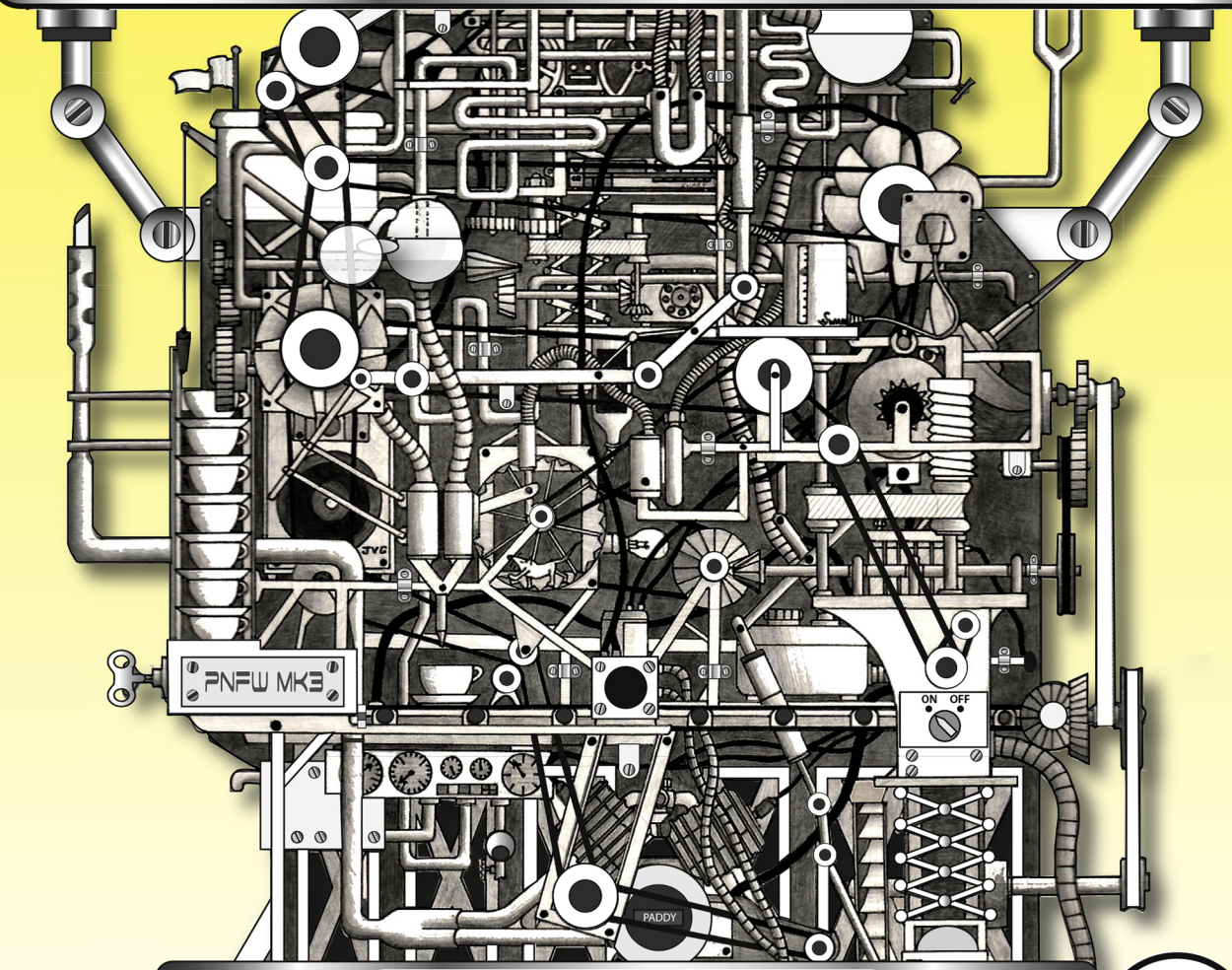
FOOD SCIENCE

AND THE CULINARY ARTS



MARK GIBSON

ILLUSTRATED BY PAT NEWSHAM

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Mark Gibson

Illustrated by Pat Newsham





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Preface

It seems that today's cooks, chefs, connoisseurs, gastronauts, critics, and plain food lovers are all very savvy when it comes to the food they eat. This has a lot to do with the positive image the industry has been receiving over the last decade or so. New technologies, the growth of the internet, and increasing gastronomic tourism have exposed a new and existing generation to diverse culinary delights far and wide. Indeed, culinary tourism, once the preserve of culinary aficionados, has long become mainstream. On top of this, food shows and celebrity chefs have glamorized the industry introducing new talent, young and old to the wonders of the palate. Furthermore, as a teacher, I find more and more of my students asking the same questions of why and how, in terms of food and their ingredients. Why do eggs coagulate? Why does milk foam? Why do emulsions split? Why do foams stabilize with protein and other substances? What is chocolate polymorphism? And why does chocolate bloom? Why do proteins denature? In fact, it is in answer to these and many other questions that piqued my interest and was the motivation behind this book.

Moreover, nowadays, not only cooks want to cook good food, but also they want to understand what it is that makes a particular dish delicious: whether it is the choice of ingredients and how they were grown, the way in which the food was prepared and cooked/presented, or the environment in which it was served. Understanding these and other processes while controlling texture not only of meats but also of sauces, soufflés, breads, cakes, pastries, etc. is a journey that encompasses a range of chemical, biological, and physical disciplines.

That said, there is one caveat, and that it is clear from the literature that the chemistry of cooking is extremely complex, making it very difficult to predict or reproduce with any great certainty. Not only will the ingredients themselves be different from batch to batch, but also the actual handling and processing of those ingredients can never be fully consistent in a real kitchen, although most cooks strive to do just that. Nor too can the timing and temperatures of cooking be replicated exactly. Therefore, while we may understand some of the general principles of the processes involved, it becomes very unlikely that a cook could ever master cookery simply from the underlying chemistry alone.

The food science in this book is written with the lay person in mind. In this way, there is not too much deviation into long complicated texts regarding hard-core esoteric scientific investigation. Instead, the book concentrates on a softer scientific approach and one that, it is hoped, will benefit both lay persons, interested cooks, and others in the culinary field alike. Also, taking the soft science approach means that a lot more can be covered in a book of this kind. Structurally, the book aims to cover a broad range of topics divided into three parts. The first part takes us on a journey of discovery into the scientific world, and while not extensively scientific, there are some concepts that require more scientific explanation than others. Secondly, part two covers the ingredients, their structure, how they behave under certain conditions, and how certain foodstuffs are formed or created. Again, there is some science involved, and once again, we have tried to make this as palatable as possible. Lastly, the appendices provide supporting material for many chapters; in this, I include a basic organic chemistry chapter that is designed to help the reader navigate portions of the book.

Having been a chef for over 20 years before I became an academic, I feel I have a good insight into the how and why of the chemistry involved. This is despite not having a science background. As such,

I have relied heavily on extensive literature reviews. Yet, despite triangulation and cross-referencing, it still seems that much in the world of food and science is not agreed upon nor fully explained. This makes for an interesting discussion and one that as cooks and lay people alike should embrace and further explore.

Lastly, this book has also been written in a way that it does not need to be read from end to end but rather can be dipped in and out depending on what's on ones' mind.

Acknowledgments

Writing this book has been a tremendous journey of discovery. After having been a chef for 20 years and after having taken both my master's and my PhD, I thought I was particularly well versed on the subject of cooking. Yet after another 18 months of studying food science, I feel I am left wanting. The things I never knew and indeed the things I wish I had known could have without a doubt made me a better chef. And yet, there is so much more to learn. Of course, this has a lot to do with the sheer breadth of the topic and the many various disciplines with which I have had to become familiar. In this respect, I have been very lucky in working alongside some professional and enthusiastic individuals who have provided both encouragement and the occasional epiphany. In this book, I impart a good deal of what I have learned. There are a few people too who have helped in this journey. In particular, I'd like to acknowledge Dr. Fanny Vong (President of the Institute for Tourism Studies, Macau SAR) whose support I found to be invaluable. I would also like to thank Pat Newsham, a lifelong friend who was particularly generous with his time and who has provided all the illustrations for this book. Another individual who I'd like thank is Flora for her patience and understanding; indeed despite her busy schedule, she always made herself accessible for advice, as a mentor or simply for a chat; in this, I am truly grateful. There are of course numerous others with whom I have corresponded with from all fields and disciplines; the name list is too long to give credit here, but they know who they are. I would lastly like to thank others including my students for their wit and energy and my office colleagues for the never-ending banter that is always a welcome aside. Collectively, these people have provided me with insight, clarification, and direction in an effort to navigate such a difficult field without which this project would have never been completed. I would especially like to thank Hans Rasmussen for his help, especially in the sous vide meat experiment. And of course, several other close friends and loved ones have also constantly been supportive and inspirational: these include Florence, David Wong, Hugo, Christy, Jerome, Jeffrey, Marieta, Miguel, David Gibson, Helen, Jamie-Leigh, Grant, Alan, Leona, and Mikey and lastly a big thank you to Harold McGee whose book *On Food and Cooking: The Science and Lore of the Kitchen* was a huge inspiration.

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PART

1

SCIENCE KNOWLEDGE AND DISCIPLINE

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FOOD GROUPS

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Many might be surprised to learn that much of the food we eat is still alive, whether raw oysters, uncooked fruit and vegetables, fresh seeds, nuts and herbs, and fermented and bacterially enhanced foods like yogurts, cheeses, sauerkraut, miso, and tempeh. They are alive in the sense that they contain cells that are still living (Field, 2011). The human body then, benefits from both raw and cooked foods. It must also be remembered that of the many foods we eat, we are never eating just one group, say vitamins (unless one is taking supplements), for example. Instead, an apple might contain several groups of foods including vitamins, minerals, fibers, and carbohydrates perhaps. It should be noted too that while certain food groups are ingested every day (some nutrients are required on a regular basis) not every food groups (in particular the micronutrients) are required on a daily basis, as certain of these can be stored in the body (Belitz et al., 2009). It is similarly noteworthy that some of these nutrients cannot be synthesized by the body and must be ingested through the food we eat.

Before we get into the mix so to speak, it is perhaps worth taking a quick look at the various nutritional components that make up our food requirements. The term "food" applies to a variety of organic materials and can be categorized in a number of ways. Foods can be grouped by whether or not they provide energy (calorific value) for the body or not or more descriptively by such terms as fish,

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meat, dairy, fruit, and vegetables. In this book, we categorize foods according to the body's needs. As such, our first foray into the vast area of food shall take the form of a quick look, not only at the nutritional profile of macronutrient food groups but also those of the loosely termed "minor" (although no less important) micronutrient food groups too. These are summarized in six categories: carbohydrates, proteins, fats, water (which comprise 99% of the dry weight of the food we eat), and vitamins and minerals (collectively making up the remaining 1%).

1.1 MACRONUTRIENTS

Macronutrients are the nutrients needed in greater quantities than those of micronutrients; these are the proteins, lipids (fats), carbohydrates, and water, which, with the exception of water, provide energy to the body at the following rates. Proteins provide around 4 Cal/g, lipids (fats) roughly 9 Cal/g, and carbohydrates supply approximately 4 Cal/g. As for water, there are no calories for energy; however, as will be seen later, it becomes clear that water is a vital and necessary component of the macronutrients (Table 1.1 and Section 1.2) (EUFIC, 2009; Wilson, 2008; WHO, 1997, 2006).

1.1.1 CARBOHYDRATES

The basic building blocks of carbohydrates are the amalgamation of carbon, hydrogen, and oxygen. Carbohydrates are also ketones, alcohols, polyhydroxy aldehydes, and acids and their derivatives. In more lay terms, carbohydrates are one of the main macronutrients within our diets; they, along with fats and proteins, supply valuable energy for the body to function. Although in terms of ranking and as will be discussed later, carbohydrates are the most important of the energy providers (Eliasson, 2016). This is partly because our digestive system readily metabolizes carbohydrates into glucose (blood

Table 1.1 Body Composition of an Average Lean Man (65–70 kg) Percent by Weight

	Gibney	FAO	Rowett Institute	Average Percent
Water	60 (26%[a], 34%[b])	61.6	60	60.4
Proteins	19.1	17	17	17.7
Fats	14.4	13.8	17	15.1
Carbohydrate	0.6	1.5		1.1
Minerals	5.3	6.1		5.7
Remaining			6%—including carbs	

[a]*Extracellular water.*
[b]*Intracellular water.*
Source: Compiled from multiple sources: Latham, M.C., 1997. Human Nutrition in the Developing World. Food and Nutrition Series—No. 29. Food and Agriculture Organisation of the United Nations, Rome; Gibney, M.J., et al., 2009. Introduction to Human Nutrition. Blackwell Publishing, Oxford; Eduweb, 2010. Fact Sheets: Body Composition. Retrieved 15 Oct 2017 from http://www.rowett.ac.uk/edu_web/; EUFIC, 1998. The European Food Information Centre: What Do We Mean by Nutrition?. Retrieved 11 November 2016, from http://www.eufic.org/article/en/health-and-lifestyle/healthy-eating/artid/nutrition-2/; Gibson, M., 2012. The Feeding of Nations: Re-defining Food Security for the 21st Century. CRC Press, Boca Raton, FL.

sugar) that in turn is used as energy for cells, tissues, and organs. Carbohydrate sugars can also be assembled according to their structural complexity, that is, three principal groups: the monosaccharides including glucose, fructose, and galactose; the disaccharides comprising two sugar units known as sucrose and lactose; and the polysaccharides that cover the starches, cellulose (fibers), and hemicellulose (Lee et al., 2014; Cummings and Stephen, 2007).

Food, because of its heterogeneity, means that carbohydrates are not consumed in isolation. Instead, they are found in a variety of foods that also bring an assortment of other nutrients to the diet; these include vitamins and minerals, dietary fiber, antioxidants, and phytochemicals. These are found in varying amounts in fruits, vegetables, grain-based foods, and several dairy products.

1.1.1.1 Monosaccharides—Simple sugars

Monosaccharides are the simplest units of carbohydrates and the simplest forms of sugar there is. The main monosaccharides are the hexoses (simple sugars in which the molecules contain six carbon atoms)—these include glucose (known also as dextrose), fructose[1] (commonly called levulose), galactose, and mannose (Eliasson, 2016). All of which are naturally found in fruit juices. These simple sugar forms are typically colorless and crystalline water-soluble solids. Monosaccharides have a sweet taste, the best examples being fructose and galactose and to a lesser degree, glucose. Glucose, however, is without doubt the most common of the monosaccharides and is also incidentally, industrially manufactured on a large scale through the hydrolysis[2] of cornstarch. Being less sweet though, glucose is often used instead of "table" sugar (the common name for the disaccharide—sucrose) in cooking, especially in the pastry kitchen. Moreover, glucose can also be prepared in relatively pure form through hydrolysis of both disaccharides and polysaccharides. Importantly, the simple monosaccharide glucose is also the easiest sugar for the body to break down and metabolize. In fact, it is only in its simplest form, that is, glucose, that sugar can be absorbed into the blood and in a relatively short space of time too (Lee et al., 2014). This is why eating sugary foods and soft drinks very quickly causes spikes in the glucose levels of the blood, sometimes referred to as a "sugar rush." Although useful in moderation, if sugar intake is continually excessive, then in the long run this can lead to heart and vascular diseases (Cummings and Stephen, 2007; Eliasson, 2016). Fructose, another simple sugar, is also found naturally in fruits, and if cane or sugar beet is hydrolyzed, one molecule of each, fructose and glucose, is created from each molecule of sucrose (see Sections 6.5 and 10.1.7.1) (Lee et al., 2014). It is also worth noting that while hydrolysis of di- or polysaccharides produces monosaccharide, monosaccharides in turn cannot be further hydrolyzed to make simpler compounds. Instead, monosaccharides in turn become the building blocks of disaccharides like sucrose (table sugar) and lactose. Sugars are used as sweeteners to improve the palatability and preservation of many foods. They are also responsible for certain functional characteristics in foods like viscosity, texture, body, and browning or caramelization properties. Sugars also increase dough yield, influence starch and protein breakdown, and control moisture, consequently preventing the drying out of certain foods (Cummings and Stephen, 2007).

[1]Fructose is the sweetest of all the sugar carbohydrates.
[2]Hydrolysis is the breakdown of a compound by a chemical reaction with water.

1.1.1.2 Disaccharides—Sugars

When it comes to disaccharides like sucrose, maltose, and lactose, they may be thought of as comprising two simple sugar molecules that come together to make one larger molecule. Sucrose is the common sugar in the cook's kitchen and at home. It is made largely from sugarcane and sugar beets. The hydrolysis of sucrose results in the formation of glucose and fructose. Another monosaccharide, maltose, is the resulting compound from the hydrolysis of starch originating from a wide variety of sources (Eliasson, 2016). In turn, maltose can be hydrolyzed into two molecules of glucose. In the alcoholic fermentation process too, maltose is the resultant product from the enzymatic[3] breakdown of starch from malted barley. The sugar then feeds the yeast producing alcohol and carbon dioxide. Lactose, the third disaccharide, is more commonly known as "milk" sugar. It can be hydrolyzed to form glucose and galactose—both simple sugars, although if they are then oxidized, both galactose and glucose form acid compounds.

1.1.1.3 Polysaccharides—Complex sugars

Although polysaccharides are condensation products[4] of both hexoses (simple sugars) and other monosaccharides; three polysaccharides in particular, starch, cellulose, and hemicellulose, are of interest in the food and organic chemistry industries. Although they form part of the saccharides, one might expect polysaccharides to share the same characteristic sweetness. Instead, starch, cellulose, and hemicellulose are predominantly (but not always) insoluble and have such complex molecular structures so as to be completely dissimilar from mono- and disaccharides (Eliasson, 2016). Sometimes, these polysaccharides go by the collective name of "dietary fibers." Fiber or dietary fiber has many different meanings in the world of nutrition. It is not a reference to a precise chemical component; instead, it is essentially a physiological concept that describes the proportion of food (derived from cellular walls of plants) that is ultimately poorly digested in human beings (Cummings and Stephen, 2007). Nondigestibility is the keyword here. Dietary fibers encompass a range of different compounds that affect many important gastrointestinal and systemic bodily processes (Brownlee, 2011). For example, the key role of the gut is to absorb nutrients following digestion in the stomach. Dietary fibers that inhibit this intestinal process results in decreased upper gastrointestinal transit times, in turn, affecting satiety. Furthermore, as complex carbohydrates, they take longer to digest because they require more time and effort to be broken down into their simpler sugar units. Dietary fiber is also known to decrease the risk of coronary heart disease (Abdul-Hamid and Luan, 2000) and other maladies (Peters et al., 2003). Additionally, indigestible seaweed polysaccharides like brown seaweeds (alginates) and edible red seaweeds (carrageenan's) are capable of forming ionic colloids that have been shown to lower serum[5] cholesterol levels. This is in part due to their ability to disperse in water while retaining cholesterol and similar active compounds and to inhibit lipid absorption in the gastrointestinal tract (Jiménez-Escrig and Sánchez-Muniz, 2000).

In short, fiber is a type of complex carbohydrate; it is a polysaccharide (made up of three or more sugar units) and is very difficult to digest. Fiber can be further classified as insoluble and soluble and is

[3]Enzymatic—is the action of enzymes at work. Enzymes accelerate or act as catalysts in chemical reactions. Most cellular metabolic processes require enzymes in order to occur at rates fast enough to sustain life.
[4]Condensation products or reactions are reactions in which two molecules combine to form a larger molecule, losing a smaller molecule in the process.
[5]Serum is the amber-colored liquid that separates out when blood coagulates.

mainly composed of cellulose that can be found in whole grains, oats, peas, beans, root vegetables, potatoes, rice, and fruits including prunes, plums, and figs. Fiber is required by the body to promote digestive health.

Cellulose—Physically, many plants rely on the cellulose polysaccharide for its structure and rigidity. As with starch, cellulose comprises beta-linked subunits or monomers[6] of glucose. As such, they cannot be enzymatically broken down by humans and animals—that is, with the exception of certain ruminants (cows in particular) who utilize bacteria in the gut that can in fact hydrolyze the *beta*-link. For the rest of the animal kingdom though, cellulose usually passes through the digestive system largely undigested (Eliasson, 2016).

Hemicelluloses—Hemicelluloses are composed of a mixture of pentose and hexose units (comprising five and six carbon atoms, respectively) including xylose, glucose, and mannose. Also, while they share certain similar characteristics to cellulose, including their names, they are in fact unrelated. Together with other complex carbohydrates like pectins, they surround the cellulose fibers of plant cells. Hemicellulose along with cellulose and pectin (a nonstarch polysaccharide), as well as lignin, a noncarbohydrate constituent of plants cell walls, collectively comprise the main components of dietary fiber as mentioned above. Also, as mentioned, dietary fibers are either water soluble or nonwater soluble. The water-soluble fibers include the gums, pectins, mucilages, and certain hemicelluloses. They are found in oats, barley, grapefruits, and the like and are generally good for the body's digestive processes. Most hemicelluloses along with cellulose and lignin, however, are not water soluble even though they can swell up with absorbed water. These substances are found in most leafy greens, and although cannot be digested, certain hemicelluloses can be partly assimilated by bacteria found along the gastrointestinal tract.

Starches—Starches are without a doubt the principal carbohydrate in most diets, and like fibers, they are also complex carbohydrates and important constituents of the human diet. Chemically, starches are polysaccharides that consist of repeating glucose units. In origin, starches turn out to be the storage carbohydrate of many varied plants such as cereals and root vegetables. Starches are found in a partially granular crystalline form comprising two polymers[7], namely, amylose[8] and amylopectin[9] (Eliasson, 2016). Some common cereal starches contain 15%–30% amylose starch, while others like corn, sorghum, rice, and barley contain largely amylopectin starch and are considered "waxy." It is this amylose/amylopectin ratio within foods that is the key to the functional properties of starches. Starch crystalline structure is lost when it is heated in water (gelatinization[10]), as it allows for easier digestion to take place (Cummings and Stephen, 2007). What that means is when starch is dispersed in a liquid and heated, the liquid penetrates into the starch granule, swelling it until it is fully hydrated. Once hydrated (gelatinized), the swollen granules may increase the viscosity of the liquid

[6]Monomers are molecules capable of reacting or binding with other molecules to form polymers.
[7]A polymer is a large or macromolecule composed of many repeated subunits. They play an essential role in everyday life from natural biopolymers including DNA and proteins. Polymers are created by combining many small molecules called monomers. Polymer's relatively large molecular mass allows for unique physical properties, including toughness, viscoelasticity, and semicrystalline structures. Put another way, a monomer is a single atom or molecule that can join with other monomers to make new substances called polymers.
[8]Amylose is the crystalline form of starch comprising long unbranched polysaccharide chains.
[9]Amylopectin is the noncrystalline form of starch, consisting of branched polysaccharide chains.
[10]Gelatinization of starch means that it absorbs moisture, swells, and then becomes semifirm.

and/or assist in forming gels. In very loose general terms, the amylose provides the gel strength, while the amylopectin provides the viscosity.

Modified starch—Natural proportions of amylose and amylopectin in starchy foods are variable, and different cultivars of common species, like rice, display quite varied amylose-to-amylopectin ratios. However, genetic breeding can alter these ratios to influence properties like appearance and texture and viscosity or simply to improve gel stability and mouthfeel of the starch involved. Furthermore, chemical tampering can help reduce retrogradation, which is part of the process of staling of bread, lowering or increasing of gelatinization temperature, and enhancing freeze—thaw stability, controlling viscosity, improving acid and heat stability, and inhibiting gel formation. However, a note of caution is warranted; by altering the chemical nature of starch, the result can lead to it becoming resistant to digestion (Cummings and Stephen, 2007; Eliasson, 2016).

So, in sum, it can be said that dietary carbohydrates are a diverse group of compounds with a range of chemical, physical, and physiological properties. While chiefly there for energy metabolism,[11] carbohydrates do indeed affect things like satiety, blood glucose and insulin, and lipid metabolism. In turn, carbs also have implications for overall health contributing to things like weight control, diabetes, and cardiovascular disease (Cummings and Stephen, 2007; Eliasson, 2016).

1.1.1.4 Sugar alcohols

A class of carbohydrates are the sugar alcohols or polyols. These are compounds that fall in between sugars and alcohols. While they are neither, they are in fact carbohydrates with structurally similar chemical compounds that partially resemble both sugar and alcohol. Common sugar alcohols include glycerine, sorbitol, mannitol, isomalt, xylitol, lactitol, erythritol, maltitol, maltitol syrup, and hydrogenated starch hydrolysates. Collectively, they are important in the food industry as sweeteners for all sorts of products. One of the main reasons for using polyols over traditional sugars is that they are generally fully metabolized by the body and subsequently contribute fewer calories than traditional sugars do. Calorie rates of the various sugar alcohols are in the range of 0.02–3 Cal/g as opposed to 4 Cal/g for traditional sugars. However, while most polyols not as sweet as sucrose, the exceptions, maltitol and xylitol, are about the same as sucrose.

1.1.2 PROTEINS

(See also Chapter 4)

Proteinaceous compounds containing carbon, hydrogen, oxygen, and nitrogen and on occasion phosphorous and sulfur are among the most complex of the organic compounds found in nature. They are commonly found in plants and animals and form an essential part of a cells' protoplasm.[12] They are also a necessary part of the human diet too in which they help to build and repair various bodily tissues

[11]Metabolism is the breaking down (catabolism) or the building up (anabolism) of food in the body. Metabolism can be considered as functionally active in three main areas—firstly, the transformation of food into energy/fuel to operate cellular processes; secondly, the transformation of food into building blocks for proteins, lipids, some carbohydrates, and nucleic acids; and lastly, the transformation of food to be used as vehicles for the safe disposal of nitrogenous wastes that would otherwise tend to form toxic ammonia.

[12]In biology, protoplasm is the living contents of a cell surrounded by a plasma membrane that effectively separates the interior of the cell from the outside environment.

(Sawyer et al., 2002). Although proteins (polypeptides[13]) can readily supply energy if required to, their primary area of responsibility is that they are the key component of most cells, the muscle, connective tissues, hair, and the skin (Latham, 1997). In turn, every protein molecule is made up of numerous combinations of amino acids. The human body requires these amino acids to retain or replace existing proteins or to make new proteins. Any excess of ingested amino acids that aren't needed by the body are simply passed through urination. There are in fact two categories of proteins, those that the body can produce (nonessential proteins—amino acids) by itself and those that it cannot (essential amino acids), which in turn must be ingested. Of the hundreds of nonproteinogenic[14] amino acids that exist, the body utilizes just 20 or so protein-making (proteinogenic) amino acids; eight of these, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, and valine (plus a ninth, histidine for infants), cannot be synthesized by the body and are the essential amino acids that must be consumed as part of the diet (Latham, 1997; WHO, 1997; Beaton and Patwardhan, 1976; Wilson, 2008; Wu, 2013). The other amino acids including glycine, alanine, serine, cystine, tyrosine, aspartic acid, glutamic acid, proline, hydroxyproline, citrulline, and arginine must either be ingested as food or synthesized in the body (Wu, 2013). Proteins can be further classified as either complete or incomplete:

Complete proteins—simply means a substance or food that contains all the essential amino acids a person requires. These include meat and animal products like milk and eggs (WFP, 2000). Although having said that while animal proteins offer complete essential amino acids, they are not necessarily the best source as animal proteins often contain unhealthy amounts of cholesterol and saturated fats (Wu, 2013).

Incomplete proteins—are those foods that do not by themselves contain all the amino acids required by the body. They are generally of fruit and vegetable origin, and as such, foods are often combined to complete the full required compliment. However, there is one noteworthy exception among fruit and vegetables and that is the humble soybean. Soybean's amino acid profile is such that it is one of the very few vegetable sources considered a "complete" protein, supplying all of the essential amino acids needed (WFP, 2000; Tovar et al., 2002; Velasquez and Bhathena, 2007; Erdman, 2000; Wu, 2013).

Proteins and satiety—General satiety can be explained by the fact that the stomach expands during eating, and as it does so, nerve receptors on the stomach wall sense the volume and pressure of the stomach contents. These feelings in turn convey signals to the brain, thus creating the sensation of fullness. Furthermore, vegetable-based proteins, as opposed to meat proteins, create the feelings of "fullness"; earlier, this means less vegetable protein needs to be ingested before one feels full (Kristensen et al., 2016). Satiety is a multifaceted construct. Studies cited by Chambers, McCrickerd, and colleagues (2016) in their paper on the satiating effects of foods suggest that cognitive and physiological sensory signals play important roles in determining whether one is and remains fully satiated. This hinges on responses by the body in terms of satiety signals that combine cognitive sensory perceptions with absorptive and ingestive signals that collectively determine the state of "fullness." Indeed, classic research in this area promotes the notion of a hierarchy of satiating macronutrients starting with protein, going on to carbohydrate then fat (Chambers et al., 2016). This is not surprising as protein has undeniably been in the limelight for a long time now when it comes to investigative and

[13]Polypeptides are organic polymers (linear) that comprise a large number of amino acid residues that are ultimately bonded together in a chain forming part of or the whole protein molecule; that is to say, amino acids are joined together by peptide bonds that form polypeptide chains.

[14]Nonproteinogenic (not protein-making) amino acids are not naturally found in the genetic code of any organisms.

real-life research about satiety. Certainly, supporting the idea of long-term weight loss through increasing one's protein intake, without altering overall energy consumption, cites Chambers et al. (2016), is a strategy that is supported by the literature. This is especially so if combined with the intake of dietary fiber, which has been shown to work though increasing the physical bulk of foods, an upsurge in gastric swelling, and slowing the flow of gastric voiding.

The literature also supports a dietary combination of high protein and fiber foods containing more carbohydrate than fat (Chambers et al., 2016). It also, surprisingly, indicates that by manipulating the physical or textural qualities of foods and playing on the psychology of a food's sensory profile (claiming fullness and satiety), so one's perception of satiety is also altered in favor of being full (Chambers et al., 2016).

1.1.3 FATS

(See also Chapter 16)

Semantics—While generally referred to as "fats," these substances are in fact lipids. They are fat-like compounds that encompass naturally occurring molecules that include fats, waxes, sterols (including cholesterol), fat-soluble vitamins (A, D, E and K), and phospholipids[15].

Fats and oils, collectively known as triglycerides[16] or triglycerols, are commonly referred to in this sense as "dietary fats." They are obtained from both animal and vegetable origin. Lipids make up the bulk of the dietary fat intake. In common with general usage, the term "fat" or "fats" in the context of this section is used to represent all edible fats and oils (triglycerides), while the term "dietary fats" (distinct from "dietary lipids") is also used interchangeably with "fat" or "fats"—once again in line with common parlance (Latham, 1997; WFP, 2000; WKU, 2010). When it comes to fat, the difficulty for us humans is that, while we ingest and store fats, fats can also be metabolized from excess carbohydrate intake as well. Thus, one has to be careful and watch both fat and carbohydrate intake. Most dietary fats are composed of some sort of fatty acid[17] arrangement; triglycerides are no different in this respect and are made of glycerol (a type of alcohol) and three fatty acids (Gibson, 2012). This separation is important as the nature of the fat depends on the specific type of fatty acids present. These can be divided into one of two groups: saturated fatty acids and unsaturated fatty acids, abbreviated to saturated and unsaturated fats, respectively. While it is true to say that all fats contain both saturated and unsaturated fatty acids, they are usually identified according to the dominant fatty acid present (Latham, 1997; WKU, 2010; Ortega, 2007).

[15]The human body is made up of cells, including phospholipids, that are important molecules providing structure and protection to cells. Phospholipids consist of a hydrophilic (water-loving) and a hydrophobic (water-fearing) tails. Phospholipids line up arranging themselves into two parallel layers, a "phospholipid bilayer." This layer makes cell membranes and is critical to a cell's ability to function.

[16]Triglycerides are derived from glycerol and three fatty acids. They are the main component of body fat in animals and humans and vegetable fat.

[17]Fatty acids are the building blocks of fat within the human body and within the food we eat. So, while we consume whole fats, the human digestive system breaks down these fats into their component fatty acids that can then be absorbed into the blood. Fatty acid molecules are usually joined together in groups of three, forming a triglyceride. Triglycerides are also made in our bodies from the carbohydrates that we eat too. Lastly, fatty acids have many important known functions in the body, including energy storage. So, if it is not available for one reason or another, fatty acid as fuel for the cells instead.

Saturated fats—Broadly speaking, these dietary fats derive predominantly from animals and animal by-products, for example, meat, eggs, milk, cream, and butter. Although, as always, there are exceptions particularly from the vegetable world; these include palm and coconut. Saturated fats are also differentiated from their unsaturated counterparts in that saturated fats have no carbon double bonds and are instead saturated with hydrogen atoms. A cautionary note, moderation must be exercised here as diets containing too much saturated fat tend to raise blood cholesterol levels affecting potential heart disease.

Unsaturated fats—Unsaturated fats predominantly originate from plants and are usually further subdivided into two types: mono- and polyunsaturated fats. While both help in lowering low-density lipoproteins (LDL cholesterol) and reducing heart disease, some consider polyunsaturates as doing the job marginally better by providing more membrane fluidity than monounsaturated fats. Unsaturated fats in general comprise carbon-to-carbon double bonds, the number and configuration of which ultimately determines health properties in the humans. Monounsaturated fats contain only one such bond, while polyunsaturated fats contain more than one. The healthy unsaturated fatty acids are those with the *cis* as opposed to the *trans* carbon configuration (WKU, 2010; WHO/EMRO, 2010; EFSA, 2008). Both the following are of the *cis* configuration:

- *Monounsaturated fats* (MUFA) include oils from peanuts, olives, canola, sesame seed, and avocados. It's worthwhile mentioning too that monounsaturated fats are also high in vitamin E, which also helps to develop and maintain healthy cells in the body.
- *Polyunsaturated fats* (PUFA) include oils from corn, cottonseed, safflower, soybean, and sunflower. Fish oil too is also polyunsaturated as are omega-3 and omega-6 fatty acids.

Although for some, polyunsaturated fats are the preferred choice; they are more vulnerable to peroxidation (rancidity) (Section 16.1). Although in an attempt to reduce and slow the onset of rancidity and prolong fats' shelf life, scientists introduced hydrogenation.[18] Unfortunately, however, partial hydrogenation, while beneficial in the reduction of rancidity and allowing fats and oils to be firm/hard at room temperature, hydrogenizing polyunsaturated fats in part transforms the original oil/fat into *trans*-fatty acids or *trans* fats for short (WKU, 2010; WHO/EMRO, 2010; EFSA, 2008).

Trans fats—Trans fats can be either *trans*-PUFA or *trans*-MUFA, and while they both can occur naturally in nature, they are not common. Instead, by far, the biggest producers and users of trans fats are humans. Trans fats are often found in processed foods such as soft or semihard margarines. They are also particularly harmful in that trans fats act like saturated fats (*see note on hydrogenation*) in that they can raise levels of cholesterol in the blood and just as disturbing contributes to fatty acid membrane loss in the brain with implications for neurodegenerative disorders such as multiple sclerosis (MS) and Parkinson's and Alzheimer's diseases (WKU, 2010; WHO/EMRO, 2010; EFSA, 2008).

Essential fatty acids—When required, the human body can produce (synthesize) most of the fatty acids it needs; in this respect, they are not essential fatty acids. Others, however, the "essential" fatty acids, are essential and must be included in the diet. Two essential fatty acids, linoleic and

[18]Trans fats and hydrogenation. In their natural state, unsaturated fats can be oxidized creating a rancid, stale, or unpleasant smell or flavor. By saturating the fat (fixing more hydrogen to natural unsaturated fats), the number of double bonds is decreased in a process called hydrogenation; this slows the process of rancidity.

alpha-linolenic, cannot be manufactured in the body and therefore must be obtained from consumed foods such as vegetables and some vegetable oils (flaxseed), nuts (walnuts), seeds (pumpkin and sunflower), soya and soya products, and fish and fish oils. Linoleic and alpha-linolenic are used to build particular fats—omega-3 and omega-6 fatty acids that aid in the normal functioning of all tissues of the body (Gropper and Smith, 2012). However, it is also important to, not only ingest these fatty acids, but just as importantly to take them in the right ratios. This is because both fatty acids are competitive in nature and therefore, excessive intake in one might inhibit the effect of the other (Lands et al., 1990). The ideal ratio of omega-6 to omega-3 should be in the region of 1:1 and 4:1 (Simopoulos, 1999). Instead, many consume these fats at a much greater ratios—as high as 10:1 and 25:1. Such a runaway imbalance is due in large part because of the greater dependence on processed foods and oils. Aiming for a lower omega-6/omega-3 ratio is desirable for reducing the risk of many chronic diseases (Simopoulos, 2008).

1.2 WATER

Water is often not seen as or is more precisely overlooked as a macronutrient, yet it is perhaps one of the most important of the macronutrients. While water does not provide the body with energy like fats, proteins, and carbohydrates do, it does however account for around 60–70% of our total body weight (Fig. 1.1) (EUFIC, 1998; DeMan, 1976). And we cannot survive without it. Water plays an important role in many nutritional processes, not least of which is homeostasis.[19] Water and homeostasis work in

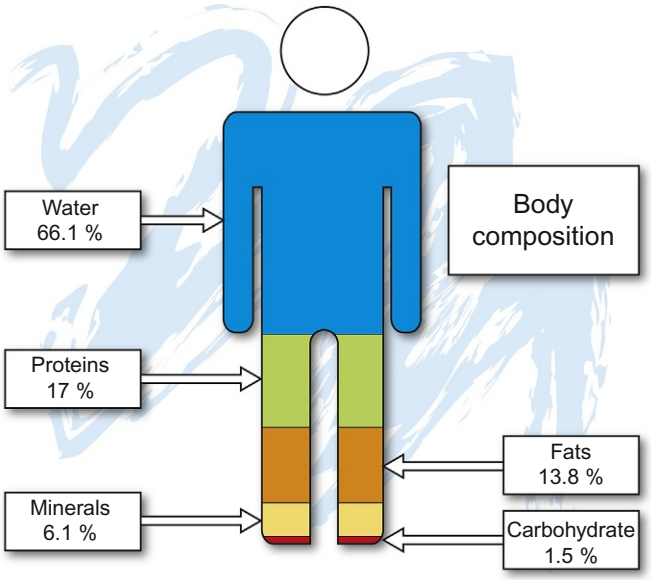


FIG. 1.1 Nutrient composition of the human body by weight.

[19]Homeostasis is the function of a system (e.g., human blood work) in which a variable (say the concentration of glucose in solution) is actively regulated to remain as constant as possible.

unison regulating the bodies fluids; it controls the body's temperature (via perspiration), aids in digestion, and enables the transportation of nutrients around the body; water is also involved on a chemical level too, to facilitate the metabolization of foods, and lastly, it also promotes efficient bodily waste management through fecal and urine excretion (WHO/EMRO, 2010; CFNI, 2004; Lipp et al., 1999; Matthys et al., 2007; Wilson, 2008; EUFIC, 2009).

Losing just 8% of the average person's body water (through dehydration, heatstroke, constant diarrhea, etc.) can have dire consequences; losing 10% can be fatal (EFSA, 2008). Yet for all its importance, water intake requirements were still, up until recently at least, prescribed solely on the need to prevent such things as dehydration and little else (Grandjean, 2004). After more research in the area, however, it has been calculated that just about 25–35 mL of fluids per kilogram body weight must be consumed daily—which is equivalent to between 2 and 3 L/day for an adult (Howard and Bartram, 2003). In short, without food, humans can survive many weeks by calling on its reserves, yet without water, humans can only survive for just a few short days (CFNI, 2004; Belitz et al., 2009). The main sources of water are from what we drink plus that found in foods we ingest.

1.3 MICRONUTRIENTS

Unlike macronutrients, micronutrients provide virtually no energy to the body and as such are only required in small does. While the term "micro"-nutrients might be suggestive of lesser importance, it must be remembered that "micro" is a volumetric term only; consequently, micronutrients should not be used to relegate to a position of secondary value. Essential micronutrients are involved in many processes in the body, without which, even in these small amounts, would result in severe problems in the body. Micronutrients promote biochemical reactions like enzyme production and aid in metabolization and producing hormones and many other compounds or substances, all of which are essential for the proper regulation of growth and development within the human body (EUFIC, 2009; WHO, 1997, 2017). Micronutrients consist primarily of vitamins, minerals, and trace elements.

1.3.1 VITAMINS

Vitamins are organic substances that are produced by plants and animals; they fall neatly into two groups: fat or water soluble. Fat-soluble vitamins including A, D, E, and K can be stored in the body, so they need not be ingested so frequently. Water-soluble vitamins on the other hand, like vitamin C and the B complex varieties (vitamins B_1 (thiamine), B_2 (riboflavin), B_3 (niacin), B_6, B_9 (folic acid or folate), and B_{12}), for example, need to dissolve in water before the body can absorb them. Because of this solubility, the body cannot store them as reserves, as a result any excesses are passed through the urinary tract. Consequently, the body requires a fresh supply of many of these micronutrients every day (Latham, 1997; WHO, 1997).

Although many need replenishing every day, vitamins are only required in very small amounts. They also have diverse biochemical functions. Some have hormonelike functions as regulators of mineral metabolism (vitamin D), or regulators of cell and tissue growth and differentiation (some forms of vitamin A). Others function as antioxidants (vitamin E and sometimes vitamin C). While the largest number of vitamins (the B complex vitamins) function mainly as precursors for enzyme cofactors

(coenzymes[20]) that aid enzymes in their work as catalysts in metabolism. Other functions of vitamins include boosting the immune system while helping cells and organs do their jobs. Vitamin K helps blood to clot (Yang and Xiong, 2012). Furthermore, if one is "running on empty" and showing signs of fatigue, tiredness, and low energy levels, despite sufficient macronutrient intake and without any underlying disease, such symptoms might just as easily be caused by a lack of vitamins and minerals in the diet (see also Appendix A and Section 1.1) (Huskisson et al., 2007).

1.3.2 MINERALS

As opposed to vitamins and proteins, minerals are inorganic chemical elements that are needed by all living beings. Yet as with vitamins, minerals are often relegated to a position of secondary status. However, this cannot be further from the truth as they provide important functions either by themselves or in conjunction with other micro- and macronutrients. Minerals are indirectly provided through plants and animals, which in turn ingest them via soil and water or, in the case of animals, through eating plants or other animals. Minerals are also carried in the water supply, the composition of which varies greatly from region to region (LPI, 2017). Moreover, it is also worth noting that certain elements including some metals occur in the form of ionic[21] compounds. Minerals are acquired, not only necessarily individually but also in complex compounds via natural inorganic sources. In other cases, certain minerals occur less frequently in nature and have to be added artificially in the form of supplements like iodine in salt, for example. There are some minerals that are essential, and they have to be consumed in larger amounts. Sometimes, these minerals are referred to as macrominerals; other times, this distinction is not made. Mineral's roles can be structural as in bones and teeth, for example, or perhaps in vital roles such as electrolytes[22] or more simply to help regulate many of the body's processes including metabolization and energy production; others might have more specific functions like providing structure in (FSA, 2010; MIT, 2010; WHO/EMRO, 2010; WHO/FAO, 2004).

As with many things, mineral data vary from individual to individual and from institution to institution. Bearing this in mind, minerals can be categorized either by their importance or functional classification, by status of essential and nonelements, by their structural compound such as metals and salts, or simply by groupings like macro- and micronutrients and macro- and microminerals and trace minerals (MIT, 2010; WHO/FAO, 2002).

This book follows the latter convention. However, as has been pointed out, just as there is a lack of agreement between people and institutions on macro and micronutrients, so there is a similar lack of mutual agreement between the separation of macro- and microminerals. That said, some system must be adopted, so this author chooses to recognize macromineral nutrients, as those needed in quantities above 100 mg and microminerals as those between 1 and 100 mg. Trace elements too, for the purposes of this book, are those that fall below this 1 mg threshold (Britannica, 2009; MIT, 2010). Importantly, while certain minerals are required in larger doses than

[20]Coenzymes are nonprotein compounds that mainly help the functioning of enzymes.
[21]An ionic compound is a chemical compound that comprises ions held together by electric charges or forces termed "ionic bonding." The compound consists of positively charged ions called cations and negatively charged ions called anions. Overall, the compound is neutral.
[22]Electrolytes are substances that produce an electrically conducting solution when dissolved in a polar solvent, such as water.

others, this does not confer upon them a greater measure of importance. Regardless of which system is used, we still need some perspective, guidelines, and recommendations on daily intake. This is where the dietary guidelines come in (next section and Appendix A) (FAO/WHO, 2001; Bogden and Klevay, 2000).

1.3.3 A GOOD BALANCED ENERGY PORTFOLIO

When it comes to energy intake, it is not sufficient to simply ingest sufficient calories to meet daily requirements. Instead, because of the body's changeable physiological needs and the preferential way it treats the different energy macronutrients (carbohydrates, fats, and proteins), a balanced energy portfolio is recommended by all major dietary guideline providers. Deciding adequate protein, carbohydrate, and fat balances is a complicated and costly exercise. Having said that, it is nevertheless important as imbalances can inevitable be costly in terms of health both from a personal and from a public health perspective (WHO/FAO/UNU, 2007; WFP, 2009). It can be seen from the appendices (Section A.4 and Table A.4) that carbohydrates, the major source of energy, can be as high as 75% of total macronutrient intake. It can also be seen from Section A.4 and Table A.3 that the figures indicate that both industrialized and nonindustrialized countries' daily fat intake can be as high as 35% (Latham, 1997). This can particularly skew energy intake as is seen in the discussion on metabolism (Section 1.4). It is also worth noting at this juncture that the energy content of fat equals 9 kcal/g, which is more than twice that of protein and carbohydrate (both at 4 kcal/g). Therefore, any intake above and beyond expenditure, as quoted by national guidelines, will result in this fat being deposited as stored fat (usually as adipose tissue). So, what are the recommended balances and who decides this? For a fuller answer, see Appendix A "Dietary Guidelines." In the meantime, we take a quick look at the body's metabolic processes vis-à-vis the macronutrients.

1.4 METABOLISM

Unlike plants (autotrophs[23]) that are able to convert sunlight into energy via photosynthesis, so animals including humans (heterotrophs[24]) rely on organic molecules or compounds (food) as starting blocks for energy and other purposes. As mentioned, foods contain six major nutrient classes: carbohydrates, proteins, fats, vitamins, minerals, and water. Between them, they provide the raw materials the body requires for energy and for building cells like proteins, certain carbohydrates, lipids, nucleic acids such as DNA and RNA, and other important components of the body. These breaking down and building up of biochemical compounds are referred to as metabolism or sometimes "cellular respiration[25]." Put simply, metabolism is the sequence of chemical reactions that happens within a cell. It is the biochemical breakdown of complex molecules in a process called "catabolism" resulting in the breakdown of larger molecules into smaller ones while releasing energy in the process or the utilization of the energy

[23]Autotrophs are organisms that serve as primary producers in a food chain. They obtain energy and nutrients by harnessing sunlight through photosynthesis.
[24]In biology, heterotrophs are organisms that require organic compounds as their principal source of food.
[25]Cellular respiration is a general term describing all metabolic reactions that are involved in the creation of usable energy from the breakdown of ingested nutrients.

of catabolized molecules for building or synthesizing other molecules in a sequence of metabolic pathways called "anabolism." The various ways or "paths" that are available to achieve the entire process of metabolism are referred to as the metabolic pathways (more later).

However, before metabolism "proper" can take place, the food we eat must first be digested; this is sometimes called intermediary or intermediate metabolism. Digestion and metabolism also involve the movement or transportation of substances and the like between and into the many varied cells (Gropper and Smith, 2012). It all begins with the digestive process, in particular, with the digestive enzymes that first break down foods into their component building blocks allowing for easier absorption into the body. The body achieves this, in part, by utilizing enzymes, proteinaceous molecules that catalyze or speed up certain chemical processes of metabolism. Specific enzymes work in specific environments, temperatures, and pH levels. Digestive enzymes are located all along the digestive tract, in the salivary glands, in cells that line the stomach, in pancreatic secretions, and from cells in both the large and small intestines. Nutrients are also broken down in cells at the cellular level. Enzymes tend to be categorized according to their particular area of speciality. Therefore, we can say that the enzyme amylase,[26] which is produced in the salivary glands, the pancreas, and the small intestine, aids in the breakdown of carbohydrates like starch and sugars into simple sugars like glucose—both in the mouth and in the small intestine. All the while, protease enzymes catalyze proteins into their constituent components (i.e., peptides and amino acids) in the stomach and small intestine. Lipases on the other hand are found in the pancreas and small intestine and accelerate the hydrolysis of lipids resulting in fatty acids and glycerol in the small intestine. Lastly, nucleases split the genetic transporters, the nucleic acids into nucleotides. Taking this one step further, foods are primarily broken down (catabolized) into food molecules (nutrients) in the digestive tract. It does this by initially using the mechanical forces of biting and chewing of food in the mouth; at the same time, the salivary glands secrete amylase. This helps digest or break down starch before the food enters the stomach where hydrochloric acid and pepsin[27] further break down various nutrients. This mix of food, saliva, and gastric juices is collectively known as chyme. This chyme then travels to the small intestine where the pancreas produces proteolytic lipases and a plethora of other digestive enzymes, which, together with the liver's bile salts, further digest (break down) nutrients for easier ingestion. After or, more precisely, during the small intestinal pathway, glucose, simple carbohydrates, and other nutrients are carried across the intestinal wall and absorbed directly into the blood. At this point, the liver's parenchymal cells along with other tissues help to finally complete the initial catabolic process by breaking down the remaining carbohydrates into simple sugars, fats into fatty acids, and proteins into amino acids. After this, nutrients are then made available to the cells at which point, if need be, these nutrients can be further altered or broken down into numerous other chemicals for the cell's requirements (King, 2010).

Moving on, howsoever, the food/nutrients are processed or digested; the metabolites (as the products of metabolism are called) are transported via the bloodstream (produced in the bone marrow) to where they need to be. The bloodstream comprises two components, cells and plasma. The cellular portion of blood contains three categories of cells: red blood cells (RBCs) (also known as erythrocytes), whose purpose is to deliver oxygen to the body's cells while taking away "spent" CO_2. Another blood cell component is the white blood cells (WBCs), which aids in the fight against infection. Then, there

[26]Amylase is an enzyme produced in saliva that works on breaking down food before entering the stomach.
[27]Pepsins are the main digestive enzyme produced in the human stomach responsible for breaking down proteins.

Table 1.2 The Body's Major Metabolic Pathways

Major Metabolic Pathways
Glycolysis converts glucose into pyruvate which in aerobic reactions enters the cell's mitochondria where it is oxidized into CO_2 and H_2O. The resultant potential energy is stored as adenosine triphosphate (ATP). In anaerobic conditions, pyruvate is reduced by nicotinamide adenine dinucleotide (NADH) to a range of useful products, especially important is lactate
Citric acid cycle aka *Krebs cycle*—is a set of chemical reactions that releases energy through oxidation of acetyl-CoA in proteins, carbohydrates, and fats into CO_2 plus energy in the form of adenosine triphosphate (ATP)
Oxidative phosphorylation—helps with the disposal of electrons that are released through glycolysis and the citric acid cycle. A lot of the energy released in this process can, if required, be stored as ATP
Gluconeogenesis—biosynthesis of sugar (glucose) from noncarbohydrate sources like amino acids and glycerol
Urea cycle is the conversion reactions involved in transforming ammonia into urea that is then excreted via the kidneys
Fatty acid beta-oxidation—fatty acids are broken down into acetyl-CoA, which then enter the citric acid cycle
Pentose phosphate pathway—this pathway functions largely to generate nicotinamide adenine dinucleotide phosphate (NADPH) for biosynthetic purposes

Source: Compiled from multiple sauces: Gropper, S.S., Smith, J.L., 2012. Advanced Nutrition and Human Metabolism. Cengage Learning; Devlin, T.M., 2010. Textbook of Biochemistry With Clinical Correlations. John Wiley & Sons, USA; Greenberg, D., 2012. Metabolic Pathways. Elsevier; Medeiros, D.M., Wildman, R.E.C., 2013. Advanced Human Nutrition. Jones & Bartlett Learning.

are the platelets (also known as thrombocytes), which are small disk-shaped colorless cell fragments without a nucleus found in large numbers in blood and which are involved in the clotting process. Lastly, the plasma (the clear yellowish blood fluid when the cells are separated out) is responsible, not only as a vehicle for carrying the cells but also, just as importantly, as a transport carrier for such things as dissolved electrolytes, nutrients, vitamins, hormones, clotting factors, and antibody[28] proteins such as albumin and immunoglobulins (Belitz et al., 2009; Gropper and Smith, 2012).

When food molecules are not being metabolized for specific purposes in the body, they are metabolized for energy. These metabolic reactions are the chemical reactions in which living organisms convert chemical compounds (metabolized food) into useable energy or other components needed by the body. Of the numerous pathways involved in metabolizing food molecules, there are a handful of important "metabolic pathways" worth noting; these are shown in Table 1.2.

1.5 ENERGY PREFERENCES

The body's first requirement is for energy and, if required, all macronutrients, that is, proteins, fats, and carbohydrates, with the exception of water, to ultimately be catabolized into functional glucose, glycerol, and free fatty acids (fats). That said, this interchangeability of energy sources is not as might seem, a randomized process; instead, the human body has its preferences. With its relatively quick and easy transformation into glucose, carbohydrates are the major source of energy for the body. In this sense, carbohydrate (in the form of glucose) is the body's fuel of choice. In the absence of sufficient intake, or

[28]An antibody, also known as immunoglobulin, is a protective protein produced by the immune system in response to the presence of a foreign substance in the body—called an antigen.

a bout of excessive physical activity whereby reserves of glucose run low, then the body first taps into its glycogen reserves. Once these are depleted or become dangerously low, so the next place the body turns to are the fatty deposits (the adipose cells). If still in need of energy, through prolonged abstinence, profoundly low continuous intake or starvation, then the body will start to convert its own existing muscle proteins into its constituent amino acids and then into glucose for energy. This has the effect of depleting muscle mass, and action must be taken to remedy this.

Just as glucose is the body's choice of fuel, so adipose (or "fat") tissue is the body's choice of fuel storage system; this is no accident. As with protein, adipose is very flexible and either can be synthesized from excess dietary fat intake or can be converted from surplus carbohydrate or protein in our body and/or diet. As it does so, so fat "reserves" are built up in case of leaner times. The first and foremost reason the body converts all this extra carbohydrate, protein, and fat into body fat is the relative energy profile of fat itself. That is to say, each type of molecule, whether fats, carbohydrates, and proteins, produces specific amounts of energy. For example, the energy yield from 1 g of fatty acid is approximately 9 kcal (37 kJ), compared with carbohydrates and proteins, which is just 4 kcal/g (kJ/g) each. Thus, it is for this reason that fats are so potent and efficient forms of energy stores. Hence, fat stores can be converted back into glucose as and when needed (Wilson, 2008).

1.5.1 CARBOHYDRATE METABOLISM

As mentioned, carbohydrates are the body's first choice when it comes to energy production within the body (WFP, 2000). Carbohydrate metabolism utilizes several of the abovementioned pathways in the production of glucose (also referred to as "blood sugar"), the cells' universal source of energy. Essentially, the human body, through the digestive tract or GI, tends to treat all carbohydrates in the same way. That is, it endeavors to break down carbohydrates into sugar molecules whereupon it converts the most digestible of these into glucose (Fig. 1.2) (HSPH, 2010). In the carbohydrate metabolic pathway, the glucose is absorbed into the cell directly from the blood. From here, it enters the cytosol (the aqueous liquid inside the cell) where through the initial process of glycolysis (the oxidation of glucose) converts glucose molecules into two molecules of pyruvic acid (pyruvate) and a modest amount of the universal energy storage molecule—adenosine triphosphate (ATP). The pyruvate then passes into the mitochondria[29] from the cytosol (Alberts et al., 2002). Two options are present at this juncture dependent on the cell's needs; this in turn determines whether the pyruvate is subsequently treated aerobically or anaerobically. In anaerobic activity, the pyruvic acid is subject to anaerobic glycolysis[30] (Hunter, 2008). If sufficient oxygen is present for aerobic conversion, pyruvic acid is further metabolically transformed into acetyl-CoA before it enters the "citric acid cycle" (also known as the Krebs cycle). In the meantime, oxygen from the lungs is dispersed into the blood. Oxygenated blood is then fed to the cell's mitochondrion. In the citric acid (the Krebs) cycle, the oxygen in the blood is made available to the cell and in turn reacts with the acetyl-CoA oxidizing it and generating a small amount of energy that is then stored as nicotinamide adenine dinucleotide hydrogen (NADH) and waste carbon dioxide (Hunter, 2008). The spent carbon dioxide travels back, via the blood, to the lungs where it is

[29]A mitochondrion is an organ found in large numbers in most cells whereby the biochemical processes of respiration and energy production occur.

[30]Anaerobic glycolysis is extremely important for tissue or skeletal muscles that have high energy requirements. It is also required at times when there is an insufficient or an absence of oxidative enzymes. Anaerobic glycolysis is produced by lactic acid fermentation and is only effective during short periods of intense exercise or energy needs.

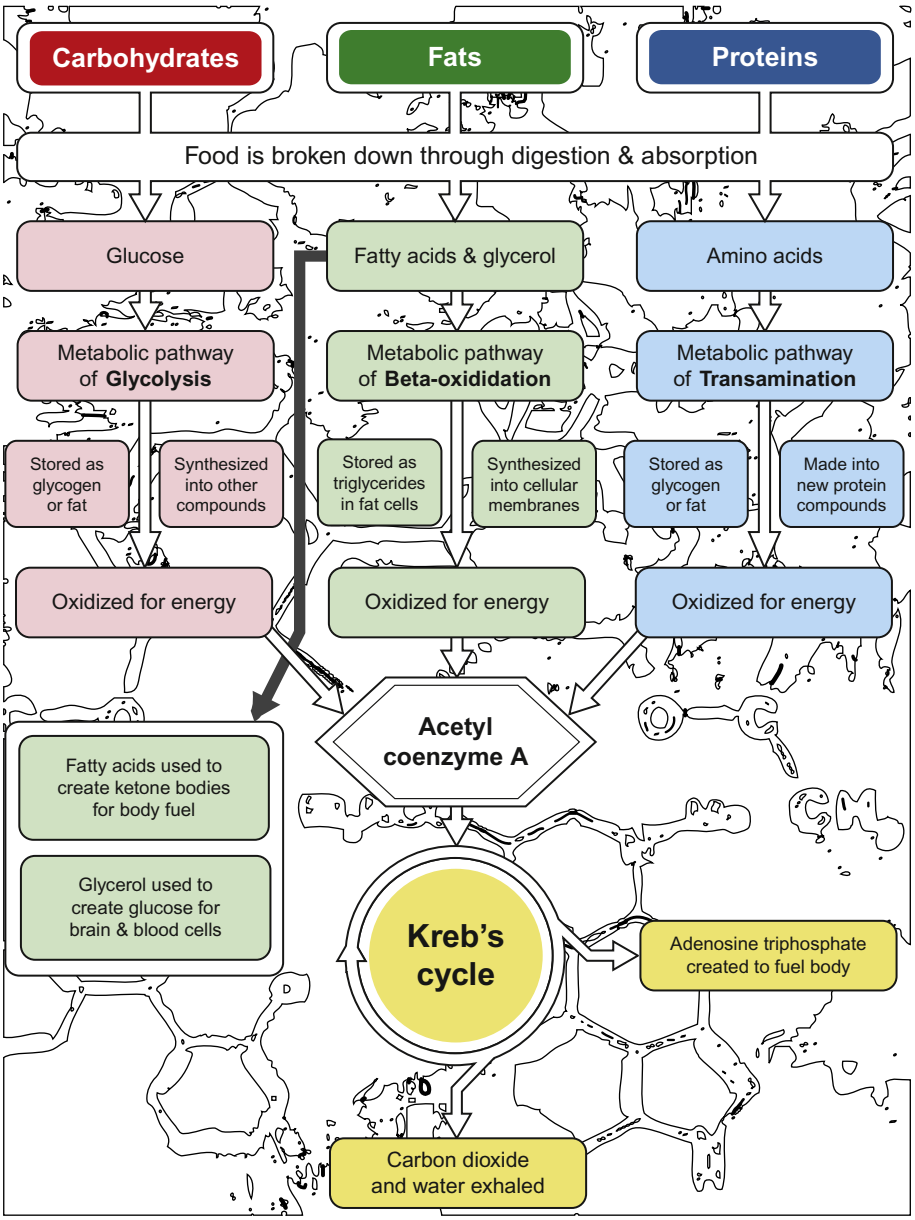


FIG. 1.2 Foods' metabolic pathways.

exhaled, while the hydrogen continues on in other reactions to further form adenosine triphosphate (ATP) molecules and water (Fig. 1.2).

The ATP molecule acts like a miniscule battery allowing it to be used for either molecular growth or energy release. If the cell requires molecular growth or repair (called biosynthesis or biogenesis), the

ATP molecule anabolizes or recombines simple molecules into complex ones; consequently, one has cellular growth or repair. If on the other hand, energy is required for movement or the metabolic process itself, the ATP molecule is degraded back to adenosine diphosphate (ADP), and sufficient energy is released for the required purpose. When the organism or cell is at rest and energy is actually not immediately required, in this case, the reverse reaction takes place, thus storing energy like a battery (Fig. 1.2).

Any excess intake of carbohydrate is first converted to glucose then stored as glycogen—a complex carbohydrate in skeletal muscle and the liver or as fat (triglycerides in adipose tissue) providing a reserve storage of energy. As and when energy stores are again needed, so glycogen is the first reserve to be called upon, and then, if further energy is required and glycogen is depleted, the body then reuses the triglycerides (fat) (Albright and Stern, 1998; UoArizona, 2004; Britannica, 2009; King, 2010; Silva, 2002; UoAkron, 2010; UoBristol, 2010).

1.5.2 LIPID (FAT) METABOLISM

As well as carbohydrates, the body requires other macronutrients like lipids (fats) and protein for energy and growth. And as with carbohydrates, any intake in excess of the body's needs is converted and stored in the body as triglycerols (or triglycerides). Then, in response to cellular energy demands, ingested fatty acids or stored fats can be utilized. Initially triglycerols are catabolized (broken down) in an enzymatic process of lipolysis into fats' component parts, that is, free fatty acid and glycerol. The free fatty acid and glycerol are treated separately. Free fatty acid is oxidized in the mitochondrion organelles[31] of liver cells in a process called β-oxidation.[32] This leads to the formation of NADH and the energy battery ATP. The glycerol on the other hand is converted to glucose in a process of gluconeogenesis,[33] which then becomes available to the citric acid cycle and subsequently is metabolized into NADH and ATP (Merck Manual, 2005; King, 2010; Albright and Stern, 1998; DeMan, 1976).

1.5.3 PROTEIN METABOLISM

Each protein comprises as many as 2000 amino acids connected by chemical links called peptide bonds. So, for this large molecule to be used in the body, it must first be catabolized into its component amino acids. This might sound a little inefficient, as amino acids usually also act as inputs for the building of the body's own proteins. Protein turnover throughout the body, for instance, including new proteins being synthesized and existing proteins being broken down, takes place constantly. However, apparent inefficiency aside, if needed for energy, amino acids are first converted to glucose by gluconeogenesis, primarily in liver cells. These are then converted into pyruvate through glycolysis before entering the citric acid cycle for oxidation and ultimately, the production of ATP. If intake, however, is in excess of the body's natural requirements, proteins are then metabolized to glycogen or triglycerols (fat) and are subsequently stored for use later as needed (Latham, 1997).

[31]In cell biology, an organelle is one of a number of structures with specialized functions suspended in the cytoplasm of a cell.
[32]In biochemistry and metabolism, β-oxidation (beta-oxidation) is the catabolic process by which fatty acid molecules are broken down to generate acetyl-CoA, which then enters the citric acid cycle.
[33]Gluconeogenesis (GNG) is a metabolic pathway that results in the generation of glucose from noncarbohydrate carbon substrates. Gluconeogenesis is one of many mechanisms used by humans and animals to maintain blood glucose levels.

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CHAPTER

FOOD PHASES

2

CHAPTER OUTLINE

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Foodstuffs, as with other materials, exist in three phases or states, as a solid, liquid, or gas. In the kitchen, cooks work with foods in all of these three phases. State transition in food phases refers to changes not only in the three phases mentioned above but also in the physical state or properties of a food. First of all, it must be said that not many foods in the kitchen exist in a single state of homogeneity; there are exceptions of course like sugar crystals and salt and other chemically pure substances, for example. Most foods instead are heterogeneous, meaning their biochemical structures are not all the same. In this way, whole foods and the cook's "dish of the day" are complicated structures comprising a great number of organic and inorganic compounds, which, inevitably, means the food exists in several different physical phases and states. Nonpolar mixtures or compounds, which mainly include the lipids (Chapter 16), exist in a separate phase from the water phase and display their own set of phase transitions and state properties. Lipid phases include crystallization and melting, which, when understood and acted upon, can give chosen characteristics to the cooks' repertoire especially in things like dairy products, spreads, and certain fat-based emulsions (Roos and Drusch, 2015).

Lipids aside, this section will concentrate on phase transition of the aqueous state as this represents the largest of the food pool. In particular, we examine phase and state transitions with regard to low-liquid and frozen foods with one eye on, inter alia, food quality and shelf life. Indeed, water-based food systems are comparatively well understood in terms of phase transitions and are successfully applied in the preservation of foods, both at the industrial and the home or cooks level. This knowledge is employed in things like freezing and dehydration to remove water from foods and by extension offering prolonged shelf life and microbiological stability. Further, in employing such treatments, it can be seen that most frozen or low-water foods, irrespective of their pretreatment phase or state, ultimately become solids (Roos and Drusch, 2015). Examples of solid, low-water, noncrystalline foods include

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things like breakfast cereals, food powders, confectionery, potato crisps, frozen solids, and of course dehydrated foods. Lipid phase aside, the low-water content of these organic frozen solids[1] and low-water foods are mostly composed of partial or fully water-soluble carbohydrates and proteins.[2] In turn, while these foods are devoid of much of their water content, the reaction of the remaining water and soluble nutrients and external factors like humidity and light collectively determine the physicochemical state of the final product.

When it comes to phases, the effects of temperature, time, and water content have a great bearing on the physical properties and the quality of particular foods. Indeed, for the cook, understanding phase and state transitions of foods, especially in terms of the relationships vis-à-vis structural relaxation, molecular mobility, and stability, will undoubtedly help the cook understand better food processing and storage techniques (Roos and Drusch, 2015). As mentioned, this is of great benefit to cooks as they often mix solids with other solid ingredients, solids with liquids, solids and gases, or multiples of all these phases to create edible dishes. The heating/cooking or cooling of ingredients too helps food to further transition from one state to another, for example, boiling water to create vapor or melting firm gelatin to create a liquid (Talarczyk, 2009; Vaclavik and Christian, 2014). One thing to note about cooking is that many such transitions are irreversible like cooking eggs, cakes, and breads that when cooled do not revert back to their original phase. Others however do like the melting of an ice cream or a simple panna cotta. It is often during the heating or cooling processes that the bonds of foods are manipulated in order to change the phase of the food. In this case, the bonds between the molecules help one to distinguish between each of the states of phases (Belitz et al., 2009; Roos and Drusch, 2015).

2.1 SOLIDS, LIQUIDS, AND GASES

In each of the phases, the molecules are constantly on the move. The bonds of a gas are weaker than a solid and are freer to move around, while a liquids' bonds are stronger but still not as strong as a those of a solid (Talarczyk, 2009). A large proportion of foods in the cook's kitchen are solids, whether a piece of meat, fruit, or vegetable, seeds or nuts, etc. In fact, solids are distinguishable because as they all have a definite shape, which is not easily changeable. This is because the molecules in a solid are packed tightly together and cannot move around so easily; in this sense, they are dense materials/foods. As heat is applied, so many solids become more flexible; this is because atoms begin to move more freely allowing the food to expand or move around little and even melt. The texture of (solid-like) foods varies from extremely light and airy foams to very hard-boiled sugars (Barham et al., 2010; Belitz et al., 2009). In liquids, molecules are densely packed together although not as much as with solids; this allows liquid molecules to move about and flow more freely. When cooled enough (below freezing), most liquids will become a solid, while heating them allows the liquid to become a gas. Some solid foods produce gas bypassing the liquid phase;

[1]In frozen foods, most of the water content exists in a separate, solid ice phase.
[2]Many carbohydrates and proteins are partially or fully soluble in water, while lipids in general are less so. In fact, lipids' solubility varies greatly among types, with some being only partially soluble while others not at all, due to most being hydrophobic in nature.

however, most gases come from liquids. By way of example, take water or stock that when heated, the molecules move around faster and faster and are able to break the bonds that keep them in a liquid state. As this happens, vapor is released into the air. In fact, it does not have to be heated to any great degree for vapor to be released and depends on its volatility—(Section 3.3). Gases have no definite shape or size; they simply disperse or spread with no particular pattern. Gases are present in the air even though we cannot see them; the aroma from the stock whether chicken, beef, or fish lets us know that gases are present (Talarczyk, 2009).

2.2 MULTIPHASIC FOODS

Most foods rarely exist in a single phase; rather, they exist in multiphasic form. In scientific parlance, this can be thought of in terms of a substance composed of very fine particles being "dispersed" in what is sometimes described as a "dispersed" medium or alternatively a "continuous" phase. Put another way, dispersed phases are the suspended particles, while continuous phases are the medium of suspension. In general, this describes colloids in which small particles are suspended in a liquid, solid, or gas medium. Depending on the properties of the continuous and dispersed phases, multiphasic foods can belong to one of eight possible types of colloids. Table 2.1 classifies these eight states based on the physical state of the dispersed phase and the continuous medium.

Table 2.1 Various Colloidal Systems

Dispersed Phase	Continuous Phase or Medium	Colloidal System	Examples
Solid	Solid	Solid sols	Solid dark chocolate, liver terrine
Solid	Liquid	Sols	Starch in water, proteins, blood, melted chocolate gelatin
Solid	Gas	Aerosols of solids	Smoke, clouds, fog
Liquid	Solid	Gels	Cheese, butter, jellies, jam, blancmange
Liquid	Liquid	Emulsions	Milk, vinaigrette, mayonnaise
Liquid	Gas	Aerosol of liquids	Fogs, clouds, mists
Gas	Solid	Solid foams	Meringue, honeycomb, marshmallows, bread, sponge cakes
Gas	Liquid	Foams	Bread dough, soufflés, whipped cream, soda water

Note: *When the continuous phase is a gas, the dispersed phase can be solid or a liquid but cannot be a gas simply because colloids are heterogeneous mixtures, so when a gas is mixed with another gas, it forms a homogeneous mixture rather than a colloidal suspension. Source, compiled from multiple data sources (Barham, P., et al., 2010. Molecular Gastronomy: A New Emerging Scientific Discipline. Chem. Rev. (110), 2313–2365; Belitz, H., et al., 2009. Food Chemistry, fourth ed. revised and extended edition. Springer; Talarczyk, M., 2009. Edible transformations. Science and Engineering in the Kitchen, vol. 3. Yale-New Haven Teachers Institute, New Haven).*

Good examples of sols are blood, melted chocolate, and cream so long as the fat particles are cold enough to be solid (Barham et al., 2010). More specifically in the kitchen, sols are often found as sauces where the thickness of the sauce is determined by the viscosity of the liquid and a higher concentration of solid particles. By contrast, the perceived creaminess of a sauce tends to be enhanced by having a higher proportion of small particles.

A solid sol can best be described as a solid phase dispersed into solid continuous phase. Dark chocolate is a prime example here where two solids, sugar and cocoa powder, are dispersed into the continuous solid fat phase. In the case of solid sols (foods), cooks need to consider whether they are looking for a hard finish like a well-tempered chocolate wafer or whether a ductile liver terrine. In each case, it's the actual continuous solid phase (in both cases, "fat") that determines the overall texture (or hardness/ductility) and mouthfeel of the food (Roos and Drusch, 2015).

A gas dispersed into a solid medium is called a solid foam. In the kitchen, the range of sold foams available to the cook are quite vast. One common component though is that the medium (continuous phase) will nearly always determine the textural properties in the mouth. For example, one has hard and brittle foams like meringue or honeycomb (cinder toffee) or soft (but nonetheless solid or ductile foams) like melt in the mouth foamed chocolate bars. Then there are the semi-solid, ductile foams like bread and sponge cakes, while further, more solid or firm continuous phases are responsible for tougher foams like stale or toasted bread. Lastly, although the medium generally determines the actual mouthfeel, it can generally be said that the size of the gas or air pockets determine how "light" the product is. In other words, the smaller and more dispersed the air or gas is, the better, smoother, or lighter the food is perceived.

Emulsions are also popular in the kitchen; in fact, they form the largest group of food colloids available in the cooks' repertoire. They are formed when a liquid phase is dispersed into another liquid phase. These include many sauces and dressings in the kitchen. As with sols, the cook is looking for "thickness" and "creaminess," as well as "stability" within the emulsion. Importantly, the overall texture and mouthfeel is usually determined by the whole product and not the individual components themselves. When it comes to stability of emulsions or all food colloids for that matter, one can say that all emulsions and food colloids are more or less unstable. A prime example here is the humble vinaigrette, which, given enough time, will eventually separate out to form two completely separate substances—oil and vinegar.

The stability of a structure can be thought of as its life span or shelf life, that is, before any severe degradation in the product is visible or detectable through the senses. A professional cook, for instance, uses his/her own experiential knowledge of stability and has built these into numerous recipes, like an emulsifier in ice creams, or pectin in jams, for instance. This also applies to new and novel recipes that a creative cook might consider. Of exceptions are the multitude of processed foods such as "bought-in" mayonnaise, in which case because of added stabilizers its stability is greater than its usable shelf life. Lastly, it is worth noting the integration of electronic repulsion between particles as this often is the main stabilizing effect in certain foods. Take mayonnaise once again, through harder and more vigorous beating of the emulsion so the droplets become charged. In turn, the increased charge on the droplets can significantly affect stability.

2.3 PHASE SEPARATION

Phase separation, or the severe degradation of structure in liquid-liquid, sols, and emulsions, is perhaps best viewed in terms of the various mechanisms of phase separation. In an emulsion where Brownian motion[3] is not sufficient on its own to keep the droplets suspended by themselves, so the larger molecules (like fat in milk) will eventually settle out (Mörters and Peres, 2010). Another example includes an emulsified vinaigrette where water droplets settle out or in milk where the fat droplets will migrate upward effectively creating a band of cream on top of the milk (Barham et al., 2010; Vaclavik and Christian, 2014).

In scientific parlance, the simplest approach to calculating stability of an emulsion is to find the "steady-state drift speed" of a droplet. Essentially, this notion boils down to the size of the droplets and the densities of the dispersed and continuous phases. Collectively, this determines something called the "drift velocity," that is, the time it takes for particles to separate out. As a rule, the smaller the particles and the more viscous the liquid, the slower the drift velocity or separation. By reducing the drift velocity, it takes longer for a mixture to separate out and the more stable the emulsion or colloid becomes. In industry, one example of achieving smaller droplet sizes is the process of homogenization. This is commonly applied to milk in order to reduce the size of all molecules present making it slightly more viscous; with a slower drift velocity and in the process, it takes longer to separate the cream and milk phases. In the kitchen, the aid of a homogenizer would greatly benefit the cook. Or alternatively, the stability of substances can be further improved by controlling the viscosity of the continuous phase. This can be achieved through the thickening of sauces using starches, cellulose, locust bean, and gums (Barham et al., 2010; Roos and Drusch, 2015).

While droplets in the dispersed phase separate out naturally under gravity, they can also accumulate into unwanted particles of a larger size through aggregation or coalescence. Due to their increased size, this may also promote separation. For example, in the case of a vinegar/oil dressing, coalescence usually takes place once the droplets become more closely crammed together. Partial coalescence is an intermediary state between complete fusion and aggregation. However, not all coalescence is a bad thing. In whipped creams, for instance, the fat globules reach a partial coalesced state, which then act as a solid-like network that gives whipped cream its physical stability (Barham et al., 2010).

In another phenomenon, a process called Ostwald ripening (or particle coarsening) occurs in the continuous phase. As with the dispersed phase, smaller, less stable droplets (molecules) become larger droplets. This is especially fast if the dispersed phase is highly soluble in the continuous phase. The result is eventual net diffusion—the movement of molecules from an area of high concentration to an area of low concentration. Ostwald ripening is very common in a wide range of phase-separating instances. This can be seen in foods that have been stored for long times such as frozen desserts like ice creams in which the recrystallization of water gives old ice creams a gritty, crunchy unpleasant texture (Pronk et al., 2005). So how does phase separation help in the average kitchen. By understanding the nature of the different phases and the effects of heat, time, and physical properties of these phases gives cooks an understanding and by extension the tools to help slow the process of phase separation. Although, that said, it is never possible to eliminate the tendency of small droplets of dispersed phases

[3]Brownian motion is the random and erratic movement of a particle as it receives a jolt or displacement, caused, for example, by other particles bumping into it or through an external force whether physical, thermal, or others.

from growing larger over time (Barham et al., 2010). However, one benefit of the commercial kitchen is the fact that dishes can be prepared and eaten over small periods of times. This cannot be translated to the wider food industry as the commercial retail industry demands products with life spans in the region of days or even months. In such circumstances, it is often necessary to introduce additional "stabilizing" or "emulsifying" compounds.

2.4 PHASE STABILITY

Regarding the stability of colloidal systems, while many are fairly stable others need a little assistance. In this regard, we are lucky in that there is a wide range of food molecules that aids in this respect. These substances are divided into two categories: emulsifiers and surfactants.[4] Typical examples include polar lipids (Chapter 16) and globular proteins.[5] These are present in an array of foods such as egg yolks (phospholipids (lecithin)), egg whites (globular proteins), milk powder (caseins and whey proteins), soybean (phospholipids and proteins), and flaxseed (flaxseed mucilage[6]). These all work by reducing excess surface tension between phases, thus decreasing the potential for phase separation. Furthermore, the emulsifiers and surfactants also act on the formation of emulsions, for instance, and act on the stability of the final product. Other stabilized products that benefit from the above also include mayonnaise, hollandaise, and béarnaise (through egg yolk lecithin) and vinaigrette (which can be stabilized by mustard). However, looking at the problem of stability within say, a restaurant environment, then the long-term stability of foam-based products, for instance, is not necessarily that important. Therefore, it is possible to prepare and use foods that are intrinsically unstable in their final state. This is because such products will be used soon after they are made and are not held in long-term storage. As a result, milk-based foams and other liquid- and protein-based foams are becoming more and more popular with experimentalists and aficionados alike.

2.5 PHASE TRANSITION

Phase transition is the physical change(s) that take place of materials and the subsequent effects this has on the physical property of the changed phase. This can be any transition from solid to liquid, solid to gas, liquid to gas, etc. caused by changes in pressure and/or temperature. The term "state" transition in food phases refers to those changes in the actual physical state or properties of a food caused by many factors such as melting and crystallization, protein denaturation, starch gelatinization, and retrogradation. Take, for example, a thick viscous sauce, once heat is applied (depending on the ingredients used), the sauce might become runnier/thinner (Roos and Drusch, 2015). Both, phase and state transitions in this respect, are important notions within food production and usually involve time, temperature, and water content of foods. While some occur naturally, others are purposefully adapted in an effort to improve quality of the product or its shelf life.

[4]Surfactants are substances that tend to reduce the surface tension of a liquid in which it is dissolved.
[5]Globular proteins, named after their shape, are one of the common protein types: other protein types include fibrous, disordered, and membrane proteins.
[6]Mucilage is a viscous secretion.

Furthermore, in phase transition of foods, physical states are described in terms of molecular mobility. In apparent solid or crystalline foods, molecules are not strictly immobile, but rather their movement is greatly restricted (Roos, 2010). In "rubbery" foods where there is no solid crystal phase, molecules are more mobile, although they are still somewhat limited in movement due to the viscosity of the medium in which they exist. For example, molecules in liquids and gases are "very" to "extremely" mobile, respectively. When it comes to natural substances or the cook's creation, for example, phase transitions have to deal with complicated substances comprising a large group of organic compounds. Unlike water though, whose phase transitions are fairly straightforward and well documented, natural compounds and food dishes are complex compositional mixtures of physical forms and states (Roos, 2010). That is, they are extremely heterogeneous comprising multiple, varied phases in their physical makeup. Consequently, knowledge of biomaterials and food properties is therefore of great benefit to the food scientist/engineer and to some degree the cook (Roos, 2010).

2.5.1 MOLECULAR MOBILITY AND GLASS TRANSITION

Water, one of the most abundant substances on earth, is also an essential constituent of all foods. Water or moisture in foods, while important, can also greatly affect a products shelf life, assuming favorable temperatures and pH values. Furthermore, water in foods is either "bound," meaning it is attached to molecules, or "free" water, which is, as the name implies—free. It is this free water that is the problem for foods' longevity as it allows for spoilage by microorganisms and chemical reactions. In microorganism spoilage, water is necessary to dissolve soluble foods allowing easier digestibility of such foods for molds, bacteria, and yeast cells that contaminate the food, for instance. It also allows for easy excretion of microbial waste products leaving behind unpleasant flavors at best or potential harmful toxins at worst. Thus, shelf life of many foods is regulated by the amount of free water in foods and time, temperature, and pH. This can be addressed and the shelf life prolonged through the process of drying, evaporation, and concentration of foods or by freezing, that is, rendering water unavailable to spoilage bacteria. Consequently, when it comes to water and the stability of food, molecular mobility (Mm), is the name used to describe the above phenomena. Key to the concept, as the name suggests, is the movement of molecules within a food substance. The notion of slowing or restricting a foodstuffs molecular movement of water promotes longevity. A molecule's ability to move within a substance is related to a liquid or foodstuffs viscosity (its water content); the more viscous a substance is, the less the water content and the more restrained the movement of molecules. Further still, mobility is altered with temperature. That is to say with higher temperatures—the greater the thermal energy—the faster the molecules move and vice versa. To completely cease molecular mobility or, more precisely, to drastically reduce movement to almost nothing, one must create a crystalline structure such as salt or sugar or in the case of freezing tiny ice crystals. In crystalline structures, because of the lack of movement, spoilage microbes cannot exist. However, most food or food elements do not form such crystalline structures so Mm is always present. Instead, if water content is reduced, solutions and other foodstuffs can become viscous and eventually behave like rubber (solid-like). If more water is removed, the rubberlike quality gives way to firmer or near-solid foods until the critical point is reached whereby mobility essentially ceases (reduces to almost nil). In this state, the foodstuff is considered to be in a "glassy" or hard structure.

Both glassy and rubbery materials are thought of as amorphous solids. Glass-liquid transition (glass transition) is a reversible transition or change in an amorphous[7] substance, in this case—food. Building on the previous section, glass transition is ultimately related to the molecular mobility of food and helps to explain how drying or freezing[8] alters or affects the storage stability of foods. The change in temperature between states is referred to as the glass transition temperature (Roos, 2010; Roos and Drusch, 2015). The glass transition temperature is the temperature required for an amorphous solid to become soft upon heating or brittle upon cooling. Such food phases can be reversed with the reintroduction of water and temperature, although the temperature involved would be lower owing to the plasticizing[9] effect of water (Kumaga and Kumaga, 2009; Fontana et al., 2008). The actual glass transition temperature that is needed to affect this state change varies depending to a large extent on the substance and the water content of the food itself. Consequently, manipulation of the temperature and water content of foodstuffs is of great importance in the food industry, especially when it comes to production, transportation, and preservation.

Glass transition states have been used to study food products longevity and have been used alongside water activity and physical and chemical changes, to determine stability in foods. Moreover, such phenomenon is also associated with factors such as crystallization, sticking, caking, nonenzymatic browning, oxidation reactions, and microbial stability of many foods (Bhandari and Howes, 1999; Balasubramanian et al., 2016). Some simple solid amorphous glassy foods, for instance, include breakfast cereals like cornflakes or rice crispies, certain confections, and dehydrated foods that have solid but porous, brittle structures. While these foods are crispy in the glassy state, this trait may be lost as a result of water absorption during storage at high relative humidity (Roos, 2010).

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[7]In scientific terms, "amorphous" means a lack of a crystalline structure, that is, something without solid shape or form.
[8]Freezing can be thought of in a similar process to drying foods. Water first crystallizes then slowly leaves the food in an increasingly dehydrated environment.
[9]In foods, water plasticizing is a nonfat, predominantly hydrophilic (water loving) process that softens or makes food flexible (plasticity). This takes place in the rehydration of dried foods like pasta and dried mushrooms, etc.

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CHAPTER

TASTE, FLAVOR AND AROMA

3

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In one sentence, it can be said that "flavor" is largely a combination of two different sensations—taste and smell. Yet, before we go into any great detail about flavor, it is worth taking an overview, brief as it may be, of the way in which we actually perceive or sense food flavors themselves. While much of what we like and dislike remains subjective, it is nevertheless true to say we all share the same set of senses that are employed to interpret taste, aroma,[1] flavor, and texture of the food we eat.

When we consider taste, we invariably think of our tongues and the sensations of salts, sweet sugars, sour acids, savory amino acids, and bitter alkaloids; yet, much more is at play here than just our palate and what it comes into contact with it. In reality, one might be surprised to learn that the majority of our nontongue senses are utilized in the appreciation of the food we eat (New World Encyclopedia, 2015). Take sight, for instance; food has visual appeal; however, compare the visual effect appeal of say a fried egg dyed red with that of a medium cooked steak cut in two, and it's not difficult to see which one gets

[1]An aroma compound is also referred to odorant, aroma, or fragrance. In its basic definition, it is a compound that has a smell or odor. A compound has a smell or odor when it is volatile, so it can be transported to the olfactory system in the upper part of the nose.

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the gastric juices flowing. The same could be said when fine dining with China plates and silver cutlery versus paper plates and plastic cutlery; in this sense, the expectation on the palate is tangible (Belitz et al., 2009; Barham et al., 2010). Sight and touch aside, the most significant senses when it comes to our appreciation of food remain the chemical senses comprising taste, smell, and chemesthesis[2] (Section 3.5). These three unique and distinct systems facilitate the passing of information about the presence of chemicals in the immediate environment. Taste (gustation) detects chemical compounds using sensors mostly in the mouth. Smell (aroma or olfaction) detects airborne chemicals, both externally through the nasal passage and from those compounds emitted from foods masticated[3] in our oral cavity—the retronasal pathway. The retronasal passage (*next sections*) is the path in olfactory perception that is just as important as, if not more so than, the nasal passage. On top of this, there is also chemesthesis involving such things as astringency and pungency (see Fig. 3.1). Lastly, before we go any further, it is worth noting that in order to enjoy the holistic sense of food, we have at our disposal, an overall sense of aroma/smell taste and flavor. In turn, to aid in these processes, we have 9000 taste buds and several million olfactory epithelium neuron receptors (New World Encyclopedia, 2015; Murray, 2017; Heilmann and Hummel, 2004).

The complex smelling and tasting processes begin the moment molecules detach from food compounds and reach our nose or mouths. The fact that we can differentiate between thousands of tastes and smells is a result of complex processes that activate various combinations of odor and taste receptors

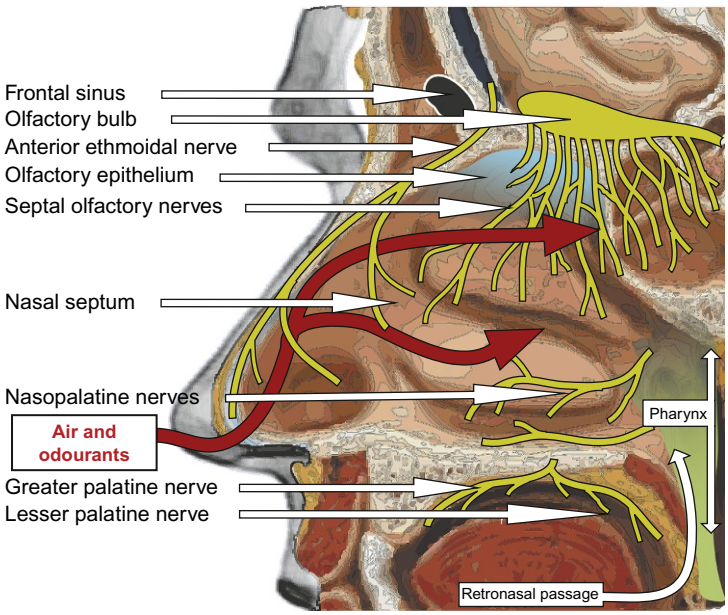


FIG. 3.1

Aroma and taste receptors.

[2]Chemesthesis arises when certain chemical compounds activate receptors normally associated with other senses that mediate pain, touch, and thermal perception, that is, false heat and false coolness.
[3]Mastication is the process of chewing food, breaking it down.

(Murray, 2017). It is also worth noting too that while the neural pathways of aroma and taste stimuli are different, the two often work in unison, especially at the dinner table. Indeed, much of what people perceive as flavor has a lot more to do with the aromas of food and drinks than people might expect. It is also noteworthy that much of what is eaten is connected to the areas of the brain responsible for emotions (Murray, 2017).

3.1 SENSE OF TASTE

There is one common misconception that must first be addressed, and that is, many believe that taste cells that respond to different tastes are bundled together in specific regions of the tongue (PubMed, 2016). In reality, taste cells scattered across the tongue and throat are able to sense a range of tastes (MSUN, 2009; Menche et al., 2014). Gustatory cells, or more commonly taste buds, are on the tongue, the palate (including the soft palate), and areas in the upper throat—in particular the pharynx and laryngopharynx. These number about 2–10,000 depending on who one reads (Ahn et al., 2011; PubMed, 2016). However, as we age, so we lose a few of these gustatory cells over time, especially after the age 50 or so. Every bud contains 10–100 receptor cells (once again depending on who one reads), each able to distinguish between all of the five basic tastes (MSUN, 2009; PubMed, 2016). At the tip of these buds is an opening onto the tongue. Within the bulb itself, the taste cells' receptor proteins (chemoreceptors[4]) embedded in the taste cell membranes function either by physically binding to a tastant[5] (sweet, bitter, and umami) or by acting as a channel to allow ions to pass through to other taste cells (salty and sour). It is these interactions that trigger a torrent of signals to the brain giving clues as to the flavors and complex compounds being tasted (DeMan, 1976). One's capacity to taste food and drink occurs when tiny molecules are released by chewing or drinking, which stimulate special sensory cells in the mouth and throat, which in turn send messages to the brain.

The five basic taste receptors are the following:

- *Sweetness*—which is usually regarded as an agreeable taste generally connected to sugars, some proteins, and other similar substances. It is also often associated with aldehydes and ketones containing the carbonyl group. Sweetness is detected by a variety of G-protein-coupled receptors. G proteins (guanine nucleotide-binding proteins) are a protein group inside cells that act as molecular switches conveying, in this sense "sweet" signals from stimuli outside the cell to its interior. The G protein in the gustatory system, specifically among the taste buds is "gustducin." Sweetness of a particular food substance is usually compared with sucrose or table sugar in which sugar has an index of 1 (UoD, 2017).
- *Sourness*—while the mechanism by which animals and humans detect sourness is still not fully comprehended, we can say that the tartness or sourness can be thought of in terms of acidity from substances such as vinegar, some unripe fruits, and lemon juice. According to the University of Delaware (UoD, 2017), although proteins are involved, evidence suggests that the protons from sour foods can enter the sour-taste cells directly without protein couplers. This ionic (proton) transfer can then trigger electric responses (neurotransmitters) in return. In this way through the

[4]Chemoreceptor is a sensory cell or organ responsive to chemical stimuli.
[5]A tastant is the masticated food molecule being tasted.

direct and indirect hydrogen ion intake. As with sweetness, the sourness of substances is measured or relatively compared with a dilute hydrochloric acid solution with a "sourness" index of 1. Using this scale, we can see that in decreasing levels, the sourness of tartaric acid, citric acid, and carbonic acid have indexes of 0.7, 0.46, and 0.06, respectively.

- *Saltiness*—it is a taste sensation produced mainly by the presence of sodium chloride (common salt) and other sodium ionic or salt compounds. These in turn belong to the alkali metal group on the periodic table. The further from sodium the substance is, the different salt "profile" is created on the palate—this is usually manifest in a less salty taste. As with other taste sensations so the index of saltiness is connected to sodium chloride that acts as a comparative measure of saltiness. Sodium chloride has an index of 1; potassium chloride, an alternative used as a salt substitute, has a saltiness index of 0.6 (UoD, 2017).
- *Bitterness*—the opposite of acids are the bases (alkaloids). These are the bitter tones that many people find unpleasant. Many alkaloids taste bitter, and for good reason, a significant number of these natural compounds are toxic. Thus, it has been suggested, particularly by evolutionary biologists, that a distaste for bitter things evolved over time allowing people to avoid toxicity and accidental poisoning. One of the more sensitive of tastes and in moderation can be quite agreeable. Common bitter foods and beverages include coffee, beer, bitters, bitter gourd, citrus peel, chicory, and quinine (found in tonic water) (UoD, 2017).
- *Savoriness (umami)*—it is difficult to describe the savoriness that is umami, so we have added the following longer description (MSUN, 2009; Ishimaru et al., 2006; PubMed, 2016).

Traditionally, it was long thought that there were only four taste receptor types on the tongue: salty, sweet, bitter, and sour—it turns out that there is a fifth—umami (Kurihara, 2009). Umami is a word adapted from the Japanese meaning a "pleasant savory taste." The subtle umami meaty or savory flavor derives from L-glutamate (an amino acid) often abbreviated to glutamate-rich foods—and while virtually all foods contain some degree of glutamate, there are some foods in which it is rich such as Roquefort cheese, seaweeds, tomatoes, and other foods (Field, 2011). Glutamates are naturally broken down through cooking or in the enzymatic processes in meat—it also happens naturally in fermented or aged foods like soy and fish sauces, Parma ham, and various natural foods like walnuts, seaweed (especially kelp), and mushrooms. The sodium salt of glutamic acid, a nonessential amino acid, is known as monosodium glutamate (MSG), also identified as sodium glutamate. This is often added to food to enhance food flavor especially in the industrial food sector, this is so even despite the MSG backlash over the last few years. Nowadays, MSG is made through the fermentation of molasses and sugar beet and is one of the world's most popular additives. The taste itself is difficult to describe; however, the Macmillan Dictionary provides a good place to start:

> Umami is subtle and not generally identified by people when they encounter it, but blends well with other tastes to intensify and enhance flavours. It therefore plays an important role in making food taste delicious. If it helps to visualise, a familiar example of the umami taste in action is parmesan cheese, maybe not as appetising as some cheeses when eaten on its own, but creating a delicious taste sensation when sprinkled on a dish of steaming spaghetti Bolognese
>
> **(MacmillanDictionary.com, 2010).**

There are of course other sensations that are experienced through the action of chemesthesis, and these include false heat and coolness including astringency and pungency (see also Section 3.5).

3.2 SENSE OF SMELL: THE OLFACTORY SYSTEM

Of the two principal senses that detect chemicals, smell and taste are an important arsenal of tools that allows one to discern food or liquid flavor profiles. Indeed, it has been said that

> only after taste is combined with smell is a food's flavour produced
>
> **(PubMed, 2016).**

Our sense of smell, just like our sense of taste, is part of our chemosensory system (the chemical senses) (Barham et al., 2010). The sense of smell in this case can be described variously as aromas, fragrances, odors, or odorants, etc. While taste receptors in the mouth detect small molecules by which foods are determined, receptors of the olfactory system (aroma/odorant receptors) detect volatile molecules in the air whether from liquids, gases, or even solids. It's worth noting too that people's sensitivity to aromas varies quite significantly between individuals.

In short, there are two pathways by which a volatile substance reaches the olfactory sensory cells in humans. Firstly, the orthonasal route whereby the chemical molecule to be smelled travels through the air, as it enters the nostrils and then travels onto to the nasal receptors called the olfactory epithelium. Secondly, the retronasal route, whereby odorants enter the mouth, then spreads through the nasopharynx that is located behind and above the soft palate and then travels on toward the olfactory epithelium then back out through the nostrils (Heilmann and Hummel, 2004; Halpern, 2009). As a result of the two pathways (ortho- or retronasal), odors, when presented, tend to be perceived differently.

The complex procedure of smelling starts the moment volatile molecules detach or are released from substances from which they belong (Murray, 2017). The sense of smell happens when aromas enter the nose (orthonasally) and are detected by olfactory receptor cells (many millions of them) located at the top of the nasal cavity properly called the olfactory epithelium neuron cells,[6] (Fig. 3.1) (New World Encyclopedia, 2015). The olfactory epithelium itself is composed of three types of cells: basal cells, olfactory receptor cells, and supporting cells, all of which are covered by the mucous membrane. This membrane is also the area in which small filaments dangling from the epithelium neuron cells known as "cilia" reside. It is these cilia cells, more specifically, the membrane receptors on the cilia that bind the chemical stimuli, that collectively determine a particular aroma (Murray, 2017; Purves, 2004). The basal cells are newborn olfactory receptor cells that are transformed over a period of approximately 40–60 days, to become new olfactory receptor cells—replenishing those that come naturally to the end of their life cycle. This is in contrast to the 10-day turnaround for the gustatory cells. Each olfactory receptor neuron (or cell) interacts with just one specific type of aroma molecule (or part of that molecule), although that said, the same molecule (different sections of which) can potentially bind with other receptors, thus interacting with more than one different receptor. This combination or pattern of the receptor types (a sort of code) ultimately triggers an aroma perception specific to that molecule (New World Encyclopedia, 2015; Heilmann and Hummel, 2004).

As well as the potential for aromas to be detected orthonasally via the nasal passages directly onto the olfactory epithelium, smells are also detected retronasally. This is the process when molecules are inhaled through the mouth and exhaled through the nose stimulating the same olfactory epithelium (Heilmann and Hummel, 2004). Retronasal identification is also the case whereby the food one eats

[6]Olfactory receptors are in fact neurons rather than cells. This is different from the gustatory receptors that are cells.

is masticated by chewing in the mouth, mixed with saliva, and releases volatile molecules that are then detected retronasally.

Howsoever, aroma molecules are released; all molecules must first be dissolved in the mucosa membrane that covers the epithelium receptor cells containing mucopolysaccharides, salts, antibodies, and enzymes. Once assimilated, dissolved aromas/odors stimulate specific neuron cell receptors (cilia), which in turn identify particular aroma molecules through their unique chemical structure. This "lock-and-key" fit (which is still debated by scientists) relays specific aroma patterns from the olfactory epithelium cells through the skull bone and to the olfactory bulb (part of the limbic system[7]) (Barham et al., 2010; Ahn et al., 2011).

Going back to the cilia (the aroma receptors) in the mucosa membrane, it is understood that the cilia are stimulated necessarily not only by a single molecular structure of a molecule but also by groups of structurally similar molecules/compounds (Murray, 2017). In this way, different smells can be distinguished quite easily because one aroma receptor might recognize a range of aromas, while a number of different aroma receptors might collectively recognize just one aroma. Consequently, the pattern or combination of aroma receptors activated gives one the ability to leverage the number of smells that we can detect. Not surprisingly then, thousands of different odors/aromas can be separated this way. As touched upon earlier, people can distinguish upward of 10,000 aromas or odorants; some are at concentrations so low (in the order of a few parts per trillion), as to defy belief. Consequently, it is not difficult to see that aromas are very complex things replete with nuances and vagaries of top, middle, and bottom notes (*next section*).

Another pathway to the olfactory epithelium happens when we chew our food. As food is masticated, so saliva mixes with the food, allowing certain molecules to become volatile and released. These molecules find their way to the olfactory epithelium retronasally (Barham et al., 2010; Heilmann and Hummel, 2004; Bender et al., 2009).

So, as discussed, the nose plays more of an important role in eating food than many might consider. We have also seen that when we taste food, it stimulates special nerve cells in both the nasal cavity. More specifically though, when we talk of aroma, we are talking of the ability to detect airborne particles that come directly through the nasal passages or from the back of the mouth/throat passage (retronasal transport) to reach the olfactory epithelium cells. These neurons then pass through the skull to reach the olfactory bulb, where they are identified. The extent to which aroma plays a part in the overall taste perception can simply be tested by tasting foods while holding one's nose closed. This has the same effect as when one has a cold; in this way, it can be seen that not all the senses are being used to the fullest; as a result, food can sometimes seem tasteless. In fact when it comes to the actual separation of taste senses, it has been estimated that only 10%–20% of a tasting experience comes directly from the tongue whereas the remaining 80–90% comes from the smell or the aroma (Ahn et al., 2011; MSUN, 2009). In this way, the words "taste," "flavor," and "aroma" are often used interchangeably. To further elucidate this, in perspective, we have around 5–10 million receptors capable of detecting aromas/smell, while we only have 2–10,000 to detect taste (Murray, 2017; PubMed, 2016). Smell or aroma makes up a large part of our sense of taste (Thierry and Hannon, 2014). Hence, flavor

[7]The limbic system is a collection of connected structures residing close to the middle of the brain. Linked within the central nervous system, these structures work together affecting a wide range of specific behavior including emotions, motivation, and memory.

results from the perception of taste and odor-active volatile compounds. It is also important to note that while taste and smell processes are quite separate and distinct, the sensation of eating and drinking work together in harmony sending the brain simultaneously signals of taste, flavor, and aroma.

3.3 VOLATILITY AND AROMA NOTES

Before one can fully appreciate the specific aromatic characteristics of smell, one must first ponder the notion of volatility, that is, the ability of a compound (liquids or solids) to become a gas or vapor—the ability of something to be smelled. Volatility is an important concept not only in organic chemistry in general but also to all flavors and fragrances in general, which, by definition, must be volatile to be smelled. At its very simplest, we can think of volatility as the ease with which a substance vaporizes. The weaker the forces holding the molecules together, the higher the volatility of a liquid or solid, the easier it becomes a gaseous vapor that releases molecules into the air. It is this quality, which allows one to smell a substance (Belitz et al., 2009; Vaclavik and Christian, 2014).

From this understanding, it can then be said that when it comes to volatility, there are three main factors that need to be considered—a compound's molecular weight, the temperature of the item to be smelled, and its intermolecular forces of attraction. The first is fairly straightforward in that it doesn't take a great leap of faith to understand that heavier molecules will require more energy to vaporize and thus are relatively lower in the volatility scale. The second is related to the first; that is, the application of heat or a change in atmospheric pressure or both are required to assist in volatility. This taps into the fact that higher temperatures excite molecules more, giving them the all-important "energy kick" that helps make the transition between a substance and vapor that much easier (Vaclavik and Christian, 2014). So, whatever the initial volatility of a substance is, as one increases the temperature, so the volatility of that substance increases too. The third item, the intermolecular forces, relates to the strength of the bonds that bind atoms and molecules alike.

Armed with the above, we can say that

- volatility is the force it takes for a substance, whether liquid or solid to release molecules—sometimes referred to as vaporization;
- all substances have different volatility thresholds;
- all substances can therefore be ranked relative to each other; that is, one might be higher than another at the same temperature and atmospheric pressure;
- volatility is connected to boiling points—boiling points are connected to polarity;
- the polarity of molecules or compounds (as determined by their intermolecular forces) represents the strength of the bond between atoms and molecules;
- the stronger the polarity, the more energy required to pull the atoms apart—equals a higher boiling point—lower volatility.

From the above, it can be seen that different flavors and fragrances (foods, liquids, or chemical compounds) have different volatility characteristics. Those with higher volatile characteristics are quickly (or easily) detected, while those with lower volatile characteristics tend to either be masked by others or have to be sought out through the nose or the palate. Herein lays the distinction—and a subtle one at that—of the different "top," "middle," and "bottom" or "base" notes of flavors and fragrances. Herein, lies the art of the connoisseur.

While tastes can be defined through a limited number of distinct groups—sweet, sour, salty, and bitter—aromas are that much more difficult to classify. Characteristically, aroma attributes tend to be much wider and more diverse than tastes; they can be fruity, flowery, spicy, resinous (of smoke, etc.), foul, rancid, pungent, and even burning, among others. The following aroma wheel (Fig. 3.2) is a visual aid that helps determine types of aromas.

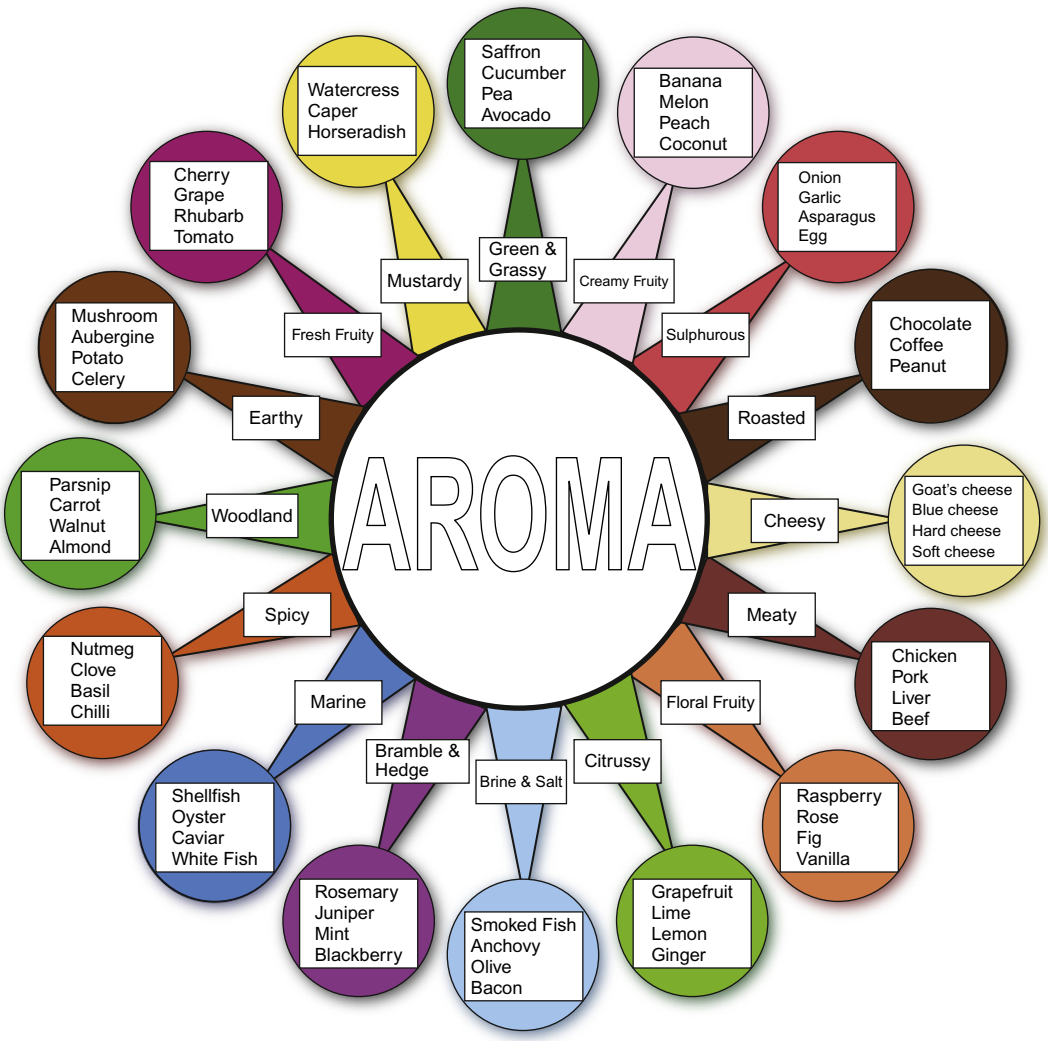


FIG. 3.2

An aroma wheel can aid in the process of identification of aroma notes.

Top notes—these generally give one a first impression, the peak notes of a substance or compound. These are usually the characteristic of the higher volatile components of a substance. In some wines, oils, and fragrances, these top notes often comprise the citrus, fresh, or green tones or notes.
Middle notes—these are thought of as the heart of compound. These usually unfold a few moments after the top note and are typical of the intermediate volatile substances. These can commonly be floral and aldehydic in nature.
Base notes—these are the "also rans" or "also founds"; this is often the clinging fragrance. The scent that remains the longest—the lower volatile compounds reminiscent of woody, powdery, or musky tones. Calling them the "also rans" is possibly a huge disservice as, despite this nomenclature, the base notes are an important dimension to any wine, oil, or fragrance.

With the above in mind then, the chemical composition of any compound being smelled or tasted and the concentration of its key volatile substances determine the individual notes of that substance and the collective overall impression. So, from this little excursion, we can see that volatility, temperature and polarity are all related. In order to understand the mechanics of this concept in more detail, it is worth reading the organic chemistry section of these appendixes (Appendix B).

3.4 SENSE OF TOUCH

It is not only the olfactory but also the gustatory senses that need to be considered when enjoying food. Physical touch provides the sensation of the texture of food too. From vision and the perception of texture, through to handling of the food (somesthesis[8] and kinesthesis[9]). During consumption, too, the oral processing, or masticating of foods is important to the overall sensations of taste and smell as there is a marked difference between the food when it first enters the mouth and the wetted bolus[10] that is subsequently swallowed. Thus, it can be said that, the whole process is the

> …summation of sensory impressions during the whole process from seeing the food, picking it up and putting it our mouths, chewing it, and eventually swallowing it…
>
> **(Barham et al., 2010)**

that we perceive as the texture of the food.

3.5 CHEMESTHESIS

As food is eaten, it activates receptors associated with senses in the mouth and nose like touch, taste, smell, and volatility. Mouths too also detect the temperature of foods; however, this sensation can be manipulated. In chemesthesis, chemical-induced reactions do not fit the traditional senses of taste and

[8]Somesthesis—sensory systems associated with the body includes skin senses and the internal organs.
[9]Kinesthesis—the sensation of movement or straining muscles, tendons, and joints, muscle sense.
[10]Bolus—a small rounded mass of a substance, especially of chewed food mixed with gustatory fluids at the moment of swallowing.

smell, but rather give the impression of false heat and false coolness. False coolness occurs when some substances activate cold trigeminal[11] receptors triggering a "cool," "fresh," or "minty" sensation in the mouth. Foods such as spearmint, menthol, ethanol, and camphor are in this category. Another phenomenon is false heat caused by chilies, ginger, mustard, horseradish, etc. This perceived burning sensation is induced by a trigeminal nerve reaction too (MSUN, 2009). The perceived heat or the "hot" or "spicy" in these cases is caused by food activating the same nerve cell ion channel as activated by hot temperatures. Such sensations of false heat and false coolness are often referred to in terms of freshness, astringency, spiciness, pungency, or piquancy, for example. Two in particular are worth looking at in more detail.

3.5.1 ASTRINGENCY

As mentioned above, for example, that dry-mouth constricting, puckering feeling that follows a sip of strong tea, red wine, or a bite into an unripe banana, is not quite a taste sensation nor an aroma. Instead, it can be thought of as a tactile sensation, a chemesthetic reaction that arises when certain chemical compounds like tannins activate receptors normally associated with other senses that mediate pain, touch, and thermal perception. Astringency physically constricts organic tissue, and the phenomenon is not widely known; instead, it is sometimes known by other terms including hard, dry, harsh, and sometimes tart (although this normally refers to sourness) (Vaclavik and Christian, 2014).

3.5.2 PUNGENCY

The painful irritation caused by chilies (active ingredient—capsaicin), mustard (active ingredient—allyl isothiocyanate (AITC)), horseradish (also allyl isothiocyanate), and black pepper (piperine), for instance, is also a chemesthetic reaction that lies somewhere between touch taste and smell. These were and still are originally intended to repel animals and humans from eating the foods in question. Some elements of these foods do actually do mild damage to the unprotected cell membranes in our mouths and nasal passages. This causes actual pain and chemesthetic pain. The receptors in the mouth lining responsible for recognition of such chemicals are the same receptors meant for registering physical pain from actual heat in the mouth. As a result, the body responds in certain ways. First, it releases sweat from sweat glands in order to cool the body and also flush out aberrant substances. This is why people sweat when eating chili, mustard, pepper-based foods, etc. The body also excretes more saliva to diffuse or flush out the offending foods. Lastly, the body generates endorphins, the body's natural painkillers. Cooking, however, will moderate the pungency of many, but not all of these types of foods.

3.6 FLAVOR

After a look at many processes involved in the perception of flavor, it has been noted that flavor is mainly a combination of the two sensations—taste and smell. Taste is perceived on the tongue and nearby regions, while smell is perceived in the upper nasal passage. In other words, flavor is the sensory impression of a food or beverage as determined by the collective chemical senses. We have also seen

[11]The trigeminal nerve sends messages to the brain.

that in the process, "smell" is the biggest factor in the flavor of our food and drinks. Indeed, smell receptors are almost limitless in their ability to detect aroma compounds. That is, not all in a scientific context flavor may be defined as

> …the complex combination of the olfactory, gustatory, and trigeminal sensations perceived during tasting. The flavours may be influenced by tactile, thermal, painful and/or kinaesthetic effects and expectations from visual presentation of the product
>
> **(Barham et al., 2010).**

This is why a food's flavor can be manipulated in a multitude of ways using texture, fragrance, or flavor compounds.[12] Take jellies of a similar taste; for example, simply by adding certain flavorings of a mainly odorific type, the jellies flavor can be altered in numerous subtle fashions. In this way, a food flavor can therefore be altered relatively easily simply by changing its odorific profile while keeping its taste similar.

3.6.1 NATURAL AND ARTIFICIAL FLAVORINGS

Flavorants focus on altering or enhancing the flavors of food products from meat to vegetables to candies and more. However, the definition of a flavorant is difficult to determine precisely as in the United States; for instance, the Food and Drug Administration's definition includes anything that contributes flavor to food:

> The term natural flavour or natural flavouring means the essential oil, oleoresin, essence or extractive, protein hydrolysate, distillate, or any product of roasting, heating or enzymolysis, which contains the flavouring constituents derived from a spice, fruit or fruit juice, vegetable or vegetable juice, edible yeast, herb, bark, bud, root, leaf or similar plant material, meat, seafood, poultry, eggs, dairy products, or fermentation products thereof, whose significant function in food is flavouring rather than nutritional
>
> **(FDA, 2015).**

While for artificial flavoring, the definition of the same code suggests that

> The term artificial flavour or artificial flavouring means any substance, the function of which is to impart flavour, which is not derived from a spice, fruit or fruit juice, vegetable or vegetable juice, edible yeast, herb, bark, bud, root, leaf or similar plant material, meat, fish, poultry, eggs, dairy products, or fermentation products thereof. Artificial flavour includes the substances listed in 172.515 (b) and 182.60 of this chapter except where these are derived from natural sources
>
> **(FDA, 2015).**

Flavorants are focused on scent and taste; for the purists, however, the problem is natural flavorings tend to be rather more expensive than the "nature-identical" chemical equivalent synthesized flavorings. The European Union has a similar stance on the above although certain flavorants are given an "E" number, which may or may not be artificial in nature. For artificial flavors, the flavor and fragrance

[12]While the terms "flavoring" or "flavorant" in lay terms denote the combined chemical sensations of taste and smell, the flavor and fragrance industries use the same terms to refer to edible chemicals and natural extracts that alter the flavor of food and food products.

industries must create a nontoxic artificial compound that denotes a specific flavor. Just like their natural counterparts, most artificial flavors are often complex mixtures of naturally occurring flavor compounds combined to either imitate or enhance a particular flavor (MSUN, 2009). As counterintuitive as it sounds, artificial flavors are an essential component in the flavor and fragrance industries if only to ensure that a batch of recipes maintains a consistent profile. Curiously too, just because something that is of a natural origin does not necessarily make it safe, and by contrast, artificial flavors might, in some instances, be considered somewhat safer to consume than their natural counterpart. This is due to the high standards of purity, consistency, and testing required of certain regulations.

Note—Umami or "savory" flavorants more commonly known as "taste enhancers" are based largely on amino acids and nucleotides.[13] These are manufactured as sodium or calcium salts such as glutamic acid salts.

> This amino acid's sodium salt, monosodium glutamate (MSG), is one of the most commonly used flavour enhancers in food processing
>
> **(MSUN, 2009).**

3.6.2 FLAVOR VARIATIONS

Of course, the flavor of plants depends on many factors from the various variety of a single species being grown to the way it is stored and prepared. Wine is a good example here; different grape varieties produce different flavored wines; even the same grape varieties grown in different soils and climates will produce a unique tasting wine. In fact, this phenomenon is not unique to grapes but in fact can be applied to all fruits and vegetables and meat and fish. Not only does the growing of goods affect flavor, but storage too also affects the way the flavors are concentrated or lost. In aromas too, much scientific effort has gone into trying to understand the chemical reactions that produce volatile aroma molecules. Cooks, by contrast, work mostly on experience and intuition backed up by an empirical understanding of techniques and processes that is the art of cooking.

The scientific approach clearly has an advantage in its objectivity and reproducible results despite given variations in ingredients used. Although a major setback in the scientific approach (and to some extent the traditional cooks approach) is the lack of a vocabulary to aid in distinguishing the nuances of both aromas and flavors (Barham et al., 2010).

3.7 COLOR OF FOOD

Alongside taste, smell, and texture, another factor to consider when describing foods is that of color; in the culinary world, for example, color sets up expectations of what we are about to eat. When the bright richness of green vegetables and red fruits are at their peak, the mouth salivates with expectations of freshness, juiciness, and flavor. This is also true of raw and cooked meats. Nowadays, the quality of meat is often judged by its immediate appearance; therefore, discoloration of meat is for many consumers, unacceptable (Barham et al., 2010). The color of meat is determined mainly by myoglobin

[13] *Nucleotides* are organic molecules that serve as the subunits of nucleic acids.

whose physiological function is that of oxygen storage in muscles. In avoiding or reducing the myoglobin oxidation, some retail venders now pack their meats in controlled or modified atmosphere packages in order to maintain the cherry red color for longer.

Pigments, the chemical compounds that reflect certain wavelengths of light, are responsible for the color of many foods we eat. Depending on the pigments involved depends on which wavelengths are absorbed. Because of this, pigments are useful to plants and other autotrophs in making their own food via photosynthesis. There are three basic classes of pigments: chlorophyll,[14] the carotenoids, and the phycobilins; however, we are only interested in the first two.

When it comes to fruit and vegetables, we can see that pigments play important physiological roles in living plants. The chlorophyll pigments in green plants, for instance, match the spectrum of sunlight for optimal conversion of light to chemical energy. In other plants of a different hue, like the blues, reds, or yellows, for example, we learn that these pigments belong to several classes of chemical compounds chief of which are the carotenoids and polyphenols. Carotenoids, also known as tetraterpenoids, are organic pigments that are found in chloroplasts[15] and chromoplasts[16] of plant cells and in other photosynthetic organisms including some bacteria and some fungi. Used primarily in the photosynthetic process, that is, the absorption and transformation of light's energy, there are over 750 naturally occurring carotenoid pigments (LPI, 2017). They are generally classified as carotenes (red and orange pigments) comprising alpha-carotene, beta-carotene, and lycopene, and xanthophylls (yellow pigments) including beta-cryptoxanthin, lutein, and zeaxanthin. Carotenoids produced in plants are also responsible for the bright red/orange colors of ripe tomatoes and carrots.

At the same time, we humans have adapted so that the bright green, red, or orange color of fruit and vegetables, for instance, provides us with the sense of perceived freshness. These carotenoids can also be passed along the food chain, providing color to other organisms. A prime example of this phenomenon happens when certain pink phytoplankton's pigmentation is transferred to krill then onto shrimp and eventually salmon. This is why when farmed salmon are fed artificial diets, their food mix is colored with pigment to mirror those found in the wild (Barham et al., 2010). Furthermore, while staying with color pigmentation, it can be seen that certain foods absorb certain amounts of color depending on seasonal variation and the food they in turn eat. Free-range chickens, for example, have access to a much wider variety of foods, so their diet is less restricted—in this way, free-range egg yolks[17] tend to have a darker, richer color than their industrially raised brethren.

Carotenoids are also useful in the health and diet of humans too. Fruit and vegetables are responsible for the greatest proportion of carotenoids (40–50) that form part of the human diet, while four carotenoids in particular, alpha-carotene, beta-carotene, gamma-carotene, and beta-cryptoxanthin, are also incidentally useful as provitamin A in the visual cycle[18] of humans (LPI, 2017).

[14]Chlorophyll, a green pigment, presents in green plants and in cyanobacteria, which is responsible for the absorption of light that provides energy for photosynthesis.
[15]Chloroplasts' main role is the action of photosynthesis, where it captures the energy from sunlight and converts it and stores it in energy-storage molecules.
[16]Chromoplasts are plant cells containing yellow or orange pigment.
[17]The color of an egg yolk is from the xanthophyll carotenoids—lutein and zeaxanthin.
[18]The visual cycle in humans is the biological conversion of light into an electric signal for the brain.

3.8 TEXTURE IN FOOD

The overall appeal of a particular food is determined not only by its flavor but also by its texture. Imagine a potato crisp; a crisp crunch is what is expected, but if allowed to go soggy, then the flavor is perceived differently, somehow not right. The same is true of limp salad greens or of ice cream that is not smooth enough due to large ice crystals contained within. All in all, texture of the food plays an important role in the overall flavor experience. Not surprisingly then, it follows that the creation, control, and modification of texture is therefore an important aspect of any skilled cook. Indeed, in a cook's parlor of tricks, they learn how to modify meat textures through tenderization, marination, and cooking. They prepare sugar sculptures resembling glass figurines. They make the lightest soufflé's and flavorsome hollandaise emulsions. Yet, when it comes to the science of the "what" and the "how" of what they do, they are left mainly a little in the dark. As Peter Barham puts it,

> A glance at any cookbook on how to produce a simple mayonnaise shows that many cooks do not have even a basic grasp of thermodynamics of emulsification
>
> **(Barham et al., 2010).**

That said, he does show optimism in the following:

> The understanding of the biological and physical chemistry to control texture in, for example, emulsions, gels, foams, and glasses has an enormous range of potential applications to produce foods of novel and interesting textures in the kitchen
>
> **(Barham et al., 2010).**

3.9 REACTIONS AFFECTING FLAVOR

Raw ingredients contain a vast array of naturally occurring flavors, for example, fragrant raspberries, sweet pumpkins, mildly acidic apples, and sharp limes. Yet, many of our most favored flavors actually do not occur naturally but are in fact created by chemical reactions within and between the food ingredients post harvest (Barham et al., 2010). Put another way, without processing technologies and chemical reactions, there would be no chocolate, no coffee, and no "meaty" flavors from the Maillard reaction, etc. (Section 5.1.2). Thus, collectively, flavor development arises from a wide variety of pre- and postharvest chemical, physical, and biological reactions as we nurture, grow, store, prepare, and cook our foods. Some reactions occur even before we start any cooking. Some happen in the ground as different soils and climates ultimately affect the foods as they grow. The same foods grown in rich, moist irrigated, and fertilized soils, for example, will taste different if grown in dry, arid, nonfertilized conditions. Another example is the different flavor profiles of grass versus grain-fed beef. Other examples include the physical processing of certain foods during cutting or mincing, fermentation or marination, for example. This is not to mention further reactions during cooking and processing including those of hydrolysis, oxidation, and Maillard and caramelization reactions (Barham et al., 2010).

In many cases when it comes to fresh ingredients, the first stage of processing involves the cutting or physical breaking down of food items into smaller pieces. The very act of fracturing the cell walls leads to the immediate release of enzymes and the start of enzymatic reactions that, given sufficient time,

temperature, and moisture, can alter the flavor and texture of the product in use. This is why in many living plant and animal cells, enzymes are compartmentalized—separated naturally from their substrate so as to avoid self-destructive enzymatic reactions in the living body. However, upon harvesting if the cellular structure is cut into, or is otherwise destroyed, flavor-altering enzymatic reactions begin to occur. Yet, it is interesting too to note that heating or cooking of these meat and vegetable enzymes above a certain temperature becomes denatured (see Section 4.2) and their enzymatic powers arrested.

3.10 TASTING NOTES: FOOD-PAIRING

A theory, which suggests dishes, recipes, or plated accompaniments that share similar flavor compounds are more likely to taste well together than those that don't, has received much attention over the last decade or so (Ahn et al., 2011; Varshney et al., 2013; Kort et al., 2010; Møller, 2013). It has even been said that Blumenthal and Lahousse are practitioners of the theory and use food pairing as a tool to inspire new dishes (Kort et al., 2010). Not only does the theory carry weight at the top echelons of various industries from culinary to food processing, but also there is a whole stack of science that helps pair foods. This is usually achieved by chemists and food scientists who identify and compare numerous foods, which in turn are paraded in fashionable food pairing trees (Ahn et al., 2011). However, a database of volatile compounds in food, which was started way back in 1963, was employed to evaluate the food pairing theory; that is, the notion that two foods sharing the same major volatile molecules would taste nice when eaten together. However, in a sensory analysis experiment, results indicated there was some doubt as to the validity of the food pairing theory (Kort et al., 2010). Moreover, in another, more in-depth global analysis, focusing on food pairing by Ahn and colleagues (2011), they examined and analyzed the cuisine habits of several regions around the world. In their conclusion, it was found that the cuisines of both the North American and Western Europeans revealed significant tendencies for recipes that shared similar flavor compounds. By contrast, however, it was also shown that both the cuisines of East Asia and Southern Europe tended to avoid dishes whose ingredients shared similar flavor compounds (Ahn et al., 2011). In conclusion, food pairing based in similar flavor contents is not looking good as a universal theory (Møller, 2013). Instead, what the data are telling us is the idea that similarly flavored foods might work in some foods and in some regions, while nonsimilar or contrasting flavored foods work in other regions.

From these and other observations, one can confidently say that when it comes to taste combinations or the matching of flavors; as a rule, there is no right or wrong. That is to say, flavor pairing has always been and will always be to a large extent subjective. However, this does not necessarily mean food pairing is without rules or experiential knowledge. Indeed, while it is generally seen as an art form or a form of craftsmanship, there is a modicum of science thrown in too. So, as has been shown, there are several schools of thought with regard to the matching of flavors of different foods or even wines and foods for that matter. For simplicity sake, though we can think of the task of matching flavors as comprising two main branches—complimentary and contrasting. In this regard, it has been noted that the Western palate generally relies heavily on food pairing of similar flavorants while the East Asian and Southern European palates tend to avoid these, relying instead on contrasting flavors (Ahn et al., 2011).

Taking these findings to their logical conclusion, it can be said that nearly all meats, vegetables, and fish benefit from both complimentary and contrasting flavors whether from the Asian or Western larders. This is an important concept and one worth remembering. The same food that one serves with the same complimentary sauce or garnish might also benefit from a sauce that is contrasting in nature and flavor. There are some cooks who have an uncanny or a natural ability to marry certain foods without much consideration or forethought of the science behind what they are doing. For most of us, however, the art of "flavor pairing" has to be learned. Take, for example, a Dover sole; there are many ways in which this is regularly served, and cooks will often create a dish from instinct with little regard to their own thought processes involved. Absolutely, there is nothing wrong with this as this tendency comes with or is developed with experience. Dover sole contains just over 1% fat; now, this author, for one, does not consider this be too much fat at all, although once again, the matter is a subjective one. So, back to the sole, with a low-fat content, oftentimes, one might come across dishes that complement the sole with added fat in the form of a "nut-brown" butter that at once, because of the butters' soft creamy after-palate taste, combines to enhance the delicate flavor of the fish. An opposite or contrasting approach, and one equally acceptable, is a simple minimal butter glaze and a contrast tartness provided by a smattering of lemon juice. Of course, the two are sometimes combined to experience yet more complex sensations. Another example is to take foods richer in fats such as duck or some cuts of lamb. In this instance, the fattiness of both meats benefits from a contrasting acidity that cuts through the cloying oiliness, something like vinegar and mint for the lamb or a nice tart red-berry sauce with the duck are not uncommon. The art here is to choose the right acidic vehicle, the right amounts, and the right complimentary or contrasting flavors. As an aside here, fat in foods is an important carrier of flavor. Others still, mainly scientists and enthusiasts of the trend, go to great lengths to use gas chromatography-coupled mass spectrometry (GC-MS) results to work on unique and novel pairings. Note that this approach works on mainly complimentary flavor compounds that share similar flavor characteristics. Little research has considered the alternative scenario (Ahn et al., 2011).

In sum, in the pursuit of flavor pairings, some have relied heavily on science. One approach uses the chemical analysis of a foods' gas chromatographic profile to determine the makeup and relative strength of each molecule. The product's flavor profile is then compared to a database of other food and beverage products. Products that have flavor components in common with the original ingredient are grouped together accordingly. The results are then often graphically presented on a food pairing tree similar to the one shown below in Fig. 3.3 (Ahn et al., 2011; Møller, 2013; Kort et al., 2010).

Others still use their own skill and intuition and draw on generations of experiential knowledge in their pursuit of flavor pairings, whether complimentary or contrasting in nature. The point is that both complimentary and contrasting flavors are equally important. Although, the greatest sin, and a cautionary note here, is the practice of overpowering a dish with any flavor or flavor combination that, rather than enhancing a particular dish, simply masks or alters it completely. Get this basic premise right, and one can experiment to their hearts content and remember, as a subjective art, what works for one person might not work for someone else. The cook's difficulty here lies in that he/she is not cooking for him- or herself but is rather trying to appeal to the wider, mass audience. In this sense, the cook often might balance a menu with some proven flavor combinations and then add one or two dishes that push the boundaries and challenge widely held perceptions. Therein lays the art of an experienced professional or accomplished home cook.

From the preceding foray into the world of flavor, it can be said with great confidence that flavor, for all its complexities, turns out to be more of a composite organoleptic sensory perception than a

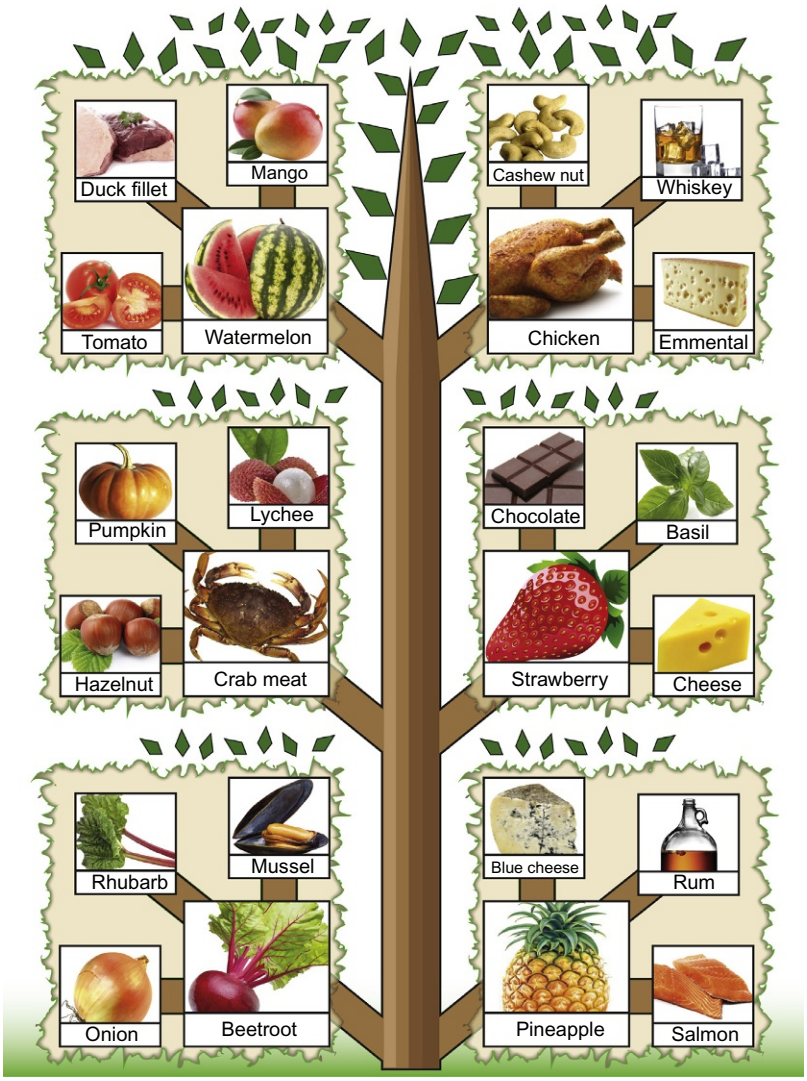


FIG. 3.3

A food pairing tree.

stand-alone sense. It is a combination of sensations that utilizes the eyes, drawing on visual cues that excite and stimulate; the taste buds, with their limited variability; and aroma, with its complex and somewhat sophisticated mechanisms. So, while there are just a scant handful of different tastes that can be leveraged, there are many thousands of different odors and colors to match (MSUN, 2009; Barham et al., 2010; Vaclavik and Christian, 2014). From there, neurotransmitters send signals to the brain about the flavor sensation of a particular food.

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CHAPTER

PROTEIN BIOCHEMISTRY

4

CHAPTER OUTLINE

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Proteins are generally large, complex chemical molecules containing carbon, hydrogen, oxygen, and nitrogen, and irregardless of source, analysis of all proteins falls within a narrow compositional band, as shown below:

- Carbon 51%–55%
- Hydrogen 6.5%–7.3%
- Oxygen 20%–24%
- Nitrogen 15%–18%
- Sulfur 0.0%–2.5%
- Phosphorus 0.0%–1.0% (Sawyer et al., 2002)

Not only are proteins important in the kitchen, but also they are essential to all life on earth. Each protein will have just one very precise job to do (Castellani, 2017). In humans, proteins are responsible for a whole host of bodily interactions; they provide structural rigidity to cells; they regulate

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metabolism[1] and the concentrations of metabolites[2] as well as controlling the flow of substances that pass through the body's membranes. Moreover, proteins act as sensors and switches responsible for motion and controlling gene functions while also being responsible for catalyzing a whole host of chemical reactions (Harvey et al., 2000). Proteins too are important building blocks of the bones, muscles, cartilage, skin, and blood. Indeed, proteins are so ubiquitous that they can be found not only within our own bodies but also in those of other animals, fish, and plants too, which also contain and require proteins to function properly.

Proteins are, by design, able to bind to almost every imaginable molecule there is from simple ionic atoms to large and complex molecules such as fats, nucleic acids, sugars, and other proteins (Jessica and David, 2016). And it is only when proteins are in their distinctive three-dimensional structure that they are able to function properly; this is a key concept in understanding just how proteins work. Put simply, a single protein's function is largely attributed to its three-dimensional structure. In turn, the three-dimensional structure is specified by its amino acid sequence (*next section*).

So much happens in the kitchen that involves proteins; it is worth taking a close look at these little marvels. Proteins are used extensively in the kitchen, through gelatin, fish or meat, eggs, cream, and fruit and vegetables. In fact, the list is endless. There are two ways to help understand the various proteins and their behavior, through their chemical and physical characteristics. For reasons explained in the next section, proteins are large polypeptides, as such the two names can and are used interchangeably (Berg et al., 2002).

4.1 AMINO ACIDS: THE BUILDING BLOCKS OF PROTEINS

Proteins are complex organic compounds the subunits of which are amino acids or more precisely amino acid residues.[3] They are thought of as comprising four structural levels: primary, secondary, tertiary, and quaternary levels. Proteins are first synthesized as a primary sequence and are then folded into secondary, then tertiary, and finally quaternary structures. Although there are several hundreds that exist in nature (Lu and Freeland, 2006), the human body requires only 20 or so amino acids to create all the proteins it requires for normal functioning. Some might question the fact that because there are only 20 or so amino acids used, aren't the number of proteins limited? In answer, a simple analogy shows that while there are only 26 letters of the alphabet, there are indeed hundreds of thousands of words that can be constructed from the different arrangements of the letters—including recursive (or repeating) letters. Mirroring this analogy, molecules of proteins are often very large,

[1]Metabolism describes the chemical reactions that are involved in maintaining the living state of an organism. Metabolism can be divided into two categories: catabolism—the breakdown of molecules—and anabolism—the synthesis of compounds needed by the cells.

[2]A metabolite is any substance produced during metabolism although the term might also be used to refer to the product that remains after the process of metabolism by the body.

[3]A protein chain will have somewhere in the range of 50–1000+ recursive amino acid residues. Residues are the correct terminology simply because a peptide chain isn't made up of whole amino acids. That is because in the aggregation of amino acids or as they combine, so a water molecule is lost in the process. The peptide chain is then made up out of what is left after the process—in other words, is made up of amino acid residues. Having said that, this book will follow customary convention and will continue to refer to amino acid residues as amino acids.

having been constructed from long chains of the 20 different amino acids numbering in the hundreds, the thousands, and the millions depending on the sequence and the recursive nature of the acids involved. Some of these, depending on their structure, are responsible for different proteins in the human body. Some of these proteins are in solution in blood and other fluids, while others are in solid form—in the framework of tissue, bone, and hair, for example (Belitz et al., 2009; DeMan, 1976).

So, while proteins are made up of amino acids—"amine" meaning "nitrogen-containing"—in turn, all amino acid chains are molecules that comprise the same end structures: a nitrogen-containing amine group (—NH_2) at one and an acid group (carboxyl group (symbolized as COOH)) at the other (Jessica and David, 2016; Berg et al., 1995). In more detail, proteins' amino acids are connected together by a type of amide bond that joins the amine group of one end of an amino acid with the opposite end (the carboxyl group end) of another amino acid through a condensation reaction; the resultant bond is called a "peptide bond."

The sequence of bonded amino acids that is repeated along the core of the polypeptide chain is also referred to as the polypeptide backbone (Berg et al., 2002; Alberts et al., 2002). What separates the thousands of amino acid combinations are the different side chains that are attached to all amino acids' backbone. Side chains are the amino acids that do not get involved in forming a peptide bond and that ultimately provide each amino acid its unique properties. Amino acids may also possess a charge whether negative, positive, or no charge at all, which coupled with the fact that their side-chain groups vary in size, reactivity, and hydrophobicity (their love or hate of water). These reactionary traits jointly determine the size and ultimately the behavior of the different amino acids and by extension the protein molecules themselves (Alberts et al., 2002; Harvey et al., 2000). Just 20 or so of these amino acids all with different side chains are the building blocks of the proteins that make up most of all living tissues (Boyle and Roth, 2012; UEN, 2016). It comes as no surprise then that proteins differ from each other in both the sequence and number of the amino acids that form a specific chain. They also differ in another way—the way in which the physical protein chain (also known as a peptide chain) is linked, coiled, or twisted (*described below*) (UEN, 2016).

4.1.1 PEPTIDES

As mentioned, amino acids have two ends: on one end is a carboxyl group, while the other is an amine group. Amino acid chains are made as one end (the carboxyl group) of an acid is joined to the amine group of the opposite end of second amino acid, thus forming a simple two-group chain. However, what distinguishes one amino acid from another is the sequence of acids involved plus the ability of the chain to branch out sideways, creating a side chain attaching to itself more amino acids. There are three overall groups of side chains: nonpolar, charged polar, and uncharged polar chains (Tornberg, 2005).

The word "peptide" can be confusing—it describes the chemical bond (the peptide bond) between amino acids and the resultant small agglomeration of amino acids or the chain itself (the peptide chain). Two or more amino acids that are joined are called dipeptides, while three are tripeptides, four are tetrapeptides, and so on and so forth. These small (two or more) amino acids, di-, tri-, and tetrapeptide molecules, while they are strictly speaking proteins, are, by convention, simply called peptides. These are generally smaller than proteins. This is so until, that is, the number of amino acids in the chain rises to about 50 or so at which point they are referred to as polypeptides or polymers (long chains of

repeating amino acids) or more commonly—proteins.[4] All proteins contain anywhere between 50 and 1000+ amino acid sequences.

In sum, peptides are the connecting blocks of amino acid chains. In turn, amino acid chains are the foundation of protein molecules (Jessica and David, 2016; Britannica, 2016). Polypeptides and proteins are formed chemically from amino acids that undergo a "condensation" reaction in which one water molecule is lost in the bond between two amino acids. Repetition of this reaction (called polymerization) converts dipeptides to polypeptides, which in turn create proteins.

We stated too (Section 1.1.2) that 8 of the 20 or so amino acids (lysine, isoleucine, threonine, methionine, tryptophan, leucine, valine, and phenylalanine) are called "essential" as they cannot be made by the body and so must be ingested while the other 12 can be synthesized in the body (UEN, 2016).

4.1.2 FOUR LEVELS OF STRUCTURE DETERMINE THE SHAPE OF PROTEINS

As we have alluded to, along with a proteins' amino acid chemical sequencing, the shape and size of the protein (polypeptide) itself goes a long way to determining its particular role whether in the body or within the kitchen. Consequently, the way the amino acids and their side chains are sequenced or arranged helps determine the folding of the protein into its final unique shape. Since protein function is partly based on shape and size, it is critical that they are created in the correct shape with the correct sequence of amino acids in order that they do their jobs correctly. There are many ways a protein takes on its final shape, and that is through a number of noncovalent interactions such as ionic interactions, van der Waals forces, hydrogen bonding, and hydrophobic packing (Tornberg, 2005). Such resultant structures are commonly referred to in terms of four hierarchical levels of organization (Fig. 4.1).

The creation of a single polypeptide chain as described above can be seen in Fig. 4.1. The first chain is referred to as the "primary" protein structure that can be defined as the linear sequence of amino acids that make up a particular protein. Primary structure "bonds" are solely linked through covalent bonding. The secondary structure deals with the details of the polypeptide chain and its folding and bonding, its spatial arrangement. This is important because, without any stabilizing interactions, a polypeptide chain assumes a random-coil structure. By adding stabilizing hydrogen bonds between certain amino acid residues, stabilizing hydrogen bonds between the arms at the surface of the protein molecule allow turns and cause the polypeptides to fold inward on itself creating regular and stable geometric spiral structures. Although there are many types of secondary structures, the most common are the forms known as the α-helix (alpha-helices that are spiral-like) and the β-sheet (in which the structure of the polypeptide backbone is nearly fully extended like a flat two-dimensional sheet). The tertiary structure is determined by how the secondary structure folds together, that is to say, the 3-D arrangement of α-helices and β-sheets. In essence, tertiary structures refer to the overall precise shape of a protein in three dimensions resulting in the overall folding of the entire polypeptide chain (Berg et al., 2002; Alberts et al., 2002). While both secondary and tertiary amino acid structural processes drastically alter the physical nature of the molecule, so it's worth noting that in the secondary structure, stability is provided by the hydrogen bonds, and in the tertiary structure, integrity is stabilized by the hydrophobic

[4]Another of the primary differences in the nomenclature of biochemistry is the difference between proteins and polypeptides being simply the molecular length.

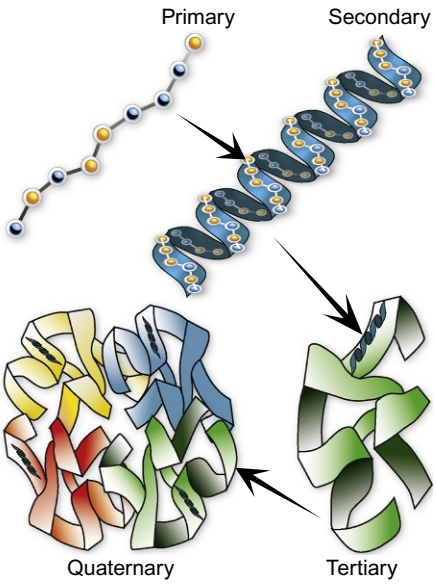


FIG. 4.1

Hierarchal structures of various protein configurations.

interactions between nonpolar (no charge) reactions. The result is the tertiary structure that looks to stabilize the α-helix and β-strands folding, twisting, and coiling of the amino acids of the secondary structures, etc. (Jessica and David, 2016). In this way, the tertiary protein's size and shape is dependent not only on its sequence of amino acids present but also on the number, size, and arrangement of its secondary structure. For those proteins comprising a single polypeptide chain (monomeric), the tertiary structure is the highest level of organization that can be applied (Berg et al., 2002; Alberts et al., 2002). In the quaternary structures, two or more polypeptide chains (multimeric) combine together through noncovalent bonds forming one large functional molecule. That means the quaternary structure describes both the number and relative positions of the subunits in a multimeric protein (Jessica and David, 2016). Resulting from these interactions, we can say that each type of protein has a particular three-dimensional structure, which is determined in turn by the order of the amino acids within its chain. Many thousands of different proteins are known to exist, each with its own particular role as determined by its shape and amino acid sequencing (Berg et al., 2002; Alberts et al., 2002).

4.1.3 GLOBULAR AND FIBROUS PROTEINS

As a general rule, proteins fold, forming two structural types: fibrous and globular (Fig. 4.2). While globular proteins are compactly folded, so fibrous proteins are more filament-like. Take the protein hemoglobin for example—it is a complex globular macromolecule.[5] The primary structure recognizes

[5]Hemoglobin contains in excess of 10,000 atoms of hydrogen, carbon, nitrogen, oxygen, and sulfur and 4 atoms of iron. It is the iron in hemoglobin that is more important as it gives blood its ability to combine with oxygen.

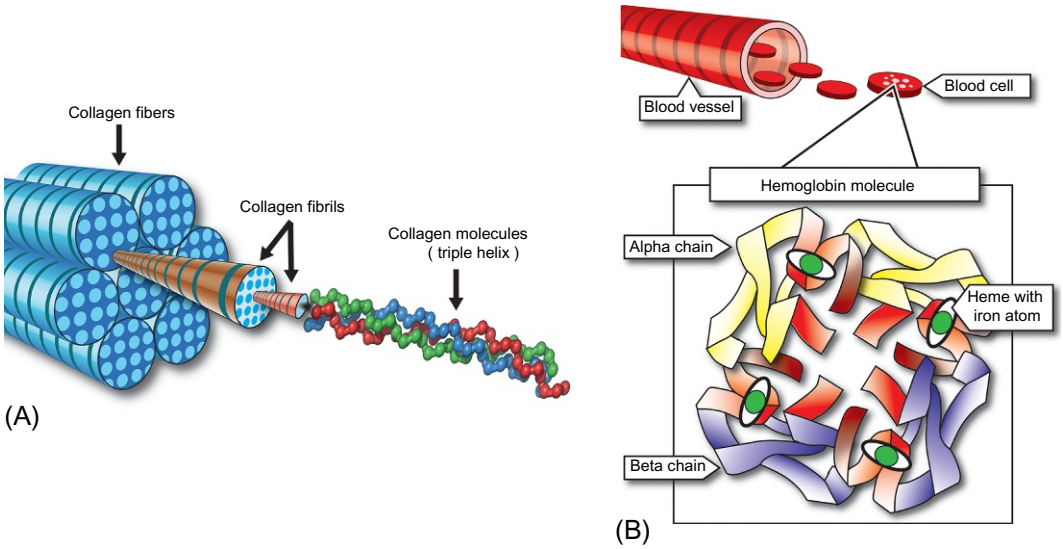


FIG. 4.2

Protein structures: collagen and hemoglobin.

the long linear polypeptide chains made up of sequential amino acids; this is probably the easiest protein structure to visualize. This sequence also defines how the final protein folds and by extension how it will function. A single change in the amino acid sequence at this stage, for instance, can mean the difference between a hemoglobin protein or a deformed protein that causes the sickle cell anemia disease (Jessica and David, 2016; Alberts et al., 2002).

Many functional proteins fold into compact globular shapes. Globular proteins are those proteins with long chains of amino acids (polypeptides) that have been folded around each other to form a fairly tight and compact mass (Fig. 4.2) (Jessica and David, 2016). Whether mono- or multimeric, heat will cause much of a protein to unfold. Indeed, as the globular protein unfolds, amino acids tend to form weak bonds with other unfolded amino acids of other proteins; this is generally irreversible with the exception of a few proteins like gelatin (Alberts et al., 2002). Further, heat will cause the proteins' loose or weak networks to solidify, while overheating tends to create too many bonds among the proteins making for a tighter mass that ends up squeezing water out. This can result in unpleasant or unwanted food textures that might be runny, lumpy, rubbery, or a combination thereof (*next section*). When it comes to globular proteins, many tend to be enzymes that, while large and complicated, most have an overall rounded shape (Alberts et al., 2002).

Fibrous proteins, by contrast, have just as equally important roles in cellular biology. Fibrous proteins, as the name suggests, are individual molecules that are required to span large distances and that usually have comparatively simple, elongated three-dimensional structures. Fibrous proteins are quite often found outside the cell, as one of the main components of the extracellular matrix that helps to bind collections of cells together to form tissues, of which animal collagen is one such example (Alberts et al., 2002). A collagen molecule consists of three long helical-like polypeptide chains. The collagen molecules then bind to one another side by side and end to end to create long and strong, tough fibrils that give connective tissue its tensile strength. In contrast to collagen's tightly woven strength, another

fibrous protein found in the extracellular matrix is elastin. Elastin molecules derive from loose relatively unstructured polypeptide chains that act like an elastic or rubberlike interlaced mesh. As far as conformation[6] goes, because the nature of its usage in animals, elastin is somewhat stretchable as in skin and similarly elastic tissues such as those found in arteries and lungs (Alberts et al., 2002).

4.2 DENATURATION

(See also Sections 12.2.1 and 12.9.1)

Protein denaturing is important in the kitchen for a variety of reasons: It helps to firm up meat making it more palatable and easier to digest, it stabilizes foams and emulsions, it thickens sauces, and it even makes gels, among many other things. However, acids, salts, and even alcohol each have the capacity to neutralize negatively charged areas of the protein molecule and in the process denature them. This allows the protein molecule to bond more easily. Cream of tartar (tartaric acid), for example, contains acid that can cause the whites of eggs to denature or coagulate without heat. Lemon juice will also do the same thing; however, the water content of the lemon juice prevents good foam (Section 7.2.2.3) from forming. Using vinegar in water too, when poaching eggs, helps denature the surface proteins of the egg, thus keeping it from falling apart before full desired coagulation can take place (Creighton, 1993). Still with eggs, if an egg-white foam is whipped, and fats somehow enter the mix, so fats coat denatured proteins preventing them from bonding; that is why even just a little of the egg yolk (which as we know contains fat), if not properly separated out of the egg white, will prevent the production of a good fully whipped foam. Furthermore, the cook's instruments have to be clean and free from fat as whipping egg whites in a bowl with any oil or fat residue will also inhibit the production of a good foam.

While it can be seen, there are many ways to denature proteins; denaturation by heat tends to be one of the most commonly used catalysts (Branden and Tooze, 1998; Creighton, 1993).

There are literally thousands of proteinaceous compounds each with their own specific denaturation temperatures. Meat, for example, is not homogenous; rather, it is a collection of globular and fibrous proteins in which numerous examples of each make up the whole. This is a great challenge for cooks in the home or professional kitchen. How to cook meat with multiple protein types with differing denaturation temperatures—suffice to say for now—the simple answer is slowly (this is explained in detail in Section 12.9.1). Other proteinaceous foods too are also cooked at lower temperatures; fish, for instance, can be and often are cooked at low sous vide temperatures, thus allowing enzymes time to break proteins down and help tenderize the food (Ophardt, 2003). Once the protein has denatured, more bond-forming areas along the unfolded protein are opened up allowing the formation of new bonding sites with other denatured proteins.

4.2.1 PROTEIN AGGREGATION: COAGULATION AND GELATION

In the properties of proteinaceous foods vis-à-vis aggregation, gelation/coagulation of proteins is related to a greater or lesser extent, on the physicochemical phenomena of protein denaturation (Schmidt, 1981). In turn, this gelation/coagulation is dependent upon the amount and specific type of protein being used, the pH, and the ionic environment, among other things.

[6]Conformation is the shape or structure of the protein.

After the denaturation process, proteins sometimes coagulate or gelate; however, there is some confusion or perhaps ambiguity in the literature regarding these processes. Gelation, for example, can, for practical reasons, be defined as the phenomenon of protein aggregation and gelation in which molecules' attractive and repulsive polarities and the polymer-polymer and polymer-solvent interactions are balanced such that a soft/firm/hard matrix is formed. Depending on the specific proteins involved plus the time and temperature, so during the process of gelation, the matrix is capable of trapping or holding proportionally large amounts of liquid (often water-based). Coagulation achieves a similar matrix but rather in a less orderly fashion, with more random aggregation in which polymer-polymer connections are favored over gelation's polymer-solvent reactions (Schmidt, 1981).

In reality though, it is not always that simple as there tends to be unavoidable overlap between the two processes; as such, the terms are often used interchangeably. However, before the process of coagulation/gelation can occur, the protein must first undergo denaturation. Denaturation as we know describes the reversible or irreversible changes in natural conformation (shape) of a protein molecule, that is, the partial or full unfolding of the protein's physical structure (Baldwin, 2012). Even once this is achieved, protein gelation/coagulation can only occur when there are sufficient protein concentrations, enough heat (if thermally denaturing), and other optimal conditions present, in order to achieve a stable matrix. In fact, heat-induced denaturation and gelation is perhaps the most common and by extension the most important aspect with regard to the cook's kitchen (Schmidt, 1981). The process of thermally induced denaturation—which proteins are denatured and to what degree they are denaturated—relies mainly on temperature and, to some extent, on time (see Section 12.9.1) (Baldwin, 2012). The two-step process of gelation starts with the unfolding (dissociation) of a protein followed by the denatured protein's association and aggregation reactions. It's "clumping" together. Individual proteins, for instance, will start to denature at low temperatures—this is just the beginning. As the temperature increases, so more of the protein denatures and will continue to do so until there comes a point in where the major change in conformation (shape) is reached. This phenomenon is called the transition temperature, also known as the molecular transition temperature (Sikorski, 2006) or, more colloquially, denatured. This is a very useful tool in, say, meats that, as discussed later, contain not only one protein but also many varieties, all with different denaturation points.

There are two types of protein denaturation states: the reversible and irreversible. Reversible denaturation allows the proteins to regain their "native" state once the denaturing stimulus is removed. Irreversible denaturation cannot be reconformed, that is, once denatured, these proteins stay denatured (Ma et al., 2003; Weijers et al., 2003). Denaturation involves, at the very least, the disruption of, or the potential destruction of, the weak forces of the secondary and tertiary structured proteins and the breakdown of quaternary protein subunits that, in essence, translates to the unraveling of the protein's structural integrity usually due to some form of external forces. With regard to the primary structure (the sequence of amino acids), the peptide bonds tend to be too strong for any denaturation reactions to break apart; thus, a meat protein will still be a meat protein even after denaturation (Ophardt, 2003). In secondary and tertiary structural conformations, denaturation interferes with the bonding processes that end up with proteins in which the alpha-helix and beta-sheets unfold into random shapes. In quaternary proteins, denaturing results in disruption or dissociation and/or the altered spatial arrangement of the proteins subunits. The process of denaturation can be reversible with certain proteins when the peptide chain is denatured and stabilized by the denaturing agent. In this process, removing the denaturing agent thus allows the native conformation to be reestablished. On the other hand, irreversible denaturation occurs when certain protein peptide chains unfolded and interact with

other chains forming bonds that stabilize the unfolded chain. This happens, for example, when eggs are boiled, meat is cooked, and crème caramels are made. Notice here that when we talk of gels and coagulation, we are not solely talking about obvious gels/coagulates; we also include the likes of eggs, meat, fish, and vegetable. When considering denaturation, say gelation/coagulation in meats, for example, we are talking of the myofibrillar and the stromal and sarcoplasmic proteins (Section 12.9.2.1.1—onward). In short, both reversible and irreversible denaturations occur when the protein molecules unravel from their "native" state. This occurs most frequently when proteins are subjected to denaturing agents like heat; being beaten (mechanical agitation); pH changes (both acids and bases[7]); inorganic salts; polar organic solvents; the action of urea and alcohol; being frozen; and even ultraviolet light (Ophardt, 2003).

4.2.1.1 Role of cross-linking in the gel structure

A gel's physical properties depend to a large extent on the type, size, and shape of the proteins involved. It is also affected by the nature of the unfolded protein strands in cross-linking (aggregation) associations. The cross-linking of proteinaceous gels (both protein and the immobilized solvent) displays a certain strength and elasticity (Schmidt, 1981). Furthermore, the stability and durability of a gel or coagulum rely to a large degree on these cross-links, whether covalent or noncovalent bonding, among other things. In complex globular gels/coagulations, protein denaturation, aggregation, and cross-linking all tend to happen simultaneously and more randomly. Consequently, this type of gel displays a lower elasticity with higher opacity and more solvent weeping (syneresis[8]) than that of a more ordered thinner-stranded fibrous gel network (Schmidt, 1981). This is a very general observation as the actual coagulation and/or gelation properties are protein-specific and are intricately interrelated to proteins' other functional properties. In this sense, one must also consider the qualitative or subjective organoleptic characteristics of protein gels, as valid cues to adequate or appropriate gelation/coagulation.

4.2.1.2 Factors affecting gelation/coagulation

The conditions of gelation/coagulation of different proteins vary over a certain range of variables including protein and nonprotein components, their concentration, pH value, and ionic and any heat-treatment conditions. When it comes to protein concentration in gelation, for example, it has been found that each protein has a critical concentration requirement, below which a gel would be difficult to form. Sufficient concentration and gel properties however are also contingent on the different proteins used. In fibrous proteins, a gel can be formed with fewer aggregated proteins, while globular protein-based gels require higher concentrations (Schmidt, 1981). As an aside, the higher the quantity of protein aggregates, the more opacity can be seen in the finished gel.

Having said all, there are certain other conditions that affect the process of gelation/coagulation. In heterogenous foods, for example, other proteinaceous components may very well interfere with or alter any gelation/coagulation reactions. Furthermore, protein pH values tend to have substantial effects on gelation reactions. For instance, moderately high pH has been shown to improve gelling ability although prolonged exposure to higher pH values actually suppresses protein aggregation (Schmidt,

[7]Baking soda is a good example of a "base" in the kitchen.
[8]Syneresis is the drawing together of the protein particles of a gel, with some separation of the liquid medium and shrinkage of the gel, that is, weeping.

1981). As unfolded, denatured proteins become extended or larger from their unraveling, so they are more likely to physically bump into each other forming single clumps or groups of clumps. When these proteins unravel and accumulate like this, so exposed, potential bonding areas of the unfolded proteins attract each other and bond in a phenomenon called aggregation (Ma et al., 2003; Weijers et al., 2003). If this happens to enough proteins, they end up forming a solid, filament-like matrix that can potentially trap inter- and intracellular fluids as in meat and eggs, or they can trap external fluids and other introduced liquids by the cook. These include such things as baked custard tarts, gelatinous terrines, quiches, and crème brûlées. This is called gelation/coagulation (Schmidt, 1981). However, as a cautionary note, if too high heat is applied or the cooking goes on for too long, many more proteins will join the matrix and will further tighten existing protein-to-protein bonds (Vaclavik and Christian, 2014). This collectively tightens or shrinks the food, simultaneously forcing out water, juices, and other fluids. Thus, one ends up with a chewy and dry steak or an overcoagulated egg custard that is effectively "split" into liquids and solid particles. The process just described doesn't just occur with heat alone; there are many ways proteins can be denatured (*previous section*); one example includes the preparation for cheesemaking—the addition of rennet or lactic acid bacteria to milk that denatures the casein proteins and squeezes out the liquid, separating the milk into curds and whey.

In sum, following denaturation, protein gelation and coagulation are important reactions in the processing and final structure of many foods. Strictly speaking, gelation is operationalized as an aggregation of denatured proteins whereby polymer-polymer and polymer-solvent interactions are balanced, such that a tertiary network is formed. This often elastic or semielastic matrix is capable of trapping large quantities of liquid whether water or others. Also, strictly speaking, coagulation occurs as denatured proteins aggregate through polymer-polymer interactions and not (as in gelation) polymer-solvent interactions. The resultant coagulation tends to be less flexible or less elastic and more rigid than that of a protein gel. Stabilizing these new gels/coagula is the association or cross-linking of protein to protein bonding whether through heat treatment, calcium-induced gels, ionic attractions, hydrogen bonding, disulfide bridging, hydrophobic attractions, and divalent cation addition reactions. In short, protein denaturation leads to gelation and/or coagulation—however, throughout this book, unless made explicit, both will be used interchangeably (Schmidt, 1981). Lastly, coagulation and gelation are not to be confused with gelatinization (Section 15.2.1) (Vaclavik and Christian, 2014).

4.3 ENZYMES

Enzymes are important protein-based workhorses in nature, operating at low temperatures and at moderate ranges of pH. They are present in all living cells and act as catalysts in the organisms' various metabolic processes. While many enzymes are simply proteins, others comprise a protein that is connected to one or more nonprotein groups. They are also bulky molecules comprising anywhere from 20 to upward of a million plus amino acids that are coiled and folded in upon themselves thousands of times. Because of this complex makeup and the chemical folding that shapes the enzyme molecule, so the specific shape is unique for each enzyme. This conformation (its three-dimensional structure) in turn determines its function and with which particular molecule it will fit and act upon (Vaclavik and Christian, 2014). This is why the shape of the biological substrate (the molecule to be acted upon) fits like a key—in this way, only substances of the right shape will be transformed (Novozymes, 2016;

DeMan, 1976). While there are many different types of proteins, for simplicity sake, we can in fact divide them into two groups. The first group is the stromal, sarcoplasmic, and myofibrillar proteins, which are the main proteinaceous elements of animal bodies (Chapter 12). The second group, however, covers the biologically active proteins in meat; these are the enzymes. However, although it must be noted that all enzymes are proteins, not all proteins are enzymes. If a protein can catalyze[9] a biochemical reaction, it is considered an enzyme. Enzymes then catalyze (or speed up) all the biochemical processes in cells in the human and animal body, that is, they are responsible for both the breaking down (catalyzing) and building up (anabolizing) of proteinaceous components. In this respect, they can breakdown, nurture, or synthesize chemical substances required by the body such as other proteins, carbohydrates, or fats (RSC, 2004). By way of example, when one eats foods, both the food and the salvia enzymes both work to break down the food into much smaller particles after which they can be converted into energy. As mentioned, this begins in the mouth where saliva containing amylase (an enzyme) works on the food helping it to partially break down the food before entering the stomach where other enzymes (gastric lipase and pepsin) continue the process. This process further continues in the intestines subsequently aiding the digestion process.

Enzymes are generally process-specific, that is, they have one purpose only. Every molecule at the beginning of the process of being broken down is called a substrate,[10] and every molecule/organism has its own unique enzyme that fits it like a key in a lock. This is an important difference with industrially produced artificial[11] non-substrate-specific enzymes. With natural enzymes, there are no side effects like runaway enzymatic reactions, whereas in the artificial or chemical variety, one has to be a little careful. The good news though is that artificial or industrial enzymes once discarded are just as readily biodegradable as their natural counterparts by microorganisms and suchlike. Enzymes will go about their business until they either are denatured themselves through cooking or are dissolved, usually by other enzymes (RSC, 2004; Novozymes, 2016). Once the enzymes have catalyzed a reaction, they do not form part of the finished product; they simply move on to the next molecule/organism and continue to do their job (RSC, 2004).

Enzymes work at the cellular level. As cell structures begin to degrade with death, they eventually break open allowing the enzymes within to react with other cells promoting enzymatic breakdown of substrates and allowing for decay of microorganisms, etc. In meat, for example, enzymatic action breaks down the meat proteins making for a more tender cut of meat, and this is why meat is hung for periods of a few days to a month or two (The American Meat Science Association, 2015). However, it must be said that meat is hung under strict temperature and humidity controls; that is why it can be hung for so long. Raw meat in the fridge however will spoil much more quickly than this. That is all well and good for as long as the enzyme is nondenatured; once cooked beyond a specific temperature, enzymes are then unable to further break down the tissues and fibers. In this way, cooked meat lasts longer than raw meat (RSC, 2004).

Lastly, it is also worth noting that different enzyme groups work on different food/molecule groups. Proteolytic enzymes, for instance, are those that break down proteins, while lipolytic enzymes break down fats, and finally, amylolytic enzymes break down carbohydrates (The American Meat Science Association, 2015).

[9]To catalyze something is to encourage a chemical reaction to happen faster.
[10]Substrates in this sense are the substance on which an enzyme acts.
[11]Industrial enzymes are complex molecules or proteins that are manufactured and aid in catalysis. They are sourced from plant or animal tissue and microbes.

4.4 GELATINE

(See also Section 15.2.4)

Gelatin (or gelatine) is a protein that is rendered from meat and fish. It is one of the most versatile ingredients in any cook's larder. Made from animal and fish, gelatin is a thermoreversible[12] protein gel that is used in both hot and cold food preparations. However, not all gelatins are the same—unlike many proteins in the cook's pantry, gelatin works a little differently than most. In the majority of food, when proteins are subjected to the heat of cooking, they unfold and form permanent bonds with each other and other protein mixtures, before coagulating to form a firm, solid mass (e.g., crème caramels). With gelatin, however, the molecules cannot form permanent bonds, and in such cases, heat simply causes them to vibrate and loosen from their existing weak bonds. Moreover, because gelatin's molecules are very long, they easily tangle with each other, and upon cooling, this gives the resultant liquid a solid matrix with a firm or soft texture depending on how much gelatin has been used.

4.4.1 ANIMAL GELATINE

As with most things, there are no free gelatin molecules floating around in meat. Instead, they form part of a tightly woven connective-tissue protein that is collagen. Collagen as seen in meat (Section 12.1.2) is the tough, tightly woven, and stretched fibrous protein that gives physical strength to the muscles, tendons, skins, and bones (Tornberg, 2005). Collagen by itself is insoluble; however, when heated in water, it becomes soluble. To obtain a stock to be used as a sauce base or a jelly, the cook first applies a long slow heating/cooking process at 50–60°C/122–140°F (temperatures may vary; see Section 12.9.2.1.2) or above. This is sufficient to dismantle much of the collagen fibers that contain most of the gelatin and squeeze out other meat juices, some of which also contain gelatin molecules. The higher the cooking temperature, the more gelatin becomes dispersed into the liquid and the richer the stock—although this is not always necessarily a good thing, as is explained below (Section 15.2.4).

Having discussed animal gelatin from a cook's perspective, it is slightly different from an industrial angle. There are essentially two ways in which collagen is processed to make gelatin: the acid process and the alkali process. The majority of industrially manufactured gelatin (at least from Europe and Northern America's perspective) is made from pigskin or sometimes cattle skin and bones. Firstly, if pigskin is used, it is soaked in a dilute acid for between 18 and 24 h in order to break down the cross-linking collagen bonds. After this, the gelatin containing collagen is gently extracted in water at about 55°C/131°F to extract the molecules with the least damaged or most intact gelatin proteins. This low-temperature cooking produces the strongest and lightest in color gelatins. After the first round of cooking, the gelatin-rich liquid is then drained and topped up with freshwater, and the process is repeated but this time at higher temperatures. This still extracts

[12]Thermoreversible—this is a process in which gelatin and its denatured proteins, for example, go from a liquid to a gel (bond) at cool temperatures; however, by applying heat, this process can be reversed; whereby the gelatin bonding is undone or unraveled and it becomes a liquid again.

gelatin but only at these higher temperatures. The problem with this is as the temperature increases so there is more damage done to the gelatin proteins that in turn produce softer setting gels and a slight yellow hue to the finished product. This whole process is repeated several times each time with increasing temperatures until the last mix is cooked to a temperature of around 90°C/194°F. In all cases, the extracts are filtered then purified, having their pH levels adjusted to an optimum pH of between 4.5 and 5.5. The liquid is then evaporated off and sterilized before being dried and set in sheets or in granules.

The alkali process is generally used on older bovine hides and other collagen sources. Collagen undergoes a pretty lengthy alkali process of liming or a shorter, equally alkali caustic soda process before extraction. In this way, the alkali hydrolyzes the asparagine side chains to glutamic acid and the glutamine side chains to aspartic acid—both of which result in gelatin. After this processing, the collagen is then washed to rid it free of alkali and is then treated with acid until the desired pH is reached (the pH has a tangible effect on the gelatin strength to viscosity ratio). The collagen is then processed and converted into gelatin using heat and an acid similar to the above procedure after which the final product is ultrafiltered and then passed through the processes of vacuum evaporation, gelation, drying, grinding, and blending.

4.4.2 FISH GELATINE

As with animals, fishes have the bones and skin that are rich in connective tissue. However, because of their relatively cool habitat and their comparative lack of physical exertion to land animals, fish collagen differs from animal collagens (Vaclavik and Christian, 2014). Perhaps, the first difference worth noting is that being less cross-linked than animals, fish collagen melts at much lower temperatures (in some cases) as low as 10–25°C/50–77°F (depending on the fish). This has practical implications in that fish collagen can be extracted at much lower temperatures and in much shorter times (from 20 min to 1 h). Prolonged cooking can affect the stock in two ways: Firstly, as the bones become disintegrated, so they cloud the stock with calcium salts; secondly, being more fragile than animals, fish collagen breaks down into smaller pieces very easily, thus creating delicate gels with loose cross-links that easily melt at lower temperatures.

There are exceptions of course including squid, octopus, and other mollusks whose collagen requires higher extraction temperatures (80°C/176°F) because of their increased cross-linking of collagen (see also Section 15.2.4).

4.4.3 COLD JELLIES

The most important influence on the consistency, texture, and mouthfeel of a chilled gelatin product depends on several things including the amount and quality of the gelatin, the gelatin molecules themselves (whether long-chained or shorter broken chains), and what other ingredients are involved as well as the way in which the mixture is cooled. Indeed, gelatin is a very variable material as even the manufactured gelatin might contain only 60–70% intact, full-length molecules, while the remainder is usually composed of smaller pieces that are less efficient gelation agents. Gelatin too is subject to continued bonding after it has apparently already set. This essentially ensures that crème caramels and Italian Panna Cotta's as well as other gelatin set products become "rubbery" over time. This

phenomenon is called "aging." When the pudding is blast-chilled, for example, the gelatin molecules are immobilized or bonded in a very short space of time. Yet, because of this, the bonds are weak, and the gel is soft, whereas allowing the same pudding to set more slowly at room temperature the bonds are formed not so quickly. This results in a firmer gel; however, that said, both methods of cooling will eventually deteriorate from "aging," that is to say, gelatin ages whether blast-chilled or set slowly. We mentioned too that certain ingredients will also affect the gelling behavior of gelatin. The following gives an example of the sorts of foods and reactions that can take place when involved with gelatin:

- Salt lowers the strength of the gel as it interferes with the bonding of the denatured protein molecules.
- Sugars in general (except fructose) tend to increase gel strength by enticing water molecules away from the gelatin molecules, thus creating a thicker bonded protein network.
- Alcohol too, as long as it remains no more than 30%–50% of the mixture to be gelled, strengthens the gel. However, beyond this proportion, it will split the gelled product.
- Acids, whether fruit juices, citrus fruits, vinegar, or even wine, in fact, anything with a pH below 4, create a weaker jelly by increasing opposing electric charges on the gelatin molecules.
- Lastly, certain fruits like papaya, melons, pineapple, and kiwi contain enzymes that digest and break down gelatin proteins into shorter chains preventing them from setting into a gel at all. However, one work-around is to cook these ingredients first to disable (denature) the enzymes before setting them into a gel.

4.4.3.1 *Aspic and fish jellies*

When making set savory jellies like fish or "aspics" from meat for terrines, buffet work, and *chaudfroid* decorations, the cook will clarify the stock with egg whites and minced meat or fish for extra flavor. These jellies usually contain about 10%–15% gelatin by weight as they should be firm enough to be cut yet tender enough that one does not need to chew them. It is worth noting too that the homemade approach to extracting collagen for fish jellies and aspics is much more aggressive than the industrial equivalent process, which tends to be gentler and more productive.

4.4.4 TYPES OF GELATINE

There are several physical forms that gelatin is sold in; these include powder form and for various grades of sheets from "bronze," "silver," and "platinum." With both granulated and sheet gelatin, they both undergo an initial soaking in cold water so that the solid gelatin can rehydrate and dissolve more readily in warm liquid. Otherwise, if added to warm water without this presoaking, then the gelatin itself would become sticky and lumpy. Although, having said that even if this were the case, the gelatin would still dissolve in the liquid eventually. There is also a "powder" form of gelatin that can be added directly to warm liquid, but this is the exception and not the rule in a cook's kitchen. And lastly, there are the hydrolysed gelatins whose cross-links have been purposefully broken into smaller pieces (too short to form a gel); instead, they're used in the industrial food manufacturing business as an emulsifying agent.

One overriding advantage, if sheet gelatin is used, is that it adds less bubbles or air into the mix whether making aspic jellies and certain desserts like crème caramels. Lastly, when working with

gelatin, it is handy to know that the average manufactured gelatin sets at about 15°C/59°F and remelts at a temperature less than about 35°C/95°F.

Gelatin quality and gelling strength are determined by its "bloom" number, in which the higher the number the stronger the gelatin; for example, a 250 bloom strength indicates high gelation power. In fact, using the term "bloom" itself can be a little confusing. Some people use it to describe the actual process of soaking gelatin in cold water to soften it rather than alluding to its strength. That aside, the term is more appropriately used to describe the strength or firmness of the gelatin being used. The "bloom" strength of gelatin runs from 125 to 250–265 bloom. Many cooks prefer sheet gelatin as they are easy to work with and create clearer gels. The following are the different strengths and representative names:

- Bronze: 125–135 bloom
- Silver: 160 bloom
- Gold: 190–220 bloom
- Platinum: 235–265 bloom

This allows the cook to choose from different grades or strengths of sheet gelatin fit for a particular purpose.

4.5 PROTEINS IN SUMMARY

Proteins can be separated into various categories based on type and usage. These might include their physicochemical properties and functionality. They can also be organized by their structural features (at the molecular level) and their molecular properties (i.e., their surface charge, hydrophilic or hydrophobicity, sulfhydryl content, conformational stability, molecular weight, association/dissociation behavior, and so on) (Morrissey et al., 1987; Farley et al., 2012). Howsoever, proteins are organized; it can be seen that the animal kingdom is made of proteins, from the largest muscle down to the smallest hormone, nerve fiber, or enzyme. In the human body, proteins comprise about 80% of the dry weight of muscle, 70% of the skin, and 90% of the blood (Novozymes, 2016). Proteins are made from building blocks called amino acids. Out of the numerous amino acids out there, the human body requires only 20 or so (8–9 essential and 12 nonessential). These 20 aside, amino acids can also be combined in many different combinations to produce thousands of different proteins. Proteins then are long threadlike particles (of amino acids) that can be straight threadlike chains or folded and coiled into a tight little bundle. As a whole, the inner part of the protein is more protected from physical and chemical damage than the outside—hence, it takes some proteins longer than others to break down (Branden and Tooze, 1998). Proteins contain four specific structures:

The primary structure is the sequence of amino acids in the peptide chain that drives the folding and intramolecular bonding of the linear amino acid chain. This ultimately determines the protein's unique three-dimensional shape. A secondary structure describes the conformation (or shape) of the protein. That is to say, the primary sequencing or main chain of the protein must organize itself to form a compact structure using secondary structure elements. In achieving this, the two most common secondary structure elements are the alpha-helices and beta-sheets, turns and coils, etc. So, by using hydrogen

bonding between the amino and carboxyl groups in the protein chain can, at times, cause certain patterns of folding to occur. There is a tertiary structure that, as most proteins comprise multiple helices and sheets, the formations and folds in a single linear chain of amino acids further describe the 3-D structure of the entire polypeptide. Lastly, the quaternary structure describes both the number and relative positions of the subunits in a multimeric protein.

Proteins are specific too in that the very unique physical three-dimensional shape dictates their specific roles; whether as enzymes, breaking down other foods, or building blocks of muscle, etc., each protein has its specific role (Harvey et al., 2000). It is also worth remembering that even a small change in the structural conformation of some proteins can affect their activity considerably (Harvey et al., 2000). That is to say that, when this specific three-dimensional structure is disrupted, the protein loses its ability to perform its natural function. In this way, it is said to have undergone denaturation.

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CHAPTER

ENERGY AND FOOD

5

CHAPTER OUTLINE

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We heat food and beverages for many reasons including the following: to make food more palatable (digestible), to add flavor, to make cooked food last longer (by killing microbes), and to aid in the conversion of starches into simple sugars so things like potatoes become more edible and sweeter (Field, 2011). We also consume foods for the health and maintenance of the body including a component for energy. In photosynthesis, plants use sunlight to convert carbon dioxide and water into the simple sugar glucose and oxygen. This creates energy and is stored in the chemical bonds that are bioavailable if eaten by other organisms. This energy is released as the bonds are broken down in the varied metabolic processes (cellular respiration). As touched upon earlier (Chapter 1), all foods contain energy, although not all energy is necessarily available to the body. By eating, animals and humans convert ingested food (carbohydrates, fats and proteins, alcohol, water, vitamins, minerals, etc.) into stored chemical energy. As humans, we require a daily intake of nutrients to provide sufficient energy for the daily functioning of the body.

5.1 BROWNING REACTIONS

There are only two ways that food browning occurs—with or without enzymes. In enzymatic reactions, browning occurs in fruits, vegetables, and in certain seafood. It is the oxidation of foods catalyzed by certain chemicals like polyphenol oxidase and catechol oxidase as well as other enzymes. While most of this type are detrimental browning processes, there are desirable browning traits in certain foods like the color and taste of coffee, tea, and chocolate, as well as raisins, prunes, etc. Enzymatic browning begins with the oxidation of phenols by polyphenol oxidase into quinones. In turn, these quinones

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are polymerized in a succession of reactions that eventually results in the formation of excessive production of melanin on the surface of tissues (melanosis) resulting in brown pigments.

Browning without enzymes can, in the process, produce flavors, colors, antioxidant properties, and some nondesirable traits like the destruction of nutrients. Having said that, nonenzymatic browning is general seen as a good thing as it imparts considerable flavor into the process. Nonenzymatic browning (whether for good or bad) can be further subdivided into four categories: caramelization, lipid oxidation, ascorbic acid oxidation, and the Maillard reaction; we will look at two of these—caramelization and the Maillard reaction (Field, 2011; Brown, 2014).

5.1.1 CARAMELIZATION

Caramelization is the action of certain carbohydrates and sugars within foods that react with each other usually in the presence of heat to form brown coloring. It is a complex process that involves the breaking down of complex sugars into simple sugars, polymerizations into larger molecules through oxidation, and isomerization, among other reactions. All in all, these reactions if taken to the right temperatures are responsible for the caramelized sugar smell so familiar in pastry kitchens around the world. When cooking sugar, the first reaction is the breakdown of complex sugars into simpler ones like fructose and glucose (Vaclavik and Christian, 2014; Field, 2011). Following this, water molecules are lost as both simple sugars are then rejoined to form sucrose *anhydride* (without water).

As the heating continues, the molecules become progressively browner in things like crème brûlées, a proportion of the browning in sautéed or roasted foods. In use, this type of browning adds a good deal of flavor to the end product, but if taken to extreme, caramelization of sugar is chemically altered several times until finally it reaches 200°C/392°F where it forms the bitter molecule *caramelan* and finally *caramelin*.

5.1.2 MAILLARD REACTION

The Maillard reaction named after the French chemist Louis Camille Maillard is not to be confused with the caramelization of sugars that is an altogether different form of nonenzymatic browning. The Maillard reaction is of great importance in the kitchen when it comes to the quality of foods, especially for heated foods. The Maillard reaction encourages the browning of foods; it has influences on nutritive value of foods and having the ability to produce antioxidative components (Field, 2011). Moreover and perhaps more significantly, it also has a large effect on the flavor of the foods we eat (Boekel, 2006; Barham et al., 2010). This creates complex flavors distinguishable from the same foods if they were boiled, poached, or steamed, for example (Field, 2011). In fact, it is safe to say that until the Maillard reaction takes place, many foods, especially meat, for example, will be less flavorsome.

The Maillard reaction is usually divided into three separate stages:

- The first is a chemical reaction that takes place between a reducing sugar[1] and an amino acid mostly (but not always) under the influence of heat. That is to say, the reactive "carbonyl" group of the

[1]A reducing agent (aka a reductant or reducer) is any element or compound that loses (donates) an electron. It is in fact any sugar that has a free aldehyde group or a free ketone group. All monosaccharides are reducing sugars along with some disaccharides, oligosaccharides, and polysaccharides.

sugar interacts with the nucleophilic[2] amino group of the amino acid producing N-substituted glycosylamine and water.
- In the intermediate stage, the unstable glycosylamine undergoes Amadori rearrangement (for aldoses) and Heyns rearrangement (for ketoses), that is, the isomerization[3] of glycosylamine catalyzed by an acid or base to form ketosamines (the combination of two organic chemistry functional groups, derived from ketose and amine). It is worth noting that at this stage, the resulting unstable compounds give neither browning nor aromas but serve as important precursors for subsequent reactions.
- In the last phase, the ketosamines further react in a multitude of ways producing either as follows:
  - Produce two water and reductones.[4]
  - Diacetyl, aspirin, pyruvaldehyde, and other short-chain hydrolytic fission products can be formed.
  - Produce brown nitrogenous polymers and melanoidins.

While a complex process, it is worth noting that the first and second stages of the Maillard reaction are all about the degradation of sugar catalyzed or initiated in part by amino acids. The final phase however is mostly about the degradation of alpha-amino acids that undergo further dehydration, fragmentation, cyclization, or polymerization reactions. This is the so-called Strecker degradation of amino acids into structurally related aldehydes, among other things (Barham et al., 2010).

The Maillard reaction is responsible for many colors and flavors in foodstuffs as shown in the table below. However, the extent to which odorants or flavor compounds are created during the Maillard reaction is controlled by the chemical and physical environment, that is, the pH value, temperature, time, moisture, and oxygen. Thus, the Maillard/Strecker reactions give way to an almost unquantifiable number of combinations and by extension a vast array of aroma, taste, and flavor compounds (Boekel, 2006; Berger, 2007; Lung, 2015). The Maillard/Strecker reaction is often at its strongest at the surface of say a joint of beef. At the surface, the water content is reduced, and as the surface dries out, so it draws moisture from within the joint refueling the reaction with more Maillard precursors such as monosaccharides and amino acids. The pH is also a factor in controlling the Maillard reaction as it influences the reactivity of free amino acids (Baldwin, 2012).

It has been reported too that in cooked meats with relatively small changes in the pH, the total quantity of volatile compounds increased as the pH decreases (Baldwin, 2012; Barham et al., 2010).

For simplicity, the aroma volatiles from the Maillard/Strecker reactions may be classified into three groups organized according to their stage of formation and origin. They include the following:

- Simple sugar dehydration and fragmentation products
- Amino acid degradation products such as Strecker aldehydes
- Products from further interactions

While a number of these compounds have relatively high aroma thresholds—these need to be generated in excess, in order to contribute to flavor. Others, belonging to the third group, include a variety of small

[2]The tendency of a molecule or group to donate electrons or react at electron-poor sites such as protons
[3]Isomerization is the process by which one molecule is transformed into a variation of the same molecule. That is, it has exactly the same atoms, but the atoms have a different arrangement, for example, A-B-C to B-A-C.
[4]Reductones are enediols with a carbonyl group adjacent to the enediol group.

heterocyclic flavor compounds that have rather low odor threshold values with aromas that are often characterized by

> … 'nutty' 'roasted' 'toasted' 'cooked vegetable' 'caramel' and 'meaty' flavour notes typically present in heat-treated foods as in coffee chocolate roasted seeds and nuts vegetables meat and cooked cereals.
>
> **(Barham et al., 2010)**

The Maillard reaction can be intensified by adding a reducing sugar such as glucose, lactose, or fructose or as mentioned by increasing the pH (a pinch of baking soda will do the trick) or by increasing the temperature (Baldwin, 2012). The Maillard reaction begins at around 130°C/265°F, but rather than being sufficiently browned and producing roasted flavors at this temperature, the effect is rather like that of boiled foods with little browning occurring. Instead, precursors to the browning "proper" are promoted. Thus, by increasing the temperature to around 150°C/300°F, significant browning and flavor improvements are noticeable. Further increasing the temperatures to 175°C/350°F and above and a significant increase, the Maillard reaction not only occurs but also increased the production of carcinogenic mutagens (*see below*).

As hinted at, there is a downside to the Maillard reaction, and, that is, in certain circumstances, the reaction produces potential carcinogens (cancer-causing), like acrylamide and furans. This is particularly so in highly processed or burnt foods (Everts, 2012). Fourteen years ago, food chemists and Eden Tareke and colleagues from Stockholm University published a paper that showed that heavily processed foods such as French fries, chips, and biscuits contained high levels of potential cancer-causing acrylamide (Everts, 2012; Tareke et al., 2002). Lastly, in order to reduce the overcooking of a piece of fish or meat's interior, high temperatures are often used in the browning stage—this includes things like sautéed tender meats and sous vide meat. This can be achieved on the stove top, the skillet or sauteuse pan, the griddle, or even a butane blowtorch (propane can leave residual off-notes) (Baldwin, 2012).

5.2 HEAT AND FLAVOUR

While heating or cooking of foods can affect the flavors of sweet, sour, and the food's saltiness, so cooking also generally tends to focus more on the bitter or savoriness (umami) of the food on the palate. Of course, looking at heat and the volatility of foods encourages molecules to part with a particular mixture or dish creating aromas. However, heating can also catalyze chemical reactions creating more aroma and flavor molecules in the process. Take fat or beef dripping, for instance, as it melts, so molecules of the dripping will be inhaled and "tasted" (see also Chapter 3). On a cautious note, it is also worth noting that not all heating is beneficial. Flavor and aroma molecules might be vaporized or "evaporated" off leaving less flavor and aroma in the product being cooked—although in reality the loss is generally insignificant. Back to fats and it can be said that heating fats can oxidize them, speeding up the process of rancidity and gives rise to unpleasant tastes or smells. The chemical composition of whether an oil or fat is saturated and unsaturated is also a factor in rancidity. The more saturated fat present in an oil or fat, for instance, the less susceptible it is to rancidity, and by contrast, the greater the amount of unsaturated fat in an oil, the more likely it is to become rancid. Since many of the healthiest plant oils are all highly unsaturated, they are especially susceptible to rancidity.

5.3 SCALING RECIPES: SURFACE-TO-VOLUME RATIO'S

At its very basic, for most recipes, scaling up or down is a simple matter of arithmetic. However, scaling up by a factor of 50, 100, 500, etc. is not so easy. In his book *Culinary Reactions*, Simon Field (2011) explains why. Imagine boiling chicken stock in a four-quart (3.8 L) saucepan—(in an 8 in round saucepan) the depth of the liquid will be about 1.15 in—the bottom heat from the stove is fixed. The surface area on the top of the liquid where evaporation occurs is also fixed. This gives it a combined surface area including the top, bottom, and depth of 129 in^2. Now picture doubling the stock, the saucepan, the bottom heat, the bottom surface area, and the top surface area remain the same; the only difference is the depth of the liquid—2.3 in. So, while the volume of the liquid has doubled, the surface area has increased only marginally from 129 to 158 in^2. This has implications that are not necessarily clear; however, by doubling the liquid volume, it takes about twice as long to boil and twice as long to reduce (Field, 2011). This is simply because while one might have doubled the volume, the surface area has in fact only increased by 158/129 or about 1.25 times. This is known as the surface-to-volume ratio (Vaclavik and Christian, 2014; Field, 2011).

This simple analogy has wider implications in the kitchen. Imagine trying to cook a loaf double the original size, does one cook it twice as long or by a factor of 6–8 times?

5.3.1 HEAT AND SURFACE-TO-VOLUME RATIO'S

Continuing with analogy, in the case of bread, by doubling say a loaf measuring 5 in wide, 4 in high, and 8.5 in long to one of $10 \times 8 \times 17$ in, one actually increases the surface area by 2 and the volume by almost 8 times. That is to say, the 5 in wide loaf's volume is 3 quarts (3.8 L), whereas the 10 in wide loaf while only doubled in dimensions is actually 24 quarts (22.7 L) (Field, 2011). Once again, the cooking of the dough is reliant on the surface area; one has to cook a loaf 8 times the volume through a surface area that is only doubled. This is further complicated by the fact that bread dough is not a good conductor of heat, and so, the likelihood is the outside will cook and brown before the inside reaches the temperature for starches to gelatinize and proteins to denature (Field, 2011).

Add in the knowledge that small things heat up quicker than larger things (Newton's law of cooling). Building on this and with all else being equal, the rate of cooking goes down as the volume goes up. Therefore, in the bread scenario as it is double in size (eight times in volume), so the temperature needed to cook the dough will have to be reduced, and the cooking time needs to be increased. Alternatively, one can reduce the height of the dough and double the depth and length only; this would have the effect of reducing the overall volume (Belitz et al., 2009).

Consider too the more food one puts in an oven or frying oil, so the temperature cools slightly. And by extension, if one tries to fry a big basket of French fries as opposed to just a small handful, the results would not be the same. Also, if one tries to fry a large potato at high temperatures, the results would not be the same either. Instead, in terms of frying a large potato, one can confit it (cooking in fat at a lower temperature for longer). If an oven is full, one can place stone slabs that help retain the heat or use a convection oven that has a fan blowing the hot air around, thus reducing the reliance on radiated heat alone. In the bread example above, if the oven was full of these larger loaves, it might be necessary to consider increasing the temperature at first and reducing it later (Vaclavik and Christian, 2014).

5.3.2 DRYING AND SURFACE-TO-VOLUME RATIO'S

Continuing the theme of surface-to-volume ratios, one naturally needs to consider drying too. In general, water evaporates at the surface; ergo, a smallest surface possible in the surface-to-volume equation is a sphere; this means food will dry out slower. If one wants to dry something out quicker, one spreads it out or slices it thin as in crisp apple or orange slices (121°C/250°F for 1 h), while attempting to dry out the whole fruit will take much longer, taking from one to several days. The smaller the surface-to-volume ratio, the quicker the drying time; examples include sea salt, breadcrumbs, apricots, coffee, and cocoa beans.

5.4 HEATING AND COLOUR

Heat also plays a role in the color of the finished and cooked product. Take green vegetables for instance, many might wonder why overcooked spinach or broccoli, for instance, loses color when they are overcooked? Well, in short, this is to do with the chlorophyll contained within vegetables and leaves. Chlorophyll has one atom of magnesium, and by adding heat, we are in effect replacing this atom with a hydrogen atom giving rise to paler greens, etc. Compounding this, plants' cells contain some of the overall plants' chlorophyll. Upon heating, the cells expand and split open releasing some of the chlorophyll, and if overcooked, this loses enough chlorophyll to make the greens and spinach pale in color. Other foods like meat and sugar are also affected by heat. Caramelization and the Maillard reaction (as described above) change the color of the food; this is because on heating, the myoglobin in the meat reacts with oxygen to produce a brown color.

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CHAPTER

CRYSTALLIZATION

6

CHAPTER OUTLINE

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Many of the ingredients we use in the average kitchen are fully or partially crystalline substances; these include certain carbohydrates, fats, and many salt compounds. These substances might very well pass through other liquid or amorphous[1] states whether through heat or solvents during the preparation of foods. However, the end result might, after heat treatment and cooling or by baking and cooking, result in the formation of new materials or even new crystalline products (Barham et al., 2010). Often too, there is little to stop multiple competing crystalline forms from coexisting.

Crystallization is not just found in the food industry, it is also a technique that chemists use to purify solid compounds. If a water sugar/salt solution is saturated (where no more sugar/salt can be dissolved), then the solution can be seeded; that is, by adding just a single extra crystal into the solution, then the dissolved crystals of sugar/salt will actually start to recrystallize and attach themselves to the single crystal. As time goes by, so the crystal becomes larger and larger. However, this simple explanation belies the importance of crystallization within the food industry. It is used to purify sugars and fats to alter the texture of certain foods like ice creams, chocolate tempering, fondant, and fudge to name but a few. Indeed, the mouth is so sensitive it can detect the graininess of crystals that are as small as 15 μm in size (Field, 2011). Properly made ice cream should contain crystals no more than 40 μm in size, larger than this and the ice cream will have a gritty texture. This also explains why, when left in the freezer over time, the small crystals will start to grow and the ice cream will become hard and grainy in texture

[1]Amorphous entities are without a clearly defined shape or form.

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(see also Section 2.2). Essentially, crystals will only grow or are only attracted to molecules of the same compound, thus crystals are pure substances.

6.1 CONTROLLING THE SIZE

In many of the foods mentioned like caramel, fudge, fondant, ice creams, and even butter or margarine for that matter, the size of the crystals (whether carbohydrates, fats, sugar, or ice) dictates the texture, the consistency, and the perceived quality of a product. Choosing ice creams once again, the size of the ice crystals that form is governed by churning and the rate of cooling (the quicker, the better). As the ice forms, so it is mixed and coated with either proteins in the milk or water. Similarly, the lactose and sucrose crystals are being coated by proteins at the same time, preventing them from joining together into larger crystals. Altogether, the aim is to keep the crystals from becoming detectable by the tongue (Field, 2011).

6.2 WATER

Of all the food molecules that occur in crystalline form, frozen water or ice is the most common. It is also one of the more versatile crystals that are present in all frozen foods. Therefore, the growth of ice crystals is paramount in considering food's long-term storage. It is important to note that in ice creams in particular, besides the ice crystals required of an ice cream, there must also be a liquid phase that is necessary to provide enough fluidity to make ice cream soft and easy to eat, without which the ice cream would remain hard and undesirable. In ice creams then, the addition of sugars or other solutes such as ethanol helps to leave an adequate portion of aqueous solution unfrozen at the typical serving temperature of −13 to −6°C/9–21°F and also at conventional storage temperatures of −15 to −20°C/5 to −4°F (Barham et al., 2010) (see also Section 11.1.3). Other frozen desserts like granitas, for example, are created with much less sugar than ice creams; therefore, the finishing of the granite relies on some kind of mechanical breaking down of the larger ice crystals. In this respect, machines like the Pacojet are excellent investments. In fact, with the introduction of the Pacojet, this has opened up a whole new world of frozen foods for the professional cook. Because it manually "crushes" (for want of a better word) the ice crystals, cooks can make all sorts of ices, whether sweet or savory ice creams, granitas, or simple frozen mousse-like juices (Vaclavik and Christian, 2014a).

When it comes to the physical storage of many foods in the freezer, ice crystals can also become the enemy. This is true in many foods with high aqueous contents like meat, fish, and fruit (think of frozen strawberries). This is because the cells contained within these foods contain water that expands on freezing leaving many cells broken, damaged, and mushy in the process. One work-around solution to this is blast freezing. The quicker an item can be frozen, the smaller the ice crystals that form. However, these small crystals are not particularly stable and are over time overpowered by the larger crystals that will grow larger at the expense of the smaller ones.

6.3 CARBOHYDRATES

Simple sugars are, more often than not, refined into crystalline powders or granules. Moreover, it should also be noted that most sugars are not in fact particularly chemically stable. Although certain reactions like caramelization are very desirable like those of the crème caramel and the crème brûlée, however, there are times when sugar needs to be melted without caramelization as in candy floss or spun sugars. For these purposes, one can select sugars that are more stable, in particular the sugar alcohols xylitol, sorbitol, and maltitol, which are stable and can be melted without any noticeable browning. A second option to this little problem involves mixtures of different sugars that can be used, for example, to make hard-boiled sweets in which sucrose and glucose are boiled to a temperature of about 146–154°C/295–309°F (just short of the caramelized stage); the candies can then cool in an environment that suppresses the recrystallization of the sugar. Crystalline sugars are not by themselves undesirable; indeed, in many dishes such as chocolate fondant, fudge, and dry meringues, they are actively sought. Crystalline sugars not only contribute to the sweet taste of foods but also

> changes the texture of the product depending on the amount and size distribution of the crystals.
> **Barham et al., 2010**

Other carbohydrates like starches are present in the form of small partly crystalline micrometer-sized starch granules, especially in many basic ingredients like flour and potatoes. In a process called starch gelatinization, water and heat are used to heat the crystalline parts of the granules, which in turn will then melt, and the granule will take up water and swell (Belitz et al., 2009).

6.4 FATS AND OILS: TRIGLYCERIDES

In this section of crystallization, we look at the fats and oils that, by themselves, can exist as relatively simple multicomponent materials to complex crystalline structures with a plethora of crystal phases that can all coexist. This makes fats and oils' crystallization and melting behavior emphatically more complex than simple systems like the sugars (Barham et al., 2010; Vaclavik and Christian, 2014a). So, what differentiates fats and oils? In general, liquid triglycerides at ambient temperatures are called oils, whereas the mainly crystalline triglycerides are called fats. Triglycerides show a richness in polymorphic (*see below*) forms; in fact, it is one of the most studied areas of fat structural characteristics as they are used widely in the processing industry in such foods as spreads, shortening, and confectionery applications.

Each polymorph has its own characteristic melting temperature, powder x-ray diffraction patterns, infrared spectral signatures, and Raman spectra (Marangoni, 2011). So far, at least three main polymorphic forms have thus far been identified. These include (in order of increasing stability, melting point, and packing density) the alpha, beta prime, and beta forms. A good-quality chocolate is associated with its content of cocoa butter in the beta, form V, polymorph, while "good shortening or spreads" are associated with the presence of fat crystallized in the beta prime form.

The sizes of individual crystallites are typically in the order of a few micrometers. For most fat types, crystals of the beta prime type give rise to the most optimal crystal size, distribution, and crystal network. These are therefore not surprisingly desirable in ingredients such as butter, margarine, and some forms of chocolate. One important factor of say butter, margarine, and other spreads is the

importance of mouthfeel. Once in the mouth, the fat crystals melt, and the water-in-oil phase is displaced by the all-important stable oil-in-water emulsion. As this happens, so it releases the water-soluble flavors and gives a "watery" rather than an "oily" mouthfeel. This is an important concept in certain fats (Povey, 2013). Some fats can be complex substances; they are considered not only multicomponent mixtures but also multiphasic. Indeed, the number of phases present in such fats is comparable with the number of different triglycerides present that, for most fats, can be greater than 10. This results in a broad range of melting temperatures.

6.5 SUGAR

Unlike a lot of other molecules and compounds like proteins (which denature and gelate/coagulate) or starch (which separate into smaller chains of glucose molecules) or fats (that oxidize and go rancid), sugars are one of the more robust of kitchen ingredients. As well as mixing to form a solution in water sugars are also tolerant of heat. However, when suitably concentrated in water or vegetable juice, sugar easily bonds to each other and amass themselves into pure solid masses or crystals (depending on the circumstances) (Hartel and Shastry, 1991; McGee, 2004). In fact, this urge to crystallize is very strong in sugar. If dissolved in enough water, for example, the water will form a bond surrounding the sugar molecules keeping them separated. But if it gets too crowded with too much sugar, as happens when water is boiled off or more sugar is added to a solution (to reach saturation[2]), then the sugar will react and start to bond with each other to form crystals (Gabarra and Hartel, 1998; McGee, 2004). The vigorously agitated water molecules in a hot saturated sugar solution can keep more sugar molecules dissolved than a cold solution can. Furthermore, the moment a hot saturated solution begins to cool, so it is at this point that the solution becomes supersaturated. Once a supersaturated sugar solution is disturbed, it will encourage sugar crystals to form and grow. As this happens, there comes a point when sugar molecules leave the solution around them less concentrated. When this happens, the concentration of sugar appropriate for its new temperature is reached, and the crystals stop forming. The sugar is now in two different states, while some remain dissolved, others are crammed into their solid crystal form surrounded by the syrup (Gabarra and Hartel, 1998).

Having said that, there are times when we want to encourage sugar crystal growth in the kitchen. As we do so, we must remember a few certain rules. Primarily, there are two steps to achieving sugar crystallization: the formation of the crystal "seeds" and then the "growth" of those seeds into mature, full-sized crystals. In any solution, seed formation regulates just how many crystals will form, while crystal growth controls how large they become.

Crystal "seeds" are the primary platform to which sugar molecules can attach themselves to, and as they do so, they amass into a solid form. The seed needs only be a few sugar molecules in size, and this can happen quite easily through stirring or agitation (this is why sugar for "pulled-sugar" work is not stirred beyond the initial successful solution). Stirring or agitation in this situation only encourages more of the solvents sugar to bump together, binding themselves to form of crystal seeds (Iswanto et al., 2006). Other things can also serve as seeds in cooling syrup and initiate crystallization. One must

[2]Saturation of a solution occurs when a dissolved substance is exactly balanced by the solvents ability to prevent bonding of the solute.

also be careful of sugar crystals that have dried on the edge of a pan or on a spoon, for instance, as these can help seed the cooking or cooling of a sugar saturated solution. In preventing this, the cook will often wash the sides of the pan with clean water in order to redissolve any crystallized sugar particles before they fall back into the boiling/cooling mixture (McGee, 2004; Vaclavik and Christian, 2014b).

6.5.1 CONTROLLING CRYSTAL SIZE

The cook has to be concerned with the premature crystallization and the right size of sugar crystals because cooking sugar for candies, fudges, and other boiled sweets, the very texture of the end product is affected by the temperature of the syrup at which crystallization begins.

As a rule, hot syrups tend to produce coarser crystals, while cooler syrups produce finer crystals. This is because more sugar molecules will bump into any seeded crystal surface in fast-moving hot syrup than in a cold sluggish one. In other words, crystals grow more rapidly in hot syrups. Simultaneously, stable crystal seeds are less likely to form at higher temperatures on account that the few sugar seedlings that do amass are more easily knocked apart in the fast-moving surroundings. Taking account of these two properties, it can be seen that as hot syrups begin to crystallize, so they produce fewer but larger crystals than a cool one—and by extension—a coarser texture. The same can be said for slower cooling of the mixture that, if seeded, can initiate larger crystals (Vaclavik and Christian, 2014b).

As noted, crystal size is also influenced by stirring or agitation of the saturated mixture. This favors the formation of crystal seeds where a syrup that is only occasionally stirred will develop just a few crystals (Iswanto et al., 2006). In contrast, by stirring vigorously or continuously, great numbers of crystals—smaller crystals—will be produced. Therefore, by logical extension, the more a syrup is stirred, the finer the uniformity or consistency of the final candy. This is why when making fudge vigorous stirring is called for. This is also why candies, fudge, and other boiled sweets with fine textures call for the syrup to be cooled extremely quickly before the cook initiates crystallization by stirring or beating (Gabarra and Hartel, 1998).

6.5.2 PREVENTING/LIMITING CRYSTAL FORMATION

All the above relies on the fact that making sugar crystals is the desired result. There are occasions where cooks require their confections to have no crystals at all as in hard candies (boiled sweets). In this case, the mixture is cooled so rapidly it does not have a chance to crystallize at all. In such cases, if no coloring is added, the candies are transparent and very hard. Such an unstructured, noncrystalline substance is called a "glass," and just like its mineral namesake, sugar glass is also brittle and transparent (Lees, 2012). Having said that, in reality, it is not always easy to control or even prevent some crystallization of sugar (sucrose), and confectioners or cooks have long relied upon the properties of other ingredients like invert sugar and corn syrup to slow the crystalline process.

Invert Sugar—Honey is a natural source of invert sugar (syrup); however, a homemade version can be made relatively easy. Invert sugar is the result of taking plain sucrose and boiling it in a solution with cream of tartar. As this happens, so the sugar is broken down into its component parts—glucose and fructose. Both glucose and fructose interfere with the crystallization process of boiled sugar syrups by temporarily bonding to sucrose crystals' surface, thus blocking the way for other sucrose molecules to attach. Artificially made "invert syrups" containing glucose-fructose mixtures are available too; however, as with honey and both their fructose content, they both readily caramelize and can, at times,

cause unwanted browning in certain preparations (Lees, 2012). Acid-inverted syrups on the other hand brown less because of their acidity that helps slow caramelization.

Corn Syrup—Because of the unpredictability of the acid-treated sucrose (invert sugar), many cooks and confectioners use corn syrups in place of sucrose as it does not readily caramelize. Corn syrup is a natural sweetener made from cornstarch also known as glucose syrup and is an effective inhibitor of the crystallization process. The inhibitor effect is more physical with corn syrup as assorted long glucose chains form a tangled mess that physically impedes the motion of both sugar and water molecules. This makes it difficult for sucrose to find another crystal onto which it can fit. Corn syrup also gives body and chewiness to certain confections, although its biggest advantage is that it is both less sweet and less expensive than other alternatives.

6.6 CHOCOLATE

(See also Chapter 17)

The wondrous appearance and consistency of chocolate are a direct expression of its physical qualities, qualities that can, with the right processes, give chocolate a certain silken, glassy quality satisfying both visual appeal and textural mouthfeel. At room temperature, the chocolate is solid, but surprisingly (with sometimes over 50% cocoa butter), it is not greasy. Further, cocoa butter is mainly saturated fat comprising three fatty acids. These fatty acids are able to form dense networks of compact, stable crystals with sufficient leftover fat that can ooze out between the crystals—this is what gives chocolate its glossy finish and an audible "snap" upon breaking. However, as mentioned above, this distinct network can only develop when fat crystallization is meticulously controlled. This process of chocolate tempering requires that the mass of chocolate be heated and cooled in a way that encourages the growth of the right types of crystals (see Section 6.6.1) (Lees, 2012). The difficulty is that chocolate's cocoa butter can solidify into six different kinds of fat crystals of which only two are the stable kinds that produce the glossy, dry, hard chocolate described above. The other four crystal types are, firstly, unstable and, secondly, produce a less organized or unified network of crystals that leaves more of the fat that can readily detach and secrete away (Wille and Lutton, 1966; Timms, 2003; McGee, 2004). As an example, when chocolate is left to melt and then resolidify in an uncontrolled fashion, it's the unstable crystals that predominate, producing a greasy, soft, and mottled chocolate. Untempered chocolate is fine if used in cooking (in meat or bakery); however, if making chocolate decorations or chocolate coverings, the cook is looking for that telltale crisp and glossiness. That said, every time a tempered chocolate melts, if it is treated properly, it does not have to be retempered every time it is melted.

Confectioners and pastry cooks for that matter often make thin chocolate sheets of tempered chocolate for use as garnishes and other delicate preparations, etc. For instance it is common practice for melted chocolate to be painted onto plant leaves, allowed to set before the leaf is peeled off—leaving a mirror image of the leaf. It is also used in piping bags to make lines, drops, and filled shapes. Chocolatiers often melt chocolate and then use chocolate as a coating for fruits like strawberries, raspberries, and bananas or for handmade truffles. Lastly, but by no means least, tempered chocolate can be used to line molds for bonbons and to produce all manner of wonderful decorations. Of course, the quickest way to do this is simply to melt (untempered) chocolate and use it as is; the problem with this method is that while it might taste fine (albeit without the sheen), it is more than likely going to look dull and be

soft instead of glossy and snappy. This is because as the chocolate cools down in a relatively short period, its cocoa fat solidifies into a loose network of unstable crystals. If appearance and consistency are important to the cook, then he/she must temper the melted chocolate or, as happens on occasion, seed it with already tempered chocolate in order to ensure the desired stable crystals of cocoa fat are encouraged to grow—just as the manufacturer does before forming chocolate into bars. Furthermore, the "snappiness" of tempered chocolate takes several days to fully develop as the crystal network continues to grow and become harder—more tightly bound (Svanberg et al., 2011; Reverend, 2009).

6.6.1 POLYMORPHISM

Perhaps the first thing one needs to know about chocolate and tempering is the fact that chocolate's fat (cocoa butter) is polymorphic—that is to say, its fat molecules can crystallize in a number of different configurations (Beckett, 2008; Talbot, 1994). As we have seen, all fats are mixtures of triglycerides, comprising three fatty acids attached to a glycerol backbone. Cocoa butter is no different; the three main acids account for over 95% of those present, which are oleic acid (35%), stearic acid (34%), and palmitic acid (26%). As the cocoa butter is melted then cooled, so the three types of fatty acids behave very differently; in other words, as the fats crystallize, they do so in a number of different ways, a characteristic known as polymorphism. Furthermore, as the structure becomes denser (with tightly packed cocoa butter crystals), so the resultant chocolate will become harder, more stable, and harder to melt (Beckett, 2008). Now this is where it gets interesting. Some fats are only stable in one form, while others might have three, namely, α, β', and β. Cocoa butter however has six, and confusingly, there are two terminologies used to describe these polymorphs—the first is used mainly by the chocolate industry that numbers them as phases I–VI, as first described by Wille and Lutton in 1966 (Wille and Lutton, 1966; Dhonsi and Stapley, 2006). The oil and fat industry on the other hand sides with Larsson (Larsson, 1994) and prefers to use Greek letters for denotation. As it turns out, forms V and VI polymorphs are considered the most stable, giving the right blend of snap and melting qualities. Thus, the cook/chocolatier must ensure that the cocoa butter takes the form of form V polymorphs when used to make confectionery. This form, as mentioned, is hard, gives a good snap, has a glossy appearance, and slows down the onset of blooming.

Understanding polymorphism should give one an understanding of why we need to temper chocolate. The crux of the matter is the fact that only good confectionary chocolate can be made from the stable crystals from phases V and VI. As a result, tempering is a time-temperature process that helps ensure the formation of these stable crystals. The process is explained in the next section, but generally, we need to melt all six crystal phases while encouraging the growth of the phase V cocoa butter crystals.

6.6.2 TEMPERING/PRE-CRYSTALLIZATION

The most common precrystallization method used in the chocolate industry today is conventional tempering. Consisting of three straightforward steps, the tempering process first involves heating the chocolate to thoroughly melt all six phases of fat crystals. After this, the chocolate must be cooled enough to allow the right kind of crystals to seed and grow. The last process requires that the mixture is then reheated in order to remelt the unstable crystals, so only the necessary stable crystals remain and are used to seed the rest of the mix. Once this is achieved, the "right" kind of crystals (the "starter" crystals of phase V) is then able to encourage more of their own type to form, thus creating a dense,

hard crystal framework as the chocolate finally cools and solidifies (Beckett, 2008; McGee, 2004). This is helped by the fact that unstable crystals melt relatively easily, while the required stable crystals (referred to as "beta," "beta prime," or "form" or "phase" V crystals) melt only at warmer temperatures (Talbot, 1994; Larsson, 1994; Wille and Lutton, 1966; Reverend, 2009).

It should also be understood too that the temperature range at which a particular kind of crystal melts is also the same range in which the same crystal forms as the chocolate cools. Therefore, the crystals need to cool quickly but not too quickly as if the chocolate is cooled too rapidly stable crystals do not have enough time to form. Instead, unstable crystals form making the finished product dull and crumbly. Once tempered, if the cook is working with the chocolate, he/she must carefully keep the chocolate at a temperature above the melting point of the unstable crystals but below the melting point of the stable crystals. The tempering range for dark chocolate is a little higher for milk and white chocolates thanks to the different mixtures of cocoa and milk fats.

Another method of utilizing chocolate that has already been tempered and left to cool—or if buying couvertures (which are mostly pretempered anyway)—is simply to melt the chocolate slowly until the desired temperature, in this case just below the phase V crystals melting point at 32°C/89.6°F and keep it at that temperature. In such cases, the cook does not need to retemper the chocolate every time.

One challenge, as with the temperature of the various phases discussed above, is that not everyone agrees on the right temperatures to temper chocolate (see Table 6.2). That said, tempering chocolate does have a margin of error based on the various percentages and composition of fat, coco solids, sugar, and milk solids, i.e., different chocolate brands may require certain increases or decreases dependent on their particular chocolate composition. As long as the range covers the table described in the previous section, then a little discrepancy is ok.

So, while the rational for the precrystallization of chocolate has been made—as mentioned, it is not always agreed which temperatures should be used in each phase. Of the two common methods, one creates stable crystals in a three-step tempering process, while the other uses a small amount of pretempered chocolate to "seed" the melted chocolate with pretempered chocolate (and by extension) stable crystals.

Precrystallization by Tempering—Tempering is treated mechanically and thermally and is the most conventional way to precrystallize chocolate. As has been mentioned (Tables 6.1 and 6.2), there are commonalities and great differences in choosing which temperatures to temper chocolate. The first stage of tempering is to melt all the crystals within the chocolate, in this case phase VI crystals. As far as temperature ranges go, we can see from Table 6.1 that for phase VI crystals, the melting range starts from a low of 34°C and reaches a high of 36.3°C/93–97°F. So, as long as we melt the chocolate above this temperature, we should have all the crystals melted. However, once again (Table 6.2), there is little consensus as to the correct temperature to use. The options range from 40–58°C to 104–136.4°F. So, as a rule and to be on the safe side, this author recommends an initial melting temperature of between 45–50°C and 104–122°F for dark chocolates and slightly less for milk and white chocolates. Then, it is a case of cooling the chocolate so as to melt all but phases V and VI. To do this, we must cool the chocolate to just below phases V and VI and above phases I–IV so as not to seed the chocolate with the wrong crystals. In this case, as the table shows, phases V and VI melting temperatures range from 31.3–36°C to 88.34–96.8°F, but do not forget the temperature needs to be above phase IV—25–28°C. This puts the cooling temperature above 28°C/82.4°F (phase IV) but below phase V 31.3°C/88.34°F. In the case of cooling then, this author recommends the chocolate to be cooled to around 29°C/84.2°F (give or take for the different chocolates). As it cools, so keep stirring the chocolate until it thickens

Table 6.1 Polymorphism, Phases and Melting Ranges for Cocoa Butter Crystals

Crystal Phase	Polymorph	Wille and Lutton (1966)	Timms (2003)	Beckett (2008)	Lechter (2009)	Zimmerman et al. (2012)
		Melting Temperature Ranges (°C)				
I	γ Sub Alpha	17.3	17.3	16–18	17.3	17
II	α	23.3	23.3	22–24	23.3	21
III	β′2	25.5	25.5	24–26	25.5	26
IV	β′1	27.5	27.5	26–28	27.3	28
V	β2	33.8	33.8	32–34	33.8	34
VI	β1	36.3	36.2	34–36	36.3	36

Beckett, S., 2008. The Science of Chocolate. Royal Society of Chemistry, Cambridge; Svanberg, L., et al., 2011. Effect of pre-crystallization process and solid particle addition on cocoa butter crystallization and resulting microstructure in chocolate model systems. Procedia Food Sci. 1910–1917; Zimmerman, A., et al., 2012. Additive manufacturing system and method for printing customized chocolate confections, Google Patents; Gunstone, F.D., 2001. Structured and Modified Lipids. CRC Press, Boca Raton, FL; Reverend, B.J.D.L., 2009. Kinetics of Cocoa Butter in Chocolate and Application to Confectionery Manufacturing, PhD. School of Chemical Engineering, The University of Birmingham, Birmingham, p. 246; Larsson, K., 1994. Lipids—Molecular Organization, Physical Functions and Technical Applications. The Oily Press LTD, High Wycombe, UK.

noticeably (an indication of crystal formation), or pour about a third to a half of the mixture onto a cool surface and scrape and mix it until it thickens—this agitation promotes the formation of the right crystals, before returning the cooled chocolate to the bowl. Once cooled, the chocolate must then be reheated in order to seed the mixture; because we want phase VI crystals at between 31.3–34°C and 88.34–93.2°F, it needs to be reheated to no more than 32°C/89.6°F.

In sum, this author's recommendation for tempering chocolate is

- melt at between *45–50°C and 104–122°F*,
- cool to around *29°C/84.2°F*,
- then reheat to *32°C/89.6°F*.

Chocolate is said to be in temper when 2%–4% of the cocoa butter is in the stable crystal form.

Precrystallization by Seeding—Another way of producing chocolate in the polymorphic phase V form is by seeding. Precrystallization by seeding can be achieved in several different ways; however, all procedures require a small batch of precrystallized chocolate in order to induce the correct formation of crystal phases. The process is quite straightforward; preseeded cocoa butter crystal or chocolate containing crystals of phase VI is added to the precooled chocolate in quantities of about 0.2%–2%. This results in a large number of well-defined core crystals, and although the seed crystals are initially of the phase VI variety, as the cocoa butter in the chocolate solidifies, so the phase VI changes into the desired phase V crystals (Dahlenborg, 2014).

Crystallization in chocolate is a very important factor in determining the way the chocolate breaks or snaps. The chocolate or more precisely the cocoa butter is tempered by controlling the heat as it cools to ensure the creation of a lot of tiny crystals. As with ice cream, the rate of the crystals growth determines the size of the crystals; the quicker the chocolate cools, the smaller the crystals are, the better the "snap"—albeit not too quickly as previously discussed (Field, 2011).

Table 6.2 Various Tempering Chocolate Temperatures

Temp. of Chocolate	Melting Temperature				Cooling Temperature				Tempering Range			
	McGee (2004)	Bau and McLachlan (2011)	Loisel et al. (1997)	Timms (2003)	McGee (2004)	Bau and McLachlan (2011)	Loisel et al. (1997)	Timms (2003)	McGee (2004)	Bau and McLachlan (2011)	Loisel et al. (1997)	Timms (2003)
Dark	45–50°C	55–58°C	50°C	45–50°C	28–29°C	28–29°C	26.1°C	27–29°C	31–32°C	31–32°C	30.5–33.3°C	29–31°C
Milk	40–45°C	45–50°C			27–28°C	27–28°C			30–31°C	29–30°C		
White	40°C	45–50°C			24–25°C	26–27°C			27–28°C	28–29°C		

Adapted from McGee, H., 2004. On Food and Cooking: The Science and Lore of the Kitchen. Charles Scribner's Sons, New York; Bau, F., McLachlan, C., 2011. Valrhona Cooking With Chocolate. Flammarion, Paris, France; Loisel, C., et al., 1997. Tempering of Chocolate in a Scraped Surface Heat Exchanger. J. Food Sci. 62 (4), 773–780; Timms, R.E. (2003). Confectionery Fat Handbook. The Oily Press, Bridgwater; Dahlenborg, H., 2014. Fat bloom on chocolate confectionery systems—From core to surface, Doctoral Thesis. Department of Food Technology, Engineering and Nutrition, Lund University, Sweden, p. 160; Wille, R.L., Lutton, E.S., 1966. Polymorphism of cocoa butter. J. Am. Oil Chem. Soc. 43 (8), 491–496.

Tempering is an Art—While an accurate thermometer and careful temperature control are both necessary for effective tempering, they are not always sufficient in themselves. That's because there is an art to the tempering process that relies on recognizing when the chocolate has accumulated sufficient stable crystals to form a dense, solid network as it cools. Insufficient tempering time, or little stirring, can produce too few stable crystal seeds, and undertempered chocolate results. Conversely, too much stirring (agitation) or time can produce too many crystals and an overtempered chocolate in which individual crystals predominate over the joined network. That said, although overtempered chocolate is stable, it can seem a little dull in appearance and feels coarse and waxy rather than the expected snappy mouthfeel.

Testing for Temper—Chocolate can be tested to see whether or not it has been tempered correctly by coating a small portion on a room-temperature surface whether a plate or piece of foil. If properly and adequately carried out, tempered chocolate solidifies in a few minutes, and one observes a clean, silky mass. Out of temper, chocolate on the other hand takes many minutes to harden and has an irregular powdery, dull and/or grainy or streaky appearance.

Working with Tempered Chocolate—Once chocolate has been properly tempered, it must be handled with care; it should be kept warm within the tempered range to keep it in temper. If pouring into molds or used as a coating for future fillings, the equipment must not be too hot (to melt the stable crystals), nor too cold, that it causes the cocoa butter to solidify too quickly (unstable). Room temperature would usually suffice in this case. Another trait of tempered chocolate sees the chocolate shrink by about 2% upon setting. This is because the stable crystals are more densely packed than their liquid counterparts. The benefit of this shrinkage is the ease with which chocolates can be easily demolded.

Fat Bloom—There are two schools of thought when it comes to fat bloom in chocolate. These are based on either phase separation or polymorphism. Under phase separation, fat bloom is considered to be the separation or the melting of certain triglycerides within the cocoa butter. Consequently, since cocoa butter is made of a diverse mix of triglycerides, each with its own unique melting point, so some triglycerides may still be liquid at room or higher storage temperatures. These liquid triglycerides then migrate to the surface of the chocolate through capillary action and subsequently solidify resulting in the blooming effect (Zimmerman et al., 2012) (see also Section 17.6).

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CHAPTER

RHEOLOGY

7

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When we talk about rheology in food, we are specifically looking at the flow or deformation of a particular food. Despite the word "flow," rheology is equally applied to solids, gases, and liquids, in other words the phases and textures of food. Having said that for the most part in the past, food rheology was restricted to liquid foodstuffs. Nowadays, rheology is more aptly applied to materials like solutions, emulsions, suspensions, foams, gels, and melts as well as semisolids like creams and pastes (McKenna and Lyng, 2003). This means that the food rheologist deals with many food phases that are often substantially inhomogeneous. By way of example, take the humble "ketchup" sauce; if an open bottle is held upside down, it will not flow unless it has been shaken or tapped vigorously—this is due to its rheological properties. In the same way, rheological properties describe the behavioral properties and the perception of certain foods. This occurs either on touching, or it can be felt in the mouth. Such properties depend not only on the rheological flow but also on the solid particles within the food (Belitz et al., 2009; Adebowale, 2012).

Rheology is important for many aspects of food production and consumer consumption: it involves the physical characteristics of fluids and semisolid foods, the engineering and process design, the development of new products, and their testing including as mentioned earlier their sensory properties. While food rheology is not directly equated with food texture, there is, however, some considerable overlap. Taking the International Standards Organization (ISO), for example, we can define food texture as

> all the rheological and structural (geometrical and surface) attributes of a food product perceptible by means of mechanical, tactile, and, where appropriate, visual and auditory receptors.
>
> **Redgwell and Fischer, 2002**

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Rheology has its own vocabulary. In lay terms, food rheology defines the consistency of the many different food products used in the kitchen and without.[1] In turn, consistency is defined by the elasticity (springiness) and viscosity (thickness) of these items (*see next section*). This knowledge is important in the making of pasta, bread, cereal, chocolate, and salad dressings, among many others (Vaclavik and Christian, 2014).

Isaac Newton thought that at a given temperature and shear stress, the viscosity of a fluid would remain constant regardless of changes to the shear rate. Although, in reality, he was only partly right. For example, a few fluids like water and honey do in fact behave this way—these fluids are called Newtonian fluids. Most fluids, though, have viscosities that fluctuate depending on the shear rate of the substance—these are called non-Newtonian fluids (Barnes et al., 1989).

7.1 ELASTICITY, VISCOSITY, AND VISCOELASTICITY

Elasticity—is the tendency of materials to return to their original shape after any deforming force is withdrawn. Examples might include bread dough, gummy bears, etc.

Viscosity—is an internal property of a fluid that offers resistance to flow. For example, pushing a spoon through a bowl of water takes little effort—little resistance—but through honey, the same force moves the spoon very slowly. An important point here is the consistency of resistance. In such compounds as water, honey, or cooking oil, the resistance is uniform and independent of any applied force. That is to say, whether a spoon is pushed through honey or not, the viscosity is the same—this property as described above is called Newtonian fluids. By contrast, in non-Newtonian compounds, viscosity increases or decreases with the increasing application of force (Adebowale, 2012).

The viscosity of a liquid then is a measure of the difficulty that molecules exhibit when passing each other in a fluid, like our ketchup example previously. Therefore, viscosity in liquids corresponds to the informal concept of "thickness." It is the fluid resistance to "shear" forces that arise from forces that exist between the molecules.

Plasticity—this type of fluid will generally behave like a solid when under little or no stress. As in the ketchup example, a force must be used to overcome the apparent solid sauce's viscosity in order for it to flow freely, and once the force is removed, so the ketchup returns to its apparent sold state (Barnes et al., 1989).

Pseudoplastic—is the type of fluid whose viscosity decreases with increased shear rates. These are perhaps the most common of the non-Newtonian fluids and include starches and pastes and are sometimes referred to as shear thinning.

Shear thinning—Most foods show a decrease in viscosity with increased forces such as chewing, kneading, or spreading. Such non-Newtonian materials include melted chocolate, peanut butter, and concentrated tomato juice, for instance. In the example of peanut butter, if one were to mix a spoonful in a bowl, the longer and faster one stirs, the thinner the peanut butter becomes. This is due to the shear-thinning effect of the compound.

[1]Rheology is also applicable to nonfood items too.

Shear thickening—by contrast, viscosity increases with more rigorous force. A good example of this is the action of corn flour in water. When agitated with a small force, the resistance is noticeable; however, mix it with greater force and the resistance is also that much greater (Adebowale, 2012).

Viscoelasticity—is another rheological property of food substances in which certain solutions, suspensions, colloids, etc. exhibit both viscous and elastic[2] characteristics (Barnes et al., 1989). Examples include bread dough, peanut butter, and cream.

Before describing some of the agents of rheology, it is worth looking at the various states of foods—that is, solutions, colloids, suspensions, gums, gels, and thickeners.

7.2 SOLUTIONS, COLLOIDS, SUSPENSIONS, GUMS, GELS, AND THICKENERS

Central to food rheology are colloids; in particular hydrocolloids. Colloids are microscopically dispersed substances evenly distributed throughout another substance—a sort of cross between a solution and an emulsion. Hydrocolloids often make up the gums, gels, and thickeners; they are hydrophilic (water-loving) colloids that can be polysaccharides or proteins of vegetable, animal, microbial, or synthetic origin and either are naturally present or are added to foods to control physical and functional properties of aqueous (water-based) foodstuffs. Technical jargon aside, food rheology is essentially the study and application of these hydrocolloids (gums, gels, and thickeners) (Vaclavik and Christian, 2014).

Gums, gels, and thickeners display several important properties and are used for foam, liquid, and emulsion stabilization; for the prevention of ice and sugar recrystallization; and for textural and other organoleptic properties. That is to say, when added to an aqueous mixture, gums, gels, and thickeners increase viscosity without substantially modifying other properties, such as taste. Such thickening agents tend to provide stability too and may also improve the suspension of other ingredients or additives. In understanding hydrocolloid science, there are two properties of particular importance that these gums, gels, and thickeners display; these are their gel and flow properties (their viscosity and viscoelasticity).

7.2.1 SOLUTIONS

A solution is a homogeneous mixture of two or more substances. The dissolving agent is the solvent, and the component that is to be dissolved is the solute. Components of a solution are atoms, ions, or molecules that make them very small at 10^{-9} m or smaller in diameter. A good example of a solution is sugar and water. That said, it does not have to be a liquid; gases, for instance, can dissolve in liquids, and even solids can be dissolved in solids. The science is fairly easy on this one; when an atom loses or gains an electron, it becomes an ion with a charge (positive or negative) (see Appendix B). Everyday table salt is an ionic compound with positively charged sodium ions and negatively charged chlorine ions. Because of this, the opposite charges are attracted to each other; however, salt becomes ionized when the chlorine atoms in salt attract electrons from the sodium. Once salt is dropped into some water,

[2]Elastic materials are those that strain when stretched then return to their original state once any stress is removed.

the positive and negative ends of water molecules are attracted to the sodium and chlorine ions. As the water molecules exert a stronger pull on the salt ions, so they are pulled into the water—they are dissolved (Vaclavik and Christian, 2014).

Another example of a solution is carbon dioxide that dissolves in water to form carbonated water. Examples of solutions are endless and include sugar, salt, soluble proteins, acetic acid, and certain soluble vitamins too. Solutions are not always either liquid or gas; take candy canes, for example, these are simply a solid solution of sugar, water, and flavorings. Liquids can also be dissolved in other liquids as well, such as water and ethanol. Because of this, alcohols can be made to any strength required from 1 to 100 percent. Even nonpolar oils can be dissolved in a strong alcohol solution (Vaclavik and Christian, 2014; Field, 2011). By design, homogeneous mixtures are solutions with particle size dimensions between 0.1 and 2 nm.

7.2.2 COLLOIDS

(See also Section 2.2)

A colloid is an intermediate phase between a solution and a suspension. Colloids are varied systems in which one substance is dispersed (called a dispersed phase) as fine particles in another substance (called the dispersed medium or the continuous phase). The dispersed phases are particles bigger than molecules and are in the range of 2–1000 nm in size and are termed colloidal particles or simply colloids. They are too large to dissolve and far too small to settle out naturally (McKenna and Lyng, 2003). Good examples of colloids are milk, fog, clouds, and smoke. These microscopically dispersed insoluble particles that are suspended in say milk, for example, are known as the colloids, whereas the whole milk (the overall mixture) is known as the colloidal suspension. Unlike a solution too (described previously) whose stable solute-solvent mixture constitutes only one phase, the colloid's suspended particles are considered multiphasic (Dickinson, 1992). Furthermore, to qualify as a true colloid, the mixture must be one that does not separate or settle out too easily. Colloids can be distinguished from solutions and suspensions using the Tyndall effect. That is—as light is passed through a colloidal dispersion, so it will be reflected or scattered by the larger particles within the colloid. There are three subclasses of colloids: hydrocolloids (gels and sols), emulsions, and foams.

7.2.2.1 Hydrocolloids: Gels and sols

There are two types of water-based colloids (hydrocolloids) often encountered in the kitchen; these are the gels and the sols (liquids made of colloidal suspensions of very small solid particles) (Field, 2011). Sols are described in Section 2.2.

Gels in the kitchen are types of mixtures involving water and solids. One of the most common forms of gel is perhaps the panna cotta, a mixture of milk and milk protein molecules that bond together to form a jelly. Another type of gel is aerated mixture in which water or cream is trapped in cell-like matrices of separate pockets as in a fruit mousse (Talarczyk, 2009). Gelatin (the agent used in both the previous examples) in fact is a prime example of a hydrocolloid, and it is also one that sits in both gel and sol categories. When cold, gelatin is a gel, yet when warmed, it becomes a sol. This strange set of affairs is also true of jellies made of other reversible gelling agents like agar, carrageenan, and pectin (Field, 2012). Gels are formed when particles are cross-linked through chemical bonding into three-dimensional shapes that behave somewhat like solids. Other gelling agents include starches (polysaccharides) and agar. Agar though has certain advantages over other gels and starches in that it has a

higher melting point (85°C/ 185°F) and a higher setting point (32°C/90°F). Agar is also used as a vegetarian option to gelatin (made from red algae or seaweed) although the varied mouthfeel and textures of the two are quite different. Carrageenan (extracted from red seaweed) is another gel that acts similar to agar, only this gelling agent is viscoelastic and liquefies under "shear" stress and returns to a solid once the stress is removed. Pectin, a soluble dietary fiber, is another gel used mainly for making jams and jellies. Pectin is usually extracted from citrus fruits like oranges or lemons or harder fruits like apples. Pectin can also be found in the softer fruits although usually in much smaller quantities. Commercially, most pectin is extracted from the apple pulp after it has been squeezed for juice. Protein gels too, like those found in egg whites, while not reversible, are nevertheless also very common in the kitchen.

7.2.2.2 Emulsions

(See also Section 15.3)

An emulsion is another form of colloid. While it is a common fact that by themselves oils or fats and water do not mix well, with a little help, they can be joined in an emulsion such as milk and milk fats or a good salad dressing. Emulsions with fats such as these are quite easy to make (if following certain rules *see below*) as the chemical bonds between them are really quite weak. The trick is to use molecules that both attract and repel oil and water—in this case, a double-ended molecule; these are called emulsifying agents. Luckily, these molecules are very easy to come by as most organic cells' membranes contain a water-loving side and a water-repelling side. These are known as phospholipids. Once ground up and introduced to oil, they form a coating around small droplets of oil, thus preventing it from combining with other small droplets of oil. A common emulsifying agent is lecithin. This is obtained commercially from soybeans, but there is another source readily available to the cook and that is egg yolks. Egg yolks contain lecithin and protein that help bind oil and vinegar together; also if mustard is used, the phospholipids present will also strengthen the emulsion (Field, 2011). Egg yolks can be used to thicken all sorts of emulsions. This is because of the various yolk components, two in particular: the proteins of low-density lipoproteins (LDL) (phospholipids and cholesterol), and secondly, the larger yolk granules (containing both LDL and high-density lipoproteins (HDL)) are both effectively strong emulsifying agents. That said, the large yolk granules are at this stage simply too big to coat any dispersed droplets; however, add some salt and it helps break down the large granules into their more effective subcomponents—LDLs, HDLs, and proteins (in particular phosvitin).

Gums (Section 7.2.4) can also be used as a stabilizer in the emulsifying process. Gums are large starch-like molecules that when in the presence of water form colloidal suspensions. Adding a pinch of xanthan gum, for instance, into a hollandaise or a mayonnaise at the right moment will stabilize the emulsion very effectively, making it very difficult to separate. Apart from lecithin, there are other emulsifying agents, most important of which is "fat" surprisingly. Fat molecules are triglycerides, i.e., made up of three fatty acids. Break these fats down into their component parts monoglycerides or diglycerides and one has more emulsifying agents to play with.

7.2.2.2.1 Emulsifiers and stabilizers

When it comes to emulsifiers, these can best be described as molecules that lower the surface tension of the dispersed phase (e.g., in mayonnaise). What happens is as the surface tension of the oil is lowered so it is easier for the egg yolks lecithin content (or other emulsifying agents) to coat the oil droplets,

helping to keep them apart from each other. Furthermore, emulsifying agents must be partly soluble in both liquids. They do this by the chemical makeup of the particular agent. Each agent must have two different regions within the same molecule, one soluble in water and the other soluble in fat. Lecithin, as mentioned, is a good emulsifier as it contains molecules with both a fat- and water-loving area. Other good emulsifiers are the larger protein molecules with their long chains of amino acids that too contain both fat- and water-compatible molecular regions. All in all, though, it can be said that the best natural emulsifiers in the cook's kitchen are lecithin (in egg yolks) and casein proteins (in milk and cream).

Emulsions, while able to help create sauces or accompaniments, are inherently unstable, and they can readily "split" or coalesce into their preemulsified fractions. This is not too much of a problem if using handmade emulsions in the home or the professional kitchen. But for longer shelf life—especially in the manufacturing industry, one also needs to consider the stability of the emulsion. Having said that, more and more professional kitchens are becoming familiar with industrial stabilizers and emulsifiers. As mentioned, while emulsifiers ease the process of making an emulsion, it does not necessarily translate into a stable emulsion. For a stabilizer to work, it must be able to "get in the way" of the droplets that are trying to rejoin (coalesce). Luckily though, there are numerous molecules and particulates that can help in this respect. Proteins, starch, pectins, gums, and fine pieces of plant tissue all stabilize emulsions well. Even tomato paste, with its substantial protein content (approximately 3%), is a useful emulsifier and stabilizer.

Making emulsions. From the above text, it might seem that emulsions are quite easy to make; in reality, a few rules must be followed if one wishes to create a stable product. In the first instance, in all cases, the dispersed phase is added to the continuous phase and not the other way around. Take mayonnaise, for example, the steps include the following:

- The liquid- or water-based mixture (water and vinegar) is mixed with suitable emulsifying agents like egg yolks and any stabilizing agents being used.
- The dispersed phase (the oil) must be added very slowly/gradually to begin with (*see below*) while the mixture is whisked or blended vigorously.
- It is prudent, too, not to add too much dispersed phase—no more than three times the volume of the continuous phase (the vinegar and water solution) should be adequate; otherwise, the final emulsion becomes too thick and less stable.

Split, coalesce, separation of emulsions. Every cook in the kitchen knows that when making an emulsion, it is important to start slowly although many perhaps do not know why beyond increasing the chance of the mix "splitting." This means adding the dispersed phase (in the case of mayonnaise, it is oil and in hollandaise, it is clarified butter) slowly. This is because, in the early stages of an emulsion, if too much dispersed phase (oil) is added too quickly, too soon, the oil cannot be dispersed into the growing emulsion quickly enough. This leaves droplets of oil unemulsified before more oil is added. This phenomenon is known as "splitting," "coalescing," or "separation." An emulsion has to grow and grow slowly at first; once the emulsion has achieved a little volume and developed some viscosity, its increased stability then allows oil to be added more quickly.

7.2.2.3 Foams

A foam is simply any liquid or solid that has a gas suspended in it. They form an important aspect of cooking, especially in baking. Foams can also take many forms including marshmallows, meringues, Genoese sponge cakes, whipped cream, foam sauces, and some cookie recipes. They are formed in

several different ways, and in many but by no means all cases, protein plays an important part in the process (Field, 2012). For the most part, many proteins are partly or wholly water-soluble and are made of long chains of amino acids curled up tight in small ball-like structures. These are held together by weak chemical bonds. That said, not all proteins are the same; instead, some are attracted to water (hydrophilic) and are repelled by oils and fats, while others are attracted to oils and fats and are repelled by water (hydrophobic). Despite these differences, when heat is applied or when proteins are physically agitated (e.g., by beating), they begin to denature (see Chapter 4). As described, denatured proteins are proteins whose weak bonds have been broken, and as a result, they have a tendency to uncurl or unravel. Denaturing can occur in three different ways: physically or mechanically as in beating, whisking, or pounding with a meat hammer; chemically/biologically through the addition of acids in lemon juice, cream of tartar, and acidic marinades; or through heat by cooking, etc. As these unraveled proteins encounter other uncurled proteins, so two things generally happen. Firstly, the untangled protein is not fully untangled; this allows it to tangle or snag onto other proteins creating physical or mechanical bonds. The second thing than can occur is new chemical bonds that are formed allowing the two proteins to bind together at the molecular level. The bonds between these proteins are stronger and more stable if the proteins are not fully uncurled or unraveled. Ultimately, as more and more proteins bind together, they form a protein web—a network that traps some of the water or oil in which the proteins reside and any air that was also incorporated as the mixture was being beaten or cooked. In other words, bubbles of air are surrounded by a tough layer (the skin) of interconnected denatured proteins. In whipped egg whites, these bubbles of air are surrounded by a film made of protein to which some water is still attached. In whipped cream, the air bubble is surrounded by a film of protein to which some fat is still attached; also, because of the different nature of the proteins in cream (being hydrophobic), so the water within the cream is pushed out and held outside this bubble (Gardiner et al., 1998; Field, 2012).

7.2.2.3.1 Egg whites

As is true for the gelling or coagulation of heated eggs (see Section 11.4), the key to a stable egg foam is the propensity of albumin proteins to unfold and bond with each other when they are being exposed to physical stress. By whipping the egg whites, we exert physical stress on the proteins. As the whisk forces itself through the white, so it drags some of the white with it creating a pulling force that physically unfolds the compacted protein molecules. As a result, egg whites readily form physical bonds with each other, and a continuous solid matrix of proteins holds both water and air in place. There are several things that we need to consider in this scenario. By increasing the connections or bonds between proteins, we can make our egg white foam more stable. Because of the predominantly hydrophilic proteins within egg whites, any oil present—whether from the yolk itself or whether introduced by accident (greasy bowl or utensils)—will adversely affect the ability of the whites to whip. Interestingly, in this respect, the type of equipment used also affects the whip; for instance, fat readily sticks to plastic, so even if it appears clean, the chances of some residual fat being present are higher in plastics than other materials. This is why metal or glass bowls are usually preferred for whipping egg whites in.

Whites can also be overwhipped. This results from the overbeaten proteins uncurling or unraveling too much, encouraging too many bonds to form, which then ends up drawing the proteins closer together effectively squeezing out bubble-trapped air rather than containing it. What happens then is egg whites look grainy and dull and will eventually collapse back on itself (McGee, 1997; Gardiner et al., 1998). So, to help stabilize egg whites and reduce excessive bond formation, we can use a few tricks. Using copper bowls to whip the whites is one trick, for instance. This is not a housewife's

tail; instead, this helps stabilize the foam because ions in the copper bowl react with the proteins that contain sulfur. In turn, this allows them to form stronger bonds with other amino acids that also contain sulfur (Field, 2011). Another trick is to add a small amount of acid such as lemon juice, vinegar, or cream of tartar into the egg white mix. This can also help stabilize foams by allowing the proteins to unravel a little and tangle together with other lightly unraveled proteins even before the whisking starts (Gardiner et al., 1998; Field, 2012). However, one thing, as cooks we see a lot of is overbeaten egg whites. In this case, by simply adding another egg white and beating it until the mixture forms peaks again can often salvage the mixture.

When it comes to optimum whipping techniques, whites at room temperature are easier to whip due to decreased surface tension that also allows the proteins to expand that much easier. Also, adding sugar at the correct stage during beating makes a positive difference. Adding sugar too soon however means the sugar molecules obstruct and slow down the egg white's proteins ability to find each other and form bonds (Gardiner et al., 1998).

Lastly, while the albumin protein allows egg whites to foam in the first place, when a meringue, for instance, is in the oven, another protein ovalbumin gives the structure rigidity upon cooking.

7.2.2.3.2 Gelatine foams

As well as the albumin of egg whites, so other proteins can also make foams. Another simple protein foam is made with gelatin. Gelatin is a protein obtained either from stock or by the acid and alkaline processing of collagen (found in animal bones, tendons, hides, etc.). It is used, among other things, to make marshmallows. Marshmallows are made by several methods, but one method involves cooking a sugar syrup to the firm ball stage (116°C/240°F) and beating the mixture into gelatin that has softened in cold water. As with other protein foams, the gelatin will denature as the hot syrup, and whisking causes it to form links with itself, forming a sturdy net, with the syrup attracting the water-loving parts of the protein, leaving the oil-loving parts facing the air in the bubbles.

7.2.2.3.3 Milk foams

Milk foams tend to be more fragile than other foams and as such are generally made shortly before serving. Milk foams too need to be heated with steam in order to foam naturally. As per the above examples, milk owes its foaming power mainly to its proteins. There are two different types of proteins in milk: the caseins responsible for around 80% of all proteins in milk and the whey proteins. While casein plays a role in the functional properties of whipping/foaming, it is the whey proteins that offer far superior foam stabilizing properties. In doing so, it creates a more rigid film at the air/water interface of the foam. As proteins amass (either by mechanical whipping or through the use of steam injection), so a thin layer around of proteins forms around the pockets of air. Milk foams, however, are more fragile and short-lived than other foams because milk's proteins are scarce (just 3% of the milk's weight compared with egg whites' 10%). On top of this, casein proteins are tough little proteins to denature making it difficult to unfold and coagulate/gelate into a solid network. This is why milk can be boiled and boiled evaporating to a fraction of its original volume without curdling. However, if we heat the milk to around 70°C/160°F, the whey proteins (just 1% of milk's weight) do unfold to some extent. If these proteins unfold at the air-water boundary of a bubble wall, then whey proteins do bond to each other and at the same time moderately stabilizes the foam. Some milks are more convivial than others at producing foams, especially those skimmed milks with reduced fat and/or fortified with proteins. However, be aware that skim milk foams lack flavor and mouthfeel, whereas full fat foams are somewhat fuller in

texture and flavor. One other point to consider is that very hot milk does not hold its foam well. Although, when it comes to fat, it must be said that, as is the case of egg whites, the addition of fat will destabilize and minimize the formation of foam. In this respect, as fats in milk increase, so foam stability decreases. This is so up to about 5% and then after close to 10% fat, so the opposite occurs, and milk foams are once again stabilized. At this point, highly more stable cream-type foams are formed.

7.2.2.3.4 Cream foams

Cream, the layer of butterfat on top of milk, is liquid at body temperature yet solidifies when chilled. There are a variety of cream types that are usually distinguished by their fat content. Ranging from 18% fat content for single creams in the United Kingdom to 30%–35% for whipping creams, and richer still at 48%, there are the double creams; moreover, some creams, especially clotted creams, can have as much as 55%–60% fat content.

Unlike foams of egg whites and milk, proteins do all the foaming; however, in whipped cream, proteins share the task with fat; that is, cream foams are mostly stabilized by fat (McGee, 2004). Also, unlike egg whites where fat inhibits the whipping process, if cream is to be whipped—only cream with a minimum 30%–35% fat content can be whipped into a foam. This is why "single" creams cannot be whipped (Field, 2012). The process of whipping cream foams works like this. Firstly, the cream must be chilled to keep the fats solid. Then as cream is whipped, so proteins are denatured and which then surround the fat globules (triglycerides) in the cream. Along with these proteins, cholesterol and molecules called phospholipids[3] work together surrounding the globules of fat. Phospholipids' unique structure comprises both water-loving (hydrophilic) and water-repelling (hydrophobic) components. This special arrangement helps keep the triglycerides floating around separately, not only from one another but also from the liquid water in the cream (Field, 2011). As part of "fats," protective membranes are exposed or stripped away so the "naked" fat globule settles in one of two regions in the cream. Either they face the pocket of air in the bubble, or they stick to another destabilized fat globule. Collectively, the fat globules (just like the proteins) stick together or, more precisely, coalesce. At this point, pockets of air are surrounded by films of solid fat and protein with trapped air inside and with the water on the outside in between the bubbles. This creates a continuous fatty network. In the process and as mentioned above, the temperature of the fat is important—that is to say, only chilled fat can coalesce; warm fat will simply not adhere to each other, and one ends up with a split cream, a demulsified solution. Additionally, cream with a higher fat content like the UK double cream (38%–40% fat) will actually whip faster while forming a stiffer, denser, and less voluminous foam.

If the whisking continues past the point at which a stable foam has been made, the congregation of fat globules continues until the process actually begins to destabilize the foam. At this point, more fat globules coalesce with each other into ever coarser clumps of butterfat. At which point, air and liquid that was held together inside the pockets of fat begin to weep; the fat loses volume, and the cream becomes granular (in kitchen parlance, it is "split"). Further whipping still and we can turn the whole thing about face, that is, instead of having a water-based solution with tiny films of fat and protein with air trapped inside; overbeating will eventually break down the membranes further forcing the fat to clump tighter together and forcing the air and water out. In this situation, we have made butter.

[3]Phospholipids, special biological "fatlike" molecules that possess hydrophilic (water-loving) and hydrophobic (water-fearing) regions.

As has been labored, to keep the whipped cream stable, the temperature of the fat needs to be kept low enough that the fat stays quite solid. Another solution to help stabilize the foam is to add more protein, such as gelatin or certain vegetable gums. In fact, as cream is inherently unstable in itself, after 24–48 h, water will naturally start to leach out of the cream, making any cakes or buns coated with it slightly soggy. One common solution is to add a small amount of gelatin that helps hold the foam together and by extension keeps the fat in place (Field, 2011; McGee, 2004). Further, if cream has already been whipped successfully (straight out of the fridge) and held at room temperature the same as above, the butterfat will soften, and bubbles will collapse leading to leakage of the liquid. If using homogenized cream, the fats are generally smaller; this gives rise to creams that are lighter in texture

7.2.2.3.5 Sugar foams

One can make foam without proteins, emulsifiers, or surfactants although as a general rule they are usually less stable. But if we make the foam out of something that hardens when it cools and before the air can escape, then we don't require proteins to stabilize the foam. One kind of confection—honeycomb or cinder toffee—does just that. One starts by cooking a saturated sugar syrup (sucrose and simple sugars) to about 150°C/302°F, to the hard-crack stage of sugar boiling. This is the stage just before the sugar starts to burn (caramelizes) and turns brown (Field, 2011). To this mixture, bicarbonate of soda is added, and then, the mixture is quickly beaten. The high heat causes the baking soda to decompose into sodium carbonate and carbon dioxide bubbles which, upon cooling, entrap the bubbles causing a sweet sugary foam that is popular around the world.

7.2.2.3.6 Leavening agents

Leavening (a raising agent) plays an important role in baking science. Specifically, leavening is the foaming action with the incorporation of either air or carbon dioxide bubbles, which helps to lighten and soften doughs and batters. Without leavening products, some traditionally leavened breads will be left dense. Leavening agents are the substances by which this is achieved, and they can take one of three forms—biological, chemical, or physical/mechanical (see also Section 10.1.6).

Biological leavening—Biological leavening is the process of using living organisms that characteristically release carbon dioxide to leaven things like doughs and batters, for example. Typical biological leaveners include sourdough starters, yogurt, buttermilk, and, more commonly, yeast. Yeast is a single-celled fungus that feeds on simple sugars and starch giving off by-products of carbon dioxide and alcohol, which give products made with yeast their distinctive flavor. In other naturally leavened breads such as certain sourdoughs, the flavor is further enhanced by various lactic acid bacteria (lactobacilli) or acetic acid bacteria (acetobacter). Unlike chemical leavening, however, biological leavening is a slower process requiring proofing times to allow the yeast time to react or ferment. Yeast comes in many forms and is known by many different names—fresh yeast, compressed yeast, active fresh yeast, cake yeast, baker's compressed yeast, wet yeast, active dry yeast, baker's yeast, bread machine yeast, brewer's yeast (aka beer yeast), and lastly nutritional yeast.

Chemical leavening—Chemical leaveners are compounds that, when the right conditions prevail, will release gases when they react with other chemical catalysts and/or moisture or with heat. Most are based on a combination of acid-like cream of tartar and a salt of bicarbonate (sodium bicarbonate or baking soda). After the reaction has finished, some say a saltiness can be detected, so it is wise to use chemical leavening agents prudently. Chemical leaveners are used in things like quick breads and

cakes, as well as cookies and untold other applications where a long biological fermentation is undesirable or indeed impractical.

Mechanical—Mechanical leavening is the physical whisking or "creaming" to use kitchen parlance. This is no more noticeable than (as has been mentioned before) beating egg whites or whipped creams. It is also the method used in making nonchemical (raising agents) cakes like Genoese, where the only aeration introduced into the mix is that of beating/whisking.

7.2.2.3.7 Sauce and puree foams

These types of foams sit on the fence between protein and nonprotein foams in the culinary kitchen. It all depends on the ingredients used. Cooks will often aerate sauces and purees to make foams by whipping or blending liquids or purees at high speeds. As a result, almost anything can be foamed using this method. However, for the large part, most of these foams are very unstable as (depending on ingredients) there might be insufficient protein or stabilizing agents to hold the foam together. What usually happens then is once the foam forms, within seconds or sometimes minutes, the foam will collapse in on itself. One work-around solution that one might see cooks doing is to keep the sauce hot (if required) and as needed; the puree or juice foam is whipped to order, i.e., one dish at a time. Foams are so popular these days, however, that cooks often make foams with a stick blenders, but remember, for it to hold, one needs a stabilizer such as agar, gelatins (or other proteins), or lecithin and other emulsifiers and foaming agents (stabilizers).

Foaming agents or more commonly foam stabilizers are surfactants,[4] that is, when present in small amounts, they reduce the surface tension of liquids in turn facilitating the formation of a foam. Alternatively, to enhance a mixture, stability surfactants inhibit the coalescence of bubbles. Using gelatin as a foaming agent is very efficient as it is a good stabilizer in its own right; it is also worth noting the fact that different gelatins have different foam stabilizing properties and as such need to be carefully selected. Using the emulsifier lecite or lecithin (one among many) as a stabilizing agent is actually very good at converting juices and watery liquids to airs and foams. To produce a stable foam using soy lecithin, it is typically used at ratios between 0.25% and 1.0% ratio by weight. That is, for every 100 g of liquid, 0.25–1 g of soy lecithin would be used.

7.2.3 SUSPENSIONS

Suspensions are created when particles of solid material are held within a fluid and are sometimes referred to as a coarse dispersion. A suspension will also have particles that are large enough to be seen under a microscope or with the naked eye. The particle size is generally larger than those found in solutions and colloids—usually greater than 1000 nm. Particles within a suspension may become distributed evenly throughout the suspension by shaking the contents vigorously or by mechanical means. They are also large enough not to dissolve in the fluid; instead, they separate out easily when disturbed. Although that said, the use of binding agents may prevent this from happening or at least slow the process down. Suspensions can either be heterogeneous[5] or homogeneous depending on the materials used. In short, we can say suspensions are types of mixtures in which solid particles do not dissolve in a liquid to form a solution and are too big to form a colloid. The large particle size gives the

[4]A surfactant is a substance that aims to reduce the surface tension of a liquid in which it is dissolved.
[5]Heterogeneous suspensions have diverse, varied, or assorted particle sizes dispersed in a suspension liquid.

suspension a murky or opaque quality, and left long enough, some may separate out on their own or can be separated at will through filtration.

7.2.4 GUMS, GELS, AND THICKENERS

(See also Section 15.2.3)

Because thickening agents provide body, increase overall stability, and improve suspension within sauces, soups, stews, etc., so they are often used as food additives. Thickening agents then are materials used to thicken and stabilize solutions, colloids, emulsions, and suspensions. It is important to know too that some thickening agents are also gelling agents. Thickeners are often based on either polysaccharides[6] including starches, vegetable gums, pectins, and even proteins. The major types of thickeners, stabilizers, and gelling agents are discussed in the next sections.

7.2.4.1 Gums, gels, and gelation

Gums and gels work by taking a volume of liquid and stabilizing it in a solid matrix-like form through a network of partially dissolved long-chain polymer molecules. When they form a complete three-dimensional network throughout the system (usually as it cools), they become a gel. The most commonly known gel is gelatin although there are many other types of gels or gelling agents. For many, in the scientific world at least, it is reasonable in many cases to treat the network as a rubber-like system. Most gels start off in an aqueous medium although in certain cases some gels operate in an alcohol or oil-based environment. The gel works when the molecules form cross-linked connections that may be chemical or physical. As these molecules form, so further heating or gelation acts to create a three-dimensional network throughout the solution, at which point it forms a gel.

Methods of Gelation—There are a very wide and complex array of possible gelation mechanisms depending on the type of cross-links and their relative stability. However, for simplicity, we can divide the connections into two broad categories, chemical and physical. The main difference being that chemical connections are generally irreversible while physical connections can often be reversed. The prime example of chemical gels in food is well demonstrated in the cooking of eggs, both the egg whites and the yolks, whether in "floating islands," "in brûlées," or by themselves (see Section 4.2). That said, most gels encountered in the kitchen are of the physical variety rather than the chemical variety. As mentioned previously, the most common of these is gelatin[7], although it must be repeated that not all gels are equal. Gels originate from a variety of sources (animals, seaweeds, fruits, other foods, etc.) and have broadly differing molecular weights. This multiplies the range of possible junction types that may also significantly differ between products. This gives the cook a variety of gelling agents that he/she may play with. Other gels and thickeners include the following:

- *Agar*—is thermoreversible with high melting and setting temperatures.
- *Alginate*—is a polysaccharide made up of chains of sugar units (guluronate, mannuronate, or guluronate-mannuronate blocks), the proportion of which determines how strong a gel is formed.
- *Carrageenan*—gels when mixed with proteins.

[6]Polysaccharides are carbohydrates (e.g., starches, cellulose, or glycogen) whose molecules consist of a number of sugar molecules bonded together.

[7]Gelatine is obtained by the thermal denaturation of collagen.

- *Cellulose derivatives*—various derivatives form gels by swelling or even wicking (the absorption or drawing off a liquid through capillary action).
- *Gelatin*—thermoreversible gels form on cooling.
- *Gellan gum*—is a water-soluble thermoreversible anionic[8] polysaccharide produced by the bacterium *Sphingomonas elodea*. It is a gelling agent developed specifically to replace agar and gelatin in conditions that are not ideal. There are two types of gellan gum: the first are gels made with low acyl, which tend to be brittle and firm. The second are made with high acyl, which are flexible and elastic.
- *Guar gum*—guar gum is a thickening agent derived from guar beans. It is especially useful as a binder in gluten-free baking.
- *Gum Arabic*—also known as acacia gum, is a natural gum made of the hardened sap of various species of the acacia tree—it also gels at high concentrations and in acidic environments too.
- *Locust bean gum*—also known as carob bean gum, is derived from the seeds of the carob tree; it is a cost-effective and simple way to stabilize certain foods.
- *Pectin*—is a naturally occurring polysaccharide found in berries, apples, and other fruits. When heated together with sugar, it causes a thickening that is characteristic of jams and jelly gels at low pH.
- *Xanthan gum*—is a polysaccharide secreted by the bacterium *Xanthomonas campestris* responsible for thickening and stabilizing—it is also thermoreversible.

Referring to the physics, the propensity for a gel to form sufficient three-dimensional cross-links depends greatly on the molecular weight of the gelling agent—the lower the weight, the more gel that is needed (Barham et al., 2010).

Take gelatin gels, for example, there is much that can affect the different phases of the product. Firstly, it is the product of the denaturation or disintegration of collagen. Further, the concentration of gelatin seems to affect the melting temperature, i.e., the more concentrated the gel, the higher the melting ranges and vice versa (Cole, 2000). Moreover, other properties like the presence of proteases[9] can also affect the inclination for junctions to form. This is especially so in fruits including pineapple, kiwi, mango, ginger root, papaya, figs, or guava where proteases hinder (by breaking down the protein) rather than aiding the gelling process. The tip in this case is not to use more gelatin but rather to cook the fruits first, effectively denaturing the enzymatic proteins (protease). Also, affecting the gelling rate of gelatin is the pH value of the product to be set. It would seem the lower the pH (more acidic), the longer the gelatin needs to set, and once it does set, it will not be as firm where the pH value is higher (Schrieber and Gareis, 2007).

Other gel-forming agents have found their way into restaurants such as "spherification" whereby flavored alginate solutions are dropped into a solution of calcium creating spheres in the process (El Bulli). Another gel with a higher melting and setting point is agar, which has been used to great effect by Heston Blumenthal in his flaming sorbets (Barham et al., 2010).

[8]A negatively charged ion.
[9]Protease refers to a group of enzymes whose catalytic function is to hydrolyze (break down) proteins. They are also called proteolytic enzymes or systemic enzymes.

7.2.4.2 Starches

(See also Section 15.2.1)

A different class of gels are those formed by starches. These not only occur when food is being cooked but also can be made inside the kitchen too. Starch granules are the main storage form of carbohydrates in plants; they are polysaccharides assembled from the simple sugar glucose and can contain anywhere from five hundred to several hundred thousand glucose molecules. Starch has many industrial applications although more importantly for us it is also an additive in foods. Chemically, vegetable starches are composed of two different molecules, amylose (20%–30%) and amylopectin (70%–80%), although the plants also incorporate some proteins within their starch.[10] Starch molecules are broken down by enzymes known as amylases, and the digestibility of a given starch is influenced by its physical form. In plants, starch is present in microscopic granules.[11] Cooking starch-containing items results in gelatinization (not to be confused with gelation, which is the process of setting something in a jellylike substance). When starch gelatinizes, its molecules hydrate, and the starch granules begin to swell. This enhances the enzymatic breakdown of the starch itself. Cold water will not greatly affect the amylose or amylopectin in a starch granule, but hot water will. Furthermore, by adding heat, the starch granules in ordered crystalline layers start to melt (>60°C/140). This disordering and opening up of the structure allow amylose molecules (quite water-soluble) to soak up the water while the branched amylopectin less so. As the starch molecules significantly overlap with one another, so they do not fully dissolve; instead, they form a soft gel. In general, starch granules can absorb (depending on variety) a considerable amount of water without losing their integrity. It is this swelling and subsequent absorption of water that provides the thickening effect of starches used in the kitchen. By way of example, potato starch granules can absorb liquids and swell up to 100 times their original volume (Barham et al., 2010). Indeed, the thickening of soups and sauces by ingredients such as flour, arrowroot, tapioca starch, or corn starch is an example of the gelatinization of starch granules into their optimal swollen state. These can serve to thicken soups and sauces as mentioned, or upon cooling, they can leave a suspension in a gel-like state, for example, a traditional "blancmange."

Of note, here is the problem of overcooking. By overcooking the starch, it can have disastrous effects on the soup or sauce as the granules disintegrate; they release amylopectin and amylose into the sauce with the resultant thinning of the product.

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[10]Importantly, different plants (and different varieties of the same plant) incorporate widely differing amounts of protein in their starch granules.
[11]A typical granule of starch may be a few micrometers across.

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CHAPTER

ACIDS AND BASES

8

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When describing acids and bases, one often gets the jargon a little wrong. This is not surprising as there are several definitions out there that at first glance may seem a little contradictory. For a fuller more detailed explanation into this, see Section B.7.3.

The first thing worth noting is that all solutions are either acid or base (basic) and that base liquids are sometimes called alkalis.

Acids and Bases—Fundamentally, acids are hydrogen-based substances in which hydrogen atoms have either been stripped of their proton or have gained electrons leaving behind charged hydrogen ions. These corrosive ions "burn" metals and in their mild palatable form are somewhat sour (depending on food type). Bases are contrary to acids in that mild, alkaline foods taste bitter or acrid on the tongue. All acids contain hydrogen, and bases tend to absorb or "soak up" hydrogen ions, and given sufficient quantity, bases can effectively neutralize acids leaving water and residual salt (Vollhardt and Schore, 2014). Both acids and bases are measured on a pH scale (potential of hydrogen) ranging from 0 to 14 where 0 equals the strongest pure acid there is and 14 the strongest base. A pH of 7 is neutral. An alkaline is simply a soluble base, and while all alkalis are bases, it is true that not all bases are alkalis; for a base to be called an alkali, it must be soluble in water (Brown and Trivieri, 2013). So, if acids and bases are present in the same solution, as previously mentioned, they end up canceling each other out through a reaction that leaves behind a salt and water (neutralization).

In food, as in chemistry, acids (measured in pH) are sour or "astringent," while bases are pungent and acrid. Examples of weak acids include vinegar (acetic acid), lemon juice (citric acid), and even soda water (carbonic acid). An example of a neutral food is water with a pH of between 7 and 7.5. Stronger acids mixed with water tend to lose all of their protons to water molecules and in the process create hydronium ions, while weaker acids are less likely to lose protons to water molecules (Field, 2011). Alkalis are bases that have an OH (oxygen-hydrogen) pairing involved. Bases or alkalis can accept protons by donating hydroxide ions. In the kitchen, strong bases include food-grade lye (sodium hydroxide or caustic soda) and baking soda (sodium bicarbonate) (see also Appendix B).

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Classifying acids and alkalis is simple; the lower the pH value, the stronger the acid; the higher the pH value, the stronger the base. A selection of common foods and their values can be found in Appendix E and Table E.1.

8.1 ACIDIC/BASE FOODS VERSUS ACID/BASE FORMING FOODS

A distinction has to be made with acidic and base foods and acidic- and base-"forming" foods once they are consumed. Essentially, acidic and base foods are just that—either acid or base in nature before they are eaten. By contrast, acidic- and base-forming foods can actively influence the body's chemistry and its chemical balance—but only in a limited fashion. Furthermore, when it comes to whether a food is acid- or base-forming in the body, it is important to remember that it has nothing to do with the actual pH of the food itself.

While the body relies on appropriate pH levels in its cells, it is thought that the body thrives on a slightly base/alkaline diet. Human blood serum too requires a controlled pH level in the alkaline range of between 7.35 and 7.45 in order to thrive and survive (Schwalfenberg, 2011). It is generally acknowledged too that today's diets are rich in saturated fats, simple sugars, chloride, and sodium as compared with diets of the distant past. As a result, this may result in something called metabolic acidosis (the acidifying of the body), which is ultimately incompatible with genetically determined nutritional requirements (Adeva and Souto, 2011; Sebastian et al., 2002; Konner and Eaton, 2010). Furthermore, alkaline diets potentially result in certain health benefits including reduction of muscle wasting, benefits to bone health, improving cardiovascular health, improvements in memory and cognition, better functioning of many of the body's enzyme systems, and mitigation of hypertension and strokes (Minich and Bland, 2007; Schwalfenberg, 2011). In fact, diets with an increase in consumption of fruits and vegetables would aid in any diet helping to reduce morbidity and mortality of chronic disease. Also, when one talks of probiotics, it can be said that the good bacteria (the probiotics) found in cultured/fermented foods naturally produce lactic acid that gives foods their characteristic sour taste. This is helpful especially in the gut that utilizes lactic acid to control the growth of competing, potentially harmful microbes. While acid reflux (heartburn) seems to only occur in the stomach, it is thought to be more to do with having less stomach acid rather than too much (Compare et al., 2011; Gates and Schatz, 2011).

Acid ions, primarily found in proteinaceous foods such as meat, poultry, fish, eggs, grains, legumes, certain nuts, and some processed foods, together with minerals like iron, sulfur, and phosphorus are produced in the body. On top of this, many soft drinks contain phosphates, which are also acid-forming foods. By contrast, the minerals calcium, potassium, sodium, and magnesium and certain foods are very useful biologically in the body. Such minerals and foods are ironically abundant in fruits and vegetables. That said, there are exceptions. Milk for one, while high in protein, sulfur, and phosphorus (which are acid-forming foods), actually contains sufficient calcium to neutralize the liquid and its potential acid-forming property. Other foods that are neither acid- nor base-forming are the pure fats and the simple sugars, starches, and other foods devoid of minerals. However, while the general benefits mentioned above are, to some, attributed to a high alkaline diet, the reality might well be that most of these benefits come as the result of a nutritionally well-balanced diet, a diet full of fruit and vegetables with less meat and dairy, the very same dietary guidelines that governments and their agencies advocate. Indeed, claims that a high alkalinity diet can alter certain bodily fluids pH are only partially true.

Indeed, from a dietary perspective, eating a healthy balance of fruits and vegetables does in fact result in the generation of alkalinity, whereas meat and dairy products tend to generate more acid. In addition to this, the average diet may well contain various other food acids and alkalis that, when ingested and ultimately absorbed through the gastrointestinal tract, contribute to the net acid-alkali load in the body (Remer and Manz, 1995; Koeppen, 2009). However, while food does affect the acid-alkali load in the body, it does so only minimally. Referring once again to the acid-base balance of the body, it can be said, in point of fact, that the acid-base balance is a means by which the stability of the body's carbonic acid to bicarbonate in the blood is kept in equilibrium. And although some small alterations do occur in the chemistry of the blood and body fluids, such changes are generally due to serious problems in either the metabolic pathways or are the result of improper functioning of the body's organs resulting from severe morbid conditions. Indeed, the effects of food on the equilibrium of the acid-base within the body have been somewhat exaggerated.

One of the more serious claims of a high alkaline diet suggests that one can alter the pH of one's blood through the food we eat; it is not borne out. In perspective, the blood is tightly regulated at around a slightly alkaline pH value of 7.35–7.45, and it is the vital role of the kidneys that is pivotal in creating a good environment in which the body can operate. For example, "acid ash" resulting from a diet of acid-forming foods is quickly moderated by bicarbonate ions in the blood (Koeppen, 2009). This results in the production of carbon dioxide, which is ultimately exhaled via the lungs, and salts, which are produced by the kidneys. During this process, the kidneys create more bicarbonate ions to replace those lost in the blood. This is the sustainable way in which the body regulates blood pH (Koeppen, 2009; Bonjour, 2013).

8.2 COOKING WITH ACIDS AND ALKALIS

Acids in cooking are quite widespread; they are used in dressings, to flavor fish, in desserts, in cheeses (*next section*), and in fact almost everywhere in the kitchen. There is a type of cooking too without heat where the denaturing of proteins occurs; in this case, the use of acid is used in the marination of foods like "ceviche" (a South American dish of macerated fish) primarily marinated in lime juice and other flavorings/seasonings. In fact, most acid cooking in the kitchen revolves around seafood. Seafood in general does not have the same tough collagen that is found in meats, so cooking tends to be gentler. The exception is with some shellfish that can be really quite tough; in cooking these, one can add some acid such as vinegar or lemon juice into the cooking liquor to help denature the proteins. Or one can simply marinate the shellfish in an acidic marinade such as the protein-digesting enzymes (proteases) extracted from a number of plants including pineapple, kiwi, and ginger before cooking.

When cooking with alkalis, it is important to note that any fats in the food will be turned into soap, which might be a culinary challenge to sell. One of the more familiar alkalis used in cooking is bicarbonate of soda (sodium bicarbonate or baking soda) (Lung, 2015). This is a weak alkali as is carbonic acid (soda water), while lye is perhaps lesser known but much stronger. Sodium bicarbonate acts with an acid (lemon juice or tartaric acid (cream of tartar)), which when combined creates carbon dioxide used in doughs and cakes to leaven them. The same sodium bicarbonate breaks down at 70°C/158°F to produce carbon dioxide and water vapor. This is the basis of making honeycomb (cinder toffee). However, perhaps one of the more widespread uses in cooking with alkalis is with corn. Mixing lime (calcium hydroxide—not to be confused with the fruit that is an acid) with boiling water will soften the

outer hull of corn kernels (Field, 2011). Furthermore, the corn absorbs the water and swells, and the resultant flour made from the corn becomes more workable. An added bonus of using lime this way is the fact that certain minerals are leeched into the corn such as calcium, iron, zinc, potassium, and copper. If using the corn whole, a hot alkali solution works to denature the kernel proteins and frees the niacin (vitamin B_3) making them both more bioavailable (Section 16.5).

8.3 PROTEINS AND ACIDS

We have seen in earlier chapters that proteins in milk are denatured by heat and when mixed with eggs and sugar make crème caramels or by enzymatic proteins to make cheese and by bacteria to make yogurt. Well, proteins can also be denatured by acids too—also in cheese making. This is because acids that naturally develop over time in the milk will eventually denature the proteins and curdle the milk (casein) (Vaclavik and Christian, 2014). However, this is not recommended as the milk will spoil before this happens. If using an acid to denature proteins, it is recommended to use a mild acid and a little warmth. Yet, that said, making cheese this way, the acid and heat tend to denature and coagulate not only the casein but also the proteins in the "whey" at the same time too (the liquid left after coagulating the milk into "curds") (Vaclavik and Christian, 2014; Field, 2011; Brown, 2014). This is not always desirable as the whey can also be used to make cheese in its own right. However, one important characteristic of making cheeses out of whey proteins, such as paneer or ricotta, this way is that they do not melt as other cheeses do. And of course, by denaturing the proteins in the whey, we also get a better yield from the milk (Belitz et al., 2009).

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CHAPTER

HYDROLYSIS, OXIDATION, AND REDUCTION

9

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9.1 HYDROLYSIS

Hydrolysis refers to the cleavage or unbinding of chemical bonds by the addition of water. Many of the nutritionally important molecules in our food like starches and proteins (polymers[1]) are not especially soluble or volatile resulting in little, if any, perceivable taste or aroma. However, when degraded into smaller molecules, a wide array of tastants[2] and aromatics can be generated. There are several different ways in which this type of degradation can occur; however, hydrolysis is probably the most important. The three macronutrients carbohydrates, proteins, and lipids can all react with water and can be degraded into smaller subunits that are more likely to possess aroma and/or flavor—which may or may not always be agreeable (Belitz et al., 2009). The monomers (sugars) of carbohydrates are linked together by glycosidic[3] bonds. These bonds may hydrolyze as a result of acid catalysis[4] or via enzymatic reactions (Sections 12.3.1 and 4.3). This is exactly what happens in brewing beer. Malting, an important development in the fermentation process, is the enzymatic hydrolysis of starch producing smaller carbohydrates, making them available for the yeast.

[1]A polymer is a large molecule composed of many repeated subunits.
[2]A tastant is the thing being tasted.
[3]A glycosidic bond is a type of covalent bond that joins a carbohydrate (sugar) molecule to another group.
[4]Catalysis is the acceleration of a chemical reaction by a catalyst.

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Proteins too may be hydrolyzed during the ripening of cheese or the boiling of meats. In this process, shorter peptides[5] are formed, which can eventually be broken down to their individual amino acids. In general, the more hydrophobic[6] an amino acid is, the more bitter the taste, and conversely, the more hydrophilic[7] an amino acid, the more neutral or sweeter the taste (Barham et al., 2010). Carrying this further, if enough peptides with specific combinations of hydrophobic amino acids are formed in cheeses, it can make the cheese very bitter and risk ruining its flavor altogether. Another amino acid, glutamic acid, is often formed during the cooking of meats, in soups, and in savory cheeses. These are, on the whole, a good example of hydrolysis as they excite the savory (umami) taste sensation in the mouth. Most foodstuffs are either acidic or fairly neutral, so base (Chapter 8) catalysis is relatively rare. However, in fish treated with lime[8] or other alkaline substances, as is the practice in some Asian and Scandinavian countries (Barham et al., 2010), hydrolysis through base catalysis plays an important role in the development of flavor.

Lipolytic[9] enzymes too can hydrolytically[10] break down lipids to form glycerol and free fatty acids. Such reactions are especially important when it comes to rancidity in oils and fats (Section 9.2). However, not all lipid hydrolysis is bad. Take the humble loaf of bread with its partially hydrolyzed lipids. These lipids act as emulsifiers in bread, for example, to reduce staling and starch crystallization (Chapter 6). Mold ripening of cheeses too through protein hydrolysis followed by lipolysis yields wonderfully complex flavors. This is especially so in blue cheeses like Danish Blue and Roquefort in which free fatty acids contribute significantly to the overall flavor.

9.2 OXIDATION AND REDUCTION

Another process that is often responsible for degrading food molecules is oxidation. In fact, it is true to say that most foods and food components are susceptible to oxidation. Once oxidized, so the flavor and color may potentially change the substances' overall flavor and nutritive value. In fact, unlike hydrolysis, in most cases, oxidation leads to flavors that are not welcome or desirable, so we go to great lengths to reduce or avoid oxidation during storage and the processing of fresh ingredients (Barham et al., 2010). The oxidation of foods may be initiated by one of several means: enzymatically, as has been shown before (see Section 4.3); by catalysis (the acceleration of a chemical reaction by a catalyst) through the transference of metal ions that potentially occur when using copper bowls or pans to whip egg whites or when frying in copper pans, for example; or, from the thermal oxidation that occurs during cooking, or lastly, from exposure to light (Section 16.3.1). In kitchens, many of us are familiar with oils or fats that have gone rancid (oxidized). In fact, when it comes to sensitivity to oxidation, the degree to which lipids are unsaturated and the nature of any antioxidants present are critical. By way of example, fish oils and fats are especially sensitive to oxidation, plant oils express intermediate sensitivity, while animal fats, especially from ruminants are the least sensitive to oxidation (Barham et al., 2010). From this, we can see heavily unsaturated oils like walnut and pumpkin oxidize

[5]Peptides are short chains of amino acid monomers linked by peptide bonds, that is, small proteins.
[6]Hydrophobic are water-hating elements.
[7]Hydrophilic are water loving elements.
[8]Calcium hydroxide, traditionally called slaked lime or calcium oxide (CaO), is commonly known as quicklime.
[9]Lipolysis is the breakdown of lipids that involves hydrolysis of triglycerides into glycerol and free fatty acids.
[10]The action of hydrolysis.

quite readily, so they should never be used for frying or cooking; they are however good for dressings. By contrast, the higher monounsaturated content of oils or fats such as olive and rapeseed (canola) is almost perfect for frying (Section 16.3).

Essentially, when it comes to oxidation, we can basically boil it down to a chemical equation using electrons and protons (see Appendix B) (Barham et al., 2010). In essence, this is what happens when avocado and apples, for example, go brown (or are oxidized); when wine[11] is oxidized into vinegar (Section 9.3); or, lastly, as described above, when oils and fats go rancid. In the oxidation of apples, the plants produce colorless phenols and the enzyme polyphenol oxidase[12]; as the apple is cut, so cells are opened allowing the two molecules to mix. Next, oxygen in the air is combined with the polyphenol to produce quinones that in turn react to make melanins (a dark colored molecule). Melanins are also responsible for the bruises one finds under the skin of fruits and the browning of avocados and bananas. Most food components are vulnerable to oxidation, and as such if oxidation occurs, this may change the flavor, color, and nutritive value of many foods. There are ways to slow and even stop the process. The polyphenol oxidase as mentioned above is an enzyme, and as we know from protein biochemistry (Chapter 4), enzymes are proteins; so by heating the enzyme (by cooking the apple or by dipping it in a pot of boiling water—blanching it), we denature the enzymatic protein effectively disarming it (Barham et al., 2010). Furthermore, as enzymes slow down or cease functioning completely as temperature drops, so by simply freezing the apple, the browning reaction will also be slowed or can even cease altogether. However, with apples, for instance, when one does not want to blanch or freeze the fruit, there is another way of slowing the oxidative process. One can rub it with a little lemon juice or place it in a bowl of water and lemon juice. This is because the enzyme only works within a narrow pH range, and by simply adding lemon juice or vinegar, it will change the environments' pH value (Field, 2011). Lastly, as the polyphenol oxidase also requires moisture to function so by freeze drying the apple slices we prevent the formation of melanins. Another dehydration method would be to cover them and place them in an oven at a low temperature to dry out. Unfortunately, the browning process is a quick process, so this method is not the most effective unless one can prevent the oxygen from reaching the apple. One option, although not available to the average kitchen, professional or otherwise, is to irradiate the apple; this in effect denatures the enzyme. Lastly, it is interesting to note that when it comes to flavor-altering enzymes, there is one enzyme in particular—the lipoxygenase enzymes (responsible for oxidation)—that is still active at the low temperatures of the freezer. It is for this reason we blanch vegetables prior to freezing, to break down this enzyme, prolong shelf-life, and protect its flavor (Barham et al., 2010).

Photooxidation, although happens with oil and certain foods left in the light, is a comparatively slow process and rarely a problem in the professional kitchen. In plants, which are out in the sunlight all day, they tackle the problem of oxidation by employing carotenoids (colored pigments) (Section 14.3); these are naturally present together with chlorophylls (the green pigment). Combined, the plant is relatively well protected against photooxidation. Having said that and as mentioned before, photooxidation can and does occur in some foods when stored in the light, albeit quite slowly. The quality of the raw material is important for the oxidative stability of certain meats too. The feeding regime of nonruminants, for example, is key to this; by feeding ruminants large quantities of unsaturated lipids (sometimes

[11]Vinegar is made from wine as the ethanol oxidizes into acetic acid in the presence of air.
[12]Oxidase is any enzyme that is capable of oxidizing something, while the polyphenol is the thing being oxidized.

mixed in the feed), so it aids in the increased risk of oxidation in the meat. By contrast, a good supply of antioxidants from fruits, vegetables, and fresh herbs. helps slow down the oxidative process postmortem (Section 16.3). In this respect, free range foods are preferred over factory intensive rearing.

9.3 VINEGAR

It was known in ancient times that while wines, because of the alcohol content, tend to inhibit the growth of most microbes, there are a few noteworthy exceptions. These are the bacteria that are able to utilize oxygen to metabolize alcohol extracting, in the process, much needed energy. When working with wines, the bacteria not only survives and prospers but also can go on to convert wines' alcohol into acetic acid (a pungently acidic wine) and water or more commonly known in French as *vinaigre* or vinegar. Vinegar, incidentally, is a much more effective antimicrobial agent than alcohol.[13] As a result, vinegar became one of the most potent preservatives in ancient and modern times used to pickle all manner of fruits, vegetables, and meats. It is not just wine either that can be made into vinegar, the ancient Chinese created complex vinegars from rice, wheat, and other grains, which were sometimes roasted before fermentation. Traditionally though, making vinegar simply meant leaving containers of wine and other alcoholic liquids exposed to oxygen allowing them to sour over a period of weeks and even months. However, this unpredictable process has been replaced in modern times allowing vinegars to be made in only a day or two.

Vinegar or acetic acid contributes to taste through its acidity on the tongue and aroma through pungency on the olfactory senses (especially when heated). It also boils at approximately 118°C/236°F, which if the water is allowed to boil off results in a concentrated vinegar. Furthermore, one of vinegars' molecular properties is the fact that the molecule tends to be fatlike, resulting in the better absorption of certain fatlike aroma compounds especially in herbs and spices, Hence the use in the kitchen of "steeped" or soaked herbed and spiced vinegars. It might also come as a surprise that vinegar was and still is in certain regions of the world used as a beverage and in its more common role in cooking and flavoring. There are literally dozens of types of vinegars available to the cook.

9.4 VINEGAR PRODUCTION

Wine left in the open air oxidizes into acetic acid. More precisely, there are three ingredients required to make vinegar; these are an alcoholic liquid like wine or cider, oxygen and bacteria from one of several genera of bacteria; in particular acetobacter, gluconobacter, and gluconacetobacter, 3 of 10 acetic acid causing bacteria (AAB) whose subspecies are commonly used in commercially produced vinegar. As these bacteria require oxygen to thrive, so the action takes place at the surface-air boundary of the alcoholic liquid. By using alcohol as a source of energy, these and other bacteria are capable of metabolizing it at temperatures between 28–40°C and 82–104°F leaving two by-products acetic acid and water. Another factor involved in the stability of the bacterial process, and by extension the final

[13]Acetic acid is an effective agent of preservation in which a weak solution (0.1%) is able to inhibit the growth of many microbes.

product, is the concentration of the alcoholic liquid used. An alcoholic content of around 5% produces vinegar with around 4% acetic acid; this is just about strong enough to prevent spoilage. Although a paradox occurs at concentrations above this threshold, while a stronger alcohol content produces a more stable vinegar, at higher concentrations, the fermentation process is slower, and there is sometimes residual alcohol in the final vinegar. This is why wines with about 10%–12% alcohol are sometimes diluted with water. Furthermore, by diluting the wine, some of the final flavors are in danger of being muted or even lost altogether. This is why artisanal producers tend to ferment their wines at a slower pace to allow for complexity and stability of flavor while reducing/removing residual alcohol.

After fermentation of the wine or alcoholic liquid is finished, almost all vinegars are subsequently pasteurized at between 65–70°C and 150–160°F to render any remaining bacteria inoperative. After filtration, many types of vinegar are aged for at least a few months to allow the flavor to mellow out and become less harsh allowing other flavor compounds to create new, often aromatic substances (Belitz et al., 2009).

There are essentially three ways of producing vinegar in the West.

9.4.1 THE ORLéANS PROCESS

The oldest, slowest, and perhaps simplest of methods involves partly filled wooden wine barrels that are diluted and injected with an acetobacter, often from a previous batch, which are then allowed to ferment. As time passes, so some of the vinegar is siphoned off and replaced with new wine. This method results in a slow fermentation (because of the low surface area of the wine) in which reactions among the alcohol, acetic acid, and other flavor molecules are encouraged. This method, while taking 2 months or perhaps more, can actually produce some of the finest flavored vinegars there are.

9.4.2 TRICKLING PROCESS

In the second method, wine is repeatedly trickled over an air-rich porous medium such as wood shavings or synthetic materials onto which acetic bacteria has been cultured. This method speeds up the vinegar-making process as the medium over which the wine is poured greatly increases the surface area and thus the reaction time resulting in production times of a matter of days only.

9.4.3 SUBMERGED CULTURES

Lastly, there is the submerged culture method whereby acetobacteria in the mix are fed or bubbled with a constant supply of oxygen in the form of air, vastly speeding up the process. This is an industrial method and reduces production to 24–48 h (Tesfaye et al., 2002b).

9.4.4 VINEGARS FOR EVERYONE

There are a variety of vinegars for cooks to choose from, from wine vinegars, fruit, malted, distilled, and Asian, among others. While all contain acetic acid, they are all distinctive, sometimes subtly so, as each are made with different starter ingredients and are either matured or not.

9.4.4.1 Wine vinegars

Made with fermented red or white grape juice, wine vinegars not surprisingly have wine-like characters reminiscent of buttery aroma compounds (diacetyl and butyric acid). Although many wine vinegars generally contain lower levels of acetic acid than white or cider vinegars. Better quality and more expensive wine vinegars are sometimes matured in wooden casks for up to 2 years, revealing complex, mellow flavors. Furthermore, wine vinegars can be made using individual varieties of wine such as champagne, sherry, balsamic, or pinot gris. Two of the most highly prized vinegars come from Italy and France; these are the balsamic and sherry vinegars.

9.4.4.2 Balsamic vinegar

Decades-long fermentation gives traditional balsamic wine vinegar its characteristic black color, its complex flavor, and syrupy texture. Made from concentrated white grape juice, balsamic is versatile in cooking, particularly in both sweet and savory products. Only traditionally made *aceto balsamico* refers to this long-aged (in wooden barrels) vinegar that concentrates and matures the flavor considerably. As a result, they can become very expensive indeed.

Traditional balsamic vinegar starts with the reduced grape juice from the trebbiano grapes that have been boiled to two-thirds of the original volume in which sugars and acids are concentrated. At this stage, the "must" also begins the browning reactions of the grape proteins and sugars. With no initial alcoholic fermentation, the liquid is placed inside ever decreasing small barrels, often made from a variety of oak, chestnut, cherry, mulberry and juniper woods. While no initial fermentation is triggered, there is some natural fermentation that takes place over the years generating aroma products.[14] At the same time, evaporation continues, and the juice (must) is transferred to smaller barrels (McGee, 2004).

While no initial alcoholic fermentation is triggered, acetification begins very slowly as a mixed culture of high-sugar-resistant yeast (*Zygosaccharomyces bailii* or *bisporus*) and bacteria that converts a portion of the abundant sugars into alcohol then into acetic acid through oxidation. As the two fermentations (natural and introduced) take place, so the process of maturation or aging simultaneously enhances balsamics' characteristic aroma and flavor profiles. One reason why traditional balsamic is so sweet (apart from the initial and subsequent reductions) is the fact that the yeast, as specialized as it is, cannot ferment all the sugars into alcohol then acetic acid (Gullo et al., 2006). As a result, balsamic vinegar might comprise anywhere from between 20 and 70% unfermented sugars. The finished product also contains about 8% acetic acids and about 4% tartaric, malic, and other nonvolatile acids. One can also expect about 1% alcohol and as much as 12% glycerol (a product of the fermentation process) contributing greatly to the silken, velvety viscosity (McGee, 2004). Balsamic vinegars come in a range of ages from younger aged balsamic—3–5 years to 6–12 years—to the much older versions ranging from 12 to over 100 years old. However, by law, a vinegar labeled "Aceto Balsamico Tradizionale di Modena" must have been wood-aged for at least a minimum of 12 years. Older variations labeled "stravecchio" must be aged for at least 25 years. These older high-quality balsamics are sometimes used as aperitifs or digestifs.

White balsamic vinegars—White balsamic vinegar is also produced in Modena, Italy; however, it is produced in a different process. In this case, the grape is cooked under pressure that affects and even

[14]Fermentation, whether natural or introduced, is very slow as the high concentration of sugars and acids inhibits the growth of all but the hardiest of microbes.

prevents the caramelization of flavors and color. Aged for only 1 year in charred wooden barrels, white balsamics flavor remains light and delicate.

Modern variations—Once again and as one would expect so, modern cheaper and less elaborate versions or imitations were popularized in the 1980s. These are produced more rapidly. The better of the mass-produced balsamic versions will generally include some concentrated grape "must" and are aged for about a year or so. Cheap nonaged versions on the other hand are simply wine vinegars with added color and caramel and, if required, sweetened with sugar.

9.4.4.3 Sherry vinegar

Sherry vinegar shares similarities to both balsamic and wine vinegars. Sherry wine has little or no residual sugar, so this has to be added to the must before fermentation can take place. Like balsamico too, sherry vinegars are aged in wooden barrels for years and sometimes even decades from (30–75 years). Also in line with balsamic production practice, so sherry vinegars are blended with older batches until the right balance is achieved. Characteristically and once again, this is found in balsamic vinegars too and sherry vinegars through concentration and extended contact with microbes and the wooden barrel, so sherry vinegars are replete with high levels of savory amino and organic acids. In older soleras,[15] acetic acid can reach concentrations of 10% and sometimes more, and although not as dark and savory as its balsamic counterpart, it is nevertheless noticeably more intense and nuttier than other wine vinegars (Tesfaye et al., 2002a).

9.4.4.4 Fruit vinegars

Fruit vinegars can be made simply through maceration of the fruit with neutral flavored vinegars, or they can be the product of fermented juices of the fruit itself.

Cider vinegar, for instance, is an example of the latter; it is produced from fermented apple juice that allows it to retain certain characteristic aroma components of the apple juice including volatile phenols (ethyl guaiacol and ethyl phenol) (Plutowska et al., 2010). Also, rich in malic acid, apple or cider vinegars go through a malolactic fermentation. Cider vinegars can sometimes go cloudy as a result of tannin-protein complexes.

9.4.4.5 Malt vinegars

Malt vinegar is simply vinegar made from unhopped beer: that is to say, from sprouted (malted) barley and cereal grains in which the grains' starch is broken down into sugars. Its flavor has nuances of malted barley—hence the name.

9.4.4.6 Asian vinegars

Asian rice and grain vinegars are often made from grains (sometimes roasted), while its starch is converted to sugars through a cultured mold rather than the sprouted grain itself. Add to this, the fact that the liquid is fermented together with the grain solids, so certain Chinese vinegars can be especially savory and full of flavor. In addition, the vinegar is also often aged in direct contact with the fermentation products witnessing the release of flavor compounds like amino acids and other organic acids and

[15]Solera is the process of aging liquids like wine, beer, vinegar, and brandy, by means of fractional blending. The purpose of this intensive process is the creation and maintenance of reliable qualities in the beverage over time.

flavor compounds into the vinegar. Rice vinegars come in three varieties comprising: white, red, and black rice vinegars.

9.4.4.7 Distilled vinegars

Distilled vinegars vary depending on geographic location. In the United Kingdom, for instance, distilled vinegar is made through fermentation of unhopped beer, after which it is distilled to concentrate the acetic acid. In the United States, distilled vinegar is produced through distillation of alcohol. Such distilled vinegars are generally higher in acetic acid giving rise to higher sour or harsh-tasting flavors. Lastly, distilled vinegars are often made from a grain-alcohol base.

9.4.4.8 White vinegars

White vinegar tends to be of the purest sources of acetic acid there is. They are produced by acetobacterial fermentation of pure alcohol that also has not been aged nor mellowed in wooden casks. As a result, the vinegar retains or contributes little in terms of savory or aromatic by-product fermentation; thus, this type of vinegar becomes very versatile in the kitchen.

9.4.4.9 Macerated herb vinegars

Herb vinegars are produced through macerating warm vinegar in fresh herbs until such time as the vinegar is properly infused with the ingredient's flavor. These vinegars may be based on a single herb or a combination of herbs and other flavorings.

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FOOD AND SCIENCE

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CHAPTER

BREAD 10

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Bread is human history's basic staple food. It has been linked to wars, survival, and religious worship. Indeed, it still plays an important role in the folklore, religion, culture, and politics. While dietary tastes have changed over the centuries, so bread, in one form or another, has remained true to its ancestral heritage. Today, bread is one of the most widely eaten foods in the world. In prehistory, there is evidence that man was already making gruel from meal (grains) and water. So, it should come as no great leap of imagination for man to simply cook the gruel over stones into a solid albeit a rudimentary bread-like form—a sort of unleavened flatbread. From here, two innovations turned this flatbread into the white fluffy stuff we know today—leavening and refined flour. These and more are discussed in the following sections.

10.1 BAKING INGREDIENTS AND THEIR USAGE

Bread is a staple food prepared by cooking a dough of flour made from ground or milled cereal grains with the addition of water, salt, and yeast (if leavened). Or in the case of enriched doughs, the previous mix is used but with added butter or fat, sugar, and eggs. Understanding how these basic ingredients behave will aid in their effective usage.

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10.1.1 GRAINS

Grains (also known as cereals) are the dry fruits (or caryopsis) of grass and grass-like plants. A distinction is made between the so-called "true" grains (grasses) and "pseudocereals" (nongrasses). All types of grain are excellent sources of complex carbohydrates and being low in fat with no cholesterol. They also contain a good selection of nutrients too. Although there are many variations of grain, they are closely related to one another in general physical and chemical structures (WGC, 2016). Compositionally, cereals consist of 12%–14% water, 65%–75% carbohydrates, 2%–6% lipids, and between 7% and 12% protein (Vaclavik and Christian, 2014; Haard et al., 1999).

Although some cereal grains may contain appreciable quantities of protein and oil, they are essentially a starchy crop composed of three parts: the endosperm, containing the starch and a large part of the protein; the germ (reproductive epicenter of the grain, Fig. 10.1), also containing protein and most of the oil and some minerals; and the bran (pericarp or seed coat), consisting mainly of cellulose and hemicelluloses together with some lignin and protein.

Any grains can be milled or ground into flour including rice, oats, corn, or barley, although wheat tends to be more common. As well as being able to use any type of grain, all parts of the chosen grain—the endosperm, the bran, and the germ—can all be used to make flour; the final characteristics of which are determined by those parts and proportions of each used. The simplest of white flours are made using the endosperm portion of the grain. Adding the bran, however, adds texture and fiber to flour giving it a distinctive brown color and rough texture. By incorporating the germ, the flour will contain more vitamins, minerals, and fiber.

Wheat grains are usually described as hard or soft depending on its protein content. This hardness translates into strong flours such as those used in breads and the like, while the softer wheat flours, with less gluten content, are used in cakes and pastries.

10.1.2 PROTEINS AND GLUTEN

With regard to proteins, there are several protein groups found in cereal grains—some water-soluble groups like albumin and globulin and two water-insoluble groups including glutenin and gliadin (Haard et al., 1999). Two of these protein groups—glutenin and gliadin—are naturally found in wheat and

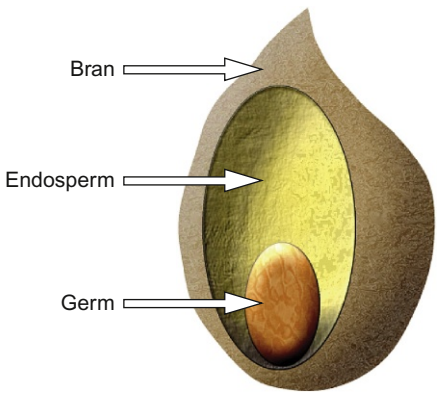


FIG. 10.1

The structure of grains.

related grain species including barley and rye. In flour, when these two proteins are mixed with water, they bond forming a new protein—gluten.[1] This gluten is composed of a crosshatched network of molecules that gives rise to glutens' characteristic elasticity (Field, 2011; Brown, 2014). As the dough is kneaded, so this encourages the formation of this crosshatching network—the longer the knead, the chewier the product—increased moisture content also enhances this network making doughs more elastic. Gluten can also be processed without the need for kneading; if the dough is left long enough (a day and a half maybe), then the gluten will be worked enough. Kneading simply speeds the process up.

In these products, the resultant elasticity is directly proportional to the quantity of gluten present and the amount of kneading undertaken. Shortening (fats) inhibits the formation of glutens' cross-linked network and, as a result, a "shorter" softer final product. Brioche is a good example of bread shortening in action giving the final cooked product a cake-like texture. Back to gluten, because of this elasticity, bread and baking products can be leavened using yeast or similar products. The resultant carbon dioxide that is produced is trapped by the protein, flour, and water dough giving rise to bread and similar products—this gives the finished dough a lighter more digestible texture. Upon heating, gluten is denatured and coagulated that, along with the starch in the flour, helps maintain the shape of the product (Cauvain, 2009).

The content of grain protein and by extension gluten is key in the baking of acceptable leavened products—as a general rule, the more protein/gluten content, the more elastic the final product. To determine the protein content of grains, near-infrared spectroscopy is used that allows the intensity of light at different wavelengths to be recorded. However, to determine the gluten content of flour, a less sophisticated and simpler method recommended by the International Association for Cereal Chemistry (ICC) is the extraction of the gluten content by washing a mix of the flour-water dough. This simply involves making a dough of flour and water and washing off the starch component using water itself. What is left after the starch is washed away is the gluten portion of the flour, which can then be dried baked and calculated/compared with the original dough (Cauvain, 2009).

10.1.3 TYPES OF GRAINS

There are a number of different types of grains available, many of which are commonly used in the manufacture of flour. These include the following:

True grains

- **Wheat** (*Triticum* spp.)—wheat and maize are the most commonly cultivated cereal crops worldwide
- **Maize or corn** (*Zea mays* ssp. *mays*)—native to the Americas
- **Rice** (genus *Oryza*)—the third most important (in terms of volume) cultivated cereal crop
- **Barley** (*Hordeum vulgare*)—the fourth most important cereal crop and high in fiber
- **Sorghum** (*Sorghum vulgare*)—the fifth most important cereal crop
- **Millet** (*Pennisetum glaucum*)
- **Rye** (*Secale cereale*)

[1]Although rye flour contains both glutenin and gliadin, it is incapable of forming gluten because certain substances in rye flour interfere with its creation. This is the reason why wheat flour is included in rye bread recipes.

- **Oats** (genus *Avena*)—native to Eurasia and low in gluten
- **Triticale** (*X Triticosecale*)—a hybrid of rye and wheat
- **Teff** (*Eragrostis tef*)—native to North Africa
- **Wild rice** (*Zizania*)

Pseudocereals

- **Buckwheat** (*Fagopyrum esculentum*)
- **Amaranth** (Amaranthaceae)
- **Quinoa** (*Chenopodium quinoa*)
- **Cockscomb** (genus *Celosia*)
- **Kaniwa** (*Chenopodium pallidicaule*)
- **Kiwichae** (*Amaranthus Caudatus*)

There are many different species of each of the grains listed here; however, of all the grains, wheat is without a doubt the most important grain of the temperate zones. Of the many species of wheat, the most common include common wheat (also known as bread wheat), club, durum, spelt, emmer, Polish, Persian, macha, shot, oriental, einkorn, and Kamuela; these species too may have several varieties within each family, and each has different properties of starch and protein contents making for a whole variety of different types of flours (Section 10.1.4) (NewCROP, 2012).

Other terminologies and grain derivatives one might come across:

- *Bulgur wheat* (sometimes referred to as parcooked) is made by soaking and cooking whole-wheat kernels, which are then dried, removing some of the bran and cracking the remaining kernel into little pieces. It can then be reconstituted and added to salads and desserts or simply used as a meat extender.
- *Cracked wheat* (also known as kibbled wheat) is made by cracking the whole-wheat kernel into small pieces. Unlike Bulgur wheat, however, it is not precooked. When added to salads or breads, cracked wheat adds a crunchy texture and nutty flavor.
- *Groats* are dehulled grains—that is, the removal of the husk, shell, or outer covering of the grain or seed.
- *Grits* are coarsely ground corn kernels (boiled).
- *Pearled barley* has the hard outer layers of the barley grain removed (dehulled).
- *Semolina* is a coarse flour made from the endosperm after milling and sifting. The term is used to describe flour from varieties of wheat and from other grains such as rice and corn. Semolina made from durum wheat (because of its high gluten content) is commonly used in the manufacture of pasta.
- *Couscous*—finely cracked wheat endosperm (semolina) that is steamed then dried. It is popular in North Africa and Middle Eastern countries.
- *Polenta* can be coarse or finally ground and is made from dried yellow or white corn (maize).

10.1.3.1 Wheat

In terms of geographic coverage and versatility, wheat's importance among the grains is undeniable. There are many varieties grown around the world. In the United States for instance, there are six predominate types of wheat. "Hard winter red" wheat is moderately high in protein (about 10.5%) making it a good all-purpose flour. "Hard spring red" wheat contains a higher protein count than hard winter at

13.5% good for bread making. "Soft winter red" wheat is a low-protein flour, while "hard winter white" wheat, with a similar protein profile to hard winter red, is good for making noodles and flat breads. "Soft spring white" wheat is similar to soft winter red wheat, and "durum wheat" is the hardest variety of all the wheats with the highest protein (or gluten) content at between 12.5% and 17%. Because of this, it's ideal for making pasta. It's also used to make couscous in Africa and Latin America, as well as in the United States. Durum wheat is rarely used to make bread although the by-product of semolina production is durum flour, which is usually sometimes enriched with four B vitamins and iron and used to make noodles.

Within these different varieties, there are also many strains and substrains offering millers and bakers an array of possibilities for soft, low-protein cake and pastry flours to medium-protein all-purpose flours right the way through to the various hard, higher-protein bread flours, pasta, and noodle flours. On top of this, there are also different degrees of grinds too from coarse, to medium, to fine. Other terms used to describe coarseness include grits, groats, chops, cracked, and mealy (Bread Experience, 2013).

10.1.4 TYPES OF FLOURS

As seen, there are many types of flours in use today, so it is not surprising that there are just as many varieties of flours in use:

- *All-purpose flour*—as the name implies, this flour is used in a variety of occasions. It is generally made from wheat, in particular the finely ground endosperm. It is made from a combination of both hard and soft wheat varieties—hence the term all-purpose—gluten content = ~10%–12%.
- *Bread (strong) flour*—this is milled and primarily used in baking. Similar to all-purpose flour, it generally is made from hard wheat's and as such has a higher gluten content, which is optimal in making yeast doughs—gluten content = ~12.5%–13.5%.
- *Self-rising flour*—this is a type of all-purpose flour that has salt and a leavening agent added, usually in the form of baking powder.
- *Cake (soft) flour*—this is usually milled from soft wheat that has a low protein (gluten) content. It is primarily used in the making of cakes, cookies, crackers, quick breads, and some pastries. Cake flour has a higher percentage of starch and less gluten than bread flour, helping keep cakes and pastries less "chewy" and more delicate—gluten content = ~7%–9%.
- *Pastry flour*—pastry flour's properties fall somewhere between those of all-purpose and cake flour. Usually made from soft wheat (for pastry making) soft flour can also be used for cookies, cakes, crackers, and similarly baked products, it has a slightly higher protein content than cake flour and less starch—gluten content = ~9%–10%.
- *Whole-wheat flour*—(aka graham flour) this is made by milling or grinding the entire wheat berry including the bran. The presence of bran reduces the development of gluten making products heavier and denser than those made from other flours. The addition of extra gluten to the flour helps counteract this.
- *Stone ground flour*—this is a type of whole-wheat flour that has been milled by crushing the kernel between two rotating stones (Prejean, 2013).

10.1.5 FLOUR BLEACHING AND MATURING

Historically, flour when freshly milled had a yellowish tint that consumers generally found unappealing. However, if allowed to age naturally, over a month or so, the color will generally fade becoming paler. But of course, time is money, and couple this with the fact that the results were not always consistent, so as a result, nowadays, chemical bleaching and maturing agents are added to speed up the process; this effectively allows flour to be used immediately after milling. With such measures, however, care is taken as certain additives can affect flour properties with some, like potassium bromate, strengthening gluten while others like benzoyl peroxide weakening it (Figoni, 2010).

According to Simon Field (2011), many reasons have been given for sifting flour. Among these are to sift out foreign obstacles, aeration, or simply to mix certain dry ingredients together. In truth, however, the quality of flour produced these days is largely free of foreign objects like husks and insects (poor storage notwithstanding). As for breaking up lumps and mixing dry ingredients, it is said a whisk will do the same job only quicker. The question then of whether to sift or not to sift relates largely to the volume of the sifted flour. Imagine an American cup full of nonsifted flour and one of nonsifted flour—would their respective weights be the same? Of course not. By sifting flour, air is incorporated into the flour making a cup of sifted flour lighter in actual weight compared with the nonsifted cup. The point is academic although it does have implications for the consistency of certain recipes. So, the answer to whether one sifts or not is more to do with personal preference as a good or experienced cook can adjust the amount of flour in their recipes through "experience."

Water is a basic ingredient in bread baking. There are several types of water—hard water (containing dissolved minerals like chalk, lime, and mostly calcium and magnesium) that produces the best-quality bread and soft (marginally more alkaline) water that ultimately weakens the gluten during mixing and fermentation. The water type can be influenced to some degree. To perform at its best, yeast prefers a slightly acidic medium, so if using soft water, this can be corrected to some degree by adding salt or vinegar (acetic acid) or lactic acid and by using mineral yeast in the recipe (Vaclavik and Christian, 2014).

10.1.6 LEAVENING

Leavening is an important function in baking science. Specifically, leavening is the foaming action either through the incorporation of air or carbon dioxide bubbles in breads and batters. This helps to lighten and soften doughs and batters without which we would be left with dense, low-volume baked goods. Leavening agents are the substances by which this is achieved, and they can take one of the three forms—biological, chemical, or physical (mechanical).

10.1.6.1 Physical or mechanical leavening

Physical leavening is the simplest of leavening methods and involves the physical or mechanical incorporation of air into a batter or dough. This is what happens when butter and sugar or eggs and sugar are beaten together. In both instances, air pockets are created adding volume to the final baked goods. Another type of physical leavening uses steam and air that expands upon heating. To facilitate this style of leavening, baking is usually done at high temperatures. A good example of this method is in the making of Yorkshire puddings. Another example of physical leavening includes the making of Genoese sponges.

10.1.6.2 Chemical leavening

Chemical leaveners are mixtures or compounds (usually a combination of acids and alkalies) that, when active, release gases (usually carbon dioxide) and a by-product—a chemical salt. Chemical leaveners are used in place of other leavening agents where long biological fermentation is either impractical, unnecessary, or undesirable. One common chemical leavening agent is baking soda. Baking soda, also known as bicarbonate of soda or sodium bicarbonate, is a "base" that readily reacts with acid forming carbon dioxide gas. This acid can take many forms such as citrus juice, buttermilk, and cream of tartar. Another common chemical leavener is baking powder; this differs from baking soda in that the baking powder contains both the acid and the base (alkali) together in one powder. That is, it contains both bicarbonate of soda (the alkali or base) and cream of tartar (the acid) (Belitz et al., 2009).

10.1.6.3 Biological leavening: yeast

Yeasts are naturally abundant in air, and they have been used for thousands of years; even if the persons using it weren't sure of the process, they somehow managed to leaven bread and make beer and wine. Yeasts however need sugar to feed on and grow, and while some batters call for sugar, others do not. In the absence of sugar, uncooked flour contains a natural enzyme that breaks down some of the starch molecules into sugar molecules. This is generally sufficient for the yeast to grow. In wine, the sugar in grapes feeds the yeast while it ferments or grows. Two by-products of yeast are carbon dioxide and alcohol (Field, 2011). Sometimes, these are both desired outcomes in, for example, beer and some sparkling wines, but in bread, while alcohol is still produced, the main requirement is the carbon dioxide.

While there are natural yeasts in bread flour, the modern practice is to add an amount of commercial yeast to the flour in order that wild yeasts[2] and bacteria do not overpower the commercial yeast's flavor. It's also worth noting that when it comes to flavor, the action of the yeast on the sugar it feeds on produces not only carbon dioxide and alcohol but also other molecules like aldehydes, ketones, aromatic heavy alcohols, and other metabolic by-products. These all add to the characteristic flavor profile of beer, wine, bread, etc.

A yeast starter (aka poolish, sponge, or levain) is a mixture of flour and water that has been colonized by wild airborne yeast and other friendly bacteria. These starters give sourdoughs and other breads made with it a unique or special character. This method of biologically leavening breads was commonplace before the commercialization of yeast cultures, and with proper care and attention, starters can last for decades. The difficulty however is the variation in quality and consistency. For this reason, starters today have yeast added to help provide an initial uniform and reliable starter

10.1.6.3.1 Yeast equivalents

1 oz fresh yeast = 3.75 teaspoons dry yeast (or 0.4 oz)

[2]Many things like sweet liquids, sour bread, and wine will spontaneously ferment and eventually sour naturally; some wild yeasts will give certain "off" flavors to the final product. So, whenever yeasts are required in a product, most people will use specific "cultured" yeasts for specific purposes.

10.1.7 CARBOHYDRATES AND SUGARS

All carbohydrates are either simple carbohydrates (sugars), complex carbohydrates (starches), or fibers. All simple, complex, and dietary fibers however are all composed of units of sugar, and as such, they are interchangeably referred to as simple and complex sugars. All digestible carbohydrates are eventually converted to glucose in our body. What distinguishes one carbohydrate from another is the number of sugar units it contains. Simple sugars are composed of only one (monosaccharide) or two (disaccharide) units of sugar. Complex sugars (complex carbohydrates—starches and fibers) on the other hand are composed of more than two units of sugar and are known as polysaccharides. Because complex carbohydrates contain multiple units of sugar, so the body takes longer to digest them, releasing glucose into the bloodstream more slowly and evenly than digesting simple carbohydrates.

10.1.7.1 Sugars

In cooking, there are many types of sugars that between them contribute to foods' texture, structure, and flavor; most too are worth about 4 cal/g. They are also responsible for controlling crystallization in certain recipes and in certain concentrations can help prevent spoilage of foods. More importantly, in the context of bread, sugars are the foods that promote the growth of yeast, although in high concentrations sugar can actually have the opposite effect and actually retard yeast activity.

In cooking and baking, there are many types of sugars that are used; some of these are described below:

- *Corn syrup* (glucose syrup): made from corn starch that has been hydrolyzed into glucose—which results in around 90%–100% glucose purity.
- *Fructose*: found in fruits, honey, and some root vegetables.
- *High-fructose corn syrup (HFCS)*: is a mixture of glucose and fructose produced from corn. The most common is composed of 55% fructose and 45% glucose.
- *Galactose*: found in milk and dairy foods. Together, galactose and glucose form the disaccharide lactose.
- *Glucose* (dextrose): is a simple monosaccharide found in plants.
- *Lactose*: called milk sugar. It is composed of one galactose and one glucose unit.
- *Maltose*: composed of two glucose units. It can be found in molasses and is used in fermentation.
- *Sucrose*: known as table or white sugar. It comprises equal parts of glucose and fructose. It is found naturally in fruits and vegetables and is especially abundant in sugarcane and sugar beets.

When talking of simple sugars, we can note that they bind more tightly to water than sucrose does; one overriding advantage of this is that they do not crystallize easily. There are two basic ways to get simple sugars into syrup. The first is to simply add them. A candy recipe that calls for corn syrup in addition to sugar, for example, is doing just that. Corn syrup is mostly composed of the simple sugar glucose. The second way is to break up sucrose into its two simple sugars—glucose and fructose. One does this by heating it in the presence of an acid. A candy recipe that calls for cream of tartar (tartaric acid) is doing that. Other recipes might call for vinegar, lemon juice, or other acids to cook with the sugar.

10.1.8 OTHER INGREDIENTS OF BREAD

Milk has a stabilizing effect on the fermentation process while also aiding in texture, flavor, taste, and keeping quality of the baked loaf. The lactose in milk also helps improve crust color. While eggs in the pastry kitchen can act as binding agents and leavening agents, egg yolks lend richness and moisture to baked goods.

Shortening can be confusing because it has two specific meanings in the kitchen. Firstly, it is the vernacular name given to a collection of fats used as shorteners, and secondly, it is also a process. Shortening is synonymous with fats like lard, margarine, and other hydrogenated vegetable oils. In the shortening process, because of the effect of fats on gluten (as described below), they are also known as shorteners or shortenings. As well as shortening the dough, fats also lubricate the dough making it more pliable and giving the final product the impression of moistness. Shortening also makes the crust tender; it improves the keeping quality of the product and also helps to produce a crumb that is soft and chewy.

In bread making, the protein gluten affects the elasticity of dough, which in turn affects the chewiness of baked wheat and other gluten-containing cereal doughs. As the dough is kneaded, so sheets of the gluten protein are produced. These crosshatched proteins trap the air and allow the dough to rise. However, adding oils and fats to the mix allows certain hydrophobic amino acids in the gluten to attach themselves to the fat, thus allowing fewer gluten proteins to connect together. This is the act of shortening and is shown in the nature of the finished product, whether cake or brioche-like or chewier like traditional breads.

Salt is an essential ingredient in baking. It has several functions; apart from the obvious flavor benefits, salt also helps regulate fermentation while at the same time strengthening the gluten. It also slows down the growth of wild yeast and bacteria:

Kneading and rising—bread is initially kneaded to help develop the gluten structure previously mentioned. After the fermentation of the first rise, the bread is "knocked" back and kneaded a second time before a second rising. This second knead helps to redistribute the yeast converting more sugars from the flour and thus helps to develop more complex flavors. The second knead and second rise also help with texture, reworking the gluten and allowing the first fermentations of carbon dioxide to be more evenly distributed giving the bread a more even crumb.

Celiac disease and allergies—celiac disease is an autoimmune condition that damages the lining of the small intestine preventing food from being properly absorbed. More and more people these days are found to be intolerant (celiac disease) or allergic to gluten. For these people, choosing the right bread grain is of great importance (WGC, 2016):

Grains with gluten—wheat, including varieties like spelt, kamut, farro, and durum, and products like bulgur, semolina, barley, rye, triticale, and oats[3]

Gluten-free grains—amaranth, buckwheat, corn, millet, Montina (Indian rice grass), oats, quinoa, rice, sorghum, teff, and wild rice

[3]Oats are inherently gluten-free but are frequently contaminated with wheat during growing or processing.

10.2 SOURDOUGHS

Sourdoughs are breads or doughs that use an acidic component like buttermilk, watered-down yogurt, or cultured bacterial "starters." This replaces any added "baker's" yeast and gives the final product its characteristic flavor. There are numerous sourdoughs around the world, each with its own "starter" and flavor. One might recall that there is some natural yeast present in flour: this is the backbone of making a sourdough starter culture. By stirring in some water to some flour and by letting it sit for a day, microbes already present in the flour will start to grow. By throwing away half of the mixture and by adding more flour and water over a period of a week, the mixture will stabilize and turn a little sour, thus creating a sourdough starter. The reason one throws away half of the mix is because the enzymes naturally present in the mix have broken down and feasted on all the sugar in the flour, rendering it useless as an ongoing food source. The yeast naturally present in the flour is acid-tolerant and is not compatible with the baker's yeast that is commonly added to make bread. This is because it cannot survive in the acidic environments of starter cultures. In actual fact, it is the friendly bacteria in the starter that forms the acidic environment through the production of lactic and acetic acids that give sourdough its distinctive flavor typical of sour bread. By varying the pH to control the growth of any of the several friendly bacteria present and/or by varying the temperature to control the growth of both yeast and bacteria, the baker can fine-tune the particular flavor of his/her bread (Field, 2011). Note too, the friendly bacteria act together with others to help kill off the harmful bacteria.

10.3 STALING OF BAKERY PRODUCTS

Simply put, staling or firming of the crumb starts to affect bread the moment it starts to cool. When warm, starch molecules consist of long chains that, upon cooling, shrink and firm up in the process of staling. This can be seen when stale products become softer when warmed and firm up again on cooling. In an effort to slow the process, bakers sometimes use emulsifiers. Emulsifiers or bread softeners such as monoglycerides, calcium stearoyl lactylate, and sodium stearoyl lactylate produce bread that will remain soft and more importantly fresher for a longer period of time.

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11.1 NONFERMENTED DAIRY PRODUCTS

11.1.1 MILK

There are likely more than 4000 different species of mammals (Baker and Bradley, 2006), from the smallest hog-nosed bat to the largest blue whale. However, irrespective of whether they live on the land or in the sea, all mammals share some common characteristics. First among which is that all mammals including humans are all warm-blooded (endothermic) vertebrates with backbones and hair. They also have a larger, more developed brain than other types of animals. Importantly too, mammals feed

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their young with milk—a complex, nutritional substance that provides nutritional and functional benefits; a breakdown of which can be seen in the following:

- 88% water
- 3.3% protein
- 3.3% fat
- 4.7% carbohydrate
- 0.7% ash

Yet, despite the vast variety of potential milk carriers out there, mankind only exploits a handful including cattle, water buffalo, sheep, goats, camels, and yaks (Table 11.1). Ruminants in particular have a highly specialized, multichambered stomach. This allows them to extract nourishment from feed (hay and grass) that is otherwise of little biological value to humans. In fact, the ruminants' mammary gland

Table 11.1 Milk Composition of Selected Animals' Average % of Whole Milk

Milk Composition of Selected Animals' Mean % of Whole Milk					
Milk	Fat	Proteins	Lactose	Minerals	Water
Human	3.83 (3.5–4.17)	1.3 (0.9–1.7)	6.71 (6.3–7.12)	6.2 (3.51–9)	88
Cattle	4.36 (3.23–5.4)	3.37 (2.54–4.19)	4.86 (4.4–5.33)	2.15 (1.5–2.8)	86.4 (85–87.8)
Buffalo	9.2 (4.9–13.39)	4.86 (3.44–6.29)	4.52 (2.95–6.1)	0.8 (0.8–0.81)	83
Sheep	6.7 (4.1–9.3)	5.17 (3.35–7)	4.45 (3.7–5.21)	0.9 (0.8–1)	81.25 (80–82.5)
Camel	4.51 (2.35–6.67)	3.64 (2.06–5.23)	4.3 (2.77–5.85)	0.77 (0.75–0.8)	87
Goat	4.4 (3–6.02)	3.4 (2.38–4.43)	4.58 (4.08–5.09)	0.8 (0.7–0.89)	86.9 (85.8–88)
Yak	7.25 (5.5–9)	6.2 (3.51–9)	4.86 (3.9–5.82)	0.8 (0.8–0.81)	82
Horse	1.25 (0.5–2)	2.15 (1.5–2.8)	6.4 (5.8–7)	0.4 (0.3–0.5)	90

Notes: *Figures in brackets are highest and lowest ranges. Water is the main component of milk and varies with species—cattle, buffalos, yaks, sheep, goats, horses, and humans (FAO, 2017).*

Source: Compiled from multiple sources: McGee, H., 2004. On Food and Cooking: The Science and Lore of the Kitchen. Charles Scribner's Sons, New York; FAO, 2011. Milk and Milk Products. W. H. Organization, Rome, p. 248; FAO, 2017. Dairy production and products: milk composition. Retrieved 20 February, 2017, from http://www.fao.org/agriculture/dairy-gateway/milk-and-milk-products/milk-composition/en/#.WJNDlPIdaVs; Kapadiya, D.B., et al., 2016. Comparison of Surti goat milk with cow and buffalo milk for gross composition, nitrogen distribution, and selected minerals content. Vet. World 9 (7), 710; Soliman, G.Z., 2005. Comparison of chemical and mineral content of milk from human, cow, buffalo, camel and goat in Egypt. Egypt J. Hosp. Med. 21, 116–130; Suárez-Vega, A., et al., 2015. Characterization and comparative analysis of the milk transcriptome in two dairy sheep breeds using RNA sequencing. Sci. Rep. 5, 18399; Barłowska, J., et al., 2011. Nutritional value and technological suitability of milk from various animal species used for dairy production. Compr. Rev. Food Sci. Food Saf. 10 (6), 291–302; Ferm, E., Kangas, N., 2011. Milk composition and milk yield in mares; Wells, S., et al., 2012. Evaluation of mare milk composition/quality during lactation. Anim. Ind. Rep. 658 (1), 51; Potočnik, K., et al., 2011. Mare's milk: composition and protein fraction in comparison with different milk species. Mljekarstvo 61 (2), 107.

is a mini biological factory producing milk from its blood and fats, sugar, and proteins; the gland's secretory cells are then released into the udder. In fact, the milk produced by these animals is a small wonder unto itself. Whether raw, pasteurized, fermented, churned, or cooked, milk is just a step or two away from luxuriant cream, golden butter, aromatic yogurts, soured buttermilks, smooth ice creams, and flavorful cheeses among all manner of other delights (Vaclavik and Christian, 2014; National Geographic, 2016; McGee, 2004).

Continuing the mini biological factory analogy, raw milk is complex and alive, teeming with live white blood and mammary-gland cells as well as bacteria and enzymes. Once pasteurized, however, very few of the living cells or active enzymes remain. So, while pasteurized milk is safer and lasts longer, some artisan cheesemakers still prefer raw milk in traditional cheesemaking where it helps with ripening and deepens flavor.

Milk contains microscopic fat globules[1] and protein bundles, salts, milk sugar, vitamins, and other proteins[2] as well as traces of many other compounds (Mistry, 2001; FAO, 2011). The only carbohydrate (complex sugar) found in any quantity in milk is lactose[3] that is comprised of two simple sugars, glucose and galactose. In milk too, water is a continuous phase in which other elements are either dissolved or suspended. For instance, lactose and some of the mineral salts are found in the solution, whereas certain proteins and the rest of the minerals are found in a colloidal suspension (following sections).

In humans, an increasing number of people lack the special enzyme required to digest lactose; these are lactose intolerant and need to be careful of the dairy products they consume.

There are literally dozens of proteins that can be found in milk that collectively represent 3.3% of total milk composition with approximately 82% of this percentage being casein while the remaining 18% are whey or serum proteins (CALS, n.d.). However, in terms of kitchen science, we can reduce the number of representative proteins to the two most important—caseins and whey. First, the caseins, of which there are around four specific species (*see below*), all of which are similar in structure. Second, all other proteins found in the milk are grouped together under the catchall "whey" proteins. The major whey proteins in cow's milk are beta-lactoglobulin and alpha-lactalbumin (Belitz et al., 2009; Hurley, 2010). Of biological value too, milk contains all nine of the essential amino acids needed by humans.

11.1.1.1 Milk proteins: Caseins proteins

Casein is the overarching name given to describe a group of related phosphoproteins[4] (αS1-casein, αS2-casein, β-casein, and κ-casein) that are commonly found in milk. Together, caseins make up to as much as 80% of the total proteins (3.3%) in some mammalian milk, but the exact amount can and does vary quite considerably across the species. Casein lays claim to being active in a wide and diverse assortment of dairy products in general (Phadungath, 2005). They are a high-quality source of amino acids too and are also very digestible, while most whey proteins are to some degree relatively less digestible. Moreover, the high phosphate content of casein proteins allows milk to hold much more calcium than would otherwise be possible if the calcium were in solution (CALS, n.d.).

[1]Milk fat accounts for about half the calories of whole milk and the fat-soluble vitamins (A, D, E, and K).
[2]Cow's milk contains more than double the protein and minerals found in mother's milk.
[3]Lactose is peculiar to milk and only a handful of plants, and therefore, very few organisms possess lactose-breaking enzymes.
[4]Phosphoproteins are common in living organisms in which they play a role in various metabolic processes such as in the regulation of cell nuclei, in ion transport, and in the oxidation processes in a cell's mitochondria.

Physicochemically, casein is somewhat hydrophobic, meaning it is not particularly soluble in water. Instead, it forms a suspension of colloidal-like particles in the water phase of milk called casein micelles[5] (Tuinier and De Kruif, 2002; CALS, n.d.). These micelles consist of the caseins (α-s1, α-s2, and β) bonded through calcium phosphate bridges on the inside of the molecule, which in turn are surrounded by a layer of 6-casein that further aids in the stabilization of the micelles in the water phase (CALS, n.d.). Each casein micelle can contain several thousands of individual protein molecules.

It has already been mentioned that casein proteins are unusual among other food proteins in that they are very tolerant of heat where cooking would normally denature and coagulate many proteins in say eggs and meat. This does not happen so easily with the casein proteins in milk and cream. Indeed, fresh milk and cream can be boiled down to a fraction of their original volume without denaturing and curdling of both the fat and protein molecules. That said, as milk boils, so a few of the proteins do indeed denature, but instead of curdling, they form bonds surrounding the fat globules making the membranes thicker and more resistant to thermodenaturing (Mistry, 2001). The hydrophilic (water-loving) part of the molecule becomes negatively charged and repels each other; this ensures that milk stays liquid and does not clot. Alas, it can be seen that most micelles are thermostable (some will inevitably denature, but not in any significant amounts) in that they can be boiled, cooled, dried, and reconstituted, without any adverse effects (CALS, n.d.). In the stomach, however, caseins clot due to the acid and the actions of enzymes that clot or curdle the milk. In the making of cheese, this is why rennet is used to help the caseins clot together in a solid.

Having said that, caseins do denature; by disrupting the micellar structure through chemical or biological means, micelles are likely to "unclump" as it were causing the casein to come out of suspension forming a curd (Mistry, 2001). This can happen with the application of gentle heat (40–42°C) simultaneously altering the pH to around 4.6 whereby casein proteins will coagulate or precipitate out. Caseins will also coagulate with the addition of an acid or enzyme, using rennet (an enzyme containing rennin from the stomachs of young mammals). In the cheese industry, one will find many and varied combinations of enzymatic hydrolysis of casein proteins and acid precipitation often using specific bacterial cultures to establish the conditions for protein denaturation at lowered pH values to form yogurts, cheeses, etc. (Belitz et al., 2009; Hurley, 2010).

11.1.1.2 Milk proteins: Serum or whey proteins

There are many serum (whey) proteins in milk although the predominant whey protein of ruminant species (but by no means in all other species including humans) is beta-lactoglobulin (at 50% of the whey proteins in milk) (lactoglobulin for short) (Kontopidis et al., 2004). Another important whey protein is alpha-lactalbumin, accounting for 20% (lactalbumin for short). Other proteins included in the remaining mix are lactoferrin; transferrin; immunoglobulins[6]; serum albumin (a serum protein); and a long list of enzymes, hormones, growth factors, and nutrient transporters, among others (Hurley, 2010; CALS, n.d.). However, unlike casein proteins, whey proteins exist in soluble form. They even remain in solution in reduced pH milk at pH of 4.6 (the coagulation of casein). Both caseins and whey proteins have very different physical structures and as such display different physicochemical properties. These include stability in denaturation in which casein can withstand prolonged high temperatures while

[5]The casein micelle also contains water and salts (mainly phosphorous and calcium).
[6]Immunoglobulins are antibodies (a blood protein) especially high in colostrum (the first milk breasts produce).

whey proteins tend to denature from around 60–78°C/150–172°F, depending on who one reads and begins to aggregate with themselves and with kappa-casein proteins, leading to the so-called whey protein/κ-casein complexes (Laurence et al., 2009; Wijayanti et al., 2014; Hillier and Lyster, 1979; Casal et al., 1988). Furthermore, many of the whey proteins' functional roles are still not clearly understood or known to be responsible for any specific function. Even the function of β-lactoglobulin is not fully comprehended, although it is thought by some to be a transporter of vitamin A.

It is also worth noting the whey protein instability to thermal processing, which leads to their denaturation, aggregation, and eventual forming of a "whey" cheese like ricotta. Also, under some conditions, whey proteins can also form fine-stranded gels under prolonged heating and at low pH. Furthermore, whey proteins are also largely responsible for the foaming stability of hot milk.

If milk and cream are frozen, however, the results are drastic to both the protein and the fat globules. In this case, the protein and fat globule membranes are pierced by the expansion of ice crystals in the water of the milk effectively breaking up of the proteins and phospholipids surrounding the fat molecules. Once thawed, the fat globules tend to clump together, and if boiled, one will end up with a puddle of fat on top of what is left of the milk (Belitz et al., 2009).

11.1.1.3 Pasteurization and sterilization

The thermal processing of foods is used to yield physical or chemical changes that make food more edible or safe to eat. Such measures can also alter the properties of certain foods—for example, reducing enzymatic processes, gelatinization of starch, or denaturation of proteins. Blanching fruit and vegetables at 100°C is undertaken to destroy surface microbes and to arrest or destroy enzyme activity that could potentially alter the quality of foods to be frozen, dried, or simply stored for later use.

Thermally processing foods for safety reasons however is a little more precise. There are two main categories employed in such instances, pasteurization and sterilization. These are used either to destroy all (sterilization) or to radically reduce microbial activity (pasteurization). Pasteurization is the heat treatment in which foods are heated to above 100°C. Widely used throughout the industry, pasteurization can be used to destroy enzymes and relatively heat-sensitive microorganisms including nonspore-forming bacteria, molds, and yeasts. In this regard, pasteurization is used routinely for the destruction of all disease-causing organisms except for two groups—the thermoduric microorganisms that can survive exposure to such high temperatures and the thermophilic microorganisms that survive and thrive at these high temperatures.

Comparatively speaking, unlike pasteurization where the existence of heat-resistant microorganisms is acceptable, the aim of sterilization is the annihilation of all bacteria—their spores included. Thus, heat treatment in such cases must be high enough and long enough to kill or at least inactivate the most heat-resistant bacterial microorganisms that are usually the *Bacillus* and *Clostridium* spores. The time and temperatures needed to achieve this are usually between 110°C (which will destroy most *Bacillus* spores within a short time) and 121°C for *Clostridium* spores (which are destroyed after a few seconds). On occasion, some treat foods as high as 130°C for a very short period of time just to err on the side of caution and to reduce the holding time. Sterilization uses one of several methods from chemical and/or physical agents such as heat, filtration, pressure, and radiation to kill absolutely all microorganisms present. Sterilization, however, has one major drawback in that at temperatures so high the process can actually alter the color and taste of certain foods—take sterilized milk for instance in which sterilization denatures 75% of the whey proteins and causes the Maillard reaction to take place, leaving the milk darker and tasting somewhat different to the unsterilized version (Verhoeckx et al., 2015).

Pasteurization of milk—if pasteurization is undertaken, as is the norm for most countries, and if stored below 5°C/40°F, then the shelf life of milk is extended from just a few days to perhaps a week or more. Pasteurization of milk by applying heat is used in order to kill any pathogens present as well as the spoilage microbes and lastly by inactivating milk enzymes.

Three basic methods are used for the pasteurization of milk. The simplest method is batch pasteurization whereby say a few hundred gallons of milk are slowly disturbed or agitated in a heated vat at a temperature of 63°C/145°F for 30–35 min. This is fine for the small-to-medium operator, but at large-scale industrialized operations, the use of high-temperature, short-time (HTST) methods is more convenient and economical. The process sees the milk continuously pumped through a heat exchanger at which point it is held at a minimum of 72°C/162°F for 15 s. Also worthy is the fact that the HTST method is in fact hot enough to denature around 10% of the whey proteins. The third method is the ultra-high-temperature (UHT) method. This increased the temperature of the milk to 130–150°C/266–302°F for about 1–3 s. This method allows the milk to be kept at room temperature for up to several months without refrigeration. The longer UHT treatment imparts a cooked flavor and slightly brown color to milk; cream contains less lactose and protein, so its color and flavor are less affected.

11.1.1.4 Homogenization

Another process often carried out in milk is that of homogenization. If left to its own devices, fresh whole milk will eventually separate out into two phases; the lighter fat molecules clump together and rise to the surface in a layer of cream. This action leaves a fat-depleted phase below (a "skimmed milk"). When homogenized—the pumping of hot milk through very small nozzles at high pressure, commotion tears the fat globules apart into smaller globules about a quarter of the size of the original. This increases the fat globule count that is made temporarily defenseless as the membranes are disrupted, which is until the naked fat surface attracts enough casein particles that ends up creating an artificial coating. In homogenized milk, the casein particles tend to weigh the new fat globules down while also interfering with the fat's usual clumping. As a result, the fat remains evenly distributed throughout the milk. There is a risk inherent in this practice, and that comes from enzymes present in the milk from attacking the unprotected fat globules (albeit momentarily unprotected) and producing rancid flavors. Consequently, the milk is either simultaneously pasteurized during the process of homogenization, or it is performed just before the procedure.

11.1.1.5 Concentrated milks

Concentrated milk products are valued for the unique tastes and for the long-shelf-life qualities. When it comes to evaporated milk for instance, it is made by heating raw milk in a partial vacuum so that the boiling point is raised to 43–60°C/110–140°F until it has lost about half its water. The resulting creamy, mildly caramel[7] flavored liquid is then homogenized and then canned and sterilized. For the other well-known concentrated milk—sweetened condensed milk, the initial evaporation is the same as for evaporated milk. After that, sugar is added until it reaches a concentration of about 55%. At these concentrations, microbes cannot grow, so the process of sterilization is redundant. However, because of the high concentration of sugars, the milk's lactose begins to crystallize. This is prevented by "seeding" the milk with preformed lactose crystals to encourage controlled crystallization to keep the crystals

[7]The cooking and concentration of evaporated milk causes some browning; this is partly due to the Maillard reaction of the protein and the part caramelization of the lactose.

small and undetectable by the tongue. Condensed milk has a lighter color and a milder flavor than evaporated milk and is of the consistency of a thick syrup.

Lastly, when making powdered milk, there are several processes and differing methods used. One such method involves first passing the milk into an evaporator where about one-third of water content is removed. This is done in a partial vacuum that allows for a lower boiling point (57°C/134.6°F); this is important because it allows the milk to evaporate at a low enough temperature so it does not alter the biochemical makeup of the original milk. Water is removed until the solids increase from the natural 12% (if one includes the butterfat) to about 50%. During this process, the milk undergoes pasteurization at temperatures of about 79°C/174.2°F or so for 20 s before it is quickly cooled. Again, this has the added benefit of killing off the microbes without destroying the integrity of the milk. In making powder, the milk then goes from the evaporator to the separator where the cream (butterfat) is removed. The butterfat is placed in a separate storage tank to be used later (Pearce, 2016). The skim milk now moves on to tanks to be standardized. In commercial plants, this means adjusting the skimmed evaporated milk by putting back the solids and some of the fat until it meets the standard requirements of the customer; this also ensures consistency of the final product from batch to batch. Milk solids (including butterfat) are standardized at around 8.8% solids and 3.4% butterfat that comes to 12.2% total solids. At this point, the remaining evaporated and condensed milk is turned into powdered milk. Powdered or dry milk is the result of one of two types of drying that are the spray nozzle and the newer atomization system. In a spray nozzle system, the drying towers are large diameter towers that can be as tall as 12 stories high. In the top of the towers, spray nozzles spray a fine mist of the condensed milk into swirling air that is present at about 204°C/399.2°F. Then, as the droplets fall, so the swirling air quickly removes water from the falling droplets of milk until all that's left is a small particle of milk powder. In the atomization system, instead of using nozzles to spray the milk, one uses an extremely high-speed turning atomizing wheel. This atomizes the milk into much finer droplets than one can get from a spray nozzle. The advantage is that because the droplets in an atomizing wheel are that much smaller than a nozzle sprayer so they dry much more quickly in the atomizer (compact dryer). On the base of this compact drying tower where the dry milk aggregates, so it is constantly agitated. At this point, any additives such as vitamins, minerals, lecithin, or lactose as well as other compounds are added to the customers' requirements (Mistry, 2001; Pearce, 2016).

11.1.2 CREAMS

(See also Sections 7.2.2.3.4 and 11.2.3)

Cream is an extraordinary natural product. In the culinary world, it is highly prized for its silken creaminess and sumptuous mouthfeel consistency. It is also both smooth and velvety and lingers in the mouth without feeling greasy. The luxuriant mouthfeel sensation results from the crowding of the tiny fat globules, which are too small for our senses to distinguish.

Cream is that portion of, often nonhomogenized, milk that is greatly enriched with fat, and if left alone, this enrichment occurs naturally (FAO, 2011). That is to say, once fully settled, the milk and cream will eventually settle out. This concentrated cream layer can then be skimmed off leaving the "skimmed" milk below. Milk with an average of 3.5% fat will yield cream with a fat content of about 20%. Milk contains approximately equal weights of protein and fat, while in cream fat outweighs protein levels by about 10–1. As a direct result of this dilution of proteins, cream is less likely to "split" or curdle (with the exception of light creams) (Mistry, 2001). And owing to its concentration of fat globules and its virtue of being a robust, forgiving ingredient, cream can be aerated into whipped

cream: a far more stable foam than milk can ever be (Section 7.2.2.3.4). Once separated from milk, cream is pasteurized; however, it is generally not homogenized (although one does find homogenized cream in their local supermarket), because it makes whipping the cream that much harder. One problem though with nonhomogenized cream is that it continues to separate in the carton. The globules of fat slowly rise and concentrate into a semisolid layer at the top of the carton. It's a common phenomenon that cooks around the world come across. At cold (refrigerator) temperatures, fats inside the globules form solid crystals. This can be disastrous as the crystal edges tend to break through the protective globule membranes after which clumping of the naked fat globules forms microscopic butter grains. This is not good for the whipping quality of the cream. Although having said that, some creams, especially the longer-shelf-life creams, are indeed homogenized—mainly to prevent separation in the carton. In fact, one can get homogenized—30% fat cream, but it just requires more care and attention when whipping.

11.1.2.1 Fat content

A number of different fat levels in cream are manufactured for particular purposes. Light creams are in general for pouring on desserts or into coffee, while the heavier creams can be whipped or are used to thicken sauces. Heavier creams can also be diluted with milk to mimic lighter creams. Light creams as well are unstable and can easily "split" or curdle when heat is applied. Some like the clotted creams are used as they are in things like the good old British afternoon tea where it is spread on scones with jam and butter. In fact, it is fair to say that a creams' fat profile pretty much determines both its consistency, its versatility, and, by extension, its usage.

When using cream, a general rule of thumb is the greater the fat content the easier it will be to work with. In sauces and creams, a high fat content will bind the liquids (hot or cold) together much better. Consequently, the high-fat cream is less likely to curdle or split when incorporated. High-fat creams also whip easier and create more stable and airy whipped creams. A few select creams are listed below in Table 11.2 and in Section 11.2.3.

Table 11.2 Different Creams and Their Fat Content

Fat Content (%)	The United Kingdom/Europe	Fat Content (%)	The United States
12%	Half fat	10.5%–18%	Half and half[a]
18%	Single cream		
18%–25%	Cultured/soured cream		
23%	Sterilized cream		
28%–48%	Crème fraiche	30%	Light whipping cream
35%	Whipping cream	36%	Heavy (whipping) cream
48%	Double cream		
55%	Clotted cream		
		70%–80%	Plastic cream

[a]*Half and half cream is equal parts of whole milk and light cream.*

Source: Compiled from various sources: Brown, A., 2014. Understanding Food: Principles and Preparation. Nelson Education; Robinson, R.K., Batt, C.A., 2014. Encyclopedia of Food Microbiology. Academic Press; Fox, P.F., et al., 2011. Encyclopedia of Dairy Sciences; BBC Worldwide, 2017. Glossary: Cream. Retrieved 3rd April, 2017, from http://www.bbcgoodfood.com/glossary/cream.

11.1.2.2 Single cream

At around 18% fat content, single cream is simply a more concentrated version of milk. One might use it for pouring into hot beverages like coffee or as a pouring cream for such things as apple crumbles or fruit pies. Beyond that, single cream is not particularly useful to the cook. This is because, as mentioned, if boiled or added to a sauce, it will curdle or "split" the sauce. It is also not available for whipping as there is insufficient fat to hold an aerated matrix together. As a result, it cannot be a substitute for the likes of whipping cream or double cream, etc. (BBC Worldwide, 2017; Brown, 2014).

11.1.2.3 Whipping cream

Whipping cream contains approximately 35%–36% fat, and unlike single cream, whipping cream can trap air bubbles in a matrix that roughly doubles its volume. It is often used in cake finishing and filling cakes and pastries. One downside is that whipping or whipped cream can "weep" a little liquid from the cream over time.

11.1.2.4 Double cream

Double cream is more stable and more versatile than whipped cream, and once whipped, it can hold its aerated volume for hours and even overnight in a fridge without "weeping." Containing 48% fat, double cream is ideal as a pouring cream or for decorating cakes and desserts. If boiled, double cream (just like whipping cream) will not separate or "split" so is a great addition to savory sauces requiring a little cream for a smooth, rich accompaniment (Brown, 2014).

11.1.2.5 Clotted cream

Clotted cream has the highest percentage of fat of all creams with at least 55% minimum. Manufactured by baking double cream until the right texture and fat content are reached, it is often served with scones, butter, and jam in the United Kingdom (BBC Worldwide, 2017) (also see Section 11.2.3).

Talking further of boiling creams, it's interesting to note that, unlike single or "light" creams, by simply boiling a heavy or double cream, the cream is very stable. Furthermore, while the heavy cream is being boiled, even a light acid or salt base fails to split the cream. It would seem that the key to this phenomenon lies (as with milk) in the caseins present in cream. With cream at about 25% or more fat, there appears to be sufficient fat to cling onto the caseins, thus taking most of the casein out of operation and ultimately no casein curds can form. Conversely, with lower percentages of fat levels in a cream, so the greater the proportion of the casein-carrying water phase, there is available to curdle. It is for this reason why "acid-curdled" mascarpone cheese can be made from milk and/or light cream, but not from heavy cream. When talking of clotted creams with a potential fat content of 55%–60%, they are fairly easy to make; simply simmer some cream in a pan for several hours evaporating some of the milk out then place in a cool area till cold enough to fridge. Let it stand for 24–48 h and then skim off the top cream, and one has clotted cream. This method melts some of the collective fats that when cooled gives a part grainy and part smooth, thick substance. Lastly, fat in creams can also be utilized to stabilize whipped cream foams (see Section 7.2.2.3.4).

11.1.3 ICE CREAM

The aim of a good ice cream is to set a flavored cream so that it leaves a sufficient portion of aqueous solution unfrozen at the typical serving temperature from −13 to −6°C/from 9 to 21°F and also at conventional storage temperatures from −15 to −20°C/from 5 to −4°F (Barham et al., 2010). This takes a lot of skill from the cook's perspective and scientific understanding from the industrial point of view. Cream by itself when frozen is as hard as a rock. So, we add sugar, which lowers the freezing point (by disrupting the freezing of water ice crystals) and makes it softer (assuming the right amount of sugar). As a result, sweetened cream freezes well below the freezing point of water. Interestingly too, if salts are added to the ice-cream mixture, the salts dissolve in the water portion of the cream, and they too help lower the freezing point that then allows the mixture to get cold enough to freeze the sugared cream. The trick to making a good ice cream is to freeze it so the ice crystals that form are small enough to be undetected on the palate rather than being coarse and grainy. To achieve this, ice cream has to be frozen as quickly as possible to help produce these very fine ice crystals. In industry, manufacturers can freeze their ice creams quicker and colder than their handmade counterparts. However, of manufacturers, while they might have the edge on ice-crystal technology (Paco-Jets aside), they do often adulterate the traditional ice-cream recipe by adding or replacing some traditional ingredients with gelatin, concentrated milk solids, stabilizers, powdered milk, and artificial flavors and colorings. Also, from a commercial perspective, one benefit is that the mixed ingredients are combined and then pasteurized. If pasteurization is carried out at a high enough temperature (above 76°C/174.2°F), the denaturing of the whey proteins can in fact improve the smoothness of the ice cream by helping to minimize the size of the ice crystals (Mistry, 2001).

When it comes to recipes, we need to achieve three phases or states; these are the tiny pure ice crystals that form the backbone of the ice cream, the concentrated flavored cream, and sufficient pockets of air that are formed as the mixture is churned during freezing. Most good recipes approximate the following: a water content of around 60%, 15% sugar, and a milk fat content between 10% and 20%. In carrying out this recipe, the result is a thick semisolidified mass of equal portions of liquid water, milk fat, milk proteins, and sugar that ultimately coats each of the many millions of ice crystals. During freezing, the mixture is agitated trapping air into pockets that help lighten the mixture making it smooth and creamy. This trapping of air is called overrun and can be anywhere from a few tens of percent (a denser ice cream) to 100% (effectively doubling the volume) and giving it a light and velvety mouthfeel.

11.1.3.1 Two types of ice cream

According to McGee (2004), there are two main types of ice creams and a few variations. The first in his words is the standard or Philadelphia-style and the second French or custard ice cream.

Standard or Philadelphia-style ice creams are generally made from cream, milk, and sugar plus one or two other ingredients like vanilla. It's appeal plays on the velvety richness and delicate flavor of cream itself. When making these types of ice creams, the first step is to take the basic ingredients—fresh cream and milk (17% milk fat from equal quantities of whole milk and heavy, "double" cream) and 15% table sugar. It is then prechilled, to aid in the subsequent freezing process. It is then, as mentioned, frozen as quickly as possible in a homemade or commercial restaurant ice-cream maker. Once rapidly chilled and aerated, the mix becomes too thick to continue in the machine; however, at this time, still only about half of the water has thus far frozen into ice crystals. At this point, it is popped

into the freezer whereupon another 40% of the water turns into ice crystals. If the hardening is too slow, some of the existing ice crystals can take up more of the mixes' water than others and coarsen the texture of the ice cream. One option to avoid this is by taking the ice cream and spreading it out onto a tray so it freezes that much quicker.

French or custard ice creams start with cooked egg custards (a Crème Anglaise) with sometimes as many as 12 egg yolks per liter of milk or cream (traditionally milk). In this case, it is the proteins in the milk and the emulsifying nature of the yolk that help keep ice crystals small and the texture smooth even at high water/low milk fat contents. A smooth but low-fat option ice cream can be made by replacing some of the milk with cream or with high-protein evaporated, condensed, or powdered milks or alternatively by replacing some of the sugar with corn syrup.

Among the few variations of the above is the Italian Gelato. Gelato's custard ice cream is made with high levels of butterfat and little overrun giving the whole cream a dense but creamy texture and flavor. Other ice creams are the reduced, low, and nonfat types. However, as one might recall, fat plays an important role in regulating the size of the ice crystals, which in reduced-, low-, and nonfat varieties is achieved through the addition of things like corn syrup, powdered milk, and vegetable gums.

To preserve its smoothness, ice cream is best stored at −18°C/−0.4°F or below to slow the ice crystal coarsening process. Partial thawing to between −13°C/8.6°F and −6°C/21.2°F (different ice creams have different ideal serving temperatures) is good for serving, but note that at these increased temperatures, a good proportion of the ice crystals melt. And while these temperatures are good from the consumers' point of view, it is not so good for the ice cream. This is because refreezing the ice cream back to −18°C/−0.4°F again encourages the free water to form larger crystals coarsening the texture until it's noticeable on the tongue. Also, if uncovered, fats on the ice cream can absorb localized air, retaining unwanted odors.

11.1.4 NONCULTURED BUTTER

We have described the phenomenon of overwhipping cream to make butter; however, in order to understand a little more of the processes of making, in this case, a cultured butter, read on. There are many varieties of butter, normal unsalted/salted, flavored and cultured (or fermented), etc. (FAO, 2011).

For basic salted butter, at its very simplest, it can be made by separating the cream from fresh whole milk. The cream is then reduced by cooking until the fat content reaches 36%–44% fat; at this point, it is also pasteurized. The mixture is then whipped, beaten, or blended until the cream separates into a coalesced fat and liquid (buttermilk) mixture. By separating the fat at this point, one has made basic butter. However, left like this, the butter's shelf life is only a few days long. To improve upon this, we need to take as much of the remaining buttermilk away to leave a butter with about 80%[8] butterfat and 16% buttermilk and about 4% protein (UK preferences). We do this by adding in some ice-cold water then reblending it. One will see that the water become cloudy; this is just the buttermilk coming out of the mixture. After blending for maybe 30 s, leave in the fridge for 30 min or until the butter has fully separated and then add in a little salt if desired, and there, one has it—homemade butter (for "Cultured Butter," see Section 11.2.2).

[8]When it comes to fat content, while 80% is a general rule, France specifies a minimum fat content of 82%, while some American producers aim for 85%. Specialty butters are also made for professional bakers and pastry cooks where higher butterfat content is desired; this leaves less water in the fat for things like puff pastry.

11.1.4.1 Clarified butter

Clarified butter is butter is just that—clarified. Simply melt the butter at a low temperature so that the water and milk solids settle out and are removed leaving behind pure milk fat. Another method is to continue the cooking of the unclarified butter at high enough temperatures (boiling point of water) that the water and milk evaporate away leaving just the butter and a film of whey protein on top and a layer of casein protein on the bottom. All one needs to do then is separate the elements until one has clarified butter. The end result is great for panfrying (sautéing) as with the milk solids and water removed the cooking temperature of the newly clarified butter can be raised in the pan. In fact, clarified butter can be heated to temperatures of 200°C/392°F before it begins to burn, which, when compared with the unclarified version that burns at about the 150°C/302°F mark, is quite an advantage.

11.1.4.2 Butter in cooking

Butter in the kitchen is used in many ways. We use it to fry foods in, in baking and pastry goods, as a coating on fresh breads and pastries, to toss vegetables in, to line molds, and to help keep some sponges moist. In fact, butter is one of those delights in the kitchen that, with its wonderful texture and aroma, is used in as many dishes as is possible. Perhaps, the most visible uses in the kitchen are in sauces. For example, cooks use it to enrich sauces giving them a fine glossy shine and a buttery aftertaste in a process called "monter au beurre" (to mount with butter). This is achieved by cutting the butter into small cubes and whisking it in to a simmering but not boiling sauce. This disperses the butter throughout and is held in an emulsified state long enough for the plate to reach the customer. Then, there are the compound butters, those cold creations containing anything from garlic and parsley, chopped prawn and dill or red bell pepper and paprika. These are usually mixed into a softened butter then left to chill before being sliced and presented atop anything from grilled fish to vegetables and meats. After this, there are the butter sauces; a good example is the "*beurre blanc*," a reduction of wine, shallots, and cream that is finished with a hefty amount of butter whisked in cold (similar to monter au beurre) only with more butter. Next come the melted butters: "beurre noisette," (hazelnut butter) and "beurre noir" (black butter (dark brown)), which are maybe the simplest of all sauces. These are melted butters cooked until the water boils off and the molecules in the whitish residue (milk, sugar, and protein) react with each in the browning reaction to form brown pigments and nutty aromas. Of course, the black butter is not black but rather dark brown; otherwise, it would simply taste acrid and bitter. Oftentimes, lemon juice and parsley are added for extra flavor and are great with things like fish and vegetables. Last but not least, there is the granddaddy of emulsions the humble hollandaise. This sauce is made by partially denaturing egg yolks, lemon, and water over a steam bath, at which point we drizzle in clarified butter until the desired thickness, taste, and textures are achieved.

11.1.4.3 Margarine

Margarine was created by the French scientist Michel Eugene Chevreul who on discovering a new fatty acid (in 1813) called it "acide margarique," later renamed margarine. Today, margarine remains relatively cheap compared with butter, and it is said that the Americans and northern Europe including the Scandinavians favor it over butter while France and Britain still put butter first. Up till about 1900 AD, animal fats were used in the process, but nowadays, modern margarines are made from vegetable oils, lard, and some refined fish oils. These vegetable oils are hydrogenated (see Chapter 16) and can be made to differing hardness depending on clients or usage. Some margarines are spreadable straight from the refrigerator, while others are still solid and unusable at the same temperature.

Some try to mimic butter, while others attempt to stand out. Overall, the composition of margarine is the same as that of butter's, that is—a minimum of 80% fat and a maximum of 16% water/skimmed milk and salt for flavor and as a microbial deterrent. Also, added are the stabilizer lecithin (0.2%), coloring agents, and flavor extracts together with vitamins A and D. One advantage margarine has over butter is the ratio of saturated to unsaturated fat in hard margarines that turns out to be 1:3, whereas in butter it is 2:1. The downside though is the trans fats in margarine. However, nowadays, manufacturers have the know-how to produce trans-fat-free margarines, although that doesn't necessarily mean all do.

There are a multitude of varieties available to the cook: hard, soft, less saturated, spreadable, low fat, no fat many with an ABC of emulsifiers, starches, gums, and/or proteins.

11.2 FERMENTED DAIRY PRODUCTS

11.2.1 LACTIC ACID BACTERIA: LACTOBACILLUS AND LACTOCOCCUS

There is a vast array of enticing options when it comes to fermented milk and dairy products. From soured creams to yogurts to cultured butters, each owes their existence to one particular family of bacteria—the lactic acid bacteria. Lactose (a sugar) can be found in milk but very few other places in nature. Lactose then is an energy source that is very rare; this requires a specialist microbe with very specific enzymes that can feed on this sugar. Lucky for us, this specialist microbe is a people-friendly bacteria—a probiotic. These bacteria digest lactose in milk extracting energy from the lactose and breaking it down into lactic acid. This is then released into the milk where it amasses and impedes the growth of most other microbes.

There are two important groups of lactic acid-causing bacteria: the various species of *Lactococcus*, found primarily in plants, and the more common genus *Lactobacillus*. The lactic acid bacteria (depends on which one is chosen) are lightly acidic or tart, causing the casein proteins in milk to gather together in semisolid curds that consequently thickens the milk. However, while this process happens naturally, very few people are willing to leave it to chance bacteria populating the milk—instead producers opt for a narrow few species of bacteria for consistency of products.

11.2.2 CULTURED BUTTER

Making cultured butter seems quite an easy process on paper; however, to achieve in the kitchen, it turns out to be quite a laborious chore. First, one needs to prepare the cream by either buying high-fat "heavy" cream (or double cream) or using the 30% whipping cream and reducing it till the butterfat content reaches 36%–44% fat. It is then pasteurized and cooled. After this cooling period, cultured butter may be inoculated with lactic acid bacteria[9] that are typically a mixture of lactic acid-producing strains from the Lactobacillus family. The mixture then is cooled to about 5°C/41°F where it is aged (or ripened and fermented) for at least 8 to 10–18 h in order that about half of the milk fat in the globules are allowed to form solid crystals. Aging is also a process that helps distort and weaken the fat globule

[9]Lactic acid bacteria are the principal organisms involved in the manufacture of cheeses, yogurt, buttermilk, sour cream, and cultured butter.

membranes so that they rupture easily upon churning. Depending on number and size of the crystals will determine how quickly the milk fat separates. The number and size of the crystals will also determine the final texture of the butter. After warming by a few degrees, the butter mixture is then churned. Churning is achieved by a variety of mechanical means that churns the butter for a few seconds or up to 15 min depending on the machine. This churning is needed to further rupture the fat globules in the mixture. Once again, these "naked" fat globules coalesce to form a continuous mass of butterfat that grows with further churning until the required wheat grain size of the separated fat is reached. After this, the butterfat is washed with cold water and then kneaded to release any trapped buttermilk and to bring the whole mass together. This can then be salted or flavored and stored in favorable conditions (fridged or even frozen). One alternative method that is used in some countries when making cultured butter is to churn the pasteurized cream then add the culture starter afterward. This then ferments in the fridge over time. This is not to be mixed with other butters where manufacturers add pure lactic acid and flavor compounds to cream butter *ex post facto*. Lastly, because butter's limited water content is dispersed among the butter in tiny droplets, so, correctly made butter greatly resists microbial contamination. As such, butter can keep well for several days at room temperature. However, its exposure to air and bright light begins to oxidize the fat molecules (Section 9.2); for this reason, butter is best kept refrigerated.

As mentioned, butter comes in many varieties, and sometimes, it's necessary to read the label to determine if a particular butter was made with plain or fermented cream or even cream flavored to taste like fermented cream butter. While raw cream (unpasteurized) butter is quite rare these days, it is still in fact prized for its "pure" creamy flavor. If one is lucky enough, one can still find small artisanal businesses still practicing this method today. Cultured butter on the other hand also has a veritable variety of tastes that can be markedly different depending on the particular culture and length of fermentation employed. In all cases of cultured butter, the bacteria used produce both acids and aroma compounds, so the butter tends to be noticeably fuller in flavor (Mistry, 2001; FAO, 2011).

11.2.3 FERMENTED/CULTURED MILKS AND CREAMS

There are literally hundreds of varieties of fermented milks and creams from around the world; however, they need not be complex things, and most are generally ready for consuming within hours or a few days. The basic premise of fermented milk is fairly straightforward; it boils down once again to the humble casein protein. As bacteria feed on lactose-producing lactic acid, so progressively, acid conditions cause the normal bundled micelles of casein proteins to unravel into their separate casein molecules. After that, they rebonded to each other forming a continuous matrix of bonded protein molecules that trap liquid and fat globules in small pockets. This turns the fluid milk into a fragile solid or gel.

As has been mentioned, traditionally, if cream or milk were left unattended, bacteria would grow spontaneously giving the derivative products made from it a characteristic aroma and tartness of flavor. Nowadays, the same products are now intentionally seeded with these same bacteria. The various species of *Lactococcus* and *Leuconostoc* are best for these creams as they also share three important characteristics. Firstly, they grow best at temperatures well below those typical of yogurt fermentation. Secondly, the bacteria used are only moderate acid producers, so overly "tartness" of taste is eliminated as a problem. Lastly, certain strains of *Lactococcus* and *Leuconostoc* are capable of converting citrate (a milk component) into diacetyl, an aromatic compound that enhances the flavor of cultured creams,

butters, and milks. Indeed, so favorable is this flavor, the manufacturers sometimes add citrate to accentuate this flavor note.

11.2.3.1 Yogurt

Raw milk can contain all manner of dangerous microbes including *Brucella*, *Campylobacter jejuni*, *Coxiella burnetii*, *Escherichia (E) coli*, *Listeria monocytogenes*, *Mycobacterium bovis*, *Mycobacterium tuberculosis*, *Salmonella*, *Staphylococcus aureus*, and *Yersinia enterocolitica*. These all survive and thrive at certain pH levels, and while, for example, *S. aureus* thrives within a neutral pH range of 7–7.5, it can in fact survive within milk as acid as pH of 4.5 (Field, 2011). Therefore, while yogurt can prohibit the growth of many of these bacteria, certain pathogens are not necessarily neutralized to a sufficient degree (FAO, 2011). For this reason, it is best to use pasteurized milk instead of raw milk when making yogurt.

There are essentially two stages in yogurt making, and they are heating the milk and partly cooling it and then fermenting the warm milk. Traditionally, milk for yogurt was boiled at length (30 min at 85°C/185°F or at 90°C/194°F for 10 min) to concentrate the proteins giving it a firmer texture. These temperatures improve yogurts consistency by denaturing the curd and whey proteins caseins and lactoglobulins, respectively. At the milk is cooled to about 40–45°C/104–112°F, the bacteria are added. Typical yogurt contains just two kinds of bacteria—*Lactobacillus delbrueckii* subspecies bulgaricus and *Streptococcus salivarius* subspecies thermophilus. Each encourages the growth of the other in a symbiotic relationship in which the outcome acidifies the milk more rapidly than either could on its own. Another option that is commonly used, by cooks and artisans, is a portion of the previous batch that is used to "seed" the new yogurt. At first, the acid-sensitive streptococci is the main agent creating lactic acid until the acidity exceeds 0.5%, at which point it slows down and the more robust lactobacilli take over taking the final acidity to about 1% or more. At this point, the mixture is kept warm until the milk sets. If untouched at this juncture, flavor compounds are produced that taste a little like green apples (acetaldehyde). However, as with most things food wise, the industry are looking for stability, consistency, and shelf life—as such one can find many yogurts with extra milk proteins, gelatin, starch, and stabilizers that help prevent the separation of curds and whey (Mistry, 2001; FAO, 2011).

The fermentation temperature has a strong impact on yogurt consistency. At the maximum tolerable temperature of 40–45°C/104–112°F, the bacteria cultivate and produce sufficient lactic acid allowing the milk proteins to gel in just 2–3 h. At just 30°C/86°F, however, the bacteria work far more leisurely, and the milk can take up to 18 h to set. There is a difference in the fast and slow processes beyond the economic impact. Rapid gelling not only generally produces a coarse network of proteins giving it the required firmness but also freely leaks whey. Slow gelling on the other hand produces a finer more delicate matrix that is better at retaining the whey (Field, 2011; McGee, 2004).

11.2.3.2 Crème fraîche

Crème fraîche in French actually means "fresh cream," so in France, crème fraîche means a pasteurized cream with 30% fat. This liquid version is unfermented and has a shelf life of 15–20 days or so. It is the thick version that we are really interested in, in this section. Non-French crème fraîche is similar in many ways to soured cream. Although, one obvious difference to sour cream is that crème fraîche has a milder flavor on the palate. Crème fraîche is customarily made (outside of France) using naturally fermented unpasteurized cream. Nowadays, however, naturally thick pasteurized cream is used for safety and quality reasons. It is soured with the addition of bacteria that incidentally is also the

thickener. This ensures a thick, high-fat (minimum 30%, some even higher up to 48%), low-protein, tart-tasting cream that complements certain fresh fruit and caviar, as well as being used in stews and casseroles, and of course as dips among other things. It comes in several forms, either liquid (liquide and fleurette) or thick (épaisse). The thick version is fermented at lower "cool-room" temperatures with a cream culture for 15–20 h. It becomes thick (like most fermented milks); after which, it is ready to eat. It has a shelf life of 10–30 days depending on who one reads. The thickening in fact is a good sign that the product has reached the optimum acidity for this product of about pH 4.6 and of course its characteristic tartness. While commercial crème fraîche is made essentially the same way, they do sometimes add a little rennet for a thicker consistency. A distinct buttery flavor is noted in certain milks rich in citrate and those diacetyl-producing strains of bacteria. In an alternative to using cream cultures, the kitchen cook can seed a batch of heavy cream with shop bought cultured buttermilk or sour cream at the proportion of 15 mL/250 mL and following the above procedure of temperature and time. Because of the high fat content, it can safely be used in the kitchen without fear of splitting or curdling (Mistry, 2001; Brown, 2014).

11.2.3.3 Sour/soured cream

Sour cream is basically a firmer, less versatile version of crème fraîche. It contains around 18%–25% upward of milk fat that upon cooking will curdle. American sour cream is heavier-bodied than its European counterpart owing largely to having the cream homogenized twice before being cultured. A small dose of the enzyme rennet is sometimes added with the bacteria, which helps the casein proteins to coagulate forming a firmer gel. In cook's kitchens around the world, they commonly acidify (coagulate) their cream literally with acids like lemon juice. This "acidified sour cream" is nonfermented. In the kitchen, sour or soured cream is very versatile and is commonly used as a base for flavoring dips, dressings, and other condiments and to finish certain sauces (although if boiled, it will split). It can also be used as a base for potato salad or in baked goods such as breads, cheesecakes, pies, and cookies. It is also sometimes used to enrich cold-set cheesecakes (Brown, 2014).

11.2.3.4 Kefir

Kefir is fermented by "kefir grains," the curds from a previous batch that acts as a starter culture in each new production. Within the curd starter are active microorganisms that comprise 83%–90% lactic acid bacteria and 10%–17% yeast (which is traditional but also optional if the final product is not to have an alcoholic content). Commercially made kefirs on the other hand have seen the development of starter cultures that make the whole process more efficient and quicker while also providing longer product shelf lives. The fermentation gives kefir a carbonated, lightly sour, and slightly alcoholic yogurt-like beverage that smells somewhat like yeast. Typically, cow, goat, and sheep milks are used for kefir production making an end product that can vary greatly in terms of flavor. In cooking, kefir can be used as alternative to salad dressings or added to baked goods such as breads, pancakes, and waffles. It can also be used in breads, cakes, and pastries as a replacement for things like yogurt or buttermilk (Brown, 2014; FAO, 2011).

11.2.3.5 Koumiss

Koumiss (kumiss, kumis, kymmyz, or kymis) is another fermented milk drink traditionally from Central Asia. It is made with horse milk or camel's milk if in Mongolia and is similar to kefir in that it is a lightly carbonated, slightly sour (from the production of lactic acid), and light as opposed to some

heavier fermented milk drinks. It differs from kefir in that it uses a liquid starter culture comprising nonlactose-fermenting yeasts and the bacteria lactobacilli (FAO, 2011; Mistry, 2001). It's worth noting too that as horse's milk has a higher sugar content than several of the other major milk-producing mammals, so the resulting koumiss' alcohol content is slightly higher than that of kefir. Today, commercial koumiss is made from cow's milk and additional sugar to better replicate the alcohol content (Table 11.3) (Brown, 2014).

11.2.3.6 Buttermilk

True buttermilk is that portion of milk that is left after the milk or cream has been churned to make cultured butter. It has a slightly sour flavor and would continue to thicken and develop flavor over time. This type of true buttermilk is subtler and provides a more complex flavor profile although it is also more prone to off-tasting flavors and early spoilage. The fragments of fat globule membranes are rich in

Table 11.3 Fermented Milk and Creams

Acidity (pH)	Product	Microbes[a]	Fermentation Temperature, Time	Shelf Life (4°C)[b]
4.0–4.4	Yogurt	*Lactobacillus delbrueckii*, *Lactococcus lactis*, *Streptococcus thermophilus*	41–45°C/ 106–114°F, 2–5 hr, or 30°C/86°F, for 6–12 h	2–3 weeks
4.5	Crème fraiche[c]	*Lactococcus lactis*, *Leuconostoc mesenteroides*	20°C/68°F, for 15–20 h	10–30 days[d]
4.5	Sour cream	*Lactococcus lactis* subsp. *lactis*, *Leuconostoc mesenteroides*	22°C/72°F, for 16 h	4 weeks
4.4–4.8	Buttermilk	*Lactococcus lactis* subsp. *lactis*, *Lactococcus lactis* subsp. cremoris, *Leuconostoc mesenteroides* subsp. dextranicum	72°F/22°C, for 14–16 h	10 days
4.3–4.5	Kefir	Lactococci, *Lactobacillus Kefir*, *Acetobacter*, yeasts	20°C/68°F, for 24 h	10–14 days
3–3.5[e]	Koumiss	Lactobacilli, nonlactose-fermenting yeasts	27°C/80°F, for 2–5 h and cool aging	10–14 days

[a]*The types of microbes, etc. being used for each fermentation are not exhaustive, but merely examples.*
[b]*The shelf life may vary with manufacturers.*
[c]*Crème fraîche in French denotes a pasteurized cream with 30% fat. The French version is unfermented and has a shelf life of 15–20 days.*
[d]*Depends on who one reads.*
[e]*Depends on strength.*
Adapted from McGee, H., 2004. On Food and Cooking: The Science and Lore of the Kitchen. Charles Scribner's Sons, New York; Puniya, A.K., 2015. Fermented Milk and Dairy Products. CRC Press; Brown, A., 2014. Understanding Food: Principles and Preparation. Nelson Education; Hess, S., et al., 1997. Rheological properties of nonfat yogurt stabilized using Lactobacillus delbrueckii *ssp. bulgaricus producing exopolysaccharide or using commercial stabilizer systems. J. Dairy Sci. 80 (2), 252–263; Mistry, V.V., 2001. Fermented milks and cream. Food Science and Technology. Marcel Dekker, New York, pp. 301–326.*

emulsifiers like lecithin that make it especially valuable in the kitchen for things like ice cream to baked goods.

However, with the arrival of the centrifuge, making butter has become that much easier. However, once separated, the remaining liquid produces sweet unfermented buttermilk that is left behind. This would then either be sold "as is" or is cultured with lactic acid-producing bacteria in order to develop a traditional consistency and flavor. In the United States, just after World War II, a shortage of true buttermilk led to the imitation of cultured buttermilks made using skimmed milk and fermenting it until thick and acidic. Today, in the United States, so-called cultured buttermilks are produced by taking heated low-fat or skimmed milk that after cooling is then fermented with cream cultures (just like yogurt treatment) until a fine protein gel is formed. The gelled milk is further cooled to stop the fermentation and gently agitated to break the curd into a thick but smooth liquid. Apart from being a refreshing beverage, cultured buttermilk is used widely in many kitchens. It is an extremely versatile product used in breads, cakes, desserts, and biscuits. It is also often used in dressings for salads and tangy sauces and even soups (Mistry, 2001; Brown, 2014).

11.2.4 COOKING CULTURED/FERMENTED MILKS AND CREAMS

When cooking with fermented or cultured milk products, it must be remembered that a fairly stable milk or cream product can easily become unstable once heat is added to the equation. Adding high, lengthy, or protracted heat treatment to such products above, combined with the high acid content characteristics of cultured/fermented foods, results are milks and creams that are highly susceptible to curdling. In fact, it takes a great deal of care and attention from the cook not to push the protein coagulation too far resulting in "split" grainy-like particles of protein. It is not just heat either, additional salt, acid, and/or strenuous stirring can all cause the product to curdle. The reality in maintaining a wholesome smooth and uncurdled consistency is gentleness in the application of heat while stirring or treating such foods with great care. However, it is not all that bad, as fermented or cultured milk products have several beneficial properties. Firstly, as the pH of the product is lowered through the fermentation process (making it more acid), bacteria find it difficult to grow, thus acting like a self-fulfilling preservative and prolonging the foods shelf life. Another benefit is that some products like crème fraîche or sour cream for instance can add "body" or a thickness to certain culinary dishes like sauces, dips, and condiments. As a flavor enhancement, most fermented milk products can also offer a characteristic sourness from the likes of lactic acid, carbon dioxide, diacetyl and ethanol, and other such products of the fermentation process. Milk proteins too are great emulsifiers helping to stabilize fat emulsions like salad dressings, soups, and foams. Lastly, there are the nutritional benefits of fermented/cultured milks and creams being probiotics and containing much needed vitamins and minerals (Brown, 2014).

11.3 CHEESE

Not unsurprisingly, the character of cheese closely reflects the animals' milk from which it came whether cow, sheep, goat, buffalo, camel, or other. In turn, the character of the milk is dependent on what it was fed on and the all-important microbes that inhabit the milk in the first place. Further considerations depend on whether it is raw (*see below*) or pasteurized and a whole host of conditions, from acid to enzymatic reactions, to molds, time, temperature, and humidity. Cheese, once a

multifaceted way of preserving the bounty of the milking season, is now a product of much desire for aficionados and laymen alike. It is practiced all around the world catering to all manner of palates and tastes. Cheeses are to be enjoyed, either paired with fruits, chutneys, and wines; cooked in sauces or in sandwiches; or simply by itself. Each type of cheese is unique in that the proteins are broken down by enzymes and microbes into a whole host of aroma and flavor compounds. More specifically, the casein proteins in milk are first broken down into smaller pieces called peptides (which can be either tasteless or bitter) and then further broken down into amino acids (usually sweet or savory) that in turn are broken down into amines producing trimethylamine (reminiscent of fish), putrescine (spoiled meat), and sulfur and ammonia (Vaclavik and Christian, 2014). When broken down like this, cheese sounds very unappetizing, but in reality, a little bit of this and a little dash of that and the magic of cheese begins. As well as breaking down the proteins, cheesemaking also processes the fats, which are enzymatically or bacterially broken down into their fatty acid components giving off peppery, blue cheese, pineapple or coconut notes, etc. In fact, the combinations are almost limitless and depend greatly on the conditions mentioned above and on the numbers and types of bacteria and enzymes being used. Indeed, a look at the following sections and one will have a better understanding of just how unique cheeses really are.

11.3.1 MAKING CHEESE

Cheese is a simple fermented dairy product, made with little more than a few basic ingredients—milk, starter culture, salt, and enzyme called rennet, which is then ripened or aged. There are several stages in the creation of most cheeses involving standardizing milk, ensuring the right temperature for inoculation, inoculation with starter and nonstarter bacteria, adding rennet, forming curds, cutting the curds, draining the whey, texturing the curd, dry salt or brining, forming the cheese into blocks, storing and aging, and packaging.

- *Standardize the milk*—milk is often standardized before the cheesemaking process begins. This is in order to optimize the protein to fat ratio so as to make a quality cheese with a high yield.
- *Milk*—milk is heated or cooled down (depending on whether or not the milk is pasteurized) to 32°C/90°F, the temperature needed for the starter bacteria to grow.
- *Starter and nonstarter bacteria*—the milk is inoculated with starter and nonstarter adjunct bacteria or molds and left to mature at 32°C/90°F for 30 min. The maturing step allows the lactic acid bacteria to grow and begin fermentation converting the lactose (milk sugar) into lactic acid that lowers the pH, while the adjunct bacteria also helps develop the flavor of the cheese.
- *Add rennet*—the rennet is an enzyme that acts on the proteins in milk to help form the curd. This is left undisturbed for about 30 min to ensure a firm coagulum.
- *Cut curds and heat*—curds are allowed to ferment until they reach a desired pH level. It is then cut into small pieces and heated to 38°C/100°F that helps to separate the curd from the whey.
- *Drain whey*—the whey is drained from the curd and the left behind curds to form a mat.
- *Texture curd*—the curds are cut into sections and piled on top of each other being flipped periodically. This helps to expel more whey while also allowing fermentation to continue again until the desired pH is reached. Further, this allows the mats to join closer together to form a tighter more matted structure. These mats are then cut into smaller pieces.
- *Dry salt or brine*—depending on the type of cheeses being made, they are sometimes put back in a vat of brine or are dry salted.

- *Store and age*—after the cheese has been pressed and shaped, they are stored in coolers for ripening until the desired age is reached. Depending on the variety of cheese and whether or not the cheese needs to ripen, assuming it does need ripening, this can be from several days to weeks, months, or even years.
- *Package*—cheese may be cut and packaged into blocks, or it may be waxed or smeared with bacteria or other materials to form a crust.

But first one must choose the right milk.

11.3.1.1 The milk: Pasteurized or raw

In modern industrial cheese production, the milk is practically always pasteurized to eliminate pathogens and spoilage bacteria. However, artisanal cheesemakers may still use raw milk (more so in the United Kingdom and Europe). That said, since the late 1940s, the US Food and Drug Administration (FDA) has mandated that cheese made from raw milk must be aged a minimum of 60 days at temperatures not lower than 2°C/96°F. At this temperature, it is thought that whatever pathogens might have been in the milk will be eliminated during that period. In fact, so great is the fear of using raw milk in the states that the United States has actually banned the importation of raw milk cheeses aged less than 60 days. This means US artisanal cheesemakers unlike many of their European counterparts cannot sell fresh raw milk cheeses (unless otherwise aged) and have been confined to making hard, aged cheeses (Knoll, 2005). Even the World Health Organization has considered completely banning the production of raw milk cheeses (FAO, 2011).

On the other hand, raw milk cheeses are exceptional nutrient-rich foods and far superior to processed pasteurized cheeses. The reason raw milk is so popular is that pasteurization tends to kill off useful milk bacteria while inactivating many of the milk's own enzymes. This it is believed to drastically affect nutrition and taste. Raw milk is also far superior for other reasons too, by providing the following:

- High-quality protein and amino acids.
- High-quality saturated and omega-3 fats.
- Vitamins and minerals, including calcium; zinc; phosphorus; and vitamins A, D, B_2 (riboflavin), and B_{12}.
- Because raw cheese is not pasteurized, the natural enzymes in the milk are well preserved.
- Grass-fed cheese is considerably higher in calcium; magnesium; beta-carotene; and vitamins A, C, D, and E.
- Organic grass-fed cheese is free of antibiotics and growth hormones.

The artisanal resurgence in cheesemaking, particularly in Europe, is providing a wealth of gourmands a veritable treasure trove of fine cheeses both raw and pasteurized. European regulations actually encourage the use of raw milk, as long as strict regulations are followed (EU, 1992). For the traditional production of a number of the world's best known cheeses, raw milk was and is still in some cases the preference in Brie, Camembert, Comté, Emmentaler, Gruyère, and Parmesan although some of these are now made using pasteurized milk.

As mentioned, whether raw or pasteurized, the milk is often standardized in order to optimize the protein to fat ratio so as to ensure a high yielding good quality cheese. The milk is taken to 32°C/90°F, the right temperature needed for the starter bacteria to grow.

11.3.1.2 Definition of raw milk

We have talked a lot about raw milk, but what exactly is raw milk? Again, the answer varies depending on who one reads. For instance, the international food health standard of the World Health Organization's (WHO) Codex Alimentarius defines raw milk that has

> …not been heated beyond 40°C [104°F] or undergone any treatment that has an equivalent effect
> **(FAO, 2011, p. 187)**

Similarly, the European Union (EU) Directive 92/46/EEC defines raw milk as

> …milk produced by the secretion of the mammary gland of farmed animals that has not been heated to more than 40°C [104°F].
> **(EU, 1992, p. 3)**

In both cases, the application of the term "raw milk" as opposed to "unpasteurized milk" recognizes that there are processes other than pasteurization that are permitted such as thermization.[10]

11.3.1.3 Starter culture/bacteria

Cheesemaking cultures are called lactic acid bacteria (LAB). Their primary source of energy is the lactose in the milk, and their primary metabolic product is lactic acid. These lactic acid-producing bacteria (starter cultures) initially acidify the milk (at 32°C/90°F); they also play crucial roles during the many phases of the cheesemaking and ripening/aging processes. Starter cultures are the first ingredient to be added to the milk to assist with coagulation by lowering the pH prior to the addition of rennet. This ensures the correct pH for coagulation and also influences the final moisture content of the cheese. The metabolism of the starter cultures contributes greatly to desirable flavor compounds while also preventing the growth of spoilage organisms and pathogens. Furthermore, adjunct cultures are often employed at the starter culture stage to provide or further enhance the characteristic flavors and textures of cheese. The rate of acid production is critical too in the manufacture of certain products like Cheddar cheese and others (Mistry, 2001).

There are two broad groups of starter cultures; these are the following:

- Coccus—*Lactococcus lactis* ssp., *Lactococcus lactis* ssp. *cremoris*, and *Streptococcus thermophilus*
- Rods—*Lactobacillus bulgaricus* and *Lactobacillus helveticus*

The moderate-temperature (mesophilic) lactococci are also used to make cultured creams, cheddar, cottage cheese, Monterey Jack, feta, Stilton, Edam, Gouda, Muenster, blue cheese, and Colby. Or the heat-loving (thermophilic) lactobacilli and streptococci are also used to make yogurt, mozzarella, provolone, Emmentaler, Comté, Gruyère, pecorino, Gorgonzola, and various blue cheeses (Hui, 2006).

Once the starter cultures and any nonstarter adjunct bacteria have been added, the milk is held at 32°C/90°F for 30 min to further develop. This maturing step allows the bacteria to thrive and grow and begin fermentation. This also lowers the pH while aiding in the development of flavor.

[10]Thermization involves heating raw milk to temperatures of around 63–65°C for 15 s, while pasteurization involves heating milk at 63°C for 30 min or up to 71°C for 15 s.

11.3.1.4 Rennet

Since plain acidity alone can cause milk to denature, then to curdle or coagulate, it is not unreasonable for one to ask why use rennet at all? In fact, there are two very good reasons. Firstly, acid by itself can cause the protein micelles "casein" and the calcium that holds them together to break up far too much. As this happens, so they get lost in the whey, what is left after this is the remaining proteins that then coagulate forming a curd that is brittle and unpliable. Secondly, a high-acid curd tends to slow down the flavor producing bacteria used, or if the mixture is too acidic, it can actually destroy the bacteria altogether.

By contrast, rennet's enzyme (rennin or chymosin) is far more gentle and takes a much more targeted approach. In milk, casein protein bundles called micelles are kept apart by the negatively charged kappa-casein. Instead of targeting all proteins indiscriminately and breaking them down at many junctures, rennet's chymosin attacks one specific protein, the kappa-casein protein. Rennet targets this protein and breaks it down in only one place, the negatively charged area of the kappa-casein protein. This effectively allows the rest of the casein micelles to better aggregate forming bonds and a very supple but solid elastic coagulum or curd. This process while not quite as fast as that of using acid, it is still relatively quick. In just 30 min, the rennet has done its work preparing the milk/cheese for the next stage.

Traditionally, rennet is taken from the fourth stomach of milk-fed calves less than 30 days old. However, there are vegetarian alternatives that can be used to make cheeses originating from thistle flower stigmas (usually from the cardoon thistle) and lady's bedstraw (*Galium verum*), among several others. Although a word of warning here in that while all vegetable coagulants (often mistakenly called rennet) are vegetarian, not all vegetarian rennets are made from vegetables. Some vegetarian rennets are produced in one of two ways, firstly by the growing of a natural enzyme produced by the microbial mold *Mucor miehei* while another way is through the genetic modification whereby the animal gene producing chymosin has been spliced into the DNA of bacteria, fungi, or yeasts.

11.3.1.5 Curdling

The curd (the denatured and coagulated/gelation of milk protein) is allowed to ferment until the desired pH is reached. The curd is then cut with into small pieces and heated to approximately 38°C/100°F (depending on the cheese) helping to separate the whey out from the curd. So, a few fresh cheeses aside, the cheesemaker nearly always uses a combination of starter culture (bacteria) and rennet. The different combinations of pH through lactic acid-causing bacteria, time, and temperature are responsible for all manner of textures and flavors that can be produced. If more acidic, one ends up with a fine grained fragile curd that is formed over many hours containing more moisture. This is the case with many fresh cheeses including goat's cheeses. With more rennet-initiated coagulation, one has a coarse but robust, firm, and rubbery curd that forms anywhere from 30 to 60 min. This is the case with hard and semihard cheeses including Emmentaler, Gouda, cheddar, and Parmesan. Another aspect to consider with hard and semihard cheeses is the choice of starter culture as it persists in the drained curd and helps generate much of the flavor during the ripening stage. This can last for weeks, months, and even years and as the bacterial activity might slow or stop, so many of their enzymes continue the breaking down of proteins into savory amino acids and other aromatic by-products.

11.3.1.6 Draining

Depending on the type and texture of the cheese to be made, the curd can be treated in several ways. For moist-rich softer cheeses, the curd can be cut, molded, and drained by gravity alone for several hours. In other instances, for the firmer cheeses, the cheesemaker cuts the curd into smaller pieces allowing more

moisture to drain, and then, the curd is pressed underweight. For harder cheeses, still, the curd can be cooked in the whey at about 55°C/131°F to expel more moisture (whey) and then pressed.

11.3.1.7 Salting and brining

To inhibit the growth of spoilage bacteria and for flavor, the cheesemaker always adds salt to the cheese. This is done by mixing dry salt with the curd and whey or by simply applying dry salt or brine to whole cheeses. Salt also aids in the aging process by drawing out moisture from the curds and slowing the growth of the ripening bacteria or molds and regulates the activity of the ripening enzymes. Most cheeses contain a lot of salt, somewhere in the region of between 1.5% and 2% salt by weight. By way of example from highest to lowest, salt content belongs to Roquefort, pecorino, and feta that contain approximately 5%, while Emmentaler is the least salty at about 0.7%.

11.3.1.8 Aging/ripening

Ripening is where the magic continues. It is the time when microbes and milk enzymes turn the salty, soft, crumbly, or rubbery curd into cheese as we know it. Some cheeses like the moist Camembert reaches its peak in a few short weeks, while the many more, most in fact, reach their peak after a few months. The real hardcore of cheeses, those like the dry Comté and Parmesan, peaks after a year or more. This is all achieved under the watchful eye of the cheesemaker who controls the growth of microbes, the activity of enzymes through the skillful manipulation of temperature and humidity.

11.3.1.9 Cheese microbes

Yeasts and molds are used in certain cheeses to provide the characteristic colors and more importantly the flavors of cheese varieties. Think of cheeses as being decomposed then recomposed by the cheesemaking process. The question that needs asking is which microbes to use for which cheese. Well, not surprisingly, perhaps no more than a scant handful of most modern cheeses are made with purified cultures, while numerous others are made with a portion of the previous batch's starter.

11.3.1.9.1 The molds

According to McGee (2004), cheese molds are microbes that require oxygen to grow. They tolerate much drier conditions than many bacteria in the cheesemaking process, and they are also responsible for the powerful protein- and fat-digesting enzymes that help mature and improve the flavor and texture of certain cheeses. While molds are useful, unwanted molds will easily develop on the rinds of most any cheese that is not periodically wiped to prevent such growth. Having said that, there are some molds that are seeded on purpose. The so-called smear bacteria (*Brevibacterium*) is responsible for Epoisses, Münster, Limburger, Port-du-Salut, Raclette, Livarot, Pont l' Eveque, and Năsal, among others, that are just a few examples of rind bacteria that give the distinctive desirable stench to the cheese. As *Brevibacterium* grow, they do so at salt concentrations of up to 15%, which is a concentration that inhibits the growth of most other microbes. Furthermore, *Brevibacterium* are less tolerant of acid and need oxygen to thrive and also only grow on the cheese surface, not inside.

Coincidentally, the variety of bacteria that contribute to the many molds in cheese comes from the same genus that gives us the antibiotic penicillin—the genus *Penicillium*, in particular two varieties, the blue and white molds:

- *Blue molds*—blue molds are responsible for many of the strong-tasting cheeses available: Roquefort (from sheep's milk) gets its characteristic blue veins, it's odor and strong flavor from the

Penicillium roqueforti, similarly, and the characteristics of Stilton and Gorgonzola are at the mercy of *Penicillium glaucum*. Furthermore, many aged goat's cheeses also owe their specific flavor notes to the same bacterium. In fact, blue penicillia are quite unique in their ability to grow in low-oxygen atmospheres (5% compared with air at 21%). The specific characteristics of *Penicillium roqueforti* and other blue cheeses flavors arise from the fact that the mold specifically breaks down between 10% and 25% of the milk's fat. More specifically, this freeing up of the short-chain fatty acids gives the slight peppery feel to sheep's and goat's milk blue cheeses. Moreover, blue penicillia are also responsible for the breaking down of the longer fatty acid chains converting them into aroma and flavor substances including methyl ketones and alcohols.

- *White molds*—in addition to the blue penicillia, there are also the white strains of *Penicillium camemberti* that are responsible for the soft cow's milk cheese like Camembert, Brie, and Neufchâtel. The white penicillia mold create their characteristic aromas and flavors of garlic, mushrooms, and ammonia through the breakdown of the cheese proteins.

11.3.1.10 How are the holes in cheese made?

The *propionibacteria*—the *propionibacteria shermanii* is an important bacterium in Swiss starter cultures and are well-known for their hole-making property. Like most others, this bacterium continues to consume the cheese's lactic acid from inception as the starter culture, through the rennet process and during ripening. As this continues on during the ripening phase, so it converts the lactic acid into a combination of propionic and acetic acids and carbon dioxide gas that is responsible for the characteristic holes in Emmentaler. The *propionibacteria* grow slowly at an unusually high temperature of 24°C/75.2°F for several weeks.

11.3.1.11 How is cheese classified?

How cheese is classified depends on who one consults (McGee, 2004; FSANZ, 2009). One popular way of organizing cheese is to group them first by the animal from which they came then secondly by their moisture content and/or finally by the microbes that were used to ripen them. Classification by moisture content from one source alone should be considered arbitrary as

> …although many classification systems utilise moisture content as a defining factor, inconsistency exists between category parameters e.g. Codex defines soft cheese as >67% moisture on a fat free basis, whereas Schultz (1952) defines soft cheese as 60–69.9% moisture content and Scott (1986) and Burkhalter (1981) both employ a limit of >55% moisture
>
> **(FSANZ, 2009, p. 18)**

Furthermore, even though moisture content is a widely used tool for classification, it suffers from a major drawback in that it tends to group together cheeses with widely differing characteristics and manufacturing protocols. As a result, the percentages given below are from McGee (2004) and as such should be treated as reference only.

A fresh (raw) cheese with 80% water for instance tends to last only a few days. A pasteurized soft cheese containing 45%–55% water can last several weeks. While a semihard cheese with 40%–45% water content can be kept a few months, and finally, a hard cheese containing 30%–40% water can last a year or more. In short, the more moisture removed from the cheese at the curd stage, the harder the cheese's eventual texture and by extension the longer its shelf life.

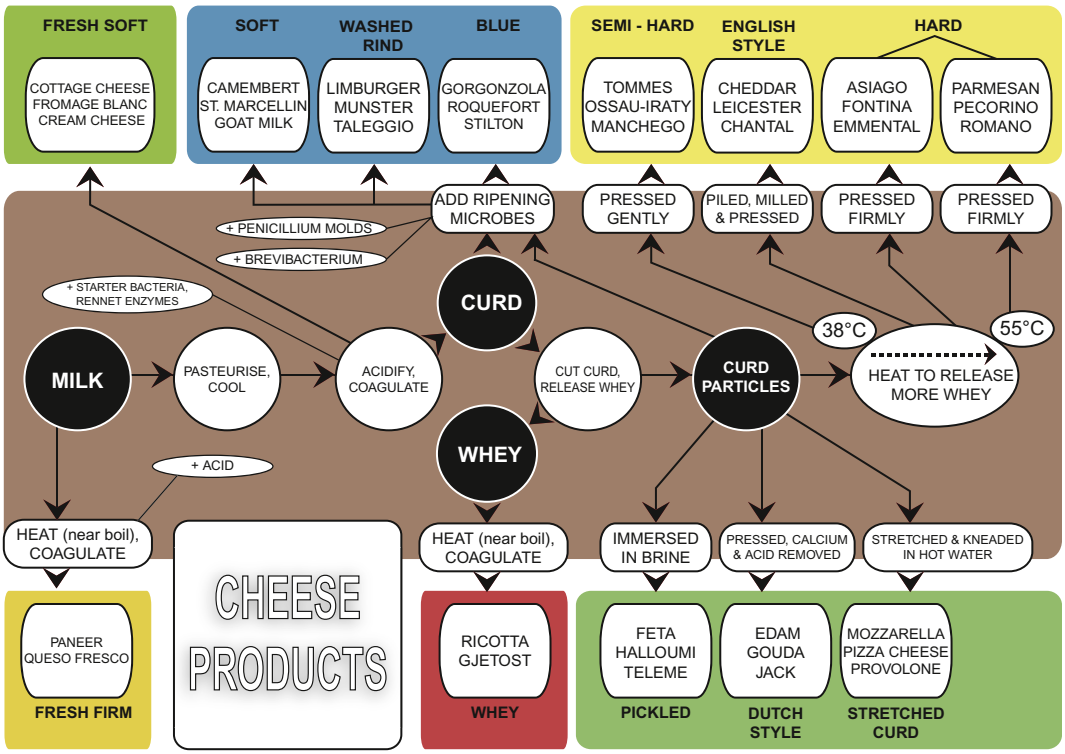


FIG. 11.1

Cheeses: production and versatility.

One other option of classifying cheeses then is through the texture, that is, from soft to hard (Fig. 11.1).

To savor the full body, aroma, and flavor of the cheese, they should ideally be served at temperatures of 12–15°C/55–60°F that is cooler than most rooms and warmer than fridge temperatures. However, storing or holding cheeses at this temperature is simply not practical as at this temperature the cheese continues to ripen. As a result, most people, commercial kitchens, and the like tend to refrigerate them. Then, perhaps, an hour or more before serving pop them into a holding cooler set at the right temperature or as is often the practice—left to come up to room temperature. Although one word of caution here, if the room is too hot, say above about 26°C/80°F, then the milk fats will melt and sweat out of the cheese.

As far as the rinds go *vis-à-vis* eating them, it mostly comes done to individual's preferences. Long-aged rinds tend to be harder and more difficult to eat and being slightly rancid from oxidation in the air. Some are coated in wax and other nonedible materials, while the others are generally ok. As said, it's largely a matter of personal preference, with softer cheeses. The rind can offer a prominent contrast to the interior in terms of both flavor and texture. But beware, if a piece of cheese develops an unusual, unattractive surface mold or sliminess or even an unusual odor, the best thing to do in this situation is to throw it away. Simply cutting the outside mold off will not remove the mold filaments (some carry toxins) that can penetrate some distance into the cheese itself (Brown, 2014).

11.3.1.12 Cooking with cheese

When using cheese as an ingredient in cooking, there is one important thing to note. Maybe surprising to some is that not all cheese melts, some merely gets drier and stiffer. Technically, cheese is a simple emulsion of dairy fat and water, bonded by a network of casein proteins. These proteins are held together by calcium atoms. Upon heating, the calcium bonds dissolve, separating the casein molecules. In fresh, younger, or unaged cheeses, the casein molecules are large and elastic as in stringy mozzarella. However, during aging, casein molecules are acted on by ripening enzymes, and the casein is broken down into small pieces. This affects the melting characteristics of the cheese.

There are certain cheeses that do not melt; these include Italian ricotta, Indian paneer, Iberian queso blanco, and many fresh goat's cheeses. The distinction with these cheeses is that almost all are curdled primarily by means of acid alone or with little rennet involved. As mentioned earlier, acid coagulation tends to ride rough shod over the micelle proteins breaking their bonds in many places and dissolving the calcium bonds that hold them together. This creates a microcosm of tiny clumps of casein proteins, which upon heating, rather than melting, the casein proteins form tighter bonds pulling themselves together and simply become firmer while expelling water. This is why these cheeses can be fried, baked, boiled, and roasted, and they will still hold their shape. Rennet on the other hand creates a more pliant, more malleable structure of casein micelles that are easily weakened by heat.

As we melt cheese, so two things happen: At around 32°C/90°F milk fats melt bringing little beads of fat to the surface and making the initial mass of cheese more supple; then, at higher temperatures—around 55°C/130°F for soft cheeses, 65°C/150°F for semihard Cheddars and Swiss cheeses, and 82°C/180°F for the Parmesan and Pecorino family of cheeses—sufficient bonds among the casein proteins collapses, and the matrix effectively falls apart, resulting in a softening of large pieces of cheese or a complete melting if finely grated. Melting behavior is also determined by the cheeses' water content, that is, low-moisture-content/low-water-content hard cheeses need more heat to melt because their protein molecules are much more firmly bonded. This means when melted, the hard cheeses flow relatively little. With continued high heat, more moisture will evaporate from these hard liquefied cheeses. In turn, the cheese gets progressively stiffer and will eventually resolidify. If cheeses are over developed, as mentioned earlier, whereby the caseins are attacked by the ongoing enzymatic process (mostly hard but some overripened soft cheeses too), then the casein matrix tends to contain smaller pieces of protein.

Stringiness can be a desirable trait in things like pizza or lasagna, for example. So, if one wants stringiness as in mozzarella, one uses cheeses from the predominantly rennet-making process. These cheeses have mostly, intact casein molecules that are then linked together by calcium into long, ropelike fibers that can stretch into ropelike threads. The stringiest or the most fibrous cheeses then are those that are moderate in moisture, acidity, salt, and age. The most common among these are the mozzarellas, Swiss-style Emmentaler, and Gruyère. Crumbly cheeses on the other hand are the Cheshire and Leicester cheeses, while the moist cheeses like Colby, Caerphilly, and Monterey Jack are the preferred choice for simply melting, but not becoming stringy in foods like Welsh rarebit and grilled cheese sandwiches. Also, Gruyère is the preferred cheese in fondues because of its moist, fat, and salt content, while hard cheeses like the Parmesans, Grana Padano, and the pecorino readily disperse in all manner of soups, sauces, risottos, and innumerable pasta dishes:

Cheese sauces and soups—certain cheeses simply need to be melted in soups and sauces without splitting or coagulating into lumps. The tip here is not to use soft stringy cheeses but rather cheeses like

the high-moist, young-aged cheeses and sometimes even aged grating cheeses. The trick here is after adding, do not overheat as excessive or long-term heating can easily overcoagulate the proteins and water, and unsightly, milk fat tends to leach out with the oil rising to the surface. It helps if one were to add these cheeses at the last minute of a cooked dish and to not let the dish cool down too much as the cheese gets tougher and lumpy and sometimes stringy, depending on the cheese used. Lastly, by adding a thickener like arrowroot, corn flour, or flour to the soup sauce or other dish, it helps stabilize the cheese by coating the protein mixture and keeping them apart. Another tip would be to add some tartaric acid, lemon juice, or wine in the preparation. This has the effect of keeping the cheese proteins apart and helps prevent seizing, splitting, or coagulating.

11.3.1.13 Cheese: Love or hate them

It is no small wonder that the smell and taste of cheese can provoke delight in some and disgust in others. This is because many of the molecules that give cheese its unique aroma and flavor are the very same molecules that are produced during uncontrolled spoilage. It is also the same story with microbial activity on warm, moist, shielded areas of human skin (e.g., armpits, toes, and belly buttons). So, we can see that it is no wonder the obvious sense of repugnance cheese is to some while for others, the limited and controlled spoilage (as the fermentation of cheeses can be thought of), is an acquired taste. In this way, an aversion by one person can be seen as a miraculous transformation for another. Furthermore, as cheeses are spoiled, so we are only a microbe or two away from possible food poisoning.

11.4 EGGS

The tradition of eggs is perhaps greater than that of any other single food item. It is used in both sweet and savory dishes; it can act as binders and as raising agents and used in cakes, meringues, and cookies. The yolks too can act as emulsifiers in sauces such as mayonnaise and hollandaise and provide structure to custards, brûlées, and crème caramels.

11.4.1 FREE RANGE AND INDUSTRIALIZATION

Year-round egg-laying hens have been made possible by the use of controlled lighting and temperature. Eggs produced under these conditions are cooled quickly and shipped using refrigerated means of transport allowing for longer shelf lives and quality control. Sadly though, this industrialization has paved the way for rising incidences of salmonella contamination. This is because once the hens have outlived their egg-laying days, they are often processed and then used in the feed mix for the next generation of productive hens.

That said, over the past two decades, give or take, enough people have become outraged by this practice and have turned to free-range hen's eggs or those fed with organic products. Although one must be cautious however as the term "free-range" can be slightly misleading in that all a chicken needs to be free range is perhaps a slightly bigger cage and minimal access to the outdoors.

11.4.2 THE EGG: ITS PHYSICAL, PROTEIN AND NUTRITIONAL VALUE

11.4.2.1 The white

When cracking open an egg, one encounters three separate components—a thin watery white substance surrounding a thicker gelled white substance, surrounding the yolk. The egg white is the main reactive component in the equation here as it contains two types of proteins, albumins and mucoproteins.[11] Under the banner of albumins, there are several different types:

- *Ovalbumin* makes up over half (54%) of the white's protein. Although while the most by percentage ovalbumin's activity is largely unknown, it does contribute greatly to the eggs flavor through its reactive sulfur groups. Some have suggested that its role is pure nourishment for the embryo.
- *Ovotransferrin* (also known as conalbumin) makes up 12% of the white's protein and is located closer to the yolk. It also binds to iron and is the first protein to coagulate when an egg is heated
- *Ovomucoid* at 11% (the main gelling agent in the egg white) that incidentally does not denature by heat alone.
- *Globulins* make up about 8% that possibly act to plug holes or defects in the shell.
- *Lysozyme* at 3.5% is an enzyme that helps break down bacterial cell walls. It also acts as a foam stabilizer too.
- *Ovomucin* is about 1.5% of the total albumen content; this protein tends to have the most influence on the thickening part of the white by pulling together many of the other proteins (up to 40 times thicker than the runny/liquid part); it also acts as a foam stabilizer too.
- *Avidin* (0.06%) helps bind the biotin vitamin (H).
- *Others*—there is also another 10% of mixed proteins of negligible amounts in the albumin responsible for various functions.

The white in total accounts for nearly two-thirds of the egg's shelled weight of which 90% is water. As seen above, the rest (around 10%) is protein and a few trace elements (minerals), some fatty material, vitamins, and glucose.

Biochemically, the albumen proteins described above are not only food for the baby chicks. Three of the proteins above bind tightly to vitamins preventing them from being bioavailable to other organisms. One binds to iron, while another protein inhibits the reproduction of viruses. With the last one digesting the cell walls of bacteria, it can be said that the egg whites' secondary role is protector, a chemical shield against things like infection and predation.

11.4.2.2 The yolk

Biologically, the yolk (accounting for just over one-third of a shelled egg's weight) is said to be almost exclusively nutritive. It comprises 75% of the calories, most of the iron, thiamine, and vitamin A. Its bright yellow color derives not from beta-carotene[12] but from plant pigments called xanthophylls, which the hens obtain from alfalfa and corn feeds or through supplements in the feed from producers.

From a culinary perspective, the yolk contains "…free-floating proteins and protein-fat-cholesterol-lecithin aggregates" (McGee, 2004) called lipoproteins that give the yolk its notable capacity for emulsifying and enriching. It is also one of the most nutritious foods we have. Including an abundant

[11]Mucoproteins are glycoproteins composed primarily of mucopolysaccharides.
[12]Beta-carotene comes from the orange pigment in carrots and other plant foods.

supply of linoleic acid (a polyunsaturated omega-6 fatty acid), several minerals, many vitamins and two plant pigments, lutein and zeaxanthin, and valuable antioxidants, not surprisingly, the yolk truly is a nutritional bounty (Belitz et al., 2009).

11.4.2.3 Cholesterol

The egg is no doubt one of the richest sources of cholesterol containing around 215 mg per large egg which, when compared with a similar size portion of meat, contains only 50 mg. While a lot of bad press surrounds cholesterol, it has been suggested that blood cholesterol is raised far more by saturated fats than by cholesterol itself. Taking this into account, in eggs favor is the fact that most of the fat in the yolk is unsaturated. Further, some evidence has been cited that other fatty constituents in the yolk (the phospholipids) actually interfere with our absorption of yolk cholesterol (Brown, 2014).

11.4.3 GOOD AND BAD EGGS

In order to determine egg quality, producers "candle" their eggs. While this might still be the terminology used, nowadays, it is nearly almost exclusively carried out by light, bright enough to pass through an egg coupled with automated scanners. Candling then, detects cracks in the shell, harmless blood spots on the yolk, and so-called meat spots in the whites (either dark blood spots or tiny bits of tissue from the hen's oviduct picked up on its way out). Candling also looks for larger than normal air pockets. Collectively, any of these defects relegate the egg to the lower grades.

The average egg is exceptional among our raw animal foods in its capacity to remain edible for weeks (if stored properly). That said, from the moment the egg leaves the hen, it starts to deteriorate in certain ways. In terms of pH levels as time goes by, so the egg (both yolk and the white) become more alkaline. This happens because of the carbon dioxide (in the form of carbonic acid) within the egg tends to dissolve out of the white and yolk and is slowly lost through the pores in the shell. As this happens, so the pH of the yolk rises from a slightly acidic pH of 6.0 to a nearly neutral 6.6; the white (albumen), however, can go from an alkaline 7.7 to a very alkaline 9.2—sometimes even higher. The result of this pH change is more noticeable in the white. When fresh, egg whites tend to be slightly cloudy as proteins cluster together. Change the pH and the same proteins are repelled from each other causing a more transparent, clearer egg white, while at the same time the thick white tends to become progressively runnier. In terms of yolk, the pH osmotic imbalance allows water from the albumin to crossover into the yolk at a rate of several milligrams per day. This swells the yolk and makes it noticeably runnier.

During the mid-1980s *Salmonella enteritidis* was identified with increasing numbers of food poisonings in Europe, Great Britain, and North America. *S. enteritidis* is a particularly persistent bug that can cause diarrhea or the chronic infection of other bodily organs. As most of these were associated with the consumption of lightly cooked eggs (and even raw eggs), further investigation showed that even the United States' clean, grade A eggs potentially carried large enough numbers of *S. enteritidis* to be of concern. Indeed, it was estimated, in the 1990s, that perhaps one egg in 10,000 US eggs carried this particularly powerful form of salmonella. Nowadays, thanks to a selection of precautionary measures, the prevalence of infected eggs is now much lower—although it is still not zero. So, by way of precautionary measures, it is always best to buy and keep eggs refrigerated and to cook any eggs to a temperature of at least 60°C/140°F for 5 min or 70°C/158°F for 1 min, or if the option is available, use pasteurized eggs.

As mentioned, there are alternative, safer alternatives to using fresh eggs—these are pasteurized eggs in the shell, dried egg whites, and salted or sugared liquid eggs. Simply put blended whole eggs, separated yolks, and whites, and whole intact eggs can all be pasteurized by heating to temperatures of 55–60°C/131–140°F (just below the temperature range at which egg proteins coagulate). Dried egg whites can also be pasteurized before or after the drying. For most purposes, using pasteurized eggs can give satisfactory results when replacing fresh eggs although if making foams, emulsions, etc., there is usually some loss in pasteurized egg's foaming and emulsifying power and stability.

11.4.4 HANDLING AND STORAGE

Eggs are collected shortly after laying and are immediately cooled and in some countries washed in detergent to sterilize the thousands of bacteria on the shell that gather laying. Traditionally, washed eggs were then given a coating of mineral oil to impede the loss of both CO_2 and moisture; today, however, with most eggs reaching market in just 2 days after laying, oiling is limited to long-haul delivery routes. The quality of an egg can deteriorate four times more quickly if held at room temperature rather than the refrigerator. So, it comes as no surprise that one should buy eggs from and store them in the refrigerator. If treated with care, there is little reason why eggs should not be kept for several weeks in the shell. Once broken open, however, they must be consumed fairly quickly, or if required, they can be frozen.

It is perhaps a little-known fact that eggs if stored deshelled and in airtight containers can be kept frozen for several months. Whites freeze fairly well, and they lose only a minor amount of their foaming power. In yolks, however, the story is different; once thawed, they defrost to a pasty consistency unusable in the traditional sense. Thorough mixing of yolks with either salt, sugar, or acid however can prevent yolk proteins (livetin, etc.) from amassing leaving the thawed mixture fluid enough to mix. As a rule of thumb, yolks require about (5 g), 1 tablespoon of sugar (15 g), or 4 tablespoons of lemon juice (60 mL) per half liter to be of use.

11.4.5 EFFECTS OF HEAT AND TIME ON EGGS: PROTEIN COAGULATION

When cooking an egg, ovotransferrin is the first protein to denature and end up binding itself not only to other denatured ovotransferrin proteins but also to other proteins whether denatured or otherwise. In this way, ovomucin is combined with the ovotransferrin and ovalbumin to form a rigid white gel.

There is much speculation over the right temperatures that eggs begin to denature upon the application of heat (Barham et al., 2010; Field, 2011; Jueneman, 2011; McGee, 2004; Baldwin, 2012). The following is a representative sample:

- 61.5–63°C/143–145°F: *conalbumin* denatures and causes the white to form a loose gel.
- 64.5°C/148°F: *livetin* denatures and causes the egg yolk to form a tender gel, while at 70–77°C/158–170°F, the yolk tends to fully coagulate.
- 70°C/158°F: *ovomucoid* denatures and causes the egg white to form a firm gel (the egg yolk also coagulates around this temperature).
- 80–84.5°C/176–184°F: *ovalbumin* overdenatures and causes the egg white to become slightly rubbery (Barham et al., 2010; Field, 2011; Jueneman, 2011; McGee, 2004; Baldwin, 2012; Sikorski, 2006; Belitz et al., 2009).

It has also been said by Barham et al. (2010) that egg whites can begin to denature forming cross-links at temperatures as low as 52°C/126°F, while those in egg yolks require a higher temperature, approximately 58°C/136°F and above (Barham et al., 2010). Another opinion cited by Baldwin is to cook eggs at a temperature between 70°C/158°F and 84.5°C/184°F, so that the conalbumin and ovomucoid will be denatured but not the ovalbumin as this will cause the egg to become rubbery. Another train of thought, according to Jueneman (2011), eggs should be cooked for enough time to heat the yolk to a temperature of around 64.5°C/148°F, yielding a soft-boiled egg with a firm, but not rubbery egg white and a soft to creamy yolk (Jueneman, 2011).

Whichever one chooses, it is clear that there are many schools of thought on what are the best ways and the best temperatures to cook eggs. At the very least, one can see from the above that the thermally activated process of denaturing proteins is different with different egg proteins (Barham et al., 2010; Field, 2011; Jueneman, 2011; McGee, 2004; Baldwin, 2012). Furthermore, from all this and from personal experience, the author can say that there is a middle ground suggesting that at 63°C/145°F egg whites begin to denature and lightly gel; then, at 65°C/149°F, they become solid and firmer but nevertheless still a tender gel. Therefore, the optimum lies between these two temperatures giving a semi-firm white while leaving the yolk soft. Any further cooking and the eggs will begin to overcoagulate as proteins clump tighter together and water is pushed out giving way to a rubbery texture.

Egg whites and whole eggs aside for now, we can see that egg yolk protein (livetin) denatures and cooks or coagulates at a fairly low temperature of about 64–70°C/147–158°F. This is important to know when making things like hollandaise sauce, because too much heat and the proteins will form tighter and tighter protein networks, and if not, careful one will ultimately end up with scrambled eggs instead of a thick butter sauce. As an aside, this is the same temperature that coagulates the proteins in salmonella and other similar pathogens. Thus, to avoid undercooking, the eggs in a hollandaise and allowing bacteria to multiply, a small trick is to add a little acid in the form of lemon juice or vinegar. This has the effect of rising the temperature required (up to 90°C/194°F) for some of the egg yolk proteins to bond.

On a trivial note, too—when considering the density of eggs, it is worth mentioning that the white of the egg is denser than the yolk. This means when cooking, the yolk rises to the highest point it can, while the whites flow toward the bottom. This is why when boiling an egg, one will sometimes see the yoke way off center when cut open. To centralize the yolk, the egg should be turned frequently in the hot water (Field, 2011).

A raw egg is essentially a cocoon of water interspersed with protein molecules. As far as egg molecules go, a single molecule consists of thousands of atoms bonded together forming a long chain that, as with many such proteins, folds upon itself forming a tight ball. Many of the egg white and yolk proteins are negatively charged and repel each other keeping them apart, while some in the yolk are bound up in fat protein, effectively bonding them together. As heat is applied, so these molecules of protein move faster and faster, colliding and denaturing them. This unfolds them and allows them to get tangled and bond with other proteins forming a matrix of water trapped by proteins. At this stage, the egg is transformed from a liquid to a solid (Chapter 4). Also, because large protein molecules in the egg have now bundled closely enough together, so the egg sufficiently deflects light rays turning the egg white or opaque. However, as we have mentioned before, simply overcooking the eggs and the proteins will pull together tighter and tighter essentially expelling the water out and leaving a rubbery white behind.

So, when it comes to cooking dishes with eggs, the trick really is to not overcook them. This is especially true of the various custard-type dishes like caramels and brûlées that if overcooked either

will become rubbery or will overcoagulate separating the mixture into watery liquid and lumpy coagulants.

11.4.5.1 Adding ingredients to eggs

More often than not, dishes require ingredients such as salt, sugar, cream, and milk that are added to eggs. As we do so, so we affect egg-protein coagulation vis-à-vis temperature and time and by extension the dish's final consistency. By diluting eggs with either cream or milk for instance, we raise the temperature at which gelation occurs. This is because dilution effectively encapsulates eggs' protein molecules with more water particles from the milk or cream. This means that egg proteins need to be hotter in order to allow the freedom or rapid movement required for eggs to find and bond to each other. By way of example—a crème caramel of eggs—milk sugar thickens not at the rate of egg proteins (at about 70°C/158°F (the temperature of gelled yolks)) but rather at 78–80°C/172–176°F. Moreover, the resultant coagulum is somewhat delicate and prone to overheating and curdling. This is also the same for other diluted egg dishes including quiches and sweet flans, crème brûlées, and cheesecakes. It is a similar story for things like custard creams that are cooked on the stove rather than in the oven—such as the thickened crème Anglaise (custard creams), crème pâtissière (pastry creams), and the humble hollandaise sauce.

Both acids and salt pretty much accomplish the same thing with regard to egg proteins; that is, they bring the proteins together at an earlier stage. Specifically, acids and salt thicken and coagulate eggs at lower cooking temperatures while actually producing a gentler texture. At the heart of this neat, little trick is the effect of the natural negative electric charge that most egg proteins carry; namely, they repel each other—thus, by adding salts or acids such as cream of tartare, lemon juice, or simply acidic fruit juices, it effectively lowers the pH of the egg and consequently weakens the proteins' mutually repelling negative charge. In this way, the proteins end up bonding together earlier in the cooking and unfolding process and at lower temperatures too.

Yolk-based custard cream gels are common in western cuisines and are almost always made with milk or cream. However, one can use almost any liquid so long as it contains minerals. Interestingly, if one tries to make a gel with just water, one ends up with hot water and coagulated bits of egg floating around in the mix. By simply adding salt to the same mix and the proteins cluster around the positively charged minerals, effectively neutralizing the proteins negative charge resulting in a uniform set gel. Fruit or savory vegetable custards on the other hand are a bit of a hit or miss affair. For example, quiches are prone to overcooking and overcoagulation unless treated with care. Juice leakage from both fruits and vegetables can be reduced by precooking them. Adding flour too will also help stabilize certain custards. Custards, like crème caramels and crème brûlées, require gentle cooking and are usually baked in a moderate oven inside a water bath, which effectively helps in keeping the cooking temperature below boiling point, radiation heat from above notwithstanding. That said, one cannot put a lid on the water bath as this can easily increase the water temperature allowing it to boil and making it more likely to overcook and coagulate the custard.

Lastly, fruit curds, one of the most common being lemon curd, are a kind of thickened sweetened fruit juice (very similar to a custard) in which milk is replaced by the juice. Fruit curds usually have a spoonable consistency that, like jams and marmalades, goes well as a topping or filling for small breakfast pastries. And while they contain no flour, they usually have more sugar, starch, and more eggs and butter than milk custards. In this way, largely because of the added ingredients, the cooking temperature can once again be raised in order to thicken and mesh all the ingredients together.

11.4.5.2 Starch as a stabilizer

Flours, cornstarch, arrowroot, or other starches can be added to egg dishes (as in the previous example) to help protect against curdling. This is so even if they are cooked quickly and over direct heat. In fact, so robust are the starches that they can even be brought to the boil as in crème pâtissière. Instrumental, here is the gelatinization of the starch granules; when heated to around 77°C/170°F and above (around the temperature at which the egg proteins denature and coagulate), the granules start to absorb water, they swell up, and the long starch molecules seep into the liquid. As the swollen granules absorb liquid, so they also slow protein binding. A cautionary note—when it comes to adding starches to things like crème pâtissière and so on, as they are heated and the starch begins to stiffen the mix, it is important to bring these mixtures to the boil. This is because of the egg yolks starch-digesting enzyme called amylase. Amylase is extraordinarily heat-resistant, and unless the egg-starch mix is taken to a full boil, the eggs' amylase will survive and eventually digest the starch, turning the stiff cream into a pourable liquid version of the original.

11.4.5.3 Boiled eggs

When it comes to boiling eggs, a cracked, leaking egg is both unsightly and at times smelly (producing a sulfurous smell). The best way to avoid this is to gently heat fresh eggs without the turbulence of boiling water but rather in a "rolling" boil. Also, when boiling eggs, a shell that doesn't peel off cleanly makes for a rather unattractive, pockmarked egg. To avoid this, it is actually better to use older eggs. This is because hard to peel eggs are characteristic of fresh eggs comprising a relatively low albumen pH. This causes the albumen to adhere more firmly to the inner shell membrane than to itself. At higher pH levels, characteristic of eggs left in the refrigerator for a few days, the shell tends to peel more easily. However, if one has fresh eggs that need to be cooked right away, simply adding a half teaspoon of baking soda to the water actually makes the cooking water slightly alkaline and the resultant eggs easier to peel. That said, with this method, one runs the risk of intensifying the sulfur (ammonia) flavor of old or bad eggs.

11.4.5.4 Green eggs

Occasionally, when boiling eggs, a ring of green-gray discoloration surrounding cooked yolk is visible. While it is a harmless compound of iron and sulfur (ferrous sulfide), it can seem quite unsightly to some. This occurs more often in older or prolonged, overcooked eggs and is the result of sulfur from egg whites reacting with iron in the yolks. The alkalinity of the egg plays an important role in the chemistry here, which is why (as we have seen) the older the egg, the more alkaline the white becomes, the easier the chemical reaction occurs. The good news is that the reaction can be minimized by using fresh eggs and cooking them as briefly as possible.

The greening of the outer layer of the yolk is not the only greening to be concerned about. In many hotels across the world, eggs on the breakfast buffet, especially scrambled eggs and omelets, are kept hot in chafing dishes or under a heat lamp. These eggs too will sometimes develop green patches. This is the same reaction as seen in the boiled eggs mentioned previously. It is also for the same reason, that is, where the eggs are slightly alkaline from age and the heat is persistent. This phenomenon can be slowed down by the addition of acid (usually lemon juice or vinegar) at proportions of about half a teaspoon (2 g) per egg, just enough to slow the reaction without affecting the flavor.

11.4.5.5 Poaching eggs

The thing about poaching eggs is the outer layer of thin white tends to spread out in the boiling water irregularly before it solidifies. Two tips here would be to use fresh eggs, which contain the least amount of runny whites, while the second tip is to use water that is not boiling but instead just close enough to the boil to arrest the bubbling and water agitation. These two measures should help with the tailing off or stringiness of the runny white by allowing the white to set on the outside as quickly as possible. Another tip is to have the water at simmering point and stir the water clockwise until enough momentum is produced creating a mini whirlpool; then, the egg is gently popped into the water and the thin outer white trails the rest of the egg and can be easily cleaned off or separated before serving. Some cookbooks call for salt or vinegar to aid in the process; however, while they do indeed speed up the coagulation process, they also produce slivers of white and a film over the surface of the egg. One lesser known practice is to crack the egg onto a perforated spoon allowing the runny white to drain away before poaching. Of course, these measures will never be 100% fool proof, but one can usually see a marked difference.

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CHAPTER

MEAT: FOOD AND SCIENCE OF THE ANIMAL KINGDOM

12

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As will be explained through the course of this chapter, animal carcasses comprise the bone, muscle, fat, connective tissue, and water in varying proportions depending on such variables as species, size, age, gender, and other considerations. Yet, while there is much variability, particularly inter- and intraspecies, there are sufficient data to be able to account for such variables. Thus, it is still possible to break down the average carcass into its component parts, which, as an exercise, can be quite illuminating. From Table 12.1, it can be seen that proportionally, with the exception of the percentage of pig

Table 12.1 General Meat Carcass Composition

Animal Product	Cattle (%)	Pig (%)	Lamb (%)
Carcass meat	34	52	32
Bones	16	17	18
Organ/viscera—the heart, kidney's, liver, etc.	16	7	10
Abdominal and intestinal innards	16	6	11
The skin and attached adipose fat	6	6	15
Blood	3	3	4
Fat tissue	4	3	3
Hoofs, feet, horns, and skull	5	6	7

Adapted from multiple data sets Goldstrand, R.E., 1988. Edible meat products: their production and importance to the meat industry. Adv. Meat Res. (USA); Bender, A.E., 1992. Meat and Meat Products in Human Nutrition in Developing Countries. Rome: FAO; Goldstrand, R.E., 1992. An overview of inedible meat, poultry and fishery by-products. Inedible Meat by-Products. Springer, pp. 1–17; Pearson, A.M., Dutson, T.R., 1992. Inedible Meat By-Products. Springer Science & Business Media; Bengtsson, O., 1984. By-products of slaughtering. A short review. Les sous-produits. Un atout economique pour les industries agro-alimentaires, Angers, France, 25–26 October 1983; Hald-Christensen, V., 1986. Industrial processing of slaughterhouse byproducts. Fleischwirtschaft 66 (1621); Filstrup, P., 1976. Handbook for the Meat By-products Industry. Alfa-Laval Slaughterhouse By-products Department.

meat and lamb's skin and fat tissues, that there are many similarities.[1] This is also the same when it comes to vitamin and mineral content, with the exception of high levels of thiamine in pork as compared with other meats (Bender, 1992; Goldstrand, 1988).

When it comes to meat, it can be said in general that most raw meat is moist, slick, and mushy in the mouth. However, as meat cooks, so proteinaceous connective tissues (collagen and reticulin) denature eventually transforming into soft gelatin. Other proteins too, like those in muscle meat, (the fibrous, myosin, actin, and titin) also denature at the right temperature and conditions, collectively making the meat more tender. One interesting fact worth noting is the water retention ability of meat. With cooking at progressively higher temperatures, so the denaturing and cross-hatching (linking) of the proteins continue and become closely knitted. Furthermore, as the meat continues to cook, so water in the fibers expand, and if the surrounding connective tissue/gelatin coating hasn't had time to adequately gelatinize, so water from the fibers will be squeezed out resulting in a tougher product (Lawrie and Ledward, 2006).

Importantly, as described later in this section and in Chapter 4, not all proteins are the same; they will not react in the same way, nor will they all react at the same temperatures. Consequently, cooking meat is not necessarily a straightforward as it may seem. In fact, there are a whole host of things to consider. Cooking certain meats more slowly on a low heat, like sous vide, for instance, will give a more tender feel as will cooking it slowly in a pan (after the initial higher temperature browning). Overcooking meat however generally means it becomes tough—up to a point that is after which additional cooking will further denature more of the proteins and the meat will eventually fall apart; however, whether it is tender or simply dry and chewy depends to a large extent on the cut of the meat, the cooking method (i.e., dry or moist heat methods), and the cut and quality of the meat.

In sum, the end goal is for the professional or home cook is to be able to cook meats in a way that makes them attractive to the eye and tasty on the palette—they also need to be tender and full of succulent juices.

To start with, raw meat has a limp feel; however, during the cooking process, muscle shrinks in volume, firms up as the proteins denature, and loses valuable juices. So, what makes meat juicy and tender and delicious? Taking a look at Fig. 12.1, one can see—this is "why" in a nutshell. By the end of this chapter, one will have an understanding of why and how meat behaves the way it does and one will be able to interpret this image without difficulty. This knowledge will also stand potential students or cooks in good stead in a future career within the hospitality industry.

Firstly, a working knowledge of the structure and composition of meat aids in understanding just how and why meat behaves the way it does during processing and cooking.

Traditionally, carcasses are thought of as comprising the following:

- *Meat*—is defined as the muscle tissue of slaughtered animals
- *Fat*—can be either adipose tissue fat or inter- or intramuscular fat
- *Offal*—the internal organs—i.e., the tongue, heart, liver, kidneys, lungs, diaphragm, esophagus, and intestines

[1]Variations *inter alia* animals of the same species being reared under the same or different management, plus errors in sampling and analytic techniques, occur frequently and result in considerable quantitative variations. Despite, this, similarities in the composition of meat carcasses according to the scientific literature, there is still general commonalities inter- and intraspecies that can be used to generalize somewhat.

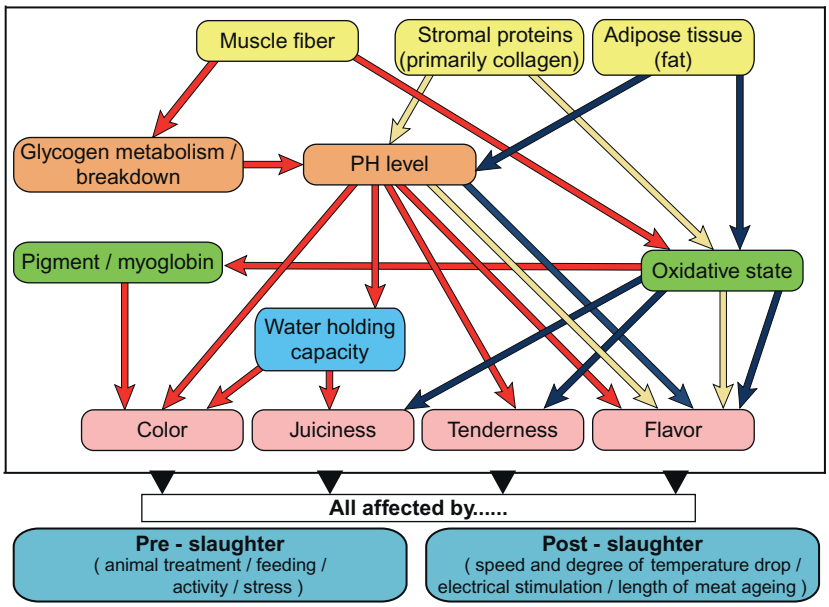


FIG. 12.1

Factors affecting meat quality.

- *Others*—other slaughter by-products including blood, soft tissues from feet, and the head (these are also sometimes referred to as offal)

However, in order to better understand the culinary importance of meat—in particular the various processes such as meat aging, tenderizing, cooking, and protein denaturing, it is worth looking at meat from different perspectives. Irrespective of the specific animal, there are two ways we can look at meat carcasses: The first is through meat physical composition, i.e., muscle, fat, and connective tissues, and the second is the biochemical composition, i.e., water, fat, protein, and carbohydrates. However, while we explore meat from both angles, there will naturally be some overlap, as such, some repetition is inevitable.

12.1 PHYSICAL COMPOSITION OF MUSCLE MEAT

The physical carcass can be broken down into its edible component parts—all of which are used in the manufacture of meat and processed meat products. The main tissue in all carcasses is the mass of muscle, i.e., the cells—the long-fibrous material that causes movement when contracted and relaxed. Surrounding these muscle fibers is the connective tissue, a kind of biological glue that connects the fibers to each other and to the bones. Lastly, intermingled among these fibers and connective tissue are the fat cells, an energy store for the muscle fibers. As we shall see, the overall quality of meat—its texture, color, and flavor juiciness—are to some degree determined by the arrangement and relative proportions of the muscle fibers, connective tissue, and fat tissue (see below) (McGee, 2004; Lawrie and Ledward, 2006). Muscle meat is only one of four classes of tissue. Meat carcasses comprise the following:

- *Muscle* (skeletal, smooth, and cardiac)
- *Connective* (adipose, areolar, dense, cartilage, blood, and the bone)[2]
- *Epithelial* (the skin)
- *Nervous tissue* (comprising the brain and nerves)

In the following sections, we will look at these in more detail.

12.1.1 MUSCLE TISSUE

Muscle is a specific type of tissue that not only provides structural support and movement but also helps maintain healthy metabolic processes. Muscle is the main component of meat and meat products; furthermore, meat proteins make up about 20% of the muscle's overall composition, making it the main constituent in the structure of meat (water notwithstanding) (Tornberg, 2005). When cooked, meats succulent texture can be as satisfying and distinctive as its flavor. Toughness, by contrast as we shall see later in the chapter, can come from any of the following—the muscle fibers, the connective tissue surrounding them and from the lack of marbling fat within the muscle itself, and more. As a rule of thumb and with all else being equal, the toughness of a cut of meat is partly determined by where it comes from on the carcass and by its age and level of activity. By way of example and in gross over simplification, we can say that grazing animals employ more forward muscles like the neck and shoulders, chest, and front and back limbs; as a result, these tend to carry the brunt of the animal's muscular workload. This leaves things like the rib eye, sirloin, and tenderloin relatively tenderer by comparison.

When considering birds too, legs tend to be tougher than breasts for the same reasons. Although when cooked, there is room for flexibility as the legs contain up to about 5%–8% collagen compared with 2% in the breast. Which brings us nicely to the question of why there are two different colors of meat, not only in birds but also in many other animals too?

12.1.1.1 Colored meats

Before we go into detail about the various muscle types we can say that the answer to the previous question of meat color, it can be said, in simple terms, that color depends on its position and workload within the carcass, that is to say, belonging to a particular type of muscle fiber. There are several different kinds of muscle fibers, and each is designed for a specific kind of work. Further, each of which has its own color and flavor.

White and red fibers—to better understand the different types of meat, it is important to know that animals move in two rudimentary ways—suddenly (rapidly but briefly), for example, when feeling threatened—when the fight of flight reaction kicks in or more leisurely (slow and casual) as the animal goes about its business of grazing. As a result, over millennia, two types of muscles have developed for these purposes the hardworking muscles—the dark or red fibers of turkey and chicken legs and other animals and the less strenuous muscles of white fibers of turkey and chicken breasts. The two types also differ in many biochemical details, although the most important difference is the energy supply each uses. As explained in the next section there are two main types of muscle fibers - fast and slow twitch fibers. The small slow-twitch fibers work aerobically: that is to say they utilize oxygen while metabolizing fatty acids and proteins; then there are the fast-twitch fibers which operate anaerobically, i.e.using no oxygen in their metabolism of glucose.

[2]For the physical components of this section, blood will be categorized according to its proper category (connective tissues), but for the remainder of the book, it will be categorized under one of the main protein components—"sarcoplasmic" proteins.

12.1.1.2 White muscle fibers

White muscle fibers dedicate themselves to applying force rapidly but briefly. These are referred to as "fast-twitch" muscle fibers. These cells are powered by a store of glycogen (carbohydrates) that resides in the fibers themselves and is rapidly converted into energy by enzymes at the cellular level. White muscle fiber cells use oxygen to "burn" glycogen; however, if the blood does not deliver sufficient oxygen on time, the cells can generate their own energy. However, generating their own energy using cellular glycogen produces a waste product called lactic acid, which accumulates until more oxygen arrives to refuel the glycogen reaction. The accumulation of lactic acid however limits the cells' durability, as does their limited fuel supply. This is why white cells work best in short sporadic bursts followed by periods of rest in between so that the lactic acid in the cells can be removed and the glycogen replaced. As a result, "fast-twitch" muscles tend to be whiter in color and more tender than the darker predominantly "slow-twitch" muscle groups.

12.1.1.3 Red muscle fibers

Red muscle fibers are used for prolonged periods of work—these are called "slow-twitch" muscles as they can produce large amounts of energy slowly over a period of time (BBC, 2014). Fueled principally by fat (in the form of fatty acids) that are metabolized using oxygen (from the blood); red fibers are comparatively thin. The cells also contain their own fat deposits and the biochemical apparatus required to convert it into energy. Part of the apparatus consists of, among other things, two proteins that give red cells their color. Myoglobin, an iron- and oxygen-binding protein, which is found in general in the muscle tissue of vertebrates and oxygen-carrying hemoglobin that carries oxygen from the respiratory organs (lungs) to the rest of the body's cells. Among the fat oxidizing proteins are also the cytochromes,[3] which, like myoglobin and hemoglobin, contain iron and are also dark in color. In general, we can say that the greater the oxygen needs of the fibrous cell, the more it tends to be exercised and the greater the content of myoglobin and cytochromes it will contain—and by extension the darker the fiber cell. The dark meat with predominantly "slow-twitch" muscle fibers tends to be tougher and requires more cooking than those of their "fast-twitch" brethren.

12.1.1.4 White meat and dark fiber variations

Putting the above in context, we can see that most animals' muscles are employed in both slow and rapid activities. This is to say their muscles contain both white fibers (short but quick, fast twitch) and red muscle fibers (long and continuous, slow twitch) as well as certain hybrid fibers that combines certain characteristics of both. In short, muscles that contain a lot of slow-twitch fibers are red in color as they comprise lots of oxygen carrying blood. Fast-twitch muscle fibers, on the other hand, do not require oxygen to make energy; therefore, they do not need a rich blood supply—ergo fewer blood vessels. This is why fast-twitch muscles tend to be lighter-colored muscle meats than those that contain a lot of slow-twitch muscle fibers (BBC, 2014).

The proportions of the different fibers depend on the actual pattern of muscle use. Frogs, among others, whose quick, sporadic movements use very few of their skeletal muscles continuously, as a result, have a very pale flesh comprising white so-called fast-twitch fibers. Chickens and turkeys, on the other hand, only fly when startled; they run occasionally, but mostly, they stand or walk for extended periods of time. This means chickens' breast muscles predominantly consist of white fast-

[3]Cytochromes function as electron transfer agents in many metabolic pathways, especially cellular respiration.

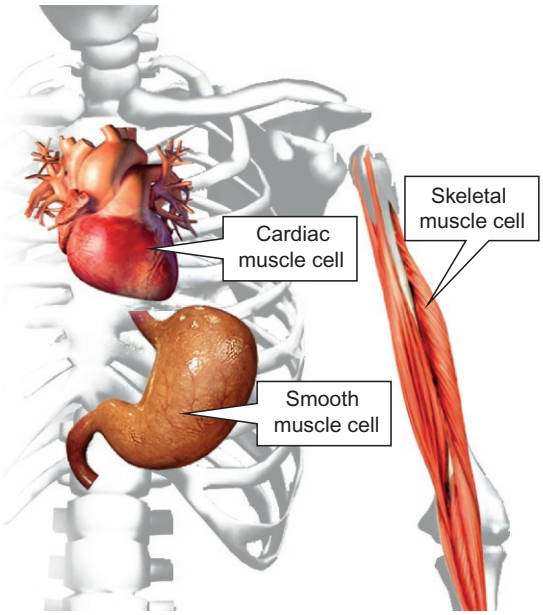


FIG. 12.2

Types of muscle groups.

twitch fibers, while their leg muscles are typically half white and half red fibers comprising both fast- and slow-twitch muscles. By contrast, the breast muscles of the majority of migratory birds such as ducks and European pigeons contain predominantly red fibers as they are used much more in as the birds fly for hundreds of miles at a time (BBC, 2014; McGee, 2004).

Fast- and slow-twitch muscles aside, there are three main muscle types: skeletal, smooth, and cardiac (Fig. 12.2).

12.1.1.5 Muscle fiber physiology

Structurally, at the very core, muscles are a collection of fibrous (threadlike) cells. A single fiber is very thin—between a tenth to a hundredth of a millimeter in diameter—about the thickness of a human hair. However, while it has miniscule diameter, each fiber can be as long as the whole muscle itself (from just a few centimeters up to 30 cm or so long) (McGee, 2004; Tornberg, 2005). Such fibers are smaller in diameter when the animal is young; however, as it grows and uses its muscles more, so the animal's muscles become stronger, not by increasing the number of fiber cells, but rather by increasing the numbers of contractile fibrils (protein) within the individual fiber cells themselves. This means the number of cells does not increase, but they do get wider or thicker. This has consequences for the toughness of the meat; that is to say, the more proteinaceous fibrils there are crammed into the fibrous cells, the harder it is to cut across them—ergo the tougher the meat. This is the reason why older, more exercised animals are tougher than their younger counterparts.

Each fiber (muscle cell) is wrapped in a protective collagen jacket called endomysium. In turn, many parcels of these fibers are combined to form bundles of muscle cells that are in turn wrapped in a tissue of collagen called perimysium (which incidentally also covers the fascicle). Once again,

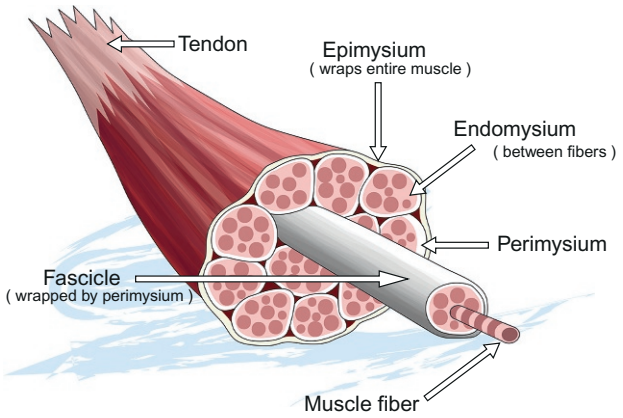


FIG. 12.3

Physical structure of muscles.

many of these perimysium-wrapped bundles in turn are further bunched together and wrapped inside another collagen-based tissue called epimysium (Fig. 12.3). Moving on, flowing between the perimysium-wrapped bundles are the intramuscular fat cells (marbling), small blood vessels (capillaries), larger blood vessels, and nerve branches. More often, several muscles collectively make up a single cut of meat (five in the case of beef rump). The tendons (connective tissue) then attach each muscle or bundle of muscles to other muscles or to the bone. These tendons and other collagen-based connective tissues (epimysium and perimysium) have different eating properties that must also be considered when preparing and cooking meat (Section 12.1.2).

However, before we go any further, the actual makeup of the muscle cells themselves, both physically and chemically, is of fundamental importance in understanding its structure and reaction to such things as pre- and postslaughter, the aging process of meats and ultimately the processing and of course cooking of meats; it is worth taking a closer look. In terms of placement, although the material transcends both the physical and chemical categories as discussed above and below this section, it is nevertheless placed here because of importance and intuitiveness.

12.1.1.5.1 The muscle cell

The muscle fibers or cells themselves vary in width and diameter depending on the age of the animal and the type of muscle itself. Lengths can be anything up to a few centimeters long, while the diameter can vary between 0.01 and 0.1 mm. The length and width of these cells are determined by the contents. Inside, the cells are wrapped by a membrane called the sarcolemma, inside of which two elements are: the *sarcoplasma* and the *myofibrils*:

- The *sarcoplasma* constitutes about 30% of the muscle cell. It is a soft protein structure containing, among other proteins, myoglobin—the red muscle pigment; these proteins are water soluble.
- *Myofibrils* constitute the remaining 70% of the cell and are by far the more important in terms of tenderness and eating quality and nutritionally. The myofibrils can number anywhere from 1000 to 2000, once again depending on age and workload of the muscle. The older the beast and/or the more used a muscle is, the bigger the myofibrils the muscle cell will contain.

By extension, the bigger and greater the number of myofibrils a cell contains, the stronger or tougher the protein structure is to break down. Each myofibril in turn is solid protein chains made of the contractile proteins actin and myosin. Actin and myosin are able to slide alongside each other allowing for the contraction and relaxation of the muscle itself. These are also lined up neatly in alternating placements giving skeletal muscle its characteristic striations (stripes). Myofibril proteins are also soluble in saline solutions.

From a culinary point of view while muscle tissue (meat) is the most important of the tissues, other important components include the following:

12.1.1.6 Smooth muscle

Smooth muscles—sometimes referred to as visceral muscles—can be found in an animal's cardiovascular, gastrointestinal, genitourinary, and respiratory systems. They are mostly composed of hollow organs (tubular or saccular) and facilitate the transport and/or storage of food, fluids, or gases within the body (with the exception of breathing and the beating of the heart). The walls of these organs are composed of smooth muscle, a type of tissue that enables constriction or dilatation. Smooth muscle is so called because of the lack of the appearance of striations (stripes) as seen in both skeletal and cardiac muscles. Striations are caused by the alternating segments of thick and thin muscle proteins that uniformly line up within muscle fibers giving the appearance of stripes. Smooth tissues like the large and small intestines are often used as casings (Fig. 12.4).

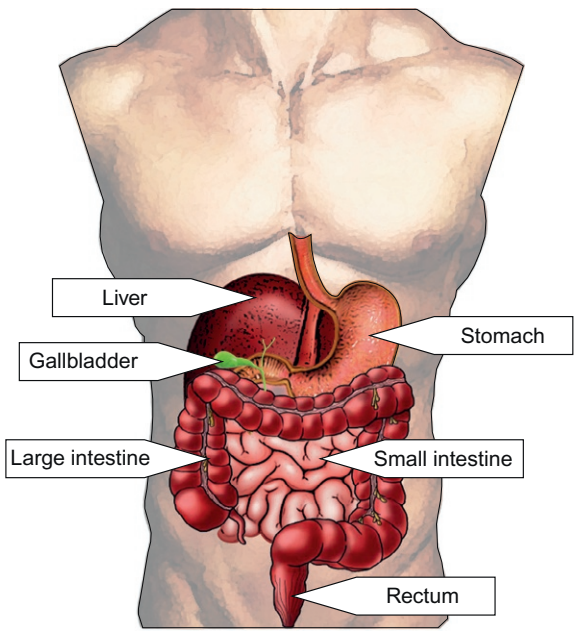


FIG. 12.4

Smooth muscle.

12.1.1.7 Cardiac muscle

Cardiac muscles are unique tissues located solely in the heart—hence the separate category. Heart muscles show some of the characteristics of smooth muscle and some of the characteristics of skeletal muscle. Its fibers, like those of skeletal muscle, have cross striations; however, like smooth muscle tissue, the heart muscle works on an involuntary basis. In contrast to skeletal and smooth muscles, however, cardiac muscle cells can also be branched and not just linear and longitudinal as in the other two types.

12.1.2 CONNECTIVE TISSUES

For the most part, connective tissues (aka stromal proteins) connect things like individual cells and other tissues to each other. In very general terms, it can be said that the younger the animal, the more soluble the meat is. The more tender the meat (Baldwin, 2012). We have already mentioned that connective tissues surround each muscle fiber and hold adjoining fibers together in bundles. They also surround ever-increasing bundles of cells until they eventually merge whole muscles with the bone (tendons) or bone to bone (ligaments). Ultimately, this means the bigger and stronger the animal, the bigger the muscle, and the bigger the muscle, the bigger the tendon. Once again, this translates into a naturally tougher piece of meat (Zhang, 1999; Farley et al., 2012).

Connective tissue principally consists of nonliving molecules in which the few living cells that do exist secrete protein filaments into the large gaps between molecules. These filaments are dispersed throughout the connective tissue effectively reinforcing it (*more details below*). One such protein, elastin is responsible for the stretchiness of ligaments and the elasticity of blood cell walls. Elastin is an especially tough protein and is not broken down by cooking. Fortunately, though, there is very little of it within tendons and ligaments. Instead, the bulk of the protein found within the skin, tendons, and bone matrices is collagen that constitutes about a third of all proteins within the living animal or carcass. Interestingly and not far off the mark, collagen comes from the Greek word meaning "glue producing," not surprisingly too; this is because when collagen is heated in water, the tough collagen partly denatures dissolving into a sticky gelatin. Once again, the amount of collagen within an animal varies with age, and while a young animal starts out with a good deal of readily dissolvable collagen, an older animal has less of the dissolvable collagen and more of the tougher type that is harder to denature and soften. Incidentally, this accounts for a great deal of the difference found in veal and beef meat tenderness. Furthermore, we mentioned in previous sections that as muscle fibers become tougher with high-heat cooking, so connective tissue generally becomes softer over time (Farley et al., 2012; Bender, 1992).

Connective tissues are not just collagen; other types of connective tissues are characterized as having cells suspended in some form of matrix whether solid of liquid—as in, for example, blood cells that are suspended in plasma or in the case of the bone (osteocyte cells) that are suspended in the bone matrix. There are many types of connective tissues, many of which are important to understand—if cooking meat is to be optimally achieved. These include the following:

- Adipose (fat)
- Areolar (loose)
- Dense (tendons and ligaments)
- Cartilage
- Blood and the bone

As a consequence, we cannot consider meat quality and tenderness in isolation, for instance, without giving thought to the many types and varieties of connective tissues—their structure and behavior (Farley et al., 2012).

12.1.2.1 Adipose: Lipids/fats

Adipose tissue (body fat) can be found in various parts of the body. These can be found under the skin (subcutaneous) forming a deposit of energy and insulation; around internal organs (visceral/abdominal fat)—once again not only to supply energy but also to act as a cushion against undesirable bumps and knocks, (interspersed between skeletal muscles are the intermuscular fats, i.e., intramuscular fat, i.e., marbling) and in bone marrow (yellow bone marrow). These are all loose connective tissues comprising approximately 80% fat whose main role is one of energy storage, although they also act, as mentioned, to insulate, cushion, or protect organs around the body. Adipose and organ fats represent between 40% and 50% of total body fat. It is also, for the most part, composed of triglycerides that contain proteinaceous cells and contain relatively little water (Bender, 1992). Fat in intermuscular tissue, i.e., between the bundles of muscle fibers, is known as "marbling" and can be as high as between 4% and 8% of the weight of lean meat. Furthermore, inside the meat, the intramuscular fat represents somewhere between 1% and 3% of the weight of a particular "lean cut"—this is also known as marbling (Bender, 1992).

In terms of meat quality, fat plays an important role, among other things:

- The looks and feel of fat on a fresh carcass can help determine its quality and freshness.
- It provides both flavor and moisture as meat cooks.
- It can also affect the tenderness of a cut of meat—through the marbling (Zhang, 1999; Farley et al., 2012).

12.1.2.2 Areolar (loose)

Loose connective tissue is the most common type of connective tissue in animals (vertebrates). It is a gelatinous-like substance made primarily of collagenous (collagen) and elastic (elastin) fibers running in many directions. Loose tissue is also versatile, strong enough to bind different tissue types together such as holding organs in place yet soft enough to provide flexibility and cushioning s of the organs too; it also attaches epithelial tissue to other tissues and surrounding the blood vessels and nerves.

12.1.2.3 Dense tissue (tendons and ligaments)

Dense connective tissues like ligaments and tendons are both soft and strong collagenous tissues:

- *Ligaments* connect bone to bone and help to stabilize joints. They are composed mostly of long, stringy collagen fibers that create short bands of tough fibrous connective tissue.
- *Tendons* on the other hand connect muscles to the bone. They are tough yet flexible enough to allow for movement.

Both ligaments and tendons are composed predominantly of collagen and other proteins that when cooked, break down, soften, or dissolve to various degrees depending on their specific collagen composition (more on this later) (Zhang, 1999; Farley et al., 2012).

12.1.2.4 Cartilage

Also, made primarily of collagen, cartilage can be found throughout the carcass in such areas as between bone joints, the rib cage, the ears, and the nose and within bronchial tubes and intervertebral disks and provide a valuable lining for bones and bone ends. It serves to provide structure and support to the body's other tissues. It falls somewhere between the bone and muscle in rigidity, not as hard as the bone but stiffer and less flexible than muscle.

There are three different types: *hyaline cartilage*, *elastic cartilage*, and *fibrocartilage*:

- *Hyaline cartilage*—e.g., on the ends of the bones
- *Elastic cartilage*—e.g., ear cartilage
- *Nonelastic cartilage (fibrocartilage)*—e.g., nose cartilage

Cartilage in mammals is mainly composed of hyaline cartilage.

Note on Collagen and Elastin

Comprising the bulk of connective tissues structure, both collagen and elastin are worth a closer look. Collagen (whitish tissue) and elastin (yellowish tissue) are two proteins that form fibers that make up the majority of connective tissues' structure within the body. Together, these proteins work in partnership. Collagen provides strength and support and is found primarily in tendons, ligaments, and other connective tissues such as the skin, blood vessels, and lungs, while elastin also forms part of the skin (dermis—the layer beneath the epidermis). Elastin lets the skin stretch and return to its original state. It is also found primarily in arterial walls, lungs, and intestines (Zhang, 1999; Farley et al., 2012).

Collagen makes up the bulk of animal protein (up to 6% body weight or up to a third of the animal's total protein content). Besides collagen and elastin, another protein reticulin, collectively makes up the connective tissues (stromal) proteins (Section 12.2.1.3).

While there are about 28 types of collagen (types 1–28), over 90% of the collagen in the body, however, is of type 1. One of these types, the white collagen (the white tissue), reacts to heat, and much of it is soluble in water. As a result, during prolonged cooking processes, white collagen can then be softened or reduced to a gelatinous substance (gelatin[4]). Elastin (the yellowish tissue), on the other, does not become soluble with heat instead; it remains largely as it was before cooking—i.e., tough and chewy in the mouth. As a consequence, the yellow tissue is usually, where possible, removed from the meat before cooking.

12.1.2.5 Blood and bone

Interestingly, despite their obvious dissimilarities in both structure and apparent function with other connective tissues, blood and bones are both considered types of connective tissues. This is because in spite of the dissimilarities they do share certain traits with other connective tissues—one obvious characteristic is that they both have an extracellular matrix (ECM). Extracellular matrices are secretions from cells, usually nonliving (composed mainly of proteins) that help fill the gaps between cells in tissues while providing support and cohesion to neighboring cells. Importantly too, ECM can be fluid or semifluid (as in blood) or solid (as in the bone). That said, because they differ so greatly from other

[4]Gelatin—collagen in beef tissue is the origin of the gelatin that is used in the making of many jellies and desserts. There are vegetarian alternatives; however, beef gelatin still remains the most popular and widely used type of gelatin today.

connective tissues, the term "connective tissue proper" is sometimes used to include all other connective tissues except blood and the bone (New World Encyclopedia, 2008).

Blood—blood connects all the body's systems transporting much needed oxygen, nutrients, hormones, and signaling molecules and helping to remove wastes. Mammalian blood is composed of blood cells suspended in liquid plasma. By volume, blood cells (red and white) make up about 45% of the blood, and the remaining 55% is plasma. Plasma in turn is composed of 90% water, while the remaining 10% contains minerals, hormones, electrolytes, and nutrients that provide energy for the body. Blood also comprises essential gases including oxygen, carbon dioxide, and nitrogen, and waste products for expulsion.

Bone—bone tissue (osseous tissue) and bones are two different things. Bone tissue specifically refers to the mineralized deposit or solid matrix of connective tissue that contains collagen and calcium phosphate (calcium carbonate)—this forms the rigid sections of the bones themselves. Bones, however, are in fact the whole thing that is the tissue (solid structure) plus the marrow, blood vessels, epithelium, and the nerves. For the remainder of this book, as per convention, blood will be categorized as part of the "sarcoplasmic" protein group.

12.1.3 EPITHELIAL

Compared with other types of animal tissue, there is very little epithelial tissue (or skin-like tissue) in the animal body. It forms the linings of external and internal surfaces of the body and protects some of the organ systems. Much of the epithelial tissue is removed during the slaughter and processing stages and that remaining is found in the blood and lymph vessels, as well as edible organs like the kidney and liver.

12.1.4 NERVOUS TISSUE

Nervous tissue makes up the autonomic and central nervous and the peripheral nervous systems of animals. This includes the brain, the spinal cord, and the peripheral nerves that regulate and control all body functions. Neurons, the basic currency of nervous tissue, are responsible for detecting stimuli and transmitting these signals between the different parts of the animal's body. However, nervous tissue as a source of food is very limited. In beef, for instance, because of the human variant of mad cow disease, it has become important to keep central nervous system tissues (especially of beef) out of the food supply. This requires strict regulation at the point of slaughter, where tissues are at risk of contaminating the rest of the meat. However, central nervous tissue is important to the quality of the meat in another way. That is in the function and treatment of the animal both immediately before and during the slaughter process, which can, as is described later, greatly influence the final quality of the meat—especially if the preslaughtered animal is overly stressed (Section 12.3.2) (Ockerman, 1996; Aberle, 2012; Zhang, 1999; Farley et al., 2012).

12.1.5 BY-PRODUCTS: OFFAL

The various nonmeat components of the slaughter process are commonly referred to as offal, by-products, or variety meats. These include the liver, brains, heart, sweetbreads (thymus and pancreas), fries (testicles), kidneys, oxtail, tripe (stomach lining of cattle), and tongue, as well as the bones, tails, lights (lungs and the esophagus), head, feet, and stomach. All of these to some extent are used

throughout the world in various regional or local cuisines whether as delicacies, main meals, accompaniments or processed into sausages, casings, and the like.

In sum, we can say there are four classes of tissue—muscle (skeletal, smooth, and cardiac), connective (cartilage, tendons, and ligaments), epithelial (the skin), and nervous tissue (Zhang, 1999; Farley et al., 2012). All of which are useful either individually or, as is quite often the case, as a heterogeneous piece of meat comprising one or more of the tissues types.

12.2 BIOCHEMICAL COMPOSITION OF MEAT

Physical structure aside, it is also useful from both a nutritional and craft or technical viewpoint to look at meat carcasses from a biochemical viewpoint. We concentrate mainly, but not exclusively, on just one type of tissue in particular—that of skeletal muscle. This is simply and solely because of the focus of the book, which is predominantly for the household and professional cook, and in that sense, we take a holistic overview of muscle meat that can and does, in many instances, apply to other broader meats and tissues of a variety of animals. That said, muscle tissue does not exist as a homogenous piece of meat; it is, as mentioned, a heterogeneous substance that usually comprises skeletal muscle itself plus connective tissue and epithelial and some periphery nervous tissues, depending on the "cut" of meat being used. Surprisingly and irrespective of which animal is used as a reference point, lean muscle meat, on a wet weight basis, is relatively comparable with compositional terms across the animal board. Moreover, compared with various vegetarian alternatives such as vegetables, nuts, or legumes—as a source of protein, meat has a great advantage. This is because of the very different nutritional profile that lean meats possess (Table 12.2). In particular, lean beef and lamb are far superior proteinaceous

Table 12.2 Content of Water, Protein, Fat, Ash (%), and Calories of Selected Meats

Product	Water	Protein	Fat	Ash[a]	Calories/ 100 g
Beef (lean muscle) (min-max)	74.05 (73.1–75)	22.8 (22.3–23.2)	2.3 (1.8–2.8)	1.2	116
Beef (carcass)	54.7	16.5	28	0.8	323
Pork (lean muscle) (min-max)	75.1	22.8	1.2	1	112
Pork (carcass)	41.1	11.2	47	0.6	472
Veal (lean muscle) (min-max)	75.6 (74.8–76.4)	23.05 (21.3–24.8)	1.15 (0.8–1.5)	1.2	98
Lamb (lean muscle)	72.9	21.9	4.7		130
Venison (deer)	75.7	21.4	1.3	1.2	103
Chicken	75	22.8	0.9	1.2	105

[a]*Incombustible inorganic residue remaining after incineration calcium, phosphorus, sodium, potassium, chlorine, magnesium, and trace elements such as iron, copper, and zinc.*

Compiled from multiple data sets Heinz, G., Hautzinger, P., 2010. Meat Processing Technology: For Small-to Medium-Scale Producers. Bangkok: Food And Agriculture Organization of the United Nations; Williams, P., 2007. Nutritional Composition of Red Meat. Nutr. Diet. 64(s4), S113–S119; Bender, A.E., 1992. Meat and Meat Products in Human Nutrition in Developing Countries. Rome: FAO.

Table 12.3 Average Animal Meat Composition—Nutritional Breakdown

Average Muscle Composition	Percent	
Water	75	
Protein	20	
Fat	3	
Soluble nonprotein substances of which are the following:	2	
• Nonprotein nitrogen-containing substances		45
• Carbohydrates		34
• Inorganic compounds		18
• Vitamins		3

Adapted from Tornberg, E., 2005. Effects of heat on meat proteins—Implications on structure and quality of meat products. Meat Science 70 (3), 493–508.

sources and are considered "complete" proteins compared with the vegetarian options, except in some cases like certain cheese and vegetables. Furthermore, when it comes to lean meats, they also contain generous quantities of niacin, zinc, and omega-3 fats, among others. Continuing in the same vein, meats are also a profitable source of vitamin B_6 and an appreciable source of vitamin B_{12} that tends to be almost completely missing in the vegetable kingdom (Williams, 2007; Farley et al., 2012).

It can also be noted that lean meat, once again irrespective of species, has similar values when it comes to vitamins, certain macronutrients as already mentioned and inorganic constituents too. In fact, the greatest variable in any animal appears to be the adipose tissue. That is the fat content that varies from species to species, according to sex, age, and to a large extent on the animal's role, i.e., whether for dairy, meat, or egg production. Even so and perhaps not unexpectedly, lean beef and lamb both contain less total fat in comparison with cheese, eggs, creams, and nuts.

Based on such various compositions in the table above, a good representative average carcass composition is often used in literature, perhaps the most notable of which comes from Tornberg's excellent assessment of meat proteins and the effects of heat (Tornberg, 2005). What Tornberg provides is non-species-, non-age-, and non-sex-specific notional animal and one that serves as a very useful guideline when considering general meat nutrition (Table 12.3).

12.2.1 ANIMAL PROTEINS

It can be seen that the average animals' total compliment of proteins is in the region of 20% (Table 12.3). This figure is made up of muscle tissue and two types of connective tissue—blood and other similar proteins and "connective tissue proper." Muscle proteins are a group referred to as myofibrillar proteins containing approximately 50%–55% of the 20% available. Blood and other similar proteins, called sarcoplasmic proteins, comprise myoglobin, hemoglobin, cytochrome[5] proteins, and a wide variety of enzymes that collectively account for a further 30%–34% of muscle meat

[5]Cytochromes are classed as those compounds that consist of a heme (an iron-containing compound) bonded to a protein.

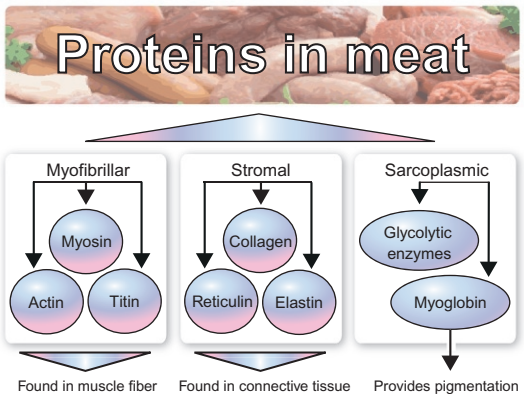


FIG. 12.5

Proteins within mammalian meat.

protein. Lastly, connective tissue proper or, more appropriately, stromal proteins make up the remaining 10%–15% of proteins in meat (Fig. 12.5) (Tornberg, 2005; Heinz and Hautzinger, 2010).

When it comes to meat, recall that there are 20 or so essential and nonessential amino acids that are required by the body for health and good maintenance. Luckily, animal meat can provide the full complement of the much needed building blocks. In this respect, meat is considered a source of "complete proteins." As a result, is not difficult to see why meat is extremely popular within the diet. Although having said that, one must remember that not all proteins are the same; indeed, some are better than others; they have more biological value due to the makeup of the specific amino acid chains (see Chapter 4) (Belitz et al., 2009; Lawrie and Ledward, 2006).

Among the many various meat proteins that exist, myoglobin is a typical globular protein (sarcoplasmic) that gives meat its distinctive color. Other equally important structural proteins are the fibrous actin, myosin, and collagen proteins that are mainly located in the muscle and connective tissues (myofibrillar and stromal proteins, respectively, Fig. 12.5). These latter proteins are all constructed from three principal amino-acid-based structures, the α-helix and the β-pleated sheet, as well as the triple helix (the last one (the triple helix) refers solely to collagen only) (Tornberg, 2005). Stabilizing these particular fibrous structures is quite often achieved through the action of hydrogen bonding. Furthermore, fibrous structures also tend to be in a constant state of being "stretched," while the globular proteins tend to be more compacted (Tornberg, 2005). With this in mind, it is also worth mentioning the different ways in which these globular- and fibrous-like protein structures behave as heat is applied. In globular proteins, the application of heat alters the bonding, weakening the bonds, and allowing the tightly packed protein to expand and partially unfold. By contrast, in fibrous proteins (Fig. 12.5), as heat is applied, so the stretched proteins' many hydrogen bonds are gradually broken, allowing the proteins to shrink or contract on cooking.

So, to sum up, skeletal meat proteins are made up of three specific groups of proteins, myofibrillar proteins, which include but are not limited to proteins like actin and myosin and which make up between 50% and 55% of the total meat protein content. Then, there are the sarcoplasmic proteins such as glycolytic enzymes, hemoglobin, and myoglobin that comprise approximately 30%–34% of muscles' protein content. Finally, stromal or connective tissue proteins like collagen and elastin account for the

final 10%–15% of proteins in meat (Fig. 12.5) (Tornberg, 2005). Furthermore, it must be noted that enzymes that are naturally present in meat continue to function even as the meat is aging. Enzymes such as the proteolytic break down proteins, while lipolytic enzymes break down the fats, and amylolytic enzymes break down what little carbohydrates there are in meats. If left to do their own thing, proteolytic enzymes continue to break down myofibrillar proteins especially in the aging process, further affecting the tenderness of meat.

Each of these proteins is further subdivided into constituent proteins of which there are many; however, the main examples are shown in Fig. 12.5.

12.2.1.1 Myofibrillar proteins in muscle meat

In muscle tissue, 20 or so different myofibrillar proteins constitute the majority of the actual muscle (50%–55%); these are the proteins that affect the muscles ability to relax and contract (contractile). Each myofibril (a component of muscle cells (Fig. 12.6)) is composed of the structural proteins myosin (55%) and actin together with lesser known proteins like tropomyosin and troponin complex

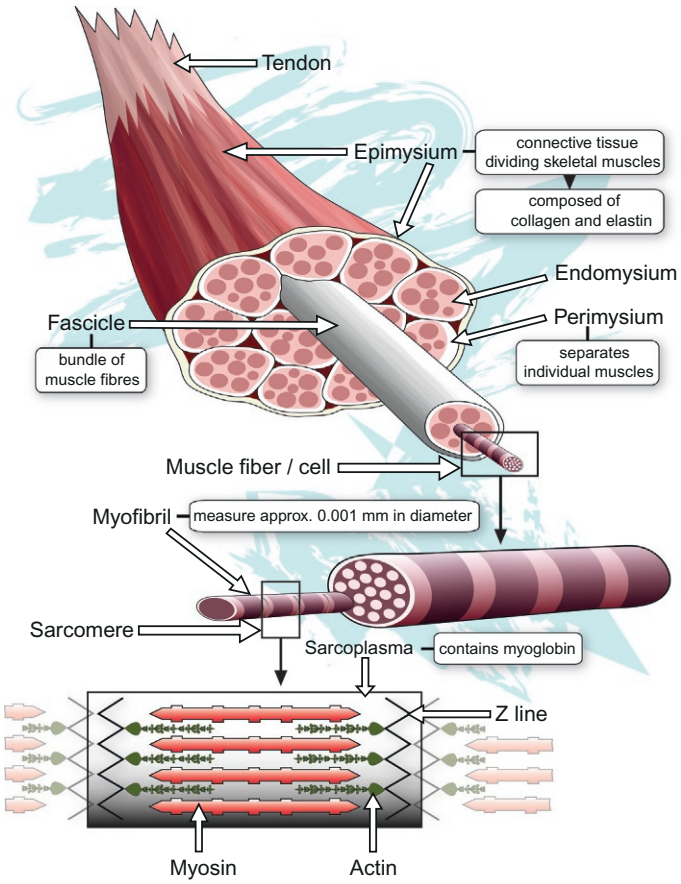


FIG. 12.6

The various striations/bands of muscle fiber protein.

(40%–45%). These help regulate muscle force, i.e., the stretching and relaxing. Found in both cardiac and skeletal muscle, one form of tropomyosin-troponin complex is a thin filament protein that controls the intracellular concentration of calcium. As the calcium content passes through the filaments, so muscles contract, whereas when calcium levels fall or is restricted, so the muscles relax. Other elastic proteins like myomesin also work together to this end (Tornberg, 2005; Spudich et al., 1972; ISU Science and Technology, 2008; The American Meat Science Association, 2015; Baldwin, 2012). Other regulatory and structural proteins that account for the remaining percentage are the α- and β-actinin microfilament proteins, while others still include the M protein (only found in fast fibers) and the C protein (the myosin-binding protein) (Tornberg, 2005). Titin, on the other hand, is a large macromolecule found especially in striated muscles (Fig. 12.6). Its main role is to stabilize the thick filament preventing any overstretching of the sarcomere and to ensure its proper recoil like releasing a stretched rubber band (Saladin, 2015) (Section 12.1.1.5). These "stretch and relax" proteins are uniformly placed within the cells and in areas where they overlap (represented by the different bands) they appear as striped—striations.

While several muscle proteins have been mentioned in regard to myofibrillar proteins, most only exist in small quantities. Myosin and actin, on the other hand, account for as much as 65% of the total muscle protein, while tropomyosin and troponins each contributes 5%, and the remaining 25% comprises structural or regulatory proteins. While myofibrillar proteins are quantitatively the most important of the muscle proteins, they are also qualitatively important too as having the highest biological value (Heinz and Hautzinger, 2010). The other myofibrillar proteins, mainly myosin and actin, are also called the salt-soluble and fat-binding proteins due to their solubility in certain salt solutions (ISU Science and Technology, 2008). The methodical arrangement of myofibrillar proteins such as actin and myosin collectively form the muscle cell's myofibril filaments. These can be seen in Fig. 12.6 as alternating light and dark bands. During contraction, actomyosin is formed when both actin and myosin filaments slide and come together; the overlapping of which causes these darker striations or bands (The American Meat Science Association, 2015).

12.2.1.2 Sarcoplasmic proteins in meat

Another important group of proteins in meat are the sarcoplasmic group. This assortment of proteins constitutes about 30%–34% of total muscle tissue like enzymes (which make up a significant proportion), mitochondrial nucleoproteins, lysosomal proteases, and of course hemoglobin and myoglobin (Tornberg, 2005; Baldwin, 2012). One such important protein is myoglobin (has a similar function to hemoglobin) in that it provides the predominant red pigmentation in fresh meat and the brown pigmentation in cooked or oxidized meat (Suman and Joseph, 2013). Furthermore, as meat is aged, it is the oxidation of myoglobin that accounts for the darkening of the meat. Lastly, although blood itself is high in tryptophan (an essential amino acid), it is nevertheless considered of lower biological value due to the deficiency of one particular essential amino acid—isoleucine.

In more detail, myoglobin is the main proteinaceous pigment found in meat; its purpose is to store the oxygen transported via hemoglobin in the blood to myoglobin in the muscle cells. Myoglobin comprises two connected structures: a molecular cage for want of a better word, attached to a nonprotein heme ring. The heme "pigment" portion of the molecule plays an important role in meat color that in turn is ultimately determined by the oxidative state of iron within the heme ring itself (Morrissey et al., 1987; Suman and Joseph, 2013; The American Meat Science Association, 2015). Interestingly, if the iron atom within the heme ring continues to hold onto a molecule of oxygen, myoglobin remains bright

red. However, as the oxygen is drawn away by enzymes, in the muscle cell, for example, so the myoglobin becomes dark purple.[6] Further still, when oxygen manages to rob the iron atom of an electron, the iron atom loses its ability to hold oxygen at all; instead, it has to settle for a water molecule; at this point, myoglobin becomes brown (Suman and Joseph, 2013).

Sarcoplasmic are soluble in water and in low concentrated salt solutions; these include proteins comprising myoglobin, hemoglobin,[7] cytochrome proteins, and a whole host of other endogenous (synthesized) enzymes. When it comes to meat muscle distinctive color, myoglobin is perhaps the most important of the pigmentation proteins, which is also associated incidentally with the perception of quality. The concentration of myoglobin in meat is related to several considerations including species, age, and muscle type. Further, those muscles that are used more frequently contain more myoglobin than those less frequently used. Moving on, the reason the surface of red meats are a richer red color is because the major pigments, myoglobin and hemoglobin, have both been oxygenated on the surface forming the bright red oxymyoglobin (The American Meat Science Association, 2015).

12.2.1.3 Stromal or connective tissue proteins in meat

Stromal proteins, also known as connective tissue proteins, predominantly comprise collagen, elastin, and reticulin. These can be found in the skin, bone, tendons, cartilage, and muscle itself. In fact, of all the animal proteins, it is the connective tissue proteins that are found in largest quantities in the whole carcass. In actual fact, connective tissue proteins can represent at least 25% and sometimes as much as 35% of total animal carcass proteins (Heinz and Hautzinger, 2010).

That said, in muscle meat, connective tissue proteins by themselves represent a mere 10%–15% of total protein content. Further, collagen, being the main structural component of connective tissues, can be as much as 55% of this figure, while at times, this figure can reach a colossal 95% (Tornberg, 2005).

While collagen is tough and fibrous, it nevertheless breaks down quite readily if cooked to the right temperature, becoming soft gelatin, both soluble and digestible. However, it is of low biological value due to it being devoid of the essential amino acid—tryptophan. Elastin, another stromal protein, contains both desmosine and isodesmosine (Becker and Yu, 2013), yet it does not break down with cooking. Instead, for elastin to be digested, it needs to be broken down by the enzyme elastase (Brown, 2005).

Individual muscle fibers (cells) are covered or wrapped in a network of a fibrous collagen-based coating called the endomysium; it does so while also supporting nerves and other capillaries. In turn, many bound and wrapped cells come together to form a bundle called the fascicle, which is in turn further bound in connective tissue called the perimysium. This collagen and elastic fiber sheath also supports capillaries like nerves and blood vessels. From here, bundles of perimysium-coated fascicles are collectively bound in yet another collagen-containing connective tissue called epimysium (Fig. 12.6). This last layer not only binds individual muscles together, but also they bind groups of muscles together while separating them from surrounding organs and other tissues. Ultimately, the connective tissues of the endomysium, perimysium, and epimysium converge and attach to either the bone as tendons or to the skin or to other muscles. In cases where the bone is connected to the bone with

[6]Similarly, this is why hemoglobin is red in animal's arteries because it's fresh from their lungs; however, after unloading oxygen into the animal's cells, deoxygenated blood appears a darker red, almost a deep purple.

[7]When it comes to hemoglobin, there is an appreciable quantity still present in meat as during exsanguination at slaughter, not all the blood is drained from capillaries, arteries, and the like.

connective tissue, these are called ligaments. Furthermore, muscles employ capillary networks like nerves and blood vessels, which enter the muscle through connective tissue partitions and which surround each muscle fiber to supply both nutrients and oxygen (Tornberg, 2005).

12.2.2 FAT

Fat can be found throughout the animal's carcass. External fat or back fat as it is referred to is found on the meats' surface, whether at the whole carcass level or the individual cuts. Intermuscular (between muscles) fat is referred to as seam fat, while intramuscular (inside the muscle) fat is the specks of fat known as marbling. Marbling contributes greatly to the flavor and "apparent" succulence of a piece of meat. Fats in the adipose, intramuscular and abdominal cells are predominantly made up of triglycerides. Collectively, they contribute greatly to both the flavor and moisture of cooked meats and help to tenderize the meat. The particular fat we are interested in are triglycerides, which comprises glycerol (a type of alcohol) and three fatty acids. This fatty acid arrangement is important as the nature and flavor of the fat is determined by the type of fatty acids involved (Bender, 1992). Fats can be divided into of two groups: saturated fatty acids and unsaturated fatty acids. While all fats actually contain both saturated and unsaturated fatty acids, fats are usually identified according to the predominant fatty acid present. Saturated fats are distinguished from their unsaturated cousins in that they have no carbon double bonds and are instead saturated with hydrogen atoms. Unsaturated fats are mainly found in plants although they are present in meat in smaller quantities. Unsaturated fats can be further subdivided into mono- and polyunsaturated fats. Monounsaturated fats (MUFA) are high in vitamin E, which helps to develop and maintain cells in the animal's body. Polyunsaturated fats (PUFA) have been suggested to be particularly good for brain development. In the diet, fats act as carriers for the fat-soluble vitamins (A, D, E, and K) and supply essential fatty acids (Heinz and Hautzinger, 2010; Owusu-Apenten, 2004) (see Chapter 16 and Section 13.7)

It is worth noting that the actual fatty acid composition of some meats is heavily dependent on several factors. In animals with simple stomachs (nonruminants such as pigs), for instance, diet can drastically alter the fatty acid composition of its meat. If these animals consume diets high in unsaturated fats, so the fat they deposit in their muscles will have elevated levels of unsaturated fatty acids. By contrast, in ruminant animals (e.g., cattle and sheep), fatty acid composition found in the lean muscle is largely unaffected by diet as microorganisms in the stomach alter the chemical structure of digested fats before they are utilized or deposited as adipose tissue (Owusu-Apenten, 2004).

One disadvantage of meats with the healthier unsaturated fatty acids is that they suffer from oxidation when exposed to the air promoting rancidity in the meat. On the flip side, meats with higher concentrations of saturated fats can generally be stored for longer periods without developing unpleasant flavors or odors (Bender, 1992). Lastly, fats in meat carcasses contribute to the "apparent" juiciness of meat by providing the feel of moisture in the mouth.

12.2.3 CARBOHYDRATES, VITAMINS, AND MINERALS

Meat contains very little or virtually no carbohydrates. This is because the glycogen, a complex sugar and principal carbohydrate found in living muscle, is almost completely broken down in the conversion of muscle to meat. The liver is one notable exception to this, containing up to 8% of the whole

carcasses' carbohydrates—equal to about half compliment of total carbs found in the carcass (The American Meat Science Association, 2015). Glucose, another carbohydrate, is found in blood and other tissues including organs and glands.

Carbohydrates aside, most meats are an excellent source of B complex (thiamine, riboflavin, and niacin) vitamins while on the other hand are somewhat poor in the fat-soluble vitamins A, D, E, and K. This is despite the fact that vitamins A, D, E, and K are found in the fat seams of meats; however, they exist in such low concentrations, and much is lost as the fat melts out in the cooking process. Saying this though, much of the animal offal, specifically the liver and kidney, generally contains appreciable quantities of fat (between 5% and 7% wet weights) in which fat-soluble vitamins, particularly A and D, reside (Bender, 1992). When it comes to the water-soluble vitamins too, it must be noted that there can be substantial loss of these vitamins due to leakage of meat juices. This is also the case when defrosting meats, as much of the defrosting, or melt liquid (depending on the meat) can be vitamin B rich. Having said that, well-fed or free-range animal meat often exhibits high intakes of carotene in the form of provitamin A, much of which is transformed into retinol (vitamin A proper) (Bender, 1992; Lombardi-Boccia et al., 2005).

In general, meat contains approximately 1% minerals (The American Meat Science Association, 2015), when it comes to minerals and trace elements in particular iron, zinc, copper, calcium, phosphorus, sodium, potassium, chlorine and magnesium. Iron in meat, in particular, has a higher bioavailability due to greater resorption and metabolism than iron in plant products. Also in terms of iron, zinc, and copper, while they differ significantly from species to species, the liver is by far the best source of such minerals in comparison with muscle tissue. That said, red meats can be excellent sources too (The American Meat Science Association, 2015). Unfortunately, high levels of minerals and trace elements in domesticated animal feed do not necessarily translate into richer sources in postmortem meat. Although by contrast, when feed or pasture is deficient in certain minerals, the resultant amounts found in meat are seen to be reduced.

12.2.4 PRE-SLAUGHTER HANDLING

It has been known for centuries that stress just before an animal's death, whether through hunger, physical work, duress during transport, fighting, storage with inadequate ventilation, handling, mixing of different groups of unfamiliar animals or the mixing of species, overcrowding, being watered, or simply through fear, has an adverse effect on meat quality. Indeed, preslaughter handling is a major concern in the livestock industry, especially the pork sector; all need to be carefully considered and indeed are considered before an animal's slaughter (Lawrie and Ledward, 2006). In this regard, many inspections both pre- and postmortem are carried out as standard regulatory practices throughout much of the world to ensure both the animals welfare and quality standards of the meat are met. In fact, it so happens by fortunate coincidence that the most humane methods of animal slaughter also result in good-quality meat (McGee, 2004). However, one trade-off in the animal's welfare and the quality of meat relates to the fact they are not fed 12–24 h prior to slaughtering—this is to ensure full bleeding (exsanguination) and ease of evisceration.[8]

[8]Evisceration means the removal of internal organs.

Moreover, in mature animals, collagen becomes more insoluble with age and subsequently less digestible. Also, if animals are poorly fed, taking a longer time to reach a marketable size, so their meat is tougher and of lower eating quality (Bender, 1992). This is also true of animals that are used for meat after a lifetime of hard work. In such cases, these meats are often not used for direct consumption but are rather used in the processing industry (Bender, 1992).

12.2.4.1 Slaughter

As far as meat, current best practice is for the animals to be generally slaughtered as untraumatically as is humanely possible. Each animal is usually stunned, usually with a bolt or a blow or an electric discharge to the head. It is then hung up by its legs whereupon one or two of the major blood vessels in the neck are cut, and the animal bleeds to death while unconscious in a process called exsanguination. About half the blood is removed to decrease the risk of spoilage. After this, the animal's head is usually removed, and the hides are stripped. The carcasses are then cut open and the inner organs removed.

Pig carcasses tend to remain intact until their skin has been scalded, scraped, and singed to remove all the bristles; only then are the head and innards then removed, while the skin remains in place. Chickens, turkeys, and other fowl too must be plucked. The slaughtered birds are usually submerged in a hot water bath to loosen the feathers, which are then plucked by machine and cooled in a cold air blast or cold water bath. Of note here is the fact that prolonged water chilling at this point can add a significant amount of water to the carcass. While the Americans practice this, the Europeans tend not to.

12.3 POST-MORTEM: FROM FLESH TO MEAT

Understanding what happens to meat post-mortem can shed light on why meat behaves the way it does (Belk et al., 2002). It also highlights the importance of pre- and postmortem considerations of animal welfare, storage, processing, and cooking.

As the life of an animal comes to an end, so significant changes help facilitate the conversion of fresh muscle to quality meat. The first and most important change is the onset of rigor mortis. However, it is worth remembering that the majority of what we are eating in meat are proteins and fats and the breakdown (softening) of the proteins and fats is what determines whether a meat is tender, juicy, and full of flavor or not. In fact, everything we do with meat whether aging, marinating or cooking, aims to tackle these three key variables. So in light of this, it is worth taking a look at just how proteins are indeed broken down or synthesized or metabolized to use the proper term (Belitz et al., 2009).

This process of breaking down proteins is in fact achieved through the action of two important processes—enzymatic action on proteins (protease) and the denaturing of proteins.

12.3.1 MEAT PROTEINS

(For a general understanding of protein denaturation, see Section 4.2. For a more in-depth view of meat protein denaturation, see Section 12.9)

The meaty flavor of animal carcasses is a delicate mixture of taste-bud-stimulating compounds and aromatic combinations. Both arise from the treatment of meat by enzymatic and cooking processes (Lawrie and Ledward, 2006). As proteins are broken down, so some of the pieces, namely,

the single amino acids and sugars, fatty acids, nucleotides,[9] and salts, are what stimulates the palate with sweet, sour, salty, and savory sensations. Furthermore, when heated (as in the cooking process), proteins react with each other to form innumerable different aromatic compounds. In general though, it can be said of cooked meats that a well-exercised muscle with a high proportion of red fibers (chicken leg or beef), for instance, makes for more flavorful meat (albeit potentially a little tougher) than less exercised, predominantly white-fibered muscles like chicken breast, and veal. Darker or red fiber meats tend to contain more substances with the potential for generating flavor, in particular, fat and fatlike components of the membranes that house the cytochromes.[10] Red fibers also contain more substances that help break down these flavor precursors into flavorful fragments. In fact, the connection between muscle exercise and flavor has been known for a long time (Lawrie and Ledward, 2006).

Two things help break down tough proteins in meat—denaturing by cooking and enzymes. Denaturing of meat proteins is covered in Section 12.9.1 while the following deals with enzymes.

Proteinaceous enzymes called proteases are a group of catalysts that speed up the degradation of other proteins without being consumed in the process. They occur naturally in foods but are altered or deactivated (broken down themselves) above certain temperatures in the cooking process. For raw meat or meat cooked at low temperatures, enzymatic degradation helps to tenderize tougher proteins. Besides this, raw meat enzymes, for instance, (part of the group of proteases like cathepsins[11]) act on muscle proteins breaking them down further, releasing peptides and amino acids in the process—that is generally smaller more palatable components (Koohmaraie, 1996). The cathepsins also weaken the collagen in older connective tissues by breaking some of the strong cross-links in mature collagen fibers (see also Section 12.4.1 and Chapter 4) (Vaclavik and Christian, 2014). Once the enzyme is degraded either by the digestive or by the cooking processes, so further, degradation of cooked and eaten foods is taken care of by enzymes within the body. This (and some denaturation) is also part of the process of aging meats.

Proteins aside and back to the process of flesh to meat, we can say that some of these processes occur naturally, while others are encouraged, catalyzed, and actively sought. Not surprisingly, the first of these considerations is the onset of rigor mortis.

12.3.2 RIGOR-MORTIS—PROTEIN CHANGES

After the animal's death and/or a brief period of time only, its muscles are relaxed. If immediately cut and cooked, this meat will make an especially tender dish. However, this is rarely practical outside the domestic slaughtering process. Instead, rigor mortis occurs soon after death as cell energy reserves are depleted. Rigor makes extremely tough dishes of cooked meat. As a result, the carcass must pass through the rigor mortis state in order to provide tasty, palatable meat (Lian et al., 2013). The exact time rigor sets in varies greatly depending on the species, the cooling rate of the carcass, and the amount of stress the animal experiences before slaughter, and of course, depending on who one reads. Usually though, rigor in the skeletal muscles varies between species and does not appear until within 1–2 h in

[9]Nucleotides form the basic structural unit of nucleic acids such as DNA.
[10]Cytochromes are any of a number of compounds consisting of heme (an iron-containing compound) bonded to a protein.
[11]Cathepsins are enzymes that digest proteins.

poultry, 4–6 h in pork, and within 7–15 h after exsanguination in beef and lamb, with maximum rigidity being attained at about 20–24 h at between 7–10°C and 45–50°F (note that these figures vary once again depending on who one reads). After this time, rigor gradually declines.

As rigor sets in, so myofibrillar proteins, actin, and myosin within the cells lose their flexibility resulting in muscle contraction and stiffening (Purslow, 2005; Bender, 1992). Over time, muscle rigor begins to decrease due to the enzymatic breakdown of proteins. In fact, there is much research and supporting evidence of three endogenous proteolytic systems in play when it comes to postmortem proteolysis[12] and meat tenderization—the calpains,[13] cathepsins, and proteasomes systems (Lian et al., 2013). As a result of these three enzymatic processes, so postmortem myofibrillar filaments, while still firmly locked together at this stage, begin to relax allowing the overall muscle structure to weaken and the meat texture to soften or tenderize. At the same time, other proteins—the connective tissue proteins—are also partly enzymatically denatured, although not to any great significance at this stage. This process is known as "resolution of rigor" or more commonly in the culinary world—as the "aging of meat." The process of aging can continue for days and sometimes even weeks after slaughter, producing meats that are more tender and palatable.

12.3.3 WATER HOLDING CAPACITY

At about 70%–80% moisture, water is the greatest proportion of muscle weight and can be found between the thick (myosin) and thin (actin) filaments of the myofibrils (Bender, 1992; Baldwin, 2012). It is also easily lost. Fifty-five percent of the muscle weight is retained by the myofibrillar proteins (ISU Science and Technology, 2008). This moisture retention is termed "water-holding capacity" or WHC for short. WHC is so important to yields, texture, and flavor, and the prevention of its loss is of great concern to the industrial sector (who sells meat by the weight) and in the kitchen—where cooked foods retain or lose moisture all too easily (Honikel, 1998). Water then can be categorized as being "bound," "free," or simply "immobilized." Bound water, as the name suggests, is a molecule of water that is chemically bonded directly to meat proteins. This represents between 4% and 5% of total moisture content of wet meat. Free water, on the other hand, is held in cellular membranes through capillary action. The breakdown of the proteins at the cellular level, i.e., through chopping or grinding, accounts for the loss of membranous water. With regard to immobilized water, water is indirectly retained through electric charges of meats' reactive proteins. This can be as much as approximately 35%–75%. Meat water retention is the goal of meat processors and cooks alike. In all of this, pH plays an important role. Postmortem protein cells, for instance, are still alive and are capable of holding water molecules (Honikel, 1998). As the pH decreases (with the increase in lactic acid), so the same proteins are able to hold less water. Therefore, getting the right balance between aging the meat and reduced water-holding capacity to provide a juicy, tender cooked steak, for instance, can be subjective. This also has implications for meat yield that is directly affected by the water content, particularly in the meat processing industry (Lawrie and Ledward, 2006).

[12]Proteolysis is the breakdown of proteins or peptides into amino acids by the action of enzymes.
[13]Calpains comprise three primary components, the proteins μ-calpain, m-calpain (known as calpains I and II), and calpastatin.

12.3.4 MEAT COLOR—MYOGLOBIN AND OXIDATION

Initial flesh color varies with the age of an animal—generally, the older and slower its basal metabolic rate, the darker the meat. Having said that, the color change of meat in freshly bled animals is largely due to a couple of factors, namely, the myoglobin content of muscle fibers and the chemical state of the iron atom within that myoglobin molecule, i.e., the slow oxidization process. Immediately after cutting, because water is bound to the iron atom of the myoglobin molecule, the meat is reddish purple in color (Honikel, 1998). After just half an hour exposure to air, the beef slowly becomes a bright cherry-red color in a process called blooming—this is the result of oxygen binding to the iron atom. After several days of exposure, the iron atom is fully oxidized and loses its ability to bind oxygen. In this oxidized state, the meat color turns brown. While the color is in no way harmful, it does suggest that the meat is no longer fresh. For aged animals, this is not a problem, but for younger unaged carcasses, this might be a subjective indication of poor quality for some people.

12.3.5 pH CHANGES

Shortly after exsanguination (bleeding out), the muscle still lives although it no longer has access to fresh oxygen. However, once existing cells' stores become depleted the cells do not immediately shut down. Instead, cellular energy production continues for a short while in a process of anaerobic glycolysis. As a result of this process, glycogen[14] stores are completely converted to lactic acid—a process that usually takes place within the first 12–24 h after slaughter. At the same time, anaerobic glycolysis effectively reduces perimortem levels of pH from approximately 7–7.2 to about 5.5 making the meat slightly more acidic (Lawrie and Ledward, 2006). This drop is also important for the storage life of meat as a lower pH inhibits the growth of harmful bacteria. On top of this, the combination of low pH, coupled with lactic acid, brings about the conversion of some of the collagen protein in extracellular connective tissue into gelatin.

The degree to which the pH of meat falls after slaughter and the time the process takes has a significant effect on taste or flavor and hence quality of the resulting meat. This is a key consideration of preslaughter treatment (transport, handling, and stress)—as poorly treated or susceptible animals can result in two equally undesirable outcomes: PSE meat—pale, soft, exudative meat; and DFD meat—dark, firm, dry meat.

12.3.5.1 PSE meat—Pale, soft, exudative meat

Pale, soft, and exudative (PSE) meat results from a rapid postmortem pH decline, while muscle temperature is still too high. This combination—low pH and high temperature—reduces muscle proteins ability to hold water resulting in paler meat with a soft almost mushy texture, which when cooked is a drier, less juicy product. PSE meat is especially problematic in the pork industry. It is known to be stress-related and inheritable—a condition known as porcine stress syndrome (PSS).

[14]Energy in mammals comes from the glucose that has been either ingested (eaten) directly or synthesized from the food eaten. If it is not needed for energy use straight away, it is converted into glycogen and stored as a form of energy primarily in the cells of the liver and the muscles. It functions as the secondary long-term energy storage deposit after adipose tissue (tissue containing fat cells).

12.3.5.2 DFD meat—Dark, firm, dry meat

An opposite phenomenon may occur in animals that have been stressed prior to slaughter. This may arise from a number of situations; perhaps the animals have not been fed for a significant period of time before slaughter, a stressful journey resulting in tired and fatigued animals, or perhaps simply poor treatment. In such cases, most of the muscle glycogen has been used up at the point of slaughter leaving little or no reserves post-mortem. This results in less glycogen for the conversion to lactic acid and a reduced ability to lower pH levels to an acceptable level (rarely going below pH 6). This results in a dark, firm, and dry (DFD) meat with a "sticky" texture. The resultant higher pH actually causes the muscle proteins to retain most of their bound water—they remain swollen retaining more moisture during curing and cooking. However, with a higher pH, this has implications for increased bacterial growth and a reduced shelf life. Incidentally, DFD meat should not be confused with similarly looking darker meat from mature animals.

Interestingly, while PSE and DFD meats are not ideal, they are certainly not unfit for human consumption; instead, in its nonprocessed form, such meats are simply not particularly well suited to the palate. PSE, as mentioned, tends to lose excessive moisture and remain dry due to low water-binding capacity, while DFD, due to the lack of acidity, means the meat remains tough and tasteless—although, despite this, it does produce a more moist, juicier piece of meat due to its water-binding abilities. Lastly, to a certain extent, both PSE and DFD can be prevented or retarded through proper and humane treatment of animals that aim to minimize stress prior to slaughter (Heinz and Hautzinger, 2010).

12.3.6 COLD SHORTENING

Another undesirable outcome of poor postmortem practice is called cold shortening. Cold shortening can cause meat to be as much as five times tougher than usual. This results from the rapid chilling of carcasses immediately after slaughter, before all the glycogen in the muscle has had the chance to be converted to lactic acid. It can happen either as mentioned through poor management of the carcass or in very lean meats that do not have much insulating fat to moderate the process.

With some glycogen still present, the rapid chilling induces an irreversible contraction of the muscle—that is to say, the actin and myosin proteins of myofibrillar filaments irreversibly shorten or contract. One way around this is the application of electric stimulation (high-voltage electric current to the carcasses immediately post-mortem); this reduces or eliminates cold shortening by forcing muscle contractions and using up muscle glycogen. However, using up too much glycogen in this way leaves little to be converted to lactic acid and by extension results in a higher pH and potential dark, firm, and dry meat (DFD)—hence, it's a trade-off!

Another condition similar to cold shortening is "thaw rigor." It produces similar results too and results from freezing meat before it enters rigor mortis. Thus, when the meat is thawed, the leftover or remaining glycogen in the cells allows for excessive muscle contraction and the meat becomes extremely tough.

12.3.7 HEAT RING

Another issue arising out of chilling meats post-mortem is something called "heat ring." Heat ring is the appearance of dark, coarse textured bands of meat around the outside of some muscles. This results from the uneven way carcasses cool—those muscles in a carcass, for instance, that have only a thin

deposit of fat to insulate them might cool faster than say a shoulder muscle that is wrapped in a thick insulative layer of fat giving rise to a slower reduction in pH. It is not just the different muscles within a carcass that can suffer from heat ring either. Larger muscles with little insulative fat might also suffer as the outside cools more rapidly than the inside resulting in a slower pH decline in the outer layer and once again creating that tell-tale heat ring. As with cold shortening, heat ring too can be moderated or alleviated by electric stimulation after slaughter causing a more even pH reduction throughout the muscle.

12.4 QUALITY, EATABILITY, AND FLAVOR

We have learned that meat quality may be affected by both the preslaughter handling of the live animals as well as the postslaughter processing of the carcass. We have already looked at stress, both psychological and physical. In addition, postmortem considerations are a delicate combination of many factors that greatly affect the quality, eatability, and ultimately the flavor of meat. Some of these are tried and tested and are used as benchmarks throughout the meat and catering industry; others however can be somewhat subjective. The following highlights some of these considerations (Vaclavik and Christian, 2014; Belk et al., 2002; Lawrie and Ledward, 2006).

12.4.1 RIPENING/AGING

When dealing with nonprocessed or comminuted[15] meat, tenderness is of paramount importance. As such, perhaps one of the first and most significant considerations of quality is the practice of ripening or aging of the meat. Indeed, in the 19th century, beef and mutton joints would be kept at room temperature for days or even weeks or at least until the outside was quite literally rotten. The French named this process "mortification." Although nowadays, modern preferences, while still somewhat diversified across the globe, tend to veer toward a less aged, less ripened product. This is especially so when it comes to game animals and birds. Consequently, many countries' aging preferences differ greatly from a few days to several weeks, depending on species and local tastes (McGee, 2004; Calkins and Sullivan, 2007).

During the aging process, meat is placed in temperature- and humidity-controlled cool rooms to slow the onset of bacterial growth. Throughout the aging period, certain physiological and biochemical changes take place that, if properly controlled, help the meat to become more tender and flavorful (Calkins and Sullivan, 2007). As we have seen, after slaughter, muscles become stiff in a process of rigor mortis whereby actin and myosin proteins, among others, become rigid. In time and under favorable environments such as the correct pH, the right temperature, time, enzymatic action and other conditions, so meat begins to relax. As the carcass relaxes, so further enzymatic action of the calpain system of protease contributes to postmortem proteolysis that weakens the supporting proteins holding the contracting myofibrillar filaments in place and by extension further tenderizing of the meat (Lian et al., 2013). At this stage, cathepsins also weaken connective tissue by degrading the cross-links between mature collagen fibers. This results in more collagen able to dissolve into gelatin during the cooking process, aiding the overall succulence and tenderness. Furthermore, by breaking down the

[15]Comminuted meat is pulverized or finely ground meat.

collagen, meat is less likely to shrink as much during cooking, thus retaining more moisture leading to greater juiciness (Lian et al., 2013). It is worth noting too that postmortem proteolysis is self-limiting because the calpains and other enzymes undergo slow autolysis.[16] As a result of the autolysis self-degradation, calpains do not overtenderize the meat (Calkins and Sullivan, 2007).

Some protein cells like collagen, however (those which have not already been converted into gelatin through enzymatic action or through lactic acid conversion—Section 12.3.5), especially in older animals, tend to resist this process. This is why one tends to get tougher meat from older carcasses.

Enzyme activity is contingent to a great degree on temperature. The calpains, for instance, begin to denature and lose their ability to break down proteins at around 40°C/104°F, while the cathepsins around 50°C/122°F. Having said that, the higher the temperature of the meat is (below these thresholds), the faster the enzymes catalyze the degradation of proteins. This includes cooking in the pan/oven. For instance, if meat is quickly seared to brown and eliminate surface microbes then is cooked sous vide or slow cooked (braised or roasted in a slow oven), then the aging enzymes calpains and cathepsins within the meat can be very active for several hours before they are themselves denatured (Belitz et al., 2009; Tornberg, 2005). That said, in sous vide cooking, while it is noted that above 50°C/122°F the calpains and the cathepsins themselves become denatured, above the temperatures (between 55–60°C and 130–140°F), so collagenases are still active and can greatly increase tenderness after about 6 h of cooking (Tornberg, 2005).

In sum, aging can be thought of as tenderization of meats brought about by the destruction of the cellular skeleton (protein-based cytoskeleton) and the resolution of rigor together with conversion of some of the collagen to gelatin. As far as aging of different meats, the following gives a general guideline for maximum quality—of course meats do not need to be aged, but there will be a marked difference between a well-hung prime rib and one still mooing on the plate (Heinz and Hautzinger, 2010):

- Chicks: 1–3 days
- Pigs: 5 days
- Bovine: 4–28 days

That said, within the processed meat industry, during the fabrication of many meat products, the toughness or tenderness of the meat used is of only minor consideration. This is because, a great deal of meat products are created using comminuted meat, a process where even tough meat is made palatable. Other processing too such as with hams or other cured and fermented or cured and cooked products gives little consideration to tenderness as the process itself renders the meat tender and palatable (Lawrie and Ledward, 2006).

All in all, this aging process can last from a few days to a few weeks—although with the caveat that the longer the process, the more moisture is lost.

12.4.2 MUSCLE ENZYMES AT WORK

As touched upon above, the aging of meat (under the right conditions) is primarily the work of enzymes. Post slaughter, the control systems that keep cells intact and working together cease and begin to break down (Lawrie and Ledward, 2006). This allows enzymes to indiscriminately degrade other cell

[16]Autolysis is the destruction of cells or tissues by their own enzymes.

molecules taking large flavorless molecules and breaking them down into smaller, flavorful fragments. Proteins are broken down into savory amino acids, glycogen becomes sweet glucose, ATP turns into the meaty substance IMP (inosine monophosphate), and fats and fatlike membrane molecules turn into aromatic fatty acids. All in all, these broken down/altered or changed products contribute significantly to the intensely meaty flavor characteristic of aged meat (Atkins, 2003; McGee, 2004; Calkins and Sullivan, 2007).

12.4.3 WET AND DRY AGING

Dry-aged meat is undertaken at around 1–3.3°C/34–38°F in conditions of about 70% humidity and for any length of time between 1 and 45 days (depending on the specific meat). Higher temperatures can be used (up to 45°C/113°F) but only for a maximum of 4 h or so, as we are in the microbial danger zone at this temperature. However, at these temperatures, even these few short hours can produce a noticeable improvement in the tenderization of meat. Recall too that enzymes are a substantial component of the sarcoplasmic proteins (Section 12.2.1.2). The calpain group of enzymes along with lysosomal cathepsins are especially important when it comes to the aging (ripening or conditioning) of meat. In aging, these specialist proteinaceous enzymes work well on the sarcomere myofibril proteins—in particular, the Z line and on myosin, actin, troponin, and collagen proteins (Baldwin, 2012; Tornberg, 2005).

Despite the contribution that aging can clearly provide to the quality of meat, the modern meat industry generally tries to minimize it as much as possible. This is simple economics; why should a meat company tie up their assets in storage losing up to about 20% of the meat's original weight (especially when it is being sold by weight) to evaporation and trimming of the rancid and sometimes moldy surfaces? Instead, most meat is now butchered into retail cuts at the processing plant shortly after slaughter. These are then wrapped and shipped to market almost immediately—although there are exceptions.

For a while, there was a trend for certain meats to be "wet"-aged, i.e., meat is kept in its plastic wrap for some days or even weeks, where it is shielded from oxygen and retains its moisture and where the enzymes continue about their work. However, one downside is that while wet-aged meat can generally develop certain similar tenderness and flavors of their dry-aged counterparts, in general, they tend not to do so to the same degree. Thus, they do not have the same concentration of flavor. As a result, dry aging, while out of fashion for a while, has made something of a comeback—artisans and even mainstream producers are offering customers more choice when it comes to aged meats. Cooks too can further age meat in the kitchen simply by purchasing the meat several days before it is required and aging it in the refrigerator—as long as conditions fall within the temperature and humidity requirements stated above. The meat can be kept either tightly wrapped or uncovered allowing for evaporation and concentration of flavors. Although unwrapping works best with large cuts, as opposed to steaks and chops, for the simple reason that too much trimming of the smaller cuts will be uneconomical (McGee, 2004; Baldwin, 2012).

12.4.4 WATER HOLDING CAPACITY

Another consideration in the quality of meat is its water-holding capacity (WHC). Water-holding capacity varies within different muscles of the body and among species. It can also be affected by the various preserving techniques such as curing, salting and drying, as well as with the variety of processing techniques like mincing/grinding and chopping. Lastly, the cooking process itself affects meat

moisture content; pan-fried steak compared with pot-roasted pheasant, for instance, if not tackled properly can result in dry unappetizing meats This is for several reasons. As high-temperature cooking commences, so proteins begin to contract and denature—the denatured proteins thus form tighter bonds effectively pulling themselves together squeezing the water out of both the intra- and intercellular matrices. Furthermore, cooking also causes water within the meat fibers to expand and burst out of the cells. Cooking aside, however, raw beef generally has the greatest water retention followed by pork then chicken, which helps explain why chicken can be dry if just even slightly overcooked (for more on meat juiciness and tenderness, see Section 12.4.7) (Belitz et al., 2009; Heinz and Hautzinger, 2010).

12.4.5 MEAT GRAIN

Meat grain is another determination of the tenderness and by extension the quality of good meats. One should recall that meat fibers are composed predominantly of myofibrillar proteins, the size and diameter of which depend on age, type, and breed of animals. Another important consideration is the workload of the muscle itself; as a general rule, it can be said that the harder a muscle works, the greater the number of fibers—the tougher the meat. So, to help reduce toughness, we generally cut across the cells length (called the "grain") of the meat. That is to say, meat myofibrillar proteins are long chains of protein groups that all align together—just like lengths of string all lined in a row (Lawrie and Ledward, 2006). If we then cut down the muscle cells length (across the grain/string), we end up with shorter lengths of myofibrillar cells. Thus, cutting across the grain physically reduces the size of the fibers making them more edible.

12.4.6 FAT

In animal meat, there are subcutaneous (under the skin), visceral/abdominal (surrounding organs), intermuscular (between muscles), and intramuscular (inside muscles that when present in high proportions, gives rise to marbling) fat deposits. During the cooking process, fat acts to flavor and moisten the meat, and meat's eating quality is particularly (in terms of flavor) enhanced (Fig. 12.7). Small amounts

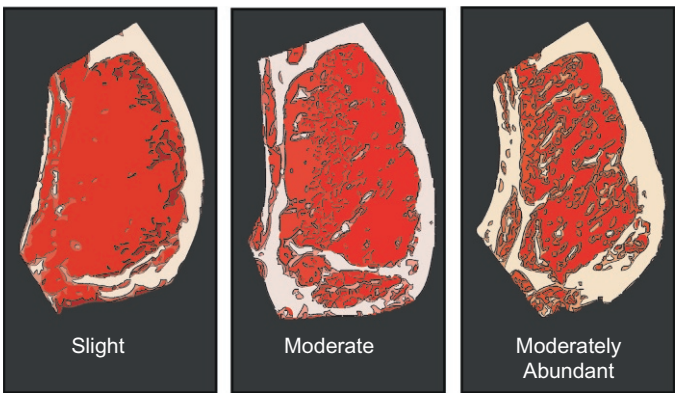


FIG. 12.7

Marbling within sirloin steaks.

of fat also improve eating quality by giving the impression of softness or moisture. Indeed, in processed meat products too, fats are added to make products feel softer on the palate.

Not all fats are equal though; this is mainly because of sensory reasons—as taste and texture of fat varies between animal species. Fat from old sheep (mutton), for example, is, to some, particularly strong, while by comparison, pork fat is almost odorless and relatively less flavorsome. In fact, concerning the latter, it is these qualities of pork fat that make it especially useful in the meat processing industry—that and its ease of availability. Examples of commonly used pork fat include jowl fat, back fat, leaf fat, belly, and soft fat. Beef fat although considered less desirable due to its firmer texture, yellow coloring, and more pronounced flavor is however used in sociocultural or religious situations that do not permit pork. Buffalo fat too, being whiter than beef, is also an acceptable alternative in meat processing. Mutton on the other hand is rarely used, while chicken fat with its neutral flavor is often used to flavor chicken-based products.

12.4.7 JUICINESS

When the scientists studied the sensation of juiciness, they came to the conclusion that it consists of two phases. In the first stage, the moisture one gets from biting down on a piece of meat comes from the meat itself—that is to say from the water-holding capacity of the meat. Secondary, juices however flow from the fat giving the consumer another dimension or impression of moisture. Then as one continues to chew, so our own saliva glands are stimulated into coating the meat being chewed. This is the tertiary sensation of juiciness, which altogether provides a well-rounded experience of meats' juiciness.

12.4.8 TASTE

Typically, the smell and taste of the meat we are used to a great extent the product of a combination of the formation of lactic acid and the enzymatic breakdown of proteins (amino acids and di- and tripeptides). Feed can also influence the flavor of the meat; examples include corn-fed chicken, heather-fed lamb, corn-fed duck, grain-fed Kobe or Wagyu beef; even fishmeal has been used to enhance livestock feed—and by extension its flavor. Lastly, in some cases, even the sex of the animal can affect the smell and flavor of its meat; most extreme example is the pronounced urine-like smell of old boar's meat (Heinz and Hautzinger, 2010).

12.4.9 TENDERNESS

When it comes to tenderness, we are talking of not only the meat fibers themselves but also the connective tissues. If one recalls, each collection of fibers is wrapped in a collage-based protective sheath that in turn are further bundled and joined and so on and so forth until the muscle is fully complete. In the end, that equates to a lot of connective tissue. As a result, the type and extent to which the protein in meat and connective tissues have broken down—either enzymatically or through marination or cooking—have huge bearing on the tenderness of meats.

In connective tissue toughness, both the collagens physical quantity and its solubility are important factors that must be considered in any cooking methods. We have also noted that any muscles that are particularly well used (and those in older animals) tend to be tougher.

All in all, the tenderness of meat then is influenced by all of the considerations of the previous sections that can be summarized to include the following:

- The age of the animal
- The length of aging (if appropriate)
- The quality of livestock management—pre- and postslaughtering
- The pH level of the meat
- The particular muscle used
- The water retention properties of the meat
- The grain of the meat
- The quality and amount of connective tissue
- To a lesser extent, the sex of the animal

However, all of the above considerations are rendered of little importance if the skill and knowledge of the cook or meat processor is lacking. The quality of any processing needs to take into consideration choosing the appropriate cuts of meat for the appropriate processing or cooking methods employed (Lawrie and Ledward, 2006; Aberle, 2012; Honikel, 1998).

The cooking method too and the competence of the cook will also determine whether a good cut of meat is presented to a customer tough and unpalatable.

So, coming back to our initial picture of meat quality (Fig. 12.8), together with the discussion above, it can be seen that there are indeed many factors that impact the final product. Indeed, by studying the picture once again, it is hoped that the many considerations become somewhat clearer. In sum, meat quality then is more than just subjective consideration—it is a science unto itself.

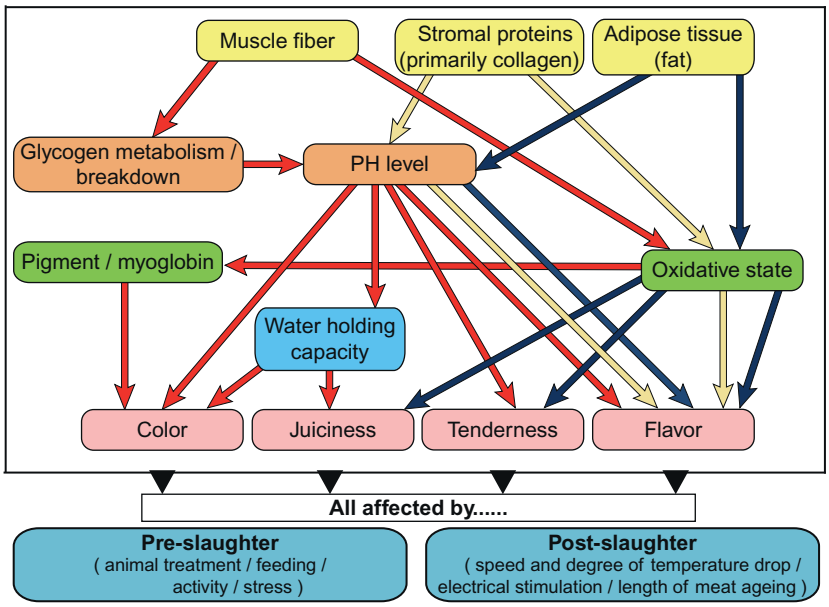


FIG. 12.8

Factors affecting meat quality.

So, having looked at the overall quality of meat and the various factors that affect its eatability, we take a foray into several other meat-related aspects from humane practices to the cooking of meats.

12.5 HUMANE AND INHUMANE MEAT PRODUCTION

In recent decades, there has been something of a backlash against many inhumane mass production practices that certain livestock have to endure. As a result, in a series of legislative acts and voluntary guidelines going back 30 years or so, the European Union and others around the world have mandated that producers pay more attention to accommodation and other welfare needs of their animals. Such things as living space, access to outdoors and to natural light, and the limited sizes of herds are now routinely considered. However, when it comes to mass production, time is critical; too long to grow, to feed, and to aging, all have a bearing on the time and cost of animal meat production. As a result, some bad practices persist (Lawrie and Ledward, 2006).

Of course, we cannot blanket the whole meat industry as being irresponsible; as in many instances, they are simply responding to consumer demand. Indeed, in some (if not many) cases, the same consumers who demand better welfare for the animals are sometimes the same consumers that demand cheaper, more affordable meats. For some industrial producers though, this paradox means that many simply cannot afford to follow recommended guidelines and produce cheaper meats at the same time.

That said, there are certain concerns regarding the industrialization of the meat production industry.

12.5.1 CONTROVERSIES IN MODERN MEAT PRODUCTION PRACTICES

There is no doubting that globally, meat production is big business. Because of meats' popularity and economic importance, both industry and government have funded research to find innovative ways in which to control meat production and its costs. As a result, there has been a steadfast increase in global supply of relatively cheap meat. Despite the good news, however, the same industry has been criticized for excessive use of unnatural practices like growth hormones and antibiotics to mention but two. Moreover, many innovations involve the use of chemicals to manipulate or promote animal metabolism (Aberle, 2012). Other innovations involve animal feed, in which it is not uncommon to find reprocessed waste materials from various other agricultural industries being used. However, the powers that be are learning, as practices like these have no doubt contributed to the onset of mad cow disease and the persistence of salmonella in chickens. Another side of the industrialization of modern meat rearing sees the growth of large-scale farming whereby perhaps hundreds or even thousands of animals are confined in a single facility. This practice contributes to localized pollution of the water table, the quality of soil and air pollution, etc. (Gibson, 2012).

Other practices of concern include the restriction of movement of animals in an effort to minimize unnecessary growth of tough meat and keep expenditure of feed under control. This kind of movement restriction is promoted as it favors the production of white muscle fibers. As such, meats raised this way are relatively pale in color and tender in eatability in comparison with their humanely farmed or wild brethren (Belk et al., 2002). Indeed, if slaughtered at a young age, animals develop fewer, strong collagen cross-links, thus aiding in the apparent quality of meat. Furthermore, younger animals are preferred for their tenderness. Therefore, they tend to be slaughtered before they reach adulthood—when muscle growth begins to slow down and toughening of muscles begins.

As a direct result of the above, there is a modest but growing segment of the industry that is devoted to meats raised on a smaller scale, with more traditional values and ethics and with more attention to the quality of the animals' life and by association it's meat.

12.5.2 HORMONES AND ANTIBIOTICS

Perhaps a little surprising to know but farmers have been unwittingly playing with animal hormones for millennia. For as long as animals have been domesticated, male castration helped render the animal more docile—this practice continues today. Not only castration does make the animal easier to handle, but also testicle removal turns out to influence the production of fat tissue over muscle. This is why steers and capons have long been preferred as meat animals over their noncastrated counterparts—bulls and cocks. However, this traditional method is being challenged as more and more people trend toward leaner, less fatty meats. As a result, this has led some producers to change tack and raise uncastrated animals or to replace certain hormones in castrated animals (McGee, 2004; Aberle, 2012).

Regarding hormones in animal rearing, it can be seen that careful manipulation of natural and synthetic hormones (including testosterone and estrogen) produce leaner, well-built cattle more swiftly and on less feed. However, this is a moot point in the EU as they have long-banned the use of hormones in the rearing of animals for meat. The situation is different for the United States and other countries, for instance, as they continue to use hormones, particularly in cattle.

Regarding antibiotics, oftentimes, it has been said that for economic industrial-scale meat production to take place, it inevitably involves abundant numbers of animals being raised in close confinement. However, such situations not surprisingly promote the rapid spread of disease throughout the community of animals (Gilchrist et al., 2007). Consequently, in order to control animal pathogens, many producers now routinely add antibiotics to animal feed. This practice turns out to have the added benefit of increasing growth rate and feed efficiency. As with hormones too, so some say antibiotic residues in meat are also minute and apparently inconsequential; however, others disagree and warn of potential "superbugs" evolving with increasing virulence both in livestock and in humans and other species (Gilchrist et al., 2007; Barton, 2000). Indeed, with the increased regular use of antibiotics in livestock, there is good evidence of the evolution of antibiotic-resistant salmonella and campylobacter bacteria. In Europe and other countries though, because resistant bacteria are more difficult to control, antibiotics are now restricted in certain animals. Furthermore, more research is also recommended in the use of hormones, antibiotics, and general feedstocks when it comes to the meat industry (Sapkota et al., 2007).

12.6 MEAT SPOILAGE

As with most fresh foods, meat is inherently unstable as a food product as it begins to change both chemically and biologically the moment it is processed. That said, there are good changes and bad changes. Those good changes, the ones described above in association with aging, tenderness, and flavor generation by enzymes, are desirable—to a point. The bad changes nevertheless are largely the result of microbial spoilage; i.e., given the opportunity, microorganisms such as molds, yeast, and bacteria will feast on meat and will multiply rapidly. The result is both uninviting for consumption and unsafe in the general sense (Rawat, 2015)

12.6.1 SPOILAGE BY BACTERIA AND MOULDS

Generally speaking, intact muscles of fit and healthy as-yet-unprocessed livestock are usually free of harmful quantities of microbes. Instead, bacteria and molds that might end up spoiling the meat are introduced during the many stages of processing, especially from the animal's hide or the plant's packing machinery. Poultry and fish are particularly disposed to spoilage because they are sold with their skin on. Many of these molds and bacteria break down cells at the meat surface and digest proteins and amino acids into molecules that smell fishy and sulfuric-like rotten eggs. Meat too, as a nutritious source of food, is especially vulnerable to colonization by microbes—mainly bacteria (Lawrie and Ledward, 2006). As mentioned, both animal skins and digestive tracts are rich reservoirs of bacteria, so it seems almost unavoidable that primarily clean meat surfaces will be contaminated through slaughter and the removal of the skin, innards, and feathers. Much of these bacteria are relatively harmless and merely spoil the meat by consuming its nutrients, eventually generating unpleasant smells and at times a slimy surface. A number, however, can occupy the cells of our digestive system producing toxins. The two most prominent causes of serious meat-borne illness are *Salmonella* and *E. coli* (Belitz et al., 2009).

12.6.1.1 *Salmonella*

Salmonella is a genus that counts among its members more than 2000 distinct bacterial types. It is also responsible for more serious food-borne diseases in Europe and North America than any other single organism. Salmonella is a resilient group especially adaptable to extremes of temperature, acidity, and moisture and is found in most if not all animals including fish, poultry, and eggs. This has a lot to do with overcrowding and the recycling of animal by-products like feathers and viscera as feed for the next generation. Salmonella often has little or no obvious effect on the carriers of the bacteria, but in humans, it causes diarrhea and chronic infection in many other parts of the body.

12.6.1.2 *Escherichia coli*

Escherichia coli or *E. coli* for short is the name given to a group of related bacterial strains that naturally inhabit the intestines of warm-blooded animals, including humans. Several strains of *E. coli*, however, are foreign to the digestive system and if ingested will cause illness. The most notorious and the most dangerous strain of *E. coli* is *O157:H7*. This causes bloody diarrhea and sometimes kidney failure. *E. coli O157:H7* is found in cattle's and other animals' digestive systems (especially calves) and their fecal matter, but its presence has little adverse effect on the animals itself. Nevertheless, meat or more precisely meats' surface is by far the most common source of *E. coli O157:H7*. This is then easily transferred and can potentially multiply quite easily, especially in minced beef with its relatively large surface area (Vogt and Dippold, 2005; Brusa et al., 2013).

12.6.1.3 *Trichinosis*

Traditionally, trichinosis is a disease caused by the infection of a small parasitic roundworm that would through multiplication become cysts. *Trichinella spiralis* can be found in a wide range of hosts. Indeed, almost any species of mammal can become infected. Adult worms live in the small intestine, while its larvae live in striated muscle cells of the same animal, long associated with undercooked pork from pigs fed rotten food waste that sometimes included infected rodents and other such delights. However, uncooked food waste was banned as feed for pork in 1980 in the United States, and since then, the incidence of trichinosis has fallen. For many years, it was recommended that pork be well cooked

to ensure the elimination of trichinae. However, it is now known that a temperature of 58°C/136.4°F or "medium" doneness is actually sufficient to kill the parasite in meat. It is also known that trichinae can also be reduced if not completely eliminated by storage in the freezer for a period not less than 20 days (Webster et al., 2006; Pozio et al., 2006).

12.6.1.4 BSE: Mad cow disease

Bovine spongiform encephalopathy (BSE) or more colloquially known as "mad cow disease" is a progressive and invariably fatal neurodegeneration disease in cattle. During the epidemic in Britain in the 1980s, it was especially worrying as it was found to be caused by a nonliving protein called a prion that was not destroyed by cooking. This prion too, it seemed, could be passed on to humans through the food chain in the new variant form of Creutzfeldt-Jakob disease (CJD). BSE was passed onto the cows via their feed of sheep by-products from those suffering from a sheep disease called "scrapie." It was hitherto thought that this disease and BSE were unable to cross the species barrier, but that was proved wrong on both accounts. In 1995–96, 10 young Britons died from this new variant of CJD, and postmortems found the prion in their bodies was closely related to that of BSE. This finally convinced the authorities that humans can contract the devastating disease by eating meat from BSE-infected cattle. The cattle brain, spinal cord, and retina are thought to be the tissues in which prions are concentrated, but a report in 2004 suggested that they may also be found in muscles and therefore in common cuts of beef. While BSE has all but been destroyed in Britain, diseased cattle have turned up elsewhere in Europe and the United States, Canada, and Japan. To date, the known numbers of human deaths from BSE-infected beef is in the in the low hundreds, and the overall risk of contracting the prion disease from beef appears to be very small (Imran and Mahmood, 2011; McGee, 2004).

Other spoilage occurs for many reasons, one of these is oxidation. Oxygen in the air and the rays of light generate off-flavors and can easily turn meat rancid or produce dull colors.

12.6.2 FAT OXIDATION AND RANCIDITY

Perhaps, the most significant chemical change undergone by meat is the breakdown of their fats by both oxygen and light into small, aromatic molecules that are redolent of rancidity. While rancid fat will not generally make us sick, they do have an unpleasant flavor. So much so that catabolism of fat can often be the limitation of the aging or storage process (Aberle, 2012). It is the unsaturated fats too that are most susceptible to rancidity—this means fish, poultry, and game birds. These go rancid before the meats of larger animals that generally contain more saturated fats rather the unsaturated. In point of fact, beef has the most saturated fats and is the most stable of all meat fats; thus, it keeps the longest.

This oxidation of fats cannot be prevented, but it can be delayed by good practices and careful handling. Raw meat should be wrapped tightly in oxygen-impermeable plastic wrap (note that polyethylene is permeable). A good practice is to overwrap meats in foil too to keep it in the dark. It should be stored in the coolest corner of the fridge or freezer. The development of rancidity in cooked meats can be hindered or delayed by minimizing the use of salt that actually boosts fat oxidation. An alternative is to use antioxidants, i.e., covering the meat in Mediterranean herbs, in particular rosemary. Lastly, browning the meat surface also generates antioxidant molecules that can delay fat oxidation; this can be done before storage (Aberle, 2012; Lawrie and Ledward, 2006).

12.6.3 PREVENTION

Prevention of bacterial infection then begins with the well-grounded assumption that all meat is contaminated with at least some disease-causing bacteria. To prevent these from spreading requires measures to ensure bacteria are, firstly, not passed onto other foods and, secondly, that they are eliminated from the meat themselves during cooking. This harks back to basic kitchen practices of clean hands, knives, cutting boards, and countertops used to prepare meats. *E. coli* bacteria, for instance, are killed or destroyed at 68°C/154.4°F, so things like minced beef needs to achieve this internal temperature before serving. If cooking burgers rare, this temperature will not be met. One workaround is to plunge the precut meats for mincing into boiling water to kill all the surface bacteria then mince the meat through a pristine machine. This is perhaps the safest way for "rare" minced beef patties. *Salmonella* and other bacteria, on the other hand, can multiply significantly at temperatures between 40–60°C and 104–160°F. So, meats should not be left in this temperature range for more than a few hours.

12.7 THE STORAGE OF MEATS

12.7.1 FREEZING AND REFRIGERATION

In the developed world, perhaps the most common domestic method for preserving meat is simply to keep it cool in the fridge or freezer. Cooling in the fridge has two great benefits; firstly, it requires little in the way of attention or preparation, simply cover, label, and let it be. Secondly, the fridge leaves meat comparatively unchanged from its fresh state. Cooling meat this way extends a products shelf life because as the temperature drops, both bacteria and meat enzymes become less active. That said, it's important to note that neither microbial nor enzymatic actions cease altogether; in fact, spoilage and enzymatic action do indeed continue.

When it comes to freezing though, meats' shelf life is greatly extended because freezing stops all biological microbial activity. This is simple biology as all life requires liquid water in order to function. Freezing immobilizes the meat's liquid water in solid crystals of ice. As a result, well-frozen meat will keep for months, years, or even indefinitely, according to the US Department of Agriculture (USDA). This according to the USDA is because freezing to −18°C/0°F inactivates any microorganisms present in foods whether bacteria, yeasts, or molds (USDA, 2017). In fact, the real test of how long food can stay in the freezer is more to do with issues of quality rather than safety. In frozen meats, for example, it is the ongoing activity of enzymes that can lead to the deterioration of food quality. This is because enzymatic activity, albeit slowed considerably, is still active at these freezer temperatures, which continue to promote chemical reactions. Chemical changes in frozen meat over time include the discoloration and development of oxidative rancidity and the over denaturation of proteins leading to texture hardening among other things. Furthermore, it is not just chemical reactions that adversely affect frozen meat quality. The packaging of the meat also influences freezing quality of meats; for instance, air-permeable plastic wrapping should be avoided or at least overwrapped with a more suitable covering so as to avoid the subzero drying process known as "freezer burn" (more in the next sections). Lastly, because meats and other foods can be stored indefinitely in the freezer, so the various frozen food shelf-life guidelines one sees around, especially the meat storage chart from US Department of Agriculture (USDA) can be found at https://www.fda.gov/downloads/Food/ResourcesForYou/

HealthEducators/UCM109315.pdf. Lastly, with such guidelines it must be remembered that the recommendations are literally "food quality" not safety guidelines only, and be used with care (Lawrie and Ledward, 2006; Aberle, 2012; USDA, 2017).

12.7.1.1 Cell Damage

As raw meat freezes, so growing ice crystals swell into their own and adjacent soft-celled membranes, puncturing them. Upon thawing, the broken cell membranes leak fluids rich in salts, vitamins, proteins, and pigments. This is not all, as the food cooks, so it further leaks more fluid than usual, and the meat readily ends up dry and dense and generally tough to eat. In order to minimize this loss, it is wise to freeze uncooked meats as quickly as is possible using a blast chiller or the industrial equivalent apparatus. In this way, just like ice cream, the ice crystals in meat become extremely small and in turn do less damage to the cellular membrane. As for crystal growth over the long period, it's best to keep the meat as cold as possible to slow the process down. Other than these measures, it is difficult to control water loss from frozen meats, vegetables, and fruits.

12.7.1.2 Fat oxidation and rancidity in frozen meat

As we have just mentioned, meat can keep for an almost limitless period of time in the freezer. However, in reality, it is the quality of the meat in question that generally determines the length of time a product can be frozen. Freezing not only causes physical damage but also causes chemical changes too. We have also mentioned the damage ice crystals can do to frozen foods; what we have not yet touched upon is the fact that moisture loss concentrates the meats salts and trace metals that in turn promotes the oxidation of unsaturated fats. As a result, rancid flavors tend to accumulate. This unstoppable process means that quality deteriorates noticeably for different meats. In fresh fish and poultry, rancidity becomes evident after only a few months while for pork after about 6 months, lamb and veal after about 9 months, and for beef after about 1 year. The quality or flavor of raw ground meats and cooked meats vis-à-vis rancidity depreciates even faster.

12.7.1.3 Freezer burn

A last side effect of freezing is the common phenomenon of "freezer burn." It is a brownish-white discoloration of the meat that develops after some weeks or months of storage, although the process is quicker if the meat is uncovered or not properly wrapped. Freezer burn is caused by water evaporation into the dry freezer air. The water exodus leaves tiny cavities in the meat surface that scatter light and can appear white or brownish (depending on meat) because of it. The meat surface (or deeper into the flesh if left for longer periods) effectively becomes a thin layer of freeze-dried meat. It is also an area in which the oxidation of fat and of pigment is hastened. In this way, texture, flavor, and color all suffer. As mentioned, freezer burn can be diminished by properly covering the meat as compactly as possible with air-impermeable plastic "cling" film or plastic wrap.

12.7.1.4 Thawing meats

Most frozen meats are thawed before cooking; the easiest thing to do would be to allow the meet to thaw to room temperature; however, this is neither safe nor efficient. This is because the surface can rise to microbe-friendly temperatures long before the interior has thawed adequately. So, a much faster and safer method is to immerse the wrapped meat in a water bath filled with ice. This keeps the surface of

the meat cool enough while transferring heat to the middle of the meat. Of course, one could defrost the meat in the fridge, but pound for pound, the water bath is the quickest route.

Cooking meats from the freezer—frozen meats can, if the need or want arises, be cooked without thawing first. This is possible especially with slow-cooked meats, maybe a large roast in the oven or sous vide in a warm water bath. However, cooking times under these circumstances will vary greatly with size and temperature.

12.8 MEAT GRADING

Meat grading is practiced around the world and can vary greatly from country to country. Generally, the grading aims to categorize meat into different classes based on a variety of considerations. For instance, meat can be graded based on a large number of variables including the following:

- The expected eating qualities, i.e., appearance, texture, and juiciness
- The fat content
- Its yield potential
- Sustainability issues such as global versus local
- Its welfare status, i.e., organic or free range

In fact, throughout the world, meat products can and are graded on any or several of the above considerations or indeed any number of other physical, social, or ethical benchmarks.

In contrast to pre-and postmortem meat inspection procedures that are fairly constant throughout the world (albeit to varying standards), consumer-centric meat-grading systems can vary significantly. These differences can be attributed to the fact that different countries produce meat for different reasons. For example, in the United States, cattle are primarily reared for the production of steaks in which a high amount of marbling achieves a greater USDA quality grade (i.e., prime, choice, or select). By contrast, Australian cattle are primarily raised for the processed ground beef industry where the highest quality grades are given to the leanest cuts of meat. In this sense, a cook needs to be aware of the various standards when importing meat from abroad.

12.9 THE COOKING OF MEAT

We cook meat for four general reasons:

- To make it microbially safe to eat
- To make it easier to chew (more palatable)
- To aid in digestion as denatured proteins are more susceptible to the body's digestive enzymes
- To make it more flavorful

Furthermore, raw meat is different from cooked meat in that it provides an altogether different flavor profile (Tornberg, 2005). Unadulterated raw meat provides savory amino acids, salts, and light acidity, while it offers little in the way of aroma. Cooking, however, strengthens or intensifies the taste of the meat creating both new aromas and flavors. This is because the chemical and physical changes to meat muscle fibers (cells) involve the release of more of the meats' fluids and therefore more stimulating

substances for the palate (Aberle, 2012; McGee, 2004). At higher temperatures, chemical changes also release molecules that combine and recombine to form new molecules giving way to yet more aroma profiles of meatiness, fruity or grassy notes, among others. These aromas are the esters, ketones, and aldehydes in action (Belitz et al., 2009). It should also be noted that the available fluid or moisture in meat is at its maximum when meat is only lightly cooked. However, this does not necessarily mean this is the best way to cook the meat. We have seen too the effects of the Maillard reaction that gives off generic "roasted" notes when tasted although the reaction can also provide certain grassy, floral, oniony, spicy, and even earthy tones too. In fact, there have been several hundred aromatic compounds that have been identified in the Maillard reaction that contributes to the overall flavor, aroma, and texture of cooked meats (Weijers et al., 2003; Berg et al., 2002; McGee, 2004).

Meat experiences significant structural and chemical changes upon cooking and by extension, the eatability and consumers perception of quality also changes considerably (Tornberg, 2005). As a generalization, we like meat to be tender and juicy rather than tough and dry (McGee, 2004). The ideal cooking method then would be the one that minimizes moisture loss and the compacting of the meat fibers while at the same time maximizing the conversion of tough connective tissue collagen into soluble or fluid gelatin. Unfortunately, these aims are sometimes incompatible with each other, and in practice, the desired result can be quite difficult to achieve—hence, the knowledge, experience, and skill of the cook is paramount (next sections) (Tornberg, 2005; Baldwin, 2012). It should also be remembered that any meat, if treated badly during the rearing, slaughtering, and postmortem stages, as discussed in previous sections, will be tough no matter the cut or the cooking method (Bender, 1992; McGee, 2004). The best practice for such meats is marination. That said, assuming a respectable level of quality assurance throughout the many stages of meat's development, then, cooking methods can be more appropriately tailored to the particular cut of meat.

12.9.1 DENATURATION, COAGULATION, AND GELATION OF MEAT PROTEINS

(See also Section 4.2)

To begin with, to ensure meat meets the four criteria described previously, one must cook (denature) the meat proteins to a desirable degree. And, as has also been discussed, the denaturation of proteins is essentially the physical unfolding of proteins. While this is true, the difficulty of this task lies in the fact that the many different meat proteins present all differ in denaturation temperatures. More confusingly, denaturation temperatures within single proteins also vary somewhat, due to certain factors or forces that try to keep protein conformation intact. These might be the density of cross-links present, the strength of side-chain hydrogen bonding, and salt bridge interactions, for example (Sikorski, 2006). What this means for the cook is the fact that there will be several degrees of unfolding; starting at low temperatures with increased denaturation over ever-increasing temperatures. Recall that when talking of thermal denaturation, it is actually defined as the temperature at which proteins reach a major change in conformation—this is also referred to as the transition temperature or the molecular transition temperature (Sikorski, 2006). It is also the point that the cook aims for when cooking meats or any proteins for that matter.

Recall too from earlier chapters that proteins themselves are a collection of amino acid residues that form long chains of repeating units that are folded upon themselves in numerous configurations. The unraveling or denaturation of these proteins can occur from either physical damage (tenderizing the meat with a meat hammer), chemical (through marination with acids or bases), or thermal (cooking)

applications. The physical break down of proteins by pounding the meat with a tenderizing hammer is self-explanatory, i.e., proteins, especially the long myofibrillar proteins in meat are physically cut into smaller fibers, thus aiding the tenderization process. Chemical breakdown occurs through the action of pH changes, among others, which also helps facilitate the unfolding of proteins. It is worth knowing too that extremes of pH levels also denature proteins. If one marinades meat, for instance, one usually has an acidic component like red wine, lemon juice, or fruits high in protein-digesting enzymes (proteases). These can be extracted from a number of plants such as pineapples, kiwis, or ginger and which serves to partially deconform individual proteins (Lung, 2015). If one were using alkaline to marinade meat on the other hand, perhaps the most well-known solution is that of baking soda or sodium bicarbonate. A lesser known, but no less effective marinade is that of aged egg whites. Egg whites are naturally slightly alkaline—just over 7.6 on the pH scale, but they become progressively more alkaline over a relatively short period of time. This sees an increase in pH to between pH 8 and even pH 9.4 depending on certain factors (Ophardt, 2003). Even salts, of a specific kind can raise the pH of a solution; although with the use of aged egg whites, one would have to be mindful of any unwanted residual flavors.

12.9.2 EFFECT OF HEAT ON MEAT

We learn from the preceding and the following sections that the cooking of meat is indeed a complex and involved process. We note too that on heating, the textural changes in the meat are related to denaturation of the fibrous and globular proteins that both behave differently (Baldwin, 2012) (see also Section 4.2).

To recap, animal carcasses comprise four main types of tissue:

- *Muscle* (skeletal, smooth, and cardiac)
- *Connective* (adipose, areolar, dense, cartilage, blood, and the bone)
- *Epithelial* (the skin)
- *Nervous tissue* (comprising the brain and nerves)

While all are important, from an economic point of view, muscle, particularly skeletal muscle meat, is the most prized of all tissues. These are used for roasts, steaks, grills, chops, pies, pasties, burgers, and sausages; in fact, the list is almost endless. Skeletal meat muscle (interchangeably referred to as muscle or simply meat) accounts for the largest proportion of protein within animals. However, muscles do not exist independently of the other tissues; in reality, muscle meat, while predominantly formed from muscle fibers, actually contains all of the other tissues mentioned above. That is to say, meat comprises (from largest to smallest) muscles, muscle bundles, muscle fibers (or cells), myofibrils, and myofilaments; each of which is encased in a film of connective tissue comprising mainly collagen and elastin proteins interlaced with fat and nerve tissues proteins. Thus, any given muscle contains various amounts of fat, collagen, nerve, and capillary tissues too. In this way, muscles are not homogenous pieces of meat, rather they contain a selection of tissues and other components each comprising multiple different groups of proteins (Fig. 12.5). The difficulty when it comes to cooking meat then is that all these tissues contain proteins, which, as mentioned before all denature at differing temperatures.

In sum, meat is composed of three main protein groups: the myofibrillar proteins (mostly myosin and actin) that account for approximately 50%–55% of total meat protein, sarcoplasmic proteins (myo- and hemoglobins) that represent about 30%–34% of meat, and stromal or connective tissue proteins (mostly collagen) that make up the remaining 10%–15% of proteins in meat (see Section 12.2.1)

(Tornberg, 2005). All these proteins can be divided into two types—fibrous and globular (Baldwin, 2012). Consequently, different proteins in turn act in their own peculiar way. When heat is applied, for instance, sarcoplasmic proteins that are predominantly globular expand, while myofibrillar proteins and the connective tissue proteins (principally collagen) are fibrous proteins that contract (Baldwin, 2012). Consequently, when it comes to cooking meat, there is not a one-size-fits-all approach; instead, cooking meat is somewhat of a trade-off, one in which Baldwin (2012) succinctly summarizes as

> Which proteins and how much we denature them mainly depends on temperature and to a lesser extent on time.
>
> **(Baldwin, 2012)**

As one reads on, it will be seen that there are numerous different and many contradictory temperatures given for denaturation, aggregation, and gelation. This is because, as mentioned, meat is a heterogeneous product containing multiple protein types that all behave in different ways not only at different temperatures but also at different time intervals. In this sense, it is important to remember that meat proteins do not react in isolation. Subsequently, it can be difficult to fully comprehend just exactly what happens inside a piece of meat as heat is applied.

All is not lost, however, as there are a number of ways—experimental ways and established methods—by which denaturation temperatures can be measured or gauged; these include but are not limited to differential scanning calorimetry (DSC), fluorescent probes, viscosity and gel rigidity measurements, circular dichroism, light scattering, and enzyme activity assays (Sikorski, 2006). Consequently, different methods are used in different experiments and for differing measurement techniques and requirements; this also applies to different meat typologies (old, young, male, female, etc.) and to different proteins and so on and so forth. That said, while it seems there are multiple measures to test the same thing, one method in particular, differential scanning calorimetry (DSC) has certain advantages over other techniques in that it can be used in complex heterogenous mixtures like meat and their multiple protein concentrations (Tornberg, 2005). Understandably, with the varied measuring techniques and the different proteins involved, as well as the different methodologies employed, it is little wonder that there is a great deal of confusion in the lay literature. Not surprisingly too, little consensus is formed when it comes to exact denaturation temperatures, and by extension the cooking of meat. The following helps to explain.

12.9.2.1 Cooking temperatures

When considering the behavior of heated globular and fibrous proteins, one must remember that globular proteins expand, while the fibrous proteins contract. The connective tissue proteins—collagen, reticulin, and elastin—are all fibrous proteins, as are the myofibrillar proteins, myosin and actin. Consequently, upon heating, they all shrink to some degree. In contrast, the sarcoplasmic proteins tend to be globular and expand with heat (Tornberg, 2005). Thus, in order to serve up a tasty morsel of steak or a medium roast, for instance, the cook must understand something of the different denaturation temperatures and the effects of protein expansion and shrinkage. In this way, the cook aims for an optimal internal meat temperature cooked under specific conditions over a specific period of time. But how does the home or professional cook know the right times and temperatures to operate within? For one, there is a whole host of experiential data from the catering industry that has been collected over the eons. There is also certain literature available to back this up, but as will be seen in the review

below, there are many figures, times, and temperatures offered that it becomes difficult at best to find consensus.

First, as has been mentioned, each type of protein denatures at different temperatures and at several different points, starting slowly at first, then becoming more denatured with increased heat. This continues until a point is reached where proteins have achieved the greatest proportion of protein denaturation or conformational change. However, once again, meat is not a homogenous product, so the denaturation point is different for different tissue proteins. The challenge for the cook is deciding the optimum point that unfolds enough of the right proteins to reach the desired goal when cooking both tender and tough cuts of meat. The result? Confusion at best and a bad dinner at worst.

McGee (2004), in his seminal book on science in the kitchen, suggests cooking tougher cuts of meat long and slow. On the other hand, he proposes that if cooking tender cuts of meat, then cooks must do so rapidly in order to maximize tenderness and minimize moisture loss. Grilling, sautéing, and frying are the typical fast-cooking methods (Breidenstein et al., 2013). Accordingly, it is suggested that tender cuts are best heated quickly to no hotter than an internal temperature of between 55–60°C and 131–140°F (McGee, 2004) or slightly contradictorily between 50–60°C and 122–140°F (Purslow, 2005). Furthermore, as will be seen, cooking potentially tender meat within a narrow desirable temperature range is difficult to achieve with fast-cooking methods. This is partly because as the meat cooks from the outside to the inside quickly that a large temperature gradient is created. That is to say, once cooked, meat does not display a uniform temperature throughout. Fast cooking means that the meat is hotter on the outside and gradually gets cooler the closer one gets to the center of the meat (assuming the meat is not cooked to the degree of "well done"). This is an area in which sous vide[17] cooking has an advantage over traditional cooking methods. With slow, low-temperature cooking, a degree of "doneness" can be achieved with very little temperature gradient, i.e., the meat is the same temperature from the outside all the way to the center.

Finding the correct temperature for cooking meat (replete with numerous different proteins) to a specific degree of doneness is difficult to find in the scientific literature. Nevertheless, one such source comes in the form of a report written for the United Nations Food and Agriculture Organization (UNFAO). In the report, it is suggested that meat is considered cooked once internal temperatures reach 65–70°C/149–158°F (Bender, 1992). At this point, proteins are said to coagulate, and the meat seemingly benefits from the partial hydrolysis of the collagen present in connective tissues (Bender, 1992). In another text, temperatures of between 35–40°C and 95–104°F have been said to exhibit the first signs of conformational changes (denaturation) across the protein range, while a transition temperature of 60°C/148°F in bovine meat is reported to be optimal (Sikorski, 2006).

While these are all useful as guidelines for whole cuts of meat, they are somewhat limiting in terms of understanding the processes involved. The next section briefly explores the literature for individual proteins and their relative properties under heat induced denaturation. From this, it gives the cook a better understanding of the whys' and wherefores' and a platform from which cooks (home and professional alike) can make informed decisions about cooking methods, times, and temperatures.

[17]In sous vide cooking, low temperatures cook food slowly in vacuumed bags in a water bath to, among other things, allow proteins to unfold, coagulate, and gelate and to allow enzymes to act in optimal temperatures. In sous vide cooking though, the water bath is generally preheated to the desired temperatures.

12.9.2.1.1 Myofibrillar proteins, 50%–55% of total muscle protein

Myofibrillar proteins are the main components of meat, and there are around 20 or so different types in this particular group. In perspective, out of the overall 50%–55% of myofibrillar protein, myosin and actin alone account for around 65%–70% of this figure. Recall too that myosin forms the bulky thick filaments of the meat muscle cell while actin forms the thin filaments. The bulk of the water content lies trapped between these two fibrous proteins.

In this arrangement, myosin is the principal protein, and actin is both physically and proportionally much smaller (Sikorski, 2006; Tornberg, 2005; Baldwin, 2012). Fibrous muscles like myosin and actin in general shrink or constrict with the application of heat, and at quite low temperatures too—beginning at around 35–40°C/95–105°F. After this, shrinkage of both myosin and actin increases progressively up to estimated temperatures of about 80°C/175°F or so (Baldwin, 2012). It is also worth noting too that Tornberg (2005), in his excellent review of the effects of heat on meat, found that as meat fibers shrunk; they do so both laterally (transversely or cross-sectionally) and longitudinally (lengthways). This shrinking ends up squeezing out a little intracellular fluid while firming up the meat in the process. It also enlarges existing gaps between fiber bundles and their surrounding endomysium that was primarily initiated at rigor. However, there have been some questions raised as to whether the same temperature simultaneously denatured fibers both laterally and longitudinally. In this respect, Bendall and Restall (1983) inform us that lateral shrinkage begins at about 40°C/104°F; while Tornberg (2005) cites another study in which lateral and longitudinal fibers shrunk concurrently at 40–60°C/104–160°F. Longitudinal shrinkage by itself has also been observed at around 60°C/160°F or at 40–50°C/104–122°F, depending on who one reads (Offer, 1984; Bendall and Restall, 1983). In Tornberg's (2005) review, he also highlighted three transitional states of denaturation for the three main protein groups; in respect of myosin, it was found that denaturation occurred at between 54–58°C and 129–156°F. In another example, Tornberg (2005) touched on experiments that denatured the same proteins in solution. In this foray, it was found that myofibrillar proteins as a whole began to unfold at slightly lower temperatures of between 30–32°C and 86–90°F. Subsequent aggregation (protein-protein association) in the same experiment occurred at around 36–40°C/97–104°F followed by coagulation or gelation at 45–50°C/113–122°F (Tornberg, 2005). Bircan and Barringer (2002) also noted that denaturation of myosin resulted at 62°C/144°F, whereas McGee (2004) suggests 50°C/122°F as the beginning of the denaturation point. In yet another study, it was found that myosin unfolded, losing its structure, between 54–58°C and 129–136°F (Martens and Vold, 1976; Wright et al., 1977; Tornberg, 2005). Additionally, other trials and literature found myofibrillar proteins denatured at around 60°C/160°F by Sikorski (2006) and at 50°C/122°F by Potter and Ruhlman (2010).

Actin, because of its behavioral properties, is perhaps the next most important protein in meat tissue. It is said to denature at around 82°C/180°F (Bircan and Barringer, 2002); while Potter and Ruhlman (2010) suggest the optimal point for actin would be reached at 66–73°C/151–163°F; Wright and colleagues, on the other hand, determined the denaturation point of actin to be between 80–83°C and 176–181°F (Wright et al., 1977).

Moving on to titin, studies have shown that both pork and beef unfold at 75.6°C/168°F and 78.4°C/194°F, respectively (Pospiech et al., 2002).

As can be seen from the review of the literature there is great variability in measurements for partly and fully denatured myofibrillar proteins. As a result, it is only through the experimentation and experience of the cook to determine what works best. From the study above, it would seem that the

myosin generally fully denatures at temperatures commonly falling in the 50–60°C/122–160°F range, while actin and titin do so at higher temperatures.

12.9.2.1.2 Sarcoplasmic proteins, 30%–34% of total muscle protein

Numerous proteins exist in the sarcoplasmic group of predominantly soluble globular proteins. Indeed, depending on who one reads, this can be anywhere between 50 and 100, of which consists of hemoglobin, myoglobin, and numerous enzymes (Tornberg, 2005; Baldwin, 2012). Although, unlike myofibrillar and stromal proteins (in particular, collagen) that shrink with increasing temperatures, as noted previously, sarcoplasmic proteins actually expand. It has also been suggested too that, upon heating or cooking, denatured sarcoplasmic proteins can coagulate forming a gel in between the structural elements of meat, thus linking them together and adding to the overall texture/firmness and mouthfeel. Also, in the case of sarcoplasmic enzymes, as with most meat-catalyzing enzymes, if cooking at low temperatures, there is a noticeable tenderizing effect on the final product if the meat is being cooked for a long time—over several hours in some instances.

A study by Davey and Gilbert (1974) experimented with sarcoplasmic proteins as a group and found that most soluble (or low ionic strength soluble[18]) sarcoplasmic proteins began to unfold, at between 40°C and 105°F. After which, the aggregation and gelation was complete at temperatures of 60°C/140°F (Baldwin, 2012). Although it was found that in certain muscle groups, this figure was as high as 90°C/194°F (Davey and Gilbert, 1974). By around 60°C/140°F though, McGee (2004) proposes more of the proteins inside the meat cells, specifically the pigment myoglobin,[19] denatures, and the meat becomes a more tan color and firms up a little more. Other temperatures put forward suggest that sarcoplasmic proteins denature at between 65–67°C and 149–153°F (Wright et al., 1977; Martens and Vold, 1976). At around 60°C/140°F, myoglobin begins to denature (Potter and Ruhlman, 2010; McGee, 2004), while another study promotes the idea that myoglobin begins to denature at 20°C/68°F before fully transitioning at 80–85°C/176–185°F (Bender, 1992). One of the sarcoplasmic enzymes, collagenase, has also been noted to operate at temperatures above 60°C/140°F, only, however, if the meat is cooked slowly, as fast cooking tends to destroy this enzyme (Tornberg, 2005; Baldwin, 2012). All in all, it can be seen that figures for sarcoplasmic proteins to fully denature tend to be around 60°C/140°F.

12.9.2.1.3 Stromal proteins, 10%–15% of total muscle protein

Stromal or connective tissue proteins (predominantly epimysium, perimysium, and endomysium) are responsible for the structural integrity of an animal. That is, they are responsible for holding muscles, bones, fat, and fibers in place. They achieve this by wrapping themselves around whole muscles, (the epimysium connective tissue), their subunits—bundles of fibers, (the perimysium connective tissue), and individual fibers themselves (the endomysium connective tissue). In turn, depending on the muscle type and position, all the connective tissues surrounding the fibers, bundles, and muscles collect together at the terminal end of a muscle or muscle group forming a strong muscle-bone connection called tendons or muscle-to-muscle connections referred to as ligaments (Fig. 12.3). In this way, connective tissues bedding themselves around and in between meat fibers, fat, the bone, and the like, connective tissues are the glue that binds all the parts together.

[18]The ionic strength of a solution is the measure of the amount or concentration of ions in the solution.
[19]Myoglobin coagulates to form the tan-colored version of the same molecule called hemichrome.

Predominantly made of collagen and elastin fibrous proteins, connective tissues begin to shrink at around 60°C/140°F, yet with further heating to about 65°C/150°F and above, the tissue shrinks more vigorously (Baldwin, 2012). If cooking at lower temperatures though, before the collagen starts to shrink, at say 55°C, collagen actually dissolves into gelatin, and interfiber (muscle cell) adhesion is reduced (This, 2006). Interestingly, Baldwin (2012) states that there is not a single specific temperature that collagen is denatured; instead, he suggests that the degree to which denaturation occurs increases exponentially with increased temperatures. He further suggests that 55°C/130°F is a practical temperature to aim for when denaturing collagen. On the other hand, Martens and Vold (1976) proposed denaturation temperatures as occurring between 65–67°C and 149–153°F. While given enough time, collagen is said by Potter and Ruhlman (2010) to denature at between 56–62°C and 122–144°F; others placed temperatures at 70°C/158°F (Bircan and Barringer, 2002), and 53–63°C/127–145°F (Martens et al., 1982), as well as 62–65°C/144–149°F (Barham et al., 2010), 70°C/158°F, or higher (McGee, 2004).

In another study, when it comes to shrinkage of collagen, Tornberg (2005) cites Bendall and Restall (1983) in proposing figures of 35–40°C/95–104°F as the point at which collagen starts to shrink, and then at around 65°C/149°F, it begins to shrink more rapidly. Yet, another study also puts forward temperatures of collagen shrinking (to approximately one-quarter of the original length) at temperatures of 60–70°C/122–158°F. Moreover, it was noted that at this temperature, both collagen and muscle fibers shrank in unison longitudinally and continued to do so with increased temperatures (Mohr and Bendall, 1969; Tornberg, 2005). Note too that Barham et al. (2010) suggest collagen gelates at between 62–65°C and 126–149°F, while McGee (2004) suggests collagen gelates at about 70°C/158°F and above. On the other hand, according to Tornberg (2005), a figure of gelatinization is said to take place at 80°C/176°F. Once again, it can be seen there is confusion and disagreement in the literature as to the temperature that collagen gelatinizes. Once again, for all the science, the solubilization of collagen boils down to tried and tested methods of cooks both now and in the past. This is not to disregard the scientific literature either; it merely points out the wide and varied temperatures and the huge gap in opinions from a host of different sources.

12.9.2.1.4 Meat temperature charts

As can be seen from our little foray into protein denaturation, it becomes clear that not all scientists, reviewers, and commentators see eye to eye on the subject. Despite this, it would seem that the process of meat denaturation is well understood (see below). Having said that, what seems to be lacking in the literature is consensus of the precise temperatures involved; one needs only glance at the minimum and maximum temperatures in Tables 12.4 and 12.5 to get a feel for the current divergence of opinion. On a positive note, what can be taken from this though, is the fact that when we cook meat, certain changes happen slowly and others more quickly. Consequently, it boils down to the notion that there are essentially two ways in which we can treat the process of cooking; one is through long and slow cooking as in sous vide, stewing, or braising; the other is fast, high-heat, and short-time cooking by sautéing, grilling, and frying and roasting—both have their merits.

As mentioned, the table above shows the temperature ranges from the literature at which specific and nonspecific proteins fully denature. This refers mainly to the fast and quick cooking temperatures, and while it is a useful guide, the lack of consensus and the varied temperatures are too vague and confusing to be of any real practical use in the kitchen. There are exceptions of course, with certain quality reviews and studies, some of which have been touched upon in this book.

Table 12.4 Meat Cooking Temperature Ranges

Meat Denaturing Temperatures	
General meat denaturing temperature range	
50–70°C	
Myofibrillar proteins	
• Myosin	54–62°C
• Actin	66–83°C
• Titin	78.4°C
Sarcoplasmic proteins	
• Mainly myoglobin and haemoglobin	60–85°C
Stromal proteins	
• Mainly collagen	53–70°C

Compiled from Numerous Data Baldwin, D.E., 2012. Sous vide cooking: a review. Int. J. Gastron. Food Sci. 1(1), 15–30; Tornberg, E., 2005. Effects of heat on meat proteins—implications on structure and quality of meat products. Meat Sci. 70(3), 493–508; Sikorski, Z.E., 2006. Chemical and Functional Properties of Food Components. CRC Press; Potter, J., Ruhlman, M., 2010. Cooking for Geeks: Real Science, Great Hacks and Good Food. O'Reilly Media, Incorporated; Bircan, C., Barringer, S.A., 2002. Determination of protein denaturation of muscle foods using the dielectric properties. J. Food Sci. 67(1), 202–205; McGee, H., 2004. On Food and Cooking: The Science and Lore of the Kitchen. New York: Charles Scribner's Sons; Martens, H., Vold, E., 1976. DSC studies of muscle tissue protein denaturation. Congress Documentation; Proceedings of the European Meeting of Meat Research Workers; Wright, D.J., et al., 1977. Differential scanning calorimetric studies of muscle and its constituent proteins. J. Sci. Food Agric. 28(6): 557–564; Davey, C.L., Gilbert, K.V., 1974. Temperature-dependent cooking toughness in beef. J. Sci. Food Agric. 25(8), 931–938; Bender, A.E., 1992. Meat and Meat Products in Human Nutrition in Developing Countries. Rome: FAO; Martens, H., et al., 1982. Texture and colour changes in meat during cooking related to thermal denaturation of muscle proteins. J. Text. Stud. 13(3), 291–309; Barham, P., et al., 2010. Molecular gastronomy: a new emerging scientific discipline. Chem. Rev. 110, 2313–2365; Purslow, P.P., 2005. Intramuscular connective tissue and its role in meat quality. Meat Sci. 70(3), 435–447.

Nevertheless, when it comes to cooking and meat temperatures, many cooks, both accomplished and otherwise, build on years of experiential knowledge of their own and from their forefathers. Accordingly, compared with the general scientific literature, one could argue that the cooks indeed have it under control.

What the literature highlights, is a collective understanding of the process of denaturing; this is where the literature in point excels. By way of example, it can be seen from the literature that myofibrillar proteins (predominantly myosin and actin) and the connective tissue proteins (predominantly collagen) tighten and contract with the application of heat, while the sarcoplasmic proteins under the same conditions expand. This, however, is where the similarities end; myofibrillar proteins, for instance, contract both transversely (cross-sectional) and longitudinally (lengthwise). Connective tissues shrink longitudinally and with temperature and time will eventually solubilize. The sarcoplasmic proteins, on the other hand, after the initial expansion, tend to aggregate and gelate (Baldwin, 2012; Tornberg, 2005). Further, recall that approximately 80% of muscle's total water content can be found in myofibril cells, in particular, between myosin (the thick) and actin (the thin) filaments. The degree too to which the meat retains this water depends on temperature, time, and skill of the cook.

We know too that in terms of protein, enzymes, and the like, muscle meat is not a single homogenous entity, so cooking methods must be tailored to the meat. Tender cuts with little connective tissue

Table 12.5 Meat Cooking Temperatures—A Measure of "Doneness"

Description	The Professional Chef (2001)	McGee (2004)	Green (2005)	Bistro Laurent Tourondel (2007)	Gisslen (2010)	USDA (2011)	Blumenthal (2011)	Baldwin (2012)	Breidenstein et al. (2013)	López-Alt (2015)	The Food Network (2016)	Gibson and Rasmussen (2017)
Extra-rare/ Blue (*bleu*)		45°C/110°F	46–49°C/ 115–120°F				45°C					45–47°C/ 113–117°F
Rare (*saignant*)	58°C/135°F	50°C 120–130°F	52–55°C/ 125–130°F	45–55°C/ 120–125°F	54°C/ 130°F		50°C	50°C/ 125°F	60°C/140°F	50°C/ 120°F	52°C/125°F	49–51°C/ 120–124°F
Medium rare (*à point*)	63°C/145°F	55°C 130–135°F	55–60°C/ 130–140°F	55–60°C/ 130–135°F		63°C/ 145°F	55°C	55°C/ 130°F	66°C/150°F	55°C/ 130°F	54–57°C/ 130–135°F	52–54°C/ 127–129°F
Medium (*à moyen*)	70°C/160°F	60°C 135–145°F	60–65°C/ 140–150°F	60–65°C/ 140–145°F	60–63°C/ 140–145° F	71°C/ 160°F	60°C	60°C/ 140°F	71°C/160°F	60°C/ 140°F	57–60°C/ 135–140°F	57–61°C/ 135–142°F
Medium well (*cuit*)		65°C 145–155°F	65–69°C/ 150–155°F	65–70°C/ 150–155°F						65°C/ 150°F	60–66°C/ 140–150°F	63–65°C/ 147–149°F
Well done (*bien cuit*)	75°C/170°F	70°C 155°F and above	71°C +/160°F+	70°C/160° F+	71°C/ 160°F	77°C/ 170°F	70°C	70°C/ 160°F	77°C/170°F	70°C/ 160°F	68°C/155°F +	68–70°C/ 155–158°F

like collagen tend to favor dry heat methods, and vice versa meat with appreciable amounts of connective tissue generally does well in moist heat environments.

In tougher cuts, however, the relative quantity of connective tissue tends to determine the tender and less tender cuts of meat. Less tender cuts of meat require long slow-cooking techniques, preferably in water or stock (which aids the gelatinization of the collagen) leaving the fibers free to uncoil. In this case, sous vide, braising, stewing, steaming, and pot roasting are good examples (Aberle, 2012; Lawrie and Ledward, 2006). Indeed, according to Baldwin in his excellent paper on sous vide cooking, he demonstrates that in cooking meats sous vide (slow cooking), it is the slow changes and lower temperatures involved that are used largely to increase meat tenderness (Baldwin, 2012).

In all this, the challenge for the cook is to implement the appropriate method of cooking for the different meats and meat cuts. The trick, according to Barham, Skibsted et al. (2010), is

> the meat should be heated to a temperature where collagen is denatured but actin is still native i.e. between 62 and 65°C [144-149°F].

In general, it is acknowledged that in cooking tender meat, it is important for the cook to understand the fast changes, as slow changes—less than 80°C—are predominantly cooked sous vide style. In sous vide cooking, with the tender (and not so tender) cuts, the cook needs only bring the meat up to temperature and hold it there as long as is required. In fast cooking, by contrast, the cook is playing with the physical and chemical properties of the proteins at much higher and faster temperatures. As such, in very loose terms, it can be said meat tenderness increases with internal temperatures of between 50–65°C and 122–150°F after which tenderness decreases as temperatures continue rising to 80°C/175°F. Post 80°C/175°F meats are essentially considered "well done," and it takes further cooking to denature the tougher proteins and any undissolved collagen. Don't forget too other connective tissue proteins like elastin of which there is much less in tissue fibers. These do not denature with heat; instead, elastin remains springy and rubberlike.

12.9.2.2 A note on sous vide

Slow cooking, like sous vide, can ensure food is cooked to the low end of denaturation points; this method of cooking also minimizes shrinkage and reduces toughness while ensuring a minimal temperature gradient. That way more of the food is cooked to the required "doneness." At temperatures of 55–60°C/131–140°F, meats' tenderness, depending on toughness, size, and length of time in the sous vide bath, is significantly increased over time. This is due to several reasons, but two in particular include the action of proteolytic and collagenase enzymes. These enzymes remain active at low temperatures and aid in the breakdown and tenderizing of myofibrillar and collagen proteins, respectively (Bouton and Harris, 1981; Baldwin, 2012; Tornberg, 2005; This, 2006). For an excellent resource on temperatures and times *inter alia* sous vide cooking, see Baldwin (2012).

As far as internal cooking temperature goes and as has been labored in the previous sections, there is no definitive temperature at which to cook meats to perfection. One cook's medium is another cook's medium rare. This results in something of a free-for-all with many (both scientific and lay) claiming optimum cooking temperatures (Table 12.5). Quite wisely though, most have adopted a range of figures rather that a single point.

This author too, after 20 years as a chef and the last 10 as a lecturer and researcher along with Hans Rasmussen, a chef of 15 years, undertook our own little sous vide study. In the study, we chose beef

sirloin steaks at a thickness of 3.5 cm, and using the sous vide method for accurate low-end temperatures starting from a temperature of 45°C/110°F, we cooked 26 steaks at 1°C intervals to 70°C/160°F for a cooking time of 1 h 30 min. In the experiment, we were not looking for tenderness or water-holding capacity, we solely concentrated on the perception of "doneness" as indicated by visual cues from 120 survey respondents. The results can be seen in Table 12.5.

12.9.3 EFFECT OF HEAT ON MEAT FAT

In the first instance, inter- and intracellular fat cells interrupt and weaken the cohesiveness of muscle fibers and by extension whole muscles or joints of meat. With the application of heat, fat cells melt rather than dry out; this further affects the strength of individual fibers and entire muscles. Furthermore, as fat melts, so it lubricates fibers and gives meat a sense of moisture in terms of mouthfeel. Indeed, without enough fat, otherwise, tender meat can give the sensation of being compacted, feeling dry, and even tough in the mouth. Additionally, fat cells can greatly affect the flavor of the meat. In this regard, it should be mentioned that fat cells are essentially storage tissues so pretty much, any sort of fat-soluble material can generally be found stored away. As the contents of fat tissue vary from species to species and intraspecies for that matter, so what's in the fat varies depending on diet and the resident gastrointestinal microbes. As a result, the flavor of beef, lamb, pork, and chicken is to a certain extent determined by the contents of the fat tissue. We can think of fat as composites of many different kinds of aroma molecules that when melted can take on characteristics of fruity or floral or even nutty aromas (Owusu-Apenten, 2004). Fats and gastrointestinal microbe compounds from forage plants contribute to the ruminant flavor of cattle, sheep, and deer. Lamb and sheep, for instance, store a number of fatty molecules including branched-chain fatty acids and gastrointestinal microbes including thymol (the same molecule that gives thyme its distinct aroma). The flavor of pork is thought to come from the intestinal microbes and their amino acid metabolism, while its sweetness comes from the same kind of molecule that also gives coconut and peach their specific aroma character (lactones).

It has been said that diets of grass or "forage" feeding results in stronger tasting meat than those animals fed on grain or concentrate feed alone. This is due to the plants' high content of various aromatic substances, reactive polyunsaturated fatty acids, and chlorophyll, which rumen[20] microbes convert into chemicals called terpenes, relatives of the aroma compounds in many herbs and spices (see Section B.7.9.3). The deep meaty flavors of beef and mutton can be a little off-putting in grain-fed animals especially in the fat that gets stronger and "gamier" as animals get older. This is so because more of the flavor compounds are put into fat storage and is the reason why lamb and its gentler flavor tend to be generally more popular than mutton from mature sheep.

12.9.4 MARINATING, BRINING AND TENDERIZING MEAT

A marinade is a mixture of seasonings used to preserve, flavor, and/or tenderize foods. Marinades usually comprise a number of ingredients to achieve this end such as oil, salt (brining), acidic liquids, and flavorings. The molecules of each of these ingredients are different sizes, and while some are attracted to certain chemicals in meats and fish, others are repelled by them. In this way, some can flow easily

[20]Rumen represents the first chamber in the alimentary canal of ruminant animals.

into and between the microscopic voids of muscle fibers, while most others are simply too large. As a result, in most instances, marinades then are essentially a surface treatment, with only the salt penetrating deep into the flesh. That is to say, marinades in general do not penetrate meats very far. So, salting thinner cuts of meat are the best way to accomplish tenderization. If there is too heavy a component of salt in the marinade, then the marinade should really be called a "brine." Liquid marinades have long been used to soften or tenderize meats while imparting certain flavors. It can be thought of as a chemical method that can both improve the perceived juiciness and the tenderness of the meat. It can also increase the weight of the product being marinated. At the commercial level, the food industry often injects marinades or "cures" into the meat directly. This is because normal, uninjected marinades work very slowly on the meat; they are more surface acting flavor enhancers then marinades *per se*. The aim in meats at least is to increase tenderness and juiciness, both usually associated with higher water-holding capacity (WHC) and the swelling of myofibrils.

While acids like lemon and other acidic fruit juices, vinegar or wine are very common ingredients in a marinade and been found to improve tenderness and water retention. However, if a cook goes down this route he/she has to contend with the possible side effects of a sour-tasting end product. The way in which these sour marinades work is through the breakdown of proteins or peptides[21] into amino acids by the action of enzymes (proteolysis) while at the same time increasing the conversion of collagen to gelatin. The pH value is also important in the swelling capacity of the meat as both high and low muscle pH, positively effects the water binding capacity and swelling of the myofibrillar proteins. This means that since an increase in WHC on either side of neutral pH is seen in myofibrillar proteins that mean alkalis solutions will also have tenderizing properties. This can be observed especially in the tenderization of meats in Chinese and Indian cookery. While generally not adopted in Western cuisine, an alkaline solution of say sodium bicarbonate or sodium phosphate has been seen to improve the WHC and color in pork and increased solubility of myofibrillar proteins (Barham et al., 2010). Comparing sodium bicarbonate with the effects of salt and phosphate[22] (also common tenderizers in the food industry), it has been shown that a considerably higher yield together with a decrease in shear force[23] can be readily achieved.

Another chemical way of tenderizing meat is by using protease[24] enzymes, specifically, papain (from papaya), actinidin (kiwi fruit), bromelain (pineapple), ficin (figs), bacillus protease (*Bacillus subtilis*), and aspartic protease (*Aspergillus oryzae*). As a bonus, enzymes increase the rate at which normal cellular reactions occur, so certain enzymes help denature the protein network of tough meat. They help break down muscle fiber proteins into their constituent amino acids. However, temperature is probably the most important (and controllable) factor influencing enzymatic activity here. Most of the exogenous[25] enzymes used to tenderize meat have an optimal activity in the range of 50–70°C/122–158°F. This means most enzymatic activity actually takes place during the cooking process especially if slow cooking in moist heat. The pH of the meat will also influence activity of the enzymes, so while most optimally work inside the normal pH range in meat, some function best either side of

[21]Peptides are biologically occurring short chains of amino acids.
[22]Phosphate is a salt or ester of phosphoric acid.
[23]Shear force is the pressure of pushing one part of a body in one direction and another part of the body in the opposite direction.
[24]Proteases speed up the breakdown of proteins.
[25]Exogenous in this sense means developed from external substances.

meat normal range for optimal protein degradation. Once again, many of the enzymes do not penetrate into the meat, so injection is also an option here (Calkins and Sullivan, 2007).

Brining is another method used to tenderize, moisten, and flavor meat. Brining involves placing meat into a solution of salt water for a couple of hours to a few days depending on how much salt is in the brine (the more salt, the less time). Then, through osmosis, the brine penetrates deep into the flesh. This means water flows from a lower concentrated salt solution—the meat cell—to a higher concentrated solution, the brine or marinade. When meat is marinated in a brine, the meat's cell fluids are, at first, less concentrated than the brining solution, so moisture is initially drawn out of the meat cells and replaced with the salted brine. However, the salt solution then dissolves some of the fiber proteins, and the meat cell fluids eventually become more concentrated in the process. As this happens, so the osmotic action is reversed, and moisture or the flavored brining liquor is drawn back in until equilibrium is met, both within and without (Brown, 2014; McGee, 2004). Brining essentially affects meat in two ways. Firstly, while in the cells, salt dissolves some of the support structure of the fibers preventing some coagulation of proteins during cooking, and secondly, brining allows for the absorption of between 10% and 25% of the brined meat's weight of the flavored brining liquid (Baldwin, 2012)

12.9.5 CARCINOGENICS

There are certain cooking processes like the browning and Maillard reactions (Section 5.1.2) that, as we have seen, transform proteins and other molecules in meat into highly reactive products that potentially damage DNA. This, it is understood, can possibly initiate the development of cancers. However, when it comes to cooking, the Maillard and browning reactions provide us great flavors to devour. The prudent rule for cooking meat then would be to minimize the creation of potential carcinogens by steaming, braising, and poaching rather than grilling, dry roasting, or frying. Once again being prudent, if one does use high, dry heat, then consider using a marinade whose moistness and acidity reduce carcinogenic production (Belitz et al., 2009; Everts, 2012).

12.9.6 THE FINAL WORD

From the preceding sections, we can say that meat is a complicated biochemical foodstuff that requires knowledge and understanding if one is to utilize it to its fullest potential. Meat too is not a homogenous substance; instead, it is a conglomeration of blood, a variety of tissue types comprising dozens if not more proteinaceous molecules. It is also heavily processed before it reaches the cook's kitchen, and numerous considerations of quality need to be considered in order to ensure consistency, humane practice, and eatability of meat.

It is both nutritious and flavorful if cooked well, although we can say that there is no ideal cooking method for all meats. Instead, methods must be tailored to particular cuts of meat's characteristics and the desired outcome. Indeed, cooks, whether home or professionally trained have been cooking meats to perfection for eons. As a result, the composition of meat on the plate can vary quite considerably. Indeed, what works for one cook might not work for another. So, with a dash of experience, a smattering of luck and a sprinkling of serendipity, common sense must prevail. Cooking, it seems, is an art form that is backed up, in certain areas by science and in other areas by experience and intuition.

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Fish and shellfish were once plentiful and inexpensive; nowadays, however, due to the increased popularity and more efficient, sophisticated fishing techniques, as well as the development or degradation of many coastal areas, demand has begun to outstrip supply. Not surprisingly, this has had an upward push on prices where once common fish like the humble cod are now prized and costly. These factors have caused many countries to pass regulations limiting commercial fishing in specific waters and introducing incentives in new start-ups like aquaculture—the farm raising of fish—to help ensure reliable sources of fresh fish for the long term. Fish and shellfish are foods from the voluminous oceans, whose depths can plunge as much as 7 mi down. So, it should come as no surprise that of all the foods we consume, fish and shellfish are the only foods that we still harvest in substantial quantities from the wild. This is despite a growing fish-farming sector that sees an increasing abundance of fish being farmed. Not surprisingly, today, more than a third of the salmon eaten in the world is farmed in Europe and North and South America, while about a third of the world's warmwater shrimp harvest is cultivated mainly in Asia. All in all, about 70 species of fish and shellfish are now regularly farmed worldwide.

When it comes to aquaculture, there are several advantages in farming practices over naturally caught fish. First and foremost, it allows the producer unparalleled control over the conditions by which the fish live and are harvested. Both of which can result in a better-quality product in the market place. Further, fish and shellfish species can be carefully chosen for particular traits, namely, rapid growth, robustness, and the ability to be raised at a uniform and ideal stage for eating. Indeed, by adjusting water temperature, flow rate, and light levels, fish and shellfish can be encouraged to grow far more rapidly than in the wild. Having said that, there are unhealthy practices and producers of farmed fish who, as with meat, take shortcuts and use unethical practices. Furthermore, aquaculture itself is not a perfect solution. Modern aquaculture is still in its infancy, and ongoing research has identified a number of serious problems. Farming in offshore pens, for instance, can contaminate the surrounding waters with fish wastes, antibiotics, and unconsumed food. It also allows any genetically enhanced fish that escape to dilute the diversity of already endangered wild populations. Also, a less serious issue but one that is still important in the kitchen is that the combination of restricted water flow, limited exercise, and artificial feeds seems to affect the texture and flavor of farmed fish. In other words, they are seemingly not as fit as their free-swimming counterparts. This, some say, results in fish that is blander in taste and softer in texture. If, however, the welfare of the fish is strictly observed and catered for, then farming fish might well turn out to be the predominant practice of the future.

In short, the increased value of seafood demands that a cook be familiar with a wide variety of fish, shellfish, and their sources; be able to select fish and shellfish of the best quality; and understand the best cooking method or methods to use in their preparation.

13.1 FISH ANATOMY/MORPHOLOGY

While fish and shellfish share many common traits, anatomy is not one of them. The main difference being of course is that fish are vertebrates (with backbones) while shellfish are invertebrates (backboneless). For millennia now, the basic shape of the average roundfish[1] (Fig. 13.1) has changed very little; that is, a streamlined shape that minimizes water's resistance to their movement while maximizing

[1]Roundfish is a general term used to describe the oval/rounded fish as compared with flatfish.

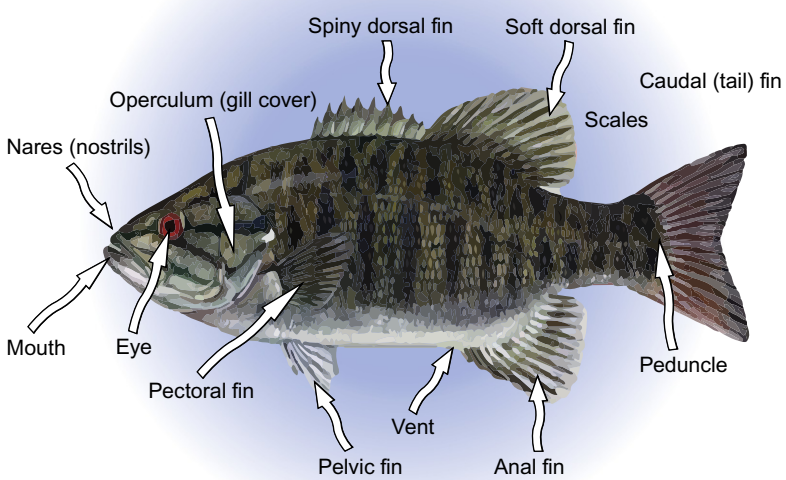


FIG. 13.1

External fish anatomy.

propulsion through their tails (caudal fin). Of course, there are just as many exceptions to this rule as there are members, but it serves to illustrate fishes' exemplary evolution. Round- and flatfish will usually have a configuration of fins whether spiny or fleshy, dorsal or pectoral, or both. Most have eyes, some are blind, and some have teeth, while others do not. In fact, the variation is diverse and complex especially when we are talking about 33,000 varieties of fishes in total (Fig. 13.1).

The skin consists of a thick underlying dermis that is rich in connective tissue comprising approximately one-third collagen and a thin outer epidermis, which are great in fish stocks.[2] In the epidermis, there are a variety of cells that secrete chemicals, usually for protection. Perhaps the most obvious of these is the slimy protein-filled mucous that can be found on many fresh fish. Also on the skin, one finds the scales, made of the same tough calcareous minerals as teeth. Scales also come in numerous shapes and configurations too (McGee, 2004).

13.1.1 BONES/CARTILAGE AND INNARDS

The main skeleton, whether (cartilage or bone) of a fish, consists of a backbone and rib cage. As well as this, there are often small so-called pinbones that help with support and aid in directing energy through the muscle of the flesh. A skilled cook can often remove the fillet in one piece and then extract the pinbones and any bones/cartilage projecting into the fins with minimal damage to the flesh.

[2]The skin is good for fish stock as the flesh can be as little as between 0.3%–3% collagen.

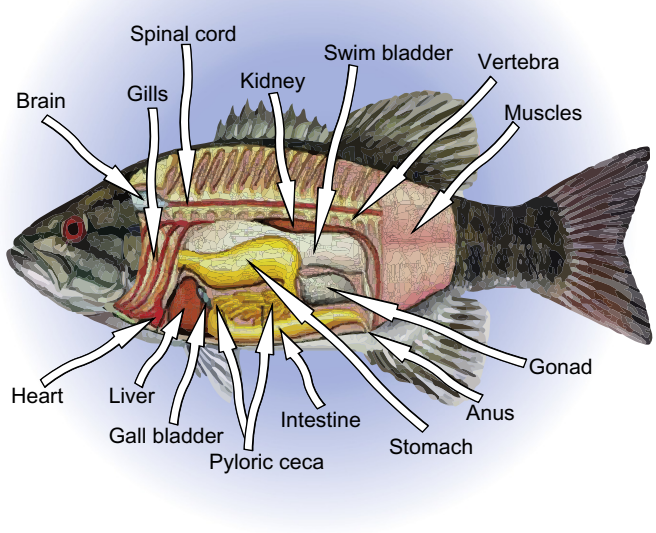


FIG. 13.2

Internal fish anatomy.

Fish innards need not always be wasted (Fig. 13.2). The obvious one that comes to mind is the various fish eggs and caviar (Section 13.11.5). After the eggs, the livers are also prized in various regions around the world; these include red mullet, monkfish, mackerel, some rays, and the cod family. Furthermore, the tongues of carp and cod plus the heads and the swim bladders[3] of many other fish are considered delicacies by many. Fish heads are often eaten in Asia by themselves either in a soup or casserole or fried until crunchy.

13.1.2 MUSCLE AND COLLAGEN

Because of the density of water, fish easily obtain neutral buoyancy from the swim bladder and the lighter-than-water fish oils in their bodies. This means that the fish need not work so hard to move from area to area. This also gives rise to a smaller skeletal frame, a delicate assembly of connective tissue and large, pale muscle mass.

In animals (Section 12.1.1), muscle fibers can be many inches long and are bundled together surrounded by tough collagen. By contrast, fish have more muscle meat than any other vertebrate (as much as 70% in some fish). Fish muscles are only a fraction of an inch thick called "myotomes," which in turn merge into very thin layers of connective tissue fibers called "myosepta." These run from the backbone to the skin. The muscle sheets are folded upon themselves into the familiar "flakes" we see when eating fish and are separated (as mentioned) from their neighbor by a sheet of connective tissue. The amount

[3]Swim bladders are balloons of connective tissue that fill with air or gas to adjust the fishes' buoyancy.

of muscle sheets can vary from a handful to about 50 or so along the length of a cod. Furthermore, like land animals, fish muscle tissue also serves as an energy store that's constantly being built up and broken down; the difference being is that in land animals, muscle tissue becomes reinforced and therefore tougher with age whereas fish muscle remains tender. In dark fleshed fish, the muscle fibers are thinner and require more connective tissue to keep the fish meat together. As a result, fishes' dark meat has a markedly finer, more gelatinous texture.

When it comes to connective tissue in fish, we can generally say it is structurally weak because its collagen contains less structure-reinforcing amino acids than beef and other animal collagens. Also, while meat collagen (depending on which animal and which cut) must be cooked for some time close or near boiling point to be liquefied into gelatine, most fishes' collagen dissolves at about 50–55°C/122–131°F. As has been discussed, both dissolved collagen (gelatine) and fat can and do contribute to the impression of moistness in the mouth. However, there are many fishes like the trout and sea bass that contain very little collagen; this gives rise to the feeling of dryness. This can be combated with cream or butter sauces in cooking for a more moist mouthfeel.

During swimming, fish use the back end of their body; as a result, the tail region contains more connective tissue than the head end. And as with meat fish, connective tissue (mostly collagen) makes the back end seemingly more succulent. Fat content varies greatly from species to species and can range from 0.5% in cod and monkfish to as much as 20% in mackerel or herring. Fish fat can be found usually directly under the skin and in the belly area, while muscle sections become increasingly leaner toward the back end by the tail. Interestingly, a center cut from say salmon may have as much as twice the fat content of a slice closer to the tail.

13.2 SPECIES IDENTIFICATION

The identification of fish can be somewhat daunting. Unlike meat livestock whereby the total number of common species the world utilizes can be counted on two hands, the volume and variety of fish that humans regularly consume around the world number in the thousands. This makes identifying the food we eat from this food group a whole different "kettle of fish"—so to speak.

So, with so many species of fish, identification is a challenge at the best of times. Compounding this problem is the fact that many fish have two names, a Latin name and a "common" name. As far as common names go, many fish are known by one name in one region and yet another in another region. With many countries and fishing fleets operating within the same waters as their geographic neighbors—especially in the diverse and densely populated Pan-Asian region, some species of fish might be known locally by several different colloquial names and yet another when describing the fish to a nonlocal. Take the cod fish—the Gadidae family—for instance. True codfish such as the grayfish, codling, *Gadus ogac* and uvac, and related species including the Arctic cod, codlet, and rock cod are all species of the cod (Gadidae) family. Yet, wholly unconnected fish going by such names as ling, Maori cod, reef cod, and trout cod are from different species altogether. Some of these names arise out of profiteering where marketers have adapted the names simply in the hope of cashing in on the popularity of the true cod fishes. Others are innocently confused by the plethora of alternative common names. Either way what is left is a legacy of misunderstanding among both professionals and laymen alike. Couple this with the sheer variety of fish on offer and it is not surprising that confusion abounds.

There are of course those fish that are used far more commonly than others, and in time, students and professionals will gain a rudimentary understanding of various fish and their groupings.

13.3 CLASSIFICATION AND IDENTIFICATION

Waterborne animals are broadly divided into two categories: fish and shellfish. At its very simplest (although there are exceptions), fish can generally be thought of as vertebrates with fins and gills, while shellfish are invertebrates—usually with shells but can also exist without.

Fish themselves are classified or categorized in several different ways, scientific classification aside for the moment, some of the more common systems are described below:

- *Freshwater and salt water*—fish are sometimes separated into freshwater and salt water. With freshwater fish, due to being less buoyant than salt water, one often sees a network of tiny, light bones throughout the flesh. Saltwater fish, on the other hand, usually contain fewer thicker bones.
- *Fat content*—fish can also be further divided into categories based on the fat content. Lean fish, often called whitefish, tend to be lighter in color and milder in flavor. However, as the fish becomes oilier (called oily fish), the flesh firms up, darkens, and is usually characterized by a stronger, more distinctive, or assertive flavor.
- *Round or flatfish*—another way of categorizing fish is by their physiological structure, i.e., round or flat. Flatfish have evolved and adapted, often specializing in swimming along the bottom of the sea. Flatfish are oval-shaped with dark skin on top and paler skin underneath. It is also not uncommon to have both eyes on the topside of the body. Roundfish on the other hand have round or elliptical bodies with eyes on opposite sides of the head and swim at all depths of the sea.
- *Pelagic and demersal*—this category defines areas of the water column in which the fish are usually found. Pelagic fish live and feed near the uppermost surface of coastal, ocean, and lake waters—in fact, most pelagic fish can be found within the 200 m epipelagic range. These fish are generally streamlined and agile making them good swimmers. They range in size from small sardines to giant tuna and sharks. Demersal fish, from the Latin word meaning "to sink," are bottom dwellers and found living and feeding on or near the bottom of seas or lakes (with the exception of the deepest of seas). Both pelagic and demersal fish can be found in both coastal (inshore) and oceanic (offshore) waters (Fig. 13.3), (Belitz et al., 2009).

On top of the above, there is of course the scientific classification system. From a scientific standpoint, each fish has its own name and is readily identifiable within a formulative system that classifies and names all organisms. This is called taxonomy—in this case Linnaean taxonomy. The system comprises different levels in a hierarchical grouping of common traits—these are the following: *domain*, *kingdom, phylum, class, order, family, genus, and species.*

Within this system, fish belong to the *kingdom Animalia* and the *phylum Chordata*; from here, all fish then belong to one of two *subphyla*—the Craniata and Vertebrata. After this each group of fish can then be assigned to a specific *class*, *order*, *family*, *genus*, and *species* (Benton, 2004; Nelson, 2006). So, from this, we can see that fish have been traditionally classified within the following structure:

- *Kingdom* ***Animalia***
  - *Phylum* ***Chordata***
    - *Class* Agnatha (**jawless fish**)
      - *Subclass* Cyclostomata (**hagfish and lampreys**)
    - *Class* Chondrichthyes (**cartilaginous fish**)
      - Subclass Elasmobranchii (**sharks and rays**)
      - *Subclass* Holocephali (**Chimaeras**)

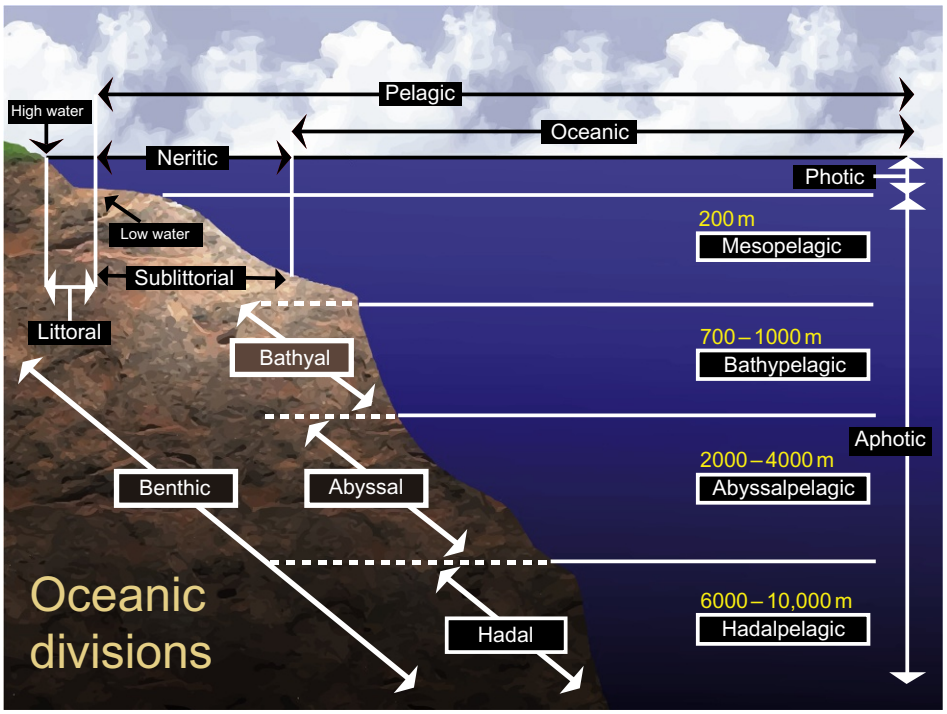


FIG. 13.3

Oceanic divisions.

- *Class* Acanthodii (**spiny sharks**, at times classified under bony fishes)
- *Class* Osteichthyes (**bony fish**)
  - *Subclass* Actinopterygii (**ray-finned fishes**)
  - *Subclass* Sarcopterygii (**lobe-finned fishes**)

13.3.1 BONY FISHES (OSTEICHTHYES)

These fish are a group of aquatic vertebrates that, in contrast to skeletal cartilaginous fishes, have bony skeletons. The class of bony fishes includes two subclasses; the ray-finned fishes and the lobe-finned fishes. As a subclass, it is the ray-finned fishes that have more numbers (close to 30,000) and a variety of species; compare these with the lobe-finned fishes that number a modest eight species. Bony fishes share similar characteristics in their skeletal structure including the pattern of their cranial bones, the structure of their lower jaw, the bones supporting their eyeballs, and the configuration of their pectoral girdles (*see* Section 13.1). Bony fishes also have the ability to view the world in color, and most species of bony fishes possess swim bladders: an oxygen (usually)-filled digestive sac that helps stability and buoyancy as the fish swim through the water (Belitz et al., 2009; Froese and Pauly, 2015).

All bony fishes have gills although not all use them as their primary source of oxygen for respiration. Indeed, some species can breathe through vascularized swim bladders or through lungs, while a few more can effectively respire through thin membranes like the skin, the intestine, or even the stomach. Most bony fishes too are cold-blooded, meaning their body temperature is determined by its warm-water or cold-water environment. Although we say most, there are in fact a few species like tuna and swordfish that have evolved some ability to regulate their own body temperature (endothermic). The largest bony fish is believed to be the ocean sunfish (*Mola mola*) that has been said to grow to 11 ft long. The smallest however is understood to be the dwarf pygmy goby (*Pandaka pygmaea*) that grows to a length of just one-third of an inch.

Bony fishes survive in a wide range of different habitats of different water temperatures, salinity, and oxygen capacities. And some species have even been known to migrate between fresh and salt water (*diadromous*). Indeed, some species like the salmon migrate from salt water to freshwater in order to spawn, while other species such as freshwater eels migrate from freshwater to salt water in order to spawn (Klappenbach, 2017).

Bony fishes are generally divided into the following taxonomic groups:

- Ray-finned fishes (Actinopterygii)
- Lobe-finned fishes (Sarcopterygii)

13.3.1.1 Ray-finned fish—(Actinopterygii)

Ray-finned (*Actinopterygii*) fish are named after their fins that are supported by rays of bony spines that in turn are supported by bony spines rather than the fleshy alternatives of the lobed-finned fishes. They are a diverse group of bony fishes forming the largest group in this class with an estimated 25,000 species to their name.

Ray-finned fish have a true bony skeleton, and they have an upper jaw that consists of two bones that allow the upper jaw to easily extend. The class of fish itself ranges from the tiny 8 mm gobies to 4 m long sturgeons (*Acipenser huso*). Ray-finned fishes are remarkable in their flexibility of habitat. They can inhabit both marine and freshwaters, from deep-sea caves (7000 m) to turbulent rivers, even desert springs and high-altitude lakes. They can also comfortably survive in water temperatures between −1.8°C and 40°C (28.7°F and 104°F), in water salinity ranging from 0 to 90 ppm and in pH values ranging from 4 pH to 10 pH. In fact, it is this very flexibility that has allowed this class of fish to survive and thrive (Klappenbach, 2017; Froese and Pauly, 2015).

Among the 46 groups (*order*) of ray-finned fishes are the mullets, puffers and filefishes, flatfishes, perch-like fishes, scorpion fishes and flatheads, spiny eels, pipefishes and seahorses, dories, whale fishes, needlefish, silversides, anglerfishes, cods, trout, salmon, pikes, catfish, carps, herrings, eels and morays, and sturgeons, among others (Froese and Pauly, 2015; Parr et al., 2014).

13.3.1.2 Lobe-finned fishes (Sarcopterygii)

The lobe-finned fishes are the sister group to the ray-finned fishes. They are characterized by their paired, fleshy pectoral, and pelvic fins that are each articulated via a single bone. Ancestral records clearly show us that terrestrial vertebrates evolved from lobe-finned fishes nearly 400 million years ago. Lobe-finned fishes share common ancestors with tetrapods[4] and are very limited in their group,

[4]Tetrapods are four-footed animals.

with only three *orders* of fishes including the coelacanths, the South American and African lungfishes, and the Australian lungfishes (Klappenbach, 2017; Froese and Pauly, 2015).

13.3.2 JAWLESS FISH (AGNATHA)

There are two groups (*classes*) that fall within the jawless fish category; these are the lampreys and the hagfish. Members of this class do not have a stomach; however, larvae do have a flexible rodlike cord along their bodies called a notochord that supports it during its embryonic stage. This is like the backbone in vertebrates and is there as support for the fish at a crucial stage of growth (Klappenbach, 2017). Once grown, most jawless fish have a skeleton made of cartilage and paired gill pockets (in some cases as many as seven). Being jawless, lampreys still have cartilaginous teeth and most being parasitic latch on and suck tissue and fluids from any fish they are attached to. Hagfish on the other hand are completely blind and have a set of tentacles around their mouth that they use to search for food—marine worms and other invertebrates. The hagfish is a slime-producing fish, which it uses for protection. It also has a really low metabolism and can therefore go for as long as 7 months without eating (Parr et al., 2014).

Lampreys can range in size from 5 to 40 in. and are found in temperate rivers and coastal seas, whereas the hagfish are found in cold ocean waters especially on muddy seafloors often living in large groups. There are around 50 living species of lampreys and about 80 species of hagfish (Parr et al., 2014; Froese and Pauly, 2015).

13.3.3 CARTILAGINOUS FISHES (CHONDRICHTHYES)

Cartilaginous fishes are jawed fish with paired fins and nares (nostrils), with scales and a two-chambered heart. Their skeletons are made of cartilage rather than bone. The class is divided into two subclasses: sharks, rays, and skates (Elasmobranchii) and Chimaeras (Holocephali), sometimes called ghost sharks and separated into a class of their own. This class of fish is subdivided as follows:

- Sharks, rays, and skates (Elasmobranchii)
- Chimaeras (Chimaeriformes)

13.3.3.1 Sharks, rays and skates (Elasmobranchii)

Between them, sharks, skates, and rays form a group of between 800 and 1150 species of ocean- and freshwater-dwelling fish. From the giant whale shark and the enormous manta ray to the tiny short-nosed electric ray, elasmobranchs come in many shapes and sizes. Despite their shape and size though, all living elasmobranchs share certain common key features. Firstly, their skeletons are made of cartilage rather than bone. Another characteristic is the fact they have rows of replaceable teeth and the five to seven gill slits on each side of their body. Further, many share the capacity in being able to perceive tiny changes in electric current around them that for some elasmobranchs is used to seek out prey making them effective hunters. This current is also used for directional purposes, while in a few others, it has been speculated that this sense might be used in various social and mating rituals (Parr et al., 2014). Oftentimes, the elasmobranchs are the top predators in their respective food chains, however, because they grow slowly as a general rule and reproduce late in life so they produce few offspring, and have trouble recovering quickly from population decline caused by overfishing (Parr et al., 2014).

13.3.3.2 Chimaeras (Chimaeriformes)

The main traits of this group are, as with sharks, skates, and rays, the fact they share a cartilaginous skeleton. They also possess no lungs or gas bladder, but instead, they rely on a large, buoyant liver. Further, because they fertilize internally, they lay large eggs. External identification characters include a large, single gill flap that covers four internal gill openings. Chimaeras have two dorsal fins, and their first dorsal fin is a "…poison-laden spine, which is erectable" (Froese and Pauly, 2015). They also have thick "front-end" bodies that taper to long thin tails and grinding tooth plates in their jaws; as such, chimaeras are largely bottom feeders grinding mollusks and crustaceans crushing them with their tooth plates (Klappenbach, 2017). Chimaeras are generally found in temperate deep ocean waters and range in size from 1 to 5 ft. There are around 50 species in this order of fish (Froese and Pauly, 2015).

13.4 FISH COLOR

If one has ever looked closely at the underside of fish skin, one sees a layer of dark meat. Also, if the fish has been too skillfully skinned, one might also see this dark meat on the flesh. These are the dark and pale meats of fish. They possess two colors for the following reasons. We have already established that because of the fishes' buoyancy, the necessity for thick, strong fibrous cells is not needed. So, unlike land animal meat, much of the fish we eat is white, pale, or translucent. This is because continuous cruising requires long-term stamina by the fish, which in turn is provided by so-called slow-twitch red fibers (see also Section 12.1.1.4), well supplied with the myoglobin (for oxygen) and fat (for fuel). Since being neutrally buoyant, cruising is relatively effortless, so fish only need to devote a small proportion of their overall muscle to the task. This is the dark meat—usually a thin layer found under the skin as described above. Having said that, when accelerating, whether for predatory or flight purposes, the fish must generate a quick burst of energy just long enough to find its prey or its safety. For this purpose, fish have developed what amounts to an emergency power pack of white muscle mass capable of occasional bursts of rapid movement—these are the fast-twitch white muscle cells that are the bulk of the fish. The different proportions of white and dark meat within fish are an indication more of the fishes' way of life than anything else—tuna, for instance, whose constant fast-paced lifestyle requires a larger proportion of slow-twitch red fibers compared with that of say a lemon sole.

In sum, when it comes to color, it can be seen that most of the muscle in pale fish, an off-white almost translucent, then becomes opaque upon both cooking and/or marination in acid. In meatier red fish, the color comes from the same oxygen-storing pigment myoglobin found in land animals. As with meat, so fish myoglobin is particularly susceptible to oxidation turning it into the brownish metmyoglobin.[5] This is especially so at freezer temperatures as low as −30°C/86°F. In fact, tuna needs to be kept well below this temperature in order to keep its color.

Orange salmons's characteristic color is due to the chemical relative of the carrot pigment—carotene. This compound, astaxanthin, comes from the salmons' diet, more specifically from the small crustaceans they prey on who in turn obtain it from the beta-carotene they acquire from their diet of algae. Although astaxanthin is not particularly uncommon in fish (many store it in their skin and ovaries), it is only the salmon family, however, that tends to store it in their muscle. Their farmed cousins however do not have

[5]Metmyoglobin is the oxidized form of the oxygen-carrying heme-protein myoglobin.

access to wild crustaceans, so they tend to have paler flesh—unless of course their feed is supplemented with crustacean shell by-products or the industrially produced carotenoid (*canthaxanthin*).

13.5 HOW MANY FISH?

So how many fish species are there? In fact, there are numerous figures being bandied around regarding the number of fish in the seas and rivers, too many in fact to cite here. However, a recent 10-year study highlighted the breadth of marine species and put a total estimate in the region of more than 230,000 species in our oceans (COML, 2010). However, this might be somewhat misleading as the study also included such species as plankton, birds, sponges, sea worms, and sea slugs. Stripping all of these out there is in fact approximately 25,000–33,000 fish in our seas (depending on, as so much else, who one reads), with a good estimate coming from two sources: the first "FishBase"—global information system on fish with a searchable database containing information on 25,585 *species* and secondly the California Academy of Sciences Institute for Biodiversity Science and Sustainability Catalog of Fishes by Eschmeyer who suggests that there are 17,535 salt water and 15,467 fresh fish (Eschmeyer, 2014).

13.6 SHELLFISH

Shellfish is a common term used to describe any aquatic invertebrate animal that often, but not always, has an exoskeleton shell. This includes various species of mollusks, crustaceans, and a few echinoderms. While most shellfish are harvested or gathered from salt and brackish waters, some are in fact found only in freshwater (Britannica, 2016).

There are three main groups of edible Shellfish; they are the following:

- *Mollusks*—which include seven varieties of which we are interested in only three—bivalves, gastropods and cephalopods
- *Crustaceans*—comprising nine varieties of which we are mainly interested in three—amphipods, stomatopods, and decapods
- *Echinoderms*—which altogether include seven varieties of which we are interested in three—Echinoidea Holothuroidea, and Asteroidea

When it comes to marketability, we can say that among the mollusks, oysters, mussels, scallops, and clams as well as abalone, whelk, and conch, octopus, squid, and cuttlefish rank among some of the most commercially important seafood in the world. On top of this, the main crustacean varieties traded around the world are shrimp, prawns, lobsters, and crabs, while among the echinoderms, the most popular are the sea urchins and sea cucumbers.

13.6.1 MOLLUSCS

Mollusks are a group of invertebrates belonging to the bivalve, gastropod, and cephalopod groups of shellfish[6] that include snails, slugs, limpets, squid, octopuses, cuttlefish and mussels, clams, oyster, and scallops as well as many lesser-known animals. Scientists estimate that there are between 50 and

[6]Shellfish can be a little misleading as not all members have a shell or an exoskeleton.

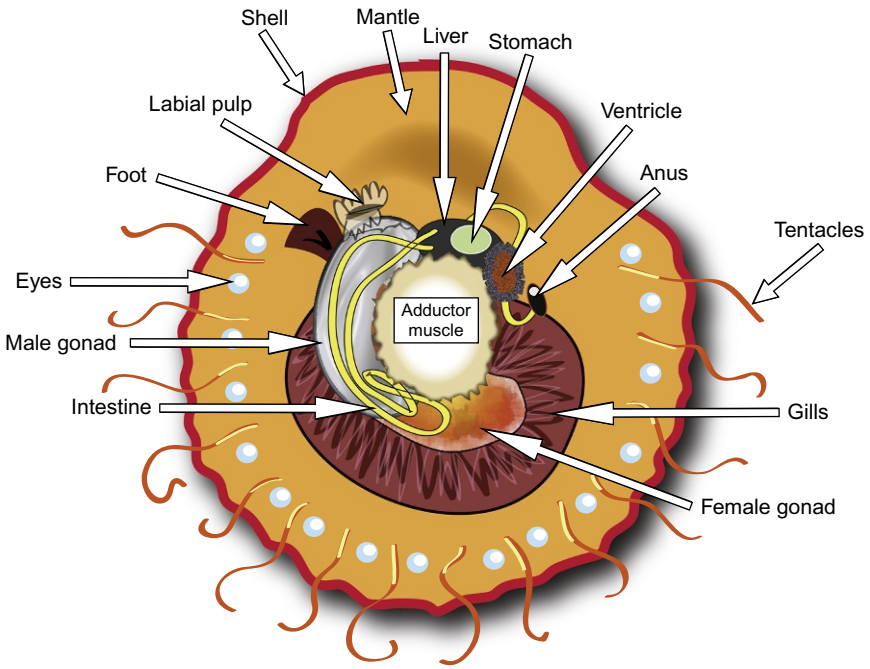


FIG. 13.4

Inside the scallop shell.

120,000 or so species of mollusks alive today (Chapman, 2009; McGee, 2004). While some mollusks have protective shells, they are not multijointed, they are either single shelled or bivalves. Their shells are made of chitin, proteins, and calcium carbonate. Because mollusks are so varied anatomically, oftentimes, one might come across textbooks describing a single hypothetical "mollusk" displaying several features common to many species. In this book, we take the same approach. So, talking generically, we can say that mollusks have soft bodies comprising three basic parts: a foot, a visceral mass, and a mantle; however, for the sake of illustration purposes, however, we have used the scallop as our sample mollusk (Fig. 13.4).

As far as the anatomical structure of the token mollusk's three main components, the following can be said:

- *The foot*—it is a muscular structure located on the underside of the body and secretes mucous to lubricate the underlying surface enabling better movement of the animal.
- *The visceral* mass—it is located below the mantle and above the foot that contains the animal's organ structure, the digestive system, the heart, the liver, and other internal organs. The circulatory system usually comprises a single pair of gills to breathe, although some species (terrestrial slugs and snails) have rudimentary lungs.
- *The mantle*—it is a layer of tissue that shelters the visceral mass, and in many mollusks, it contains glands that secrete the hard shell, supports eyes, and has small tentacles that can either detect food or danger, and being able to contract and relax in order to control the flow of water into the interior.

13.6.1.1 Gastropods

Previously known as univalves, gastropods include some very familiar organisms. Along with bivalves, they are also one of the most diverse mollusk groups. The word itself is a combination of the Greek words "Gastir" meaning stomach and "Podi" meaning foot, "stomach footed." These can sometimes be quite large and are used for crawling along. They typically have a well-defined head with two or four sensory tentacles with eyes. Except for slugs that nearly all have an outer shell (sometimes called a valve) that can be both small and large conical, twisted, or simply cone shaped. Of the numerous species, available small example includes snails, sea snails, rock snail, bubble snail, mud snail abalone, black-lip abalone, green abalone, red abalone, white abalone, green ormer, limpets, winkles, periwinkles, conchs, whelks, channeled whelk, lightning whelk, knobbed whelk, tooth shells, worm shells, and vermetids (worm snails), sundial shells and sea hares, to name but a few.

13.6.1.2 Bivalves

Bivalves are mollusks with a two-part hinged shell (called valves) that encloses and protects the delicate body. Water is passed through a sheetlike gill allowing it to breathe, while most bivalves including clams, mussels, oysters use their comblike gills for filtering food particles out of the water that the mantle sucks in and expels. Also by opening and closing the bivalve shell very quickly, an efficient propulsion system allows some bivalves to move about. Others just attach themselves to stable objects and never move. Bivalves also inhabit both marine and freshwater environments. Among the bivalves, we have the quahogs, cherrystone, top-neck and soft-shell clams, oysters, mussels and scallops, clams, razor shells, cockles, venus shells, borers, arcs, among numerous other families.

13.6.1.3 Bivalves' adductor muscle

The adductor muscle in bivalves (Fig. 13.4) performs two jobs. The first is to very quickly close the shell to expel sediment, waste products, and eggs or simply to keep predators at bay. The other is to keep the shell tightly closed for hours or even days until any danger passes. These two jobs are completed by adjoining parts of the same muscle. The fast contracting "quick" part of the muscle (similar to the fast-twitch muscles of fish) is white, translucent, and relatively tender when cooked. By contrast, the slow, tension-sustaining "catch" portion of the muscle is among the strongest muscles known. The catch muscle is a smooth muscle that usually makes up part of the adductor muscle in bivalve mollusks, this in turn allows the valve to remain closed while utilizing less energy (Galler et al., 2009). Indeed, with very little energy expenditure, the "catch" muscle can maintain its contraction by locking the muscle fibers with connective tissue (collagen). Catch muscles are very much like the tough tendons in a chicken or lamb leg that means they are also tough to eat unless cooked for a long period of time. It is for this reason (in the scallop especially) that the small catch muscle is usually cut away.

13.6.1.4 Cephalopods

There are only two of the original three groups of cephalopods alive today, the Nautiloidea (nautiluses) and the Coleoidea (squids, cuttlefish, and octopuses). Overall, there are about 650 species of cephalopods thriving today, and they are without doubt the most advanced of the mollusks. The cephalopods are carnivores with large eyes and arms. They appear to be mollusks turned inside out where the mantle is on the outside acting as a specialized muscular sheet of flesh that expands and contracts

providing jetlike propulsion through a small funnel derived from the foot muscle. The octopus, species, has eight arms grouped around its mouth with which it scrambles along the sea bottom where it hunts for prey. By contrast, the cuttlefish and squid have short arms with two long tentacles (Belitz et al., 2009).

13.6.2 CRUSTACEANS: SHRIMPS, LOBSTERS, CRABS, AND RELATIVES

Crustaceans are shellfish that have segmented external skeletal support systems with jointed legs and other appendages and sometimes claws. This exoskeleton supports the muscle, internal organs, and the head sac. Common varieties include lobsters, crayfish, shrimps, prawns, and crabs and the lesser-known barnacles, pill bugs, amphipods, copepods, krill, sea fleas, clam shrimps, and fairy shrimps, among many others. In fact, today, there are between 30 and 70,000 species of crustacean (depending on who one reads) (Meyer, 2006; Arthur and Arthur, 2014; McGee, 2004). Crustaceans form part of the group of organisms called arthropods; not surprisingly then, crustaceans are relatives of insects. Most edible crustaceans are from a group called "decapods," which means they have five pairs of legs, although sometimes one pair is enlarged into claws.

When it comes to anatomy, nearly all crustaceans share the same basic body arrangement that can roughly be divided into two main components. The forward portion (in some animals, this means just the head) called the *cephalothorax*. The *cephalothorax* includes the mouth, any sensing antennae present, its eyes, and the five pairs of crawling legs or appendages as well as the main innards—the organs of the digestive, circulatory, respiratory, and reproductive systems. The rear portion, the abdomen, sometimes simply called the "tail," is largely the meaty swimming muscle that moves the finlike plates at the end of the tail. Of course, there are exceptions, and perhaps, the major exceptions to this body layout are the various crabs. Crabs rarely swim, so its abdomen is devolving, and one can find it tucked away on the underside of the enlarged *cephalothorax*. It has been said that the liver is the most important part of the crustacean as this is where the enzymes are released to digest food and where the fat is stored. From a flavor-aroma perspective, this is very true; consequently, it is one of the richest and most flavorful parts of the animal and is particularly prized in crabs and lobsters. However, the liver is also what allows crustaceans to spoil so easily.

The liver is made up of tiny, fragile tubes, and when crustaceans are killed, the tubes are subsequently attacked and damaged by their own enzymes. This then spreads into the muscle tissue and breaks it down into a mushy-like substance. Having said that there are several ways one can slow this process or even avoid it altogether. With lobsters and crabs, they are sold either live or cooked. In both cases, there is no problem as their enzymes are either held in check (if alive) or the enzymes are inactivated by the cooking. The shrimp's liver on the other hand is relatively small and is found in the head section (*cephalothorax*). This is why when buying fresh or frozen raw prawns and shrimps, these are often sold headless. Once again, this is not always the case as one can still buy "head-on" prawns—both fresh and frozen; in these cases, they must be handled with greater care.

13.6.2.1 Molting and seasonal quality

One more defining trait of most crustaceans is the shell or "cuticle" that, as mentioned before, is made of chitin. In shrimp, the cuticle is lean and transparent, while in larger crustaceans, it tends to be a thicker, more opaque, and hardened mass with calcium minerals filling the gaps between chitin fibers.

As crustaceans grow, so they periodically cast off the old cuticle in order to create a bigger more comfortable shell in a process called molting. It does this by creating the new shell that is at first soft and leathery. It then squeezes itself out of the old shell and pumps up its body with water to between 150% and 200% its original size. This effectively stretches the new cuticle to the desired size that then sets hard in a few days. On the downside, it also means that the quality of the meat at this juncture is very variable. That is to say that an actively growing crustacean has dense, plentiful muscle, while the same crustacean preparing to molt loses muscle; further, a newly molted crustacean may be as much water as it is muscle. In crabs, it is after molting and before the new shell sets that they are taken to the market to be sold as soft-shell crabs.

13.6.2.2 Crustacean color

Crustacean shells provide some of the most vivid colors in kitchens and buffets as well as on the plate. Many are usually a dark green-blue-red-brownish color when alive but change to a deep orange-red color when cooked. The original coloring is a self-protecting mechanism that crustaceans create by attaching bright carotenoid pigments resulting from the plankton in their diet (astaxanthin, canthaxanthin, beta-carotene, and others) to protein molecules that help to mute or alter their color. However, simply cooking the crustacean denatures the proteins in the shell that are then freed up to reveal the carotenoids true color.

13.6.3 ECHINODERMS

In the scientific world, the *echinoderms* have no skeleton—either internal or external; instead, they are sometimes stiffened by hard calcified plates and/or spines just beneath the skin. In the culinary world, few have any real appeal although several do provide popular delicacies. These would be the edible starfish, sea urchins, and sea cucumbers.

13.6.3.1 Sea cucumber

Sea cucumbers live in every marine environment from tidal waters to the deepest channels; they do not live however in fresh water. They have a flexible body comprising both circular and longitudinal muscles and a skeleton made up of calcite particles, called ossicles that tend to toughen the skin. Characteristically, a sea cucumber is a drawn-out cylinder lying on its side, a mouth at one end, and an anus at the other. Along its length, it has five rows of tube feet while around its mouth are usually one or two feeding tentacles, which are actually modified tube feet. Most sea cucumbers are less than 12 in. long and are a popular food item in Asia where they have largely been overfished. This has led to the development of large aquaculture operations in China, Japan, and Australia, among others (Anderson et al., 2011; Purcell et al., 2013).

13.6.3.2 Sea urchins

Spiny sea urchins are members of the echinoderm groups. There are about a half-dozen commercial species of whose average diameter of 6–12 cm. Physically, they are almost entirely enclosed in a sphere of calcified plates that in turn are covered by protective spines. For the most part, the only part of the sea urchin that is eaten is the golden-colored richly flavored reproductive organs/tissues (Pearce et al., 2002). These organs in fact make up the bulk of the tissue inside the body and can account for up to two-thirds of the internal tissue mass. The sexual organs are hard to tell apart, but both the testes

and the ovaries are highly prized. Sea-urchin gonads average 15%–25% fat and 2%–3% savory amino acids, peptides, and IMP (inosine monophosphate[7]) (Politi et al., 2004).

13.6.3.3 Starfish

Starfish are adept at pulling open the shells of bivalves and then exuding their stomach into its shell, digesting the occupant in place. There are not a lot of edible starfish out there, and they are mainly eaten in Asia. Live starfish should be dropped into boiling water for about 4 min and then refreshed in cold water. To eat, simply break off a leg and split it open along the bottom side although its flesh is gray and tends to have little in the way of flavor.

13.7 SEAFOOD AND HEALTH

The common belief and one that is not unfounded is that fish is good for us. Indeed, there is good evidence suggesting that fish oils can significantly contribute to our long-term health. However, a major caveat here is that of all the foods we consume, fish and shellfish are among the widest source of health hazards known to us. From bacteria, viruses, parasites, pollutants, and strange and exotic toxins, cooks and consumers should be aware as to how to choose, handle, store, and cook fish and shellfish in an appropriate manner.

Just like land animals' meats, fish and shellfish are also good sources of proteins, B vitamins, and various minerals including iodine and calcium. Many fish are very lean and so offer these and other nutrients with relatively few calories attached. Even the fish fat/oils of ocean fish turn out to be especially valuable. Ocean fish provide a highly unsaturated[8] fat that, because of its cool environment, turns out to be good for us. This is because oceanic waters are cold, and most fish are cold-blooded, so the cell membranes and energy stores of ocean fish (and the plankton they feed on) must remain fluid and workable at temperatures approaching 0°C/32°F. As a result, the fishes' fatty acids are irregular in structure and do not solidify into uniform crystals until the temperature becomes very low indeed. These unsaturated fats are rich in valuable highly unsaturated omega-3 fatty acids, which is great for the human body.

Omega-3 fatty acids are crucial to the function and development of the brain and for the health of the central nervous system. It has also been observed that a diet rich in omega-3 fatty acids not only helps limit the inflammatory response lowering the incidence of strokes and heart disease but also reduces the risk of cancer. Lastly, it also helps lower the artery-damaging form of blood cholesterol (Vaclavik and Christian, 2014).

Farmed fish mostly have lower levels of omega-3 than their wild cousins. This is because wild fish obtain their quota from phytoplankton, whereas farmed fish on formulated feed usually contain much lower levels and by extension less remains in their flesh. Freshwater fish too do not have access to oceanic phytoplankton and so provide negligible amounts of omega-3 in their meats.

[7]Inosinic acid or inosine monophosphate (IMP) is a nucleotide monophosphate that is important in the process of metabolism.
[8]Monounsaturated and polyunsaturated fats are known by other names omegas. There are three types of omega fatty acids: omega-3, omega-6 and omega-9.

13.8 QUALITY OF FISH AND SHELLFISH

Buying seafood can often be more challenging than cooking or eating it. So, it's worth keeping these little tips in mind when shopping for fish and shellfish. Furthermore, the quality of many fish and shellfish species can vary quite considerably from season to season. This is because they live out life cycles that typically include two phases. During the first phase, fish and shellfish expend their time and energy on growing and maturing. During the growing period, they are actually at their peak in terms of culinary appeal. During maturity, they then expend their collected energy reserves in migration and spawning. At this stage, the animals' muscle mass is being used as an energy supply, so they diminish in bulk and culinary appeal. This is because fish do not store their reserves as fat but rather as proteins in their muscles. So, during migration and spawning, they amass protein-digesting enzymes in their muscle that literally transforms their own flesh into energy and sperm or eggs for the next generation. After this, their muscles are generally "spent" leaving a spongy if not mushy texture to the fish. For these reasons and the fact that different fish have different cycles, they can be in different phases dependent on which part of the world they were caught in and which part of the phase they are in. Indeed, from the market or cook's perspective, there are very few telltale signs, so it's hard for a cook to know until it's too late, i.e., after the fish has been cooked.

13.8.1 FRESH AND FROZEN FISH

Knowing how to select fresh or frozen fish or seafood is an important skill for the student or cook. Unless one catches the fish oneself, there really is no way of knowing exactly how fresh the fish is. But buying fresh need not be fraught with anxiety. Fresh fish have a particular odor, but before we get into that, we can have some general pointers of things to look for. First of all, look at the eyes; they should be bright and glossy, whereas dull-eyed fish may well be safe enough to eat but in truth are past their prime. The next thing to look at is the fish itself; is it clean and shiny? Or does it have discolored or dulled patches on it? If so, it is borderline. Now, look at the gills; they should be bright red, not the shade of rust. And if allowed, gently press the flesh; firm fresh and nonfrozen fish should recover from the pressure leaving no trace of a fingerprint. Lastly, this is where the fun begins, smell it—it should certainly have no pungent aromas. Both fish skin and plant leaves contain enzymes (lipoxygenases[9]) that break down the nonsmelly fatty acids in both fish and plants into the same small, aromatic fragments. This is why fresh fish with between six and eight carbon-catalyzed atom fragments smell of several things depending on species and the arrangement of these atom fragments. The smells range from freshly cut grass; earthy fragments; green, geranium leaves; and slightly metallic smells. Some freshwater and migratory species also produce fragments typical of cucumbers and melons.

Ocean fish, while also reminiscent of crushed plant leaves, often have an added characteristic aroma of the sea. This "aroma note" seems to be provided by compounds called bromophenols. Bromophenols are present in marine worms and in algae. They are believed to cause the typical sealike aroma and flavor of seagoing fish (Belitz et al., 2009; Hassenklövera et al., 2005). This is the same "seaweedy" or sealike smell one gets near the coast as wave action makes these aroma fragments more volatile.

[9]Lipoxygenases are a group of iron-containing enzymes that catalyze the dioxygenation of polyunsaturated fatty acids.

Also, when considering the freshness of the fish, the skin should be moist, and if the fish has scales, they should stick closely to the skin and not be dry or disheveled looking.

Frozen fish should be firmly frozen with no soft patches, and good-quality fish should not really have much of a smell. Avoid fish too with signs of freezer burn, i.e., white and dehydrated. It is also worth checking the inside of the packaging if possible for ice crystals as water moisture can gather from damaged cells or it can be the result of thawing and refreezing. While it's best to thaw in the fridge, placing under cold running water is also an acceptable option.

13.8.2 SHELLFISH: CHOOSING AND HANDLING

Healthy shellfish should be lively and alert, and in the case of bivalves, their shells should be intact and their adductor muscle actively holding the shells tightly together. When buying fresh bivalves in the shell, they should be alive and healthy as they spoil very quickly. To tell if the mollusks are alive, their shells will be closed. If they are open, simply tap them, and alive clams and mussels will quickly close their shells. If they close sluggishly, then this is an indication of shellfish that has been kept just a little too long. Nonetheless, they are still edible albeit not in its prime. They should also be iced or at least refrigerated dry or on ice and covered with a damp cloth. Mollusks tend to fair better if kept on ice covered with a damp cloth. If keeping sea creatures, they must be kept in a container of seawater—not tap water, and for some, like clams, this even helps by cleaning themselves of residual sand. One acceptable alternative is to buy certain shellfish shelled and frozen—as is often the practice with scallops and clams etc. or in the shells like lobsters and prawns.

When shucking bivalves, say clams or oysters, it is the hinge ligament and adductor muscles that must be dealt with. Usually, the cook would aim to cut through the hinge ligament before cutting the adductor muscle or muscles away from the shells.

13.9 PERISHABILITY OF SEAFOOD

Talking of cold-water and warmwater fish and shellfish, a group of cold-water creatures tend to spoil faster than other fish and land animals for two reasons. Firstly, fish rely on highly unsaturated fatty acids that need to work (remain fluid) at low temperatures. Upon death, these fatty acids are highly susceptible to being broken down by oxygen into stale or rancid off-smelling molecule fragments in a relatively short space of time. Secondly and more importantly, cold-water fishes require enzymes that work well at low temperatures. Furthermore, the bacteria that live in and on the fish also prosper at such temperatures. This means that once again, upon death and storage, the same enzymes and spoilage bacteria thrive at refrigerator temperatures. Therefore, among the fishes, it is the cold-water species particularly the oily ones that spoil faster than tropical fish.

13.9.1 HEALTH HAZARDS

Seafood is highly perishable; however, in general terms, there are a few types of hazardous substances that contaminate this group. These range from industrial and biological toxins to disease-causing microbes and parasites. Overall though, it is in the postharvesting stage of fish and shellfish that causes the greatest problems (Britannica, 2016).

13.9.1.1 Toxic metals and pollutants

Water quality can be a problem when it comes to fishes' welfare. Toxic rain, for example, starts out as your regular everyday rain; however, as it rains in polluted areas, so the clean rain ends up washing chemical pollutants out of the air and carries them into the ground and potentially into the water table, rivers, and oceans where pollutants can accumulate in fish and shellfish. Of all the potentially hazardous pollutants found in fish, the most noteworthy are heavy metals and organic pollutants, predominantly dioxins and polychlorinated biphenyls, or PCB's for short. Heavy metals include mercury, lead, cadmium, and copper that are particularly bad for sea creatures as they interfere with oxygen absorption and the transmission of signals within the nervous system. In humans, heavy metals are also known to cause brain damage. Organic pollutants too accumulate in fishes' body fat and have long been associated with liver damage, cancer, and hormonal disturbances in laboratory animals. When it comes to chemical toxins, these can be found in fish but more often within "filter-feeding" shellfish or long-lived predatory fish at the top of the food chain. In fact, the fish/shellfish that are least likely to be contaminated are those farmed in controlled waters or the short-lived fish from the open ocean. Cooking does not eliminate the contaminants in fish and shellfish, and neither is there any way for consumers to tell whether fish contain unhealthy levels of the above contaminants.

13.9.1.2 Infectious and toxin-producing microbes

From a risk analysis, seafood carries the same hazards of bacterial infections and poisonings as found in land animal meats. However, the riskiest of these are those shellfish served raw or undercooked. This is especially true in bivalves that, being filter feeders, filter and trap bacteria and viruses throughout their lives. Furthermore, when we eat these foods raw, we generally eat and digest the whole organism, digestive tract, and all. Although that said, proactive government monitoring of water quality and regulation of shellfish harvesting around the world has greatly reduced the problem. As a general rule of thumb, bacterial infections by parasitic organisms in fish and shellfish can be prevented by cooking seafood to a minimum of 60°C/140°F while to be rid of some viruses requires an internal temperature of 82°C/179.6°F or more. Moreover and perhaps more scary is the fact that, some chemical toxins created by certain microbes can actually survive the cooking process altogether. Thus, both raw and cooked fish and shellfish are in need of consideration on this point. Among the most significant microbes in fish and shellfish include the following:

- *Vibrio bacteria* are natural inhabitants of river mouths, brackish, or saltwater waters in which they thrive in the warm summer months. One species (*Vibrio cholerae*) causes cholera, while another, a milder diarrheal disease, and a third (*Vibrio vulnificus*) found in some raw oysters and other seafood is the deadliest of the seafood-related diseases. Sufferers from this particular virulent strain can expect high fever, a drop-in blood pressure, septicemia, and damage to skin and flesh. Scarily, it also has the reputation of killing about half of those infected (McGee, 2004; CDC, 2013; JW et al., 2006).
- *Paralytic shellfish poisoning* (PSP) is caused by dinoflagellates. They are red-brownish in color and can grow to such numbers that great swathes of red streaks appear in the ocean and are referred to as "red tides." The toxin caused by dinoflagellates is known to concentrate within certain shellfish including mussels, cockles, clams, scallops, oysters, crabs, and lobsters. Symptoms are generally mild, but in cases of severe poisoning, respiratory failure and muscle paralysis can occur. In such cases, death may occur in 2–25 h (CDC, 2005).

- *Botulism bacteria*, which grow and thrive in the digestive system of fish, produce a deadly nerve toxin that can also be especially virulent. Most cases of fish-borne botulism, however, are caused by improperly cold-smoked, salt-cured, or fermented fish products.
- *Intestinal viruses*, the norovirus (formerly the Norwalk), attack the lining of the small intestine and cause vomiting and diarrhea. In fact, it is the most common cause of viral gastroenteritis in humans in the world. It affects people of all ages and is transmitted by fecally contaminated food or water or from person-to-person contact, among others (CDC, 2015).
- *Hepatitis viruses A and E* can and do cause long-lasting liver damage.

There are also other disease-causing microorganisms although to what degree they are serious depends on locale, the degree of microbial activity, the toxin involved, etc. These include the following:

- *Scombrotoxic fish poisoning* is also known as scombroid or histamine fish poisoning.
- *Ciguatera poisoning* or ciguatera is caused by eating contaminated tropical reef fish.
- *Neurotoxic shellfish poisoning* is caused by a third type of dinoflagellate with another toxin that occasionally accumulates in clams, oysters, mussels, etc.
- *Amnesic shellfish poisoning* is a rare syndrome caused by a toxin made by a microscopic, red-brown, saltwater plant, or diatom called *Nitzchia pungens*.

13.9.1.3 Other hazards

Other hazards in fish include certain parasites; these include species of *Anisakis* and *Pseudoterranova* (anisakids or cod worms), which can be up to 2.5 cm long and sometimes more. Furthermore, with a diameter of just a few human hair thick, both parasites can commonly be found in the flesh of cod, halibut, herring, mackerel, rockfish, salmon, and squid. These are generally destroyed by cooking although one can ingest this parasite from eating raw fish such as lightly marinated salmon, cold smoking, and even sushi. Symptoms of infection can range from a simple (and harmless) tingling in the throat through invading the lining of the stomach or the small intestine causing pain, nausea, and diarrhea. Interestingly, one is much less likely to be infected from farmed salmon than their wild counterparts. Other parasites include the legendary tapeworm (*Diphyllobothrium latum*). If ingested, tapeworm's larvae tend to make their home in the intestines and can grow to as long as 27 ft or 9 m. The larvae are found in freshwater fish of temperate regions around the world. More serious than the tapeworm though are the flukes, or flatworms, hosted by freshwater and brackish-water crayfish, crabs, and some fish species. These parasites can damage the human liver and lungs after being consumed.

13.10 POTENTIAL CARCINOGENS

As mentioned in the cooking of meat, any cooking process involving high, dry heat, especially when the Maillard reaction is involved, transforms proteins into highly reactive products. All can potentially damage fish DNA and may therefore initiate the development of cancers. So once again, avoid if possible the Maillard reaction or at least use a marinade before so. Ideally, fish should be braised, steamed, or poached rather than grilling, frying, and sautéing. However, this is unrealistic, and the advice just given is more for one's own knowledge rather than practicality. After all, who doesn't enjoy a mouth-watering grilled halibut, a pan-fried tuna steak, or good old fish and chips?

13.10.1 THE FLAVOR AND QUALITY OF FISH AND SHELLFISH

Fish flavor, the cook's touch notwithstanding, is simply a product of its species and the category it belongs and ultimately of course its environment—that really is it. Firstly, the flavor depends greatly on the kind of fish it is (over 33,000 varieties), whether it's oily or not or white or dark, the salinity of the water it lives in or whether it inhabits freshwater instead, and to a large extent on the food it eats, among many other variables. Of particular interest though is the freshwater-saltwater differential. This is because the optimum level of dissolved minerals secreted within animal cells (including sodium chloride aka table salt) is less than 1%. Ocean fish then breathe and swallow salt water at concentrations of up to 3%, as a result they have had to develop a way of maintaining their body fluids at the correct concentration of dissolved minerals, etc. Most balance this need by utilizing more amino acids and amines within their cells. Fin fish contain some of these amino acids and amines but still rely largely on a relatively tasteless amine called *trimethylamine oxide* (TMAO). Many sharks, skates, and rays use a different substance; they use a slightly salty and bitter urea.[10] However, there is one major setback with TMAO and urea, and that is, after the fish is dead, bacteria and fish enzymes easily convert TMAO into the foul-smelling trimethylamine (TMA) and the urea into the cleanser—ammonia. These are the rotten fish smells that accompany fish that have been dead for more than a few days. The environment for freshwater fish on the other hand is considerably less salty, so they have no need to accumulate amino acids, amines, or urea within their cells. This is why their flesh is comparatively milder, both when fresh and when a few days old (Vaclavik and Christian, 2014; McGee, 2004).

Shellfish are especially rich in glycine (a sweet-flavored amino acid) and savory glutamic acid in the form of monosodium glutamate (MSG) and other flavorful amino acids. However, the moment fish are killed, so other aromas begin to develop and take over. The first and most obvious of the marine species is the "fishy" smell associated with the compound mentioned above trimethylamine oxide (TMAO) that bacteria on the fishes' surface break down to the malodorous trimethylamine (TMA) and may also be split into dimethylamine (DMA)[11] and formaldehyde (FA) by enzymatic processes in the fish. Fortunately, the "fishiness" of TMA and fish past its prime can be significantly reduced by employing a couple of simple tips. TMA on the surface of the fish can simply be washed off with freshwater, and secondly, acidic ingredients like lemon juice, vinegar, and tomatoes, for example, aid in two ways. The acidity encourages the decaying molecules to react with water becoming less volatile in the process. The second way is acidity contributes a hydrogen ion to both TMA and DMA, thereby taking on a positive electric charge that then bonds with water and other neighboring molecules reducing their volatility.

Freshwater fish on the other hand tend not to accumulate TMAO, and crustaceans only accumulate a relatively minor amount, so neither becomes as "fishy" as ocean fish. Although unsaturated fats and fresh-smelling molecules (aldehydes) produced from fresh fish (upon aging after death) react slowly to produce other molecules with stale, cheesy notes, some of which accentuate the fishiness of any TMA present. Lastly, when it comes to storing fish in the freezer, we note that the fish's own enzymes are also responsible for converting some of the TMA to DMA making the fish smell weakly of ammonia.

[10]Urea is what most animals turn protein waste into before they excrete it.
[11]DMA smells weakly of ammonia.

13.10.2 COOKING FISH

Fish bones are smaller, lighter, and are less mineralized with calcium than land animal bones. Because of this and the fact that fishes' collagen is less tough, this means they can be softened—even dissolved by a relatively short period at temperatures near to the boil. Look closely at a fillet of fresh salmon, cod, or halibut, and pearlescent webbing can be seen between the striations of muscle. This is the connective tissue collagen, a structural protein that holds together short, thick muscle fibers. In fish, muscle fibers are much shorter than they are in beef, and collagen dissolves easily during cooking. Therefore, fish cooks quickly, and there is no tenderizing to do. In fact, the biggest challenge in preparing fish is to keep them from overcooking and falling apart, after the fact.

As fish cooks, so proteins in the muscle fibers coagulate, and the flesh changes from translucent to opaque in appearance. Further, when the fishes' collagen softens in heat, it loses its structure and turns to gelatin at around 46–49°C/115–120°F (Belitz et al., 2009); the muscle fibers have little to hold them together, and the fish separates easily into flakes. The process of fiber coagulating and collagen softening happens almost simultaneously and at lower temperatures than with beef. So, it's easy to understand why fish is easily overcooked. Thus, the transition from "almost done" to perfectly cooked happens in moments. Remember too that residual heat means that the fish continues to cook for a few minutes, more after it has been removed from the heat. Fish that seems tough and dry when bitten into are probably overcooked. As it moves from done to "overdone," the flesh continues to firm then shrinks, pushing out moisture, which evaporates and leaves the fish dry and chewy (McGee, 2004). Fresh fish needs little in the way of embellishment as its flavor is as fragile as its flesh. To enhance the dish is an ideal goal, yet to overpower its delicate meat, spoils a perfectly fine dish. The idea is to keep it simple, use a sprinkling of salt and no more, a "soupçon" of freshly ground pepper, perhaps a squeeze of fresh lemon, and a few well-chosen fresh herbs. From this, it can be seen that very few foods other than fish require so little in the way of preparation to be outstanding. However, it should be noted that the preference of cooking say salmon and arctic char to 42°C/108°F (rare) and many other fin and shellfish to 49°C/120°F (medium-rare) these days is too low to destroy any food pathogens. In such cases, preparatory health and safety should be applied rigorously to minimize contamination (Baldwin, 2012). In the end, cooking fish beautifully rests as much on science as it does on the art of restraint.

13.10.2.1 Softness

There is a state of fish muscle that can be unpleasant and very unappetizing in the mouth—this happens when fish become overly mushy. This can happen for several reasons; when the fish is thawed from the freezer, as with meat, the same ice crystals can break through adjacent cell membranes liberating enzymes that then attack the rest of the muscle fibers and leaking valuable juice upon thawing, thus giving it a too-soft, mushy mouthfeel. Another reason for soft mushy flesh can be after the migration or the spawning period, in which muscle gets depleted and whereby fish proteins bond to each other, but only very loosely. In extreme cases, muscle proteins are so tenuously bonded that they can seem to be almost liquefied.

13.10.2.2 Fish taste

As a general rule, seafood is said to be more fully flavored than land animal meats or freshwater fish. This is because ocean-dwelling creatures accumulate amino acids that serve to counteract the salinity of seawater. On top of this ocean fishes' flesh contains about the same amount of sodium chloride (salt)

as beef or freshwater trout, but ocean fish differ in the amount of free amino acids they contain—astonishingly to the tune of between 3 and 10 times as much. Most notable is the sweet amino acid, glycine, and savory amino acid, glutamate. This is especially so in the herring and mackerel family of fishes, the sharks and rays as well as shellfish, etc. Moreover, as the salt content of seawater varies between the open oceans and near river mouths, so fishes amino-acid content fluctuates depending on the location of its natural habitat. One additional element concerning fish flavor and aroma profile depends on the energy-carrying compound adenosine triphosphate (ATP). When a cell uses up energy from ATP, it is converted or transformed into a series of smaller molecules, one of which has a savory taste similar to that of glutamate—inosine monophosphate (IMP). Having said that, IMP is a fleeting substance, and while the savoriness of fish can increase as IMP levels rise for a period of time after death, it then declines again as IMP disappears.

13.10.3 COOKING SHELLFISH

Shellfish have much in common with fish in terms of delicate bodies and chemical makeup. One of the main common things is that shellfish too contain between 3 and 10 times as much free amino acids as land animal do. However, unlike fish, most shellfish are invertebrates in that they do not have a backbone or internal skeleton, and most of them do not swim all that much. As a result, many shellfish benefit from brief and gentle cooking, whereas, with high-heat cooking, shellfish might very well disintegrate or become very chewy. Conch and abalone as well as others like them, on the other hand, are naturally tough and must be pounded or cooked long and slow in order to tenderize the tough meat. It is also important to remember that there are many types of shellfish that are cooked live to protect the customer against the effects of bacterial spoilage too. Lastly, another advantage shellfish has over their fish cousins are the exoskeletons or shells from things like crabs, shrimp, and lobsters. Many of these are cooked[12] and crushed allowing their flavor and color to add richness to dishes, sauces and soups.

13.10.3.1 Mollusc texture

Whether eaten raw or cooked, it is often the adductor muscle that largely determines the texture of certain bivalves. When bivalve bodies are eaten whole, people are eating quite a collection that includes one or two adductor muscles together with miscellaneous innards or entrails; small tubes and thin panes of muscle and connective tissue; potentially a soft mass of eggs, sperm, and food particles; and a general protein-based mucous that lubricates and binds food particles. Thus, clams, mussels, and oysters are slick, tender, and perhaps a little crunchy when raw and maybe a little chewy when cooked. This all depends on the "catch" or fast-twitch muscle——i.e., the greater the proportion of this type of muscle tissue, the chewier the mollusk will be. Moreover, abalone, octopus, and squid meat as well as others that comprise mainly muscle tissue and a lot of collagen connective tissue couple this with a complex fiber arrangement, and it should come as no surprise that they either become chewy or just about eatable when lightly cooked or tough as leather when cooked further until finally edible when cooked slowly over a low heat to collagen's denaturation temperature of 50–55°C/122–131°F.

[12]In shells, because carotenoid pigments are much more soluble in fat than in water, you can gain more color if the cooking liquid is mainly fat or oil or butter.

The texture of mollusks is also strongly affected by the animals' reproductive state; as they approach spawning, so their bodies produce eggs and/or sperm that, when cooked, develops a soft creaminess that sets like a custard. Immediately after spawning, however, the depleted tissues become thin and slack.

13.10.3.2 Mollusc flavor

When eaten raw, oysters, clams, and mussels are highly prized for their rich, satisfying taste. The savory taste comes about due to the mollusk's accumulation of internal taste-active substances, mostly amino acids. Unlike marine fish though, which utilizes tasteless TMAO and relatively small amounts of amino acids to balance out osmotic salinity, most mollusks rely almost entirely on amino acids, in particular the flavorsome glutamic acid. Further, instead of fat storage in muscles like those that marine fish utilize, mollusks accumulate proline, arginine, alanine, and certain combined forms of these and other amino acids as well as glycogen. It's also worth noting that the more saline the home water is for the mollusk, the more amino acids it uses to counteract salt concentration, the more savory the shellfish.

When mollusks are cooked, however, they become less savory. This is because heat traps some of the amino acids in the coagulated protein web withholding them from the tongue. On the plus side, though, cooking both alters and intensifies the mollusks aroma, which is commonly dominated by the compound dimethyl sulfide (DMS) that mollusks accumulate from certain algae upon which they feed (McGee, 2004).

13.10.3.3 Cephalopods—squid and octopus

Just as with abalone and clams, both squid and octopus must be cooked lightly either for a brief period of time to avoid the muscle fibers toughening or for a longer period of time in order to break down the collagen. Cooked quickly to between 55°C and 57°C or 131°F and 134.6°F and the squid or octopuses' flesh is moist yet at 60^{+}°C/140^{+}°F, and it begins to curl and shrink as the collagen layers contract squeezing out moisture from the muscle fibers. If this happens, simply cooking for another hour or so at approximately 60°C/140°F will dissolve the softened collagen into gelatine giving the flesh a smooth succulence. Of course, pounding too will also help break down and tenderize the flesh.

Again, as with fish, squid, and octopus preserve their osmotic balance principally with tasteless TMAO rather than the more flavorsome free amino acids. As a result, their flesh is less sweet and savory than that of other mollusks. Another downside with TMAO as discussed before is that when slightly old, bacteria convert TMAO to "fishy"- smelling TMA.

The muscle fibers of octopus and squid are extremely thin. In fact, compared to fish and cattle, the fibers are less than a tenth the diameter (0.004 mm) of a typical fish or steer cell fiber (0.05–0.1 mm). This makes the muscle fibers of these cephalopods dense and fine-textured. Furthermore, they are also arranged in several layers that are greatly reinforced with toughening connective tissue (collagen), about three to five times more than fish muscle has. So, unlike the delicate and fragile fish collagen, squid and octopus' collagen is extensively cross-linked, behaving more like the collagen of land animals.

13.10.4 ECHINODERMS

Sea cucumbers are firm, gelatinous creatures whose flavor is very mild. The black sea cucumbers have the most flavor followed by the red ones. It would seem that their main function in cooking is to add texture and to absorb the flavors of a dish. When cooking sea urchins, the reproductive organs are eaten sometimes lightly cooked in a sauce or, as is most common, raw, especially in Asia. In Japan, sea urchins are popular and are eaten raw in sushi or are salted and fermented to become a savory paste, while in France, they are sometimes added to scramble eggs, soups, and sauces or are simply poached by themselves.

13.10.5 CRUSTACEA

As with the flesh of most fish, flesh from the Crustacea family mainly comprises white, fast-twitch muscle fibers. Crustacea are also collagen rich with more connective tissue than fish collagen that is less easily dissolved by heat. Consequently, meat from crustaceans is less delicate and easily dried. However, as discussed before, the protein-breaking enzymes in the muscle when raw remain very active, eventually turning the meat into a kind of mushy texture. As a result, these enzymes must be arrested through the process of cooking. These enzymes work to break down the flesh most actively in the temperature range of 55–60°C/131–140°F, so the choice here for the cook is to cook the crustacean until it reaches the above temperature and serve immediately or cook it beyond this range as quickly as possible. Boiling, steaming, or sautéing are the most rapid cooking methods and the usual treatments for many shellfish (Belitz et al., 2009) (Fig. 13.5).

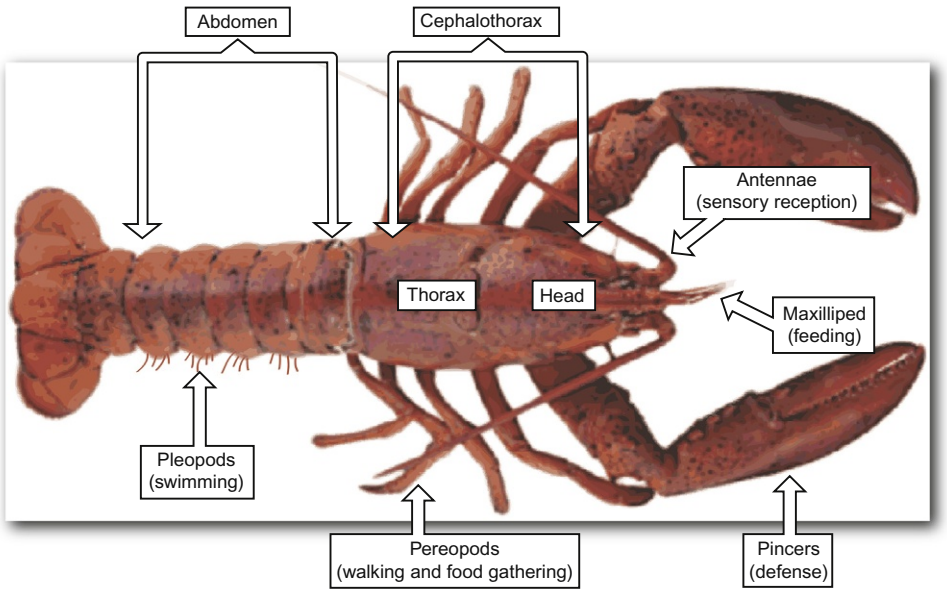


FIG. 13.5

Lobster anatomy.

The aroma profiles of cooking shrimp, lobster, crawfish, and crab, among others, are somewhat distinct from either mollusks or fish aromas. These are due in large part to an abundance of pyrazine and thiazole[13] molecules. These are generally produced because of the Maillard reactions when amino acids and sugars react together at high temperatures.[14] It would seem that such reactions take place at lower temperatures in crustaceans than in land animals, perhaps because of the higher concentrations of free amino acids and sugars in crustaceans' muscle tissue. Furthermore, it has been noted that crustaceans seem to be more flavorful when cooked in their shells. This is because the shell reduces the leaching of flavor compounds from the flesh, while at the same time, the outer layer of flesh is flavored by the shell that is also in itself a concentrated mass of proteins, sugars, and pigment molecules.

As an aside

As mentioned once dead, the flesh of crustaceans is very easily damaged by their own enzymes. As a result, they are generally sold raw frozen, cooked, or alive. In all cases, live crustaceans should be active and come from a clean tank. Like mussels and other bivalves, they can also survive for several days in a moist cloth or newspaper wrapping. If someone is looking for real quality, small lobsters and crabs will have finer muscle fibers and therefore a finer texture on the palate. There are many anecdotal stories on how best to cook a lobster the most humane way. The truth is while these creatures don't have a central nervous system as such (the brain receives input only from the antennae and eyes), each body segment has its own nerve cluster so it's hard to know how pain can be minimized. As a result, according to McGee (2004), the most prudent advice would be to anesthetize the animal in iced salt water for 30 min before cutting up, steaming, or boiling.

13.11 PRESERVING FISH AND SHELLFISH

Few foods spoil faster than fish and shellfish. As a result, history has taught us how to best preserve these delicacies against spoilage microbes by drying, salting, smoking, and fermenting or combination thereof. However, as refrigeration technology grew, so people were able to gain access to fresh fish on a regular basis. That meant less preservation was needed. However, instead of giving up on preservation, sometimes, it is so ingrained in a particular culture that the practice forms a part of a country's or a region's cultural food heritage. Nowadays, many people are interested in preserved seafood as a genuine option to fresh fish.

13.11.1 DRIED FISH

One method of preservation is the drying of foods in the sun and wind. We mentioned earlier that fresh fish is approximately 80% water; by drying, we can take the moisture content down to around 25% or below, at which degree bacteria have trouble growing. By taking more moisture out (below 15%), even molds' growth too can be inhibited. The good part about drying is that it not only preserves the food but also intensifies and alters flavors. It does this through the disruption of the cellular structure, thus freeing and promoting enzymatic action. As drying continues, so these flavor molecules also begin to react

[13]Pyrazine and thiazoles are heterocyclic aromatic organic compounds.

[14]There are many amino acids that sea creatures tend to accumulate when balancing the salt in the seawater, crustaceans seem to favor glycine, which has a sweet taste that reflects in the meat.

with each other to form additional, complex flavors. Having said that, one downside to drying fish and shellfish is the eventual unavoidable fat oxidation leading to certain rancid flavors. Consequently, only lean fish and shellfish are generally utilized in the drying process. Indeed, historically, those fatty fish and shellfish that do not qualify for drying are usually smoked. Whether drying or smoking, seafood is usually salted or brined and/or cooked; this draws further moisture from the seafood, making them (particularly the surface) more inhospitable for microbial bacteria. From a global perspective, China and Southeast Asia are the largest producers and not surprisingly consumers of dried seafood. Various dishes call for steamed reconstituted products like abalone, octopus, jellyfish, squid, sea cucumbers, and shark fins before adding them to soups, stews, and the like.

13.11.2 SALTED FISH

Preservation by drying in natural environments works best in cold or hot climes. In temperate Europe, however, humidity and temperatures are not conducive for air drying in the traditional sense. Instead, dried seafood must be dried in specially designed indoor areas controlling both humidity and temperature. A day's salting (with a little salt) generally preserves fish for several days, while steeping fish with around 25% salt keeps it stable for a year or more. In the right zones, lean cod and other similar families are, then and now, salted before air drying. This is in contrast to fish like herrings and their families that are protected from air-induced rancidity by brining and/or by smoking. The best examples of salted seafood are the gastronomic equivalent of some of the world's best cured hams and beef.

When salting (dry curing) or brining (wet curing), it is important to understand that salt slows down spoilage bacteria and molds while maximizing the time allowed for friendly bacteria and local enzymes to populate and break down fishes' relatively flavorless protein molecules and fats into more savory substances. This in turn reacts further to create even more complex flavors.

Salt herring—because of herrings and similar species can be up to as much as 20% fat by weight, traditional dry curing leads quickly to rancidity. Historically, to overcome this, air was taken out of the equation, and the fish was wet-cured in a moderate brine (16%–20% salt solution) allowing the fish to be kept for up to a year. Then, about AD 1300, a technique was developed that left part of the intestine rich in digestive enzymes (the pyloric caecum) inside the fish. That meant, along with the fish muscle and skin enzymes, the digestive enzymes of the pyloric caecum all worked together breaking down proteins creating a more tender, texture, and a complex flavor-aroma, slightly meaty, fishy, and cheesy. This practice continues today, and these herrings are eaten as they are, without desalting or cooking (Stefansson, 1995; McGee, 2004).

Cured anchovies—anchovies, distant relatives of the herring, are simply dry-cured and layered with enough salt to saturate the fishes' tissue. This is then placed under weight and kept at high temperatures 15–30°C/86°F for between 6 and 10 months. This is a very traditional Mediterranean delicacy sold as is or further processed to make fish sauce or ground and mixed with oil or butter to form a paste. The muscle, skin, blood cells, and enzymes together with bacteria and the warm curing temperature all work together stimulating the early stages of the browning reactions and generating, in the process, many aromatic flavors. The result, in the words of Harold McGee,

> …is a remarkably full flavor that includes fruity, fatty, fried, cucumbery, floral, sweet, buttery, meaty, popcorn, mushroom, and malty notes.
>
> **(McGee, 2004)**

Salt cod—when it comes to salting and drying cod, in the right conditions, it can be dry-cured for about 15 days or so with about 25% salt marinade. At this point, the fish can then be held for months during which time *Micrococcus* bacteria break down molecules producing TMA and flavorful free amino acids. On top of this, oxygen too works on the small amounts of fat substances producing fatty acids contributing to the aroma of the fish. Artificial drying in a controlled cold room for a further 3 days completes the process.

Gravlax, gravadlax, and gravlaks[15]—the original gravlax meaning "buried salmon" (*next section*) hales from Scandinavia. It was a lightly salted, pressed salmon that was preserved by burying it and allowing it to ferment. As time went by, so the dish evolved, still lightly salted but this time pressed and unfermented. Nowadays, gravlax recipes call for varying amounts of salt, sugar, dill, and curing time. The salmon is first salted[16] and sugared and such flavorings as dill and lemon are added; after that, the fillets are weighted down and refrigerated for 1–4 days depending on preference, size, and amount of salt used.

13.11.3 FERMENTED FISH

When it comes to the fermentation of fish versus salting, it can become all too confusing; this is because, as with both the salting and fermentation processes, both salt and bacteria play a part. Anchovies are a good example of the difficulty in distinguishing one from the other. Bacterium, for instance, plays a role in the curing of anchovies, while salt plays a larger role. On the other hand, most seafood fermentations start with salt to control the initial bacterial population before the bacterial growth "proper," kicks in. Indeed, many cultures from around the world utilize microbes to transform fishes' texture and flavor into a delicacy at best or an "acquired" flavor at worst. Without doubt though, it is the Asians, specifically the East Asians who have taken fermentation and made it an art form. In Asia, fermentation serves to both preserve seafood and to act as a stimulating flavor enhancer, particularly important are the flavors of monosodium glutamate (MSG) and certain other amino acids within these fermentations.

Talking of the actual fermentation process, it seems that over the years, two distinct techniques have evolved. The first involves basically salting fish or fish parts and then leaving them to ferment. In this way, the amount of salt is usually sufficient by itself to preserve the fish from spoilage, while the bacteria are important mainly as flavor enhancers. In the second, the fish is salted first before being inserted into an already fermenting mass of grains, vegetables, or fruits. In this "mixed" fermentation, the light salting preserves the fish for a few days or weeks, while the grains or plant-based materials feed the microbes—the same ones that sour milk or ferment grape juice into wine. The fish is then preserved and flavored by many microbes' waste or by-products, i.e., acids or alcohols. In this way, there are literally dozens of fermented fish and shellfish products on the market today. Perhaps the most widely known and used within Asia at least are the many fish sauces available.

Asian seafood pastes and sauces—fish sauces generally replace soy sauces in regions where soy beans do not grow that well. In terms of preparation and very generally speaking, it turns out that both fish pastes and sauces are merely two phases of the same preparation. Firstly, when making pastes, a quantity of seafood is saturated with about 10% salt and then sealed in a container for about 1 month. These pastes tend to have moderate to strong fish and cheese aroma notes.

[15]Gravlax means "buried salmon."
[16]Salt also dissolves the myosin protein found in the muscle fibers.

When making sauces, however, these are saturated with up to 30% salt and are held for up to 24 months after which they are sometimes boiled, aged, and flavored; this transformation gives fish sauces welcome meaty and savory tones. Like some oils (olive oil is a good example), some of the most prized sauces are those of the first extractions or "tappings" of the fermented seafood. Second-tapped sauces from the extracted mass might well be supplemented with other ingredients in cooking to add a certain depth of flavor to a complex dish (McGee, 2004).

Soured buried fish of Scandinavia—the original gravlax, the Norwegian "rakfisk" and "rakørret" and the Swedish "surlax" and "sursild" are fermented fishes that originated perhaps out of need. A glut of fish with a shortage of salt in which to cure the catch and shortages of other commodities like barrels, and other suitable containers meant that a new method of preservation had to be found. Ingeniously, the solution was to lightly salt the fish and bury it in a hole in the ground and sometimes wrapped in the bark of the birch tree or covered with malted barley, whey, or flour. As it turned out, in Scandinavia at least, the combination of low temperatures, the lack of air in the buried fish, minimal salt, and any added carbohydrates as mentioned above all work together to encourage the right bacterium to produce lactic acid that then covers the fish surface. After acidification, the same bacteria break down the fishes' proteins and fish oils producing an overall sharp cheesy aroma together with a buttery texture.

Asian mixtures of rice and fish—as with the Scandinavian examples, so there are numerous Asian fermentations that mix fish and grains. The main grain, because of its popularity and abundance, is rice. During the process of fermentation, so various bacteria consume the carbohydrates in rice producing an assortment of organic acids that then protect the seafood against spoilage. The same acids also act to soften the fishes' skeletal structure while also contributing greatly to the characteristic richness of acidic/tart flavor full of buttery, cheesy, and vinegary aroma notes. Perhaps one of the most famous of the above process is the traditional Japanese sushi "narezushi," of which the best known is "funazushi," which is also fermented with rice. This practice of fermentation of sushi is ancient and traditional that incidentally contrasts modern day sushi/sashimi production in which the freshness of raw unfermented sushi is combined with vinegared rice.

13.11.4 SMOKED FISH

It's not clear just how smoking fish was discovered, but over the centuries, numerous incarnations have brought us delicacy after delicacy. One clue might be in the fact a lot of the more familiar smoked fish hale from the cooler northern regions. The same regions that has given us smoked haddock and cod (from Britain), smoked herring (Germany, Holland, and Britain), smoked skipjack (from Japan), and smoked sturgeon (Norway, Scotland, Russia, and Nova Scotia). Howsoever, smoking came about, we know that smoking not only disguises the smell of staleness but also imparts a unique, smoky flavor all its own while also preserving the fish. Smoking is successful for the simple fact that it either kills food poisoning and spoilage bacteria or renders them innocuous by changing the chemistry of the environment in which they need to survive and thrive. Traditionally, achieving this end was crucial to the eatability of the fish, but it also meant that the process of salting, drying, and smoking was extreme, resulting in high-salt and low-moisture content products. While historically this practice was out of necessity, modern people's appetites tend not to have the palatability for these extreme flavors of traditional smoking practices. Instead, contemporary smoking methods tend to be a milder version of the original. These "lesser"- smoked products are made possible because of refrigeration, freezing, and other modern storage techniques.

Smoking foods, whether meat or fish, are prepared in two basic ways, hot smoking and cold smoking. Both hot- and cold-smoked fish are preserved primarily by controlling water content and temperature.

Salting and drying—nowadays, fish is "cured" first, either salted or brined in concentrations of salt close to 3% or so (the same salinity as seawater), for a few hours to a few days that by itself is not quite enough to inhibit microbial activity. Instead, what it does is draw muscle fiber proteins, most notably myosin to the surface that, when the fish is hung and allowed to dry, creates a tacky covering of salt dissolved myosin on the surface known as a "pellicle"— a gel-like skin.

Cold and hot smoking—sawdust is often used for initial smoking whether subsequent hot or cold smoking follows, as it can produce more smoke at lower temperatures than whole pieces or "chips" of wood. This is undertaken at about 30°C/104°F or less. The aim of which is to remove some of the interior moisture without a "hardening" of the surface pellicle.[17] At this point, the fish meat becomes denser without actually being cooked. After this initial smoking, fish is next smoked for several hours in one of two temperature ranges—hot (65–75°C/149–167°F) or cold (below 32°C/90°F). If cold-smoked, the fish retains the texture of raw fish, albeit with less moisture content—a good example is with smoked salmon. If hot smoked, the fish is cooked and ends up having a firm but flaky texture. Slow, prolonged cold smoking allows the fish to keep for several months, while lesser-smoked products (whether hot or cold) will last only a few days or weeks. If cold smoking, it is also recommended to use prefrozen produce to ensure that any parasitic worms or bugs that might not otherwise be destroyed during the process are actually killed. Industrial smoked products tend to be brined less and smoked less. This is simple economics as such fish and meats are sold by the weight.

Hot-smoked fishes' rich and slightly darkened color is in part generated by browning reactions between amino acids in the pellicle and the aldehydes in the smoke and condensation of dark resins from the smoking vapor.

Smoked salmon—a good smoked salmon may be brined with salt and sometimes sugar for anywhere between a few hours to a few days. This is then rinsed and air-dried before being cold-smoked for between 5 and 36 h. Sometimes, the temperature is increased to about 30–40°C/86–104°F toward the end of smoking to bring some oil to the surface giving it an attractive oily sheen.

13.11.5 FISH AND SHELLFISH EGGS

There are two types of fish egg preparations; these are either unsalted roes[18] and eggs or salted roes and eggs including caviar.[19] Certain fish eggs, specifically eggs from the sturgeon fish, can be some of the most expensive and most luxurious items from the sea. Fish ovaries or "roes" amass enormous numbers of eggs in readiness for spawning: in fact, in salmon alone, they can produce as many as 20,000 eggs in a single spawning, while sturgeon, carp, or shad can accumulate several millions at one go. As with chicken eggs too (as explained earlier), fish eggs comprise all the necessary nutrients that the offspring require to grow, and in many cases, the egg is a more concentrated form of nutrition than the fish[20]

[17]Hardening of the pellicle would create a barrier to the movement of moisture from the interior to the exterior.
[18]Roes consist of separate eggs held loosely together in a weak protein solution all encased in a thin, fragile membrane.
[19]Although "caviar" should refer only to the salted eggs of sturgeon, it has come to mean any lightly salted eggs.
[20]Fish eggs contain, among other things, fat and savory amino acids and nucleic acids.

itself. Furthermore, roes and caviars often contain striking pigments whether pink or yellow carotenoids or sometimes brown-black melanins.

It transpires that the best eggs for eating, cooking, or salting are neither fully ripened nor particularly young. This is because immature eggs are hard and small and possess little flavor, whereas, by contrast, eggs for spawning are soft, easily crushed, and can rapidly develop off-flavors. As it happens, there are more fish eggs eaten salted than unsalted. Of course, as with all preservation techniques, the original idea of salting was simply a means of prolonging the shelf life of goods. Nowadays, however (albeit to a lesser degree), such techniques are practiced more for their flavor than for anything else.

As well as the eggs, another source of proteinaceous delicacies is the sperm mass, called white roe or milt. It tends to be creamy, and the milts from sea bream and cod are especially prized in Japan (McGee, 2004; Vaclavik and Christian, 2014).

13.11.5.1 Bottarga

For a long time, tuna and mullet ovaries have been dry-salted, then pressed, and dried to make what's known in Italy as bottarga. During the process, the salting and drying concentrate the fatty materials, sugars, and the amino acids that consequently react with each other in browning reactions that serve to darken the roe to a deep red-brown while creating rich flavors in the process. Today's bottarga is a mild form of its recent ancestor, but it is still nonetheless a delicacy that might be grated over pasta or sliced and served as an antipasto.

13.11.5.2 Caviar

Caviar, the salted roe of a handful of sturgeon species (Acipenseridae family), is the seafood's version of truffle, foie gras, and champagne. While the term "caviar" had for many centuries referred only to a small handful of sturgeon species' loose eggs, it is nowadays used extensively to describe any lightly salted loose fish eggs. But, just like champagne and truffles, there are the good varieties, and there are the bad; in this respect, the eggs from sturgeon native to the Russian and Iranian rivers that drain into the Caspian Sea still remain, for many, the cream of the caviar crop.

From a scientific standpoint, it transpires that by lightly salting moist fresh fish eggs, through osmosis, some of the salt enters the egg, triggering protein-digesting enzymes; this in turn boosts the levels of flavor-stimulating free amino acids. It further triggers another enzyme called transglutaminase that helps bond proteins, effectively cross-linking them in the outer egg membrane. This helps strengthen the membrane, plumps up the egg as a whole, thus giving it more texture and a firmer mouthfeel in the process. Furthermore, as salt ions affect the proteins within the eggs, so bonded proteins act as a thickening agent where watery egg fluids display greater viscosity in the final product.

13.11.5.3 Making caviar

Traditional "sturgeon" caviar making has something of a bad reputation. Because sturgeons' roe must be extracted from living fish, they are first captured, stunned, or anesthetized, and their roe sacs were removed before being killed. However, things are changing; because of the endangered species listing of sturgeons, wild beluga sturgeon caviar is all but banned in many countries. This has led to the growth of farmed sturgeon and the admiral pursuit on how to remove the roe without killing the fish.

Next, the egg sacs are passed through screens (sieves) in order to separate them from the ovary membrane while simultaneously sorting and grading the eggs. They are then dry-salted at saturations

of between 3% and 10% for 2–4 min. Traditionally, sodium borate (borax[21]) replaced some of salt. Borax is an alkaline that allows the eggs to be salted more lightly while making the caviar taste sweeter and aiding in the improvement of its shelf life. Although it must be noted that the United States, among other countries, prohibit imports containing borax for fear of health reasons (Shin et al., 2010). After salting, the eggs are allowed to drain for between 5–15 min before being placed into large cans and chilled to −3°C/26.6°F.[22]

Caviar can be "fresh" (nonpasteurized) or pasteurized at 50–70°C/122–158°F for between 1 and 2 h, although it has been said by many that with pasteurization, the eggs flavor noticeably diminishes, while its texture becomes chewier, but its shelf life is prolonged somewhat (McGee, 2004).

Fresh caviar should be refrigerated, never frozen; as we have seen, the freezing process breaks down the integrity of the preserved eggs, particularly the eggs membranes. Unopened, the egg quality is maintained for 4 weeks although once opened, it is best consumed on that occasion.

The characteristic Caspian caviars have distinctive sizes, colors, and flavors. In total, there are four types of caviar:

Malossol—is a Russian word roughly translated meaning "little salt." However, strictly speaking, it is a term that describes a style of caviar rather than those coming from a particular species of sturgeon.[23] Malossol caviars (whether beluga, oscietra, or sevruga) have lower salt concentrations than is generally used—between 2.5% and 3.5% salt. Some caviar aficionados tend to prefer Malossol caviar as they believe, with less salt, the flavors are crisp and intensified allowing the full complex flavors to shine through. Nonetheless, while some consider it the most highly prized caviar, it is also the most perishable.

Beluga—is the largest, the rarest, and the most expensive of the caviars. Beluga caviar comes from the beluga sturgeon *Huso huso* that can live for 80–100 years and matures after about 20 years. It is principally found in the Caspian Sea (the world's largest saltwater lake), which is bordered by Russia, Iran, Azerbaijan, Kazakhstan, and Turkmenistan, but can also be found in the Black Sea and occasionally in the Adriatic Sea. The eggs range from very dark gray to light gray on color—the lighter colors, coming from older fish are among the most valued.

Oscietra (ossetra or osetra)— comes mainly from the Black, Caspian, and Azov seas. Living for up to 50 years, the osetra matures and is ready for spawning after 10 years. The oscietra sturgeon produces a medium- to large-grain caviar that tends to be firmer than the other sturgeon species. Next to the beluga, this is the second-largest species of sturgeon, producing eggs in shades of dark gray to golden brown, even golden highlights. Slightly smaller than the beluga eggs, some connoisseurs prefer its more intense but subtle nutty, slightly fruity, and oyster flavors compared with beluga.

Sevruga—is the smallest of all the caviar-producing sturgeons and is also the most commonly found sturgeon in the Caspian Sea. Because of this, it is the backbone of the Caspian caviar industry. While the Sevruga sturgeon is the most widespread, it is the least productive of the sturgeons. It lives to about 30 years and is ready for spawning at age 7– 10 years. Its eggs are generally smaller than those of the oscietra and beluga sturgeons.

[21]Borax is used as an ingredient in caviars as a preservative, allowing less salt to be used; however, it is banned in some countries because of perceived detrimental to public health.
[22]At this temperature, the salt prevents the eggs from freezing.
[23]There are 27 varieties of sturgeon.

13.11.5.4 Other "caviars"

Pressed caviar—is a relatively inexpensive and a great alternative to traditional caviars. It is usually made from overmature sturgeon eggs that are judged to be unsuitable as whole-grain caviars. The eggs are less salted (reaching 7% saturation) and pressed turning it into a strong-tasting paste. This caviar is then suitable for slicing and spreading and continues to be sought after by those who prize its unique, intense flavor. This caviar, unlike the others, can be frozen.

Salmon caviar—is an appealing alternative to traditional caviars of the sturgeon. Salmon eggs are large grain eggs with an orange/reddish translucence. These are soaked in saturated brine for between 2 and 20 min achieving acceptable final salt levels of between 3.5% and 4%. These are then drained and then dried for up to 12 h.

Lumpfish caviar—lumpfish are native to Scandinavian countries (near their North Atlantic habitat). Their eggs are the size of Sevruga and are lightly crunchy giving that pleasing "poppiness" in the mouth. Lightly salted lumpfish roe can be used just like other caviars to accompany various dishes. The eggs develop in a rainbow of colors, but most are usually dyed to a vibrant red or black color in an attempt to fit into people's expectations. Nonetheless, lumpfish is still seen as a poor man's caviar and is often frowned upon by true aficionados, where it need not be.

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CHAPTER

FRUITS, VEGETABLES, HERBS, AND SPICES

14

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Before we look at the technicalities of the complexities of what constitutes fruits, vegetables, seeds, legumes, grains, nuts, etc., we can look a little into the inception of plants as we know them today. Before photosynthesis, the earth's atmosphere comprised very limited oxygen; this meant that the destructive ultraviolet rays from the sun bore all the way to the ground and several feet into the oceans. This also meant that organisms could only survive in deeper waters. Then, approximately 3 billion years ago, some archaic bacteria evolved, creating chlorophyll. Chlorophyll, the green pigment we see in vegetation all around us, is the molecule that absorbs the sun's rays and uses the energy to synthesize carbohydrates from CO_2 and water in a process known as photosynthesis. In the same process, as early photosynthetic bacteria and algae bloomed, the by-product of oxygen made its way to the upper atmosphere where radiation converted it to ozone. This in turn absorbed ultraviolet light, and voila, land life was finally possible. In this way, chlorophyll is the basis for sustaining plant life's processes, and by extension, since animals and humans obtain their food supply either directly or indirectly through eating plants, photosynthesis can be said to be the source of all animal life too (Kingsbury, 2009).

Plants are not as mobile as their animal counterparts; instead, their survival depends on their ability as virtuosic alchemists. Plants use colors, tastes, textures, scents, and all manner of chemical creations to ward off enemies and attract friends. Comprising simple elements, plants are constructed out of the very earth itself; that and a smattering of water, air, and light effectively transforms the earth into food on which all animal life ultimately depends. Furthermore, plants and animals are fundamentally different, not only in their mobility but also in the way they nourish themselves in order to grow and reproduce. Plants in essence nourish themselves by building their tissues out of minerals, air, and water while harvesting sunlight for its energy requirements. Animals, however, cannot extract energy from the sun nor can they construct tissue, blood, and bones from the earth's primitive materials. For this, they must obtain them premade in the form of plants or other living things making them predatory heterotrophs[1] and plant autotrophs.[2]

Unfortunately, over the years, since the beginning of the domestication of agriculture, (approximately 10,000 years ago), only a few grains, seeds, fruits, nuts, etc. were used on a regular basis. This drastically reduced the variety of plant foods in the human diet. Moreover, a millennium or so later, the intensification and extensification of agriculture further reduced these numbers to the point that only a

[1]Heterotrophs are organisms that cannot manufacture its own food, so they obtain their food and energy by taking in organic substances usually from autotrophs (plant and algae) or other heterotrophs.
[2]An autotroph is a self-feeder or a producer of complex organic compounds such as carbohydrates, fats, and proteins from very simple substances using predominantly energy photosynthesis or through inorganic chemical reactions (chemosynthesis). In this way, autotrophs are the producers in a food chain, like plants (on land) or algae (in water).

fraction of available plants, seeds, fish, and animals are now eaten on a regular basis (Gibson, 2012). Having said that, people are now beginning to open their eyes to new possibilities. Indeed, if one were to look around, one would find plants offering a veritable feast of earthy roots and tubers, bitter or sharp tasting leaves, perfumed flowers, juicy fruits, crunchy vegetables, a plethora of nuts and seeds, and a bounty of herbs and spices and of course oils and aromas by the thousands (Kingsbury, 2009; Royal Botanic Gardens, 2016).

14.1 PLANT STRUCTURE: PHYSIOLOGY

There are six major plant organs: the root, stem, leaf, flower, fruit, and seed:

Roots—they firmly anchor the plant in the ground giving it support. Roots also absorb and pass along moisture and nutrients to the rest of the plant (*see vascular tissue below*). While most roots are tough, fibrous, and for the large part barely edible, there are exceptions. These are the roots that swell up mainly with nonfibrous storage cells; that is, they allow plants to survive temperate-zone winters, so they can flower later in the year, for example, carrots, parsnips, and radishes, or they can survive seasonal dryness in the tropics like the sweet potatoes and cassava (manioc).

Stems and stalks—their main function is to transport nutrients between the root and the leaves, thus providing support for the aboveground plant organs. As a result of this function, they tend to be fibrous and chewy. This is why we often need to peel asparagus and broccoli stems and devein celery and cardoons (a thistlelike plant in the same family as the artichoke) before cooking.

Leaves—they concentrate their efforts in the production of high-energy sugar molecules through photosynthesis. As such, they are the most fragile and short-lived parts of any plant. In order to maximize sunlight, plant leaves are nearly always flat, providing a large surface area in which photosynthetic cells (chloroplasts) are predominant. Furthermore, to promote the exchange of gas (CO_2 and oxygen), the leaf interior is filled with many thousands of tiny air pockets. This explains why leafy vegetables shrink so much when cooked.

Flowers—these by design are the plant's reproductive organs whereby the male pollen and female ovules are formed. They are often dazzlingly colored and aromatic in order to attract pollinating insects. Having said that some very familiar plants protect their flowers from animal predators such as ourselves with toxins, so a flower's edibility should be checked before use in the kitchen. We also eat a few flowers such as broccoli, cauliflower, and artichokes.

Fruits—fruits are the organs that generally originate from the flower's ovary or its adjacent stem tissue. It contains the seed(s) of the next generation and often promotes a dispersal mechanism that spreads the seeds away from the mother plant. Some fruits however are inedible and are designed to float away on the wind or the fur of a passing animal for instance. That said, the fruits that animals and ourselves eat are often prepared by the plant to be eaten. When ready and ripe, the fruit is usually the most flavorful and most tender part of the plant.

Seeds—seeds are small embryonic plants enclosed in a seed coat or husk. Most plants generally grow from seeds and fall into two groups: angiosperms and gymnosperms. Angiosperms are the flowering plants whose seeds develop inside the ovary—the female reproductive part of the flower. These usually, but not always, ripen into a protective fruit. Gymnosperms on the other hand do not have flowers or ovaries. Instead, their seeds mature inside cones (Royal Botanic Gardens, 2016).

14.1.1 IN MORE DETAIL

In plants, just like animals, the physical structure comprises numerous miniscule compartments called cells (Fig. 14.1). Each is contained within a thin cell membrane constructed from fatlike molecules and proteins. This membrane is also permeable to water and other small molecules. Inside this membrane is the cytoplasm, the substance that is rich in much of the complex chemical machinery required for the cell's growth and function. This includes the starch (storage cells are often filled with amyloplasts, which

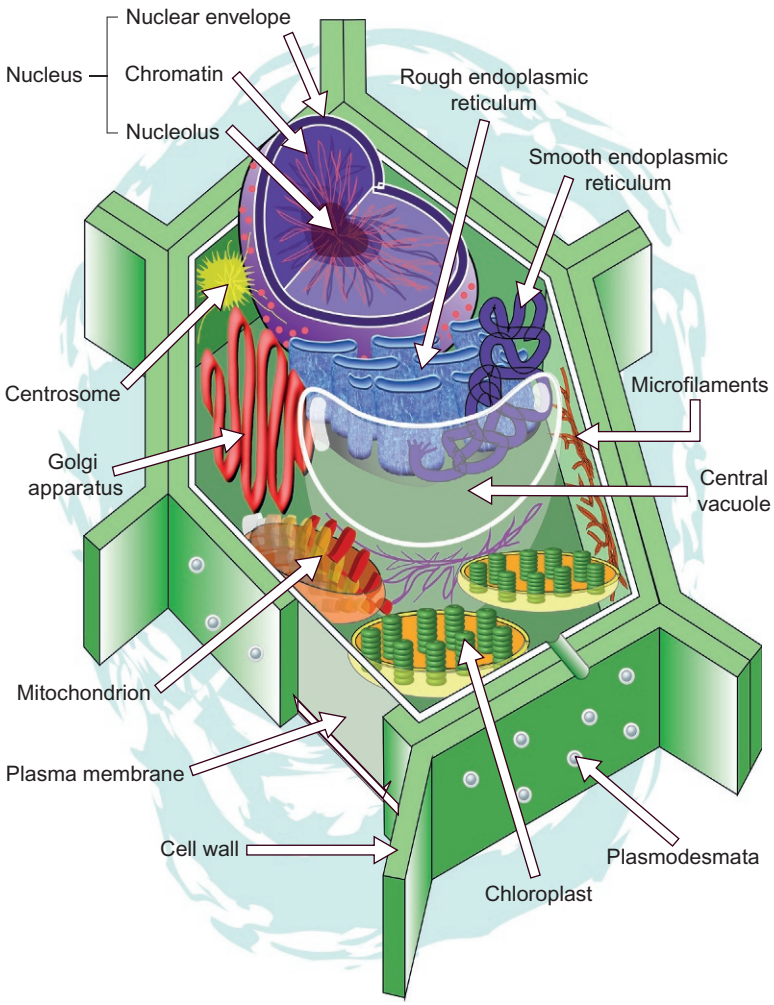


FIG. 14.1

Plant cell structure.

hold many long sugar chains called starch together). chloroplasts[3] (which can number in the dozens to hundreds and perform the functions of photosynthesis), and the nucleus of the cell (containing most of the cell's DNA). Also, inside the membrane, nearly all plant cells comprise a large watery-like vacuole that, depending on the plant, may be filled with sugars, proteins, enzymes, acids, water-soluble pigments, and waste and/or defensive compounds. The cells of fruits often contain chromoplasts[4] too, which among other things concentrates the yellow, orange, and red pigments. Lastly, but no less important, among the physiology of plant cells is the cell wall itself, something that animal cells lack entirely. The plant cell walls surround the membrane mentioned above. It is strong and rigid, lending much needed structural support. As a general rule, the very texture of plant foods is determined not only through the strength of the cell walls but also by the fullness of the storage vacuole and the presence/absence of any starch granules. Color is determined by chloroplasts and chromoplasts and sometimes by water-soluble pigments within the vacuoles themselves, while flavor is determined from the contents of the storage vacuoles (Fig. 14.1) (Royal Botanic Gardens, 2016).

When it comes to plant tissues, groups of cells are organized to perform a common function. There are four basic tissues:

Ground tissue—it makes up the bulk of the tissues within cells, and its purpose depends on its location within the plant. In leaves, the ground tissue is responsible for photosynthesis, while elsewhere ground tissue is responsible for storing nutrients and water. Cells in the ground tissue usually have thin cell walls, which in turn makes the tissue tender. Most of the fruits and vegetables we eat are mainly ground tissues (McGee, 2004; Zeng, 2010).

Vascular tissue—it often aids ground tissue in support of the plant rigidity; unlike ground tissue though, vascular tissue is often tough and fibrous. The main purpose of the vascular tissue is to act like veins running through the plants' ground tissue. In essence, it is a system of microscopic tubes transporting nutrients throughout the whole plant. The work is divided between the xylem, which carries water and minerals to all regions of the plant, and the phloem, which carries sugars down from the leaves to areas where it is needed.

Dermal tissue—like humans, dermal tissue acts as the skin or outer surface of the plant. It helps to protect the plant while also retaining moisture. The tissue can take one of two forms either epidermis or periderm. The epidermis is most often a single layer of cells that secrete surface coatings including a fatty material called cutin and wax (long-chain molecules made from joined fatty acids and alcohols). The periderm is found on a plant underground organs and older tissues like the skins of potatoes and beets.

Secretory tissues—these are isolated cells usually found on the surface or within the plant itself. These cells are similar to human oil and sweat glands and are responsible for storing or producing various aroma compounds. These are often used to attract or repel animals. Some herbs like mint, thyme, and basil are characterized by glandular hairs on stems and leaves that contain aromatic oils, hence the strong aromas. Vegetables like the carrot family on the other hand concentrate their aromas in inner secretory cells (Zeng, 2010; McGee, 2004; Royal Botanic Gardens, 2016).

[3]Chloroplasts' main role is to conduct photosynthesis, whereby the photosynthetic pigment—chlorophyll—takes sunlight, converts it, and stores it in the energy-storage molecules ATP and NADPH.

[4]Chromoplasts are plastids (double-membraned "saclike") other than chloroplasts that produce and store pigments. They are found in roots, leaves, flowers, and ripe fruits. Chromoplasts contain carotenoids that are lipid-soluble pigments from yellow to red in color that give color to the plant tissues containing them.

14.2 PLANT TEXTURE

Besides the existence of chloroplasts, one major difference between plant and animal cells is the presence of a cell wall that surrounds the plasma membrane. The cell walls are primarily made up of the most abundant macromolecule on Earth—cellulose. Celluloses are long linear complex carbohydrate fibers comprising hundreds if not thousands of glucose molecules. In addition, cell walls contain two groups of branched polysaccharides, the pectins and cross-linking glycans. When it comes to the secondary cell wall (inside the primary wall) while almost identical to the primary, the secondary wall also contains additional substances, in particular lignin that is hard and wood-like adding strength to the structure of the secondary wall. In sum, plant cell walls are a matrix of cellulose microfibrils cross-linked by hemicellulose, pectin, and extension. Plant's cell walls serve a variety of functions. Besides protecting intracellular contents, the structure adds vital rigidity to the plant. It also offers a porous medium for the circulation and distribution of water, minerals, and valuable nutrients, among other things. The thickness and the composition of cell walls vary significantly from plant to plant. Furthermore, many plant cells have a primary cell wall that houses the cell as it grows and a secondary wall that develops inside the primary wall after the cell has ceased growing. These components have a great bearing on the texture of fruits and vegetables. When munching on raw fruit and vegetable, they might end up seemingly crisp and crunchy, soft, melt in the mouth or hard, juicy, dry, or just simply chewy. These traits are all dependent on the way the plant tissues break down as we chew them. In turn, this is contingent on two main factors: the construction of the fruit or vegetable cell wall in question and the amount of water minerals and proteins held in and between the walls[5] (Vaclavik and Christian, 2014).

Crisp or limp—cell walls then act as firm but flexible containers. As the cell wall contains mostly water, there is a relationship between the two, which results in the perceived texture of the fruit and vegetable. If the cell approaches its maximum water storage capacity, it presses against the cell wall increasing the pressure and subsequently those cells that surround it (which are more than likely maxed out with water too). The resultant pressure exerted can reach 50 times the pressure of the surrounding air, which results in a fully firm fruit or vegetable. By contrast, less water in the cell equates to less pressure and sagging cell walls—these fruits and vegetables then become limp or flaccid. In sum, the same fruit or vegetable can be seen as crisp, firm, and juicy when its cells are bulging with water but might be seen as limp and chewy when its cells are depleted of most of its water. Fortunately, though water loss is sometimes reversible, simply soak a limp fruit or vegetable in water for a few hours, and its semipermeable cell walls will absorb water and reinflate.

Grainy, dry, or melt-in-the-mouth feel—when talking of grainy- or dry-textured fruits and vegetables, we are looking specifically at the mixture or cement-like semisolid mixture of water, carbohydrates, minerals, and proteins positioned between neighboring cells. If this mixture is weakly bonded together, chewing these fruits and vegetables tend to merely break the cells apart rather than breaking them open. When this happens, we end up with masses of tiny separate cells in our mouth giving the fruit or vegetable in question a grainy, dry mouthfeel. Once again, by contrast, if the cement-like matrix between cells is even more weakened to the point the cell walls have all but disintegrated, the fruit or vegetable is soft and melt in the mouth (Vaclavik and Christian, 2014).

[5]The mixture is akin to a kind of cement whose stiffness varies according to the proportions of its ingredients.

This is also the case with ripened fruit and some vegetables, although there is more to it than that (as will be shown). Other fruit and vegetables though, when the intercellular cement is weakened, some especially those containing starch grains like potatoes will not have a melting mouthfeel but rather chalky.

14.2.1 CELLULOSE AND LIGNIN

Cellulose is very resistant to change. It is one of the most abundant plant biomasses on earth. And as mentioned, like starch, cellulose contains strings of glucose sugar molecules bound so tightly that makes it indigestible to animals and invulnerable to chemical treatment or extreme heat. Cellulose's strength and stability are valuable in many ways (wood is one-third cellulose, while cotton and linen are almost 100% pure); however, this makes it a nightmare for the cook as it simply will not be made pliable or softened by any known kitchen techniques. In fact, it can be something of a nuisance in certain stems and stalks like the stringiness of celery and the artichoke-like thistle cardoons. Lignin is also a cellular strengthening agent very resistant to breakdown, but it has little role to play in the kitchen. This is because most vegetables are harvested well before any appreciable amounts of lignin are formed although on occasion we do come across woody and toughened broccoli stems (Belitz et al., 2009). The only remedy for this kind of toughness as mentioned before is to simply peel the vegetables involved, ridding it of the worst excesses.

14.3 PLANT COLORS

(See also Section 14.9.1)

Plant colors (called pigments) are designed to function in plant energy conversion process—photosynthesis. The colors help to capture as much light energy as possible while also attracting insects to flowers to encourage pollination. There are four groups or families of plant pigments each with different functions in a plant's life. All of them are large molecules. The challenge for the kitchen cook is to preserve the vividness and appeal of these remarkable colored fruits and vegetables during cooking and processing. The difference in a fruit or vegetable's color is determined by the different proportions of these pigments (Davies, 2009).

14.3.1 GREEN CHLOROPHYLLS

Green chlorophylls are everywhere. These humble molecules harvest sunlight channeling it directly to the photosynthetic system that converts it into sugar (energy) molecules. There are two varieties: chlorophyll *a* that tends to be a bright bluey green color, while chlorophyll *b* is a more subdued olive color. In most leaves, the chlorophyll *a* form dominates the b-form by 3:1. Physically, the chlorophylls are concentrated in plant cell bodies (in particular embedded in the cell's membrane) whereby they are called chloroplasts. Each chlorophyll molecule is composed of two parts. The first is a ring of carbon and nitrogen atoms with a magnesium atom at the center. These are soluble in water and do the work of absorbing light. The second fat-soluble tail of 16 carbon atoms is colorless and anchors the whole molecule in the chloroplast membrane. These molecules are easily altered during cooking and are the

reason why the bright green of fresh vegetables is so fragile. Therefore, attention to temperatures, acidity, and cooking times is essential to serving bright rather than dull green vegetables (Belitz et al., 2009; Davies, 2009).

Homemade chlorophyll—cooks nowadays have access to many coloring agents, especially the green pigments. However, good cooks can also utilize vegetable extracts from natural ingredients by making it themselves. When it comes to culinary chlorophyll, for instance, this is made by finely grinding dark green leafy vegetables in order to isolate and break open cells. This preparation is then soaked in water to dilute pigment-damaging enzymes and acids while separating out solid fibers and other cell-wall debris. This is then gently simmered for a brief period of time to inactivate enzymes and allow cells and free chloroplasts to rise to the surface. After straining off the green mass, the cook can then use it to color foods and sauces at the last minute, although culinary chlorophyll will, like its natural cousin, still become a dull green with prolonged heating.

14.3.2 YELLOW, ORANGE, AND RED CAROTENOIDS

The first member of the large family of carotenoids to be chemically isolated came from carrots—hence the name carotenoids. These pigments (beta-carotene, xanthophylls, zeaxanthin, anthocyanins, lycopene, capsanthin, and capsorubin) are responsible for most of the yellow and orange colors found in fruits and vegetables and some of the reds found in tomatoes, capsicums, watermelons, etc. Carotenoids are chains of around 40 carbon atoms that are predominantly soluble in fats and oils. They are also relatively stable, so fruits and vegetables tend to stay bright when cooked in water. Carotenoids are found in two different spaces within plant cells: The first is in special pigment bodies (chromoplasts), which signals when fruit or vegetables are ripe, while the second, like chlorophyll, resides in the photosynthetic membranes of chloroplasts. The main role of carotenoids in chloroplasts is to protect chlorophyll and other parts of the photosynthetic system by absorbing potentially harmful light wavelengths while acting as antioxidants during the high-energy chemical photosynthesis (Vaclavik and Christian, 2014; Davies, 2009).

There is a nutritional component to carotenoids too; several are converted to vitamin A in the human intestinal wall. Although, strictly speaking, only animal-derived foods contain vitamin A itself, whereas fruits and vegetables contain only vitamin A precursors. However, without these pigment precursors, there would be no vitamin A in humans and animals.

14.3.3 RED AND PURPLE ANTHOCYANINS

After chlorophylls and carotenoids, anthocyanins are the third major class of plant pigments. Anthocyanins are responsible for most of plants' yellow red, purple, and blue colors. They are susceptible to the acid-alkaline balance of foods with alkalies pushing the color toward the blue spectrum. Their main function is for signaling purposes in fruits and flowers. Anthocyanins are also a subgroup of the huge phenolic family (*see appendixes*). These particular phenols are water-soluble that means the colors leech out into cooking liquid when boiling. They are also valuable antioxidants, and there are about 300 known anthocyanins with most fruits or vegetables usually containing a mixture of a dozen or more.

Table 14.1 Major Pigments Found in Fruit and Vegetables

Pigment	Common Varieties	Where They Originate	Example of Typical Colors
Chlorophylls	Chlorophyll *a* and chlorophyll *b*	Green plants	Green
Carotenoids (tetraterpenoids)	Carotenes and xanthophylls	Carrots, corn, egg yolks, rutabagas, and bananas	Oranges, reds, yellows, pinks
Flavonoids	Anthocyanins, aurones, chalcones, flavonols, and proanthocyanins	Common in plants like berries, eggplant, and citrus fruits. Also found in certain teas, wine, and chocolate	One of the most important plant pigments producing yellow, red, blue/purple
Betalains	Betacyanins and betaxanthins	Found in vibrant lowers and fungi	Red to violet, also yellow to orange

Multiple sources including Vaclavik, V., Christian, E.W., 2014. Essentials of Food Science. New York: Springer; Davies, K., 2009. Annual Plant Reviews, Plant Pigments and Their Manipulation. Boca Raton, FL: John Wiley & Sons; Belitz, H., et al., 2009. Food Chemistry, 4th Edition revised and extended edition. Heidelberg: Springer.

14.3.4 PALE YELLOW ANTHOXANTHINS

Anthoxanthins are a type of flavonoid pigment found in plants. They range in color from white or colorless to a creamy yellow, often found in flower petals or vegetables like potatoes, onions, and cauliflowers. As with anthocyanins, anthoxanthins are susceptible to foods acid-alkaline balance. In this respect, these pigments are generally whiter in a lightly acid base and yellower in an alkaline medium. Anthoxanthins are water-soluble pigments whose color is also very vulnerable to changes in mineral content and metal ions. As with all flavonoids, anthoxanthins are important in nutrition; they also display antioxidant qualities and are sometimes used as food additives.

14.3.5 RED AND YELLOW BETAINS

The fourth group of plant pigments is the betaine. They are relatively scarce and are found in only a handful of distantly related species. That said, they appear in several popular varieties of vegetables: beets, chard, amaranth, and prickly pear. The betaines (also known as betalains) are similar to anthocyanins in that they are water-soluble, sensitive to heat and light, and trend toward the blue in alkaline conditions. There are approximately 50 red betaines and 20 yellow betaxanthins, which when combined produce the stem and vein colors of novelty chards. The red betaines contain a phenolic group and are good antioxidants, while the yellow ones do not (see Table 14.1).

14.4 PLANTS: DEFINITIONS AND CLASSIFICATIONS

So, what is the difference between a fruit and a vegetable? Fruits and vegetables collectively have a technical and a common meaning. However, according to Thompson and colleagues,

> …there is no universal agreement on the meaning of 'fruits' and 'vegetables'.
>
> (Thompson et al., 2011)

Despite the sentiment, technically, a fruit is thought of as being the edible part of a plant developed from a flower's ovary's like those of the sweet, fleshy foods like oranges, bananas, and peaches for instance. In a biological sense, however, fruits are also technically those from seed-bearing plants (MacmillanDictionary.com, 2016). That said, this does not address those fruits and vegetables such as cucumbers, pea pods, nuts, capsicums, cereals (like corn, wheat, and rice), and pumpkins, which are also technically fruits but are not treated as such. Under the technical sense too, there are fruits that are not traditionally "true fruits" since they are not derived from the ovary. Examples include figs, pineapples, and strawberries (Jolles, 2010; Royal Botanic Gardens, 2016).

Having said that, a common, well-defined system of crop classification is important not only in crop science but also in the agricultural, culinary, and everyday world. Furthermore, there is a lot of confusion surrounding such questions as what exactly are the differences between fruits and vegetables? Thus, standardizing fruits, vegetables, legumes, nuts, seeds, herbs, and spices, among others, can serve to simplify communication, dissemination, and retrieval of information.

Despite this obvious advantage, however, classifications of crops (especially in agriculture) vary from place to place and even from country to country. The confusion is due to the absence of a universal standard, and this is a concern for professionals and laypeople alike. Indeed, it is not uncommon to have two or more classifications used simultaneously: a good example of this is the humble peanut that, depending on where the information comes from, can be a groundnut; a legume seed crop; an oil seed crop; an industrial crop; or even a plantation crop. This is not a local problem either in the FAO report of 2010 "crops statistics–concepts, definitions, and classifications" (FAO, 2010); the FAO expresses this very difficulty, and the trouble it has in estimating statistical data on fruit and vegetables due to differences in concepts, definitions, coverage, and classifications of crops from country to country.

Plants then can be classified in many different ways depending on one's requirement or viewpoint. That is, they can be classed according to their botanical, descriptive, or agricultural features.

14.4.1 THE BOTANICAL CLASSIFICATION OF CROPS

The International Code of Botanical Nomenclature (ICBN) and the International Code of Nomenclature for Cultivated Plants (ICNCP) are the governing bodies that set the rules on botanical classification of crop plants. However, like so many bodies of its type, the ICBN has no legal status and is wholly dependent on the voluntary acceptance of its rules by authors, editors, and other users of plant names (McNeill, 2003; Royal Botanic Gardens, 2016). The ICBN is revised every 6 years, as of the last meeting in the following hierarchical ranking, the taxa of plant categories serve as criteria of botanical classifications. Note that each taxon is usually subdivided by other groups immediately below each division (Fig. 14.2).

14.4.2 DESCRIPTIVE CLASSIFICATION OF CROPS

As one can see over the next few sections, there are many ways in which crops, plants, fruits, vegetables, and the like can and are classified. Each is used in a different context, but the difficulty lies in knowing which to use when.

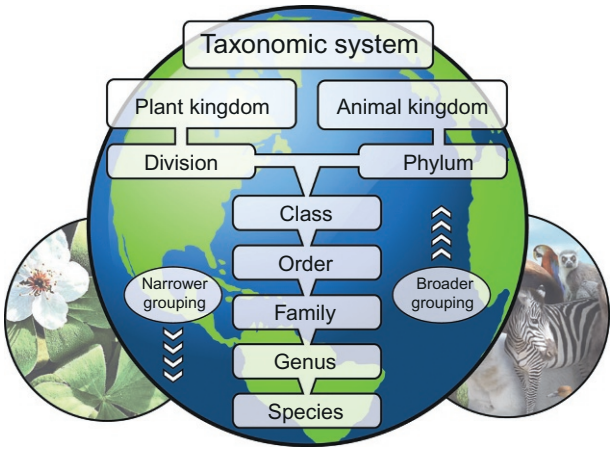


FIG. 14.2

Divisions of taxonomic classification.

Crop Classification Referred to by Method of Pollination

- *Naturally self-pollinated plants*—is the principal way in which both pollen and the embryo sac are produced either within the same flower or alternatively in different flowers within the same plant. Examples include most pulses, rice, okra, tomato, and tobacco plants.
- *Naturally cross-pollinated plants*—are those that require fertilization whereby pollen is transferred from one flower to the stigma of another flower in a separate plant. Examples include corn, grasses, grapes, avocadoes, and mangoes.
- *Both self- and cross-pollinated* plants—not only are usually self-pollinating but also occur with varying amounts of cross-pollination. Examples include cotton and sorghum.

Crop Classification Based on Growth Habit

- *Vines*—are herbaceous plants meaning they have no woody self-supporting stems above ground. These may be climbing or twining annuals, biennials,[6] or perennials.[7] Examples include cucumbers, sitaws (varieties of beans), and yams (Bareja, 2011).
- *Lianas*—are long-stemmed woody climbing or twining plants. As with vines, they depend on other plants for vertical support. Examples include grape, rattans (manila or Malacca), and passion fruit.
- *Shrubs*—are small treelike and erect woody plants that produce several branches from the base. Examples include Barbados cherry, pink jasmine, and *Lantana*.
- *Trees*—are continuous growing plants with a large biomass of woody tissue; trees usually but not always display a single distinct stem or trunk reaching a height of 5 m or more.

[6]Biennials (not to be confused with biannual—which occur twice a year) either live for 2 years or have their life cycle that is a 2-year long process.
[7]Perennial plants are those plants that live for more than 2 years.

Crop Classification Described by their Life Spans

- *Annual*—a plant that lives for a short period of time from a few weeks to a few months. In short, a plant that germinates, grows, flowers, produces seed, and dies all in one season. Examples include corn, rice, mung bean, and squash.
- *Biennial*—a plant that has a life cycle of two growing seasons: The first year is usually required for vegetative growth and the amassing of food reserves, and the second season is for the production of reproductive parts. Examples include bulb onion, celery, carrot, and radish.
- *Perennials*—are plants, including all trees, shrubs, and many herbaceous plants that live indefinitely. Perennial plants continue to grow and produce seeds yearly either from a single plant or from succeeding regrowth.

Crop Classification based on Leaf Retention

- *Evergreens*—are plants that maintain their leaves through continually replacing them throughout the year. Examples include pines, palms, papaya, and most tropical plants.
- *Deciduous*—are plants that annually shed leaves for extended periods. Natural leaf shedding is more pronounced in deciduous trees living in temperate zones.

14.4.3 AGRICULTURAL CLASSIFICATION OF PLANTS

Another classification is based on whether or not a crop is a weed or not. This can be somewhat confusing as a basic definition of weed is an unwanted plant or crop. This then suggests that, for example, if one is purposefully growing corn but radishes begin to grow amidst the corn planting, then radishes are considered weeds. This is a very loose description but highlights the delicate demarcation of crops and weeds.

Crop vs. Weeds

- *Crops/plants*—in agricultural classification, crop/plants are considered either a crop or a weed. Crops/plants are any useful plants grown for any purpose. This could be for food, animal feed, spices, drinks, fibers, clothing, medicines, tannins, rubber, oils, ornamentation, fuels, beverages, construction materials, sugar, landscaping, and much more (Bareja, 2011).
- *Weeds*—on the other hand, weeds are unintended crops/plants that grow where they are not wanted. Ironically, if it is growing and competing with other plants/crops for space, nutrients, and light, it becomes a nuisance and must be removed. In this respect, any plant can be a weed. That is to say if corn and wheat grass plants are sown, they will eventually begin to sprout throughout the crop, and the normally desirable wheat grass is considered a weed and will be treated as such.

Agricultural Classifications Based on Primary Usage

Another important classification based partly on the United Nation's food organization is to group crops by their primary usage. This is perhaps more familiar to cooks and laypeople alike and are generally divided into two simple categories—edible and nonedible crops. These are illustrated in the following:

- *Food crops*—are an important group of plants grown chiefly for their harvest (which could be any part of the plant) that is then used by man directly as food or indirectly through its processing into a food product. This classification is a collective term for all those crops that are variously

subdivided into smaller groups such as cereals, roots and tubers,[8] legumes, seeds, beverage crops, sugar crops, fruits, and vegetables.

- *Nonfood crops*—are those grown for creation of nonfood products for humans like fodder or forage (animal feed) fiber, tobacco, alcohol, rubber, biofuel essential and industrial oils, pharmaceuticals, gums and resins, dyes and tannins, or those simply for ornamentation.

Food/ Edible Crops

- *Vegetable crops*—these are plants (except mushrooms) grown for their edible parts such as their roots, leaves, stems, or seeds for use in the culinary world. In this, the FAO notes that certain gramineous and leguminous plants harvested "green" (*see below*) are classified as belonging to this group. That is to say, in as far as they are harvested for the green grains and/or for their green pods (e.g., maize, green peas, green beans, string beans). If harvested for their dry pulses, they belong among the cereals and pulses (*see legume seed crops below*). Lastly and perhaps more importantly, the FAO distinguish vegetables as only those vegetables cultivated principally for human consumption as belonging to this group (FAO, 2010).
- *Pomological or fruit crops and nuts*—these are plants grown primarily for their edible fruits. All fruits and berries are permanent crops characterized by their sweet taste and their high organic acid content and pectin. Fruits from trees are, not surprisingly, called tree fruits, among which are the apple, pear, durian, mango, mangosteen, and papaya. Fruits harvested on low-growing plants such as shrubs and vines are called small fruits or berries, including the grape, passion fruit, and strawberry. Important sources of vitamin C, they are high in cellulose yet usually have little or no fat, protein, or starch.
- Some nuts on the other hand are tree crops yielding dry hard-shelled fruits or kernels of plants. They are characterized by their high fat, woody shells, or hard husks that are removed at harvesting time. Examples include cashew, groundnut, walnuts, and macadamia (FAO, 2010; Royal Botanic Gardens, 2016).
- *Nuts*—these are an important source of nutrients for man; there is also a lot of confusion between a seed and a nut (*see edible seeds below*). In short, we can say that some nuts are fruits, and some are seeds. Some examples of nuts are brazil nut, butternut, candlenut, chestnuts, cobnut, hazelnut, hickory nut, juniper berry, macadamia, maya nut, para nut, paradise nut, pecan, pili nut, pine nut, pistachio nut, Polynesian chestnut, royal walnuts, rush nut, sweet chestnut, tiger nut, walnut, and water caltrop.
- *Edible seeds*—a seed is a small embryonic plant enclosed in a seed coat or husk; a nut, on the other hand, is a hard-shelled fruit that contains a single seed. Put another way, seeds are the fertilized and ripened ovule, comprising the plant embryo, a protective outer seed coat, and stored food material (see Fig. 14.3). Some examples include almond, cashew, chia seed, flaxseed, hemp seed, poppy seed, pumpkin seeds, sesame seed, safflower, and sunflower seed (see also cereal, grain crops below).
- *Staple crops*—staple foods are those foods regularly consumed in such quantities as to form the basis of a traditional people's or region's diet. They also form a major proportion of this group energy and nutrient necessities (Bareja, 2011). Examples of staple crops include wheat, bananas and plantains, millet, breadfruit, potatoes, and yam, among others.

[8]Tubers are short, thickened, fleshy parts of an underground stem.

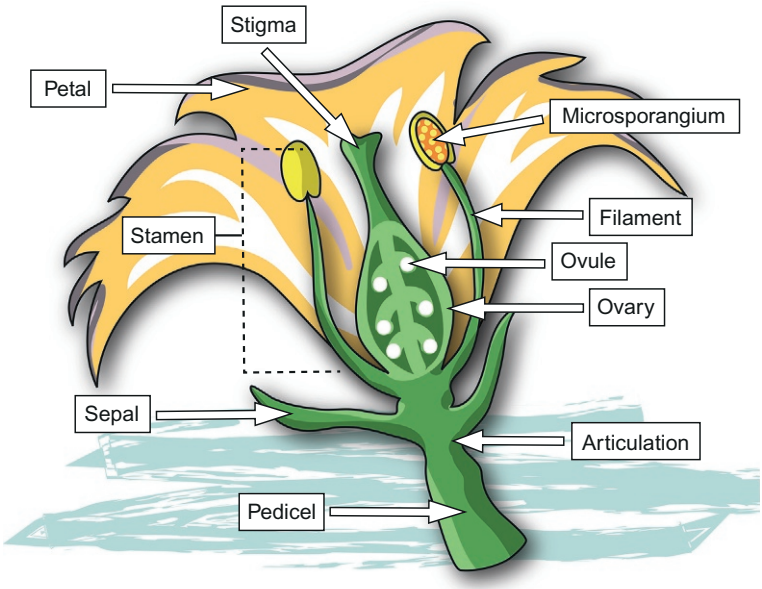


FIG. 14.3

Physiology of flowers.

- *Cereal or grain crops*[9]—these annual, herbaceous plants belong to the "true grasses" of the Poaceae (or Gramineae) family and some of the sedges (Cyperaceae) and the rushes (Juncaceae). All of which are grown for their seeds or grains. While strictly speaking, these include sprouted grain or shoots; the FAO defines cereals or grains as that that is used for food, feed, seed, and industrial purposes, e.g., ethanol. They exclude rhizomes and legumes (like pulses) but include rice, wild rice, wheat, corn (or maize), barley, millet, sorghum, oats, rye, triticale, teff, spelt, canary grass, and buckwheat. The FAO also specifies that cereals are those limited to crops harvested for dry grain only, excluding crops harvested green for forage, silage, grazing, etc. (FAO, 2010; Bareja, 2011).
- *Roots and tubers* or tuberous crops—these are plants that have evolved developing a swollen root or underground stem that include varieties of roots, tubers, rhizomes, and corms. They are generally rich in carbohydrates and are frequently used as staples, as livestock feed, or as raw materials for industrial purposes (including alcohol and starch production, among other things) (Bareja, 2011). Modified root crops are different from those with modified stems. A fleshy root is often an enlarged primary root like carrots and sugar beets, while a tuberous root, for instance, is a thickened secondary root like cassavas, sweet potatoes, and yams. While such crops can produce high yields, they generally contain low amounts of nutritional protein, minerals, and vitamins than cereal crops (FAO, 2010).

[9]Grains or cereals are used more often than not interchangeably. Cereals are plants in the grass family, the Gramineae, whose members produce edible and nutritious seeds (or grains).

- *Fungi*—there are five kingdoms of organisms, the plant, animal, Protista, Monera, and fungi. So, while not strictly a vegetable, for this agricultural classification, however, we have included it here. Fungi range from yeasts and mushrooms to truffles and others (Royal Botanic Gardens, 2016).
- *Legume seed crops* (*pulses*)—leguminous crops are annual plants that produce edible, protein-rich seeds called pulses; more precisely, the seeds are inside pods that split into two halves. Although on this front, the FAO once again prefers to use the term "pulse" to describe the dry seeds for food and feed only, preferring instead to use the term "legumes" for those harvested green seeds for food, i.e., green beans and peas, which are considered vegetables. Examples of dried and fresh legumes/pulses include beans, peas, lentils, soybeans, cowpeas, mung beans, peanuts, and peas.
- *Sugar crops*—these are a catchall for plants grown primarily for their sugar or other sweet-tasting products and secondarily for the production of alcohol. These sugars are simple carbohydrates, such as sucrose, (common table sugar), glucose (called dextrose), and fructose (levulose or fruit sugar) (Bareja, 2011). Other sweet-tasting organic compounds like alcohol, diterpene glycosides, and monellin can be harvested from various plant parts such as from stems, bulbs, leaves, flowers, seeds, fruits, resins, and sap. Other more familiar examples include sugarcane, sugar beet, sweet sorghum, corn, sweet potato, cassava, and many palms.
- *Oilseed crops*—these are annual plants grown for their seeds that are processed for their rich source of culinary and industrial oils (excluding essential oils). The most common oilseed crops are the soybean, peanut, sunflower, sesame, and cotton. As with cereals and pulses, oilseed crops (according to the FAO) should be limited to crops harvested for the dry seed only and not harvested green for food, feed, or grazing (FAO, 2010). Permanent oil-bearing crops are perennial plants whose seeds and fruits (olives, nuts, etc.) are used mainly for culinary or industrial oils (Bareja, 2011).
- *Essential oil crops*—these plants, grown for their essential oils, are mostly aromatic, volatile elements that often used in the cosmetic and perfumery industries. As a result, strictly speaking, these plants sit on the fence as being more inedible than edible, but we list them here as more and more cooks are turning to essential oils in the kitchen (see Section 16.4). Examples include citronella, eucalyptus, lavender, and peppermint.
- *Spice crops*—these plants grown for their strongly flavored, aromatic materials including plant components such as rhizomes, bark, fruits, berries, and seeds. Spices can also be rich in essential oils that are increasingly being used in the food industry. Spices are of high commercial value and include black pepper, garlic, hot pepper, onion, turmeric, ginger, vanilla, cinnamon, cloves, nutmeg, mace, cardamoms, ginger, anise, and fennel (FAO, 2010).
- *Beverage crops*—these are plants that are harvested as raw materials in the production of various drinks. Some of these drinks provide certain nutrients in the form of vitamins and minerals, while others are stimulants and relaxants too. Examples include tea, coffee, cocoa, fruit juices, coconut, and beer and wine (see also Section 14.6).

Non-Edible and Fodder Crops

- *Rubber, latex, and gum crops*—the production of latex (a form of rubber) is industrially processed into rubber, chewing gum,[10] and many nonedible industrial products such as surgical tapes, dental

[10]Chewing gum is the exception in this group of nonedible plants.

supplies, insulation, waterproofing, and adhesives. Examples of such plants include para, Castilla, Ceara, chicle rubber trees, and guayule (Bareja, 2011).

- *Dye and tannin crops*—plants grown for its content of tannin are used either as coloring, aromatic, or phenolic substances depending on the plant and the type of tannin. They are generally found in barks and other plant structures and are used in numerous industries including the tanning, pharmaceutical, ink, and dyeing industries (Bareja, 2011).
- *Pasture and forage crops*—these are also known as fodder crops; these plants, as the name suggests, are explicitly cultivated primarily for use as animal feed. Such crops contain three major groups of fodder plants: grasses including cereals (harvested green), legumes, pulses (also harvested green), and root crops specifically cultivated for fodder. All can be used as green feed, as hay (crops harvested or left to dry once harvested green) or as silage[11] products (FAO, 2010).
- *Fiber crops*—these are plants grown to be used as sources of fiber. These are mostly used for their soft but strong threadlike fibrous plant material that then goes on to produce yarn. From these beginnings, a large industry has grown up around the manufacture of innumerable fabrics including textiles, rope, twine, and similar materials (Bareja, 2011). Fibers are extracted from leaves, bark, coconut husks, and other plant organs. Primary fiber crops include cotton, jute, and flax (FAO, 2010).
- *Biofuel crops*—these are plants grown especially for the production of fuel. The main biofuel products (alcohol, biodiesel, and bioethanol) are processed from the fermented sugar or starch of such plants. Examples include sugarcane, corn, cassava, and coconut (Royal Botanic Gardens, 2016; FAO, 2010; Bareja, 2011).

14.5 FRUITS: REPRODUCTION AND RIPENING

Higher animals and plants reproduce joining genetic material from male and female sex organs. While animals have the advantage of being mobile and can thus initiate contact, plants do not have this luxury. Instead, they have to depend on mobile go-betweens whether wind, animals, or insects, which ultimately facilitates the connection of the male pollen and the female ovule. However, some encouragement is usually needed here, and the more advanced plants have evolved the flower, an organ designed to attract a specific assistant, most often an insect or a bird. As the animal flies around and collects nectar or pollen for food, it spreads the pollen from one plant to another.

Once both male and female cells have joined and developed into offspring, they should be given a good start in life. However, in this respect, plants need considerable help. That is to say, if the seeds merely dropped to the ground, they would end up competing with each other and with their parent for sunlight and much needed minerals. So, effective plant families have developed some ingenious and sometimes natural mechanisms for scattering their seeds far and wide. Some offspring (seed) containers pop open as they fall from the parent and propel the seeds in all directions away from the mother crop. Others rely on the wind or hitch a ride on the fur of a passing animal. More ingeniously are fruit containing seeds that plant organs actively encourage animals to eat. In this way, animals eat

[11]Silage or ensilage is a method of green fodder preservation through which fermentation is used to slow spoiling.

the fruit and will carry their seeds away eventually passing them through their digestive systems and depositing them far and wide. So, while plants have an arsenal of weaponry at hand to ward of animals and insects from destroying the plant itself, fruits are meant to be eaten. As a result, fruits (once ripened) are attractive in their own way, whether color, texture, odor, or flavor; they are appealing to animals and humans alike (Royal Botanic Gardens, 2016).

As mentioned previously, fruit is a distinctive tissue that develops from the flower, often from the female tissue or more specifically the thickened wall of the ovary—(Fig. 14.3) which usually envelops the plant seeds.

Not surprisingly then because of this, confusion spreads to vegetables too. As such, commonly interpreted, vegetables usually denote the edible plant or part of a plant that is neither a fruit nor a seed. In this way, depending on one's viewpoint, many plant parts can therefore be seen as either vegetables or fruits. A common popular work-around relates to the kitchen where the meanings of fruits and vegetables are usually based on culinary and cultural traditions (Jolles, 2010). In this way, an important distinction is the notion that we predominantly (but by no means always) serve vegetables as accompaniments to main courses and fruits as the center of a dessert—although this is a loose generalization as more and more cooks these days experiment with swapping traditional roles of certain fruits and vegetables. Both fruits and vegetables are intended for us to eat (stalks, and other indigestible plant biomass, etc. notwithstanding) although one culinary distinction is that fruits are the natural world's candy so to speak. They come in all colors and have distinct and complex aroma profiles (involving up to several hundred chemicals). They become tender and more flavorful with ripening and importantly are sweeter in order to satisfy an innate liking for sweetness that is shared by nearly all animals. By contrast, foods we regard as vegetables remain firm, either possessing mild flavors like cucumbers, green beans, and potatoes, or they go the other way with excessively strong flavors and aromas like onions and chilies (Royal Botanic Gardens, 2016; McGee, 2004).

While most of earth's plants are relative newcomers (around 200 million years), an even more recent development is the herbaceous[12] species of plants. In fact, most food plants are not, as we imagine, long-lived trees but are in reality small, delicate herbaceous plants that grow, produce their seeds, and die in a single growing season. In doing so, plants show greater flexibility in adjusting to changing conditions that, in turn, allows us to grow crops to full maturity in just a few short months.

14.6 HERBS AND SPICES

Given the difficulty in describing fruits and vegetables luckily, herbs and spices are a little more straightforward. While both are primarily used to flavor foods, herbs come from the green parts of any number of aromatic or flavorful plants (usually leaves), while spices can be thought of as any other part of the plant whether, seeds, bark, buds, fruits, stems, or roots (Herman, 2015). Of note also is the fact that we tend to consume herbs and spices in small quantities; thus, in this respect, they possess negligible nutritive value. Despite all this though from early history, herbs and spices have been some of the most coveted and costly of all ingredients. Even today, herbs are significant additions to the cook

[12]Herbaceous plants are those plants with little or no woody tissue, which generally persist for only one growing season.

in the kitchen, and many flavors can be enjoyed that remind us of regionally specific origins. Interestingly, few might be aware that herbs and spices also include both the numerous varieties of tea leaves and of coffee beans (seeds). In this way, herbs and spices can be thought of as regional and cultural emissaries of their homegrown countries (Royal Botanic Gardens, 2016).

Herbs and spices as we have noted are strong, concentrated potent sources of aromas and tastes. In fact, chew on a clove or a piece of cinnamon bark and chili, and one finds the experience not particularly pleasurable; instead, one finds their mouths replete with pain, acrid, astringent, numbed, or sufficient to simply irritate our senses. This harks back to the primary function of the plants herb or spice—that of self-preservation. That is to say, herbs and spices in particular are defensive, chemical weapons protecting themselves from predators and microbes. Having said that, we use these potentially toxic foods in the kitchen in sufficiently dilute quantities to ensure such ingredients are rendered not only harmless but also simultaneously tasty, pleasurable, complex, and appealing.

If extracting flavors or the essences from herbs and spices, one might end up with the active component or essence of many plants—essential oils (see Section 16.4). To mimic essential oils, some cooks end up infusing neutrally flavored oils with herbs and spices. Of course, essential oils can be used instead, but they must be food-grade essential oils that tend to be stronger, more difficult to come by, more potent, and more expensive. Thus, essential oils can be thought of as concentrated essences. In perspective, it can be seen that some dry spices might contain as much as 5%–15% essential oil by weight, while dried herbs contain much less, as little as 1%.

There are two groups of flavor compounds that are worth mentioning here: the terpenes and the phenolics (see also Appendix B and Section 14.9).

Terpene compounds—because of their chemical makeup (building blocks of five carbon atoms), it turns out that terpenes are remarkably versatile. Its chemical profile allows itself to be combined, twisted, and reformed into tens and thousands of different molecules. Plants, especially herbs and spices, have been shown to produce a mixture of defensive terpenes. The manifest in all manner of ways includes the needles and bark of coniferous trees, of citrus fruits, and of course in the flowers themselves. As a result, they produce the fresh notes like pine, floral, citrusy, and leaflike qualities in the cook's kitchen. Moreover, as a family, terpenes and their derivatives tend to be especially volatile and reactive, meaning they are often the first molecules to reach the olfactory senses. The downside, however, means that they are readily boiled away or modified by even the briefest of cooking. This is why some cooks leave adding herbs and spices just before serving.

Phenolic compounds—are created from a simple closed ring of six carbon atoms with at least one water molecule fragment. Different from terpene aromatics (which might seem a little generic), the phenolic aromatics are very distinctive in their aromas and flavors. These include herbs and spices like anise, cinnamon, cloves, thyme, oregano, and vanilla. Moreover, the pungency of chilies, black pepper, and ginger is also fashioned from a phenolic base.

As we have already shown in previous chapters, flavor is a composite quality of many aroma and tastants. This is no less true of the herb and spice family too; so, while we might distinguish a particular herb or spice as containing one specific taste or aroma, they are in fact made up of several hundred different compounds. That said on occasion, a single compound might well dominate or provide the main character, although in other cases most main flavors are in reality combinations of many unifying compounds.

14.6.1 PRESERVING AND STORING AROMA COMPOUNDS

The main goal of having a selection of herbs and spices on hand is knowing how best to preserve them without too much loss of aroma and flavor compounds. The very volatility and chemical reactant nature of herbs and spices that give us so much pleasure in cooking is also its Achilles heel. Herbs and spices are generally very volatile and are reactive when in contact with oxygen, heat, light, moisture, and temperature. As such, these variables can easily alter delicate and even robust flavors of the plant material. Thus, in order to preserve herbs and spices, most are dried, so that they do not decompose. This has to be undertaken as gently as possible so that water is removed without removing all the flavor. This, as mentioned, is because by the nature of the herbs and spices that, being very volatile, means any evaporation of water will also speed up the evaporation of the volatile molecules, potentially altering the herb or spices core aroma profile hence the drying of these materials. Once dried, they must be kept dry in a cool, dark storage area. Ideally, this would be in containers in the freezer; however, practically, this is not always possible or even desirable. In general, the keeping quality of herbs and spices are OK as long as they are not habitually exposed to strong light, in room temperature, and away from strong light. If stored properly, these flavorants can be optimally kept for over a year, while ground spices only for a few months.[13]

Fresh herbs—when it comes to fresh herbs, they should never be stored in closed containers; as when cut, the ethylene hormone is released and encourages general deterioration. Instead, loosely wrapping them in a moist cloth or tissue paper will slow down the growth of spoilage microbes. Another option with fresh herbs is to store them in the freezer, bearing in mind that the thawed product would be less than attractive. If these are then to be used as flavorings, then freezer storage is fine; however, if they are for decoration, then freezing would defeat the purpose as the herbs will come out limp and lifeless. Another alternative to refrigerating and freezing fresh herbs is to immerse them in oil and keep them in the fridge (for bacterial reasons). This protects the tissue from oxygen and can even be held for a few weeks in this condition.

Drying fresh herbs—as some herbs contain up to 90% water, drying them can be problematic. This is because, as mentioned, there are many aroma chemicals that are more volatile than water, so processing fresh herbs through evaporation of water will also evaporate most of the volatile flavor aromas. This is one of the major downfalls of drying herbs, as once dried herbs can taste more like hay than their fresh counterparts. There are of course exceptions, and these include many of the hotter countries herb crops like those of the Mediterranean that are not overly affected by the drying process. These include herbs such as oregano, thyme, rosemary, and bay leaves. Also, when it comes to drying, freeze-drying is the preferred method, as it retains more of the aroma chemicals. Sun drying, while sounding romantic destroys more of herb aroma profile, instead a few days in the shade, is better although much slower. Another option is oven-drying, yet, although this method is quicker, the higher temperatures involved are also a downside. Surprisingly, the microwave turns out to be marginally better than sun or oven-drying as a method of preservation of herbs as, thanks to its rapid vibration of water molecules, evaporation occurs while leaving many nonpolar, oil-like flavor molecules moderately unaffected. Using the microwave is also an advantage when it comes to time as the process, depending on the amount to be dried, will usually just take a few minutes.

[13]The fine particles of powdered spices lose their aroma molecules to the air more rapidly due to the large surface area of these items.

A cook's arsenal of flavor—one of the trickiest things a cook needs to develop in their careers is just how to extract the most flavor from their aromatics as they can. For fragile herbs and spices, this often means simply mixing them into the dish at the last minute whether in stews or in soups and other dishes like some Thai soups for instance. For the more robust herbs and spices, they might require chopping shredding or crumbling and popping them directly into the dish at an early stage. If a spice is to be used, one can either pop in the whole spice or in the case of spices like whole nutmeg and the like can be ground to break open and give more surface area, thus exposing more of the key aromatics to the dish.

Once herbs and spices are added to a recipe, they are immediately exposed to oxygen, heat, and other ingredients and begin to undergo a multitude of chemical reactions. Not surprisingly, after all that has been said on the subject of aroma profiles, some proportion of the original aromatic is altered by the above factors. The test of a good cook is the art of moderation, i.e., one does not add sage to a stewed dish and expect to have that sage overpower the final dish. Instead, two things happen; part of the sage profile is altered during the cooking process in a way that should complement but not overpower the various other elements or flavors in the dish. In this sense, the cook's experience once again comes to the fore. Another example is of an Indian cook toasting mustard seeds, cumin, fenugreek, or coriander in a pan; in the process, the sugars and amino acids undergo browning reactions that generate other savory aroma molecules typical of roasted and toasted foods (pyrazines). In turn, this adds a depth of flavor that complements the original raw aroma. This knowledge comes from years of experience and knowledge from traditions being handed through the generations.

Herb and spice extracts—when making flavored oils, vinegars, and alcohols, the herb or spice is usually chopped, crushed, bruised, or otherwise damaged in order to crush the cells allowing the chosen aromatics (liquid or otherwise) to seep out. Oils, vinegars, and alcohols are often heated before the process to kill bacteria and to enable herbs and spices initial seepage into the liquid medium. The length of time it takes to make a culinary extraction depends on the medium used and the herb or spice in question. This could take anything from just a few short hours for flowers and alcohol or a few weeks for seeds and the hardier of the herbs. On the bacterial front, it is important to know that most of these mediums do not encourage the growth of microbes, while the herbs and spices concerned do not provide enough nutrients under these conditions to encourage spoilage bacteria. There is one exception though and that is garlic and oil. A cautionary note—oils actually encourage the growth of the pathogen *Clostridium botulinum*, whose spores survive brief boiling and can germinate when there is no air. Infused garlic oils are safest when they're made and immediately refrigerated.

Commercial extracts—commercial extracts, unlike their kitchen counterparts, tend to be highly concentrated, so they must be used with care. Some familiar flavors include vanilla, mint, and almond. While some are produced naturally using actual herbs and spices, others are synthetically prepared from one or chemical flavorings (see Section 16.4).

14.7 SEASONS AND FRUIT AND VEGETABLES

Eating seasonally fresh produce is constantly being touted for its health, economic, and environmental benefits. Yet, the big elephant in the room here is that "seasonal" varies depending on where one lives and the length of a particular region's growing season. More specifically, foods are now grown all over the world: across a diverse pattern of climates, soils, and agricultural systems; in frost-ridden climes to

cool or temperate zones; and to sub- and tropical regions. Furthermore, temperature aside, once such variables as humidity, wet or dry areas, latitude, and topography are factored in, one ends up with a plethora of options in which to grow fruits and vegetables. What this means operationally is the notion that seasonal foods are regional and climate-specific, so what works in one area might not necessarily work in another. Put another way, growing strawberries to be harvested in Washington in June and July can be harvested all year round in California.

What this translates to, for the humble cook, is that wherever the cook is contemplating local seasonal foods on his/her menu, this will mean one thing in the Philippines, another in Morocco, and another in Britain. This is all very well if a cook is local to the region and is aware of local produce seasons, but if one is a career cook with many continents under his/her belt, then it becomes that much more difficult to discern local versus global fruit and vegetable.

One rule of thumb is offered by the United States-based "Produce for Better Health Foundation" in which it advocates knowing the temperatures and climes that are preferential to fruits and veggies like. Once that is known, it becomes a little easier to determine if they were grown locally or in other favored temperature locations (Vaclavik and Christian, 2014; Pivonka, 2014). However, such is the advances in agritechnology these days that many fruits and vegetables can now be grown in non-native regions and even in local areas that does not help with the demarcation of the "local-global" debate.

14.8 POST-HARVEST CONSIDERATIONS

The moment fruits and vegetables are harvested, they begin to change. For the most part, these changes are not good, while exceptions might see some postharvest fruit or vegetables overripening, while other vegetables tend to hibernate such as onions and potatoes (see "Metabolism" below). Although having said that, one great advantage that plant cells have over animal cells is the fact that plant cells are hardier and can therefore last for weeks or months under the proper conditions. Although it must be noted that both fruit and vegetable need constant nutrient replenishment during storage otherwise, they end up consuming their own flesh in an attempt to prolong life. As this happens, it affects both flavor and texture. As extreme examples, take the pea and some varieties of corn that can end up converting as much as half their natural sugars into starch for energy in order to stay alive—this can begin within just a few hours after picking. Eventually, both fruit and vegetable cells ultimately run out of energy, wither, and die as their enzymes act upon themselves—effectively catabolizing themselves. Hastening this process are microbes that are always present on the surface skins and in the air. Especially, microbes like bacteria, molds, and yeasts that are ever present attack the cell walls and the contents of the cell (WSU, 2017). Although all microbes affect the quality of postharvest crops, the biggest threats are bacteria that grow faster than other microbes. Although fruits are generally more acidic than vegetables, they are more resistant to many opportunistic bacteria. Fruits instead are more readily attacked by yeasts and molds such as *Penicillium* and *Botrytis*. In terms of preparation, for optimum quality, cutting fruits and vegetables tends to break open cells and their walls, so they should be cut at the last minute or cut and stored properly, perhaps in modified atmosphere bags. As the fruit or vegetable is cut, two things happen: The first is that tissue damage encourages more defensive activity and, in the process, depletes their remaining nutrients causing such changes as browning and/or the rise of bitter and astringent flavors. Secondly, cutting also exposes the nutrient-rich interior to infection by microbes.

Metabolism

When storing fruit and vegetable, the aim is to slow the inevitable deterioration. Metabolism is something we think of as an animal/human trait, yet metabolism is just as much a part of the plant world. For instance, mushrooms, berries, papayas, figs, avocados, and apricots all have naturally high metabolic rates, so they end up deteriorating faster than the slower apples, pears, cabbages, kiwi fruits, carrots, and others that end up keeping better. On the other hand, soil harbors large numbers of microbes and should be removed from the surfaces of sturdier fruits and vegetables before storing them. In both cases, though, oxygen plays an important role in the shelf life of both crops. While fruit and vegetables still require oxygen for the metabolic process, reducing its presence for instance will help slow down the process. One work-around solution found more and more in stores these days is the innovative practice of using modified atmosphere packaging containing a mixture of nitrogen, carbon dioxide, and just enough oxygen (about 8% or less) to help keep the plant cells functioning normally. On the flip side, when it comes to too little oxygen, fruits and vegetables switch to anaerobic metabolism. This has the side effect of producing alcohol and other odorous by-products characteristic of fermentation. Low oxygen also aids in internal tissue damage and browning process. However, in the kitchen, the average cook does not have, at his/ her disposal, the necessary equipment to achieve modified packaging and tight plastic wrapping around fruit and vegetables, while common is not the answer to keeping them fresh. Instead, placing these items in a sealable plastic bag with most of the air taken away goes a long way to keeping fresh produce fresh. That said, as a cautionary note here, as plastic-bagged fruits and vegetables (fruit especially) excrete ethylene gas,[14] so produce may pass from ripe to overripe quicker than is perhaps wanted (WSU, 2017).

14.8.1 TEMPERATURE CONTROL

Having said all that, the most effective and efficient way to prolong shelf life of fresh produce is to control its temperature. As a rule, cooling slows chemical reactions; in general, this includes the metabolic rate of the plant cells themselves and the growth of deteriorating microbes. Indeed, a mere 5°C/41°F reduction in temperature can nearly double storage life of certain foods. While the author understands, this is a gross generalization; it is mentioned simply as an example. This is because the optimum storage temperature is different for different fruits and vegetables and with produce from different climes. For instance, fresh produce specifically native to temperate climates are best kept near freezing point. In this way, controlling the storage atmosphere (oxygen, temperature, humidity, nitrogen, and carbon dioxide) and the temperature of apples may actually keep for up to a year. Yet, fruits and vegetables native to warmer climates such as banana skins that turn black at cooler fridge temperatures, avocados (which darken and fail to soften or ripen), melons, eggplants, tomatoes, squash, cucumbers, peppers, beans, and citrus fruits (which can develop spotted skins), if kept at lower temperatures, have a tendency to promote uncontrolled enzyme action. This in turn causes damage to cell walls and the possibility of discoloration and which can, simultaneously develop off-flavors. Chilling injury may not become apparent while in the fridge; instead, the symptoms described above might only manifest after taken out of the fridge and brought to room temperature. The answer then is to keep tropical and

[14]Ethylene gas is a hormone that accelerates ripening in fruits and incites defensive activity and accelerated aging in other tissues.

subtropical fruits and vegetables at the moderately high temperatures of 10°C/50°F or alternatively at room temperature.

Another method of storing harvested produce is to freeze it. This has the effect of terminating all metabolic activity of fruits, vegetables, and spoilage microbes. Furthermore, freezing crystallizes most of the water in plants, effectively immobilizing molecules that in turn suspend most other chemical activity. While defrosting, however, microbes will revive, yet plant tissues die. Further, as plants are frozen, they suffer in two ways. One way is through the action of frozen water within and around cells. As water freezes, it expands becoming crystalline; as this happens, water crystals piercing cell walls and cell membranes, consequently, as the food thaws, so cell fluids leak out resulting in lost crispness and limp and wet fruits and vegetables. One work-around solution that helps to some degree is to reduce the size of the water crystals. This can be achieved by freezing the food as quickly as possible (like ice cream) using a blast freezer or similar apparatus.

As well as the general physical and chemical breakdown of plant cells through freezing, another aspect that is heightened, rather than reduced, is the enzymatic breakdown of vitamins and pigments. Another work-around in this case is to blanch the fruits and vegetables long enough to inactivate the enzyme's responsibility (usually a minute or two in boiling water). Also, when it comes to freezing fruits, enzymatic browning can be reduced or prevented by packing the fruit in a sugar syrup enhanced with ascorbic acid. Lastly, fruits and vegetables should be covered as air- and watertight as possible (previous caveats withstanding) as areas of produce left exposed to the relatively dry atmosphere of the freezer can, if exposed, readily develop freezer burn.[15]

14.9 PLANT FOODS AND HEALTH

Despite meat's appeal and nutritional value, plant foods can in fact provide us with all the nourishment we need to live and thrive. Indeed, nowadays, nutritional science focuses more on defining the elements of an "optimal" diet. And in doing so, we discover that minor, seemingly nonessential, food components found in fruits and vegetables can have a beneficial cumulative effect on our long-term health. In actual fact, there are many animals and cultures that eat nothing but plant foods. This is despite the fact too that the industrialization of meats is effectively pushing fruits and vegetables aside. Sadly, it is only in relative recent years that the full nutritive value of such plants is becoming fully recognized (Gibson, 2012; Grassi and Ferri, 2012).

14.9.1 PHYTOCHEMICALS

While fruits and vegetables contain a rich variety of vitamins, minerals, and fibers, they also contain things called phytochemicals. Phytochemicals are those chemical compounds found naturally in plants that, although, are still not established as essential nutrients and possess protective or disease preventive properties (LPI, 2017). In fact, as many as 5000 individual phytochemicals have been identified, and many more are as yet undiscovered (Pivonka, 2014). Although many but not all phytochemicals are plant-coloring pigments, some are in fact colorless, and others are responsible for

[15]Freezer burn is the drying out of produce caused by the evaporation of frozen water molecules (sublimation) which in turn develop "burned" patches leaving a tough texture and stale flavor.

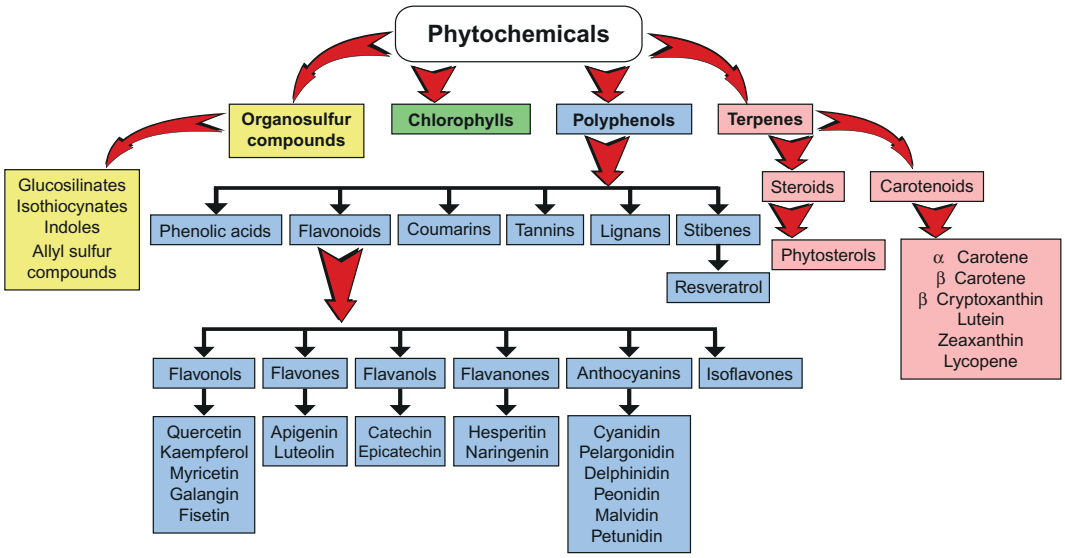


FIG. 14.4

Classes of phytochemicals in plants.

taste. Furthermore, while they are also responsible for certain organoleptic properties such as color and smell, there is mounting evidence that phytochemicals might also have more biological significance than at once thought (Pivonka, 2014). So, while they are nonessential nutrients,[16] it is thought that plants produce these chemicals to help protect themselves (LPI, 2017). A small but not exhaustive list of phytochemicals include carotenoids, chlorophyll and chlorophyllin, curcumin, fiber, flavonoids, garlic, indole-3-carbinol, isothiocyanates, lignans, phytosterols, resveratrol, and soy isoflavones (Fig. 14.4).

As the diagram shows (Fig. 14.4), flavonoids are the most copious of the polyphenols incorporating several subclasses. Recent research, while scarce, has tentatively demonstrated that they can also protect humans against certain diseases, particularly when it comes to the reduced risk of chronic diseases including cardiovascular disease, stroke, and certain types of cancer. The answer then, as to whether phytochemicals are healthy, lies in studies that show that the best health benefits appear to come from eating the whole fruit or vegetable as opposed to taking isolated nutrients (Fig. 14.4) (Belitz et al., 2009; Carkeet et al., 2012; Heneman and Zidenberg-Cherr, 2008; Pivonka, 2014).

So how are phytochemicals beneficial?

Phytochemicals are found in edible portions of all fruits and vegetables[17] and in animals. It appears too that nutrients and certain phytochemicals seem to work together producing greater benefits as a whole than they may produce in isolation (Pivonka, 2014).

There is still not enough known about the bioavailability of phytochemicals although scientists have identified certain ways that phytochemicals work. Many phytochemicals appear to have strong

[16]Phytochemicals are nonessential nutrients, meaning that they are not required by the human body for sustaining life.
[17]Phytochemicals are frequently concentrated in the skins of fruits and vegetables.

antioxidant properties (*see below*), moderating the damage to cells from oxidation. There is also evidence to suggest that phytochemicals also have a role to play in the many metabolic pathways within the body. Furthermore, others seem to prevent blood cells from sticking together, and others still work to reduce inflammation that occurs in arterial walls. Lastly, phytochemicals may also augment the body's ability to detoxify chemicals (Pivonka, 2014).

Looking at the figure above (Fig. 14.4), it can be seen that phytochemicals are grouped according to their chemical structure. This diagram suggests (albeit tentatively) that phytochemicals in the same group are more likely to act in a similar fashion within plants and within the human body. Phytochemicals are clustered into subgroups: carotenoids, flavonoids, organosulfur compounds, etc. (Pivonka, 2014; LPI, 2017).

14.9.1.1 Carotenoids

(See also Section 14.3)

As discussed previously, carotenoids are the sources or pigments of the yellow, orange, and red colors of many plants. With more than 600 known carotenoids, they are broadly grouped into two classes: carotenes (α-carotene, β-carotene, and lycopene) and xanthophylls (β-cryptoxanthin, lutein, and zeaxanthin). Some of these carotenoids (β-cryptoxanthin, α-carotene, and β-carotene) are precursors to vitamin A production in the body, and the key to releasing their potential is through the usual processing of fruits and vegetables such as chopping, cutting, pureeing, and cooking in oil (as most carotenoids are soluble in oil). As far as colors go, lycopene provides fruits and vegetables their reddish colors, while α-carotene and β-carotene offer yellow-orange pigments and β-cryptoxanthin offers the reddish-orange hues (Pivonka, 2014). Their biological activity extends to the following:

- Vitamin A activity
- Antioxidant activity
- Light filtering
- Intercellular communication
- Immune system function

14.9.1.2 Chlorophyll

(See also Section 14.3)

Chlorophyll traps light for photosynthesis and is, as mentioned previously, responsible for plants green color. As with the carotenoids, chlorophyll is fat-soluble; however, beyond that, little is known about its bioavailability or metabolic pathways. Being the most abundant pigments in plants, the richest source of chlorophyll is found in the darkest green leafy vegetables. According to some, it is estimated that flavonoids account for roughly two-thirds of the polyphenols in our average diet while the bulk of the remaining is from phenolic acids. In terms of biological activity, these phytochemical activities are thought to be more related to their cell-signaling pathway qualities than to their antioxidant benefits.

14.9.1.3 Polyphenols

Within this catchall, flavonoids are the most plentiful of the polyphenols accounting for approximately two-thirds of our diets, with the majority of the remaining coming from phenolic acids. It has been observed that much of the biological effects of flavonoids are less known for their antioxidant activity

but more for their ability to control cell-signaling pathways in humans (Pivonka, 2014). Their biological activity extends to the following:

- Its antioxidant activity.
- Metal chelation.[18]
- Helps to manage normal cell-cycle regulation.
- Helps to regulate cell growth and death.
- Polyphenols stimulate detoxification enzyme activity.
- Inhibits cancer cell proliferation.
- Decreases inflammation.
- Increases arterial relaxation (vasodilation).
- Helps decrease platelet aggregation.

Organosulfur compounds—are sulfur-containing compounds called glucosinolates. These are found in cruciferous (Cruciferae) vegetables from the Brassicaceae family that includes vegetables like bok choy, cauliflower, cabbage, broccoli, brussel sprouts, and a host of similar green leafy vegetables. Their biological activity extends to the following:

- Helps eliminate chemicals including drugs, toxins, and carcinogens
- Aids in the normal cell-cycle regulation
- Inhibits the proliferation of cancer cells
- Anti-inflammatory activity
- Antibacterial activity

14.9.1.4 Antioxidants

We have talked a lot about antioxidants but have not fully expressed what they are or what they do; this section addresses this. Antioxidants can be vitamins, minerals, or phytochemicals. They are found in generous quantities in fruit and vegetables. Antioxidants are important to help battle the cumulative effect of "free radicals" in the human body. Free radicals come about through the chemical wear and tear of human energy pathways and other essential bodily processes involving oxygen. Oxygen through breathing reacts with fats and sugars to generate the chemical energy we need to operate the cellular machinery within our bodies. Unfortunately, however, this energy generation and other crucial processes involving oxygen create chemical by-products—free radicals. Normal cell functions in the body produce damaged molecules; these are called free radicals. They are highly unstable and end up stealing molecules of fat, protein, or DNA from other cells. This can create a chain reaction that can lead to entire cells becoming damaged or dying. This process is called peroxidation[19] (see also Section 16.1). Our bodies counter this destructive process through the use of antioxidants that react with free radicals before they have a chance to do any real damage. Because the processes involving oxidation is a continual one, we need a continuous and abundant source of antioxidants to sustain our

[18]Chelation therapy is a medical process that involves administering of chelating agents to remove heavy metals from the body.
[19]Lipid peroxidation is the degradation of lipids through oxidation. It is the process in which free radicals take away electrons from lipids cell membranes, resulting in cell damage.

good health. Furthermore, while the body does produce a few antioxidant molecules of its own, plants turn out to be a treasure trove of antioxidants (Belitz et al., 2009; Barham et al., 2010).

The process of photosynthesis in plants is a high-stake energy conversion game. The oxidative stress caused by plant leaves using sunlight to split water molecules into hydrogen and oxygen for essential energy leaves it extremely vulnerable. To compensate, plant leaves and other exposed elements evolved and developed an abundance of antioxidants to keep these high-energy reactions from damaging essential proteins. The numerous plant antioxidants are carotenoid pigments, yellow lutein and zeaxanthin, and red lycopene and green chlorophyll and vitamins C and E. Moreover, there are thousands of different "phenolic" compounds; in fact, each plant part, fruit and vegetable, has its own characteristic group of antioxidants each either protecting against certain kinds of molecular damage or helping to regenerate other protective molecules (Barham et al., 2010; McGee, 2004).

14.9.2 FRUIT AND VEGETABLE FIBER

Health benefits of plants, among numerous other things, include being good sources of fiber or dietary fiber. The majority of fiber as discussed in earlier chapters is the material in plant foods that our digestive enzymes find difficult to break down into usable nutrients. The fibers comprise four main components—each is a form of carbohydrates from plant cell walls. They are cellulose and lignin that are solid fibers that are insoluble in our digestive fluids and pectins and hemicelluloses that do dissolve. Other minor components of fibrous cell walls include uncooked starch, various gums, mucilages, and certain other carbohydrates. The bulk of the fiber is insoluble and therefore is not absorbed in the small intestine; instead, it passes intact into the large intestine. Here, some fiber is broken down by intestinal bacteria; however, unlike other digestible carbohydrates, soluble and insoluble fibers slow digestion and make stools softer and easier to pass. As an aside, soluble fiber has been shown to lower blood cholesterol while keeping blood sugar stable, all the while making it easier to lose weight. Although different foods contain insoluble and soluble fibers, they are usually richer in one type than the other. Foods rich in soluble fibers include oatmeal, beans, nuts, apples, and blueberries. Apart from the lowering of cholesterol, other benefits include helping to protect humans from diabetes while also bulking out stool for healthy bowel movements. On the other hand, foods rich in insoluble fiber, found in skins of fruits and seeds, brown rice, and whole wheat bread, help promote satiety, weight loss, and digestive health. In conclusion, the indigestible portion of fruits and vegetables is very beneficial, while fruit and vegetable juices are all the rage presently; in fact, a glass of juiced fruit or vegetable is not as valuable as the whole fruit or vegetable (Zeng, 2010; Vaclavik and Christian, 2014).

14.9.3 HERBS, SPICES AND ESSENTIAL OILS

The idea that herbs, spices, and essential oils have medicinal value is as old as medicine itself. Indeed, plants, being the skillful alchemists that they are, have been responsible for many original sources of medications including but are certainly not limited to aspirin, digitalis, and quinine, among many others. Of note here too is the fact that three important qualities of this group are that they are phenolic and terpene compounds and antioxidants. Phenolic compounds often provide antioxidant activity, while terpenes help to minimize the body's cancer causing production of DNA-damaging molecules. Further, some phenolic compounds and terpenes are also anti-inflammatories in that they moderate the body's reaction to cell damage while also helping to reduce the risk of both heart disease and cancer.

14.9.4 TOXINS IN SELECTED FRUITS AND VEGETABLES

Many plants contain natural toxins that help protect it and create resistance to diseases, fungi, insects, and other predators. The fruits and vegetables that we eat are no exception (Vaclavik and Christian, 2014).

- *Alkaloids*—these are bitter-tasting toxins. In high doses, all known alkaloids are poisonous, and at lower doses, alkaloids can effectively alter animal metabolism. Familiar foods like the potato can accumulate potentially worrying alkaloid levels, especially green-skinned potatoes and potato sprouts making them bitter and toxic.
- *Cyanogens*—when certain plant tissues are damaged by chewing, cyanogens are mixed with plant enzymes, which causes them to break apart releasing hydrogen cyanide (HCN). Cyanogen-rich foods include cassava (manioc), bamboo shoots, and certain tropical varieties of lima beans that need to be treated before consumption. This includes open boiling and soaking (leaching) in water or fermentation. Certain seeds too like citrus, apples, and pears also generate cyanide as well as some stone-fruit seeds (McGee, 2004; CFS, 2015).
- *Hydrazines*—these are nitrogen-containing substances found in the common white mushroom and other mushroom varieties. The difficulty here is that they persist during cooking. When fed to laboratory mice, mushroom hydrazines cause cancer and liver damage although it has no effect in rats. That said, it is not yet clear whether mushroom hydrazines pose a noteworthy hazard to humans (CFS, 2015). So, the advice would be to eat mushrooms in moderation (Coultate, 2009).
- *Protease inhibitors and lectins*—these are proteins that interfere with digestion; that is, they block the action of protein-digesting enzymes. Moreover, lectins bind to intestinal cells preventing them from absorbing adequate nutrients. Troublingly, lectins can also enter the bloodstream where they bind red blood cells to each other. Both protease inhibitors and lectins are neutralized by lengthy boiling; however, they can survive in beans that are eaten raw or are undercooked causing symptoms similar to food poisoning. They are found mainly in soy, kidney, and lima beans (McGee, 2004; Freeman and Beattie, 2008; CFS, 2015).
- *Flavor chemicals*—while these are generally consumed in small quantities, a few may cause complications when over indulged. *Myristicin*, for instance, the major flavor in nutmeg, when ingested in large quantities appear to be responsible for intoxication and hallucinations. *Glycyrrhizin*, on the other hand, the sweet-tasting substance in licorice root, can induce high blood pressure, while *coumarin* that gives melilot (sweet clover) its sweet aroma and is also found in lavender can interfere with blood clotting (McGee, 2004).
- *Toxic amino acids*—these are unusual forms of protein building blocks that interfere with proper protein functioning. Canavanine for instance affects certain cell functions and has also been associated with the development of lupus. Canavanine is found in large quantities especially in jack bean and alfalfa sprouts. Vicine and convicine in fava beans are responsible for blood-cell-destroying anemia called favism, which can occur in susceptible people.
- *Oxalates* (salts of oxalic acid)—these are waste products of some plant's metabolic processes found in certain foods such as spinach, beets, chard, rhubarb, and amaranth. While sodium and potassium salts are soluble, calcium salts are not and form crystals instead, which in turn can irritate the mouth and digestive system. Soluble oxalates on the other hand can combine with calcium in the human kidney creating kidney stones. In very large doses (in the order of a few grams), oxalic acid is corrosive and can indeed be fatal.

- *Bracken-fern toxins* (*Pteridium*)— certain fern leaves can cause blood disorders and cancer in animals that graze on them. Humans too tend to use fern leaves as a vegetable but in the form of the younger "fiddlehead ferns."[20] Ostrich ferns (*Matteuccia*) are thought to be a safer source of fiddleheads. Whichever is used, it is probably wise to use fiddleheads in moderation and to avoid bracken-fern fiddleheads altogether (Freeman and Beattie, 2008).
- Psoralens—these are any of the constituents of certain plants, such as within the seeds of *Psoralea corylifolia* and in celery, parsley, figs, anise, cumin, caraway, chervil, coriander, fennel, dill, mustard, and all citrus fruits. Psoralens produce phototoxic dermatitis when someone is first exposed to it and then to sunlight. Furthermore psoralens possess mutagenic and photocarcinogenic effects and can subsequently damage animal and fish DNA and/or cause blistering skin inflammations in humans (Freeman and Beattie, 2008). Psoralens are absorbed through the skin while handling or through eating either raw or cooked vegetables. Once contact has been made or the vegetables ingested psoralens lie dormant in skin cells until they're struck by ultraviolet light. This causes them to bind to DNA and allows psoralens to damage both DNA and some cell proteins. Luckily, it takes a high intake of psoralen for these manifestations to present. Furthermore, and oddly enough, despite the potential safety concerns, the same chemical psoralens are used in the treatment for dermatitis, eczema, psoriasis, and vitiligo, among others.

In addition to the above, there are numerous other toxins that fruit and vegetables produce as chemical defenses. Other toxins include nonnatural toxins introduced through agricultural chemicals (pesticides, herbicides, fungicides, etc.) and air and soil pollutants (dioxins, polycyclic aromatic hydrocarbons, etc.). Although one must not live in fear, in general, the usual levels of these extra contaminants do not constitute an immediate health hazard. But on the other hand, they are toxins, so moderation and washing the produce goes a long way in mitigating any excesses (McGee, 2004; Zeng, 2010).

Other food poisoning—generally, when we talk of food poisoning, it is the animal kingdom that often comes to mind, yet fruits and vegetables are also a significant source. Indeed, fruits and vegetables have been associated with almost every food pathogen known to exist. The reasons for this are not hard to fathom. First and foremost, fruits and vegetables are grown in the soil, an abundant reservoir of microbes. On top of this, botanical produce is easily contaminated whether by people, containers, or machinery. This may have a lot to do with the lack of field facilities in certain production areas—especially during harvest time—such as toilets and wash basins and being contaminated in postharvest processing and packing departments. Furthermore, there is much produce that is eaten raw like fruits, some vegetables, and salad. Fruit and vegetable juices too are often made by crushing whole fruits, which are easily contaminated by a small number of infected microbes. As a result, many manufacturers now pasteurize their juices. Knives and fingers too can introduce surface bacteria to the flesh (even if the skins are to be thrown away); the answer is to wash all produce to be eaten raw with commercial produce washes.

[20]Fiddleheads or fiddlehead ferns are the curled fronds of a young fern leaf. They are harvested for use as a vegetable.

14.10 DISCOLORATION AND ENZYMATIC BROWNING

(See also Section 9.2)

When some fruits and vegetables such as bananas, apples, mushrooms, and potatoes are cut, chewed on, or bruised, they are quick to develop a reddish-brown discoloration. This is caused by three possibilities, namely, plant enzymes, 1- and 2-ring phenolic compounds, and oxygen. In a healthy, intact fruit or vegetable, phenolic compounds are kept in the storage vacuole, while the enzymes are situated in the surrounding cytoplasm. When the cell structure is damaged, bruised, or bitten into, the phenols are mixed with the cytoplasm's enzymes and oxygen. The enzymes then oxidize the phenols making molecules that react with each other and bond together forming large brown pigments. This system is one of the plant's oldest chemical defenses. As the animal, insect, or microbe injures the plant's cells, (although oxidization occurs), the plant also releases reactive phenols that in turn attack the assailants' own enzymes and membranes.

Minimizing browning—as mentioned in previous chapters, enzymatic browning can be discouraged or at least slowed down in several ways. This happens mainly by the reduction of runaway plant enzymatic processes, the decrease in phenolic compounds, and the prevention of the oxidation process. The browning enzymes work very slowly in acidic conditions, so the single most often used method in the antibrowning arsenal is to coat cut surfaces with lemon juice. Another acid that also inhibits browning because of its antioxidant properties is ascorbic acid (vitamin C). Failing that chilling the food below about 4°C/39°F will also slow the enzymes from causing discoloration. Immersing the cut pieces in cold water also helps by limiting the availability of oxygen. Not surprisingly too (as we have learned from the denaturation process), boiling fruits and vegetables will effectively destroy the browning enzyme. However, these short-term remedies aside, high temperatures can actually encourage phenolic oxidation in the absence of enzymes, so cooks beware (Fig. 14.5).

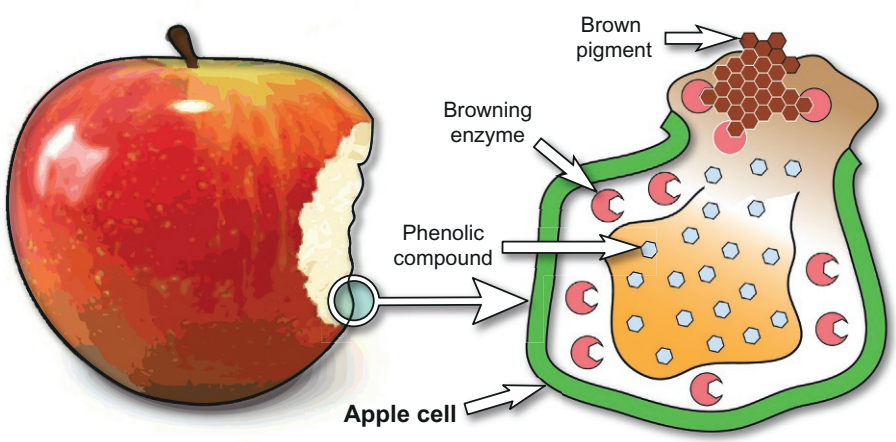


FIG. 14.5

Browning reactions in certain cut, bruised, or bitten fruits and vegetables.

14.11 FRUIT AND VEGETABLE FLAVORS

While flavors have already been covered in a general sense, it is worth delving a little more into the specifics of fruits and vegetable flavors. Of the five generally recognized tastes discussed earlier, four, sweetness, sourness, bitterness, and savory/umami are particularly conspicuous in fruits and vegetables. While tasteless starch is generally stored in unripened fruits, as they ripen, the starch is converted into sugar, making the fruits more appealing to seed-scattering animals. In fact, so abundant is this product of photosynthesis on average ripe fruit can contain as much as 10%–15% sugar by weight (Vaclavik and Christian, 2014). Moreover, as fruits ripen, their acidity typically drops too further adding to their appeal. That said, there still remain organic acids[21] present in many fruits whether for chemical defenses, metabolic waste, or simply energy stores. As such, this sweet-sour balance is particularly prevalent in fruits.

Most vegetables, on the other hand, comprise only modest amounts of sugar and acid, and those vegetable cells that do tend to use them up quickly postharvest. This is why the freshest of produce is more fully flavored than the general mass harvests of industrial agriculture, which can be days or weeks before the produce can reach the market. While we associate fruits with sweetness, we generally do not do so with vegetables (with a few exceptions of course). Instead, savoriness and bitterness tend to dominate the vegetable world. Bitterness can be found in certain vegetables like radicchio, chicory, Asian bitter gourd, and eggplants as well as alkaloid-containing cocoa beans and coffee. After this, savory foods containing amino acids, more typical of protein-rich animal foods, can be found in glutamic acid (the active portion of MSG) containing tomatoes and many seaweeds (Vaclavik and Christian, 2014).

The subject of aroma has already been sufficiently covered (Chapter 3); however, just a few words here will help with context. Aroma profiles involve many hundreds of diverse chemicals, and there are two essential facts that need to be borne in mind when contemplating the aroma of any food, fruit, vegetable, herb, or spice. Firstly, the characteristic aroma of specific food is created by the distinctive volatile chemicals that make up that food. Secondly, nearly all food aromas are mixtures of many different volatile molecules. In vegetables, herbs, and spices, this might mean just a few dozen, but with fruits, this number can run into the hundreds. Once again, just a handful of aromas typically create the dominant volatile element of a food, while others create the middle and background (supporting) notes. This sheer complexity helps explain why we might encounter echoes of one food in another. It might also explain why certain foods pair well, through either complimentary or contrasting aroma profiles (Freeman and Beattie, 2008; McGee, 2004).

14.12 COOKING FRESH FRUITS AND VEGETABLES

Fruits and vegetables contain large amounts of carbohydrates, and while carbohydrates are robust molecules, they are relatively easy to cook with. This is especially so when compared with meats (animal tissues), eggs, and dairy products in which many contain appreciable quantities of proteins that are, relatively speaking, very sensitive to the cooking process. Having said that, the art of fruit and vegetable cooking does have its finer points that do require careful consideration. For example, as we shall see, plant pigments, flavor, textures, and nutrients are all sensitive to some degree, to heat, and to the

[21]There are several organic acids that plants accumulate including citric, malic, tartaric, and oxalic.

chemical environment. On a very fundamental level, the art of cooking fruit and vegetable is to create an appealing product that does not compromise texture, color, flavor, or nutritive value (Vaclavik and Christian, 2014). However, while rich in vitamins and minerals, plain boiled or steamed vegetables tend to lose valuable water-soluble vitamins and other nutrients to the cooking liquor. This is an altogether different situation when cooking vegetables in vacuum bags in sous vide cooking, for instance (Baldwin, 2012).

14.12.1 HEAT AND THE QUALITIES OF FRUITS AND VEGETABLES

14.12.1.1 Heat and texture

Cell softening—we have already determined that the texture of fruits and vegetables is affected by two main factors: the water pressure within plant cells and the structure of the cell walls. Cooking generally softens fruit and vegetable by breaking down cell walls and cell membranes releasing water and nutrients and by extension reducing cell pressure. This gives most fruit and vegetable a limp or flaccid texture. This is because as temperatures rise, cell walls in particular are physically damaged by the heat and nutrients leach into the surrounding waters or stock. Having lost their natural crisp crunch, cell structure in some fruit and vegetable walls remain strong enough to maintain a chewy consistency. Further cooking fruit and vegetable to boiling point, the cell walls then start to further weaken. Remember that plant walls comprise a number of materials including cellulose fibers enmeshed or held together in a cement-like material of pectin and hemicellulose, among other things. So, as we reach boiling point, plant material softens, not due to the cellulose fibers, which remain mostly intact, but rather to the "cement" (the soluble pectin and hemicellulose), which softens and eventually dissolves making the fruit or vegetable more edible. Prolonged cooking however will further dissolve this cement until all that is left is a puree like consistency.

The degree to which pectin and hemicellulose dissolve is not solely governed by heat. The more acid the cooking solution contains (like tomato or sweet and sour sauces), the less hemicellulose liquefies and the firmer the fruit or vegetable and vice versa—the more alkalies in the cooking solution, the more soluble hemicellulose becomes the softer the outcome. In neutral liquid (neither acid nor alkalies), fruit and vegetable soften in a moderate amount of time. Putting salt[22] in a neutral cooking liquid (like soft water) helps speed the softening process because sodium ions displace the calcium ions that strengthen the cement molecules in fruit and vegetable cell walls, thus aiding the dissolution of hemicellulose. Using hard water, the opposite is true: the salt and minerals tend to reinforce the cement cross-links. In short, acid and hard water maintain firmness, while salt and alkalinity speed the softening process.

The cook can make good use of this knowledge and adjust cooking times, environments, and methods accordingly. If he/she wants a softer vegetable in a tomato sauce, simply precooking the vegetable in salted soft water, for example, can give the required result. Or the cook can compensate for hard water with a pinch of alkaline baking soda to help soften the cooking liquid. Incidentally, to help green vegetables keep their vibrant chlorophyll color, the cook can shorten the cooking time while adding salt and a small dose of baking soda.

[22]Salt in a neutral cooking liquid can make the solution either acidic or basic depending on what fruit or vegetable is added to it.

Starch—when raw, starchy vegetables like potatoes, squash, cassava, and other similar vegetables are hard, closely packed, and have a distinct granular or chalky mouthfeel when eaten raw. Upon cooking, these starchy foods owe their characteristic "mealy" or "pastiness" texture to their starch granules. That is because during cooking, starches begin to soften at about the same temperature plus or minus a few degrees (58–66°C/136–150°F for potatoes) as the cell's cytoplasm and vacuole membrane proteins denature. At this point, starch granules start to absorb water and other cell liquid molecules. This allows the starch granules to swell up to several times their original size, forming a soft gel-like food in the process. This results in a tender but to some extent dry texture in the mouth. One answer is to add lubricating butter or other oils and fats to the starchy vegetable cooking liquor or, if being pureed, directly to the mix, giving the final product a better, more moist feel in the mouth.

Precooking/blanching—when cooking certain fruits and vegetables including potatoes, beets, carrots, and apples, the typical softening that occurs can be reduced by precooking. By precooking or blanching, these items in a cooking liquid at approximately 55–60°C/131–140°F for 20–30 min, these foodstuffs develop a firmness that endures prolonged final cooking so to speak (McGee, 2004; Vaclavik and Christian, 2014). This can be valuable for vegetables that need to hold their shape in say a casserole or potatoes in a potato salad.

Cooking from cold—when it comes to root vegetables, if cooked in boiling water, the outer portions of the vegetables can often become over soft and disintegrate, while the inside remains firm and undercooked. This is especially so in vegetables like potatoes. Two solutions here are as follows: The first is the precooking method described above. The second is to start the cooking process with cold water so that the outer regions will firm up during the slow temperature rise.

Crisp vegetables—there are a few stem vegetables noteworthy for their capacity to remain crunchy after prolonged cooking. These include the Chinese water chestnut, bamboo shoots, lotus root, and certain beets. The reason is fairly straightforward in that the robustness originates from particular phenolic compounds, called ferulic acids. These acids are found in cell walls, forming strong bonds with the cell-wall carbohydrates, thus slowing and partially preventing them from being softened during cooking.

14.12.1.2 Heat and color

Many water- and fat-soluble plant pigments are transformed by the cooking process, and it is through this altered state (the color) that we can often gauge how judiciously fruit and vegetables have been prepared by the cook. As always, there are exceptions, and in this case, it is the yellow-orange-red carotenoid group that is more soluble in fat than in water. That said, even these carotenoids are altered a little by cooking in water-based stocks. As we cook carrots, for instance, the beta-carotene changes hue from red-orange toward the yellow spectrum. However, it is the green chlorophylls and the multihued anthocyanins that have the most to lose in the culinary world.

Green chlorophyll—it is the name given to a collection of green pigments. Most are vulnerable to two specific chemical variations during cooking. Chlorophyll is not initially soluble in water; however, under the heat of cooking, the first reaction is the loss of its long carbon-hydrogen tail, thus leaving the pigment partially water-soluble and allowing it to leech out into the cooking liquid. The loss of this tail is aided by a key enzyme in chlorophyll's metabolism called chlorophyllase[23] and is encouraged by

[23]Chlorophyllase is most active between 66°C and 77°C or 151°F and 170°F and only destroyed near the boiling point.

both acid and alkaline environments. Once the pigment has been rendered water-soluble, the second chemical change sees a further dulling down of its vibrant natural color. This happens under heat or through enzymatic activity whereby the magnesium atom at the center of the chlorophyll molecule is nudged out and replaced by hydrogen at which point chlorophyll *a* turns into the gray-green pheophytin *a* and chlorophyll *b* into yellowish pheophytin *b*. In fact, this is the most common cause of food discoloration in cooked vegetables (Coultate, 2009). Further, green vegetables need not be cooked in liquid either for them to lose color. This is because when the cooking temperatures rises above 60°C/140° F, membranes in and around the chloroplast are damaged, and chlorophyll is exposed to the plant's own natural acids. Hence, stir-frying, grilling, and barbecuing, for example, will all cause a color change. Lastly, we have mentioned freezing, but pickling, dehydrating, and plain old aging also conspire to damage chloroplasts and chlorophyll. This is the reason we see so many unappetizing dull, olive-green vegetables.

Having said that, it is not all doom and gloom for chlorophyll; indeed, there are certain chemical tricks that can aid in the endeavor to keep green vegetables bright and vivid. The first is to deacidify the cooking liquid and cook the greens in alkaline water (by adding baking soda (sodium bicarbonate)), as alkalies solutions have very few hydrogen ions capable of displacing the magnesium in chlorophyll. The other trick is to use metal, specifically, copper and zinc that can replace magnesium in the chlorophyll molecule, thus resisting displacement by hydrogen. However, both have disadvantages, as for instance excessively alkaline conditions can turn vegetable texture to mush, while copper and zinc in doses of more than a few milligrams can be toxic (McGee, 2004; Vaclavik and Christian, 2014).

There are nonchemical options available to the cook too. The first is to keep the cooking times as short as possible—if at all feasible—as short as 5–7 min. The next is to avoid acidity; for this reason, microwaving is not the best cooking method. This is because microwaves work on a cellular level exposing chlorophyll wholly to the cells' own acids. The next trick in avoiding acidity is to cook the foods in copious amounts of boiling water / cooking liquid. This goes back to the general cooking process whereby as the cells break open during cooking, the acid inside the cells leaks into the boiling water. Using more water dilutes this acidification. If the cook is inclined, another option is to test the water's pH using litmus paper, and if acidic, add a small pinch of baking soda to adjust it to neutral or slightly alkaline pH. Lastly, as the vegetables are cooked, either serve immediately or, if dressing with vinaigrette, lemon juice, etc., protect them by tossing them in butter. If not serving immediately, then refresh the vegetables (as the foods continue to cook slightly once removed from the water) at once in cold water to arrest the cooking process.

Red-purple anthocyanins and pale-yellow anthoxanthins—reddish anthocyanins and pale-yellow anthoxanthins are naturally water-soluble. This inevitably results in the vegetables bleeding color into the boiling water / cooking liquid. Both are also sensitive to pH and to the presence of metal ions, but on this occasion, acidity helps rather than hinders the vegetable. In acidic conditions, certain vegetables can change the color of the fruit or vegetable completely. Take red cabbage as an example. Cooked with sugar and citric or acetic acid, the red cabbage takes on a vivid red hue, while cooking in plain or alkalies water, the cabbage turns blue. This is the same principle that can turn blueberries and garlic green or blue.

As acid is good for most of these (anthocyanins and anthoxanthins) color compounds, alkalinity is usually not beneficial. When these classes of anthocyanins and anthoxanthins containing fruit and vegetables are cooked so the cells break open and pigments escape, their color becomes diluted and can fade or even disappear. The produce's remaining pigments are in turn affected by the resultant slightly

acidic (from the plant cell material) cooking environment. In acid conditions, anthocyanins tend to move toward the red, while in alkaline conditions, they become bluish. By contrast, pale anthoxanthins become a deeper yellow as alkalinity rises. All the while, traces of metals in the cooking liquid can actually generate very unusual colors: some anthocyanins and anthoxanthins form gray-green, blue, red, or even brown colors when in the presence of iron, aluminum, and tin.

In essence then, the key to maintaining natural anthocyanin colors, the cook must keep fruits and vegetables sufficiently acidic and avoid the addition of trace metals. Lemon juice is good for this. Placed in the cooking liquid or on the over, the fruit or vegetable in question can help stabilize coloration. Incidentally, citric acid also helps bind metal ions inactivating them by making them unavailable.

14.12.1.3 Heat and flavor

The flavors of fruits and vegetables are altered and sometimes intensified by cooking, through the breakdown of plants cell walls, which allows the cell contents (like sweet sugars and sour acids) to readily escape and—if not lost in any cooking liquor—can reach our taste buds. Carrots are a good example of this; as they cook, the sweetness is released in the softened cells as we chew. Cooking also allows aromatic compounds to become more volatile and hence add to the aroma of cooking and cooked fruits and vegetable. Further, cooking can also create completely new molecules through increased enzyme activity, mixing of cell contents, and other general chemical reactivity (Coultate, 2009). In other words, the more the food is cooked, the original aroma molecules tend to become modified and supplemented giving it a more complex cooked flavor. Interestingly, if cooking temperatures exceed that of boiling water (through methods such as frying and baking), all manner of browning reactions can occur from the Maillard reaction to caramelization of the fruit and vegetable's own carbohydrates (Section 5.1). This allows the cook more flexibility in the cooking process.

Astringency—one sensory component plants provide is astringency, which is especially prominent in such foods as unripe fruits and nuts. Unadulterated, this makes them quite unpleasant to eat. However, there are ways to control tannins influence in such foods. One work-around when cooking with fruit and vegetables that are not fully ripened is to avoid the use of acids and salt (which intensifies the perception of astringency). Instead, by adding sugars and proteins like milk, gelatine, or similar to a dish, it can act to reduce its astringency. This works by inducing astringent tannins to bind to less astringent food proteins. This works too with ingredients rich in pectin or gums that also reduce the tannin flavor.

14.12.1.4 Heat and nutritional value

Nutrition—cooking fruits and vegetables can seem like a contradiction in terms of nutrition. On the one hand, cooking aids in the elimination of potentially harmful microbes. It also softens foods making them easier to eat in sufficient quantity and can actually improve the availability of some nutrients. Two important examples of this are starch and the carotenoid pigments. Starch itself comprises long chains of sugar molecules compacted into masses called granules. The problem is when raw, human digestive enzymes cannot penetrate past the outer layer of these granules, while cooking unravels the starch chains allowing more access by our enzymes. Furthermore, because beta-carotenes (precursors to vitamin A) and its chemical relative, lycopene (an antioxidant), and other important carotenoid pigments are not very soluble in water, so thorough cooking of the vegetables in question instead breaks down plant tissues more thoroughly allowing one to extract much more in the way of nutrition from them.

Unfortunately, on the other hand, while cooking can make some nutrients more bioavailable, it can also destroy certain other, equally valuable ones. This occurs through a combination of uncontrolled enzyme activity, high temperatures of cooking, and exposure to oxygen and to light. In this way, nutrients, such as vitamins, minerals, and antioxidants, can be destroyed or leech out of fruit and vegetable tissues into the cooking liquid. There are of course exceptions to this; however, these losses can be mitigated by brief, rapid, and appropriate cooking. Take baked potatoes, for example, as they heat up relatively slowly; they lose much more vitamin C to enzyme action than boiled potatoes do (McGee, 2004).

So how does the cook speed up the cooking process? In reality, it becomes a trade-off. Despite what has been advocated before in this chapter, i.e., cutting the produce into smaller pieces and cooking them in a large pot of boiling water, while this can help speed up cooking, the effect of the smaller pieces actually creates a larger surface area that allows more, not less, leeching of nutrients. Also, mentioned earlier too, the microwave oven agitates water molecules at the cellular level breaking open cells and cell walls. That said, to maximize nutrient retention, the cook should cook smaller batches of fruits and vegetables with a minimal amount of added water (McGee, 2004). This seeming contradiction is one of the reasons why both raw and cooked fruit and vegetables are encouraged in our diets (Vaclavik and Christian, 2014).

14.13 PULVERIZING AND EXTRACTION

Typically, in kitchens on any given day, one will more likely than not, come across juices, purees or pastes. In some preparations, cooks blend raw or cooked fruit and vegetable plants—cell wall and all. In other instances, cooks separate out food's flavorless, colorless cell-wall fibers in order to concentrate the food's essence.

The simplest and most common version of this process is the purees. Cooks do this by applying sufficient physical force to crush cell-wall tissue, break open its cells, and mix cell's organelles. The high water content of most cells ensures that most purees are fluid and velvety, thanks to the thickening powers of cell-wall carbohydrates. Failing that, the cook can boil off the excess liquid, thus concentrating the carbohydrates until the desired consistency is achieved. Purees are very versatile in the cook's kitchen; they are the foundation of soups, sauces, or frozen into ices, sorbets, etc. While many sufficiently ripened fruits have adequately weakened cell walls, they are easily pureed raw, yet most vegetables are first cooked to soften tough cell walls. Precooking also has the additional benefit of inactivating cell enzymes that while uncooked would otherwise render vitamins and pigments useless. Moreover, uncooked purees can alter flavors and cause unsightly browning (Coultate, 2009; McGee, 2004). Considering the textural features of a puree, some can be smooth and velvety, while others watery and grainy. These nuances can be explained by the size of solid particles in the puree that in turn is determined by how thoroughly ripening, cooking, or methods used have managed to dismantle the cell walls. Hand mashing is not really a substitute for mechanical blenders, processors, or pulverizers, as handmade purees leave large cell aggregates intact. Persistent granular purees or cellulose fibers can be removed by passing the puree through a strainer. Important exceptions to this rule are cooking and pureeing potatoes and other starchy vegetables: this is because starch granules, once crushed or pureed, continue to absorb much of the free moisture in cell tissues. As a result, these are best pureed with added moisture, whether cream, milk stock, or water.

14.13.1 JUICES

Unlike purees, when a cook juices a fruit or vegetable, he/she blends the food and then separates out the solid cell walls leaving the main fluid contents of the plant. However, a cautionary note here: the extraction of living cells, including lively, still active enzymes and various reactive and oxygen sensitive substances from fresh juices are inevitably unstable and change rapidly. By way of example, apple and pear juices turn brown almost immediately thanks to the action of oxidative browning. To stabilize juices, they are either best kept chilled or frozen or are preboiled and then chilled or frozen. This might not seem the intuitive or logical thing to do; however, by using this method, preboiling kills microbes that may be present while also deactivating (denaturing) enzymes responsible in part for enzymatic browning.

14.13.2 FRUIT AND VEGETABLE FOAMS, EMULSIONS AND ICE CREAMS

Foams and emulsions (as discussed in Sections 7.2.2.2 and 15.2) are notoriously unstable, without the presence of certain ingredients. As a result, most foams will just crash in on themselves. In purees and juices alike, it is important to strain out the solids from the juice or puree before foaming. Remember too that you require a certain amount of liquid when foaming as one cannot foam a think pasty puree. The remaining carbohydrates, from the cell walls with added xanthan gum, can help to stabilize both a foam of air bubbles and an emulsion of oil droplets (Vaclavik and Christian, 2014; McGee, 2004). If puree or juices are then whipped, beaten, or otherwise aerated to incorporate air bubbles, cell-wall carbohydrates then act to slow the flow of escaping air and liquid from the subsequent mixture, and the resultant bubbles or foam then takes longer to collapse. Similarly, when oil is added to a puree or juice to make an emulsion, so once again, plant carbohydrates essentially insulate the oil droplets from each other. This allows more time to work with the foam as the oil and water phases separate out more slowly. The cook then benefits by adding the rich dimensions of fruit and vegetable emulsions and foams to his/her repertoire. As a general rule, the thicker the puree, the more stable and less delicate the foam or emulsion.

Whether fruit of vegetable, if these same purees and juices are frozen, they form a semisolid mass known by a variety of names including sorbet, granita, and sherbet (depending on the method and sugar content). Unadulterated and left pure, the flavor of the fruit or vegetable essentially remains that of the fruit or vegetable (or herb, spice, flower, coffee, or tea) in question. Although to stop them freezing into a single solid block, the cook can, in most cases, add sugar and acid (to reach 25%–35% and 0.5%, respectively). Without getting into too much detail about ices, granita's, and sorbets, it is worth clarifying the term "sherbet." In the United States, this term applies to fruit ices that contain between 3% and 5% milk solids that help fill out the flavor and soften its texture.

As observed in Chapter 6 the texture of the above ices granita's, sherberts, and sorbets can vary from granular to coarse or to creamy, dependent in large part on the proportions of ingredients and the temperature at which it is to be served. During the freezing process, water in the juice or puree solidifies into millions of tiny crystals, which are then surrounded by all the other substances in the mix. This might be leftover liquid water (which forms a syrup with dissolved sugars of the fruit plus any added sugar) and contents of the plant cells and cell walls themselves. The more syrup and plant debris there is in the ice, the more the ice crystals are lubricated and subsequently the softer the ice's texture.

Successful fruit and vegetable ice creams also depend on the sugar content and the agitation process. As the mix is cooled, this helps ensure smaller ice crystals and by extension smoother texture in the mouth.

In sum, ice's coarseness or creaminess is a result of the size of the crystals that, in turn, is decided on the ice's sugar content, plant solids, and amount of agitation during freezing. Ices served right from the freezer are relatively solid and crystalline, by allowing them to warm slightly produces a softer, smoother consistency in the mouth.

14.14 PRESERVING FRUITS AND VEGETABLES

Fruits and vegetables can be preserved almost indefinitely by killing off the living tissue of the produce to inactivate the products enzymes, thus making it unwelcome or unavailable to microbes. Some of these techniques are ancient, while others are the product of the creative industrial age.

14.14.1 FLAVORED OILS, VINEGARS, SYRUPS, AND ALCOHOLS

As we have seen, cooks steep fruits, vegetables, herbs, and spices into a variety of liquids. However, if there is no rush, the freshest tasting extracts come from slowly immersing raw fruits or herbs intact at room or refrigerator temperatures for a few days or even weeks.[24] The immersion liquid can be vinegar, sugar syrups, oils (see below), or alcohols. All of these mediums of preservation help prevent the growth of spoilage-causing microbes that makes them relatively trouble-free for the cook. That said, preserving fruit and vegetables in oil requires special consideration. This is because of the air-free environment in which oil marinades can actually encourage the growth of botulism bacteria that incidentally have spores that survive relatively high cooking temperatures. Thus, preserving in oil is achieved best at cold temperatures; this means that both cooked and uncooked flavored oils should be stored in the refrigerator.

14.14.2 DRYING AND FREEZE-DRYING

Drying is one of the oldest preservative techniques known to man. By reducing fruit and vegetable tissues' water content from around 90% to between 5% and 35%, it preserves the food by making it an inhospitable environment where little can grow including harmful microbes. Yet even before, these stage fruits and vegetables benefit through quickly being blanched to inactivate the enzymes that damage vitamins and colors. Apart from the kitchen, this is also practiced commercially; however, commercial drying also dips and sprays fruits and vegetables in certain sulfur compounds to prevent oxidation and the loss of antioxidant phenolic compounds, vitamins and, of course, flavor.

Sun drying used to be the treatment of choice, yet its reliance and variability meant that one was always at the mercy of the weather. Nowadays, hot air-drying has now widely become a popular method of drying, albeit not via the sun. Cooks tend to use the ovens and specifically made electric driers whose temperature is reliable and easier to control. Fruits and vegetables are dehydrated at relatively low temperatures of between 55°C and 70°C, in order to minimize the loss of flavor and color and to slow surface drying that, if happens too fast, can impede moisture loss from within. Pureed fruits

[24]Flavors of dried herbs and spices are less affected by heat so can be extracted more rapidly in hot liquids.

too are spread out onto thin sheets to make "fruit leather." Lastly, while the degree to which food is dried can be controlled by the cook, he/she must be careful if semidrying is the goal as relatively moist dried fruits and vegetables, while nicely soft with concentrated flavors, they are also susceptible to some hardy yeasts and molds. Therefore, semidried fruits and vegetables are best stored in the refrigerator.

Freeze-drying—freeze-drying could well be thought of as a controlled form of freezer burn. In this method, food is dehydrated via a number of processes that seeks to prolong or preserve the shelf life of foodstuffs. It is also a phase transitional process (see Chapter 2) called sublimation. In this process, ice crystals go straight from being frozen to water vapor without the in-between phase of melting into water. The first stage of freeze-drying is to completely freeze the item as quickly as low as possible (down to −50°C) at atmospheric pressure of 1 bar. In the second stage, the food is then placed inside a vacuum well below the "triple point of water"[25]; with the aid of a little heat, the food's ice crystals are evaporated or sublime (sublimation). At this point, up to 95% of water in the food is evaporated. This process can take up to several days. After this, in the secondary drying phase, pressure might be lowered, while further heat (in some foods above 0°C) is added. Thus, through careful control of the environment, the remaining 5% can be removed leaving foods with prolonged shelf lives with many that need not be refrigerated.

The big advantage to this method of preservation is that they are not heated or exposed to oxygen so their colors and flavors remain relatively fresh. Indeed, many foods, including fruit and vegetables, are freeze-dried these days and used as snack foods for general consumption, reconstituted in water, as camping foods and as emergency ration packs (Vaclavik and Christian, 2014).

14.14.3 FERMENTATION AND PICKLING

Fermentation is one of the simplest means of preserving foods as it requires no specific type of climate and no cooking. In a quirk of semantics, an overlapping practice is that of pickling, so named as foods are immersed in brine or strong acids that often, but not always, encourage fermentation, while fermentation in turn produces preservative acids. The result—the term "pickle" is applied to both fermented and unfermented produce (Coultate, 2009).

Fermentation—it is the preservation of fruits and vegetables that work by allowing benign microbes to flourish in fruit and vegetables while suppressing spoilage- and disease-causing microbes. Plants are the natural home of some of these benign microbes that, when active, act upon the plants readily metabolized sugars. In turn, these produce a variety of antimicrobial substances among which are lactic and other acids, alcohol, and carbon dioxide. This, as mentioned, encourages the growth of good fermentation microbes while arresting the growth of spoilage bacteria. These benign lactic acid-producing bacteria are the same microbes that turn milk into yogurt, cheeses, and fermented piquant sausages. Furthermore, during the fermentation process, new volatile substances are generated, thus enriching fermenting foods' aroma.

Some fruits and vegetables are simply left to ferment alone in tightly covered containers, most either through dry-salting or brining, which helps draw water, sugars, and other nutrients out of the plant

[25]The triple point of water is the point when temperature and pressure are in equilibrium to allow the three phases (solid, liquid, and gas) can coexist.

tissues and provide enough liquid to cover the food and limit its exposure to oxygen (McGee, 2004). Confusingly, this marinade is also called the "pickle." The characteristics of which are determined by the concentration of salt and the fermentation temperature that combine to determine which friendly microbes dominate and which substances they produce. *Leuconostoc mesenteroides* favor low temperatures and salt concentrations producing a complex yet mild mixture of acids, alcohols, and other aroma compounds. On the other hand, *Lactobacillus plantarum* prefers higher temperatures almost exclusively producing lactic acid. Naturally, fermentation does not come without challenges. Problems in fruit and vegetable fermentations are usually caused by salt concentrations or temperatures being inadequate or excessive or alternatively through simple exposure to air. All of which promote the growth of undesirable microbes. A couple of common mistakes for the uninitiated are as follows: the first happens when fermented products are not weighted down to keep them below the surface of the brine, while the second occurs if the brine surface itself is not tightly covered or the brine has access to the air. Such occurrences might result in one or a number of problems including a thin film of yeasts, molds, and/or "air-requiring" bacteria to form. If this happens, one might see the lowering of brine acidity as lactic acid is consumed and the growth of spoilage microbes take over. Clues to these unfortunate occurrences can include the softening of the fermented produce, discoloration, and unpleasant odors as the breakdown of fats and proteins take place.

Unfermented pickles—there are a multitude of fruit and vegetables that are pickled by the direct addition of acid rather than by fermentation as described above. In these circumstances, the simplest and most often used acids are wine and/or vinegar. As with fermentation, the acidity inhibits the growth of spoilage microbes, it is also quicker and allows more control over salt content and by extension—texture. However, this simple method produces simpler flavors hence the augmentation of all sorts of herbs and pickling spices in the "pickling" liquor. Nowadays, one common method is to control the acetic acid (diluted vinegar) environment by adding enough hot vinegar and water to produce a final concentration of around 2.5% by volume, compared with the 3%–9% of standard vinegars.[26] Nonfermented pickles are usually heat-treated at about 85°C for 30 min to prevent spoilage. Non-heat-treated pickles should remain in the fridge.

Most pickles are eaten raw and are very often crisp in texture. Using sea salt aids in this crispness due to calcium and magnesium impurities in the salt that helps pectin in strengthening cross-linking in fruit and vegetables' cell walls. Especially, crisp are pickled cucumbers that are sometimes made either by adding alum (aluminum hydroxide) or through presoaking the raw materials in a solution of "pickling lime" (a strong alkaline) that must be washed off thoroughly before pickling to avoid counteracting the pickles' acidity. Thus, once presoaked, fruits and vegetables are then cooked; the cell walls tend to stabilize, keeping the final product crisp and crunchy. If more tender pickles are required, they can be cooked until the produce is soft (McGee, 2004).

14.14.4 SUGAR PRESERVES: JAMS AND JELLIES

Another favored technique for preserving fruits, in particular, is to increase their sugar content and turn it into a jam or jelly. Like salt, sugar makes the environment inhospitable to spoilage microbes; however, the molecules of sugar are larger and heavier than those of salt, so it takes a little more sugar to

[26]Vinegar is roughly 3%–9% acetic acid by volume; the rest is water.

achieve the same goal. Proportion wise, sugar is added by weight to achieve 55% fruit to 45% added sugar. At these concentrations, sugar dissolves, tying up water molecules, and further attracts moisture out of the living cells (Vaclavik and Christian, 2014).

Needless to say, sugar preserves are very sweet, although for many, this is the appeal. The result is a firm yet moist jellylike substance that can range from firm and slightly chewy like "gummy" candies to fragile apple jellies. Talking of apples or quince jams and jellies, for instance, the gelation of these preserves is made possible by the nature of pectin (a component of the plant cell wall) and the interaction with the fruit's acids and any added sugar.

Pectin gels—fruit preserves form a physical structure called a gel (see Section 7.2.2.1): these are a mixture of water and other molecules bonded to create a continuous gel-like network. The key to this is the long pectin chain that when fruit is heated near the boil, the cell-wall chains dissolve and release cell fluids into the mix. Initially, pectins are not attracted to each other as they carry a negative charge and are too diluted. However, by reducing the liquid through evaporation and by adding sugar, the water molecules, which are subsequently drawn away from the pectin, allow pectins to come closer together. Then, by adding acid, the cook neutralizes the electric charge finally allowing pectin chains to bond to each other to form a gel. The optimal conditions for pectin gelation are acidities between a pH of 2.8 and about 3.5 (similar to that of orange juice), a pectin concentration of between 0.5% and 1.0%, together with a sugar concentration of 60%–65% (McGee, 2004).

Preparing Preserves:

Making preserves, gels, jams, and jellies begin with cooking the fruit to draw out the pectin. This is easy with apples and citrus fruits as they are especially rich in pectin. Other fruits might require adding pectin to form the necessary bonds. This preliminary cooking in a combination of heat acid and water should be brief and somewhat gentle as the pectin is quite fragile and could just as easily break the pectin chains into pieces too small to form a network. At this point, the sugar is added together with any extra pectin, and the mixture is then rapidly boiled removing water and concentrating the other ingredients. Once the temperature reaches 103–105°C/217–221°F, the sugar concentration should have reached 65% (a saccharometer can be used to test the sugar density). At this point, supplemental acid is added. It is added late so as to avoid breaking down the pectin chains (Vaclavik and Christian, 2014). When ready, the final gel is poured into sterilized jars and starts to set as it cools below about 80°C/176°F.

A cautionary note—if the mixture fails to set, one of two possibilities could have happened. One common problem is inadequate amounts of either acid or pectin; another issue might be the over- or prolonged cooking that ends up damaging the pectin. However, all is not lost as failures can sometimes be rescued with the addition of a more pectin and/or the addition of a little cream of tartar or lemon juice together with a brief reboiling.

14.15 CANNING

While canning preserves fruits and vegetables without the leathery texture of drying, or the sweetness of sugar preserves, or the saltiness or sourness of fermentation practices—there is however no doubting that the foods have been cooked—oftentimes overcooked. In essence, canning is essentially the heating of hermetically sealed foodstuffs. During the process, heat deactivates or denatures plant enzymes and destroys spoilage microbes, while the hermetically sealed container prevents recontamination. The food can then be stored at room temperature without spoiling.

The main concern surrounding the canning process is the bacterium *Clostridium botulinum*. The problem is that this bacterium prospers in low-acid, airless conditions, which if left to multiply produce a deadly nerve toxin. The good and the bad thing here is that while the botulism toxin is easily destroyed by boiling, the dormant spores that can produce these toxins are very robust and can survive prolonged boiling. If the canning process was left just at the boiling stage, then the spores may well waken becoming active bacteria, meaning as the can cools, the toxin is refabricated. The answer is a higher than boiling cooking process, in a process called the "botulinum cook" that means foods are typically heated in a pressure cooker at 121°C/250°F for 3 min (the time and temperature vary with pressure). Of note—while preserving foods through the canning process, because of the extreme temperatures involved, it does not always bode well for the fruit or vegetable concerned. Furthermore, many high-acid foods like fruits do not require such high temperatures as the acidity hinders the production of botulism (McGee, 2004).

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CHAPTER

SAUCES

15

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There are literally thousands of different flavor molecules that can be arranged in an almost infinite number of ways, each of which will be perceived differently by the consumer. In this regard, when it comes to sauces, the cook can make a sauce out of almost anything and tantalize us with textures and flavors—from soft, smooth, coarse, grainy, thick, thin, lightly or heavily flavored, oil- or water-based sauces, emulsion, foam, and suspension—in fact, the options are endless. Yet, for the cook, it is not a hit or miss affair—a lot of thought goes into preparing and matching the right sauce with the right food. Indeed, when considered as carriers of flavor, sauces form a broad spectrum of flavors from the rich, subtle butter sauces like hollandaise, compound butters, and melted brown butters, to the tart vinaigrettes and creamy mayonnaises, to the tartness and pungency of well-made salsas. While at the other end, there are the complex flavor mixtures of the meat-based sauces in which complex flavor sensations are largely from the extraction and concentration of savory amino acids and other taste molecules, from the generation of meat-based stocks that have undergone browning reactions between amino acids and sugars.

It is also important to know that when we talk of sauces that accompany the primary ingredient(s) of a dish, their purpose is to enhance or compliment the flavor of the chosen ingredients in one of two ways; either complementing the dish by enhancing it with like-for-like ingredient flavor profile foods

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or by providing contrasting flavors to complement the main ingredients(s). As well as amplifying flavor, the cook can also create sauces that can give tactile pleasure by the way they move and feel in the mouth, further stimulating or augmenting the whole experience. Fluidity is also of concern to the budding cook as the way a sauce coats the food or lingers in the mouth can prolong the experience of the meal in a good way. As an aside, sauces can also provide the diner with a visual treat using vibrant natural colors like beetroot vinaigrette or smoked vegetable sauces for instance.

15.1 MAKING SENSE: FLAVOR AND CONSISTENCY

There are a number of ways for a cook to make sauces. Many involve the extraction of juices from plant or animal tissues, whereby they can be combined with other extractions, herbs, spices, or any number of flavorful materials. These types of sauces though tend to be watery thin, in which case they end up benefiting from some kind of thickening or emulsifying agent that ultimately thickens the sauce while also aiding in the lingering on the food on the palate. So, while there are many thousands of flavor molecules to choose from, it is still prudent to review a few basic facts about flavor in general when constructing a sauce. As we have noted (Chapter 3), flavor is a combination of two different sensations—taste and smell. Taste is sensed on the tongue and is characterized by five different sensations comprising salt, sweet, sour (acids), savory (amino acids), and bitter (alkaloids). Next are the astringent and pungent flavors (tannins and chemesthesis) as found in red wine and tea, as well as in chilies, peppers, and mustard, for example. Smell on the other hand is perceived in the upper nasal region in the olfactory epithelium. In fact, it all boils down to the fact that it is taste and taste alone, that we experience with food in the mouth while pinching the nostrils, and likewise, it is smell alone that we experience while we smell foods without taking a bite. This little foray goes to show that neither taste nor smell by itself is fully satisfying, and only by employing the full senses in unison can we begin to appreciate the bounty before us. Sauces are accompaniments and not the centerpiece of a dish; they are also eaten in small quantities and therefore have to be a little concentrated in terms of flavor. Thickening agents too have a habit of reducing the intensity of flavor, so this must be taken into account too.

A well-made sauce gives great satisfaction to a meal, yet getting it wrong and the dish can be left somewhat lacking. The challenge for the cook then is to serve a full dish, maintaining overall balance and harmony, not only of the main components but also of garnishes like sauces. The main aim of the sauce is its flavor and complimentary/contrasting nature to the main element of the dish. Yet, even if it is not forefront in the diner's mind, a bad or misjudged sauce might simply feel like something is missing or out of place. Alas, problems with sauces are not uncommon and, in many instances, are just as likely to be the fault of poor consistency as it is flavor and/or texture. A sauce's physical structure, for instance, can make a sauce unusable; it might be curdled, congealed, split, or separated—this reduces desirability (their mouthfeel) considerably. As a result, it's good to have some fundamental knowledge of the what, the why's, and the how's of sauces.

The base ingredient in many but by no means all sauces is water; the task then is to enrich the watery base giving it a desirable, more substantial consistency. This can be achieved through obstructing the free movement of obstacles via the addition of starch or other vegetable or animal particles, through the addition of oil or even bubbles of air (Belitz et al., 2009).

15.1.1 OBSTRUCTING THE MOVEMENT OF WATER MOLECULES

How does this work? Firstly, we need to understand the molecular makeup of water—it is just three molecules in size, H_2O, and left to their own devices, water is very mobile and very runny. Compare this with oil molecules, which comprise three fatty acid chains stuck together and each 14–20 atoms long; this creates more friction, so they drag against each other and move more slowly (more viscous), and watery sauces by comparison seem less attractive. So, introducing oil droplets or air bubbles (depending on the sauce being made) slows the movement of the free-running water molecules. Of course, all cooks are familiar with thickening agents, which often work in very similar ways. Some thickening agents quite literally bind water molecules to each other that have the effect of reducing the fluidity and increasing the viscosity of the sauce. Other elements can also give "character" to a sauce; certain substances in the dispersed phase, for instance, can bestow upon the sauce's various textures. Solid tiny particles can give a sauce an unwanted grainy mouthfeel, while oil or butter droplets can give the impression of creaminess. Other dispersed molecules on the other hand that show a tendency to stick together may give the impression of stickiness or sliminess, whereas air bubbles have an effect on sauces, giving them a light airy feel, an almost fleeting evanescence (Belitz et al., 2009; Vaclavik and Christian, 2014).

15.2 THICKENING SAUCES

Whether of animal or vegetable origin, there are several ways we regularly thicken watery fluids. Each has its own characteristics and gives the finished sauce certain idiosyncrasies that set them apart from others. Sauces are thickened with a boggling variety of oils, butters, air (foams), starches, gelatins, carrageenan, pectins, and agar-agar to name but a few. However, before we delve into many of these alternatives, it is perhaps worth noting the most common form of thickening agent a cook employs on a regular basis, that is, the various starches at their disposal.

15.2.1 STARCHES

(See also Section 7.2.4.2)

Diminishing flavors—before we get into any detail about starch, there is one thing that must be discussed as it affects all starch-based thickened sauces. Cooks concoct sauces both intense and rich; the reasons for this richness are twofold; firstly, the sauce is only eaten as an accompaniment to a main dish, so consequently, they are eaten in small quantities. Therefore, to make any impact on the meal, one must ramp up the flavor. Secondly, starches have little flavor of their own, and their use subsequently does two things; it waters down the flavor of the sauce and also binds some of the sauce molecules together, so our palates never get to sense or taste them. In this respect, sauces, if made with starch, are best made on the thin side. Oily or butterfat sauces also suffer the same problem to some degree, as some of the flavor molecules are soluble in oil—thus, a thick oil-based sauce like a hollandaise or a *beurre blanc* entraps some of the aroma and flavor molecules within the sauce itself. Having said that, these tendencies are minor, and if the cook is aware of them, they can easily be rectified.

Of course, an alternative to thickening sauces is simply to boil off some of the continuous phase in order to allow any natural thickeners already present to concentrate the texture and the flavor.

Adding to this, research has shown that thickeners reduce our perception of aroma not only because of the reasons mentioned above but also because in part they reduce our perception of saltiness. It has been suggested that this happens as a result of the long-chain carbohydrates, including starch, which decrease the perceived saltiness of the sauce by binding sodium ions to themselves. This "apparent" reduced saltiness decreases the intensity of the sauce aroma. This suggests that simply thickening a sauce with flour or starch has the effect of diminishing its overall flavor. Although in short, both taste and aroma can be reinstated by the addition of more salt.

So, onto starch, one might recall that starch molecules are complex carbohydrates comprising long chains of numerous glucose molecules linked together. One also might recall that there are in fact two types of starch molecules: the long straight-chained amylose and the short branched-chain starches called amylopectins. As plants deposit these starch molecules in a myriad of microscopic granular particles of differing sizes and structures within their cells, amylose and amylopectin starches in cooking greatly vary depending on the size and the shape of the starch granules that differ sometimes considerably from species to species. In sum, unlike other thickening agents, starch is perhaps one of the least expensive and most versatile thickeners a cook has to work with. The cook can choose from several different kinds of starch, each with its own qualities and characteristics.

15.2.1.1 Amylose and amylopectin

As hinted at, the size and shape of both amylose and amylopectin molecules have a direct effect on the way they thicken a sauce. When dissolved in water, the straight-chained amylose starch coils up into long helical structures while retaining their basic linear shape. This linearity makes it easy for the largish amylose molecules to bump into each other when dispersed in a liquid and thus thicken the sauce. By contrast, the shorter branched chains of amylopectin are compact and therefore are less likely to collide with others. Moreover, as it collides, it is also less likely to get snarled up and inhibit the motion of other molecules in its vicinity. As a result of these characteristics, the job of thickening a sauce is that much easier with a small number of long amylose molecules than with the much shorter amylopectin molecules. Furthermore, the cook can achieve the same degree of thickening with a small amount of amylose potato starch than if they were to use moderate-length amylose wheat and corn starches.

15.2.1.2 Swelling, gelation, thickening and congealing

What makes starch so useful in the kitchen is the way it behaves in water—more specifically, hot water or liquids. The structure of starch is such that it contains both strong and weak regions. Simply adding starch to cold liquid and it can be seen that little else happens other than the starch absorbs about 30% its own weight in liquid. Now, if heated, the starch granules absorb more liquid and swell up placing pressure on the stronger granule regions. At specific ranges of heat (each starch is different) but usually at around 50–60°C/122–140°F, the granules lose their organized structure completely and end up absorbing a larger volume of liquid. This temperature is known as the gelation range on account of the starch granules morphing into individual closely packed gels or liquid-containing networks of long-chain molecules (see Chapter 7).

During swelling and gelation and depending on the quantities of starch, liquid and heat involved; the mixture might noticeably thicken at various stages and reach their maximum thickness after the gelated granules start to leak amylose and amylopectin molecules into the surrounding liquid. As this happens, so the long-chain amylose molecules form three-dimensional fishnet-like networks that not only reduce the movement of liquid but also block the movement of the large but unbroken

liquid-swollen starch granules. However, caution must be exercised by the cook at this point because as the sauce/mixture achieves its thickest consistency, so the starch-liquid mixture will begin to thin out again.

There are three specific things that cooks do that aid in the thinning process whether intentional or otherwise: the first is heating a starch-thickened sauce, for instance, for a long period of time; second by briskly boiling and continuous stirring; and lastly by vigorous stirring alone. All these processes have same effect, and that is they break the swollen and fragile granules into very small fragments. And while we mentioned earlier that the breaking up or releasing of more amylose into the liquid mixture (which is a good thing), this also means that the liquid has fewer large bodies able to be entrapped in the amylose network. Also, while this thinning effect can be seen in sauces, they are more frequently observed in pastes, etc. For some, this thinning process is a desired consequence that is seen as going hand in hand in the making of a good sauce, ensuring greater refinement of texture. Once starch in a sauce has gelated, that is, the amylose has leaked out of the starch molecules, so the sauce is considered finished. As cooking is halted, so the temperature of the sauce starts to fall. As this happens, so liquid and starch molecules move about with increasingly less energy. It is at this juncture (temperatures vary depending on starches) that we see the temporary bonds begin to gradually hold the longer amylose molecules together forming stable bond within the liquid. As this takes place, the sauce's liquid molecules settle in the pockets between the starch chains resulting in a mixture that as it cools, it becomes progressively thicker. Furthermore, there is sufficient concentration of amylose molecules and if the temperature falls far enough, the mixture congeals into a solid gel. Of note, sauces made with shorter amylose chains or "bushy" amylopectin starch molecules ensure that the thickened sauce takes longer to bond and slow to congeal. It is also worth remembering that sauces tend to be evaluated for taste, texture, and consistency while they are being made—when they are hot. So, it is important for any cook to understand the thickening and process of cooling—that is to say, a sauce with a great consistency in the kitchen might not necessarily translate into a great sauce on the plate, due to thickening, cooling, and congealing. As a result, McGee (2004) recommends that sauces be thinner at the stove than on the table.

15.2.1.3 Different starches and their characteristics

Cooks have a number of different starches to choose from when it comes to thickening, each with its own particular quality or characteristics. For ease of comprehension, we can say that starches fall into two respective families; they are starches from grains (wheat flour, cornstarch, etc.) and starches from tubers and roots (i.e., potato starch and arrowroot).

15.2.1.4 Cereal and grain starches

Starches from grains generally share several characteristics—chief of which is the fact that their starch granules are generally medium sized. Further, cereal or grain starches also contain small but substantial amounts of lipids and proteins. While they are impurities within the starch, they do in fact aid in the thickening process. This is because such impurities give the starch granules a certain structural stability, which means in reality that it takes higher temperatures to gelate them. Moreover, grain starches also contain a high quantity of moderately long amylose molecules that in turn forms stable networks with each other giving the characteristic sauce qualities that easily and quickly thicken and congeal when cooled. Lastly, while lipids inhibit gelation by stabilizing granule structures, this also means that sauces made from them have less pronounced flavors.

Wheat flour—made by grinding wheat grains and removing both the bran and germ from the starch-rich endosperm, the end product gives us wheat flour. In this form, flour comprises approximately 75% starch; the rest is protein (10%) and other substances (15%). As a result of being 75% starch, this makes it a less efficient thickener than say pure potato or cornstarch. This also means that it takes more flour to thicken the sauce or at least to obtain the same consistency as other starches. Furthermore, flour has a distinct wheat flavor that cooks often "cookout" by precooking it before adding it to a sauce. The suspended protein particles (mostly gluten) influence the opacity of the sauce giving it a dull, matte-like finish, unless, that is, the sauce is cooked for hours and skimmed to remove the gluten.

Corn starch—unlike wheat flour that is milled dry, cornstarch is produced by soaking the whole grain and then milling it removing the germ and hull. It is then ground, sieved, and centrifuged to separate out the seed proteins. The resultant starch is then washed, dried, and reground into a fine powder consisting of single granules. After this process, the starch is for all intents and purposes—pure starch, making it one of the most efficient thickeners available.

Rice starch—rice starch is more commonly used in Asia-Pacific regions than in the Western world, although many good craft and even supermarket stores are increasingly adding it to their shelves. Rice starch granules are the smallest size of the cereal/grain starches, consequently producing a particularly fine texture in the early stages of thickening.

15.2.1.5 Roots and tuber starches

One overriding difference between the cereal/grain starches and those from roots and tubers is the fact that roots and tuber starches are moist to begin with and tend to comprise larger granules. These moist underground storage structures also maintain more water molecules; they cook a lot quicker and are able to release starches at lower temperatures. As a rule, they contain less amylose, although having said that, roots and tubers' amylose chains can be as much as four times longer than those of cereal/grain origin. On top of that, root and tuber starches only contain a small percentage of the lipids and proteins normally associated with cereal starches. This has a positive effect in cooking as it makes them more willing to gelate. The properties of root starches mean that less is actually required to obtain a desired thickness that can also be achieved much quicker.

Potato starch—it is perhaps in a league of its own in the world of starches; not only is it an important food starch in Europe, but also it possesses certain unusual characteristics too. Firstly, its amylose granules are up to a tenth of a millimeter in size, which in molecular terms is enormous; as well as being large, they are also very long too. This combination gives potato starch an edge over its brethren in that it displays initial thickening power far more superior than that of any other starch. As the long chains of amylose starches entangle themselves with each other and with the unbroken giant granules, they work together to inhibit easy movement of the sauce liquid. At first, the large swollen granules give the consumer a perceptible graininess to sauces, although this is only temporary as the granules are fragile and readily splinter into finer particles. That is to say, a sauce thickened with potato starch will initially be thick and grainy, but as cooking continues, so the consistency of a potato starch sauce becomes both finer and thinner. There is also one more trick up the sleeve of the potato starch and that is it carries an electric charge (due to its large number of phosphate groups). This causes the starch chains to repel one another and to keep the starch chains evenly distributed within the sauce contributing to the thickness of the sauce and its low tendency to congeal upon on cooling.

Tapioca—it comes from the root of the tropical plant cassava. A root starch, tapioca, is used mainly in puddings and desserts. This is because it tends to become "stringy" in liquid-based sauces, so it is

usually made into largish pregelatinized pearls that are subsequently cooked long enough to be softened. One advantage tapioca has over other starches is that it does not develop any strong lasting aromas that one sometimes finds in other starches—in this sense, it has a neutral flavor.

Arrowroot—it is refined from the roots of a West Indian plant named *Maranta arundinacea*. It has smaller granules than tapioca or potato starches and does not thin out as much if prolonged cooking takes place. Its gelation temperature is higher too than other similar root starches and is in fact more in line with that of cornstarch in this matter. Confusingly, starches from a number of other plants from Asia and Australia are also deemed "arrowroots" (species of *Tacca*, *Hutchenia*, and *Canna*), for example.

Other root starches include but are not limited to millet, water chestnuts, sweet potato, yams, and lotus roots.

15.2.1.6 Modified starches as thickeners

Due to considerations of the many industrial food production cycles, that is, production, distribution, and storage, food manufacturers are always looking to create starches that are stable throughout the full cycle of a product "life." As a result, certain engineered varieties of starch have been developed to help stabilize products throughout the many processes. One obvious form of modified starch is the "waxy" variety of corn that has been bred to contain little or no amylose starch in favor of corn with nearly all amylopectin. This species of corn does not mesh or form network as easily as amylose, and as such, they make sauces and gels that resist congealing and separation when cooled and allow products to be defrosted without liquid "leakage" or watery residue, a problem of which is common in high-amylose starches.

Ingredient manufacturers also use a number of physical and chemical treatments in order to modify standard plant starches to make them less prone to such things as breaking down during cooking or to enhance them, making them more effective or efficient emulsion stabilizers or any number of traits that are not so easy to process from natural products or which are uneconomical in their natural relatives. That said, natural starches too might be modified in several ways, they might be precooked and dried, for instance, to produce powders or granules that might readily absorb cold water rather than hot, or they might be modified to disperse in and thicken liquids without heat. Lastly, chemical changes might also be made to oxidize them or substitute fat-soluble side groups along the chains. These, just like the corn example above, are the "modified" starches, and in this way, modified starches are a whole category unto themselves.

15.2.1.7 The influence of other ingredients on starch sauces

Starches are influenced in many ways from many seemingly harmless products.

Salt, *sugar*, *and acid*—starch and water (or liquid) form the basis for many of todays' sauce's structure, while salts, acids, and sugars are often added to enhance flavor. However, salt, sugar, and acids have other effects on the physiology of the sauce. For one, salt lowers the gelation temperature of starch, even if only slightly, while sugars increase it. Acids too have an effect on starch-based sauces, especially wine and vinegar that both encourage the disintegration of the long starch chains into much shorter lengths. So much so, in fact that starch granules disintegrate and gelate at lower temperatures giving the final product less viscosity than otherwise should have been. Root starches in particular are noticeably affected by moderate acidity levels of less than pH 5. Further, it transpires that grain starches can withstand the pH values of around pH 4—similar to those of yogurt and certain fruits.

Proteins and fats—two other materials, proteins and fats, are frequently found in flour-thickened sauces and exert some influence on the sauce texture and consistency. Many flours[1] contain variable quantities of protein much of which is insoluble gluten. Although, in general, some gluten might get caught in the starch network ultimately increasing the viscosity of the sauce, pure starches on the other hand are generally more powerful thickeners. There are plenty of protein-based sauces, and some are founded on concentrated meat stocks in which a good deal of protein (gelatin) can be found. Moreover, fats like butter, oil, or meat "drippings[2]" do not mix with water- or liquid-soluble sauces, although they do slow down the infiltration of water into starch granules. Yet, when used in a "roux,[3]" these oils coat the flour particles preventing them from "caking[4]" together in the water subsequently safeguarding against lumpy sauces. Fat too, as mentioned before, does add to the sensations of smoothness and moistness to a sauce.

15.2.2 USING STARCHES IN SAUCES

From personal experience getting starch into a sauce to thicken it can be trickier than it seems. If one adds flour or starch, for instance, directly into a hot sauce, the moment they enter the heated liquid, the starch granules become partly gelated, which instantly seals or clumps the dry granules together, thus preventing them from fully dispersing. That said, all is not lost as there are many ways in which starch can be incorporated into dish.

Slurries, *beurre manié*, *floured meats*, *and roux*—cooks typically utilize several methods for incorporating starch into a sauce, four of which are discussed here.

In the first method, the flour or starch is mixed with cold water in order to wet and separate the granules making a starch-liquid "slurry"; this in turn is added to hot or cold sauces until they are cooked and reach gelation temperatures. If they do not reach gelation temperatures, the granules do not sufficiently thicken the sauce and also end up giving it a grainy-like texture in the mouth.

The second way of adding starch to a sauce is to first mix butter and flour (or starch) together in the French *beurre manié*, or "kneaded butter," in order to once again separate the starch or flour particles. This entails working the flour with an equal weight of butter into a paste that can then be added to hot sauces at the last minute.

An alternative to this is to melt the butter or oil (or other fats) in a pan first before adding an equal quantity of flour and then cooking out the starch either just a little so that it remains white or not fully cooked or taken a little farther until it turns yellow or brownish, with varying degrees of "cookedness." A roux can then be added at the start of the sauce, or if the cook is experienced enough, they can add the yellow or brown roux further into the cooking process.

A fourth way of thickening sauces if making long, slow-cooked stews, etc. is to introduce it early in the cooking process. This is achieved by dusting or rolling pieces of meat in flour and shaking off the excess. These pieces are then sautéed in oil or fats, and water or a cooking liquor is added that will then

[1]Wheat starch is different from wheat flour in that the wheat starch is the carbohydrate component that is left after processing wheat flour to remove the protein portion.
[2]Dripping is the fat that is extracted by rendering meat until the fat melts away.
[3]A "roux" is a classical French-based mixture of oil/butter and flour that is used in thickening sauces.
[4]Caking is the tendency of some dry goods like flour and starch to clump together and cause lumps in sauces.

form part of the finished dish's sauce. In this way, the starch is dispersed over the large surface area of the meat, while sautéing the fat prevents clumping or lumps when the liquid is added.

Cooking the starch—the starch introduced into the sauce is usually left for a few minutes, to tens of minutes, or to several hours to cook out the raw cereal or root flavors that can linger and make a sauce taste "unfinished." In cereal-based starches, cooking out the starch can give the sauce an extra dimension of nutty or toasted flavors—for this reason, cooks use certain thickeners in certain dishes. Lastly, as the cooking proceeds, the starch molecules, especially the longer chains, start to split and break down into smaller units. With prolonged cooking, these smaller chained or branched starches are less able to thicken sauces as efficiently. Overcooked sauces can sometimes, after the initial thickening, end up thinning them down somewhat. So, cooks not only need to judge the right starch to use but also needs to be aware of the amount of cooking time involved. There are other alternatives to thickening and gelling agents that are worth discussing; however, they are often used in the making of desserts. These are discussed in the next sections.

15.2.3 OTHER THICKENING AND GELLING AGENTS

Gelatine, as a protein, not only thickens sauces but also sets mixtures in a gel. However, gelatine is not the only ingredient that cooks use to turn a liquid into solid gel. Starch gels give the cook various options to make such things as Turkish delight and variety of pectin set fruit jellies and jams. With regard to seaweeds, they fall into three fairly broad groups based on their pigmentation: brown, red, and green seaweeds. From the cook's point of view, red and brown seaweeds are also used to manufacture the hydrocolloids, alginate, agar-agar, and carrageenan that are used as thickening and gelling agents (each has its own benefits and drawbacks) (McHugh, 2003). Many types of seaweeds are used directly not only for human consumption but also as an ingredient for the global cosmetics, to fertilizer, and in the animal feed additive industries. Seaweeds too used to be mainly collected from the wild, but more and more so nowadays, they are being farmed, just like any other vegetable commodity. It is handy that cooking certain seaweeds in hot water releases viscous or gelatinous substances into the water that then sets upon cooling. These gelatinous substances are not proteins but rather carbohydrates with some unusual properties. Many too are used as stabilizers in emulsions like ice creams in the manufacturing sector and as an alternative to animal-based gelatins.

Agar (*or agar-agar*)—it is a combination of several different carbohydrates from the red algae[5] genera (of which there are many thousands). The gels from these seaweeds are made simply by boiling them in water, draining, and filtering the liquid (after which it remains translucent) and then freeze drying the liquid, forming strands that can then be used as is or ground to a powder. Before use, these strands or powder needs to be soaked in cold liquid before being heated to 85°C/185°F in order to fully melt or dissolve the carbohydrate chains. As well as a higher melting point than gelatine, agar also sets within a higher range, around 35–50°C/95–122°F,[6] (McHugh, 2003) too. Like gelatine, agar is also thermoreversible in that once set, it can be remelted at about 85–100°C/185–212°F (again, temperatures vary depending on the source) (McHugh, 2003). Importantly, this also means it does not melt in

[5]All seaweeds are algae but not all algae are seaweeds. Seaweeds tend to be easily visible, comprise many cells, and grow in the sea. There are red, brown, and green seaweeds. However, many algae are microscopic single-cell diatoms consisting of a single cell.

[6]Gelatine is different in that it tends to set at about 15°C and remelts at a temperature less than about 35°C.

the relative coolness of the mouth; instead, it has to be chewed that itself brings a whole new mouthfeel or sensation to a dish. One advantage of the higher melting points though is that it can be used in warmer environments and on main course dishes too as opposed to just desserts. A set agar jelly is opaque or translucent.

Carrageenan—from certain edible, red algae are used quite extensively in the food industry for their gelling, thickening, and stabilizing properties and their ability to create strong bonds with food proteins. Carrageenans are quite bulky and very versatile molecules that form helical structures allowing them the innate ability to form a variety of different gels. More specifically, carrageenans differ in their chemical structure, consequently their properties, and by extension their uses. The carrageenans of interest are iota, kappa, and lambda. As a result of their differing chemical structures, their ability to form thick solutions or gels is also different; the three classes of carrageenans are the following:

- *Iota*—in the presence of calcium ions/salts, iota forms soft elastic gels. Produced mainly from E*ucheuma denticulatum*, it is a clear gel that does not bleed liquid when set (a phenomenon known as syneresis). Interestingly too, this gel is also freeze/thaw stable.
- *Kappa*—it forms strong, rigid gels with potassium salts and brittle gels with calcium salts. Although slightly translucent, the gel becomes clear with the addition of sugar. In kappa carrageenans, there is a little bleeding of liquid from the set gel (some syneresis).
- *Lambda*—this carrageenan does not form gels; instead, it is used as a stabilizer or a thickener, altering the viscosity of liquids.

All three carrageenans are soluble in hot water, but in cold water, only the lambda carrageenan and the salts of the other two are in fact soluble. When it comes to manufacturing carrageenans, like agar, the process is fairly simple. Postharvest seaweed is dried, ground, and then sieved to remove impurities. After which, they are treated with a hot alkali solution such as potassium hydroxide. Then, by centrifuge and filtration, the cellulose is removed after which the resulting carrageenan is dried and ground once again (McHugh, 2003).

Alginates—these are produced from brown seaweeds and are unique in that they only form gels in the presence of calcium—in milk or cream or calcium chloride, for example. These are used not only as thickeners but also by cooks who use alginate to make small spherical delights. Firstly, they prepare an alginate solution (calcium-free) of a particular flavor and color and then drop carefully into a calcium chloride solution, where it immediately sets in a gel, often spherical.

Gellan gum—it is a water-soluble gum similar to xanthan gum in that it is produced by bacterial fermentation (*Sphingomonas elodea*). A polysaccharide (carbohydrate), gellan gum is a multifunctional gelling agent that can be used alone or in combination with other products producing a wide variety of differing textures.

15.2.3.1 Cloudy suspensions

When making sauces, most of the raw ingredients the cook uses, whether fruits or vegetables, meat or fish, etc. all comprise microscopic cells that are filled with watery fluids. Once ground, pureed, pulverized, blended, or any other physical breakdown of the food, they are effectively turned inside out—with the watery (continuous) phase containing the remains of cell tissues, cell walls, etc. These in turn block or bind liquid-like molecules, thus forming a thickened suspension (see Section 7.2.3). Of course, the thickness of the suspension depends on the size of its particles: the smaller they are, the thicker the liquid; moreover, the less distinguishable they are on the tongue, the creamier the mouthfeel. As has

been noted before, suspensions will eventually settle out of the liquid unless starch, droplets of oils, or other long molecules are added to improve the stability and consistency.

15.2.3.2 Emulsions and droplets

(See also Section 7.2.2.2)

As has been noted, due to the structure and properties of water and oil molecules, neither one can dissolve in the other. However, all is not lost; by simply adding an emulsifier that coats the oil droplets in order to prevent them from coalescing together, then, one has the ingredients to make an emulsion. Several diverse substances can be used to achieve this function; these include proteins, cell-wall fragments, or group of hybrid molecules like lecithin from egg yolks. To make an emulsified sauce such as mayonnaise, the cook adds oil to a mixture of water, vinegar, and egg yolks (the emulsifier). As the mixture is whisked, so the oil droplets are broken up into microscopic droplets, after which the emulsifier immediately coats and stabilizes the mixture. Another option is to begin or seed an emulsified sauce with a premade emulsion such as cream. Cream, as an emulsion, is especially versatile and is a considerably robust base for emulsified sauces like the French "beurre blanc" where butter is added to a mixture of wine and hot cream reduction. Such a mixture of two generally incompatible liquids, where droplets of one liquid dispersed in a continuous phase of the other, is called an emulsion.

15.2.3.3 Foams and bubbles

(See also Section 7.2.2.3)

To some, the idea that a fluid can be thickened using bubbles just seems absurd, yet take a moment to consider the bubbles in a caffe latte or the whipped cream on top of a dessert, and it becomes a little easier to imagine. In a fluid, for example, air bubbles pretty much behave as solid particles in that they obstruct the movement of a liquid's molecules. The overriding disadvantage of foams, however, is that they are fragile and simple gravity alone drains fluid from bubble walls—to the point where the walls end up collapsing in on themselves. That said, this can be delayed by the cook who can thicken the fluid with anything from lecithin or failing that they can slow bubble drainage from cell walls by using other emulsifiers and stabilizers.

15.2.3.3.1 In more detail

As with emulsions, foams are a dispersion of one substance (gas or air) into another, in this case a liquid. While it might be hard to imagine a sauce thickened with bubbles, imagine a foamed cappuccino and its thicker-than-water consistency, and it becomes easier to envisage. Although, as the bubbles impede the flow of the liquid in a sauce thus thickening it, the instability of the sauce requires that it is made at the last minute before being served. Bubbles too, because of the large surface area and the low surface tension of the liquid, can also release more aroma as they "pop" so to speak. In the mouth, they also have a unique effervescent quality that seems to accompany almost all foods for the better. In heavy sauces, too, foams can lighten their texture and give a good, sometimes, unexpected mouthfeel.

Bubbles are not a new invention although some cooks are finding ingenious way of making them and using flavors and ingredients that or not so common. One classic foam sauce is the sabayon, in which egg yolks are whipped as they cook, although sometimes this is an intermediary step for further use in cakes, mousses, etc. More and more so nowadays though, foams are finding their way into savory meat and fish dishes. Other foams like whipped cream and egg whites can be folded into a base liquid;

however, chefs nowadays prefer to create all types of foams from all manner of liquids including reductions, protein- or starch-thickened sauces, and juices, purees, and emulsions—these can all benefit from an infusion of bubbles.

Stabilizing foams—bubbles in a typical foam can be anywhere in size between 0.1 mm and up in size. Being so small means that, in terms of stabilizing the foam, they require less emulsifier than is probably expected: typically, just 0.1% of the sauce by weight—equal to 1 g/L. However, as bubbles are notoriously fickle when it comes to stability, cooks use several methods at their disposal. We have mentioned one way and that is to fold in some whipped cream or egg whites into the sauce, but some purists prefer to make them from scratch. By simply whipping a protein rich sauce by hand or preferably with a stick blender for instance can give a fairly notable mass of bubble foam, solid, and stable enough for its intended use—albeit measured in minutes. Another method is to use the common whipping canister that uses pressurized carbon dioxide to inject gas into the sauce. Foams can also be stabilized by other stabilizing agents like carbohydrate thickeners like starch, pectin, and gums. However, a note of caution concerning fat, fat or oils destroy foams because they settle at the interface between the sauce and the air preventing the stabilizers from being there, where they are needed, in order to stabilize the foam.

15.2.4 GELATINE AND OTHER PROTEIN THICKENERS

(See also Sections 7.2.4 and 4.4)

Animal gelatine stocks and sauces—while the properties of gelatin are similar across both animal and fish proteins, there are some subtle differences that need to be pointed out (Section 4.4.2). When making a beef gelatin sauce or stock, the bones are first browned with a few vegetables and then added to a pot of cold water. The stock is brought to simmer and then is further reduced over several hours (depending on the animal). This concentrates the juices and the collagen (gelatine) and forms the base for many sauces whether it is fully reduced to form a meat glaze,[7] thickened only by the gelatine in the stock, or reduced then thickened with a brown roux to form a brown stock (espagnole) or half (a demi-glace). It is very common for beef stocks to incorporate a good ratio of veal (young calf) bones in the making of the beef stock and pig skin (optional) as there is more gelatin present as compared with an old animal that has extra-toughened collagen fibers.

When making a stock, there are soluble and nonsoluble proteins. The soluble and dispersible constituent protein elements in general include approximately the following:

- 20% collagen found in bones
- 1% by weight of collagen (not from bones)
- 30% pig skin and around (optional)
- 40% cartilaginous veal knuckles
- 5% other cell proteins
- 2% amino acids and other savory molecules
- 1% sugars and other carbohydrates
- 1% minerals, mainly phosphorus and potassium

[7]Meat glazes are slowly simmered until they are reduced to about a tenth of their original volume. This produces a thick, syrupy, sticky consistency due to the high gelatin content (about 25%). This type of stock is called a *glace de viande*, which cools to a solid jelly.

So, when it comes to making the stock, one can see that the bones, skin, and veal knuckles are relatively rich in collagen protein. Having said that, the bones, skin, and knuckles provide only minimal extra soluble molecules that enhance or provide flavor in the finished stock and ultimately the sauce. As a way of adding more flavorful molecules to the stock, both meat and roasted vegetables are often used and their juices and flavor molecules extracted. In this sense, the meat in the stock is thoroughly cooked and releases about 40% of its weight in juice. Making animal stocks can be a lengthy process with times varying from a few hours for chicken and up to a day or so for beef stocks. However, a cautionary note here, with long extraction times and higher temperatures comes certain problems, chief of which is the fact that the gelatin molecules that have already been dissolved are damaged if cooking temperatures are too high or if the cooking process is too lengthy (Coultate, 2009; McGee, 2004).

As a thickener, gelatin is relatively inefficient because its molecules are very physically flexible and are unable to interfere with the flow of liquid in the sauce the same way starch and carbohydrates can. In fact, a sauce thickened with gelatin alone requires large concentrations to be effective as a thickener. However, the problem with this concentration of gelatin is that the sauce will quickly congeal on a cooling plate. This is because single gelatin molecules are proteins with chains of around 1000 or more amino acids that create weak, reversible bonds that essentially undo (or untangle) with heat just as easily as they set (gelate) in the cold.

However, when it comes to setting stocks, gelled deserts, etc., a gel forms when the concentration of gelatin is relatively high, around 1% or more by weight; although even at these concentrations, the cooled stock or dessert is still fragile. That said, such concentrations are adequate for warm or hot sauces. If we were to make any semisolid set desserts, then we would have to ramp up the percentage of gelatine to say 3% or more by weight.

Fish and shellfish sauces—when making stocks or sauces from the bones and skin of fish, it is important to remove the gills so as not to color or cloud the end result. Also unlike the browning process of beef and other similar animals, the cook usually aims for a clear white fish stock. Also because of the lower extraction temperatures of collagen in fish (between 10–25°C and 50–77°F depending on climate and habitat of the fish), the stock can be made at a much lower temperature and for a reduced length of time than their animal counterparts. We also noted (Section 4.4.2) that fishes' bones and skin are rich in connective tissue, while its collagen is generally less cross-linked making for a softer gel when cooled. We also observed that the more cross-linked collagen there is in the fish or shellfish, so it requires higher extraction temperatures; this is the case with squid and octopus whose collagen might need a full hour or so at 80°C/176°F or above, in order to extract the maximum amount of collagen. After this, the stock can be reduced as a glaze or thickened with a roux or *beurre manié*. As mentioned, fish stocks need to be treated gently as their gelatin is relatively fragile and is easily broken down into smaller pieces of denatured proteins when cooked. This makes it harder for them to bond with each other, thus resulting in a weak network of proteins to thicken sauces or if cold—a softer set gel.

With shellfish sauces, while there is no collagen in the shells, they are still used in the making of the sauce. Firstly, the shells are roasted or panfried in a little butter or oil to dissolve the flavors and pigmentation, seeing as the elements the cook wants are more soluble in fat than in water. Then, by adding a good fish stock among other ingredients, the stock is then reduced to make the sauce for the dish.

15.2.4.1 Other protein thickeners

Gelatin is the without doubt the easiest and most forgiving of protein thickeners cooks can hope to work with. Simply add some heat, and water and protein molecules unbond with each other and become redispersed among the water or liquid molecules. Cool it down, and they once again rebond to each

other, and so, the cycle goes. However, while it is very common and popular among cooks, practically, all other proteins, in plants and animals, behave in the opposite manner. That is to say, as heat unfolds the proteins, so they become entangled with each other forming strong bonds that then coagulate permanently and irreversibly into a firm solid. This is why raw eggs, when cooked, solidify, or once pliable, meat tissue becomes stiff, and why milk curdles. All these solid pieces of coagulated protein cannot be reversed, but it is possible with a little patience and temperature control to govern protein coagulation so that they can thicken sauces. The theory, however, while straightforward, does take some practice not to curdle or coagulate the sauce; this is where the experienced cook shines. Firstly, a sauce is made without any other thickening agents, and at the right moment, the cook adds a suspension of tiny protein particles to thicken the sauce.

Take for example a white stew, in which the liquid or stock will become the sauce. At the moment, the stock has the consistency of water. If we then add a protein source, in this case egg yolks,[8] and heat the mixture gently, at some point, the proteins unfold and begin to form bonds. The temperature is critical here as too low and the sauce will not thicken and too high and the sauce coagulates or "splits." For the most part, animal proteins coagulate around 60°C/140°F or so, and we are careful to say "for the most part" as this crucial temperature can indeed vary to some degree (see earlier discussion). In the end, there really is no substitute for experience and careful monitoring of the sauce's stability. Anyway, as the sauce noticeably thickens, it clings to a spoon rather than running off like water. The observant cook immediately takes the sauce off the heat and keeps stirring to prevent proteins from forming anymore strong bonds.

If the protein thickener is popped directly into the sauce, then some of the protein will become instantly overheated and will separate out into grainy particles. There are many work-arounds, and one of them is to add the protein (the puree liver, for instance) into softened butter and cool it, so, when it's time to thicken the sauce, the butter slowly melts dispersing the liver thickener evenly in the sauce. The same trick can be applied to high protein animal and fish organs. Furthermore, one need not stick to one method of thickening alone. Adding a little flour, for instance, helps enormously with the stability of the sauce.

Egg yolks—egg yolks comprise 50% water, 16% protein, and about 34% lipids. They are one of the most efficient of the protein thickeners; this has a lot to do with the percentage of protein present and the fact that they are already well dispersed in an emulsion of water and lipids. This makes them easy and versatile to work with, whether custard sauces, mayonnaises, etc.; egg yolks are also cheap, very adaptable, and usually can be found in most professional and private kitchens.

Liver—as well as providing a thickening agent, the liver also provides flavor. However, before it can be used, the liver must first undergo some preparation. The proteins in the liver are found inside the cells, so to break them open, one must puree or pound the liver in order to separate the cell membranes and connective tissues. Once they are sieved, they can be used on their own, with a little flour or starch, or some classic French dishes require that a sauce be finished with the liver. Furthermore, the liver is the binding and solidifying substance in pâtés and parfaits.

Blood—this is the traditional thickening agent in the British "Jugged Hare" and the French "coq au vin"; blood is made up of approximately 17% protein and about 80% water and consists of the various

[8]In adding protein to hot liquids, one must be careful not to coagulate the proteins on contact. It is generally more prudent to add a little of the hot liquid into the protein to gently bring up the heat before adding the protein mix to the sauce.

blood cells and a fluid called plasma in which the cells float. This plasma makes up two-thirds of pig and cattle blood with dispersed proteins about 7% by weight. Albumin, at temperatures of about 75°C/167°F, is the protein responsible for thickening sauces and stews.

Cheese and yogurt—the overriding difference with using yogurt and cheese as thickeners is the fact that they have already had their proteins coagulated by enzymatic activity and/or acidity. In this sense, they operate in a slightly different way—cooks can, and often do, use these products by simply adding them to sauces to thicken and enrich. The best cheeses for thickening sauces are soft and creamy rather than the hard cheeses as the creamier cheese protein network has already been broken down into small, easily dispersed molecules. Both cheese and yogurt are best subjected to moderate heat only as cooking close to the boil can cause "splitting" or curdling. Also, it might be necessary to aid the process and to stabilize the sauce by adding a little starch or flour to the mix.

15.2.5 PUREE-TYPE SAUCES

Purees like apple or ubiquitous tomato sauces are simply made with little preparation by cooking and blending fruits and vegetables, passing them through a sieve and seasoning them to taste. Sometimes though, just pureeing fruits and vegetables, either raw or cooked, can leave the puree (the juice and the suspended cellular debris[9]), with a sauce coarse in texture and a thin fluid that bleeds out on the plate. This bleeding happens as the puree's particulates are usually too big and act as inefficient thickeners or stabilizers. One option to avoid this is to heat the sauce and reduce it sufficiently until any excess fluid is evaporated off, but in this case, the cook is in danger of producing a thick gloopy puree that acts more like a fruit or vegetable accompaniment than as a sauce. As mentioned, purees can be sieved to extract these floating cellular particles giving the remaining juice a smoother more "saucy" feel. However, in this case, the removal of the cell particles (which originally helped to thicken the sauce, albeit inefficiently) must be replaced by some other thickeners as the remaining juice/puree will, more likely than not, be too watery. There are many ways to do this, but one way in particular that gives the puree sauce a creaminess and rich buttery flavor is to literarily add butter. However, as suggested in Section 15.3.4, this must be done with caution so as to keep the butter in emulsion without allowing the reconstituted fat droplets to separate.

15.3 EMULSIONS AS SAUCES

(See also Section 7.2.2.2)

So far, we have looked at thickening sauces with a fine diffusion of solid materials such as starches, proteins, cell-wall molecules, and plant tissues. Another option or more precisely, an alternative to traditionally thickened sauces is to modify a sauce into an emulsion. The idea, as laid out in Section 7.2.2, describes the principles of a simple emulsion. Firstly, one has to take a continuous phase, say water, for example, and mix it with a stabilized dispersed phase, in this example, oil, and the whole thing is stabilized by the lecithin in egg yolks to make a thick creamy emulsion. Simply add vinegar, capers, gherkins, and parsley, and the cook has made a simple tartar sauce. Other very simple emulsions

[9]The solid particles in a puree are plant cell walls—an agglomeration of many thousands of carbohydrate and protein molecules.

that are used as sauces include *beurre blanc*, hollandaise, and oil-and-vinegar-based salad dressings. The trick or the art of a good emulsion is to stabilize the sauce as they are inherently unstable. Taking our above example of mayonnaise, the aim is to get the oil droplets (the dispersed phase) as small as is possible; along with the egg yolk emulsifier, this helps stabilize the mixture. In terms of options, the humble whisk (if vigorous enough), a cook can disperse the oil into 3 thousandths of a millimeter across; this is the same as a domestic blender. Once we start getting into commercial and industrial blenders, they become smaller still until one happens across an industrial homogenizer that can reduce the size of oil droplets to less than 1 thousandth of a millimeter. These small droplets are easier to emulsify with egg yolks or other substances and are less likely to separate or coalesce into its two separate phases (split). However, adding emulsifiers alone, while sufficient in the home and professional kitchen, is not always enough at the commercial level where one might need to add a stabilizer too.

Once the emulsion has been made, the temperature at which it is kept impacts on the texture and quality of the sauce. Mayonnaises and other cold emulsions are generally fine at fridge or room temperatures. However, hot or warm emulsions like *beurre blanc* or hollandaise cannot be allowed to become too cold or too hot. This is because as molecules heat up, they are agitated; they move faster with an increased risk of collision with other dispersed molecules ultimately reaching a point where the sauce is destabilized and threatens to "split" or coalesce. At temperatures above approximately 60° C/140°F, proteins tend to denature and unfold and coagulate. Bear in mind too that a cooked emulsion that is "held" for a period of time on a low heat might also lose sufficient continuous phase (usually water based) through evaporation allowing the remaining dispersed droplets to become overcrowded and threaten its stability. Furthermore, the sauce must also not be allowed to get too cold, with the exception of mayonnaise, which can stand fridge temperatures quite well; other sauces containing butter, oils, and fats that solidify at room or lower fridge temperatures will tend to coalesce or have its dispersed phase (fats and oils) set. This produces fat or oil crystals that then rupture the emulsification agent surrounding these fats so that eventually they will split or separate when stirred or reheated.

Recovering a split sauce—when an emulsified sauce splits, there are at least two ways it can be recovered or reemulsified. The first is to simply pop it into a blender that, if sufficient emulsifying and stabilizing molecules are still present, can allow the blender to break down the enlarged dispersed molecules. That said, this process will not work for overheated protein-based emulsified sauces like hollandaise as the irreversible denatured proteins in the egg yolks cannot be "uncoagulated." The second and often the easiest technique to restore the emulsion is to start again with a small amount of the continuous phase (optional egg yolk or other emulsifiers added) and gently and carefully whisk the split sauce back into the new base. If in the case of hollandaise, the sauce is split, and the proteins coagulated, so this can be recovered by sieving out the proteins and use the remaining butterfat to restart another emulsion (Vaclavik and Christian, 2014).

15.3.1 EGG EMULSIONS

When it comes to emulsification, egg yolks work best when raw and warmed. If too cold, the yolk particles will only move slowly and cannot effectively coat fat droplets. If cooked, yolks' proteins are already denatured and coagulated, although that said sometimes cooked yolks are used in place of raw yolks in some emulsions. The difficulty is the denaturation of the proteins and the fact that phospholipids are more likely encased in the coagulated network. Thus, they have far less emulsifying power with an additional downside of potentially giving the final emulsion a grainy texture

(Coultate, 2009). As for the less concentrated protein in egg whites, while they are not useful as an emulsifier, they do have some value as emulsion stabilizers.

15.3.1.1 Hollandaise sauce

In hot egg sauces like hollandaise, only clarified or separated butter is used; the liquid portion of the butter only serves to thin the sauce, whereas clarified butter thickens the sauce. The trick here is to heat the mixture sufficiently that yolks thin out and easily coat the butter particles but not too hot that the yolks cook—which happens at between 70–77°C and 158–170.6°F. Occasionally, cooks add an acidic substance like lemon juice or vinegar—this is because if the resultant mix pH drops to about 4.5, then this has the effect of stabilizing egg yolks and allowing them to be taken to higher temperatures to as much as 90°C/194°F without curdling. This happens as a result of the lower pH causing the proteins to repel each other, thus allowing them to unfold in the heat without forming too many bonds and coagulating the mixture too early.

As mentioned, when it comes to keeping the hollandaise warm for use during "restaurant service," there is a tricky trade-off. Too hot and the yolk proteins coagulate and split the sauce; too cold and the butter starts to solidify. The best temperature for holding a stable hollandaise is around 63°C/145.4°F. Also, when holding the sauce on the heat, it is worth considering the evaporation of moisture that could affect the stability of the emulsion. Further, when holding the emulsion on heat, bonds are still being made that tends to thicken the sauce and once again threatens to destabilize it. To solve both risks, it is worth covering the pot to prevent moisture loss and control the overbonding by occasional stirring or adding some liquid back into the mix (Coultate, 2009).

15.3.2 VINAIGRETTE EMULSIONS

Perhaps one of the easiest of the emulsion sauces/dressings to make is the humble vinaigrette. With three parts oil and one part vinegar, these dressings are not usually emulsified; instead, the oil, vinegar, and flavorings are simply whisked, or if bottled, then shaken to disperse the droplets of vinegar in the oil. This is a very standard dressing used variously for cold salads, vegetables, and other foods. If an emulsified vinaigrette is wanted, then first, the cook uses less oil, perhaps dilutes the vinegar if it is too strong or too acidic, and then emulsifies the ingredients using mustard paste like Dijon or English. Nowadays, cooks are learning to play with more unusual vinaigrettes where the vinegar is augmented with things like fruit and vegetable juices or purees, pan juices, or stock reductions (McGee, 2004). The oil or fat is also being swapped out for things like olive oil or various nut and seed oils and rendered poultry fats and even butter. Emulsifiers are also changing as the cook becomes more educated and inventive; emulsions can be made with gelatine, certain gums, and cream too. All in all, emulsified sauces are fast becoming very versatile dressings in the modern cook's kitchen.

15.3.3 MILK AND CREAM EMULSIONS

Milk is a dispersion in which water is the continuous phase and the dispersed phase is a complex mix of microscopic fat droplets and casein proteins. The fat droplets are coated with a thin membrane of emulsifiers and casein proteins that are very tolerant of heat. This is why milk and cream can be boiled without its fat globules coalescing or splitting or the proteins coagulating.

While whole milk is about 4% fat, it is not enough to make a substantial or fulfilling sauce. Cream on the other hand is milk whose proportion of fat has been concentrated to between 18% and 60% depending on usage (McGee, 2004; Field, 2011). In top of this, cream contains other proteins and emulsifying molecules that help stabilize other, more fragile emulsions. So, creams make excellent sauces by themselves and stable emulsions like *beurre blanc*. However, while boiling milk and lower fat creams, the casein proteins within are stable enough, yet when they come into contact with anything acidic, the proteins denature and curdle or split. This is why in many sauces, whose pan sediments have been deglazed with wine or brandy or the like, so reducing the deglazed liquid evaporates or burns off sufficient alcohol that only then can cream be added to finish the sauce. The higher fat sauces tend to have, so few casein proteins that acidity has little effect on the outcome.

15.3.4 BUTTER EMULSIONS

Like cream, butter is also an emulsion but an unusual emulsion in which fat (80%) is the continuous phase and what little water there is (15%) constitutes the dispersed phase; the remaining 5% is formed from the milk solids. By itself, butter makes a rich and versatile sauce, whether whole of clarified (whereby the butter is melted and continued on the heat until all the water boils off leaving the milk solids to turn brown), giving it a nutty aroma. These are how classic browned French butters *beurre noisette* (hazelnut) and *beurre noir* (black) are made (Page and Dornenburg, 2008).

Beurre monté/monté au beurre—butter is used to enrich many sauces. This makes butter useful as a finishing agent for so many sauces giving sauces a silken rich, creamy flavor and texture that is not to be forgotten. First, the cook must begin by heating the sauce that acts as the continuous phase. Then, cubes of butter are added to the sauce while hot but not boiling. It is then whisked in. As the butter melts and is vigorously whisked into the sauce, the fat is released along with the constituents of the butter's water droplets (containing milk proteins and other nutritive components). This method works in proportions of one part butter to three parts sauce (McGee, 2004). Of note, however, because of the partial remnants of the emulsifiers and proteins in the sauce, the sauce is fragile and must not be reheated above 60°C/140°F lest the fat begins to seep out of the sauce. If a sauce is accidentally overheated and begins to leek fat, it can usually be saved by briskly whisking in a small amount of cool water. Any water-based sauce can be treated in this manner especially if the sauce does not contain much in the way of gelatin or starch thickeners. In this way, a butter-sauce emulsion is a good way to go; in fact, this is the basis for the famous *beurre blanc* that has been referred to on more than one occasion throughout this book.

Beurre blanc—the French *beurre blanc* is a butter-emulsion sauce made by reducing wine and/or vinegar/lemon with flavorants such as shallots and other things. Once reduced and the alcohol burned off, so cream or velouté is added, and pieces of butter are vigorously whisked into the reduction. The butter's watery component containing phospholipids and proteins is capable of emulsifying 2–3 times the volume of butterfat contained within. Also, once the initial emulsion has been formed, the consistency can be made thicker with the addition of more either whole butter or (as in *hollandaise*) its clarified component. One must also be aware that if temperature rises above 58°C/136°F, the *beurre blanc* can separate leaking butterfat. Although as with other butter emulsions, so the addition of cool water or cream can often bring the sauce back. Likewise, if the temperature falls below around 30°C/86°F, the fat solidifies, and its crystals pierce the stabilizing thin membrane coating and begin to coalesce, which then separates out upon reheating. The best temperature for holding a *beurre blanc* is about 52°C/125°F (McGee, 2004).

All said and done, in reality, a cook's sauces are seldom simple suspensions, dispersions, emulsions, or foams; instead, they are, more often than not, a combination of several techniques. Purees, for instance, might be both a suspension and a dispersed molecular solution, while a starch-thickened sauce can just as easily contain both a dispersion of protein molecules and remnants of starch granules. Foam sauces might include proteins from milk and carbohydrate from starches, while gelatin-based sauces might just as easily be thickened at the last minute with a knob of butter or a spoonful of cream. Indeed, when it comes to sauces, the experienced cook really can be a wizard in the kitchen (Gisslen, 2010).

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CHAPTER

LIPIDS, OILS, FATS, AND EXTRACTS

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Fats and oils are esters of the trihydroxy alcohol (glycerol[1]), while waxes are esters of long-chain monohydroxy alcohols. Since both can be hydrolyzed to fatty acids and alcohols they are important foods for humans and some bacteria. Lipids are oil-like/fatlike chemical compounds that cover a wide variety of naturally occurring molecules that include oils/fats, waxes, sterols (including cholesterol), fat-soluble vitamins (A, D, E, and K), and phospholipids. These are important nutrients in that the body as the body cannot produce them for itself. Often used synonymously with oils and fats, it can be seen that they are, in fact, very different. Strictly speaking, lipids are a group of naturally occurring molecules; three major types of lipid molecules exist—these are the following:

[1]Glycerol, a clear, viscous, sweet-tasting liquid that belongs to the humble polyol compound. (A polyol is an alcohol containing multiple hydroxyl groups).

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- *Phospholipids*—are made up of two fatty acids and a phosphate group; these are the type of lipids found in the cell membranes of all animals.
- *Steroids*—are made up of four connecting carbon rings and a functional group that determines which particular steroid molecule it is. These lipid compounds generally create hormones such as testosterone and estrogen from the cholesterol steroid molecule (Belitz et al., 2009).
- *Triglycerides*—from the cook's perspective, triglycerides are made up of three fatty acid molecules linked to a glycerol molecule that together forms glycerides (with one, two, or three attached fatty acids)—hence the triglyceride or triglycerides. These are the typical oil/fat molecules found in the bloodstream before being deposited in adipose tissue. It is in this third group—the triglycerides that we are mainly interested in (Vaclavik and Christian, 2014; Latham, 1997; Ortega, 2007; WKU, 2010).

Generally speaking, the main focus of fats in our diets is for health and nutrition. However, they are also an important ingredient in the manufacture and the taste and texture of many food products. Fats contribute to aeration in ice creams, moisture retention in cakes and puddings, in glossy appearances like chocolate coverings and bonbons, and in textures like margarines (NEODA, 2016). So, what determines if a triglyceride is oil or a fat?

16.1 OILS AND FATS IN COOKING

Just to recap, oils/fats are made up of just three elements: carbon, oxygen, and hydrogen atoms. These elements come together to form chains called fatty acids. If three of these chains, then join together, they form a molecule—a triglyceride. The triglyceride molecule is the basis of all oils and fats. However, what distinguishes "oil" from a "fat" is the makeup of the fatty acid chains within the oil or fat itself. Individual fatty acids can be either saturated or unsaturated and unsaturated fats can be further subdivided into mono- and polyunsaturated fatty acids (Vaclavik and Christian, 2014; NEODA, 2016; Larsson, 1994). This separation is important as the nature of the fat depends on the type of its fatty acids involved.

Saturated fats—broadly speaking, these fats are predominantly of animal origin; for example, they are found in meat, milk, cream, butter, and in small quantities in eggs, although exceptions from the vegetable kingdom with high saturated fats include palm, cocoa, and coconut oils. The levels of saturates found in certain fats are generally higher in those that are solid at ambient temperatures. From a cooking point of view, they are good; however, from a health point of view, they are bad. These fats are also distinguished from their unsaturated companions in that they have no carbon double bonds and are instead saturated with hydrogen atoms. Diets high in saturated fats tend to raise blood cholesterol levels leading to possible heart disease.

Unsaturated fats—mainly derive from plants and can be further subdivided into poly- and monounsaturated fats. While both poly- and monounsaturated fats help in lowering low-density lipoproteins (LDL cholesterol) and subsequently reducing the risk of heart disease, some consider polyunsaturated fats as being marginally better for their health. At the molecular level, unsaturated fats contain carbon-to-carbon double bonds, and their configuration ultimately determines their health properties in the human diet.

- *Monounsaturated fats* (MUFA[2]-)—contain one double carbon bond, hence mono- and as such include oils from the olive, peanut, sesame, rapeseed, and avocados plants. These "healthier" fats contain *cis*- as opposed to the *trans*- carbon arrangements[3] (EFSA, 2008; WHO/EMRO, 2010; WKU, 2010)
- *Polyunsaturated fats* (PUFA)—for some, polyunsaturated fats are the preferred choice for many people; however, they do tend to be more prone to lipid peroxidation (see Section 12.6.2). In an attempt to prolong the shelf life of these oils, scientists introduced hydrogenation that changes the degree of saturation of the fat. In essence, scientists found a way of converting the liquid vegetable oil into a more solid or semisolid fatlike margarine, for example. Unfortunately, partial hydrogenation of these fats creates trans-fatty acids or trans fats (see below). Polyunsaturated fats come from corn, cotton seed, safflower, soybean, and sunflower oil. Fish oils too are also polyunsaturated as are omega-3 and omega-6 that are also fatty acids believed to be good for health too (EFSA, 2008; WHO/EMRO, 2010; WKU, 2010).

Trans fats—can either be trans-MUFA or trans-PUFA, and while these can naturally occur in nature, they are not particularly common, instead, and, by far the biggest intake of human trans fats, are derived artificially. Because prolonged shelf-life properties of hydrogenation many common processed foods contain trans fats. Trans fats are particularly harmful in that they act like saturated fats and raise levels of blood cholesterol.

While this separation is good for generalization, in truth, all fats contain a combination of both saturated and unsaturated fatty acids. Consequently, fats are usually identified according to the predominant fatty acid present. Furthermore, because all oils and fats contain different proportions of most of those fatty acids described above, it is this combination that determines whether it will be solid fat or liquid oil at ambient temperature. As a loose rule of thumb, those oils that contain a greater proportion of unsaturated fatty acids tend to be liquid at room temperature whereas those with higher amounts of saturated fatty acids are generally solid. Another characteristic of oils and fats is that their molecules tend to be larger so they are not as volatile as say water or alcohol (Belitz et al., 2009).

16.2 VEGETABLE OIL

Vegetable oil is generic term used to describe cooking oil derived from vegetable sources. They are generally lower in saturated fats than animal-based fats and oils so have a higher smoking point (see below) making them good for frying. Chemically speaking, the particular physical alignment (the varied branching of the atoms) of the fatty acids that make up the triglyceride molecules means that there is less friction between molecules making them liquid at ambient temperature. Many specific oils exist, like rapeseed, sunflower, and olive oils, yet many vegetable oils are often a blend of different types of oil. As such, it is not always possible to determine the ratio between the different types and components of fat within. The following (Table 16.1) helps differentiate various oils and their relative fat contents (Gunstone, 2001; Larsson, 1994).

[2]Monounsaturated and polyunsaturated fats are known by other names - omegas. There are three types of omega fatty acids: omega-3, omega-6 and omega-9.

[3]Cis and trans isomerism describes molecules with the same chemical makeup but that have different physical structures.

Table 16.1 Common Oils and Fats—Constituent Fatty Acids

Percent by Weight of Total Fatty Acids								
	Fatty Acids							
	Saturated					Monounsaturated	Polyunsaturated	
Oil or Fat	Capric Acid	Lauric Acid	Myristic Acid	Palmitic Acid	Stearic Acid	Oleic Acid	Linoleic Acid	Alpha Linolenic Acid
Almond oil	–	–	–	7	2	69	17	–
Borage oil	–	–	–	11	4	16	39	0
Butterfat (cow)	3	3	11	27	12	29	2	1
Butterfat (human)	2	5	8	25	8	35	9	1
Canola oil	–	–	–	4	2	62	22	10
Cocoa butter	–	–	–	25	38	32	3	–
Cod liver oil	–	–	8	17	–	22	5	–
Coconut oil	6	47	18	9	3	6	2	–
Corn (maize) oil	–	–	–	11	2	28	58	1
Cottonseed oil	–	–	1	22	3	19	54	1
Flaxseed oil	–	–	–	3	7	21	16	53
Evening primrose	–	–	–	6	1	11	72	1
Grape seed oil	–	–	–	8	4	15	73	–
Lard (pork fat)	–	–	2	26	14	44	10	–
Olive oil	–	–	–	13	3	71	10	1
Palm oil	–	–	1	45	4	40	10	–
Palm kernel oil	4	48	16	8	3	15	2	–
Peanut oil	–	–	–	11	2	48	32	–

Perilla oil	–	–	–	6	2	17	15	61
Safflower oil	–	–	–	7	3	15	75	–
Sesame oil	–	–	–	9	4	41	45	–
Soybean oil	–	–	–	11	4	24	54	7
Sunflower oil	–	–	–	7	5	19	68	1
Walnut oil	–	–	–	11	5	28	51	5

Compiled and adapted from LaMorte, W.W., 2016. Diet and Heart Disease. School of Public Health. http://sphweb.bumc.bu.edu/otlt/mph-modules/ph/ph709_heart/ph709_heart8.html (retrieved 02.04.17.); Cummings, J., Stephen, A., 2007. Carbohydrate terminology and classification. European Journal of Clinical Nutrition 61, S5–S18; SkillsYouNeed, 2013. Cooking Fats and Oils.

16.2.1 SMOKING (SMOKE) POINT

The smoking point or smoke point of an oil or fat is the temperature at which it starts to burn and degrade. As the name suggests, oils and fats literally start to smoke and can easily ignite at this point. Those oils and fats with higher smoking points are best for sautéing or frying foods, while those with lower smoking points are good for salad dressings, confits, and other warm or cold uses. Interestingly, smoking points vary within the same type of oil of fat due to the different extraction methods and storage methods (SkillsYouNeed, 2013).

16.3 RANCIDITY

The term "rancidity" is used to describe two different processes: oxidative rancidity caused by fat oxidation and hydrolytic rancidity caused by fat hydrolysis.

16.3.1 OXIDATIVE RANCIDITY

Oxidative rancidity of oils and fats such as lard, shortenings, and cooking oils refers to the unwanted odors and flavors that develop over time when they are exposed to oxygen in the air. These can be oils and fats by themselves or foods containing them, including fish, poultry, meat, and dry milk, which can all become rancid as the fats in the products react with the oxygen in the air. The polyunsaturated fatty acids within the foods, oils, and fats react with oxygen to form peroxides. The peroxides in turn decompose giving rise to complex mixtures of aldehydes, ketones (see Appendix B), and other volatile products. It is these products that give the rancid foods and oils that distinct rancid aromas and flavors (Belitz et al., 2009; Sebranek and Neel, 2008).

The chemistry is fairly complex and involves free radicals (Section 14.9.1.3) causing a chain reaction. Light or heat can react with oils and fats to break bonds of hydrogen and carbon in fatty acids in the oil leaving behind free radicals (in this case carbon atoms with an unpaired electrons). This electron, in turn, reacts with oxygen breaking the double bond and after pairing with one of the unpaired electrons to leave a peroxide radical attached to where the hydrogen had been in the oxygen molecule. The remaining unpaired electron in the peroxide radical then adsorbs hydrogen from the linoleum, thus closing the circle to start over again. Hence the chain reaction, which by definition can go on and on *ad-infinitum*. This causes the oils and fats to chemically break down—degrading them, affecting the color, the taste and the performance, effectively shortening their useful life span. That said, the chain reaction can be broken simply by storing oils and fats in a dark place or by popping it in the fridge (Belitz et al., 2009; Sebranek and Neel, 2008). Another way to arrest the chain reaction is to use antioxidants that bind with the free radicals preventing or slowing the process. This is because antioxidants contain stable radicals that bond with free radicals found in the chain reaction, thus preventing further oxidization. Many antioxidants exist that prolong shelf life in oils and fats the most common of which is vitamin E.

16.3.2 HYDROLYTIC RANCIDITY

Hydrolytic rancidity develops when triglycerides in particular are hydrolyzed and free fatty acids are released; the process sometimes requires a catalyst. It is also the reason short-chain fatty acids, such as butter fats, are odorous. Rancidity in foods ranges from barely noticeable, indicating a loss of freshness—to very severe complete with strong aromas (Sebranek and Neel, 2008). Small or slight

degrees of rancidity are much more common in foods, oils and fats than severe rancidity is, yet it is the slight rancidity that is of much more concern. This is especially observable in meat—even though it is kept refrigerated or even frozen, the polyunsaturated fat within meat will continue to oxidize and slowly become rancid. This process starts from the moment of slaughter and continues under cool temperatures although it must be said that, at refrigerated or even frozen temperatures, rancidity happens at a slower rate (see Section 9.2), (Gunstone, 2001).

16.4 ESSENTIAL OILS

Essential oils are the highly concentrated, volatile, aromatic essences of plants. These natural plant oils are appreciated for both their aromatic and flavoring qualities. While common, fruit, vegetable, and other plant oils are readily available for the flavor and aroma industries, for manufacturing and mass production, and for use by the humble cook. That said, essential oils are the lesser known components of the cook's repertoire. As such, we introduce essential oils here, and while the following sections mainly describe essential oils and their properties and extraction methods, with a little consideration, much of this can also be applied to common vegetable oils in general.

At its very simplest, Ernest J. Parry described essential oils in 1922 as

> …odouriferous bodies of an oily nature obtained almost exclusively from vegetable sources…
> **(Parry, 1922)**

An essential oil is an oil that is generally (but not always) distilled by steam or water from the leaves, stems, flowers, bark, roots, seeds, fruits, or other elements of a plant (SADC, 2006).

They are the purest and most potent form of predominantly plant extracts available. While not a bad starting point, in actual fact, essential oils are complex mixtures of volatile[4] constituents biosynthesized by living organisms. They can be of plant, animal, or microbial origin although, as the quote hints at, aromatic plants are the major source of most commercially important essential oils. Interestingly, essential oils' actual function in nature is still an unanswered question and the focus of much ongoing research. However, there is suggestion that such oils might be produced for defence, for signaling, or even as part of the secondary metabolic processes (Stewart, 2005). In plants, they are distilled from the leaves, stems, flowers, bark, roots, or other elements of the plant usually by steam or by water. Essential oils are highly volatile—that is, they quickly dissipate into the air, even at room temperature, and are hydrophobic in that they refuse to mix with water. The total essential oil content of plants in general may vary considerably from one season to the next due in part to the age of the plant, the plant genotype, and just as importantly, the weather. In general, yields can range from a few tenths of 1% of a plants' biomass to about 1% maximum (Surburg and Panten, 2006). In pure lavender oil (*L. angustifolia*), for example, essential oil content is very low—in some cases between 0.4% and 0.7% but again always less than 1%. A good yield of lavender oil returns just over 400 g of oil per 80 kg batch of distilled plant material.

16.4.1 GENERAL PROPERTIES OF ESSENTIAL OILS

(For a detailed look at the various chemical classes or chemical groups that make up most essential oils' compositions, see Appendix C).

[4]Volatility—in chemistry, volatility refers to a substances tendency to vaporize (see Section 3.3).

What we can take from this foray is that essential oils are compounds of terpenoid or nonterpenoid origin. These are hydrocarbons, with their structure based on the isoprene unit, known as terpenes[5] and the oxygenated compounds of these hydrocarbons. These oxygenated compounds are the result of reactive functional groups[6] attaching themselves to hydrocarbons. These include alcohols, aldehydes, esters, ketones, phenols, and oxides. Some may also contain other groups beside the hydrocarbon and oxygen compounds and include those nitrogen-, sulfur-, and halogen-containing compounds. In addition, phenylpropanoids, fatty acids and their esters, or their decomposition products are also encountered as volatiles in essential oils. Collectively then, these compounds are responsible for giving essential oils their distinctive physiological, psychological, and aromatic qualities.

Chemistry aside for now, it is generally accepted that many if not most, oils display common characteristics as a whole. This can be partly attributed to the fact that a lot of essential oils comprise many of the main chemical classes discussed in the appendixes and, by doing so, exhibit many similar qualities, depending on concentration of course. In this respect, many would suggest that the aromatic, therapeutic, and psychological effects of the whole oil are synergistic—that is, they are greater than the individual benefits of each constituent component chemicals.

It has also been said that such overarching properties generally include first and foremost being volatile, in which they are all able to be absorbed by the human body, while oily (ish) they are in fact nongreasy; they tend to be soluble in both alcohol and carrier oil while only being partially water soluble; they are inflammable; stress relieving; potentially prophylactic[7] while displaying a pronounced sedative or calming effect on the central nervous system—especially lavender's *angustifolia*.

16.4.2 OIL PROCESSING

There are several methods available that can be used to extract oils (essential oils included); these include cold pressing, distillation using water or steam (or a combination of both), enfleurage, solvent extraction, and CO_2 extraction. The method chosen is not an arbitrary choice based on preference; instead, the method chosen depends to a large extent on factors required of the desired results (different methods affect the oils chemical compounds differently) to the best method that suits the particular plant material itself among others (Hoard, 2012). The amount and quality of the oil depends on the particular type of plant and the weather during the season.

16.4.2.1 Cold pressing (expression)

Cold pressing or expression is a mechanical method used primarily with citrus peels such as lemon, lime, orange, and grapefruit and others including fruit and seeds such as olives, peanuts, and sunflowers. Oils produced this way contain not only all of the essential ingredients of a good oil but also other things including colorants and waxes. The overriding advantage of this method is that in the absence of heat, these oils themselves are more refreshing or flavorsome and truly reminiscent of the fruit, seed, or plant itself. In fact, when it comes to certain oils, while they can be distilled using

[5]Terpenes are a large class of naturally occurring organic compounds derived from multiples of five hydrocarbon structural units called isoprenes (a contraction of the word isoterpene).
[6]Functional group, in organic chemistry, is a reactive portion of a molecule that characterizes the chemical reactions of those molecules.
[7]Prophylactic—disease preventing.

water or steam, they might very well be fragile and can easily be altered chemically during the heating method; in such cases, cold pressing is recommended.

16.4.2.2 Distillation

The separation of a liquid's various components through the process of distillation depends on the differences in boiling points of the individual component parts. This taps into the principles of volatility, a detailed explanation of which can be found in Section 3.3. Distillation is also similar in practice to the distillation methods of fortified alcoholic beverages and the like (Section 20.1).

This can be achieved principally in one of two ways—water or steam distillation:

- *Water distillation*—water distillation involves boiling plant material in water. Volatiles evaporate along with the water vapor that is then condensed by the different fractions (components) on the surface of a cooling condenser.
- *Steam distillation*—steam distillation is a technique that must be mastered—too hot or too much pressure may actually alter the molecular structure of important chemical compounds affecting both oils' chemical and aroma profiles; in this respect, oils properties are altered with heat. In operation, the stills are loaded and steam is passed through the biomass for about half an hour. In lavender oil, for example, because it has a lower evaporation point than steam, the steam causes the oil in the flowers to vaporize. The oil and steam vapors then travel along to the condenser where the mixture is cooled until it condenses back into liquid. Because of the different densities, the oil floats atop the water that can then be tapped off.

16.4.2.3 Extraction

Sometimes, extracting or drawing out oils from plants is best achieved using liquid solvents or gases carbon dioxide CO_2. These methods are generally used when the heat of distillation threatens to damage delicate oils or when the quantity of oil in the plant is so low that distillation would not be an effective extraction method.

Solvent extraction—solvent extraction today has evolved into an efficient chemical process. In the past, there were hot and cold enfleurage processes (next section) although these have largely become obsolete as a result of being uneconomic and wasteful—ultimately inefficient. The most common method of solvent extraction these days is with the use of liquid hydrocarbon-based compounds. Liquid solvents might take the form of petroleum, toluene, methanol, and even ethanol. These solvents are gently heated with the plant biomass that helps to absorb the aromatic compounds after which the solvent is evaporated off. The residue that is left behind is called a "concrete"; however, at this stage, the concrete contains insoluble waxes. The next stage is to turn this concrete into an "absolute" through a similar process as above. This time, the concrete is gently heated with an alcoholic solvent after which the solution is filtered and the alcohol is recovered as before (TESFAYE, 2007).

Enfleurage—another method, although one not in common use today involves the pressing of flowers on glass coated with animal fats. The fat in turn absorbs the blossoms fragrance although it might have taken several pressings of fresh flowers to reach saturation point. This saturated fat is called "pomade." This is then "washed out" using alcoholic solvents that are than evaporated off to leave a fragrant "absolute."

16.4.2.4 CO_2 extraction

Carbon dioxide extraction—is a relatively new process that allows oil to be recovered from plant biomass under much lower temperatures. All else being equal, this method would undoubtedly be the preferred method as employing these lower temperatures means that the extracted oil is less chemically altered and exceptionally true to those of the plant. Unfortunately, however, in the present circumstances the high cost of the equipment and complexity of the process involved makes the cost of these oils, in most cases, prohibitive. Of all the above processes, the least destructive in terms of finished product is the cold-pressing method. However, this is usually confined to citrus fruits, some berries including olives, and other similar edible and nonedible plants.

16.4.3 EXTRACTS

There is a class of oil extracts derived from plants that for the moment we have chosen to keep separate. Some of these are made from the same plant materials as regular edible oils, while others use the flower and other plant biomass to obtain the oils (Burt, 2004). However, the extraction processes are different when considering pomades, concretes, absolutes, resinoids, and tinctures, and they are variously named according to the method of their preparation. It is important to note too that not all plants are capable of producing any of the above, i.e., while some plants can be treated to produce all of those mentioned; some might only produce an essential oil, while others still, might only produce concretes and/or absolutes or resinoids. As with other oils, all of these are essences of plants or seeds; the difference between these and essential oils proper are subtle but of great importance to purists, aromatherapists, and industry alike. Essential oils tend to be seen as the simplest, least destructive ("pressing" aside) of the processes and, for many, are the most natural or more representative of the plant's soul—its essence, while solvent extracted products are not seen as "pure" and will not potentially possess the same therapeutic "powers" of a so-called pure essential oil.

Pomades—are fats containing saturated fragrance substances produced by the enfleurage process that incidentally, is the oldest known procedure for preserving plant fragrance substances. Although originally developed in France during the 19th century, the process, owing to cost prohibitive and labor-intensive practices, as a method of fragrance extraction, has been largely confined to small-scale artisans of traditional practices. Today's pomades are generally less connected to the process of "animal-fat" enfleurage (with the exception of lanolin) but rather to a collection of products that are waxy or greasy based on petroleum jellies, beeswax, and other similar substances. They are used in such things as hair-styling products, polishes, and the like.

Concretes—are the essence of plants—wholly similar in many respects to essential oils. The key difference is in the method of extraction. As mentioned before, the use of solvents like toluene, hexane, or petroleum ether to dissolve out the plants' juices is what makes a concrete a concrete. Once this solvent has evaporated off, the remaining residue (the concrete) is a mixture of both near-solid volatile and nonvolatile substances similar to the waxy compounds of pomades. As with pomades, concretes have a limited role to play in the fragrance and cosmetic industries.

Absolutes—if we were to take the above concretes and dissolve as much of it as we could in an alcohol solution, we would find a soluble mixture of essential oil, some waxes, fixed oils, and fats. If this alcohol is then distilled off, then the remaining liquid substance is called an absolute. These are the most concentrated and by extension the costliest of the plant extracts and as such are used sparingly—mostly in the perfume industry.

Resinoids—resins are clear/yellow to brown, solid or semisolid viscous substances of plant origin. These sticky gumlike substances are naturally exuded from tree bark or woody plants, which flows out to the exterior when they are cut or damaged. By dissolving the plant material in a solvent to extract this gum or resin, this becomes a resinoid. Resinoids are used primarily not only in the production of lacquers, varnishes, inks, adhesives, synthetic plastics and pharmaceuticals but also in the fragrance industry to prolong the fragrant notes of perfumes and certain food additives, etc.

Tinctures—are solutions where the extractive solvent is alcohol although it can also be an acetic acid, ether, or similar. Alcohol is more often used as this is a more versatile solvent able to handle both acid and base substances. This way more can be drawn out of the plant. For those who prefer not to take alcohol, glycerol-based extracts offer a suitable alternative for ingestible preparations and cooking.

Tinctures are not to be confused with tisanes that are simply water (usually hot)-based tealike drinks made from infusing plant material.

Hydrosols—are the pure, distillate waters that remain after an oil has been separated by the distillation process; essentially a by-product of the essential oil steam distillation process. As the essential oil and steam condenses, so the remaining steam distillate (the water) is referred to as the hydrosol or variously as floral waters, hydroflorates, flower or aromatic waters, or simply distillates. While these contain all of the essence of the plant, they are much more subtle and milder. Most hydrosols tend to give off an herby or grassy note characteristic of the fresh plant (Rose, 1999). Used primarily in perfumeries and cosmetics in such things as facial splash, body perfume, deodorant, and even air fresheners, they are also used in the kitchen—rose water is a good example—or they can be taken as a tonic or combined in beverage drinks. The main chemical component in hydrosols is primarily acids. These are hydrophilic that is to say they are water-loving.

In some applications, an isolate or oil fraction is preferred over the whole oil itself. Specifically, fractioned oils are those oils that have constituent compounds removed from the whole oil for perceived benefits. This is common practice among essential oils like star anise and fennel where undesirable (antheole) notes are removed (UNIDO and FAO, 2005). Lemon oil is also fractionated to increase its stability especially within the beverage industry.

16.4.4 USES

The uses of essential oils extracted by the above methods is as diverse as it is varied, the following looks at some of these:

16.4.4.1 Perfumery and cosmetics

Essential oils and their fractions are of great importance in the perfumery and cosmetic industries. Lavender itself historically, ranks as one of the major components although nowadays, *angustifolia* is being used less and less in favor of more economical lavandin oils. Saying that, English lavender is still widely used in the small-scale upmarket (or higher-priced) fragrances, cosmetics, essential oils, skin creams, etc. and is still widely regarded for its clean, fresh aromatic notes. Other varieties too, albeit the less camphoraceous of the species, are also particularly useful as a "lifter." This is because of its general pleasant fragrance but more importantly because of the oils' high volatility that helps to emphasize the top notes of other, less volatile oils.

Spike lavender oil, being more camphoraceous, tends to blend well with both lavender and lavandin oils and as such is often used in soap production. Although having said that, because of

its supposed tainted color (caused by the camphor), it is very common to find spike lavender oil being used in domestic cleaning products too.

16.4.4.2 Aromatherapy

Aromatherapy is big business and one could be forgiven for thinking that essential oils were almost specifically and universally designed with aromatherapy in mind. A thoughtful idea, however in reality, aromatherapy is in fact a collection of therapeutic practices including inhalation therapy, massage, and oral consumption of aromatic waters. Aromatherapists are in fact one of the most rigorous groups in their demand for quality among pure essential oils. Quality and purity are important attributes when choosing appropriate suppliers for many of the reasons already discussed.

Oils are used to treat ailments, to enhance moods, or simply for their aromatic qualities. Whether physiological, psychological, or even psychosomatic, the therapeutic effects are of huge importance, both inside and outside of the industry. In the medical profession, for instance, there is an increasing propensity in the uptake of aromatherapy by nurses as a real complementary therapeutic modality, particularly in palliative care facilities.

Its core clinical benefits tend to concentrate on the central nervous components—both the limbic and the autonomic systems. Indeed, there have been many studies designed to understand the oft reported sedative, anxiolytic, and mood-modulating benefits. Although, as previously discussed, there is still a long way to go before consensus can dictate the reality and degree to which the effects are real or otherwise. That said, aromatherapy is increasingly taking a reverential position among the alternative or more precisely complimentary therapies.

16.4.4.3 Cooking with essential oils

Generally speaking, essential oils are the stock in trade of the aromatherapy and cosmetic industries. Although a little-known fact among kitchen aficionados is that essential oils have actually been widely used by large-scale commercial food industries almost since their inception. When using these oils, however, it is important to be aware that too much heating of foods containing essential oils will destroy the molecules health benefits although not the actual flavor. Pure, steam-distilled essential oils are safe up to approximately 260°F. Citrus oils, however, because of their larger molecule size should not be heated above 100°C/212°F. Whether sweet or savory, essential oils can add depth and vibrant flavors to food and beverages in a way that working with dried and powdered herbs and spices cannot (Burt, 2004; Smith-Palmer et al., 2001).

Many essential oils are suitable for use in cooking or as flavorings. That said, not all essential oils are food safe especially the synthetic ones or those containing residual solvent or petrochemicals. Very few food bodies around the world in fact actually test these products for suitability in the kitchen. So how does one know what they can or cannot use? One can always find a cookbook or two with many essential oil recipes, but it is a bit more complicated than that. It is also important to know that orange essential oil, for example, might be great to use in aromatherapy straight from the distillation or extraction process; however, it might not be food-grade safe to use in the kitchen, because of the very extraction method used. In this instance, a first pressing of orange oil might be more suitable—it all depends on the extraction method and any further processing. That said, we are in luck, the US Food and Drug Administration offers a list of tested food-grade essential oils, oleoresins (solvent-free), and natural extractives (including distillates) that are generally recognized as safe for kitchen use (Burt, 2004). They offer a list under the auspices of

Title 21 - food and drugs chapter I-food and drug administration department of health and human services subchapter b-food for human consumption (continued) Subpart a--general provisions sec.182.20 essential oils, oleoresins (solvent-free), and natural extractives (including distillates).

Indeed, when cooking with essential oils, only 100% pure essential oils from controlled cultivation motivation and extraction should be used. Oils, particularly those that are cold-pressed, should be checked for pesticide residue—in this sense, a guarantee by the manufacturing company should be available on the label or upon request. Furthermore, when talking of food-grade essential oil labeling, one should note that it contains the oil or plant's name, including its Latin descriptor; the country of origin and the method of extraction used; the fact that it is indeed food-grade; and the date of expiry; the label should also include information on whether the oil has been thinned, and if—with what and to what ratio; furthermore, if solvents have been used they should be mentioned (Baser and Buchbauer, 2015).

16.4.4.3.1 Why use essential oils in the kitchen

So why would cooks choose an essential oil over real herbs and spices and other flavorings? For one thing, the average shelf life for dried herbs, for full potency is approximately 6 months. The shelf life of food-grade essential oils, on the other hand, in general, runs to several years. Although citrus oils by contrast have a shelf life of only about 1 year. Also, while perhaps, a little more expensive upfront, essential oils can be more economical in the long run due in large part to their potency. Take oregano for example—one drop of oregano can replace three tablespoons of the dried herb, then consider that the average 15 mL bottle contains up to 250 drops, and then, the math is straightforward. Of course, many people would still prefer to use the real thing, but in many instances, the real herb, extract, or flavoring might be impossible to find in certain areas.

In fact, there's almost no limit to the endless culinary creations one can create with essential oils. And indeed, more and more cooks nowadays are finding creative and ingenious ways of using them in their recipes. Herbaceous oils are great for meats, fish, soups, sauces, casseroles, and baked goods. Citrus oils, on the other hand, are lighter and are good in marinades, in salad dressings, and in beverages and desserts. Flower oils are best used in baked goods, desserts and sweets, although it must be said that unlike other kitchen oils, essential oils are so concentrated and potent that one only needs to add a tiny amount to a particular recipe to be effective. Using essential oils in cooking:

- For most herbaceous oils, one drop of essential oil is enough to replace between 1 and 3 teaspoons of dried herb or spice.
- For milder herb oils, use only 1–2 drops at the end of the cooking process, or simply add a drop of oil before serving for a great addition to the cook's repertoire.
- For the stronger and more pronounced flavored oils such as thyme, oregano (origanum), rosemary, and marjoram, it is sufficient to simply dip a toothpick into the bottle and stir into the recipe just before serving. These stronger flavored oils can also be simmered in soups and stews to produce a milder flavor.
- Many alcohol-based extract flavorings in the kitchen—especially for baking can be replaced by essential oils. The dosage of which is determined by the fact that the essential oils are several times stronger/more potent, although some, like peppermint and clove, are even stronger and should be used with caution.

In fact, in reality, there is no dish whose flavor cannot be enhanced with essential oils.

16.5 BIOACTIVITY AND BIOAVAILABILITY OF OILS

Bioavailability is a term used to describe how readily available a substance is to the body for use in bodily processes. For instance, some foods, say whole kernel sweetcorn, for example, while it might be nutritious in and of itself, yet it is not easily broken down (digested) by the body. As such, it often ends up passing through the gastrointestinal tract without useful nutrients being properly absorbed into the circulatory system. In short, while the food itself might be nutritious, it is not easily taken up by the body; in this respect, it is considered to have low bioavailability.

When talking of ingesting essential oils, metabolism, and poor absorption create barriers to bioavailability. In such instances, much of the potential benefits are lost to the body. One medical example is the intravenous injection of drugs. In this case, there are no metabolic processes or barriers involved, and the drugs are immediately in the circulatory system—this method is considered 100% bioavailable. Of note here is not whether or not the substances can be utilized in the most efficient way or not by the body; irrespective of this, intravenously injected drugs are still considered 100% bioavailable.

The same principals can be applied to essential oil constituents. If they are intrinsically beneficial yet are not easily absorbed or otherwise digested (i.e., there are too many absorption and metabolic barriers), then they are not particularly bioavailable. Of course, no one intravenously injects essential oils, so how does the body absorb and utilize their potential benefits? The answer is in three ways: through the skin via absorption, through inhalation, and lastly via oral ingestion.

However, before we examine these, it is important to understand that there are many factors that can affect the bioavailability of essential oils including an individual's physiological characteristics, life stage, their diet, and their metabolic characteristics. To this end, understanding the specific uptake, retention, and utilization of oils reported beneficial constituent compounds would greatly help in this understanding. Yet sadly, in this regard, there is a less than stellar body of research undertaken in this area. Indeed, those studies that do exist are themselves predominantly based on animal models. That said, what we can take from this is that most essential oils are rapidly absorbed after dermal, oral, or pulmonary administration.

A note concerning the bioavailability of essential oils—one of the difficulties in the area of bioavailability is the notion that the sum of the oil is quite often seen as being greater than its constituent parts. Indeed, many of the supposed benefits of essential oils have been attributed to the whole oil, in its entirety, and understanding which constituent component might be responsible for say an oil's antimicrobial properties or its relaxation or perhaps its calming qualities is not always clear (Bakkali et al., 2008). Of course, while there is evidence to support certain chemical compound' properties acting as say antibactericides, for instance, such evidence is often (although not always) the result of lab-based testing where the compounds have been separated into their pure and concentrated fractions. While testing in this way might tell us much about how the chemicals act on isolated organisms, this does not always give us insight into the way the same chemical might act on humans, especially in terms of bioavailability (Burt, 2004) or, for that matter, how such chemicals (as one component of an essential oil) might interact with others—their synergistic properties. As such and as has been reported in numerous publications, there remains a lot of uncertainty about how essential oils biologically act, react, or interact with the human subject. This is likely to remain so for the foreseeable future too as the

potential synergistic combinations of the numerous bioactive constituents within essential oils in general (without turning to statistical probabilities) surely must run into the thousands if not tens of thousands (Bakkali et al., 2008).

16.5.1 ORAL INGESTION

Of course, care needs to be taken when orally ingesting any essential oil products due to the potential toxicity of some oils. That said, there are many natural dietary sources of oils and one can quite easily ingest numerous essential oil compounds on a regular basis without even knowing it. Some might be obvious such as citrus peelings and lemongrass, while others perhaps possibly wouldn't even be considered like caraway, cherry, or spearmint. The point worth noting here is that exposure to essential oils through the diet is both common and widespread.

So, having orally ingested essential oil and after metabolism and absorption, those compounds that remain can be of use to the body. In this case, due to the lipophilic[8] character of volatile compounds and their physically small size, many of these compounds are in fact readily able to cross the blood-brain barrier and interact with receptors in the central nervous system (Bakkali et al., 2008). This in turn might affect any relevant biological functions such as relaxation, sleep, or digestion.

16.5.2 ABSORPTION THROUGH THE SKIN (TRANSDERMAL)

Based on a combination of lipophilic qualities along with a certain ability to partially reduce the polarity of the stratum corneum (the outermost skin layer), essential oils, to varying degrees, seem to have the ability to overcome the natural barrier function of the skin. Indeed, one study showed that linalool from lavender oil could be detected in human blood samples 5 min after skin application. Another showed that carvone had exhibited peak plasma concentration after about 30 min. In this way, chemical constituents of essential oils can readily be absorbed into the cutaneous microcirculation that ultimately finds its way into the body's systemic circulation and by extension the various organs.

16.5.3 INHALATION

Another way by which essential oils enter the body is through inhalation. As a result of their volatility and their relatively small molecular mass, essential oils are inhaled through the respiratory tract passing into the lungs. These are then distributed into the bloodstream and act in the same ways described above.

However, they get there, once in the body essential oils are available to take effect in three ways. The first is biochemically (or pharmacologically) affecting anything from neurotransmitters to hormones and enzymes. The second is through physiological interactions such as muscle relaxants, etc. Last and by no means least are the psychological effects that might be triggered say by the olfactory area of the brain (the limbic system), which in turn might positively affect a person's mood, and consequently, their potential outlook, etc.

Also for the sake of completeness, there is one last action of essential oils that should not be overlooked, and this is the psychosomatic effects of essential oils—the placebo effect. Although in

[8]Lipophilic refers to the ability of chemical compounds to dissolve in fats, oils, lipids, and nonpolar solvents such as hexane or toluene.

truth, using the term placebo might be doing essential oils a disservice, for whatever the outcome, whether an uplifted mood is achieved or a physiological improvement to the body has taken place, the psychosomatic results whether real or imagined are nevertheless, all too genuine for the person concerned to be fully dismissed.

16.6 ADULTERATION OF OILS

There are two ways to look at adulteration of essential oils. The first is the very legitimate need to standardize certain oils for the sake of quality and consistency issues. Take lavandin for example, standardizing the oil for certain cosmetic or perfumery "recipes," as when producing "lavender 40–42 essential oil," for instance, might involve combining this with certain chemical constituents of pure lavender oil or a completely separate plant species such as linalyl acetate from *Mentha citrate* to produce a consistent product. Although for some this is not a bad product, many aromatherapists find this unacceptable. In other cases, manufacturers might require oil with a longer shelf life, and as some terpenes oxidize rapidly, they can have the effect of changing the aroma profile over a short period. For this reason, the practice of "fractioning" or redistilling is undertaken that can alter or isolate certain constituent properties. Other forms of adulteration might include diluting an oil—variously referred to as "extending," "cutting," or "stretching"(Bakkali et al., 2008). This practice involves diluting the original with perhaps a pure vegetable oil, isolates,[9] or other oils (usually cheaper), as well as alcohols or perhaps other solvents.

Lastly, another method that, not so much attempts to stretch an existing oil so to speak but rather attempts to recreate a quality oil. This involves synthesizing oils by attempting to reconstitute or "copy" the main components of natural oils with synthetic (often petroleum-based) products that aim to imitate the original. The industry in this regard might specify, to the manufacturers, the level of accuracy to the real thing they require (usually anywhere between 51% and 96% accuracy). That said though, even with the higher accuracy target there will still be a large number of trace elements missing from this reconstituted oil. Once again for the sake of standardization though, perhaps, in the cleaning product industry, this is not necessarily a bad thing.

Secondly and more disturbingly, because of the commercial importance of essential oils, the potential for adulteration to optimize profits by using cheaper artificial (synthetic) material is, unfortunately, a common occurrence. Once again using lavender oils by way of example, one finds that the most frequent, systematic adulteration involves adding synthetic linalool and linalyl acetate. Consequently, this might well introduce impurities like dehydrolinalool and dihydrolinalool into the oil. Therefore, authenticating the origin and naturalness of these oils is an important area of note.

So, while there are many legitimate and acceptable reasons for the adulteration of oils, if the consumer is informed and understands the choices he or she is making, there is little to worry about here. However, what are unforgivable, are attempts from individuals or manufacturers to deceive or mislead consumers for the sake of profiteering. For a particularly detailed and in alarming look at adulterated

[9]Isolate is the term used to describe specific constituents from essential oils or other natural materials—for instance, eucalyptol from eucalyptus.

essential oils in general and lavender in particular, there is an interesting report published by Tony Burfield that, although is 12 years old, highlights some of the practices and cautiousness one needs to take when dealing with essential oils.

16.7 AUTHENTICATING ESSENTIAL OILS

For big commercial enterprises, ensuring that a crop of oil firstly is authentic and has not been adulterated and that it meets quality standards is an important consideration. Setting the chemical standards for essential oils are several international organizations, these are the International Organisation for Standardization (ISO), the Association Française de Normalisation (AFNOR), and the Essential Oil Association of the United States (EOA).

Understanding the chemical signature of essential oils can be achieved using analytic techniques that examine the specific chemical profile of any oil. There are a number of methods available including standard analytic techniques of gas chromatography with mass spectrometry (GC/MS) or infrared spectroscopy (GC/IRFT). However, these methods have their limitations and without getting into too much detail another, more informative methodology, involves detecting specific optically active enantiomeric chiral molecules for species and potential geographic origin. Collectively, these methods too not only help to determine the authenticity or not of such oils but also can establish whether the oils themselves meet international standards expected for or not.

For those of us who cannot afford to go to such lengths, perhaps the best method of determining the quality and purity of an oil is the reputation of the vendor.

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CHAPTER

CHOCOLATE/CACAO 17

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From the astringent, bitter, and generally tasteless seeds of the tropical *Theobroma cacao* tree comes one of our most prized foods in the cook's arsenal—chocolate. The tree can top out at 15 or so meters but is usually only allowed to grow to approximately 7–8 m in height for ease of harvesting. The tree blooms and bears fruit twice a year and produces fruits in fibrous pods that can vary significantly (15–25 cm long by 7.5–10 cm in diameter) and that contain a sweet-tart pulp within which are buried about 20–75 seeds (beans) (depending on who one reads). Each bean is about 1–3 cm long (Wolfe and Shazzie, 2005; Coe and Coe, 2007; McGee, 2004). The beans are treated to both fermentation and roasting, after which this otherwise bland seed turns into a complex, rich, and versatile ingredient that graces both home cooking and Michelin restaurants with equal style. Yet chocolates' contemporary incarnation—the dense, smooth, sweet, solid, and melt-in-the-mouth treat—has existed in its modern form for only a relatively short period of its full history. Another point to be made here is the confusion between the usage of "cacao" and "cocoa," which are often used interchangeably. There is a difference and a lot of misunderstanding surrounding the subject.

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Cacao is in fact the raw, largely untreated beans from the cacao tree that are usually either unroasted and cold-pressed into powder or as nibs.[1] This process removes the fat (cacao butter) and allows enzymes to live on. Cocoa or cocoa powder, on the other hand, looks the same but is, instead, raw cacao that's been roasted at high temperatures (Wolfe and Shazzie, 2005). To understand more about chocolate, a little history is in order.

17.1 A LITTLE CHOCOLATE HISTORY

Chocolate/cacao's humble beginnings predate recorded history, but evidence of its use and cultivation has been found all around the world in warm climates (25–27°C/77–80°F) with high humidity, from equatorial Central and South America to Africa and Indonesia and as high as about 600 m above sea level (McGee, 2004; Beckett, 2008; Grivetti and Shapiro, 2011). From their wild origins, alternate scenarios about the domestication of chocolate have been put forward (McGee, 2004; Grivetti and Shapiro, 2011; Coe and Coe, 2007). In one situation, chocolate was likely first domesticated in the western regions of the Amazon basin around 3000 or so years ago (Henderson et al., 2007). Yet, another suggests that domestication of the cacao plant first took place in areas encompassing the modern states of southern Mexico, northern Guatemala, and Belize. Either way, cacao became a very important commodity very quickly, in fact it became so important to local economies that during this early period, the beans themselves were distinguished into two primary types: the best-quality beans, termed *quauhcacahuatl* was used as a form of currency, while lower-quality beans *tlalcacahuatl* were used to prepare frothy beverages sometimes flavored with aromatic flowers, vanilla, chili, honey, etc. (Grivetti and Shapiro, 2011; McGee, 2004). In fact, according to linguistic specialists, it has been said that these and other chocolate-related terms quite possibly originated with the early Olmec civilization and were then passed to the Mayans and in turn to the Mexican/Aztecs.

It was also used in the same fashion (as a currency and as a beverage) among the indigenous people at the time of Spain's 16th century conquest of Central America (Coe and Coe, 2007; Grivetti and Shapiro, 2011). How the bean and beverage made its way back to Europe and North America, again, is the subject of much debate. Yet, it can be said that within a century of the arrival of the Spanish in Central America, chocolate's culinary and medicinal qualities had spread from Mexico to Spain, England, France, and other regions in Western Europe and into North America (Grivetti and Shapiro, 2011). During this time, both tea and coffee were popular beverages of the time, and chocolate quickly found itself a niche market that only grew in popularity to eventually rival that of both tea and coffee.

As with the indigenous peoples of cacao-growing regions, so some Europeans also began to add their own flavorings to the cacao beverage including sugar, vanilla, cloves, cinnamon, anise, orange-flower water, almonds hazelnuts, and musk.[2] However, the beverage was also popularly drunk with little else added, other than sugar and vanilla. Milk at some point was added to the mix, giving us that popular beverage that we know and love today—hot chocolate (Vaclavik and Christian, 2014).

[1]Raw cacao nibs are simply cacao beans that have been ground into smaller pieces.
[2]Musk is a strong-smelling substance, used predominantly in perfumes, and is either artificially made or obtained from a gland of an Asian (musk) deer.

For the first couple of centuries, Europe utilized chocolate almost exclusively as a beverage, and using cacao in confectionary, for instance, was rarely heard of. That was until a couple of innovations paved the way introducing something similar to the modern incarnation of the chocolate that we know today. The first came about as the paste from ground chocolate did not have a good mouthfeel with its course, gritty, and crumbly texture. The answer came in 1828 from a Dutch businessman called Conrad van Houten who, trying to make a less "oily" chocolate drink, used a screw press that removed most of the "oil" (cocoa butter) and in the process ended up with a powder for making hot chocolate that carries nearly all the flavor and much less of the oil (Coultate, 2009).

The pure cocoa butter extracted by van Houten's press also by chance turned out to be key in the development of modern chocolate sweets. Sugar was later added (1847 by Fry and Sons) to a paste of ordinary ground cacao beans, thus providing a rich, melting solid "eatable" chocolate (McGee, 2004). Later still in 1876, two further developments helped expand chocolate's appeal. Firstly, a Swiss confectioner, Daniel Peter, used the newly developed dried milk powder to make the first solid milk chocolate.[3] Secondly, in 1878, another Swiss manufacturer, Rodolphe Lindt, invented the conche, a machine that slowly ground cacao beans with milk powder and sugar for hours, sometimes even days. This helped develop a much finer consistency than had been possible before and one that is reminiscent of today's chocolate bars.

17.2 CACAO BEAN VARIETIES

Of the 101–155 or so various types and origins (genotypes[4]) of *Theobroma cacao* L., only three main groups and their cultivars,[5] largely based on the beans morphological traits and characteristics, are cultivated for their cacao beans. These are criollo, forastero, and trinitario (N'Goran et al., 1994; Lerceteau et al., 1997).

Criollo—the criollo tree and its cultivars are native to Central and South America as well as the Caribbean islands and Sri Lanka. They typically produce red or yellow fruit pods, although some also are green or white (their beans have a pinkish-white hue), while the beans taste has been described as delicate yet complex with spicy and fruity notes (Argout et al., 2011; Henderson et al., 2007). In fact, even though they produce a relatively mild and delicate bean, criollo is considered, among many, as the finest of the cacao beans there are and is, in fact, highly prized as an ingredient in the very finest of chocolates (Argout et al., 2011). However, being disease prone and vulnerable to a variety of environmental threats, these trees are the lowest yielding of the three varieties, providing less than 5% of the world's total harvest (N'Goran et al., 1994; Lerceteau et al., 1997).

Forastero—the most commonly grown cacao comes from the forastero tree. Today, forastero is mainly cultivated in Africa, Ecuador, and Brazil and is a high-yielding tree accounting for approximately 80% of the world's total cacao supply (N'Goran et al., 1994; Lerceteau et al., 1997). Unlike the criollo tree though, the forastero is among the hardier of the trees, being less susceptible to diseases. It also boasts a much better yield than the other varieties. Forastero cocoa pods are relatively smooth

[3]Milk powder dilutes the strong bitter and slightly astringent chocolate flavor and helps make it taste milder.
[4]Genotype—in a very broad sense, the term *genotype* refers to the genetic makeup of an organism. That is to say, it describes an organism's complete set of genes.
[5]Cultivars are plant varieties that have been propagated not only from seeds but also from bulbs and stem cuttings.

and more bulbous compared with criollo pods. In addition, the pods may resemble the red or yellow coloring of the criollos, or they might just as easily become orange or purple upon maturity. They have purple-colored beans and are mostly used to give chocolate its "full-bodied" (more chocolaty) flavor (Henderson et al., 2007). However, flavor-wise while some see the Forastero as being rich, it is also a little bitter and unsupported by secondary flavors. For this reason, forastero is often used as a blending or "bulking" bean to be mixed with other, more superior cacaos. Indeed, because of forastero's flavor profile, chocolatiers might typically use forastero as a base for their chocolate blends creating a rich, chocolate flavor body before adding a variety of flavor beans to ensure the final flavor profile is more complex and interesting. There are many forastero subspecies, but among the most notable are *amelonado*, *cundeamor*, *calabacillo*, and *nacional* (Henderson et al., 2007; Beckett, 2008).

Trinitario, the hybrid—due to cacao's general susceptibility to disease, more vigorous hybrids have been created. The best known among this is the trinitario. Trinitario is a wonderfully complex hybrid combining the benefits of hardiness from the forastero together with the sophisticated taste of criollo. That said, however, the quality of the trinitario bean can be very variable, that is, between average and superior. This, as has been speculated, is the result of both parents highly contrasting characters (Henderson et al., 2007). It is also worthy of note that, just like forastero, trinitario's popularity has also ensured its growth throughout the world. Although that said, the volumes of cultivated forastero trees dwarf those of trinitario—even if trinitario has a finer flavor. Not surprisingly, today, trinitario cacao is very sought after by chocolatiers from around the world for its fine flavor either to flavor, bulk forastero or to create a premium chocolate by itself.

17.3 MAKING CHOCOLATE

As it is, the cacao bean is bitter and astringent, so it is up to the farmers and chocolate manufacturers to develop its potential. They do this in several distinct processes:

- *Fermenting and drying*—Once harvested, farmers ferment the crop of beans with their fruit pulp in order to help develop precursors to the chocolate flavor. These are then dried, usually in the sun.
- *Roasting*—Once the beans are ready, the manufacturers roast them further transforming flavor precursors into flavors.
- *Grinding*—The roasted beans are then grounded, sugar is added, and the mixture is physically worked to refine the flavor and to give it a silken texture.
- *Conching and refinement*—After grinding, further refining to create even smaller smoother pieces of chocolate is accomplished in the conching process.
- *Cooling and tempering*—The final chocolate is cooled and tempered ensuring an even "snap" and glossy texture to the finished product.

The processes described above can best be seen in Fig. 17.1.

17.3.1 FERMENTATION AND DRYING

Once the cacao pods are harvested, they are broken open, and both the beans and the pulp are allowed to ferment together in the warm climate air. Microbes then begin growing on the nutrient-rich sugary pulp that can last for between 2 and 8 days. During the process, the beans generally go through three phases. In the first phase, yeasts convert the sugars into alcohol and begin metabolizing some of the pulps acids.

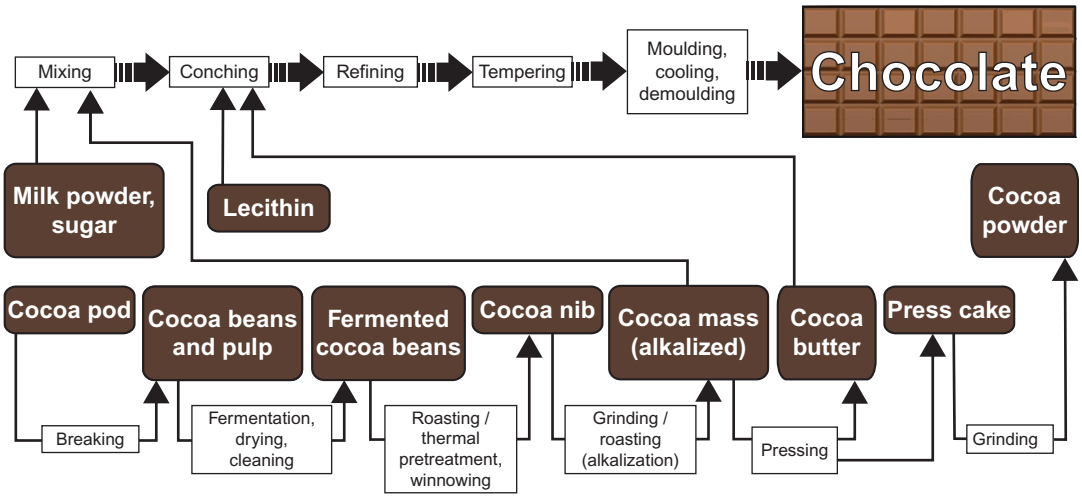


FIG. 17.1

Chocolate manufacturing process.

As the mass of pulp is depleted of oxygen, so the yeasts begin to die off and are succeeded by lactic acid bacteria.[6] Then, as the pile of beans and pulp are turned and aerated, so the lactic acid bacteria are themselves succeeded by acetic acid bacteria.[7] In time, acetic acid bacteria consume the yeasts' alcohol converting it into acetic acid (Vaclavik and Christian, 2014). All these processes are in fact just fermenting the pulp and not the bean; however, in the last stage, the acetic acid penetrates into the bean and breaks open some of the cells allowing three things to happen. The first are the flavors from the fermenting pulp itself, which seep into the perforated beans, adding certain sweet, sour, fruit, and flowery notes. Secondly, the beans own enzymes start to break down proteins and sucrose into their building blocks (amino acids and simple sugars). This helps produce more aromatic molecules during the roasting process to come. Lastly, astringent phenolic compounds mix with proteins, oxygen, and each other forming substances much less astringent. Therefore, properly fermented beans convert astringent and previously bland beans into containers loaded with sumptuous flavors and flavor precursors.

Once fermentation has taken place the beans are then dried usually in the sun until moisture levels reduce to about 5%–7%. This can take several days in which time growers have to be careful so as not to allow unwanted bacteria and mold to grow.

Fermentation and drying is the first and one of the most important steps in the development of chocolate as we know it. That said, the process is also the least controlled and predictable. That is because the timing and results are dependent on the farmer's skill when it comes to fermentation and whether or not the crop is underfermented, overfermented, or even in some cases just fermented to the point of being moldy. Not surprisingly then, there is a great gap in the quality of the raw beans, so the first and hardest challenge for the manufacturer is to find good-quality, fully fermented beans for the next process of roasting.

[6]Many of the lactic acids are the same species found in fermented dairy products and vegetables.
[7]Acetic acid bacteria are the makers of vinegar.

17.3.2 ROASTING

Fermentation takes place to improve the cacao beans flavor making it less astringent and much more flavorful than their unfermented counterparts. The challenge now is, although they have acquired new flavor compounds, they are not fully developed and still retain some of the overpowering vinegary acetic acid. As a result, the beans are roasted to harmonize flavors and allow reactive amino acids and sugars to participate in the Maillard browning (Grivetti and Shapiro, 2011). This takes between 30–60 min at 120–160°C/248–320°F depending on whether the beans are to be roasted whole, as nibs, in their thin shells, etc. This gentle roasting not only creates and balances flavors but also helps preserve some of the beans intrinsic flavors developed during fermentation (McGee, 2004).

17.3.3 GRINDING AND REFINING

After roasting, the beans are separated from the shells by a "winnower."[8] The resulting pieces of beans are called nibs. At this stage, the nibs pass through several pressings (steel rollers), thus transforming the nibs from solid chunks of bean into a thick, dark fluid called cocoa liquor. This stage serves two purposes: the first is to separate the beans from the chaff while simultaneously freeing up the cocoa butter; the second is to grind the beans into particles whose sizes are too small for the tongue to detect as gritty or grainy (Wolfe and Shazzie, 2005; McGee, 2004). This penultimate grinding reduces particle sizes to around 0.02–0.03 mm, while the Swiss and the Germans tend to grind the nibs even smaller. Nibs are around 54%–55% cocoa butter, so essentially, this becomes the continuous phase, while the solid fragments (protein, fiber, and starch) become suspended in the fat (see also Chapter 2). Grinding alone nowadays actually pulverizes the various solids to the proper dimensions before any conching takes place, so if required, manufacturers can utilize the cocoa solid and cocoa powder mix as is, in all manner of manufactured chocolate tastes and flavors. If it is to be left as cocoa liquor (cocoa butter and solids) for use as chocolate bars, then the resulting mixture is further processed by conching.

17.3.4 CONCHING

The problem with pure cocoa liquor at this stage is that it has a concentrated chocolate taste that is relatively rough, bitter, astringent, and acidic. Although this is good for cooking if we are manufacturing chocolate candy/bars, then we need to add a few more ingredients before conching. These include sugar for dark chocolate, sugar, and dry milk solids for milk chocolate and in some cases vanilla. On top of this, the addition of pure cocoa butter is sometimes required—depending on the manufacturer requirements. After these additions, the mixture is then conched. The process of conching simultaneously rubs and smears the mixture of cocoa liquor, sugar, and milk solids against a solid surface—the combination of which produce friction and the raising of heat (Ziegleder, 2009). As this happens, the temperature of the mix increases to about 45–80°C/113–176°F (for milk chocolate 43–57°C/109–135°F). Depending on the machine and manufacturers preferences, conching may last anytime between 8 and

[8]Winnowing is the practice of blowing a current of air through (usually grain) in order to remove the chaff or outer papery coverings.

36 h (McGee, 2004). So, if conching is an optional extra, what purpose does it serve? There are two main reasons, the first is to further break up the tiny pieces of cocoa beans and coat them evenly with cocoa butter, in order that the finished chocolate melts, smoothly in the mouth. Second, conching greatly improves the flavor of the chocolate by ensuring the flavor of the mix is mellowed. This happens in the following way: as the mixture is conched, so it is aerated and moderately heated. This allows as much as 80% of the undesirable volatile aromatic compounds and any excess moisture to evaporate away. As a result, many of the undesirable volatiles, including various acids and aldehydes, steadily decline during conching. Simultaneously, certain desirable volatiles, those with roasted, caramel, and malty aromas like the pyrazines, furaneol, and maltol, are improved by the heating and mixing. Furthermore, at this stage, toward the end of conching, both a little cocoa butter and the emulsifier lecithin are added to the mix. The cocoa butter provides extra lubrication for the added sugar particles in order to make the mixture creamy and fluid rather than pasty as it melts in the mouth. Lecithin helps coat the sugar particles, in turn, reducing the amount of additional cocoa butter required.

17.3.5 COOLING AND SOLIDIFYING

After conching, the dark chocolate is basically a warm fluid mass of cocoa butter containing particles of the cocoa beans and sugar in suspension, while milk chocolate contains cocoa fat, lactose, milk proteins, and slightly less bean solids. At this stage, the mixture must now be cooled to room temperature, although, as it turns out, the transition from fluid to solid is not so straightforward. The chocolate must be tempered. Without tempering, the chocolate doesn't have the "snap" or the familiar gloss required of the finished product. This involves stabilizing cocoa butter crystals by carefully cooling to a certain degree and then rewarming it to become liquid again and then cooling once more at which time it finally cools to room temperature and solidifies (see Section 6.6).

17.4 CHOCOLATE FLAVOR

Over time, chemists have identified more than 600 different kinds of volatile molecules in chocolate. This accounts for the fact that chocolate comprises one of the richest, most complex flavors of any of the foods discussed thus far. According to some (Ziegleder, 2009; McGee, 2004), this has a lot to do with the following building blocks of flavor:

- From the bean—bitter and astringent notes from theobromine and the phenolic compounds
- From the fermented pulp—fruit, wine, sherry, and vinegar from acids, acetic acid, esters, alcohols, and acetaldehydes
- From the beans, enzymatic process—almond, dairy, and flowery notes from benzaldehyde, diacetyl, methyl ketones, and linalool
- From roasting and browning reactions—comes the roasted, nutty, earthy, sweet, and spicy notes resulting from pyrazines and thiazoles, phenyls, phenyl alkanes, and dienals
- From added sugar and vanilla—sweetness and the warm appeal of the spice
- From added milk solids—a light touch of caramel and butterscotch and cooked-milk notes

Some confectioners even add a touch of salt to their chocolates, especially milk chocolates as this is the one basic taste missing from sweetened chocolate.

17.4.1 KINDS OF CHOCOLATE

Manufacturers produce a wide range of chocolates; some are designed for eating as is, some are meant for cooking, and others are still for confectionery. Most inexpensively produced chocolates are made with the minimum amount of comparatively expensive cocoa solids and cocoa butter and the maximum amounts of cheaper sugar, milk solids, and vanilla. In such cases, the flavor of the chocolate is pretty mild and unremarkable. By contrast, the higher the proportion of cocoa solids, the more intense the chocolate flavor.

Dark chocolate—contains cocoa solids and cocoa butter but no milk solids; it also contains enough sugar that is often used to distinguish the type of chocolate—these range from bitter (less sugar) to bittersweet to sweet.

Milk chocolate—is without doubt the most popular form of chocolate and the mildest in flavor. As mentioned earlier, milk chocolate contains milk solids and enough sugar that, combined, usually outweigh the combination of cocoa solids and cocoa butter. Because of the small ratios of coco butter to sugar and milk solids, milk chocolate tends to be softer and less "crisp" than the darker chocolates.

White chocolate—is almost a misnomer as it contains no cocoa particles whatsoever. Consequently, white chocolate contains little or no chocolate flavor. It is a mixture of purified, cocoa butter together with milk solids and sugar.

Couverture chocolate (French—"to cover") is any chocolate, milk, or dark that has been processed to flow easily upon melting. This aids in the cook's efforts in tempering chocolate or using it in cooking and as a covering. This also means adding more cocoa butter to the chocolate mix (as much as 31%–38% or more) allows the sugar and cocoa particles to move around more freely.

So-called fine "expensive" chocolates—(whether dark or milk) are made from premium beans prized for their excellent characteristic complex flavors. They are also often treated in small batches so as to bring out their full potential. In such cases, more cocoa solids and cocoa butter are added during processing to ensure a premium velvety texture and superior flavor. As people become more aware of the speciality of chocolate, so some manufacturers are now labeling their premium chocolates with the content of cocoa beans, that is, 70% chocolate means the chocolate contains 70% cocoa butter and cocoa solids (collectively known as cocoa solids) by weight. In effect, the higher the percentage of cocoa solids, the less the sugar and milk solids, the more intense the chocolate flavor, especially when it comes to bitterness and astringency (McGee, 2004).

17.5 COCOA POWDER

Cocoa powder is produced from the slabs of roasted cocoa bean particles left behind when cocoa butter is extracted. As the pressing does not remove all the cocoa butter, so the particles remain coated with a thin layer of cocoa butter, all in all fat content of cocoa powder varies from 8% to 26%. These solid particles (the cocoa powder) are the basis of chocolate's flavor (and not as one might imagine—the cocoa butter). As a result, cocoa powder is the most concentrated version of chocolate there is. It is also very versatile in both cooking and chocolate making, it also has a pH of around 5 (McGee, 2004; Wolfe and Shazzie, 2005). Sometimes (especially in Europe and the United States), cocoa beans

are treated, either before or after roasting, with an alkaline substance like potassium carbonate after which they are ground into cocoa powder. This treatment is sometimes called "dutching" after its inventor—Conrad van Houten—the Dutch chocolatier. The process effectively raises the cocoa's pH to between 7 and 8. This has the effect of reducing the levels of astringent, bitter phenolics, and the roasted, caramel-like molecules (pyrazines, thiazoles, pyrones, and furaneol). The effect is a cocoa powder with a less bitter and astringent tone and one that is milder in flavor and darker in color than traditional cocoa powder. "Dutched" cocoa can come in shades ranging from light brown to near black each with their own mild flavor profiles.

17.6 STORAGE AND FAT BLOOM

Chocolate bloom is a whitish coating that appears on the surface of chocolate for two main reasons—fat and sugar bloom—and some say, through improper tempering. That said, while there is some disagreement as to the exact processes involved (Aguilera et al., 2004; Altimiras et al., 2007; Kinta and Hartel, 2010; Lonchampt and Hartel, 2006), there is general agreement on the main protagonists. Fat "bloom" occurs when the chocolate is stored in constantly fluctuating temperatures that in turn encourage the melting and resolidification of the cocoa butter fats. As the fat melts, so it migrates through capillary action to the surface of the chocolate where it recrystallizes into what looks like a white patchy coating. This can usually be prevented by proper storage at an optimum temperature of 15–18°C/59–64°F. It is important this temperature is kept steady, so chocolate's crystals do not melt and resolidify or recrystallize. Stored properly chocolate has quite a long shelf life too (many months at room temperature); this is because of its chemically stable saturated fats and its plentiful antioxidant molecules. While contrastingly white chocolate (with less antioxidants) has a shelf life of only a few weeks; after that, its fats are degraded, and it develops a stale, rancid flavor (Coultate, 2009). The second type of chocolate bloom occurs in humid conditions. As chocolate soaks up moisture from the atmosphere, so condensation on the surface of the chocolate causes the sugar crystals to absorb this moisture which upon evaporation recrystallizes leaving behind whitish "dust-looking" patches.

17.7 WORKING WITH CHOCOLATE

Both chocolate and cocoa are adaptable ingredients. They're incorporated into many recipes, not only sweets but also savory sauces and some meat stews where it blends well with the depth and complexity of chocolate, especially the darker, bitter varieties. In cakes and pastries, chocolate and cocoa powder provide a rich silken product. It is also structure-enhancing as the dry particles contain both starch and protein that absorbs moisture contributing to depth and solidity to baked goods, etc. (McGee, 2004). Chocolate is also a fully cooked, entirely developed ingredient in its own right, all one needs to do sometimes is simply to melt it, mix in a few ingredients and voila- chocolate mousse. It is also versatile in that it can be melted and solidified repeatedly. Although saying that, milk and white chocolates contain more milk solids, so they are best melted gently over a lower heat.

Chocolate can be melted in several different ways; if the cook is experienced, it can be achieved by using a tempering machine. The best temperature to do this is between 45°C and 50°C or 113°F and 122°F. For precision and comfort, chocolate can also be melted over a pan of hot but not boiling water. Lastly, the cook can also use the microwave, but one must be careful of hot spots, so stopping to stir

frequently is important. Also, because chocolate is a poor conductor of heat, so its best if the chocolate is cut into smaller pieces to aid in the melting process (McGee, 2004).

17.7.1 CHOCOLATE SEIZING

There is one odd facet to melted chocolate and that the enormous number of sugar and cocoa particles whose surfaces entice or attract moisture. The problem is, while they are immersed in a vat of cocoa butter, if even the smallest amount of water is mixed into molten chocolate, the chocolate will "seize" up. This seizing has the effect of turning the velvety smooth liquid into a dry stiff paste. The small amount of water acts as a kind of glue, attracting millions of cocoa and sugar particles with just enough moisture to coat the molecules and stick them together separating them out from the liquid cocoa butter. Not surprising then, it's important either to keep chocolate completely dry or to add enough liquid to dissolve the sugar and milk solids into a syrup. But it is not all bad, as seized chocolate can be salvaged by simply adding more warm liquid until the stiff unyielding paste turns into a thick fluid; of course, that probably ruins the recipe the cook was working on, but at least, the chocolate is not wasted (Belitz et al., 2009; McGee, 2004; Brown, 2014).

17.7.2 GANACHE

One of the modest and most familiar of chocolate preparations to the pastry cook is the humble ganache. A mixture of cream and chocolate that can be flavored with almost anything, it can also be whipped as a topping or filling or further enriched with butter. Ganaches are one of the foundations of chocolate work in the modern kitchen. A soft ganache is made with equal weights of cream and chocolate, while a firmer ganache can be made with two parts chocolate to every one part cream. Initially, the cream is scalded, and the chopped chocolate is melted into it forming a complex combination of an emulsion and a suspension (see Section 7.2). The continuous phase of this mixture is a syrup made from the cream's water and the chocolate's sugar. Suspended in this syrup are the milk fat and cocoa butter droplets as well as the solid cocoa particles from the chocolate. While in a weak ganache (more cream and less chocolate), there is an abundance of the syrup phase to hold the fat and particles, yet in a firmer (less cream and more chocolate) mixture, there is less syrup. This latter situation can cause problems in that the more, dry cocoa particles there are, the more they can soak up moisture from the syrup. Depending on the numbers of cocoa particles, they can eventually absorb so much of the moisture that the cocoa particles might swell and stick to each other. The water-deprived emulsion then fails and the fats coalesce and separate from the swollen particles. This is why high-chocolate-content ganaches are sometimes unstable and coarsen over time (McGee, 2004). This is why some confectioners rest their ganache at room temperature overnight before using them. This gradual overnight cooling allows the cocoa butter crystals to crystallize in such a way so that when the ganache eaten it softens and melts more slowly.

17.8 CHOCOLATE AND HEALTH

Cocoa beans are very nutritious; they consist mainly of fat and carbohydrates as well as proteins; theobromine; minerals (including calcium, iron, potassium, magnesium, sodium, and phosphorus); and vitamins A, B_1, B_2, B_3, and B_6. Cocoa has the highest amount of polyphenols on a per-weight basis

contributing greatly to the total dietary intake of flavonoids. Sadly, the manufacturing process destroys up to 95% of these polyphenols (Visioli et al., 2012). All too often too, polyphenols are solely equated with their antioxidant capabilities and little else (Gutiérrez-Salmeán et al., 2015). However, while cocoa's main polyphenolic flavonoid subclass—flavanols (in particular, catechin and epicatechin)—exact mechanism of action is unknown, consumption has been seen to decrease blood pressure and promote cardiovascular protective properties like vasorelaxation (vasodilation[9]) (Ottaviani et al., 2009; Gutiérrez-Salmeán et al., 2015; Loffredo and Violi, 2012).

It would seem in fact that there are a plethora of health-giving properties attributed to chocolate such as lowering blood pressure, reducing high-density lipoproteins (HDL), reducing insulin-resistance indexes, and reducing depressive states, increasing cognitive capacity, and acting as an anti-inflammatory. Yet, the reality is there is little evidence in support of most of these claims (Brillo and Di Renzo, 2015).

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[9]Vasodilation (or vasodilatation) refers to the widening of blood vessels, which results from relaxation of smooth muscle cells within blood vessel walls.

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CHAPTER

TEA AND COFFEE

18

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Strictly speaking, tea and coffee belong in the herbs and spices section, but they are of sufficient importance to denote a small exclusive chapter to these popular beverages. It should come as no surprise really that among all the colas, sodas, wines, whiskies, and other popular beverages, tea and coffee are collectively the most popular and widely consumed drinks (water notwithstanding) around the world today. Again, not surprisingly, tea (an herb) and coffee (a spice) contain within their cells numerous chemicals and chemical defenses that are common to both groups. Both tea leaves and coffee beans share a bitter alkaloid[1] called caffeine and quantities of similar phenolic compounds. That said, they are both very different beverages. On the one hand, tea is a plant whose leaves are rich in enzymes that are carefully captured and preserved through minimal heat and drying. On the other hand, coffee starts its cycle as a seed, rich in proteins, carbohydrates, and oil, but unlike its opposite number, coffee is the product of a more robust process of high heat and grinding.

[1]Alkaloid is a term used to describe substances produced as end products of nitrogen metabolism in some plants.

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18.1 CAFFEINE

Caffeine is the common name for 1,3,7-trimethylxanthine also known as theine, mateine, guaranine, or methyl theobromine. Naturally produced by several plants, such as coffee beans, cacao beans, and tea, caffeine acts as a natural pesticide against predators (Gimba et al., 2014). In humans, we have managed to dilute, adapt, and accept this bitter substance in our everyday lives. In fact, such is the popularity of tea and coffee in terms of caffeine and its stimulative effects that, many other foods and drinks are now routinely supplemented with caffeine; with that, it makes caffeine the world's most widely consumed behavior-altering chemical.

Caffeine has pronounced physiological effects on humans. As an alkaloid, it affects the human body in different ways. First and foremost, caffeine increases the secretion of epinephrine (a hormone that initiates the "fight-or-flight" mechanism in animals), thus stimulating the central nervous system (CNS). There are also more direct ways that caffeine affects the CNS here. The most important seems to be caffeine's ability to interfere with the neurotransmitter "adenosine" in binding to its nerve cell receptor. These can also lead to secondary metabolic changes that can positively affect physical or mental performance. That is, the speed at which information is processed such as awareness, attention, and reaction times, that is, the "fight-or-flight" mechanism in process, is heightened (Gimba et al., 2014; MAYO Clinic, 2014). Caffeine can also help relieve lethargy and tiredness and allegedly improve mood. Furthermore, caffeine can increase energy production in muscles and their capacity for work.

All these sound fine and dandy, but with all good things, there must be some caution exercised. In high doses, caffeine may cause headaches, heart palpitations, heartburn, nervousness, restlessness, and insomnia. On the heart too, it has complex effects that can sometimes produce an unusually fast heartbeat. There are some studies too that suggest that caffeine can (at doses of 75–150 mg) contribute to enhanced alertness and performance after a night of acute sleep loss. Having said that, an overall healthy adult, enjoying a moderate daily caffeine intake of $\leq$400 mg, is not associated with any adverse effects (MAYO Clinic, 2014). Lastly, caffeine is absorbed into the bloodstream at any time between 10 min and 2 h after consumption, and its levels are persistent, only reducing to half within 3–7 h while completely gone by 12 h. Withdrawal symptoms too can be very unpleasant with headaches, dizziness, etc., but they do not generally persist beyond 2–3 days of abstention (Gimba et al., 2014; McGee, 2004).

Table 18.1 Common Tea and Coffee Caffeine Content

Coffee Type	Caffeine (mg/1 oz)
Brewed coffee	11.9–25
Brewed decaffeinated	0.25–1.5
Espresso	47–75
Instant	3.38–21.63
Instant decaffeinated	0.25–1.5

Source: *Adapted from MAYO Clinic, 2014. Caffeine Content for Coffee, Tea, Soda and More. Healthy Lifestyle: Nutrition and Healthy Eating. Retrieved 2nd September, 2016, from: http://www.mayoclinic.org/healthy-lifestyle/nutrition-and-healthy-eating/in-depth/caffeine/art-20049372; USDA, 2016. Coffee: World Markets and Trade. U.S. Department of Agriculture, Washington, p. 9.*

Oddly enough, though tea leaves are richer in caffeine (2%–3%) by weight than in coffee (1%–2%), tea uses less tea leaves per cup than brewed coffee; thus, coffee contains more caffeine on a per cup basis (see Table 18.1).

The origins and histories of both tea and coffee are long, colorful, and fraught with swashbuckling adventures that fill the entire volumes. However, we are not a book about tea or coffee history; we are interested in the production and science of tea and coffee. That said, for the sake of context and completeness within this book, we will cover a soupçon of both histories.

18.2 TEA

Tea and tea drinking have been established in China's long history, as evidenced by tea containers (in which tea was probably boiled and then dried for later use), which were found in tombs dating from the Han dynasty (from 206 BC to AD 220) (McGee, 2004). However, it was not until the Tang dynasty (AD 618–906) that tea firmly established itself as the national drink in China. It has been suggested that during the 8th century, tea leaves were stir-fried before drying resulting in a green/yellow leaf giving a mild but bitter and astringent infusion. In fact, such was the popularity of tea in China that a writer (Lu Yu) wrote the first known book ("Ch'a Ching" or Tea Classic) entirely devoted to tea. Not long afterward, tea was introduced to Japan by Japanese Buddhist monks. As with many cultures, tea drinking has become a vibrant part of Japanese culture (UK Tea and Infusions Association, 2016). By the 17th century, stronger flavored orange-red teas such as oolongs were developed, around which time China began to trade extensively with Europe and Russia. In doing so, the new, more complex style of tea had won the hearts of English (McGee, 2004; Teasource, 2016). Until the late 19th century, all the tea traded in the world was Chinese, that is, until China started to object to the Britain's practice of paying for its tea with opium. This resulted in the British increasing tea production in some of their own colonies, chiefly in India, in which, because of the warm climate, an indigenous variety, camellia (*sinensis var. assamica*) known as Assam tea, was cultivated. The resulting tea contained more phenolic compounds with a richer caffeine content giving it a stronger flavor and darker color than the Chinese rivals. At about the same time, Britain went on to plant hardy Chinese tea crops in the Himalayan foothills of Darjeeling (*Camellia var. sinensis*) and at high elevations in the south. In fact, today, India has gone on to become the world's largest black tea producer producing about three-quarters of the world's black tea.[2]

18.2.1 THE TEA PLANT

Many might be surprised to learn that all teas, whether white, yellow green, oolong, black, red, and pu-erh, are made from the leaves of the same genus of tea plant, namely, *Camellia sinensis*. That said, there is one major variety in particular that is used for the production of Chinese teas, *Camellia sinensis var. sinensis*, while a second is used to make another variety of black Assam teas, *Camellia sinensis var. assamica*, while of the same genus—*Camellia* plants, together with weather and soil conditions, contribute to the ultimate taste of the final tea. So employing a single variety (or two if one counts Assam) of the above types, one can produce very different teas; that is to say, while the leaf remains

[2]The strong "black" tea that is most familiar in the West today is the result of the processing the Chinese developed in the 1840s specifically for export to the West.

similar in terms of varietal species, significant differences of tea flavors are in the processing and development of the leaves (Royal Botanic Gardens, 2016).

Originally indigenous to China, the tea plant is a tropical evergreen, from the *Camellia* family (*Camellia sinensis*) that grows best in warm, humid regions with rainfall measuring 100 cm or more a year. The plant also prefers deep, lightly acidic, and well-drained soils. In fact, given the right conditions, tea will grow in almost any area from sea level up to altitudes as high as 2000 m or so (UK Tea and Infusions Association, 2016). Nowadays, for ease of plucking, tea is grown as a bush roughly 1 m high and trained into a flat-topped fan shape called a plucking plateau. Dependent on altitude, tea can take between 3 and 5 years to reach maturity (Royal Botanic Gardens, 2016). The plant's small young shoots and unopened leaf buds (the "pluck") make the best teas as they contain the highest concentrations of chemical defenses and related enzymes. This high-quality "pluck" from the abovementioned plucking plateau is the terminal (end) bud and two adjacent leaves. Yet nowadays, however, most teas are harvested mechanically, so it should come as no surprise that the tea leaves end up containing more of the older and less flavorful leaves than just the pluck (Wood, 2014; McGee, 2004).

18.2.2 TEA LEAF PROCESSING: HOW TEA IS MADE

Once mature, every 7–14 days, only the top two leaves and a bud (pluck) of the tea bushes are plucked. However, take a fresh camellia tea leaf and chew on it, and one finds it bursting with unpleasant, bitter, and astringent flavors and little else. This is a reflection of a host of phenolic substances whose purpose is to make the leaf as unattractive to animals as possible. The transformation of these bitter leaves into a variety of light fragrant teas requires work as the aromatic molecules are locked up in nonvolatile combinations with sugar molecules. While teas are said to be "fermented," in reality, the process doesn't involve any significant microbial activity; instead, what we are talking about here is enzymatic transformation. In effect, two types of enzymatic processes occur at this stage. The first is achieved by pressing (or rolling) the leaves, physically breaking them open, and allowing enzymes to work on the aroma compounds, breaking them apart from the bound sugars holding them back. The second transformation takes the small, three-ring phenolic compounds (which by themselves are astringent, bitter, and colorless) to create large molecules using the browning enzyme—polyphenol oxidase. This enzyme utilizes atmospheric oxygen to join the small phenolic compounds together altering color, body, and ultimately flavor. One particular phenolic combination creates a kind of molecule that's yellowish in color (theaflavin), which is less bitter but still astringent. Another complex formed in the same process but with more phenols are the less astringent, orange-red molecules (thearubigens). Even larger molecules are also created that are brown and not astringent at all. In short, the more the tea leaves are pressed, together with the longer time they are allowed to so-called ferment before the enzymes are ultimately destroyed by heating, the more colored the leaves become while the less bitter and astringent they taste (Wood, 2014; McGee, 2004; UK Tea and Infusions Association, 2016).

The above describes the main chemical processes involved in making teas; however, there is more to making tea than crushing leaves. The following is a quick summary of the process:

- The harvested leaves are usually allowed to wilt, from a few minutes to a few hours in order to modify their metabolism in flavor-altering ways and to become physically more fragile. The longer the withering is allowed to take place, the deeper the flavor and color of the leaves.
- The leaves are almost always pressed (or rolled) in order to break down the tissues, thus allowing enzymes and oxygen to transform (oxidize) cell fluids and generate additional color, flavor, and body.

- After a sufficient length of time, the leaves may be heated to arrest the enzymatic production of flavor and color and to preserve them for longer shelf life.
- The leaves are then allowed to dry before being sieved and then graded by size ranging from whole leaves to dust—when brewing, the smaller the piece of leaf, the faster the extraction of flavor.

All around the world, cultures pride themselves on their tea, although perhaps no more so than in China and Japan—these are where the most variety in terms of colors and flavors can be found. Incidentally, in China, teas are generally named after their color and/or the length of fermentation; as such, there are six or seven types of black tea that is sometimes referred to as red tea.

18.2.3 TEA CHEMISTRY

Apart from the caffeine (a methylxanthine), it might surprise people to know that tea leaves on the bush contain thousands of chemical compounds. Consequently, when we brew our tea, our senses are tantalized by thousands of volatile and nonvolatile compounds (Harbowy et al., 1997). While we do not always understand particular compounds functions, in a very general sense, many of tea's chemicals are categorized into broad functional groups, which collectively give us some idea of what happens during processing and what flavors and aromas they are responsible for (Tea Research Association, n.d.). From research over the years though, what we can say today with confidence is that the most important compounds in fresh tea leaves responsible for appearance, aroma, and flavor are polyphenols, amino acids, pigments, enzymes, carbohydrates, minerals, methylxanthines, and many other compounds such as the volatile flavor and aromatic complexes. During processing and eventual steeping, these compounds react and interact to produce that special brew so beloved around the world (Tea Research Association, n.d.).

18.2.3.1 Chemical compounds

Polyphenols—these are the most abundant chemical group in tea with as many as 30,000 compounds within the fresh and processed tea leaves. They are plant metabolite compounds derived from amino acids that act as a defense mechanism. The same polyphenols are largely responsible for the astringent sensation in tea (Gebely, 2015; Zhen, 2002; Harbowy et al., 1997). The largest concentration of polyphenols resides in the bud and first two leaves, and as we go further down the branch, so leaves have less and less. Flavonoids (a group of polyphenols) are probably without doubt, the most important group of phenols linked with antioxidants and other health benefits. Within this flavonoid group, flavanols (also known as flavan-3-ols) are the most predominant. Also referred to as tannins, these flavanols, through oxidation, are converted to theaflavins and thearubigins, compounds that are responsible for the dark color and full-bodied flavors most notably present in black teas (Gebely, 2015). Of the main flavanols found in tea such as catechin (C), epicatechin (EC), epicatechin gallate (ECG), epigallocatechin (EGC), gallocatechin (GC), and epigallocatechin gallate (EGCG), it is epigallocatechin gallate that is the most active. Not surprisingly, tea flavanols are sometimes jointly referred to as catechins. Besides flavanols, tea flavonoids also comprise flavones, isoflavones, and anthocyanins, all of which contribute to teas color and aroma and flavor profiles (Harbowy et al., 1997; Gebely, 2015).

Amino Acids—tea leaves contain many amino acids, the most abundant being theanine, or more specifically L-theanine. As sunlight falls upon the leaves, these amino acids are converted into

polyphenols. Once again, as we go further down the bush or tree, there is less sunlight for the leaves. This results in the retention of more amino acids than those grown in direct sunlight. Having said that, tea bushes are sometimes deliberately shaded for several weeks before harvest in order to increase the tea's amino acid content. In steeped tea, amino acids can be present in concentrations up to as much as 6% of the extract solids (Gebely, 2015). As an aside, theanine is also responsible for promoting alpha brain-wave activity, thus promoting relaxation. It has also been said that L-theanine, in conjunction with caffeine, can actually encourage a state of "mindfulness" or "alertness" in the tea drinker.

Enzymes—browning through oxidation is not always an undesirable reaction. Take polyphenol oxidase (PPO) and peroxidase enzymes for instance; these compounds are responsible for the enzymatic browning of tea leaves. During tea processing, these enzymes come into play, and when the timing is right, the enzymes are denatured by heat. This happens at precise points, depending on whether one is making green or black teas, so control over whether browning (the extent of oxidation) is needed can be controlled (Quesnel and Jugmohunsingh, 2006).

Pigments—plant pigments are responsible for using light in the energy-producing photosynthetic process, but more than that, they also give leaves their color. In fresh tea leaves, there are two important groups of pigments: the chlorophylls (responsible for the green colors) and the carotenoids (composed of carotenes) that are responsible for the orange color, while another carotene, xanthophyll, is responsible for the yellow colors. When tea leaves are wilted, the pigments condense giving the leaf a darker hue to its original color. During oxidation, however, the chlorophyll is converted to black pigments known as pheophytins, leading to the dark appearance of familiar oxidized "black" teas. Depending on the processing of the leaf, certain desired colors (or flavors) are required. Through gentle wilting or a little oxidation or through other carotenoids and xanthophylls are all responsible for certain colors of finished tea leaves (Gebely, 2015; Harbowy et al., 1997).

Carbohydrates—energy formed during photosynthesis in plants is stored in the form of carbohydrates (sugars and starches). Plants use some of this energy to fuel enzymatic reactions in the oxidation process during tea making. Carbohydrates are also responsible for the creation of polyphenols in young tea leaves, while in the finished brew, carbohydrates give the steeped brew a little sweetness as well as making up approximately 11% of extract solids (Harbowy et al., 1997).

Methylxanthines—these are a group of compounds that include the stimulant caffeine and two other related compounds: theobromine and theophylline. As natural insect and animal repellents, these closely related alkaloids can comprise up to between 2% and 5% methylxanthines in tea leaves (by weight) of the fresh leaves (Zhen, 2002). Methylxanthines, because of their alkaline properties, tend to contribute to tea's bitter taste.

Minerals—according to Zhen (2002), tea has a higher than average amount of mineral elements, 28 in total including aluminum, arsenic, fluorine, iodine, nickel, manganese, potassium, and selenium, compared with other plants. That said, the quantity of each mineral varies with any given harvest, and many are modified greatly during processing of the tea leaves.

Volatiles—the volatile organic compounds (VOC) in tea leaves are largely responsible for the tea's aroma and taste and, by extension, its flavor. The aroma complex itself is made up of hundreds (potentially even thousands) of taste and aroma compounds although many do not exist in fresh leaves rather they are created during the processing stages. Compounds, such as linalool and linalool oxide, are responsible for teas' sweetness, while geraniol and phenylacetaldehyde compounds give the tea

certain floral aromas. Nerolidol, benzaldehyde, phenyl ethanol, and methyl salicylate on the other hand tend to promote fruity flavors, while *n*-hexanal, *cis*-3-hexenol, *trans*-2-hexenal, and *b*-ionone give tea its fresh flavor (Tea Research Association, n.d.). Altogether, the aroma, taste, and flavor profile is a complex mix of compounds and processes that are not always fully understood.

18.2.4 TYPES OF TEA

White teas—these are a specialty of the Fujian province on China's east coast; they are the most delicate and the least processed of all teas. White tea undergoes the least processing of any tea. The buds (and leaves) are merely picked and allowed to wilt and simply either dried through sun drying or are baked dry at low temperatures—with very little oxidization occurring or steaming methods. White tea is prized for its subtle complexity and natural sweetness and its mellow creamy, nutty quality. Using the youngest shoots of the plant, there is little or no oxidation, and when brewed correctly—with low heat and a short steeping time—white teas benefit from high antioxidants and low amounts of caffeine. Indeed, loose white tea is often valued for its health benefits. Varieties of white tea include White Peony (Bai Mudan), Silver Needle (Baihao Yinzhen), Long Life Eyebrow (Shou Mei), and Tribute Eyebrow (Gong Mei).

Yellow teas—the yellow tea is a speciality of Anhui, Sichuan, and Hunan provinces in China and is among the rarest and most expensive of all teas (Teasource, 2016). Being just a handful of yellow teas, production is limited. Historically, they are used as tribute teas. Produced in a similar fashion to green teas, yellow tea has the added step, after oxidation of being steamed under a damp cloth or simply wrapped in paper and left in humid conditions for 48 h. This gives the leaves a slight yellow tinge while imparting a mellow and less grassy taste than is found in green teas. Varieties include Meng Ding Hu Yellow and Jun Shan Silver Needle, which is one of China's most sought-after teas found exclusively on an island in Hunan province.

Green teas—green teas are withered very lightly after being picked, after which the oxidation process takes place over a shortened period after which time it is abruptly stopped by rapidly heating the leaves. As such, many varieties tend to produce more subtle flavors with many hints and accents that tea lovers treasure (Wood, 2014). The production process is similar to that of white tea that, after wilting, is followed shortly after by panfrying or steaming to destroy the enzymatic process, thus allowing very little oxidation to occur. After this, they are then rolled to give the desired shape and then dried. Making up about 10% of the world's total tea production, green tea is greenish yellow in color, and its flavor is slightly astringent with grassy notes reminiscent of fresh leaves. Varieties include Sencha, Fukamushi Sencha, Gyokuro, Kabusecha, Matcha, Tencha, Genmaicha, Hojicha, Shincha, Ichibancha, Nibancha, and Sanbancha (UK Tea and Infusions Association, 2016; McGee, 2004).

Black (red) teas—black teas, sometimes known by the Chinese as "red" teas owing to their brewed reddish brown color, contain a higher proportion of caffeine compared with other teas. Being the most common variety of tea around the world, many consider Chinese black tea far superior to Indian or other regional types. The withering or wilting of black tea is a longer process than those for oolong and green teas so as to create deeper, more concentrated flavors (Wood, 2014). After this, the leaves are rolled and slowly oxidized in varying levels of temperature and humidity. This turns the leaves a dark brown/black color after which a final heat drying process stops oxidation and reduces the moisture

level of the leaf to around 3 %. Further, because these teas are usually fully oxidized, they are typically more robust with more pronounced, fully assertive flavors. Varieties of black teas include Lapsang Souchong, Keemun Hao Ya, Bai Lin Gong Fu, Dian Hong (Yunnan black), Fu Shou Mei (sugarcane black), and Yunnan Gold Pearls.

Oolong tea—this is also known as wulong tea or "the champagne of teas" and is considered among the finest and most expensive teas in the world. Oolong tea is a "semifermented" tea, or in real terms, it goes through a relatively short period of oxidation that leaves the final leaf with a caffeine content somewhere between that of green and black teas (Teasource, 2016). Tea made from oolong is pale yellow, and flavor-wise oolong is typically not as full-bodied as black teas or as subtle as green teas. Instead, it has its own very distinctive, fragrant, and intriguing aroma and flavor notes of floral, fruity tones, and some say with a hint of smokiness. Varieties of oolong teas include Iron Buddha (Tie Guan Yin), Big Red Robe (Da Hong Pao), Dan Cong Tea, and Ali Shan.

Pu-erh tea—pu-erh tea (Puer, pu'er, po lei, bolay, or dark tea) is in a class all of its own. There is a lot of secrecy surrounding the making of the tea, yet it can be said that pu-erh is an aged black tea that has been "fermented" twice (Wood, 2014). The process of double oxidation is followed by a period of maturation in which a thin layer of mold is added imparting a distinctive earthy tone to the beverage. While not bitter, it does have a very rich and full-bodied flavor and is prized for its medicinal properties including that of being a powerful digestive aid (Teasource, 2016). When it comes to varieties, there is really only one kind; for a tea to be called pu-erh, they must be made from the large-leaf subspecies *Camellia sinensis var. assamica*. Pu-erh comes in three categories:

- *Young "raw"*—it is the first state that all pu-erh teas go through. They are aged anywhere from 2 to 3 years and after which it looks like green tea; at this stage, it is not yet old enough to develop any of the aged characteristics of more mature pu-erh. Young and raw pu-erh presents more "grassy" tones reminiscent of Japanese green teas.
- *Cooked "ripe"*—because of the unfinished sense of "green and grassy" notes of "raw" pu-erh, a shortcut, in which dried pu-erh leaves are heaped in rooms then left to effectively compost for months amid the heat and humidity generated from their own biomass. This speeds up the fermentation process, which helps to bring out the aged flavor characteristic tones of a "cooked" or "ripened" pu-erh tea.
- *Aged "matured"*—many believe that the height of a fine pu-erh tea is a raw pu-erh that has been aged for decades. Because of this aging, many pu-erhs are expensive and often out of the reach of many tea drinkers. In fact, the more aged it is, the better the perceived quality, the more expensive the product. Depending on how long pu-erh has been aged for will affect the flavor of the tea from light vegetal, "grassy" notes (for the lightly aged) to a complex, full-bodied flavor with many subtle tones. In many older, aged pu-erh teas, a cigar-like smokiness is often said to be detected (Wood, 2014).

Tisanes and herbal infusions—the word "tea" is often loosely employed as a catchall for teas and beverage made with the leaves of any plant. However, technically speaking, true "tea" is made from the *Camellia var. sinensis* plant. Connoisseurs and enthusiastic tea professionals often suggest that all leaf-, herb-, or spice-derived drinks other than true "tea" should, in reality, be referred to as tisanes or herbal infusions. Tisanes are what many people describe as "herbal teas" that, in essence, are any beverage made by steeping various herbs, spices, flowers, etc. in warm or boiling water.

18.3 COFFEE

Genetic analysis of the origins of coffee trees shows that they were indigenous to the Great Rift Valley of Ethiopia. In fact, there are over 40 species of *Coffea* found in Africa, over 50 in Madagascar, and only a handful found in the Mascarenes[3]; other than that, there are no naturally occurring *Coffea* species found outside of these three areas. That is to say, the species found all around the world have all come from plantings taken from these three regions (Davis et al., 2006). So while Ethiopia remains the birthplace, coffee was first cultivated commercially in the Yemen (Aga et al., 2003). In fact, nowadays, all commercially grown coffee is from what is known as the "coffee belt." This is an imaginary line (loosely formed around the Tropics of Cancer and Capricorn) that wraps around the globe covering all of Africa's, Central and South America's, and Asia's best coffee-growing regions. This gives coffee trees the necessary moderate sunshine, rain, and stable temperatures around 20°C/68°F. The tropics also offer rich, porous soil profiles replete with a good selection of nutrients (National Geographic, 2016a; Charrier and Berthaud, 1985).

Some say that the coffee tree was originally valued for its sweet cherry-like fruits before the process of transforming beans into coffee was introduced, how much of this is true is speculative. That said, from Africa and the Middle East, the coffee tree eventually made its way around the world just like tea trees. Today, Brazil, Vietnam, and Colombia are the largest exporters of coffee; African countries contribute a large proportion of world production (USDA, 2016; McGee, 2004).

Coffee trees are generously pruned in order to conserve energy and aid in harvesting. When flowering, they are borne in the axils (the juncture of the leaf and the trunk/branch). And depending on the conditions of heat and moisture that prevails in a particular region's seasonal pattern, especially in lowland plantations where rain is perennial, several crops are produced in the one season. That is to say, in the right conditions, flowering and fruiting can continue practically all year round with trees displaying ripe fruits, green fruits, open flowers, and buds at the same time on the same tree. However, if the conditions are not favorable as in the semidry high districts of Costa Rica or Guatemala, there tends only to be one blossoming season.

Depending on the variety and whether or not the plant was grown from seed, it can take approximately 3–5 years of growth to reach full fruit production, and once flowering occurs, it can take another year for the cherries to mature. Coffee plants too can live to be a hundred years old, although their production life might last only 30 years or so. Once in the production cycle, a single tree can produce anywhere up to 12 lb of coffee cherries or 2 lb of green beans per year (Royal Botanic Gardens, 2016; NCA, 2016). Propagation can happen without using seeds; instead, a coffee plant's cutting can be used. This has two distinct advantages over propagation by seed. The first is it saves on seed production that can be rather expensive, and second, it also allows for hybridization, which, if lucky, can lead not only to very interesting coffees but also to very profitable new cultivars[4] (Charrier and Berthaud, 1985).

In botanical terms, coffee traces its origin to a genus of plants known as *Coffea*; overall, the genus has about 103 species, only a few of which are commercially relevant (Davis et al., 2006; Aga et al., 2003). Of those, there are just two coffee bean species that account for about 95% of commercial coffee production. The first is *C. arabica*, known as "arabica" that accounts for about 60%–80%, while

[3]The Mascarene Islands is a group of islands in the Indian Ocean.
[4]Cultivars are plant varieties that have been propagated not only from seeds but also from bulbs and stem cuttings.

C. canephora, known as "Robusta," accounts for another 20%–40%—the exact figures differ depending on who one reads (USDA, 2016; Griffin, 2006). A lesser known variety—making up just about 2% of the production—is *C. liberica* (Liberian) (Davis et al., 2006).

18.3.1 THE ANATOMY OF THE COFFEE CHERRY

The coffee beverage we all know and love is actually made from the roasted seeds from the fruit of a *Coffea* tree called a coffee cherry (Fig. 18.1). And while it may be called a bean, it is in fact a seed. As can see from the figure, the cherry's outer skin is called the exocarp, which covers a thin layer of pulp called the mesocarp. Underneath this, there is a layer of sticky/slimy mucilage-type texture of pectin. Covering the beans themselves are paper-like tissues called endocarp, or more frequently parchment. Inside this is yet another membrane (the epidermis) or silverskin within which the bean (or the endosperm) is finally uncovered. Two seeds are found inside each coffee cherry, yet in about 5% of the world's coffee, there is only one bean inside—these are known as peaberries and are sometimes isolated for separate sale (NCA, 2016).

18.3.2 THE PROCESSING OF COFFEE

Harvesting the bean—when ripe, the coffee cherry usually forms a bright, deep red or yellow color depending on variety. In most countries, cherry picking is a labor-intensive handpicking process. However, in places like Brazil where the coffee fields are large expanses of flat lands, mechanical harvesting is preferred. This mechanized process can be somewhat indiscriminate though in that it can harvest many of the unripened cherries and those in full bloom. Selective handpicking ensures that only the ripened cherries are processed, although this too has its drawbacks in the fact that the process is labor-intensive and much slower (NCA, 2016).

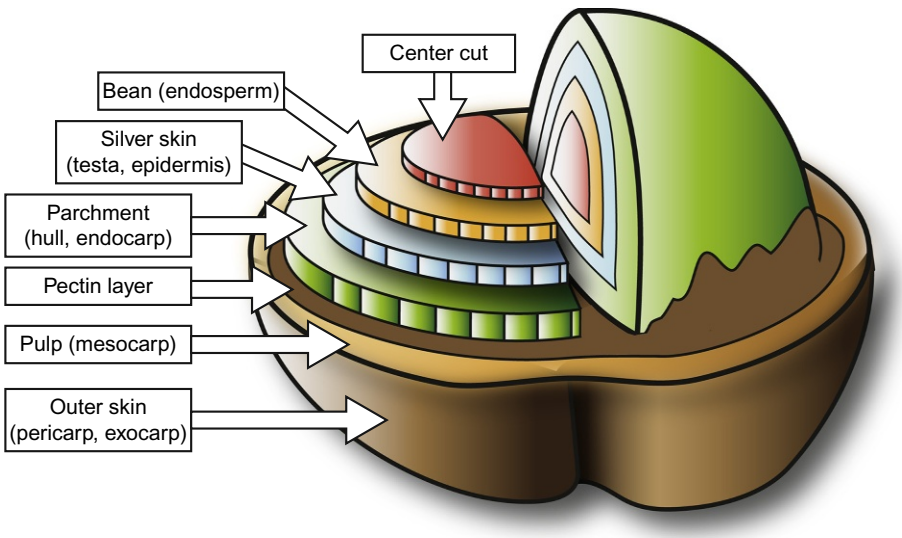


FIG. 18.1

The anatomy of the coffee cherry (bean).

Dry and wet processing—once picked, the seeds are "cleaned" of the fruit pulp by one of two methods. The dry method allows the fruit to ferment for a few days after which they are then left in the sun until the moisture content of the fruit is reduced to between 8% and 12% (Gloess et al., 2014). Alternatively, the berries are not fermented at this stage but are simply left in the sun to dry. After drying, the fruit is removed by machine.

In the wet method, the bulk of the unwanted fruit pulp is stripped away and what is left is allowed to ferment for a few days. After the remaining fruit pulp is removed, the beans are then sorted by size and by weight. These are then fermented (with naturally occurring enzymes) for 24–48 h in large, water-filled fermentation tanks. Depending on a combination of factors including the climate and the altitude, the fermentation process will remove the slick layer of mucilage surrounding the bean (USDA, 2016; Griffin, 2006). Due to the wet processing of beans, some of the minerals and sugars leach out producing a final coffee bean with less body and more acidity than dry-processed beans. If the beans were processed by the wet method, then they still have the parchment surrounding the bean.

Drying and milling—the next step in the process is to dry the beans—these can be sundried (turned regularly) or dried mechanically using tumblers to reduce the beans' moisture content to about 8%–12%. At this stage, the dried beans from the wet-processed method are known as "parchment coffee." After further drying, the beans are then milled (or hulled) whereby the parchment is removed. If dry processing was carried out, the bean goes through the milling/hulling process at this stage to remove the entire dried husk—the *exocarp, mesocarp*, and *endocarp* of the dried cherries. An optional process called "polishing" might take place at this stage in order to remove any last remnants from the bean. Although some feel this superior to nonpolishing, others believe otherwise.

Roasting—once the raw green beans are dried to between 8% and 12% of its original moisture content, they are very hard and unusable. So, to be able to use the bean, it must first be roasted, which does two things: First, it softens the bean, and secondly, it further develops the flavor. The beans are roasted at temperatures ranging from 190 to 220°C/374 to 428°F for around a few seconds to a few minutes up to 15 min or so, during which time the remaining moisture puffs the bean up. At these progressively higher temperatures, proteins, sugars, phenols, and other compounds begin the caramel and Maillard browning reactions, breaking down fragments that react with each other creating complex aromas and flavors. If the roasting continues long enough at the right temperatures, oil (caffeol) begins to coat the bean giving it a visible gloss while further developing the brown pigments and desirable roasted aromas (Belitz et al., 2009).

When the beans have reached the desired degree of roast, the beans are then cooled with water or cold air immediately in order to halt further molecular breakdown and/or interaction. The result of roasting is a brown, brittle bean that has infinite possibilities. The roasting process is fundamental to the development of distinctive flavors and as such is looked at in a little more detail.

Roasting—the development of coffee flavor—in roasted beans, the color is a good indicator of its potential flavor profile.

The process that beans go through when being roasted (as with other foods) is called pyrolysis—this is the thermochemical and physical breakdown of organic tissue in the absence of oxygen. Thus, it involves the simultaneous modification of both chemical composition and the physical phase that is also irreversible. While the vast bulk of global coffee is commercially roasted on a large scale, small-scale commercial roasting is making a comeback and is growing significantly, especially with the trend toward "single-origin" coffees that are becoming very popular. A cautionary note here, if one reads around, one will find a whole host of names to fit the color of roasts while also coming across some wildly differing roasting temperatures. With this in mind, color and temperature are somewhat

subjective and differ from coffee house to coffee house. Bear this in mind when reading the following guide:

- The first stage of the coffee bean process dries the green beans until they become yellow in color. This phase of roasting is endothermic (meaning heat absorbing) and occurs at or around 50°C where the vast majority of heat goes toward the denaturing of proteins and the evaporation of water (Belitz et al., 2009). Furthermore, in this early stage of roasting, plant compounds like chlorophyll and anthocyanins begin to change inducing subtle changes in aroma from grassy to more toast or some say popcorn notes. Then, at approximately 100°C/212°F, browning occurs (due to pyrolysis of the beans organic compounds), and water inside the bean turns to steam creating a pressure gradient. This happens around 150°C and results in the swelling of the bean. Further heating to around 175–200°C/347–365°F brings about the eventual rupturing of cells within the bean creating the audible "popping" sound known as "first crack." Also at this stage, the bean nearly doubles in volume and also, depending on the extent of roasting and caramelization, the full roasting phase is now complete. At this point, the moisture levels have been reduced from a preroasting of 8%–12% moisture content to as low as between 1.5% and 5%, again depending on who one reads (Gloess et al., 2014; Belitz et al., 2009).
- If beans are roasted quite lightly say, "light to medium" (196–205°C/385–401°F), the beans end up with a mild to medium brownish hue and a light tartness to the brew. This is because at this early to midstage of roasting, the beans' own organic acids (citric and malic) are mixed with sugars that have broken down (through pyrolysis) into other acids (formic, acetic, and lactic), giving the final coffee a mild to medium flavor.
- As the roast progresses to a "fuller medium" roast (210–225°C/410–437°F), the bean's color becomes a darker medium brown, and the acids—the astringent phenol chlorogenic acid—are both mostly destroyed: this reduces the coffee's astringency and acidity and highlights the origin and character marking this type of roast as very popular for aficionados. This is because it is believed that a medium roast gives a fuller body and flavor than most other types of roasts. At higher temperatures (above 200°C/392°F), the second "crack" or popping sounds can be heard. This is due, not to the steam (as in the first "pop"), but rather to the buildup of pressure from the formation of CO, CO_2, and other gases.
- Lastly, as the beans are "dark roasted" (225–230°C/437–446°F), acids, tannins, and soluble carbohydrates further decline resulting in the loss of the brew's richness of body. Bitterness too, from some of the browning reactions, now increases, which actually masks some of the beans' original distinctiveness in favor of a more generic roasted coffee flavor (Gloess et al., 2014) (Fig. 18.2).

Decaffeinated coffee—when making decaffeinated coffee, it can be made from two slightly different methods. In the first instance, a solvent such as methylene chloride or ethyl acetate is used, while in the second, hot water is employed. In the solvent method, the first task is to soak the beans in methylene chloride or ethyl acetate, thus extracting the caffeine. In this method, the soaked decaffeinated beans are then steam heated to evaporate off any remaining solvent. When using the water method, caffeine is simply removed from the beans soaked in water through charcoal filters, and any remaining organic solubles are then added back to the beans:

Instant coffee—this is made by brewing ground coffee twice, the first is near the boil to obtain essential coffee aroma and flavor; this is then put aside, and the second brewing occurs at 170°C/338°F

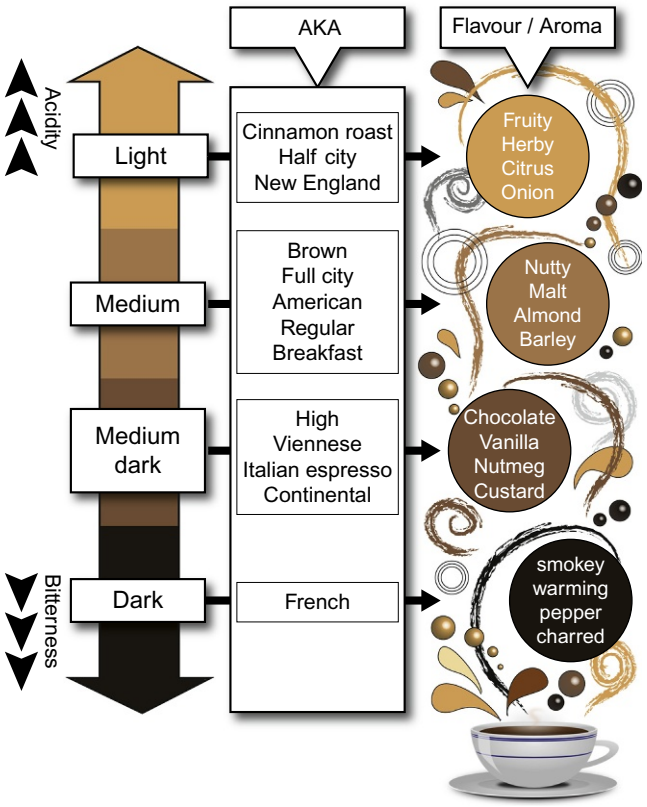


FIG. 18.2

Coffees' different roasting profiles.

under high pressure so as to maximize the extraction of pigments and body-producing carbohydrates. Water is then removed from the two liquids either through hot spraying or freeze drying.[5] Then, the two dried ingredients are then blended and supplemented if necessary.

Once roasted, whole coffee beans keep freshest (before becoming perceptibly stale) in the freezer for several months. This is aided by the high content of CO_2 within the bean that slows down oxidization. After the freezer, whole beans keep well at room temperature for about 2 weeks and finally once ground—just a few days. It is also important to note that if beans are to be stored for any length of time, they are best stored "green" as they can last quite a while without any loss of quality.

In terms of the best flavor, that is of course up to the individual but considering the chemical makeup, somewhere between a light medium to a full medium roast, where the tartness all but disappears and the acids, especially the astringent phenol chlorogenic acid, is milder (Gloess et al., 2014).

Brewing coffee—not only is it the processing of coffee that affects the overall taste profile, but also the way it is made (or brewed) which has a big impact on the final flavor. Perhaps, not surprising, the

[5]Freeze drying retains more of the volatile aroma compounds and produces a fuller flavor than hot spraying.

first thing to note is the particle size of the grind. That is to say, a consistent particle size appropriate to the brewing method is key in getting the best out of roasted coffee beans. Too small a particle size, the larger the surface area there is, and the potential for over extraction is greater; by contrast, the larger the particle size, the opposite is true. Brewing also affects the volatile organic compounds (VOC) and browning pigments and carbohydrates,[6] which cumulatively contribute coffee's flavor too. In fact, according to McGee (2004), the flavor, color, and body of the coffee are affected not only by how much coffee is used for a given amount of water but also of the contact time with water and the temperature of the hot water being used. In inadequate extraction, from coarsely ground beans, and inadequate contact time between coffee and water for instance, one suffers from a watery, acidic brew. Conversely, too fine a grind and too much contact time with the water plus a high brewing temperature and the resultant coffee can end up a harsh, bitter brew. Also, as a rule of thumb that the ideal brewing temperature be between 85 and 93°C/185 and 100°F, anything higher extracts more bitter compounds much too quickly. A guide to brewing time for a fine ground coffee should range from anywhere between 1 and 3 min, while with a coarser grain 6–8 min should suffice (McGee, 2004).

18.4 WATER FOR MAKING TEA AND COFFEE

It might be surprising to know just how important a role, water plays in the making of the perfect brew. Both teas and coffees are around 95%–98% water, so the quality of the water must be considered. The flavor of water is affected by many things from the amount of disinfectant chlorine compounds, whether it is hard (high in calcium and magnesium carbonates) or soft or distilled water. In each case, the water brings certain characteristics to the table when brewing either tea or coffee. Any off-flavors like chlorine compounds for instance are generally boiled off, while hard water affects the brew in several ways. Firstly, in coffee, minerals slow the flavor extraction process; it also clouds the brew and reduces the crema (foam) in espressos. In teas, a surface scum can sometimes be seen comprising precipitated calcium carbonate and phenolic aggregates. Soft water tends to overextract both coffee and teas leaving a hint of saltiness on the palate, while distilled water gives a brew a kind of flat flavor. So, what is the ideal water profile in tea and coffee? The answer is somewhere between hard and soft, that is, a moderate mineral content and a pH close to neutral (7) that upon brewing make the final brew a modest acid pH of around 5, which is just about right to balance the flavor profile of both.

18.4.1 COFFEE SPECIES/VARIETIES

There are several varieties of coffee that have all derived from the three species of the Rubiaceae family:

- *Coffea arabica*
- *Coffea canephora* (robusta)
- *Coffea liberica* (Liberian)

[6]Carbohydrates provide body to the coffee.

Although two (major) species of coffee (arabica and robusta) are global in production, they display significant biological differences. That said, there are a healthy number of cultivars in existence too. These are grown in much smaller quantities and are not always sold on the world market; however, they do make delicious additions to the coffee repertoire. Cultivars are plants and seeds that are selected or selectively bred for certain beneficial properties. Having said that, these cultivars are still (biologically speaking) the same species of their host parent. The exception to this is that the arabica and robusta hybrids, which have either been crossed, or the mutants that have evolved over the years.

So with this in mind, as has been noted, out of the 100 or so varieties, there are only about 25 major species within the genus *Coffea*. From this, there are in reality only two that are harvested for commercial consumption: *C. arabica* (arabica) and *C. canephora*, more commonly known as robusta. There is a third coffee, *C. liberica* (or Liberian coffee) native to western and central Africa; however, production represents a mere 2% of the world's coffee harvest. There are many cultivars in all two major coffee species—arabica and robusta, as well as the lesser produced, but no less important Liberian coffee used around the world. As mentioned, cultivars are any variety of plants in this case *Coffea* that are produced by horticultural or agricultural breeding techniques. They are also not normally found in natural populations—many specialty coffees are in fact cultivars. Bourbon and Typica are some of the most widely known cultivars. Many too are used either to boost production volumes or to add favorable traits like the increase of disease resistance and/or the improvement of cup quality. Other lesser known varieties too have been used in blends to meet the same ends (Fig. 18.3).

Coffee flavors can vary considerably from continent to continent, from region to region (within the same continent), as well as from the soil profile, humidity, rainfall, and through temperature. All these variables have a remarkable effect on the coffee's flavor profile. A look at some of the individual varieties will help elucidate this point.

18.4.1.1 Arabica varieties/cultivars

Coffea arabica (arabica)—trees are directly related to the original coffee trees discovered in Ethiopia, Madagascar, and Mascarenes. These trees' beans produce a smooth, mild aromatic coffee that commands a higher price than the robustas, and at the same time, they are also lower in caffeine content. The more prized arabicas are high-altitude (2000–6000 ft) coffees, although height alone does not make a great bean; as mentioned, temperature and moisture must all be within optimal parameters for the bean to flourish (Davis et al., 2006; Griffin, 2006; NCA, 2016; Aga et al., 2003). Each cultivar is the result of different botanical varieties whereby different species or subspecies are interbred. There are different cultivars of arabica coffee beans, all of which have their own characteristics, different flavors, and attributes. Of the many cultivars in existence, some of the most popular include the following:

- *Typica*—this cultivar is very flexible and can be grown in any coffee-producing region; in fact, it is the cultivar from which many other cultivars are derived. Typica coffees are low yielding, yet they are considered one of the finest arabica cultivars around.
- *Bourbon*—as with Typica, there are many cultivars originating from Bourbon. Bourbon grows best at 3500–6500 ft above sea level; it has broader leaves and denser cherries than Typica, and just like Typica, it also has a conical-shape plant—albeit less pronounced. Bourbon produces 20%–30% more fruit than Typica and similarly produces a rich-tasting brew.

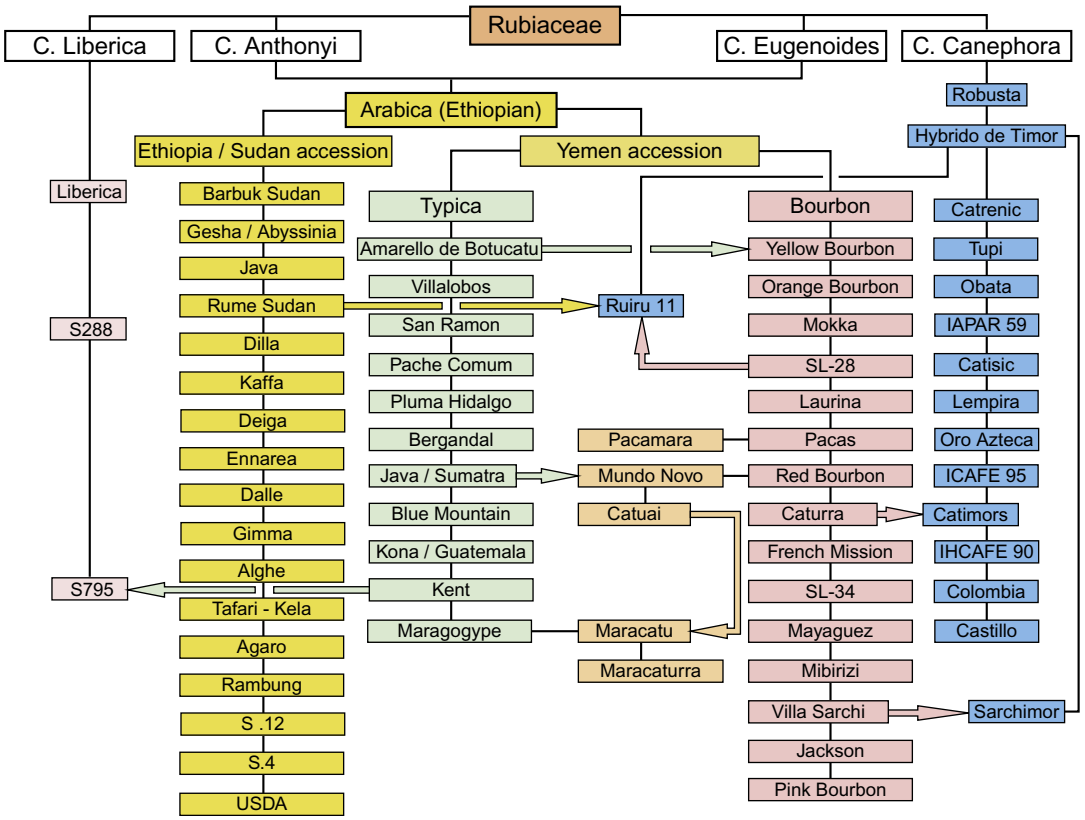


FIG. 18.3

Various coffee cultivars.

- *Blue mountain*—another Typica cultivar grown in Jamaica is the popular Blue Mountain coffee well-known for its resistance to the coffee berry disease. That said, it cannot be grown in all coffee-growing regions; instead, Blue mountain coffee not only thrives at high altitudes and is commonly grown on the Blue Mountains of Jamaica (hence the name) but is also known to thrive in Kona and Hawaii.
- *Caturra*—this cultivar is a mutated variety of Bourbon, and although it was first discovered in Brazil, it flourishes better in Colombia and South America. It is a high-quality coffee with a better than average yield. Although Caturra has a higher yield than Bourbon, it requires a lot of care and attention in order to thrive. Caturra produces a light but vibrant brew with a zesty essence.

18.4.1.2 Robusta (coffee Canephora)

Coffea canephora (robusta)—the name is thought to reflect the more robust nature of the coffee it produces; with more caffeine and a more pronounced bitter flavor, it has a distinct "kick" to the brew. That said, it is also generally agreed that the resultant coffee from robusta is on an inferior quality than

arabica. So much, in fact, instant or blended coffees are largely made using the robusta bean.[7] It is also widely used as filler for blended coffees. Robusta is cultivated around the world producing (once again, depending on who one reads) about 25%–40% of the world's coffee beans (USDA, 2016; Griffin, 2006; Aga et al., 2003). While the tree itself is hardier than the arabica, making it easier and cheaper to cultivate, the brew itself has a distinctive stronger, harsher, grain-like taste. It also contains much more caffeine than the arabica (Griffin, 2006; NCA, 2016).

Robusta coffee is not especially known for its hybrids, cultivars, and varietals. However, there are several interspecific[8] hybrids bred from arabica and robusta among which include the following:

- *Arabusta*—Arabusta is a hybrid of arabica and robusta. This cultivar has been used widely in Africa as the plants do well in lowland areas, especially in West Africa. It is not known for its quality brew so is usually used in blended coffees.
- *Hibrido de Timor* (Tim Tim (short for Timor Timur (East Timor in English)) or Bor Bor)—Hibrido de Timor or HDT for short is a hybrid of arabica and robusta. The variety is widely cultivated around the world today mainly for its hardy resistance toward leaf rust. As such, it is used quite widely in different breeding projects with the purpose of breeding into any new hybrids a higher resistance toward leaf rust and other diseases. Other cultivars of this particular variety include Catimor, Sarchimor, Colombia, and Costa Rica 95.
- *Sarchimor* (bred from HDT and a Costa Rican Arabica mutation)—Sarchimor is a hybrid between Costa Rican Villa Sarchi and Hibrido de Timor. It is grown widely throughout India and Costa Rica and displays good resistance to coffee leaf rust; some are also resistant to coffee berry disease (berry or stem borer). Sarchimor also adapts well in low- or medium-altitude zones that at such altitudes, the cup quality is good.
- *Catimor* (a hybrid of HDT and Cattura)—it is a highly productive plant, with poor cup quality used for blends. Because of the breeding with HDT, some resistance to coffee berry disease and leaf rust is present. While the plant is quite hardy, it tends to require a lot of maintenance and generally only has a short fruit blooming production of between 5 and 10 years.

18.4.1.3 *Coffea Liberica* (Liberian)

Coffea liberica (Liberian coffee)—it is another commercial coffee species that is grown on the world market, albeit in small quantities. Originating from the low-altitude growing areas of West Africa and Malaysia, it grows as a large tree (up to 18 m high), with large leathery leaves, and is comparable with *C. robusta* in flavor. There are not as many varieties or cultivars as the two main species *C. arabica* and *C. robusta*, but a couple worth mentioning include the following:

- *Kape Barako* (Baraco or Barako coffee)—it is a cultivar grown in the Philippines. It is not a particularly common coffee variety accounting for less than about 1% of global commercial coffee grown. That said, it is fairly abundant in Southeast Asia especially in the Philippines and Malaysia. It tends not to be exported as most is sold locally to the tourist market. It also has the largest leaves and beans of all the coffee varieties.

[7]Not all robustas are of inferior quality; some are valued especially in espressos for their deep flavor and good crema.
[8]Robusta and arabica plants are sometimes used for crossbreeding of both species.

- *Excelsa* (*Coffea excelsa* or *Coffea liberica var. dewevrei*)—Excelsa grows on large, hardy trees at medium altitudes whose beans have a characteristic teardrop shape. Growing mainly in Southeast Asia, where it is used as a blending coffee, it adds complexity and depth. By itself, Excelsa has a pronounced tart, fruity, and dark flavor giving the brew more substance and power.

18.4.1.4 Other coffee varieties

As mentioned previously, there are many varietals or hybrids and mutations that exist among the world's coffee beans; while some of the above are good examples, there are in fact a lot more. The Coffee Commission lists many more, and they are categorized by their method of creation, that is, hybrid or mutation: some of these include the following:

- *French Mission, N39, Mayaguez, Arusha, Jackson, K20, Kenya Selected, SL35*—all subvarieties of Bourbon
- *Pointu, Semperflorens, Caturra, SL34, Tekisic, Pacas*—mutations from Bourbon
- *Acaiá, Mundo Novo*—intraspecific hybrids from subvariety Typica and Bourbon mutation
- *Sumatra, Bergendal, Rume Sudan, Amarelo de Botucatú, Blawan Paumah, Java Mocha*—subvarieties of Typica
- *Mokka, Arabigo, Sáo Bernando, Pluma Hidalgo, Garundang, Chickumalgur, Creole, Ethiopian Harrar, Criollo, Kent, Maragogipe, Pache Común, Villa Lobos, Blue Mountain, Villa Sarchi, Ethiopian Sidamo, Ethiopian Yiragacheffe, San Ramón, Sidikalang*—all mutations from Typica
- *Hibrido de Timor, Icatú, Devamachy, Arla, Bogor Prada*—interspecific hybrids from Canephora
- *Laurina*—interspecific hybrid from Mauritania
- *Kalimas, Kawisari, S26, S228*—interspecific hybrids from Liberica
- *Pache Colis*—intraspecific hybrid from Caturra (Bourbon mutation) and Pache Común (Typica mutation)
- *Ouro Verde*—intraspecific hybrid from Acaiá (intraspecific hybrid) and Catuai (intraspecific hybrid)
- *Catuai Garnica*—intraspecific hybrid from Caturra (Bourbon mutation) and Mundo Novo (intraspecific hybrid)
- *Sarchimor*—intraspecific hybrid from Hibrido de Timor (Interspecific hybrid) and Villasarchi (Typica mutation)
- *Pacamara*—intraspecific hybrid from Pacas (Bourbon mutation) and Maragogipe (Typica mutation)
- *Catimor*—intraspecific hybrid from Caturra (Bourbon mutation) and Hibrido de Timor (interspecific hybrid)
- *Rasina*—intraspecific hybrid from Typica subvariety
- *Maracatu*—intraspecific hybrid from Caturra (Bourbon mutation) and Maragogipe (Typica mutation) (Coffee Co-Mission, 2015; Diniz et al., 2005)

18.4.2 TEA, COFFEE AND HEALTH

Tea—while all teas originate from the same plant family—*Camellia sinensis*—each style of tea has a unique taste and chemical content due in large part to the way they are processed. All the teas described above, with the exception of the tisanes, are a rich source of natural plant-derived antioxidant

compounds called flavonoids,[9] a class of polyphenols. Flavonoids, while providing antioxidant protection against harmful free radicals, the amounts in each type of tea vary by type and by amount due to the degree of oxidization of the leaf—but only by a small percentage. In other words, while there is some difference in antioxidant activity across the varieties of teas, it varies only by a small degree (Dam, 2016).

Less oxidized green teas have more catechins (simple flavonoids), while fully oxidized black teas acquire the more complex flavonoids (theaflavins and thearubigins). Oolong teas contain a flavonoid profile somewhere between the green and black teas. The green teas have six primary catechin compounds: catechin, gallocatechin, epicatechin, epigallocatechin, epicatechin gallate, and epigallocatechin gallate (known as EGCG), which are thought to give health benefits to the drinker through its antioxidant properties. Further, while whole leaf green teas contain high levels of the antioxidants, they also contain vitamins C, K, B_{12}, B_6, and E as well as many minerals including potassium, manganese, magnesium, calcium, and other compounds like the amino acid L-theanine and significant amounts of fluoride. Alkaloids are also present including the stimulants caffeine (as discussed above), theobromine, and theophylline (Wood, 2014).

The main benefits from tea is protection against cancer, reduced risk of cardiovascular disease, and reduced risk of high blood pressure (Nechuta et al., 2012; Lee et al., 2013; Kuriyama, 2008; Dam, 2016).

Coffee—it is also recognized as a major source of antioxidants, especially in the America medium roasts, which have the highest antioxidant activity. Moreover, while it is considered safe to drink up to perhaps six cups per day ($\leq$400 mg caffeine), certain brewed coffees can in fact affect blood cholesterol levels. Two lipid (fatlike) substances, namely, cafestol and kahweol, can raise LDL cholesterol levels, although they are only present in coffee when the brewing technique doesn't filter them out. That means coffee that uses plunger pot and espresso machines contains these substances. Some people may want to consider staying away from coffee or switching to decaf, especially those who are pregnant or those who need to control their blood pressure or blood sugar (Dam, 2016). Other benefits include the possible reduction in heart disease and stroke risk (Lopez-Garcia et al., 2009; Dam, 2016) and a lower risk of developing type 2 diabetes, for although coffee initially raises blood sugar levels, the antioxidants are thought to improve insulin sensitivity (Bhupathiraju et al., 2013). Coffee is also said to protect against gallstones through studies over 10 years that show significant reduction as a result of regular coffee drinking (Dam, 2016). Lastly, coffee drinking has been linked to a significantly lower risk of developing Parkinson's disease (Saaksjarvi et al., 2008).

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[9]Tea has one of the highest flavonoid contents of all plants taking up as much as 15% of the dry leaf weight.

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CHAPTER

WINE AND BEER

19

CHAPTER OUTLINE

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(See also Appendix B)

Alcoholic beverages can be subdivided into beers, wines, and spirits, which all contain ethyl alcohol of agricultural origin (Wiśniewska et al., 2016). In turn, alcohol is both a source of energy and a drug. In moderate amounts, alcohol allows many people to feel and express emotions more readily, while in large amounts, it can act as a narcotic,[1] clouding thoughts and affecting judgment. Abuse aside, as with teas and coffees, so certain wines, beers, and spirits are among some of the most finely crafted beverages that exist today. Alcoholic beverages, while being ubiquitous, are also uniquely enriched with regional and cultural traditions that are often handed down through the ages. Indeed, much of the pleasure of a good beer, wine, or spirit comes with the recognition that its essence is not only the expression of its cultural heritage but also an appreciation of the craftsman's art expressed in the choice of materials; the course of fermentation and maturation; and the nose and the sense of taste of the maker or artisan.

[1]Narcotics are drugs or other substances like alcohol that affect mood and modify behavior usually in nonmedical usage.

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As mentioned, common to all wines, beers, and spirits (nonalcoholic versions aside) is alcohol, which is made possible by the action of microscopic yeasts that actively break down (ferment) food sugars into molecules of alcohol. As they do so, so the fermentation process also adds dimensions of aromas and flavors that a skilled technician of the trade can manipulate and transform (with other ingredients) into a harmonious nectar, an operatic ensemble (McGee, 2004; Dougherty, 2012; Lea and Piggott, 2011). Alcohol is also a highly volatile fluid capable of creating new dimensions to the aroma and flavor of grapes and grains. In many living cells, not only alcohol is a by-product of breaking down sugars for their potential chemical energy, but also alcohol can, in turn, be broken down for its energy content too. As always though, there are exceptions in the form of some yeast strains that actually excrete alcohol into their surroundings (Belitz et al., 2009; Wiśniewska et al., 2016).

19.1 FERMENTATION AND YEASTS

The alcoholic beverages we discuss in this chapter come about through two transformative processes: fermentation (for wines and beers and spirits) and distillation (applied mainly to spirits—Chapter 20). Fermentation is a naturally occurring biochemical reaction, a phenomenon in which sugary liquids come into contact with either natural airborne or purposefully introduced yeasts. During the process, this sugar is converted into alcohol through the interaction of the yeasts. Yeasts, all 160 species or so belong to a group of single-celled microscopic molds of which not all are harmless. Some yeasts cause human diseases like the fungal infection—*Candida*, while others cause food to spoil. Most alcohol-producing yeasts, however, belong to the *Saccharomyces* genus (meaning "sugar fungus"). This sugar fungus cultivates efficiently while crowding out other less helpful or more unpleasant microbes[2] (McGee, 2004; Wiśniewska et al., 2016). While most living cells utilize oxygen to break down fuel molecules (like sugar) for energy, leaving carbon dioxide and water in their wake, so most yeasts in this genus, vital to their production of alcohol, is their ability to survive on very little oxygen. On top of this, yeasts, as stated, bring a whole host of flavors to the show. They are responsible for producing savory succinic acid while also helping to combine alcohols with acids to make fruit-smelling esters. The action of the yeast also aids in the conversion of amino acids into longer-chain alcohol molecules while also helping to creating sulfur compounds and others including acetic acid, acetate, acetaldehyde, diacetyls, ethyl, esters glycerol, and phenols (Belitz et al., 2009; Lea and Piggott, 2011; McGee, 2004; Tippling Bros, 2017).

As the biochemical reaction takes place, so compounds are changed, altered, or created. The process can be summarized in the following way: sugars (glucose, fructose, and sucrose) plus yeast creates alcohol, carbon dioxide, and heat. When talking of alcohol in this sense, it is the common form—ethyl alcohol (ethanol) that we are referring to. However, this is not the only alcohol produced in the process; indeed, as fermentation occurs, so other alcohols including methanol, propanol, and butanol are also produced, albeit it in varying doses. That said, ethanol is the main component of all alcoholic beverages.

While the sugars the yeasts feed off occur naturally in fruits including grapes, so beers on the other hand require the starch in the grain to be first turned into useable sugars before it can begin to be fermented. This is achieved in several ways, but essentially, all aim to initiate "germination" or "sprouting" of the grain—in a process called "malting." Once, the grain starches have been converted

[2]A microbe is any microorganism, especially a bacterium, which causes disease or fermentation.

to sugars, so the subsequent "mash" (Section 19.8.2.4.1) begins to react with the natural or added yeast (Belitz et al., 2009; Lea and Piggott, 2011; Tippling Bros, 2017; Barham et al., 2010).

As with yogurt and cheese and other similar foods, creating a convivial environment for beneficial microorganisms can, by its very nature, become less appealing to some harmful organisms. This is the case with yeast in general and specifically in the production of wines, beers, and spirits. This is because one of the yeasts' by-products is alcohol, which acts as a controlling agent for many spoilage microbes who find the environment inhospitable (Field, 2011; Barham et al., 2010). Combining this with the initial sterilization of the water used in the making of wines, beers, and spirits and controlling fermentation temperatures and the end products tend to be safe with a long shelf life—wine and spirits more so than beer because of the relative alcohol content. As an added measure of consistency, extra yeast is usually added rather than relying on natural yeasts and other microorganisms to control fermentation and flavor. Also, yeast fermentations produce gas that is sometimes funneled back into the fermenting liquor bubbling up through the mixture removing impurities.

Lastly, a hydrometer, which measures density in alcohol production, is used to check the density of the mixture. This works because as the yeast feasts on sugar in the mixture, so the alcohol content increases, and the sugar content decreases, thus making the solution less dense.

To facilitate the process of creating sparkling wines and carbonated beers, sugar is sometimes added just before bottling. This allows what remaining yeast there is to create more alcohol and more carbon dioxide that, as the pressure rises, so CO_2 dissolves in the wine creating a more gaseous product (Field, 2011).

Another somewhat different fermentation process occurs when lactic acid bacteria (e.g., *Oenococcus oeni*) convert malic acid[3] to lactic acid in a process known as malolactic fermentation. By itself, malic acid is perceived as rather "tart," tasting of apples, so the transformation of malic-to-lactic acid in wines especially is considered beneficial as lactic acid has a softer, more rounded flavor with buttery overtones produced from diacetyl, another by-product of malolactic fermentation. Indeed, under favorable conditions and if intended, malolactic fermentation in wine is desirable; however, sometimes, it occurs unintentionally after the wine is bottled. This is caused by wild or "bad" bacteria in the wine that also can cause the malolactic fermentation. The result is a slightly gaseous wine that tastes bad or slightly "off." Consequently, many winemakers try to avoid accidental malolactic fermentation in their wines from bad bacteria by inoculating their wines with a culture of desirable bacteria (Barham et al., 2010). Wine and beer aside, by far, the largest application of lactic acid-producing bacteria is in the fermentation of dairy products producing a plethora of milk-based derivatives like yogurts, soured creams, acidified milks, and of course cheeses with all manner of by-products. These might include diacetyl (a buttery flavor), carbon dioxide, ethanol, and acetaldehyde (characteristic of yogurts). Even some Swiss cheeses owe their distinctive holes to the effect of certain carbon dioxide-producing bacteria (Barham et al., 2010).

19.2 CHEMICAL AND PHYSICAL QUALITIES OF ALCOHOL

In the chemical world, the word "alcohol" is applied to a large group of substances with similar or comparable molecular structures. That is, all alcoholic molecules are created from chains of carbon (C) atoms and hydrogen (H) atoms that form a chemical group ending in –OH. The difference between

[3]Malic acid is a component of many of the foods that we eat daily and is found as a naturally occurring organic compound in various fruits.

the many alcohols is merely the length of these chains. By contrast, as cooks and drinkers of the everyday libation, "alcohol" refers to one particular group called *ethyl alcohol* or *ethanol* for short. Other alcohols aside, any mention of alcohol in this chapter, unless otherwise stated refers to *ethyl alcohol* or *ethanol*. Alcohol then, is a clear liquid whose small molecule comprises one end (CH_3) that is similar to fats and oils, while the other end (OH) resembles that of a water molecule (Wiśniewska et al., 2016). As such, alcohol is a useful liquid that mixes well with both water and fatty materials (Belitz et al., 2009; Lea and Piggott, 2011).

Because of alcohol's chemical versatility and in particular its fat-loving end of the molecule, so it readily penetrates living cells' membranes, which are also, in part, made of fatlike molecules. As alcohol penetrates in high enough concentrations, it interrupts the work of membranous proteins to the point where the membrane fails and the cell dies exposing sugars and other natural substances for the yeast to act on. This cellular breakdown however can happen to yeasts too. This is illustrated by the fact that alcohol-producing yeasts can tolerate alcohol environments in concentrations of about 20%, a figure at which most other microbes are long destroyed. However, alcohol-producing yeasts succumb to the same cellular breakdown produced by their own alcohol production in environments exceeding 20% (Lea and Piggott, 2011; McGee, 2004). Moreover, if an alcoholic solution also comprises sugar and/or acid like those found in distilled spirits, fortified wines like port and sherry, and the like, then alcohol is an even stronger microbial killer. This is why, unlike beer and wine, such concentrated alcoholic drinks do not spoil easily once they are opened.

Note that in this mix of alcohols, methanol is the smallest alcohol molecule and usually exists in very small quantities in fermented products. Yet even in small doses, methanol can be harmful with symptoms ranging from mild sickness to blindness and on occasions, even to madness and death. All alcoholic beverages contain methanol in minute amounts; however, as methanol is the smallest and lightest in size, this means it will boil first in any distillation process and by extension is contained in the head or foreshots of the distillate (later sections), (Lea and Piggott, 2011). By contrast, propanol and butanol (commonly referred to as fusel oils) comprise larger molecules than both ethanol and methanol molecules. As a result, fusel oils can be found in the "tail" or "feints" of a distillate (Wiśniewska et al., 2016). Also, while they are relatively harmless in small doses, increased dosage can result in nausea and headaches (Chapter 20).

Chemistry aside, several physical properties have important consequences for the amateur or professional cook. Alcohol is very volatile and is more readily evaporated than water; it also boils at a much lower temperature than water (around 78°C/172°F). Alcohol can also affect frozen foods like "champagne sorbets" and ice creams too in that alcohol freezes at a much lower point than water (−114°C/237°F); this means an excess of alcohol in any sorbet will slow and even arrest the freezing process. Alcohol is also flammable, which makes for great flambés in the restaurant or at dinner parties too. As a volatile chemical, alcohol has its "own" aroma that can best be detected in distilled spirits (Section 20.1), especially unflavored grain alcohols like vodka. On the palate, the alcohol molecule has a slightly sweet flavor, and at high concentrations such as those found in distilled spirits, it can even be lightly irritating in the mouth and nose, producing a hot, pungent-like sensation—that "burning" feeling brought about by chemesthesis.

Of note is the fact that, as alcohol is very flexible with water- and oil-loving molecules, so it binds well with other ingredients in cooking and can at times inhibit the volatility or release of other aroma volatiles. In this case, less is more. In fact, alcohol compliments cooking at concentrations of around 1% or less. That is to say, alcohol actually enhances the volatility of substances' aroma molecules into

the air like fruity esters. This is one reason why adding alcohol can enhance a dish, provided either it is in small amounts. However, even if added to food and if cooked thoroughly, the levels of alcohol in a long-stewed dish retains as much as about 5% of the initial alcohol added, while shorter cooked dishes can retain anywhere between 10% and 50%. Lastly, flambés can retain as much as 75% of the original added alcohol (Belitz et al., 2009; Lea and Piggott, 2011; McGee, 2004).

19.3 METABOLIZING ALCOHOL

In humans, alcohol is eliminated or broken down and converted into energy in a series of chemical reactions in two particular organs—the stomach and the liver. In the stomach, metabolism of alcohol varies between the sexes, but in general, 30% of alcohol consumption in men and 10% in women is broken down and transformed into energy by the stomach enzymes. This is because metabolism varies with size, i.e., a heavier person can consume more than a lighter person can before the effects are felt. This is partly why men can generally drink more alcohol than women. After the stomach, what is left of the alcohol passes through into the small intestine, whereby it is absorbed into the blood and into every region in the body. This can be slowed if there is food already in the stomach, which slows the passage of alcohol into the intestine allowing more time for the enzymes to act. By contrast, drinking on an empty stomach allows the quicker passage of alcohol into the system. When it comes to breaking down alcohol for its energy (around 7 cal/g), in general, the average person can metabolize between 10 and 15 g of alcohol every hour. Also, the alcohol available, after the stomach enzymes have consumed their share, reaches the blood a maximum of 30–60 min after consumption. Ultimately, the extent to which someone is inebriated is contingent on the absorption of alcohol in the cells. Once absorbed from the digestive tract, the blood quickly circulates the alcohol to all body fluids and across membrane walls penetrating all cells. The resulting degree of intoxication depends on levels of alcohol in the blood—that is, a concentration of alcohol in the blood of between 0.02% and 0.03%, and the person starts to display impulsive behavior and impaired coordination. Further deterioration of the human faculties occurs at about 0.15% blood alcohol levels, while 0.4% can end up being fatal (Lea and Piggott, 2011).

Next comes the hangover, which is partly indicative of withdrawal symptoms, as the previous drinking session left the body adjusted to high levels of alcohol. Headaches, dry mouth (dehydration), and acute sensitivity to sound and light, for example, may be the price to pay for the overall depression of the nervous system. And the notion of a drink the morning after supposedly helps as it partly restores conditions to which the body had become used to while under the effects of alcohol although this method only prolongs any withdrawal symptoms.

19.4 ALCOHOLIC BEVERAGES AND WOODEN BARRELS

Just as microbes "spoil" (for want of a better word) fruit juice and gruel into flavorful wines and beers, so simply storing alcoholic beverages and vinegars in wooden barrels also aids in the development of complementary flavors.

Why oak?—while other wooden barrels made of chestnut, redwood, and cedar, among others, have been used throughout the world, most brewers and distillers still prefer oak barrels for aging wines and spirits. However, these barrels are made from a specific portion of the oak tree—the inner "dead wood,"

referred to as oak heartwood. This is because this part of the tree's cells is full of flavor-giving compounds. These compounds include a good amount of tannins, but more importantly, they also contain aromatic compounds like volatile phenols such as eugenol (reminiscent of cloves), phenolic aldehydes like vanillin (vanilla-like), and lactones—commonly known as "oak lactones" (Lea and Piggott, 2011). Between 90% and 95% of oak heartwood cell-wall molecules are made of cellulose, hemicellulose, and lignin, yet while mostly insoluble, in conditions of strong alcohol, lignin can be partly broken down and complimentary flavors extracted. On top of this (as is described later), cellulose, hemicellulose, and lignin can all be altered during the heating of the barrel-making process and turned into new aromatic molecules. When it comes to oak, coopers mainly rely on a couple of European and nearly a dozen or so North American species; the European species are most often made into wine barrels, while the American species are preferred when aging distilled spirits.[4]

Forming and cooking the barrels—in making wooden barrels' coopers, take the heartwood and form them into elongated planks and dries them. These are then heated (to make them more pliable) and hooped. Once tightly hooped, the inside of the barrel is heated to between 150°C and 200°C/302°F and 392°F for 5–20 min, depending on the degree of "toasting" required, generally, longer for spirits and shorter for wine barrels. The exact method varies from region to region whereby some might char the inside of the barrel with an open flame, while others might heat or toast the inside twice.

When it comes to flavor of the alcoholic beverages stored in these barrels, several chemical and physical things occur. The libation absorbs soluble materials that lend color, aroma, and flavor to the beverage. These range from tannins, to eugenol, vanillin and oak lactones to sugars and browning-reaction products as well as the smoky volatiles fashioned when the barrel was toasted. Further, the barrels, being semiporous, allow a limited amount of oxygen into the mix that interacts with the wine or spirit, further aiding the numerous reactions that help toward maturation. Lastly, new oak barrels can affect a pronounced flavor, one that, if not careful, can overpower delicate beverages like wine. In this case, the winemaker uses their judgment to limit the aging of the wine in new barrels or reverts to used barrels that are milder on the palate (Lea and Piggott, 2011; McGee, 2004).

Alternatives to barrels—oak barrels tend to be expensive; so one generally finds the more expensive of the wines and spirits aged in them. However, all is not lost for the cheaper wines and spirits as there are alternative ways in which the "oakiness" can be imbued. One way is to boil wood chips in water and use the extract as a flavor enhancer (particularly common in brandies). More recently, certain large-scale winemakers have taken to adding barrel planks, sawdust, or wood chips directly into wines as they mature in steel (and other inert materials) rather than wood containers.

19.5 WINE

Grape's naturally sweet juice is well suited to the preparation of a diverse family of alcoholic beverages. The grapevine is an adaptable plant in terms of wide-ranging soils and climates; it is also a very productive plant. Grape juice also brims with tartaric acid, an unusual occurrence in fruits and one that only a few microbes and certain yeasts can metabolize (Lea and Piggott, 2011; Wiśniewska et al.,

[4]American oak species tend to possess lower quantities of tannins while maintaining higher levels of oak lactones and vanillin.

2016). As a result of these qualities and together with demand for wine, grapes are one of the world's largest and most versatile fruit crops.

19.5.1 WINE: A LITTLE HISTORY

The art of viti- and viniculture[5] has a long and illustrious history spanning millennia and is covered by volumes of literature that makes any detailed comprehensive study beyond the scope of this book. As such, this book merely skips through wine's history in such a way as to give the reader some background context while highlighting a few important key ideas.

One of the earliest pieces of evidence there is for grape-based wines is residues found at the bottom of a western Iran pot dating from around 6000 BC. Then, by about 3000 BC onward, wine had become a prominent product of trade in Egypt and Western Asia. In Egypt, wines were sealed in clay pots, graded, and left for years to ferment; indeed, many wine amphorae[6] found can be dated quite precisely as those found in the tombs of the pharaohs were labeled and dated during the period they were made (Giuliani et al., 2011; Lea and Piggott, 2011). Greek and Phoenician (modern-day Syria, Lebanon, and northern Israel) traders were initially responsible for cultivating vines throughout the Mediterranean basin. And by about 700 BC, wines with strong alcohol contents were often watered down and drunk as a very common beverage in Greece. Its graded quality separated the good wines for the freemen and the poor ones for slaves. In Italy, however, it took another 500 years (c.200 BC) before the culture of wine production took hold, but when it did, it did so with a vengeance. In fact, in during the following two centuries or so, Rome had become so adept at winemaking that the Greeks referred to southern Italy as the Oenotria—"the land of the grape."

During this period, Pliny the Elder[7] wrote of an infinite number of grape varieties and promoted the notion that a single grape variety could produce remarkably different wines. He even acknowledged places like Greece, Egypt, France, and of course Italy as venerable sources of wine. Also when it came to storing or aging wine, the Romans (as with the Egyptians) used airtight clay amphorae that allowed them to ripen wine for years without spoiling (Phillips, 2002; Soleas et al., 1997). It was also about this time that northern Europe innovated the wooden casks, and the Romans (over the centuries) adopted this as a standard alternative to the clay amphorae. However, while casks had many advantages over the amphorae, they had one distinct disadvantage; that is, they were not airtight. This meant wines could only be aged for a shorter period (a handful of years) before they became overoxidized and disagreeable to the palate. This meant that as the Romans and many others adopted the wooden cask, so outstanding aged wines more or less disappeared. This was the case for more than a thousand years until the appearance of the cork-stoppered bottle.

By about the 5th century AD, Europeans or more precisely the Christian monasteries of Europe requiring wine for the Holy Communion, and as a beverage for visiting guests, brought order to the art of winemaking through the systematic study of the grape itself and through the various processes

[5]Viticulture is the science, production, and study of grapes in general, while viniculture refers same thing only for grapes specifically used for wine.
[6]An amphora (amphorae plural) is a type of container with of a characteristic shape and size, usually but not always made of clay or other ceramic materials.
[7]Pliny the Elder was a Roman author of the much celebrated "Natural History" volume of books of which one was dedicated solely to the humble grape.

of winemaking. Consequently, during this period, wines and winemaking techniques spread rapidly through the various regions of France, Germany, and others alike (Phillips, 2002). By the Middle Ages, wines from Burgundy became celebrated and renowned, and from this point forward, France gradually attained the foremost distinguished reputation as having some of the best wines in all of Europe. It was about this time too that Italy started to lag behind in quality, knowledge, and international trade, due in part to political upheaval and excessive wine tariffs in the country at the time. Beginning in the late Middle Ages and through to early modern times, things really started happening to advance both vini- and viticulture. From the 16th century, the Spanish found that they could both stabilize the fermented grape juice and give new character or dimension to it by fortifying the wine with brandy resulting in what we now know as sherry. By the 17th century, the Hungarians cultivated wines from an otherwise destructive fungus (the "noble rot"[8]) giving us the very sweet concentrated Tokaji wine, the forerunner of French Sauternes and similarly sweet German wines too (Giuliani et al., 2011).

Bringing us up to the 17th and 18th centuries, two important innovations gave winemakers the opportunity once more, to age wines for many more years without spoiling and oftentimes with noticeable improvements in flavor, a situation that had vanished with the adoption of wooden barrels' centuries before. These were the glass bottle and cork stoppers (McGee, 2004; Karbowiak et al., 2009; Soleas et al., 1997). During this period, English importers of white wines from the Champagne region found they could make sparkling wine by transferring it from the wooden barrel to bottles before it had fully finished fermenting. Further developments by merchants bringing strong red wines back from Portugal found that they could also stabilize and extend the shelf life of the wine being transported by adding distilled alcohol. In doing so, they realized the pleasures of fortified sweet red wines—known as Ports.

During the 19th century, Louis Pasteur wrote the seminal *Études sur le vin*. Previous to this, Pasteur and his peers had already shown yeast to be a living microbe that made his work on understanding the so-called maladies of wine that much easier in identifying and controlling the specific types of yeasts responsible for the production and the spoilage of wine (Barnett, 2000). In his work, Pasteur was also pivotal in demonstrating the key roles of oxygen, wooden barrel aging and glass bottles in the successful production of winemaking. His findings showed that the wooden barrel was key in supplying oxygen to the young wine (aiding in maturation and flavor), while the bottle was important in preventing oxygen from reaching the newly bottled wine in turn preventing overoxidization—effectively helping to preserve the wine instead. In his work, Pasteur introduced the scientific approach to winemaking. About this time (1880s), two institutions the University of Bordeaux and the University of California both established institutes of oenology.[9] Both with the remit of furthering the knowledge of traditional methods of producing fine wines, in the process, the nature of malolactic[10] fermentation was discovered. By the 20th century, winemaking methods by Pasteur, the universities, and others from that time

[8]Noble rot is a gray fungus—*Botrytis cinerea*—that affects wine grapes that, in the wrong conditions, can destroy whole crops. However, under the right conditions, i.e., dry, less humid conditions, the gray rot becomes beneficial, and as the grapes become a little dried, like raisins, this type of infection is known as noble rot. This produces particularly fine and sweet, concentrated wines.

[9]Oenology is the science and study of wine and winemaking; it is separate from viticulture, the science of vine growing and of grape harvesting. Oenology is the overarching field of study.

[10]Malolactic fermentation is the conversion of malic acid into lactic acid through the actions of bacteria as opposed to yeasts. This has the added benefit of reducing tartness in the wine giving it a softer taste on the palate.

to the present were so advanced and widely disseminated that the modern global winemaking industry now produces more good wine in more regions of the globe than ever before (Phillips, 2002). Moreover, as a result of all this, there are now numerous ways and means employed by winemakers around the globe, both privately and industrially that produce a wide selection of wines to choose from. On the one side is the fairly straightforward traditional approach, in which the grapes are grown, crushed, and fermented then matured for some time and bottled, in situ. On the other side, there are the advanced production processes that aim to replicate the qualities of traditionally fashioned wine through nontraditional means. This usually means less labor-intensive and less expensive production methods. In the industrialization of winemaking, the grapes need not be at the ideal or optimal ripeness. This is because nowadays the has, at its disposal, a variety of separation tools that specifically adjust the water, sugar, acid, alcohol, and other qualities of the grapes and winemaking processes. Further, the effects of wooden barrel aging and oxygenation can be also replicated as mentioned before, through various means, in large steel vats (Lea and Piggott, 2011).

Both traditional and industrial winemakings have their advantages and disadvantages. The quality of industrial wines, for example, means that the process can be monitored, checked, and "tweaked" if necessary ensuring a consistent product that is often (purists aside) not bad and indeed quite tasteful. Small-scale wineries, on the other hand, can produce quality wines with little interference or manipulation. However, their quality can sometimes be less predictable. This is not necessarily a bad thing either as wine made on a small scale with minimal manipulation is less predictable in its quality, simply because such methods tend to reflect the local growing environment. That is to say, the small wineries' wines tend to reflect a more distinctive expression of the grapes unique character, the soil, the year, the weather and other local environmental factors, and the wineries' winemaking processes. As a result, these wines tend to be more distinctive and unique, but they also often come with a heavier price tag.

19.5.2 WINE GRAPES: VARIETIES AND CLONES

Central to any wines' characteristics are the grapes themselves. Wine grape varieties and their clones number in the thousands; some say up to 15,000 collectively (McGee, 2004; Almadanim et al., 2015; Giuliani et al., 2011). The most important components a grape possesses are sugars, acids, tannins, pigmentation, and aromas. Sugars (mainly glucose and fructose) enable yeasts to feed and convert the sugar into alcohol. At their optimum, wine grapes are generally harvested when they ripen sufficiently reaching a sugar content of 20%–30%. Next is acid, which is important for flavor and controls the growth of the wrong microbes during fermentation. Acids like tartaric and some malic are the more commonly used acids. Tannins and other associated phenolic compounds contribute the astringent sensation giving the wine a fuller body and weight to the final wine. Molecules of the grapes pigmentation can also contribute to astringency but are more importantly used for color—the skins' red grapes comprise anthocyanin, while white grapes contain flavanols (a different set of phenolic compounds). Lastly, the aroma is distinctive to each variety, although many aromatics are bound chemically to other molecules—usually sugars, which need to be enzymatically broken down during fermentation releasing their uniqueness to the final wine (Lea and Piggott, 2011; Almadanim et al., 2015; Giuliani et al., 2011).

The grapevine tends to grow vigorously in springtime and is usually fairly easily propagated by "cuttings." Vines also readily lend themselves to being "cloned," thus producing identical versions of any given plant. Yet in all of this, the same grape variety can offer a multitude of different wines

owing to habitat or the microcosm in which they are cultivated (Almadanim et al., 2015; McGee, 2004; Dougherty, 2012). The large number of varieties and clones tend to reflect the fact that over millennia, small isolated wineries with little connection to each other developed their own varieties of grapes and wines unique to that region—terroir (see below).

As mentioned, there are said to be approximately 15,000 varieties of the Eurasian grape, *Vitis vinifera* of which a single variety like the humble Pinot noir or the Cabernet Sauvignon grape might very well exist as hundreds of varying clones; each is unique in its characteristics (Lea and Piggott, 2011; Almadanim et al., 2015).

Terroir is a concept that suggests the final wine is influenced by the entire physical environment surrounding the vineyard. This notion includes the soil in which the grapes are grown—its composition and mineral makeup including its water content; the vineyard's physical orientation, slope, and elevation; and the microclimate of the region, i.e., sunlight, temperature, humidity, and rainfall (Almadanim et al., 2015). Of course, it doesn't take a genius to understand the notion that regional differences, even those of a few short miles, change the microcosm or mini ecosystem in which the grapes are grown and by extension the taste of the final wine. This is not a new concept, although it has developed over recent years to become part and parcel of the unique expression of a vineyard's wine. What is new, however, is the degree to which terroir can be lessened by altering the grapes composition and ultimately its wine through manipulation of the grape post harvest. This reduces the effect of terroir, and the wine becomes less a product of a specific place and year and more a result of modern fermentation technologies (Lea and Piggott, 2011). Lastly, many agree that the best wines are cultivated within a narrow band of conditions, which include just enough water, light, heat, and minerals (Almadanim et al., 2015). The reasoning is that such conditions encourage slow and gradual ripening that people believe produces a better wine. This in turn might not result in a wine that is realized in a single year. In this case, the year in which the grape was grown and harvested becomes the "vintage" of the wine—and in this sense, it can be seen that certain years produce better wines than others.

19.5.3 MAKING WINE

Basically, in winemaking, there are only three stages: the first is crushing the grapes to extract the juice, the second step is to ferment the juice through the action of alcohol-producing yeasts, while the third and last stage is the aging or maturation of the wine. Yet, as simple as these steps sound, they belie the art and craft of the winemaker in all of this, so while the steps can be simply defined as they are above, the actual craft is that much more involved and complicated (Belitz et al., 2009; Lea and Piggott, 2011).

19.5.3.1 Crushing the grapes

Crushing grapes extracts the liquid, known as the "must" that will eventually become the wine. This is an important step too as it largely determines the wines final characteristics; its potential composition and qualities. The "free run" or the first mechanical pressing usually ends up being extracted from the middle of the grape. This free run is usually clear, sweet, and essentially tannin-free. However, this is not enough; elements that are important to the grape are not just in the first pressing of the grape. Importantly, the skin contains much of the grapes' phenolic compounds, i.e., the tannins and the pigments, as well as many other compounds that give the grape its distinctive individual taste and aroma as well as most of the acid. What is not wanted are the stems and the seeds as these contain more bitter-tasting tannins, oils, and resins. So as more pressure is applied to the press, a second pressing must be

careful not to break the seeds or overly crush the stems. Instead, the goal is to get the juice from under the skins and around the seeds. The degree of all pressings will have a significant effect on the appeal or character of the final wine produced (Lea and Piggott, 2011). The liquid portion the must comprises between 12% and 27% sugars (as previously mentioned—in the form of glucose and fructose), 70%–85% water, and lastly about 1% acids (Belitz et al., 2009; McGee, 2004).

As is shown in the figure above (Fig. 19.1) when it comes to white wines, the skins are left in the "must" for a few hours to impart some of the yellow pigmentation and a little tannin before being removed for fermentation. The same is true of rosé and red wine "musts," yet these are left in partly during the fermentation for the same reasons of pigmentation and tannins. The longer the skin and seeds are suspended in the must, the richer the color and the more astringent the wine. Lastly, before fermentation begins two substances are added—sulfur dioxide and sugar or acid. The first, sulfur dioxide helps inhibit the growth of unwanted wild yeasts and bacteria while also lessening the oxidation of pigment and flavor molecules. The second treatment is adding either sugar or acid depending on the region of the world one is in and the practice of the individual wineries. The reason for this is simply to adjust the "musts" sugar-acid balance. In cooler climes, wines can often lack sufficient sugar to convert into alcohol, while in warmer climes, sometimes, the grapes can metabolize some acid content (Belitz et al., 2009; Lea and Piggott, 2011).

19.5.3.2 Fermentation

Recall from previous sections, grape skins often contain wild fermentation yeasts such as *Kloeckera*, *Candida*, *Pichia*, and *Hansenula*—so when it comes to fermentation, the winemaker can either allow one of these to ferment the wine or he/she can add a starter culture instead. Each of the above yeasts adds their own unique flavor to the wine before they are eventually destroyed—see below. If adding yeast, however, there is a plethora of different strains of *Saccharomyces* at the winemaker's disposal. If using no starter culture and relying on the wild yeasts, they will always be displaced naturally as *Saccharomyces cerevisiae* invades the must through its greater tolerance for alcohol. Although yeasts' first duty is to convert sugar into alcohol, it also creates many varied aroma compounds from long-chained esters, a group of compounds that combine acid with phenol or an alcohol. Moreover, further aromatic molecules are also liberated through the enzymatic action of both yeast and grape enzymes and the acid condition itself. All these occurrences add to the complexity of the final wine's aroma and flavor profiles (Lea and Piggott, 2011; Wiśniewska et al., 2016).

During the fermentation period, time and temperature are critical. It is the time in which chemical components of the must interact with the fermentation products and with oxygen. This is where the greatest skill of the winemaker is put to the test as he/she can vary the numerous conditions under which these reactions occur—dependent on the type of wine being made. In robust red wines, for example, as we mentioned, the must is fermented along with the skins to extract color pigments, tannins, and other flavors (Belitz et al., 2009). This is achieved from anywhere between 4 and 14 days and at temperatures of 18–27°C/64–81°F. After this, the skins are filtered out, and the must is further fermented for another 2–3 weeks. If fermenting white wines, the must is fermented for between 4 and 6 weeks at temperatures of 16°C/61°F or so (Lea and Piggott, 2011). Temperature in fact is one of the crucial factors that can be manipulated; as a rule, a long slow ferment at low temperatures allows for more aromatic molecules. Usually, when all the sugar in the must has been converted into alcohol, the main fermentation process is complete—this is how "dry" wines are made. By contrast, if the winemaker is making "sweet" wines,

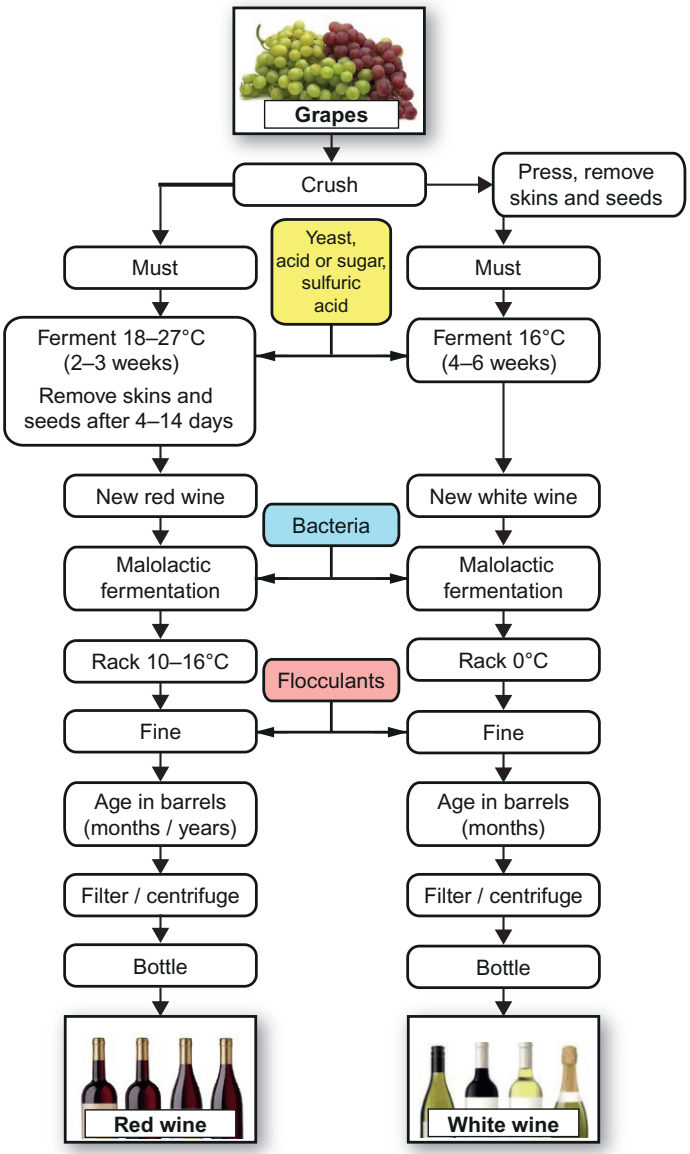


FIG. 19.1

Winemaking steps.

the main fermentation is halted before all the sugar has been converted, or alternatively, some reserved sweet grape juice is added to a dry wine after the yeast has been removed.

Malolactic fermentation—some wines are sharp and a little "tart" from the first fermentation, and in some wines, this is a desired trait. Yet not all winemakers and connoisseurs like these strong and

sour(ish) wines; variety is the key. In order to mellow the wine out, a second bacterial fermentation is induced to convert the existing tart malic acid into a sweeter, less strong alcoholic wine. This is achieved using the bacterium *Leuconostoc oenos* in a "malolactic" fermentation. As a bonus, this second fermentation also results in a number idiosyncratic aroma compounds among which is the distinctive buttery diacetyl (Lea and Piggott, 2011).

19.5.3.3 Maturing and ageing

Once complete, the newly made wine is drained ready for clarification and aging, in which a cloudy, rough-around-the-edges wine is allowed to mature and develop into a clear, smooth flavored libation full of character. The first step is to siphon off the solid particles of residual yeast and grape in a process of racking. Racking is simply a means by which sedimentary particles are allowed to naturally settle out before the wine is carefully drained off; this process is generally repeated every few months. There are exceptions to racking and that is to allow a wine to mature for months, even years in contact with the grape and yeast particles. This is a process, whereby the yeast cells slowly break down further imparting flavor and body to wines like champagne and muscadet in a procedure called *sur lie* or "on the lees."

Racking temperatures −0°C/32°F for whites and 16°C/61°F for reds unfortunately reduces the solubility of proteins, carbohydrates, and tannins, which causes them to come out of solution creating a cloudy wine. The answer to this problem is to have the wine "fined." That is to say substances like egg whites, gelatin, and others are added to attract these particles that bind to them allowing them to settle as sediment. Some even go to the extent of centrifuging the wine or passing it through a very fine filtration system in order to clarify the wine. However, a compromise here must be made between removing some of these flavorful molecules and clarifying the wine. In traditional winemaking, the months of racking and transferring the wine from container to container periodically exposes the liquid to oxygen in the air. Thus, a chemical evolution occurs, albeit slowly; these reactions tend to reduce a wine's bitterness and astringency. All the while, other reactions see molecules break apart or react with oxygen reducing the hard-earned floral and fruity notes in favor of a more subdued generic less than flavorful wine (Belitz et al., 2009).

Barrel aging—for the reasons above, new wines generally possess an unassuming, a modest aroma, and a fresh raw flavor that requires fine-tuning. Aging the wine after fermentation allows a cornucopia of often slow-acting chemical reactions to develop body and soul. This final complex balance of harmonious flavors can be heightened by aging the wine in wooden barrels. Once again, the amount of time a wine is aged in barrels depends on the type, style, and composition required of the winemaker. This means barreled wine and their controlled access to oxygen can vary from months to 2 years or so, after that time, the wine is then bottled to age further (Lea and Piggott, 2011).

After barrel aging and before bottling, most wines are usually a blend of two or more wines, which once again test the winemaker's skill in his craft. After this, the wine might go through another filtration method and being given another shot of sulfur dioxide to inhibit unwanted microbial growth during its period of storing. Sometime too, the wine might be pasteurized as is the case of some Burgundy in which the wine is taken to a temperature of around 72°C/162°F for no more than 2–3 s.

19.5.3.4 Bottle aging

Whites and light reds are commonly bottled after 6–12 months of barrel aging, while astringent dark reds might require a year or 2 to mature and mellow out a little. So, in general, between a few short months to 2 years, it is now time to bottle the wine for further aging or maturation. A cork stopper was

the sealant of choice over the last few centuries; however, this is still a semipermeable material that allows oxygen into the mix, which some cases causes the wine to overoxidize or spoil "corked." In an effort to reduce this problem, more and more wineries are increasingly using plastic or metal stoppers as a more secure barrier against the air. That said the wine, even bottled, continues to be exposed to oxidation, this occurs at several points. After leaving the cask, the wine is bottled, and during this process, air is introduced into the mix and into the bottle especially in the bottles neck—i.e., the gap between the wine level and the stopper. So even though the little oxygen present continues to oxidize the wine, it is a relatively slow process.

Also at the bottling stage, while the chemistry is not particularly well understood, continued aging can include the release of aromatic molecules from nonaromatic complexes. This also applies to other reactions that affect tannins further lowering astringency levels. All the while pigment reactions tend to push the color of the wine toward the brownish end of the spectrum. Needless to say, different wines have different aging times; many reds, for example, benefit and improve greatly after a year or so in the bottle, while others might take decades. Whites, however, require less aging and usually max out in a few short months to a year. That said, one thing in common to both whites and reds is the fact that all wines have a finite life span after which their quality deteriorates (Belitz et al., 2009; Lea and Piggott, 2011).

19.5.4 SPECIALITY WINE TYPES

While in the previous pages, we have generalized about the whole process of winemaking; there are some speciality wines worthy of further explanation. These include sparkling, sweet, and fortified wines.

Champagnes and other sparkling wines—as has been mentioned, certain by-products of yeast fermentation include not only alcohol but also carbon dioxide. In normal winemaking processes, the CO_2 usually evaporates into the air during fermentation. Sparkling wines, however, make use of this CO_2. By being made under pressure, either in special tanks or in the bottle itself, the carbon dioxide is prevented from escaping; instead, it is dissolved into the wine until the wine is saturated. As an example, champagne is bottled at pressures of 3–4 atm and can also hold about six times its own volume in carbon dioxide. As the wine is opened, so the pressure is reduced, and carbon dioxide falls out of solution and bubbles to the surface. While many countries around the world have their own versions of sparkling wine, only sparkling wine from the region of champagne can actually be called champagne.

When it comes to making sparkling wines in general and champagne in particular, the first stage involves the production of a base wine, usually from Pinot noir and/or chardonnay grapes. After this, extra sugar is added to feed the yeast after which, the wine goes through a second fermentation process under pressure in closed vats or directly in the bottle. Whichever method is chosen, both must be air-tight so as not to lose the CO_2. The wine is then kept at about 13°C/55°F. After this second fermentation, which lasts for about 2 months or thereabouts (depending on quantities of yeast and sugar added), the wine is left to age in contact with the yeast cells for anytime between a few months to several years. Following this, the sediment is removed, and the wine is either bottled from the vats or rebottled if already aged in the bottle. During the aging period, as has been described before, most of the yeast cells die releasing more flavor into the mix (Lea and Piggott, 2011; Dougherty, 2012). While traditional methods are great for original true champagnes and quality sparkling wines,

it can be seen that it is in fact quite labor-intensive, time-consuming, and somewhat more expensive. Industry, being the great innovator it is, aims to minimize these variables through several methods. One such method is simply to minimize or eliminate altogether the aging of the wine on the yeast sediment. Another method leaves out the second fermentation and introduces CO_2 using the same method employed in the soft drinks industry, that is, carbonated using tanks of pressurized carbon dioxide (Lea and Piggott, 2011).

Sweet wines—as mentioned before, sweet wines containing 10%–20% "residual" sugar is usually made after the wine has consumed all the sugar and converted it into alcohol (dry wines) then either more sugar is added, or the wine is topped up with sweet unfermented grape juice. Prevention of further fermentation is halted by the addition of sulfur dioxide, or the wine can be filtered to remove all yeast and bacteria from the wine. However, there are other options available to the winemaker. One answer is to moderately freeze the grapes and gently crush them while partly frozen in order to separate the resultant concentrated juice leaving behind the ice crystals. This concentrated juice is then fermented into a stable wine containing residual sugar as is typical of the German *Eiswein*. Another solution is to allow the grapes to partly dry on the vine until the concentration of sugars reach 35% by weight, or more. Thus, during fermentation, once the yeast has used up its quota of sugar, so the fermentation process ceases, once again leaving residual sugar in the wine. Good examples of this method are the Italian *Recioto* and the German *Trockenbeerenauslese*. Lastly, as has been mentioned before, sweet wines can purposefully be infected with *Botrytis cinerea* (noble rot) that effectively dehydrates the grapes, concentrating their flavors and sugars. Following this is a controlled fermentation period during which the rot metabolizes some, but not all of the musts' tartaric acid and some of the sugars, in a way that keeps a good balance of sweetness and moderate tartness. A good example of this method is evident in Hungary's *Tokaji*, but the method has also has also been adopted in certain regions in Germany and France (Dougherty, 2012).

19.5.4.1 Fortified wines

By adding pure distilled spirits to a base wine until it reaches between 18% and 20% alcohol, one has made a very simple fortified wine. With this much alcohol, the finished product is more robust, inhibiting spoilage and vinegar bacteria and other microbes. Fortified wines also react well with oxygen, to the point where winemakers expose them to air for months and sometimes years. Most fortified wines are stable and once opened keep well for weeks.

Port—although originally a generic term used to describe any Portuguese wine in the 18th century, so merchants found that the addition of brandy was a simple way of stabilizing the wine on the long return trip to England. Nowadays, Ports are sweet red purposely fortified and fermented wines. They are produced by halting the fermentation process of a base red wine leaving half the grape sugar intact and unfermented. Add to this distilled spirits to achieve an alcohol content of around 20% and then age it in barrel, ultimately bottling it for any length of time from 2 to 50 years, and one has a very desirable Port on one's hand (Dougherty, 2012; Lea and Piggott, 2011).

Sherry—is another fortified white wine from around the 17th century. True modern sherry's characteristic flavor is a product of the "solera" system of barreling. This involves maturing wine using a series of casks each containing the fortified wine of a particular year. The barrels are not completely filled, and a good area of the wine is in contact with the air, thus promoting a strong oxidized flavor. Next, as the cask contents evaporate and are concentrated, so the remaining wine is replenished with wine from the next younger cask and so on and so forth. Finally, the sherry is bottled from the casks

containing the oldest wines that, in turn, are a blend of wines and vintages and grades of development (Dougherty, 2012; Lea and Piggott, 2011).

Madeira—early in the 16th century, merchants discovered that on their regular trips to the Indies, barrels of Madeiran wines aged very well. The extreme climate coupled with the agitation of the barrels at sea produced an unusually nice wine; so much so that by the 1700s, ships were sailing to the East Indies and back simply to age Madeiran wine. Nowadays, however, the base wine (either red or white), is fortified and occasionally sweetened, before being heated to about 50°C/122°F for about 3 months (Dougherty, 2012; Lea and Piggott, 2011; Hancock, 2009).

Vermouth—a traditional medicinal wine is the basis of the modern-day vermouth. It is essentially a fortified wine (18% alcohol) flavored with dozens of herbs and spices and, as with Madeira, is sweetened up to about 16% sugar content although unsweetened or "dry" vermouths are customarily bitter and both have different alcohol levels. Vermouth, once fortified is aged for several months before bottling. Vermouths are also known as an aromatized liquor, and while usually made from grapes, vermouths can also be made from mangoes, plums, apple, and pears (Panesar et al., 2009).

19.6 STORING AND SERVING WINE

While wines have traditionally been aged for months and years, wines are still sensitive libations requiring care and attention. The optimum conditions for storing wine mimics the traditional "cellar," that is, cool, dark, and moderately humid. Bottles are always stored on their sides in order to prevent the cork from drying on the inside of the bottle, while the outside humidity moistens the cork from the outside. Both arrest the drying and shrinking of the cork that might otherwise allow air to flow into the wine. When it comes to temperature, the constant coolness tends to minimize pressure changes in the wine and air inside the bottle. While the darkness prevents high-energy light from giving the wine (sparkling and other whites) a sulfur-like aroma, further, low temperatures between 10°C and 15°C/50°F and 59°F somewhat slows the wine's overdevelopment. In this way, the wine lasts longer (Lea and Piggott, 2011).

Serving temperatures—most people will agree that different wines are at their best at different temperatures. A colder wine gives the impression of being less tart, sweet, or aromatic. This is the case for some of the more tart and/or somewhat aromatic wines that usually tend to be the light whites and rosé wines. Although that said, the more robust of the white wines may be served at slightly higher temperatures; The optimum temperatures for these wines range from 5 to 13°C/41 to 55.4°F. The less tart the wine is and the more apparent body, especially in full-flavored aromatic red wines, are at their best at temperatures between 16 and 20°C/61 and 68°F. That said, as with reds, stronger fuller-bodied whites are served warmer, and delicate reds can be served at cooler temperatures. Furthermore, as the alcohol content increases as with the Ports, Madeiras and Sherrys, for example, these are best served at warmer temperatures of between 18 and 22°C/64 and 71°F.

Aeration or breathing—on occasion, some wines benefit from a period of "breathing" (aeration) before being served. By aeration, one is not talking about uncorking the bottled wine and leaving it to stand, as very little aeration occurs in this way. First of all, the wine is decanted into a large broad, shallow, flat-bottomed glass decanter that gives the wine a large surface area in which oxygen from the air reacts with the volatile substances altering the wines aroma. Among other things, aeration can also improve a wine's aroma by allowing certain off-odors, like excess sulfur dioxide in some white wines,

to escape. Moreover, aeration can also provide a short burst of accelerated aging to young, underdeveloped red wines. The trade-off, of course, is by allowing the wine to breathe in this way, so it also allows other "desirable" volatiles to escape into the air, effectively undoing the complexity of a mature wine that has taken years to develop in the bottle (Lea and Piggott, 2011).

19.7 ENJOYING WINE

For the wine lover, whether hobbyist or connoisseur, the art and craft can be infinitely intriguing especially when one considers the complexities involved, the grape varieties, where they were grown, under what circumstances, the weather, the soil, the yeasts, the years spent in oak and/or bottles, and the skill of the winemaker. All this affects the taste and aroma and makes wines one of the most complex of all beverages we consume. Because of this complexity, not surprisingly, a whole elaborate and evocative vocabulary has grown up around the industry, one that aims to express the nuances of character, body, aroma, and all manner of idiosyncrasies of the art of wine.

Take the clarity and color of a wine, for example; these can give certain clues as to the expectations of taste. If a wine is cloudy and doesn't settle out, (except for the usual salt crystals of excess tartaric or oxalic acids), this can mean the wine has undergone further unintentional bacterial fermentation in the bottle—this is an undesirable outcome and one that means the wine is likely to be "off" or spoiled. Whites range in color from a straw-like yellow hue to a deeper amber, and in general, we can say that the darker the hue or color, so the older the wine and the more mature the wine's flavor. Reds on the other hand maintain a rich, ruby-like color for many years. Furthermore, as reds, further age so the pigments and some tannins and other precipitates settle out leaving the wines' flavor "deeper" or more full-bodied, more pronounced. In the process, the wine progresses from a simple ruby-like or a tawnier shade or even a reddish-brown hue, which can incidentally compliment the aged wines less fruity, more complex flavor.

When we take a sip of wine in the mouth, the senses of touch, aroma and taste come into play. When it comes to touch, we have already talked about astringency—the sensation one has when tannins in wine make the mouth physically constrict or "pucker." Together with the smoothness and viscosity of the wine and other extracted components, so the wine possesses more "body,", more substance Yet if there's too much tannin present so the wine feels "dry and harsh" (Lea and Piggott, 2011). In tasting wines, it often boils down to a fine balance between a wine's sweetness, its sourness, and its savory quality (attributed to succinic acid and other yeast metabolites). And while phenolic compounds can at times deliver a slight bitterness, the acid content of any particular wine is important in averting a bland or flat taste; indeed, there are some who say the acid content provides the wine with "backbone" in its overall flavor profile. Whites usually contain around 0.85% while reds about 0.55% acid. Therefore, when considering wines' aroma profile, one can think of acid as its backbone and astringency and viscosity its body. Together, these traits bring the full complexity in terms of aroma to an art form, the wines "animated spirit" so to speak. Indeed, when one considers the notion that any one wine can give off hundreds of different kinds of volatile molecules, such molecules have many different odors—the top, middle, and bottom notes. In fact, in the olfactory world, there are many similarities of wine-bound aromas that mimic those found in nature. Certainly, many of these wines' aroma molecules can be found in tropical and/or temperate grape varieties themselves, in the leaves, the woods, and spices, and in fruits and flowers, and even in animal scents or cooked foods, for instance. Even

hydrocarbons, reminiscent of fuel tanks and nail polish remover, can sometimes be invoked in the profile of a wines aroma. For these reasons, wine can be difficult to "read," with many people experiencing many different evocative aromas. Further, one must also not forget the grape and the yeast flavor, which is prevalent in any aroma profile; in fact, the primary architects of wine's final aroma are the yeasts—these create many of the stimulating volatile molecules.

19.8 BEER

Wine and beer are two very fundamentally different beverages; wines are made from fruits, while beers are made from grains—usually barley. Another major difference between beer and wine is that while fruits generate sufficient quantities of sugars in their ripening stages, grains are full of starches instead. Consequently, yeasts cannot exploit the starch directly in the grains; therefore, before yeasts can work their magic, grains must be treated in order to break down the starch into sugars. Furthermore, the raw material for beer is grain that is much cheaper than grapes, while the fermentation process is also less drawn out and less difficult to master.

Grains though have several distinct advantages over using fruits as wine. For a start, grains are easier and somewhat quicker to grow than the grapevine; furthermore, acre for acre grains produce a greater yield; they are also hardier and can be stored for several months before being fermented that allows more freedom in the fact that grains (because of their storage ability) can be made into beer any day of the year and not (as with grapes), just at harvest time (Lea and Piggott, 2011).

Thanks to our forefathers, the fruition of beer (turning grains into alcohol) came into being in three different regions and in three different ways, although the key to each was the same—enzymatic action that transformed ordinary grain starch into fermentable sugars. In Inca times, women used the enzymes in their saliva to ferment the grain, while in the Far East, brewers used the enzymes in a mold called *Aspergillus oryzae*, and in the Near East, the grain itself supplied the enzyme. In fact, it is the process used in the near East that provided generations of followers the know-how and the inspiration resembling today's methods of production. In this method, brewers soaked grains in water for several days allowing the grain to germinate that was then combined and heated with ungerminated ground seedlings. This process is called "malting," and as mentioned, it is the primary or most widely used method in use today. As an analogy, malting can be thought of as allowing seeds to sprout just as many have done in school biology, making them moist, softer, and altogether sweeter.

Hops and lagering—while the history of beer is also beyond the remit of this book, a little taster is in order. It was in medieval Germany that two important innovations made present-day beer what it is today. The first was the preservation and flavoring by hops,[11] while the second involved fermenting the brew slowly in the cold that resulted in a mild-flavored "lager" (Lea and Piggott, 2011). Over the years, many variations of herbs and spices were experimented with to flavor beer while also attempting to delay the onset of off-flavors in a mixture called gruit—a mixture of herbs used for bittering and flavoring beer. Yet it was not until about the 10th century that hops were used both as a flavoring agent and also as a stabilizer. By the 14th century, gruit was more or less fully replaced by hops albeit with a few exceptions and, by the 1700s even English beer ended up using hops as a matter of course. Right up to the Middle Ages, however, beer was made with little control over the fermentation process or

[11]Hops are flowers of the hop plant *Humulus lupulus*.

temperatures involved. Consequently, fermentation took only a few short days before it was ready. However, this beer was unstable and had to be drunk within a few days to a matter of weeks. Then, by the early 15th century in the Bavarian Alps, a different kind of beer making was developed. In this method, fermentation took place in cooler caves for a period of a week or more. But more importantly, a type of yeast was used that grew under the surface of the liquid and not on top as was the case previously. After this, the brew was then packed in ice for a few months before the yeast was drawn off and became ready for drinking (Lea and Piggott, 2011). In this method, the cool, slow fermentation temperatures imbued the beer with a distinctively mild flavor, while the cooler climes and relatively long settling time produced altogether a clearer, more palatable beer. Lager beer as it became known (from the German *lagern*, meaning to store or lay down) remained unique to Bavaria up until the 1840s by which time the established techniques were adopted by Czechoslovakia, the United States, and Copenhagen, which in turn, became the prototype of most modern beers (McGee, 2004). That is except for Belgium and England who stuck to the traditional methods of warm fermentation temperatures and top-fermenting yeasts.

England's gaseous ales—while the British were late to the game in accepting hops, they made up for it in the development of gaseous bottled beers. Ale (as beer was known in the United Kingdom) was traditionally fermented in open tanks, whereby all the carbon dioxide was lost to the air. Yet, sometime around the early 17th century, it was found that if the ale was kept in a corked bottle, it would retain its carbon dioxide bubbles. By about a century or so later, glass-bottled ales, sealed with cork and thread had become popular even if they were still seen as novelties. As most beer was still drunk relatively flat, straight from the barrel, it wasn't until a few centuries later, with the advent of airtight kegs and carbonation, that gaseous beer became the rule and not the exception.

19.8.1 SPECIALTY MALTS

Britain, during the 18th and 19th centuries, was pivotal in brewing innovation, especially with the advent of coke and coal that, as a means of temperature, gave the brewer more control over the malting process. Greater control meant that gentle heat could now be applied to the malt, marking the introduction of pale ales. Further innovation came with the very dark roasted malts that were solely used for adjusting color and flavor of other ales and beers and not to provide fermentable sugars. Thus, very heavy stouts and porters were created using a very dark coloring malt, yet even so, these new dark malted brews were still much lighter and less calorific than their predecessors of some years before (Lea and Piggott, 2011). In the United States, a natural preference for lighter brews, possibly because heavier beers were less refreshing, especially in the hot climates of some parts of the country, persisted. So, without a strong tradition of beer making, German immigrants around the mid-19th century paved the way for a whole new industry of lighter lager brewing and so gave America such brews as Miller, Anheuser and Busch, and Coors, of which several remain prominent today. All the while, in the United States, the stronger, more traditional brews reminiscent of British and German tastes tended to only appeal to a relatively small number of aficionados. In a very general sense, American beer is very bland compared with their European counterparts, but even despite this, sales of beer in the United States still represent about three-quarters of all alcoholic drinks consumed. Also, as people become more savvy and open to the idea of European beers, so small microbreweries are opening up making specialty beers in small quantities and catering to an ever-increasing niche market in the United States (Lea and Piggott, 2011).

19.8.2 MAKING BEER

Like wines and spirits, beers are a varied group of beverages that tend to be savored for their flavor, heritage, and intrinsic qualities. These range from the following:

- *Color* from pale yellow to a browny-black
- *Body*, a sense of *weightiness* resulting from the long starch molecule remnants in the malt
- *Savoriness* from malt's amino acids
- *Astringency* from the malts' phenolic compounds
- *Taste* that might contain sweet or salty flavors from unfermented malt sugars and water, respectively, and/or acidity from the roasted malt and the fermentation microbes, while hops might give the beer a characteristic bitterness
- *Aroma* from the floral, citrus-like almost woody hops to the near smoky malt, or malty caramel notes that may seem at once fruity (pears, apple and citrus) to flowery and even buttery notes, while others may encounter straw or hay-like aromas (McGee, 2004)

In fact, there are tremendous variations in aroma, taste, flavor, and color, etc. When it comes to basic beers and this is all due to the following processes:

19.8.2.1 Malting

While other grains like oats, corn, millet, wheat, and sorghum are all used to make beer, the grain of choice for most remains barley. This is simply for the reason that barley is best at generating starch-digesting enzymes. In malting, the first sage is to soak or steep the grain in cool water for several days before raising the temperature to 18°C/64°F allowing the grain to germinate. As this happens, so several enzymes start to break down cell walls, while others begin to break down starch and proteins within the cells and the endosperm. As time progresses, the endosperm's cell walls are dissolved, further allowing enzymes into the cells themselves. Once inside, enzymes begin digesting some of the starch and protein while also secreting gibberellin (a hormone), stimulating in the process, the aleurone protein[12] in cells that go on to produce yet more enzymes. The aim in all of this is to catabolize (break down) as much of the endosperm cell walls as possible while maximizing the production of the starch- and protein-catabolizing enzymes. As the process continues (about 5–9 days), so the shoot of the embryo reaches the end of the kernel. At this stage, if a pale malt is required, the brewer controls the starch digestion, keeping it to a minimum; darker malts that require more sugar and browning reactions benefit from a longer malting process and holding the moist barley at between 60 and 80°C/140–176°F in which to maximize the starch-digesting, sugar-producing enzymes (Lea and Piggott, 2011).

19.8.2.2 Kilning

Once, the barley achieves the right balance of enzymes and sugars, so the brewer arrests any further enzymatic processes by drying and heating the barley in a kiln. High heat and dehydration in the kilning process kills the embryo while generating color and flavor. However, if the brewer (the maltster) wants to make pale, light-colored and light-flavored brew, he/she must treat the barley to lower kiln temperatures over a 24 h or so period before taking the barley slowly up to temperatures of around 80°C/176°

[12]Aleurone is the granular protein in the cells of plant seeds.

F. These temperatures do not destroy the enzymes; on the contrary, it creates malts with high enzymatic potential. If a darker more flavorful brew is desired, the brewer kilns the barley at much higher temperatures of between 150 and 180°C or 302/356°F; this encourages browning reactions that create flavors ranging from smoky, sharp, and astringent to toasted and caramelized flavors. The degree to which the brewer germinates and kilns the barley gives him/her a range of malts to choose from. These include pale or lager, ale, crystal, amber, brown, caramel, chocolate, and black. However, in reality, these malt stages can be mixed to obtain a single brew with a specific profile in terms of color, flavor, and enzymatic power (Lea and Piggott, 2011).

Once kilned, the dried kernels can be stored for up to several months until they are required, at which point, they are ground into a coarse powder.

19.8.2.3 Hops

Hops, the female flowers (cones) of the *Humulus lupulus* vine, possess resin and aromatic oil glands that are essential ingredients for flavoring beers. Choosing the right hop from several dozen brewing varieties dictates a good proportion of the final flavor of the brew. Hops are added to the brew at a rate between 0.5 and 5 g/L. The lower the concentration the blander the brew, and conversely, the higher hop content gives rise to stronger more flavorful brews. Hops themselves provide both bitterness from phenolic "alpha acids"[13] predominantly from humulone and lupulone[14] (found in the resins of the hop) and aroma from the plants' essential oil. Needless to say, the different species of hops give many variable options in terms of the different flavors and bitterness that they can contribute to the brew. The downside of boiling the bittering compounds humulone and lupulone, however, is that many of the much-needed volatile aroma compounds are evaporated away. In this case, brewers may add another portion of unboiled hops to the brew in order to add back the important lost aroma compounds (Plutowska et al., 2010; Lea and Piggott, 2011).

19.8.2.4 Brewing beer

As with wine, there are several steps involved when brewing beer; these include mashing, boiling, fermentation, conditioning, lagering (if necessary), additives, and bottling (Fig. 19.2).

19.8.2.4.1 Mashing

The first step in making the "brew" is to soak the ground malted barley in hot water at between 54°C and 70°C or 129°F and 158°F for a couple of hours in proportions of around eight parts water to one-part malt. This process awakens the hitherto dormant barley enzymes that then catalyze and gelate the starch into fermentable sugar chains and sugars, and proteins into their amino acid component parts. The resultant drained fluid is a sweet, brown liquid full of color and flavor called the "wort." The leftover barley solids are then rinsed or "sparged" to capture any remaining useable material for the wort. During the mashing process, different enzymes work well under different temperature environments. So, in order to obtain the right balance of fermentable sugars to sugar chains and amino acids to

[13]Alpha acids are chemical compounds found in the resin glands of the flowers of the hop plant and are the source of hop's bitterness.

[14]The important bittering alpha acids *humulone* and *lupulone* are not very soluble in water; however, prolonged boiling transforms the acids into soluble flavorful structures.

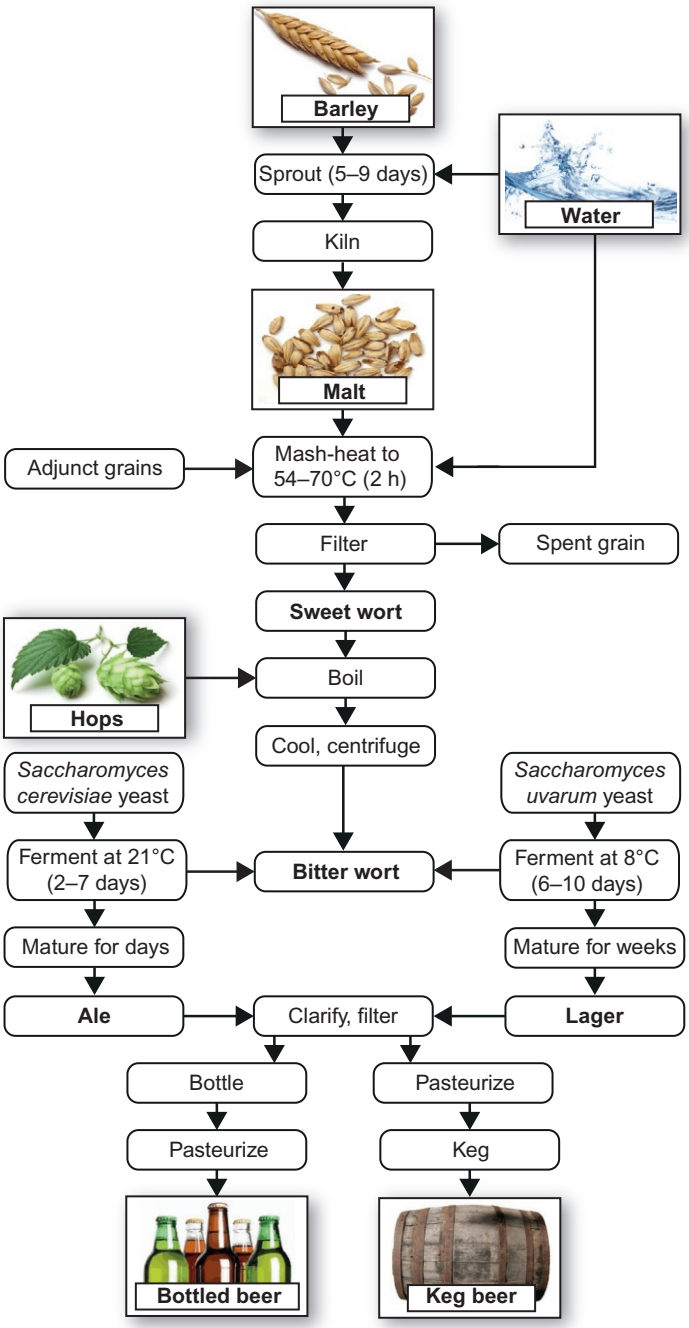


FIG. 19.2

The process of making beer.

amino acid chains, the brewer varies the time and temperature until the optimum outcome is obtained. This process also controls the brews final body and stability of its foam (Lea and Piggott, 2011).

As an example of the process of mashing, we can see that in malt, 85% of the carbohydrates were starch, while in the wort, as much as 70% of the carbohydrate have been converted into sugar (mainly maltose) with the remaining 5%–25% carbohydrates are dextrins—sugar chains of between four to a few hundred glucose units, which ultimately become entangled with each other, impeding the free flow of the liquid providing a full-bodied uniformity to the final beer. Moreover, the dextrins coupled with the amino acid chains will also impede the draining of the beer from any bubble walls of foam contributing to its stability when poured.

19.8.2.4.2 Cereal adjuncts

Having described the process of mashing above, there are some things we need to know. While the above example of making the wort with little else other than malted barley and hot water is standard practice in Germany and many microbreweries, this does not represent the whole industry. In many large breweries, supplementary unmalted "adjuncts" are added to lower the amount of malt needed. Adjunct carbohydrates range from rice, wheat, corn, unmalted barley, and even sugar. These are added for economic purposes to keep production costs down because unlike malt, the adjuncts provide little in the way of flavor of their own, but they do water down the malted flavor. As a result, adjuncts are mostly added to pale, milder brews (Lea and Piggott, 2011).

19.8.2.4.3 Boiling the wort

After drawing off the liquid wort from the grain solids, the brewer adds the hops and boils it vigorously for up to 1.5 h. This process aids in the conversion of hitherto insoluble hop "alpha acids" into its soluble form, thus developing beers distinctive bitterness. This also helps extract hop resins that ultimately concentrate the flavor of the beer while sterilizing (killing off any microbes) and enriching the color (through browning reactions between maltose and the amino acid proline). It also deactivates the enzymatic process fixing the carbohydrate (sugar) mix that can now be converted into alcohol (Lea and Piggott, 2011). Furthermore, boiling aids the brew's clarification by the coagulation of large proteins that bind with tannins and allows them to precipitate out of solution.

19.8.2.4.4 Fermentation

At this point, a bland barley grain liquid has now been transformed into a sterile, tasty, and sweetened liquid. At this juncture, yeast is added to the cooled wort, allowing the conversion of sugar into alcohol until the desired proportions of each are reached. The result is a beer that is less sweet but richer in body and flavor. There are two main fermentation methods. Firstly, rapid high-temperature fermentation (18–25°C/64–77°F for between 2 and 7 days) uses ale yeasts (strains of *Saccharomyces cerevisiae*). This so-called "top" fermentation sees the rise of yeast cells to the surface of the wort where they are skimmed off periodically. Alternatively, slow, low-temperature fermentation (at between 6°C and 10°C/43°F and 50°F, over a period of 6–10 days) uses lager yeasts (*Saccharomyces uvarum* or *carlsbergensis*) that ultimately drift to the bottom of the wort when the fermentation process is over—hence the term "bottom" fermentation.

Both produce distinctive results, that is to say top (warm) fermentation encourages the generation of certain aroma compounds (like esters and volatile phenols), which produce fruity and spicy notes while

cooler, slow fermentation processes, yield sharp, or crisp beverages with dry, bread-like flavors (Lea and Piggott, 2011; McGee, 2004).

19.8.2.4.5 Conditioning

The newly created "green" beer as it is referred to at this stage, is left for some time to condition it or clear itself of yeasts and other cloudy materials. It also has a harsh sulfurous taste that mellows with time; while lastly, conditioning is used to enhance carbonation. This after-fermentation conditioning varies according to whether "top" or "bottom" fermentation was used in the first instance. Usually, this means brief treatment for "top"-fermented and longer treatment for "bottom"-fermented beers.

Top-fermented beers are placed inside a closed cask or tank where a second fermentation is created through the addition of either more yeast and sugar or some fermenting wort from another batch (called Kräusening[15]). Inside the closed container, carbon dioxide is produced and absorbed by the beer. Although these days, such techniques might just as easily be forsaken by directly carbonating the beer through the pumping of carbon dioxide into the mix. Other modern techniques include adding hops or extract of hops to balance the beer's aroma and bitterness. After a couple of days of cooling, the beer might still be cloudy with suspended proteins, yeast cells, tannins, and other detritus, so it is further treated with a "fining" agent like fish gelatin (isinglass[16]), or sometimes vegetable gums and even clay in a process called cold stabilization. This helps precipitate these suspended particles after which a final centrifuge purifies the beer further before being pasteurized and bottled (Lea and Piggott, 2011).

In bottom-fermented beers, the process is a little different. In years gone by, lager was allowed to rest and age directly in contact with yeast residues for months that slowly carbonated the brew that, as a side benefit, also aided in purging any sulfur-like off-odors. While these days, certain lagers are still aged for several months, but for economic reasons, the inclination is to lager green beers at just above freezing for no more than 2–3 weeks. And as with "top"-fermented beer shortcuts, so carbon dioxide might also be pumped in directly to carbonate the bottom-fermented beer while also purging unwanted aromas. The clarification of the beer is also similar to that of top-fermented beers.

Lastly, in beer, additives act as preservatives or enzymes to break down proteins into smaller molecules that help clarify the brew, while vegetable gums might be used as foaming agents.

19.8.3 STORING AND SERVING BEER

In complete contrast to wines, most beers do not improve with age. There are exceptions of course, which include certain British and Belgium beers that start out with high-soluble carbohydrate contents, in turn, allowing for continued slow fermentation in the bottle. These tend to improve with age (perhaps a year or 2) and usually end up with increased alcoholic contents, in the region of 8% or so.

However, as mentioned, most beers do not improve over time and as such, most are at their best when they are freshly made. This is mainly because of a plethora of reactions that occurs over time; these might be anything from a harshness induced by phenolic compounds, to stale aromas from oxidation caused by fatty acid fragments (nonenal[17]) and to browning reactions that affect flavor. When

[15]Most ales are fermented rapidly that the yeast is still active at bottling time. In such cases, Kräusening is seldom necessary.
[16]Obtained from the dried swim bladders of fish.
[17]Nonenal is an unsaturated aldehyde; an important aroma component of aged beer.

storing beer, staling and malodors are generally seen to slow at low temperatures away from direct sunlight. This is why beer is best stored in a cold, dark place (Lea and Piggott, 2011).

When it comes to serving beer, an ice-cold refreshing brew can be really thirst quenching; however, to do justice to lager beers, they are often best served a little warmer than fridge temperature (about 10°C/50°F) and top-fermented ales at about 10–15°C/50–59°F. In enjoying beer, many pay attention to the foaming qualities too, that is, the beer's "head." There is even a name that describes the ability of the foam to cling to the side of the glass as the beer level drops; this is known as "lacing." Many aspects influence the stability and quality of a beer's "head"; these include medium-sized proteins originally from the malt or more importantly from any cereal adjuncts, whose proteins tend to be better preserved during the beer-making process than malts. Acids from the hop also contribute stability. Other than proteins, nitrogen gas also plays a part, especially in creamy foams (Lea and Piggott, 2011). However, this tends to be added after brewing as an artificial adjunct solely for the purpose of creating a creamy head similar to that of many stouts.

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CHAPTER

SPIRITS 20

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Spirits are alcoholic beverages of at least 15% alcohol by volume that has been produced either directly, through the distillation of naturally fermented products like wines, beers, and plant juices like potatoes or sugarcane, or through the maceration[1] or similar processing of plant materials in alcohol, in particular ethyl alcohol (ethanol) (EUR-Lex, 2008; Wiśniewska et al., 2016). Spirits are governed worldwide by national and international decrees, legislation, and other standards (Christoph and Bauer-Christoph, 2007).

[1]Maceration in this sense is the process whereby phenolic compounds, coloring agents (anthocyanins), and flavor component are leached from plant material into ethyl alcohol.

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A "crude" undistilled spirit comprises fractions or components that make up the whole. These components have different volatile temperatures and as such can be distilled or evaporated off creating the final product—the spirit. Therefore, an understanding of the different fractions gives the distiller options in terms of collecting different components, and by extension, controlling the composition of the final distillate is paramount. Using this method, the best way for a distiller to determine if a batch of distilled spirits requires further treatment, such as the addition of flavorings and/or the further addition of alcohol or dilution with water, can be made. Furthermore, the higher the ethyl alcohol content, the purer the distillate, the lower the proportion of higher alcohols (fusel oils—*see below*), and the better the spirit (Wiśniewska et al., 2016; Plutowska et al., 2010; Berry and Slaughter, 2003).

So, how does one concentrate the alcohol in wines and beers? This is achieved through distillation.

20.1 DISTILLATION

Distillation does not produce alcohol—that is the job of fermentation; instead, distillation merely concentrates the alcoholic content as well as the flavor and aroma contents of an alcoholic beverage. Why distill alcoholic beverages in the first place? The reason is that all yeasts[2] and microbes can only operate and thrive within certain alcoholic concentrations after which point they are killed or destroyed by the very essences (ethanol and other alcohols) they create (Rogers, 2014). Therefore, to create alcoholic beverages of greater alcohol content than say wines and beers, they must be distilled—concentrated. The alcoholic liquid to be distilled is called the "wash," that is to say the concentrated essences of wine,[3] beer, and other juices fermented from plants (EUR-Lex, 2008; Biernacka and Wardencki, 2012). These fermented juices originate from but are not limited to plants such as potatoes, sugarcane, sugar beet, corn, rice, barley, and various fruits including grapes (wine), apples, and peaches (Belitz et al., 2009; Lea and Piggott, 2011; Encyclopaedia, 2001; Plutowska et al., 2010). The finial distilled product is called the distillate or distilled spirit.

As mentioned, the main alcoholic component of all wines, beers, and spirits is called ethyl alcohol or ethanol; however, these are not the only alcohols present in the wash. The following are the main alcohols with their respective boiling points:

- Methanol 64.7°C/148.5°F
- Ethanol 78.4°C/173.2°F
- Propanol 97°C/206.6°F
- Butanol 117.7°C/243.9°F

Here, we come to the crux of distillation. Some of the above alcohols are desirable for reasons explained later, while others are not. Moreover, alongside the alcohols themselves, much of the beer or wine's flavor and aroma compounds are also highly volatile with differing boiling points. Collectively, all these components are called "congeners," and importantly, they vary significantly in concentration depending on type of beverage and the manufacturing process itself (French, 2011).

[2]Yeasts for brewing cannot tolerate more than approximately 20% alcohol concentration.
[3]Distillates of wine are called brandies.

There are literally dozens, hundreds, and sometimes even thousands of different volatile congeners that are present in various alcoholic beverages. Also noteworthy is the fact that certain congeners are desirable while others are not (Kostik et al., 2013). Congeners may be volatile or nonvolatile compounds like acids, alcohols, esters, ketones, and aldehydes as well as other components like carbohydrates, coloring agents, tannins, phenols, metals, histamine, minerals, and any other pharmacologically active compounds or substances (Kostik et al., 2013).

Because of the varied boiling points of the volatile congeners, it then becomes possible to evaporate or separate out the desirable volatiles or fractions[4] from the substrate (the wash). Distillation then is a process in which fractions of the wash are first boiled, then evaporated, and separated, or distilled out (through condensation) into its component parts (Plutowska et al., 2010). As a result, the end product is a more concentrated spirit with a stronger flavor and a higher concentration of alcohol than the original predistilled product (Tippling Bros, 2017; Pacult, 2016; Lea and Piggott, 2011; McGee, 2004). The resultant distillate is known by many names such as "aqua vitae," "aquavit," "eau-de-vie," and "whisky[5]", all variations of the term "water of life" (Belitz et al., 2009).

The process of distilling alcohol is quite complicated but very versatile—as such, all distilled alcohols are made in the same way through pot or column stills (*as described below*). In the first instance, carbohydrates (malted grains, fruits and others) are fermented with yeasts to produce a wash with alcohol content in the range of between 5% and 12%. This is then heated, and the various alcohol, aroma, and flavor vapors are collected and passed along cooler surfaces where they condense into the spirits' component fractions. For stronger spirits, this process might be repeated several times to further purify and concentrate a spirit characteristic nature (Rogers, 2014). Further, some spirits, in turn, might be flavored with various herbs or spices and/or aged in wooden barrels (Lea and Piggott, 2011; Plutowska et al., 2010).

The more volatile of the alcohols (those with the lowest boiling points) are the first to evaporate; these are known as the "heads" or "foreshots," while the "heart" of the spirit—the ethanol—comes next. Following on with the analogy, the last and least desirable of the alcohols as well as the proteins, carbohydrates, and other compounds are collectively known as the "tails" or "feints" (Rogers, 2014).

20.1.1 CHEMICAL COMPOUNDS FOUND IN AGRICULTURAL DISTILLATES

Including ethanol, yeast fermentation also creates both volatile and nonvolatile by-products or congeners, which collectively influence the final product quality. During distillation, certain congeners remain in the fermentation mix, while many others find their way into the distillate. As previously mentioned, there are hundreds and sometimes thousands of different volatile congeners found in various alcoholic beverages in general, but several tend to be commonly found in many beers, wines, and distilled spirits. These include congeners like acetaldehyde, ethyl acetate, ethyl formate, methyl alcohol, and small aliphatic alcohols: n-propyl alcohol, isobutyl alcohol, and n-butanol (Kostik et al., 2013). Other by-products or congeners of the distillation process might also include the higher alcohols, esters, fatty acids, and carbonylic compounds like acetones, aldehydes, and ketones (Stanisz et al., 2009; Wiśniewska et al., 2016). Thus, the presence of any of these or numerous other congeners in spirits directly influences the flavor and aroma

[4]Fractions are the different components that make up the wash to be distilled. Desirable components (fractions) like ethanol are evaporated or distilled in order to separate them out.
[5]Whisky is the anglicized term of the Gaelic "water of life."

of the final agricultural distillate in question. The fermented alcoholic beverage is then, as mentioned, distilled into its fractions: *the heads*, *the heart*, and *the tails*. This separation is an art the distiller acquires over time; however, experience and some guidance helps maintain a consistent final product. The wash or distillation is then mixed with the foreshots and the feints from previous distillations, and together, the collective mix comprises the "run" or batch to be distilled. Why add the "heads" and "tails" back into the wash? This is simply because in the first distillation, some of the desirable congeners are not particularly volatile although they are soluble in higher strengths of alcohol. Thus, at low alcohol strengths of the first "wash," these congeners (fatty acids and their esters) are only found in the "heads" and "tails" and not in the heart of the spirit. In the second distillation, however, the alcoholic strength is much greater, and the desirable congeners are dissolved. These are then evaporated and swept up alongside the stronger alcoholic spirit to be fractioned and used as required in the finial distillate (Belitz et al., 2009).

The head is the first part of the liquid to be distilled that mainly comprises those unpleasant congeners that would give spirits a sour-like taste. These are best eliminated from the final distillate so, as previously mentioned, are collected along with the tails (feints) to be added back into the next run. Separating these out though is in part the art of the distiller as he/she must ascertain when the head actually ends and the heart (the ethyl alcohol and the aromatic and flavor substances) begin. After this comes the "heart" of the distillation, the ethanol, and other congeners that make up the bulk of the final distillate. Once again, it is up to the experience of the distiller to determine when the heart finishes and the tails begin. The tails are also generally somewhat undesirable as they contain the unwanted fatty and oily substances.

The following details a few of those compounds that can be found in the heads, the heart, and the tails of certain distillates (Wiśniewska et al., 2016). This is a very general list as all distillates will vary in terms of congeners present and their quality and quantity.

20.1.1.1 The heads

Heads, also commonly known as "foreshots," are low-boiling (highly volatile) alcohols together with other chemical compounds that evaporate within a low range of temperatures. The first 5% or so of the run generally contains large amounts of congeners (volatile chemical compounds), such as acetone, aldehydes, esters, and certain fusel oils—some desirable, some not. They have lower boiling points relative to ethanol (Claus and Berglund, 2005).

Aldehydes—like acetaldehyde, aldehydes are usually produced by the metabolic process in plants. They can be somewhat pungent with a metallic apple fruity odor and a boiling point of 21°C/70°F.

Acetone—belonging to the ketone family, acetone is a colorless liquid that boils at 56°C/133°F. More commonly found in paint thinners or cleaning fluids.

Esters—esters are desirable heads as they are responsible for many desired "sweet and fruity" notes. Intensely odorous, the most commonly found ester in alcoholic spirits is ethyl acetate (which boils at 77°C/171°F), and while in low concentrations, this can act to "smooth out" severe odors. In large doses though, esters can give spirits a vinegar-like flavor. Then, there is ethyl formate (54°C/129°F), ethyl butyrate (121°C/250°F), and hexyl acetate (171.5°C/340°F) (Stanisz et al., 2009; Wiśniewska et al., 2016; Rogers, 2014).

Methanol—this is also known as methyl alcohol, wood alcohol, or wood naphtha boils at 64.7°C/148°F. It has a unique profile in that it is found in higher concentrations in both the head and tail cuts while present in lower concentrations in the heart cut (or middle fraction) (Claus and Berglund, 2005). However, one must be cautious with methanol, as even in small quantities it is in fact dangerous and

somewhat toxic[6] (Wiśniewska et al., 2016; Rogers, 2014). Weeding out this unwanted volatile (fraction) is difficult as methanol bonds very well to ethanol. However, it must be distilled out as it is highly toxic, even as little as 4–5 parts per million can lead to damage of the optic nerve and even blindness, while larger doses can be fatal.

20.1.1.2 The heart or middle cut

The main component of the "heart" of a spirit is the ethanol and certain aroma and flavor compounds. In fact, ethanol is the main concern for most distilleries; this is the portion of the distilled spirit that is most desirable. Once separated out, the distillate is still fairly raw and unpolished; as a result, many distilleries redistill the raw spirit increasing the strength of the distillate while also removing many of the distillate's impurities that were retained in the first distillation step (Gardner, n.d.). Distillers often mix the hearts with small quantities of heads and then dilute the blend that is then aged, if required, to make flavorful spirits.

Ethanol—this, also known as ethyl alcohol, pure, grain, or drinking alcohol, is volatile (boiling at 78.37°C/173°F); it is also the main alcohol in all alcoholic beverages. And as mentioned previously, it is also used to macerate fruits and other botanicals creating herbal drinks and remedies.

20.1.1.3 The tails

Variously known as the feints or faints, the tails with their higher boiling points evaporate last in the distillation process—hence the name—tails. These include such compounds as propanol, butanol, and amyl alcohols that can sometimes be found in higher concentrations in the tail cut, and collectively, they have boiling points higher than that of ethanol. The tail is also not particularly tasty and mostly comprises proteins, carbohydrates, and less volatile alcohols with higher boiling points—the fusel alcohols. Certain of these are desirable in small doses, while others are not so. As a result, much of this portion of the mix is set aside to be added back into new batches of wash that are then redistilled later.

1-Propanol—formed in small doses, propanol boils at 97.2°C/207°F; it is also known as propan-1-ol, 1-propyl alcohol, *n*-propyl alcohol, and *n*-propanol and is known as one of the fusel alcohols (fuselol and sometimes fusel oils) (*see below*) (Unmack, 2011).

Butanol alcohol—also known as butyl alcohol, it is common in wine and beer as it is a product of the fermentation process. Boiling at 118°C/244°F butanol also belongs to the group of fusel alcohols.

Amyl alcohol—amyl alcohol or isobutyl carbinol boils at 131.6°C/267°F and also belongs to the group of fusel alcohols.

Fusel alcohols—aka *fuselol* and sometimes *fusel oils or higher alcohols*—fusel/higher alcohols comprise a group of congeners found in the tails of the distillation process that in large quantities adversely influences the quality of agricultural distillates (Kostik et al., 2013; Wiśniewska et al., 2016). This group comprises those alcohols (mainly fusel alcohols) that are vaporized at higher temperatures and are largely characterized by strong disagreeable odors and flavors (Wiśniewska et al., 2016). These alcohols, with their longer fatlike tails, give spirits a somewhat oily-like viscous body or weight that in small doses adds character (in brandies and the like), while in large doses, fusel alcohols can be very undesirable. As a result, fusel alcohols, with their higher boiling points, are almost entirely removed during the distillation process (Rogers, 2014; Wiśniewska et al., 2016). That that is left after distillation is usually mellowed over time through aging or maturation.

[6]Methanol can be lethal if consumed in amounts greater than 30–50 g.

Acetic acid—it is a natural product of fermentation as the alcohol is oxidized to acetic acid. Both sour and slightly pungent acetic acid (vinegar) boils at 118.1°C/244.5°F.

Furfural—this is an aldehyde, a colorless (when not oxidized), oily liquid that boils at 161.7°C/323° F and smells like almonds.

Generally speaking, there are two ways in which distillers separate the fractions into desirable heads, the necessary body (or heart) of alcohol, and the certain desirable tails: the pot still and the column still.

20.1.2 POT STILL

One way is pot distillation whereby a batch of beer or wine is heated in a copper pot over a 12 h or so period. Once capped, sealed, and heated sufficiently, the volatile "head" vapors evaporate off, rising to the top of the still that are then are drawn off into a coil. The coil in turn is submerged in cool water, which condenses the alcohol back into liquid form. The alcohol then runs out of the coil and into a collection vessel. Once the head vapors (mostly methanol) are extracted, the main desirable alcohol, which is the next fraction to be collected, follows the same path as above (Fig. 20.1). This applies too to the less volatile fractions (fusel-oil tails), which are collected last (Lea and Piggott, 2011; Plutowska et al., 2010).

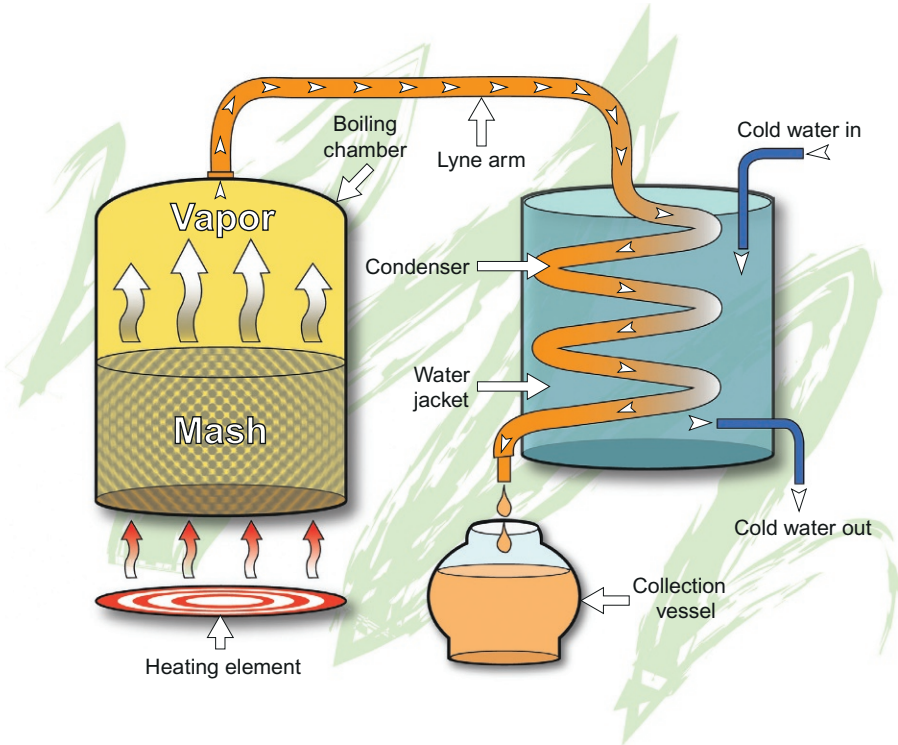


FIG. 20.1

A pot still.

This process, in the first instance, gives the cumulative collected liquid an alcohol content of about 20–30%; as a result, the process is repeated as many times as is needed until the run reaches alcohol levels of between 50%–70% by volume (see Appendix D) (Biernacka and Wardencki, 2012). The downside to this method is the pot still that can only be used for one batch before requiring cleaning and reassembling for the next batch (Lea and Piggott, 2011).

20.1.3 THE COLUMN STILL—CONTINUOUS DISTILLATION

The other method of distillation is to use a "continuously fed column still" in which the different fractions can be separated from the rest of the volatiles simply by their position in an elongated chamber called a "column still." In a column still, the liquid to be distilled remains in a column at the top of the unit, while steam heats the base or bottom of the still. This separation of heat—the hottest at the bottom and the coolest at the top—allows the spirit to separate leaving the methanol and other low-boiling substances in a vaporized state throughout all but at the top of the column (Fig. 20.2) (Plutowska et al., 2010).

In this way, each fraction can be separated out at different levels within the column in a continuous fashion.

20.1.4 FINISHING THE SPIRIT

Maturation and aging—once distilled, the base spirit tends to be colorless and in some instances a little rough around the edges. As a result, certain distilled liquors are aged or matured with differing periods for specific spirits. The process can range from no aging to aging for a few short hours, to months, and even years. The actual length of time required depends on a variety of factors, including the spirit involved and the flavor or type of spirit to be achieved by the distiller. If aged in barrels, there are several factors that affect the length of time involved. This applies especially to wooden barrels that are porous and effectively allow the liquor to breathe. Thus, it follows that the wooden barrel's external environment takes on greater importance, whether warm humid weather (giving rise to shorter aging processes) or, by contrast, cooler, less variable weather in say Scotland means longer maturation times before any perceptible changes in the spirit occurs (Lea and Piggott, 2011; Tippling Bros, 2017). Then, three is the oxygen and its oxidative effect; the size of the aging vessel; or the process involved in making wooden barrels vis-à-vis burning or heating the wood, toasting, charcoaling, etc. All these factors must be considered. In essence, then, it can be seen that as with other aged alcoholic beverages like wine and beer, aging spirits can also dramatically affect the complexity, flavor, and character of a spirit.

So-called white or clear spirits such as vodka and "eaux-de-vie" made from fruits are not generally aged (although they might well be flavored before bottling). Brown spirits on the other hand that include whiskies, rums, and brandies are so called because they are aged in wooden barrels, giving color and complex characteristic flavors from the extraction, absorption, and oxidation processes. The aging process also sees both water and alcohol evaporate from the liquor further concentrating the spirit in the barrel. In all cases, though, high-alcohol spirits are both chemically and biologically stable enough that they can be stored for years without spoiling (Lea and Piggott, 2011; McGee, 2004).

After aging, spirits are often blended and watered down to ensure consistency of quality and flavor. Sometimes, additives are also used to enhance particular traits expected of a certain spirit (Plutowska et al., 2010). Aside from the laudable aim of a consistent product, there is a growing market for single-cask spirits that relish and favor atypical characteristics like extra smoky flavors and other traits.

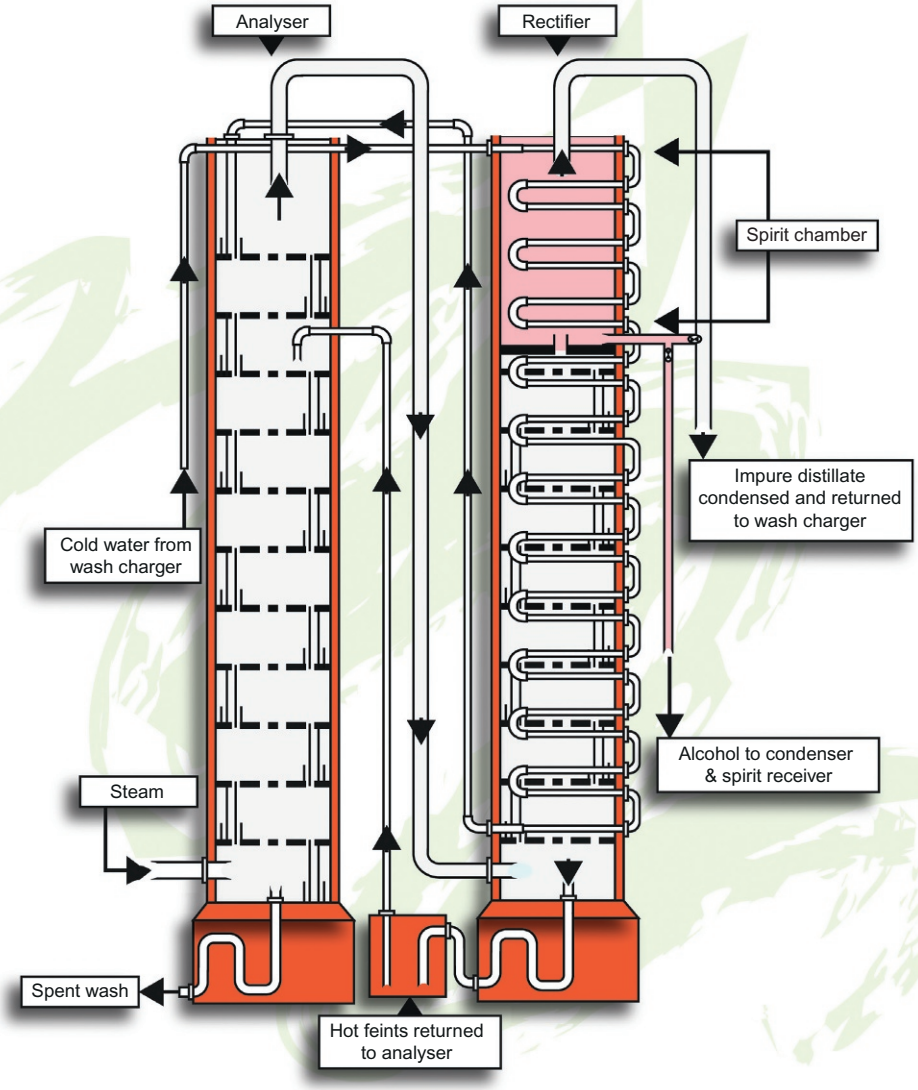


FIG. 20.2

A column still.

Filtration and chaptalization—in the distillation process, much of the congeners are left behind as the spirit is distilled. The more times a spirit goes through this process, the less the impurities. Another way of separating out unwanted impurities and the heavier fusel oils is to use filtration whether several feet of lightly condensed charcoal or other similar processes. Chaptalization is the process whereby extra sugar (either natural or artificial) is added to either to the fermenting mash or to the final product. This is undertaken in order not to add sweetness but rather to aid in the formation of more alcohol. It is also a process that is illegal in some countries around the world.

Dilution, flavoring, and coloring—if the final spirit is too rich in alcohol or if the product is a little unpalatable in its near finished form, then water may be used to dilute the spirit to address both these issues. This is also the point in which any flavorings are added that might include aromatic ingredients like bark or spices to spirits, thus adding flavor and smoothing out any harsh distillates. Compounding is one way to add flavor; this involves adding sugar solution to the spirit (bearing in mind the caveat mentioned above). Another way of adding flavor to a distillate is to use the spirit to macerate fruits and other delicate herbs and spices directly in the distilled spirit. This infuses the alcohol with fresh delicate flavors that would otherwise be destroyed or severely diminished if they were exposed to the heat of the distillation process. A similar method sees the spirit heated and percolated through a concoction of delicate fruit as well as herbs, plants, and spices. The process is similar to that of percolating coffee.

20.2 VARIETIES OF SPIRITS

Distilled spirits or just "spirits" made from all types of base ingredients are found worldwide where each is a characteristic of the region, method, and flavorings used (Table 20.1).

20.2.1 EAU DE VIE AND WHITE ALCOHOLS

There are many names used to describe spirits distilled from fermented fruits other than grapes—among them perhaps "eau-de-vie" is one of the most widespread. In these spirits, the liquor truly captures the concentrated and distinctive essence "of the fruits from which they're made" (McGee, 2004).

Table 20.1 Distillates—Origin and Base Ingredients

Base Ingredients		Spirits and Liqueurs
Grains	Barley, wheat, corn, rye, and other grains	Whiskey, vodka, arrack
Herbs, roots, and vegetables	Sugar cane	Rum, gin, vodka, arrack, cachaça
	Sugar beet	Rum, pinga
	Molasses	Rum, cachao
	Potato	Vodka
	Agave	Tequila
	Herbs and spices	Absinthe, blanca, aquavit
	Fruits and herbs	Benedictine, chartreuse
	Coffee	Jägermeister, Kahlúa
Fruits	Grapes	Brandies, cognac, armagnac
	Apples, pears	Calvados, Poire
	Plums	Schnapps, mirabelle
	Prune	Slivovitz
	Coconut flowers	Arrack
	Strawberry, raspberry	Framboise, fraise
	Cherries	Kirsch, schnapps, maraschino
	Apricot Pits, almonds	Amaretto
	Oranges	Cointreau

Adapted from Burroughs, D., Bezzant, N., 1990. The New Wine Companion. Heinemann Professional Publishing, Oxford and Cunningham, S.K., 2012. The Bartenders Black Book. Board and Bench Publishing.

Examples include Calvados (apple), Poire Williams (pear), Kirsch (cherry), Mirabelle (plum), Framboise (raspberry), Abricot (apricot), Boukha (figs from North Africa and Middle East). It may take up to 5–12 kg of fruit simply to make one bottle of eau-de-vie. Such alcohols are usually double-distilled until they reach approximately 70% (alcohol by volume—ABV); they are also not barrel aged. One notable exception to this is Calvados that is distilled from a blend of apple varieties too bitter or sour for eating. Instead, the fruit is fermented into cider after which it is then distilled. The apple distillate is then matured in old barrels for at least 2 years (Lea and Piggott, 2011; McGee, 2004).

20.2.2 VODKA

Vodka is a distilled alcoholic beverage (38% + ABV) made from grains or vegetables (or any other raw carbohydrates like potatoes, sugar beet, and corn for that matter). Vodka is one of those spirits in which the delicate flavor of the base ingredient used may or may not be tasted in the final product. It is almost always sold unaged, and today's vodka is considered one of the purest forms of distilled spirit available (Tippling Bros, 2017; Encyclopaedia, 2001). However, this was not always the case as early pot-distilled vodkas of Polish, Russian, and Scandinavian origin were poorly produced, being fiery and reminiscent of oily fusel oils; that was, until filtration was introduced. In modern times, many vodkas are now being sold flavored, but this is not something new; indeed historically, the Russians and Polish have been flavoring vodka with all manner of products from carrots to chocolate, fresh herbs, etc. for hundreds of years. Unfortunately, modern flavored vodkas are seasoned in a number of artificial ways although that said, there are the true artisans who insist on using all natural ingredients (Lea and Piggott, 2011; Tippling Bros, 2017).

20.2.3 GIN

There are essentially five types of distilled gin made today—London Dry, Plymouth, Old Tom, German, and Dutch. Traditionally, originating from Holland, the Dutch process involves distilling a fermented mixture of malted barley, corn, and rye several times in pot stills. The mixture is then distilled one final time in which it gets its final distinctive flavor from the botanicals that it is added in the last distillation process. Some common ingredients added at this last redistillation include juniper berries, coriander, cassia bark, and angelica root. The mix is then distilled until it reaches an alcoholic content of about 37.6% (ABV) The final product is full-bodied and reminiscent of the aromatic herbs and spices used and is sold unaged or on occasion aged (Lea and Piggott, 2011). London Dry gin on the other hand often starts with a neutral base that contains more grain (corn) or molasses than other gins and is generally column distilled several times reaching alcohol levels of up to 190 proof (96% ABV). This particular incarnation possesses stronger juniper flavors and aromas and is bottled—diluted if necessary until the required alcohol content settles at between 37.5% and 47% alcohol by volume. Another British method of producing gin is called the Plymouth style. Firstly, according to legislation, Plymouth gin must be produced in Plymouth using wheat and soft local water. Flavor-wise, while a little sweeter, nevertheless tends to be a little more nuanced than London Dry gin. Another, Old Tom gin, is a sweetened style of gin that after losing popularity is now making a comeback in Europe and the United States. Lastly, German gin is tripled distilled and flavored with juniper berries. In nearly all cases, the primary aromas arise from the terpene aromatics (pinene, limonene,

linalool, and myrcene) displaying aroma and tasting notes of spices, herbs, especially those of pine, citrus, flowers, and wood (Tippling Bros, 2017; Plutowska et al., 2010; Lea and Piggott, 2011).

20.2.4 AQUAVITS

While, initially, aquavits were produced in Scandinavian countries, they are now made all around the world. Aquavits are most commonly distilled from potatoes although other grains might be used. Aquavit is usually distilled into a neutral alcohol using two distillations after which it is then distilled for a third time with aromatics such as anise and caraway, although other flavorings are occasionally used (Tippling Bros, 2017). As a result, they bear some resemblance to gin. Popular in cocktails, aquavit has waned in popularity until, that is, the more recent past where it is making something of a comeback (Lea and Piggott, 2011; McGee, 2004).

20.2.5 GRAPPA, MARC

These are spirits distilled from the pomace[7] of grapes usually (Grappa and Marc), although other pomace distillates use various other types of fruits. As a spirit or wine is made, the remaining pomace still contains ample sugar, flavor, and characteristics of the grape for instance. This is then given another fermentation (with added sugar if need be) generating flavors that can be concentrated through the distillation process. Pomace distillates were originally a by-product often distilled without condensing out the heads and tails, giving grappas and marcs a strong and often harsh edge to them (Lea and Piggott, 2011; Porto, 1998). In recent decades though, the image of these pomace spirits is changing, becoming refined and something to savor as producers become more selective in the process while sometimes aging the distillates to further enhance the quality of the beverage. The names grappa and marc are the Italian and French names for the final distilled spirit (Tippling Bros, 2017).

20.2.6 JAPANESE SHOCHU

Japanese shochu is a clear spirit produced using a diverse set of ingredients that includes rice, sweet potatoes, barley, among others. The spirit is deliberately distilled in a single pot distillation at lower proofs in order to preserve the unique character of the base ingredient(s). A key difference between these and vodka production is the fact that the grains are malted using the koji—a starch-digesting mold—to convert grain starches into glucose that the yeast requires for the fermentation process (Lea and Piggott, 2011; Tippling Bros, 2017).

Other white spirits from the same stable as those shown above include American Moonshine, Bier schnapps, German Korn, Irish Poitín, Okinawan awamori, and Schnapps.

[7]A pomace is the pulpy residue remaining after fruit has been crushed in order to extract its juice, that is, skins, seeds, and stems.

20.2.7 RUM

Rum gets its name from Latin word for sugar *Saccharum*, and originally, it came about as a by-product of sugar making. It is popular all around the world, and as the Latin name suggests, it is distilled from fermented sugar cane or molasses. Rum can be classified as light, dark, or simply flavored. There are two particular styles of rum—the modern "light" style and traditional rums. The modern "light" style is produced through the fermentation of a molasses solution using yeast for 12–20 h. It is then distilled in a continuous still until it reaches about 95% alcohol, after which time it is aged for a few short months in order to eliminate or mellow the rough edges in the flavor. It is then bottled at around 43% alcohol. Lighter rums are generally given shorter aging times in barrels and are then filtered through charcoal to remove any color.

Traditional rums on the other hand are produced very differently resulting in darker colors and stronger flavors. Nowadays, most traditional rums are fermented for between one and two days with mixed yeast cultures dominated by the *Schizosaccharomyces* strain. This particular yeast produces an abundance of esters. The mix is then pot-distilled to a lower alcohol content, which as a result ends up with about four- to fivefold in number of the aroma compounds compared with light rums. The resultant spirit is then aged in wooden casks introducing most of the spirit's color. Caramel is also sometimes added to aid the depth of color and flavor. Lastly, rum is one of two types of spirits that can be sold aged or unaged (Lea and Piggott, 2011; Tippling Bros, 2017).

20.2.8 TEQUILA AND MESCAL

Tequila is a distillate made from the aguamiel (honeyed water) of the blue agave plant from the lily family (Agavaceae), which incidentally resembles a cactus—hence the oft misunderstanding that tequila is the product of cactus. Like Scotch whisky, Cognac, and others, tequila is a product of a particular region in Mexico and is governed by specific legislation that dictates that the spirit is made with at least 51% blue agave; otherwise, it is considered mescal. Furthermore, any tequila that is not produced using 100% blue agave is then considered a mix too. The plant's carbohydrate comprises simple fructose and long fructose chains called inulin. However, because we lack specific enzymes for digesting inulin, inulin-rich foods like the blue agave are first cooked to render the inulin down to its component sugars before the process of fermentation begins (Lea and Piggott, 2011).

Made in one of two ways, tequila is produced either using the cooked heart of the agave plant called the piña[8] or by augmenting the natural agave plant sugars with a mixture of other sugars in order to create the ferment. There are three types of tequila classification:

- *Blanco* (white, silver, or plata)—this type is either legally aged in oak for up to 30 days, but more often, it spends 60 days in stainless steel vats. In either case, it must be bottled within 60 days of being produced
- *Joven abocado* (gold)—it is young and unaged; this type of tequila gets is flavor and color from added caramel. This type is generally always mixto.

[8]Piña is often roasted in earth or stone pits, giving them their distinctive smoky character.

- *Reposado* (rested)—rested tequila is aged from 2 to 11 months in oak (typically used Cognac or bourbon barrels). Aging results in a mellow, easier on the palate than blanco tequila.
- *Añejo*—it is matured/aged for at least 1 year or more in small oak barrels, while extra añejo is a blend in which the youngest tequila must be aged for at least 3 years minimum.

20.2.9 BRANDY

Cognac and Armagnac are two famous brandies distilled from white grape wines. The better brandies are distilled first because, as the white wine ages, it loses esters at the same time as developing a certain acidity. Cognac is double-distilled (with yeast) reaching an alcohol content of about 70%, while most Armagnac is single distilled (without yeast) until it reaches about 55% (McGee, 2004). Both are then aged in oak barrels for a minimum of 6 months although some Cognacs can be aged for as long as 60 years or more. After aging and before bottling, both Cognacs and Armagnacs are diluted to approximately 40% alcohol by volume. While it is said that Cognac possess a fruity-cum-flowery character (due to the distillation of esters), Armagnac tends to be rougher and more complex on the palette—in no small part to the higher content of volatile acids (Tippling Bros, 2017; Lea and Piggott, 2011; McGee, 2004). In both cases, however, longer aging tends to develop certain rancid notes as the conversion of fatty acids to methyl ketones takes place (Plutowska et al., 2010).

20.2.10 WHISKIES AND WHISKEYS

There are many types of whisky/whiskies (the United Kingdom) and whiskey/whiskeys (elsewhere). Among the better known and more popular are the Scotch, Irish whiskey, and the American Rye, Tennessee, and Bourbon whiskeys.

Scotch whisky/whiskies—Scotch whisky from the European's point of view is simply (and legislatively) a whisky that has been produced in Scotland while observing the rules set forth in the Scotch Whisky Regulations act of 2009 (Crown Publications, 2009). Essentially, there are two types of Scotch whisky: single-malt Scotch and single-grain Scotch. From these two basic types, all Scotch blends are made. Single malt Scotch is produced from water and malted barley at a single distillery through the batch distillation process using pot stills. Single grain Scotch, while also distilled at a single distillery, uses, in addition to water and malted barley, other whole grains of other cereals—malted or otherwise (Tippling Bros, 2017; Crown Publications, 2009). From these two base spirits come the blended Scotch whiskies. A blended malt Scotch is strictly a blend of two or more single-malt Scotch whiskies originating from different distilleries, while blended grain Scotch is a blend of two or more single-grain Scotch whiskies from different distilleries. Blended Scotch whisky on the other hand is a blend of both single-malt and single-grain whiskies (Fig. 20.3).

Scotch is fermented only through the addition of yeast and distilled to an alcoholic strength not exceeding 94.8% by volume. It is then aged in barrels with the addition of water and caramel coloring for a minimum of 3 years. After this, it can be diluted to taste—albeit retaining a minimum alcoholic content of no less than 40% alcohol by volume (Crown Publications, 2009). Lastly, the stated age of blended Scotch whiskies signifies the youngest scotch in the mix.

American whiskey/whiskeys—there are several different types of whiskeys produced in the United States; a few are described in the following section.

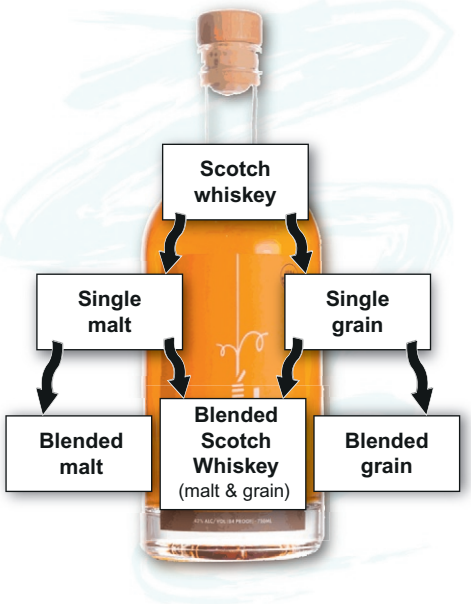


FIG. 20.3

Types/categories of Scotch whisky.

Bourbon—although it takes its name from Bourbon County, Kentucky, bourbon can in fact be made anywhere in the United States as long as the legal minimum of 51% corn (maize) is used in the mash. That said, it is not uncommon for many producers to use as much as 80% corn. In most cases, too, between 5% and 15% of malted barley is added in the fermentation process with either rye or wheat making up the remaining mash. This mix is then fermented for between 2 and 4 days after which time the mash (grain residues and yeast too) are column distilled. To be called "straight" bourbon, the whiskey must be matured or aged for a minimum of 2 years in new, heavily scorched American oak barrels. This gives the bourbon a deep rich amber color. Younger bourbons can be made, but they cannot be labeled straight bourbons. Lastly, unlike Canadian whiskeys or French brandies, American bourbon cannot be sweetened, flavored, or otherwise colored; in fact, the only permissible addition is water, and the required concentration of alcohol is 80 proof or 40% alcohol by volume (Pacult, 2016; Lea and Piggott, 2011; Tippling Bros, 2017).

Tennessee whiskey—as with Scotch whiskies, Tennessee whiskeys must be made in a specific geographic region—Tennessee. It is made with at least 51% corn and sometimes as high as 79%. The rest of the grain mix is often made up with malted barley, rye, or wheat. As with bourbon, Tennessee whiskey's aging requirements are the same at 2 years minimum. Furthermore, also in line with bourbon, there are no additives such as colorings and flavorings allowed except water. All Tennessee whiskey is twice filtered through charcoal—clarifying and shaping its flavor in a process known as the Lincoln County process (Pacult, 2016; Lea and Piggott, 2011; Tippling Bros, 2017).

Rye whiskey—rye whiskey must be made from a minimum of 51% rye. Other grains making up the mix include malted barley and corn. As with bourbon, "straight rye" must be matured in new, heavily

charred American oak barrels for at least 2 years. Also, if the spirit is aged for less than 4 years, it must be mentioned as such on the bottle. Lastly, like bourbon and Tennessee whiskey, no flavors or coloring can be added to the distillate (Pacult, 2016; Tippling Bros, 2017).

20.2.11 BITTERS AND LIQUEURS, BITTERS AND OTHER FLAVORED ALCOHOLS

In deference to alcohol's peculiar chemical properties, that is, alcohol can resemble either fats or water in their behavior. As such, it becomes an outstanding solvent for other volatile aromatic molecules. Therefore, the ability of alcohol to extract and hold flavors from all manner of botanicals such as bark, leaves, herbs, spices, flowers, and fruit means that there are literally thousands of bitters and liqueurs on the market today (Tippling Bros, 2017). Most spirits of this nature fall into two categories: bitters, which are, as the name suggests, quite bitter, and liqueurs that are sweetened with varying amounts of sugar (Lea and Piggott, 2011).

Bitters—these can be thought of as the offspring of medicinal brews first produced from wine. These alcohols are complex mixtures that are made either by maceration of the plant material or through its distillation. Bitters are often added to other spirits in a condiment-like fashion creating a unique flavor profile quite often used as aperitifs and digestifs. Examples of bitters include Angostura (*Galipea cusparia*), Peychaud bitters, and others including Gentian (*Gentiana* species), Chinese rhubarb root, orange peel, wormwood, chamomile, saffron, and myrrh (*Commifera molmol*) to name but a few (Lea and Piggott, 2011).

Liqueurs—these, also known as cordials, are best described as sweetened alcoholic beverages into which flavorings like fruit, herbs, nuts, and spices as well as flowers or cream have been added. Flavorings may be added through soaking (macerating) the distilled spirit; alternatively, flavorings may also be distilled along with the alcohol itself. In either case, many if not most liqueurs use a neutrally flavored cane or grain alcohol as the base, but there are also some that use brandy or whisky. Well-known liqueurs include Irish cream, sambuca, Curaçao, anisette, Grand Marnier, Drambuie, Limoncello, Pernod, and Raki. Generally, the methods of production will vary greatly among the liqueurs.

20.2.12 MIDDLE GROUND—CHINESE JIU AND JAPANESE SAKE

One distinctive form of alcoholic beverages that do not fit neatly into any of the above categories are certain alcoholic drinks that originating from Asia—like Chinese jiu[9] and Japanese sake. These beverages when compared with traditional Western alcoholic drinks do not fit easily in either category of wines or beers for several reasons two of which are the base product used or the type of fermentation. Firstly, the two beverages' main ingredient is fermented starchy grains, usually rice. Secondly, the grains' starches are not fermented by grain enzymes into sugars as is the case with barley but rather using a specific mold that is introduced into the liquid. This mold works in unison with yeasts—as the starch is broken down into its sugar components by the mold, the yeasts convert the sugars into alcohol. As a result, the beverage can reach higher alcoholic concentrations—of up to 20% by volume (much stronger than traditional Western style unfortified wines and beers). Furthermore, because both are made solely from the starch of the grain and little else, sake in particular is thought of as the purest,

[9]Jiu is the Chinese word that refers to all alcoholic beverages. It is a word often mistranslated into English as "wine," whereas the meaning is more akin to alcoholic beverage or simply liquor. Interestingly, the same Chinese characters are used to describe jiu are also used in Japan where it is pronounced "sake" and in Korean where it is shortened to "ju."

unadulterated manifestation of the resultant aroma, flavor, and taste of the fermentation process itself, which according to McGee (2004) is "…surprisingly fruity and flowery even though no fruit or flower has come near it."

While the modernization of the production of jiu and sake has undergone something akin to a mini revolution in modern times, there are still numerous traditionalists who insist on using more traditional methods. Jiu made with rice, sorghum, millet, or wheat may very well be roasted or even left raw; however, most grains are usually steamed, ground, and shaped into cake-like bricks and left to mold for several weeks. This process allows the growth of *Aspergillus*[10] on the outside and *Mucor*[11] and *Rhizopus*[12] on the inside (Lea and Piggott, 2011).

By contrast, Japanese sakes are simply introduced to a single mold—*Aspergillus oryzae* (known as koji) that effectively breaks down the grain starches into sugar. Furthermore, as with jiu, a yeast starter (*Saccharomyces cerevisiae*) known as "moto" is added to the mix converting the newly made sugar into alcohol. Traditional moto is made through the addition of a starch-digesting mold, koji, together with the cooked rice and a mixture comprising mainly lactic acid-producing bacteria (*Lactobacillus sakie* and *Leuconostoc mesenteroides*) and others. To this is added a yeast culture that is allowed to multiply. However, this microbe-soured moto takes over a month to mature, so not surprisingly, it has to a large degree been replaced by the time-saving addition of organic acids and sometimes concentrated yeasts to the moto mash. As a result, it is left to the artisanal producer to make the traditional the more substantial, more complex sakes. Combined, this gives the consumer a broad range of sakes of various qualities (Kanauchi, 2013).

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[10]*Aspergillus* is the same type of mold used in the production of soybean sauce.
[11]*Mucor* is important in certain aged cheeses.
[12]*Rhizopus* is the major mold in soybean tempeh—soy product from Indonesia. It is made by natural culturing and controlled fermentation. This binds soybean into a cake form.

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PART

APPENDICES

3

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APPENDIX

DIETARY GUIDELINES

A

In recent times, obtaining a relative dietary balance of macro- and micronutrients has taken on more significance, and as has been mentioned, it is becoming commonplace to recommend a range of values over a single numerical requirement, instead. However, as of 2017, there is no single international standard on dietary guidelines. This is partly because the current practice is for most countries to establish their own appropriate nutrient guidelines at the government level. Having said that, there are three major international bodies that have attempted to put together comprehensive guidelines for a "general" figurative adult male and female. Not surprisingly, when comparing the three, there is a general lack of agreement on the fundamental requirements and a plethora of confusing nomenclature to boot. Thus, navigating a maze of variously described dietary guidelines (DG), dietary reference intakes (DRI), dietary recommendations (DR), and dietary reference values (DRV), among others (*see the coming sections*), can be detrimental to the point that determining suitable nutritional requirements is at best confusing and at times contradictory (Wilson, 2007; Doets et al., 2008; Rodriguez and Garlick, 2008; BNF, 2009; USDA, 2009; IoM, 2001; WHO, 2017).

The goals of all reference intakes (howsoever they are described) look to provide optimum recommendations for the various energy-giving nutrients and essential minerals and vitamins to aid in general health and vitality (WFP, 2009b). From a user's point of view, dietary guidelines (for want of a general "catchall") tend to be used as prescriptive rather than as recommendations. Although having said that, many guidelines specifically state that such recommendations are overarching, that is, they are prescriptive of a general population as opposed to individual requirements. Also, used by policy makers, they are employed for assessing, among other things, the adequacy of national food supplies in relation to nutritional planning and populations' needs (Weisell, 2002; Brooks et al., 2004). This means accurate and up-to-date information must be available, yet in this respect, while the data are there, it is not (in this author's opinion) adequately disseminated. Also, worthy of note is the fact that universal agreement is conspicuously lacking in the final values. Although, to be fair, there is a growing convergence of opinion on many of the most important nutrients, this often comes in a range of values as opposed to a single specific value (WHO, 2017). This is generally because of the heterogeneous[1] nature of populations and any recommended intake levels that might create balance in one person but may not do so in another. This results from any number of reasons, not least of which include an individuals' basal metabolic rate (BMR), age, gender, and the bioavailability of a specific nutrient, especially in its

[1]Heterogeneous populations are diverse, varied, disparate, and multifarious. This differing nature means recommended daily intakes of nutrients vary quite differently.

interactions with other nutrients. Having said that, there is surprisingly little overarching supporting scientific evidence, and sadly, the fallback position is that of the status quo (see Table A.14) (WFP, 2000; WHO/FAO, 2004; Bourne, 2002).

Calculating requirements are continually changing over time, and it must be noted that prescribing daily requirements is never going to be easy. Three reference value groupings—those of the United States, the UN, and the EU—are examined here. It is also important to note the respective vernacular of each institution/body—which is displayed under each heading.

A.1 UN (WHO/FAO): DIETARY RECOMMENDATIONS/NUTRITIONAL REQUIREMENTS

As mentioned, those countries that do not undertake measurements of dietary requirements for themselves tend to rely heavily on the World Health Organization (WHO) and the Food and Agriculture Organization (FAO) of the United Nations. If a country goes down this road, the dietary allowances are sometimes adopted "as is" or are simply used as guidance in their own national nutrient guidelines. As far as the FAO/WHO data go, it is usually compiled and updated every 10–15 years (WHO/FAO, 2004; WHO, 1996, 2017; FAO/WHO/UNU, 2004; WHO/FAO/UNU, 2007). In the latest report from the World Health Organization (WHO), Food and Agriculture Organization (FAO) of the United Nations, and United Nations University (UNU) group, their most recent recommendations (as of 2017) concerning vitamin, mineral, and energy requirements are still based on the findings published in the 2004 report, while some trace elements of the latest report remain the same as those of 1996.

In the World Health Organization's (WHO) vernacular, the following terminologies are used:

A.1.1 MACRONUTRIENTS (ENERGY)

- *Energy requirements (ER)*: often referred to as daily requirements (DR) or recommended daily intakes (RDI). These are calculations of energy needs based on a balance between energy input (food) and energy expenditure.
- *BMR/PAL*: the basal metabolic rate (BMR) and physical activity level (PAL) determine the amount of calories required on a daily basis; in addition to the set values, there are certain provisions in any allowances for growth, pregnancy, or lactation (FAO/WHO/UNU, 2004). Calculations on energy expenditure are also broken down into their various basic component parts (i.e., carbohydrates, proteins, and fats) and given a range of values as a percentage of total energy requirements.

A.1.2 MICRONUTRIENTS

- *Estimated average requirement (EAR)*: this is the estimated daily average nutrient intake needed to meet the needs of at least half the healthy population (WHO/FAO, 2004).
- *Recommended nutrient intake (RNI)*: the RNI is based on the EAR, and its values are set at EAR figures plus two standard deviation (SD) points. Or if these data are absent, then EAR plus about 10%–12.5% is used. This value is anticipated to meet at least 97.5% of a healthy population's requirements.

- *Protective nutrient intake (PNI)*: the notion of protective nutrients is those intake guidelines of the RNI that is thought to guard against public health risks (WHO/FAO, 2004).
- *Upper tolerable limits (ULs)*: these are used to denote the absolute maximum intake of micronutrients that will likely not pose any adverse health risks in almost all (97.5%) "apparently" healthy individuals.

A.2 EU: DIETARY REFERENCE VALUES (DRVS)

The European Union (EU) via the European Food Safety Authority (EFSA) is the body responsible for general dietary guidelines within the EU. Although having said that, many countries still produce their own guidelines independent of or at least based on these general recommendations. The latest dietary reference values (as of 2017) are those updated in 2006 (EFSA, 2008, 2009, 2010a; SCF, 1993). Within the EU's overall dietary reference values (DRVs), there are six reference values to be considered:

A.2.1 MACRONUTRIENTS (ENERGY)

- *Recommended intake ranges for macronutrients (RI)*: these are the suggested energy requirements expressed as a range of tolerable values based on a percentage of overall energy intake (EFSA, 2008).

A.2.2 MICRONUTRIENTS

The EU micronutrient vernacular is as follows:

- *Lowest threshold intake (LTI)*: this value is the intake below which most people will not be able to maintain their body's metabolic integrity.
- *The average requirement (AR)*: this is the average (assuming a normal distribution curve) of nutrient requirements that satisfies half a population's needs.
- *Adequate intake (AI)*: this value is used when PRI is not available or cannot, with any great certainty, be reasonably established. Such values in cases like this are based on empirical studies and understood to be adequate.
- *Tolerable upper intake level (UL)*: this is thought to be the maximum daily intake levels unlikely to pose any adverse health risks (EFSA, 2008).

A.3 US: DIETARY REFERENCE INTAKES (DRIS)

In the United States, dietary guidelines are those proposed by the Institute of Medicine (IOM) of the National Academy's US Food and Nutrition Board (FNB). The FNB provides judgements based on the relationship between food, health, and nutrition (USDHHS/USDA, 2005; NAS, 2017). Originally called "recommended dietary allowances" (RDAs), the recommendations have been renamed the dietary reference intakes (DRIs), the latest of which (as of 2011) are those for 2005 (IoM, 2005). The DRIs are a collection of references for both macro- and micronutrients. In the US vernacular, the following terminologies are also used.

A.3.1 MACRONUTRIENTS (ENERGY)

In the case of nutrients for energy, that is, carbohydrates, fats, and proteins, recommendations from the United States are based on average requirements:

- *Estimated energy requirement (EER)*: this is the average dietary intake required to maintain equilibrium in terms of energy. Within the Institute of Medicine (IOM) of the National Academy's US Food and Nutrition Board (FNB), necessary macronutrient intake is calculated solely based on estimated energy requirements (EERs), and no provision is made for any recommended dietary allowance (RDA) (IoM, 2005).

A.3.2 MICRONUTRIENTS

In regards to micronutrient recommendations, the United States uses four reference values:

- *Estimated average requirement (EAR)*: this measurement is in line with the UN/FAO as EAR considers the daily intake of nutrients expected to provide half a healthy population's requirement.
- *Recommended dietary allowance (RDA)*: this is the average daily intake sufficient to meet the nutrient requirement of approximately 97%–98% of a healthy group individuals.
- *Adequate intake (AI)*: in the absence of any shortfall in knowledge, the RDA determines an adequate intake recommendation based on empirical data.
- *Tolerable upper intake level (UL)*: this metric reflects the highest perceived daily intake likely to pose no adverse health risks to nearly all (97.5%) individuals (IoM, 2005).

So as can be seen from the above foray into just three bodies, there are numerous dissimilarities in terms of categories of dietary reference values. That said, while they collectively might seem a little confusing, putting it in perspective, the following table (Table A.1) shows that there are in fact sufficient similarities so as to be able to make objective comparisons.

Determining adequate energy requirements for groups or individuals has been no mean task that draws on over a century of empirical research (Gibson, 2012). For now, however, a brief appraisal of the various challenges, measurements, and calculations of the various components of energy requirements is looked at.

Table A.1 Comparative of Important Nomenclature of Macro- and Micronutrient Guidelines

		Micronutrients			
		Low	Ideal		
Institution/Body	Macronutrient Energy	50%	97.5%	Upper Safe/Protective Levels	
FAO/WHO Dietary recommendations	ER	EAR	RNI		UL
The United States Dietary guidelines	EER	EAR	RDA	AI[a]	UL
EU Dietary reference values	RI	AR	PRI	AI[a]	UL

[a]*Adequate intake is used as a reference figure when no ideal value is present; note—it is not the same as a recommendation.*
Source: EFSA, 2010d; WHO/FAO, 2002a; NAS, 2017.

A.4 MACRONUTRIENTS: ENERGY REQUIREMENT GUIDELINES

Macronutrients, as the name suggests, are those nutrients that are required in large measures. As such, most nutritional guidelines generally comprise a component of energy intake in the form of carbohydrates, fats, or proteins—often referred to in various terms such as "average energy requirement." Such requirements are usually summed up in total calorie intake for a reference man or woman of a particular age, living a particular lifestyle in order to maintain long-term good health. However, one must also understand that the fundamental goal of these requirements is to achieve harmony or balance; that is to say, total energy intake should be balanced by the total energy expenditure (IoM, 2005; FAO/WHO/UNU, 2004). Furthermore, when calculating energy requirements, special consideration is given to those with special needs, such as those with extra energy needs like infants, growing children, and pregnant and lactating mothers (Shetty, 2005). The challenge begins with just how one determines or measures the critical energy requirement below which a person is considered to be "underprovided." The main debate in this regard is whether or not there exists a single measurement of good nourishment or whether there should be varying measures based on a range of different situations, that is, physical activity level, age, gender, and body weight (Seckler, 1984; Osmani, 1987). In answer to this question, Svedberg echoes Payne and Cutler's idea of two opposing paradigms. In the first notion, the "genetic potential paradigm" (GP), an individual is suggested to have a single optimum state of nourishment that the body aims to achieve (Payne and Cutler, 1984; Svedberg, 2000). In the opposing "adjustment and adaptation paradigm," it is suggested that all individuals can achieve equilibrium of energy intake versus expenditure over a range of possible pseudo-optimal states whereby one

> can adjust his energy requirements through changes in his body weight and by varying his PAL in accordance with changes in his external environment without any harmful effects on health or functions
>
> **(Svedberg, 2000, p. 19).**

So, in answer to the question of an optimum state of nourishment, in the early stages of nutritional recommendations, the approach, over the years, tended to focus on calculating intakes that maintained a person's caloric equilibrium. That meant a single measure is given that ensures sufficient intake that an individual would neither lose nor gain weight. However, as suggested, contemporary wisdom takes the view that energy requirements be considered as a range of values (Warwick et al., 1988; Brooks et al., 2004; IoM, 2005; FAO/WHO/UNU, 2004). Indeed, this is backed up by evidence and borne out over numerous BMI studies over the years that indicate the need for a range of nutritional values in which a person can be in nutritional equilibrium. Today, this view is also adopted by the UN and many other institutions.

A.4.1 CALCULATING TOTAL ENERGY EXPENDITURE (TEE)

So, how does one go about determining a range or a set of values for nourishment of a heterogenous population? In short answer, there are certain considerations that must be factored into the equation, namely, the determinants of age and weight and living style must be taken into account. These can be summed up in three specific variables: a person's basal metabolic rate (BMR), their physical activity level (PAL), and the thermic effect of food (TEF). All this is required to determine the total energy

expenditure (TEE) measured in kcal/day of a person or a group of people (Shetty, 2005; FAO/WHO/UNU, 2004; WFP, 2009b; IoM, 2005):

- *Basal metabolic rate (BMR)*—this is best described as the required energy needed in order to maintain life at rest. In other words, it is the minimal energy required for basic essential bodily functions such as preserving core body temperature, breathing, eating, and sleeping. And as a major element of energy requirement, BMR can be as much as 60%–70% of total energy needs (Shetty, 2005; FAO/WHO/UNU, 2004)
- *Physical activity level (PAL)*—physical activity level is the most variable element of the three variables at hand. Sedentary individuals (those with very light activity rates) might require just one-third of total energy expenditure (TEE) to maintain a "light" lifestyle, while very active physical people might warrant twice the TEE (Shetty, 2005; FAO/WHO/UNU, 2004). Physical activity levels (PAL) then need to be calculated for various lifestyles and activity levels—this is the basis of the physical activity level index. The WHO/FAO commonly organizes PAL into three different typical or average days: sedentary (light activity), active (moderately active), and vigorous (vigorously active) types. The United States on the other hand describes four nutritional descriptors: sedentary, low active, active, and very active (FAO/WHO/UNU, 2004; IoM, 2005). Whichever system one uses in terms of PAL, it now becomes possible to assign energy values to each category. To do this, however, conventional wisdom determines energy requirements in terms of multiples of BMR that is calculated as a ratio of TEE/BMR (see factorial approach below).
- *Thermic effect of food (TEF)*—**as** well as BMR and PAL, the body also requires energy in order to digest (metabolize) the food it eats. This spent energy (calories burned) is termed "thermic" effect of food (TEF) and can, in overall energy required of the body, be as much as 6%–15% of total energy expenditure (TEE).

Many methods have been used to calculate total energy expenditure (TEE) needs over the years; previously, the most accurate was considered to be the use of calorimetry (the direct measurement of energy expenditure). However, direct measurement using this method is somewhat cumbersome and difficult, so indirect measures tend to be used instead. Two methods that are in common use today are the traditional factorial analysis approach (factorial approach for short) and the doubly labeled water method (DLW).

A.4.1.1 Factorial approach

The factorial approach looks to calculate overall TEE energy requirements through the aggregated measurements of BMR, PAL, and TEF. Nowadays, even in spite of numerous suggested alternatives, this method is still preferable in determining estimates of BMR using extrapolative equations based on height, weight, and age. This method espoused by Schofield's meta-analysis of 1985 (Schofield et al., 1985; Schofield, 1985) is considered by many to be a suitable proxy in the absence of direct or indirect calorimetric measures. Nowadays, it is also the adopted calculation used by FAO and others in predictive BMR calculations (Schofield et al., 1985; Woodward, 2003; Shetty, 2005; Wong et al., 1996). The next step in the factorial approach is to calculate PAL. The challenge here is we mentioned earlier that PAL can be thought of as light, medium, or heavy energy expenditure lifestyles. The reality however is the reality that an average person does not actively participate in say a medium physical activity level

Table A.2 Factorial Calculations of Total Physical Activity Ratio (PAR) for Sedentary or Light Activity

"Light" Sedentary Lifestyle	Time Allocation	Energy Cost	Time × Energy Cost	Mean PAR
Main daily activities				
Driving car to and from work	1	2	2	
Personal care (dressing, showering)	1	2.3	2.3	
Sitting (office work, merchandising, shop tending)	8	1.5	12	
General household duties	1	2.8	2.8	
Walking at varying speed without a load	1	3.2	3.2	
Eating	1	1.5	1.5	
Cooking	1	2.1	2.1	
Light leisure activities (watching TV, talking)	2	1.4	2.8	
Sleeping	8	1	8	
Total physical activity ratio	*24*		*36.7*	*24/36.7 =1.53*

Source: Compiled from Human Energy Requirements: Report of a Joint FAO/WHO/UNU Expert Consultation (Rome, 17–24 October 2001. Rome, FAO/WHO/UNU, 2004).

for the whole day. Instead, there will be moments, perhaps hours of light, medium, and/or heavy activity levels throughout the course of a single 26 h period. The answer is to break the day up into component parts each corresponding to fractions of light, medium, and heavy activity days. As shown in Table A.2, one can see the light sedentary group of activities as reported by the FAO for a typical "light" day that is somewhat mixed. So rather than attempting to negotiate a single "light" figure for the whole day, current practice is to provide fractional PALs based on considered activities within the whole day. Note here that the metabolic rate or the thermic effect of food (TEF) is already factored into the PAL equation. Collectively, this is called the physical activity ratio (PAR) and is a figure that collectively mirrors activity levels and the thermic effect of food. By calculating BMR and then multiplying it by the PAR ratio, one arrives at the total energy expenditure (TEE) requirements for the day.

A.4.1.2 DLW approach

The doubly labeled water (DLW) approach to calculating energy requirements builds on the work of Lifson's animal studies of 1966 in which heavy isotopic water was used to calculate energy requirements. This, as it turns out, is perhaps one of the most accurate means of testing energy needs in both animals and humans alike (Weisell, 2002; Shetty, 2005; Brooks et al., 2004). In this method, two nonradioactive forms of "heavy" water—the isotopes D_2O and $H_2^{18}O$ (deuterium and oxygen-18)—enter the body; their dilution from body fluids, like blood and urine, can be measured; and TEE can be quantified (Wolfe and Chinkes, 2005). This works on the basis that as concentrations of the isotopes in body fluids decline (through the sampling of saliva, blood, urine, etc.), CO_2 can be measured. This is an indirect form of calorimetry, and to adequately gauge, the CO_2 levels at least two measures are

required. The primary measure is taken once the isotopes have found equilibrium in the body, and in humans, another measure is taken up to 2 weeks or so later (Westerterp, 2014). The difference is then calculated, and because CO_2 is a product of the oxidative metabolization of fats, carbohydrates, and proteins, a measure of TEE can be accurately determined.

Being accurate and noninvasive, DLW is considered by many as the "gold standard" of total energy expenditure analysis, although it does have its detractors who see DLW as a complimentary technique rather than a methodology in its own right (Burrows et al., 2010). It also has its supporters; the Institute of Medicine (IoM) of The National Academies of Sciences, for instance, has since stopped using the traditional factorial approach in favor of DLW (NAS, 2017). Similarly, the WHO/FAO chooses to use the noninvasive DLW approach in their estimations for infants, children, and adolescents (FAO/WHO/UNU, 2004). Conversely, for men and nonpregnant and nonlactating women, the WHO/FAO prefers to employ the traditional method of calculating energy requirements through the tried and tested factorial approach. This, they cite, is despite a growing database of DLW figures, there still remain insufficient data from underdeveloped nations to allow for universal application (FAO/WHO/UNU, 2004).

Adults and children—Calculating energy requirements for adults, whether based on factorial analysis or the DLW approach, utilizes the BMR and PAL allowance. For infants (0–12 months) however it is based on weight and is expressed as energy requirements per kilogram per day. This is simply because there is a close connection between an infant's weight and its TEE. This is irrespective of the infant's age, gender, and body length. However, that is not all; these guidelines not only are based solely on body weight but also include a component taking into account extra energy for growth, that is, the deposition of tissue (FAO/WHO/UNU, 2004). Regarding children and adolescents aged between 1 and 18 years old, total energy needs are determined on comparable lines, that is to say, by utilizing a child's weight as the predictor of energy requirements. This is for the same reason as the infant's close correlation between weight and energy needs; the only other consideration taken into account for children is the adjustment needed for their weight-for-age. Children's energy needs are stated both as daily requirements in terms of overall millijoules (MJ) or kilocalories (kcal) per day and MJ or kcal per kg per day.

A.4.2 AVERAGE AND MINIMUM ENERGY GUIDELINES

It is significant that when talking of daily energy guidelines (macronutrient intake) versus daily micronutrient recommendations, one deals with the low end of estimated needs for macronutrients while the other offers a quota, based on daily needs plus two standard deviations the micronutrients. That is to say, in the daily energy recommendations, it is noted that any energy intake over and above the daily requirements would result in excess calories deposited as fat—stored energy. Put simply, excess calories equal excess fat (FAO/WHO/UNU, 2004).

While on the subject of energy requirements, another aspect worth consideration is the notion of recommendations below which the average person becomes undernourished. This is an important notion when considering a country or region's undernourished population. The nomenclature, as with all things nutritional, varies with, *inter alia*, institutions and their preferences. This notional cutoff point then is variously termed the "minimum dietary energy requirement" (MDER), the "minimum per capita calorie requirement" (MPCCR), etc. In establishing a baseline, both the FAO and the US Economic Research Service (ERS) differ slightly in their approach. The FAO calculates minimum daily food requirements for countries built on explicit demographic and physiological needs of the people

ranging from 1990 kcal in the likes of the Czech Republic and Estonia to as low as 1680 kcal for Ethiopia, Eritrea, etc. (FAO, 2011a). Although as an all-purpose figure that can be generalized to all people across all countries, the FAO suggests a minimum of 1800 kcal/day (FAO, 2011b), which by the way is also the same figure used, below which is their definition of hunger (SOFI, 2008; EarthTrends, 2010). The USDA's ERS in contrast uses a flat rate of 2100 kcal as their per person minimum energy requirement (Svedberg, 2002; Blössner and Onis, 2005; FAO, 2008; USDA/ERS, 2008). The following table (Table A.3) highlights the average and minimum requirements that the various organizations use in issues of nutrition.

A.4.3 A BALANCED ENERGY PORTFOLIO

As has been noted, it is not enough simply to ingest sufficient calories; rather, a balanced approach to energy intake is highly recommended by the three major dietary guideline providers (Table A.4). One of the difficulties regarding a person's variable energy source requirements relates to the preferential way the body utilizes the different macronutrients (carbohydrates, proteins, and fats). In determining suitable carbohydrate, protein, and fat balances, it is indeed a complicated but necessary process as potential imbalances can turn out to be costly not only from a personal perspective but also in terms of public health (WHO/FAO/UNU, 2007; WFP, 2009a). On average, we can say that carbohydrates and proteins provide approximately 4 kcal/g each while fats provide as much as 9 kcal/g. Taking this into account, it has been noted that the world's nutrition is not particularly well balanced (WHO/GHO, 2010; WHO, 2017). In some cases, carbohydrates provide up to 80% of energy requirements, while in others, over 35% of fat supplies the energy calories one needs. The question then is what are the suggested balances and who determines these levels? In answer to this, all countries design their own, well, many do. Others are derivatives of the three main international agencies: the World Health Organization, the Institute of Medicine's National Science Academy via the US Department of Agriculture, and the European Union, while others still use the three main body's recommendations in their entirety. Looking at Table A.4, it can be seen that even these, the top worldwide institutional guidelines, highlight disagreement among the various bodies.

Establishing a relational dietary balance of macronutrients these days has taken on more importance, and as has been noted, it has become commonplace to recommend a range of values instead of a single quantitative requirement. Lastly, while we have highlighted the various disparities between the main agencies, Table A.4 shows that despite general differences, there does appear to be some convergence on the relative standing of each of the macronutrients.

A.5 MICRONUTRIENTS: THE SMALL STUFF

While macronutrients deal with the nutrients required in bulk, the micronutrients and trace elements deal with the smaller intake requirements. However, much of the same contradictory and competing information exists in the micronutrient world too. We will first take a quick look at the various vitamins, their chemical names, and where they can be found, before moving onto the minerals and trace elements and exactly what they are needed for. For the sake of clarity, the micronutrient vitamins are dealt with before an examination of the mineral-based micronutrients as discussed in Section A.5.2.

Table A.3 Varied Institutional Average and Minimum Energy Requirements (kcal)

Body	Reference	Average Intake (kcal)	Minimum Intake (kcal)	
WHO/FAO				
Industrialized nations	Men (age 18–29.9, 70 kg)	2550–2800[a]		
	Women (age 18–29.9, 60 kg)	2000–2200[a]		
Developing nations		Year		
		1996[b]	1996[b]	2009[c]
Sub-Saharan Africa (SSA)		2100	1800	1760
Middle East[i] and North Africa (MENA)		2150	1840	1835
East and Southeast Asia (EA, SE)		2220	1880	1812
South Asia (SA)		2110	1790	1768
Latin America and the Caribbean (LAC)		2200	1870	1833
	Regional average	**2156**	**1836**	**1802**
FAO all country minimum requirement + FAO hunger definition[e]			1800	
WFP Full Food Ration		2100[d]		
European EFSA[f]	Men and women	2000–2600		
US USDA[g] Domestic	Men (age 19–30, 70 kg)	2400		
	Women (age 19–30, 57 kg)	2000		
USDA[h] All developing nations			Approx. 2100 cal	

[a] *Based on sedentary or "light" physical activity levels (PAL) (FAO/WHO/UNU, 2004).*
[b] *Regional figures are found in the Sixth World Food Survey of the FAO (1996).*
[c] *Updated minimum kcal requirements for countries are offered as of 2009 starting from 1680 to 1980 kcal per person; however, regional aggregations have not been published; instead, estimated calculations based on such data show parallels with average decreases for each region of just under 2% (FAO, 2011a).*
[d] *The FAO denotes that daily requirements on average should be no less than 1800 kcal per day—below which, incidentally, is also FAO's threshold of hunger (FAO, 2011b; EarthTrends, 2010).*
[e] *The World Food Program's (WFP) emergency food ration equates to 2100 kcal per day (WFP, 2009b, 2011).*
[f] *European Food Safety Authority (EFSA) figures (EFSA, 2013).*
[g] *This calculation represents the sedentary PAL of a reference man and woman of 70 and 57 kg, respectively (USDHHS/USDA, 2005; IoM, 2005).*
[h] *The USDA, the Economic Research Service (ERS), and the USAID employ an average "minimum" energy requirement for each country averaging around 2100 kcal/person/day in all developing countries studied.*
[i] *Middle East—formerly Near East.*
Source: Compiled from multiple sources including Naiken, 2002; WHO/FAO, 2004; EFSA, 2009; USDA/ERS, 2008; USAID, 2009; Meade, 2010; and SCF, 1993.

Table A.4 Energy Balance Portfolio for Optimum Health

Dietary Factor	Institution		
	WHO/FAO	USDA	EU
Total carbohydrate of which are free sugars	55%–75% >10%	45%–65%	45%–60%
Total fat	15%–30%	20%–35%	20%–35%
Saturated fatty acids	<10%	<10%	As low as possible while maintaining a nutritionally acceptable diet
Polyunsaturated fatty acids (PUFAs)	6%–10%	5.6%–11.2%	No DRV[b]
n-6 Polyunsaturated fatty acid (PUFA) (linoleic acid)	5%–8%	5%–10%	No DRV[b] (AI 4%[c])
n-3 Polyunsaturated fatty acid (PUFA) (α-linolenic acid)	1%–2%	0.6%–1.2%	No DRV[b] (AI 0.5%[c])
Trans fatty acids	<1%	<300 mg	As low as possible while maintaining a nutritionally acceptable diet
Monounsaturated fatty acid (MUFA)	By difference[a]		No DRV[b]
Protein	10%–15%	10%–35%	0.83 g protein/kg body weight = 52–62 g/day[d]
Cholesterol	<300 mg/day	<300 mg/day	No DRV[b]

[a] *EU's figures are largely based on European Food Safety Authority recommendations (EFSA).*
[b] *It was decided not to propose a reference value for cholesterol beside the limitations set for saturated fatty acids (SFA).*
[c] *When there is insufficient evidence for a recommended DRV value, the EU suggests an AI value (adequate intake), although that said AI's are not considered de facto recommendations.*
[d] *Based on 62.1–74.6 kg for females/males, respectively, further, European dietary surveys show the average protein varies between about 12% and 20% of total energy intake.*
Source: Compiled from multiple data sources: WHO, 2017; USDA, 2010; EFSA, 2010c; EFSA, 2012; IoM, 2005; WHO, 2010; WHO/FAO, 2003; WHO/FAO/UNU, 2007; EFSA, 2010b; EFSA, 2008.

A.5.1 VITAMINS

Vitamins are nutrients, more specifically organic compounds, that humans require to function properly. The difficulty is that humans cannot synthesize vitamins, so they obtain them through the food one eats or through supplements. There are 13 vitamins that are essential to the body—4 fat-soluble vitamins (A, D, E, and K) and 9 water-soluble vitamins (8 B vitamins and vitamin C). The fat-soluble vitamins are mainly found in fatty foods such as milk, cheese, other dairy foods, eggs, meat, and oily fish; in vegetable oils; etc. However, fat-soluble vitamins not only are available in apparent fatty foods but also can be found in fruits and vegetables especially orange colored examples (carotenoids), dark leafy greens, seeds, and nuts, as well as turnips or beet greens. Because these vitamins are fat-soluble, one does not need to ingest them daily as excess vitamins of this group are stored in the human liver and fatty tissues for later use. Water-soluble vitamins on the other hand are not stored in the body and must be ingested regularly as excesses pass through the body, excreted in feces, sweat, urine, etc. Water-soluble vitamins are to be found in leafy vegetables, whole grains, nuts, seeds, dairy products,

meat and fish, and many fruits (Harvard Medical School, 2009). These are discussed in more detail—first the fat-soluble vitamins followed by the water-soluble vitamins.

Vitamin A is a fat-soluble vitamin also known as retinol and includes retinoids, the most important of which is retinal, which is the chemical basis of vision and provitamin A (vitamin A precursors), which simply means they can easily be converted into vitamin A in the body. Several provitamin A carotenoids, α-carotene, β-carotene, and β-cryptoxanthin, can be readily converted by the body to retinol (vitamin A). Various other vitamers (chemically and molecular similar compounds) are the retinoids (retinal, retinoic acid, and retinyl esters), which are all useful within the body (Table A.5).

A.5.1.1 Vitamin D

Vitamin D denotes a group of fat-soluble types of steroid that aids in the intestinal absorption of certain minerals like calcium, iron, magnesium, phosphate, and zinc. In humans, an important source of vitamin D is obtained directly from sunlight where vitamin D precursors form under the skin; at this point, it is biologically unavailable to the body. It is made bioavailable through enzymatic conversion (hydroxylation) of the steroid-like compound. However, the average person's exposure to sunlight is usually insufficient for daily dietary needs, so the rest must be ingested (Table A.6).

Table A.5 Vitamin A—Characteristics, Function, and Sources

Vitamin	Chemical Name(s)	Characteristics/Function	Sources
Vitamin A	Retinol	Vitamin a helps cells reproduce normally—differentiation. It is almost one of the most versatile vitamins, essential for vision, that is to say, the neural transmission of light to the brain. It also plays a key role in the immune and reproductive systems, especially in developing fetus. Vitamin A is also of use in the health and vitality of epithelial cells, that is, the skin, membrane, and soft tissue. It is also found to be beneficial to the growth of the body and bone formation, as well as reproduction and the healing of wounds	Vitamin A is derived from both animal and vegetable origin. In animals and animal products, retinol can be found in meat, milk, eggs, cheese, cream, the kidneys, the liver, cod and halibut, and other fish oils. Vitamin A can be found in vegetables too, especially via the carotenoids and particularly through beta-carotene—the most commonly consumed form of provitamin A. Beta-carotene is the orange, yellow pigment found in oranges, pink grapefruit, apricots, cantaloupe, carrots, pumpkin, and sweet potatoes and the dark green pigment originating in spinach and broccoli, as well as most dark green leafy vegetables. As a very general rule, the stronger the pigmentation, the greater the vitamin A content. Vegetable sources of beta-carotene have one overriding advantage in that they are generally low or free of fat and cholesterol

Source: Compiled from multiple sources: WHO/FAO, 2004; MedlinePlus, 2010; Britannica, 2009; FSA, 2010; Harvard Medical School, 2009; UMMC, 2017.

Table A.6 Vitamin D—Characteristics, Function, and Sources

Vitamin	Chemical Name(s)	Characteristics/Function	Sources
Vitamin $D_{1,2,3}$	Ergocalciferol cholecalciferol	Vitamin D is required by the body in order to maintain and regulate balanced levels of minerals like calcium, phosphate, and others in the blood. The minerals in turn are needed for a variety of jobs including the mineralization of bone, muscle contraction, nerve conduction, and skin and all round good cellular functioning. Furthermore, vitamin D also helps moderate cell-cycle proteins, which in turn control cell proliferation and differentiation	Dietary vitamin D is only found in a small number of foods. These include the liver, oily fish, oysters, eggs, cheese, butter, fortified milk, and cream, as well as fortified cereals

Source: Compiled from multiple sources: FSA, 2010; MedlinePlus, 2010; WHO/FAO, 2004; Harvard Medical School, 2009; UMMC, 2017.

A.5.1.2 Vitamin E

The vitamin E family is major dietary fat-soluble organic components; the family comprises eight different compounds—four tocotrienols (alpha, beta, gamma, and delta) and four tocopherols (alpha, beta, gamma, and delta). They all have antioxidant properties that help neutralize unstable molecules that might damage the body's cells (Table A.7).

Vitamin K is a group of fat-soluble, structurally similar vitamins that are synthesized by plants and the bacteria that line the gastrointestinal tract. They are involved in blood clotting, prevention of blood vessel mineralization, bone metabolism, and regulation of various cellular functions (Table A.8).

Vitamin B complex vitamins despite being chemically different are nevertheless similar in many aspects of their biological and physiological functioning. These include but are not limited to their coenzymatic capacities. In fact, perhaps the most significant of their duties is that all the B vitamins aid the body in converting the food in the form of carbohydrates that we eat into glucose fuel. The B complex vitamins, as they are sometimes called, also help in the metabolism of fats and protein and being useful cofactors in the body's chemical reactions, etc. Indeed, in these respects, the vitamin B family often overlaps somewhat in their duties. They are all water-soluble and often coexist in the same food groups, and lastly, grouped together, they also help the nervous system to function properly (LPI, 2017) (Table A.9).

Choline is not strictly a vitamin; it is a vitamin-like essential nutrient. Although the body can synthesize choline in small quantities for bodily maintenance of health, it must be ingested from the diet to preserve adequate levels. It is also involved in many physiological processes from metabolism, through transport of lipids, to neurotransmitter synthesis (Table A.10) (LPI, 2017).

Vitamin C is a water-soluble vitamin that the body cannot synthesize and is needed for healthy growth and development. Vitamin C is also an enzyme cofactor and an important electron donor while also being a strong protective nonenzymatic antioxidant. In fact, vitamin C can help protect the body's

Table A.7 Vitamin E—Characteristics, Function, and Sources

Vitamin	Chemical Name(s)	Characteristics/Function	Sources
Vitamin E	Vitamin E is a family of eight organic compounds that include four tocopherols (alpha, beta, gamma, delta) and four tocotrienols (alpha, beta, gamma, delta)	Vitamin E plays a central role in the formation of red blood cells, although the vitamin's primary role is as an inhibitor of cellular oxidation. Just as importantly, vitamin E is also an antioxidant that protects the body from both endogenous (within the body) and exogenous (from outside the body) free radicals[a]. Lastly, vitamin E group also aids the body to utilize vitamin K	Vitamin E is found in animal fats and vegetable oils including palm, rice, and bran nut oils. Other goods include nuts and seeds, soya beans, egg yolks, chickpeas, red peppers, avocados, carrots, parsnips, sweet corn, olives, tomatoes, sweet potatoes, watercress, spinach and other green leafy vegetables, parmesan, cheddar, wheat germ, and oatmeal

[a]Free radicals—normally, atomic bonds do not easily split leaving atoms or groups of atoms with an odd, unpaired electron. But when it does, they are called free radicals. They can be formed naturally in the body as part of the metabolic process, through the immune system that might on occasion create them in order to neutralize threats like bacteria or viruses. Finally, external factors like pollution and radiation can cause free radicals to form in the body. The problem is free radicals are unstable and react quickly by stealing an electron from another atom or molecule; this in turn creates another free radical and so on and so forth creating a chain reaction that can permanently damage a cell's DNA or even destroy a living cell entirely. Free radical damage accumulates with age. All else being equal, the body can usually keep these under control through the presence of antioxidants. However, if insufficient antioxidants are present, then the balance is disrupted. Antioxidants can safely interact with these radicals effectively arresting the chain reaction. Antioxidants can be in several forms, but the most powerful and readily available to humans are the vitamins with antioxidant properties—vitamin E, beta-carotene, and vitamin C. Selenium, a trace element, also possesses antioxidant properties too (Rice University, 2017).

Source: Compiled from multiple sources: FSA, 2010; MedlinePlus, 2010; WHO/FAO, 2004; Harvard Medical School, 2009; UMMC, 2017.

Table A.8 Vitamin K—Characteristics, Function, and Sources

Vitamin	Chemical Name(s)	Characteristics/Function	Sources
Vitamin K	K_1—phylloquinones (plants) K_2—menaquinones (bacteria) 14 in total designated MK_n, that is, MK_1-MK_{14} Several synthetic vitamins including the following: K_3—menadione K_4—menadiol diacetate K_5—2-methyl-4-amino-1-naphthol	Vitamin K storage capacity in the body is limited; as such, the body recycles it in the vitamin K oxidation-reduction cycle. Not surprisingly then, vitamin K deficiency increases the risk of hemorrhaging or excessive bleeding. Relatedly, vitamin K is also essential for the synthesis of certain proteins that promote the clotting of blood (a procoagulant)	K_1 phylloquinone from plants makes up the main dietary intake of vitamin K. It is plentiful in green vegetables, particularly so in spinach, kale, asparagus, Brussel sprouts, peas, soybean, avocado, kiwi, lettuce, broccoli, and certain vegetable oils like sunflower and olive K_2 menaquinones—dairy products are chiefly rich in vitamin K_2, Camembert, for example. While it contains about 40 ng/g of vitamin K_1, it also contains about 600 ng/g of K_2

Source: Compiled from multiple sources: WHO/FAO, 2004; MedlinePlus, 2010; Britannica, 2009; FSA, 2010; LipidBank, 2010; Fain, 1971; LPI, 2017; Harvard Medical School, 2009; UMMC, 2017.

Table A.9 Vitamin B—Characteristics, Function, and Sources

Vitamin	Chemical Name(s)	Characteristics/Function	Sources
Vitamin B_1	Thiamine	Thiamine, a coenzyme[a], helps with the metabolism of carbohydrates in the body's cells converting them into useable energy. This particular vitamin is also essential for the normal functioning of the heart, muscle, and nervous system while also being useful in the production of hydrochloric acid used in the digestive process	Thiamine can readily be found in all the main food groups but is especially prevalent in lean meat (especially pork), milk, eggs, and cheese, as well as fish, dried beans, whole-grain breads, peas and soybeans, and of course in many fruits and vegetables, yet while they do not contain very high quantities of thiamine—as this food group is consumed in large amounts, so they soon become an important source of thiamine
Vitamin B_2	Riboflavin	Riboflavin is also a coenzyme and aids in carbohydrate metabolization. Riboflavin also helps maintain the nervous system, eyes, skin, and mucous membrane. Lastly, this vitamin has a role in the production of steroids and red blood cells	Riboflavin is found only in small quantities, particularly in foods like lean meats, dairy products, eggs, legumes, nuts, and green leafy vegetables
Vitamin B_3	Niacin (nicotinic acid and nicotinamide)	Niacin, another coenzyme, helps in the body's energy conversion process. It is also important for the good health of the skin and the digestive and nervous systems	Niacin can be found in lean meats, like chicken, beef, and pork. It is also present in fish, dairy products, nuts, and legumes, and cereals like wheat and maize
Vitamin B_5	Pantothenic acid	Vitamin B_5 aka pantothenic acid assists in the breakdown or metabolism of proteins, carbohydrates, and particularly fatty acids. It is also critical in the creation of red blood cells and also helps in the maintenance of the digestive tract	Pantothenic acid is present in a wide variety of foods. Some of the best sources include brewer's yeast, avocado, broccoli, cauliflower, corn, kale, tomatoes, legumes, lentils, egg yolks, milk, split peas, peanuts, soybeans, sweet potatoes, sunflower seeds, whole-grain breads and cereals, beef (especially organ meats like the kidneys and liver), chicken, duck, lobster, wheat germ, and salmon
Vitamin B_6	Pyridoxine, pyridoxamine, and pyridoxal	Vitamin B6 helps make neurotransmitters (chemicals that carry signals between nerve cells). It also helps to regulate brain function and development. B_6 also produces the hormones serotonin	Good sources of vitamin B_6 can be found in dairy products, eggs, pork, chicken, turkey, beef liver, cod, tuna, salmon, shrimp, lentils, beans, spinach, carrots, bran, sunflower seeds, bananas, soya

Continued

Table A.9 Vitamin B—Characteristics, Function, and Sources—cont'd

Vitamin	Chemical Name(s)	Characteristics/Function	Sources
		and norepinephrine (mood enhancers) and regulates the body clock through the production of melatonin. Lastly, the human body relies on B_6 in order to aid in the absorption of B_{12} and to make cells—both red blood and immune system cells	beans, nuts, legumes, potatoes, whole grains such as oatmeal, wheat germ, and rice
Vitamin B_7	Biotin	Biotin (another coenzyme) is crucial in the metabolism of the macronutrients, proteins and carbohydrates for energy, and in the production of hormones and cholesterol	Biotin is found in many foods, especially noteworthy are meats, the kidney and liver, salmon, eggs, sardines, and certain fruits and vegetables. B_7 can also be found in brewer's and nutritional yeast products
Vitamin B_9	Folic acid or folate	Folic acid is crucial for good brain function playing a significant role in mental and emotional health. It also acts with B_{12} and vitamin C in the creation of protein molecules. Aiding in the production of DNA and RNA, vitamin B_9 is also particularly important in times of rapid cellular and tissue growth, especially in pregnancy, infancy, and growing children. Folic acid also works closely with vitamin B_{12} to form red blood cells. Vitamin B_9 also helps reduce neural tube defects including spina bifida in fetal babies	Folate is found in small amounts in many food sources including brewer's yeast; dark green leafy vegetables like spinach and mustard greens; root vegetables and legumes such as white beans, turnips, mung beans, lima beans, soybeans, beets, beans, Brussels sprouts, kidney beans, chickpeas, avocado, and asparagus and peas; milk; orange juice; meat and fish including beef liver, pork, poultry, salmon, and shellfish; and certain grains like wheat bran, bulgur wheat, germ, and other whole grains
Vitamin B_{12}	Cobalamin (cyanocobalamin, hydroxocobalamin, methylcobalamin)	Vitamin B_{12} is important for protein metabolism and as an aid in processing folic acid. It also helps in the formation of the body's red blood cells and keeps the central nervous system in good health	Vitamin B_{12} is found in some algae (seaweed), meat and meat organs (especially beef liver), poultry, salmon, cod, shellfish, milk, cheese, and other dairy foods, as well as in eggs and yeast extract

[a]*A coenzyme is a nonproteinaceous compound that aids in the proper functioning of an enzyme.*
Source: Compiled from multiple sources: FSA, 2010; MedlinePlus, 2010; WHO/FAO, 2004; Harvard Medical School, 2009; UMMC, 2017.

Table A.10 Choline—Characteristics, Function, and Sources

Name	Chemical Name(s)	Characteristics/Function	Sources
Choline		Choline has many functions in the body from promoting the synthesis of cell structures to aiding the formation of cell signaling precursors. Chromium is also involved in the transmission of nerve impulses and assisting the brain in neurotransmitter production. Choline also slows fat accumulation in the liver and the buildup of cholesterol. Lastly, it also aids in the removal of toxins and wastes	Much choline in foods takes the form of phosphatidylcholine. Phosphatidylcholine in turn is a major component of lecithin. Therefore, foods rich in lecithin tend to be good sources of choline: these include meat and their livers, egg yolks, milk, soybeans, peanuts, oatmeal, cabbage, and cauliflower

Source: Compiled from multiple sources: LPI, 2017; MedlinePlus, 2010; WHO/FAO, 2004; FSA, 2010; Harvard Medical School, 2009; UMMC, 2017.

Table A.11 Vitamin C—Characteristics, Function, and Sources

Vitamin	Chemical Name(s)	Characteristics/Function	Sources
Vitamin C	Ascorbic acid, ascorbate	Vitamin C is necessary for the growth and repair of tissue in the body. It is also indispensable in the formation of collagen (a protein in the skin, tendons, ligaments, and blood vessels). Lastly, vitamin C is also employed by the body in wound healing and in the maintenance of teeth, bones, and cartilage	Sources of vitamin C—all fruits and vegetables contain at least some vitamin C. However, some of the richer sources available are citrus fruits, cantaloupe, strawberries, blueberries, mango, watermelon, cranberries, kiwi, raspberries, papaya, pineapples, and certain vegetables like cauliflower, Brussels sprouts, winter squash, cabbage, leafy greens, red and green peppers, tomatoes, broccoli, and also potatoes

Source: Compiled from multiple sources: FSA, 2010; MedlinePlus, 2010; WHO/FAO, 2004; Harvard Medical School, 2009; UMMC, 2017.

proteins, carbohydrates, lipids, and the nucleic acids (DNA and RNA) from free radicals that are created in the normal metabolic process (Table A.11) (LPI, 2017; Rice University, 2017; UMMC, 2017; Harvard Medical School, 2009).

A.5.2 MINERALS AND TRACE ELEMENTS

Certain minerals are those chemical inorganic substances (elements) that the body cannot synthesize but which are also essential to the normal daily functioning of the body. The human body employs minerals in many functions: they look after the skeletal framework, the heart, the muscles, and the

brain. Minerals are also important for making enzymes and hormones, among other things. Some of these are collaborative in nature and work with other nutrients, minerals, or vitamins to regulate certain bodily processes including metabolization and energy production, while other nutrients have specific functions like calcium, for instance, in bones and teeth (FSA, 2010; MIT, 2010; WHO/EMRO, 2010; WHO/FAO, 2004). Minerals can be categorized in many ways, and while there is no general consensus, a few common categorizations include as essential elements or electrolytes; their importance in their functional classifications or by their structural component, that is, metals or salts; or simply by their grouping—macro- (major) or microminerals and trace minerals, which is based on the quantitative amount required by the body each day (MIT, 2010; WHO/FAO, 2002b). This book follows the latter convention. Once again however, there is no accepted quantitative measure separating the macro- and microminerals. However, common orthodoxy designates macrominerals as those required in quantities above 100 mg and microminerals as those between 1 and 100 mg. This is the convention followed throughout the following sections. Lastly, trace elements will be those elements that fall below this 1 mg threshold (Britannica, 2009; MIT, 2010). That said, it must be noted that this categorization does not reflect or confer any relative importance to the minerals—they are simply organized according to their quantitative daily requirements. These are examined in the following sections (Table A.12).

Table A.12 Minerals—Characteristics, Function, and Sources

Mineral	Characteristics/Function	Sources
Potassium	Potassium is an important mineral for the good functioning of all tissue and organ cells in the human body. It is also an electrolyte (a substance that conducts electricity in the body). As an electrolyte, potassium, together with sodium and chloride, helps maintain the body's fluid balance by acting as a sort of chemical pump. Potassium also regulates a cell's membrane electric "potential" when it comes to nerve impulse functions. It also helps in the regulation of the heartbeat, the synthesis of proteins, and the metabolization process in general	Many good sources of potassium include all meats and certain fish including salmon, cod, flounder, and sardines. Potassium can also be found in many fruits and vegetables like broccoli, peas, sweet potatoes, lima beans, tomatoes, squash, potatoes, citrus fruits, cantaloupe, bananas, kiwi, prunes, and dried apricots; milk yogurt; and nuts
Chloride	Chloride is also an electrolyte—it is, in fact, ionized chlorine, that is, a chlorine element that has gained an electron to form an anion (negatively charged ion). In this form, chloride can join positively charged sodium ions (cations) to create sodium chloride (table salt) or to form hydrochloric acid (stomach acid) if bonded with a hydrogen cations. As an electrolyte, chloride is important in helping to regulate both inter- and intracellular equilibrium of fluid. Chloride is also used by the kidneys; it acts to keep the blood pH—levels in balance	Much of the chloride in the diet is derived from table salt or sea salt (sodium chloride). It can also be found in many vegetables including seaweed, lettuce, and cereals such as rye. Other foods high in chloride include tomatoes, lettuce, celery, and olives

Table A.12 Minerals—Characteristics, Function, and Sources—cont'd

Mineral	Characteristics/Function	Sources
Sodium	Sodium is an essential element for all people and one that plays a central role in multiple life-sustaining processes. As with potassium and chloride, sodium is also an electrolyte that collectively makes up the principal ions in extracellular liquids and helps balance the body's fluids. These include interstitial fluids and blood plasma. Also, just like potassium but with an opposite negative charge, sodium ions called anions create the potential difference in cell membranes that allow for electric impulses to generate muscle and nerve impulses	As with chloride, sodium makes up the other component of table salt (sodium chloride). Natural foods containing sodium include seafood; meats such as beef and poultry; many vegetables including carrots, celery, beets, artichokes, and kelp; and other sea vegetables
Calcium	Calcium is the most abundant mineral in the body. It is a major structural constituent requiring for the bone and teeth (representing 99% of total intake), and a small but essential amount is required for blood and soft tissue. For structural formation, the absorption of calcium is assisted by vitamin D. There is also a need for calcium in the signaling of cells and the regulation of muscle contraction, as well as the proper functioning of the nerve cells. Calcium also promotes blood clotting	Sources of calcium can be found in milk, cheese, and other dairy products; in fish, especially prawns and sardines eaten with the bones; in seaweed; in vegetables including olives, celery, carrots, sweet potatoes, cabbage and all the greens, artichoke, many beans and pulses, spinach, watercress, broccoli, and parsley; and in fruits like rhubarb, dried figs, apricots, and black currants, as well as foods like molasses, brewer's yeast and many nuts and some seeds, wheat germ, barley, brown rice, and carob flour
Phosphorous	Like calcium, an essential requirement of mineral bone means that 85% of phosphorus intake goes to the bone factory. Further, much of the body's phosphorous is in the form of phosphate (PO_4). It is also an essential mineral found in every cell, helping with the metabolic processing of carbohydrates and fats and in the synthesis of proteins. Phosphorous is also active in supporting both nerve and muscle signals and contractions, functioning of the kidneys, and binding with hemoglobin in order to facilitate the transport of oxygen around the bloodstream. Lastly, phosphorus is also functional in the nucleic acids DNA and RNA	Phosphorous can be sourced from proteinaceous food groups such as red meat, fish, poultry, and dairy products. It can also be found in rice, bread, and oats, while fruits and vegetables usually only contain small amounts of phosphorus. Yet, while an abundance of phosphorous is located in whole grains, it is in a form (phytin) not bioavailable to the body
Magnesium	When it comes to bones and the element magnesium, it can be seen that once again the bulk (60%) of required intake is devoted to bone formation. However, it cannot be underestimated as it is also an important component present in every cell type in the body to help with the numerous essential metabolic reactions that create energy. Magnesium is also required in cell signaling and aids in the correct functioning of the parathyroid glands	The richest sources of magnesium are vegetables especially the green leafy varieties like spinach. Nuts and spices, bread, fish, meat, and dairy foods, as well as cereals and cocoa, are also good sources of magnesium

Continued

Table A.12 Minerals—Characteristics, Function, and Sources—cont'd

Mineral	Characteristics/Function	Sources
Manganese	Manganese aids in metabolism, that is, the anabolism (production) of some of the many enzymes in the body and the catabolism (the breaking down) of carbohydrates, amino acids, and cholesterol for energy. Also at the cellular level, a number of manganese-activated enzymes work as antioxidants that slow down the oxidative process and the ultimate formation of free radicals. Manganese is also involved, albeit indirectly, in the process of wound healing and in promoting healthy cartilage and bone	Manganese is found in tea, pineapple, and nuts; in green vegetables like peas, runner beans, and spinach; and in brown rice and whole grains like rye, spelt, and oats. Manganese can also be found in some breads
Iron	There are essentially two varieties of iron Iron is available in both plants and animals. While they are both iron, they are two different chemical forms of iron. Animal and animal products' iron is mostly attached to a hemeprotein, hence the nomenclature heme iron while plants' iron is not attached to a hemeprotein and is consequently called a nonheme iron. Those of animal origin are readily absorbed—more bioavailable, than those of plant origin. Iron has a number of important roles in the body, being essential for metabolism, growth, healing, DNA synthesis, and playing a role in reproduction and the immune system. It is also a cofactor in many enzymatic reactions helping to create a multitude of proteins. Iron is particularly central (together with vitamin A) in preventing anemia. It is also important in the oxygen-carrying protein hemoglobin (in blood) and myoglobin (in muscles), both transporters of oxygen around the body	Some rich sources of iron can be found in meat—especially the liver; in eggs; in fish and shellfish like oysters, salmon, and tuna; in whole grains, beans, nuts, dried fruit, and soybean flour; and in most dark green leafy vegetables (except, contrary to popular belief)—spinach as it contains oxalic acid that makes it difficult for the body to absorb spinach's iron
Zinc	Zinc is extant in all bodily tissues and fluids and is involved in several aspects of metabolism. It also acts as a cellular stabilizer at the molecular level and contributes to the general maintenance of cell integrity. Zinc deficiency is responsible for stunted growth, acute and slow wound healing, etc. As such, zinc plays an important role in growth and development, immune system, and neurological and reproduction functions	Good sources of zinc in foods include meat, milk, and dairy produce, as well as shellfish, bread, and cereal products like wheat germ

Source: Compiled from multiple sources: LPI, 2017; WHO/FAO, 2004; MIT, 2010; FSA, 2010; MedlinePlus, 2010; Harvard Medical School, 2009; UMMC, 2017.

A.5.2.1 Trace elements

Just like macrominerals, trace elements are classified in various ways; however, in this book, the convention used is to determine trace elements as those whose daily requirements fall below the 1 mg threshold. Once again, it is important to remember that this does not confer any less importance in the diet than macronutrients as they can be just as significant in the body's many structural and functional processes (MIT, 2010; Latham, 1997; UMMC, 2017) (Table A.13).

Table A.13 Trace Elements—Characteristics, Function, and Sources

Mineral	Characteristics/Function	Sources
Copper	Just like iron, copper aids in the creation of both red and white blood cells. Copper is also a trigger for the release of iron to form hemoglobin. On top of this, copper also has a role to play in the functioning of energy production, in synthesis of neurotransmitters, and in the central nervous system. Copper also aids in antioxidation, keeping the blood vessels healthy and lastly acting in part as a regulator of gene expression	Good sources of copper can be found in shellfish in particular oysters, the liver, the kidneys, potatoes, beans, dried fruits, dark leafy greens, cocoa, black pepper, yeast, nuts, and whole grains
Iodine	Iodine in soil varies a good deal from region to region, although most of the planets source can be found in oceans. That said, wherever dietary iodine is from, when ingested, it boasts 100% bioavailability, that is, it is fully absorbed from food and water. Iodine is needed mainly for two purposes: firstly, for the cells to convert food into energy and, secondly, for normal thyroid functions and the production of thyroid hormones	The main food source of iodine is probably fortified table salt; however, other good rich supplies include seafood (especially cod, haddock, sea bass, and perch), various seaweeds including kelp, dairy products, and plants grown in iodine-rich soil
Selenium	Selenium is a trace element with a variety of functions. It aids in the preparation of an antioxidant that helps prevent cell damage. It also plays a role in the immune system while also aiding in thyroid hormone metabolism. Selenium also has been said to stimulate antibodies and help to boost fertility, especially among men, but that is generally hearsay	Sources of selenium can be found in fish and shellfish, red meats and their livers, chicken, grains, eggs, garlic, brewer's yeast, wheat germ, and Brazil nuts
Chromium	Chromium not only aids in the metabolism of fats and carbohydrates into energy but also helps in the upkeep of healthy insulin and blood sugar levels. Further, chromium helps to transfer blood sugar (glucose), from the bloodstream and into the cells for use as energy. On top of this, chromium also stimulates fatty acid and aids in cholesterol synthesis that is important for brain functioning and other body processes	Chromium is ubiquitous; it can be found in the air, water, and soil. In addition to plants and animals, chromium can be sourced from meat and the liver, oysters, eggs, green peppers, apples, bananas, spinach, tomatoes, onions, and potatoes, as well as whole grains, lentils, and brewer's yeast

Source: Compiled from multiple sources: MIT, 2010; FSA, 2010; MedlinePlus, 2010; WHO/FAO, 2004; LPI, 2017; Harvard Medical School, 2009; UMMC, 2017.

There are of course numerous other elements than just those described above that can be found in the human body. That said, from the perspective and limitations of this book and public health, there is little or no evidence of those elements described below that deficiencies in these would cause any major health problems if absent from the diet. These elements include, inter alia, arsenic, cobalt, fluoride, molybdenum, nickel, silicon, vanadium, and tin (Latham, 1997; MIT, 2010; FSA, 2010; MedlinePlus, 2010; WHO/FAO, 2004; LPI, 2017; Harvard Medical School, 2009; UMMC, 2017).

Thus far, this book has examined both the macro- and micronutrients in some detail. From a food or health perspective, it is worth noting the importance of many of these and their value not only in terms of health but also from the chef's perspective. This is especially prevalent in today's modern cooks as not only are we tasked with developing menus and dishes with color, texture, and an aroma and flavor appeal but also we are increasingly asked to consider nutritionally balanced dishes (Table A.14).

Regarding nutrients whether macro-, micro-, and trace elements, it just remains to determine the actual guidelines. As with previous discussions on this, while there are many nutritional guidelines available to the general public, some guidelines are more acceptable than others, especially at the international level. These include those of the World Health Organization (WHO), the United States (US), and the European Union (EU). The following table summarizes the various nutrient guidelines in question (Table A.12).

Table A.14 Macro- and Micronutrient Guidelines of the EU, the United States, and the WHO for Adult Men and Women

		Energy																			
			Carbohydrate			Fat				Protein											
	Water[i]	Energy/Daily Calories	Total	Sugar	Fiber	Total	Saturated Fat	n-6 PUFA Linoleic Acid	n-3 PUFA α-Linolenic Acid	Total	Vitamin A	B_1 Thiamine	B_2 Riboflavin	B_3 Niacin	B_5 Pantothenic Acid	B_6 Pyridoxine	B_7 Biotin	B_9 Folate	Vitamin B_{12} cobalamin
Body	**(L/d)**	**kcal**	**(g/d)**	**(g/d)**	**(g/d)**	**(g/d)**	**(g/d)**	**(g/d)**	**(g/d)**	**(g/d)**	**(µg/d)**	**(mg/d)**	**(mg/d)**	**(mg/d)**	**(mg/d)**	**(mg/d)**	**(µg/d)**	**(µg/d)**	**(µg/d)**
USDA[a]	2.7–3.7[m]	W, 2000 M, 2400	130[c] W, 225–325[e] M, 270–390[e]	Less than > W, 125[e] M, 150[e]	25–38[m]	ND W, 44–67[e] M, 53–93[e]	<10%	12–17[m] 5–10%	1.1–1.6[m] 0.6%–1.2%	46–56 W, 50–175[e] M, 60–210[e]	7–900[j]	1.1–1.2	1.1–1.3	14–16	5[m]	1.3	30[m]	400	2.4
EU	2–2.5	W&M, W, 2000 M, 2600	230[d] W, 225–300[e] M, 292–390[e]	90[f]	25	70[d] W, 45[f] M, 100[f]	20[d]	W, 9 M, 11.5[e]	2	41.5–58.1[f] W, 65 M, 94	800	1.1	1.4	16	6	1.4	50	200	2.5
FAO/WHO[b]	1.4–2 (3)[m]	W, 2100 M, 2550	W, 275–375[e] M, 350–480[e]	Less than > W, 52.5[e] M, 63.8[e]	-	W, 33–66[e] M, 42–84[e]	Less > W, 52.5[e] M, 63.8[e]	W, 12–19 M, 14–23	W, 2–5 M, 3–6	54–58[g] W, 50–75[e] M, 64–96[e]	5–600	1.1–1.2	1.1–1.3	14–16	5	1.3	30	400	2.4

	Vitamin C	Vitamin D[k]	Vitamin E	Vitamin K	Calcium	Chloride	Choline	Chromium	Copper	Fluoride	Iodine	Iron	Magnesium	Manganese	Molybdenum	Phosphorous	Potassium	Selenium	Sodium	Zinc
Body	**(mg/d)**	**(µg/d)**	**(mg/d)**	**(µg/d)**	**(mg/d)**	**(g/d)**	**(mg/d)**	**(µg/d)**	**(µg/d)**	**(mg/d)**	**(µg/d)**	**(mg/d)**	**(mg/d)**	**(mg/d)**	**(µg/d)**	**(mg/d)**	**(g/d)**	**(µg/d)**	**(g/d)**	**(mg/d)**
USDA[a]	75–90	15	15	90–120[m]	1000[n]	2.3[m]	425–550[m]	25–35[m]	900	3–4[m]	150	8–18	310–420	1.8–2.3[m]	45	700	4.7[m]	55	>2.3	8–11
EU	80	5	12	75	800	0.8	425–550[m]	40	1000	3.5	150	14	375	2	50	700	2	55	0.575 – 3.5	10
FAO/WHO[b]	45	5	7.5–10	55–65	1000	0.75	750[m]	-	900–1100	3–4[m]	130–150	8–20[h]	220–260	-	—	550–700	2[m]	26–34	0.5[m]	3–14[h]

Notes: *W = Woman and M = Male both aged 19–50.*

[a] *USDA adult needs for 19- to 30-year-olds based on the IoM National Academy of Sciences recommended dietary allowance (RDA) to meet 97%–98% of the population.*

[b] *Adults approximately 19- to 50-year-olds.*

[c] *Is the RDA value that is set at 130 g/d for both adults and children based on carbohydrate's role as the primary energy source for the brain. Remaining carbohydrate needs are to ensure adequate bodily functions.*

[d] *From the EU labeling reference intake values and scientific opinion in consultation and subject to change.*

[e] *Calculation based on energy intake values then adjusted using the recommended energy balance portfolio in Table A.4.*

[f] *Based on EU's current labeling values.*

[g] *Calculated for an adult of 65–70 kg.*

[h] *Depending on bioavailability.*

[i] *Total water includes that contained in food and beverages.*

[j] *USDA figures are the retinol activity equivalents (RAEs).*

[k] *In the absence of adequate sunlight.*

[l] *Based on an adult weighing 50–70 kg.*

[m] *Without firm reference values in the form of RDAs, RNIs, and PRIs, individual institutional adequate intakes (AIs) or equivalents are used based on factorial analysis, balance studies, daily intakes, and/or biochemical indicators.*

Source: Compiled from multiple data sources including: Gibson, 2012, and Agostoni et al., 2010; SCF, 1993; SCF, 2000; WHO/FAO/UNU, 2007; WHO/FAO, 2004; WHO/FAO, 2002b; WHO/FAO, 2002a; Europa, 2003; WHO/FAO, 2003; FAO/WHO/UNU, 2004; IoM, 2005; IoM of The National Academies, 2017; EUFIC, 2006; EFSA, 2009; EFSA, 2010a; EFSA, 2010d; EFSA, 2010b; EFSA, 2012; EFSA, 2013; CIAA, 2010; Gibson, 2012; WHO, 2015; NAS, 2017; WHO, 2017; FAO/WHO, 2001; Lagiou et al., 2009; FDF, 2013; and USDA, 2010.

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APPENDIX

BASIC ORGANIC CHEMISTRY B

For a long time, organic chemistry was translated as the study of living organisms, or more precisely, the study of compounds from living organisms. However, the concept was challenged when in 1828 Friedrich Wöhler showed it was in fact possible to create an organic compound from a mineral (nonorganic) substance, namely, urea. What this and later experiments highlighted was the fact that "organic" molecules could be handled, manipulated, and synthesized just as minerals and metals could. What also altered with these changes was the meaning of the concept of organic chemistry. That is to say, organic chemistry was no longer the study of "living" things but rather of those molecules or compounds that contain carbon atoms (Seager and Slabaugh, 2013; Boudreaux, 2013). In this new incarnation, it was understood that carbon atoms can be linked to each other and other elements that collectively account for the majority of chemistry's broad field. Many, if not most, organic compounds will also contain other elements like hydrogen and/or sometimes oxygen, nitrogen, sulfur, and phosphorus. There are exceptions too regarding those compounds created solely from carbon such as diamond and graphite and also carbon dioxide, salts such as carbonates and cyanides that incidentally are considered to be inorganic compounds—this is mainly for historical reasons (Owusu-Apenten, 2004).

As this chapter unfolds, it will be shown that carbon atoms can, in their physical form, produce complex structures like long or branched chains and rings or chiral compounds and other complex 3-D shapes (Boudreaux, 2013). But first, look at some basic building blocks of all elements, molecules, compounds, etc.

B.1 ATOMS, ELEMENTS, MOLECULES, COMPOUNDS AND MIXTURES

Forming the basic units of all matter are tiny particles called "atoms." Each atom comprises a dense central nucleus composed of a mix of positively charged protons and neutral (no charge) neutrons. The nucleus is then surrounded by a cloud of electrons with a negative charge equal to the positive charge of the protons. As there are equal numbers of protons and electrons, all atoms start out with a neutral electric charge. All atomic nuclei contain one or more protons along with neutrons (Fig. B.1).

Structurally, if one takes two or more identical atoms of the same type, for example, hydrogen (H_2), oxygen (O_2), or nitrogen (N_2), then these are called "elements." Building on this, if we join or bond two or more atoms of different elements, for example, water (H_2O), then we have a "molecule." It is important to note here that elements of the same atoms as described above are molecules but not "compounds," whereas water, carbon dioxide (CO_2), and methane (CH_4) are compounds because each is made from more than one type of element—in short, all compounds are elements, while not all elements are compounds (Gaman and Sherrington, 1996). Compound molecules are also called chemical

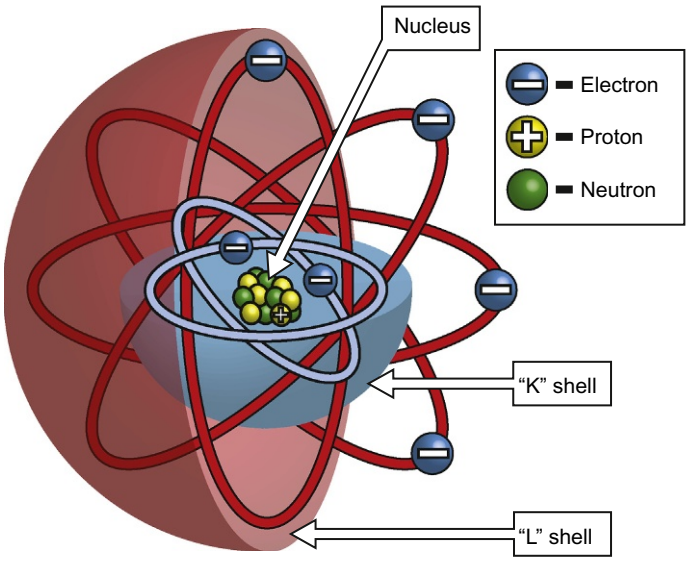


FIG. B.1

The atom and its component parts.

compounds, chemical substances, or simply compounds, and they can only be created or separated by chemical reactions. This distinguishes chemical compounds from simple chemical *mixtures,* whereby mixtures can be separated by simple, nonchemical procedures such as filtration and evaporation or by centrifugal force (Hoenig, 2001).

B.1.1 THE NUCLEUS

As mentioned, the nucleus consists of protons and neutrons:

Protons—the proton is a subatomic hadron particle[1] comprising a positive electric charge of 1 elementary charge (or electric charge denoted as e). All atomic nuclei contain at least one or more of these protons along with neutrons. The number of protons in a nucleus is considered its atomic number.

Neutrons—neutrons are also subatomic hadron particles. However, unlike protons, these have no net electric charge—hence the derivation of the name neutron from "neutral."

Isotopes—the number of neutrons in a nucleus can vary and is referred to as the neutron number. All nuclei of the same element contain the same number of protons, but as the number of neutrons in the nucleus varies, the atoms become different isotopes of the same element, for example, take the element carbon that has six protons—its atomic number therefore is 6; consider then, for example, carbon 12, carbon 13, and carbon 14, these are carbon isotopes with 6, 7, and 8 neutrons, respectively.

[1]Hadrons—the subatomic hadron particle is a composite particle made up of three quarks that are themselves held together by the strong force—a force similar in effect to the electromagnetic force. The best-known hadrons are the neutrons and the protons.

B.1.1.1 Outside the nucleus

Electrons—unlike protons and neutrons, the electron is a subatomic particle that is considered an elementary particle as it contains no known subcomponents or substructure. It has a negative charge, and thus, it reacts with other charged or negative particles. Electrons move in orbits around the nucleus in energy levels known as electron shells. Shells closest to the nucleus have the most negative energy, and shells further away from the nucleus have progressively higher energies. The first shell or one shell (closest to the nucleus) can contain up to two electrons—its full complement of electrons. When this is filled up, electrons occupy a second orbit, the two shell, which has a complement of eight. When this is filled, so electrons then occupy the third shell that has a complement of 13 and so on and so forth. The outermost shell, whether it's the second, third, or fourth shell, is known as the valence shell. The electrons in this valence shell (which can be partially filled) are known as valence electrons, and they are free to interact with valence electrons from other atoms. It is this property that leads to chemical bonding between atoms, joining them together to form molecules. If the valence shell itself has a full complement of electrons, it is considered a closed shell and because of this, it tends not to react with other atoms—it is considered inert like the element gold. When a valence shell, however, has fewer electrons than the full complement it might have, then it is considered potentially reactive, and the number of "missing" electrons determines the chemical properties of that particular atom (Seager and Slabaugh, 2013; Gaman and Sherrington, 1996).

Ions—an atom that contains an equal number of positive protons and negative electrons is a neutrally charged atom. However, if an atom contains more protons than electrons, it becomes a positively charged atom known as a positive ion (more precisely a "cation"). On the other hand, an atom that has more electrons than protons is a negatively charged atom also called a negative ion (more precisely an "anion") (Vollhardt and Schore, 2014).

In sum, things to take from this are the following:

- Different atoms are classified according to their atomic number—that is, the number of protons that each nucleus contains.
- Each atom with a specific atomic number is a unique chemical element on the periodic table.
- Molecules are two or more atoms that are chemically combined.
- The chemical properties of an atom (or element) are determined by the number of electrons in the valence shell.
- Adding electrons to an atom produces negative ions, whereas removing electrons produces positive ions.

Lastly, so far, 94 naturally occurring elements have been discovered, and a further 24 that have been synthesized/created giving a total as of 30 December 2015 of 118 (Gaman and Sherrington, 1996) tabular arrangement of the chemical elements is shown in Fig. B.2.

B.2 SO WHAT'S SO GREAT ABOUT CARBON?

Carbon atoms (C) possess the ability to bond with other carbon and often hydrogen atoms (H) to form long or branched chains and ring structures. In this way, carbon atoms can form molecules that contain one to an infinite number of C or CH atoms. Grouped atoms create molecules or compounds (*previous section*), so if one considers that chemical compounds number in the millions, 95% of which contain

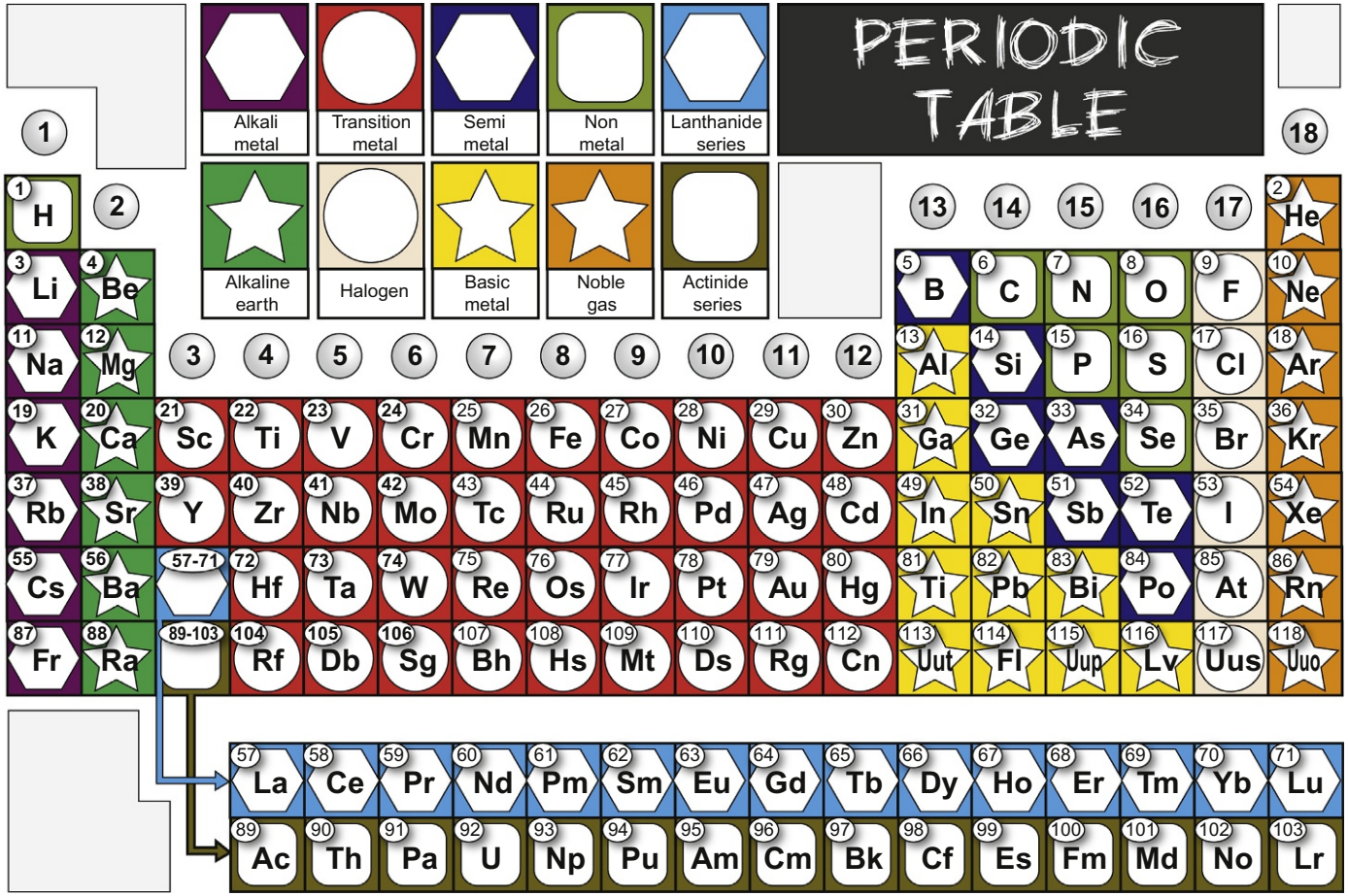


FIG. B.2

The periodic table of all known natural and synthetic elements.

carbon, one can see that carbon atoms are really quite remarkable. Also, worthy of note is the fact that organic compounds are usually held together by weak covalent bonds while inorganic compounds are held together by strong ionic bonds. By the same token, organic compounds are usually either gases, liquids, or solids with low melting points, while inorganic compounds are often found to be solids with high melting points (Seager and Slabaugh, 2013; Boudreaux, 2013; Pretsch et al., 2009; Belitz et al., 2009). The two elements (hydrogen and carbon) are collectively known as hydrocarbons—so, the study of hydrocarbons as basic organic building blocks is the foundation of organic chemistry.

B.3 HYDROCARBON COMPOUNDS

The simplest of all organic compounds are the carbon and hydrogen bonded compounds—these are called hydrocarbons. Being composed solely of carbon and hydrogen atoms, they are generally classified according to the nature of the bonds between their atoms—their physical structure whether straight or branched chains and rings. Thus, hydrocarbons can be divided into two groups—aliphatic (open chains) and cyclic (connected to form a ring). In their natural form, they are found mainly in plants, petroleum, natural gas, coal, and oil shale. Hydrocarbons can also be gases (e.g., methane and propane), liquids (e.g., hexane and benzene), waxes or low melting solids (e.g., paraffin wax and naphthalene), or polymers[2] (e.g., polyethylene, polypropylene, and polystyrene). In crude oil, hydrocarbons are all mixed together, and through a process of fractional distillation, the mixture is heated and separated on the basis of each component boiling point—the same principle as distillation of alcoholic spirits (Section 20.1). Light hydrocarbons with low boiling points separate from those with higher boiling points in a distillation tower, where the distillate is fractioned off. Most burn easily (combustible) or are dissolved more readily in alcohol than in water. Not surprisingly then, some are toxic, while some are explosive. As a result, hydrocarbons are used as fuels, explosives, solvents and extensively in the manufacture of industrial chemicals such as plastics and synthetic rubber.

B.4 THE BUILDING BLOCKS OF BIO- AND FOOD CHEMISTRY

In food chemistry, it is worth noting too that as well as the above carbon atoms' ability to bond with itself creating long chains, they also contain four valence electrons. Any one of these electrons can combine with other carbon atoms or other elements. These include hydrogen, oxygen, nitrogen, sulfur, and phosphorus that together form hydrocarbon (CH) compounds bonded to one or more elements that, if in the right configuration, can form reactive elements within a molecule called functional groups (*more later*). For now, suffice to say that the ability of carbon to bond with other elements allows for complex structures such as long or branched chains, rings, chiral compounds, and complex 3-D shapes. Furthermore, with four valence electrons bonding, other atoms can take one of several forms. A single bond arises when one electron is employed from two atoms; a double bond is when two electrons each (four in total) are shared, while triple bonds result from three shared electrons each (six in total). This is called covalent bonding (*more on this later*) and is peculiar to carbon compounds;

[2]Polymers are interesting, and an important property of carbon is that it forms linked chains quite readily. This linking process is referred to as polymerization; the finished linked items are polymers, while the individual link units are the monomers.

conversely, inorganic compounds are usually held together by ionic bonds. As a result of this variety and flexibility in bonding, carbon atoms form an enormous diversity of compounds—literally, many millions of organic compounds as opposed to several hundred thousand or so inorganic compounds (Manning, 2008; Boudreaux, 2013; Seager and Slabaugh, 2013). In this way, it can be said that carbon, along with hydrogen atoms (hydrocarbons), the so-called backbone of nearly all organic compounds, can attach to one or more functional groups forming the basis of biochemistry and food chemistry. This gives rise to varied complex organic compounds with useful biological functions ranging from vitamins, carbohydrates, proteins, lipids, enzymes, fats, and to things like RNA and DNA (Gaman and Sherrington, 1996; Seager and Slabaugh, 2013).

B.5 CHEMICAL BONDING

Recall that an atom containing an equal number of positive protons and negative electrons is a neutrally charged atom, while atoms containing more protons than electrons have a positive charged atom known as an ion or more specifically a cation (a positively charged ion). Recall too that atoms with more electrons than protons have a negative charge and are also called ions, again, more specifically—an anion (a negatively charged ion). This then forms the basis of atomic bonding. This is referred to in chemistry as the intermolecular force—in short, the forces of attraction or repulsion that act between neighboring particles, atoms, molecules, or ions. This allows molecules, substances, or compounds to be created or formed by the joining the atoms of two or more elements—furthermore, the same molecules are not just created but are also altered and broken down. The resulting chemical reactions—the bonding or dissociative abilities (breaking apart and detaching) of atoms and molecules—form the basis of the study of chemistry. These reactions are discussed in Section B.7; however, before that, take a look at chemical bonding (Manning, 2008; Seager and Slabaugh, 2013; Belitz et al., 2009).

In bonding, outer orbit (valence) electrons as discussed can participate in the formation of bonds by interacting with the valence electrons of other atoms. This chemical bonding is the result of either an atom sharing valence electrons with another atom, or alternatively one atom just stealing valence electrons completely from the atom with which it is bonding. The electrons in bonds exist in pairs. The way the different atoms bond together in a complex molecule goes some way toward determining the substance's reactivity, its solubility, and its applicability and is therefore very important.

B.5.1 ELECTRONEGATIVITY, POLAR AND NONPOLAR MOLECULES

Electronegativity is the ability of a nucleus to pull electrons in toward itself. The stronger the electronegative nucleus is, so the stronger the ability it has to attract electrons from atoms that are less electronegative. When one examines the periodic table, one finds that (with the exception of the noble gases) the electronegativity values of each element tend to increase as one travels from left to right along the table (Fig. B.2). This also increases as one goes up the table too. Now, if we take a chlorine atom bonded covalently[3] to another chlorine atom, because they are identical atoms with identical electronegativities, the electrons are shared equally between both atoms. This is called a nonpolar bond; one

[3]A covalent bond is a bond between two nonmetallic elements characterized by the sharing of pairs of electrons between the two atoms.

in which the electrons that make up the covalent bond rest halfway between the two atoms leaving it with an overall neutral charge. Now, consider what happens when two bonded atoms do not have the same electronegativity—that is, the two nuclei have different attractive forces; they "pull" or attract the electron pair to different degrees. The outcome is that the paired electrons in the bond are shifted toward the more electronegative atom. This means that the electron density is not in the center of the bond, but rather has shifted to one side. The resultant outcome is the bonded atoms' paired electrons are shifted toward the more positive atoms nucleus that incidentally makes this atom slightly more negative (after the electrons have moved over); this is called a polar covalent bond. To summarize, two atoms with equal electronegativity will make nonpolar covalent bonds, while an inequality in another two atom's electronegativity creates a polar covalent bond.

There is an important note to be made here and that is the notion of symmetrical bonding forces on atoms. It is important because while a pair of bonded atoms (a molecule) might have a polar bond, the resultant molecule might not be polar. To explain, one can use a simple analogy; imagine a tug of war—two teams pulling in opposite directions. Each team is an atom. If each team was pulling with the same force, the combined forces would cancel each other out, and the rope would remain stationary; this can be thought of as a nonpolar bond (two equal opposing forces). However, competitions are rarely that fair, so if one team was much stronger than the other, the two pulling forces would be different, and the rope would move toward the stronger team. This would represent a polar bond (Gaman and Sherrington, 1996; Vollhardt and Schore, 2014).

In sum, the properties of polar molecules are such that one end of the molecule has a positive electric charge while the other side has a negative charge. The extent of this polarity determines the strength of the forces of attraction within bonds—the more polar the bond, the stronger the bond. Nonpolar molecules are neutral and do not have charges at their ends.

These are important considerations when understanding functional groups that are combinations of atoms and molecules that react very specifically (Section B.7.4). In general, we can say from this that the higher the polarity on a functional group, the more reactive it is. If a functional group is nonpolar, this means it doesn't react with much without a great deal of energy.

Armed with the above, we now have enough information to contemplate the reactivity of chemicals, the fun and important stuff—the stuff that gives us coal, alcohols, plastics, and of course food reactions and essential oils, among others.

One more thing before we move on. Isomers—when dabbling in inorganic chemistry, a compound's molecular formula is specific to just one compound, yet in organic chemistry, most molecular formulas are not representative of a particular single compound. By way of example, the molecular formula, C_2H_6O, does not confer a specific compound but rather represents two separate compounds both with the same molecular formula. In this case, the two compounds sharing this formula are ethanol and methoxymethane. Such compounds sharing the same molecular formula are called isomers.

B.6 CHEMICAL CATEGORISATION AND FUNCTIONAL GROUPS

Once one understands that hydrocarbons quite literally form the backbone of organic chemistry and that when they are bonded to one or more "functional groups," then the number of structural arrangements of organic compounds literally runs into the millions. The next thing one needs to consider then is just how to categorize the various collections of atoms and molecules. Individually, of course, these

all have their own names, but generally for ease of understanding, they can and are organized in several different ways. The three particular naming conventions we are interested in are on the basis of characteristic structural or physical arrangement of the elements, using the homologous system, or simply by the compound functional groups. In the first, a structural type of categorization represents any family of compounds that shares the same physical shape whether acyclic or cyclic (closed or open compounds) (*next section*). The second common naming convention is through the functional grouping itself, while the third is by categorization within homologous groupings.

B.6.1 CLASSIFICATION BASED ON STRUCTURE

All organic compounds are divided into two main types or groups; these are the acyclic (open-chain compounds, whether straight or branched) and the cyclic (closed-chain compounds) (Fig. B.3).

Acyclic (aliphatic) open-chain compounds—these are organic compounds whereby the carbon atoms are linked to each other in a way that forms open, chain-like structures whether straight or branched. They are also known as aliphatic compounds and may be either saturated, that is, a chemical compound comprising a chain of carbon atoms linked together by single bonds or saturated compounds that contain double or triple bonds. The saturated group includes the alkanes and their derivatives, while the unsaturated hydrocarbons are compounds that contain carbon-carbon double or triple bonds.[4] These include the alkenes and alkynes and their derivative compounds (Fig. B.4).

Cyclic or closed-chain compounds—these are compounds that contain at least one closed chain of atoms called a ring or a loop, irrespective of whether it is a triangle, square, or circle in structure

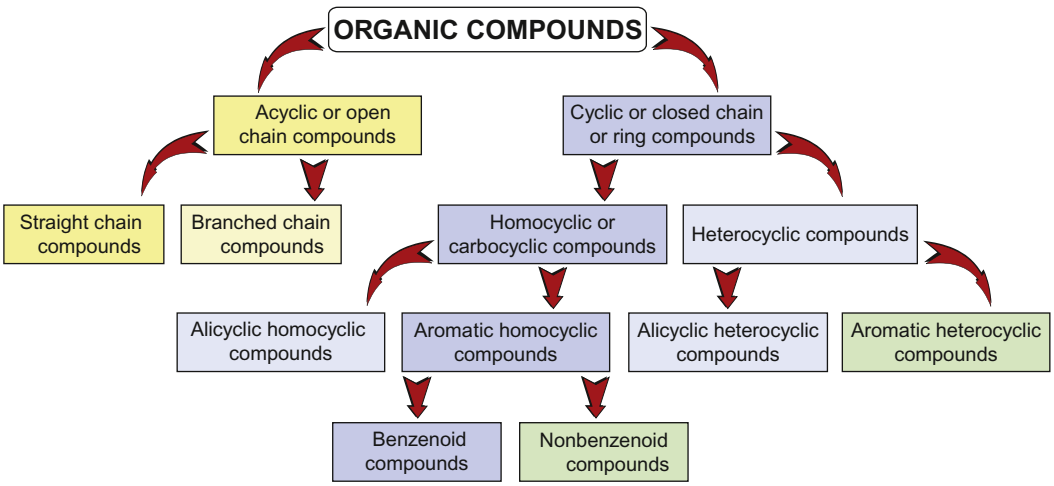


FIG. B.3

Simple organic compound classifications by structure.

[4]Saturated and unsaturated compounds might comprise simple straight or branched or ring arrangements, or they may also contain functional groups too.

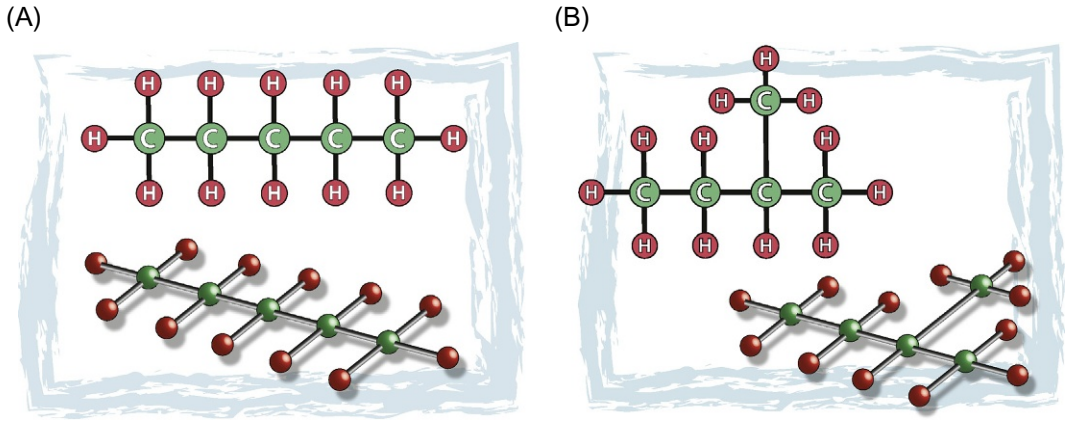


FIG. B.4

Acyclic/open-chain compounds.

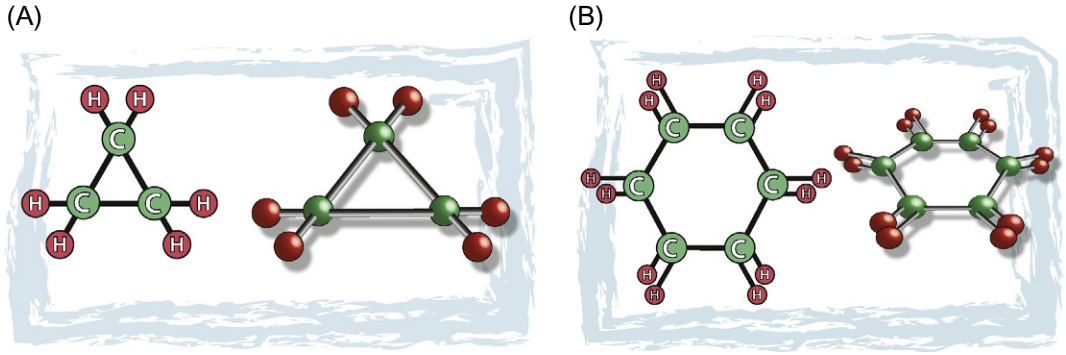


FIG. B.5

Cyclic or closed-chain compounds.

(Fig. B.5). Compounds with a single ring in the molecule are known as monocyclic, while those with more than one ring are called polycyclic. This category includes such cyclic compounds as cycloalkanes, cycloalkenes, and cycloalkynes. The cyclic (closed-chain) compounds are further divided into two subgroups homocyclic (aka carbocyclic) and alicyclic (a contraction of *aliphatic cyclic*) compounds.

Continuing with the structural classification of organic compounds for the moment, we can see that beneath the cyclic or closed-chain compounds, the following aids in the comprehension of Fig. B.3

- *Homocyclic or carbocyclic*—are those compounds that contain only rings of carbon atoms within the molecule. This group, in turn, is also subdivided into alicyclic and aromatic compounds:
  - *Alicyclic compounds*—are the compounds that contain rings of three or more carbon atoms. Chemically, these closely resemble aliphatic compounds rather than the aromatic compounds in many respects.

- *Aromatic compounds*—consist of at least one benzene ring, that is, a six-membered homocyclic ring comprising alternate single and double bonds. Generally speaking and as the name suggests, these compounds possess a fragrant odor. Underneath this are the benzenoid and nonbenzenoid aromatics:
  - *Benzenoid aromatics*—this grouping covers all those compounds that contain a stable benzene ring (Fig. B.6), and those classified as benzenoid aromatic compounds fall into this group.
  - *Nonbenzenoid aromatics*—these are those aromatic compounds that possess different structural units than those of the group of benzenoid aromatics and are known as nonbenzenoid aromatics.

- *Heterocyclic compounds*—are cyclic hydrocarbon compounds that besides comprising hydrocarbons also contain one or more heteroatoms (i.e., containing nitrogen (N), oxygen (O), or sulfur (S)). Heterocycles quite possibly constitute the largest and most varied family of organic compounds and can be further subdivided into mono-, bi-, and tricyclic compounds depending on the presence of one, two, or three rings in their molecules, respectively. Heterocyclic compounds can also be subdivided into alicyclic compounds and aromatic compounds:
  - *Alicyclic compounds*—are those compounds that resemble and act like aliphatic compounds in their properties.
  - *Aromatic compounds*—once again are those heterocyclic compounds that resemble aromatic benzene and other similar compounds in their properties and are referred to as aromatic heterocyclic compounds.

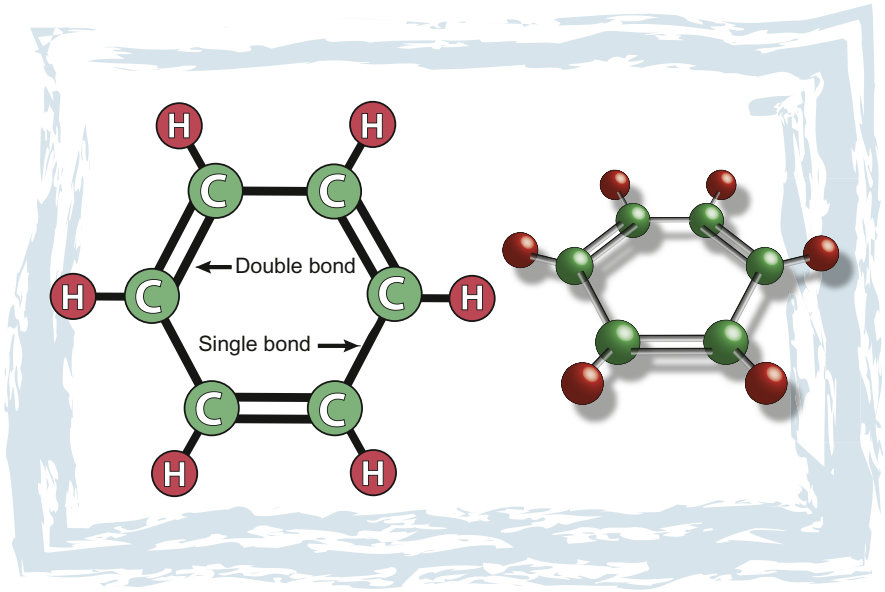


FIG. B.6

Heterocyclic aromatic compound benzene ring.

B.7 CHEMICAL REACTIVITY PROCESSES

Having classified organic chemistry structurally, we can now look a little closer at some of the reactions that occur in organic chemistry. Organic chemistry is about elements and their chemical reactions. A large number of important chemical reactions involve the transfer of electrons in redox reactions (oxidation-reduction) or hydrogen ion (acid/base) reactions and between reacting ions, molecules, or atoms. In other reactions, chemical bonds are broken by heat or light; yet others form new bonds from reactive radicals and electrons. Organic chemical reactions then are those reactions involving organic compounds that in some way affect or change those molecules and compounds involved. Although there are literally hundreds of possible reactions, some basic reactions include addition, elimination, substitution, rearrangement, and redox reactions:

- *Addition reactions*—in its simplest form are organic reactions whereby two or more molecules (with multiple atomic bonds) such as the alkenes and alkynes (carbon-carbon double and triple bonds, respectively) or heteroatoms such as imines (C═N) or carbonyls (C═O) simply combine to form a larger molecule. Types of addition reactions include electrophilic addition, nucleophilic addition, and radical addition.
- *Elimination reactions*—are just that—they eliminate atoms from a molecule. This reaction takes place in order to create carbon-carbon double bonds and is achieved using an acid or a base. If a base is used for the reaction, then an alkyl halide is employed as the reagent while elimination reactions using an acid employ alcohols as the reagent. Types of elimination reactions include the E1cB elimination reaction and dehydration.
- *Substitution reactions*—are reactions between molecules where a single or a group of atoms replace an existing atom in the original molecule. Imagine a hydrogen atom, for example, the substitution reaction would see this atom being replaced with a different atom. There are two specific types of substitution reactions possible; these are the nucleophilic and electrophilic. They differ solely in the particular type of atom that is being attached to the original molecule. In nucleophilic reactions, the new atom is electron-rich (with a tendency to donate electrons), while in electrophilic reactions, the new atom is electron-deficient (with a tendency to attract or acquire electrons). Types of substitution reactions include nucleophilic aliphatic substitution and aromatic substitution.
- *Rearrangement reaction*—the key feature defining rearrangement reactions is that a bond shifts from one site of attachment to another. The simplest example is an intramolecular reaction in which the product is simply a carbon molecule rearrangement whereby a structural isomer of the original molecule is created. Types of rearrangement reactions include 1,2-rearrangements, pericyclic reactions, and metathesis.
- *Redox reactions*—oxidation-reduction is an important aspect in organic chemistry that is very different to the redox concepts in general chemistry. In organic chemistry, metabolism of the foods that fuel the energy that keeps us alive involve redox reactions. A reaction in which reduction and oxidation occur simultaneously is a useful accounting procedure that helps reflect the changes in the bonding environment of electrons. In other words, it is a theoretical way of keeping track of collective atoms' (molecules and compounds) "electric state." Traditionally, the old definition of oxidation simply meant the reaction of oxygen on another element or compound producing a resultant oxide. As understanding over the years progressed resulting in the discovery that an oxygen atom was not always required for oxidation (although was still often involved)—as a result, the

definition was refined to describe what actually happens in true oxidation and that is the change in the "electric state" of an atom (although the name "oxidation" remained). Remember that free elements or atoms (unbonded) start out with an equal number of protons and electrons and that this resulted in the atom possessing a neutral electric state. Well, one can say that the oxidation state of this free element (unbonded) is zero. Carrying on from this, we noted previously too that electronegativity reflects the strength of attraction an atom's nucleus has for the electrons in its orbit. When bonded atoms form covalently, the more electronegative atom gains electron control over both atoms. The atom with electron control effectively draws the new electron closer to its own nucleus, thus polarizing the atom and by extension both atoms. Two things to note here: firstly, the "oxidation state" is an algebraic sum given to reflect the change in the atoms' collective charge (the net charge on the molecule). Secondly, as one atom gains an electron, so the other loses an electron. The atom that gains control is said to be "reduced," while the other atom is said to be "oxidized"—in short, reduction means "adding electrons," and oxidation means "removing electrons." This is called the *oxi*dation-*red*uction system or *redox* for short (*re*duction-*ox*idation). This is not to be confused with reactions that involve the gain or loss of one or more oxygen atoms which, are usually referred to as "oxygenase" and "reductase" reactions (see also Section 16.3.1) (Hoenig, 2001; Pretsch et al., 2009; Seager and Slabaugh, 2013).

It is important to remember that many groups of chemicals are rarely resigned to one type of reaction; on the contrary, many organic chemical groups can create other chemicals and being created themselves through one or more of the chemical functions and their derivatives described above. Furthermore, one chemical need not be exposed to a single reaction, but in fact may take many types of reactions before a stable molecule or compound is created. Apart from the chemical reactivity and the functional groups, there are also some other aspects of organic chemistry worthy of note. The following briefly describes some of these processes:

B.7.1 BOILING POINT

This is also evidenced in the various boiling point characteristics of functional groups too. The greater the forces of attraction = the stronger the bond = the higher the polarity. This results in more energy needed to excite molecules sufficiently to allow evaporation, that is, the higher the boiling point. Put another way, polar bonds are stronger than nonpolar bonds, and more energy is required to break them apart (Hoenig, 2001).

B.7.2 SOLUBILITY

In addition, the electronegativity differences of molecule atoms (i.e., the polarity) determine their solubility properties. A solution is where one or more substances are dissolved into another—a simple example is sugar and water that combine to make a syrup-like solution. There are two parts to any solution—the solute and the solvent. The solute in this example is the sugar, while the solvent is water. Solubility of a substance changes with temperature—hotter water is easier to dissolve sugar in. So back to polarity and electronegativity, from this, we can see that mixing molecules of the same polarity usually results in the molecules forming a solution or "like dissolves like." In other words, polar molecules dissolve in polar solvents, while nonpolar molecules dissolve in nonpolar solvents (Vollhardt and Schore, 2014).

B.7.3 ACIDS AND BASES

Understanding polarity also allows us to touch on another reactive component of functional groups in organic chemistry: that of acids and bases. When thinking of acids and bases, we often get the terminology a little mixed up. This is not surprising as there are multiple definitions out there. In 1923, two chemists—Johannes Nicolaus Brønsted and Thomas Martin Lowry—both independently established definitions of acids and bases. Both theories were based on a particular compound's ability to either donate or accept protons (H+ ions). Collectively, the theory defines acids as proton donors, whereas bases are proton acceptors this is referred to as the Brønsted-Lowry theory of acids and bases (LibreTexts, 2017). This theory has been used ever since it was introduced; however, there was a glitch in that the model did not fit every occasion. There was something missing. The theory seemed quite restrictive and primarily focused on acids and bases ability to donate or receive protons. So, chemists began to look around for an alternative to this theory and once again traveled back in time to 1923 where it turned out that there was a third person—G.N. Lewis from UC Berkeley who also proposed a definition, this one slightly more generalized, more favorable to most conditions of acids and bases. His theory concentrated on the explanation of acids and bases based on structure and bonding. Lewis' theory described acids through the lens of electrons instead of protons and suggested that acids accepted electron pairs, while bases donated electron pairs. Consequently, through the use of Lewis' definition, chemists are able to predict a wider variety of acid-base reactions (LibreTexts, 2017). Hybrid-like speaking, one can say that acids are chemicals that donate protons and/or accept electrons. Either way, it can be said that the higher the hydrogen ion concentration, the higher its acidity and the lower the pH of the overall solution.

So, back to basics, the first thing to note is that all solutions are either acid or base and that base liquids are often called alkali.

Acids—at their simplest, these are the hydrogen-based substances where the hydrogens have been stripped of their protons or have gained electrons leaving behind a concentration of hydrogen ions. Acids are corrosive to metals; they taste sour on the tongue, and when touched by litmus paper (a dye extracted from lichens), the paper changes color to red.

Bases or basics—these are the opposite of acids; they are more likely to taste bitter on the tongue; they have a caustic action on plant and animal tissue, feel slippery on the skin, and turn litmus paper blue.

Hydrogen is the simplest of all the atoms; it has only one proton and one electron. If this hydrogen loses its proton or gains an electron, it then becomes an ion containing more electrons than protons. As all acids contain hydrogen so an acid can be further defined as any compound, which forms hydrogen ions in solution. However, while many acids can be made with water (aqueous), there are some organic acids that must be dissolved in a solvent other than water, while others still can be in a solid state.

Interestingly, as an aside, in plain water (H_2O), a small number of the molecules naturally dissociate (split-up). As these water molecules lose a hydrogen atom, they become hydroxyl ions (OH^-). The "lost" hydrogen ions are then available to join up with other H_2O (water) molecules to form hydronium ions (H_3O^+) (a combination of H^+ ions and H_2O molecules). For simplicity, hydronium ions are referred to as hydrogen ions H^+. In pure water, the number of molecules splitting and reforming is small and balances out making the solution neither acid nor base (Vollhardt and Schore, 2014).

Concerning bases now, these are substances that accept hydrogen ions. In effect, the base absorbs or "soaks up" hydrogen ions; the result is a solution with more hydroxyl ions (OH^-) than hydrogen ions (H^+). This kind of solution is alkaline.

From a scalar perspective, the pH (potential of hydrogen) is used to determine an acid or bases' strength. The scale ranges from 0 equating to pure acid to 14 meaning a total basic compound. A pH of 7 is neutral, so anything below this is considered an acid, and anything above this is a base. Going back to the common confusion concerning alkalies, we can say that bases are substances that neutralize acids. An alkaline is simply a soluble base. From this standpoint, we can say that while all alkalies are bases—not all bases are alkalies. That is, if a base successfully dissolves in water, it is an alkali. Copper oxide is a base because although it reacts with acids, it is not an alkali as it does not dissolve in water. Examples of acid and bases include the following substances: stomach acid is 1, and wine is around 3.5, while water is 7–7.5 (neutral), blood is between 7.35 and 7.4, sea water is 8.5, and baking soda is 12 (Brown and Trivieri, 2013).

The thing to take from this is that both hydronium ions (H_3O^+) and hydrogen ions (H^+) are commonly referred to as hydrogen ions (H^+). So, in the case of water, any substance added to water that either creates (donates) hydrogen ions (H^+) or promotes hydronium ions (H_3O^+) is considered an acid compound. While nonaqueous (nonwater-based) solvents, any substance creating hydrogen ions (H^+) is an acidic compound. Lastly, acids and bases are opposites in that an acidic substance is neutralized by a base substance reducing the combined solution to salt and water (neutralization).

In organic chemistry, the most common organic acids are the carboxylic acids whose acidity is a product of the carboxyl group —COOH. In terms of strength, these are the sulfonic acids, containing the group —SO_2OH, and are the stronger acids, while alcohols, with —OH, can act as acids but are generally weaker. Other groups too can also impart acidity although usually more weakly than the above. In biological systems, organic compounds containing acidity as described are generally referred to as organic acids.

B.7.4 CLASSIFICATION BASED ON HOMOLOGOUS AND FUNCTIONAL GROUPS

As we have seen, organic molecules/compounds belong to various different families, and while all organic compounds are based on carbon (C) and often hydrogen (H), they can also bond with other elements such as oxygen, nitrogen, phosphorous, and sulfur. Furthermore, as has been mentioned, there are literally millions of organic compounds so one needs a way in which to group them. Apart from the structural classification above, another method is grouping molecules and compounds by their functional and/or homologous groupings.

A functional group—this is a specific atom or group of atoms within an organic molecule/compound that reacts in a specific way regardless of other atoms present. In this way, the "functional" part of the molecule determines the chemical properties of the whole. Furthermore, chemists group similar reactive atoms within molecules within an overarching functional group classification. Functional groups then can be as small as one or more atoms to many thousands and more; they can also comprise atoms of identical or different elements (Vollhardt and Schore, 2014; Gordon and Passlow, 1960; Manning, 2008; Seager and Slabaugh, 2013; Belitz et al., 2009). Not surprisingly too, molecules and compounds within a particular functional group share certain similar physical and chemical properties such as appearance and melting/boiling points, as well as solubility and chemical reactions characteristics. Lastly, chemical compounds are not restricted to one single functional group; on the contrary, most will include several such functional groupings. As a result, interactions and reactions are potentially complex and complicated and go a long way to explaining the lack of full understanding of chemical reactions of many compounds.

So how many functional groups exist? Well, this depends to a large degree on how one separates or divides up the active components within a molecule/compound. If we have several active atoms or atom groups within a single compound and depending on the counting convention, one could end up with literally thousands of functional groupings (Hoenig, 2001; Vollhardt and Schore, 2014).

Homologous series—a homologous series is a group of organic compounds that have similar molecular structures and that differ simply by the number of CH_2 units in the main carbon chain. As the compounds within the same group increase, with ever more CH_2 units, so the structure's properties will vary slightly depending on its size. Take the property boiling point, for example; while structurally the increasing groups are the same, the boiling points will vary slightly with each new addition of carbon units. Other properties that will also trend with varying additional carbon units include density, melting point, diffusion rate, solubility, refractive index, and conductivity. Another function that is common to compounds in the same homologous series is the presence of common functional group or groups. As a result, the various compounds will behave in a common chemical reactive fashion, although once again taking the above caveat in consideration. In short, one can think a homologous series as a "family" of compounds that have the same general formula, similar molecular structure, and similar chemical properties, further, because they have the same functional group of atoms—hence the same or similar chemical reactions (Belitz et al., 2009).

As mentioned above, the most common structural units in organic chemistry are the covalent carbon-to-carbon bonds. Indeed, one will find networks of single-, double-, and triple-bonded carbon-to-carbon atoms (or at times to hydrogen atoms). Couple this with the fact that these basic backbones of organic chemistry can attach to groups of atoms like oxygen, nitrogen, and sulfur, and in doing so, create units called functional groups. With this in mind, the following sections look at several of the more important hydrocarbons and functional groups.

There are about 7–8 key important homologous series in organic chemistry that deals with food that between them contain upward of 20 or so functional groups.

B.7.5 COMPOUNDS CONTAINING HYDROCARBONS

There are several types and subtypes of hydrocarbon compounds. Most of the compounds in crude oil are hydrocarbons and are separated into their fractions through the distillation process.

B.7.5.1 Alkanes

Alkanes are saturated hydrocarbons; they are the simplest form of organic molecules, containing single covalently bonded carbon-to-carbon atoms and sometimes hydrogen. With few elements involved and with no double or triple bonds (unsaturated), alkanes are the least chemically reactive of the numerous organic molecules. That said, there is an enormous amount of energy to be found within the single covalent carbon-carbon or the carbon-hydrogen bonds that allow for the rapid oxidation yielding a large quantity of heat, typically in the form of fire. The various types of alkanes include methane (the simplest of all hydrocarbon molecules), ethane, propane, and butane. Alkanes have limited use in the food industry although they are represented in certain mineral oil waxes. A mineral oil is a very generic term, as is its other names including white oil, liquid paraffin, *paraffinum liquidum* (Latin), microcrystalline wax, petroleum jelly, and liquid petroleum. Generally speaking, mineral oil is a liquid by-product of refining crude oil (part of the petroleum-refining process), in which the mineral oil fraction is a transparent, colorless oil composed predominantly of alkanes and cycloalkanes. In terms of

food, mineral oil or more specifically microcrystalline wax is known as the additive E-905 and is used as a surface treatment on nonchocolate confectionery (typically used for its glossy effect), in chewing gum bases and coatings in jars and cans, and as a coating for hard cheeses and various fillings. It is also used in the surface treatment of melons, mango, papaya, and lastly avocadoes (EFSA, 2013).

B.7.5.2 Alkenes

Alkenes are also known as olefins, they are produced from the alkanes in crude oil. The unsaturated, double-bonded hydrocarbon is perhaps the first and simplest of hydrocarbon functional groups. The physical properties of alkenes and alkanes are similar. At room temperature, they are both nonpolar gaseous molecules that are colorless, combustible, and practically odorless. While linear alkenes of about 5–16 carbon chain long are liquids, the higher number of carbons are responsible for the waxy solids. As well as being produced from crude oil, they can also derive from the dehydration of ethanol. Several simple examples of alkenes include ethene, propene, and butene. Alkenes are not only fairly stable molecules, but also they partake in many chemical reactions. They can be involved in addition reactions such as hydration (the addition of water across the double bond) of alkenes, which in turn yield alcohols, or in redox reactions like those involving oxidation. Perhaps, the most well-known reaction, in terms of food, is the hydrogenation of room-temperature oils with hydrogen and a metal (nickel) catalyst to allow double bonds to be converted to single bonds. This hydrogenation process results in semisolid "margarines" and other similar substances at room temperature. Furthermore, ethene (also known as ethylene), if released, stimulates the start of the ripening process in many plants, certain fruits, and vegetables. In this way, they can be picked before ripening allowing for longevity and better transportation after which the release of ethylene gas triggers the ripening process at or before reaching the point of sale.

B.7.5.3 Alkynes

Alkynes being triple bonded are unsaturated hydrocarbons that are usually found in gaseous form and that are also soluble, not in water, but in organic solvents such as benzene and acetone. In general, as one delves into the hydrocarbons and goes from the alkanes through to the alkenes and alkynes, so the potential for reaction processes increases as does the density and hence the respective boiling points. Ethyne, also known as acetylene, is perhaps the better known of the alkynes because of its flexibility and potential reactivity; it is useful to many industries not least of which is the plastics industry.

B.7.5.4 Aromatic (cyclic) hydrocarbons

It has been noted that atoms of hydrocarbons can be arranged to form closed loops, rings, or circles. These are essentially single-bonded hydrocarbons called cycloalkanes, which are regular alkanes that are formed into rings or loops. Further, because cycloalkanes are saturated compounds, they are not very reactive—just like linear or branched alkanes. Examples of these loops or rings include cyclopropane, cyclobutane, and cyclopentane. In fact, life on earth would not be possible without such compounds, as the majority of the naturally occurring organic compounds found contain hydrocarbon rings in their molecules. Many indeed turn out to be medical compounds, color pigments, and fragrances. The aromatic hydrocarbons are derivatives of the benzene hydrocarbon that contain double bonds. Benzene is not an alcohol; instead, it is a colorless liquid with an aromatic odor. It is for this reason that the benzene group is categorized under aromatic compounds. Benzene is less dense and does not mix with water. However, benzenes are able to dissolve in nonpolar solvents, and in turn,

it can dissolve in fats, resins, and rubber. Lastly, although a carcinogen, benzene is a useful compound in chemistry serving as a reactant in numerous organic compound reactions.

B.7.6 COMPOUNDS CONTAINING OXYGEN

In functional molecules and compounds that contain oxygen, there do several noteworthy examples comprise a hydrocarbon backbone plus a functional group; these include the following:

- *Alcohols*—containing the backbone and a hydroxyl group bound to an sp3-hybridized carbon
- *Ethers*—containing the backbone and an oxygen atom between two sp3-hybridized carbons
- *Epoxides*—containing the backbone and three atom ring containing one oxygen atom and two carbon atoms in which all atoms are sp3 hybridized
- *Aldehydes*—containing the backbone and a carbonyl group in which the carbon is bound to a hydrogen and another carbon
- *Ketones*—containing the backbone and a carbonyl group in which the carbon is bound to two other carbons.
- *Acetals*—containing the backbone and an alkoxy group (OR and R = alkyl) bound to an sp3-hybridized carbon
- *Esters*—containing the backbone and a carbonyl group in which the carbon is bound to an alkoxy group (OR and R = alkyl) and another carbon
- *Carboxylic acids*—containing the backbone and a carbonyl group in which the carbon is bound to a hydroxyl group (OH) and another carbon

B.7.6.1 Alcohols

In the oxygen class of compounds, the alcohol group is an important organic compound containing the hydroxyl functional group (—OH). This is further attached to an alkyl group (which is an unbranched alkane with a hydrogen atom removed from the terminal, or end, carbon). Alcohols can essentially be thought of as alkanes in which single hydrogen atoms are replaced with an —OH group. In this way, the simplest and smallest form of alcohol is methyl alcohol (methanol). On the other hand, ethyl alcohol (ethanol), the next smallest form of alcohol compounds is one of the oldest known pure organic compounds known to exist. While alcohol compounds are used a great deal in the fragrance, pharmaceutical, and fuel industries, ethyl alcohol (also referred to as grain alcohol) is also the alcohol found in alcoholic beverages. Alcohols can be further classified according to the number of alkyl groups attached to the hydroxyl functional group. They are classified as primary (1°) with one alkyl group attached to the carbon bound to the —OH, secondary (2°) with two alkyl groups, or tertiary (3°) with three alkyl groups (Rowe, 2005).

The —OH group makes the molecule polar. Alcohols contain a hydroxyl group (OH) directly attached to a terpene structure (a carbon chain); this molecular make up also allows for benzene rings to be attached somewhere along this line; however, it is not directly attached to the OH group (otherwise, this would become a phenol). They are very versatile compounds able to be created from or turned into many other compounds. Pale color or colorless alcohols are free-flowing liquids. Their physical properties are influenced by the hydrogen bonding ability of the —OH group involved. Solubility is determined by the carbon chains of specific alcohols. Those with up to 4 carbon chains are soluble in water, while those containing 5–10 carbon chain atoms are progressively viscous or oily and effectively

insoluble in water. Some alcohols containing more than 12 carbon atoms are solids at room temperature (Britannica, 2017).

Capable of forming hydrogen bonds with water molecules, so alcohols such as methanol, ethanol, and propanol are highly soluble in water; although those with longer carbon chain lengths are generally less soluble. When it comes to reactivity of alcohol, two of the most common are the dehydration and oxidation processes. When heated in the presence of a strong acid catalyst, alcohols undergo loss of water (dehydration). In this process, an —OH, an —H atom is removed from adjacent carbon atoms creating an alkene in the process. This can be reversed through the hydration of alkenes. Oxidation of alcohols is in fact the increase of oxygen and/or the loss of hydrogen atoms. In the case of the primary alcohols, once oxidized, they become aldehydes; these aldehydes if further oxidized become carboxylic acids. Secondary alcohols, however, can also be oxidized to ketones, while tertiary alcohols do not normally oxidize (Sawyer et al., 2002). Most nonindustrial alcohols these days tend to be created through the fermentation process previously described in this book. Pure hydrocarbons aside, it is the oxygenated and to a lesser extent the nitrogenous and sulfuric hydrocarbon derivatives of alcohol that contributes the bulk of aroma profiles in many foods. Unsaturated aliphatic alcohols generally provide relatively soft, herbaceous, or woody aromas, while others are reminiscent of green leaves and fresh-cut grass. Acyclic terpene alcohols on the other hand like geraniol, linalool, and citronellol tend to be fruitier and citrus-like.

B.7.6.2 Phenols

When it comes to phenols[5] (aka phenolics or carbolic acid), they consist of a hydroxyl group (—OH) group bonded directly to an aromatic group—oftentimes a benzene ring. Phenols are both the name of the group of compounds and a compound in its own right. The simplest of the group is phenol, which is also called carbolic acid. While similar to alcohols in their chemical makeup, there are differences—in phenols, the hydroxyl group is not bonded to a saturated carbon atom as in alcohols (Huang, 1992). As such, it is important to remember that phenols have unique properties of their own and are not classified as alcohols. They also tend to have greater acidity due to the aromatic ring's tight coupling with oxygen while displaying a relatively weak or loose bond between the oxygen and hydrogen atoms. Phenols can be industrially synthesized too; however, they are also produced in abundance by plants and microorganisms and are closely associated with the perception of quality (Ho, 2005). Phenols are everywhere—synthesized for use in adhesives, nylons, polycarbonate plastics, epoxy resins, varnish removers, lacquers, paints, rubber, ink, illuminating gases, tanning dyes, perfumes, and soaps. However, many naturally occurring phenolic and polyphenolic compounds occur in nature and are manufactured for use in flavor and aroma compounds in the food industry. Being aromatic compounds, they can have saccharinely sweet, sometimes strongly herbal, and at times distinctly tarry odorous qualities. Other phenols can also be found naturally in many fruits and vegetables including tomatoes, apples, peanuts, bananas, oranges, cocoa, red grapes, red fruits, and milk. Phenols also tend to be good sources of antioxidants. Generally speaking, common phenolic compounds found in foods can be divided into three groups: simple phenol and phenolic acids, hydroxycinnamic acid derivatives, and flavonoids. Out of these, perhaps, the most important are the flavonoids, consisting predominantly of catechins, proanthocyanidins, anthocyanidins, and flavones and flavonols and their glycosides (Rowe, 2005).

[5]The term phenol is both the name of a compound and that of a family of compounds.

Flavonoids exist in a wide variety of types, and with at least 2000 or so naturally occurring flavonoids, it is easier to further classify them into seven subgroups: flavones, flavanones, flavonols, flavanonols, isoflavones, flavanols (catechins), and anthocyanidins, which are, to some degree or other, discussed throughout the book. Flavanoids then, are omnipresent in plants with almost all plant tissues being able to synthesize them (Giada, 2013). Flavonoids are present in edible fruits, leafy vegetables, roots, tubers and bulbs, herbs and spices, legumes, tea and coffee, and red wine.

B.7.6.3 Ethers

Ethers are formed through the reaction of dehydrating agents removing one molecule of water from two molecules of alcohol; after which, the two alcohol molecules combine to form ether. These alkyl groups are bonded by an oxygen atom to form a carbon-to-oxygen-to-carbon bond. As a result, they are somewhat peculiar and therefore distinguished from other organic compounds in that they lack a continuous chain of carbons within their hydrocarbon backbone. The best-known ether is diethyl ether commonly called ether. Ethers are highly flammable, with a low molecular weight that also makes them very volatile. They are also used widely as solvents and are fairly resistant to biological oxidation. Ethers are widespread in nature and are common linkages in carbohydrates and lignin. On their own, they are a colorless, sweet-smelling liquid. The absence of an —OH group in an ether also has important consequences for its chemical properties, and unlike alcohols, ethers are somewhat inert—although that said, they are still more chemically reactive than the alkanes. Of note too is that as a result of the oxygen atom bonded to two carbons, the functional group of ethers performs many different and important functions marking it out as an important character in organic and synthetic chemistry.

B.7.6.4 Aldehydes and ketones

Aldehydes and ketones each contain a carbonyl group—that is, a carbon atom double bonded to an oxygen atom (C═O). There is an important difference too between aldehydes and ketones in the fact that aldehydes have at least one hydrogen atom that is directly attached to the carbonyl carbon, whereas in ketones, only carbon atoms (not hydrogen atoms) are directly attached to the carbonyl carbon.

Aldehydes belong to the carbonyl function group with the ever-present C═O double bond; however, in this case, it is also attached to at least one hydrogen atom to form the terminal (end) connection. Formed from the partial oxidation of primary alcohols, aldehydes can be further oxidized to form carboxylic acids. Low-molecular-weight aldehydes, such as formaldehyde and others, have sharp, unpleasant odors, while the higher molecular weighted aldehydes like benzaldehyde have pleasant, often flowery aromas found in certain essential oils. Aldehydes are also used in the manufacture of synthetic resins, dyestuffs, flavorings, preservatives, disinfectants, and perfumes, among others (Rowe, 2005). When it comes to reactivity, once again, the oxidation process is probably the more noteworthy of potential chemical reactions. As stated above, the primary alcohols oxidize to aldehydes, and aldehydes in turn can further oxidize to carboxylic acids, while secondary alcohols oxidize to ketones after which ketones cannot be further oxidized.

Ketones, although related to the aldehydes, are less chemically active. They are nonsoluble in water and are thought to have wide-ranging therapeutic influences—these include a calming effect on people, as a sedative, as an aid in digestion, an analgesic, a spasmolytic, a stimulant, an expectorant, to stimulate cell regeneration, an anti-inflammatory, an anti-infective agent, and as a lipolytic (breaks down fats). They have also been reported to have cell regeneration properties and a mucolytic (the ability to liquefy mucous—great in cold and flu situations). More importantly, many aldehydes and ketones are

produced or synthesized industrially as flavor and aroma chemicals. They are particularly important in the food industry where they are used as artificial and/or natural additives to food (Baser and Buchbauer, 2015; Hüsnü et al., 2007).

B.7.6.5 Acids

If compounds were continually oxidized, they would eventually attain the highest possible oxidative state—that of carboxylic acid. After this, any further oxidation would result in carbon dioxide and water (which is classed as inorganic compound).

Carboxylic acids contain the functional carboxyl group; acids with just one of these carboxyl groups are known as monocarboxylic acids, while those with two or more are called polycarboxylic acids both of which may be saturated (single bonds) or unsaturated (double bonds and more). Some of these compounds might also contain hydroxy groups too. There are plenty of examples of mono- and polycarboxylic acid in nature—perhaps, the most pertinent of these include constituents of compounds that make up the group of oils, fats, and waxes known as "fatty" acids. Furthermore, oleic,[6] linoleic, and linolenic acids are also components of the glycerides (the ester that is formed by combining glycerol with oleic, linoleic, and linolenic acids) of many if not most fats and oils. Another type of acid group is the hydroxy acids; these are organic acids that contain both a carboxyl and a hydroxyl group. As a result, a hydroxyl acid displays properties or characteristics of both an alcohol and an acid. Lactic acid belongs in this group; lactic acid is created through the process of bacterial fermentation of milk, moreover, leftover whey from making cheese contains considerable quantities of lactic acid (Sawyer et al., 2002). On top of this, there are many hydroxy polycarboxylic acids, most notable of which are tartaric and citric acids. Tartaric acids are found naturally in fruits and are present in certain winemaking wastes. Citric acid too tends to be the dominant acid in most fruits especially in the obviously acidic lemons, limes, oranges, grapefruits, etc. In general, it can be said that aldehydes, ketones, and carboxylic acids are widespread in the plant and animal kingdom while also playing an important role in certain biochemical processes (Rowe, 2005). They are the aroma, flavor, and fragrances in nature.

B.7.6.6 Esters

Esters are often derived from an organic acid (carboxylic acid) in which, at least one —OH (hydroxyl) group is replaced by an —O-alkyl (alkoxy) group. In other words, esters are formed by condensing an acid with an alcohol in a chemical reaction called dehydration synthesis[7] (condensation or more commonly—esterification). Esters are also found naturally in fats and oils in the form of the fatty acid esters of glycerol. Other esters are sometimes synthesized on an industrial scale to be used in the fragrance and essential oil industries and the food industry to improve aroma and/or taste. Widespread in nature, esters with long-chain carboxylic acids commonly occur as animal and vegetable fats, oils, and waxes while also responsible for many tastes and aromas in flowers and fruits such as apples, pears, strawberries, bananas and pineapples. Oils containing esters with low molecular weights, such as ethyl acetate, are usually volatile fragrant liquids used mainly in industry as a solvent but are also in the food sector in decaffeinating tea and coffee and an additive in confectionary too. Esters with a smaller number of carbon atoms tend to be sweet and fruity and sometimes blossomy, yet this changes to a fatty,

[6]In human and animal diets, oleic acid is considered an essential acid.

[7]Dehydration synthesis or condensation reaction (esterification)—this is where two molecules join together by removing H_2O to form one larger molecule (the ester) and water as a by-product.

soapy, and at times even displaying a metallic quality as the number of carbon atoms increase (Baser and Buchbauer, 2015). In sum, esters are important compounds in organic chemistry responsible for dominant aromas and flavors found in flowers and fruits, among other things.

B.7.7 COMPOUNDS CONTAINING NITROGEN

- *Amines* are neutral, sp3-hybridized nitrogen atoms, bound to sp3-hybridized carbons and/or hydrogen atoms.
- *Nitriles* are carbon-nitrogen triple-bonded molecules.
- *Aziridines* are three atom rings containing sp3-hybridized atoms—one of nitrogen and two of carbon.
- *Nitro groups* are atoms of nitrogen bound to two oxygen atoms, through one single and one double bond.
- *Imines* are double-bonded carbon-nitrogen molecules in which the carbon atom is also bound to two other carbon atoms.
- *Amides* are carbonyl group whereby a carbon atom is bound to an amino group.

Simple aliphatic chemical compounds containing nitrogen include amines, amides, and nitriles. Although there are many groups in the same family of functional groups, the two main ones are the amines and the amides although others include nitro (—NO_2), cyano (—CN), isocyano (—NC), nitrite (—ONO), imine, imide, and azide groups.

B.7.7.1 Amines

Just as there are primary, secondary, and tertiary alcohols, so amines also comprise primary, secondary, and tertiary structures too. It should be noted that amines are also derivatives of ammonia (NH_3) whereby one or more hydrogen atoms are replaced by an alkyl or aryl group. Nearly all amines are basic in nature and as a result react with water to form basic solutions giving the final compound a bitter taste and a slippery feeling. Due to this basicity, amines react with acids to form salts. Furthermore, amines usually have strong disagreeable odors, as both amines and ammonia are produced by decomposition of nitrogen-containing compounds. More specifically, low-molecular-weight amines tend to have sharp, penetrating odors similar to ammonia, while the higher molecular weighted amines are more pungent and can smell like rotting fish or decaying animals. All proteins contain amines in the form of amino acids:

Amino acids—amines are often found in molecules containing carboxylic acid groups (—COOH). These are the amino acids,[8] and they are an important group of compounds in all living things. There are 20 or so common amino acids, and each can come together in different formations that create nearly all proteins in human beings.

B.7.7.2 Amides

Another nitrogenous substance, amides are somewhat distinct from amines even in spite of containing the same $-NH_2$ group and being closely associated with ammonia. Amides are mostly derived from a reaction between an amine and a carboxylic acid, but they can also be prepared from amines,

[8]Amino acids are molecules containing an amine group, a carboxylic acid group, and a side chain that is specific to each amino acid.

anhydrides, esters, and nitriles. The simplest amine is called methanamide that is a liquid at room temperature, while other amides are solid. In nature, amides are pervasive and are often employed as structural materials as the amide linkage resists hydrolysis and confer flexibility and structural rigidity. Low-molecular-weight amides are commonly used as industrial solvents, in the plastic, rubber, and paper and in the water and sewage industries. In terms of the biochemical context, amide linkages are called peptide linkages and as such are involved in the formation of amino acids, the building blocks of proteins, and in many vitamins. In food, especially when baking, grilling, and frying, acrylamide is the chemical that is formed in carbohydrate-rich foods at temperatures at 120°C/248°F and above.

B.7.7.3 Nitriles

Nitriles are any organic compounds that have a —C≡N functional group. That is to say, nitriles are a category of chemical compounds that include a nitrogen atom connected to a carbon atom by a triple covalent bond. Inorganic compounds containing the same —C≡N group, however, are not referred to as nitriles, but rather cyanides. Organic nitriles are readily converted to carboxylic acids, amides, amines, aldehydes and ketones, and other groups (Rowe, 2005). They are therefore found in widespread use in organic synthesis. Nitriles occur naturally in nature and can be found in a diverse group of plant and animal sources from fruit stones or pits, like almonds, and during cooking of vegetables such as cabbages, cauliflower, and brussel sprouts. The cooking process actually releases nitriles through the hydrolysis chemical reaction. Nitriles have similar aromas to aldehydes and are sometimes used in place of aldehydes. They also tend to be more stable and are fairly resistant to oxidation (Herrmann, 2005; Rowe, 2005). Nitriles also occur naturally in marine sources.

B.7.8 COMPOUNDS CONTAINING SULFUR

- *Thiols* comprises thiol group (SH) bound to a sp3-hybridized carbon.
- *Sulfides* are compounds of a sulfur atom between two sp3-hybridized carbons.
- *Thioesters* are carbonyl groups in which the carbon atom is bound to a sulfide group and another carbon atom.

B.7.8.1 Thiols

Thiols—(sometimes referred to as mercaptans) contain a carbon-bonded sulfhydryl group and are the sulfur equivalent of alcohol's hydroxyl group (—OH) whereby sulfur replaces the oxygen in the equation (—SH). Indeed, since sulfur and oxygen are closely associated on the periodic table, so they share certain similar chemical bonding properties. As far as odors go, thiols (sulfuric compounds) have strong repulsive tendencies reminiscent of rotting flesh, feces, skunk sprays, and body odor and when sulfur in wine reacts with yeast giving off unpleasant smells. That said, however, not all thiols produce unpleasant odors; some fruit chemicals like that of grapefruit's monoterpenoid thiol are responsible for the sweet acidic aroma of the fruit. On top of that, the pleasant aromas of garlic (Lee et al., 2014) and shitake mushrooms are possible because volatile organosulfur compounds. The same can be said of the sometimes—subtle characteristic flavors present in wine, nuts, chocolate, cheese, coffee, and tropical fruit flavors.

Sulfur too is important to most living beings; this can be seen in the 20 or so required amino acids, of which two in particular—cysteine and methionine—are organosulfur compounds. Furthermore, thiols, as the functional group of the amino acid cysteine, participate in protein folding through the oxidation

reaction potentially contributing to a protein's tertiary and quaternary structure. Thiols are also active in carbohydrate and fat metabolism through coenzyme A, marking thiols out as having important roles in biological systems.

B.7.9 COMPOUNDS CONTAINING OTHER ELEMENTS

- *Haloalkanes* is an atom of halogen bound to a carbon atom in an alkyl group.
- *Benzene derivatives* are one to six substituents on benzene ring.
- *Nonaromatic heterocycles* are rings containing at least one atom other than carbon, which does not satisfy the rules of aromaticity or antiaromaticity.
- *Aromatic heterocycles* are rings containing at least one atom other than carbon, which satisfies the rules of aromaticity.
- *Terpenes* are a class of hydrocarbons in which the molecules are composed of isoprene units.

B.7.9.1 Haloalkanes

Haloalkanes also referred to as halogenoalkanes or alkyl halides are saturated[9] organic chemical compounds whereby one or more hydrogen atoms in an alkane have been replaced by one or more halogen atoms (often fluorine, chlorine, bromine, or iodine). It is a white crystalline solid, many of which are highly toxic but are nevertheless useful as solvents and as fire extinguishants, propellants in industry. They are also synthesized to create chlorofluorocarbon (CFCs). CFCs were widely used as a propellant and refrigerant because of the high heat required for vaporization and its low toxicity. However, CFCs were found to cause ozone depletion, so hydrochlorofluorocarbon HCFCs are now used as a substitute. In nature, there are many halogen-containing organic compounds that occur and are useful to the medicinal industry, while in agriculture, haloalkanes are applied as herbicides and fungicides. Others still are useful in the production of the iodine-containing hormone, thyroxine—an important thyroid hormone.

B.7.9.2 Aromatic organic compounds

All aromatic compounds are either entirely made up of ring compounds or at least have cyclic groups of aromatics in their structures that can be either saturated or unsaturated. As a rule, cyclic compounds are divided into alicyclic and aromatics (also called arenes). Regarding the alicyclic compounds—the cycloalkanes present with only single bonds of which the simplest member is the three-membered cyclopropane. Cycloalkenes and cycloalkynes contain multiple bonds and usually exist only in the form of large rings, the macrocycles.

Considering aromatic hydrocarbons for the moment, it can be said that they contain multiple double bonds. The simplest and most commonly known of all aromatic compounds is the eponymous hydrocarbon, the benzene ring. Known as the parent ring, aromatics based on this benzene ring can exist "fused" with other rings on an edgewise plane to create polycyclic compounds or "fused" on a corner so that one atom has two bonds connecting one ring and two connecting to another. This arrangement is called a spiro and is important in certain natural products. Also, it is possible to change the

[9]Haloalkanes are saturated organic chemical compounds in which all of the chemical bonds between the atoms within the molecule are single bonds.

characteristic properties of the aromatic hydrocarbons. For instance, if one were to replace one of the external carbon elements with a heteroatom (usually oxygen, sulfur, or nitrogen), one creates either an aromatic heterocycle or alicyclic heterocycles (depending on the position of the heteroatom).

B.7.9.3 Terpenes

Terpenes are perhaps one of the most important classes of natural organic chemical compounds. They are widely found in essential oils as well as being used in the flavor and aroma industries. Synthesized by plants, terpenes are probably the most widespread group of natural products. While the majority is found in plants, some of the larger and more complex terpenes are present in animals. They are difficult to classify through conventional means of functional groupings simply because terpenes exist in most of the common groupings. Instead, a useful means of classification is through the number of terpene units each subunit a molecule contains. These include the monoterpenes (with two isoprene units), sesquiterpenes (with three isoprene units), diterpenes (with four isoprene units), and so on and so forth. These isoprenes are exuded from plant leaves as a natural by-product of the metabolic process. "Terpene" at times is used as a catchall to include the terpenoids; these are simply terpenes that have been chemically modified through reactions like oxidation. After methane, the most common volatile organic compounds found in the atmosphere are the isoprenes and terpenes. While terpenes have many different functions in both plants and animals, their main role in food are important mainly as aroma compounds (Manahan, 2011).

B.8 SUMMARY OF ORGANIC CHEMISTRY

It is helpful at this point to summarize a little of what we have discovered:

- *Atoms* are the building blocks of matter; they are also elements; there are 118 elements in the periodic table.
- Atoms are composed of a *nucleus* (a collection of *protons* and *neutrons*) surrounded by a cloud of *electrons*; collectively, atoms have an "*electric charge*" that by themselves[10] are neutral (*nonpolar*).
- *Electronegativity* reflects the attraction of electrons to an atom or molecule the higher the charge the stronger the force.
- *Electronegativity* gives rise to *polarity*.
- When atoms combine, they form *molecules/substances/compounds*, and their charge may change.
- It is the electrons in any atom, their number, and *electronegative* force that determine an atom's (an element's) *reactive properties*—that is, boiling point, solubility, and volatility.
- As atoms/elements/compounds combine (bond), so these *reactions can be affected*, as in redox, altered polarity, change in pH, the combined boiling point, volatility, etc.
- *Carbon* is the backbone of organic chemistry. It is also responsible for the coal, crude oil, and diamonds that we so covet.
- *Polar* molecules dissolve in polar solutions, while *non*polar molecules dissolve in nonpolar solutions.
- Most organic compounds are *nonpolar* or are *weakly polar*. This generally results in *low melting* and *boiling* points and high vapor pressure (*volatility*).

[10]There are some exceptions to this rule, but they are not important in the context of this book.

- *Hydrocarbons* (combination of hydrogen and carbon) are the simplest of all organic compounds.
- Hydrocarbons form the building blocks; by attaching specific functional groups to these backbones, they form the alcohols, esters, and phenols and a whole host of important compounds.

B.9 SUMMARY OF FUNCTIONAL GROUPS

- Compounds can be classified according to their molecular structures or their chemical properties.
- Structural hydrocarbons can be categorized as *aliphatic* (straight chained), *cyclic* (ringed nonaromatic rings), and aromatic (comprising benzene rings).
- Aliphatic compounds can be *saturated* (joined by single bonds—i.e., alkanes) or *unsaturated* (joined by double bonds (the alkenes, etc.) or triple bonded like the alkynes).
- Some important chemical reactions and processes include *oxidizing* and *reducing agents*, *acids* and *bases*, *combustion* and *corrosion*.
- Functional groups describe these chemical reactive collections of molecules.
- *Common groups* include aromatics, alkanes, alkenes, alkynes, alcohols, phenols, aldehydes, ketones, acids, esters, amines, amides, nitriles, thiols, sulfides, and alkyl halides.
- Polarity ranking of the functional groups with the most polar first is amide > acid > alcohol > ketone > aldehyde > amine > ester > ether > alkane.

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APPENDIX

ESSENTIAL OILS

C

(See also Appendix B)

There are maybe upward of about 3000 essential oils, out of which there are 300 or so that are of sufficient commercial importance to be traded on the world market (Zuzarte and Salgueiro, 2015). While they are called oils, they should not be confused with "fixed" or fatty oils that actually comprise lipids and may or may not necessarily be volatile. Essential oils then differ from fixed oils both chemically and physically. A simple test to distinguish between the two can be achieved by placing a drop of oil on filter paper, and while essential oil evaporates completely leaving no trace, fixed oil leaves a permanent stain—even if heated (Bauer et al., 2008). It is important to note too that essential oils are "whole" oils that are distilled from plants, and it is not the same as the perfume or fragrance oils that are artificially created, even if from organic components (Hüsnü et al., 2007). Essential oils too are also to be distinguished from "distillates" that are products distilled from plant materials using ethanol or with ethanol-water mixtures (Adams, 2012).

It is interesting too that were one to take all of the chemical constituents of an essential oil and combine them in the same proportions as those naturally found in the plants themselves, it is considered unlikely that you will be able to replicate the health or therapeutic properties of the original oil itself, let alone the aromatic qualities (Hüsnü et al., 2007). In this respect, the whole of the true plant is widely accepted as being greater than the sum of its parts. This is why many alternative practices, whether medicinal or therapeutic as in aromatherapy, insist on using high-quality, clinical grade, pure essential oils (Adams, 2012). Another reason why whole essential oils are used is that were one able to similarly synthesize an oil-specific properties, it is unlikely it could be achieved at a competitive price.

C.1 THE CHEMISTRY OF ESSENTIAL OILS

Essential oils comprise volatile compounds of hydrocarbons and their many oxygenated derivatives—although nitrogen, halogen, and sulfur derivatives are not uncommon in the mix either. The hydrocarbons, as we learned from the previous section, are mainly composed of the monoterpenes and the sesquiterpenes, while the oxygenated derivatives are composed of alcohols, acids, esters, aldehydes, ketones, etc. (Baser and Buchbauer, 2015; Hüsnü et al., 2007). The nitrogen-based derivatives include amines, imines, and nitriles. The sulfur-based derivatives take the form of thiols and sulfides, while the alkyl halides form the halogen-based derivatives, etc. In addition to these components, there are also the phenylpropanoids, the fatty acids, and their esters. These then, between them, make up the bulk of most essential oils' chemical profiles (Hüsnü et al., 2007; Adams, 2012).

While the previous section concerned itself with generalities of organic chemistry, the following section gives an indicative look at some of each chemical group's properties in context of essential oils. Of note here is the subjective and speculative nature of much of the information. That is, while aromas themselves can be fairly confidently described and while certain chemical substances might be proved to have antifungal properties or perhaps act as stimulants, much else is based on numerous personal subjectivities, hearsay, and anecdotal evidence. Saying that, there have been and continues to be studies looking into many of the claims, and while there might be reason to be confident of certain claims, proof of such is beyond the scope of this book. As such, we reiterate that any described properties are subjective and are the result of a widespread literature review—unless of course it is otherwise stated. As an aide to the various aroma profiles, there is a valuable resource called the "the common fragrance and flavor materials" by Horst Surburg and Johannes Panten; it has various incarnations, but the fifth edition is out and is very comprehensive.

In essence, every essential oil contains perhaps one, two, or three dominant chemical components. These collectively determine the oil's overall qualities, therapeutic properties, and best uses. Bear in mind too that other chemical constituents within each oil might act to enhance, accentuate, or even subdue certain qualities, be they citrus, floral, herbaceous, camphoraceous, spicy, resinous, woody, or earthy.

Some common names of the various food-grade essential oils—as denoted by the Food and Drug Agency of the USDA—are as follows:

Common name—Alfalfa, allspice, almond, bitter (free from prussic acid) ambrette (seed), Angelica root, Angelica seed, Angelica stem, angostura (cusparia bark), anise, asafoetida, balm (lemon balm), balsam of Peru, basil, bay leaves, bay (myrcia oil), bergamot (bergamot orange), bitter almond (free from prussic acid), bois de rose, cacao, camomile (chamomile) flowers, Hungarian camomile (chamomile) flowers, Roman or English cananga, capsicum, caraway, cardamom seed (cardamom), carob bean, carrot, cascarilla bark, cassia bark, Chinese cassia bark, Padang or Batavia cassia bark, Saigon celery seed, chervil, chicory, cinnamon bark, Ceylon cinnamon bark, Chinese cinnamon bark, Saigon cinnamon leaf, Ceylon cinnamon leaf, Chinese cinnamon leaf, Saigon citronella, citrus peels, clary (clary sage), clover, coca (decocainized), coffee, cola nut, coriander, cumin (cummin), Curacao orange peel (orange, bitter peel), Cusparia bark, dandelion, dandelion root, dog grass (quack grass and triticum), elder flowers, estragole (esdragol, esdragon, and tarragon), estragon (tarragon), fennel, sweet fenugreek, galanga (galangal), geranium, East Indian geranium, geranium rose, ginger, grapefruit, guava, hickory bark, horehound (hoarhound), hops, horsemint, hyssop, immortelle, jasmine, juniper (berries), kola nut, laurel berries, laurel leaves, lavender, lavender spike, lavandin, lemon, lemon balm (see balm), lemon grass, lemon peel, lime, linden flowers, locust bean, lupulin, mace, mandarin, marjoram, sweet mate, melissa (see balm), menthol, menthyl acetate, molasses (extract), mustard, naringin, neroli, bigarade, nutmeg, onion, orange bitter flowers, orange bitter peel, orange leaf, sweet orange, orange sweet flowers, orange sweet peel, origanum, palmarosa, paprika, parsley, black pepper, white pepper, peppermint, Peruvian balsam, petitgrain, petitgrain lemon, petitgrain mandarin or tangerine, pimenta, pimenta leaf, pipsissewa leaves, pomegranate, prickly ash bark, rose absolute, rose (otto of roses and attar of roses), rose buds, rose flowers, rose fruit (hips), rose geranium, rose leaves, rosemary, saffron, sage, Greek sage, Spanish sage, St. John's bread, savory summer, savory winter, *Schinus molle*, sloe berries (blackthorn berries), spearmint, tamarind, tangerine, tarragon, tea, thyme, white thyme, wild or creeping thyme, triticum (see dog grass), tuberose, turmeric, vanilla, violet flowers, violet leaves, wild cherry bark, ilang-ilang, and zedoary bark.

C.2 SUMMARY OF ESSENTIAL OILS

As can be seen from both the sections in the book and the complimentary study in the appendices, essential oils are both therapeutic and important and interesting component that will only gain more popularity in the kitchen, especially among those inventive cooks looking for novelty ways in which to enhance their culinary creations.

Furthermore, as mention, in a therapeutic capacity, essential oils can be seen to interact with the cell membranes by means of their physiochemical properties, and once contact has been made, they can influence the cell's enzymes, carriers, ion channels, and receptors. Studies concerning the physiological effects on humans include brain stimulation, anxiety-relieving sedation, and antidepressant activities, as well as increasing the cerebral blood flow. Studies also describe the effects of odors on cognition, memory, and mood. The most important suggested areas of essential oil use are in urology, dermatology, sleep and nervous disorders, laxatives, erosive gastritis, cardiac and vascular systems, immunomodulation drugs, colds and coughs, stress-related illnesses, formation of stomach ulcers, and tumor growth. Effects have also been noted on blood circulation nerve growth, antiviral activity, antioxidants, antimicrobial, chemical defense against plant pathogenic diseases, etc.

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APPENDIX

A NOTE ABOUT UNITS OF MEASUREMENT

D

Joules or Calories?

A caveat on joules and calories—in the International System of Units (SI), energy values are officially quantified in joules (J). That said, it is still routine for people to continue to express energy in pre-SI thermal energy units (calories, Calories, kilocalories, and kcal), more out of familiarity or habit than any other reason. Further, there is an important distinction and a certain amount of confusion in the terms "calories," "Calories," and "kilocalories." So, in terms of proper usage:

A calorie or *"gram" calorie*—this is the amount of energy it takes for 1 g of water to be raised by 1° C/33.8°F; this is known as a "small" calorie and is denoted by a small "c," sometimes written as "cal."

A Calorie or *"kilogram" calorie*—this is similar to the small calorie except it refers to the energy required to raise 1 kg of water by 1°C/33.8°F; this is expressed as a "large" Calorie with a capital "C" or also as kcal. Not surprisingly, confusion comes about when, as is common, "calorie," "Calorie," "cal," and "kcal" are used interchangeably. Having said that, a user's intentions when using any of the above can usually be extrapolated from the context in which it is being used. It is also worth mentioning that in spite of the different meanings of calorie and Calorie (kcal), it has almost become accepted convention to accept the interchangeability of the words.

Joules—converting a single calorie to the standard SI unit of energy equates to 4.184 J; conversely, 1 J equals 0.239 calories (EUFIC, 2010; Hargrove, 2006; IoM, 2005).

Alcohol "proof" and "alcohol by volume"—in the early 18th century, the alcohol content of distilled beverages in the United Kingdom was determined by using gunpowder. A beverage would only be considered acceptable by pouring it on gunpowder and lighting it. If the flame burned steadily with a blue hue, only then was it considered 100° "proof." This meant too that it contained 57.15% ethanol by volume.

In the United States by contrast, alcoholic proof is simply defined as double the percentage of alcohol contained in a solution at 15.6°C/60°F. Thus, 100 proof is equal to 50% alcohol.

Internationally, however, a beverage's alcohol content is measured according to the recommendation set forth in the International Organization of Legal Metrology. It is measured by actually distilling off the alcohol in the beverage and weighing the components of the alcoholic fraction against the non-alcoholic fraction, with the resultant figure expressing the percentage of alcohol by weight (ABW). Alternatively, the volume of the alcoholic fraction is measured and expressed as a percentage of alcohol by volume (ABV) at a temperature of 20°C/68°F. Alcohol by weight (ABW) can then, if needed, be converted to alcohol by volume (ABV) by dividing ABW by 0.079.

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COMMON FOOD pH VALUES

E

The table presented here is compiled from multiple sources and discloses various food and nonfood pH values. As can be seen, there are a great deal of foods that we eat which are quite acidic in nature yet there are very few alkaline foods. In fact, microorganisms, including yeasts, molds, and bacteria, are sensitive to a food's pH in that very low or high pH values help prevent microbial growth. Indeed, by dividing the group into high and low pH value foods, it can be said that no unprocessed high pH food has much of a preservative value against microbial growth, yet there are some low pH value foods that allow some protection against microbes. Having said that, very few foods possess low enough pH values to completely inhibit the growth of microorganisms by themselves. Consequently, if preservation is required, then most foods require some form of microbial control such as heat processing, refrigeration or frozen storage, and drying. A combination of those mentioned is often used in the industrial food sector, although the most common of food preservation techniques in such cases is heat processing or canning.

As can be seen from the Table E.1 there are many more acidic foods than there are alkaline foods. The pH value of a food item is a direct cause of the free hydrogen ions present within that particular food.

Table E.1 pH Table of Common Food and Other Material pH Values

Acid or Base	pH	Common Examples
Acid	0	Hydrochloric acid
	1	Stomach acid
	2	Lemon juice 2.00–2.60, lime 2.00–2.80, cranberry juice 2.30–2.52, vinegar 2.40–3.40, loganberries 2.70–3.50, gooseberries 2.80–3.10, plums, blue 2.80–3.40, plums, damson 2.90–3.10, grapefruit juice 2.90–3.25, grapes, seedless 2.90–3.82, pomegranate 2.93–3.20
	3	Tamarind 3.00, Yangsberries, frozen 3.00–3.70, grapefruit 3.00–3.75, strawberries 3.00–3.90, rhubarb 3.10–3.40, blueberries 3.11–4.5, quince, fresh, stewed 3.12–3.40, pineapple 3.20–4.00, raspberries 3.22–3.95, sauerkraut 3.30–3.60, peaches 3.30–4.05, apricots 3.30–4.80, cherries, frozen 3.32–3.37, tangerine 3.32–4.48, guava, canned 3.37–4.10, sherry-wine 3.37, mangoes, ripe 3.40–4.80, cherries, maraschino 3.47–3.52, pears 3.50–4.60, tomatoes, canned 3.50–4.70, tomatoes, paste 3.50–4.70, mustard 3.55–6.00, plums, green gage 3.60–4.30, plums, red 3.60–4.30, prune, pureed 3.60–4.30, Worcestershire sauce 3.63–4.00, kumquat, Florida 3.64–4.25, oranges 3.69–4.34, honey 3.70–4.20, raisins, seedless 3.80–4.10, tomatillo 3.83, ketchup 3.89–3.92, plums, yellow 3.90–4.45, nectarines 3.92–4.18, prune juice 3.95–3.97

Continued

Table E.1 pH Table of Common Food and Other Material pH Values—cont'd

Acid or Base	pH	Common Examples
	4	Tomatoes, juice 4.10–4.60, cheese, cream, Philadelphia 4.10–4.79, cucumbers, pickled 4.20–4.60, tomatoes, puree 4.30–4.47, tomatoes 4.30–4.90, pimiento 4.40–4.90, soy sauce 4.40–5.40, buttermilk 4.41–4.83, persimmons 4.42–4.70, herring, pickled 4.50–5.00, bananas 4.50–5.20, mangosteen 4.50–5.00, peppers 4.65–5.45, lychee 4.70–5.01, milk, sour 4.70–5.65, cheese, cottage 4.75–5.02, jackfruit 4.80–6.80, pumpkin 4.90–5.50, peas, pureed 4.90–5.85, basil pesto 4.9, rambutan (Thailand) 4.9, straw mushroom 4.9, figs, canned 4.92–5.98
	5	Oyster mushrooms 5.00–6.00, bread, white 5.00–6.20, shrimp paste 5.00–6.77, greens, mixed 5.05–5.22, loquat (may be acidified to pH 3.8) 5.1, pickles 5.10–5.40, cheese, Roquefort 5.10–5.98, bamboo shoots 5.10–6.20, macaroni, cooked 5.10–6.41, cucumbers 5.12–5.78, watermelon 5.18–5.60, barley, cooked 5.19–5.32, baby corn 5.2, cheese, parmesan 5.20–5.30, bread, rye 5.20–5.90, peppers, green 5.20–5.93, papaya 5.20–6.00, chives 5.20–6.31, cabbage 5.20–6.80, turnips 5.29–5.90, sweet potatoes 5.30–5.60, parsnip 5.30–5.70, shallots, cooked 5.30–5.70, onions, red 5.30–5.80, codfish, boiled 5.30–6.10, truffle 5.30–6.50, beets beans 5.30–6.60, onions, yellow 5.32–5.60, horseradish, freshly ground 5.35, salmon, fresh, broiled 5.36–6.40, onion white 5.37–5.85, cheese, edam 5.4, bread, pumpernickel 5.4, potatoes 5.40–5.90, kidney beans 5.40–6.00, walnuts 5.42, bran flakes 5.45–5.67, bread, whole wheat 5.47–5.85, fennel (anise) 5.48–5.88, leeks, cooked 5.49–6.10, ackees 5.50, artichokes 5.50–6.00, red ginseng 5.5, leeks 5.50–6.17, eggplant 5.50–6.50, okra, cooked 5.50–6.60, green cabbage 5.50–6.75, spinach 5.50–6.80, yams, cooked 5.50–6.81, coconut, fresh 5.50–7.80, radishes, white 5.52–5.69, all bran 5.59–6.19, string beans 5.6, cauliflower, raw 5.6, red cabbage 5.60–6.00, beans 5.60–6.50, yeast 5.65, oysters 5.68–6.17, cheese, Swiss Gruyere 5.68–6.62, zucchini, cooked 5.69–6.10, cheese, stilton 5.7, hearts of palm 5.7, shad roe, sautéed 5.70–5.90, caviar, American 5.70–6.00, celery 5.70–6.00, parsley 5.70–6.00, lettuce, iceberg 5.70–6.13, sardines 5.70–6.60, kippered, herring 5.75–6.20, melon, casaba 5.78–6.00, romaine lettuce 5.78–6.06, calamari (squid) 5.8, garlic 5.8, mangoes, green 5.80–6.00, lettuce 5.80–6.15, vermicelli, cooked 5.80–6.50, grass jelly 5.80–7.20, radishes, red 5.85–6.05, watercress 5.88–6.18, carrots 5.88–6.40, cheese, cheddar 5.9, chicory 5.90–6.05, tuna fish, canned 5.90–6.20, milk, evaporated 5.90–6.30, corn 5.90–7.30, spaghetti, cooked 5.97–6.40
	6	Capers 6, carp 6, curry sauce 6, oyster, smoked 6, scallop 6, sea snail (top shell) 6, water chestnut 6.00–6.20, Brussels sprout 6.00–6.30, octopus 6.00–6.50, wild rice 6.00–6.50, squid 6.00–6.50, soy beans 6.00–6.60, melons, honey dew 6.00–6.67, asparagus 6.00–6.70, mushrooms 6.00–6.70, white rice 6.00–6.70, mussels 6.00–6.85, olives, black 6.00–7.00, clams 6.00–7.10, olives, ripe 6.00–7.50, gelatine, plain jell 6.08, aloe vera 6.10, egg yolk 6.1, herring 6.1, noodles, boiled 6.08–6.50, abalone 6.10–6.50, flounder, boiled 6.10–6.90, coconut milk 6.10–7.00, cantaloupe melon 6.13–6.58, Swiss chard, cooked 6.17–6.78, haddock, filet, broiled 6.17–6.82, cod liver 6.2, eel 6.2, razor clams 6.2, sturgeon 6.2, scallion 6.2, trout, sea 6.20–6.33, dates, canned 6.20–6.40, brown rice 6.20–6.80, peas, cooked 6.22–6.88, mackerel, king 6.26–6.50, raspberry 6.27, avocados 6.27–6.58, peanut butter 6.28, cuttlefish 6.3, kelp 6.3, broccoli, cooked 6.30–6.52, lentils, cooked 6.30–6.83, milk, condensed 6.33, kale, cooked 6.36–6.80, congee 6.4, milk, cow 6.40–6.80, peas, dried (split yellow), cooked 6.43–6.62, cream, 40% 6.44–6.80, cauliflower, cooked 6.45–6.80, peas, dried (split green), cooked 6.45–6.80, milk, goat's 6.48, peas, chick, garbanzo 6.48–6.80, lima beans 6.50, anchovies 6.5, cream, 20% 6.50–6.68, crab meat 6.50–7.00, shrimp 6.50–7.00, eggs, new-laid, whole 6.58, sea bass 6.58–6.78, spinach, cooked 6.60–7.18, crabmeat, cooked 6.62–6.98, palm, heart of 6.7, lotus root 6.9+, soybean milk 7, soy bean curd (tofu) 7.2, tea 7.2, tofu (soybean curd) 7.2, pollack, filet, broiled 6.72–6.82

Table E.1 pH Table of Common Food and Other Material pH Values—cont'd

Acid or Base	pH	Common Examples
Neutral	7	Pure water, lobster, cooked 7.10–7.43, tea 7.20, bird's nest soup 7.20–7.60, conch 7.52–8.40, cheese, camembert 7.44
Base/alkaline	8	Egg whites 7.0–9.0, seawater 8.3
	9	Baking soda
	10	Milk of magnesia
	11	Ammonia
	12	Soapy water
	13	Bleach, oven cleaner
	14	Lye (sodium hydroxide), liquid drain cleaner

Compiled and modified from multiple sources: Bridges, M.A., Mattice, M.R., 1939. Over two thousand estimations of the pH of representative foods. Am. J. Dig. Dis. 9, 440–449; Anon, 1962. pH values of food products. Food Eng. 34 (3), 98–99; Grahn, M.A., 1984. Acidified and Low Acid Foods From Southeast Asia, US Food and Drug Administration, Silver Spring, MD; Warren, L.L. et al., 1995. Examination of canned foods. In: FDA Bacteriological Analytical Manual, eighth ed. AOAC International, Gaithersburg, MD (Chapter 21, Table 11); USFDA, 2007. Approximate pH of Foods and Food Products, vol. 13. Department of Health and Health Services, Food and Drug Administration, Silver Spring, MD.

Indeed, it is these acids in foods that release the hydrogen ions. This in turn gives acidic foods their distinct sourness. Thus, in short, pH may simply be defined as a measure of foods' free acidity.

FURTHER READING

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Glossary

A

Acetic acid bacteria These are the makers of vinegar.

Acetic acid This is an effective agent of preservation in which a weak solution (0.1%) is able to inhibit the growth of many microbes.

Aleurone This is the granular protein in the cells of plant seeds.

Alkaloid It is a term used to describe substances produced as end products of nitrogen metabolism in some plants.

Alpha acids These are chemical compounds found in the resin glands of the flowers of the hop plant and are the source of hop's bitterness.

American oak species These tend to possess lower quantities of tannins while maintaining higher levels of oak lactones and vanillin.

Amino acid residues A protein chain will have somewhere in the range of 50–1000+ recursive amino acid residues. Residue is the correct terminology simply because a peptide chain isn't made up of whole amino acids. That is because in the aggregation of amino acids or as they combine, a water molecule is lost in the process. The peptide chain is then made up out of what is left after the process—in other words, it is made up of amino acid residues. Having said that, this book will follow customary convention and will continue to refer to amino acid residues as amino acids.

Amino acids These are molecules containing an amine group, a carboxylic acid group, and a side chain that is specific to each amino acid.

Amorphous entities These are without a clearly defined shape or form.

Amorphous In scientific terms, "amorphous" means a lack of a crystalline structure, i.e., something without solid shape or form.

Amphora An amphora (amphorae plural) is a type of container with a characteristic shape and size, usually but not always made of clay or other ceramic materials.

Amylase It is an enzyme produced in saliva that works on breaking down food before entering the stomach.

Amylopectin It is the noncrystalline form of starch, consisting of branched polysaccharide chains.

Amylose It is the crystalline form of starch comprising long unbranched polysaccharide chains.

Anaerobic glycolysis It is extremely important for tissue or skeletal muscles that have high energy requirements. It is also required at times when there is an insufficient or an absence of oxidative enzymes. Anaerobic glycolysis is produced by lactic acid fermentation and is only effective during short periods of intense exercise or energy needs.

Antibody An antibody, also known as immunoglobulin, is a protective protein produced by the immune system in response to the presence of a foreign substance in the body—called an antigen.

Aroma compound An aroma compound is also referred to odorant, aroma, or fragrance. In its basic definition, it is a compound that has a smell or odor. A compound has a smell or odor when it is volatile, so it can be transported to the olfactory system in the upper part of the nose.

Aspergillus It is the same type of mold used in the production of soybean sauce.

Autolysis It is the destruction of cells or tissues by their own enzymes.

Autotroph An autotroph is a self-feeder, or a producer of complex organic compounds such as carbohydrates, fats, and proteins from very simple substances using predominantly energy photosynthesis or through inorganic chemical reactions (chemosynthesis). In this way, autotrophs are the primary producers in a food chain, like plants (on land) or algae (in water).

B

β-Oxidation In biochemistry and metabolism, β-oxidation (beta-oxidation) is the catabolic process by which fatty acid molecules are broken down to generate acetyl-CoA, which then enters the citric acid cycle.

Baking soda This is a good example of a "base" in the kitchen.

Beta-carotene It comes from the orange pigment in carrots and other plant foods.

Biennials (Not to be confused with biannual—which occur twice a year) they either live for 2 years or their life cycle is a 2-year long process.

Black tea The strong "black" tea that is most familiar in the West today is the result of the processing the Chinese developed in the 1840s specifically for export to the West.

Bolus It is a small rounded mass of a substance, especially of chewed food mixed with gustatory fluids at the moment of swallowing.

Borax It is used as an ingredient in caviars as a preservative, allowing less salt to be used; however, it is banned in some countries because of perceived detrimental to public health.

Brownian motion It is the random and erratic movement of a particle as it receives a jolt or displacement, caused, for example, by other particles bumping into it or through an external force whether physical, thermal, or others.

Butterfat When it comes to fat content while 80% is a general rule, France specifies a minimum fat content of 82%, while some American producers aim for 85%. Specialty butters are also made for professional bakers and pastry cooks where higher butterfat content is desired; this leaves less water in the fat for things like puff pastry.

C

Cacao nibs Raw cacao nibs are simply cacao beans that have been ground into smaller pieces.

Caking It is the tendency of some dry goods like flour and starch to clump together and cause lumps in sauces.

Calcium hydroxide Traditionally called slaked lime or calcium oxide (CaO), it is commonly known as quicklime.

Calpains These comprise three primary components, the proteins μ-calpain, m-calpain (known as calpains l and ll), and calpastatin.

Carbohydrates These provide body to the coffee.

Carotenoid pigments in shells Because carotenoid pigments are much more soluble in fat than in water, you can gain more color if the cooking liquid is mainly fat or oil or butter.

Casein micelle The casein micelle also contains water and salts (mainly phosphorous and calcium).

Catalysis It is the acceleration of a chemical reaction by a catalyst.

Catalyst To catalyze something is to encourage a chemical reaction to happen faster.

Cathepsins These are enzymes that digest proteins.

Caviar Although "caviar" should refer only to the salted eggs of sturgeon, it has come to mean any lightly salted eggs.

Cellular respiration This is a general term describing all metabolic reactions that are involved in the creation of usable energy from the breakdown of ingested nutrients.

Chelation therapy It is a medical process that involves administering of chelating agents to remove heavy metals from the body.

Chemesthesis It arises when certain chemical compounds activate receptors normally associated with other senses that mediate pain, touch, and thermal perception, i.e., false heat and false coolness.

Chemoreceptor This is a sensory cell or organ responsive to chemical stimuli.

Chlorophyll It is a green pigment, present in green plants and in cyanobacteria, which is responsible for the absorption of light that provides energy for photosynthesis.

Chlorophyllase It is most active between 66–77°C/151–170°F and only destroyed near the boiling point.

Chloroplast Its main role is to conduct photosynthesis, whereby the photosynthetic pigment, chlorophyll, takes sunlight, converts it, and stores it in the energy-storage molecules ATP and NADPH.

Chromoplasts These are plastids (double-membraned "saclike") other than chloroplasts that produce and store pigments. They are found in roots, leaves, flowers, and ripe fruits. Chromoplasts contain carotenoids that are lipid-soluble pigments from yellow to red in color, which give color to the plant tissues containing them.

Cis and trans isomerism It describes molecules with the same chemical makeup but has different physical structures.

Coenzymes These are nonprotein compounds that mainly help the functioning of enzymes.

Comminuted meat It is pulverized or finely ground meat.

Condensation products or reactions These are reactions in which two molecules combine to form a larger molecule, losing a smaller molecule in the process.

Conformation It is the shape or structure of the protein.

Covalent bond A covalent bond is a bond between two nonmetallic elements characterized by the sharing of pairs of electrons between the two atoms.

Cow's milk It contains more than double the protein and minerals found in mother's milk.

Cultivars These are plant varieties that have been propagated not only from seeds but also from bulbs and stem cuttings too.

Cytochromes These are any of a number of compounds consisting of heme (an iron-containing compound) bonded to a protein. They function as electron transfer agents in many metabolic pathways, especially cellular respiration.

D

Dehydration synthesis or condensation reaction (esterification) This is where two molecules join together by removing H_2O to form one larger molecule (the ester) and water as a by-product.

Distillates Distillates of wine are called brandies.

Dripping It is the fat that is extracted by rendering meat until the fat melts away.

E

Elastic materials These are those that strain when stretched then return to their original state once any stress is removed.

Electrolytes These are substances that produce an electrically conducting solution when dissolved in a polar solvent, such as water.

Energy Energy in mammals comes from the glucose that has been either ingested (eaten) directly or synthesized from the food eaten. If it is not needed for energy use straight away, it is converted into glycogen and stored as a form of energy primarily in the cells of the liver and the muscles. It functions as the secondary long-term energy storage deposit after adipose tissue (tissue containing fat cells).

Enology It is the science and study of wine and winemaking; it is separated from viticulture, the science of vine growing and of grape harvesting. Enology is the overarching field of study.

Enzymatic This is the action of enzymes at work. Enzymes accelerate or act as catalysts in chemical reactions. Most cellular metabolic processes require enzymes in order to occur at rates fast enough to sustain life.

Enzyme substrates In this sense, these are the substance on which an enzyme acts.

Ethylene gas It is a hormone that accelerates ripening in fruits and incites defensive activity and accelerated aging in other tissues.

Evaporated milk The cooking and concentration of evaporated milk causes some browning; this is partly due to the Maillard reaction of the protein and the part caramelization of the lactose.

Evisceration This means the removal of internal organs.

Exogenous In this sense, exogenous means developed from external substances.

F

Fatty acids These are the building blocks of fat within the human body and within the food we eat. So, while we consume whole fats, the human digestive system breaks down these fats into their component fatty acids that can then be absorbed into the blood. Fatty acid molecules are usually joined together in groups of three, forming a triglyceride. Triglycerides are also made in our bodies from the carbohydrates that we eat too. Lastly, fatty acids have many important known functions in the body, including energy storage. So, if it is not available for one reason or another, fatty acids act as fuel for the cells instead.

Fermentation Whether natural or introduced, fermentation is very slow as the high concentration of sugars and acids inhibits the growth of all but the hardiest of microbes.

Fiddleheads or fiddlehead ferns These are the curled fronds of a young fern leaf. They are harvested for use as a vegetable.

Fish eggs These contain, among other things, fat and savory amino acids and nucleic acids.

Flavorant While the terms "flavoring" or "flavorant" in lay terms denote the combined chemical sensations of taste and smell, the flavor and fragrance industries use the same terms to refer to edible chemicals and natural extracts that alter the flavor of food and food products.

Fractions These are the different components that make up the wash to be distilled. Desirable components (fractions) like ethanol are evaporated or distilled in order to separate them out.

Freeze drying It retains more of the volatile aroma compounds and produces a fuller flavor than hot spraying.

Freezer burn It is the drying out of produce caused by the evaporation of frozen water molecules (sublimation) that in turn develop "burned" patches leaving a tough texture and stale flavor.

Freezing This can be thought of in a similar process to drying foods. Water first crystallizes and then slowly leaves the food in an increasingly dehydrated environment.

Fructose It is the sweetest of all the sugar carbohydrates.

Functional group In organic chemistry, it is a reactive portion of a molecule that characterizes the chemical reactions of those molecules.

G

Gelatin Collagen in beef tissue is the origin of the gelatin that is used in the making of many jellies, desserts, etc. There are vegetarian alternatives; however, beef gelatin still remains the most popular and widely used type of gelatin today.

Gelatin It is obtained by the thermal denaturation of collagen.

Gelatinization Gelatinization of starch means that it absorbs moisture, swells, and then becomes semifirm.

Genotype In a very broad sense, the term "genotype" refers to the genetic makeup of an organism. That is to say, it describes an organism's complete set of genes.

Globular proteins These, named after their shape, are one of the common protein types: other protein types include fibrous, disordered, and membrane proteins.

Gluconeogenesis (GNG) It is a metabolic pathway that results in the generation of glucose from noncarbohydrate carbon substrates. Gluconeogenesis is one of many mechanisms used by humans and animals to maintain blood glucose levels.

Glycerol It is a clear, viscous, sweet-tasting liquid that belongs to the humble polyol compound. (A polyol is an alcohol containing multiple hydroxyl groups.)

Glycosidic A glycosidic bond is a type of covalent bond that joins a carbohydrate (sugar) molecule to another group.

Grains or cereals These are used more often than not interchangeably. Cereals are plants in the grass family, Gramineae, whose members produce edible and nutritious seeds (or grains).

Gravlax This means "buried salmon."

H

Hadrons The subatomic hadron particle is a composite particle made up of three quarks that are themselves held together by the strong force—a force similar in effect to the electromagnetic force. The best-known hadrons are the neutrons and the protons.

Hemoglobin It contains in excess of 10,000 atoms of hydrogen, carbon, nitrogen, oxygen, sulfur, and four atoms of iron. It is the iron in hemoglobin that is more important as it gives blood its ability to combine with oxygen.

Haloalkanes These are saturated organic chemical compounds in which all of the chemical bonds between the atoms within the molecule are single bonds.

Herbaceous plants These are those plants with little or no woody tissue and that generally persist for only one growing season.

Heterogeneous Heterogeneous populations are diverse, varied, disparate, and multifarious. This differing nature means recommended daily intakes of nutrients vary quite differently.

Heterogeneous Heterogeneous suspensions have diverse, varied, or assorted particle sizes dispersed in a suspension liquid.

Heterotrophs These are organisms that cannot manufacture their own food, so they obtain their food and energy by taking in organic substances usually from autotrophs (plant and algae) or other heterotrophs.

Homeostasis It is the function of a system (e.g., human blood work) in which a variable (say the concentration of glucose in solution) is actively regulated to remain as constant as possible.

Hops These are flowers of the hop plant *Humulus lupulus*.

Humulone and lupulon The important bittering alpha acids humulone and lupulon are not very soluble in water; however, prolonged boiling transforms the acids into soluble flavorful structures.

Hydrolysis It is the breakdown of a compound by a chemical reaction with water.

Hydrophilic These are water-loving elements.

Hydrophobic These are water-hating elements.

I

Ice phase in frozen foods Most of the water content exists in a separate, solid ice phase.

Immunoglobulins These are antibodies (a blood protein) especially high in colostrum (the first milk breasts produce).

Industrial enzymes These are complex molecules or proteins that are manufactured and aid in catalysis. They are sourced from plant or animal tissue and microbes.

Inosinic acid or inosine monophosphate (IMP) It is a nucleotide monophosphate that is important in the process of metabolism.

Ionic An ionic compound is a chemical compound that comprises ions held together by electric charges or forces termed "ionic bonding." The compound consists of positively charged ions called cations and negatively charged ions called anions. Overall, the compound is neutral.

Isolate This is the term used to describe specific constituents from essential oils or other natural materials, for instance, eucalyptol from eucalyptus.

Isomerization It is the process by which one molecule is transformed into a variation of the same molecule. That is, it has exactly the same atoms, but the atoms have a different arrangement, for example, from A-B-C to B-A-C.

J

Jiu It is the Chinese word that refers to all alcoholic beverages. It is a word often mistranslated into English as "wine," whereas the meaning is more akin to alcoholic beverage or simply liquor. Interestingly, the same Chinese characters are used to describe jiu are also used in Japan where it is pronounced "sake" and in Korean, where it is shortened to "ju."

K

Kinesthesis It is the sensation of movement or straining muscles, tendons, and joints—muscle sense.

L

Lactic acid bacteria These are the principal organisms involved in the manufacture of cheeses, yogurt, buttermilk, sour cream, and cultured butter.

Lactic acids Many of the lactic acids are the same species found in fermented dairy products and vegetables.

Lactose It is peculiar to milk and only a handful of plants, and therefore, very few organisms possess lactose-breaking enzymes.

Limbic system The limbic system is a collection of connected structures residing close to the middle of the brain. Linked within the central nervous system, these structures work together affecting a wide range of specific behaviors including emotions, motivation, and memory.

Lipid peroxidation It is the degradation of lipids through oxidation. It is the process in which free radicals take away electrons from lipid cell membranes, resulting in cell damage.

Lipolysis It is the breakdown of lipids that involves hydrolysis of triglycerides into glycerol and free fatty acids.

Lipophilic This refers to the ability of chemical compounds to dissolve in fats, oils, lipids, and nonpolar solvents such as hexane or toluene.

Lipoxygenases These are a group of iron-containing enzymes that catalyze the dioxygenation of polyunsaturated fatty acids.

M

Maceration In this sense, it is the process whereby phenolic compounds, coloring agents (anthocyanins), and flavor component are leached from plant material into ethyl alcohol.

Malic acid It is a component of many of the foods that we eat daily and is found as a naturally occurring organic compound in various fruits.

Malolactic fermentation It is the conversion of malic acid into lactic acid through the actions of bacteria as opposed to yeasts. This has the added benefit of reducing tartness in the wine giving it a softer taste on the palate.

Mascarene Islands The Mascarene Islands is a group of islands in the Indian Ocean.

Mastication It is the process of chewing food, breaking it down.

Meat glazes These are slowly simmered until they are reduced to about a tenth of their original volume. This produces a thick, syrupy, sticky consistency due to the high gelatin content (about 25%). This type of stock is called a "glace de viande," which cools to a solid jelly.

Metabolism It is the breaking down (catabolism) or the building up (anabolism) of food in the body. Metabolism can be considered as functionally active in three main areas—firstly, the transformation of food into energy/fuel to operate cellular processes; secondly, the transformation of food into building blocks for proteins, lipids, some carbohydrates, and nucleic acids; and lastly, the transformation of food to be used as vehicles for the safe disposal of nitrogenous wastes that would otherwise tend to form toxic ammonia.

Metabolite A metabolite is any substance produced during metabolism although the term might also be used to refer to the product that remains after the process of metabolism by the body.

Methanol It can be lethal if consumed in amounts greater than 30–50 g.

Metmyoglobin It is the oxidized form of the oxygen-carrying heme protein myoglobin.

Microbe A microbe is any microorganism, especially a bacterium causing disease or a fermentation.

Milk fat This accounts for about half the calories of whole milk and the fat-soluble vitamins (A, D, E, and K.)

Milk powder It dilutes the strong bitter and slightly astringent chocolate flavor and helps make it taste milder.

Mitochondrion A mitochondrion is an organ found in large numbers in most cells whereby the biochemical processes of respiration and energy production occur.

Monomers These are molecules capable of reacting or binding with other molecules to form polymers.

Monounsaturated and polyunsaturated fats These are known by other names—omegas. There are three types of omega fatty acids: omega-3, omega-6, and omega-9.

Mucilage It is a viscous secretion.

Mucoproteins These are glycoproteins composed primarily of mucopolysaccharides.

Mucor This is important in certain aged cheeses.

Musk It is a strong-smelling substance, used predominantly in perfumes, and is either artificially made or obtained from a gland of an Asian (musk) deer.

Myoglobin It coagulates to form the tan-colored version of the same molecule called hemichrome.

N

Narcotics These are drugs or other substances like alcohol that affect mood and modify behavior usually in non-medical usage.

Noble rot It is a gray fungus—*Botrytis cinerea*—that affects wine grapes that in the wrong conditions can whole destroy crops. However, under the right conditions, i.e., dry, less humid conditions, the gray rot becomes beneficial, and as the grapes become a little dried, like raisins, this type of infection is known as noble rot. This produces particularly fine and sweet, concentrated wines.

Nonenal It is an unsaturated aldehyde, an important aroma component of aged beer.

Nonproteinogenic (not protein making) amino acids These are not naturally found in the genetic code of any organisms.

Nucleotides They form the basic structural unit of nucleic acids such as DNA.

O

Oats These are inherently gluten-free but are frequently contaminated with wheat during growing or processing.

Oleic acid in human and animal diets Oleic acid is considered an essential acid.

Olfactory receptors These are in fact neurons rather than cells. This is different from the gustatory receptors, which are cells.

Organelle In cell biology, an organelle is one of a number of structures with specialized functions suspended in the cytoplasm of a cell.

Organic acids There are several organic acids that plants accumulate including citric, malic, tartaric, and oxalic.

Oxidase It is any enzyme that is capable of oxidizing something, while the polyphenol is the thing being oxidized.

P

Pellicle Hardening of the pellicle would create a barrier to the movement of moisture from the interior to the exterior.

Pepsins These are the main digestive enzyme produced in the human stomach responsible for breaking down proteins.

Peptides These are biologically occurring short chains of amino acids.

Perennial plants These are those plants that live for more than 2 years.

Phenol The term phenol is both the name of a compound and that of a family of compounds.

Phosphate It is a salt or ester of phosphoric acid.

Phospholipids The human body is made up of cells, including phospholipids, which are important molecules providing structure and protection to cells. Phospholipids consist of a hydrophilic (water loving) and a hydrophobic (water fearing) tails. Phospholipids line up arranging themselves into two parallel layers, a "phospholipid bilayer." This layer makes cell membranes and is critical to a cell's ability to function.

Phosphoproteins These are common in living organisms in which they play a role in various metabolic processes such as in the regulation of cell nuclei, in ion transport, and in the oxidation processes in a cell's mitochondria.

Phytochemicals These are nonessential nutrients, meaning that they are not required by the human body for sustaining life.

Piña It is often roasted in earth or stone pits, giving them their distinctive smoky character.

Plasticizer In foods, water plasticizing is a nonfat, predominantly hydrophilic (water loving) process that softens or makes food flexible (plasticity). This takes place in the rehydration of dried foods like pasta and dried mushrooms.

Pliny the Elder It was a Roman author of the much celebrated "Natural History" volume of books of which one was dedicated solely to the humble grape.

Polymer A polymer is a large or macromolecule composed of many repeated subunits. They play an essential role in everyday life from natural biopolymers including DNA and proteins. Polymers are created by combining many small molecules called monomers. Polymer's relatively large molecular mass allows for unique physical properties, including toughness, viscoelasticity, and semicrystalline structures. Put another way, a monomer is a single atom or molecule that can join with other monomers to make new substances called polymers.

Polypeptides These are organic polymers (linear) that comprise a large number of amino acid residues that are ultimately bonded together in a chain forming part of or the whole protein molecule That is to say, amino acids are joined together by peptide bonds that form polypeptide chains.

Polysaccharides These are carbohydrates (e. g., starches, cellulose, or glycogen) whose molecules consist of a number of sugar molecules bonded together.

Pomace A pomace is the pulpy residue remaining after fruit has been crushed in order to extract its juice, i.e., skins, seeds, and stems.

Prophylactic It prevents disease.

Protease This refers to a group of enzymes whose catalytic function is to hydrolyze (breakdown) proteins. They are also called proteolytic enzymes or systemic enzymes.

Proteases They speed up the breakdown of proteins.

Proteins In adding protein to hot liquids, one must be careful not to coagulate the proteins on contact. It is generally more prudent to add a little of the hot liquid into the protein to gently bring up the heat before adding the protein mix to the sauce.

Proteolysis It is the breakdown of proteins or peptides into amino acids by the action of enzymes.

Protoplasm In biology, protoplasm is the living contents of a cell surrounded by a plasma membrane that effectively separates the interior of the cell from the outside environment.

Purees The solid particles in a puree are plant cell walls—an agglomeration of many thousands of carbohydrate and protein molecules.

Pyrazine and thiazoles These are heterocyclic aromatic organic compounds.

R

Reductant/reducer A reducing agent (aka a reductant or reducer) is any element or compound that loses (donates) an electron. It is in fact any sugar that has a free aldehyde group or a free ketone group. All monosaccharides are reducing sugars along with some disaccharides, oligosaccharides, and polysaccharides.

Reductones These are enediols with a carbonyl group adjacent to the enediol group.

Rheology It is also applicable to nonfood items too.

Rhizopus This is the major mold in soybean tempeh—a soy product from Indonesia. It is made by natural culturing and controlled fermentation. This binds soybean into a cake form.

Robusta and *arabica* plants These are sometimes used for cross breeding of both *Coffea* species

Robusta Not all robustas are of inferior quality; some are valued especially in espressos for their deep flavor and good crema.

Roes These consist of separate eggs held loosely together in a weak protein solution all encased in a thin, fragile membrane.

Roundfish It is a general term used to describe the oval/rounded fish as compared with flatfish.

Roux A "roux" is a classical French-based mixture of oil/butter and flour that is used in thickening sauces.
Rumen This represents the first chamber in the alimentary canal of ruminant animals.
Rye flour Although rye flour contains both glutenin and gliadin, it is incapable of forming gluten because certain substances in rye flour interfere with its creation. This is the reason why wheat flour is included in rye bread recipes.

S

Saturated and unsaturated compounds These might comprise simple straight or branched or ring arrangements, or they may also contain functional groups too.
Saturation of a solution It occurs when a dissolved substance is exactly balanced by the solvent's ability to prevent bonding of the solute.
Seaweeds All seaweeds are algae, but not all algae are seaweeds. Seaweeds tend to be easily visible, comprise many cells, and grow in the sea. There are red, brown, and green seaweeds. However, many algae are microscopic single-cell diatoms consisting of a single cell.
Serum It is the amber-colored liquid that separates out when blood coagulates.
Shear force It is the pressure of pushing one part of a body in one direction and another part of the body in the opposite direction.
Shellfish This can be a little misleading as not all members have a shell or an exoskeleton.
Silage or ensilage It is a method of green fodder preservation through which fermentation is used to slow spoiling.
Skin It is good for fish stock as the flesh can be as little as between 0.3% and 3% collagen.
Solera It is the process of aging liquids like wine, beer, vinegar, and brandy, by means of fractional blending. The purpose of this intensive process is the creation and maintenance of reliable qualities in the beverage over time.
Solubility Many carbohydrates and proteins are partially or fully soluble in water, while lipids in general are less so. In fact, lipids' solubility varies greatly among types, with some being only partially soluble while others, not at all, due to most being hydrophobic in nature.
Somesthesis Sensory systems associated with the body; it includes skin senses and internal organs.
Sous vide cooking In sous vide cooking, low temperatures cook food slowly in vacuumed bags in a water bath to, among other things, allow proteins to unfold, coagulate, and gelate and to allow enzymes to act in optimal temperatures. In sous vide cooking though, the water bath is generally preheated to the desired temperatures.
Sturgeons These are fish from which caviar are made—there are 27 varieties of sturgeon.
Surfactant A surfactant is a substance that aims to reduce the surface tension of a liquid in which it is dissolved.
Swim bladders These are balloons of connective tissue that fill with air or gas to adjust the fishes' buoyancy.
Syneresis It is the drawing together of the protein particles of a gel, with some separation of the liquid medium and shrinkage of the gel, i.e., weeping.

T

Tastant A tasting is the thing being tasted.
Tea It has one of the highest flavonoid contents of all plants taking up as much as 15% of the dry leaf weight.
Terpenes These are a large class of naturally occurring organic compounds derived from multiples of five hydrocarbon structural units called isoprenes (a contraction of the word isoterpene).
Tetrapods These are four-footed animals.
Theobroma In Greek, it means the food of the gods.
Thermization It involves heating raw milk to temperatures of around 63–65°C for 15 s, while pasteurization involves heating milk at 63°C for 30 min or up to 71°C for 15 s.
Thermoreversible This is a process in which gelatin and its denatured proteins, for example, go from a liquid to a gel (bond) at cool temperatures; however, by applying heat, this process can be reversed whereby the gelatin bonding is undone or unraveled and it becomes a liquid again.

Trans fats and hydrogenation In their natural state, unsaturated fats can be oxidized creating a rancid, stale, or unpleasant smell or flavor. By saturating the fat (fixing more hydrogen to natural unsaturated fats), the number of double bonds is decreased in a process called hydrogenation; this slows the process of rancidity.

Trigeminal nerve The trigeminal nerve sends messages to the brain.

Triglycerides These are derived from glycerol and three fatty acids. They are the main component of body fat in animals and humans and vegetable fat.

Triple point of water The triple point of water is the point when temperature and pressure are in equilibrium to allow the three phases (solid, liquid, and gas) can coexist.

Tubers These are short, thickened, fleshy parts of an underground stem.

U

Urea It is what most animals turn protein waste into before they excrete it.

V

Vasodilation (or vasodilatation) It refers to the widening of blood vessels result from relaxation of smooth muscle cells within blood vessel walls.

Vinegar It is made from wine as the ethanol oxidizes into acetic acid in the presence of air.

Visual cycle The visual cycle in humans is the biological conversion of light into an electric signal for the brain.

Viticulture It is the science, production, and study of grapes in general, while viniculture refers same thing only for grapes specifically used for wine.

Volatility In chemistry, volatility refers to a substances tendency to vaporize.

W

Wheat starch This is different from wheat flour in that the wheat starch is the carbohydrate component that is left after processing wheat flour to remove the protein portion.

Whisky It is the anglicized term of the Gaelic "water of life."

Wild yeasts Many things like sweet liquids, sour bread, and wine will spontaneously ferment and eventually sour naturally; some wild yeasts will give certain "off"-flavors to the final product. So, whenever yeasts are required in a product, most people will use specific "cultured" yeasts for specific purposes.

Winnowing It is the practice of blowing a current of air through (usually grain) in order to remove the chaff or outer papery coverings.

Y

Yeasts Yeasts for brewing cannot tolerate more than approximately 20% alcohol concentration.

Yolk pigment The color of an egg yolk is from the xanthophyll carotenoids—lutein and zeaxanthin.

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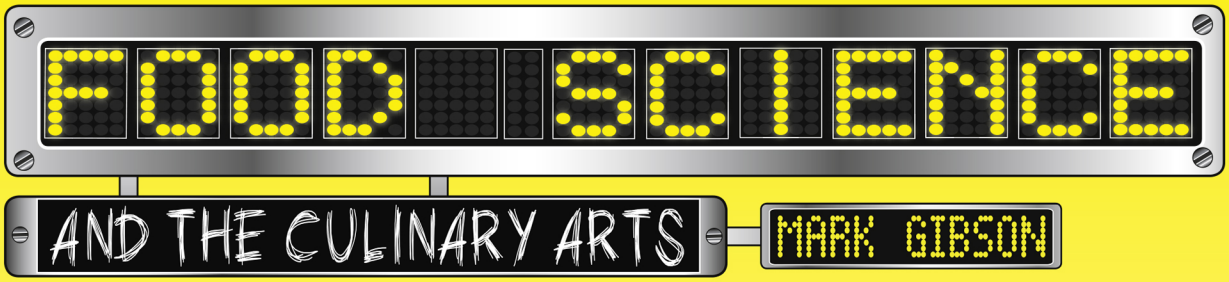
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This book offers comprehensive coverage of all aspects of food and beverage science, from the principles underpinning the subject to factors affecting a range of ingredients from whole and processed foods

- Provides foundational food science information to culinary students and specialists
- Integrates principles of food science into practical applications
- Spans food chemistry to ingredients, whole foods, and baked and mixed foods
- Includes a comprehensive glossary of terms in food science

Food Science and the Culinary Arts is a unique reference that incorporates the principles of food and beverage science with practical applications in food preparation and product development. The first part of the book covers the various elements of the chemical processes that occur in the development of food products. It includes exploration of sensory elements, chemistry, and the transfer of energy and heat within the kitchen. The second part looks in detail at the makeup of specific foodstuffs from a scientific perspective, with chapters on meat, fish, vegetables, sugars, chocolate, coffee, and wine and spirits, among others. It provides a complete overview of the food science relevant to culinary students and professionals training to work in the food industry.

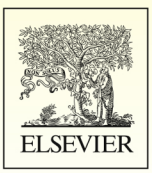
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