3 Carbohydrates

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Carbohydrates comprise more than 90% of the dry matter of plants. As a result, they are abundant, widely available, and inexpensive. Carbohydrates are common components of foods, both as natural components and as added ingredients. Both the quantities consumed and the variety of products in which they are found are large. They have many different molecular structures, sizes, and shapes, exhibit a variety of chemical and physical properties, and differ in their physiological effects on the human body. They are amenable to both chemical and biochemical modification, and both modifications are employed commercially in improving their properties and extending their use.

Starch, lactose, and sucrose are digested by normal humans, and they, along with D-glucose and D-fructose, are human energy sources, providing 70–80% of the calories in the human diet worldwide. In the United States, they supply less than that percentage with widely varying amounts from individual to individual.

The term carbohydrate suggests a general elemental composition, namely, $C_x(H_2O)_y$, which signifies molecules containing carbon atoms along with hydrogen and oxygen atoms in the same ratio as they occur in water. However, the great majority of natural carbohydrate compounds produced by living organisms do not have this simple empirical formula. Rather, most natural carbohydrates are in the form of oligomers (oligosaccharides) or polymers (polysaccharides) of simple and modified sugars. The source of low-molecular-weight carbohydrates is often the depolymerized natural polymers. However, this chapter begins with a presentation of simple sugars and builds from there to larger and more complex structures.

3.1 MONOSACCHARIDES

Carbohydrates contain chiral carbon atoms. A chiral carbon atom is one that can exist in two different spatial arrangements (configurations). Chiral carbon atoms have four different groups attached to them. The two different arrangements of the four groups in space (configurations) are nonsuperimposable mirror images of each other (Figure 3.1). In other words, one is the reflection of the other that one would see in a mirror, with everything that is on the right in one configuration on the left in the other and vice versa.

D-Glucose, the most abundant carbohydrate and the most abundant organic compound (if all of its combined forms are considered), belongs to the class of carbohydrates called monosaccharides. Monosaccharides are carbohydrate molecules that cannot be broken down to simpler carbohydrate molecules by hydrolysis, so they are sometimes referred to as simple sugars. They are the monomeric

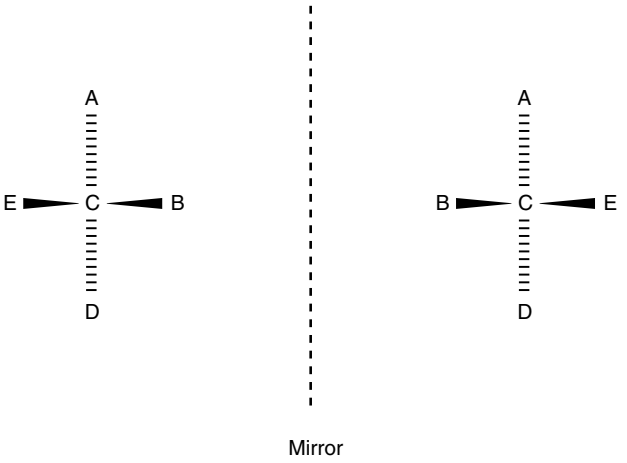

FIGURE 3.1 A chiral carbon atom. A, B, D, and E represent different atoms, functional groups, or other groups of atoms attached to the carbon atom C. Wedges indicate chemical bonds projecting outward from the plane of the page; dashes indicate chemical bonds projecting into or below the plane of the page.

TABLE 3.1
Classification of Monosaccharides

	Kind of Carbonyl Group	
Number of Carbon Atoms	**Aldehyde**	**Ketone**
3	Triose	Triulose
4	Tetrose	Tetrulose
5	Pentose	Pentulose
6	Hexose	Hexulose
7	Heptose	Heptulose
8	Octose	Octulose
9	Nonose	Nonulose

units that are joined together to form larger structures, namely, oligosaccharides and polysaccharides (see Sections 3.2 and 3.3), which can be converted into their constituent monosaccharides by hydrolysis.

D-Glucose is both a polyalcohol and an aldehyde. It is classified as an aldose, a designation for sugars containing an aldehyde group (Table 3.1). The suffix -ose signifies a sugar; the prefix ald- signifies an aldehyde group. When D-glucose is written in an open or vertical, straight-chain fashion (Figure 3.2) known as an acyclic structure, with the aldehyde group (carbon atom 1) at the top and the primary hydroxyl group (carbon atom 6) at the bottom, it is seen that all secondary hydroxyl groups are on carbon atoms 2, 3, 4, and 5, all of which have four different substituents attached to them and are, therefore, chiral. Naturally occurring glucose is designated as the D form; specifically, it is D-glucose. It has a molecular mirror image, termed L-glucose. Since each chiral carbon atom has a mirror image, there are 2^n arrangements for these atoms. Therefore, in a six-carbon aldose such as D-glucose (with its four chiral carbon atoms), there are 2^4 or 16 different arrangements of the carbon atoms containing secondary hydroxyl groups, allowing formation of 16 different six-carbon sugars with an aldehyde end. Eight of these belong to the D-series (Figure 3.3); eight are their mirror images and belong to the L-series. All sugars that have the hydroxyl group on the highest-numbered chiral carbon atom (C-5 in this case) positioned on the right-hand side are arbitrarily called D-sugars

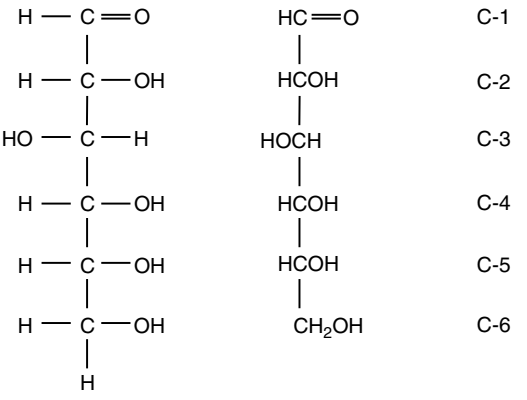

FIGURE 3.2 D-Glucose (open-chain or acyclic structure).

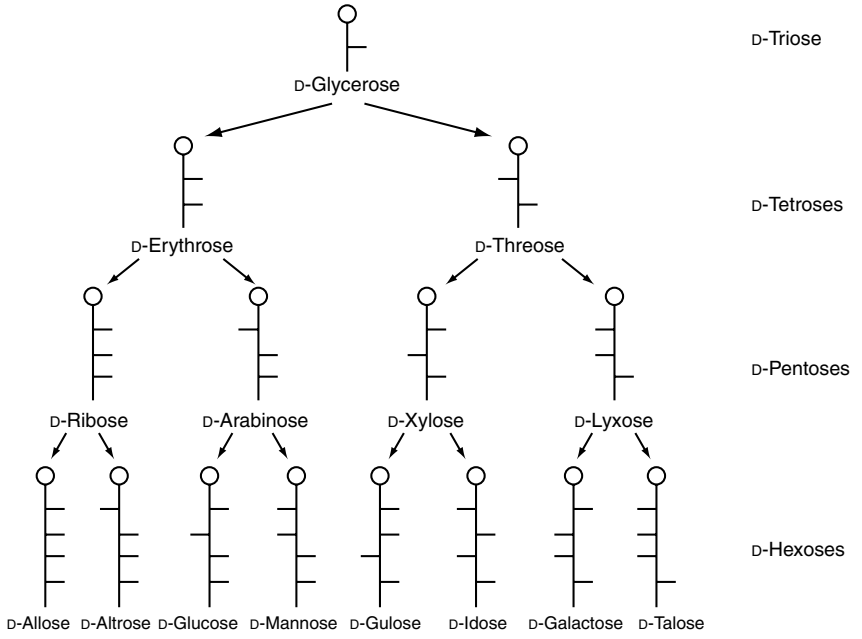

FIGURE 3.3 Rosanoff structure of the D-aldoses containing from 3 to 6 carbon atoms.

and all with a left-hand positioned hydroxyl group on the highest numbered chiral carbon atom are designated L-sugars. Two structures of D-glucose in its open-chain or acyclic form (called the Fischer projection) with the carbon atoms numbered in the conventional manner are given in Figure 3.2. In this convention, each horizontal bond projects outward from the plane of the page and each vertical bond projects into the plane of the page. (It is customary to omit the horizontal lines for covalent chemical bonds to the hydrogen atoms and hydroxyl groups as in the structure on the right.) Because the lowermost carbon atom is nonchiral, it is meaningless to designate the relative positions of the atoms and groups attached to it. Thus, it is written as $-CH_2OH$.

D-Glucose and all other sugars containing six carbon atoms are called hexoses, the group of aldoses present in nature in the greatest amount. The categorical names are often combined, a six carbon atom aldehyde sugar being termed an aldohexose.

There are two aldoses containing three carbon atoms. They are D-glyceraldehyde (D-glycerose) and L-glyceraldehyde (L-glycerose), each possessing but one chiral carbon atom. Aldoses with four

carbon atoms, the tetroses, have two chiral carbon atoms; aldoses with five carbon atoms, the pentoses, have three chiral carbon atoms and comprise the second most common group of aldoses. Extending the series above six carbon atoms gives heptoses, octoses, and nonoses, which is the practical limit of naturally occurring sugars. Development of the eight D-hexoses from D-glyceraldehyde is shown in Figure 3.3. In this figure, the circle represents the aldehyde group; the horizontal lines designate the location of each hydroxyl group on its chiral carbon atom, and at the bottoms of the vertical lines is the terminal, nonchiral, primary hydroxyl group ($-CH_2OH$). This shorthand way of indicating monosaccharide structures is called the Rosanoff method. Sugars whose names are in italics in Figure 3.3 are commonly found in plants, almost exclusively in combined forms, that is, in glycosides, oligosaccharides, and polysaccharides (see later). D-Glucose is the only free aldose usually present in natural foods, and that too only in small amounts.

L-Sugars are less numerous and less abundant in nature than are the D-forms, but nevertheless, have important biochemical roles. Two L-sugars found in foods are L-arabinose and L-galactose, both of which occur as units in carbohydrate polymers (polysaccharides).

In the other type of monosaccharide, the carbonyl function is a ketone group. These sugars are called ketoses. (The prefix ket- signifies the ketone group.) The suffix designating a ketose in systematic carbohydrate nomenclature is -ulose (Table 3.1). D-Fructose (systematically D-*arabino*-hexulose) is the prime example of this sugar group (Figure 3.4). It is one of the two monosaccharide units of the disaccharide sucrose (see Section 3.2.3) and makes up about 55% of common high-fructose syrup (HFS) and about 40% of honey. D-Fructose has only three chiral carbon atoms (C-3, C-4, and C-5). Thus, there are but 2^3 or eight ketohexoses. D-Fructose is the only commercial ketose and the only one found free in natural foods, but, like D-glucose, only in small amounts.

3.1.1 Monosaccharide Isomerization

Simple aldoses and ketoses containing the same number of carbon atoms are isomers of each other, that is, a hexose and a hexulose both have the empirical formula $C_6H_{12}O$ and can be interconverted by isomerization. Isomerization of monosaccharides involves both the carbonyl group and the adjacent hydroxyl group. By this reaction, an aldose is converted into another aldose (with the opposite configuration of C-2) and the corresponding ketose, and a ketose is converted into the corresponding two aldoses. Therefore, by isomerization, D-glucose, D-mannose, and D-fructose can be interconverted (Figure 3.5). Isomerization can be catalyzed by either a base or an enzyme.

3.1.2 Monosaccharide Ring Forms

Carbonyl groups of aldehydes are reactive and readily undergo nucleophilic attack by the oxygen atom of a hydroxyl group to produce a hemiacetal. The hydroxyl group of a hemiacetal can react further (by condensation) with a hydroxyl group of an alcohol to produce an acetal (Figure 3.6). The carbonyl group of a ketone reacts similarly.

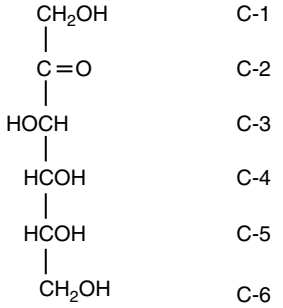

FIGURE 3.4 D-Fructose (open-chain or acyclic structure).

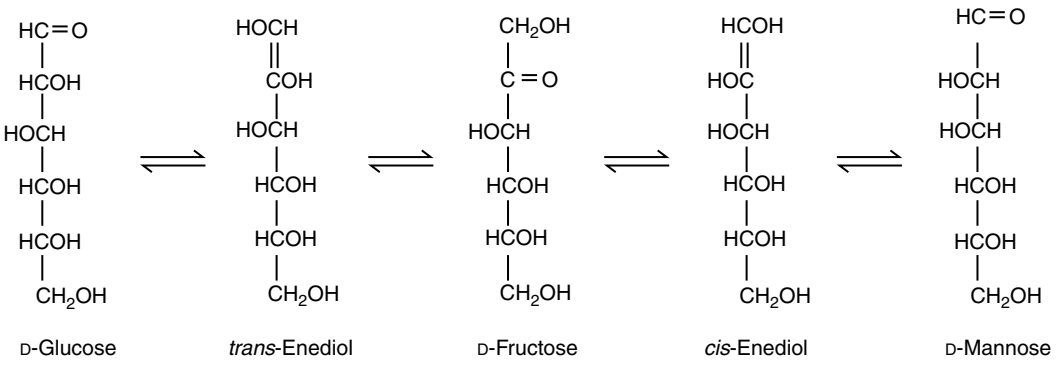

FIGURE 3.5 Interrelationship of D-glucose, D-mannose, and D-fructose via isomerization.

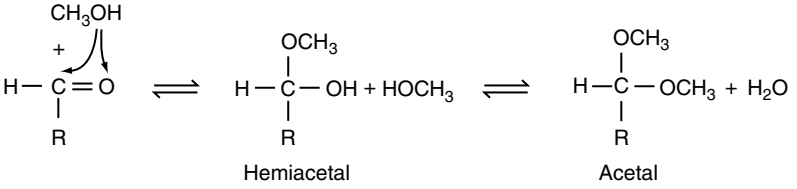

FIGURE 3.6 Formation of an acetal by reaction of an aldehyde with methanol.

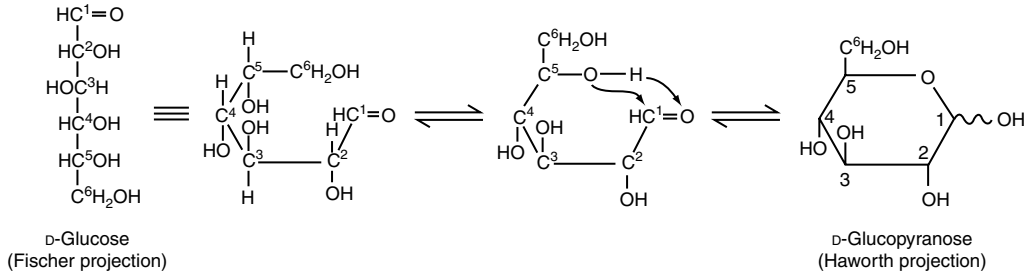

FIGURE 3.7 Formation of a pyranose hemiacetal ring from D-glucose.

Hemiacetal formation can occur within the same aldose or ketose sugar molecule, that is, the carbonyl group of a sugar molecule can react with one of its own hydroxyl groups, as illustrated in Figure 3.7 with D-glucose laid coiled on its side. The six-membered sugar ring that results from reaction of an aldehydo group with the hydroxyl group at C-5 is called a pyranose ring. Notice that, for the oxygen atom of the hydroxyl group at C-5 to react to form the ring, C-5 must rotate to bring its oxygen atom upward. This rotation brings the hydroxymethyl group (C-6) to a position above the ring. The representation of the D-glucopyranose ring used in Figure 3.7 is termed a Haworth projection.

Sugars also occur in five-membered (furanose) rings (Figure 3.8), but less frequently than they do in pyranose rings.

To avoid clutter in writing the ring structures, common conventions are adopted wherein ring carbon atoms are indicated by angles in the ring and hydrogen atoms attached to carbon atoms are eliminated altogether. A mixture of chiral (anomeric*) forms is indicated by a wavy line (Figure 3.9).

* The α and β ring forms of a sugar are known as anomers. The two anomers comprise an anomeric pair.

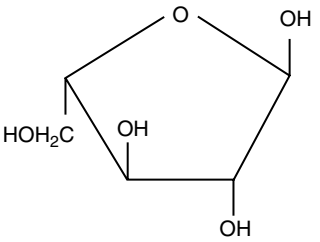

FIGURE 3.8 L-Arabinose in the furanose ring form and α-L-configuration.

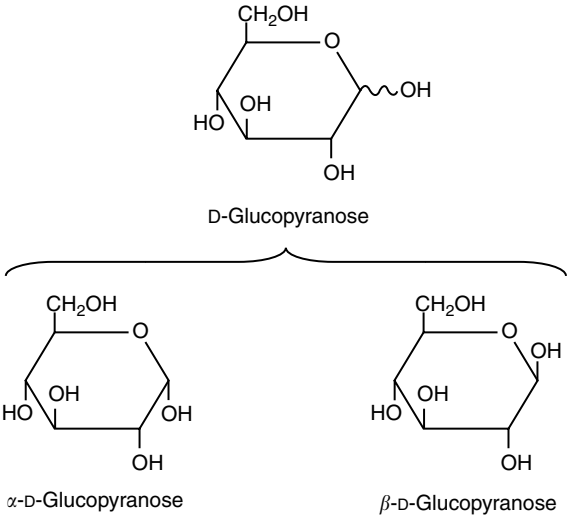

FIGURE 3.9 D-Glucopyranose as a mixture of two chiral forms.

When the carbon atom of the carbonyl group is involved in ring formation, leading to hemiacetal (pyranose or furanose ring) development, it becomes chiral. With D-sugars, the configuration that has the hydroxyl group located below the plane of the ring (in the Haworth projection) is the alpha form. For example, therefore, α-D-glucopyranose is D-glucose in the pyranose (six-membered) ring form with the configuration of the new chiral carbon atom, C-1, termed the anomeric carbon atom, alpha (below the plane of the ring). When the newly formed hydroxyl group at C-1 is above the plane of the ring (in the Haworth projection), it is in the beta position, and the structure is named β-D-glucopyranose. This designation holds for all D-sugars. For sugars in the L-series, the opposite is true, that is, the anomeric hydroxyl group is up in the alpha anomer and down in the beta anomer (see Figure 3.8). This is so because, for example, α-D-glucopyranose and α-L-glucopyranose are mirror images of one another.

However, pyranose rings are not flat with the attached groups sticking straight up and straight down as the Haworth representation suggests. Rather, they occur in a variety of shapes (conformations), most commonly in one of two chair conformations, so-called because they are shaped somewhat like a chair. In a chair conformation, one bond on each carbon atom does project either up or down from the ring; these are called axial bonds or axial positions. The other bond not involved in ring formation, is either up or down with respect to the axial bonds but, with respect to the ring, projects out around the perimeter in what is called an equatorial position (Figure 3.10).

Using β-D-glucopyranose as an example, C-2, C-3, C-5, and the ring oxygen atom remain in a plane, but C-4 is raised slightly above the plane and C-1 is positioned slightly below the plane as in Figures 3.10 and 3.11. This conformation is designated $^4C_1$. The notation C indicates that the

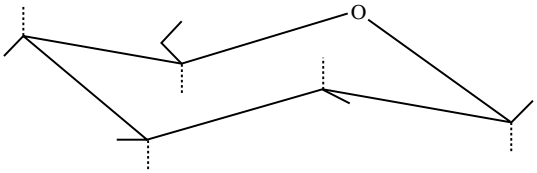

FIGURE 3.10 A pyranose ring showing the equatorial (solid line) and axial (dashed line) bond positions.

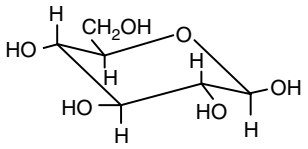

FIGURE 3.11 β-D-Glucopyranose in the $^4C_1$ conformation. All bulky groups are in equatorial positions and all hydrogen atoms in axial positions.

ring is chair-shaped; the superscript number indicates that C-4 is above the plane of the ring and the subscript number indicates that C-1 is below the plane. (There are two chair forms. The second, $^1C_4$, has all the axial and equatorial groups reversed.) The six-membered ring distorts the normal carbon and oxygen atom bond angles less than do rings of other sizes. The strain is further lessened when the bulky hydroxyl groups are separated maximally from each other by the ring conformation that arranges the greatest number of them in equatorial, rather than axial, positions. The equatorial position is energetically favored and rotation of carbon atoms takes place on their connecting bonds to swivel the bulky groups to equatorial positions as far as possible.

As noted, β-D-glucopyranose has all its hydroxyl groups in the equatorial arrangement, but each is either slightly above or slightly below the true equatorial position. In β-D-glucopyranose, the hydroxyl groups, all of which are in an equatorial position, alternate in an up-and-down arrangement, with that on C-1 positioned slightly up, that on C-2 slightly down, and continuing with an up-and-down arrangement. The bulky hydroxymethyl group, C-6 in hexoses, is almost always in a sterically free equatorial position. If β-D-glucopyranose were in a $^1C_4$ conformation, all the bulky groups would be axial. Being, a much higher energy form, little of D-glucopyranose exists in the $^1C_4$ conformation.

Six-membered sugar rings are then quite stable if bulky groups such as hydroxyl groups and the hydroxymethyl group are in equatorial positions. Thus, β-D-glucopyranose dissolves in water to give a rapidly equilibrating mixture containing the open-chain form and its five-, six-, and seven-membered ring forms. At room temperature, the six-membered (pyranose) ring forms predominate, followed by the five-membered (furanose) ring forms. The configuration of the anomeric carbon atom (C-1 of aldoses) of each ring may be alpha or beta. The equilibrium ratio of the ring forms varies with the sugar and the temperature. Examples of the distribution are given in Table 3.2.

The open-chain, aldehydo form constitutes only about 0.003% of the total forms; but because of rapid interconversion with the ring forms, a sugar can readily and rapidly react as if it where entirely in the free aldehyde form (Figure 3.12).

3.1.3 Glycosides

The hemiacetal form of sugars can react with an alcohol to produce a full acetal; the product is called a glycoside. In the laboratory, the reaction occurs under anhydrous conditions in the presence of the acid (as a catalyst) at elevated temperatures, but glycosides are most commonly made in nature, that is, in aqueous environments by enzyme-catalyzed reactions in pathways involving several intermediates. The acetal linkage at the anomeric carbon atom is indicated by the -ide suffix. In the case of D-glucose reacting with methanol, the product is mainly methyl α-D-glucopyranoside, with

TABLE 3.2
Equilibrium Distribution of Cyclic and Anomeric Forms of Monosaccharides

	Pyranose Ring Forms		Furanose Ring Forms	
Sugar	**α-**	**β-**	**α-**	**β-**
Glucose	36.2	63.8	0	0
Galactose	29	64	3	4
Mannose	68.8	31.2	0	0
Arabinose	60	35.5	2.5	0.5
Ribose	21.5	58.5	6.5	13.5
Xylose	36.5	63	<1	<1
Fructose	4	75	0	21

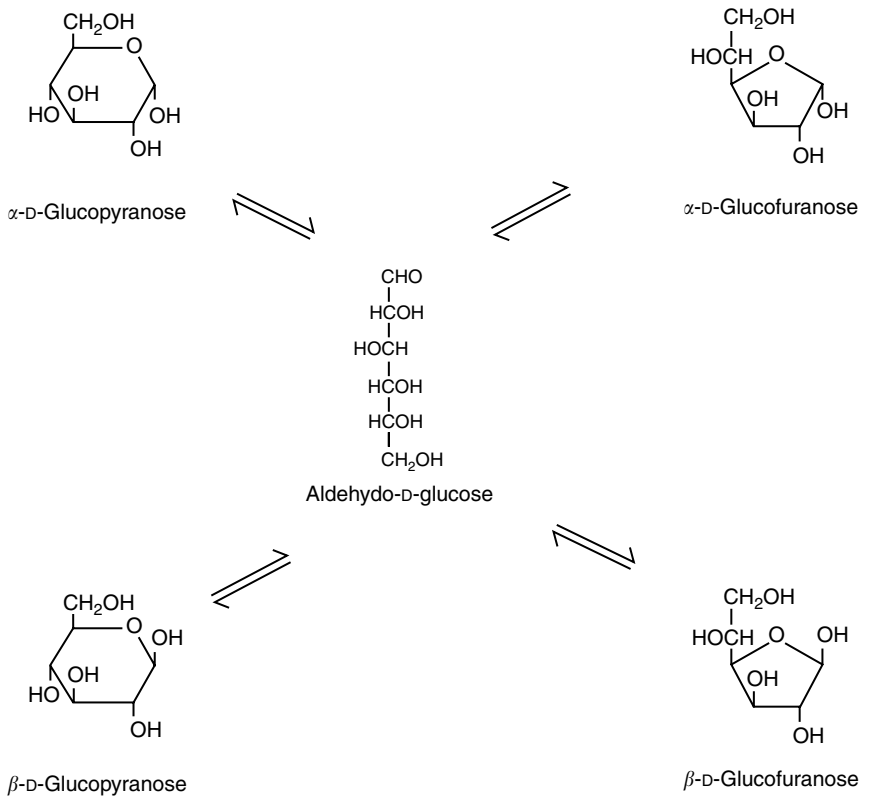

FIGURE 3.12 Interconversion of the acyclic and cyclic forms of D-glucose.

less methyl β-D-glucopyranoside (Figure 3.13). The two anomeric forms of the five-membered-ring furanosides are also formed; but being higher energy structures, they reorganize into more stable forms under the conditions of formation and are present at equilibrium in low amounts. The methyl group in this case, and any other group bonded to a sugar to make a glycoside, is termed an aglycon. Glycosides undergo hydrolysis in acidic environments to yield a reducing sugar (see Section 3.1.4.1) and a hydroxylated compound. Hydrolysis becomes more and more rapid as the temperature is raised.

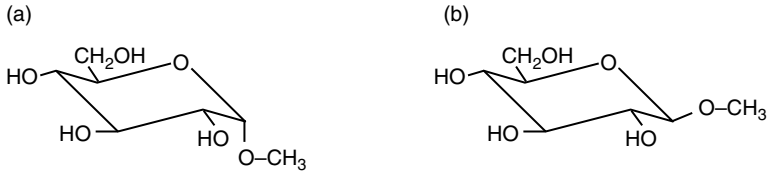

FIGURE 3.13 Methyl α-D-glucopyranoside (a) and methyl β-D-glucopyranoside (b).

3.1.4 Monosaccharide Reactions

All carbohydrate molecules have hydroxyl groups available for reaction. Simple monosaccharides and most other low-molecular-weight carbohydrate molecules also have carbonyl groups available for reaction. Formation of pyranose and furanose rings (cyclic hemiacetals) and glycosides (acetals) of monosaccharides have already been presented.

3.1.4.1 Oxidation to Aldonic Acids and Aldonolactones

Aldoses are readily oxidized to aldonic acids by oxidation of the aldehydo group to a carboxyl/carboxylate group. The reaction is commonly used for quantitative determination of sugars. One of the earliest methods for detection and measurement of sugars employed Fehling solution. Fehling solution is an alkaline solution of copper(II) that oxidizes an aldose to an aldonate and in the process is reduced to copper(I), which precipitates as brick-red Cu_2O. Variations (the Nelson–Somogyi and Benedict reagents) are still used for determining amounts of reducing sugars in foods and other biological materials.

$$2Cu(OH)_2 + R-\underset{\displaystyle H}{\underset{|}{C}}=O \longrightarrow R-\underset{\displaystyle O}{\underset{\|}{C}}-OH + Cu_2O + H_2O \qquad (3.1)$$

In the process of oxidizing the aldehydo group of an aldose to the salt of a carboxylic acid group, the oxidizing agent is reduced, that is, the sugar reduces the oxidizing agent; thus, aldoses are called reducing sugars. Ketoses are also termed reducing sugars because, under the alkaline conditions of the Fehling test, ketoses are isomerized to aldoses. The Benedict reagent, which is not alkaline, will react with aldoses, but not with ketoses.

A simple and specific method for quantitative oxidation of D-glucose to D-gluconic acid uses the enzyme glucose oxidase, the initial product being the 1,5-lactone (an intramolecular ester) of the acid (Figure 3.14). The reaction is commonly employed to measure the amount of D-glucose in foods and other biological materials, including the D-glucose concentration in blood and urine. D-Gluconic acid is a natural constituent of fruit juices and honey.

The reaction given in Figure 3.14 is also used for the manufacture of commercial D-gluconic acid and its lactone. D-Glucono-delta-lactone (GDL), D-glucono-1,5-lactone, according to systematic nomenclature, hydrolyzes largely to completion in water in about 3 h at room temperature, affecting a decrease in pH. Its slow hydrolysis, producing slow acidification and mild taste makes GDL unique among food acidulants. It is used in meats and dairy products, but particularly in refrigerated dough as a chemical leavening component.

3.1.4.2 Reduction of Carbonyl Groups

Hydrogenation is the addition of hydrogen to a double bond. When applied to carbohydrates, it entails addition of hydrogen to the double bond between the oxygen atom and the carbon atom of the carbonyl group of an aldose or ketose. Hydrogenation of D-glucose is readily accomplished with hydrogen gas under pressure in the presence of Raney nickel as a catalyst (Figure 3.15). The product

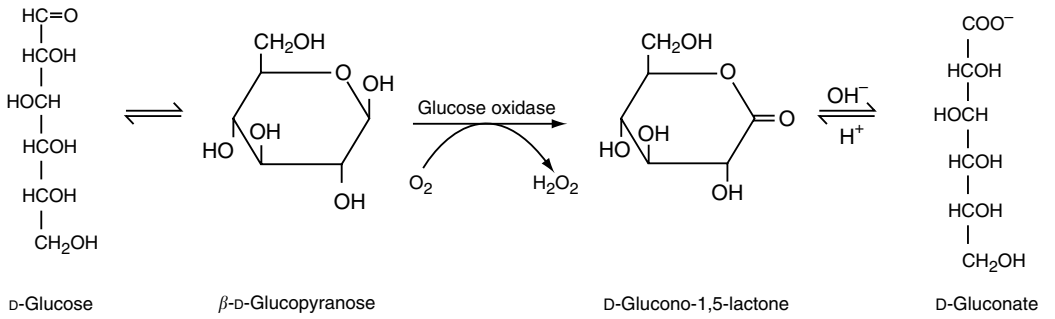

FIGURE 3.14 Oxidation of D-glucose catalyzed by glucose oxidase.

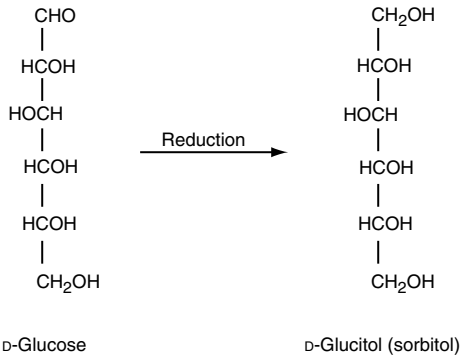

FIGURE 3.15 Reduction of D-glucose.

is D-glucitol, commonly known as sorbitol, the -itol suffix denoting a sugar alcohol (an alditol). Alditols are also known as polyols and polyhydroxy alcohols. Because it is derived from a hexose, D-glucitol (sorbitol) is specifically a hexitol. Sorbitol is widely distributed in plants, ranging from algae to higher plants, where it is found in fruits and berries; but the amounts present are generally small. It is about half as sweet as sucrose, is sold both as a syrup and as crystals, and is used as a general humectant, that is, a substance that will hold/retain moisture in a product.

D-Mannitol can be obtained by hydrogenation of D-mannose. Commercially, it is obtained along with sorbitol from hydrogenolysis of sucrose. It is a product of hydrogenation of the D-fructose (Figure 3.16) component of sucrose and from isomerization of D-glucose, which can be controlled by the alkalinity of the solution undergoing catalytic hydrogenation. D-Mannitol, unlike sorbitol, is not a humectant. Rather, it crystallizes easily and is only moderately soluble. It has been used as a nonsticky coating on candies. It is 65% as sweet as sucrose and is used in sugar-free chocolates, pressed mints, cough drops, and hard and soft candies.

Xylitol (Figure 3.17) is produced from hydrogenation of D-xylose obtained from hemicelluloses, especially from birch trees. Its crystals have a high negative heat of solution. This endothermic heat of solution of crystalline xylitol produces a cooling effect in the mouth. This cooling effect makes xylitol desirable as an ingredient in mint candies and in sugarless chewing gum. Its sweetness is about equal to that of sucrose. Xylitol is noncariogenic because it is not metabolized by the microflora of the mouth that produce dental plaques.

3.1.4.3 Uronic Acids

The terminal carbon atom (at the opposite end of the carbon chain from the aldehyde group) of a monosaccharide unit of an oligo- or polysaccharide may occur in an oxidized (carboxylic acid) form.

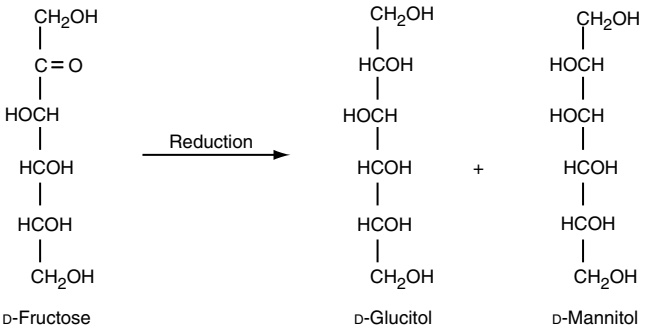

FIGURE 3.16 Reduction of D-fructose.

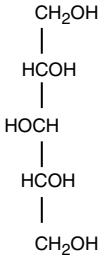

FIGURE 3.17 Xylitol.

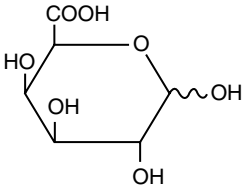

FIGURE 3.18 D-Galacturonic acid.

Such an aldohexose with C-6 in the form of a carboxylic acid group is called a uronic acid. When the chiral carbon atoms of a uronic acid are in the same configuration as they are in D-galactose, for example, the compound is D-galacturonic acid (Figure 3.18), the principal component of pectin (see Section 3.3.13).

3.1.4.4 Hydroxyl Group Esters

The hydroxyl groups of carbohydrates, like the hydroxyl groups of simple alcohols, form esters with organic and some inorganic acids. Reaction of hydroxyl groups with an activated form of a carboxylic acid, primarily a carboxylic acid anhydride, in the presence of a suitable base produces an ester:

$$\mathrm{ROH + R'-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R' \quad or \quad R'-\overset{\overset{O}{\|}}{C}-Cl \rightarrow R-O-\overset{\overset{O}{\|}}{C}-R' + HO-\overset{\overset{O}{\|}}{C}-R' \quad or \quad HCl} \tag{3.2}$$

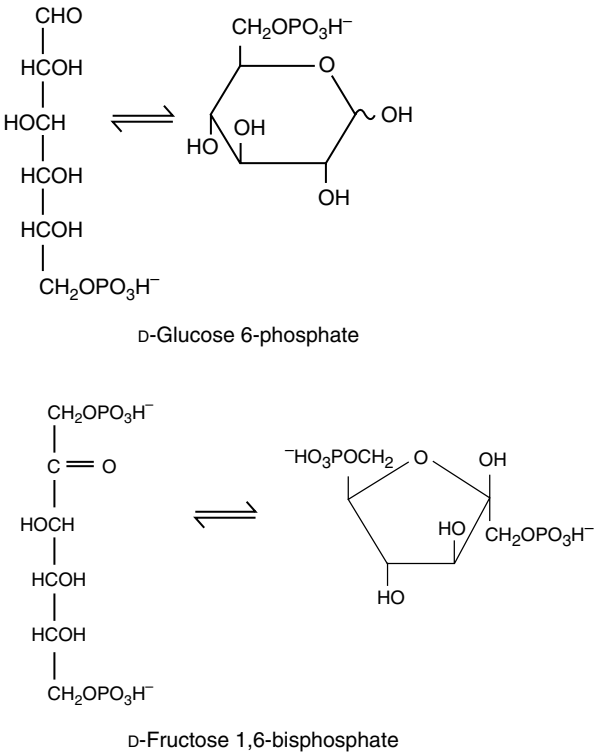

FIGURE 3.19 Examples of sugar phosphate metabolic intermediates.

Acetates, succinate half-esters, and other carboxylic acid esters of carbohydrates occur in nature. They are especially found as components of polysaccharides. Sugar phosphates are common metabolic intermediates (Figure 3.19).

Monoesters of phosphoric acid are also found as constituents of polysaccharides. For example, potato starch contains a small percentage of phosphate ester groups. Corn starch contains even less. In producing modified food starch, corn starch is often derivatized with mono- and distarch ester groups or both (see Section 3.3.6.10). Other esters of starch, most notably the acetate, succinate and substituted succinate half-esters, and distarch adipates, are modified food starches (see Section 3.3.6.10). Sucrose (see Section 3.2.3) fatty acid esters are produced commercially as water-in-oil emulsifiers. The family of red seaweed polysaccharides, which includes the carrageenans (see Section 3.3.10), contain sulfate groups (half-esters of sulfuric acid, $R{-}OSO_3^-$).

3.1.4.5 Hydroxyl Group Ethers

The hydroxyl groups of carbohydrates, like the hydroxyl groups of simple alcohols, can form ethers as well as esters. Ethers of carbohydrates are not as common in nature as are esters. However, polysaccharides are etherified commercially to modify their properties and make them more useful. Examples are the production of methyl ($-O-CH_3$), sodium carboxymethyl ($-O-CH_2-CO_2^-Na^+$), and hydroxypropyl ($-O-CH_2-CHOH-CH_3$) ethers of cellulose and hydroxypropyl ethers of starch, all of which are approved for food use.

A special type of ether, an internal ether linkage between carbon atoms 3 and 6 of a D-galactosyl unit (Figure 3.20), is found in the red seaweed polysaccharides, specifically agar, furcellaran, κ-carrageenan, and ι-carrageenan (see Section 3.3.10). Such an internal ether is known as a 3,6-anhydro ring; the name derives from the fact that it can be viewed as the product formed by removal of the elements of water (HOH) from the hydroxyl groups on C-3 and C-6.

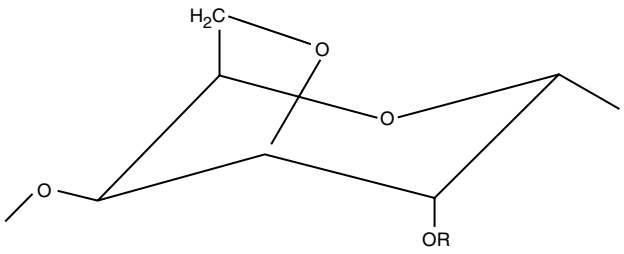

FIGURE 3.20 A 3,6-anhydro-α-D-galactopyranosyl unit found in red seaweed polysaccharides.

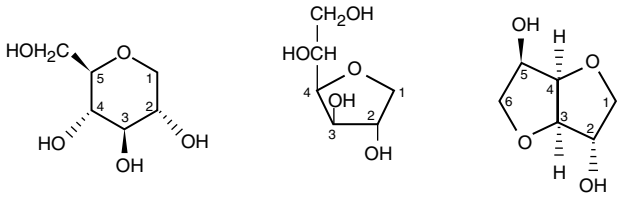

FIGURE 3.21 Anhydro-D-glucitols (sorbitans). Numbering refers to the carbon atoms in the original molecule of D-glucose (and of sorbitol).

A family of nonionic surfactants based on sorbitol (D-glucitol) are used in foods as water-in-oil emulsifiers and as defoamers. They are produced by esterification of sorbitol with fatty acids. Cyclic dehydration accompanies esterification (primarily at a primary hydroxyl group, that is, C-1 or C-6) so that the carbohydrate (hydrophilic) portion is, not only sorbitol, but also its mono- and dianhydrides (cyclic ethers of sorbitol called sorbitans, Figure 3.21). The products are known as sorbitan esters. Products called mono-, di-, and triesters (Spans) are formed. (The designation mono-, di-, and tri- simply indicates the ratio of fatty acid ester groups to sorbitan.) The product called sorbitan monostearate is actually a mixture of partial stearic (C_{18}) and palmitic (C_{16}) acid esters of sorbitol (D-glucitol), 1,5-anhydro-D-glucitol (1,5-sorbitan), 1,4-anhydro-D-glucitol (1,4-sorbitan), both internal (cyclic) ethers, and 1,4:3,6-dianhydro-D-glucitol (isosorbide), an internal dicyclic ether. Sorbitan fatty acid esters, such as sorbitan monostearate, sorbitan monolaurate, and sorbitan monooleate, are sometimes modified by reaction with ethylene oxide to produce so-called ethoxylated sorbitan esters called Tweens, which are also nonionic detergents approved by the U.S. FDA for food use.

3.1.4.6 Nonenzymic Browning [4,36,69]

Under some conditions, reducing sugars produce brown colors that are desirable and important in some foods. At other times, brown colors obtained upon heating or during long-term storage of foods containing reducing sugars are undesirable. Common browning of foods on heating or on storage is usually due to a chemical reaction between reducing sugars, mainly D-glucose, and a primary amino group (a free amino acid or amino group on a side chain of a protein molecule.) This reaction is called the Maillard reaction and the overall process is sometimes designated Maillard browning. It is also called nonenzymic or nonenzymatic browning to differentiate it from the more rapid, enzyme-catalyzed browning commonly observed in freshly cut fruits and vegetables, such as apples and potatoes.

When aldoses or ketoses are heated with amines, a variety of reactions ensue, producing numerous compounds (some of which are flavors, aromas, and dark-colored polymeric materials); but both reactants disappear only slowly. The flavors, aromas, and colors may be either desirable or undesirable. They may be produced slowly during storage and much more rapidly at the high temperatures encountered during frying, roasting, or baking.

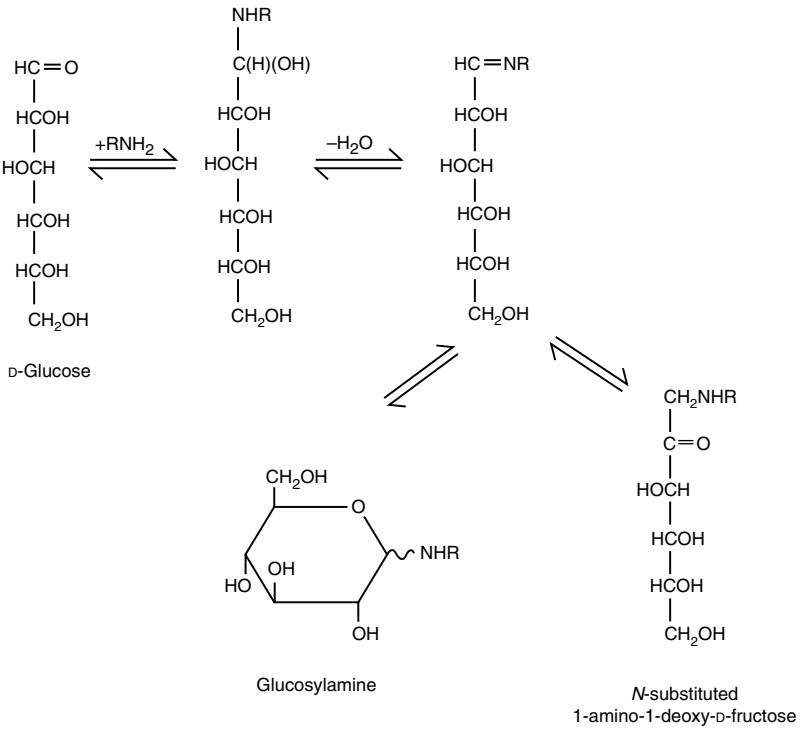

FIGURE 3.22 Products of reaction of D-glucose with a primary amine (RNH_2).

The reducing sugar reacts reversibly with the amine to form a Schiff base (an imine, RHC = NHR′), which may cyclize (in the same way that an aldose cyclizes) to form a glycosylamine (sometimes called a *N*-glycoside), as illustrated with D-glucose (Figure 3.22). The Schiff base undergoes a reaction called the Amadori rearrangement to give, in the case of D-glucose, a derivative of 1-amino-1-deoxy-D-fructose a so-called Amadori compound. Amadori compounds are early intermediates in the browning reaction sequence.

Amadori compounds undergo transformation via four known pathways starting with four different intermediates formed from them. The result is a complex mixture of intermediates and products. Three of the four intermediates formed by rearrangements and eliminations are 1-, 3-, and 4-deoxydicarbonyl compounds, usually known by their common names that are 1-, 3-, and 4-deoxyosones. Formation of these intermediates occurs most readily at pH 4–7. The most prevalent of these intermediates is usually the 3-deoxyosone (more properly called a 3-deoxyhexosulose, Figure 3.23).

Osones can cyclize in the same way that aldoses and ketoses do. They also will undergo dehydration, especially at high temperature. Reaction continues, especially at pH 5 or lower, to give an intermediate that dehydrates. Eventually, a furan derivative is formed: that from a hexose being 5-hydroxymethyl-2-furaldehyde, commonly known as hydroxymethylfurfural (HMF) (Figure 3.23); that formed from a pentose is furfural (furaldehyde). Under less acidic conditions, that is, pH > 5, the reactive cyclic compounds (HMF, furfural, and others) and compounds containing amino groups polymerize to a dark-colored, insoluble material containing nitrogen called melanoidin. Amino acids and furans (furfural and/or HMF) are almost always incorporated into the polymeric end products. Individual polymers constituting melanoidin vary in color (brown to black), molecular weight, nitrogen content, and solubility.

When higher concentrations of compounds containing primary amino groups (such as proteins containing higher proportions of L-lysine) are present, the primary products are pyrroles (products in which the ring oxygen atom of HMF and furfural is replaced with N—R).

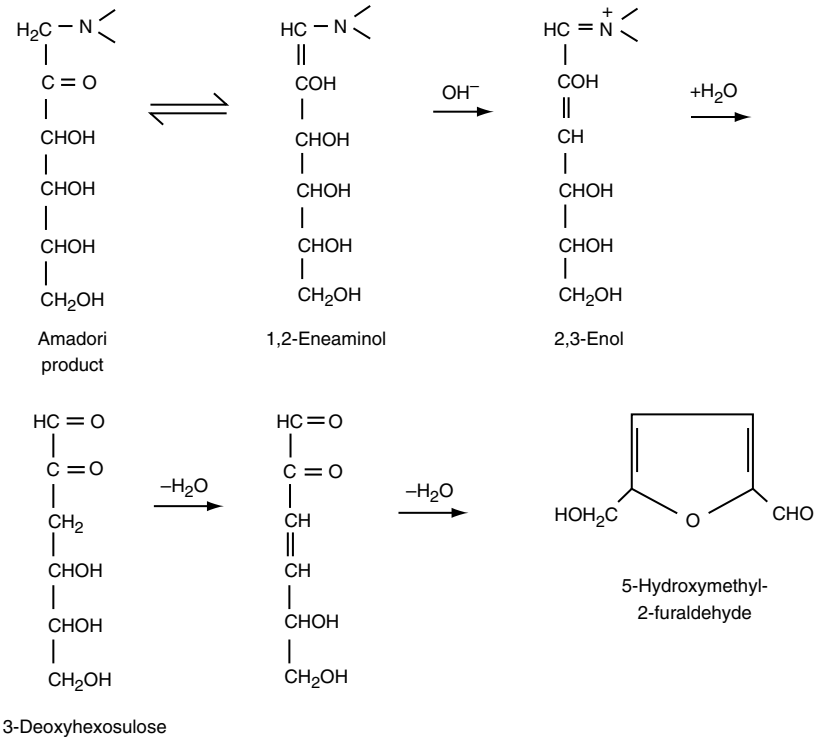

FIGURE 3.23 Conversion of the Amadori product into HMF.

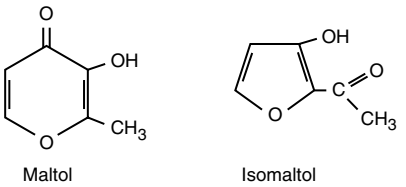

FIGURE 3.24 Maltol and isomaltol.

Maltol and isomaltol, both of which contribute to the flavor and aroma of bread, are formed from 1-deoxyosone (Figure 3.24).

Intermediates in the formation of melanoidin called reductones are also formed from 1-deoxyosones. Reductones are antioxidants. Because reductones can be involved in redox reactions, other intermediates can be formed from them (Figure 3.25).

Osones will also undergo cleavage, either between the two carbonyl groups or at the site of an enediol (—COH═COH—) forming shorter-chain products, primarily aldehydes that can undergo various reactions. Another important reaction of dicarbonyl compounds (osones and deoxyosones) is the Strecker degradation. Reaction of one of these compounds with an α-amino acid ($R—CHNH_2—CO_2H$) results first in a Schiff base being formed, then decarboxylation (releasing CO_2), dehydration, and elimination to produce an aldehyde that is one carbon atom shorter than the original amino acid. Aldehydes produced from amino acids often are major contributors to the aroma produced during nonenzymic browning. Among important aroma compounds produced in this way are 3-methylthiopropanal (methional, $CH_3—S—CH_2—CH_2—CHO$) from L-methionine, phenylacetaldehyde ($Ph—CH_2—CHO$) from L-phenylalanine, methylpropanal ($(CH_3)_2—CH—CHO$)

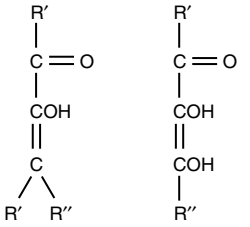

FIGURE 3.25 Two of several types of structures of reductones.

from L-valine, 3-methylbutanal ($(CH_3)_2{-}CH{-}CH_2{-}CHO$) from L-leucine, and 2-methylbutanol ($(CH_3{-}CH_2)\ (CH_3){-}CH{-}CHO$) from L-isoleucine.

A variety of the colored compounds collectively called melanoidins are formed. The variety arises from the variety of intermediates and the variety of possible condensation reactions. Some contain nitrogen; some contain only carbon, hydrogen, and oxygen atoms. All contain aromatic rings and conjugated double bonds.

Other products of the Maillard browning reaction are modified proteins. Protein modification primarily is the result of their reaction (especially reaction of the side chains of their L-lysine and L-arginine units) with carbonyl-group-containing compounds such as reducing sugars, osones, furfural, HMF, and pyrrole derivatives. For example, reaction of the ε-amino group of a unit of L-lysine in a protein molecule followed by the Amadori rearrangement converts the L-lysine unit into a unit of *N*-fructofuranosyl-lysine. Further reactions result in substituted furan and pyrrole rings being formed from the fructofuranosyl unit and being attached to the protein molecule. Reactions of this kind destroy the amino acid. Since L-lysine is an essential amino acid, its destruction in this way reduces the nutritional quality of the food. Losses of lysine and arginine of 15–40% in baked and roasted foods are common.

The product mixture formed is a function of temperature, time, pH, the nature of the reducing sugar, and the nature of the amino compound for the following reasons. Different sugars undergo nonenzymic browning at different rates. For example, D-glucose undergoes the browning reaction faster than does D-fructose. Secondary amines give different reaction products than do primary amines. Because the reaction has a relatively high energy of activation, application of heat is generally required. The rate of the Maillard reaction is also a function of the water activity (a_w) of a food product, reaching a maximum at a_w values in the range 0.6–0.7. Thus, for some foods, Maillard browning can be controlled by controlling water activity as well as by controlling reactant concentrations, time, temperature, and pH. Sulfur dioxide and bisulfite ions react with aldehyde groups, forming addition compounds, and thus will inhibit Maillard browning by removing at least some of a reactant (reducing sugar, HMF, furfural, etc.). Color, taste, and aroma are, in turn, determined by the product mixture. Reaction variables that can be controlled to increase or decrease the Maillard browning reaction are the following: (1) temperature (decreasing the temperature decreases the reaction rate) and time at the temperature; (2) pH (decreasing the pH decreases the reaction rate); (3) adjustment of the water content (maximum reaction rate occurs at water activity values of 0.6–0.7 [about 30% moisture]); (4) the specific sugar; and (5) presence of transition metal ions that undergo a one-electron oxidation under energetically favorable conditions, such as Fe(II) and Cu(I) ions (a free radical reaction may be involved near the end of the pigment-forming process).

In summary, Maillard browning products, including soluble and insoluble polymers, are found where reducing sugars and amino acids, proteins, and/or other nitrogen-containing compounds are heated together, for example, in soy sauce and bread crusts. Browning is desired in baking, for example, in bread crusts and cookies, and roasting of meats. The volatile compounds produced by nonenzymic browning (the Maillard reaction) during baking, frying, or roasting often provide desirable aromas. Maillard reaction products are also important contributors to the flavor of milk

chocolate, caramels, toffees, and fudges, during which reducing sugars react with milk proteins. The Maillard reaction also produces flavors, especially bitter substances, which may be desired, for example, in coffee. On the other hand, the Maillard reaction can result in off-flavors and off-aromas. Off-flavors and -aromas are most likely to be produced during pasteurization, storage of dehydrated foods, and grilling of meat or fish. Application of heat to intermediate moisture foods is generally required for nonenzymic browning.

3.1.4.7 Caramelization [4,59]

Heating of carbohydrates, in particular sucrose (Section 3.2.3) and reducing sugars, without nitrogen-containing compounds affects a complex group of reactions involved in caramelization. Reaction is facilitated by small amounts of acids and certain salts. Although it does not involve amino acids or proteins, carmelization is similar to nonenzymic browning. The final product, caramel (as in Maillard browning) contains a complex mixture of polymeric compounds, formed from unsaturated, cyclic (five- and six-membered ring) compounds. Also, as in Maillard browning, flavor and aroma compounds are also found. Heating causes dehydration of the sugar molecule with introduction of double bonds or formation of anhydro rings. As in Maillard browning, intermediates such as 3-deoxyosones and furans are formed. The unsaturated rings may condense to form useful, conjugated double-bond-containing, brown-colored polymers. Catalysts increase the reaction rate and are used to direct the reaction to specific types of caramel colors, solubilities, and acidities.

Caramel is produced commercially both as a coloring material and as a flavoring material. To make caramel, a carbohydrate is heated alone or in the presence of an acid, a base, or a salt. The carbohydrate most often used is sucrose, but D-fructose, D-glucose (dextrose), invert sugar, glucose syrups, HFSs, malt syrups, and molasses may also be used. Acids that may be used are food-grade sulfuric, sulfurous, phosphoric, acetic, and citric acids. Bases that may be used are ammonium, sodium, potassium, and calcium hydroxides. Salts that may be used are ammonium, sodium, and potassium carbonates, bicarbonates, phosphates (both mono- and dibasic), sulfates, and bisulfites. So, there are a very large number of variables, including temperature, in caramel manufacture. Ammonia may react with intermediates, such as 3-deoxyosones, produced by thermolysis to produce pyrazine and imidazole dervatives (Figure 3.26).

There are four recognized classes of caramel. Class I caramel (also called plain caramel or caustic caramel) is prepared by heating a carbohydrate without a source of either ammonium or sulfite ions; an acid or a base may be employed. Class II caramel (also called caustic sulfite caramel) is prepared by heating a carbohydrate in the presence of a sulfite, but in the absence of any ammonium ions; an acid or a base may be employed. This caramel, which is used to add color to beers and other alcoholic beverages, is reddish brown, contains colloidal particles with slightly negative charges, and has a solution pH of 3–4. Class III caramel (also called ammonium caramel) is prepared by heating a carbohydrate in the presence of a source of ammonium ions, but in the absence of sulfite ions; an acid or a base may be employed. This caramel, which is used in bakery products, syrups, and puddings, is reddish brown, contains colloidal particles with positive charges, and gives a solution

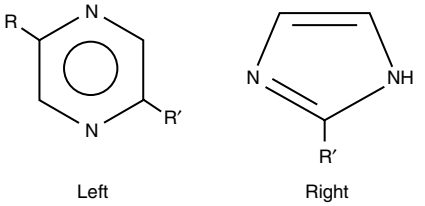

FIGURE 3.26 Pyrazine (left) and imadazole (right) derivatives formed during carmelization in the presence of ammonia R = $-CH_2-(CHOH)_2-CH_2OH$, R′ = $-(CHOH)_3-CH_2OH$.

pH of 4.2–4.8. Class IV caramel (also called sulfite ammonium caramel) is prepared by heating a carbohydrate in the presence of both sulfite and ammonium ions; an acid or a base may be employed. This caramel, which is used in cola soft drinks, other acidic beverages, baked goods, syrups, candies, pet foods, and dry seasonings, is brown, contains colloidal particles with negative charges, and gives a solution pH of 2–4.5. In this case, the acidic salt catalyzes cleavage of the glycosidic bond of sucrose, and the ammonium ion participates in the Amadori rearrangement reaction. The pigments in all four types of caramel are large polymeric molecules with complex, variable, and unknown structures. It is these polymers that form the colloidal particles. Their rate of formation increases with increasing temperature and pH. Of course, caramelization may also occur during cooking or baking, especially when sugar is present. It occurs along with nonenzymic browning during the preparation of chocolate and fudge.

3.1.4.8 Formation of Acrylamide in Food [3,18,50,70,73]

The Maillard reaction has been implicated in the formation of acrylamide in many foods that have been heated to high temperatures during processing or preparation. Levels of acrylamide (typically <1.5 ppm) have been reported in a wide range of food products that are made by frying, baking, puffing, roasting, or other elevated-temperature processing schemes during production or preparation (Table 3.3). Acrylamide is not detected in unheated or even boiled foodstuffs, such as boiled potatoes, because the temperature during boiling does not go above $\sim$100°C. Acrylamide is undetected or detected at only very low levels in canned or frozen fruits, vegetables, and vegetable protein products (vegetable burgers and related products) with the exception of pitted ripe olives, in which the measured levels ranged from 0 to 1925 ppb. Acrylamide is a known neurotoxicant and probably a weak human carcinogen at exposure levels much higher than are obtained from food.

Acrylamide is derived primarily from the second-order reaction between reducing sugars (carbonyl moiety) and the α-amino group of free L-asparagine (Figure 3.27). The reaction requires

TABLE 3.3
Ranges of Acrylamide Found in Common Food Products Containing High Levels

Food	ppb Acrylamide[a]
Almonds (roasted)	236–457
Bagels	0–343
Breads	0–364
Breakfast cereals (RTE)	34–1057
Cocoa	0–909
Coffee (unbrewed)	3–374
Coffee with chicory	380–609
Cookies	36–432
Crackers and related products	26–1540
French fries	20–1325
Potato chips	117–196[b]
Pretzels	46–386
Tortillas	10–33
Tortilla chips	117–196

[a] Extreme values, especially extremely high values, are usually representative of only a small number of sampled products.
[b] A sample of sweet potato chips contained 4080 ppb acrylamide.

Source: Center for Food Safety and Applied Nutrition, USDA.

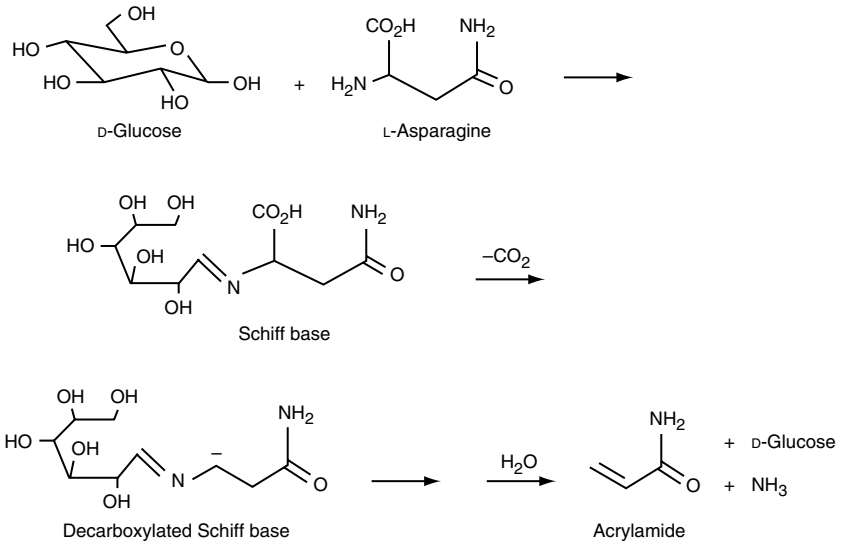

FIGURE 3.27 A proposed mechanism of acrylamide formation in foods.

the presence of both substrates. Fried potato products, such as potato chips and French fries, are particularly susceptible to acrylamide formation because potatoes contain both free D-glucose and free L-aspargine. The reaction most likely occurs via a Schiff base intermediate, which then undergoes decarboxylation, followed by carbon–carbon bond cleavage to form acrylamide, whose atoms are known to be derived solely from L-asparagine. Though acrylamide is not the favored product of this complex series of reactions (reaction efficiency $\approx 0.1\%$), it is able to accumulate to detectable levels in food products subjected to prolonged heating at high temperatures. Acrylamide formation requires a minimum temperature of 120°C, which means that it cannot occur in high-moisture foods, and is kinetically favored with increasing temperatures approaching 200°C. With extended heating at temperatures above 200°C, acrylamide levels may actually decrease via thermal elimination/degradation reactions. Food levels of acrylamide are also impacted by pH. Acrylamide formation is favored as the pH is increased over the range of 4–8. Reduced acrylamide formation in the acid range is thought to be due in part to protonation of the α-amino group of asparagine, reducing its nucleophilic potential. Furthermore, acrylamide appears to undergo increased rates of thermal degradation as the pH decreases. Acrylamide levels increase rapidly in the latter stages of the prolonged heating process as the water at food surfaces is driven off to allow surface temperatures to increase above 120°C. Products with high amounts of surface area, such as potato chips, are among those high-temperature processed foods that exhibit the highest acrylamide levels. Thus, exposed surface area of a food can be an additional factor, provided that reaction substrates and processing temperatures are sufficient for acrylamide formation.

Efforts to minimize formation of acrylamide in food generally involve one or more of three strategies: (1) removal of either one or both of the substrates, (2) alteration of processing conditions, and (3) acrylamide removal from food following its formation. Through blanching or soaking in water, it is possible to achieve up to a 60% reduction in acrylamide levels within processed potato products through removal of reaction substrates (reducing sugars and free asparagine). Reagent modification (e.g., protonation of asparagine by lowering the pH or conversion of asparagine to aspartic acid with asparaginase), addition of competing substrates that do not yield acrylamide (e.g., amino acids other than asparagine or protein), and incorporation of salts have been shown to mitigate acrylamide formation. Where possible, better control or optimization of thermal processing conditions (temperature/time relationships) may also prove beneficial to minimizing acrylamide

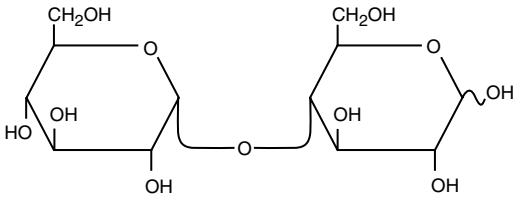

FIGURE 3.28 Maltose.

levels. It is likely that a combination of mitigation methods will be required to effectively limit acrylamide formation within food products, with the employed methods likely varying according to the nature and needs of a particular food system.

Although studies to date have uncovered no association between acrylamide consumption in foods and the risk of cancer, long-term carcinogenicity, mutagenicity, and neurotoxicity studies are still ongoing as are efforts to reduce acrylamide formation during food processing and preparation.

3.2 OLIGOSACCHARIDES

An oligosaccharide contains from 2 to 10 or from 2 to 20 sugar units, depending on who is defining the term, joined by glycosidic bonds. When a molecule contains more than 20 units, it is a polysaccharide.

Disaccharides are glycosides in which the aglycon is a monosaccharide unit. A compound containing three monosaccharide units is a trisaccharide. Structures containing from 4 to 10 glycosyl units, whether linear or branched, are tetra-, penta-, hexa-, octa-, nona-, and decasaccharides, and so on. Only a few oligosaccharides occur in nature. Most are produced by hydrolysis of polysaccharides into smaller units. Because glycosidic bonds are part of acetal structures, they undergo acid-catalyzed hydrolysis in the presence of aqueous acid and heat.

3.2.1 Maltose

Maltose (Figure 3.28) is an example of a disaccharide. The reducing end unit (on the right as customarily written) has a potentially free aldehyde group and in solution will be in equilibrium with alpha and beta six-membered ring forms, as described earlier for monosaccharides. Since O-4 is blocked by attachment of the second D-glucopyranosyl unit, a furanose ring cannot form. Maltose is a reducing sugar, because its aldehyde group is free to react with oxidants and, in fact, to undergo almost all reactions as though it were present as a free aldose.

Maltose is produced by hydrolysis of starch using the enzyme β-amylase (see Section 3.3.6.9). It occurs only rarely in nature and only in plants as a result of partial hydrolysis of starch. Maltose is produced during malting of grains, especially barley, and commercially by the specific enzyme-catalyzed hydrolysis of starch using β-amylase from *Bacillus* species, although the β-amylases from barley seed, soybeans, and sweet potatoes may be used. Maltose is used sparingly as a mild sweetener for foods. Maltose is reduced to the alditol maltitol, which is used in sugarless chocolate.

3.2.2 Lactose

The disaccharide lactose (Figure 3.29) occurs in milk, mainly free, but to a small extent as a component of higher oligosaccharides. The concentration of lactose in milk varies with the mammalian source from 2.0 to 8.5%. Cow and goat milk contains 4.5–4.8%, human milk about 7%. Lactose is the primary carbohydrate source for developing mammals. In humans, lactose constitutes 40% of the energy consumed during nursing. Utilization of lactose for energy must be preceded by hydrolysis to the constituent monosaccharides, D-glucose and D-galactose, because only monosaccharides are

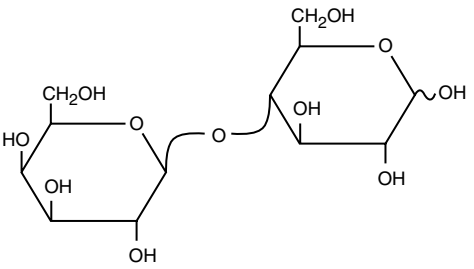

FIGURE 3.29 Lactose.

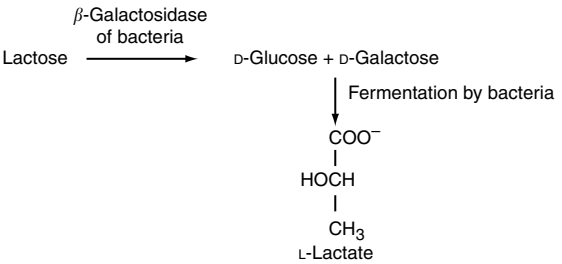

FIGURE 3.30 The fate of lactose in the large intestine of persons with lactase deficiency.

absorbed from the small intestine. Milk also contains 0.3–0.6% of lactose-containing oligosaccharides, many of which are important as energy sources for growth of a specific variant of *Lactobacillus bifidus*, which, as a result, is the predominant microorganism of the intestinal flora of breast-fed infants.

Lactose is ingested in milk and other unfermented dairy products, such as ice cream. Fermented dairy products, such as most yogurt and cheese, contain less lactose because, during fermentation, some of the lactose is converted into lactic acid. Lactose stimulates intestinal adsorption and retention of calcium. Lactose is not digested until it reaches the small intestine, where the hydrolytic enzyme lactase is present. Lactase (a β-galactosidase) is a membrane-bound enzyme located in the brush border epithelial cells of the small intestine. It catalyzes the hydrolysis of lactose into its constituent monosaccharides, D-glucose and D-galactose, both of which are rapidly absorbed and enter the blood stream:

$$\text{lactose} \xrightarrow{\text{lactase}} \text{D-glucose} + \text{D-galactose} \tag{3.3}$$

If for some reason the ingested lactose is only partially hydrolyzed, that is, only partially digested, or is not hydrolyzed at all, a clinical syndrome called lactose intolerance results. If there is a deficiency of lactase, some lactose remains in the lumen of the small intestine. The presence of lactose tends to draw fluid into the lumen by osmosis. This fluid produces abdominal distention and cramps. From the small intestine, the lactose passes into the large intestine (colon) where it undergoes anaerobic bacterial fermentation to lactic acid (present as the lactate anion) (Figure 3.30) and other short-chain acids. The increase in the concentration of molecules, that is, the increase in osmotic strength, results in still greater retention of fluid. In addition, the acidic products of fermentation lower the pH and irritate the lining of the colon, leading to an increased movement of the contents. Diarrhea is caused both by the retention of fluid and the increased movement of the intestinal contents. The gaseous products of fermentation cause bloating and cramping.

Lactose intolerance is not usually seen in children until after about 6 years of age. At this point, the incidence of lactose-intolerant individuals begins to rise and increases throughout the

life span with the greatest incidence in the elderly. Both the incidence and the degrees of lactose intolerance vary by ethnic group, indicating that the presence or absence of lactase is under genetic control.

There are three ways to overcome the effects of lactase deficiency. One is to remove the lactose by fermentation as in yogurt and cultured buttermilk products. Another is to produce reduced-lactose milk by adding lactase to it. However, both products of hydrolysis, D-glucose and D-galactose, are sweeter than lactose, and at about 80% hydrolysis, the taste change becomes quite evident. Therefore, most reduced-lactose milk has the lactose reduced as close as possible to the 70% government-mandated limit for a claim. The third is for the lactase-deficient individual to consume β-galactosidase along with the dairy product.

3.2.3 Sucrose [40,46]

When the total amount of sucrose, usually called simply sugar or table sugar, used in the United States is divided by the total population, it is calculated that the per person daily utilization averages about 160 g; but sucrose is also used extensively in fermentations, in bakery products where it is also largely used up in fermentation, and in pet food; so the actual average daily amount consumed by individuals in foods and beverages is much less, estimated to be about 55 g (20 kg or 43 lb/yr). Sucrose is composed of an α-D-glucopyranosyl unit and a β-D-fructofuranosyl unit linked head-to-head (reducing end-to-reducing end) rather than by the usual head-to-tail linkage (Figure 3.31). Since it has no reducing end, it is classified as a nonreducing sugar.

There are two principal sources of commercial sucrose—sugar cane and sugar beets. Also present in sugar beet extract are (1) a trisaccharide, raffinose, which has a D-galactopyranosyl unit attached to sucrose and (2) a tetrasaccharide, stachyose, which contains another D-galactosyl unit (Figure 3.32). These oligosaccharides, also found in beans, are nondigestible. These and other carbohydrates that are not completely broken down into monosaccharides by intestinal enzymes and are not absorbed pass into the colon. There, they are metabolized by microorganisms producing lactate and gas. Diarrhea, bloating, and flatulence result.

Sucrose has a specific optical rotation of $+66.5°$. The equimolar mixture of D-glucose and D-fructose produced by hydrolysis of the glycosidic bond joining the two monosaccharide units has a specific optical rotation of $-33.3°$. Early investigators, noticing this, called the process inversion and the product invert sugar.

Sucrose and most other low-molecular-weight carbohydrates (e.g., monosaccharides, alditols, disaccharides, and other low-molecular-weight oligosaccharides), because of their great hydrophilicity and solubility, can form highly concentrated solutions of high osmolality. Such solutions, as

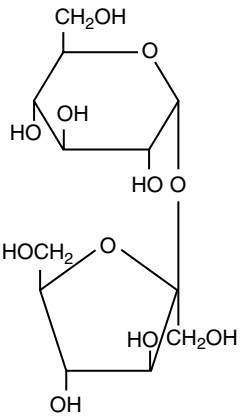

FIGURE 3.31 Sucrose.

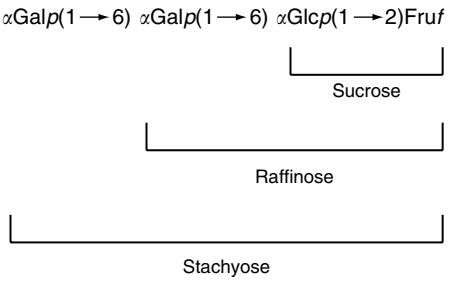

FIGURE 3.32 Sucrose, raffinose, and stachyose. (For explanation of the shorthand designations of structures, see Section 3.3.1.)

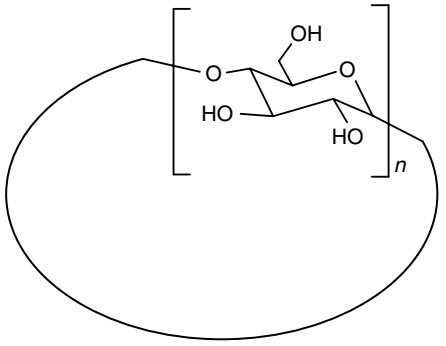

FIGURE 3.33 Generalized chemical structures of α- ($n = 6$), β- ($n = 7$), and γ- ($n = 8$) cyclodextrins.

exemplified by honey, need no preservatives themselves and can be used, not only as sweeteners (although not all such carbohydrate syrups need have much sweetness), but also as preservatives and humectants.

A portion of the water in any carbohydrate solution is nonfreezable. When the freezable water crystallizes, that is, forms ice, the concentration of solute in the remaining liquid phase increases, and the freezing point decreases. There is a consequential increase in viscosity of the remaining solution. Eventually, the liquid phase solidifies as a glass in which the mobility of all molecules becomes restricted and diffusion-dependent reactions become very slow (see Chapter 2) and, because of the restricted motion, water molecules become unfreezable, that is, they cannot form crystals. In this way, carbohydrates function as cryoprotectants and protect against the dehydration that destroys structure and texture caused by freezing.

The sucrase of the human intestinal tract catalyzes hydrolysis of sucrose into D-glucose and D-fructose, making sucrose one of the three carbohydrates humans can digest and utilize for energy, the other two being lactose and starch. Monosaccharides (D-glucose and D-fructose being the nutritionally significant ones in our diets) do not need to be transformed before absorption.

3.2.4 Cyclodextrins [48,56]

Cyclodextrins, formerly known as Schardinger dextrins and cycloamyloses, comprise a family of cyclic oligosaccharides comprised of (1→4)-linked α-D-glucopyranosyl units (Figure 3.33). These cyclic structures are formed from soluble, partially hydrolyzed starch polymers (Section 3.3.6.9) through action of the enzyme, cyclodextrin glycosyltransferase (CGTase), which catalyzes the intramolecular cyclization of glucosyl chains. Cyclodextrins consist of six, seven, or eight glucosyl

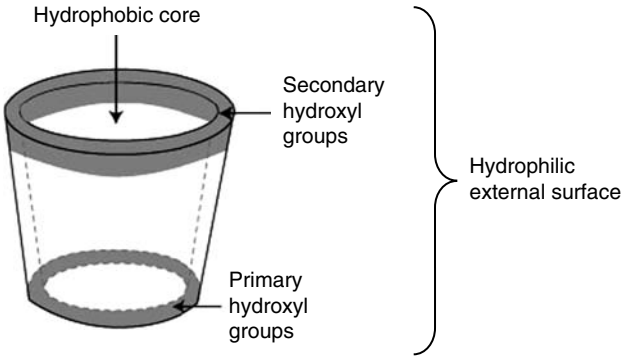

FIGURE 3.34 Depiction of the idealized geometric shape of cyclodextrins.

TABLE 3.4
Chemical Characteristics of α-, β-, and γ-Cyclodextrins

Characteristic	α	β	γ
No. of glucosyl units	6	7	8
Molecular weight	972	1135	1297
Solubility (g/100 mL at 25°C)	14.5	1.9	23.2
Cavity diameter (Å)	4.7–5.3	6.0–6.5	7.5–8.3

units; these cyclodextrins are referred to as α-, β-, and γ-cyclodextrins, respectively. In commercial production schemes, cyclodextrins may be isolated by selective crystallization (following treatment of the reaction broth with glucoamylase) or differential precipitation involving addition of a substrate-specific complexing agent (typically an organic solvent). While α-, β-, and γ-cyclodextrins are all permitted for use in food (self-affirmed GRAS regulatory status), only β-cyclodextrin is utilized to any appreciable degree due to its lower cost (relative to the other two) and established function.

Cyclodextrins possess a truncated funnel- or doughnutlike geometry with an internal hydrophobic core or cavity and a hydrophilic external surface (Figure 3.34). The solubility of cydodextrins in water, which is attributable to the presence of the hydroxyl groups on their outer molecular surface, is different for α-, β-, and γ-types (Table 3.4). γ-Cyclodextrin is the most water soluble, followed by α-cyclodextrin, while the β-type, due to an extensive band of intramolecular hydrogen bonds spanning the entire outer molecular perimeter, has the lowest water solubility. In contrast, the internal cavity provides a hydrophobic environment for formation of inclusion complexes with nonpolar guest molecules through hydrophobic and other noncovalent associations. The size of the inner cavity increases as the number of cyclodextrin glycosyl units increases ($\gamma > \beta > \alpha$) (Table 3.4). This complexing ability is the most significant property of cyclodextrins and is the driving force for cyclodextrin use in almost all food and industrial applications. Within food systems, cyclodextrins may be used to complex flavors, lipids, and color compounds for an array of purposes. Cyclodextrins may be used to complex undesirable constituents (such as masking of off-flavors, odors, and bitter compounds and removal of cholesterol and free fatty acids [FFAs]), to stabilize against chemical oxidation (e.g., protection of flavor compounds, binding of enzymic browning phenolic precursors), to enhance nonwater-soluble (lipophilic) flavor compounds, and to improve physical stability of food ingredients (encapsulation of volatiles, controlled release of flavor).

3.3 POLYSACCHARIDES [54,65]

3.3.1 Polysaccharide Chemical Structures and Properties

Polysaccharides are polymers of monosaccharides. Like the oligosaccharides, they are composed of glycosyl units in linear or branched arrangements, but most are much larger than the 10- or 20-unit limit of oligosaccharides. The number of monosaccharide units in a polysaccharide, which is termed its degree of polymerization (DP), varies. Only a few polysaccharides have DPs less than 100; most have DPs in the range 200–3,000. The larger ones, such as cellulose, have a DP of 7,000–15,000. Starch amylopectin is even larger, having an average molecular weight of at least 10^7 (DP > 60,000). It is estimated that more than 90% of the carbohydrate mass in nature is in the form of polysaccharides. The general scientific term for polysaccharides is glycans.

If all the glycosyl units are of the same sugar type, they are homogeneous as to monomer units and are called homoglycans. Examples of homoglycans are cellulose (Section 3.3.7) and starch amylose (Section 3.3.6.1), which are linear, and amylopectin (Section 3.3.6.2), which is branched. All three are composed only of D-glucopyranosyl units.

When a polysaccharide is composed of two or more different monosaccharide units, it is a heteroglycan. A polysaccharide that contains two different monosaccharide units is a diheteroglycan; a polysaccharide that contains three different monosaccharide units is a triheteroglycan, and so on. Diheteroglycans generally are either linear polymers of blocks of similar units alternating along the chain, or consist of a linear chain of one type of glycosyl unit with a second present as single-unit branches. Examples of the former type are algins (Section 3.3.11) and of the latter guar and locust bean gums (LBGs) (Section 3.3.8).

In the shorthand notations of oligo- and polysaccharides, the glycosyl units are designated by the first three letters of their names with the first letter being capitalized, except for glucose which is Glc. If the monosaccharide unit is that of a D-sugar, the D is omitted; only L-sugars are so designated, for example, L-Ara for L-arabinose. The size of the ring is designated by an italicized *p* for pyranose or *f* for furanose. The anomeric configuration is designated with α or β as appropriate, for example, an α-D-glucopyranosyl unit is indicated as αGlc*p*. Uronic acids are designated with a capital A, for example, an L-gulopyranosyluronic acid unit (see Section 3.3.11) is indicated as LGul*p*A. The position of linkages are designated either as, for example, 1→3 or 1,3, the latter being more commonly used by biochemists and the former more commonly used by carbohydrate chemists. Using the shorthand notation, the structure of lactose is represented as βGal*p*(1→4)Glc or βGal*p*1,4Glc and maltose as αGlc*p*(1→4)Glc or αGlc*p*1,4Glc. Note that the reducing end cannot be designated as α or β or as being in a pyranose or furanose ring (except in the case of a crystalline product) because the ring can open and close; that is, in solutions of both lactose and maltose and other oligo- and polysaccharides, the reducing end unit will occur as a mixture of α- and β-pyranose ring forms and the acyclic form, with rapid interconversion between them (see Figure 3.12).

3.3.2 Polysaccharide Solubility

Most polysaccharides contain glycosyl units that, on average, have three hydroxyl groups. Each of the hydroxyl groups has the possibility of hydrogen bonding to one or more water molecules. Also, the ring oxygen atom and the glycosidic oxygen atom connecting one sugar ring to another can form hydrogen bonds with water. With every sugar unit in the chain having the capacity to hold water molecules, glycans possess a strong affinity for water and most hydrate readily when water is available. In aqueous systems, polysaccharide particles can take up water, swell, and usually undergo partial or complete dissolution.

Polysaccharides, like lower-molecular-weight carbohydrates, modify and control the mobility of water in food systems, and water plays an important role in influencing the physical and functional properties of polysaccharides. Polysaccharides and water together control many functional properties of foods, including texture.

The water of hydration that is naturally hydrogen bonded to polysaccharide molecules is often described as nonfreezable water, that is, water whose structure has been sufficiently modified by the presence of the polymer molecule so that it will not freeze. This water has also been referred to as plasticizing water. The molecules that make up this water are not energetically bound in a chemical sense. While their motions are retarded, they are able to exchange freely and rapidly with other water molecules. This water of hydration makes up only a small part of the total water in gels and fresh tissue foods. Water in excess of the hydration water is entrapped in capillaries and cavities of various sizes in the gel or tissue.

Polysaccharides are cryostabilizers, rather than cryoprotectants. They do not increase the osmolality or depress the freezing point of water significantly, because they are large, high-molecular-weight molecules and osmotic strength and freezing point depression are colligative properties. When a polysaccharide solution is frozen, a two-phase system of crystalline water (ice) and a glass consisting of perhaps 70% polysaccharide molecules and 30% nonfreezable water is formed. As in the case of solutions of low-molecular-weight carbohydrates, the nonfreezable water is part of a highly concentrated solution in which the mobility of the water molecules is restricted by the extremely high viscosity. While some polysaccharides provide cryostabilization by producing this freeze-concentrated matrix that severely limits molecular mobility, others provide cryostabilization by restricting ice crystal growth by adsorption to nuclei or active crystal growth sites. Some polysaccharides in nature are ice nucleators.

So both high- and low-molecular-weight carbohydrates are generally effective in protecting food products stored at freezer temperatures (typically −18°C) from destructive changes in texture and structure, with various degrees of effectiveness. The improvement in product quality and storage stability is a result of controlling both the amount (particularly in the case of low-molecular-weight carbohydrates) and the structural state (particularly in the case of polymeric carbohydrates) of the freeze-concentrated, amorphous matrix surrounding ice crystals.

Most, if not all, polysaccharides, except those with very bushlike, branch-on-branch structures, exist in some sort of helical shape. Certain linear homoglycans, such as cellulose (see Section 3.3.7), have flat, ribbon-like structures. Such uniform linear chains undergo hydrogen bonding with each other so as to form crystallites separated by amorphous regions (Figure 3.35). It is these crystallites of linear chains that give cellulose fibers, such as wood and cotton fibers, their great strength, insolubility, and resistance to breakdown; the latter because the crystalline regions are nearly inaccessible to enzyme penetration. These polysaccharides with high degrees of orientation and crystallinity are exceptions. Most polysaccharides are not so crystalline and readily hydrate and dissolve in water.

Unbranched diheteroglycans containing nonuniform blocks of glycosyl units and most branched polysaccharides cannot form micelles because their chain segments are prevented from becoming closely packed over lengths necessary to provide enough intermolecular bonding to form sizeable crystallites. Hence, these chains have a degree of solubility that increases as chains become less able to fit closely together. In general, polysaccharides become more soluble in proportion to the degree of irregularity of the molecular chains, which is another way of saying that, as the ease with which molecules fit together decreases, the solubility of the molecules increases.

Water-soluble polysaccharides and modified polysaccharides used in food and other industrial applications are known as gums or hydrocolloids. Food gums are sold as powders of varying particle size.

3.3.3 Polysaccharide Solution Viscosity and Stability [12,20]

Polysaccharides (gums, hydrocolloids) are used in foods primarily to thicken and/or gel aqueous systems and otherwise to modify and/or control the flow properties and textures of liquid products and the deformation properties of semisolid products. They are generally used in food products at concentrations of 0.25–0.50%, indicating their great ability to produce viscosity and to form gels.

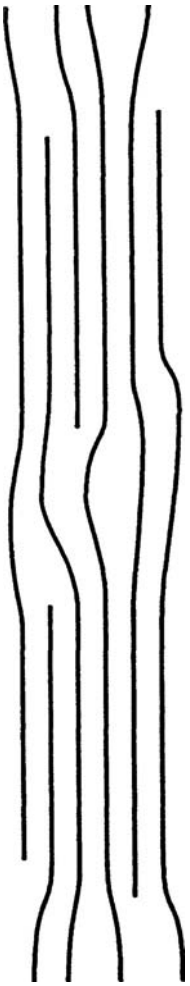

FIGURE 3.35 Crystalline regions in which the chains are parallel and ordered separated by amorphous regions.

The viscosity of a polymer solution is a function of the size and shape of its molecules and the conformations they adopt in the solvent. In foods and beverages, the solvent is an aqueous solution of other solutes. The shapes of polysaccharide molecules in solution are a function of rotations around the bonds of the glycosidic linkages. The greater the internal freedom at each glycosidic linkage, the greater the number of conformations available to each individual segment. Chain flexibility provides a strong entropic drive, which generally overcomes energy considerations and induces the chain to approach disordered or random coil (Figure 3.36) states in solution. However, most polysaccharides exhibit deviations from strictly random coil states, forming stiff coils, the specific nature of the coils being a function of the monosaccharide composition and linkages.

The motion of linear polymer molecules in solution results in their sweeping out a large space. When they collide with each other, they create friction, consume energy, and thereby produce viscosity. Linear polysaccharides produce highly viscous solutions, even at low concentrations. Viscosity depends both on the DP (molecular weight) and the shape and flexibility of the solvated polymer chain, with the longer, more extended, and/or more rigid molecules producing the greatest viscosity. With respect to DP, carboxymethylcellulose (CMC) (see Section 3.3.7.2) and products obtained from the parent CMC can have solution viscosities at 2% concentration that can vary from <5 to $>100{,}000$ mPa · S.

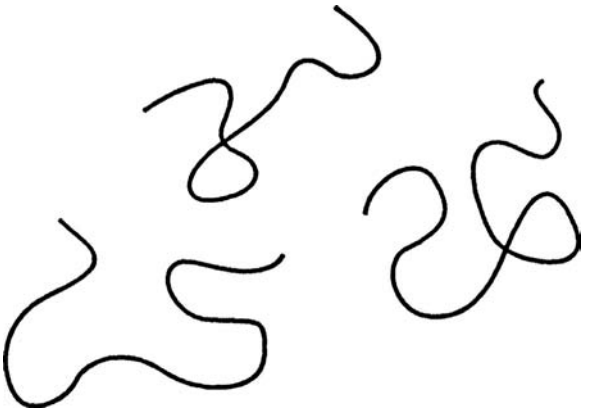

FIGURE 3.36 Randomly coiled polysaccharide molecules.

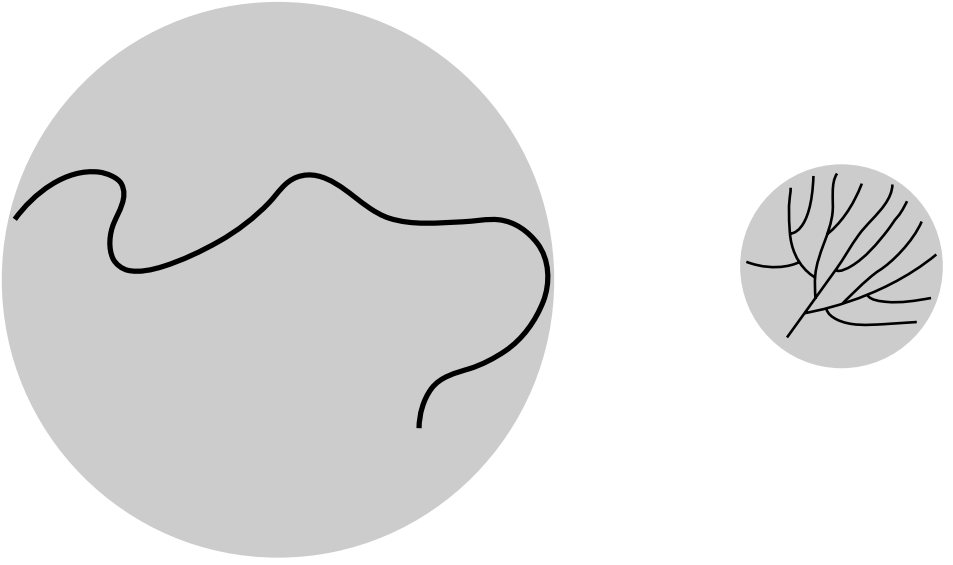

FIGURE 3.37 Relative volumes occupied by a linear polysaccharide and a highly branched polysaccharide of the same molecular weight.

A highly branched polysaccharide will sweep out much less space than a linear polysaccharide of the same molecular weight (Figure 3.37). As a result, highly branched molecules will collide less frequently and will produce a much lower viscosity than will linear molecules of the same DP. This also implies that a highly branched polysaccharide must be significantly larger than a linear polysaccharide to produce the same viscosity at the same concentration.

Likewise, linear polysaccharide chains bearing only one type of ionic charge (almost always a negative charge imparted by ionized carboxyl or sulfate half-ester groups) cause them to assume an extended configuration due to repulsion of the like charges, increasing the end-to-end chain length and, thus, increasing the volume swept out by the polymer. Therefore, these polymers tend to produce solutions of high viscosity.

Unbranched glycans with regular repeating unit structures form unstable aqueous dispersions that precipitate or gel rapidly. This occurs as segments of the long molecules collide and form intermolecular bonds over the distance of a few units. Initial short alignments then extend in a

zipper-like fashion to greatly strengthen intermolecular associations. Other segments of other chains colliding with this organized nucleus bind to it, increasing the size of the ordered, crystalline phase. Linear molecules continue to bind to fashion a fringed micelle that may reach a size where gravitational forces cause precipitation. For example, starch amylose, when dissolved in water with the aid of heat and then cooled to below 65°C, undergoes molecular aggregation and precipitates, a process called retrogradation. During cooling of bread and other baked products, amylose molecules associate to produce firming. Over a longer storage time, the branches of amylopectin associate (and may partially crystallize) to produce staling (Section 3.3.6.7).

In general, molecules of unbranched, neutral homoglycans have an inherent tendency to associate and partially crystallize. However, if linear glycans are derivatized, or occur naturally derivatized, as does guar gum (Section 3.3.8), which has single-unit glycosyl branches along a backbone chain, their segments are prevented from association and stable solutions result.

Stable solutions are also formed if the linear chains contain charged groups so that Coulombic repulsions prevent segments from approaching each other. As already mentioned, charge repulsion also causes chains to extend, which provides high viscosities. Such highly viscous, stable solutions are seen with sodium alginate (Section 3.3.11), where each glycosyl unit is a uronic acid unit having a carboxylic acid group in the salt form, and in xanthan (Section 3.3.9), where one out of five glycosyl units is a uronic acid unit and another carboxylate group from a cyclic acetal of pyruvic acid is present at a frequency of about one per every ten monosaccharide units. But, if the pH of an alginate solution is lowered to 3, where ionization of carboxylic acid groups is repressed because the pK_a values of the constituent monomers are 3.38 and 3.65, the resulting less-ionic molecules can associate and precipitate or form a gel as expected for an unbranched, uncharged glycan.

Carrageenans are mixtures of linear chains of nonuniform structures that have a negative charge due to numerous ionized sulfate half-ester groups along the chain (Section 3.3.10). These molecules do not precipitate at low pH because the sulfate group remains ionized at all practical pH values.

Solutions of gums are dispersions of hydrated molecules and/or aggregates of hydrated molecules. Their flow behavior is determined by the size, shape, ease of deformation (flexibility), and presence and magnitude of charges on these hydrated molecules and/or aggregates. There are two general kinds of flow exhibited by polysaccharide solutions: pseudoplastic (by far the most common) and thixotropic; both are characterized by shear thinning.

In pseudoplastic flow, a more rapid flow results from an increase in shear rate, that is, the greater the applied force, the less viscous it becomes (Figure 3.38). The applied force can be that of pouring, chewing, swallowing, pumping, mixing, or anything else that induces shear. The change in viscosity is independent of time, that is, the rate of flow changes instantaneously as the shear rate is changed.

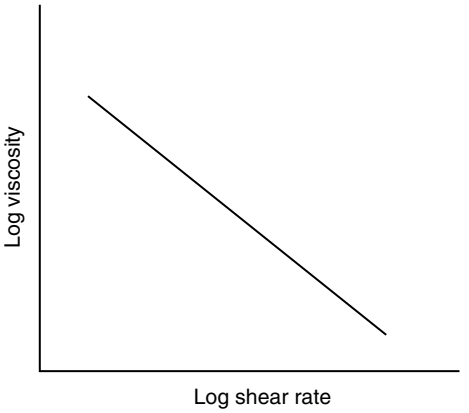

FIGURE 3.38 The logarithm of viscosity as a function of the shear rate for a pseudoplastic shear-thinning fluid.

In general, higher-molecular-weight gums form more pseudoplastic solutions. Certainly, stiffer, linear molecules produce the more pseudoplastic flow.

Gum solutions that are less pseudoplastic are said to give long flow;* such solutions are generally perceived as being slimy. More pseudoplastic solutions are described as having short flow and are generally perceived as being nonslimy. In food science, a slimy material is one that is thick, coats the mouth, and is difficult to swallow. Sliminess is inversely related to pseudoplasticity, that is, to be perceived as being nonslimy, there must be marked thinning at the low shear rates produced by chewing and swallowing.

Thixotropic flow is a second type of shear-thinning flow. In this case, the viscosity reduction that results from an increase in the rate of flow does not occur instantaneously. The viscosity of thixotropic solutions decreases under a constant rate of shear in a time-dependent manner and regains the original viscosity after cessation of shear, but again only after a clearly defined and measurable time interval. This behavior is due to a gel → solution → gel transition. In other words, a thixotropic solution at rest is a weak (pourable) gel (Section 3.3.4).

For solutions of most gums, an increase in temperature results in a decrease in viscosity. This loss of viscosity as the temperature is raised is often an important property, for it means that higher solids can be put into solution at a higher temperature; then the solution can be cooled for thickening. (Xanthan gum is an exception because the viscosity of its solutions is essentially constant at temperatures between 0°C and 100°C. See Section 3.3.9.)

3.3.4 Gels [12,13,26]

A gel is a continuous, three-dimensional network of connected molecules or particles (such as crystals, emulsion droplets, or molecular aggregates/fibrils) entrapping a large volume of a continuous liquid phase, much as does a sponge. In many food products, the gel network consists of polymer (polysaccharide and/or protein) molecules or fibrils formed from polymer molecules joined in junction zones by hydrogen bonding, hydrophobic associations (i.e., van der Waals attractions), ionic cross bridges, entanglements, or covalent bonds, and the liquid phase is an aqueous solution of low-molecular-weight solutes and portions of the polymer chains.

Gels have some characteristics of solids and some characteristics of liquids. When polymer molecules or fibrils formed from polymer molecules interact over portions of their lengths to form junction zones and a three-dimensional network (Figure 3.39), a fluid solution is changed into a material that can retain its shape (partially or entirely). The three-dimensional network structure offers sufficient resistance to an applied stress to cause it to behave in part as an elastic solid. However, the continuous liquid phase, in which molecules are completely mobile, makes a gel less stiff than an ordinary solid, causing it to behave in some respects as a viscous liquid. Therefore, a gel is a viscoelastic semisolid, that is, the behavior of a gel in response to an applied stress is partly that of an elastic solid and partly that of a viscous liquid.

Although gel-like or salve-like materials can be formed by high concentrations of particles (much like tomato paste), to form a gel from dissolved gum/hydrocolloid molecules, the polymer molecules or aggregates of molecules must partially come out of solution in junction zone regions to tie them together in a three-dimensional gel network structure. In general, if the junction zones grow after formation of the gel, the network becomes more compact, the structure contracts, and syneresis results. (The appearance of fluid droplets on the gel surface is called syneresis.)

* "Short flow" is exhibited by shear-thinning, primarily pseudoplastic, viscous solutions and "long flow" by viscous solutions that exhibit little or no shear-thinning. These terms were applied long before there were instruments to determine and measure rheological phenomena. They were arrived at in this way. When a gum or starch solution is allowed to drain from a pipette or a funnel, those that are not shear-thinning come out in long strings, while those that shear-thin form short drops. The latter occurs because as more and more fluid exits the orifice, the weight of the string becomes greater and greater, which causes it to flow faster and faster, and which causes it to shear-thin to the point that the string breaks into drops.

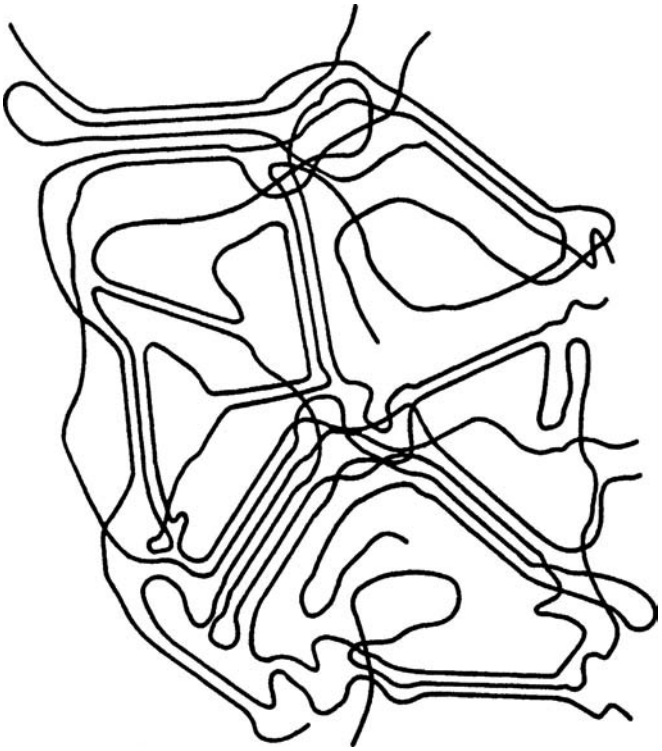

FIGURE 3.39 A diagrammatic representation of the type of three-dimensional network structure found in gels. Parallel side-by-side chains indicate the ordered, crystalline structure of a junction zone. The gaps between junction zones contain an aqueous solution of dissolved segments of polymer chains and other solutes.

Although polysaccharide gels generally contain no more than 1% polymer, that is, they may contain as much as 99% water, they can be quite strong. Examples of polysaccharide gels are dessert gels, aspics, structured fruit pieces, structured onion rings, meat-analog pet foods, jams, jellies, and confections such as gum drops.

Choice of a specific gum for a particular application depends on the viscosity or gel strength desired, the desired rheology, the pH of the system, temperatures during processing, interactions with other ingredients, the desired texture, and the cost of the amount needed to impart the desired properties. Consideration is also given to desired functional characteristics. These include a gum's ability to function as a binder, bodying agent, bulking agent, crystallization inhibitor, clarifying agent, cloud agent, coating agent/film former, emulsifier, emulsion stabilizer, encapsulating agent, fat mimetic, flocculating agent, foam stabilizer, mold release agent, suspension stabilizer, swelling agent, syneresis inhibitor, and whipping agent and its ability to effect water absorption and binding (water retention and migration control). Each food gum tends to have an outstanding property (perhaps several unique properties), which is often the basis for its choice for a particular application (Table 3.5).

3.3.5 Polysaccharide Hydrolysis

Polysaccharides are relatively less stable to hydrolytic cleavage than are proteins and may, at times, undergo depolymerization during food processing and/or storage of foods.* Often, food gums are

* On the other hand, polysaccharides do not undergo denaturation.

TABLE 3.5
Predominantly Used, Water-Soluble, Nonstarch Food Polysaccharides

Gum	Source	Class	General Shape	Monomer Units and Linkages (Approx. Ratios)	Noncarbohydrate Substituent Groups	Water Solubility	Key General Characteristics	Major Food Applications
Algins (alginates) (generally sodium alginate)	Brown algae	Seaweed (algal) extract Poly(uronic acid)	Linear	Block copolymer of the following units: →4)-βMan*p*A (1.0) →4)-αLGul*p*A (0.5–2.5)		Sodium alginate soluble	Gels with Ca^{2+} Viscous, not very pseudoplastic solutions	Forms nonmelting gels (dessert gels, fruit analogs, other structured foods) Meat analogs
						Alginic acid insoluble		Alginic acid forms soft, thixotropic, nonmelting gels (tomato aspic, jelly-type bakery fillings, filled fruit-containing breakfast cereal products)
					Hydroxypropyl ester groups in propylene glycol alginate (PGA)	Soluble	Surface active Solutions stable to acids and Ca^{2+}	Emulsion stabilization in creamy salad dressings Thickener in low-calorie salad dressings
Carboxymethyl-cellulose (CMC)	Derived from cellulose	Modified cellulose	Linear	→4)-βGlc*p*-(1→	Carboxymethyl ether (DS 0.4–0.8)[a]	High	Clear, stable solutions that can be either pseudoplastic or thixotropic	Retards ice crystal growth in ice creams and other frozen dessert products Thickener, suspending aid, protective colloid, and improver of mouthfeel, body, and texture in a variety of dressings, sauces, and spreads Lubricant, film former, and processing aid for extruded products Batter thickener and humectant in cake and related mixes Moisture binder and retarder of crystallization and/or syneresis in icings, frostings, toppings, fillings, and puddings Syrup thickener Suspending aid and thickener in dry powder, hot and cold drink mixes Gravy maker in dry pet food

(Continued)

TABLE 3.5
(Continued)

Gum	Source	Class	General Shape	Monomer Units and Linkages (Approx. Ratios)	Noncarbohydrate Substituent Groups	Water Solubility	Key General Characteristics	Major Food Applications
Carrageenans	Red algae	Seaweed (algal) extracts Sulfated galactans	Linear		Sulfate half-ester			Secondary stabilizer in ice cream and related products Preparation of evaporated milk, infant formulas, freeze–thaw stable whipped cream, dairy desserts, and chocolate milk Meat coating Improves adhesion and increases water-holding capacity of meat emulsion products Improves texture and quality of low-fat meat products
				κ types: $\rightarrow$3)-βGal*p* 4-SO_3^- (1$\rightarrow$4)-3,6An-αGal*p* (1$\rightarrow$		κ types: Na^+ salt soluble in cold water, K^+ and Ca^{2+} salts insoluble; all salts soluble at temperatures > 65°C; soluble in hot milk, insoluble in cold milk	Forms stiff, brittle, thermoreversible gels with $K^+ > Ca^{2+}$; thickens and gels milk at low concentration; synergistic gelation with LBG	

				ι types: →3)-β-Gal*p* 4-SO_3^- (1→4)-3,6An-α-Gal*p* 2-SO_3^-(1→		ι types: Na^+ salt soluble in cold water, K^+ and Ca^{2+} salts insoluble; all salts soluble at temperatures > 55°C; soluble in hot milk, insoluble in cold milk	Forms soft, resilient, thermoreversible gels with $Ca^{2+} > K^+$; gels do not synerese and have good freeze–thaw stability	
				λ types: →3)-β-Gal*p* 2-SO_3^- (1→4)-α-Gal*p* 2,6-diSO_3^-(1→		λ types: all salts soluble in hot and cold water and milk	Thickens cold milk	
Curdlan	Fermentation medium	Microbial polysaccharide	Linear	→3)-β-Glc*p*-(1→		Soluble	Gels irreversibly upon heating of solutions	Layered, nonmelting dessert gels
Gellan	Fermentation medium	Microbial polysaccharide	Linear	→4)-α-LRha*p*-(1→3)-β-Glc*p*-(1→4)-β-Glc*p*A-(1→4)-β-Glc*p*-(1→	Native type contains an acetate and a glycerate ester group on each repeating unit	Soluble in warm water	Gels with any cation Solutions have high yield values Low-acyl types form firm, brittle, nonelastic gels High-acyl types form soft, elastic, nonbrittle gels	Bakery mixes Nutrition bars Nutritional beverages Fruit toppings Sour cream and yogurt products

(Continued)

TABLE 3.5
(Continued)

Gum	Source	Class	General Shape	Monomer Units and Linkages (Approx. Ratios)	Noncarbohydrate Substituent Groups	Water Solubility	Key General Characteristics	Major Food Applications
Guar gum	Guar seed	Seed galacto-mannan	Linear with single-unit branches (behaves as a linear polymer)	→4)-βMan$p$(~0.56) αGal$p$ 1 ↓ 6 →4)-βMan$p$(~1.0) (Man:Gal = ~ 1.56:1)		High	Stable, opaque, very viscous, moderately pseudoplastic solutions Economical thickening	Binds water, prevents ice crystal growth, improves mouthfeel, softens texture produced by carrageenan + LBG, and slows meltdown in ice cream and ices Dairy products, prepared meals, bakery products, sauces, pet food
Gum arabic (gum acacia)	Acacia tree	Exudate gum	Branch-on-branch, highly branched	Complex, variable structure, contains polypeptide		Very high	Emulsifier and emulsion stabilizer Compatible with high concentrations of sugar Very low viscosity at high concentrations	Prevents sucrose crystallization in confections Emulsifies and distributes fatty components in confections Preparation of flavor oil-in-water emulsions Component of coating of pan-coated candies Preparation of flavor powders
Inulin	Chicory root	Plant extract	Linear	→2)-βFru$f$(1→		Soluble	Gels when hot solutions are cooled Can be used as a fat mimetic	Ingredient in nutrition, breakfast, and energy bars and vegetable patties as a source of dietary fiber and fat mimetic
Locust bean gum (carob gum, LBG)	Locust bean (carob) seed	Seed galacto-mannan	Linear with single-unit branches (behaves as a linear polymer)	→4)-βMan$p$(~2.5) αGal$p$ 1 ↓ 6 →4)-βMan$p$(~1.0) (Man:Gal = ~ 3.5:1)		Soluble only in hot water; requires 90°C for complete solubilization	Interacts with xanthan and carrageenan to form rigid gels; rarely used alone	Provides excellent heat shock resistance, smooth meltdown, and desirable texture in ice creams and other frozen dessert products

Methylcelluloses (MC) and hydroxy-propylmethyl-celluloses (HPMC)	Derived from cellulose	Modified cellulose	Linear	→4)-βGlc*p*-(1→	Hydroxypropyl (MS 0.02–0.3)[a] and methyl (DS 1.1–2.2)[a] ether groups	Soluble in cold water; insoluble in hot water	Clear solutions that are thermal gelling; surface active	MC: Provides fat-like characteristics Reduces fat absorption in fried products Imparts creaminess through film and viscosity formation Provides lubricity Gas retention during baking Moisture retention and control of moisture distribution in bakery products (increases shelf life and imparts tenderness) HPMC: Nondairy whipped toppings, where it stabilizes foams, improves whipping characteristics, prevents phase separation, and provides freeze–thaw stability
Pectins	Citrus peel Apple pomace	Plant extract Poly(uronic acid)	Linear	Primarily composed of →4)-αGal*p*A units	Methyl ester groups May contain amide groups	Soluble	Forms jelly- and jam-type gels in presence of sugar and acid or with Ca^{2+}	HM pectin: high-sugar jellies, jams, preserves, and marmalades Acidic milk drinks LM pectin: dietetic jellies, jams, preserves, and marmalades
Xanthan	Fermentation medium	Microbial polysaccharide	Linear with trisaccharide unit; branches on every other main chain unit (behaves as a linear polymer)	βMan*p* 1 ↓ 4 βGlc*p* A 1 ↓ 2 αMan*p* 6-Ac 1 ↓ 3 →4)-βGlc*p*-(1→4)-βGlc*p*-(1→	Acetyl ester Pyruvyl cyclic acetal on some βMan*p* end units	High	Very pseudoplastic, high viscosity solutions; excellent emulsion and suspension stabilizer; solution viscosity unaffected by temperature; solution viscosity unaffected by pH; excellent salt compatibility; synergistic increase in viscosity upon interaction with guar gum; heat reversible gelation with LBG	Stabilization of dispersions, suspensions, and emulsions Thickener

[a] For definitions of DS and MS (see Sections 3.3.6.10 and 3.4.3).

deliberately depolymerized. One reason why food gums would be deliberately depolymerized is so that a relatively high concentration can be used to provide body (*mouthfeel*) without producing undesirable viscosity.

Hydrolysis of glycosidic bonds joining monosaccharide (glycosyl) units in oligo- and polysaccharides can be catalyzed by acids (H^+) and/or enzymes. The extent of depolymerization, which has the effect of reducing viscosity, is determined by the pH (acid), temperature, time at that temperature and pH, and structure of the polysaccharide. Hydrolysis occurs most readily during thermal processing of acidic foods (as opposed to storage) because of the elevated temperature. Defects associated with depolymerization during processing can usually be overcome by using more of the polysaccharide (gum) in the formulation to compensate for breakdown, using a higher-viscosity grade of the gum, again to compensate for any depolymerization, or using a relatively more acid-stable gum. Depolymerization can also be an important determinant of shelf life.

Polysaccharides are also subject to enzyme-catalyzed hydrolysis. The rate and end products of this process are controlled by the specificity of the enzyme, pH, temperature, and time. Polysaccharides, like any and all other carbohydrates, are subject to microbial attack because of their susceptibility to enzyme-catalyzed hydrolysis. Furthermore, gum products are very seldom, if ever, delivered sterile, a fact that must be considered when using them as ingredients.

3.3.6 Starch [66,68]

The unique chemical and physical characteristics and nutritional aspects of starch set it apart from all other carbohydrates. Starch is the predominant food reserve substance in plants and provides 70–80% of the calories consumed by humans worldwide. Starch and starch hydrolysis products constitute most of the digestible carbohydrate in the human diet. Also, the amount of starch used in the preparation of food products—without counting that present in flours used to make bread and other bakery products, that naturally occurring in grains used to make breakfast cereals, or that naturally consumed in fruits and vegetables—greatly exceeds the combined use of all other food hydrocolloids.

Commercial starches are obtained from cereal grain seeds, particularly from normal corn, waxy corn (waxy maize), high-amylose corn, wheat, and various rices, and from tubers and roots, particularly potato and cassava (tapioca starch). Starches and modified starches have an enormous number of food uses, including adhesive, binding, clouding, dusting, film forming, foam strengthening, gelling, glazing, moisture retaining, stabilizing, texturizing, and thickening applications.

Starch is unique among carbohydrates because it occurs in nature as discrete particles called granules. Starch granules are insoluble; they hydrate only slightly in cold water. As a result, they can be dispersed in water, producing low-viscosity slurries that can be easily mixed and pumped, even at concentrations greater than 35%. The viscosity building (thickening) power of starch is realized only when a slurry of granules is cooked. Heating a 5% slurry of most unmodified starch granules to about 80°C (175 F) with stirring produces a very high viscosity dispersion called a paste. A second uniqueness is that most starch granules are composed of a mixture of two polymers: an essentially linear polysaccharide called amylose and a highly branched polysaccharide called amylopectin.

3.3.6.1 Amylose

While amylose is essentially a linear chain of (1→4)-linked α-D-glucopyranosyl units, many amylose molecules contain a few branches connected by α-D-(1→6) linkages at the branch points. Perhaps, 1 in 180–320 units, or 0.3–0.5% of the linkages, are branch points. The branches in branched amylose molecules are either very long or very short, and most branch points are separated by large distances so that the physical properties of amylose molecules are essentially those of linear molecules. Amylose molecules have molecular weights that are, on average, about 10^6.

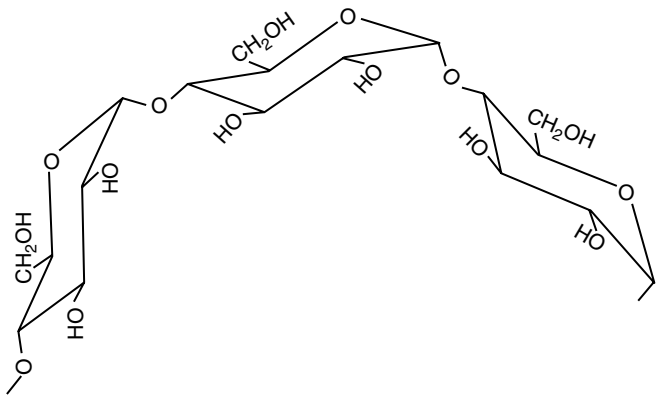

FIGURE 3.40 A trisaccharide segment of an unbranched portion of amylose or amylopectin molecule.

TABLE 3.6
General Properties of Some Starch Granules and Their Pastes

	Common Corn Starch	Waxy Maize Starch	High-Amylose Corn Starch	Potato Starch	Tapioca Starch	Wheat Starch
Granule size (major axis, μm)	2–30	2–30	2–24	5–100	4–35	2–55
% Amylose	28	<2	50–70	21	17	28
Gelatinization/pasting temp. (°C)[a]	62–80	63–72	66–170[b]	58–65	52–65	52–85
Relative viscosity	Medium	Medium high	Very low[b]	Very high	High	Low
Paste rheology[c]	Short	Long	Short	Very long	Long	Short
Paste clarity	Opaque	Very slightly cloudy	Opaque	Clear	Clear	Opaque
Tendency to gel/retrograde	High	Very low	Very high	Medium to low	Medium	High
Lipid (% DS)	0.8	0.2	—	0.1	0.1	0.9
Protein (% DS)	0.35	0.25	0.5	0.1	0.1	0.4
Phosphorus (% DS)	0.00	0.00	0.00	0.08	0.00	0.00
Flavor	Cereal (slight)	"Clean"		Slight	Bland	Cereal (slight)

[a] From the initial temperature of gelatinization to complete pasting.
[b] Under ordinary cooking conditions, where the slurry is heated to 95–100°C, high-amylose corn starch produces essentially no viscosity. Pasting does not occur until the temperature reaches 160–170°C (320–340 F).
[c] For a description of long and short flow (see Section 3.3.3).

The axial → equatorial position coupling of the (1→4)-linked α-D-glucopyranosyl units in amylose chains gives the molecules a right-handed spiral or helical shape (Figure 3.40). The interior of the helix contains a predominance of hydrogen atoms and is hydrophobic/lipophilic, while the hydroxyl groups are positioned on the exterior of the coil. Looking down the axis of the helix gives a view very much like that of looking down a stack of α-cyclodextrin molecules (Section 3.2.4) because each turn of the helix contains about 6 α-D-glucopyranosyl units linked (1→4).

Most starches contain about 25% amylose (Table 3.6). The two high-amylose corn starches that are commercially available have apparent amylose contents of about 52% and 70–75%.

3.3.6.2 Amylopectin [39]

Amylopectin, is a very large, very highly branched molecule, with branch point linkages constituting 4–5% of the total linkages. Amylopectin consists of a chain containing the only reducing end group, to which are attached numerous branch chains, to which are attached one to several third layer branch chains. The branches of amylopectin molecules are clustered (Figure 3.41) and

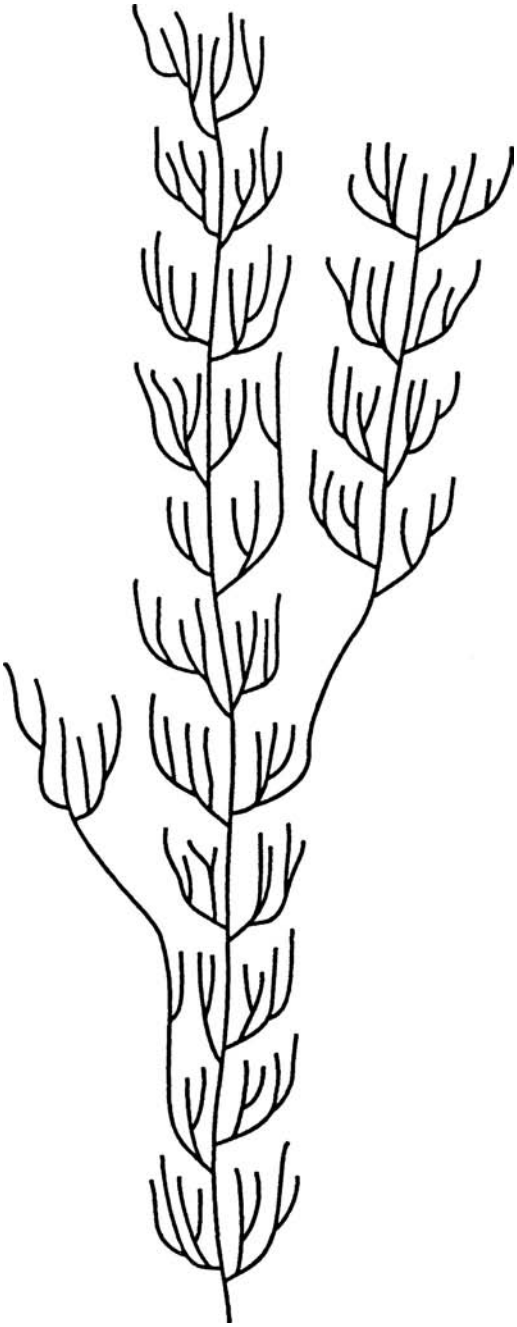

FIGURE 3.41 A diagrammatic representation of a portion of an amylopectin molecule.

occur as double helices. Molecular weights from 10^7 (DP ~60,000) up to perhaps 5×10^8 (DP ~3,000,000) make amylopectin molecules among the largest, if not the largest, molecules found in nature.

Amylopectin is present in all starches. It constitutes about 75% of most common starches (Table 3.6). Some starches consist entirely of amylopectin and are called waxy or amylopectin starches. Waxy corn (waxy maize), the first grain recognized as one in which the starch consists only of amylopectin, is so termed because, when the kernel is cut, the new surface has a vitreous or waxy appearance. Most other all-amylopectin starches are also called waxy although, as in corn, there is no wax present.

Potato amylopectin is unique among the commercial starches in having more than trace amounts of phosphate ester groups. These phosphate ester groups are attached most often (60–70%) at an O-6 position, with the other third at O-3 positions. These phosphate ester groups occur about once in every 215–560 α-D-glucopyranosyl units.

3.3.6.3 Starch Granules [72]

Starch granules are made up of amylose and/or amylopectin molecules arranged radially. They contain both crystalline and noncrystalline regions in alternating layers.* The clustered branches of amylopectin occur as packed double helices. The packing together of these double-helical structures forms small crystalline lamellae. The more dense layers of starch granules, which alternate with less dense amorphous layers, contain greater amounts of the crystalline lamellae. The radial, ordered arrangement of starch molecules in a granule is evident from the birefringence of granules, evidence for which is the polarization cross (white cross on a black background) seen in a polarizing microscope with the polarizers set at 90° to each other. The center of the cross is at the hilum, the origin of growth of the granule.

Corn starch granules, even from a single source, have mixed shapes, some being almost spherical, some angular, and some indented (for the size, see Table 3.6). Wheat starch granules are lenticular and have a bimodal size distribution (roughly <10 and >10 μm), with the larger granules being lenticular in shape. Rice granules are the smallest of the commercial starch granules (1–9 μm), although the small granules of wheat starch are almost the same size. Many of the granules in tuber and root starches, such as potato and tapioca starches, tend to be larger than those of seed starches and are generally less dense and easier to cook. Potato starch granules may be as large as 100 μm along the major axis.

All commercial starches contain small amounts of ash, lipid, and protein (Table 3.6). The phosphorus content of potato starch (0.06–0.1%, 600–1000 ppm) is due to the presence of the phosphate ester groups on amylopectin molecules. The phosphate ester groups give potato starch amylopectin a slight negative charge, resulting in some Coulombic repulsion that may contribute to the rapid swelling of potato starch granules in warm water and to several properties of potato starch pastes, namely, their high viscosities, good clarity (Table 3.6), and low rate of retrogradation (Section 3.3.6.7). Cereal starch molecules either do not have phosphate ester groups or have much smaller amounts than do potato starch molecules. Only the cereal starches contain endogenous lipids in the granules. These internal lipids are primarily FFA and lysophospholipid (LPL), largely lysophosphatidyl choline (89% in corn starch), with the ratio of FFA to LPL varying from one cereal starch to another.

3.3.6.4 Granule Gelatinization and Pasting [6,52]

Undamaged starch granules are insoluble in cold water, but can imbibe water reversibly, that is, they can swell slightly, and then return to their original size on drying. When heated in water,

* Starch granules are composed of layers somewhat like the layers of an onion, except that the layers cannot be peeled off.

starch granules undergo a process called gelatinization. Gelatinization is the disruption of molecular order within granules. Evidence for the loss of order includes irreversible granule swelling, loss of birefringence, and loss of crystallinity. Leaching of amylose occurs during gelatinization, but some leaching of amylose can also occur prior to gelatinization. Total gelatinization of a population of granules occurs over a temperature range (Table 3.6). The apparent temperature of initial gelatinization and the range over which gelatinization occurs depends on the method of measurement and on the starch:water ratio, granule type, and the degree of heterogeneity within the granule population under observation. (All populations of starch granules are heterogenous.) Several aspects of gelatinization of a population of granules can be determined. These are the initiation temperature, the midpoint temperature, and the completion temperature.

Continued heating of starch granules in excess water results in further granule swelling, additional leaching of soluble components (primarily amylose), and eventually, especially with the application of shear forces, total disruption of granules. These phenomena result in the formation of a starch paste. (In starch technology, what is called a paste is what results from heating a starch slurry.) Granule swelling and disruption produces a viscous mass (the paste) consisting of a continuous phase of solubilized amylose and/or amylopectin molecules and a discontinuous phase of granule remnants (granule ghosts* and fragments). Complete molecular dispersion is not accomplished except, perhaps, under conditions of high temperature, high shear, and excess water—conditions that are seldom, if ever, encountered in the preparation of food products. Cooling of a hot, normal corn starch paste results in a viscoelastic, firm, rigid gel.

Because gelatinization of starch is an endothermic process, differential scanning calorimetry (DSC), which measures both the temperature and the enthalpies of gelatinization, is widely used to follow the process. Although there is no complete agreement on the interpretation of DSC data and the events that take place during gelatinization of starch granules, the following general picture is widely accepted. Water acts as a plasticizer. Its mobility-enhancing effect is first realized in the amorphous regions, which physically have the nature of a glass. When starch granules are heated in the presence of sufficient water (at least 60%) and a specific temperature (T_g, the glass transition temperature) is reached, the plasticized amorphous regions of the granules undergo a phase transition from a glassy state to a rubbery state.† However, the peak for absorption of energy associated with this transition is not often, if ever, seen by DSC because the regions of crystallinity, that is, the ordered, packed, double-helical branches of amylopectin, are contiguous and connected by covalent bonds to the amorphous regions and melting of the crystallites immediately follows the glass transition. Because the enthalpy of initial melting (T_m) is so much larger than that of the glass transition, the latter is usually not evident.

Melting of lipid–amylose complexes occurs at much higher temperatures (100–120°C in excess water) than does melting of the amylopectin double-helical branches packed in crystalline order. Lipid–amylose complexes are made with single-helical segments of amylose molecules when a starch paste containing fatty acids or monoacyl glycerolipids is cooled. A DSC peak for this event is absent in waxy starches (without amylose).

Under normal food processing conditions (heat and moisture, although many food systems contain limited water as far as starch cooking is concerned), starch granules quickly swell beyond the reversible point. Water molecules enter between chains, break interchain bonds, and establish hydration layers around the separated molecules. This plasticizes (lubricates) chains, so they become more fully separated and solvated. Entrance of large amounts of water causes granules to swell to several times their original size. When a 5% starch suspension is gently stirred and heated, granules imbibe water until much of the water is absorbed by them, forcing them to swell, press against

* The granule ghost is the remnant remaining after cooking under no shear to moderate shear. It consists of the outer portion of the granule. It appears as an insoluble, outer envelope.

† A glass is a mechanical solid (a supercooled liquid) capable of supporting its own weight against flow. A rubber is an undercooled liquid that can exhibit viscous flow (see Chapter 2 for further details).

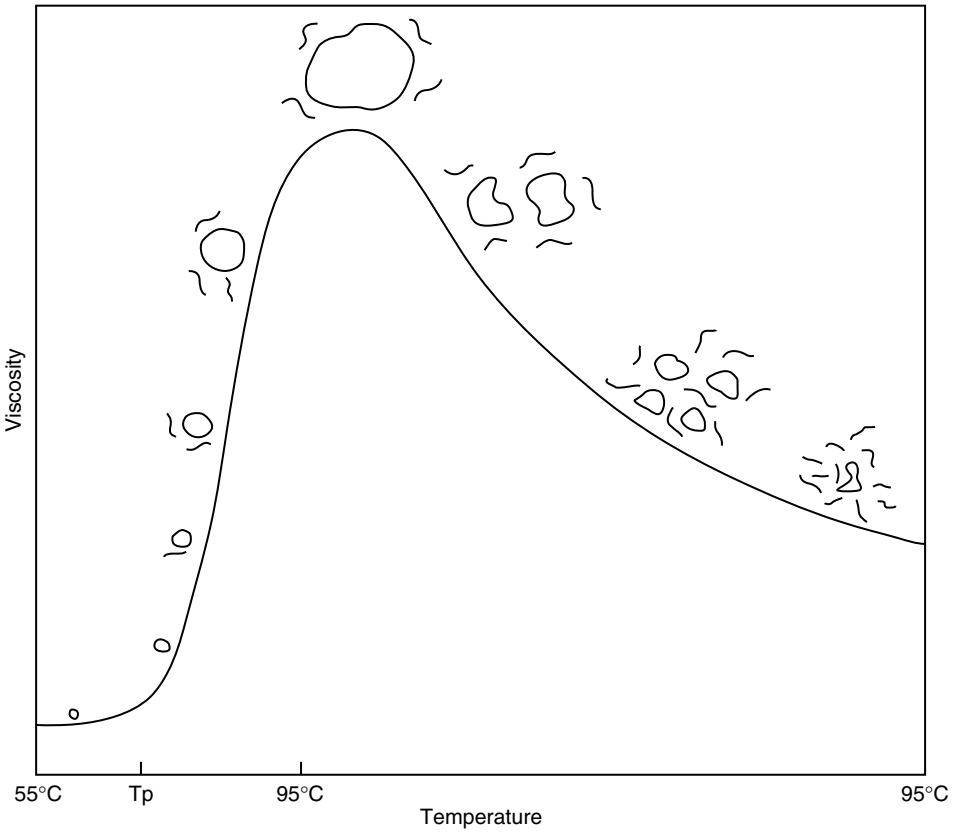

FIGURE 3.42 Representative cooking/pasting curve showing viscosity changes related to typical starch granule swelling and disintegration as a granule suspension is heated to 95°C and then held at that temperature using an instrument that imparts low shear.

each other, and fill the container with a highly viscous starch paste with most of the water inside the swollen granules. Such a starch paste has viscosity like that of a pudding because most of the space is composed of swollen granules that move past one another only with great difficulty. Such highly swollen granules of native starches are easily broken and disintegrated by stirring, resulting in a decrease in viscosity. As starch granules swell, hydrated amylose molecules diffuse through the mass to the external phase (water), a phenomenon responsible for some aspects of paste behavior. Results of starch swelling can be recorded using various instruments that record the viscosity continuously as the temperature is increased, held constant for a time, and then decreased (Figure 3.42).

Most suspensions of starch granules are stirred while being heated to prevent the granules from settling to the bottom of the container. Instruments that record changes that occur during starch pasting and paste behavior as a function of temperature to produce curves like those in Figure 3.42 also employ stirring. By the time peak viscosity is reached, some granules have been broken by stirring. With continued stirring, more granules rupture and fragment, causing a further decrease in viscosity. On cooling, some starch molecules partially reassociate to form a precipitate or gel. This process is called retrogradation (Section 3.3.6.7). The firmness of the gel depends on the extent of junction zone formation (Section 3.3.4). Junction zone formation is influenced (either facilitated or hindered) by the presence of other ingredients such as fats, proteins, sugars, and acids and the amount of water present.

3.3.6.5 Uses of Unmodified Starches

Starches serve a variety of roles in food production. Principally they are used to produce desired texture qualities (Section 3.3.6.9). Primarily, they provide body and bulk. The extent of starch gelatinization in baked goods strongly affects product properties, including storage behavior and rate of digestion. In baked products made from low-moisture doughs, many wheat starch granules remain ungelatinized. In higher-moisture products, most or all of the granules become gelatinized.

Most starch used as a food ingredient is "modified food starch" (Section 3.3.6.10) because, for the most part, textures of cooked suspensions of native starches, especially of native normal corn starch, are undesirable. The clear, cohesive pastes produced from waxy maize starch are somewhat more desirable, but even waxy maize starch is usually chemically modified to improve the functionalities it imparts. Unmodified potato starch is used in extruded cereal and snack food products and in dry mixes for soups and cakes. Rice starch produces opaque gels useful for baby food. Waxy rice starch gels are clear and cohesive. Wheat starch gels are weak and have a slight flavor due to residual flour components. Tuber (potato) and root (tapioca) starches have weak intermolecular bonding and swell greatly to give high-viscosity pastes (Table 3.6), but if shear is applied, the viscosity decreases quickly because the highly swollen granules break easily.

3.3.6.6 Starch Gelatinization within Vegetable Tissues [1,29,30,45]

The majority of dietary starch occurs within grain- and vegetable-based food products that contain starch as the predominant dry matter. Thus, it is important to understand the thermal properties of starch within these native environments as it relates to acceptability and texture of processed foods. The degree to which starch is gelatinized within food systems is generally dependent upon both the amount of water present and the extent of the heat treatment. As already mentioned, in some baked products, starch granules may remain ungelatinized even when heated to high temperatures. In pie crust and some cookies that are high in fat and low in moisture, about 90% of the wheat starch granules remain ungelatinized. In bread and cakes, which have higher moisture contents, about 96% of the wheat starch granules are gelatinized, but because they are heated without shear, the granules are still evident and can be isolated, although many are deformed.

Thermal processing (blanching, baking, boiling, steaming, frying) of vegetables is generally sufficient to induce a desired tissue softening. Following a heating process, vegetable tissue becomes more susceptible to fracture between (as opposed to through) its parenchyma cells.

Parenchyma tissue is the most abundant type of tissue in edible plants. In general, parenchyma tissue is comprised of aggregates of polygonally-shaped cells, each of which contains clusters of starch granules surrounded by a cellulosic cell wall. Adjoining cells are attached or cemented together by a middle lamella, which consists primarily of pectic substances. Water, which is the predominant constituent of most vegetable tissues, resides primarily in vacuoles within cells (84%), while the balance is associated with starch granules (13%) and cell wall components (3%).

As plant tissue is heated, the semicrystalline starch granules take up available water within cells and undergo swelling and gelatinization (Figure 3.43). The native moisture within parenchyma tissue is generally sufficient to plasticize starch granules and facilitate gelatinization, though the temperature at which these thermal events occur is slightly higher for starch granules housed within native plant cells compared to isolated starch. The higher gelatinization temperature of *in situ* starch has been attributed to the presence of solutes. Though starch gelatinization is complete within plant tissue (molecular order is fully lost), granule swelling is limited by the boundaries of the surrounding cell walls. Starch granules swell (with some leaching of amylose from cells) to fill most of the entire volume of their respective cells, producing a swollen starch mass that may still possess some subtly discernable granule remnants. Granule swelling during heating has been shown to exert an observable internal pressure on parenchyma cell walls (estimated at 100 kPa). Though the magnitude of swelling pressure is itself insufficient to bring about cell rupture (cells generally remain

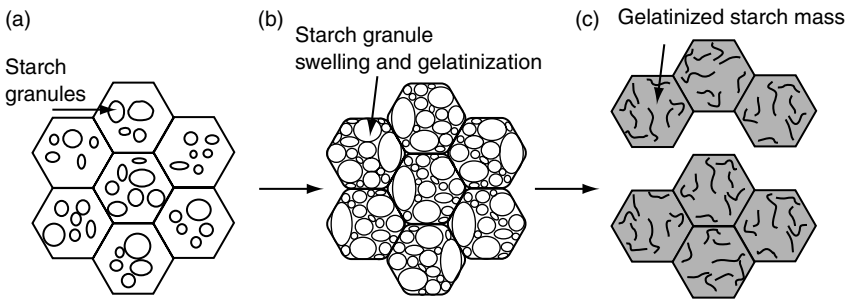

FIGURE 3.43 Within plant parenchyma tissue, starch granules (a) within cells undergo swelling and gelatinization during heating to exert a temporary "swelling pressure" on surrounding cell walls (b). With further heating, starch granules evolve into a fairly uniform gelatinized starch mass within cells (c). Heated tissue becomes prone to increased sloughing (cell separation), which is primarily attributable pectin degradation within the middle lamella, though starch swelling pressure is thought to contribute a significant secondary role.

intact), isolated potato parenchyma cells temporarily increase in size and become more spherical as a result of starch gelatinization. This phenomenon, referred to as cell "rounding off," occurs in concert with pectin degradation by β-elimination within the middle lamellae to cause softening of the parenchyma tissue. As the characteristic softening phenomenon is observed in tissues that do not contain appreciable starch contents, such as tomatoes, this effect is primarily attributed to pectin degradation within the middle lamellae.

Nevertheless, in starch-containing tissues, such as potato, a high starch content and/or degree of starch granule swelling is associated with a softer, more friable cooked tissue. It is thought that the cell "rounding off" phenomenon exerts physical pressure on a partially degraded or weakened middle lamellae, contributing secondarily to cell separation or tissue sloughing. Also, the degree to which gelatinized starch swells to fill the volume of parenchyma cells is thought to influence the human perception of tissue moistness in the mouth. A high starch content and swelling capacity is generally more effective in binding up free moisture within the cooked tissue, producing a corresponding dry mouthfeel. Cooked potato texture has been traditionally classified in terms of "mealiness" and "waxiness." A mealy texture is characterized by a dry-appearing tissue that crumbles or sloughs easily. In contrast, a waxy tissue (not to be confused with a waxy starch) is defined by a moist appearance, a gummy mouthfeel, and a firm texture. Generally, mealy potatoes are deemed more suitable for the majority of processed products (French fries, mashed potatoes, etc.). Waxy potato varieties find application in boiling and canning. In conclusion, starch gelatinization behavior appears to exert significant influence on cooked vegetable texture and end-use potential through its secondary role in tissue softening (cell "rounding off") and its water-binding capabilities within parenchyma tissue.

3.3.6.7 Retrogradation and Staling [23,42,43,52]

As already pointed out, cooling a hot starch paste generally produces a firm, viscoelastic gel. The formation of the junction zones of a gel can be considered to be the first stage of an attempt by starch molecules to crystallize. As starch pastes are cooled and stored, the starch becomes progressively less soluble. In dilute solution, starch molecules will precipitate. The collective processes of the starch molecules in a solution or paste becoming less soluble is called retrogradation. Retrogradation of cooked starch involves both of the two constituent polymers, amylose and amylopectin, with amylose undergoing retrogradation at a much more rapid rate than amylopectin. The rate of retrogradation depends on several variables, including the molecular ratio of amylose to amylopectin; structures of the amylose and amylopectin molecules, which is determined by the botanical source of the starch; temperature; starch concentration; and presence and concentration of other ingredients, primarily surfactants and salts. Many quality defects in food products, such as bread staling and loss of viscosity and precipitate formation in soups and sauces, are due, at least in part, to starch retrogradation.

Staling of baked goods is noted by an increase in crumb firmness and a loss in the perception of product freshness. Staling begins as soon as baking is complete and the product begins to cool. The rate of staling is dependent on the product formulation, the baking process, and storage conditions. Staling is due, at least in part, to the gradual transition of amorphous starch to a partially crystalline, retrograded state. In baked goods, where there is just enough moisture to gelatinize starch granules (while retaining a granule identity), amylose retrogradation (insolubilization) may be largely complete by the time the product has cooled to room temperature. Retrogradation of amylopectin is believed to involve primarily association of its outer branches and requires a much longer time than amylose retrogradation, giving it prominence in the staling process that occurs with time after the product has cooled.

Most polar lipids with surfactant properties retard crumb firming by forming complexes with starch polymer molecules. Compounds such as glyceryl monopalmitate (GMP), other monoglycerides and their derivatives, and sodium stearoyl 2-lactylate (SSL) are incorporated into doughs of bread and other baked goods, in part to increase shelf life.

3.3.6.8 Starch Complexes [7]

Because amylose chains are helical with hydrophobic (lipophilic) interiors, they are able to form complexes with linear hydrophobic portions of molecules that can fit in the hydrophobic tube. Iodine (as I_3^-) complexes with both amylose and amylopectin molecules. Again, the complexing occurs within the hydrophobic interior of the helical segments. With amylose, the long helical segments allow long chains of poly(I_3^-) to form and produce the blue color used as a diagnostic test for starch. The amylose–iodine complex contains 19% iodine and determination of the amount of complexing can be used to measure the amount of apparent amylose present in a starch. Amylopectin forms a reddish-purple color with iodine because the branch chains of amylopectin are too short for formation of long chains of poly(I_3^-).

Polar lipids (surfactants/emulsifiers and fatty acids) can affect starch pastes and starch-based foods in one or more of three ways as a result of complex formation: (1) by affecting the processes associated with starch gelatinization and pasting (i.e., the loss of birefringence, granular swelling, leaching of amylose, melting of the crystalline regions of starch granules, and viscosity increases during cooking), (2) by modifying the rheological behavior of the resulting pastes, and (3) by inhibiting the crystallization of starch molecules associated with the retrogradation process. Here too, complexation with emulsifiers occurs much more readily with, and has a much greater effect on, the amylose component than on the amylopectin component, so emulsifiers affect normal starches much more than waxy maize starch.

Certain flavor and aroma compounds also complex with starch, resulting in reduced perception in starchy foods. The binding of such compounds to starch, primarily amylose, molecules appears to be complex with competitive, synergistic, and antagonistic effects. However, the major reason all polysaccharides (starches and food gums) reduce the perception of flavors and aromas is a limitation of diffusion of flavor molecules to taste buds and aroma molecules to the surface where they can escape due to the increased viscosity starches and gums impart. Which of these processes and specific changes occur depends on the structure of the polar lipid, the starch employed, and the product to which it is added.

3.3.6.9 Hydrolysis of Starch [51,61]

Starch molecules, like all other polysaccharide molecules, are depolymerized by hot acids. Hydrolysis of the glycosidic bonds occurs more or less randomly to produce, initially, very large fragments. Commercially, hydrochloric acid is sprayed onto well-mixed starch, or stirred slightly moistened, granular starch is treated with hydrogen chloride gas, and the mixture is then heated until the desired degree of depolymerization is obtained.

TABLE 3.7
Functional Properties of Starch Hydrolysis Products

Properties Enhanced by Greater Hydrolysis[a]	Properties Enhanced in Products of Less Conversion[b]
Sweetness	Ability to produce viscosity
Hygroscopicity and humectancy	Ability to provide body
Freezing point depression	Foam stabilization
Flavor enhancement	Ice crystal growth prevention
Fermentability	Sugar crystallization prevention
Browning reaction	

[a] High-conversion (high-DE) syrups.
[b] Low-DE syrups and maltodextrins.

The acid is neutralized, and the product is recovered, washed, and dried. The products are still granular, but break up (cook out) much more easily than does the parent untreated starch. They are called acid-modified, thin-boiling, or thinned starches. Even though only a few glycosidic bonds are hydrolyzed, the starch granules disintegrate much more easily during heating in water. Acid-modified starches form gels with improved clarity and increased strength, even though they provide less solution viscosity. Thin-boiling starches are used as film formers and adhesives in products such as pan-coated nuts and candies and whenever a strong gel is desired, for example, in gum candies (such as jelly beans, jujubes, orange slices, and spearmint leaves) and in processed cheese loaves. To prepare products that form especially strong and fast-setting gels, a high-amylose corn starch is used as the base starch. The functional properties of the hydrolysis products of starch are given in Table 3.7.

More extensive depolymerization of granular starch with acid produces dextrins. Dextrins produce lower viscosities at equal concentrations than do thin-boiling starches and can be used at high concentrations in food processing. They have film forming and adhesive properties and are useful in products such as pan-coated, roasted nuts and candies. They are also used as fillers, encapsulating agents, and carriers of flavors, especially spray-dried flavors. They are classified by their cold water solubility and color. Dextrins that retain large amounts of linear chains or long chain fragments form strong gels.

Incomplete hydrolysis of cooked, that is, pasted, starch dispersions with either an acid or an enzyme produces mixtures of maltooligosaccharides,* which are referred to industrially as maltodextrins. Maltodextrins are usually described by their dextrose equivalency (DE). The DE is related to the DP through the following equation:

$$\mathrm{DE} = 100/\mathrm{DP}$$

where both DE and DP are average values for populations of molecules. Therefore, the DE of a product of hydrolysis is its reducing power as a percentage of the reducing power of pure D-glucose (dextrose); thus, DE is inversely related to average molecular weight. Maltodextrins are defined as products with DE values that are measurable, but <20, that is, their average DPs are >5. Maltodextrins of lowest DE, that is, highest average molecular weight, are nonhygroscopic, while those of highest DE tend to absorb moisture. Maltodextrins are bland with virtually no sweetness and are excellent for contributing body or bulk to food systems. Hydrolysis to DE values of 20–60 gives mixtures of molecules that, when dried, are called corn syrup solids. Corn syrup solids dissolve rapidly and are mildly sweet.

* Oligosaccharides from starch are known as maltooligosaccharides.

Continued hydrolysis of starch produces a mixture of D-glucose, maltose, and other maltooligosaccharides. Syrups with these components in various ratios are produced in enormous quantities. One of the most common has a DE of 42. These syrups are stable because crystallization does not occur easily in such complex mixtures. They are sold in concentrations of high osmolality (about 70% solids), high enough so that ordinary organisms cannot grow in them. An example is waffle and pancake syrup, which is colored with caramel coloring and flavored with maple flavoring.

Three to four enzymes are used for the industrial hydrolysis of starch to D-glucose. α-Amylase is an endo-enzyme that cleaves both amylose and amylopectin molecules internally, producing oligosaccharides. The larger oligosaccharides may be singly, doubly, or triply branched via (1→6) linkages, since α-amylase acts only on the (1→4) linkages of starch. α-Amylase does not attack double-helical starch polymer segments or polymer segments complexed with a polar lipid (stabilized single-helical segments).

Glucoamylase (amyloglucosidase) is used commercially, in combination with an α-amylase, for producing D-glucose (dextrose) syrups and crystalline D-glucose. The enzyme acts upon fully gelatinized starch as an exo-enzyme, sequentially releasing single D-glucosyl units from the nonreducing ends of amylose and amylopectin molecules, even those joined through (1→6) bonds. Consequently, the enzyme can completely hydrolyze starch to D-glucose, but is always used on starch that has already been depolymerized with α-amylase to generate fragments and, thus, more nonreducing ends.

β-Amylase releases the disaccharide maltose sequentially from the nonreducing ends of starch polymer chains. When amylopectin is the substrate, it attacks the nonreducing ends, sequentially releasing maltose, but it cannot cleave the (1→6) linkages at branch points; so it leaves a pruned amylopectin residue termed a limit dextrin, specifically a β-limit dextrin.

There are several debranching enzymes that specifically catalyze hydrolysis of (1→6) linkages in amylopectin, producing numerous linear, but low-molecular-weight molecules. One such enzyme is isoamylase; another is pullulanase.

Cyclodextrin glucanotransferase is a unique *Bacillus* enzyme that forms rings of (1→4)-linked α-D-glucopyranosyl units from starch polymers called cyclodextrins (Section 3.2.4). Glucose syrup, often called corn syrup in the United States, is the major source of D-glucose and D-fructose. To make a syrup, a slurry of starch in water is mixed with a thermally stable α-amylase and put through a special cooker where rapid gelatinization and enzyme-catalyzed hydrolysis (liquefaction) takes place. After cooling to 55–60°C (130–140 F), hydrolysis is continued with glucoamylase, whereupon the syrup is clarified, concentrated, carbon-refined, and ion-exchanged. If the syrup is properly refined and combined with seed crystals, crystalline D-glucose (dextrose) can be obtained.

For production of D-fructose, a D-glucose solution is passed through a column containing bound (immobilized) glucose isomerase. The enzyme catalyzes the isomerization of D-glucose to D-fructose (see Figure 3.5), forming an equilibrium mixture of approximately 58% D-glucose and 42% D-fructose. Higher concentrations of D-fructose are usually desired. (The HFS most often used as a soft drink sweetener contains approximately 55% D-fructose.) To make a syrup with a concentration of D-fructose greater than 42%, the isomerized syrup is passed through a bed of cation-exchange resin in the calcium salt form. The resin binds D-fructose that can be recovered and added to the normal syrup to produce a syrup enriched in D-fructose.

3.3.6.10 Modified Food Starches [5,66,68]

Food processors generally prefer starches with better behavioral characteristics than provided by native starches. Native starches produce weak-bodied, cohesive, rubbery pastes when cooked and undesirable gels when the pastes are cooled. Modification is done to improve the characteristics of the pastes and gels. Some modifications are done so that resultant pastes can withstand the conditions of heat, shear, and acid associated with particular processing conditions; others are done to introduce specific functionalities. Modified food starches are functional, useful, and abundant food macroingredients and additives.

Modifications can be chemical or physical. Chemical modifications make crosslinked, stabilized, oxidized, and depolymerized (acid-modified, thin-boiling; Section 3.3.6.9) products. Physical modifications make pregelatinized (Section 3.3.6.11) and cold-water-swelling (Section 3.3.6.12) products. Chemical modifications have the greatest effects on functionalities, and the majority of modified food starch products have been derivatized with reagents that react with hydroxyl groups to form ethers or esters. Modifications can be single modifications, but modified starches often are prepared by combinations of two, three, and sometimes four processes.

Chemical reactions currently both allowed and used to produce modified food starches in the United States are as follows: esterification with acetic anhydride, succinic anhydride, the mixed anhydride of acetic and adipic acids, 1-octenylsuccinic anhydride, phosphoryl chloride, sodium trimetaphosphate, sodium tripolyphosphate, and monosodium orthophosphate; etherification with propylene oxide; acid modification with hydrochloric and sulfuric acids; bleaching with hydrogen peroxide, peracetic acid, potassium permanganate, and sodium hypochlorite; oxidation with sodium hypochlorite; and various combinations of these reactions.

Approved and used esterified and etherified modified food starches include the following:

Stabilized starches

- Hydroxypropyl starches (starch ether)
- Starch acetates (starch ester)
- Starch octenylsuccinates (monostarch ester)
- Monostarch phosphate (ester)

Crosslinked starches

- Distarch phosphate
- Distarch adipate

Crosslinked and stabilized starches

- Hydroxypropylated distarch phosphate
- Phosphorylated distarch phosphate
- Acetylated distarch phosphate
- Acetylated distarch adipate

Crosslinked starches have higher gelatinization and pasting temperatures, increased resistance to shear, and increased stability to low pH conditions and produce pastes with greater viscosities and stability as compared to the base starch.

Stabilized products have lower gelatinization and pasting temperatures, are easier to redisperse when pregelatinized, and produce pastes and gels with a reduced tendency for retrogradation, that is, greater stability, improved freeze–thaw stability, and greater clarity as compared to the base starch.

Hypochlorite-oxidized products are whiter, have lower gelatinization and pasting temperatures, produce a lower maximum paste viscosity, and result in softer, clearer gels as compared to the unmodified starch.

Starches that have been both crosslinked and stabilized generally have lowered gelatinization and pasting temperatures, produce pastes with greater viscosity, and demonstrate the other attributes of crosslinking and stabilization as compared to the base starch.

Thinned, that is, very slightly depolymerized, products have lower gelatinization and pasting temperatures and produce pastes with less viscosity as compared to the base starch.

Any starch (corn, waxy maize, potato, tapioca/cassava, wheat, rice, etc.) can be modified, but modification is practiced significantly only on normal corn, waxy maize, and potato starches and to a much lesser extent on tapioca and wheat starches. Modified waxy maize starches are especially popular in the U.S. food industry. Pastes of unmodified common corn starch will gel, and the gels will

generally be cohesive, rubbery, and prone to syneresis (i.e., to weep or exude moisture). Pastes of waxy maize starch show little tendency to gel at room temperature, which is why waxy maize starch is generally preferred as the base starch for food starches, but pastes of waxy maize starch will become cloudy and chunky and exhibit syneresis when stored under refrigerator or freezing conditions; so even waxy maize starch is usually modified to increase the stability of its pastes. The most common and useful derivative employed for starch stabilization is the hydroxypropyl ether (see later).

Specific property improvements that can be obtained by proper combinations of modifications are reduction in the energy required to cook (improved gelatinization and pasting), modification of cooking behaviors, increased solubility, either increased or decreased paste viscosity, increased freeze–thaw stability of pastes, enhancement of paste clarity, increased paste sheen, reduction or enhancement of gel formation and gel strength, reduction of gel syneresis, improvement of interaction with other substances, improvement in stabilizing properties, enhancement of film formation, improvement in water resistance of films, reduction in paste cohesiveness, and improvement of stability to acid, heat, and shear.

Starch, like all carbohydrates, can undergo reactions at its various hydroxyl groups. In modified food starches, only a very few of the hydroxyl groups are modified. Normally, ester or ether groups are attached at very low degrees of substitution (DS) values.* DS values are often <0.1 and generally in the range 0.002–0.2, depending on the modification. Thus, there is, on average, one substituent group on every 500-5 D-glucopyranosyl units, respectively. Small levels of derivatization change the properties of starches dramatically and greatly extend their usefulness.

Starch products that are esterified or etherified with monofunctional reagents resist interchain associations, which reduces the tendency of the starch paste to gel, and the tendency for precipitation to occur. Hence, this modification is often called stabilization and the products are called stabilized starches (see below). Use of bifunctional reagents produces crosslinked starches. Modified food starches are often both crosslinked and stabilized.

Acetylation of starch to the maximum allowed in foods (DS = 0.09) lowers the gelatinization temperature, improves paste clarity, provides stability to retrogradation, and provides some freeze–thaw stability (but generally not as effectively as hydroxypropylation). Starch phosphate monoesters (Figure 3.44) are made by treating starch with sodium tripolyphosphate or monosodium orthophosphate. They can be used to make pastes that are clear and stable and have freeze–thaw stability. Monostarch phosphates have a long, cohesive texture. Paste viscosity is generally high and can be controlled by varying the concentration of reagent, time of reaction, temperature, and pH. Phosphate esterification lowers the gelatinization temperature. In the United States, the maximum allowable DS with phosphate groups is 0.002.

Preparation of an alkenylsuccinate ester of starch attaches a hydrophobic, hydrocarbon chain to its polymer molecules (Figure 3.45). Even at very low DS, starch 1-octenylsuccinate molecules concentrate at the interface of an oil-in-water emulsion because of the hydrophobicity of the alkenyl group. This characteristic makes them useful as emulsion stabilizers. Starch 1-octenylsuccinate products can be used in a variety of food applications where emulsion stability is needed, such as in flavored beverages. The presence of the aliphatic chain tends to give the starch derivative a sensory perception of fattiness, so it is possible to use the derivative as a partial replacement for fat in certain foods. Higher-DS products are nonwetting and are used as release agents for dusting on dough sheets and as processing aids.

Hydroxypropylation is the most often used reaction to prepare a stabilized starch product. Hydroxypropylstarch (starch$-O-CH_2-CHOH-CH_3$) is prepared by reacting starch with propylene oxide to produce a low level of etherification (DS 0.02–0.2, 0.2 being the maximum

* The degree of substitution (DS) is defined as the average number of esterified or etherified hydroxyl groups per monosaccharide unit. Both branched and unbranched polysaccharides composed of neutral hexopyranosyl units have an average of three hydroxyl groups per monomeric unit. Therefore, the maximum DS for a starch and cellulose is 3.0, although the maximum possible is not allowed in products used as food ingredients.

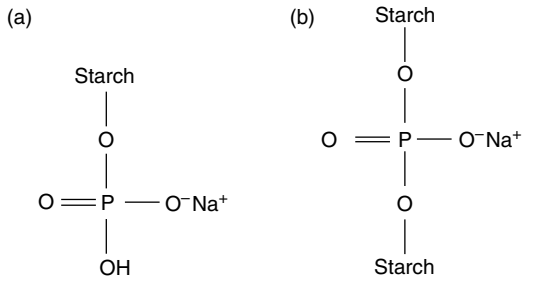

FIGURE 3.44 Structures of starch monoester phosphate (a) and diester phosphate (b). The diester joins two molecules together, resulting in crosslinked starch granules.

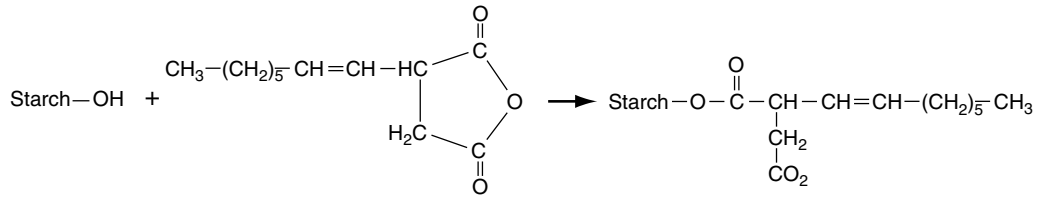

FIGURE 3.45 Preparation of the 2-(1-octenyl)succinyl ester of starch.

allowed). Hydroxypropylstarch has properties similar to those of starch acetate, because it similarly has "bumps" along the starch polymer chains that prevent the interchain associations that lead to retrogradation. Hydroxypropylation reduces the gelatinization temperature. Hydroxypropylstarches form clear pastes that do not retrograde and withstand freezing and thawing. They are used as thickeners and extenders. To improve viscosity, particularly under acidic conditions, acetylated and hydroxypropylated starches are often also crosslinked with phosphate groups.

Monostarch phosphates (sodium phosphate monoesters of starch) are prepared by impregnating and reacting starch granules with solutions of sodium tripolyphosphate or monosodium orthophosphate. Monostarch phosphates produce stable pastes that are clear and have a long, cohesive texture. Pastes viscosity can be controlled by varying the concentrations of phosphate salt, time of reaction, temperature, and pH. Increasing substitution lowers the gelatinization temperature; products undergo cold-water swelling at DS 0.07. Corn starch phosphates of DS 0.01–0.03 produce pastes with hot viscosity, clarity, stability, and texture more like those of potato starch. Starch phosphates are good emulsion stabilizers and produce pastes with improved freeze–thaw stability.

The majority of modified food starch is crosslinked. Crosslinking occurs when starch granules are reacted with bifunctional reagents that react with hydroxyl groups on two different molecules within the granule. Crosslinking is accomplished most often by producing distarch phosphate esters (Figure 3.44). Starch is either reacted with phosphoryl chloride ($POCl_3$) in an alkaline slurry or reacted with sodium trimetaphosphate—$POCl_3$ being the reagent most often used for crosslinking. The linking together of starch chains with phosphate diester or other crosslinks reinforces the granule and reduces both the rate and the degree of granule swelling and subsequent disintegration. Thus, granules exhibit reduced sensitivity to processing conditions (high temperature; extended cooking times; low pH; high shear during mixing, milling, homogenization, and/or pumping). Cooked pastes of crosslinked starches are more viscous,* heavier bodied, shorter textured, and less likely to break down during extended cooking or during exposure to low pH and/or severe agitation than

* Note in Figure 3.42 that maximum viscosity is reached when the system contains highly swollen granules. Crosslinked granules are less prone to disintegrate as shear is applied. Thus, there is less loss of viscosity after the peak is reached.

are pastes of the native starches from which they are prepared. Only a small amount of crosslinking is required to produce a noticeable effect; and with lower levels of crosslinking, granules swell in inverse proportion to DS. As crosslinking is increased, the granules become more and more tolerant to physical conditions and acidity, but less and less dispersible by cooking. Energy requirements to reach maximum swelling and viscosity are increased. For example, treatment of a starch with only 0.0025% of sodium trimetaphosphate greatly reduces both the rate and the degree of granule swelling, greatly increases paste stability, and changes dramatically the pasting/paste viscosity profile and textural characteristics of its paste. Treatment with 0.08% of trimetaphosphate produces a product in which granule swelling is restricted to the point that a peak viscosity is never reached during the hot holding period. As the degree of crosslinking increases, the starch also becomes more acid stable. Though hydrolysis of glycosidic bonds occurs during heating in aqueous acid, chains tied to each other through phosphate crosslinks continue to provide large molecules and an elevated viscosity. The only other crosslink permitted in a food starch is the distarch ester of adipic acid.

Most crosslinked food starches contain less than one crosslink per 1000 α-D-glucopyranosyl units. Trends toward continuous cooking require increased shear-resistance and stability to hot surfaces. Storage-stable thickening is also provided by crosslinked starches. In retort sterilization of canned foods, crosslinked starches, because of their reduced rate of gelatinization and swelling, maintain a low initial viscosity long enough to facilitate the rapid heat transfer and temperature rise that is needed to provide uniform sterilization before granule swelling brings about the desired viscosity, texture, and suspending characteristics. Crosslinked starches are used in canned soups, gravies, and puddings and in batter mixes. Crosslinking of waxy maize starch gives the clear paste sufficient rigidity so that, when used in pie fillings, the cut sections hold their shape.

Depolymerization, viscosity reduction, and decreased pasting temperature can be achieved by oxidation with sodium hypochlorite (chlorine in an alkaline solution). Oxidation also reduces association of amylose molecules, that is, results in some stabilization via introduction of small amounts of carboxylate and carbonyl groups. Oxidized starches produce less viscosity and softer gels (as compared with the base starch) and are used when these properties are needed. They are also used to improve adhesion of starch batters to fish and meat and in breading. Mild treatment with sodium hypochlorite, hydrogen peroxide, or potassium permanganate simply bleaches the starch and reduces the count of viable microbes.

So-called thin-boiling starches are prepared by treating a suspension of a native or derivatized starch with dilute mineral acid at a temperature below the gelatinization temperature. When a product that gives the desired paste viscosity is reached, the acid is neutralized, and the product is recovered washed, and dried. Even though only a few glycosidic bonds are hydrolyzed, granules disintegrate more easily and after only a small degree of swelling. Acid-modified starches form gels with improved clarity and increased strength, even though their pastes are less viscous. Thin-boiling starches are used as film formers and adhesives in products such as pan-coated nuts and candies and whenever a strong gel is desired, for example, in gum candies such as jelly beans, jujubes, orange slices, and spearmint leaves and in processed cheese loaves. To prepare especially strong and fast-setting gels, a high-amylose corn starch is used as the base starch.

Modified food starches are tailor-made for specific applications. Properties that can be controlled by combinations of crosslinking, stabilization, and thinning of corn, waxy maize, potato, wheat, and other starches include, but are not limited to, the following: adhesion, clarity of solutions/pastes, color, emulsion stabilization ability, film forming ability, flavor release, hydration rate, moisture holding capacity, stability to acids, stability to heat and cold, stability to shear, temperature required to cook, and viscosity (hot paste and cold paste). Some characteristics imparted to the food product include, but are not limited to, the following: mouthfeel, reduction of oil migration, texture, sheen, stability, and tackiness.

Starches that are both crosslinked and stabilized are used in canned, frozen, baked, and dry foods. In baby foods and fruit pie fillings in cans and jars, they provide long shelf life. They also allow frozen fruit pies, pot pies, and gravies to remain stable under long-term storage.

3.3.6.11 Cold-Water-Soluble (Pregelatinized or Instant) Starch

Starch that has been pasted/cooked and dried without excessive retrogradation can be partially redissolved in cold water. Such starch is called pregelatinized or instant starch. It has been gelatinized, but it has also been pasted, that is, many granules have been destroyed; so it should more properly be called precooked or prepasted starch. There are two basic approaches to making pregelatinized products. In one, a starch–water slurry is introduced into the nip between two nearly touching and counterrotating, steam-heated rolls or applied to the top of a single rotating, steam-heated roll. In either case, the starch slurry is gelatinized and pasted almost instantaneously, and the paste that coats the rolls dries rapidly. The dry film is scraped from the roll and ground to a powder. The resulting products are cold-water soluble and will produce viscous dispersions when stirred into room-temperature water, although some heating is often required to achieve maximum viscosity. The second method of preparation uses extruders. In this process the heat and shear in an extruder gelatinizes and destroys the moistened starch granules. The puffed, crispy, glassy extrudate is ground to a powder.

Both chemically modified and unmodified starches can be used to make pregelatinized starches. If chemically modified starches (Section 3.3.6.10) are used, properties introduced by the modification(s) carry through to the pregelatinized products; thus, paste properties such as stability to freeze–thaw cycling can also be characteristics of pregelatinized starches. Pregelatinized, slightly crosslinked starch is useful in instant soup, pizza topping, and extruded snacks and breakfast cereals.

The advantage of pregelatinized starches is that they can be used without cooking. Like a water-soluble gum, finely ground pregelatinized starch forms small gel particles when added to water, but when properly dispersed and dissolved, gives solutions of high viscosity. More coarsely ground products disperse more easily and produce dispersions of lower viscosity and with a graininess or pulpiness that is desirable in some products. Many pregelatinized starches are used in dry mixes, such as instant pudding mixes. They disperse readily with high-shear stirring or when mixed with sugar or other dry ingredients.

3.3.6.12 Cold-Water-Swelling Starch

Granular starch that swells extensively in cold water is made by heating common corn starch in 75–90% ethanol or by a special spray-drying process. This product is also categorized as a pregelatinized or instant starch by some. The difference between it and conventional pregelatinized starch is that, while the crystalline order and birefringence of the granules have been destroyed by the treatment, the granules are intact. Therefore, when added to water, they swell as if they were being cooked. The dispersion made by incorporating cold-water-swelling starch into sugar solutions or glucose syrups by rapid stirring can be poured into molds, where it sets to a rigid gel that can be sliced. The result is a gum candy. Cold-water-swelling starch is also useful in making desserts and in muffin batters containing particles, such as blueberries, that otherwise would settle to the bottom before the batter is thickened by heating during baking.

3.3.7 Cellulose: Forms and Derivatives [71]

Cellulose is a high-molecular-weight, linear, insoluble homopolymer of repeating β-D-glucopyranosyl units joined by (1→4) glycosidic linkages (Figure 3.46). The axial → equatorial (1→4) linkages joining the α-D-glucopyranosyl units of starch polymer molecules produce a coiled structure (an α-helix). In contrast, the equatorial → equatorial (1→4) linkages joining the β-D-glucopyranosyl units of cellulose molecules give them a flat, ribbon-like structure in which each glucopyranosyl unit in the chain is turned upside down as compared to the units preceding and following it. Because of their flat and linear nature, cellulose molecules can associate with each

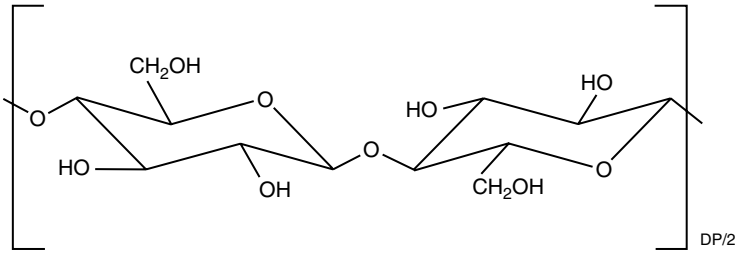

FIGURE 3.46 Cellulose (repeating unit).

other via hydrogen bonding over extended regions, forming polycrystalline, fibrous bundles. Crystalline regions are separated by, and connected to, amorphous regions. Cellulose is insoluble in water because, in order for it to dissolve, most of its very many hydrogen bonds would have to be released at once. Cellulose can, however, through derivatization, be converted into water-soluble gums.

Cellulose and its modified forms serve as dietary fiber because they are undigested and do not contribute significant nourishment or calories as they pass through the human digestive system. Dietary fiber is important to human nutrition (see Section 3.4).

A purified cellulose powder is available as a food ingredient. High-quality cellulose can be obtained from wood through pulping and subsequent purification. Chemical purity is not required for food use because cellulosic cell walls are components of all fruits and vegetables. The powdered cellulose used in foods has negligible flavor, color, and microbial contamination. Powdered cellulose is most often added to bread to provide noncaloric bulk. Reduced-calorie baked goods made with powdered cellulose not only have an increased content of dietary fiber, but also stay moist and fresh longer.

3.3.7.1 Microcrystalline Cellulose [58]

A purified, insoluble cellulose termed microcrystalline cellulose (MCC) is made by partial hydrolysis of purified wood pulp cellulose, with hydrolysis taking place in the amorphous regions, followed by separation of the released microcrystals. Cellulose molecules are fairly rigid, completely linear chains of about 3000 β-D-glucopyranosyl units and associate easily in long junction zones. However, the long and unwieldy chains do not align over their entire lengths. The end of the crystalline region is simply the divergence of cellulose chains away from order into a more random arrangement, forming the amorphous region. When purified wood pulp is hydrolyzed with acid, the acid penetrates the lower-density, hydrated amorphous regions where the polymer chains have greater freedom of movement and effects hydrolytic cleavage of chains in these regions, releasing individual, fringed crystallites.

Two types of MCC are produced, both of which are stable to both heat and acids. Powdered MCC is a spray-dried product. Spray-drying produces porous aggregates of microcrystals. Powdered MCC is used as a flavor carrier and as an anticaking agent for shredded cheese. The second type, colloidal MCC, is water dispersible and has functional properties similar to those of water-soluble gums. To make colloidal MCC, considerable mechanical energy is applied after hydrolysis to tear apart the weakened microfibrils and provide a major proportion of colloidal-sized aggregates (<0.2 μm in diameter). To prevent rebonding of the aggregates during drying, sodium CMC (Section 3.3.7.2), xanthan (Section 3.3.9), or sodium alginate (Section 3.3.11) is added. The anionic gum aids in redispersion and acts as a barrier to reassociation by giving the particles a stabilizing negative charge.

The major functions of colloidal MCC are to stabilize foams and emulsions, especially during high-temperature processing; to form gels with salve-like textures (MCC does not dissolve, nor does it form intermolecular junction zones; rather it forms a network of hydrated microcrystals);

to stabilize pectin and starch gels to heat; to improve adhesion; to replace fat and oil in products like salad dressings and ice cream; and to control ice crystal growth. MCC stabilizes emulsions and foams by adsorbing at interfaces and strengthening interfacial films. It is a common ingredient of reduced fat ice cream and other frozen dessert products.

3.3.7.2 Carboxymethylcelluloses [14,33]

Carboxymethylcellulose (Table 3.5) is widely and extensively used as a food gum. Treatment of purified wood pulp with 18% sodium hydroxide solution produces alkali cellulose. When alkali cellulose is reacted with the sodium salt of chloroacetic acid, the sodium salt of the carboxymethyl ether (cellulose—O—CH_2—$CO_2^-Na^+$) is formed. Most commercial CMC products have a DS (see Section 3.3.6.10) in the range 0.4–0.8. The most widely sold type for use as a food ingredient has a DS of 0.7.

Since CMC consists of long, fairly rigid molecules that bear a negative charge due to numerous ionized carboxyl groups, electrostatic repulsion causes its molecules in solution to be extended. Also, adjacent chains repel each other. Consequently, CMC solutions tend to be both highly viscous and stable. CMC is available in a wide range of viscosity grades. CMC stabilizes protein dispersions, especially near the isoelectric pH value of the protein.

3.3.7.3 Methylcelluloses and Hydroxypropylmethylcelluloses [24,25]

To make methylcellulose (MC) products (Table 3.5), alkali cellulose is treated with methyl chloride to introduce methyl ether groups (cellulose—O—CH_3). Many members of this family of gums also contain hydroxypropyl ether groups (cellulose—O—CH_2—CHOH—CH_3). Hydroxypropylmethylcelluloses (HPMCs) are made by reacting alkali cellulose with both propylene oxide and methyl chloride. The DS with methyl ether groups of commercial MCs ranges from 1.1 to 2.2. The moles of substitution (MS)* with hydroxypropyl ether groups in commercial HPMCs range from 0.02 to 0.3. (Both the MC and HPMC members of this gum family are generally referred to simply as MCs.) Both products are cold-water soluble because the methyl and hydroxypropyl ether group protrusions along the chains prevent the intermolecular association characteristic of cellulose.

While a few added ether groups spread along the chains and enhance water solubility, they also decrease chain hydration by replacing water-binding hydroxyl groups with less polar ether groups, giving members of this family unique characteristics. The ether groups restrict solvation of the chains to the point that they are on the borderline of water solubility. When an aqueous solution is heated, the water molecules hydrating the polymer dissociate from the chain and hydration is decreased sufficiently so that intermolecular associations increase (probably via van der Waals interactions) and gelation occurs. Lowering the temperature of the gel allows the molecules to rehydrate and redissolve, so the gelation is reversible.

Because of the ether groups, the gum chains are somewhat surface active and absorb at interfaces. This helps stabilize emulsions and foams. MCs also can be used to reduce the amount of fat in food products through two mechanisms: (1) they provide fat-like properties so that the fat content of a product can be reduced and (2) they reduce adsorption of fat in products being fried, for the gel structure produced by thermogelation provides a barrier to oil, holds moisture, and acts as a binder.

* The moles of substitution or molar substitution (MS) value indicates the average number of moles of substituent attached to a glycosyl unit of a polysaccharide. Because reaction of a hydroxyl group with propylene oxide creates a new hydroxyl group with which propylene oxide can react further, poly(propylene oxide) chains, each terminated with a free hydroxyl group, can form. Because more than three moles of propylene oxide can react with a single hexopyranosyl unit, MS rather than DS is used.

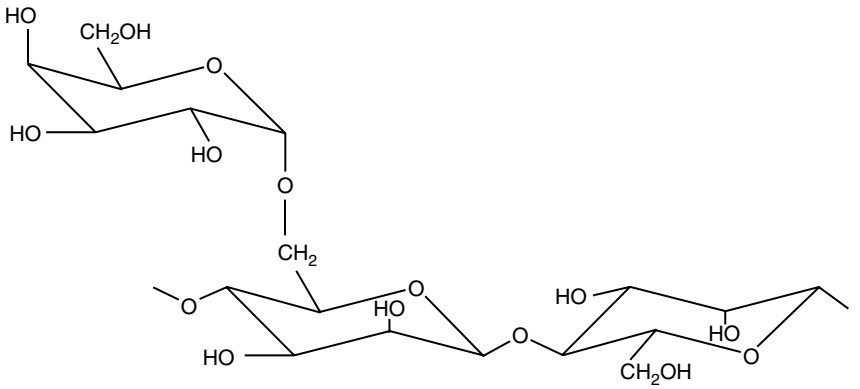

FIGURE 3.47 A representative segment of a galactomannan molecule.

3.3.8 Guar and Locust Bean Gums [27,28,38]

Guar and LBGs are important thickening polysaccharides (Table 3.5). Guar gum produces the highest viscosity of any natural, commercial gum. Both gums are the ground endosperm of seeds. The main component of both endosperms is a galactomannan. Galactomannans consist of a main chain of β-D-mannopyranosyl units joined by (1→4) bonds with single-unit α-D-galactopyranosyl branches attached at O-6 (Figure 3.47). The specific polysaccharide that makes up most of guar gum is guaran. In guaran, about one-half of the D-mannopyranosyl main chain units contain an α-D-galactopyranosyl unit.

The galactomannan of LBG (also called carob gum) has fewer branch units than does guaran and its structure is more irregular, with long stretches of about 80 underivatized D-mannosyl units alternating with sections of about 50 units in which most of the main chain units have an α-D-galactopyranosyl group glycosidically connected to their O-6 positions.

Because of the difference in structures, guar gum and LBG have different physical properties, even though both are galactomannans and are composed of long, rather rigid chains that provide high solution viscosity. Because guaran has its galactosyl units fairly evenly placed along the chain, there are few locations on the chains that are suitable for formation of junction zones. However, LBG with its long "naked chain" sections, can form junction zones. LBG molecules interact with xanthan (Figure 3.48; Section 3.3.9) and carrageenan (Section 3.3.10) helices, forming junction zones and rigid gels.

Guar gum provides economical thickening to numerous food products. It is frequently used in combination with other food gums, for example, in ice cream, where it is often used in combination with CMC (Section 3.3.7.2), carrageenan (Section 3.3.10), and LBG.

Typical products in which LBG is found are the same as those for guar gum. About 85% of LBG is used in dairy and frozen dessert products. It is rarely used alone; rather it is used in combination with other gums such as CMC, carrageenan, xanthan, and guar gum. It is used in combination with κ-carrageenan and xanthan to take advantage of the synergistic gel-forming phenomenon. A typical use level is 0.05–0.25%.

3.3.9 Xanthan [32,47]

Xanthomonas campestris, a bacterium commonly found on leaves of plants of the cabbage family, produces a polysaccharide, termed xanthan, that is produced in large fermentation vats and is widely used as a food gum. The polysaccharide is known commercially as xanthan gum (Table 3.5).

Xanthan has a backbone chain identical to that of cellulose (Figure 3.48; compare with Figure 3.46). In the xanthan molecule, every other β-D-glucopyranosyl unit in the cellulose backbone

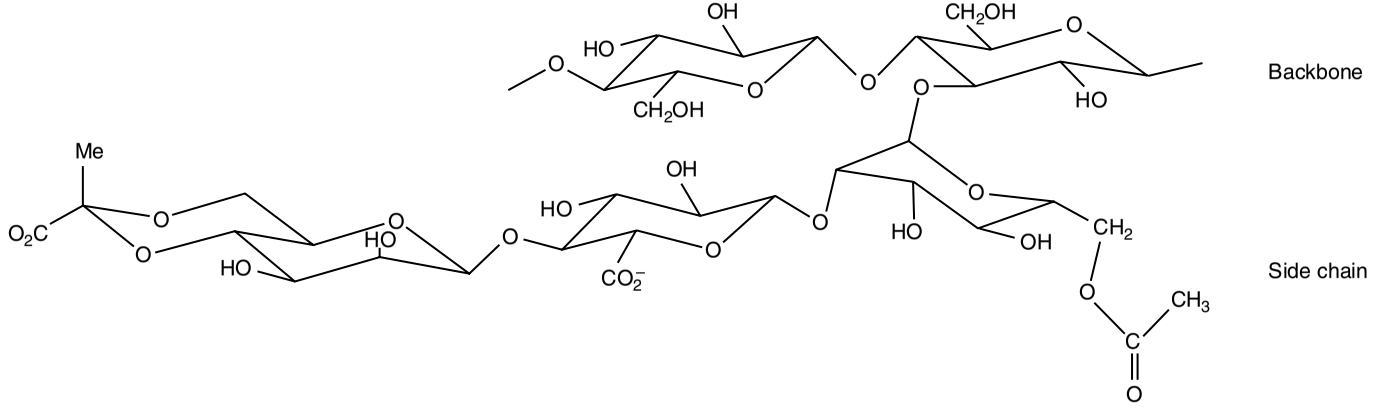

FIGURE 3.48 Structure of the pentasaccharide repeating unit of xanthan. Note the 4,6-*O*-pyruvyl-D-mannopyranosyl nonreducing end-unit of the trisaccharide side chain. Normally, about one-half of the side chains are pyruvylated.

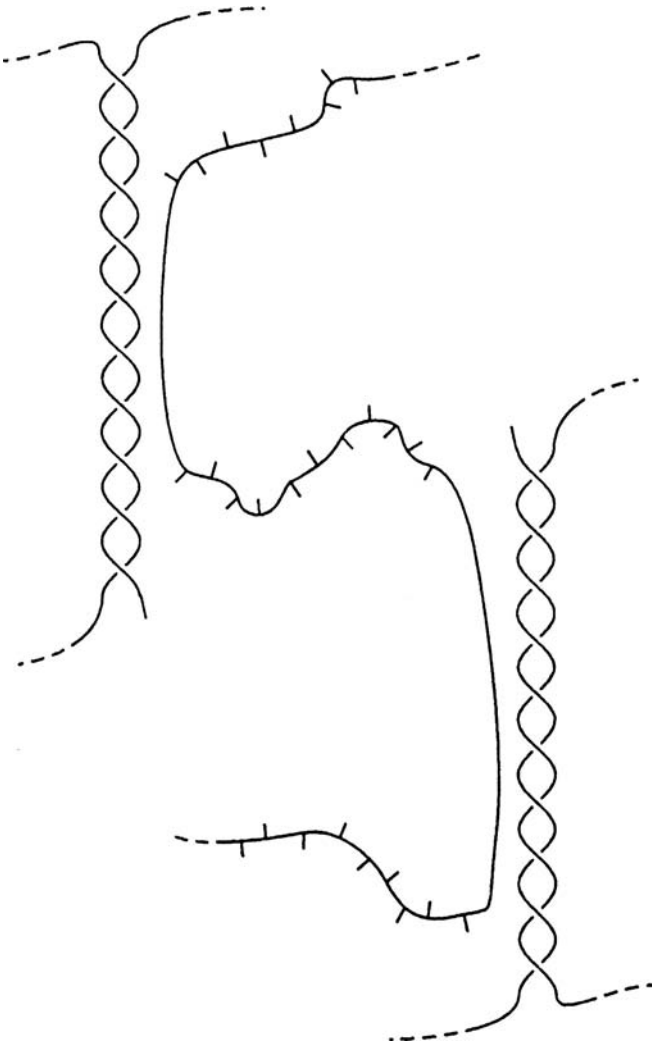

FIGURE 3.49 Representation of the hypothesized interaction of a locust bean gum molecule with double-helical portions of xanthan or carrageenan molecules to form a three-dimensional network and a gel.

has attached, at the O-3 position, a β-D-mannopyranosyl-(1→4)-β-D-glucuronopyranosyl-(1→2)-6-*O*−acetyl-β-D-mannopyranosyl trisaccharide unit.* About half of the terminal β-D-mannopyranosyl units have pyruvic acid attached as a 4,6-cyclic acetal. The trisaccharide side chains interact with the main chain and make the molecule rather stiff. The molecular weight is probably in the order of 2×10^6, although much larger values, presumably due to aggregation, have been reported.

Xanthan interacts with guar gum synergistically to produce an increase in solution viscosity. The interaction with LBG produces a heat-reversible gel (Figure 3.49).

Xanthan is widely used as a food gum because of the following important characteristics: it is soluble in both hot and cold water; it produces high solution viscosity at low concentrations; there is no discernible change in solution viscosity in the temperature range from 0 to 100°C, which makes it unique among food gums; it is both soluble and stable in acidic systems; it has excellent

* Bacterial heteroglycans, unlike plant heteroglycans, have regular, repeating unit structures.

compatibility with salt; it forms gels when used in combination with LBG; it is a remarkable stabilizer of suspensions and emulsions; and it imparts stability to products exposed to freezing and thawing. The unusual and very useful properties of xanthan undoubtedly result from the structural rigidity and extended nature of its molecules, which in turn result from its linear, cellulosic backbone that is stiffened and shielded by the anionic trisaccharide side chains.

Xanthan is ideal for stabilizing aqueous dispersions, suspensions, and emulsions. The fact that the viscosity of its solutions changes very little with temperature, that is, its solutions do not thicken upon cooling, make it irreplaceable for thickening and stabilizing such products as pourable salad dressings and chocolate syrup, which need to pour as easily when taken from the refrigerator as they do at room temperature, and gravies, which should neither thicken appreciably as they cool nor thin too much when hot. In regular, pourable salad dressings, it serves both as a thickener and as a stabilizer for both the suspension of particulate materials and the oil-in-water emulsion. It is also used as a thickener and suspending agent in no-oil (reduced-calorie) dressings. In both oil-containing and no-oil salad dressings, xanthan is almost always used in combination with propylene glycol alginate (PGA) (Section 3.3.11). PGA decreases the viscosity of the xanthan-containing system and reduces its pseudoplasticity. Together they give the desired pourability associated with the pseudoplastic xanthan and the creaminess sensation associated with a nonpseudoplastic solution.

3.3.10 Carrageenans, Agar, and Furcellaran [22,57]

The term carrageenan denotes a group or family of sulfated galactans extracted from red seaweeds with dilute alkaline solutions; the sodium salt of a carrageenan is normally produced. Carrageenans are mixtures of several related sulfated galactans (Table 3.5). Carrageenans are linear chains of D-galactopyranosyl units joined with alternating (1→3)-α-D- and (1→4)-β-D-glycosidic linkages, with most sugar units having one or two sulfate half-ester groups esterified to the hydroxyl groups at carbon atoms C-2 and/or C-6. This gives a sulfate content ranging from 15 to 40%. Units often contain a 3,6-anhydro ring. The principal structures are termed kappa (κ), iota (ι), and lambda (λ) carrageenans (Figure 3.50). The disaccharide units shown in Figure 3.50 represent the predominate building block of each type, but are not repeating unit structures. Carrageenans, as extracted, are mixtures of nonhomogeneous polysaccharides. Carrageenan products, of which there may be more than 100 from a single supplier for different specific applications, contain different proportions of the three main behavioral types (kappa, iota, and lambda) produced by starting with mixtures of red seaweed species. Other substances, such as potassium ions and sugar (for standardization), may be added to the obtained powder.

Carrageenan products dissolve in water to form highly viscous solutions. The viscosity is quite stable over a wide range of pH values because the sulfate half-ester groups are always ionized, even under strongly acidic conditions, giving the molecules a negative charge. However, carrageenans undergo depolymerization in hot acidic solutions, so these conditions are to be avoided when using a carrageenan product.

Segments of molecules of κ- and ι-type carrageenans exist as double helices of parallel chains. In the presence of potassium or calcium ions, thermoreversible gels form upon cooling a hot solution containing double-helical segments. Gelation can occur in water at concentrations as low as 0.5%. When κ-type carrageenan solutions are cooled in the presence of potassium ions, a stiff, brittle gel results. Calcium ions are less effective in causing gelation. Potassium and calcium ions together produce a high gel strength. Gels made with κ-type carrageenans are the strongest of the carrageenan gels. These gels tend to synerese as junction zones within the structure grow in length. The presence of other gums retards syneresis.

ι-Type carrageenans are a little more soluble than are the κ-types, but again, only the sodium salt form is soluble in cold water. ι-Types gel best with calcium ions. The resulting gel is soft and resilient, has good freeze–thaw stability, and does not synerese, presumably because ι-type carrageenans are more hydrophilic and form fewer junction zones than do κ-type carrageenans.

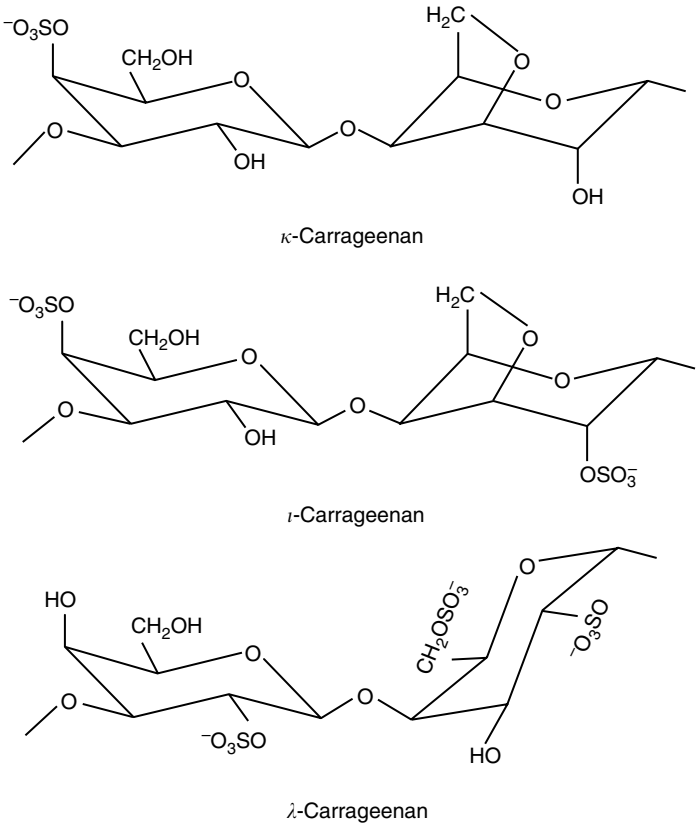

FIGURE 3.50 Idealized unit structures of κ-, ι-, and λ-type carrageenans.

During cooling of solutions of κ- or ι-type carrageenans, gelation occurs because the linear molecules are unable to form continuous double helices due to the presence of structural irregularities. The linear helical portions then associate to form a three-dimensional gel in the presence of the appropriate cation (Figure 3.51). All salts of λ-type carrageenans are soluble and nongelling.

Under conditions in which double-helical segments are present, carrageenan molecules, particularly those of the κ-type, form junction zones with the naked segments of LBG to produce rigid, brittle, syneresing gels. This gelation occurs at a concentration one-third that needed to form a pure κ-type carrageenan gel.

Carrageenans are most often used because of their ability to form gels with milk and water. Mixtures of carrageenan types are used to provide a wide range of products that are standardized with various amounts of sucrose, glucose (dextrose), buffer salts, or gelling aids, such as potassium chloride. The available commercial products form a variety of gels: gels that are clear or turbid, rigid or elastic, tough or tender, heat-stable or thermally reversible, and do or do not undergo syneresis. Carrageenan gels do not require refrigeration because they do not melt at room temperature. They are freeze–thaw stable.

A useful property of carrageenans is their reactivity with proteins, particularly those of milk. κ-Type carrageenans complex with κ-casein micelles of milk, forming a weak, thixotropic, pourable gel. The thickening effect of κ-carrageenans in milk is 5–10 times greater than it is in water. This property is used in the preparation of chocolate milk, in which the thixotropic gel structure prevents settling of cocoa particles. Such stabilization requires only about 0.025% gum. This property is also utilized in the preparation of ice cream, evaporated milk, infant formulas, freeze–thaw stable whipped cream, and emulsions in which milk fat is replaced with a vegetable oil.

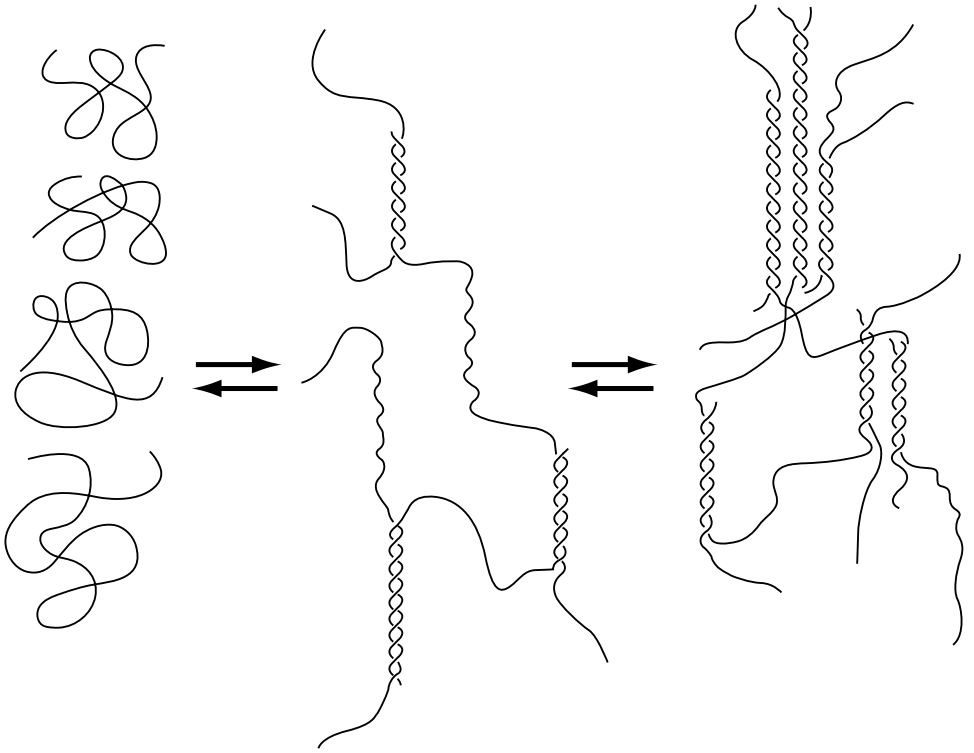

FIGURE 3.51 A representation of the hypothesized mechanism of gelation of κ- and ι-type carrageenans. In a hot solution, the polymer molecules are in a coiled state. As the solution is cooled, they intertwine in double-helical structures. As the solution is cooled further, the double helices are believed to nest together with the aid of potassium or calcium ions.

The synergistic effect between κ-carrageenan and LBG (Figure 3.49) produces gels with greater elasticity and gel strength, and with less syneresis than gels made with potassium κ-carrageenate alone. As compared to κ-type carrageenan alone, the κ-type carrageenan–LBG combination provides greater stabilization and air bubble retention (overrun) in ice cream, but also a little too much chewiness, so guar gum is added to soften the gel structure.

Cold hams and poultry rolls take up 20–80% more brine when they contain 1–2% of a κ-type carrageenan. Improved slicing also results. Carrageenan coatings on meats can serve as a mechanical protection and a carrier for seasonings and flavors. Carrageenan is sometimes added to meat analogs made from casein and vegetable proteins. Carrageenan is used to hold water and maintain water content, and therefore, to maintain softness of meat products, such as wieners and sausages, during the cooking operation. Addition of a κ- or ι-type carrageenan in the Na^+ form or processed Euchema seaweed/Philippine natural grade (PES/PNG) carrageenan (see next paragraph) to low-fat ground beef improves texture and hamburger quality. Normally, fat serves the purpose of maintaining softness, but because of the binding power of carrageenan for protein and its high affinity for water, carrageenans can be used to replace in part this function of natural animal fat in lean products.

Also prepared and used is an alkali-modified seaweed flour that was formerly called PES or PNG carrageenan, but is now often just called carrageenan. To prepare PES/PNG carrageenan, red seaweed is treated with a potassium hydroxide solution. Because the potassium salts of the types of carrageenans found in these seaweeds are insoluble, the carrageenan molecules are not solubilized and not extracted out. Primarily low-molecular-weight soluble components are removed

from the plants during this treatment. The remaining seaweed is dried and ground to a powder. PES/PNG carrageenan is, therefore, a composite material that contains not only the molecules of carrageenan that would be extracted with dilute sodium hydroxide, but also other cell wall materials.

Two other food gums, agar and furcellaran (also called Danish agar), also come from red seaweeds and have structures and properties that are closely related to those of the carrageenans. Like gellan (Section 3.3.13), the primary use of agar is in bakery mixes to which it is added to hold moisture in the final product without increasing the viscosity of the initial dough or batter (because it is not soluble in room-temperature water).

3.3.11 Algins [11,34]

Commercial algin is a salt, most often the sodium salt, of a linear poly(uronic acid), alginic acid, obtained from brown seaweeds (Table 3.5). Alginic acid is composed of two monomeric units, β-D-mannopyranosyluronic acid and α-L-gulopyranosyluronic acid units. These two monomers occur in homogeneous regions (composed exclusively of one unit or the other) and in regions of mixed units. Segments containing only D-mannuronopyranosyl units are referred to as M-blocks and those containing only L-guluronopyranosyl units as G-blocks. D-Mannuronopyranosyl units are in the $^4C_1$ conformation, while L-guluronopyranosyl units are in the $^1C_4$ conformation (see Section 3.1.2, Figure 3.52), which gives the different blocks quite different chain conformations. M-Block regions are flat and ribbon-like, similar to the conformation of cellulose (see Section 3.3.7) because of the equatorial → equatorial bonding. G-Block regions have a pleated (corrugated) conformation as a result of its axial → axial glycosidic bonds. Different percentages of the different block segments cause algins (alginates) from different seaweeds to have different properties. Algins with greater G-block contents produce gels of higher strength.

Solutions of sodium alginates are highly viscous. The calcium salt of alginates is insoluble. Insolubility results from interactions between calcium ions and the G-block regions of the chain. The holes formed between two G-block chains are cavities that bind calcium ions. The result is a junction zone that has been called an "egg box" arrangement with the calcium ions being likened to

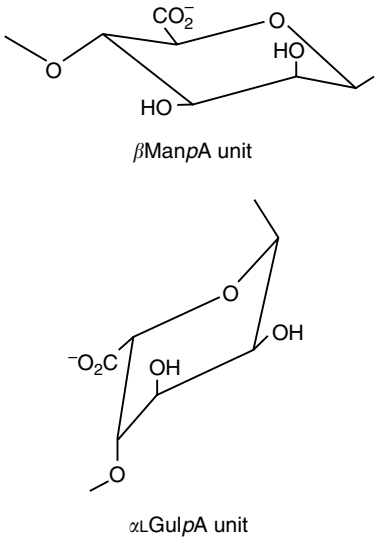

FIGURE 3.52 Units of β-D-mannopyranosyluronic acid (βMan*p*A) in the $^4C_1$ conformation and α-L-gulopyranosyluronic acid (αLGul*p*A) in the $^1C_4$ conformation.

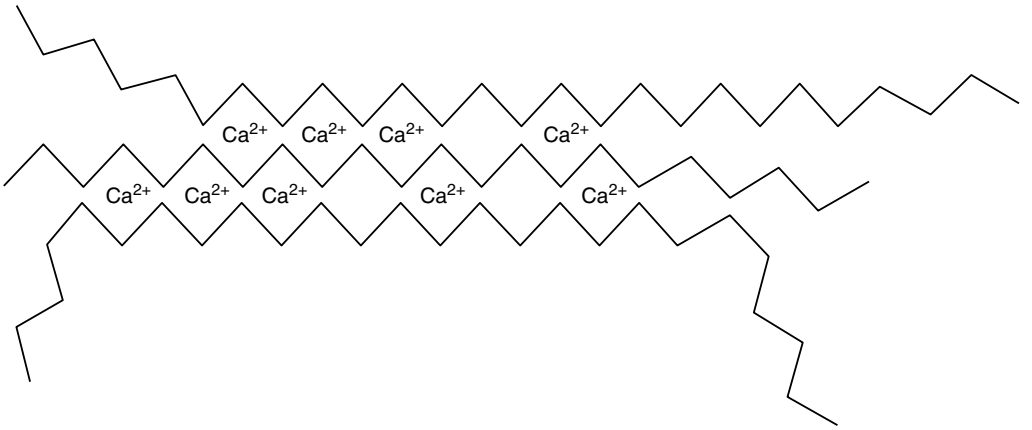

FIGURE 3.53 A representation of the proposed formation of a junction between G-block regions of three alginate molecules promoted by calcium ions.

eggs in the pockets of an egg carton (Figure 3.53). The strength of the gel depends on the content of G-blocks in the alginate used and the concentration of calcium ions.

Propylene glycol alginates are made by reacting moist alginic acid with propylene oxide to produce a partial ester with 50–85% of the carboxyl groups esterified. Solutions of PGAs are much less sensitive to low pH values and polyvalent cations, including calcium ions and proteins, than are solutions of nonesterified alginates, because esterified carboxyl groups cannot ionize. Also, the propylene glycol group introduces a "bump" on the chain that prevents close association of chains. Therefore, PGA solutions are stable. Because of its tolerance to calcium ions, PGAs can be used in dairy products. The hydrophobic propylene glycol groups also give the molecule mild interfacial activity, that is, foaming, emulsifying, and emulsion-stabilizing properties. PGA is used when stability to acid, nonreactivity with calcium ions (e.g., in milk products), or its surface active property is desired. Accordingly, it finds use as a thickener in salad dressings (Table 3.5). In low-calorie dressings, it is often used in conjunction with xanthan (Section 3.3.9).

Alginate salts are most often used as food ingredients because of their ability to form gels. However, they can be used to provide high viscosity at low concentrations and are particularly effective when a low concentration of calcium ions is present. If PGA is used, some calcium ion crosslinking of chains still occurs through the remaining carboxylate groups and results in thickening of solutions (rather than gelling).

Calcium alginate gels are obtained by diffusion setting, internal setting, and setting by cooling. Diffusion setting can be used to prepare structured foods. A good example is the structured pimento strip. In the production of pimento strips for stuffing green olives, pimento puree is first mixed with water containing a small amount of guar gum as an immediate thickener, and then with sodium alginate. The mixture is pumped onto a conveyor belt and gelled by addition of calcium ions. The set sheet is cut into thin strips and stuffed into olives. Internal setting for fruit mixes, purees, and fruit analogs involves a slow release of calcium ions within the mixture. The slow release is obtained by the combined action of a slightly soluble organic acid and a sequestrant on an insoluble calcium salt. Setting by cooling involves mixing the components required to form a gel at a temperature above the gel's melting temperature and allowing the mixture to set on cooling. Alginate gels are reasonably heat stable and show little or no syneresis. Unlike gelatin gels, alginate gels are not thermoreversible and, like carrageenan gels, do not require refrigeration and can be used as dessert gels that do not melt, even at high ambient temperatures; but as a result, they do not melt in the mouth like gelatin gels.

Alginic acid, that is, an alginate solution whose pH has been lowered, with and without addition of calcium ions, is employed in the preparation of soft, thixotropic, nonmelting gels (Table 3.5).

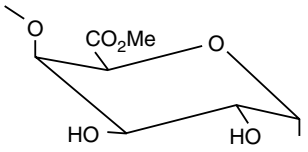

FIGURE 3.54 The most prevalent monomeric unit of an HM pectin.

3.3.12 Pectins [10,49]

Commercial pectins are galacturonoglycans (poly[α-D-galactopyranosyluronic acids]) with various contents of methyl ester groups (Table 3.5). The native molecules present in the cell walls and intercellular layers of all land plants, from which commercial pectins are obtained, are more complex molecules that are converted into methyl esterified galacturonoglycans during extraction with acid. Commercial pectin is obtained from citrus peel and apple pomace. Pectin from lemon and lime peel generally is the easiest to isolate and is of the highest quality. Pectins have a unique ability to form spreadable gels in the presence of sugar and acid or in the presence of calcium ions and are used primarily in these types of applications.

The compositions and properties of pectins vary with source, the processes used during preparation, and subsequent treatments. During extraction with mild acid, some hydrolytic depolymerization and hydrolysis of methyl ester groups occurs. Therefore, the term pectin denotes a family of compounds. The term pectin is usually used in a generic sense to designate those water-soluble poly(galacturonic acid) (galacturonoglycan) preparations of varying methyl ester contents and degrees of neutralization that are capable of forming gels. In all natural pectins, some of the carboxyl groups are in the methyl ester form. Depending on the manufacturing conditions, the remaining free carboxylic acid groups may be partly or fully neutralized, that is, partly or fully present as sodium, potassium, or ammonium carboxylate groups. Typically, they are present in the sodium salt form.

By definition, preparations in which more than half of the carboxyl groups are in the methyl ester form ($-COOCH_3$) are classified as high-methoxyl (HM) pectins (Figure 3.54); the remainder of the carboxyl groups will be present as a mixture of free acid ($-COOH$) and salt (e.g., $-COO^-Na^+$) forms. Preparations in which less than half of the carboxyl groups are in the methyl ester form are called low-methoxyl (LM) pectins. The percentage of carboxyl groups esterified with methanol is the degree of esterification (DE) or degree of methylation (DM). Treatment of a pectin preparation with ammonia (often dissolved in methanol) converts some of the methyl ester groups into carboxamide groups (15–25%). In the process, a LM pectin (by definition) is formed. These products are known as amidated LM pectins.

The principal and key feature of all pectin molecules is a linear chain of (1→4)-linked α-D-galactopyranosyluronic acid units. Neutral sugars, primarily L-rhamnose, are also present. In citrus and apple pectins, the α-L-rhamnopyranosyl units are inserted into the polysaccharide chain at rather regular intervals. The inserted L-rhamnopyranosyl units may provide the necessary irregularities in the structure required to limit the size of the junction zones and effect gelation (as opposed to precipitation/complete insolubility). At least some pectins contain covalently attached, highly branched arabinogalactan chains and/or short side chains composed of D-xylosyl units. The presence of side chains may also be a factor that limits the extent of chain association. Junction zones are formed between regular, unbranched pectin chains when the negative charges on the carboxylate groups are removed (addition of acid), hydration of the molecules is reduced (by addition of a cosolute, almost always sugar, to a solution of HM pectin), and/or when polymer chains are bridged by calcium cations.

High-methoxyl pectin solutions gel when sufficient acid and sugar is present. As the pH of a pectin solution is lowered, the highly hydrated and charged carboxylate groups are converted into uncharged, only slightly hydrated carboxylic acid groups. As a result of losing some of their charge

and hydration, the polymer molecules can now associate over a portion of their length, forming junctions and a network of polymer chains that entraps the aqueous solution of solute molecules. Junction zone formation is assisted by the presence of a high concentration (~65%, at least 55%) of sugar, which competes with the pectin molecules for the water molecules and reduces hydration of the chains, allowing them to interact with one another.

Low-methoxyl pectin solutions gel only in the presence of divalent cations that provide crossbridges. Increasing the concentration of divalent cations (only calcium ion is used in food applications) increases the gelling temperature and gel strength. The same general egg box model used to describe the formation of calcium alginate gels (Section 3.3.11) is used to explain gelation of solutions of LM (both standard and amidated) pectins upon addition of calcium ions. Since it does not require sugar for gelation, LM pectin is used to make low-sugar jams, jellies, and marmalades.

3.3.13 Gellan [44]

Gellan, known commercially as gellan gum (Table 3.5), is an extracellular, anionic polysaccharide produced by the bacterium *Sphingomonas elodea.* The gellan molecule is linear and is composed of β-D-glucopyranosyl, β-D-glucuronopyranosyl, and α-L-rhamnopyranosyl units in a molar ratio of 2:1:1. Native gellan (also called high-acyl gellan) contains two ester groups, an acetyl group and a glyceryl group, both on the same glucosyl unit. On average, there is one glycerate ester group per tetrasaccharide repeat unit and one acetate ester group for every two repeat units.

Some gellan is de-esterified by treatment with alkali. Removal of the acyl groups has a dramatic effect on the gel properties of gellan. The de-esterified form is known as low-acyl gellan. Its tetrasaccharide repeat unit structure is $\rightarrow$4)-αLRha*p*-(1$\rightarrow$3)-βGlc*p*-(1$\rightarrow$4)-βGlc*p*A-(1$\rightarrow$4)-βGlc*p*-(1$\rightarrow$. Three basic forms of the gum are available: high-acyl (native), low-acyl clarified, and low-acyl unclarified. The majority of gellan used in food products is the low-acyl, clarified type. Blending of high- and low-acyl types results in products with intermediate properties.

Gellan can form gels with both monovalent and divalent cations, divalent cations (Ca^{2+}) being about ten times more effective. Gels can be formed with as little as 0.05% gum (99.95% water). Gelation is often affected by cooling a hot solution containing the required cation. Shearing during cooling of a hot gellan solution prevents the normal gelation mechanism from occurring and produces a smooth, homogeneous, thixotropic fluid (a pourable gel) that stabilizes emulsions and suspensions very effectively. Gentle agitation of a weak gellan gel will also disrupt the gel structure and turn the gel into a smooth, pourable, thixotropic fluid with excellent emulsion and suspension stabilizing properties.

The low-acyl types of gellan form firm, brittle, nonelastic gels (with textures similar to those of gels made with agar and κ-carrageenan). The high-acyl (native) type forms soft, elastic, non-brittle gels (with textures similar to those made with mixtures of xanthan and LBG). A range of intermediate gel textures can be achieved by mixing the two basic types of gellan.

When gellan is used as an ingredient in bakery mixes, it does not hydrate appreciably at room temperature, nor increase the viscosity of the batter. It does, however, hydrate upon heating and holds moisture in the baked product. Gellan is used in formulating nutrition bars because of its moisture retaining ability. The ability of its solutions to suspend at low concentration (without producing high viscosity) makes it useful in nutritional and diet beverages.

3.3.14 Curdlan [37]

Curdlan is a bacterial polysaccharide produced by *Agrobacterium biovar* (Table 3.5). It is a 1,3-linked β-glucan that has the unique property of forming gels when solutions of it are heated. Curdlan forms two types of gels that differ in thermoreversibility. A thermally reversible gel is formed when solutions of curdlan are heated to about 65°C, then cooled to about 60°C. However, when curdlan solutions are heated to about 80°C, a strong, thermally irreversible gel forms, that is, a solution is

not reformed upon cooling. Gel strength continues to increase with increasing temperature up to about 130°C.

3.3.15 Gum Arabic [21,63]

When the bark of some trees and shrubs is injured, the plants exude a sticky material that hardens to seal the wound and give protection from infection and desiccation. Such exudates are commonly found on plants that grow in semiarid conditions. Since they are sticky when freshly exuded, dust, insects, bacteria, and/or pieces of bark adhere to the exudate tears (as they are called). Gum arabic (gum acacia), gum karaya, and gum ghatti are exudates of trees; gum tragacanth is the exudate of a shrub. Of the exudate gums, only gum arabic is a major food gum today.

Gum arabic (gum acacia) is an exudate of acacia trees, of which there are many species distributed over tropical and subtropical regions (Table 3.5). The most important growing areas for the species that give the best gum are Sudan and Nigeria. Purified, spray-dried forms of gum arabic are commonly used.

Gum arabic is a heterogeneous material, but generally consists of two primary fractions. One, which accounts for about 70% of the gum, is composed of polysaccharide chains with little or no protein. The other fraction contains molecules of higher molecular weight that have protein as an integral part of their structures. The protein–polysaccharide fraction is itself heterogeneous with respect to protein content. The polysaccharide structures are covalently attached to the protein component by linkage to hydroxyproline and, perhaps, serine units, the two predominant amino acids in the polypeptide. The overall protein content is about 2 wt%, but fractions may contain as much as 25 wt% protein.

The polysaccharide structures, both those attached to protein and those that are not, are highly branched, acidic arabinogalactans with the following approximate composition: D-galactose, 44%; L-arabinose, 24%; D-glucuronic acid, 14.5%; L-rhamnose, 13%; 4-*O*-methyl-D-glucuronic acid, 1.5%. They contain main chains of (1→3)-linked β-D-galactopyranosyl units having two- to four-unit side chains consisting of (1→3)-linked β-D-galactopyranosyl units joined to it by (1→6) linkages. Both the main chain and the numerous side chains have attached α-L-arabinofuranosyl, α-L-rhamnopyranosyl, β-D-glucuronopyranosyl, and 4-*O*-methyl-β-D-glucuronopyranosyl units. The uronic acid units occur most often as nonreducing end units.

Gum arabic dissolves easily when stirred in water. It is unique among the food gums, except for gums that have been depolymerized to produce low-viscosity types, because of its high solubility and the low viscosity of its solutions. Solutions of 50% concentration can be made. Above this concentration, dispersions are somewhat gel-like.

Gum arabic is both a fair emulsifying agent and a very good emulsion stabilizer for flavor oil-in-water emulsions. It is the gum of choice for emulsification of citrus oils, other essential oils, and imitation flavors used as concentrates for soft drinks and baker's emulsions. In the United States, the soft drink industry consumes about 30% of the gum supply as an emulsifier and stabilizer. For a gum to have an emulsion stabilizing effect, it must have anchoring groups with a strong affinity for the surface of the oil and a molecular size large enough to cover the surfaces of dispersed droplets. Gum arabic has surface activity and forms a thick, sterically stabilizing, macromolecular layer around oil droplets. Emulsions made with flavor oils and gum arabic can be spray dried to produce dry flavor powders that are nonhygroscopic and in which the flavor oil is protected from oxidation and volatalization. Rapid dispersion and release of flavor without affecting product viscosity are other attributes. These stable flavor powders are used in dry package products such as beverage, cake, dessert, pudding, and soup mixes.

Another important characteristic of gum arabic is its compatibility with high concentrations of sugar. Therefore, it finds widespread use in confections with a high sugar content and a low water content. More than half the world's supply of gum arabic is used in confections such as caramels, toffees, jujubes, and pastilles. In confections it prevents sucrose crystallization, emulsifies and

distributes fatty components, and helps prevent bloom (the surface whitening caused by polymorphic transitions of lipids). Another use is as a component of the glaze or coating of pan-coated candies.

3.3.16 Inulin and Fructooligosaccharides [15–17,19,55]

Inulin (Table 3.5) occurs naturally as a storage carbohydrate in thousands of plant species, including onion, garlic, asparagus, and banana. The primary commercial source is chicory (*Chicorium intybus*) root. Some is also obtained from Jerusalem artichoke (*Helianthus tuberosus* L.) tubers.

Inulin is composed of β-D-fructofuranosyl units linked $2\rightarrow1$. The polymer chains are often, but not always (because of degradation, either natural or during isolation), terminated at the reducing end with a sucrose unit. Inulin's DP rarely, if ever, exceeds 60. It occurs in plants together with fructooligosaccharides, giving an overall DP in the range of 2–60.

Molecules containing furanosyl units, such as molecules of inulin and sucrose, undergo acid-catalyzed hydrolysis much more easily than do those containing pyranosyl units. Inulin is a storage, that is, a reserve food, polysaccharide, so it is seemingly apparent that, at any time, molecules in various stages of synthesis and, perhaps, breakdown are present. As a result, inulin preparations are mixtures of fructooligosaccharides and small polysaccharides molecules.

Inulin is often deliberately depolymerized into fructooligosaccharides. Both inulin and the fructooligosaccharide products produced from it are prebiotics. (Prebiotics are nondigestible food ingredients that have a beneficial effect on the host by selectively stimulating the growth and/or activity of one or a limited number of bacterial species already present in the colon. Prebiotics are most often used for the nutritional/health benefits they impart.)

Aqueous solutions of inulin can be made at concentrations as high as 50%. When hot solutions of inulin of concentrations greater than 25% are cooled, thermoreversible gels are formed. Inulin gels are described as particle gels (especially after shearing) with a creamy, fat-like texture. Hence, inulin can be used as a fat mimetic in reduced-fat products. It improves the texture and mouthfeel of low-fat ice creams and sauces. Inulin is an ingredient in nutrition, breakfast, meal replacement bars, sports/energy bars, soy beverages, and vegetable patties.

Neither inulin nor fructooligosaccharides are digested by enzymes in either the stomach or small intestine. Therefore, they are components of dietary fiber (Section 3.4). They have a glycemic index of zero, that is, they raise neither the glucose nor the insulin levels in the blood.

3.4 DIETARY FIBER AND CARBOHYDRATE DIGESTIBILITY [2,8,9,15,16,31,35,41,53,60,62,64,67]

Carbohydrates have always been the principal source of metabolic energy for humans and the means for maintaining health of the human gastrointestinal tract. Carbohydrates are also the principal providers of the bulk and body of food products.

Plant cell wall materials, primarily cellulose, other nonstarch polysaccharides and lignin, are components of dietary fiber. The only common feature of these polymers is that they are nondigestible, which is the principal criterion for being classified as a component of dietary fiber. Therefore, not only do natural components of foods contribute dietary fiber, so also do gums that are added to provide the functionalities described in Sections 3.3.7–3.3.16. The definition of dietary fiber also includes substances other than polymers. The key characteristic is that the substance not be digested in the human small intestine, so nondigestible oligosaccharides, for example, raffinose and stachyose (Section 3.2.3), are included as dietary fiber substances.

Oligo- and polysaccharides may be digestible (most starch-based products), partially digestible (retrograded amylose, so-called resistant starch), or nondigestible (essentially all other polysaccharides). When digestive hydrolysis to monosaccharides occurs, the products of digestion are absorbed

and catabolized. (Only monosaccharides can be absorbed through the wall of the small intestine, and only D-glucose is produced by digestion of polysaccharides in humans because only starches can be digested.) Those carbohydrates not digested to monosaccharides by human enzymes in the small intestine (all others except sucrose, lactose, and products, such as maltodextrins, made from starch) may be metabolized by microorganisms in the large intestine, producing low-molecular-weight acids that are partially absorbed and catabolized for energy. Therefore, carbohydrates of all molecular sizes may be caloric, partially caloric, or essentially noncaloric.

The most common bulking agents in natural food are remnants of plant cells that are resistant to hydrolysis by enzymes in the digestive tract. This material includes cellulose, hemicelluloses, pectin, and lignin. Dietary fiber is important in nutrition because it maintains the normal functioning of the gastrointestinal tract. Dietary fiber increases intestinal and fecal bulk, which lowers intestinal transit time and helps prevent constipation. Its presence in foods induces satiety at meal time. Nutritionists set requirements of dietary fiber at 25–50 g per day. Insoluble fiber is claimed to decrease blood cholesterol levels, lessening the chance of heart disease. It also reduces the chances of colonic cancer, probably due to its sweeping action.

Soluble gums have similar effects in the gastrointestinal tract and on the level of cholesterol in blood, but to different extents. Some gums that have been specifically examined in this regard are pectin, guar gum, xanthan, and hemicelluloses (e.g., guar gum ingested at a rate of 5 g/day results in a lowering of the hyperglycemic spike, a 13% lowering of serum cholesterol, and no decrease in the high-density lipoprotein [HDL] fraction, the beneficial cholesterol carrier.) In addition to cereal brans, kidney and navy beans are especially good sources of dietary fiber. A product based on psyllium seed hulls has high water-binding properties, leading to rapid transit time in the gastrointestinal tract, and is used to prevent constipation. A product with a MC base is sold for the same purpose.

The starch polysaccharides are the only polysaccharides that can be hydrolyzed by human enzymes. They, of course, provide D-glucose that is absorbed by microvilli of the small intestine to supply the principal metabolic energy of humans. Other polysaccharides consumed normally as natural components of edible vegetables, fruits, and other plant materials and those food gums added to prepared food products are not digested in the stomach or small intestine of humans, but they pass into the large intestine (colon) with little or no change. (The acidity of the stomach is neither strong enough, nor is the residence time of polysaccharides in the stomach sufficiently long to cause significant chemical cleavage.) When the undigested polysaccharides reach the large intestine, they come into contact with normal intestinal microorganisms, some of which produce enzymes that catalyze hydrolysis of certain polysaccharides or certain parts of polysaccharide molecules. The consequence of this is that polysaccharides not cleaved in the upper intestinal tract may be broken down and utilized by the bacteria within the large intestine.

Sugars that are split from the polysaccharide chain are used by the microorganisms of the large intestine as energy sources in anaerobic fermentation pathways that produce lactic, propionic, butyric, and valeric acids. These short-chain acids can be absorbed through the intestinal wall and metabolized, primarily in the liver. In addition, a small, though significant in some cases, fraction of the released sugars can be taken up by the intestinal wall and transported to the portal blood stream where they are conveyed to the liver and metabolized. It is calculated that, on average, ~7% of human energy is derived from sugars split from polysaccharides by microorganisms in the large intestine or from the short-chain acids produced from them via anaerobic fermentation pathways. The extent of polysaccharide cleavage depends on the abundance of the particular organism(s) producing the specific enzymes required. Thus, when changes occur in the type of polysaccharide consumed, utilization of the polysaccharide by colonic microorganisms may be temporarily reduced until organisms capable of splitting the new polysaccharide proliferate.

Some polysaccharides survive almost intact during their transit through the entire gastrointestinal tract. These, plus larger segments of other polysaccharides, give bulk to the intestinal contents and lower the transit time. They can be a positive factor in health through a lowering of blood cholesterol concentration, perhaps by sweeping out bile salts and reducing their chances for reabsorption from

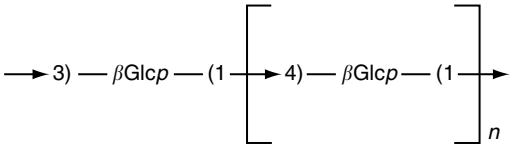

FIGURE 3.55 Representative structure (shorthand notation) of a segment of oat and barley β-glucans where n usually is 1 or 2, but occasionally may be larger.

the intestine. In addition, the presence of large amounts of hydrophilic molecules maintain sufficient water content in the intestinal contents that results in stool softness and consequent easier passage through the large intestine.

One natural component of dietary fiber is a water-soluble polysaccharide, β-glucan, that is present in oat and barley brans. Oat β-glucan has become a commercial food ingredient because it has been shown to be effective in reducing the level of serum cholesterol. The oat β-glucan molecule is a linear chain of β-D-glucopyranosyl units. About 70% are linked as (1→4) and about 30% as (1→3). The (1→3) linkages occur singly and are separated by sequences of two or three (1→4) linkages. Thus, the molecule is composed of (1→3)-linked β-cellotriosyl [→3)-βGlc*p*-(1→4)-βGlc*p*-(1→4)-βGlc*p*-(1→] and β-cellotetraosyl units (Figure 3.55). Such (1→4,1→3)-β-glucans are often called mixed linkage β-glucans.

When taken orally in foods, β-glucans reduce postprandial serum glucose levels and the insulin response, that is, they moderate the glycemic response, in both normal and diabetic human subjects. This effect seems to be correlated with viscosity. They also reduce serum cholesterol concentrations in rats, chickens, and humans. These physiological effects are typical of those of soluble dietary fiber. Other soluble polysaccharides have similar effects but to differing degrees.

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