

Sweeteners are the primary ingredients in the manufacture of confections. Chemically, the primary sweeteners in confections are carbohydrates, which consist of a group of widely varied chemical substances present in both plants and animals. For example, in dry corn, approximately 55% of the solids are carbohydrates. The word “carbohydrates” itself means hydrated carbon. Thus, carbohydrate chemistry mostly deals with chains of carbon atoms hydrated with water, with a general formula of $C_x(H_2O)_y$.

Although only three atoms are involved, the chemistry of sweeteners can be very complex. Variations such as carbon chain length and branching, among others, allow for the existence of numerous combinations of the three atoms that provide the range of chemical characteristics of carbohydrates. The main groups of interest for confectionery manufacture are monosaccharides (e.g., glucose and fructose), oligosaccharides (e.g., the disaccharides including sucrose, maltose, and lactose, and starch hydrolysates), and polysaccharides (e.g., starches). Oligosaccharides are carbohydrates consisting of 2–20 monosaccharide units joined by glycosidic linkages. Compounds containing three saccharides are trisaccharides, while four to ten are tetra-, penta-, hexa-, hepta-, octa-, nona-, decasaccharides, respectively. Various oligo- and polysaccharide products are used in confections. However, sweetening power generally decreases as carbon chain length increases (although other factors affect sweetness as well). Most confections con-

tain primarily smaller saccharides, but with a balance of oligosaccharides for functional properties (i.e., control of crystallization).

A wide range of sweeteners is used in the manufacturing of confections and chocolates, with the most common being cane or beet sugar (sucrose), glucose (corn) syrup, high fructose syrup, liquid sugar (67% sucrose dissolved in water), and invert sugar, the hydrolysis product of sucrose. Sugar alcohols (or polyols) are used for “diabetic” candies since they induce no insulin response. High intensity sweeteners are used to enhance sweetness, particularly when sugar alcohols are used.

The original candies probably were sweetened naturally, with materials like honey and maple syrup. As sucrose became more available, confectioners began using it as the primary sweetener in confections, with its hydrolysis product, invert sugar, used as the first doctoring agent (to control crystallization). As the sweetener industry matured, more and more different types of sweeteners have become available that provide excellent control for the confectioner. Knowledge of the physical and chemical properties of carbohydrates has made it possible for the confectionery industry to develop the many products available on the market today.

Sweeteners, beyond providing sweetness to confections, play an important role in determining the texture. Crystallization of sucrose in some products is encouraged, while in others, complex carbohydrates such as glucose (corn) syrup are

added to control or prevent crystallization. Chemical differences between carbohydrates similarly can result in different product characteristics. For example, the color of a number of candies is impacted by the choice of sweetener used in manufacturing. Sweeteners also aid in moisture control. Properly chosen, they either prevent moisture loss or moisture uptake. In addition, they add bulk in candies. The following sections discuss the basic chemistry of saccharides and some of their chemical properties. Their physical properties are the subject of Chapter 2.

1.1 Monosaccharides

Saccharides are composed of three basic building blocks, a carbon chain ($-\text{C}-\text{C}-\text{C}$), hydroxyl groups ($-\text{OH}$), and either an aldehyde ($-\text{CHO}$) or ketone ($-\text{CH}_2\text{COCH}_2-$) group. The chain length for monosaccharides can vary from three carbons in the simplest sugar to as many as seven. The monosaccharides most important to the confectionery industry are those containing six carbons (glucose, fructose). The presence of either an aldehyde or a ketone group in glucose and fructose gives rise to two categories known as aldose and ketose sugars. The structural difference between the two six-carbon sugars is that glucose contains an aldehyde group while fructose contains a ketone group.

The three most important monosaccharides in candies are glucose, fructose and galactose because their free aldehyde group makes them reducing sugars (defined later) and therefore, they can participate in the browning reactions. In older literature, glucose and fructose are referred to as dextrose and levulose, respectively. These terms arise from the direction in which a plane of polarized light is rotated when passing through a solution of each sugar: glucose rotates a plane of light to the right (dextro) and fructose rotates a plane of light to the left (levulo).

The word dextrose is still used in describing dextrose equivalent (DE), an important property that describes the reducing capacity of starch hydrolysate syrups. The confectionery industry uses the term dextrose when pure glucose is used.

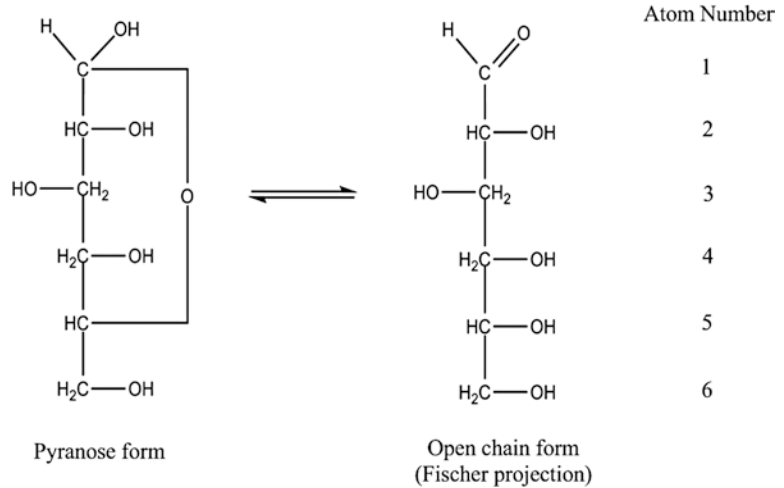
The term “glucose” is often used to describe the hydrolysate product of starch, more correctly called starch hydrolysate or glucose syrup.

1.1.1 Glucose/Dextrose

Glucose is widely distributed in nature, including the blood of animals and in the sap of plants. It also forms the base unit in one of the most important polysaccharides, starch, and is an important component of confectionery sweeteners.

Glucose contains asymmetric carbons, those that have four different substitute groups attached, which gives rise to two isomers, designated as D or L glucose. The structure of D-glucose is shown in Figure 1.1. In solution, glucose exists in the pyranose, or ring, configuration in equilibrium with a small amount of the open chain form. By convention, the assignment of the D-form in glucose, or any other monosaccharide, depends on the configuration of the hydroxyl group around the highest-numbered asymmetric carbon. This is most easily seen in the simplest monosaccharide, glyceraldehyde (Figure 1.2). Glyceraldehyde has a three-carbon chain in which only the number two carbon represents an asymmetric carbon. If the hydroxyl group at carbon 2 is written to the right, the structure represents the D-form, whereas if the hydroxyl group is written to the left, the structure represents the L-form. In Figure 1.1, the open chain form (Fisher projection) of glucose has four asymmetric carbons, while the pyranose form has five asymmetric carbons. If the hydroxyl group around the highest-numbered asymmetric carbon, carbon number 5 in glucose, is written to the right, the D form is represented. The isomer of a D-sugar is designated as the L-sugar (Figure 1.3). The open-chain form of glucose has four asymmetric carbons. Since two isomers exist for each asymmetric carbon, in a six-carbon sugar, 4^2 or 16 isomers are possible, eight of which will be in the D-configuration and eight in the L-configuration. The Fisher projections of all D-sugars with chain length between three and six carbons are illustrated in Figure 1.4. Among this family of monosaccharides, glucose, galactose and xylose

Figure 1.1 Pyranose and open chain forms of D-glucose



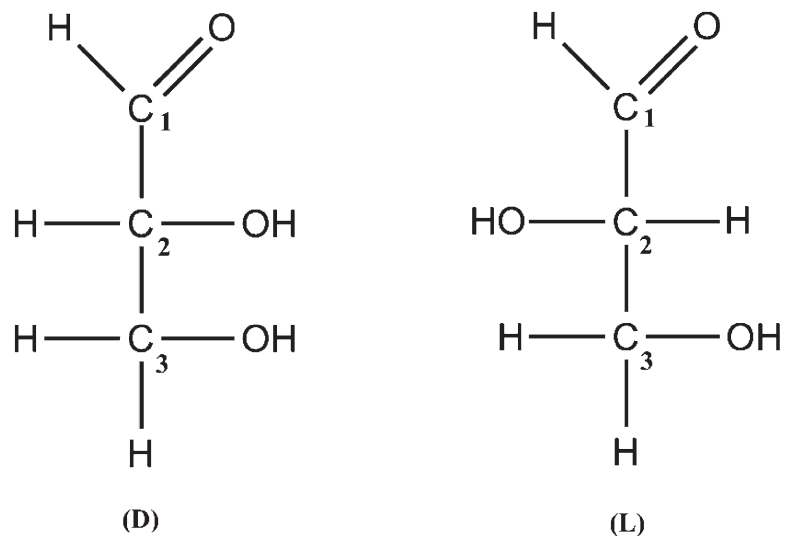
are of particular interest to the confectionery industry.

In solution, glucose molecules continuously change from open chain to ring structure and back again. The formation of the pyranose ring introduces an anomeric carbon in the first position (carbon 1), which allows two different orientations of the hydroxyl group as the ring closes. The two possible forms are designated by a Greek letter prefix as α and β . When the carbon 1 hydroxyl group is *cis*- (meaning on the same side) to the hydroxyl group at the carbon 2, the compound is termed α -D-glucopyranose or α -D-glucose. If the two hydroxyl groups are *trans*-

(meaning on opposite sides) to one another, the compound is β -D-glucopyranose or β -D-glucose. The structures of α - and β -D-glucose are shown in the pyranose form and in the cyclic Haworth configuration in Figure 1.5. In the cyclic form, the pyranose ring is considered to be perpendicular to the plane of the paper, with the substituents written to the right below the plane of the ring and those written to the left above the plane of the ring.

Glucose is present in confections primarily through the use of either sucrose or glucose syrups. At times, however, pure glucose/dextrose may be used. Commercial dextrose is made

Figure 1.2 Structures of D and L glyceraldehyde



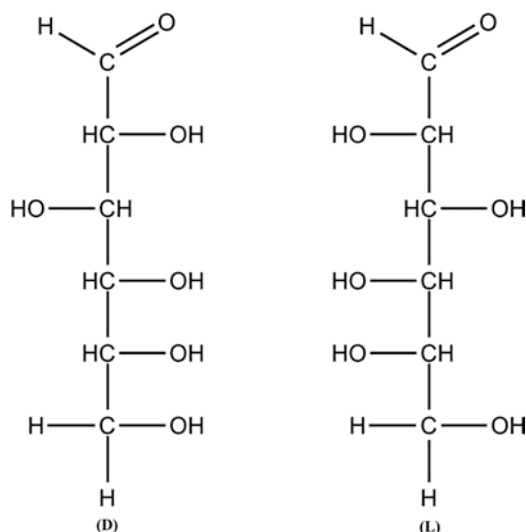


Figure 1.3 D and L isomers of glucose

through purification of fully hydrolyzed starch syrup followed by crystallization and refining. Dextrose crystallizes in different forms, with the monohydrate being the most commonly used. After drying, crystalline dextrose monohydrate is used in a variety of confections. It is often used, for example, directly in pressed tablet confections because of its compression characteristics (see Chapter 7). Anhydrous dextrose is sometimes used in commercial baking chips.

1.1.2 Fructose

The ketose sugar of greatest interest in confections is fructose. Fructose is abundant in nature and occurs in many fruits and vegetables and is a component of honey. Besides honey, it is a component of invert sugar and high fructose glucose (corn) syrup.

The D-forms of fructose in the open-chain, pyranose (six carbon ring), and furanose (five-carbon ring) forms are illustrated in Figure 1.6. These forms coexist in solution, with the pyranose ring form being most prevalent especially at elevated temperatures. As noted above, fructose is also a reducing sugar and, as such, also is found in the α and β isomers.

Until recently, fructose was only available in liquid form; in recent years, processes have been developed for the manufacture of crystalline fructose. However, crystalline fructose is very hygroscopic and care must be exercised in handling to prevent moisture uptake.

The sweetening power of fructose is from 1.3 to 1.7 times greater than sucrose and therefore, it takes less fructose to achieve the same sweetness. Further, since its metabolism does not require insulin, fructose often finds applications in diabetic foods.

1.1.3 Galactose

Galactose is a third monosaccharide of interest in confections. Although it is not used in confections directly, it is of interest because it is one saccharide component of lactose, the milk sugar. The structural comparison of glucose and galactose is shown in the Fischer projection in Figure 1.4.

1.2 Disaccharides

A number of disaccharides are used in confections, although sucrose is far and away the most common. Other disaccharides of interest include maltose and lactose. The chemical structures of these disaccharides are shown in Figure 1.7.

1.2.1 Sucrose

Sucrose is composed of two monosaccharides, α -D-glucose and β -D-fructose, with the glycosidic linkage between the one-carbon of glucose and the two-carbon of fructose. This linkage makes sucrose a nonreducing sugar because it involves the reducing groups of each monosaccharide. Mutarotation is therefore not possible; thus, sucrose cannot participate in the browning reactions unless it is first hydrolyzed (for example, by heat or low pH) into glucose and fructose.

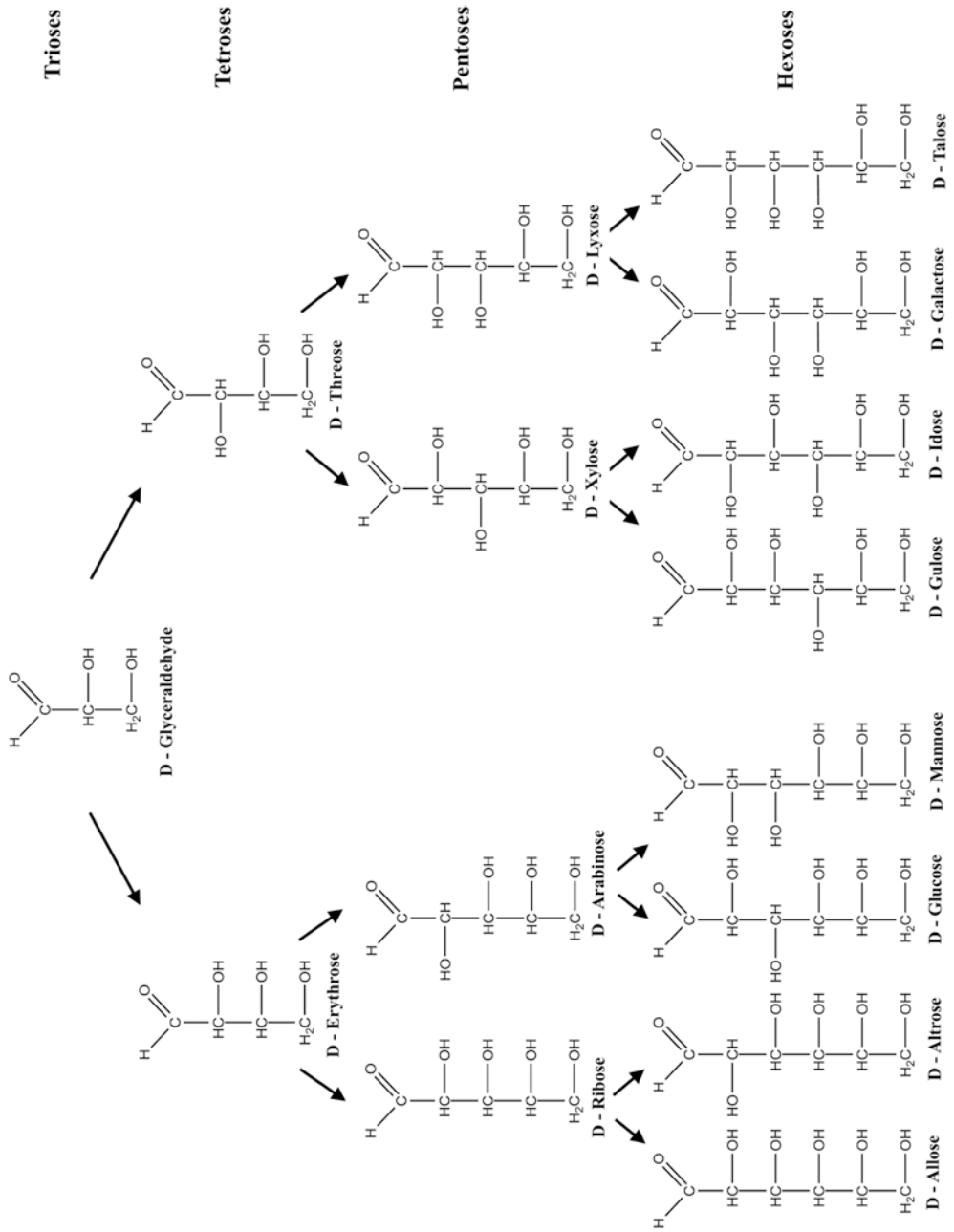


Figure 1.4 Configurational relationship of D-monosaccharides

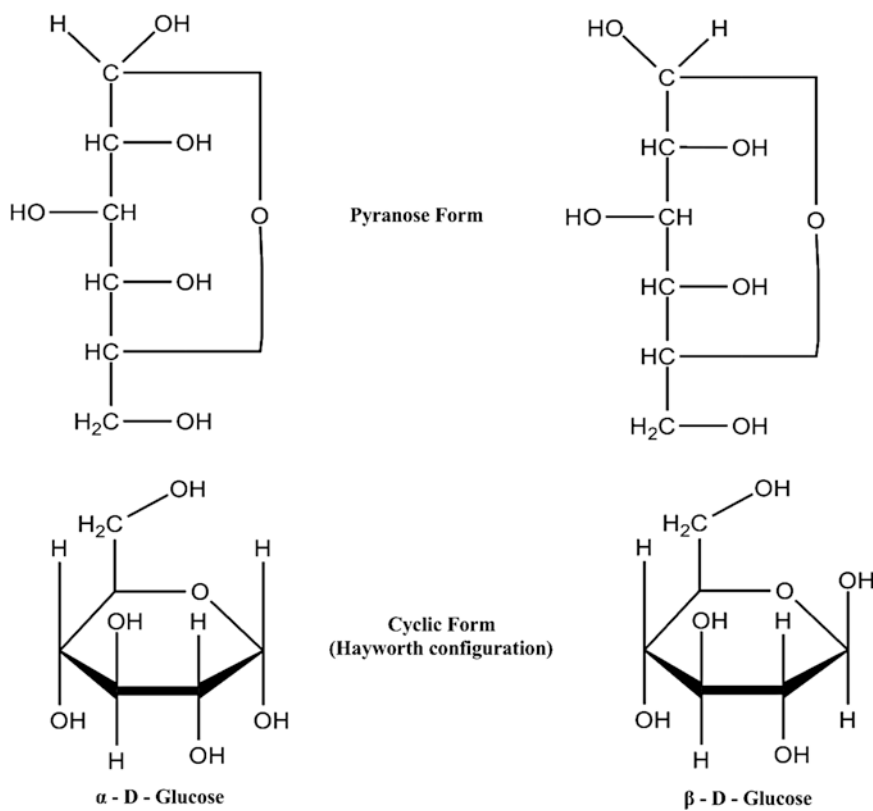


Figure 1.5 Configuration of α - and β -D-glucose

1.2.1.1 Sources of Sucrose

Sugar cane and sugar beets are the two sources of sucrose. Both yield juices rich in sugar that allow, after additional processing, the crystallization of sucrose. In each, the process is complex and a detailed description is beyond the scope of this book. The following summaries give the main steps.

1.2.1.1.1 Cane Sugar

Sugar cane is a tropical grass. It grows up to 7 m tall with stems that reach a diameter of more than 2 cm. At harvest time, the stalks are cut at ground level. Already the next day, sprouts start forming below ground level. Thus, a field of sugar cane, once planted, is self-perpetuating. The pulp in the stalks contains sugar at all times and therefore, there is no real maturity stage. The sugar content increases somewhat with cooler temperatures and decreases with warmer temperatures. Sugar cane typically contains 15% sucrose at optimum

maturity, but still contains 12% sucrose several months before and after optimum maturity. This allows for long harvest seasons. However, it is advantageous to harvest cane with the highest possible sugar content.

At the cane processing factory site, the cane is washed to remove as much dirt and debris as possible. One to 2% sugar is lost during this step in the process. Next, the cane is cut into 10–20 cm long sticks, which is followed by a cutting and hammer action to further reduce the cane. The crushed cane is then passed over several mills, which separate the cane into juice and a fibrous residue, called bagasse. Before the last step of milling, the bagasse is washed with water to achieve maximum extraction. Bagasse is waste material, mostly used for fuel.

The juices obtained during crushing and milling are combined and subjected to clarification. At this stage the juice looks brown and muddy. The dissolved materials are sucrose, invert sugar,

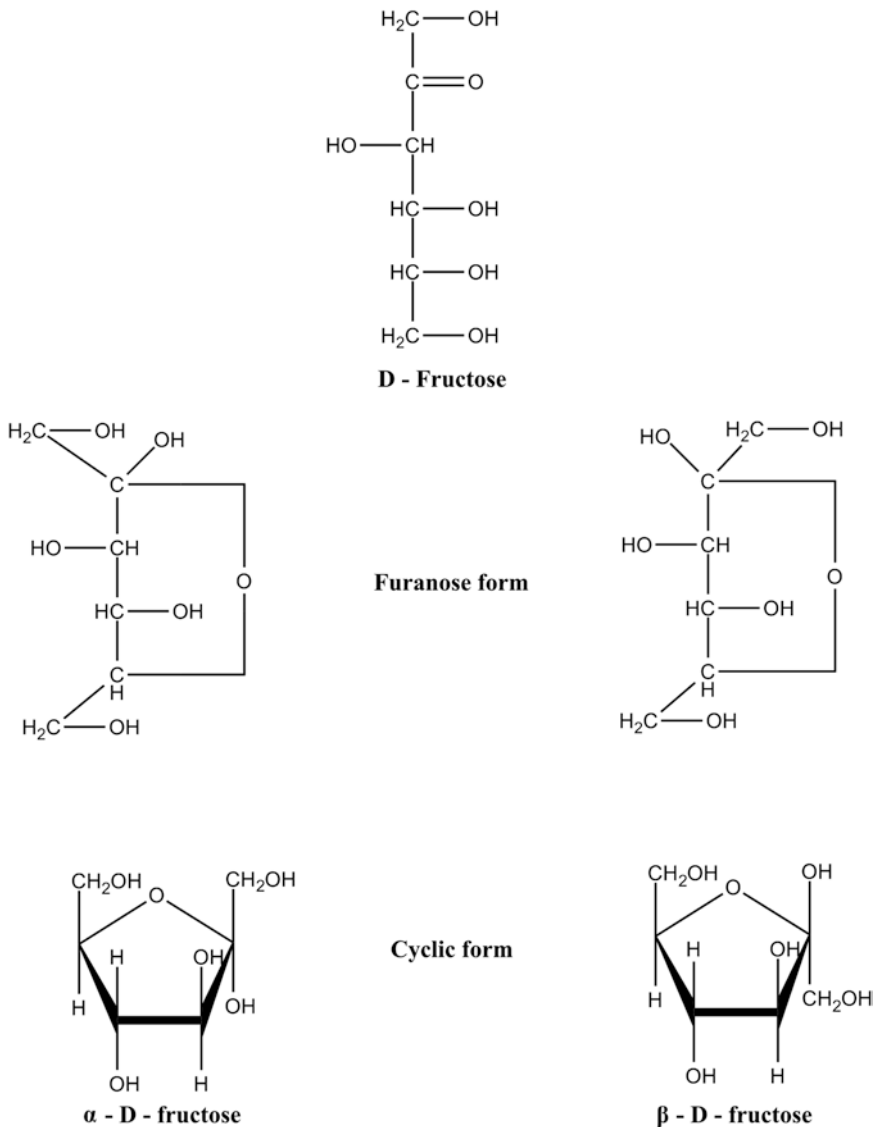
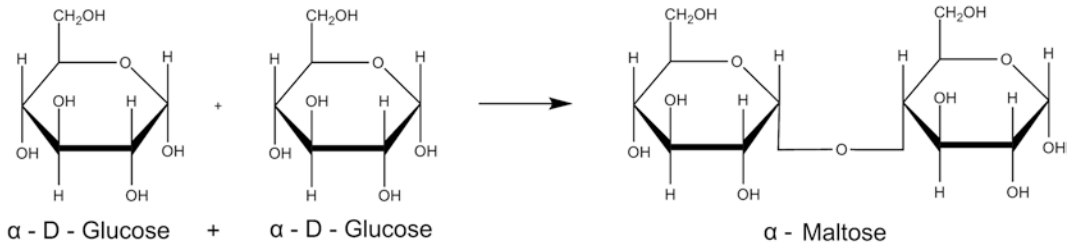
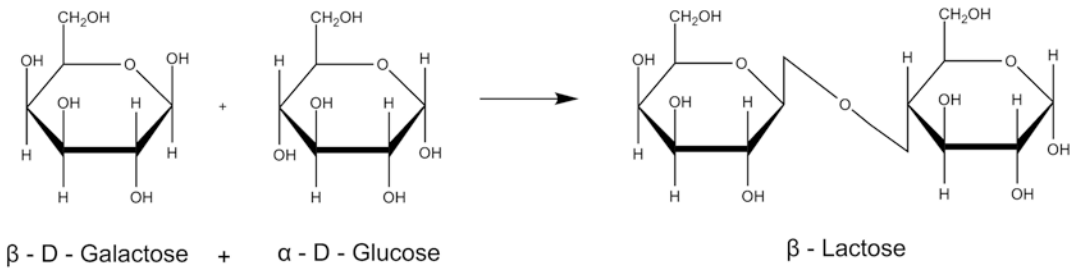
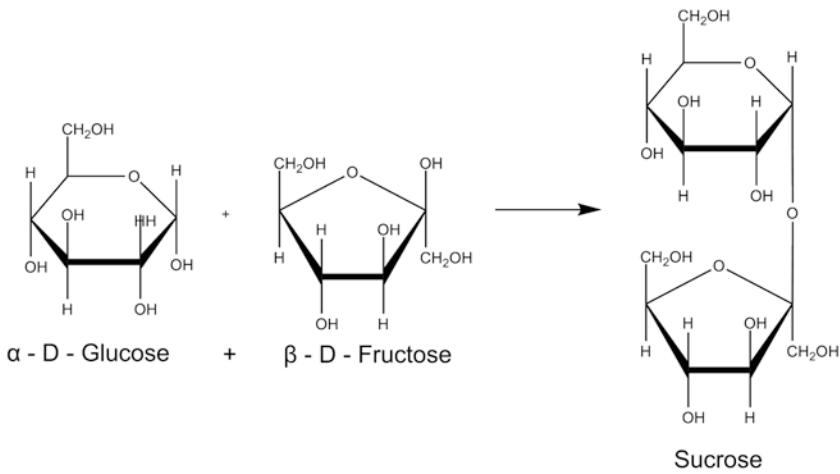


Figure 1.6 Structure of D-fructose and its α and β configurations

salts, silicates, proteins, enzymes, and organic acids. The suspended materials are cane fiber, microorganisms, chlorophyll, gums, starch, waxes, and fat. The first step in clarification is to raise the pH and heat the juice to stop microbial action and to inactivate the enzyme, invertase, which is native to sugarcane. The pH is raised by the addition of lime, which has the added advantage of adding calcium, thus forming and precipitating insoluble calcium salts. Clarification by heat and lime is a process known as “defecation”.

The precipitate, or mud, is removed and returned to the field. Following clarification, the juice is called syrup and is dark brown, almost black, in color.

The crystallization and harvesting of sucrose from syrup is accomplished by further evaporation, crystallization and centrifugation. The products of the initial processing steps are raw sugar (crystalline) and molasses. Raw sugar is shipped from the producing areas to the consuming areas, where it is further refined. Refining consists of a

Maltose**Lactose****Sucrose****Figure 1.7** Common disaccharides

series of washing and crystallization steps, up to three times, until the final sugar crystals are white with purity greater than 99%. Brown sugar is made by adding some molasses back to the refined sugar crystals.

1.2.1.1.2 Beet Sugar

Sugar beets are grown in northern climates. In the U.S., the largest sugar beet area is the Red River Valley, which lies between Minnesota and North Dakota. This region produces more than 30% of all sugar beets. Sugar beets are seeded in the spring and harvested in October. At harvest time, sugar beets weigh, on average, 1 kg. If not processed immediately after harvest, beets are stored in buildings or in piles as high as 9–10 m (29–32 ft) and as long as 1.5 km (1 mile). Sugar losses during storage are minimal and thus, storage of the beets extends throughout the processing season.

Sugar production begins when beets are removed from the storage facility and enter the factory for a thorough washing to remove soil residues. The cleaned beets are sliced with razor sharp knives into cossettes, which then enter a counter-current diffuser containing hot water. The advantage of cutting cossettes is that it allows for maximum surface area and therefore, maximum sugar extraction. The juice leaves the diffuser for further processing. The cossettes are dried and sold as animal feed. The raw juice from the diffuser is clarified with the addition of lime, similar to the process described for sugarcane, with the impurities removed by filtration. The thin juice is then evaporated to remove excess moisture before it enters a vacuum-pan, where additional water is removed and crystallization is initiated by seeding the syrup with pulverized sugar. Centrifugation separates the white crystals from beet molasses. As for sugar cane, several crystallization and centrifugation steps are used to obtain refined white sucrose.

Beet molasses is not suitable for human consumption and can only be utilized as animal feed or for the production of alcohol. For this reason, brown sugars are not made from beet sugar due to the nature of the molasses.

There has been much discussion as to the merits of the use in confections of cane sugar vs. beet sugar. Today's refined sugars from either cane or beet are practically pure sucrose, 99.9% purity and thus, are virtually indistinguishable. In raw sugars, the differences are greater. Cane sugar has a pleasant flavor and smell, whereas raw beet sugar is bitter and has an unpleasant taste. Less refined beet sugar can have a slight odor and cause excessive foaming. The foaming is the result of incomplete removal of proteins and their breakdown products, saponins and mucilages, neither of which is likely to exist in cane sugar. Less refined cane sugar has been found to contain cane wax, which will act as a foam inhibitor.

1.2.1.2 Sugar Forms and Types

Sugars can be purchased in many forms and crystal sizes. The confectionery industry takes advantage of almost every type of sugar produced. Highly refined sugars are used in chocolate, hard candy, and fondant; brown sugars are used for flavor, for example, in caramel and fudges.

Sucrose may be purchased in many granular sizes. The granular structure of crystallized sugar is determined by the size, shape and the distribution of the crystals. Although the names of the different types of sugar differ between suppliers, they generally fall into five classes, as listed in Table 1.1, based primarily on size. Each of these grades of sugar finds application in the candy industry, although most sugar use is either fine or

Table 1.1 Crystal size and names of sugars

Grain size (μm)	Name of sugar type
	Sanding sugar
>650	Confectioners A
	Confectioners AA
380–635	Coarse
	Granulated
	Fine granulated
175–380	Extra fine
	Granulated
	Baker's special
50–175	Industrial fine
	Crushed fine
<25	Powdered sugar

Table 1.2 Composition of sugars

Sugar type	Component (%)				
	Sucrose	Moisture	Invert	Ash	Others
Sanding	99.98	0.015	0.001	0.002	0.002
Granulated	99.94	0.02	0.015	0.01	0.01
Golden C, (light brown)	89.3	2.7	4.2	1.4	2.4
Yellow D (dark brown)	87.9	2.8	4.6	1.7	3.0

coarse granulated. Larger sizes are used for sanding and decorating while smaller sizes are used when the sugar will not be dissolved and recrystallized, as in pastes and lozenges. Smaller sizes are also used in soft panning to ensure a smooth candy surface.

Table 1.2 gives the composition of some sugar types. For the most part, granulated sugars are highly refined to give greater than 99.9% purity. Brown sugars contain less sucrose and more of the components found in molasses. Powdered sugar generally contains a few percent of starch granules to control moisture and prevent clumping.

Today, a specially manufactured fondant sugar is available to the industry. It is prepared with a fine sugar containing about 3% invert sugar and up to 10% maltodextrin. Fondant sugar allows the manufacturing of a fondant (often called rolled or extruded fondant) without boiling and crystallization procedures (see Chapter 9).

Whether from cane or beet, sugars are most often used in solid form. However, liquid sugar, 67% sucrose dissolved in water (based on the solubility of sucrose in water at room temperature, see Chapter 2), is available and is used in some places in the candy industry. It has the advantage of being pumpable and does not require time for dissolution prior to use. For example, large hard candy manufacturers can pump liquid sugar and glucose syrup together into the evaporator to save both time and energy. While liquid sugars allow for tank storage and economical handling procedures, care must be exercised to avoid microbial spoilage due to the high water activity. Further, crystallization (in containers and even pipes) can occur if temperature is reduced substantially below room temper-

ature and the solution becomes supersaturated (see Chapter 2).

1.2.2 Maltose

Maltose is the combination of two α -D-glucose units. The glycosidic linkage is made between the one carbon of one glucose unit and the four carbon of the second glucose unit. This linkage is referred to as a 1–4 α linkage because the hydroxyl group of the carbon number 1 is in the α position. Maltose is therefore an α -glycoside. It is also a reducing sugar.

Maltose is generally found in confections through addition of glucose syrups (high maltose syrups). It is much less sweet than sucrose (about 0.3 times as sweet).

1.2.3 Lactose

Lactose is the disaccharide found in the milk of mammals. It is the combination of a unit of α -D-glucose and β -D-galactose through the four – carbon of glucose. Lactose, therefore, is a β -glycoside. As a reducing sugar, it participates in the Maillard browning reaction, one of its desired effects in caramel, fudge and toffee.

In confections, lactose is usually introduced through a milk ingredient, as in sweetened condensed milk used for caramel or fudge. Lactose powder is available through refining of whey or whey permeate (after separation of whey proteins). Here, the whey or permeate is evaporated to 60–70% total solids, which supersaturates the lactose. The condensed stream fills a lactose crystallizer, which is then cooled over 18–24 h to

produce a crop of lactose monohydrate crystals. These are separated, washed and screened to produce lactose powder. Edible grade lactose is about 97% purity, whereas pharmaceutical-grade lactose is considerably more pure. Crystalline lactose finds its way into many confections, including being used as a nutritive sweetener in chocolate. Its very low sweetening power (0.15–0.25 times that of sucrose) and low solubility (16% at room temperature) are disadvantages in some applications.

1.3 Invert Sugar

Hydrolysis of a sucrose solution yields an equimolar (50/50) mixture of glucose and fructose, a product known as invert sugar, an ingredient that plays an important role in candy manufacturing. In the early days of candy making, before the development of starch hydrolysates, invert sugar was the primary doctoring agent for controlling sucrose crystallization. Often, the presence of invert sugar in confections was, and still is to some extent, due to deliberate processing or ingredient addition that generated a portion of invert sugar in the candy mass. Addition of cream of tartar in production of grained dinner mints, for example, is a holdover of old-time candy making. In principle, a candy maker could now simply add a specified amount of commercial invert sugar and forgo the addition of cream of tartar in making grained mints.

Invert sugar may also be used in confections as a humectant and for flavor release. Due to the low molecular weight of glucose and fructose, invert sugar provides a substantial reduction in water activity (compared to the disaccharide sucrose). This makes it a valuable humectant for products such as fondant and creams. A small amount of invert sugar may also be added to hard candy to enhance flavor release. Also, the combination of glucose (less sweet than sucrose) and fructose (more sweet) ends up being slightly sweeter than sucrose.

Note that invert sugar is formed under normal commercial candy cooking conditions, although the extent of inversion depends on the

temperature-time-pH relationship. Slow open kettle boiling to temperatures suitable for hard candy (146–152 °C; 295–305 °F) may create up to 5% (or more if cook time is extended) invert sugar production from sucrose hydrolysis even at neutral pH. In contrast, high throughput vacuum boilers have such a short residence time at elevated temperatures that a negligible amount of inversion occurs.

Commercial invert sugar is produced by either acid or enzyme hydrolysis of a sucrose solution. Most candy companies that use invert sugar in their formulations simply purchase it from a supplier, although some companies still produce their own invert syrups prior to use. However, some of these commercial products are likely to still contain up to 50% unreacted sucrose, which can significantly affect product characteristics.

1.3.1 Acid Hydrolysis

Invert sugar can be produced from sucrose solution with the use of organic acids such as citric, tartaric or acetic acids. With these acids, concentrations of approximately 1% and heating at boiling temperature for 30–45 min are required for inversion, which causes degradation of glucose and fructose and leads to the formation of a dark, generally undesirable, color. A more desirable process for making invert sugar uses hydrochloric acid since it requires a much lower acid concentration (0.1%) and, if allowed to react for 2 h, results in a colorless product. A colorless invert sugar is particularly important in white or pastel colored fondants.

Acid hydrolysis of sucrose is temperature and pH dependent and can be catalyzed by heavy metals. At temperatures above 160 °C, hydrolysis of sucrose will occur regardless of the pH value. It is for this reason that in the manufacturing of hard candy for example, it is important to cool the candy as soon as possible to prevent hydrolysis of sucrose, thereby preventing an increase in the candy's hygroscopic nature that otherwise could cause stickiness. It is for the same reason that in the manufacturing of an acid flavored hard candy, the acid is added during

Table 1.3 The effect of temperature on the hydrolysis of sucrose at pH 2.0

Temperature °C	Time for 99.9% conversion (h)
20	3,511
40	209
80	2

cooling to prevent or minimize hydrolysis and prevent possible stickiness. The influence of temperature of sucrose hydrolysis at pH 2.0 is illustrated in Table 1.3.

1.3.2 Enzyme Hydrolysis

The enzyme invertase, typically extracted from cultures of yeast, converts sucrose into invert sugar. There are two enzymes that are capable of hydrolyzing sucrose: β -fructosidase and α -glucosidase. The former acts on the fructose and the latter on the glucose portion of the molecule. The optimum activity for these enzymes is at pH 4–5 and pH 6–7, respectively. Mild temperatures (40–50 °C) are needed for enzyme production of invert syrup since significant losses in enzyme activity occur above 65.6 °C (150 °F), as shown in Table 1.4.

Since the enzyme is also inhibited by soluble solid concentration, enzymatically produced invert syrup should be produced with sucrose concentrations of about 50%. Silver and Karel (1981) document the effects of water activity on the invertase reaction, showing how the reaction rate decreased as water activity decreased (solute concentration increased).

Table 1.4 The effect of temperature on invertase activity

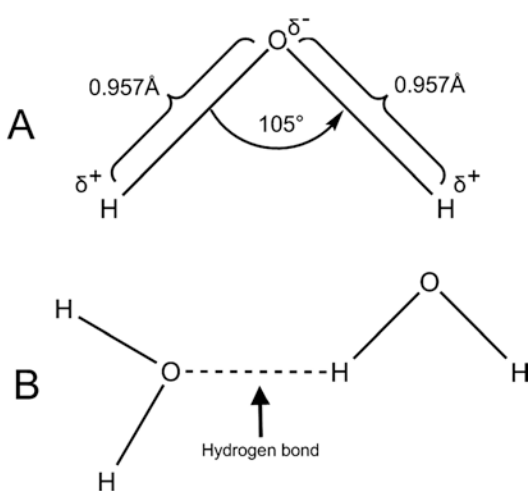
Temperature °C	% loss of activity in	
	20 min	30 min
60.0	4	6
65.6	8	12
71.1	15	20
76.7	20	30

1.4 Sugar Reactions

Although there are other sweeteners used in confections that have not yet been discussed (e.g., glucose syrup), it is important to touch on some of the chemical properties and important reactions of sugars first. Although some of these concepts have been touched on briefly already, this section will provide more details on several important chemical reactions of sugars, including hydrogen bonding, reducing sugars and mutarotation, and browning reactions. Physico-chemical properties, such as sweetness, viscosity, heat of solution, specific optical rotation, refractive index, density, colligative properties, solubility, glass transition, and crystallization, will be covered in more detail in Chapter 2.

1.4.1 Hydrogen Bonding

Water has an enormous ability to hydrogen bond. In a water molecule, the atoms are arranged at an angle of about 105° and the distance between the nuclei of oxygen and hydrogen is 0.957 Å. Each atom carries a slightly positive (hydrogen) or negative (oxygen) charge. Because of the charges, water molecules are attracted to each other with higher than normal van der Waals forces. The

**Figure 1.8** (a) Structure of a water molecule, (b) Attraction of neighboring water molecules through hydrogen bonding

binding energy for a hydrogen bond is approximately 5 kcal per mole. Similar bonding interactions occur, for example, between OH and NH groups. Hydrogen bonding is the reason for the strong affinity of carbohydrates to water.

The structure of a water molecule, and the attraction of neighboring water molecules bonded through hydrogen bonds, is shown in Figure 1.8. The impact of hydrogen bonding can easily be seen by comparing the boiling points of liquids in ascending order of hydrogen bonding capacity. Acetone (CH_3COCH_3) has less hydrogen bonding capacity compared to methanol (CH_3OH) or water (H_2O). The boiling points of these liquids are 53°, 63° and 100 °C, respectively. Thus, it takes far more energy, more hydrogen bonds must be broken, to bring water to its boiling point than to bring methanol to its boiling point.

Water interacts with sweeteners through hydrogen bonding. In fact, a sucrose molecule in solution has on average about five water molecules hydrogen bonded with it (Starzak et al. 2000). But these are not always the same water molecules; since the bonding energy is quite low, there is a continuous interchange of water molecules hydrogen bonding with a sugar molecule. That is, water molecules are continually bonding and releasing from the sugar molecule in an endless interplay. These hydrogen-bonding interactions explain why sugars are so readily dissolved in water.

The nature of the interaction between water and sugar changes as concentration of sugar in solution increases. At higher sugar concentration, sugar molecules begin to interact more with each other and somewhat less with water molecules. This increase in self-association (through hydrogen bonding) continues as concentration increases through and above the solubility concentration, although there is no discontinuity in any chemical property above and below the solubility concentration. In supersaturated solutions, the hydrogen bonding interactions between sugar molecules are thought to form the precursors for the crystalline lattice (Starzak et al. 2000).

Once crystals form in supersaturated solution, hydrogen bonding between sugar molecules becomes predominant. Depending on the sugar,

the interactions with water must be released, at least in part, for a crystal to form. In fact, what holds a sugar crystal together is the hydrogen bonding interactions between neighboring molecules in the crystal lattice. Sucrose, for example, forms an anhydrous crystal so that all water molecules must be completely desolvated from a sucrose molecule prior to incorporation of that molecule into the crystal lattice. Other sugars (i.e., glucose, fructose, and lactose) form hydrated crystal lattices, meaning that one (or more) water molecule remains hydrogen bonded to the sugar molecule as that unit incorporates into the crystal lattice.

Hydrogen bonding also influences other interactions of importance in confections. For example, gelatinization of starches is heavily affected by the ability of starch molecules to hydrogen bond. Similar interactions allow hydrocolloids (proteins, gums, etc.) to form the gels needed to provide texture in gummy and jelly candies.

1.4.2 Reducing Sugars and Mutarotation

A reducing sugar is a sugar that contains an aldehyde group or is capable of forming one. In solution, a reducing sugar undergoes mutarotation to form two isomers, α and β . Because a reducing sugar spends a portion of its time in solution in an open form (not a ring form), it is capable of reducing Fehling's solution (Cu^{++} to Cu^{\ominus}), as shown in Figure 1.9. The presence of the aldehyde form, an intermediate in the transformation between isomers, allows for the reduction of a cupric ion (Fehling's solution) to a cuprous ion and the formation of gluconic acid. This changes solution color from blue to red.

Mutarotation establishes an equilibrium between the α and β isomers in solution that can be followed by observing the change in optical rotation versus time. For example, if a pure crystalline isomer (say α lactose) is dissolved in solution, the optical rotation (see Chapter 2 for more details) would initially read the value for that isomer. To attain the equilibrium between isomers in solution, some of the α isomer will begin to trans-

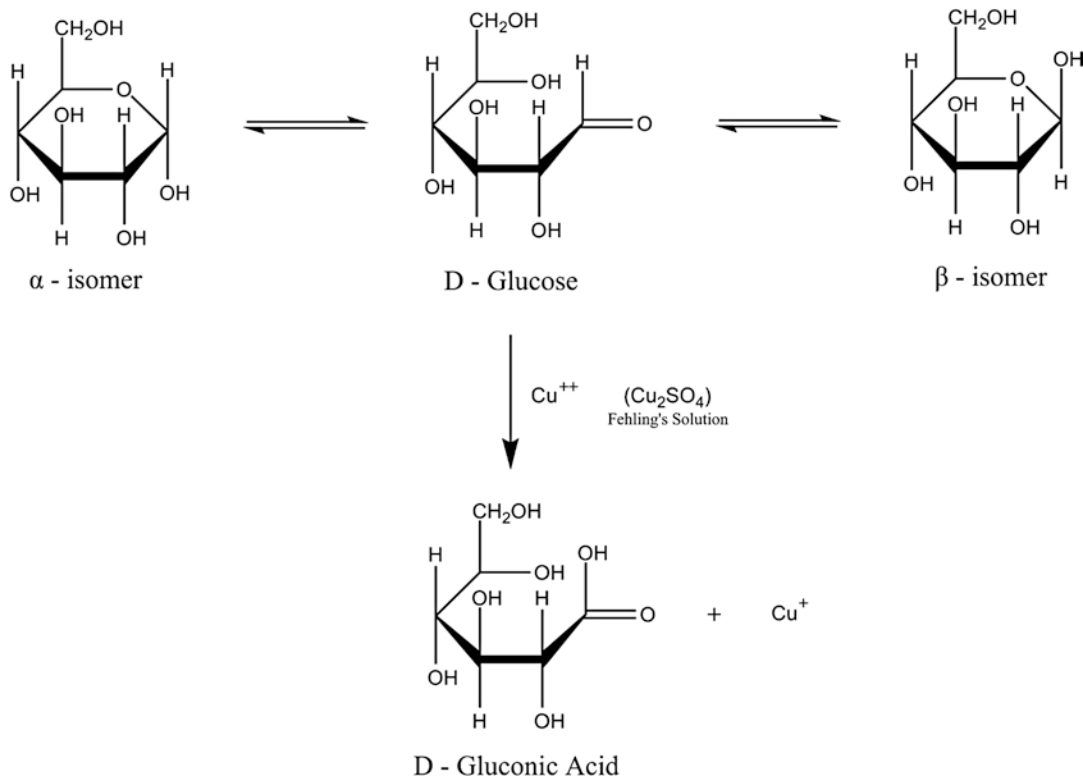


Figure 1.9 Mutarotation of glucose and reduction of cupric ion to cuprous ion

form to the β form, causing a shift in optical rotation dependent on the relative concentrations of the two isomers in solution. Eventually, equilibrium between the two isomers will be reached and the optical rotation of the mixture at equilibrium will be read. Mutarotation equilibrium depends on such solution properties as temperature and pH.

One of the most important properties of reducing sugars is their ability to participate in browning reactions. For one, they can react with proteins in the Maillard browning reaction (often called nonenzymatic browning). Reducing sugars are also needed to initiate the caramelization reaction.

1.4.3 Browning Reactions

In confections such as peanut brittle, caramel, toffee and fudge, the products of caramelization and/or the Maillard reaction are desired for the

brown color and some of the flavor. In other products, particularly hard candy, the results of caramelization reactions are undesired since they result in off-color and off-flavor. These reactions are referred to as nonenzymatic browning, in contrast to the often rapid enzymatic (e.g., polyphenol oxidase) browning reaction that occurs in freshly cut vegetables, such as potatoes and apples.

1.4.3.1 Maillard Reaction

Reducing sugars (glucose, fructose, lactose, maltose, etc.) react in the presence of an amine source (typically provided by protein) to form a variety of flavor and color (melanoidins) compounds. The reaction is named after LC Maillard, a French scientist (Billaud and Adrian 2003), who first characterized the reaction. Note that sucrose, as a nonreducing sugar, does not participate by itself in the Maillard reaction. It is only after sucrose has been hydrolyzed (inverted) to

form glucose and fructose, both reducing sugars, that Maillard browning can proceed.

The Maillard browning reaction is actually a series of steps that starts with reducing sugars and proteins, develops flavor compounds along the way, and ends with production of high molecular polymers that provide color (van Boekel 2006). Three distinct phases (initial, intermediate, and final, or advanced) are involved, although multiple reactions may take place within each phase:

1. The sugar-amine condensation and Amadori rearrangement,
2. Sugar dehydration and fragmentation, and amino acid degradation by the Strecker reaction, and
3. The formation of heterocyclic nitrogen-containing polymers and copolymers.

To initiate the reaction, the reducing sugars react with the amine to produce a glycosylamine. The amine source can either be an amino acid, a free amino group as part of a protein, or ammonia. This reaction is illustrated in Figure 1.10 with glucose as an example. The next step is referred to as the Amadori rearrangement, which results in the formation of 1-amino-1-deoxy-D-fructose. The reaction continues, even at low pH (<5), to give an intermediate that dehydrates and eventually forms the furan derivative, 5-hydroxymethyl-2-furaldehyde (HMF). The reactive cyclic compounds, such as HMF, quickly polymerize into larger compounds called melanoidins, which are both soluble and insoluble, protein-containing polymers (Wang et al. 2011). The melanoidins are primarily responsible for the color arising as a result of the Maillard reaction.

Numerous flavors are generated in the Maillard reaction with the specific compounds formed dependent on the reactants involved and the reaction conditions. Compounds such as pyrazines, pyrroles, pyridines, pyranones, oxazoles, oxalines, furans, and furanones are volatile compounds produced during the Maillard reaction that contribute to flavor. These compounds provide various flavor/aroma characteristics, including caramel-like, cooked, roasted, sweet, burnt,

pungent and nutty characteristics (van Boekel 2006). Individual reaction products contribute to overall flavor and aroma with varying intensities. The key to the overall attributes of Maillard browning are determined by the relative concentrations of the individual components produced, which is why the Maillard browning reaction can produce such widely different flavors and aromas.

For example, in chocolate, Maillard reaction products contribute significantly to the desirable flavor and provide the deep rich brown color. The simple sugars present in the cocoa bean react with proteins and peptides, both developed during fermentation. In caramel, fudge, and toffee, the reducing sugars (lactose, glucose syrup polymers, and any sucrose molecules inverted during cooking) react with milk proteins to develop the desired flavor/aroma as well as the desirable brown color.

Differences in Maillard reaction products, and hence color and flavor differences among products, are related to differences in substrate molecules, concentrations, and reaction conditions. Numerous factors have been shown to influence the rate and extent of the Maillard reaction and modify the nature of the compounds produced. Some of these factors are discussed below.

Reactant concentration As with all chemical reactions, the rate of reaction is dependent on reactant concentration, with rate increasing as reactant concentration increases. However, since the Maillard reaction is multi-step, no simple reaction order can be assigned to the entire reaction.

Sugar type The reaction rate is affected by the sugar structure, with reaction rate increasing in the order D-xylose>L-arabinose>hexoses>disaccharides. In general, differences in reaction rate for different sugars are thought to be related to the availability of the open-chain form of the sugar. Sugars that spend more time in the open-chain form undergo Maillard browning more rapidly. Ketoses are less reactive than aldoses, so glucose undergoes the browning reaction faster than fructose. Also, different reaction products

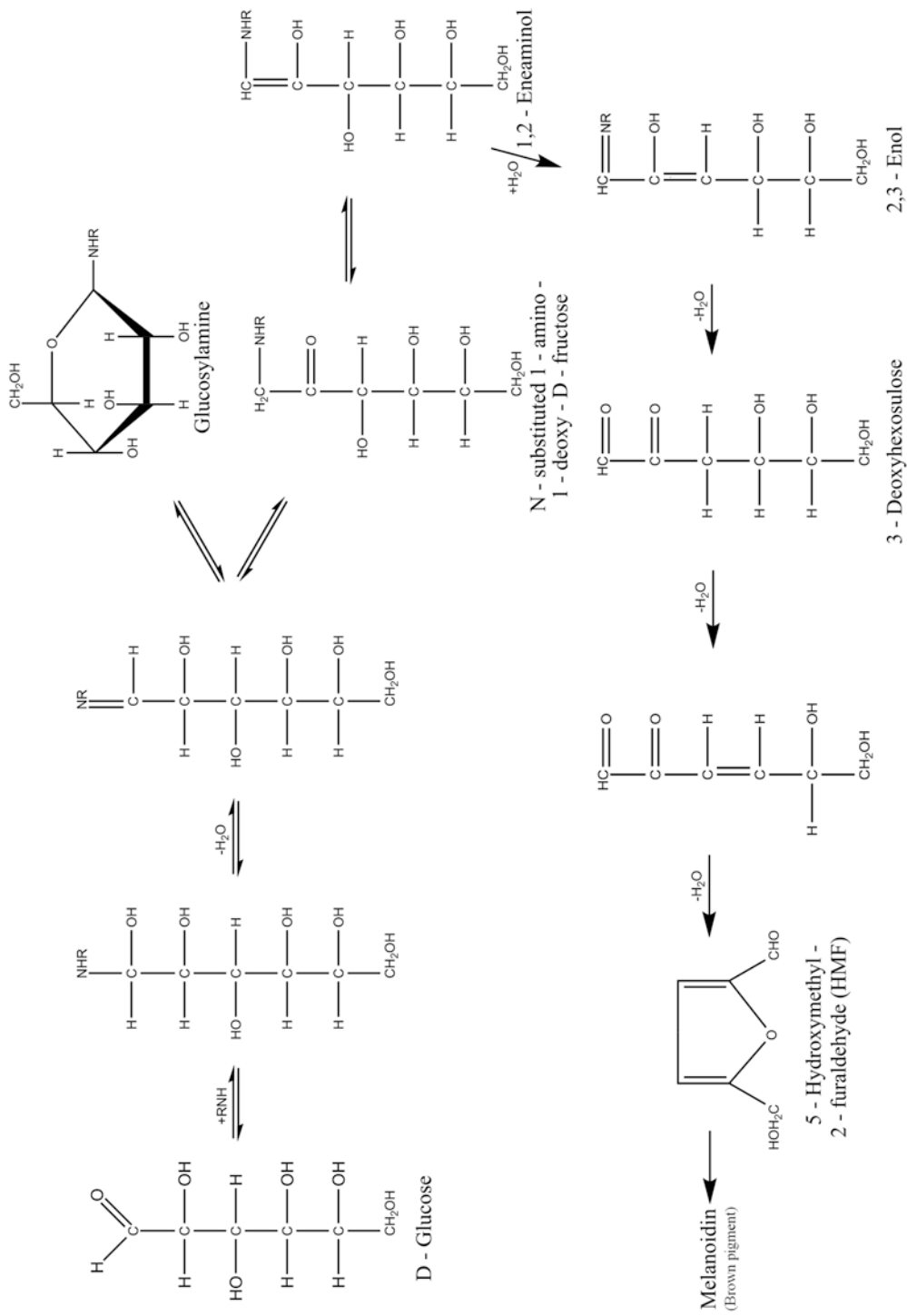


Figure 1.10 Illustration of the Maillard reaction with glucose

are formed with different sugar substrates. In confections, the typical reducing sugars present include glucose and glucose polymers, fructose (hydrolyzed sucrose), and lactose, although they are present at different concentrations and ratios in different confections. This is one of the reasons why the Maillard reaction in caramel (between milk and sugars) gives different flavors from the Maillard reaction on fermented cocoa beans.

Amine source As with the sugar component of the reactants, changing the amino group that participates in the Maillard reaction also influences both the rate of reaction and the nature of the resulting products. Some amino acid groups are more reactive than others, with lysine being a particularly labile group. With proteins, there may be more than one reactive amino group present, further complicating the reaction pathways and products produced.

Temperature As for most chemical reactions, the rate of the reaction increases with increasing temperature, although the effect is complex due to the multi-reaction characteristic of Maillard browning. Each individual reaction that contributes to Maillard browning has its own inherent temperature sensitivity, meaning that the products created vary depending on the temperature of the reaction. Color intensity increases with increasing temperature, as does the carbon content of the melanoidins produced.

pH Both rate and extent of Maillard browning increase with increasing pH over the range of pH 3–9. Due to a change in the reaction pathway as pH changes, the nature of the flavors and color pigments changes as well, although the specific changes are related to the specific reactants. The effects of pH are due to changes in the chemical nature of the reactants, specifically the extent of unprotonated amines and open-chain sugars. In caramel products, buffering salts are sometimes used to control pH, which changes the nature of the browning reaction. Buffers typically increase the rate of Maillard browning although the specific mechanism(s) are still unclear.

Moisture content The rate of Maillard browning exhibits a complex dependence on moisture content due to competing effects. At high moisture content, the reactants are diluted, which decreases reaction rate. As moisture content goes down, the rate goes up, but only to a point. When reactant concentrations are sufficiently high (low moisture content), the viscosity increases dramatically, which ultimately leads to a decrease in molecular mobility and a decrease in the rate of Maillard browning. Thus, there is an optimal water content (about 30%) where browning occurs at the fastest rate.

Minerals and metals Metal ions such as copper and iron act as catalysts and enhance the browning reactions. Fe^{+++} is more effective than Fe^{++} . Also, the mineral components in a confectionery formulation, whether added through hard water and/or milk ingredients, can influence the reaction path by helping to stabilize intermediates and allowing the reaction path to differ. Further, addition of phosphates or carbonates in confections (e.g., caramel) also can influence the reaction path, altering the nature of the flavors, aromas, and color compounds produced.

For more details on the specific nature of the Maillard browning reaction, the reader is referred to van Boekel (2006) and Wang et al. (2011) as well as chapters in food and flavor chemistry books (e.g., Belitz et al. 2004).

1.4.3.2 Caramelization Reaction

Caramelization is the browning reaction that occurs when reducing sugars are heated in the absence of protein (amine groups). In confections, it is an important reaction in production of caramels, particularly in the type of caramel process that first involves browning the sugars prior to cream addition (see Chapter 10). Caramel flavoring (and coloring) is produced in the same way, with sugar being heated in the presence of acid and then base to generate a dark, flavorful mixture that can be added to various products (e.g., licorice, etc.). In hard candy manufacture (Chapter 8), caramelization during cooking of the sugar mass is generally unacceptable since the brown color produced interferes with the normal

coloring. Rapid continuous cooking techniques produce essentially colorless cooked sugar syrups by minimizing the time at elevated temperatures to reduce the rate of caramelization.

In the first step of caramelization, reducing sugars undergo dehydration, with glucose being converted into its anhydro sugars, glucosan (1,2-anhydro- α -D-glucose) and levoglucosan (1,6-anhydro-(3-D-glucose)). Fructose, when similarly treated, gives rise to lenulosan (2,3-anhydro- β -D-fructofuranose). For sucrose to undergo caramelization, it must first be hydrolyzed into glucose and fructose (which is why acid is added at the start of caramel color/flavor production). Subsequent reactions in caramelization, including fragmentation and polymerization, generally follow the same pathways as seen in the Maillard reaction. In fact, one can think of the two reactions being similar, with the Maillard reaction being catalyzed at lower temperatures by the amine reaction whereas heat (higher temperature) is needed to initiate the sugar dehydration reactions that start caramelization.

Because the general caramelization reaction scheme is similar to that of Maillard browning (after the initial amine reaction), the products of the two reactions are often quite similar, particularly the volatile flavor compounds. Caramelization forms five- and six-membered cyclic ketones such as furanones, cyclohexones and pyrones. The Maillard browning reaction can also form these compounds, but in addition can form nitrogen-containing cyclic structures such as pyrazines, pyrroles and pyridines. Recent studies have begun to provide in-depth characterization of specific odorants found in caramelized sugar samples (Golon and Kuhnert 2012; Paravisini et al. 2012).

The color compounds produced from caramelization are also different from those of Maillard browning due to the lack of protein. In caramelization, color compounds are generally carbohydrate polymers that include caramelan, caramelen, and caramelin, with increasing molecular weight, color and solubility. The specific composition of these brown dyes depends on the type of sugar undergoing the reaction (Golon and Kuhnert 2012).

Due to the similarity of the two reactions, the factors that affect caramelization are generally the same as those that affect Maillard browning, with the exception of the amine group of course.

1.5 Glucose (Corn) Syrup

Glucose syrups created by starch hydrolysis from various plants were first discovered in Russia in 1811, with the presence of dextrose in these syrups confirmed in 1814 (Hull 2010). Discovery of sweet syrups from starch hydrolysis was a fortuitous development due to the sugar shortages during the Napoleonic wars. Interestingly, it was about the same time period when sucrose from sugar beets was first developed, making the history of these two sweeteners, both alternatives to sucrose from sugar cane, follow somewhat parallel paths.

Starch molecules found in plants, such as corn, potato, wheat, rice, tapioca, and the like, are extremely long glucose polymers, either in straight chains (amylose) or branched chains (amylopectin). Glucose syrups, products of starch hydrolysis with sweetness depending on extent of hydrolysis, are produced either by acid, enzyme or a combination of acid and enzyme hydrolysis. According to the standard of identity for sweeteners, the official name is glucose syrup. However, if the syrup is derived from the starch of a specific plant, the name may indicate the source of the starch, which is why in the United States, corn syrup is used almost exclusively. In this book, the term glucose syrup will be used to indicate the increasing trend worldwide.

According to Hull (2010), the industry uses the term “glucose” to indicate a syrup, whereas dextrose is used to indicate the crystalline product (i.e., dextrose monohydrate or anhydrous dextrose).

1.5.1 Glucose Syrup Specifications

In specifying glucose syrups, two properties are of importance: dextrose equivalent (DE) and density, expressed as °Baumé (°Be). Most commer-

cial glucose syrups provide DE and °Be as the primary specifications, with specific saccharide distribution becoming increasingly common as people recognize the importance of knowing the breakdown of individual components. °Be of glucose syrups, as a physical attribute, is covered in more detail in Chapter 2.

1.5.1.1 Dextrose Equivalent

Dextrose equivalent (DE) is a measure of the reducing power of a product, calculated in terms of glucose (dextrose) equivalents and expressed as percent of total dry substance. When starch is hydrolyzed by either acid or enzyme, smaller saccharide fractions (glucose polymers) are formed. Each fraction's terminal unit has a reducing group, regardless of the number of glucose units present in the polymer. In the determination of the DE of syrups, all reducing groups are measured and each is expressed in terms of glucose. Table 1.5 shows a typical glucose syrup composition profile along with the observed DE for each saccharide class. Glucose contributes 100 DE per unit weight, maltose contributes 58 DE, and so on to the longer chain polymers, which contribute less to the overall DE because of their larger molecular weight.

To calculate DE from a saccharide distribution, the relative weight (%) of each saccharide class is multiplied by its observed DE to obtain the contribution of that saccharide class to the total DE. For example, the glucose syrup in Table 1.5 contains 20% dextrose, with a DE of 100. Thus, glucose contributes 20 DE to the total. With 14% maltose in this syrup and an observed

DE for maltose of 58.0, the contribution to the total DE is 8.12. Similarly, trisaccharides (maltotriose) contribute 4.74 DE and tetrasaccharides 2.68 DE to the total in accordance with the principle that larger molecules contribute less to dextrose equivalents. Summing the contributions of saccharide class gives the total DE of the syrup. Due to the difficulty in measuring glucose polymers with greater than seven glucose units and their shrinking contribution to DE, the larger molecules are simply lumped into one category for the calculation. The total DE of any glucose syrup can be found in this way, once the saccharide composition has been determined.

It is often necessary to calculate the DE of a glucose syrup blend or a glucose syrup-sucrose blend. In calculating the DE of a mixture, it is important to remember that DE is expressed on a dry weight basis. As an example, calculate the DE of a blend of 60 kg of sucrose with 40 kg of a 36 DE glucose syrup with a solids content of 80.3%. The dry solids (DS) in the mixture are:

$$\begin{aligned} 60\text{kg sucrose} &= 60 \times 1.00 \text{ DS} = 60\text{kg DS} \\ 40\text{kg glucose syrup} &= 40 \times 0.803 \text{ DS} = 32.1\text{kg DS} \\ \text{Total dry solids} &= 92.1\text{kg.} \end{aligned}$$

To calculate the % DS of each component, divide the DS of each component by the total DS in the blend:

Table 1.5 Determination of dextrose equivalent (DE) from composition of glucose syrup.

Component	Composition (%)	Observed DE ^a	Contribution to DE
Monosaccharide (glucose)	20	100.0	20.0
Disaccharides (maltose)	14	58.0	8.12
Trisaccharides	12	39.5	4.74
Tetrasaccharides	9	29.8	2.68
Pentasaccharides	8	24.2	1.94
Hexasaccharides	7	20.8	1.46
Heptasaccharides and higher	30	10.2	3.06
Total	100	–	42.0

^aEquivalent DE of each saccharide

$$\begin{aligned} \text{Sucrose} & (60/92.1) \times 100 = 61.15\% \\ & \text{of the total DS is sucrose} \\ \text{Glucose Syrup} & (32.1/92.1) \times 100 = 34.84\% \\ & \text{of totals DS is glucose syrup solids} \\ \text{Total solids} & = 100.00 \end{aligned}$$

To calculate the DE of the blend, multiply the DE of each component by its %DE.

$$\begin{aligned} \text{Sucrose} & : 65.1\% \times 0\text{DE} = 0\text{DE} \\ 36\text{DE glucose syrup} & : 34.85\% \times 0.36\text{DE} = 12.55\text{DE} \end{aligned}$$

The DE of the blend is $0 + 12.55 = 12.55$ DE. Calculations like this are often important in developing formulations that meet quality specifications, as in hard candy for example, where typical DE of the sugar mixture is about 20 DE, to give the desired physical properties.

1.5.2 Production of Glucose Syrups

Production of glucose syrup is accomplished by the hydrolysis of starch (from corn, wheat, etc.) by either acid or enzyme hydrolysis or both.

1.5.2.1 Acid Hydrolysis

The first glucose syrup produced was produced by acid hydrolysis. Acid hydrolysis will hydrolyze starch randomly, cleaving both α -1-4 and α -1-6 linkages between glucose molecules. Under similar conditions of acid, heat and time, the products of starch hydrolysates are the same. Thus, it is possible to produce glucose syrup with the same saccharide composition time after time. Table 1.6 lists the saccharide composition of acid converted corn syrups (43°Be') in the range of

Table 1.6 Typical saccharide composition of acid converted 43° Baume (Be') glucose syrup in the range of dextrose equivalent (DE) 25–55

Saccharide (%)	DE			
	25	35	42	55
Glucose	8	13	19	31
Maltose	8	11	14	18
Higher saccharides	84	76	67	51

DE 25–55. In theory, it is possible to convert starch by acid hydrolysis to yield only glucose. However, trying to achieve corn syrups with higher than 58–60 DE causes individual mono- and di-saccharides to degrade, forming undesirable colors and flavors that are difficult to remove. Higher DE corn syrups can be produced with additional enzyme hydrolysis.

1.5.2.2 Enzyme Hydrolysis

Enzyme hydrolysis is very specific in contrast to acid hydrolysis, which is random. There are a number of enzymes that have specific action on starch. The actions of the amylase enzymes are shown in Figure 1.11. The enzyme α -amylase (Figure 1.11a) randomly attacks 1-4 glycosidic linkages producing a mixture of saccharides including glucose, maltose, trisaccharides and higher polymer saccharides, or maltodextrins. The formation of maltodextrins occurs because α -amylase is unable to attack 1-6 linkages. The enzyme β -amylase (Figure 1.11b) is more specific. It too attacks α -1-4 linkages, but splits off individual maltose units, thus producing corn syrups with a high maltose content.

There are a series of enzymes that are able to attack either the α -1-4 linkages of amylase or the α -1-6 linkages of amylopectin. Limited dextrinase acts on α -dextrin by attacking α -1-6 linkages, but it requires the presence of some α -1-4 linked glucose residues. It cannot attack amylopectin directly. The R-enzyme can act on amylopectin directly, but it produces only small amounts of simple sugars. Amyloglucosidase has the ability to attack both α and β linkages. Syrups containing a high amount of glucose can be produced by the use of this enzyme.

1.5.3 Composition

The ability to hydrolyze starch by acid, enzymes or a combination of the two allows for the production of various glucose syrups. Glucose syrups produced by both acid and enzyme conversions are referred to as dual converted syrups. In addition, specific blends can be made available to meet manufacturer's specifications.

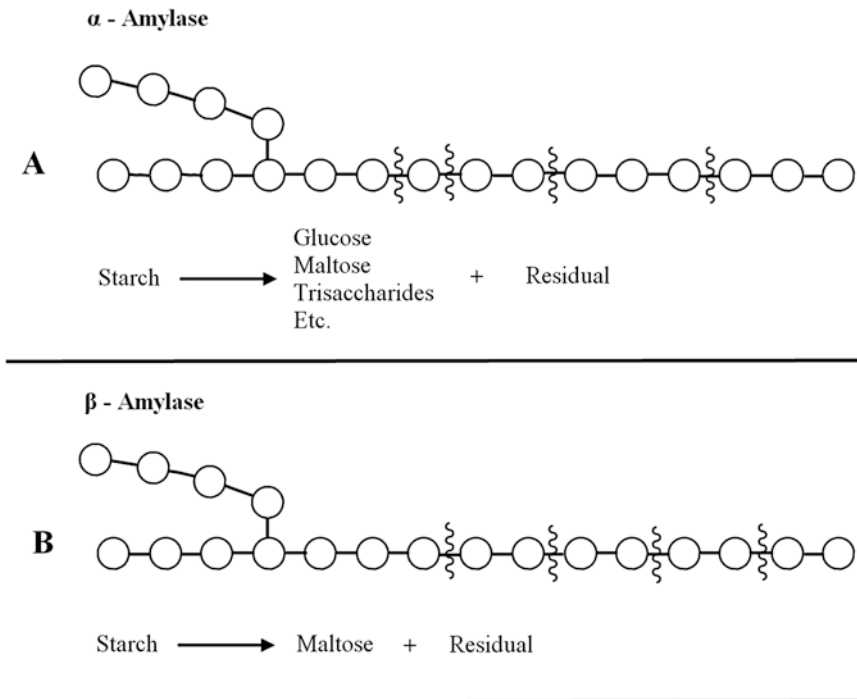


Figure 1.11 Action of amylase enzymes on starch (a) α-amylase; (b) β-amylase

High maltose syrups can be produced utilizing acid hydrolysis in combination with saccharification by the enzyme, β-amylase. Table 1.7 gives the saccharide composition of several high maltose syrups. The use of other glucoamylase enzymes will result in syrups of different compositions. The application of different types of enzymes has made it possible to produce glucose syrups with DEs higher than 60. The saccharification by amyloglucosidase of an already acid/enzyme converted glucose syrup has produced syrups with DE's ranging between 63 and 95 (Table 1.8). These syrups contain a high percentage of glucose. Typical saccharide compositions of 42 DE glucose syrups hydrolyzed by

different methods are shown in Table 1.9. Glucose syrups are often referred to by the degree of conversion – low, regular, intermediate, high and extra high. The range in DE for each is given in Table 1.10.

Because of the unique saccharide distribution, each glucose syrup has a different average molecular weight, depending on degree and nature of the hydrolysis. Technically, calculation of average molecular weight is done by first calculating the mole fraction of each saccharide and the summing the mole fractions times molecular weight of each saccharide. Pancoast and Junk (1980) provide average molecular weight values for certain types of glucose syrups. For example, they

Table 1.7 Typical saccharide composition of high maltose syrups with different dextrose equivalent (DE) converted by acid/enzyme

Saccharide (%)	DE		
	36	42	50
Glucose	6	8	10
Maltose	35	40	50
Higher saccharides	59	52	49

Table 1.8 Typical saccharide composition of high dextrose equivalent (DE) glucose syrups converted by either acid/enzymes or enzyme/enzyme

Saccharide (%)	DE		
	63	70	95
Glucose	38	45	94
Maltose	34	31	3
Higher saccharides	28	24	3

Table 1.9 Typical saccharide composition of 42 dextrose equivalent (DE) glucose syrups converted by three different methods

Saccharide (%)	Type of conversion		
	Acid	Acid/enzyme	Enzyme
Glucose	19	6	2
Maltose	34	45	55
Trisaccharides	12	12	18
Higher saccharides	55	35	25

quote 36 and 42 DE acid-converted syrups to have average molecular weights of 543 and 430, respectively, while a 62 DE acid-enzyme converted glucose syrup has an average molecular weight of 296. As expected, average molecular weight decreases as DE increases since more lower molecular weight fragments are produced with higher degree of hydrolysis. Although average molecular weight is what influences properties such as boiling point elevation, it is rare that candy makers use this level of detail.

The final end product of starch hydrolysis is the production of glucose (dextrose), when each polymer unit is completely hydrolyzed. It can be further refined, and sold as crystalline dextrose monohydrate, which contains one molecule of water for every molecule of glucose, or anhydrous dextrose. Dextrose is also sold as a liquid, but it has the disadvantage that it must be stored between 49 and 52 °C to prevent crystallization.

In the late 1960s, a process was developed to isomerize glucose to fructose in starch hydrolysates. The process is an enzyme reaction with glucose isomerase in an immobilized enzyme reactor. The product is known as high fructose (corn) syrup (HFCS). The first HFCS available was a syrup containing 71% solids composed of 42% fructose, 52% glucose, and 6% other sac-

charides. Because of the high glucose concentration, storage temperatures between 27 and 32 °C are required to prevent glucose crystallization. In 1976, a 55% HFCS was developed. The process involves a fructose enrichment step, since isomerization of glucose to fructose by enzymes above 42% is not possible. Typically, 55% HFCS contains 77% solids composed of 55% fructose, 42% glucose, and 4% other saccharides. This syrup can be used to replace invert sugar. Its other advantage, because of its lower glucose content, is that it can be stored at lower temperatures, from 24 to 29 °C. Today, a 90% HFCS product is available. This syrup has a typical solid content of 80% and contains 90% fructose, 7% glucose, and 3% other saccharides. It can be stored at lower temperature, but 21–26 °C is recommended, mainly to facilitate handling of materials containing 80% solids.

1.5.4 Properties

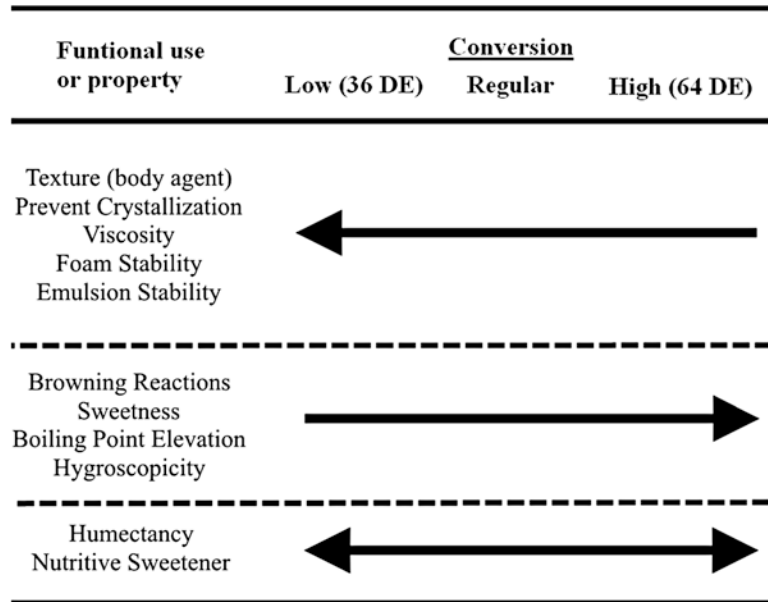
Glucose syrups are major ingredients in confections. In addition to the food value they provide, glucose syrups are used to control sweetness, texture, crystallization, browning, and humectancy. Because of the greater solubility of glucose syrups compared to sucrose, a mixture of sucrose and glucose syrup has a greater concentration than sucrose alone, with soluble solid concentrations of 75% and higher easily reached. The relationship of functional uses or properties of glucose syrups as affected by the degree of conversion is illustrated in Figure 1.12. As the DE increases, the degree of hydrolysis increases, the syrup contains more glucose and maltose, and becomes sweeter. In practice, sweetness is also affected by temperature, pH, and other substances. Table 1.11 compares the sweetness of a number of glucose syrups against sucrose.

Lower DE glucose syrups, because of their greater percentage of long-chain residuals, increase the texture or body strength and are said to increase the ability to prevent crystallization. In the latter case, the long chain residuals are thought to prevent sucrose molecules from associating to form a crystal.

Table 1.10 Common nomenclature of glucose syrups by dextrose equivalent (DE)

Corn syrup	DE range
Low conversion	26–37
Regular conversion	38–47
Intermediate conversion	48–57
High conversion	58–67
Extra high conversion	68 and higher

Figure 1.12 Relation of functional use or property of glucose syrup to the degree of conversion



High DE glucose syrups have greater numbers of reducing groups and therefore, products of the caramelization and/or Maillard reaction increase. Similarly, as the DE of a glucose syrup increases, it becomes more hygroscopic, and confections containing high levels of high- conversion syrups must be physically protected to minimize water up-take. Products containing low DE syrups are less hygroscopic and are therefore less likely to absorb water. They will also retain their moisture for longer periods of time. The use of glucose syrups to control humectancy will depend on the characteristics of the product.

Two other properties of glucose syrups that are affected by the DE are the boiling point and viscosity. As the DE of glucose syrup increases,

the boiling point increases and the viscosity decreases. The elevation of the boiling point of a solution is dependent on the number of molecules in solution. A solution containing a high DE glucose syrup will have higher boiling point than a solution containing low conversion glucose syrup.

With the reduction of high molecular weight fractions, or polysaccharides, in high conversion glucose syrups, the viscosity is reduced. Therefore, a 36 DE glucose syrup has significantly higher viscosity than a 62 DE glucose syrup at the same temperature and solids concentration.

More details on the physical properties of glucose syrups are provided in Chapter 2.

Table 1.11 Sweetness of glucose syrups of different dextrose equivalent (DE) compared to sucrose

Glucose syrup	Relative sweetness
30 DE acid – converted	30–35
36 DE acid – converted	35–40
42 DE acid – converted	45–50
62 DE acid – converted	60–70
HFCS ^a 42% fructose	100
HFCS 55% fructose	100–110
HFCS 90% fructose	120–160

^aHigh fructose corn syrup

1.6 Polysaccharides

Polysaccharides are used in candies primarily as bulking agents. There are three major types: maltodextrin, polydextrose, and inulin.

1.6.1 Maltodextrin

Maltodextrin is a dried starch hydrolysate with a low DE, from as low as 1 and up to a maximum of 20 (above 20, it is technically called glucose syrup). Depending on DE, maltodextrins contain predominantly longer-chain, higher molecular weight saccharides between 3 and 17 glucose units (degree of polymerization, or DP, from 3 to 17). A 10 DE maltodextrin, for example, contains on the order of 64% saccharides above DP 11.

Functionally, maltodextrin is not hygroscopic and dries into a noncrystalline (amorphous) powder. Because of its low sweetness, it must be used in combination with other alternative sweeteners. In confections, besides acting as a bulking agent, maltodextrins may be used to provide foam stabilization (due to high viscosity), control sucrose crystallization, form barrier layers prior to sugar panning, act as a glaze on panned goods, and serve as a binder in tabletted confections.

1.6.2 Polydextrose

Polydextrose is a randomly-bonded polymer of glucose with minor quantities of sorbitol and citric acid incorporated into the polymeric chain. It is prepared by vacuum condensation of a molten mixture of glucose, sorbitol, and citric acid at a ratio of 89:10:1. The polymer size is controlled by the presence of the sorbitol, with most polymers having molecular weight less than 5,000 g/mole. For this reason, polydextrose is very water soluble. However, solutions containing more than 70% solids become impractical to work with because of the high viscosity. Polydextrose is a white to light tan powder with a bland to slight bitter taste. Several different forms are available on the market depending on the application.

Human enzymes do not recognize most complex polymers because of their random nature. Therefore, polydextrose contains only 1 kcal/g and is considered a soluble fiber. It has no sweetness, but possesses most of the other chemical and physical properties of sucrose, making it a good sugar replacer.

1.6.3 Inulin

Inulin, another soluble fiber, is a natural occurring polysaccharide – a polymer of fructose (Izzo 2002). It is found naturally in onion, leek, chicory, and Jerusalem artichoke, among other plants. It is a β (2–1) fructan with chain length ranging from 2 to more than 60 fructose units (average of about 10 units), with a glucose molecule typically at the polymer terminus. Manufacturing processes involve similar steps as used for refining sucrose – water extraction from the plant source, purification followed by spray drying. It has a slightly sweet taste and low water solubility. It has low reducing power, but is subject to acid hydrolysis, yielding fructose. As with polydextrose, it is not digested and thus, has reduced caloric value of approximately 2 kcal/g.

Inulin contributes to texture in confections. It can be used to replace sugar and provide a source of fiber in fruit chews, caramels, high fiber lozenges, and chocolates and coatings (Izzo 2002).

1.7 Other Natural Sweeteners

Honey, maple syrup, molasses, and malt extract are also sweeteners in confections. Although they have sweetening properties, they are mostly used as flavor ingredients.

1.7.1 Honey

Honey, no doubt, is the oldest and original sweetener. Its use long preceded the development of sugar. In essence, honey is a natural high invert

Table 1.12 Composition (%) of United States honey

Composition	Average	Range
Moisture	17.2 ± 1.5	13.4–22.9
Fructose	38.2 ± 2.1	27.2–44.3
Glucose	31.3 ± 3.0	22.0–40.7
Free acid (as Gluconic)	0.43 ± 0.16	0.13–0.92
Lactone	0.14 ± 0.07	0.00–0.37
Ash	0.169 ± 0.15	0.020–1.028

sugar, containing primarily glucose and fructose. The composition of honey can vary considerably, depending on a variety of factors. Table 1.12 lists the average composition of U.S. honey. The fructose content is always higher than the glucose content with the ratio varying between 1.15 and 1.35.

Honey is used essentially for flavor purposes in confectionery, although it also retards sucrose crystallization. The flavor depends on the source of nectar. Clover and orange blossom honey have a very delicate flavor and are preferred. Alfalfa and buckwheat honey have very strong flavors. Honey varies in color from amber to white.

1.7.2 Maple Syrup

Maple syrup is produced in northeastern and midwestern United States and Canada. It is prepared by evaporating the sap from the maple tree. Sap contains between 2 and 3 wt% solids of which approximately 96% is sucrose and the remainder other carbohydrates, protein, organic acids, ash, and lignin-like materials. Maple syrup, by federal specification, must contain 66 wt% solids with a specific gravity of 1.35 (37.75 Be'). Flavor and color develop during the evaporation process as a result of both the caramelization and Maillard reactions (see Section 4.3).

Typical saccharide composition of maple syrup is 88–99 wt% sucrose and 0–12 wt% invert sugar. Crystallized maple syrup candies must be made with minimal invert sugar content to attain the desired crystallinity and texture.

In confections, maple syrup is primarily used for its unique flavor. Because of price considerations, artificial maple flavor is often substituted; however, real maple syrup still finds application in fudges and creams, particularly in combination with walnuts.

1.7.3 Molasses

Edible molasses as described earlier is the by-product of cane sugar refining. In the refining process, several sugar crystallization steps take

place to further purify the sucrose for separation. After the first crystallization, the mother liquid is called first molasses. First molasses is recrystallized, resulting in additional sucrose separation and a second molasses. After a third crystallization, the third molasses is sold as blackstrap, final or can molasses. The raw sugar obtained from these crystallizations is combined with water to dissolve residual molasses and is separated by centrifuge. The separated syrup is called affination liquor. The sugar is dissolved in water and subjected to several crystallizations. The mother liquid from the final crystallization is combined with the affination liquor and crystallized to produce a dark sugar and a mother liquid refiners molasses. It is similar to final molasses, but of better quality.

Typical molasses contains 80 wt% solid with 60 wt% as invert sugar. It also contains numerous vitamins and minerals. Because of this large amount of invert sugar, molasses inhibits sucrose crystallization. Molasses can be dried and is available in powdered form.

Molasses is commonly used as a flavorant in licorice, but also may be used in such confections as taffy, hard candy, creams, and caramel to provide unique flavoring. One unique candy made with molasses (and peanut butter) is the Mary Jane, a chewy (taffy-like) old-time candy.

1.7.4 Malt Extract

Malt extract, available as either a concentrated extract or a powder, is manufactured from high grade brewing barley. It is considered a sweetening ingredient because of its high maltose content. To make malt extract, barley kernels are wetted and allowed to germinate under controlled conditions of temperature and humidity. During germination, the starch is solubilized by enzyme action and the protein is partially degraded to peptides and amino acids. This step is followed by kiln drying in which the enzymes are retained. The germinated and dried grain is then extracted with water, and the extract filtered and concentrated to 80% total solids. The concentrate may be vacuum dried to produce a powder. The sac-

charide composition of an extract of 80% solids is approximately 55% maltose, 4% sucrose, 2% glucose, 2% fructose and 13% dextrans. Such a syrup resembles a high-maltose syrup but also contains some protein as well as amino acids, vitamins and minerals.

Malt extract has specific application in confections as a flavoring ingredient. Arguably the most popular candy containing malt extract is the malted milk ball, a puffed sugar candy coated with chocolate.

1.8 Alternative Sweeteners

Sucrose has been and remains a main ingredient in confections. Its desirable physical and chemical properties have made possible the development of many different confections; it has made confections popular throughout the world. In addition, sucrose is an excellent source of energy, at relative low cost.

Over the past few decades, however, sucrose has been a subject of controversy over its nutritional role in the diet. Studies and debates have centered around the involvement of sucrose in such issues as dental caries, obesity, diabetes, hypertension, hypoglycemia, and behavioral problems. Each of these issues have influenced the consuming public's attitude toward sucrose and has created a demand for no-sucrose or "sugar-less" confections to avoid the negative nutritional aspects of sugar, whether real or perceived. The challenge, therefore, has been to find sugar alternatives that both retain most of the beneficial properties of sucrose yet eliminate, or at least minimize, the concerns of the consumer. The most used sucrose alternatives are sugar alcohols, hydrogenated starch hydrolysates (HSH), polydextrose, and intense sweeteners.

1.8.1 Sugar Alcohols

Sugar alcohols, also known as polyols, are not sugars, but are the reduced form of sugars. They occur in nature, but at low concentrations, which make extraction impractical. They are industri-

ally derived from the corresponding saccharide by catalytic hydrogenation, with the exception of erythritol, which is prepared by fermentation of glucose. The general reaction to form the alcohol from a sugar is shown in Figure 1.13 for hydrogenation of glucose into sorbitol. In the reaction, a hydroxyl group replaces either the ketone or aldehyde group of the sugar. Hydrogenation of fructose yields mannitol, xylose yields xylitol, maltose yields maltitol, lactose yields lactitol, and finally, hydrogenation of glucose syrup yields hydrogenated starch hydrolysates (HSH).

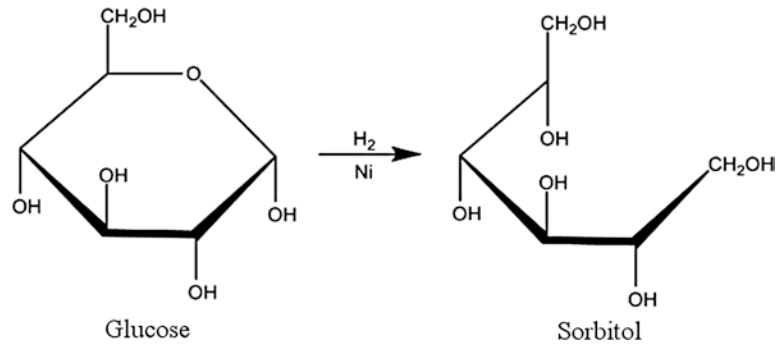
Polyols play an important role in confectionery products, particularly those targeted towards the diabetic market because of their lack of an insulin response. They are also used to provide caloric reduction due to their limited absorption in the stomach despite the laxative effect due to their subsequent fermentation in the intestines. Polyols can also provide humectancy, reduction of water activity and control of crystallization in confections. Most polyols provide a significant cooling effect and are noncariogenic. Because they are nonreducing, they also do not participate in either browning reaction. A summary of various properties of polyols is provided in Table 1.13.

1.8.1.1 General Properties of polyols

Polyols do not exhibit reducing power, because the aldehyde group of the sugar has been reduced to an alcohol. They therefore do not undergo the caramelization or the Maillard reactions. Thus, if the typical brown color generated in these reactions is desirable in a confection, as in caramel, fudge or toffee, artificial colors must be added to a sugar-free version based on polyols. Polyols are also mostly stable to acids and can withstand high temperatures for extended time. If discoloration does occur in polyol solutions, hydrolysis must first take place. For example, maltitol hydrolysis yields glucose and sorbitol, and the glucose molecule can now participate in either or both browning reactions.

Polyols, with the exception of xylitol, are less sweet than sucrose (Table 1.13). In many confectionery applications, the lower sweetness of polyols is offset with the addition of intense

Figure 1.13 Catalytic hydrogenation of glucose



sweeteners, but this depends to a large extent on which polyols are used in a formulation.

Polyols have a higher negative heat of solution compared to sucrose, with the exception of maltitol, which has a negative heat of solution similar to sucrose (Table 1.13). When the crystalline forms dissolve in water a cooling effect is observed. This pleasant cooling sensation can be an advantage in enhancing consumer enjoyment in such products as mint-flavored candies. More details are provided on heats of dilution and solution in Chapter 2.

Polyols are virtually nonfermentable and are, therefore, considered noncariogenic. The nonfermentable characteristic by oral bacteria prevents acid production and reduction in pH value, conditions that are associated with tooth decay. In the intestine, they are slowly absorbed and enter the liver without the need for insulin. They are converted to fructose and ingestion of polyols therefore results in lower plasma glucose. For this reason, polyols are recommended for diabet-

ics. Products that are sold for use by diabetics are required by the United States Food and Drug Administration (FDA) to carry the labeling statement “Diabetics: This product may be useful in your diet on the advise of a physician.” However, the incomplete digestion and slow absorption of polyols can lead to gastrointestinal problems. This can occur if excessive amounts are consumed at one time, but in some people, there can also be a cumulative effect. The extent of the laxative effect depends on the polyol consumed. A daily threshold value for each polyols is given in Table 1.13. FDA requires that if it is reasonably foreseeable that consumption may exceed the threshold value, the label statement, “excessive consumption may have a laxative effect” must be given.

The slow absorption rates of polyols are responsible for their lower caloric content compared to sugar. Caloric content (in kcal/g) for different polyols are listed in Table 1.13. The values listed are those for the United States. Other coun-

Table 1.13 Properties of polyols

Polyol	Relative sweetness	Laxation threshold	Solubility 25 °C (g/100ml)	Heat of solution (cal/g)	Caloric content (kcal/g)
		(g/day)			
Erythritol	60–70	High	61	–43.9	0
Xylitol	100	50	200	36.6	2.4
Sorbitol	60	50	235	–26.5	2.6
Mannitol	50	20	22	–28.9	1.6
Maltitol	90	100	175	–5.5	3.0
Lactitol	40	20–50	140	–13.9	2.0
Isomalt	40–50	50	39	–9.4	2.0
Sucrose	100	–	185	–4.5	4.0

tries may use slightly different values. In fact, Europe simply states that caloric content of all polyols is 2.4 kcal/g, regardless.

One final property of note for polyols is viscosity. As with all sugars, viscosity of polyol syrups increases with increasing concentration in solution and with decreasing temperature. However, the viscosity of a saturated solution of polyols follows a different trend from that of sucrose and this can have significant ramifications where solution viscosity is important, as in hard panning (see Chapter 13). Unlike for sugars, where viscosity at saturation decreases with increasing temperature, the viscosity of some saturated polyol solutions increases with increasing temperature, dependent on the relative effects of temperature on solubility and viscosity. See Chapter 2 for more on sweetener viscosity.

1.8.2 Monosaccharide Alcohols

The monosaccharide sugar alcohols comprise a major category of polyols used in confections. Of particular interest are sorbitol, mannitol, xylitol, and, to some extent, erythritol.

1.8.2.1 Sorbitol

Sorbitol is the most widely distributed natural polyol. It is found in many fruits such as cherries, plums, apples and pears. It is commercially produced by catalytic conversion of D-glucose (Figure 1.13). It was first isolated from a mountain berry called “sorb apple”, from which it derived its name. It is available in either crystalline or liquid form at concentration of 70%. The liquid form may contain small amounts of mannitol to prevent crystallization. It is most often found in sugar-free gum, but may also be used in pressed tablets and hard candy. Its high hygroscopic nature makes it an excellent humectant. In chewing gum, for example, sorbitol retards the loss of moisture and prevents drying out of the gum. Sorbitol can also be used for hard panning although it is not widely used for that purpose.

Crystalline sorbitol is polymorphic, meaning that it can exist in multiple crystalline forms. The γ polymorph is the most stable, with a melting

point of about 98–99 °C (Nezzal et al. 2009). The α and β forms are very hygroscopic and therefore, have limited application. Under the influence of moisture and heat, the unstable forms transform to the stable, γ , form.

1.8.2.2 Mannitol

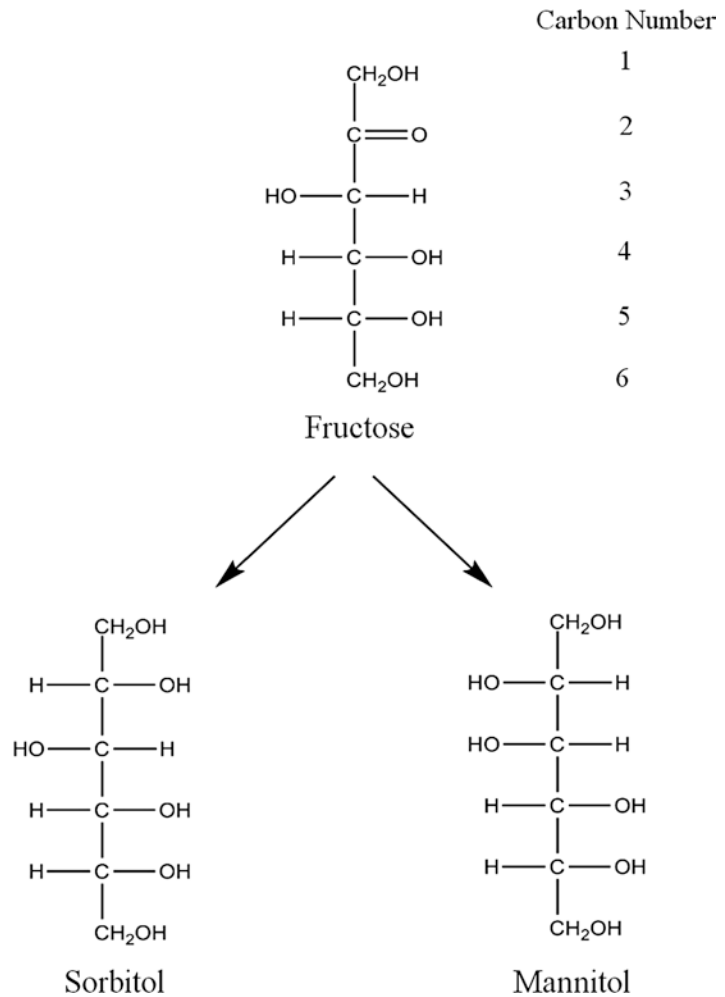
Mannitol is found in nature in algae, mushrooms, celery and olives. Originally, it was commercially extracted from algae, but today it is produced by hydrogenation of fructose. The hydrogenation of fructose yields both mannitol and sorbitol. The reaction is shown in Figure 1.14, as illustrated in the Fischer projection to clearly show that hydrogenation creates an asymmetric carbon at carbon 2 and thus, results in two isomers, sorbitol and mannitol. Because of the mixture of polyols during hydrogenation, the manufacturing process must include a separation step, which makes the manufacturing of mannitol a more expensive process. Pure mannitol, because of its low solubility (Table 1.13), can be crystallized and is available only as a powder. Its low hygroscopicity and excellent flow characteristics make mannitol a valuable ingredient in tableted confections. It may also be used in sugar-free chocolate and as a dusting powder in chewing gum.

1.8.2.3 Xylitol

Xylose is found in nature in woody plants and a number of fruits and vegetables. Xylitol was first produced by hydrolyzing xylan from birch trees to form xylose and then hydrogenating xylose to form xylitol. It is a pentahydric alcohol, which means it has a five-carbon chain, in contrast to sorbitol and mannitol, which are polyhydric alcohols and have six-carbon chains. Today, any hemicellulose source, such as corn cobs, may be used as raw material. It is commercially available as a white crystalline powder.

Xylitol is hygroscopic, with moisture uptake accelerating rapidly at relative humidity above 80%. It is less hygroscopic compared to sorbitol, which begins to absorb moisture above 70% relative humidity. Xylitol solutions are heat stable, withstanding temperatures as high as 200 °C. The viscosity of xylitol is lower than sucrose or other polyols. The low viscosity may affect the texture

Figure 1.14 Catalytic hydrogenation of fructose



of confections and the addition of a bodying agent such as polydextrose may be required. Because of its high cost of production, and its sweetness level similar to sucrose, it is often mixed with other, less expensive sweeteners. Xylitol is recognized as the most effective among all polyols in preventing caries. There is evidence to suggest that xylitol may even be anticariogenic.

In confections, xylitol is most often used in sugar-free gums, both within the gum as well as in a hard-panned shell. Its relatively rapid crystallization rate makes it useful in hard-panned shells. It may also be used in pressed tablets. Its high cost often limits its use.

1.8.2.4 Erythritol

Erythritol is the only 4-carbon chain polyol. It is the reduced form of erythrose (Figure 1.4). Erythritol is produced by yeast fermentation of glucose, meaning it can potentially be used in natural products. In human metabolism, it is absorbed and excreted unchanged via the kidney, which explains its low caloric content (Table 1.13). It has the highest negative heat of solution among all polyols, which is its major functional limitation. While the extreme cooling sensation when eaten goes well with mint pieces, it is not generally a desired effect.

1.8.3 Disaccharide Alcohols

Disaccharide alcohols have become important confectionery ingredients. These include isomalt, maltitol, and lactitol.

1.8.3.1 Isomalt

Isomalt is produced from sucrose in a unique two-step process. Sucrose, a nonreducing sugar,

is first transformed by the enzyme sucrose-glucosylfructose-mutase into a reducing sugar, isomaltulose. In this transformation the 1-2 linkage is converted to a 1-6 linkage, thus forming a free ketone group at the fructose molecule. Isomaltulose is then hydrogenated to give isomalt, an equimolar mixture of gluco-sorbitol (α -D-glucopyranosyl- (1-6)-D-sorbitol) and gluco-mannitol (α -D-glucopyranosyl-

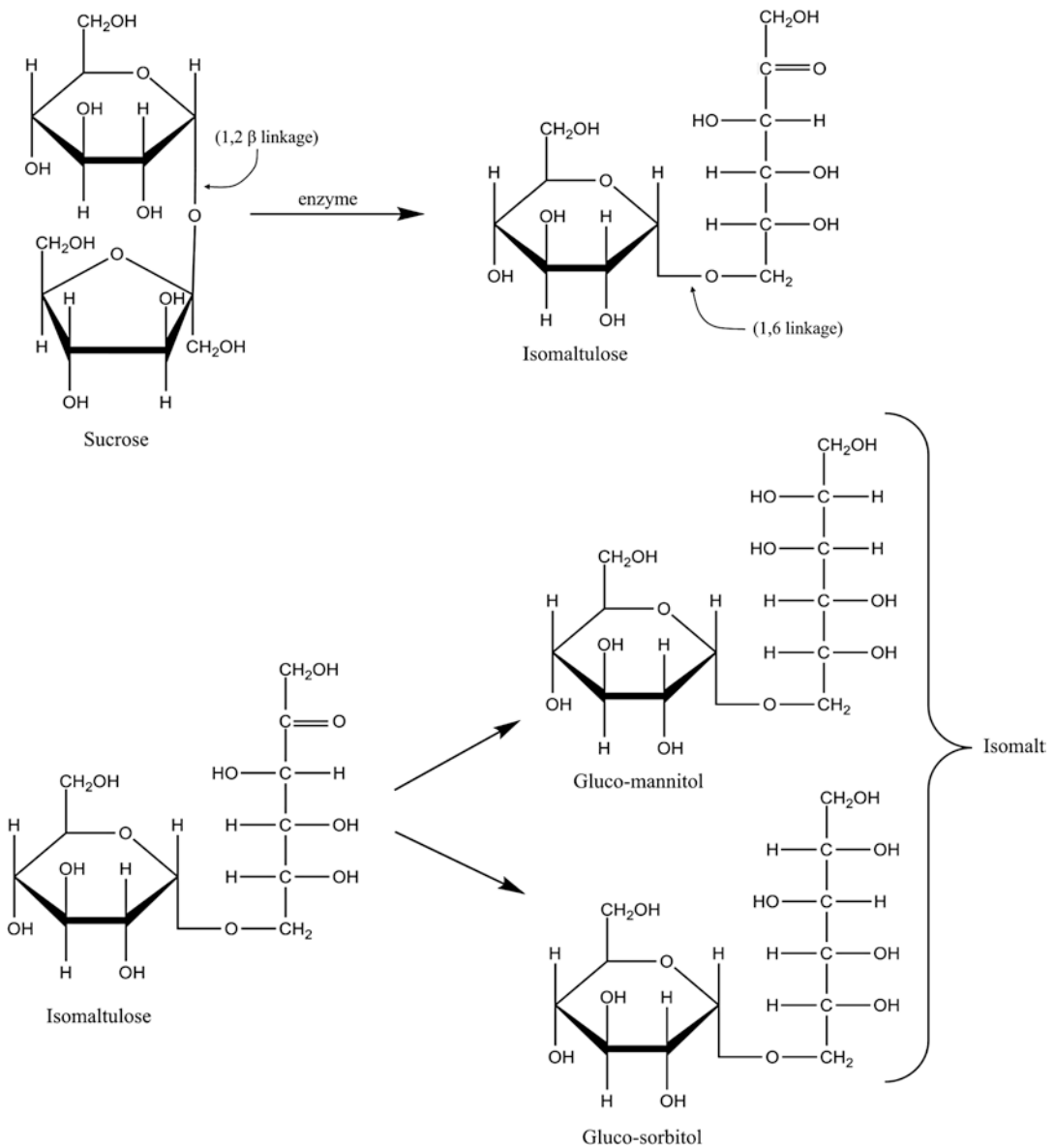


Figure 1.15 Conversion of sucrose to isomalt

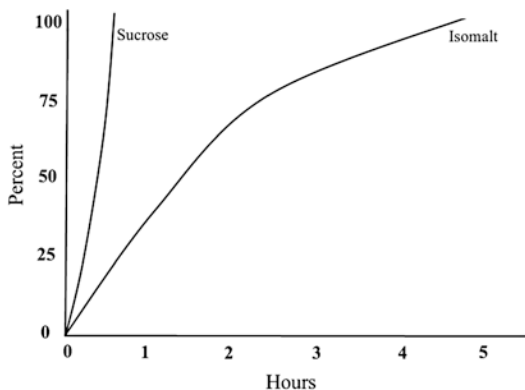


Figure 1.16 Hydrolysis of isomalt vs. sucrose in 1% HCL at 100 °C

(1-6)-D-mannitol). The reactions are shown in Figure 1.15.

Isomalt is a white, odorless, crystalline, non-hygroscopic substance. Many of its properties are similar to sucrose, which allows, in many applications, the direct substitution for sucrose. It is very stable and, because it is only half as sweet as sucrose, isomalt serves as an excellent bulking agent. A comparison of the stability of sucrose and isomalt in 1% HCL at 100 °C is shown in Figure 1.16. As seen, isomalt is more resistant to hydrolysis under acidic conditions than sucrose.

Because of its similar properties to sucrose, isomalt is often used as a direct sucrose replacement. For example, hard candies are often made with isomalt, with similar physical properties and shelf life as sucrose-based hard candies. Isomalt can also be used in sugar-free hard panning, giving a shell with similar crisp character as sucrose.

1.8.3.2 Maltitol

Maltitol is the product of hydrogenation of maltose, produced by hydrolysis of starch. Maltitol is used in confections as either a crystalline powder or as hydrogenated high maltose syrup (see below). Powdered maltitol is produced either by crystallizing from a maltitol syrup or by direct extrusion crystallization of the syrup. The former method produces maltitol powders of higher purity than the latter.

Refined crystalline maltitol has many similar properties as sucrose, including sweetness, solu-

bility and low hygroscopicity. It may be used to replace sucrose in fondants and creams, chocolates and coatings, or hard-panned candy shells.

1.8.3.3 Lactitol

Lactitol, like mannitol, is produced by hydrogenation of its parent disaccharide, in this case lactose. Hydrogenation occurs at the glucose portion of the molecule. Lactitol is primarily found as a crystalline powder with high stability to both temperature and acid. Both lactitol and maltitol are sweeter than their parent disaccharide (Table 1.13).

Lactitol is not used widely in confections, but finds application in hard candy, hard-panned shell candy, and sugar-free chocolates and coatings.

1.8.4 Hydrogenated Starch Hydrolysate (HSH) and Maltitol Syrups

HSH syrups are manufactured by the hydrogenation of glucose syrups (or starch hydrolysates). HSH syrups are mixtures of various chain length polyols, with composition dependent on the type of glucose syrup used as the starting point. In the hydrogenation of glucose syrups, glucose is converted to sorbitol, maltose to maltitol and so on through the range of glucose polymers present in the glucose syrup (Figure 1.17). Analogous to glucose syrups, the composition of HSH syrups are described based on the chain length or degree of polymerization (DP) of the saccharides. Specifications will give the amounts of monosaccharide polyols (DP 1), disaccharide (DP 2), tri- to hexa- (DP 3–6), and over DP 6. Maltitol syrups are a subset of HSH, made by hydrogenating high-maltose syrup. They must contain a minimum of 50% maltitol (dry basis).

As with glucose syrups, HSH syrups have different properties when used in confections, dependent on the composition. HSH syrups with low average molecular weight provide enhanced humectancy and sweetness and are more hygroscopic than those with higher average molecular weight. However, HSH syrups with larger mole-

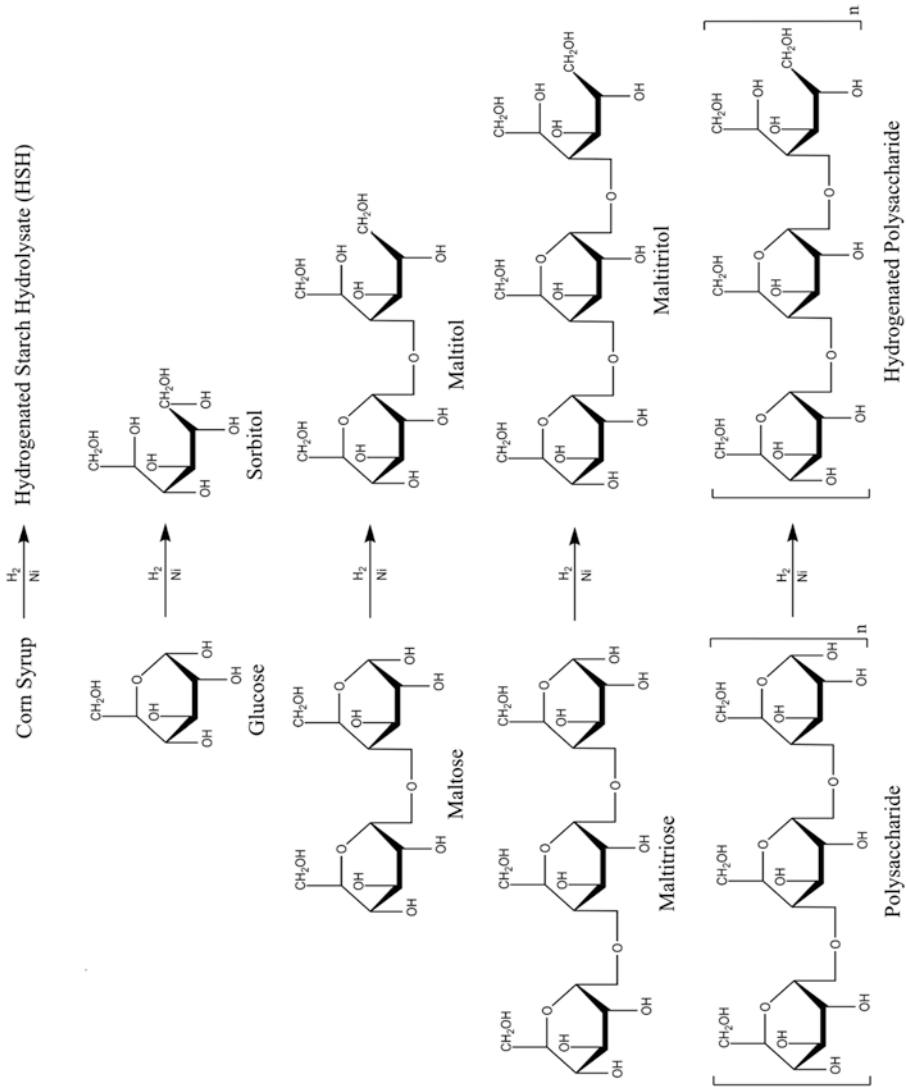


Figure 1.17 Catalytic hydrogenation of glucose syrup

cules provide enhanced viscosity and stability. During digestion or heating, particularly under acid conditions, HSH syrups may be hydrolyzed into glucose and sorbitol. The reducing groups formed will then participate in reactions that require reducing groups including fermentation, which could promote dental caries.

HSH syrups find wide application in confections. They are often used in the same manner as glucose syrup in sugar confections, to provide bulking capacity and for controlling crystallization. As such, they can be used in sugar-free versions of chewing gum, hard candy, gummies and jellies, fondants and creams, and caramels and taffy. In gum, for example, HSH can be used to moderate the recrystallization of sorbitol and to provide humectancy.

1.9 High Intensity Sweeteners

High intensity sweeteners are used with bulking agents that are less sweet than sucrose. A number of these sweeteners have been developed, including sucralose, aspartame, acesulfame-Potassium (Ace-K), alitame, thaumatin, neotame, and stevia, with new ones continually being studied.

Reviews of these noncaloric sweeteners can be found in DuBois and Prakash (2012) and Pawar et al. (2013). Their use is often limited by regulatory status and/or limitations related to their physical properties. Fortunately, usage levels in confections are very low, less than 0.1%. Chemical structures of some high intensity sweeteners are shown in Figure 1.18.

1.9.1 Sucralose

Sucralose, or trichlorogalactosucrose (Figure 1.18), is 600 times as sweet as sucrose with a clean sweet taste with lingering sweetness in the aftertaste. It is a nonnutritive sweetener that is stable to acid hydrolysis. It is hygroscopic and if slightly moist at low pH, hydrolysis can occur. Its solubility in water at 20 °C is 283 g/L.

1.9.2 Aspartame

Aspartame, marketed as Nutrasweet®, is the methyl ester of the peptide aspartylphenylalanine (Figure 1.18). It has a sweet taste 180–200 times as intense as sucrose. Aspartame has a clean

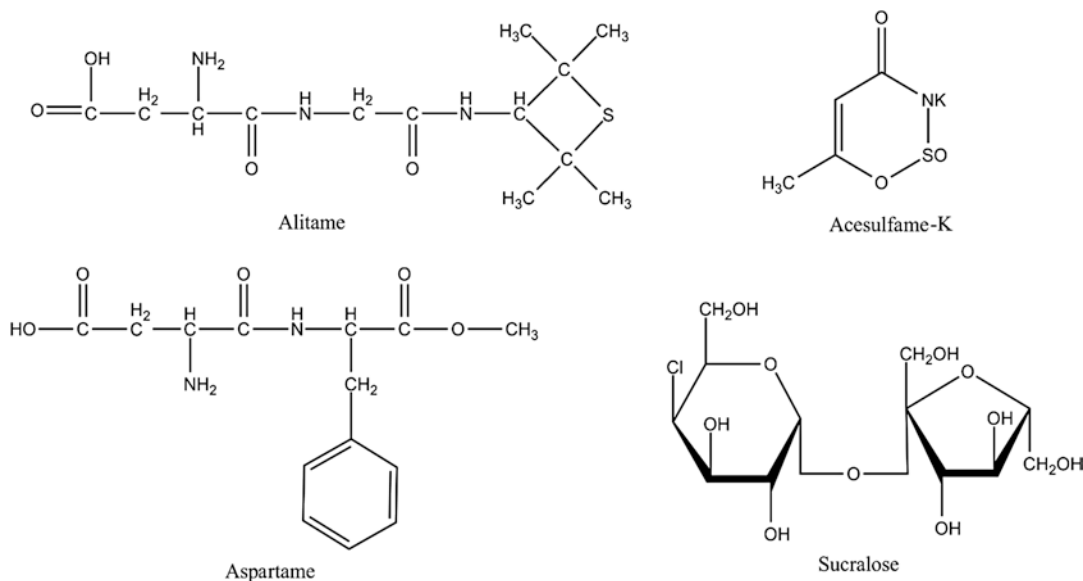


Figure 1.18 Structure of some high intensity sweeteners

Table 1.14 Solubility (%) of aspartame in water as affected by pH value

pH	Temperature (°C)		
	4.5	20	30
1.0	3.5	4.5	7.0
2.0	6.0	7.5	10.0
3.0	2.0	2.5	3.0
4.0	0.75	1.0	1.35
5.0	0.5	0.75	0.9

sweetness, with a sweet aftertaste. It has a low solubility (Table 1.14) and is not heat stable. Even at room temperature, it degrades into its component parts, including the amino acid phenylalanine, which some people cannot tolerate. This limits its usage in confections, due to the heat treatment required for most candies. Its primary use is in gum products, although, even in gum, deterioration of aspartame is of sufficient concern that significant efforts have gone into means of protecting it to retard or prevent its degradation. Although a nutritive sweetener, because of its low usage level, it contributes little to the caloric value of a product.

1.9.3 Acesulfame-Potassium

Acesulfame-K (Figure 1.18) is a nonnutritive sweetener, marketed under the trade name Sunette© and Sweet One©. Its sweet sensation is 200 times that of sucrose, with a bitter/metallic

Table 1.15 Solubility (%) of alitame in water as affected by pH

pH	Temperature (°C)				
	5	20	30	40	50
2.0	42	49	56	50	54
3.0	32	39	47	51	54
4.0	13	14	17	20	38
5.0	12	13	15	17	29
6.0	12	13	15	20	33
7.0	12	14	18	30	52
8.0	15	25	47	56	52

taste. Acesulfame-K is highly water-soluble and heat stable. At 0, 20 and 100 °C the solubility in water is 14, 27 and 130 g/100 ml, respectively. It has a synergy with other sweeteners and reduces some of their undesirable effects; thus, it has much promise when used in combination with other intense sweeteners.

1.9.4 Alitame

Alitame is a dipeptide (Figure 1.18) with a clean sweet taste and sweetness approximately 2,000 times that of sucrose. Since it is partially metabolized, it contributes 1.4 cal/g, although because of the low usage level, its caloric contribution is negligible. It is stable to hydrolysis, but has potential for off-flavor development during storage. Alitame is fairly soluble in water, primarily at pH values below 3 and above 7 (Table 1.15).

1.9.5 Thaumatin or Talin

Thaumatococcus is a plant protein extract. It is a single chain polypeptide of 207 amino acids with 8 disulfide bonds and a molecular weight of 22,209. As with alitame, it is 2,000 times sweeter than sucrose. The sweet sensation has a slow onset and is long lasting with a licorice aftertaste. Its solubility at 20 °C is 60.0 g/100 ml. The stability toward heat is pH dependent. It is most stable at pH 2.7–6.0, with optimal stability at pH 2.8–3.0. In the United States, it is considered a flavor ingredient.

1.9.6 Neotame

Neotame is chemically similar to aspartame, but with a dimethylbutyl group attached to the amino group of the aspartic acid component. This modification causes neotame to be about 8,000 times sweeter than sucrose (about 400 times sweeter than aspartame), meaning that very low levels are needed for sweetening purposes. Neotame is also much more stable than aspartame. It is not used widely in confections at this time.

1.9.7 Stevia

The steviol glycosides, extracted from the stevia plant, are made up primarily of stevioside, rebaudside A, and rebaudside C. Stevioside is 250–300 times as sweet as sucrose, while rebaudside A is 350–450 times sweeter. Commercial products based on stevia are primarily composed of rebaudside A since it is the sweetest component with least bitterness. Rebaudside A is separated from the stevia leaf extract through a crystallization refining operation. In some countries, stevia may be considered natural.

1.9.8 Luo Han Guo (Monk Fruit) Concentrates

The luo han guo fruit (often called Monk fruit) contains mogroside V, along with several mogrol glycosides, with varying degrees of sweetness. Mogroside V is about 250 times sweeter than sucrose. Commercial products are dried fruit juice concentrates with a sweetness potency of about 100. Because it is derived from the fruit itself, these dried concentrates can be considered natural.

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