

Introduction

Carbohydrates are organic compounds containing carbon, hydrogen, and oxygen, and they may be simple or complex molecules. Historically, the term “carbohydrate” has been used to classify all compounds with the general formula $C_n(H_2O)_n$ as the hydrates of carbon. Important food carbohydrates include simple sugars, dextrans, starches, celluloses, hemicelluloses, pectins, and gums. They are an important source of energy or fiber in the diet, and they are also important constituents of foods because of their functional properties. Carbohydrates may be used as sweeteners, thickeners, stabilizers, gelling agents, and fat replacers.

The simplest carbohydrates are known as *monosaccharides* or sugars, and they have the general formula $C_nH_{2n}O_n$. The most common ones contain six carbon atoms. *Disaccharides* contain two sugar units, *trisaccharides* contain three, *oligosaccharides* contain several units, and *polysaccharides* are complex polymers containing as many as several thousand units linked together to form a molecule. These carbohydrates are discussed in this chapter.

Monosaccharides

Monosaccharides are simple carbohydrates containing between three and eight carbon atoms,

yet only those with five or six carbon atoms are common. Two of the most important ones in foods are the six-carbon sugars glucose and fructose. These have the general formula $C_6H_{12}O_6$.

Examples of Monosaccharides

Glucose. Glucose is known as an *aldose sugar* because it contains an aldehyde group (CHO) located on the first carbon atom of the chain:

Glucose and an aldehyde group:

It is conventional to number the carbon atoms along the chain so that the carbon atom with the highest number is farthest away from the aldehyde (or functional) group. The aldehyde group is therefore located on carbon one in glucose (and in all other aldose sugars). The numbering of the carbon atoms in glucose is shown in Fig. 3.1.

Two isomers of glucose exist, which are mirror images of each other, D-glucose and L-glucose. D-Glucose is the isomer that occurs naturally.

In fact, there are two series of aldose sugars, known as the D-series and the L-series, each formed by adding CHO groups to build the carbon chain, starting from the smallest aldose sugar, which is D- or L-glyceraldehyde (see Fig. 3.2).

Each H—C—OH group within the chain is asymmetrical (since the H and OH groups are different). The highest-numbered asymmetric carbon atom of each D-series sugar has the same configuration as D-glyceraldehyde, rather than its L-isomer. In glucose, the highest-numbered

For use with subsequent Carbohydrate food chapters

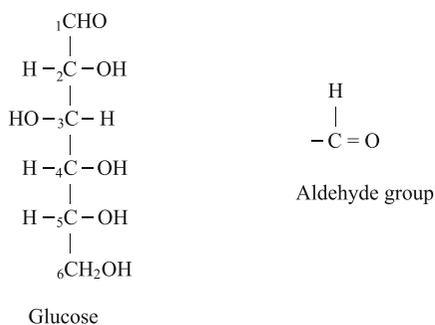


Fig. 3.1 Glucose and an aldehyde group

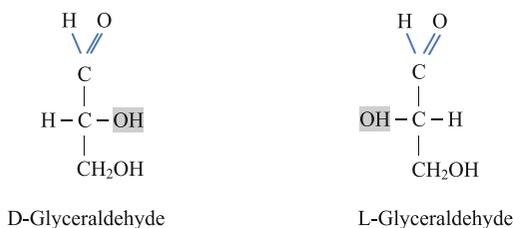


Fig. 3.2 Mirror images of glyceraldehyde

asymmetric carbon atom is carbon-5. This is termed the **reference carbon atom**, because its configuration determines whether the sugar belongs to the D-series or to the L-series. The hydroxyl group attached to it is called the **reference hydroxyl group**. This group is always on the right side in a D-series sugar.

The straight-chain configuration of glucose (and of other monosaccharides) does not account for all the properties of the molecule. In reality, the straight-chain form exists in equilibrium with several possible ring configurations. In other words, the different configurations exist together in solution in a delicate balance. Glucose can exist in four ring structures: two pyranose or six-membered ring forms, and two furanose or five-membered ring forms. These exist along with the straight-chain form, as shown in Fig. 3.3.

The most common configurations for glucose are the **pyranose** structures, drawn according to the Haworth convention in Fig. 3.4. These are **anomers** and are designated **alpha** (α) and **beta** (β). They are formed when the hydroxyl group on the fifth carbon reacts with the carbonyl group

(located on the first carbon, designated as C1). As the ring closes, a new hydroxyl group is formed on C1. This is termed the **anomeric hydroxyl group**, and the carbon atom to which it is attached is termed the **anomeric carbon atom**. For glucose and the other aldoses, the anomeric carbon atom is always the first carbon atom of the chain.

The anomeric hydroxyl group can project towards either side of the ring, as shown in Fig. 3.4. Hence, there are two possible pyranose structures.

For glucose and all the hexoses, the α -anomer has the anomeric hydroxyl group on the *opposite* face of the ring to carbon-6 (i.e., pointing in the opposite direction to carbon-6), when drawn according to the Haworth convention, whereas the β -anomer has the anomeric hydroxyl group on the *same* face of the ring as carbon-6 (i.e., pointing in the same direction as carbon-6). For the D-series sugars, when the ring closes, carbon-6 is always located above the plane of the ring. Therefore, in the case of the α -anomer, the anomeric hydroxyl group points *down*, or *below* the plane of the ring, whereas in the case of the β -anomer, the anomeric hydroxyl group points *up*, or *above* the plane of the ring.

Alpha-anomer—anomeric hydroxyl group is on the **opposite** face of the ring to carbon-6
D-series sugars—anomeric hydroxyl group points **down**

Beta-anomer—anomeric hydroxyl group is on the **same** face of the ring as carbon-6
D-series sugars—anomeric hydroxyl group points **up**

[For the chemists who prefer to define the alpha- and beta-configurations according to the reference carbon, when the anomeric hydroxyl group is formed on the same side of the ring as the reference hydroxyl group (as seen in the Fischer projection formula), the anomer is denoted alpha, whereas, when it is formed on the opposite side, it is denoted beta.]

Fig. 3.3 The main isomers of D-glucose (Fischer projections)

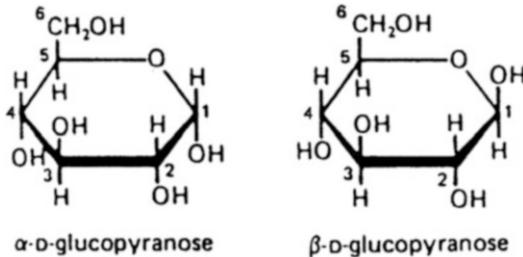
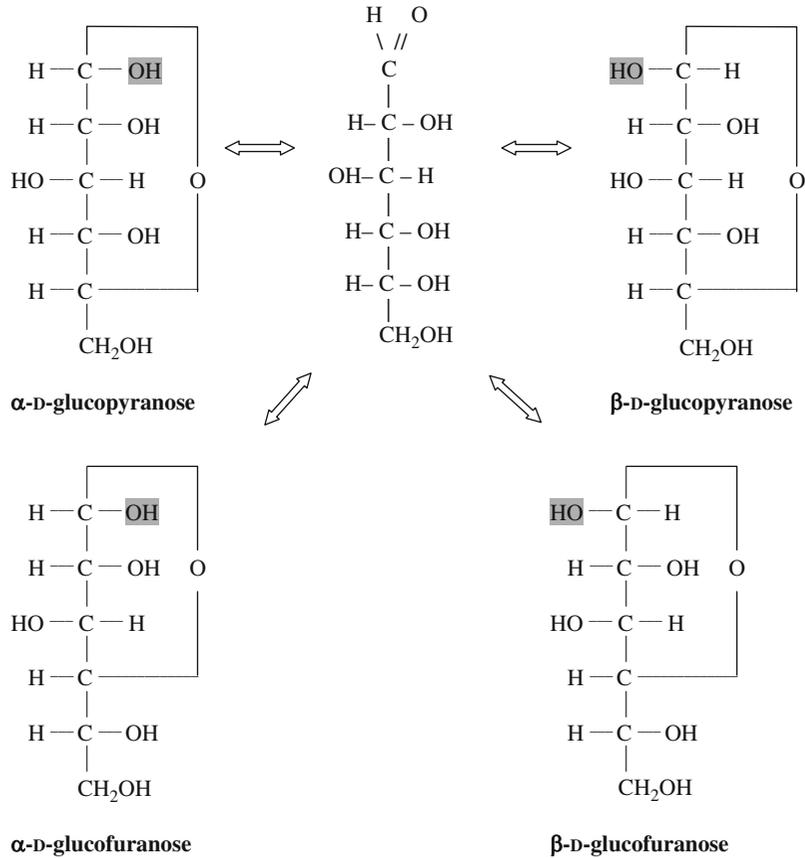


Fig. 3.4 The D-glucopyranose anomers, drawn according to the Haworth convention

In solution, the alpha- and beta-forms are in equilibrium, yet the configuration can be fixed if the molecule reacts to form a disaccharide. It is important to know whether the configuration is fixed as the alpha- or beta-configuration, because this affects properties of the molecule, including digestibility. For example, starch contains

α -D-glucose molecules, and so can be digested, although cellulose contains β -D-glucose molecules and is indigestible.

Although the ring structures are drawn with flat faces in the Haworth formulae, in reality they are not planar rings, yet, rather, they are bent, and could be visualized more as a boat or a chair configuration, as shown in Fig. 3.5.

The different configurations of glucose and the relationships between them are complex, and are beyond the scope of this book. For a more in-depth treatment, interested readers are referred to books such as Food Chemistry, edited by Owen Fennema, or to basic biochemistry textbooks.

Glucose is the most important aldose sugar. Two other aldose sugars important in foods include galactose and mannose. Galactose is important as a constituent of milk sugar (lactose),

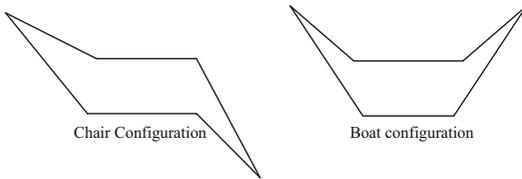


Fig. 3.5 Chair and boat configurations of monosaccharides

and mannose is used to make the sugar alcohol mannitol, which is used as an alternative sweetener in chewing gum and other food products. These are both D-series sugars. In fact, almost all naturally occurring monosaccharides belong to the D-series.

Fructose. Fructose is a six-carbon sugar, like glucose, although despite this, it is a **ketose sugar**, not an aldose, because it contains a ketone group, and not an aldehyde group (see Fig. 3.6):

Similarly to the aldose sugars, there is a D-series and an L-series of ketose sugars, but D-fructose is the only ketose of importance in foods. All **ketose sugars** contain a ketone group, not an aldehyde group.

In fructose, the ketone group is located on the second carbon of the chain. The second carbon atom is therefore the anomeric carbon in fructose. Fructose occurs mainly in the α - and β -*furanose*, or five-membered ring configurations, as shown in Fig. 3.7.

Both the ketone groups of a ketose sugar and the aldehyde group of an aldose sugar may be called a **carbonyl group**. A carbonyl group contains a carbon atom double-bonded to an oxygen atom, but the other atoms are not specified. Hence, an aldehyde group is a specific type of carbonyl group, with both a hydrogen atom and an oxygen atom attached to the carbon atom. A ketone group is also a carbonyl group, because it contains an oxygen atom double-bonded to a carbon atom located within a hydrocarbon chain.

Disaccharides

Disaccharides contain two monosaccharides joined together with a special linkage, called a **glycosidic**

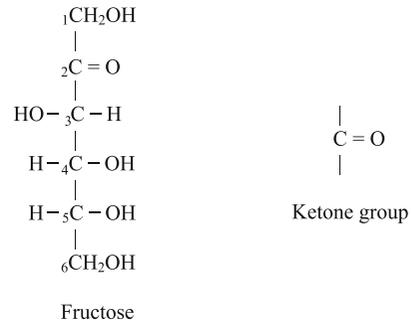


Fig. 3.6 Fructose and a ketone group

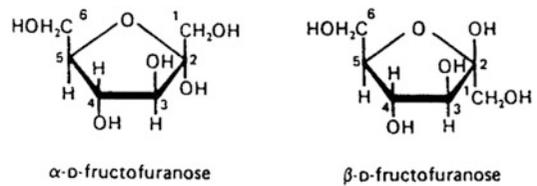


Fig. 3.7 The main configurations of D-fructose

bond. Several disaccharides are important in foods—sucrose or table sugar is the most common and contains glucose and fructose. There are other important disaccharides, such as maltose, containing two glucose units, and lactose, which contains glucose and galactose. Lactose is also known as milk sugar because it is found in milk. It is the least sweet and least soluble of the sugars.

Glycosidic Bonds

A **glycosidic bond** is formed when the carbonyl group of one monosaccharide reacts with a hydroxyl group of another molecule and water is eliminated (see Fig. 3.8).

Formation of a glycosidic link fixes the configuration of the monosaccharide containing the involved carbonyl group in either the α - or β -position. Therefore, it is necessary to specify whether the link is an α - or a β -link. The position of the bond must also be specified. For example, when two glucose molecules are joined to make maltose, the glycosidic link occurs between carbon-1 of the first glucose molecule and carbon-4 of the second, and the configuration of the first glucose molecule is fixed in the α -position. Maltose therefore contains

Fig. 3.8 A glycosidic bond between the carbonyl and hydroxyl groups of monosaccharides

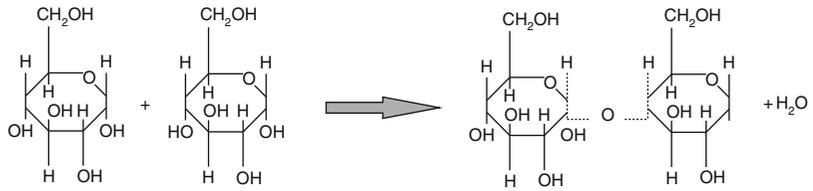
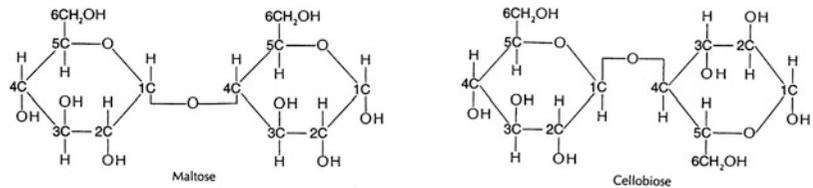


Fig. 3.9 Maltose and cellobiose



two glucose units linked by an α -1,4-glycosidic bond. The anomeric hydroxyl group that is not involved in the glycosidic bond (i.e., the one on the second glucose molecule) remains free to assume either the α - or β -configuration. Therefore, there are two forms of the disaccharide in equilibrium with each other.

Glycosidic bonds are stable under normal conditions yet can be hydrolyzed by acid and heat, or by enzymes such as sucrase, invertase, or amylases.

and carbon-4 of the second monosaccharide, as occurs in maltose

- Readily hydrolyzed by
 - Heat and acid
 - Certain enzymes, such as sucrase, invertase, and amylases

Glycosidic Bond

- Formed between the free carbonyl group of one monosaccharide and a hydroxyl group of another monosaccharide
- Fixes the configuration of the monosaccharide containing the involved carbonyl group in either the α - or β -position
- It is necessary to specify
 - The **configuration** of the link—whether it is an α -link or a β -link
 - The **position** of the link—it is numbered according to the respective positions of the two carbon atoms it links together. For example, an α -1,4 glycosidic link would occur between carbon-1 of the first monosaccharide

(continued)

Examples of Disaccharides

Maltose and Cellobiose. As has already been mentioned, maltose contains two glucose units linked by an α -1,4-glycosidic bond. When two glucose molecules are joined together and the configuration of the first glucose molecule is fixed in the β -position, cellobiose is formed. Cellobiose contains a β -1,4-glycosidic bond. The chemical formulas for maltose and cellobiose are shown in Fig. 3.9.

Maltose is the building block for *starch*, which contains α -1,4-glycosidic bonds. Alpha links can be broken down by the body, so starch is readily digested. Cellobiose is the building block for *cellulose*, which contains β -1,4-glycosidic bonds. Cellulose cannot be digested in the human body because the β -linkages cannot be broken down by the digestive enzymes. Therefore, cellulose is known as dietary fiber. (The glycosidic bonds in cellulose cross the plane of the monosaccharide

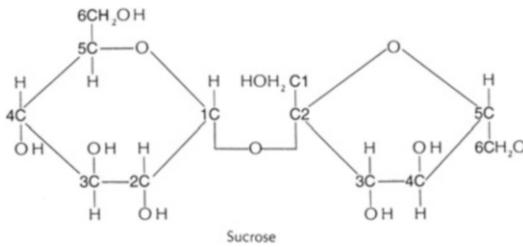


Fig. 3.10 Sucrose

units they join together, and so they may be termed **cross-planar bonds**. It is because they are cross-planar that they are not digestible. In reality, because of the orientation of the bonds, the monosaccharide units tend to twist or flip over, as drawn in Fig. 3.9, which results in a twisted ribbon effect for the polymer chain.)

Sucrose. Sucrose is the most common disaccharide, and it contains glucose and fructose joined together by an α -1,2-glycosidic link (see Fig. 3.10). The carbonyl groups of both the glucose and the fructose molecule are involved in the glycosidic bond; thus, the configuration of each monosaccharide becomes fixed. Glucose is fixed in the α -configuration, whereas fructose is fixed in the β -configuration. Sucrose can be hydrolyzed to glucose and fructose by heat and acid, or by the enzymes invertase or sucrase. The equimolar mixture of glucose and fructose produced in this way is called **invert sugar**. Production of invert sugar is important during the formation of candies and jellies, as invert sugar prevents unwanted or excessive crystallization of sucrose. (For further discussion of crystallization of sucrose, see Chap. 14.)

Various Properties of Sugars

Sweetness

The most obvious sensory property of sugars such as glucose, fructose, and sucrose is their **sweetness**, which varies depending on the specific sugar. Lactose (milk sugar) is the least sweet, whereas fructose is the sweetest sugar. Sugars are used as sweeteners in candies and many other food products.

Formation of Solutions and Syrups

Sugars are soluble in water and readily form syrups. If water is evaporated, crystals are formed. Sugars form **molecular solutions** due to hydrogen-bond interchange. When sugar is placed in water, the water molecules form hydrogen bonds with the sugar molecules, thus hydrating them and removing them from the sugar crystals. Solubility increases with temperature; thus, a hot sucrose solution may contain more solute than a cold one. (For a discussion of molecular solutions, see Chap. 2.)

If a hot saturated sucrose solution is cooled without disturbance, it will supercool, and a supersaturated solution will be obtained. A **supersaturated solution** contains more solute than could normally be dissolved at that temperature. It is unstable, and if stirred or disturbed, the extra solute will rapidly crystallize out of solution. Supersaturated solutions are necessary in candy-making. For more detail on sugar crystallization and candies, see Chap. 14.

Body and Mouthfeel

Sugars contribute body and “mouthfeel” to foods. In other words, the addition of sugar makes a food more viscous or gives it a less runny consistency. If sugar is replaced by a non-nutritive or high-intensity sweetener such as aspartame or saccharin, the consistency of the food will be watery and thin. To prevent this, another substance has to be added to give the expected body or mouthfeel to the food. Modified starches or gums are usually added to such food products to give the desired consistency without addition of sugar.

Fermentation

Sugars are readily digested and metabolized by the human body and supply energy (4 cal/g). They are also metabolized by microorganisms. This property is important in breadmaking, where sugar is fermented by yeast cells. The

yeast feeds on the sugar, producing carbon dioxide, which is the leavening agent and causes bread dough to rise before and during baking.

Preservatives

At high concentrations, sugars prevent growth of microorganisms, because they reduce the water activity of food to a level below which bacterial growth cannot be supported. Sugars can, therefore, be used as preservatives. Examples of foods preserved in this manner include jams and jellies.

Reducing Sugars

Sugars that contain a free carbonyl group are known as **reducing sugars**. All monosaccharides are reducing sugars. Disaccharides are reducing sugars only if they contain a free carbonyl group. Sucrose is not a reducing sugar because it does not contain a free carbonyl group. The carbonyl groups of glucose and fructose are both involved in the glycosidic bond and are, therefore, not free to take part in other reactions. Maltose, on the other hand, has one carbonyl group involved in the glycosidic bond, and the other carbonyl group is free; thus, maltose is a reducing sugar.

Reducing sugars give brown colors to baked goods when they combine with free amino acid groups of proteins in a browning reaction called the **Maillard reaction** (this reaction is discussed further in Chap. 8).

Caramelization

Sugars **caramelize** on heating, giving a brown color. Caramelization is caused by the decomposition of the sugars and occurs at extremely high temperatures. A variety of compounds are formed as a result, including organic acids, aldehydes, and ketones. The reaction does not involve proteins and should not be confused with the Maillard browning reaction.

Sugar Alcohols

Reduction of the carbonyl group to a hydroxyl group gives **sugar alcohols** such as xylitol, sorbitol, and mannitol. These compounds are sweet, although not as sweet as sucrose. However, they are not fermented as readily as sugar by microorganisms in the mouth, and so they are noncariogenic. (In other words, they do not cause tooth decay.) Therefore, they are used in chewing gum, breath mints, and other products that may be kept in the mouth for a while. Although products containing sugar alcohols may be labeled as “sugar-free,” it is important to realize that sugar alcohols are not free of calories. They are not metabolized as efficiently as sugars and have a lower caloric value (between 1 and 3 kcal/g).

Sugar alcohols may be used as a low-energy bulk ingredient (in place of sugar) in many food products. Since sorbitol is mostly transformed to fructose in the body rather than glucose, it is tolerated by diabetics. Hence, it can be used to replace sugar in diabetic foods.

Oligosaccharides

Oligosaccharides contain a few (3–10) monosaccharide residues linked together by glycosidic bonds. Common ones include raffinose and stachyose. Raffinose is a **trisaccharide** and contains galactose, glucose, and fructose. Stachyose contains glucose, fructose, and two galactose units. Both occur in legumes such as dry beans and peas. They are not hydrolyzed or digested by the human digestive system, and become food for bacteria in the large intestine. The bacteria metabolize the carbohydrates and produce gas, causing varying degrees of discomfort.

Polysaccharides

The most important food **polysaccharides** are the starches, pectins, and gums. All are complex carbohydrate polymers with different properties,

which depend on the sugar units that make up the molecule, the type of glycosidic linkages, and the degree of branching of the molecules. Starches are discussed in Chap. 4 and pectins and other polysaccharides are covered in Chap. 5.

Dextrins and Dextrans

Dextrins are intermediate-chain length glucose polymers formed when starch is broken down or hydrolyzed. They are larger than oligosaccharides, considerably shorter than starch molecules. Dextrins contain glucose molecules joined by α -1,4-glycosidic bonds, and they are linear polymers. They are found in corn syrups, produced by hydrolysis of starch.

Dextrans are also intermediate-chain length glucose polymers, but they contain α -1,6-glycosidic bonds. They are produced by some bacteria and yeasts.

Starch

Starch is a glucose polymer that contains two types of molecules, known as amylose and amylopectin. These are shown in Figs. 3.11 and 3.12, respectively. Both are long chains of glucose molecules joined by α -1,4-glycosidic bonds; however, amylose is a linear chain, whereas amylopectin contains branches. For every 15–30 glucose residues there is a branch, joined to the main chain by an α -1,6-glycosidic link. The branches make amylopectin less soluble in water than amylose. Usually, the two types of starch occur together, although starches may contain only amylose or only amylopectin. They have different properties, which are discussed in Chap. 4.

Starches can also be modified to give specific functional properties in food products, so knowledge of the properties of different starches is important in the food industry. Chapter 4 gives detailed information on characteristics of different starches and their uses in foods.

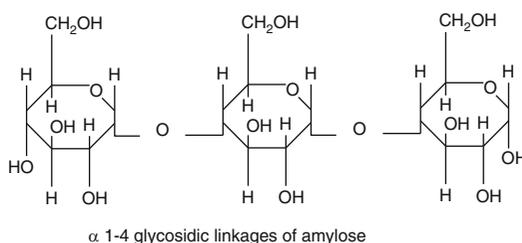


Fig. 3.11 Amylose

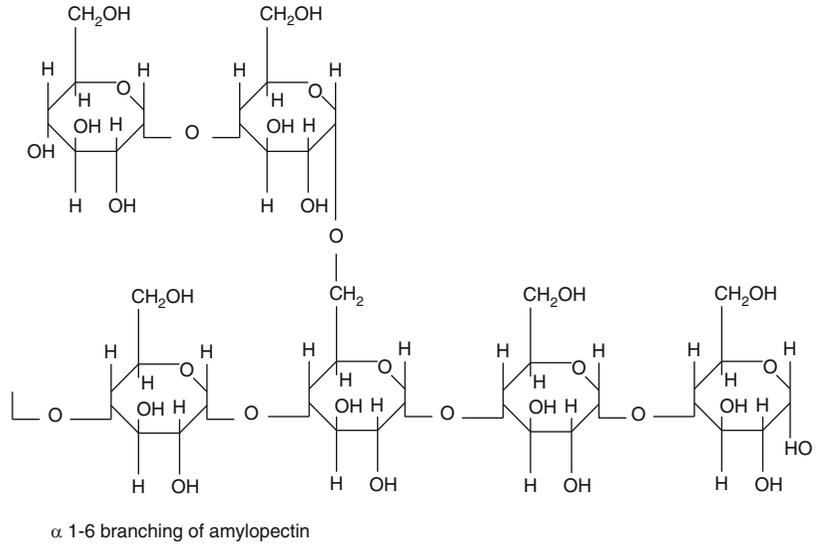
Pectins and Other Polysaccharides

Pectins, gums, and seaweed polysaccharides are also important carbohydrates used in food products. They are discussed further in Chap. 5. Pectins occur naturally in plant food products, yet gums and seaweed polysaccharides do not come from edible plant sources. They are extracted and purified and then added to food products.

Pectins are used mainly as gelling agents in jellies, jams, and other products. They are also used as stabilizers and thickeners. They are found in fruits and vegetables, and they help to hold the plant cells together. Structurally, they are long-chain polymers of α -D-galacturonic acid, which is an acid derived from the simple sugar galactose. They are soluble in water, and, under appropriate conditions, they form gels. Their structure and properties are discussed in Chap. 5.

Gums are mainly plant extracts and include gum tragacanth and guar gum. They are highly branched polysaccharides that form very viscous solutions, trapping large amounts of water within their branches. Most do not form gels because of the high level of branching. They are useful as thickeners and stabilizers, particularly in reduced-fat salad dressings and in other convenience foods.

Seaweed polysaccharides include the agars, alginates, and carrageenans. They are classified as gums, although they are able to form gels, unlike most gums. They are useful as gelling agents, thickeners, and stabilizers in foods.

Fig. 3.12 Amylopectin

Cellulose and *hemicellulose* are structural polysaccharides that provide support in plant tissues. They are not digested in the body, so they do not supply energy. However, they provide insoluble dietary fiber, which is an important part of a healthy, balanced diet.

Regarding *fiber*, food items may make the claim “good source of fiber” if 2.5–4.9 g of fiber per serving are present. When 5 g per serving, or more, are present, a food item may be labeled “high fiber.” It is recommended by health agencies and Dietary Guidelines for Americans that men should consume 38 g of fiber per day, and that women should consume 25 g per day. There is soluble and insoluble fiber and they are structurally different (see Chap. 4).

Inulin is a polysaccharide with the general formula $(C_6H_{10}O_5)_n$. It is found in tubers and

the roots of various plants and, when hydrolyzed, yields fructose.

Conclusion

Carbohydrates come in various shapes and sizes, from small sugar molecules to complex polymers containing thousands of simple sugar units. The digestible carbohydrates provide energy (4 cal/g), whereas the indigestible ones are an important source of dietary fiber. In addition to their nutritional value, carbohydrates are important as thickeners, stabilizers, and gelling agents. They are used in a wide spectrum of convenience foods, and, without them, the range of food products relished today would be greatly diminished.

Notes

CULINARY ALERT!

Glossary

Aldose Sugar containing an aldehyde group monosaccharide—single sugar unit.

Alpha-anomer The anomeric hydroxyl group is on the opposite face of the ring from carbon-6 (i.e., the two groups point in opposite directions).

Anomeric carbon atom The carbon atom that is part of the free carbonyl group in the straight-chain form of a sugar.

Anomers Isomers that differ only in the orientation of the hydroxyl group on the anomeric carbon atom; there are two forms—alpha (α) and beta (β).

Beta-anomer The anomeric hydroxyl group is on the same face of the ring as carbon-6 (i.e., the two groups point in the same direction).

Carbonyl group Contains an oxygen atom double-bonded to a carbon atom. The aldehyde group and the ketone group can both be described as a carbonyl group.

Caramelization Decomposition of sugars at very high temperatures resulting in brown color.

Cross-planar bond Formed when the hydroxyl groups on the carbon atoms involved in the formation of a glycosidic bond are oriented on opposite faces of the sugar rings. Cross-planar bonds occur in cellobiose and in cellulose. They also occur in pectin. They are not digested in the human digestive system.

Dextrans Glucose polymers joined by α -1,6-glycosidic bonds. Produced by some bacteria and yeasts.

Dextrins Glucose polymers joined by α -1,4-glycosidic bonds. Product of starch hydrolysis. Found in corn syrups.

Disaccharide Two sugar units joined together by a glycosidic bond.

Furanose Five-membered ring.

Glycosidic bond Bond that links two sugar units together; it is formed between the free carbonyl group of one sugar and a hydroxyl group of another sugar; the orientation (α or β) and position (e.g., 1,4) of the link must be specified.

Hydroxyl group The —OH group on the carbon atom.

Invert sugar An equimolar mixture of glucose and fructose, formed by hydrolysis of sucrose, either by acid and heat, or by enzymes such as invertase or sucrase.

Ketose Sugar containing a ketone group.

Maillard reaction (Maillard browning reaction) Nonenzymatic browning reaction involving a reducing sugar and a free amino acid group on a protein.

Monosaccharide Single sugar unit.

Oligosaccharide Several (3–10) sugar units joined together by a glycosidic bond.

Polysaccharide Many (hundreds or thousands of) sugar units joined together.

Pyranose Six-membered ring.

Reducing sugar Sugar that contains a free carbonyl group.

Reference carbon atom The highest-numbered asymmetric carbon atom; C5 in glucose and fructose.

Reference hydroxyl group The hydroxyl group attached to the reference carbon atom.

Sugar alcohol The result of reduction of carbonyl group to a hydroxyl group.

Supersaturated solution Solution that contains more solute than could normally be dissolved at a particular temperature.

Trisaccharide Three sugar units joined together by a glycosidic bond.

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