

1 Classifying, Identifying, Naming, and Drawing Sugars and Sugar Derivatives

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Structure and Nomenclature of Monosaccharides

Sugars are polyhydroxycarbonyls that occur in single or multiple units as monosaccharides, disaccharides, trisaccharides, tetrasaccharides, or oligosaccharides (typically three to ten sugar units). Monosaccharides (also known as simple sugars) exist as aldoses or ketoses, with glucose and fructose being the most common examples. **Glycose** is a generic term for sugars. Sugars are also classified according to the number of carbon atoms in the molecule (e.g., trioses, tetroses, pentoses, hexoses, heptoses, etc.).

Aldoses and Ketoses

Aldoses contain an aldehyde functional group at carbon-1 (C-1), whereas ketoses contain a carbonyl group that is almost always located at carbon-2 (C-2). C-1 for aldoses and C-2 for ketoses are the reactive centers for these molecules and are known as the **anomeric carbon atoms**. Figure 1.1 shows the structure for D-glucose, D-fructose, and, in addition, D-arabinose. Sugars have common or trivial names with historical origins from chemistry, medicine, and industry. There is also a systematic procedure for naming sugars (some examples are shown in Table 1.1). Glucose is also commonly known as dextrose. In systematic nomenclature, its suffix is hexose, indicating a 6-carbon aldose sugar, and the prefix is *gluco-*, which shows the orientation of the hydroxyl groups around carbons 2–5. The symbol D refers to the orientation of the hydroxyl group on C-5, the

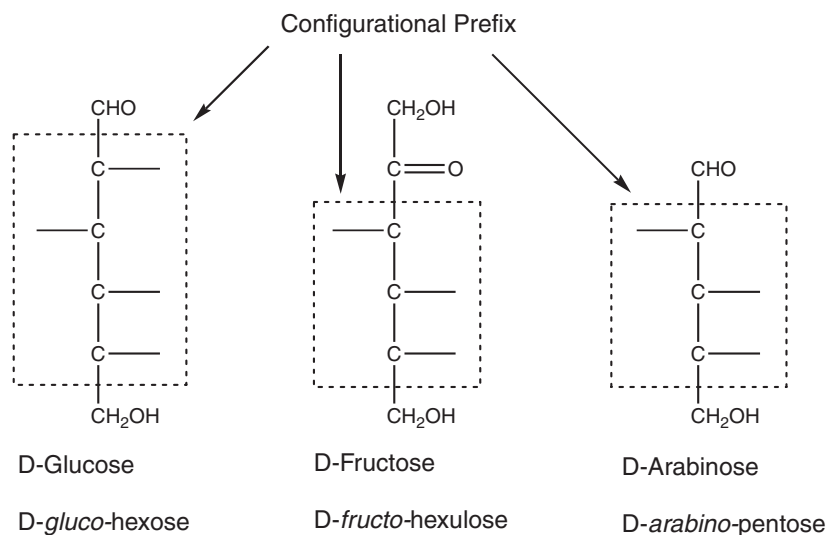


Figure 1.1 Structure and nomenclature of glucose, fructose, and arabinose.

Table 1.1 Trivial and Systematic Names of Selected Sugars

Trivial (or Common)	Systematic ^a
D-Erythrose	<i>D-erythro</i> -tetrose
D-Threose	<i>D-threo</i> -tetrose
D-Arabinose	<i>D-arabino</i> -pentose
D-Lyxose	<i>D-lyxo</i> -pentose
D-Ribose	<i>D-ribo</i> -pentose
D-Xylose	<i>D-xylo</i> -pentose
D-Allose	<i>D-allo</i> -hexose
D-Altrose	<i>D-altro</i> -hexose
D-Galactose	<i>D-galacto</i> -hexose
D-Glucose	<i>D-gluco</i> -hexose
D-Gulose	<i>D-gulo</i> -hexose
D-Idose	<i>D-ido</i> -hexose
D-Mannose	<i>D-manno</i> -hexose
D-Talose	<i>D-talo</i> -hexose

^aIn the systematic name, the configurational prefix is italicized, and the stem name indicates the number of carbon atoms in the molecule.

highest numbered asymmetric carbon atom, also known as the **reference carbon atom**. Since fructose (also known as levulose) has just three asymmetric carbon atoms, its configurational prefix is the same as that for the pentose sugar arabinose. Thus, the systematic name for glucose is *D-gluco*-hexose and fructose is *D-arabino*-hexulose.

Configurations of Aldose Sugars

Figure 1.2 shows all possible configurations around the asymmetric carbon atoms for the triose, tetrose, pentose, and hexose D-aldose sugars. **Diastereoisomers** are molecular isomers that differ in configuration about one or more asymmetric carbon atoms; there are eight hexose diastereoisomers. **Epimer** is yet another term in sugar chemistry that refers to diastereoisomers that differ in configuration about only one asymmetric carbon atom (e.g., D-galactose is the 4-epimer of D-glucose). The term has historical significance because the melting point of dinitrophenylhydrazone derivatives was a classical procedure used in identifying sugars. The 2-epimers (e.g., glucose and mannose, allose and altrose, etc.) gave identical dinitrophenylhydrazone derivatives.

D- vs. L-Sugars

L-sugars are the mirror images of D-sugars. Figure 1.3 depicts the structures of D- and L-glucose in the Fischer and conformational projections. (Note: When drawing an L-sugar, the orientation of the hydroxyl groups

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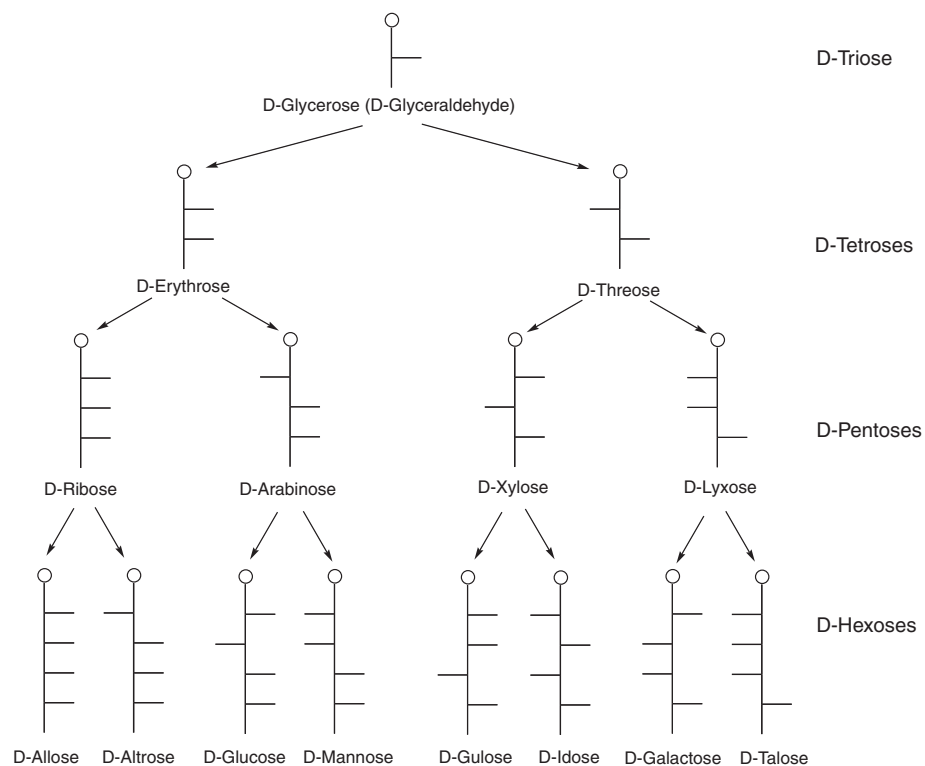


Figure 1.2 Structures of the D-aldoses containing from 3 to 6 carbon atoms as depicted by the Rosanoff shorthand convention.

on every asymmetric carbon atom need to be reversed; a frequent error is to only change the orientation on the reference carbon atom.) D- and L-glucose are **enantiomers**, nonsuperimposable stereoisomeric molecules that are mirror images. L-sugars occur rarely in nature. A pair of

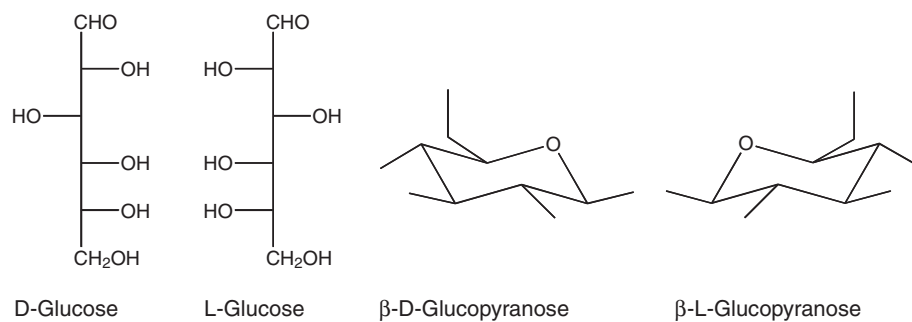


Figure 1.3 D- and L-glucose as depicted in the Fischer and conformational projections.

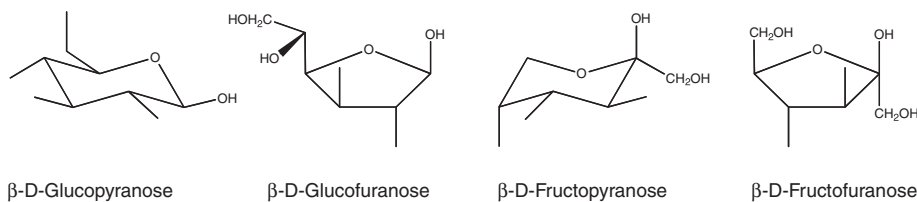


Figure 1.4 Furanose and pyranose structures of β -D-glucose and β -D-fructose.

enantiomers are identical in chemical reactivity, and they have the same taste properties. They are handled differently in biological systems, however. Although humans absorb L-sugars, L-sugars are not metabolized and thus have no caloric value.

Different Ways of Depicting Sugar Structures

Fischer, Haworth, Mills, and Conformational Structures

It is important to realize that pentose and hexose sugars exist as ring forms, and only a small amount will occur in the acyclic form. Thus, the Fischer projections shown in Figure 1.2 are in no way representative of actual structural form. The Fischer projections are useful in that they provide a code for the orientation of hydrogen and hydroxyl substituents on adjacent carbon atoms. Sugars exist as both six-membered (pyranose) and five-membered (furanose) ring structures (Figure 1.4). The furanose ring is relatively planar, whereas the pyranose ring is "puckered," existing in chair and boat forms. Figure 1.5 illustrates β -D-glucopyranose by the Haworth, Mills, and conformational conventions. The Haworth representation is troublesome because it shows the pyranose ring as being planar. The Mills structure takes an aerial view with hydroxyl groups depicted as

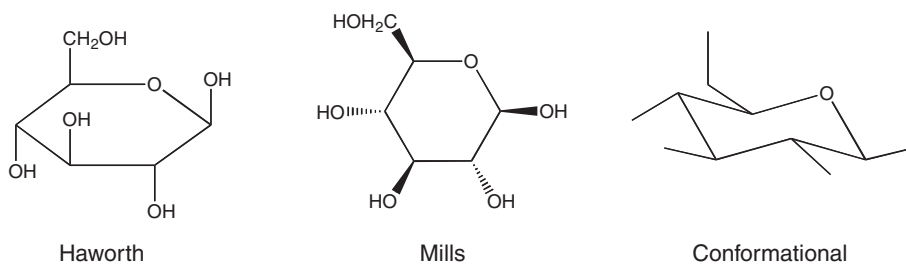


Figure 1.5 β -D-glucopyranose as depicted by the Haworth, Mills, and conformational conventions.

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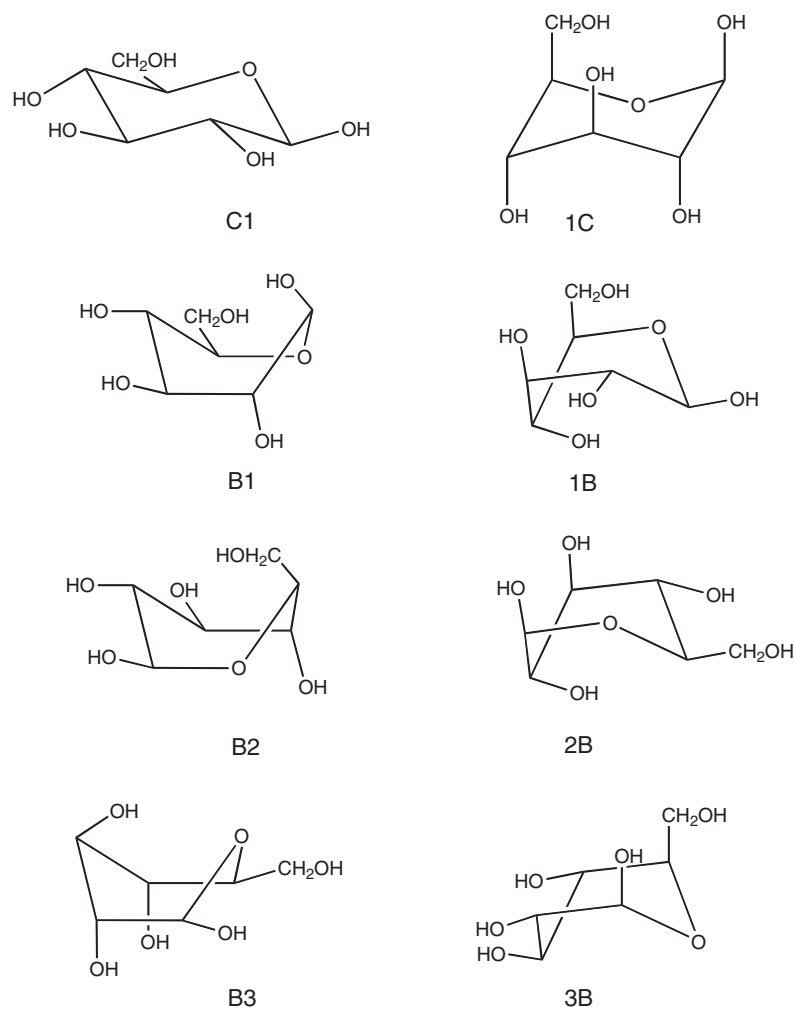


Figure 1.6 Basic chair and boat conformations for β -D-glucopyranose.

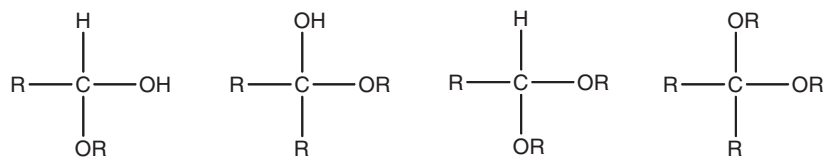
being either "upward" or "downward." The conformational representation shows perspective where the ring oxygen is remote, equatorial substituents are drawn at an angle, and axial substituents are vertical. The conformational representation is highly preferred and will be used predominately throughout this book.

There are two stable chair forms and six stable boat forms for pyranose sugars; the forms for β -D-glucopyranose are shown and named in Figure 1.6. Sugar conformation is best visualized and demonstrated using molecular models. Relatively inexpensive and stereochemically accurate kits are

available, and practice with them is highly recommended. Showing three-dimensional structure on the two-dimensional printed page has obvious limitations. Given the conformational structure of a pyranose sugar, one should be able to make the correct molecular model; and, vice versa, given a molecular model, one should be able to draw the correct conformational structure. An exercise is included in the Appendix for making molecular models of sugar molecules with molecular model kits.

Classifying Sugars by Compound Class—Hemiacetals, Hemiketals, Acetals, and Ketals

Aldehydes and ketones will condense with alcohols to form hemiacetals and hemiketals. In excess alcohol and dehydrating conditions, further condensation will take place to form acetals and ketals. A generalized reaction of an aldehyde with alcohol is shown in Figure 1.7, and the generalized structures of hemiacetals, hemiketals, acetals, and ketals are shown below.



Structure 1.1 Hemiacetal, Hemiketal, Acetal, Ketal

Pyranose and furanose ring forms of sugars are hemiacetals or hemiketals and are formed from intramolecular condensation of the carbonyl group with a hydroxyl substituent. When this reaction occurs, two products are formed, as the hydroxyl group on the anomeric carbon has two possible orientations, as illustrated by α - and β -D-glucopyranose. They have different chemical properties, with the β -form being more stable because of its equatorial disposition. They are known as **anomers**, diastereoisomers that differ in configuration only at C-1 for aldoses and C-2 for ketoses.

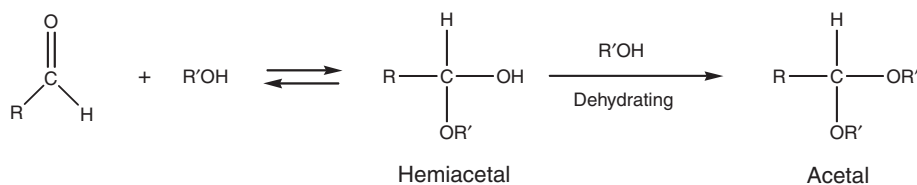


Figure 1.7 Reaction of an aldehyde with an alcohol to form a hemiacetal and an acetal.

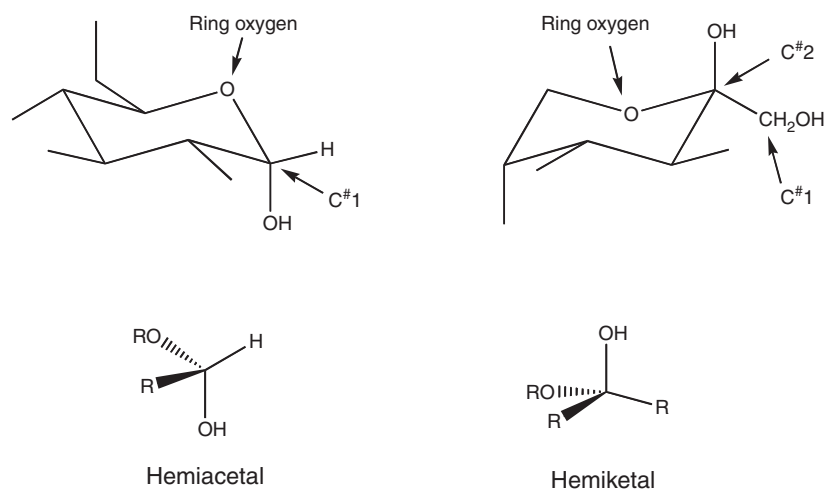


Figure 1.8 Location of the hemiacetal and hemiketal functional groups in β -D-glucopyranose and β -D-fructopyranose.

Being able to recognize hemiacetal, hemiketal, acetal, and ketal functional groups is critical to carbohydrate chemistry. The chemical reactivity and functionality of different sugars is directly related to the presence of those functional groups. Figure 1.8 illustrates the location of the hemiacetal and hemiketal functional groups for β -D-glucopyranose and β -D-fructopyranose. To correctly recognize these functional groups, one should proceed as follows:

- Locate the anomeric carbon atom. This will be C-1 for aldose sugars and C-2 for ketose sugars.
- The anomeric carbon atom will be to one side of the ring oxygen.
- The carbon on the other side of the ring oxygen may or may not be the reference carbon atom. The reference carbon atom is C-5 for hexoses and C-4 for pentose sugars. Once the anomeric carbon atom has been located, it helps to number all carbon atoms.

An exercise for identifying hemiacetal, hemiketal, acetal, and ketal functional groups in sugars is included in the Appendix.

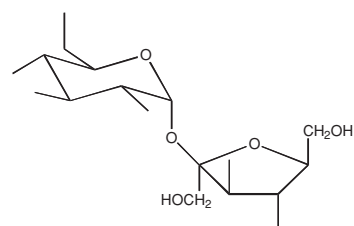
Structure and Nomenclature of Disaccharides

Disaccharides are either reducing or nonreducing, and a reducing disaccharide can be identified by the presence of a hemiacetal or hemiketal

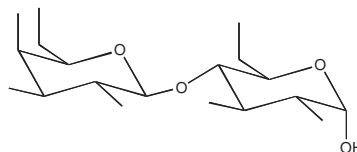
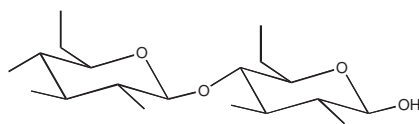
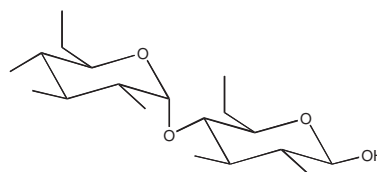
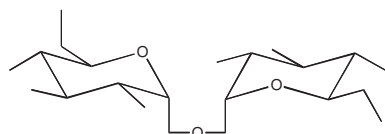
functional group. Disaccharides are formed from the reaction of an anomeric carbon atom with the hydroxyl group of another sugar. This acetal or ketal linkage is also referred to as a glycosidic linkage. The hydroxyl group reacting with the anomeric carbon may be an alcohol functional group of another sugar, or it could be the hydroxyl substituent located on the anomeric carbon. When the condensation is between two anomeric carbons, the compound will not contain a hemiacetal or hemiketal functional group, and it will be a nonreducing sugar. Reducing disaccharides are systematically named by having the nonreducing sugar moiety be a substituting group on the reducing sugar. The nature of the glycosidic linkage, whether α or β , the number of the carbon atom where the sugar is substituted, and the ring size all need to be indicated. Importantly, reducing disaccharides have an -ose suffix. For example, the systematic name for lactose is 4-O- β -D-galactopyranosyl-D-glucopyranose. Reducing disaccharides will have both α and β forms, the designation being for the orientation of the anomeric hydroxyl, not the glycosidic linkage. If the glycosidic linkage is changed from β to α , a different sugar is formed (e.g., the sugar will no longer be lactose). The structures along with systematic and trivial names for disaccharides that are important in foods are shown in Figure 1.9. Lactose is also known as milk sugar and has nutritional relevance because of lactose intolerance (inability to digest lactose) that is prevalent in some human populations.

Sucrose is a nonreducing sugar; hence, both anomeric carbons participate in the glycosidic linkage. There is no need to indicate which carbons are involved in systematic nomenclature, because it is known that both C-1 of glucose and C-2 of fructose are involved. Either sugar can be the substituting sugar, and the nature of both glycosidic linkages needs to be given. The suffix for nonreducing sugars is -ide. The correct name for sucrose is either α -D-glucopyranosyl- β -D-fructofuranoside or β -D-fructofuranosyl- α -D-glucopyranoside. The relevance of sucrose to food technology, nutrition, and world trade is monumental. Maltose (4-O- α -D-glucopyranosyl-D-glucopyranose) is the building unit of starch, whereas cellobiose (4-O- β -D-glucopyranosyl-D-glucopyranose) is the building unit for cellulose. Trehalose (α -D-glucopyranosyl- α -D-glucopyranoside) consists of two glucose molecules linked head-to-head and is nonreducing. It occurs in mushrooms and insects and is metabolized by humans. (This gives credence to the hypothesis that insects played an important role in man's diet from an evolutionary perspective.) The nonreducing and moderate sweetness properties of trehalose make possible some innovative food applications. The structures and names for an extensive list of known disaccharides are given in Unit 9 of the Appendix.

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Sucrose

 α -Lactose β -Cellobiose β -Maltose

Trehalose

Figure 1.9 Structures of five disaccharides of particular importance in foods: sucrose (β -D-fructofuranosyl- α -D-glucopyranoside or α -D-glucopyranosyl- β -D-fructofuranoside), lactose (4-O- β -D-galactopyranosyl-D-glucopyranose), maltose (4-O- α -D-glucopyranosyl-D-glucopyranose), cellobiose (4-O- β -D-glucopyranosyl-D-glucopyranose), and trehalose (α -D-glucopyranosyl- α -D-glucopyranoside).

Structure and Optical Activity

Enantiomers were previously defined as nonsuperimposable stereoisomeric molecules that are mirror images. This is best demonstrated with molecular models by making a model of β -D-glucopyranose, for example, and then also creating its mirror image, β -L-glucopyranose. The two molecules can be visualized as mirror images by placing them head-to-head or, alternatively, placing one below the other. They are nonsuperimposable, meaning that they cannot be stacked with C-1 being over C-1,

Table 1.2 Specific Rotation $[\alpha]_D^{20}$ of Selected Pairs of D- and L-Sugars at Equilibrium

Sugar	$[\alpha]_D^{20}$	Sugar	$[\alpha]_D^{20}$
D-Glyceraldehyde ^a	+13.5°	L-Glyceraldehyde	+13.5°
D-Threose ^b	-12°	L-Threose	+12°
D-Ribose ^c	-21°	L-Ribose	+21°
D-Arabinose ^c	-105°	L-Arabinose	+105°
D-Xylose ^c	+19°	L-Xylose	-19°
D-Lyxose ^c	-14°	L-Lyxose	+14°
D-Allose ^d	+14°	L-Allose	-14°
D-Glucose ^c	+52°	L-Glucose	-52°
D-Mannose ^c	+14°	L-Mannose	-14°
D-Gulose ^e	-26°	L-Gulose	+26°
D-Galactose ^c	+80°	L-Galactose	-80°
D-Talose ^c	+21°	L-Talose	-21°
D-Fructose ^c	-92°	L-Fructose	+92°

Sources: ^aWeast 1970; ^bHockett 1935; ^cPigman and Isbell 1968; ^dBates 1942; ^eIsbell 1937.

C-2 over C-2, etc. They are asymmetric, they have "handedness," and they are **chiral**. They have the property of being able to rotate plane-polarized light in equal amounts but in opposite directions. (**Optical activity** is the ability to rotate plane-polarized light.) The specific rotations of several D- and L-sugars are shown in Table 1.2. Note that some D-sugars (e.g., D-glucose and D-xylose) are **dextrorotary**, having the ability to rotate plane-polarized light to the "right" or in a clockwise direction, whereas other D-sugars (e.g., D-arabinose, D-ribose, D-gulose, and D-fructose) are **levorotary**, having the property of rotating plane-polarized light to the "left" or in a counter-clockwise direction. Thus, being a D- or L-sugar does not predict whether a sugar is dextrorotary or levorotary. The designation D and L should not be confused with *d* and *l*, which denotes having optical activity that is dextrorotary or levorotary. (The trivial names dextrose and levulose for glucose and fructose, respectively, have their origin from D-glucose being dextrorotary and D-fructose being levorotary.) The appendix contains instructions for demonstrating the existence of polarized light and the ability for sugar solutions to rotate it using plastic polarizing material, a light source such as a flashlight, and sugar solutions.

Anecdotal information

D- and L-glucose have identical physical and chemical properties (i.e., the same solubility, reactivity, and taste properties). L-Sugars are not used by humans, however, and are noncaloric. In 1981, Biospherics Inc. of

Beltsville, MD received a patent for use of several L-sugars as low-calorie sweeteners in foods (Levin and Zehner 1991). Their petition to the FDA for its use, however, was denied. The medical and nutritional communities supported the FDA's action, as the wisdom of having considerable quantities of reactive L-sugars circulating in the bloodstream from consumption of L-sugars was questionable.

Specific rotation is a physical property of sugars that is useful in identifying sugars and measuring their concentration. Measurements are taken with a polarimeter that has a source of plane-polarized light, and a prism that enables measurement of the degree that a sugar solution in a cell through which the light is being transmitted will be rotated. The equation for calculating specific rotation is shown below. α is the observed rotation in degrees, c is the concentration of the sugar solution in g/mL, l is the path length of the cell in dm, and D is the wavelength for the D line of Na, 589.3 nm.

$$\text{Specific Rotation} = [\alpha]_D = \alpha / c \times 1 \quad (1.2)$$

Table 1.3 gives the specific rotation for several different sugars. Not only do different sugars (e.g., sucrose vs. trehalose) have different specific

Table 1.3 Specific Rotation $[\alpha]_D^{20}$ of Selected Sugars^a

Sugar	$[\alpha]_D^{20}$ (Initial)	$[\alpha]_D^{20}$ (Final)
α -D-Glucose	+112°	+52°
β -D-Glucose	+19°	+52°
α -D-Galactose	+144°	+80°
β -D-Galactose	+52°	+80°
α -D-Mannose	+34°	+15°
β -D-Mannose	-17°	+15°
β -D-Fructopyranose	-133°	-92°
β -D-Fructofuranose	-21°	-92°
α -D-Xylose	+92°	+19°
β -D-Xylose	-20°	-19°
α -D-Lactose	+90°	+55°
β -D-Lactose	+35°	+55°
α, α -Trehalose	+197°	+197°
Sucrose	+66.5°	+66.5°
Raffinose	+124°	+124°
Stachyose	+148°	+148°
Invert Sugar		-20°
α -L-Glucose	-96°	-52°
Levoglucofan	-67°	-67°

^aSource: Shallenberger and Birch 1975; Shallenberger 1982.

rotation, but different anomeric and ring forms of the same sugar also have different specific rotation. When crystalline α -D-glucopyranose is dissolved in water, its initial rotation will approach +112. Reducing sugars in aqueous solution will "mutarotate" until they come to an equilibrium mixture of α and β , furanose and pyranose, and open-chain forms. Nonreducing sugars (e.g., sucrose and trehalose) will not mutarotate, that is their initial and final rotations will be the same because they are not undergoing structural transformations. Observing whether a crystalline sugar will mutarotate is another method for determining whether it is reducing or nonreducing. The Appendix includes a laboratory exercise on polarimetry of sugars.

Whether a sugar is D or L will not predict whether it is dextrorotary or levorotary. Being *d* or *l* is a fairly reliable predictor of sugar conformation, however. D-Pyranose sugars that favor the C-1 conformation are dextrorotary, whereas those favoring the 1-C conformation are levorotary.

A Systematic Procedure for Determining Conformation (C-1 or 1-C), Chiral Family (D or L), and Anomeric Form (α or β) of Sugar Pyranoid Ring Structures

The conformational structures of D-glucopyranose and D-fructopyranose are typically shown as depicted in Figures 1.3, 1.4, and 1.8. Conventionally, the structures are drawn with C-1 oriented to the right of the ring oxygen for glucose and C-2 to the right of the ring oxygen of fructose. The molecules, of course, will not always be oriented in this direction, and drawing them with a different spatial orientation, as per the structures of glucose in trehalose (Figure 1.9), can be challenging. Drawing L-sugars can be particularly troublesome. One approach is to make the molecular model and then draw the conformational structure. Shallenberger and others (1981) developed a systematic procedure for determining the conformation, chiral family, and anomeric form for sugar pyranoid ring structures. The step-wise procedure requires that one locate the anomeric carbon atom and the reference carbon atom. One determines whether the structure is drawn with the ring oxygen above or below the plane of the ring and whether the structure is oriented clockwise or counterclockwise. Plus (+) and minus (−) assignments are made for these different features, and a series of algebraic multiplications will determine whether the ring structure is C-1 or 1-C, D or L, and α or β . The C-1 conformation of β -D-glucopyranose serves as the basic reference with all assignments being positive. The Appendix contains an exercise for determining the above features for selected sugars. The protocol is useful for determining

whether or not a structure is properly drawn, and the process requires correct identification of anomeric and reference carbon atoms.

Structure and Nomenclature of Sugar Derivatives with Relevance to Food Chemistry

Glycols (Alditols)

Glycols (**alditols**) are sugar alcohols, the carbonyl group being reduced to an alcohol. The rules for systematic nomenclature are to replace the -ose suffix with -itol; that is, the alditol derivative of D-glucose is D-glucitol. The trivial name for D-glucitol is sorbitol, which is widely distributed in nature. Sorbitol is present in trace amounts in many fruits and in substantial quantities in apples (5% of total sugars), pears (18%), cherries (15–20% of total sugars), and chokeberries (*Aronia melanocarpa*; up to 50% of total sugars). Commercially, sorbitol is manufactured by catalytic reduction of glucose (Figure 1.10). The body will passively absorb sorbitol, and it is converted to glucose in the liver, thus it is **glucogenic** (the body can convert it to glucose) and caloric. Some diabetics can accommodate sorbitol because of its slow absorption rate; it is found as an ingredient in diabetic confections and jams. Sorbitol that is not absorbed in the small intestine will go to the colon, where it can cause diarrhea because of its **hygroscopic** (affinity for water) quality. Sorbitol is used to retard sugar crystallization in confections, and to provide viscosity and body in some beverage formulations. Because it is nonreducing, it will not react with amino acids in Maillard browning, and for that reason, one application is to use it as a

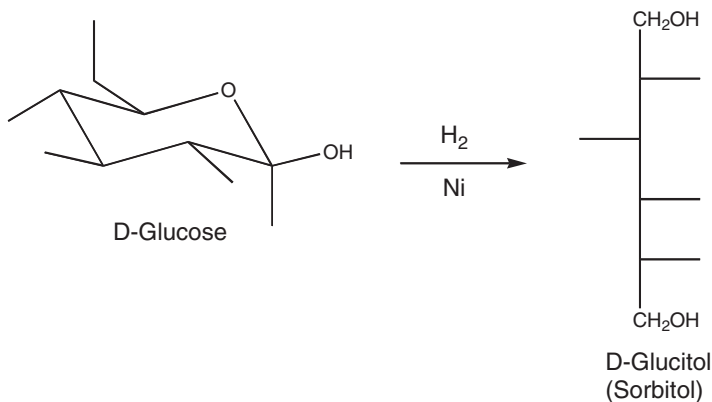
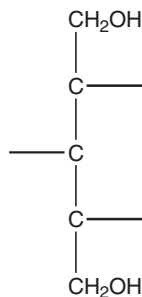


Figure 1.10 Catalytic reduction of glucose to form sorbitol.

cryoprotectant in surimi manufacture, in which a white appearance is a critical quality factor.

Xylitol has some unique properties and is approved for use in some special dietary foods.



Structure 1.3 Xylitol

It is **noncariogenic** (will not support the growth of bacteria, such as *Streptococcus mutans*, in dental plaque). Food applications are in chewing gums and some candies. It has a negative heat of solution, its endothermic enthalpy of dissolution being approximately ten times that of sucrose. Thus, it will provide a cooling effect when dissolved in the mouth. Xylitol has symmetry and is not optically active. Therefore, it is neither D nor L with respect to its configuration. Additional alditols that are **achiral** (without handedness) and optically inactive are glycerol, erythritol, ribitol, allitol, and galactitol.

Glyconic, Glycuronic, and Glycaric Acids

Mild oxidation of an aldose sugar will produce a **glyconic acid** that can cyclize intramolecularly to form lactones. Aldonic acids are named by replacing the suffix -ose with -onic acid. Figure 1.11 shows oxidation of glucose to form D-gluconic acid, which subsequently reacts intramolecularly to form δ -gluconolactone and γ -gluconolactone. δ -Gluconolactone is an approved food additive and has the property of being neutral but becomes acid when dissolved in water. This slow release of acid finds application in certain leavening systems. Salts of gluconic acid are water-soluble; calcium gluconate provides a means of increasing water solubility to effectively deliver calcium in dietary calcium supplements. Ferrous gluconate is an approved color additive in the United States; its major application is for black olives. The gluconate function renders water solubility to the salt, which permits iron to be distributed throughout the fruit where it can complex with phenolics to produce a black color.

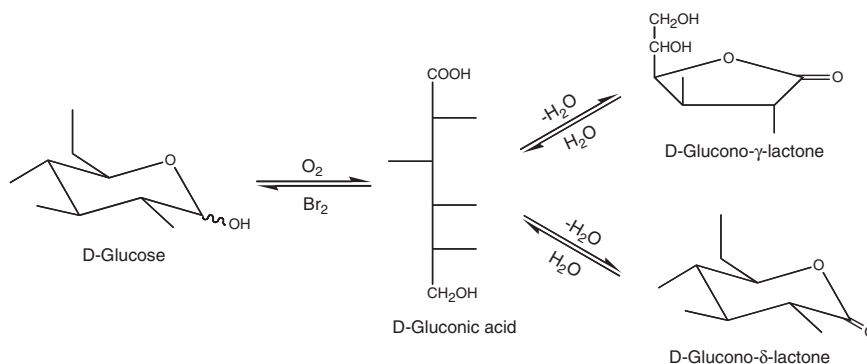
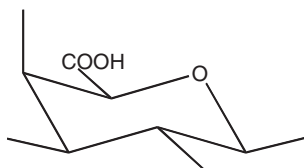


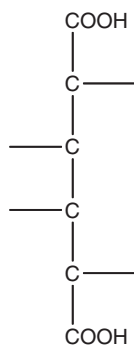
Figure 1.11 Oxidation of D-glucose to form D-gluconic acid, followed by intramolecular cyclization to form γ -gluconolactone and δ -gluconolactone.

Oxidation of the primary alcohol group of an aldose sugar to a carboxylic acid produces a **glycuronic acid**. Glycuronic acids are named by replacing the suffix -ose of an aldose sugar with -uronic acid. The structure of D-galacturonic acid, a major constituent of pectin, is shown below.



Structure 1.4 D-Galacturonic acid

Oxidation of both the aldehyde and primary alcohol functional groups of an aldose sugar to carboxylic acids gives a sugar derivative known as an **aric acid**. Galactaric acid (also known as mucic acid) serves as an example.

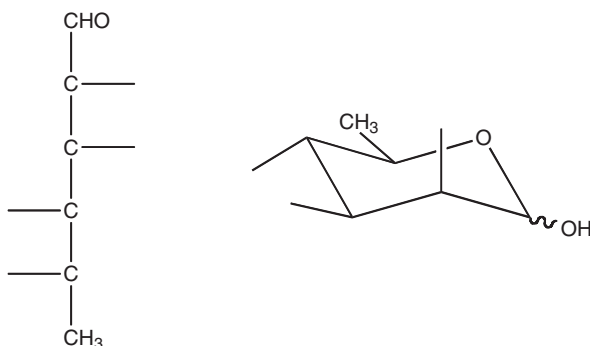


Structure 1.5 Galactaric acid

Galactaric acid can form mono- or dilactones, and it is used in some baking powders as a slow-release acidulant. Galactaric acid has symmetry and is not optically active. Additional aric acids will have this property, as discussed previously for alditol derivatives.

Deoxy Sugars

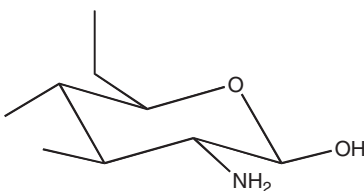
Substitution of a hydroxyl group with a proton forms a doxy sugar, which is named by indicating the carbon number containing no oxygen as a prefix, for example, 2-deoxy-D-ribose (an important constituent of nucleic acids) and 6-deoxy-L-mannose (trivial name = rhamnose). Rhamnose has an important structural role in the polysaccharide pectin and is frequently found as a phenolic glycoside in plants.



Structure 1.6 Rhamnose (6-deoxy-L-mannose)

Amino Sugars and Glycosyl Amines

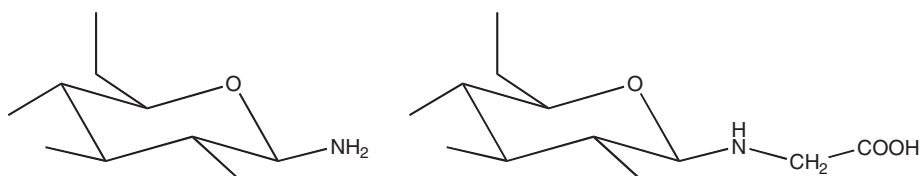
An **amino sugar** is a sugar derivative that has the hydroxyl group on any carbon other than the anomeric carbon atom replaced with an amino group. They are named as a substituted deoxy sugar, placing in alphabetical order the substituting group and the prefix deoxy (e.g., 2-amino-2-deoxy-D-glucose).



Structure 1.7 D-glucosamine (2-amino-2-deoxy-D-glucose)

Chitin, a polymer of D-glucosamine, is a major structural component of the exoskeleton of crustacea. Better use of the wastes from crab, lobster, and shrimp processing is a continuing research topic for seafood processors. Chitin is also present in insect exoskeleton and in molds. Its detection has been proposed as an index for mold contamination in foods (Cousin 1996).

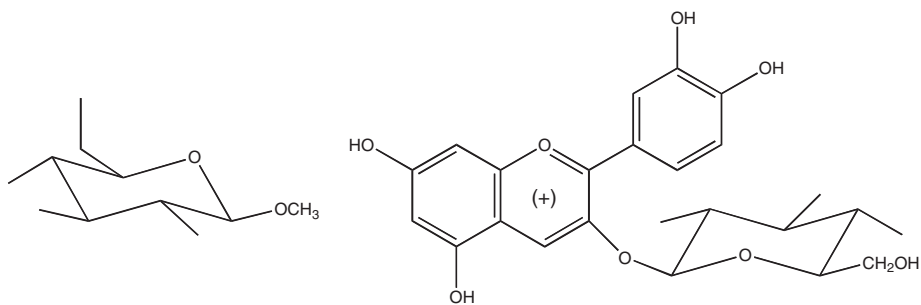
Glycosyl amines are sugar derivatives that have the anomeric hydroxyl group replaced with an amino function. They are named as a substituted amine, for example, β -D-glucosyl amine and β -D-glucosyl glycine. Not only are amino sugars and glycosyl amine named differently, they are also very different with respect to chemical reactivity.



Structure 1.8 β -D-glucosyl amine, β -D-glucosyl glycine

Glycosides

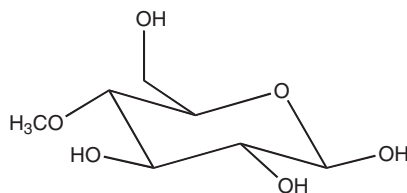
Glycosides are sugar derivatives that have been formed by reaction of a reducing sugar with an alcohol or phenol, resulting in substitution of the anomeric hydroxyl with an OR group of the alcohol or phenol. They are named by first listing the substituting group followed by the sugar with the suffix -ose replaced with -ide. Two examples are methyl- β -D-glucopyranoside and the anthocyanin pigment cyanidin-3- β -D-glucoside.



Structure 1.9 Methyl- β -D-glucopyranoside and cyanidin-3- β -D-glucoside

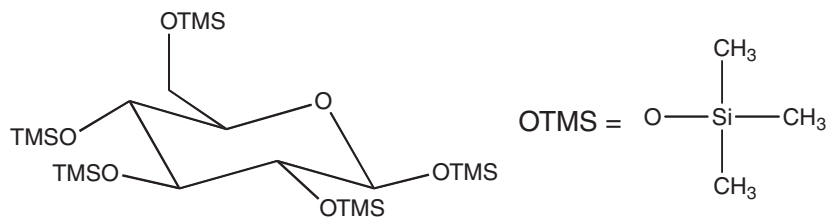
Sugar Ethers and Sugar Esters

Sugar ethers are derivatives where the hydroxyl group on carbon atoms other than the anomeric carbon atom is substituted with an -OR group. They are named by designating the number of the substituted carbon, followed by -O- and the substituting group, and then the sugar. If the sugar is a reducing sugar, the -ose suffix is retained. For example, 4-O-methyl- β -D-glucopyranose. Trimethylsilyl ethers are sugar derivatives that permit sugar analysis by gas-liquid chromatography (see Chapter 6).



Structure 1.10 4-O-methyl- β -D-glucopyranose

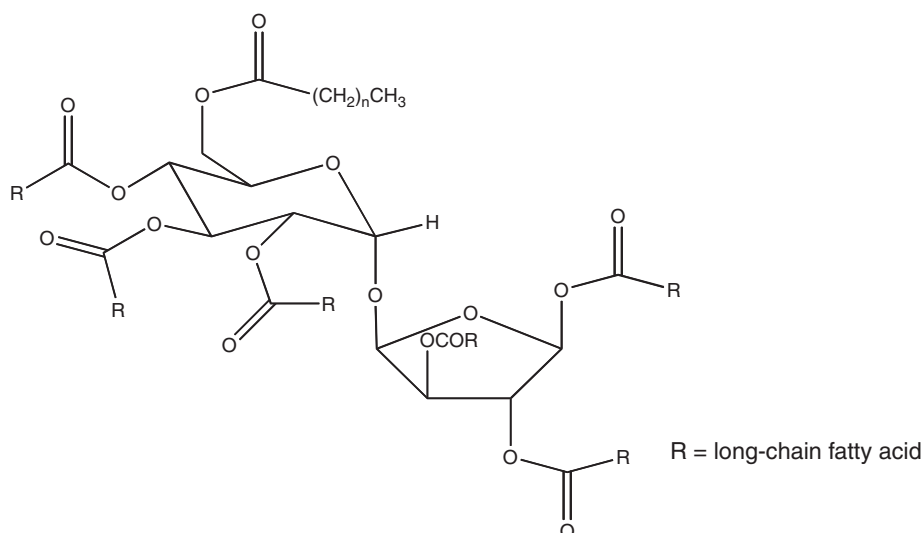
Trimethylsilyl-2,3,4,6-O-tetra-trimethylsilyl- β -D-glucopyranoside is shown below. Note that the trimethylsilyl function on the anomeric carbon is a glycoside, and so named.



Structure 1.11 Trimethylsilyl-2,3,4,6-O-tetra-trimethylsilyl- β -D-glucopyranoside

All hydroxyl groups of sugars must be substituted with trimethylsilyl groups in order for the sugar to have sufficient volatility for gas-liquid chromatographic analysis.

Sugar hydroxyls can combine with organic and inorganic acids to form **sugar esters**. Sugar acetates and succinates occur in nature, and sugar phosphates are important metabolic intermediates. Sucrose polyester (trade name OlestraTM) is an approved food additive in which sucrose is fully esterified with fatty acids. It is a lipophilic, nondigestible and nonabsorbable fat-like molecule. Hence, it is noncaloric and approved for limited use in foods as a fat substitute.



Structure 1.12 Sucrose polyester (trade name Olestra™)

Vocabulary

Achiral—Without handedness

Anomers—Diastereoisomers differing in configuration only at C-1 for aldoses and C-2 for ketoses

Anomeric carbon atom—C-1 for aldoses and C-2 for ketoses

Chiral—Possessing handedness, having no element of symmetry; being asymmetric

Configuration—The arrangement in space of substituents about the tetrahedral carbon atom

Conformation—The shape of a molecule that may be altered simply by rotation (twisting) about single covalent bonds

D-Sugars—Sugars in which the hydroxyl group on the highest numbered asymmetric carbon atom is oriented to the "right"

Dextrorotary—Having the ability to rotate plane-polarized light to the "right" or in a clockwise direction

Diastereoisomers—Isomers that differ in configuration about one or more asymmetric carbon atoms (e.g., glucose and galactose)

Epimers—Diastereoisomers that differ in configuration about only one asymmetric carbon atom

Glucogenic—The ability to be metabolically converted to glucose

Glycose—Generic name for sugars

- L-Sugars—Sugars in which the hydroxyl group on the highest numbered asymmetric carbon atom is oriented to the "left"
- Levorotary—Having the ability to rotate plane-polarized light to the "left" or in a counterclockwise direction
- Optical activity—The ability to rotate plane-polarized light
- Reference carbon atom—The highest numbered asymmetric carbon atom (e.g., C-5 for hexoses and C-4 for pentose sugars)

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