

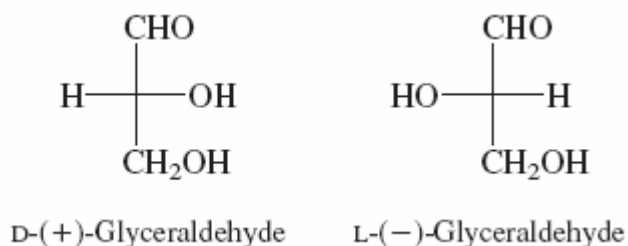
# Carbohydrates

## SUMMARY

Section 25.1 Carbohydrates are marvelous molecules! In most of them, every carbon bears a functional group, and the nature of the functional groups changes as the molecule interconverts between open-chain and cyclic hemiacetal forms. Any approach to understanding carbohydrates must begin with structure.

Carbohydrates are polyhydroxy aldehydes and ketones. Those derived from aldehydes are classified as **aldoses**; those derived from ketones are **ketoses**.

Section 25.2 Fischer projections and D–L notation are commonly used to describe carbohydrate stereochemistry. The standards are the enantiomers of glyceraldehyde.

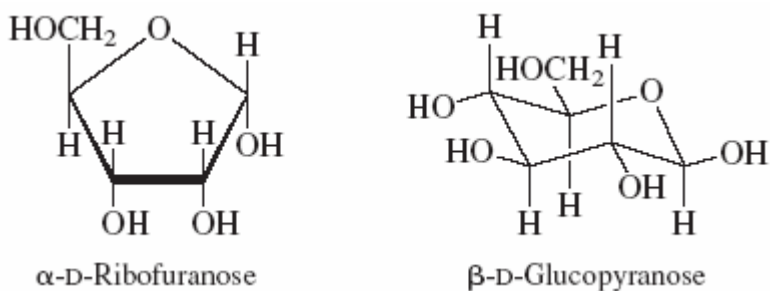


Section 25.3 Aldotetroses have two chirality centers, so four stereoisomers are possible. They are assigned to the D or the L series according to whether the configuration at their highest numbered chirality center is analogous to D- or L-glyceraldehyde, respectively. Both hydroxyl groups are on the same side of the Fischer projection in erythrose, but on opposite sides in threose. The Fischer projections of D-erythrose and D-threose are shown in Figure 25.2.

Section 25.4 Of the eight stereoisomeric aldopentoses, Figure 25.2 shows the Fischer projections of the D-enantiomers (D-ribose, D-arabinose, D-xylose, and D-lyxose). Likewise, Figure 25.2 gives the Fischer projections of the eight D-aldohexoses.

Section 25.5 The aldohexoses are allose, altrose, glucose, mannose, gulose, idose, galactose, and talose. The mnemonic “All altruists gladly make gum in gallon tanks” is helpful in writing the correct Fischer projection for each one.

Sections 25.6–25.7 Most carbohydrates exist as cyclic hemiacetals. Those with five-membered rings are called **furanose** forms; those with six-membered rings are called **pyranose** forms.



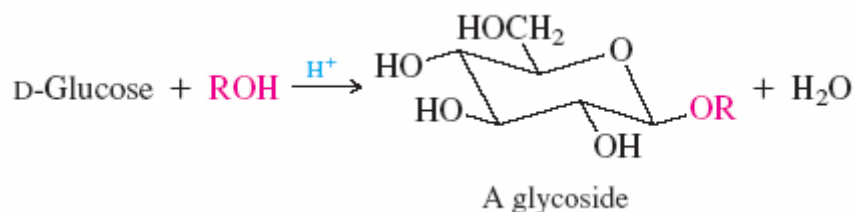
The **anomeric carbon** in a cyclic acetal is the one attached to *two* oxygens. It is the carbon that corresponds to the carbonyl carbon in the open-chain form. The symbols *a* and *b* refer to the configuration at the anomeric carbon.

Section 25.8 A particular carbohydrate can interconvert between furanose and pyranose forms and between the  $\alpha$  and  $\beta$  configuration of each form. The change from one form to an equilibrium mixture of all the possible hemiacetals causes a change in optical rotation called **mutarotation**.

Section 25.9 Ketoses are characterized by the ending *-ulose* in their name. Most naturally occurring ketoses have their carbonyl group located at C-2. Like aldoses, ketoses cyclize to hemiacetals and exist as furanose or pyranose forms.

Sections 25.10–25.12 Structurally modified carbohydrates include **deoxy sugars**, **amino sugars**, and **branched-chain carbohydrates**.

Section 25.13 Glycosides are acetals, compounds in which the anomeric hydroxyl group has been replaced by an alkoxy group. Glycosides are easily prepared by allowing a carbohydrate and an alcohol to stand in the presence of an acid catalyst.



Sections 25.14–25.15 **Disaccharides** are carbohydrates in which two monosaccharides are joined by a glycoside bond. **Polysaccharides** have many monosaccharide units connected through glycosidic linkages. Complete hydrolysis of disaccharides and polysaccharides cleaves the glycoside bonds, yielding the free monosaccharide components.

Sections 25.16–25.22 Carbohydrates undergo chemical reactions characteristic of aldehydes and ketones, alcohols, diols, and other classes of compounds, depending on their structure. A review of the reactions described in this chapter is presented in Table 25.2. Although some of the reactions have synthetic value, many of them are used in analysis and structure determination.

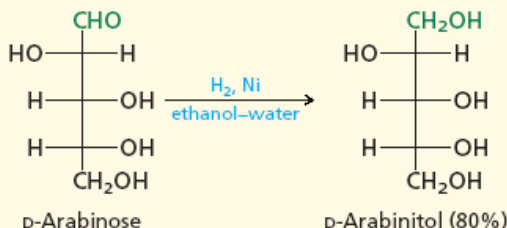
**TABLE 25.2** Summary of Reactions of Carbohydrates

Reaction (section) and comments

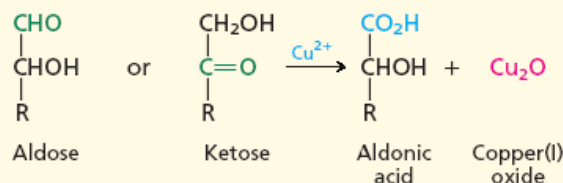
Example

**Transformations of the carbonyl group**

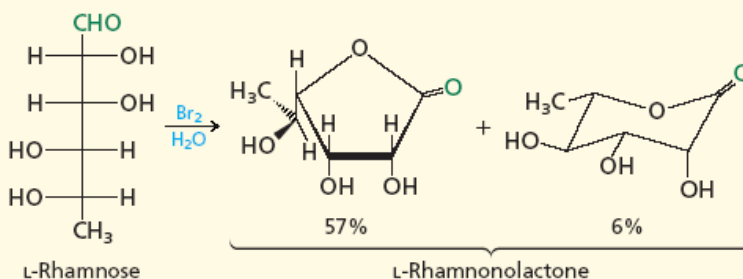
**Reduction (Section 25.18)** The carbonyl group of aldoses and ketoses is reduced by sodium borohydride or by catalytic hydrogenation. The products are called *alditols*.



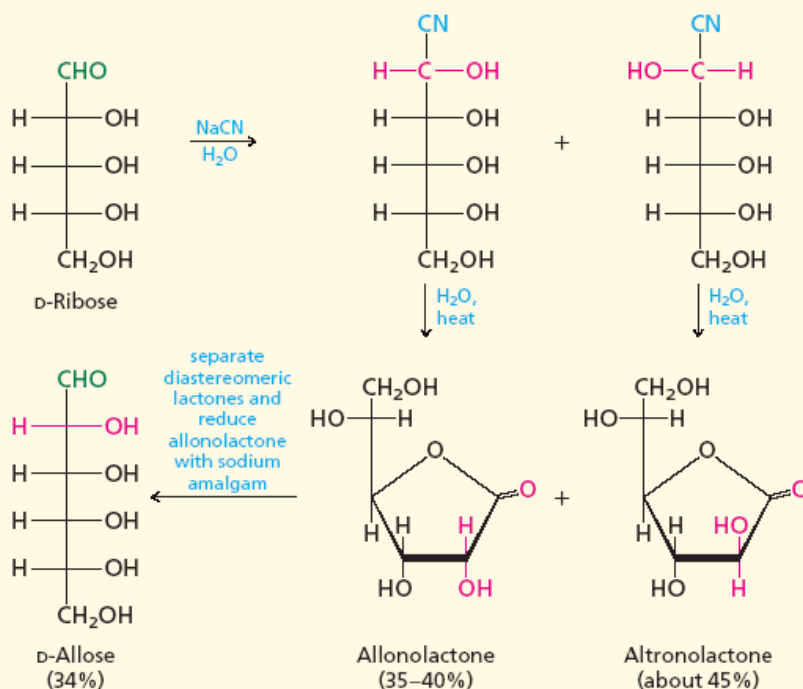
**Oxidation with Benedict's reagent (Section 25.19)** Sugars that contain a free hemiacetal function are called reducing sugars. They react with copper(II) sulfate in a sodium citrate/sodium carbonate buffer (Benedict's reagent) to form a red precipitate of copper(I) oxide. Used as a qualitative test for reducing sugars.



**Oxidation with bromine (Section 25.19)** When a preparative method for an aldonic acid is required, bromine oxidation is used. The aldonic acid is formed as its lactone. More properly described as a reaction of the anomeric hydroxyl group than of a free aldehyde.



**Chain extension by way of cyanohydrin formation (Section 25.20)** The Kiliani-Fischer synthesis proceeds by nucleophilic addition of HCN to an aldose, followed by conversion of the cyano group to an aldehyde. A mixture of stereoisomers results; the two aldoses are epimeric at C-2. Section 25.20 describes the modern version of the Kiliani-Fischer synthesis. The example at the right illustrates the classical version.



**TABLE 25.2** Summary of Reactions of Carbohydrates (*Continued*)

Reaction (section) and comments	Example
<p><b>Enediol formation (Section 25.21)</b> Enolization of an aldose or a ketose gives an enediol. Enediols can revert to aldoses or ketoses with loss of stereochemical integrity at the <math>\alpha</math>-carbon atom.</p>	<p>D-Glyceraldehyde      Enediol      1,3-Dihydroxyacetone</p>
<p><b>Reactions of the hydroxyl group</b></p> <p><b>Acylation (Section 25.22)</b> Esterification of the available hydroxyl groups occurs when carbohydrates are treated with acylating agents.</p>	<p>Sucrose</p> <p>(AcO = CH<sub>3</sub>CO)</p> <p>Sucrose octaacetate (66%)</p>
<p><b>Alkylation (Section 25.22)</b> Alkyl halides react with carbohydrates to form ethers at the available hydroxyl groups. An application of the Williamson ether synthesis to carbohydrates.</p>	<p>Methyl 4,6-O-benzylidene-<math>\alpha</math>-D-glucopyranoside</p> <p>Methyl 2,3-di-O-benzyl-4,6-O-benzylidene-<math>\alpha</math>-D-glucopyranoside (92%)</p>
<p><b>Periodic acid oxidation (Section 25.23)</b> Vicinal diol and <math>\alpha</math>-hydroxy carbonyl functions in carbohydrates are cleaved by periodic acid. Used analytically as a tool for structure determination.</p>	<p>2-Deoxy-D-ribose</p> <p>Propanedial      Formic acid      Formaldehyde</p>