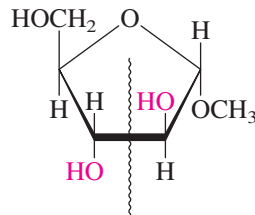
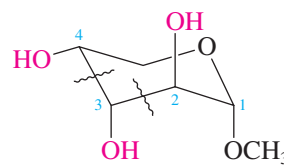


D-arabinose with methanol and hydrogen chloride. The size of the ring was identified as five-membered because only one mole of periodic acid was consumed per mole of glycoside and no formic acid was produced. Were the ring six-membered, two moles of periodic acid would be required per mole of glycoside and one mole of formic acid would be produced.



Only one site for periodic acid cleavage in methyl α -D-arabinofuranoside



Two sites of periodic acid cleavage in methyl α -D-arabinopyranoside, C-3 lost as formic acid

PROBLEM 25.20

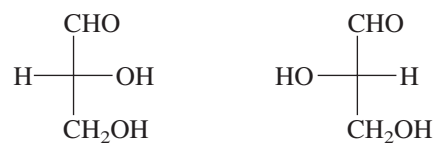
The α -methyl glycosides of the pyranose forms of all four aldopentoses give the same product on periodic acid oxidation. What is this product?

25.23 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.



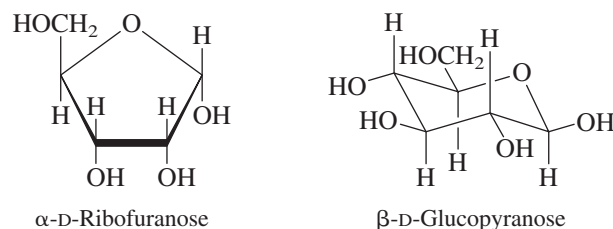
D-(+)-Glyceraldehyde L-(–)-Glyceraldehyde

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 α and β refer to the configuration at the anomeric carbon.

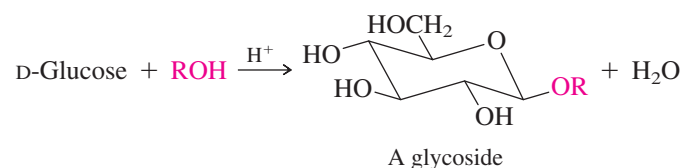
Section 25.8 A particular carbohydrate can interconvert between furanose and pyranose forms and between the α and β configuration of each form. The change from one form to an equilibrium mixture of all the possible hemiacetals causes a change in optical rotation called **mutarotation**.

In carbohydrates, the **anomeric effect** causes an axial substituent at the anomeric carbon of a pyranose ring to be more stable than an equatorial one. The effect is believed to be due to delocalization of an electron pair of the ring oxygen into an antibonding orbital of the anomeric substituent.

Section 25.9 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.

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

Reaction (section) and comments	Example
Acylation (Section 25.21) Esterification of the available hydroxyl groups occurs when carbohydrates are treated with acylating agents.	<p style="text-align: center;">Sucrose</p> <p style="text-align: center;">Sucrose octaacetate (66%)</p> <p>(AcO = CH_3CO)</p>
Alkylation (Section 25.21) Alkyl halides react with carbohydrates to form ethers at the available hydroxyl groups. An application of the Williamson ether synthesis to carbohydrates.	<p style="text-align: center;">Methyl 4,6-<i>O</i>-benzylidene-α-D-glucopyranoside</p> <p style="text-align: center;">Methyl 2,3-di-<i>O</i>-benzyl-4,6-<i>O</i>-benzylidene-α-D-glucopyranoside (92%)</p>
Periodic acid oxidation (Section 25.22) Vicinal diol and α -hydroxy carbonyl functions in carbohydrates are cleaved by periodic acid.	<p style="text-align: center;">2-Deoxy-D-ribose</p> <p style="text-align: center;">Propanedial Formic acid Formaldehyde</p>

PROBLEMS

25.21 Refer to the Fischer projection of D-(+)-xylose and give structural formulas for

- (-)-Xylose (Fischer projection)
- Xylitol
- β -D-Xylopyranose
- α -L-Xylofuranose
- Methyl α -L-xylofuranoside
- D-Xyloic acid (open-chain Fischer projection)
- δ -Lactone of D-xyloic acid
- γ -Lactone of D-xyloic acid
- Xylaric acid (open-chain Fischer projection)

25.22 What are the *R,S* configurations of the three chirality centers in D-xylose?

