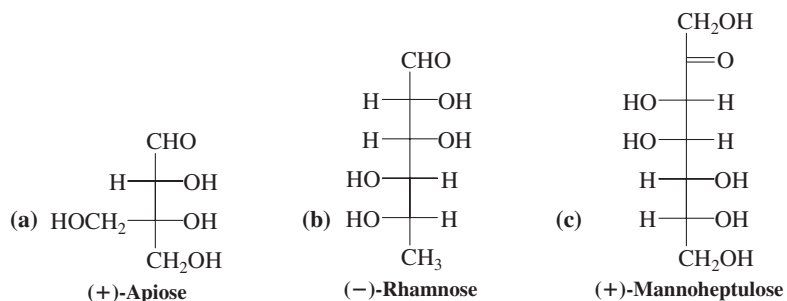


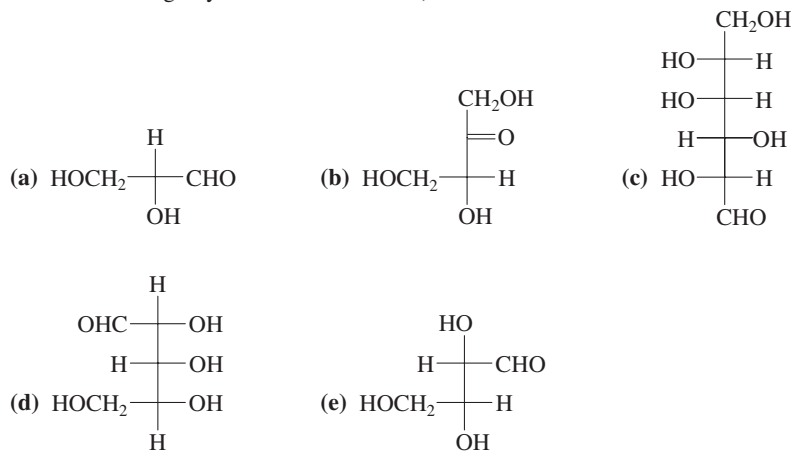
8. Sugars containing hemiacetal functions are called **reducing sugars**, because they readily reduce Tollens's and Fehling's solutions. Sugars in which the anomeric carbon is acetalized are nonreducing.
9. The synthesis of higher sugars is based on **chain lengthening**, the new carbon being introduced by cyanide ion. The synthesis of lower sugars relies on **Ruff chain shortening**, a terminal carbon being expelled as CO_2 .
10. The **Fischer proof** uses the techniques of chain lengthening and shortening together with the symmetry properties of aldaric acids to determine the structures of the aldoses.
11. **Di-** and **higher saccharides** are formed by the combination of hemiacetal and alcohol hydroxy groups of two sugars to give an acetal linkage.
12. The change in optical rotation observed in acidic aqueous solutions of sucrose, called the **inversion of sucrose**, is due to the equilibration of the starting sugar with the various cyclic and anomeric forms of its component monomers.
13. Many sugars contain modified backbones. Amino groups may have replaced hydroxy groups, there may be substituents of various complexity (**aglycons**), the backbone carbon atoms of a sugar may lack oxygens, and (rarely) the sugar may adopt the L configuration.

Problems

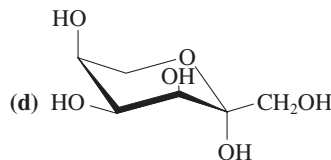
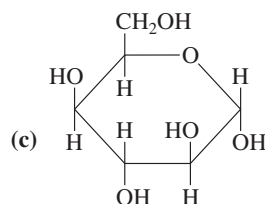
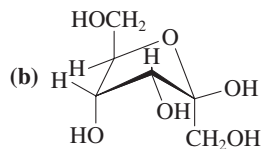
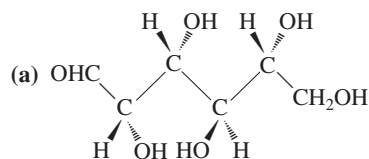
33. The designations D and L as applied to sugars refer to the configuration of the highest-numbered stereocenter. If the configuration of the highest numbered stereocenter of D-ribose (Figure 24-1) is switched from D to L, is the product L-ribose? If not, what is the product? How is it related to D-ribose (i.e., what kind of isomers are they)?
34. To which classes of sugars do the following monosaccharides belong? Which are D and which are L?



35. Draw open-chain (Fischer-projection) structures for L-(+)-ribose and L-(-)-glucose (see Exercise 24-2). What are their systematic names?
36. Identify the following sugars, which are represented by unconventionally drawn Fischer projections. (**Hint:** It will be necessary to convert these projections into more conventional representations *without* inverting any of the stereocenters.)



37. Redraw each of the following sugars in open-chain form as a Fischer projection, and find its common name.



38. For each of the following sugars, draw all reasonable cyclic structures, using either Haworth or conformational formulas; indicate which structures are pyranoses and which are furanoses; and label α and β anomers.

(a) (-)-Threose; (b) (-)-allose; (c) (-)-ribulose; (d) (+)-sorbose;
(e) (+)-mannoheptulose (Problem 34).

39. Are any of the sugars in Problem 38 incapable of mutarotation? Explain your answer.

40. Draw the most stable pyranose conformation of each of the following sugars. (a) α -D-Arabinose; (b) β -D-galactose; (c) β -D-mannose; (d) α -D-idose.

41. Ketoses show positive Fehling's and Tollens's tests not only by oxidation to α -dicarbonyl compounds, but through a second process: Ketoses isomerize to aldoses in the presence of base. The aldose then undergoes oxidation by the Fehling's or Tollens's solution. Using any ketose in Figure 24-2, propose a base-catalyzed mechanistic pathway to the corresponding aldose. [Hint: Review Section 18-2.]

42. What are the products (and their ratios) of periodic acid cleavage of each of the following substances: (a) 1,3-dihydroxyacetone; (b) rhamnose (Problem 34); (c) glucitol.

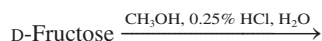
43. Write the expected products of the reaction of each of the following sugars with (i) $\text{Br}_2, \text{H}_2\text{O}$; (ii) $\text{HNO}_3, \text{H}_2\text{O}, 60^\circ\text{C}$; (iii) $\text{NaBH}_4, \text{CH}_3\text{OH}$; and (iv) excess $\text{C}_6\text{H}_5\text{NHNH}_2, \text{CH}_3\text{CH}_2\text{OH}, \Delta$. Find the common names of all the products. (a) D-(-)-Threose; (b) D-(+)-xylose; (c) D-(+)-galactose.

44. Draw the Fischer projection of an aldohexose that will give the same osazone as (a) D-(-)-idose and (b) L-(-)-altrose.

45. (a) Which of the aldopentoses (Figure 24-1) would give optically active alditols upon reduction with NaBH_4 ? (b) Using D-fructose, illustrate the results of NaBH_4 reduction of a ketose. Is the situation more complicated than reduction of an aldose? Explain.

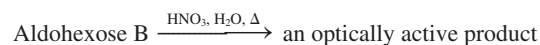
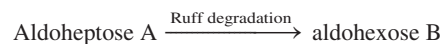
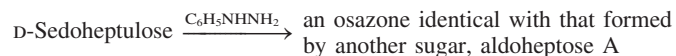
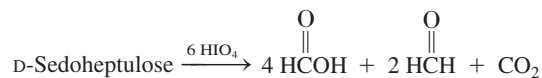
46. Which of the following glucoses and glucose derivatives are capable of undergoing mutarotation? (a) α -D-Glucopyranose; (b) methyl α -D-glucopyranoside; (c) methyl α -2,3,4,6-tetra-O-methyl-D-glucopyranoside (i.e., the tetramethyl ether at carbon 2, 3, 4, and 6); (d) α -2,3,4,6-tetra-O-methyl-D-glucopyranose; (e) α -D-glucopyranose 1,2-acetone acetal.

47. (a) Explain why the oxygen at C1 of an aldopyranose can be methylated so much more easily than the other oxygens in the molecule. (b) Explain why the methyl ether unit at C1 of a fully methylated aldopyranose can be hydrolyzed so much more easily than the other methyl ether functions in the molecule. (c) Write the expected product(s) of the following reaction.



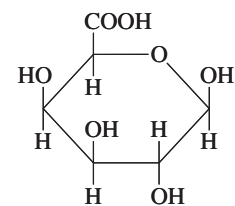
48. Of the four aldopentoses, two form diacetals readily when treated with excess acidic acetone, but the other two form only monoacetals. Explain.

49. D-Sedoheptulose is a sugar intermediate in a metabolic cycle (the *pentose oxidation cycle*) that ultimately converts glucose into 2,3-dihydroxypropanal (glyceraldehyde) plus three equivalents of CO_2 . Determine the structure of D-sedoheptulose from the following information.



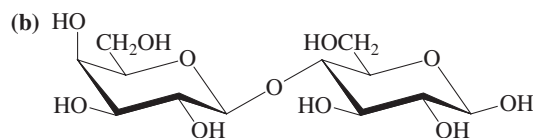
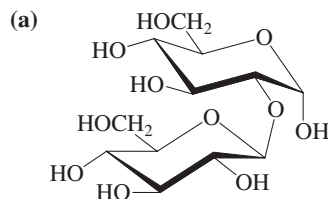
50. Is it possible for two different diastereomeric aldoses to give the same product upon Kiliani-Fischer chain elongation? Why or why not?
51. In each of the following groups of three D aldoses, identify the two that give the same product upon Ruff degradation. (a) Galactose, gulose, talose; (b) glucose, gulose, idose; (c) allose, altrose, mannose.
52. Illustrate the results of chain elongation of D-talose through a cyanohydrin. How many products are formed? Draw them. After treatment with warm HNO_3 , does the product(s) give optically active or inactive dicarboxylic acids?
53. **CHALLENGE** (a) Write a detailed mechanism for the isomerization of β -D-fructofuranose from the hydrolysis of sucrose into an equilibrium mixture of the β -pyranose and β -furanose forms. (b) Although fructose usually appears as a furanose when it is part of a polysaccharide, in the pure crystalline form, fructose adopts a β -pyranose structure. Draw β -D-fructopyranose in its most stable conformation. In water at 20°C , the equilibrium mixture contains about 68% β -D-pyranose and 32% β -D-furanose. (c) What is the free-energy difference between the pyranose and furanose forms at this temperature? (d) Pure β -D-fructopyranose has $[\alpha]_D^{20^\circ\text{C}} = -132$. The equilibrium pyranose-furanose mixture has $[\alpha]_D^{20^\circ\text{C}} = -92$. Calculate $[\alpha]_D^{20^\circ\text{C}}$ for pure β -D-fructofuranose.

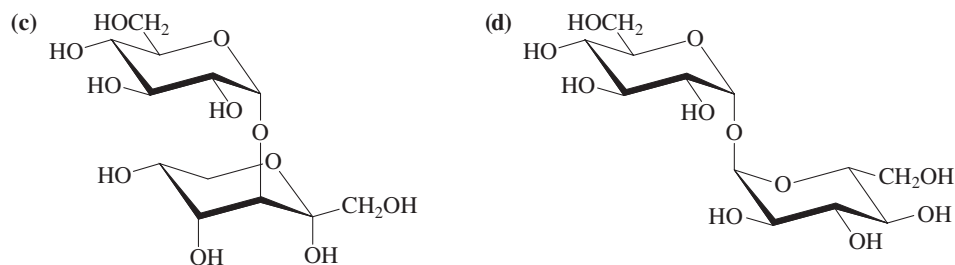
54. Classify each of the following sugars and sugar derivatives as either reducing or nonreducing. (a) D-Glyceraldehyde; (b) D-arabinose; (c) β -D-arabinopyranose 3,4-acetone acetal; (d) β -D-arabinopyranose acetone diacetal; (e) D-ribulose; (f) D-galactose; (g) methyl β -D-galactopyranoside; (h) β -D-galacturonic acid (as shown in the margin); (i) β -cellobiose; (j) α -lactose.
55. Is α -lactose capable of mutarotation? Write an equation to illustrate your answer.



β -D-Galacturonic acid

56. Trehalose, sophorose, and turanose are disaccharides. Trehalose is found in the cocoons of some insects, sophorose turns up in a few bean varieties, and turanose is an ingredient in low-grade honey made by bees with indigestion from a diet of pine tree sap. Identify among the following structures those that correspond to trehalose, sophorose, and turanose on the basis of the following information: (i) Turanose and sophorose are reducing sugars. Trehalose is nonreducing. (ii) Upon hydrolysis, sophorose and trehalose give two molecules each of aldoses. Turanose gives one molecule of an aldose and one molecule of a ketose. (iii) The two aldoses that constitute sophorose are anomers of each other.



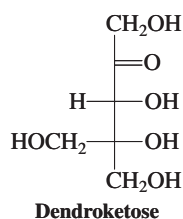


57. Identify and, using the information in Sections 24-1 and 24-11, provide names for the carbohydrates that are contained in the structure of stevioside (Chemical Highlight 24-3).

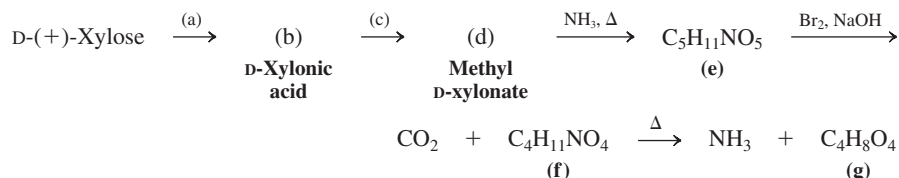
58. The disaccharide at the terminus of the oligosaccharide attached to the surface of type B red blood cells is an α -D-galactopyranosyl- β -D-galactopyranose. The linkage is an acetal from C1 of the first galactose to the C3 hydroxy group of the second. In other words, the full name is 3-(α -D-galactopyranosyl)- β -D-galactopyranose. Draw the structure of this disaccharide, using conformationally accurate chairs for the six-membered rings.

59. Glucose reacts with ammonia in the presence of a trace of acid to give predominantly β -D-glucofuranosylamine (Section 24-12). Propose a reasonable mechanism for this transformation. Why is only the hydroxy group at C1 replaced?

60. (a) A mixture of (*R*)-2,3-dihydroxypropanal (D-glyceraldehyde) and 1,3-dihydroxyacetone that is treated with aqueous NaOH rapidly yields a mixture of three sugars: D-fructose, D-sorbose, and racemic dendroketo (only one enantiomer is shown here). Explain this result by means of a detailed mechanism. (b) The same product mixture is also obtained if either the aldehyde or the ketone alone is treated with base. Explain. [Hint: Closely examine the intermediates in your answer to (a).]

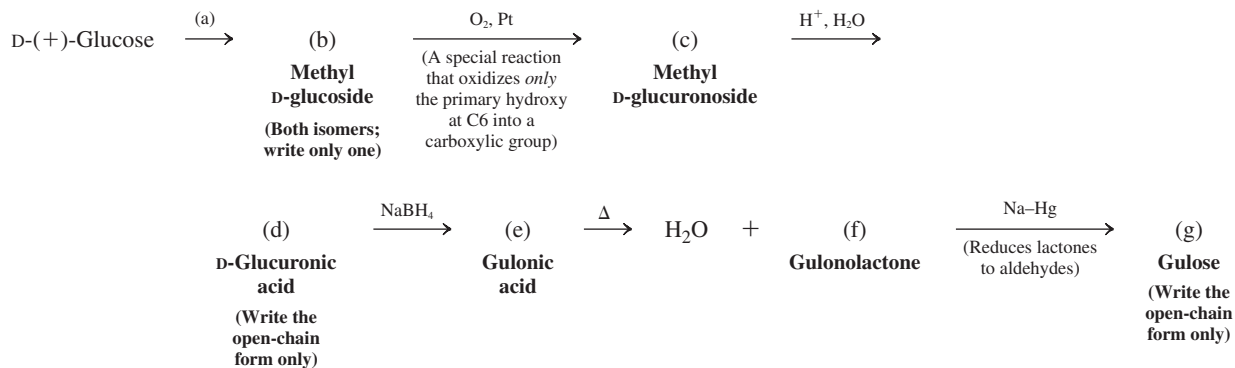


61. Write or draw the missing reagents and structures (a) through (g). What is the common name of (g)?

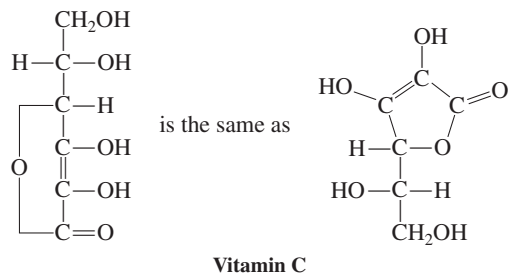


The preceding sequence (called the *Weerman degradation*) achieves the same end as what procedure described in this chapter?

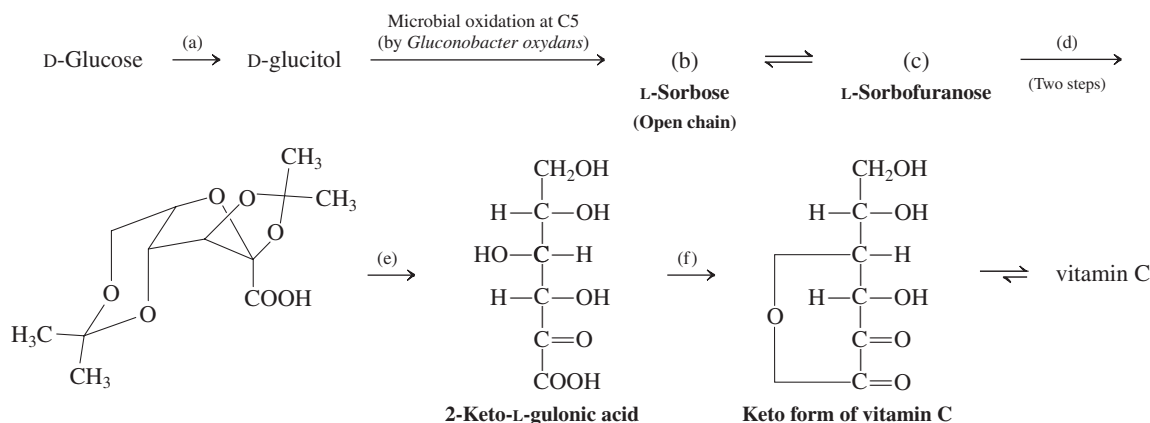
62. **CHALLENGE** Fischer's solution to the problem of sugar structures was actually much more difficult to achieve experimentally than Section 24-10 implies. For one thing, the only sugars that he could readily obtain from natural sources were glucose, mannose, and arabinose. (Erythrose and threose were, in fact, not then available at all, either naturally or synthetically.) His ingenious solution required a way to exchange the functionalities at C1 and C6 of glucose and mannose in order to make the critical distinction described at the end of the section. (Of course, had gulose existed in nature, all this effort would have been unnecessary, but Fischer wasn't so lucky.) Fischer's plan led to unexpected difficulties, because at a key stage he got a troublesome mixture of products. Nowadays we solve the problem in the manner shown below. Fill in the missing reagents and structures (a) through (g). Use Fischer projections for all structures. Follow the instructions and hints in parentheses.



63. **CHALLENGE** Vitamin C (ascorbic acid, Section 22-9) is present almost universally in the plant and animal kingdoms. (According to Linus Pauling, mountain goats biosynthesize from 12 to 14 g of it per day.) Animals produce it from D-glucose in the liver by the four-step sequence D-glucose \rightarrow D-glucuronic acid (see Problem 62) \rightarrow D-glucuronic acid γ -lactone \rightarrow L-gulonic acid γ -lactone \rightarrow vitamin C.



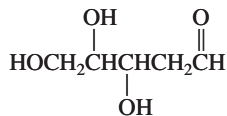
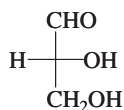
The enzyme that catalyzes the last reaction, L-gulonolactone oxidase, is absent from humans, some monkeys, guinea pigs, and birds, presumably because of a defective gene resulting from a mutation that may have occurred some 60 million years ago. As a result, we have to get our vitamin C from food or make it in the laboratory. In fact, the ascorbic acid in almost all vitamin supplements is synthetic. An outline of one of the major commercial syntheses follows. Draw the missing reagents and products (a) through (f). (**Hint:** See Chemical Highlight 24-1.)



Team Problem

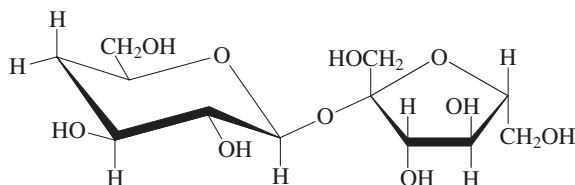
64. This problem is meant to encourage you to think as a team about how you might establish the structure of a simple disaccharide, with some additional information at your disposal. Consider D-lactose (Section 24-11) and assume you do not know its structure. You are given the knowledge that it is a disaccharide, linked in a β manner to the anomeric carbon of only one of the sugars, and you are given the structures of all of the aldohexoses (Table 24-1), as well as all of their possible methyl ethers. Deal with the following questions as a team or by dividing the work, before joint discussion, as appropriate.

- Mild acid hydrolyzes your "unknown" to D-galactose and D-glucose. How much information can you derive from that result?
- Propose an experiment that tells you that the two sugars are not connected through their respective anomeric centers.
- Propose an experiment that tells you which one of the two sugars contains an acetal group used to bind the other. (**Hint:** The functional group chemistry of the monosaccharides described in the chapter can be applied to higher sugars as well. Specifically, consider Section 24-4 here.)
- Making use of the knowledge of the structure of all possible methyl ethers of the component monosaccharides, design experiments that will tell you which (nonanomeric) hydroxy group is responsible for the disaccharide linkage.
- Similarly, can you use this approach to distinguish between a furanose and pyranose structure for the component of the disaccharide that can mutarotate?



Preprofessional Problems

65. Most natural sugars have a stereocenter that is identical to that in (*R*)-2,3-dihydroxypropanal, shown as a Fischer projection in the margin. What is the (very popular) common name for this compound? (a) D-(+)-Glyceraldehyde; (b) D-(-)-glyceraldehyde; (c) L-(+)-glyceraldehyde; (d) L-(-)-glyceraldehyde
66. What kind of sugar is the compound shown in the margin? (a) An aldopentose; (b) a ketopentose; (c) an aldohexose; (d) a ketohexose
67. Which one of the following statements is *true* about the oxacyclohexane conformer of the sugar β -D-(+)-glucopyranose?
- (a) One OH group is axial, but all remaining substituents are equatorial.
 (b) The CH₂OH group is axial, but all remaining groups are equatorial.
 (c) All groups are axial. (d) All groups are equatorial.
68. The methyl glycoside of mannose is made by treating the sugar with
- (a) AlBr₃, CH₃Br; (b) dilute aqueous CH₃OH; (c) CH₃OCH₃ and LiAlH₄;
 (d) CH₃OH, HCl; (e) oxacyclopropane, AlCl₃
69. One of the statements below is correct about the sugar shown. Which one?



- (a) It is a nonreducing sugar. (b) It forms an osazone.
 (c) It exists in two anomeric forms. (d) It undergoes mutarotation.