

## Chapter 25 – Biomolecules: Carbohydrates

### Chapter Outline

- I. Classification of carbohydrates(Section 25.1).
  - A. Simple vs. complex:
    1. Simple carbohydrates can't be hydrolyzed to smaller units.
    2. Complex carbohydrates are made up of two or more simple sugars linked together.
      - a. A disaccharide is composed of two monosaccharides.
      - b. A polysaccharide is composed of three or more monosaccharides.
  - B. Aldoses vs. ketoses:
    1. A monosaccharide with an aldehyde carbonyl group is an aldose.
    2. A monosaccharide with a ketone carbonyl group is a ketose.
  - C. *Tri-*, *tetr-*, *pent-*, etc. indicate the number of carbons in the monosaccharide.
- II. Monosaccharides (Sections 25.2 – 25.7).
  - A. Configurations of monosaccharides (Section 25.2 – 25.4).
    1. Fischer projections (Section 25.2).
      - a. Each chirality center of a monosaccharide is represented by a pair of crossed lines.
        - i. The horizontal line represents bonds coming out of the page.
        - ii. The vertical line represents bonds going into the page.
      - b. Allowed manipulations of Fischer projections:
        - i. A Fischer projection can be rotated on the page by 180°, but not by 90° or 270°.
        - ii. Holding one group steady, the other three groups can be rotated clockwise or counterclockwise.
      - c. Rules for assigning *R,S* configurations.
        - i. Assign priorities to the substituents in the usual way.
        - ii. Perform one of the two allowed motions to place the lowest priority group at the top of the Fischer projection.
        - iii. Determine the direction of rotation of the arrow that travels from group 1 to group 2 to group 3, and assign *R* or *S* configuration.
      - d. Carbohydrates with more than one chirality center are shown by stacking the centers on top of each other.

The carbonyl carbon is placed at or near the top of the Fischer projection.
    2. D,L sugars (Section 25.3).
      - a. (*R*)-Glyceraldehyde is also known as D-glyceraldehyde.
      - b. In D sugars, the –OH group farthest from the carbonyl group points to the right.

Most naturally-occurring sugars are D sugars.
      - c. In L sugars, the –OH group farthest from the carbonyl group points to the left.
      - d. D,L designations refer only to the configuration farthest from the carbonyl carbon and are unrelated to the direction of rotation of plane-polarized light.
    3. Configurations of the aldoses (Section 25.4).
      - a. There are 4 aldotetroses – D and L erythrose and threose.
      - b. There are 4 D,L pairs of aldopentoses: ribose, arabinose, xylose and lyxose.
      - c. There are 8 D,L pairs of aldohexoses : allose, altrose, glucose, mannose, gulose, idose, galactose, and talose.
      - d. A scheme for drawing and memorizing the D-aldohexoses:
        - i. Draw all –OH groups at C5 pointing to the right.
        - ii. Draw the first four –OH groups at C4 pointing to the right and the second four pointing to the left.

- iii. Alternate  $\text{-OH}$  groups at C3: two right, two left, two right, two left.
- iv. Alternate  $\text{-OH}$  groups at C2: right, left, etc.
- v. Use the mnemonic "All altruists gladly make gum in gallon tanks" to assign names.

#### B. Cyclic structures of monosaccharides (Section 25.5).

##### 1. Hemiacetal formation.

- a. Monosaccharides are in equilibrium with their internal hemiacetals.
  - i. Glucose exists primarily as a six-membered pyranose ring, formed by the  $\text{-OH}$  group at C5 and the aldehyde.
  - ii. Fructose exists primarily as a five-membered furanose ring.
- b. Structure of pyranose rings.
  - i. Pyranose rings have a chair-like geometry.
  - ii. The hemiacetal oxygen is at the right rear for D-sugars.
  - iii. An  $\text{-OH}$  group on the right in a Fischer projection is on the bottom face in a pyranose ring, and an  $\text{-OH}$  group on the left is on the top face.
  - iv. For D sugars, the  $\text{-CH}_2\text{OH}$  group is on the top.

##### 2. Mutarotation.

- a. When a monosaccharide cyclizes, a new chirality center is generated.
  - i. The two diastereomers are anomers.
  - ii. The form with the anomeric  $\text{-OH}$  group trans to the  $\text{-CH}_2\text{OH}$  group is the  $\alpha$  anomer (minor anomer).
  - iii. The form with the anomeric  $\text{-OH}$  group cis to the  $\text{-CH}_2\text{OH}$  group is the  $\beta$  anomer (major anomer).
- b. When a solution of either pure anomer is dissolved in water, the optical rotation of the solution reaches a constant value.
  - i. This process is called mutarotation.
  - ii. Mutarotation is due to the reversible opening and recyclizing of the hemiacetal ring and is catalyzed by both acid and base.

#### C. Reactions of monosaccharides (Section 25.6).

##### 1. Ester and ether formation.

- a. Esterification occurs by treatment with an acid anhydride or acid chloride.
- b. Ethers are formed by treatment with methyl iodide and  $\text{Ag}_2\text{O}$ .
- c. Ester and ether derivatives are crystalline and easy to purify.

##### 2. Glycoside formation.

- a. Treatment of a hemiacetal with an alcohol and an acid catalyst yields an acetal.
  - i. Acetals aren't in equilibrium with an open-chain form.
  - ii. Aqueous acid reconverts the acetal to a monosaccharide.
- b. These acetals, called glycosides, occur in nature.
- c. Glycosides are named by first citing the alkyl group and then replacing the *-ose* suffix of the sugar with *-oside*.
- d. The laboratory synthesis of glycosides is achieved by the Koenigs-Knorr reaction.
  - i. Treatment of the acetylpyranose with  $\text{HBr}$ , followed by treatment with the appropriate alcohol and  $\text{Ag}_2\text{O}$ , gives the acetylglycoside.
  - ii. Both anomers give the same product.
  - iii. The reaction involves neighboring-group participation by acetate.

##### 3. Phosphorylation.

- a. Monosaccharides can be phosphorylated by ATP.
- b. The resulting glycosyl phosphate can react with a second nucleoside triphosphate.
- c. This product can react with a lipid or a protein to form a glycoconjugate.

##### 4. Reduction of monosaccharides.

Reaction of a monosaccharide with  $\text{NaBH}_4$  yields an alditol.

5. Oxidation of monosaccharides.
    - a. Several mild reagents can oxidize the carbonyl group to a carboxylic acid (aldonic acid).
      - i. Tollens reagent, Fehling's reagent and Benedict's reagent all serve as tests for reducing sugars.
      - ii. All aldoses and some ketoses are reducing sugars, but glycosides are nonreducing.
      - iii. In the laboratory, aqueous  $\text{Br}_2$  is used to oxidize aldoses (not ketoses).
    - b. The more powerful oxidizing agent, dilute  $\text{HNO}_3$ , oxidizes aldoses to dicarboxylic acids (aldaric acids).
  6. Chain-lengthening: the Kiliani–Fischer synthesis.
    - a. In the Kiliani–Fischer synthesis, an aldehyde group becomes C2 of a chain-lengthened monosaccharide.
    - b. The reaction involves cyanohydrin formation, reduction and hydrolysis.
    - c. The products are two diastereomeric aldoses that differ in configuration at C2.
  7. Chain-shortening: the Wohl degradation.
    - a. The Wohl degradation shortens an aldose by one carbon.
    - b. The reaction involves treatment of the aldose with hydroxylamine, dehydration and loss of HCN from the resulting cyanohydrin.
- D. Eight essential monosaccharides (Section 25.7).
1. Glucose, galactose, mannose and xylose are monosaccharides.
  2. Fucose is a deoxy sugar.
  3. *N*-Acetylglucosamine and *N*-acetylgalactosamine are amino sugars.
  4. *N*-Acetylneuraminic acid is the parent compound of the sialic acids.
  5. All of the essential monosaccharides arise from glucose.
- III. Other carbohydrates (Sections 25.8 – 25.11).
- A. Disaccharides (Section 25.8).
1. Cellobiose and maltose.
    - a. Cellobiose and maltose contain a 1→4-glycosidic acetal bond between two glucose monosaccharide units.
    - b. Maltose consists of two glucopyranose units joined by a 1→4- $\alpha$ -glycosidic bond.
    - c. Cellobiose consists of two glucopyranose units joined by a 1→4- $\beta$ -glycosidic bond.
    - d. Both maltose and cellobiose are reducing sugars and exhibit mutarotation.
    - e. Humans can't digest cellobiose but can digest maltose.
  2. Lactose.
    - a. Lactose consists of a unit of galactose joined by a  $\beta$ -glycosidic bond between C1 and C4 of a glucose unit.
    - b. Lactose is a reducing sugar found in milk.
  3. Sucrose.
    - a. Sucrose is a disaccharide that yields glucose and fructose on hydrolysis.
      - a. Sucrose is called "invert sugar" because the sign of rotation changes when sucrose is hydrolyzed.
      - b. Sucrose is one of the most abundant pure organic chemicals in the world.
    - b. The two monosaccharides are joined by a glycosidic link between C1 of glucose and C2 of fructose.
    - c. Sucrose isn't a reducing sugar and doesn't exhibit mutarotation.

## B. Polysaccharides and their synthesis (Section 25.9).

1. Polysaccharides have a reducing end and undergo mutarotation, but aren't considered to be reducing sugars because of their size.
2. Important polysaccharides.
  - a. Cellulose.
    - i. Cellulose consists of thousands of D-glucose units linked by 1→4-β-glycosidic bonds.
    - ii. In nature, cellulose is used as structural material.
  - b. Starch.
    - i. Starch consists of thousands of D-glucose units linked by 1→4-α-glycosidic bonds.
    - ii. Starch can be separated into amylose (water-soluble) and amylopectin (water-insoluble) fractions.

Amylopectin contains 1→6-α-glycosidic branches.
    - iii. Starch is digested in the mouth by glycosidase enzymes, which only cleave α-glycosidic bonds.
  - c. Glycogen.
    - i. Glycogen is an energy-storage polysaccharide.
    - ii. Glycogen contains both 1→4- and 1→6-links.
3. An outline of the glycan assembly method of polysaccharide synthesis.
  - a. A glycal (a monosaccharide with a C1–C2 double bond) is protected at C6 by formation of a silyl ether and at C3–C4 by formation of a cyclic carbonate ester.
  - b. The protected glycal is epoxidized.
  - c. Treatment of the glycal epoxide (in the presence of ZnCl<sub>2</sub>) with a second glycal having a free C6 hydroxyl group forms a disaccharide.
  - d. The process can be repeated.

## C. Other important carbohydrates (Section 25.10).

1. Deoxy sugars have an –OH group missing and are components of nucleic acids.
2. In amino sugars, an –OH is replaced by a –NH<sub>2</sub>.

Amino sugars are found in chitin and in antibiotics.

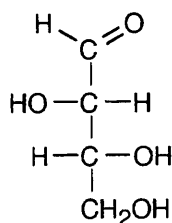
## D. Cell surface carbohydrates and carbohydrate vaccines (Section 25.11).

1. Polysaccharides are involved in cell surface recognition.
  - a. Polysaccharide markers on the surface of red blood cells are responsible for blood-group incompatibility.
  - b. Red blood cells have two types of markers (antigenic determinants) – A and B.
  - c. Unusual carbohydrates are components of these markers.
2. Possible anticancer vaccines have been synthesized from antibodies to cell-surface polysaccharides found on the surface of cancer cells.

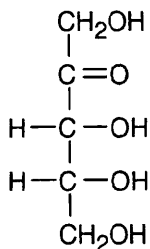
## Solutions to Problems

## 25.1

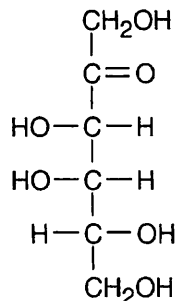
(a)

**Threose***an aldotetrose*

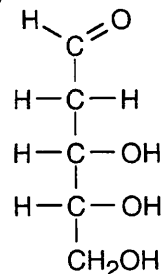
(b)

**Ribulose***a ketopentose*

(c)

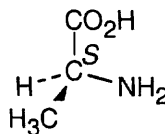
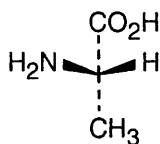
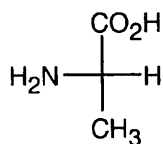
**Tagatose***a ketohexose*

(d)

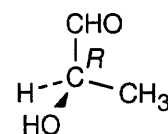
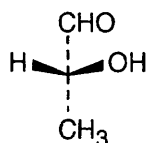
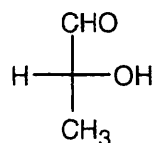
**2-Deoxyribose***an aldopentose*

**25.2** Horizontal bonds of Fischer projections point out of the page, and vertical bonds point into the page.

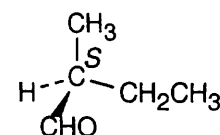
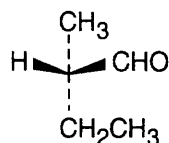
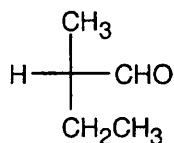
(a)



(b)



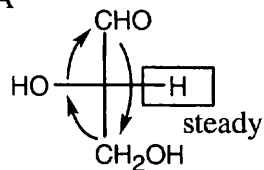
(c)



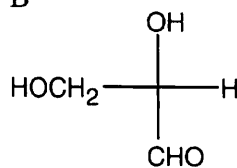
**25.3** To decide if two Fischer projections are identical, use the two allowable rotations to superimpose two groups of each projection. If the remaining groups are also superimposed after rotation, the projections represent the same enantiomer.

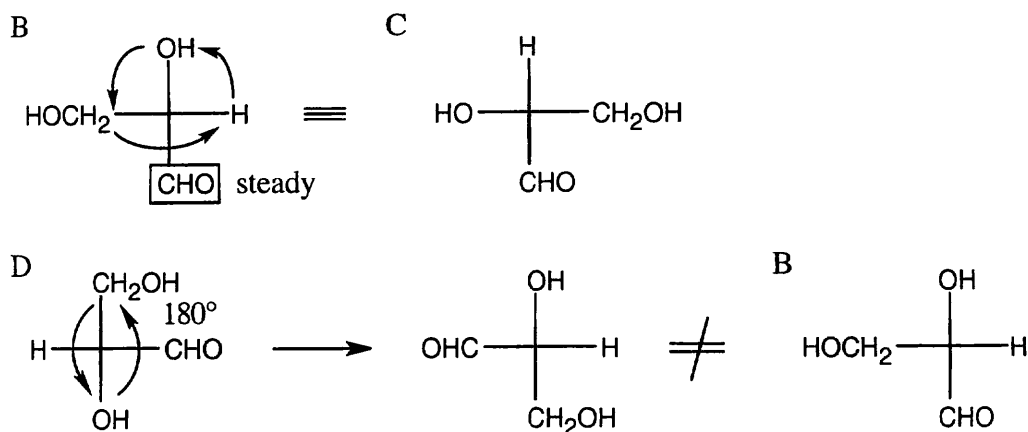
(a) Since  $-\text{H}$  is in the same position in both A and B, keep it steady, and rotate the other three groups. If, after rotation, all groups are superimposed, the two projections are identical. If only two groups are superimposed, the projections are enantiomers. Thus, A is identical to B.

A



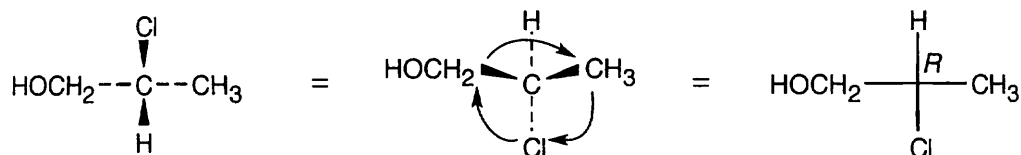
B





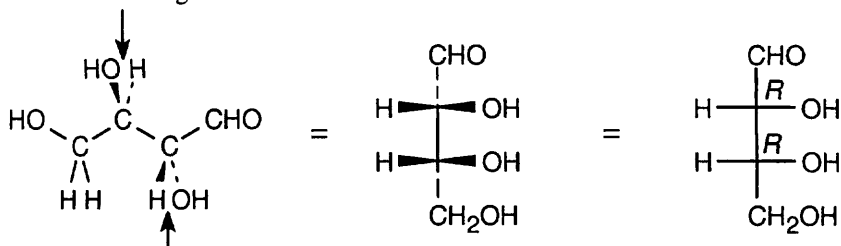
Projections A, B and C are identical, and D is their enantiomer.

- 25.4** Rotate the structure  $180^\circ$  around the horizontal axis to arrive at a drawing having the hydrogen at the rear. Assign the *R,S* configuration as usual, and draw the Fischer projection



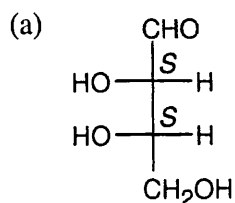
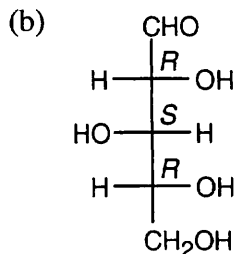
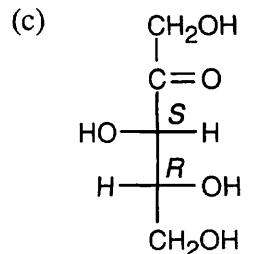
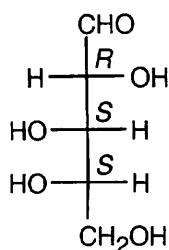
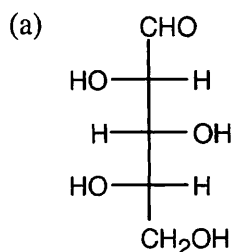
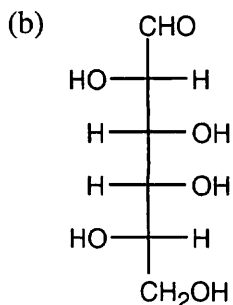
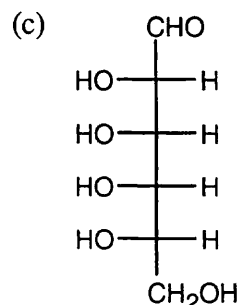
- 25.5** Draw the skeleton of the Fischer projection and add the  $-\text{CHO}$  and  $-\text{CH}_2\text{OH}$  groups to the top and bottom, respectively. Look at each carbon from the direction in which the  $-\text{H}$  and  $-\text{OH}$  point out of the page, and draw what you see on the Fischer projection.

View C3 from this side;  
 $-\text{OH}$  is on the right.



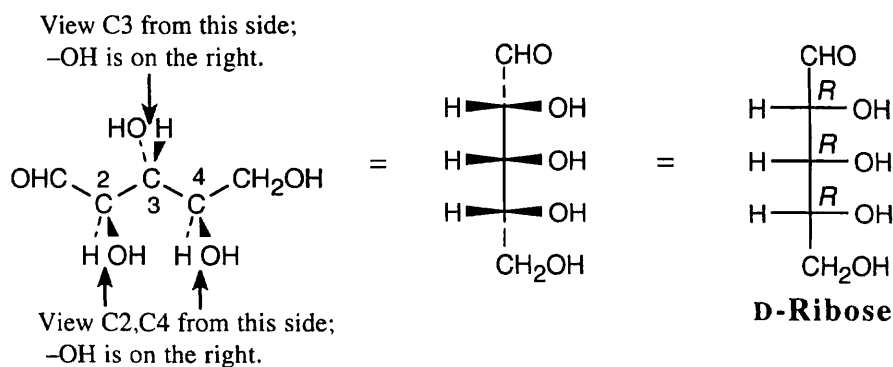
View C2 from this side;  
 $-\text{OH}$  is on the right.

**25.6** The hydroxyl group bonded to the chiral carbon farthest from the carbonyl group points to the right in a D sugar, and points to the left in an L sugar.

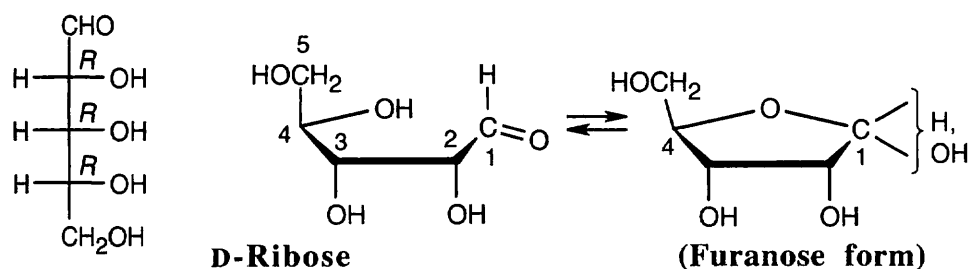
**L-Erythrose****D-Xylose****D-Xylulose****25.7****L-(+)-Arabinose****25.8****L-Xylose****L-Galactose****L-Allose**

**25.9** An aldohexose has 5 chirality centers. Thus, there are  $2^5 = 32$  aldohexoses – 16 D aldohexoses and 16 L aldohexoses.

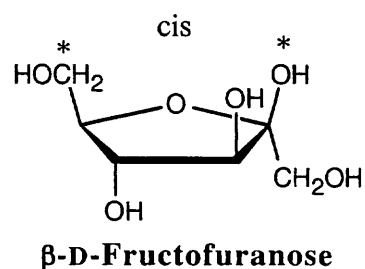
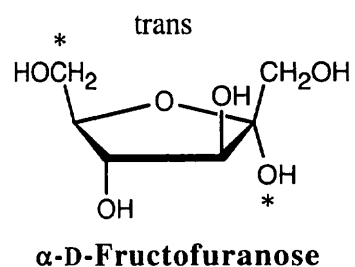
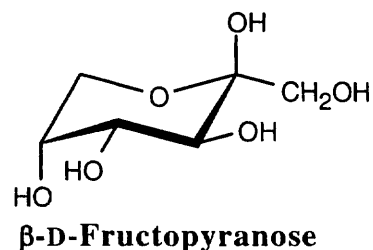
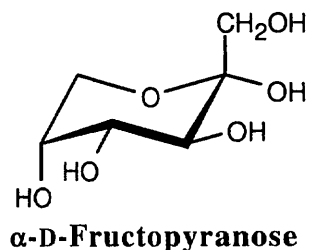
**25.10** See Problem 25.5 for the method of solution.



**25.11** The steps for drawing a furanose are similar to the steps for drawing a pyranose. Ring formation occurs between the  $\text{-OH}$  group at C4 and the carbonyl carbon.

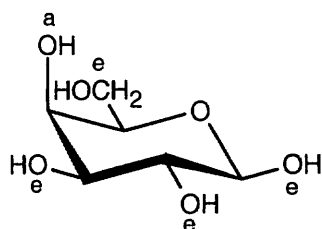
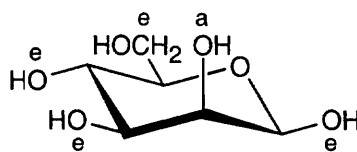


**25.12** The furanose of fructose results from ring formation between the  $\text{-OH}$  group at C5 and the ketone at C2. In the  $\alpha$  anomer, the anomeric  $\text{-OH}$  group is trans to the C6  $\text{-CH}_2\text{OH}$  group, and in the  $\beta$  anomer the two groups are cis. In the pyranose form, cyclization occurs between the  $\text{-OH}$  group at C6 and the ketone. The more stable chair conformations are shown.



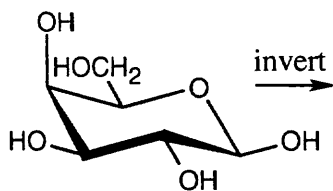


- 25.13** There are two ways to draw these anomers: (1) Following the steps in Worked Example 25.3, draw the Fischer projection, lay it on its side, form the pyranose ring, and convert it to a chair, remembering that the anomeric  $-\text{OH}$  group is cis to the  $\text{C6}$  group; (2) Draw  $\beta\text{-D-glucopyranose}$ , and exchange the hydroxyl groups that differ between glucose and the other two hexoses.

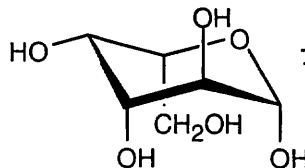
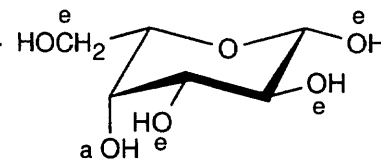
 **$\beta\text{-D-Galactopyranose}$**  **$\beta\text{-D-Mannopyranose}$** 

$\beta\text{-D-Galactopyranose}$  and  $\beta\text{-D-mannopyranose}$  each have one hydroxyl group in the axial position and are therefore of similar stability.

- 25.14** In the previous problem we drew  $\beta\text{-D-galactopyranose}$ . In this problem, invert the configuration at each chirality center of the D enantiomer and perform a ring-flip to arrive at the structure of the L enantiomer.

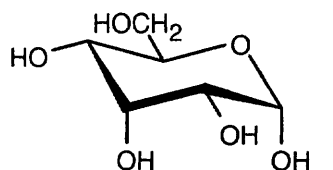
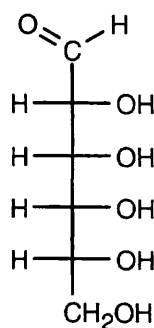
 **$\beta\text{-D-Galactopyranose}$** 

invert

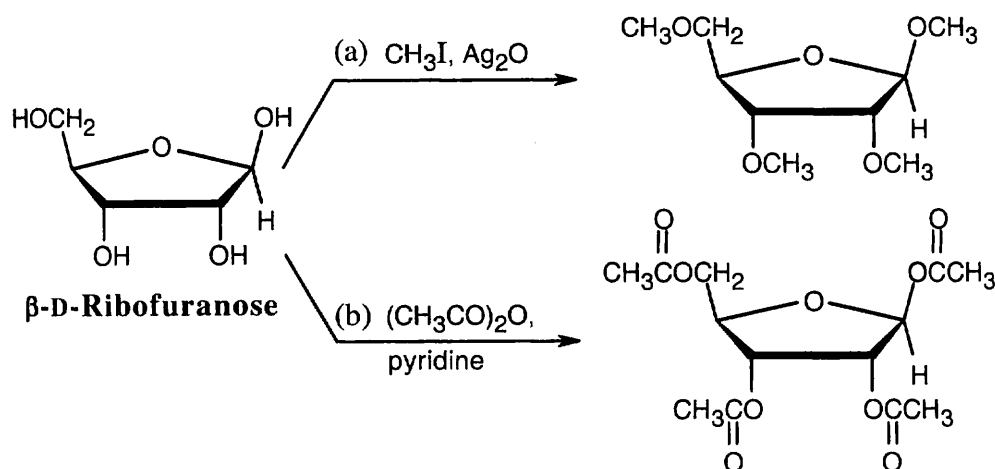
ring-  
flip **$\beta\text{-L-Galactopyranose}$** 

All substituents, except for the  $-\text{OH}$  at  $\text{C4}$ , are equatorial in the more stable conformation of  $\beta\text{-L-galactopyranose}$ .

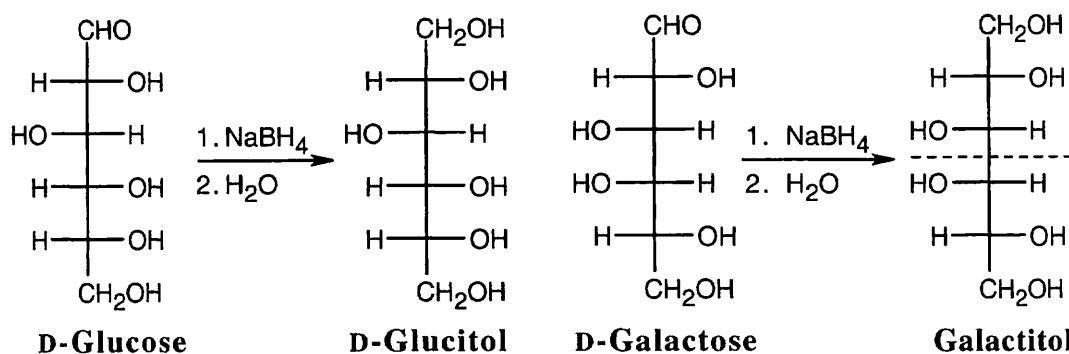
- 25.15** From the model, we can see that the monosaccharide is the pyranose form of a D-hexose. It is an  $\alpha$ -anomer because the anomeric hydroxyl group is trans to the group at  $\text{C6}$ . Comparing the model with  $\alpha\text{-D-glucopyranose}$ , we see that all groups have the same axial/equatorial relationship, except for the hydroxyl group at  $\text{C3}$ , which is axial in the model and equatorial in  $\alpha\text{-D-glucopyranose}$ . The monosaccharide is  $\alpha\text{-D-allopyranose}$ .

 **$\alpha\text{-D-Allopyranose}$** **D-Allose**

## 25.16

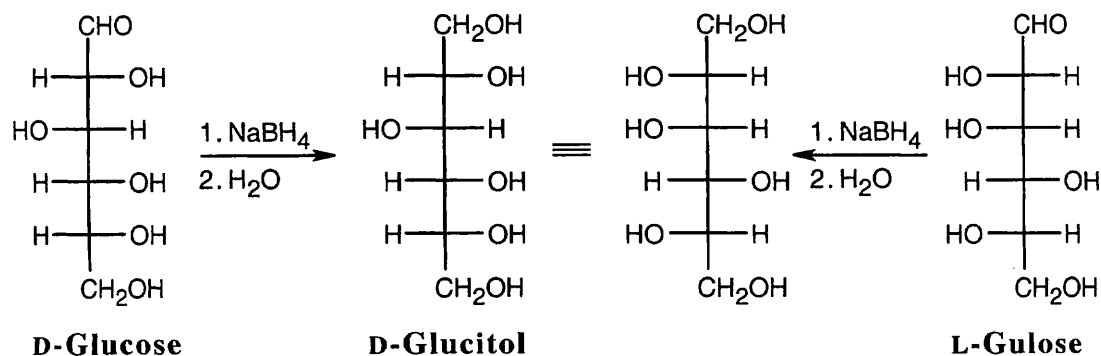


## 25.17



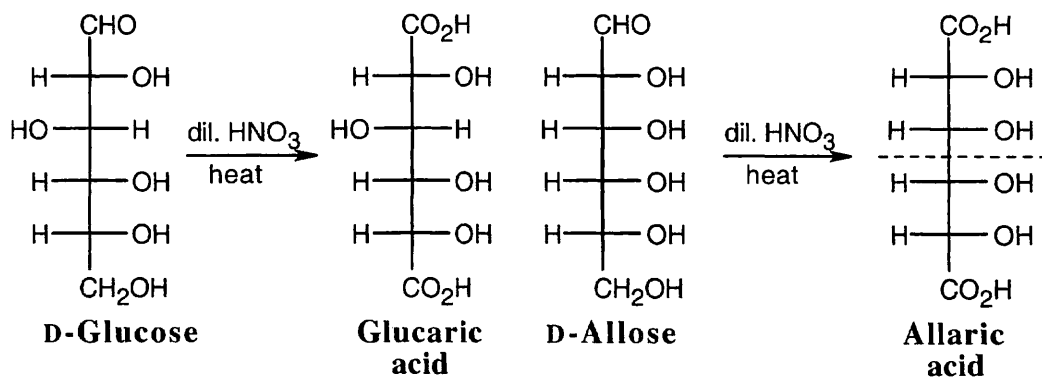
Reaction of D-galactose with  $\text{NaBH}_4$  yields an alditol that has a plane of symmetry and is a meso compound.

## 25.18



Reaction of an aldose with  $\text{NaBH}_4$  produces a polyol (alditol). Because an alditol has the same functional group at both ends, two different aldoses can yield the same alditol. Here, L-gulose and D-glucose form the same alditol (rotate the Fischer projection of L-gulitol  $180^\circ$  to see the identity).

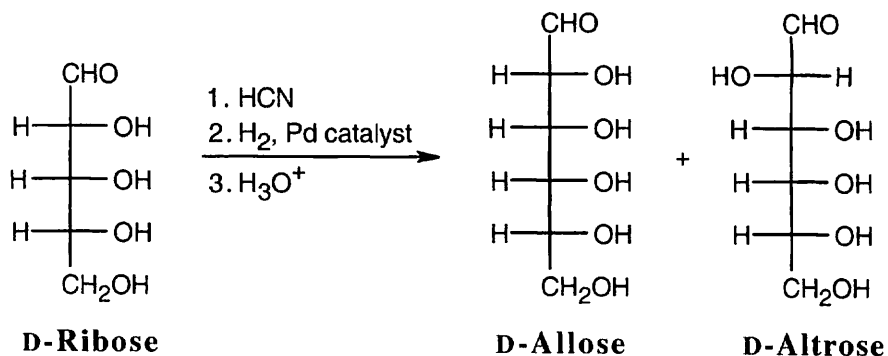
## 25.19



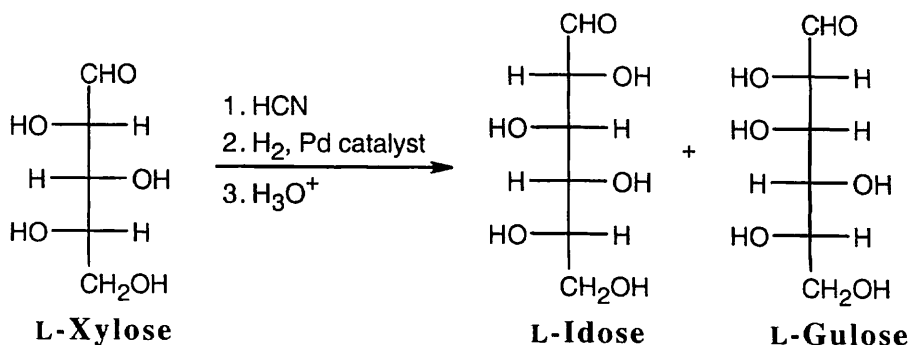
Allaric acid has a plane of symmetry and is an optically inactive meso compound. Glucaric acid has no symmetry plane.

**25.20** D-Allose and D-galactose yield meso aldaric acids. All other D-hexoses produce optically active aldaric acids on oxidation.

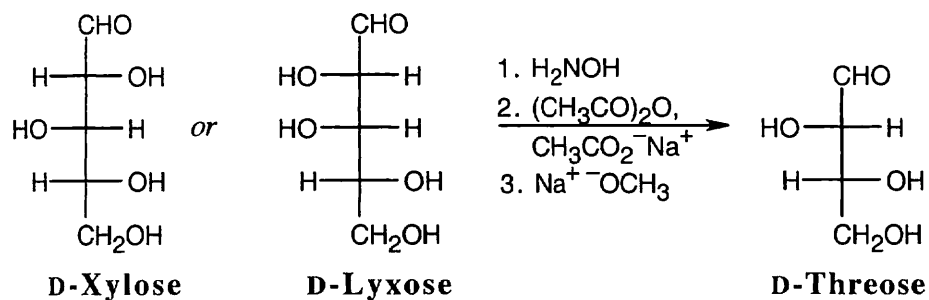
**25.21** The products of Kiliani–Fischer reaction of D-ribose have the same configuration at C3, C4 and C5 as D-ribose.



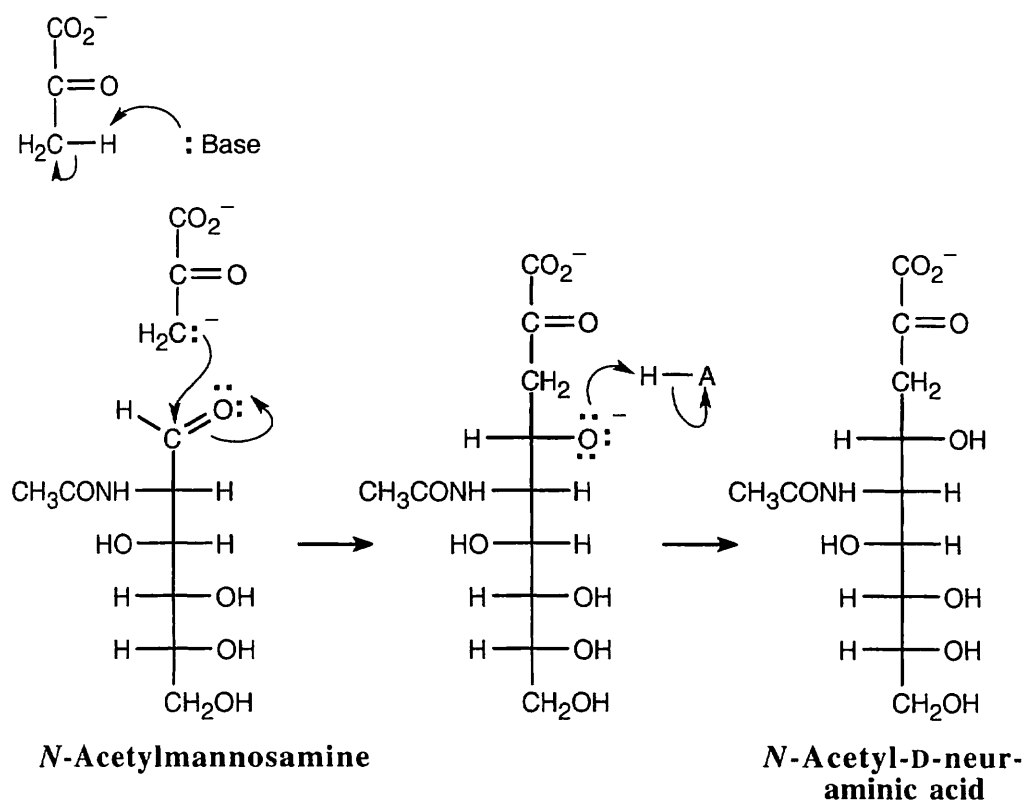
**25.22** The aldopentose, L-xylose has the same configuration as the configuration at C3, C4 and C5 of L-idose and L-gulose.



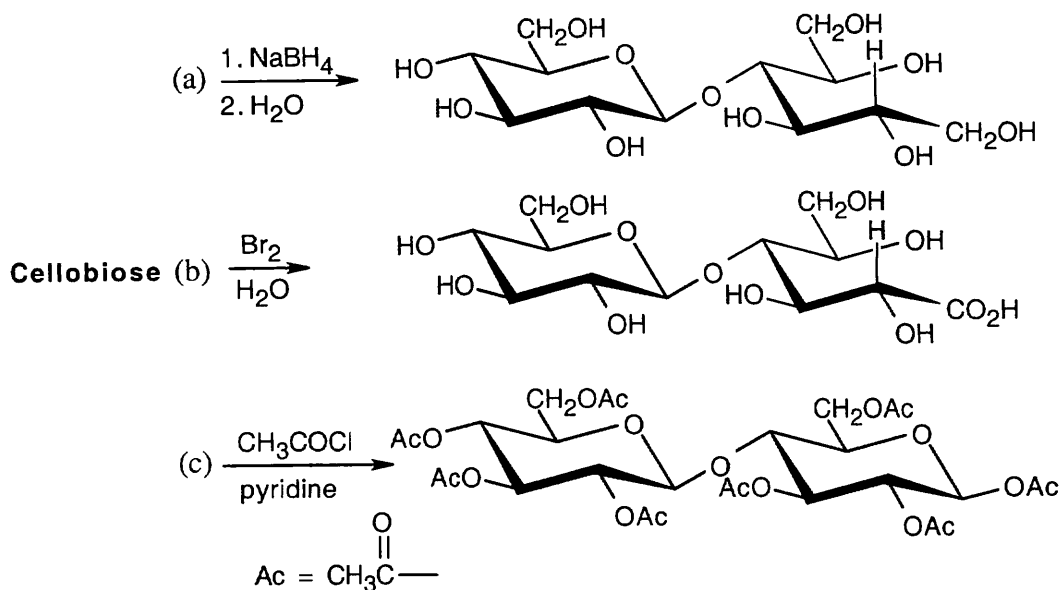
**25.23** The aldopentoses have the same configurations at C3 and C4 as D-threose.



**25.24**

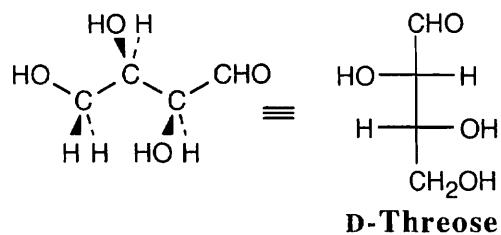


## 25.25

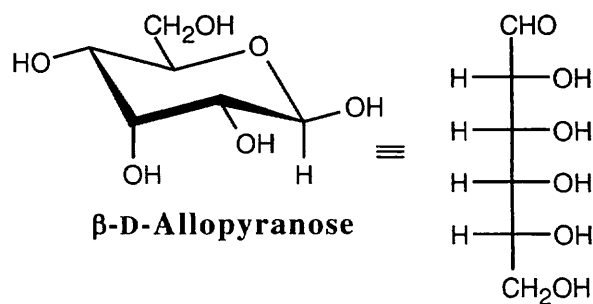


## Visualizing Chemistry

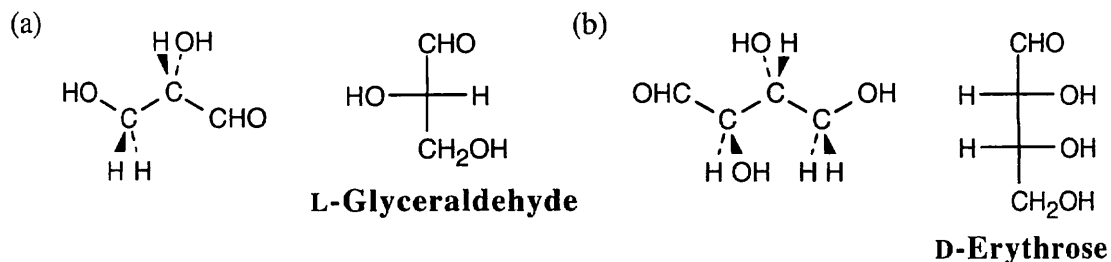
**25.26** (a) Convert the model to a Fischer projection, remembering that the aldehyde group is on top, pointing into the page, and that the groups bonded to the carbons below point out of the page. The model represents a D-aldose because the  $-\text{OH}$  group at the chiral carbon farthest from the aldehyde points to the right.



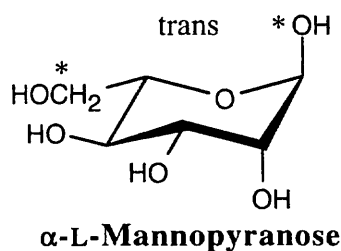
(b) Break the hemiacetal bond and uncoil the aldohexose. Notice that all hydroxyl groups point to the right in the Fischer projection. The model represents the  $\beta$  anomer of D-allopyranose.



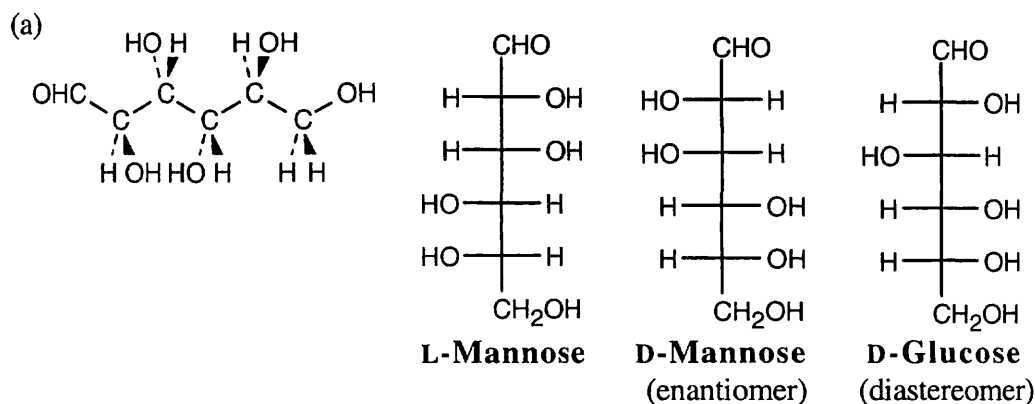
**25.27** The hints in the previous problem also apply here. Molecular models are also helpful.



**25.28** The structure represents an  $\alpha$  anomer because the anomeric  $-\text{OH}$  group and the  $-\text{CH}_2\text{OH}$  group are trans. The compound is  $\alpha$ -L-mannopyranose because the  $-\text{OH}$  group at C2 is the only non-anomeric axial hydroxyl group.

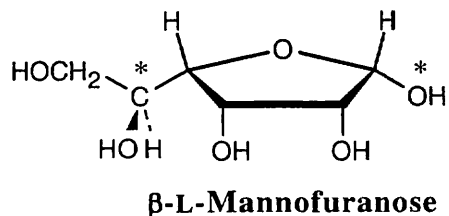


**25.29**



(b) The model represents an L-aldohexose because the hydroxyl group on the chiral carbon farthest from the aldehyde group points to the left.

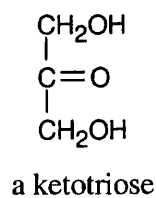
(c) This is tricky! The furanose ring of an aldohexose is formed by connecting the  $-\text{OH}$  group at C4 to the aldehyde carbon. The best way to draw the anomer is to lie L-mannose on its side and form the ring. All substituents point down in the furanose, and the anomeric  $-\text{OH}$  and the  $-\text{CH}(\text{OH})\text{CH}_2\text{OH}$  group are cis.



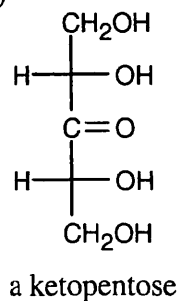
## Additional Problems

## 25.30

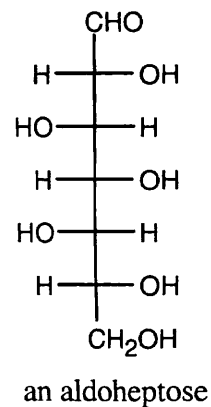
(a)



(b)

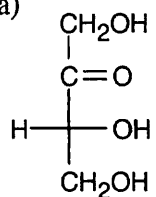


(c)

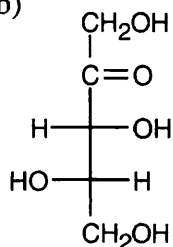


## 25.31

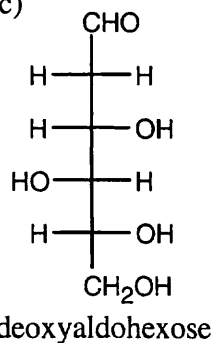
(a)



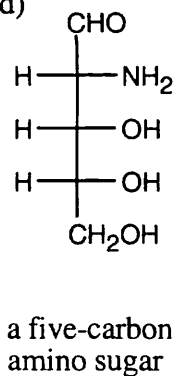
(b)



(c)

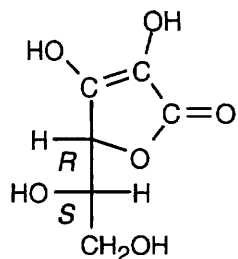


(d)

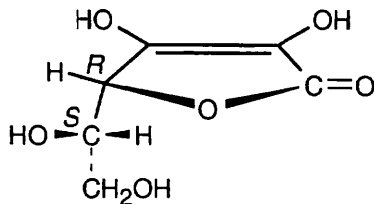


## 25.32 – 25.33

Ascorbic acid has an L configuration because the hydroxyl group at the lowest chirality center points to the left.

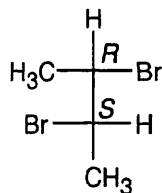


L-Ascorbic acid

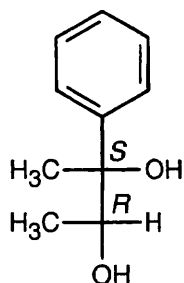


## 25.34

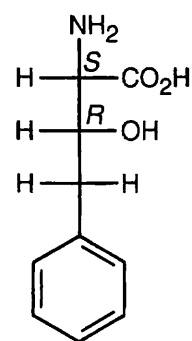
(a)



(b)

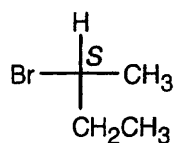
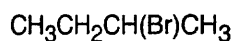


(c)

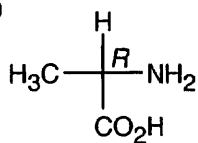
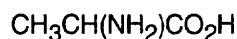


## 25.35

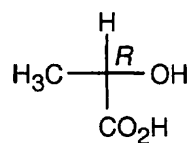
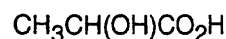
(a)

**(S)-2-Bromobutane**

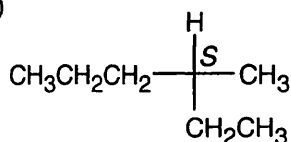
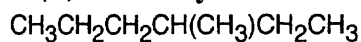
(b)

**(R)-Alanine**

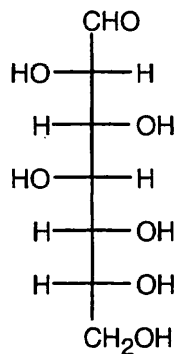
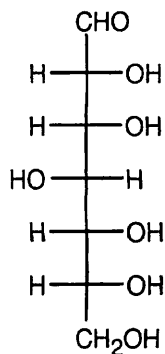
(c)

**(R)-2-Hydroxypropanoic acid**

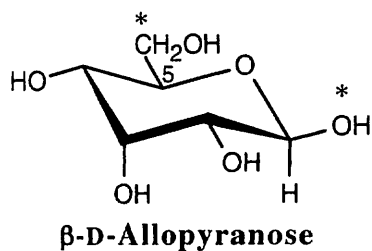
(d)

**(S)-3-Methylhexane**

## 25.36



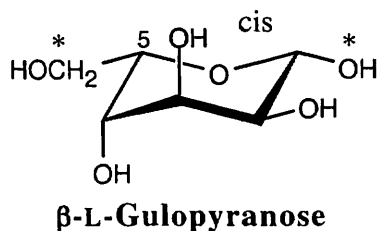
## 25.37



This structure is a pyranose (6-membered ring) and is a β anomer (the C1 hydroxyl group and the  $-\text{CH}_2\text{OH}$  groups are cis). It is a D sugar because the  $-\text{OH}$  at C5 is on the right in the uncoiled form.



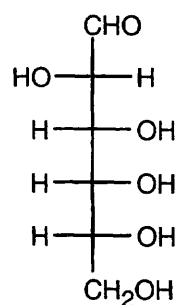
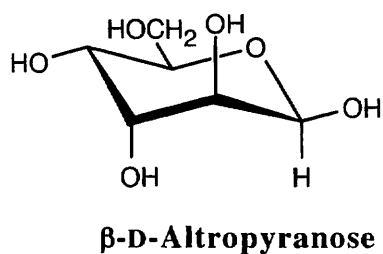
25.38



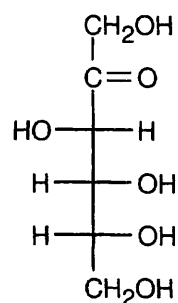
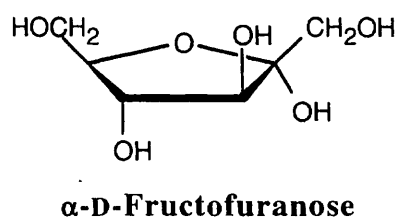
This sugar is a  $\beta$ -pyranose. It is an L sugar because the -O- at C5 points to the left in the uncoiled form. It's also possible to recognize this as an L sugar by the fact that the configuration at C5 is S.

25.39

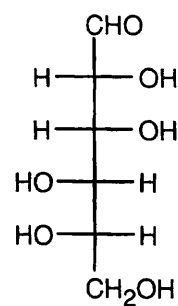
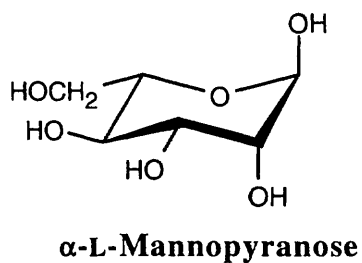
(a)



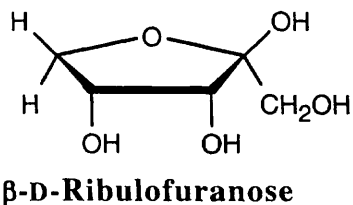
(b)



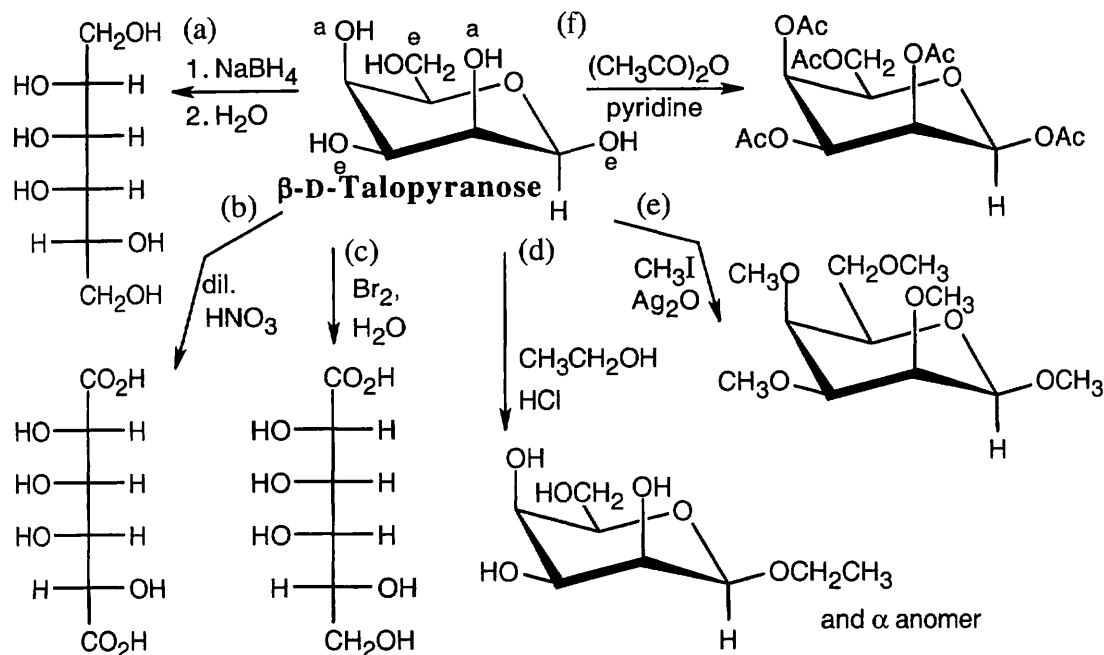
(c)



25.40

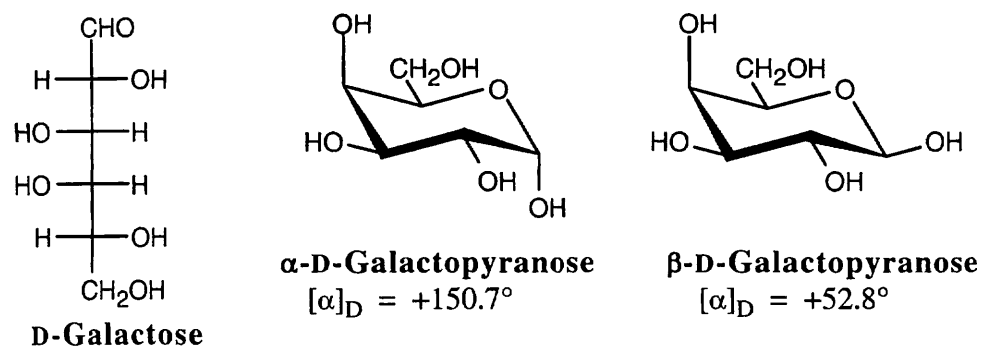


## 25.41–25.42



**25.43** D-Ribose and L-xylose are diastereomers and differ in all physical properties (or if they have identical physical properties in one category, it is a coincidence).

## 25.44

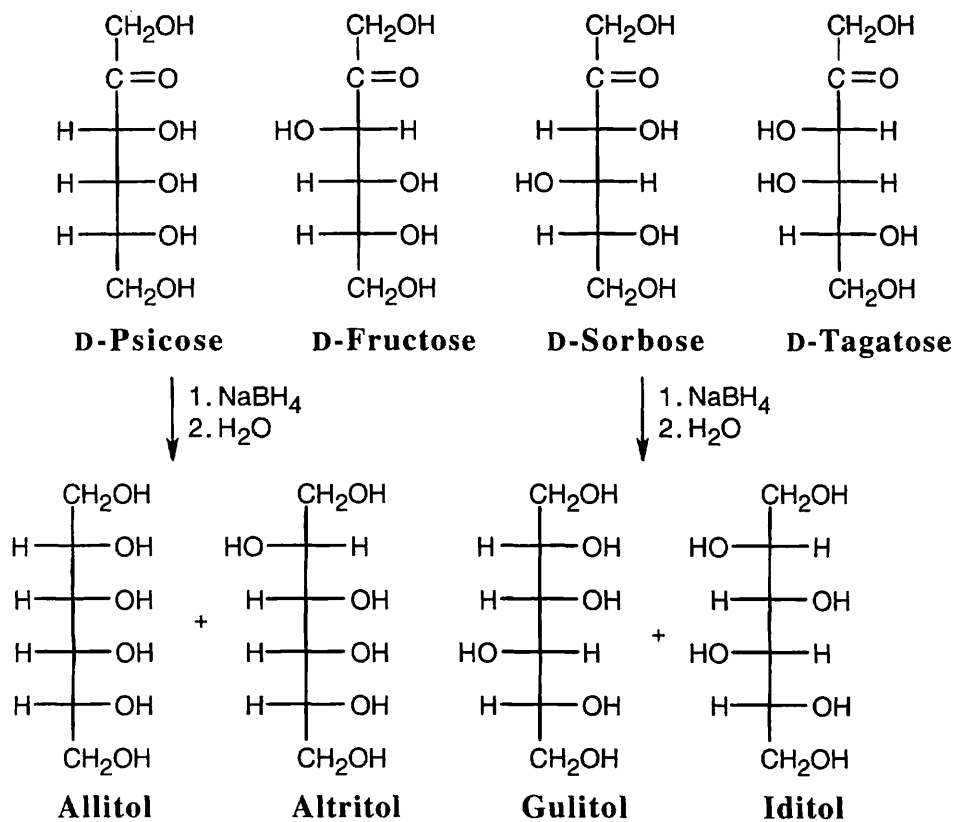


Let  $x$  be the percent of D-galactose present as the  $\alpha$  anomer and  $y$  be the percent of D-galactose present as the  $\beta$  anomer.

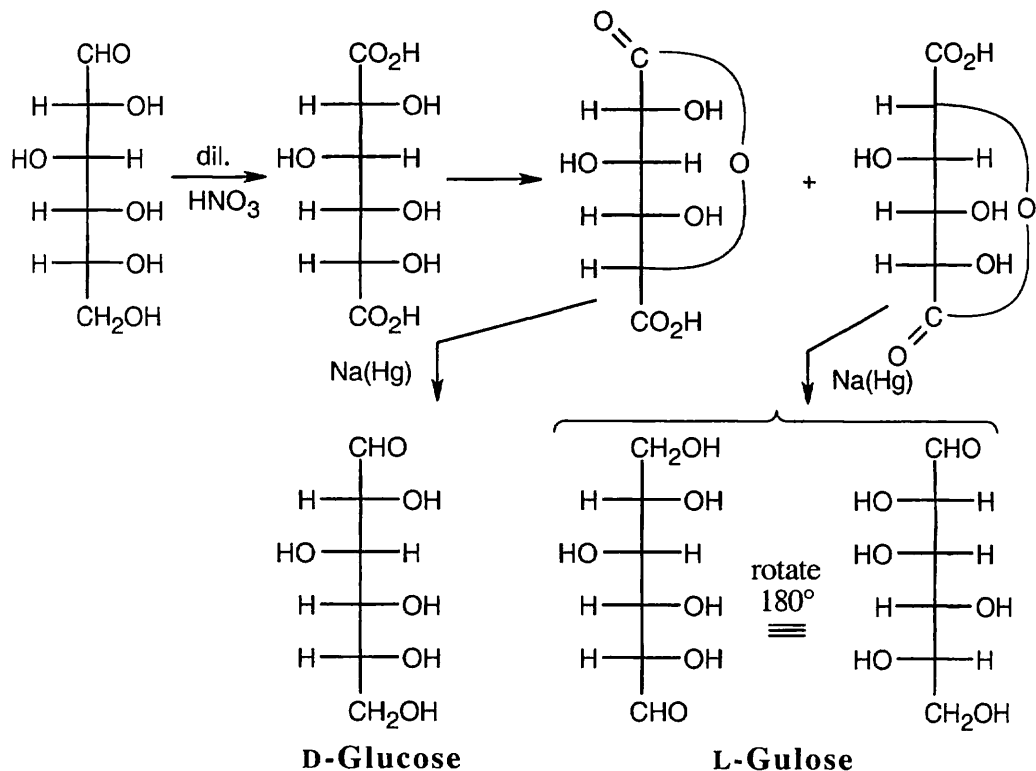
$$\begin{aligned}
 150.7^\circ x + 52.8^\circ y &= 80.2^\circ & x + y &= 1; & y &= 1 - x \\
 150.7^\circ x + 52.8^\circ (1 - x) &= 80.2^\circ \\
 97.9^\circ x &= 27.4^\circ \\
 x &= 0.280 \\
 y &= 0.720
 \end{aligned}$$

28.0% of D-galactose is present as the  $\alpha$  anomer, and 72.0% is present as the  $\beta$  anomer.

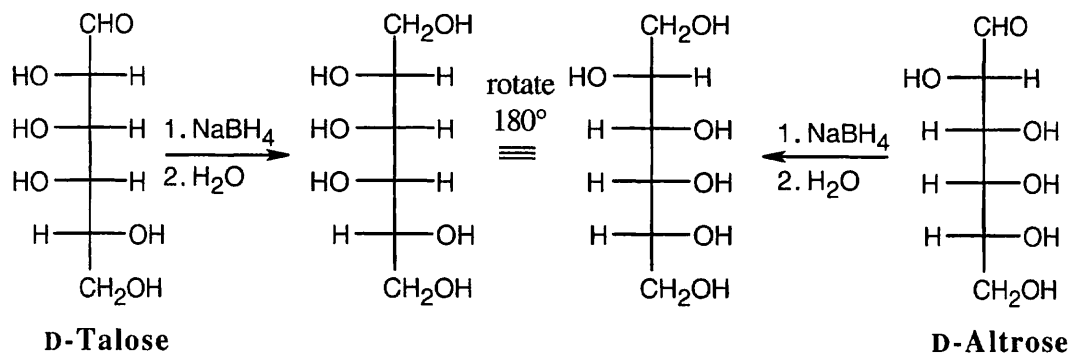
**25.45–25.47** Four D-2-ketohexoses are possible.



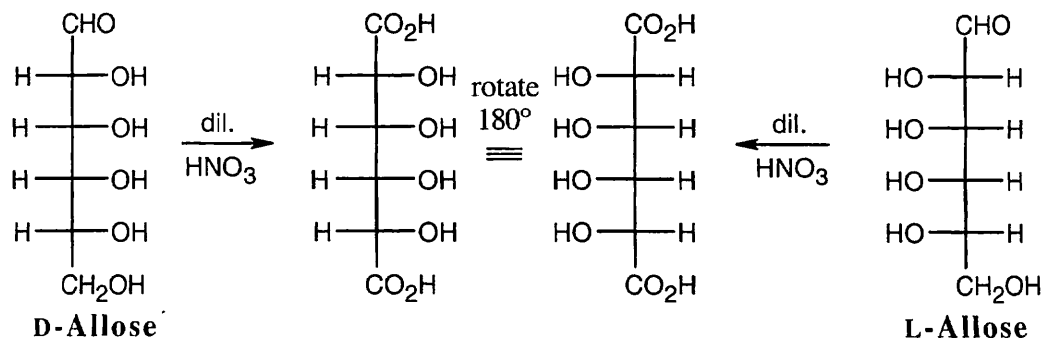
**25.48** The two lactones are formed between a carboxylic acid and a hydroxyl group 4 carbons away. When the lactones are reduced with sodium amalgam, the resulting hexoses have an aldehyde at one end and a hydroxyl group at the other end.

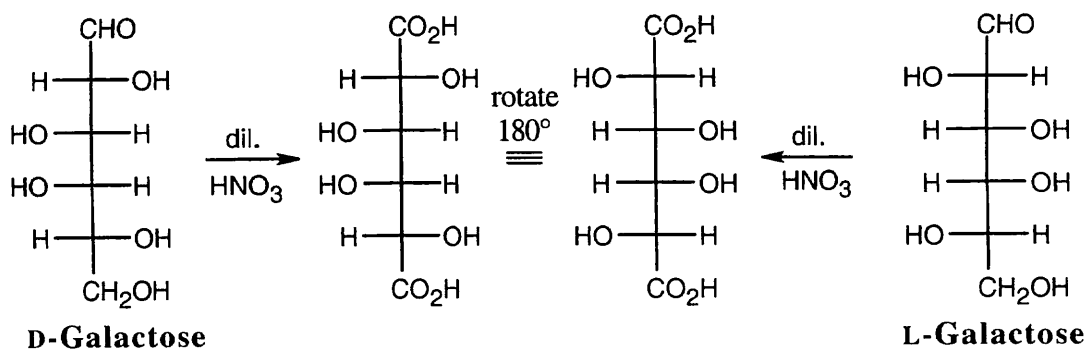


**25.49**

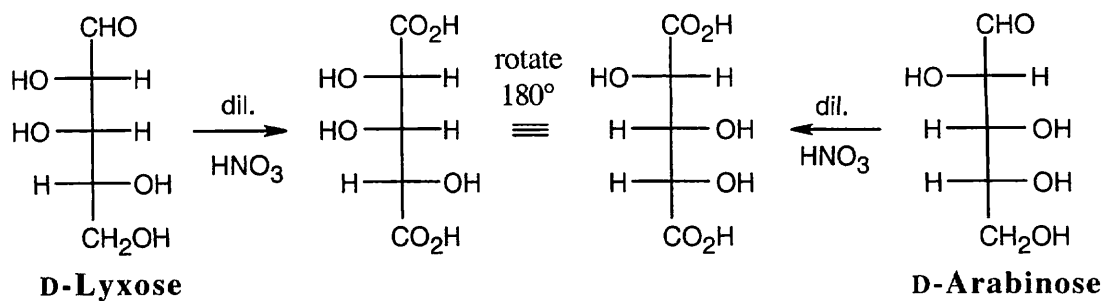


**25.50**

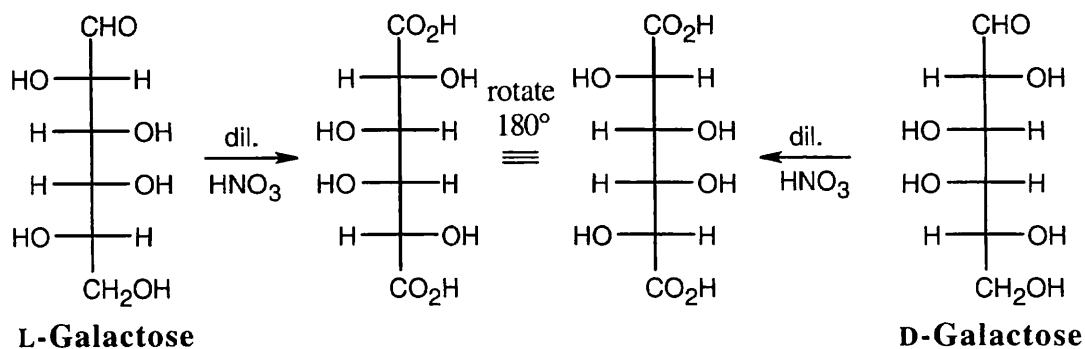




25.51

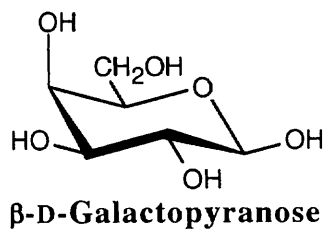


25.52 (a) D-Galactose gives the same aldaric acid as L-galactose.

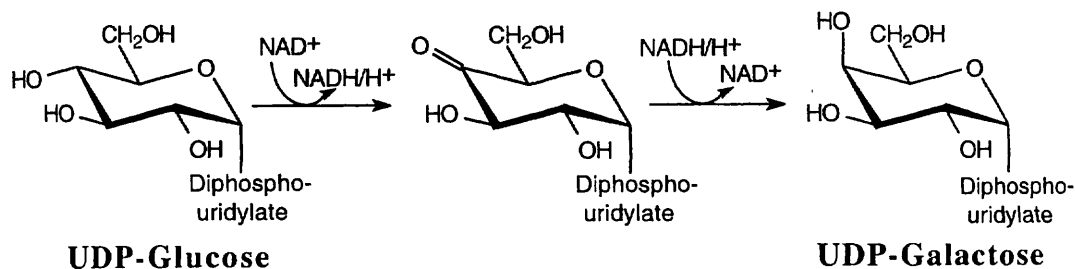


(b) The other aldohexose is a D-sugar.

(c)

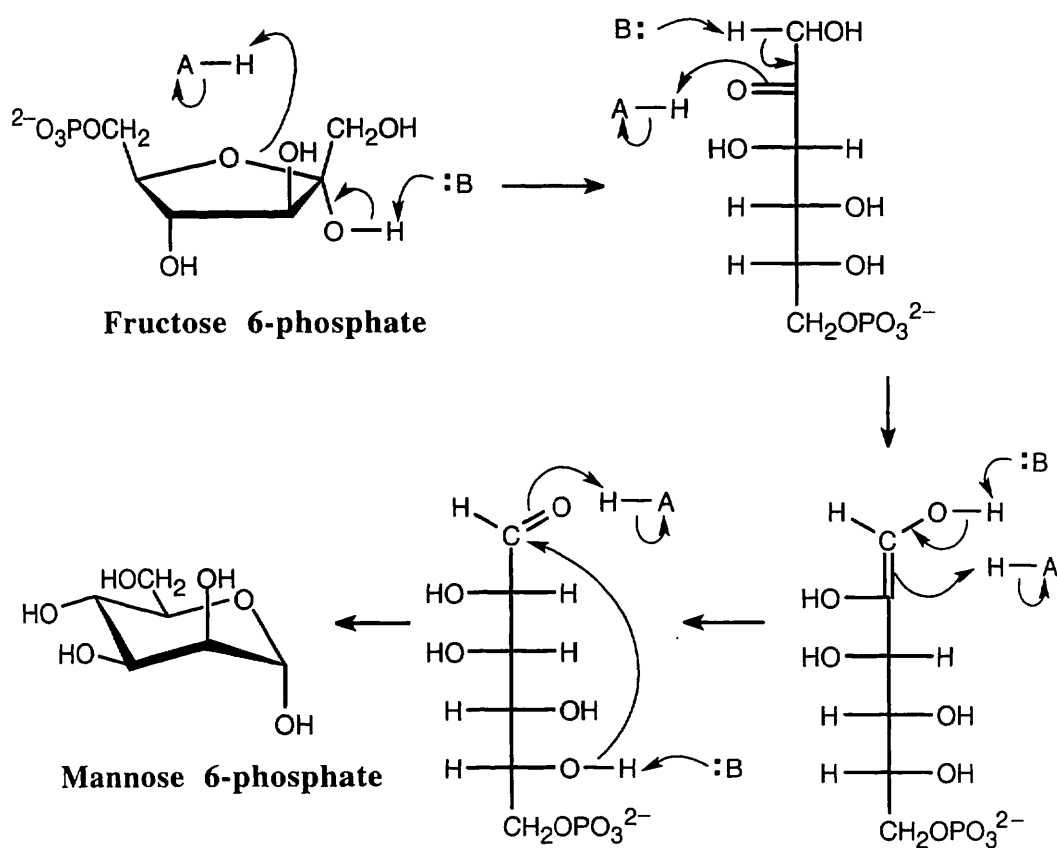


## 25.53



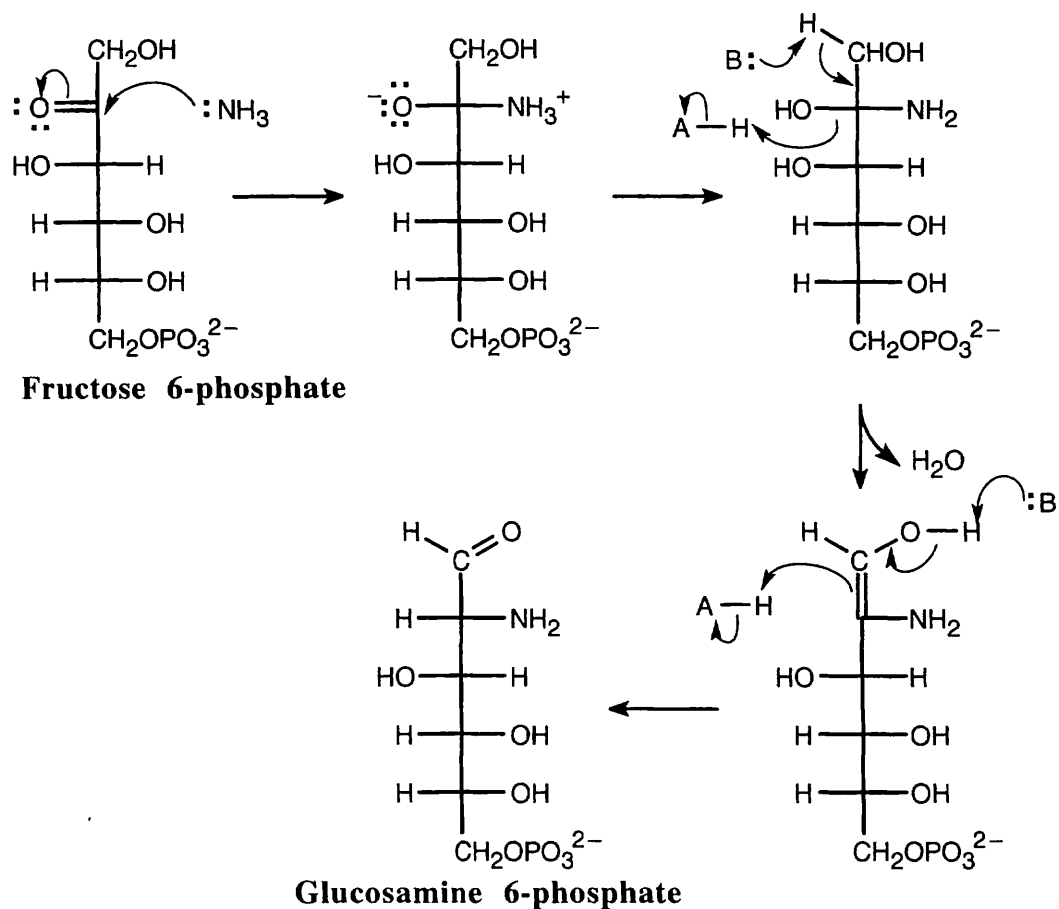
Oxidation of the C4 hydroxyl group by  $\text{NAD}^+$  forms a ketone plus  $\text{NADH}$ , and reduction of the ketone by  $\text{NADH}$  yields  $\text{UDP-galactose}$ . The result is an epimerization at carbon 4 of the pyranose ring.

## 25.54



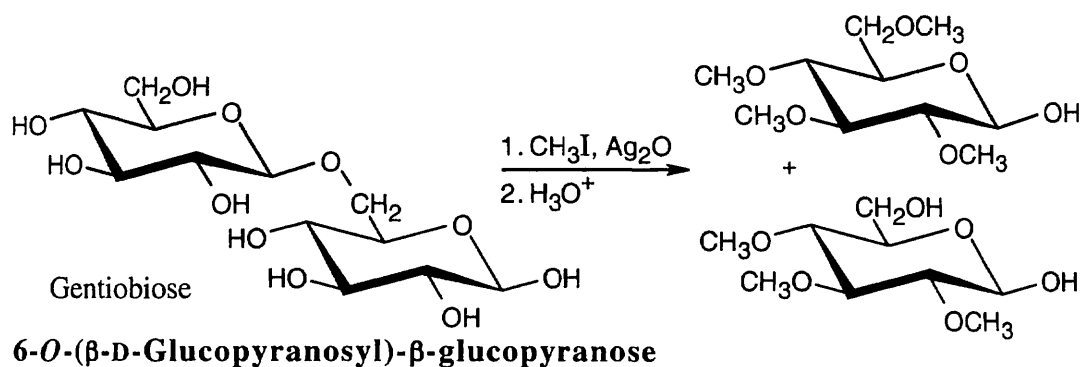
All of these reactions are acid/base catalyzed enolizations or hemiacetal openings/formations.

25.55

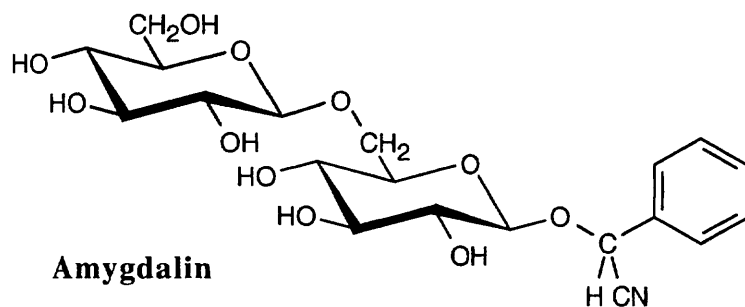


Nucleophilic acyl substitution and tautomerization lead to the formation of glucosamine 6-phosphate from fructose 6-phosphate. The mechanism of opening of the fructofuranose ring was shown in the previous problem.

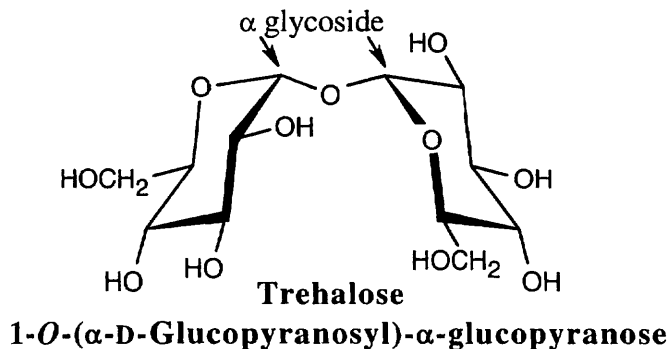
- 25.56** The hard part of this problem is determining where the glycosidic bond occurs on the second glucopyranose ring. Treatment with iodomethane, followed by hydrolysis, yields a tetra-*O*-methyl glucopyranose and a tri-*O*-methyl glucopyranose. The oxygen in the tri-*O*-methylated ring that is not part of the hemiacetal group and is not methylated is the oxygen that forms the acetal bond. In this problem, the C6 oxygen forms the glycosidic link.



- 25.57** Amygdalin has the same carbohydrate skeleton as gentiobiose. Draw the cyanohydrin of benzaldehyde, and form a bond between the hemiacetal oxygen and the carbonyl carbon of benzaldehyde, with elimination of water.

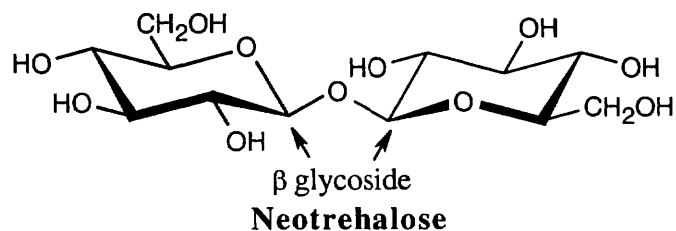
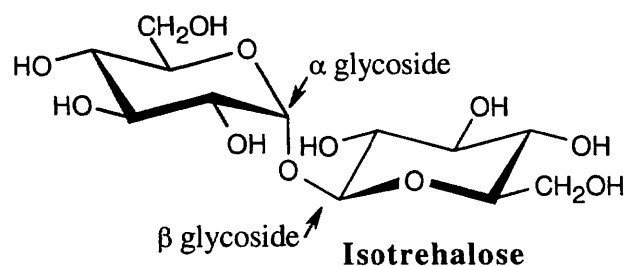


- 25.58** Since trehalose is a nonreducing sugar, the two glucose units must be connected through an oxygen atom at the anomeric carbon of each glucose. There are three possible structures for trehalose: The two glucopyranose rings can be connected ( $\alpha,\alpha$ ), ( $\beta,\beta$ ), or ( $\alpha,\beta$ ).
- 25.59** Since trehalose is not cleaved by  $\beta$ -glycosidases, it must have an  $\alpha,\alpha$  glycosidic linkage.





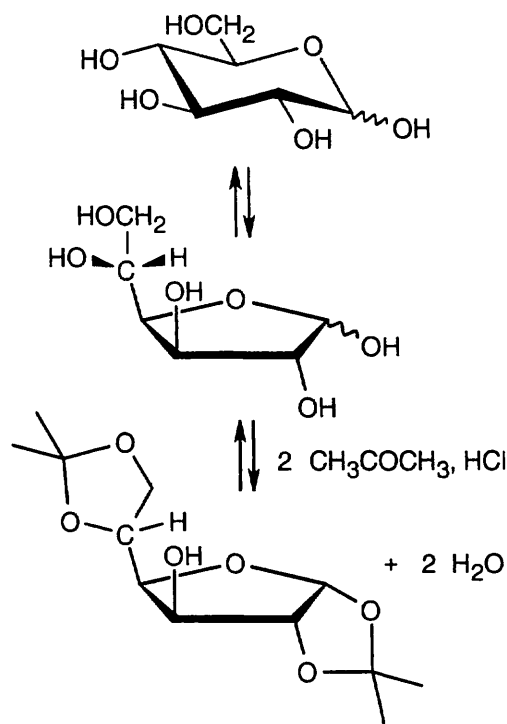
## 25.60

1-*O*-( $\beta$ -D-Glucopyranosyl)- $\beta$ -glucopyranose1-*O*-( $\alpha$ -D-Glucopyranosyl)- $\beta$ -glucopyranose

## 25.61

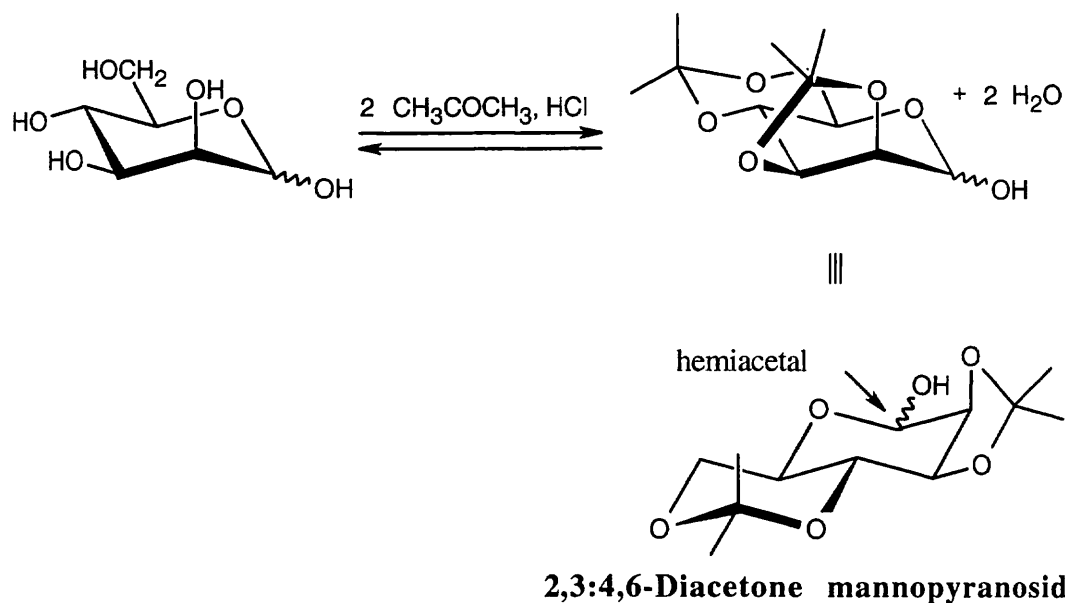
Glucopyranose is in equilibrium with glucofuranose

Reaction with two equivalents of acetone occurs by the mechanism we learned for acetal formation (Sec 19.10)



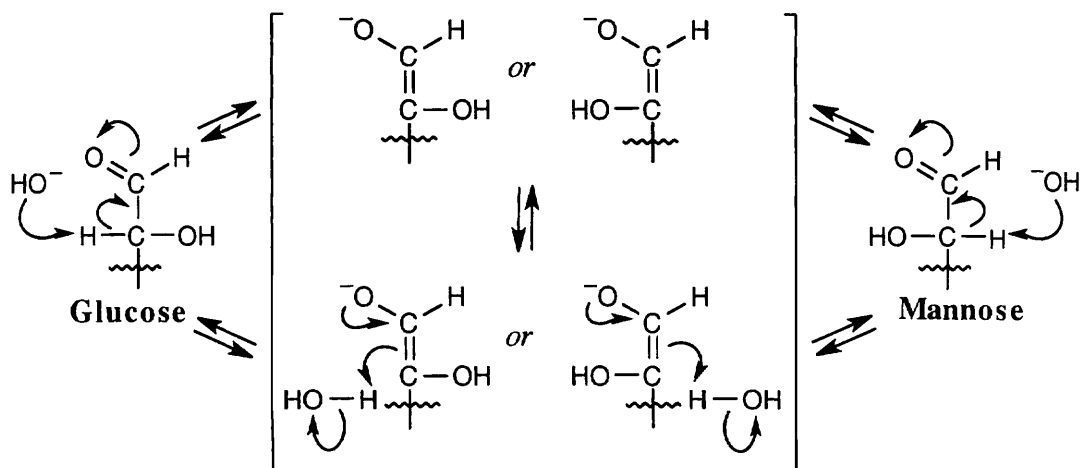
A five-membered acetal ring forms much more readily when the hydroxyl groups are cis to one another. In glucofuranose, the C3 hydroxyl group is trans to the C2 hydroxyl group, and acetal formation occurs between acetone and the C1 and C2 hydroxyls of glucofuranose. Since the C1 hydroxyl group is part of the acetone acetal, the furanose is no longer in equilibrium with the free aldehyde, and the diacetone derivative is not a reducing sugar.

## 25.62

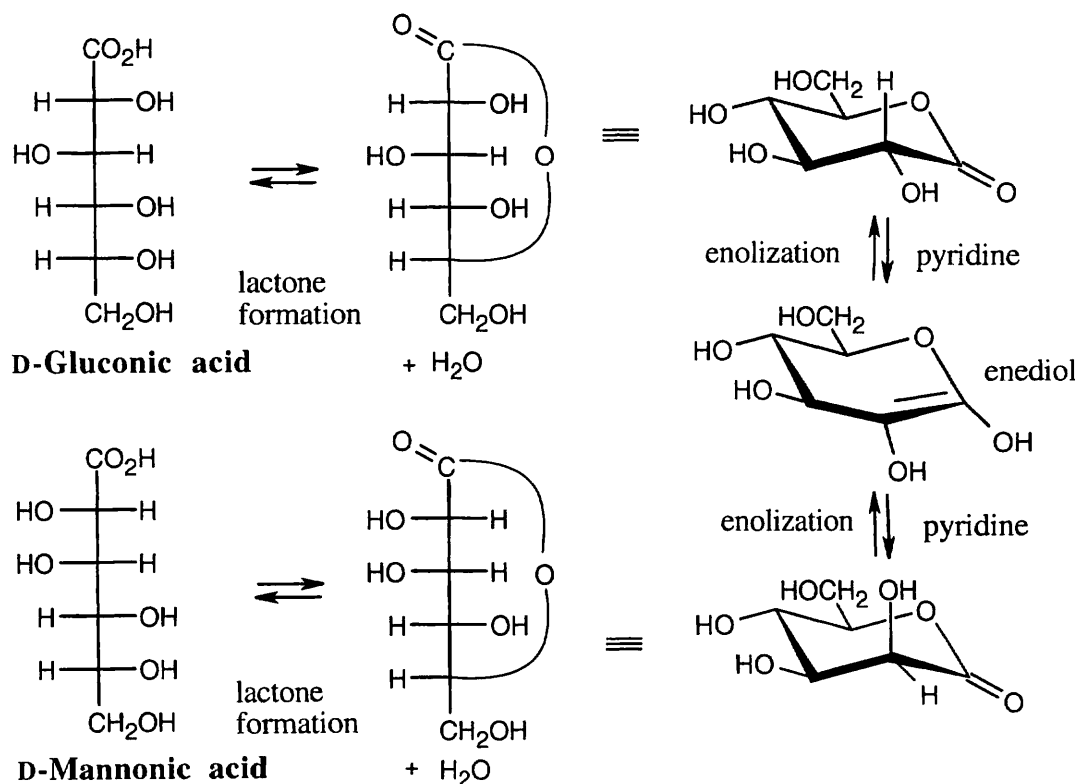


Acetone forms an acetal with the hydroxyl groups at C2 and C3 of D-mannopyranoside because the hydroxyl groups at these positions are cis to one another. The pyranoside ring is still a hemiacetal that is in equilibrium with free aldehyde, which is reducing toward Tollens' reagent.

**25.63** Dilute base abstracts a proton  $\alpha$  to the carbonyl carbon, forming an enolate. The enolate double bond can be protonated from either side, giving either mannose or glucose as the product.

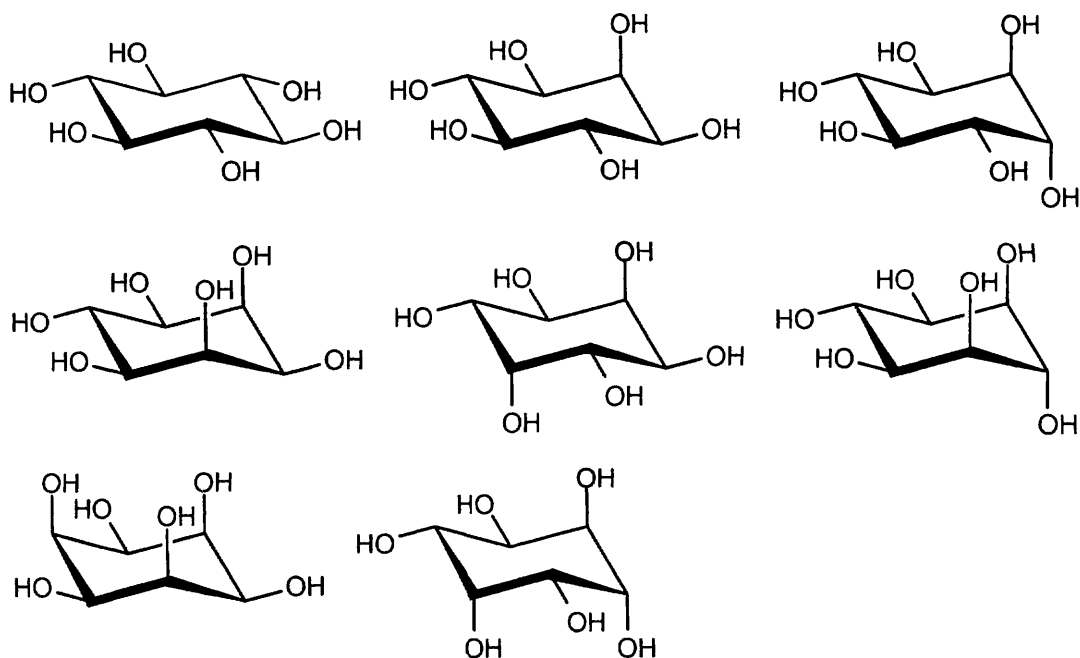


## 25.64

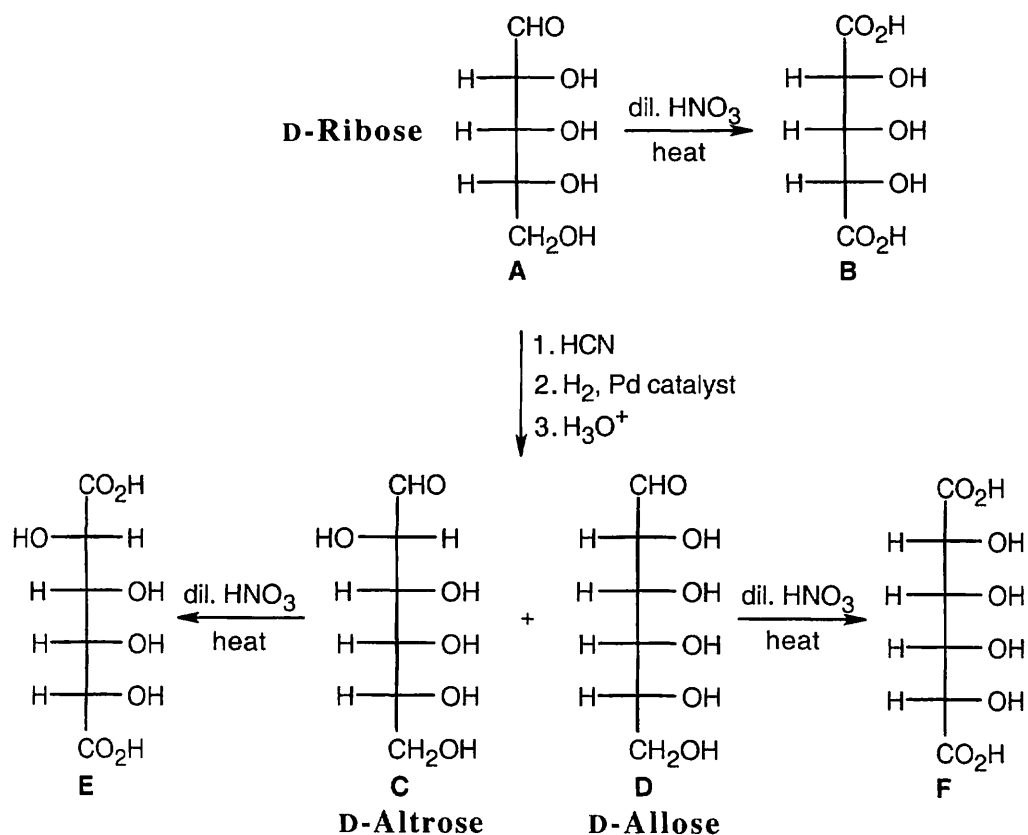


Isomerization at C2 occurs because the enediol can be reprotonated on either side of the double bond.

## 25.65 There are eight diastereomeric cyclitols.

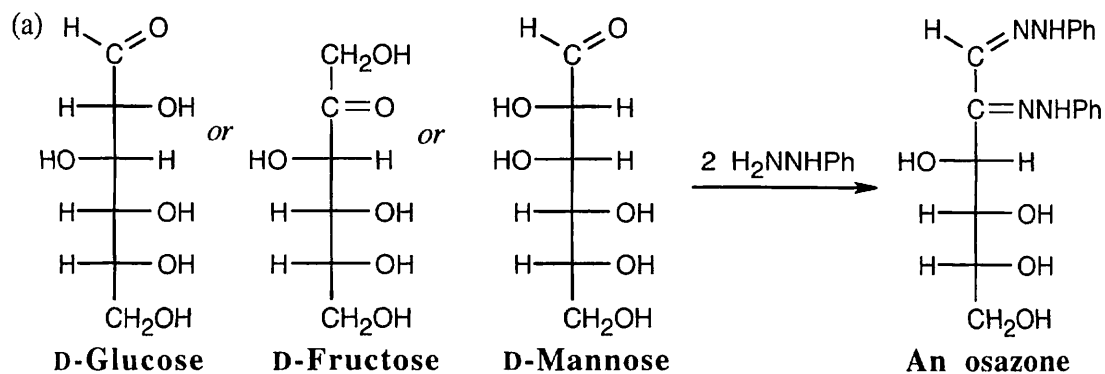


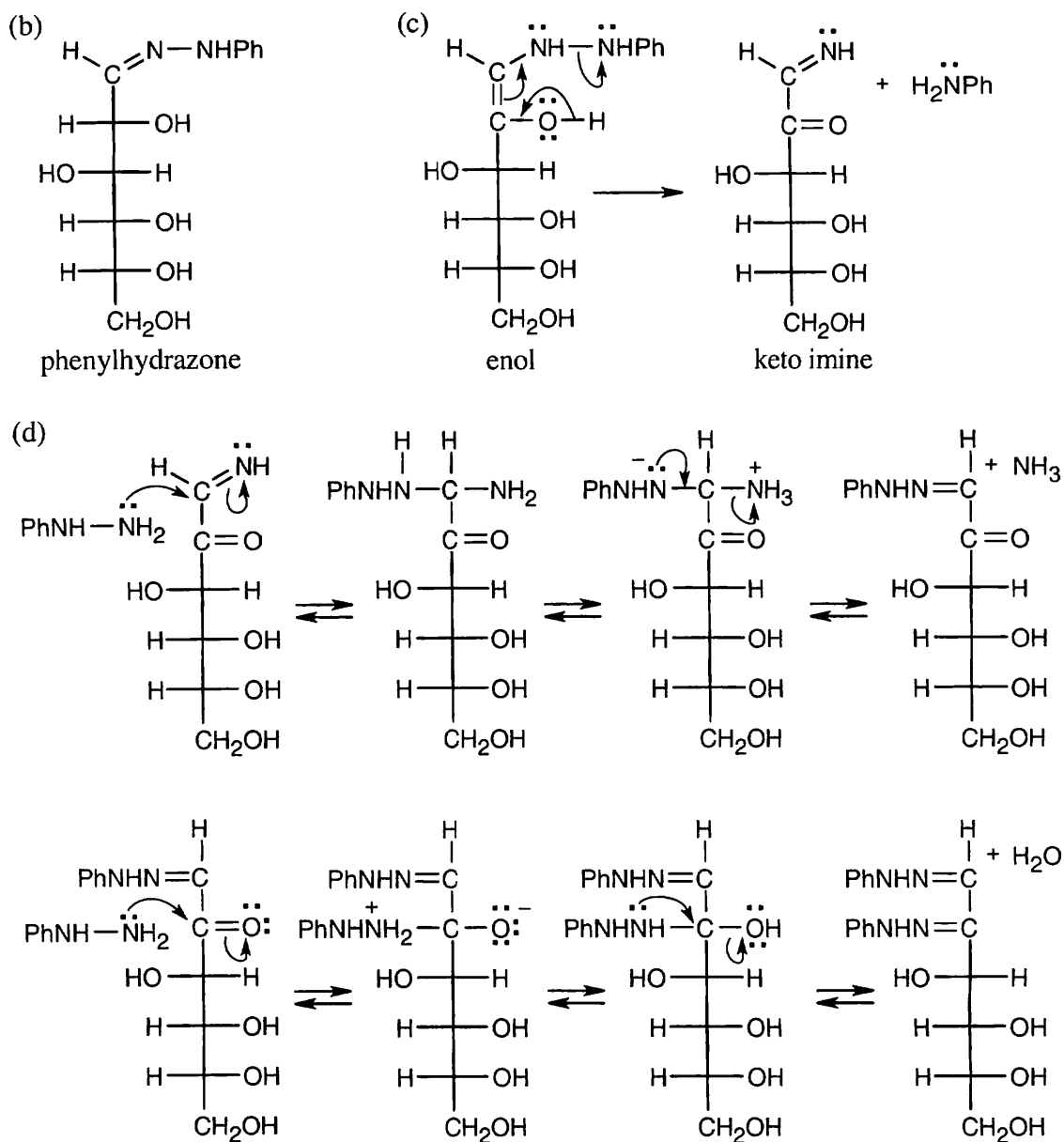
## 25.66



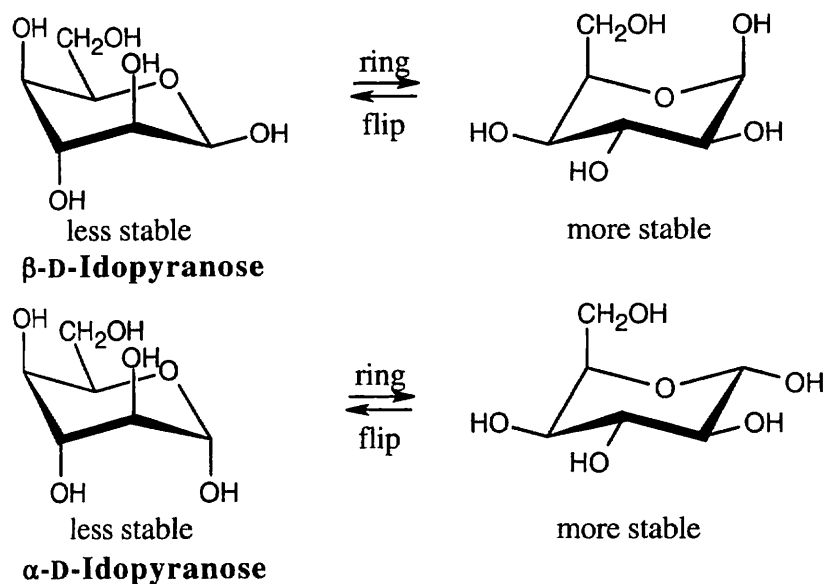
Because **A** is oxidized to an optically inactive aldaric acid, the possible structures are D-ribose and D-xylose. Chain extension of D-xylose, however, produces two hexoses that, when oxidized, yield optically active aldaric acids.

## 25.67



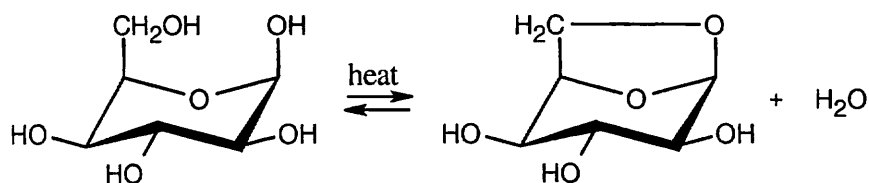


## 25.68 (a)



(b)  $\alpha$ -D-Idopyranose is more stable than  $\beta$ -D-idopyranose because only one group is axial in its more stable chair conformation, whereas  $\beta$ -D-idopyranose has two axial groups in its more stable conformation.

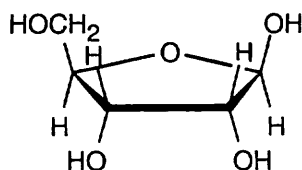
(c)



1,6-Anhydro-D-idopyranose is formed from the  $\beta$  anomer because the axial hydroxyl groups on carbons 1 and 6 are close enough for the five-membered ring to form.

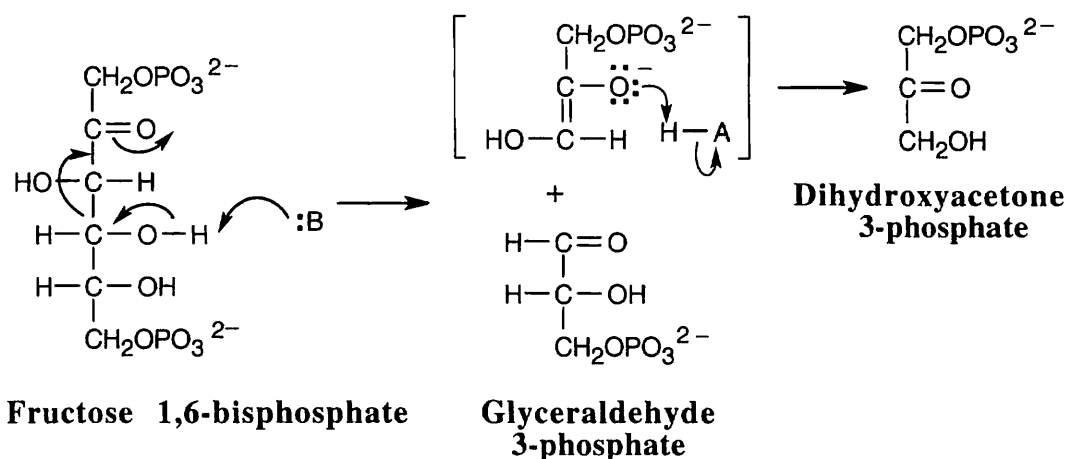
(d) The hydroxyl groups at carbons 1 and 6 of D-glucopyranose are equatorial in the most stable conformation and are too far apart for a ring to form.

## 25.69

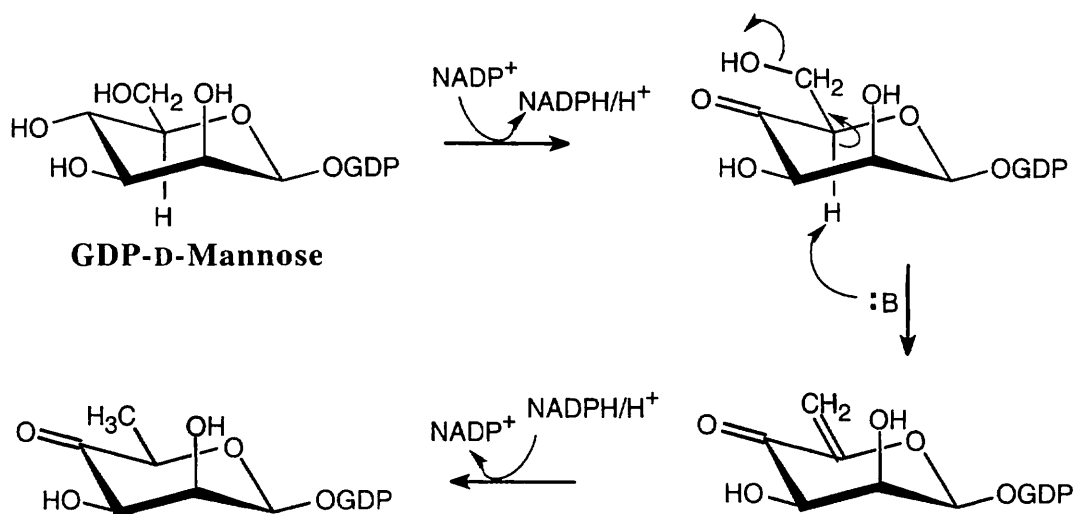


D-Ribofuranose is the sugar present in acetyl CoA.

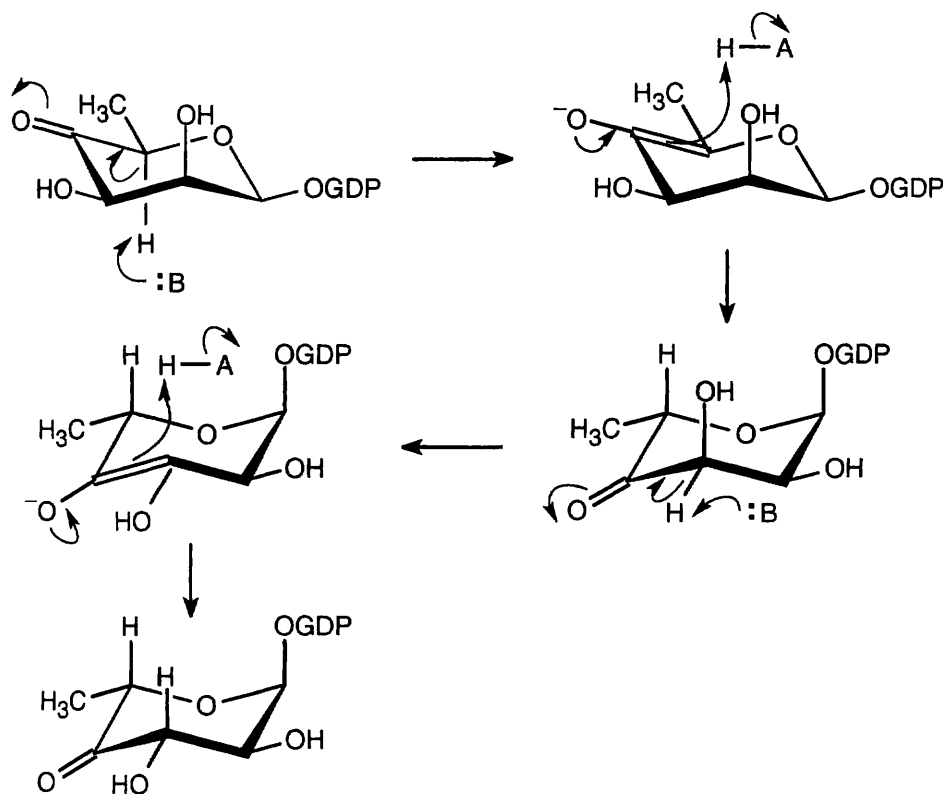
**25.70** Cleavage of fructose 1,6-bisphosphate occurs by a reverse aldol reaction.



**25.71** (a) Oxidation by  $\text{NADP}^+$ , elimination, and conjugate reduction by  $\text{NADPH}$  give the observed product. Notice that there is no net consumption of  $\text{NADP}^+$ . The mechanism of  $\text{NADP}^+$  oxidations and reductions has been shown many times in this book and also appears in part (c).



(b) Two epimerizations, both  $\alpha$  to the carbonyl group, cause a change in stereochemistry.



(c) Reduction by NADPH forms GDP-L-fucose.

