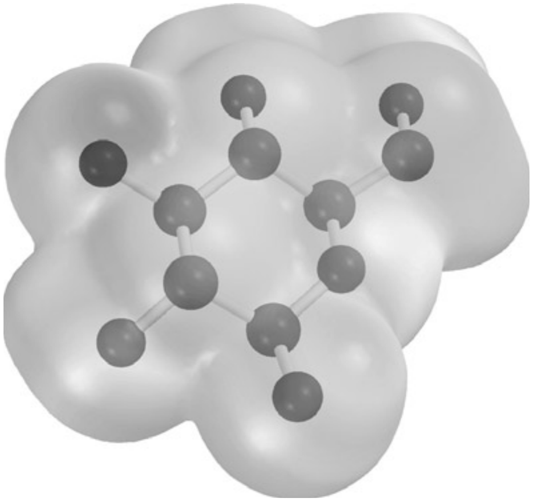
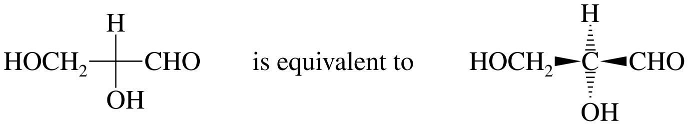


CHAPTER 25

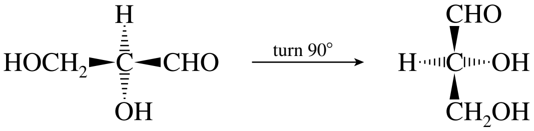
CARBOHYDRATES

SOLUTIONS TO TEXT PROBLEMS

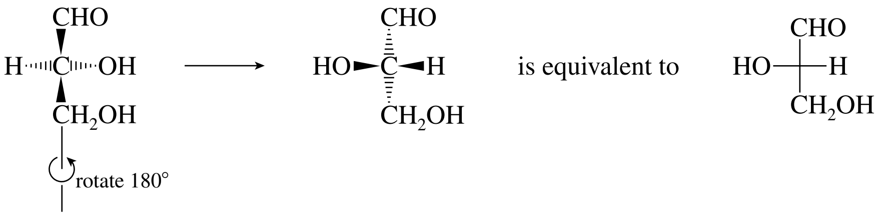
25.1 (*b*) Redraw the Fischer projection so as to show the orientation of the groups in three dimensions.



Reorient the three-dimensional representation, putting the aldehyde group at the top and the primary alcohol at the bottom.

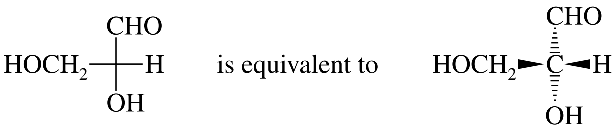


What results is not equivalent to a proper Fischer projection, because the horizontal bonds are directed “back” when they should be “forward.” The opposite is true for the vertical bonds. To make the drawing correspond to a proper Fischer projection, we need to rotate it 180° around a vertical axis.

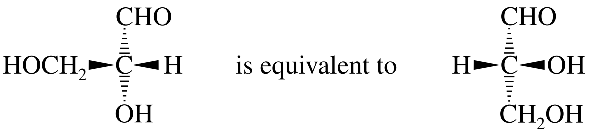


Now, having the molecule arranged properly, we see that it is L-glyceraldehyde.

(*c*) Again proceed by converting the Fischer projection into a three-dimensional representation.

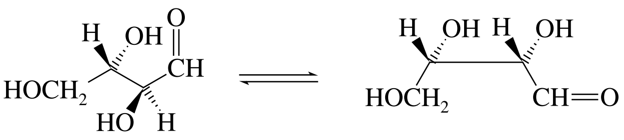


Look at the drawing from a perspective that permits you to see the carbon chain oriented vertically with the aldehyde at the top and the CH_2OH at the bottom. Both groups should point away from you. When examined from this perspective, the hydrogen is to the left and the hydroxyl to the right with both pointing toward you.



The molecule is D-glyceraldehyde.

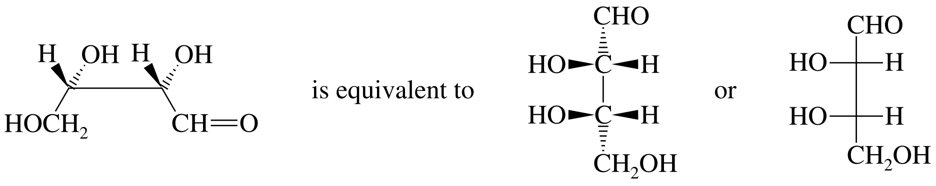
25.2 Begin by drawing a perspective view of the molecular model shown in the problem. To view the compound as a Fischer projection, redraw it in an eclipsed conformation.



Staggered conformation

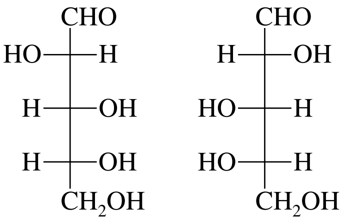
Same molecule in eclipsed conformation

The eclipsed conformation shown, when oriented so that the aldehyde carbon is at the top, vertical bonds back, and horizontal bonds pointing outward from their stereogenic centers, is readily transformed into the Fischer projection of L-erythrose.



L-Erythrose

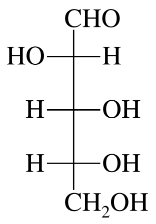
25.3 L-Arabinose is the mirror image of D-arabinose, the structure of which is given in text Figure 25.2. The configuration at *each* stereogenic center of D-arabinose must be reversed to transform it into L-arabinose.



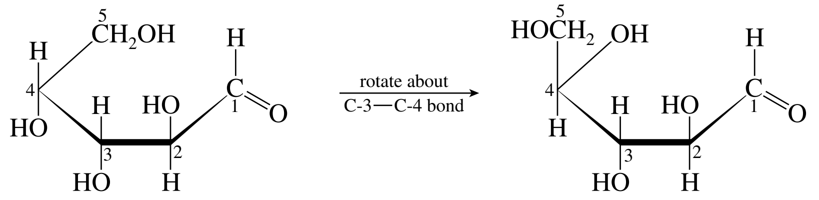
D-(−)-Arabinose L-(+)-Arabinose

25.4 The configuration at C-5 is opposite to that of D-(+)-glyceraldehyde. This particular carbohydrate therefore belongs to the L series. Comparing it with the Fischer projection formulas of the eight D-aldohexoses reveals it to be in the mirror image of D-(+)-talose; it is L-(−)-talose

25.5 (*b*) The Fischer projection formula of D-arabinose may be found in text Figure 25.2. The Fischer projection and the eclipsed conformation corresponding to it are



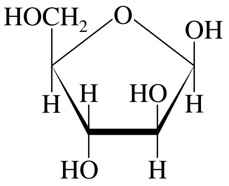
D-Arabinose



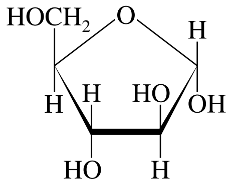
Eclipsed conformation of D-arabinose

Conformation suitable for furanose ring formation

Cyclic hemiacetal formation between the carbonyl group and the C-4 hydroxyl yields the α- and β-furanose forms of D-arabinose.

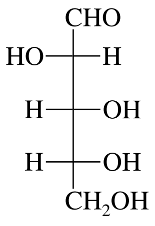


β-D-Arabinofuranose

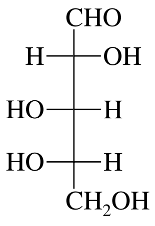


α-D-Arabinofuranose

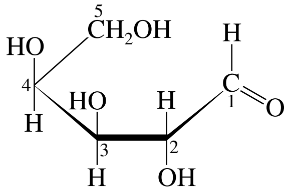
(*c*) The mirror image of D-arabinose [from part (*b*)] is L-arabinose.



D-Arabinose

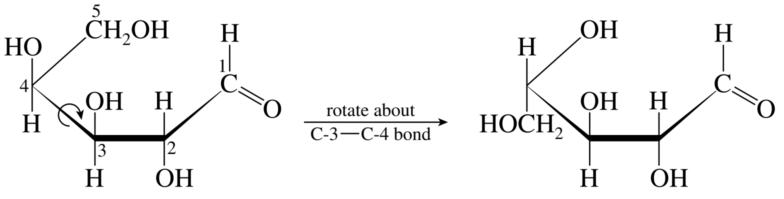


L-Arabinose



Eclipsed conformation of L-arabinose

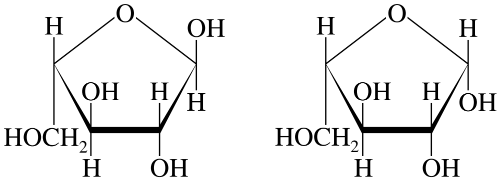
The C-4 atom of the eclipsed conformation of L-arabinose must be rotated 120° in a clockwise sense so as to bring its hydroxyl group into the proper orientation for furanose ring formation.



Original eclipsed conformation of L-arabinose

Conformation suitable for furanose ring formation

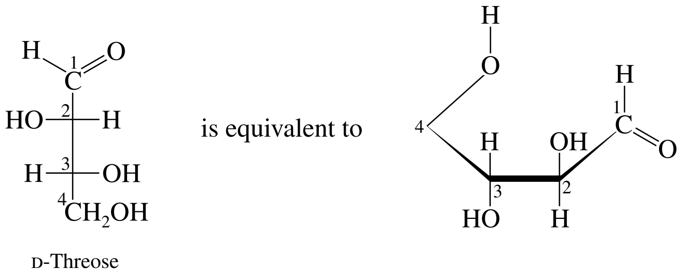
Cyclization gives the α- and β-furanose forms of L-arabinose.



α-L-Arabinofuranose β-L-Arabinofuranose

In the L series the anomeric hydroxyl is up in the α isomer and down in the β isomer.

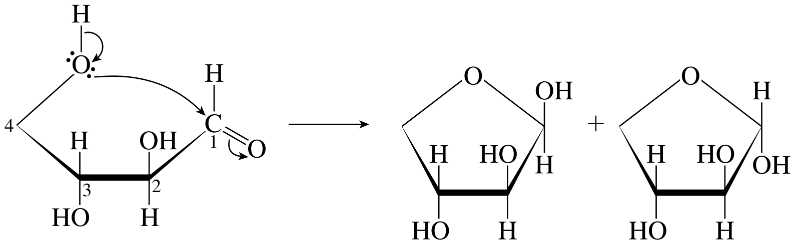
(*d*) The Fischer projection formula for D-threose is given in the text Figure 25.2. Reorientation of that projection into a form that illustrates its potential for cyclization is shown.



D-Threose

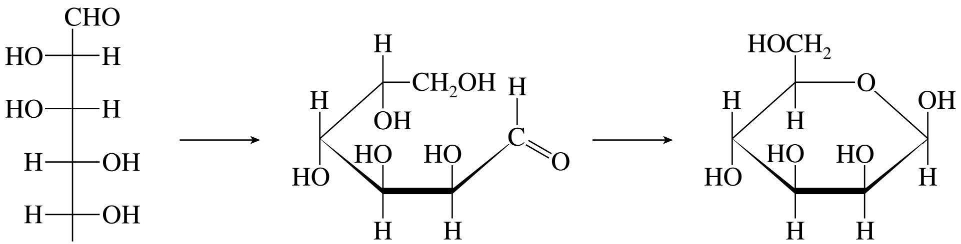
is equivalent to

Cyclization yields the two stereoisomeric furanose forms.



β-D-Threofuranose α-D-Threofuranose

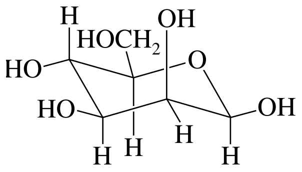
25.6 (*b*) The Fischer projection and Haworth formula for D-mannose are



D-Mannose

β-D-Mannopyranose
(Haworth formula)

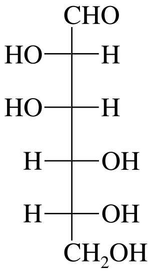
The Haworth formula is more realistically drawn as the following chair conformation:



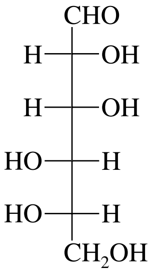
β-D-Mannopyranose

Mannose differs from glucose in configuration at C-2. All hydroxyl groups are equatorial in β-D-glucopyranose; the hydroxyl at C-2 is axial in β-D-mannopyranose.

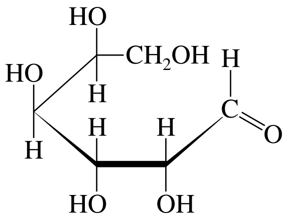
(*c*) The conformational depiction of β-L-mannopyranose begins in the same way as that of β-D-mannopyranose. L-Mannose is the mirror image of D-mannose.



D-Mannose

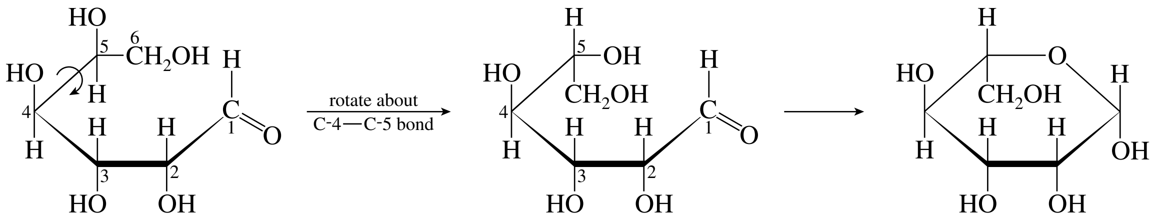


L-Mannose



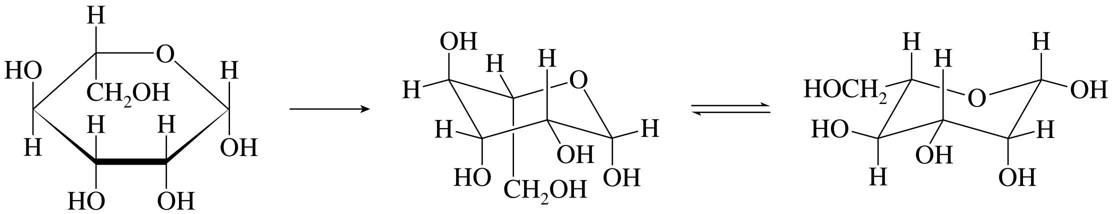
Eclipsed conformation of L-mannose

To rewrite the eclipsed conformation of L-mannose in a way that permits hemiacetal formation between the carbonyl group and the C-5 hydroxyl, C-5 is rotated 120° in the clockwise sense.



β-L-Mannopyranose (remember, the anomeric hydroxyl is down in the L series)

Translating the Haworth formula into a proper conformational depiction requires that a choice be made between the two chair conformations shown.

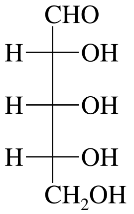


Haworth formula of β-L-mannopyranose

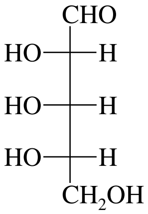
Less stable chair conformation; CH_2OH is axial

More stable chair conformation; CH_2OH is equatorial

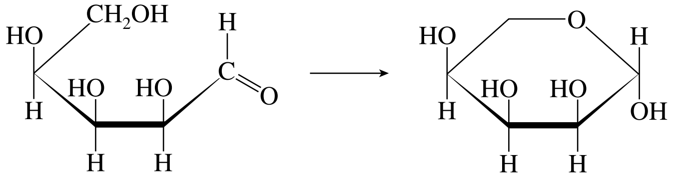
(*d*) The Fischer projection formula for L-ribose is the mirror image of that for D-ribose.



D-Ribose



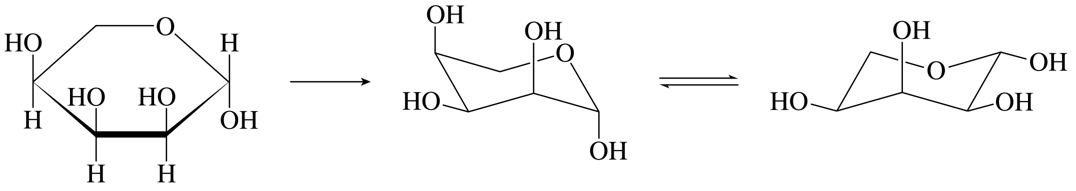
L-Ribose



Eclipsed conformation of L-ribose is oriented properly for ring closure.

Haworth formula of β-L-ribopyranose

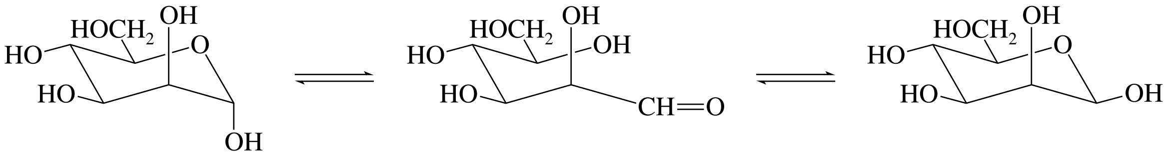
Of the two chair conformations of β-L-ribose, the one with the greater number of equatorial substituents is more stable.



Less stable chair conformation of β-L-ribopyranose

More stable chair conformation of β-L-ribopyranose

25.7 The equation describing the equilibrium is



α-D-Mannopyranose $[\alpha]_D^{20} + 29.3°$

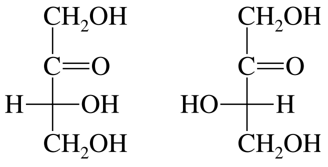
Open-chain form of D-mannose

β-D-Mannopyranose $[\alpha]_D^{20} - 17.0°$

Let A = percent α isomer; 100 − A = percent β isomer. Then

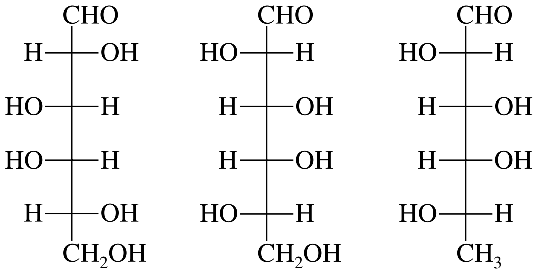
$$A(+29.3°) + (100 - A)(-17.0°) = 100(+14.2°)$$
$$46.3A = 3120$$
$$\text{Percent } \alpha \text{ isomer} = 67\%$$
$$\text{Percent } \beta \text{ isomer} = (100 - A) = 33\%$$

25.8 Review carbohydrate terminology by referring to text Table 25.1. A **ketotetrose** is a four-carbon ketose. Writing a Fischer projection for a four-carbon ketose reveals that only one stereogenic center is present, and thus there are only two ketotetroses. They are enantiomers of each other and are known as D- and L-erythrulose.



D-Erythrulose L-Erythrulose

25.9 (*b*) Because L-fucose is 6-deoxy-L-galactose, first write the Fischer projection formula of D-galactose, and then transform it to its mirror image, L-galactose. Transform the C-6 CH_2OH group to CH_3 to produce 6-deoxy-L-galactose.

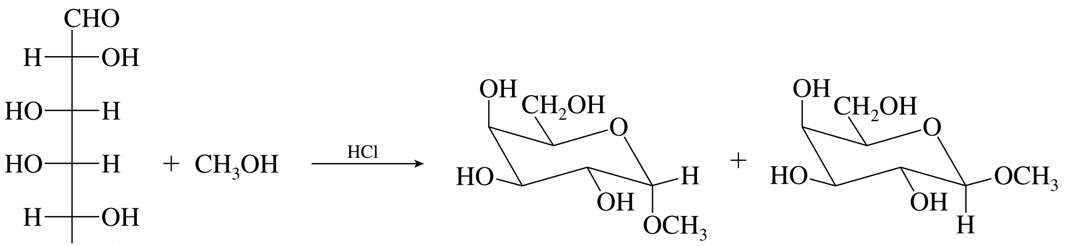


D-Galactose (from Figure 25.2)

L-Galactose

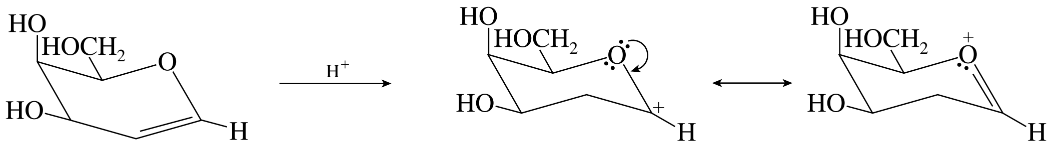
6-Deoxy-L-galactose (L-fucose)

25.10 Reaction of a carbohydrate with an alcohol in the presence of an acid catalyst gives mixed acetals at the anomeric position.



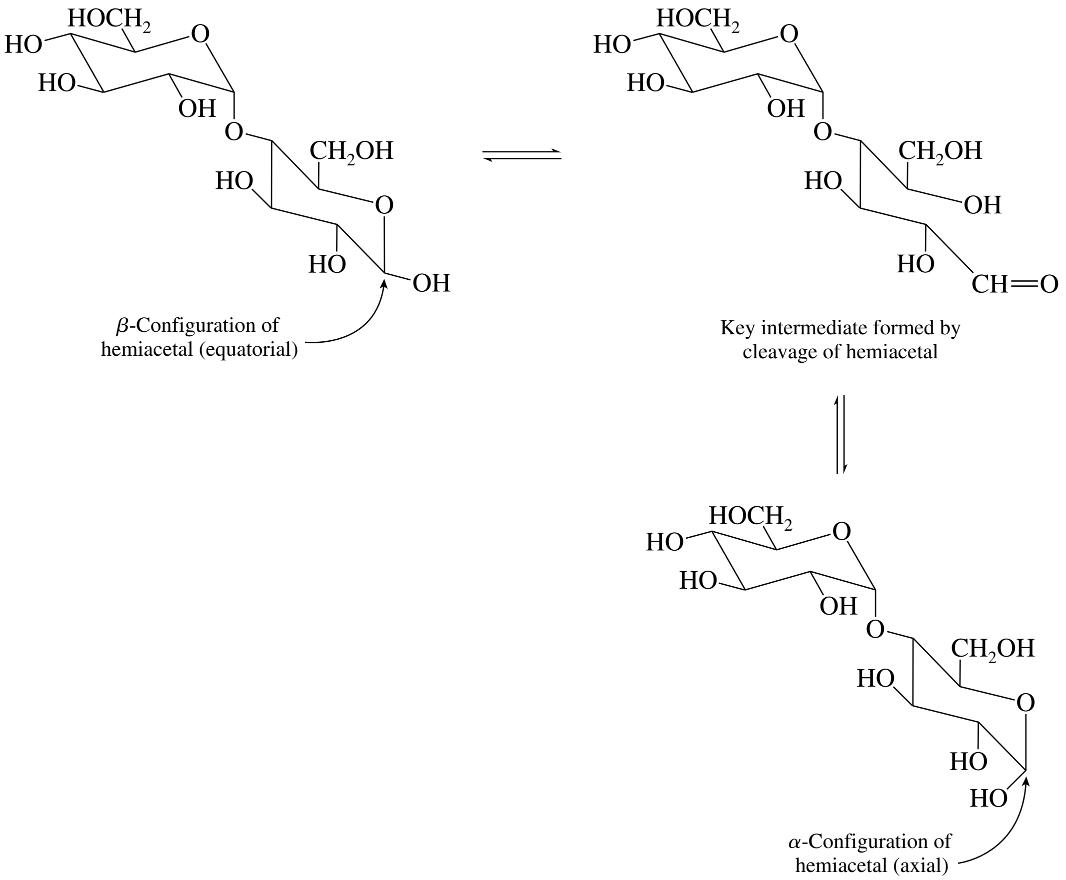
D-Galactose Methanol Methyl α-D-galactopyranoside Methyl β-D-galactopyranoside

25.11 Acid-catalyzed addition of methanol to the glycal proceeds by regioselective protonation of the double bond in the direction that leads to the more stable carbocation. Here again, the more stable carbocation is the one stabilized by the ring oxygen.



Capture on either face of the carbocation by methanol yields the α and β methyl glycosides.

25.12 The hemiacetal opens to give an intermediate containing a free aldehyde function. Cyclization of this intermediate can produce either the α or the β configuration at this center. The axial and equatorial orientations of the anomeric hydroxyl can best be seen by drawing maltose with the pyranose rings in chair conformations.



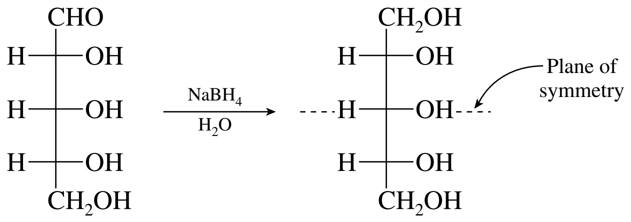
β-Configuration of hemiacetal (equatorial)

Key intermediate formed by cleavage of hemiacetal

α-Configuration of hemiacetal (axial)

Only the configuration of the hemiacetal function is affected in this process. The α configuration of the glycosidic linkage remains unchanged.

25.13 Write the chemical equation so that you can clearly relate the product to the starting material.

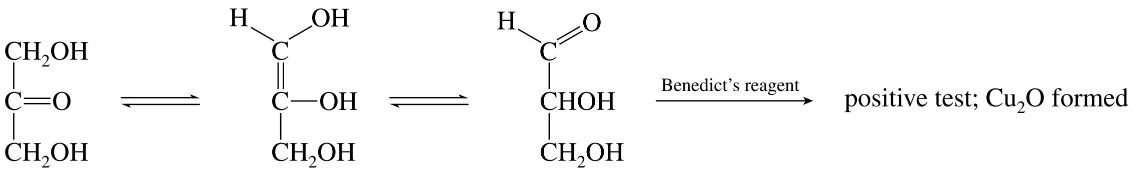


D-Ribose Ribitol

Ribitol is a meso form; it is achiral and thus not optically active. A plane of symmetry passing through C-3 bisects the molecule.

25.14 (*b*) Arabinose is a reducing sugar; it will give a positive test with Benedict's reagent, because its open-chain form has a free aldehyde group capable of being oxidized by copper(II) ion.

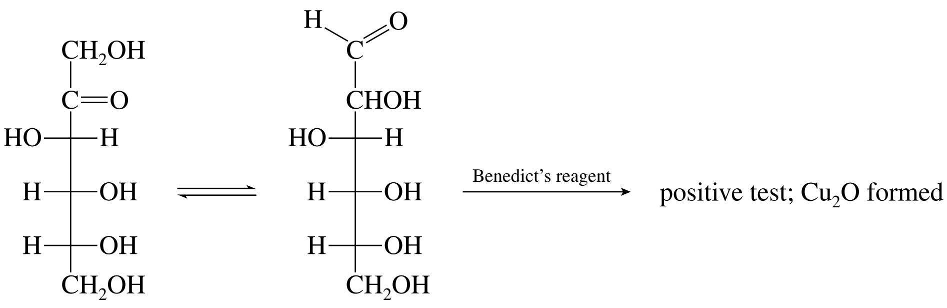
(*c*) Benedict's reagent reacts with α-hydroxy ketones by way of an isomerization process involving an enediol intermediate.



1,3-Dihydroxyacetone Enediol Glyceraldehyde

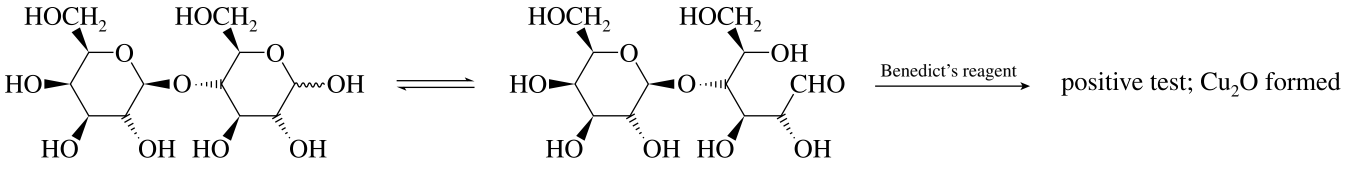
1,3-Dihydroxyacetone gives a positive test with Benedict's reagent.

(*d*) D-Fructose is an α-hydroxy ketone and will give a positive test with Benedict's reagent.



D-Fructose

(*e*) Lactose is a disaccharide and will give a positive test with Benedict's reagent by way of an open-chain isomer of one of the rings. Lactose is a reducing sugar.

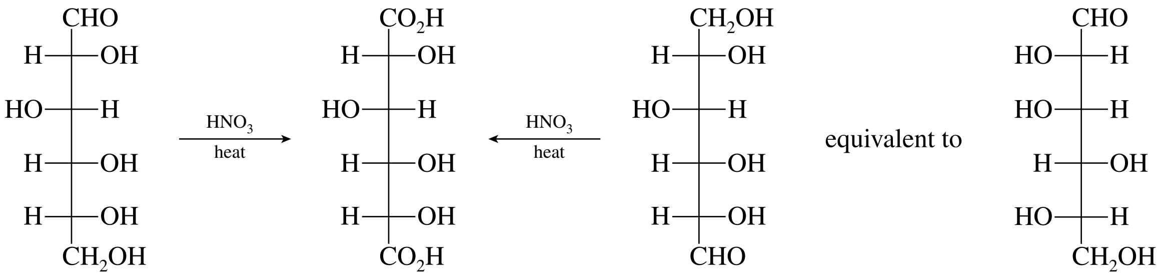


Lactose
(structure presented in Section 25.14)

Open-chain form

(*f*) Amylose is a polysaccharide. Its glycoside linkages are inert to Benedict's reagent, but the terminal glucose residues at the ends of the chain and its branches are hemiacetals in equilibrium with open-chain structures. A positive test is expected.

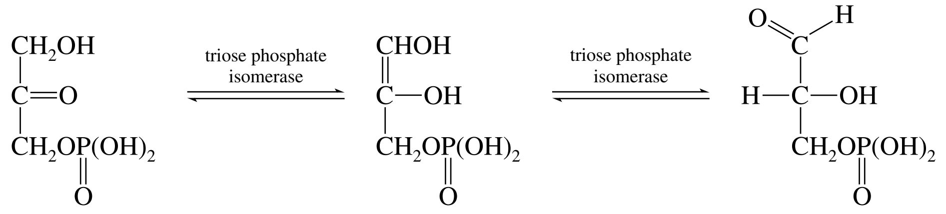
25.15 Because the groups at both ends of the carbohydrate chain are oxidized to carboxylic acid functions, two combinations of one CH_2OH with one CHO group are possible.



D-Glucose D-Glucaric acid L-Gulose

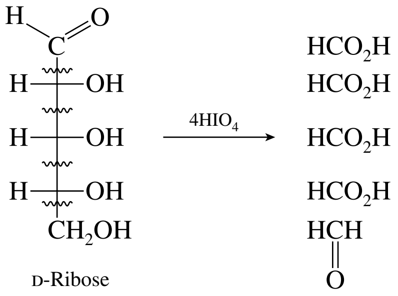
L-Gulose yields the same aldaric acid on oxidation as does D-glucose.

25.16 In analogy with the D-fructose ⇌ D-glucose interconversion, dihydroxyacetone phosphate and D-glyceraldehyde 3-phosphate can equilibrate by way of an enediol intermediate.



Dihydroxyacetone phosphate Enediol D-Glyceraldehyde 3-phosphate

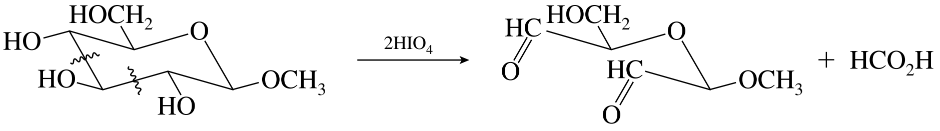
25.17 (*b*) The points of cleavage of D-ribose on treatment with periodic acid are as indicated.



D-Ribose

Four moles of periodic acid per mole of D-ribose are required. Four moles of formic acid and one mole of formaldehyde are produced.

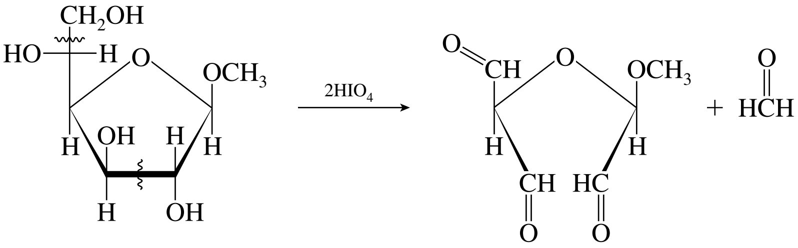
(*c*) Write the structure of methyl *β*-D-glucopyranoside so as to identify the adjacent alcohol functions.



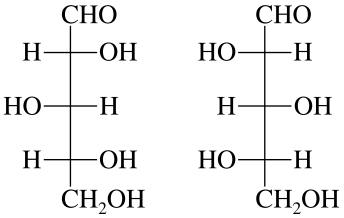
Methyl *β*-D-glucopyranoside

Two moles of periodic acid per mole of glycoside are required. One mole of formic acid is produced.

(*d*) There are two independent vicinal diol functions in this glycoside. Two moles of periodic acid are required per mole of substrate.

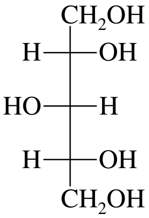


25.18 (*a*) The structure shown in Figure 25.2 is D-(+)-xylose; therefore (−)-xylose must be its mirror image and has the L-configuration at C-4.



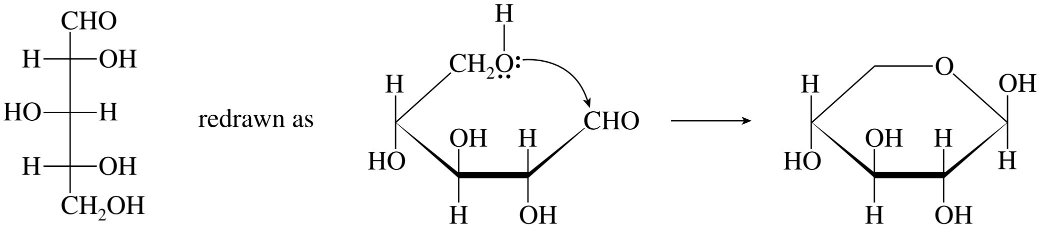
D-(+)-Xylose L-(−)-Xylose

(*b*) Alditols are the reduction products of carbohydrates; D-xylitol is derived from D-xylose by conversion of the terminal —CHO to —CH_2OH.



D-Xylitol

(*c*) Redraw the Fischer projection of D-xylose in its eclipsed conformation.



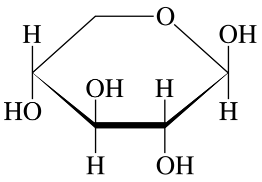
D-Xylose

Eclipsed conformation of D-xylose

Haworth formula of β-D-xylopyranose

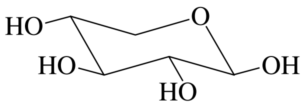
The pyranose form arises by closure to a six-membered cyclic hemiacetal, with the C-5 hydroxyl group undergoing nucleophilic addition to the carbonyl. In the β-pyranose form of D-xylose the anomeric hydroxyl group is up.

The preferred conformation of β-D-xylopyranose is a chair with all the hydroxyl groups equatorial.



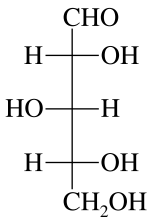
Haworth formula of
β-D-xylopyranose

is better represented as

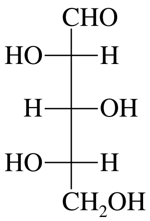


Chair conformation of
β-D-xylopyranose

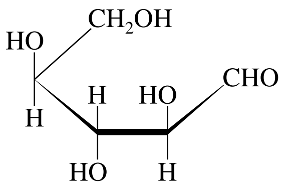
(*d*) L-Xylose is the mirror image of D-xylose.



D-Xylose

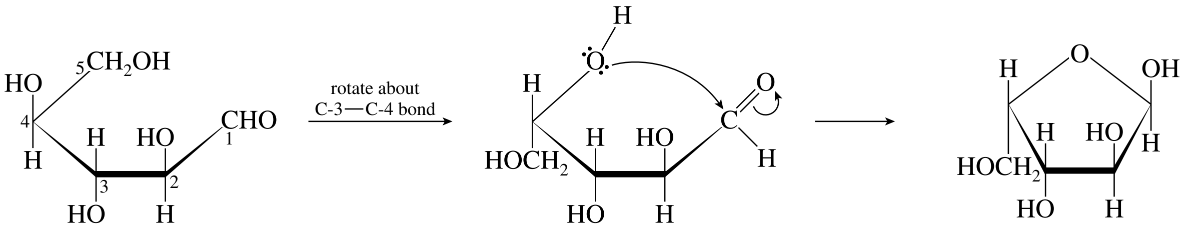


L-Xylose



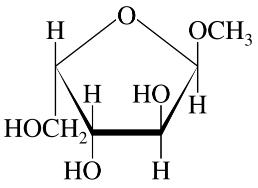
Eclipsed conformation
of L-xylose

To construct the furanose form of L-xylose, the hydroxyl at C-4 needs to be brought into the proper orientation to form a five-membered ring.

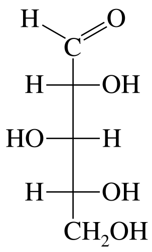


The α anomeric hydroxyl group is up in the L series.

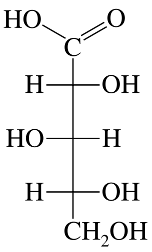
(*e*) Methyl α-L-xylofuranoside is the methyl glycoside corresponding to the structure just drawn.



(*f*) Aldonic acids are derived from aldoses by oxidation of the terminal aldehyde to a carboxylic acid.

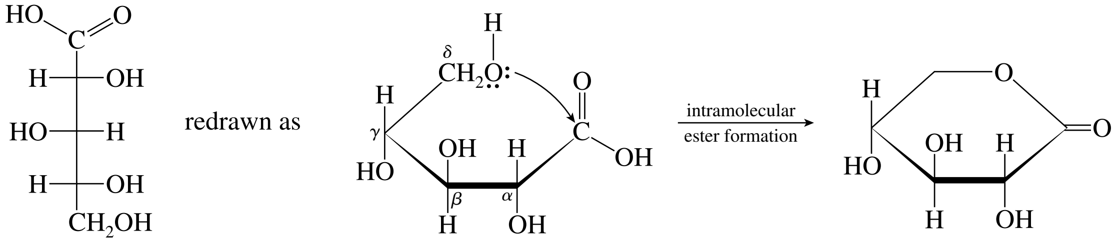


D-Xylose



D-Xylonic acid

(*g*) Aldonic acids tend to exist as lactones. A δ-lactone has a six-membered ring.

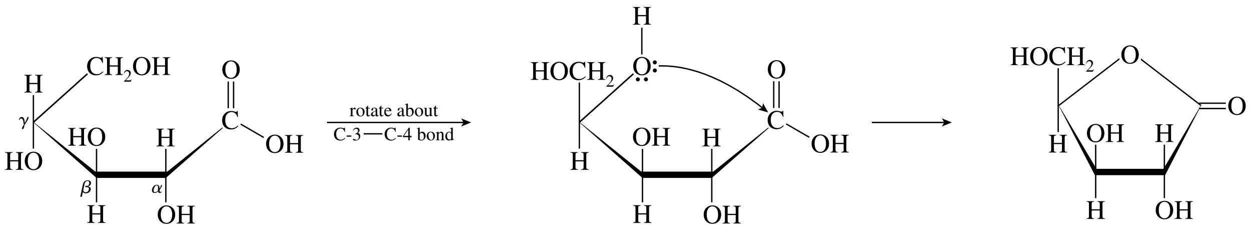


D-Xylonic acid

Eclipsed conformation of D-xylonic acid

δ-Lactone of D-xylonic acid

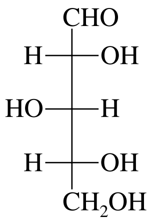
(*h*) A γ-lactone has a five-membered ring.



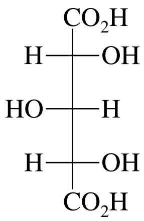
D-Xylonic acid

γ-Lactone of D-xylonic acid

(*i*) Aldaric acids have carboxylic acid groups at both ends of the chain.

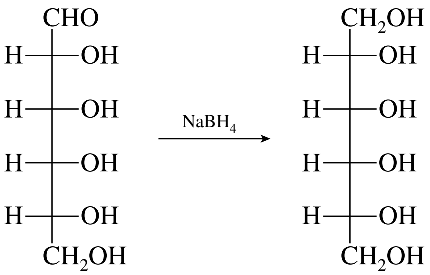


D-Xylose



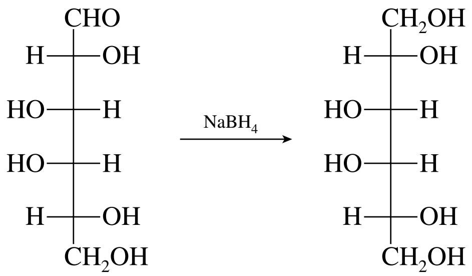
D-Xylaric acid

25.19 (*a*) Reduction of aldoses with sodium borohydride yields polyhydroxylic alcohols called **alditols.** Optically inactive alditols are those that have a plane of symmetry, that is, those that are meso forms. The D-aldohexoses that yield optically inactive alditols are D-allose and D-galactose.



D-Allose

Allitol (meso compound)

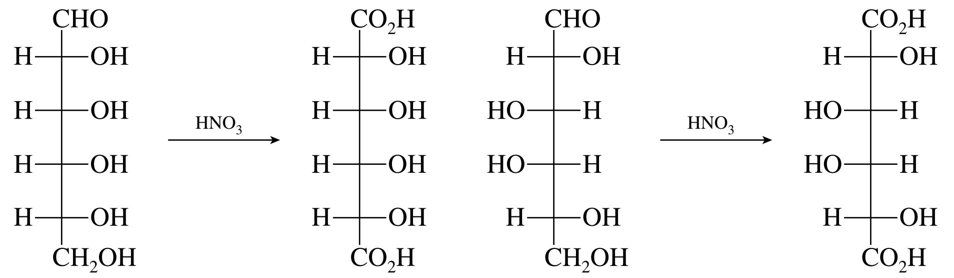


D-Galactose

Galactitol (meso compound)

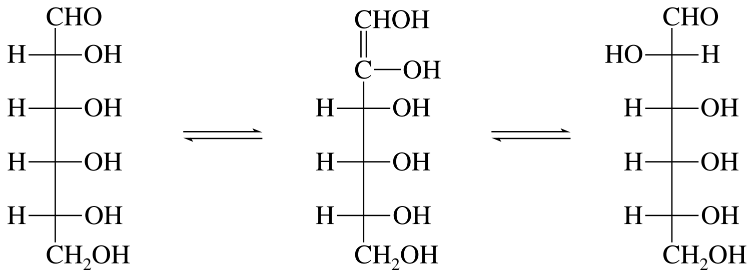
(*b*) All the aldonic acids and their lactones obtained on oxidation of the aldohexoses are optically active. The presence of a carboxyl group at one end of the carbon chain and a CH_2OH at the other precludes the existence of meso forms.

(*c*) Nitric acid oxidation of aldoses converts them to aldaric acids. The same D-aldoses found to yield optically inactive alditols in part (*a*) yield optically inactive aldaric acids.



D-Allose | Allaric acid (meso compound) | D-Galactose | Galactaric acid (meso compound)

(*d*) Aldoses that differ in configuration only at C-2 enolize to the same enediol.



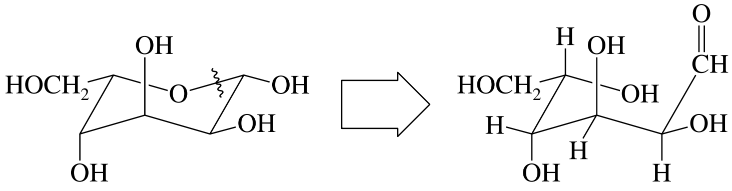
D-Allose | Enediol | D-Altrose

The stereogenic center at C-2 in the D-aldose becomes sp^2-hybridized in the enediol.

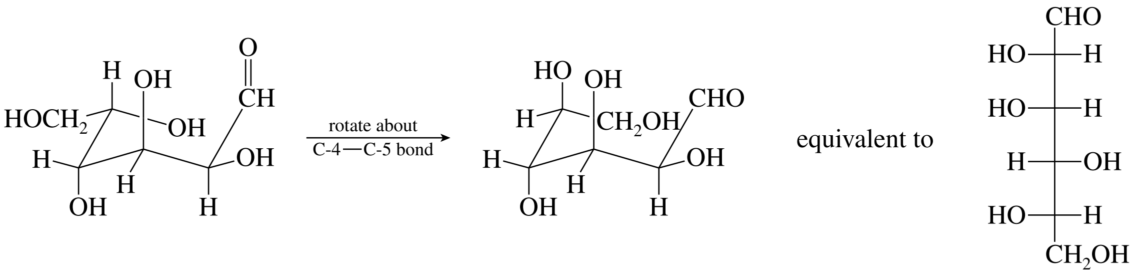
The other pairs of D-aldohexoses that form the same enediols are

D-Glucose and D-mannose
D-Gulose and D-idose
D-Galactose and D-talose

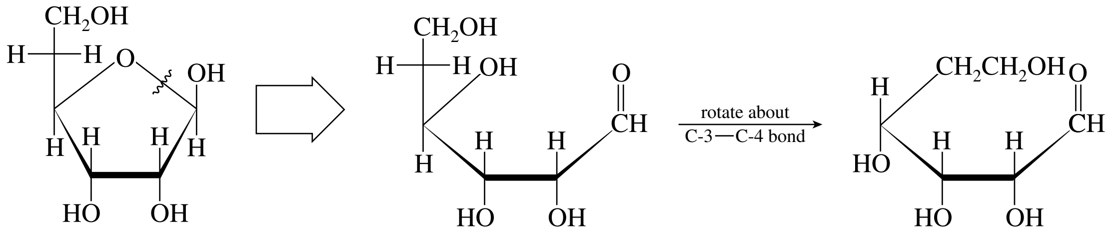
25.20 (*a*) To unravel a pyranose form, locate the anomeric carbon and mentally convert the hemiacetal linkage to a carbonyl compound and a hydroxyl function.



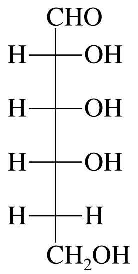
Convert the open-chain form to a Fischer projection.



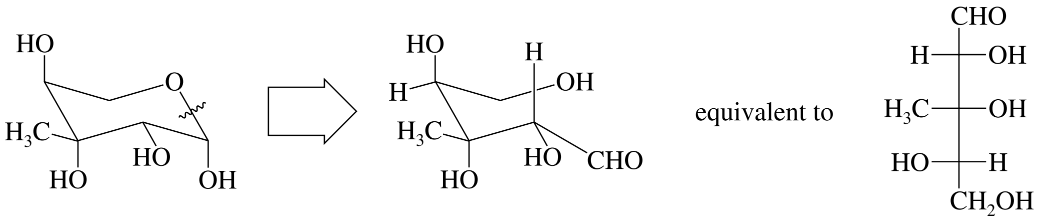
(*b*) Proceed in the same manner as in part (*a*) and unravel the furanose sugar by disconnecting the hemiacetal function.



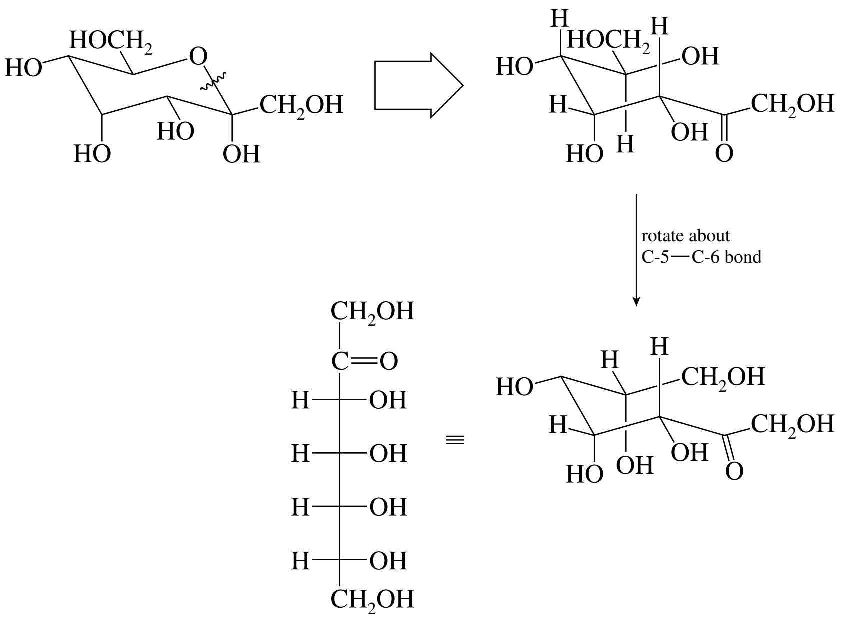
The Fischer projection is



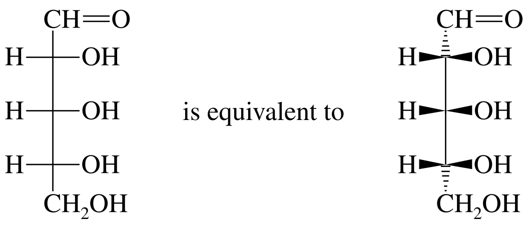
(*c*) By disconnecting and unraveling as before, the Fischer projection is revealed.



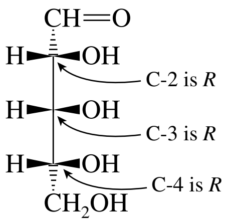
(*d*) Remember in disconnecting cyclic hemiacetals that the anomeric carbon is the one that bears two oxygen substituents.



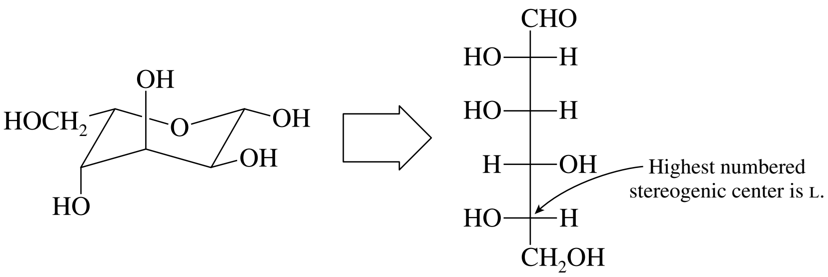
25.21 Begin the problem by converting the Fischer projection of D-ribose to a perspective view. Remember that the horizontal lines of a Fischer projection represent bonds coming toward you, and the vertical lines are going away from you.

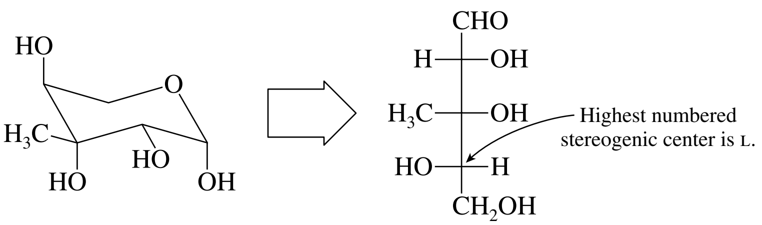


Rank the groups attached to each stereogenic center. Identify each stereogenic center as either *R* or *S* according to the methods described in Chapter 7. Remember that the proper orientation of the lowest ranked group (usually H) is away from you. Molecular models will be helpful here. Each of the stereogenic centers in D-ribose has the *R* configuration. The IUPAC name of D-ribose is (2*R*,3*R*,4*R*)-2,3,4,5-tetrahydroxypentanal.

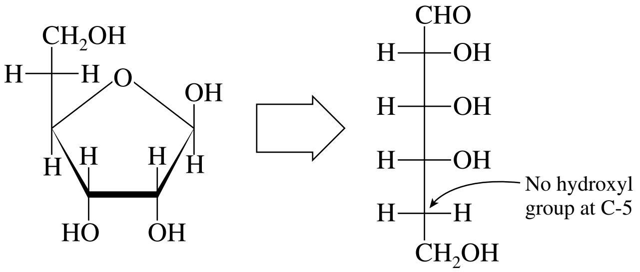


25.22 (*a*) The L sugars have the hydroxyl group to the left at the highest numbered stereogenic center in their Fischer projection. The L sugars are the ones in Problem 25.20*a* and *c*.

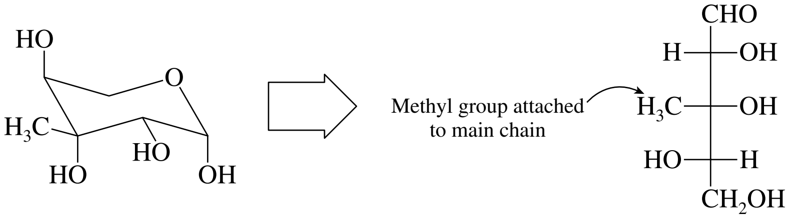




(*b*) Deoxy sugars are those that lack an oxygen substituent on one of the carbons in the main chain. The carbohydrate in Problem 25.20*b* is a deoxy sugar.

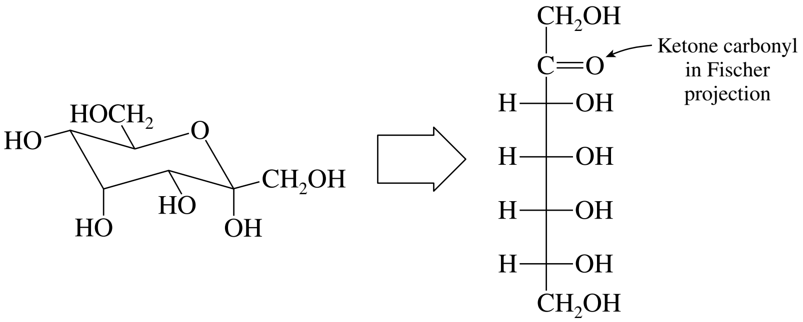


(*c*) Branched-chain sugars have a carbon substituent attached to the main chain; the carbohydrate in Problem 25.20*c* fits this description.



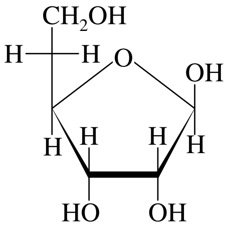
Methyl group attached to main chain

(*d*) Only the sugar in Problem 25.20*d* is a ketose.

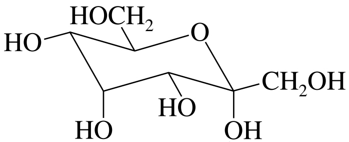


Ketone carbonyl in Fischer projection

(*e*) A furanose ring is a five-membered cyclic hemiacetal. Only the compound in Problem 25.20*b* is a furanose form.



(*f*) In D sugars, the α configuration corresponds to the condition in which the hydroxyl group at the anomeric carbon is down. The α-D sugar is that in Problem 25.20*d*.

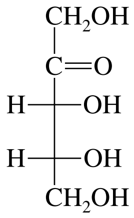


Anomeric hydroxyl is down.

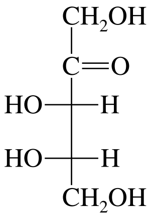
α-Pyranose form of a D-ketose

In the α-L series the anomeric hydroxyl is up. Neither of the L sugars—namely, those of Problem 25.20*a* and *c*—is α; both are β.

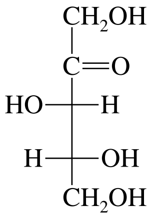
25.23 There are seven possible pentuloses, that is, five-carbon ketoses. The ketone carbonyl can be located at either C-2 or C-3. When the carbonyl group is at C-2, there are two stereogenic centers, giving rise to four stereoisomers (two pairs of enantiomers).



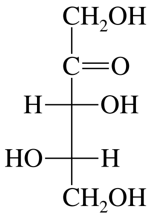
D-Erythropentulose
(D-ribulose)



L-Erythropentulose
(L-ribulose)

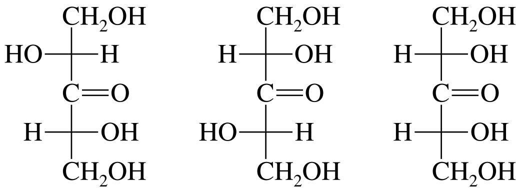


D-Threopentulose
(D-xylulose)

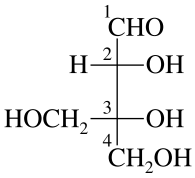


L-Threopentulose
(L-xylulose)

When the carbonyl group is located at C-3, there are only three stereoisomers, because one of them is a meso form and is superposable on its mirror image.



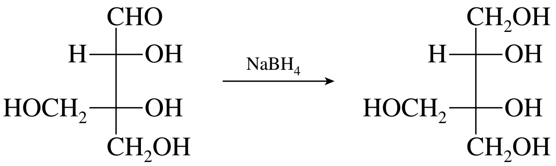
25.24 (*a*) Carbon-2 is the only stereogenic center in D-apiose.



D-Apiose

Carbon-3 is not a stereogenic center; it bears two identical CH_2OH substituents.

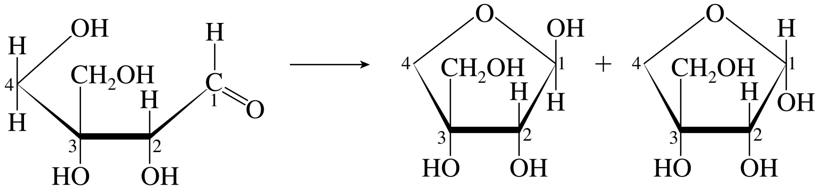
(*b*) The alditol obtained on reduction of D-apiose retains the stereogenic center. It is chiral and optically active.



D-Apiose
(optically active)

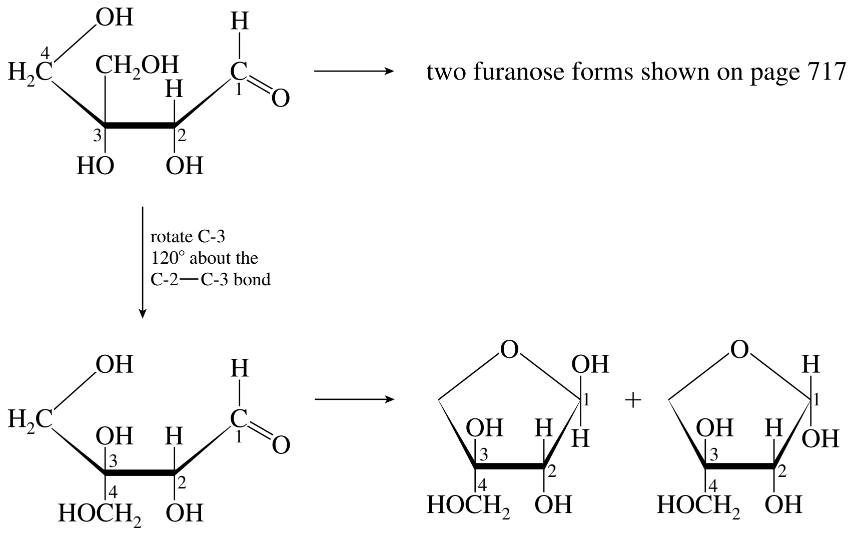
D-Apiitol
(optically active)

(*c*, *d*) Cyclic hemiacetal formation in D-apiose involves addition of a CH_2OH hydroxyl group to the aldehyde carbonyl.

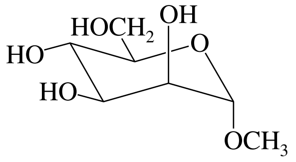


Three stereogenic centers occur in the furanose form, namely, the anomeric carbon C-1 and the original stereogenic center C-2, as well as a new stereogenic center at C-3.

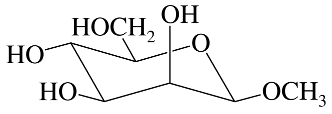
In addition to the two furanose forms just shown, two more are possible. Instead of the reaction of the CH_2OH group that was shown to form the cyclic hemiacetal, the other CH_2OH group may add to the aldehyde carbonyl.



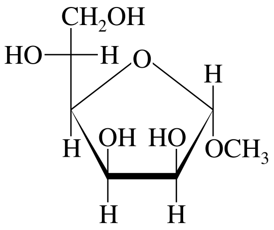
25.25 The most reasonable conclusion is that all four are methyl glycosides. Two are the methyl glycosides of the α- and β-pyranose forms of mannose and two are the methyl glycosides of the α- and β-furanose forms.



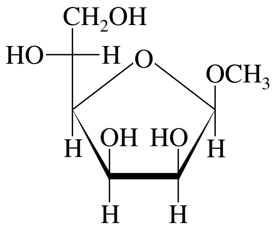
Methyl
α-D-mannopyranoside



Methyl
β-D-mannopyranoside



Methyl
α-D-mannofuranoside



Methyl
β-D-mannofuranoside

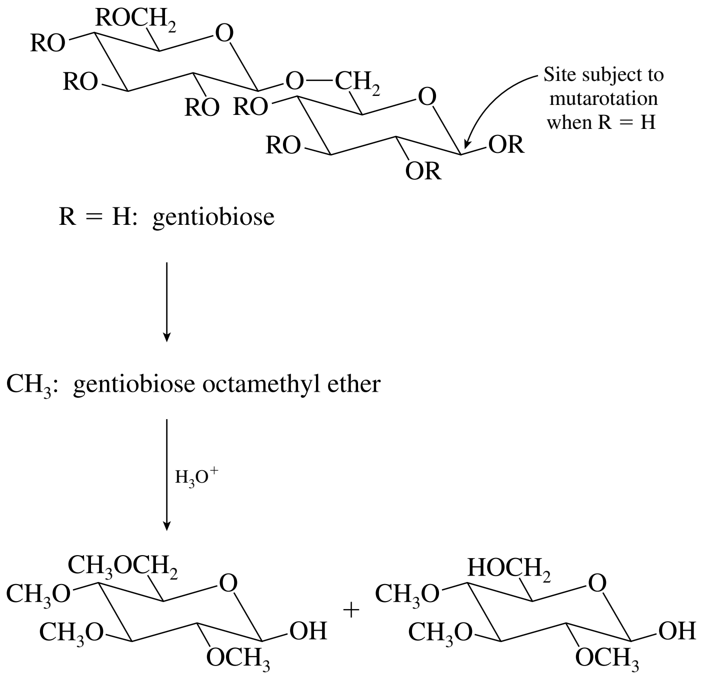
In the case of the methyl glycosides of mannose, comparable amounts of pyranosides and furanosides are formed. The major products are the α isomers.

25.26 (*a*) Disaccharides, by definition, involve an acetal linkage at the anomeric position; thus all the disaccharides must involve C-1. The bond to C-1 can be α or β. The available oxygen atoms in the second D-glucopyranosyl unit are located at C-1, C-2, C-3, C-4, and C-6. Thus, there are 11 possible disaccharides, including maltose and cellobiose, composed of D-glucopyranosyl units.

$\alpha,\alpha(1,1)$	$\alpha,\beta(1,1)$	$\beta,\beta(1,1)$
$\alpha(1,2)$		$\beta(1,2)$
$\alpha(1,3)$		$\beta(1,3)$
$\alpha(1,4)$ (maltose)		$\beta(1,4)$ (cellobiose)
$\alpha(1,6)$		$\beta(1,6)$

(*b*) To be a reducing sugar, one of the anomeric positions must be a free hemiacetal. All except $\alpha,\alpha(1,1)$, $\alpha,\beta(1,1)$, and $\beta,\beta(1,1)$ are reducing sugars.

25.27 Because gentiobiose undergoes mutarotation, it must have a free hemiacetal group. Formation of two molecules of D-glucose indicates that it is a disaccharide and because that hydrolysis is catalyzed by emulsin, the glycosidic linkage is β. The methylation data, summarized in the following equation, require that the glucose units be present in pyranose forms and be joined by a $\beta(1,6)$-glycoside bond.



Site subject to mutarotation when R = H

R = H: gentiobiose

R = CH_3: gentiobiose octamethyl ether

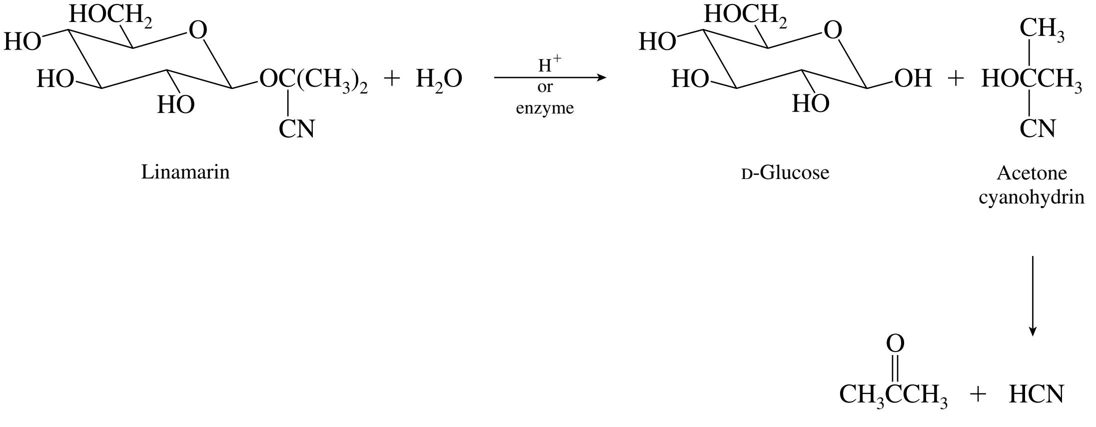
H_3O^+

2,3,4,6-Tetra-*O*-methyl-D-glucose

2,3,4-Tri-*O*-methyl-D-glucose

25.28 Like other glycosides, cyanogenic glycosides are cleaved to a carbohydrate and an alcohol on hydrolysis.

(*a*) In the case of linamarin the alcohol is recognizable as the cyanohydrin of acetone. Once formed, this cyanohydrin dissociates to hydrogen cyanide and acetone.



Linamarin

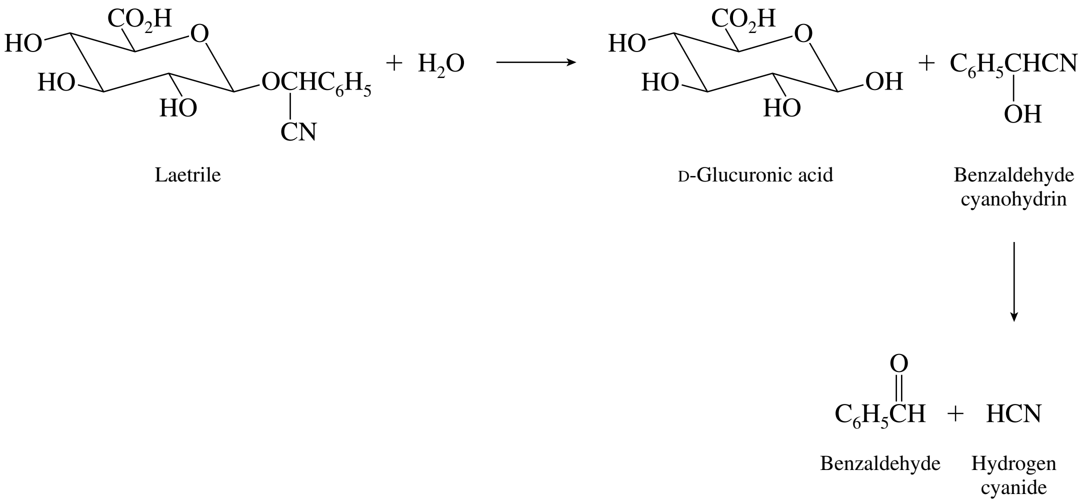
D-Glucose

Acetone cyanohydrin

Acetone

Hydrogen cyanide

(*b*) Laetrile undergoes an analogous hydrolytic cleavage to yield the cyanohydrin of benzaldehyde.



Laetrile

D-Glucuronic acid

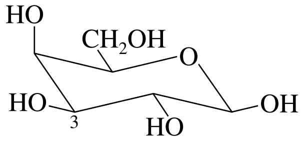
Benzaldehyde cyanohydrin

Benzaldehyde

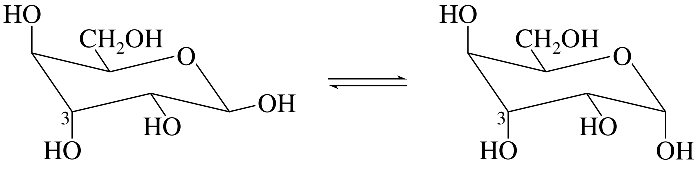
Hydrogen cyanide

25.29 Comparing D-glucose, D-mannose, and D-galactose, it can be said that the configuration of C-2 has a substantial effect on the relative energies of the α- and β-pyranose forms, but that the configuration of C-4 has virtually no effect. With this observation in mind, write the structures of the pyranose forms of the carbohydrates given in each part.

(*a*) The β-pyranose form of D-gulose is the same as that of D-galactose except for the configuration at C-3.



β-D-Galactopyranose (64% at equilibrium)

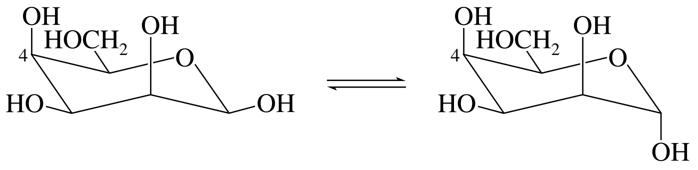


β-D-Gulopyranose

α-D-Gulopyranose (1,3 diaxial repulsion between hydroxyl groups)

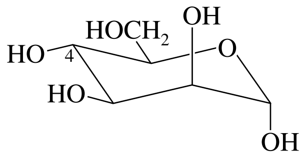
The axial hydroxyl group at C-3 destabilizes the α-pyranose form more than the β form because of its repulsive interaction with the axially disposed anomeric hydroxyl group. There should be an even higher β/α ratio in D-gulopyranose than in D-galactopyranose. This is so; the observed β/α ratio is 88 : 12.

(*b*) The β-pyranose form of D-talose is the same as that of D-mannose except for the configuration at C-4.



β-D-Talopyranose

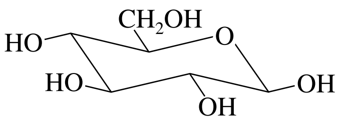
α-D-Talopyranose



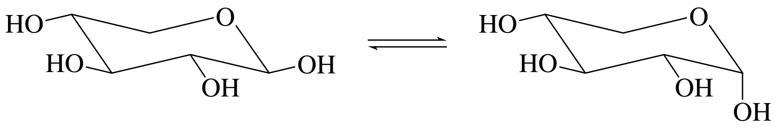
α-D-Mannopyranose (68% at equilibrium)

Because the configuration at C-4 has little effect on the α- to β-pyranose ratio (compare D-glucose and D-galactose), we would expect that talose would behave very much like mannose and that the α-pyranose form would be preferred at equilibrium. This is indeed the case; the α-pyranose form predominates at equilibrium, the observed α/β ratio being 78 : 22.

(*c*) The pyranose form of D-xylose is just like that of D-glucose except that it lacks a CH_2OH group.



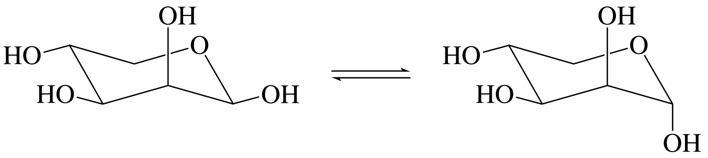
β-D-Glucopyranose
(64% at equilibrium)



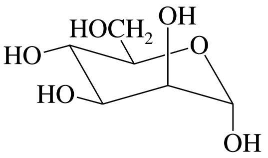
β-D-Xylopyranose α-D-Xylopyranose

We would expect the equilibrium between pyranose forms in D-xylose to be much like that in D-glucose and predict that the β-pyranose form would predominate. It is observed that the β/α ratio in D-xylose is 64 : 36, exactly the same as in D-glucose.

(*d*) The pyranose form of D-lyxose is like that of D-mannose except that it lacks a CH_2OH group. As in D-mannopyranose, the α form should predominate over the β.



β-D-Lyxopyranose α-D-Lyxopyranose

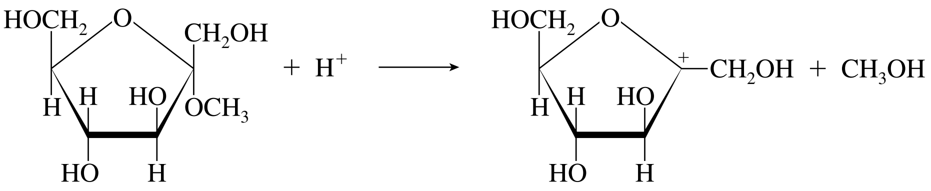


α-D-Mannopyranose
(68% at equilibrium)

The observed α/β distribution ratio in D-lyxopyranose is 73 : 27.

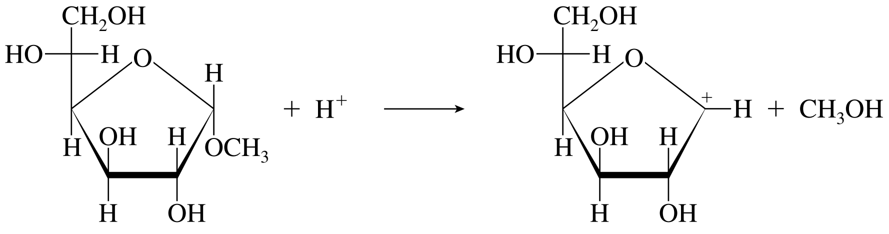
25.30 (*a*) The rate-determining step in glycoside hydrolysis is carbocation formation at the anomeric position. The carbocation formed from methyl α-D-fructofuranoside (compound A) is tertiary and therefore more stable than the one from methyl α-D-glucofuranoside (compound B), which is secondary. The more stable a carbocation is, the more rapidly it will be formed.

Faster:



A Tertiary carbocation

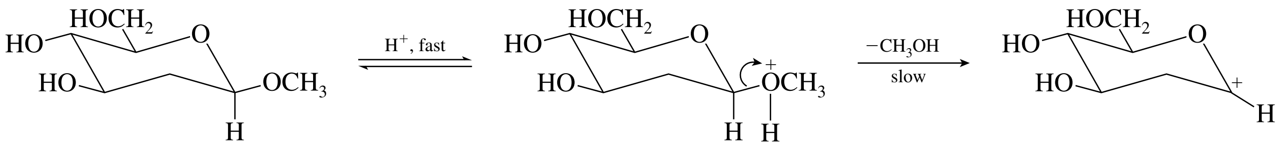
Slower:



B Secondary carbocation

(*b*) The carbocation formed from methyl β-D-glucopyranoside (compound D) is less stable than the one from its 2-deoxy analog (compound C) and is formed more slowly. It is destabilized by the electron-withdrawing inductive effect of the hydroxyl group at C-2.

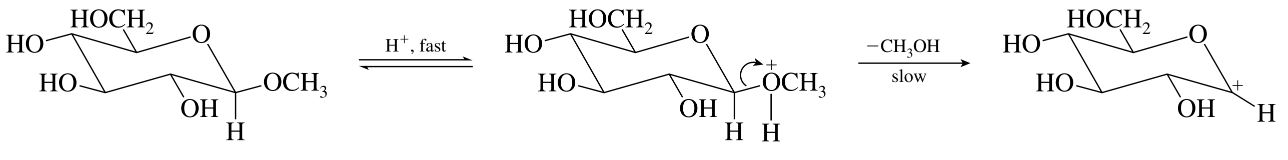
Faster:



C

More stable

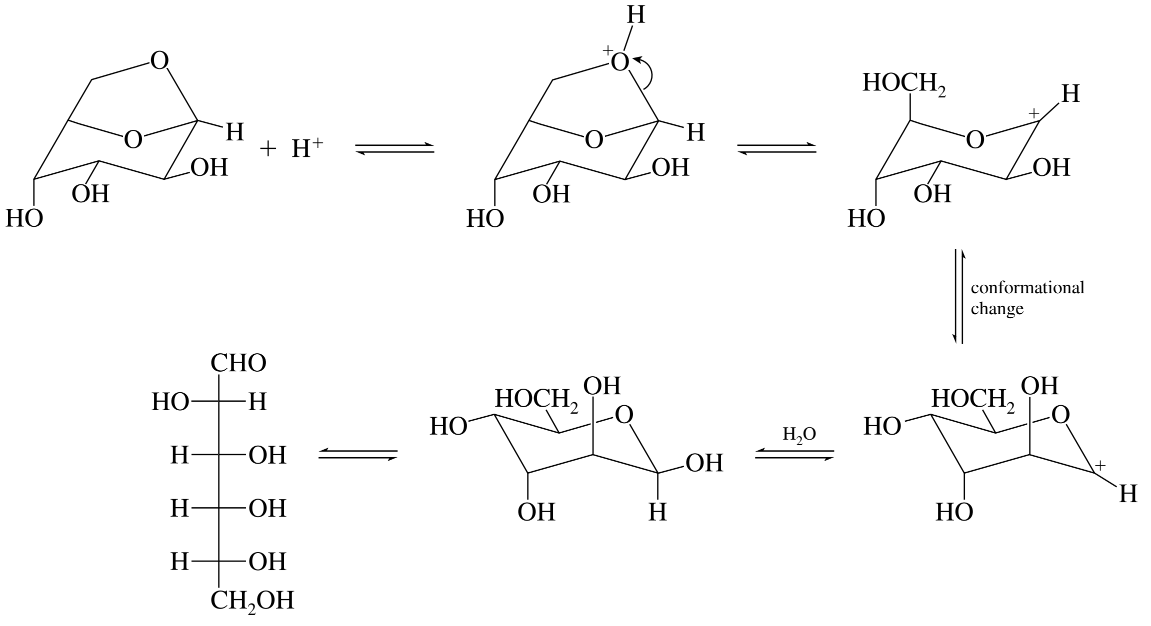
Slower:



D

Less stable

25.31 D-Altrosan is a glycoside. The anomeric carbon—the one with two oxygen substituents—has an alkoxy group attached to it. Hydrolysis of D-altrosan follows the general mechanism for acetal hydrolysis.

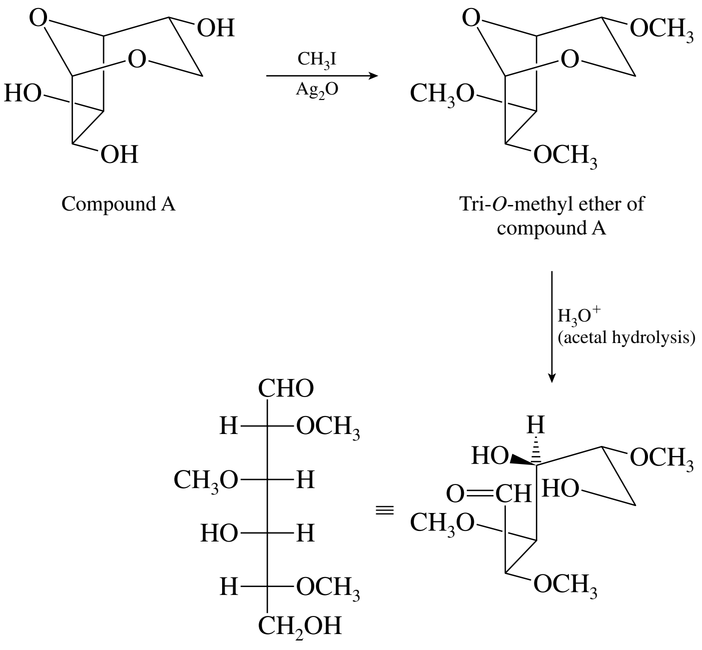


D-Altrose

25.32 Galactose has hydroxyl groups at carbons 2, 3, 4, 5, 6. Ten trimethyl ethers are therefore possible.

2,3,4
2,3,5
2,3,6
2,4,5
2,4,6
2,5,6
3,4,5
3,4,6
3,5,6
4,5,6

To find out which one of these is identical with the degradation product of compound A, carry compound A through the required transformations.

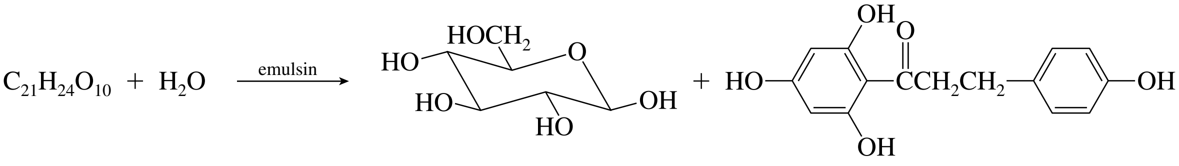


Compound A

Tri-*O*-methyl ether of compound A

2,3,5-Tri-*O*-methyl-D-galactose

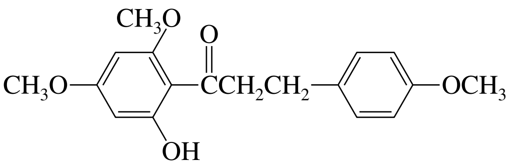
25.33 The fact that phlorizin is hydrolyzed to D-glucose and compound A by emulsin indicates that it is a β-glucoside in which D-glucose is attached to one of the phenolic hydroxyls of compound B.



D-Glucose ($C_6H_{12}O_6$)

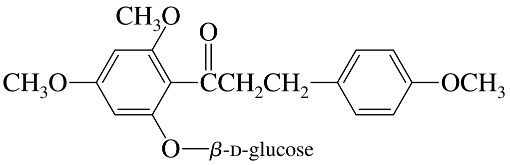
Compound A ($C_{15}H_{14}O_5$)

The methylation experiment reveals to which hydroxyl glucose is attached. Excess methyl iodide reacts with all the available phenolic hydroxyl groups, but the glycosidic oxygen is not affected. Thus when the methylated phlorizin undergoes acid-catalyzed hydrolysis of its glycosidic bond, the oxygen in that bond is exposed as a phenolic hydroxyl group.

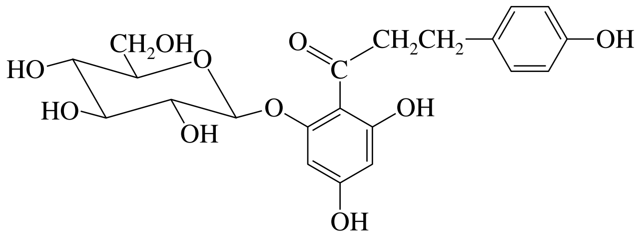


Compound B

This compound must arise by hydrolysis of



The structure of phlorizin is therefore



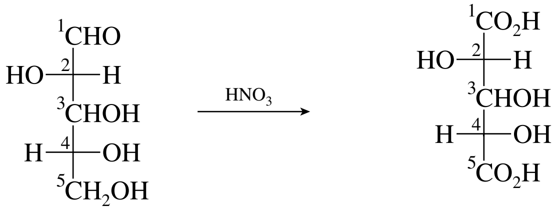
25.34 Consider all the individual pieces of information in the order in which they are presented.

1. *Chain extension of the aldopentose (−)-arabinose by way of the derived cyanohydrin gave a mixture of (+)-glucose and (+)-mannose.*

   Chain extension of aldoses takes place at the aldehyde end of the chain. The aldehyde function of an aldopentose becomes C-2 of an aldohexose, which normally results in two carbohydrates diastereomeric at C-2. Thus, (+)-glucose and (+)-mannose have the same configuration at C-3, C-4, and C-5; they have opposite configurations at C-2. The configuration at C-2, C-3, and C-4 of (−)-arabinose is the same as that at C-3, C-4, and C-5 of (+)-glucose and (+)-mannose.

2. *Oxidation of (−)-arabinose with warm nitric acid gave an optically active aldaric acid.*

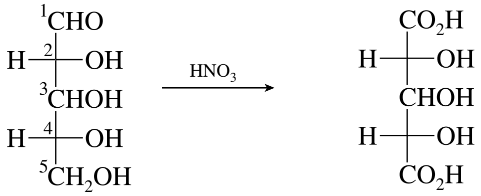
   Because the hydroxyl group at C-4 of (−)-arabinose is at the right in a Fischer projection formula (evidence of step 1), the hydroxyl at C-2 must be to the left in order for the aldaric acid to be optically active.



Partial stereostructure of (−)-arabinose

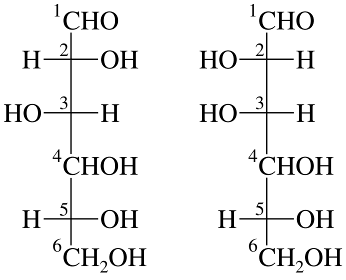
Aldaric acid from (−)-arabinose; optically active irrespective of configuration at C-3

If the C-2 hydroxyl group had been to the right, an optically inactive meso aldaric acid would have been produced.



Achiral meso form; cannot be optically active

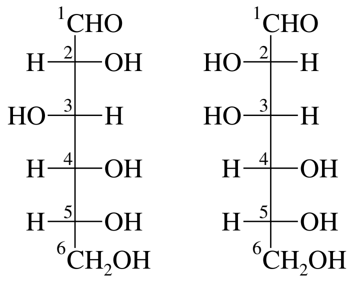
Therefore we now know the configurations of C-3 and C-5 of (+)-glucose and (+)-mannose and that these two aldohexoses have opposite configurations at C-2, but the same (yet to be determined) configuration at C-4.



[One of these is (+)-glucose, the other is (+)-mannose.]

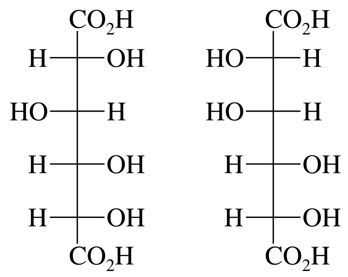
3. *Both (+)-glucose and (+)-mannose are oxidized to optically active aldaric acids with nitric acid.*

Because both (+)-glucose and (+)-mannose yield optically active aldaric acids and both have the same configuration at C-4, the hydroxyl group must lie at the right in the Fischer projection at this carbon.

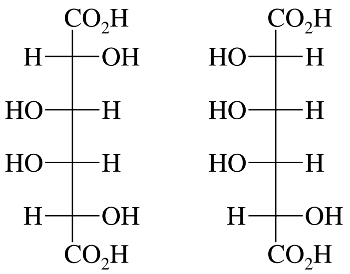


[One of these is (+)-glucose, the other is (+)-mannose.]

The structures of the corresponding aldaric acids are



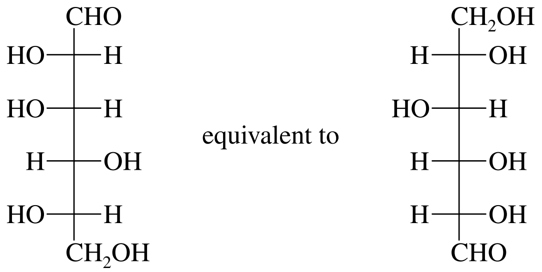
Both are optically active. Had the C-4 hydroxyl group been to the left, one of the aldaric acids would have been a meso form.



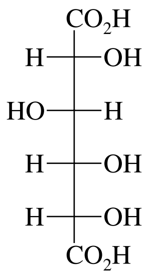
(This aldaric acid is optically inactive.)

4. *There is another sugar, (+)-gulose, that gives the same aldaric acid on oxidation as does (+)-glucose.*

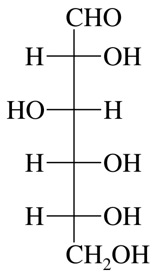
This is the last piece in the puzzle, the one that permits one of the Fischer projections shown in the first part of step 3 to be assigned to (+)-glucose and the other to (+)-mannose. Consider first the structure



Oxidation gives the aldaric acid

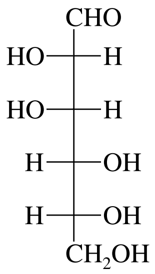


This is the same aldaric acid as that provided by one of the structures given as either (+)-glucose or (+)-mannose. That Fischer projection therefore corresponds to (+)-glucose.

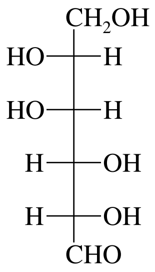


This must be (+)-glucose.

The structure of (+)-mannose is therefore



A sugar that yields the same aldaric acid is



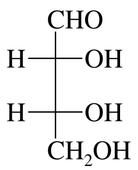
This is, in fact, not a different sugar but simply (+)-mannose rotated through an angle of 180°.

SELF-TEST

PART A

A-1. Draw the structures indicated for each of the following:

(*a*) The enantiomer of D-erythrose



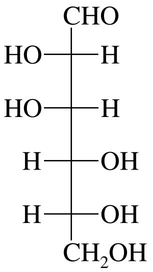
(*b*) A diastereomer of D-erythrose

(*c*) The α-furanose form of D-erythrose (use a Haworth formula)

(*d*) The anomer of the structure in part (*c*)

(*e*) Assign the configuration of each stereogenic center of D-erythrose as either *R* or *S*.

A-2. The structure of D-mannose is



D-Mannose

Using Fischer projections, draw the product of the reaction of D-mannose with

(*a*) $NaBH_4$ in H_2O

(*b*) Benedict's reagent

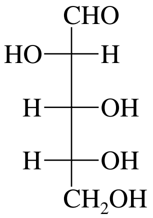
(*c*) Excess periodic acid

A-3. Referring to the structure of D-arabinose shown, draw the following:

(*a*) The α-pyranose form of D-arabinose

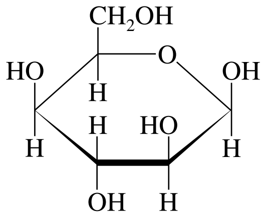
(*b*) The β-furanose form of D-arabinose

(*c*) The β-pyranose form of L-arabinose



D-Arabinose

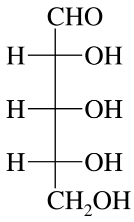
A-4. Using text Figure 25.2, identify the following carbohydrate:

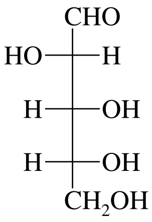


A-5. Write structural formulas for the α- and β-methyl pyranosides formed from the reaction of D-mannose (see Problem A-2 for its structure) with methanol in the presence of hydrogen chloride. How are the two products related—are they enantiomers? Diastereomers?

PART B

B-1. Choose the response that provides the best match between the terms given and the structures shown.


1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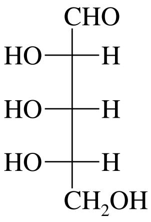
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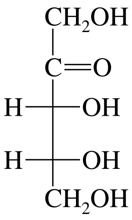
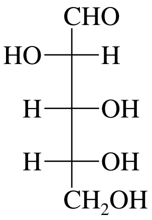
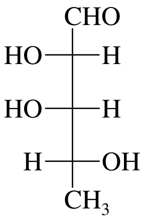

4

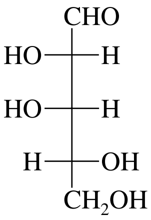
	Diastereomers	Enantiomers
(*a*)	1, 3, and 4	1 and 3
(*b*)	1 and 2	1 and 3
(*c*)	1, 2, and 3	1 and 3
(*d*)	1 and 4	1 and 2

B-2. A D carbohydrate is
(*a*) Always dextrorotatory
(*b*) Always levorotatory
(*c*) Always the anomer of the corresponding L carbohydrate
(*d*) None of the above

B-3. Two of the three compounds shown yield the same product on reaction with warm HNO_3. The *exception* is

(*a*)


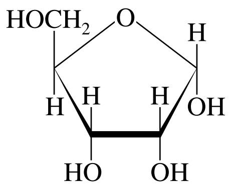
(*b*)


(*c*)


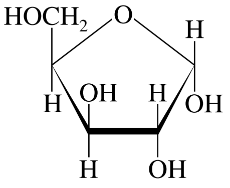
(*d*) None of these (all yield the same product)

B-4. The optical rotation of the α form of a pyranose is +150.7°; that of the β form is +52.8°. In solution an equilibrium mixture of the anomers has an optical rotation of +80.2°. The percentage of the α form at equilibrium is
(*a*) 28% (*b*) 32% (*c*) 68% (*d*) 72%

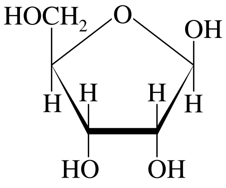
B-5. Which of the following represents the anomer of the compound shown?



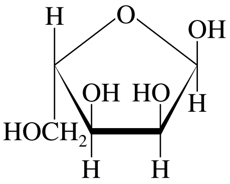
(*a*)



(*c*)

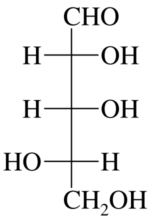


(*b*)

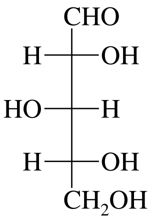


(*d*) None of these

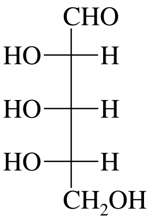
B-6. Which of the following aldoses yields an optically inactive substance on reaction with sodium borohydride?



1



2



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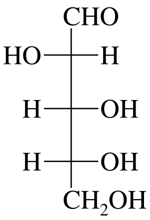
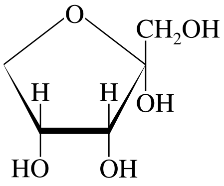


4

(*a*) 3 only
(*b*) 1 and 4
(*c*) 2 and 3
(*d*) All (1, 2, 3, and 4)

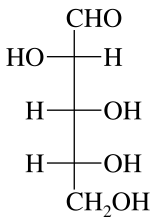
B-7. Which set of terms correctly identifies the carbohydrate shown?

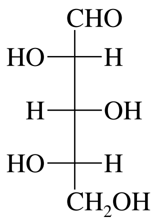


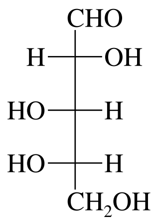
1. Pentose
2. Pentulose
3. Hexulose
4. Hexose
5. Aldose
6. Ketose
7. Pyranose
8. Furanose

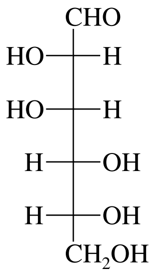
(*a*) 2, 6, 8
(*b*) 2, 6, 7
(*c*) 1, 5, 8
(*d*) A set of terms other than these

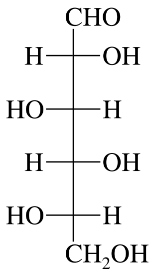
B-8. The structure of D-arabinose is shown in Problem A-3. Which of the following is L-arabinose?


(*a*)

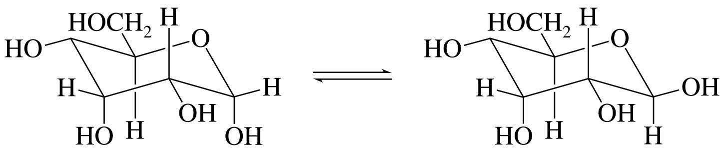

(*b*)


(*c*)


(*d*)

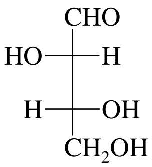

(*e*)

B-9. Which one of the statements concerning the equilibrium shown is true?



(*a*) The two structures are enantiomers of each other. They have equal but opposite optical rotations and racemize slowly at room temperature.
(*b*) The two structures are enantiomers of each other. They racemize too rapidly at room temperature for their optical rotations to be measured.
(*c*) The two structures are diastereomers of each other. Their interconversion is called mutarotation.
(*d*) The two structures are diastereomers of each other. Their interconversion does not require breaking and making bonds, only a change in conformation.
(*e*) The two structures are diastereomers of each other. One is a furanose form, the other a pyranose form.

B-10. The configurations of the stereogenic centers in D-threose (shown) are



(*a*) 2*R*,3*R* (*b*) 2*R*,3*S* (*c*) 2*S*,3*R* (*d*) 2*S*,3*S*