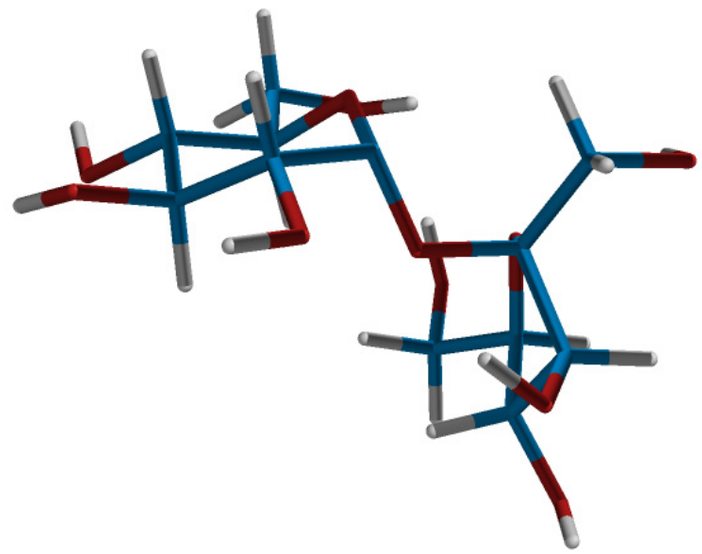
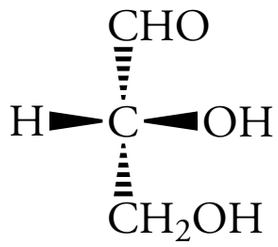
26

Carbohydrates



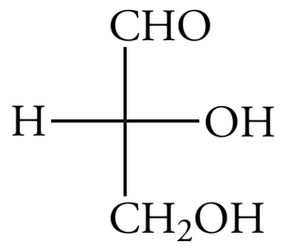
Sucrose

26.3 CHIRALITY OF MONOSACCHARIDES



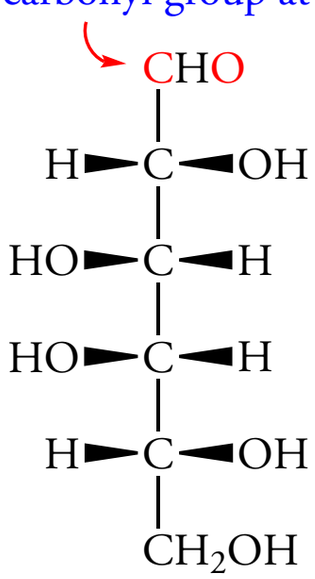
(R)-glyceraldehyde

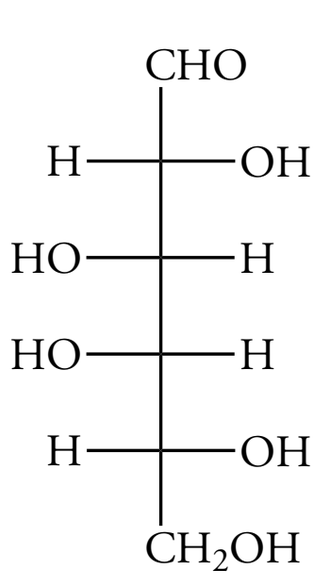
$[\alpha]_D^{25} = +13.5^o$



Fischer projection

carbonyl group at top

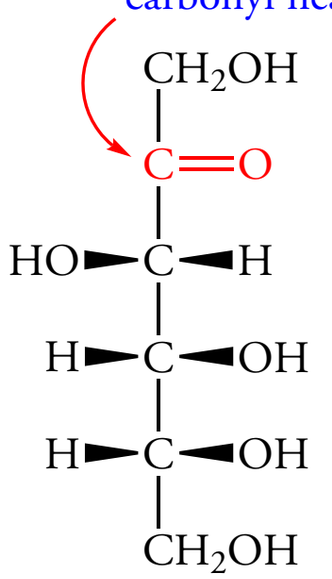


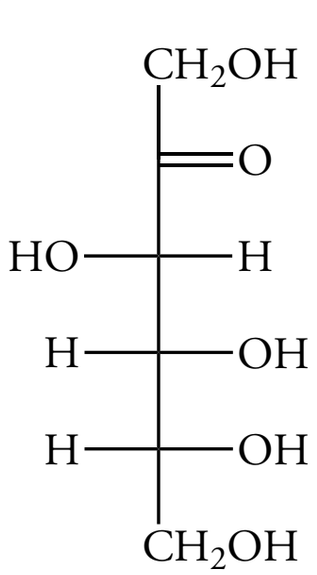


Fischer projection

D-galactose

carbonyl near top



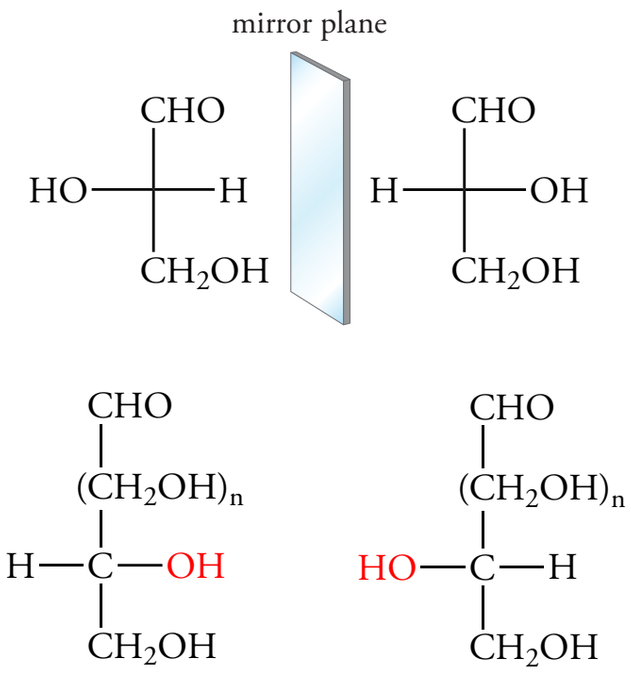


Fischer projection

D-fructose

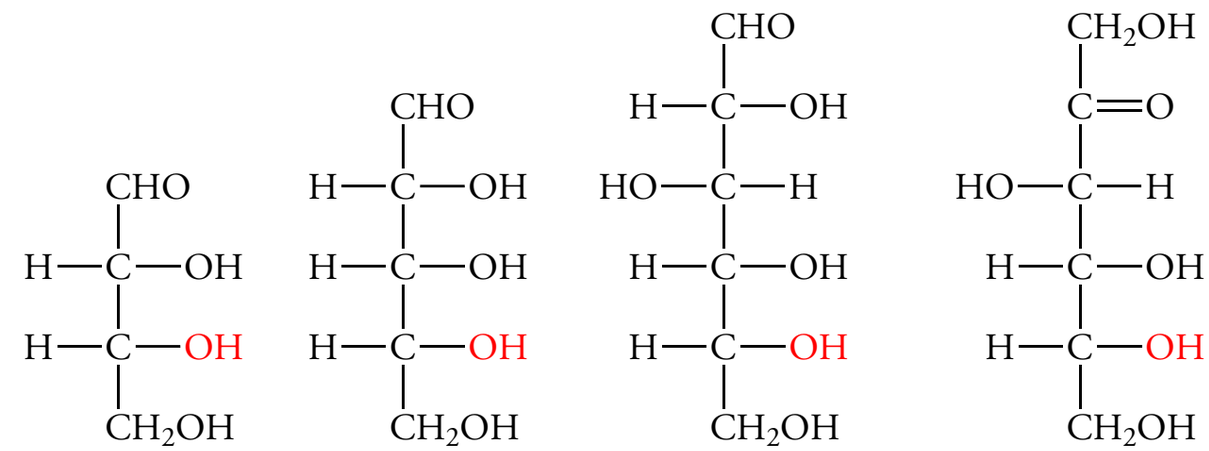
26.3 CHIRALITY OF MONOSACCHARIDES

Aldoses



a D aldose

an L aldose



D-glyceraldehyde

D-ribose

D-glucose

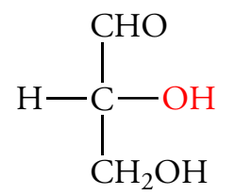
D-fructose

26.3 CHIRALITY OF MONOSACCHARIDES

Aldoses

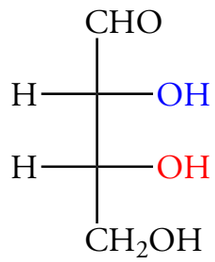
Figure 26.1 Structures of D-Aldoses

Aldotriose

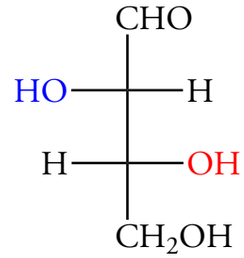


D-glyceraldehyde

Aldotetroses

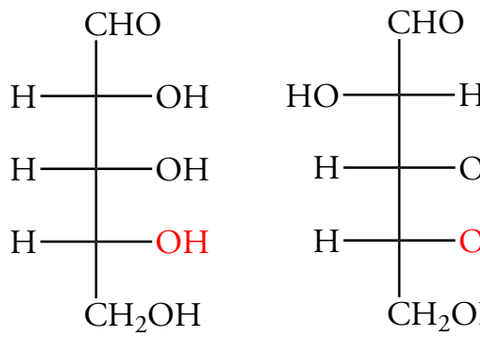


D-erythrose



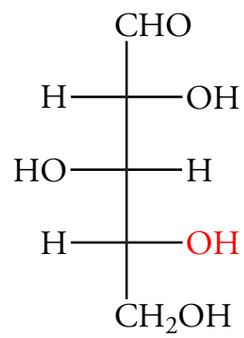
D-threose

Aldopentoses

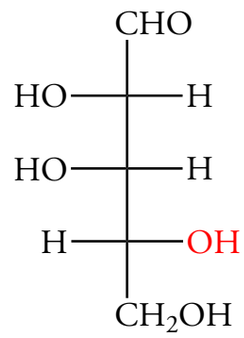


D-ribose

D-arabinose

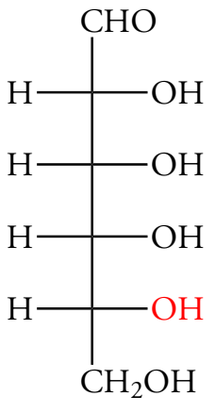


D-xylose

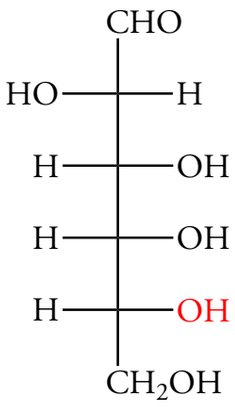


D-lyxose

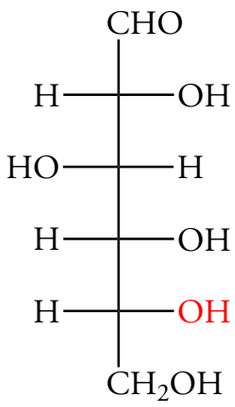
Aldohexoses



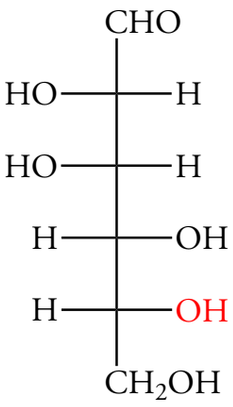
D-allose



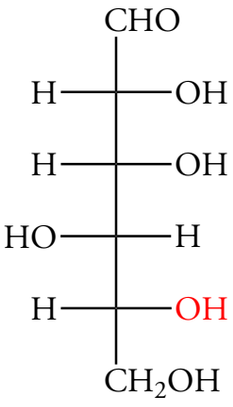
D-altrose



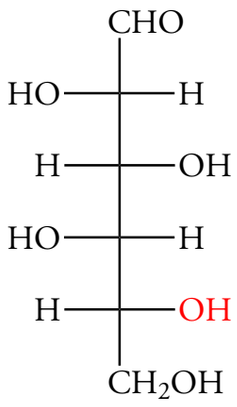
D-glucose



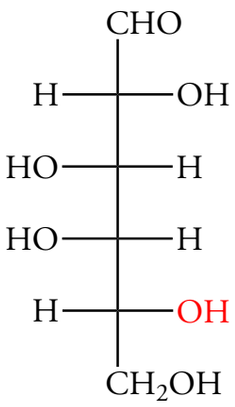
D-mannose



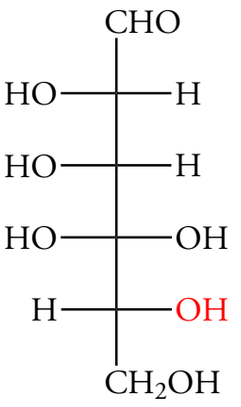
D-gulose



D-idose



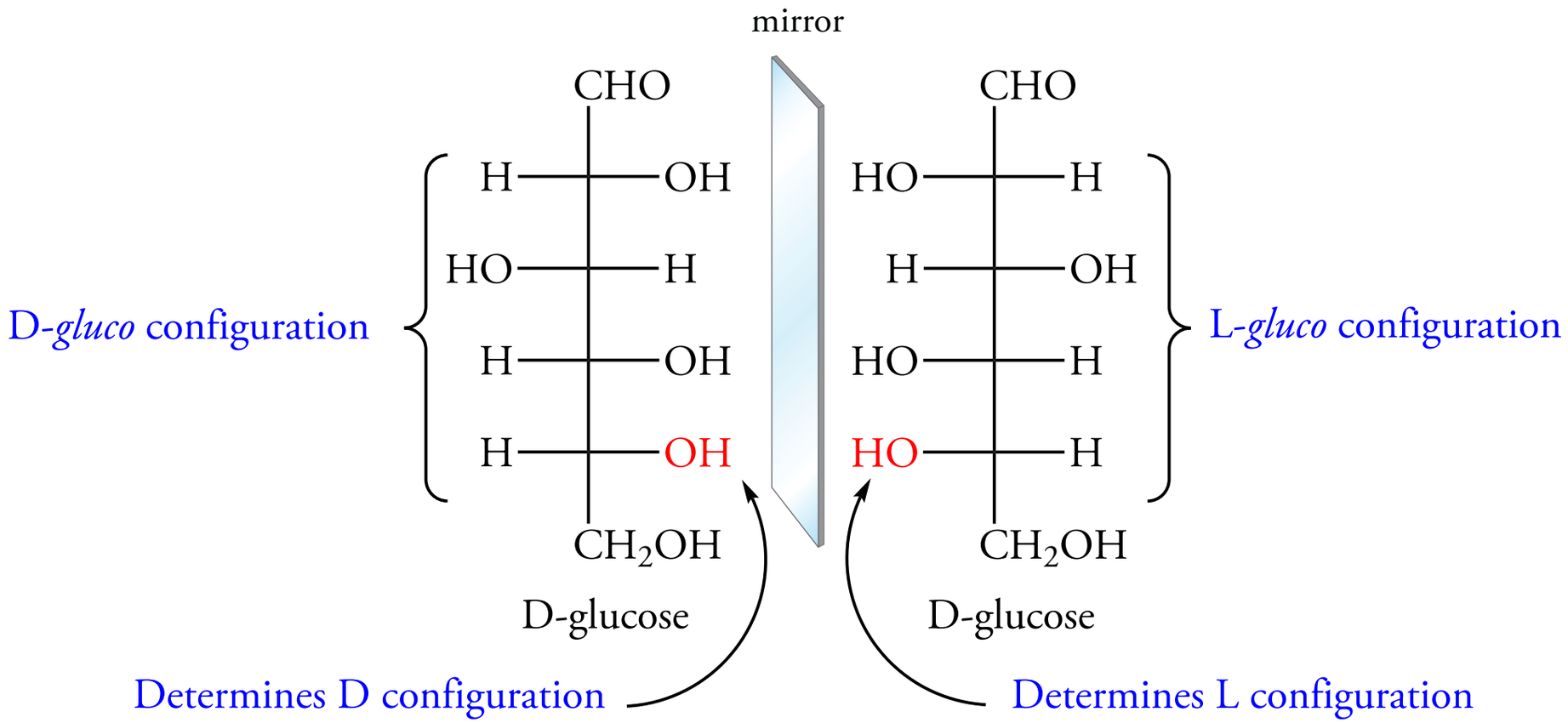
D-galactose



D-talose

Figure 26.2 Enantiomeric Relationship of D- and L-Monosaccharides

The D- and L-monosaccharides have reversed, mirror image configurations at every chiral center.

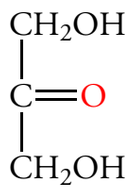


26.3 CHIRALITY OF MONOSACCHARIDES

Ketoses

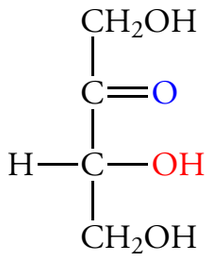
Figure 26.3 Structures of D-2-Ketoses

Ketotriose



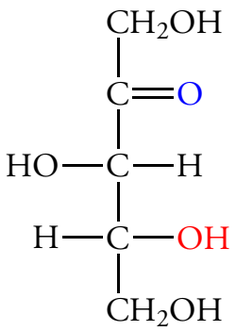
dihydroxyacetone

Ketotetrose

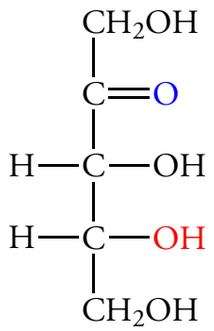


D-erythulose

Ketopentoses

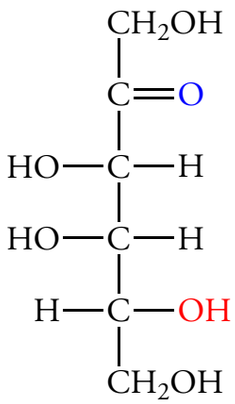


D-xylulose

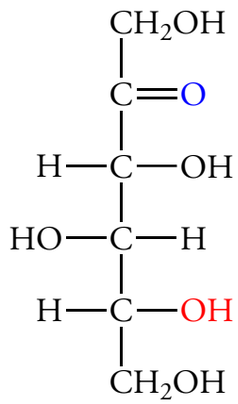


D-ribulose

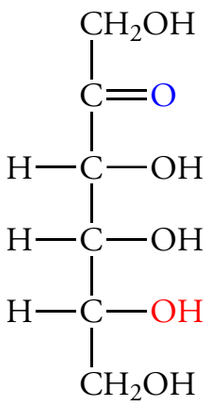
Ketohexoses



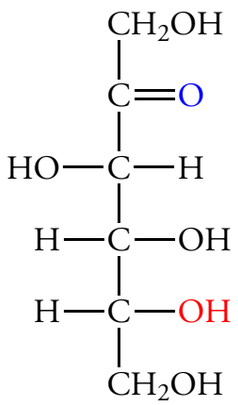
D-tagatose



D-sorbose



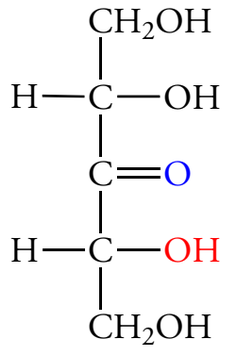
D-psicose



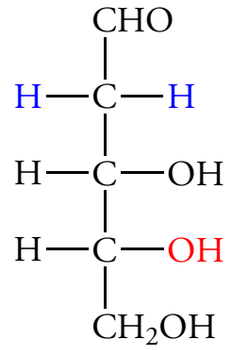
D-fructose

26.3 CHIRALITY OF MONOSACCHARIDES

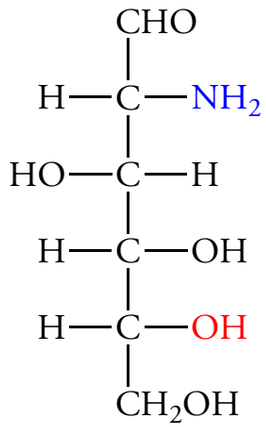
Less Common Monosaccharides



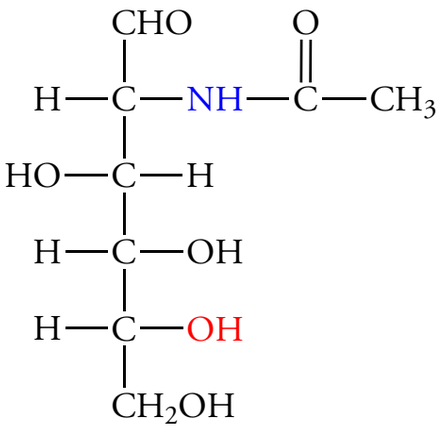
(a 3-ketopentose)



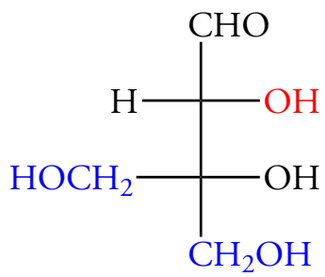
2-deoxy-D-ribose



D-2-glucosamine



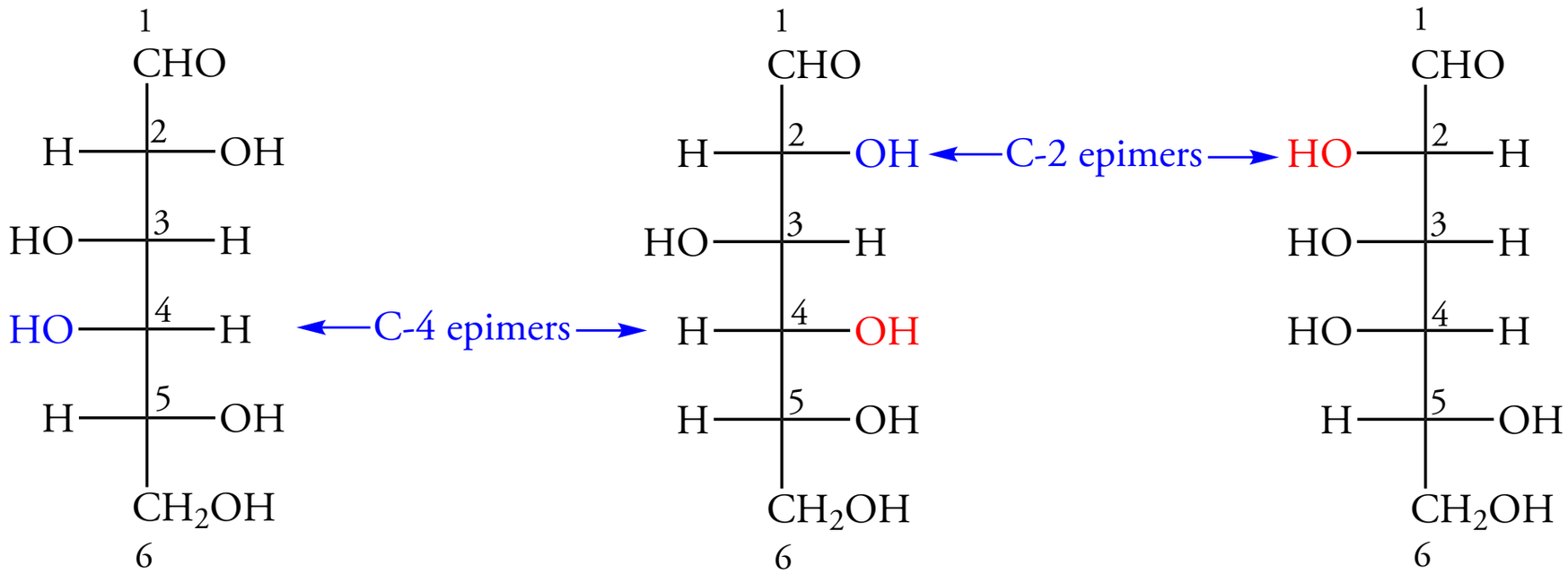
N-acetyl-D-2-glucosamine



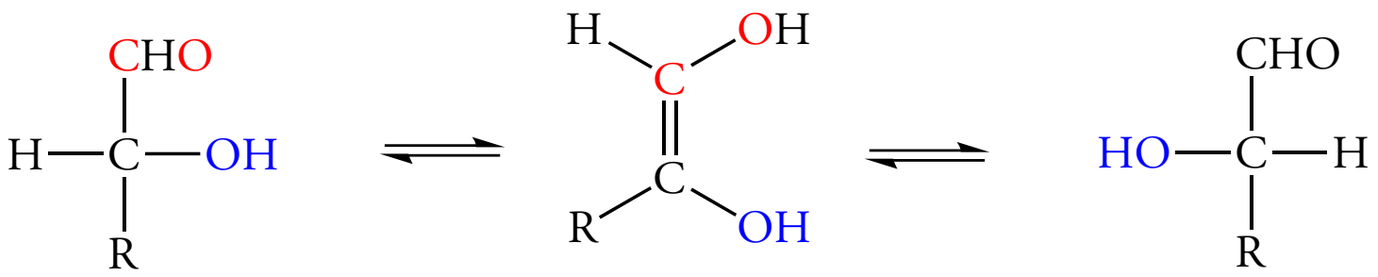
D-apiose

26.4 ISOMERIZATIONS OF MONOSACCHARIDES

Epimers



D-galactose D-glucose D-mannose

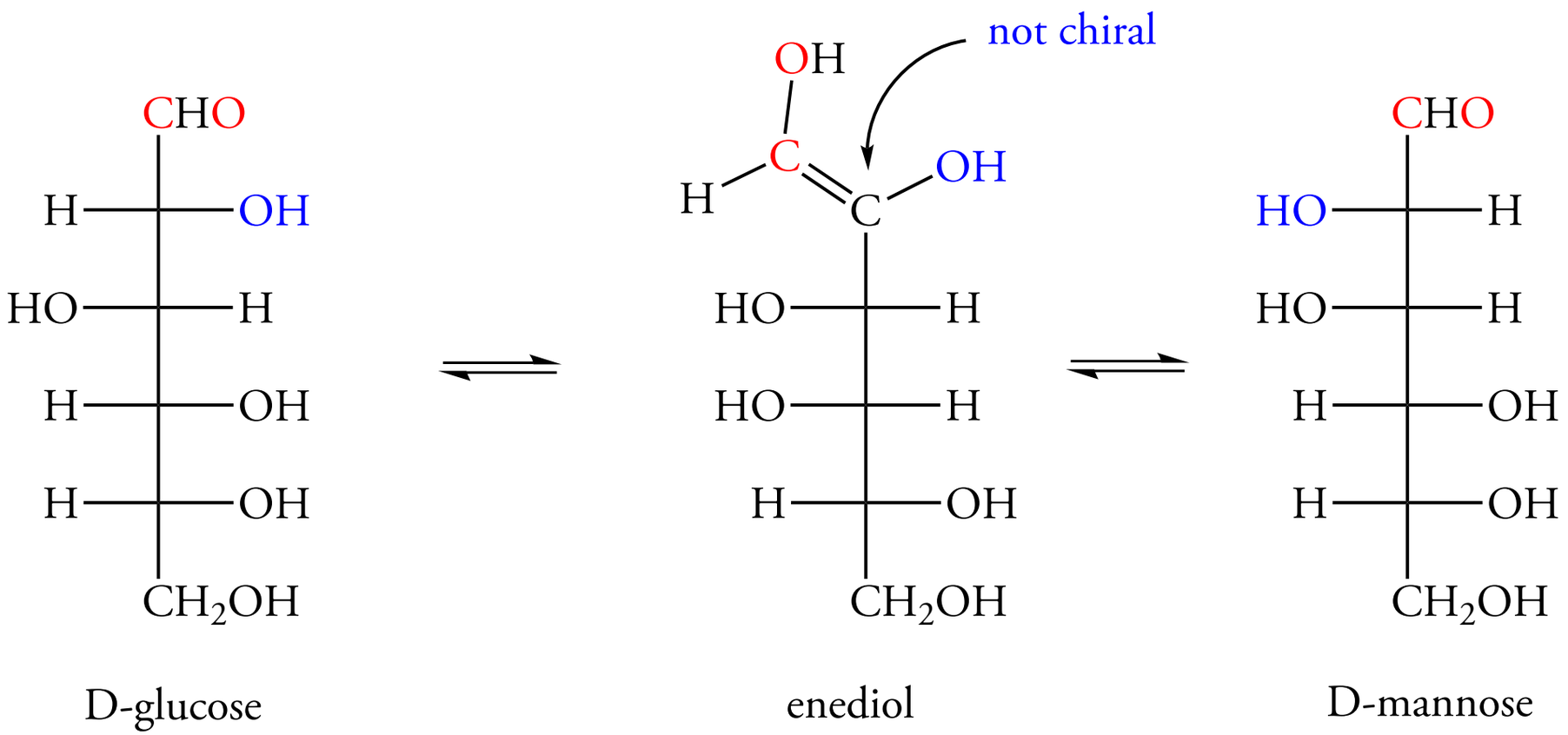


epimer 1 enediol (E and Z) epimer 2

26.4 ISOMERIZATIONS OF MONOSACCHARIDES

Epimers

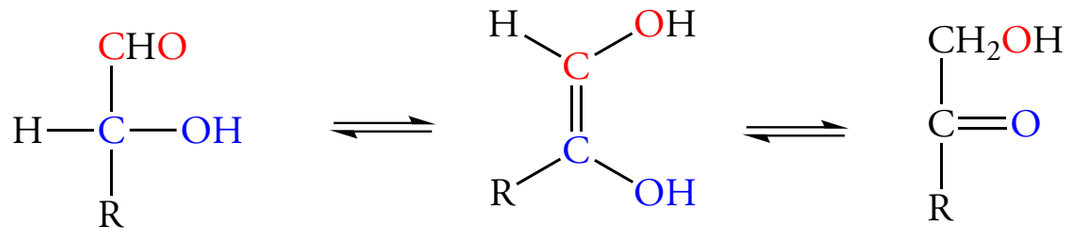
Figure 26.4 Isomerization of Aldoses via an Enediol Intermediate



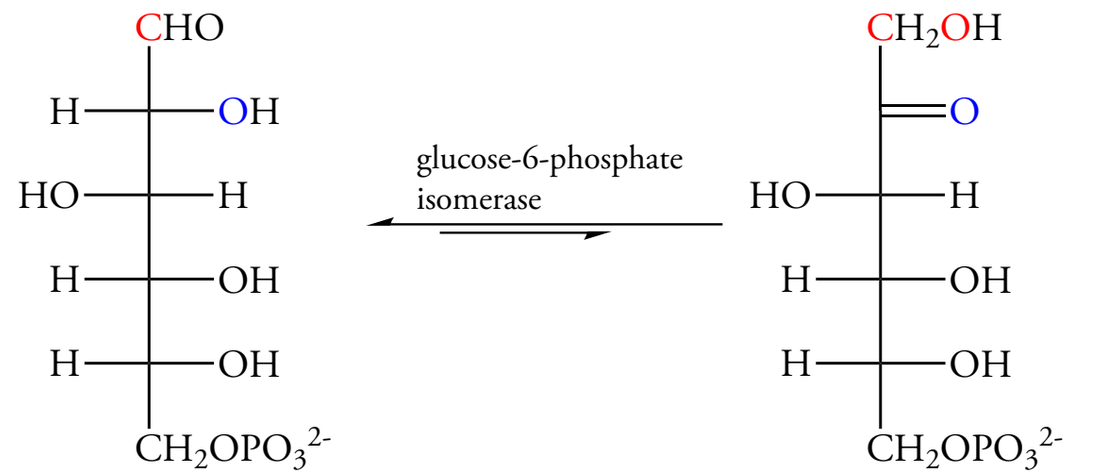
D-glucose enediol D-mannose

26.4 ISOMERIZATIONS OF MONOSACCHARIDES

Interconversion of Aldoses and Ketoses

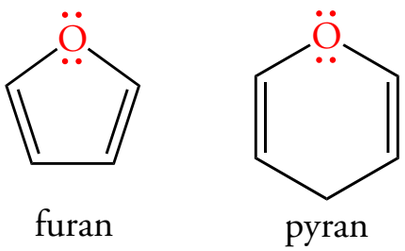


(an aldolse) (an enediol) (a ketose)



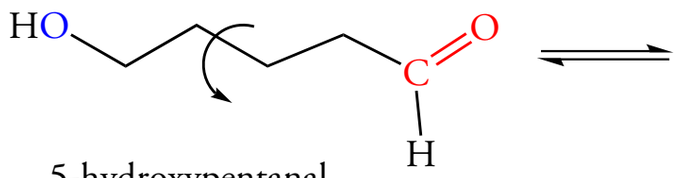
D-glucose-6-phosphate D-fructose-6-phosphate

26.5 CYCLIC MONOSACCHARIDES: HEMIACETALS AND HEMIKETALS

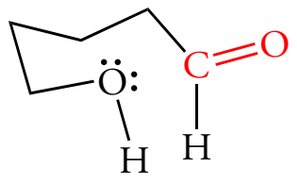


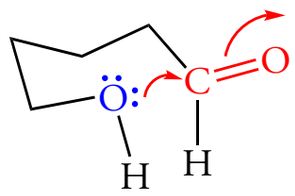
furan

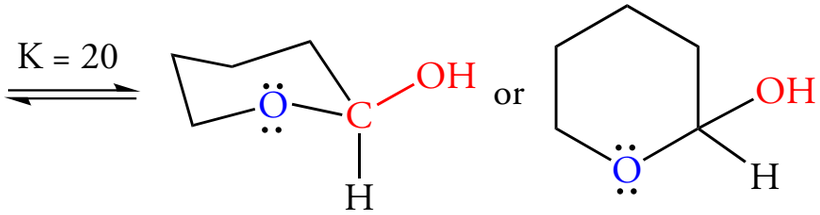
pyran

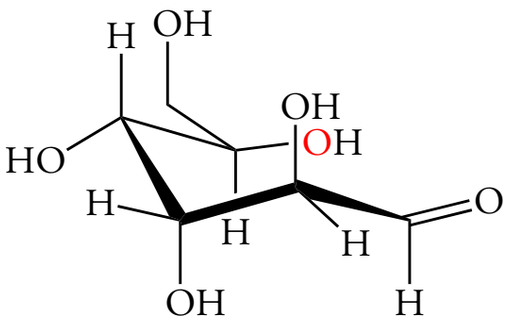


5-hydroxypentanal

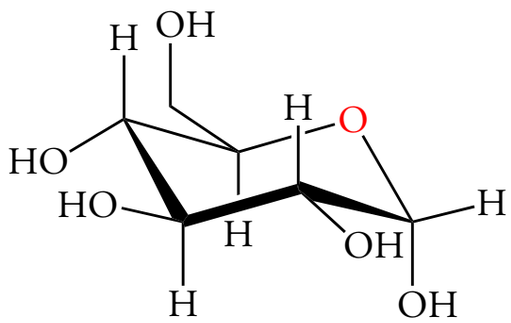






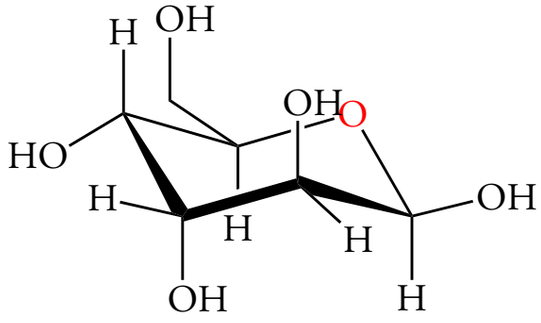


D-glucose



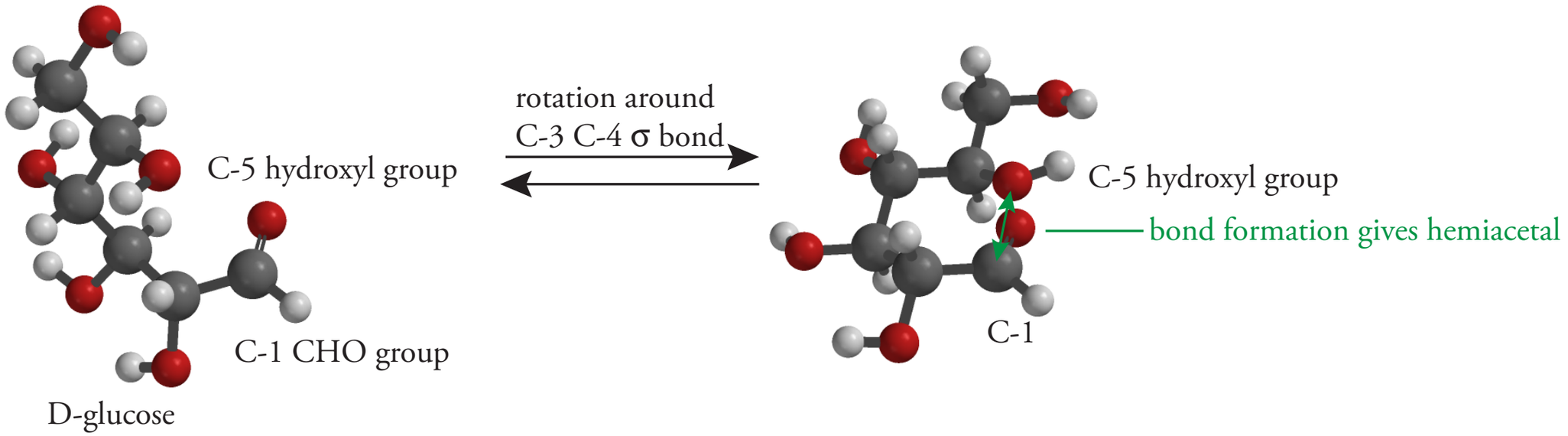
α-D-glucopyranose

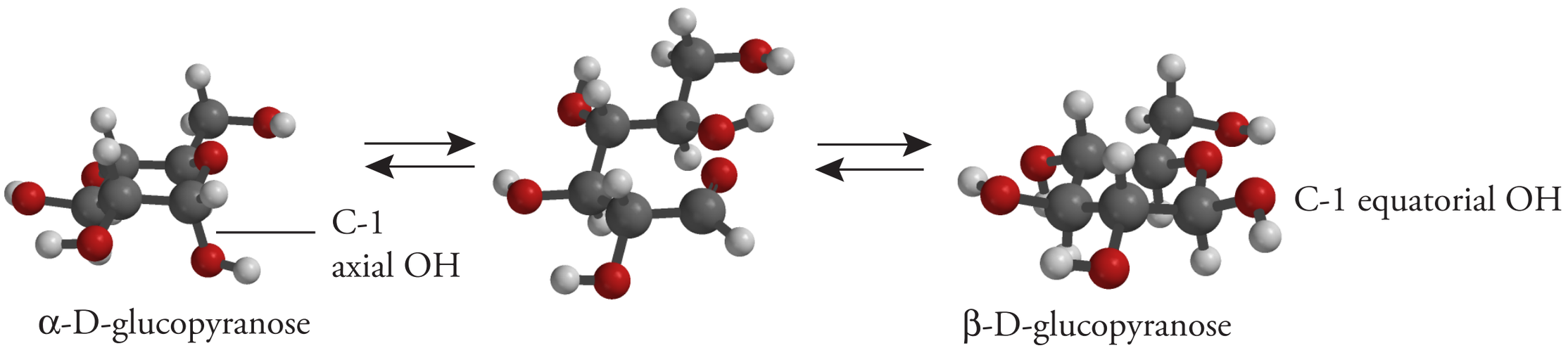
+



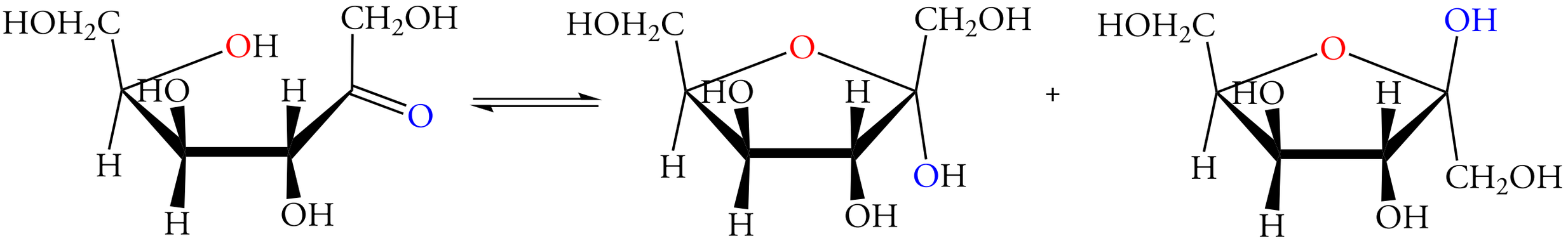
β-D-glucopyranose

26.5 CYCLIC MONOSACCHARIDES: HEMIACETALS AND HEMIKETALS





26.5 CYCLIC MONOSACCHARIDES: HEMIACETALS AND HEMIKETALS



D-fructose

α-D-fructofuranose

β-D-fructofuranose

26.5 CYCLIC MONOSACCHARIDES: HEMIACETALS AND HEMIKETALS

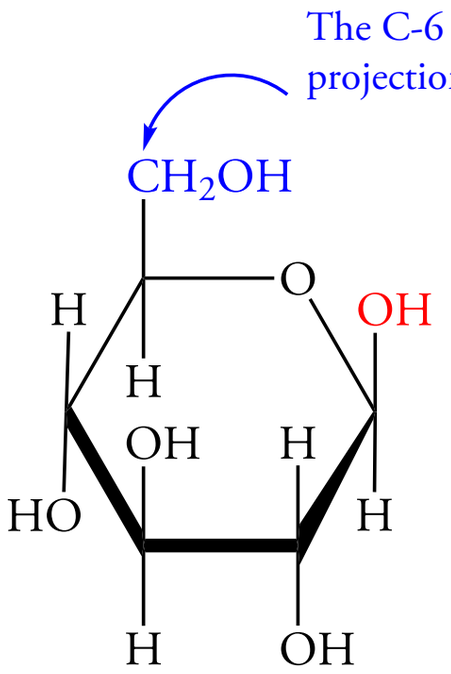
Table 26.1
Composition of Monosaccharides at Equilibrium in Solution (in percent)

Monosaccharide	Pyranose		Furanose	
	α	β	α	β
D-glucose	36	64		
D-mannose	67	32	0.8	0.2
D-galactose	31	69		
D-allose	18	70	5	7
D-altrose	27	40	20	13
D-idose	38	38	10	14
D-talose	40	29	20	11
D-arabinose	63	34	2	1
D-ribose	20	56	6	18
D-xylose	27	63		
D-fructose	2	66	7	25

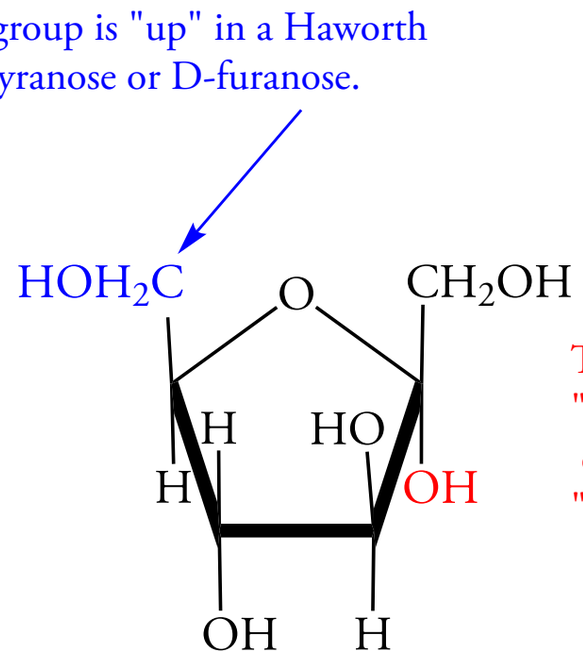
26.5 CYCLIC MONOSACCHARIDES: HEMIACETALS AND HEMIKETALS

Haworth Projection Formulas

Figure 26.5 Haworth Projections of a Pyranose and a Furanose



Haworth projection of
β-D-glucopyranose

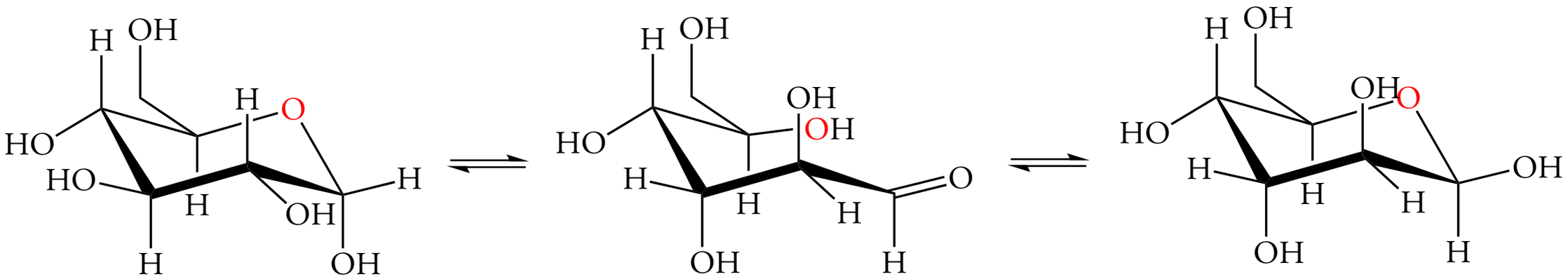


Haworth projection of
α-D-fructofuranose

The α-hydroxy group at C-1 is "down" in a Haworth projection of an α-D-pyranose or furanose. It is "up" in the β anomer.

26.5 CYCLIC MONOSACCHARIDES: HEMIACETALS AND HEMIKETALS

Mutarotation



α-D-glucopyranose ⇌ D-glucose ⇌ β-D-glucopyranose

crystalize from methanol

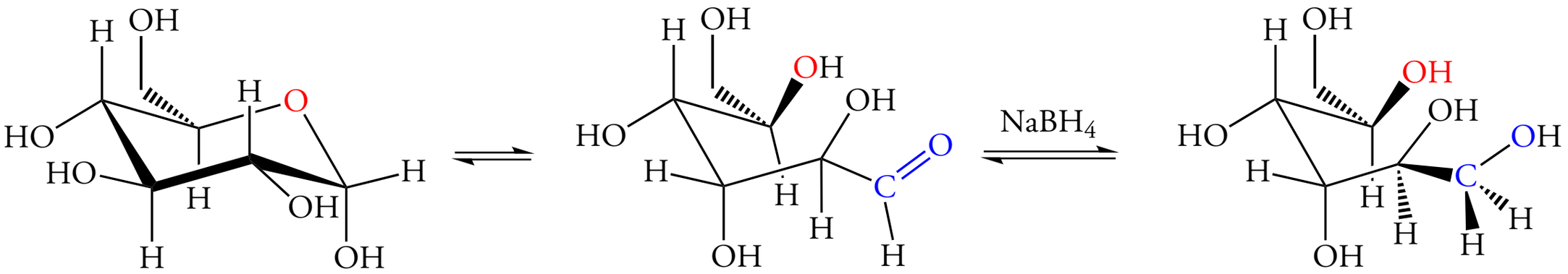
α-D-glucopyranose
mp 146°
$[\alpha]_D$ = + 112.2°

crystalize from acetic acid

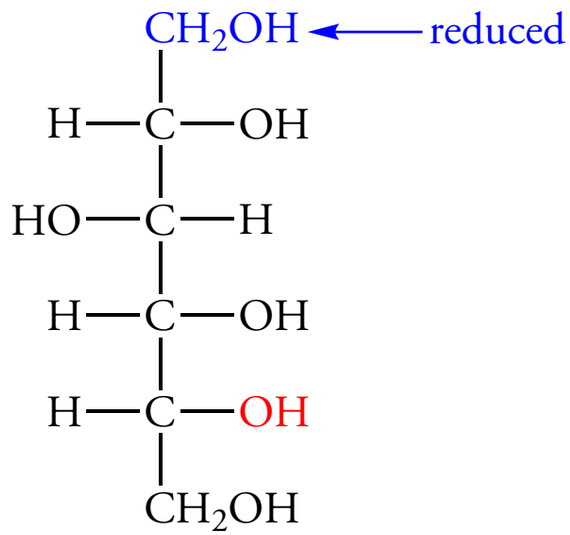
β-D-glucopyranose
mp 150°
$[\alpha]_D$ = + 18.7°

26.6 REDUCTION AND OXIDATION OF MONOSACCHARIDES

Reduction of Monosaccharides



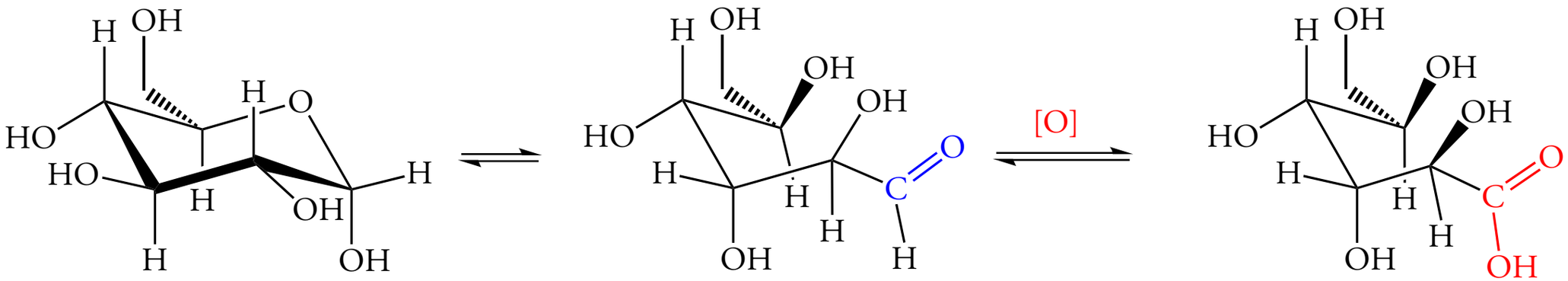
α-D-glucopyranose ⇌ D-glucose $\xrightarrow{NaBH_4}$ D-glucitol



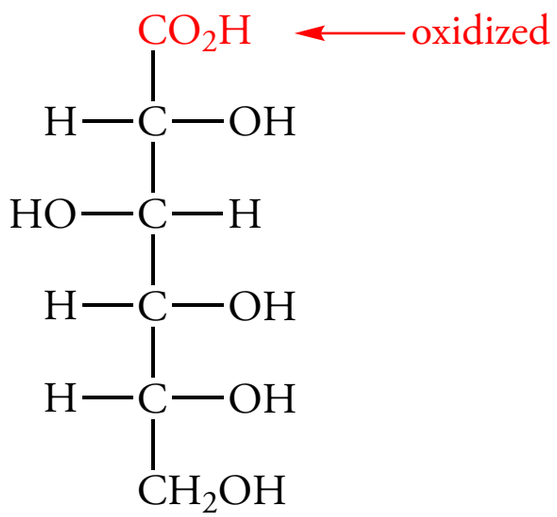
D-glucitol (D-sorbitol)
(an alditol)

26.6 REDUCTION AND OXIDATION OF MONOSACCHARIDES

Oxidation of Monosaccharides



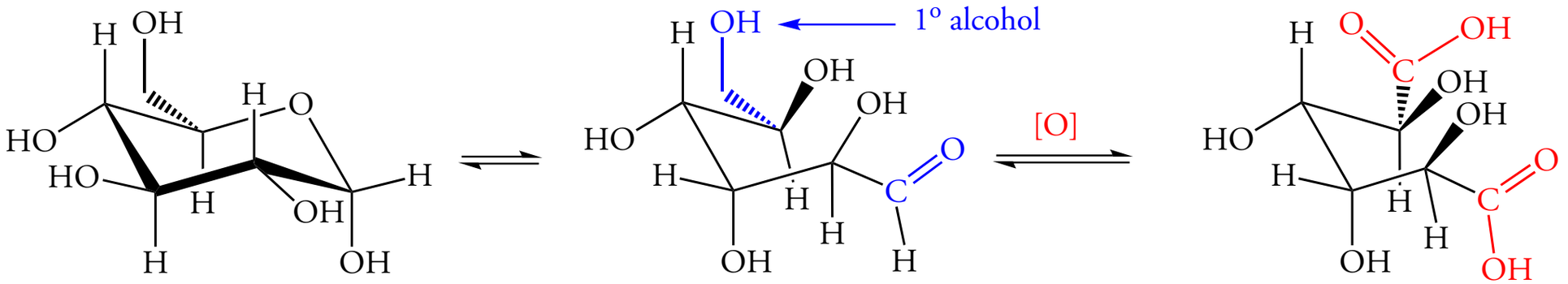
α-D-glucopyranose ⇌ D-glucose ⇌ D-gluconic acid



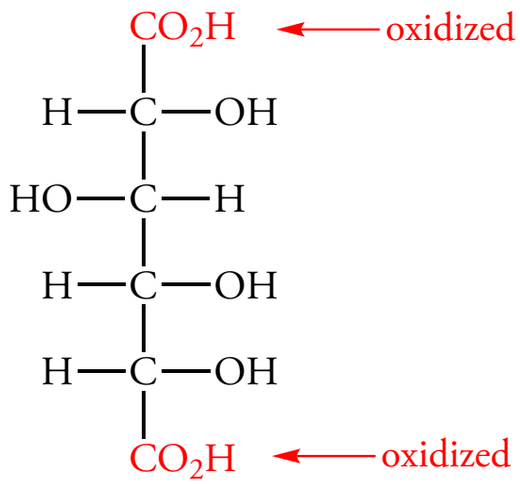
D-gluconic acid
(an aldonic acid)

26.6 REDUCTION AND OXIDATION OF MONOSACCHARIDES

Oxidation of Monosaccharides



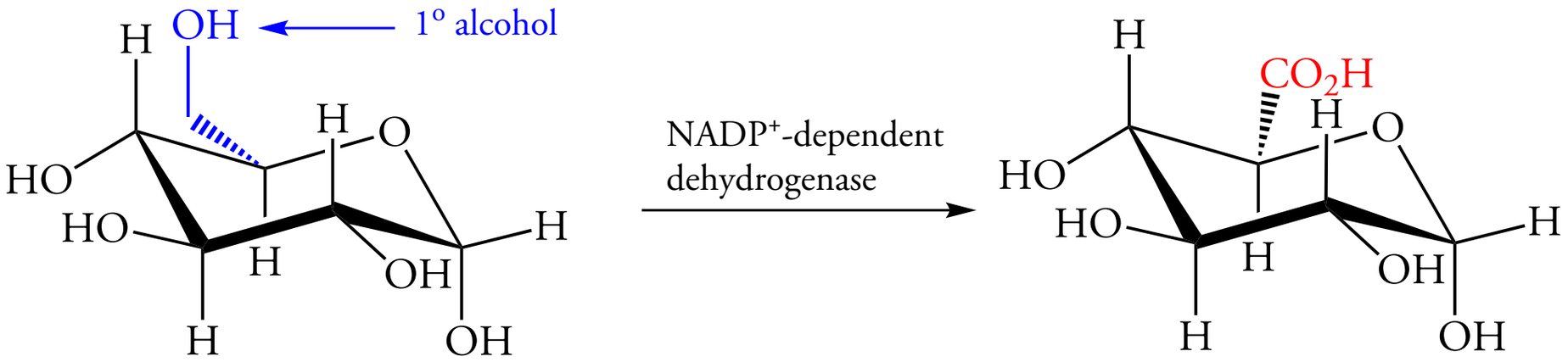
α-D-glucopyranose D-glucose D-glucaric acid



D-glucaric acid
(an aldaric acid)

26.6 REDUCTION AND OXIDATION OF MONOSACCHARIDES

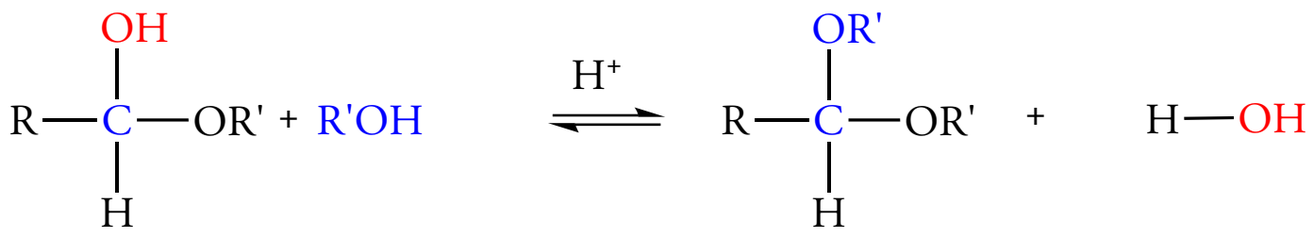
Oxidation of Monosaccharides



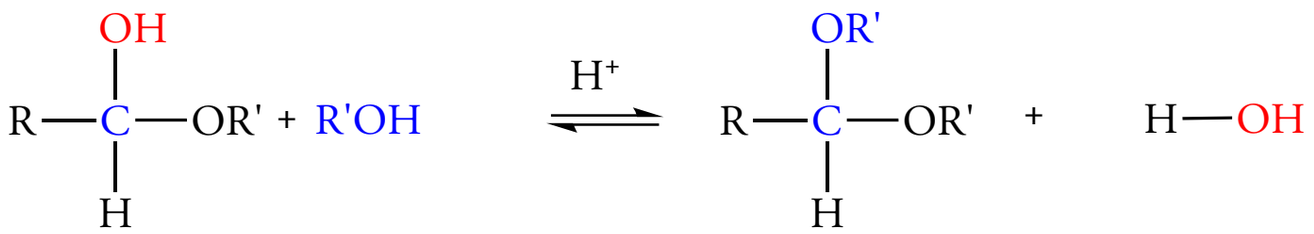
α-D-glucopyranose

D-glucuronic acid

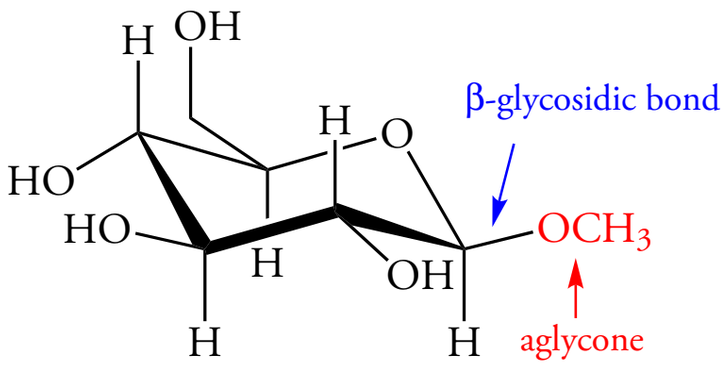
26.7 GLYCOSIDES



(a hemiacetal) (an acetal)

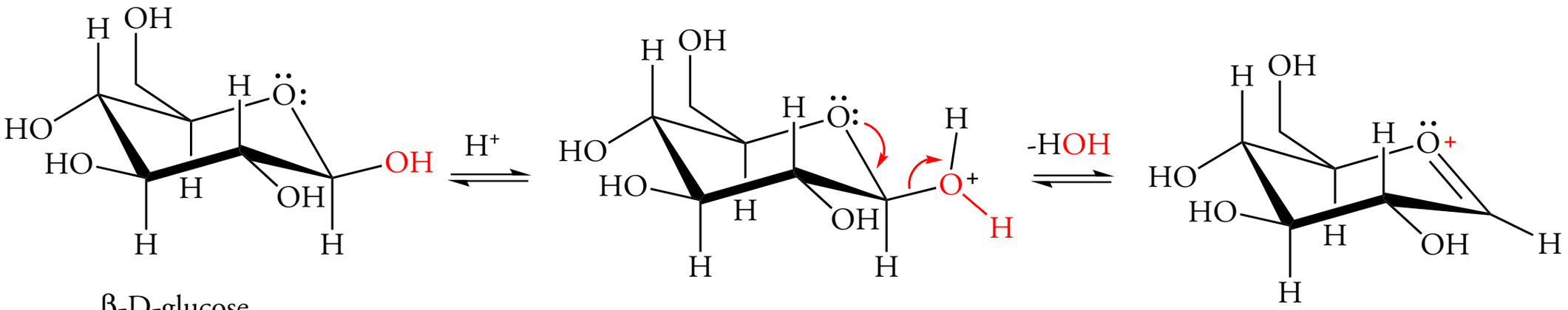


(a hemiketal) (a ketal)

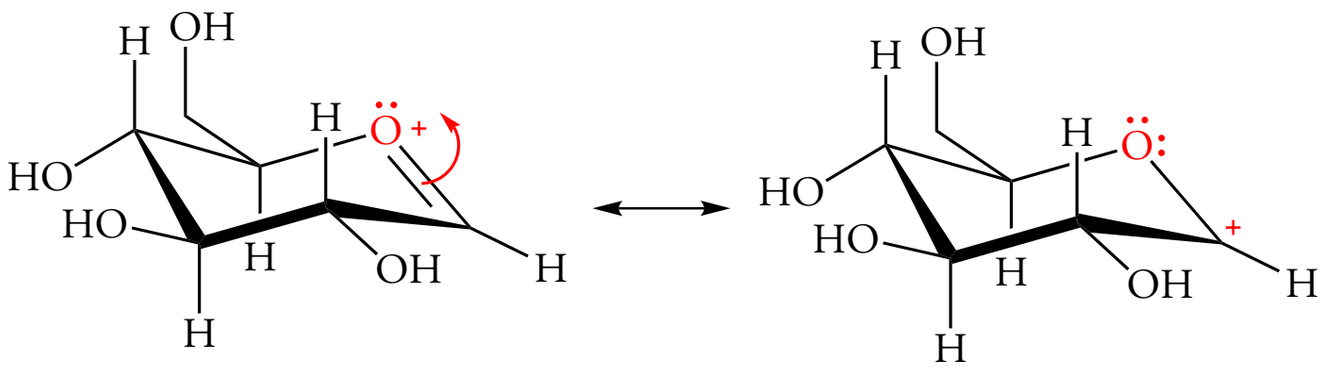


methyl β-D-glucopyranoside

26.7 GLYCOSIDES



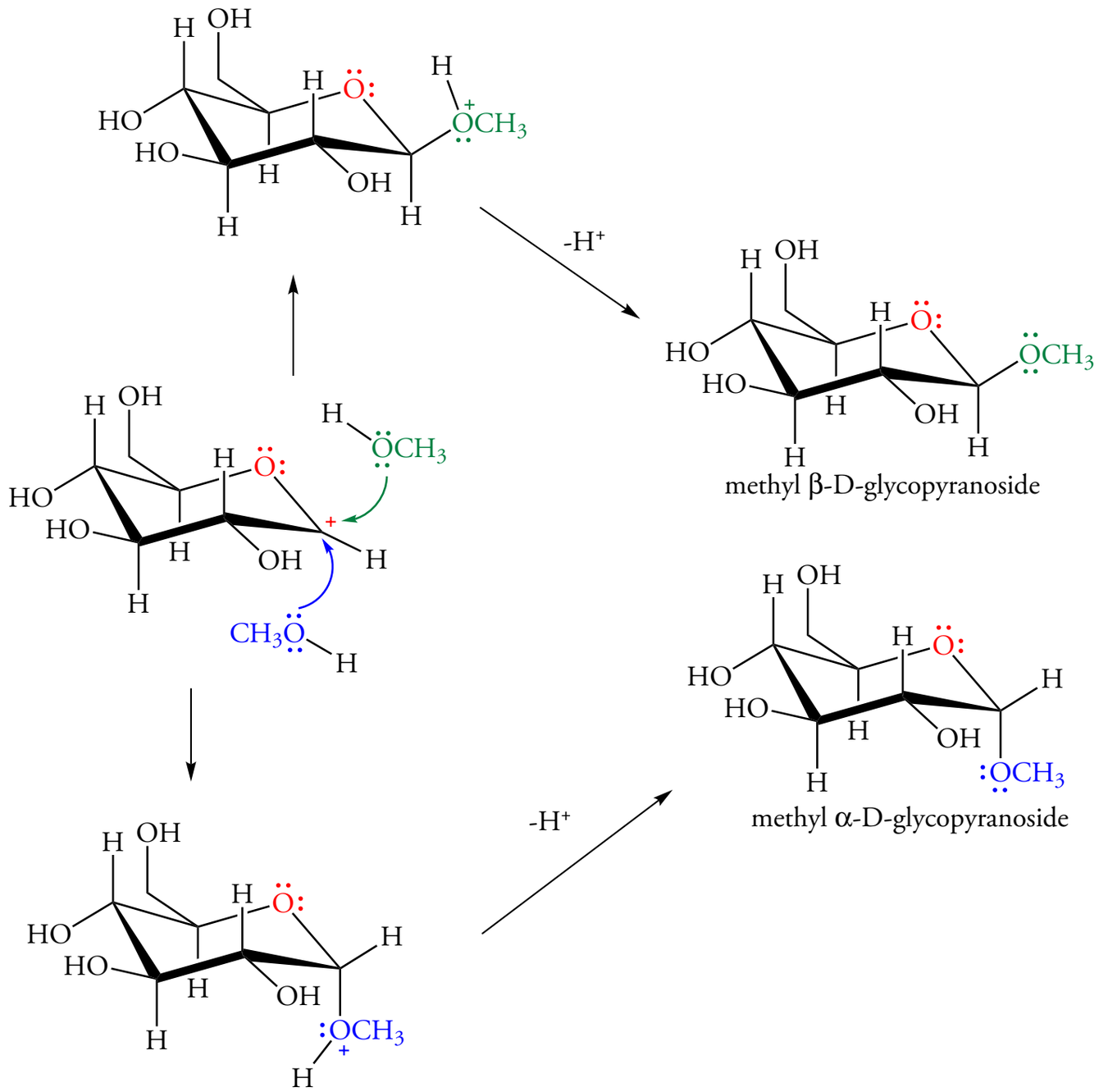
β-D-glucose



resonance-stabilized oxocarbocation intermediate

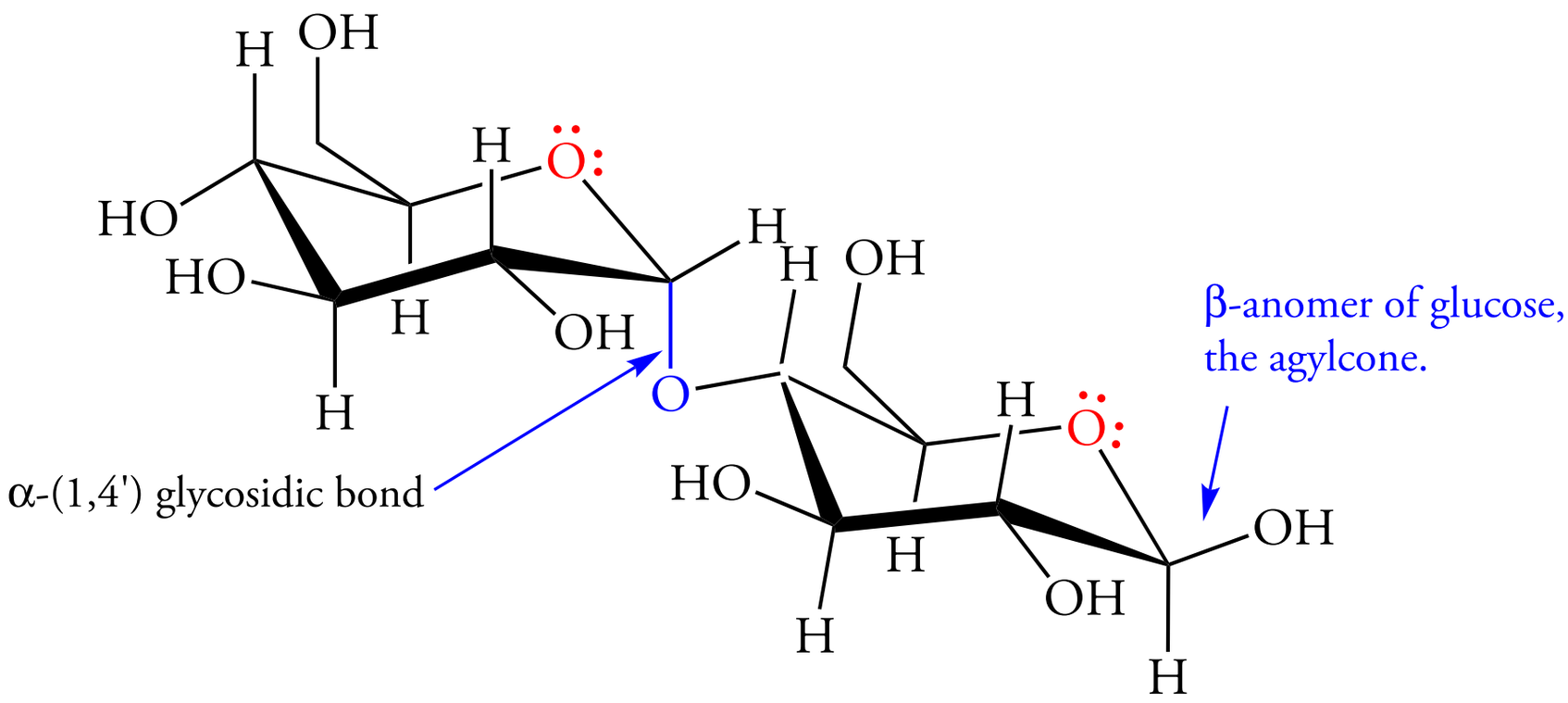
26.7 GLYCOSIDES

Figure 26.7 Formation of α and β Glysosides



26.8 DISACCHARIDES

Maltose



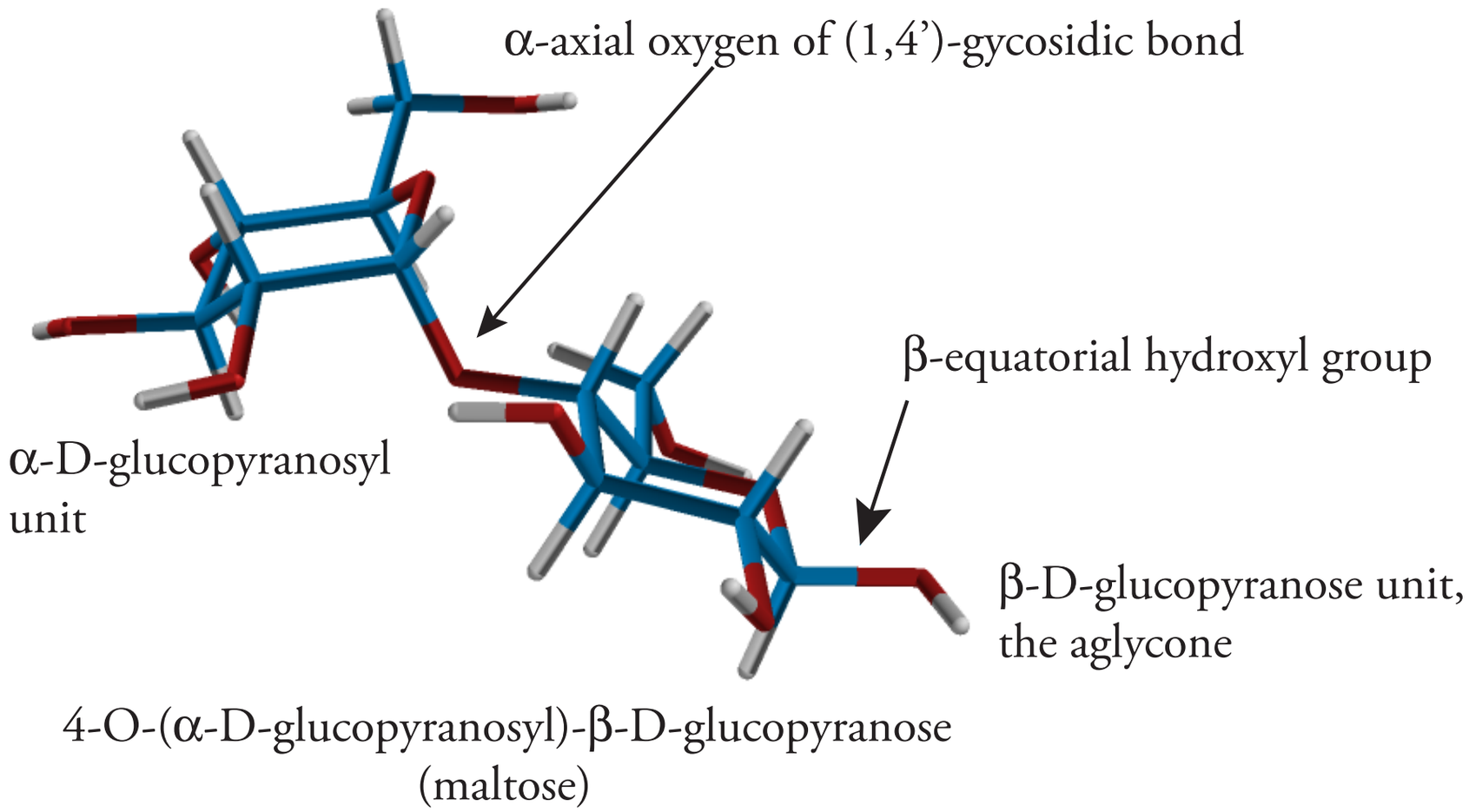
4-O-(α-D-glucopyranosyl)-β-D-glucopyranose
(maltose)

26.8 DISACCHARIDES

Maltose

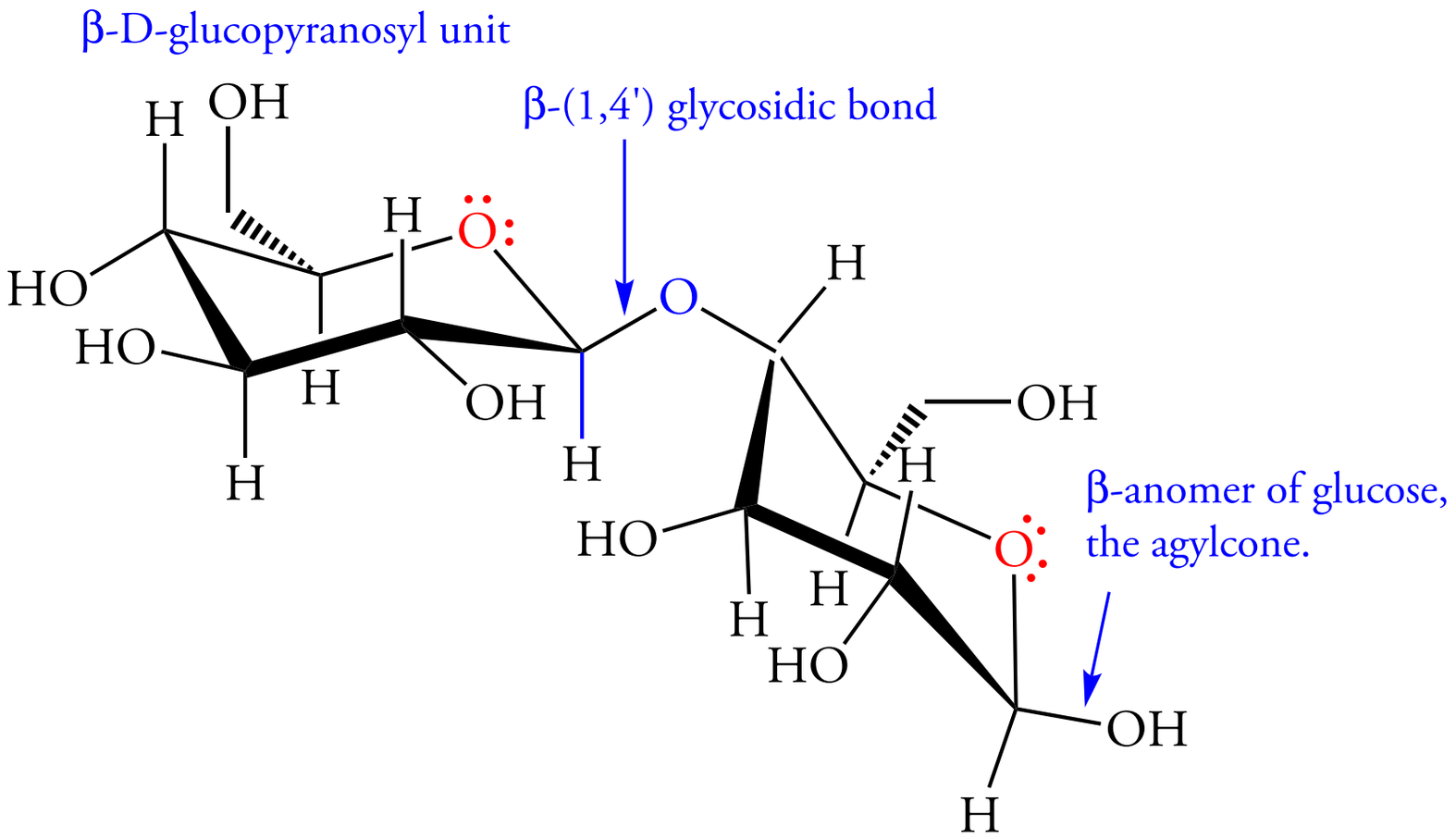
Figure 26.8 Molecular Model of Maltose.

The monosaccharide unit on the left is the hemiacetal of the α-D-glucopyranosyl unit. It is linked by an α-(1,4') glycosidic bond to β-D-glucopyranose, the aglycone. The oxygen atom of the glycosidic bond is approximately in the center of the structure, between the two rings. It is projected down, axial, and therefore α. It is linked to C-4 of the aglycone, and so the link is axial-equatorial.



26.8 DISACCHARIDES

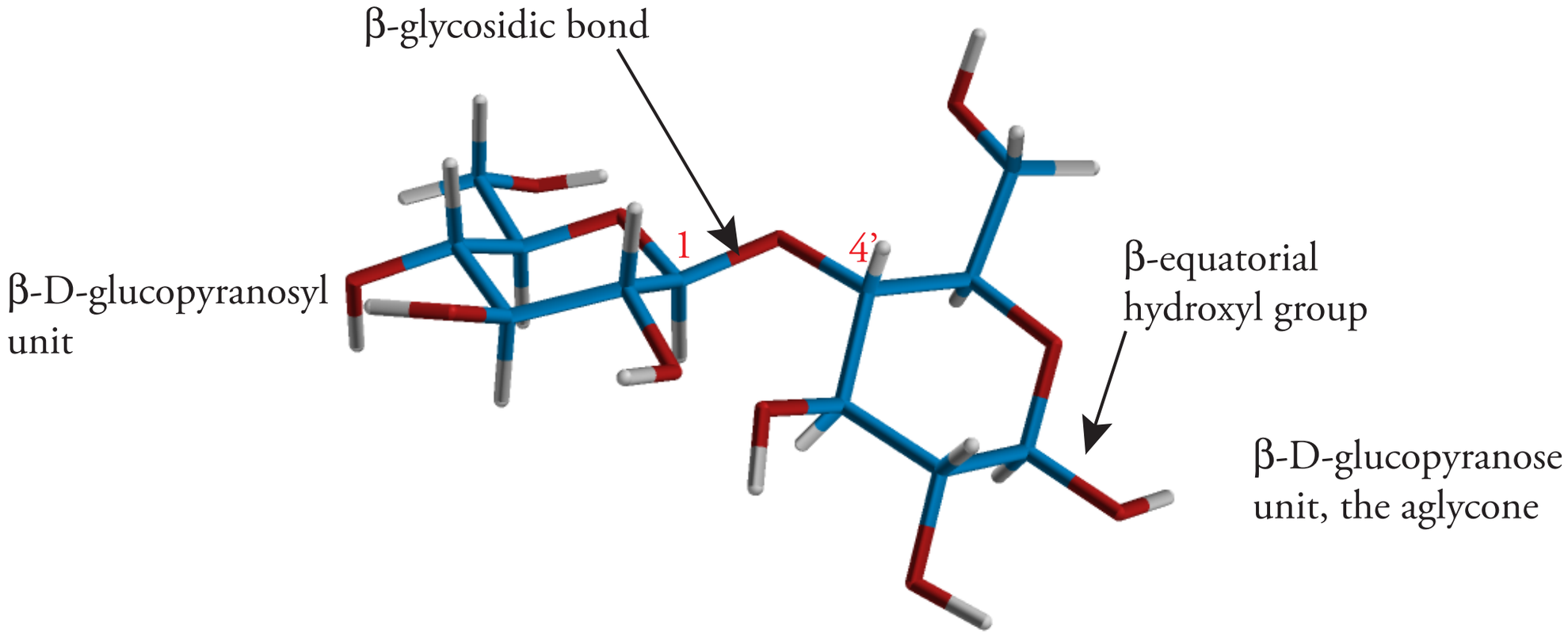
Cellobiose



4-O-(β-D-glucopyranosyl)-β-D-glucopyranose
(cellobiose)

Figure 26.9 Molecular Model of Cellobiose

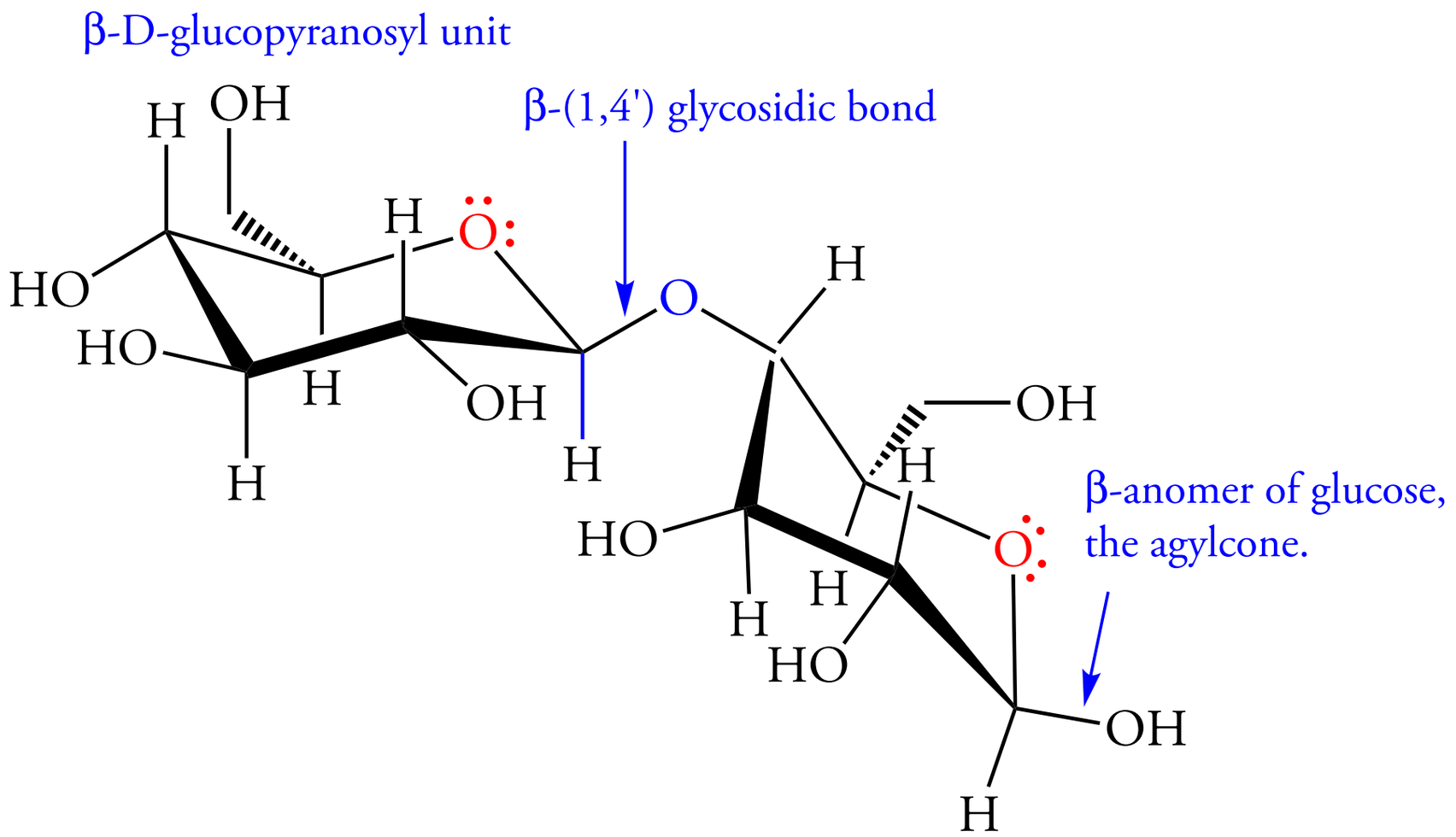
The monosaccharide unit on the left is the β-D-glucopyranosyl portion of cellobiose. It is linked by a β-(1,4') glycosidic bond to β-D-glucopyranose, the aglycone. The oxygen atom of the glycosidic bond is approximately in the center of the structure, between the two rings. It is projected up, equatorial, and therefore it is β. It is linked to C-4 of the aglycone, and so the link is equatorial-equatorial.



4-O-(β-D-glucopyranosyl)-β-D-glucopyranose
(cellobiose)

26.8 DISACCHARIDES

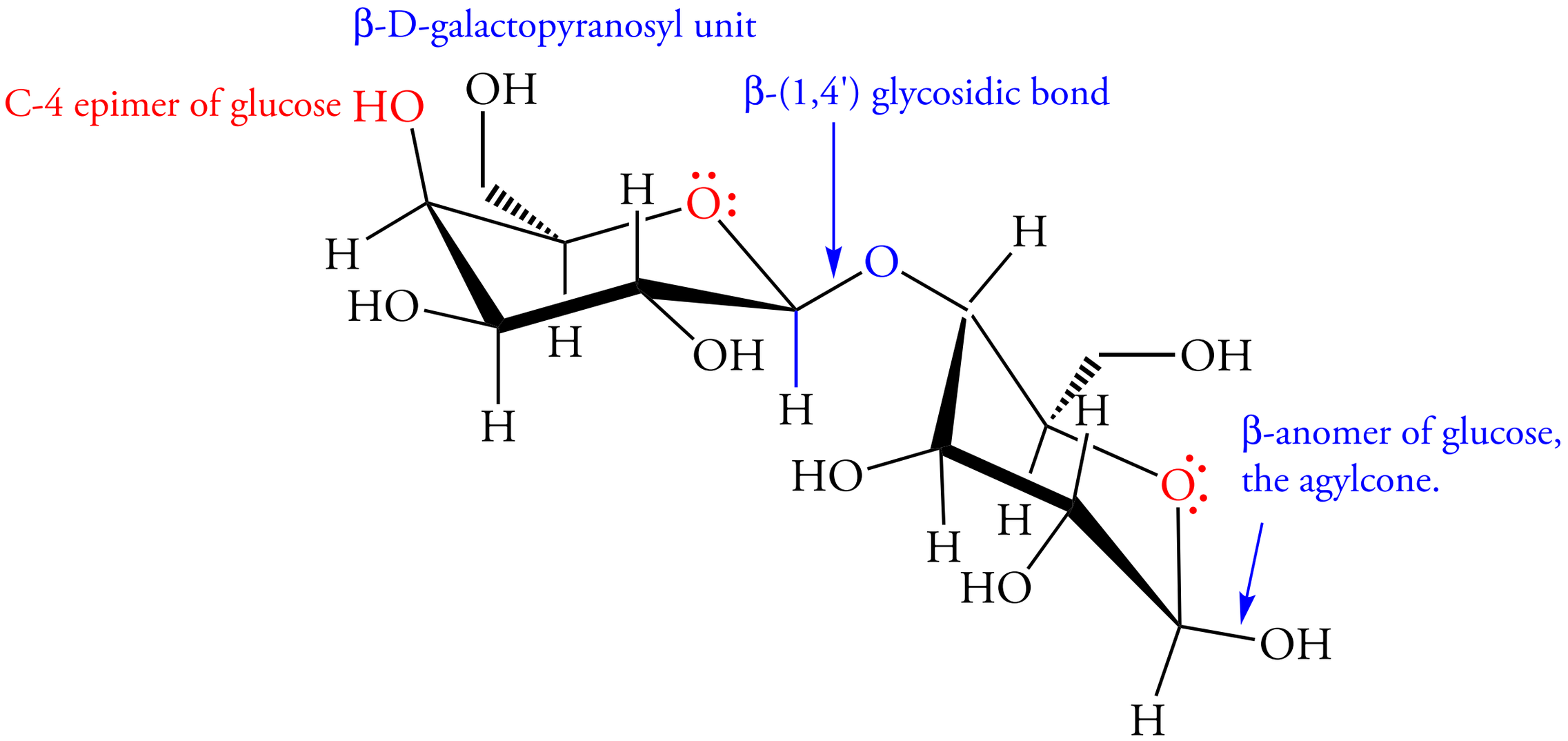
Lactose



4-O-(β-D-glucopyranosyl)-β-D-glucopyranose
(cellobiose)

26.8 DISACCHARIDES

Lactose



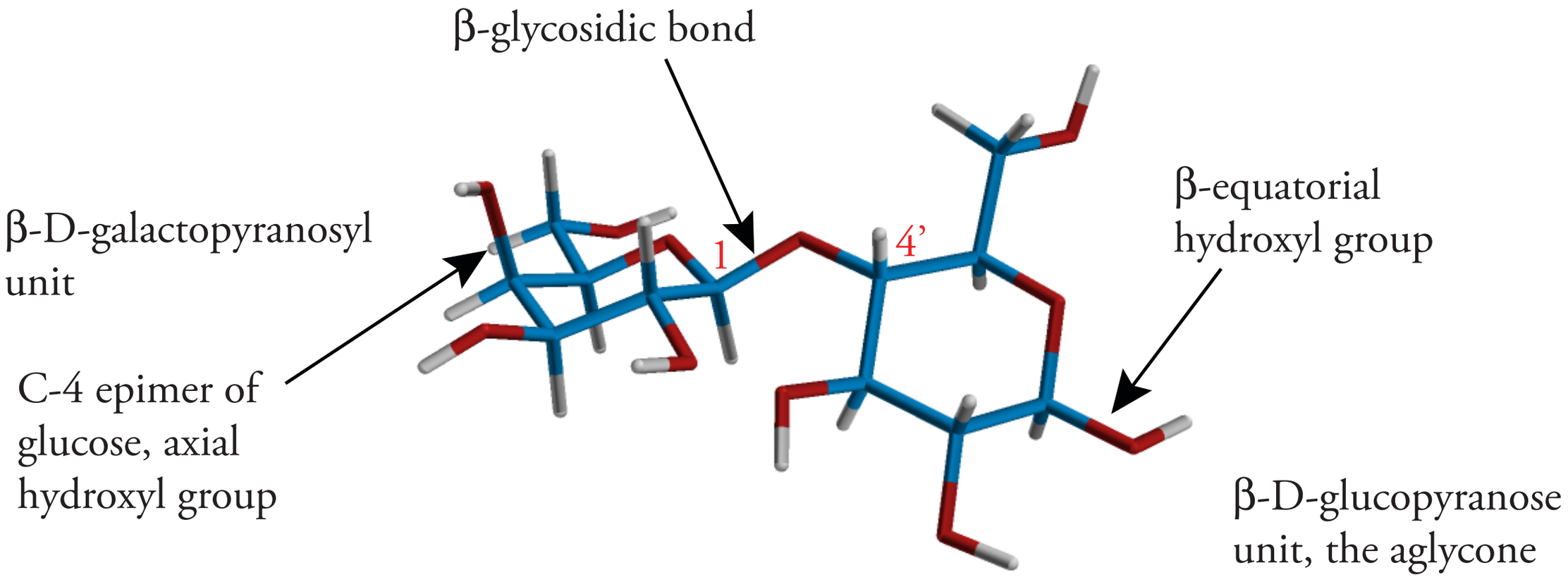
4-O-(β-D-galactopyranosyl)-β-D-glucopyranose
(lactose)

26.8 DISACCHARIDES

Lactose

Figure 26.10 Molecular Model of Lactose

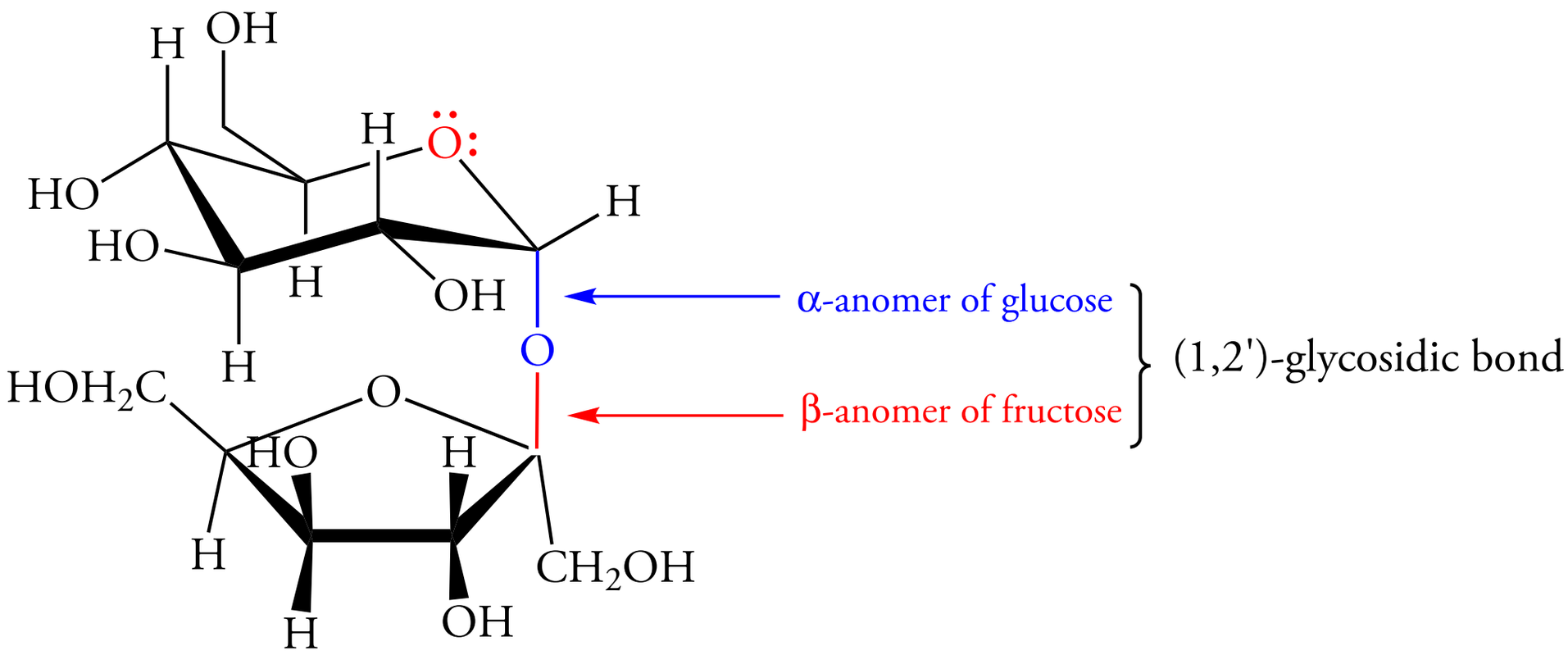
The monosaccharide unit on the left is the β-D-galactopyranosyl portion of cellobiose. It is linked by a β-(1,4') glycosidic bond to β-D-glucopyranose, the aglycone. Galactose is the C-4 epimer of glucose. Thus, the hydroxyl group at C-4, which is equatorial in glucose, is axial in galactose.



4-O-(β-D-galactopyranosyl)-β-D-glucopyranose
(lactose)

26.8 DISACCHARIDES

Sucrose



α-D-glucopyranosyl-β-D-fructofuranoside
(sucrose)

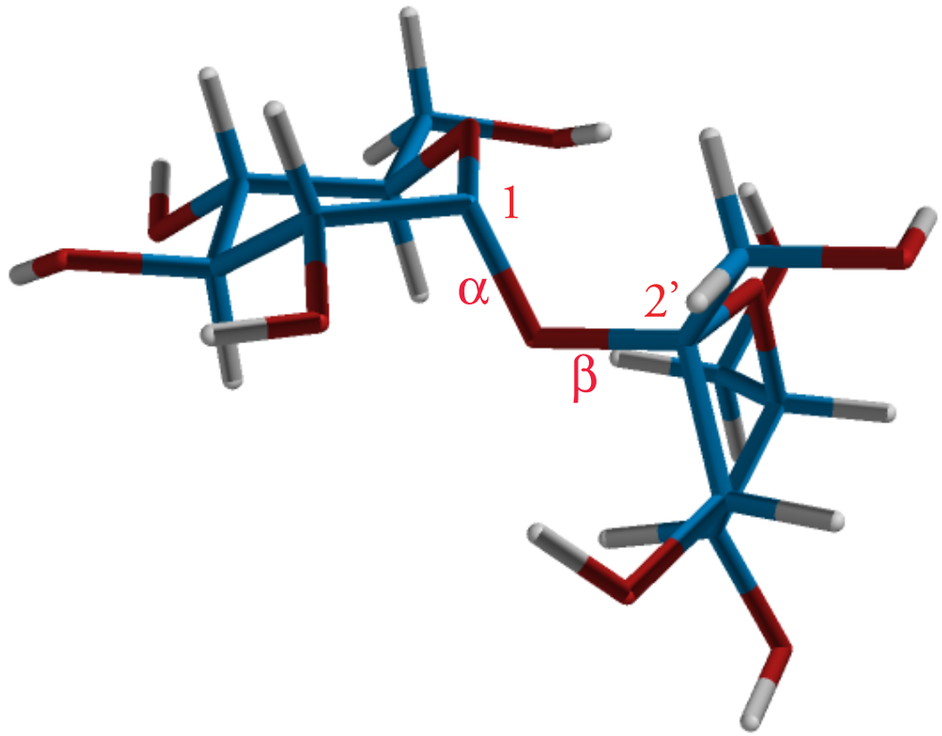
26.8 DISACCHARIDES

Sucrose

Figure 26.11 Molecular Model of Sucrose

The monosaccharide unit on the left is the α-D-galactopyranosyl portion of sucrose. It is linked by a (1,2') glycosidic bond to β-D-fructofuranose. Thus, the anomeric carbons of the monomers are linked by a glycosidic bond. Sucrose is an acetal. Therefore, it is a nonreducing sugar.

α-D-glucopyranosyl unit



β-D-fructofuranose unit

α-D-glucopyranosyl-β-D-fructofuranoside
(sucrose)

26.9 POLYSACCHARIDES

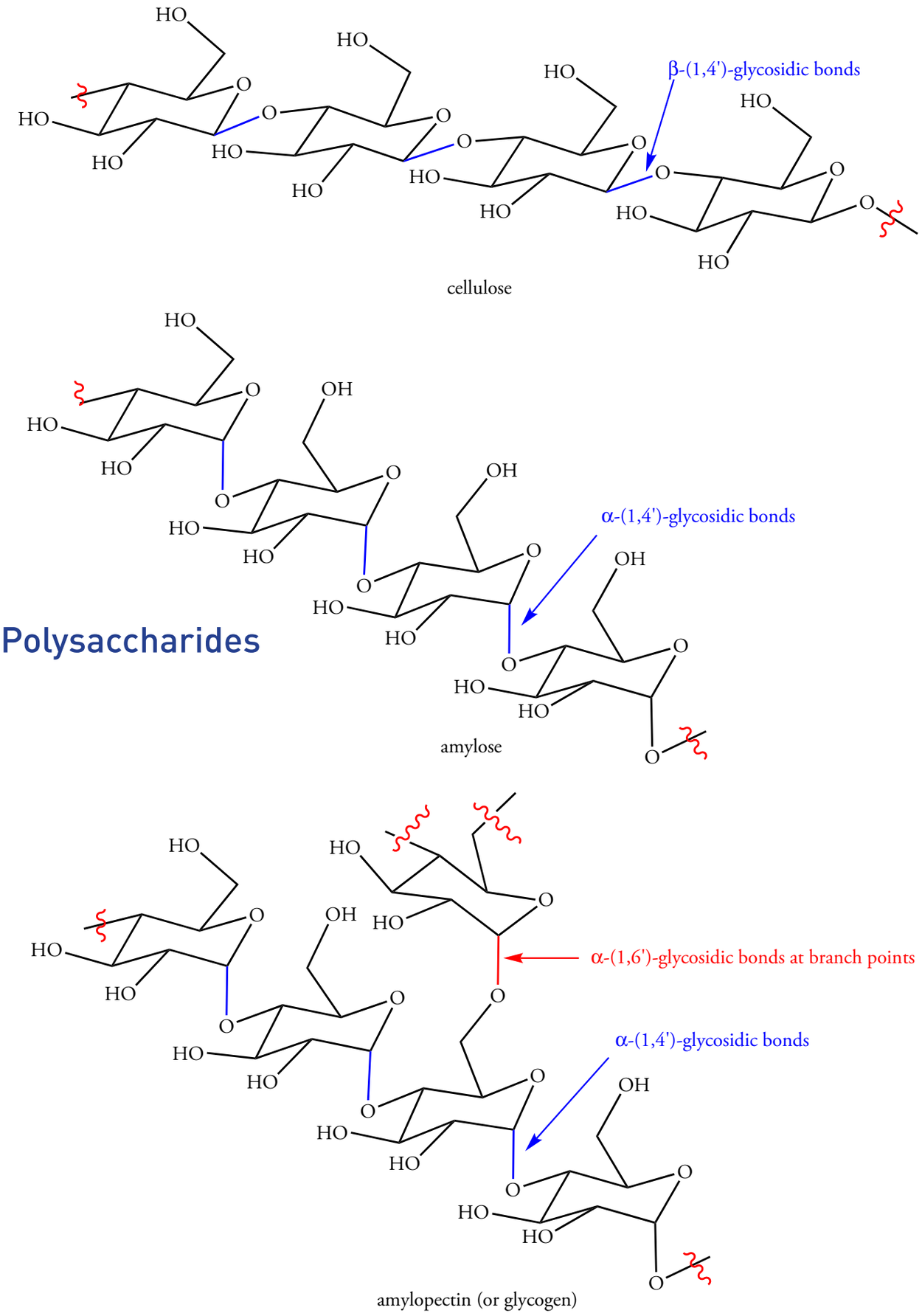
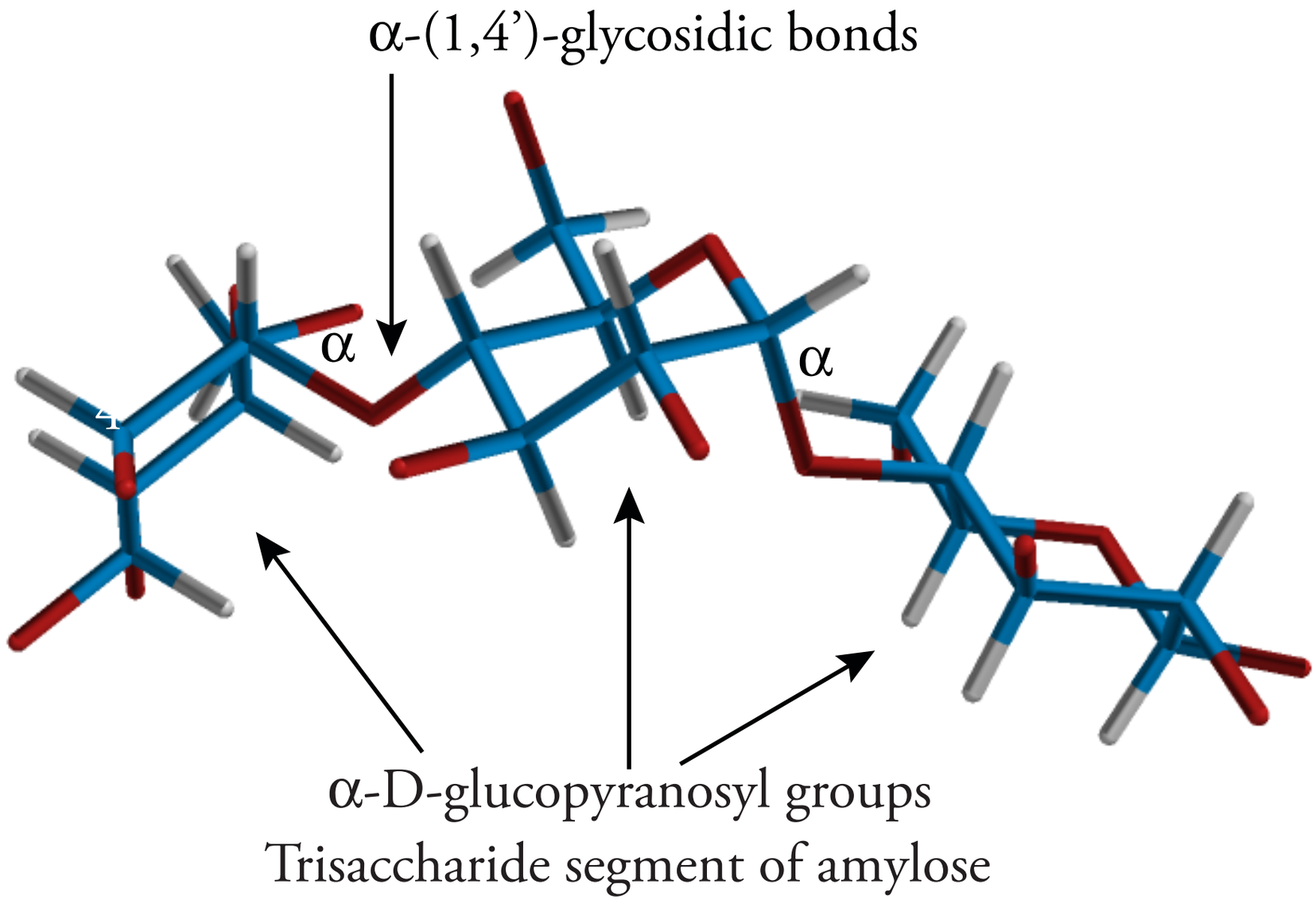


Figure 26.12 Structures of Polysaccharides

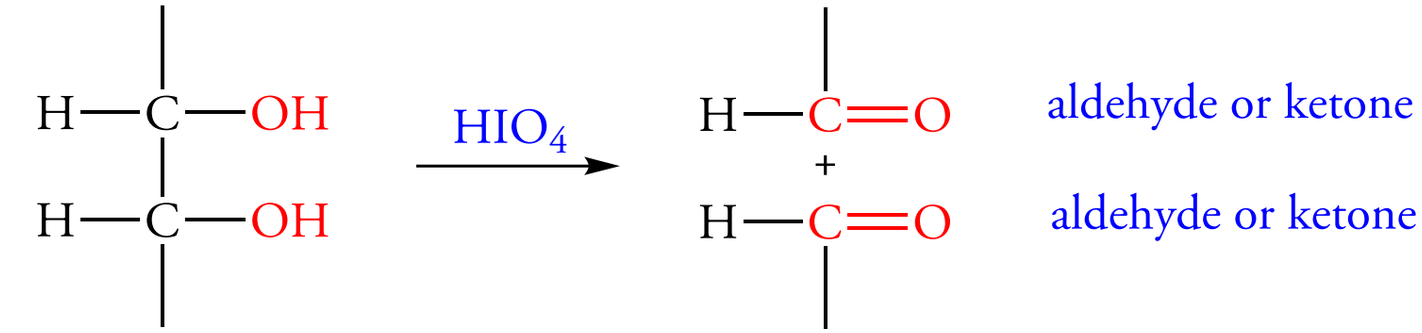
Figure 26.13 Three α-D-Glucopyranosyl Groups in Amylose

When we say that a polymer is "linear" we mean that the polymer contains no branches. Amylose coils into a helix.

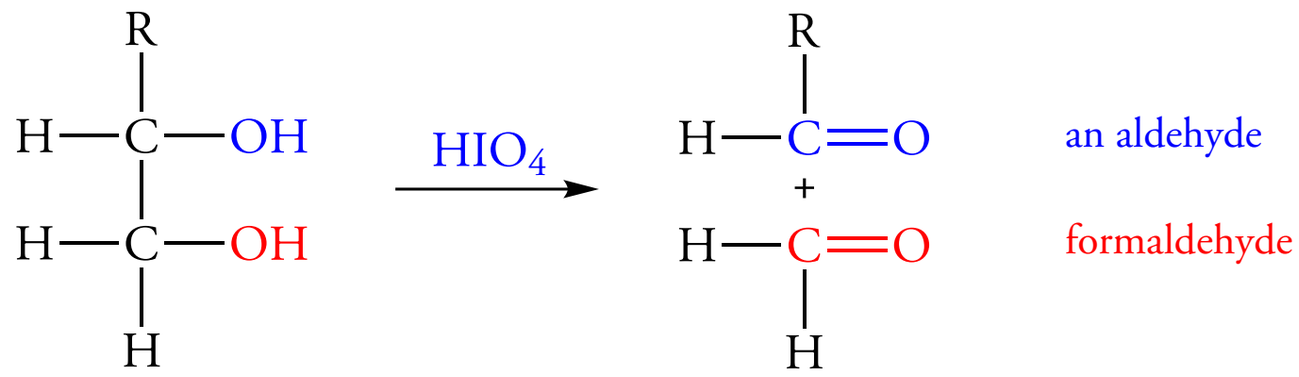


26.10 CHEMICAL DETERMINATION OF MONOSACCHARIDE STRUCTURES

Periodate Oxidation



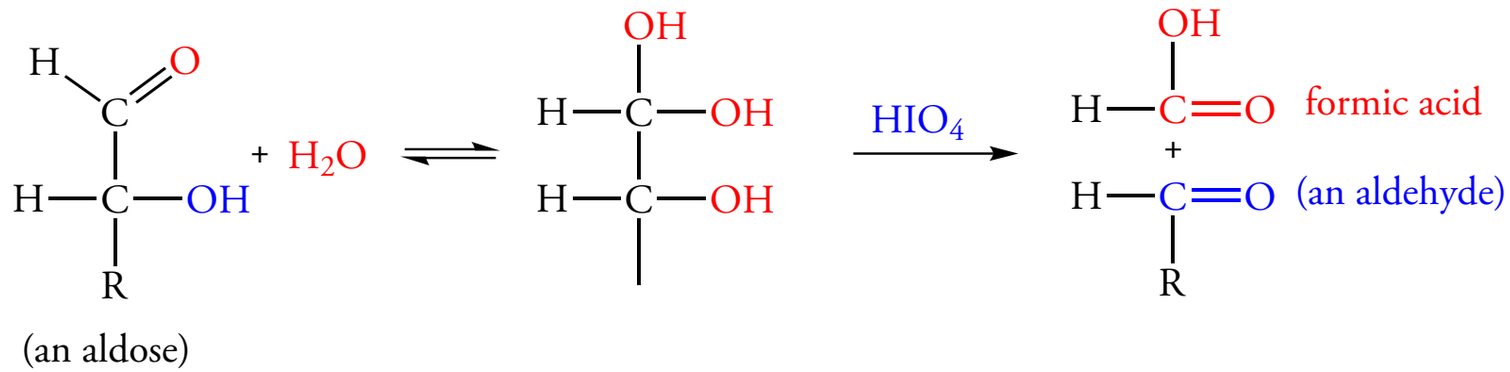
vicinal diol in
monosaccharide

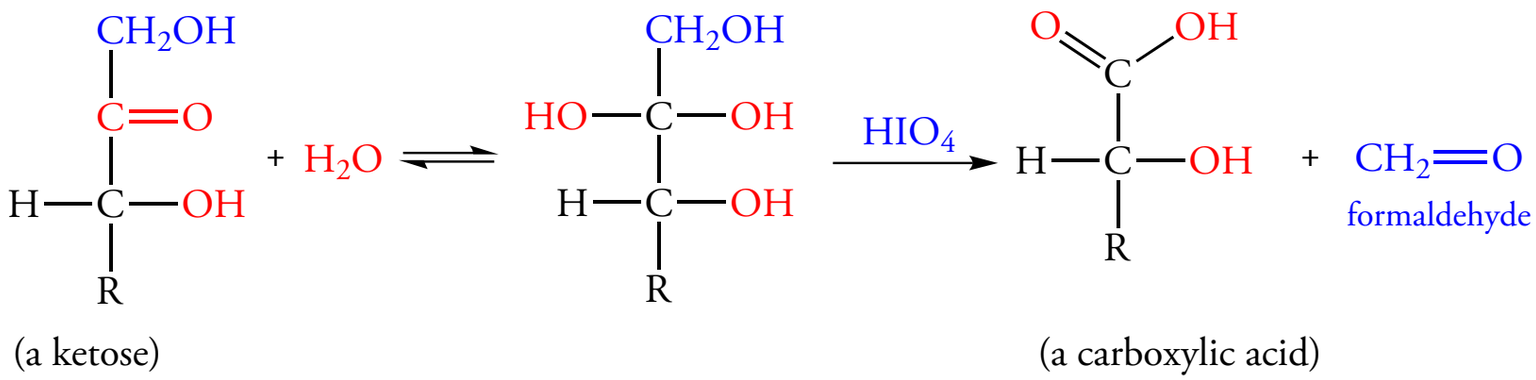


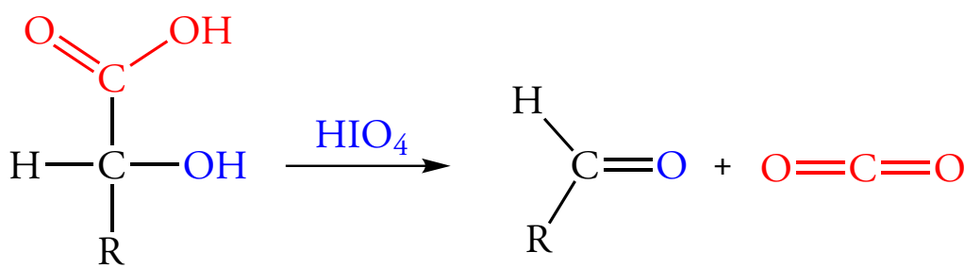
vicinal diol at
1° alcohol

26.10 CHEMICAL DETERMINATION OF MONOSACCHARIDE STRUCTURES

Periodate Oxidation

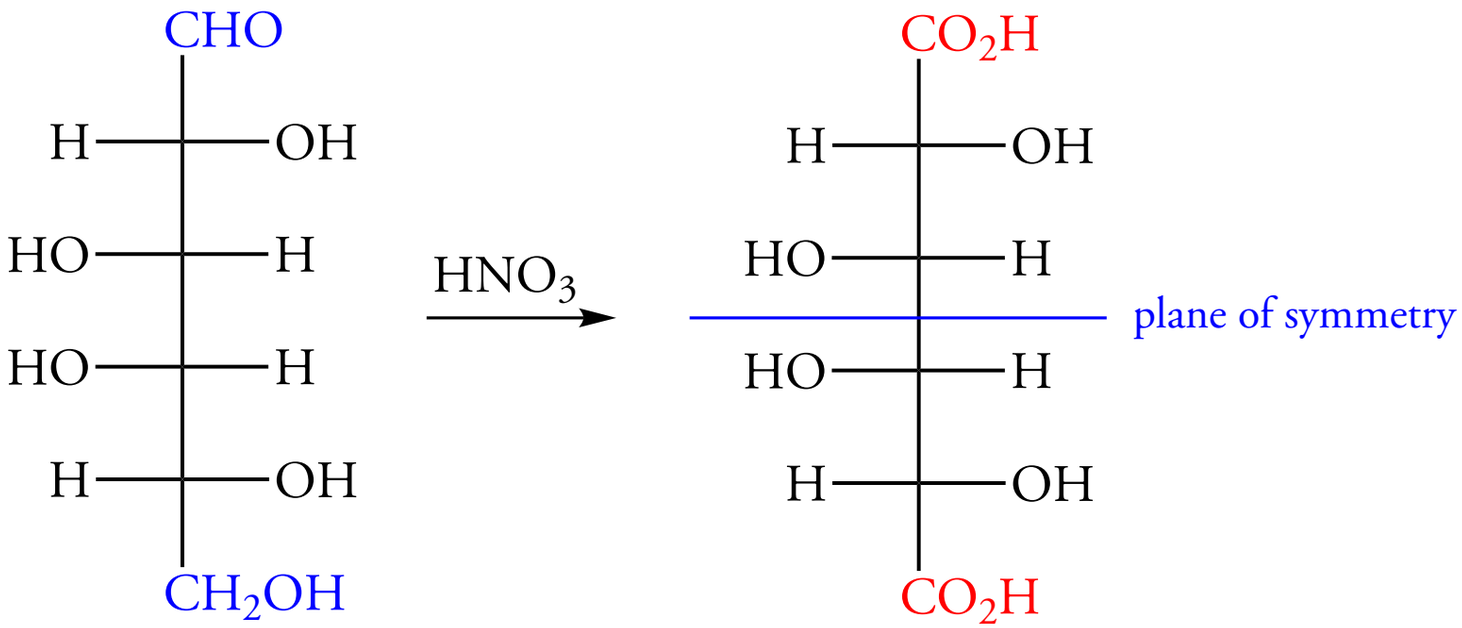






26.10 CHEMICAL DETERMINATION OF MONOSACCHARIDE STRUCTURES

Oxidation and Optical Activity

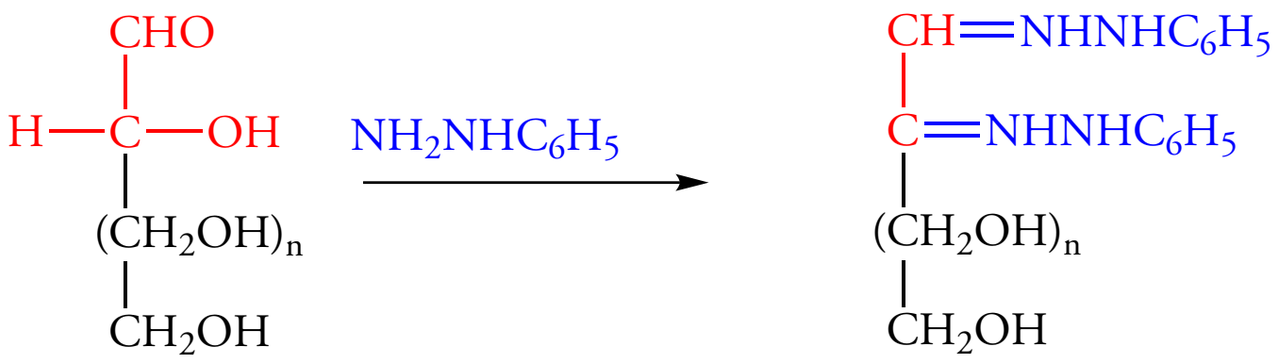


D-galactose

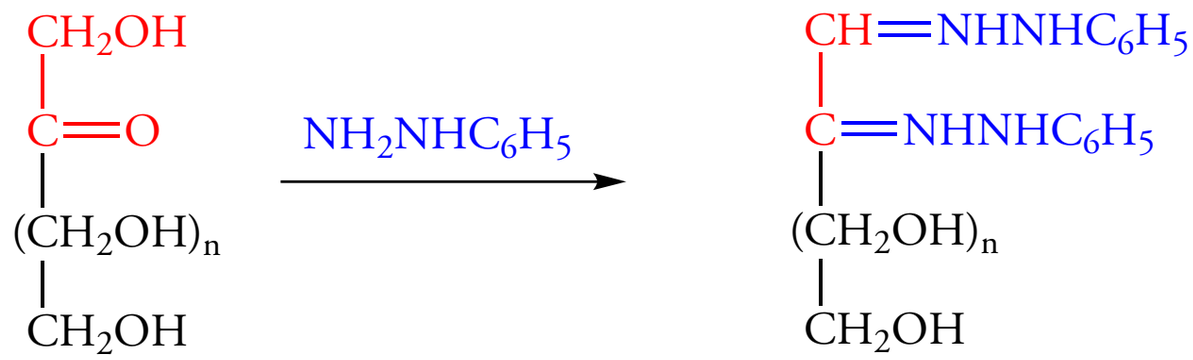
optically inactive aldaric acid

26.10 CHEMICAL DETERMINATION OF MONOSACCHARIDE STRUCTURES

Formation of Osazones



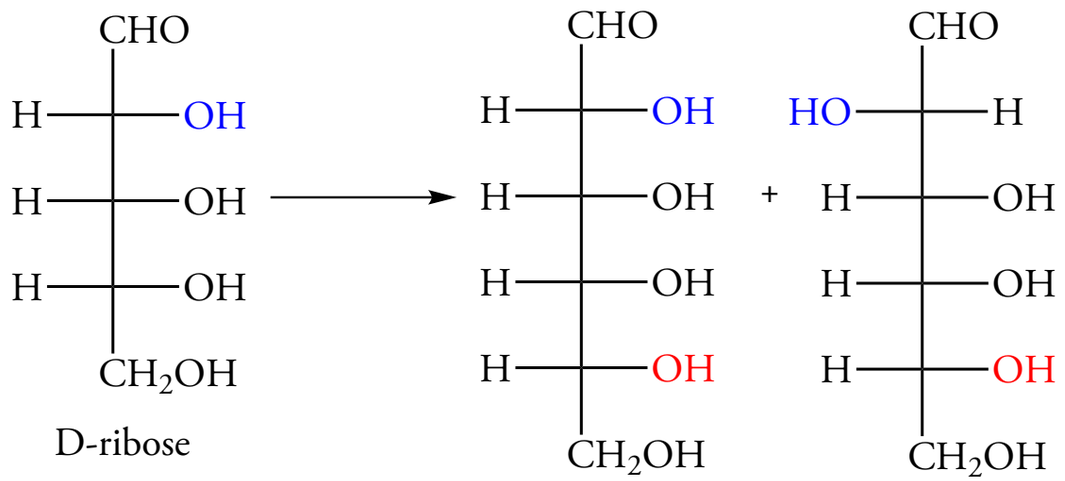
(an aldose) (an osazone)

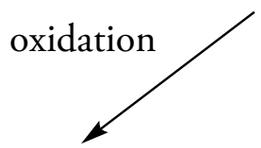


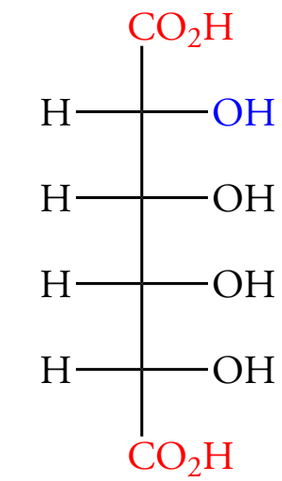
(a ketose) (an osazone)

26.10 CHEMICAL DETERMINATION OF MONOSACCHARIDE STRUCTURES

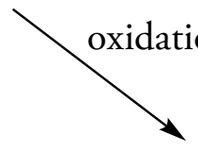
Chain Extension of Aldoses

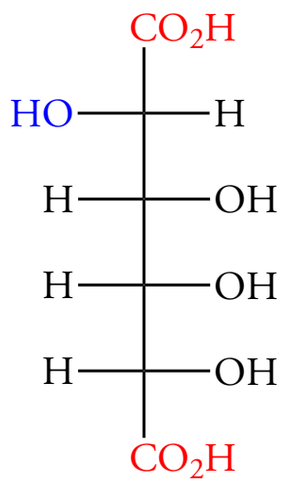






D-aldaric acid
(optically inactive)

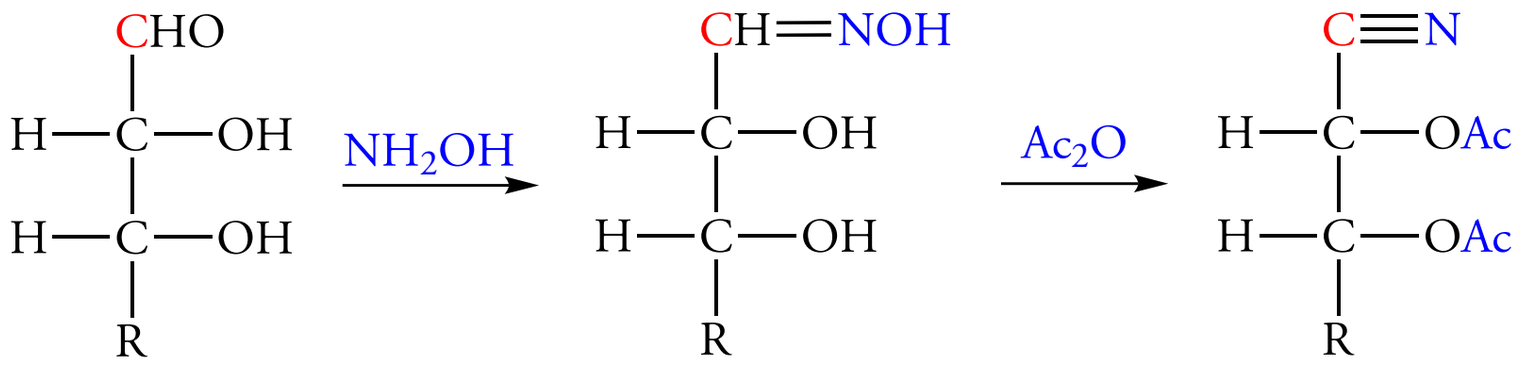




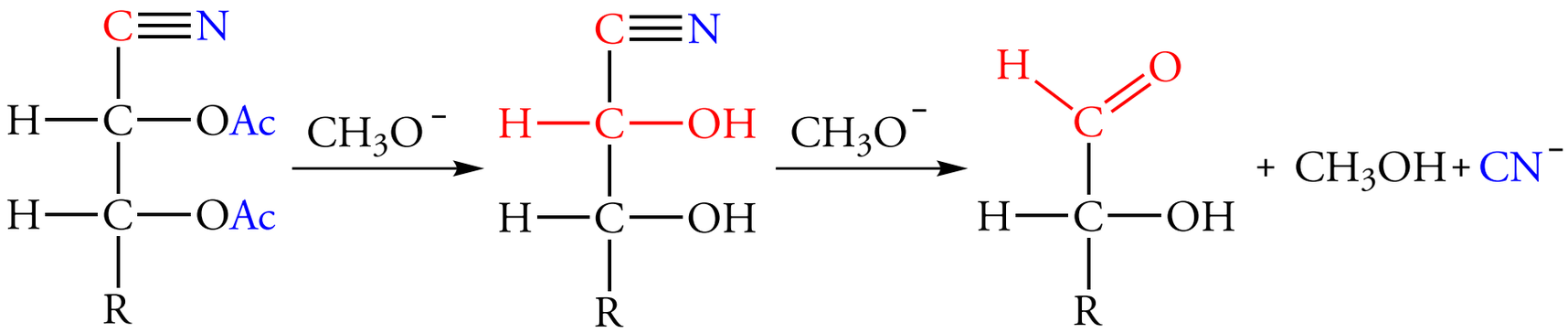
(+)-D-altraric acid

26.10 CHEMICAL DETERMINATION OF MONOSACCHARIDE STRUCTURES

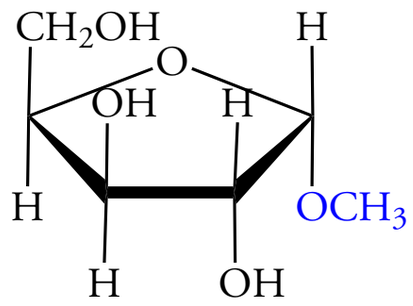
Chain Shortening of Aldoses



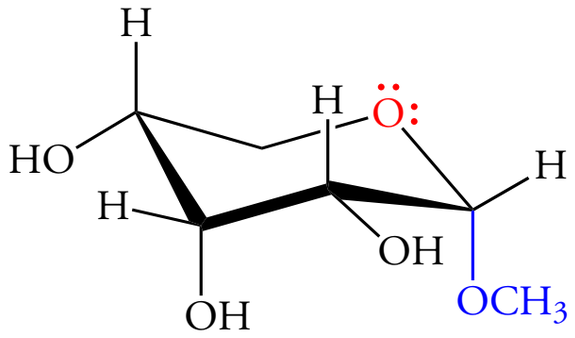
(one diastereomer) (an oxime)



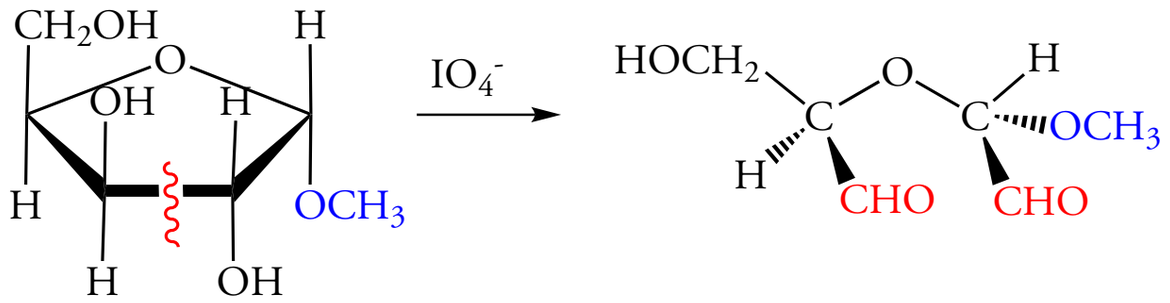
26.11 DETERMINATION OF RING SIZE



methyl α-D-ribofuranoside

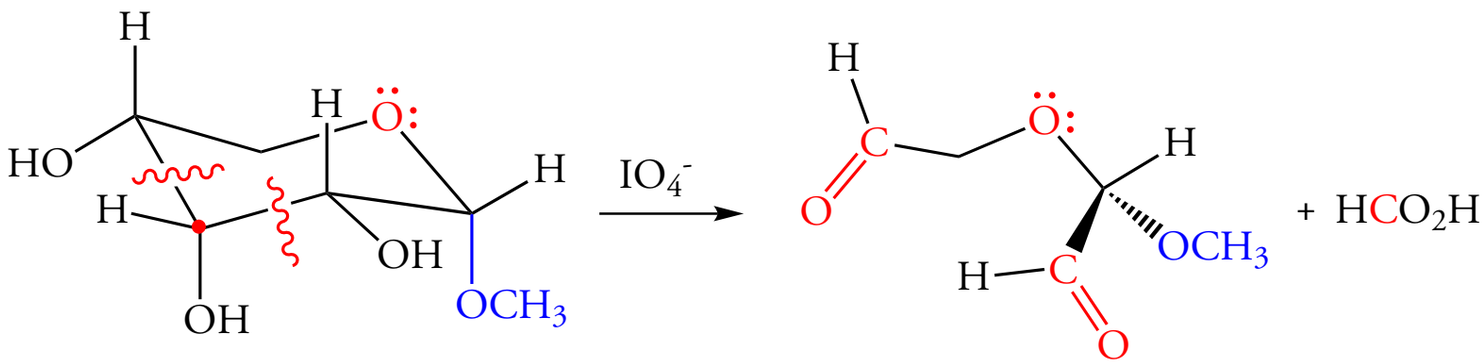


methyl α-D-ribopyranoside



methyl α-D-ribofuranoside

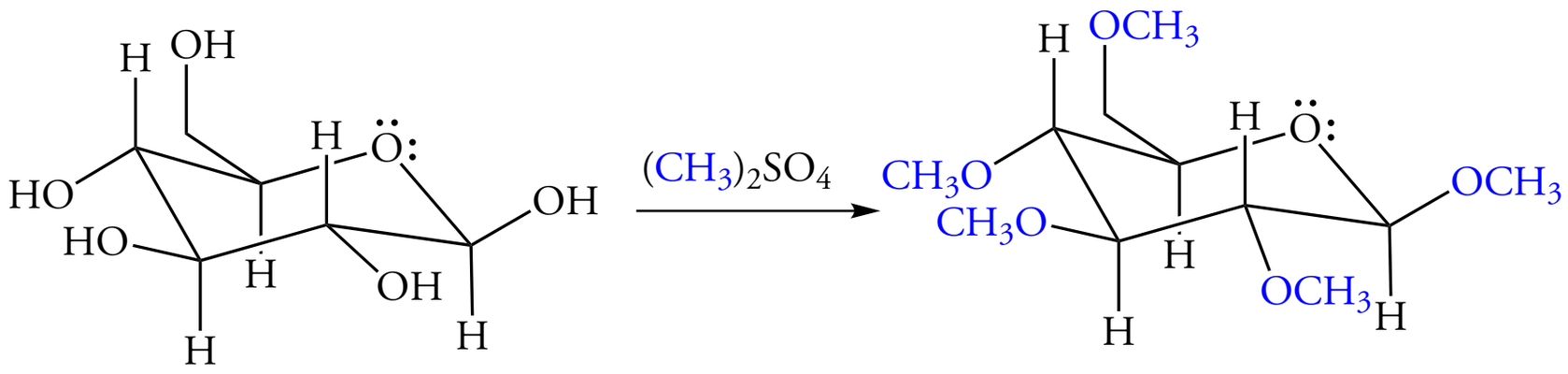
dialdehyde product



methyl α-D-ribopyranoside

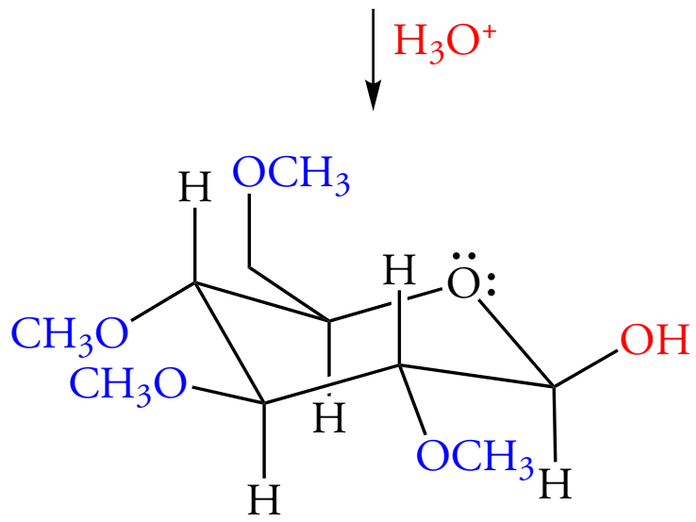
dialdehyde product

26.11 DETERMINATION OF RING SIZE



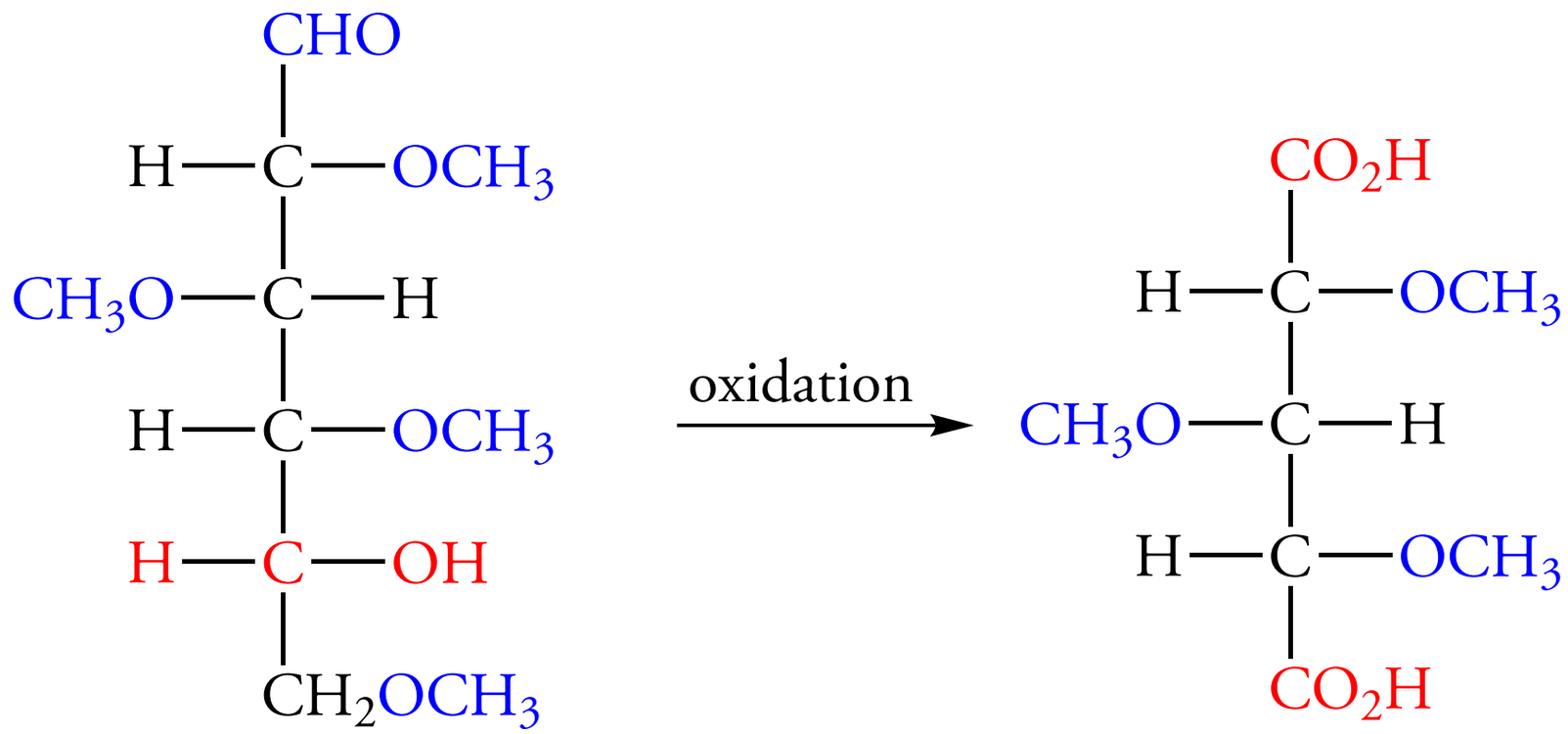
β-D-glucopyranose

methyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside



2,3,4,6-tetra-*O*-methyl-β-D-glucopyranose

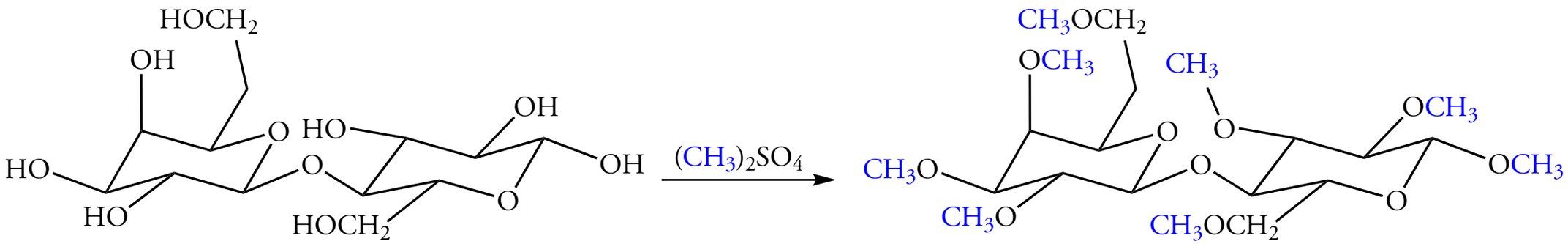
26.11 DETERMINATION OF RING SIZE



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

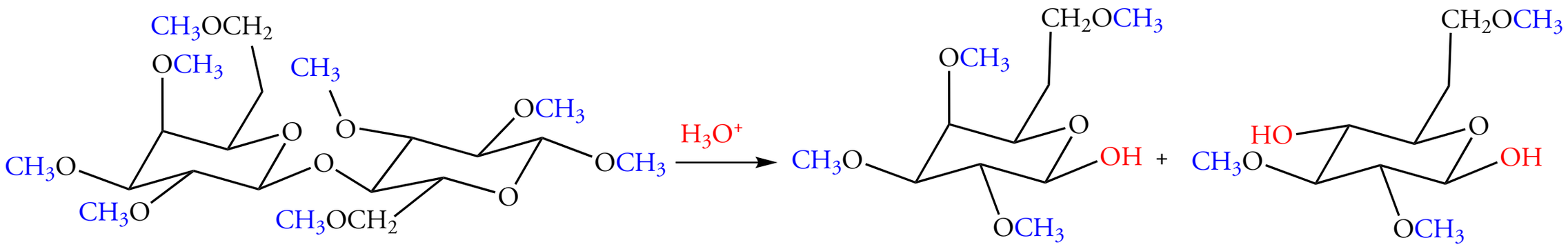
dicarboxylic acid product

26.12 CHEMICAL DETERMINATION OF DISACCHARIDE STRUCTURE



lactose

octamethyllactose

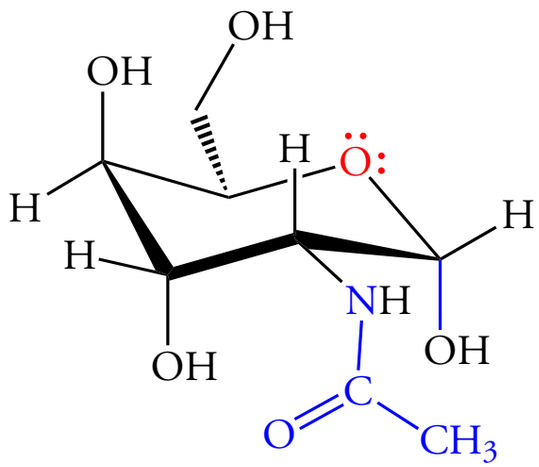


octamethyllactose

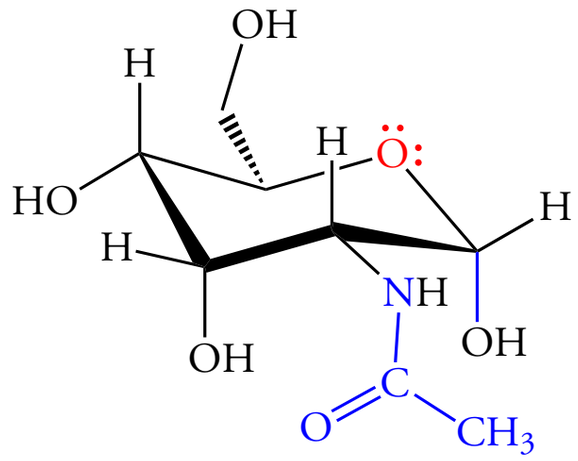
2,3,4,6-tetra-*O*-methyl-D-galactose

2,3,6-tri-*O*-methyl-D-glucose

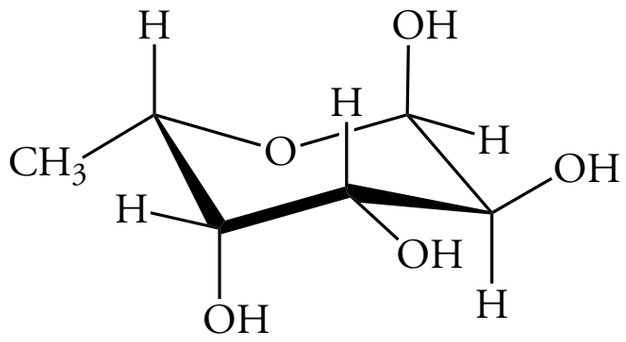
26.13 HUMAN BLOOD GROUP ANTIGENS



N-acetylgalactosamine
(GalNAc)



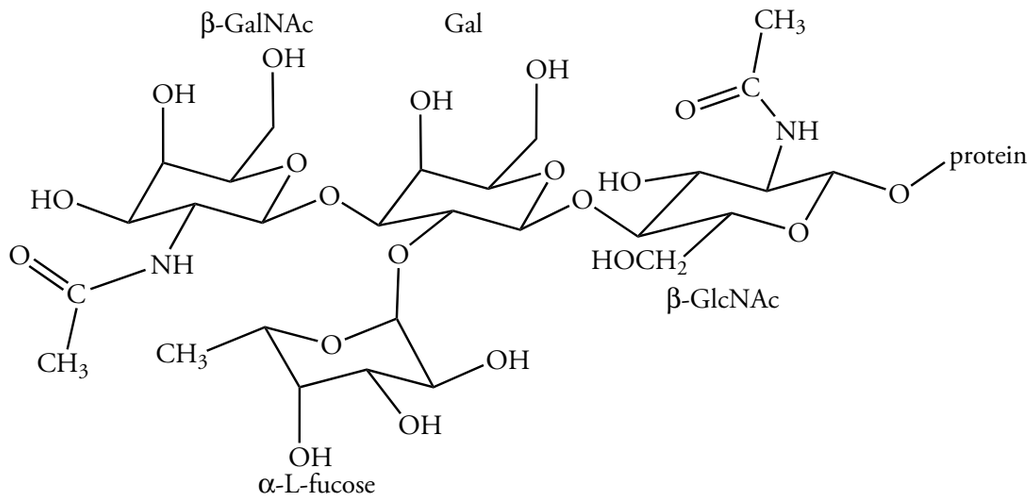
N-acetylglucosamine
(GlcNAc)



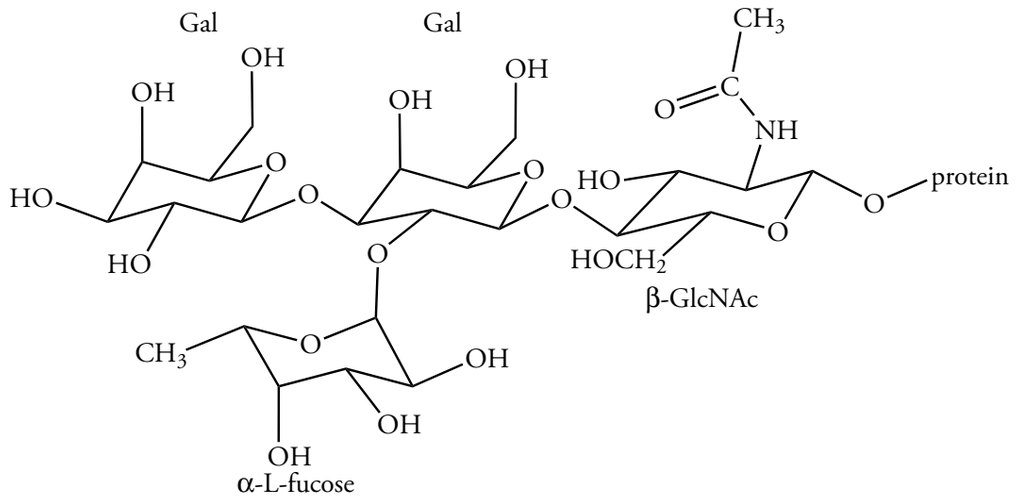
6-deoxy-a-L-galactose
(a-L-fucose)

26.13 HUMAN BLOOD GROUP ANTIGENS

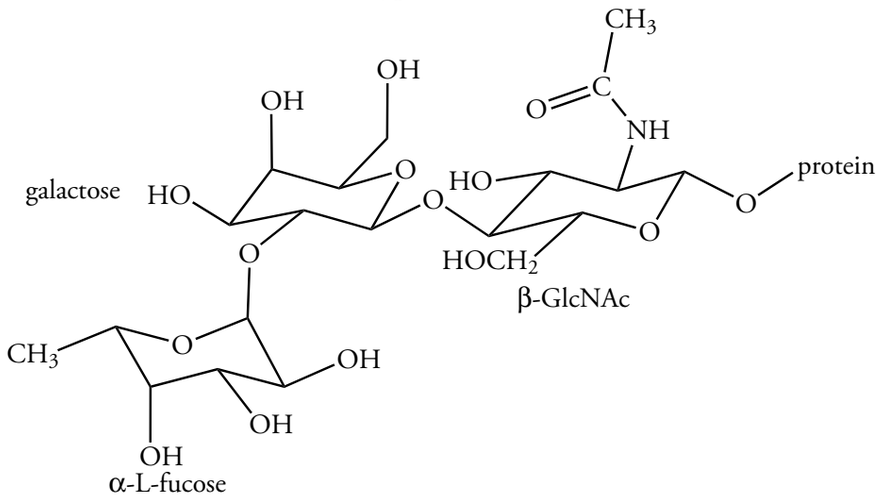
Type A



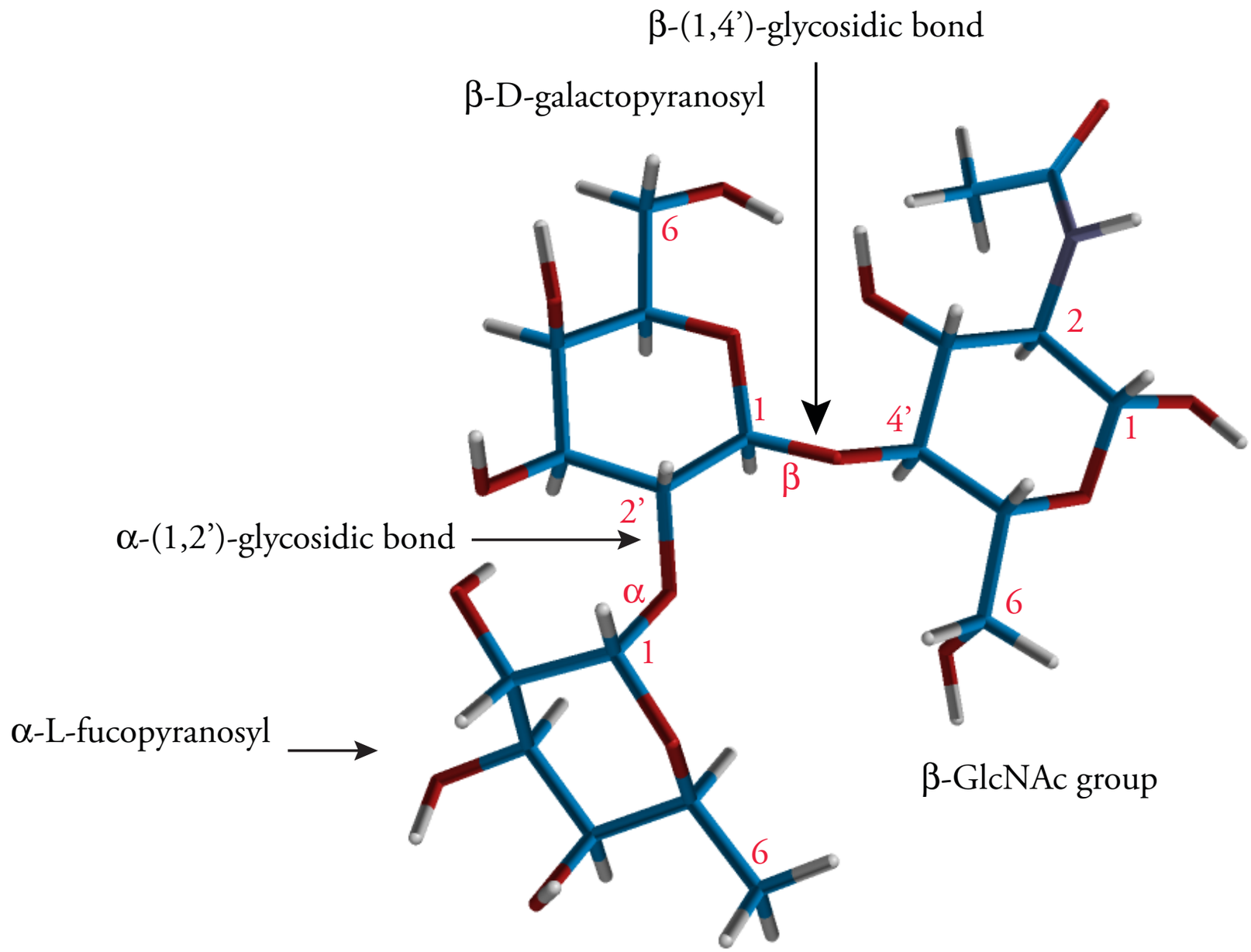
Type B



Type O



26.13 HUMAN BLOOD GROUP ANTIGENS



Type O Blood Group Antigen