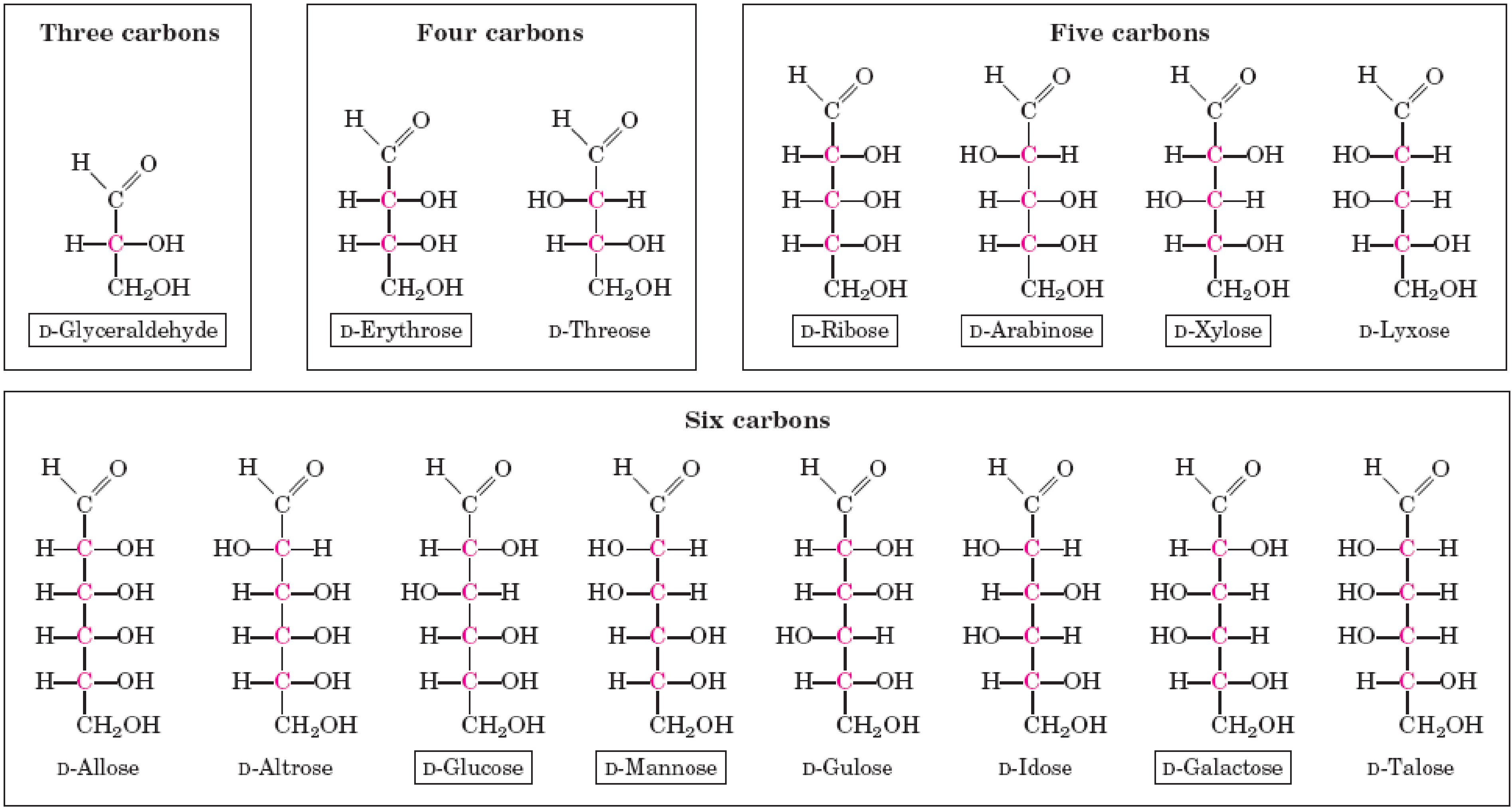
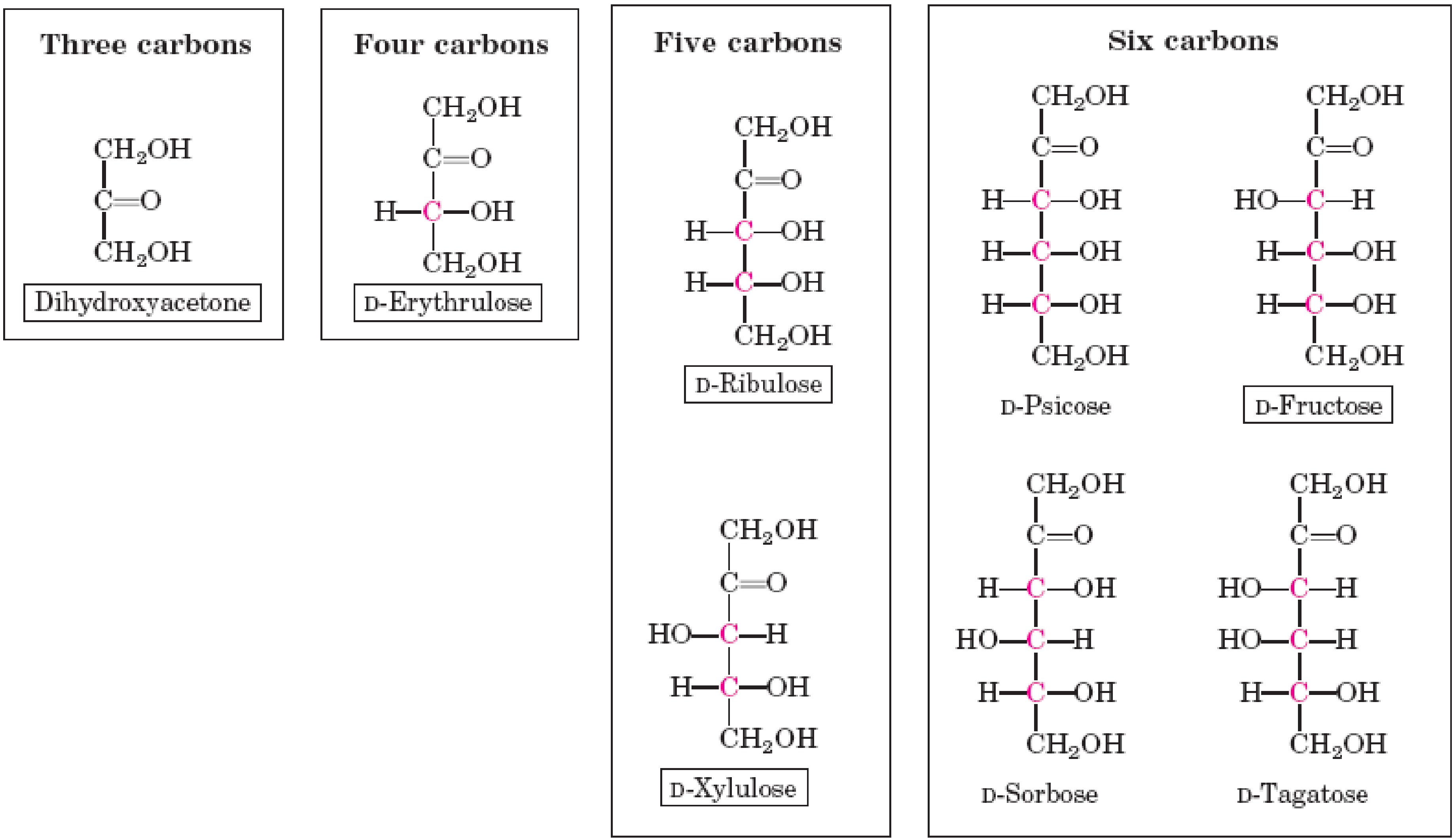
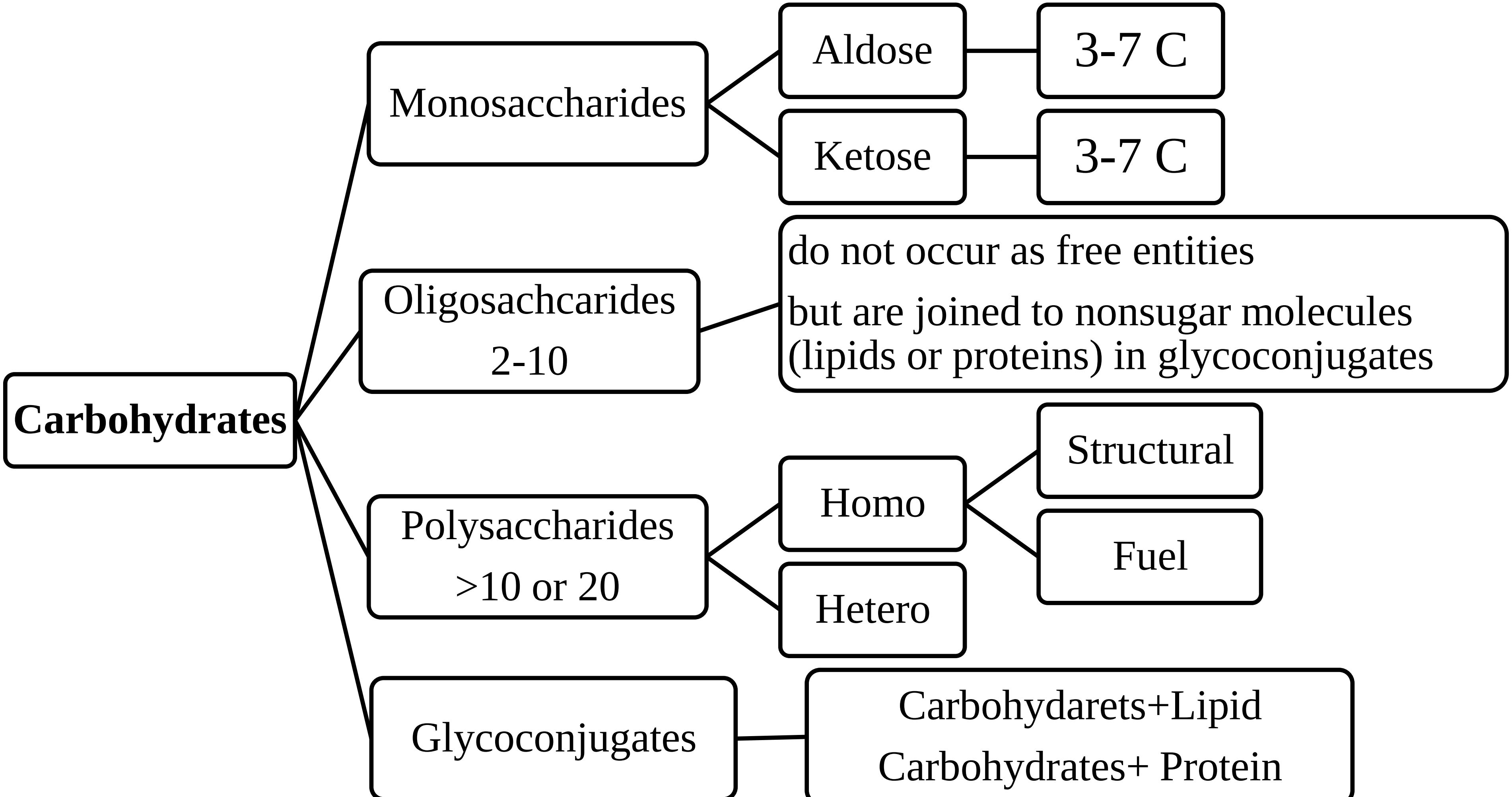
Carbohydrates


Three carbons
D-Glyceraldehyde
Four carbons
D-Erythrose
D-Threose
Five carbons
D-Ribose
D-Arabinose
D-Xylose
D-Lyxose
Six carbons
D-Allose
D-Altrose
D-Glucose
D-Mannose
D-Gulose
D-Idose
D-Galactose
D-Talose

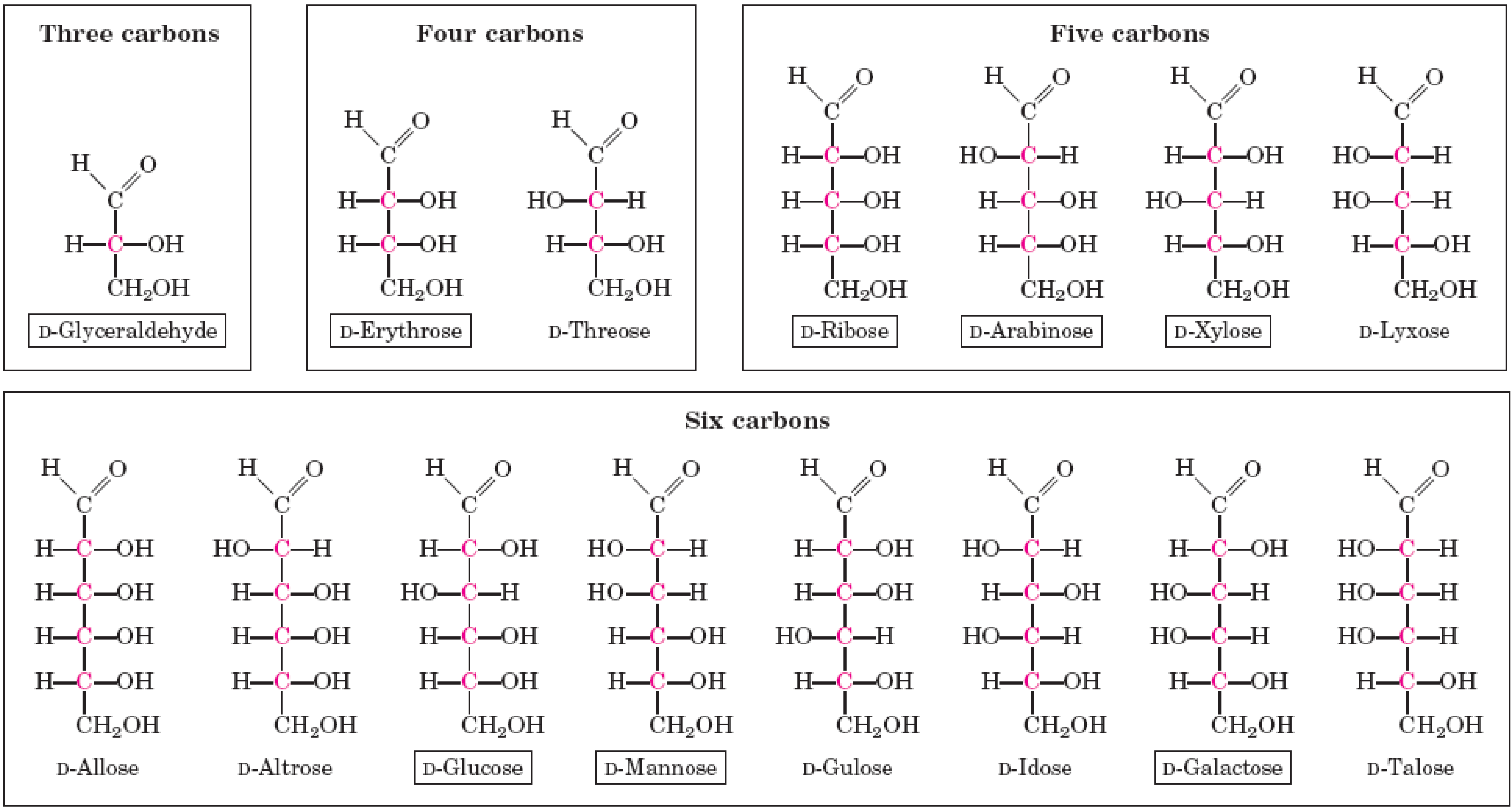
D-Aldoses


Three carbons
Dihydroxyacetone
Four carbons
D-Erythrulose
Five carbons
D-Ribulose
D-Xylulose
Six carbons
D-Psicose
D-Fructose
D-Sorbose
D-Tagatose

D-Ketoses

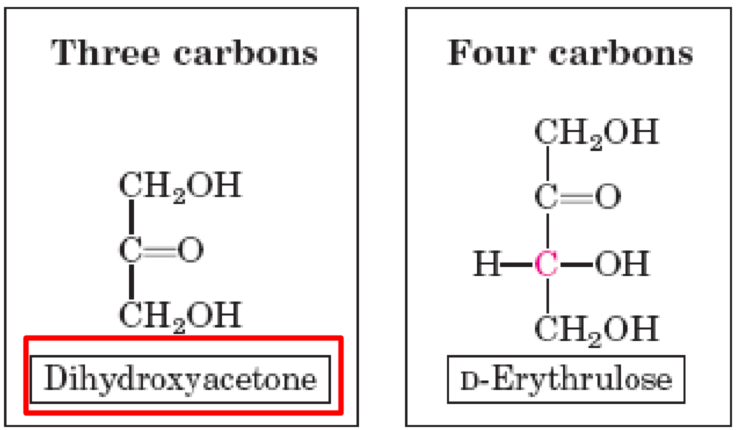

Carbohydrates
Monosaccharides
Aldose
3-7 C
Ketose
3-7 C
Oligosachcarides
2-10
do not occur as free entities
but are joined to nonsugar molecules
(lipids or proteins) in glycoconjugates
Polysaccharides
>10 or 20
Homo
Structural
Fuel
Hetero
Glycoconjugates
Carbohydarets+Lipid
Carbohydrates+ Protein

مونوساکاریدها دارای مراکز نامتقارن می باشند.

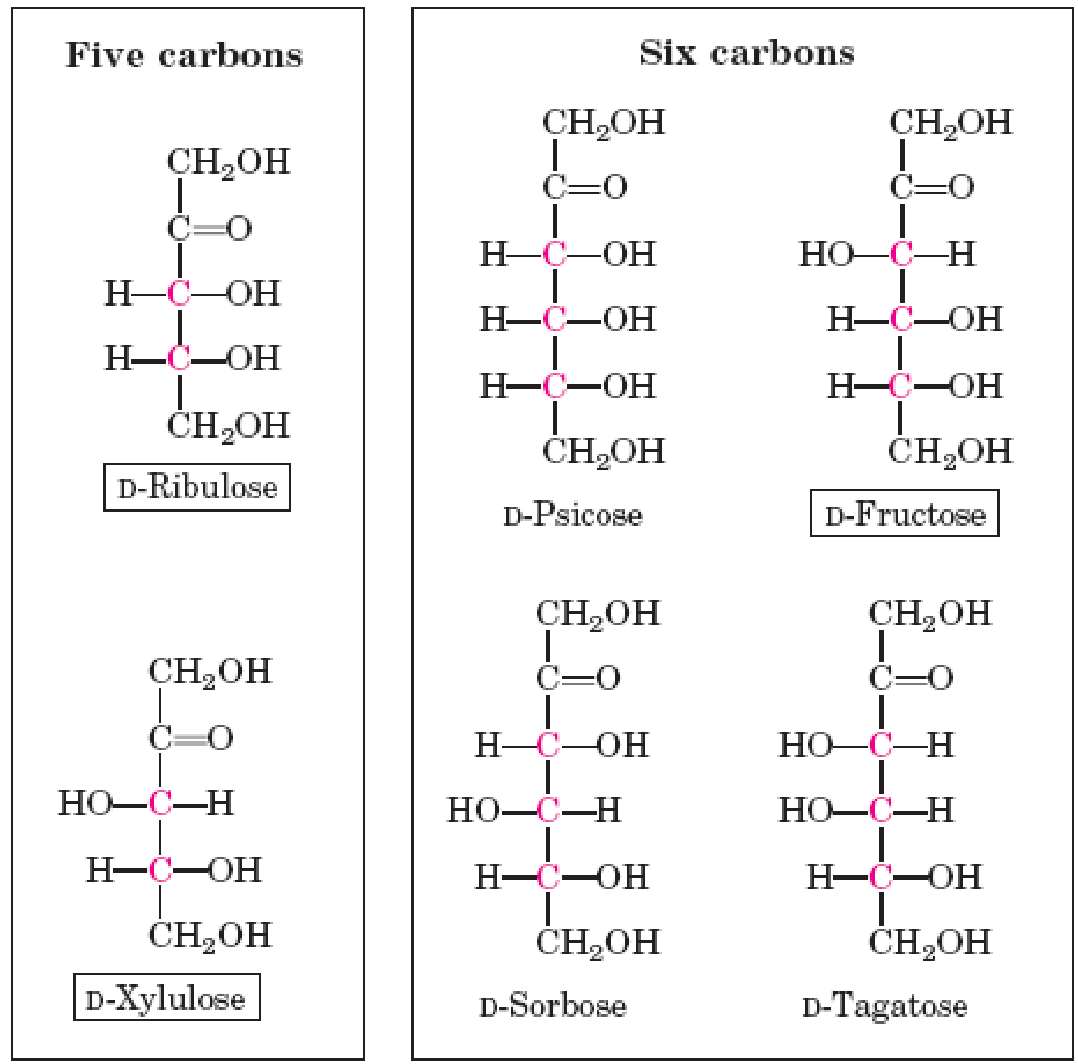


D-Aldoses

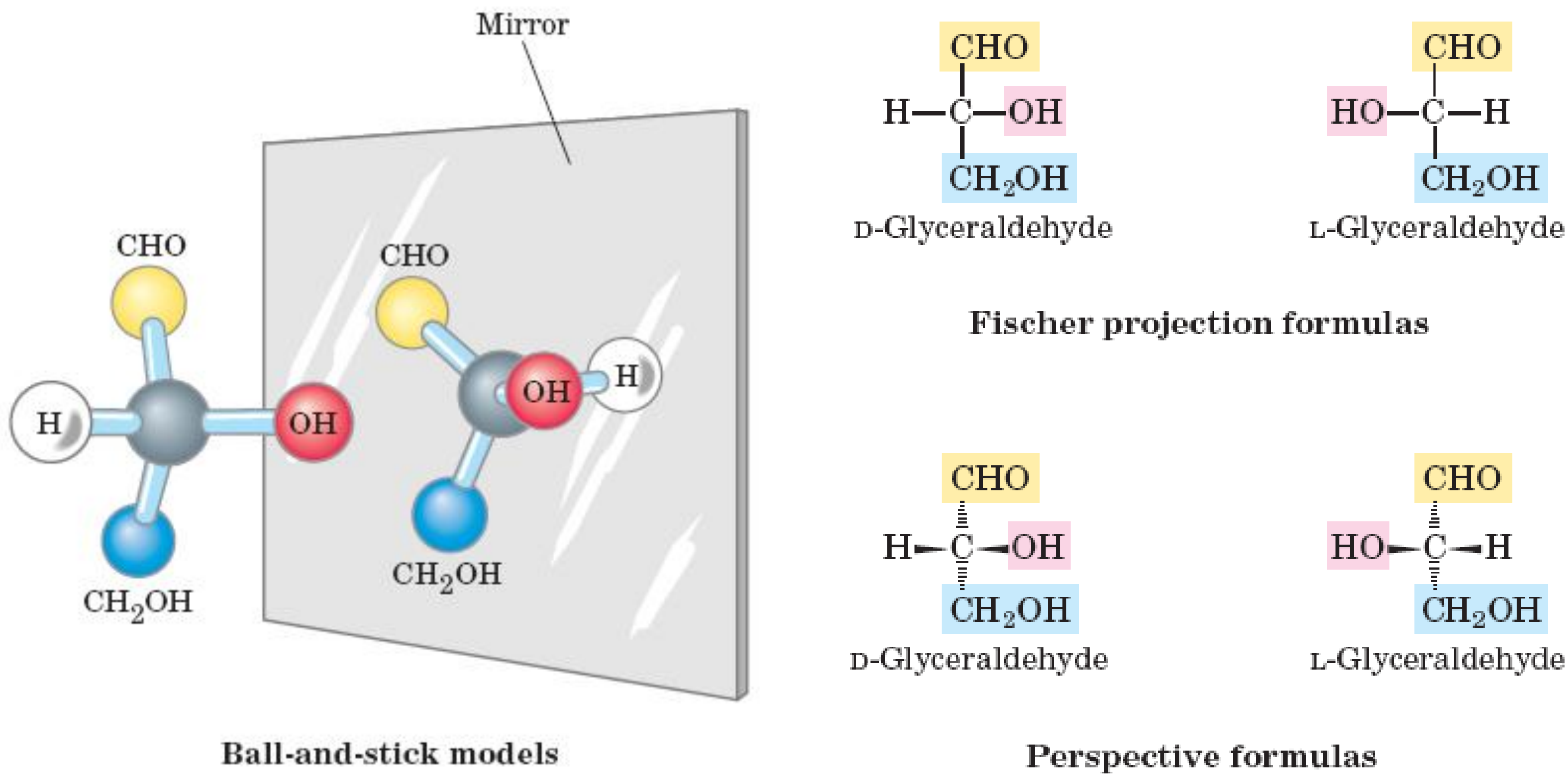
مونوساکاریدها دارای مراکز نامتقارن می باشند.



All the monosaccharides except dihydroxyacetone contain one or more asymmetric (chiral) carbon atoms and thus occur in optically active isomeric forms.



D-Ketoses

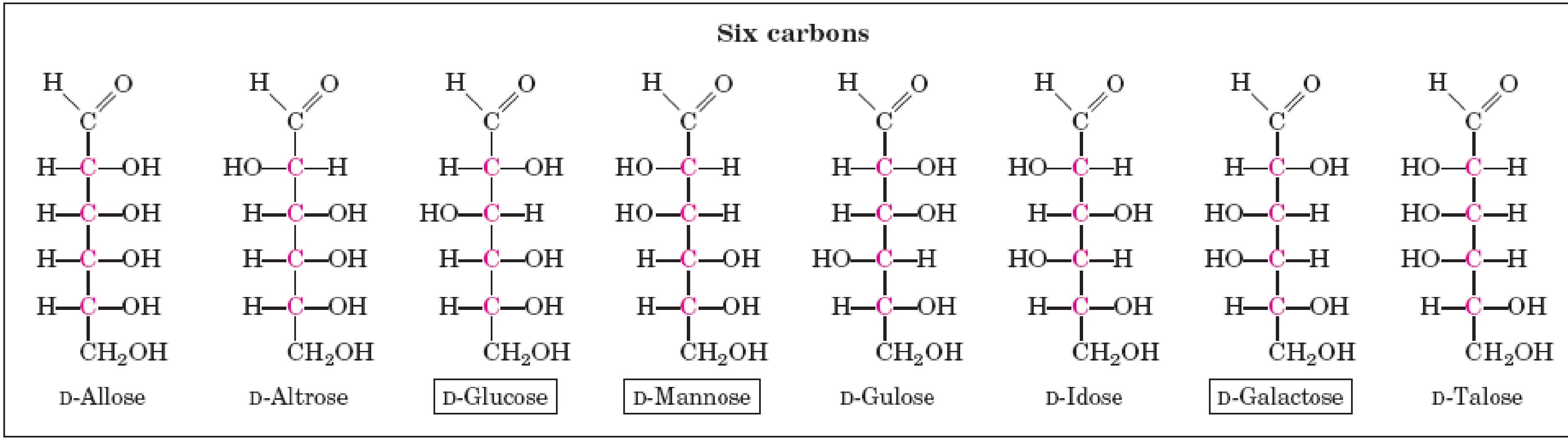


Enantiomer

تعداد ایزومرهای فضایی مولکولی با n مرکز کایرال = ؟؟؟؟

فرم D و L

تعداد ایزومرهای فضایی مولکولی با n مرکز کایرال = 2^n $\quad 2^4 = 16$



D-Aldoses

تعیین ایزومر D و L در مونوساکاریدهای با بیش از یک مرکز کایرال:

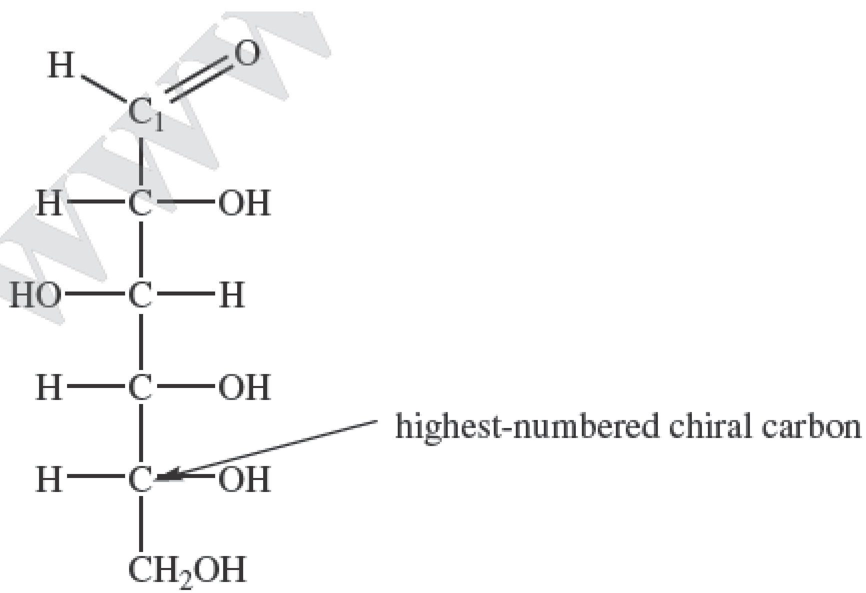
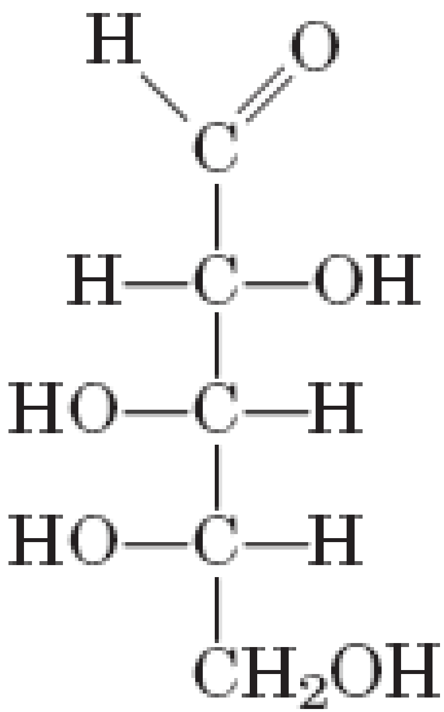
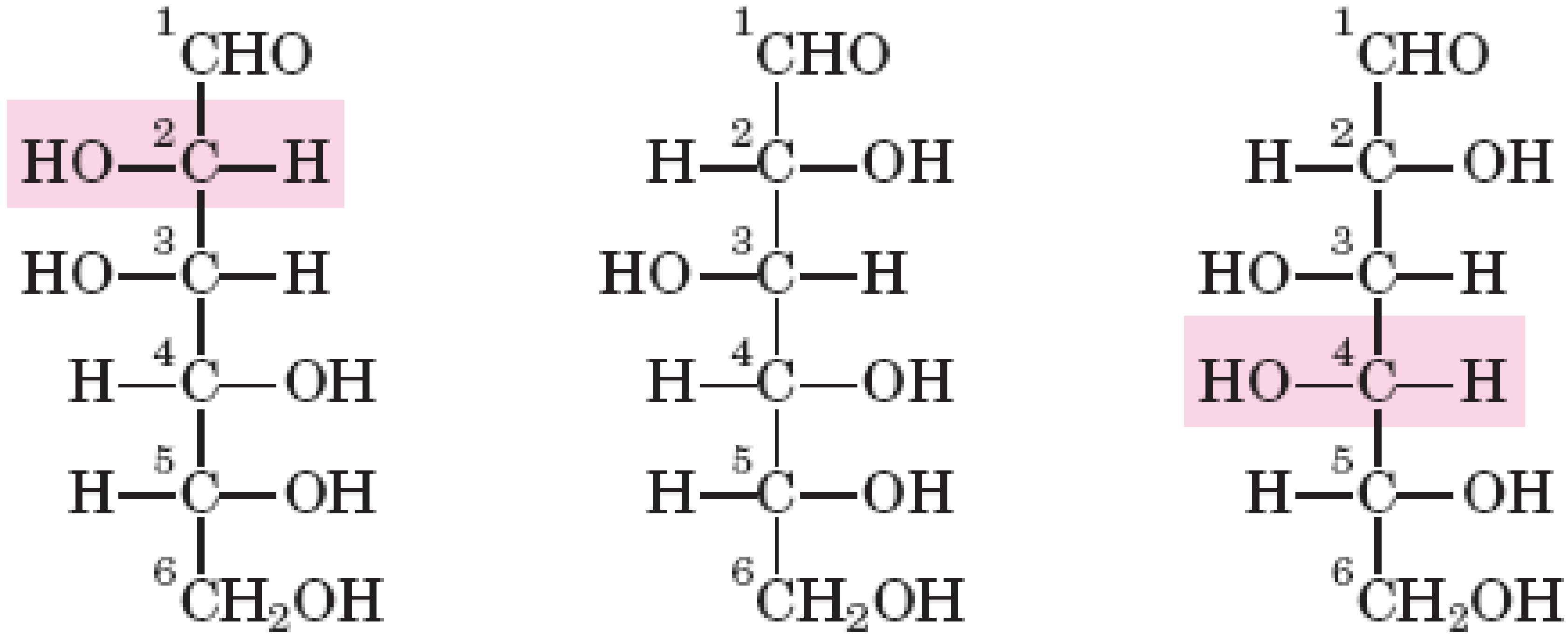


Figure 7-2: Structure of D-glucose.

بیشتر قندهای موجود در طبیعت از نوع ایزومر D هستند.



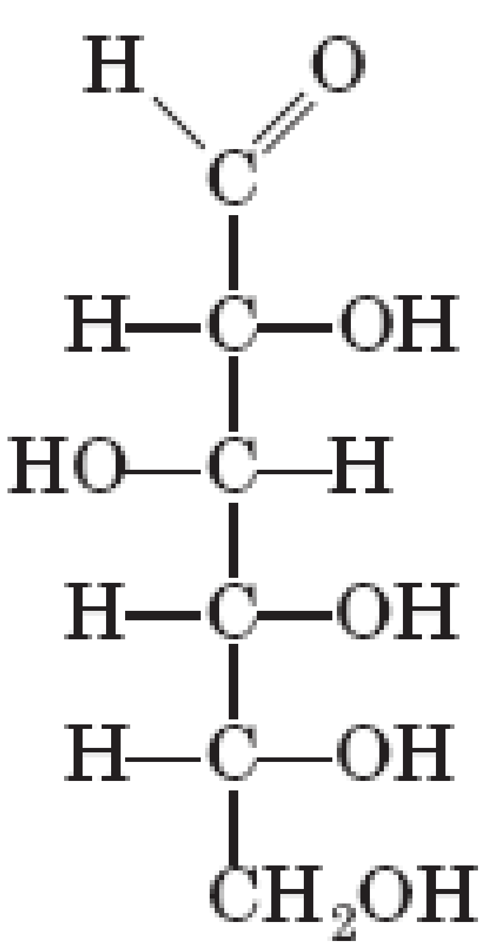
L-Arabinose



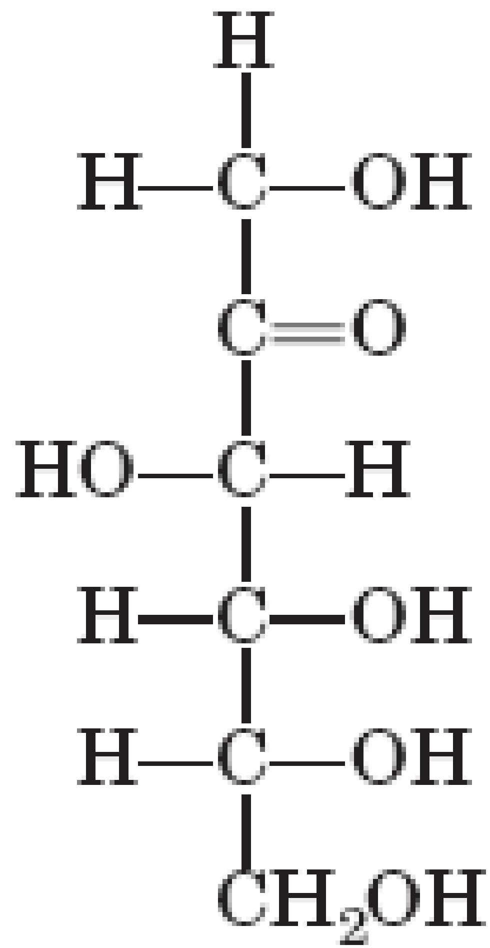
D-Mannose (epimer at C-2) | D-Glucose | D-Galactose (epimer at C-4)

FIGURE 7–4 **Epimers.** D-Glucose and two of its epimers are shown as projection formulas. Each epimer differs from D-glucose in the configuration at one chiral center (shaded red).

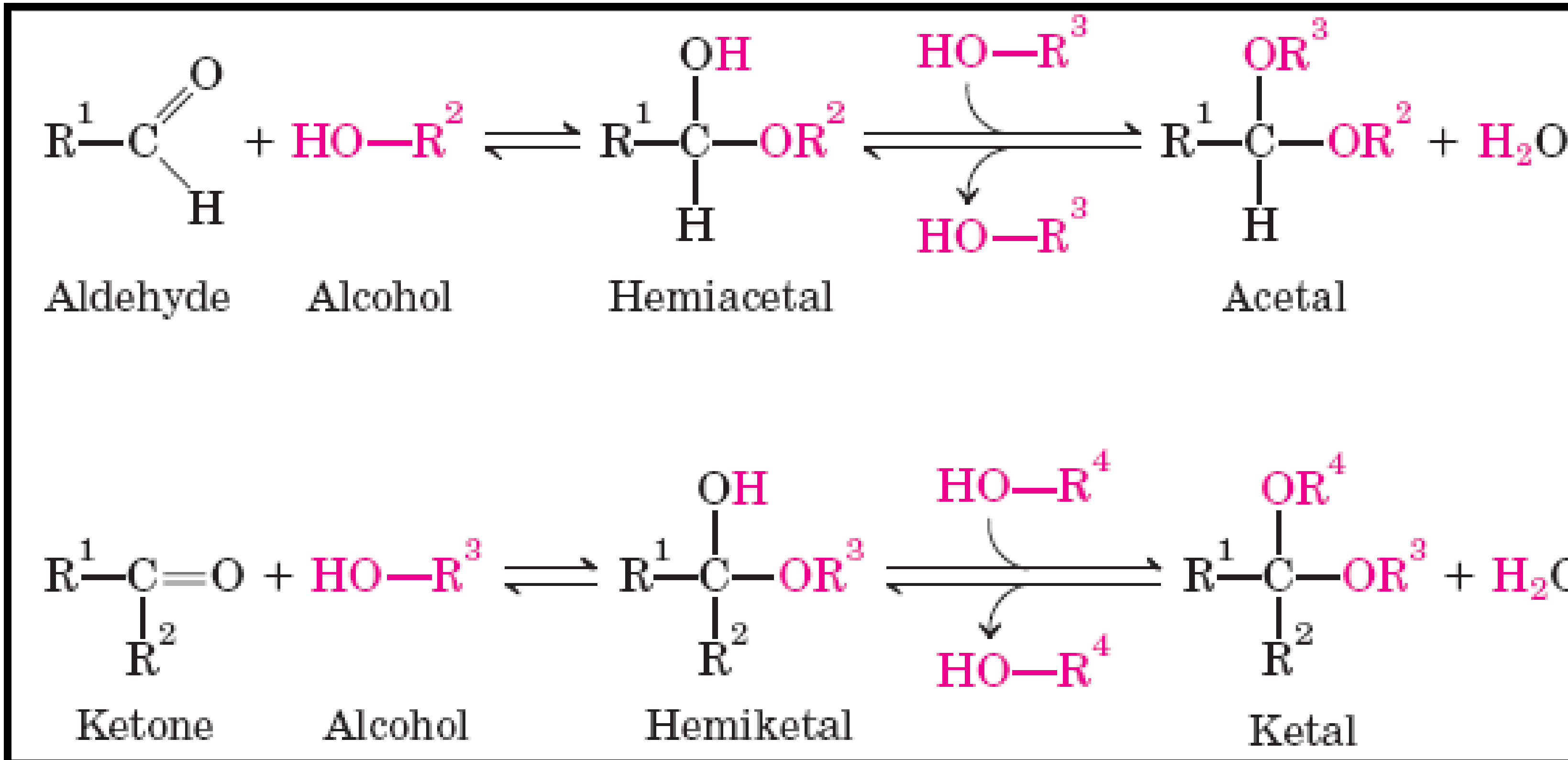
The Common Monosaccharides Have Cyclic Structures



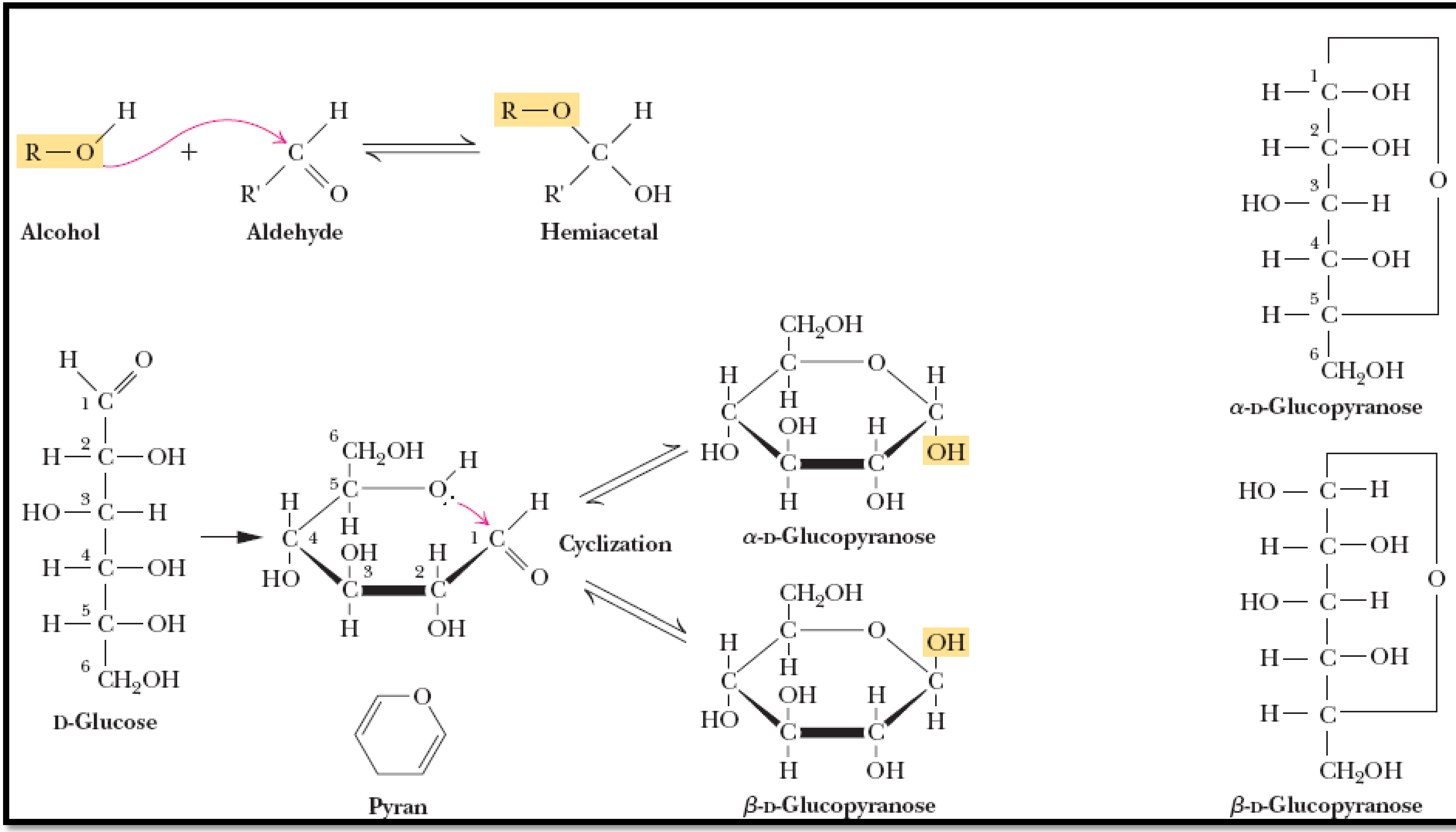
D-Glucose,
an aldohexose

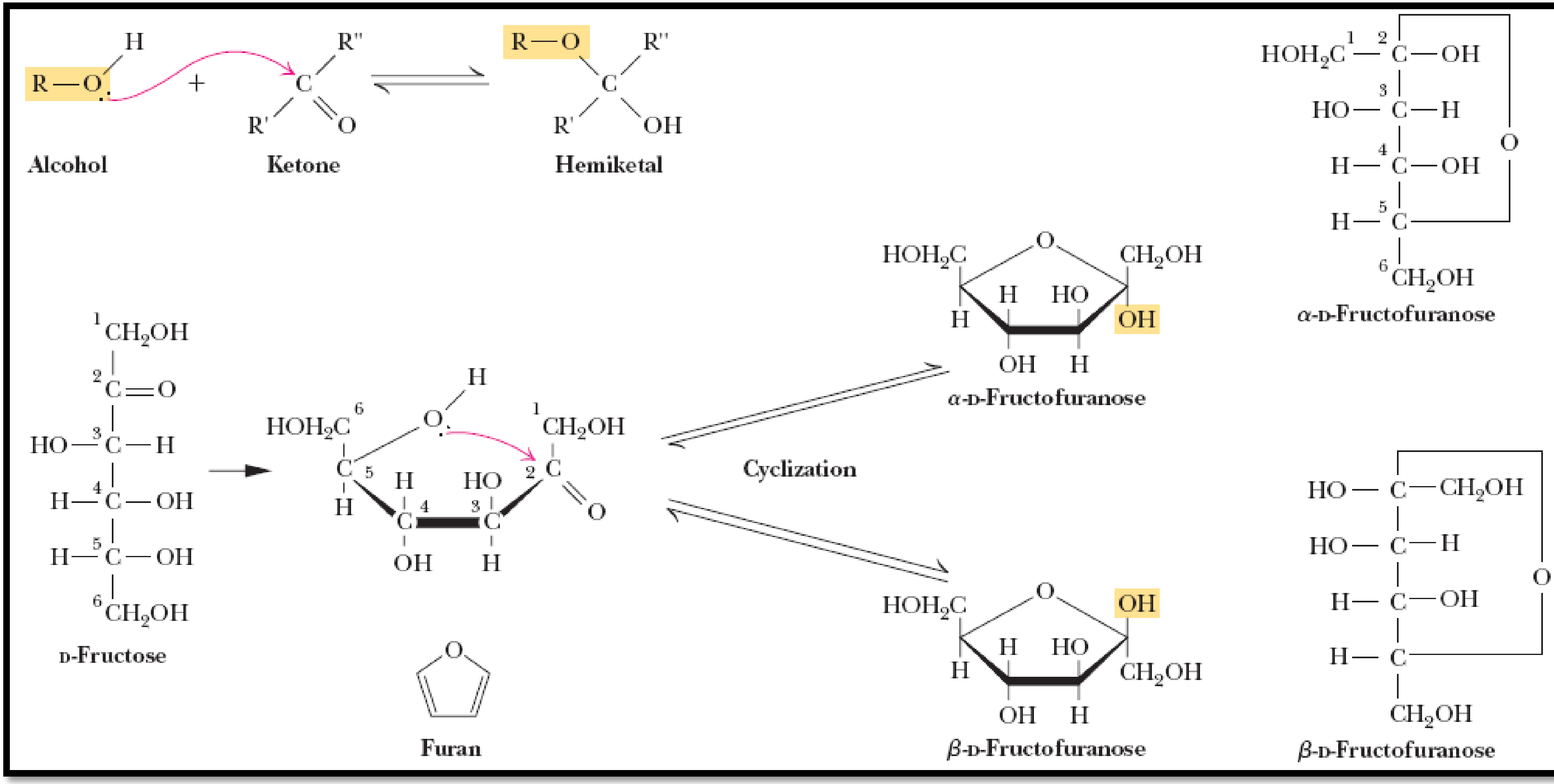


D-Fructose,
a ketohexose


Aldehyde
Alcohol
Hemiacetal
Acetal
Ketone
Alcohol
Hemiketal
Ketal

> 4 C has cyclic in aques solution





Alcohol
Ketone
Hemiketal
D-Fructose
Furan
Cyclization
α-D-Fructofuranose
α-D-Fructofuranose
β-D-Fructofuranose
β-D-Fructofuranose

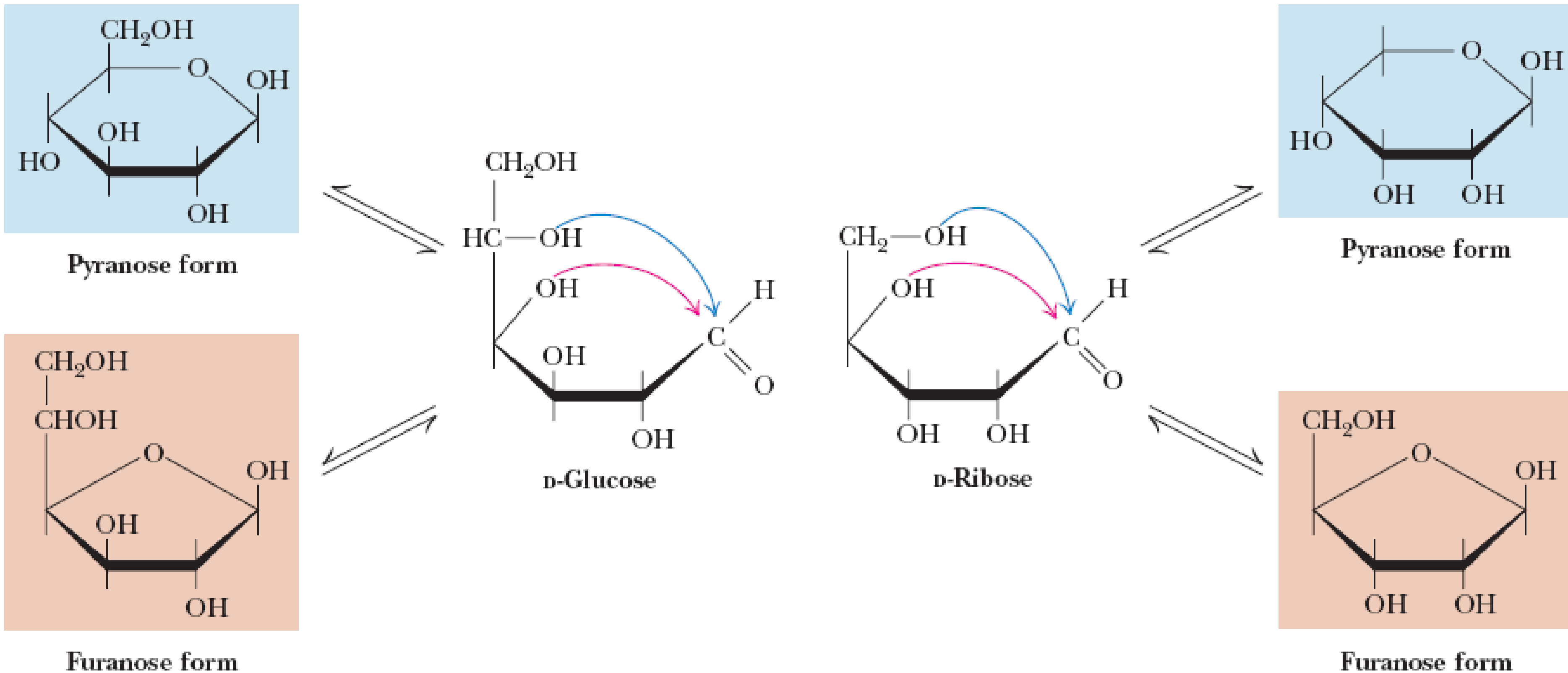


FIGURE 7.7 D-Glucose, D-ribose, and other simple sugars can cyclize in two ways, forming either furanose or pyranose structures.

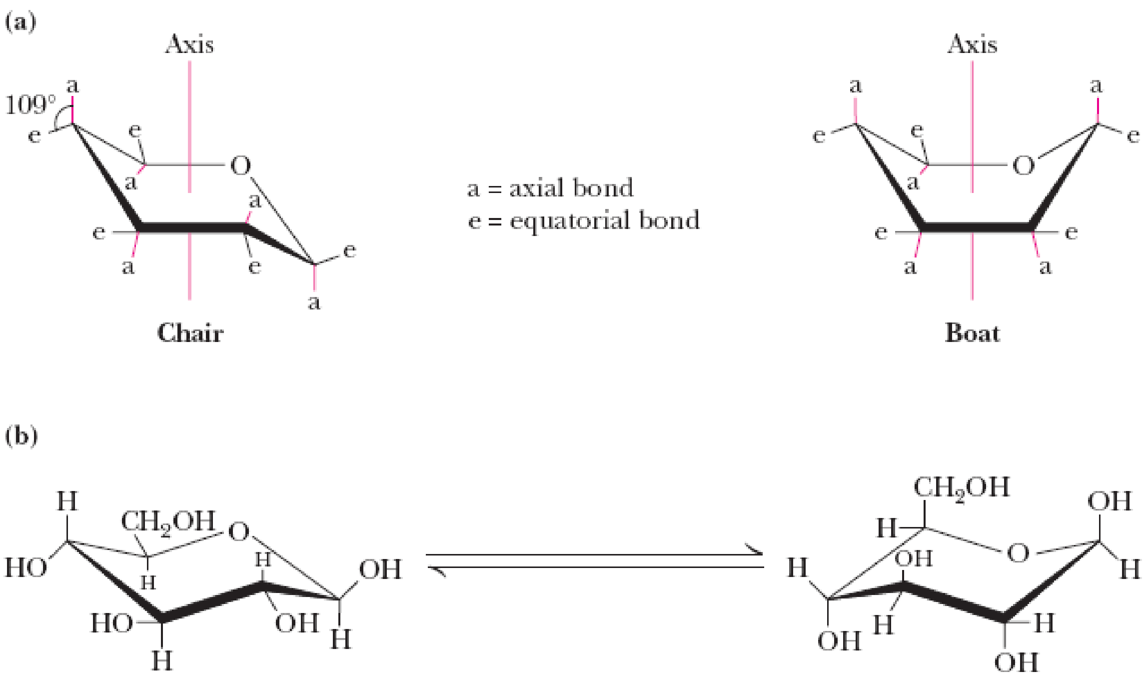
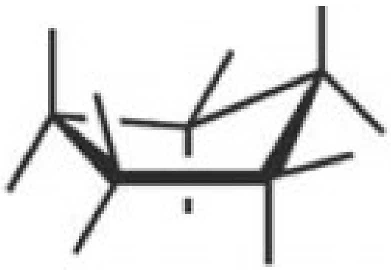
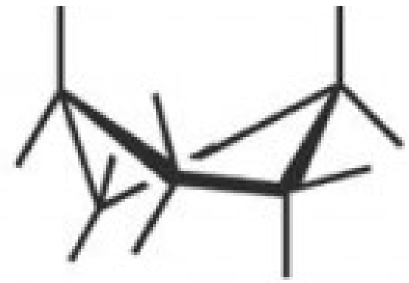


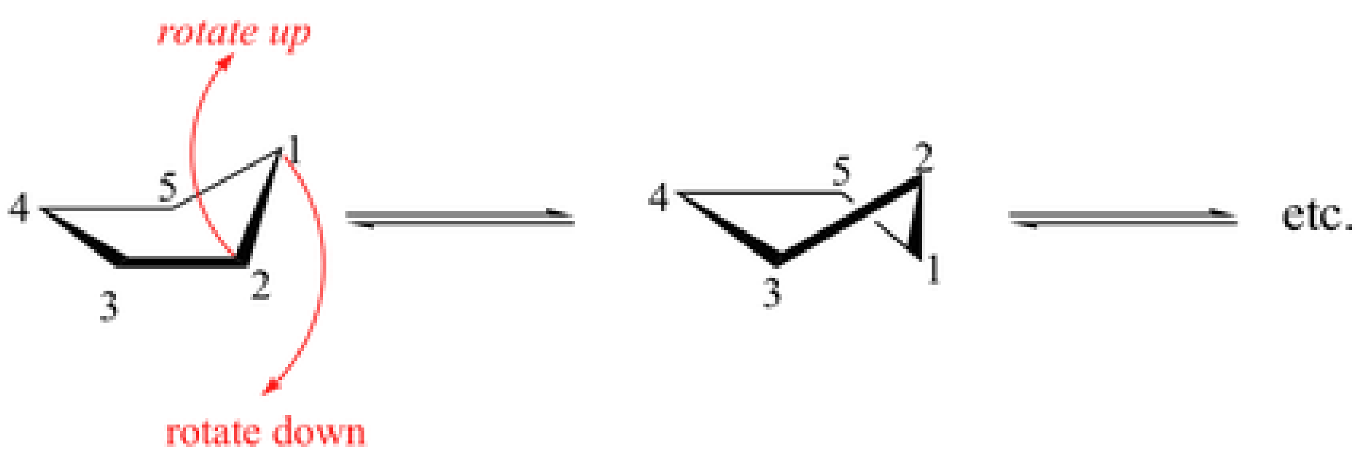
FIGURE 7.8 **(a)** Chair and boat conformations of a pyranose sugar. **(b)** Two possible chair conformations of β-D-glucose.

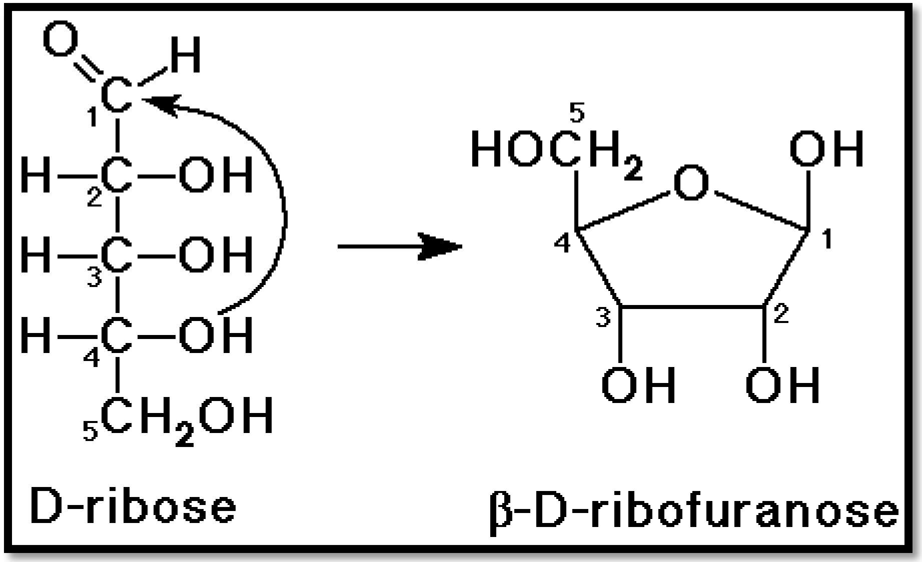


Envelope



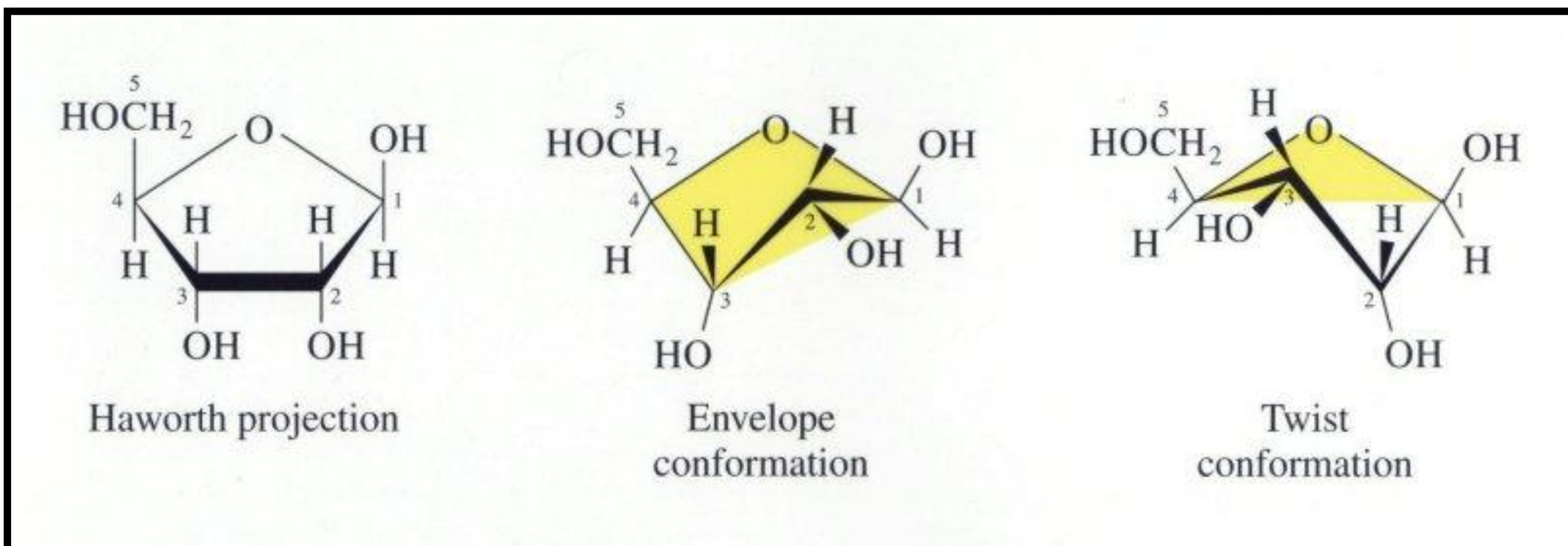
Twist

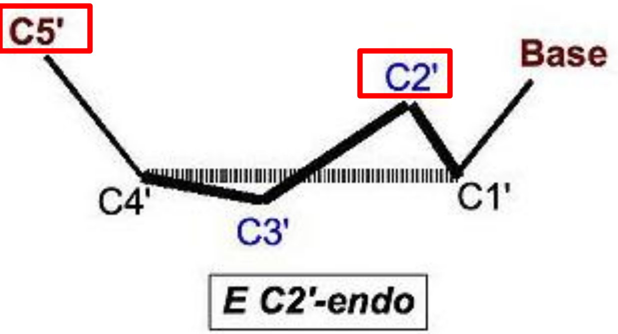


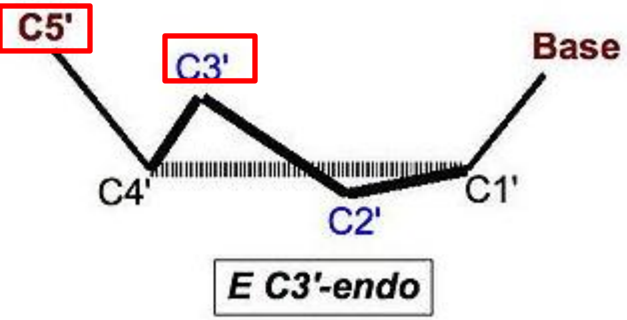


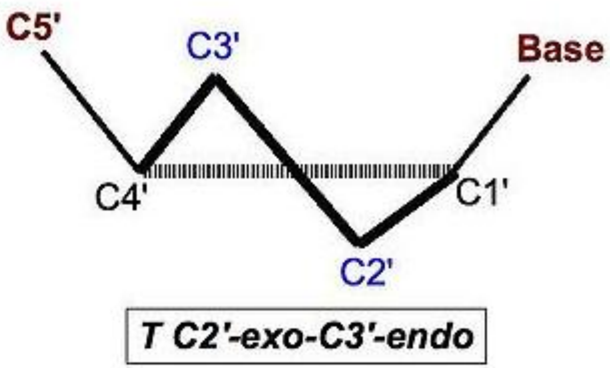
<u>In solution</u>, the straightchain (aldehyde) and ring (β-D-furanose) forms of **free** ribose are in <u>equilibrium</u>.

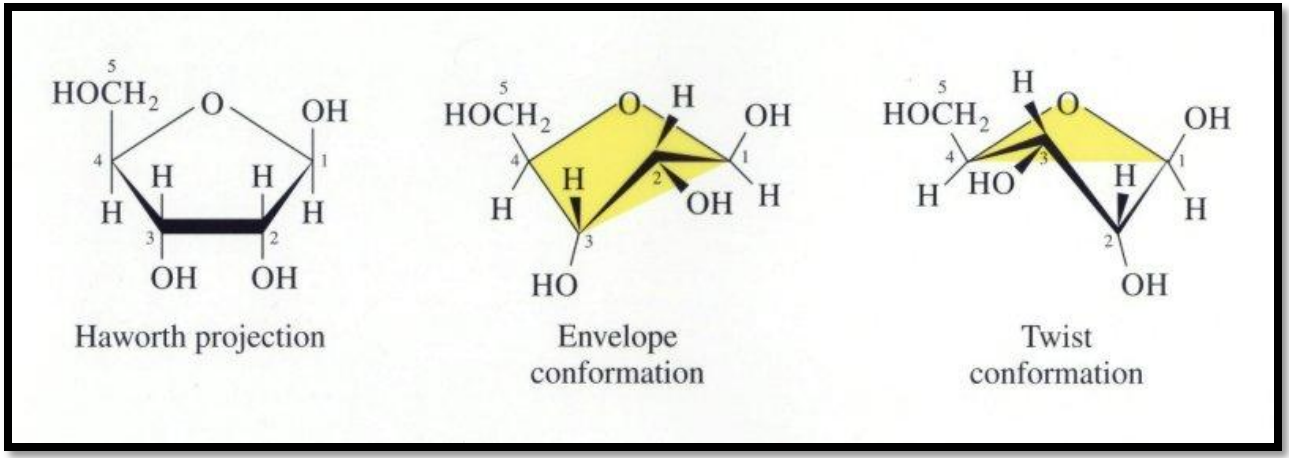
Envelope: only a single atom is displaced
Twists: Two atoms is displaced

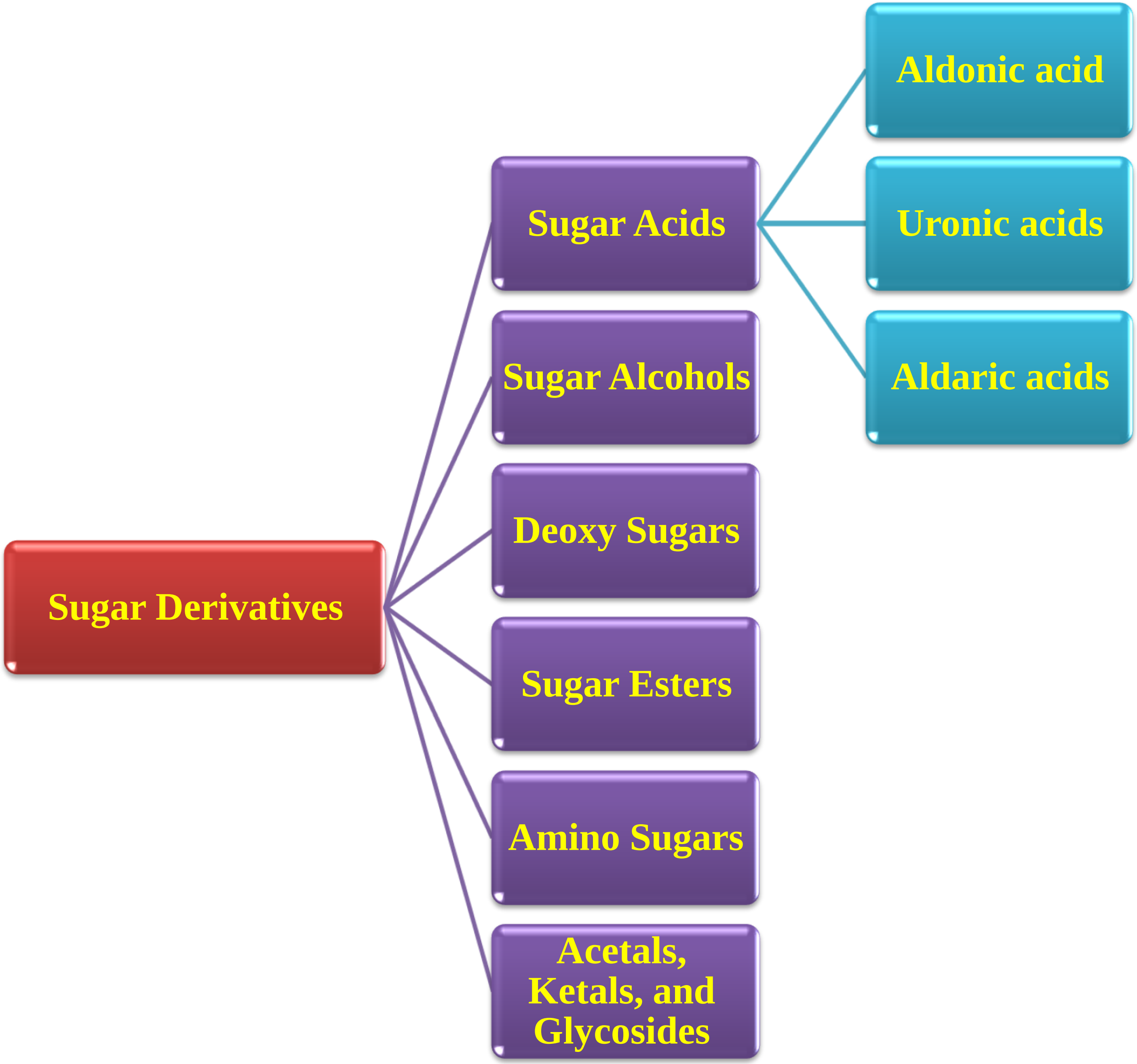



C5'
C2'
Base
C4'
C3'
C1'
E C2'-endo


C5'
C3'
Base
C4'
C1'
C2'
E C3'-endo


C5'
C3'
Base
C4'
C1'
C2'
T C2'-exo-C3'-endo


HOCH2
O
OH
H
OH
Haworth projection
Envelope conformation
HO
Twist conformation


Sugar Derivatives
Sugar Acids
Sugar Alcohols
Deoxy Sugars
Sugar Esters
Amino Sugars
Acetals, Ketals, and Glycosides
Aldonic acid
Uronic acids
Aldaric acids

Sugar Acids

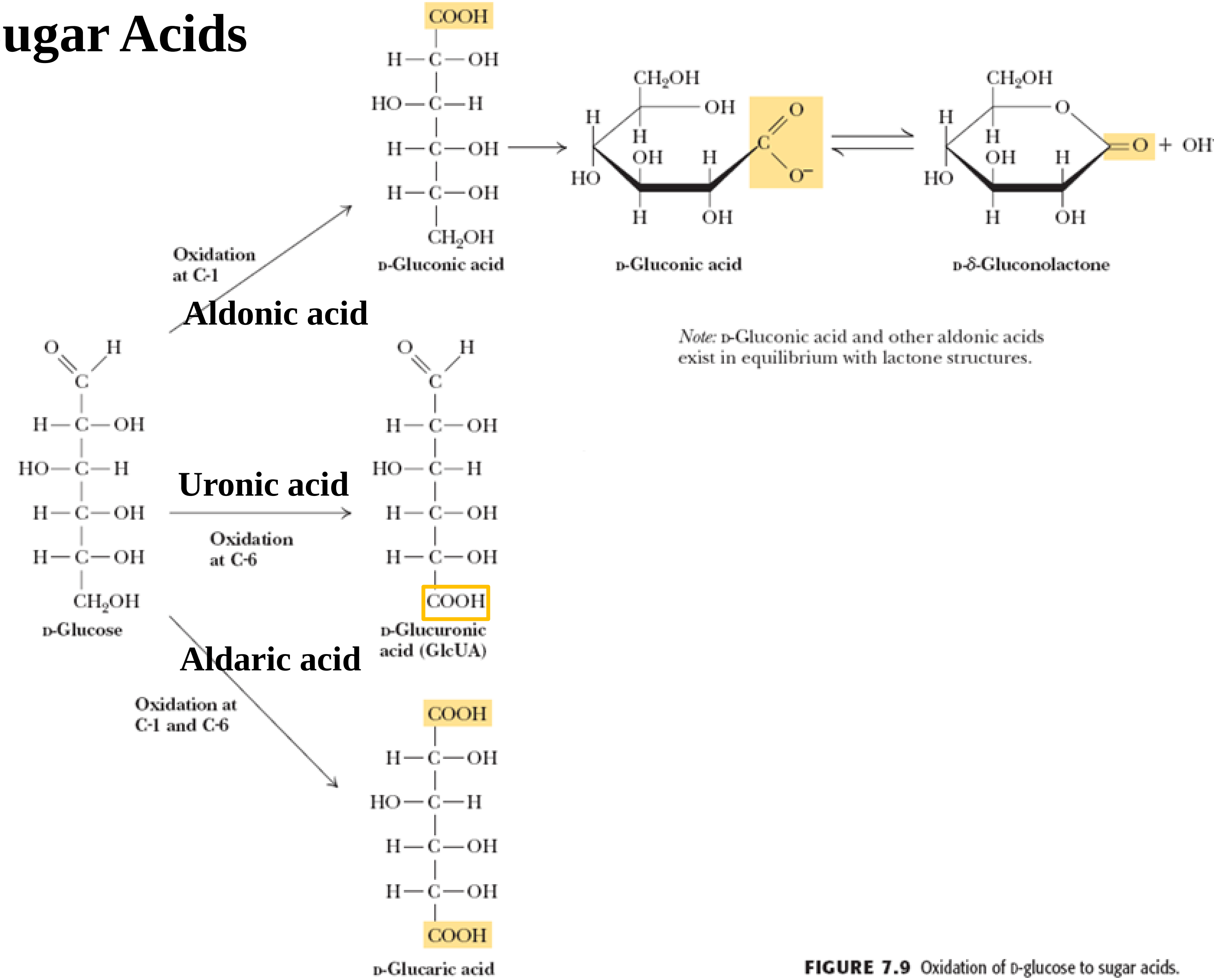
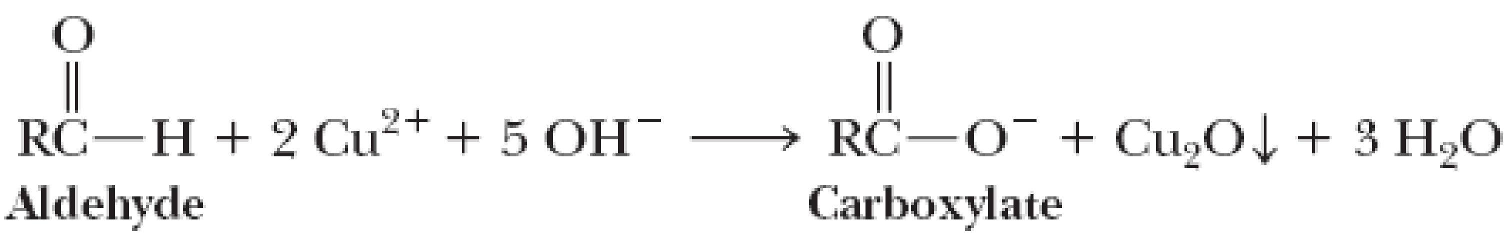


FIGURE 7.9 Oxidation of D-glucose to sugar acids.

addition of alkaline $CuSO_4$ (called *Fehling's solution*) to an aldose sugar produces a red cuprous oxide (Cu_2O) precipitate:



Sugar Alcohols

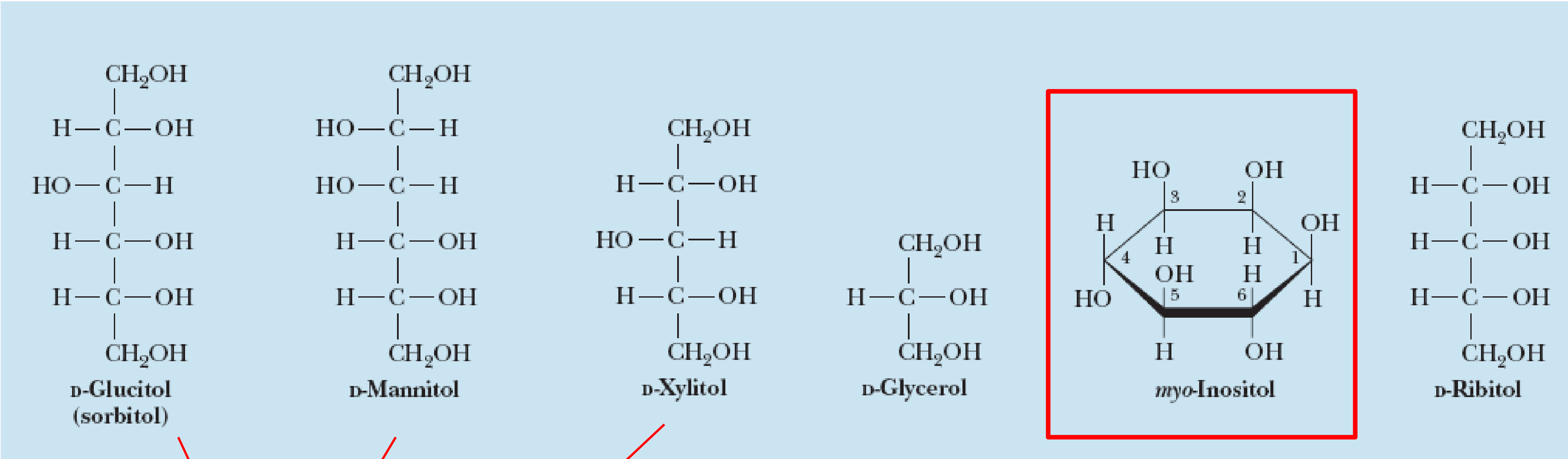


FIGURE 7.10 Structures of some sugar alcohols. (Note that *myo*-inositol is a polyhydroxy cyclohexane, not a sugar alcohol.)

FIGURE 7.11 Sugar alcohols such as sorbitol, mannitol, and xylitol sweeten many "sugarless" gums and candies.

Deoxy Sugars

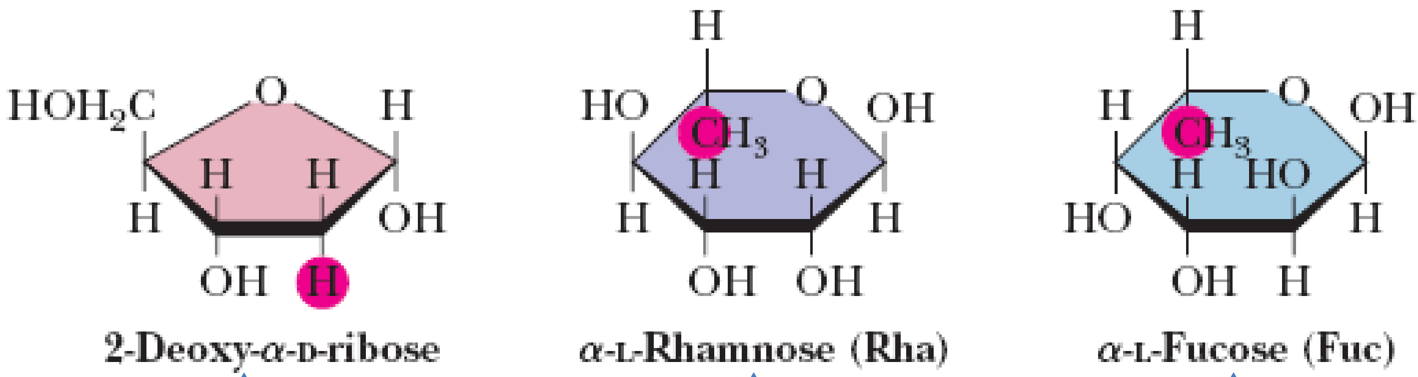
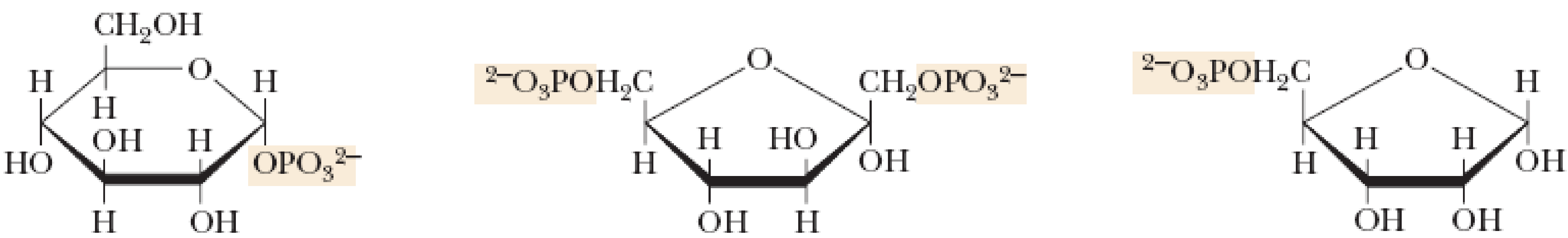


FIGURE 7.12 Several deoxy sugars. Hydrogen and carbon atoms highlighted in red are "deoxy" positions.

Ribose **Mannose** **Galactose**

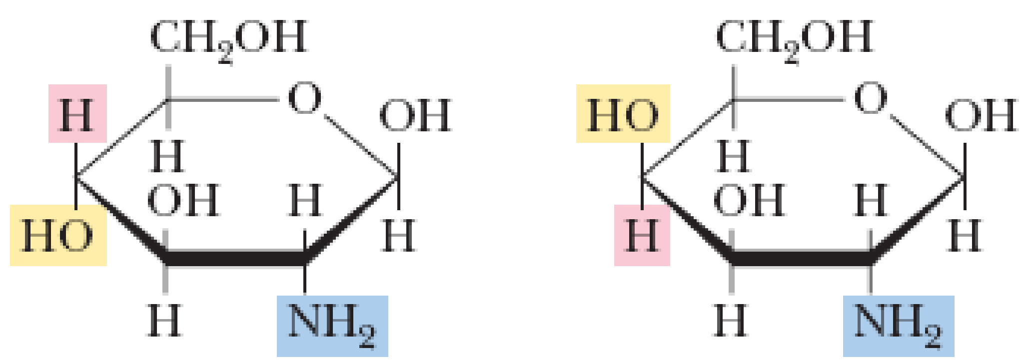
Sugar esters



α-D-Glucose-1-phosphate α-D-Fructose-1,6-bisphosphate α-D-Ribose-5-phosphate

FIGURE 7.13 Several sugar esters important in metabolism.

Amino Sugars



β-D-Glucosamine β-D-Galactosamine

FIGURE 7.14 Structures of D-glucosamine and D-galactosamine.

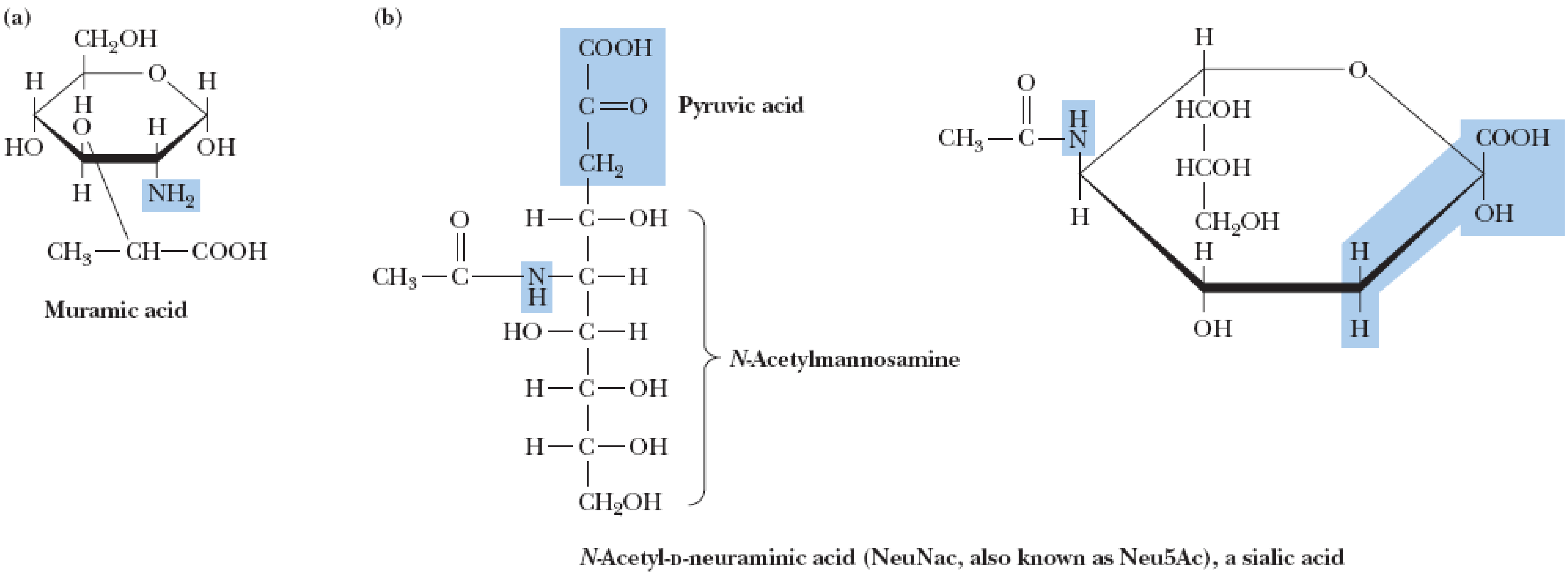


FIGURE 7.15 Structures of (a) muramic acid and (b) several depictions of a sialic acid.

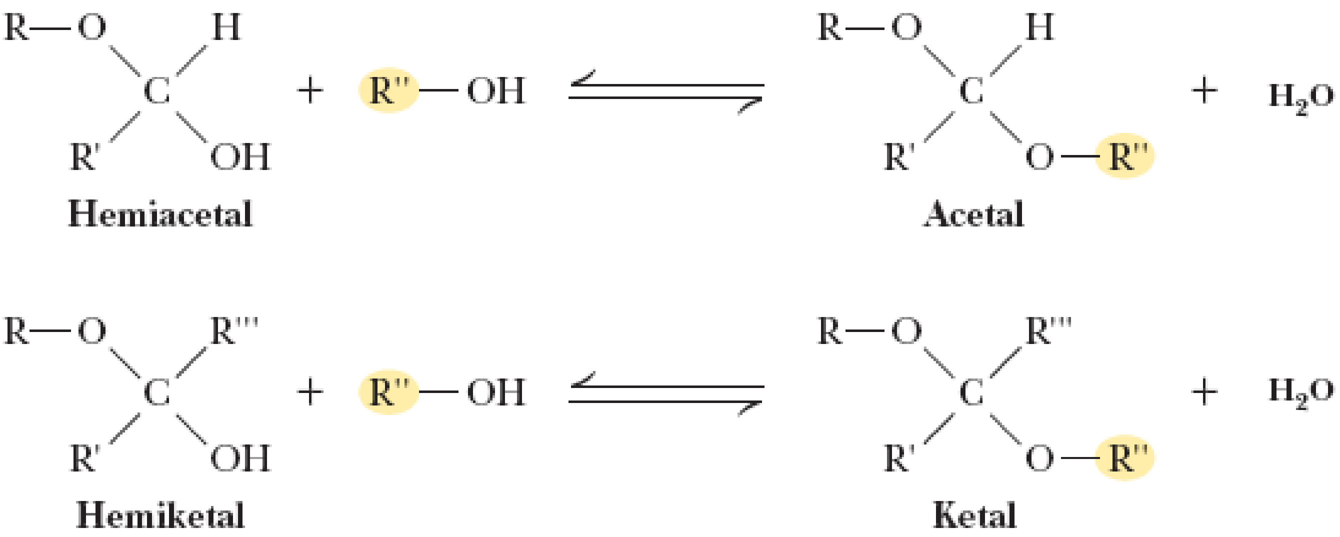


FIGURE 7.16 Acetals and ketals can be formed from hemiacetals and hemiketals, respectively.

Acetal, Ketals and Glycosides

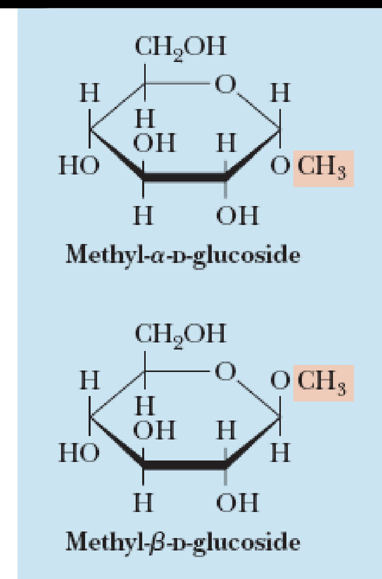
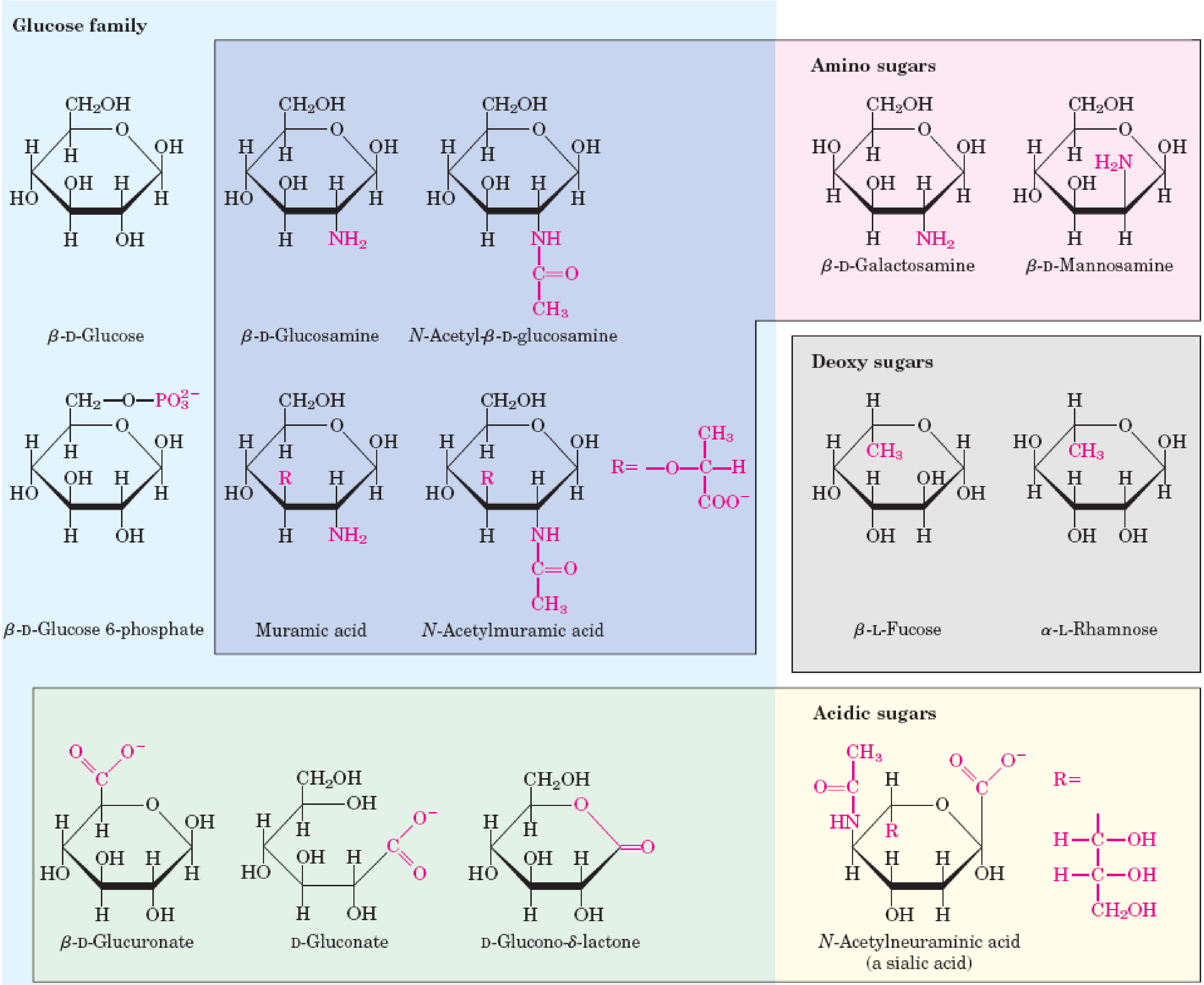
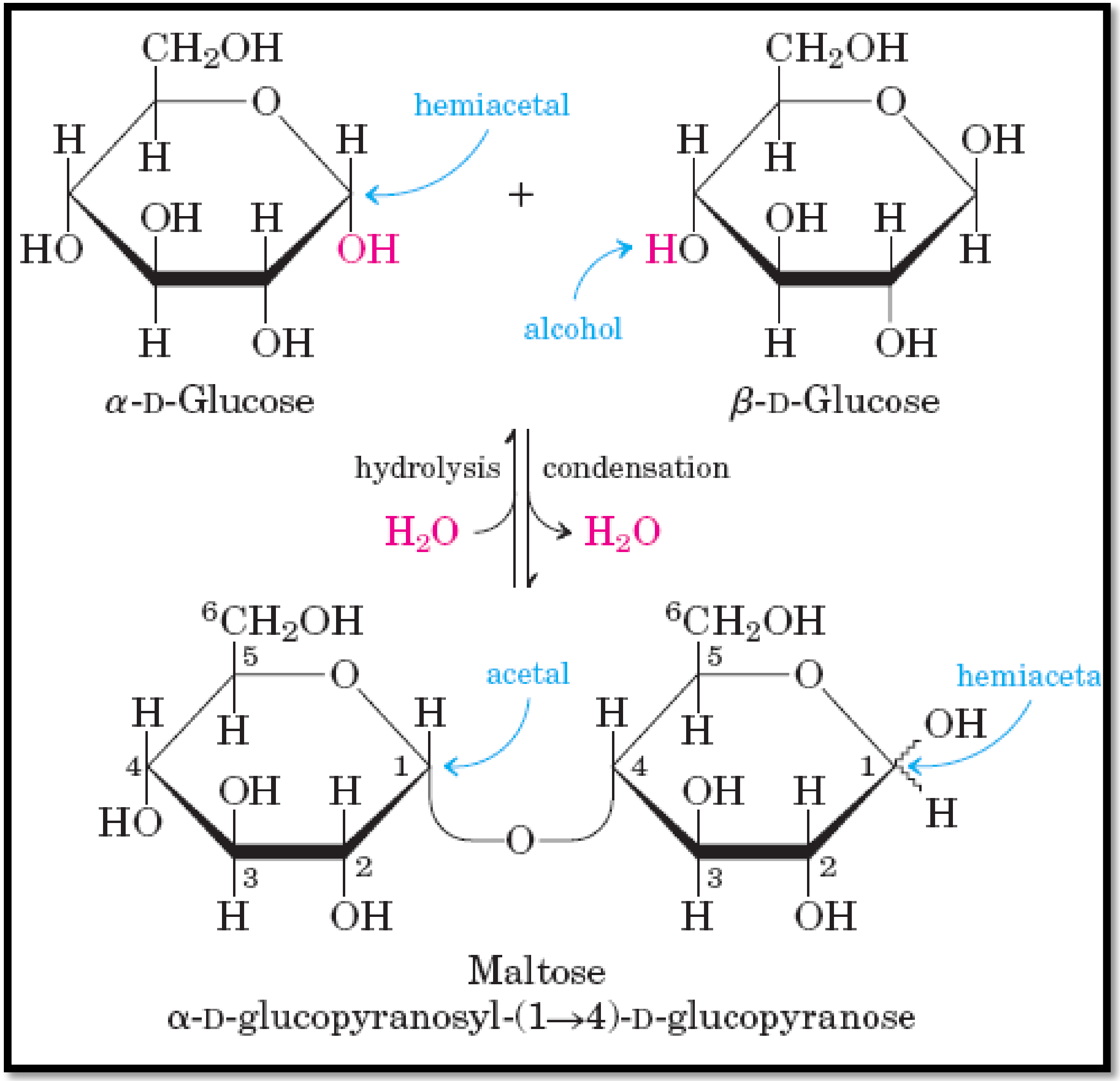


FIGURE 7.17 The anomeric forms of methyl-D-glucoside


Glucose family
Amino sugars
Deoxy sugars
Acidic sugars
β-D-Glucose
β-D-Glucosamine
N-Acetyl-β-D-glucosamine
β-D-Galactosamine
β-D-Mannosamine
β-D-Glucose 6-phosphate
Muramic acid
N-Acetylmuramic acid
β-L-Fucose
α-L-Rhamnose
β-D-Glucuronate
D-Gluconate
D-Glucono-δ-lactone
N-Acetylneuraminic acid
(a sialic acid)


CH2OH
hemiacetal
+
HO
alcohol
OH
α-D-Glucose
β-D-Glucose
hydrolysis
condensation
H2O
H2O
acetal
hemiaceta
Maltose
α-D-glucopyranosyl-(1→4)-D-glucopyranose

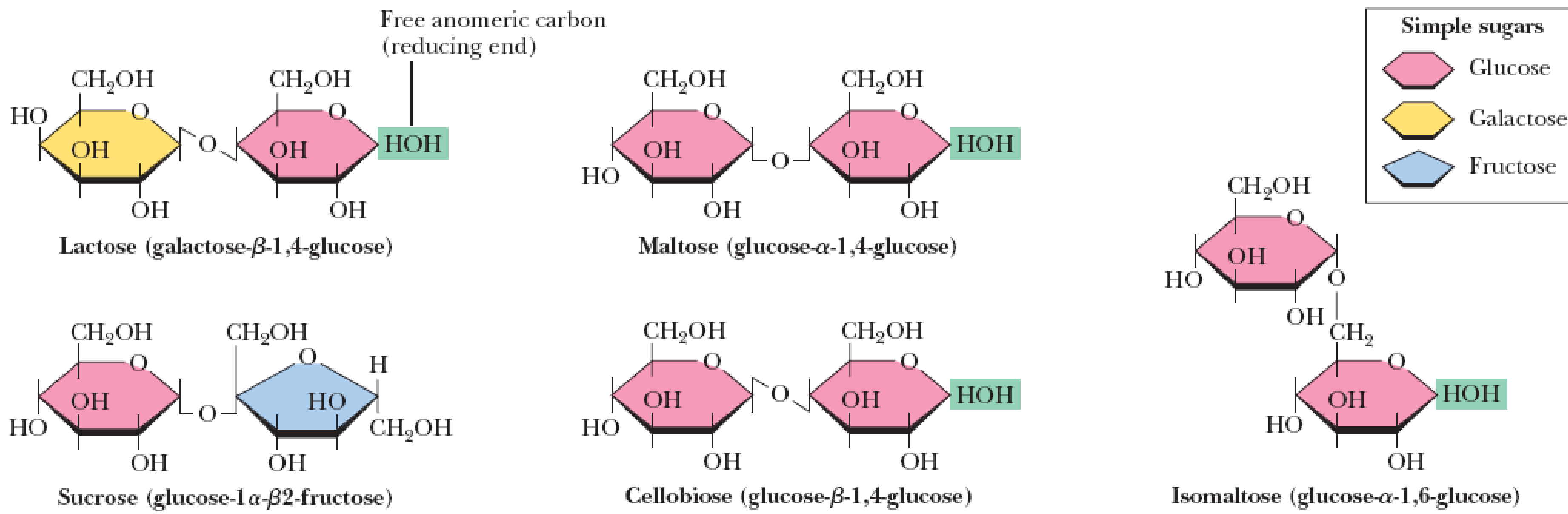
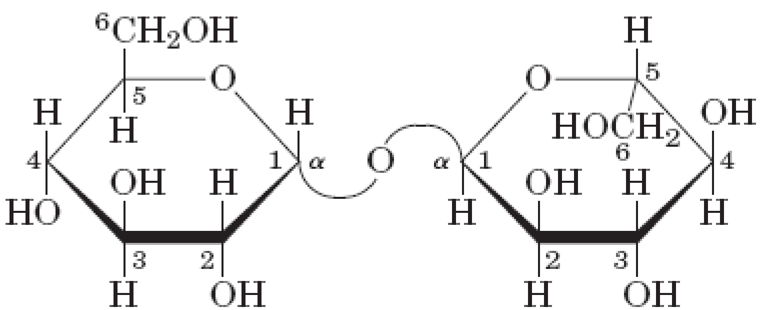


FIGURE 7.18 The structures of several important disaccharides. Note that the notation "HOH" means that the configuration can be either α or β. If the —OH group is above the ring, the configuration is termed β. The configuration is α if the —OH group is below the ring. Also note that sucrose has no free anomeric carbon atom.



Trehalose
α-D-glucopyranosyl α-D-glucopyranoside
Glc(α1↔1α)Glc

Erythromycin **Streptomycin** (a broad-spectrum antibiotic)

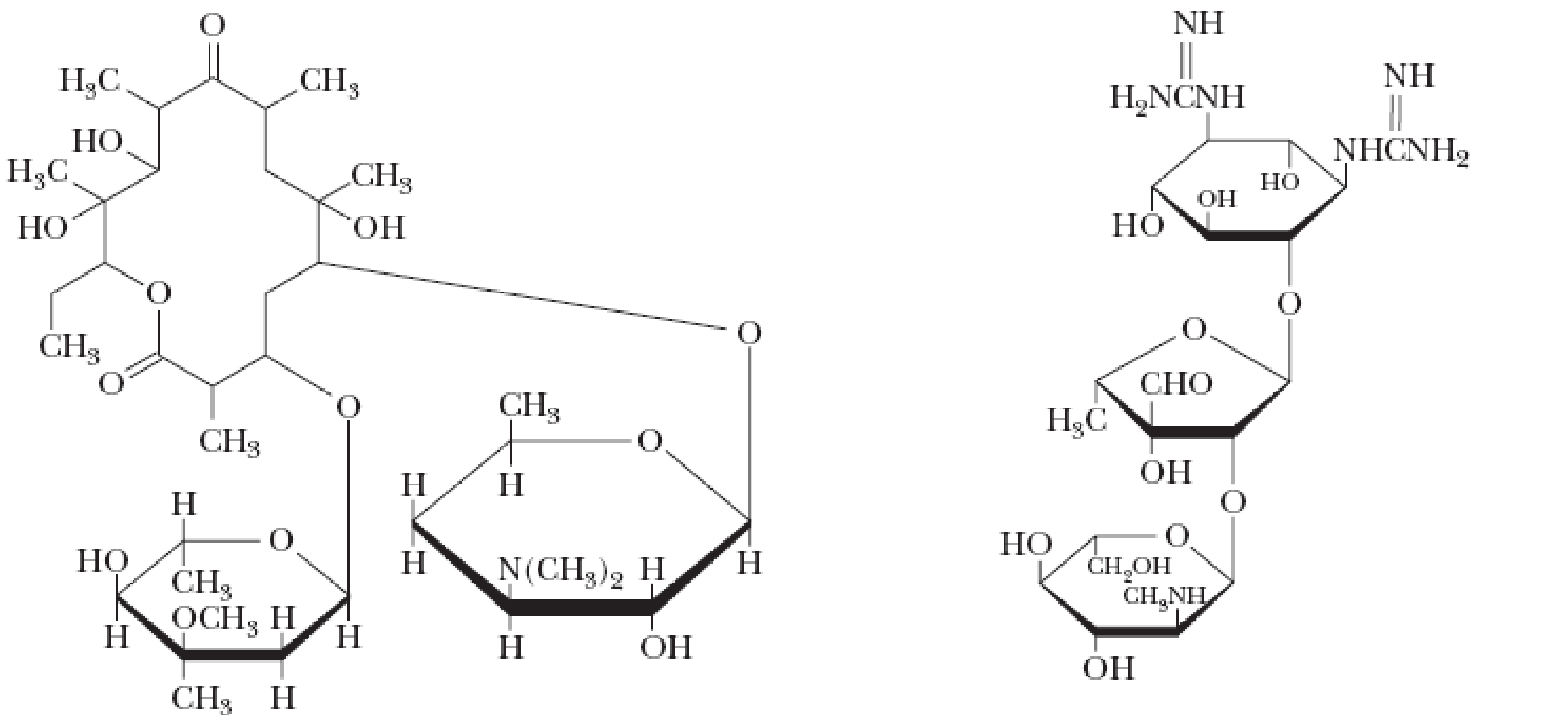


FIGURE 7.19 Some antibiotics are oligosaccharides or contain oligosaccharide groups.

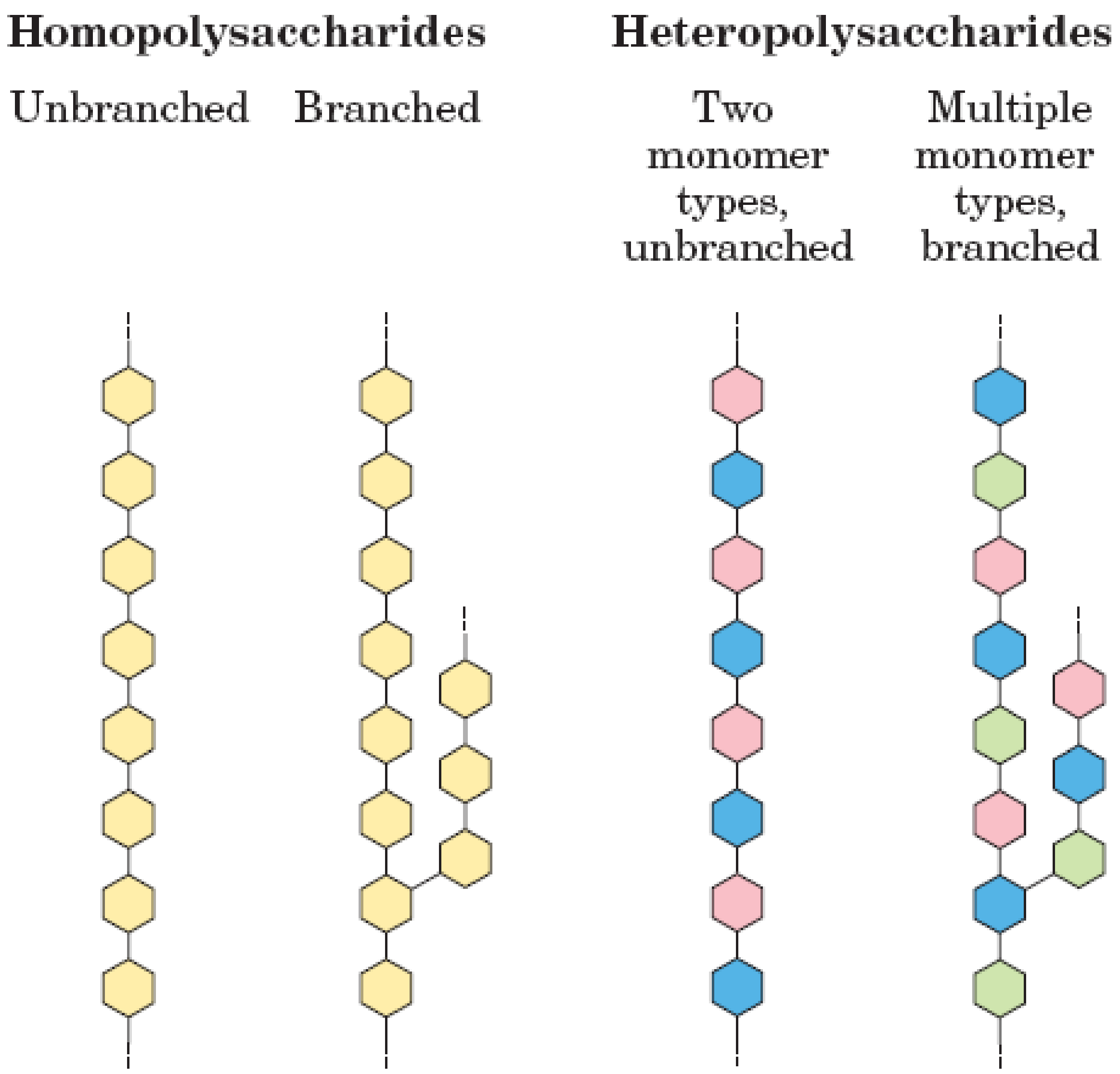
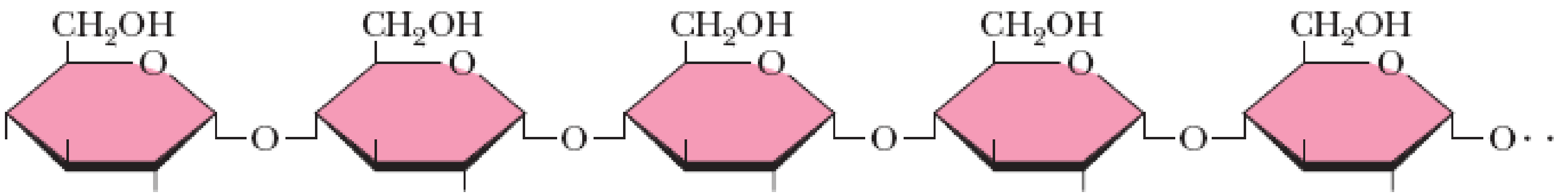
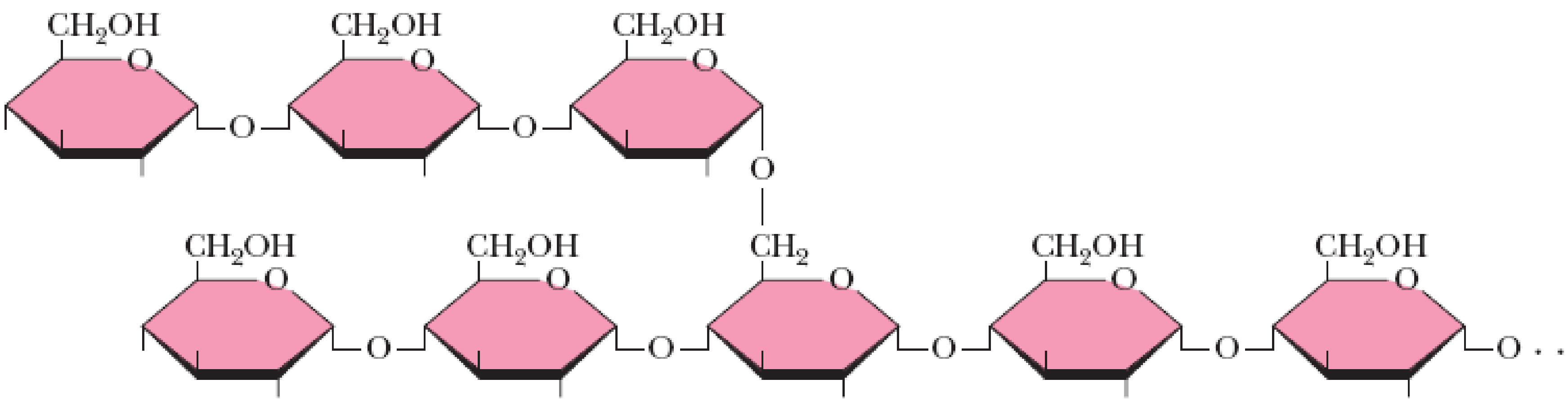


FIGURE 7–13 Homo- and heteropolysaccharides. Polysaccharides may be composed of one, two, or several different monosaccharides, in straight or branched chains of varying length.



Amylose

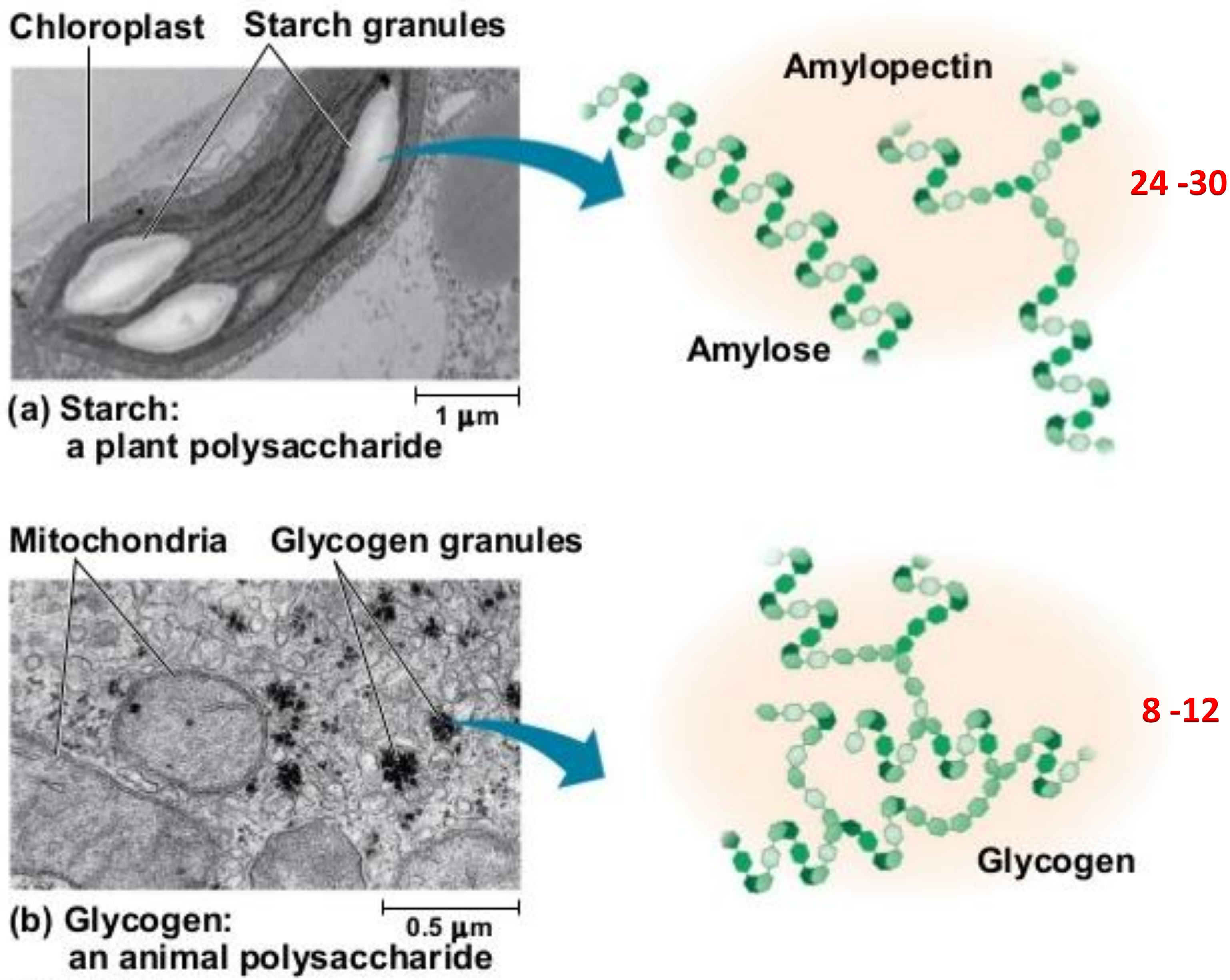
10 -30 %

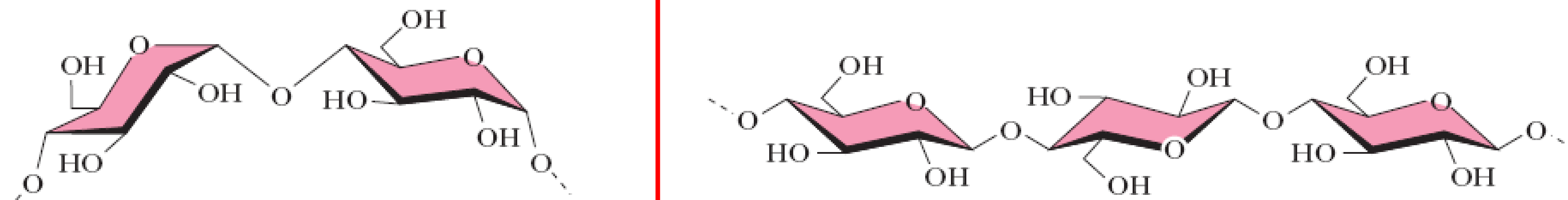


Amylopectin

70 - 90%

FIGURE 7.20 Amylose and amylopectin are the two forms of starch. Note that the linear linkages are $\alpha(1\longrightarrow4)$ but the branches in amylopectin are $\alpha(1\longrightarrow6)$. Branches in polysaccharides can involve any of the hydroxyl groups on the monosaccharide components. Amylopectin is a highly branched structure, with branches occurring every 12 to 30 residues.


Chloroplast
Starch granules
Amylopectin
24 -30
Amylose
(a) Starch:
a plant polysaccharide
1 μm
Mitochondria
Glycogen granules
8 -12
Glycogen
(b) Glycogen:
an animal polysaccharide
0.5 μm



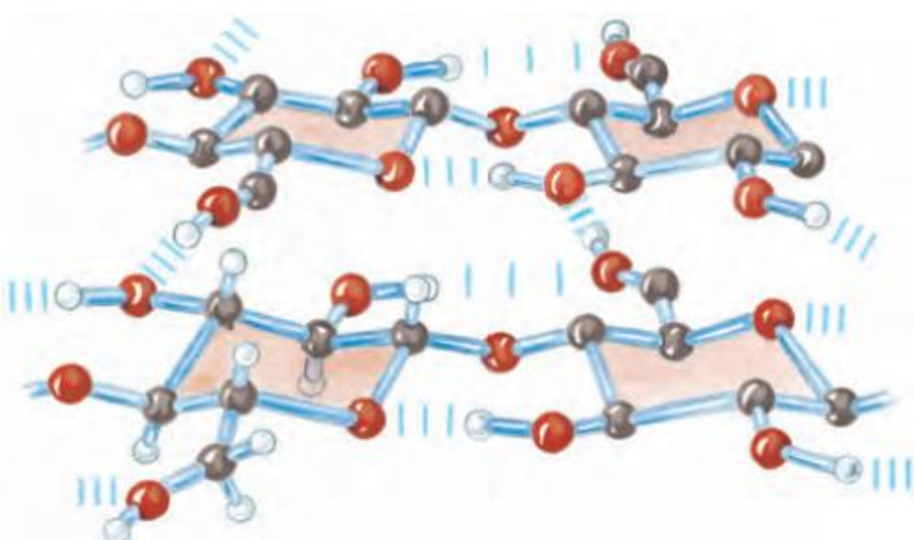
α-1,4-Linked D-glucose units

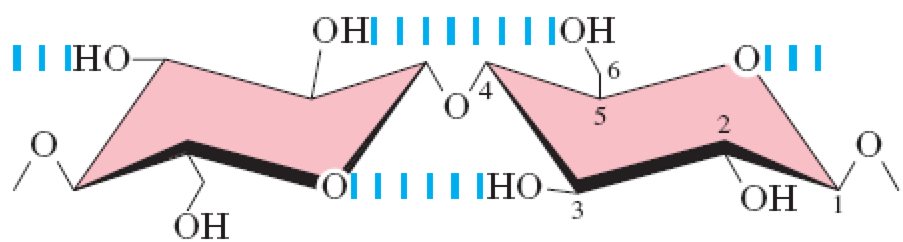
(a)

β-1,4-Linked D-glucose units

(b)

FIGURE 7.23 (a) Amylose, composed exclusively of the relatively bent $\alpha(1 \longrightarrow 4)$ linkages, prefers to adopt a helical conformation, whereas (b) cellulose, with $\beta(1 \longrightarrow 4)$-glycosidic linkages, can adopt a fully extended conformation with alternating 180° flips of the glucose units. The hydrogen bonding inherent in such extended structures is responsible for the great strength of tree trunks and other cellulose-based materials.





(β1→4)-linked D-glucose units

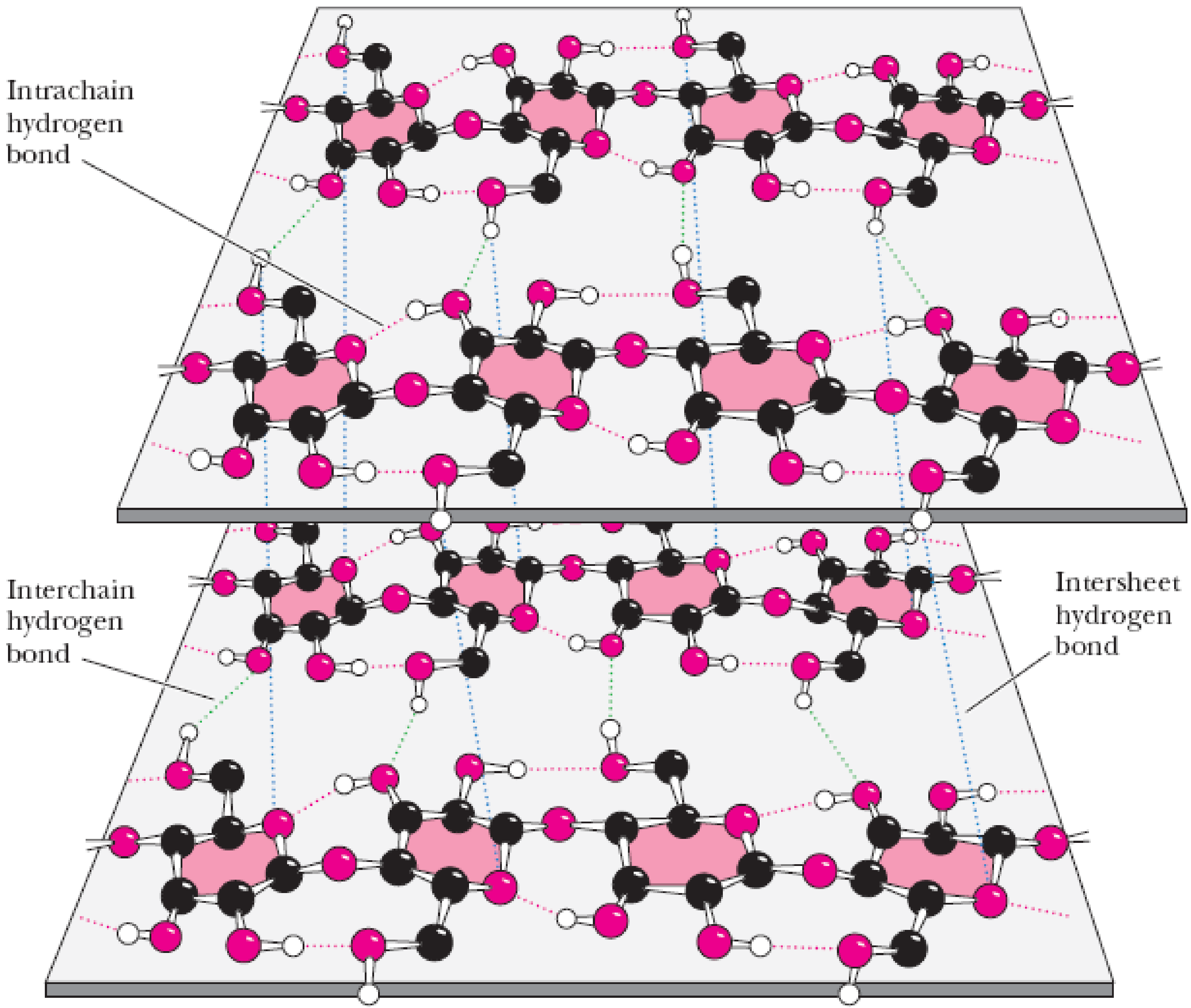


FIGURE 7.24 The structure of cellulose, showing the hydrogen bonds (blue) between the sheets, which strengthen the structure. Intrachain hydrogen bonds are in red, and interchain hydrogen bonds are in green. (Illustration: Irving Geis. Rights owned by Howard Hughes Medical Institute. Not to be reproduced without permission.)

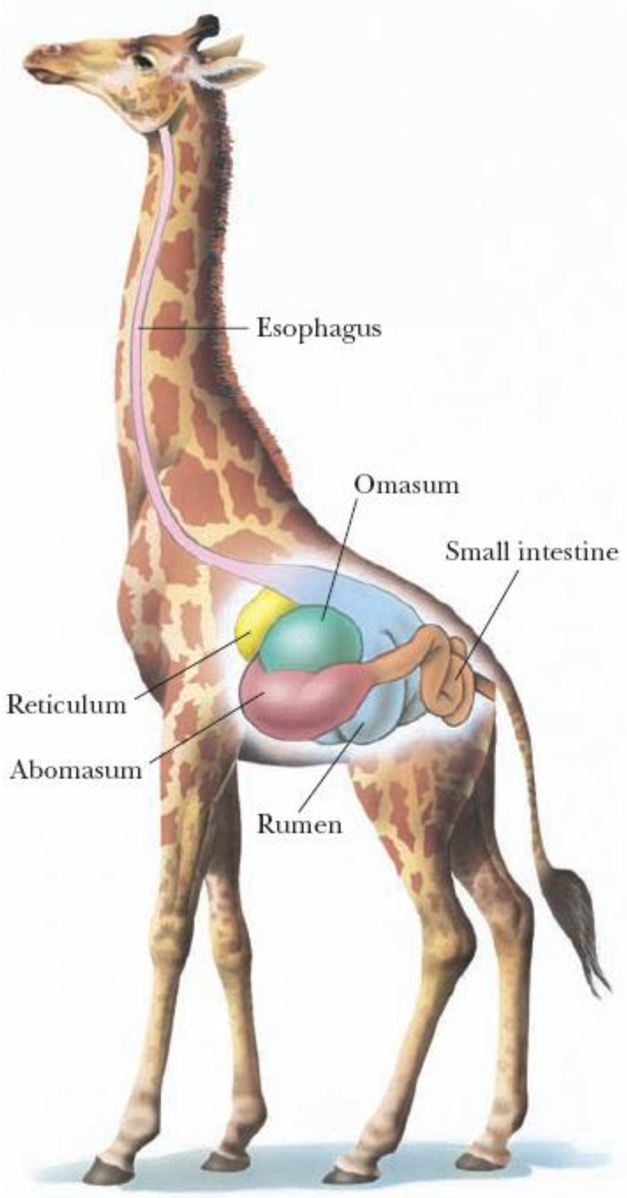
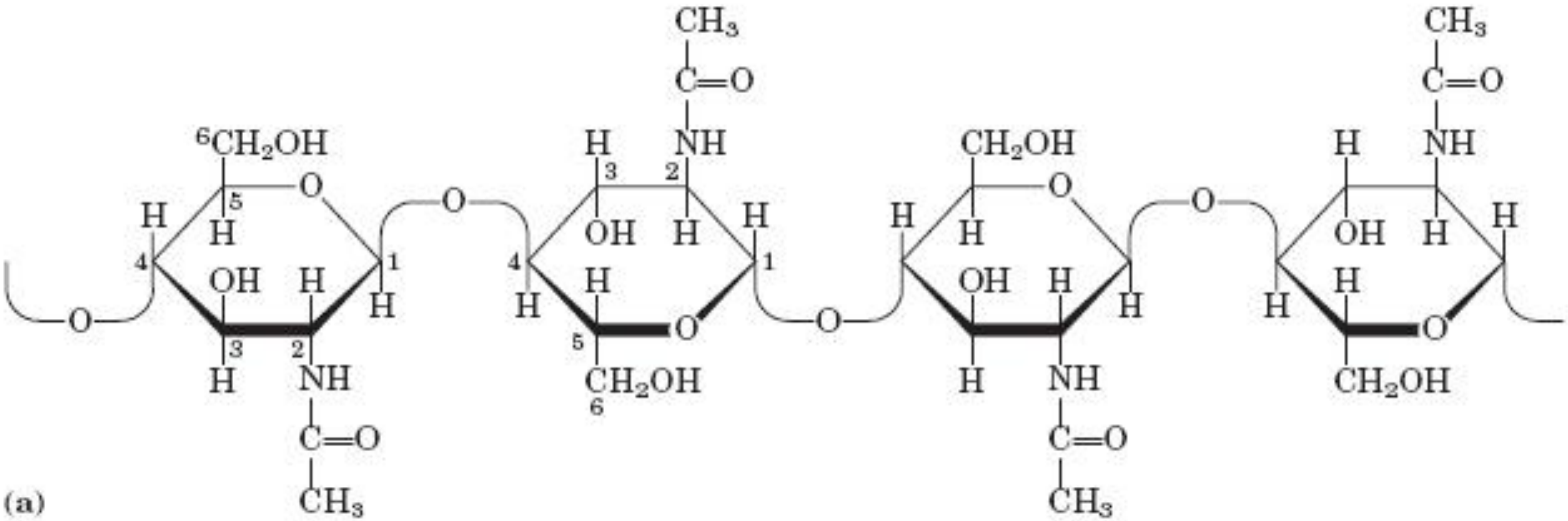


FIGURE 7.25 Giraffes, cattle, deer, and camels are ruminant animals that are able to metabolize cellulose, thanks to bacterial cellulase in the rumen, a large first compartment in the stomach of a ruminant.



(a)

(b)

FIGURE 7–18 Chitin. (a) A short segment of chitin, a homopolymer of *N*-acetyl-D-glucosamine units in (β1⟶4) linkage. (b) A spotted June beetle (*Pellidnota punetatia*), showing its surface armor (exoskeleton) of chitin.

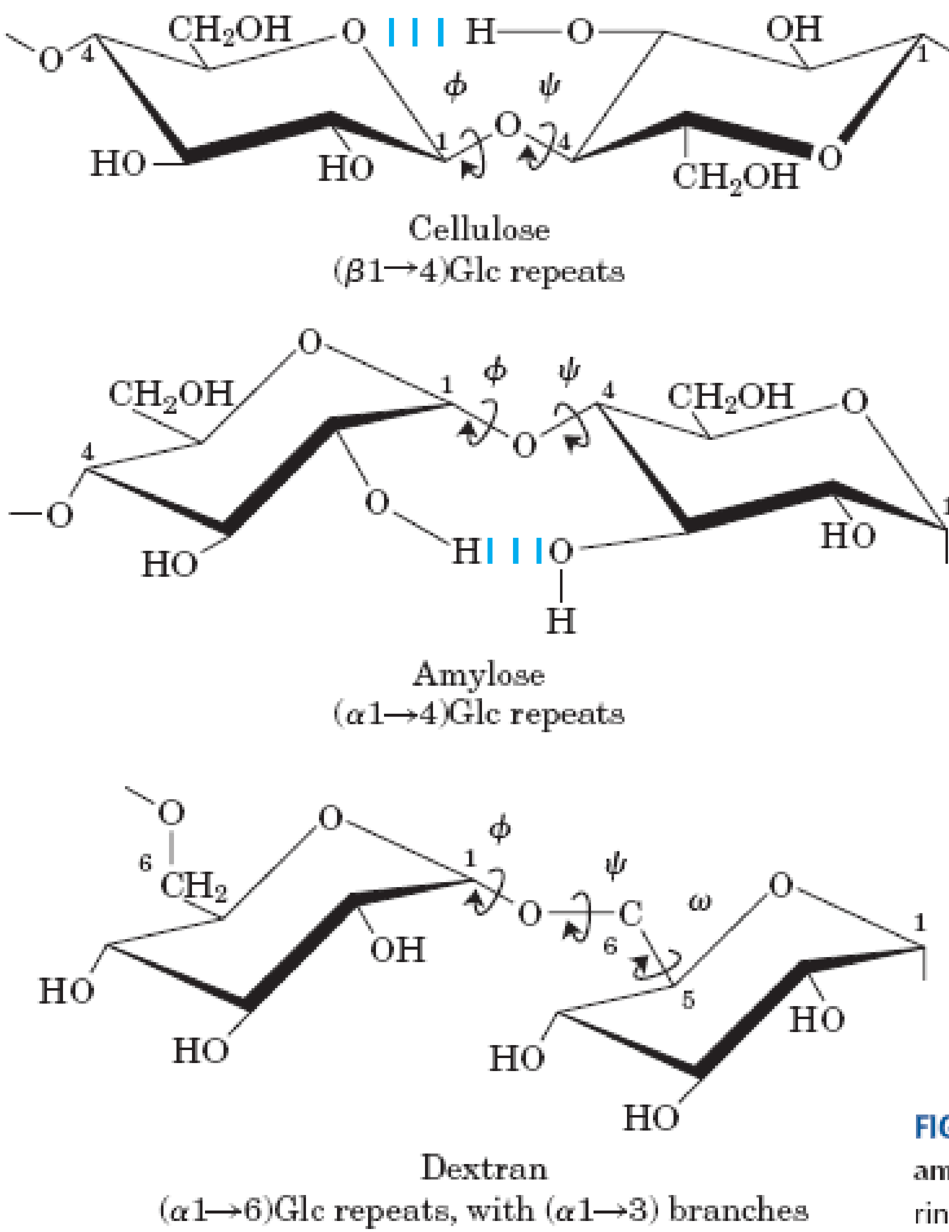
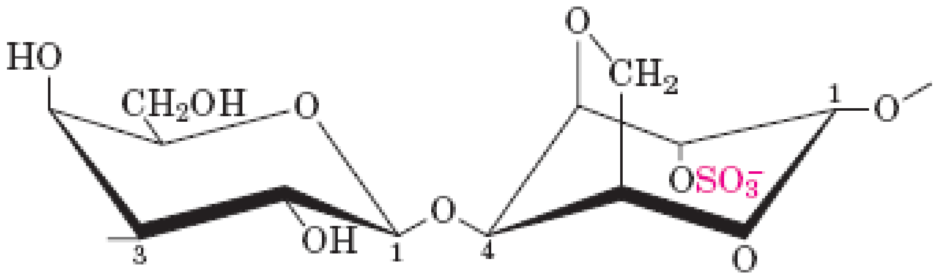


FIGURE 7–19 Conformation at the glycosidic bonds of cellulose, amylose, and dextran. The polymers are depicted as rigid pyranose rings joined by glycosidic bonds, with free rotation about these bonds. Note that in dextran there is also free rotation about the bond between C-5 and C-6 (torsion angle ω (omega)).

Bacterial and Algal Cell Walls Contain Structural Heteropolysaccharides



Agarose
3)D-Gal(β1→4)3,6-anhydro-L-Gal2S(α1 repeats

FIGURE 7–23 The structure of agarose. The repeating unit consists of D-galactose (β1→4)-linked to 3,6-anhydro-L-galactose (in which an ether ring connects C-3 and C-6). These units are joined by (α1→3) glycosidic links to form a polymer 600 to 700 residues long. A small fraction of the 3,6-anhydrogalactose residues have a sulfate ester at C-2 (as shown here).

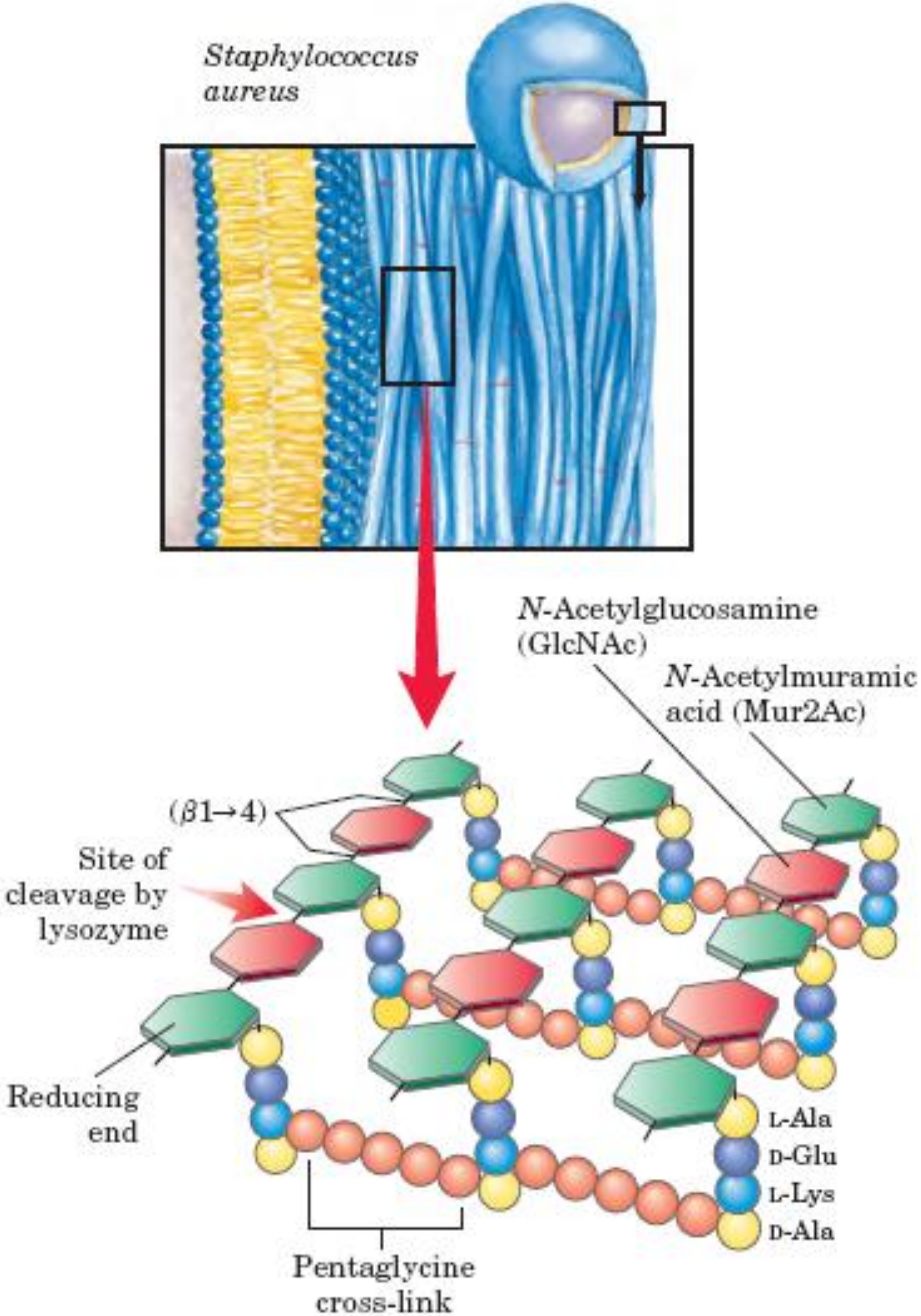
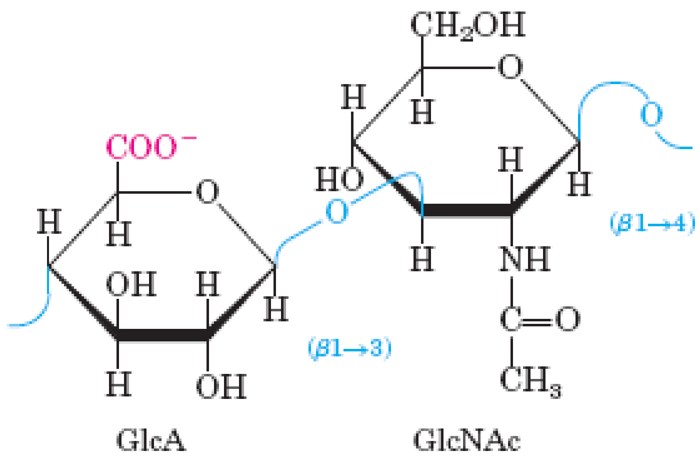
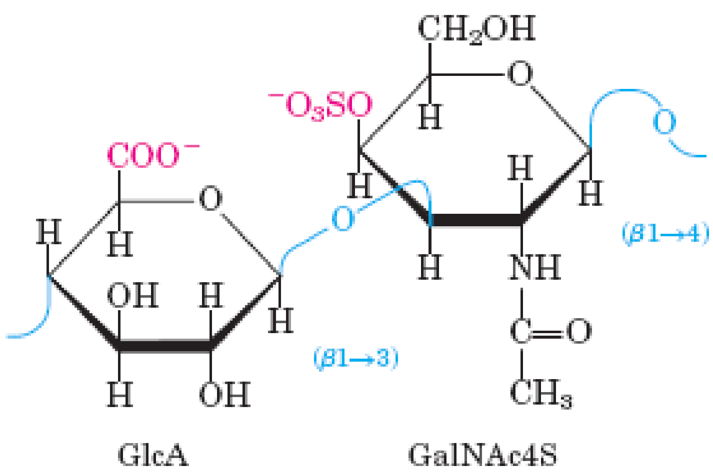
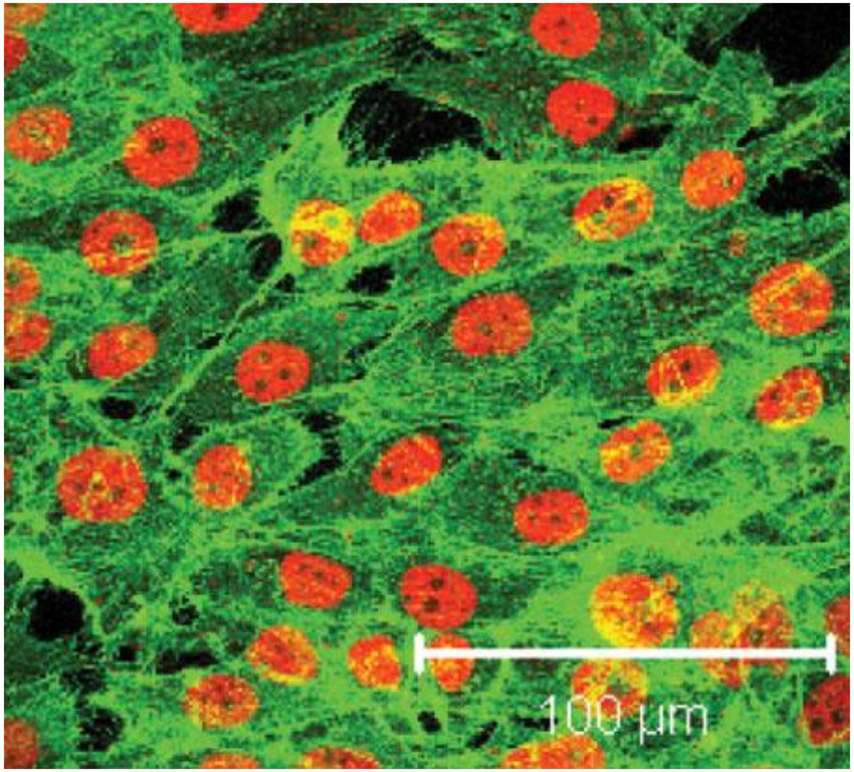
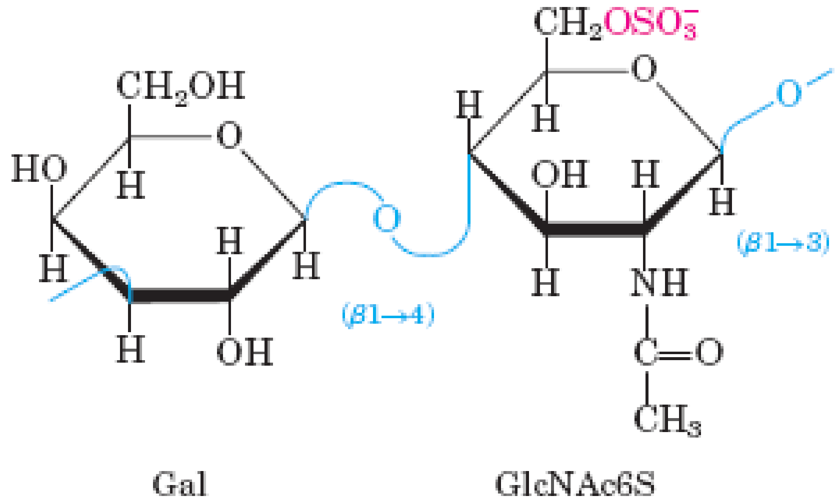
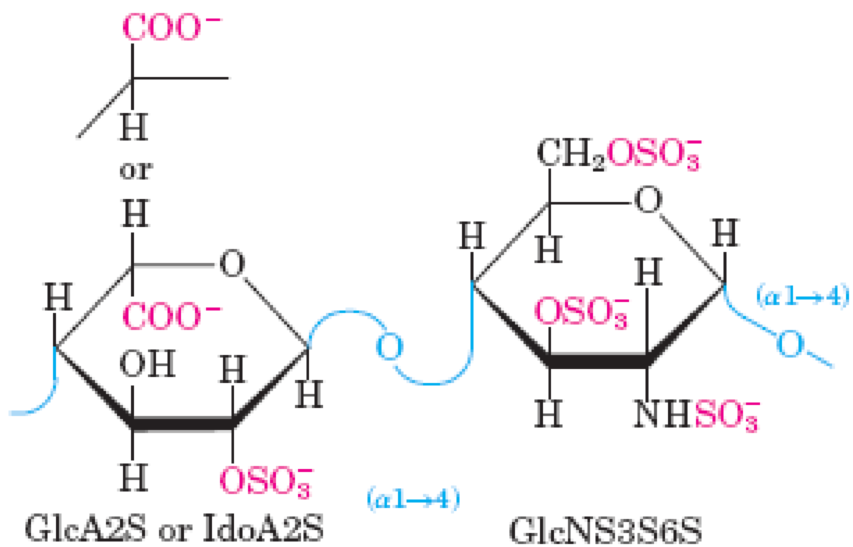


FIGURE 7–22 Peptidoglycan. Shown here is the peptidoglycan of the cell wall of *Staphylococcus aureus,* a gram-positive bacterium. Peptides (strings of colored spheres) covalently link *N*-acetylmuramic acid residues in neighboring polysaccharide chains. Note the mixture of L and D amino acids in the peptides. Gram-positive bacteria have a pentaglycine chain in the cross-link. Gram-negative bacteria, such as *E. coli,* lack the pentaglycine; instead, the terminal D-Ala residue of one tetrapeptide is attached directly to a neighboring tetrapeptide through either L-Lys or a lysine-like amino acid, diaminopimelic acid.

Glycosaminoglycans Are Heteropolysaccharides of the Extracellular Matrix

Glycosaminoglycan Number of disaccharides per chain	Repeating disaccharide
Hyaluronate ~50,000	
Chondroitin 4-sulfate 20–60	



Glycosaminoglycan Number of disaccharides per chain	Repeating disaccharide
Keratan sulfate ~25	
Heparin 15–90	

Glycoconjugates:

- ✓Proteoglycans
- ✓Glycoproteins
- ✓Glycolipids
- ✓ Lipopolysaccharides

نقش گلیکوکونژوگه ها

- ❑در میان کنش سلول با محیط خارج سلولی آن نقش دارد.
- ❑نشان دار کردن پروتئین ها برای انتقال به یک ارگانل یا مکان خاص در سلول و یا تخریب پروتئین های misfold
- ❑جایگاه شناسایی مولکول های پیام رسان خارج سلولی (مانند فاکتورهای رشد) یا انگل های خارج سلولی (باکتری یا ویروس)

هر سلول یوکاریوتی دارای یک پوشش الیگوساکاریدی به ضخامت چندنانومتر به نام Glycocalyx است (بخش های الیگوساکاریدی به غشای پلاسمایی سلول متصل هستند). این الیگوساکاریدها نقش های مهمی دارند:

- cell–cell recognition and adhesion,
- cell migration during development,
- blood clotting,
- immune response,
- wound healing,
- other cellular processes

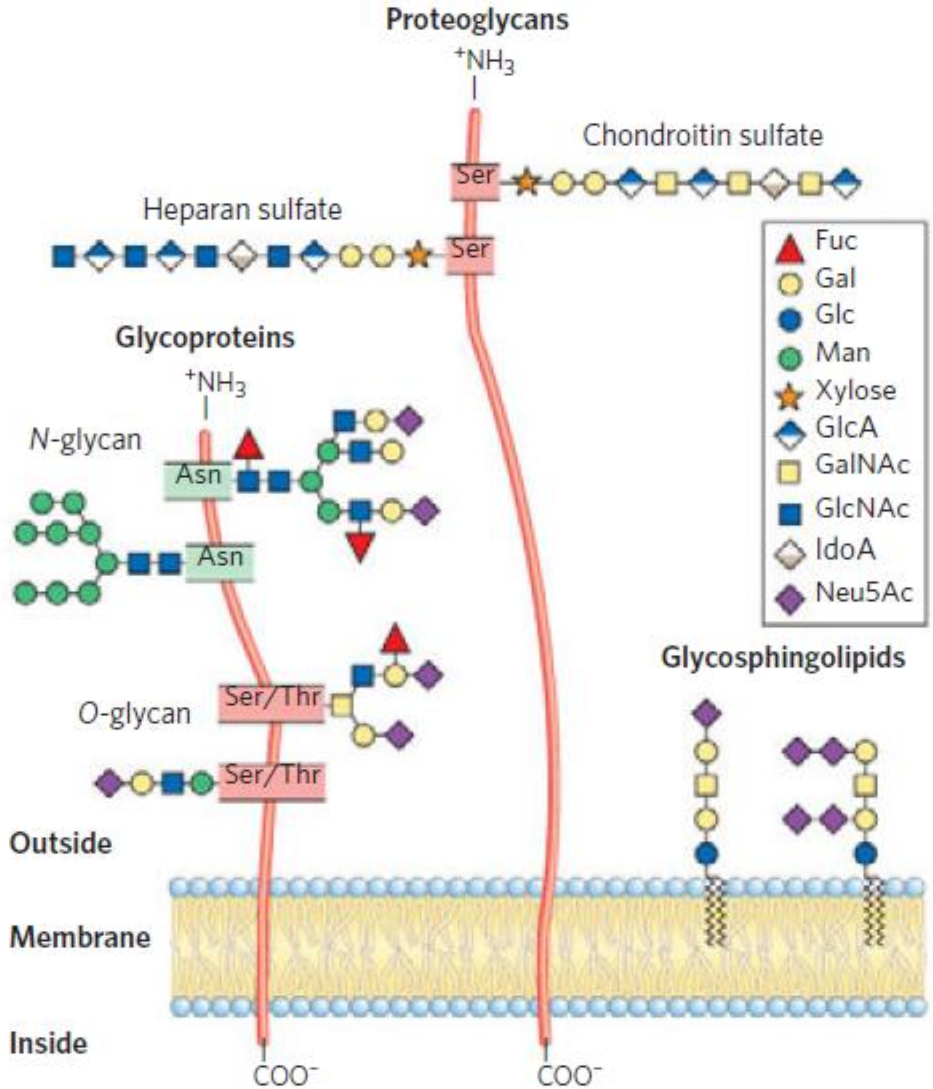


FIGURE 7–24 Glycoconjugates. The structures of some typical proteoglycans, glycoproteins, and glycosphingolipids described in the text.

Proteoglycans Are Glycosaminoglycan-Containing Macromolecules of the Cell Surface and Extracellular Matrix

Proteoglycans

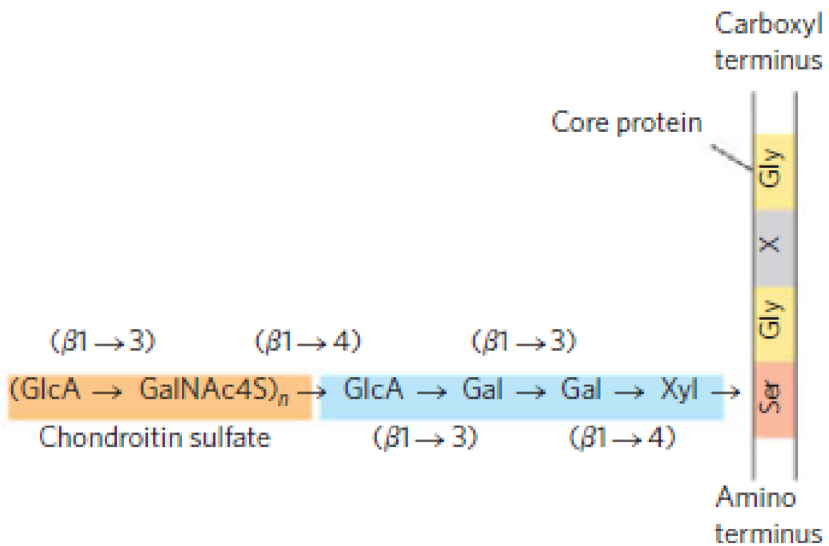
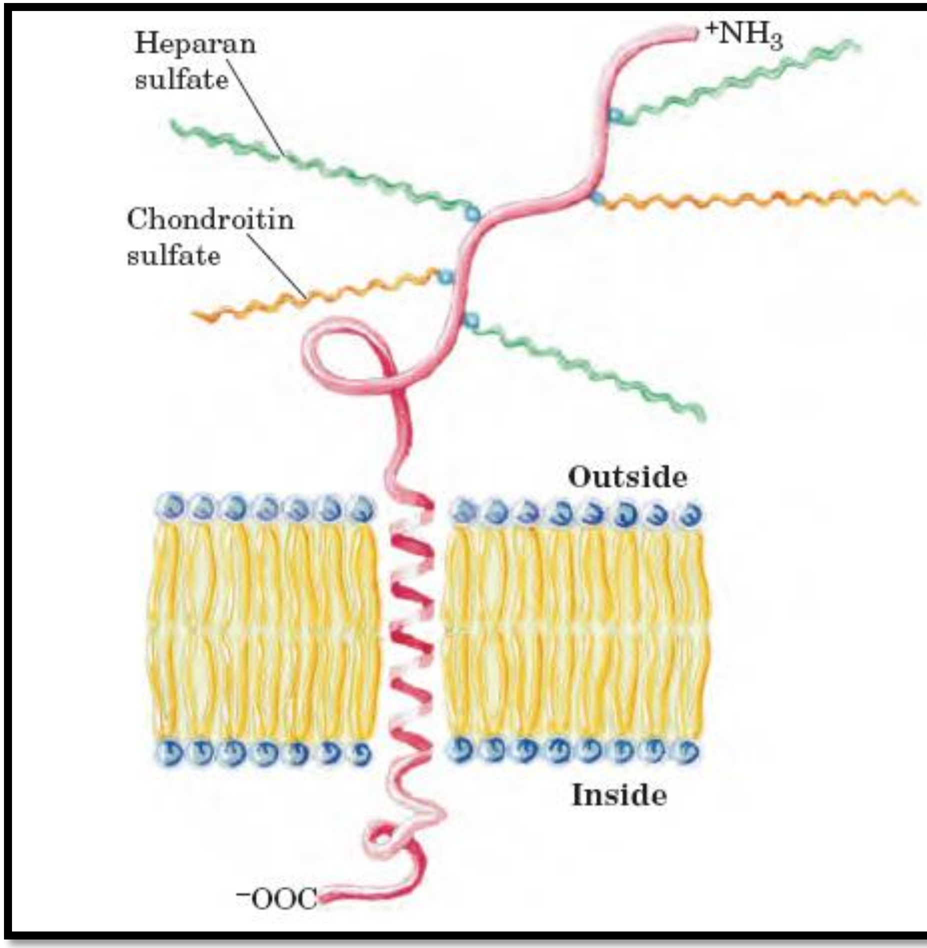


FIGURE 7–25 Proteoglycan structure, showing the tetrasaccharide bridge. A typical tetrasaccharide linker (blue) connects a glycosaminoglycan—in this case chondroitin 4-sulfate (orange)—to a Ser residue in the core protein. The xylose residue at the reducing end of the linker is joined by its anomeric carbon to the hydroxyl of the Ser residue.



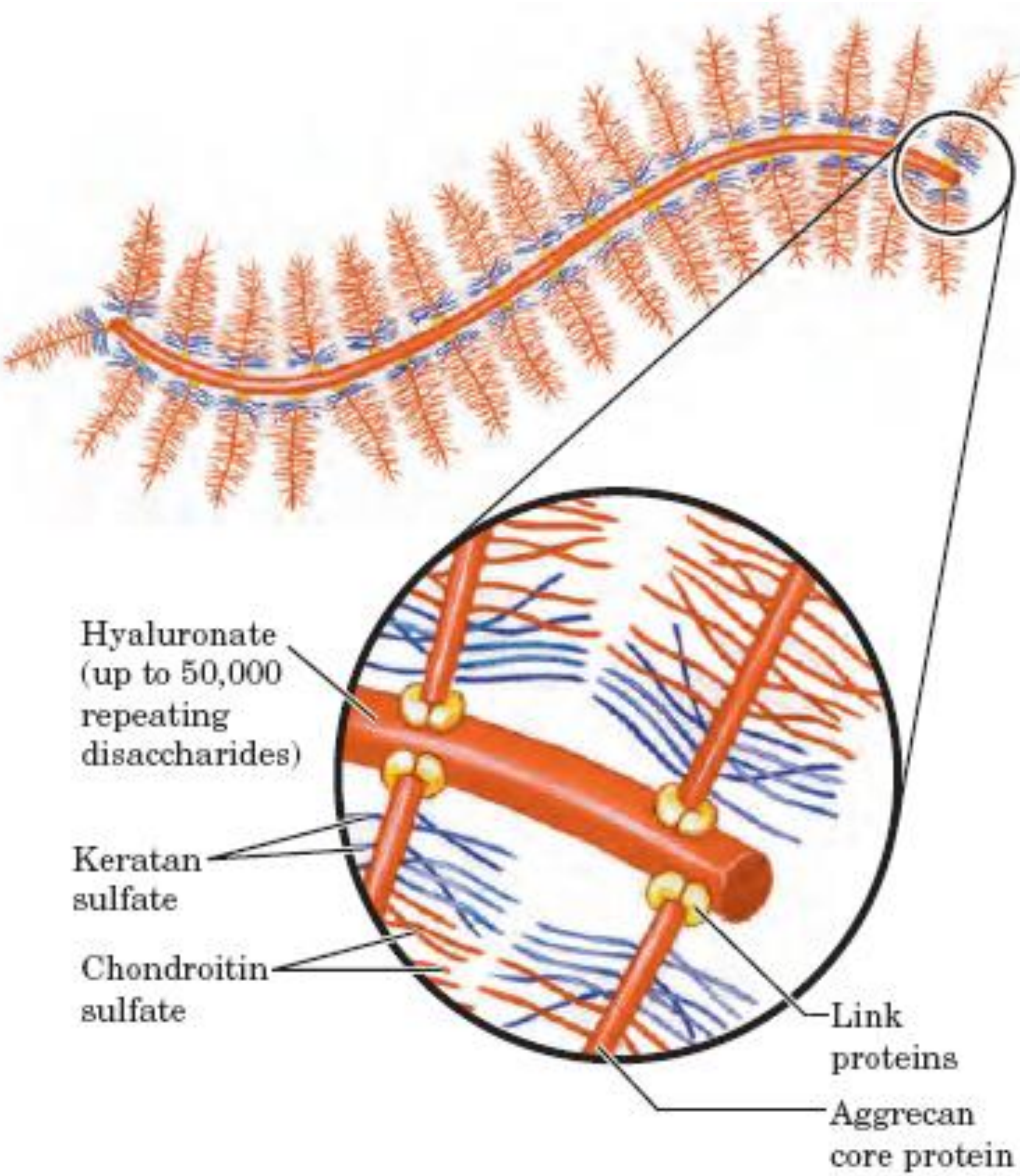
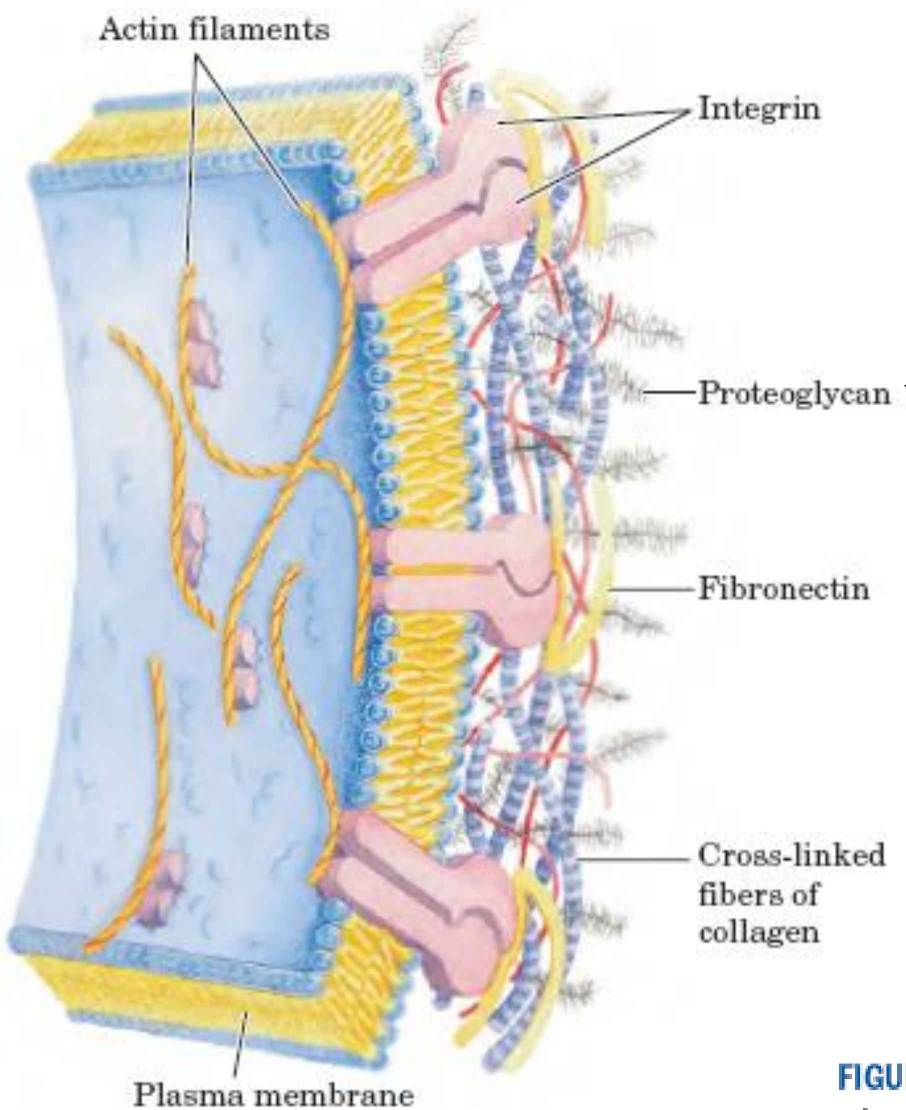


FIGURE 7–29 Proteoglycan aggregate of the extracellular matrix. One very long molecule of hyaluronate is associated noncovalently with about 100 molecules of the core protein aggrecan. Each aggrecan molecule contains many covalently bound chondroitin sulfate and keratan sulfate chains. Link proteins situated at the junction between each core protein and the hyaluronate backbone mediate the core protein–hyaluronate interaction.



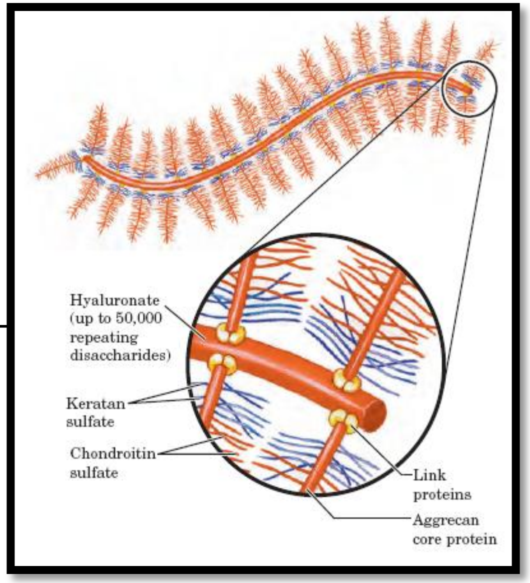


FIGURE 7–30 Interactions between cells and the extracellular matrix. The association between cells and the proteoglycan of the extracellular matrix is mediated by a membrane protein (integrin) and by an extracellular protein (fibronectin in this example) with binding sites for both integrin and the proteoglycan. Note the close association of collagen fibers with the fibronectin and proteoglycan.

Glycoproteins

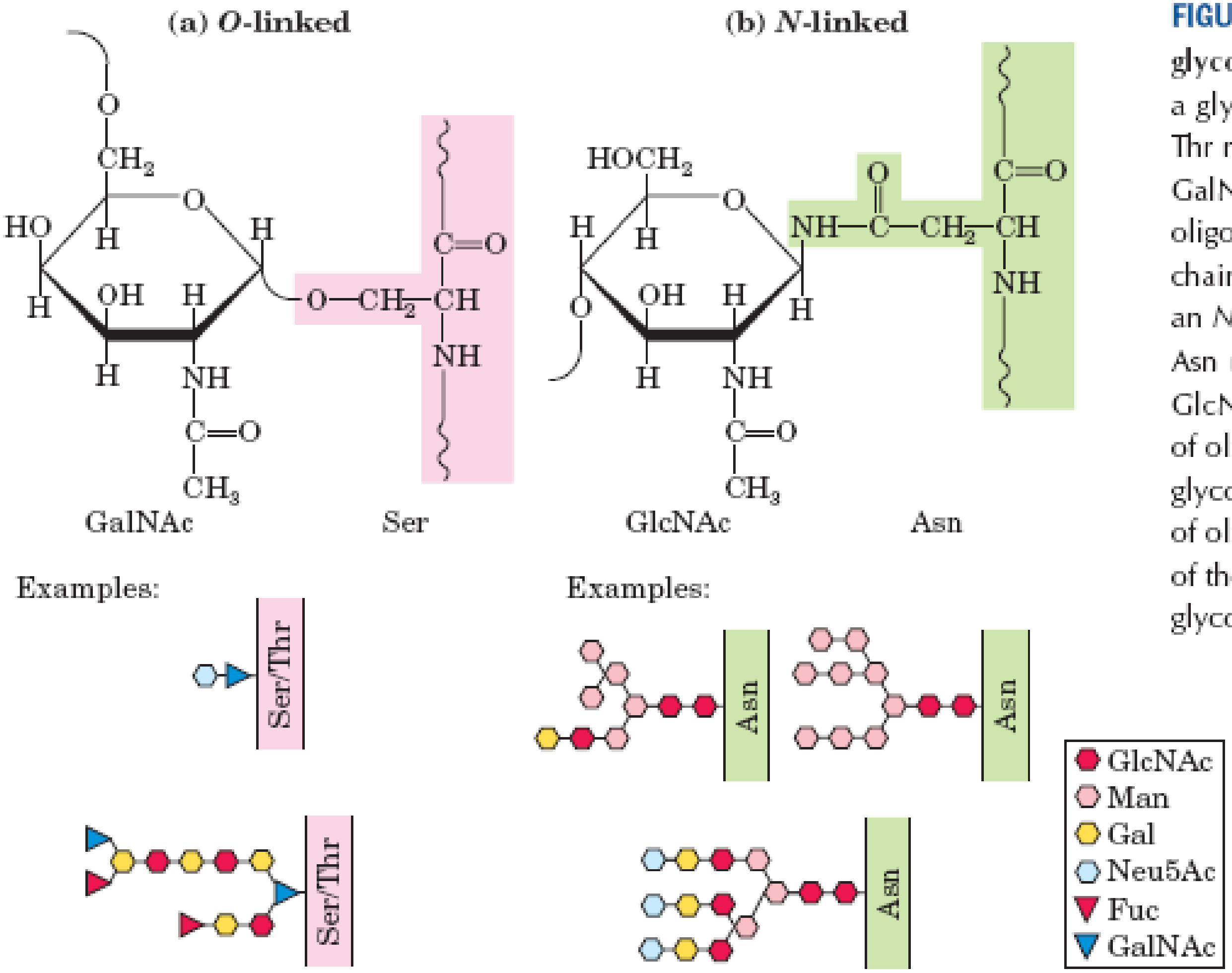


FIGURE 7–31 Oligosaccharide linkages in glycoproteins. (a) *O*-linked oligosaccharides have a glycosidic bond to the hydroxyl group of Ser or Thr residues (shaded pink), illustrated here with GalNAc as the sugar at the reducing end of the oligosaccharide. One simple chain and one complex chain are shown. (b) *N*-linked oligosaccharides have an *N*-glycosyl bond to the amide nitrogen of an Asn residue (shaded green), illustrated here with GlcNAc as the terminal sugar. Three common types of oligosaccharide chains that are *N*-linked in glycoproteins are shown. A complete description of oligosaccharide structure requires specification of the position and stereochemistry (α or β) of each glycosidic linkage.

Glycolipids

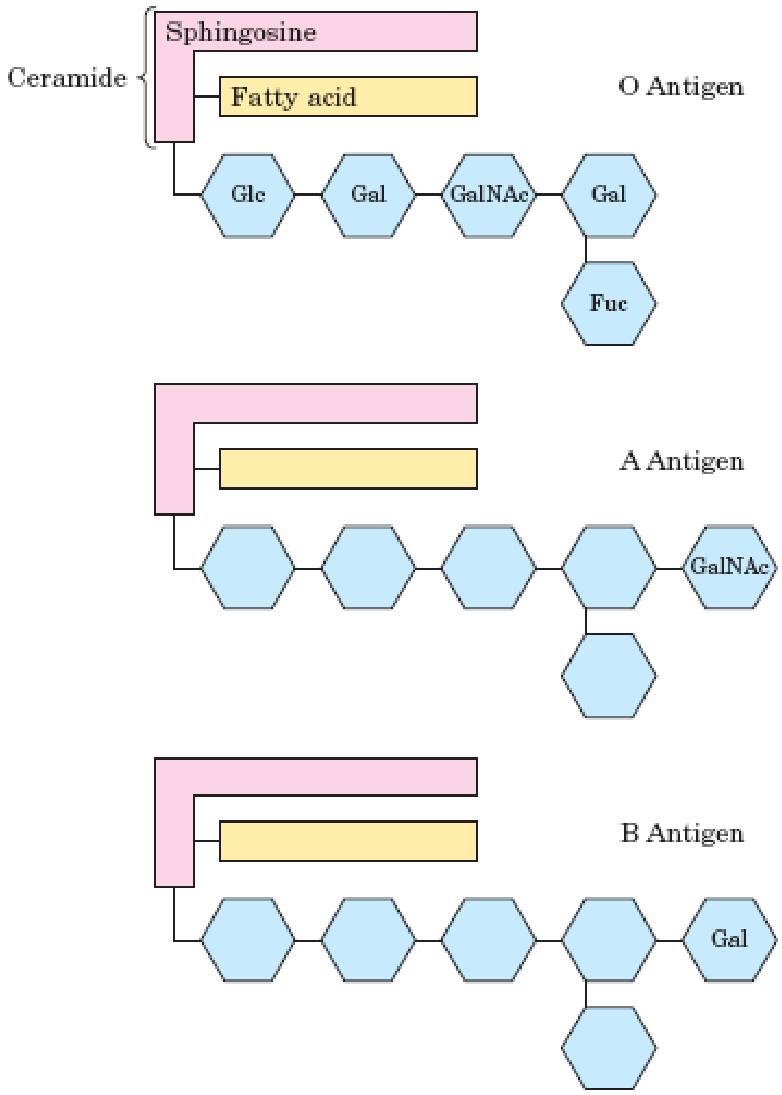
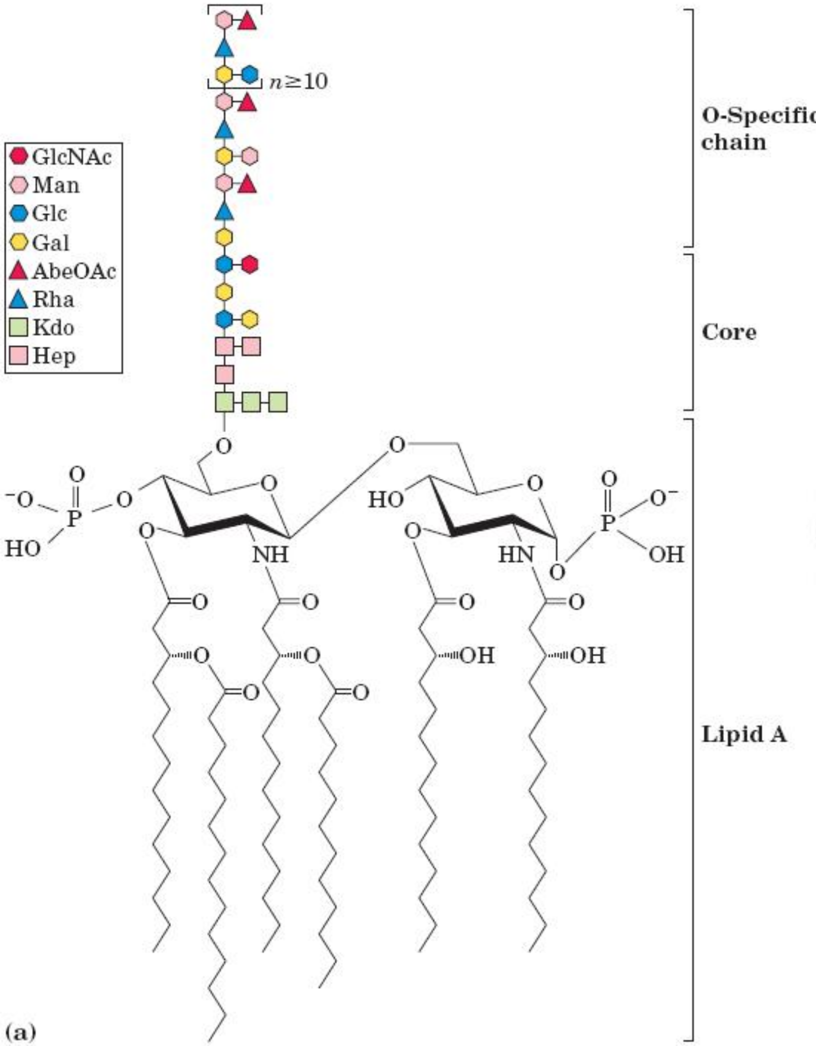


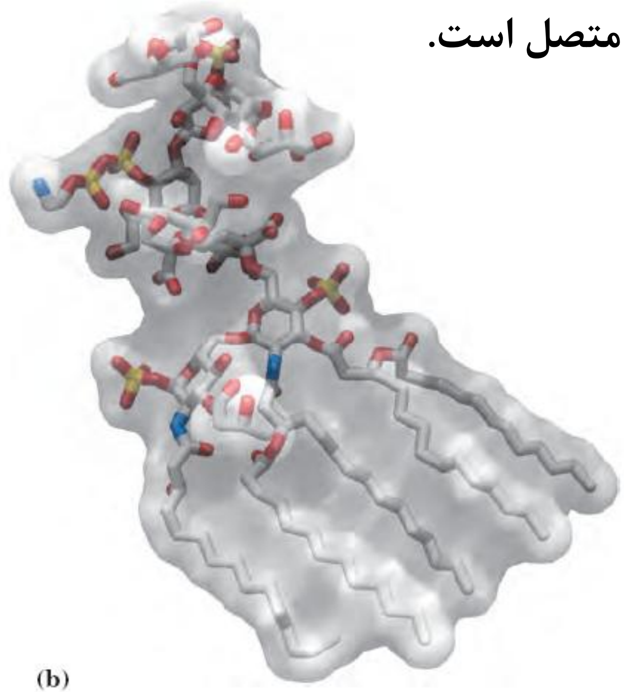
FIGURE 10–14 Glycosphingolipids as determinants of blood groups. The human blood groups (O, A, B) are determined in part by the oligosaccharide head groups (blue) of these glycosphingolipids. The same three oligosaccharides are also found attached to certain blood proteins of individuals of blood types O, A, and B, respectively. (Fuc represents the sugar fucose.)

•شش اسید چرب متصل به دو N–استیل گلوکز آمین

•یکی از N–استیل گلوکز آمین ها به یک کمپلکس الیگوساکاریدی متصل است.



(a)



(b)

FIGURE 7–32 Bacterial lipopolysaccharides. **(a)** Schematic diagram of the lipopolysaccharide of the outer membrane of *Salmonella typhimurium.* Kdo is 3-deoxy-D-manno-octulosonic acid, previously called *ketodeoxyoctonic* acid; Hep is L-glycero-D-mannoheptose; AbeOAc is abequose (a 3,6-dideoxyhexose) acetylated on one of its hydroxyls. There are six fatty acids in the lipid A portion of the molecule. Different bacterial species have subtly different lipopolysaccharide structures, but they have in common a lipid region (lipid A), a core oligosaccharide, and an "O-specific" chain, which is the principal determinant of the serotype (immunological reactivity) of the bacterium. The outer membranes of the gram-negative bacteria *S. typhimurium* and *E. coli* contain so many lipopolysaccharide molecules that the cell surface is virtually covered with O-specific chains. **(b)** The stick structure of the lipopolysaccharide of *E. coli* is visible through a transparent surface contour model of the molecule. The position of the sixth fatty acyl chain was not defined in the crystallographic study, so it is not shown.

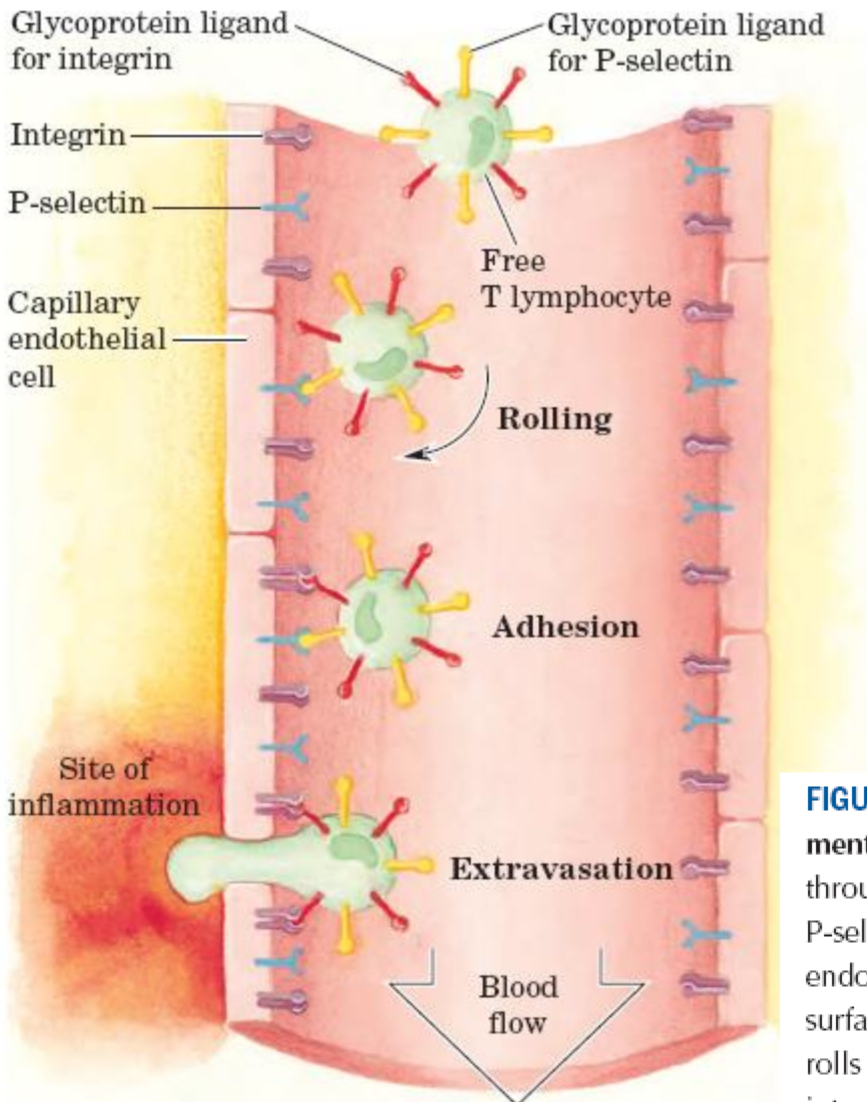


FIGURE 7–33 Role of lectin-ligand interactions in lymphocyte movement to the site of an infection or injury. A T lymphocyte circulating through a capillary is slowed by transient interactions between P-selectin molecules in the plasma membrane of the capillary endothelial cells and glycoprotein ligands for P-selectin on the T-cell surface. As it interacts with successive P-selectin molecules, the T cell rolls along the capillary surface. Near a site of inflammation, stronger interactions between integrin in the capillary surface and its ligand in the T-cell surface lead to tight adhesion. The T cell stops rolling and, under the influence of signals sent out from the site of inflammation, begins extravasation—escape through the capillary wall—as it moves toward the site of inflammation.

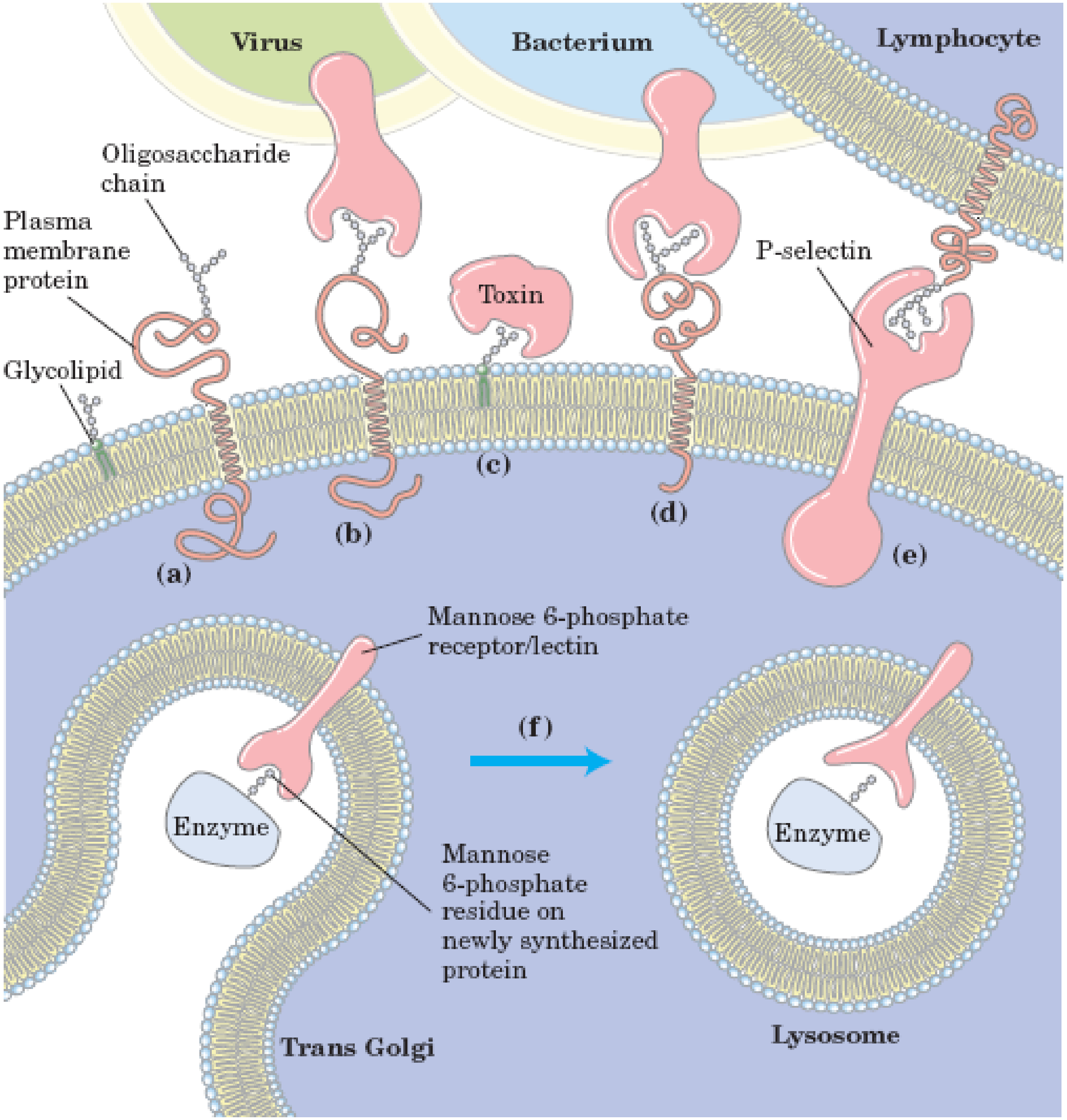


FIGURE 7–37 Roles of oligosaccharides in recognition and adhesion at the cell surface. (a) Oligosaccharides with unique structures (represented as strings of hexagons), components of a variety of glycoproteins or glycolipids on the outer surface of plasma membranes, interact with high specificity and affinity with lectins in the extracellular milieu. (b) Viruses that infect animal cells, such as the influenza virus, bind to cell surface glycoproteins as the first step in infection. (c) Bacterial toxins, such as the cholera and pertussis toxins, bind to a surface glycolipid before entering a cell. (d) Some bacteria, such as *H. pylori*, adhere to and then colonize or infect animal cells. (e) Selectins (lectins) in the plasma membrane of certain cells mediate cell-cell interactions, such as those of T lymphocytes with the endothelial cells of the capillary wall at an infection site. (f) The mannose 6-phosphate receptor/lectin of the trans Golgi complex binds to the oligosaccharide of lysosomal enzymes, targeting them for transfer into the lysosome.