

BIOCHEMISTRY: LS2101

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Syllabus

Introductory biochemistry: biological interactions.

Amino acids

•Protein structure and folding, Enzymology, Enzyme kinetics, and allostery. vitamins and coenzymes.

•Overview of techniques in protein purification.

•Nucleic acid structure.

•Introduction to intermediary metabolism: Glycolysis, TCA cycle, Electron transport

Glycolysis, TCA cycle, Electron transport

Glycolysis: Greek glykys, meaning “sweet,” and lysis, meaning “splitting”: Glucose to Pyruvate by Enzymes

CARBOHYDRATES: Most abundant biomolecules on earth

Empirical Formula : $(\text{CH}_2\text{O})_n$

Monosaccharides

Glucose, Fructose,
Ribose

Oligosaccharides

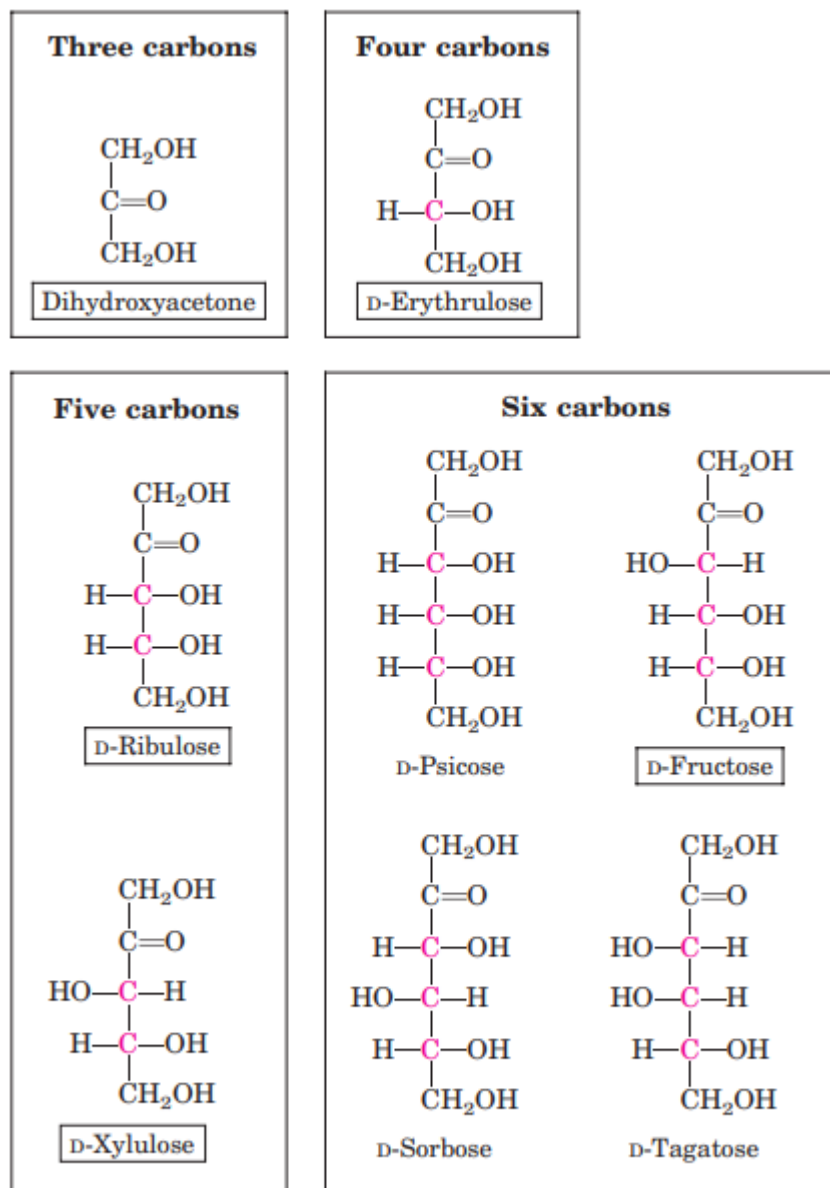
Disaccharides
Cane Sugar

Polysaccharides
Starch

The oxidation of carbohydrates is the central energy-yielding pathway in most non-photosynthetic cells.

$$\begin{array}{c} \text{H} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{C} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$$
$$\begin{array}{c} \text{H} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{C} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array} \quad \begin{array}{c} \text{H} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{C} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$$

O=C[C@@H](O)[C@H](O)[C@H](O)CO
O=C[C@@H](O)[C@@H](O)[C@H](O)CO
O=C[C@@H](O)[C@H](O)[C@@H](O)CO
O=C[C@@H](O)[C@@H](O)[C@@H](O)CO



D-Ketoses
(b)

FIGURE 7-3 Aldoses and ketoses. The series of (a) D-aldoses and (b) D-ketoses having from three to six carbon atoms, shown as projection formulas. The carbon atoms in red are chiral centers. In all these D isomers, the chiral carbon *most distant from the carbonyl carbon* has the same configuration as the chiral carbon in D-glyceraldehyde. The sugars named in boxes are the most common in nature; you will encounter these again in this and later chapters.

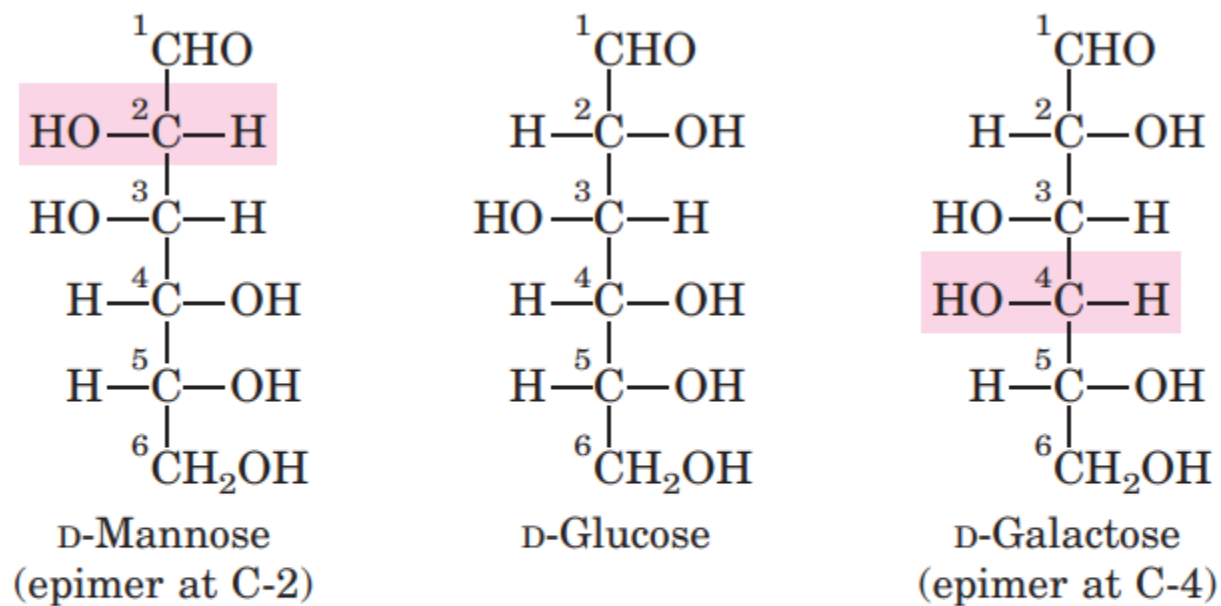
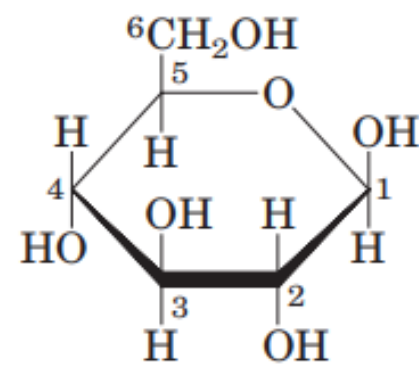
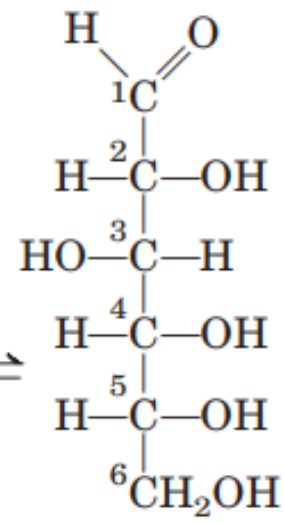


FIGURE 7-4 Epimers. D-Glucose and two of its epimers are shown as projection formulas. Each epimer differs from D-glucose in the configuration at one chiral center (shaded red).

(a)



β -D-Glucose



D-Glucose
(linear form)

(a)

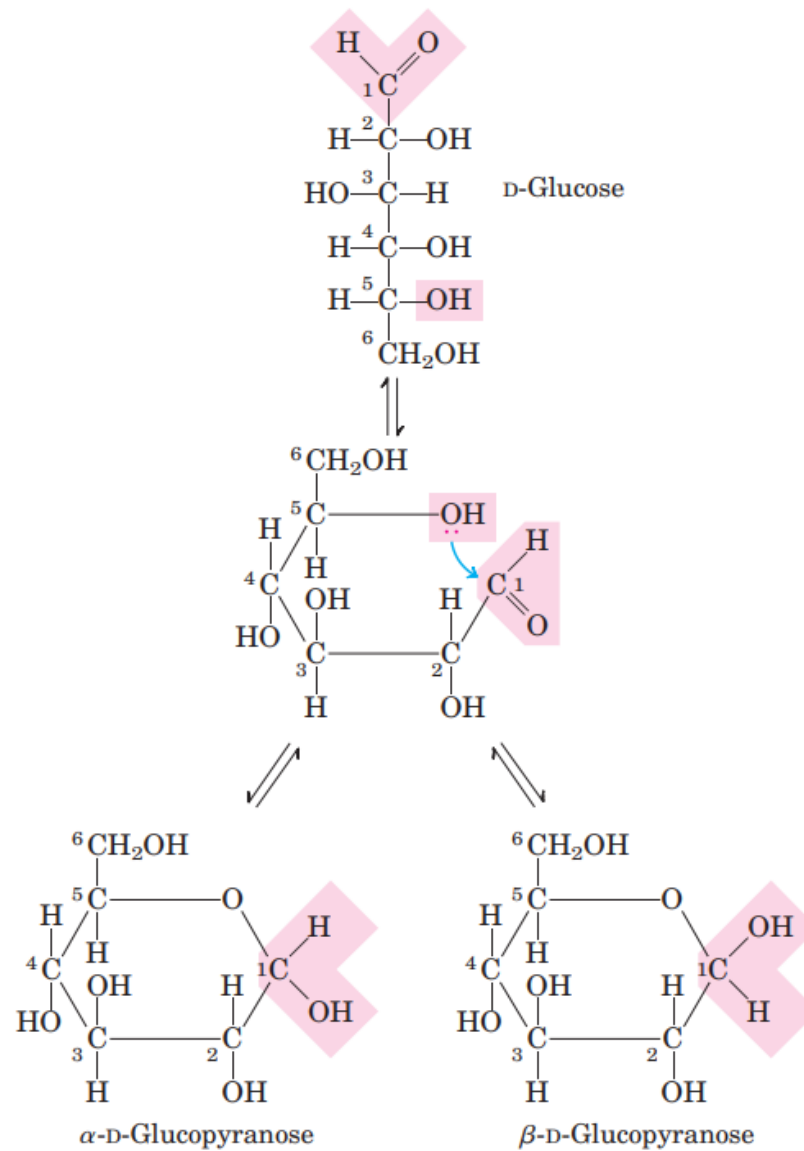
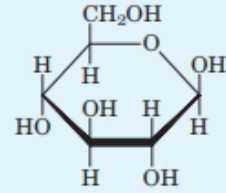
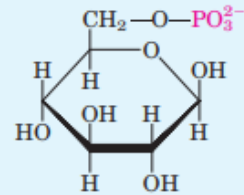


FIGURE 7-6 Formation of the two cyclic forms of D-glucose. Reaction between the aldehyde group at C-1 and the hydroxyl group at C-5 forms a hemiacetal linkage, producing either of two stereoisomers, the α and β anomers, which differ only in the stereochemistry around the hemiacetal carbon. The interconversion of α and β anomers is called mutarotation.

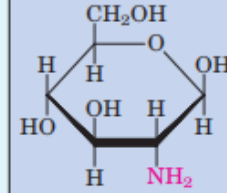
Glucose family



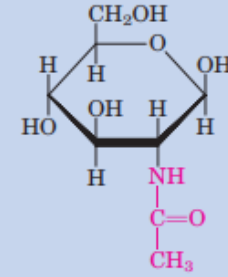
β -D-Glucose



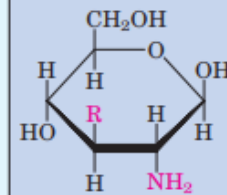
β -D-Glucose 6-phosphate



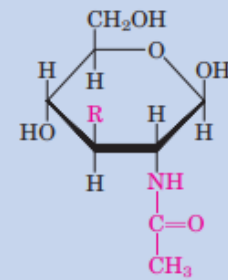
β -D-Glucosamine



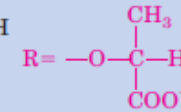
N-Acetyl- β -D-glucosamine



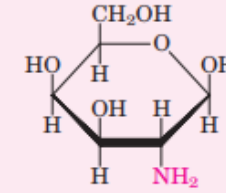
Muramic acid



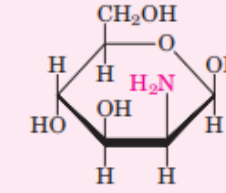
N-Acetylmuramic acid



Amino sugars

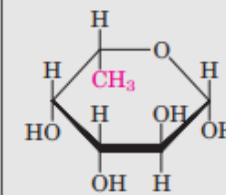


β -D-Galactosamine

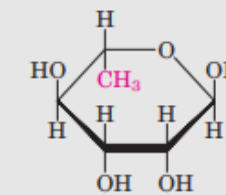


β -D-Mannosamine

Deoxy sugars

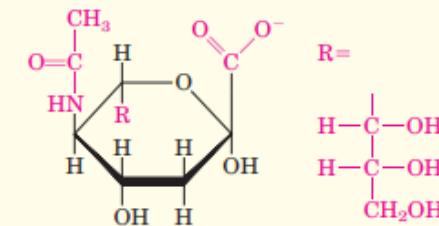


β -L-Fucose



α -L-Rhamnose

Acidic sugars



N-Acetylneuraminic acid
(a sialic acid)

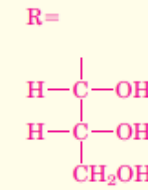


FIGURE 7-9 Some hexose derivatives important in biology. In amino sugars, an —NH_2 group replaces one of the —OH groups in the parent hexose. Substitution of —H for —OH produces a deoxy sugar; note that the deoxy sugars shown here occur in nature as the L iso-

mers. The acidic sugars contain a carboxylate group, which confers a negative charge at neutral pH. D-Glucono- δ -lactone results from formation of an ester linkage between the C-1 carboxylate group and the C-5 (also known as the δ carbon) hydroxyl group of D-gluconate.

glycosidic bonds

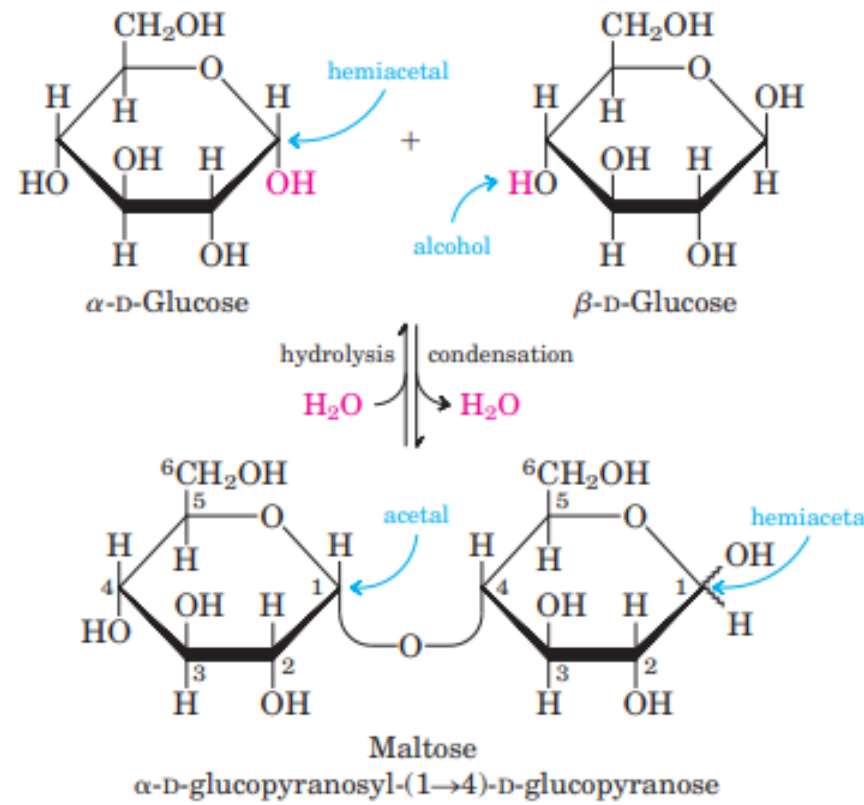
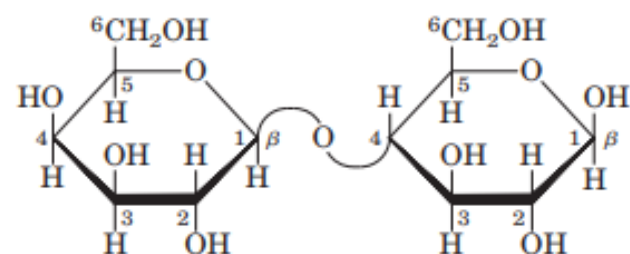
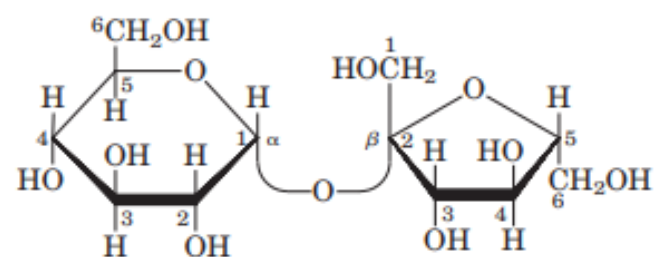


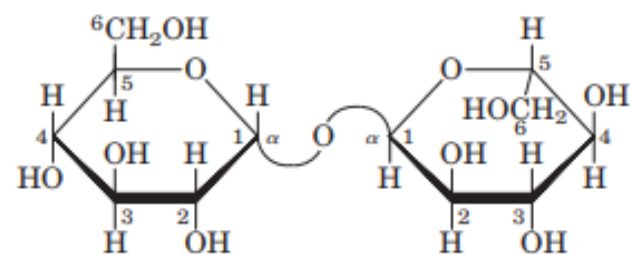
FIGURE 7-11 Formation of maltose. A disaccharide is formed from two monosaccharides (here, two molecules of D-glucose) when an —OH (alcohol) of one glucose molecule (right) condenses with the intramolecular hemiacetal of the other glucose molecule (left), with elimination of H₂O and formation of an O-glycosidic bond. The reversal of this reaction is hydrolysis—attack by H₂O on the glycosidic bond. The maltose molecule retains a reducing hemiacetal at the C-1 not involved in the glycosidic bond. Because mutarotation interconverts the α and β forms of the hemiacetal, the bonds at this position are sometimes depicted with wavy lines, as shown here, to indicate that the structure may be either α or β .



Lactose (β form)
 β -D-galactopyranosyl-(1 \rightarrow 4)- β -D-glucopyranose
 Gal(β 1 \rightarrow 4)Glc



Sucrose
 α -D-glucopyranosyl β -D-fructofuranoside
 Glc(α 1 \leftrightarrow 2 β)Fru

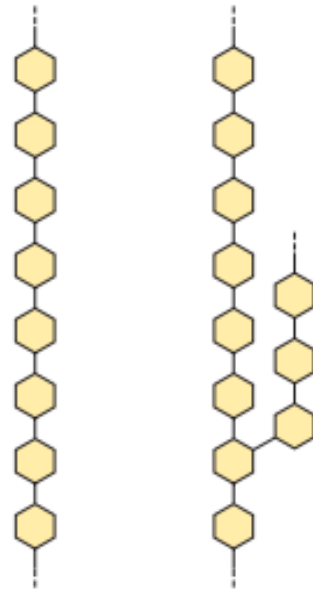


Trehalose
 α -D-glucopyranosyl α -D-glucopyranoside
 Glc(α 1 \leftrightarrow 1 α)Glc

FIGURE 7-12 Some common disaccharides. Like maltose in Figure 7-11, these are shown as Haworth perspectives. The common name, full systematic name, and abbreviation are given for each disaccharide.

Homopolysaccharides

Unbranched Branched



Heteropolysaccharides

Two
monomer
types,
unbranched

Multiple
monomer
types,
branched

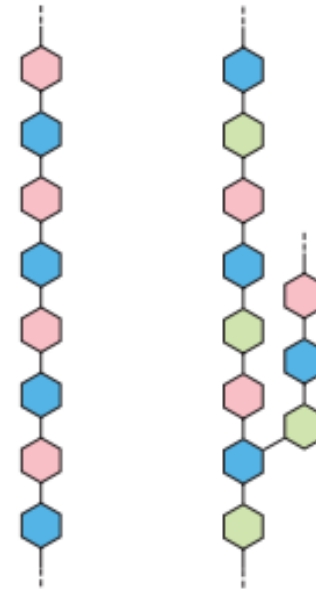


FIGURE 7-13 Homo- and heteropolysaccharides. Polysaccharides may be composed of one, two, or several different monosaccharides, in straight or branched chains of varying length.

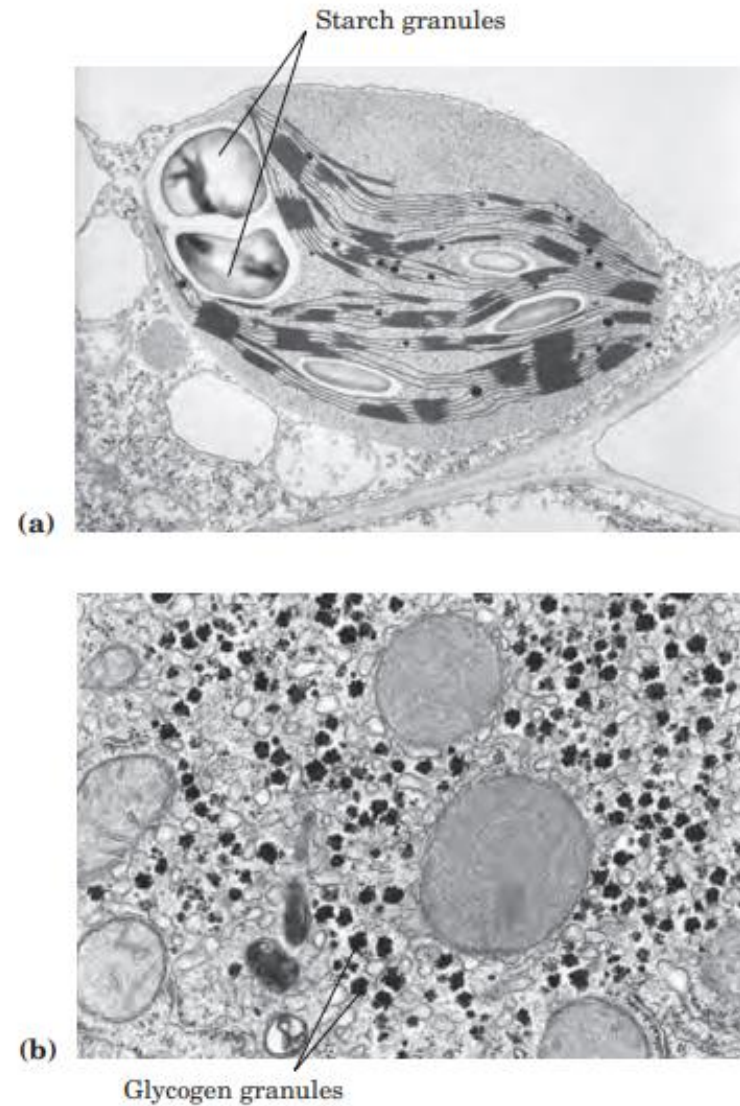


FIGURE 7-14 Electron micrographs of starch and glycogen granules. (a) Large starch granules in a single chloroplast. Starch is made in the chloroplast from D-glucose formed photosynthetically. (b) Glycogen granules in a hepatocyte. These granules form in the cytosol and are much smaller ($\sim 0.1 \mu\text{m}$) than starch granules ($\sim 1.0 \mu\text{m}$).

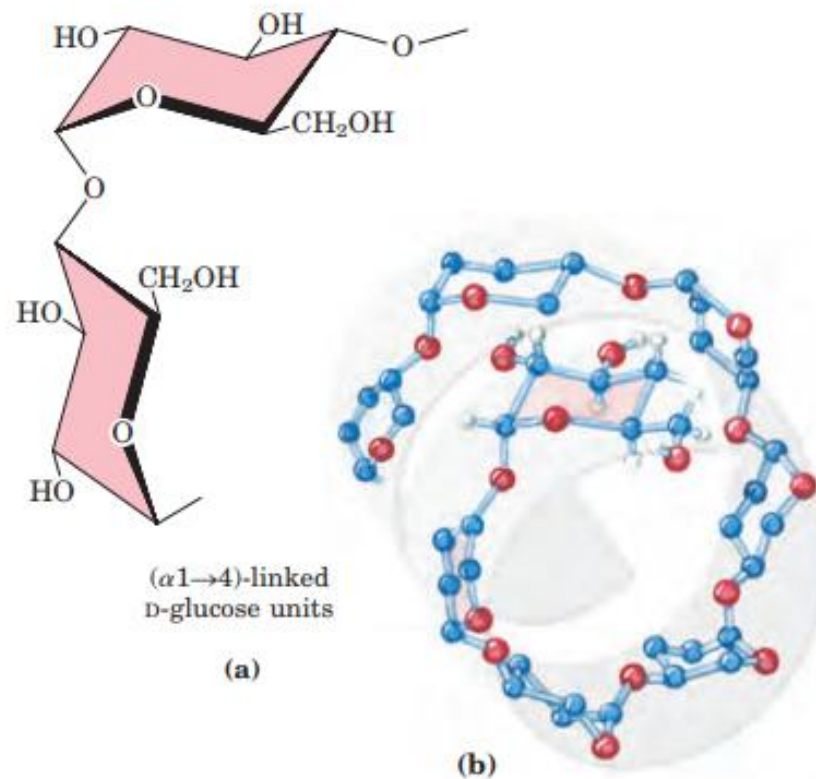


FIGURE 7-21 The structure of starch (amylose). (a) In the most stable conformation, with adjacent rigid chairs, the polysaccharide chain is curved, rather than linear as in cellulose (see Fig. 7-16). (b) Scale drawing of a segment of amylose. The conformation of $(\alpha 1 \rightarrow 4)$ linkages in amylose, amylopectin, and glycogen causes these polymers to assume tightly coiled helical structures. These compact structures produce the dense granules of stored starch or glycogen seen in many cells (see Fig. 7-14).

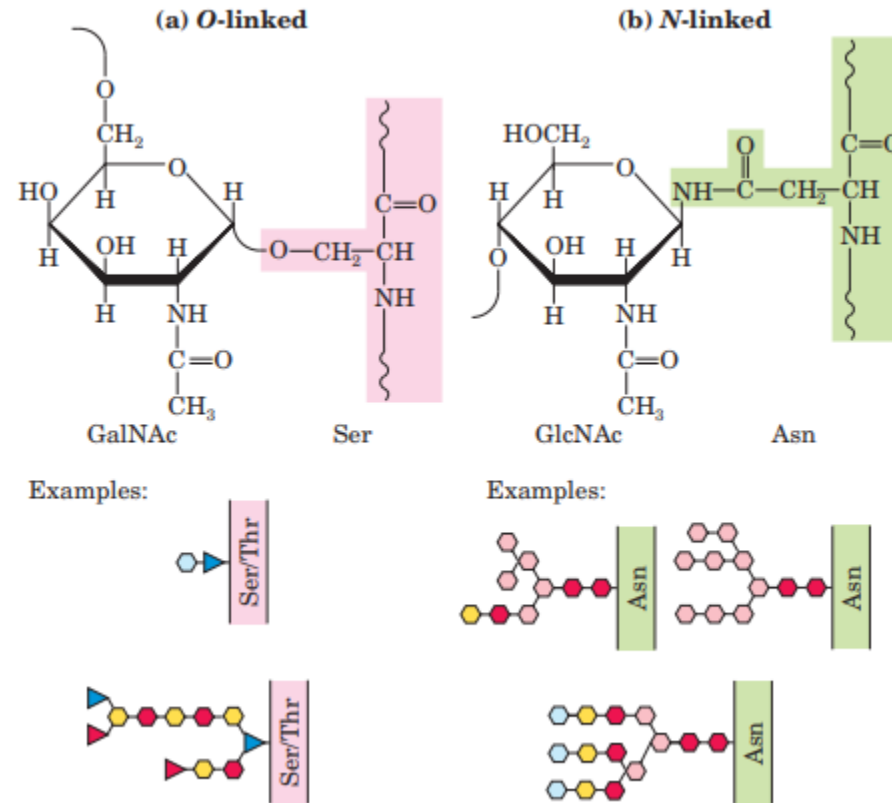


FIGURE 7-31 Oligosaccharide linkages in glycoproteins. (a) *O*-linked oligosaccharides have a glycosidic bond to the hydroxyl group of Ser or Thr residues (shaded pink), illustrated here with GalNAc as the sugar at the reducing end of the oligosaccharide. One simple chain and one complex chain are shown. (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.

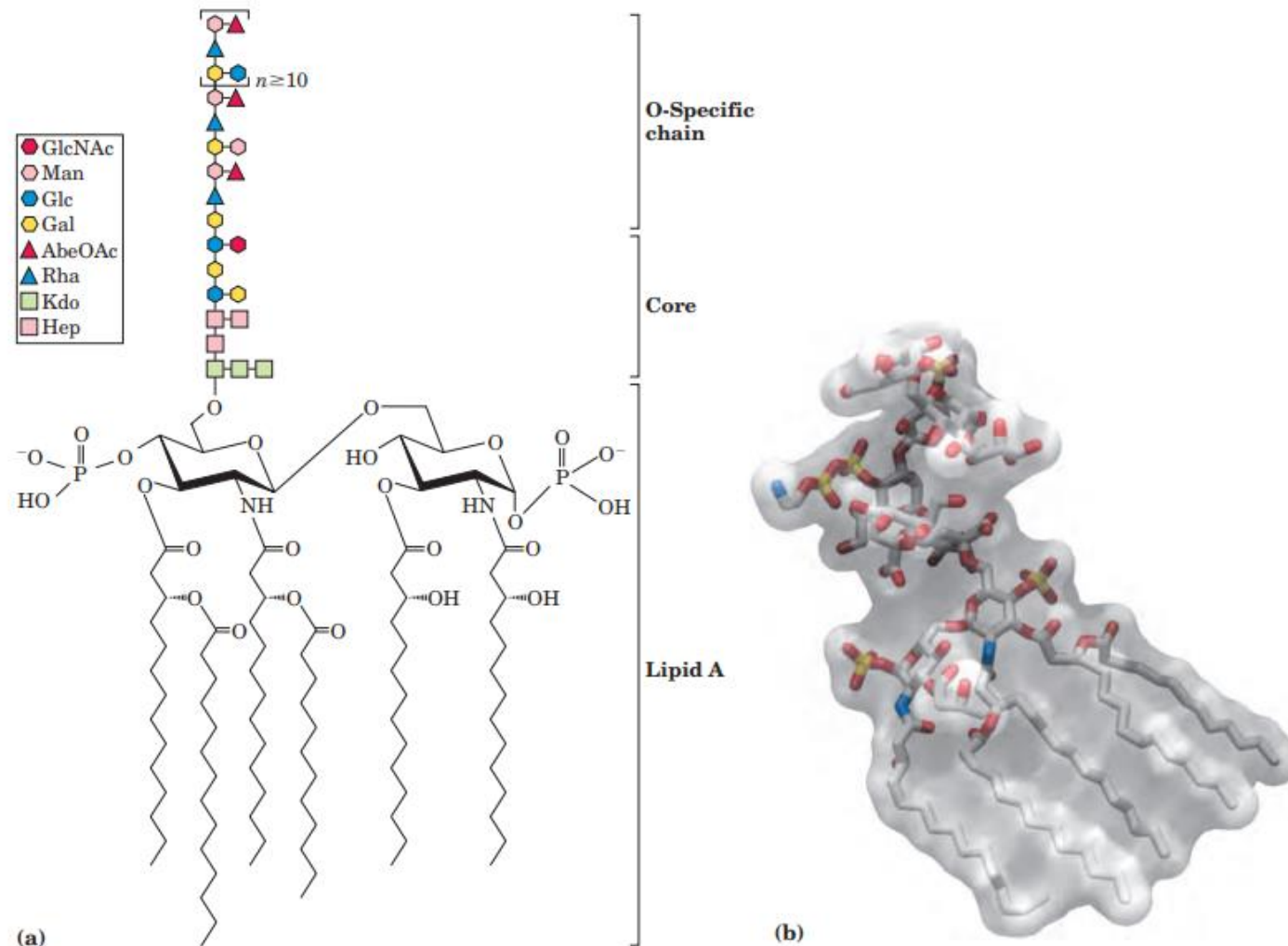


FIGURE 7-32 Bacterial lipopolysaccharides. (a) Schematic diagram of the lipopolysaccharide of the outer membrane of *Salmonella typhimurium*. Kdo is 3-deoxy-D-manno-octulosonic acid, previously called ketodeoxyoctonic acid; Hep is L-glycero-D-mannoheptose; AbeOAc is abequeose (a 3,6-dideoxyhexose) acetylated 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 prin-

cipal 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.