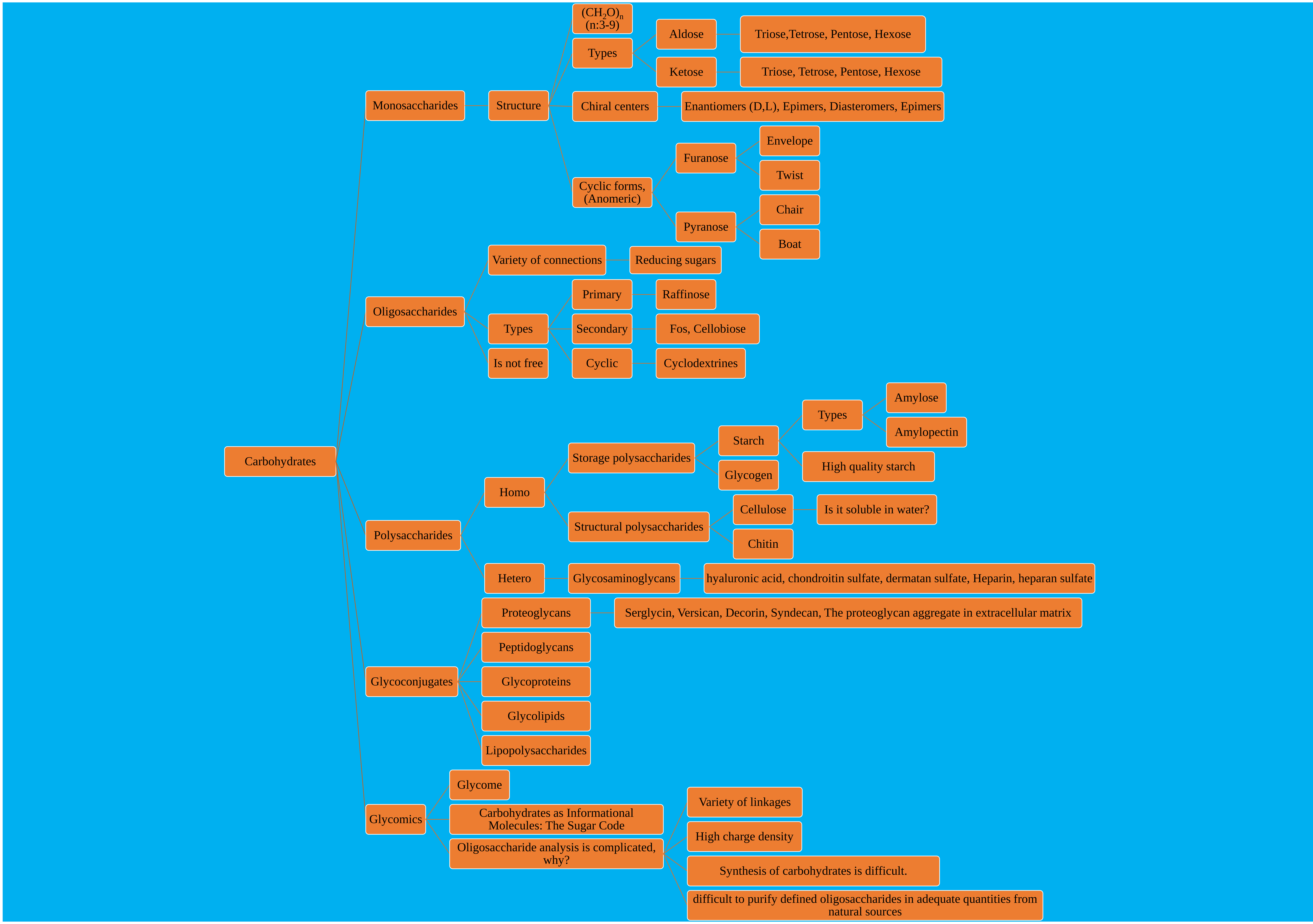
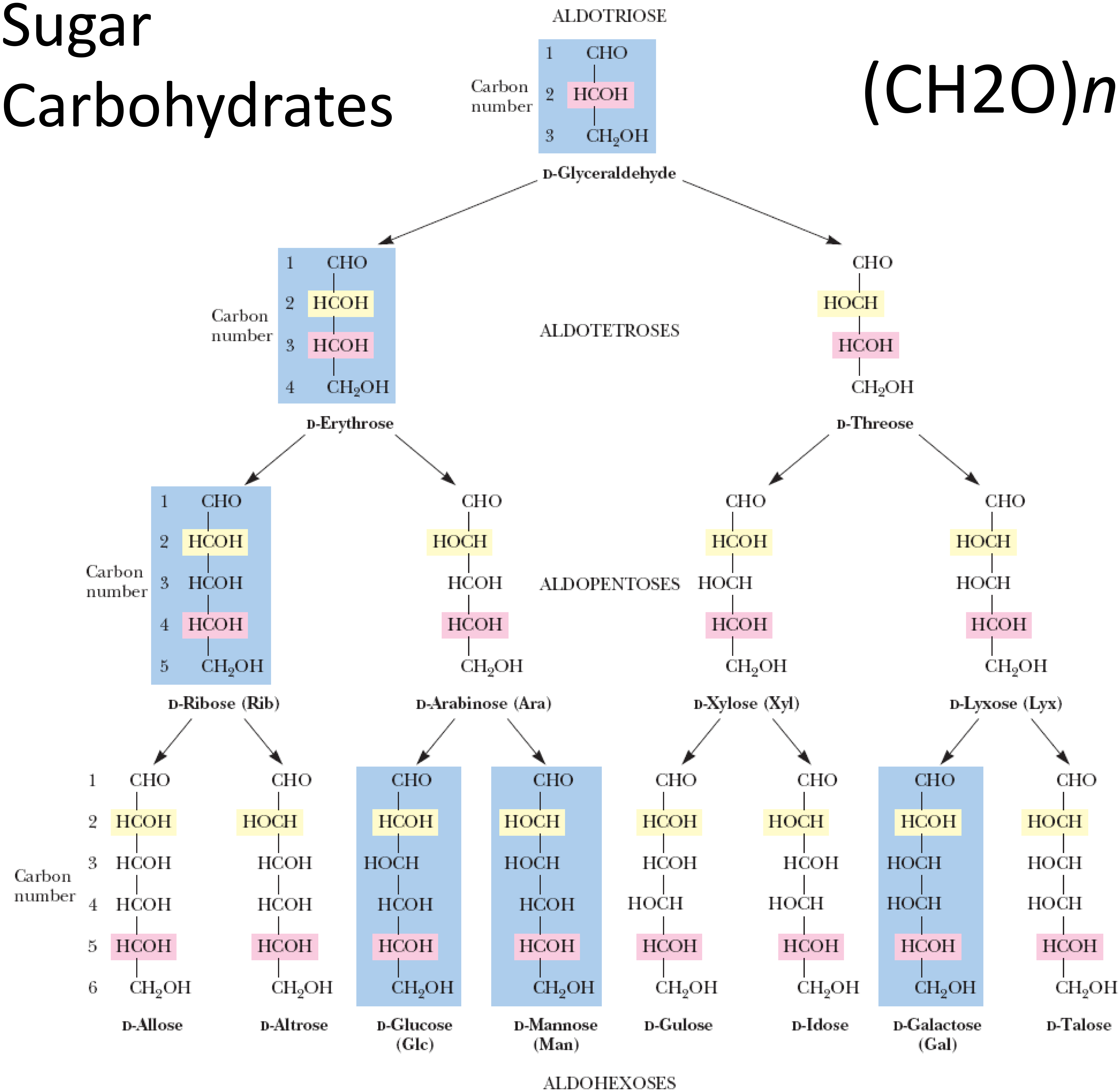
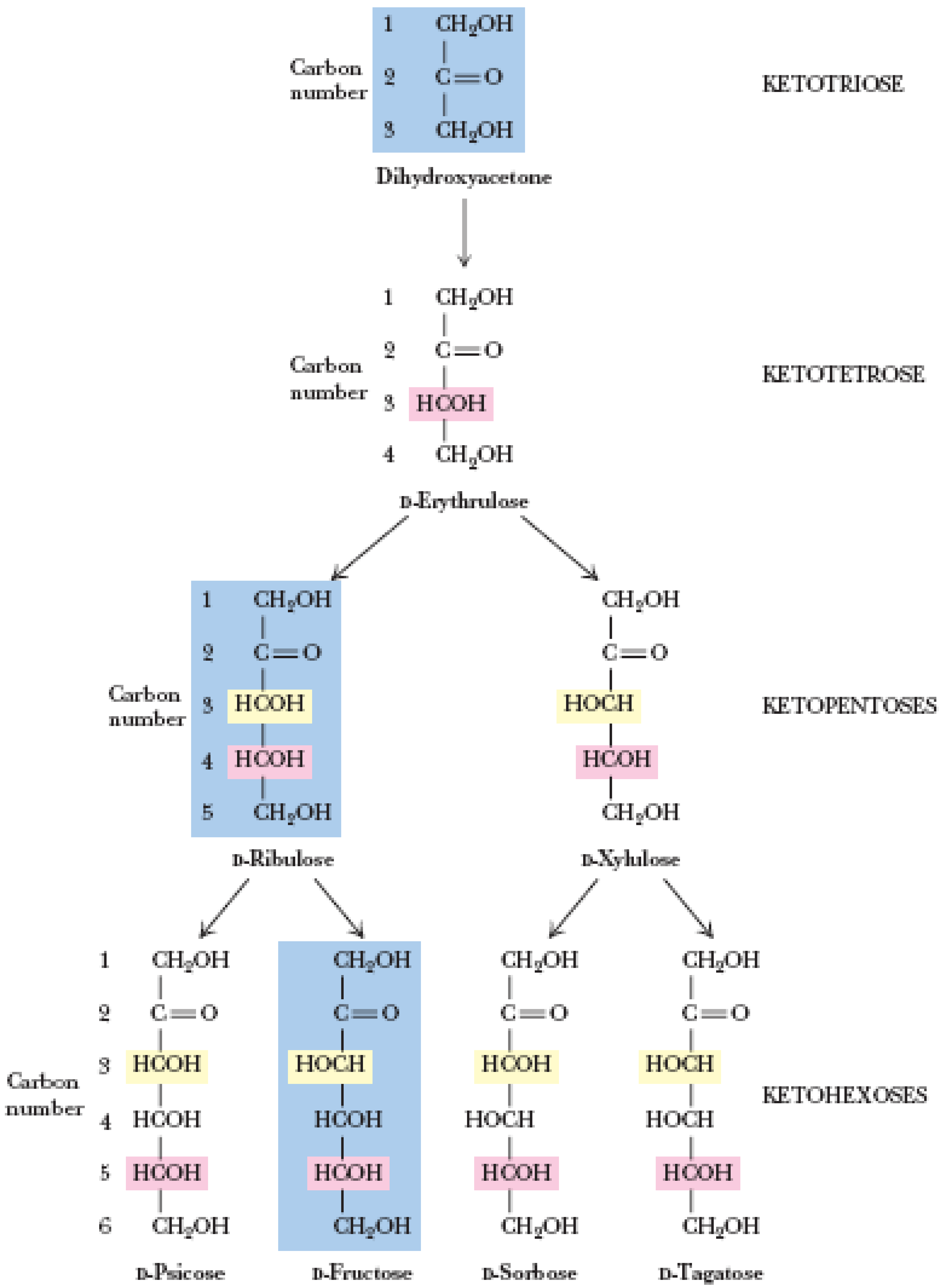
ساختار ماکرومولکول‌های زیستی (کربوهیدرات‌ها)

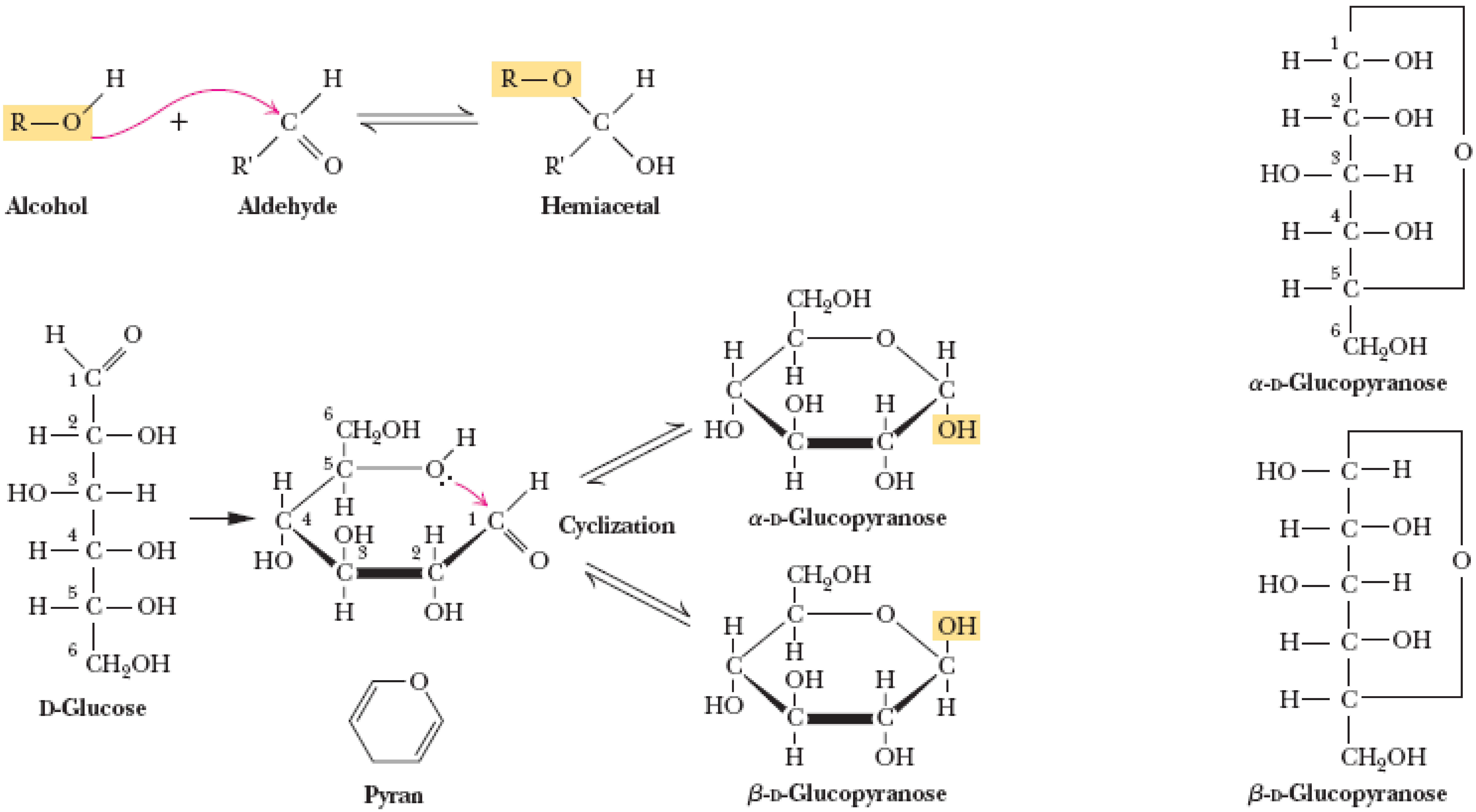


- ❑ Sugar
- ❑ Carbohydrates

$(CH2O)n$ n = 3-9

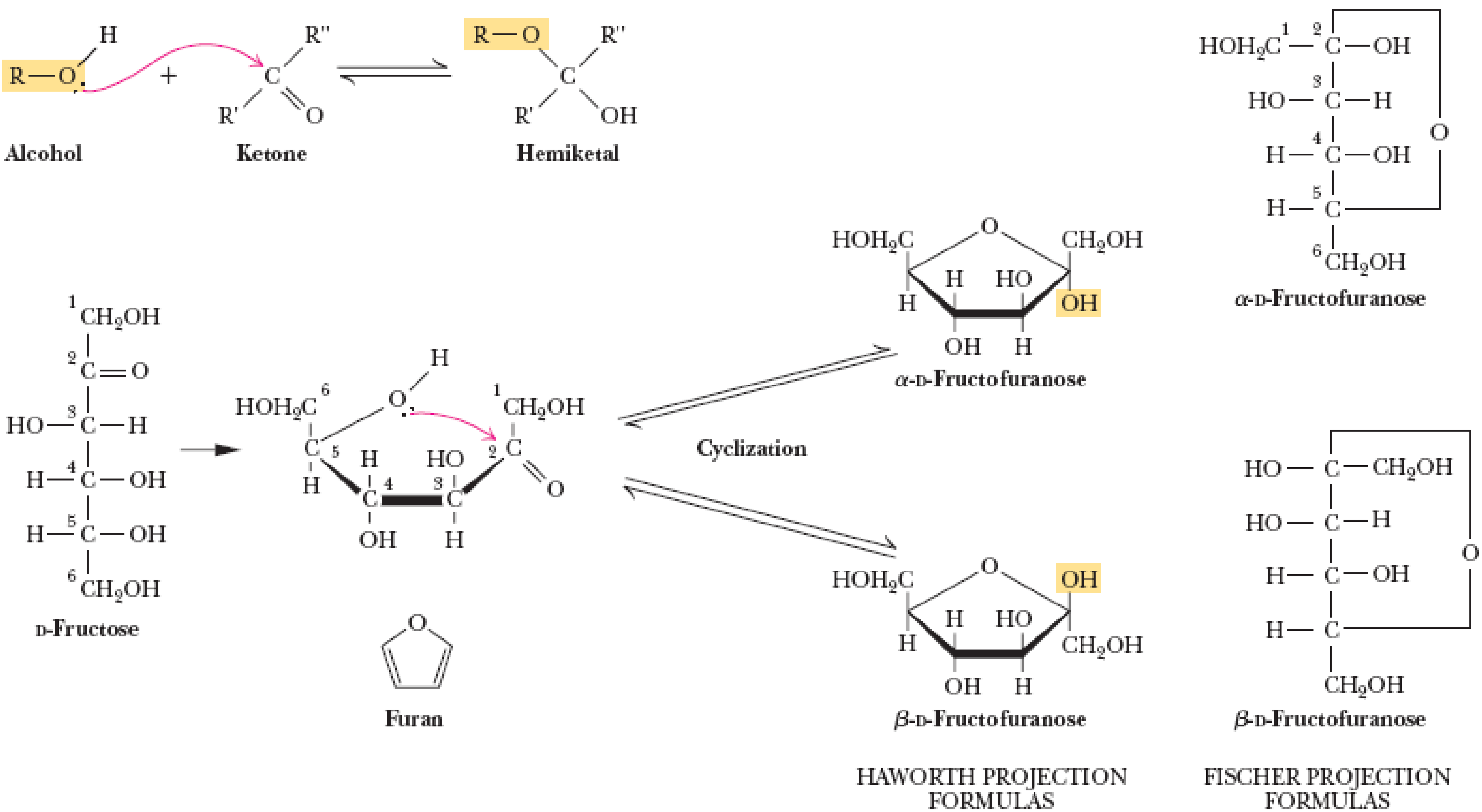



KETOTRIOSE
Carbon number
Dihydroxyacetone
KETOTETROSE
D-Erythrulose
KETOPENTOSES
D-Ribulose
D-Xylulose
KETOHEXOSES
D-Psicose
D-Fructose
D-Sorbose
D-Tagatose



HAWORTH PROJECTION FORMULAS

FISCHER PROJECTION FORMULAS


Alcohol
Ketone
Hemiketal
D-Fructose
Furan
Cyclization
α-D-Fructofuranose
β-D-Fructofuranose
α-D-Fructofuranose
β-D-Fructofuranose
HAWORTH PROJECTION FORMULAS
FISCHER PROJECTION FORMULAS

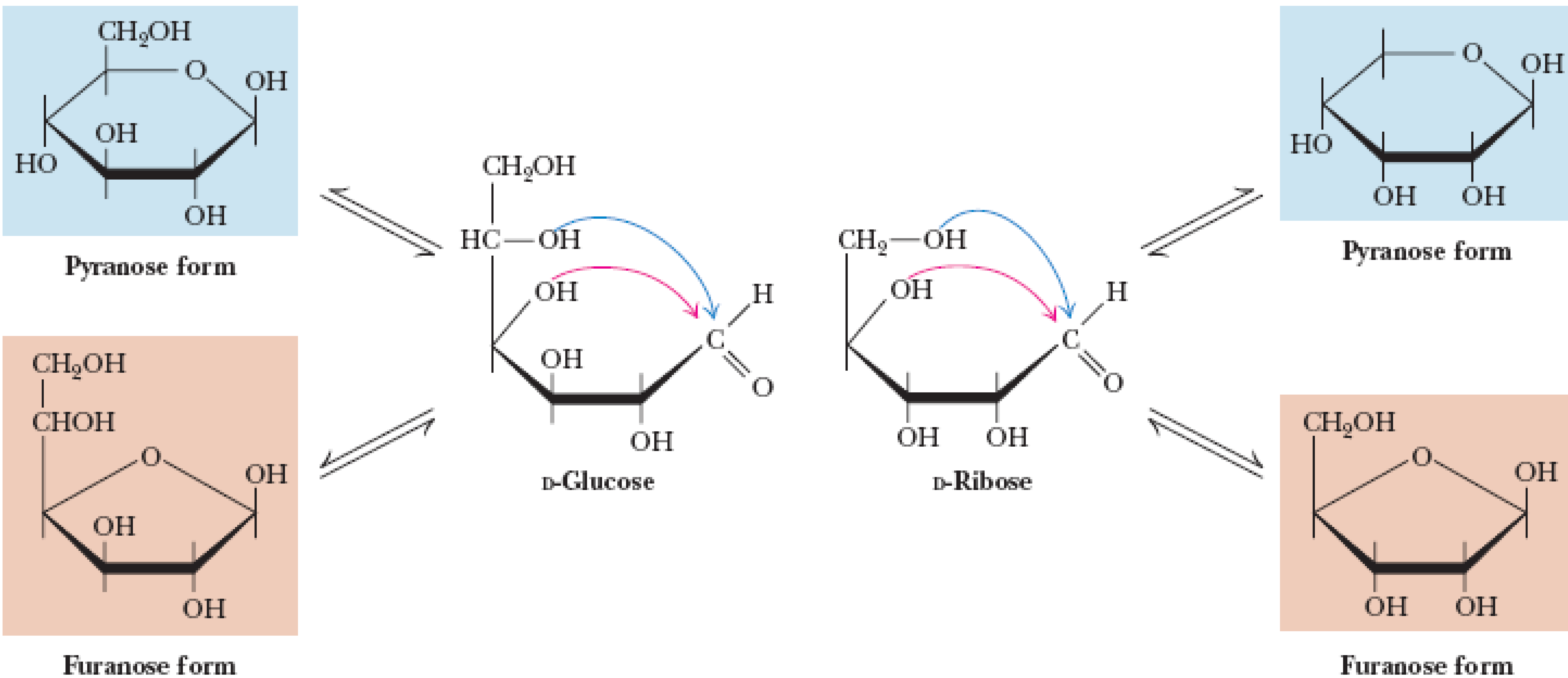


FIGURE 7.7 D-Glucose, D-ribose, and other simple sugars can cyclize in two ways, forming either furanose or pyranose structures.

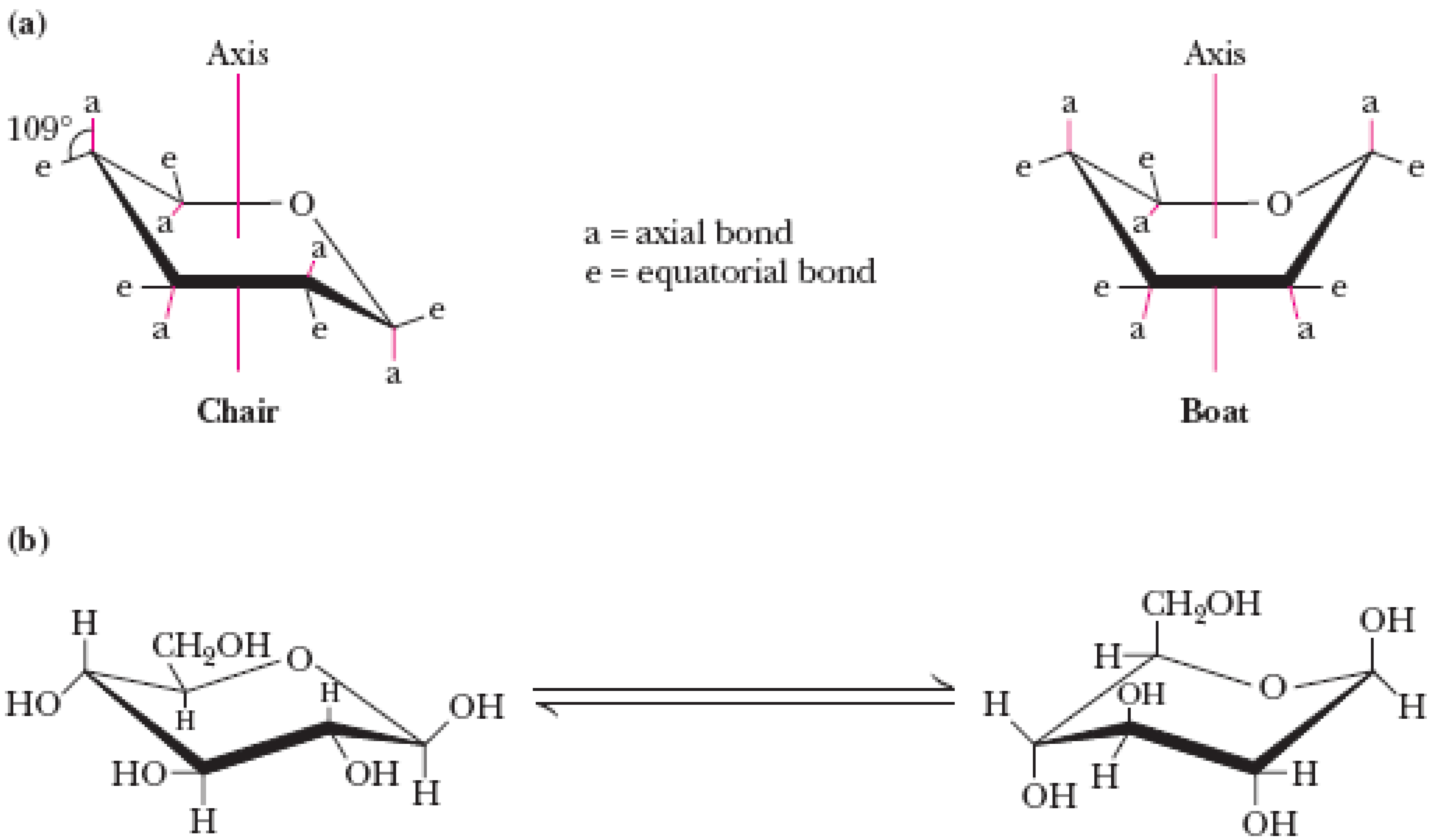
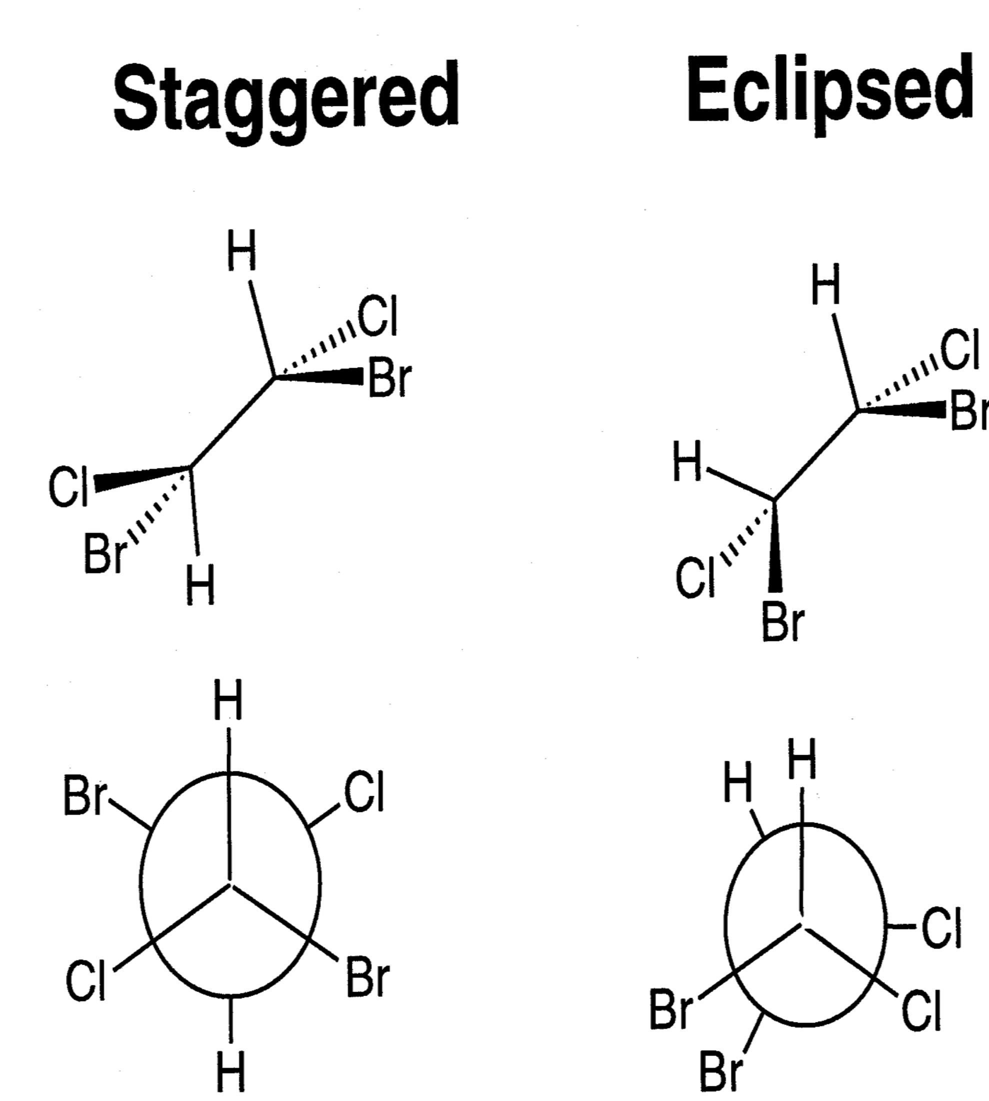
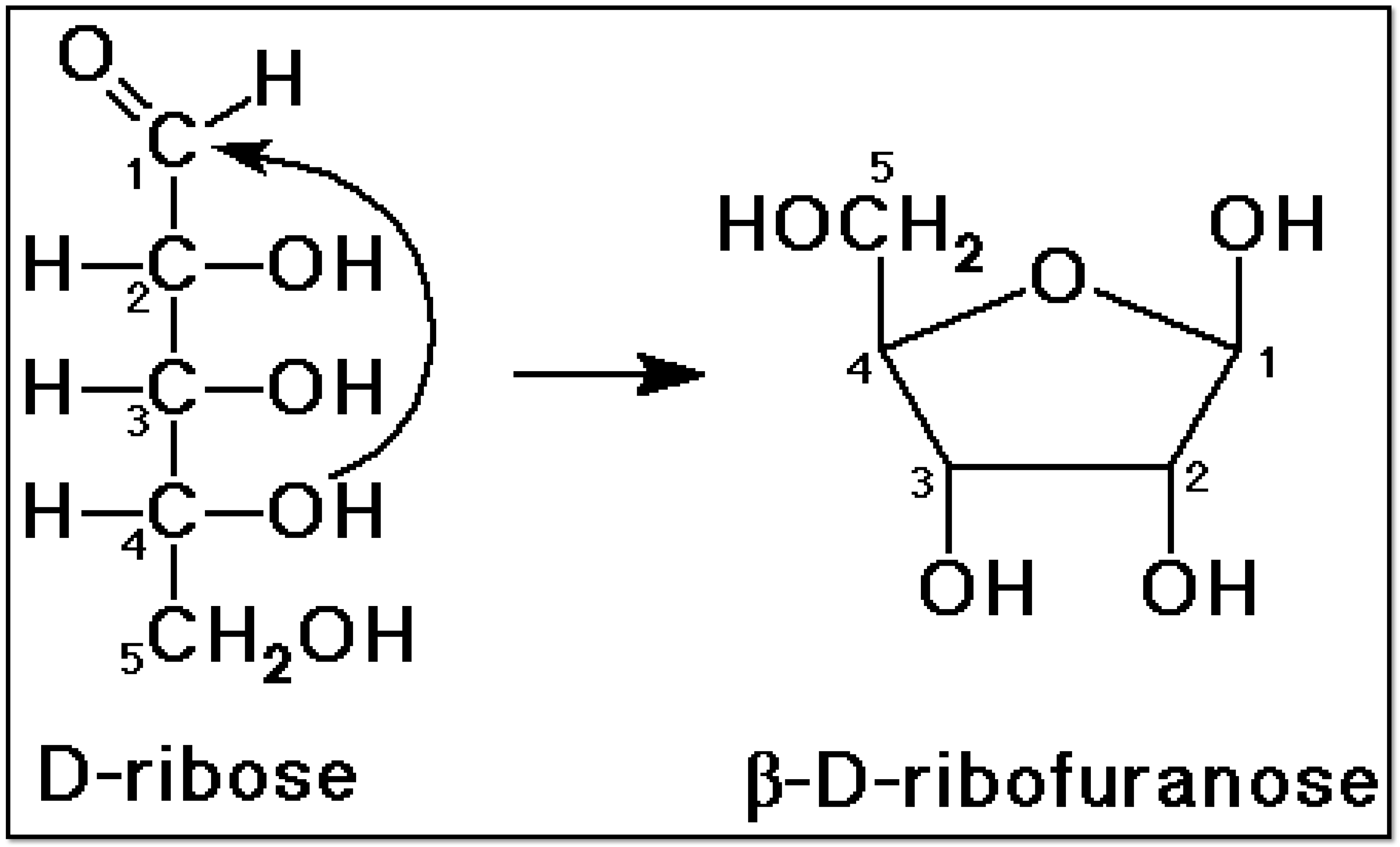


FIGURE 7.8 (a) Chair and boat conformations of a pyranose sugar. (b) Two possible chair conformations of β-D-glucose.



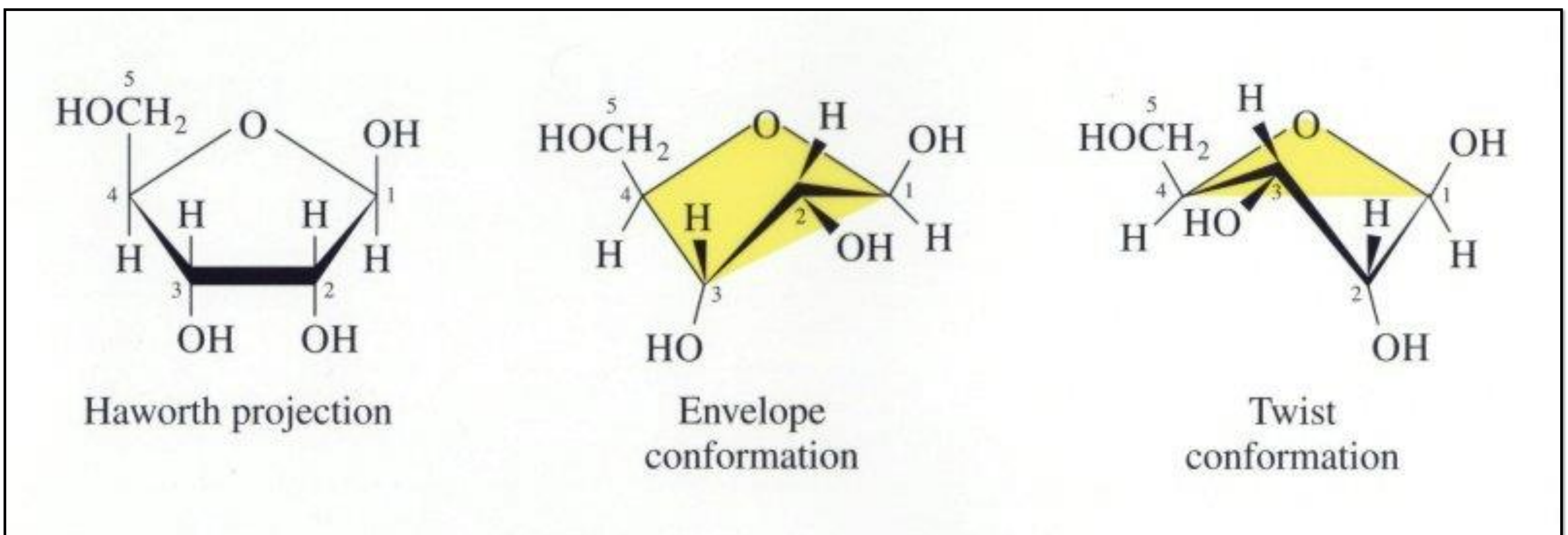


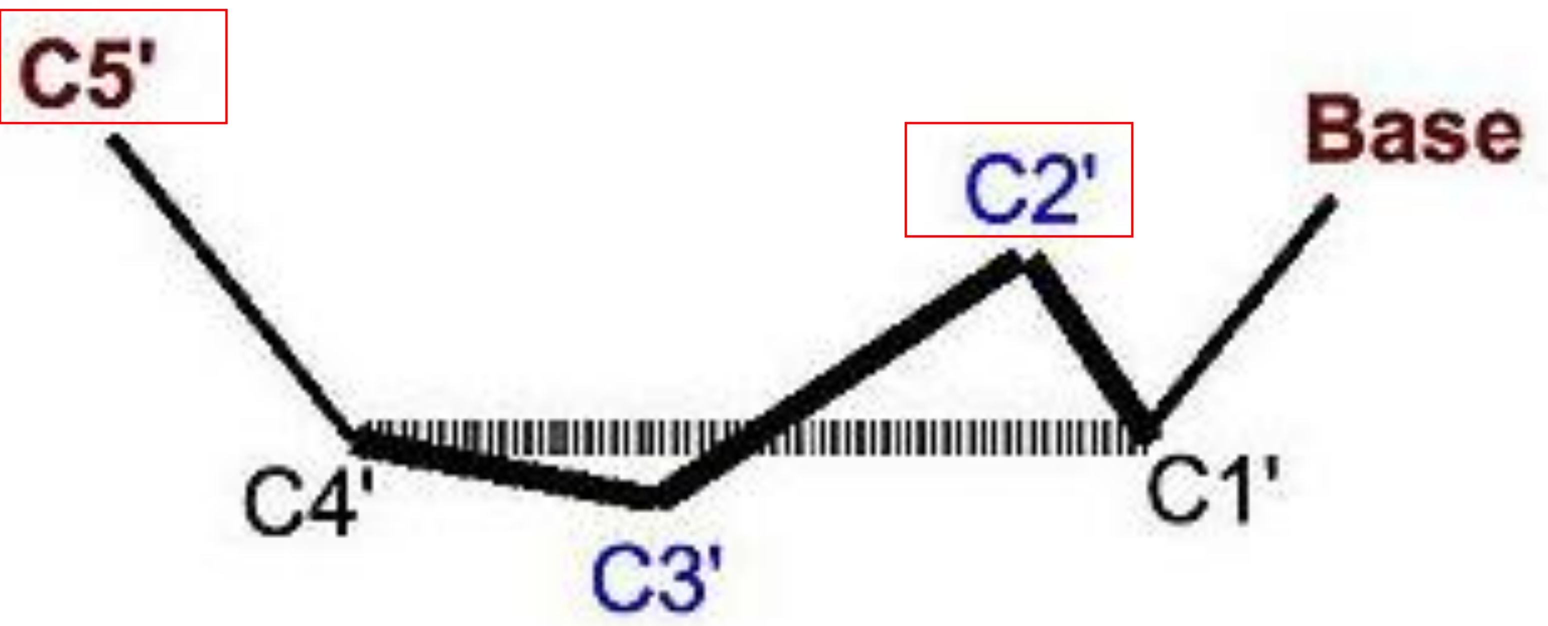
<u>In solution</u>, the straight chain (aldehyde) and ring (β-D-furanose) forms of **free** ribose are in <u>equilibrium</u>.

In RNA, exists solely as β-D-ribofuranose.

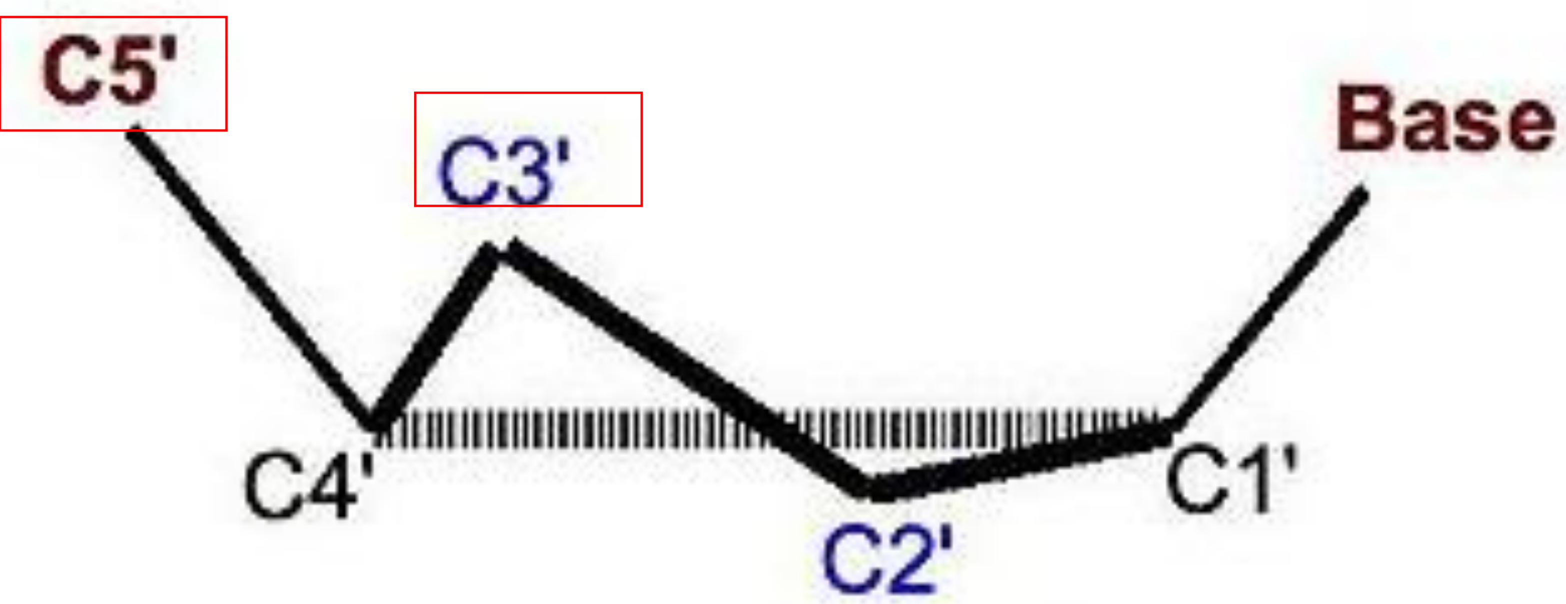
In DNA, exists solely as 2’-β-D-deoxyribofuranose.

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

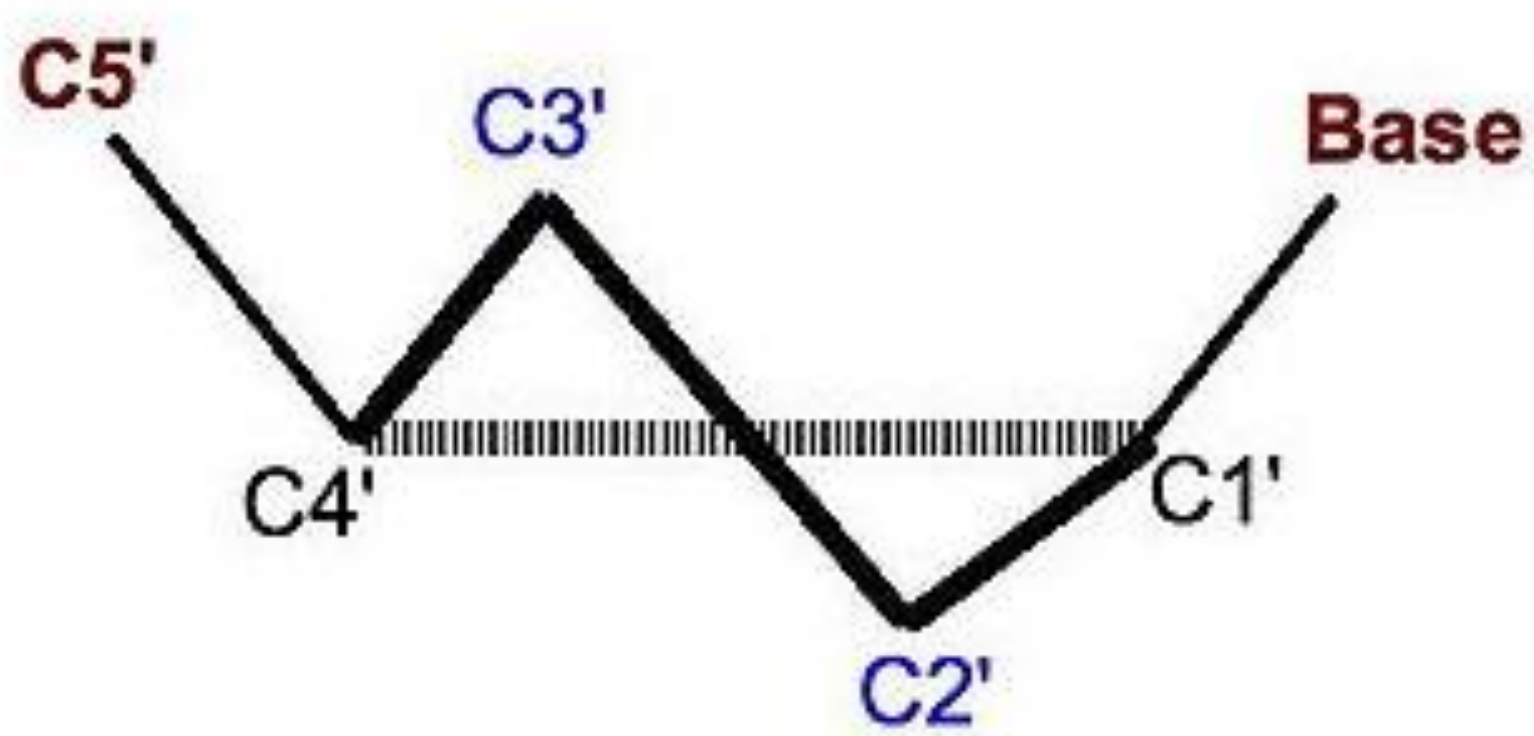




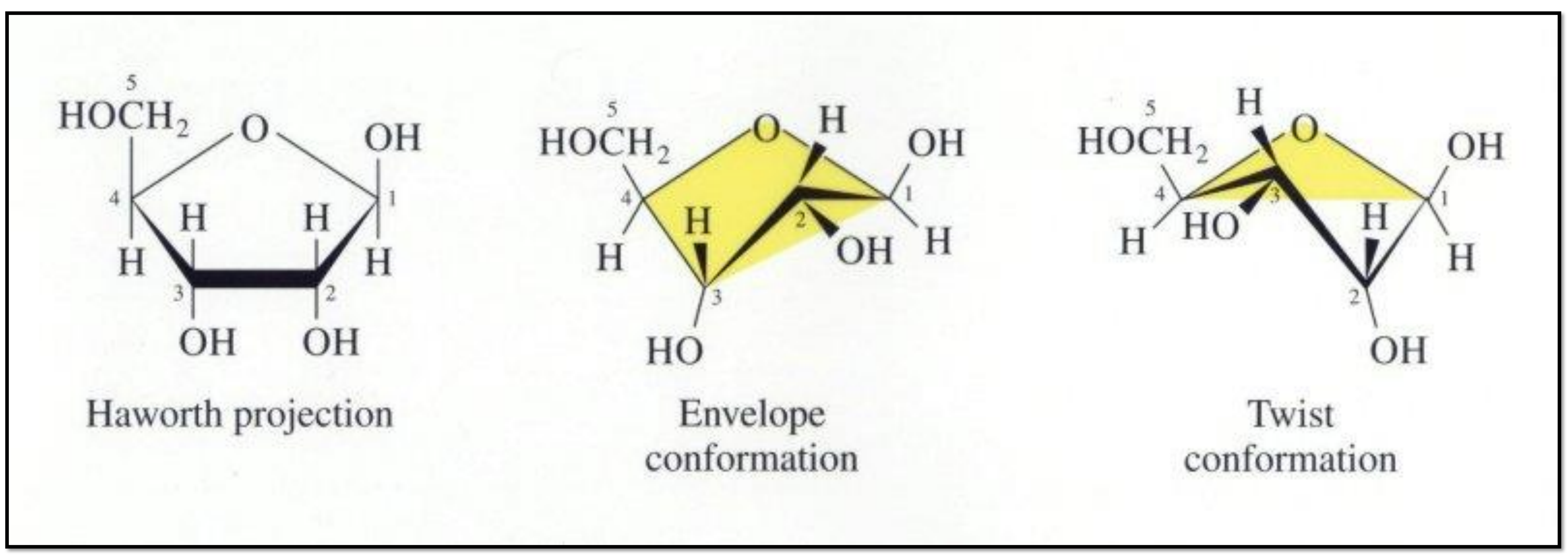
E C2'-endo



E C3'-endo



T C2'-exo-C3'-endo



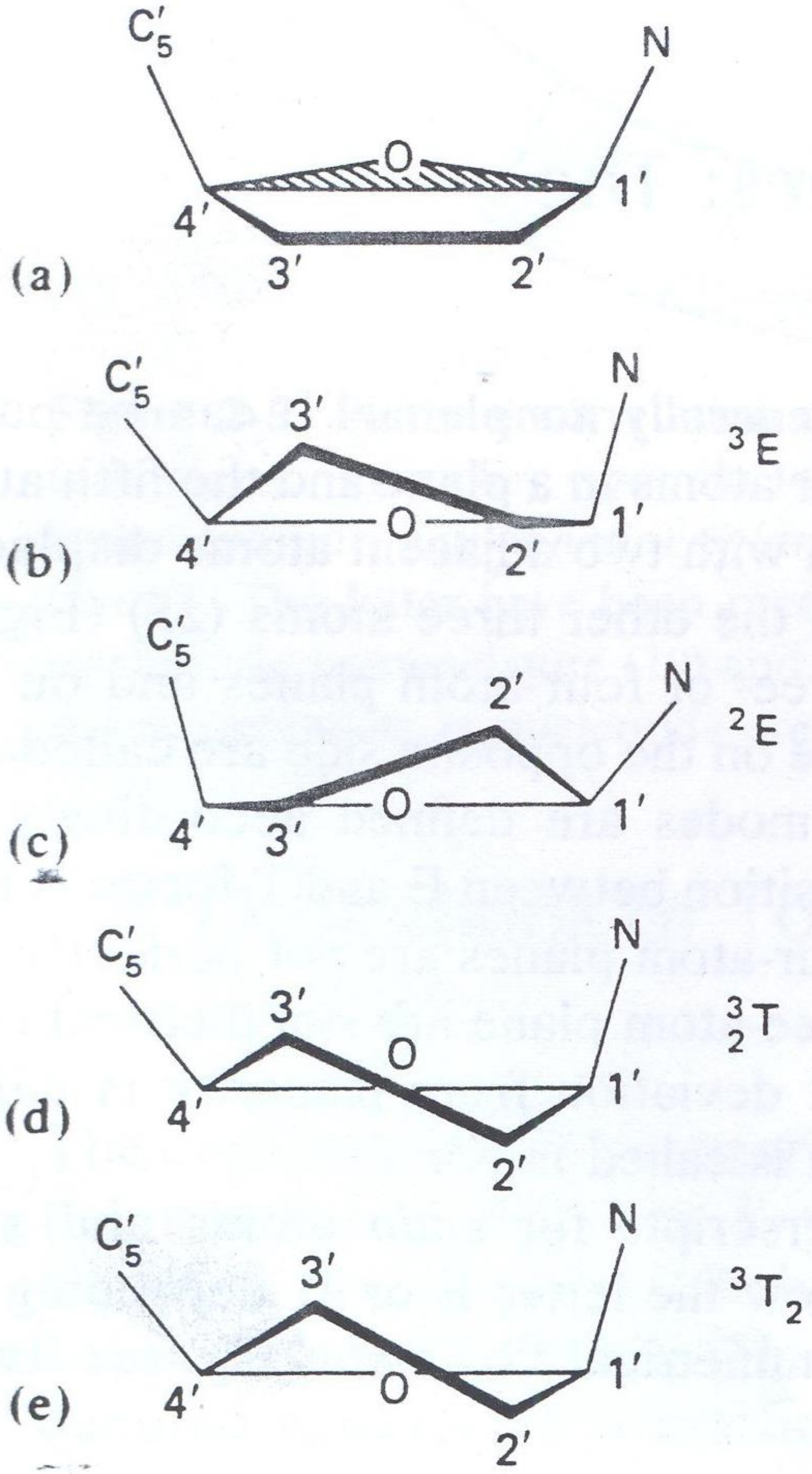
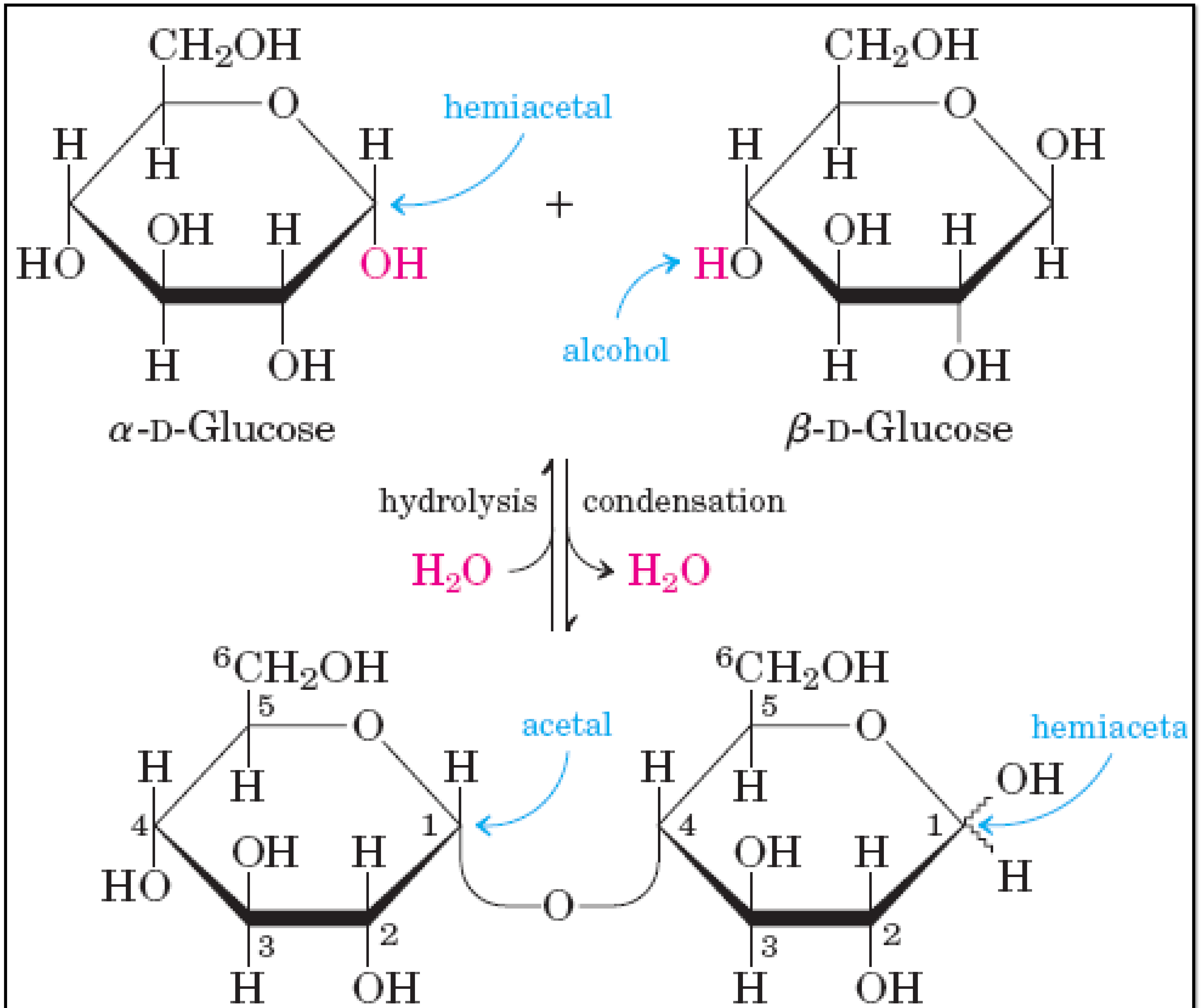


Figure 2-7. Definition of sugar puckering modes. (a) Starting position with flat five-membered sugar, a situation never observed. Place $C_{1'}–O_{4'}–C_{4'}$ is shown hatched. (b-e) View with this plane perpendicular to the paper. (b) Envelope $C_{3'}$–*endo*, ^{3}E. (c) Envelope $C_{2'}$–*endo*. ^{2}E. (d) Symmetrical twist or half-chair $C_{2'}$–*exo*–$C_{3'}$–*endo*. $^{3}_{2}T$. (e) Unsymmetrical twist with major $C_{3'}$–*endo* and minor $C_{2'}$–*exo* pucker, $^{3}T_{2}$.

Oligosaccharides and Polysaccharides



Maltose
α-D-glucopyranosyl-(1→4)-D-glucopyranose

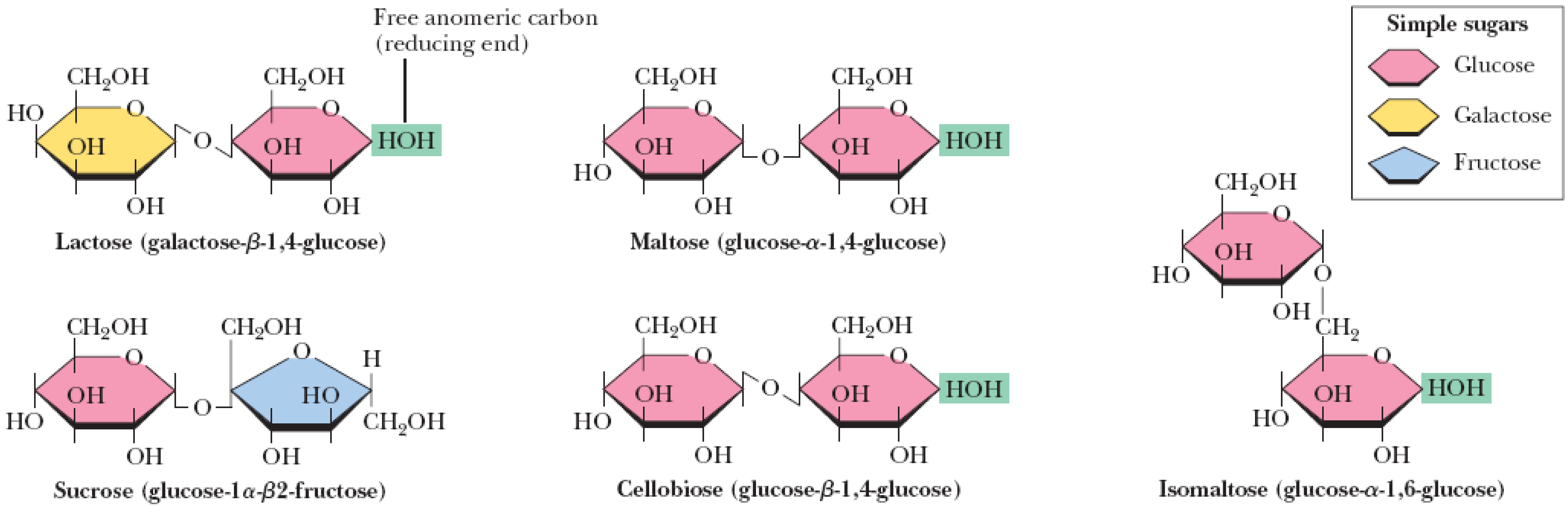
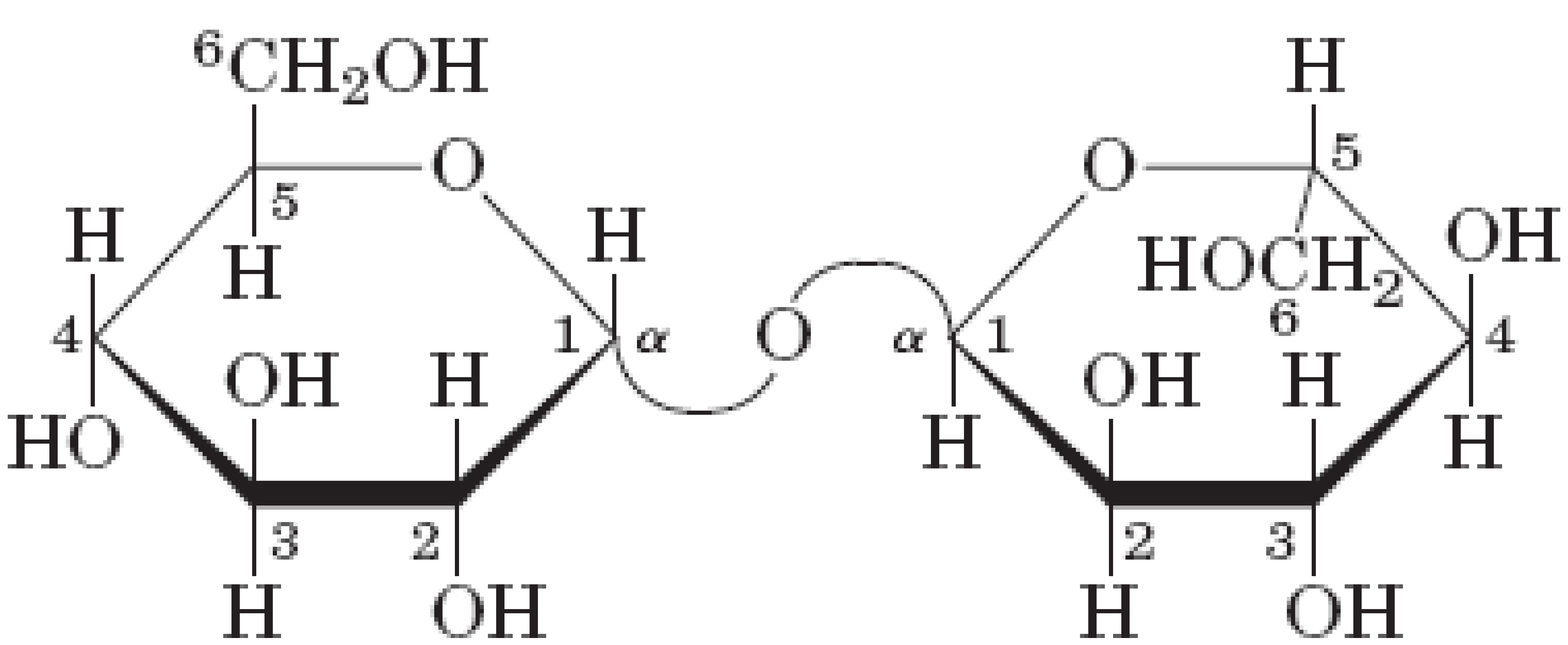


FIGURE 7.18 The structures of several important disaccharides. Note that the notation "HOH" means that the configuration can be either α or β. If the —OH group is above the ring, the configuration is termed β. The configuration is α if the —OH group is below the ring. Also note that sucrose has no free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



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

<u>αα</u> (Trehalose)

αβ (neotrehalose)

ββ (isotrehalose)

Primary oligosaccharides:

Raffinose Gal α1→6 Glc α1 →2β Fru

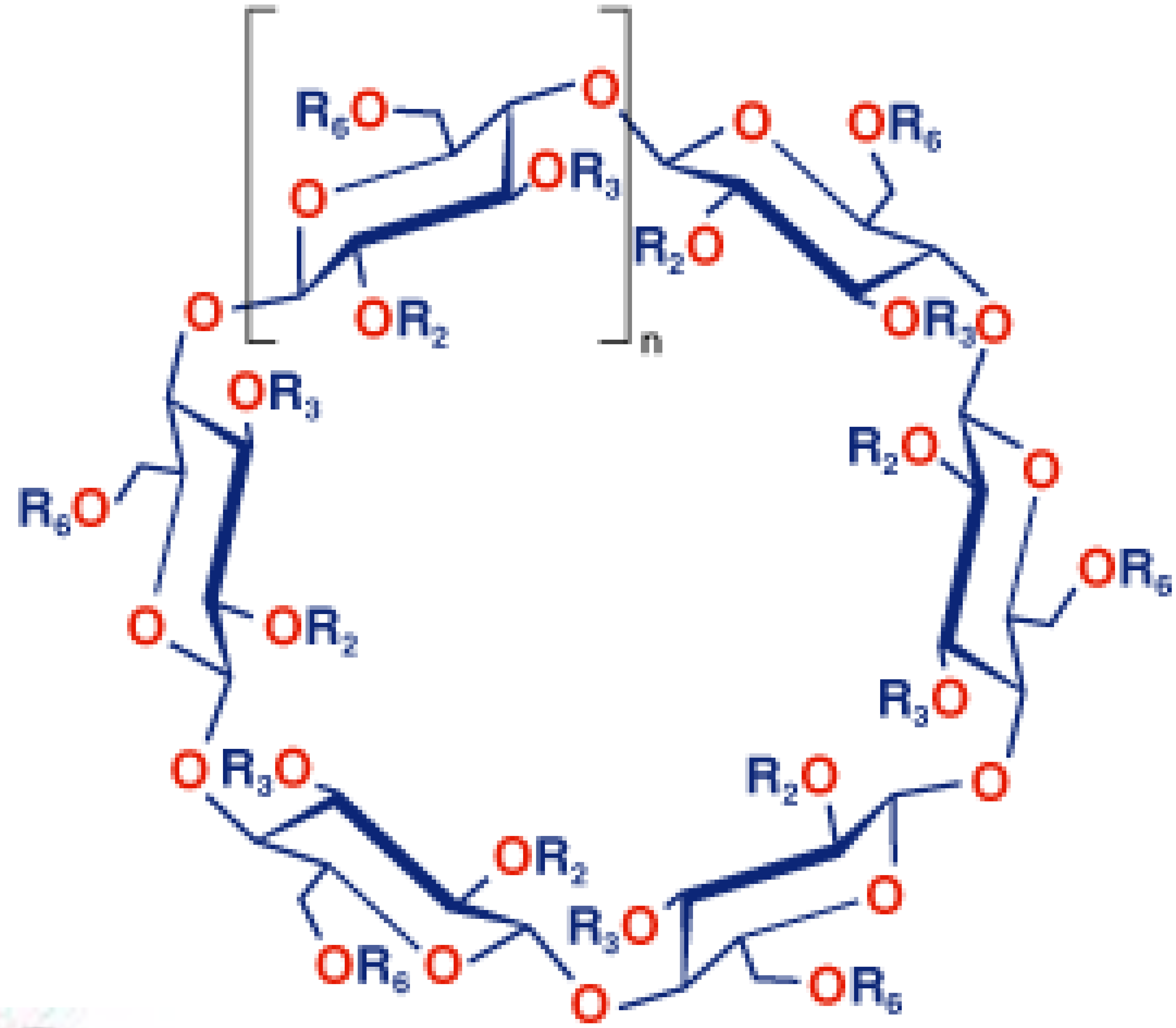
Secondary oligosaccharides:

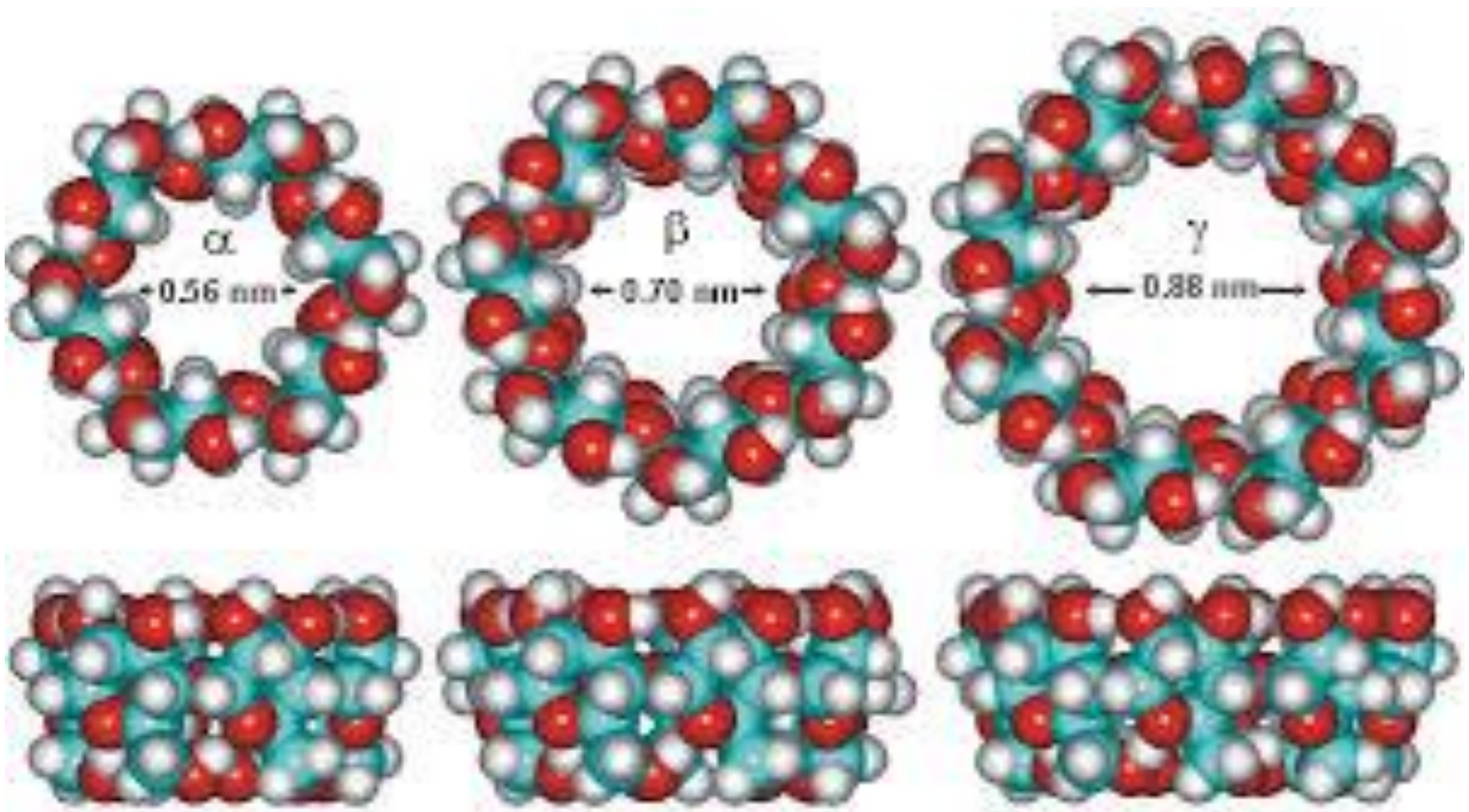
Cellobiose, Fos, Isomaltose

Cyclic oligosaccharides:

Cyclodextrins

The cyclodextrins are produced by the partial degradation of starch

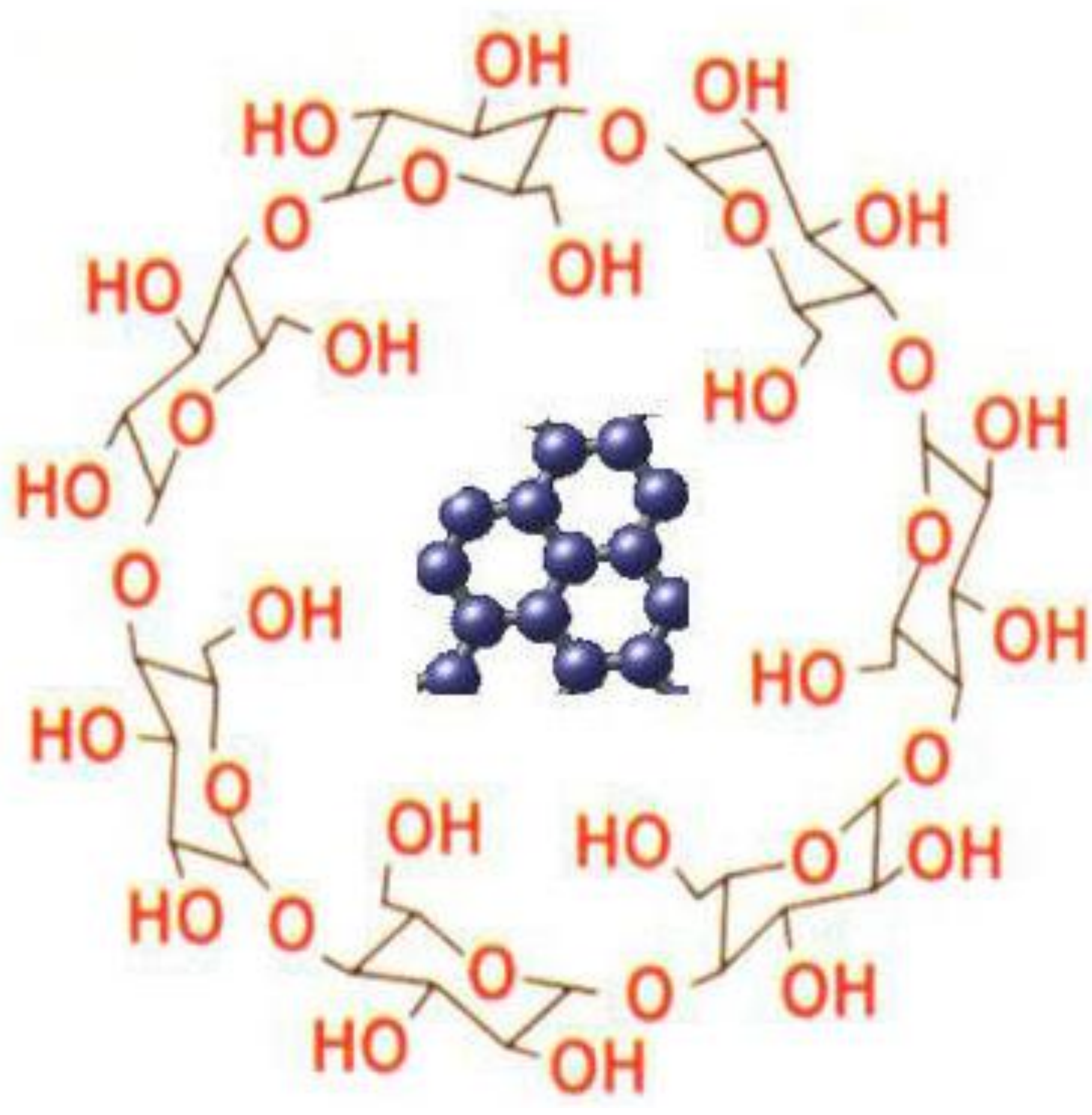


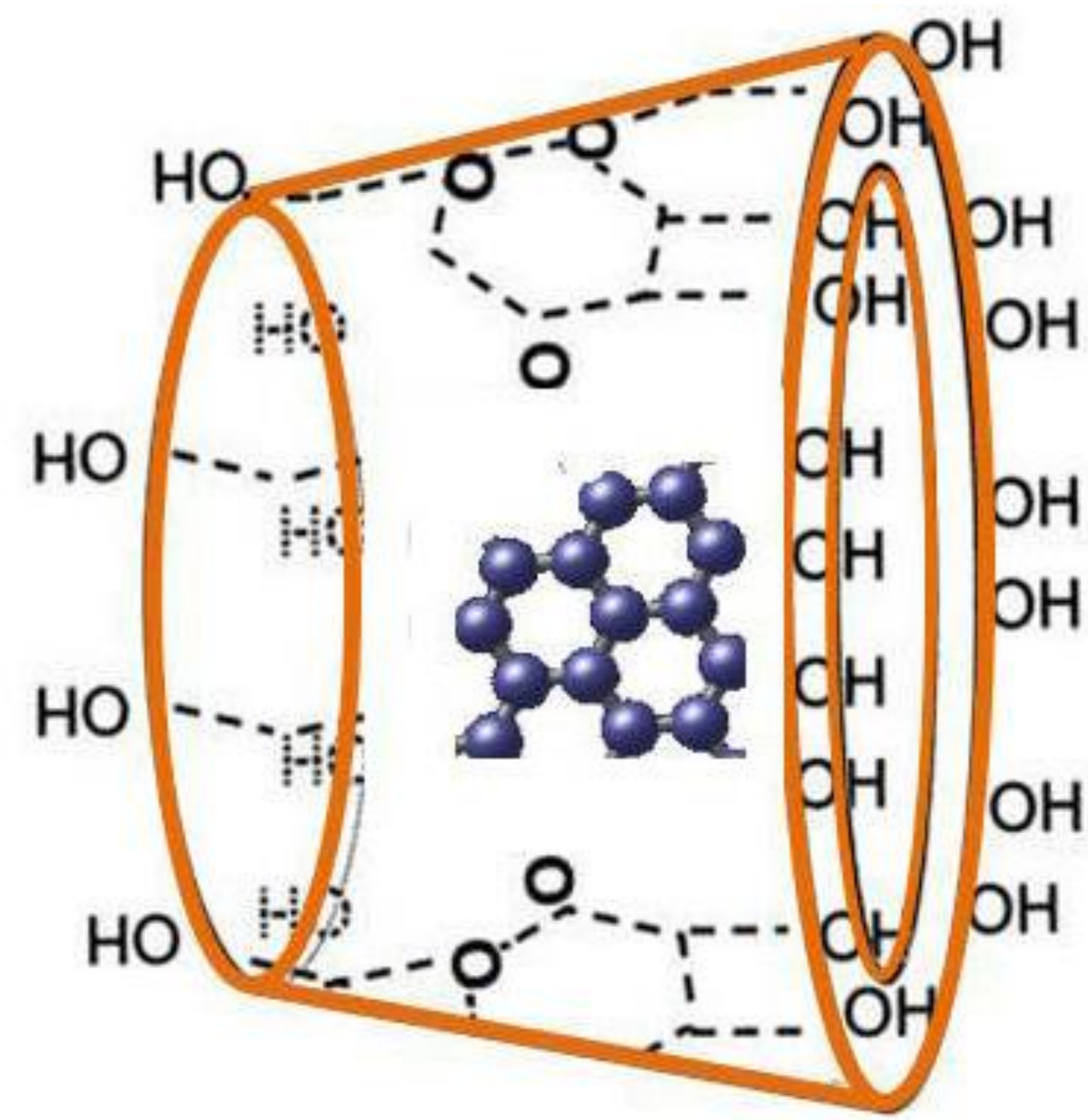


❑ non-reducing cyclic dextrins known as cyclodextrins

❑ The cyclodextrins are complex cyclic carbohydrates whose structure resembles a hollow, truncated cone with a hydrophobic (water-hating) core and hydrophilic (water-loving) exterior

❑ They are a vehicle for drug delivery. For example, cyclodextrins have been used in eyedrops to deliver the antibiotic chloramphenicol





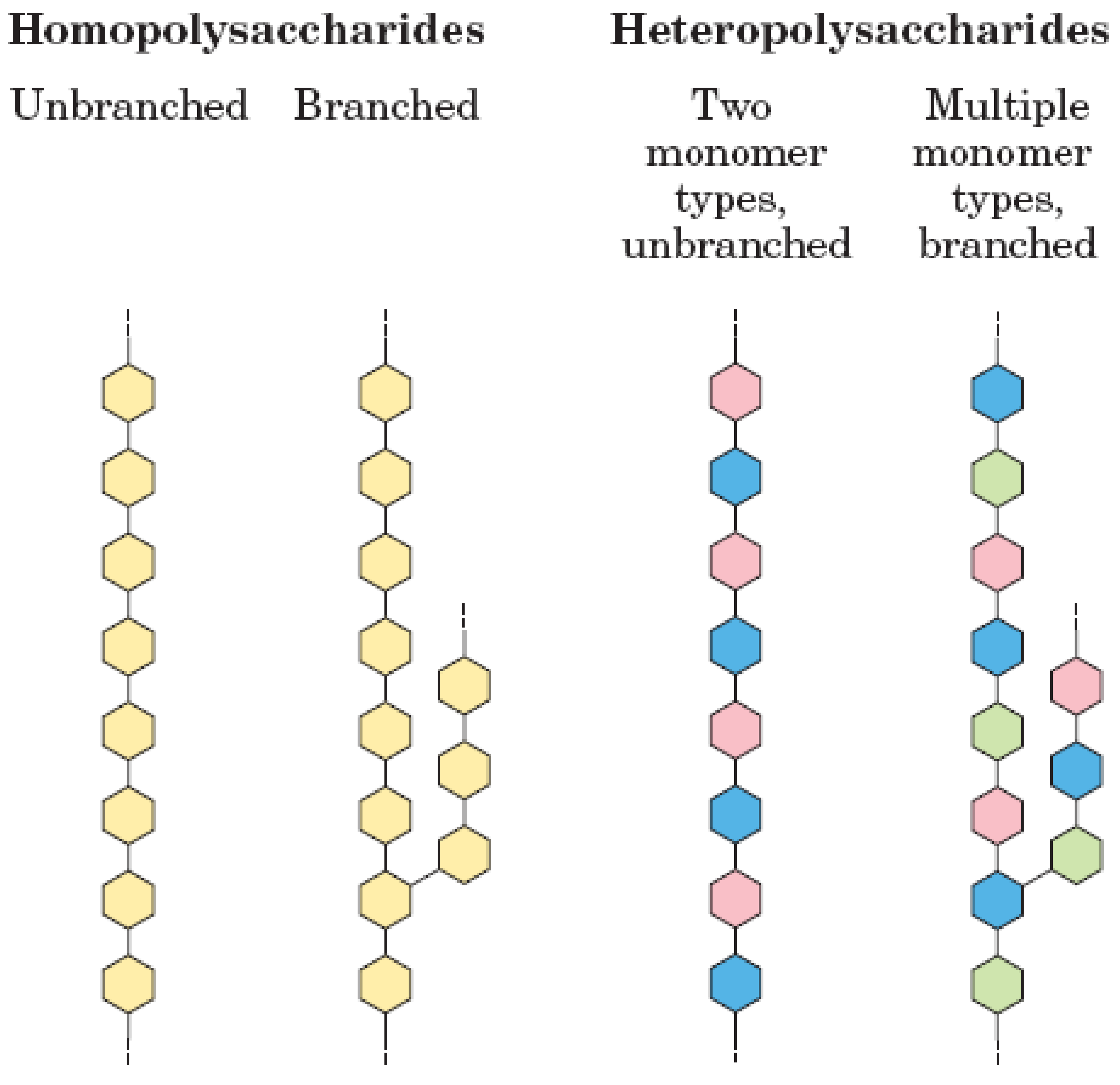
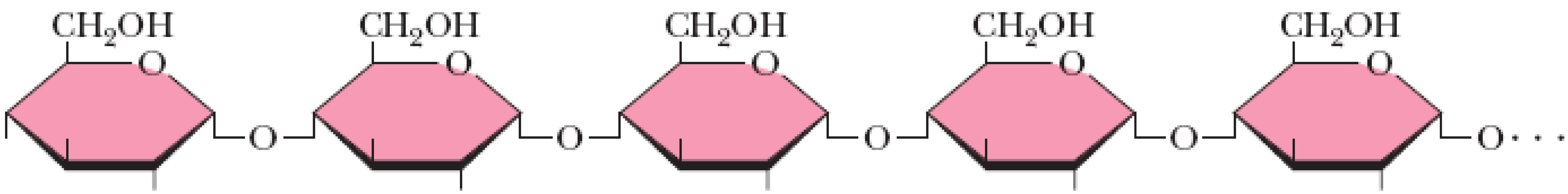
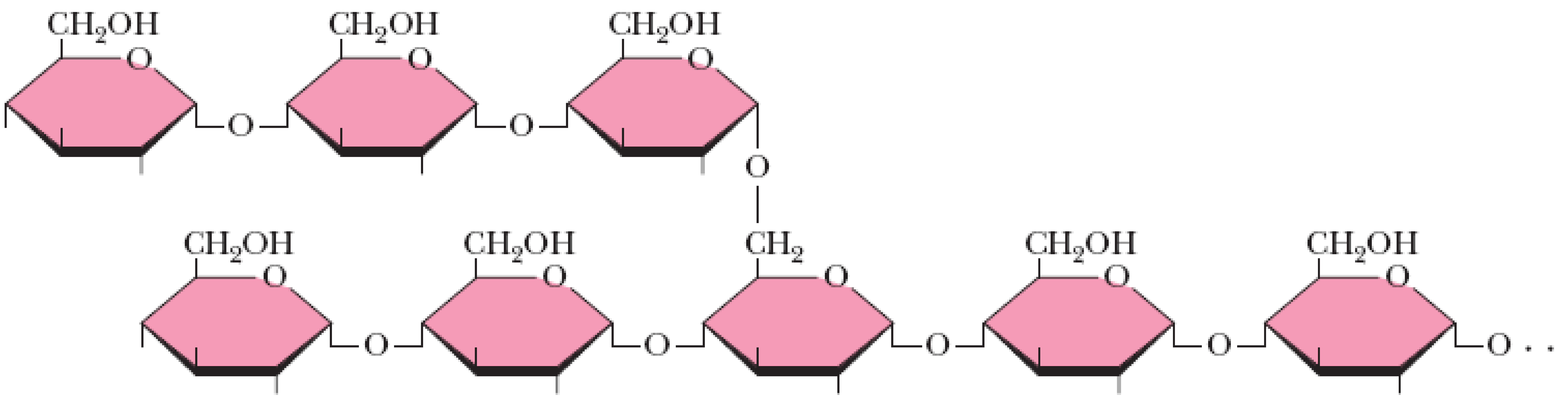


FIGURE 7–13 Homo- and heteropolysaccharides. Polysaccharides may be composed of one, two, or several different monosaccharides, in straight or branched chains of varying length.

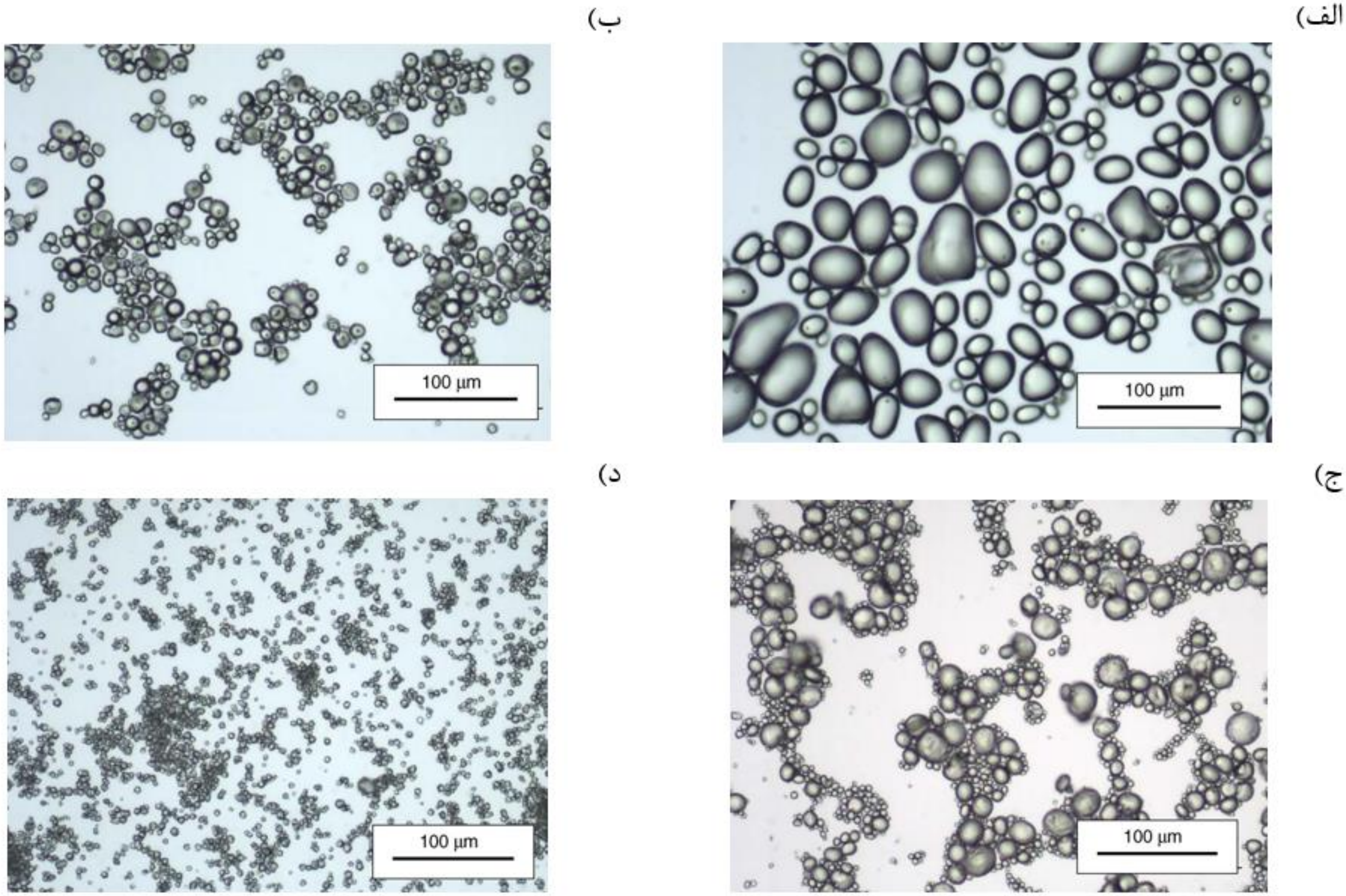


Amylose **10 -30 %**

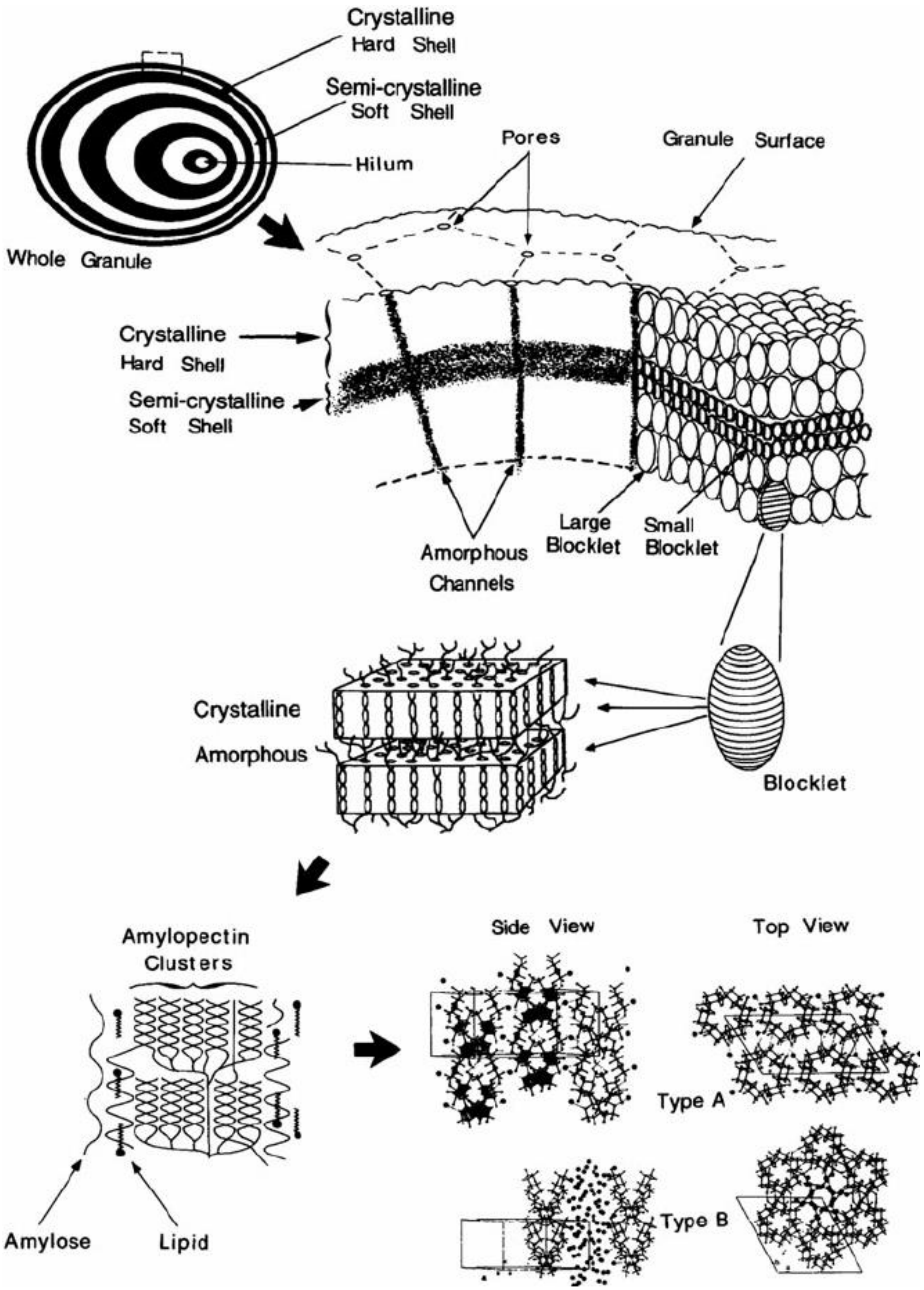


Amylopectin **70 - 90%**

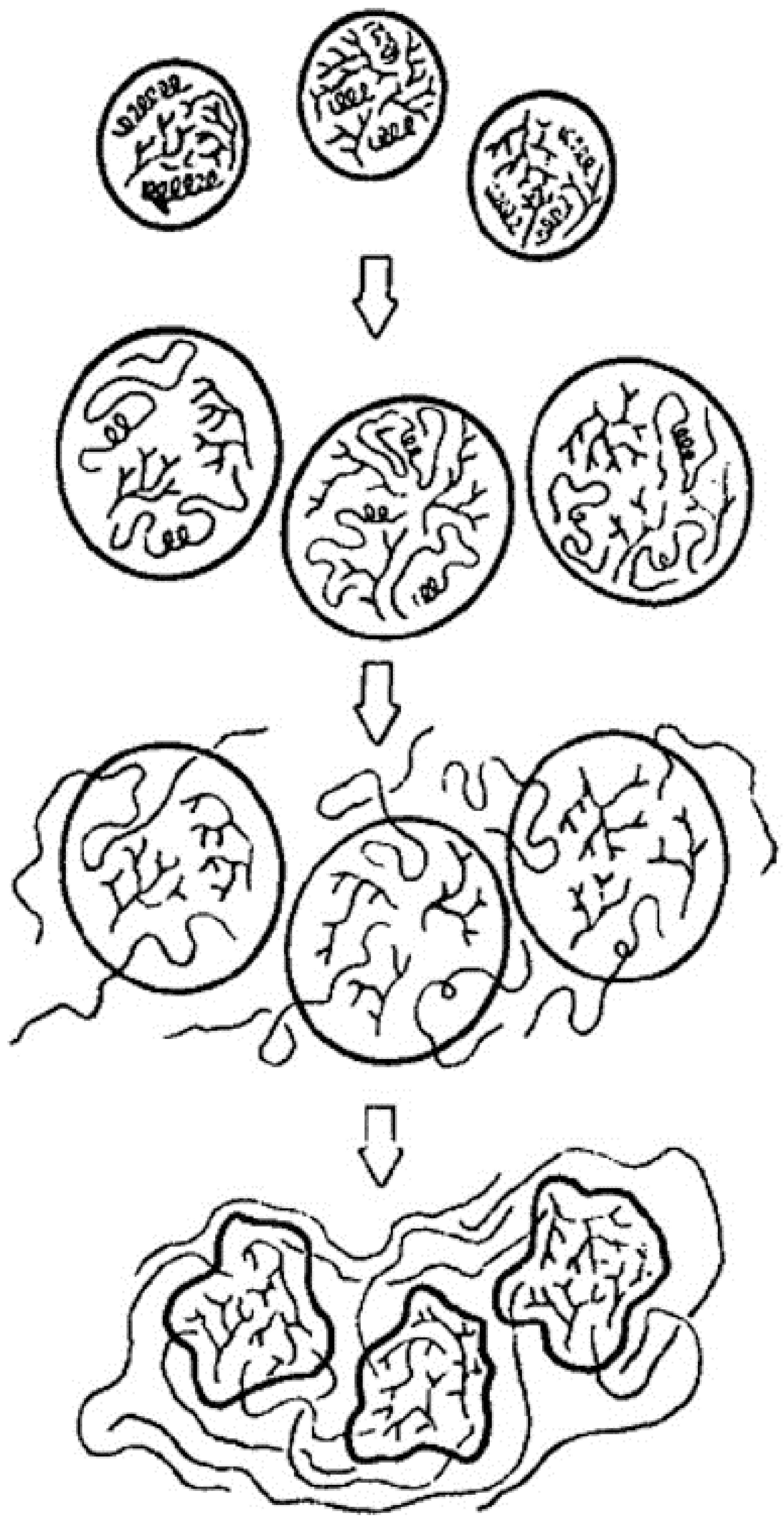
FIGURE 7.20 Amylose and amylopectin are the two forms of starch. Note that the linear linkages are $\alpha(1 \longrightarrow 4)$ but the branches in amylopectin are $\alpha(1 \longrightarrow 6)$. Branches in polysaccharides can involve any of the hydroxyl groups on the monosaccharide components. Amylopectin is a highly branched structure, with branches occurring every 12 to 30 residues.



شکل: میکروگراف نوری گرانول‌های نشاسته. الف) نشاسته‌ی سیب‌زمینی، ب) نشاسته‌ی ذرت، ج) نشاسته‌ی گندم، د) نشاسته‌ی برنج [۲۸].



Crystalline
Hard Shell
Semi-crystalline
Soft Shell
Hilum
Whole Granule
Pores
Granule Surface
Crystalline
Hard Shell
Semi-crystalline
Soft Shell
Amorphous
Channels
Large
Blocklet
Small
Blocklet
Crystalline
Amorphous
Blocklet
Amylopectin
Clusters
Amylose
Lipid
Side View
Top View
Type A
Type B

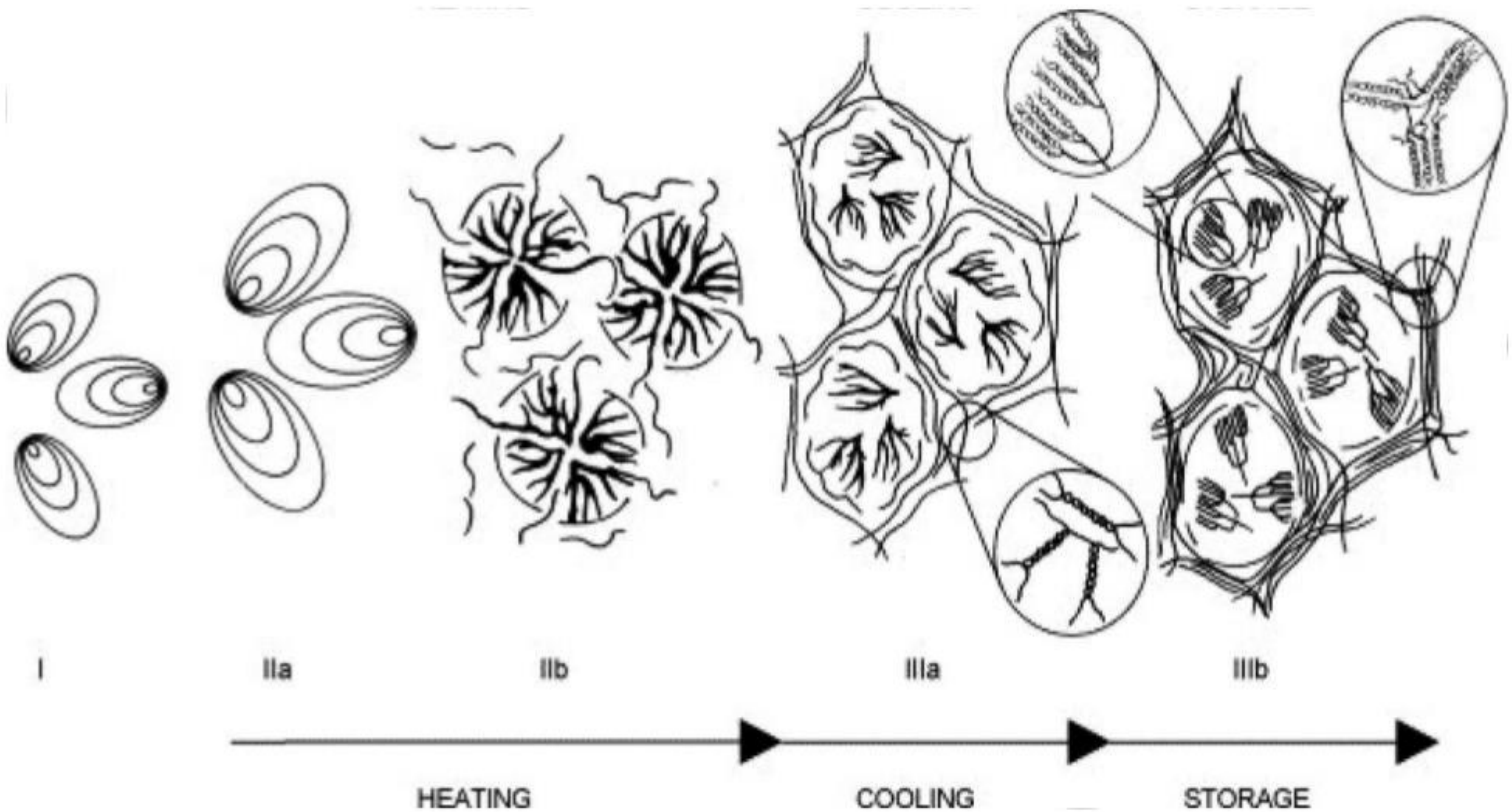


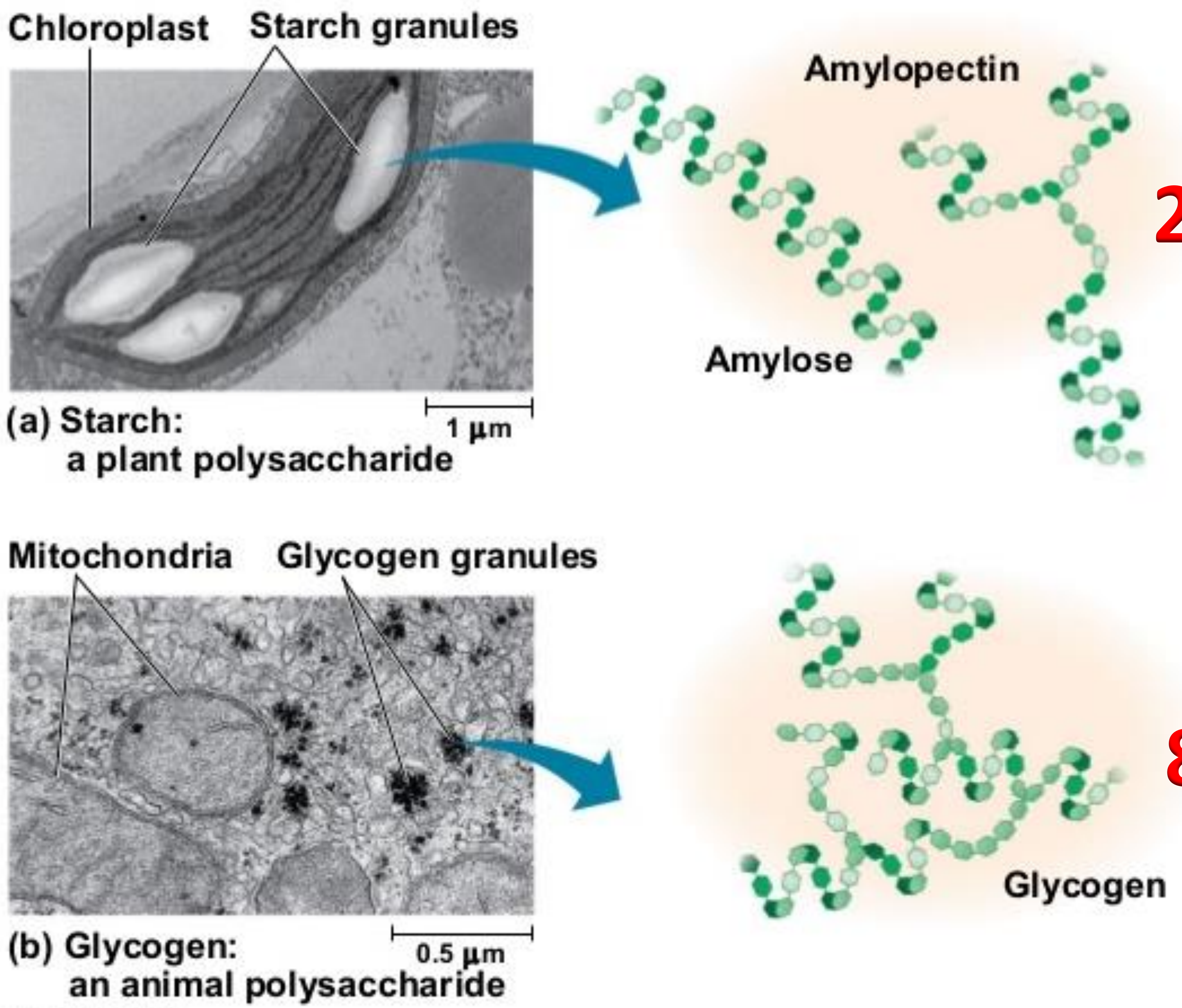
Raw starch granules made up of amylose (helix) and amylopectin (branched)

Addition of water breaks up amylose crystallinity and disrupts helices.
Granules swell

Addition of heat and more water cause more swelling.
Amylose begins to diffuse out of granules.

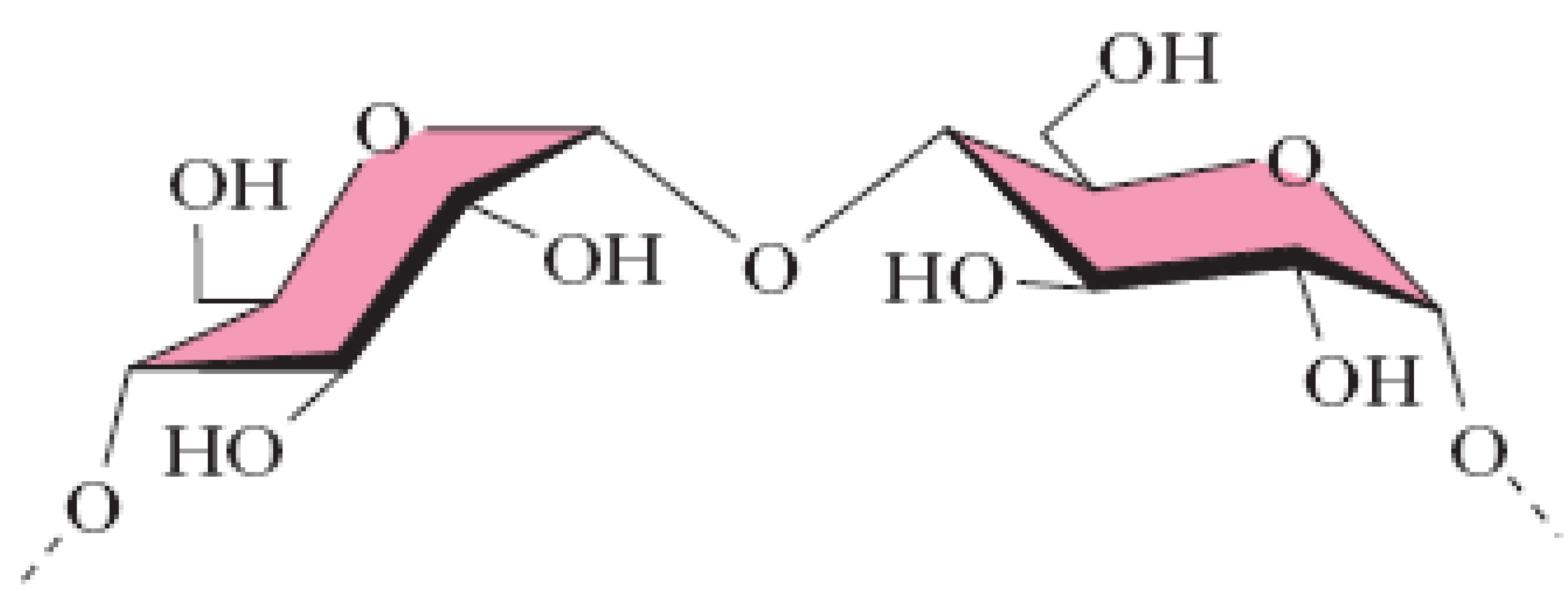
Granules, now containing mostly amylopectin, have collapsed and are held in a matrix of amylose forming a gel


I
IIa
IIb
IIIa
IIIb
HEATING
COOLING
STORAGE


Chloroplast
Starch granules
Amylopectin
Amylose
1 µm
(a) Starch: a plant polysaccharide
Mitochondria
Glycogen granules
Glycogen
0.5 µm
(b) Glycogen: an animal polysaccharide

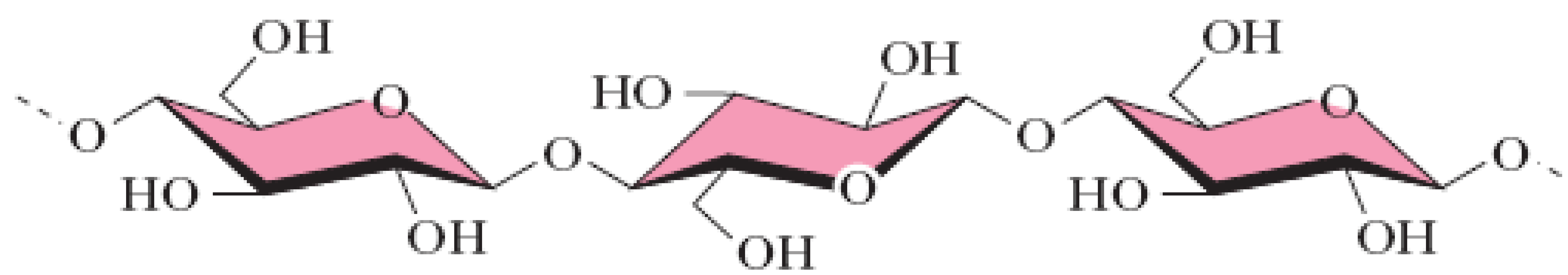
24 -30

8 -12



α-1,4-Linked D-glucose units

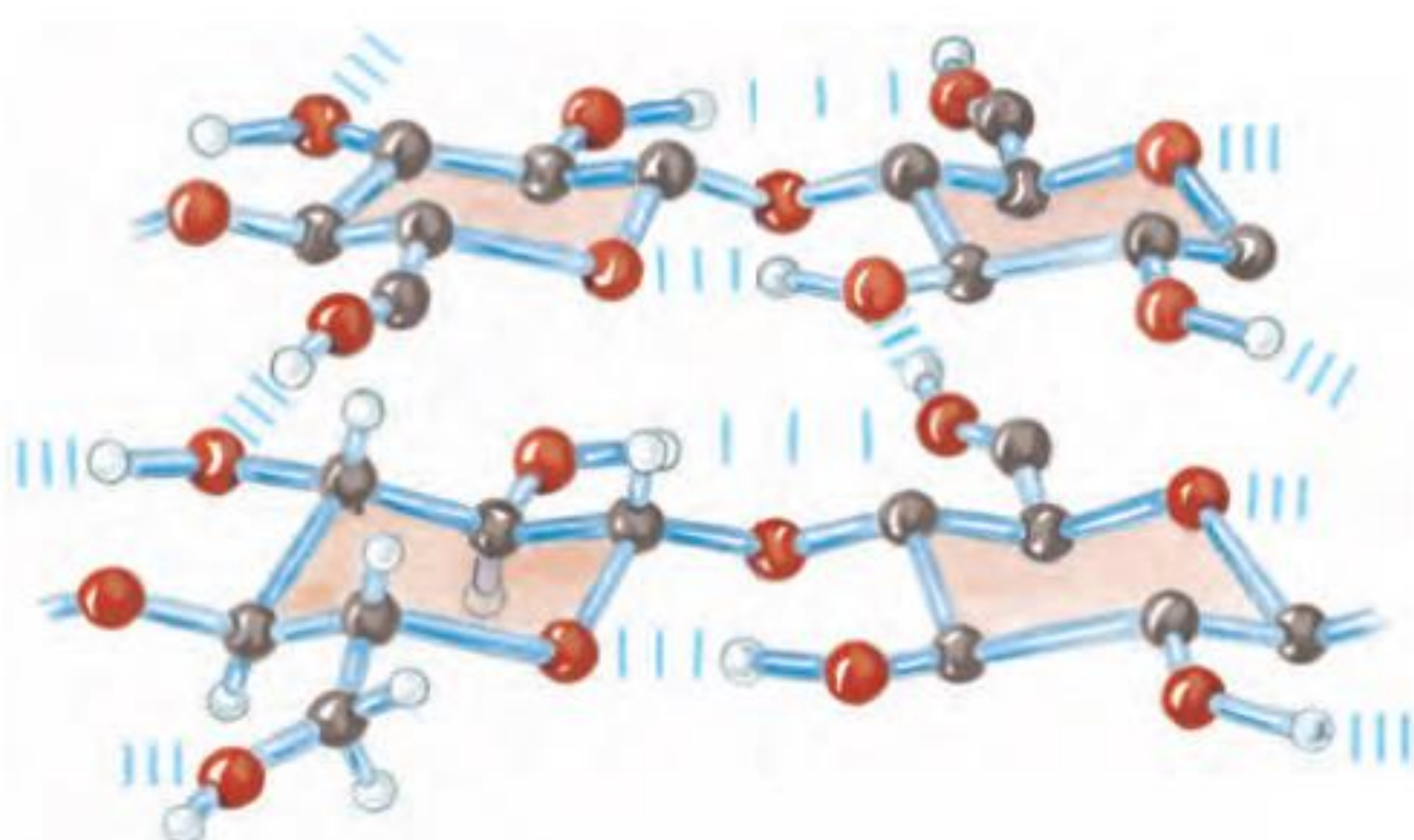
(a)

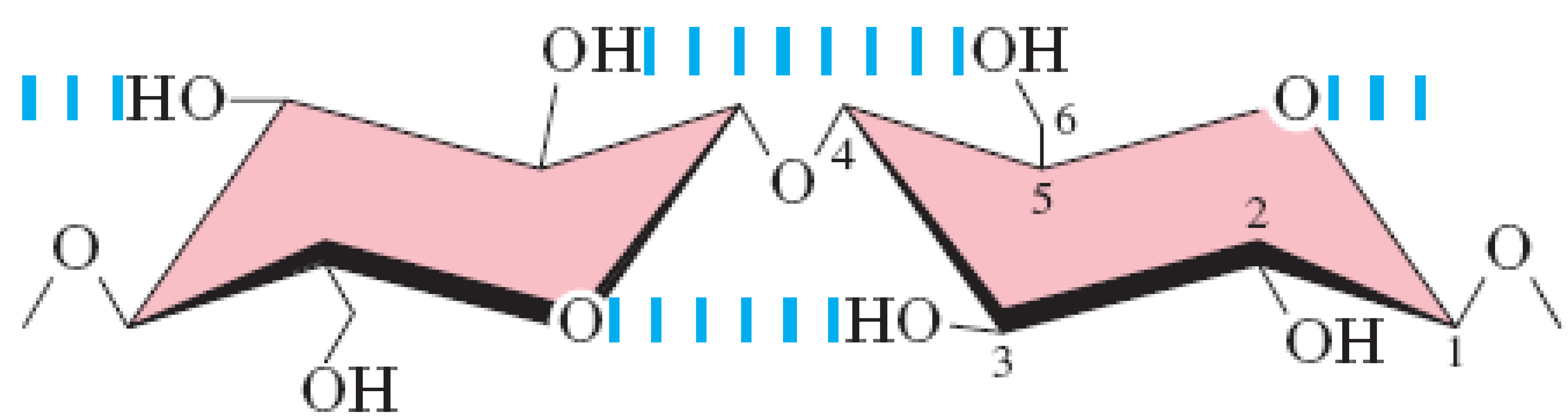


β-1,4-Linked D-glucose units

(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

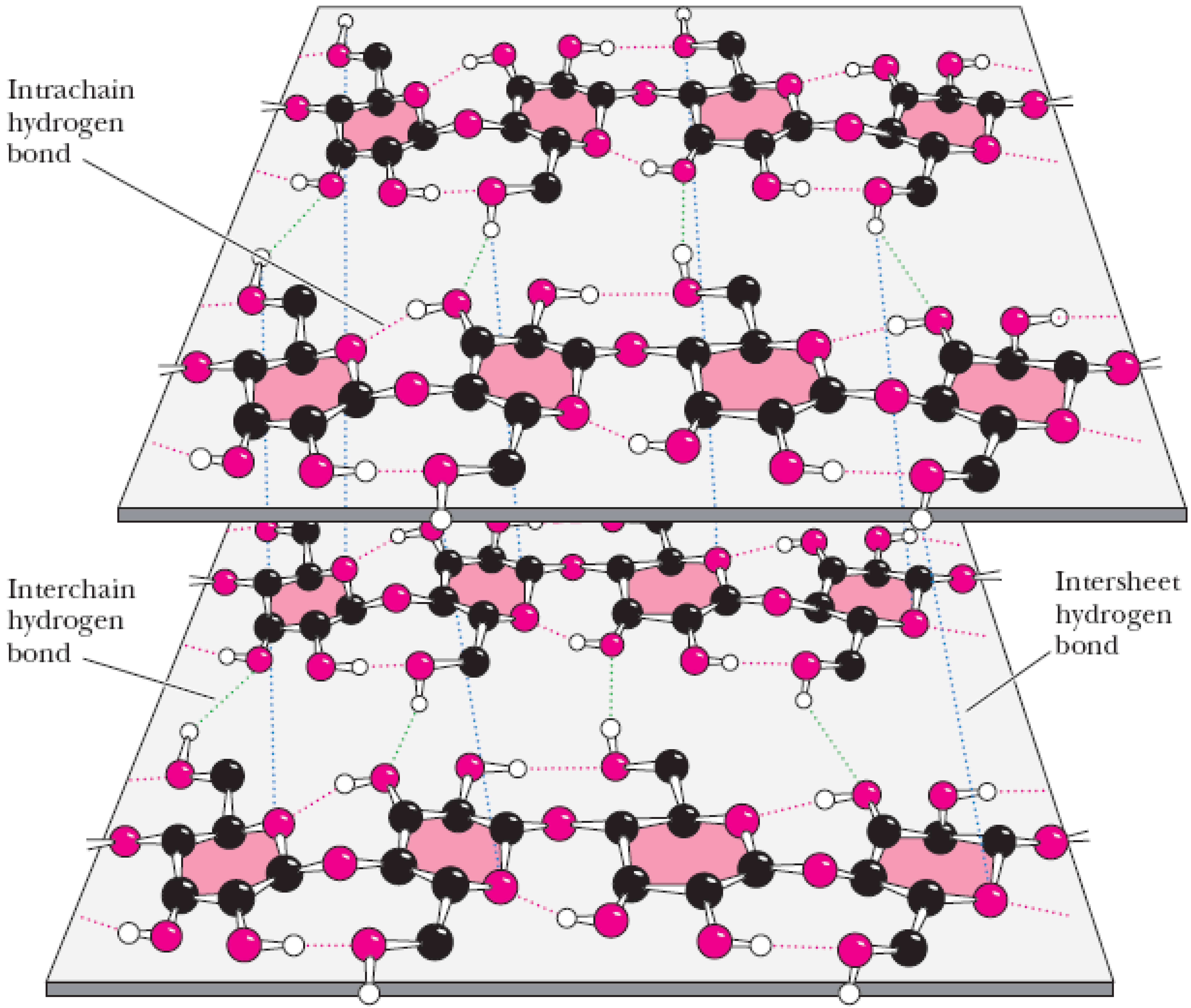
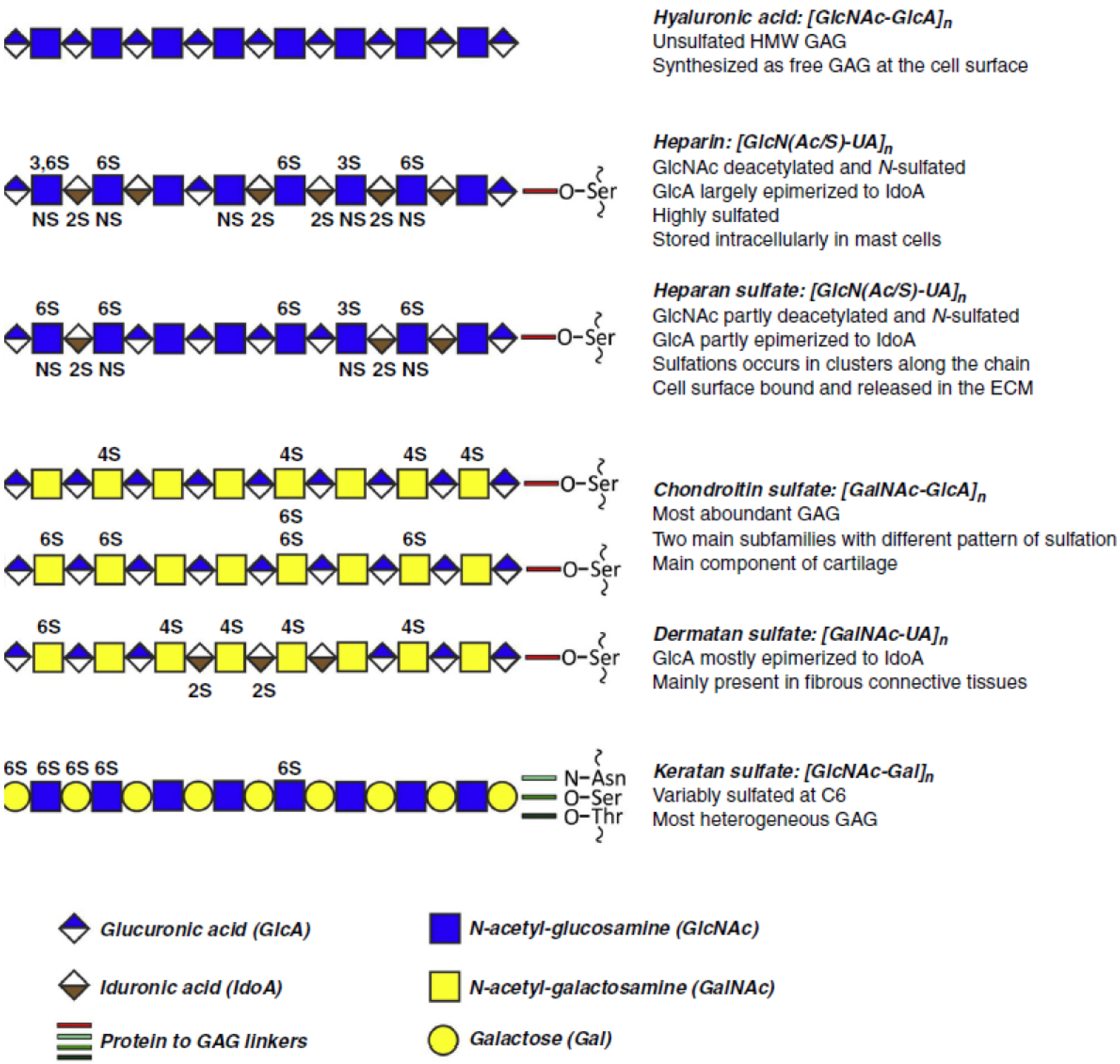
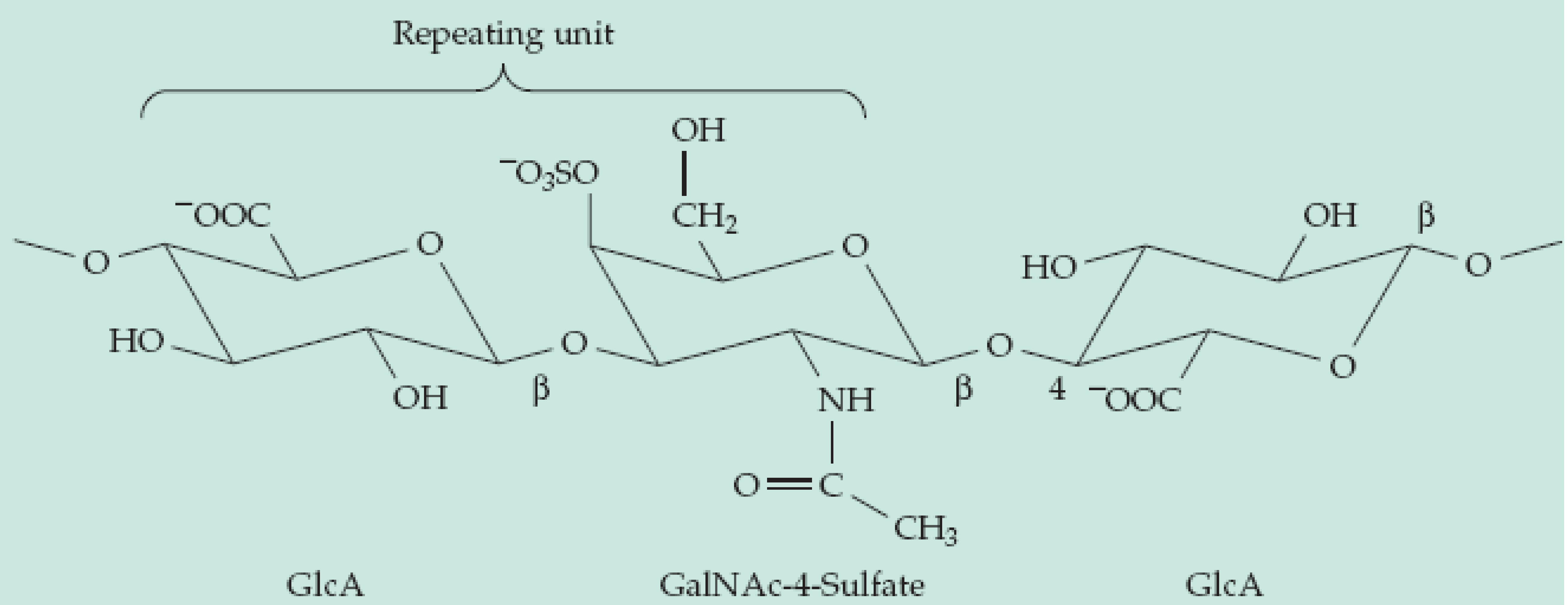


FIGURE 7.24 The structure of cellulose, showing the hydrogen bonds (blue) between the sheets, which strengthen the structure. Intrachain hydrogen bonds are in red, and interchain hydrogen bonds are in green. (Illustration: Irving Geis. Rights owned by Howard Hughes Medical Institute. Not to be reproduced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



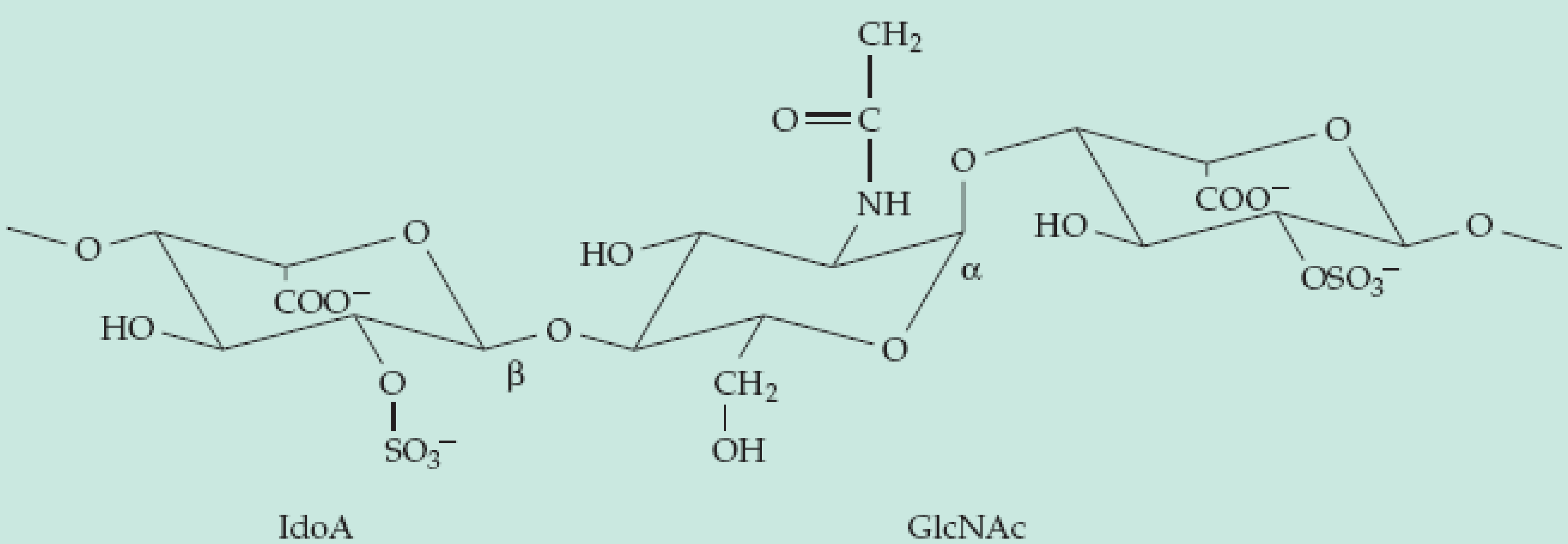
شکل ٤-١: اعضای خانواده‌ی گلیکوزآمینوگلیکان. علامت‌های اختصاری: HMW: وزن مولکولی بالا، GAG: گلیکوزآمینوگلیکان، ECM: ماتریکس خارج‌سلولی [٥٦].

Type I Chain. Alternating 1→3 and 1→4 linkages; all β, (equatorial).

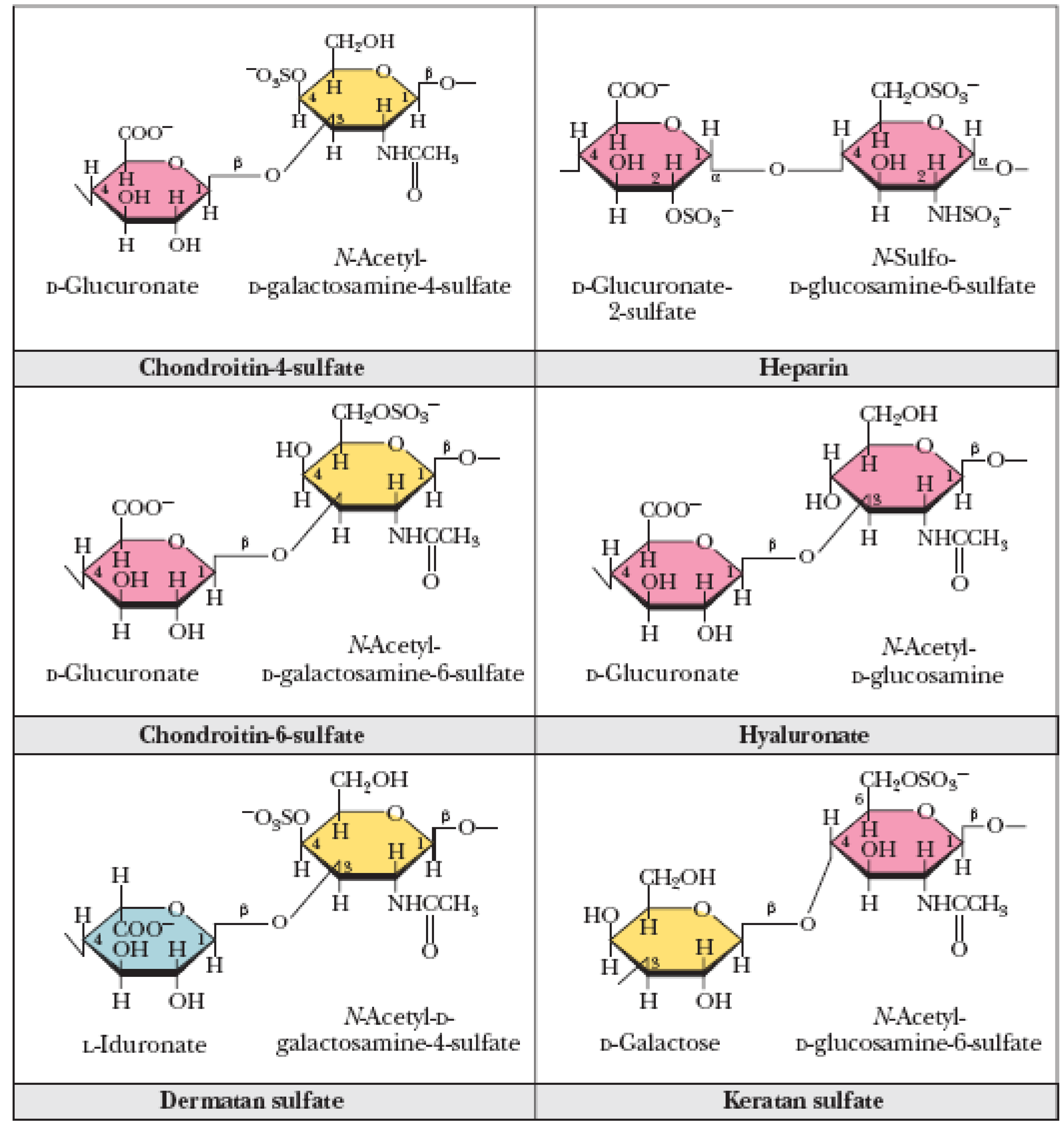


Name	Repeating unit	Variations
Hyaluronan	[–4GlcAβ1→3GlcNAcβ1→]$_n$	None. Homogeneous.
Chondroitin sulfate	[–4GlcAβ1→3GalNAc(SO_3^-)β1→)$_n$	Some GlcA-2-SO_3^-, GalNAc-4- or 6-SO_3^- or both.
Dermatan sulfate	[–4IdoAα1→3GalNAc(4-SO_3^-)β1→)$_n$	Some L-IdoA-2-SO_3^-.
Keratan sulfate	[–3Galβ1→4GlcNAc(6-SO_3^-)β1→)$_n$	Some Gal-6-SO_3, some Sia, Man, Fuc

Type II Chain. All 1→4 linkages, alternating β and α (axial).



Name	Repeating unit	Variations
Heparan sulfate	[–4-GlcAβ1→4GlcNAc]$_n$	Some IdoA, sulfation.
Heparin	[–4-L-IdoA(SO_3^-)α1→4GlcN(SO_3^-)α1→]$_n$	Some IdoA-2-SO_3^-, GlcNAc. 24 different disaccharides possible.



Peptidoglycan Is the Polysaccharide of Bacterial Cell Walls

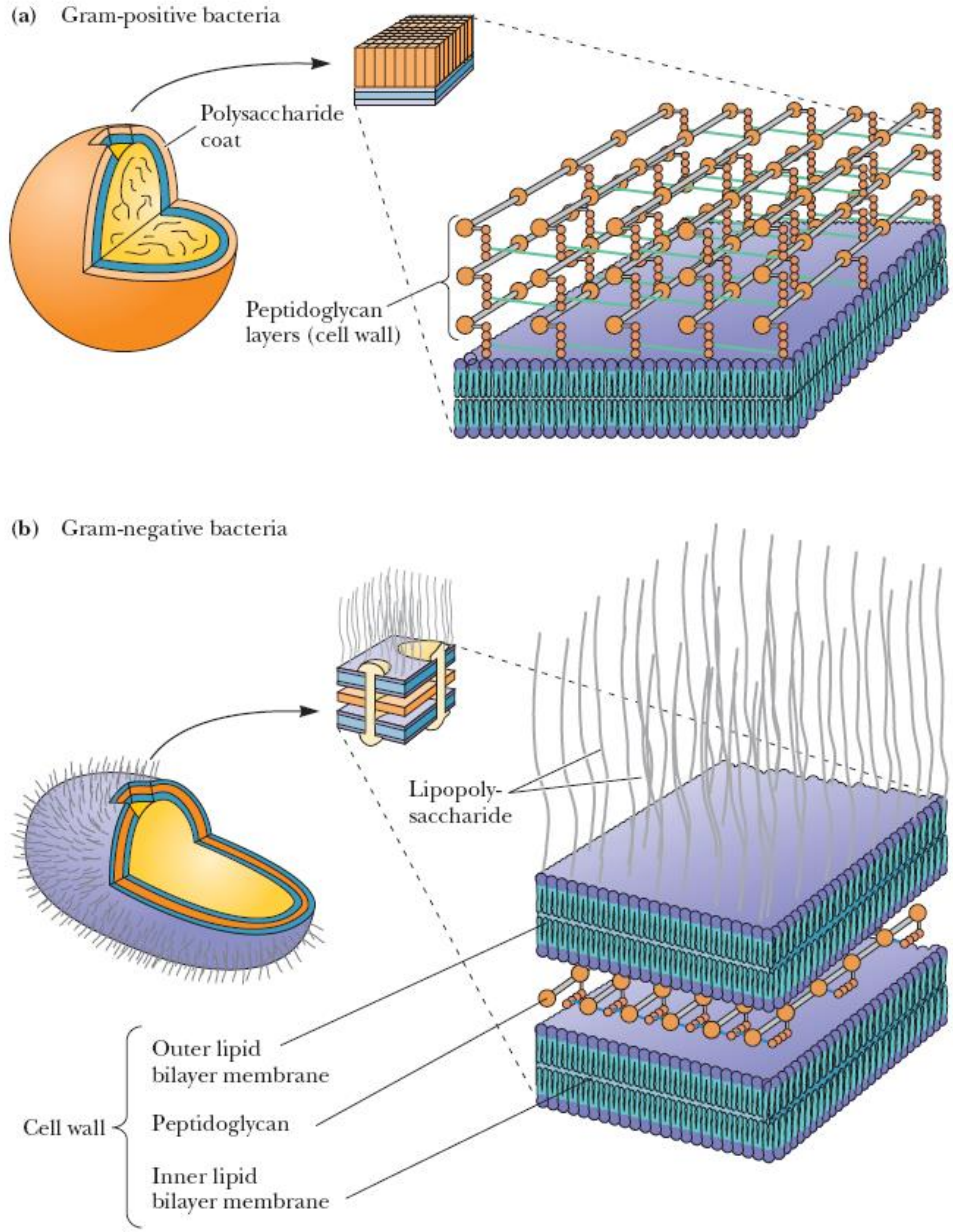


FIGURE 7.30 The structures of the cell wall and membrane(s) in Gram-positive and Gram-negative bacteria. The Gram-positive cell wall is thicker than that in Gram-negative bacteria, compensating for the absence of a second (outer) bilayer membrane.

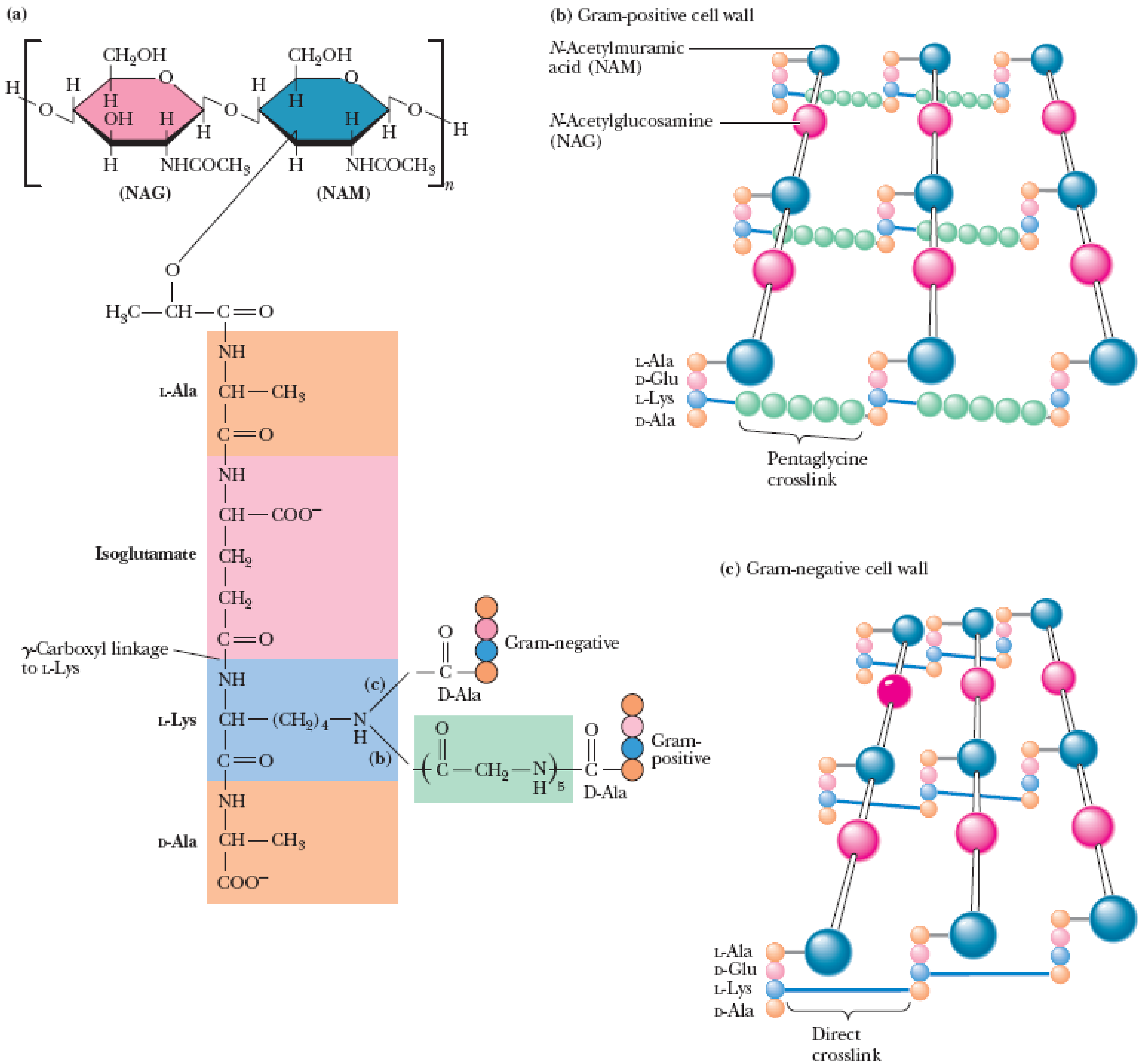
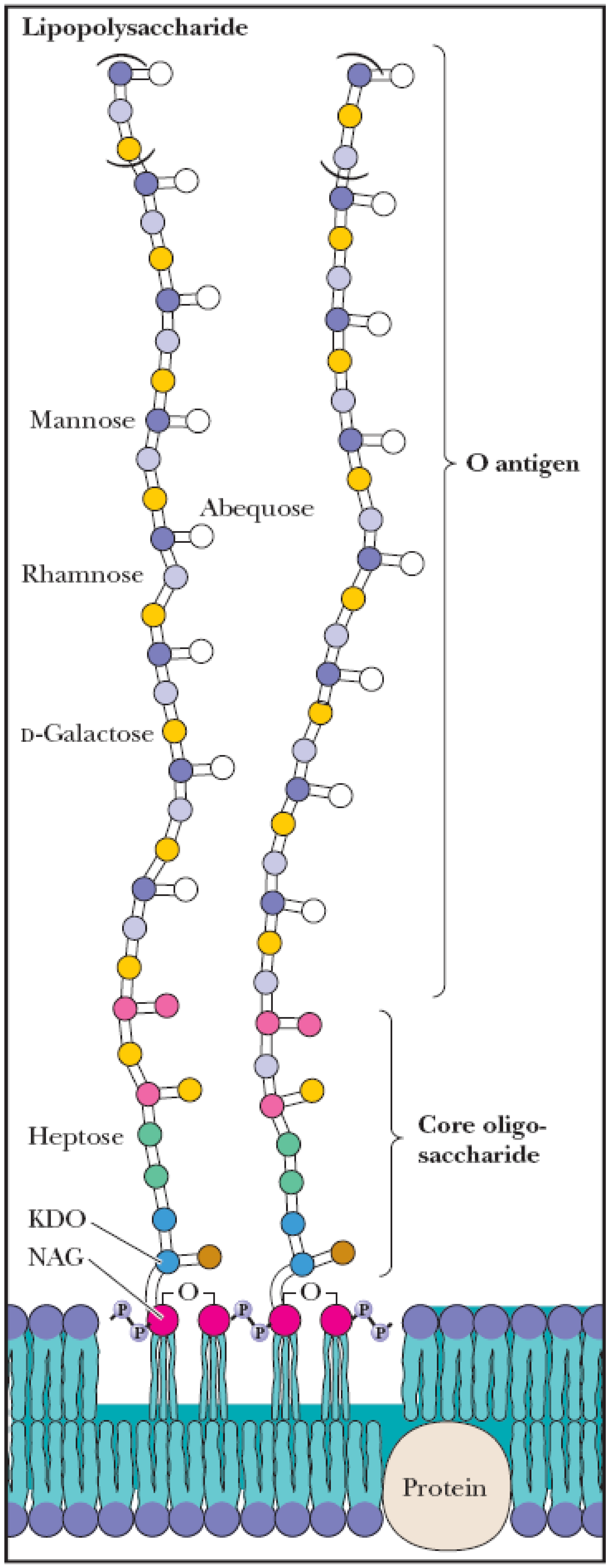
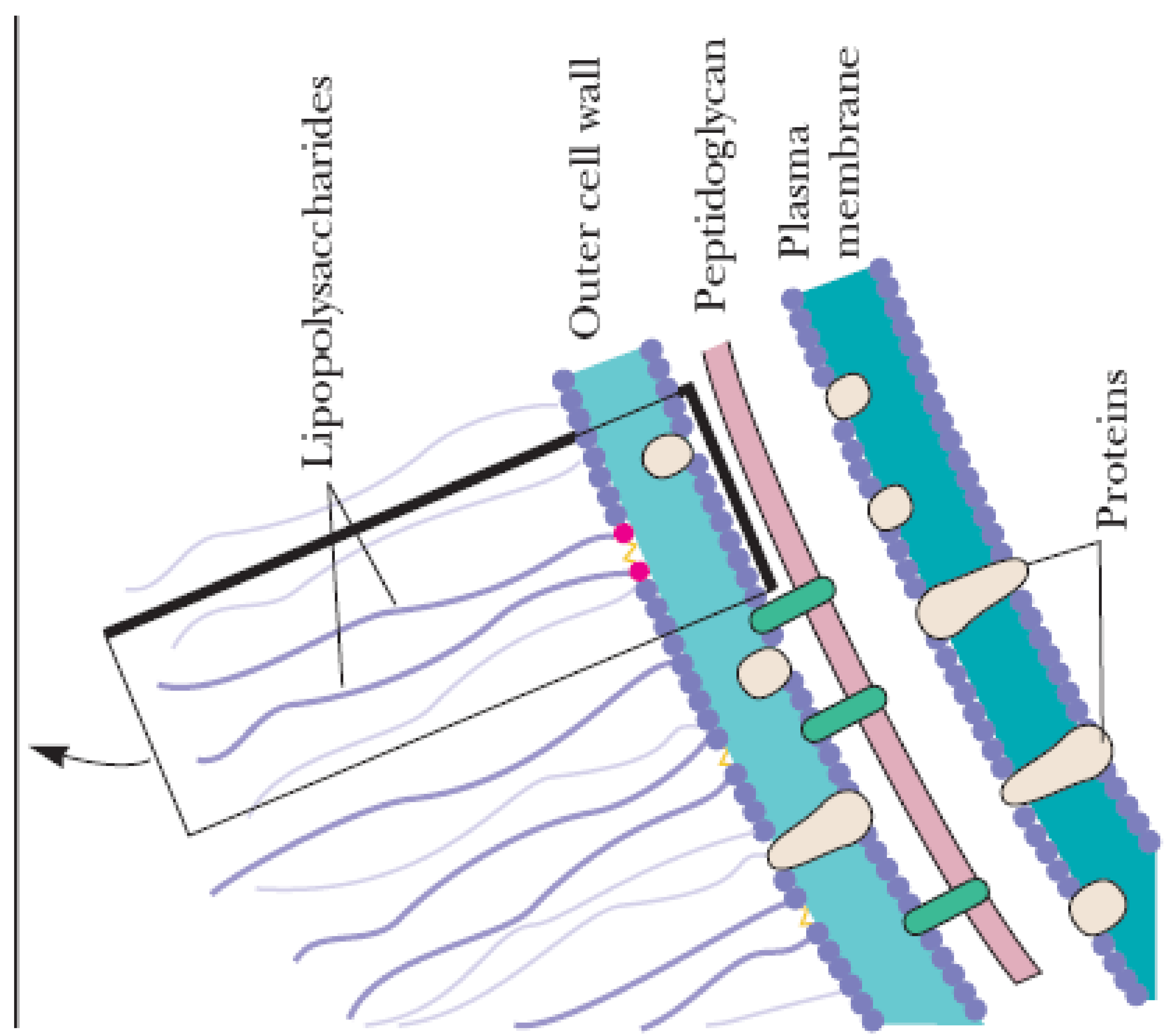


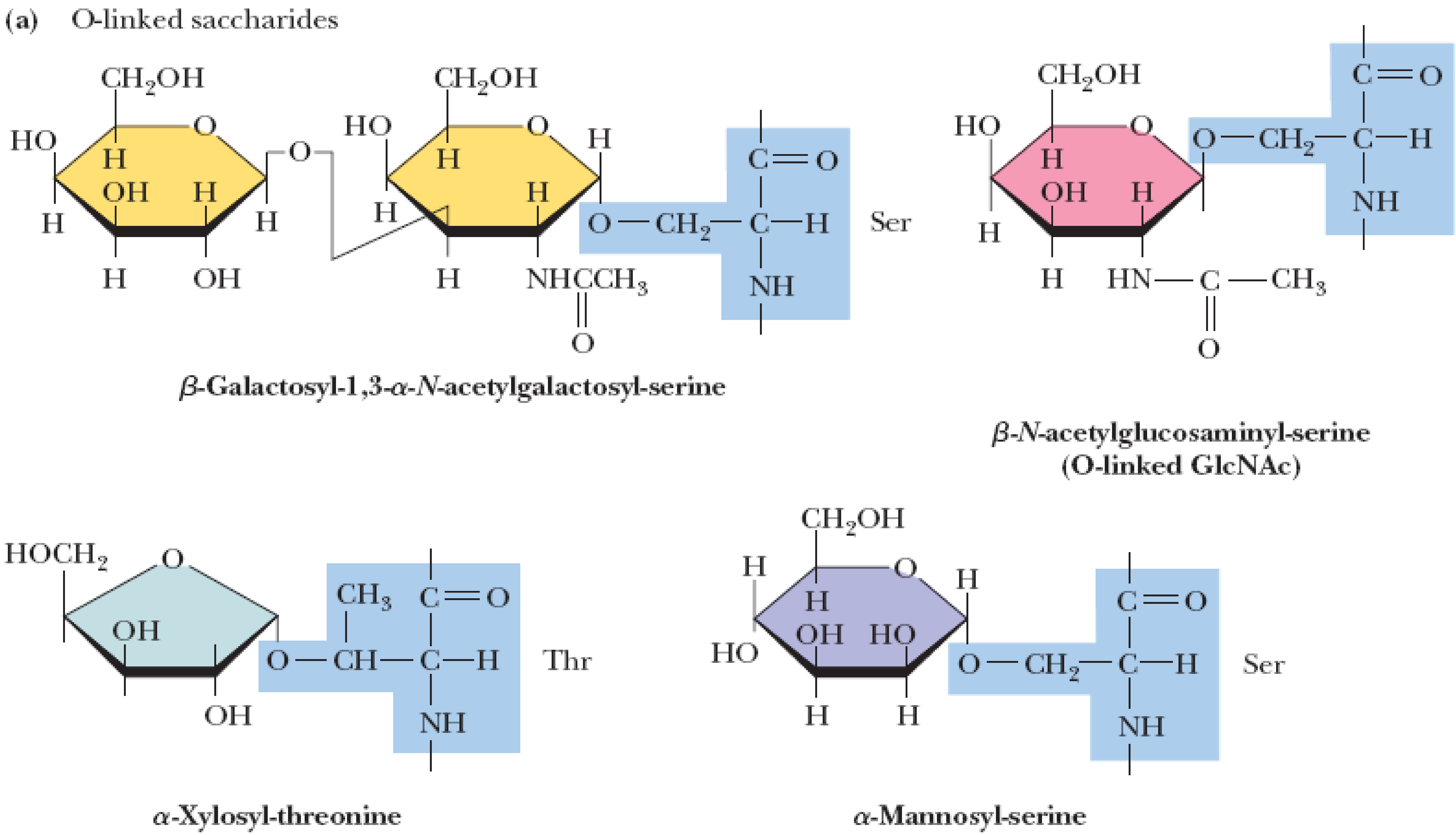
FIGURE 7.29 **(a)** The structure of peptidoglycan. The tetrapeptides linking adjacent backbone chains contain an unusual γ-carboxyl linkage. **(b)** The crosslink in Gram-positive cell walls is a pentaglycine bridge. **(c)** In Gram-negative cell walls, the linkage between the tetrapeptides of adjacent carbohydrate chains in peptidoglycan involves a direct amide bond between the lysine side chain of one tetrapeptide and D-alanine of the other.



Lipopolysaccharide
Mannose
Abequose
Rhamnose
D-Galactose
Heptose
KDO
NAG
O
P
O antigen
Core oligo-
saccharide
Protein



Lipopolysaccharides
Outer cell wall
Peptidoglycan
Plasma
membrane
Proteins



The carbohydrate residue linked to the protein in O-linked saccharides is usually an *N-acetylgalactosamine, but mannose, galactose, and xylose residues linked to protein* hydroxyls are also found.

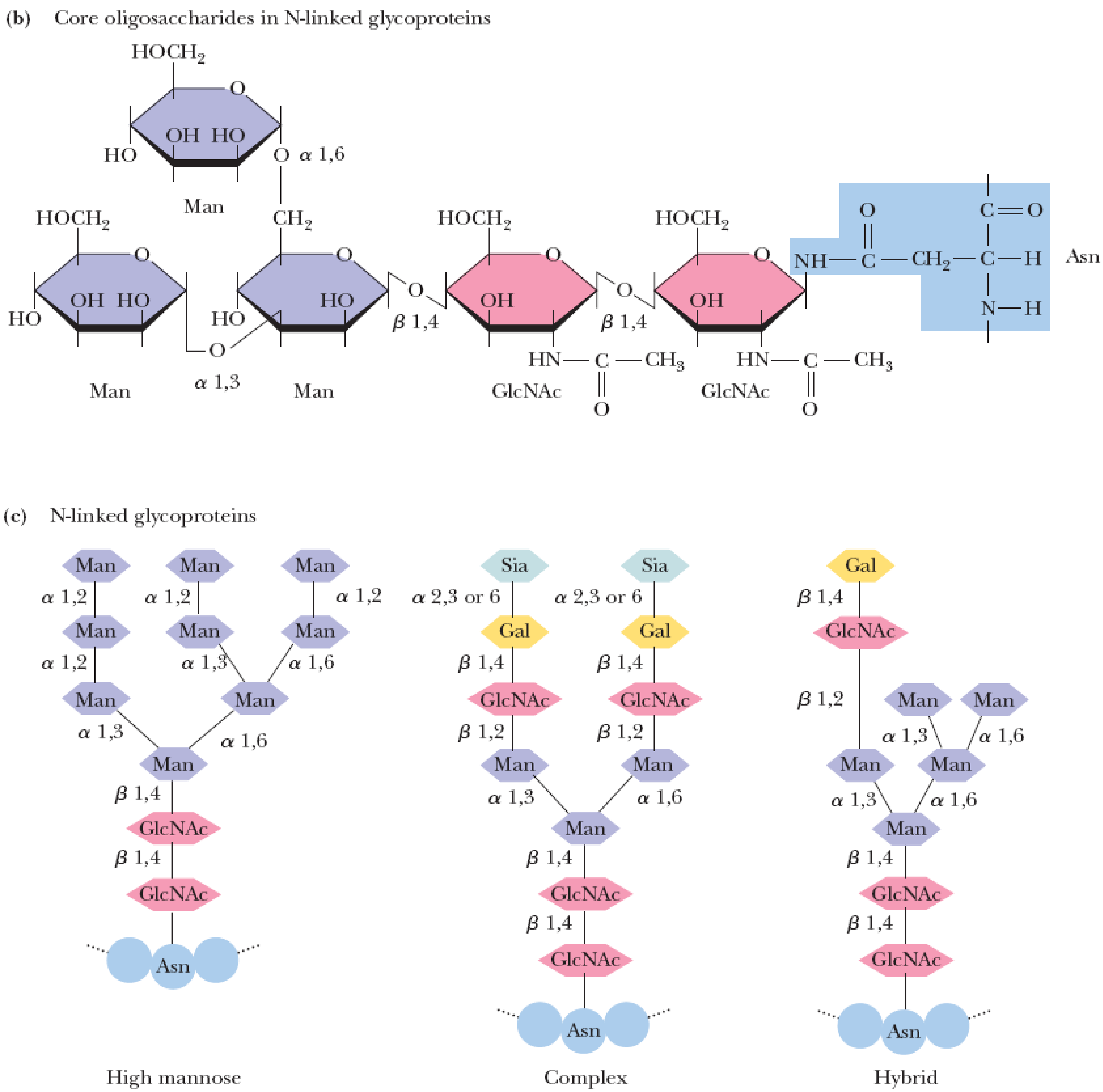


FIGURE 7.32 The carbohydrate moieties of glycoproteins may be linked to the protein via (**a**) serine or threonine residues (in the O-linked saccharides) or (**b**) asparagine residues (in the N-linked saccharides). (**c**) N-linked glycoproteins are of three types: high mannose, complex, and hybrid, the latter of which combines structures found in the high mannose and complex saccharides.

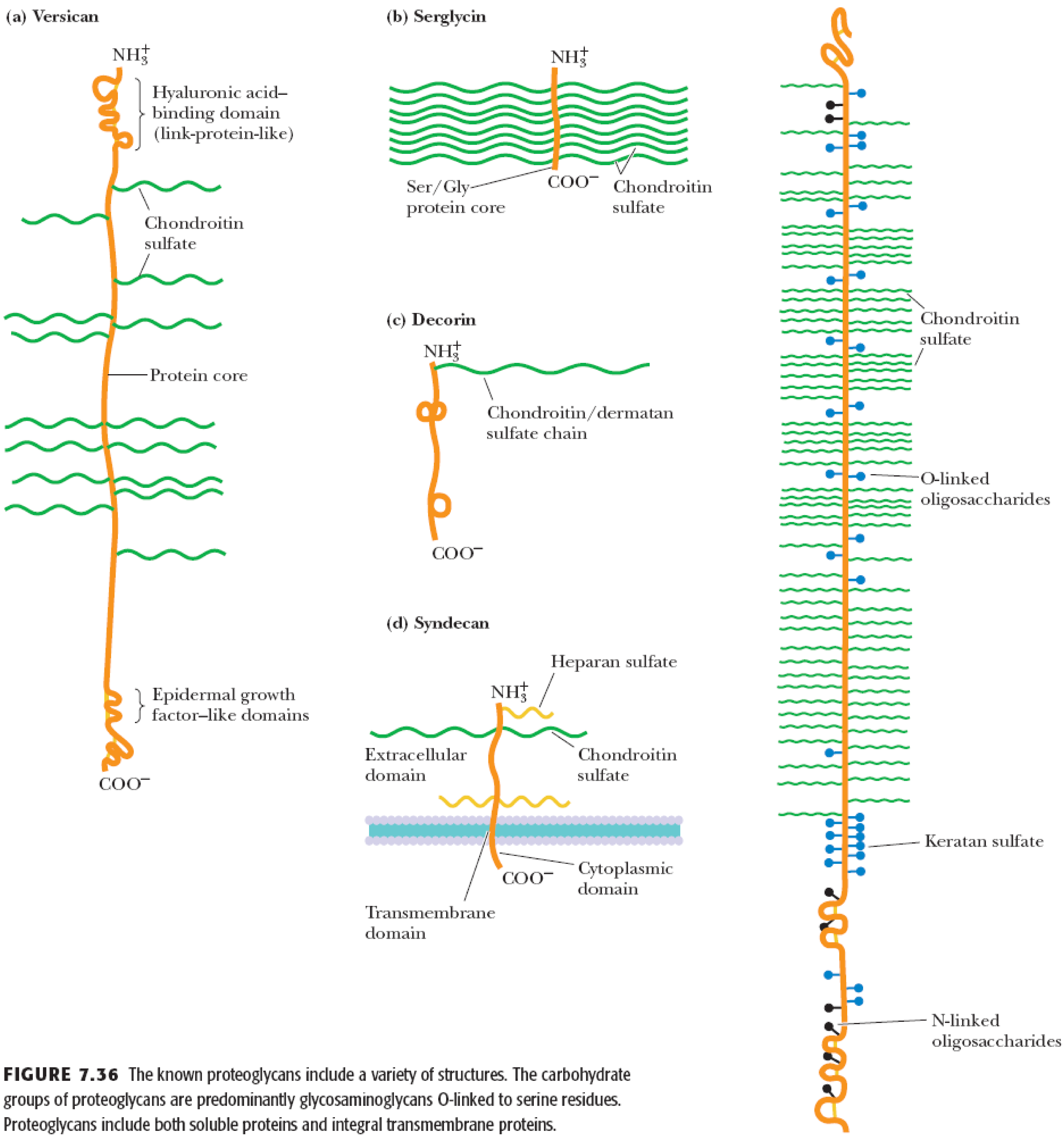


FIGURE 7.36 The known proteoglycans include a variety of structures. The carbohydrate groups of proteoglycans are predominantly glycosaminoglycans O-linked to serine residues. Proteoglycans include both soluble proteins and integral transmembrane proteins.

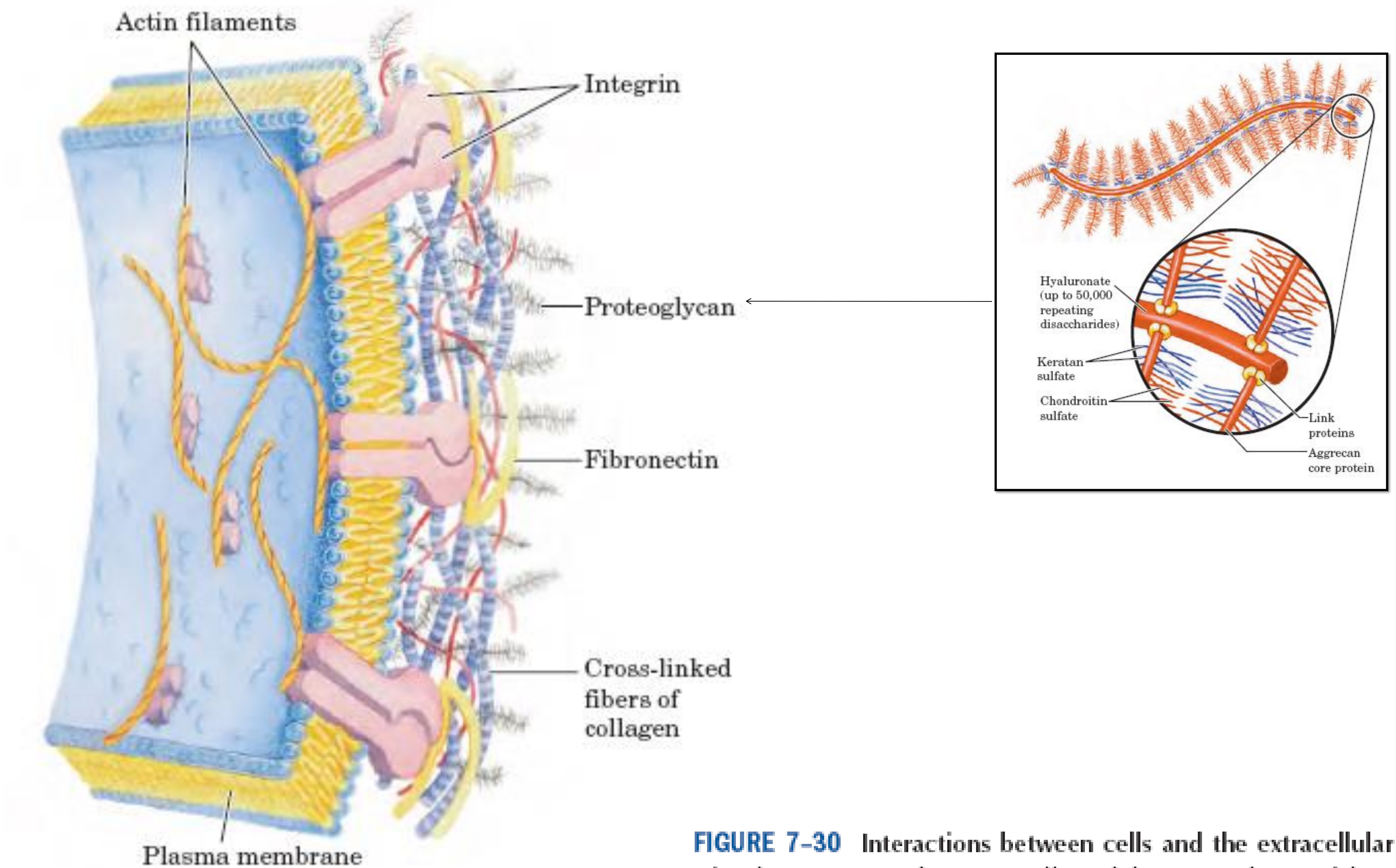


FIGURE 7–30 Interactions between cells and the extracellular matrix. The association between cells and the proteoglycan of the extracellular matrix is mediated by a membrane protein (integrin) and by an extracellular protein (fibronectin in this example) with binding sites for both integrin and the proteoglycan.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

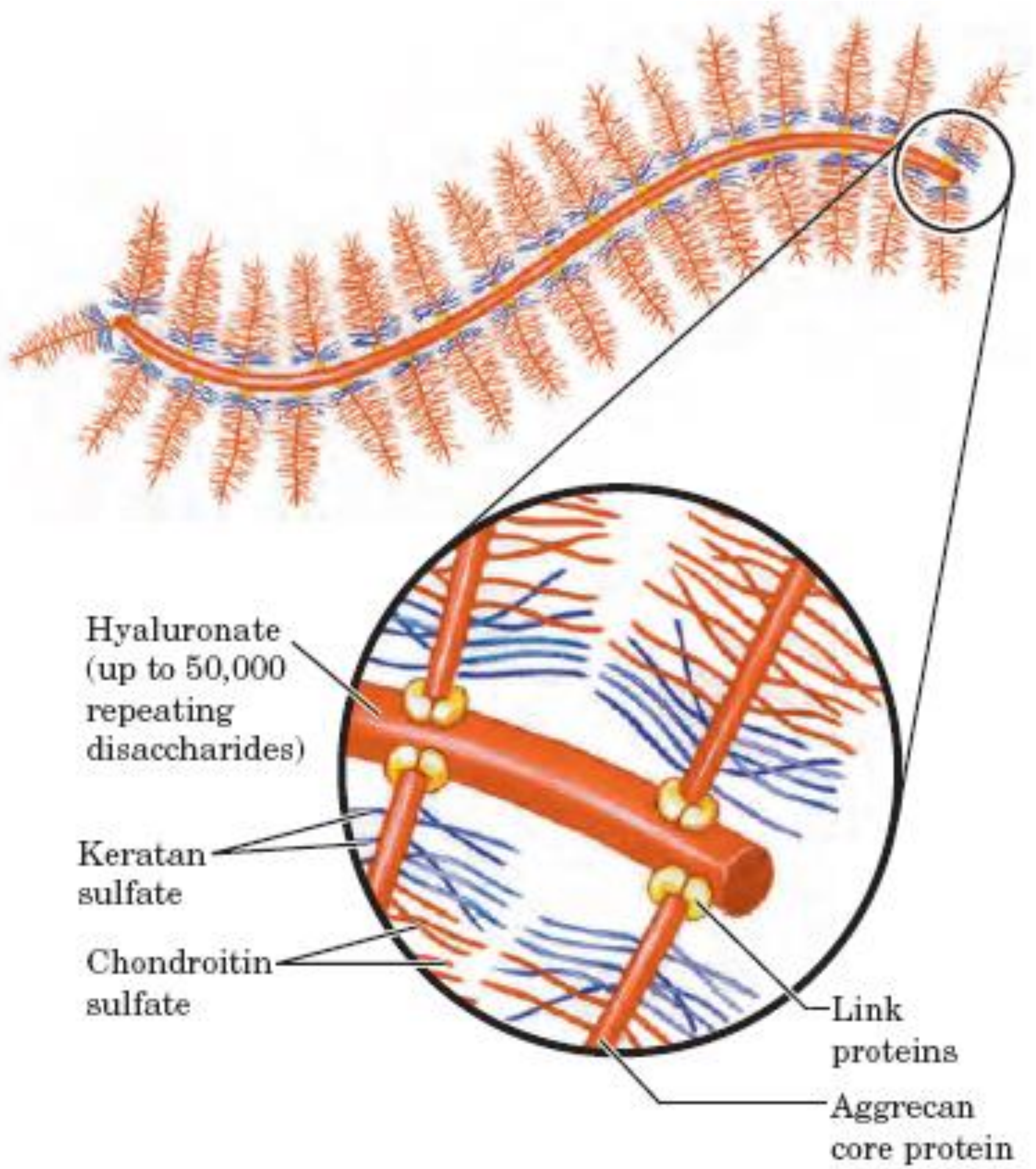


FIGURE 7–29 Proteoglycan aggregate of the extracellular matrix. One very long molecule of hyaluronate is associated noncovalently with about 100 molecules of the core protein aggrecan. Each aggrecan molecule contains many covalently bound chondroitin sulfate and keratan sulfate chains. Link proteins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

Carbohydrates as Informational Molecules: The Sugar Code

- ***Glycobiology***, the study of the structure and function of glycoconjugates, is one of the most active and exciting areas of biochemistry and cell biology.
- It is becoming increasingly clear that cells use specific oligosaccharides to encode important information about *intracellular targeting of proteins*, *cell-cell interactions*, *cell differentiation and tissue development*, and *extracellular signals*.
- Our discussion uses just a few examples to illustrate the diversity of structure and the range of biological activity of the glycoconjugates.

Carbohydrates as Informational Molecules: The Sugar Code

- Improved methods for the analysis of oligosaccharide and polysaccharide structure have revealed ***remarkable complexity and diversity in the oligosaccharides of glycoproteins and glycolipids***.

- Consider the oligosaccharide chains in Figure 7-30, typical of those found in many glycoproteins. The most complex of those shown contains 14 monosaccharide residues of four different kinds, variously linked as (1→2), (1→3), (1→4), (1→6), (2→3), and (2→6), some with the α and some with the β configuration.

- ***Branched structures***, not found in nucleic acids or proteins, are common in oligosaccharides.

- With the reasonable assumption that ***20 different monosaccharide subunits*** are available for construction of oligosaccharides, we can calculate that many billions of different hexameric oligosaccharides are possible; this compares with 6.4×10^7 (20^6) different hexapeptides possible for the 20 common amino acids, and 4,096 (4^6) different hexanucleotides for the four nucleotide subunits.

- If we also allow for variations in oligosaccharides resulting from sulfation of one or more residues, the number of possible oligosaccharides increases by two orders of magnitude.

- In reality, only a subset of possible combinations is found, given the restrictions imposed by the biosynthetic enzymes and the availability of precursors.

Working with Carbohydrates

- Another important tool in working with carbohydrates is chemical synthesis, which has proved to be a powerful approach to understanding the biological functions of glycosaminoglycans and oligosaccharides.
- The chemistry involved in such syntheses is difficult, but carbohydrate chemists can now synthesize short segments of almost any glycosaminoglycan, with correct stereochemistry, chain length, and sulfation pattern, and oligosaccharides significantly more complex than those shown in Figure 7-30.
- Solid-phase oligosaccharide synthesis is based on the same principles (and has the same advantages) as peptide synthesis, but requires a set of tools unique to carbohydrate chemistry: blocking groups and activating groups that allow the synthesis of glycosidic linkages with the correct hydroxyl group.
- Synthetic approaches of this type currently represent an area of great interest, because it is difficult to purify defined oligosaccharides in adequate quantities from natural sources.