

ساختار ماکرومولکولهای زیستی (کربوهیدراتها)



ALDOHEXOSES





KETOTRIOSE

KETOTETROSE

KETOPENTOSES

KETOHEXOSES









FISCHER PROJECTION FORMULAS



Alcohol

Ketone

Hemiketal



Furan











β-D-Fructofuranose

FISCHER PROJECTION FORMULAS







Furanose form

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

Furanose form



a = axial bond e = equatorial bond

(b)



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









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



In solution, 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.

solely DNA, exists In as deoxyribofuranose.

















³T₂

Figure 2-7. Definition of sugar puckering modes. (a) Starting position with flat fivemembered 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, ³E. (c) Envelope C_{2'}-endo. ²E. (d) Symmetrical twist or half-chair $C_{2'}-exo$ - $C_{3'}$ -endo. ${}_{2}^{3}T$. (e) Unsymmetrical twist with major $C_{3'}$ -endo and minor $C_{2'}$ -exo pucker, ³T₂.

Oligosaccharides and Polysaccharides







Isomaltose (glucose- α -1,6-glucose)

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.

<u>αα</u> (Trehalose)
αβ (neotrehalose)
ββ (isotrehalose)



Primary oligosaccharides: Raffinose Gal $\alpha 1 \rightarrow 6$ Glc $\alpha 1 \rightarrow 2\beta$ Fru Secondary oligosaccharides: Cellobiose, Fos, Isomaltose

Cyclodextrins



Inon-reducing cyclic dextrins known as cyclodextrins loving) exterior

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



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









FIGURE 7.20 Amylose and amylopectin are the two forms of starch. Note that the linear linkages are $\alpha(1 \rightarrow 4)$ but the branches in amylopectin are $\alpha(1 \rightarrow 6)$. Branches in polysaccharides can involve any of the hydroxyl groups 30 residues.

on the monosaccharide components. Amylopectin is a highly branched structure, with branches occurring every 12 to





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

()







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



HEATING





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FIGURE 7.23 (a) Anylose, composed exclusively of the relatively bent $\alpha(1 \rightarrow 4)$ linkages, prefers to adopt a helical conformation, whereas (b) cellulose, with $\beta(1 \rightarrow 4)$ -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.





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 گلیکوز آمینو گلیکان. علامتهای اختصاری: HMW: وزن مولکولی بالا، GAG: گليكوز آمينو گليكان، ECM: ماتريكس خارج سلولي [٥٦].

Hyaluronic acid: [GlcNAc-GlcA]_n

Unsulfated HMW GAG Synthesized as free GAG at the cell surface

Heparin: [GIcN(Ac/S)-UA]_n

GIcNAc deacetylated and N-sulfated GlcA largely epimerized to IdoA Highly sulfated Stored intracellularly in mast cells

Heparan sulfate: [GIcN(Ac/S)-UA]

GIcNAc partly deacetylated and N-sulfated GlcA partly epimerized to IdoA Sulfations occurs in clusters along the chain Cell surface bound and released in the ECM

Chondroitin sulfate: [GalNAc-GlcA]_n

Most aboundant GAG Two main subfamilies with different pattern of sulfation Main component of cartilage

Dermatan sulfate: [GalNAc-UA]_n

GlcA mostly epimerized to IdoA Mainly present in fibrous connective tissues

Keratan sulfate: [GIcNAc-Gal]n

Variably sulfated at C6 Most heterogeneous GAG





Peptidoglycan Is the Polysaccharide of Bacterial Cell Walls





Gram-negative bacteria (b)



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 p-alanine of the other.







 β -Galactosyl-1,3- α -N-acetylgalactosyl-serine



 α -Xylosyl-threonine

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



 β -N-acetylglucosaminyl-serine (O-linked GlcNAc)



 α -Mannosyl-serine



Core oligosaccharides in N-linked glycoproteins (b)



N-linked glycoproteins (c)



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 7.32 The carbohydrate

linked to the protein via (a) serine or

moieties of glycoproteins may be





trix. 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.

Link proteins

Aggrecan core protein

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

- extracellular signals.
- structure and the range of biological activity of the glycoconjugates.

• 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,

• Our discussion uses just a few examples to illustrate the diversity of

Carbohydrates as Informational Molecules: The Sugar Code

- oligosaccharides of glycoproteins and glycolipids.
- some with the β configuration.
- **Branched structures**, not found in nucleic acids or proteins, are common in oligosaccharides.
- possible for the 20 common amino acids, and 4,096 (4⁶) different hexanucleotides for the four nucleotide subunits.
- increases by two orders of magnitude.
- precursors.

Improved methods for the analysis of oligosaccharide and polysaccharide structure have revealed remarkable complexity and diversity in the

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 $(1 \rightarrow 2)$, $(1 \rightarrow 3)$, $(1 \rightarrow 4)$, $(1 \rightarrow 6)$, $(2 \rightarrow 3)$, and $(2 \rightarrow 6)$, some with the α and

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 × 10⁷ (20⁶) different hexapeptides

If we also allow for variations in oligosaccharides resulting from sulfation of one or more residues, the number of possible oligosaccharides

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

Working with Carbohydrates

- approach to understanding the biological functions of glycosaminoglycans and oligosaccharides.
- and oligosaccharides significantly more complex than those shown in Figure 7-30.
- that allow the synthesis of glycosidic linkages with the correct hydroxyl group.
- defined oligosaccharides in adequate quantities from natural sources.

• Another important tool in working with carbohydrates is chemical synthesis, which has proved to be a powerful

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,

• 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

Synthetic approaches of this type currently represent an area of great interest, because it is difficult to purify

