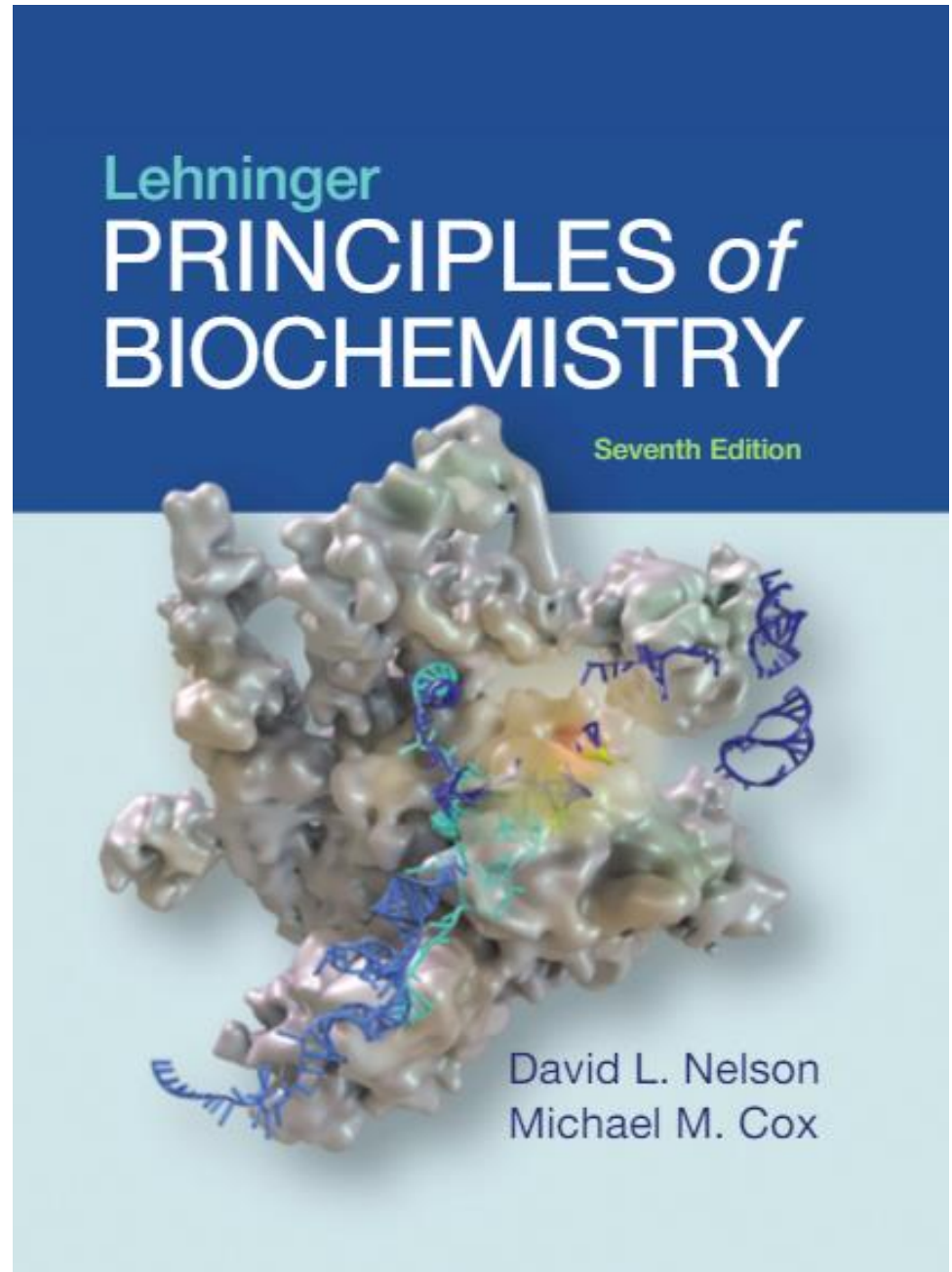


7 | Carbohydrates and Glycobiology

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CHAPTER 7

Carbohydrates and Glycobiology

Learning goals:

- Structures and names of monosaccharides
- Open-chain and ring forms of monosaccharides
- Structures and properties of disaccharides
- Biological function of polysaccharides
- Biological function of glycoconjugates

Carbohydrates

- Named so because many have formula $C_n(H_2O)_n$
- Produced from CO_2 and H_2O via **photosynthesis** in plants
- Range from as small as glyceraldehyde ($M_w = 90$ g/mol) to as large as amylopectin ($M_w > 200,000,000$ g/mol)
- Fulfill a variety of functions, including:
 - **energy source and energy storage**
 - **structural component of cell walls and exoskeletons**
 - **informational molecules in cell-cell signaling**
- Can be covalently linked with proteins and lipids

Carbohydrates

- **Monosaccharides** (simple sugars) – one polyhydroxy aldehyde or ketone unit (glucose)
- **Disaccharides** – two monosaccharide units joined together by a glycosidic linkage (sucrose)
- **Oligosaccharides** – few monosaccharide units joined together (in cells, most oligosaccharides are joined to nonsugar molecule)
- **Polysaccharides** – sugar polymers consisting of >20 monosaccharide units

Carbohydrates

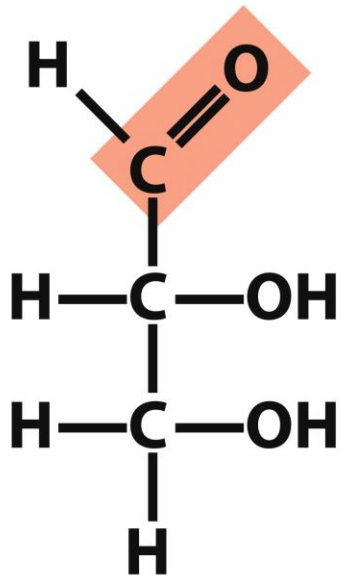
- Basic nomenclature:
 - number of carbon atoms in the carbohydrate + -ose
 - example: three carbons = triose
- Common functional groups:
 - All carbohydrates initially had a carbonyl functional group.
 - aldehydes = aldose
 - ketones = ketose

Monosaccharide Carbon backbone

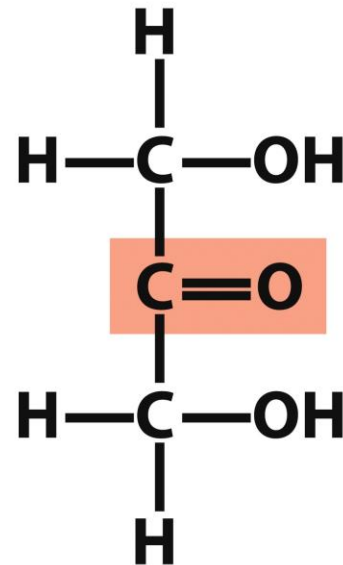
- 3 C → triose
- 4 C → tetrose
- 5 C → pentose
- 6 C → hexose
- 7 C → heptose

Aldoses and Ketoses

- An **aldose** contains an **aldehyde** functional group
- A **ketose** contains a **ketone** functional group



**Glyceraldehyde,
an aldotriose**



**Dihydroxyacetone,
a ketotriose**

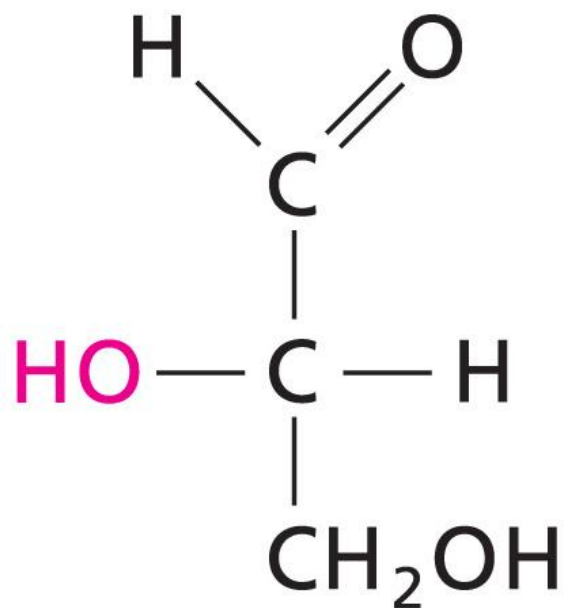
Figure 7-1a
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Stereoisomers

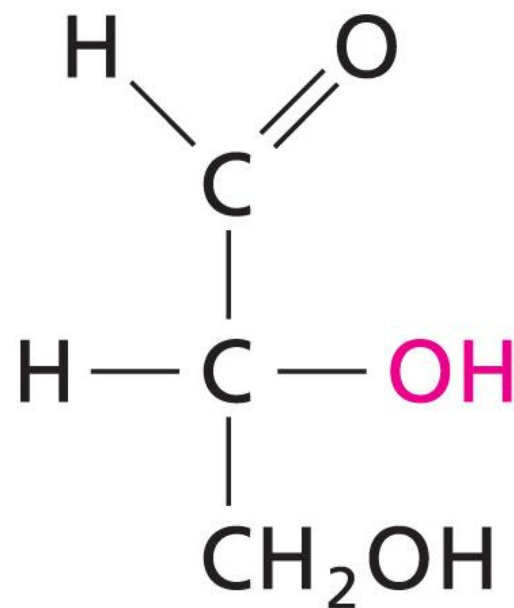
- **All monosaccharides** (except dihydroxyacetone) are chiral compounds, with **at least** one chiral carbon
- A molecule with n chiral centers can have 2^n stereoisomers
- E.g. glyceraldehyde has $2^1 = 2$
aldohexoses have $2^4 = 16$ stereoisomers

Carbohydrates Can Be Stereoisomers

- **Enantiomers**
 - Stereoisomers that are non-superimposable mirror images
- In sugars that contain many chiral centers, only the one that is **most distant from the carbonyl carbon** is designated as D (right) or L (left)
- D and L isomers of a sugar are enantiomers
 - For example, L and D glucose have the same water solubility
- Most hexoses in living organisms are D stereoisomers
- Some simple sugars occur in the L-form, such as L-arabinose

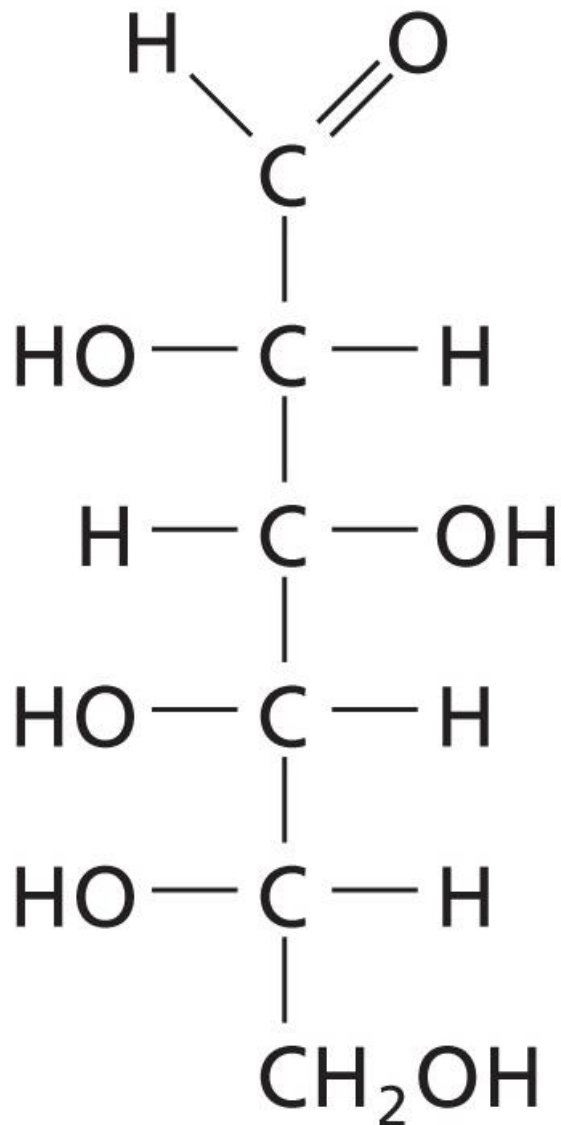


L-Glyceraldehyde



D-Glyceraldehyde

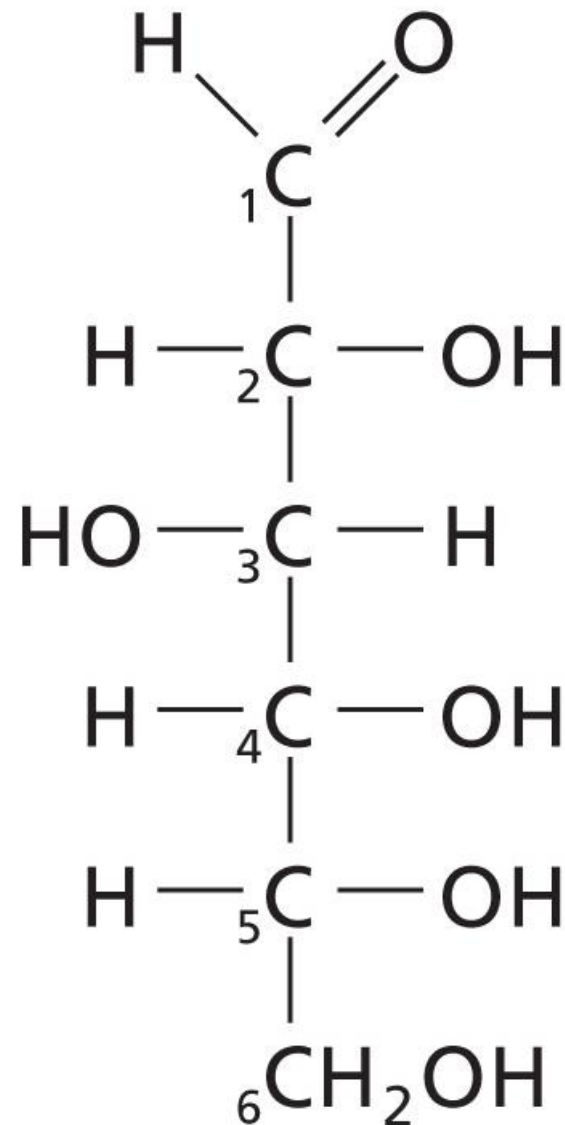
Non-
superimposable
mirror images



L-Glucose



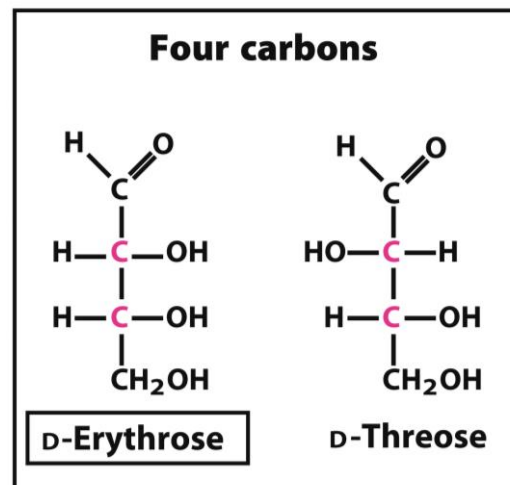
Non-
superimposable
mirror images



D-Glucose

Carbohydrates Can Be Stereoisomers

- **Epimers** are two sugars that differ only in the configuration around **one carbon atom**
- Epimers are NOT mirror images, and therefore are NOT enantiomers.
- Epimers are diastereomers; diastereomers have different physical properties (i.e., water solubility, melting temp).
 - example: D-Threose is the C-2 epimer of D-erythrose.
 - Both are D sugars because they both have the same orientation around the last chiral carbon in the chain.



Epimers

- D-Mannose and D-galactose are both epimers of D-glucose.
- D-Mannose and D-galactose vary at more than one chiral center and are diastereomers, but not epimers.

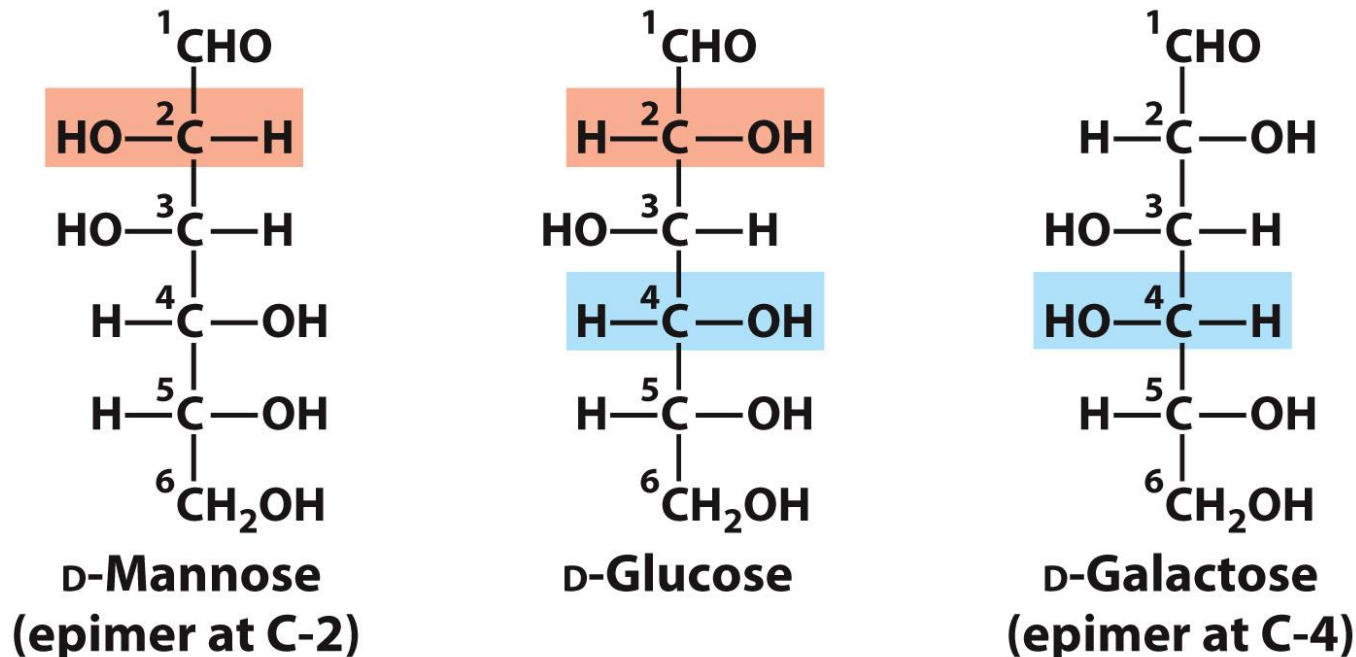
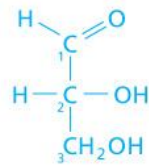


Figure 7-4
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Structures to Know

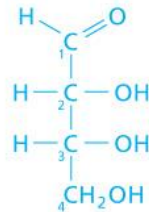
- Glyceraldehyde & dihydroxyacetone are the standard three-carbon sugars
- Ribose is the standard five-carbon sugar
- Glucose is the standard six-carbon sugar
- Galactose is an epimer of glucose
- Mannose is an epimer of glucose
- Fructose is the ketose form of glucose

Aldotriose

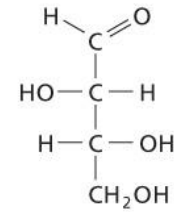


D-Glyceraldehyde

Aldotetroses

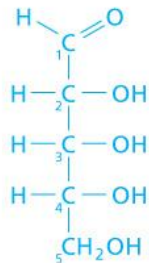


D-Erythrose

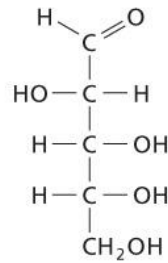


D-Threose

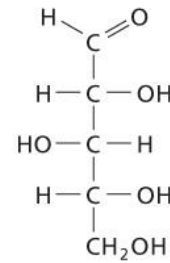
Aldopentoses



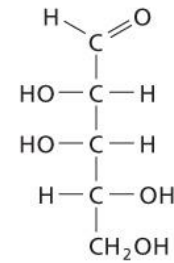
D-Ribose



D-Arabinose

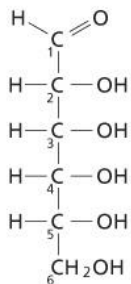


D-Xylose

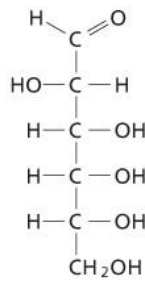


D-Lyxose

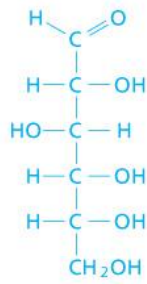
Aldohexoses



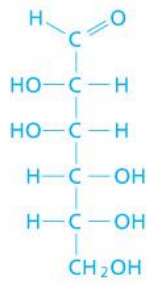
D-Allose



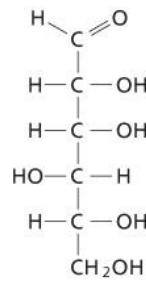
D-Altrose



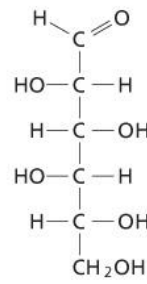
D-Glucose



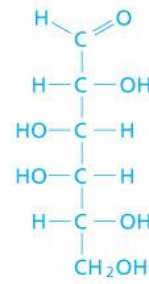
D-Mannose



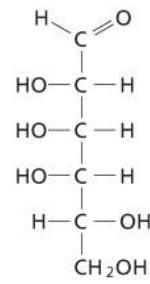
D-Gulose



D-Idose

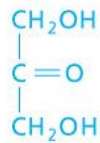


D-Galactose



D-Talose

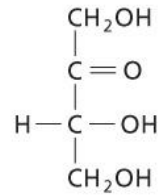
Ketotriose



Dihydroxyacetone



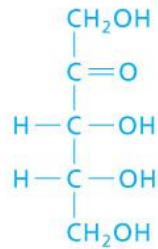
Ketotetrose



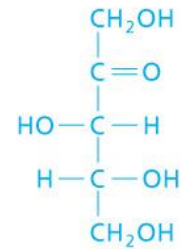
D-Erythrulose



Ketopentoses



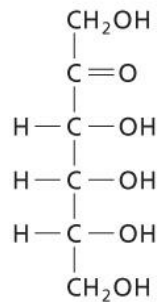
D-Ribulose



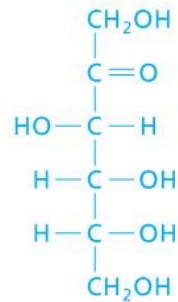
D-Xylulose



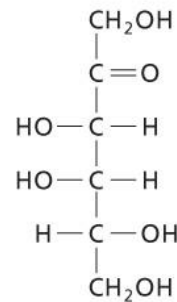
Ketohexoses



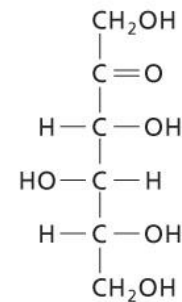
D-Psicose



D-Fructose



D-Tagatose



D-Sorbose

Common Monosaccharides Have Cyclic Structures

- In solution, monosaccharides with 4 or more carbons form cyclic compounds (ring structures)
- Carbonyl C is attacked by the hydroxyl O forming a covalent bond

Hemiacetals and Hemiketals

- Aldehyde and ketone carbons are **electrophilic**
- Alcohol oxygen atom is **nucleophilic**
- When **aldehydes** are attacked by alcohols, **hemiacetals** form
- When **ketones** are attacked by alcohols, **hemiketals** form
- These reactions form the basis of cyclization of sugars.

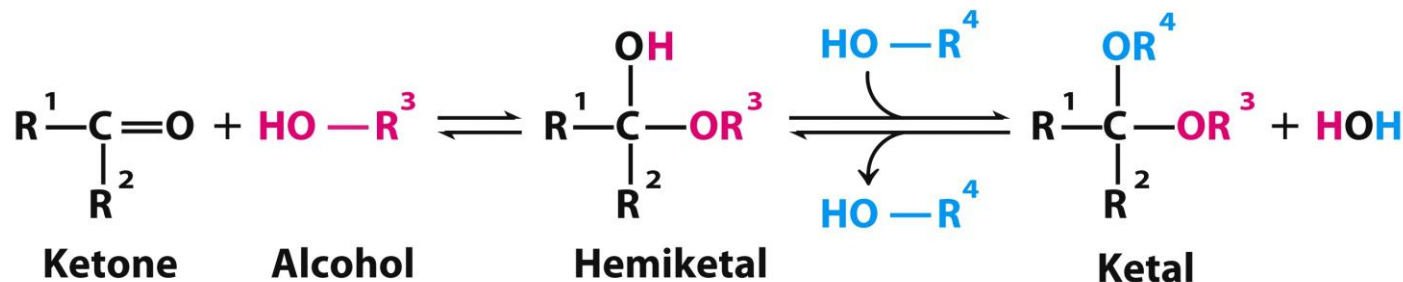
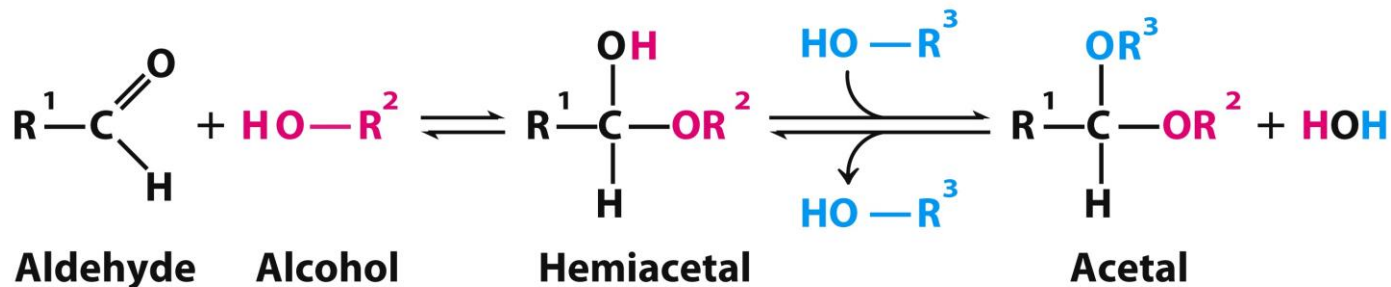


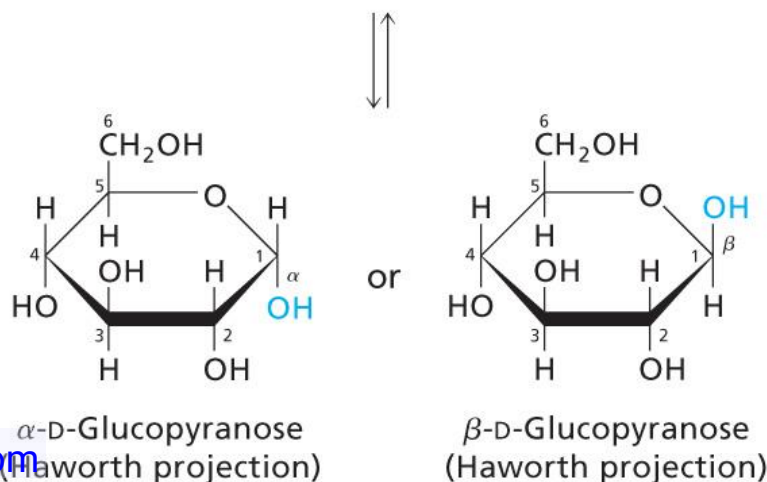
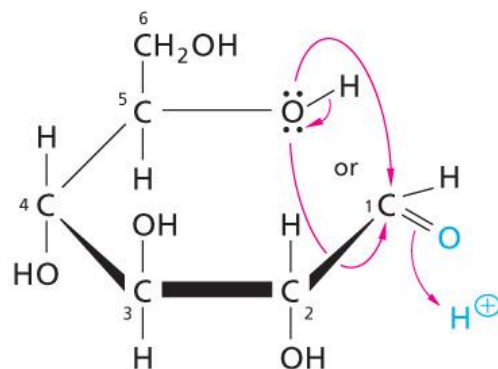
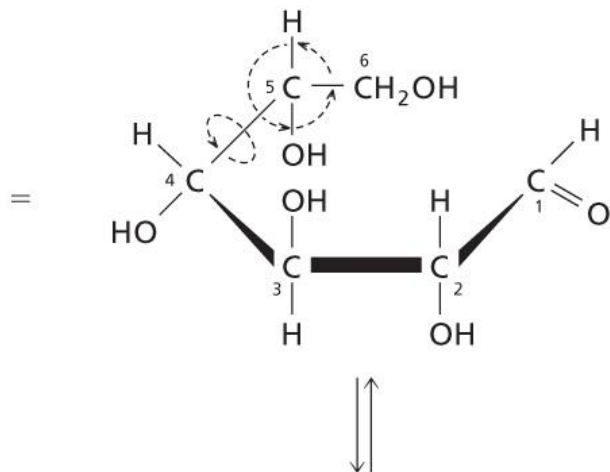
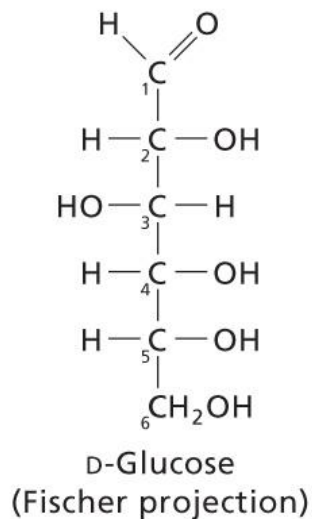
Figure 7-5

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When the second alcohol is part of another sugar molecule, the bond produced is a **glycosidic bond**.

Cyclization of Monosaccharides

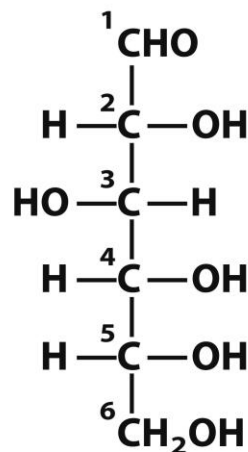
- Pentoses and hexoses readily undergo intramolecular ring formation
- The former carbonyl carbon becomes a new chiral center, called the **anomeric carbon**
- The former carbonyl oxygen becomes a hydroxyl group; the position of this group determines if the anomer is α or β
- If the *hydroxyl group* is on the **opposite side** (**trans**) of the ring as the CH_2OH moiety the configuration is α
- If the *hydroxyl group* is on the **same side** (**cis**) of the ring as the CH_2OH moiety, the configuration is β



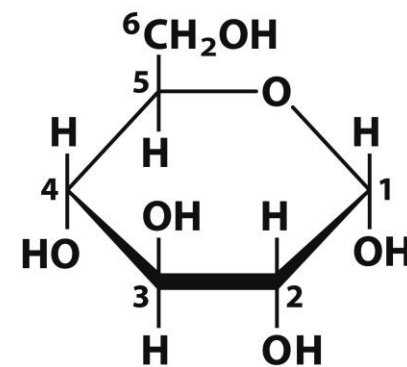
Mutarotation – the interconversion of α and β anomers.

Pyranoses and Furanoses

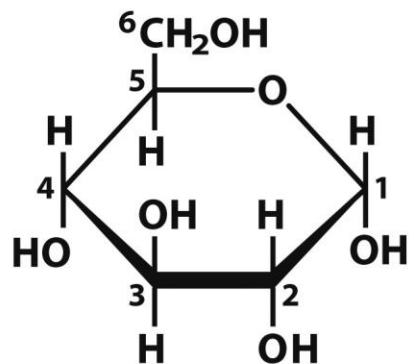
- Six-membered oxygen-containing rings are called **pyranoses**
- Five-membered oxygen-containing rings are called **furanoses**
- The **anomeric** carbon is usually drawn on the **right side**
- Cyclic sugar structures are more accurately represented in **Haworth perspective formulas**



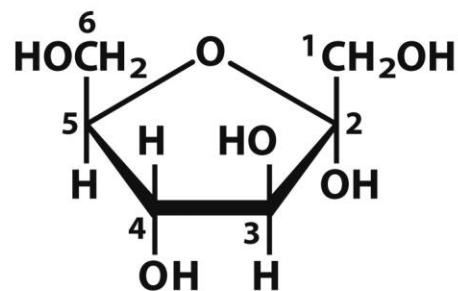
D-Glucose
Fischer projection



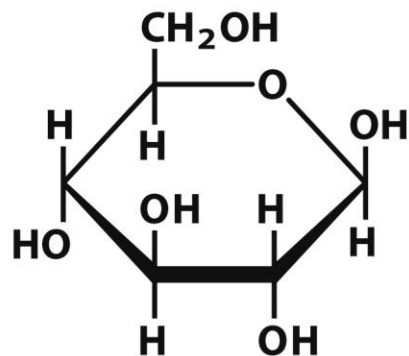
α-D-Glucopyranose
Haworth perspective
Uploaded By: Rawan Rous



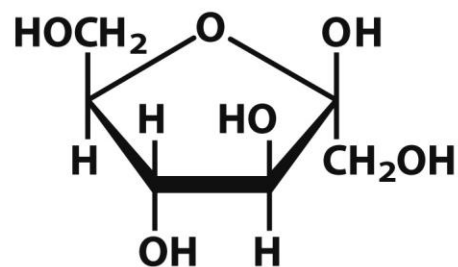
α -D-Glucopyranose



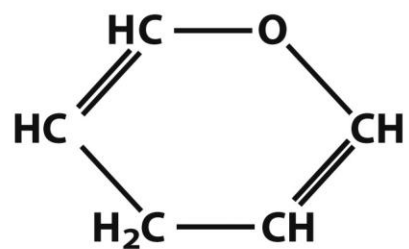
α -D-Fructofuranose



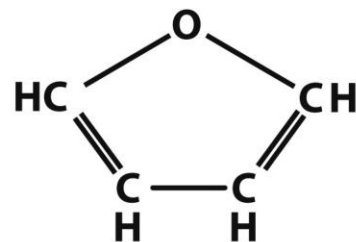
β -D-Glucopyranose



β -D-Fructofuranose



Pyran



Furan

Figure 7-7

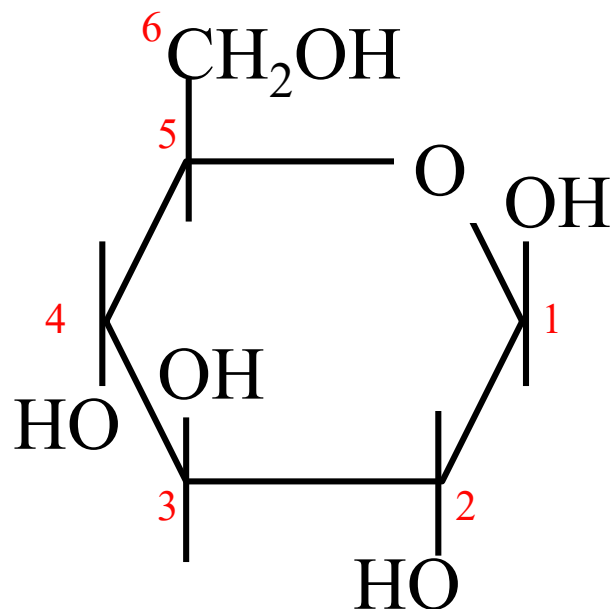
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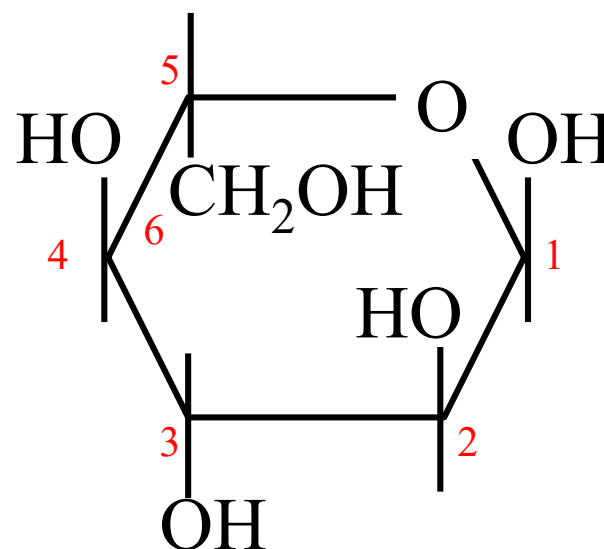
Converting linear to cyclic structures

- For any linear hexose:
 1. Draw 6-membered ring (O at the upper right)
 2. Number C's clockwise (start with anomeric)
 3. Insert the -OH
 - a. if -OH is on the **right**, draw it pointing **down**
 - b. if -OH is on the **left**, draw it pointing **up**
 4. Insert the terminal $\text{-CH}_2\text{OH}$
 - a. if the sugar is the **D-isomer**, draw it **upwards**
 - b. if it is the **L-isomer**, draw it **downwards**
 5. Draw the -OH on the anomeric C
 - a. if it faces the **same side** as the $\text{-CH}_2\text{OH}$, it's **β**
 - b. if it faces the **opposite side**, it's **α**

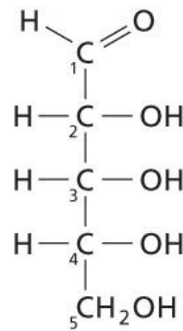
Example



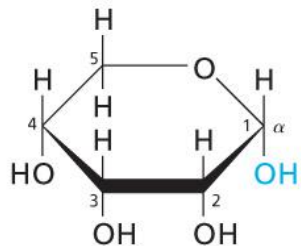
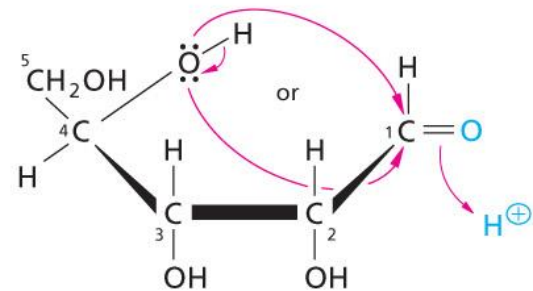
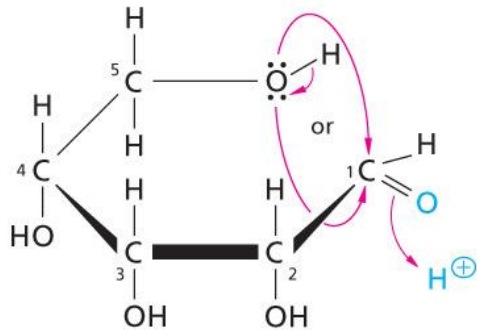
β -D-glucose
(C¹-OH points up,
cis to C⁶H₂OH)



α -L-glucose
(C¹-OH points up,
trans to C⁶H₂OH)

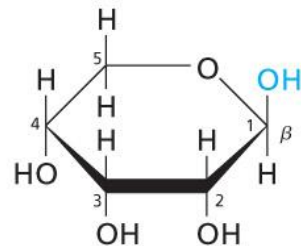


D-Ribose
(Fischer projection)

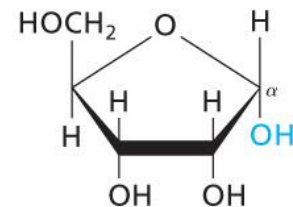


α -D-Ribopyranose
(Haworth projection)

or

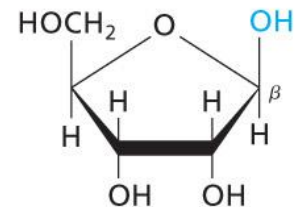


β -D-Ribopyranose
(Haworth projection)



α -D-Ribofuranose
(Haworth projection)

or



β -D-Ribofuranose
(Haworth projection)

The ring is not planar

- In solution pyranose ring is not planar but it can assume two chair conformations
- Boat conformation is possible but very rare
- Multiple “chair” conformations are possible but require energy for interconversion (~46 kJ/mole)

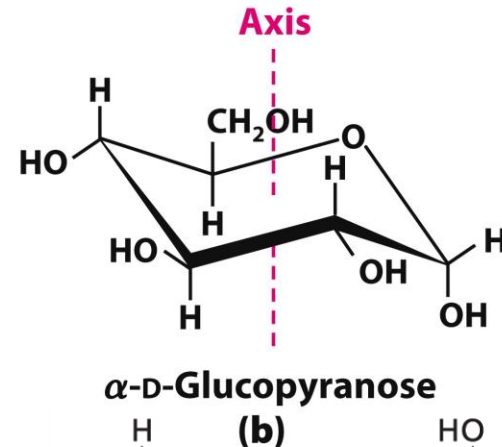
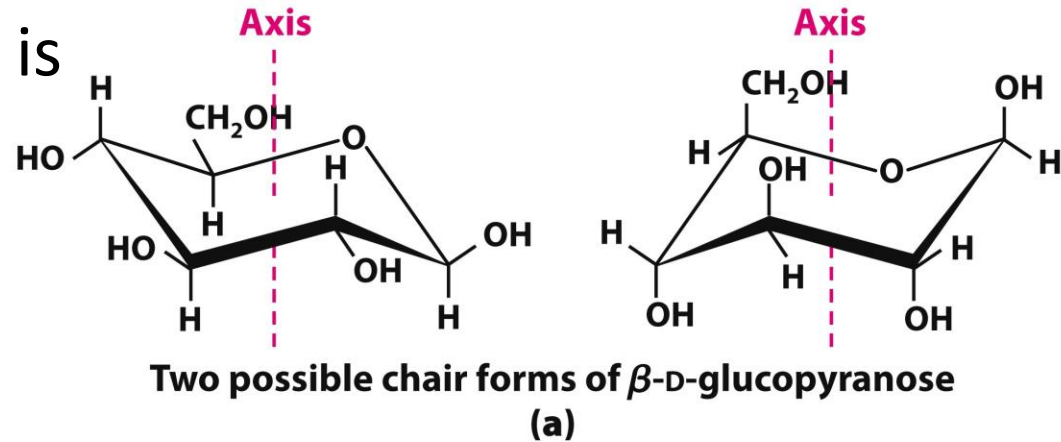
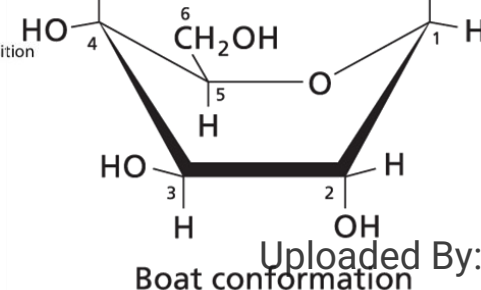
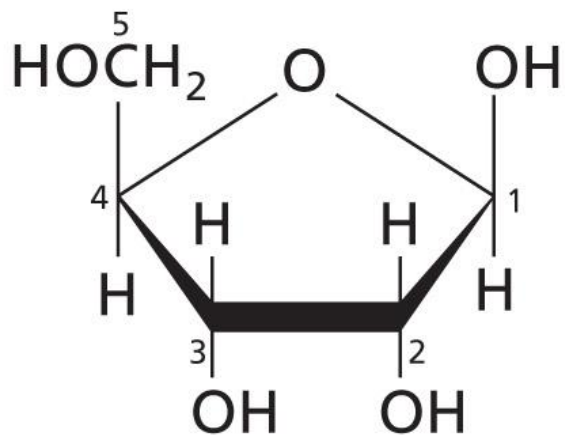


Figure 7-8
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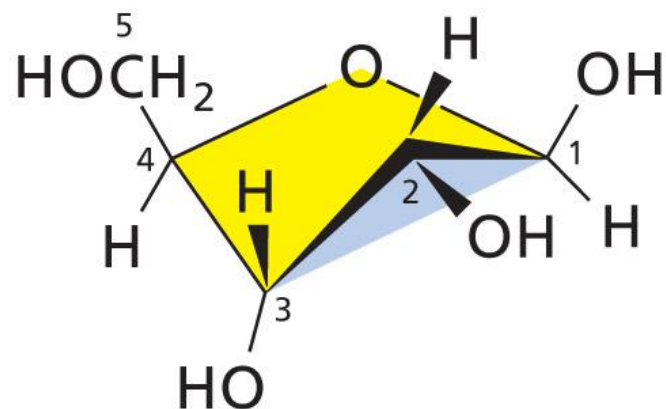


(a)



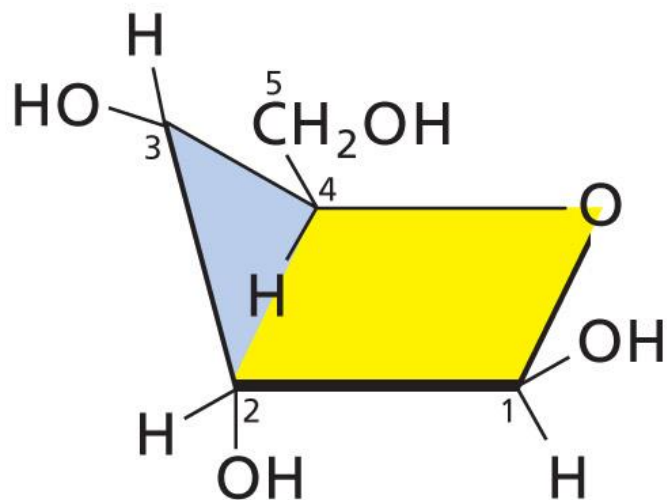
Haworth projection

(b)



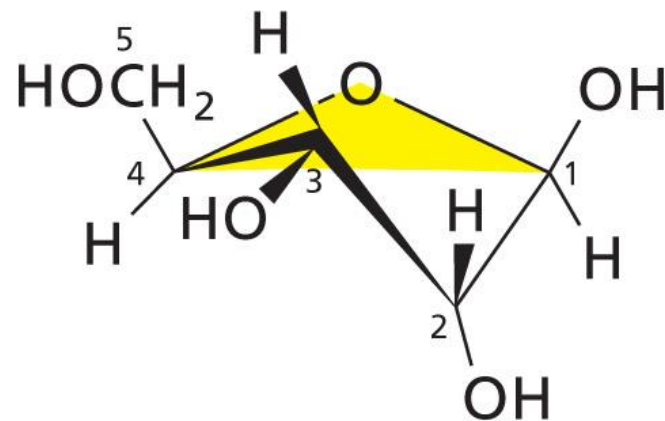
C₂-endo envelope conformation

(c)



C₃-endo envelope conformation

(d)



Twist conformation

Chain-Ring Equilibrium and Reducing Sugars

- The ring forms exist in equilibrium with the open-chain forms
- Reducing sugars have a free anomeric carbon
- Aldehyde can reduce Cu^{2+} to Cu^+ (Fehling's test)
- Aldehyde can reduce Ag^+ to Ag^0 (Tollens' test)
- Allows detection of reducing sugars, such as glucose (by measuring the amount of oxidizing agent reduced by a sugar solution, the sugar concentration can be estimated)

The cuprous ion (Cu^+) produced forms a red cuprous oxide precipitate.

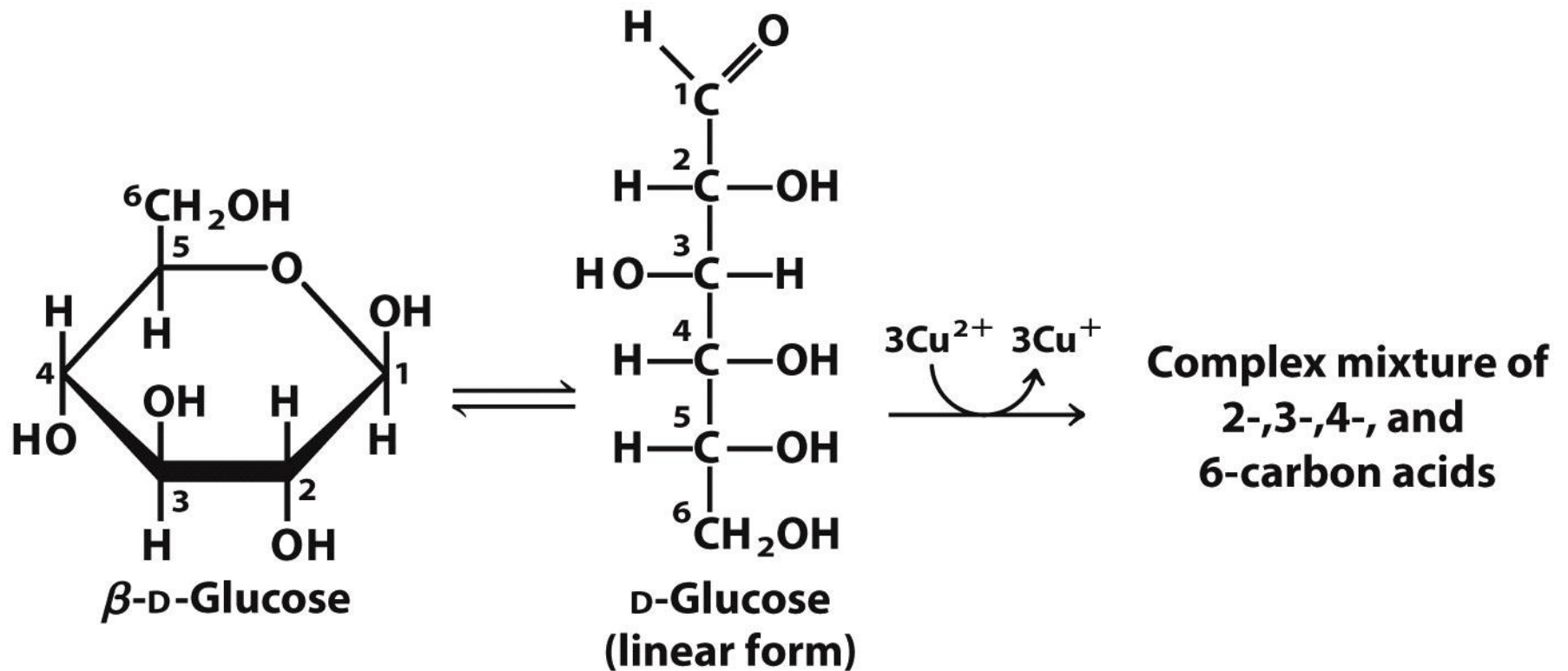


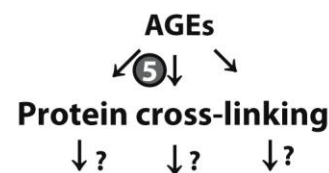
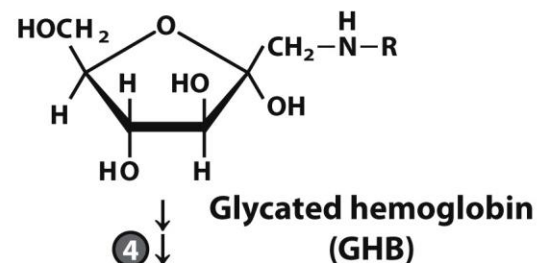
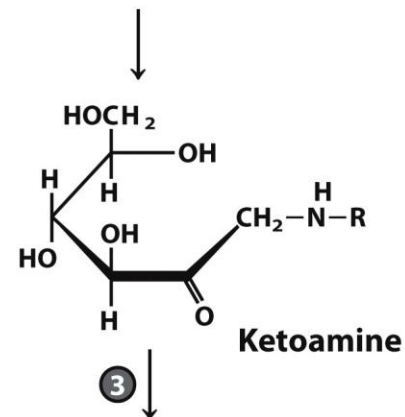
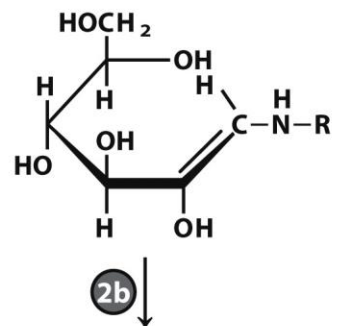
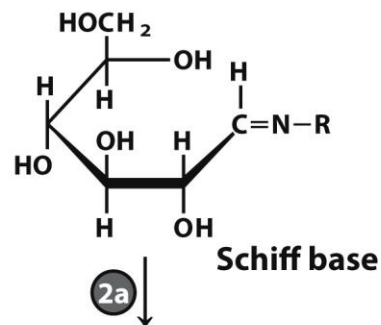
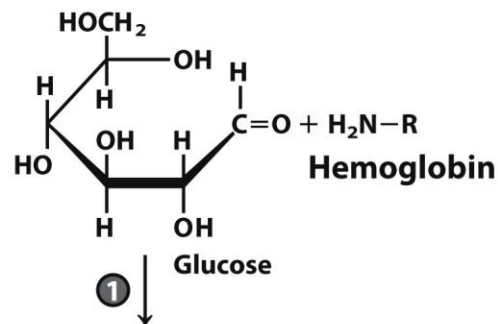
Figure 7-10

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Blood glucose measurements in the diagnosis and treatment of diabetes

- Untreated diabetes has several long-term consequences: kidney failure, cardiovascular disease, blindness, impaired wound healing, etc.
- Average $[\text{glc}]_{\text{blood}}$ over days can be measured because of a nonenzymatic reaction between glc and primary amino groups in Hb
- The amount of glycated Hb (GHb) reflects the average $[\text{glc}]_{\text{blood}}$ over the circulating lifetime of RBC (~120 days)
- Normal levels ~5% of Hb is GHb
- Diabetic people may have it as high as 13%
- Advanced glycation endproducts (AGEs) contribute to the long term problems associated with diabetes



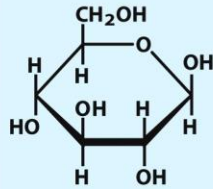
Damage to kidneys, retinas, cardiovascular system

Box 7-1 figure 1

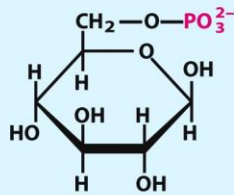
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Organisms contain many hexose derivatives

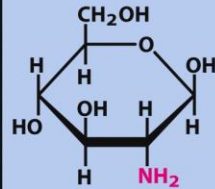
Glucose family



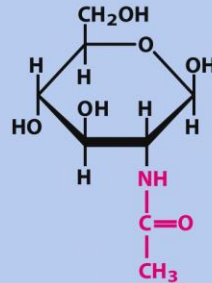
β -D-Glucose



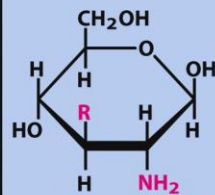
β -D-Glucose 6-phosphate



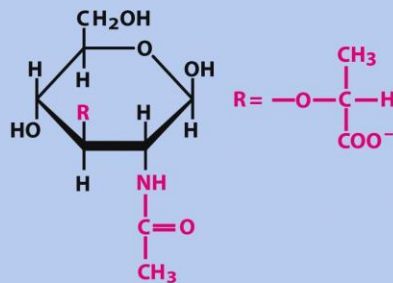
β -D-Glucosamine



N-Acetyl- β -D-glucosamine

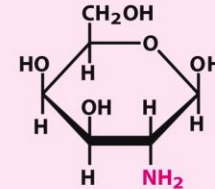


Muramic acid

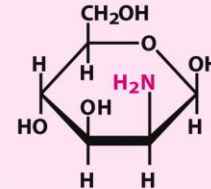


N-Acetylmuramic acid

Amino sugars

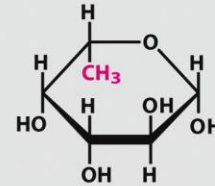


β -D-Galactosamine

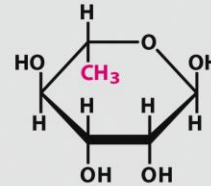


β -D-Mannosamine

Deoxy sugars



β -L-Fucose

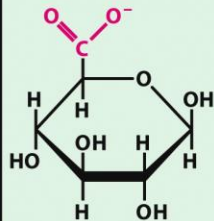


α -L-Rhamnose

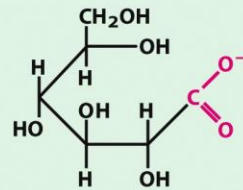
Acidic sugars



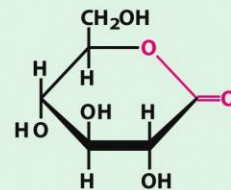
N-Acetylneuraminic acid
(a sialic acid)



β -D-Glucuronate



D-Gluconate



D-Glucono- δ -lactone

Figure 7-9

The Glycosidic Bond

- Two sugar molecules can be joined via a **glycosidic bond** between an anomeric carbon and a hydroxyl carbon
- The resulting compound is a **glycoside**
- The **glycosidic bond** (an **acetal**) between monomers is less reactive than the hemiacetal at the second monomer
 - Second monomer, with the hemiacetal, is reducing
 - Anomeric carbon involved in the glycosidic linkage is nonreducing
- The disaccharide formed upon condensation of two glucose molecules via 1 → 4 bond is called **maltose**

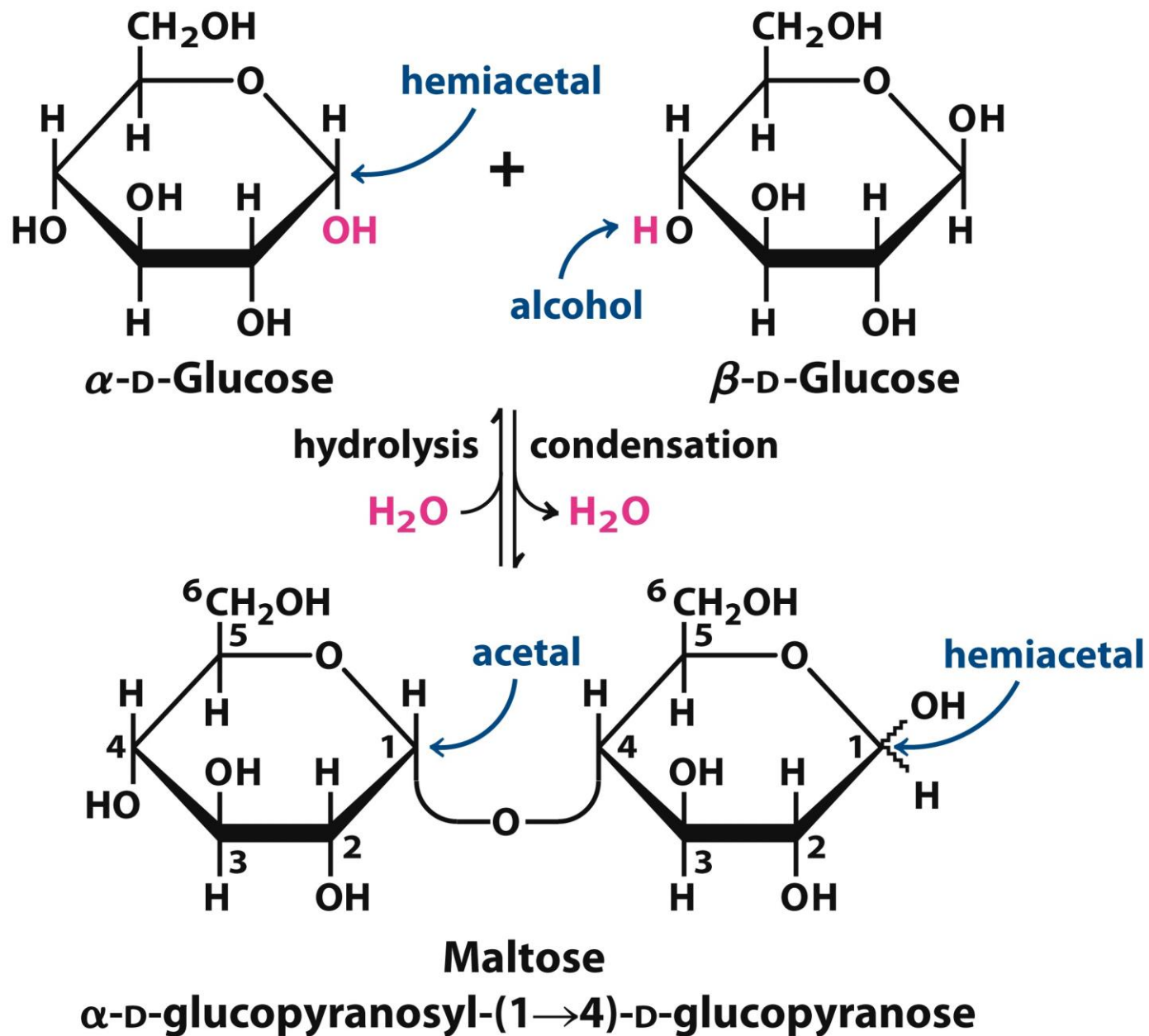


Figure 7-10

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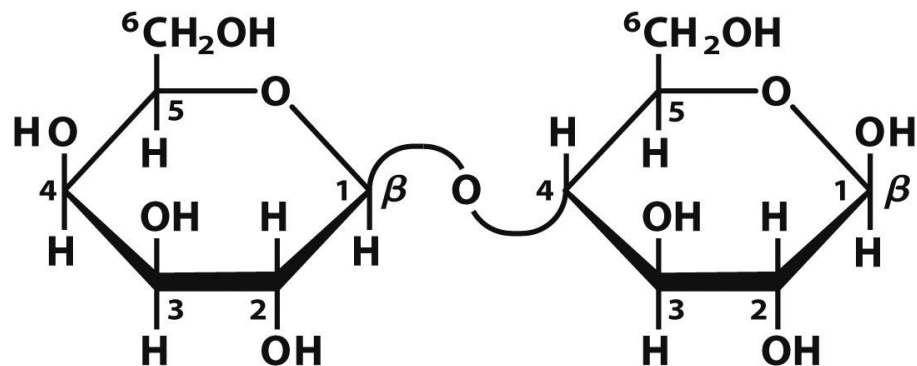
Nonreducing Disaccharides

- Two sugar molecules can be also joined via a **glycosidic bond** between two anomeric carbons
- The product has two acetal groups and no hemiacetals
- There are **no reducing ends**, this is a nonreducing sugar
- Trehalose is a constituent of hemolymph of insects
 - Provides protection from drying

Naming disaccharides

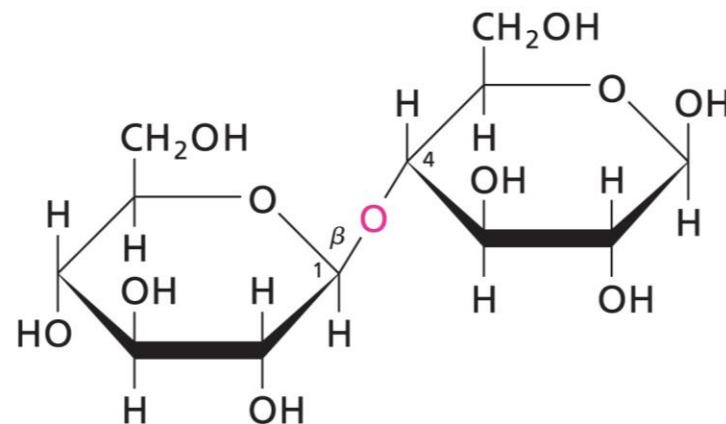
1. Find the nonreducing end
2. Give the configuration (α or β) at the anomeric C joining the first monosaccharide to the other
3. Name the nonreducing residue (use “furano” for 5-membered rings or “pyrano” for 6-membered rings)
4. Add the glycosidic bond in parenthesis (from which C to which C)
5. Name the second residue
6. If there are more residues, repeat step 2

* Abbreviations can be used (Glc, Fru, Gal, Man, GlcN, etc.)



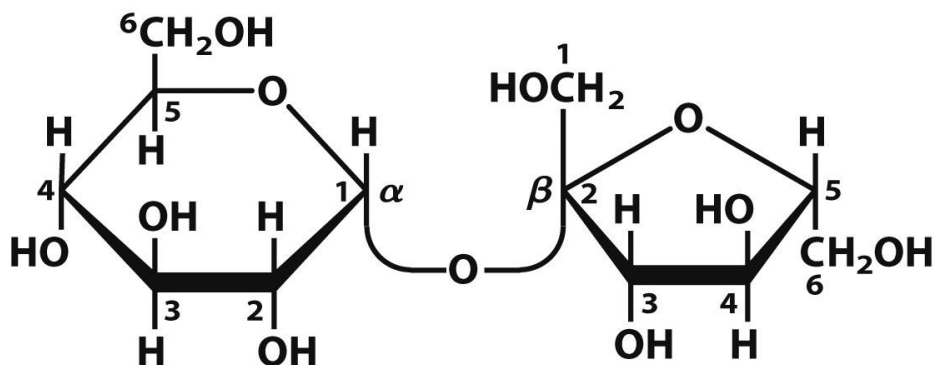
Lactose (β form)

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



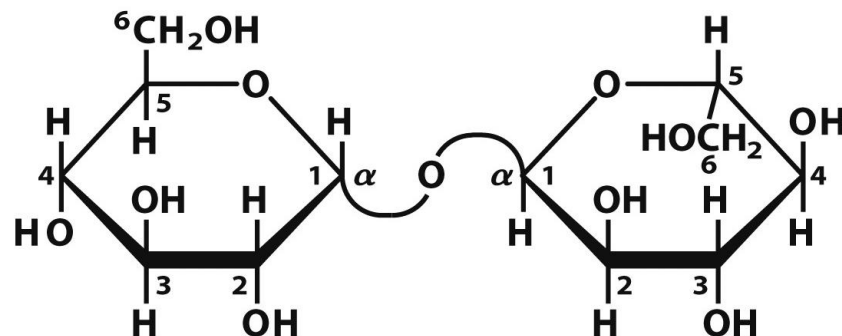
β anomer of cellobiose

(β -D-Glucopyranosyl-(1 $\rightarrow$ 4)- β -D-glucopyranose)



Sucrose

β -D-fructofuranosyl α -D-glucopyranoside
Fru(2 β $\leftrightarrow$ α 1)Glc $\equiv$ Glc(α 1 $\leftrightarrow$ 2 β)Fru



Trehalose

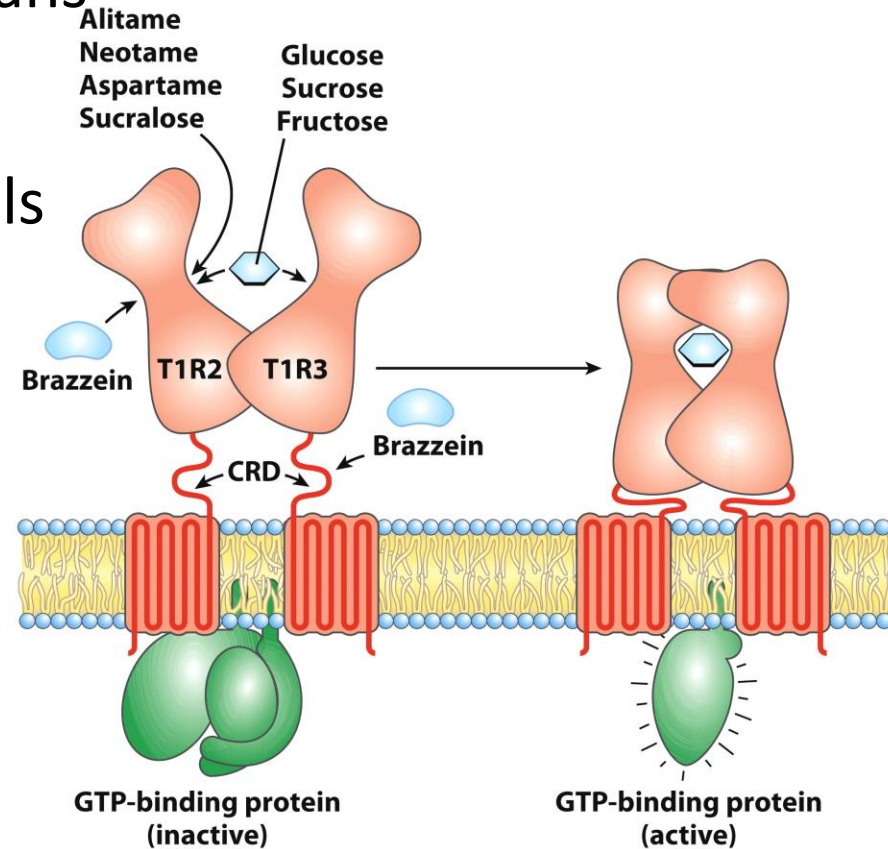
α -D-glucopyranosyl α -D-glucopyranoside
Glc(α 1 $\leftrightarrow$ 1 α)Glc

Sweet tooth? Anyone?



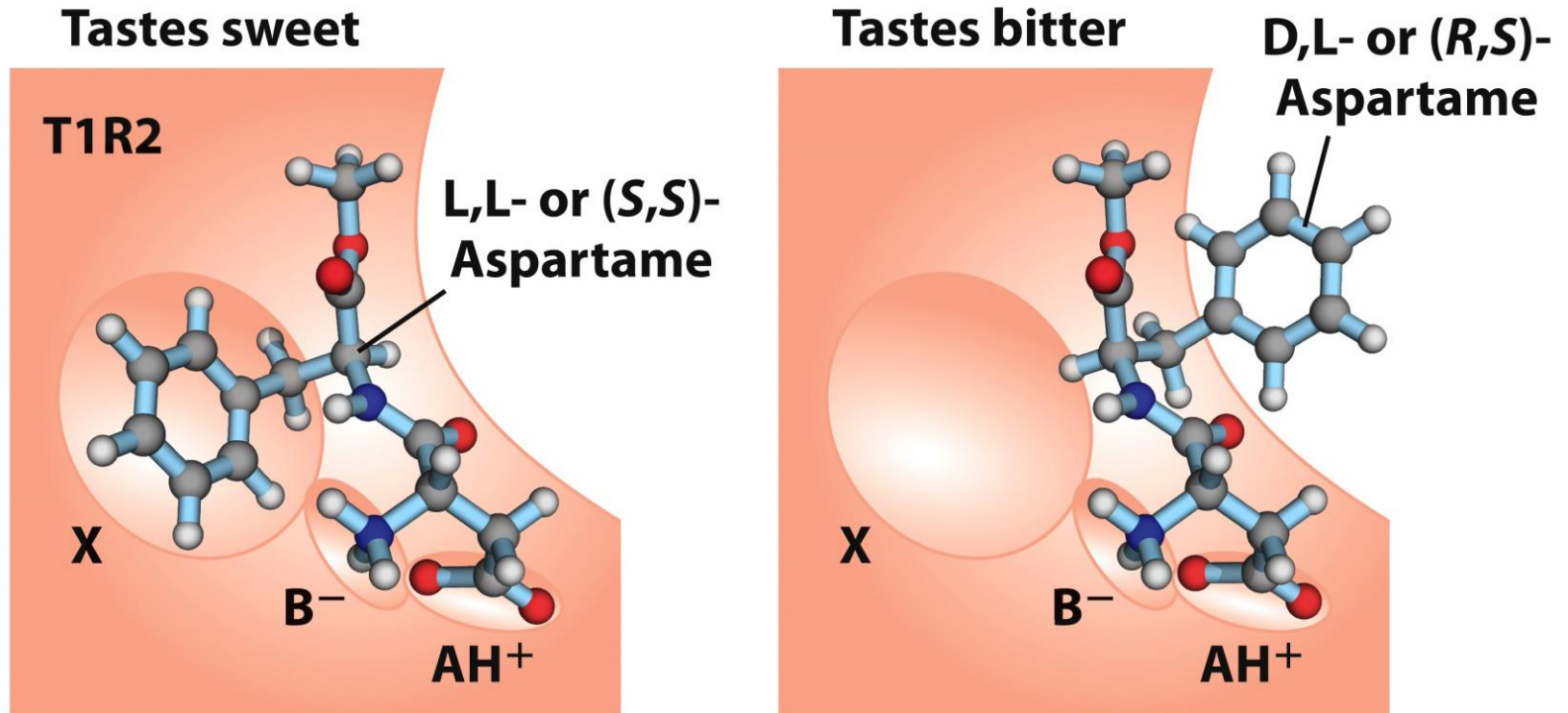
Box 7-2 Figure 1
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- Most people like sweets
- Sweetness is one of 5 tastes humans can taste
- Due to receptors on gustatory cells on the surface of tongues... T1R2 and T1R3
- Stevioside (few hundred times sweeter than sugar). Brazzein protein ~17000x sweeter
- Binding of molecules to these receptors, signals are transduced to give the sweet taste



Box 7-2 figure 2
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L,L-Aspartame is sweet; D,L-Aspartame is bitter



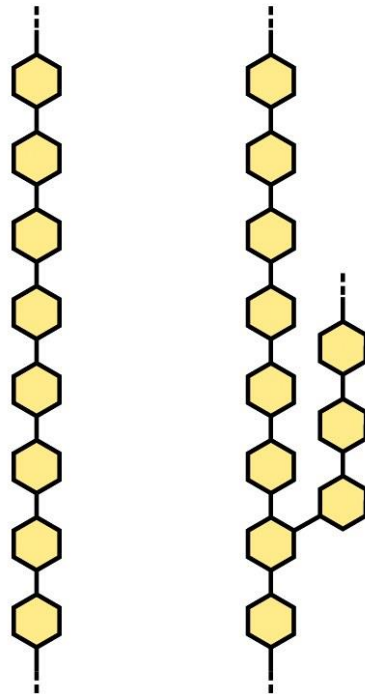
Box 7-2 figure 3
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Polysaccharides

- Natural carbohydrates are usually found as polymers
- These polysaccharides can be
 - homopolysaccharides
 - heteropolysaccharides
 - linear
 - branched
- Polysaccharides do not have a defined molecular weight.
 - This is in contrast to proteins because unlike proteins, no template is used to make polysaccharides

Homopolysaccharides

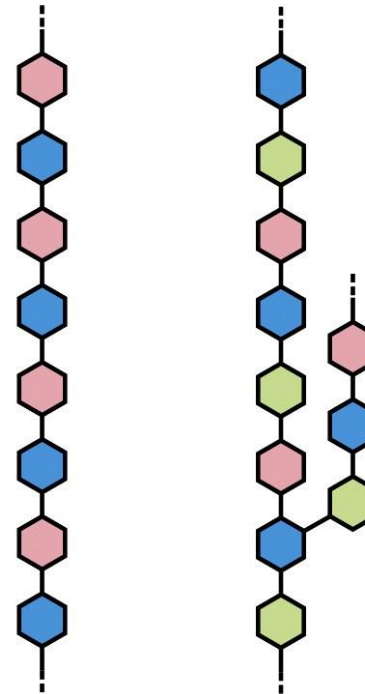
Unbranched Branched



Heteropolysaccharides

Two
monomer
types,
unbranched

Multiple
monomer
types,
branched



Can be:

- 1) Storage forms of monosaccharides, used for fuel (starch and glycogen)
- 2) Structural elements in plant cell walls and animal exoskeletons (cellulose and chitin)

Provide extracellular support for organisms of all kingdoms,

E.g.

- 1) Bacterial cell envelope is composed in part of a heteropolysaccharide
- 2) Extracellular matrix in animal cells

Table 8.2 Structures of some common polysaccharides

Polysaccharide^a	Component(s)^b	Linkage(s)
Storage homoglycans		
Starch		
Amylose	Glc	α -(1 → 4)
Amylopectin	Glc	α -(1 → 4), α -(1 → 6) (branches)
Glycogen	Glc	α -(1 → 4), α -(1 → 6) (branches)
Structural homoglycans		
Cellulose	Glc	β -(1 → 4)
Chitin	GlcNAc	β -(1 → 4)
Heteroglycans		
Glycosaminoglycans	Disaccharides (amino sugars, sugar acids)	Various
Hyaluronic acid	GlcUA and GlcNAc	β -(1 → 3), β -(1 → 4)

^aPolysaccharides are unbranched unless otherwise indicated.

^bGlc, Glucose; GlcNAc, *N*-acetylglucosamine; GlcUA, D-glucuronate.

TABLE 7-2

Structures and Roles of Some Polysaccharides

Primer	Type ^a	Repeating unit ^b	Size (number of monosaccharide units)	Roles/significance
Starch				Energy storage: in plants
Amylose	Homo-	($\alpha 1 \rightarrow 4$) Glc, linear	50–5,000	
Amylopectin	Homo-	($\alpha 1 \rightarrow 4$) Glc, with ($\alpha 1 \rightarrow 6$) Glc branches every 24–30 residues	Up to 10^6	
Glycogen	Homo-	($\alpha 1 \rightarrow 4$) Glc, with ($\alpha 1 \rightarrow 6$) Glc branches every 8–12 residues	Up to 50,000	Energy storage: in bacteria and animal cells
Cellulose	Homo-	($\beta 1 \rightarrow 4$) Glc	Up to 15,000	Structural: in plants, gives rigidity and strength to cell walls
Chitin	Homo-	($\beta 1 \rightarrow 4$) GlcNAc	Very large	Structural: in insects, spiders, crustaceans, gives rigidity and strength to exoskeletons
Dextran	Homo-	($\alpha 1 \rightarrow 6$) Glc, with ($\alpha 1 \rightarrow 3$) branches	Wide range	Structural: in bacteria, extracellular adhesive
Peptidoglycan	Hetero-; peptides attached	4)Mur2Ac($\beta 1 \rightarrow 4$) GlcNAc($\beta 1$	Very large	Structural: in bacteria, gives rigidity and strength to cell envelope
Agarose	Hetero-	3)D-Gal ($\beta 1 \rightarrow 4$)3,6- anhydro-L-Gal($\alpha 1$	1,000	Structural: in algae, cell wall material
Hyaluronan (a glycosaminoglycan)	Hetero-; acidic	4)GlcA ($\beta 1 \rightarrow 3$) GlcNAc($\beta 1$	Up to 100,000	Structural: in vertebrates, extracellular matrix of skin and connective tissue; viscosity and lubrication in joints

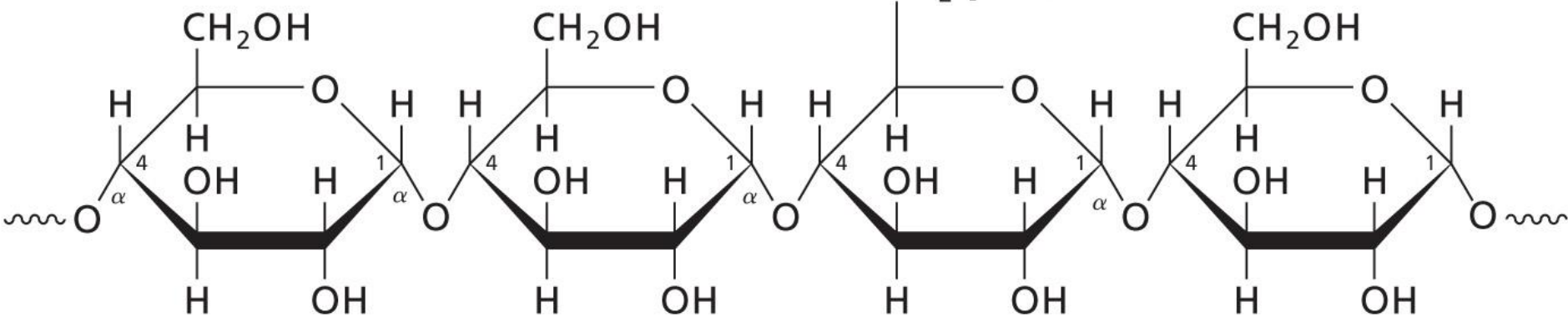
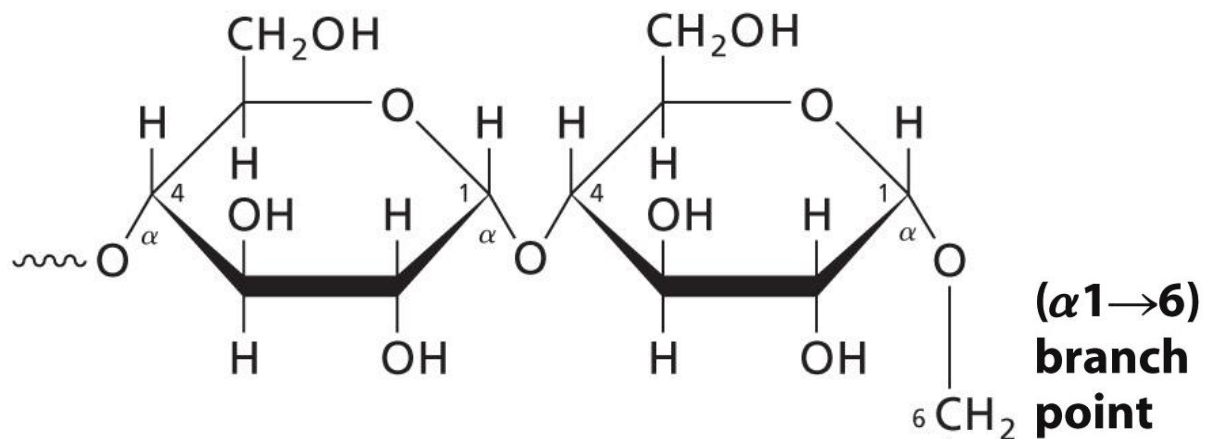
^aEach polymer is classified as a homopolysaccharide (homo-) or heteropolysaccharide (hetero-).

^bThe abbreviated names for the peptidoglycan, agarose, and hyaluronan repeating units indicate that the polymer contains repeats of this disaccharide unit. For

example, in peptidoglycan, the GlcNAc of one disaccharide unit is ($\beta 1 \rightarrow 4$)-linked to the first residue of the next disaccharide unit.

Glycogen

- Glycogen is a branched homopolysaccharide of **glucose**
 - Glucose monomers form ($\alpha 1 \rightarrow 4$) linked chains
 - **Branch-points** with ($\alpha 1 \rightarrow 6$) linkers every 8–12 residues
 - Molecular weight reaches several millions
 - Functions as the main **storage polysaccharide in animals**



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Starch

- Starch is a **mixture** of two homopolysaccharides of **glucose**
 - **Amylose** is an unbranched polymer of ($\alpha 1 \rightarrow 4$) linked residues
 - **Amylopectin** is branched like glycogen but the branch-points with ($\alpha 1 \rightarrow 6$) linkers occur every 24–30 residues
 - Molecular weight of amylopectin is up to 200 million
- Starch is the main **storage polysaccharide in plants**

Glycosidic Linkages in Glycogen and Starch

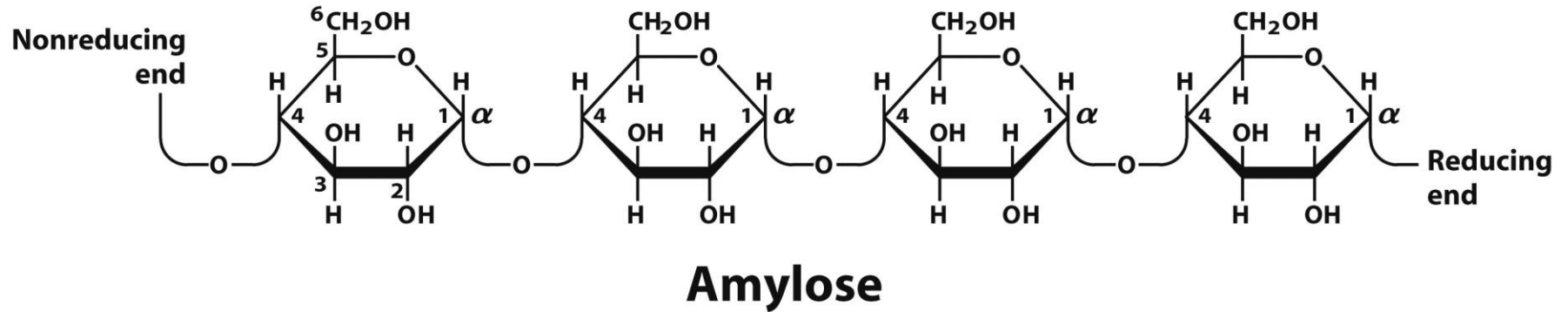
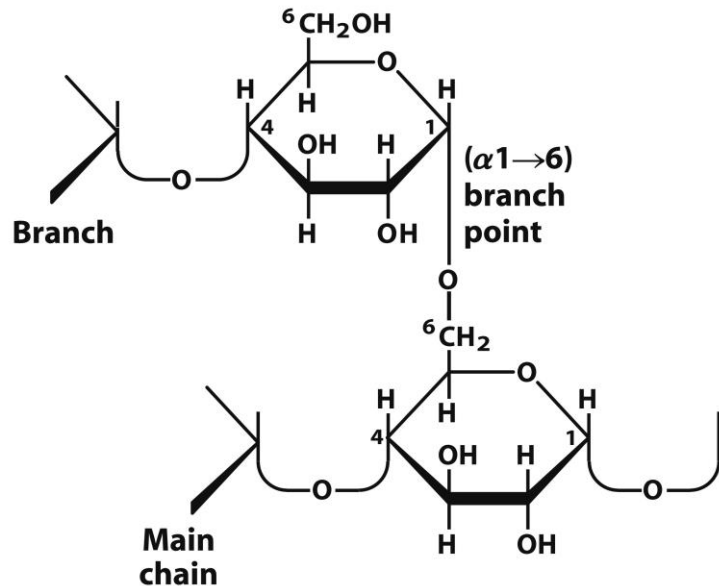


Figure 7-13a
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Mixture of Amylose and Amylopectin in Starch

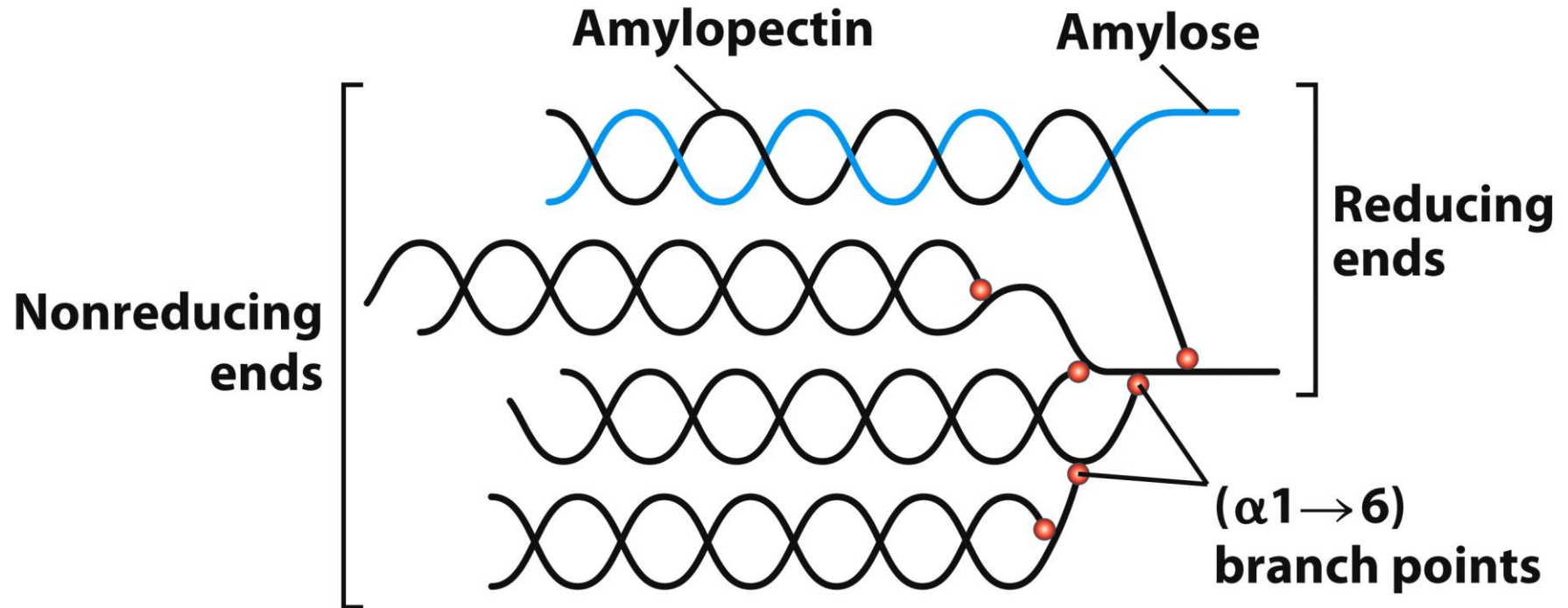


Figure 7-13c

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In starch granules, strands of amylopectin (blue) form double-helical structures with each other or with amylose strands (black). Glucose residues at the nonreducing ends of the outer branches are removed enzymatically during the mobilization of starch for energy production.

Glycogen has a similar structure but is more highly branched and more compact.

Metabolism of Glycogen and Starch

- Glycogen and starch often form **granules** in cells
- Granules contain enzymes that synthesize and degrade these polymers
- Glycogen and amylopectin have one reducing end but **many nonreducing ends** (a polymer with n branches has $n + 1$ nonreducing ends and only 1 reducing end)
- Enzymatic processing occurs simultaneously in many nonreducing ends

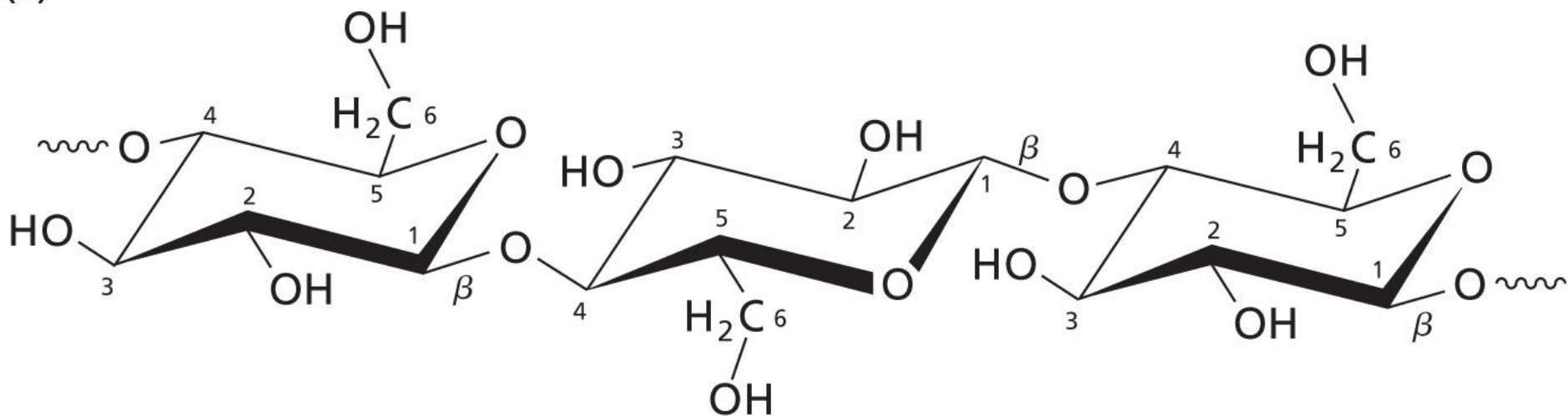
Dextrans

- Bacterial and yeast polysaccharides
- ($\alpha 1 \rightarrow 6$)-linked poly-D-glucose
- All units have ($\alpha 1 \rightarrow 3$) branches
- Some have also ($\alpha 1 \rightarrow 2$) or ($\alpha 1 \rightarrow 4$) branches
- Dental plaque (formed by bacteria on the surface of teeth) is rich in dextrans

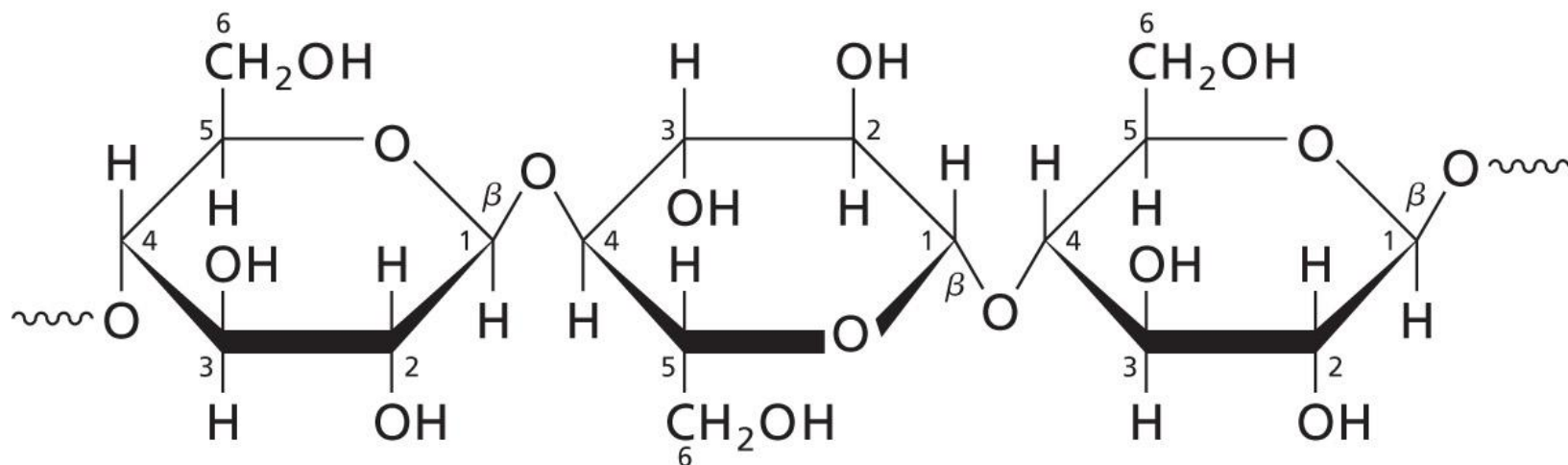
Cellulose

- Cellulose is an **unbranched homopolysaccharide** of glucose
 - Glucose monomers form ($\beta 1 \rightarrow 4$) linked chains
 - **Hydrogen bonds** form between adjacent monomers
 - Additional H-bonds between chains
 - Structure is now tough and water-insoluble
 - Most abundant polysaccharide in nature
 - Cotton is nearly pure fibrous cellulose

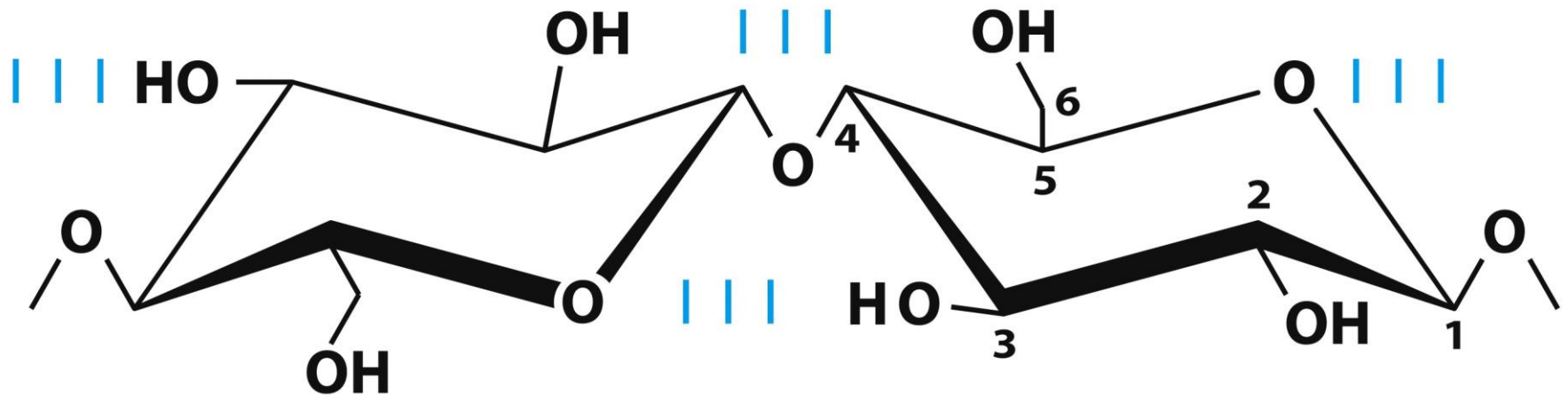
(a)



(b)



Hydrogen Bonding in Cellulose



$(\beta 1 \rightarrow 4)$ -linked D-glucose units

Figure 7-14

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Cellulose Metabolism

- The fibrous structure and water-insolubility make cellulose a difficult substrate to act on
- Fungi, bacteria, and protozoa secrete **cellulase**, which allows them to use wood as source of glucose
- Most animals cannot use cellulose as a fuel source because they lack the enzyme to hydrolyze ($\beta 1 \rightarrow 4$) linkages
- **Ruminants and termites** live symbiotically with microorganisms that produces cellulase
- Cellulases hold promise in the fermentation of biomass into biofuels

A wood fungus growing on an oak log



Figure 7-16

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Chitin Is a Homopolysaccharide

- Chitin is a linear homopolysaccharide of *N*-acetylglucosamine.
 - N*-acetylglucosamine monomers form ($\beta 1 \rightarrow 4$)-linked chains.
 - forms extended fibers that are similar to those of cellulose
 - hard, insoluble, cannot be digested by vertebrates
 - structure is tough but flexible, and water insoluble
 - found in cell walls in mushrooms and in exoskeletons of insects, spiders, crabs, and other arthropods

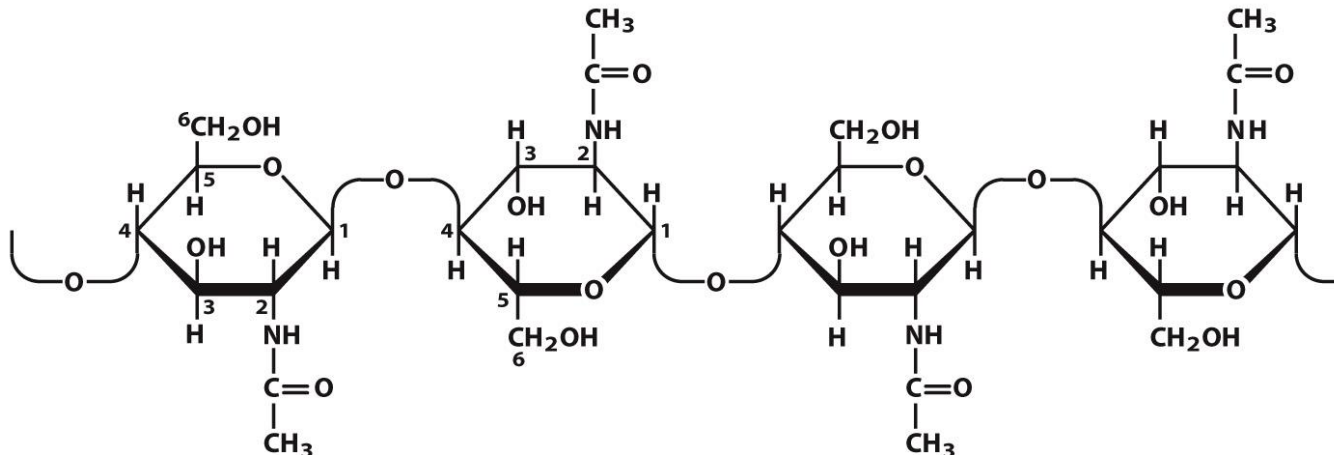


Figure 7-16a



Figure 7-16b

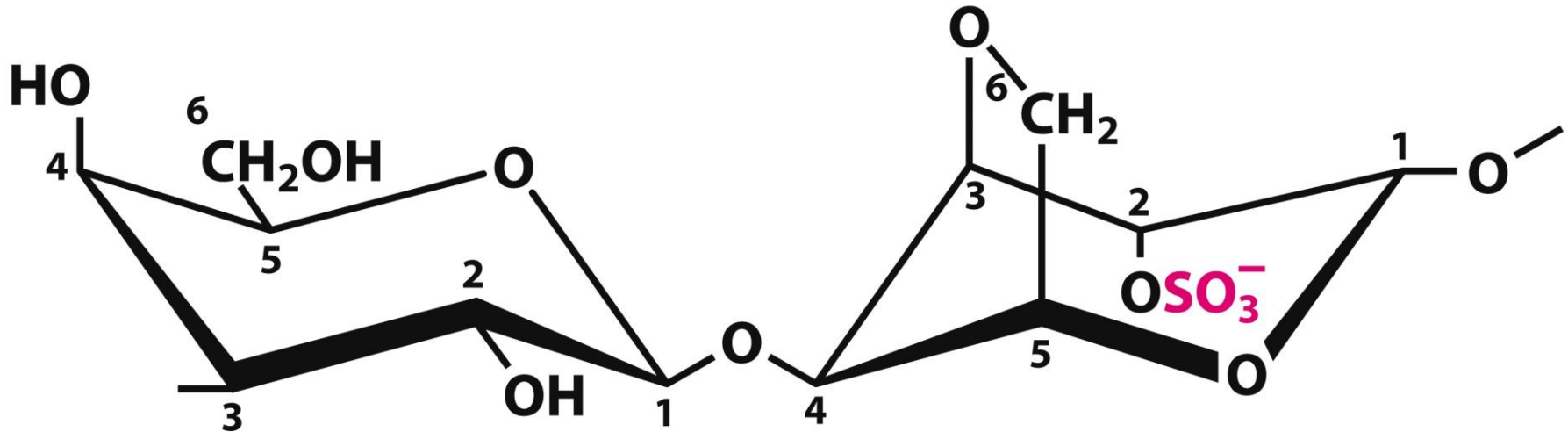
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Agar and Agarose

- Agar is a complex mixture of complex heteropolysaccharides composed of **agarose** and **agaropectin** (containing **modified galactose** units)
- Agar serves as a component of cell wall in some seaweeds
- Agar solutions form gels that are commonly used in the laboratory as a surface for **growing bacteria**
- Agar is also used for capsules in which some drugs and vitamins are packaged
- Agarose solutions form gels that are commonly used in the laboratory for **separation DNA** by electrophoresis

Agar and Agarose



Agarose

3)D-Gal(β 1 $\rightarrow$ 4)3,6-anhydro-L-Gal^{2S}(α 1 repeating units)

Figure 7-21

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Glycosaminoglycans

- Linear polymers of **repeating disaccharide units**
- One monomer is either
 - N-acetyl-glucosamine or
 - N-acetyl-galactosamine
- Negatively charged
 - **Uronic acids** (C6 oxidation)
 - **Sulfate esters**
- Extended hydrated molecule
 - Minimizes charge repulsion
- Forms meshwork with fibrous proteins to form **extracellular matrix**
 - Connective tissue
 - Lubrication of joints

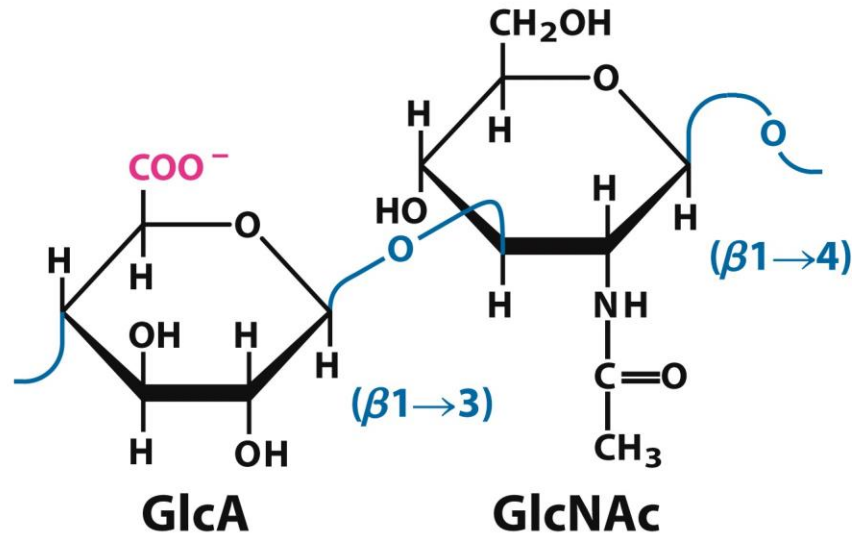
Glycosaminoglycan

Repeating disaccharide

Number of
disaccharides
per chain

Hyaluronate

~50,000



Chondroitin
4-sulfate

20 – 60

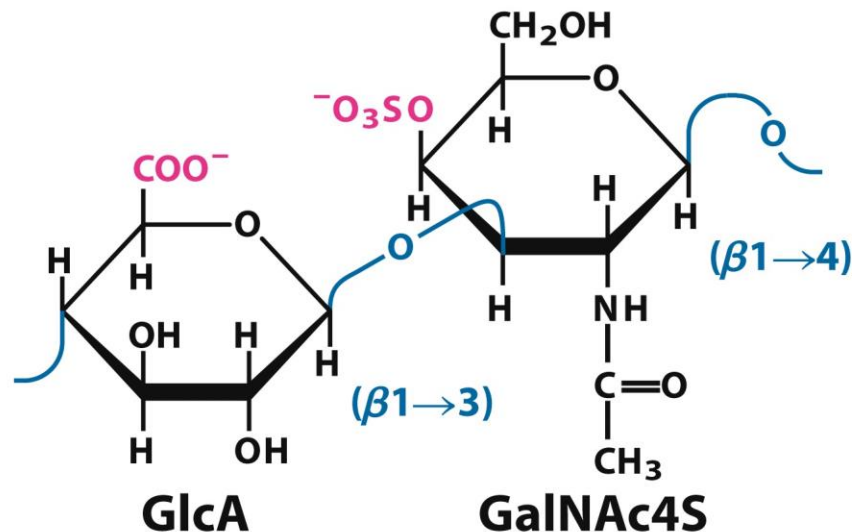


Figure 7-22 part 1a

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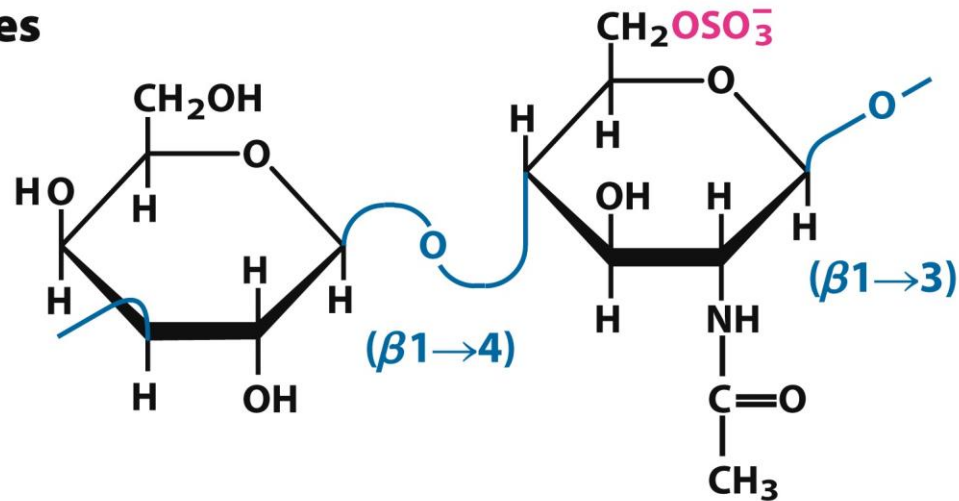
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Glycosaminoglycan

Repeating disaccharide

Number of
disaccharides
per chain

Keratan
sulfate
~25



Heparin
15-90

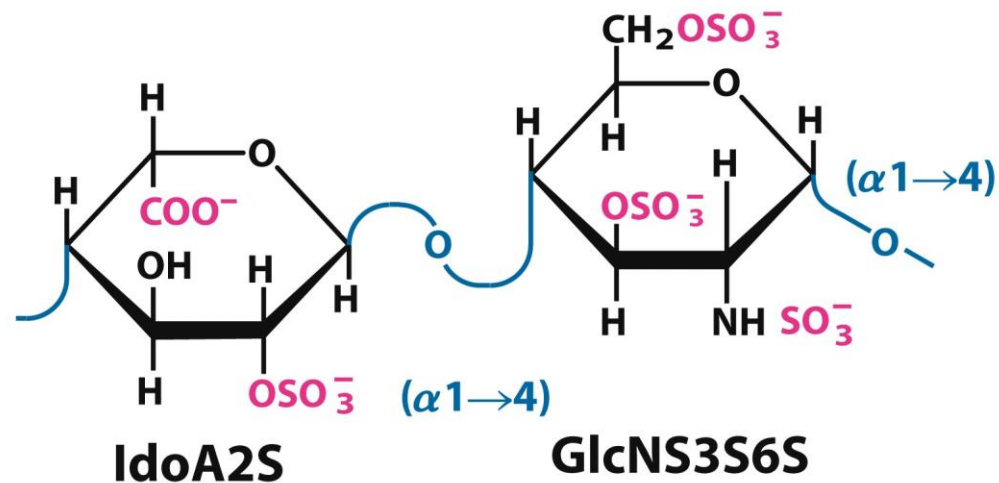


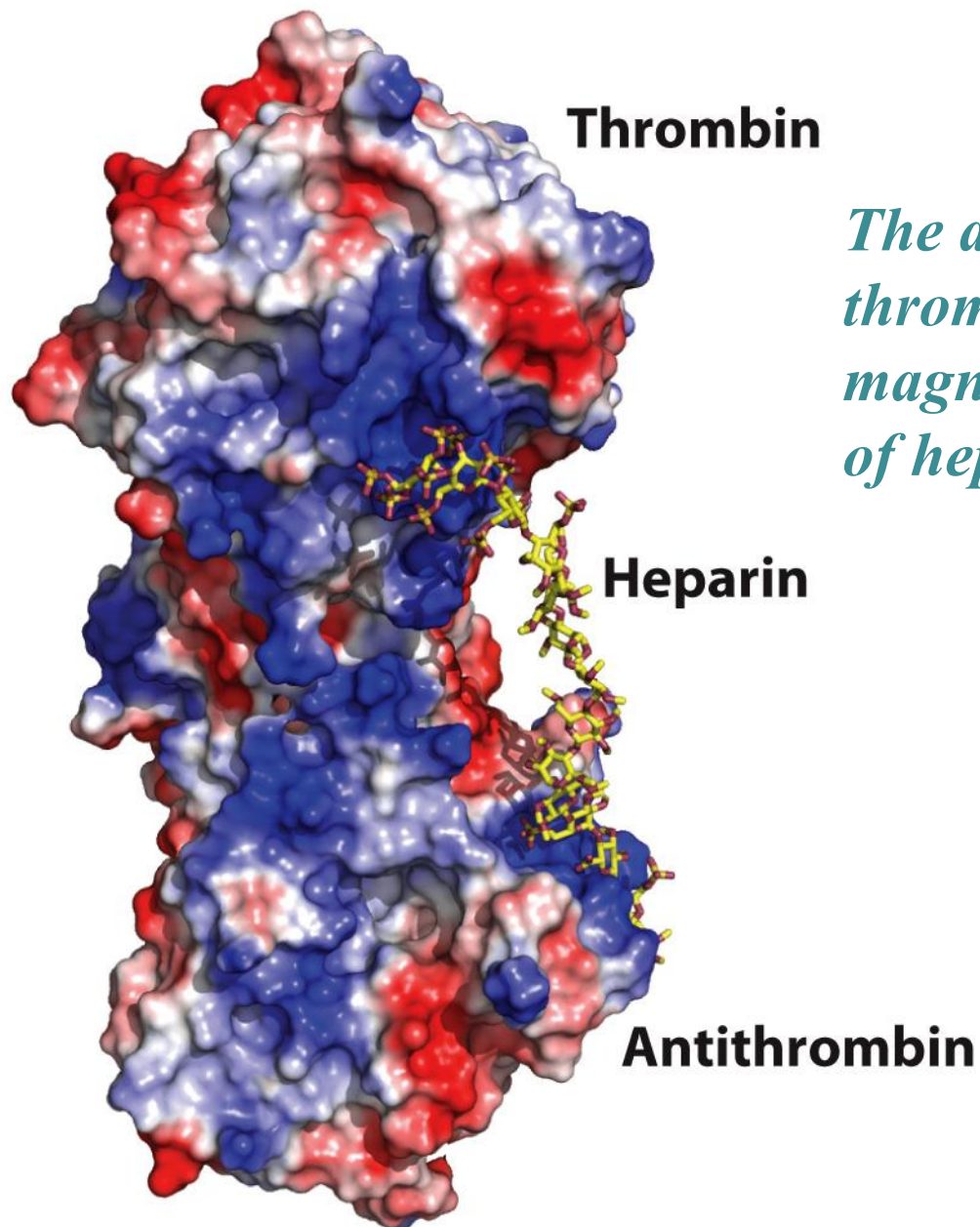
Figure 7-22 part 1b

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Heparin and Heparan Sulfate

- Heparin is linear polymer, 3–40 kDa.
- Heparan sulfate is heparin-like polysaccharide but attached to proteins.
- Highest negative-charge density biomolecules
- Prevent blood clotting by activating protease inhibitor antithrombin
- Binding to various cells regulates development and formation of blood vessels.
- Can also bind to viruses and bacteria and decrease their virulence



The affinity of antithrombin for thrombin is three orders of magnitude greater in the presence of heparin than in its absence.

Figure 7-27

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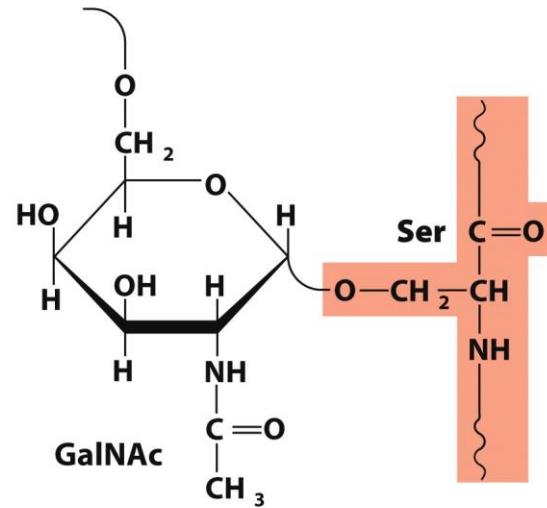
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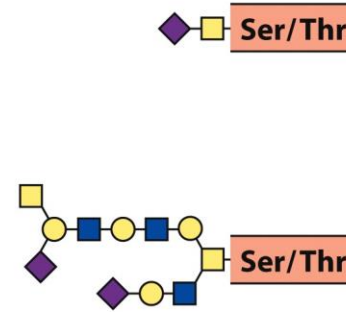
Glycoconjugates: Glycoprotein

- A protein with small oligosaccharides attached
 - Carbohydrate attached via its **anomeric carbon**
 - About half of mammalian proteins are glycoproteins
 - Carbohydrates play role in **protein-protein recognition**
 - Only some bacteria glycosylate few of their proteins
 - Viral proteins heavily glycosylated; helps **evade the immune system**

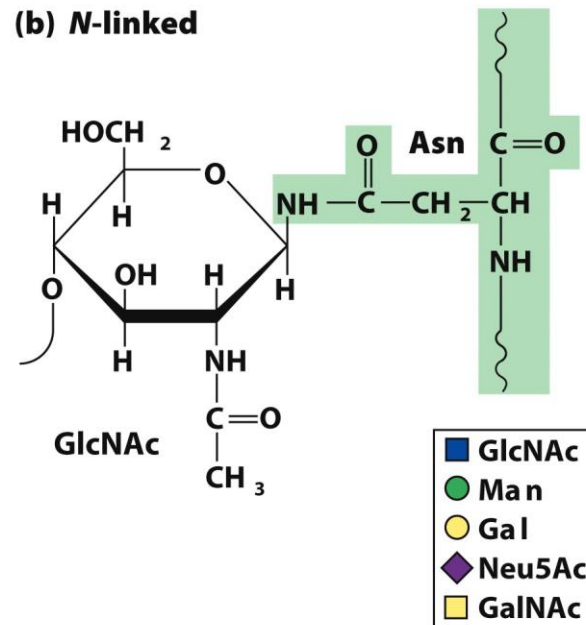
(a) O-linked



Examples:



(b) N-linked



Examples:

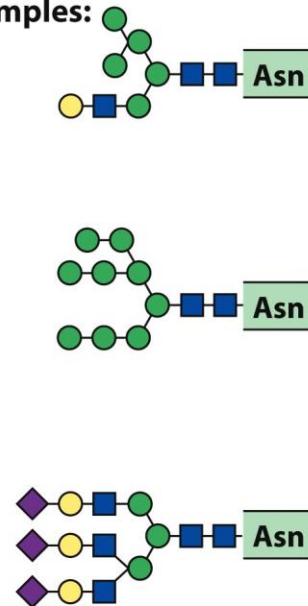
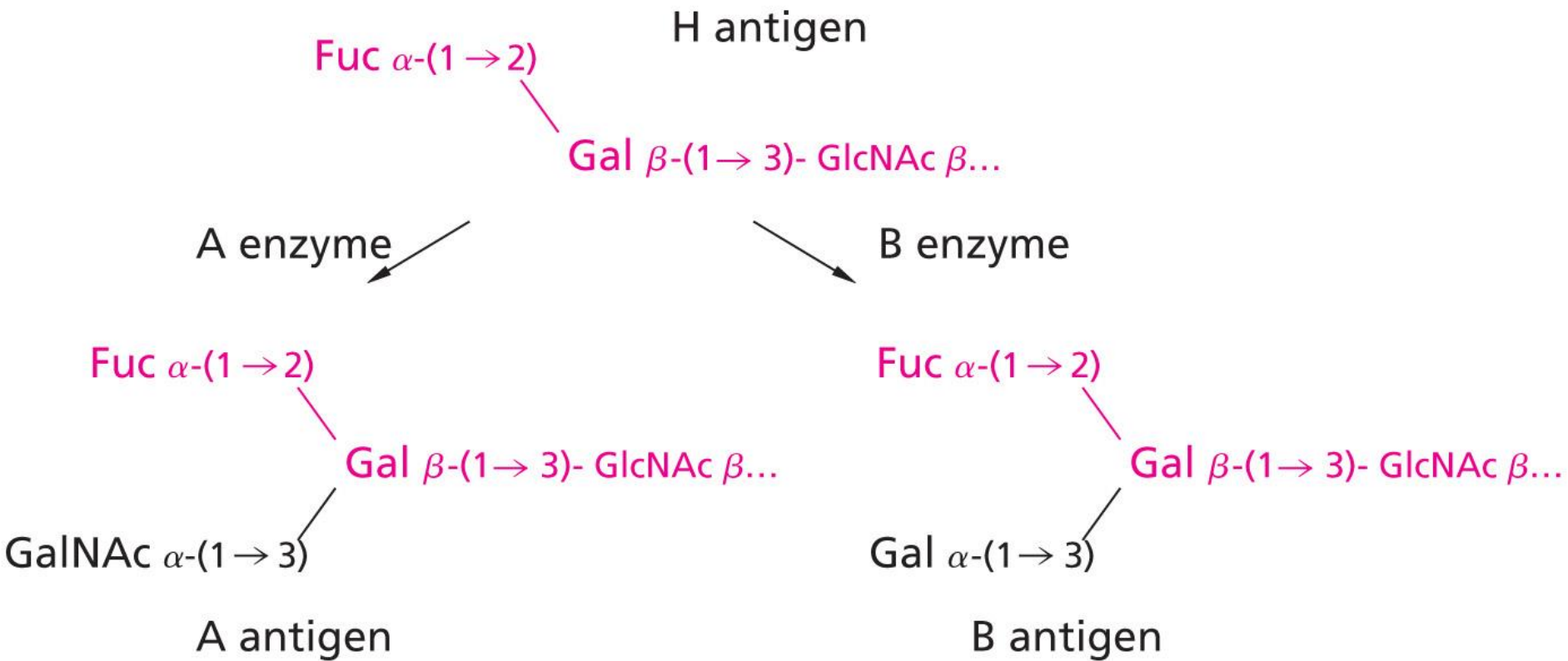


Figure 7-30

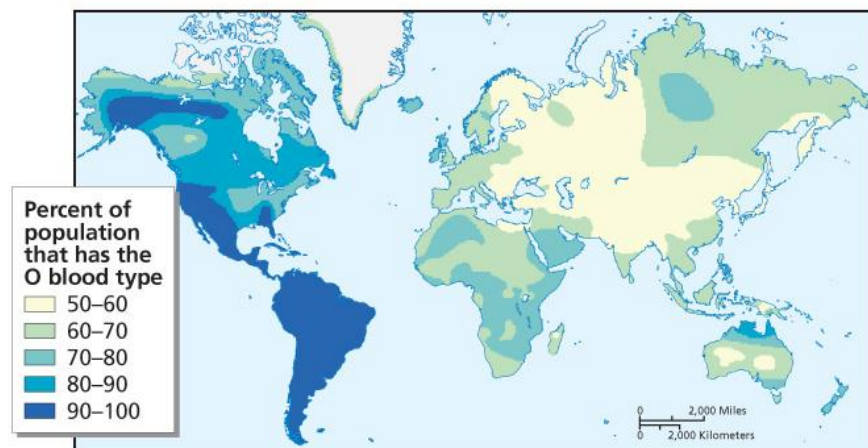
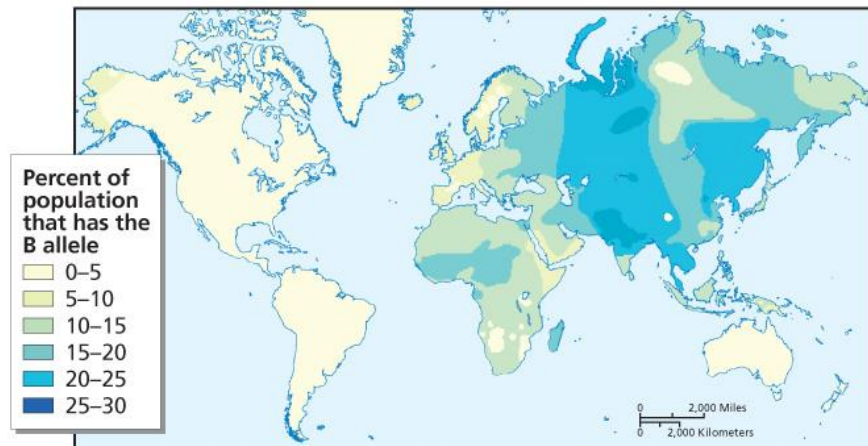
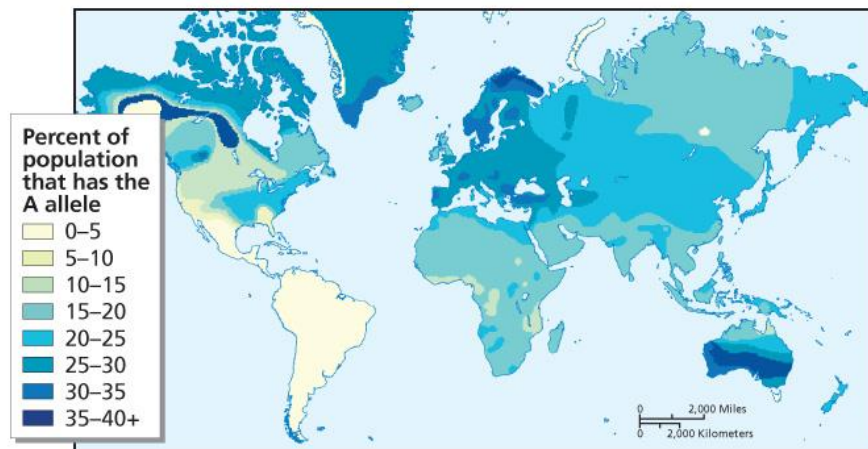
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Glycoconjugates: Glycolipids

- A lipid with covalently bound oligosaccharide
 - Parts of plant and animal cell membranes
 - In vertebrates, ganglioside carbohydrate composition determines **blood groups**
 - In gram-negative bacteria, **lipopolysaccharides** cover the peptidoglycan layer



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Glycoconjugates: Proteoglycans

- Sulfated **glucoseaminoglycans** attached to a large rod-shaped protein in cell membrane
 - Syndecans: protein has a single transmembrane domain
 - Glypicans: protein is anchored to a lipid membrane
 - Interact with a variety of receptors from neighboring cells and regulate cell growth

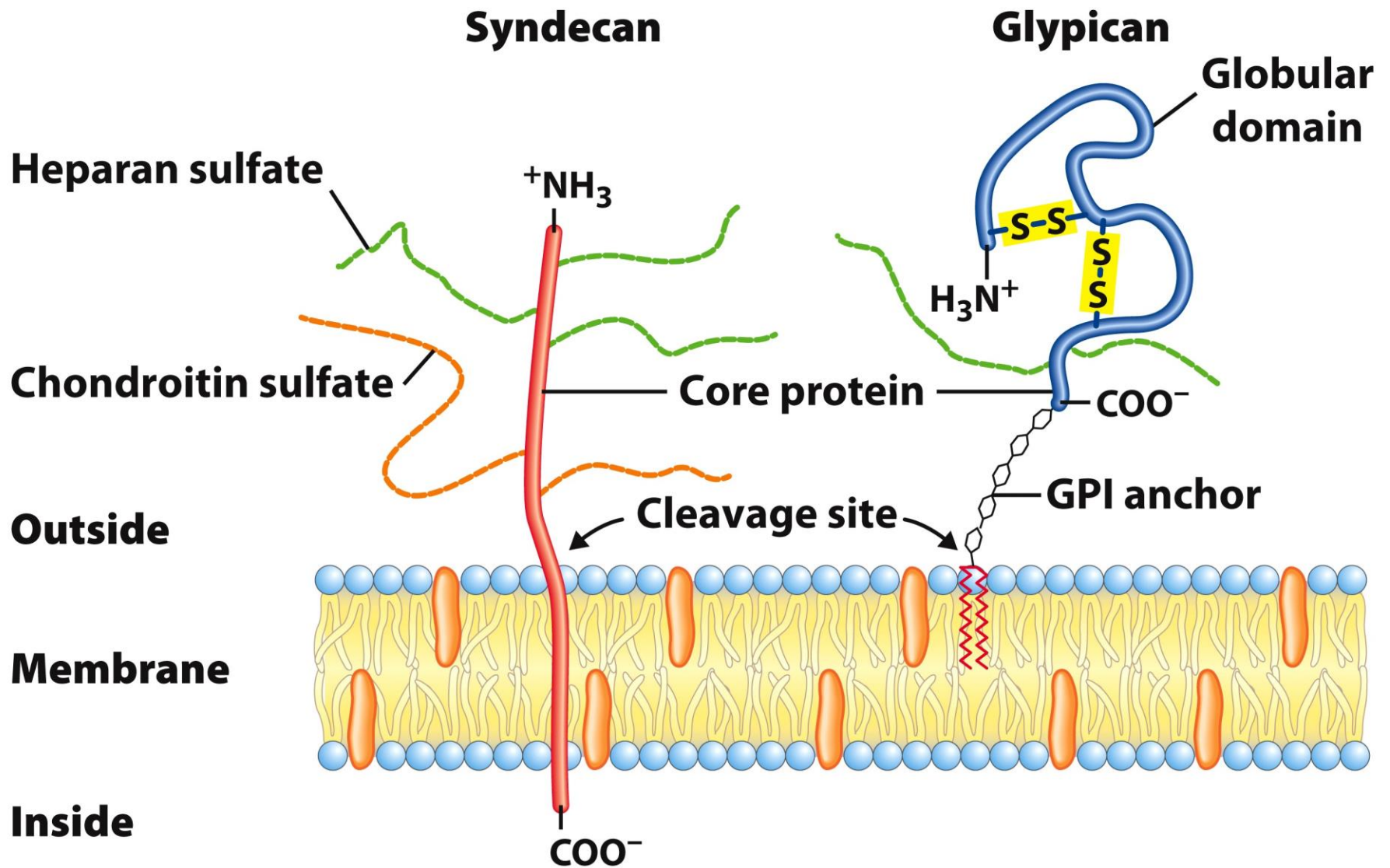


Figure 7-26a
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Proteoglycan Aggregates

- Hyaluronan and aggrecan form huge ($M_r > 2 \cdot 10^8$) noncovalent aggregates
- Hold lots of water (1000× its weight); provides lubrication
- Very low friction material
- Covers joint surfaces: **articular cartilage**
 - Reduced friction
 - Load balancing

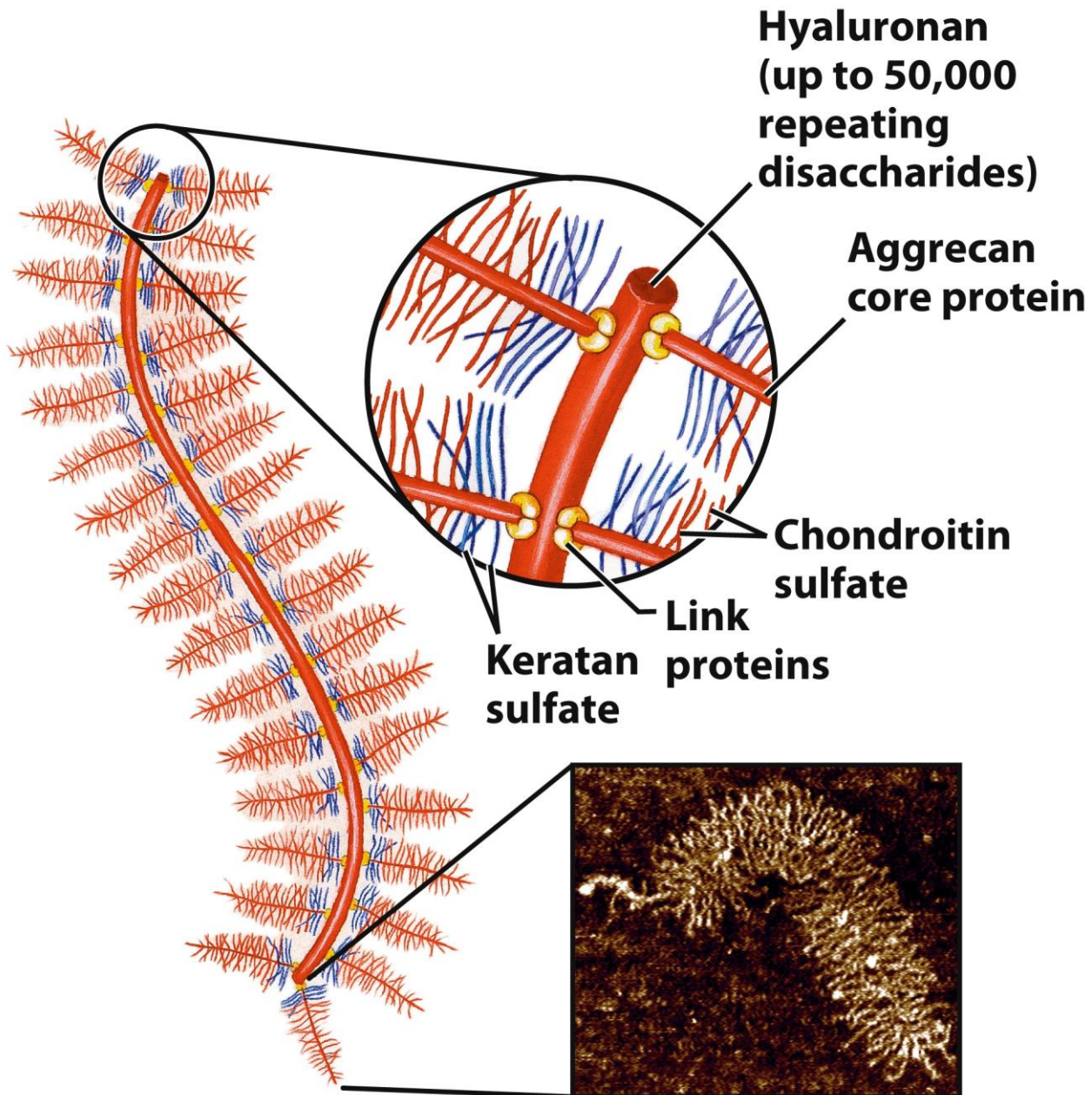


Figure 7-28

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Oligosaccharides in Recognition

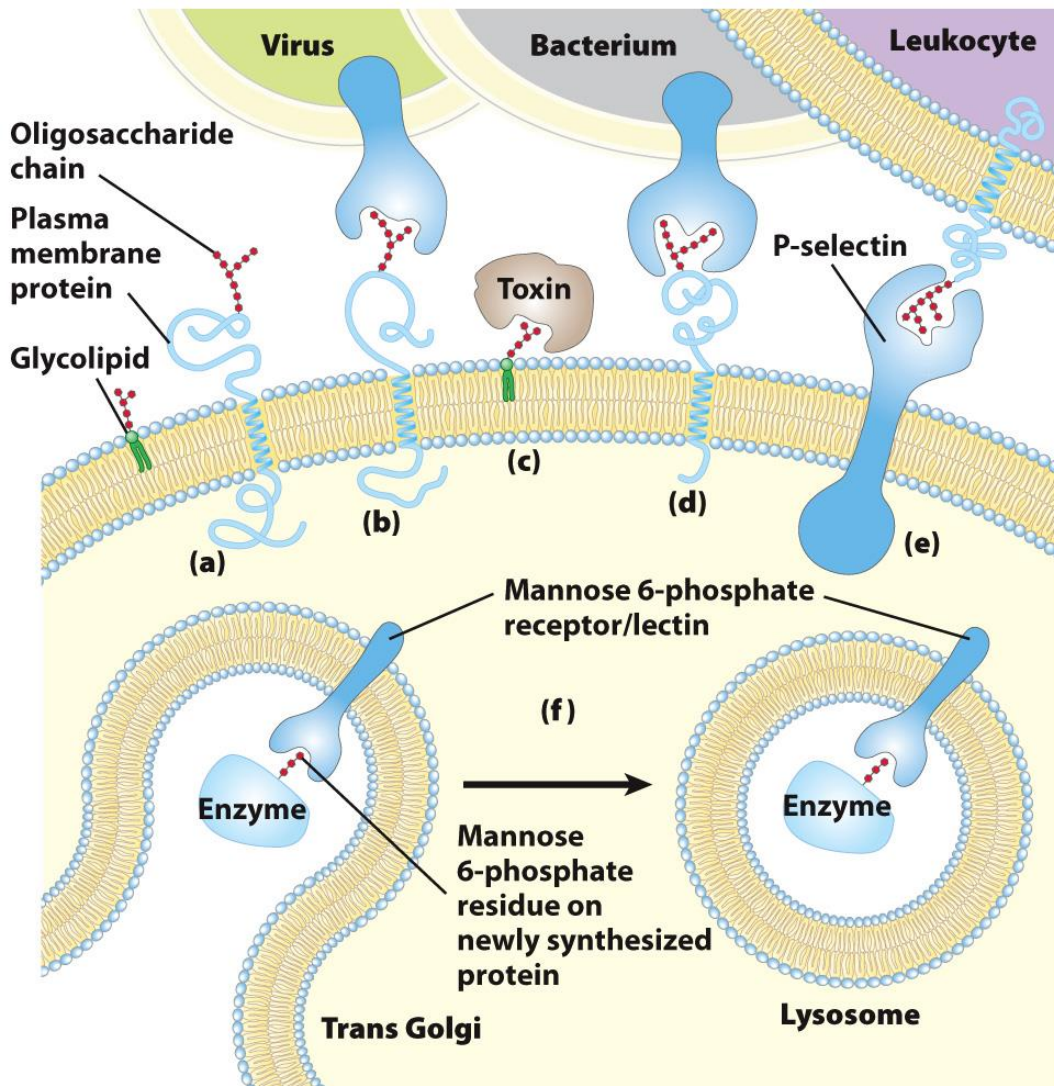


Figure 7-37

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