CARBOHYDRATES

- Most abundant biomolecules
- Each year, photosynthesis converts >100 billion metric tons CO_2 & H_2O into cellulose & other plant products
- Part of human diet - sugar and starch
- Oxidation - central energy-yielding pathway
- Carbohydrate polymers – Structural elements
  - -in the cell walls of bacteria, plants
  - -in connective tissues, cell coats of animals

- Carbohydrates polymers
  - -lubricate skeletal joints
  - -provide adhesion between cells
- Complex carbohydrate polymers

-covalently attached to proteins or lipids

-act as signals

Carbohydrates are polyhydroxy aldehydes or ketones, or the substances that yield such compounds on hydrolysis

- Most have empirical formulas suggesting - they are carbon "hydrates," Ratio of C:H:O is 1:2:1. $(CH_2O)n$

- For example, the empirical formula of glucose is $C_6H_{12}O_6$, which can also be written as $(CH_2O)_6$ or $C_6(H_2O)_6$

- Others do not; e.g. deoxyribose $C_5H_{10}O_4$ and rhamnose $C_6H_{12}O_5$

- Although Some non-carbohydrates do follow this empirical formula

- Some carbohydrates also contain N, P, S

Classification

1.Monosaccharides, 2.Oligosaccharides
3.Polysaccharides

- Word "Saccharide" is derived from Greek ***sakkharon***, meaning "sugar"

1. Monosaccharides

-Simplest sugars

-Consist of a single polyhydroxy aldehyde or ketone unit

-Most abundant monosaccharide in nature is the six carbon sugar D-glucose

2. Oligosaccharides

- Short chains of monosaccharide units **(2-10 OR 3-11)**
- Joined together by characteristic glycosidic linkages
- Most abundant – disaccharides (2 monosaccharide units)
- -Sucrose (cane sugar) consist of six-carbon sugars D-glucose and D-fructose
- Most are joined to non-sugar molecules (lipids or proteins) in hybrid structures (glycoconjugates)

3. Polysaccharides

-Long chains 100-1000 monosaccharide units

-Some polysaccharides, such as cellulose occur in linear chains

-Others, such as glycogen have branched chains

-Most abundant polysaccharides - starch and cellulose

Classification of polysaccharides

1. Storage & structural polysaccharides

Example: Starch, glycogen, chitin, cellulose

2. **Homo-polysaccharides & hetero-polysaccharides**

Example: Starch, glycogen, cellulose, hyaluronic acid

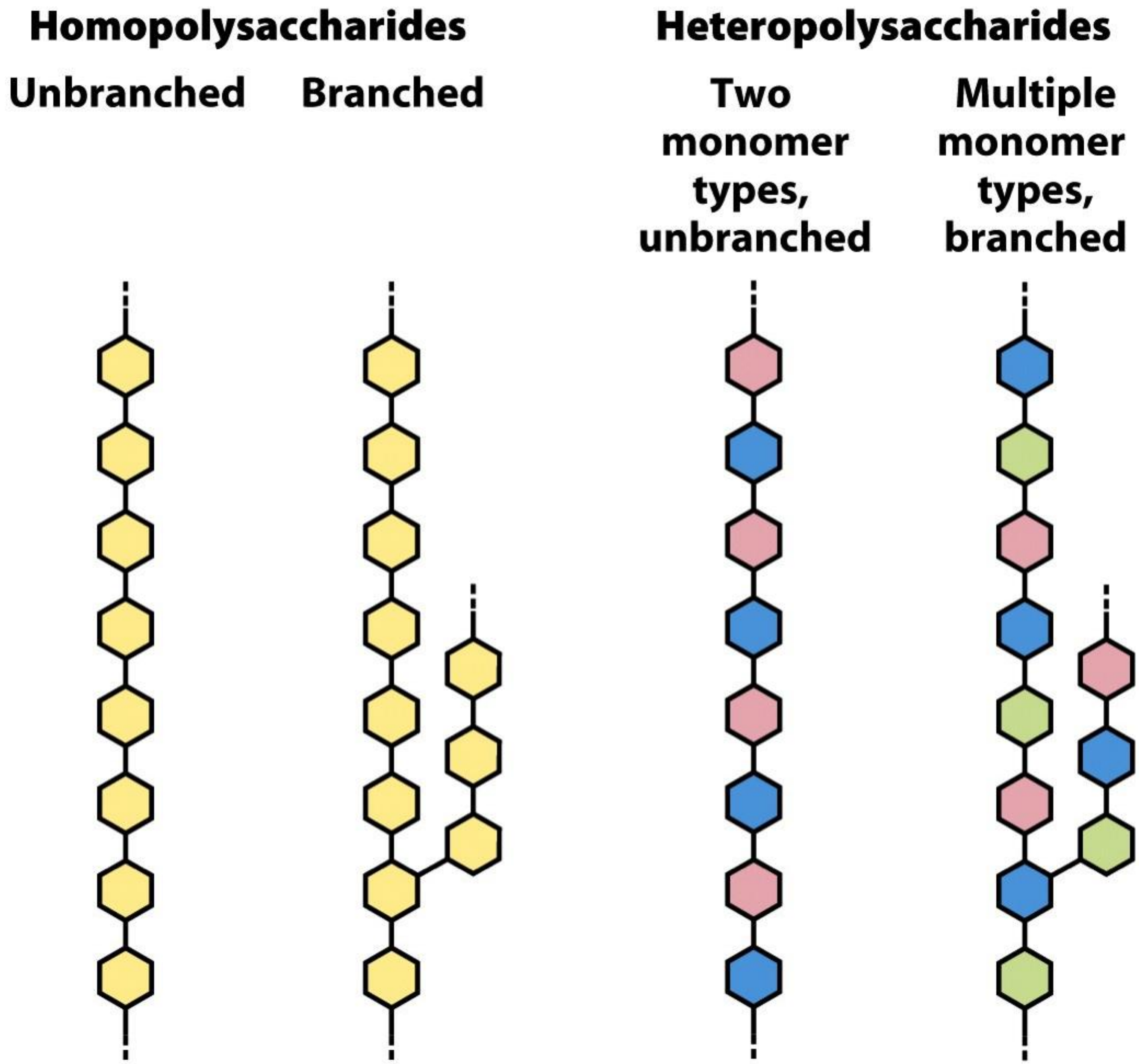

Figure 7-13
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Figure 7-17b
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Monosaccharides

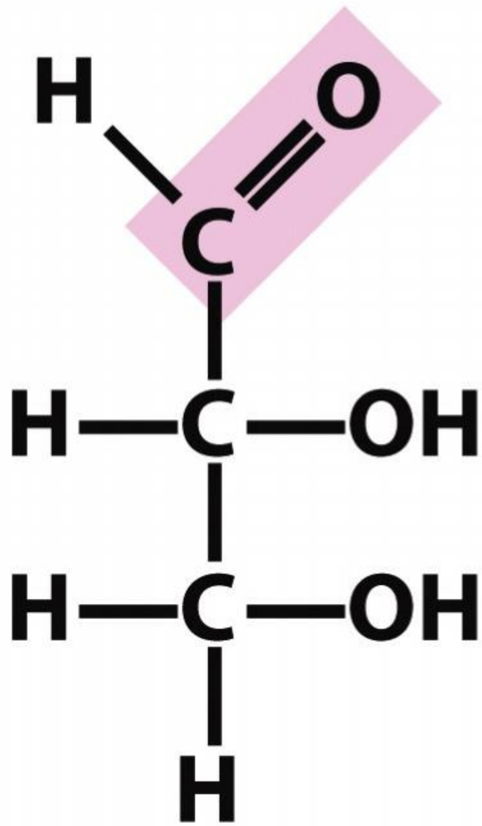
- Simplest of carbohydrates
- Subunits from which oligosaccharides, polysaccharides are constructed
- Either aldehydes or ketones
- With 1 OR > hydroxyl groups
- 6-C monosachharide glucose, fructose have 5 hydroxyl groups
- C atoms to which hydroxyl groups are attached are often chiral centers

Monosaccharides

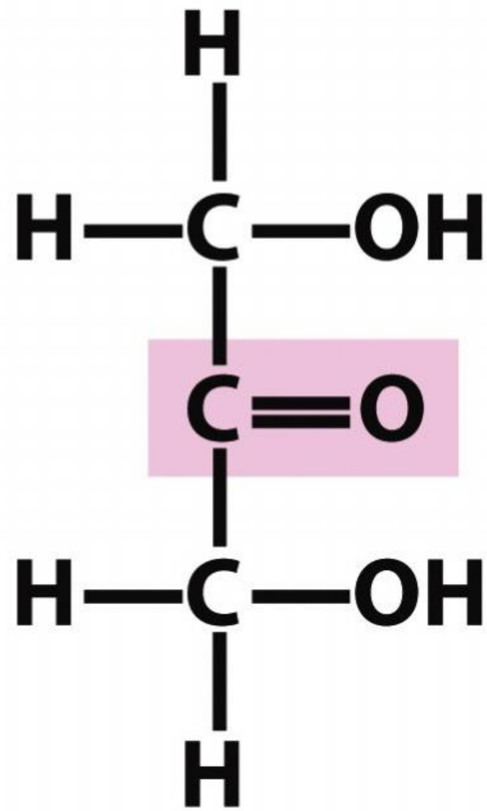
- Colorless, crystalline solids
- Freely soluble in water but insoluble in non-polar solvents
- Most have a sweet taste
- Backbone of monosaccharides -an unbranched C chain
- All C atoms linked by single bonds

Monosaccharides

- One of the C atoms is double-bonded to an O atom to form a carbonyl group
- Other C atom has a hydroxyl group
- If the carbonyl group is at an end of C chain, the monosaccharide is an aldehyde (aldose)
- If the carbonyl group is at any other position, the monosaccharide is a ketone (ketose)
- Simplest monosaccharides -three-carbon triose: glyceraldehydes, an aldose and dihydroxyacetone, a ketone



Glyceraldehyde, an aldotriose



Dihydroxyacetone, a ketotriose

Figure 7-1a

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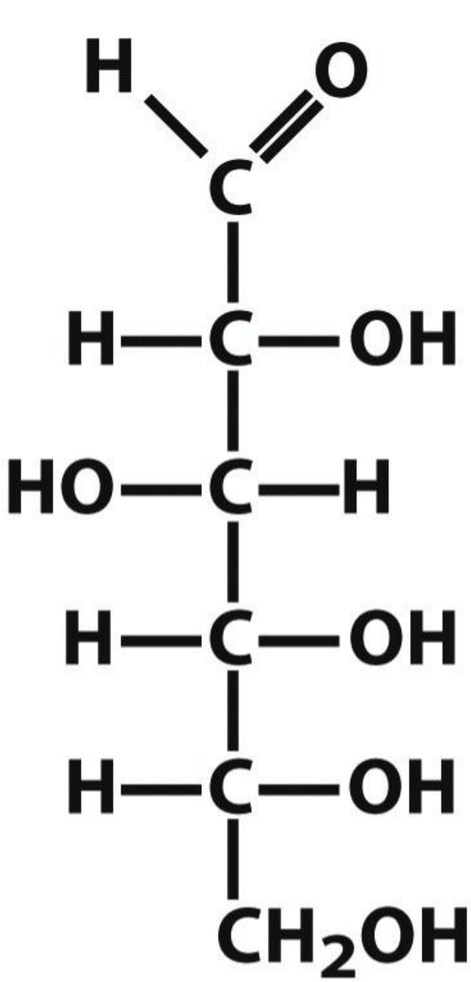
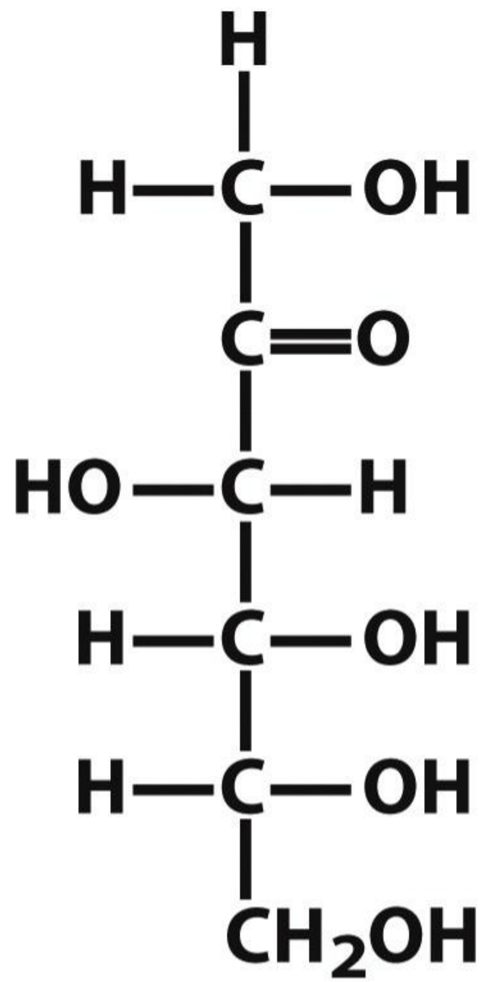
Monosaccharides

- Monosaccharides with 4, 5, 6 and 7 C atoms in their backbone called tetroses, pentoses, hexoses and heptoses
- There are aldoses and ketoses of each of these chain lengths
- The hexoses, which include the aldohexose D-glucose and ketohexose D-fructose, are the most common monosaccharides in nucleic acids



D-Glucose,
an aldohexose



D-Fructose,
a ketohexose

Figure 7-1b
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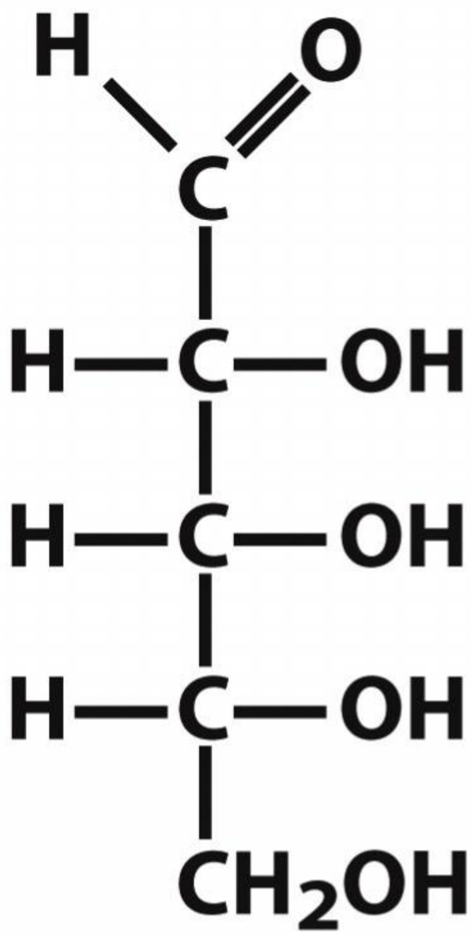
Monosaccharides

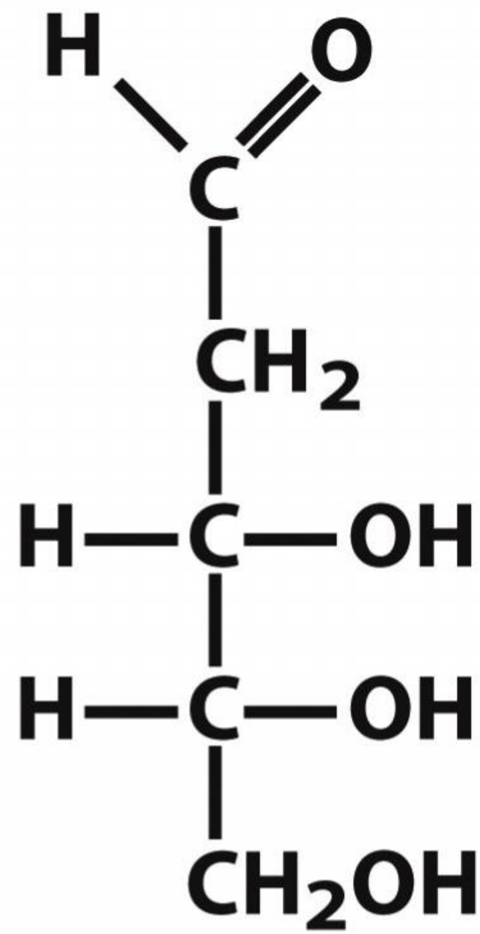
- Aldopentose D-ribose, 2-deoxyderibose - components of nucleotides

Monosaccharides Have Asymmetric Centers

- Monosaccharides except dihyroxyacetone contain 1 or > asymmetric (chiral) C atoms
- Thus occur in isomeric forms
- Simplest aldose, glyceraldehydes -1 chiral center (middle C atom), So has 2 different isomers or enantiomers



D-Ribose,
an aldopentose



2-Deoxy-D-ribose,
an aldopentose

Figure 7-1c
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Monosaccharides

ENANTIONMERS

- 1 is designated the D isomer; other is the L isomer

Stereoisomers

Compounds that have the same structural formula but differ in spatial configuration (arrangement in space) are known as stereoisomers

- Presence of asymmetric carbon or chiral carbon atom allows the formation of isomers

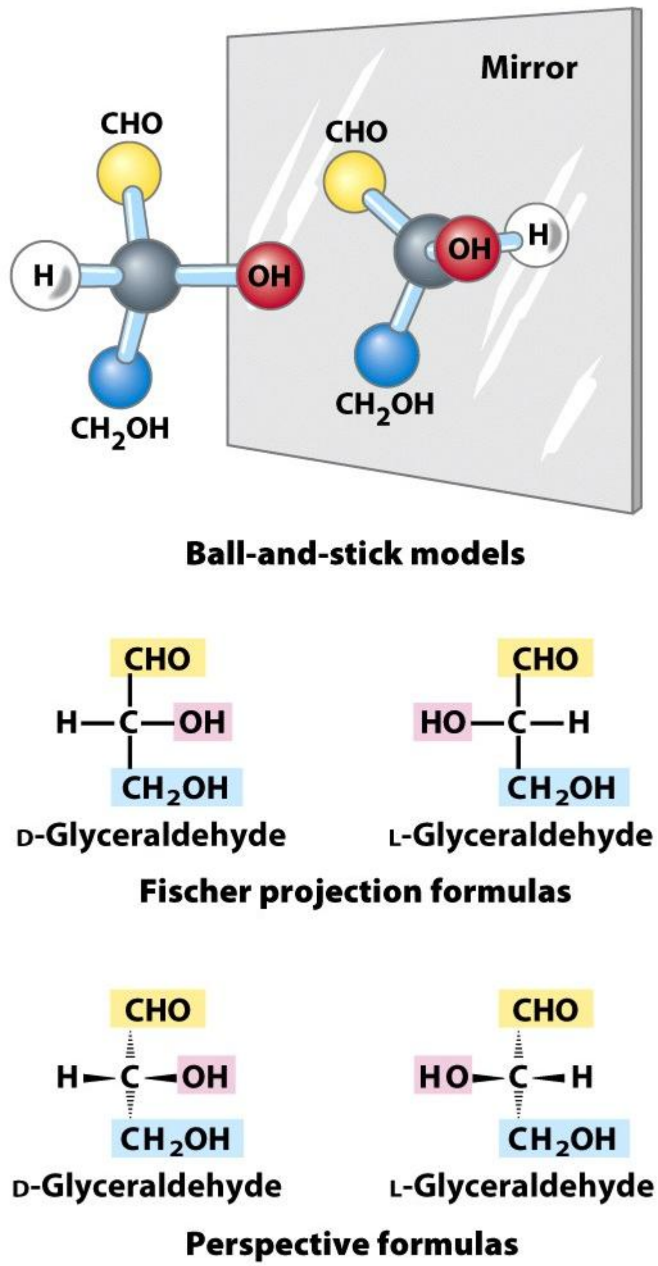

Figure 7-2
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Monosaccharides

- In general, a molecule with n chiral centers can have 2^n stereoisomers
- **Example:** Aldotriose Glyceraldehyde has 2^1 = 2; the aldohexoses, with four chiral centers, have 2^4 = 16 stereoisomers

No. of asymmetric carbon atoms	No. of possible stereoisomers
1	$2^n = 2^1 = 2$
2	$2^n = 2^2 = 4$
3	$2^n = 2^3 = 8$
4	$2^n = 2^4 = 16$

Monosaccharides

- Stereoisomers of monosaccharides of each C chain length can be divided into 2 groups, which differ in configuration about the chiral center most distant from the carbonyl carbon;
- Those with the same configuration at this reference C as that of D-glyceraldehyde are designated D-isomers
- Those with the configuration of L-glyceraldehyde are L isomers

Monosaccharides

- When the hydroxyl group on the reference C is on the right side in the projection formula, the sugar is the D isomer
- When on the left, the L isomer
- D and L glyceraldehydes are mirror images, enantiomers
- Except for the difference in the direction of rotating plane polarized light, all of their physical and chemical properties are the same

Monosaccharides

- Of the 16 possible aldohexoses, 8 are D forms and 8 are L
- Most of the hexoses found in living organisms are D isomers
- Each of the eight D-aldohexoses, which differ in the stereochemistry at C-2, C-3 and C-4 has its own name: D-glucose, D-galactose, D-mannose etc
- Ketoses are commonly designated by inserting *ul* into the name of the corresponding aldose

D-Aldoses

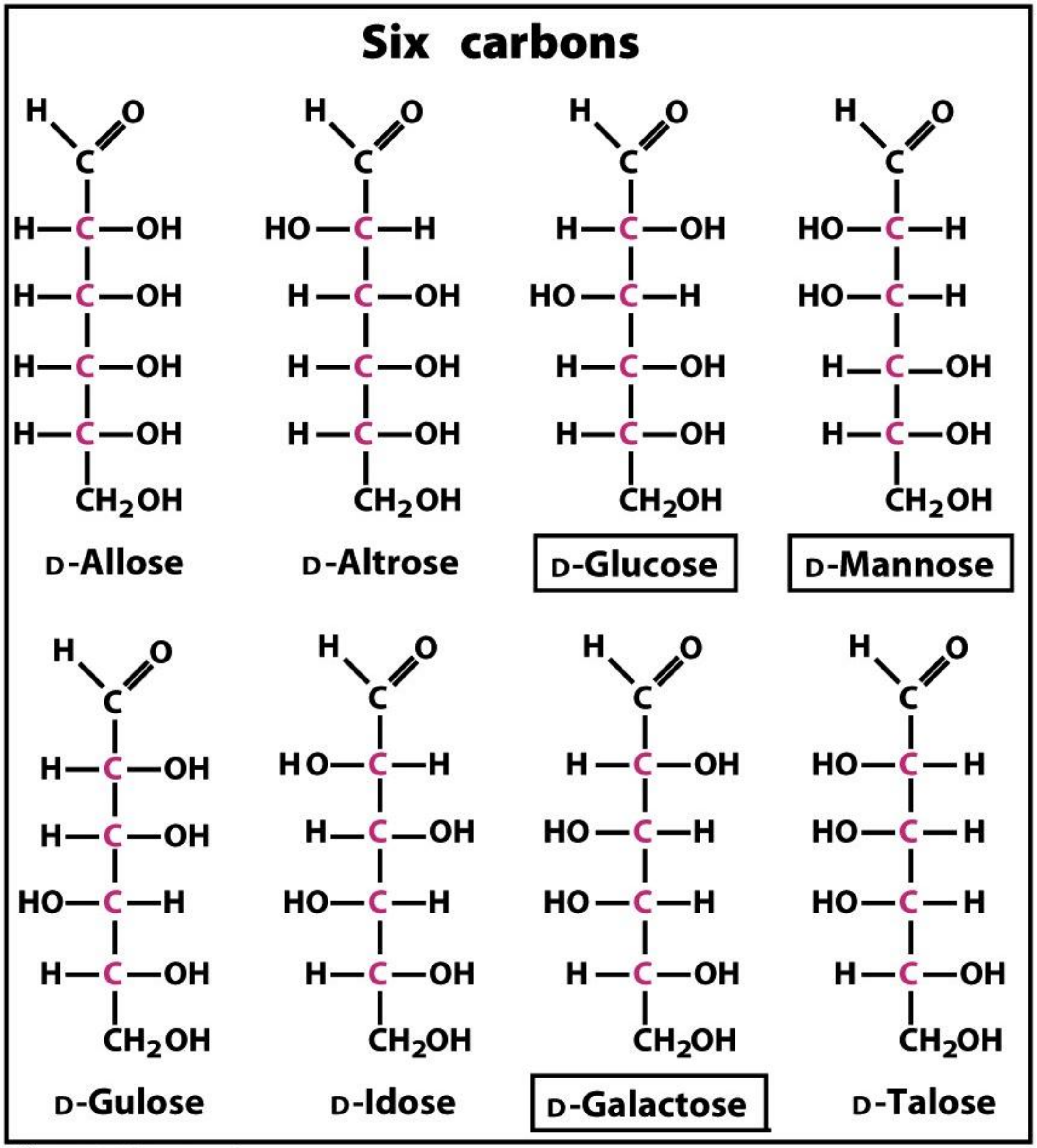

Figure 7-3a part 3
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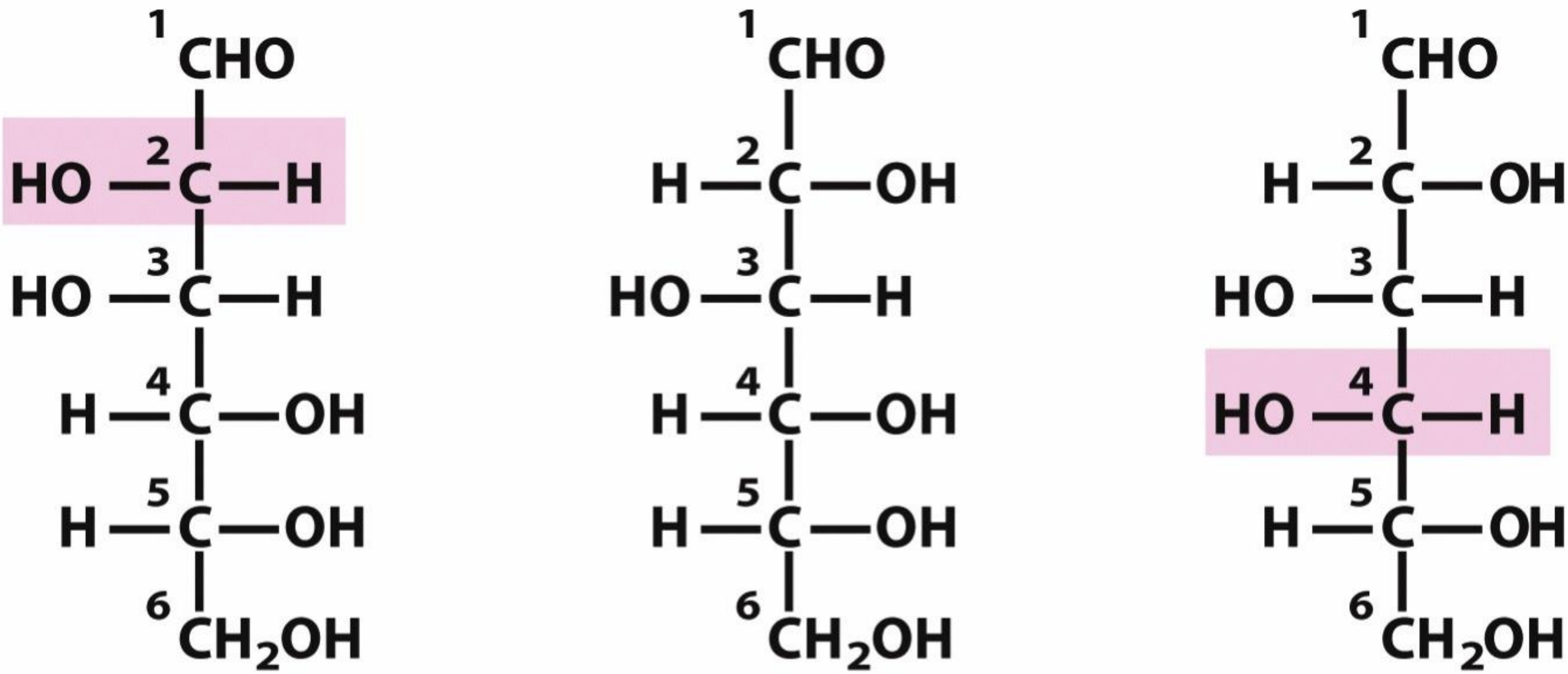
Monosaccharide Classification

# Carbons	Category Name	D-aldoses	D-ketoses
3	Triose	Glyceraldehyde	Dihydroxyacetone
4	Tetrose	Erythrose	Erythrulose
5	Pentose	Ribose, xylose	Ribulose, Xylulose
6	Hexose	Glucose, Galactose, Mannose	Fructose

Monosaccharides

- Few ketoses are named otherwise, such as fructose (from Latin fructus, meaning “fruit”; fruits are a good source of this sugar)
- When 2 sugars differ only in the configuration around 1 C atom, they are called **epimers**
- D-glucose and D-mannose, which differ only in the stereochemistry at C-2 are epimers, as are D-glucose and D-galactose (at C-4)



D-Mannose (epimer at C-2)

D-Glucose

D-Galactose (epimer at C-4)

Figure 7-4
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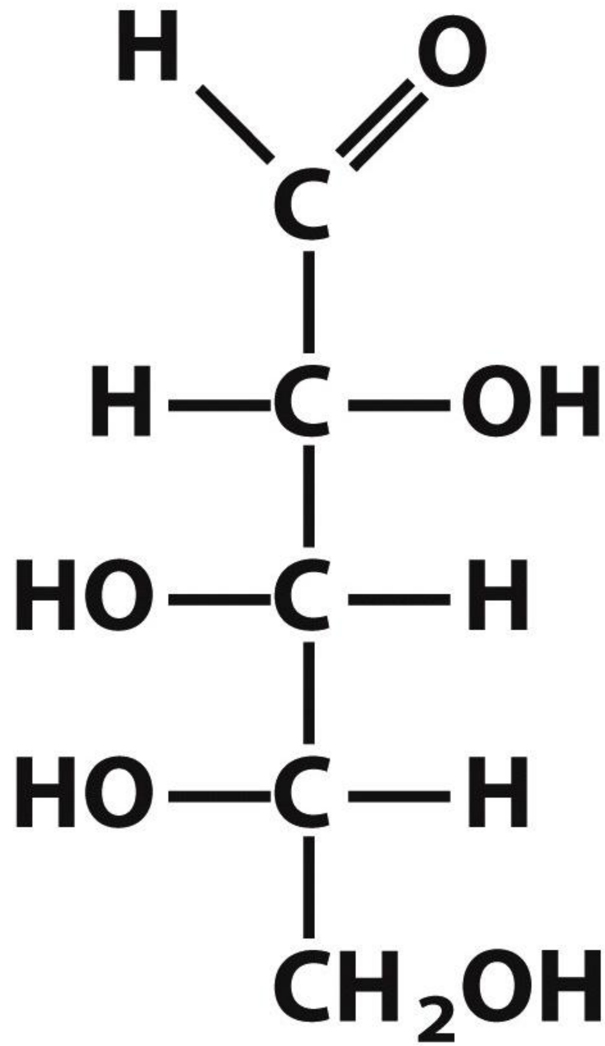
Monosaccharides

- Some sugars do occur naturally in their L forms
- Examples: L-arabinose, L-Rhamnose, L-Fucose and L isomer of some sugar derivatives that are common components of glycoproteins



L-Arabinose

Unnumbered 7 p238
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Common Monosaccharides Occur in Cyclic Forms

- Monosaccharides with 5 or > C atoms -cyclic (ring) structures
- α- D-glucose, β- D –glucose (ANOMERS)
- α & β isomers of D-glucose

Pyranoses, pyran

- D-glucose - α- D-glucopyranose & β- D-glucopyranose
- α & β forms of D-glucose interconvert in aqueous solution, by a process called mutarotation

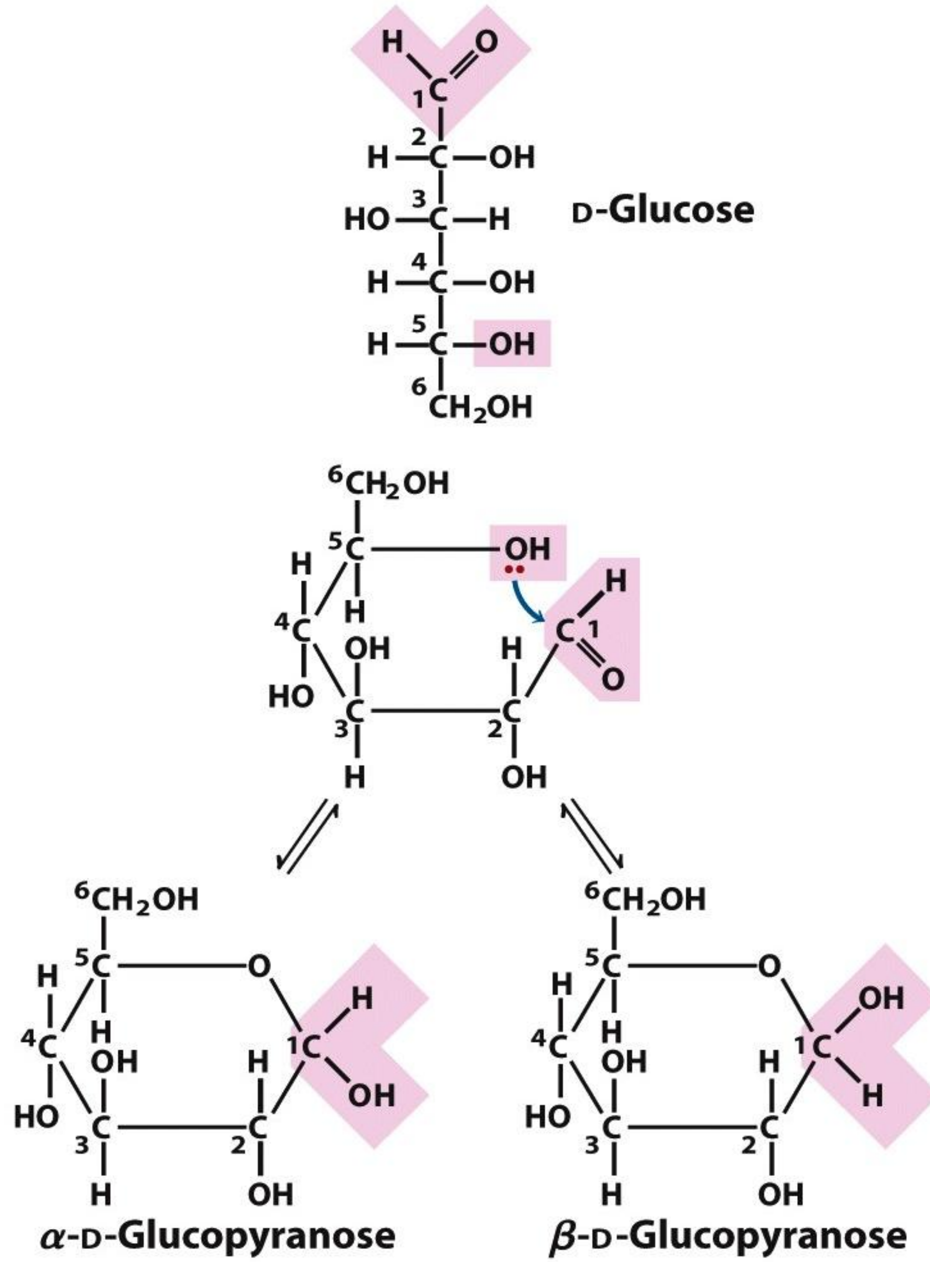

Figure 7-6
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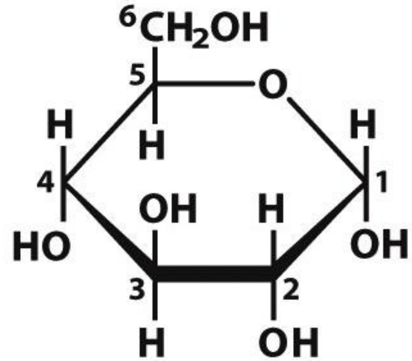
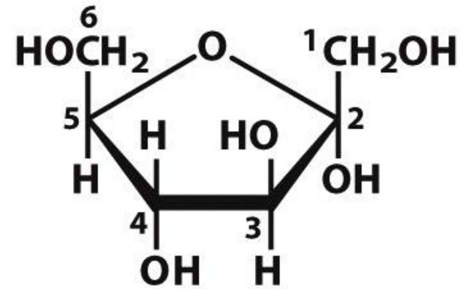
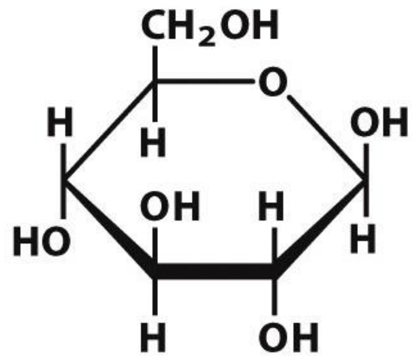


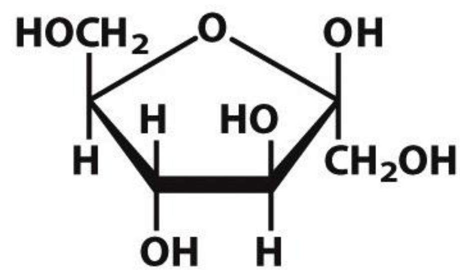
α-D-Glucopyranose



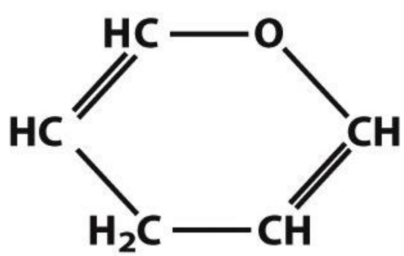
α-D-Fructofuranose



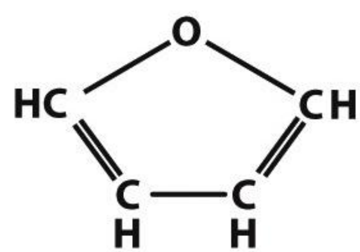
β-D-Glucopyranose



β-D-Fructofuranose



Pyran



Furan

Figure 7-7

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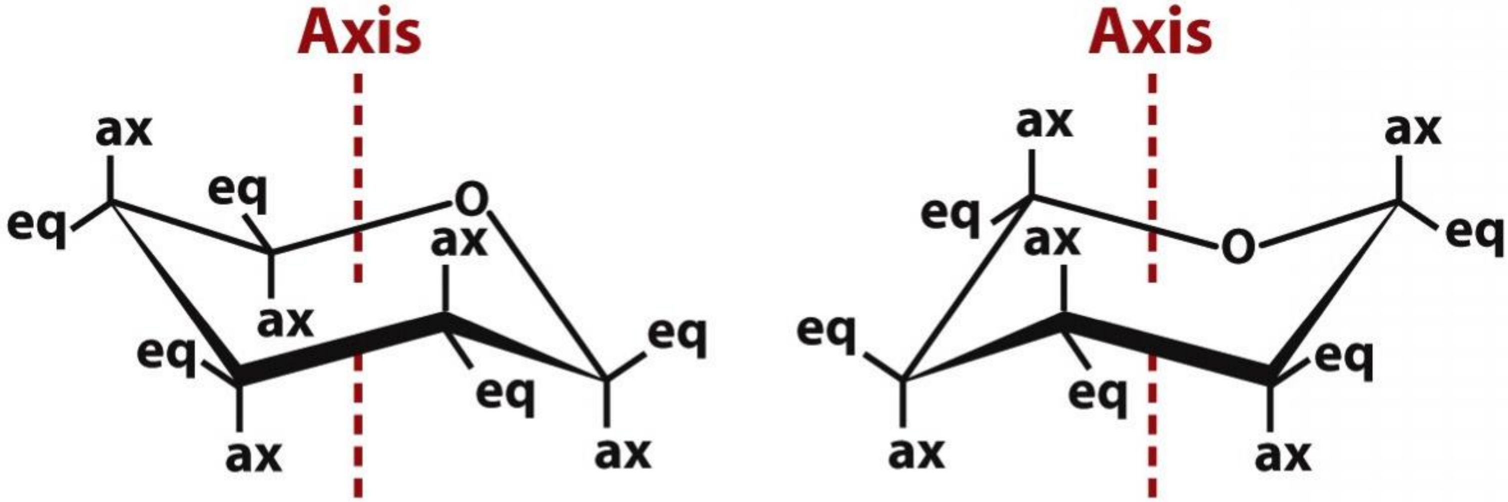
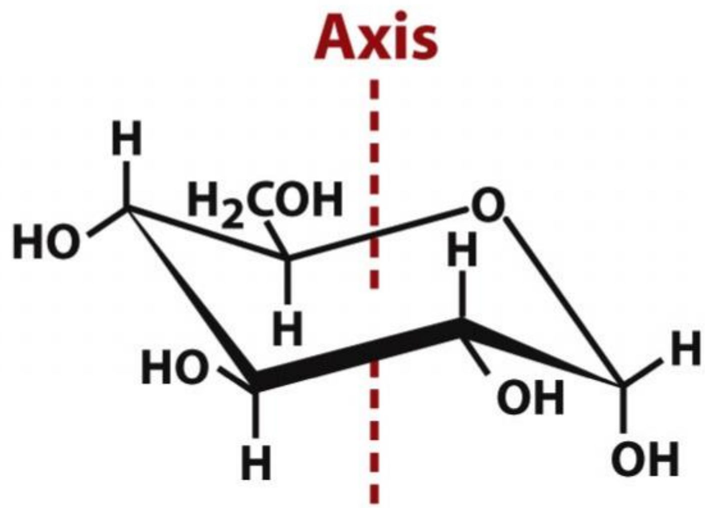


Two possible chair forms



α-D-Glucopyranose

Figure 7-8
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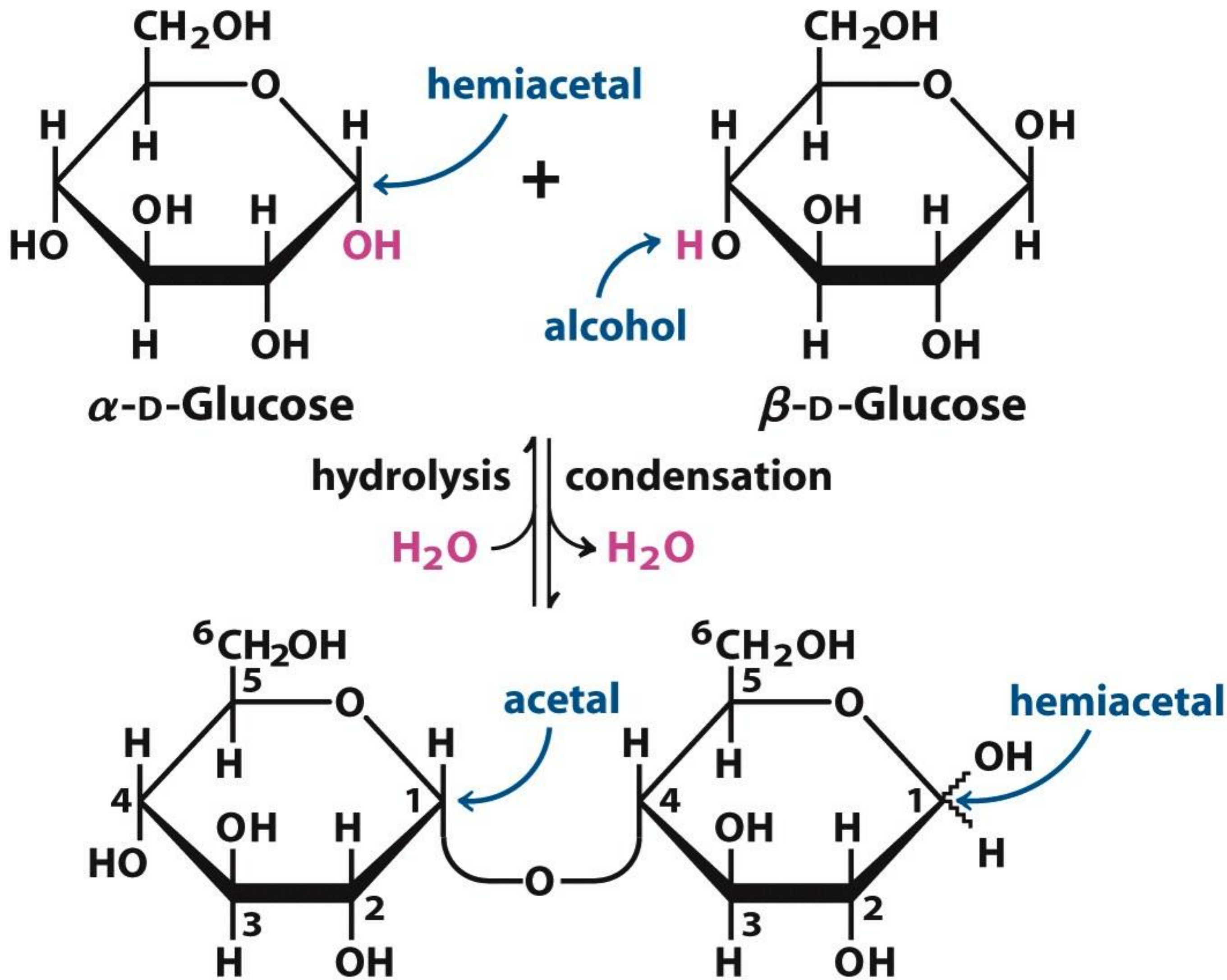

Maltose

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

Figure 7-11
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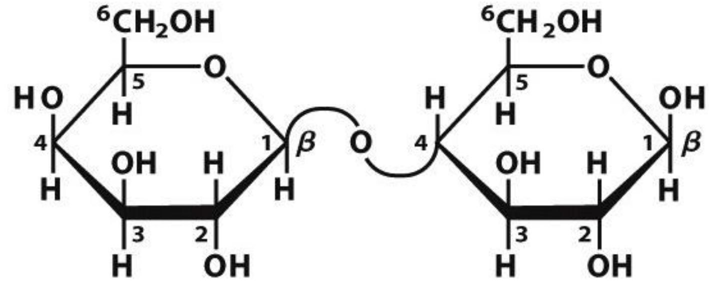
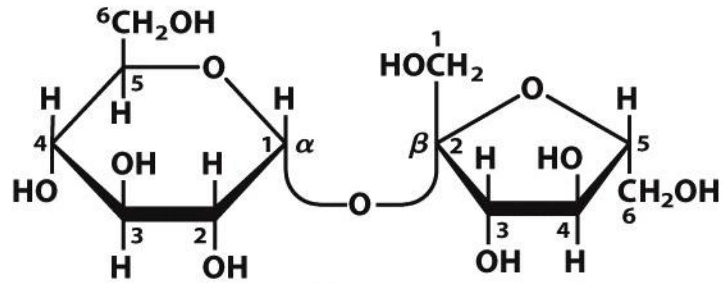
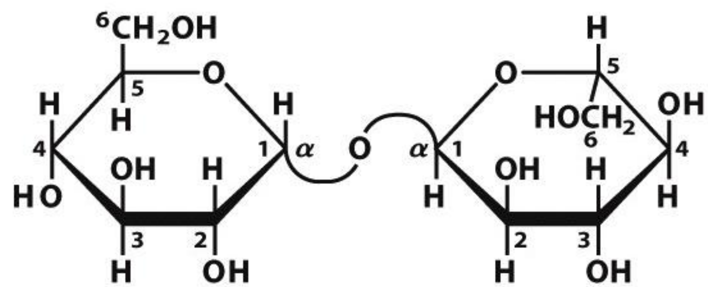


Lactose (β form)
β-D-galactopyranosyl-(1→4)-β-D-glucopyranose
Gal(β1→4)Glc



Sucrose
β-D-fructofuranosyl α-D-glucopyranoside
Fru(2β↔α1)Glc ≡ Glc(α1↔2β)Fru



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

Figure 7-12
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Polysaccharides/Glycans

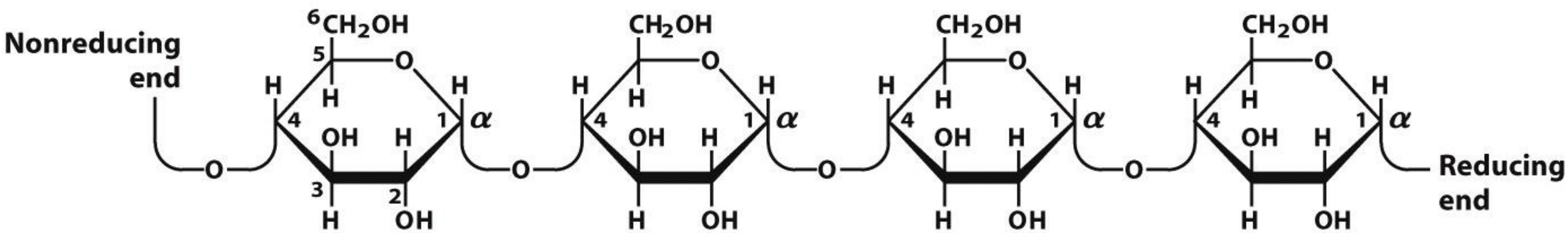
- Most of the carbohydrates found in nature occur as polysaccharides, polymers of high molecular weight
- Polysaccharides, also called glycans, differ from each other:

-in identity of their recurring monosaccharide units

-in length of their chain

-in type of bonds linking the units

-in degree of branching



Amylose

Figure 7-14a
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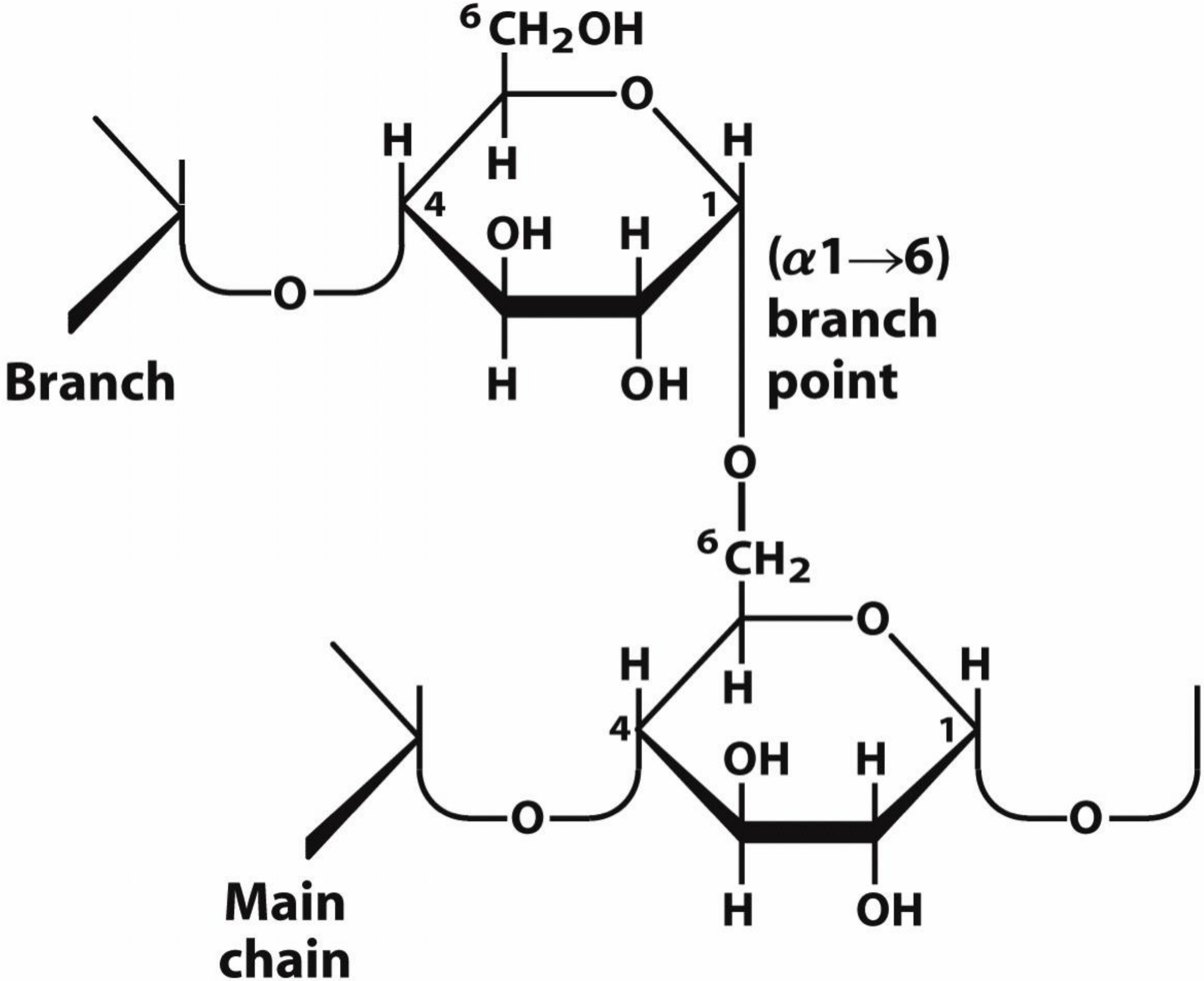

Figure 7-14b
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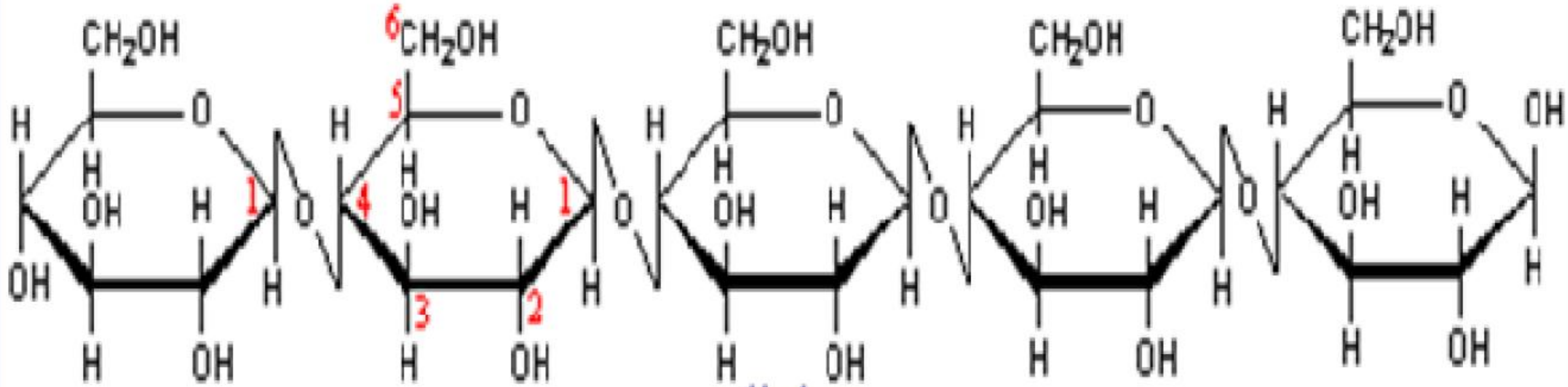

cellulose

TABLE 7–2 Structures and Roles of Some Polysaccharides

Polymer	Type*	Repeating unit†	Size (number of monosaccharide units)	Roles/significance
Starch				**Energy storage: in plants**
Amylose	Homo-	(α1→4)Glc, linear	50–5,000	
Amylopectin	Homo-	(α1→4)Glc, with (α1→6)Glc branches every 24–30 residues	Up to 10^6	
Glycogen	Homo-	(α1→4)Glc, with (α1→6)Glc branches every 8–12 residues	Up to 50,000	Energy storage: in bacteria and animal cells
Cellulose	Homo-	(β1→4)Glc	Up to 15,000	Structural: in plants, gives rigidity and strength to cell walls
Chitin	Homo-	(β1→4)GlcNAc	Very large	Structural: in insects, spiders, crustaceans, gives rigidity and strength to exoskeletons
Dextran	Homo-	(α1→6)Glc, with (α1→3) branches	Wide range	Structural: in bacteria, extracellular adhesive
Peptidoglycan	Hetero-; peptides attached	4)Mur2Ac(β1→4) GlcNAc(β1	Very large	Structural: in bacteria, gives rigidity and strength to cell envelope
Agarose	Hetero-	3)D-Gal(β1→4)3,6-anhydro-L-Gal(α1	1,000	Structural: in algae, cell wall material
Hyaluronan (a glycosamino-glycan)	Hetero-; acidic	4)GlcA(β1→3) GlcNAc(β1	Up to 100,000	Structural: in vertebrates, extracellular matrix of skin and connective tissue; viscosity and lubrication in joints

*Each polymer is classified as a homopolysaccharide (homo-) or heteropolysaccharide (hetero-).

†The 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 (β1→4)-linked to the first residue of the next disaccharide unit.

Table 7-2

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