Carbohydrates

Chapter 16

Carbohydrates

- **Carbohydrate or Saccharides** are essential components of all living organisms and the most abundant class of biological molecules

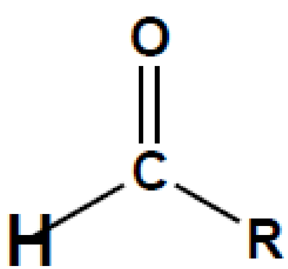
- **Monosaccharide:** a carbohydrate that cannot be hydrolyzed to a simpler carbohydrate

- **Oligosaccharides** consist of a few covalently linked monosaccharide units

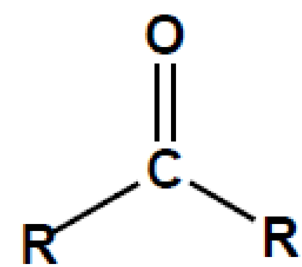
- **Polysaccharides** consist of many covalently linked monosaccharide units**.**

Carbohydrates

- Building blocks of all carbohydrates are **Monosaccharide**
- They have the general formula **C***n* **(H_2O)***n*
- **Aldose :** a monosaccharide containing an aldehyde group
- **Ketose :** a monosaccharide containing a ketone group



Aldehyde



Ketone

Monosaccharides

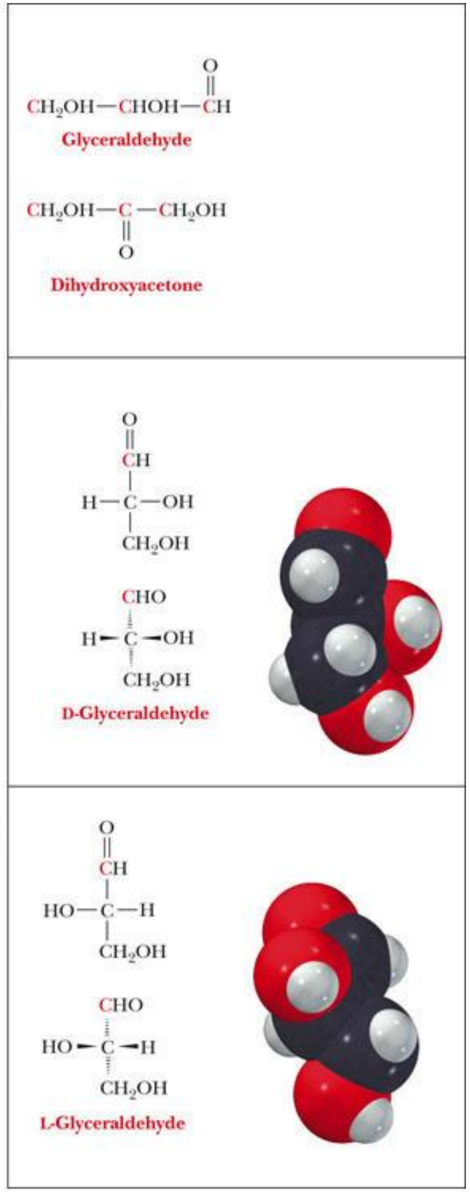
- Monosaccharides are classified by their number of carbon atoms
- 3 C atoms are simplest carbohydrate monosaccharides
- Dihydroxyacetone is the ketose (a ketotriose)
- Glyceraldehydes is the aldose with (aldotriose)
- L- and D- Glyceraldehyde ⇨ non-superimposable mirror-image (stereoisomers) also called enantiomers.

Monosaccharides

1 A comparison of glyceraldehyde (an aldotriose) and dihydroxyacetone (a ketotriose).

2 The structure of D-glyceraldehyde and a space-filling model of D-glyceraldehyde.

3 The structure of L-glyceraldehyde and a space-filling model of L-glyceraldehyde.

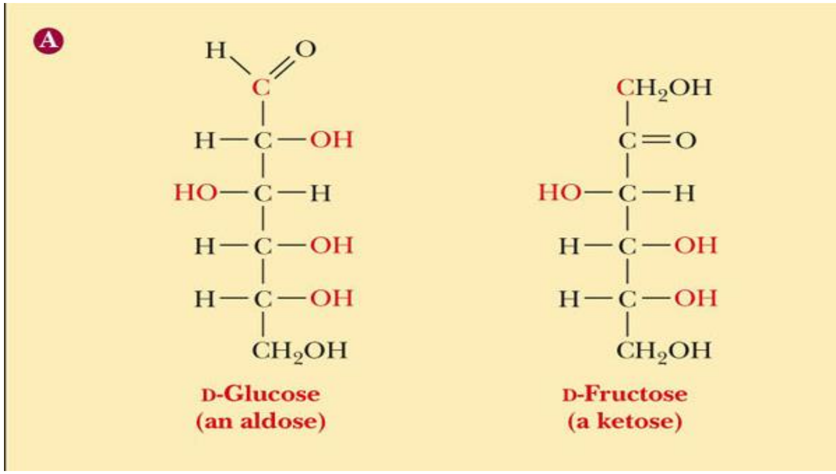


Fischer Projections

- **Fischer projection:** bonds are written in a two dimensional representation showing the configuration of tetrahedral stereocenters

  - Horizontal lines represent bonds projecting **in front the paper**

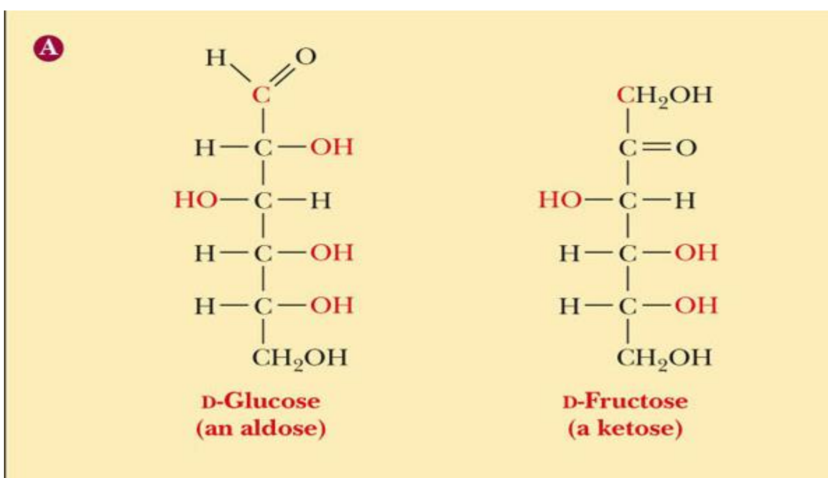
  - Vertical lines represent bonds projecting to the **behind the paper**

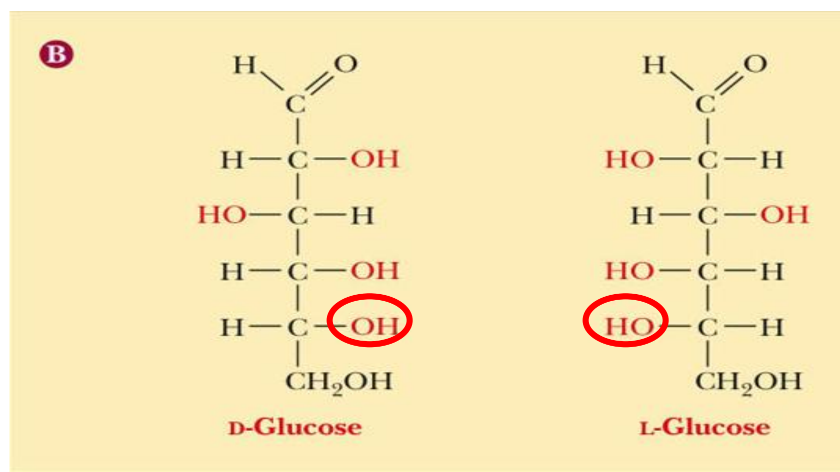


Fischer Projections

- According to the conventions proposed by Fischer:

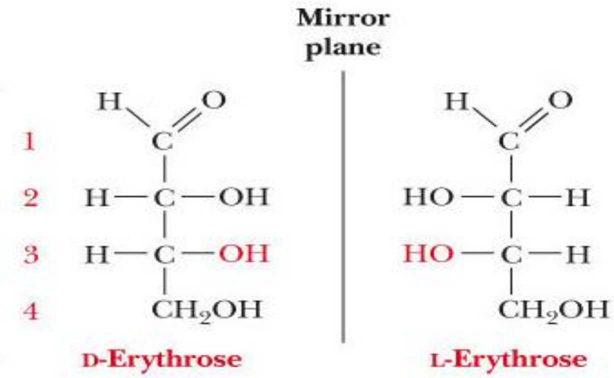
- **D-monosaccharide:** a monosaccharide that, when written as a Fischer projection, has the -OH on its fifth carbon (**highest-numbered chiral carbon)** on the right.
-
- **L-monosaccharide:** a monosaccharide that, when written as a Fischer projection, has the -OH on its fifth carbon (**highest-numbered chiral carbon)** on the left





Aldotetroses

- Enantiomers**:** stereoisomers that are mirror images
  - Example: D-erythrose and L-erythrose



Aldotetroses

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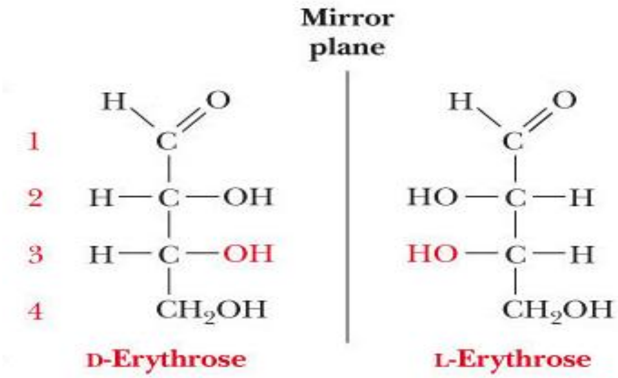
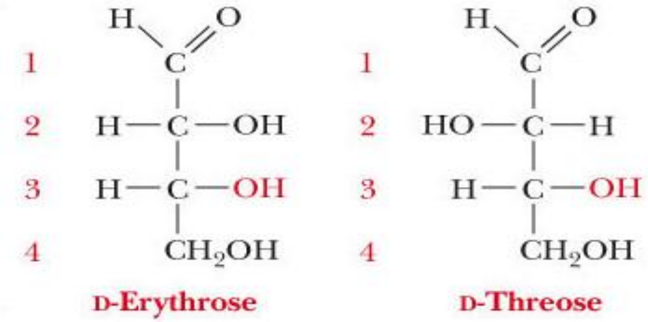
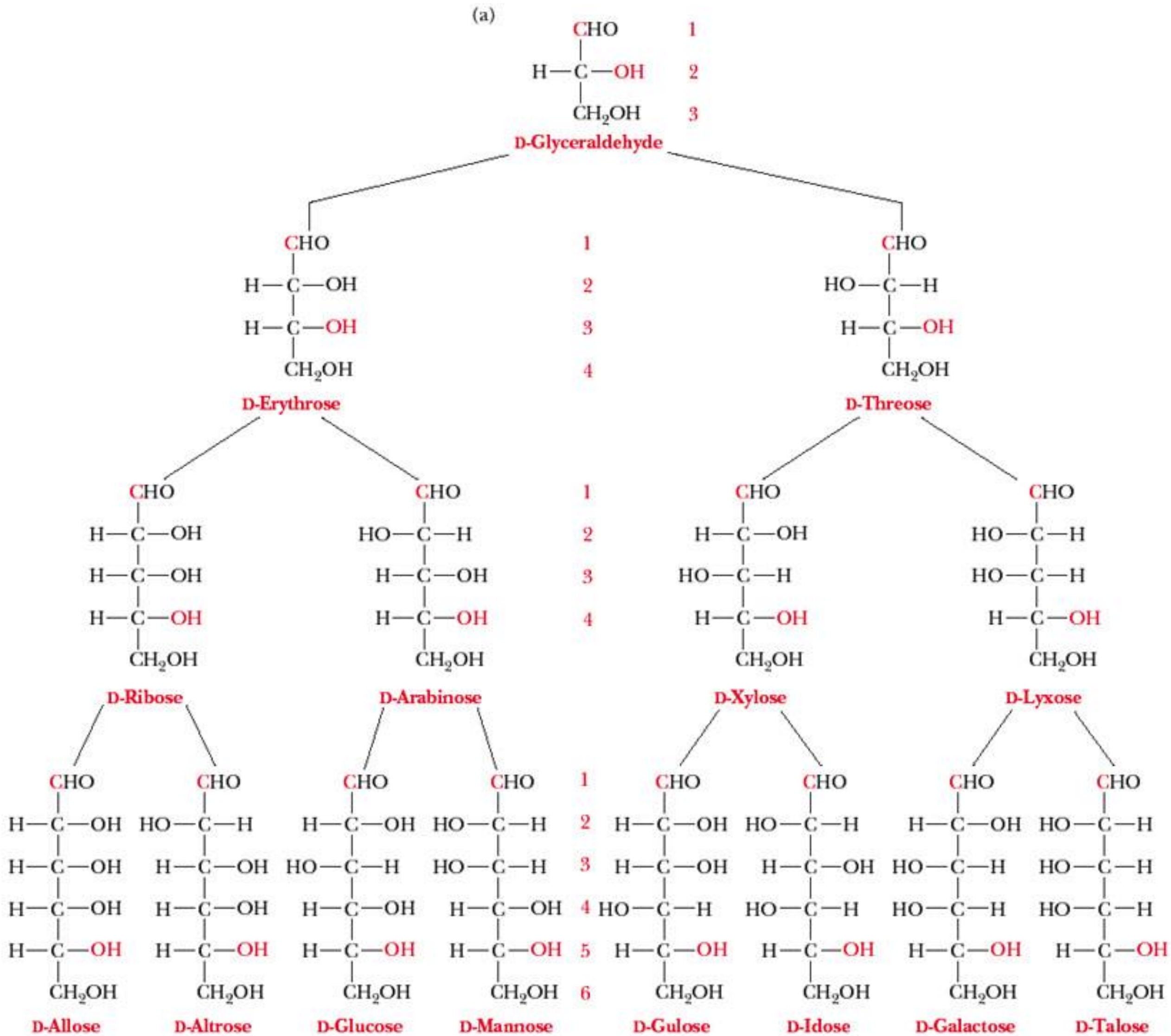


- Diastereomers**:** stereoisomers that are not mirror images
  - Example: D-erythrose and D-threose
  - Epimers: are diastereomers differ in their structures in only one chiral C

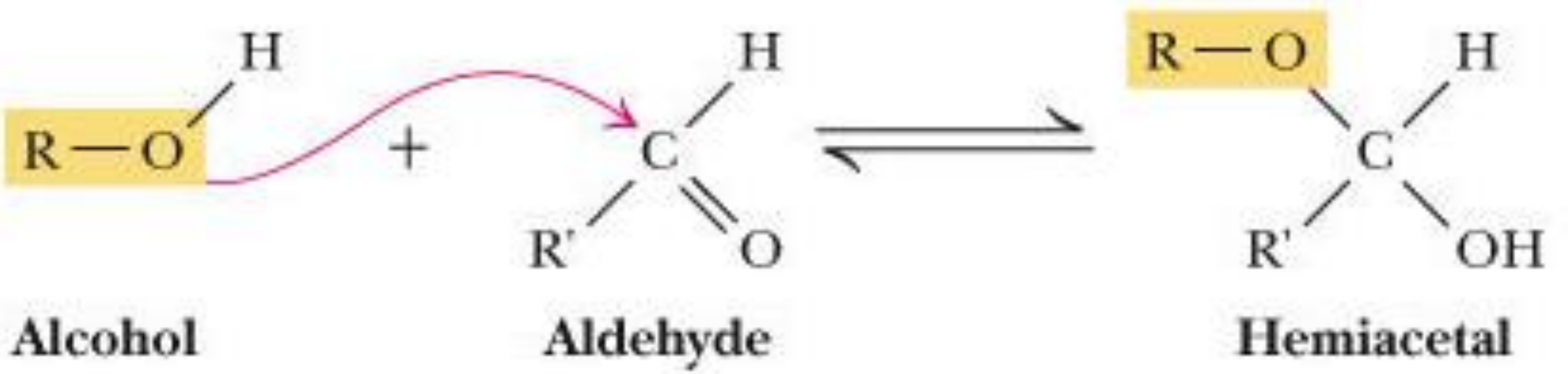


- Aldopentose has 8 possible steroeisomers (4 d and 4L forms)
- n-carbon aldose have 2^{n-2} stereoisomers.
- n-carbon ketoses have 2^{n-3} stereoisomers.



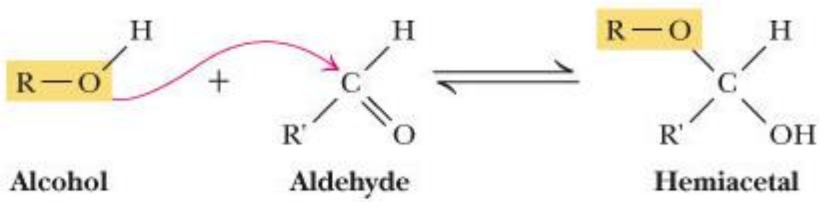
What Happens if a Sugar Forms a Cyclic Molecule?

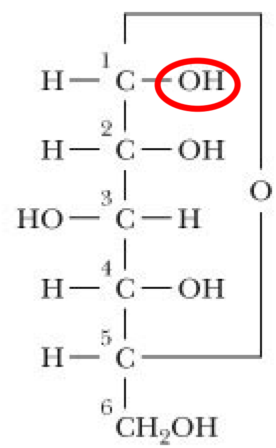
- Cyclization of sugars takes place due to interaction between functional groups on distant carbons
  - C1 to C5, to make a cyclic **hemiacetal**
  - C2 to C5 results in **hemiketal** formation



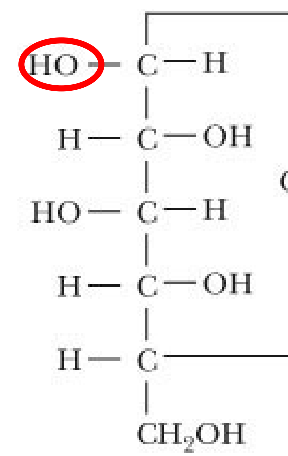
What Happens if a Sugar Forms a Cyclic Molecule?

- In both cases, the carbonyl carbon is new chiral center and becomes an **anomeric carbon.**
- **Anomeric carbon:** the new stereocenter resulting from cyclic hemiacetal formation
- **Anomers:** carbohydrates that differ in OH only at their anomeric carbons
- An α anomer according to Fischer is at the right while β is at the left
- α-D-glucose or α-D-glucose





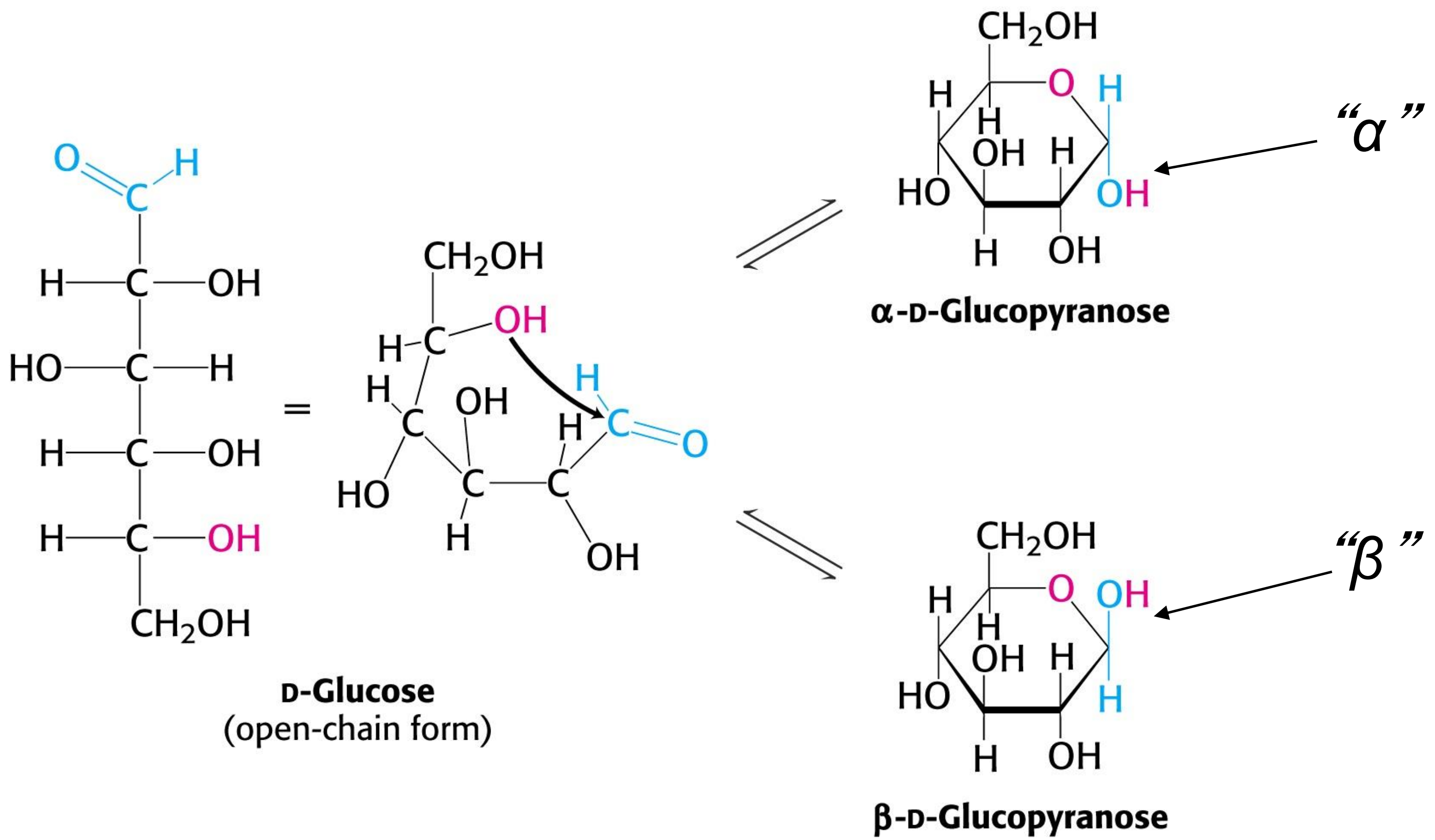
α-D-Glucopyranose



β-D-Glucopyranose

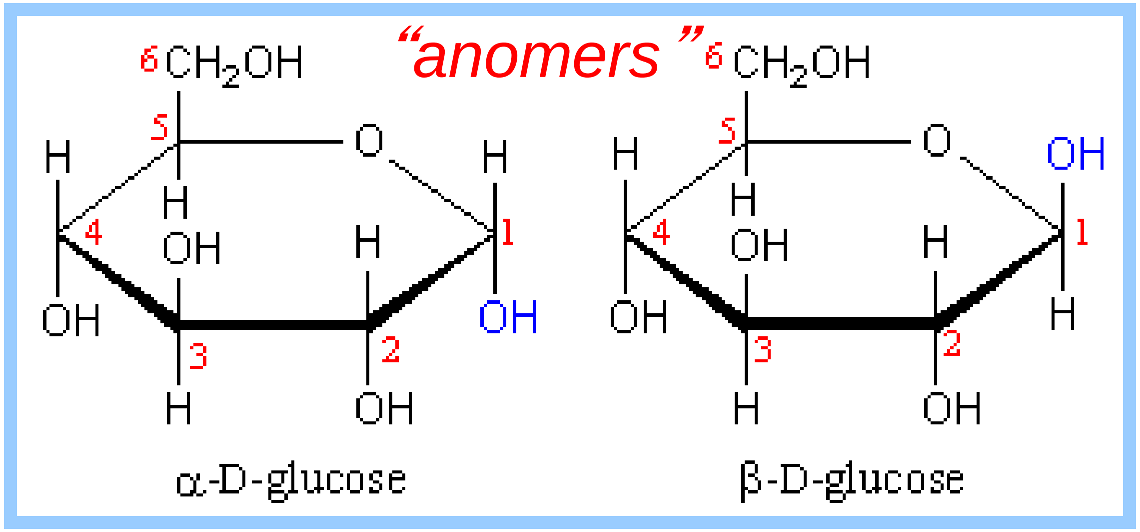
Anomers

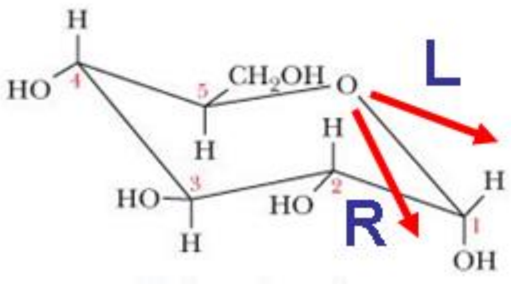
- Formation of the cyclic structures occurs as a distant hydroxyl group attacks the carbonyl carbon (the “anomeric” carbon atom).



Haworth Projections

- Five- and six-membered hemiacetals are represented as planar pentagons or hexagons
- Most commonly written with the anomeric carbon on the right and the hemiacetal oxygen to the back right
- The designation β- means that -OH on the anomeric carbon is upward to the terminal $-CH_2OH$; α- means that it is downward





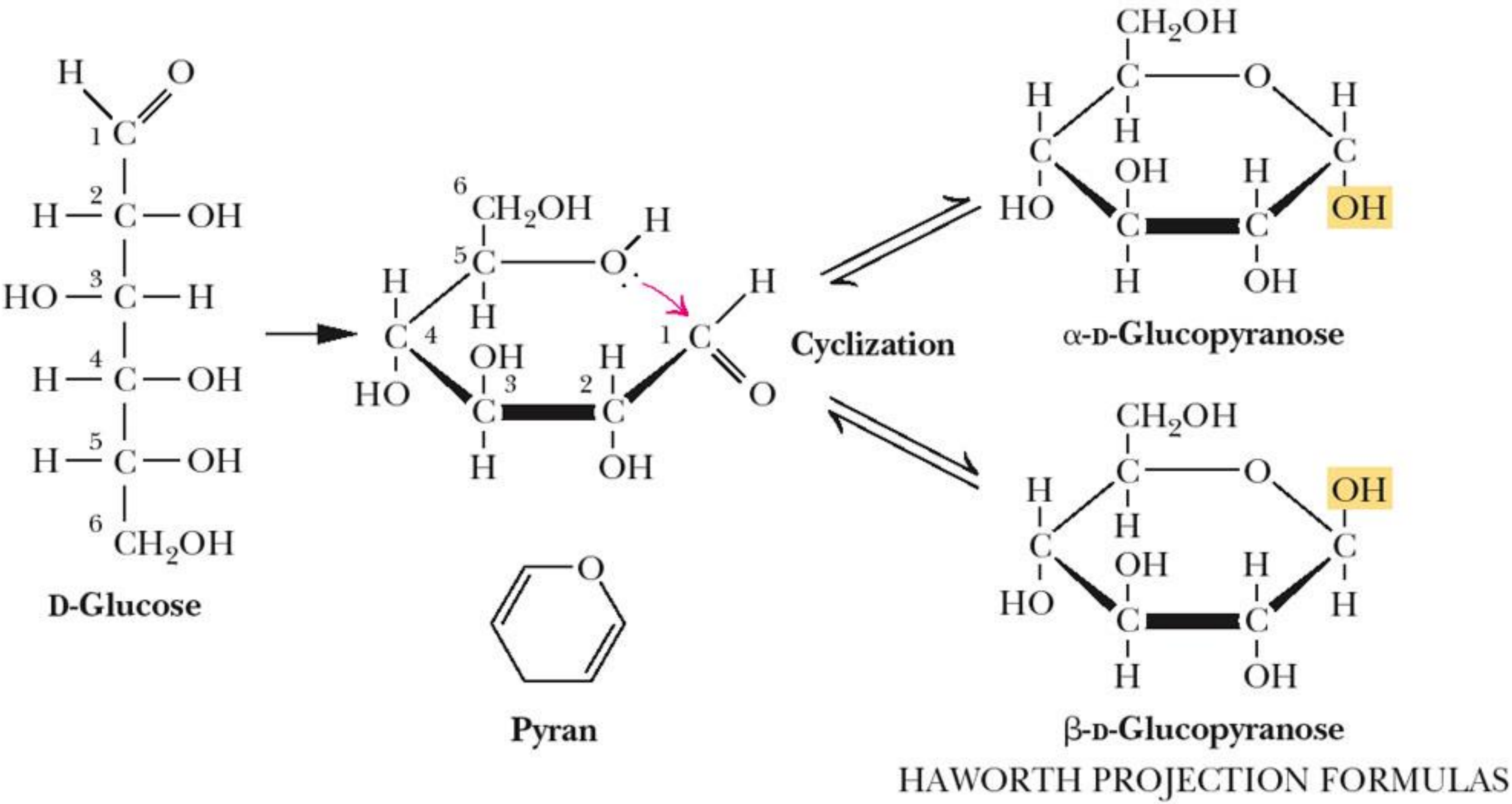
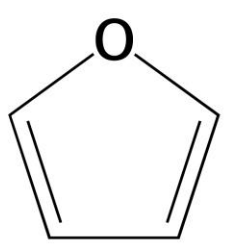


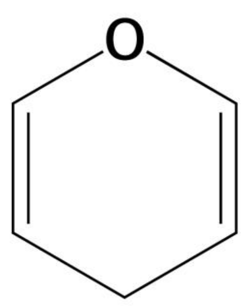
Fig. 16-5b, p.439

Haworth Projections

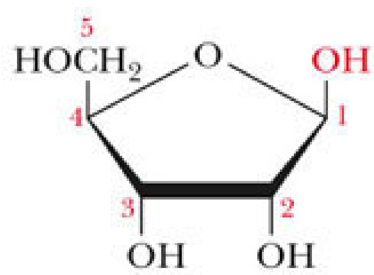
- A six-membered ring is shown by the infix –**pyran** - (pyranose)
  - For pyranoses, the six-membered ring is more accurately represented as a **chair** conformation
- A five-membered ring is shown by the infix –**furan** - (furanose)
  - Five-membered rings are so close to being **planner** that Haworth projections are adequate to represent furanoses

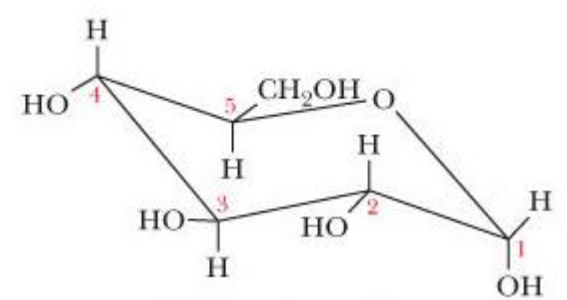


Furan



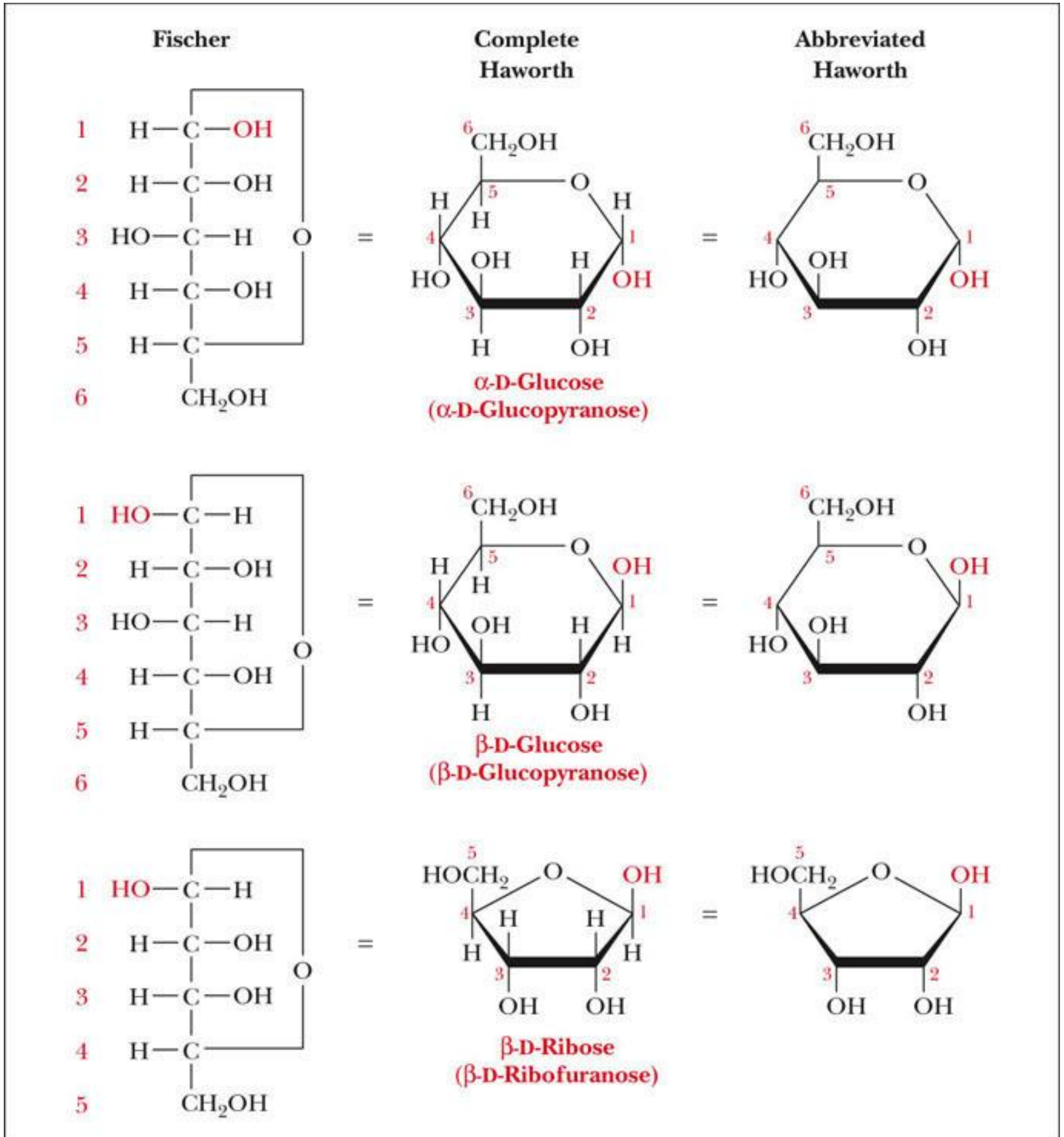
Pyran





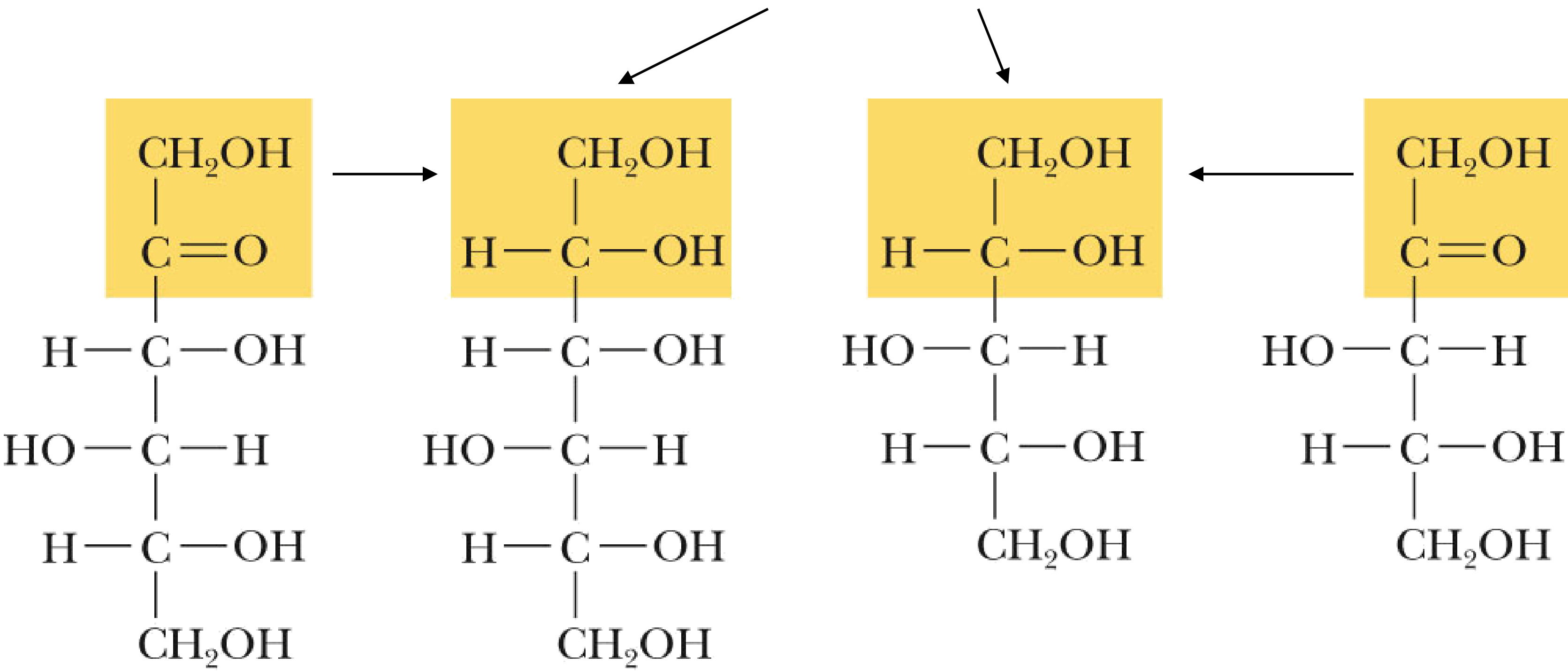
Chair conformation

Comparison of Fischer & Haworth Representations



Reaction of Monosaccharides

- The carbonyl group of a monosaccharide can be reduced to an hydroxyl group by a variety of reducing agents, such as $NaBH_4$
- Reduction of the C=O group of a monosaccharide gives a polyhydroxy compound called an **aldito (sweeteners)**



D-Sorbose D-Sorbitol D-Xylitol D-Xylulose

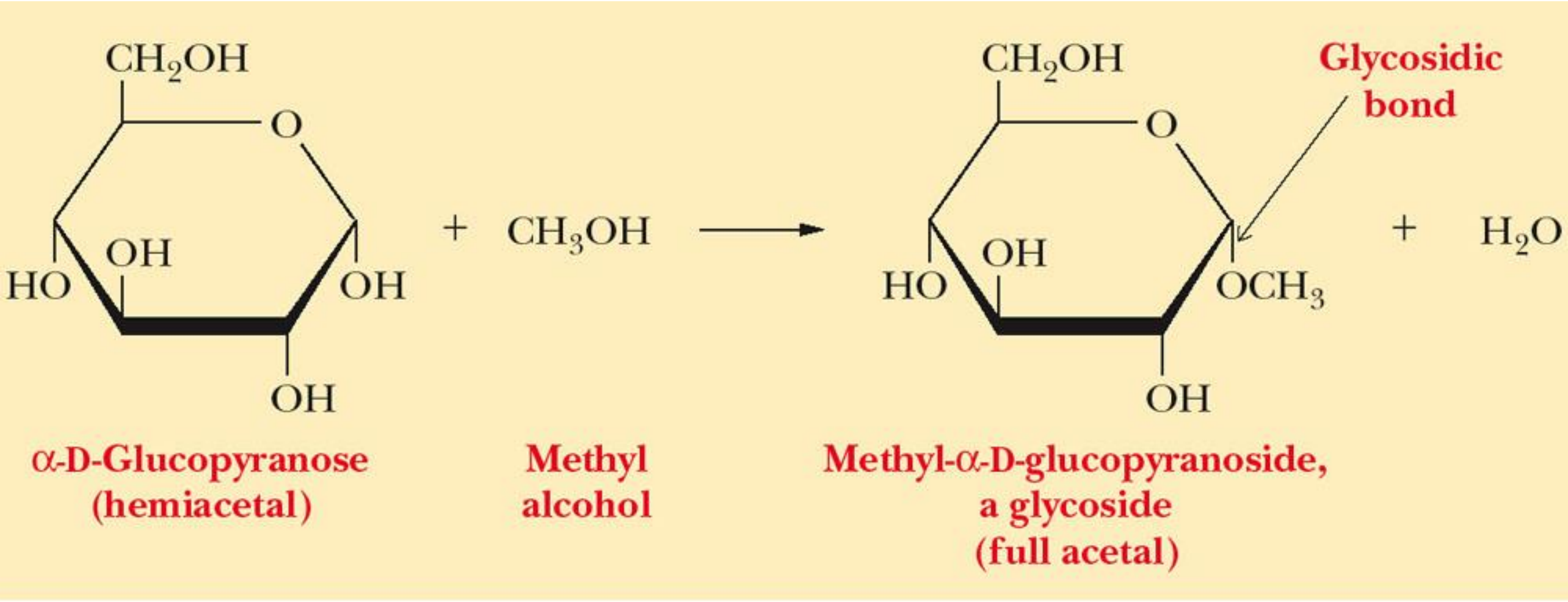
Glycosidic Bond Formation

- **Glycoside:** a carbohydrate in which the -OH of the anomeric carbon react with another OH to form

- R---O----R
  - Those derived from furanoses are **furanosides**
  - Those derived from pyranoses are **pyranosides**

- **Glycosidic bond** is the basis for the formation of **Oligosaccharides** and **Polysaccharides**

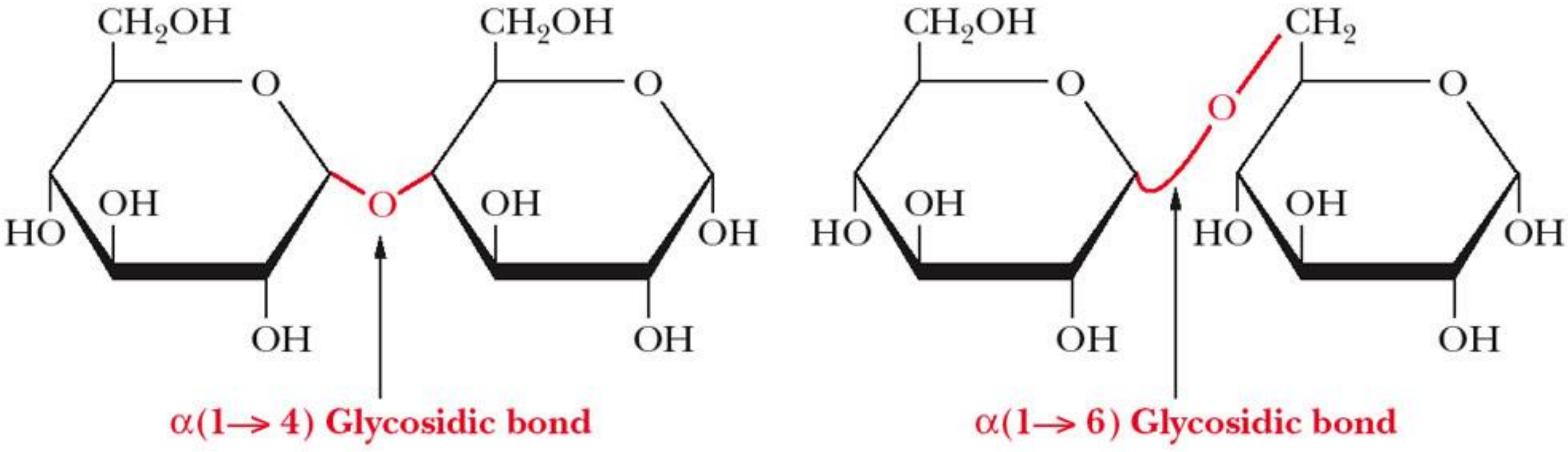
Glycosidic Bond Formation



Two Different Disaccharides of α-D-Glucose

- Glycosidic linkages can take various forms.

- The anomeric carbon of one sugar to any of the -OH groups of another sugar to form an α- or β – Glycosidic linkage



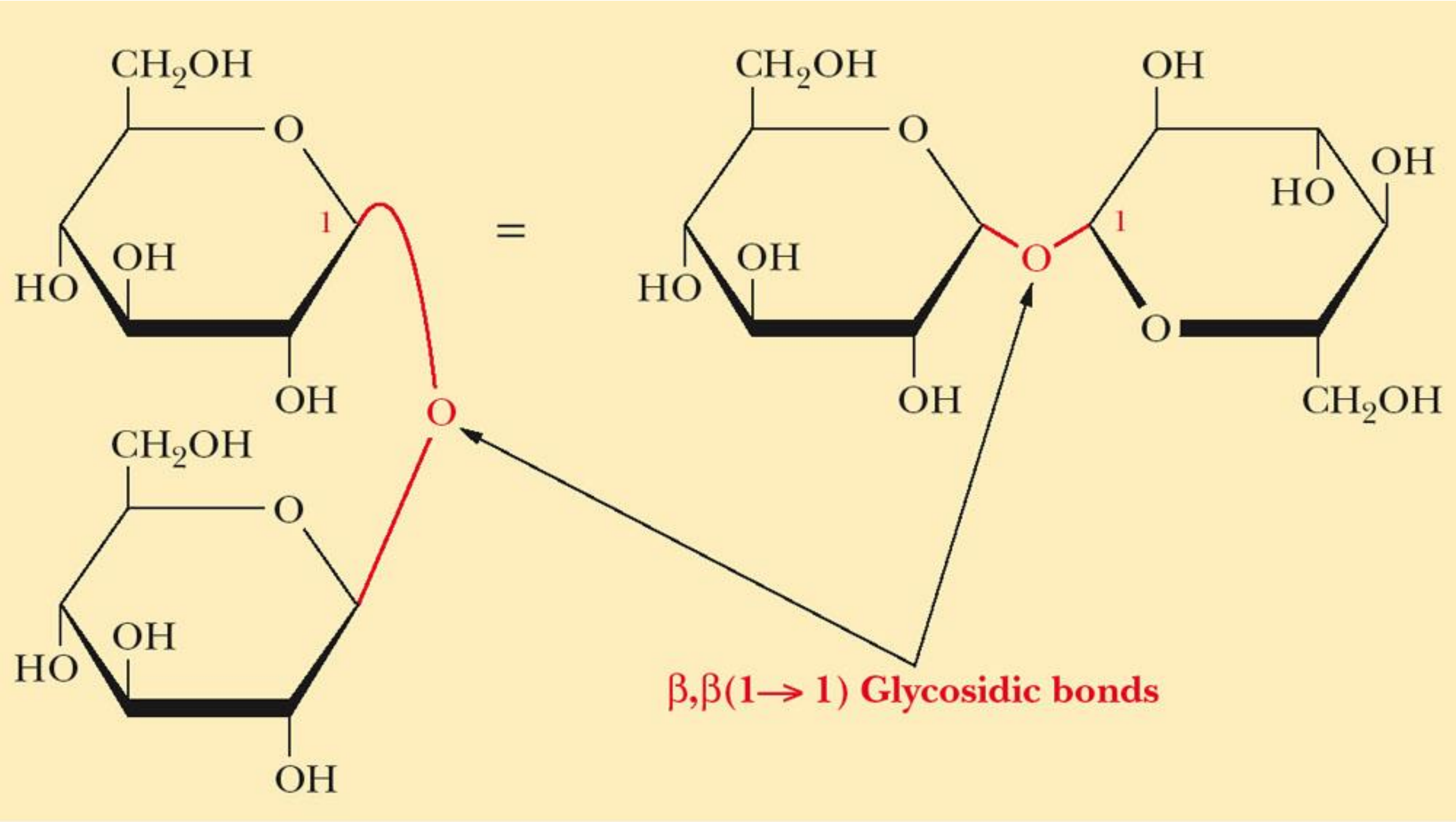


Fig. 16-14, p.445

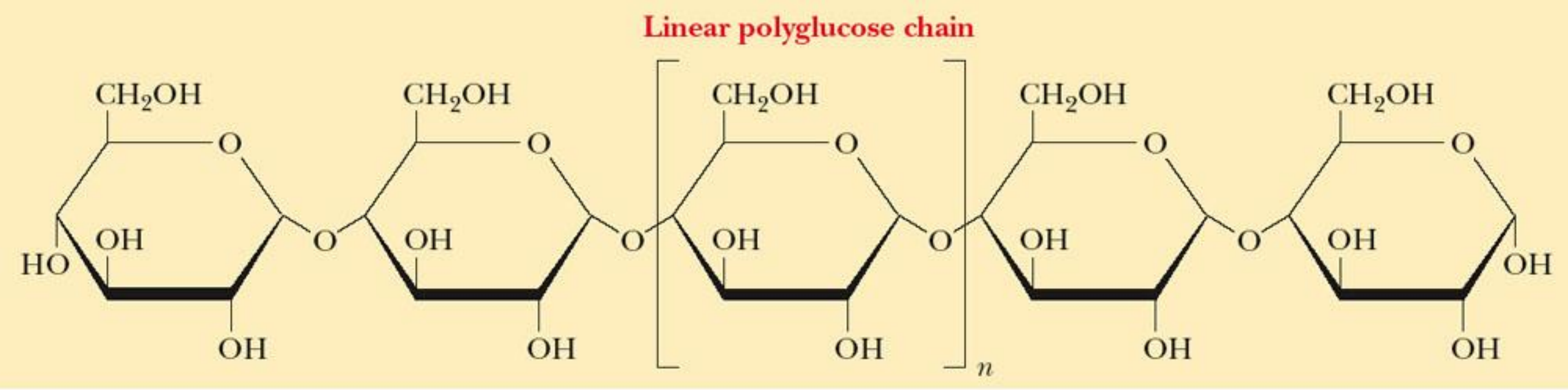


Fig. 16-15a, p.445

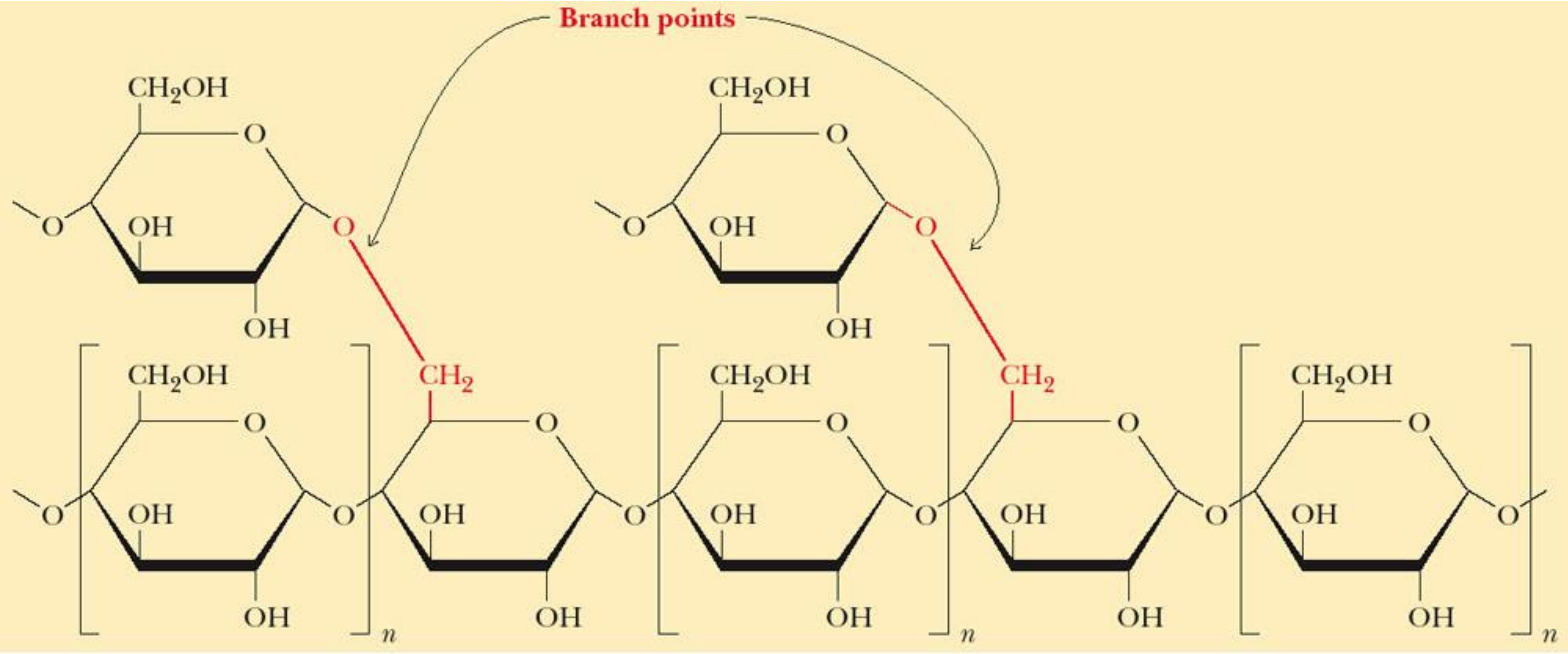
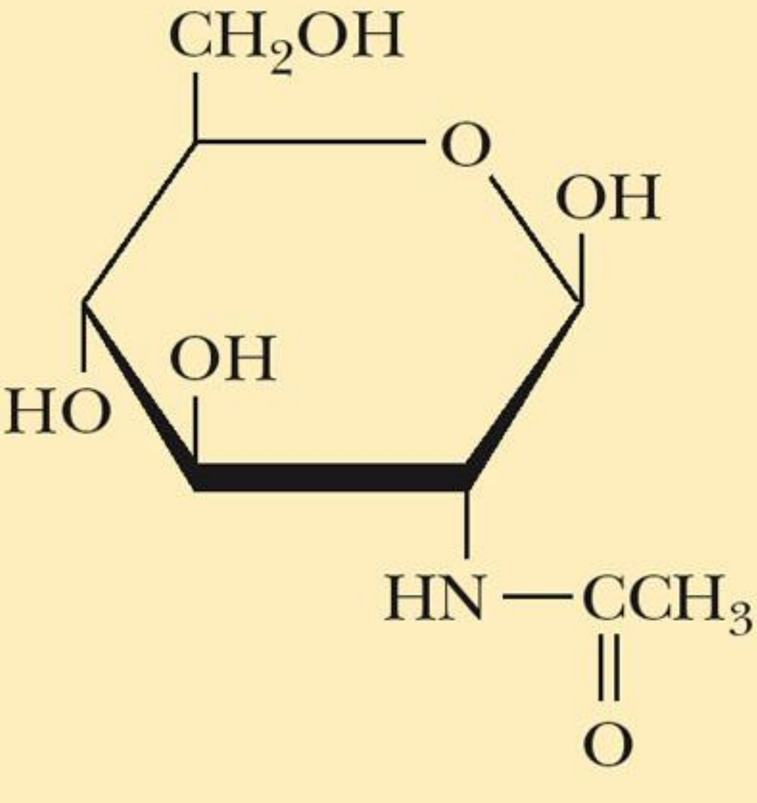
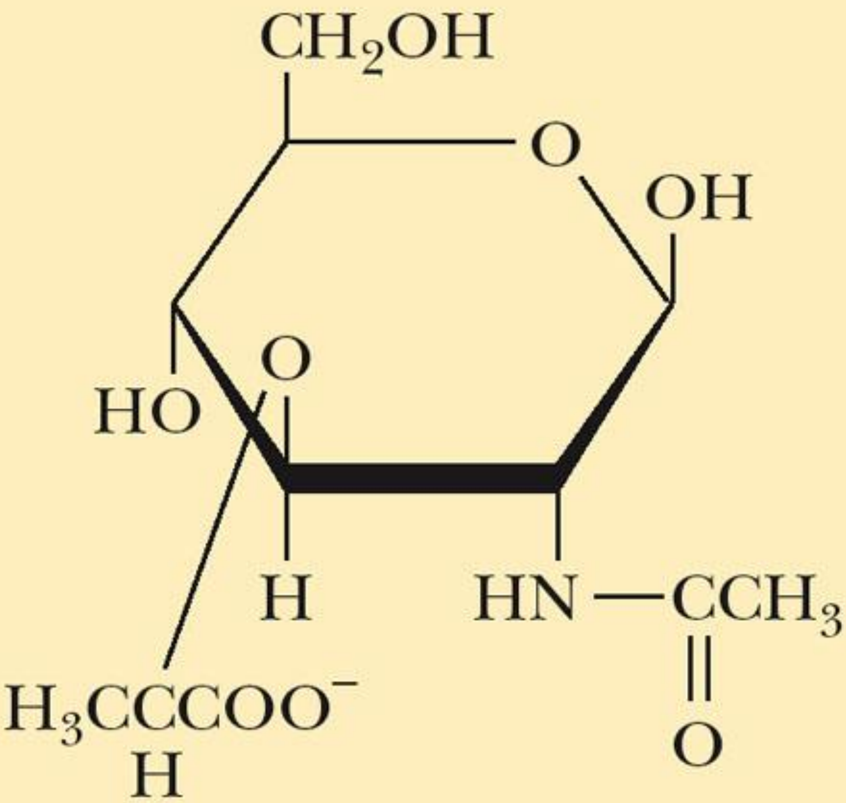


Fig. 16-15b, p.445

Amino Sugars



N-Acetyl-β-D-glucosamine



N-Acetylmuramic acid

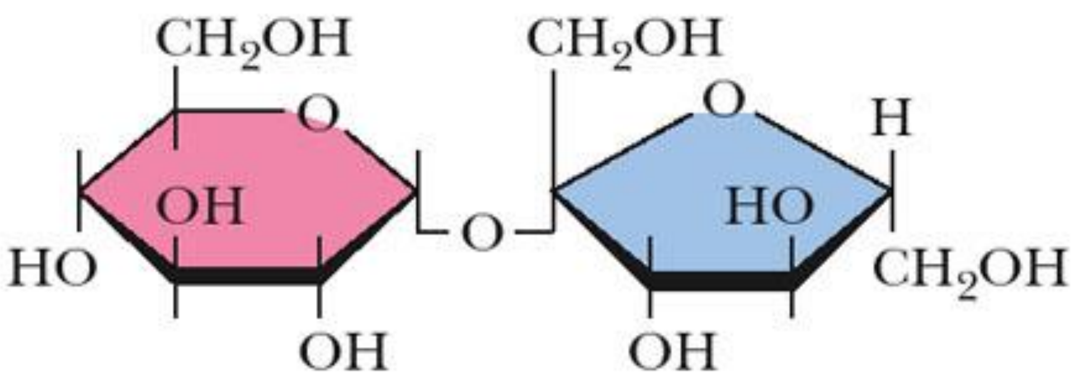
Disaccharides

Sucrose:

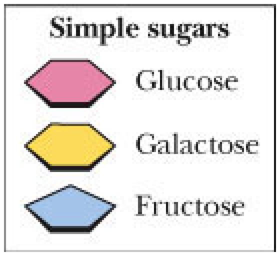
- Table sugar; obtained from the juice of sugar cane and sugar beet

- One unit of D-glucose and one unit of D-fructose joined by an α-1,β2-glycosidic bond

- Both anomeric involve in glycosidic linkage (non reducing sugar)



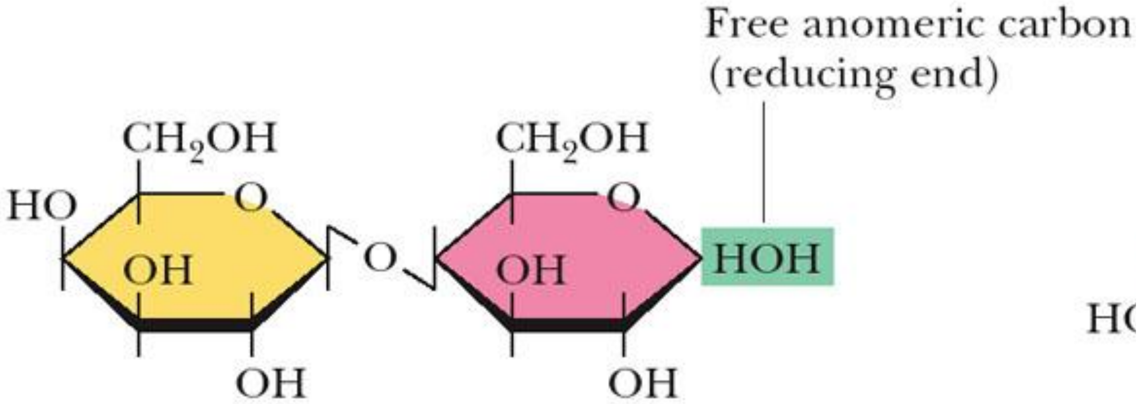
Sucrose (glucose-α-1,2-fructose)



Disaccharides

Lactose:

- Found in milk
- Made up of D-galactose and one unit of D-glucose joined by a β-1,4-glycosidic bond
- Galactose is a C-4 epimer of glucose
- Only different in one inversion at C4
- Reducing sugar free anomeric glucose

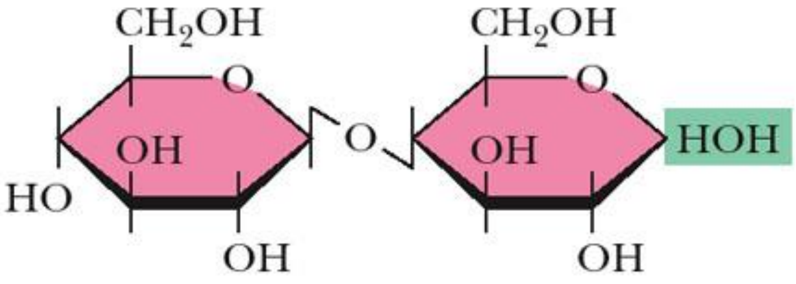


Lactose (galactose-β-1,4-glucose)

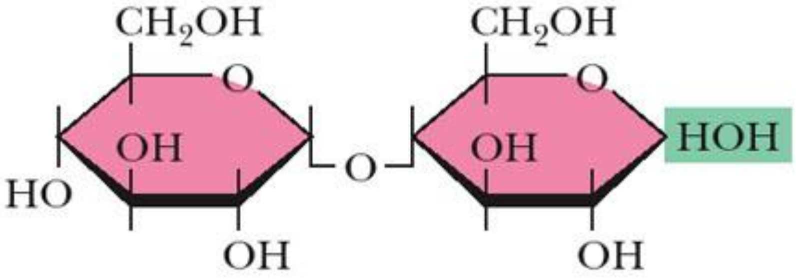
Disaccharides

Maltose:

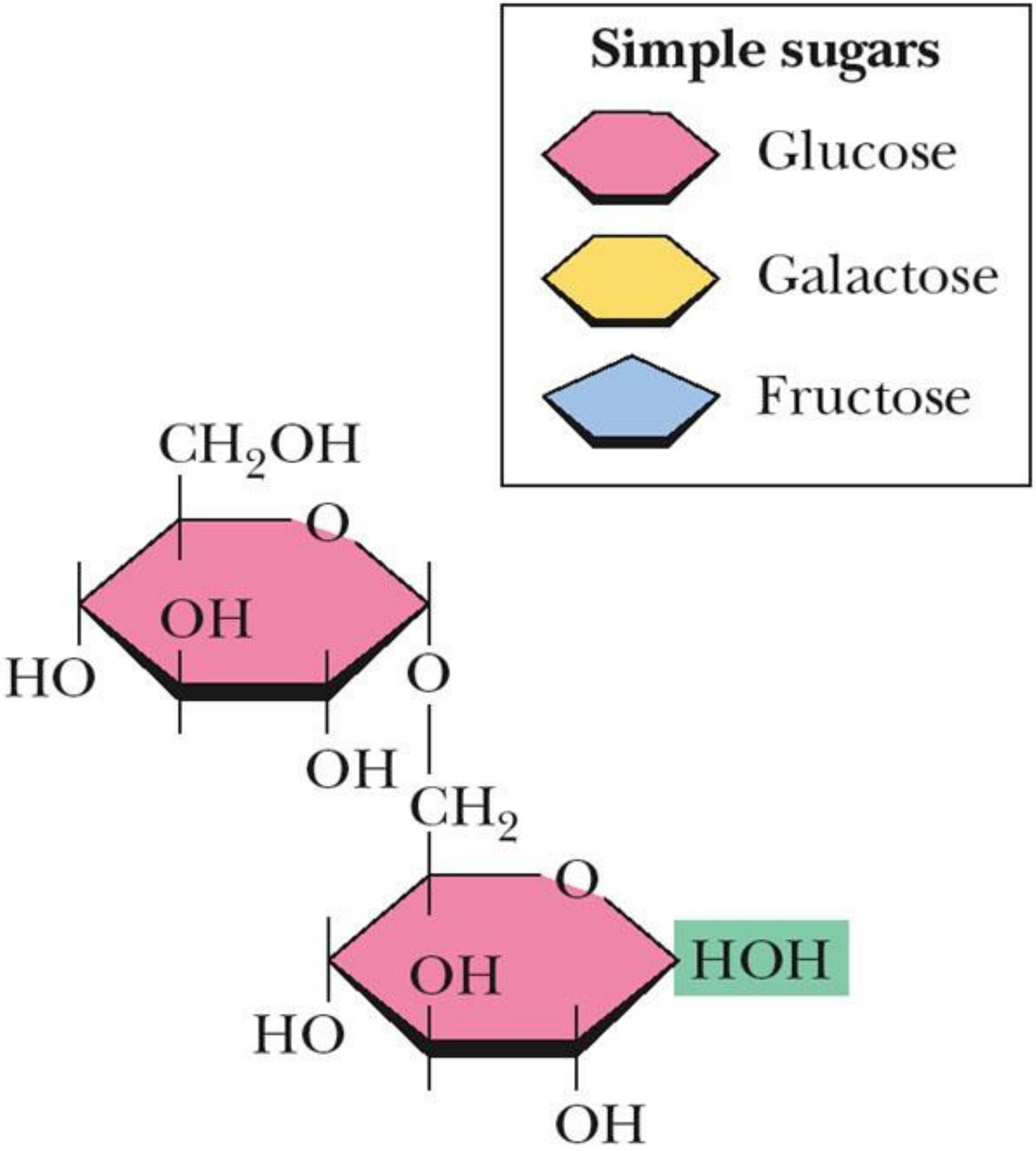
- Two units of D-glucose joined by an α-1,4-glycosidic bond
- Formed from the hydrolysis of starch
- Differs from cellobiose by the conformation of the glycosidic linkage
- Cellobiose: Obtained from hydrolysis of cellulose



Cellobiose (glucose-β-1,4-glucose)



Maltose (glucose-α-1,4-glucose)



Isomaltose (glucose-α-1,6-glucose)

Fig. 16-18b, p.448

Polysaccharides

- **Homopolysaccharides:** a polymer that consists of only one type of monosaccharide components.

- **Heteropolysaccharides:** a polymer that consists of more than one type of monosaccharide components.

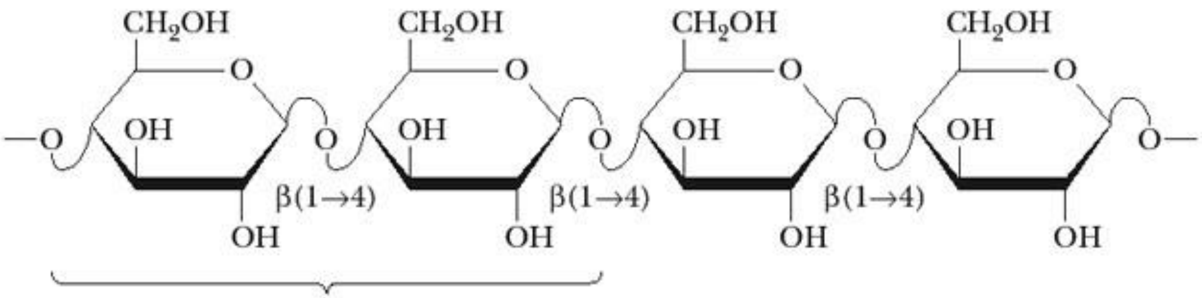
Polysaccharides can be characterized by:

- Specification of which monomers are present
- Type of glycosidic linkage (β or α glycosidic linkage)

Structures and Function of Polysaccharides

Cellulose:

- The major structural component of plants, especially wood and plant fibers
- A linear polymer of d-glucose units joined by b-1,4-glycosidic bonds
- Extensive intra- and intermolecular hydrogen bonding between chains
- Gives mechanical strength to plant fiber
- Animals!?? (Bacteria !!) lack enzymes, called cellulase, that hydrolyze cellulose to glucose.



Repeating disaccharide
in cellulose
(β-cellobiose)

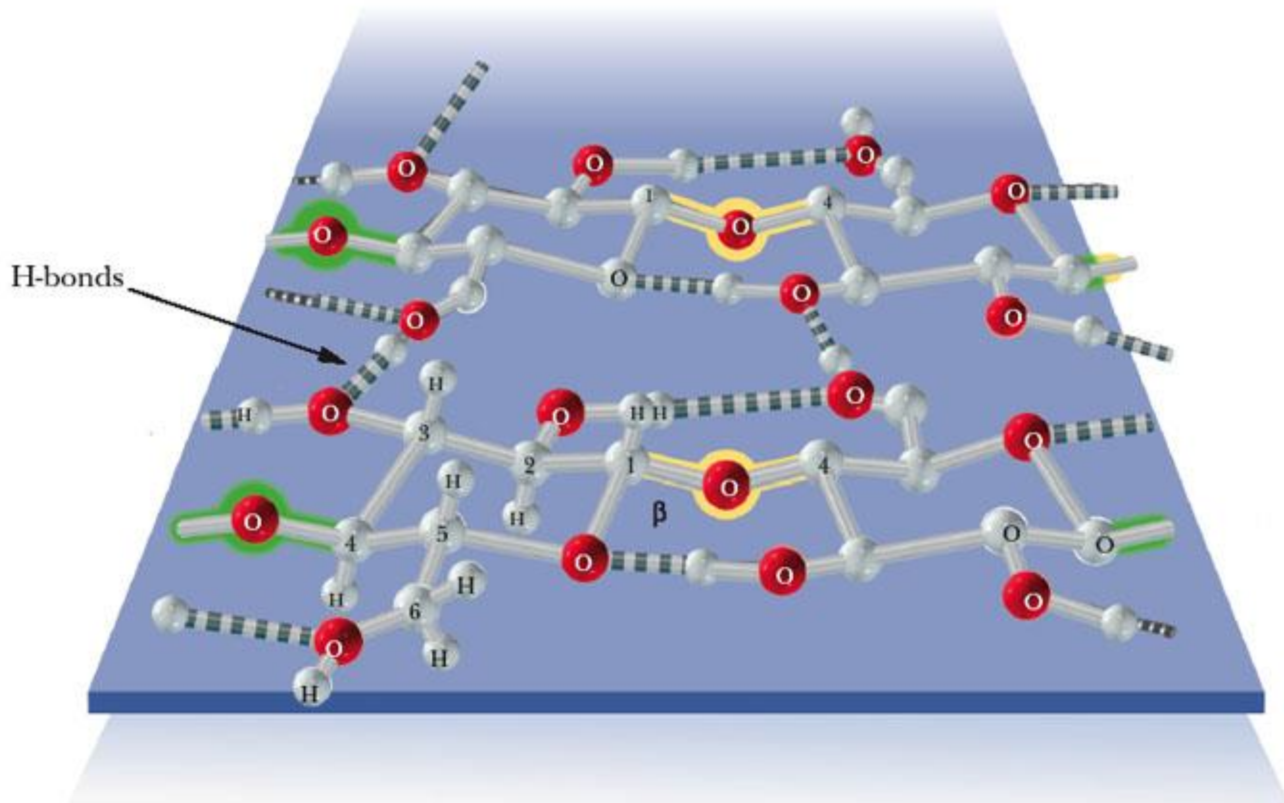


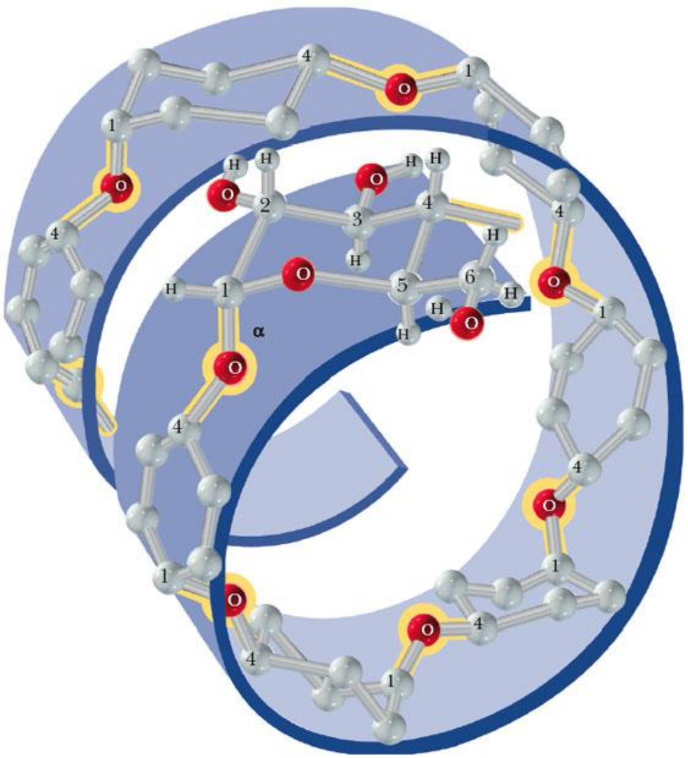
Fig. 16-19, p.451

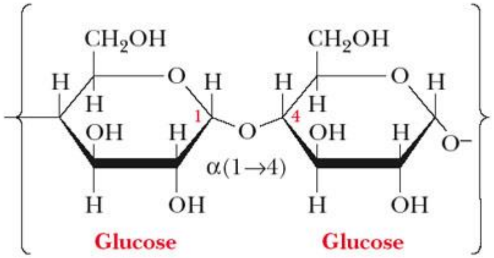
Polysaccharides

- Carbohydrate is used for energy storage in plants

Starch

- Continuous chains of a-D-glucose units joined by α-1,4-glycosidic bonds



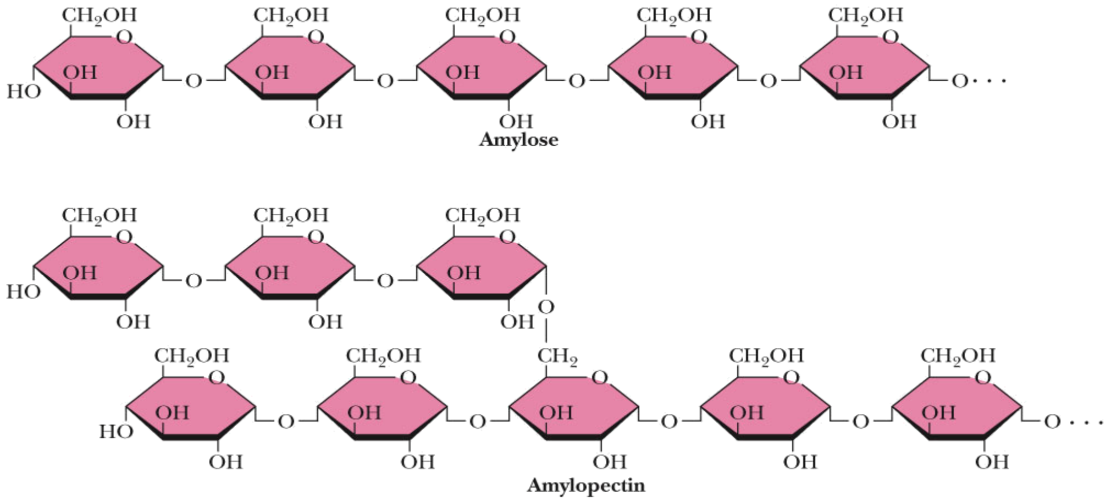


Polysaccharides

Degrees of branching:

- **Amylose:** is linear polymer consisting D-glucose joined by α-1,4-glycosidic bonds
  - Form helical structure
  - Iodine inserted inside which gives dark blue color (indicator of starch)

- **Amylopectin:** a highly branched polymer consisting of units of D-glucose joined by α-1,4-glycosidic bonds and branches created by α-1,6-glycosidic bonds
  - Iodine binds to amylopectin (glycogen) gives red blue
  - Different structure from Amylose

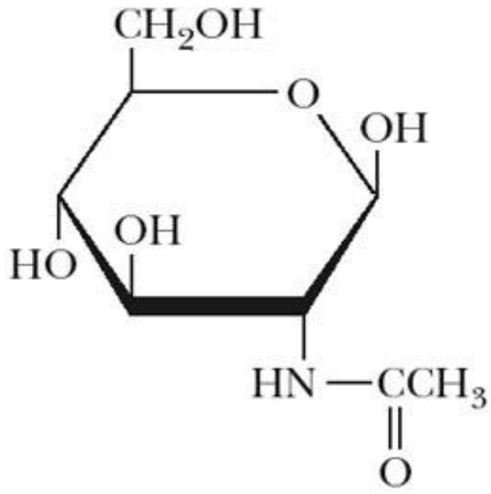


Polysaccharides

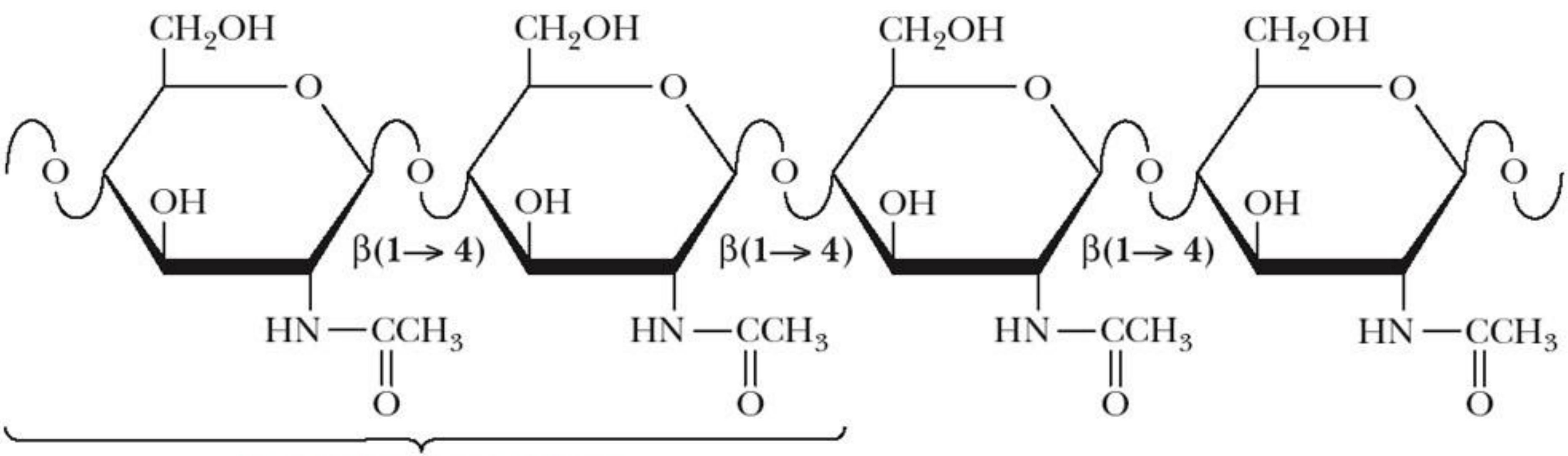
- α and β amylase catalyze hydrolysis of a-1,4-glycosidic bonds
- β-amylase is an exoglycosidase and cleaves from the non-reducing end of the polymer
  - Maltose is the product for the reaction
- α-amylase is an endoglycosidase and hydrolyzes glycosidic linkages anywhere along the chain
  - produce glucose and maltose
- Debranching enzymes catalyze the hydrolysis of a-1,6-glycosidic bonds
  - Required for complete degradation of amylopectin

Chitin

- **Chitin:** the major structural component of the exoskeleton of invertebrates, such as insects and crustaceans; also occurs in cell walls of algae, fungi, and yeasts
- Composed of units of **N-acetylglucosamine** joined by □-1,4-glycosidic bonds
- Linear homopolysaccharides
- Similar to cellulose in structure and function
- Held together by H bond



N-Acetyl-β-D-glucosamine

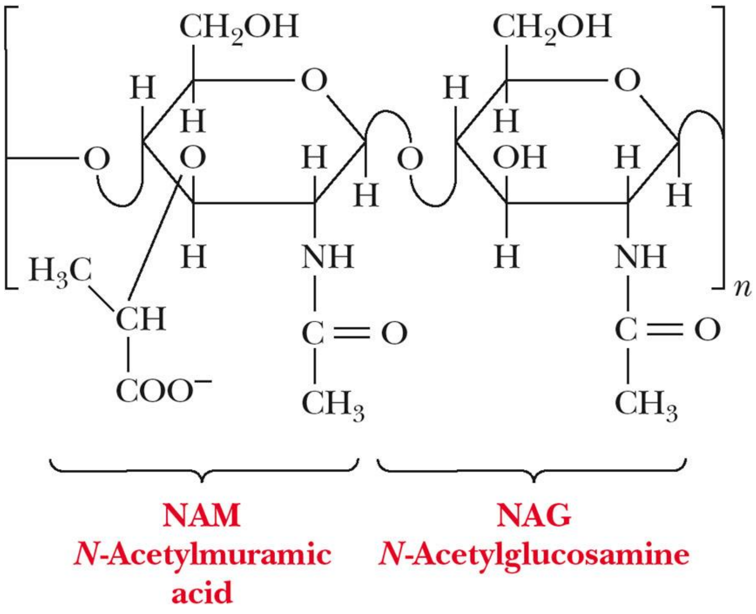


Repeating disaccharide in chitin

Fig. 16-24, p.455

Polysaccharides

- **Bacterial cell walls** : prokaryotic cell walls are constructed on the framework of the repeating unit
  - NAM-NAG joined by β (1-4) glycosidic bonds – prokaryotics
  - Heteropolysaccharides
  - NAM has lactic acid bond to C3 and replace –OH
  - NAM does not occur in Eukaryotic cells



Peptidoglycan

- Bacterial cell walls cross-linking between NAM-NAG with of small peptides
- Lactic acid join with Tetrapeptides
- Further cross linked by other small peptide (5 a.a. long(Gly))
  - Two cross links
- Peptide might contain L and D-amino acid
- D-amino acid and NAM occur in Prokaryotic but not in plants cell wall
  - Cross-linking gives strength

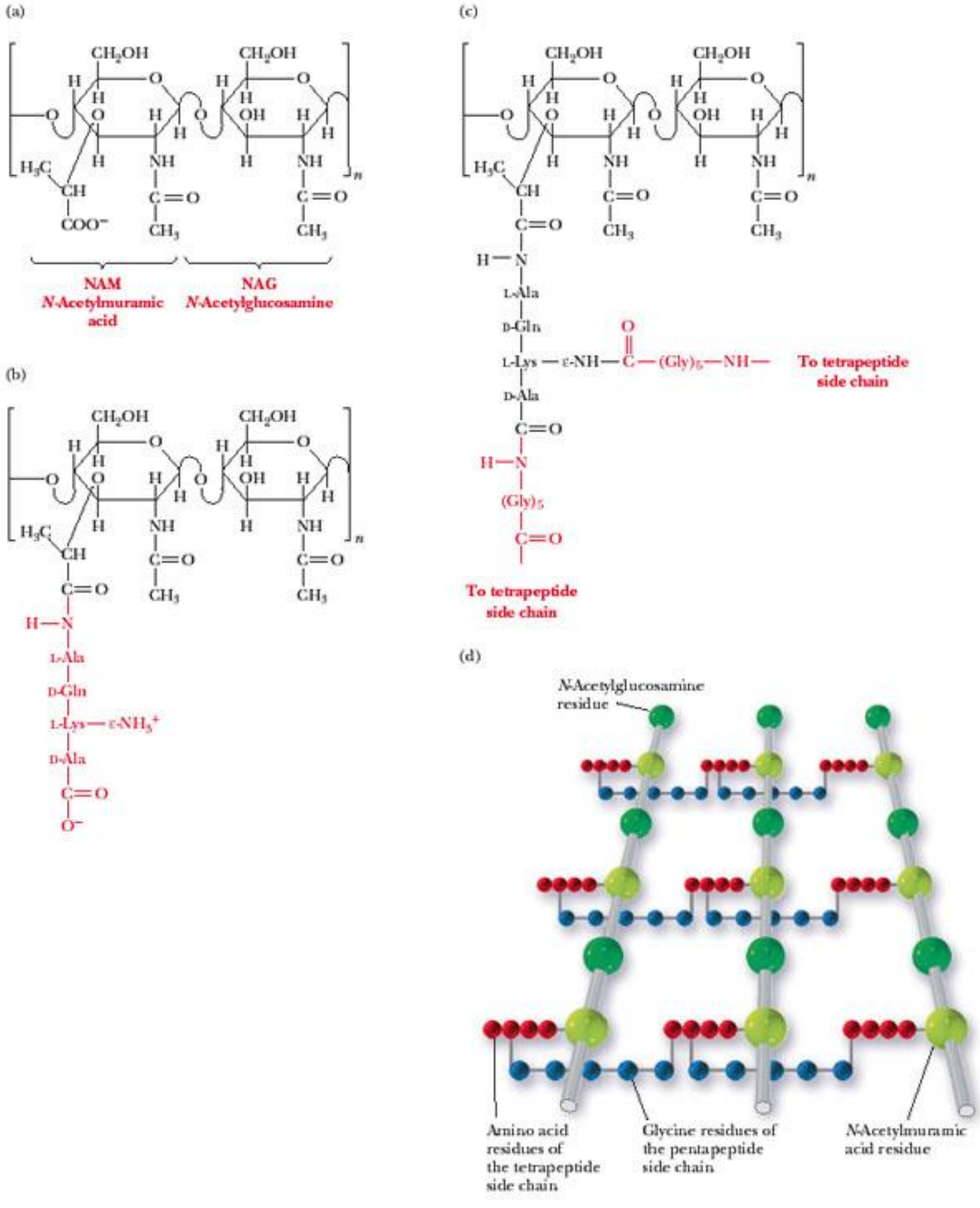


Fig. 16-25, p.456

Plant Cell Walls

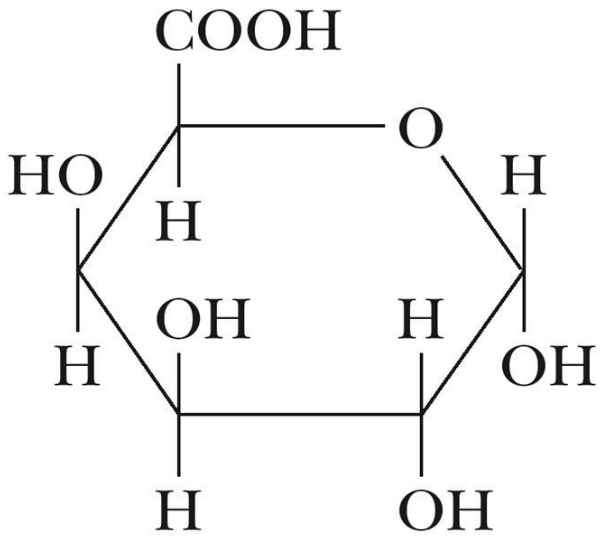
- Contain little peptides and or protein

- Consist largely of cellulose
  - Also contain pectin which functions as an intercellular cementing material

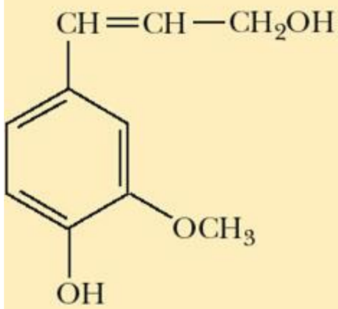
- **Pectin** is a polymer of D-Galactouronic acid joined by α-1,4-glycosidic bonds
  - Galactose derivative where OH on C6 is oxidized to carboxyl group
  - Gelling agent in food processing
    - Jams, yogurt and jellies

- **Lignin** is non-polysaccriade component of plant (woody plant)
  - Consist of coniferyl alcohol

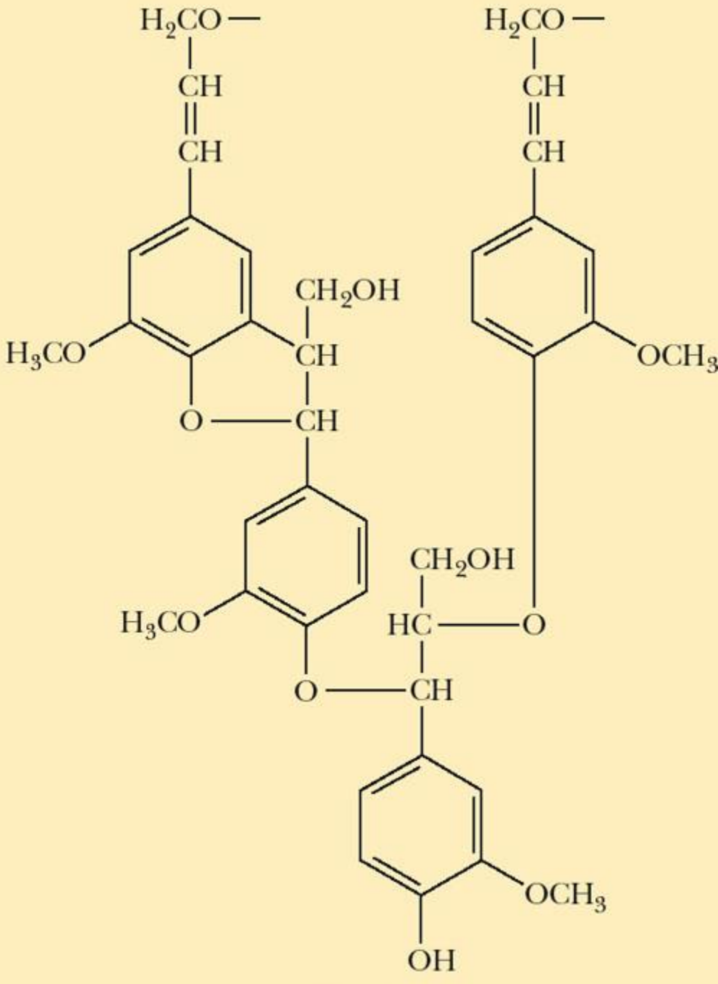
Plant Cell Walls



D-Galacturonic acid



Coniferyl alcohol

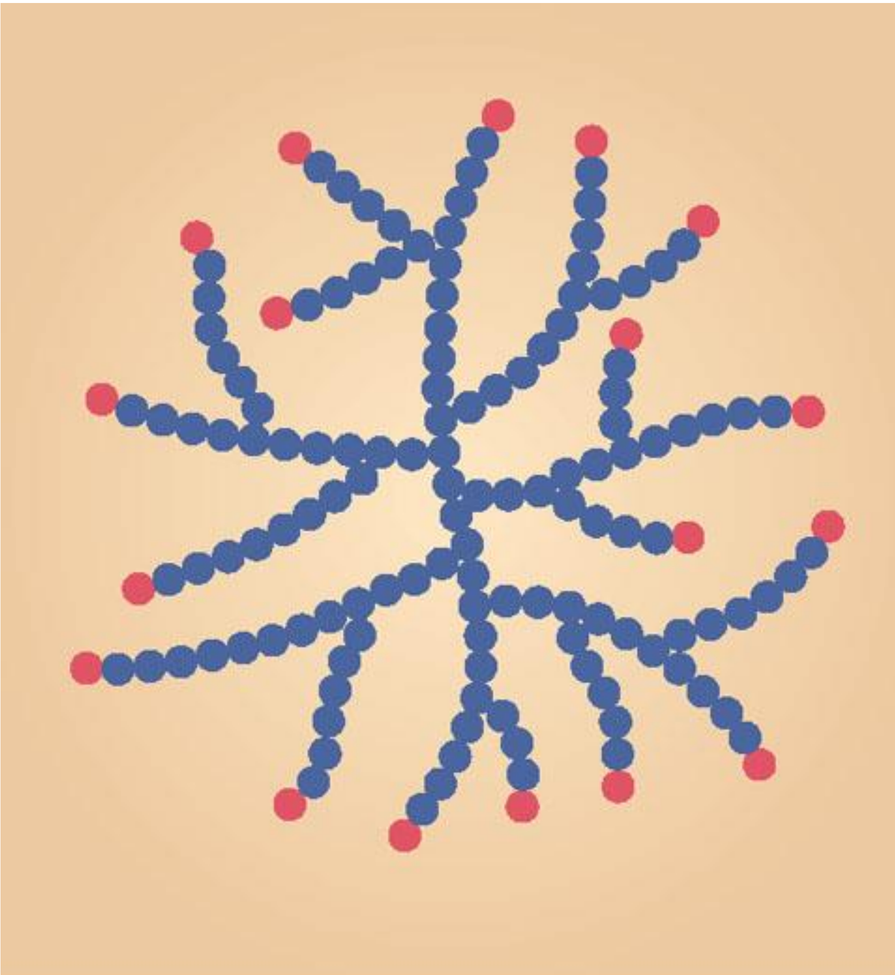


Lignin

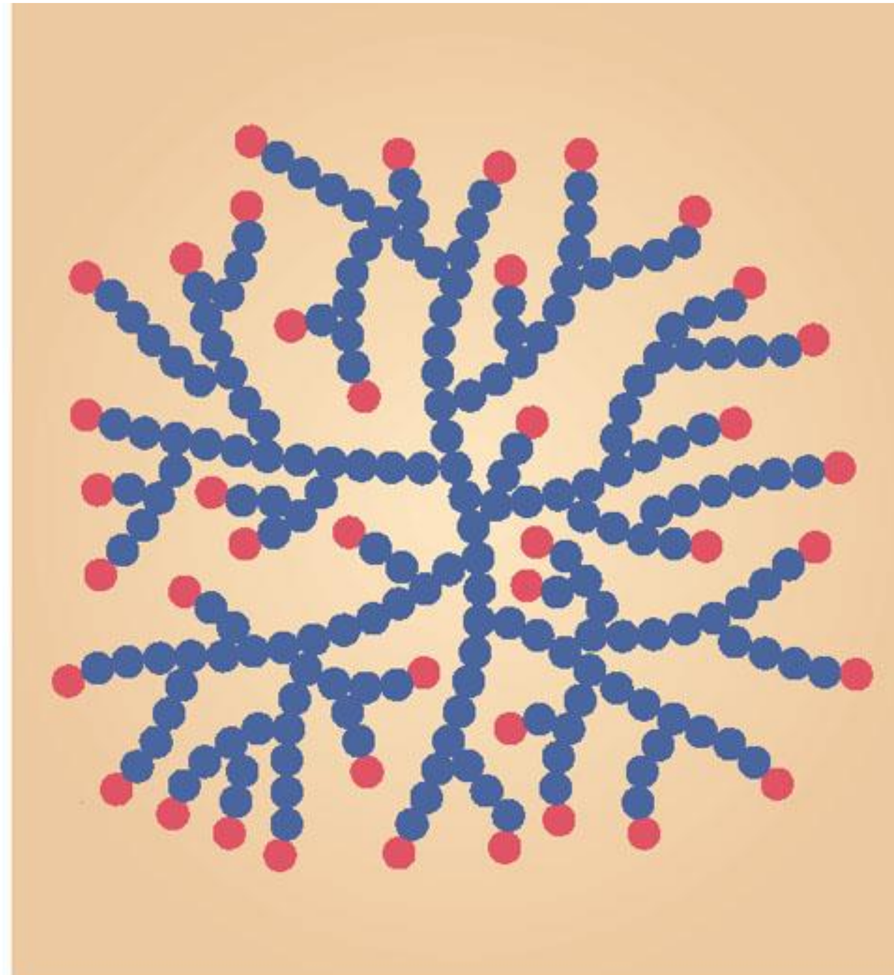
Glycogen

- Animal carbohydrate storage polymer.
- Branched-chain polymer of α-D-glucose (like amylopectin) ⇨ α (1→6) linkage along the chain of ⇨ α (1→4).
- The main difference between glycogen and amylopectin ⇨ Glycogen is more highly branched
  - Branch point occur ~ every 10 residues in glycogen and ~every 25 residues in amylopectin.
  - More branching mean more water soluble
    - Glycogen storage disease (crystals in muscle and liver)
  - Phosphorylase cleaves glucose from non-reducing end
    - Branching increase efficacy for cleavage and freeing glucose
  - Debranching enzymes also present and result in complete glycogen breakdown

Branching



Amylopectin



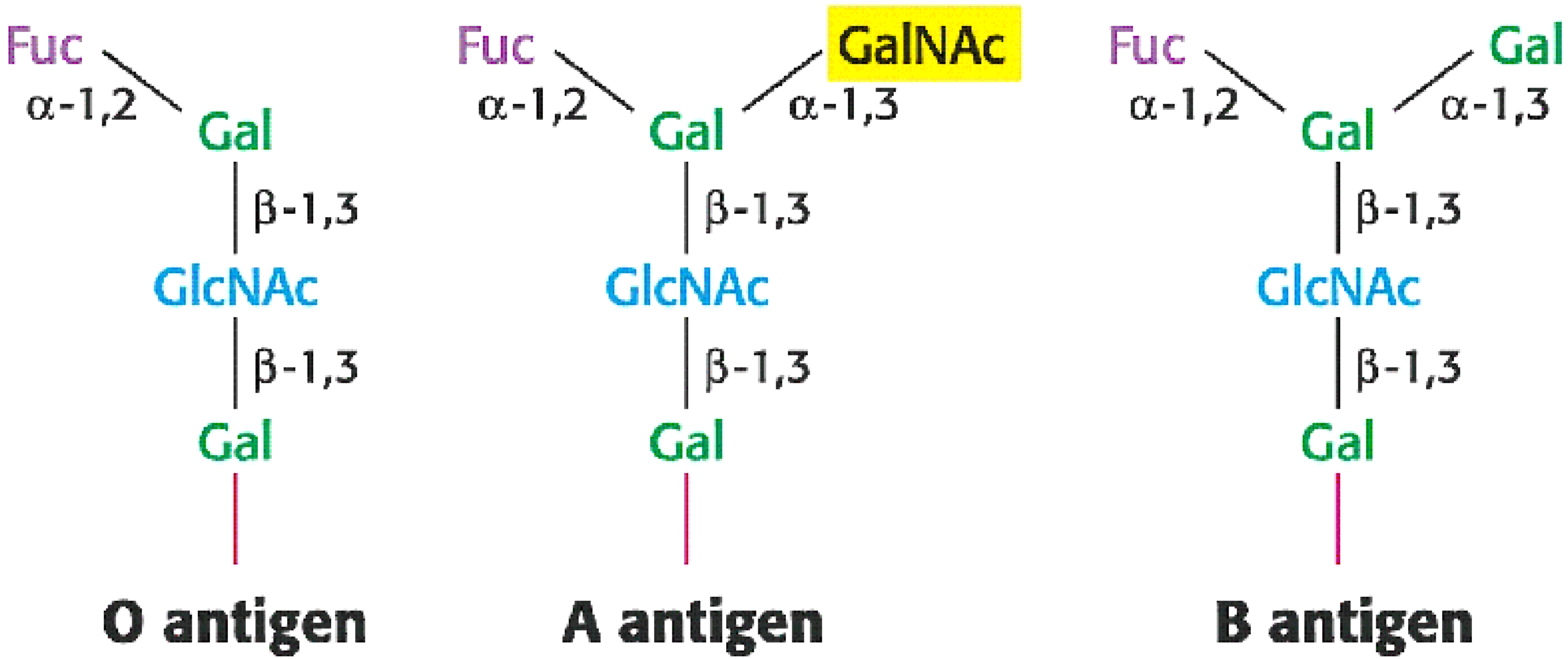
Glycogen

Glycoproteins

- Glycoproteins contain CHO units covalently bonded to a polypeptide chain
  - Proteoglycans in CHO rich cell membrane
  - Antibodies are glycoproteins
  - Oligosaccharide portion of glycoproteins act as antigenic determinants
    - Among the first antigenic determinants discovered were the blood group substances
    - In the ABO system, individuals are classified according to four blood types: A, B, AB, and O
    - At the cellular level, the biochemical basis for this classification is a group of relatively small membrane-bound carbohydrates

ABO system

- These carbohydrates are attached to glycoproteins and glycolipids on the surfaces of red blood cells where they act as specialized anitgenic determinants.



Summary

- Polysaccharides are formed by linking monomeric sugars through glycosidic linkages
- Starch and glycogen are energy-storage polymers or sugars
- Cellulose and chitin are structural polymers
- Polysaccharides are important components of cell walls in bacteria and plants
- Sugars can be found in specific bonding arrangements in some proteins
- Glycoproteins frequently play a role in the immune response