BIOL 158: CARBOHYDRATES

by

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Structure and Function of Carbohydrates

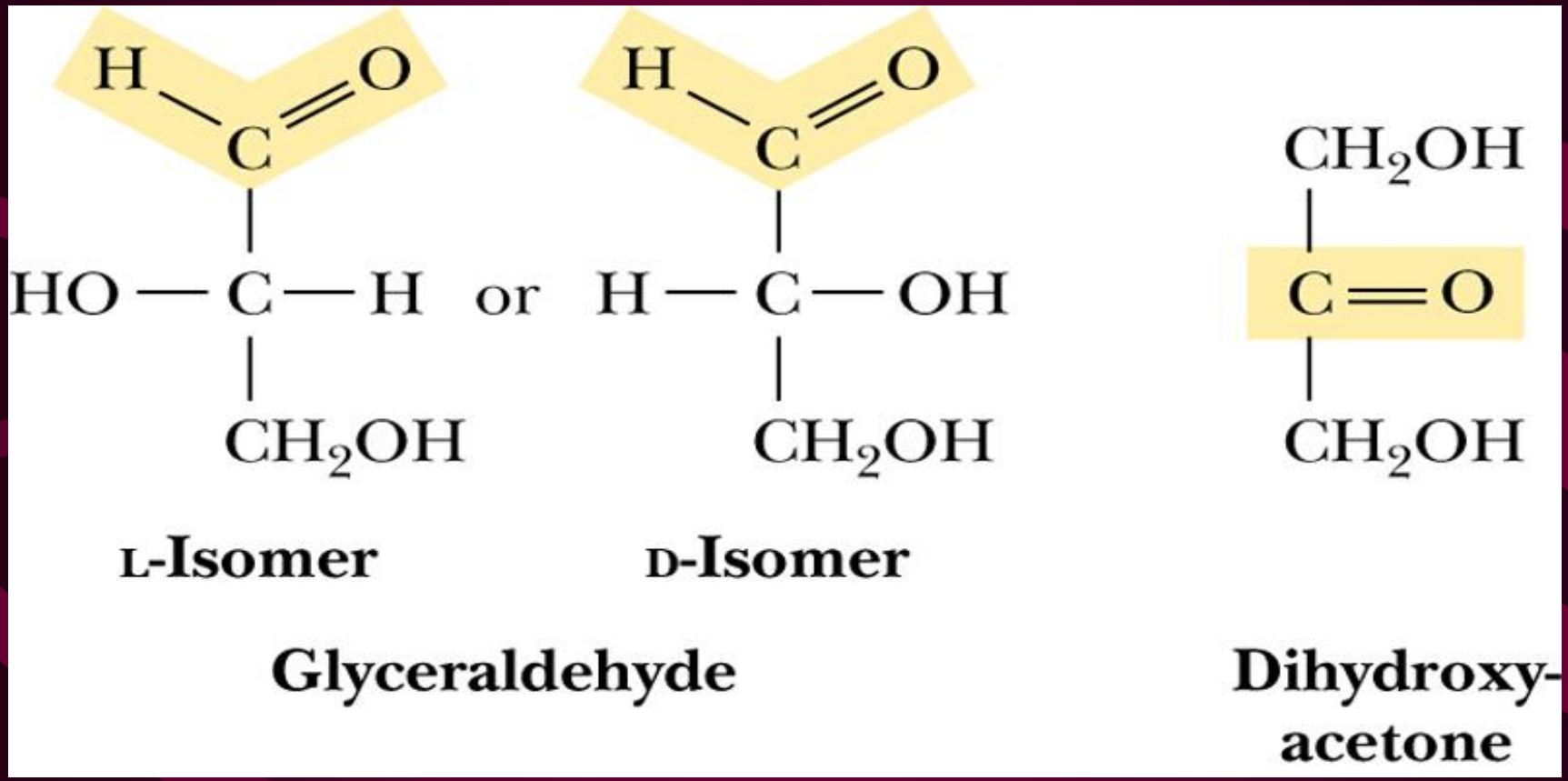
- Defined as polyhydroxy carbonyl compounds or polyhydroxy hemiacetals/hemiketals/acetals/ketals and their derivatives
- Major form of **stored energy** in organism and also the **metabolic precursors** of virtually all other biomolecules.
- The basic molecular formula $(CH_2O)_n$

Carbohydrates
- Monosaccharides: simple sugars
- Oligosaccharides: 2 ~ 10 simple sugars
- Polysaccharides: > 10 simple sugars

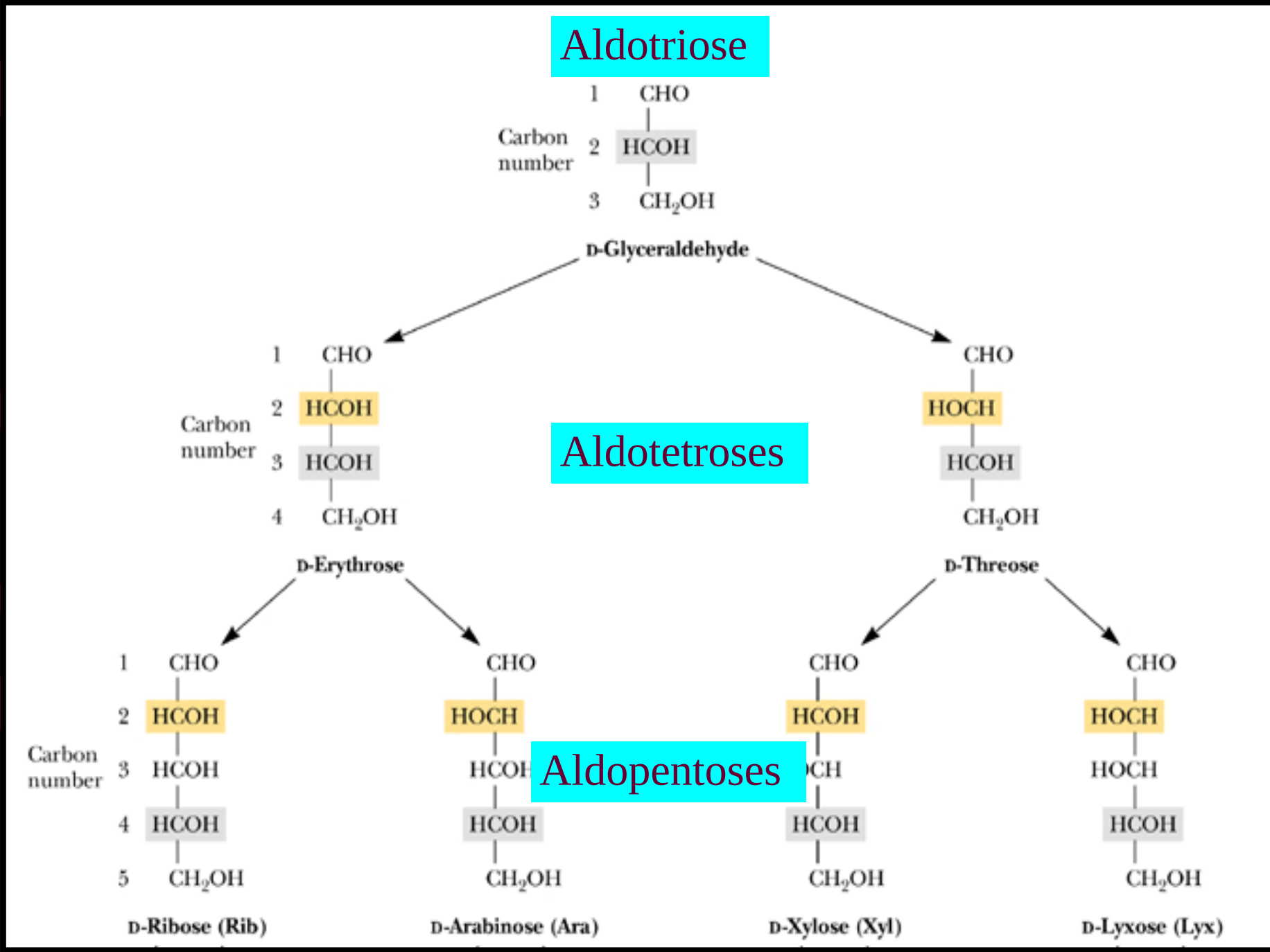
Monosaccharides are classified as aldoses and ketoses

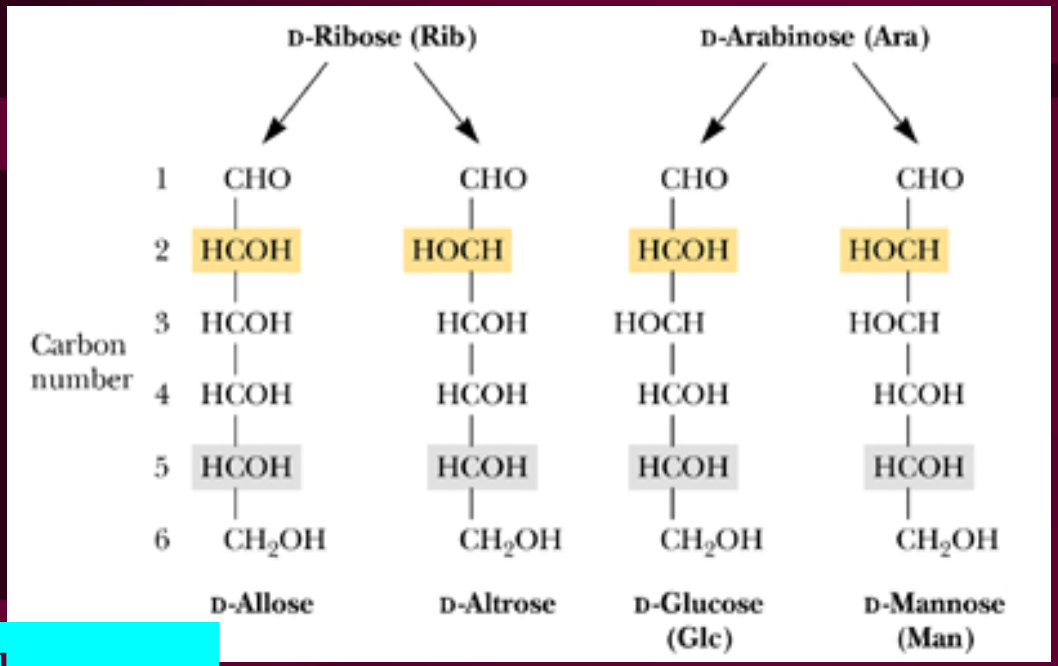
Aldose

Ketose

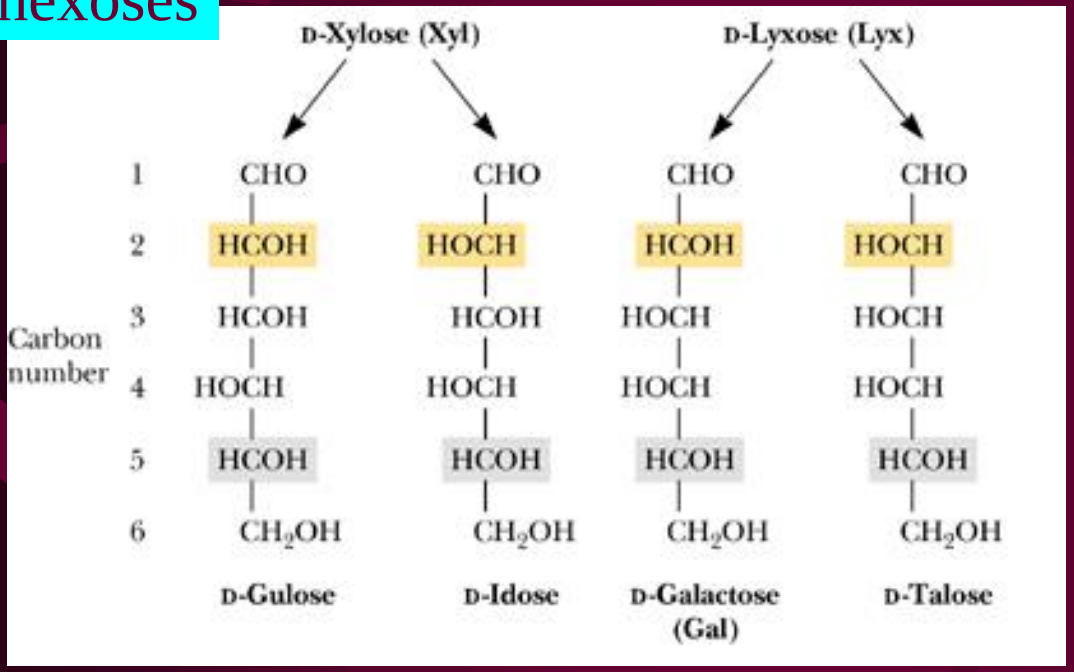


Triose: 3C


Aldotriose
Carbon number
1 CHO
2 HCOH
3 CH2OH
D-Glyceraldehyde
Aldotetroses
Carbon number
1 CHO
2 HCOH
3 HCOH
4 CH2OH
D-Erythrose
CHO
HOCH
HCOH
CH2OH
D-Threose
Aldopentoses
Carbon number
1 CHO
2 HCOH
3 HCOH
4 HCOH
5 CH2OH
D-Ribose (Rib)
CHO
HOCH
HCOH
HCOH
CH2OH
D-Arabinose (Ara)
CHO
HCOH
HCOH
HCOH
CH2OH
D-Xylose (Xyl)
CHO
HOCH
HOCH
HCOH
CH2OH
D-Lyxose (Lyx)



Aldohexoses



Aldoses names

Aldotriose

Aldotetrose

Aldopentose

Aldohexose

Aldo *** ose

Configuration

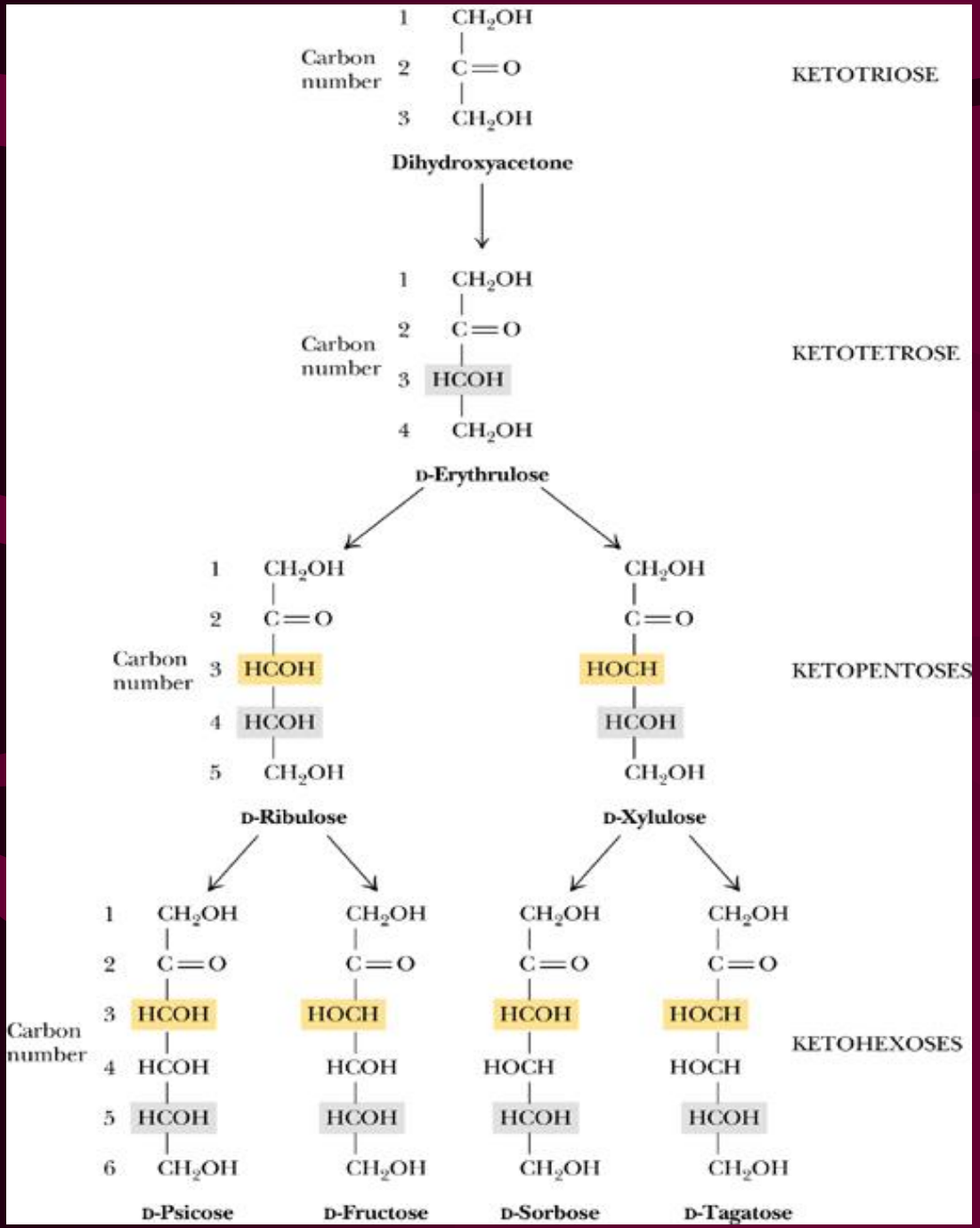
D- or L-

(+) dextrorotatory

(-) levorotatory

Abbreviation:

Glc, Man, Gal



Ketoses names

Ketotriose : triulose

Ketotetrose : tetrulose

Ketopentose : pentulose

Ketohexose : hexulose

Keto***ose : *** ulose

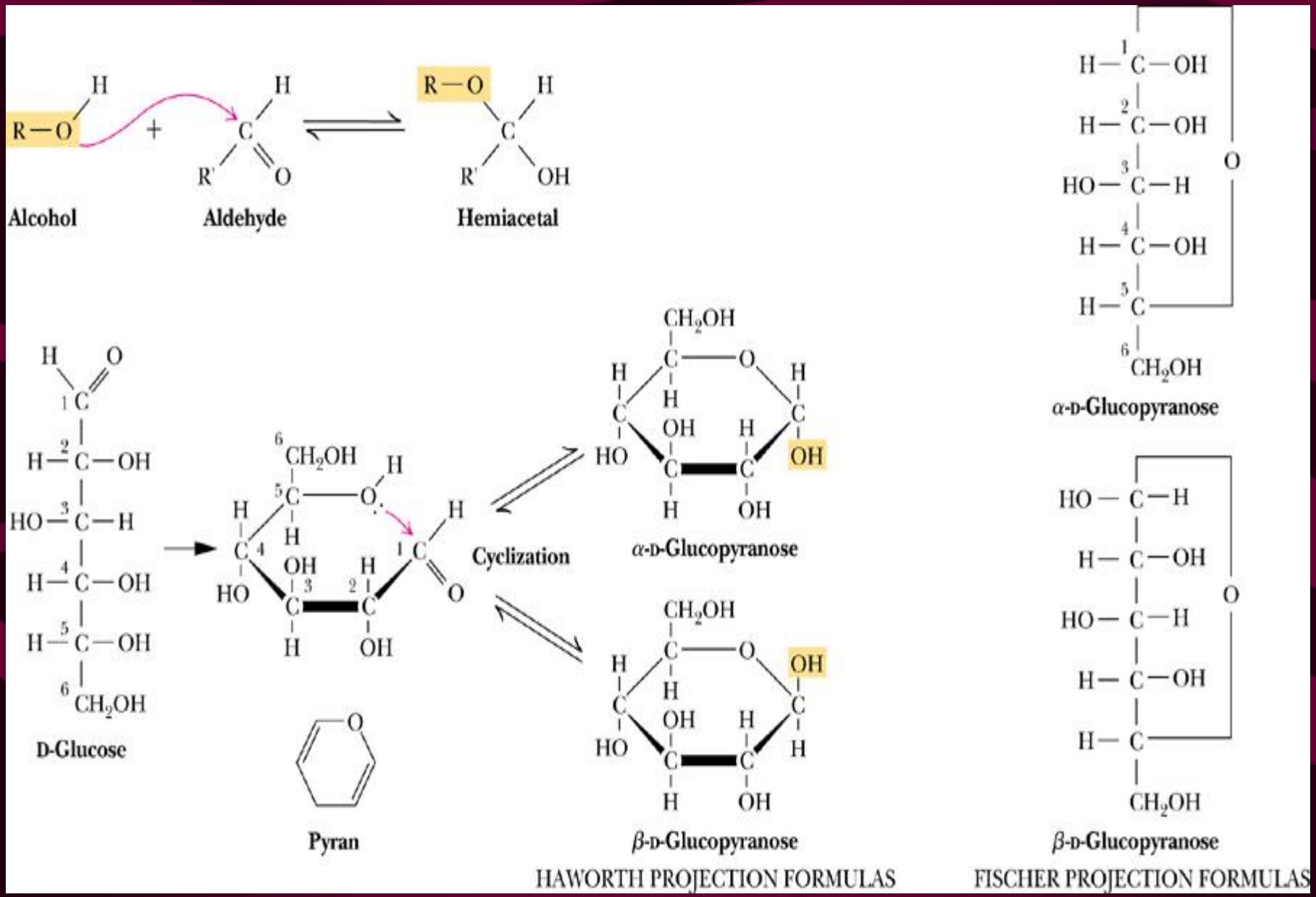
Steroisomers

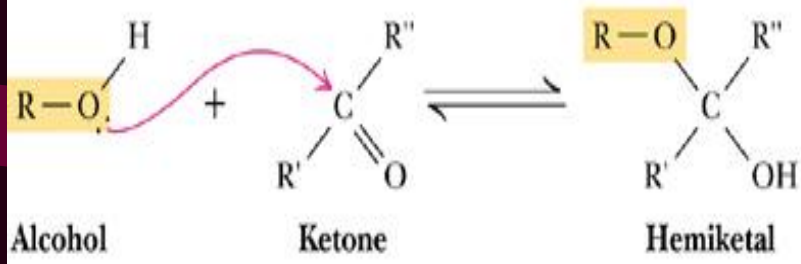
Enantiomers: mirror images of each other

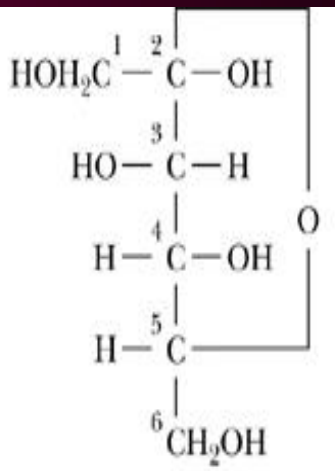
Diastereomers: isomers not mirror images

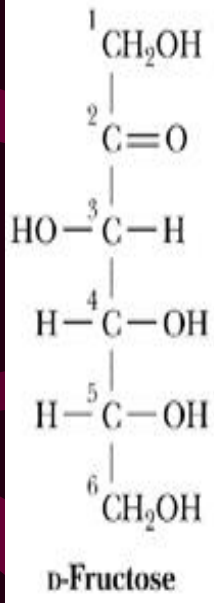
Epimers: only 1 chiral C different

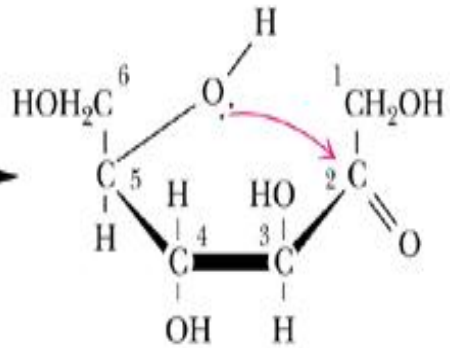
Monosaccharides exist in cyclic and anomeric forms

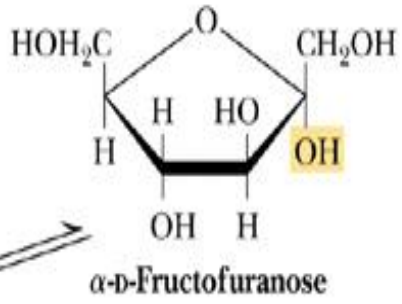




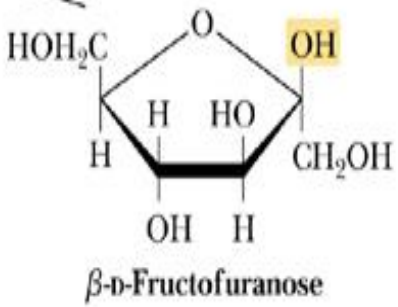


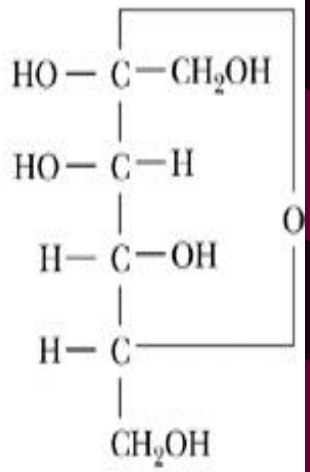






Cyclization

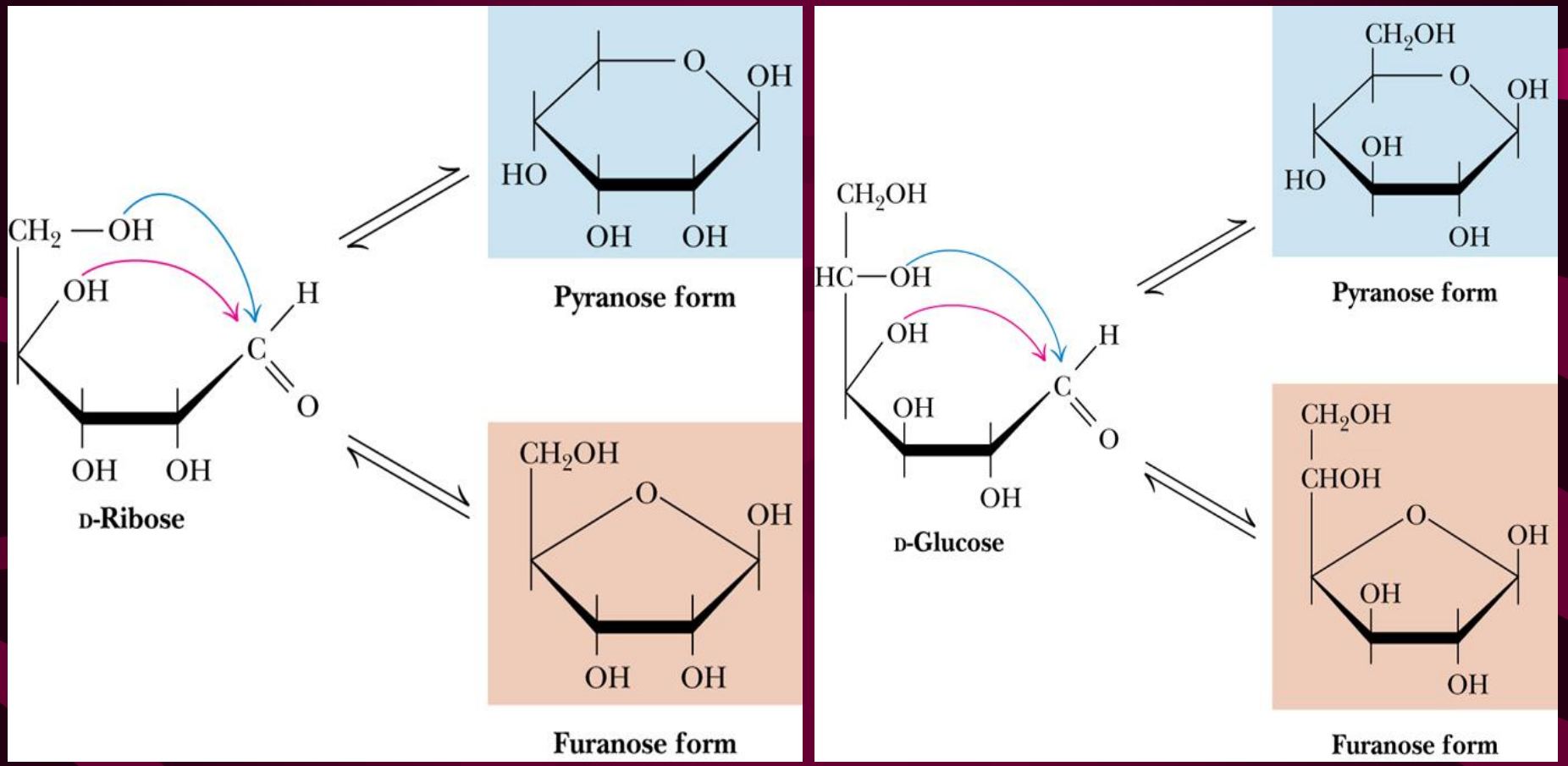




HAWORTH PROJECTION FORMULAS

FISCHER PROJECTION FORMULAS

Monosaccharides can cyclize in two ways



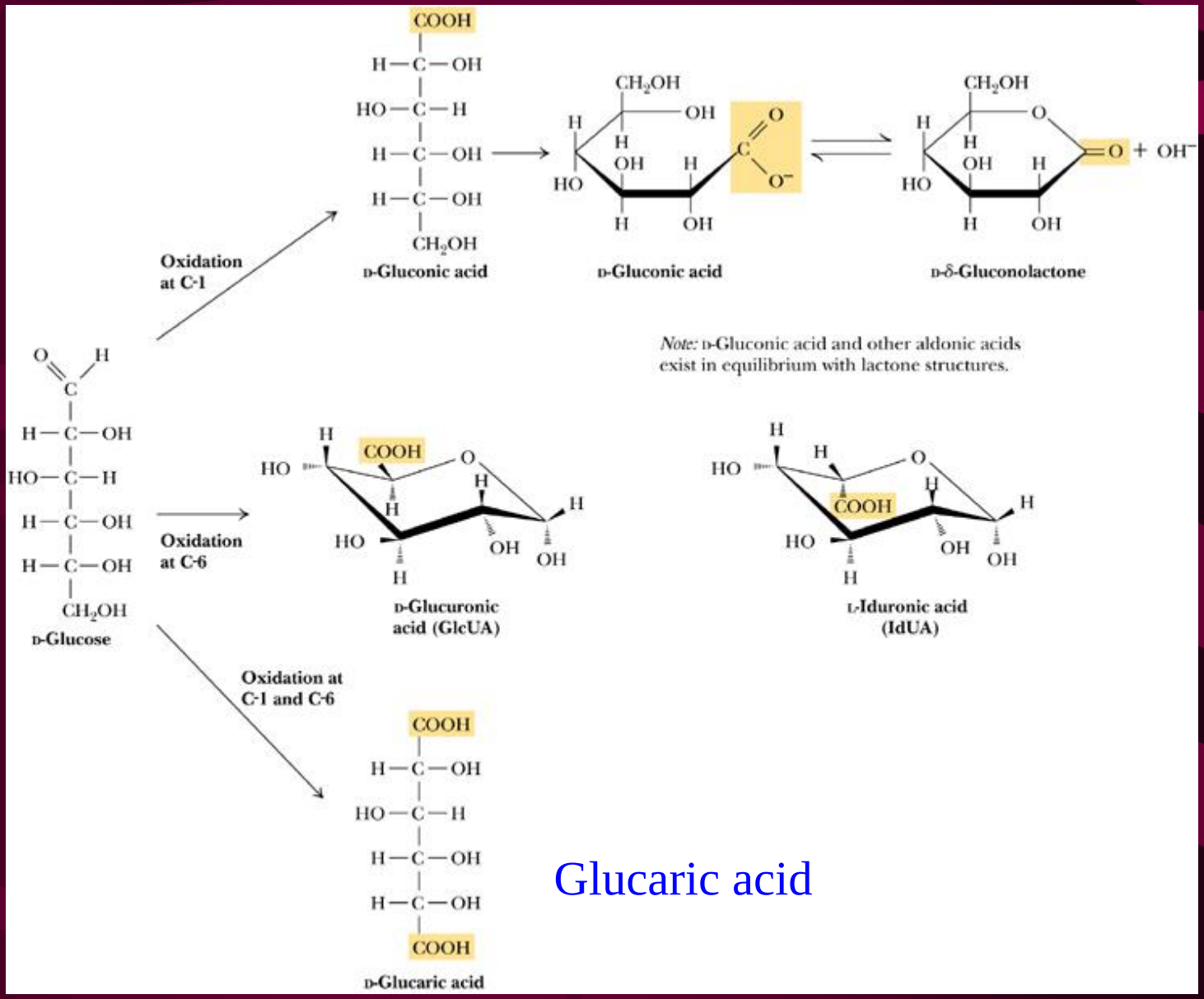
Ketohexose : Furanose form is more stable

Aldohexose : Pyranose form is more stable

Derivative forms of Monosaccharides

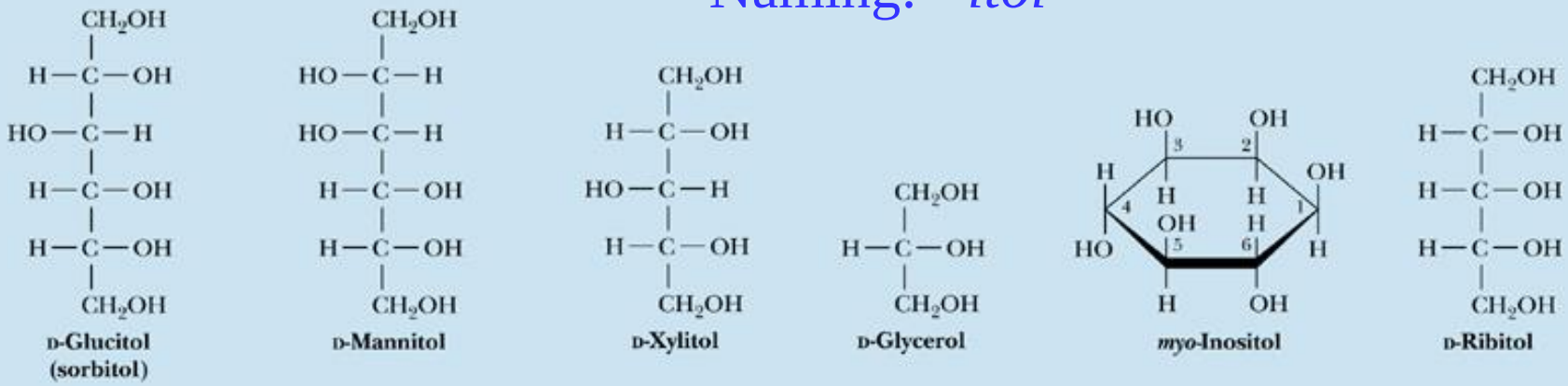
I. Sugar acids:

Oxidation of sugars

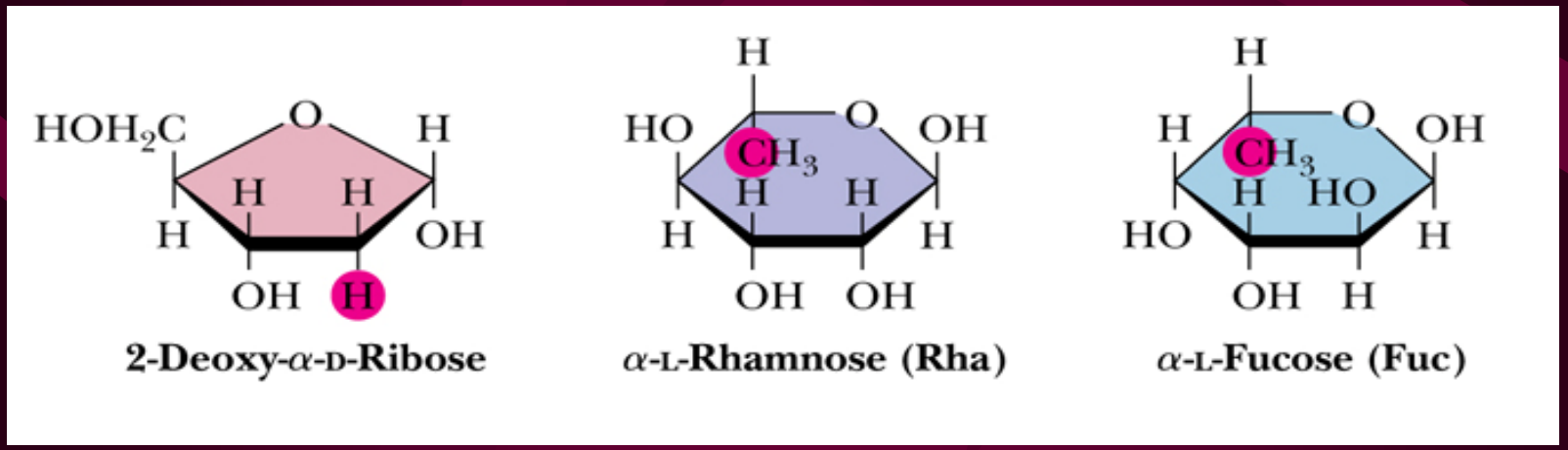


II. Sugar alcohols: Reduction of the carbonyl groups of aldoses and ketoses

Naming: *-itol*

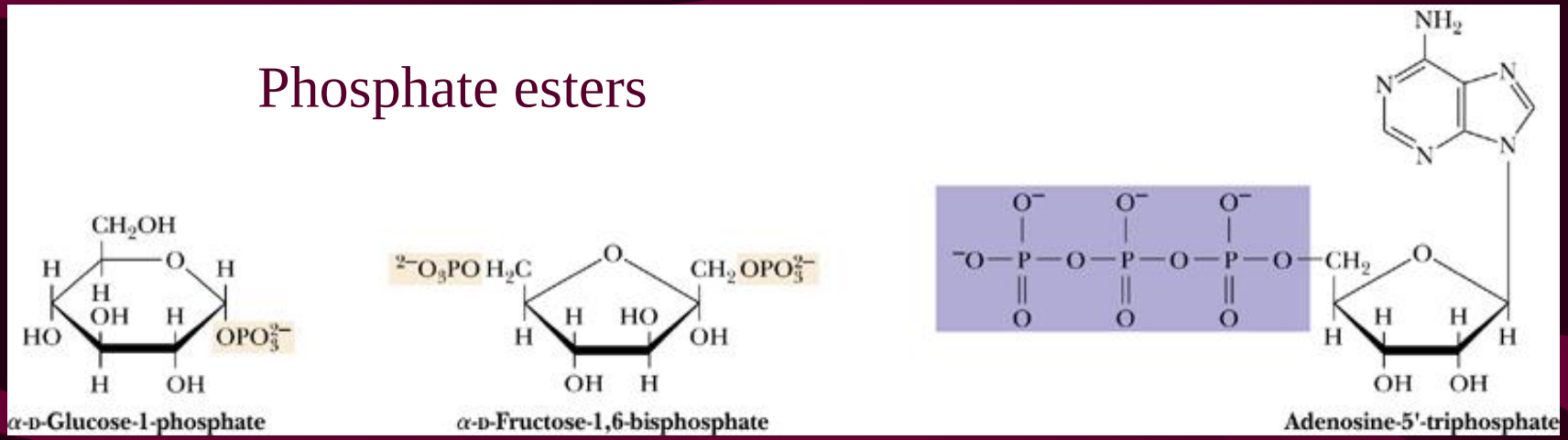


III. Deoxy Sugars:

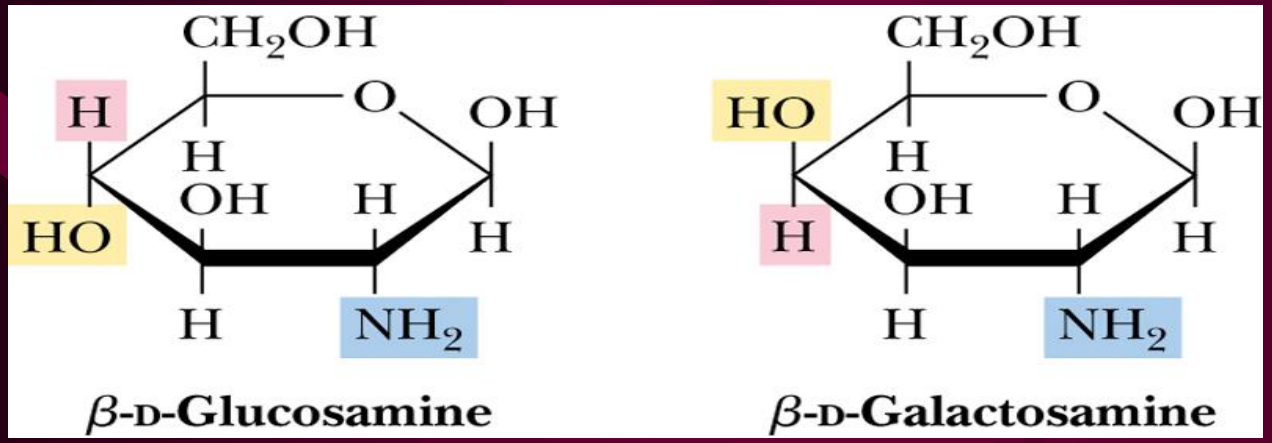


IV. Sugar Esters:

Phosphate esters

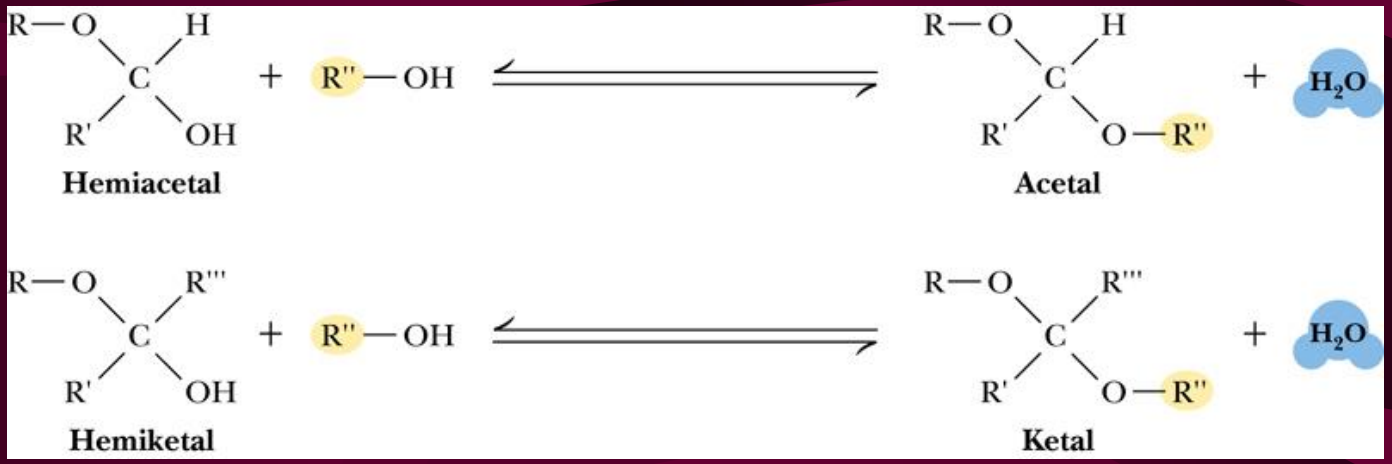


V. Amino Sugars:

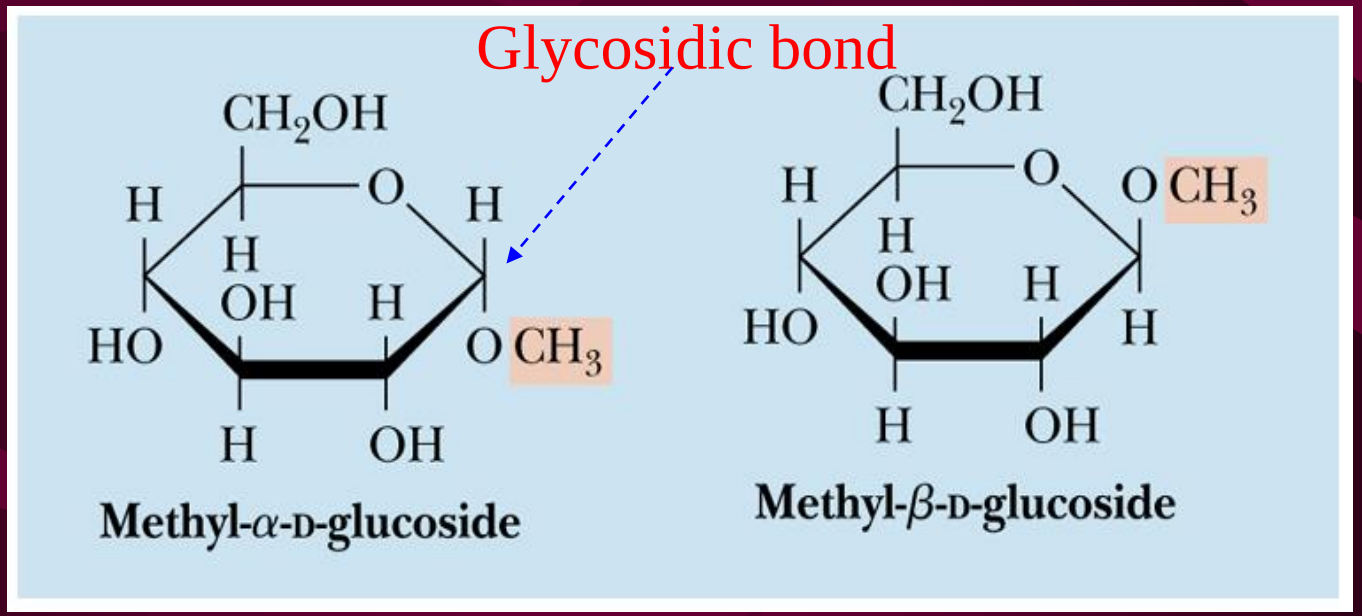


Polysaccharides of cell membranes

VI. Acetals, Ketals:



VII. Glycosides: Monosaccharides react with alcohols

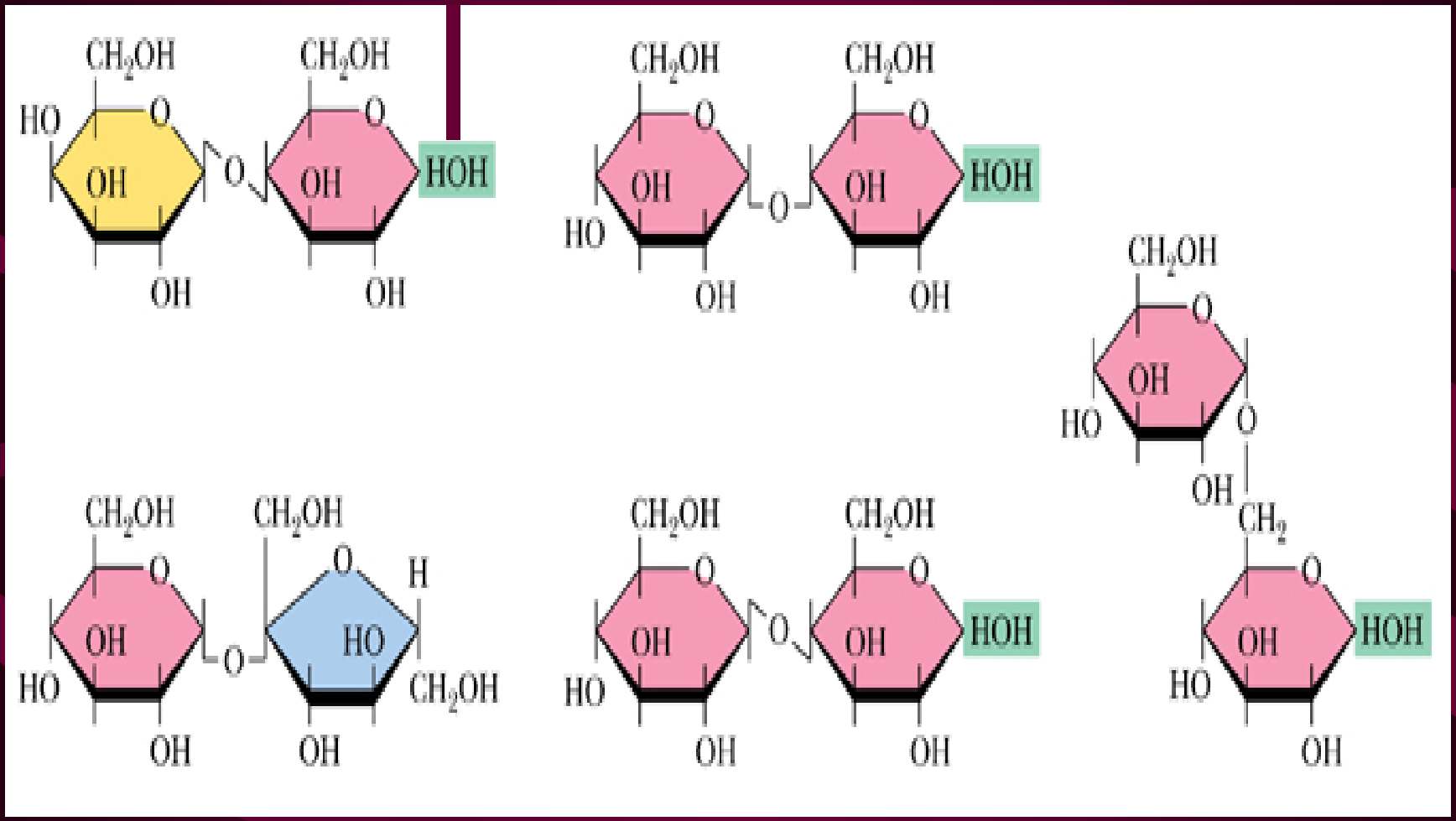


Specific Common Chemical Reactions of Monosaccharides

- Molisch's Test-indicates the presence of Carbohydrate.
- Bial's Test- differentiate between hexoses and pentoses.
- Seliwanoff's Test-differentiate between aldoses and ketoses.
- O- Toluidine Test-quantitative determination of glucose and other simple sugars.

Oligosaccharides

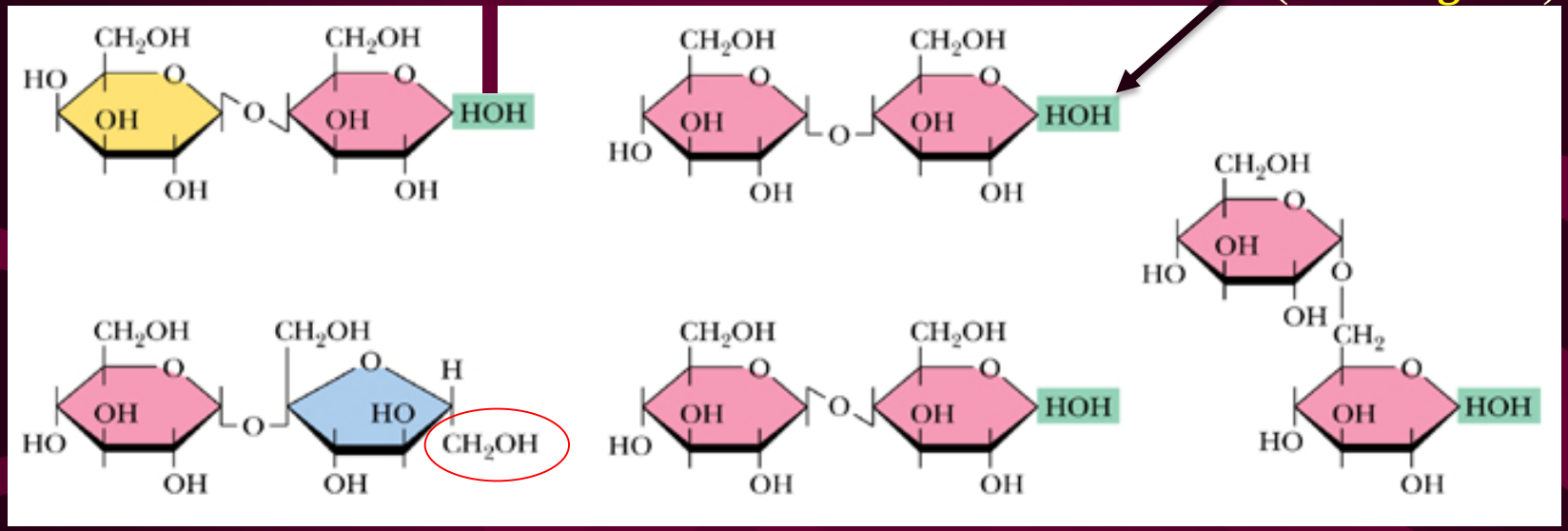
Disaccharides are the simplest oligosaccharides.



Lactose
(galactose-β-1,4-glucose)

Maltose
(glucose-α-1,4-glucose)

Free anomeric carbon
(**reducing end**)



Sucrose
(glucose-α-1, 2 fructose)

Cellobiose
(glucose-β-1,4-glucose)

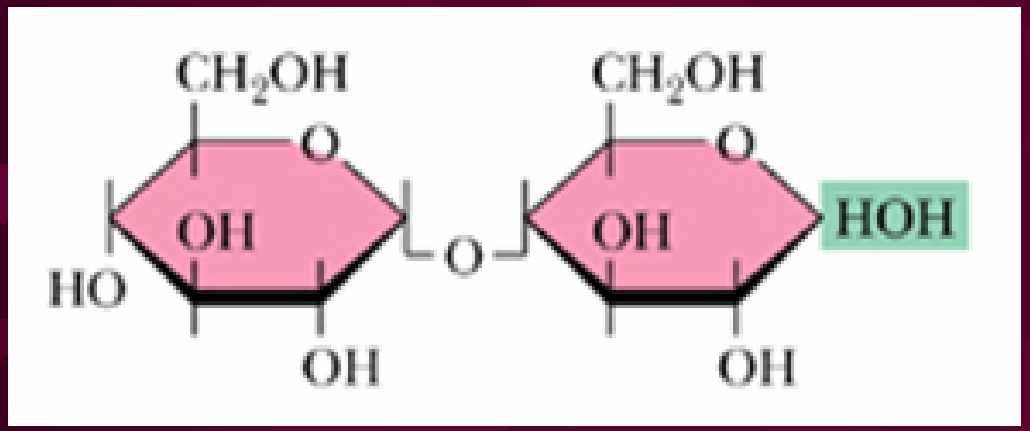
Isomaltose
(glucose-α-1,6-glucose)

Glycosidic bonds

Maltose (glucose-α-1,4-glucose): a component of malt.

Diastase produced during the germination process, catalyzes the hydrolysis of starch to maltose.

Fermented by yeast, important in the brewing of beer.

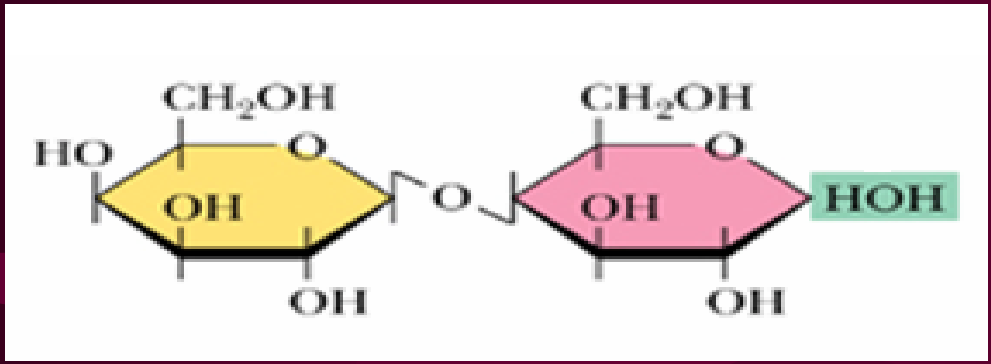


Glycosidic bonds:

Maltose (glucose-α-1,4-glucose): Glcα1 → 4Glc; Glcα4Glc

β-D-**Lactose** (galactose-β-1,4-glucose)

Galβ1→ 4Glc or Galβ4Glc

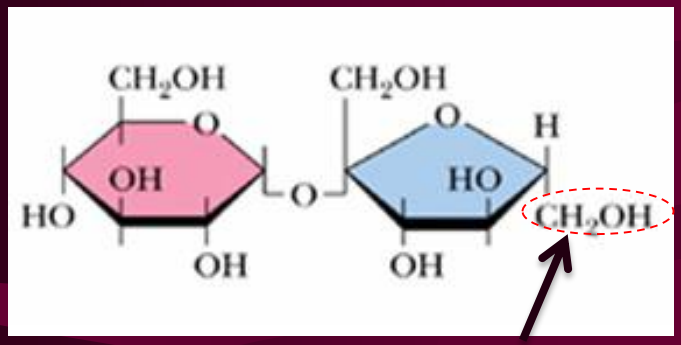


- β-D-Lactose is the principal carbohydrate in milk, a critical nutrition in the early stages of mammals.

- It can not be absorbed directly into the bloodstream, it must first broken down into galactose and glucose by **lactase,** an intestinal enzyme.

Sucrose (glucose-α-1,4 frucose)

Glcα1→ 4Fru or Galβ4Glc

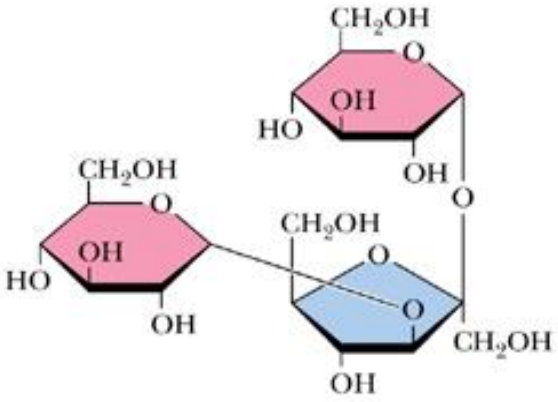


No reducing end

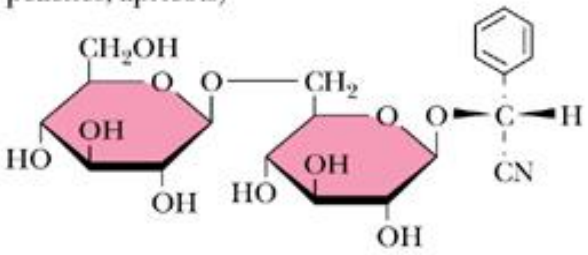
- Sucrose is a disaccharide produced by many higher plants (photosynthesis), commonly known as table sugar.
- It cannot be absorbed directly (similar to lactose), is hydrolyzed by the sucrase in the human intestine.

A variety of higher oligosaccharides occur in nature

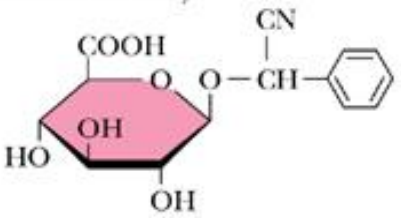
Melezitose (a constituent of honey)



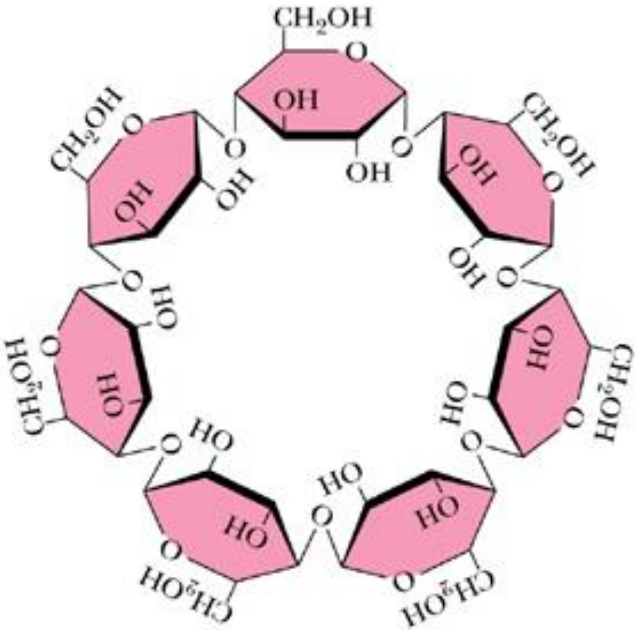
Amygdalin (occurs in seeds of *Rosaceae;* glycoside of bitter almonds, in kernels of cherries, peaches, apricots)



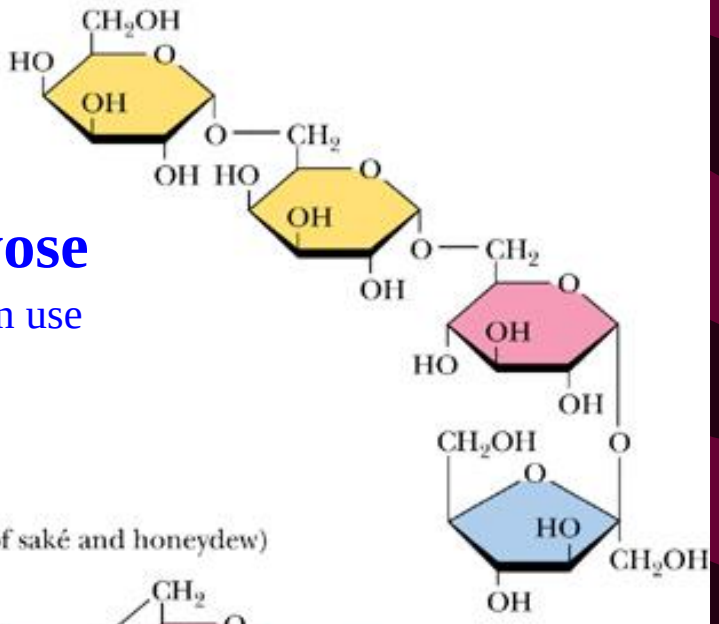
Laetrile (claimed to be an anticancer agent, but there is no scientific evidence for this)



Cycloheptaamylose (a breakdown product of starch; useful in chromatographic separations)



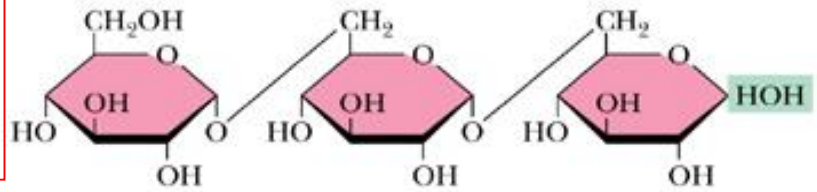
Stachyose (a constituent of many plants: white jasmine, yellow lupine, soybeans, lentils, etc.; causes flatulence because humans cannot digest it)



Stachyose

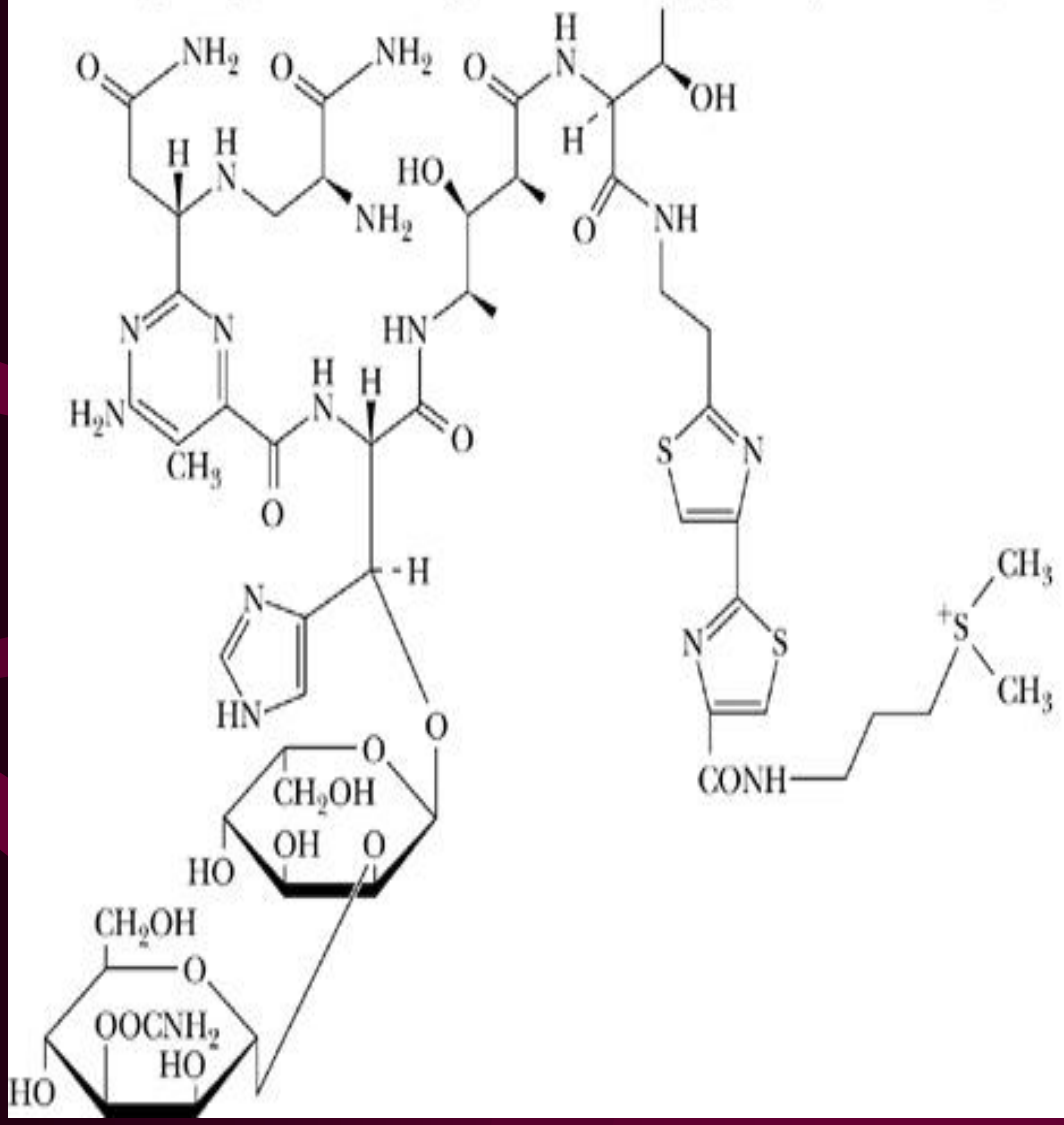
Bacteria can use

Dextrantriose (a constituent of saké and honeydew)

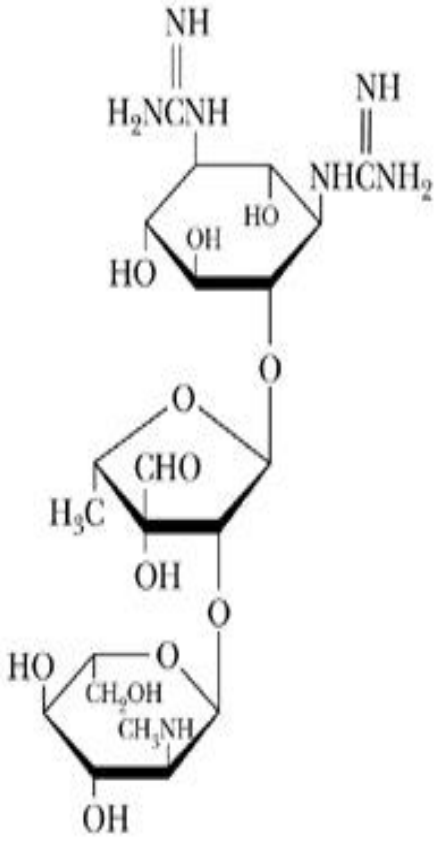


Oligosaccharides occur widely as components of antibiotics

Bleomycin A_2 (an antitumor agent used clinically against specific tumors)



Streptomycin (a broad-spectrum antibiotic)



Systematic Naming of Disaccharides

- Maltose: O-α-D-glucopyranosyl-(1→4)-D-glucopyranose
- Lactose: O-β-D-galactopyranosyl-(1→4)-D-glucopyranose
- Sucrose: O-β-D-fructofuranosyl-(2→1)-D-glucopyranose

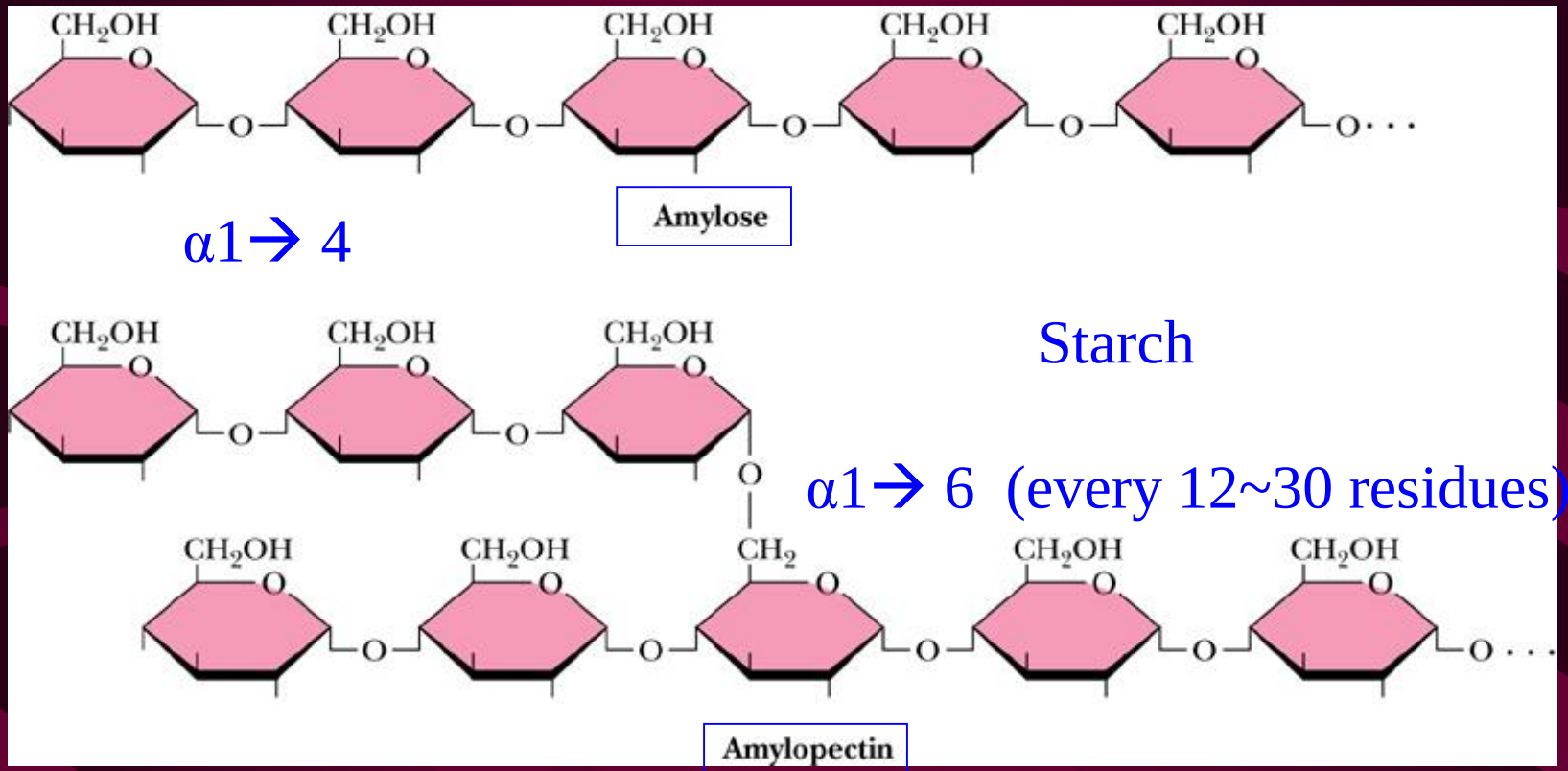
Polysaccharides

Nomenclature for polysaccharides composition and structure

Polysaccharides
Glycans

- Heteropolysaccharides (> one kind of monosaccharides
- Homopolysaccharides
  homoglycan
  - Glucans: glucose
  - Mannans: mannose
  - Galacturonans: Galactose
  - Arabinans: arabinose

Branched structure of polysaccharides



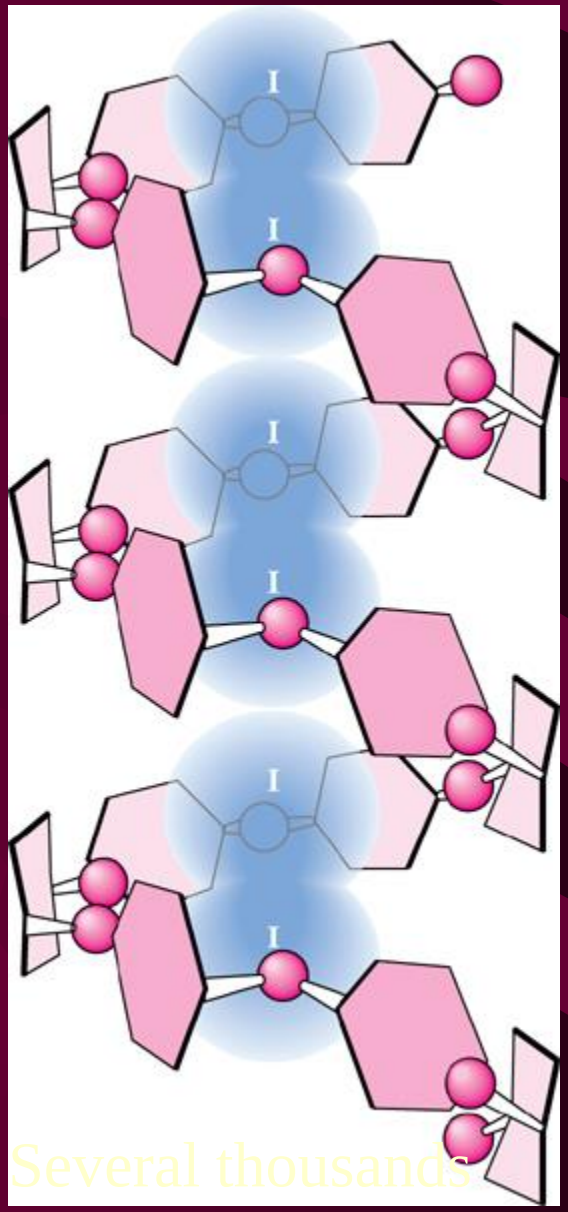
Functions of polysaccharides

I. Stores of energy

Starch: 10%~30%: amylose;
70%~90% amlyopectin

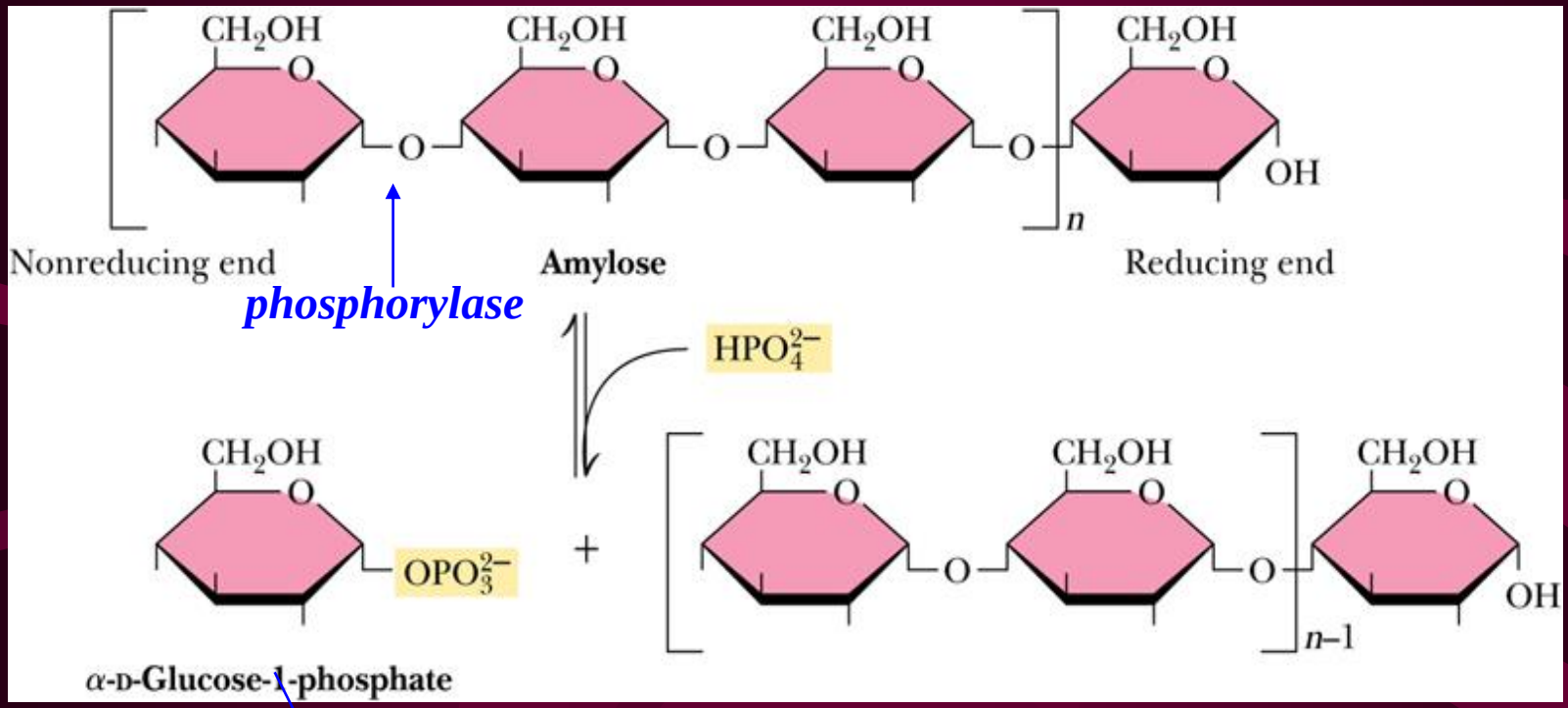
Helical amylose + I_2 → ***blue color***

Suspensions of amylose in water adopt a helical conformation. Iodine (I_2) can insert into the middle of the amylose helix to give a ***blue color*** that is characteristic and diagnostic for starch.



Split into monosaccharide:

stepwise phosphorolytic cleavage by ***starch phosphorylase***



Glycolytic pathways: produce energy (ATP)

Amylase digests starch

α-amylase :

Salivary α-amylase in animals : endoamylase,

splits α(1→4) glycosidic linkages only within the chain

Cooked starch is more digestible: Heating swell granules

Inactivated in stomach: Low pH

Pancreatic α-amylase in animals : endoamylase, small intestine

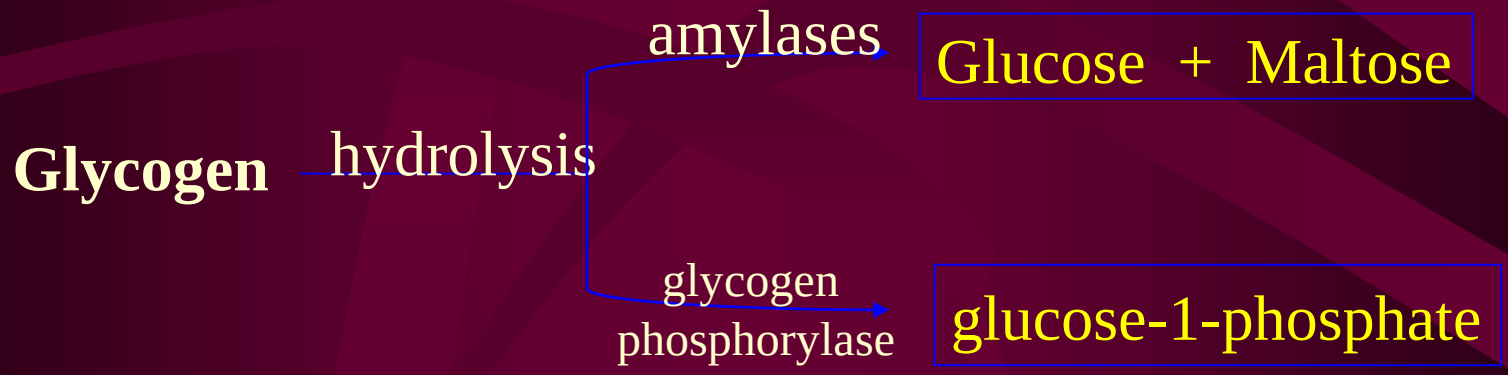
***β*-amylase** only in some plants and microorganisms: exoamylase

α(1→6) –**glucosidase:** splits α(1→6) glycosidic linkage

cleave at the branch points of starch

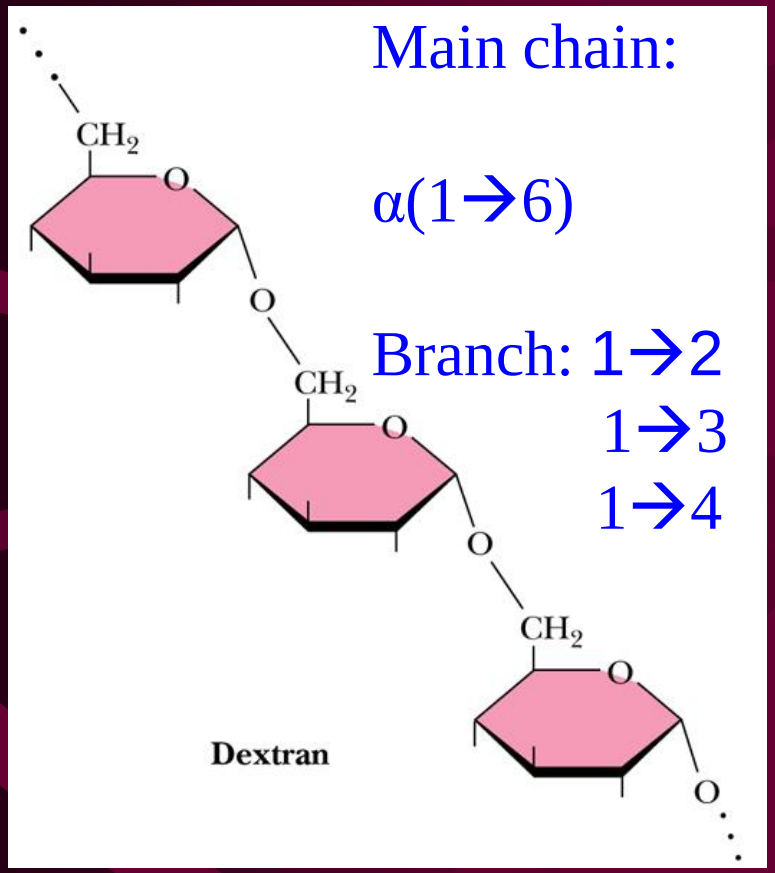
Glycogen: The major form of stored polysaccharide in animals
mainly in the liver (10% of liver mass)
and skeletal muscle (1% ~ 2% of muscle mass)

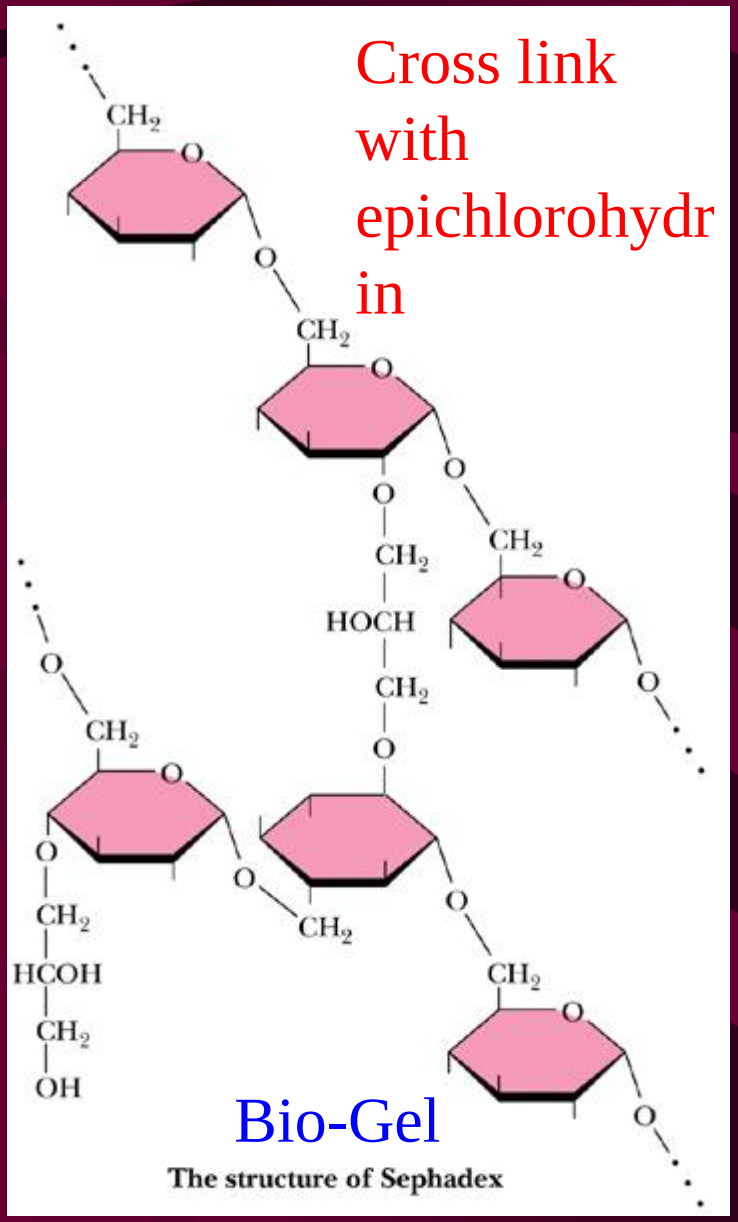
Liver Glycogen : highly branched, every 8 ~12 residuces α(1→6)



Dextran:

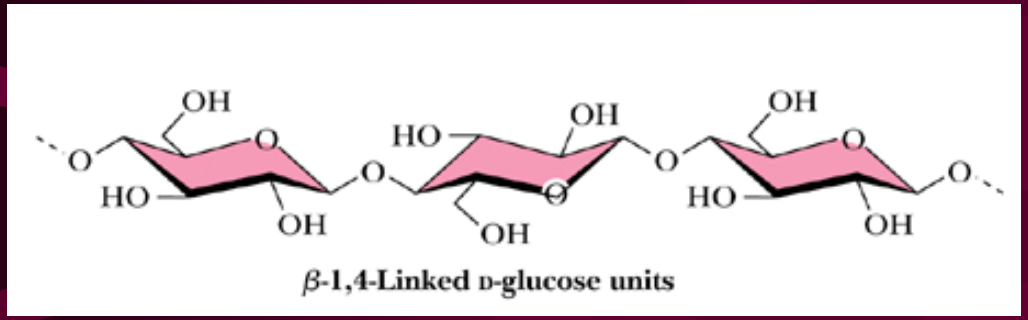
Polysaccharide of D-Glc





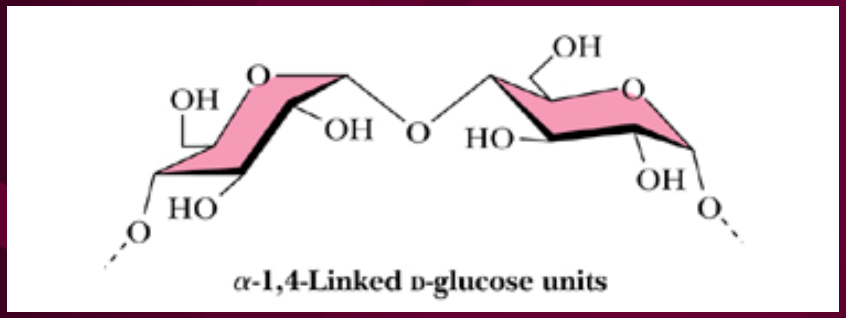
Polysaccharides provide physical structure and strength to organisms

Cellulose: structural polysaccharide,
Found in cell walls of nearly all plants

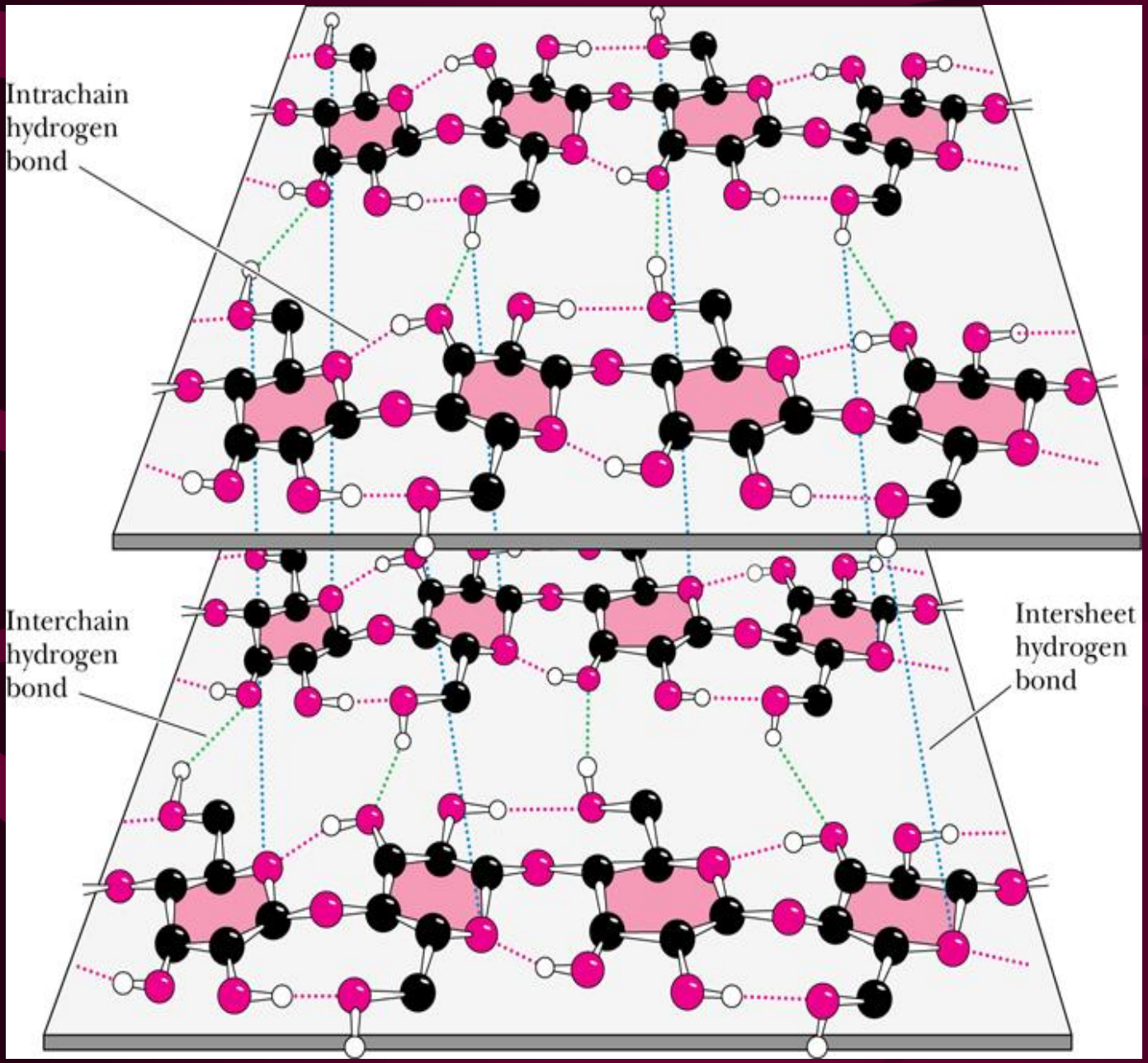


Cellulose:
extended conformation
Glc flips: H-bonds, stable

Homopolymer of D-glucose: $\beta(1\rightarrow4)$ glycosidic linkages



Starch:
helical conformation



Hydrolyzed
by cellulase,
β -glucosidase

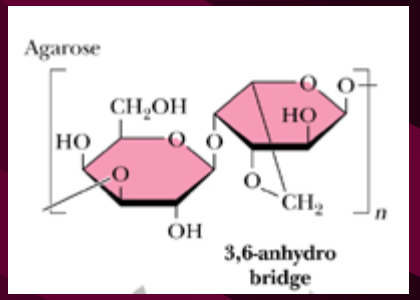
Some other polysaccharides:

Chitin: in the cell walls of fungi, exoskeletons of crustaceans, insects.

$\beta(1\rightarrow4)$: *N-acetyl-D-glucosamines*

Alginates: in marine brown algae, Ca^{2+} binding

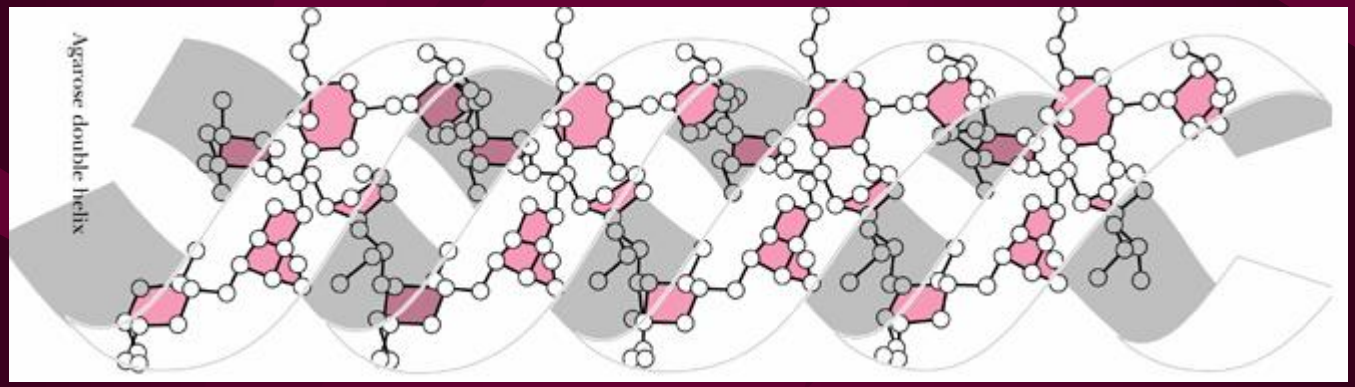
$(1\rightarrow4)$: *β-D-mannuronate*, *α-L-guluronate*



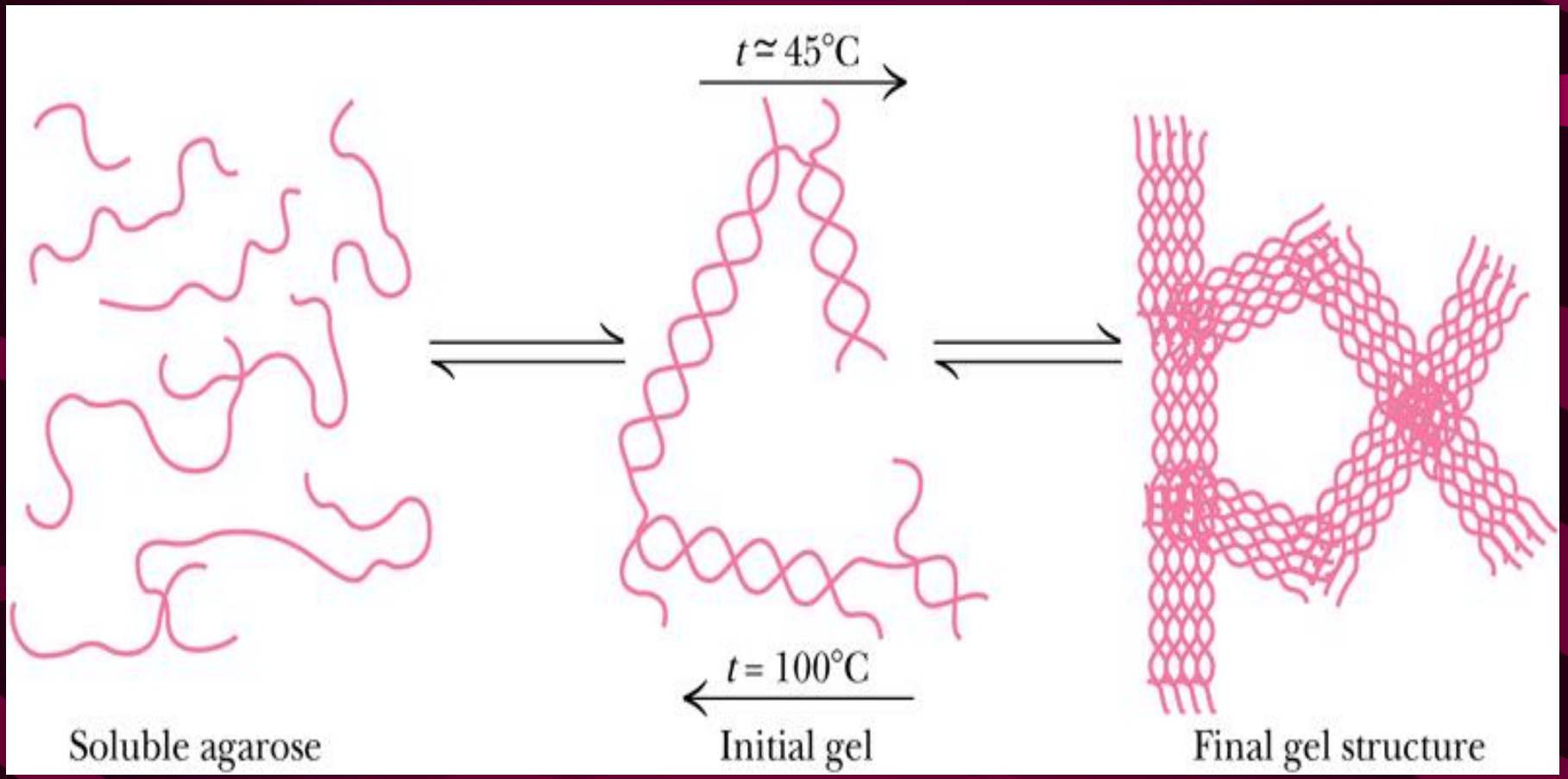
Agarose: in marine red algae

D-galactose and *3,6-anhydro-L-galactose*

3D conformation: double helix:



Agarose Gel

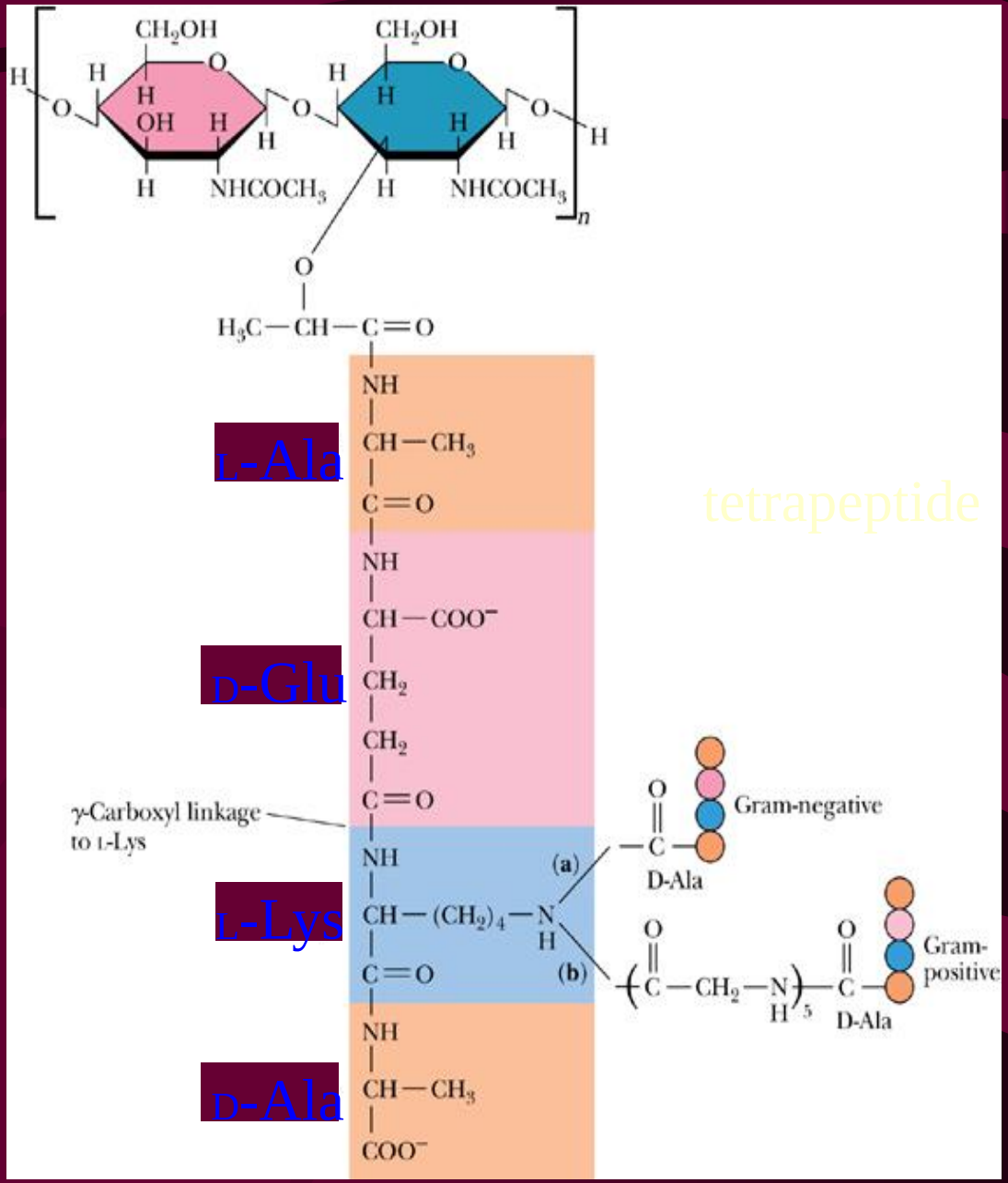


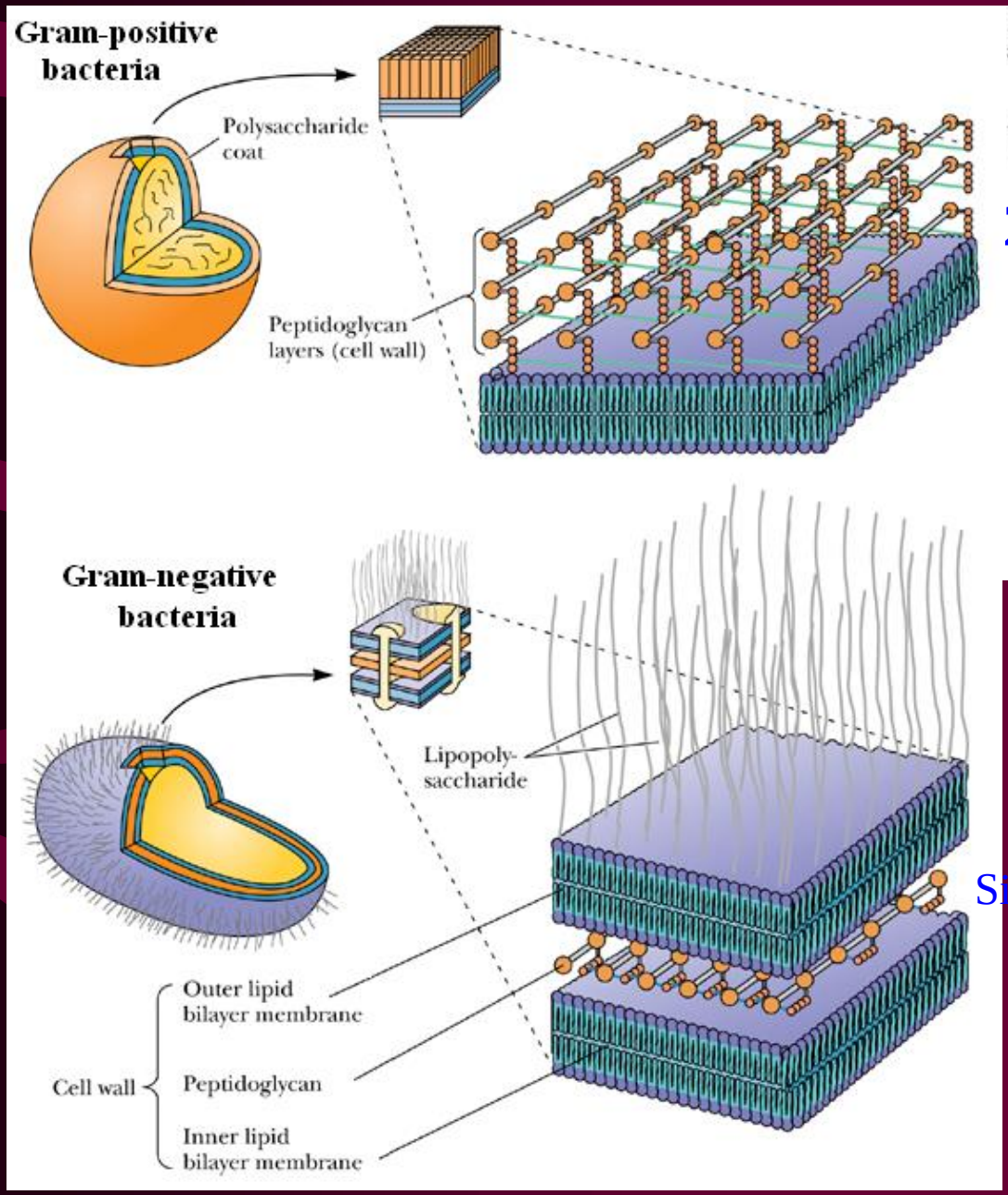
Form gels containing 99.5% water

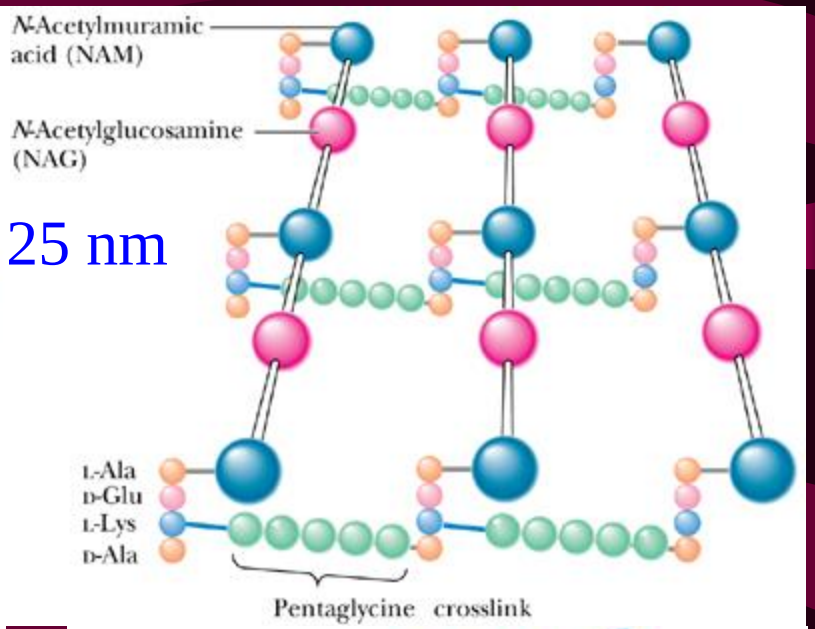
Polysaccharides provide strength and rigidity to bacterial cell walls

Peptidoglycan:

a strong, protective peptide-polysaccharide layer of bacteria

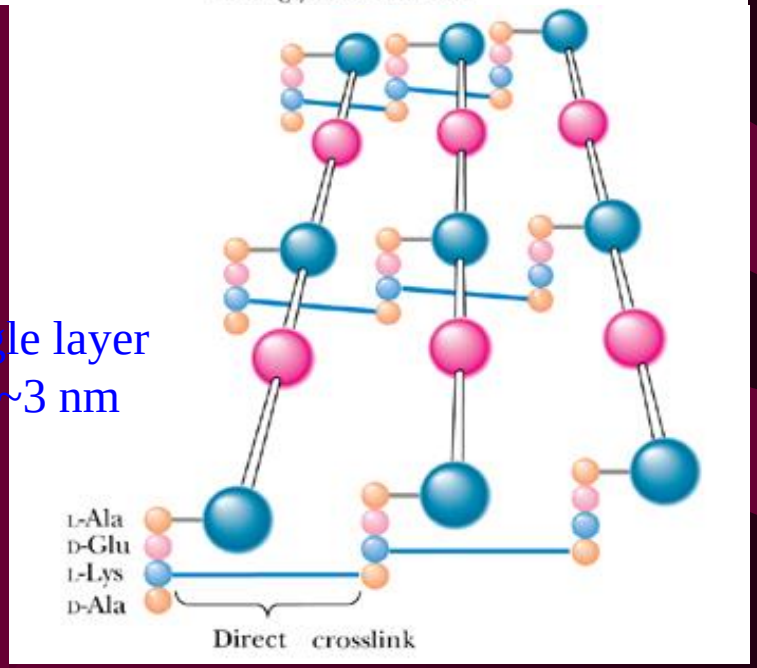




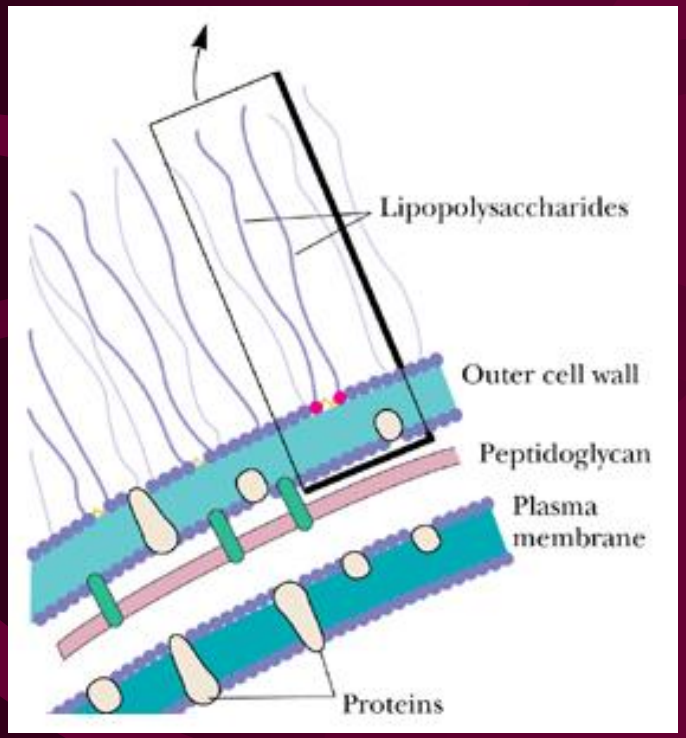


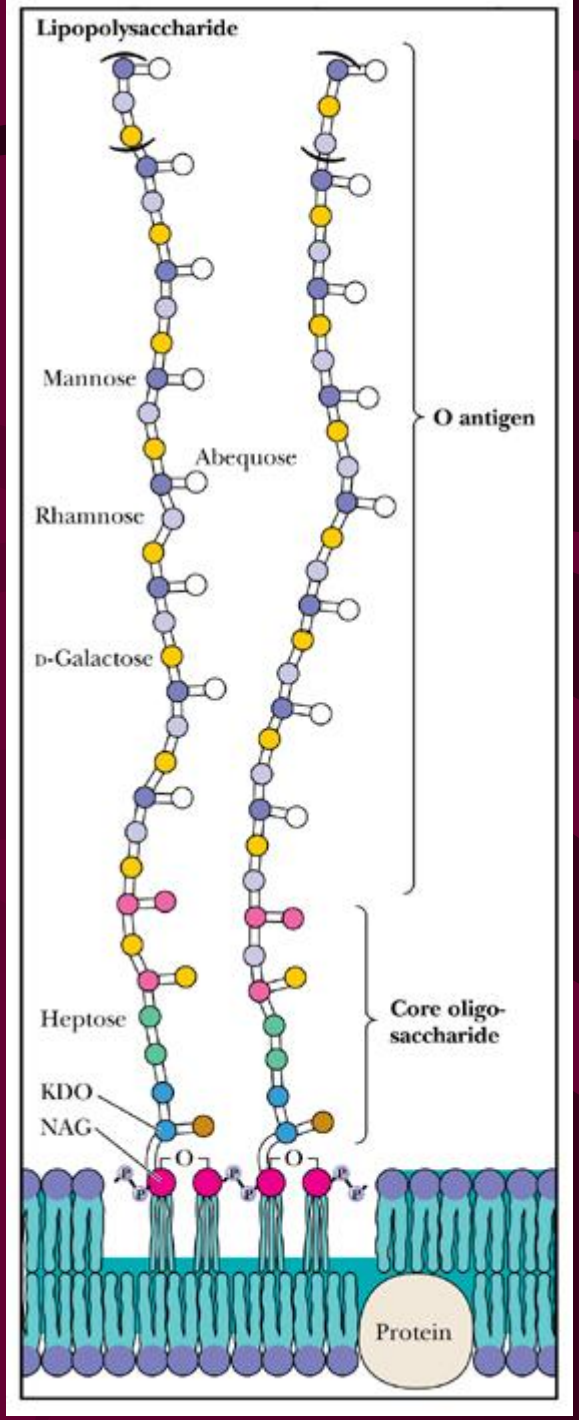
25 nm

Single layer
2~3 nm



Lipopolysaccharides: in Gram-negative bacteria





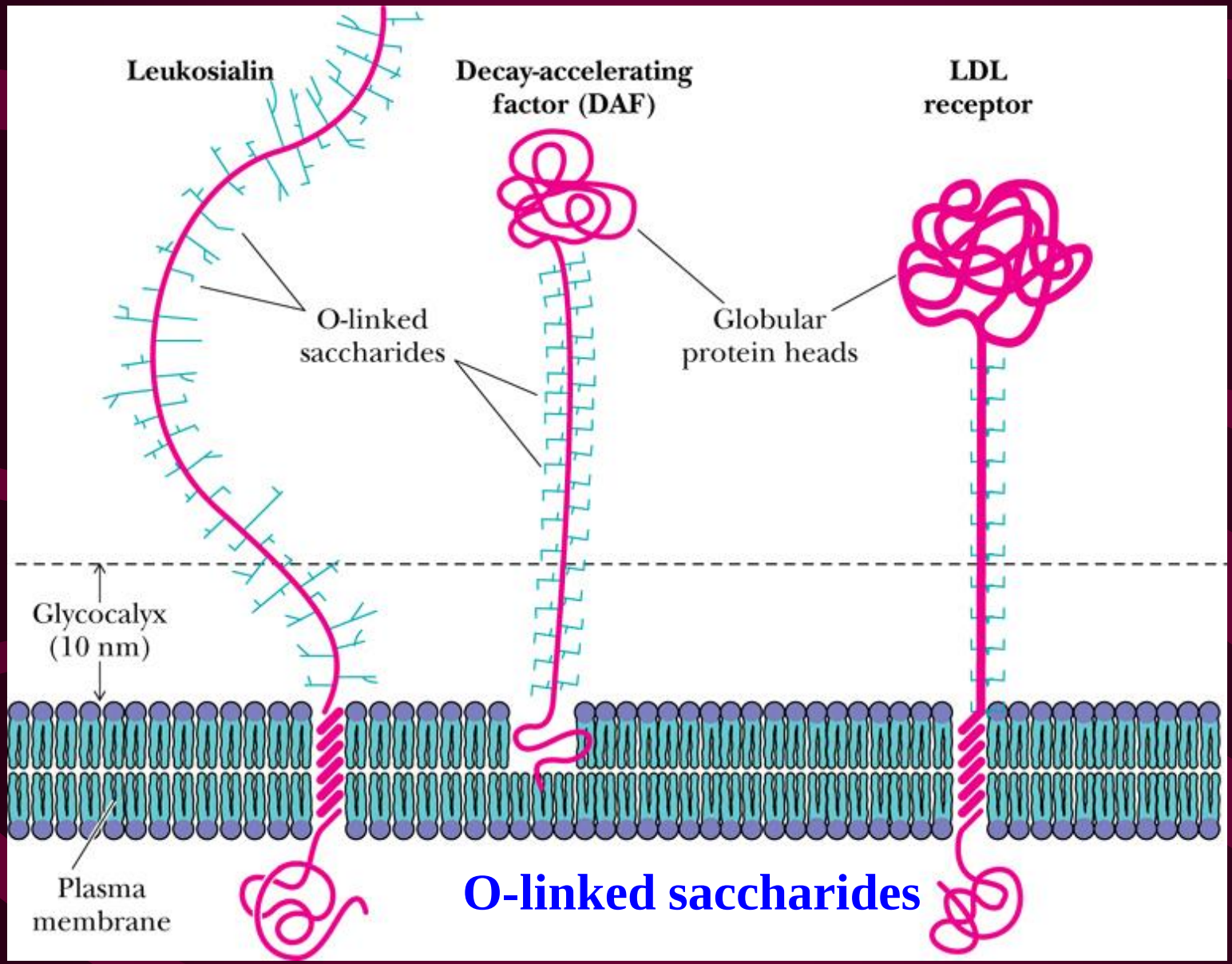
Glycoproteins and proteoglycans

Glycoproteins

- Carbonhydrate groups link to polypeptide chains,
- Include structural proteins, enzymes, membrane receptors, transport proteins, and immunoglobulines.

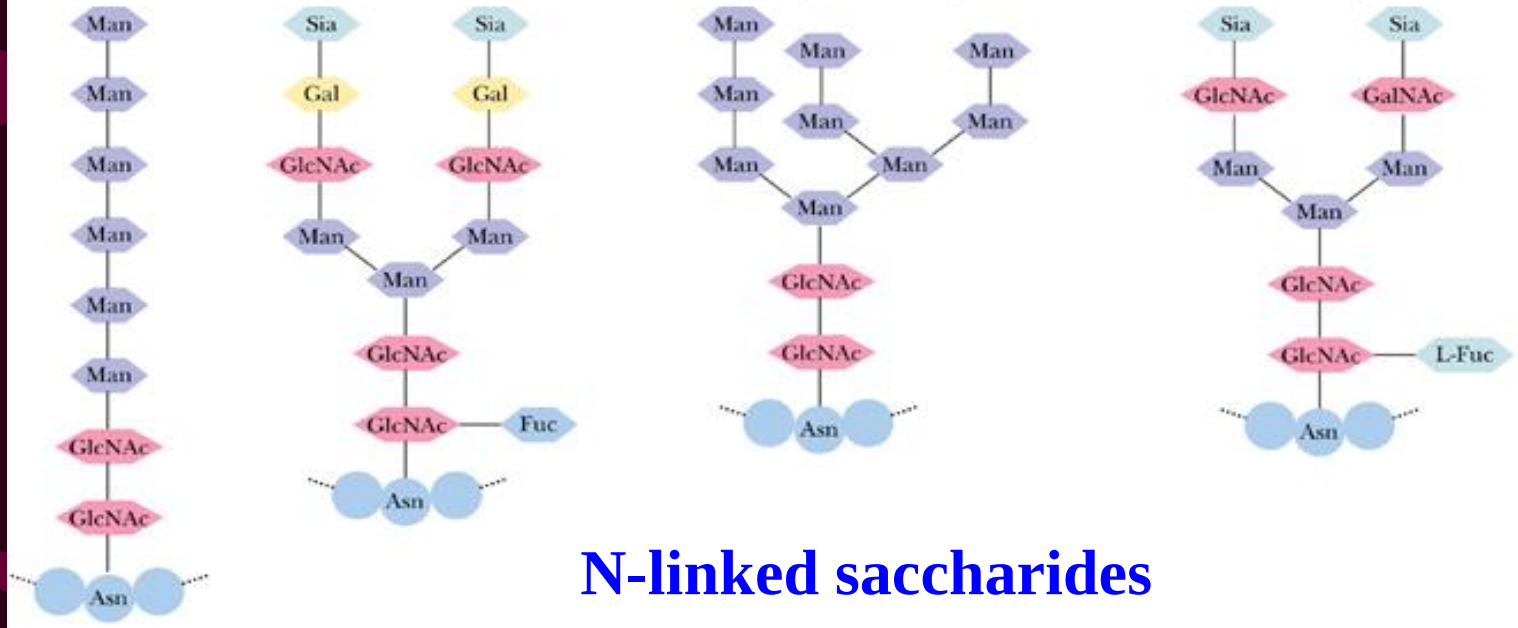
O-linked saccharides: -OH of Ser, Thr, or hydroxylysine
N-acetylgalactosamine

N-linked saccharides: amide N of Asn



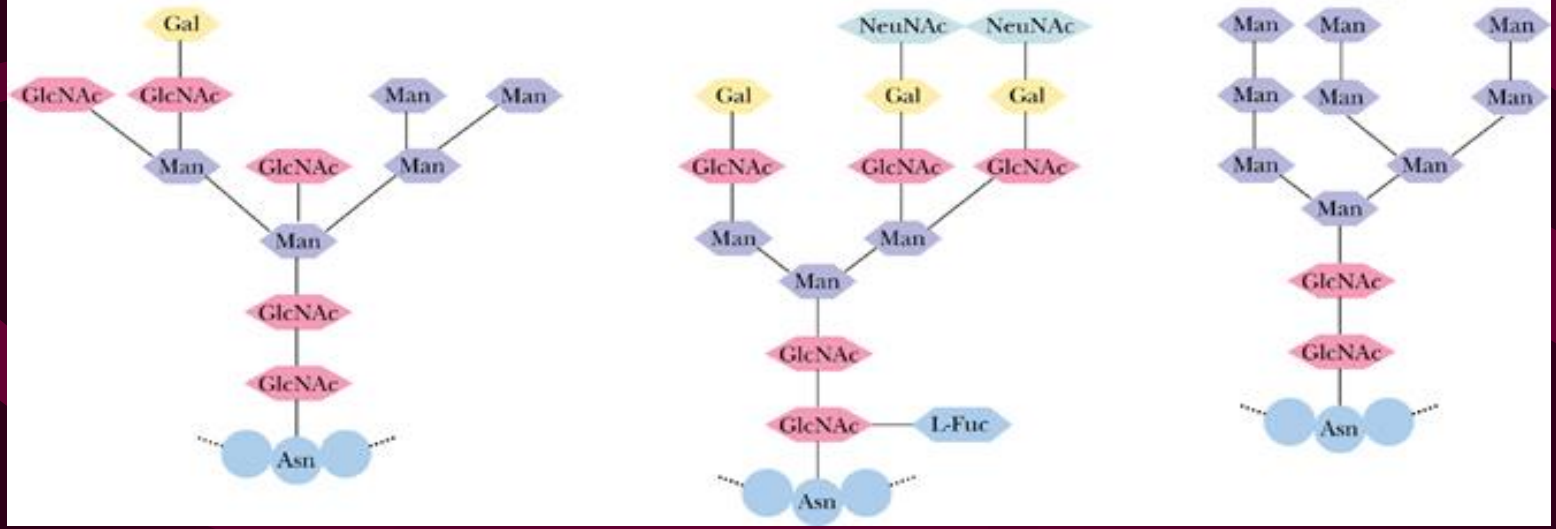
Keep the core of peptide in extended and rigid conformation

Ribonuclease B IgG lysosomal enzymes bovine luteinizing hormone



N-linked saccharides

Ovalbumin serum glycoproteins Soybean agglutinin



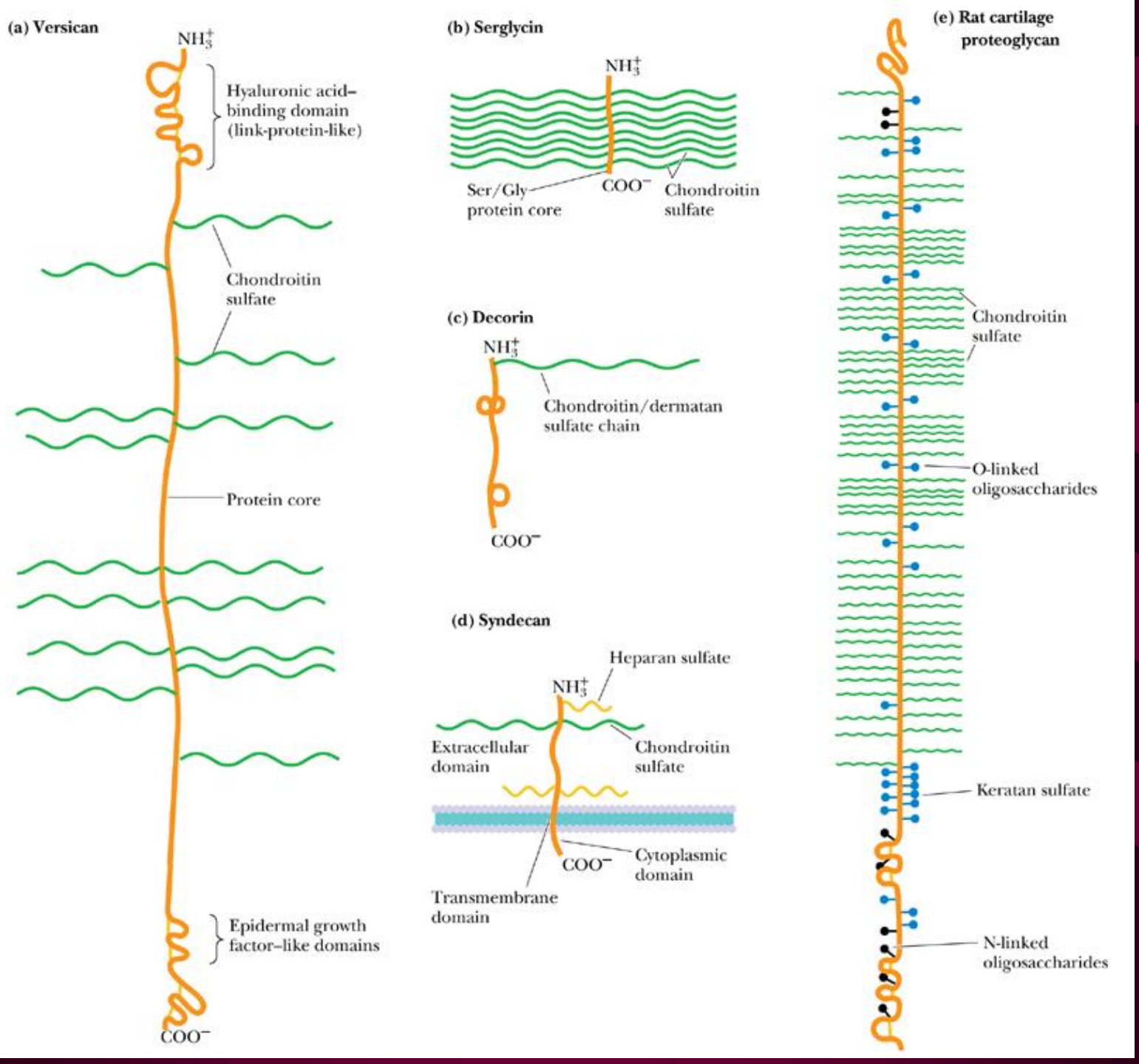
Stabilize protein conformations; Protect proteins against proteolysis

Proteoglycans

- A family of glycoproteins whose carbohydrate moieties are predominantly **glycosaminoglycans**.

Glycosaminoglycans are O-linked to Ser-Gly

- Proteoglycans may be soluble and located in the extracellular matrix.
- Functions by interacting with a variety if other molecules through their glycosaminoglycans components and specific receptor domains of polypeptide.
- Proteoglycans modulate cell growth processes and are also responsible for the flexibility an resilience of cartilage tissue in the body.


(a) Versican
NH_3^+
Hyaluronic acid–binding domain (link-protein-like)
Chondroitin sulfate
Protein core
Epidermal growth factor–like domains
COO^-
(b) Serglycin
NH_3^+
Ser/Gly protein core
COO^-
Chondroitin sulfate
(c) Decorin
NH_3^+
Chondroitin/dermatan sulfate chain
COO^-
(d) Syndecan
Heparan sulfate
NH_3^+
Extracellular domain
Chondroitin sulfate
COO^-
Cytoplasmic domain
Transmembrane domain
(e) Rat cartilage proteoglycan
Chondroitin sulfate
O-linked oligosaccharides
Keratan sulfate
N-linked oligosaccharides

Key points:

- **Carbohydrates name**: Mono/ oligo/ polysaccharides;
  Glycoconjugates
- **Monosaccharides:** aldoses and ketoses;
  cyclic forms:
- **Oligosaccharides:** Glycosidic bonds
- **Polysaccharides:** Branched structure;
  Functions: Stores of energy: Starch and amylase
  Provide physical structure and strength to organisms: Cellulose
  Provide strength and rigidity to bacterial cell walls

- **Glycoproteins and proteoglycans**