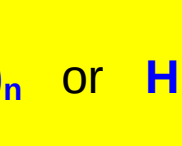
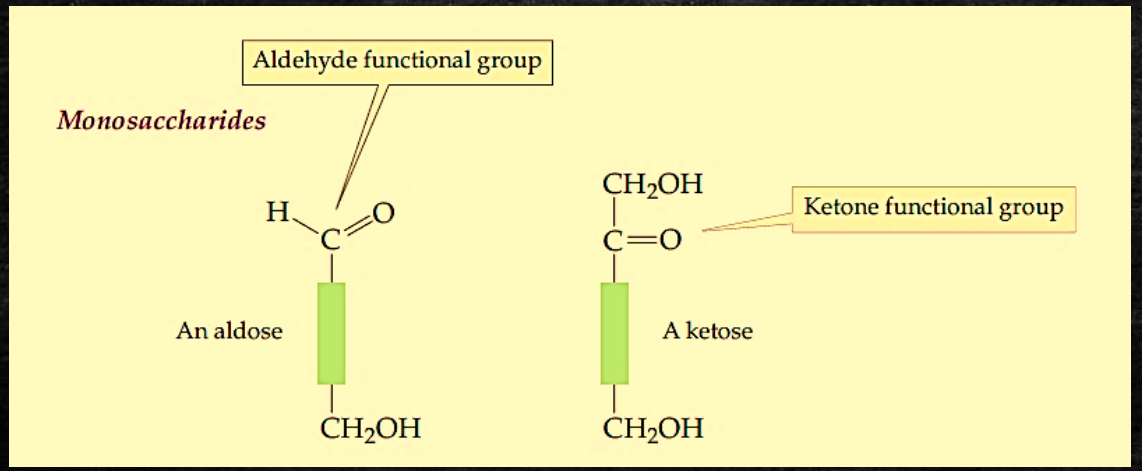
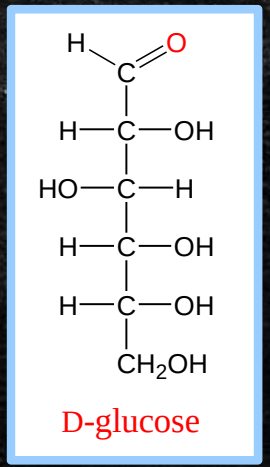
Carbohydrates

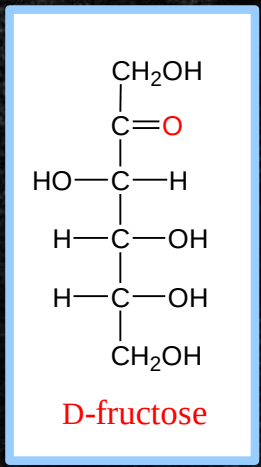
Carbohydrates "Saccharides"
"Carbo" & "Hydrate"

$(CH_2O)_n$ or 

- Glycans with basic formula (n varies from 3-8)
- It is a polyhydroxy (aldehyde) or (ketone), or a substance that gives these compounds on hydrolysis
- Monosaccharide: a carbohydrate that cannot be hydrolyzed to a simpler one
- Aldoses vs. ketoses: glyceraldehyde & dihydroxyacetone are the simplest





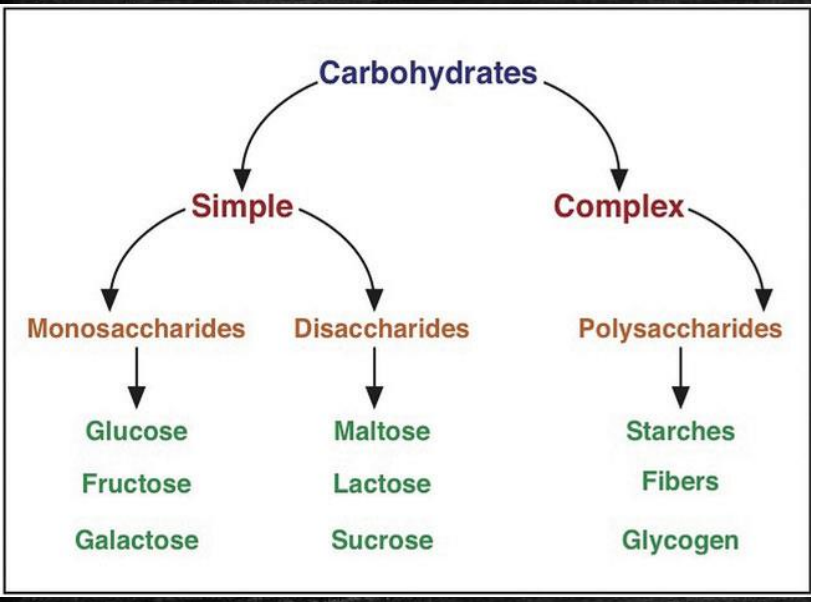


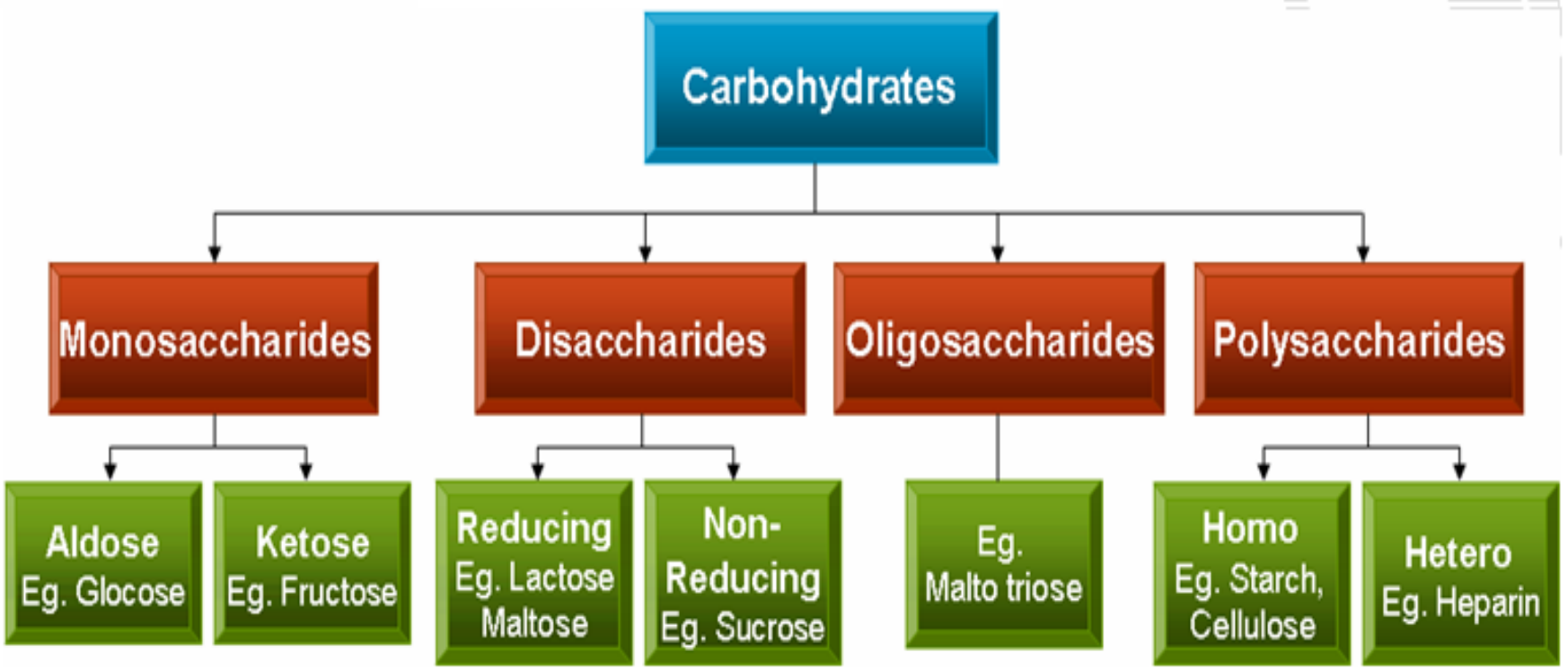
Structural Forms

- Monosaccharides – carbohydrates that cannot be hydrolyzed to simpler carbohydrates (glucose or fructose)
- Disaccharides – carbohydrates that can be hydrolyzed into two monosaccharide units (sucrose → glucose & fructose)
- Oligosaccharides (3 to 10 units) – carbohydrates that can be hydrolyzed into a few monosaccharide units (fructo-oligosaccharides (FOS) found in many vegetables, Raffinose)
- Polysaccharides – carbohydrates that are polymeric sugars (starch or cellulose)

Natural Forms

- Most carbohydrates are found naturally in bound form rather than as simple sugars
  - Polysaccharides (starch, cellulose, inulin, gums)
  - Glycoproteins and proteoglycans (hormones, blood group substances, antibodies)
  - Glycolipids (cerebrosides, gangliosides)
  - Glycosides
  - Mucopolysaccharides (hyaluronic acid)
  - Nucleic acids (DNA, RNA)



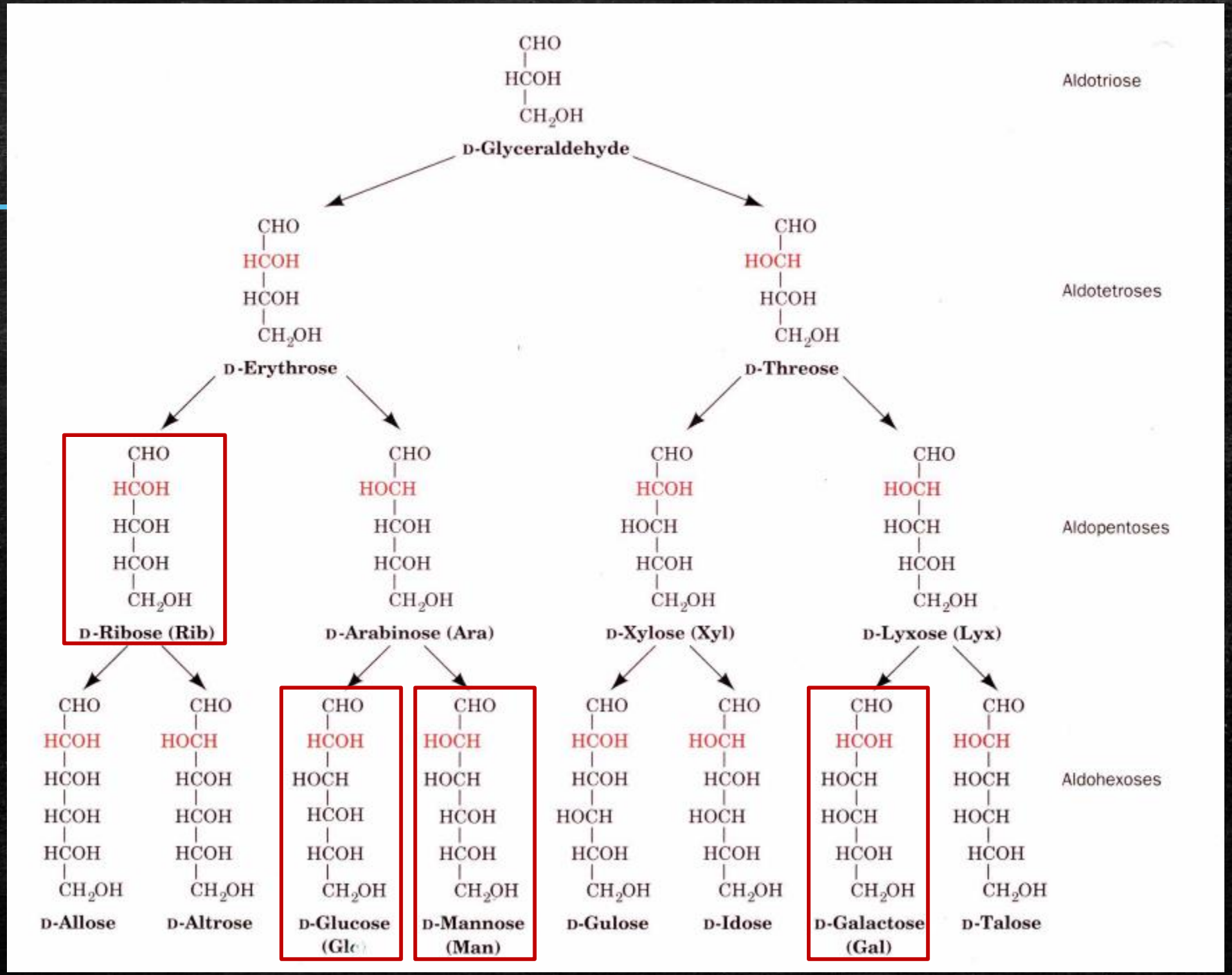


Classification

Carbon Atoms	General terms	Aldehydes	Ketones
3	Triose	Aldotriose	Keto triose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose
7	Heptose	Aldoheptose	Ketoheptose

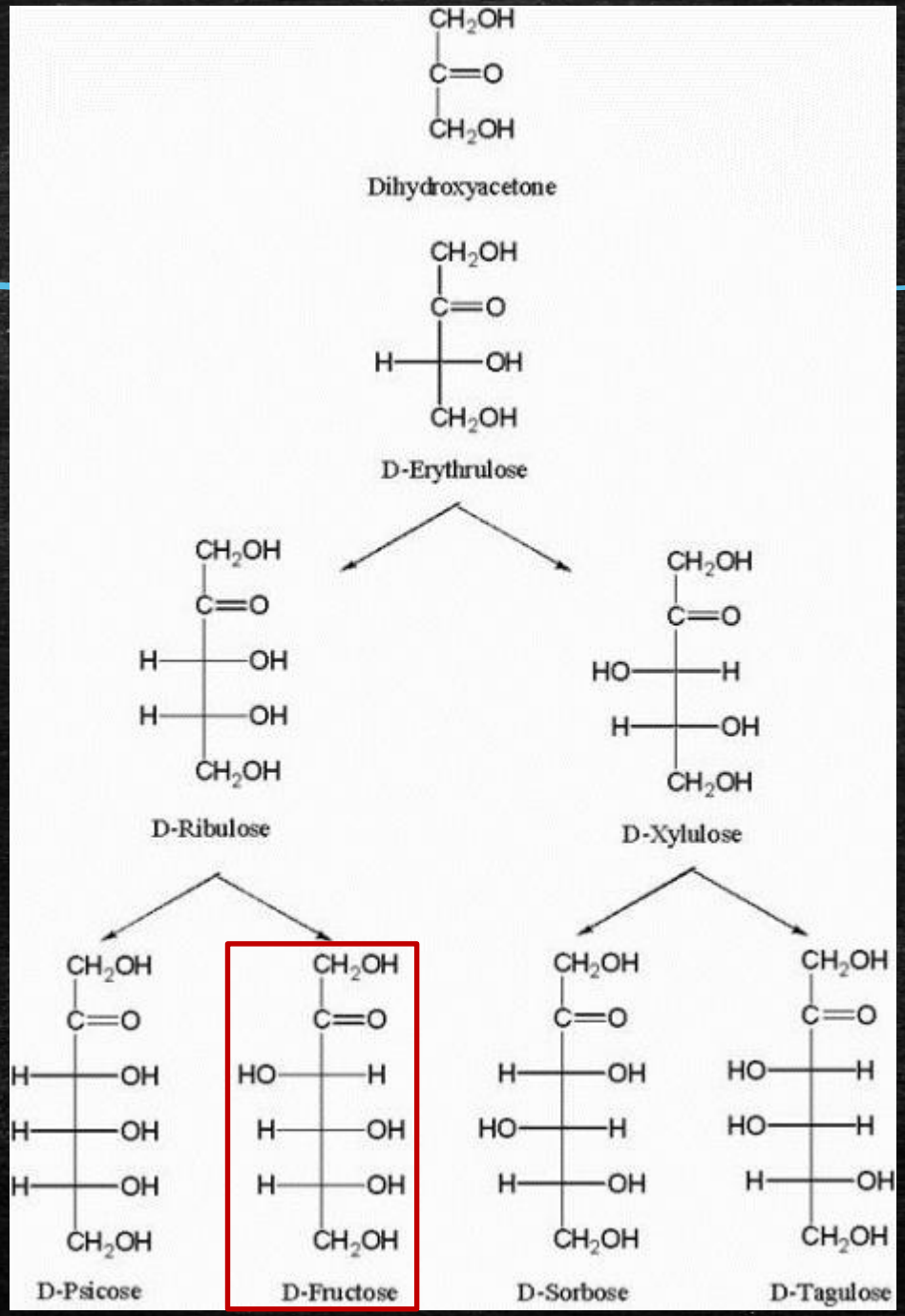
Aldoses

Classification



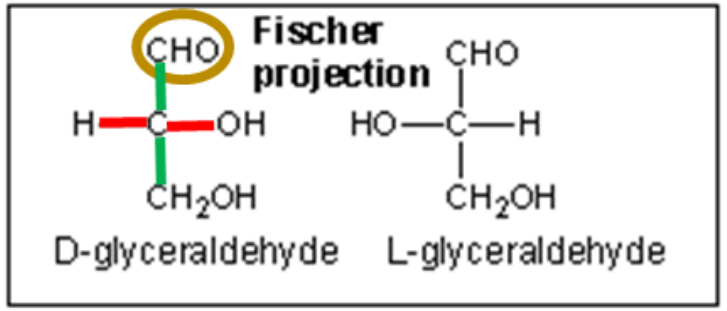
Ketoses

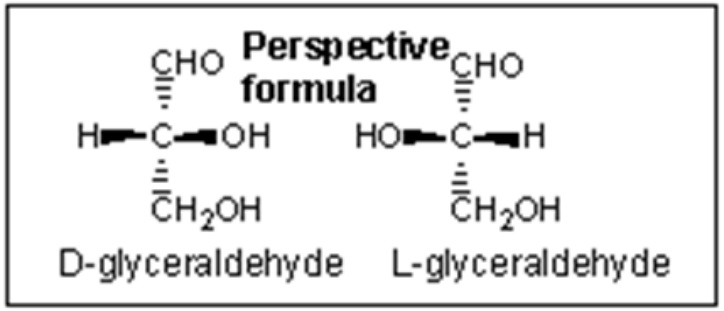
Classification



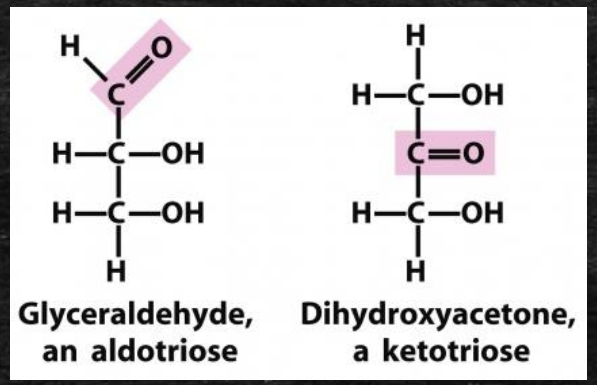
Monosaccharides

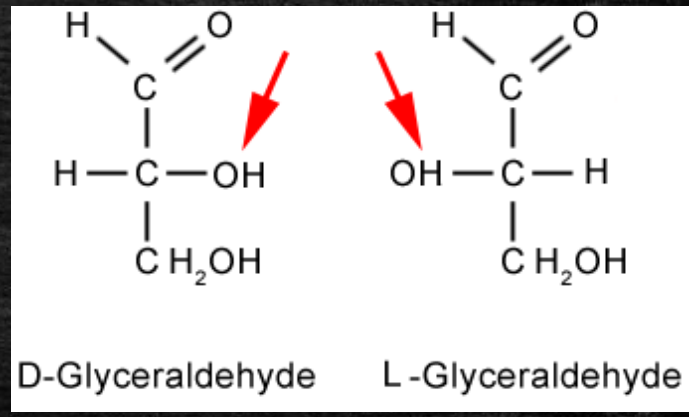
- Basic chemical formula: $(CH_2O)_n$
- Stereocenters
- D or L
- D sugars predominate in nature
- The 2-D representation (Fischer Projections)

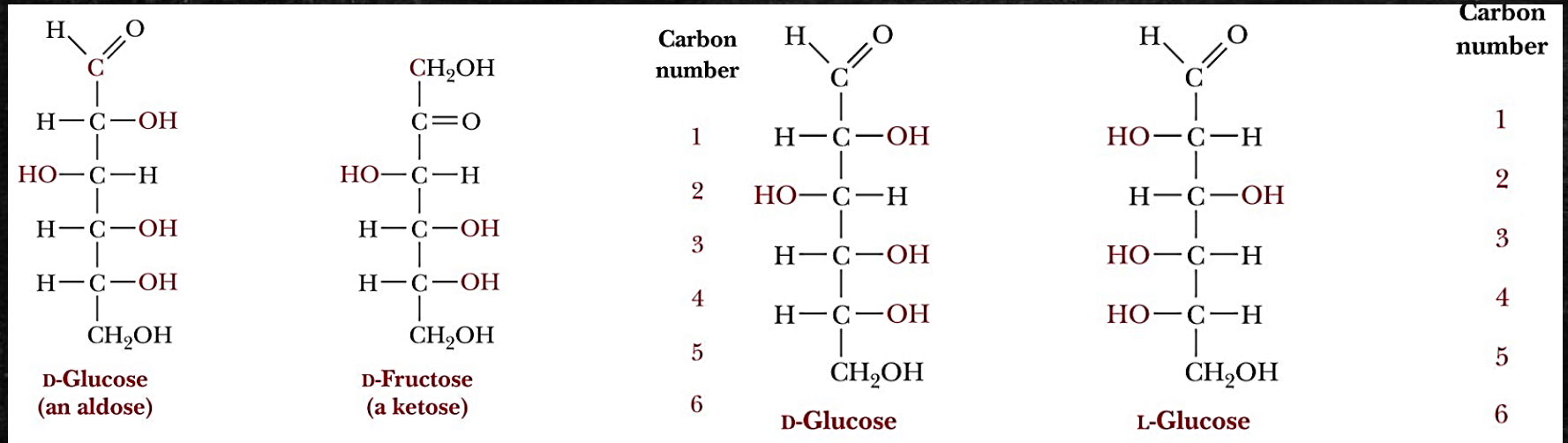


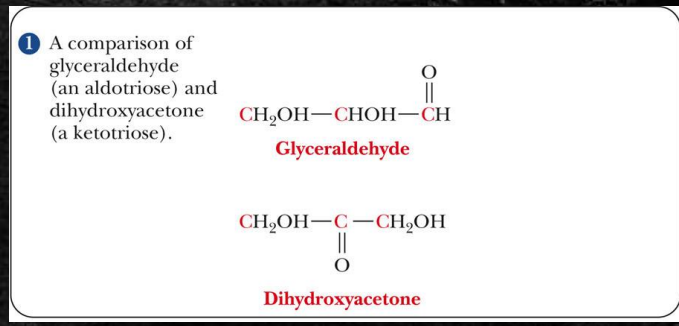


Forward | Backward | Top (C1): Most highly oxidized C



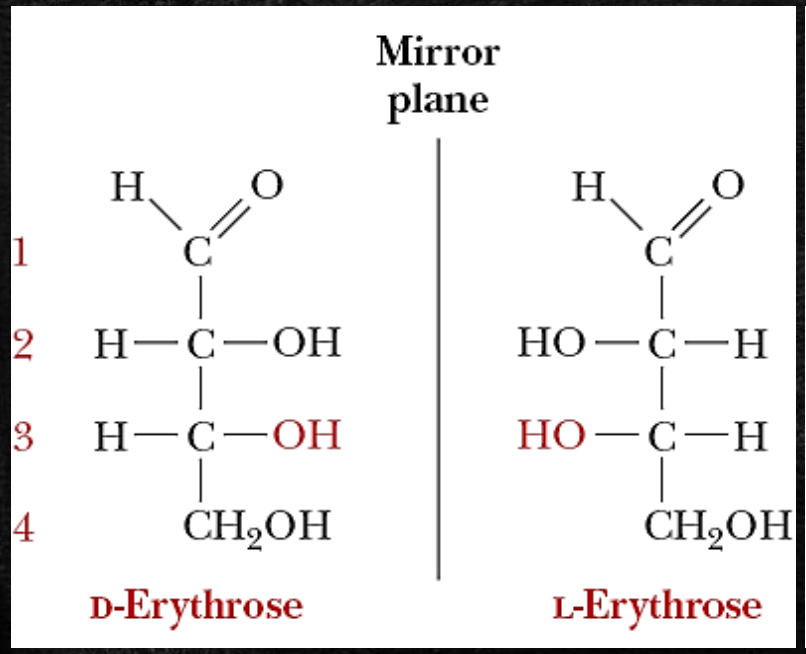


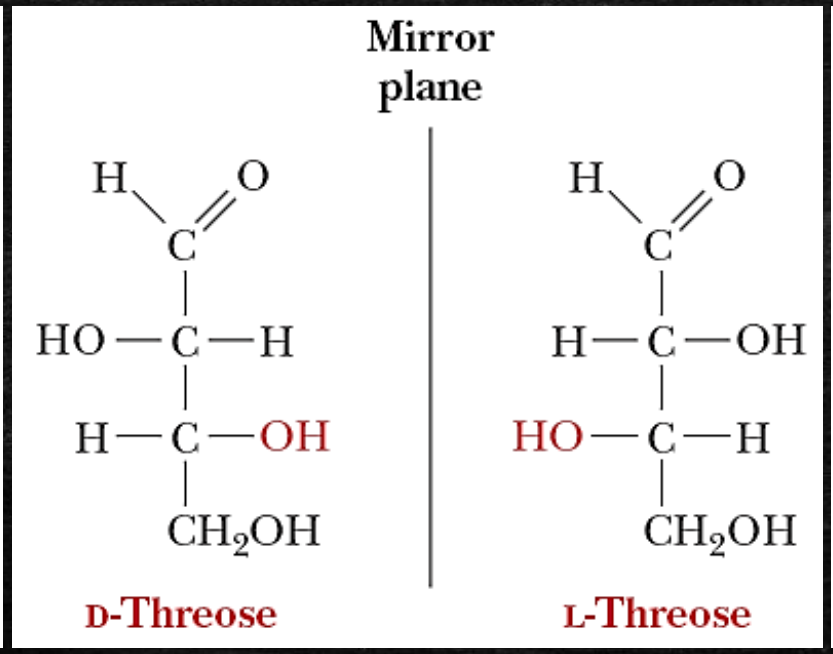


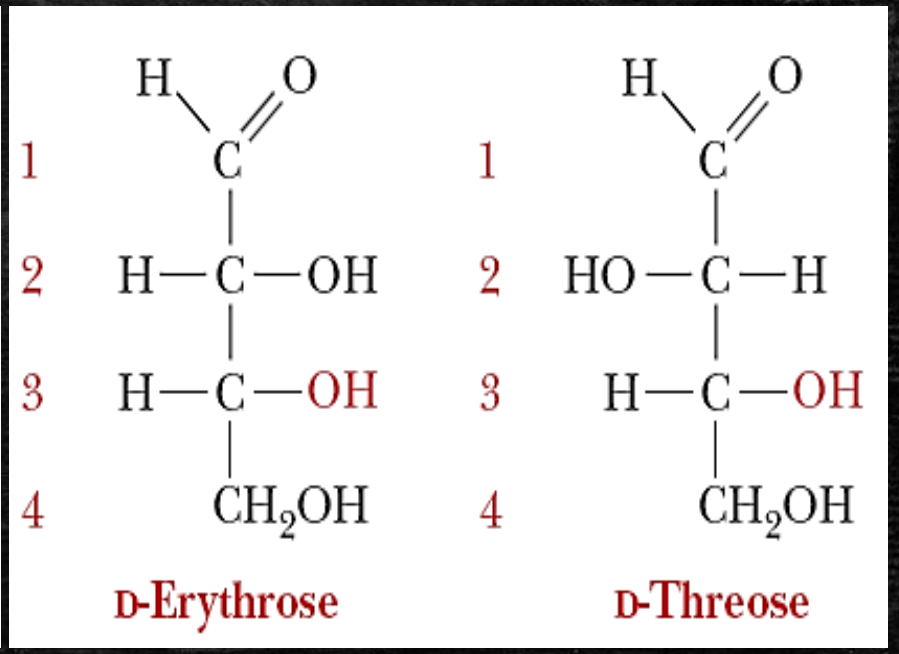


Aldotetroses

- D-erythrose & L-erythrose (enantiomers)
- D-erythrose & D-threose (diastereomers)

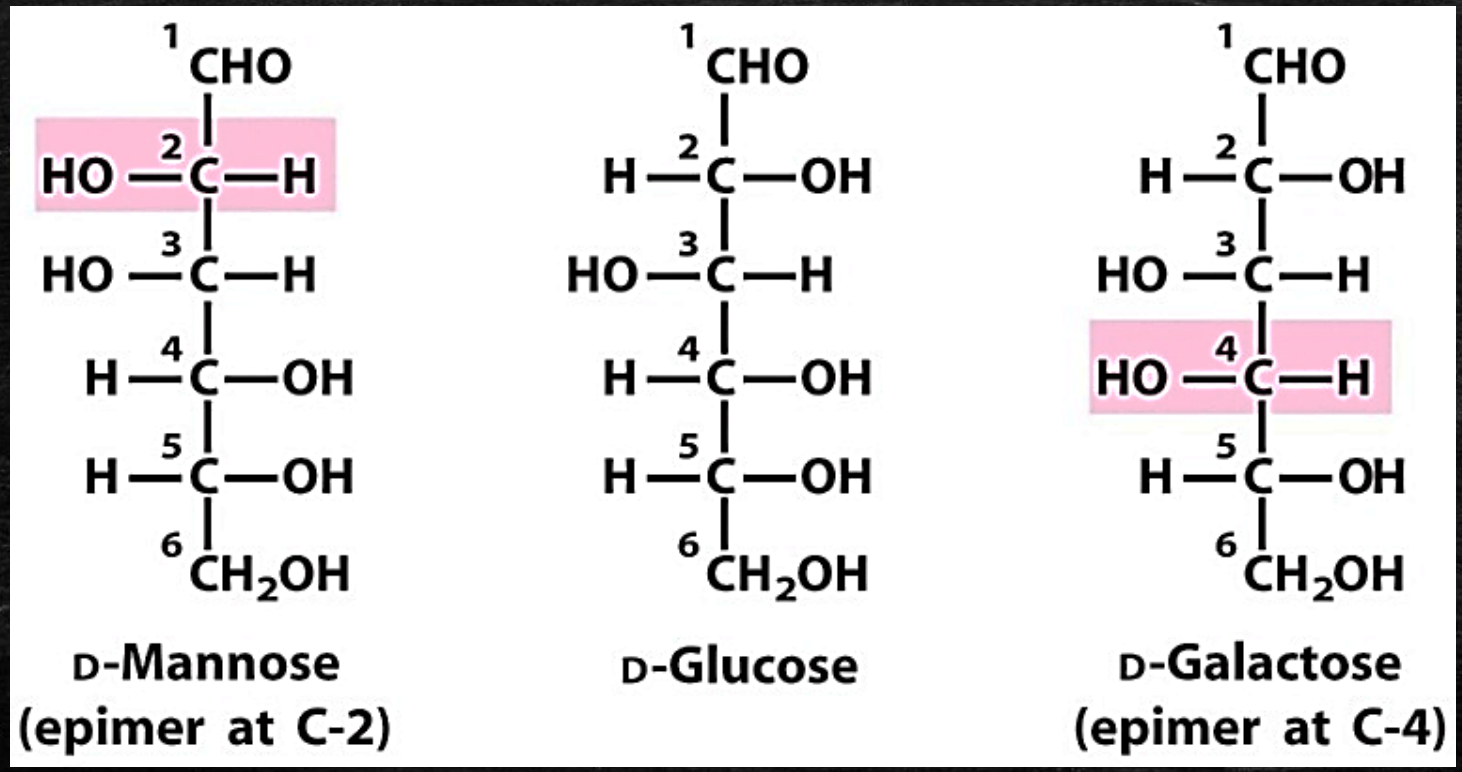




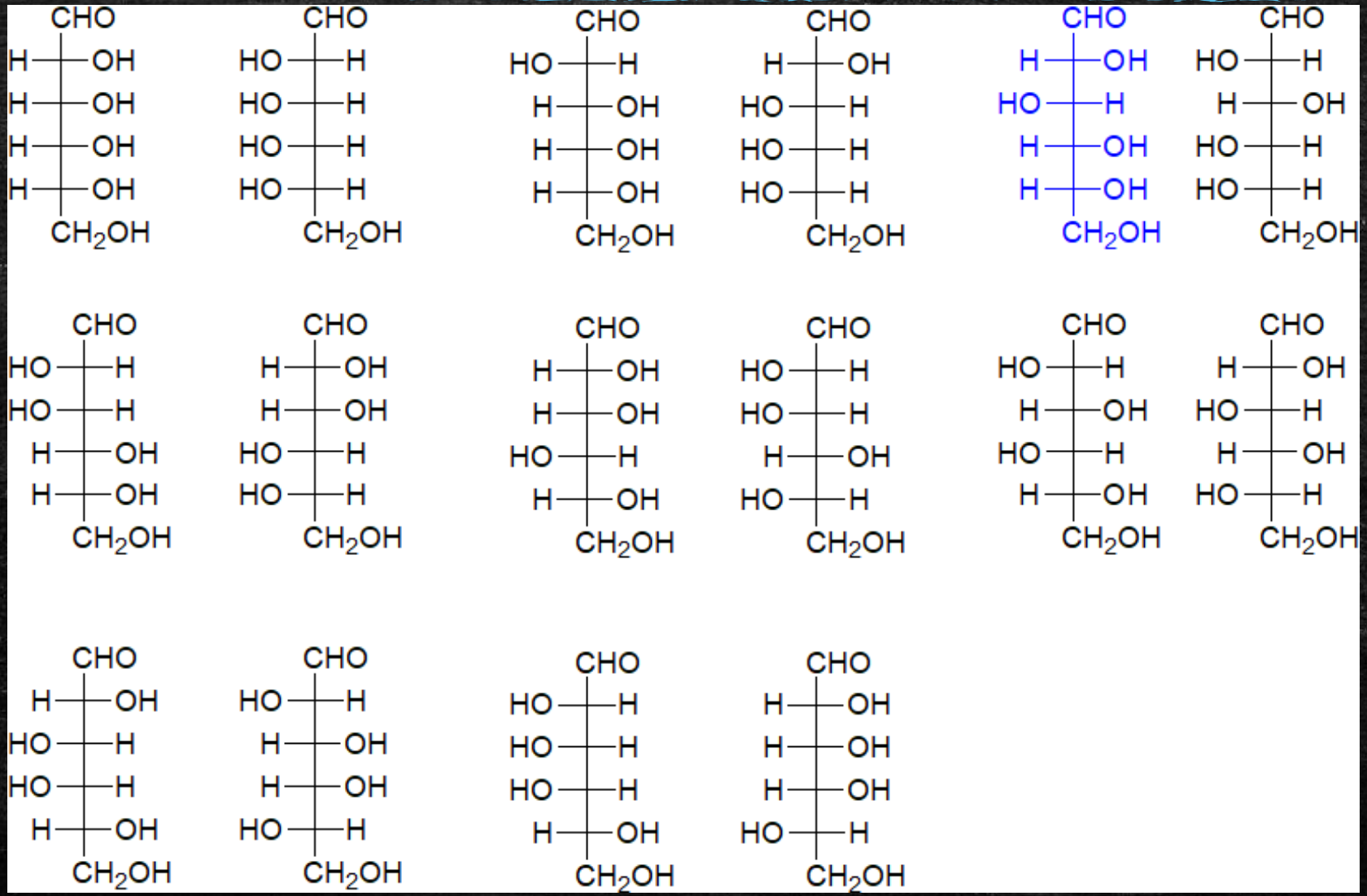


Pentoses & Hexoses

- Most of the sugars we encounter in nature, especially in foods
- Aldopentoses & Aldohexoses (how many chiral carbons? How many stereoisomers?) 2^n

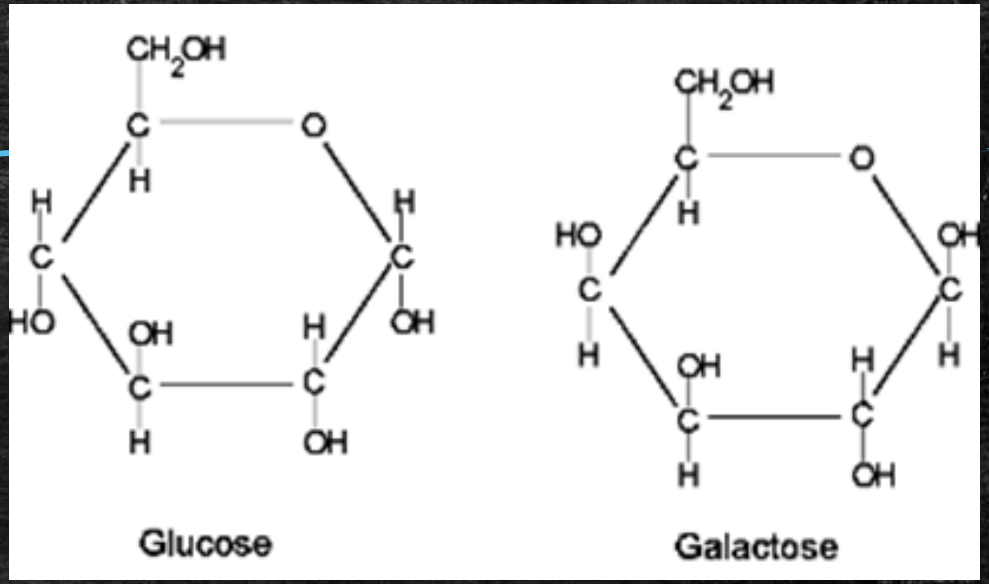


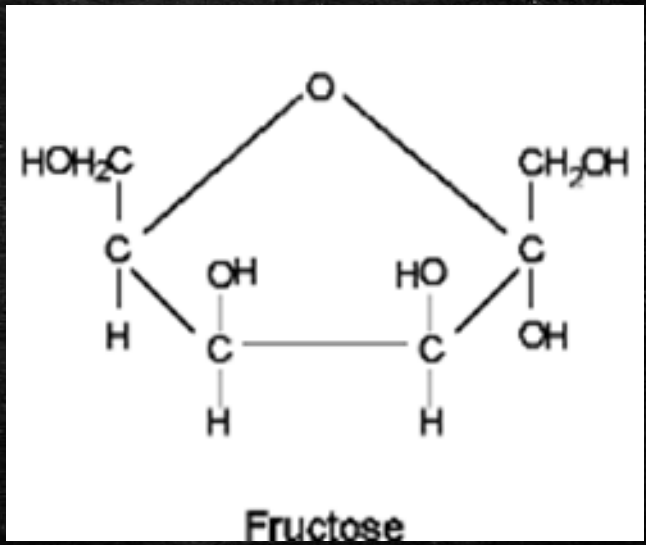
Glucose Isomers



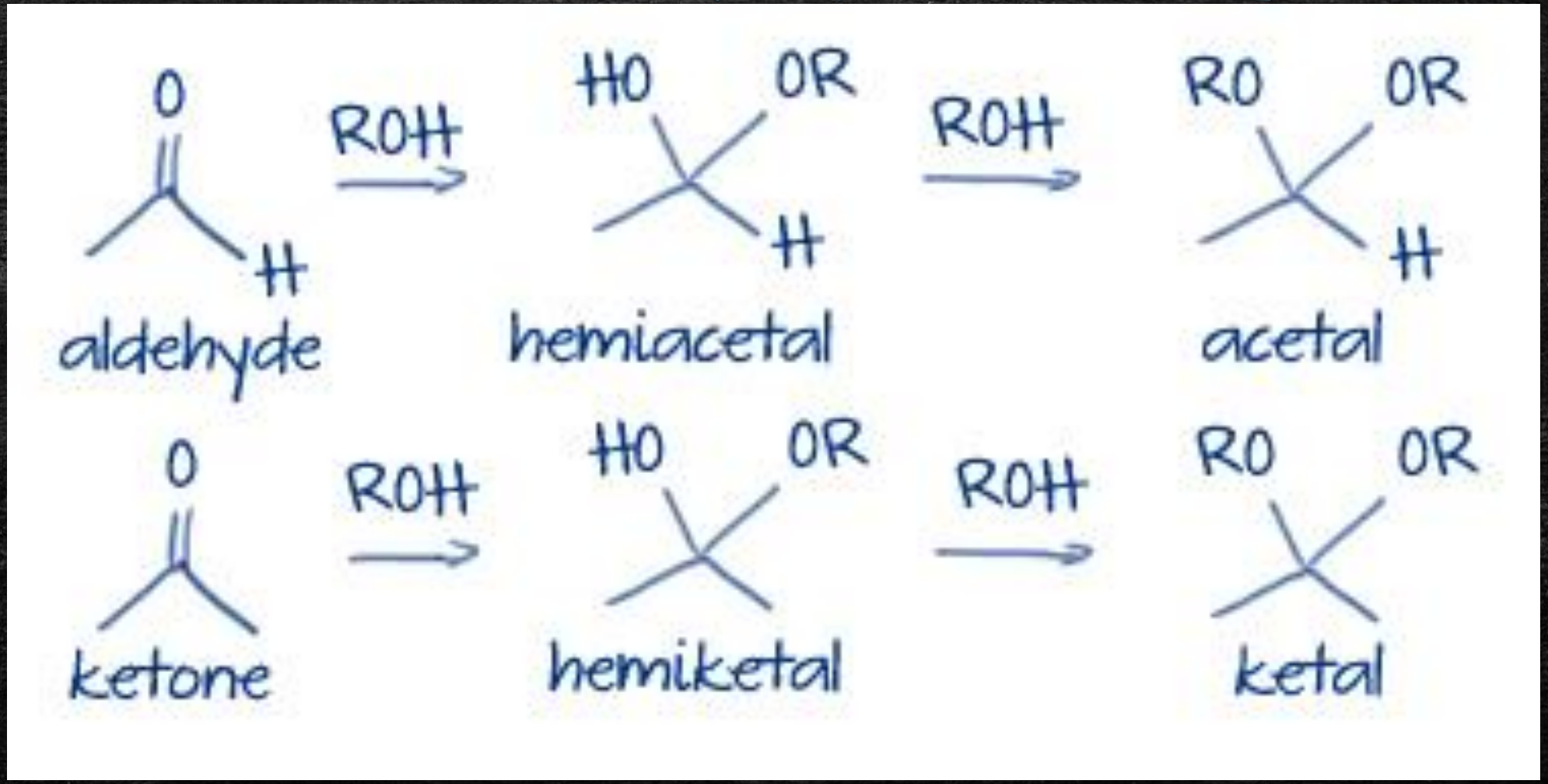
Common Monosaccharides

- Glucose:
  - Mild sweet flavor
  - Known as blood sugar
  - Essential energy source
  - Found in every disaccharide and polysaccharide
- Galactose:
  - Hardly tastes sweet & rarely found naturally as a single sugar
- Fructose:
  - Sweetest sugar, found in fruits and honey
  - Added to soft drinks, cereals, desserts



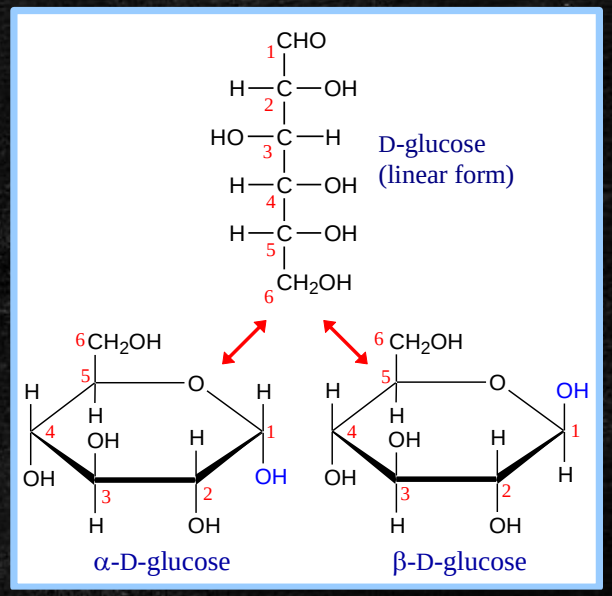


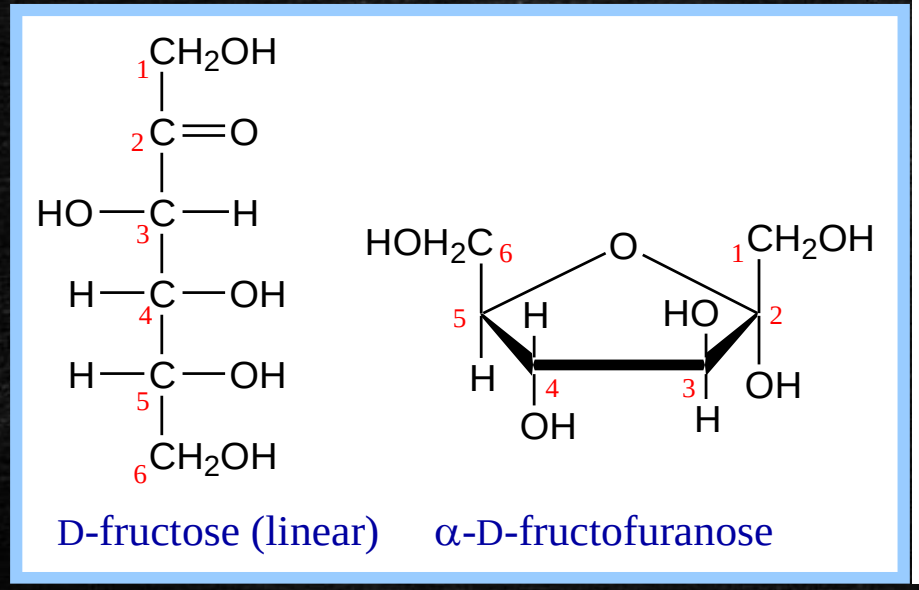
Cyclization of sugars

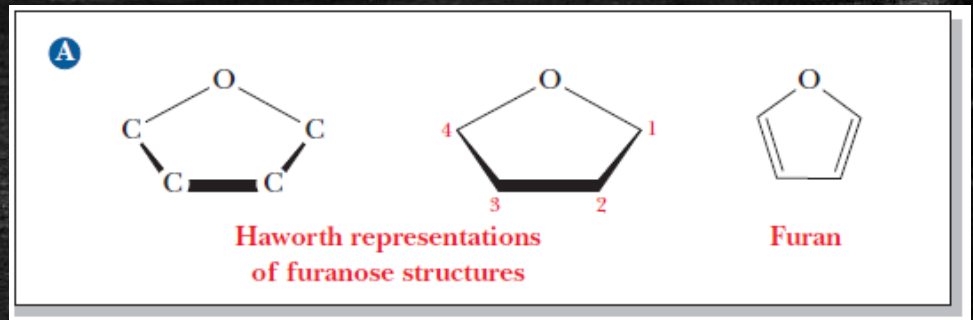


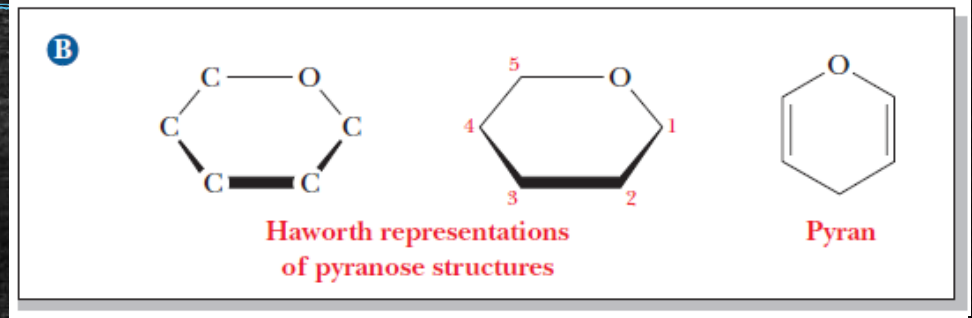
Cyclization of sugars

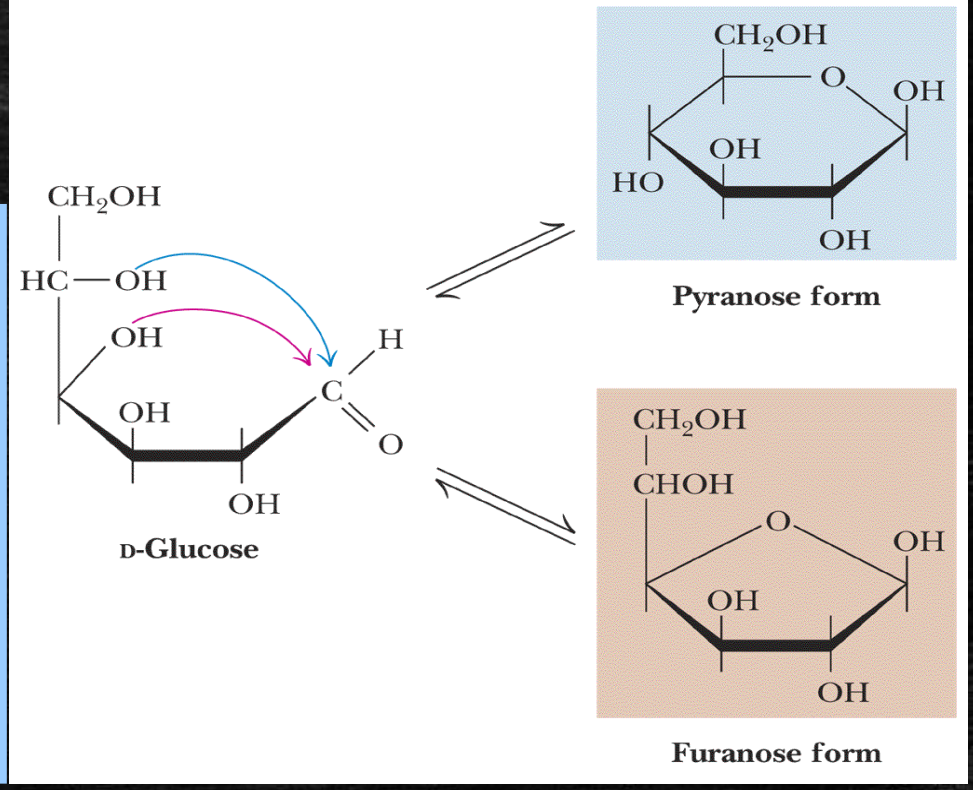
- In the cell 99% of pentoses and hexoses are in the ring form
- **Haworth Projection**: the carbonyl carbon is a new chiral center and becomes an anomeric carbon
- Anomers: differ only at their anomeric carbon, either **α or β (equilibrium)**



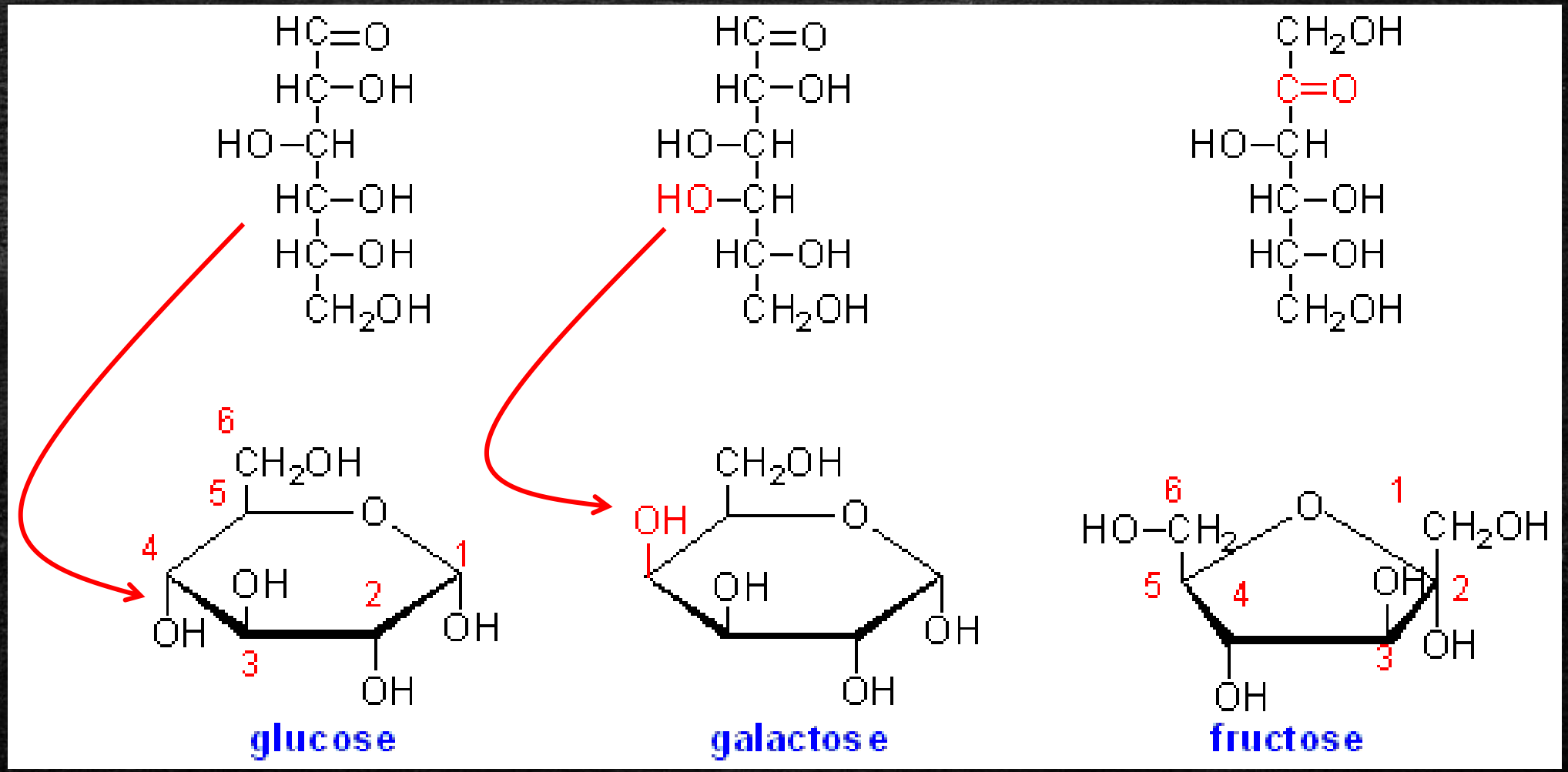








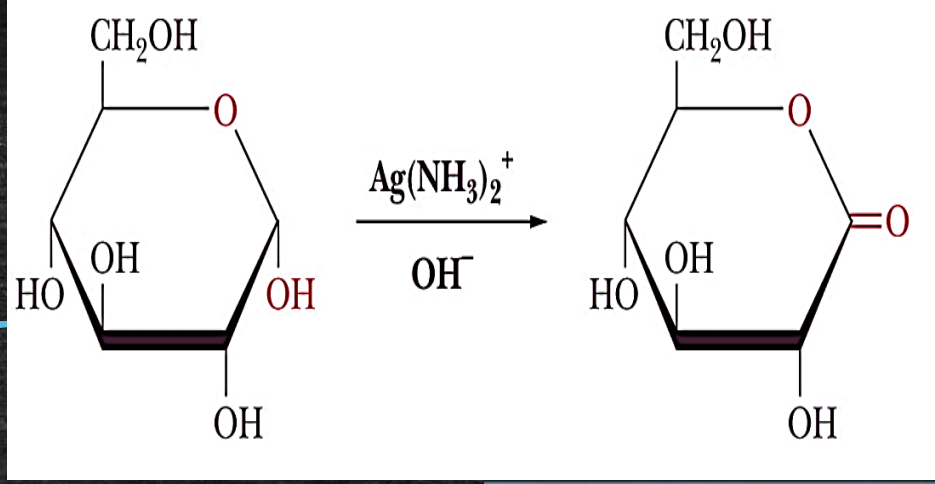
Chain to ring
Left-up, right-down



Reactions of monosaccharides – modified sugars

- Oxidation
- Reduction
- Esterification
- Glycosidic bond formation

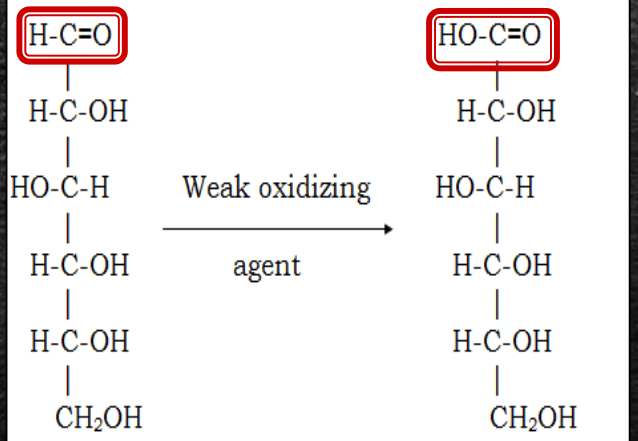
Oxidation



- Oxidation of a cyclic hemiacetal form gives a lactone
- Reducing sugars
- Tollens solution (oxidizing agent); silver ammonia complex ion, $Ag(NH_3)^{2+}$
- Specific for glucose: detection of glucose, but not other reducing sugars, is based on the use of the enzyme glucose oxidase

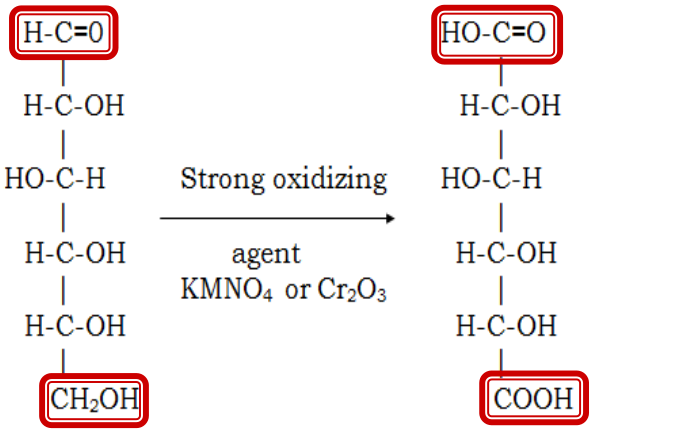
Oxidation - Naming

a. Weak oxidizing agent

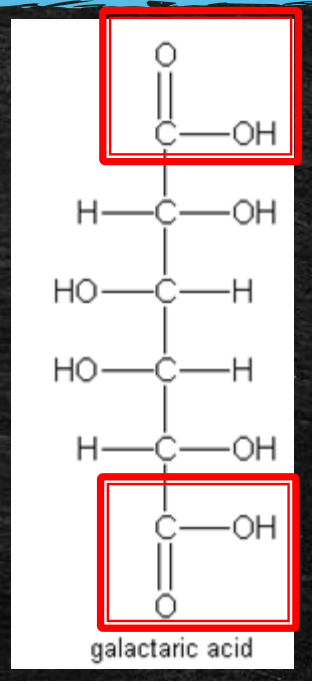


--onic acid

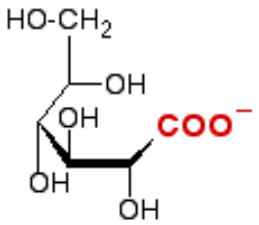
b. Strong oxidizing agents



-aric acid
A dicarboxylic acid

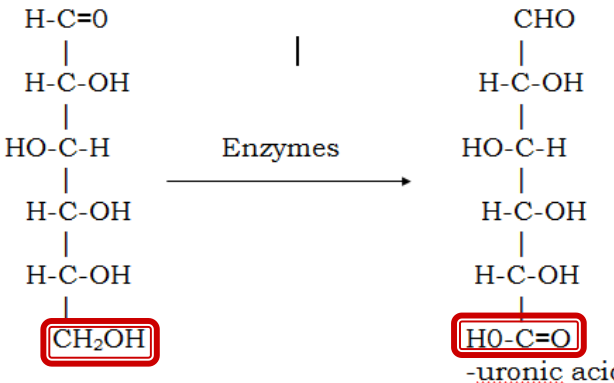


galactaric acid

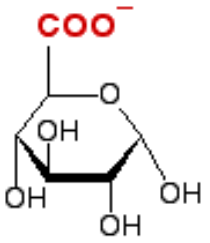


D-gluconate
(D-gluconic acid, **GlcA**)
from **oxidation of glucose C1 aldehyde)**

c. Oxidation of primary alcohol end in biological systems



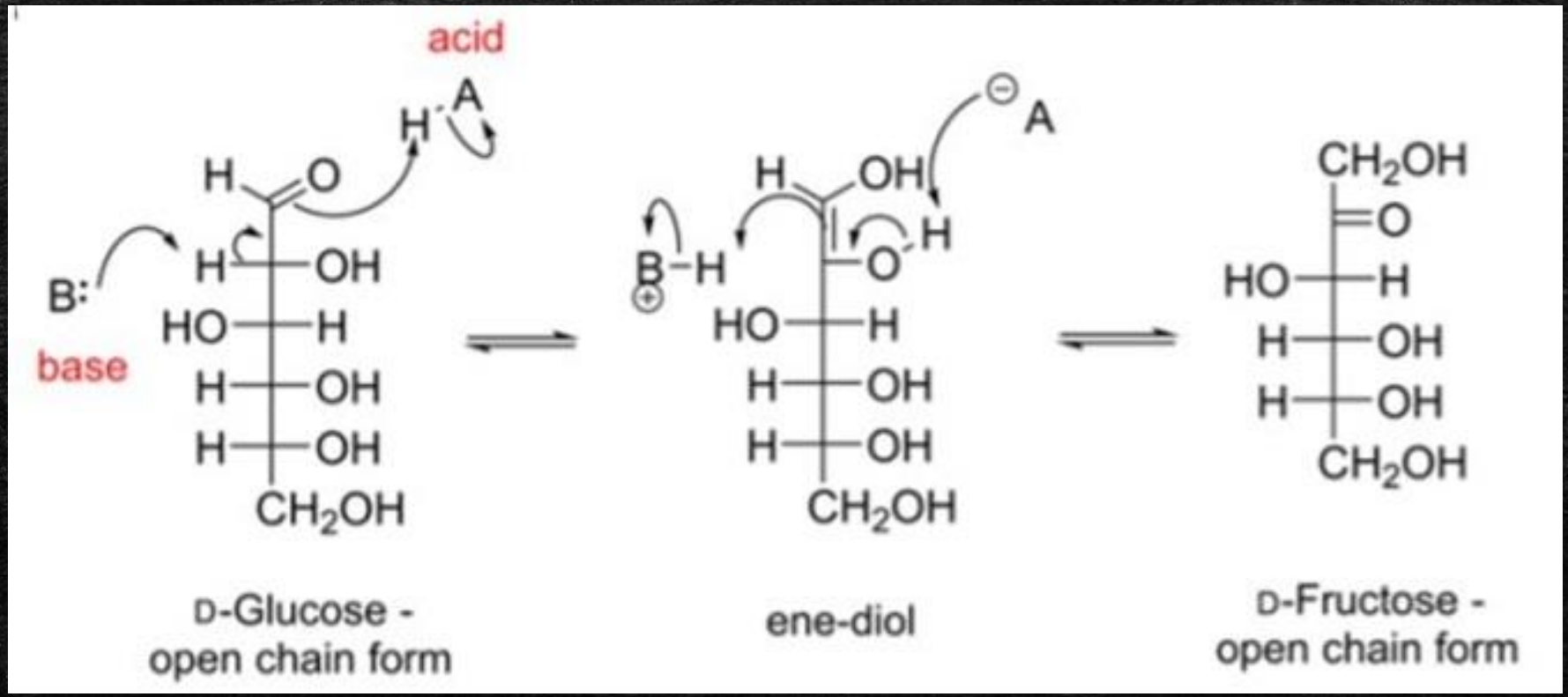
-uronic acids



α-D-glucuronate
(D-glucuronic acid, **GlcUA**)
from **oxidation of glucose C6 OH**

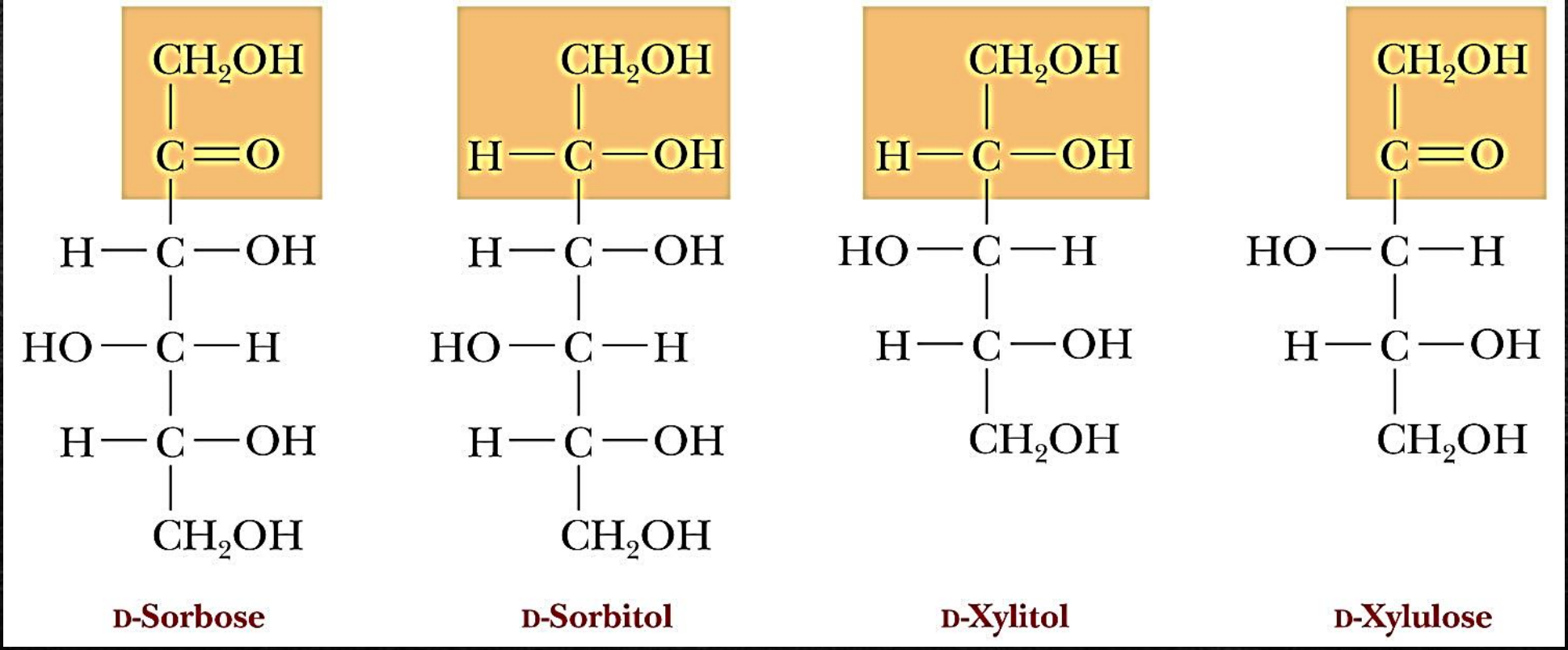
Note

- Oxidation of ketoses to carboxylic acids does not occur, but they can be oxidized because of formation of ene-diol form



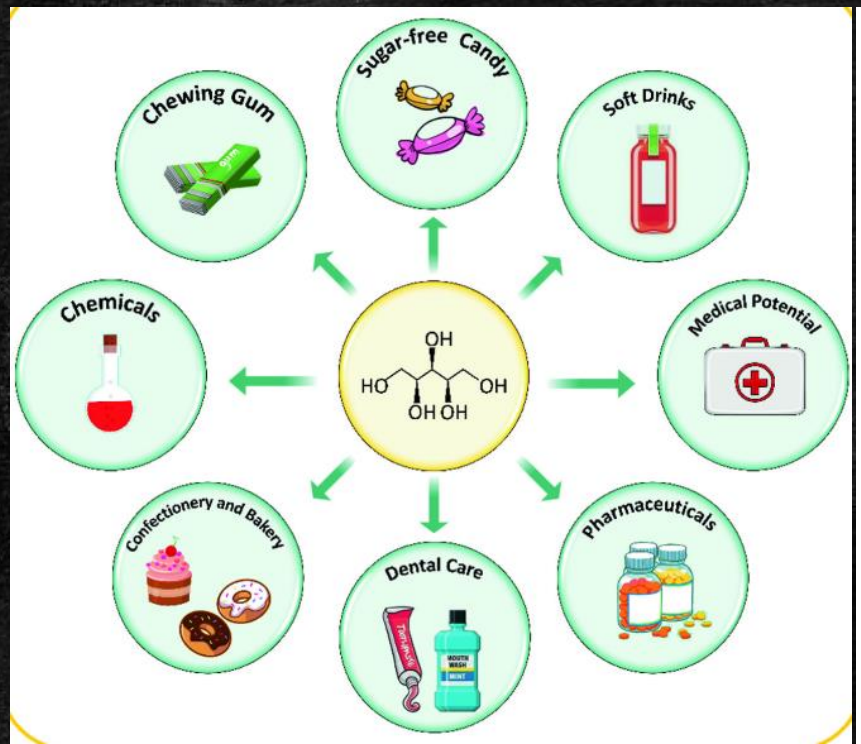
Reduction

- Xylitol & sorbitol: derivatives of xylulose & sorbose, have commercial importance (sweeteners in sugarless chewing gum & candy)



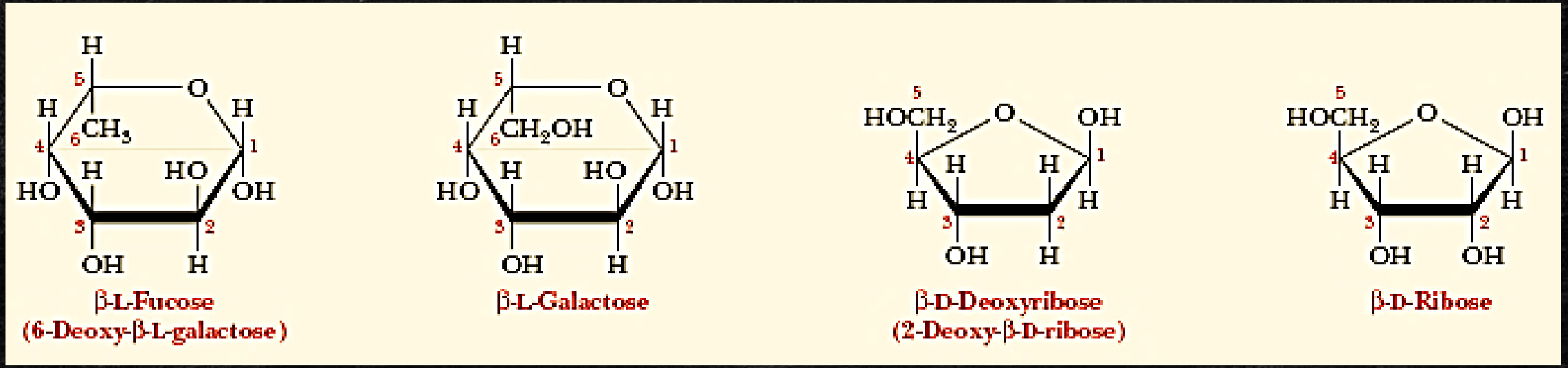
Xylitol, sorbitol, and mannitol (sugar alcohols)

- Sweetners, cosmotics and personal care (absorb moisture), pharmaceuticals (Antihypertensive drugs, diuretics)

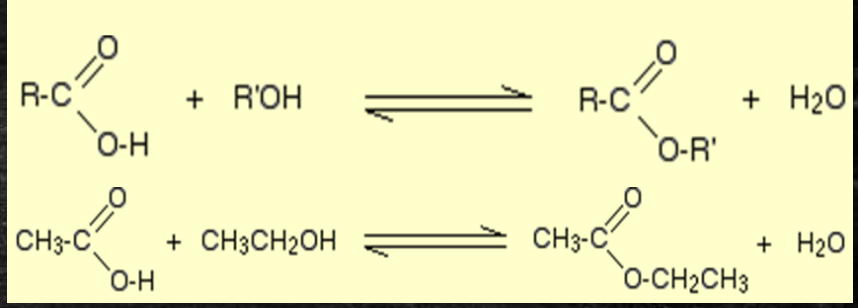


Reduction

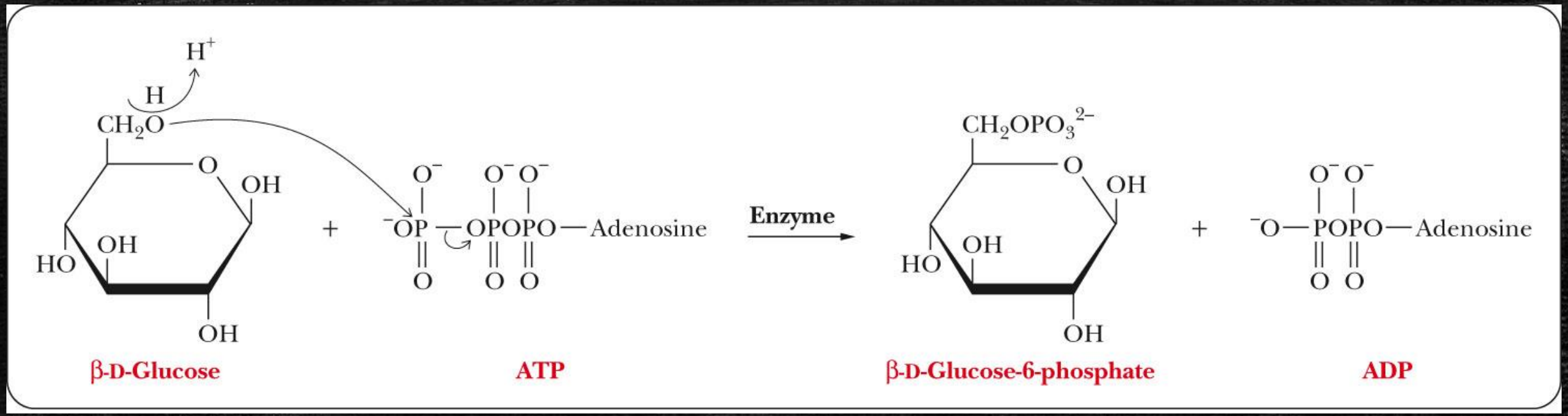
- L-fucose (L-6-deoxygalactose): some glycoproteins including the ABO blood-group antigens
- D-2-deoxyribose: in DNA



Esterification
Phosphoric Esters

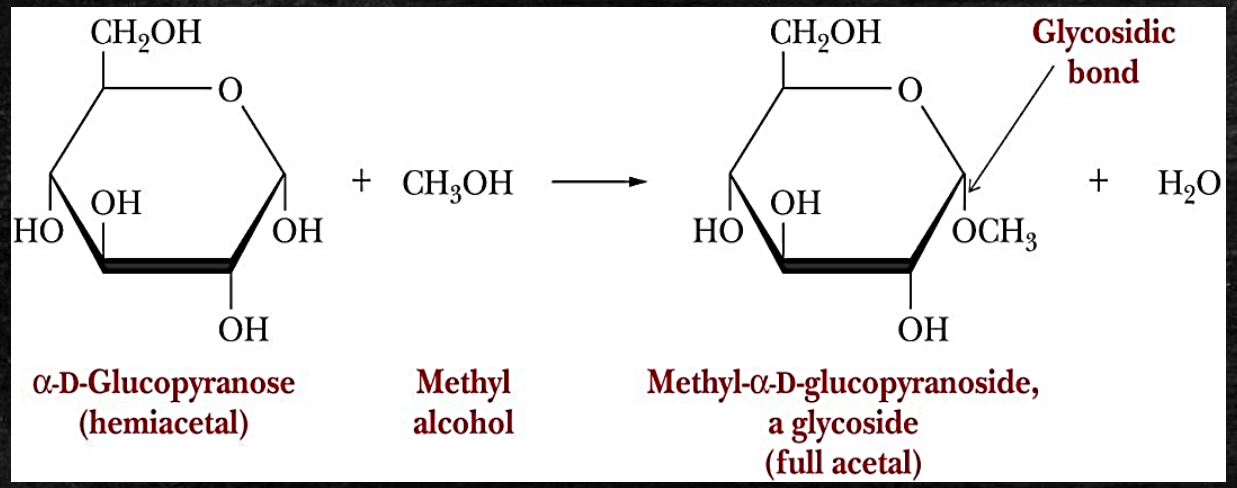


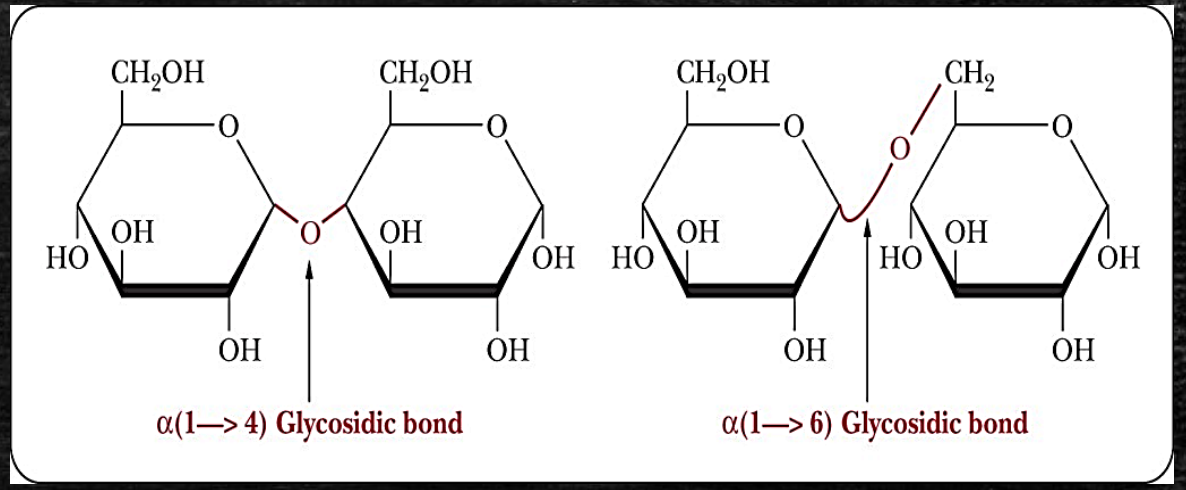
- Breakdown of carbohydrates to provide energy
- Frequently formed by transfer of a phosphate group from ATP



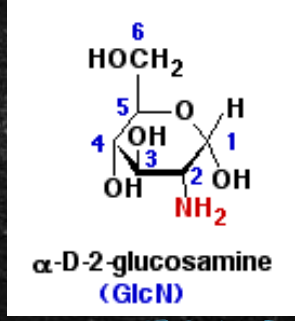
Glycosidic Bond Formation
formation of full acetal

- The -OH of the anomeric carbon is replaced by –OR
- Glycosidic bond: bond from the anomeric carbon to the -OR group
- This type of reaction involves the anomeric carbon of the sugar in its cyclic form
- This is the basis for the formation of (di/oligo/poly)saccharides





Glycosidic Bond Formation



glycosidic link

anomeric carbon

glycosidic bond

Anomeric carbon

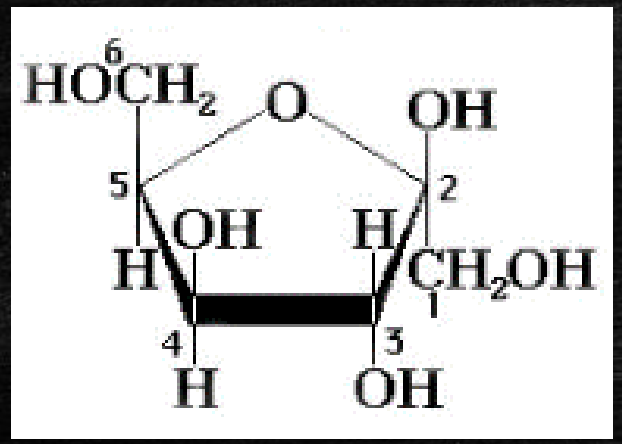
N-glycoside

N-Acetyl-β-D-glucosamine

N-Acetylmuramic acid

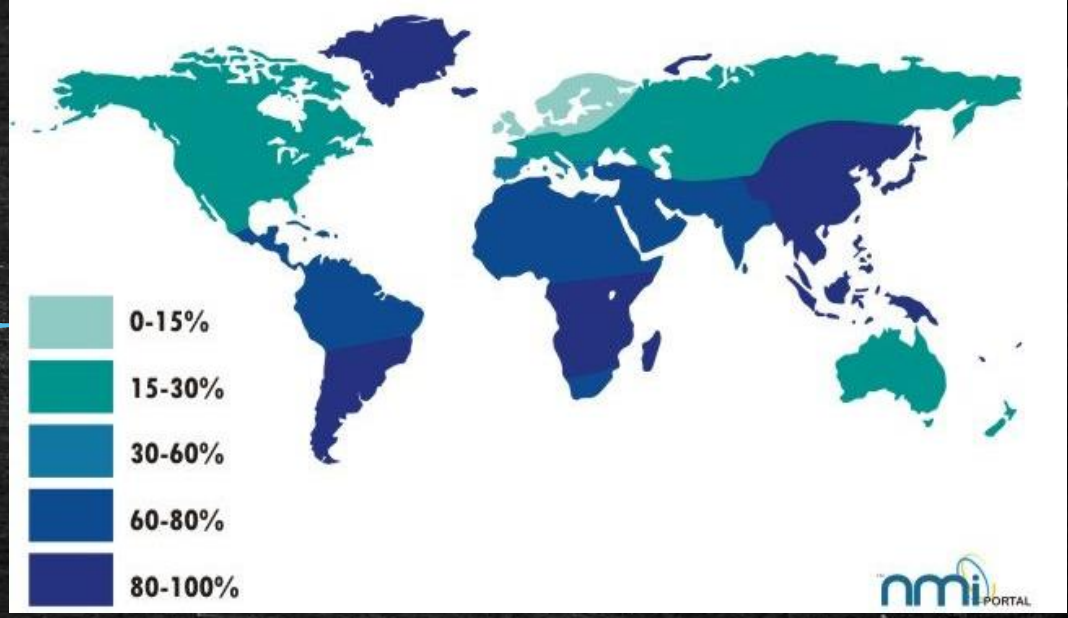
Disaccharides

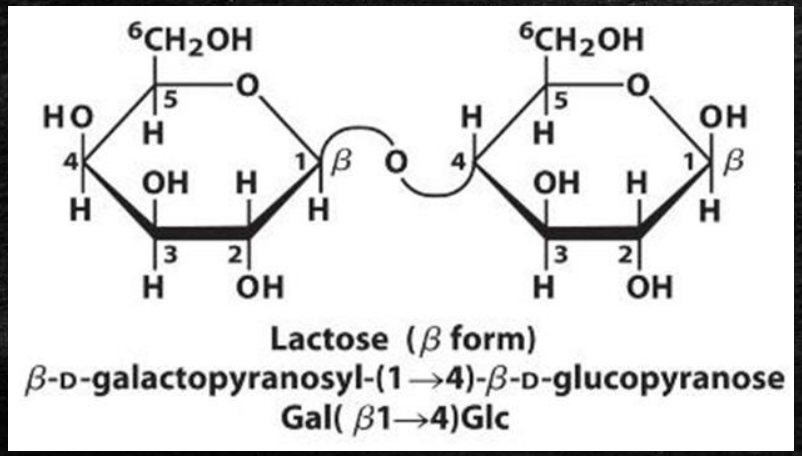
- Maltose is produced during the germination of seeds and fermentation
  - Formed from the hydrolysis of starch
- Sucrose is refined from sugarcane, tastes sweet, and is readily available
- Lactose is found in milk and milk products

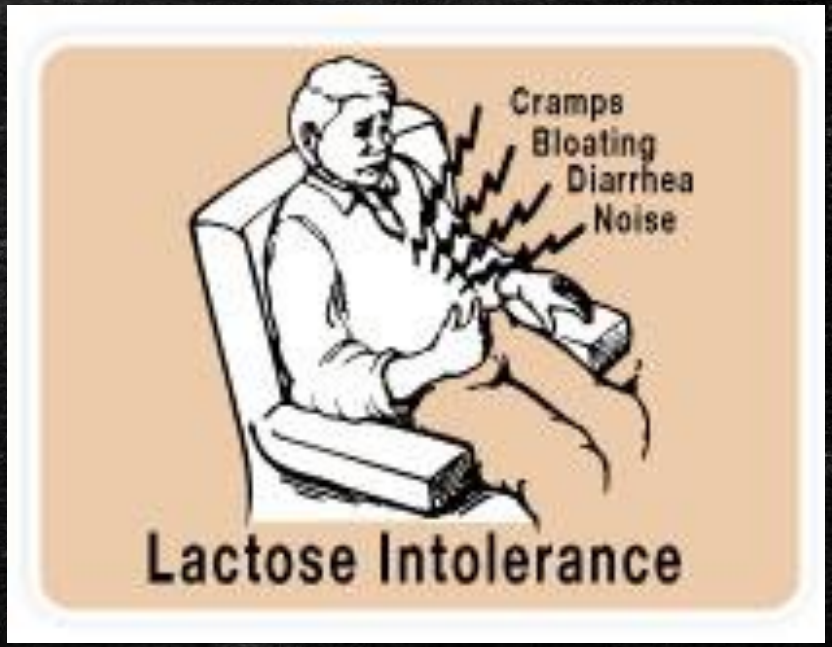


Lactose intolerance

- It is a condition caused by defective lactase
- lactose remains in the intestines & draws excess water
- Bacteria ferment lactose to produce CO_2 and methane
- Symptoms: bloating, cramps, flatulence, and diarrhea

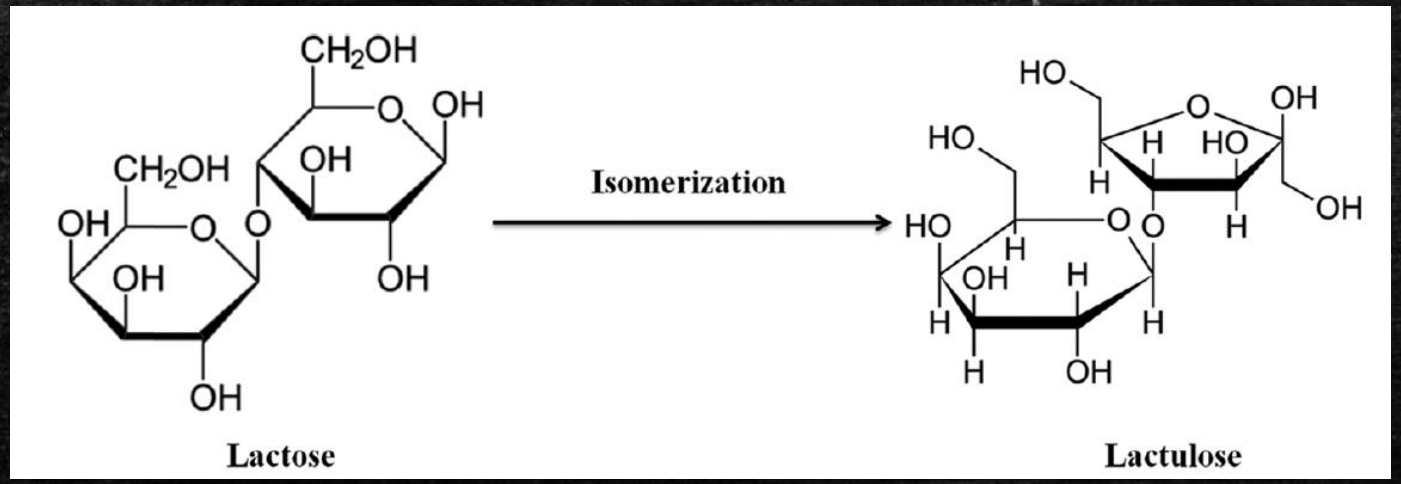


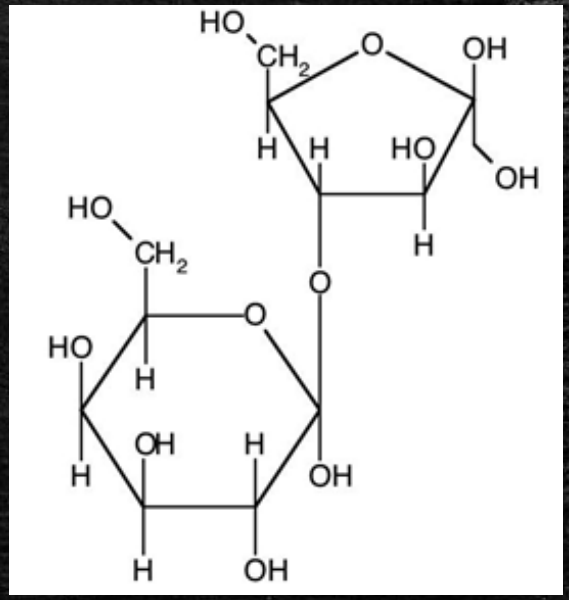




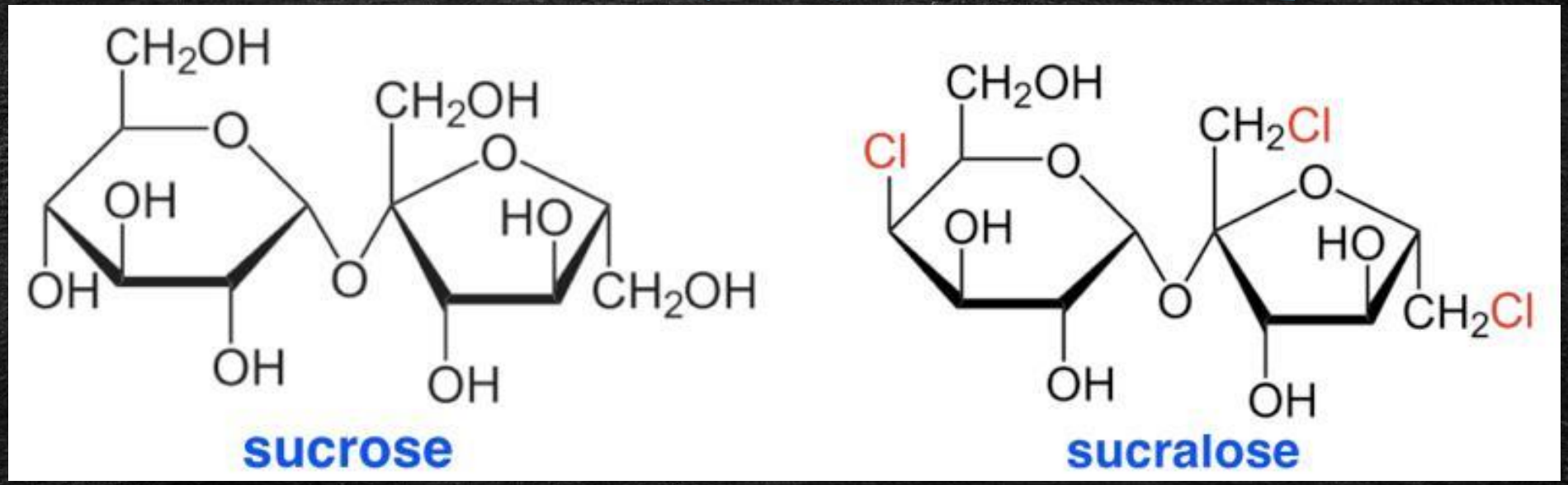
Lactulose

- Synthetic (isomerization)
- In medicine as an osmotic laxative (treatment of constipation)



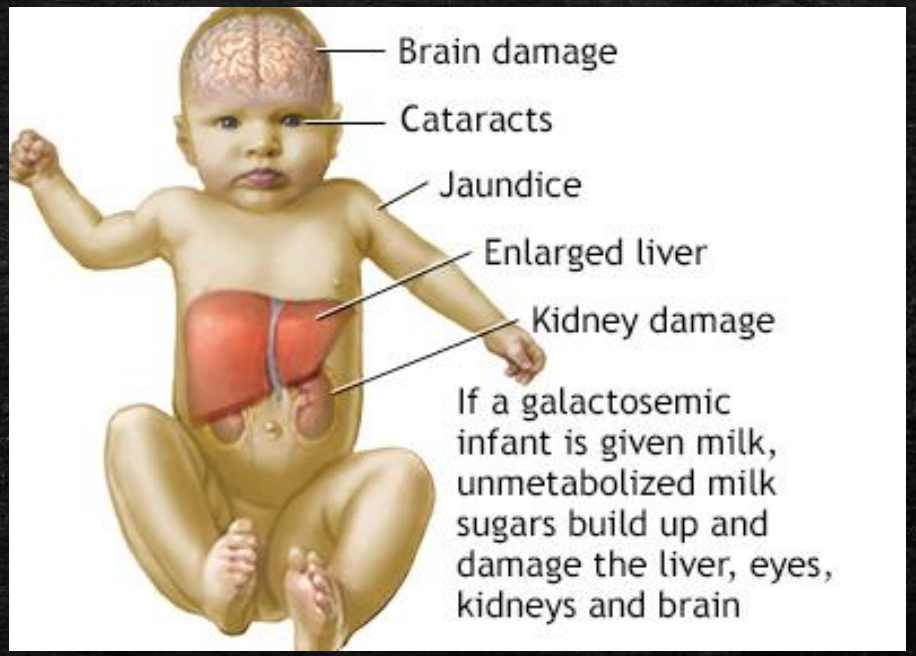


Sucralose (artificial sweetener)



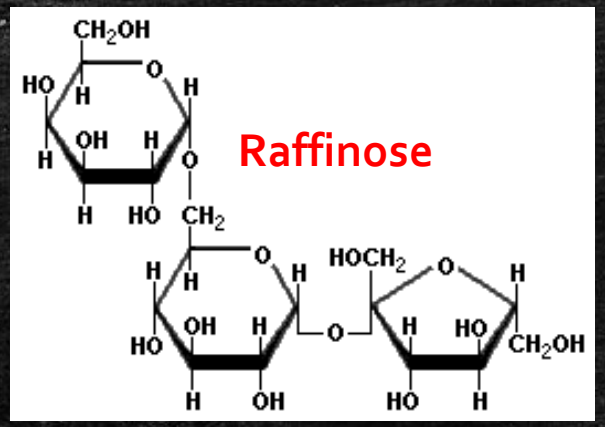
Galactosemia

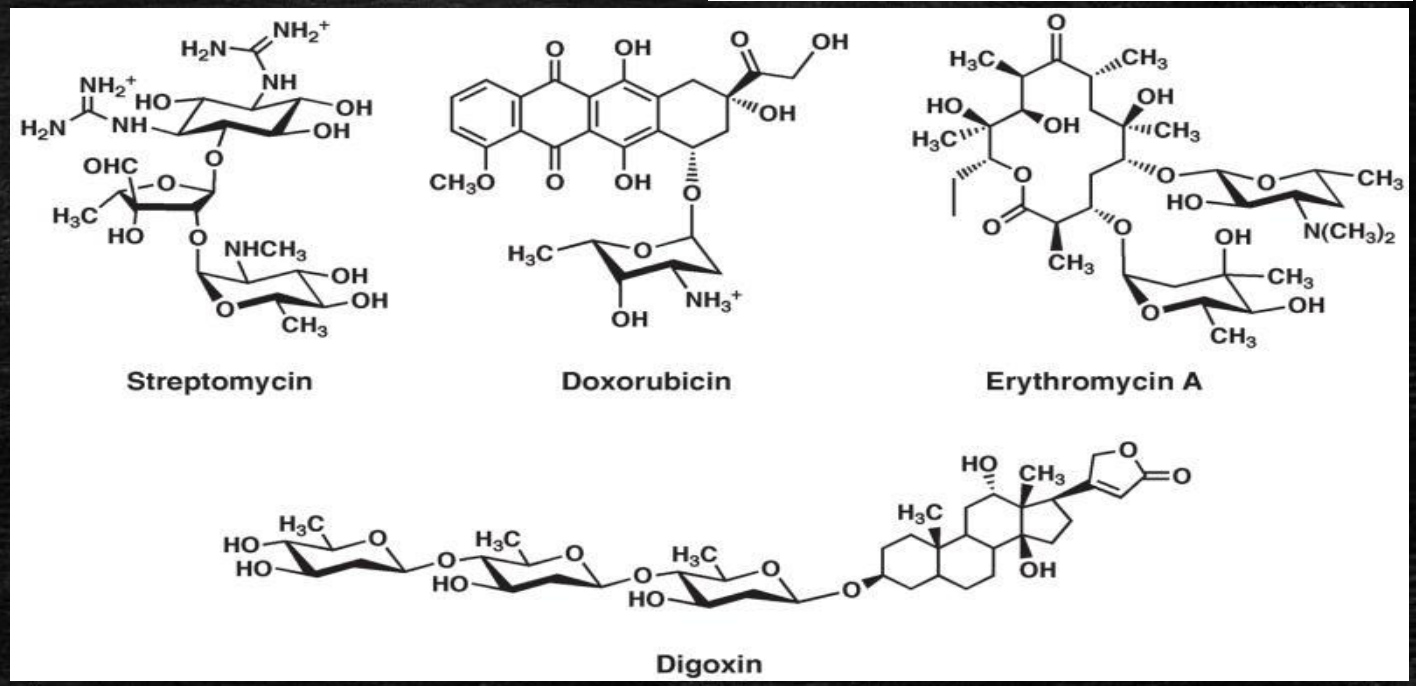
- Missing a galactose-metabolizing enzyme
- Converted to the hydroxy-sugar galactitol (cannot escape cells)
- Swelling and cell damage (brain; severe and irreversible retardation)
- Cataract



Oligosaccharides

- Raffinose; found in peas and beans
- Composed of galactose, fructose, and glucose



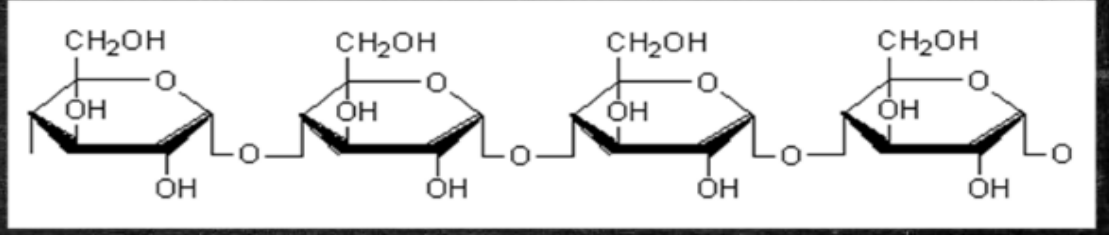


Polysaccharides

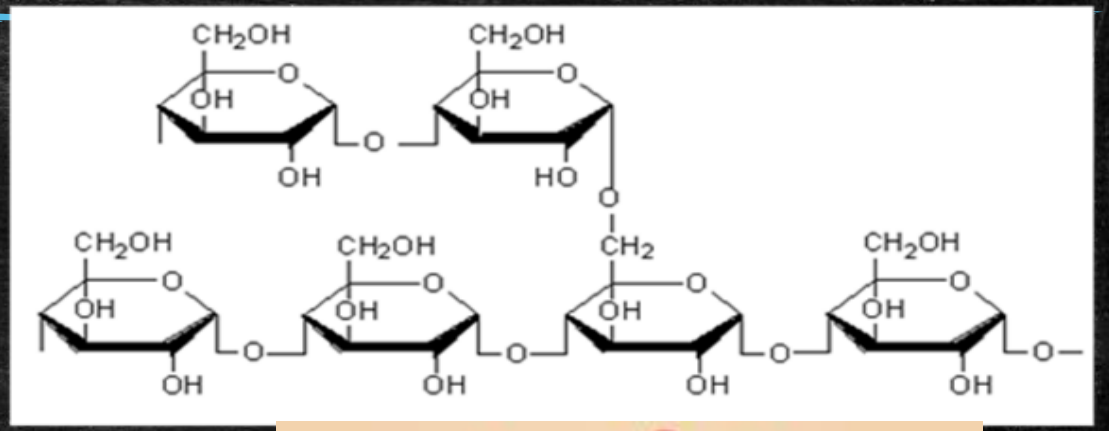
- Homopolysaccharide vs. Heteropolysaccharide
- Cellulose & chitin: β-glycosidic linkages
- Starch, glycogen, and dextran: α-glycosidic linkages

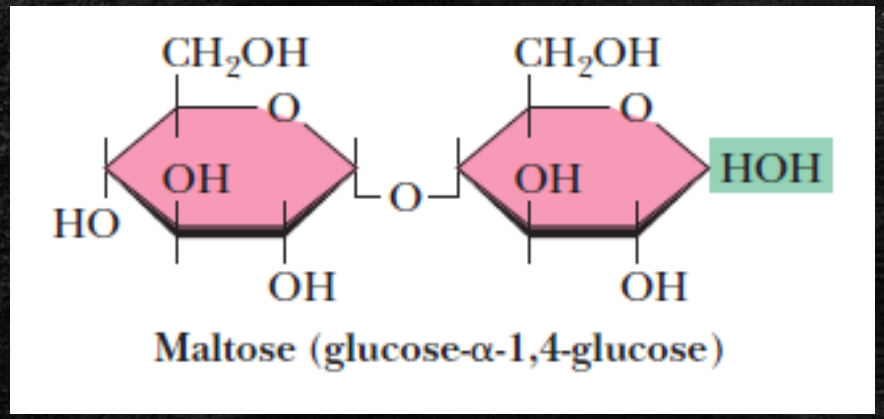
Starch

- Which organisms?
- Forms:
  - amylose (10-20%)
  - amylopectin (80-90%)
    - every 25 residues

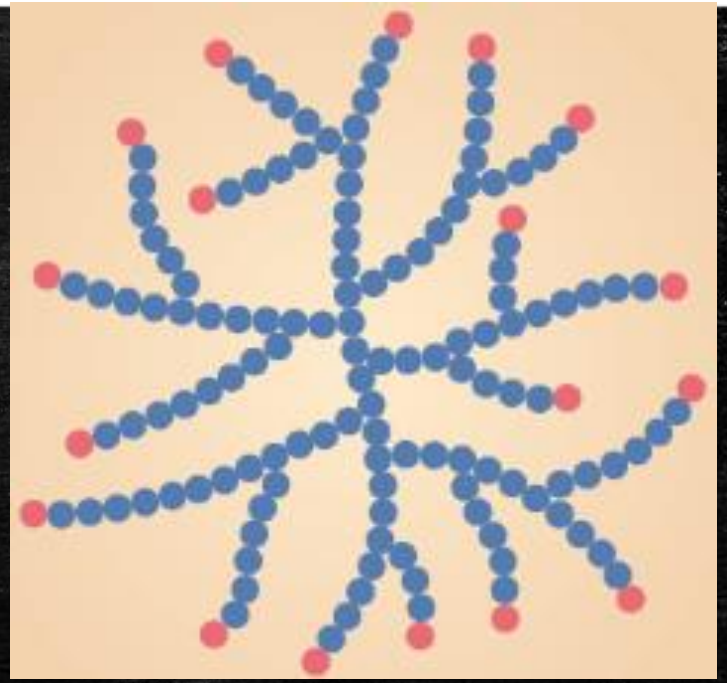


Amylose Structure



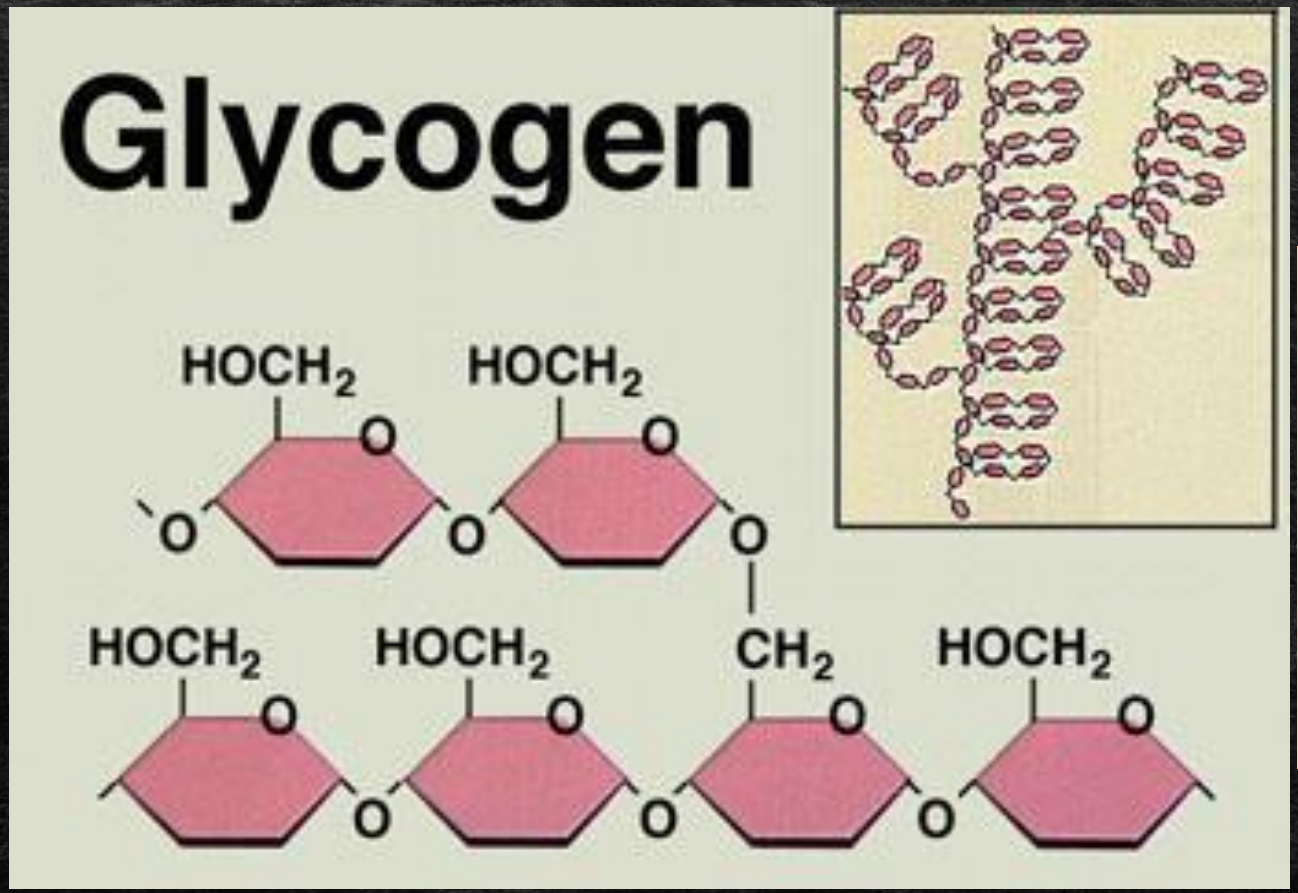


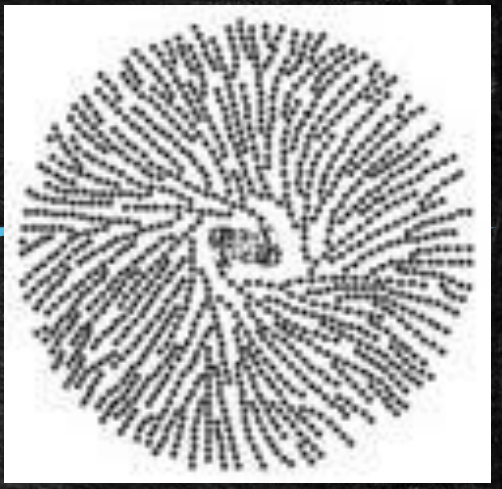
Maltose (glucose-α-1,4-glucose)

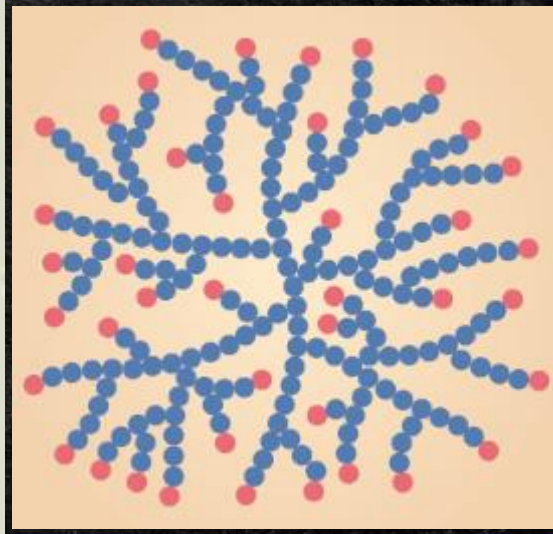


Glycogen

- More highly branched
- Every 10 residues
- More water-soluble
- Easy enzyme access to glucose residues

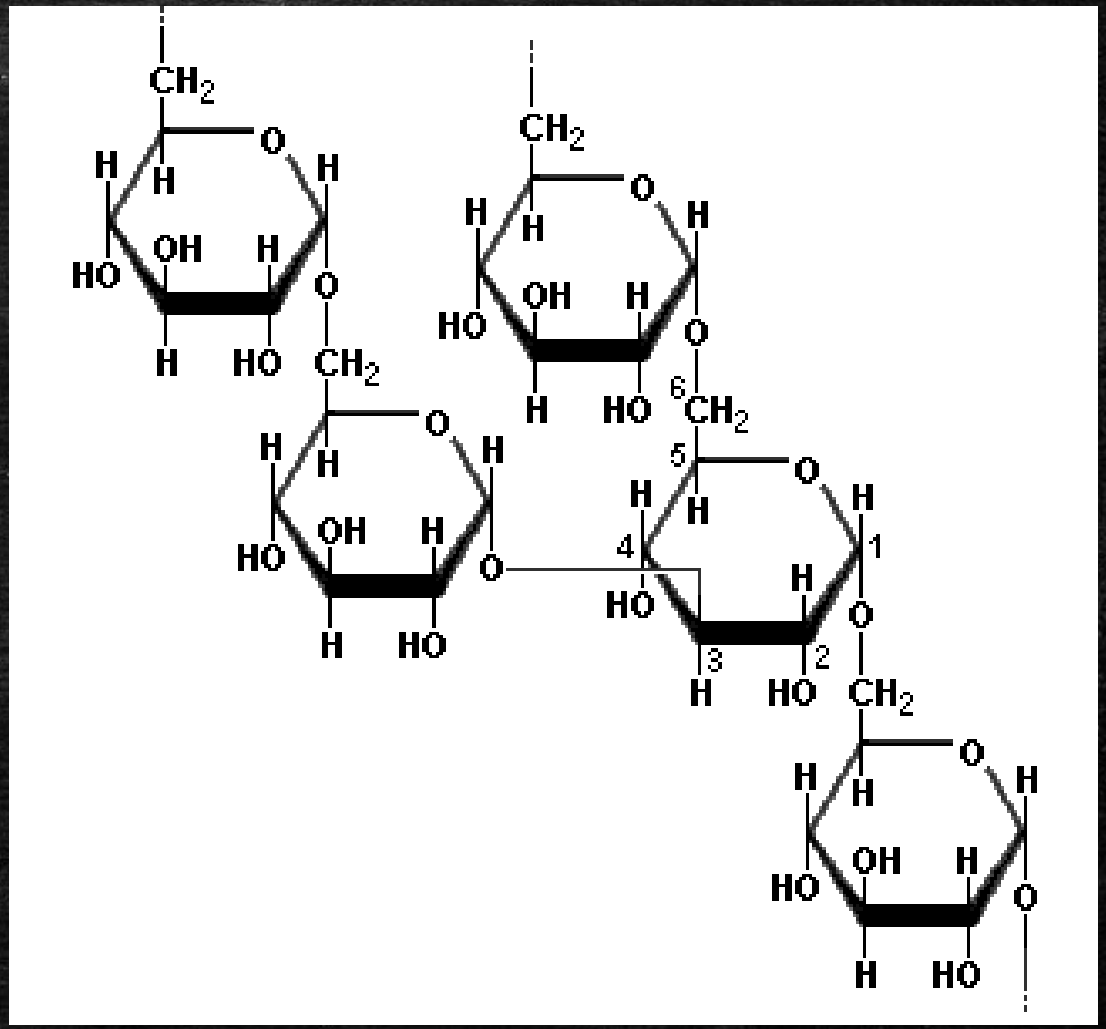






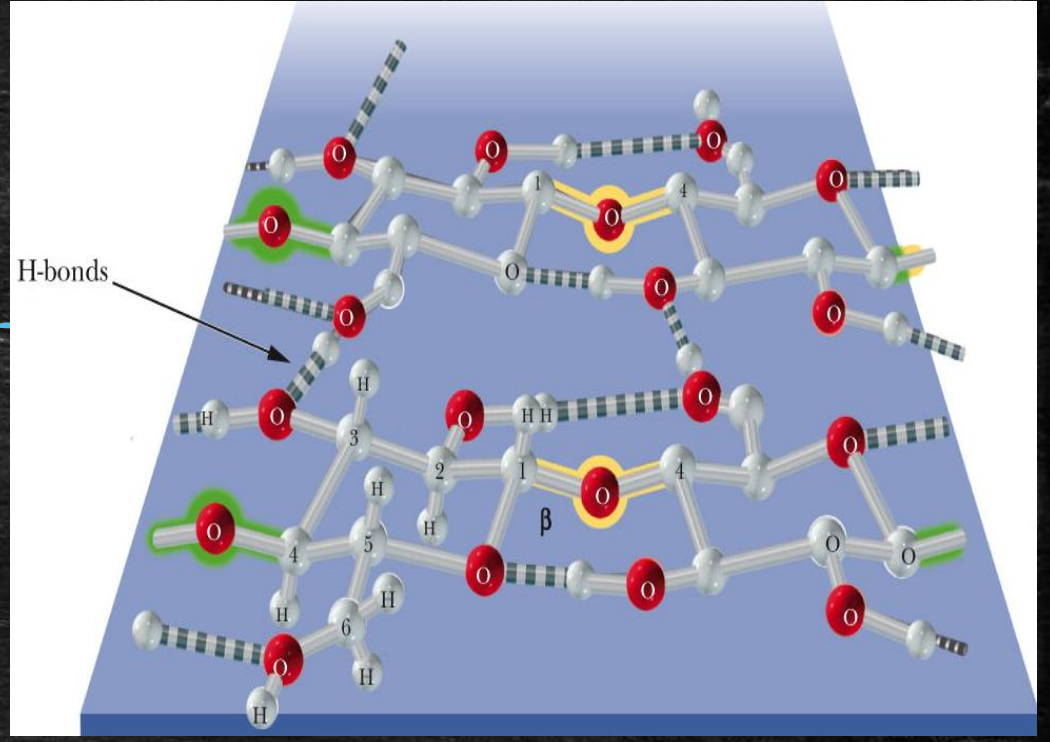
Dextran

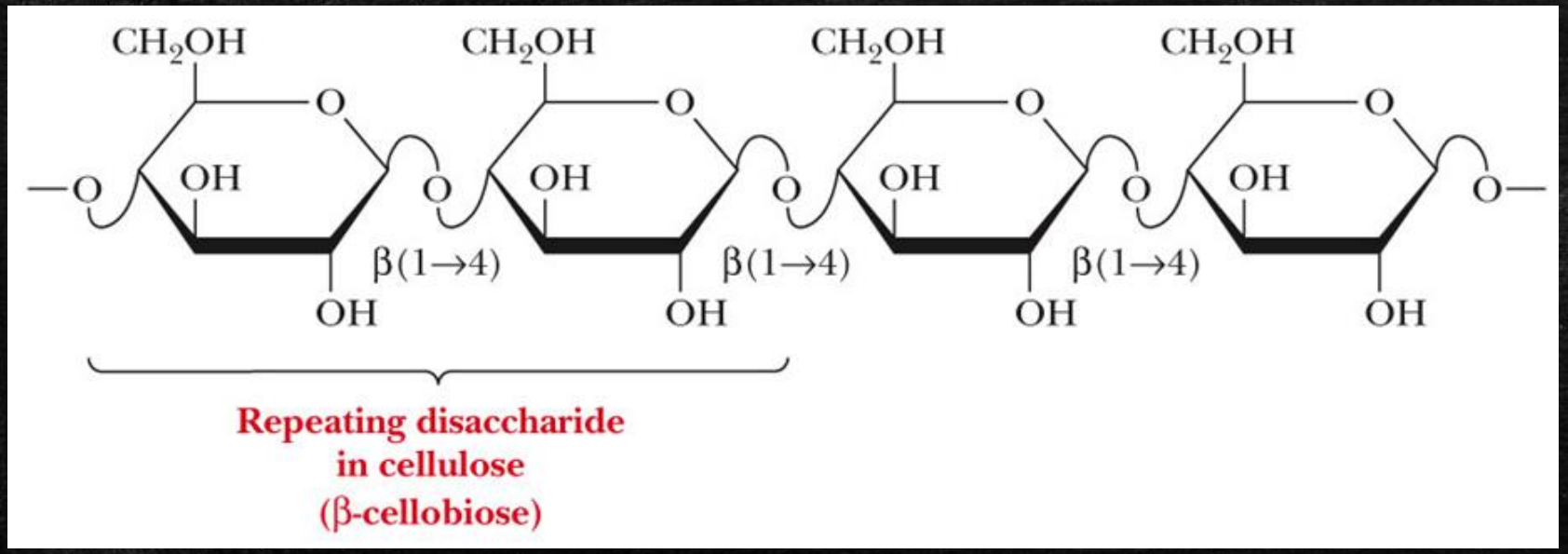
- A storage polysaccharide
- Yeast and bacteria
- α-(1-6)-D-glucose with branched chains
- Branches: 1-2, 1-3, or 1-4

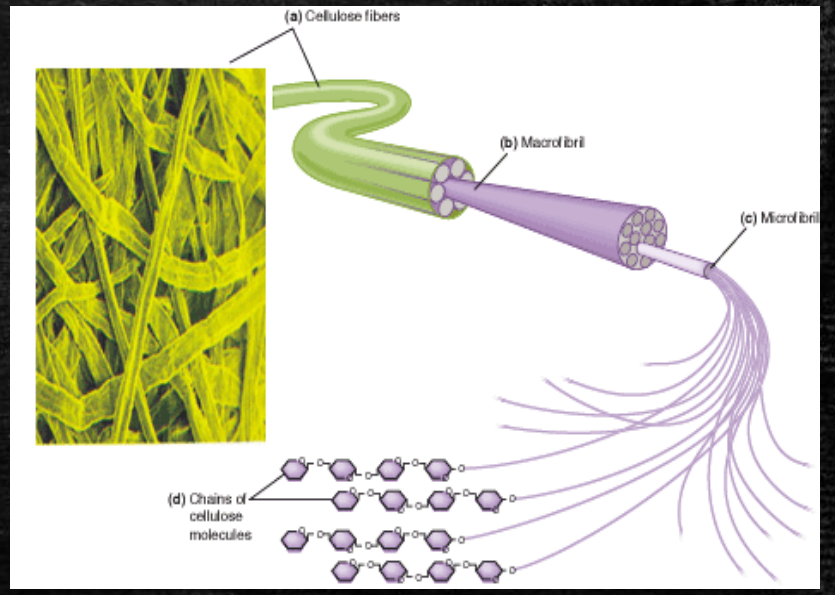


Cellulose

- Plants, linear, ~3000 unit, β-1,4-glycosidic bonds, Cellulases

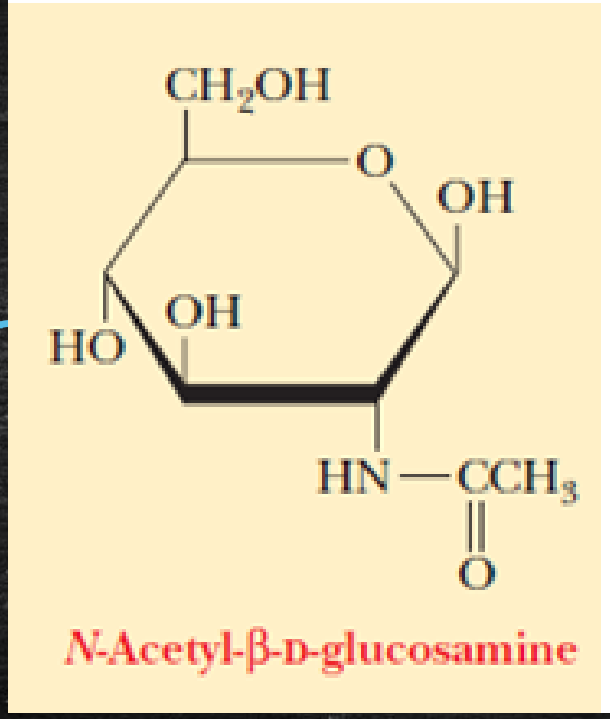


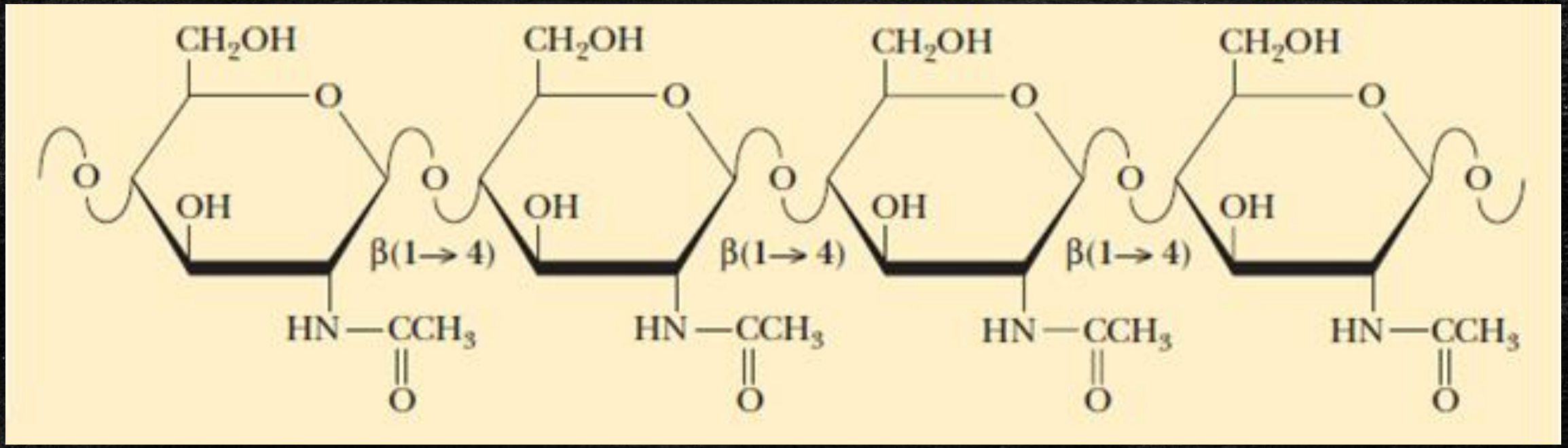




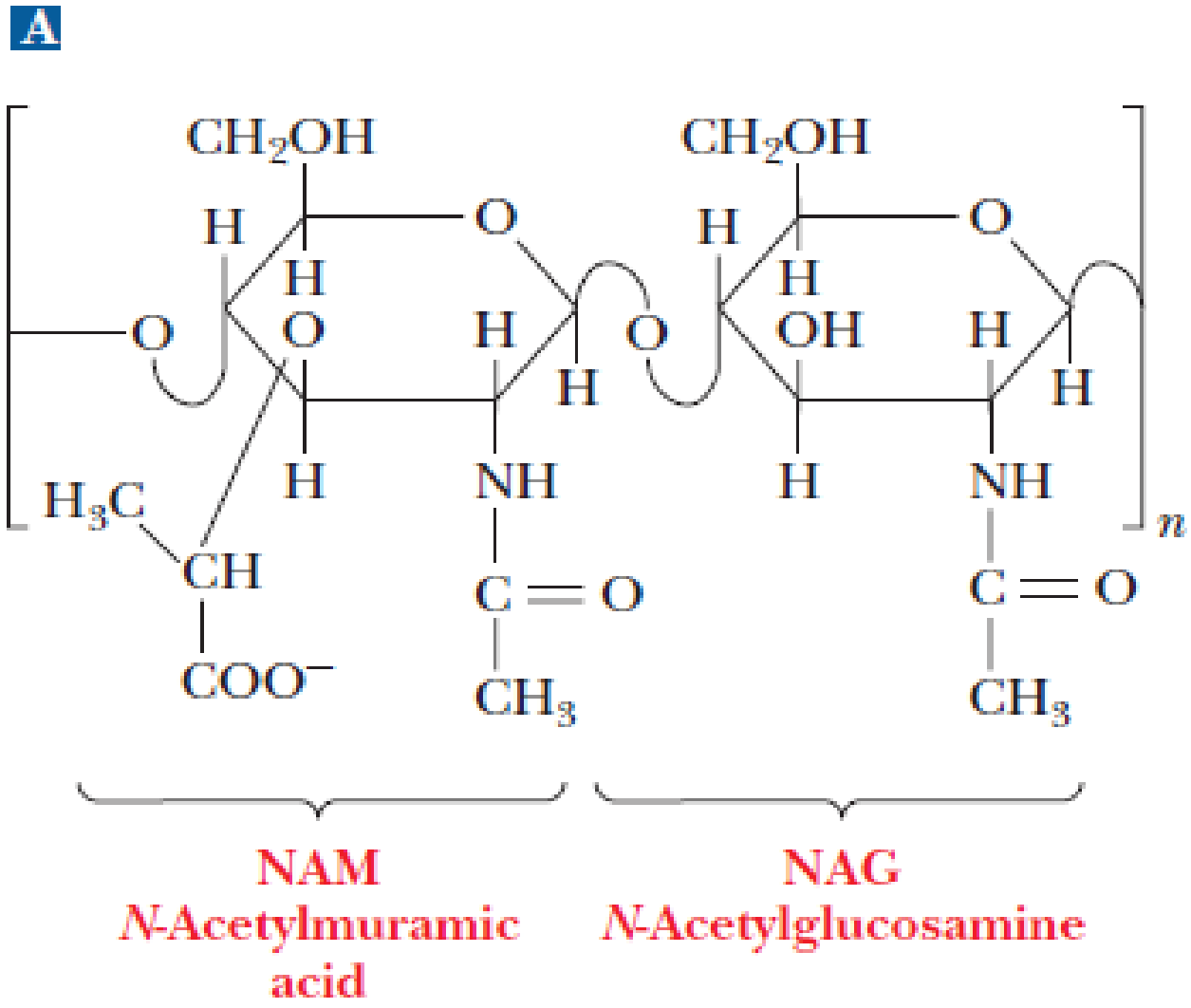
Chitin

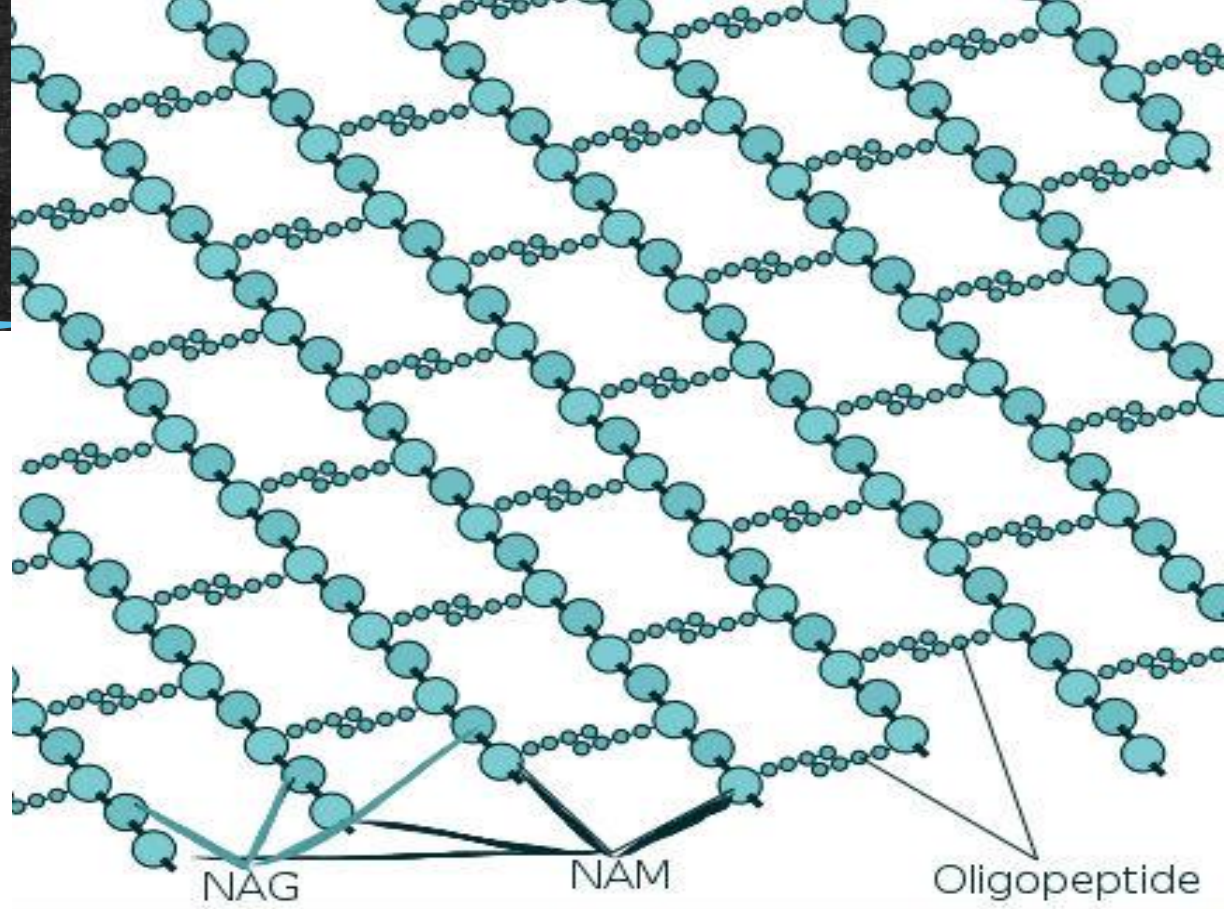
- What is the precursor?
- Where does it exist?

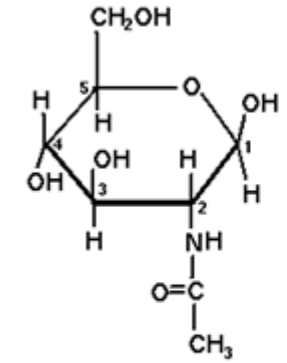




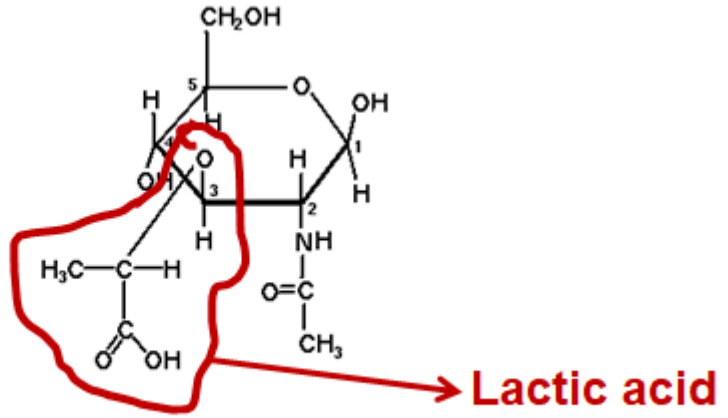
Bacterial cell wall







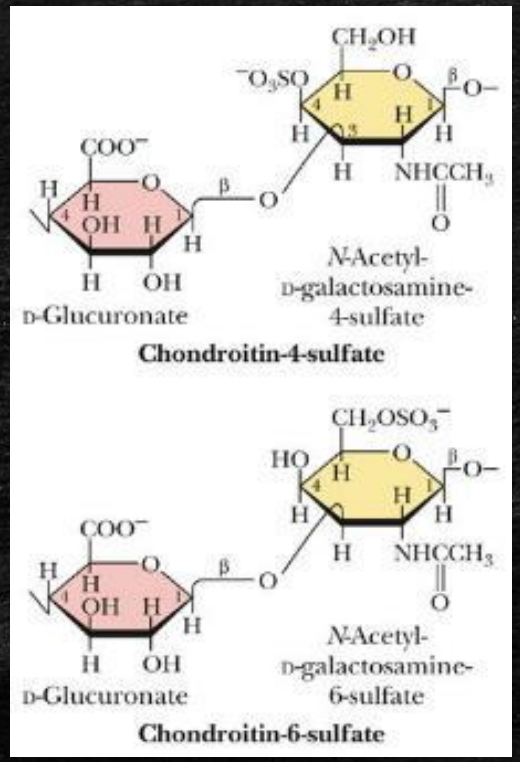
N–acetylglucosamine (NAG)

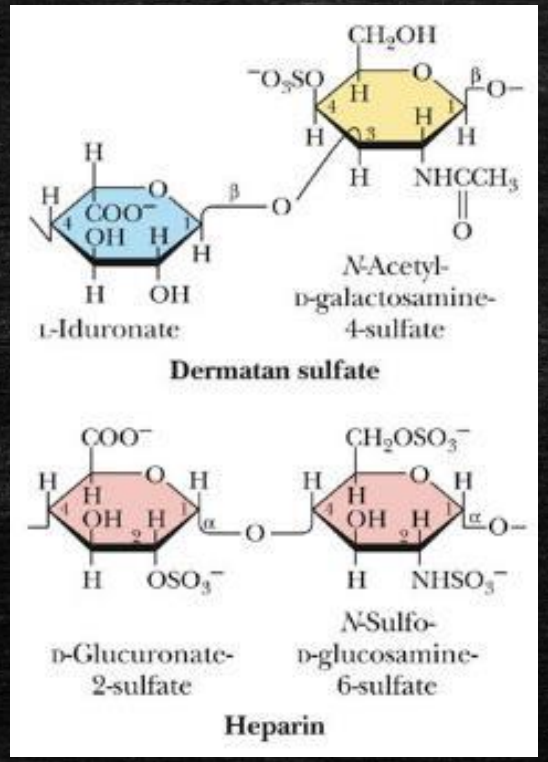


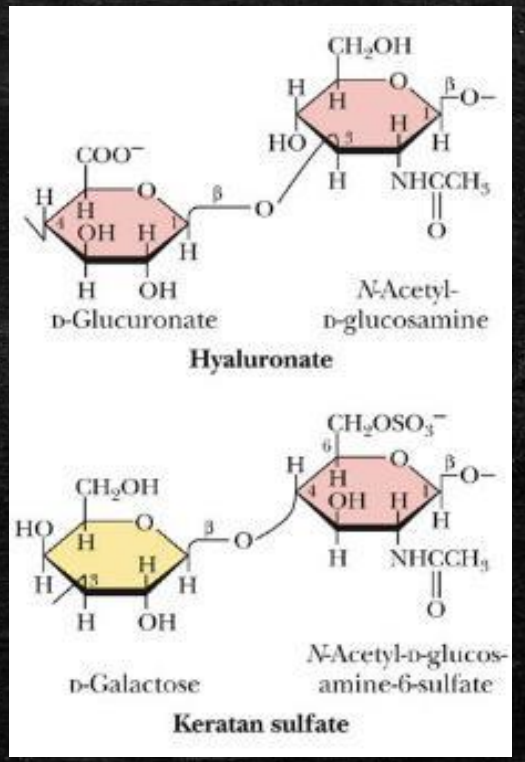
N–acetylmuramic acid (NAM)

Glycosaminoglycans

- What are they? Where are they located?
- Derivatives of an amino sugar, either glucosamine or galactosamine
- At least one of the sugars in the repeating unit has a negatively charged carboxylate or sulfate group





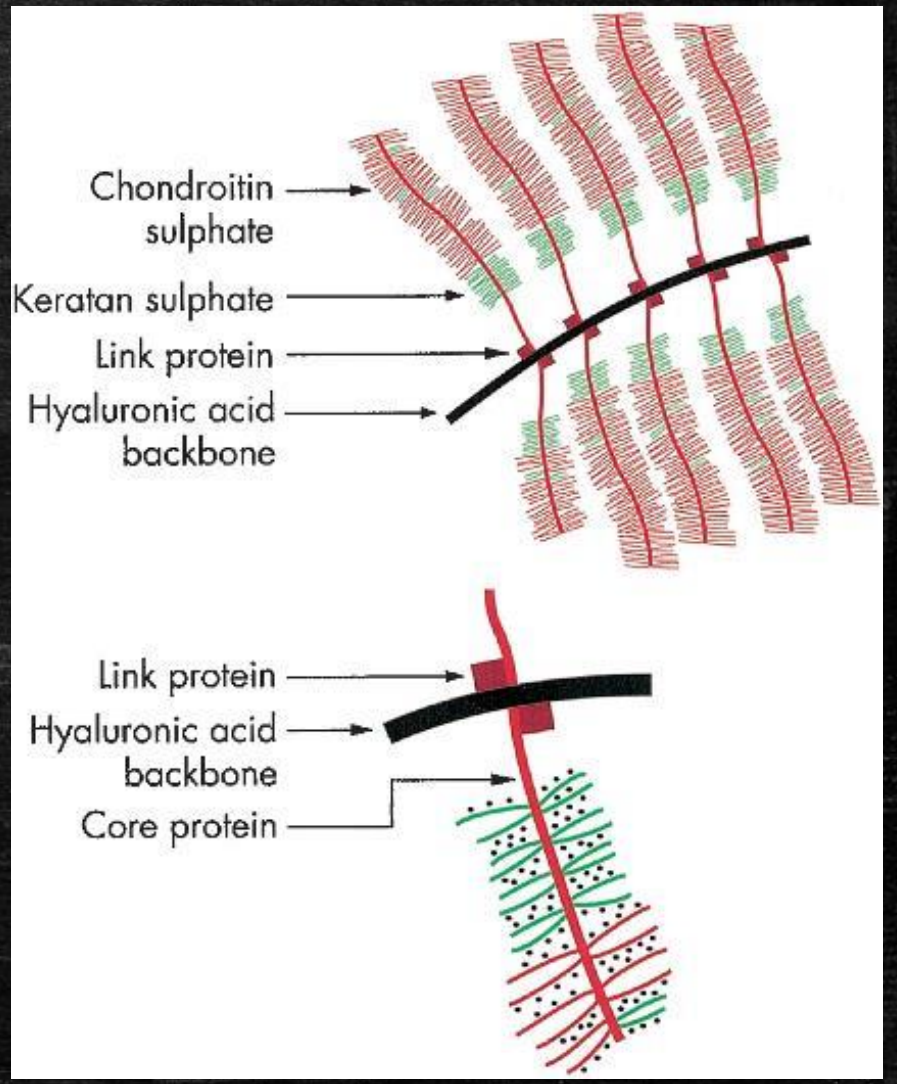


Localization and function of GAG

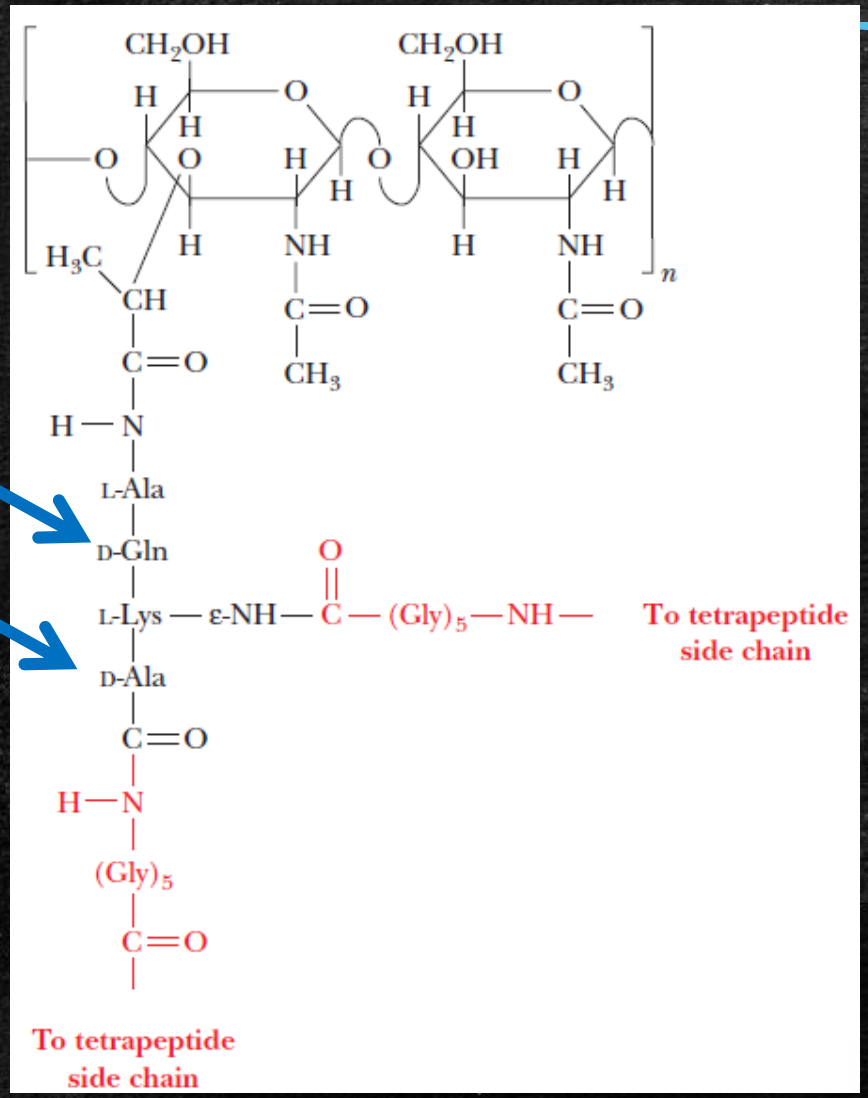
GAG	Localization	Comments
Hyaluronate	synovial fluid, **vitreous humor, ECM of loose connective tissue**	**the lubricant fluid , shock absorbing** As many as 25,000 disaccharide units
Chondroitin sulfate	**cartilage**, bone, heart valves	**most abundant GAG**
Heparan sulfate	basement membranes, components of cell surfaces	contains higher acetylated glucosamine than heparin
Heparin	component of intracellular granules of mast cells lining the arteries of the lungs, liver and skin	**A natural anticoagulant**
Dermatan sulfate	skin, blood vessels, heart valves	
Keratan sulfate	cornea, bone, cartilage aggregated with chondroitin sulfates	Only one not having uronic acid

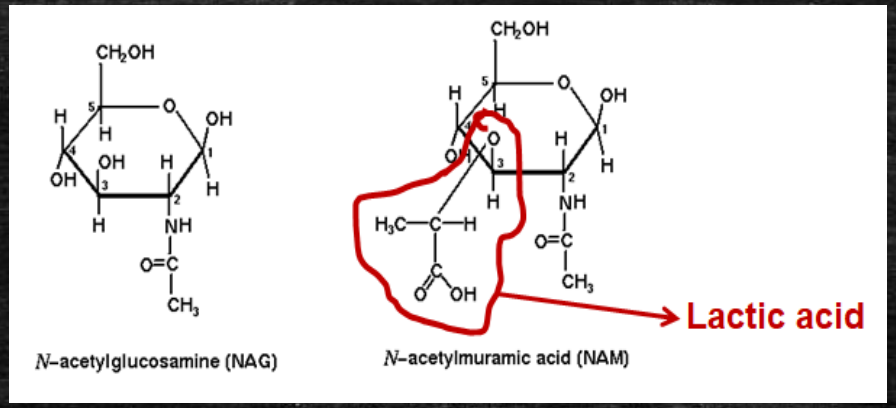
Proteoglycans

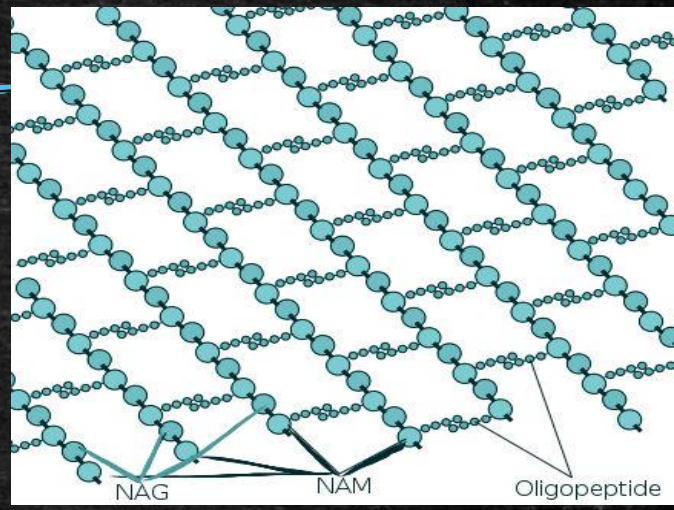
- Lubricants
- Structural components in connective tissue
- Mediate adhesion of cells to the extracellular matrix
- Bind factors that stimulate cell proliferation

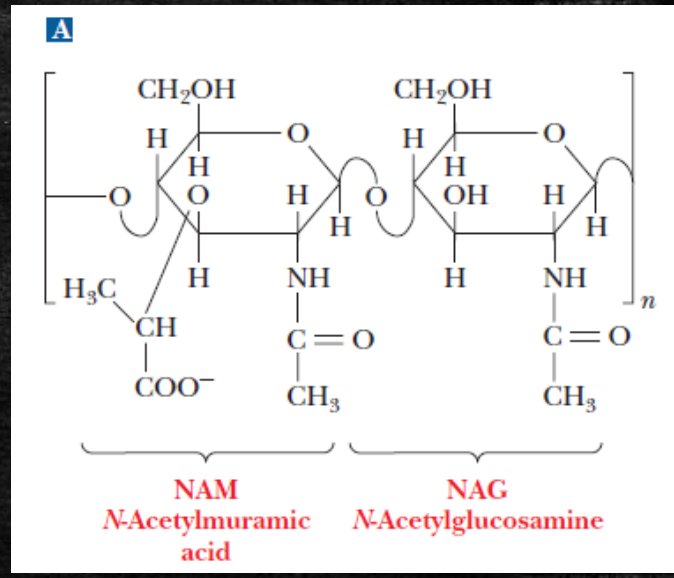


Bacterial cell wall



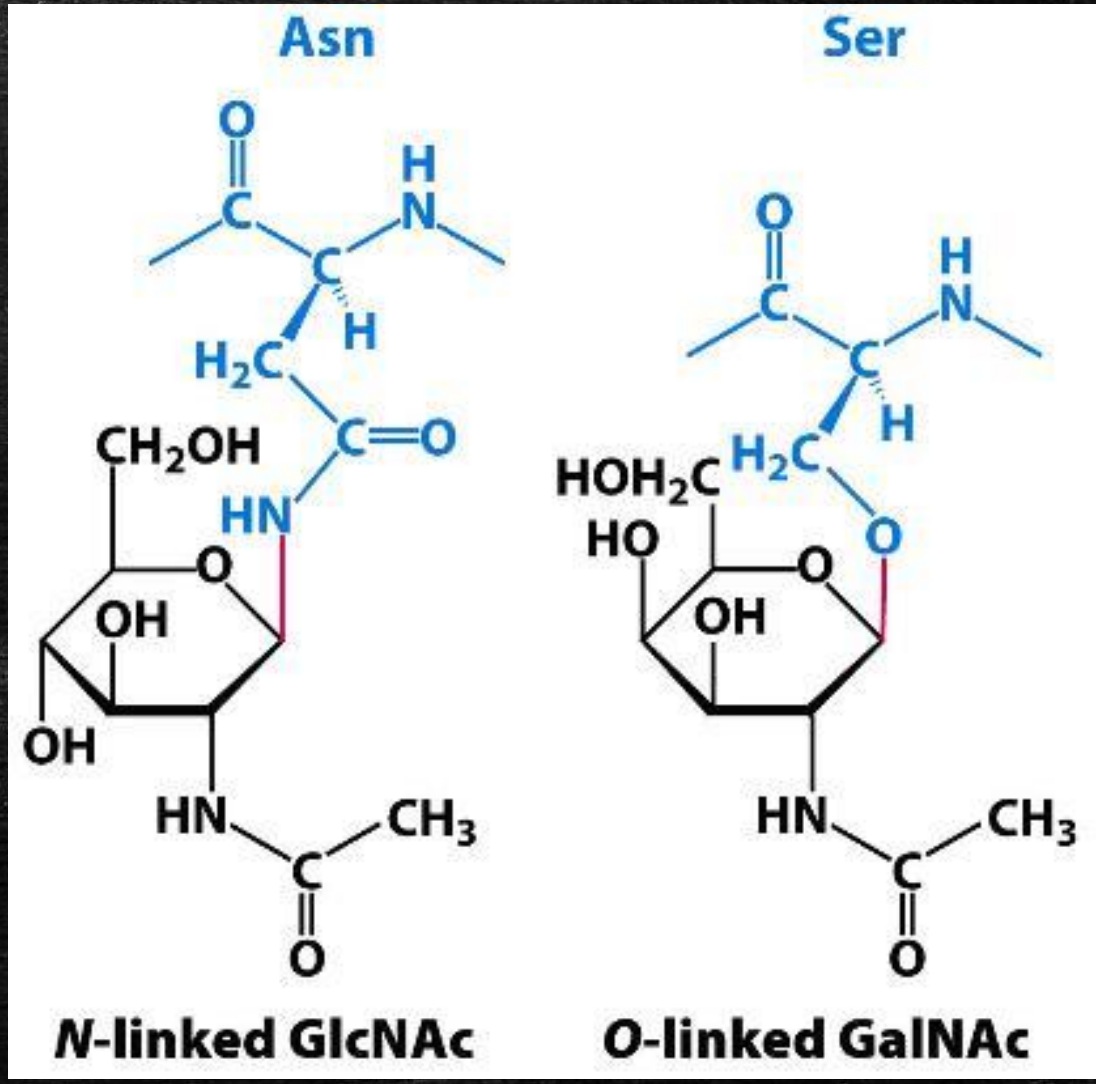




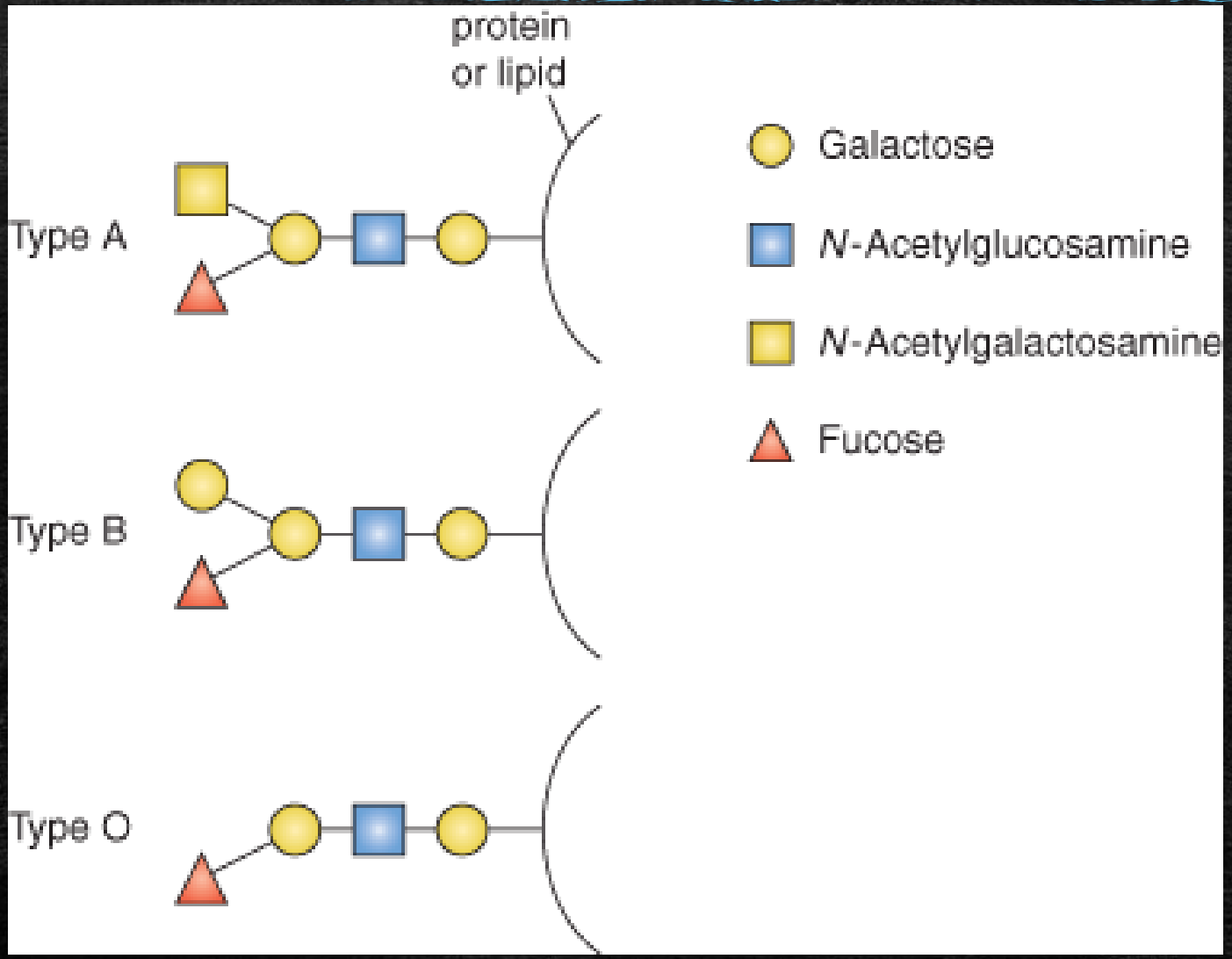


Glycoproteins

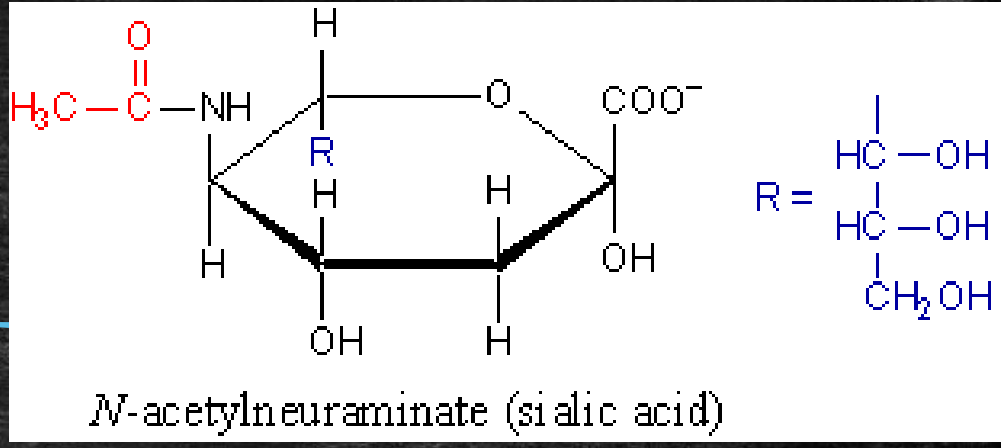
- O-glycosidic; hydroxyl group of serine (Ser, S), threonine (Thr, T) or hydroxylysine (hLys)
- N-glycosidic bonds; through the amide group of asparagine (Asn, N)
- Significance:
  - Protein folding
  - Protein targeting
  - Prolonging protein half-life
  - Cell-cell communication
  - Signaling



Blood typing



Sialic acid



- A terminal residue of oligosaccharide chains of glycoproteins and glycolipids