Carbohydrates

Summer semester 2023-2024

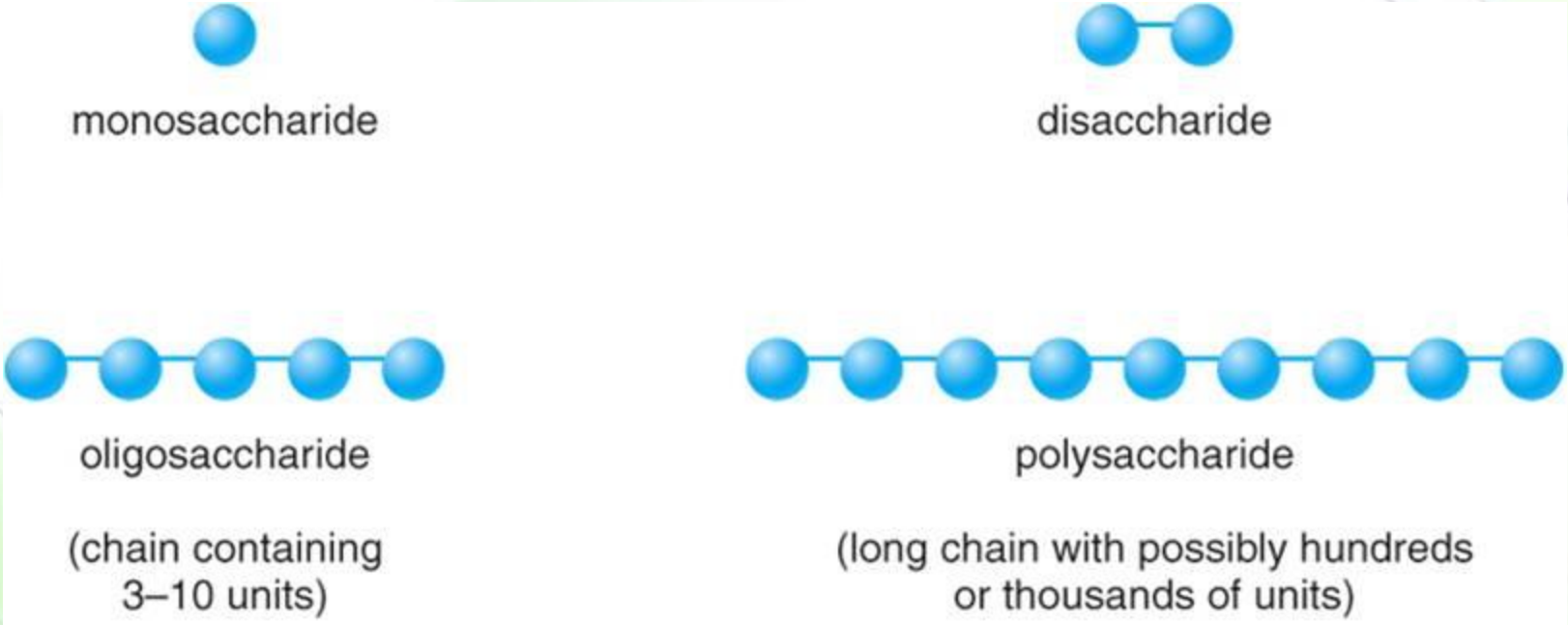
What are they?

- Carbohydrates are polyhydroxy aldehydes or ketones.
- Saccharide is another name for a carbohydrate

- Functions:
  - Source of energy (glycogen and starch)
  - Structure (cellulose and chitin)
  - Building blocks (glycosaminoglycans)
  - Cellular recognition (glycoproteins)

Classification I

- By the number of sugars that constitute the molecule
  - Monosaccharides, Disaccharides, Oligosaccharides, Polysaccharides

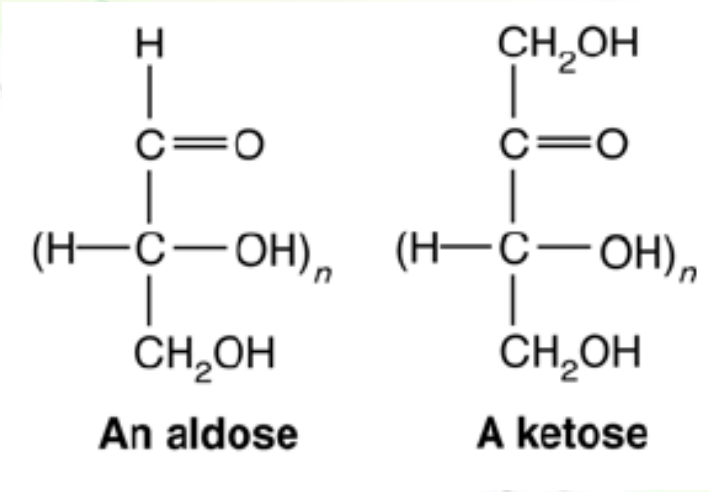


Carbohydrates – natural forms

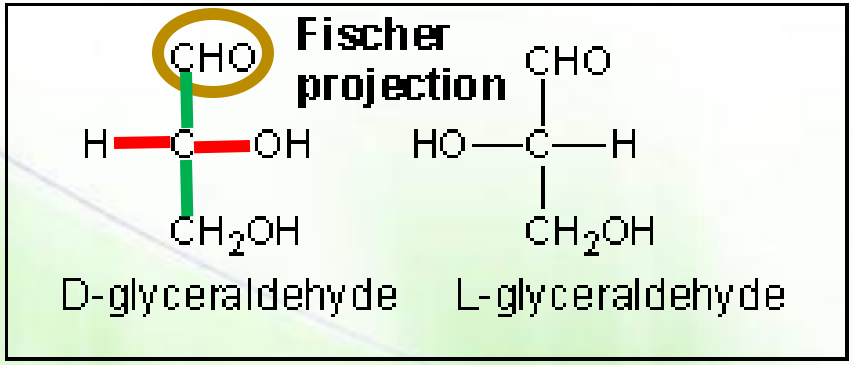
- Most carbohydrates are found naturally in bound form rather than as simple sugars.
  - Polysaccharides (starch, cellulose, inulin, gums)
  - Glycoproteins and proteoglycans (hormones, blood group substances, antibodies)
  - Glycolipids (cerebrosides, gangliosides)
  - Glycosides
  - Mucopolysaccharides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

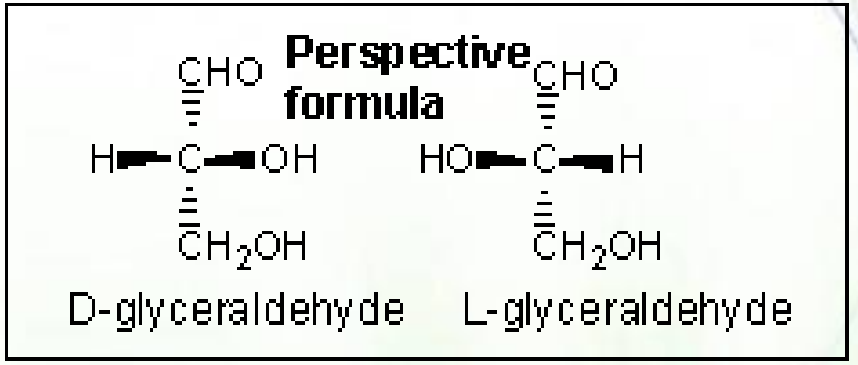
Monosaccharides

- Basic chemical formula: $(CH_2O)n$
- They contain two or more hydroxyl groups.



Fisher projections or perspective structural formulas.

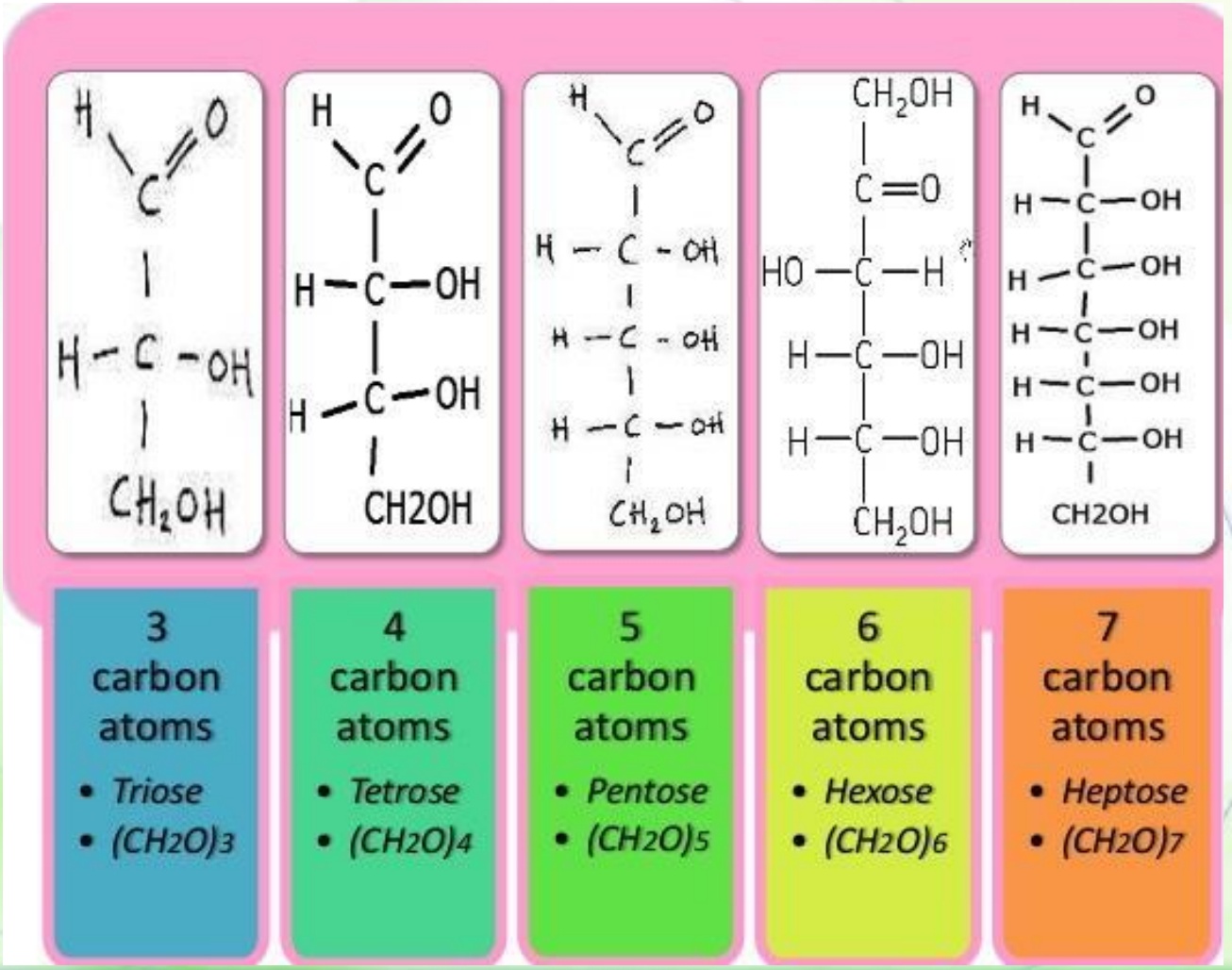




Forward **Backward** **Top (C1): Most highly oxidized C**

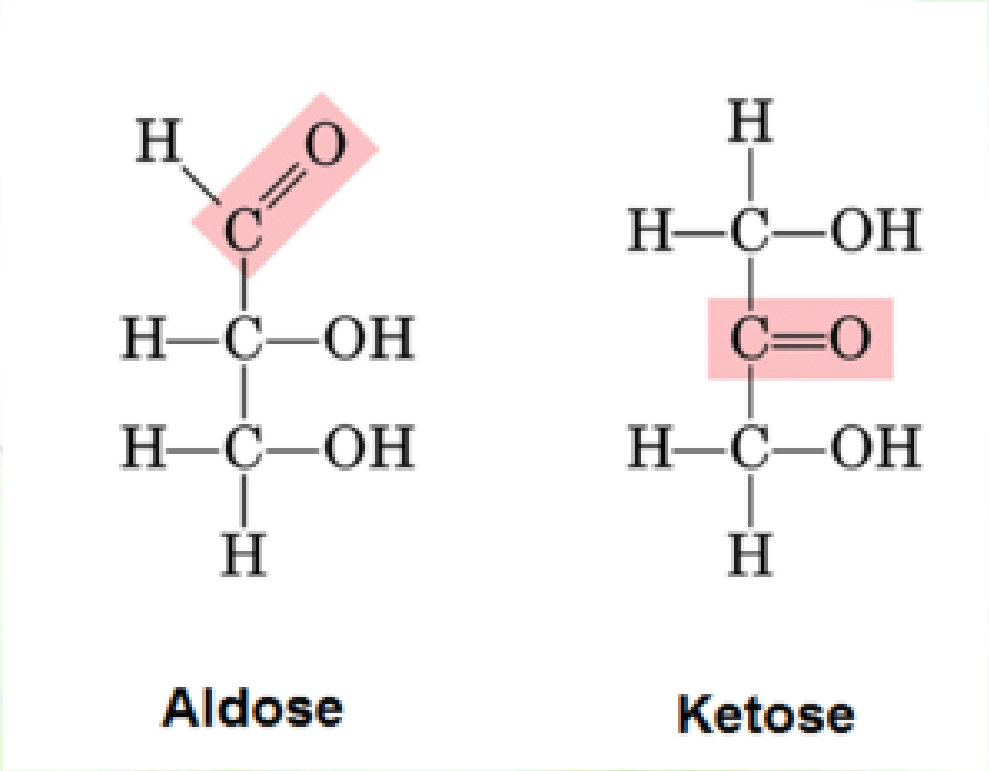
Classification 2

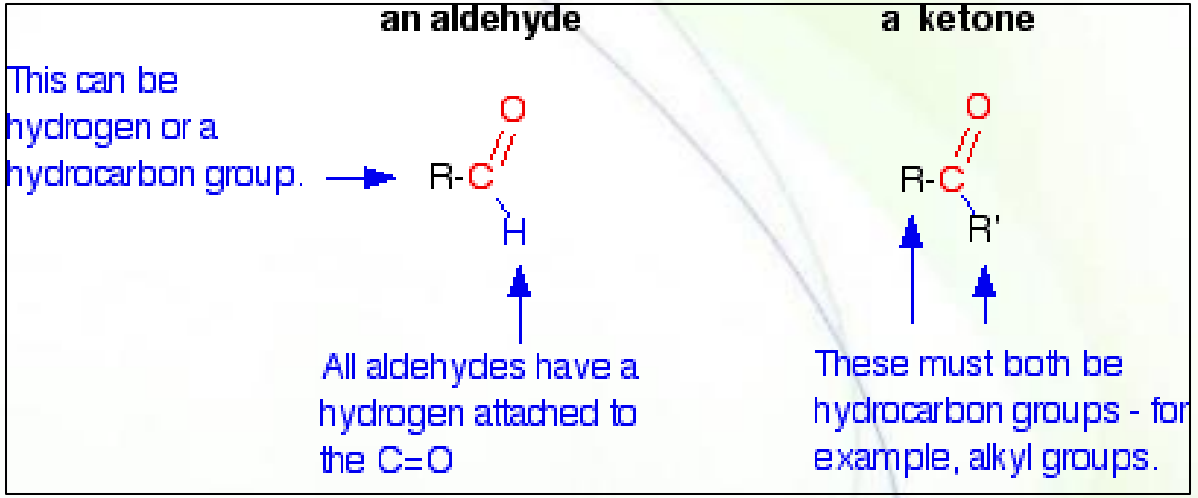
- By the number of carbon atoms they contain.
  - Triose
  - Tetrose
  - Pentose
  - Hexose
  - Heptose
  - …



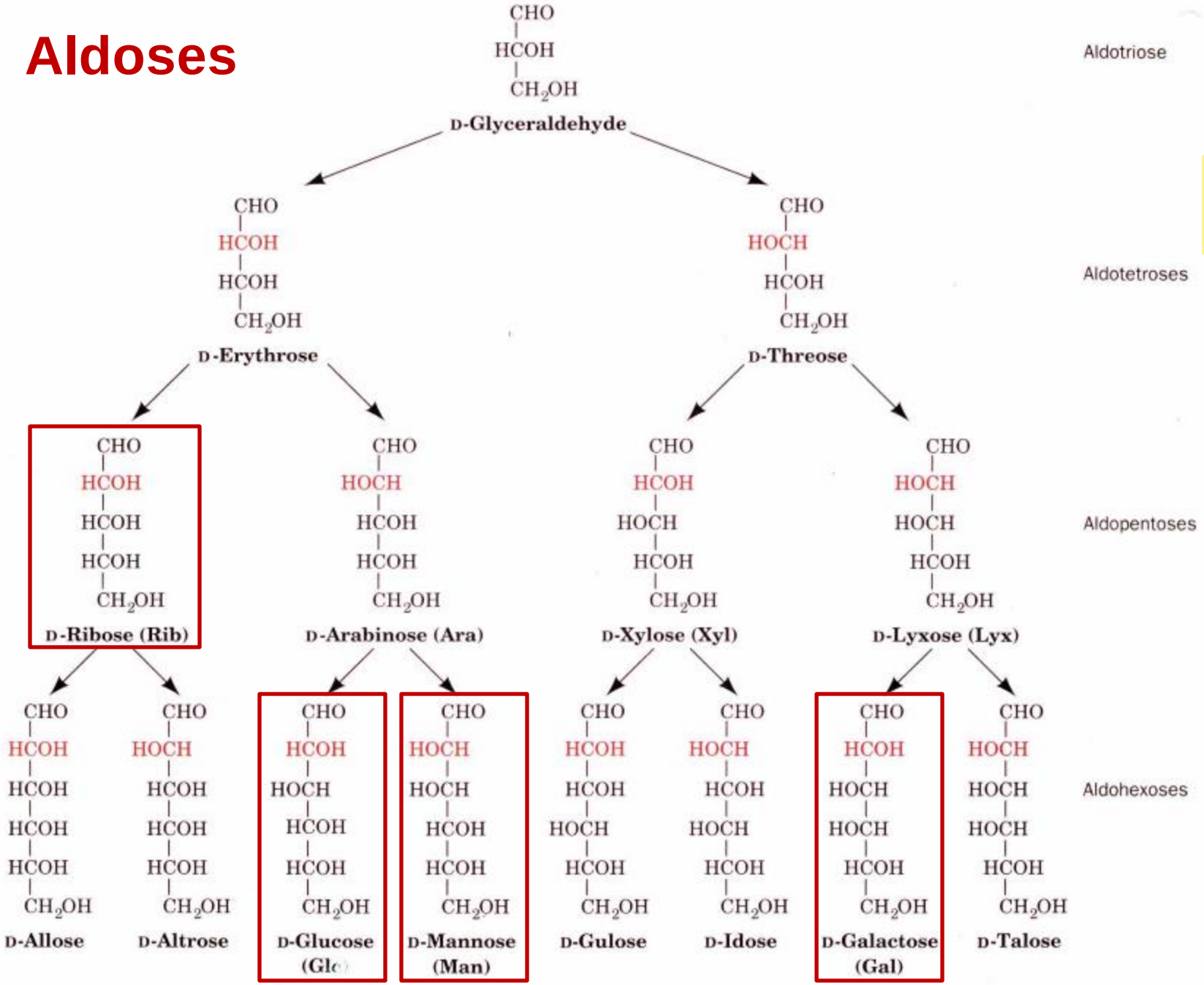
Classification III

- By the functional group



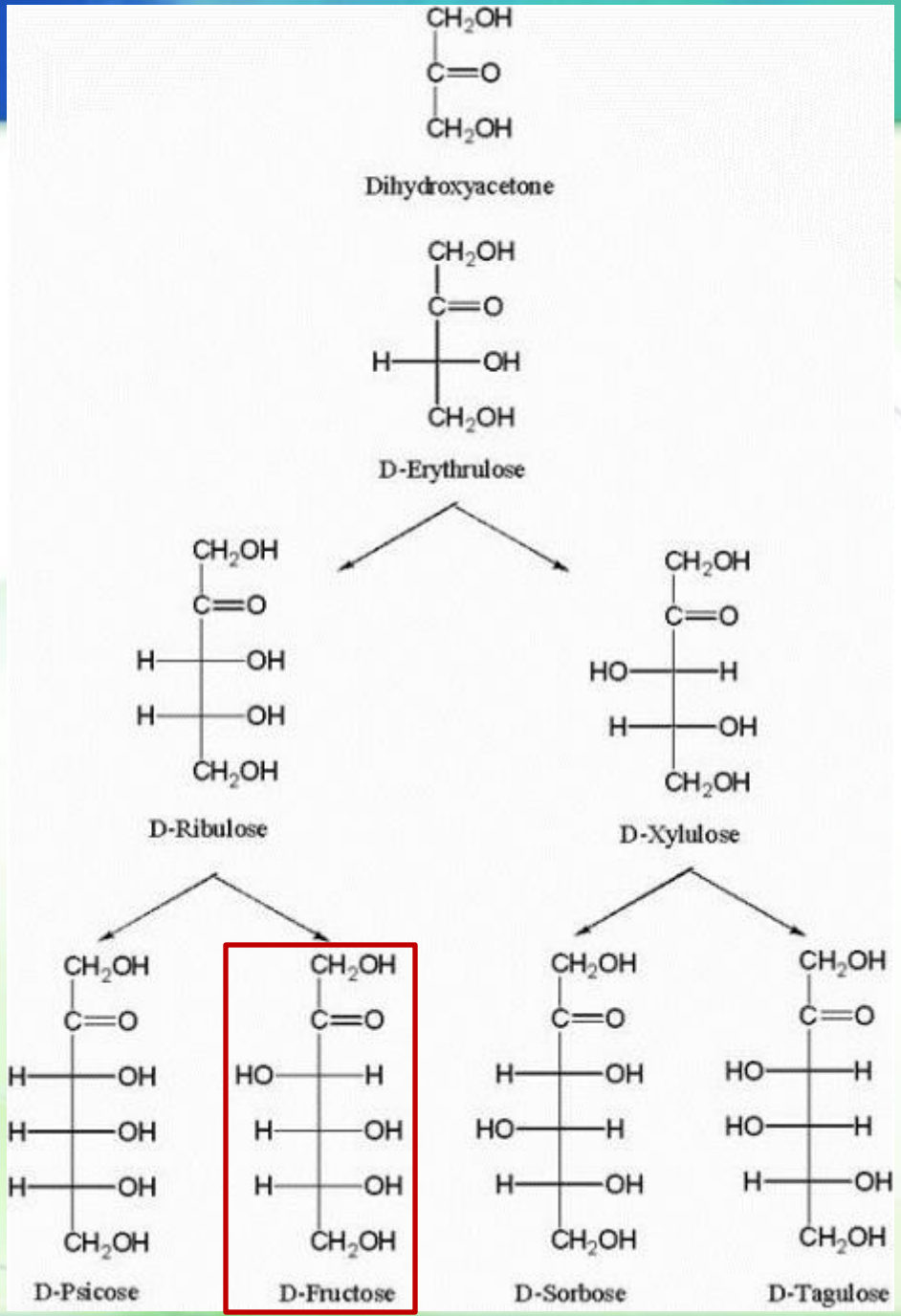


Aldoses



Memorize the ones in boxes.

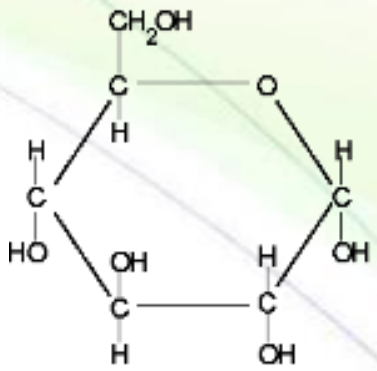
Ketoses



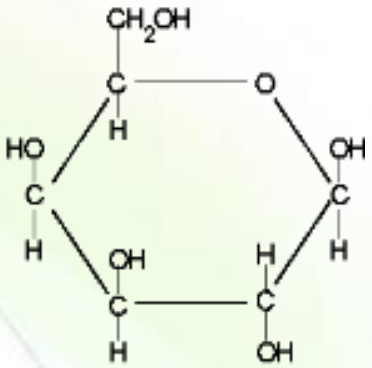
Memorize the ones in boxes.

Common Monosaccharides

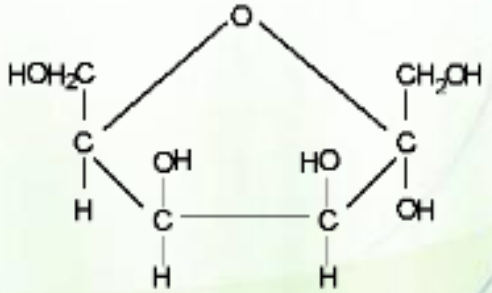
- Glucose:
  - Mild sweet flavor
  - Known as blood sugar
  - Essential energy source
  - Found in every disaccharide and polysaccharide
- Galactose:
  - Hardly tastes sweet & rarely found naturally as a single sugar
- Fructose:
  - Sweetest sugar, found in fruits and honey
  - Added to soft drinks,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



Glucose



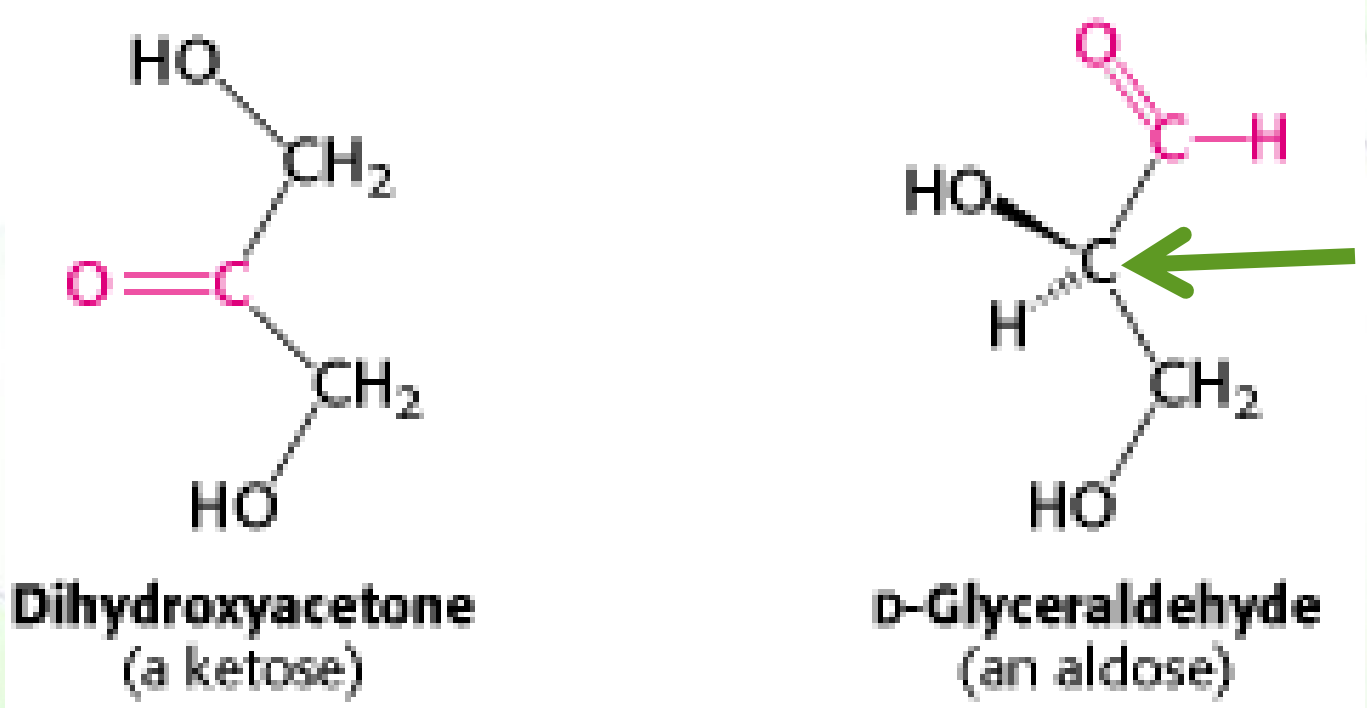
Galactose



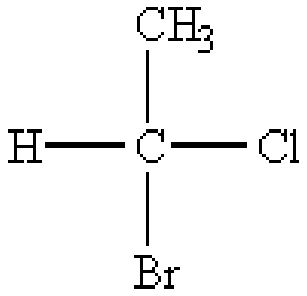
Fructose

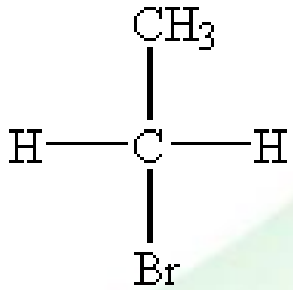
Trioses

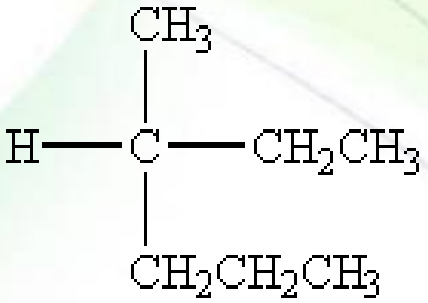
What is a chiral carbon?

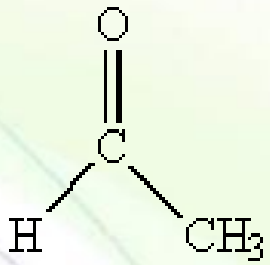


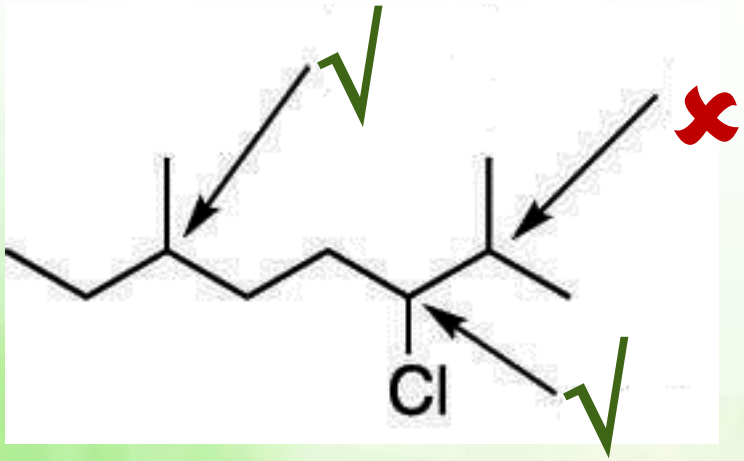
Note what a chiral carbon is...





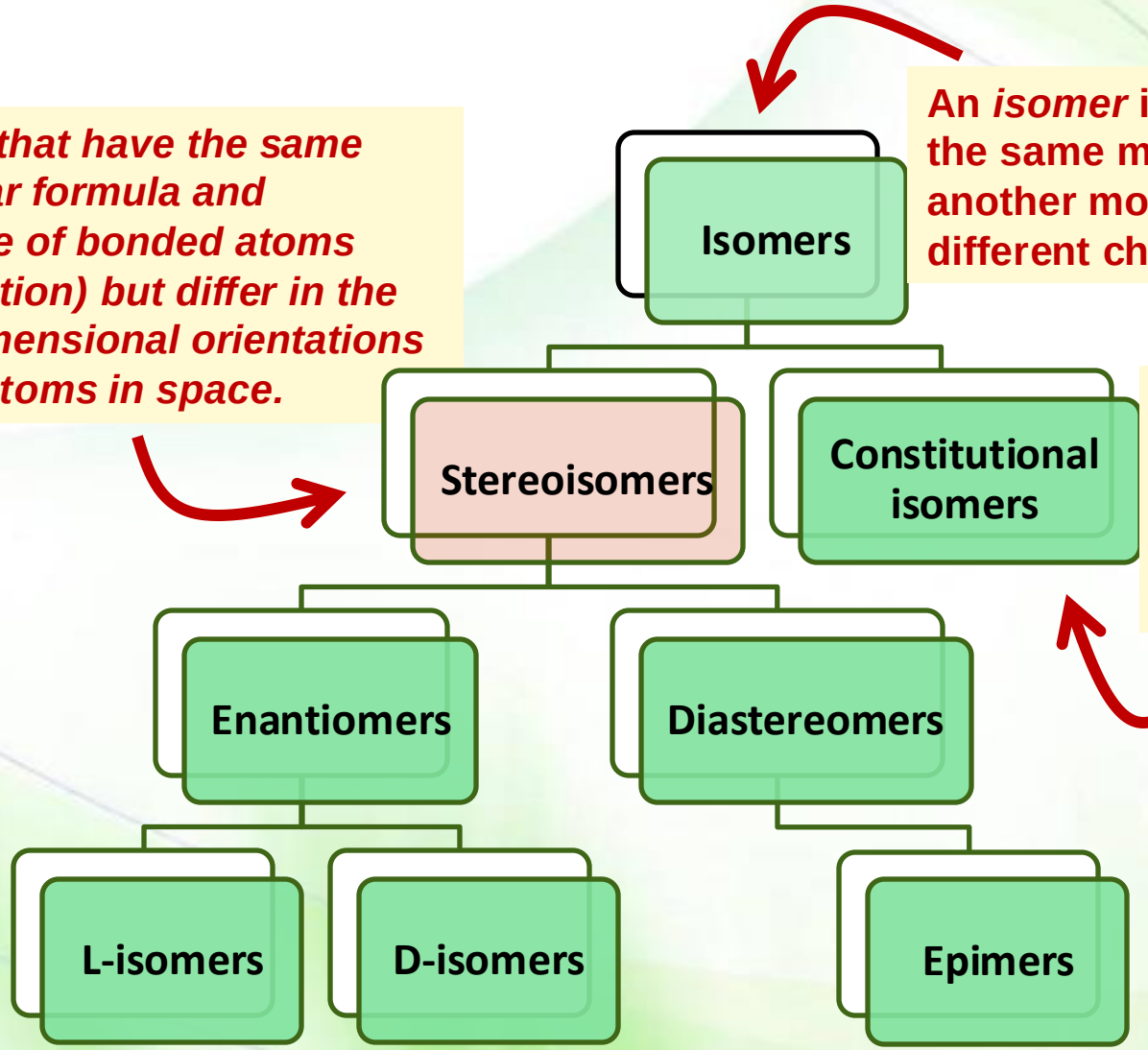






Isomerism

An *isomer* is a molecule with the same molecular formula as another molecule, but with a different chemical structure.



Isomers that have the same molecular formula and sequence of bonded atoms (constitution) but differ in the three-dimensional orientations of their atoms in space.

Molecules with the same molecular formula but have different bonding patterns and atomic organization.

Isomers of glucose

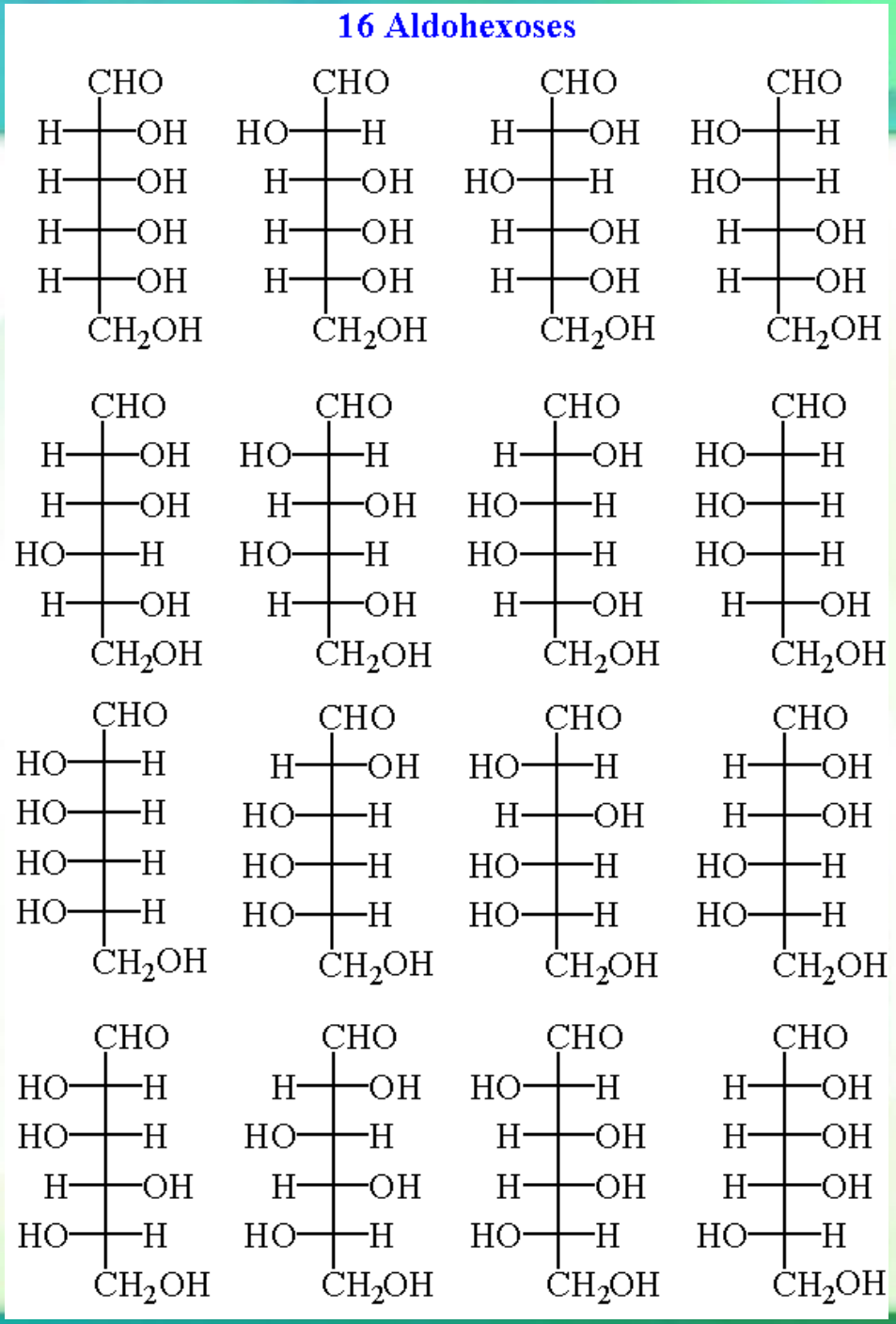
2^n (n is the number of chiral carbons in a sugar molecule)

Search for:

Glucose,

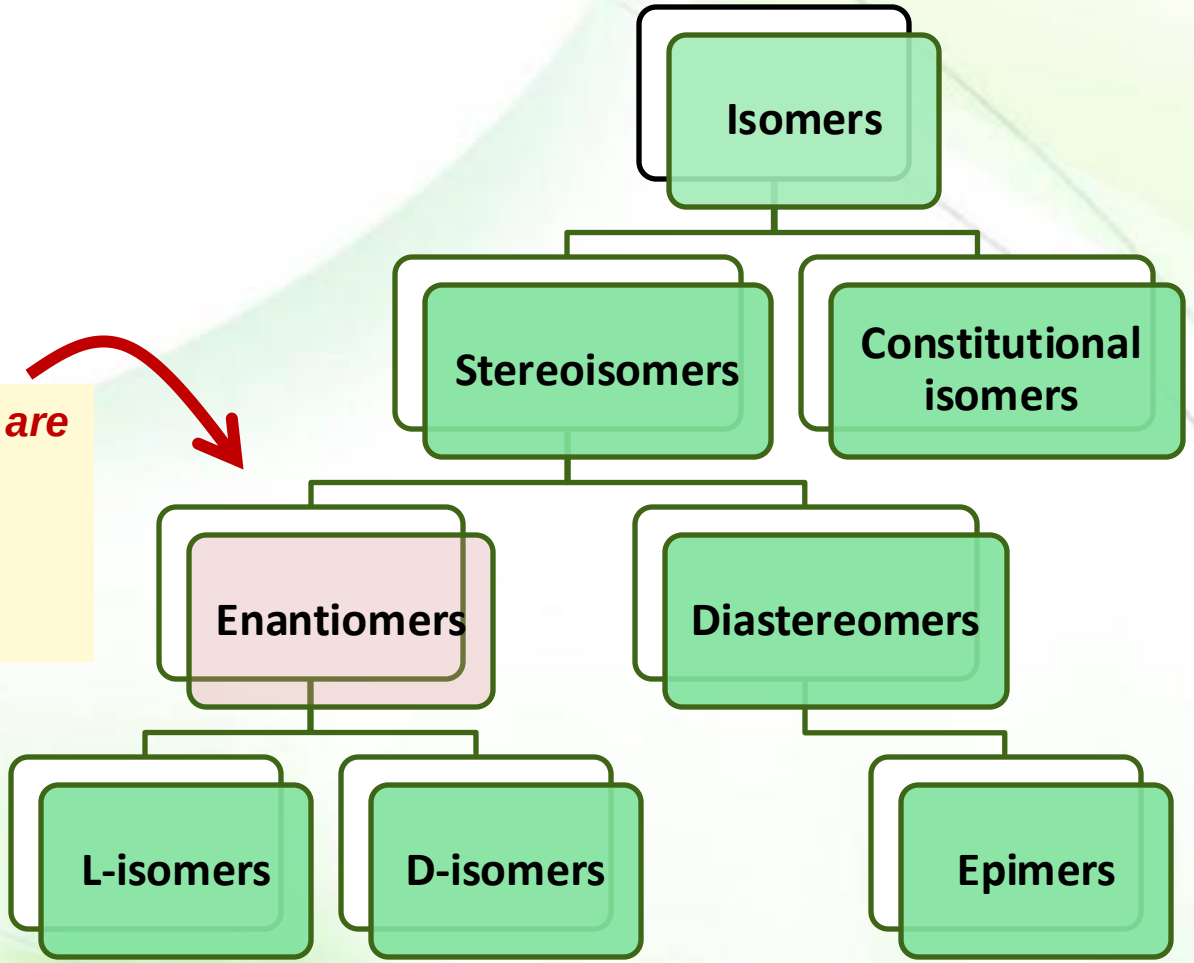
Galactose

Mannose

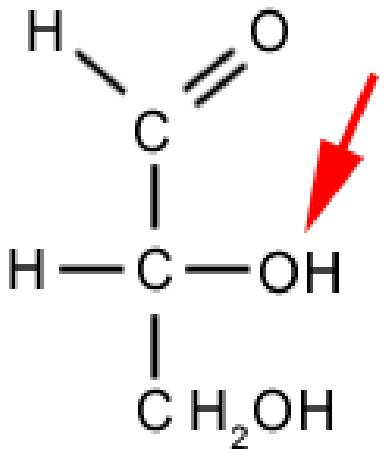


Enantiomers

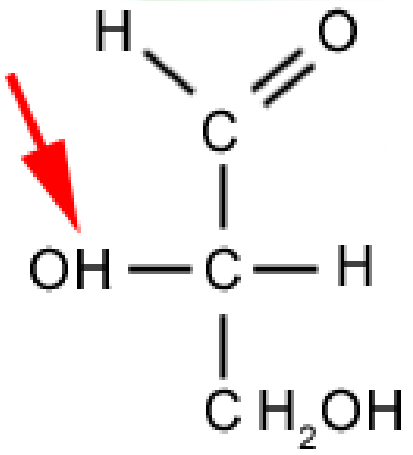
Two stereoisomers that are mirror images of each other and are non-superimposable (not identical)



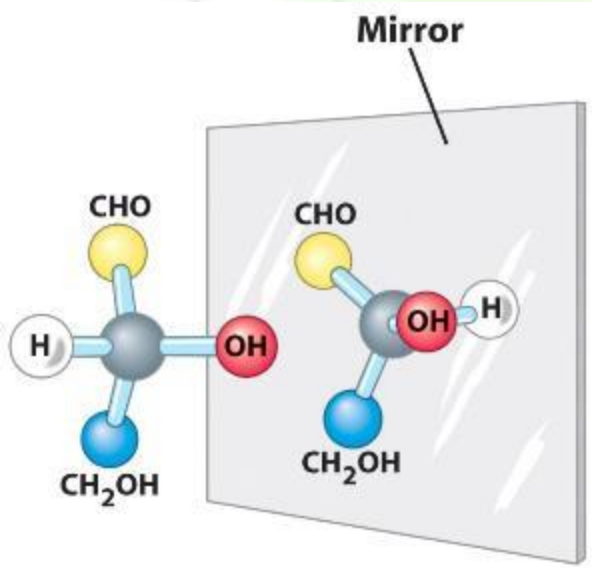
Sugar enantiomers (D- vs. L-)



D-Glyceraldehyde

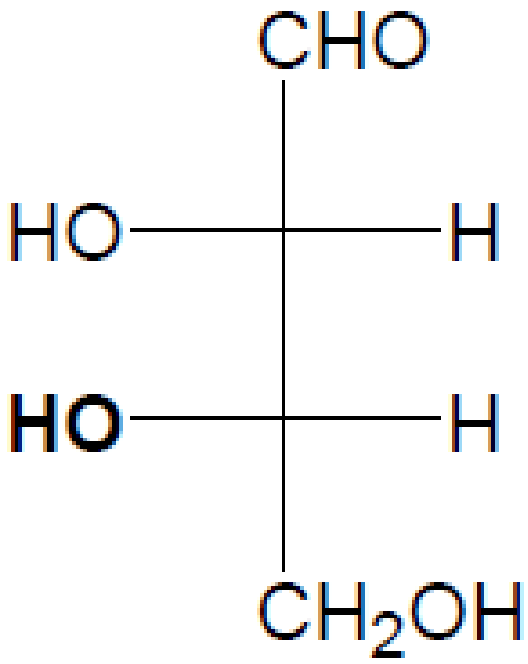


L -Glyceraldehyde

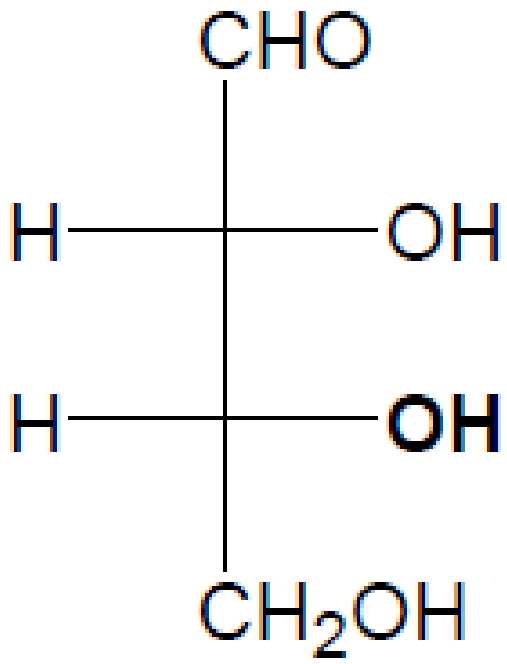


Ball-and-stick models

Which one(s) is a chiral carbon?



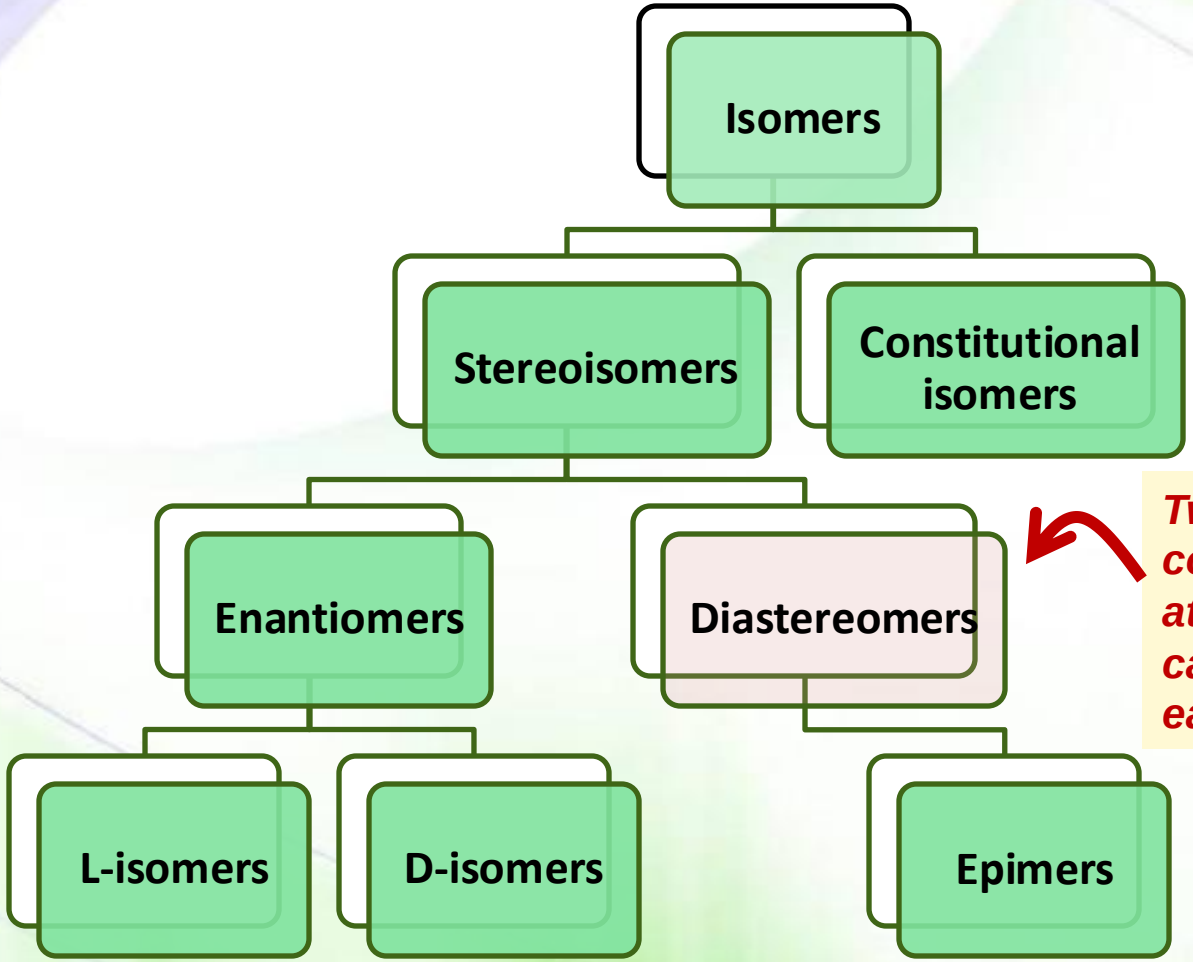
L-erythrose



D-erythrose

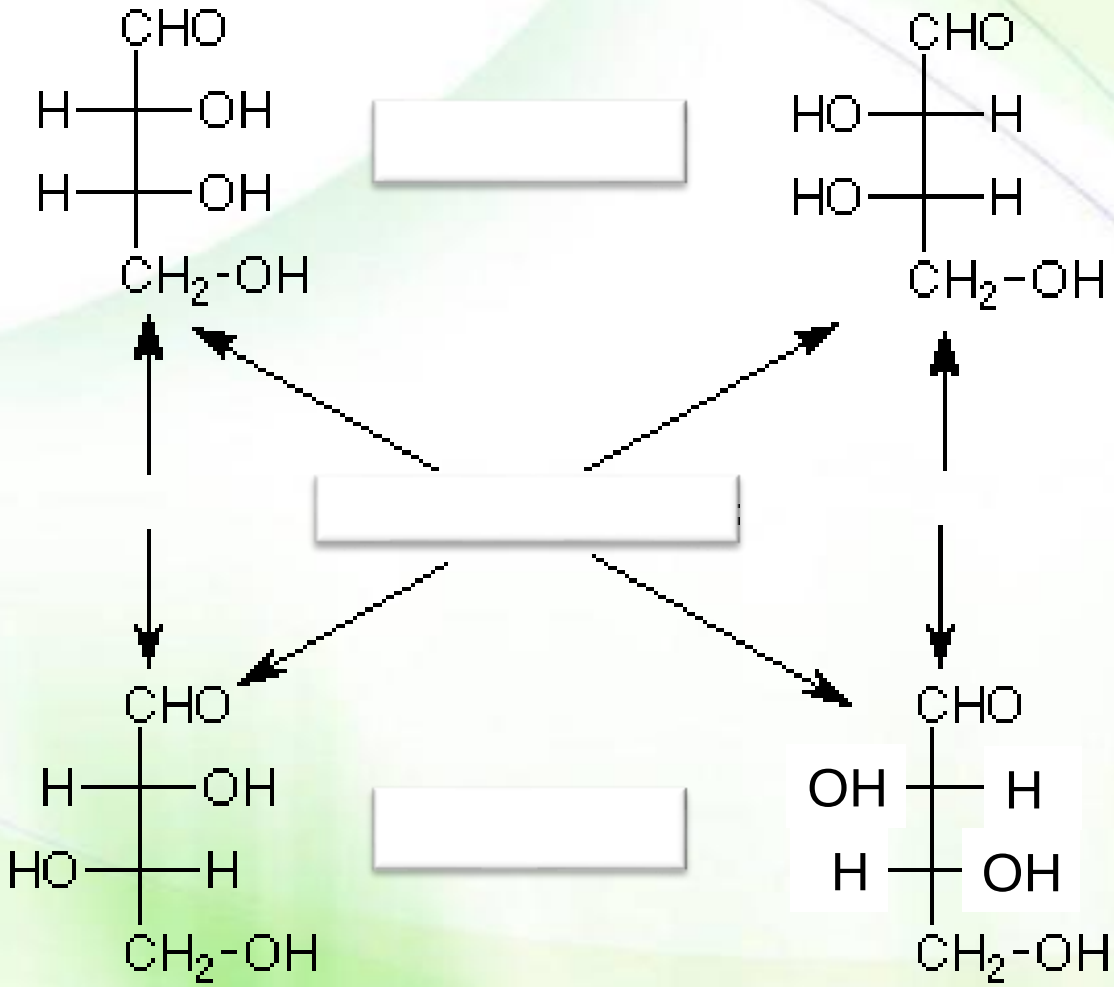
Do not memorize but study them.

Isomerism

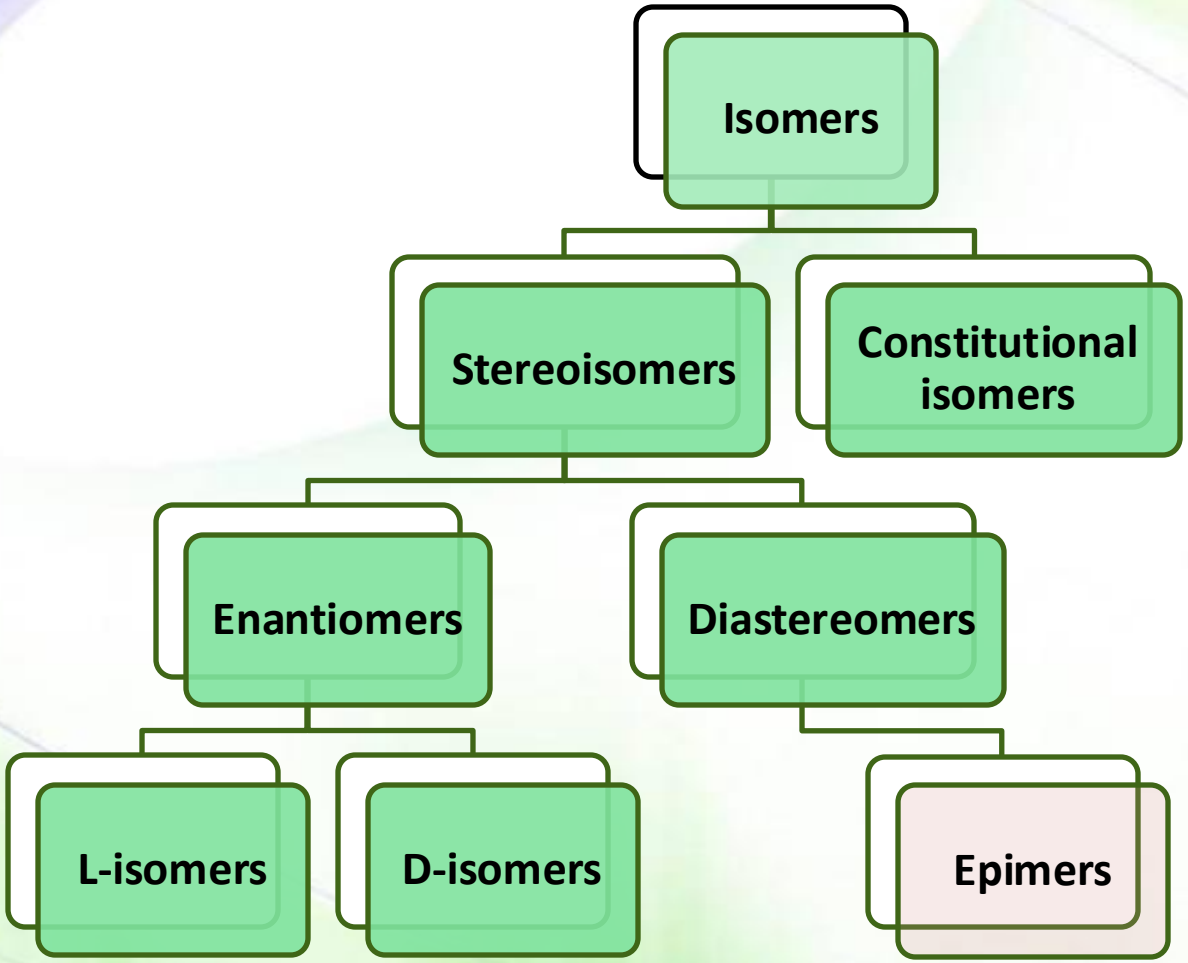


Two or more stereoisomers of a compound having different configurations at one or more (but not all) of the chiral carbons and are not mirror images of each other.

Stereoisomers, but non-mirror images and non-superimposable, then…*diastereomers*



Isomerism

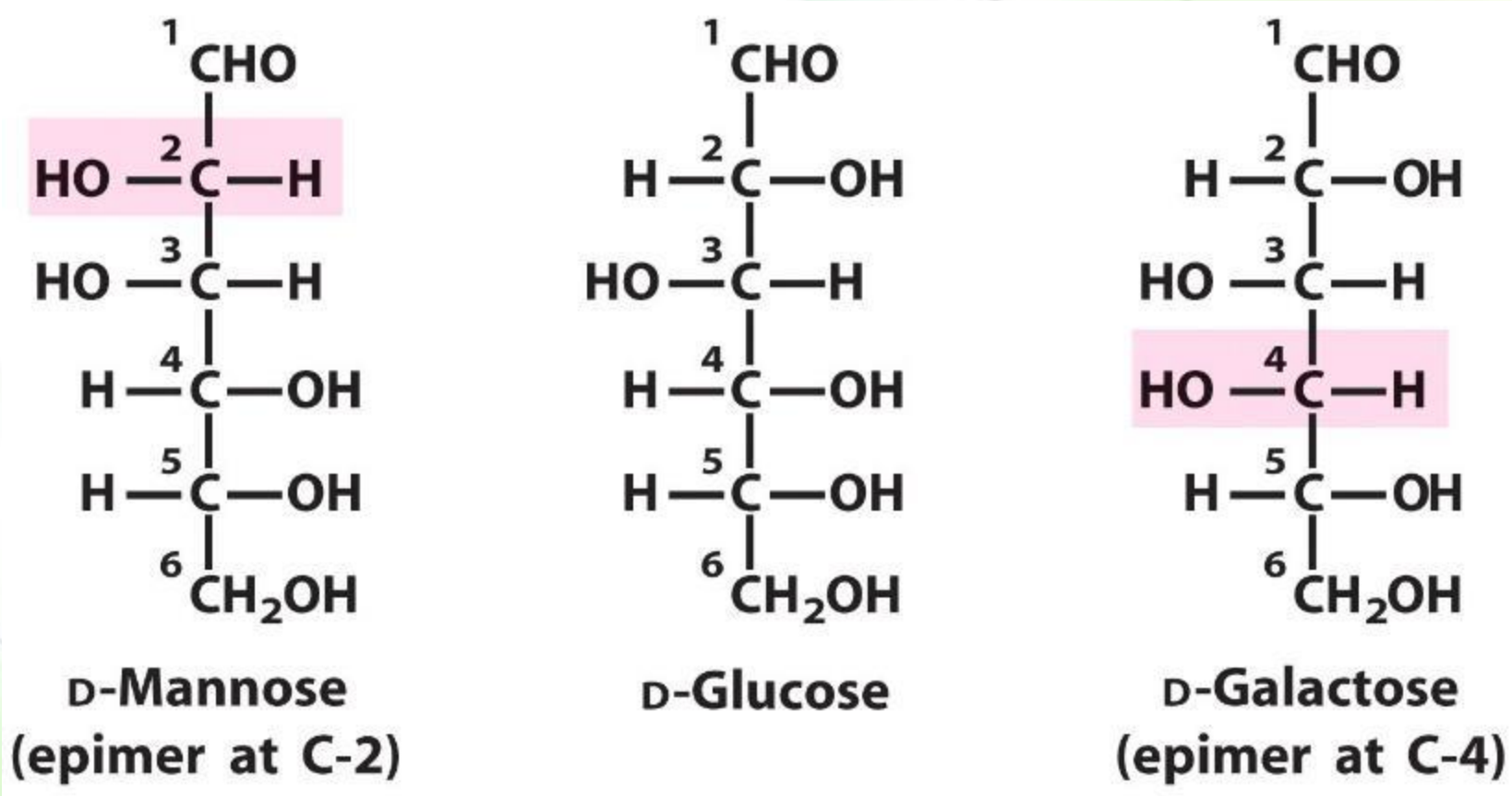


Epimer refers to one of a pair of stereoisomers whereby two isomers differ in configuration at only one chiral carbons.

Diastereomers with different orientation of one chiral carbonm

then... *epimers*

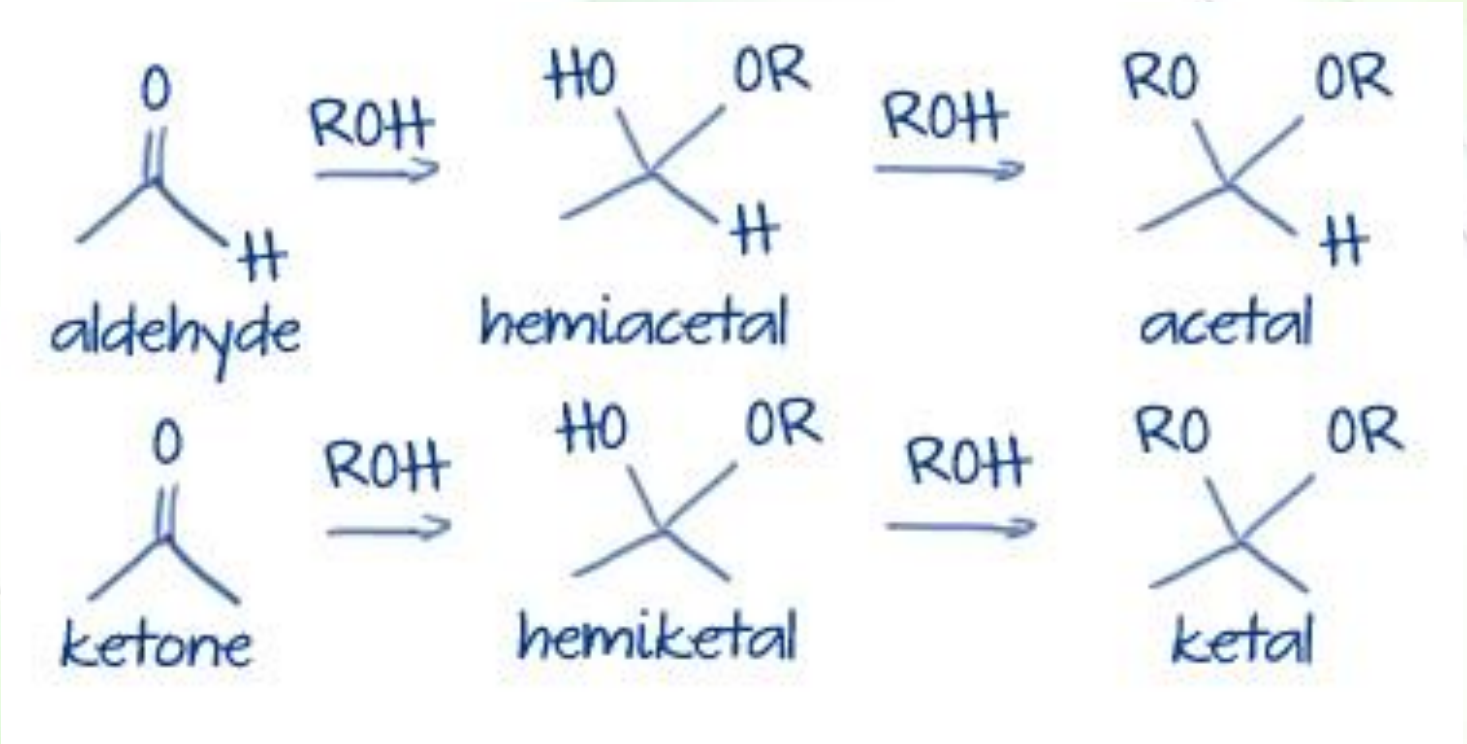
Memorize and study them.



Is L-glucose an epimer with D-mannose and D-galactose?

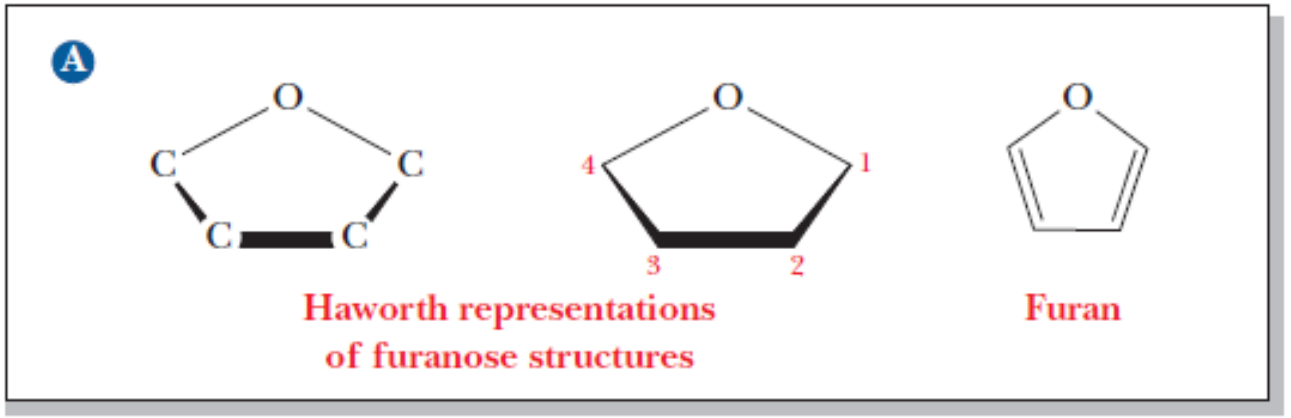
Acetal/ketal vs. hemiacetal/hemiketal

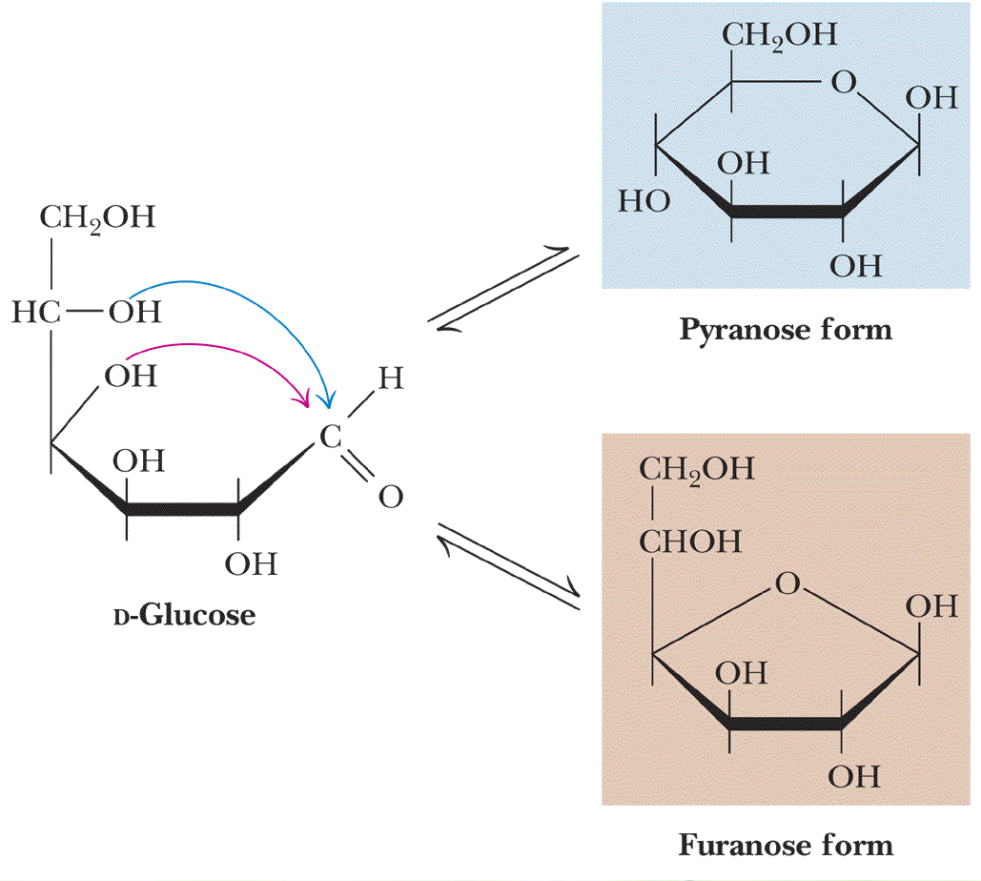
Hemiacetal and hemiketal: ether and alcohol on same carbon
Acetal and ketal: two ethers on same carbon



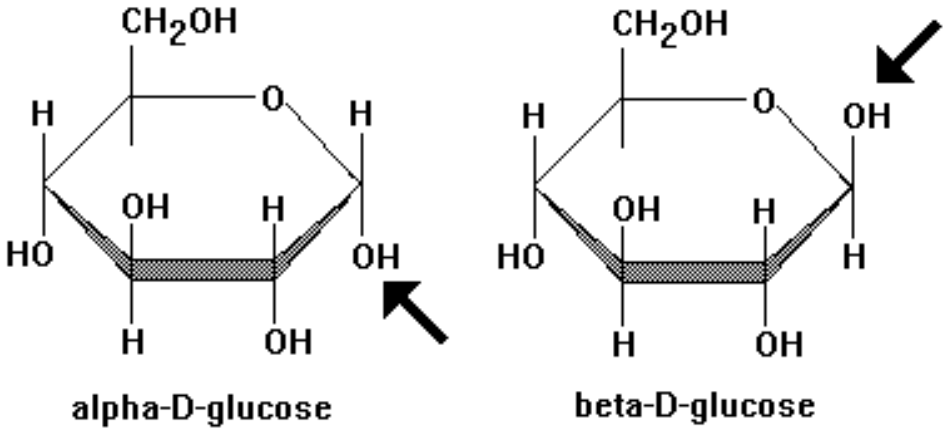
What is the difference between hemiacetal and hemiketal and the difference between acetal and ketal?

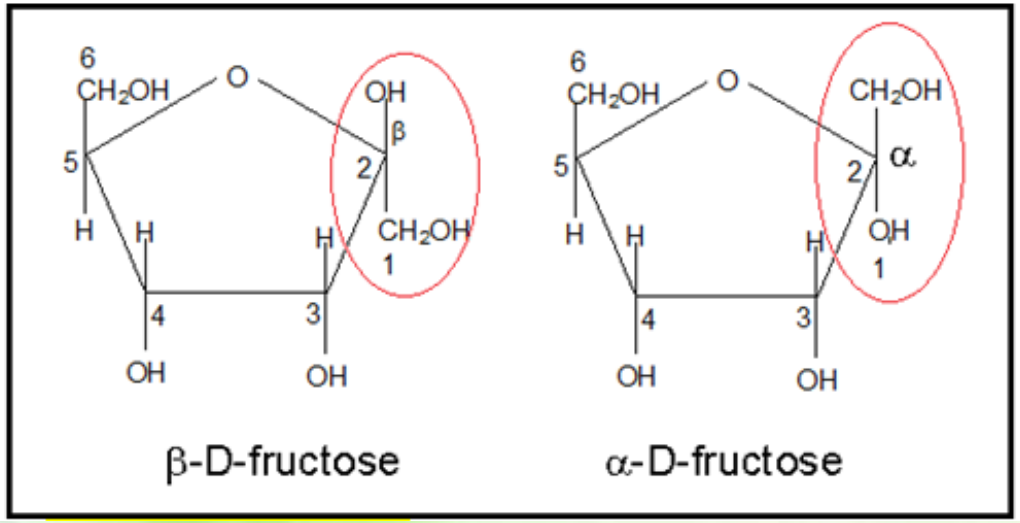
Formation of a ring structure





Anomers

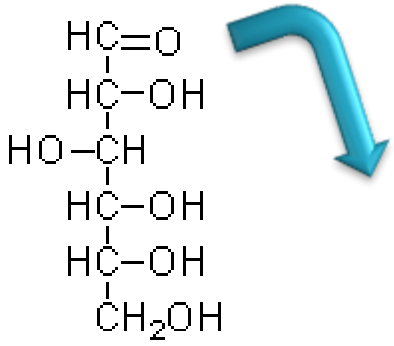

CH2OH
O
H
OH
HO
H
OH
alpha-D-glucose
beta-D-glucose

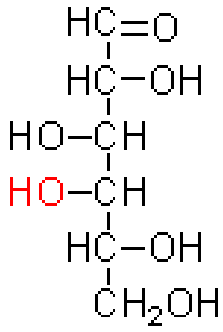

β-D-fructose
α-D-fructose

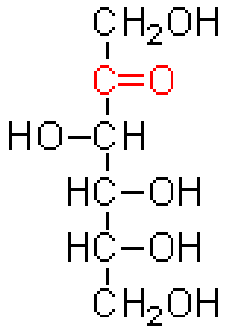
Chain to ring

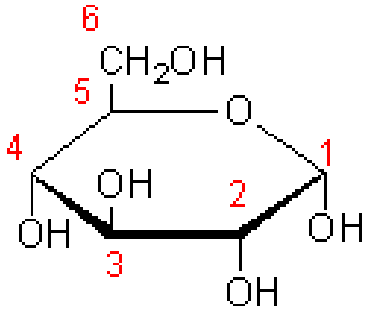
Left-up, right-down

Face the sugar and go down to <u>YOUR</u> right

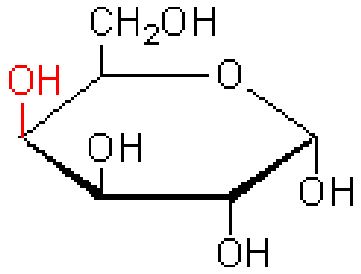




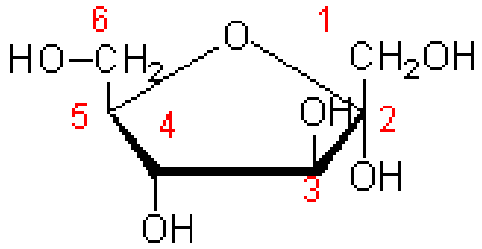




glucose



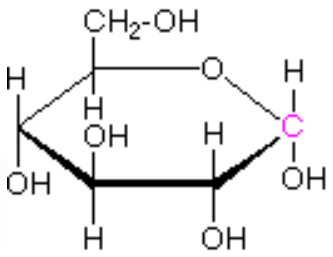
galactose



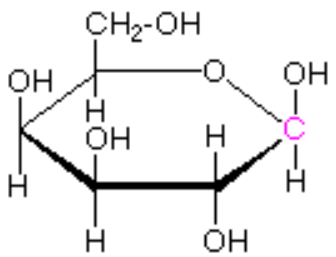
fructose

Cyclic aldohexoses

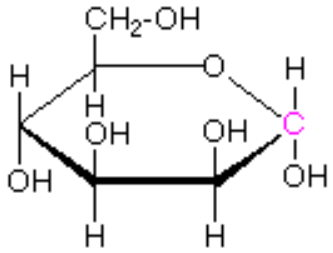
Examples of Some Pyranose Forms of Hexoses



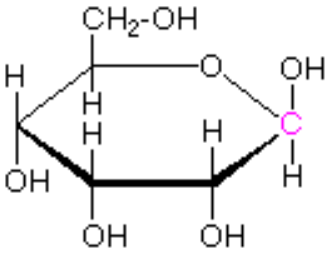
α-D-glucopyranose



β-D-galactopyranose

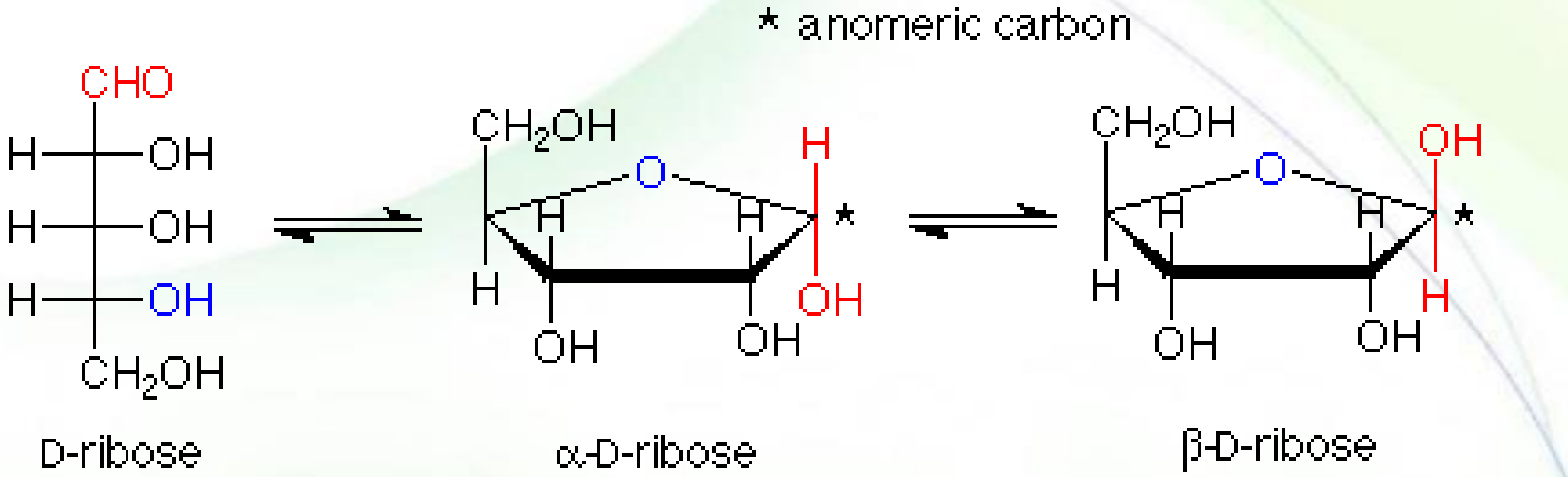


α-D-mannopyranose



β-D-allopyranose

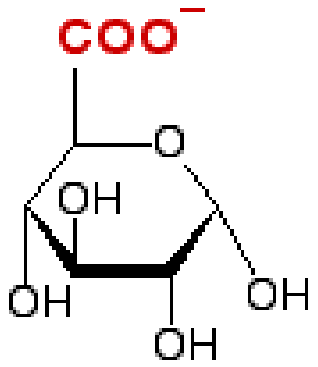
Cyclic ribofuranose



Modified sugars

Sugar acids (oxidation)

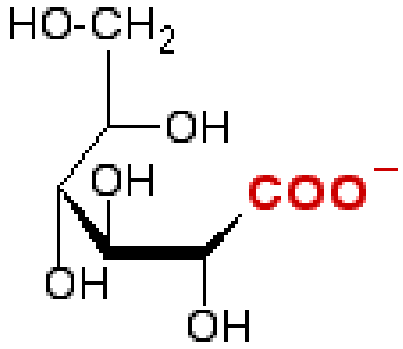
- Where is it oxidized? What does it form?



α-D-glucuronate

(D-glucuronic acid, **GlcUA**)

from **oxidation of glucose C6 OH**



D-gluconate

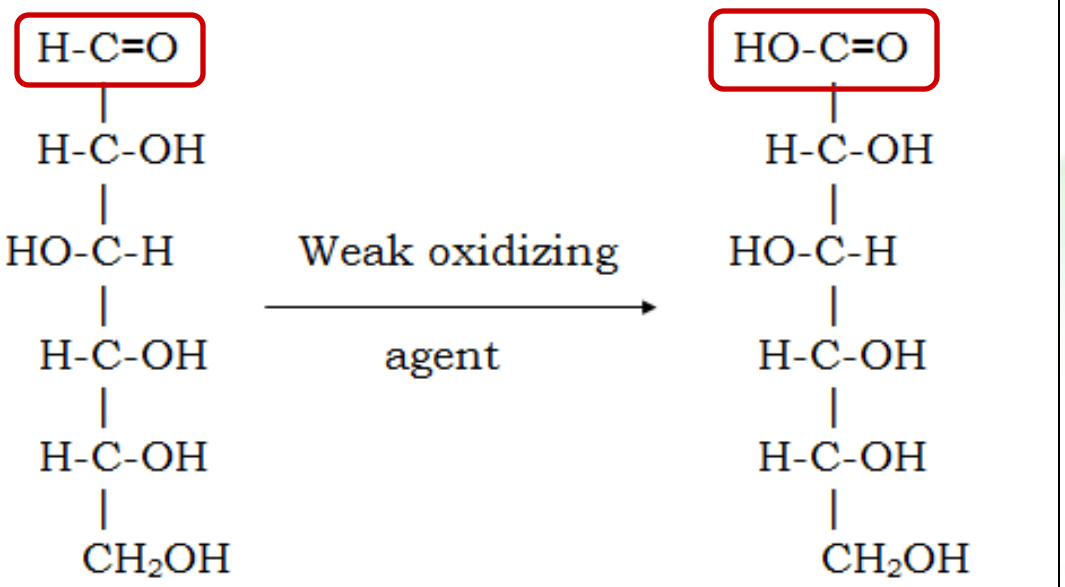
(D-gluconic acid, **GlcA**)

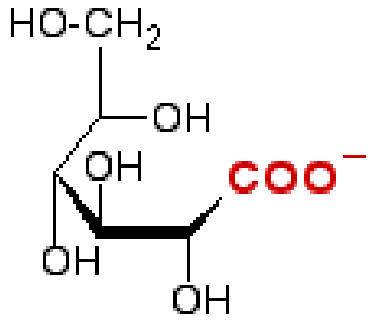
from **oxidation of glucose C1 aldehyde)**

Do not memorize the structure but study it.

Gluconate

a. Weak oxidizing agent



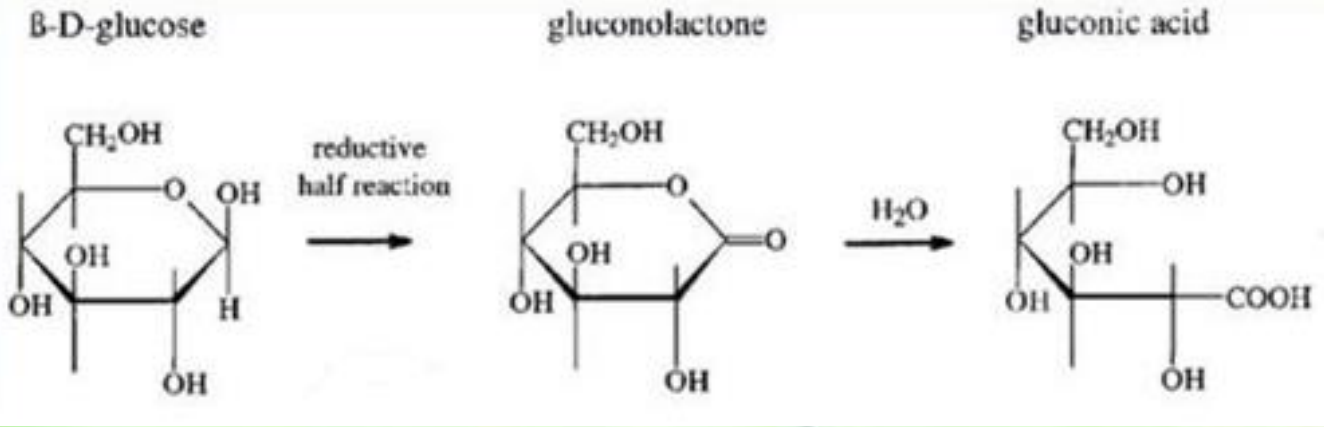


D-gluconate

(D-gluconic acid, **GlcA**)

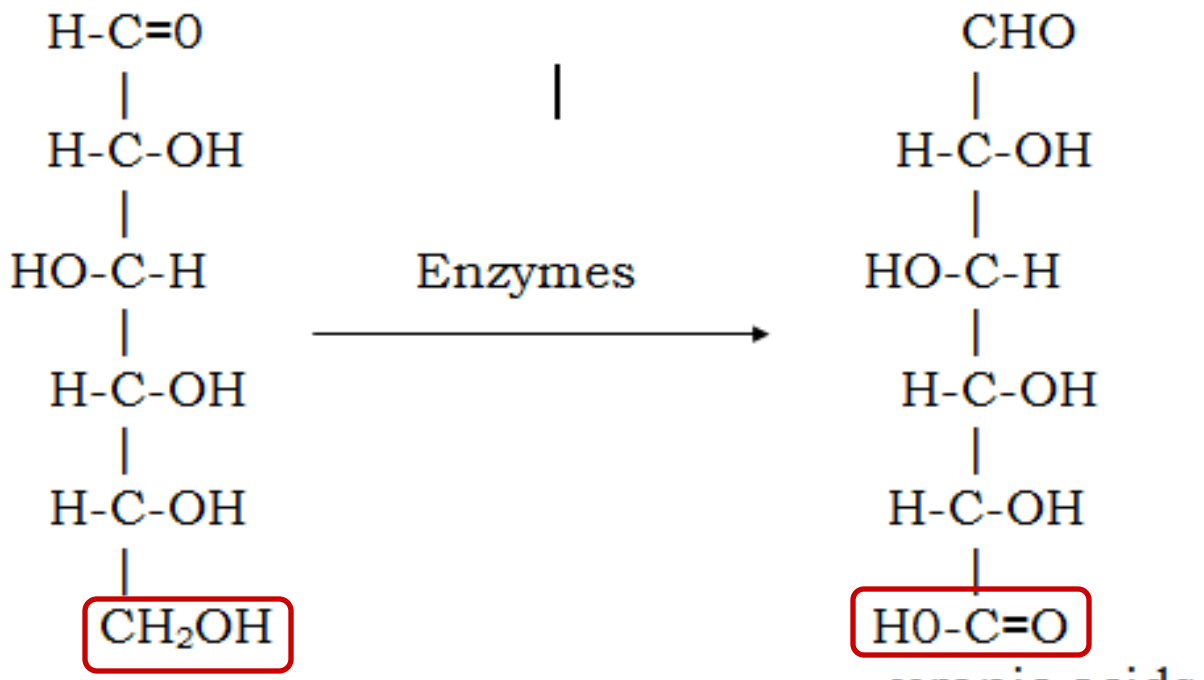
from **oxidation of glucose C1 aldehyde)**

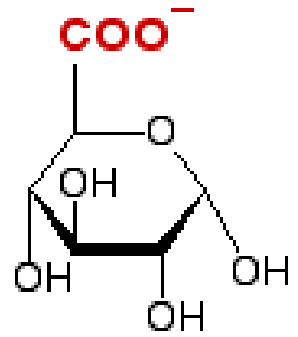
Do not memorize the structure but study it.



Glucoronate

c. Oxidation of primary alcohol end in biological systems



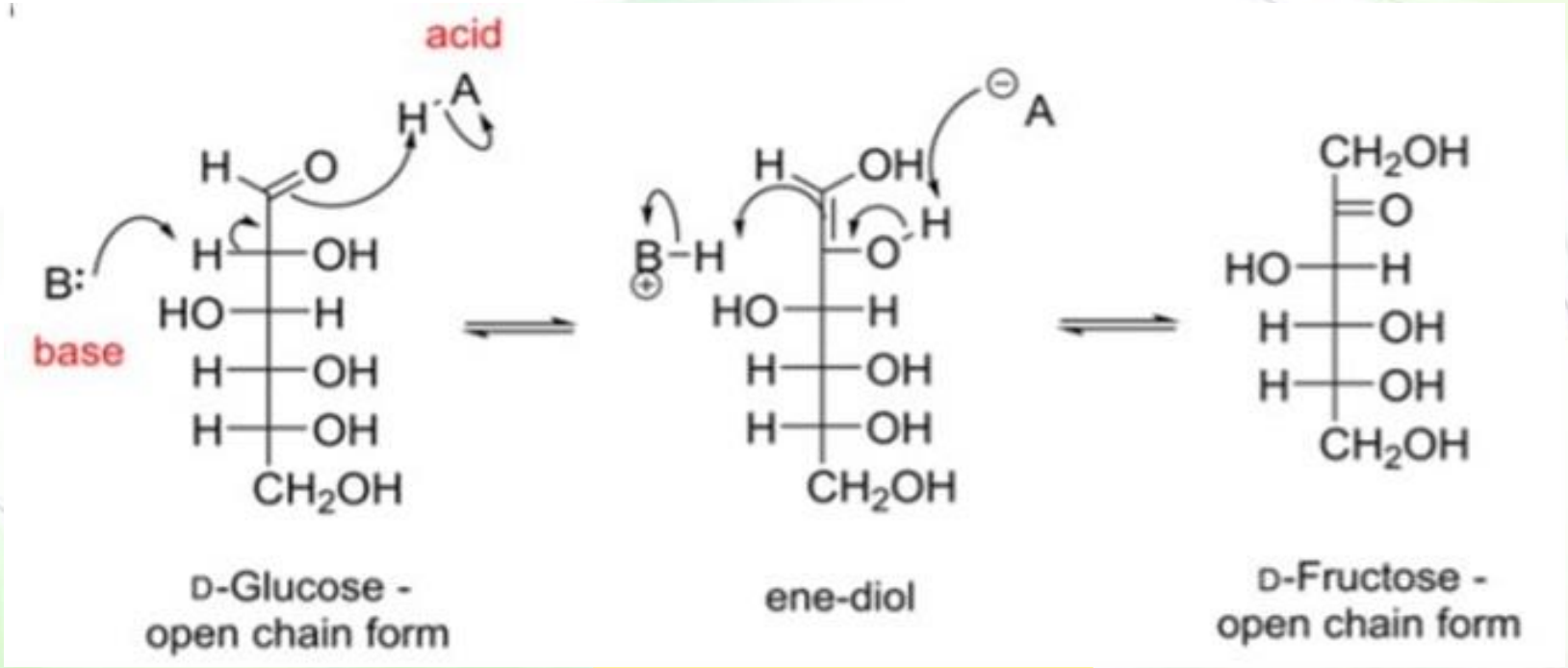


α-D-glucuronate
(D-glucuronic acid, **GlcUA**)
from **oxidation of glucose C6 OH**

Do not memorize the structure but study it.

Note

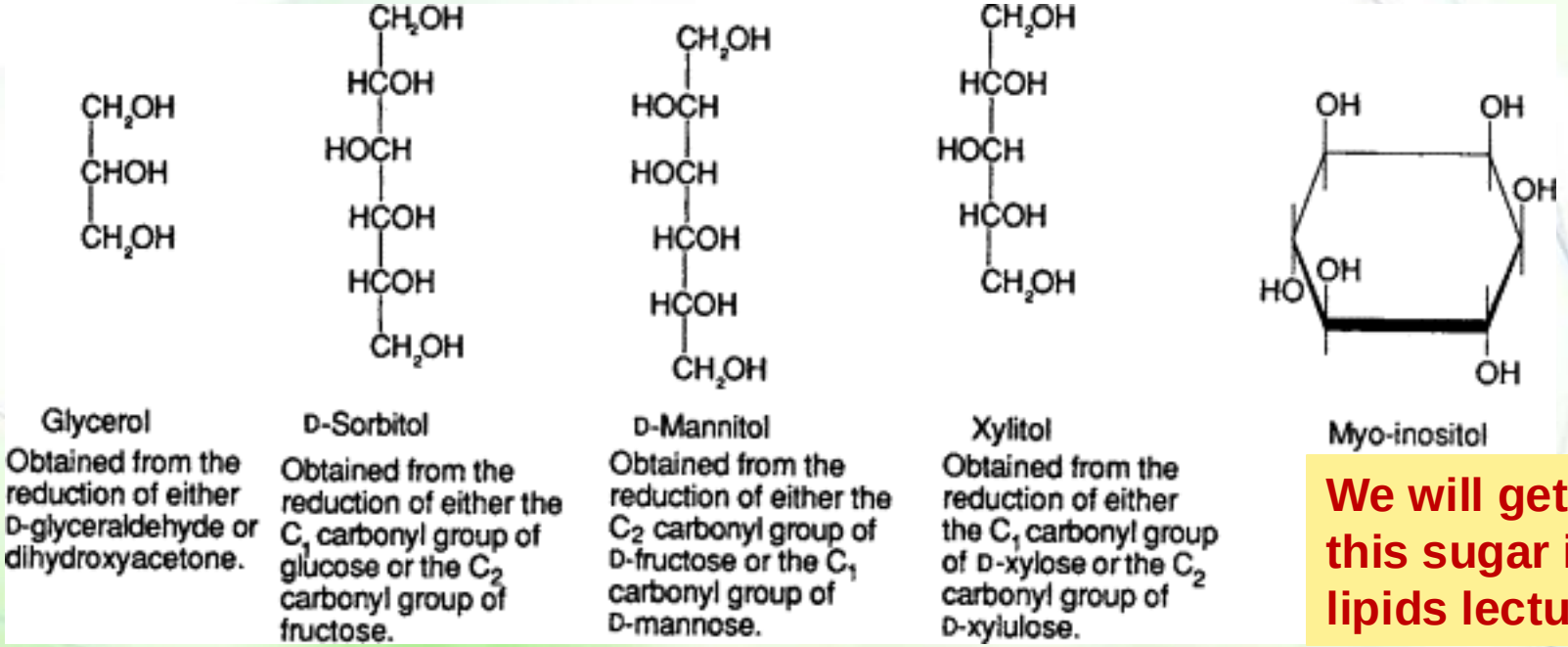
- Oxidation of ketoses to carboxylic acids does not occur, but they can be oxidized indirectly.



Do not memorize the ene-diol structure but study it.

Sugar alcohols (reduction)

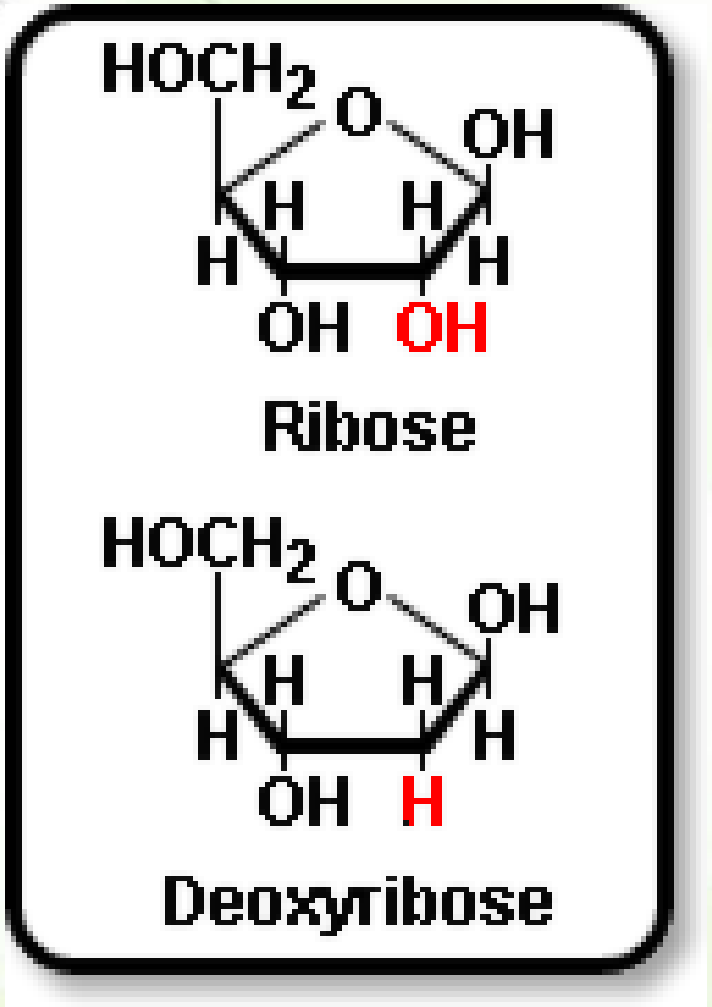
- What does it form?
- Examples include sorbitol, mannitol, and xylitol, which are used to sweeten food products



We will get to this sugar in the lipids lecture

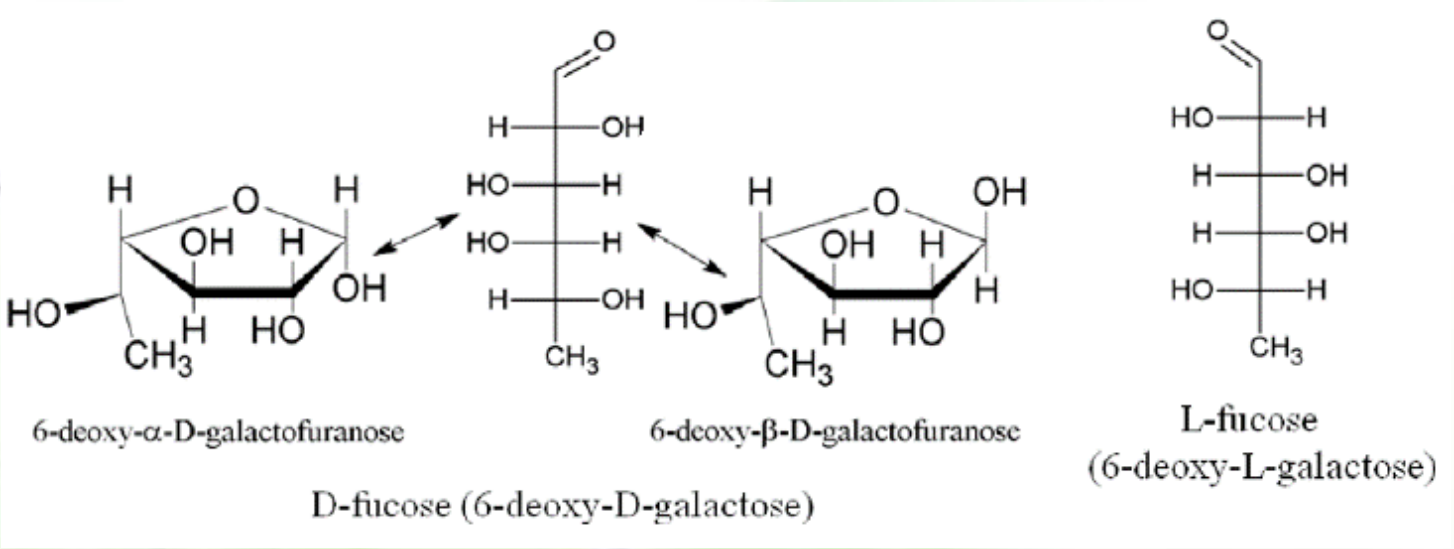
Deoxy sugars (reduced sugars)

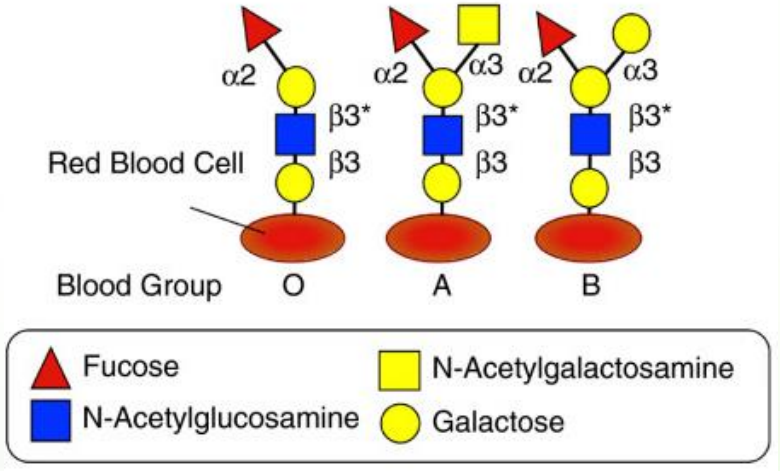
- One or more hydroxyl groups are replaced by hydrogens.
- An example is 2-deoxyribose, which is a constituent of DNA.



Another deoxy sugar

- L-fucose (L-6-deoxygalactose)
  - found in the carbohydrate portions of some glycoproteins



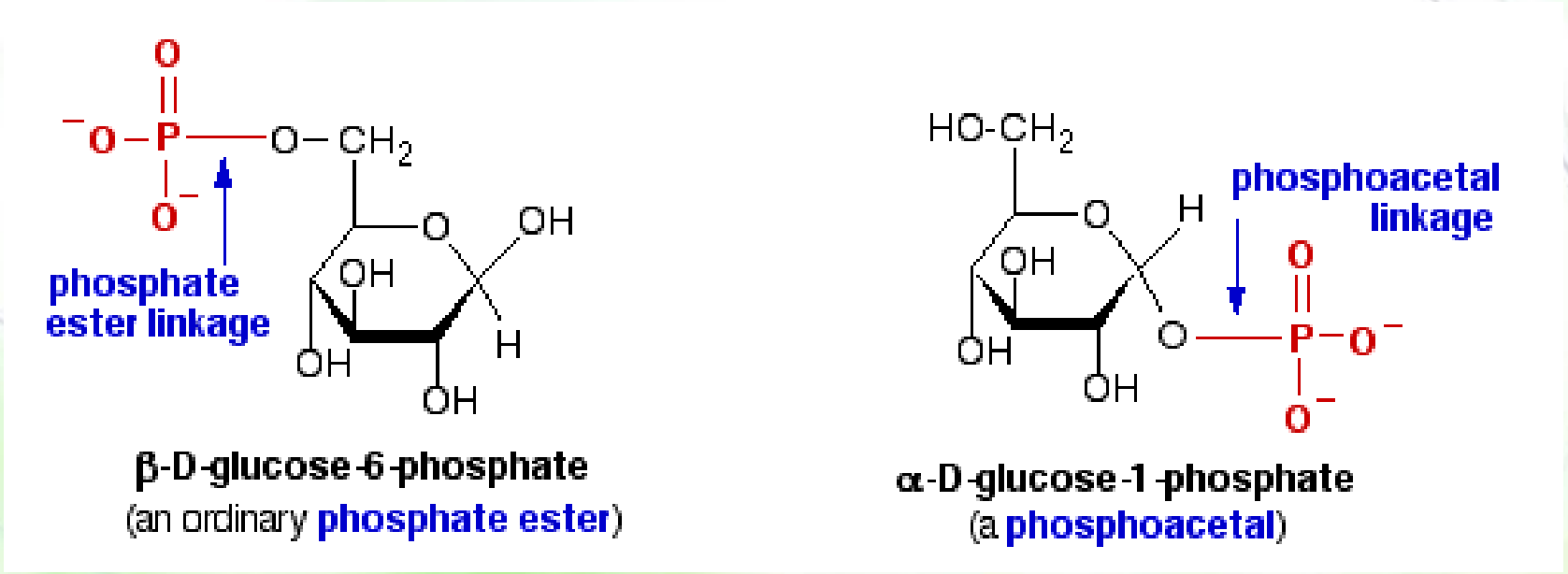


Do not memorize the structure but study it.

Do not memorize the components except for fucose.

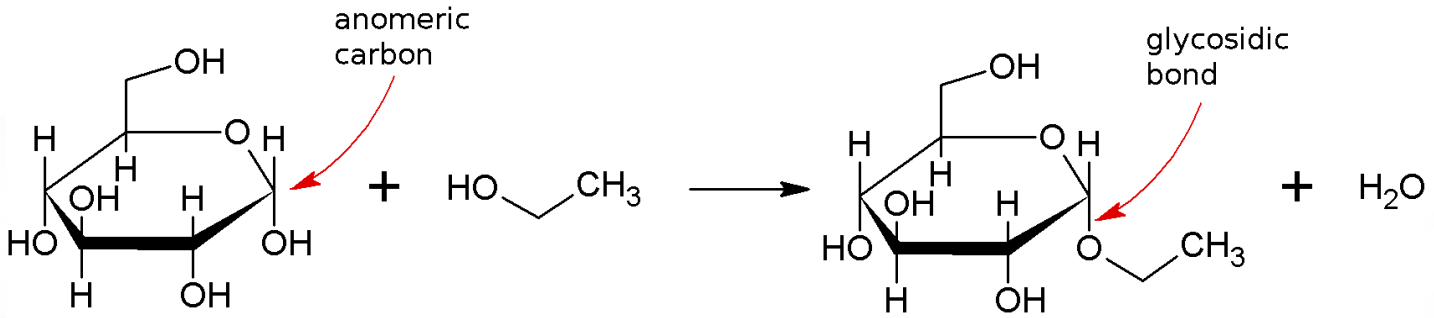
Sugar esters (esterification)

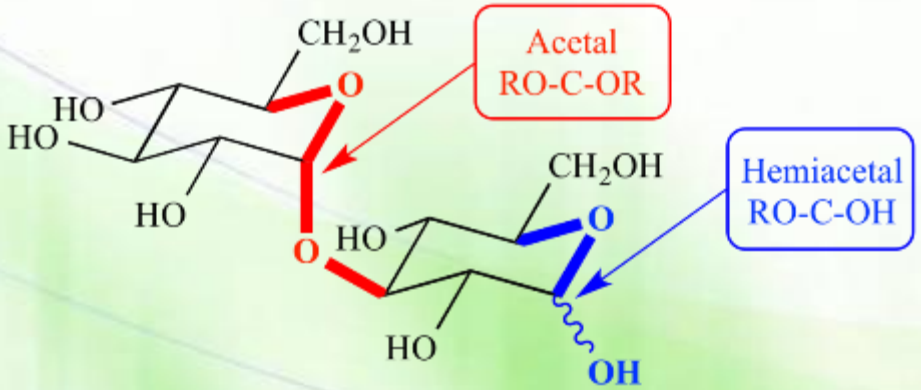
- What is the reacting functional group? Where does it react? What are the end products? Where are they used?

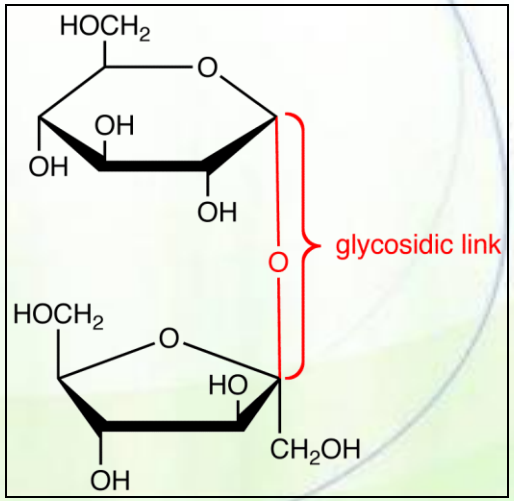


O-Glycosides

- What is the reacting functional group? Where does it react? What are the end products? Where are they used?

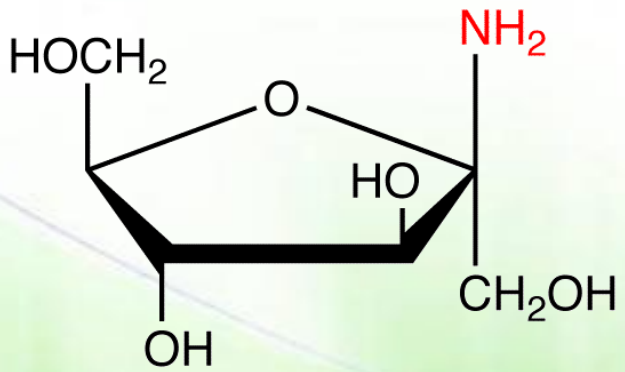




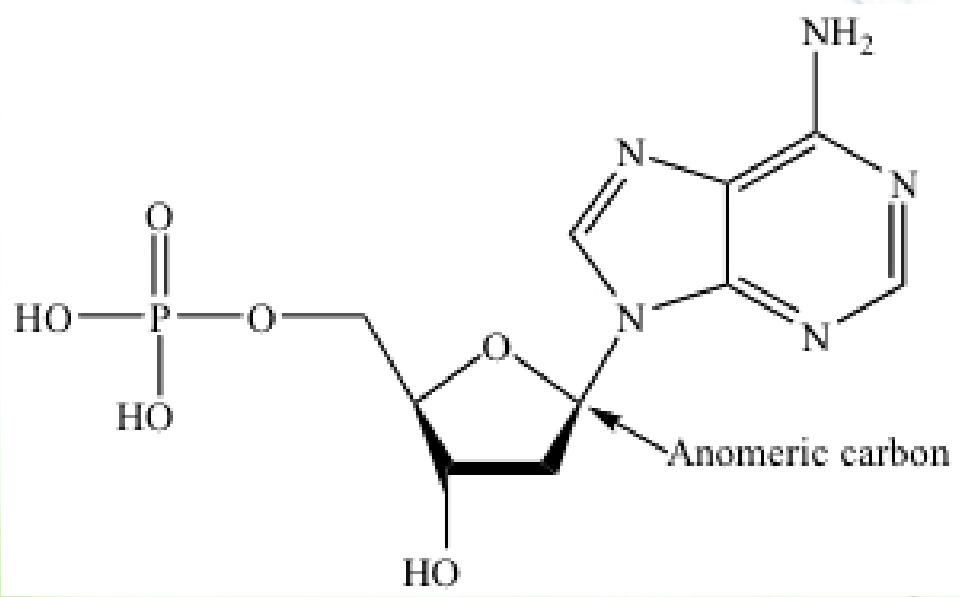


N-Glycosides

- What is the reacting functional group? Where does it react? What are the end products? Where are they used?
- Examples: nucleotides (DNA and RNA)

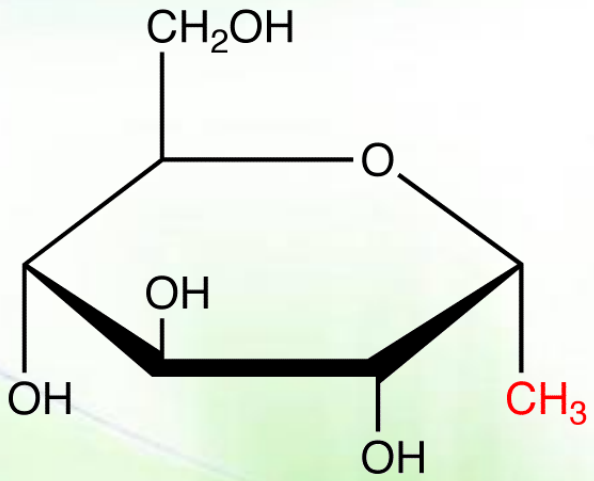


N-glycoside

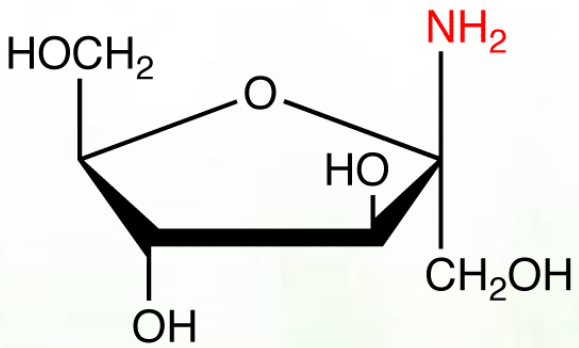


Note

- Glycosides derived from furanoses are called furanosides, and those derived from pyranoses are called pyranosides, regardless if they are N- or O-linkded.



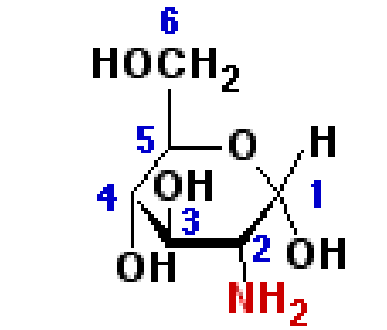
C-glycoside



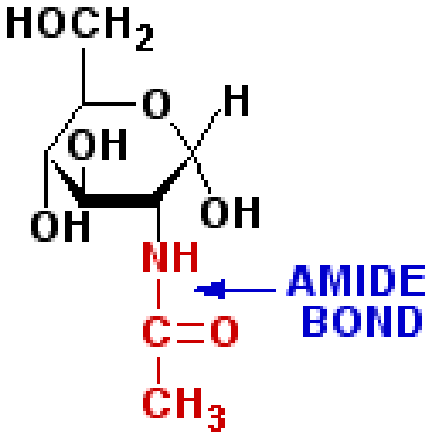
N-glycoside

Amino sugars

- What is the reacting functional group? Where does it react? What are the end products? Where are they used?
- Further modification by acetylation



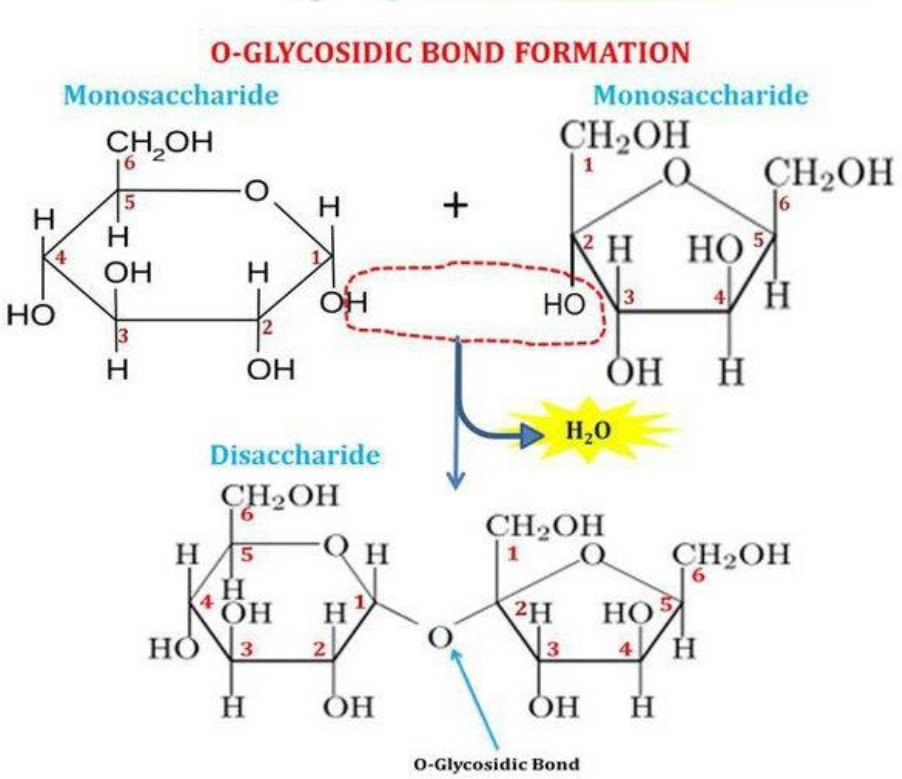
α-D-2-glucosamine
(GlcN)



N-acetyl-α-D-2-glucosamine
(GlcNAc)

Disaccharides

- What are disaccharide? Oligosaccharides? Hetero- vs. homo-?
- What is the type of reaction?
- What is a residue?
- Synthesizing enzymes are glycosyltransferases.
- Do they undergo mutarotation?
- Are products stable?

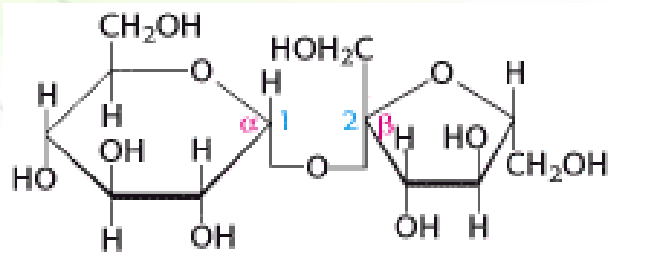


Distinctions of disaccharides

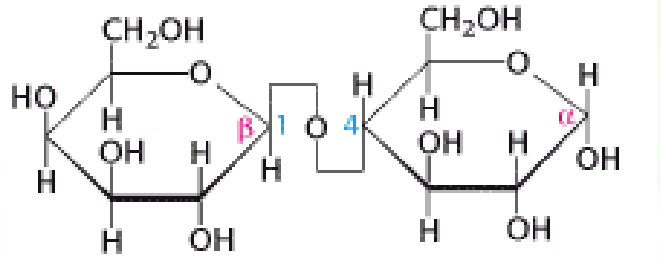
- The 2 specific sugar monomers involved and their stereoconfigurations (D- or L-)
- The carbons involved in the linkage (C-1, C-2, C-4, or C-6)
- The order of the two monomer units, if different (example: galactose followed by glucose)
- The anomeric configuration of the OH group on carbon 1 of each residue (α or β)

Abundant disaccharides

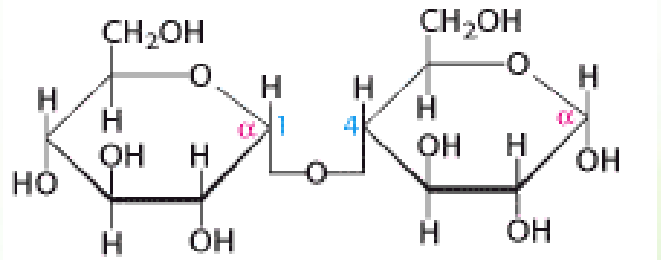
- Configuration
- Designation
- Naming (common vs. systematic)
- Reducing vs. non-reducing



Sucrose
(α-D-Glucopyranosyl-(1→2)-β-D-fructofuranose

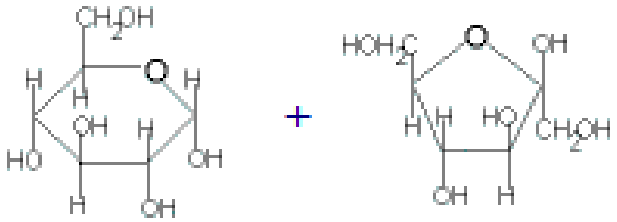


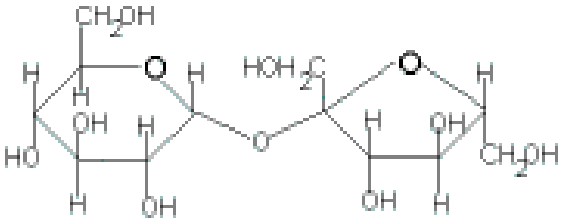
Lactose
(β-D-Galactopyranosyl-(1→4)-α-D-glucopyranose

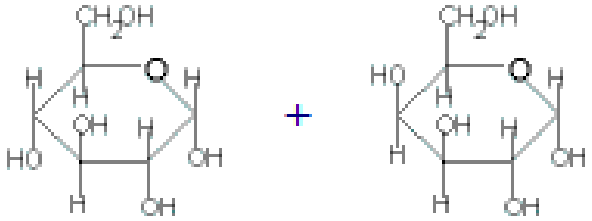


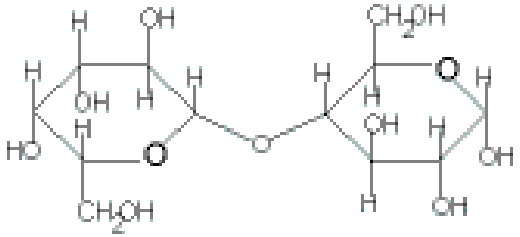
Maltose
(α-D-Glucopyranosyl-(1→4)-α-D-glucopyranose

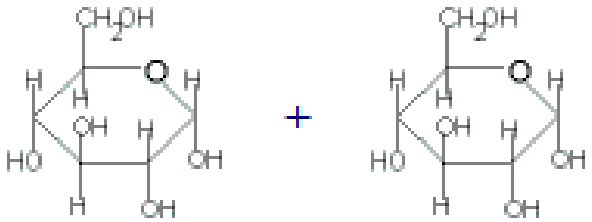
Name	Formula	Formed from	Structure
sucrose	$C_{12}H_{22}O_{11}$	glucose + fructose	---> sucrose + H_2O
lactose	$C_{12}H_{22}O_{11}$	glucose + galactose	---> lactose + H_2O
maltose	$C_{12}H_{22}O_{11}$	glucose + glucose	---> maltose + H_2O

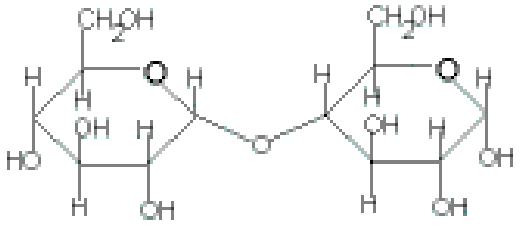




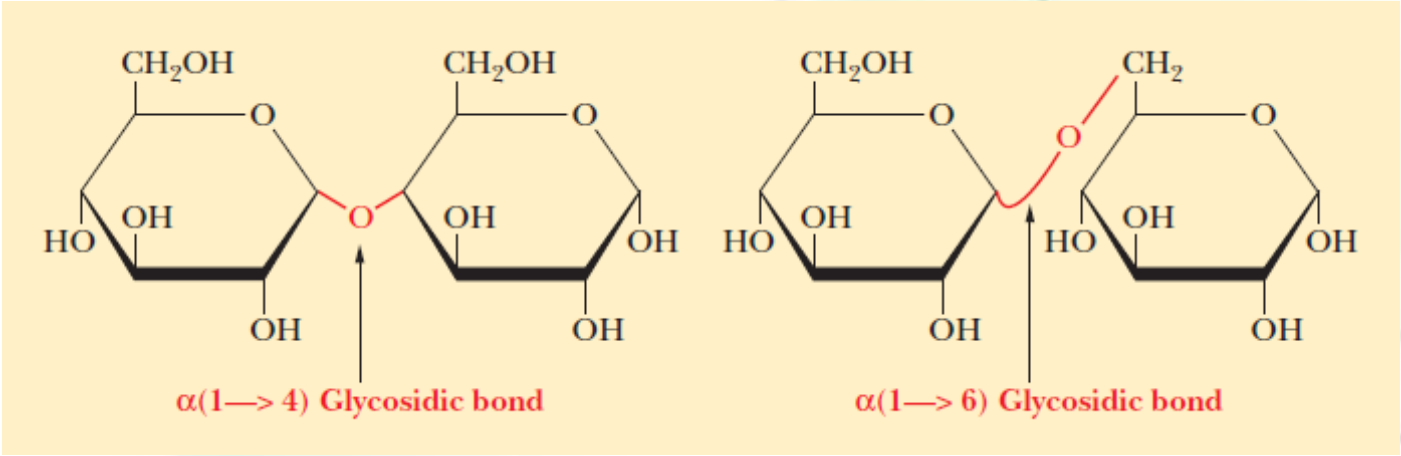


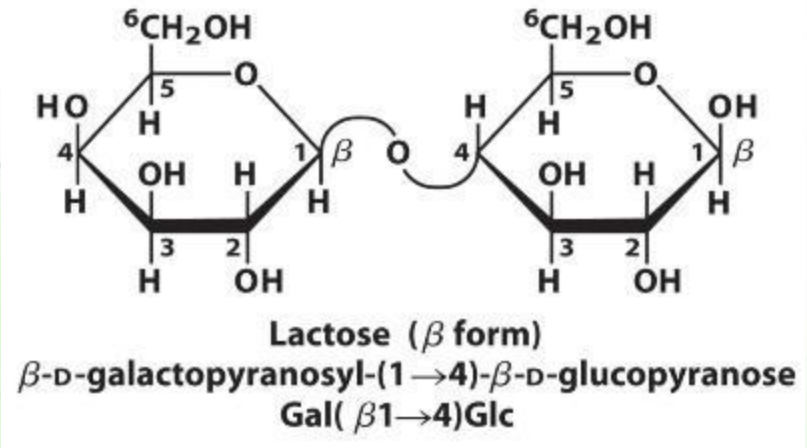


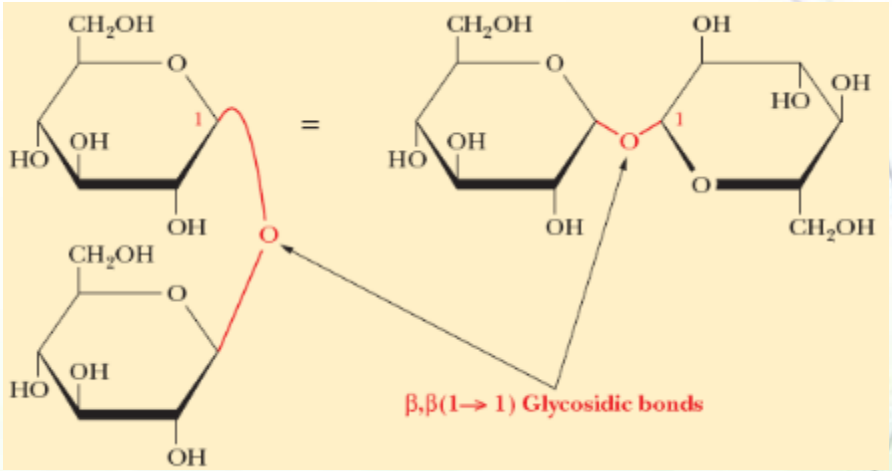




Different forms of disaccharides

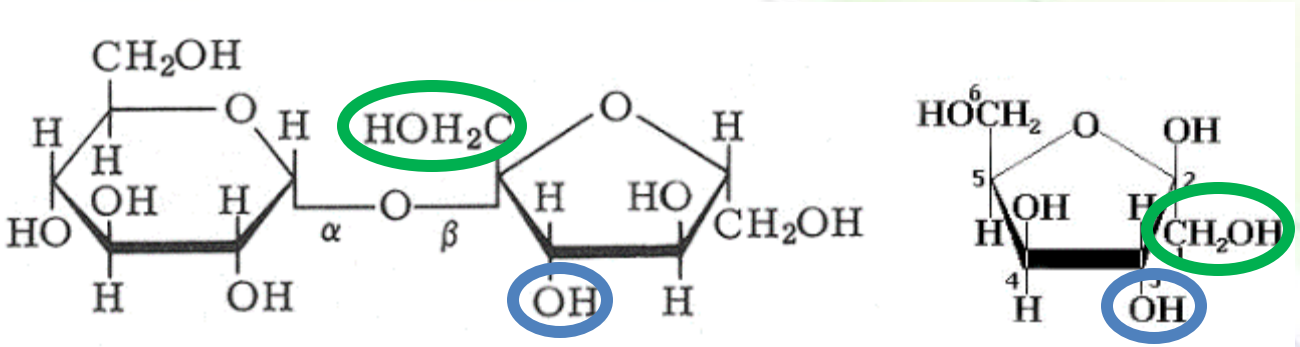


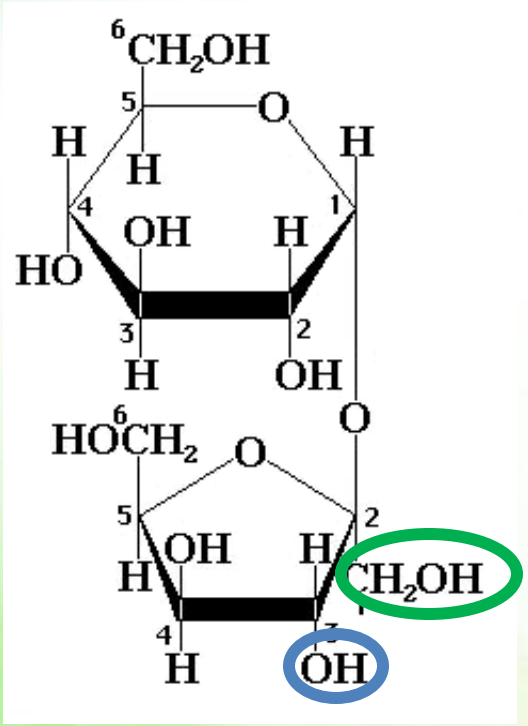




A disaccharide of β-D-glucose.

Sucrose



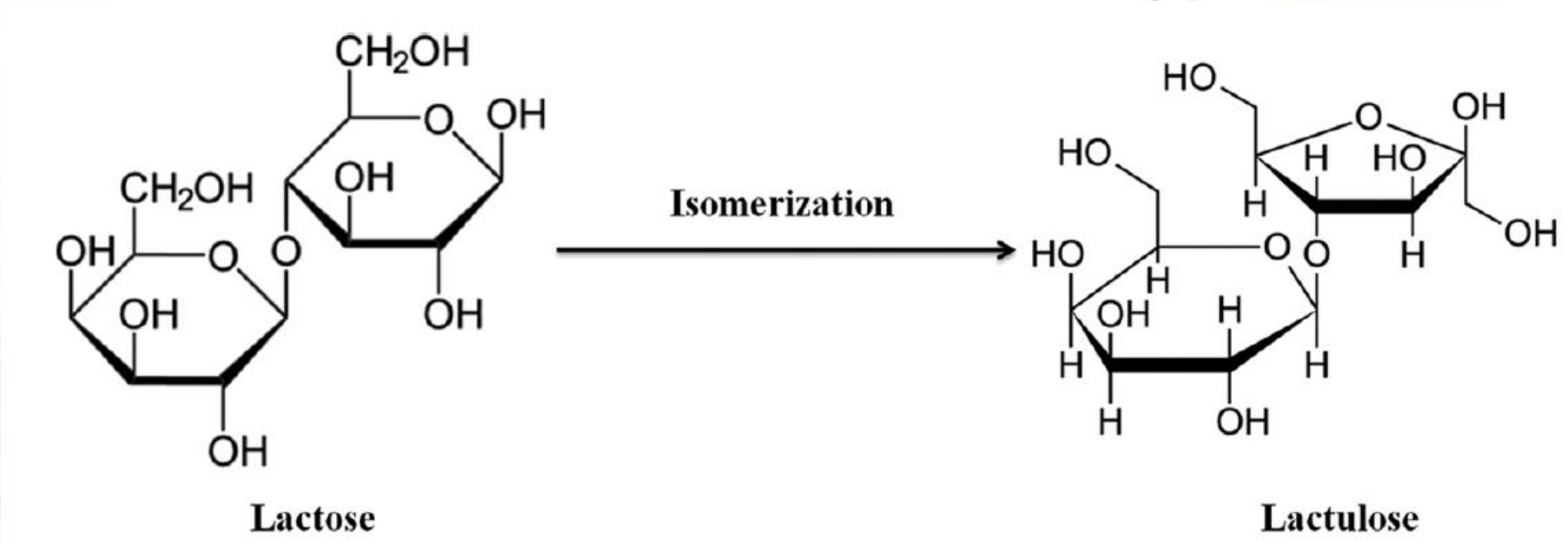


This is extra

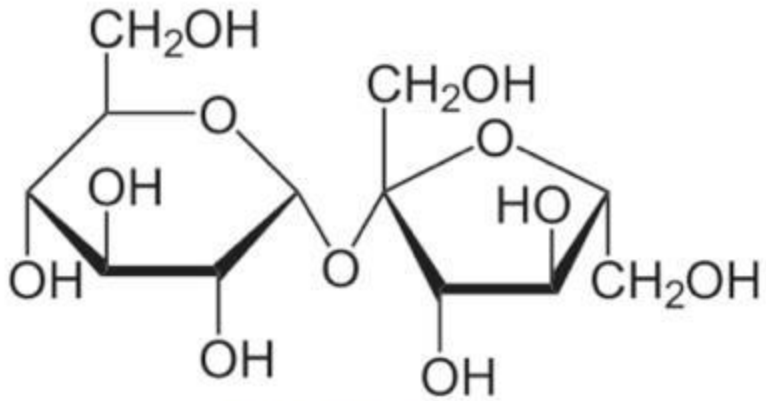
Lactulose

- It is formed by the isomerization of lactose.
- It has health benefits:
  - It is used in treating constipation.
  - It promotes the growth of health-promoting gut bacteria.
  - It modulates the immune system.

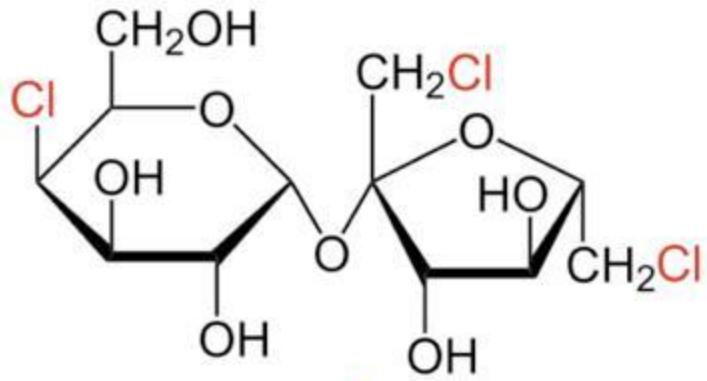
Do not memorize the structure but study it.



Sucralose (artificial sweetener)



sucrose



sucralose

News > WebMD Health News

Sucralose Damages DNA, Linked to Leaky Gut: Study

Lisa O'Mary
June 01, 2023

Sucralose, a Common Artificial Sweetener, May Increase Cancer Risk

WebMD

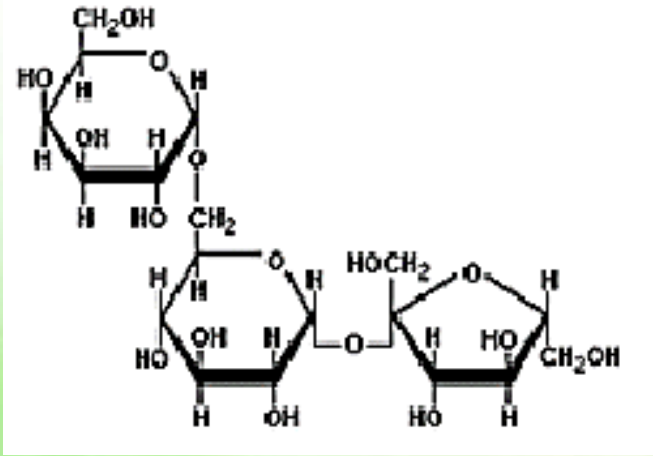
Milk problems

- Lactose Intolerance: A deficiency of the enzyme lactase in the intestinal villi allows lactase of intestinal bacteria to digest it producing hydrogen gas, carbon dioxide, and organic acids and leading to digestive problems (bloating and diarrhea).
- Galactosemia: Missing a galactose-metabolizing enzyme can result in galactosemia where nonmetabolized galactose accumulates within cells and is converted to the hydroxy-sugar galactitol, which cannot escape cells. Water is drawn into cells and the swelling causes cell damage, particularly in the brain, resulting in severe and irreversible retardation. It also causes cataract.

Raffinose

- What are oligosaccharides?
- Example: raffinose
- It is found in beans and vegetables like cabbage, brussels, sprouts, broccoli, and asparagus.

Humans lack the alpha-galactosidase enzyme that is needed to break down raffinose, but intestinal bacteria can ferment it into hydrogen, methane, and other gases.

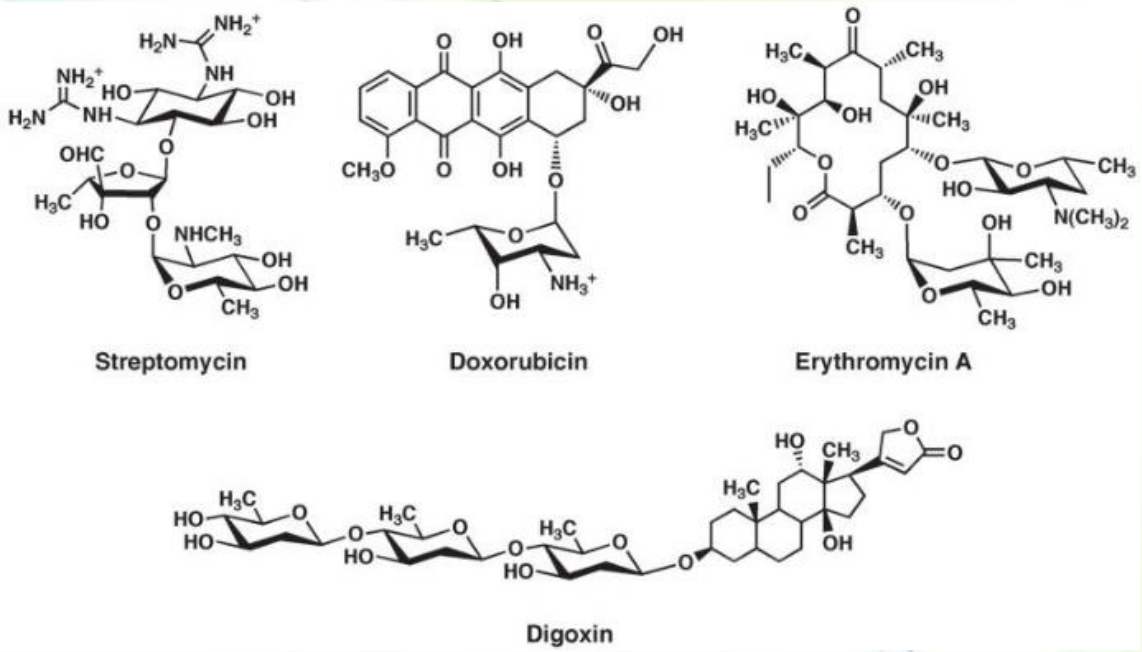


Homework

1. Recognize the monosaccharides that make up raffinose.
2. What is the monosaccharide that is attached to *what* disaccharide?

Oligosaccharides as drugs

- Streptomycin and erythromycin (antibiotics)
- Doxorubicin (cancer chemotherapy)
- Digoxin (cardiovascular disease)



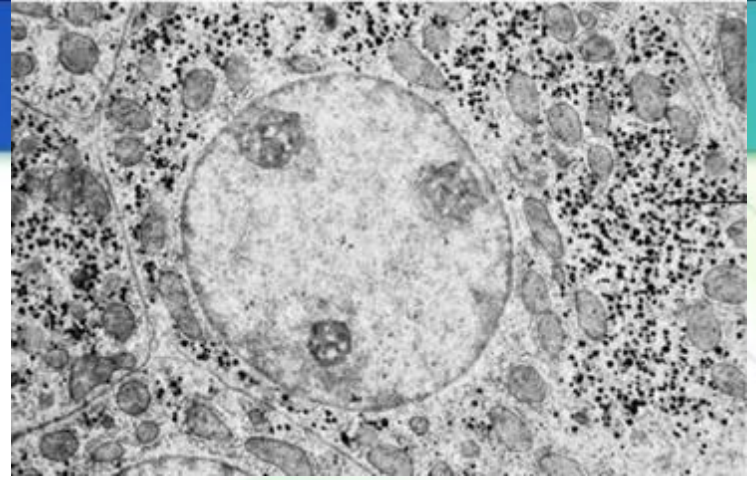
Do not memorize or study the structures.

Polysaccharides

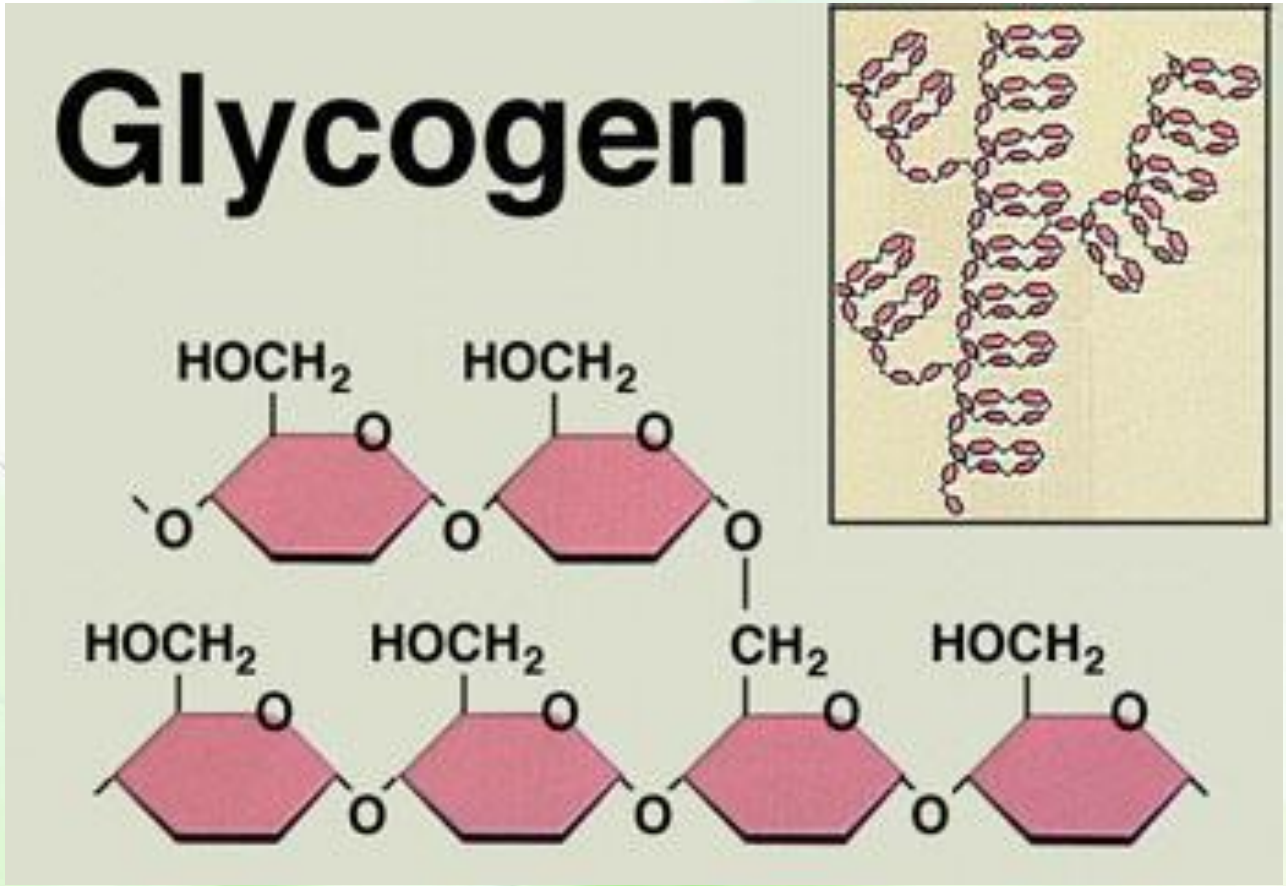
- What are polysaccharides?
- Homopolysaccharide (homoglycan) vs. heteropolysaccharides

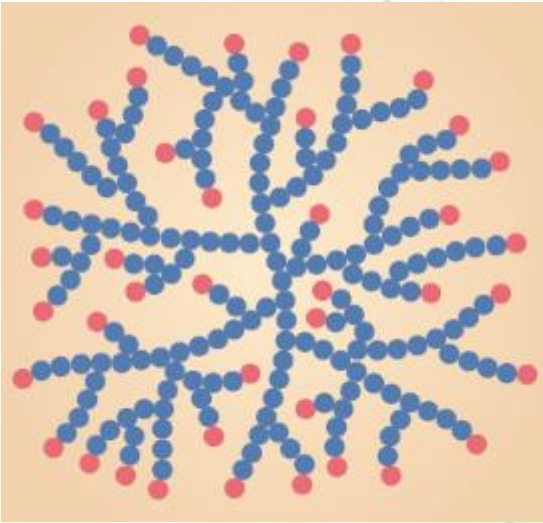
- Features of polysaccharides:
  - Monosaccharides
  - Length
  - Branching
  - Purpose:
    - Storage (glycogen, starch, dextran)
    - Structural (cellulose, pectin, chitin)

Glycogen



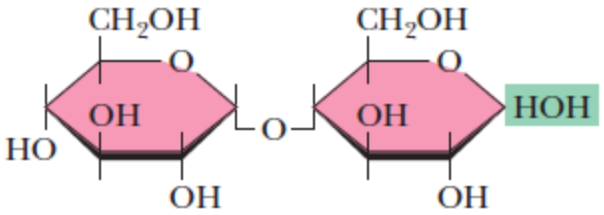
Memorize



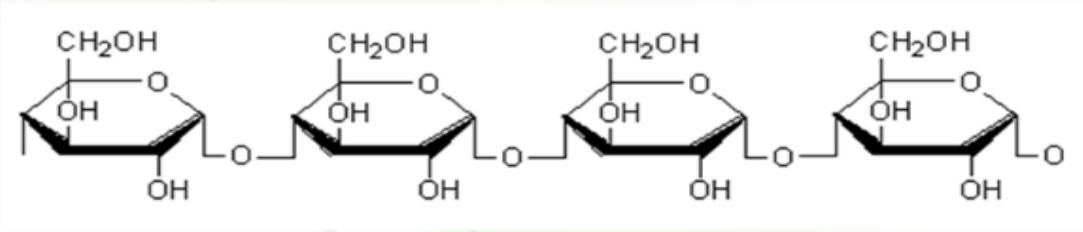


Starch

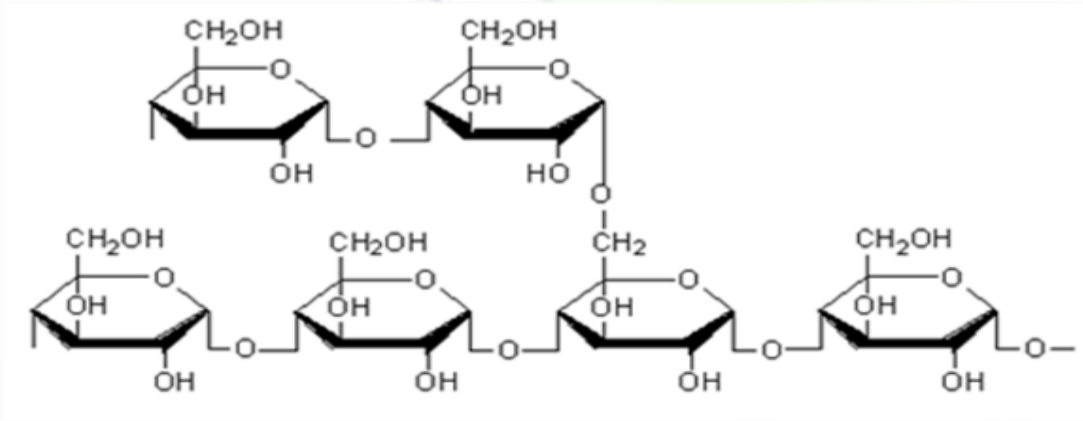
- Which organisms?
- Forms:
  - amylose (10-20%)
  - amylopectin (80-90%)



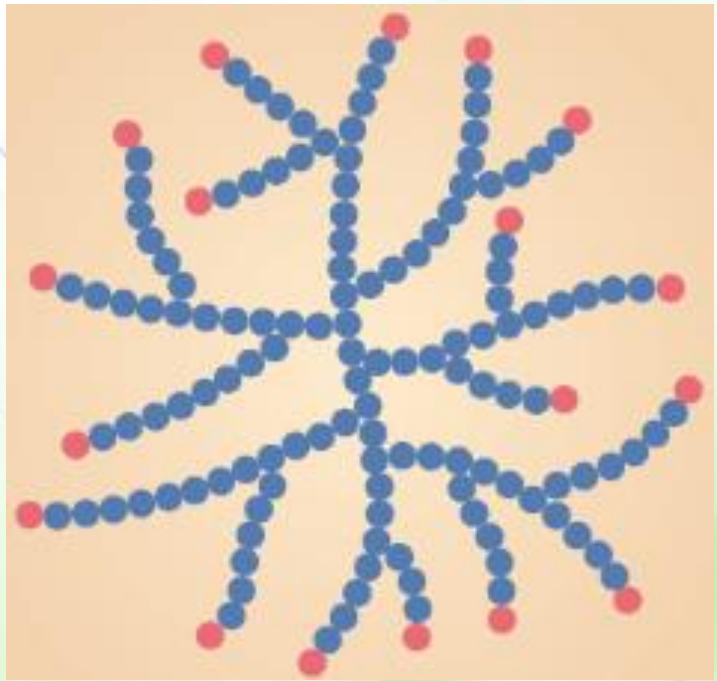
Maltose (glucose-α-1,4-glucose)



Amylose Structure



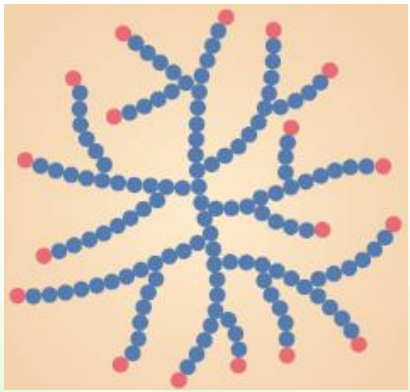
Amylopection Structure

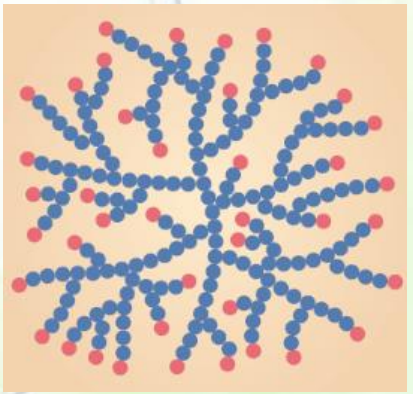


Memorize

Glycogen vs. amylopectin

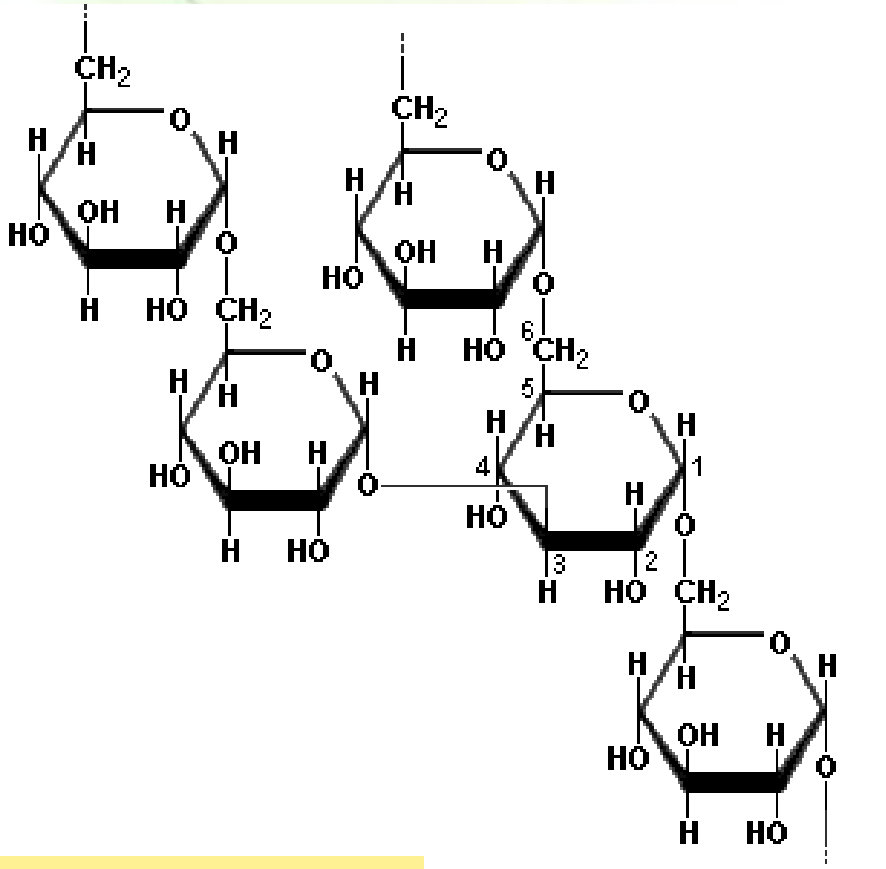
- Both are made from the same monomer and both are branched.
- Glycogen exists in animals and amylopectin in plants.
- Glycogen is more highly branched.
  - Branch points occur about every 10 residues in glycogen and about every 25 residues in amylopectin.
- Why is branching important?
  - It makes it more water-soluble and does not crystallize.
  - Easy access to glucose residues.





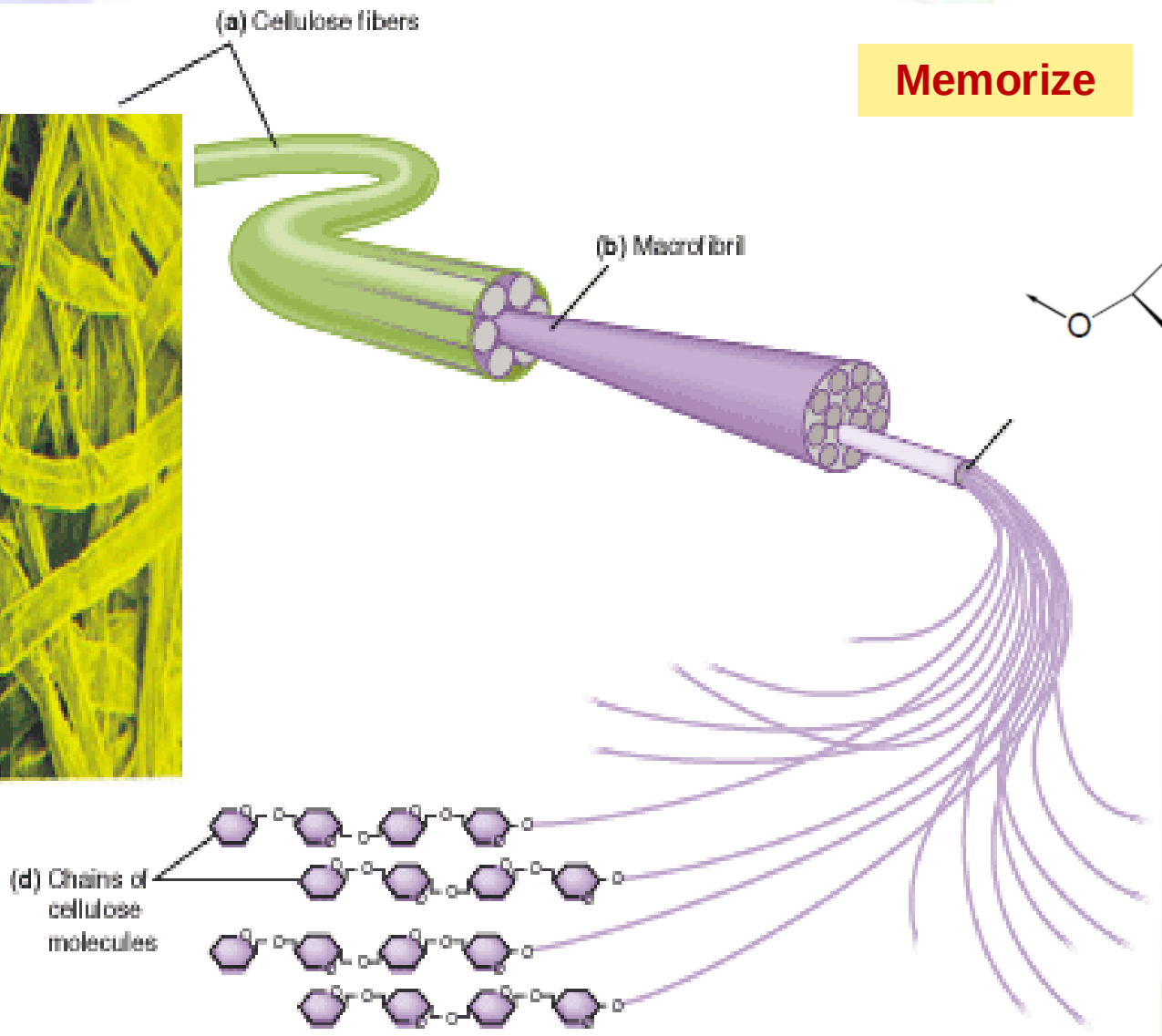
Dextran

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

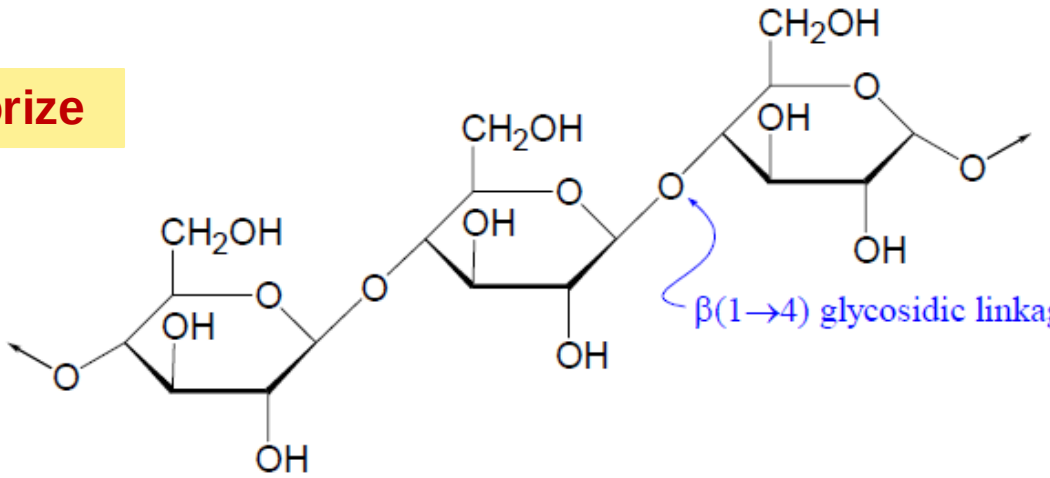


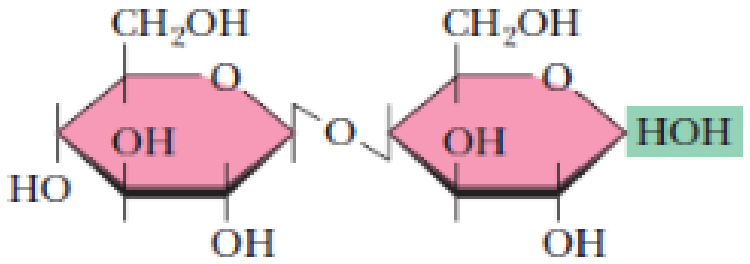
Do not memorize or study the structures.

Cellulose



Memorize

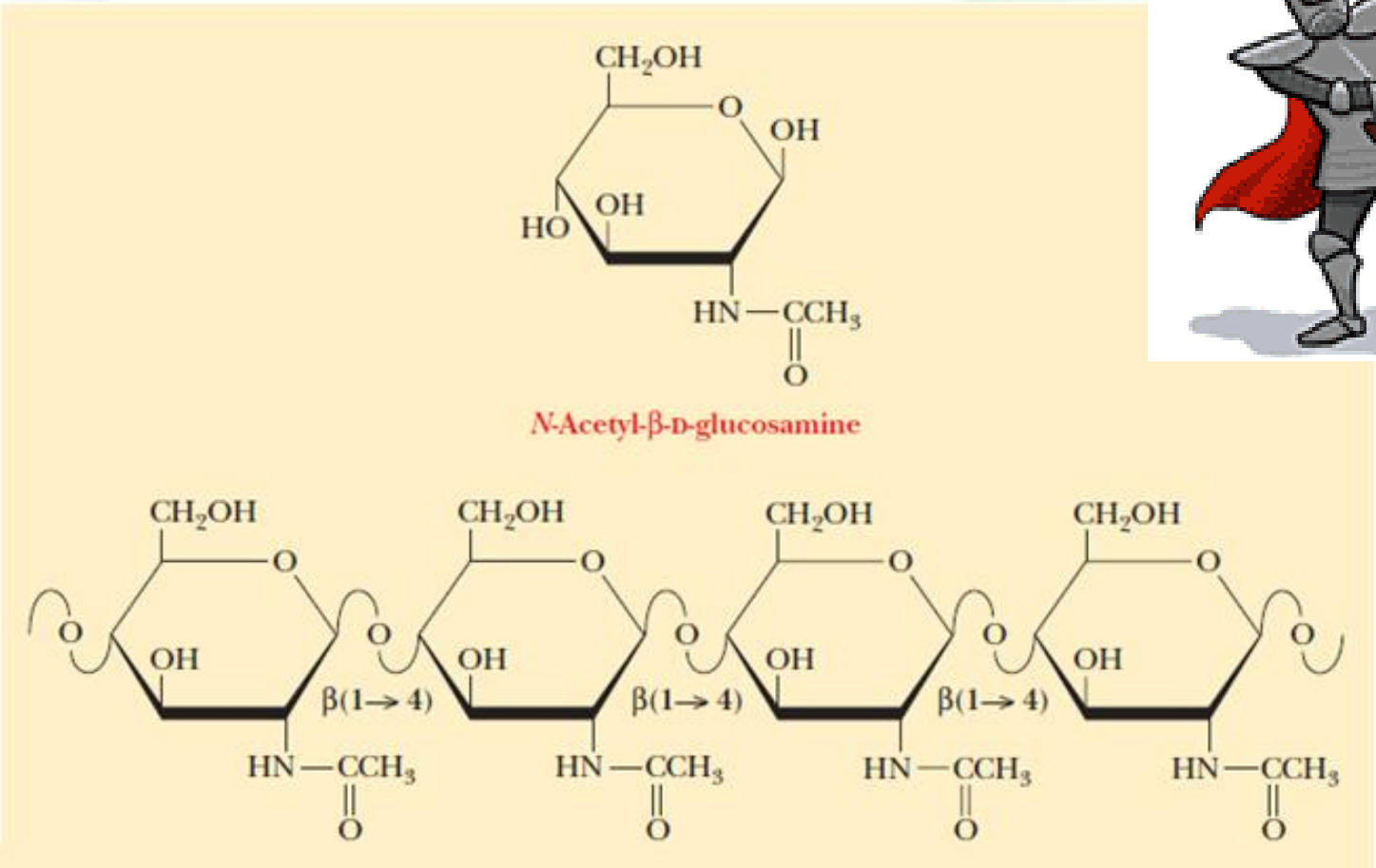




Cellobiose (glucose-β-1,4-glucose)

Chitin

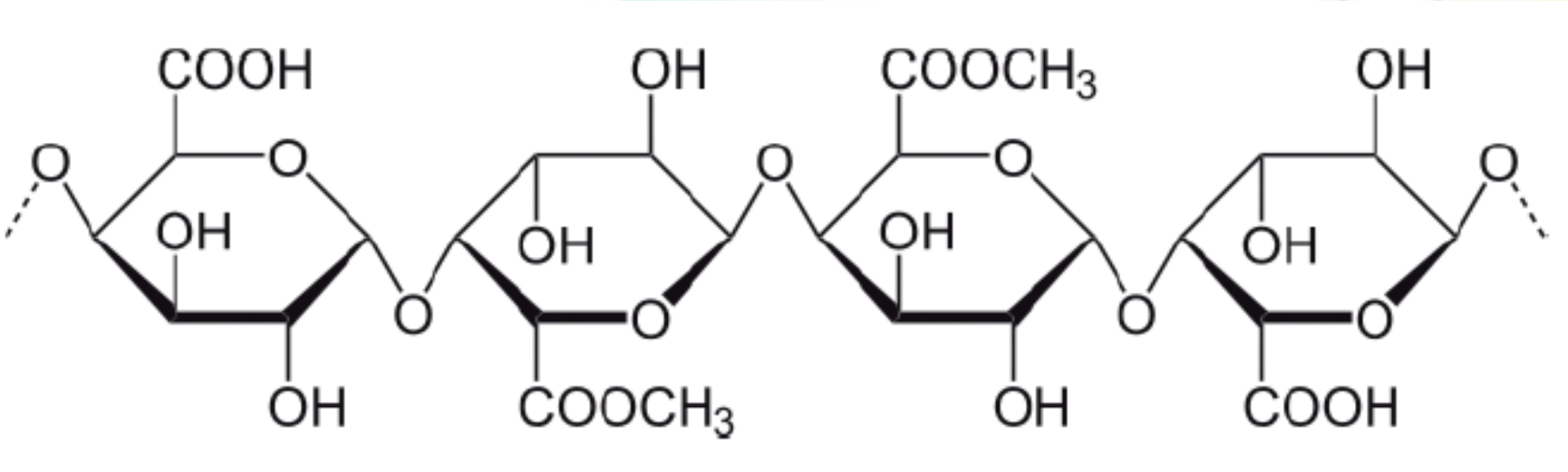
- What is the precursor?
- Where does it exist?



Do not memorize or study the structures.

Pectin

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



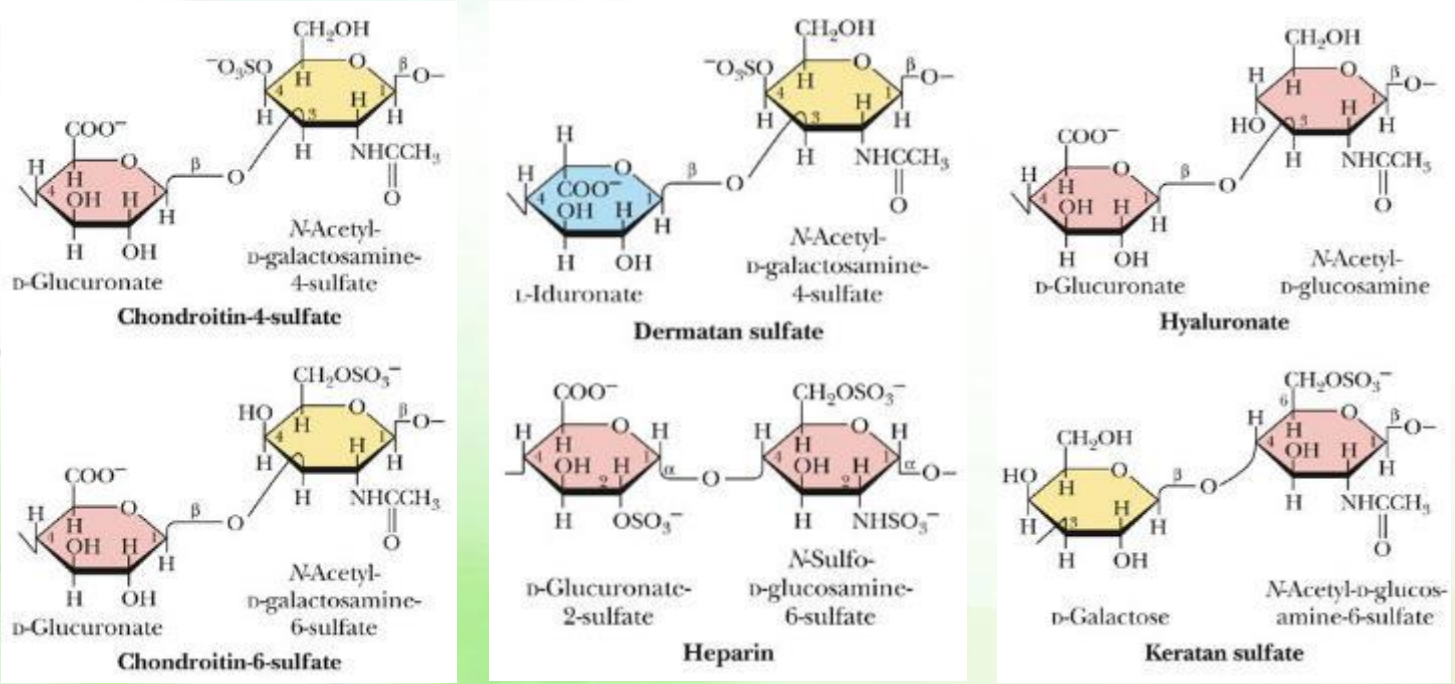
Do not memorize or study the structures.

Are polysaccharides reducing?

- A sample that contains only a few molecules of a large polysaccharide, each molecule with a single reducing end, might well produce a negative test because there are not enough reducing ends to detect.

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



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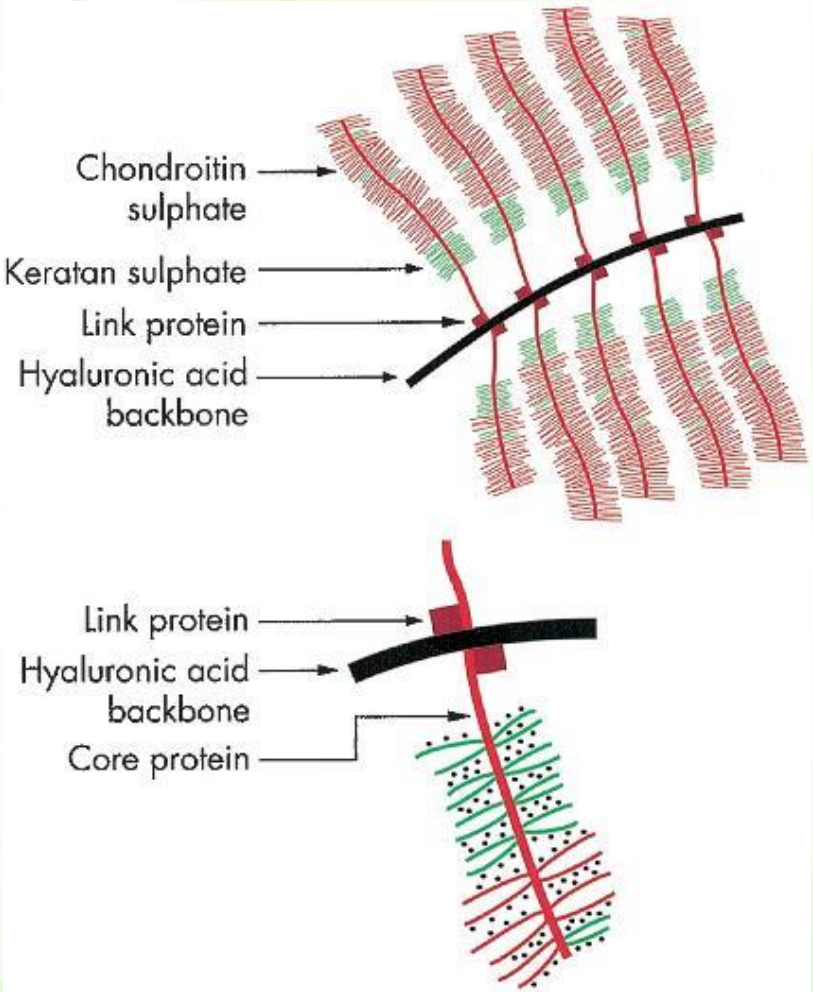
Localization and function of GAG

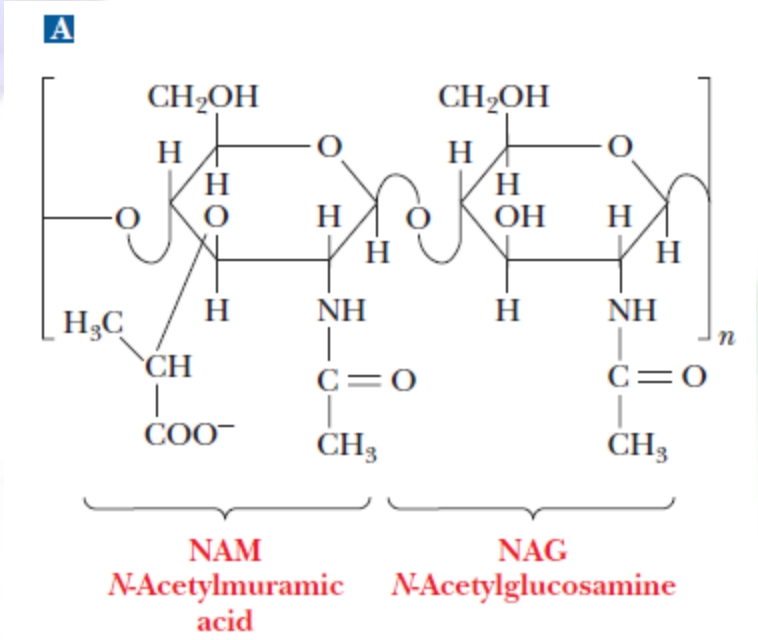
GAG	Localization	Comments
Hyaluronate	synovial fluid, **vitreous humor,** **ECM of loose connective tissue**	**the lubricant fluid , shock absorbing** As many as 25,000 disaccharide units
Chondroitin sulfate	**cartilage**, bone, heart valves	**most abundant GAG**
Heparan sulfate	basement membranes, components 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

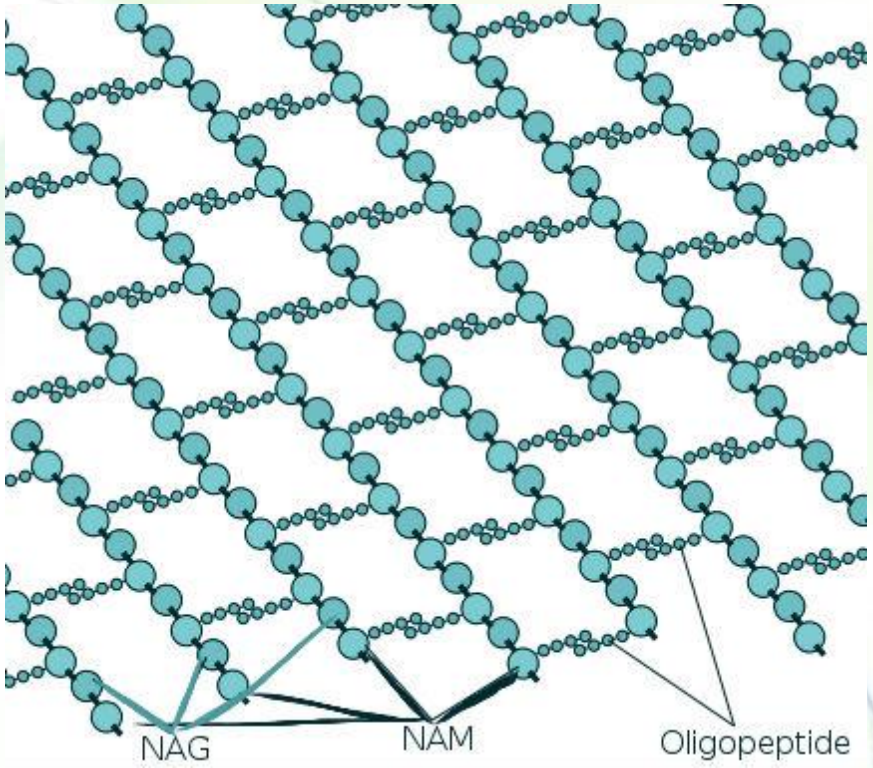
Proteoglycans

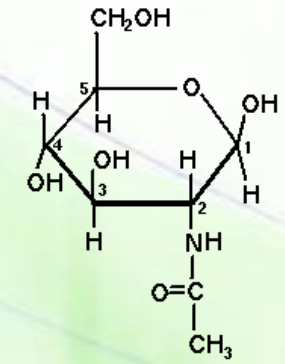
- Lubricants
- Structural components in connective tissue
- Mediate adhesion of cells to the extracellular matrix
- Bind factors that stimulate cell proliferation



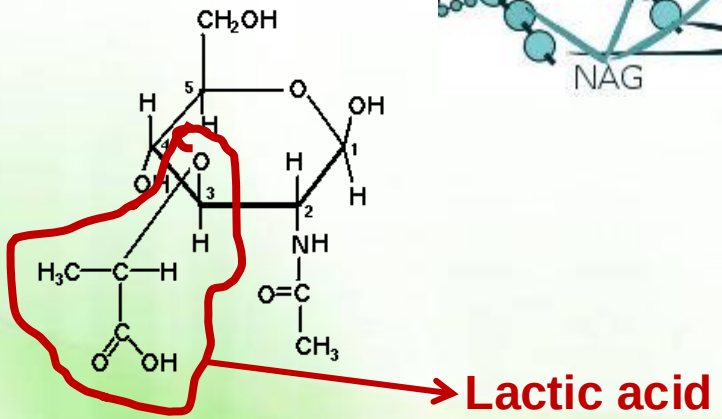
Bacterial cell wall







N–acetylglucosamine (NAG)



N–acetylmuramic acid (NAM)

Lactic acid

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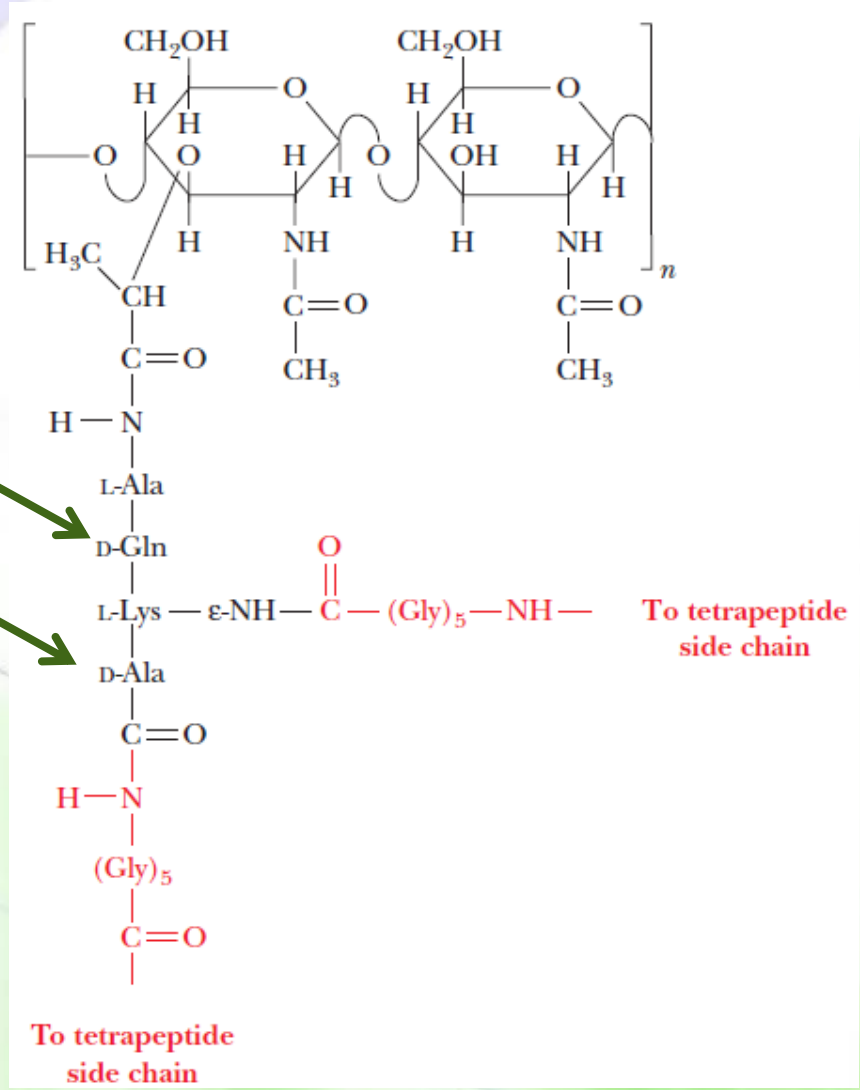
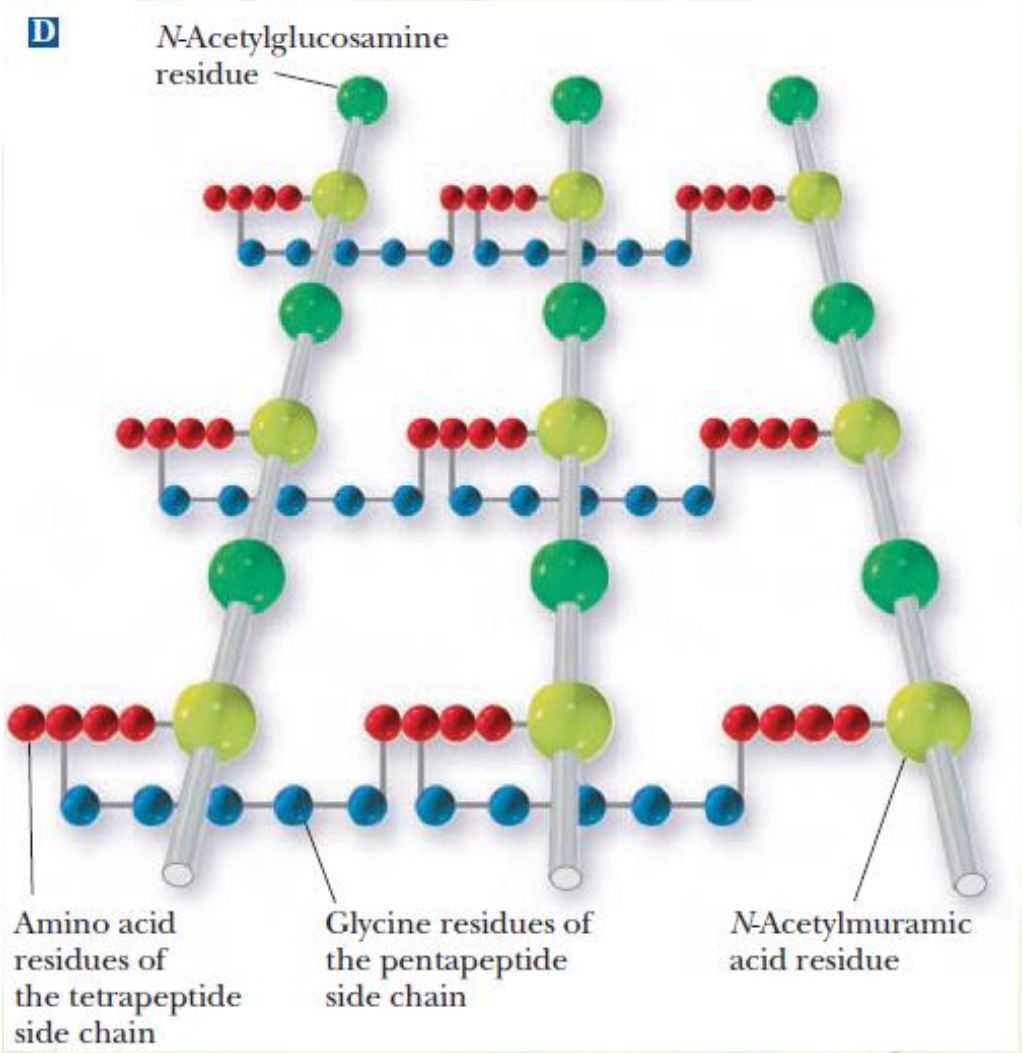
Peptidoglycan





Glycoproteins

- The carbohydrates of glycoproteins are linked to the protein component through either O-glycosidic or N-glycosidic bonds
  - The N-glycosidic linkage is through the amide group of asparagine (Asn, N)
  - The O-glycosidic linkage is to the hydroxyl group of serine (Ser, S), threonine (Thr, T) or hydroxylysine (hLys)

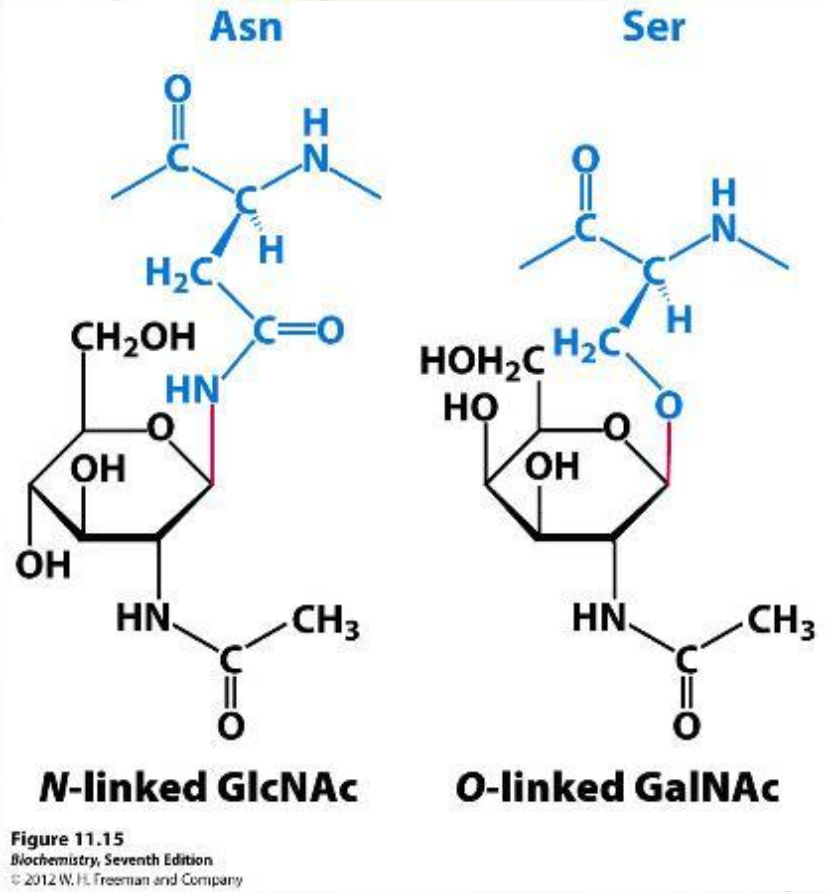


Figure 11.15
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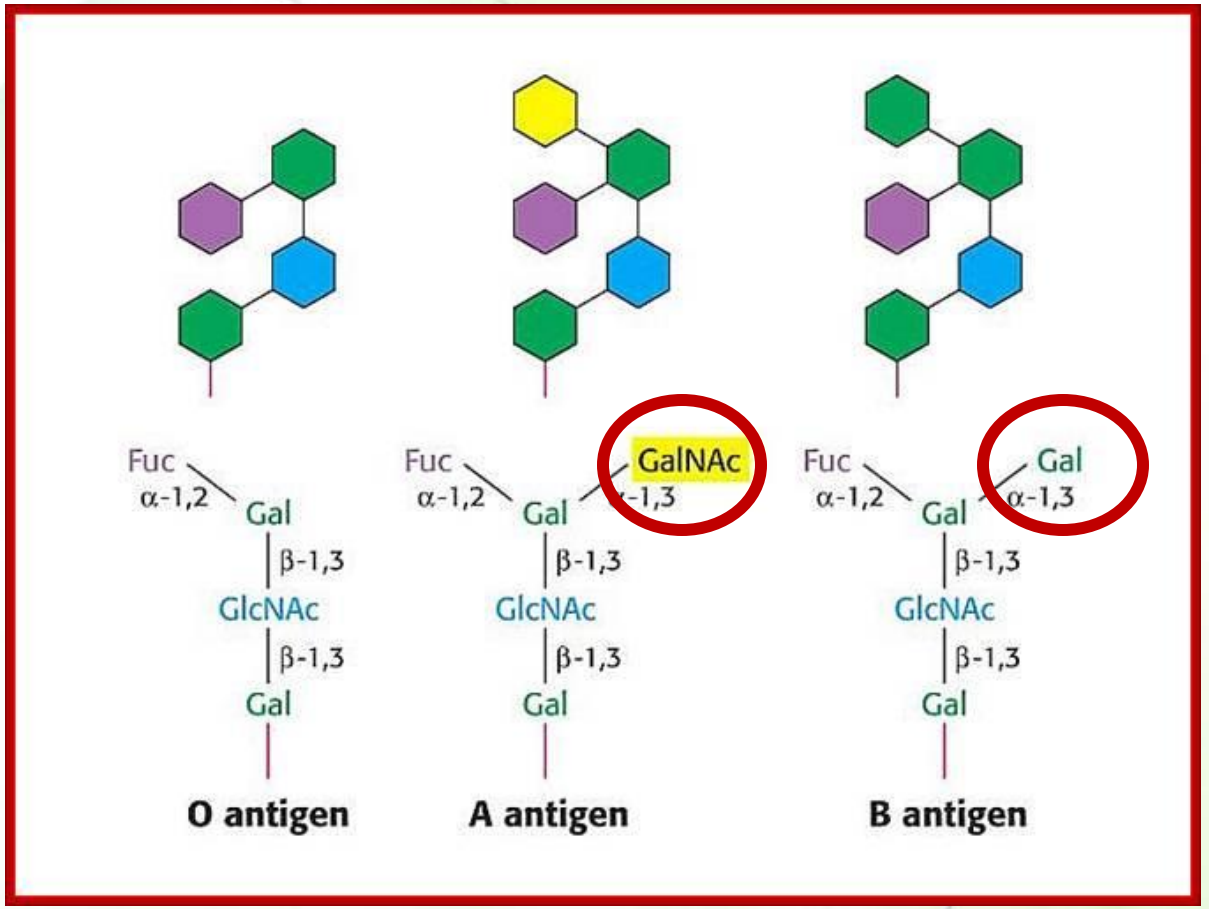
Significance of protein-linked sugars

- Soluble proteins as well as membrane proteins
- Purpose:
  - Protein folding
  - Protein targeting
  - prolonging protein half-life
  - Cell-cell communication
  - Signaling

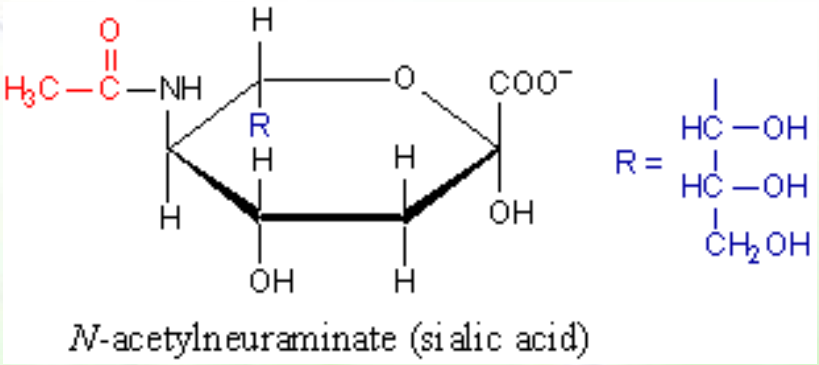
Blood typing and glycoproteins

- Three different structures:
  - A, B, and O
- The difference:
  - N-acetylgalactosamine (for A)
  - Galactose (for B)
  - None (for O)



Sialic acid

- N-acetylneuraminate
- Precursor: the amino sugar, neuraminic acid
- Location: a terminal residue of oligosaccharide chains of glycoproteins and glycolipids.



N-acetylneuraminate (sialic acid)

Do not memorize or study the structures.