Carbohydrates and Fatty Acids

September 13, 2016

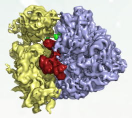
Primary Objectives

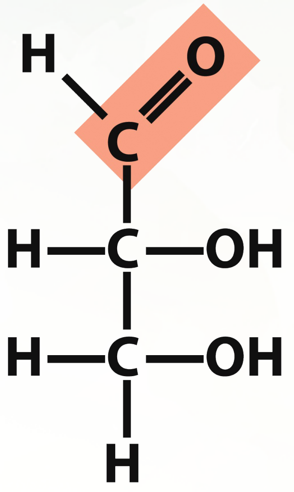
- Understand the relationship between different sugars.
- Interconvert between Fischer and Haworth structures.
- Understand the glycosidic bond.
- Comprehend the structural features of fatty acids and triacylglycerols.
- Understand the hierarchy of lipids.

Section 1

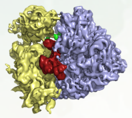
Carbohydrates

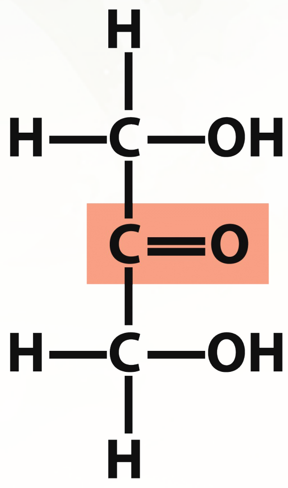
Carbohydrates Are Polyhydroxy Biomolecules





Glyceraldehyde,
an aldotriose

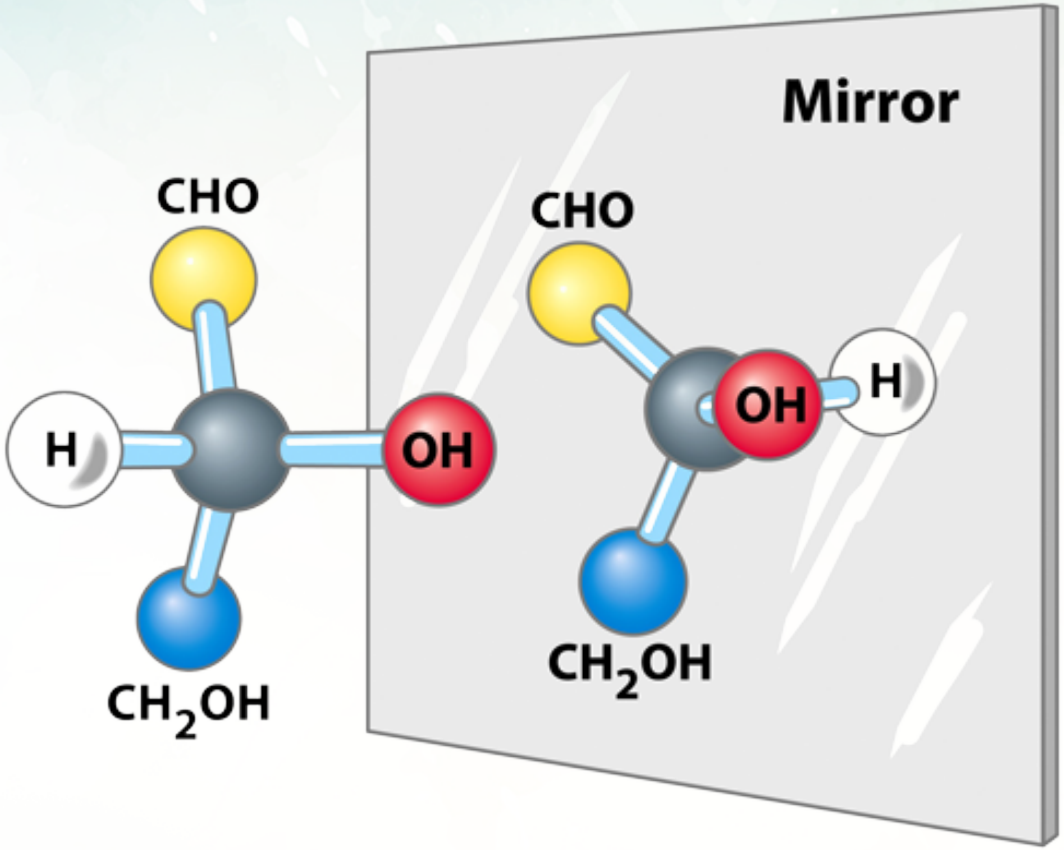




Dihydroxyacetone,
a ketotriose

- Empirical formula: $(CH_2O)n$
- Polyhydroxy aldehydes or ketones
  - Aldose → carbonyl group is in an aldehyde group
  - Ketose → carbonyl group is in a ketone group
- Naming conventions are important

Carbohydrates Exist As Enantiomers, Designated D- or L-

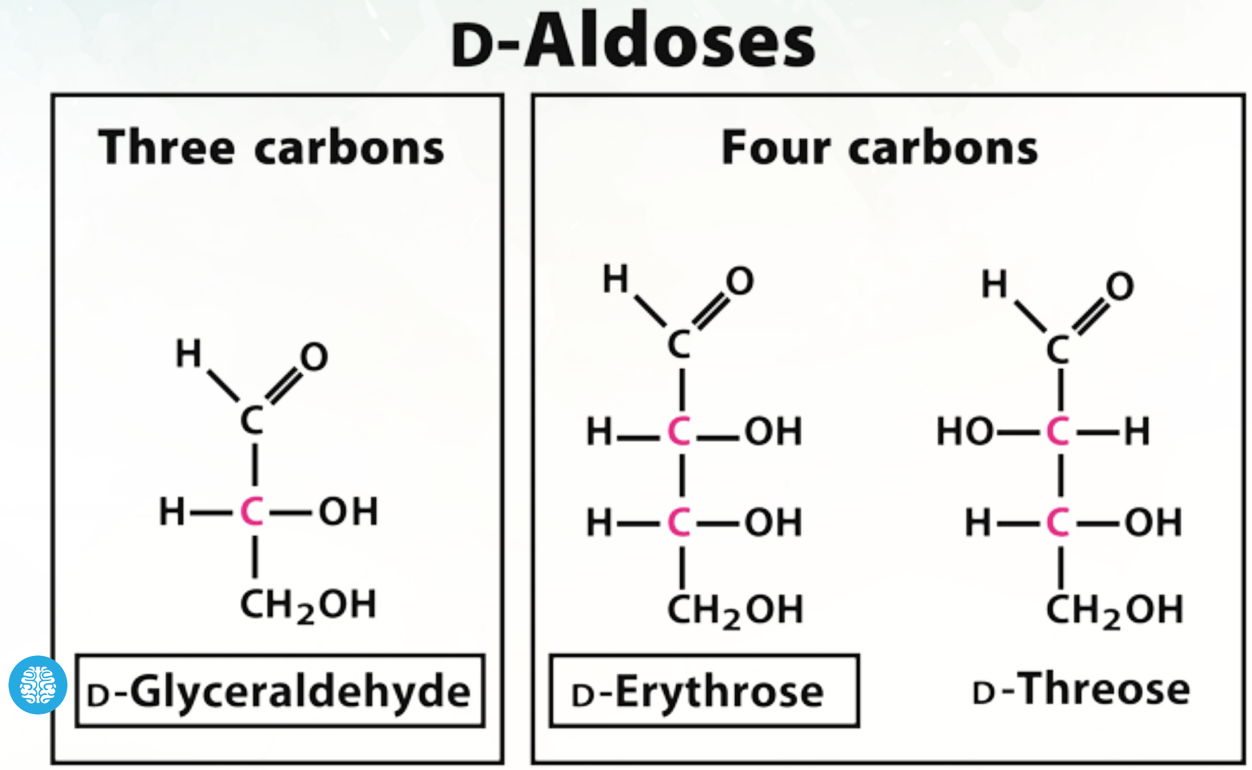


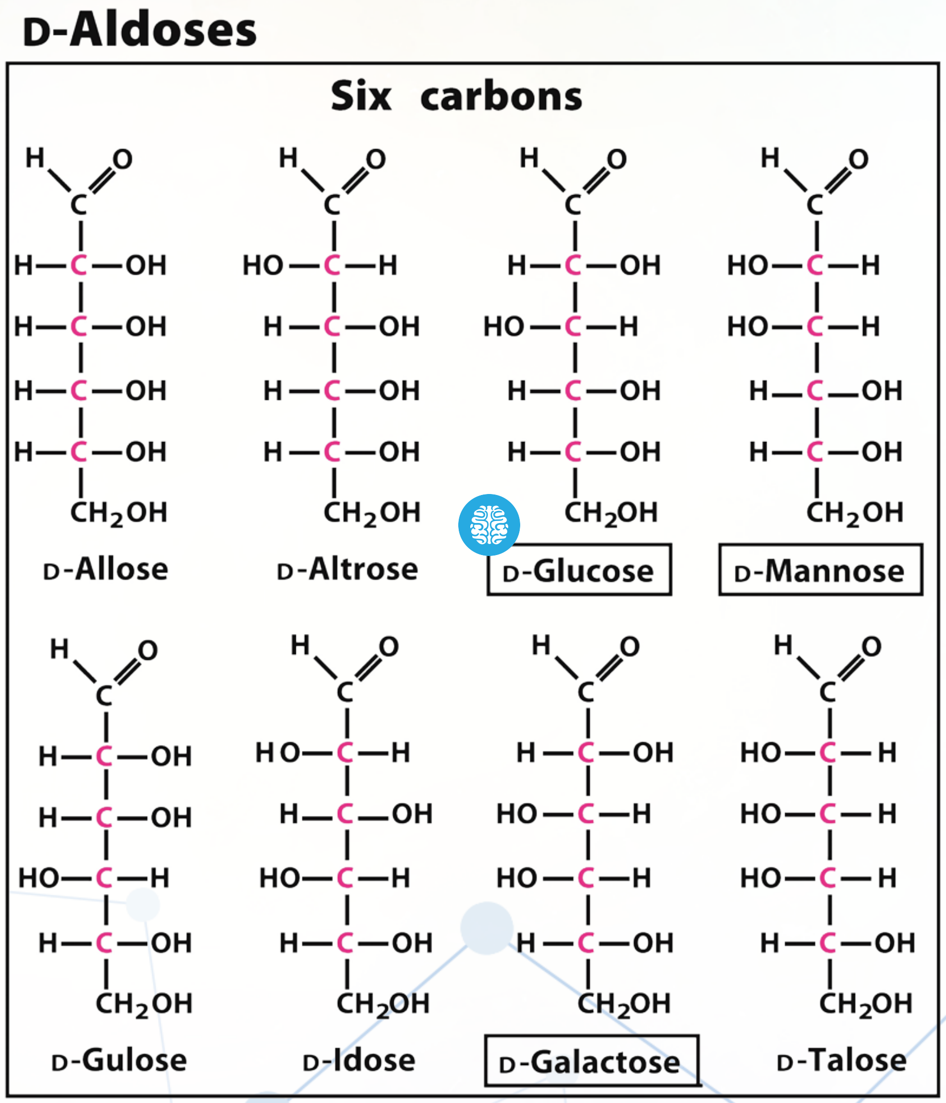
Ball-and-stick models

Fischer projection formulas

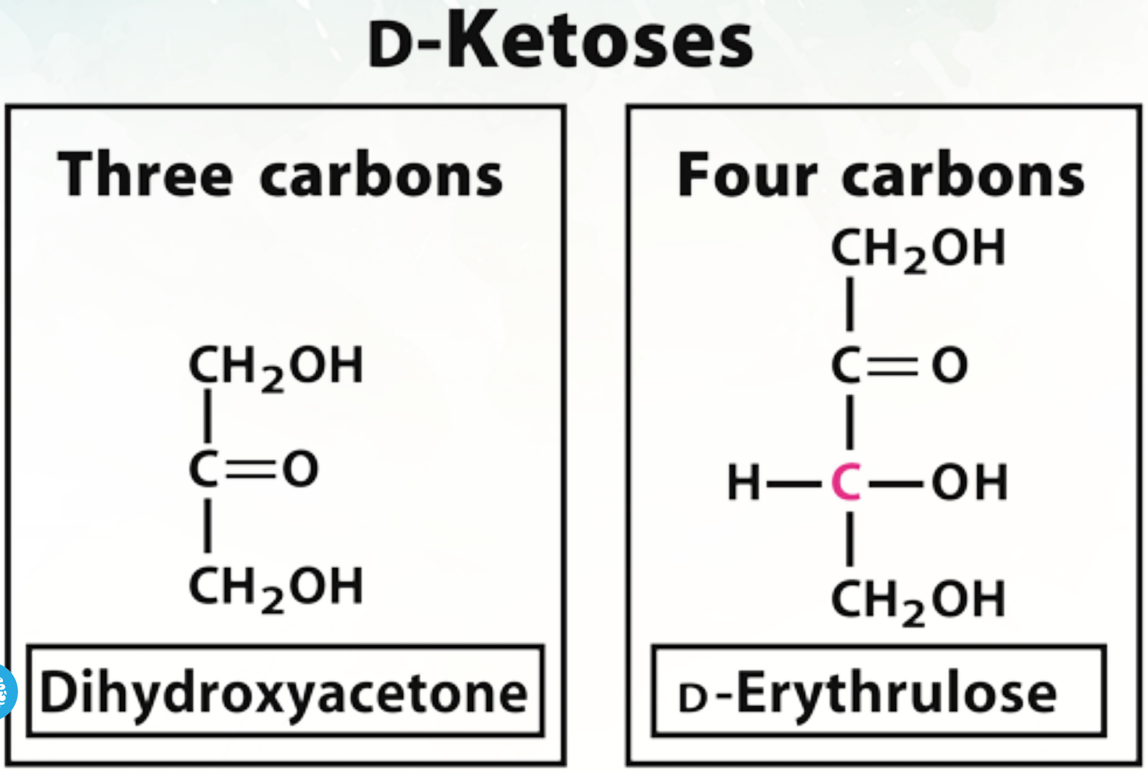
Perspective formulas

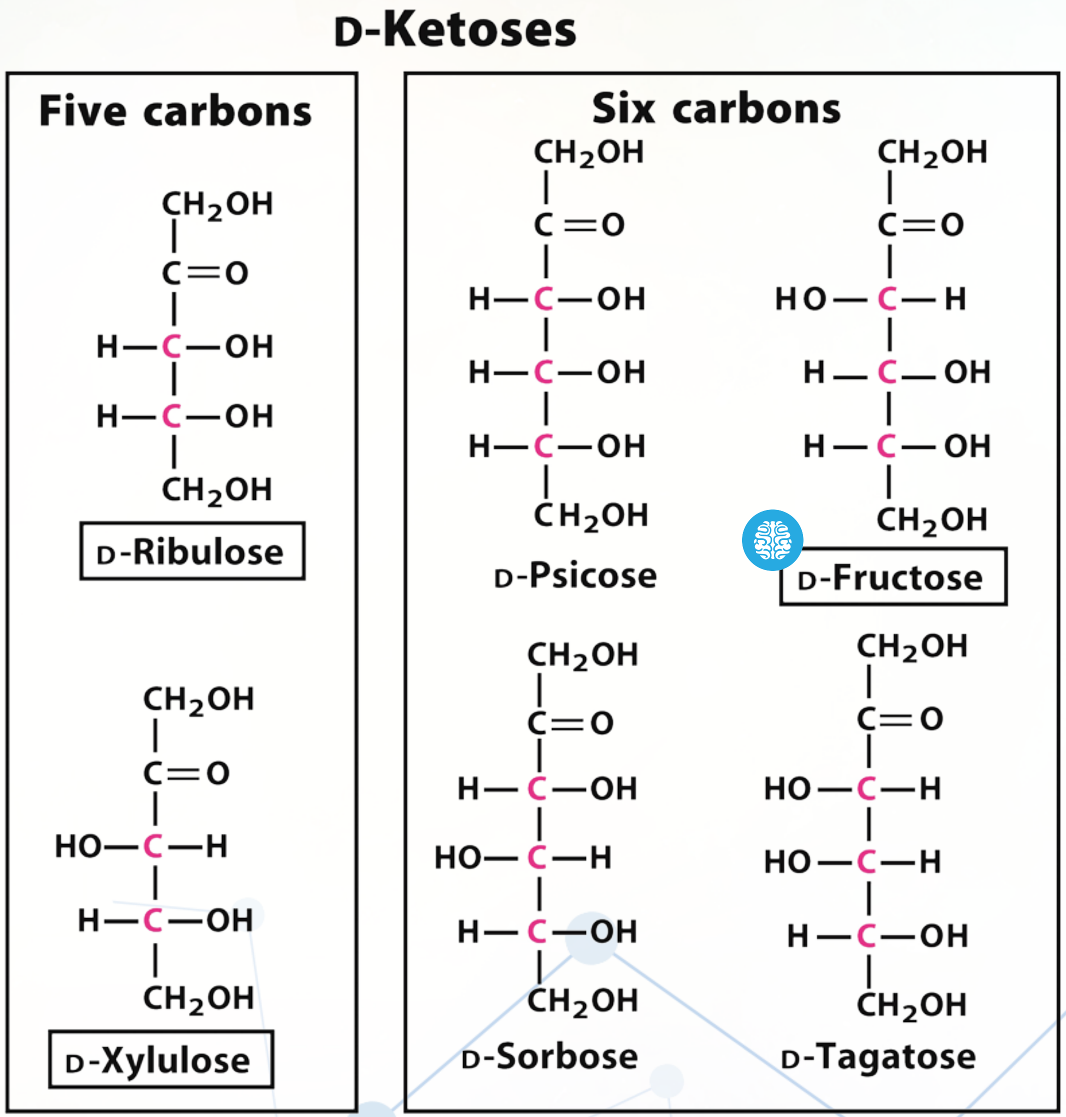
The Aldoses Are Carbohydrate Aldehydes



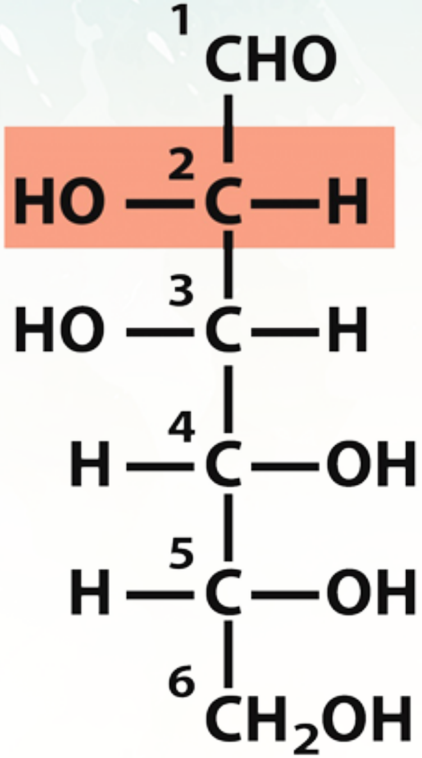


The Ketoses Are Carbohydrate Ketones

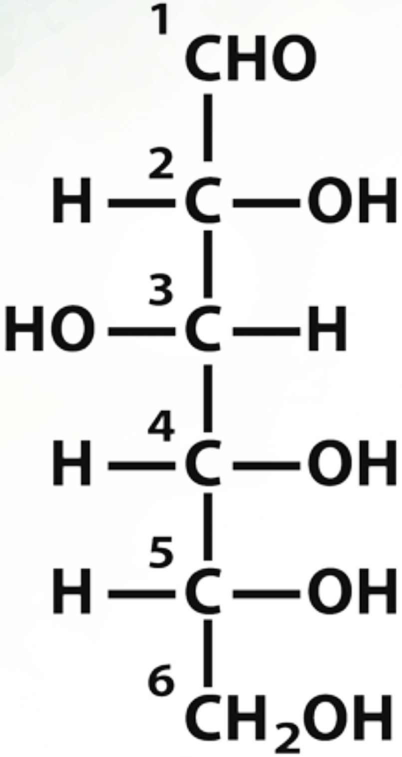




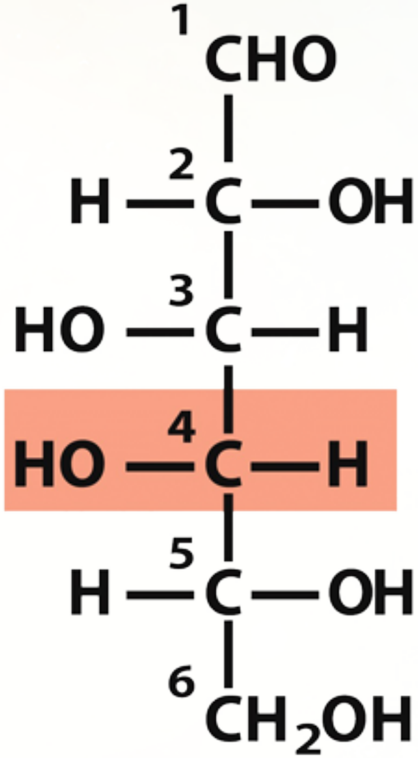
Epimeric Pairs Differ From One Another at a Single Chiral Carbon



D-Mannose
(epimer at C-2)

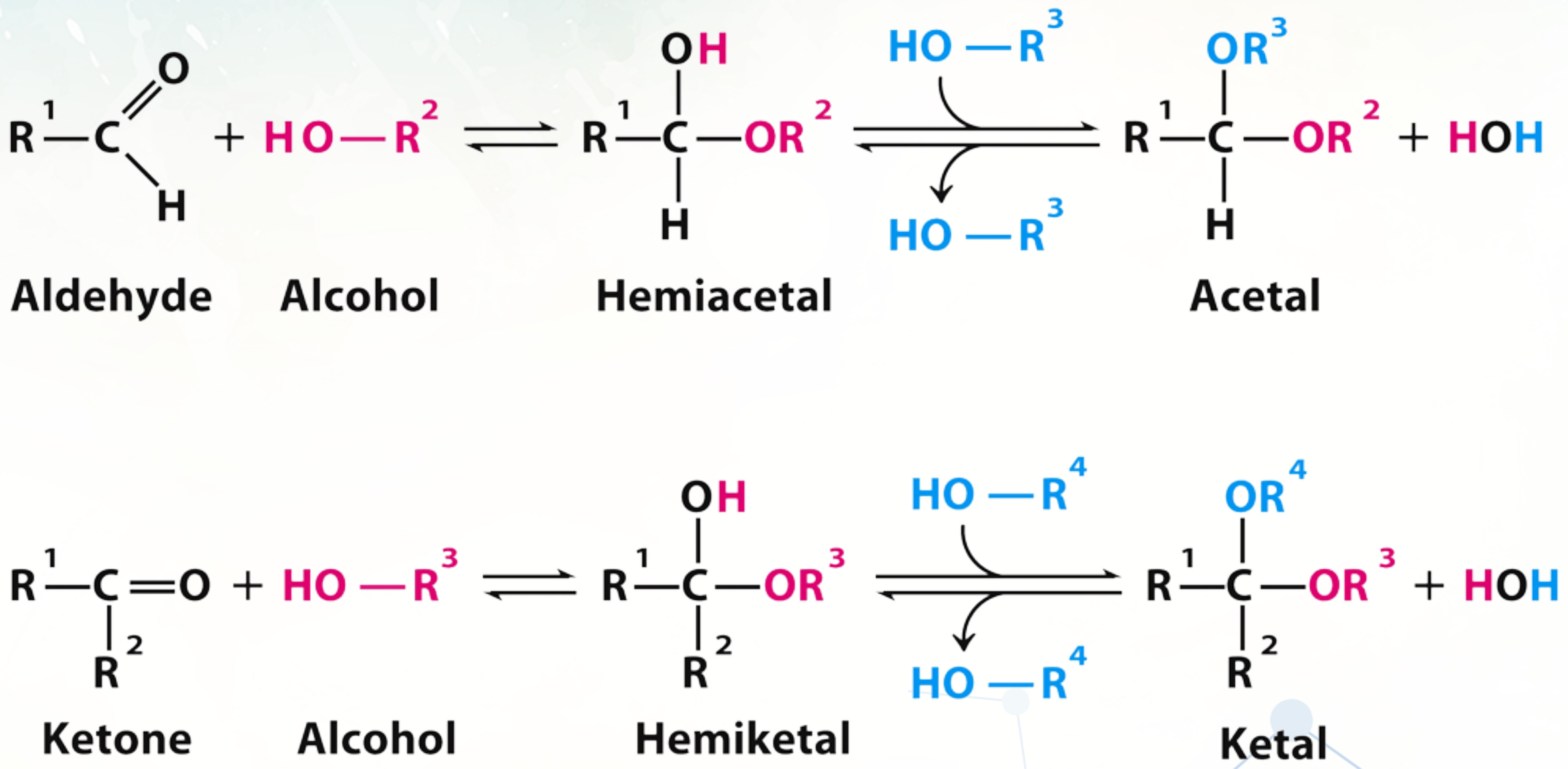


D-Glucose

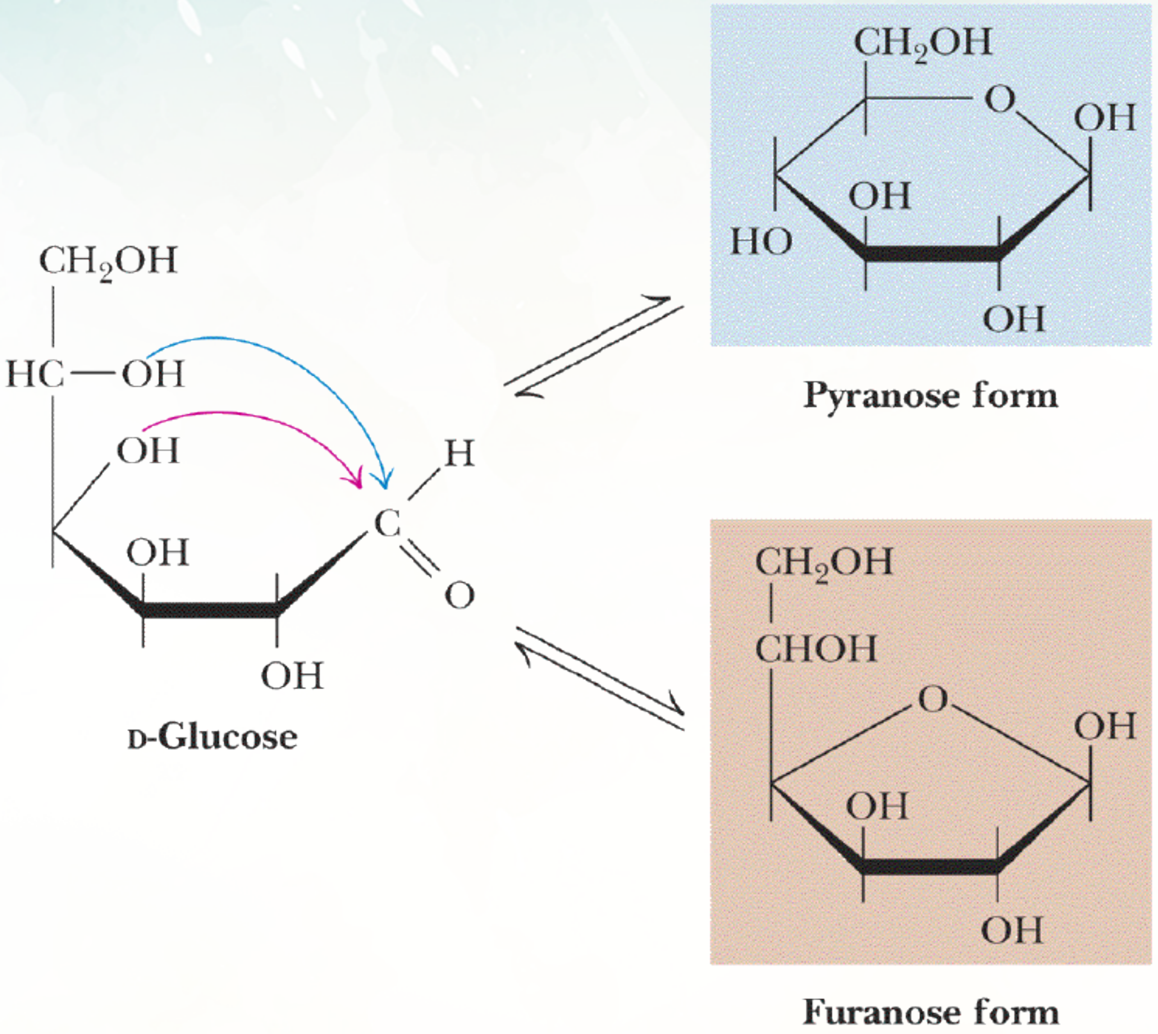


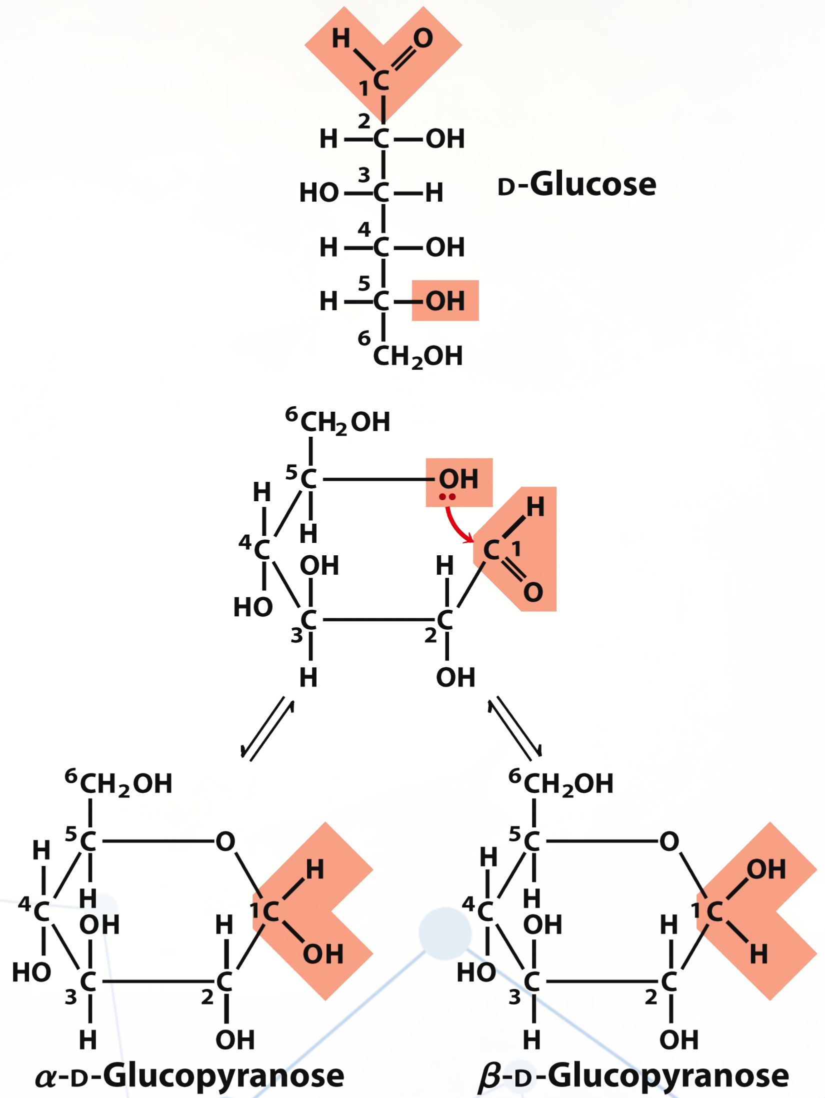
D-Galactose
(epimer at C-4)

Carbohydrate Cyclization Follows the Hemiacetal and Hemiketal Mechanism

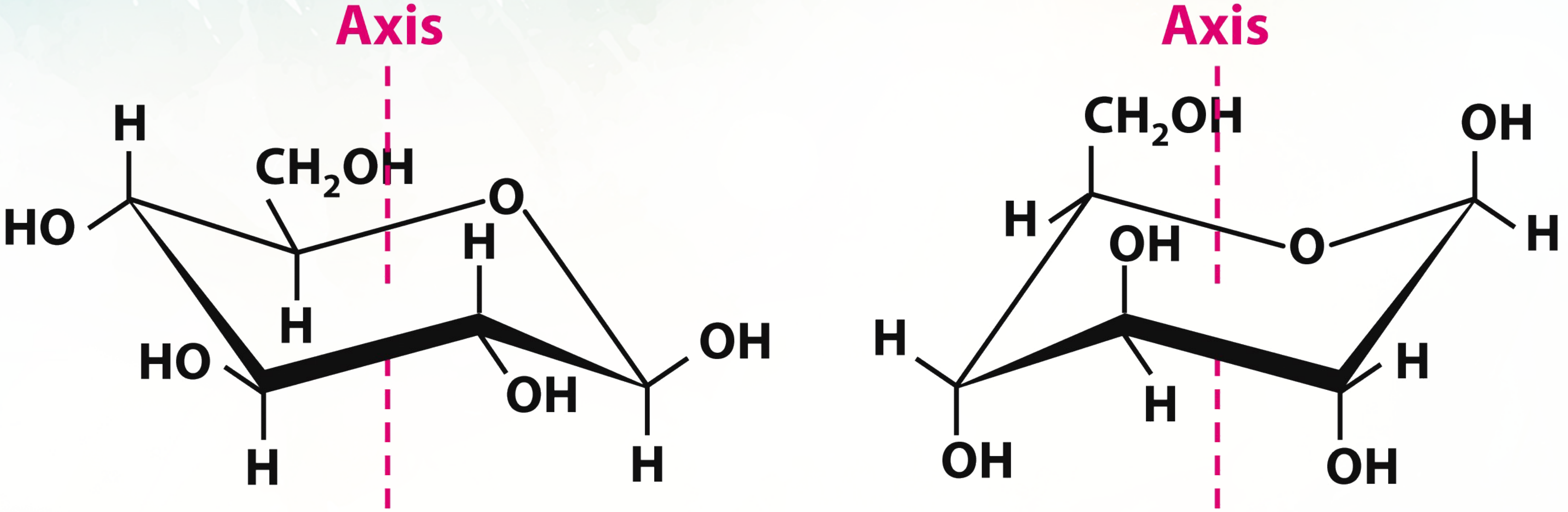


There Are Multiple Possible Cyclic Forms of a Single Carbohydrate



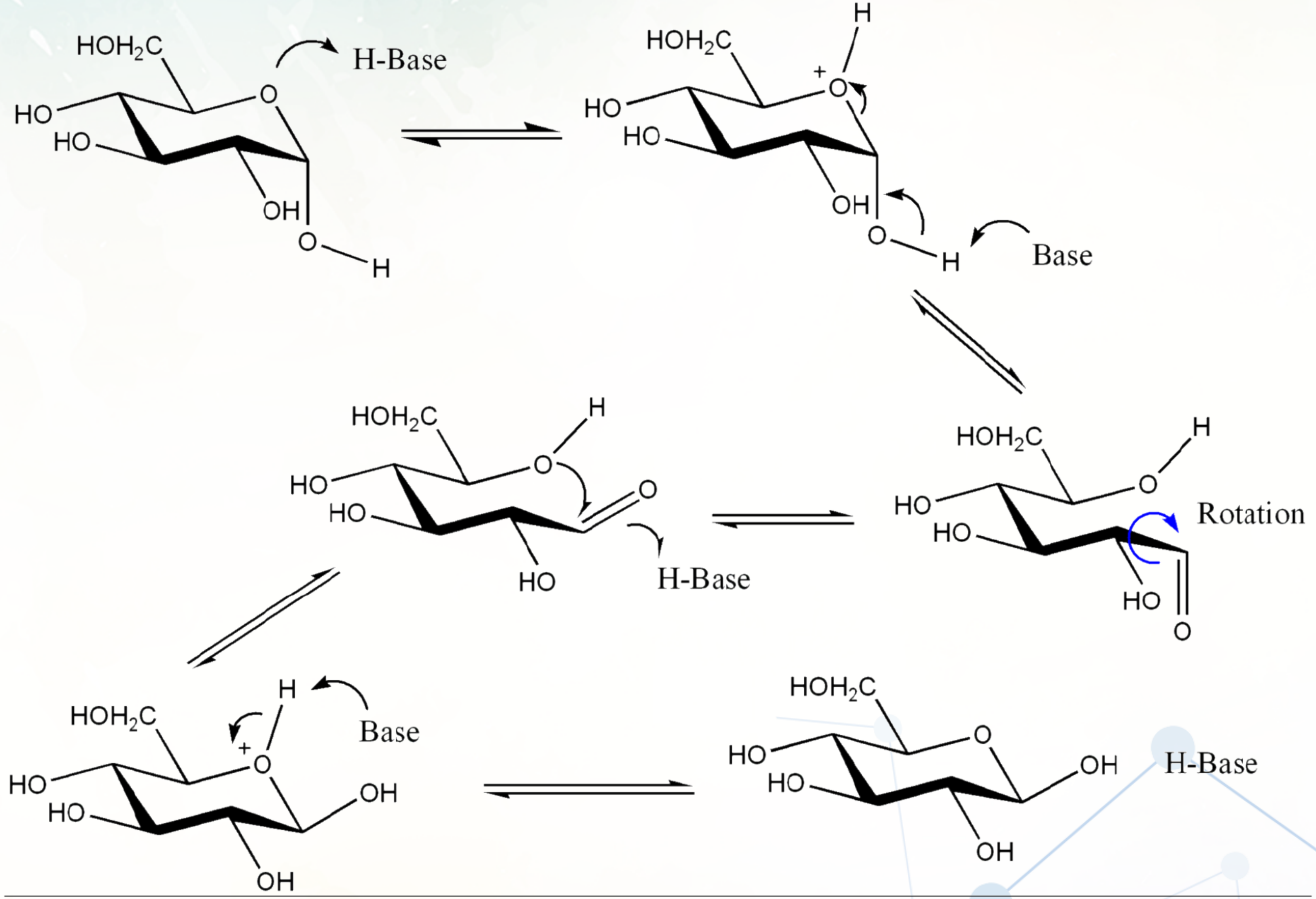


Positions of the Hydroxyl Groups Stay Constant Regardless of Chair Form

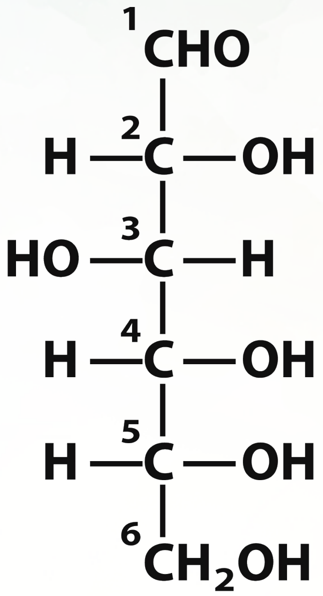


Two possible chair forms of *β*-D-glucopyranose

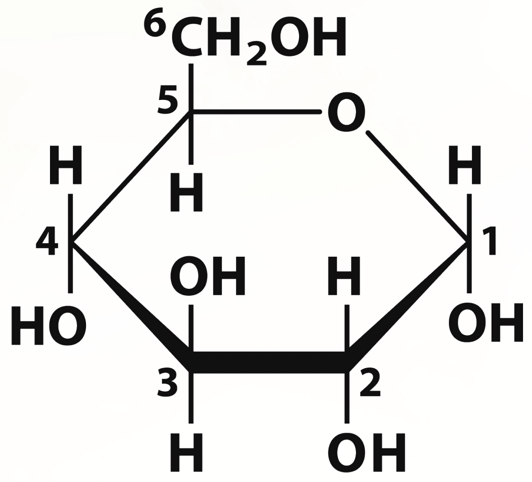
Mutarotation Switches the Configuration of the Anomeric Carbon's Hydroxyl Group



Fischer Projection and Haworth Perspective Are Two Ways To Draw Carbohydrate Structure



D-Glucose
Fischer projection

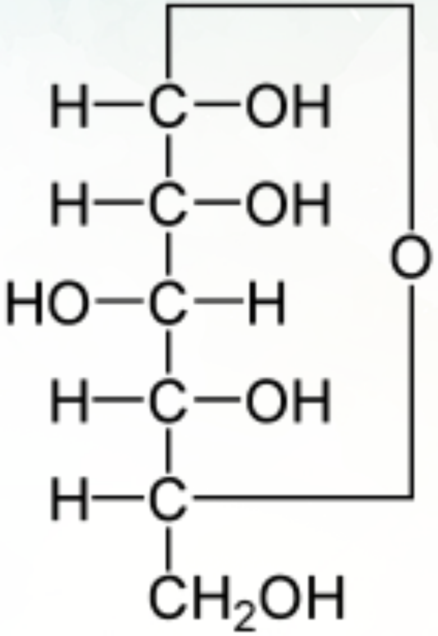


α-D-Glucopyranose
Haworth perspective

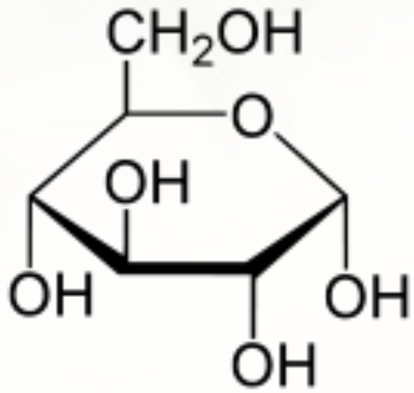
Converting to Haworth:

- Place the nucleophilic oxygen at the top (or top right) of the ring
- Number carbons clockwise beginning with anomeric carbon
- Place hydroxyl groups
    - Up → OH points left in Fischer projection
    - Down → OH points right in Fischer
- Place terminal CH_2OH group for terminal group
    - Up →for D-enantiomer
    - Down → for L-enantiomer
- Note that placement of the terminal CH_2OH group is very specific to this class, as we deal exclusively with D-sugars
- Hydroxyl group on anomeric carbon can point up (β) or down (α)

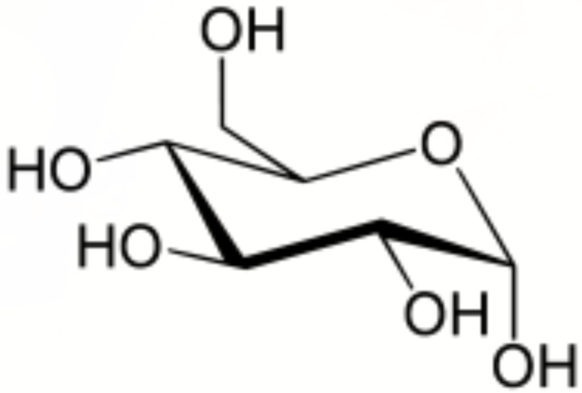
Not All Projections of α-Glucopyranose Are Easily Comprehensible



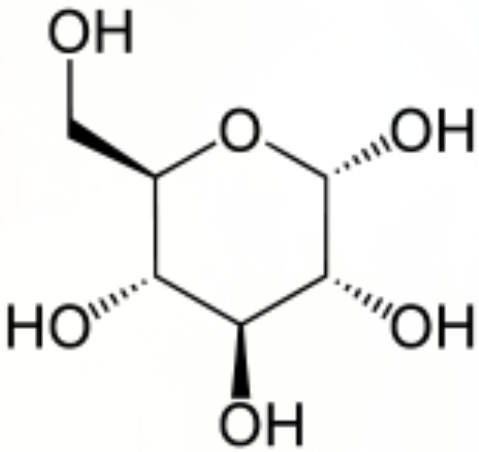
1



2



3



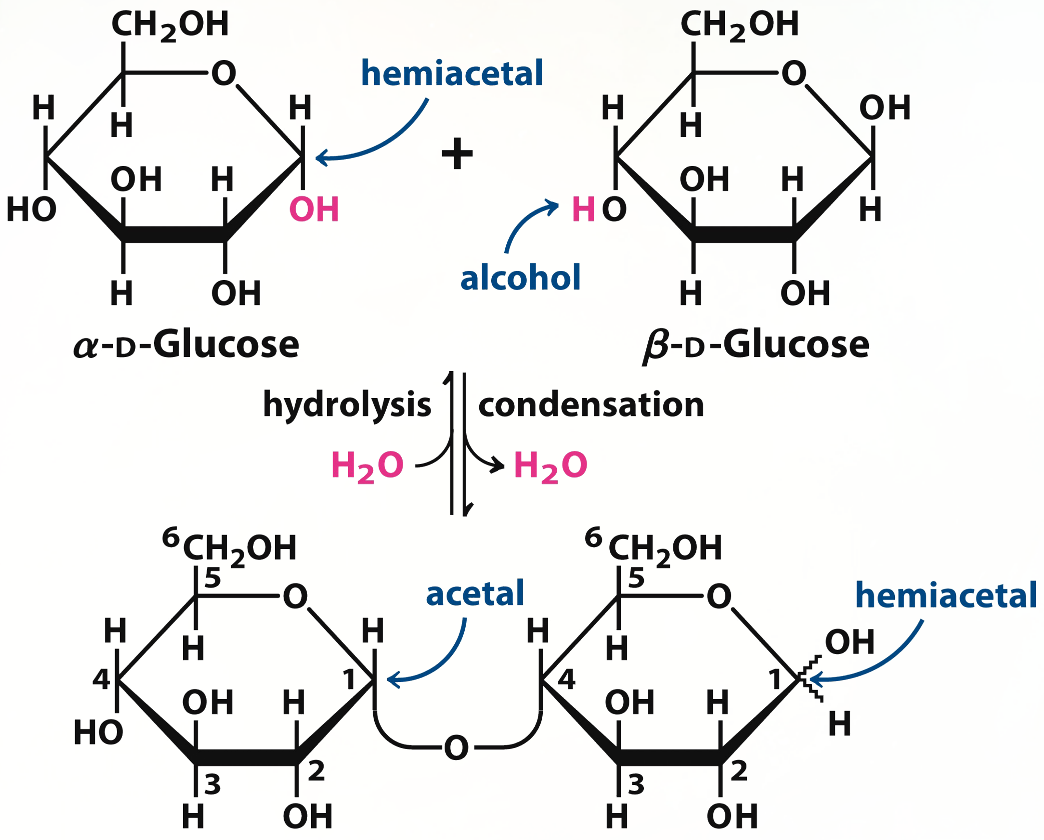
4

IN-CLASS EXERCISE:

- Draw D-glucose in its four cyclic forms as Haworth projects.

Disaccharide Formation is a Condensation Reaction

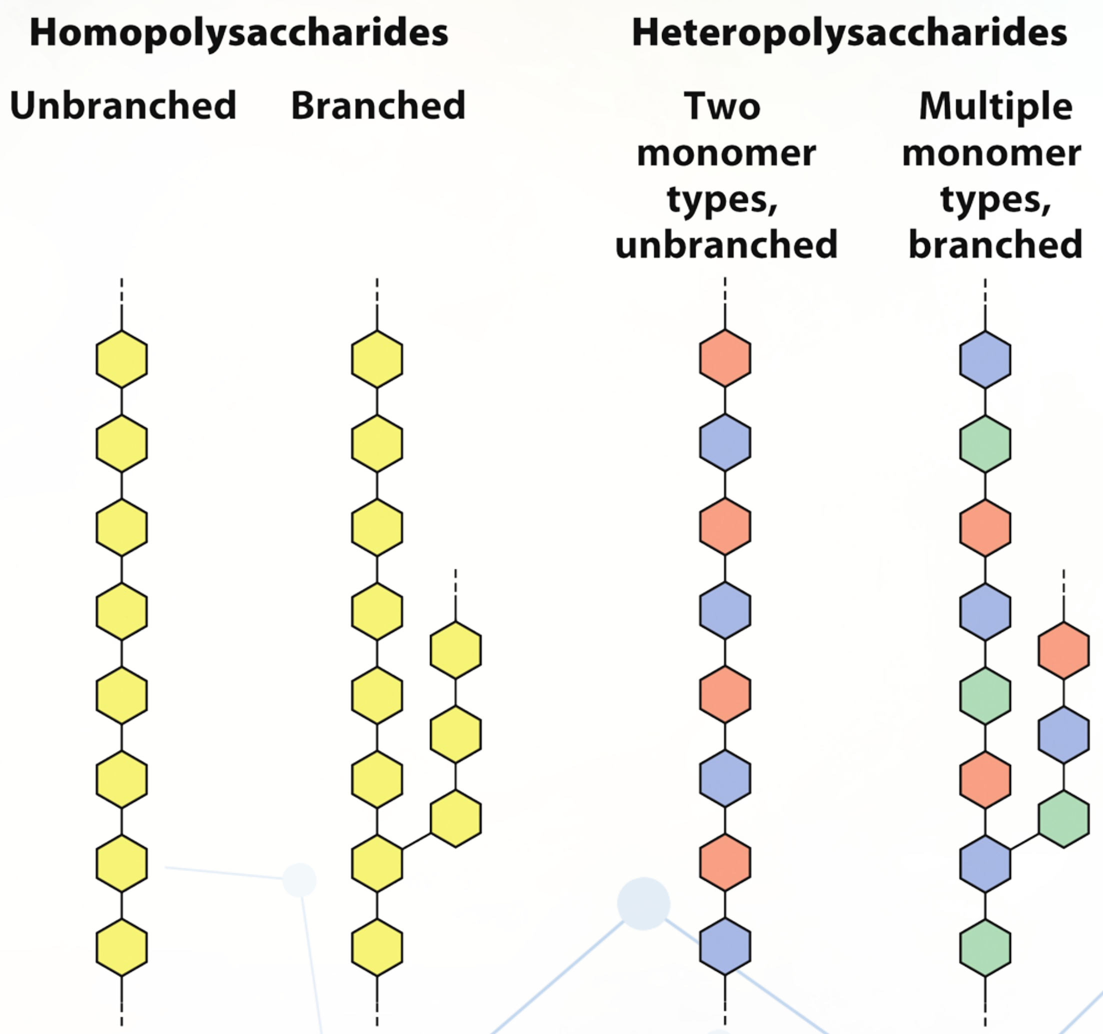
- Formation → condensation reaction
- Breakdown → hydrolysis reaction
- Once formed, interconversion between linear and ring form is prevented
- The end of a chain with a free anomeric carbon is called reducing end



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

Polysaccharides Come in Two General Forms

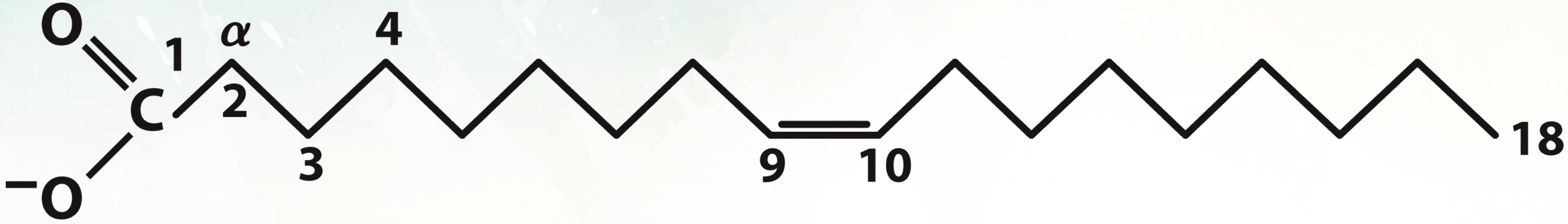
- Repeated condensation reactions result in multiple monosaccharides linked together
- Two general kinds of polysaccharides:
  - Homopolysaccharides
  - Heteropolysaccharides



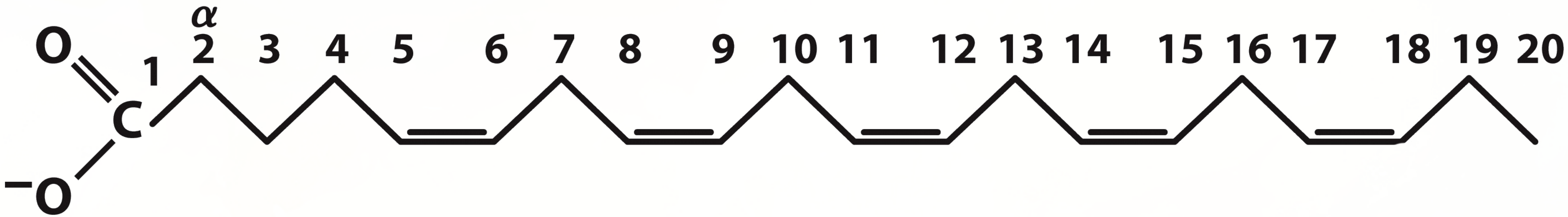
Section 2

Fatty Acids

Fatty Acids Are Long Hydrocarbon Chains

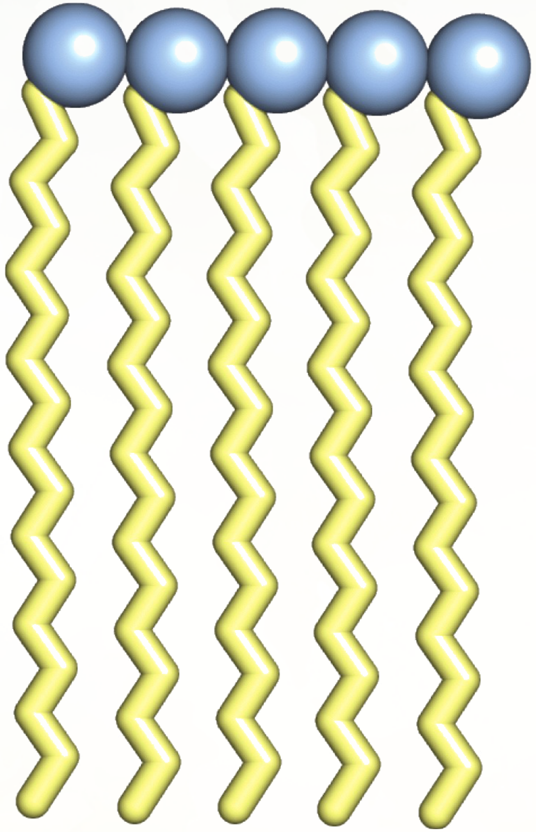


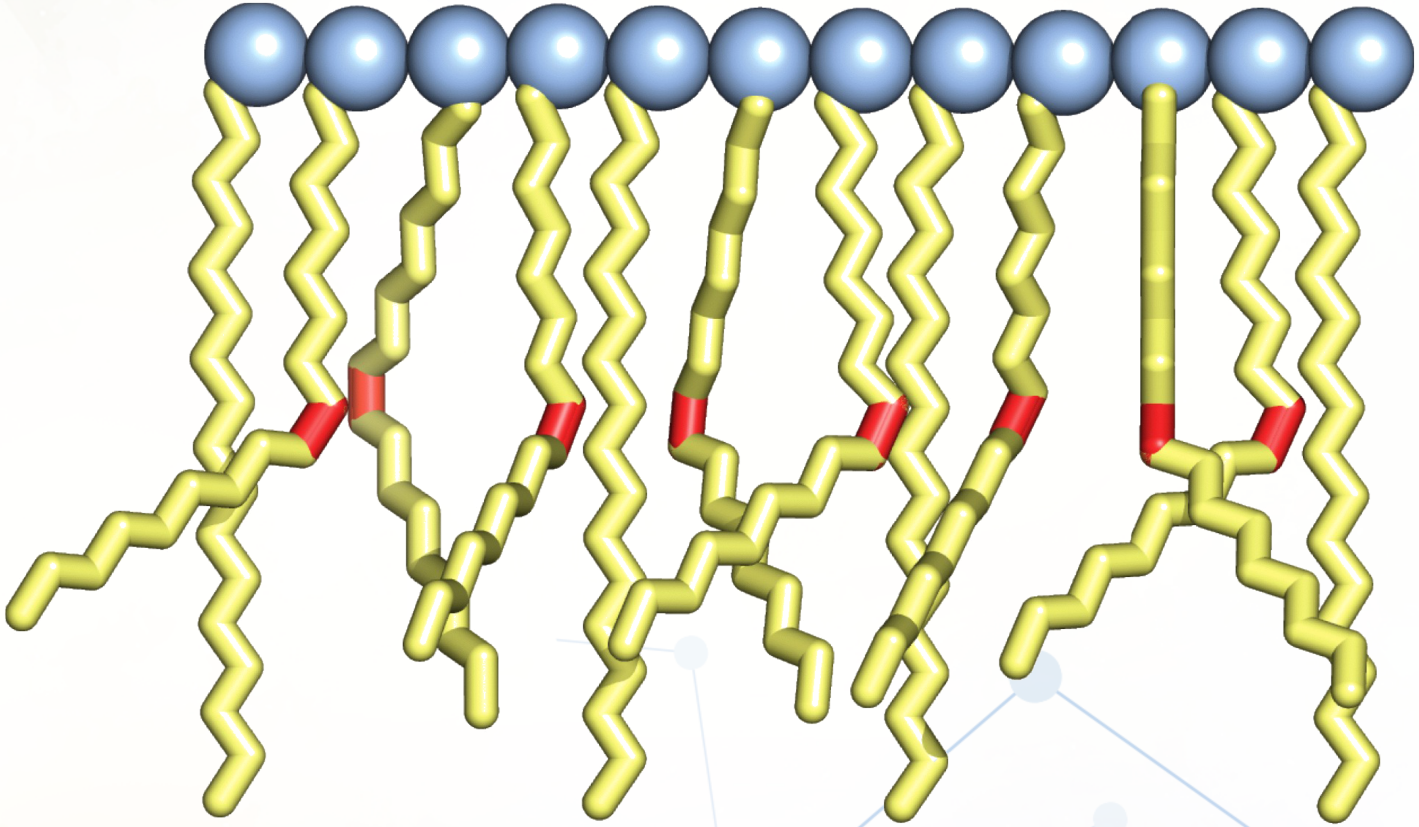
18:1(Δ^9) *cis*-9



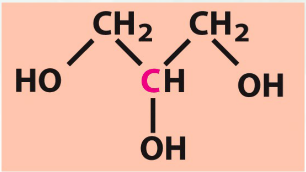
20:5($\Delta^{5,8,11,14,17}$) *cis-,cis-,cis-,cis-*5,8,11,14,15

Saturated and Unsaturated Fatty Acids Have Different Properties

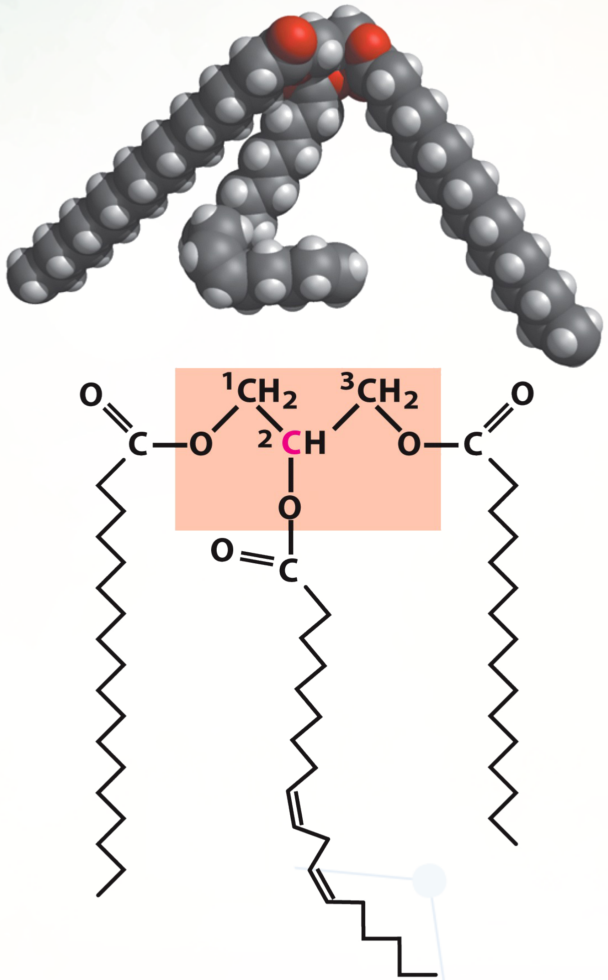




Triacyglycerols Consist of Three Fatty Acids Connected to a Glycerol

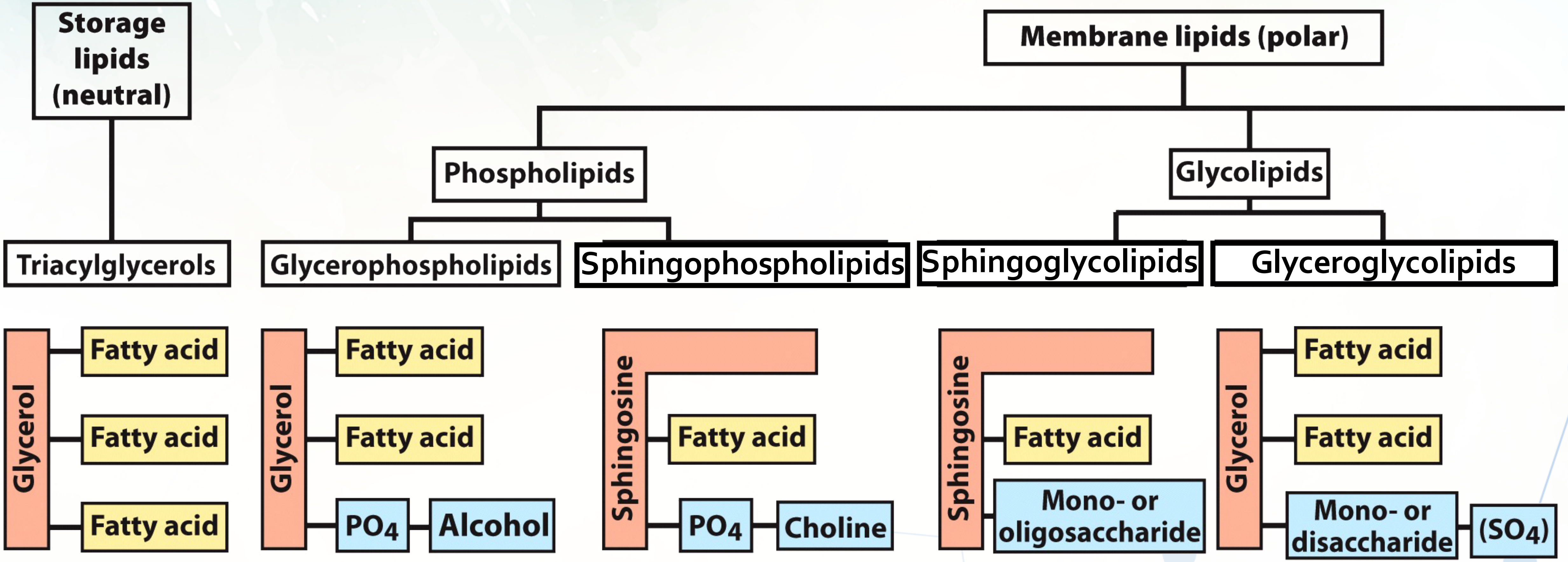


Glycerol

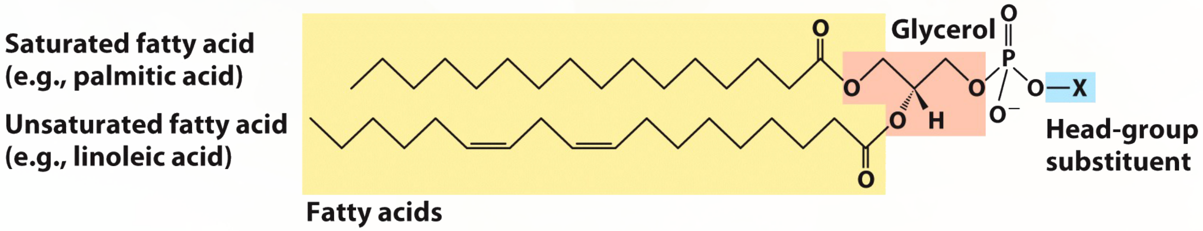


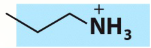
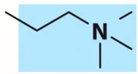
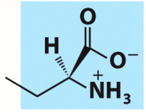
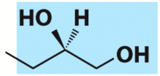
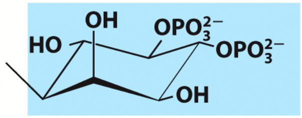
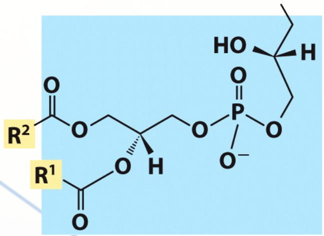
1-Stearoyl, 2-linoleoyl, 3-palmitoyl glycerol,
a mixed triacylglycerol

Classification of Lipids Is Hierarchical

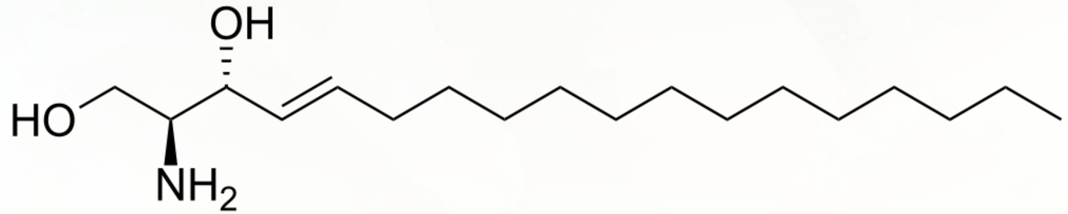


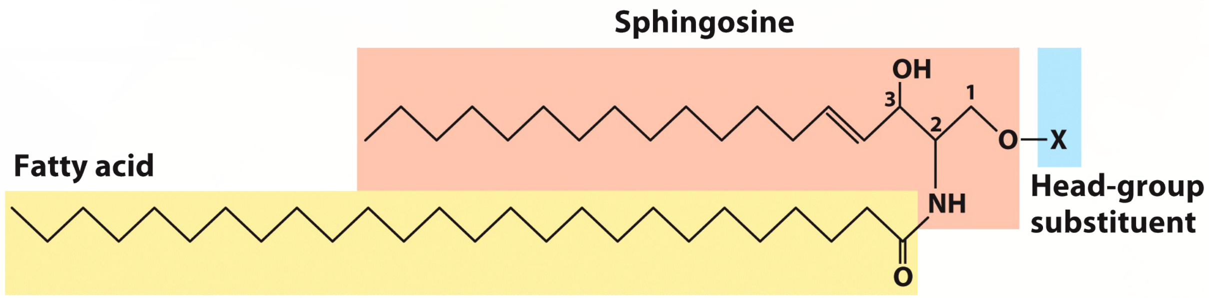
Glycerophospholipids Can Have Different Head-Group Substituents

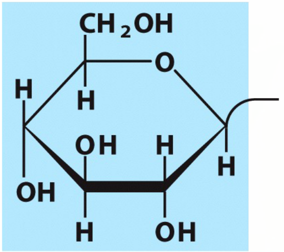
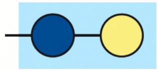


Name of glycerophospholipid	Name of X—O	Formula of X	Net charge (at pH 7)
Phosphatidic acid	—	—H	−2
Phosphatidylethanolamine	Ethanolamine		0
Phosphatidylcholine	Choline		0
Phosphatidylserine	Serine		−1
Phosphatidylglycerol	Glycerol		−1
Phosphatidylinositol 4,5-bisphosphate	*myo*-Inositol 4,5-bisphosphate		−4*
Cardiolipin	Phosphatidyl-glycerol		−2

Sphingolipids Can Have Signaling Polysacchrides As Head-Group Substituents





Name of sphingolipid	Name of X—O	Formula of X
Ceramide	—	—H
Sphingomyelin	Phosphocholine	$-\overset{O}{\overset{\Vert}{\underset{O^-}{\underset{\vert}{P}}}}-O-CH_2-CH_2-\overset{+}{N}(CH_3)_3$
Neutral glycolipids Glucosylcerebroside	Glucose	
Lactosylceramide (a globoside)	Di-, tri-, or tetrasaccharide	
Ganglioside GM2	Complex oligosaccharide