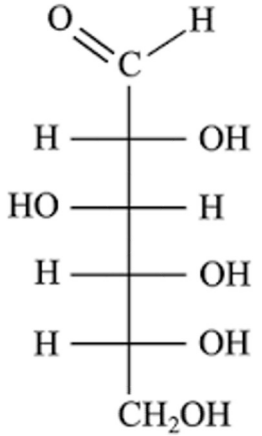




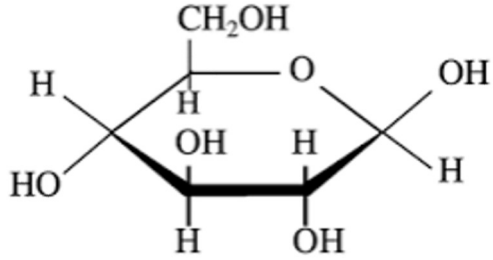
The M-CATs

Biochemistry Chapter 4: Carbohydrates

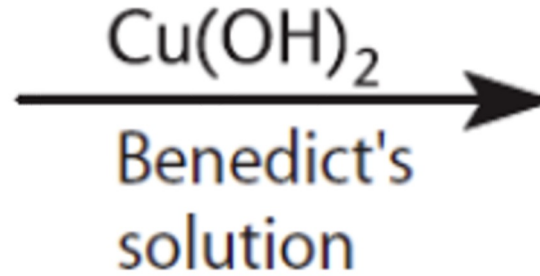
This Chapter Includes:



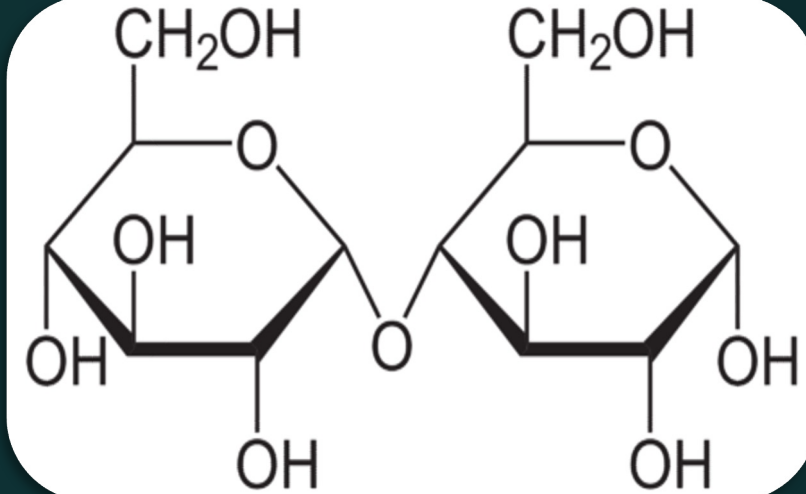
Linear Carbs



Cyclic Carbs



Carb Reactions



Carbs Linked Together

This Chapter Builds On:

Organic Chem Chapters 2, 5, 6, Biochem Chapter 2, Misc.
Bio topics

4.1

Linear Carbohydrates and Classification

+ some organic nomenclature

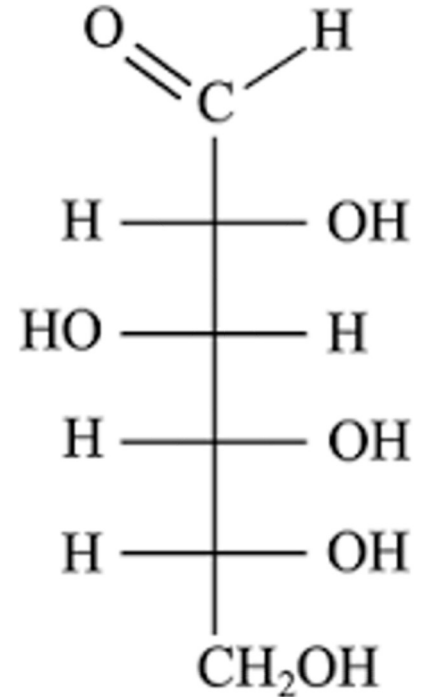
Definition of Carbohydrate

Old definition based off of empirical formula: Anything with formula $C_n(H_2O)_n$ is a carbohydrate

This means that each carbon is bonded to an H and OH, typically (except at chain ends)

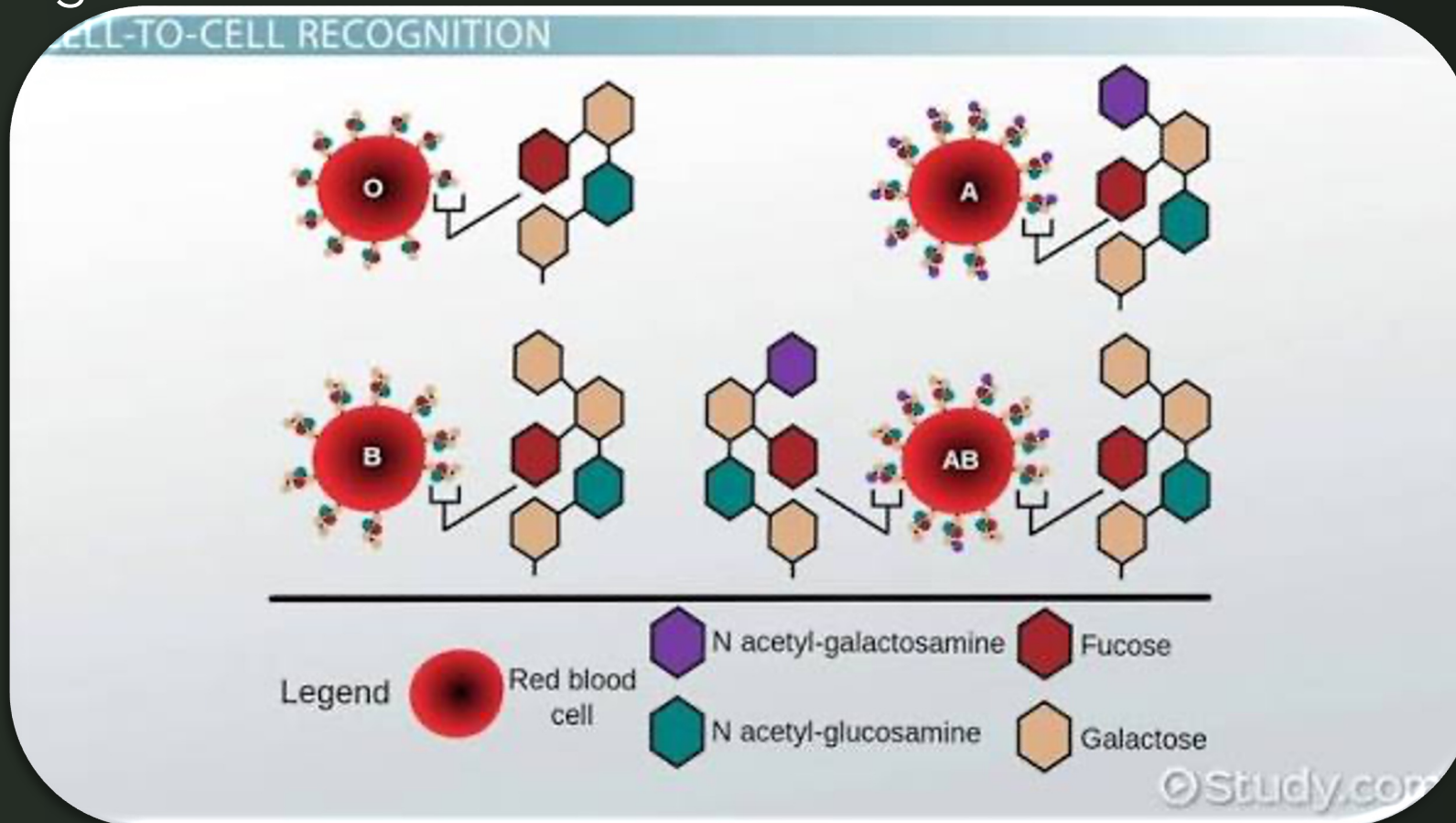
Carbohydrates include all sugars, as well as macromolecules composed of sugars – starches and fibers. Sugar polymers are considered carbs, and those are formed by dehydration (removal of H_2O).

New definition: anything with formula $C_n(H_2O)_m$ is a carbohydrate. N doesn't have to equal m, necessarily



Definition of Carbohydrate

This definition is loosey-goosey: some sugars (important, common ones too) contain amine groups; they contain nitrogen.



Carb names end in -OSE

List some carbohydrates you know that fit
this rule

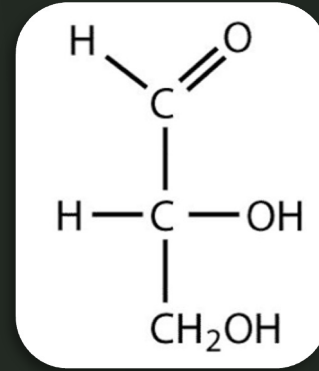
Carb names end in -OSE

List some carbohydrates you know that fit
this rule

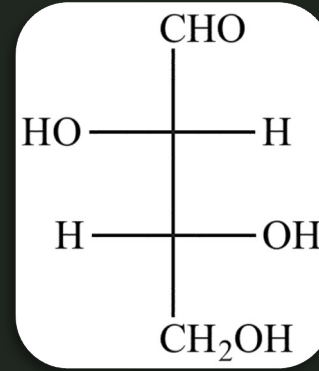
Glucose, Fructose, Sucrose, Maltose, Cellulose, Lactose, Galactose,
Mannose, amylose, Sucralose, Glycogen?

Carbs are Classified by Size

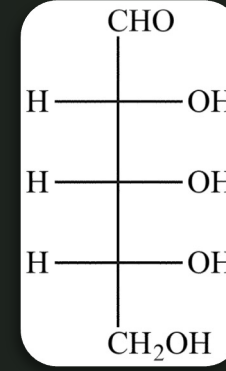
1. Simple sugars (monomers) are classified by number of carbon atoms using Greek numerical prefixes (we start at 3 carbons)



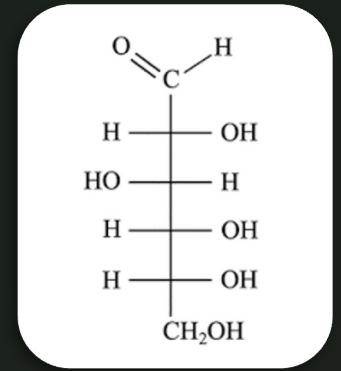
Triose



Tetrose

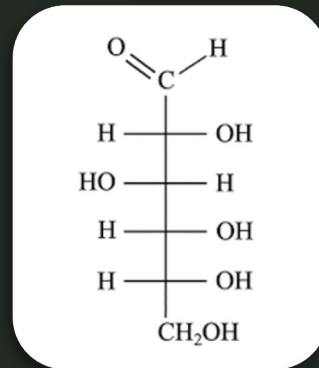


Pentose

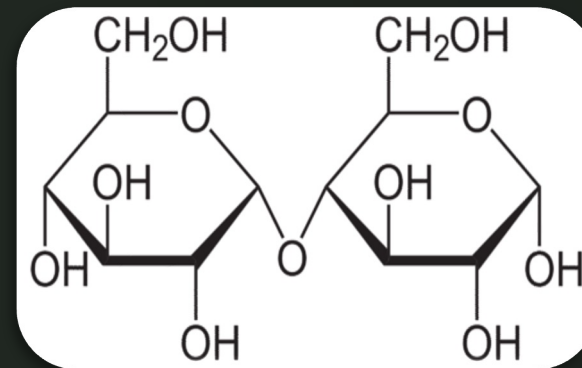


Hexose

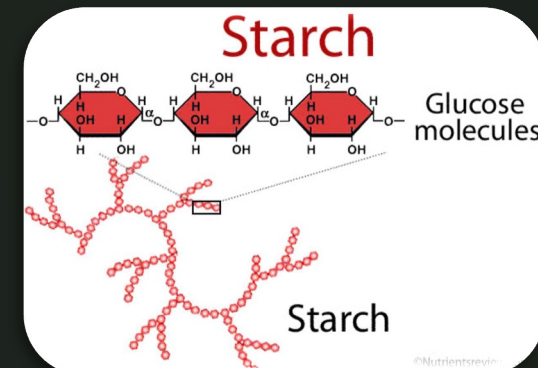
2. Carbohydrates are classified by number of monomers using Greek numerical prefixes



Monosaccharide



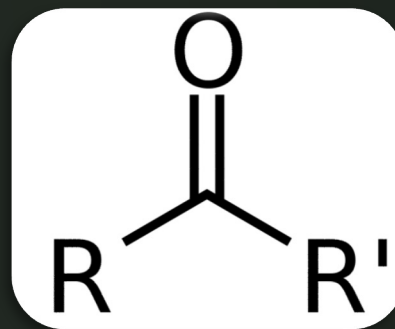
Disaccharide



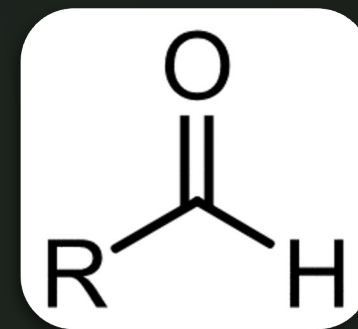
Polysaccharide

Carbs are Classified by Functional Groups

Ketones and Aldehydes are Functional groups in Organic Chemistry

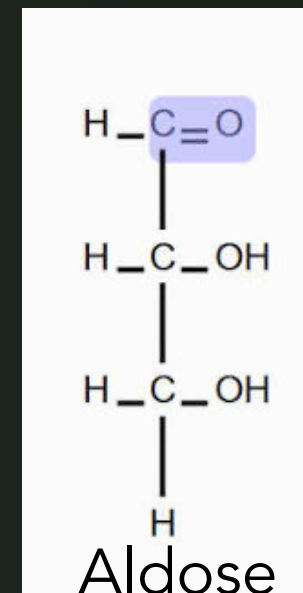
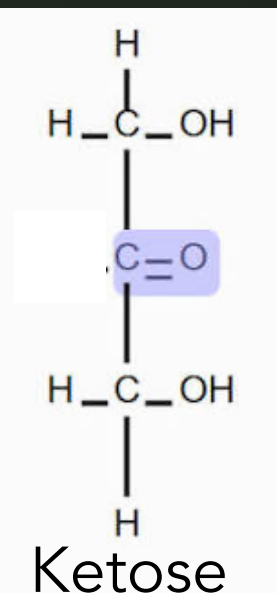


Ketone

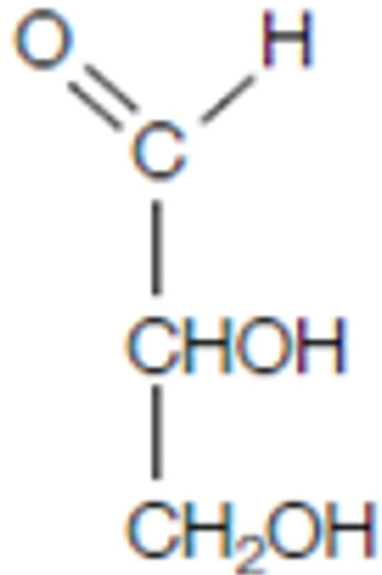


Aldehyde

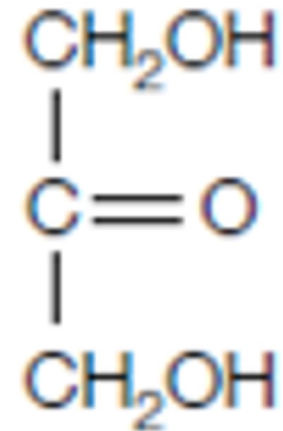
Carbohydrates are classified by if they contain Ketone or Aldehyde groups: Ketose or Aldose)



Smallest Ketose and Smallest Aldose



Glyceraldehyde
(an aldose)
 $\text{C}_3\text{H}_6\text{O}_3$



Dihydroxyacetone
(a ketose)
 $\text{C}_3\text{H}_6\text{O}_3$

Combining Terminology

Functional group prefix followed by numerical prefix.
For example:

Ketopentose – sugar that has ketone group and 5 carbons

Aldotriose – sugar with aldehyde group and 3 carbons

Fischer Projection

Vertical Lines are bent into the page, horizontal lines are bent away from the page (towards you)



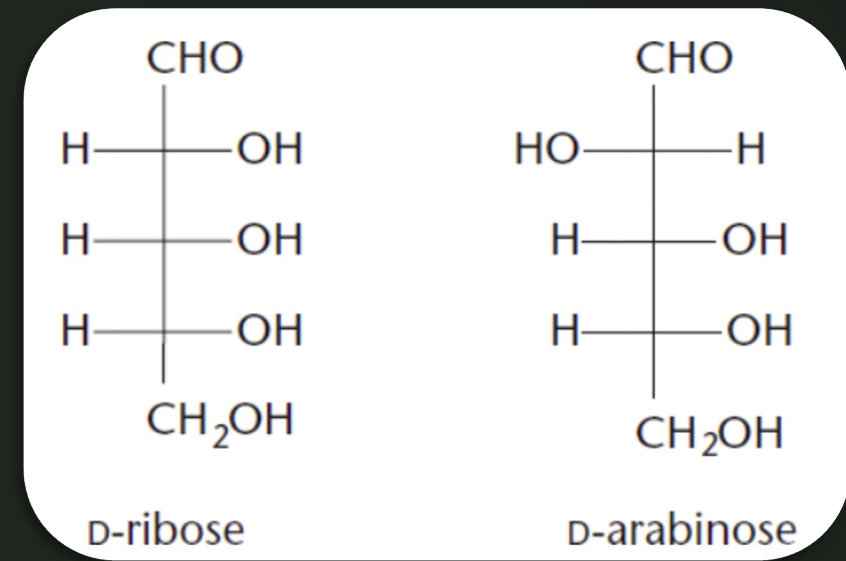
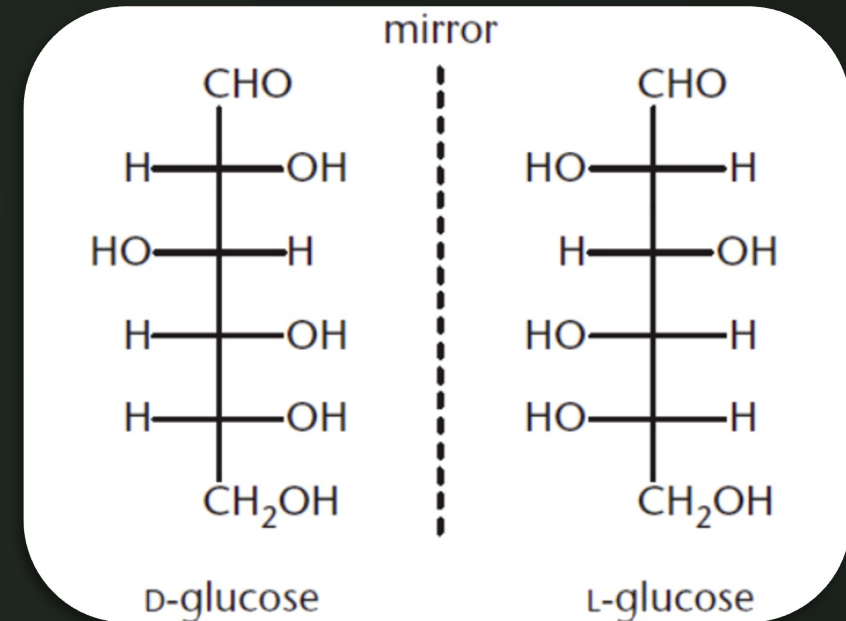
Isomers of Carbohydrates

Enantiomers are mirror reflections – every chiral center is inverted

D/L conformations are relative – depend on rotation of light through the molecule. D-carbose is the enantiomer of L-carbose

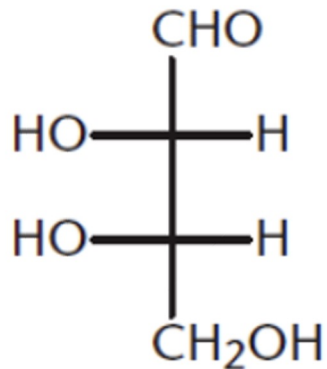
For all D-enantiomers of simple sugars, the bottom (highest-numbered) chiral carbon has hydroxyl on the RIGHT (hydroxyl on the Left = L-enantiomer)

Epimers differ at ONLY 1 chiral center

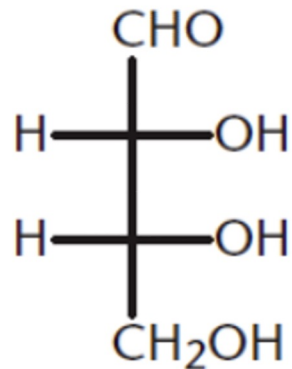


Isomers of Carbohydrates

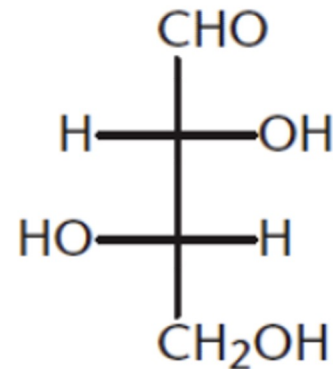
For the same backbone of n chiral centers and molecular formula, there are 2^n different stereoisomers



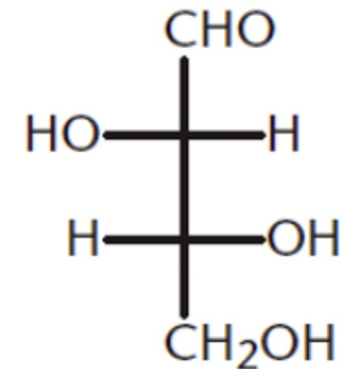
L-erythrose



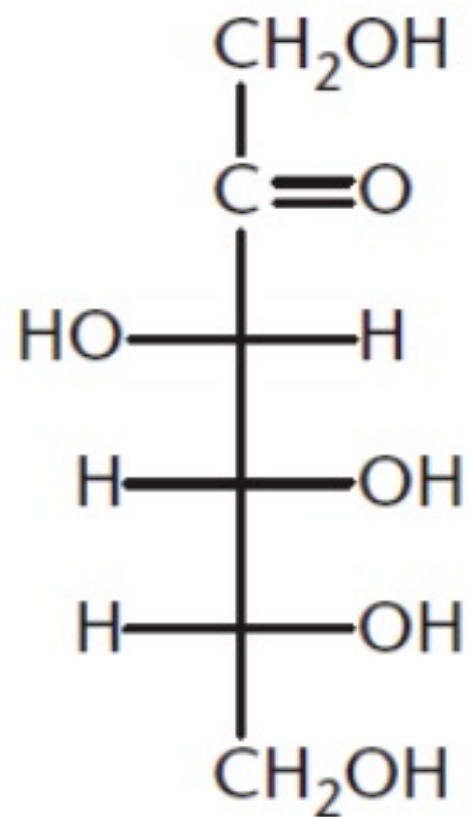
D-erythrose



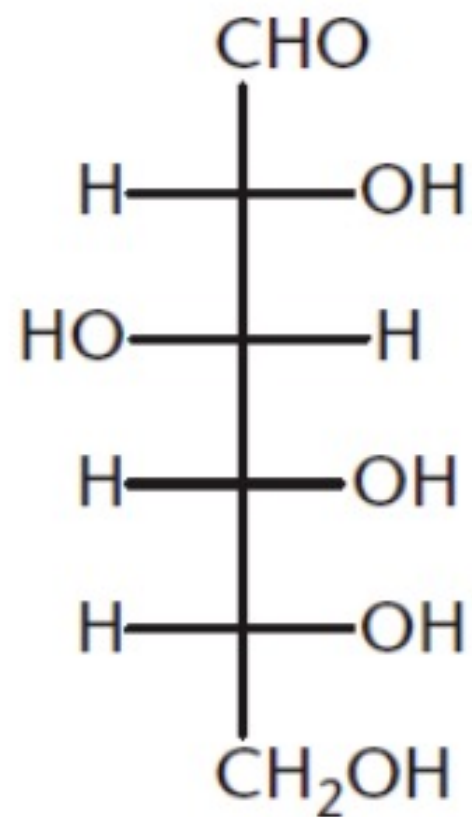
L-threose



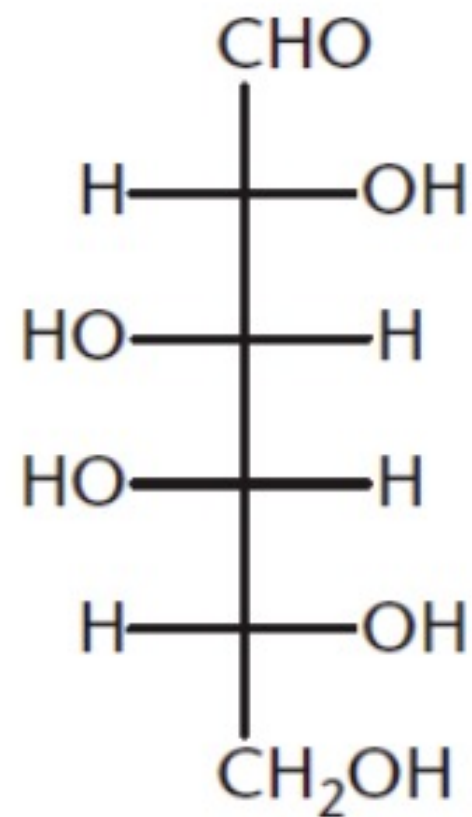
D-threose



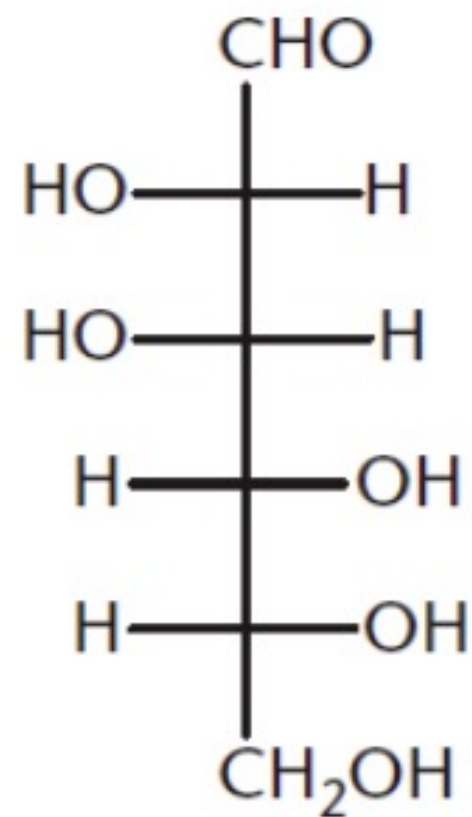
D-fructose



D-glucose

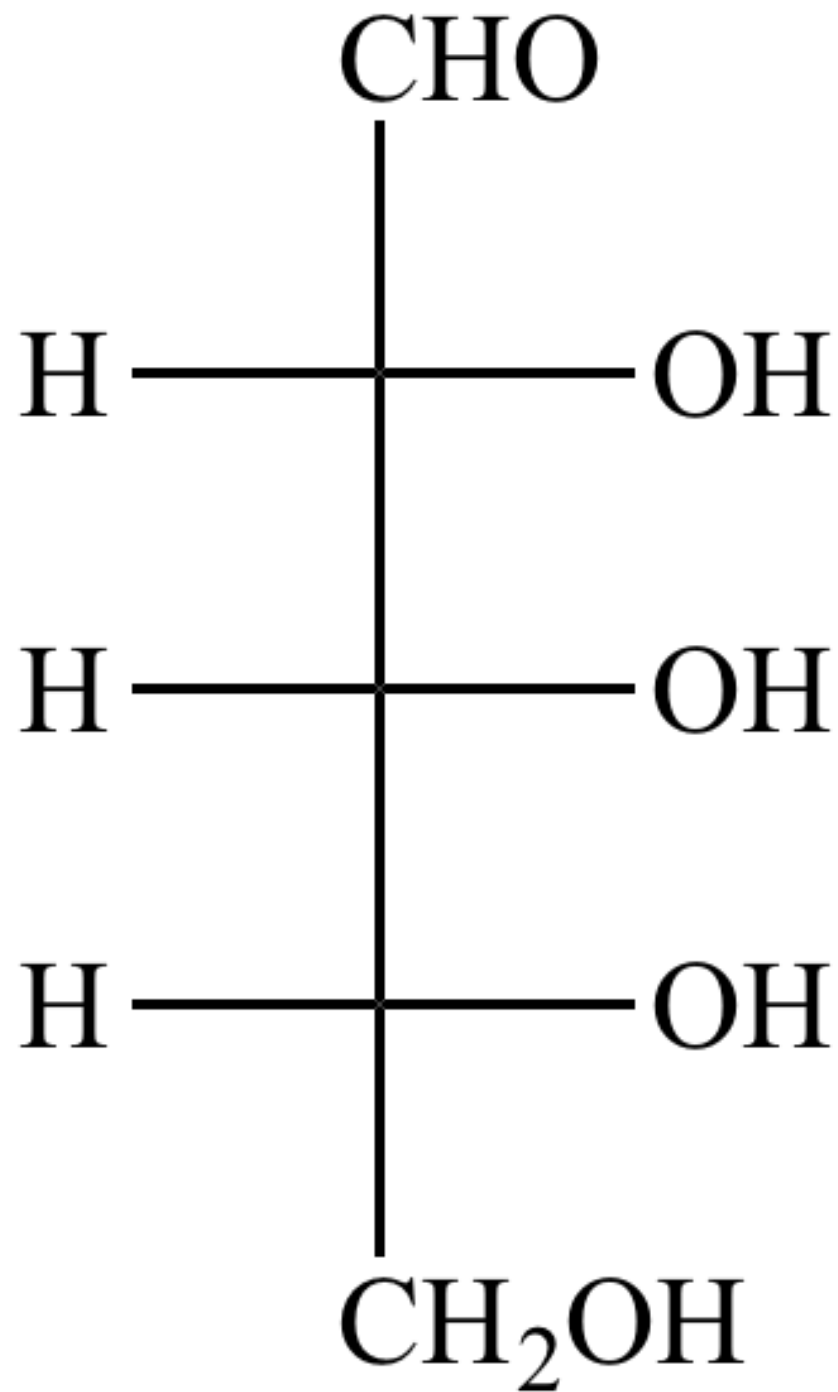


D-galactose

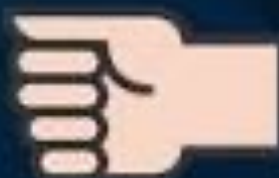
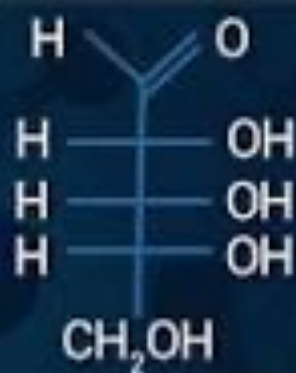


D-mannose

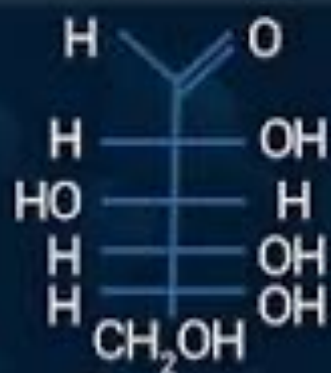
D-Ribose



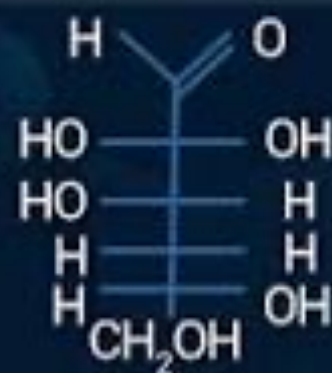
Ribose



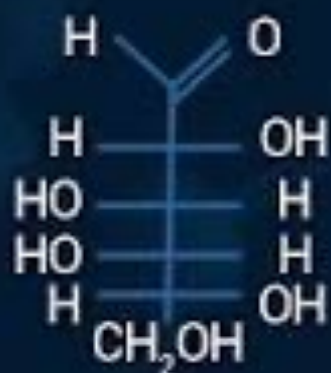
Glucose



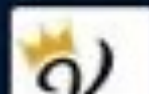
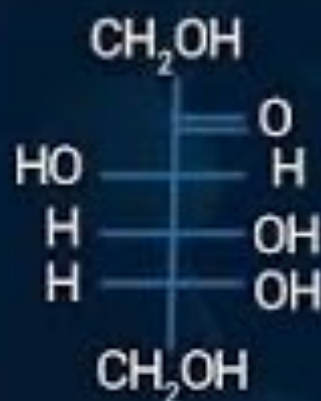
Mannose



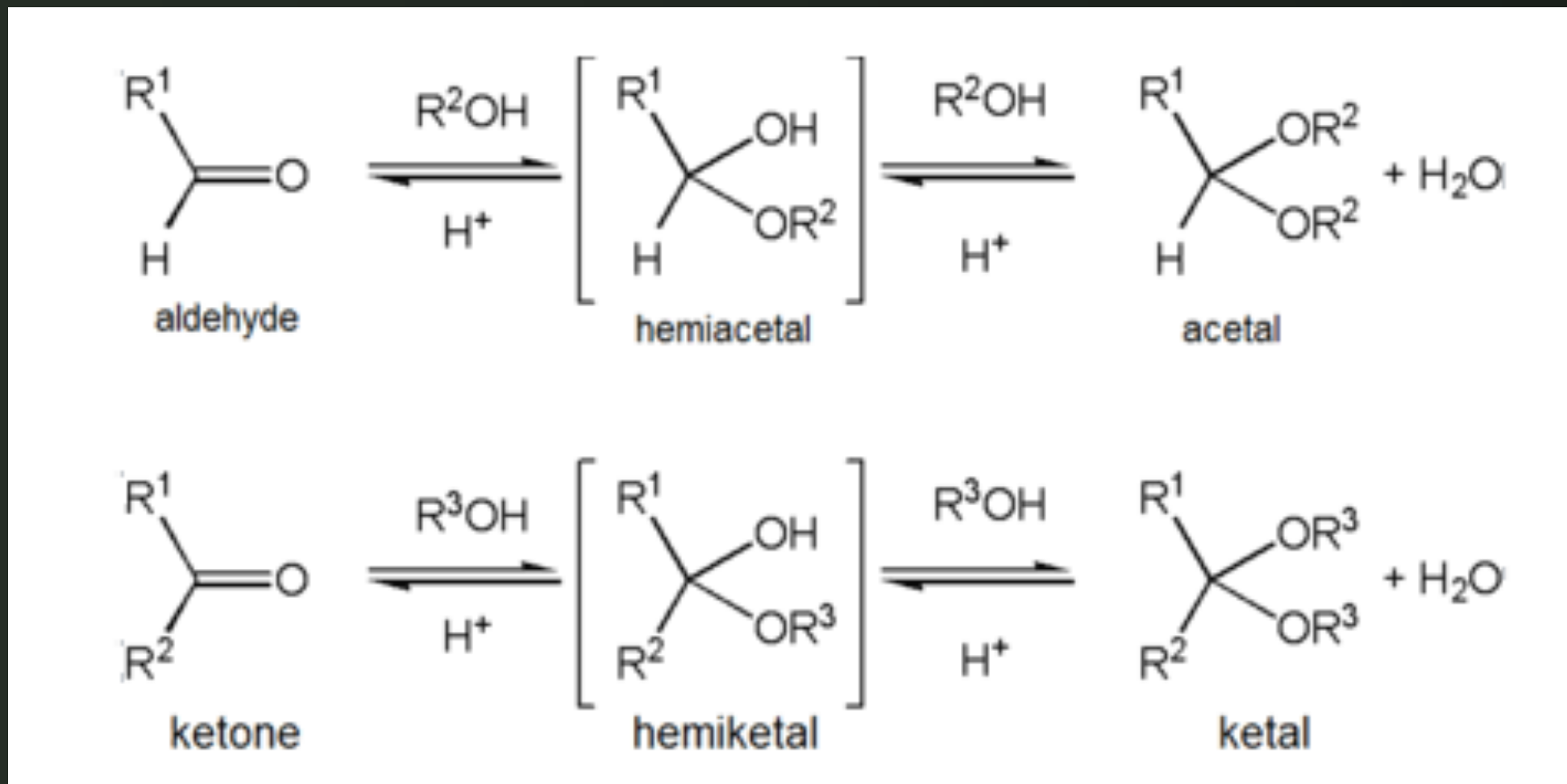
Galactose



Fructose



Acetals and Ketals



These functional groups are defined by 1 carbon with multiple ether/alcohol groups.

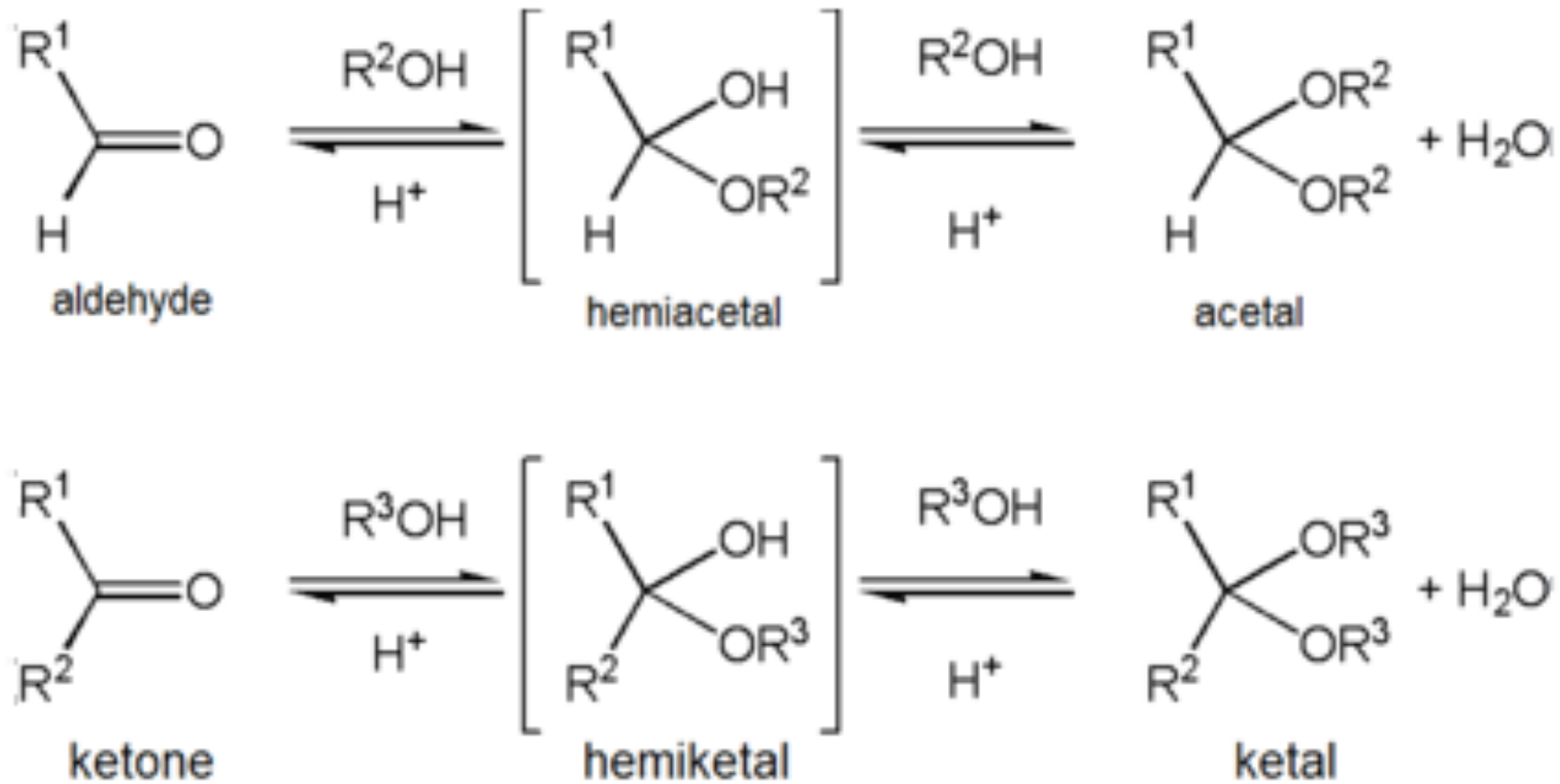
Aldehydes, ketones, hemis can form bonds with molecules by reacting to hydroxyl group

4.2

Cyclic Carbohydrates

+ one important reaction

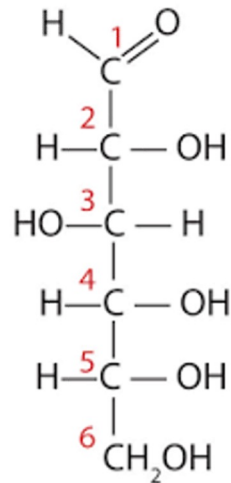
Acetals and Ketals



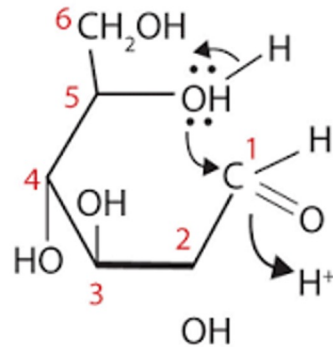
These functional groups are defined by 1 carbon with multiple ether/alcohol groups.

Aldehydes, ketones, hemis can form bonds with molecules by reacting to hydroxyl group

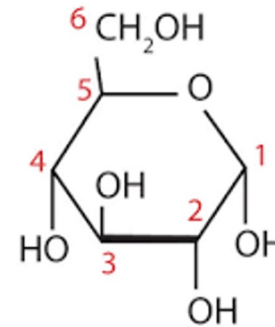
Ring-Chain Interconversion



(a) Fischer projection

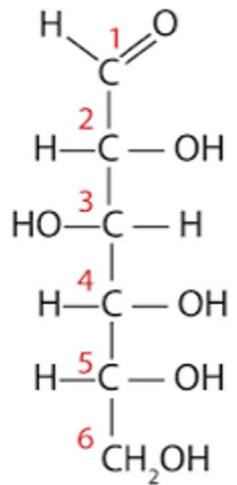


(b) Three-dimensional representation



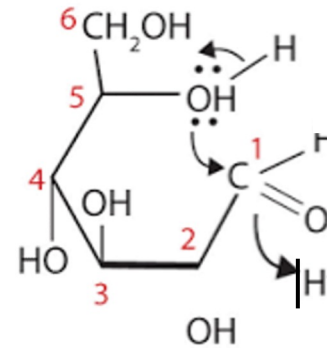
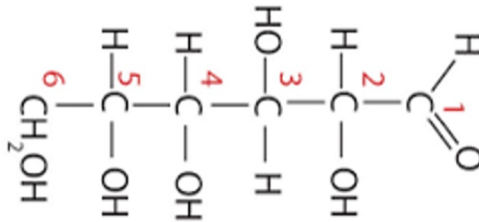
(c) Cyclic monosaccharide

Ring-Chain Interconversion

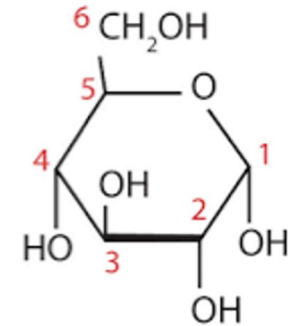


(a) Fischer projection

(a) Fischer projection

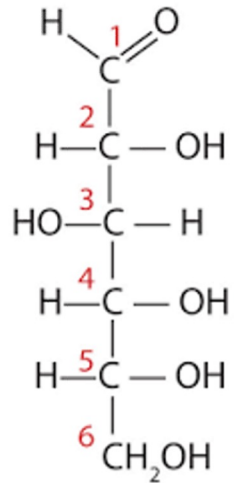


(b) Three-dimensional representation

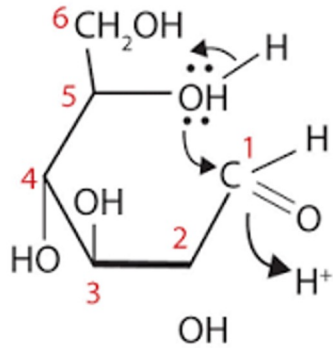


(c) Cyclic monosaccharide

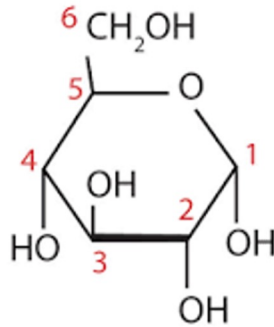
Ring-Chain Interconversion



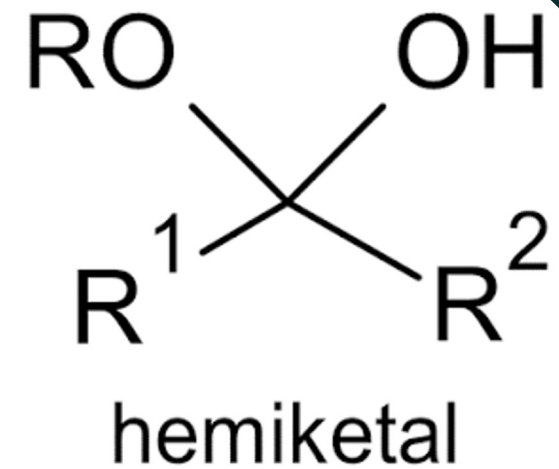
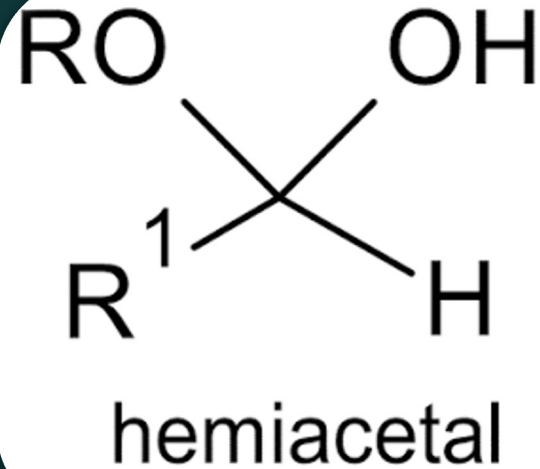
(a) Fischer projection



(b) Three-dimensional representation

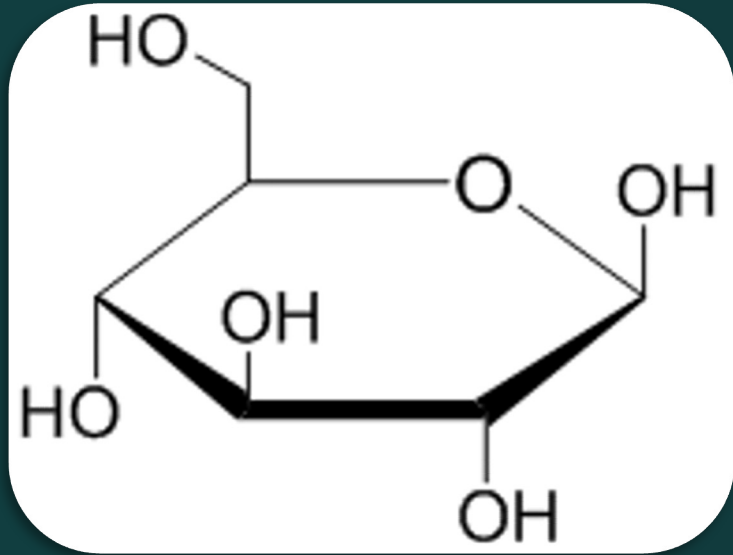


(c) Cyclic monosaccharide

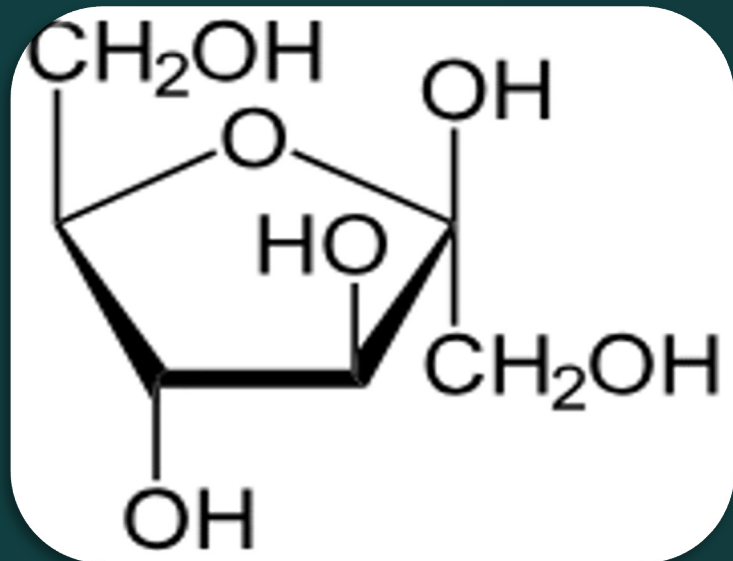


Conversion of a straight-chain sugar to a cyclic sugar IS a conversion from an Aldehyde to a hemiacetal or Ketone to a hemiketal

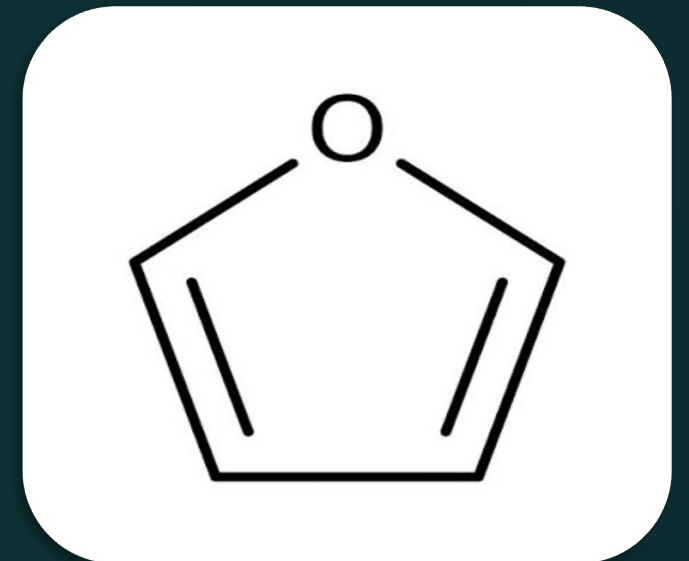
Pyranose and Furanose



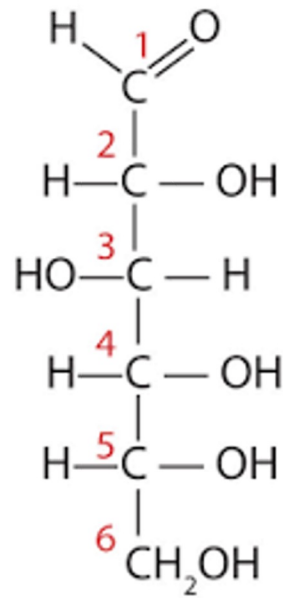
6-membered rings are called
pyranoses
Ex: glucopyranose



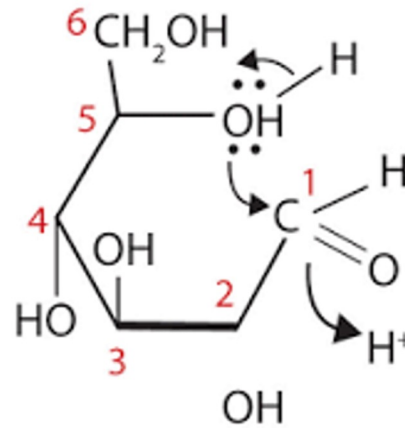
5-membered rings are
called furanoses
Ex: ribofuranose



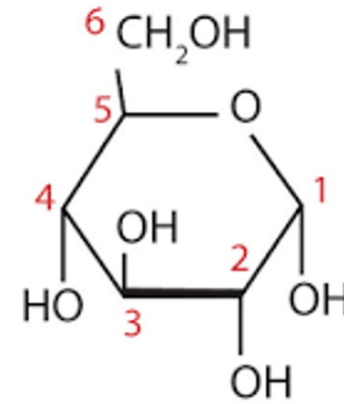
Anomers and Anomeric Carbon



(a) Fischer projection

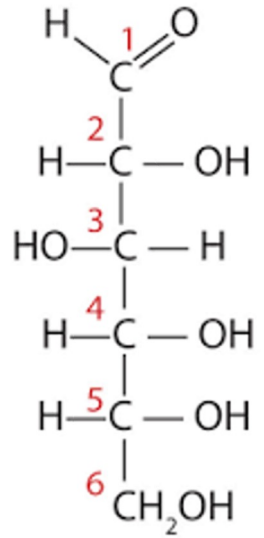


(b) Three-dimensional representation

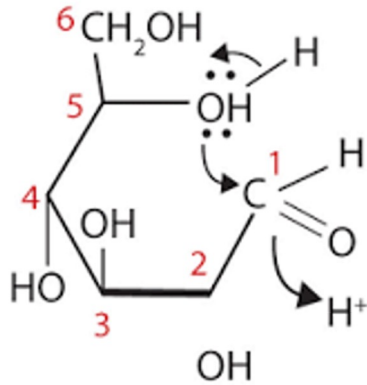


(c) Cyclic monosaccharide

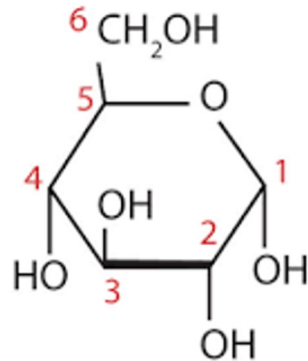
Anomers and Anomeric Carbon



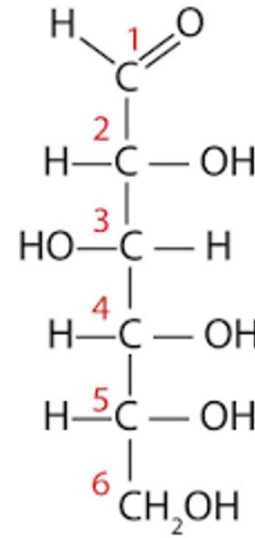
(a) Fischer projection



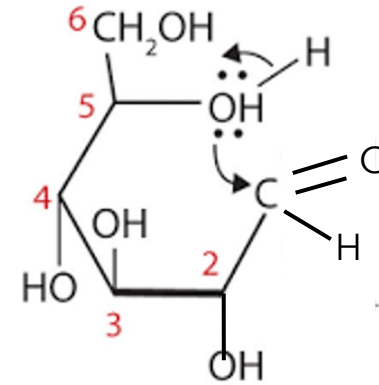
(b) Three-dimensional representation



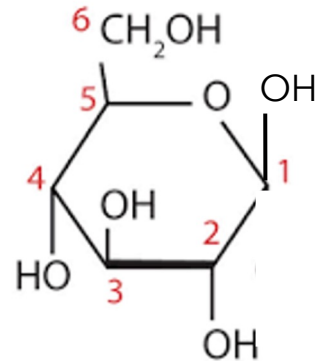
(c) Cyclic monosaccharide



(a) Fischer projection



(b) Three-dimensional representation



(c) Cyclic monosaccharide

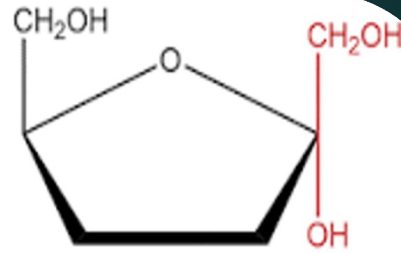
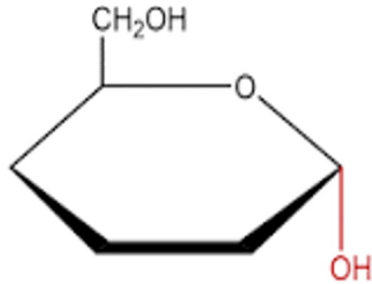
The two cyclic sugars above are anomers (type of isomer)

The carbon with varying stereochemistry is called the anomeric carbon

The same straight-chain carb can form either anomer; anomers can convert between each other (mutorotation)

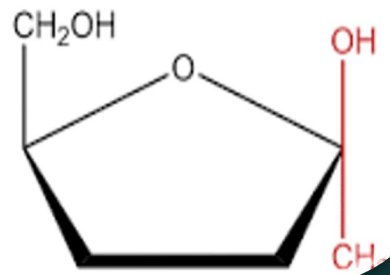
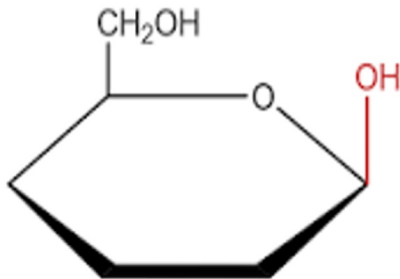
Naming Anomers

α anomers



α -anomers have hydroxyls on opposite side (trans- to) the CH_2OH group

β anomers



β -anomers have hydroxyls on same side (cis- to) the CH_2OH group

Ex: in RNA, the backbone sugar is called β -D-2-ribofuranose

Naming Anomers

So, the full naming convention for cyclic sugars is
(anomeric conformation) - (relative configuration) - [parent sugar name][ring type][suffix]

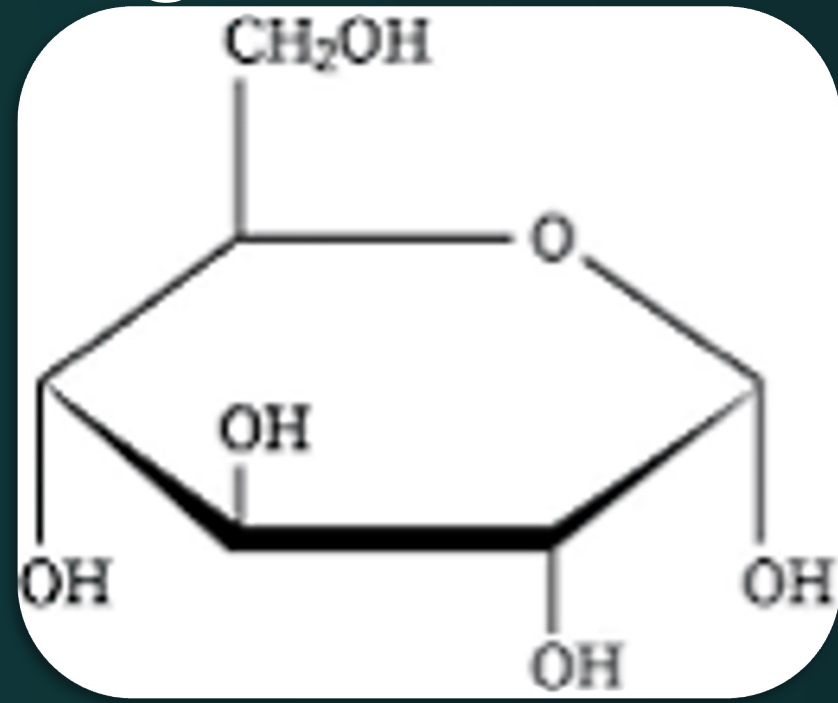
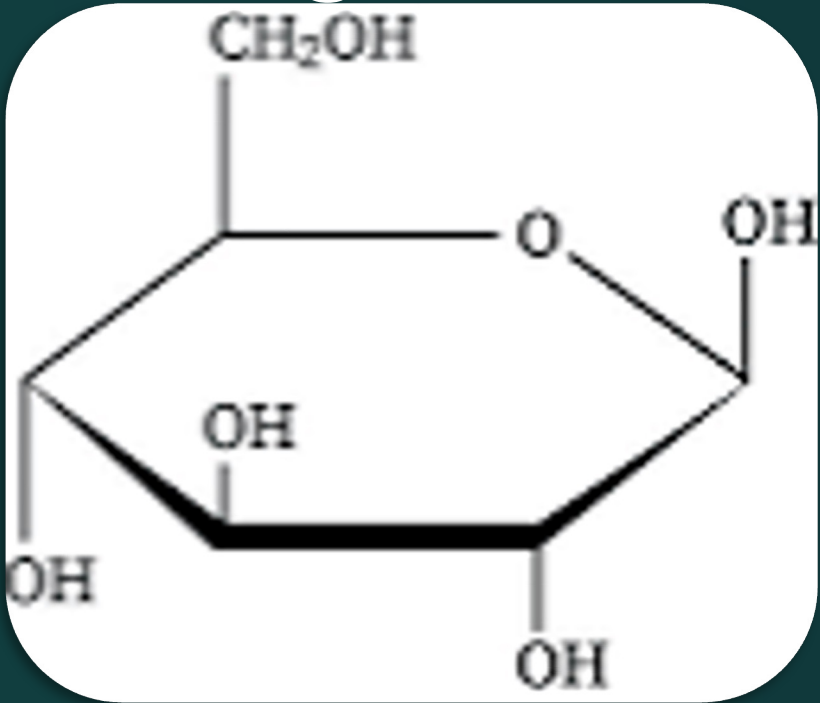
Or

(α/β)-(D/L)-[gluco/fructo/etc][pyran/furan][ose]

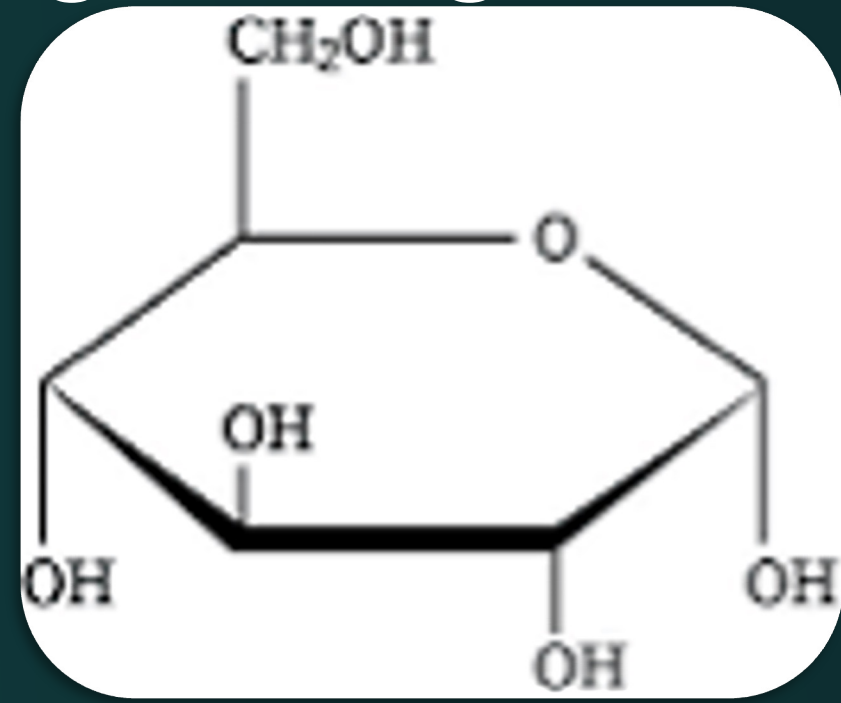
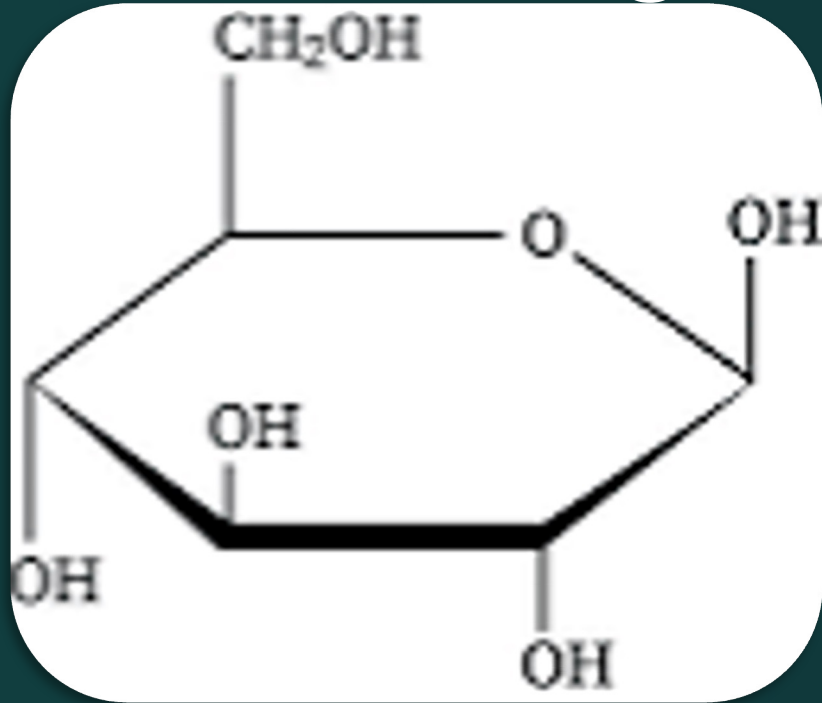
For example:

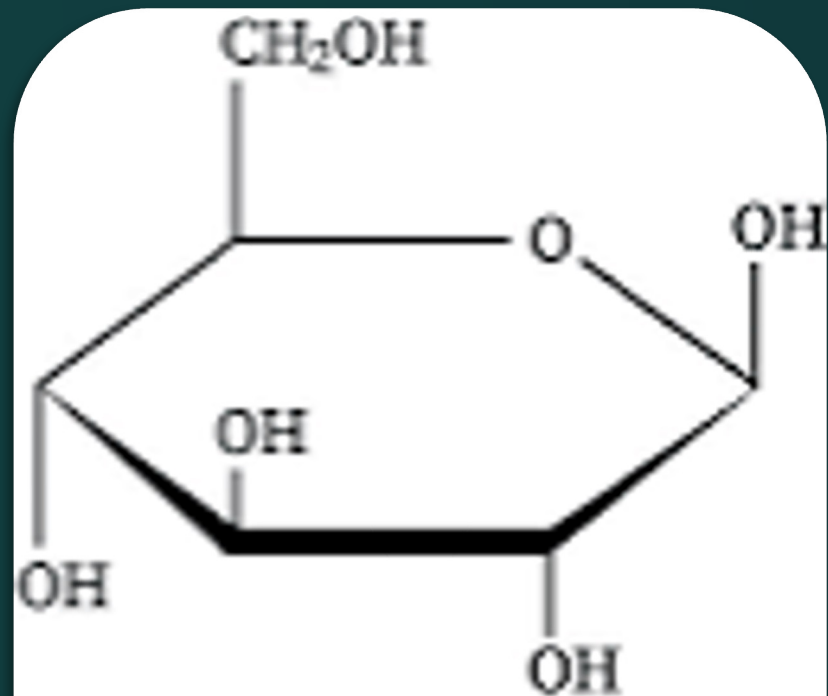
β -D-2-ribofuranose

Name These Anomers!
(I'll give hints about straight-chain carb)

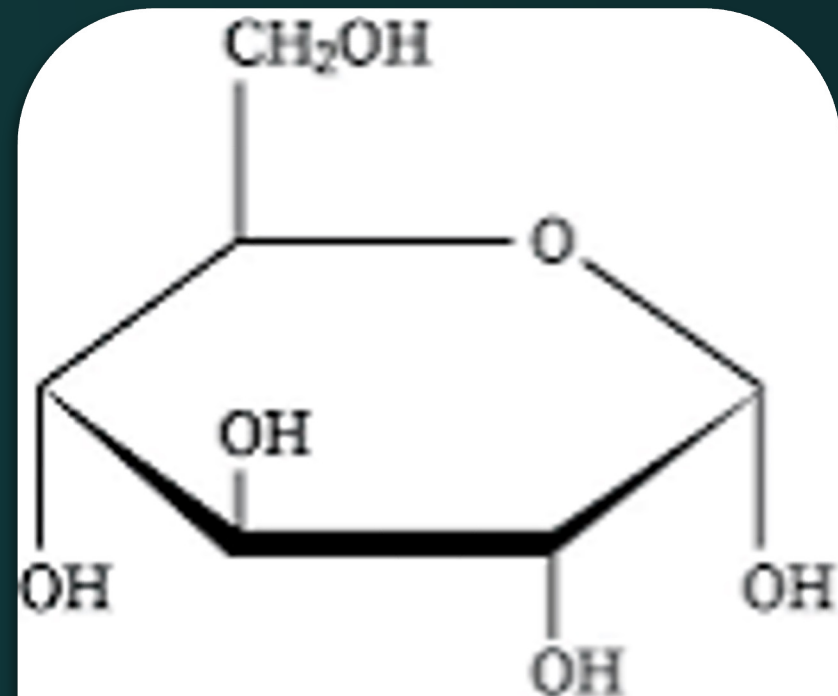


Name These Anomers!
(The straight-chain sugar is D-glucose)





(β -anomer of
D-glucopyranose
(β -D-glucopyranose))



(α -anomer of
D-glucopyranose
(α -D-glucopyranose))

β -Anomers Are Preferred

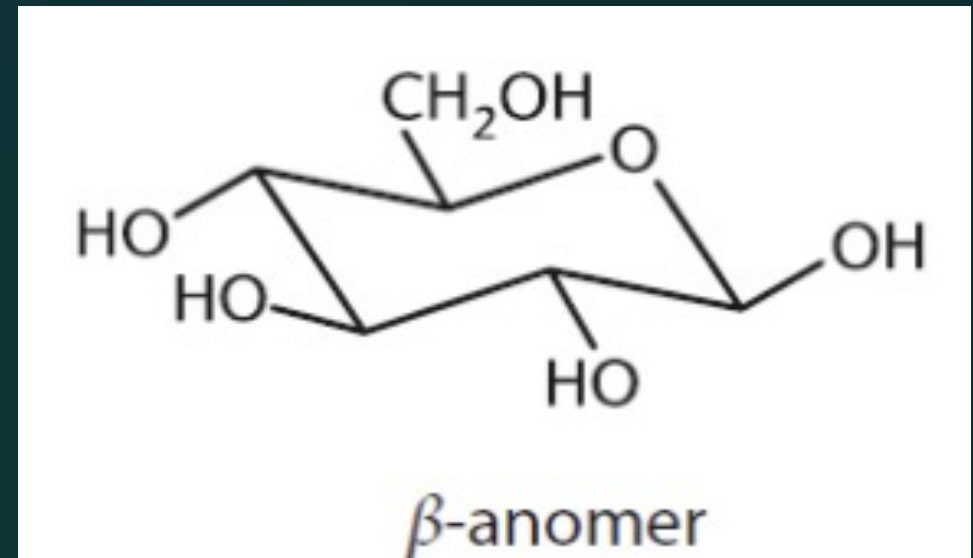
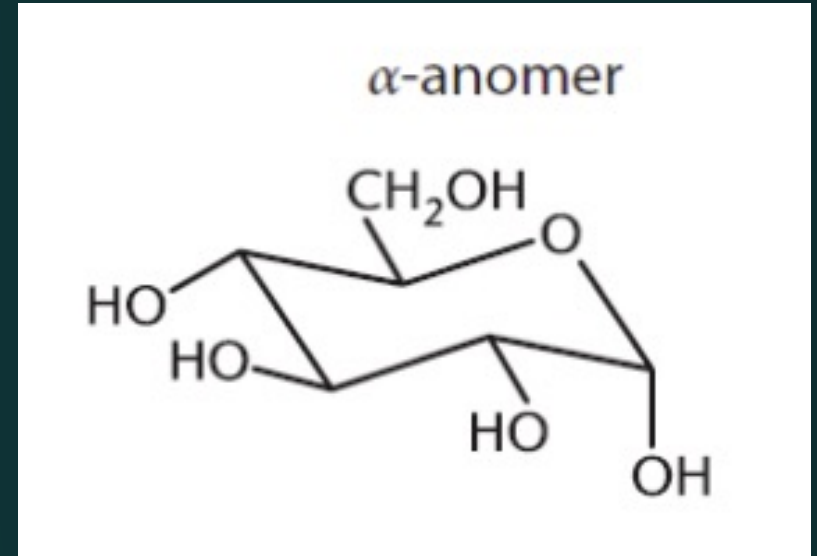
In chair conformation, CH₂OH group is Equatorial (more stable)

If OH is biggest group on anomeric carbon, sugar is more stable when OH is equatorial

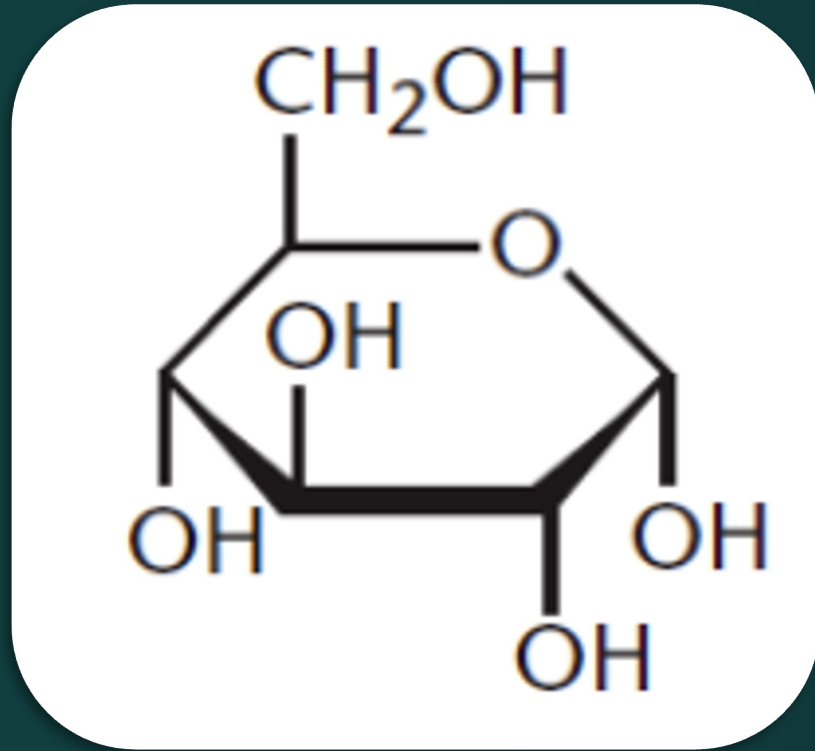
β -anomers have both CH₂OH and anomeric OH at equatorial position

64% β -anomer, 36% α -anomer

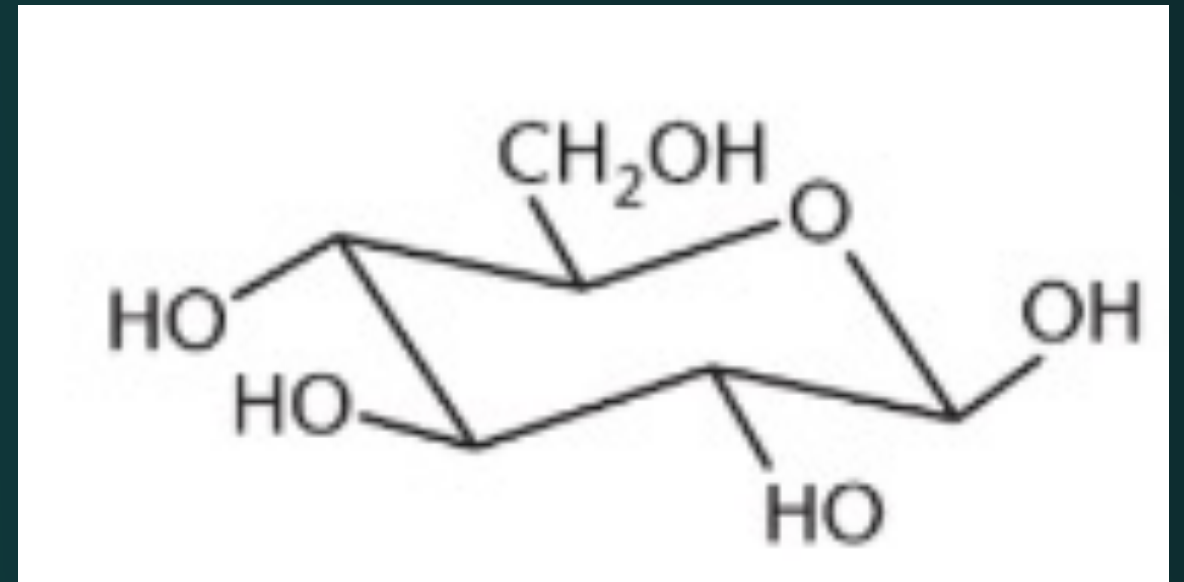
Cyclic is more stable than chain carb



Haworth Projection



Not Haworth Projection (Chair Conf.)

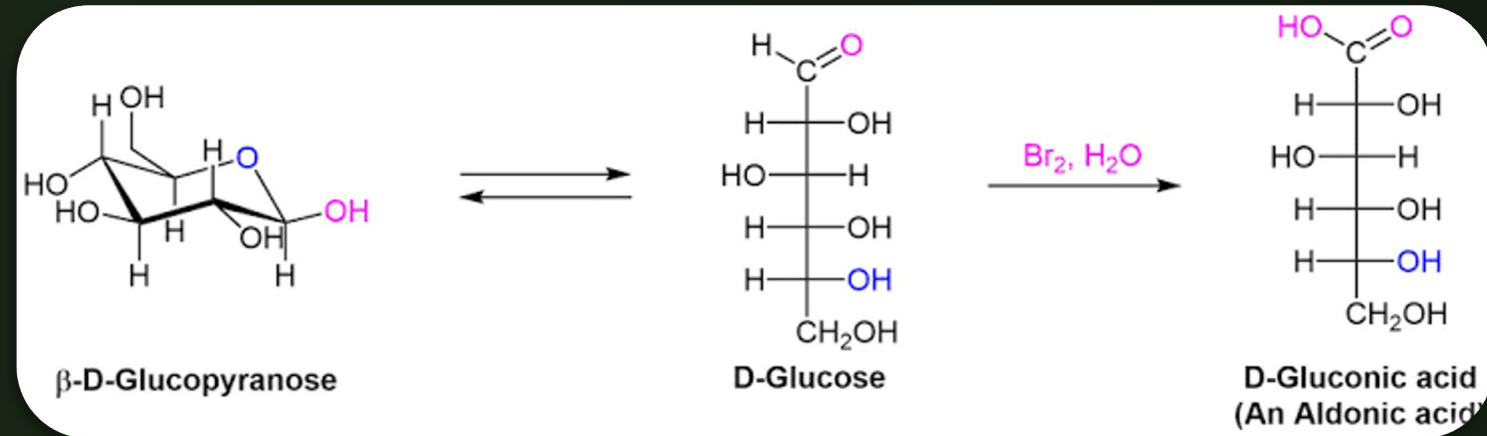


4.3

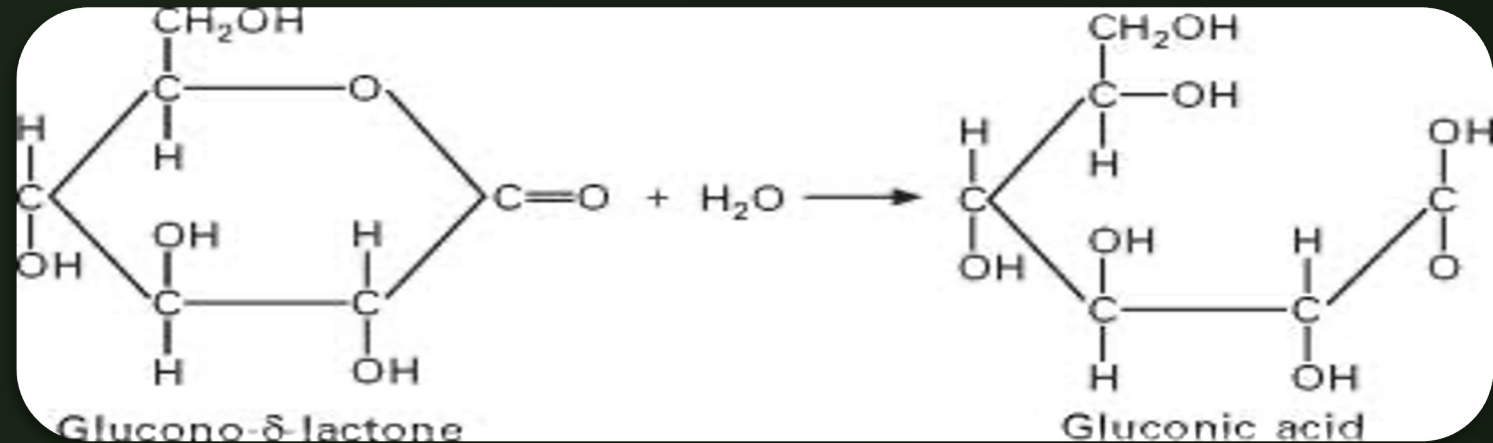
Reagents and Reactions

Oxidation of Aldoses

Like all aldehydes, Aldoses can be oxidized into a carboxylic acid.
Carboxyl sugar is called Aldonic Acid



Aldonic Acid can again assume ring structure, forming a Lactone (not often tested, vitamin C is a Lactone)



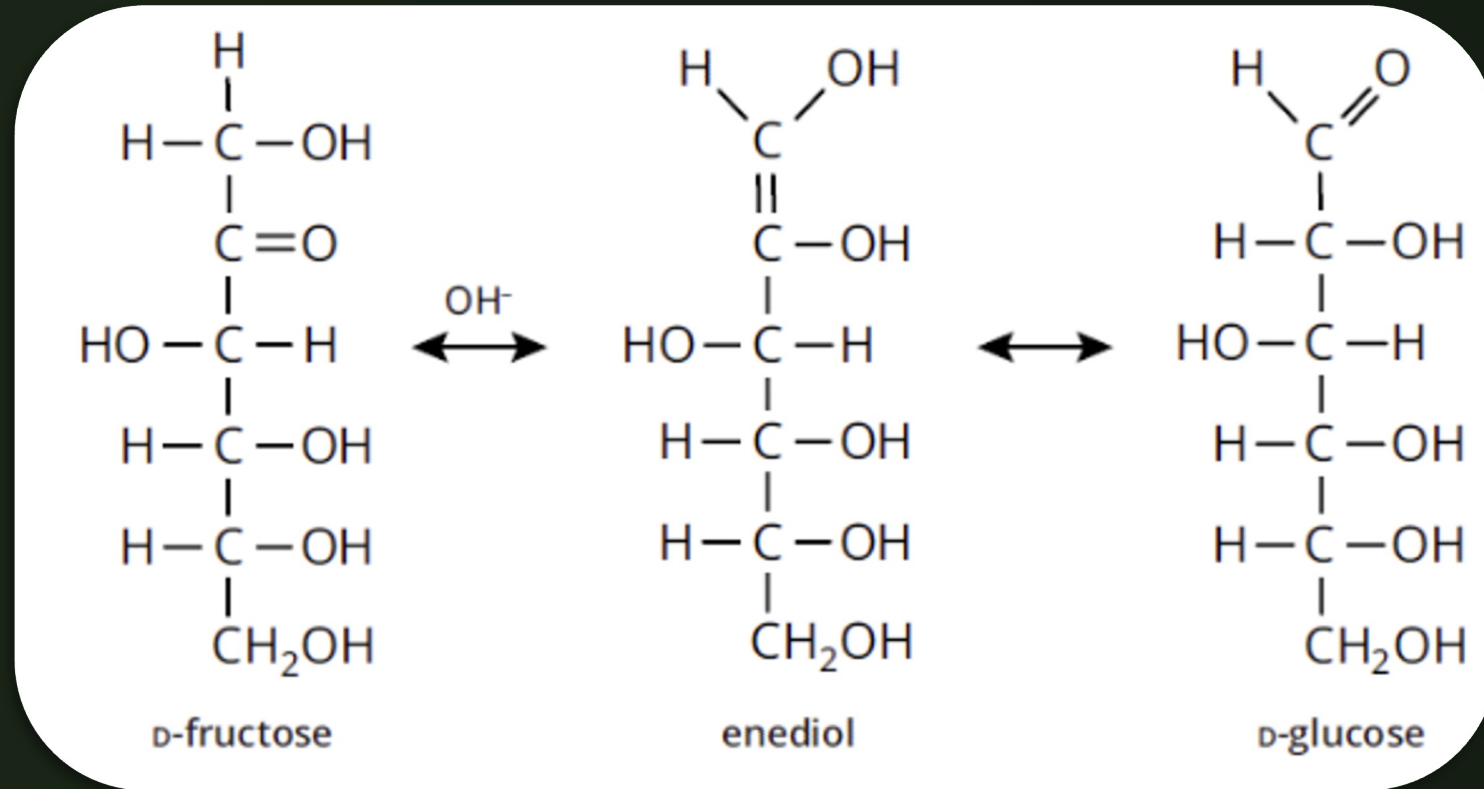
Aldoses can be oxidized by $\text{X} =$
Aldoses can *reduce* $\text{X} \Rightarrow$
Aldose monosaccharides are reducing sugars

Oxidation of Ketoses

Many Ketoses (like fructose) can convert into an Aldose through an enediol intermediate (tautomerization)

Formed Aldose can then be oxidized = can reduce other molecules

Ketose Monosaccharides are Reducing Sugars, too

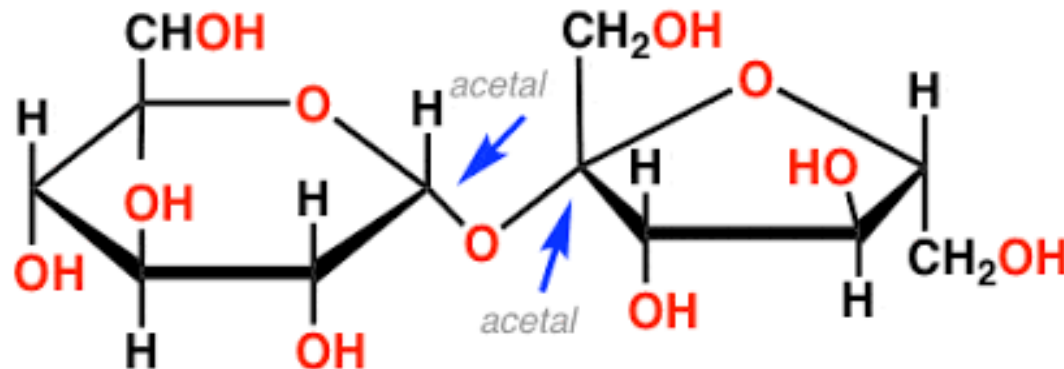


Nonreducing Sugars

Only sugars with buried/bonded reducing end will be nonreducing

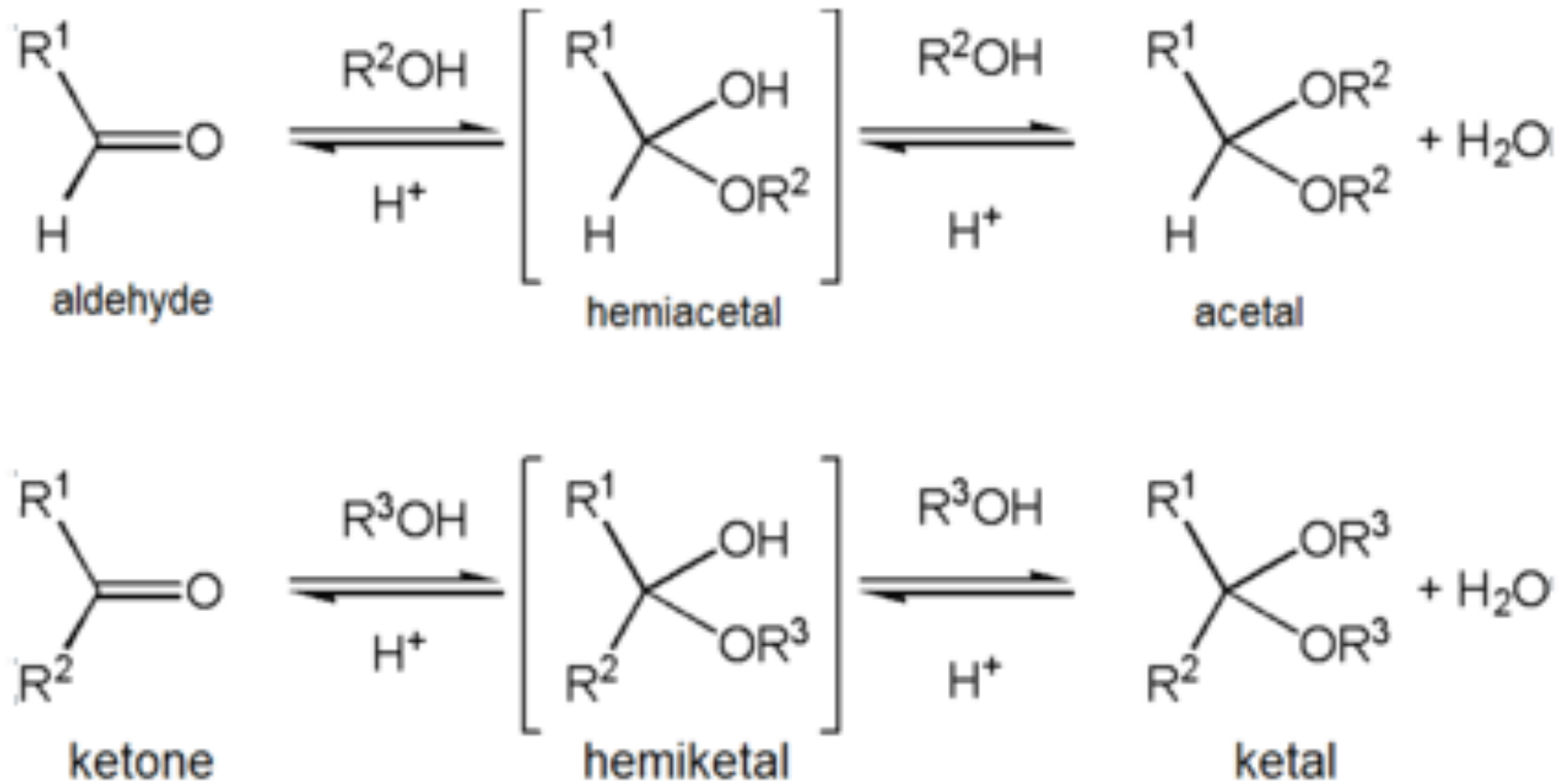
Test for reducing sugars with Benedict's Reagent or Tollen's Reagent

Sucrose is a non-reducing sugar



The structure lacks any hemiacetal functional groups and is therefore "locked" in its cyclic form

Acetals and Ketals



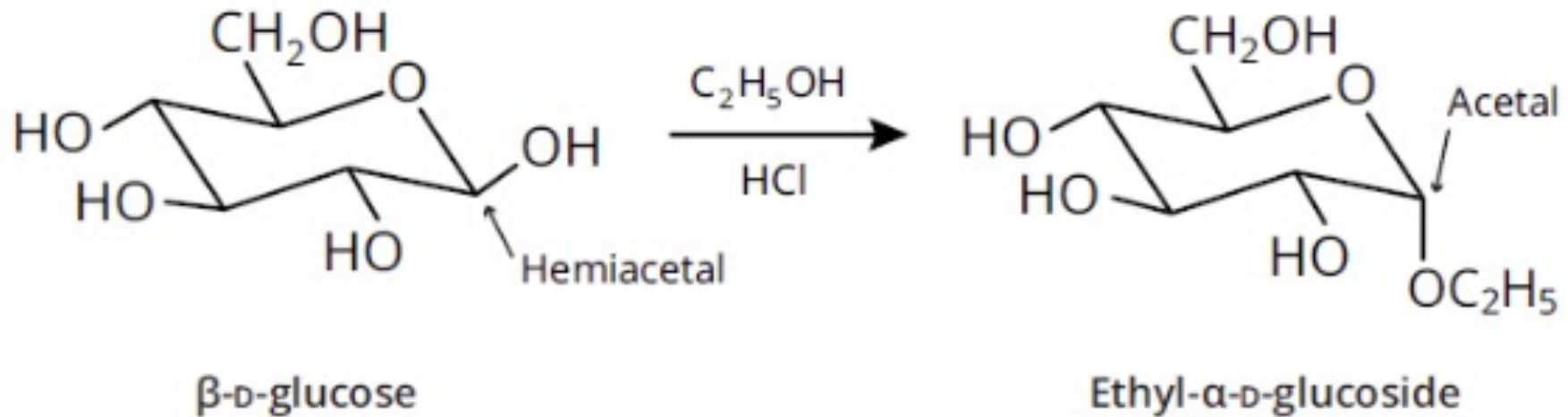
These functional groups are defined by 1 carbon with multiple ether/alcohol groups.

Aldehydes, ketones, hemis can form bonds with molecules by reacting to hydroxyl group

Glycosidic linkages

Reducing end reacts with alcohol (hydroxyl) to form a Glycosidic linkage

Entire Sugar is called a "glycoside" group



4.4

Disaccharides and Polysaccharides

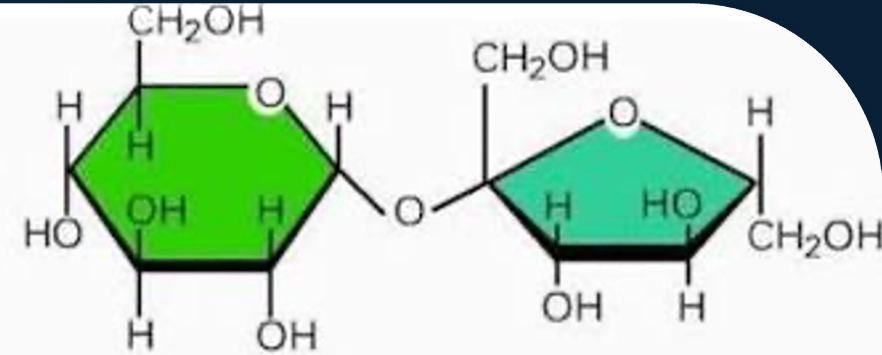
+ some related enzymes

Common Disaccharides

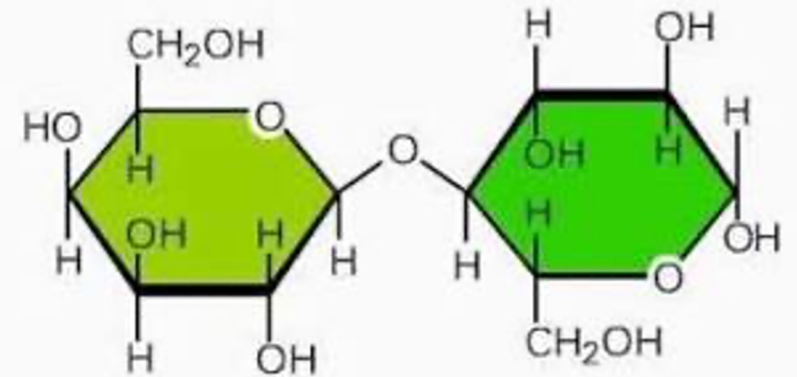
Need to know names, components, and linkage types

Commonly produced or metabolized by organisms

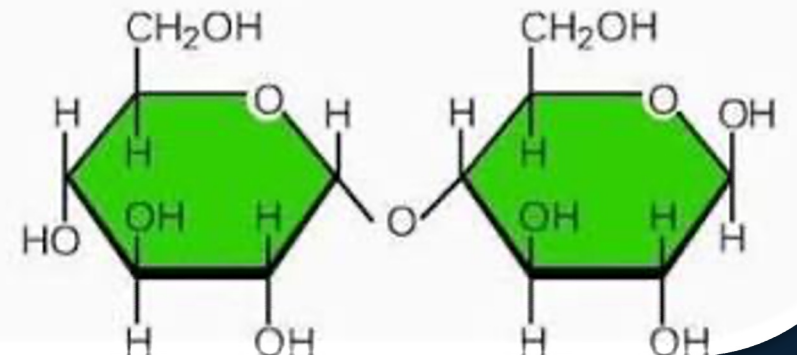
Sucrose
(glucose and fructose)



Lactose
(galactose and glucose)



Maltose
(glucose and glucose)



Glycosidic Linkages Between Sugars

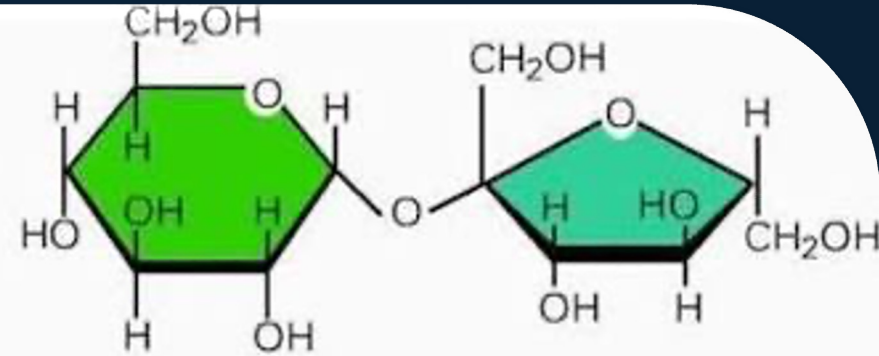
The reducing end of one sugar can bond to any hydroxyl of another sugar, forming a bond (with a specific naming convention)

We describe the first sugar's participating carbon, then describe second sugar's participating carbon.

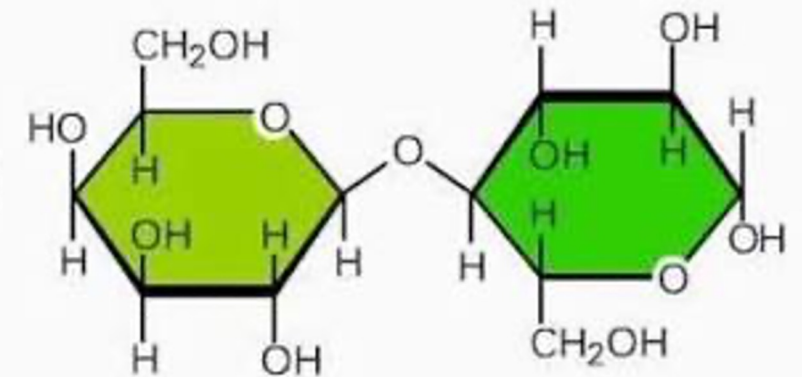
Lactose: galactose- β -1,4-glucose

Sucrose: glucose- α -1,2-fructose

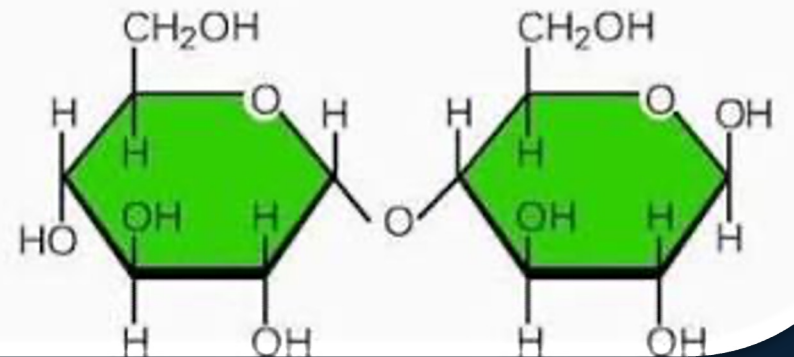
Sucrose
(glucose and fructose)



Lactose
(galactose and glucose)



Maltose
(glucose and glucose)



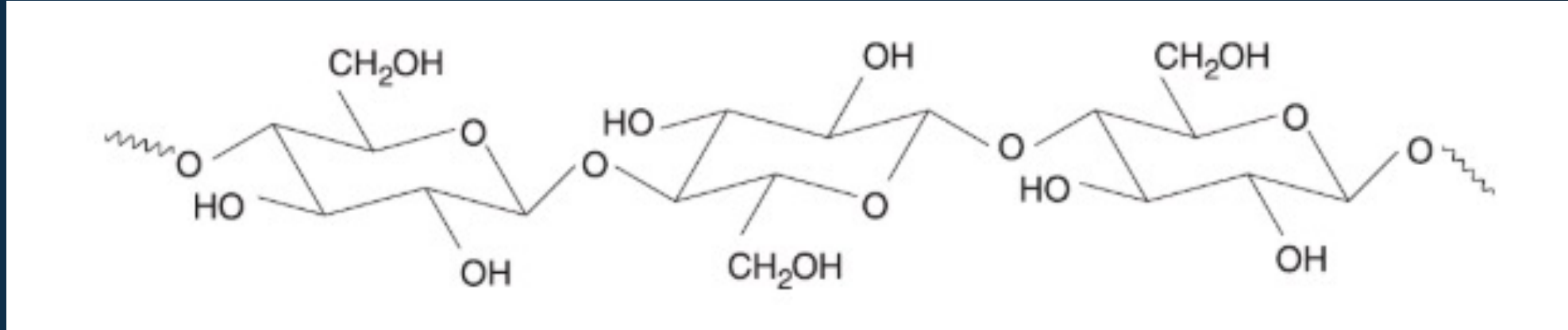
Hetero-/Homo- Polysaccharide

Homopolysaccharide – all same monomer

Heteropolysaccharide – different monomers

Most important polysaccharides are all
composed entirely of glucose
(homopolysaccharides)

Cellulose



Contains β -1,4 glycosidic bonds, does not branch, H-bonds keep strands together. β -bonds make sugars flip orientation

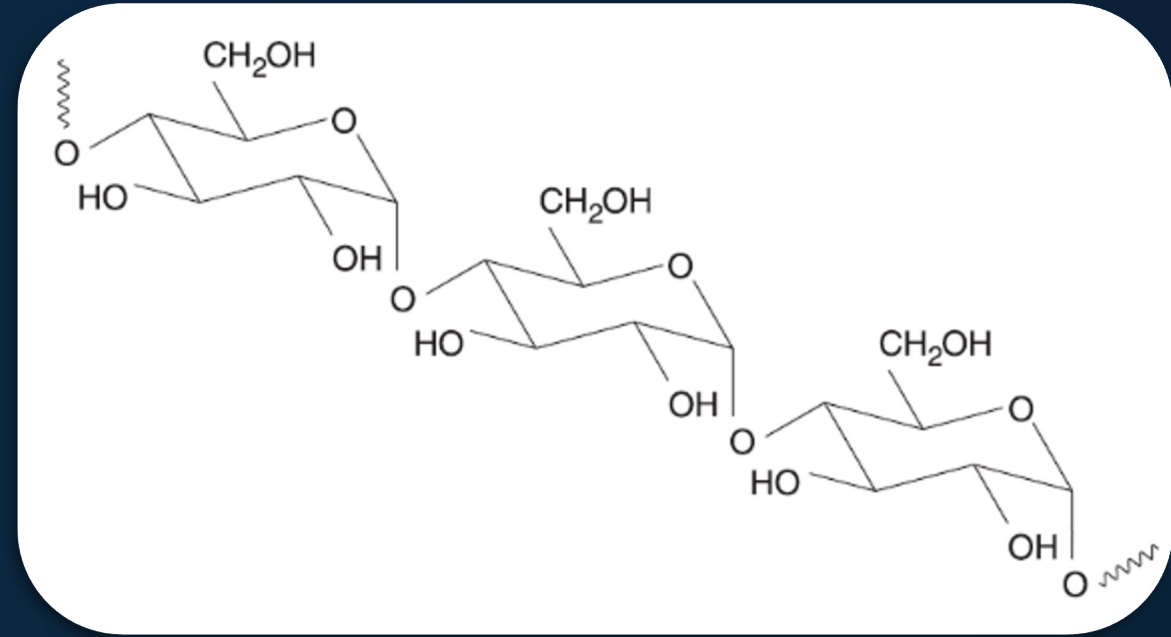
Humans do not have cellulase, so cannot digest cellulose (fiber)

Starch - Amylose

Contains α -1,4 glycosidic bonds, so sugars stay in orientation but take on a helix formation

Also unbranching

We CAN digest starches with alpha-amylase and beta-amylase

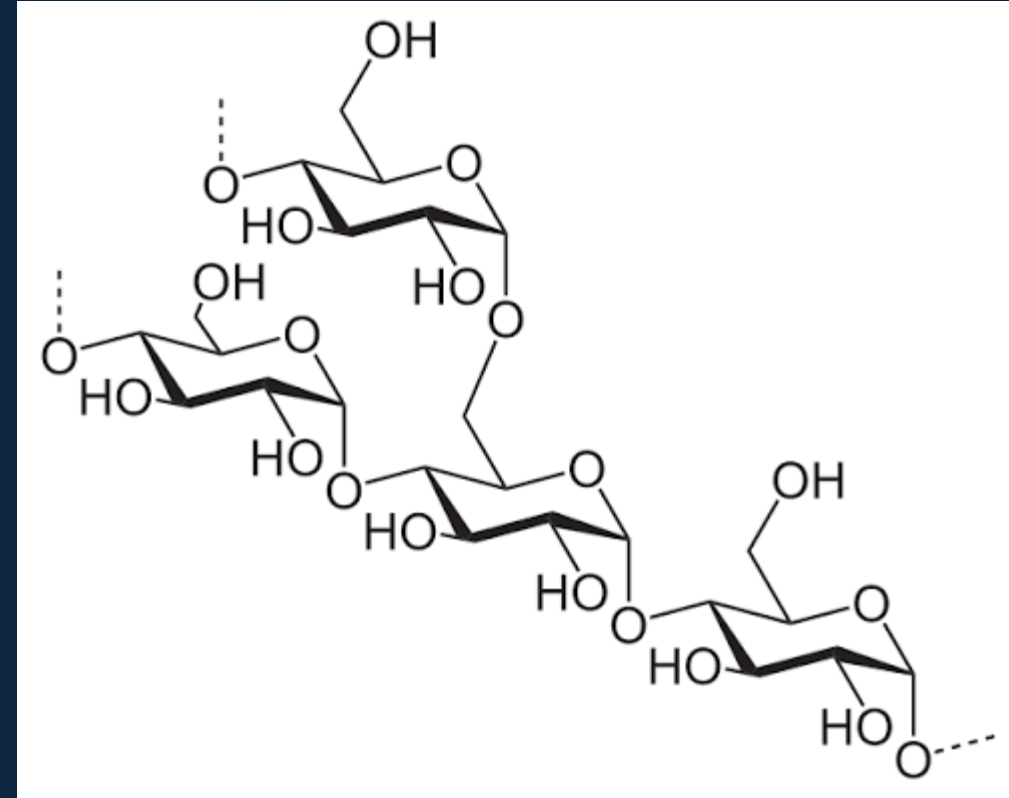


Starch - Amylopectin

Contains α -1,4 glycosidic bonds, so sugars stay in orientation but take on a helix formation

Also contains α -1,6 glycosidic bonds, so branches

We CAN digest starches with alpha-amylase and beta-amylase



Glycogen

Contains α -1,4 glycosidic bonds, so sugars stay in orientation but take on a helix formation

Also contains α -1,6 glycosidic bonds, so branches

Same as Amylopectin, except has more branches (more α -1,6 glycosidic bonds)

