Carbohydrates

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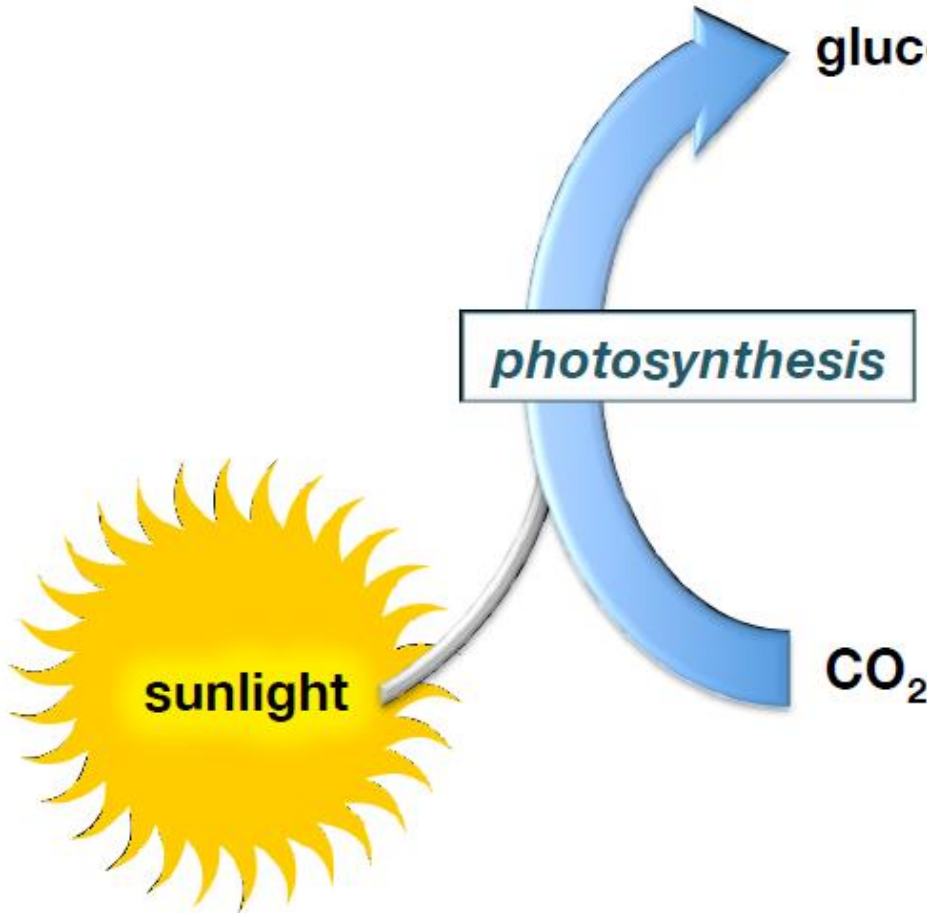
carbohydrates

- The name carbohydrates arose from the idea of compounds having empirical formula $C_n(H_2O)n$ meaning “hydrates of carbon”.
- now we know that there are carbohydrates such as amino sugars, thio sugars, deoxy sugars etc. which do not fit into the empirical formula Cn(H2O)n.
- **At present carbohydrates are defined as, polyhydroxy aldehydes or ketones.**

Carbohydrate metabolism

The energy that is contained in food can be traced back to the ***sun***.



In photosynthesis, energy from the sun's light does not vanish; it is converted to ***chemical potential energy*** within ***glucose***.

Uses of carbohydrates

- ❑Serving as an energy source for living organisms.

  e.g. glucose

- ❑Serving as energy reserves.

  e.g. starch, glycogen

- ❑As structural materials, which give strength to plants and certain animals.

  e.g. chitin, the exoskeleton of crustaceans (prawns, crabs and lobsters), cellulose and xylans in plants.

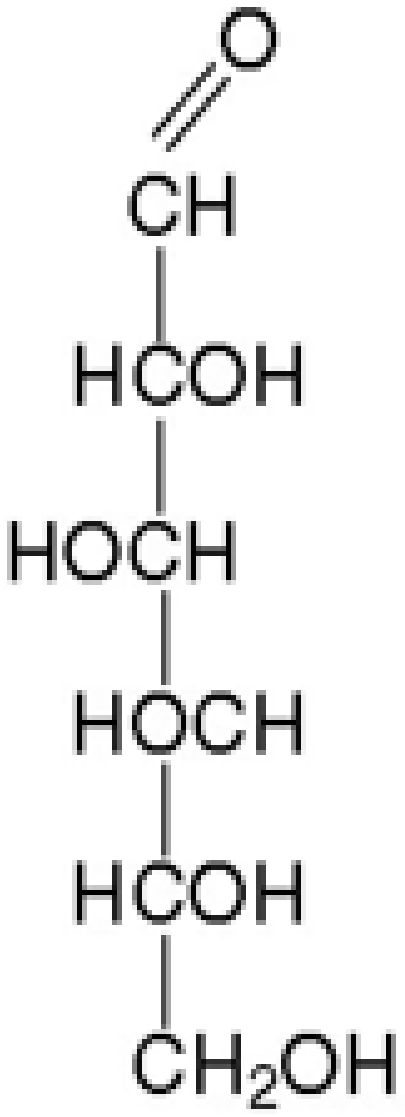
- ❑ Involvement in recognition mechanisms in biological systems.

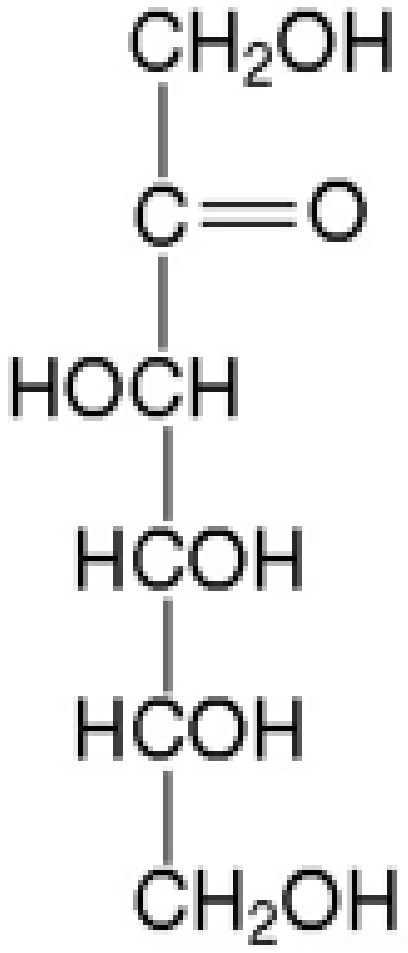
  e.g. (a) Capsular polysaccharides of many bacteria are antigenic and are used as protective vaccines against those micro- organisms (pneumococcal and meningococcal vaccines).

  (b) They act as elicitors (inducers) of phytoalexins in plants upon microbial infections.

Classifications of carbohydrates

- Names of all sugars end with “ose”.
- They are primarily classified as aldoses and ketoses.
- Aldoses consist of aldehyde functional group while ketoses consist of ketone functional group.





Classifications of carbohydrates

- Further they are classified according to the number of carbon atoms present.

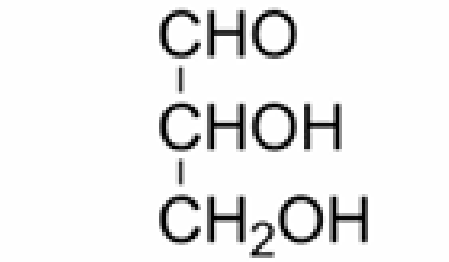
eg:carbohydrates consisting of 5 carbon atoms with aldehyde

functional group are classified as **aldopentoses**.

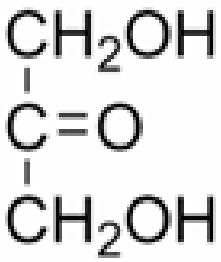
- Ketohexoses are the carbohydrates consisting of six carbons with ketone functional group.

Aldose and Ketose

- The first member of the aldose series is glyceraldehyde
- The first member of the ketose series is 1,3-dihydroxy acetone



glyceraldehyde

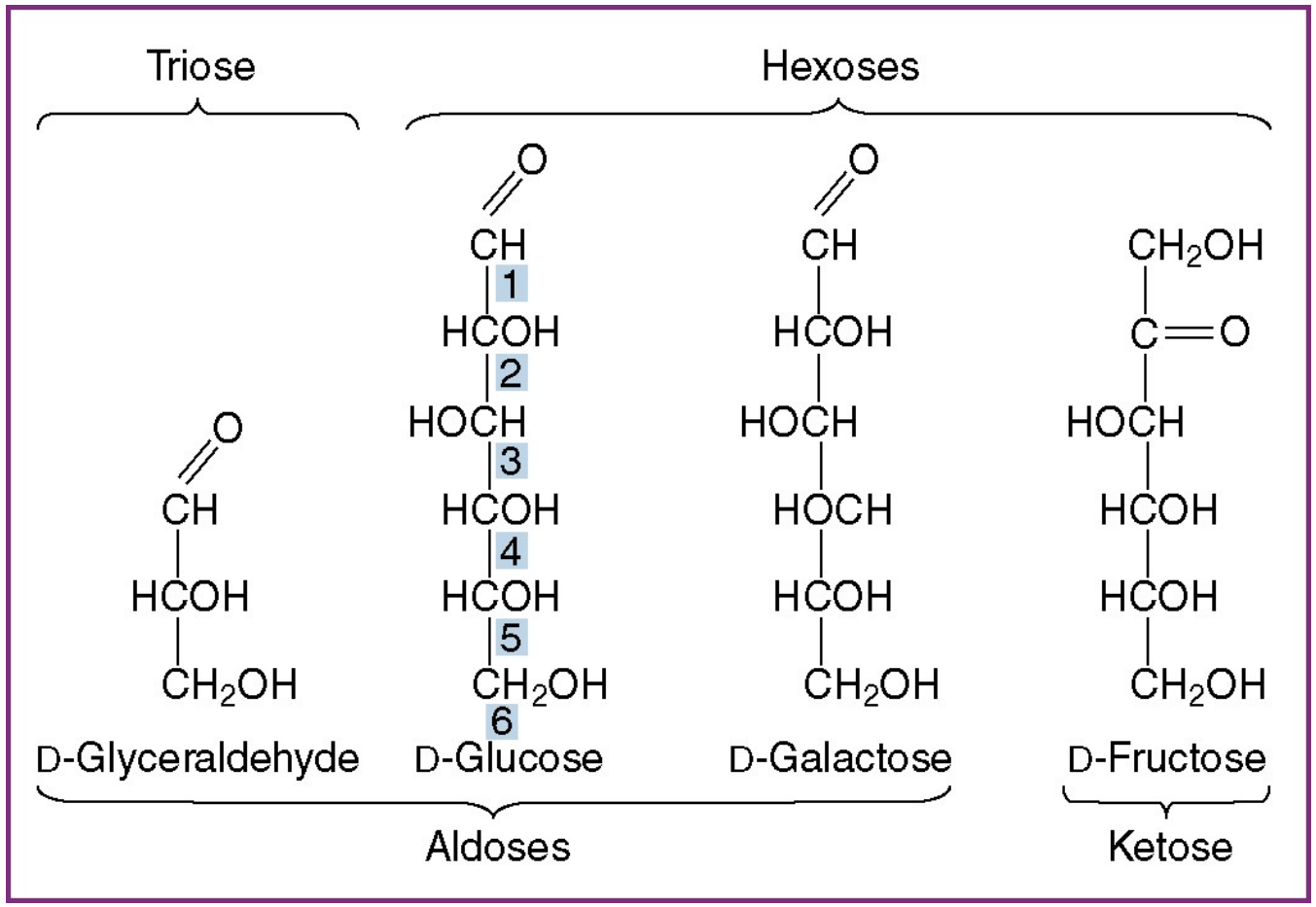


1,3-dihydroxyacetone

- Glyceraldehyde carry one stereocenter.
- 2^n stereoisomers are possible for compounds containing n number of stereocenters (chiral centres).
- Then glyceraldehyde exists in two stereoisomeric forms, D-glyceraldehyde and L-glyceraldehyde.

Classification of carbohydrates

- According to the Number of Carbons
- According to the functional group



Q: How would you classify a carbohydrate consisting of:
(a) four carbons with aldehyde group?
(b) five carbons with ketone group?
(c) six carbons with aldehyde group?

(a) aldotetrose
(b) ketopentose
(c) aldohexose

Classification of Carbohydrates

Units/Molecule	Classification
1	Monosaccharide
2	Disaccharide
3	Trisaccharide
3 – 10	Oligosaccharide*
> 10	Polysaccharide

Carbohydrates – polyhydroxyaldehydes or polyhydroxy-ketones of formula $(CH_2O)_n$, or compounds that can be hydrolyzed to them. (aka sugars or saccharides)

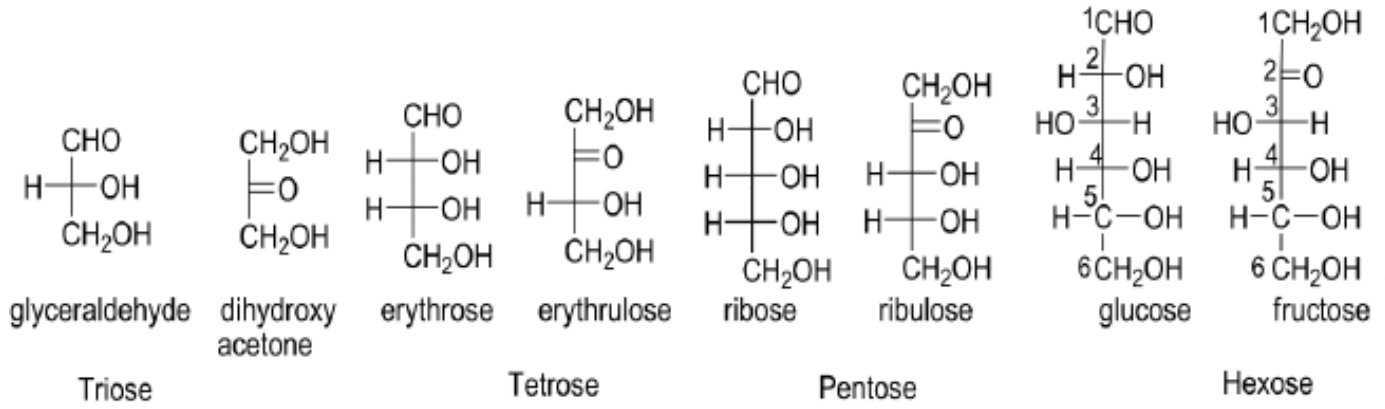
Monosaccharides – carbohydrates that cannot be hydrolyzed to simpler carbohydrates; eg. Glucose or fructose.

Disaccharides – carbohydrates that can be hydrolyzed into two monosaccharide units; eg. Sucrose, which is hydrolyzed into glucose and fructose.

Oligosaccharides – carbohydrates that can be hydrolyzed into a few monosaccharide units.

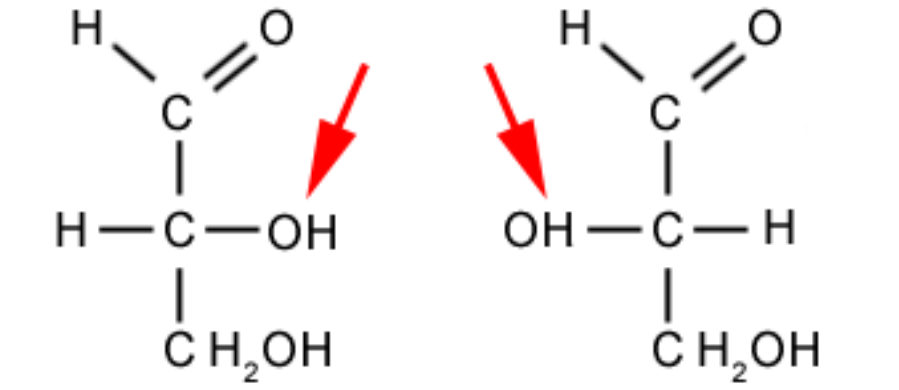
Polysaccharides – carbohydrates that are are polymeric sugars; eg Starch or cellulose.

Monosaccharides



- The monosaccharides include simple sugars and their derivatives.
- They are the basic carbohydrate units from which more complex compounds are formed.
- Monosaccharides consist of carbon atoms to which are attached hydrogen atoms, at least one hydroxyl group, and either an aldehyde (RCHO) or ketone (RCOR) group

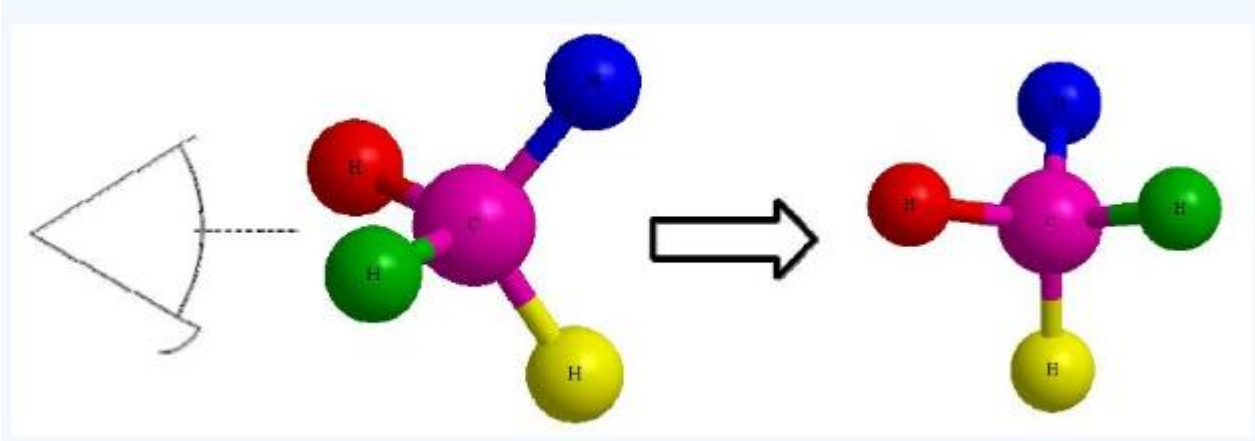
Glyceraldehyde



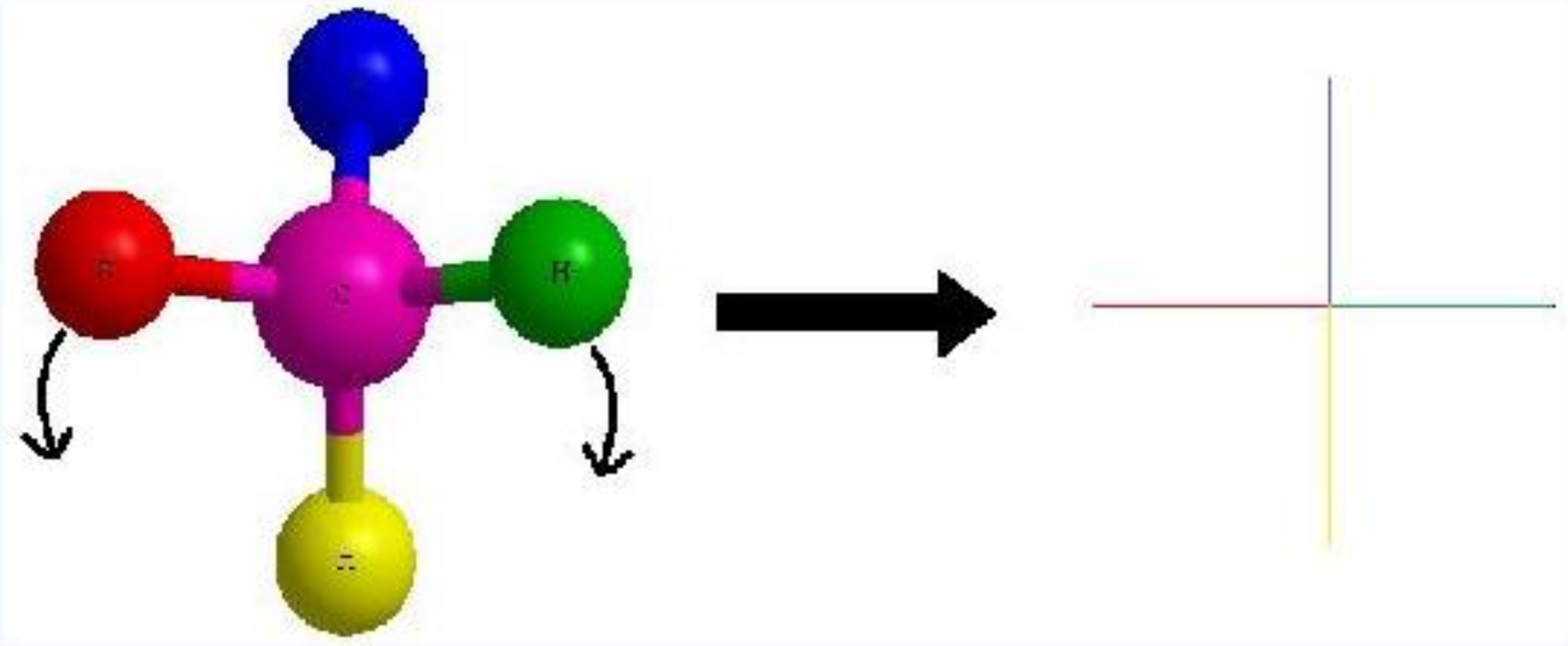
D-Glyceraldehyde L -Glyceraldehyde

- **Configuration of the chiral center with the highest number determines the L and D**
- No relation to optical rotation
- D- and L-is an old but still-convenient shorthand for saying that molecules are enantiomers.
- D-glucose and L-glucose are non-superimposable mirror images without having to write out a long IUPAC name with lots of (R) and (S) descriptors

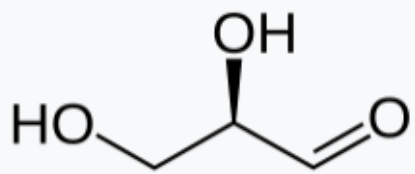
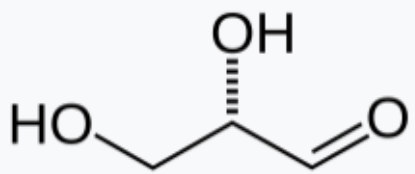
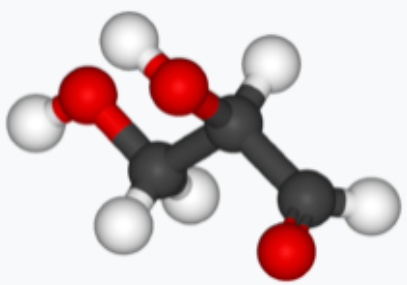
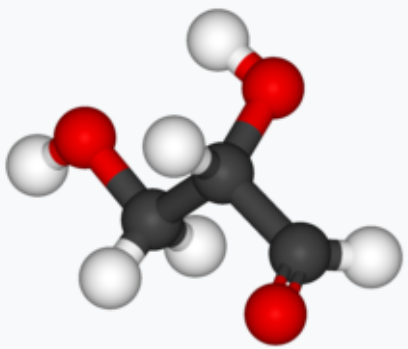
Fischer projection

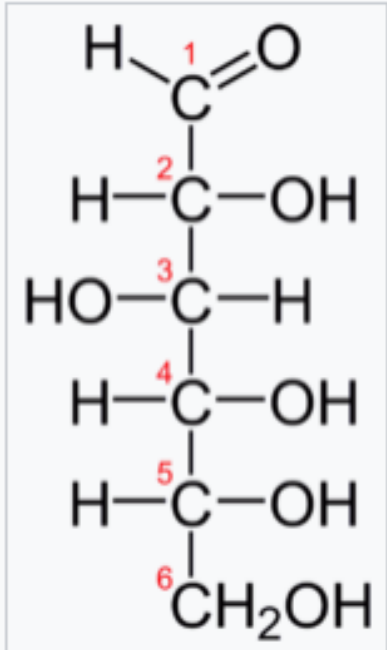


- Lets start with this 3D image and work our way to a dashed-wedged image.
- Start by imagining yourself looking directly at the central carbon from the left side.
- Now take this Figure and flatten it out on the surface of the paper and you should get an image of a cross.

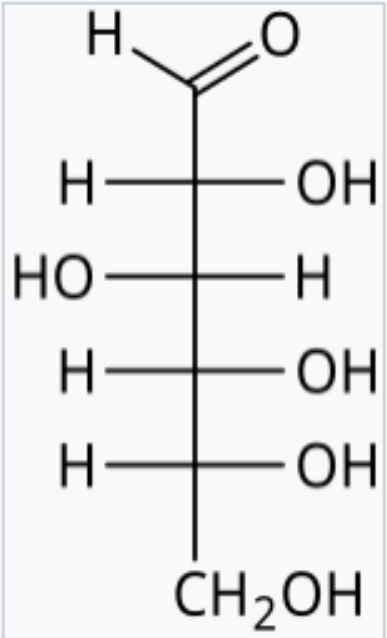


- the horizontal line represents atoms that are coming out of the paper and the vertical line represents atoms that are going into the paper.
- The cross image to the right of the arrow is a Fischer projection.

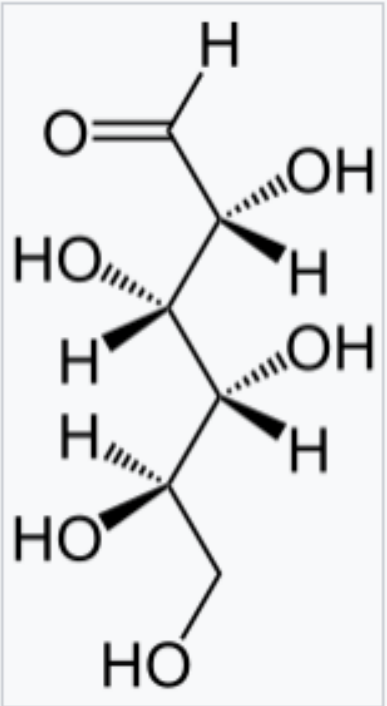
	D-glyceraldehyde (*R*)-glyceraldehyde (+)-glyceraldehyde	**L-glyceraldehyde** (*S*)-glyceraldehyde (−)-glyceraldehyde
Skeletal formula		
Ball-and-stick model		



Fischer projection with carbon atoms



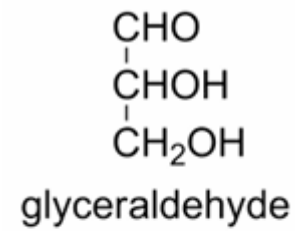
Fischer projection without carbon atoms



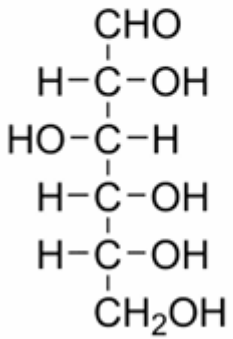
Natta projection

Three different projections of the same molecule (D-glucose)

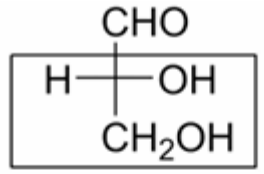
- Let us look at how we could designate D and L configurations to molecules containing more than one stereocenters.
- Draw the Fischer projection formula of the sugar as described.
- **The D and L configurations are designated by considering the stereochemistry of the highest numbered asymmetric carbon atom in the sugar chain (the bottom most asymmetric carbon atom).**



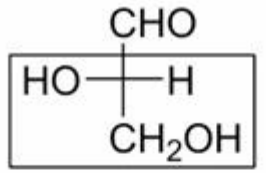
glyceraldehyde



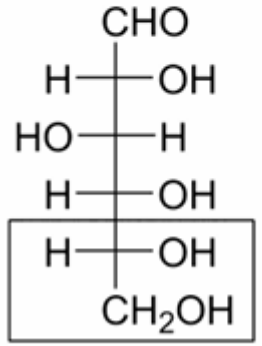
Glucose
(aldohexose)



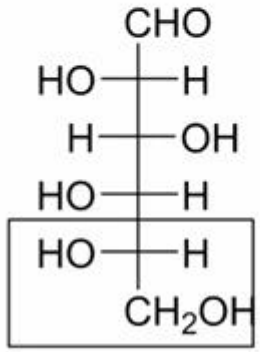
D-glyceraldehyde



L-glyceraldehyde



D-glucose

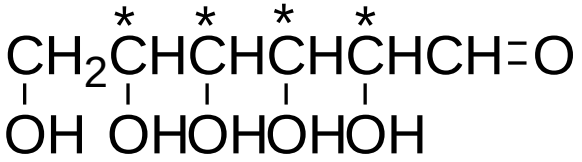


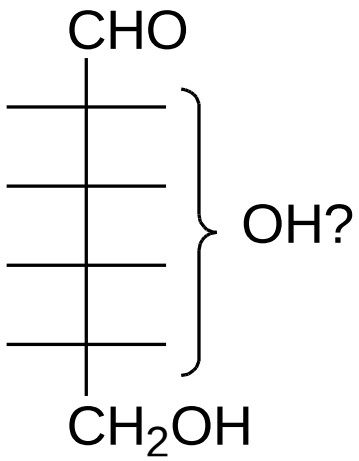
L-glucose

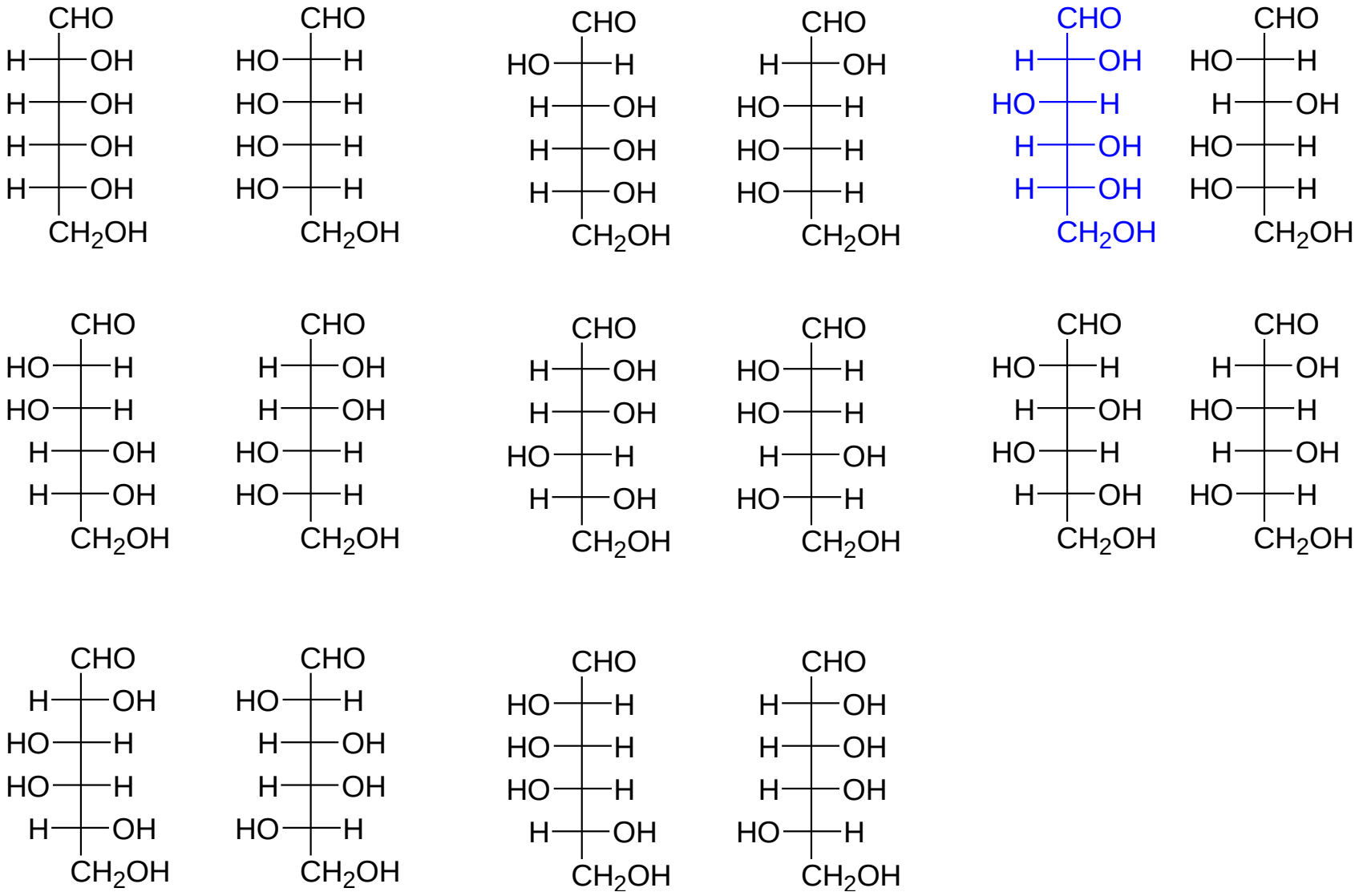
D and L has no relationship to the optical rotation usually denoted as (+) or (–)

Glucose - An aldohexose

Four chiral centers, $2^4 = 16$ stereoisomers



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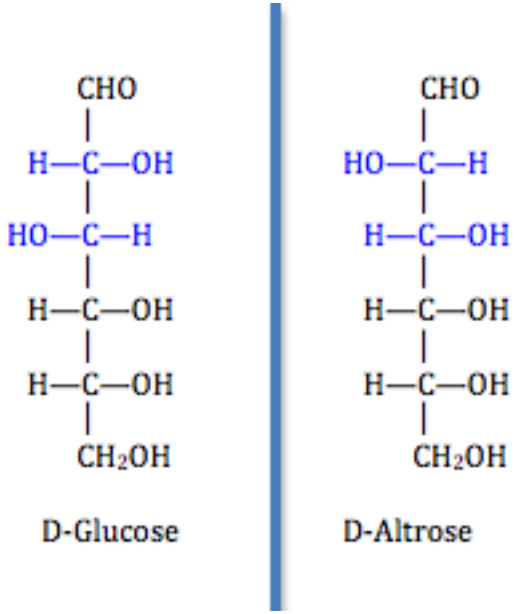
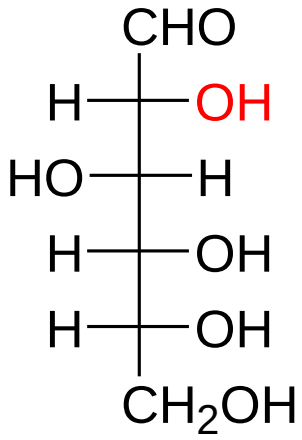
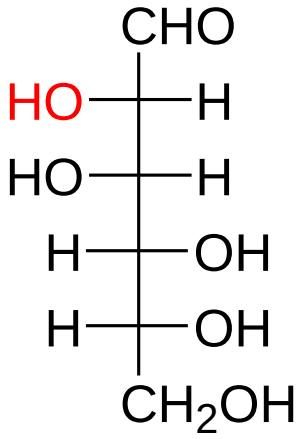
Diastereomers occurs when two or more stereoisomers of a compound have different configurations at one or more of the equivalent stereocenters and are not mirror images of each other.



Epimers – stereoisomers that differ only in configuration about one chiral center.

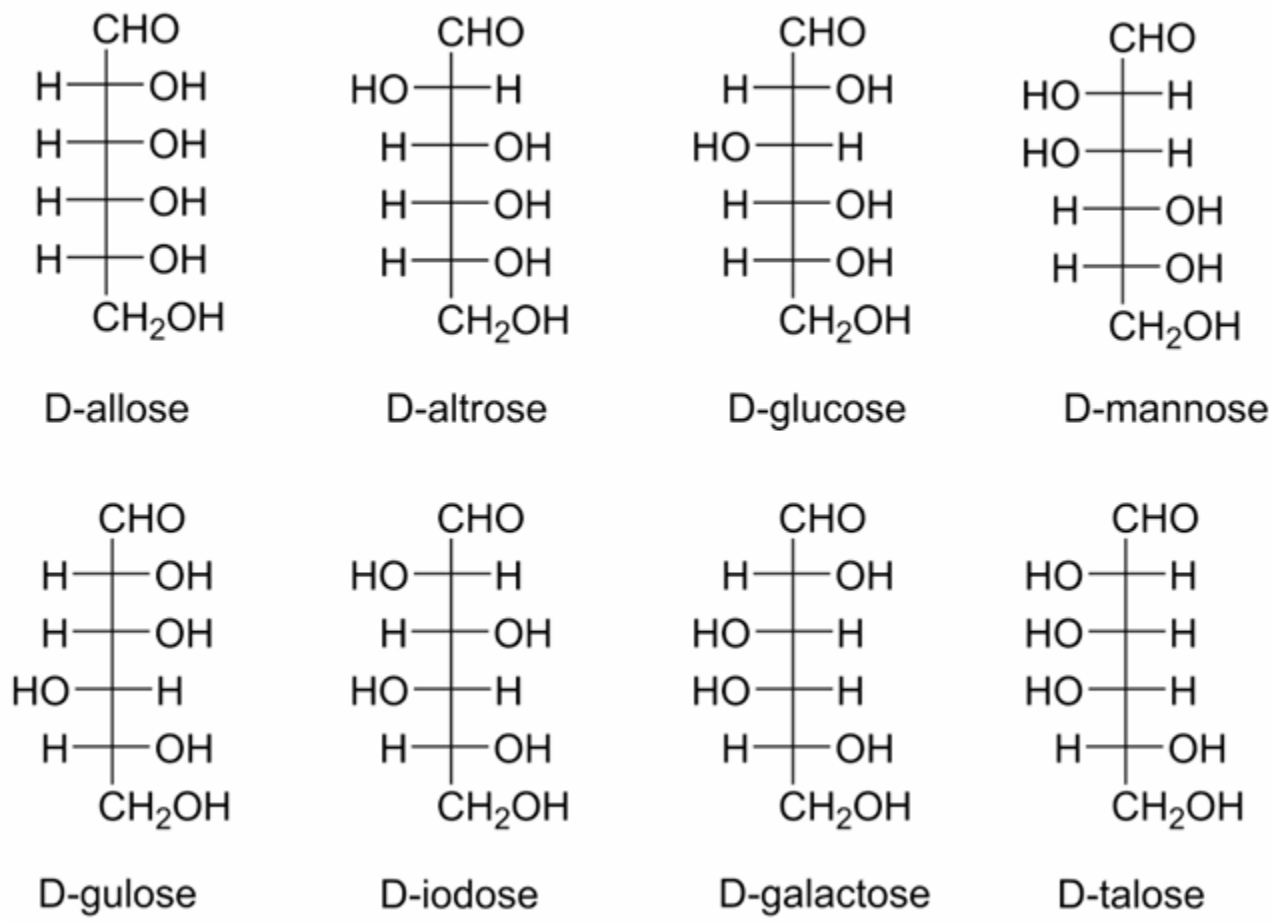


D-glucose



D-mannose

epimers



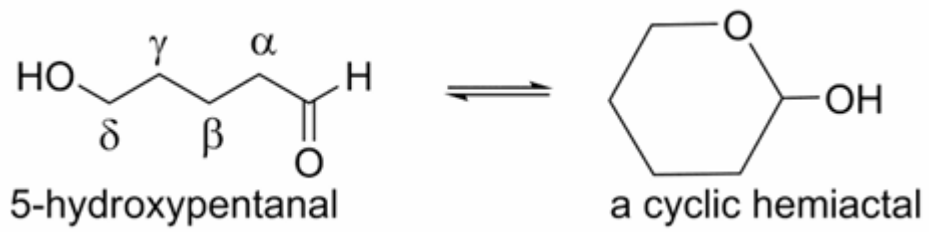
What is the C-3 epimer of glucose?

C-3: D-allose

Structural types of sugars

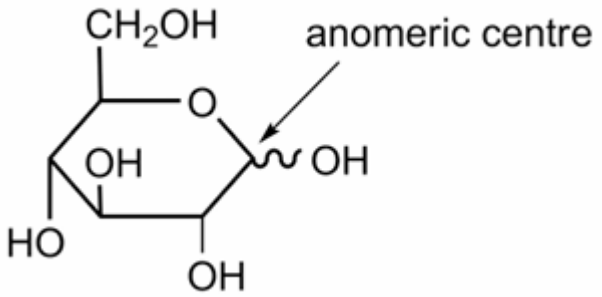
2. Ring structure

- Even though the straight chain form was proposed for sugars, in reality they do not behave as true aldehydes or ketones
- In aqueous solutions they are usually in ring forms
- cyclization of the straight chain creates two different ring sizes called “pyranose” and “furanose”.
- These names are derived from the six-membered oxygen heterocycle pyran and the five membered oxygen heterocycle furan, respectively.

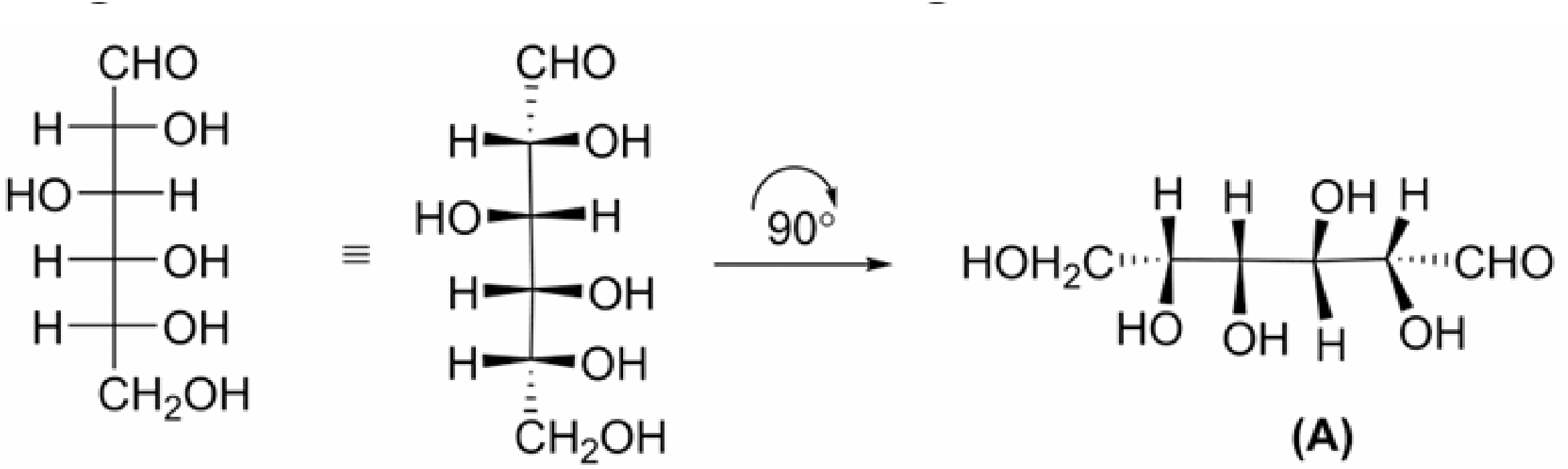


A hemiacetal is an **alcohol** and **ether** attached to the same carbon

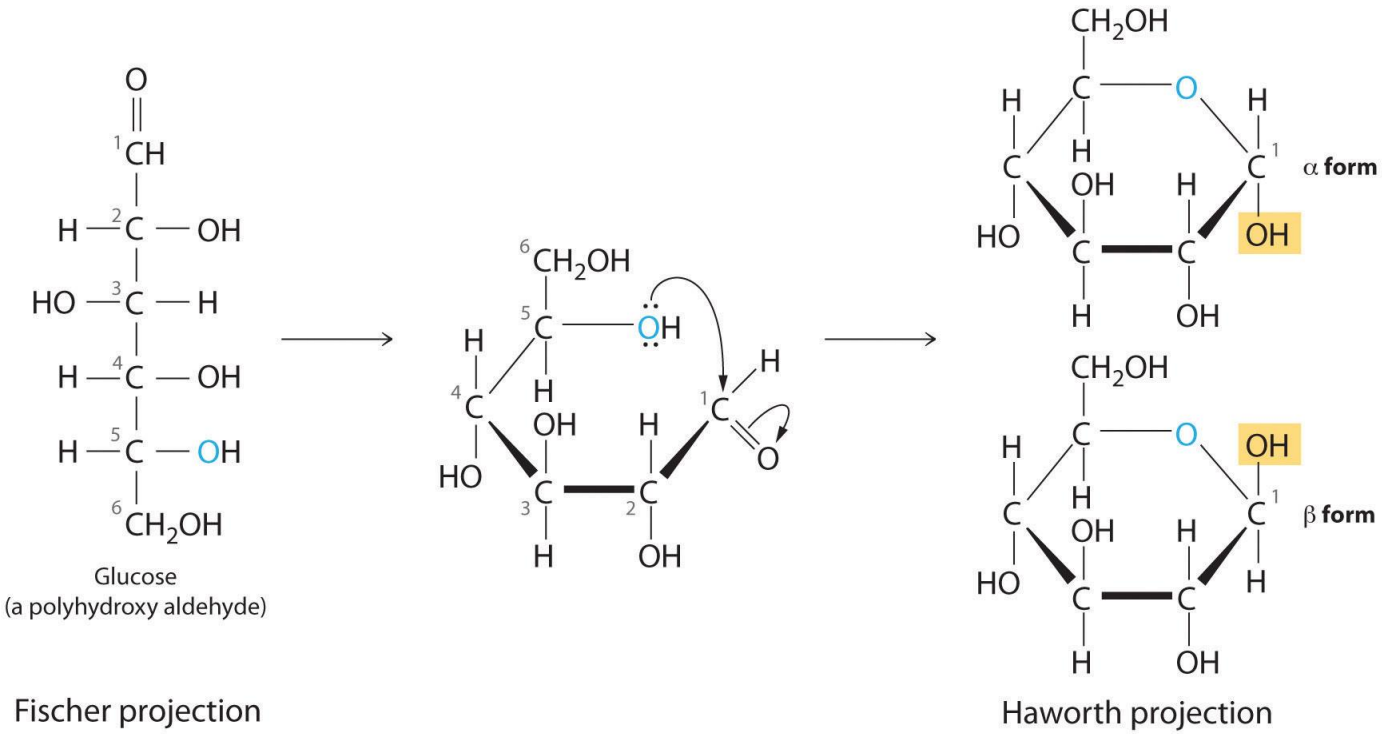
The formation of a cyclic hemiacetal creates a new chiral centre at the place where the aldehyde/keto function had been before, and it is called as the "**anomeric centre**".



Haworth projection



Haworth projection

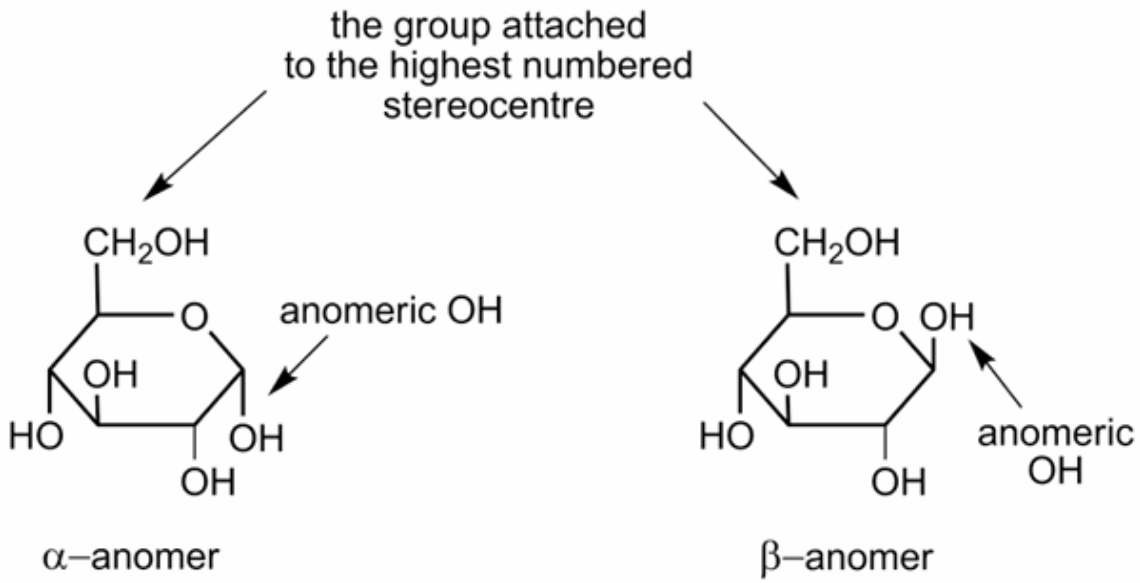


ANOMERIC CARBON ATOM

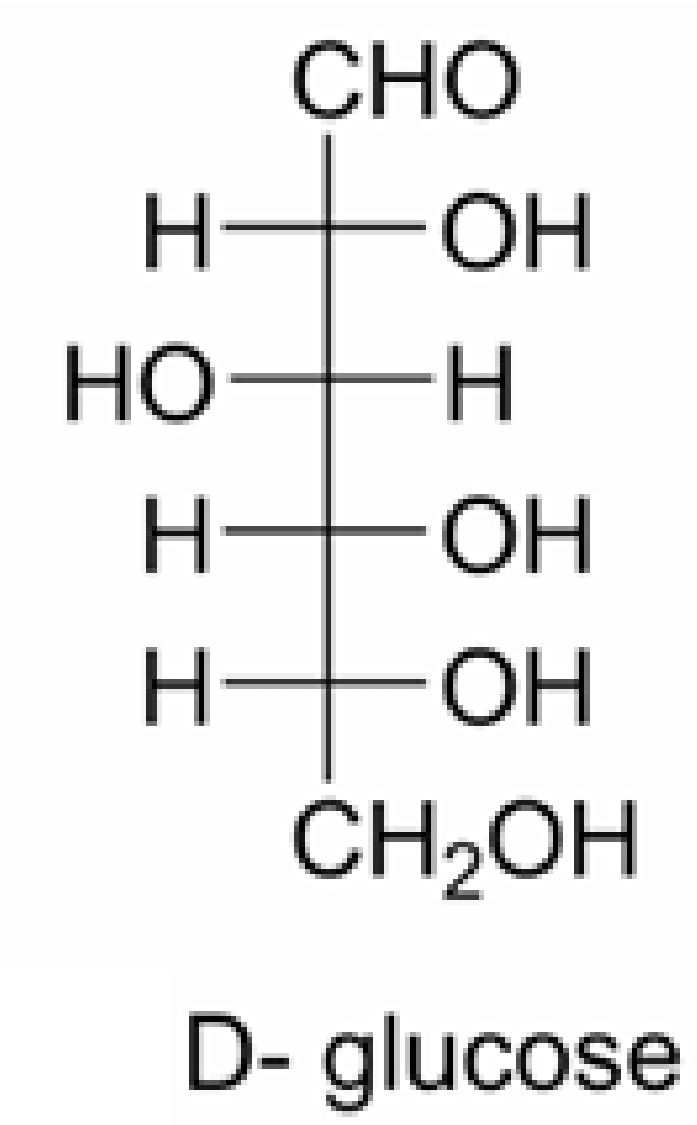
- The carbon atom which is part of the carbonyl group
- Alpha(α) and Beta(β) anomers differ from each other only in respect to configuration around anomeric carbon atom.

α–anomer and β–anomer

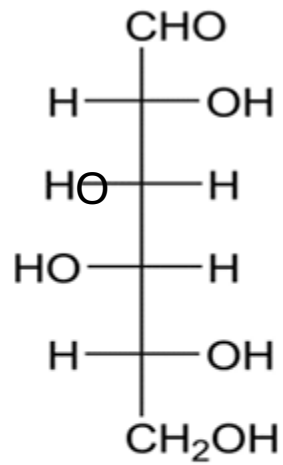
- If the oxygen substituent at the anomeric centre is trans (opposite sides) to the group attached to the highest numbered chiral carbon, the isomer is called the "α–anomer".
- If this arrangement of groups is cis (same side) the isomer is called the "β–anomer"



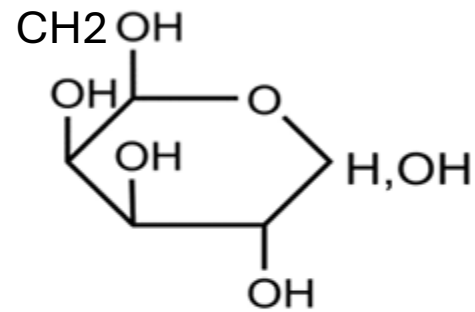
Draw the Fischer projection and Haworth formulae of the C−4 epimer of D−glucose.



D- glucose

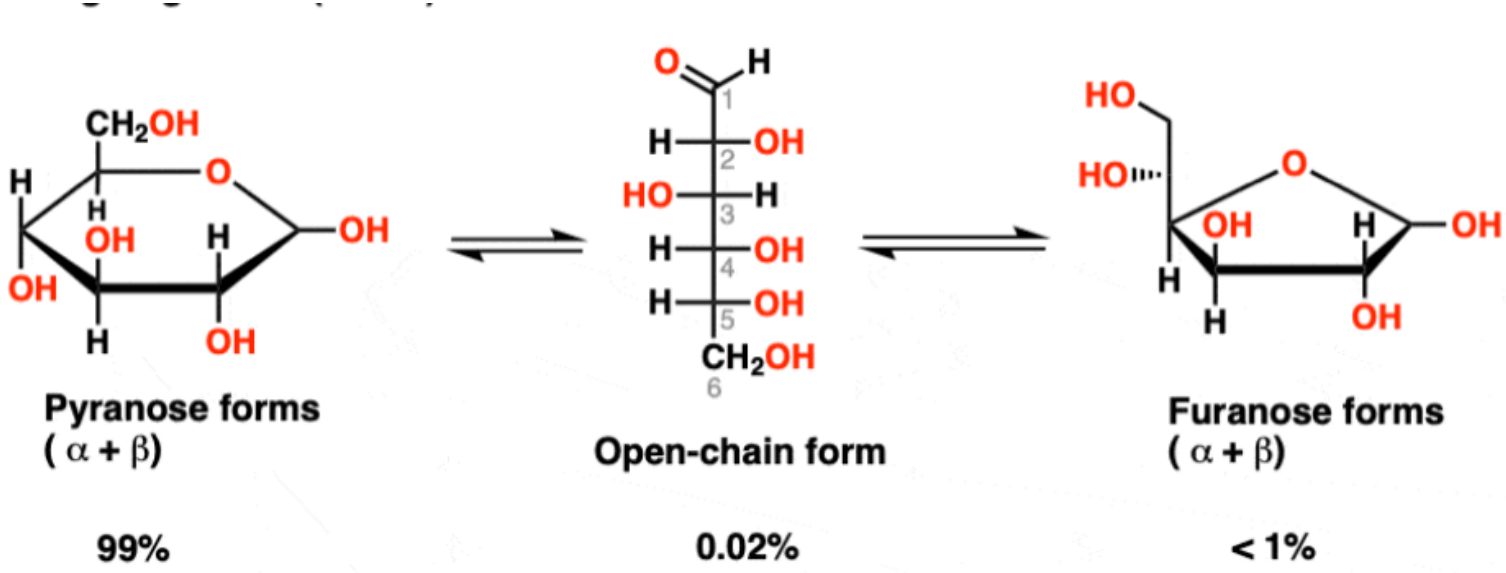


Fischer projection formula

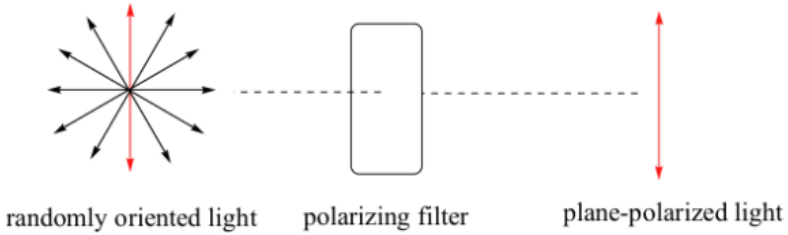


Harworth projection formula

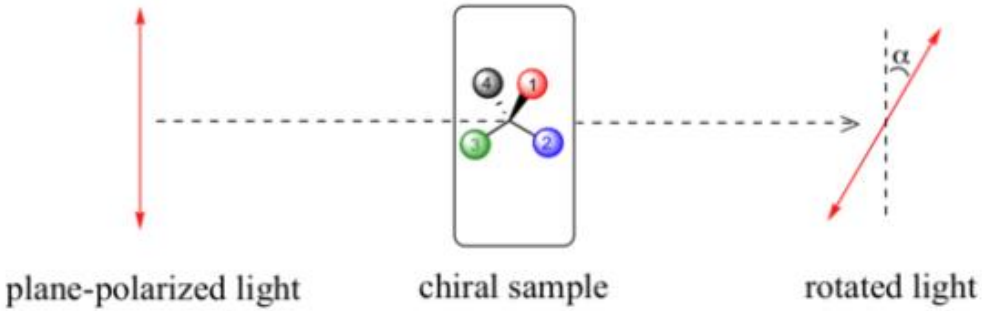
Furanose form of Glucose



Optical Activity of Sugars



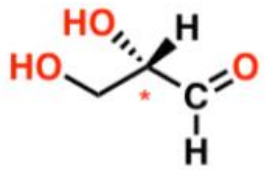
- Chiral molecules, have optical property
- A beam of plane-polarized light, when passed through a sample of a chiral compound, interacts with the compound in such a way that the angle of oscillation will rotate. This property is called optical activity.



- If a compound rotates plane polarized light in the clockwise (+) direction, it is said to be dextrorotatory, while if it rotates light in the counterclockwise (-) direction it is levorotatory.
- The magnitude of the observed optical activity is dependent on temperature, the wavelength of light used, solvent, concentration of the chiral sample, and the path length of the sample tube
- The **specific rotation** of a pure chiral compound at 25° is expressed by the expression:

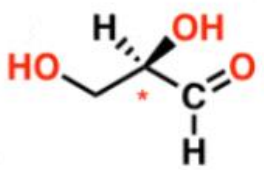
$$[\alpha]_{\mathrm{D}}^{25} = \frac{\alpha_{\mathrm{obs}}}{lc}$$

where α_{obs} is the observed rotation,
l is path length in decimeters
c is the concentration of the sample in grams per 100 mL



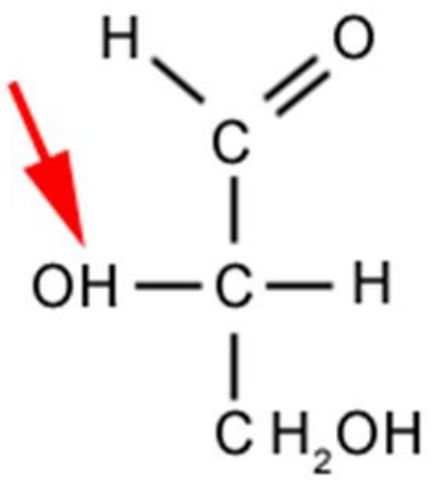
(S)-(–)-glyceraldehyde

$[\alpha]_D^{25}$ = –8.7° (c = 2, H_2O)

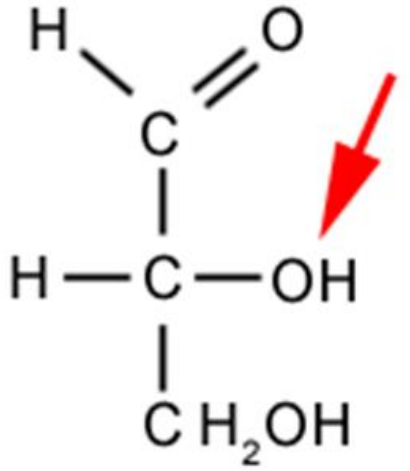


(R)-(+)-glyceraldehyde

$[\alpha]_D^{25}$ = +8.7° (c = 2, H_2O)

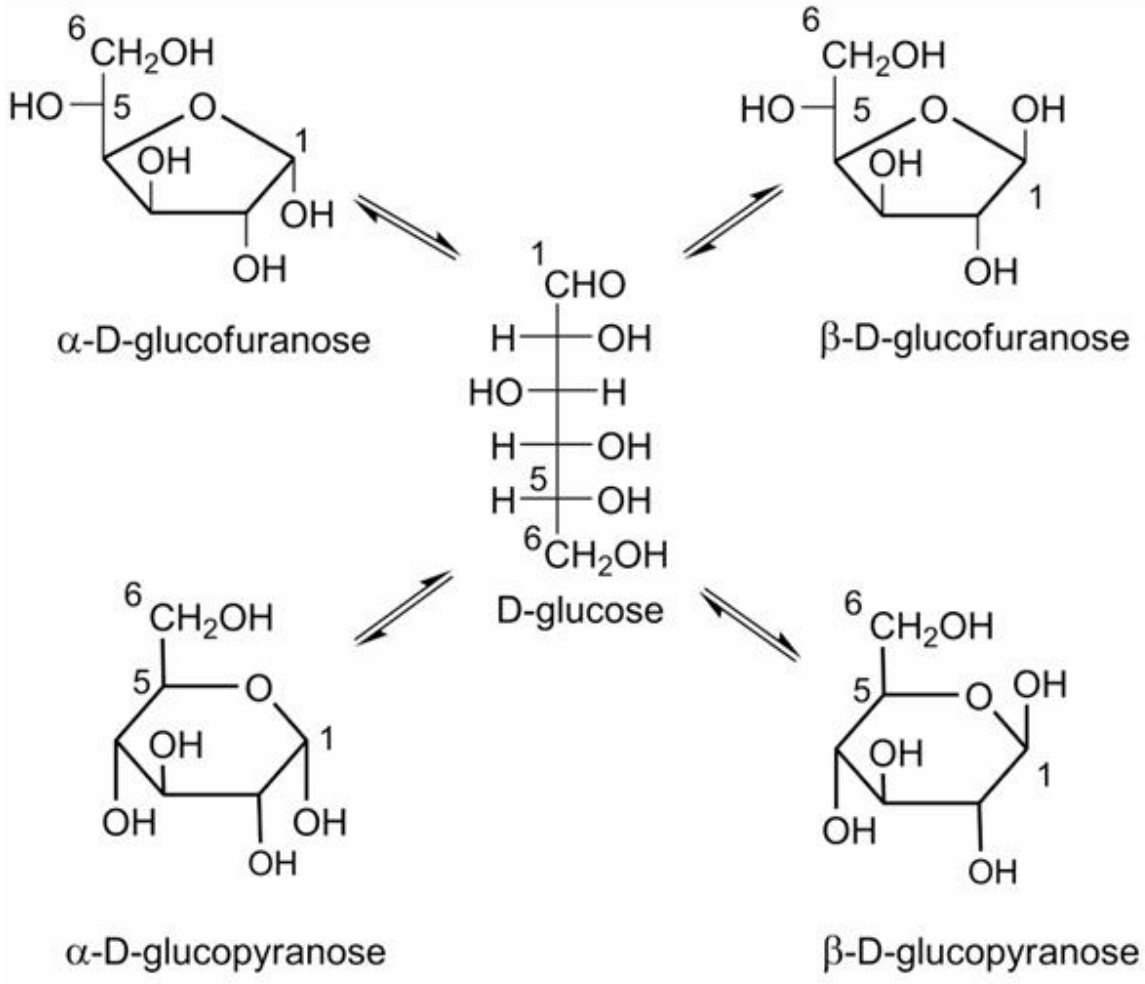


L -Glyceraldehyde



D-Glyceraldehyde

Possible pyranoses and furanoses of D-glucose



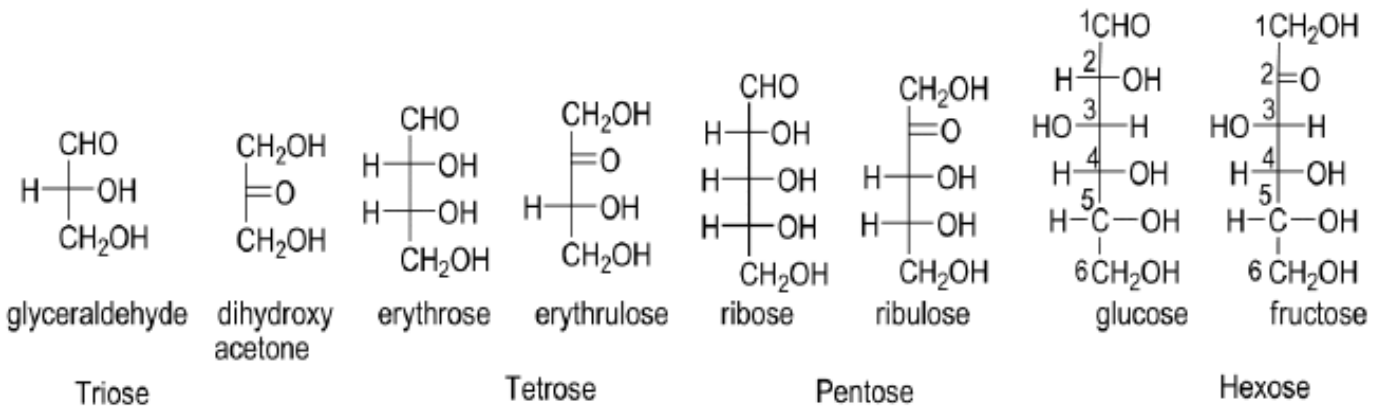
(i) pyranose: if the ring has six carbon atoms *e.g.* glucopyranose

(ii) furanose : if the ring has five carbon atoms *e.g.* fructofuranose

Classification according to the number of carbon atoms

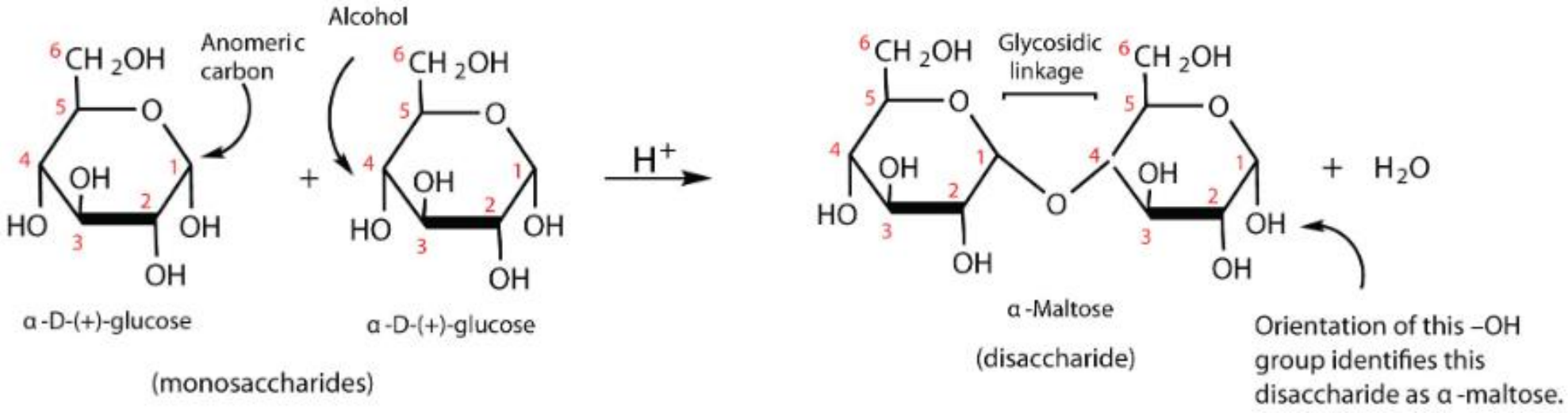
Monosaccharides are classified according to the number of carbon atoms in the chains

(i)	triose	-	3 carbon atoms
(ii)	tetrose	-	4 carbon atoms
(iii)	pentose	-	5 carbon atoms
(iv)	hexose	-	6 carbon atoms



Disaccharides

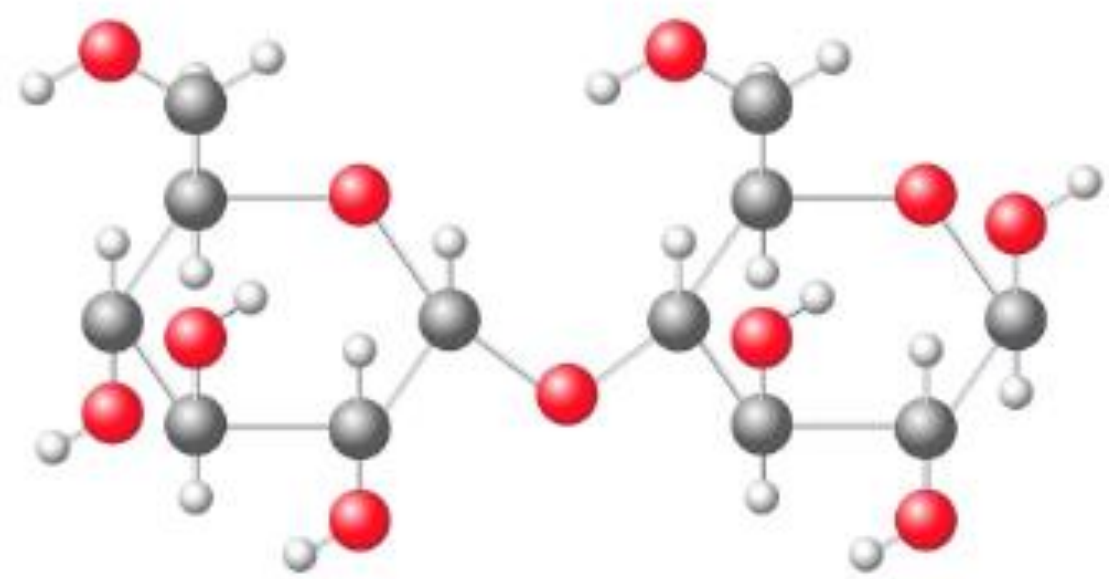
- A disaccharide is a double sugar formed when two monosaccharides are joined via dehydration synthesis.
- Disaccharides are sugars composed of two monosaccharide units that are joined by a carbon–oxygen-carbon linkage known as a **glycosidic linkage**.
- There are three common disaccharides: maltose, lactose, and sucrose

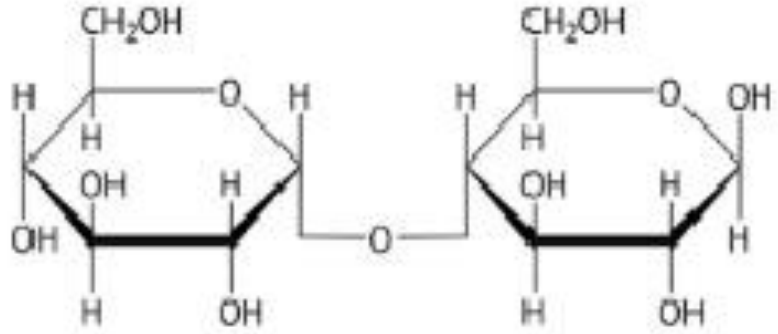


maltose

- The glucopyranose units in maltose are joined in a head-to-tail fashion through an α-linkage from the first carbon atom of one glucopyranose molecule to the fourth carbon atom of the second glucopyranose molecule

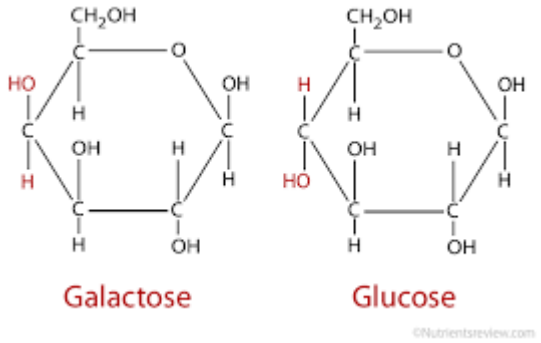
- an α-1,4-glycosidic linkage

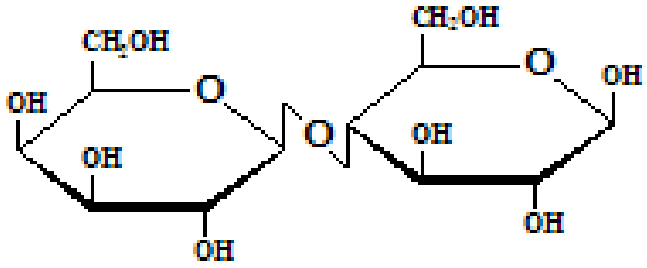




Lactose

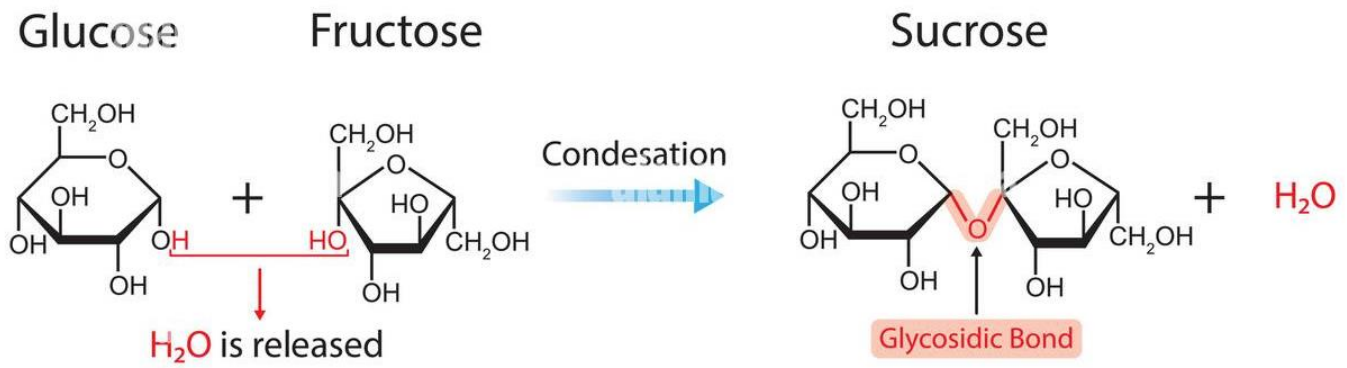
- Lactose is known as milk sugar because it occurs in the milk of humans, cows, and other mammals.
- Lactose is a disaccharide composed of one molecule of D-galactopyranose and one molecule of D-glucopyranose
- joined by a β-1,4-glycosidic bond





Sucrose

- largest-selling pure organic compound in the world,
- -1,β-2-glycosidic (head-to-head) linkage

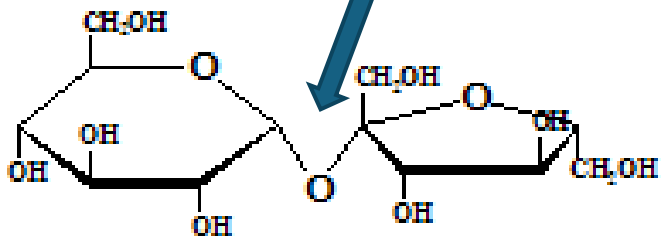


Disaccharides

Glycosidic linkage

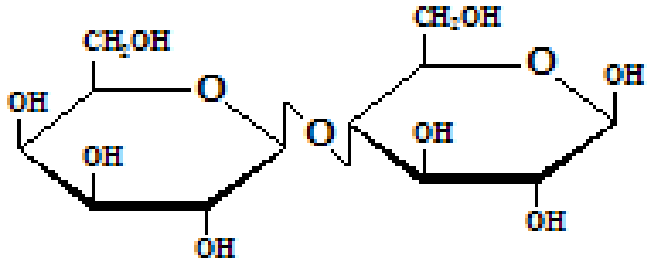
Sucrose

(Glucose-fructose)



Lactose

(Galactose-glucose)



Maltose

(Glucose-glucose)