



Carbohydrates

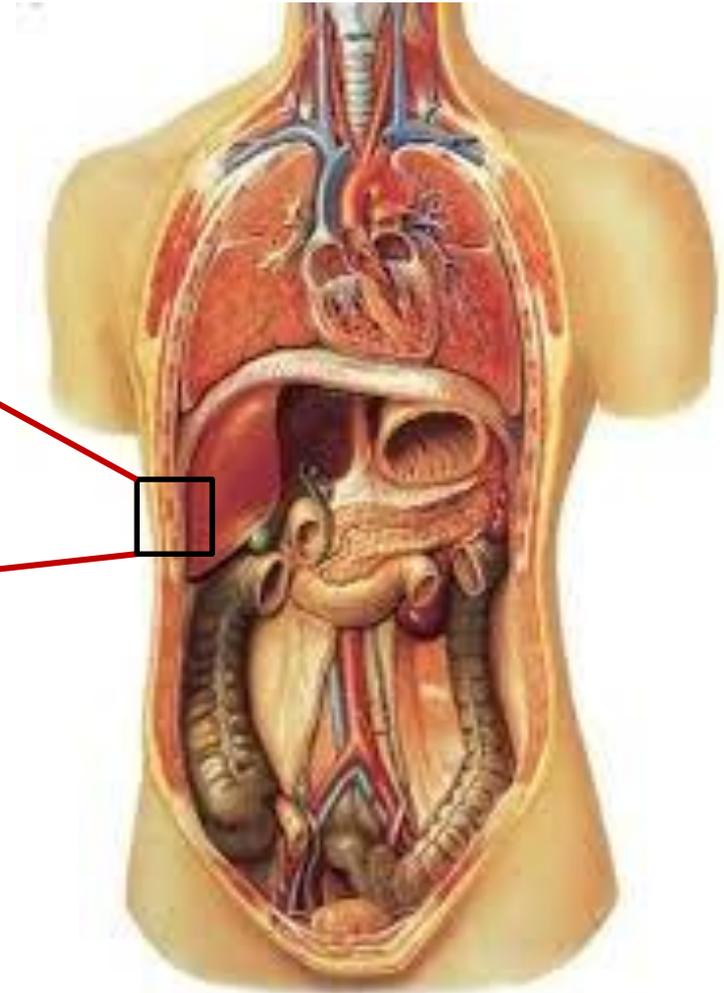
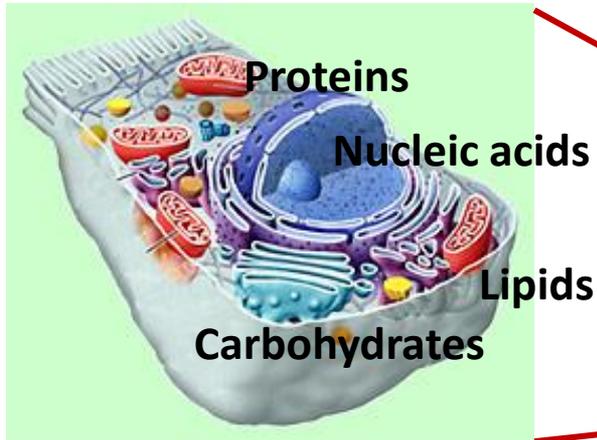


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Major Types of Macromolecules



Classification of Carbohydrates



- ❑ Carbohydrates are “Sugars” or “Saccharides” consist of the empirical formula $(CH_2O)_n$ where $n \geq 3$.
- ❑ Empirical formula, Molecular formula, Structural formula

Carbo**hydrates**

C

H2O

Classification of Carbohydrates

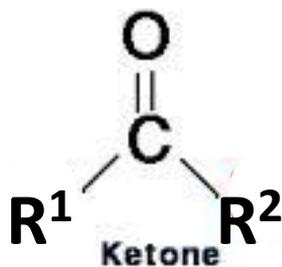
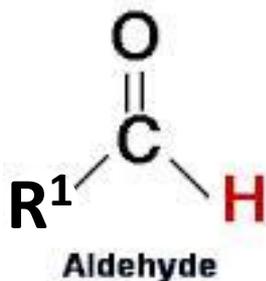
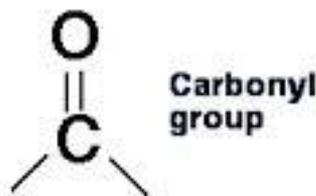


- ❑ Carbohydrates are “Sugars” or “Saccharides” consist of the empirical formula $(\text{CH}_2\text{O})_n$ where $n \geq 3$.
 - ❑ Monosaccharides: The basic units of CHO which cannot be hydrolyzed into smaller sugars like glucose, galactose and fructose
 - ❑ Disaccharides: contain two monosaccharides covalently linked by glycosidic bond like sucrose which consists of glucose and fructose
 - ❑ Polysaccharides: are polymeric molecules composed of long chains of monosaccharides linked together via glycosidic bonds like starch, cellulose and glycogen

Monosaccharides



- They are classified according to the number of carbon atoms: trioses, tetroses, pentoses, **hexoses**etc
- Also classified according to the chemical nature of the carbonyl group C=O either to Aldoses (the carbonyl group is an aldehyde) or Ketoses (the carbonyl group is a ketone)



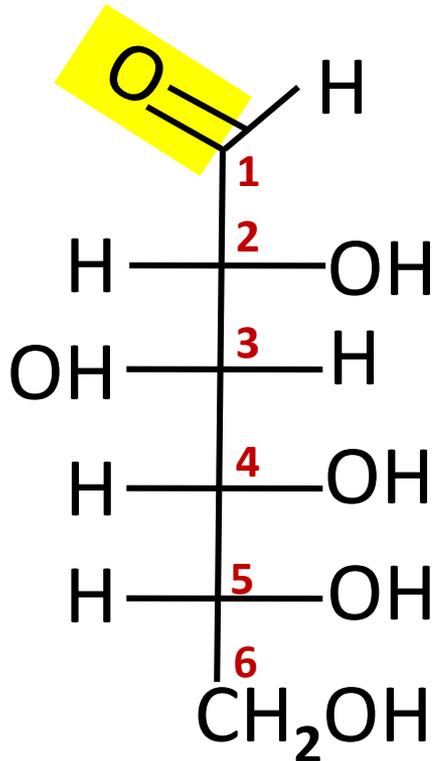
Aldehyde: $R^1 = \text{H}$, alkyl or aryl

Ketone: R^1 and $R^2 =$ alkyl or aryl

Monosaccharides



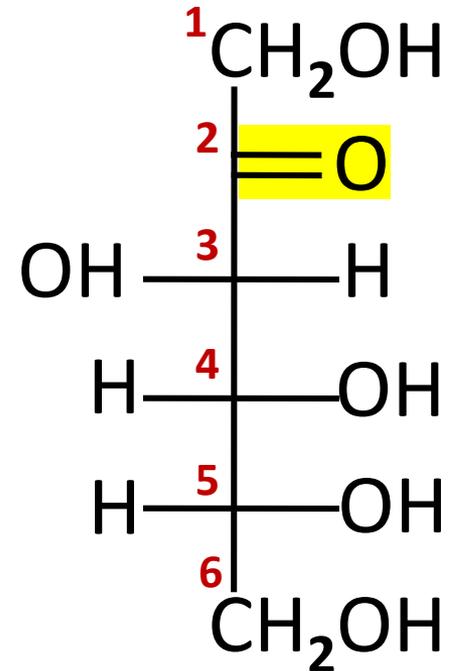
Hexoaldehyde \ Aldohexose



“grape or blood sugar”

Fischer projections

Hexoketose \ Ketohexose



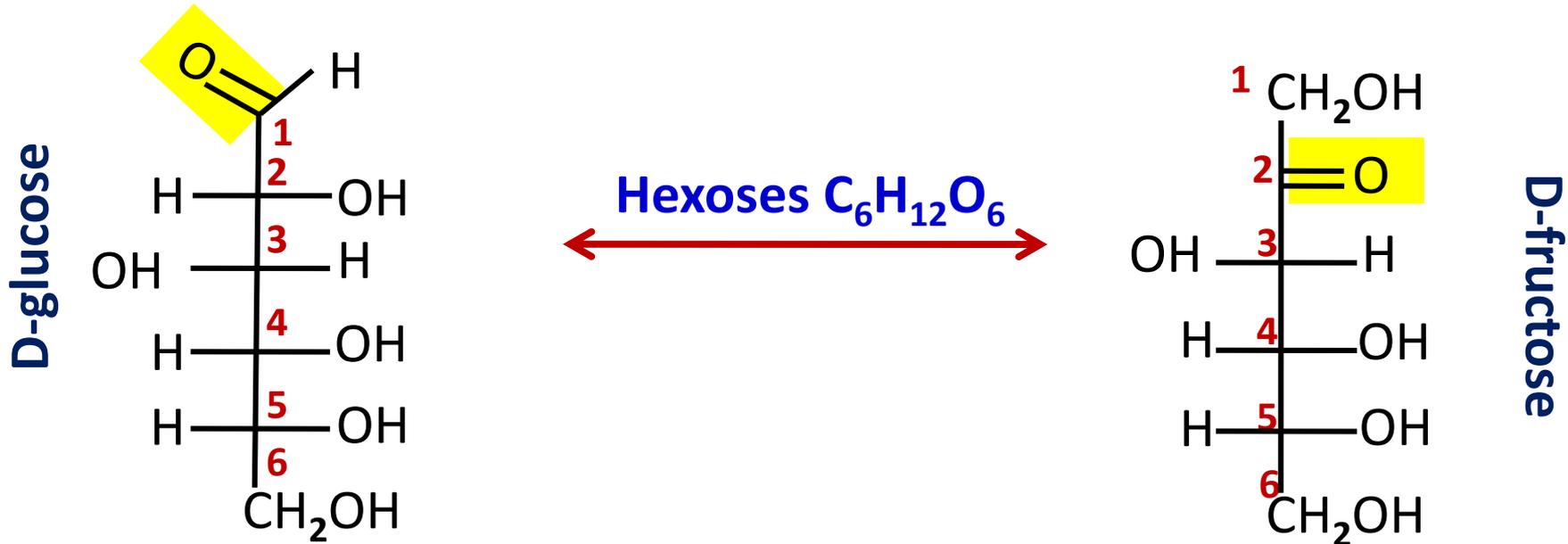
“fruit sugar”

Isomerization



□ Isomers: are molecules with same molecular formula but different chemical structures

1. Constitutional (structural) isomers: atoms and functional groups bind together in different ways (e.g. glucose and fructose)



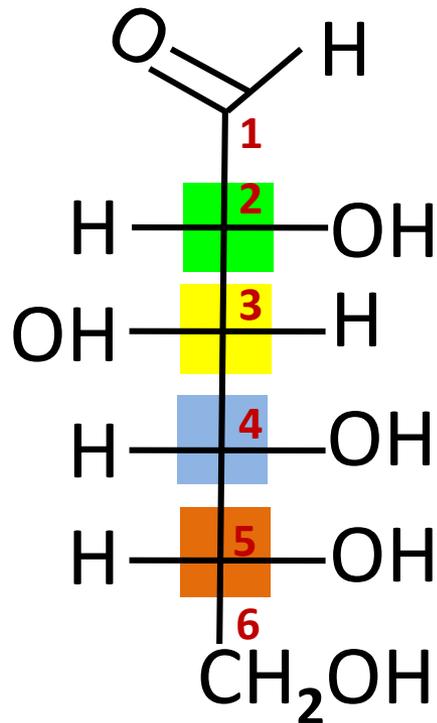
Isomerization



□ Isomers: are molecules with same molecular formula but different chemical structures

1. Constitutional (structural) isomers: atoms and functional groups bind together in different ways (e.g. glucose and fructose)
2. Stereoisomers (spatial isomers): differ in the configuration of atoms in space rather than the order of atomic connectivity
 - Chiral carbon: asymmetric carbon atom attached to 4 different groups of atoms
 - The number of stereoisomers for any given molecules = 2^n where n represents the number of chiral centers

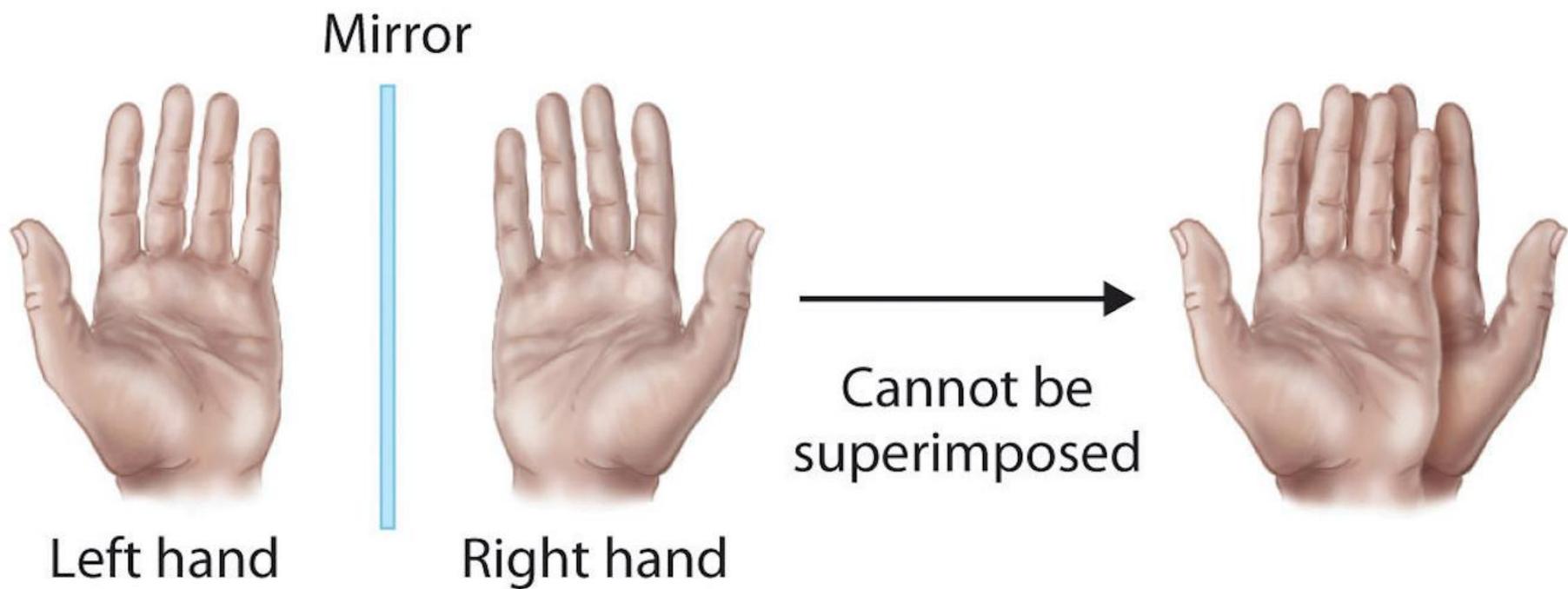
Isomerization



D-glucose

Number of stereoisomers = 2^4
= 16

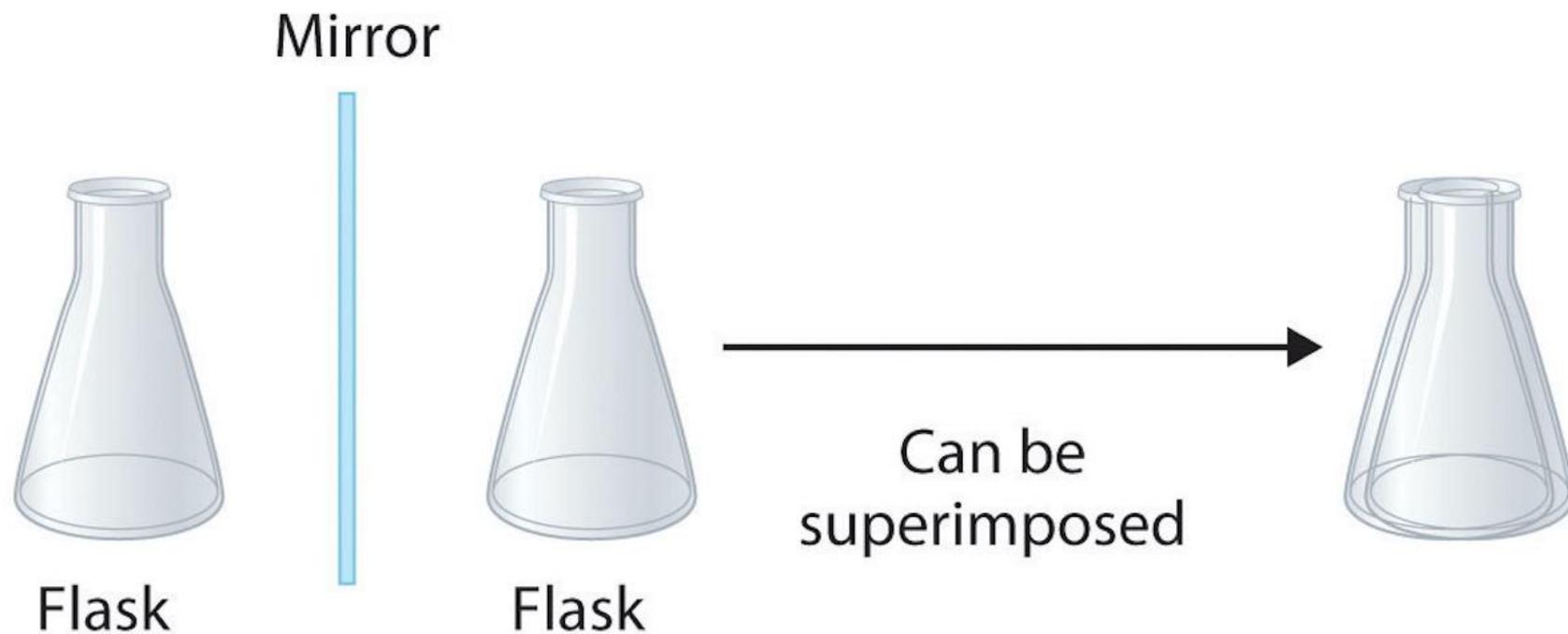
Chirality & Chiral Object



(a) Chiral objects



Chirality & Chiral Object



(b) Achiral objects

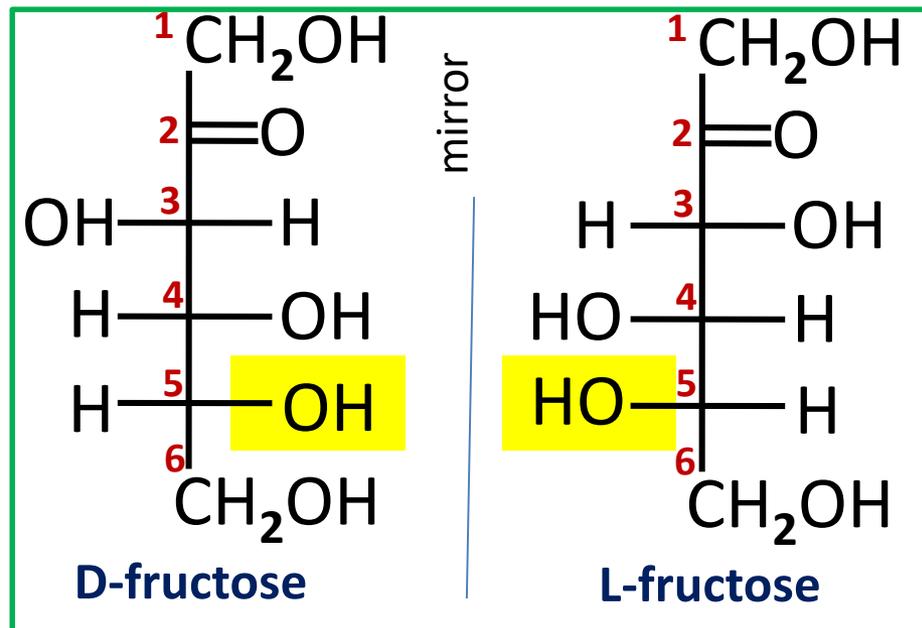
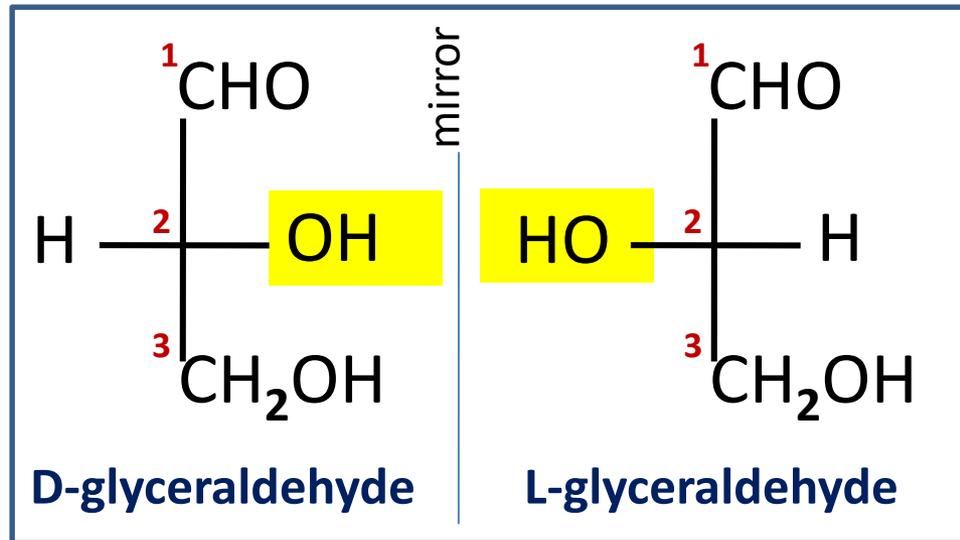
- Chiral molecules should contain at least one chiral center (**usually a carbon atom**)

Stereoisomers

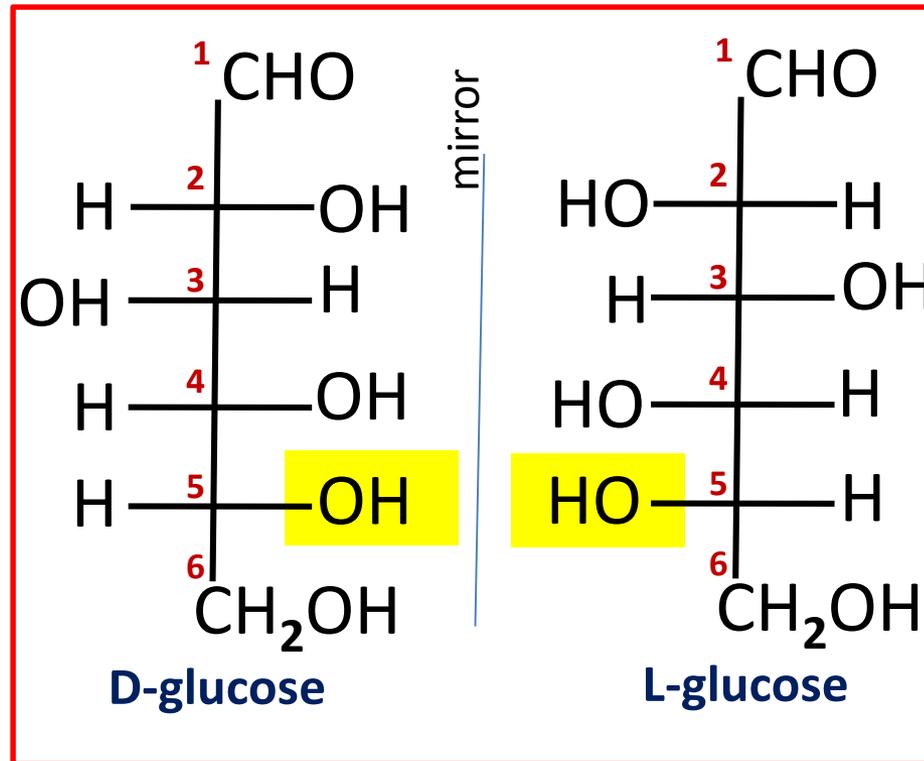


- ❑ Enantiomers: are two stereoisomers that are mirror images to each other but not superimposable

D/L Monosaccharides



D/L Monosaccharides



Isomerization

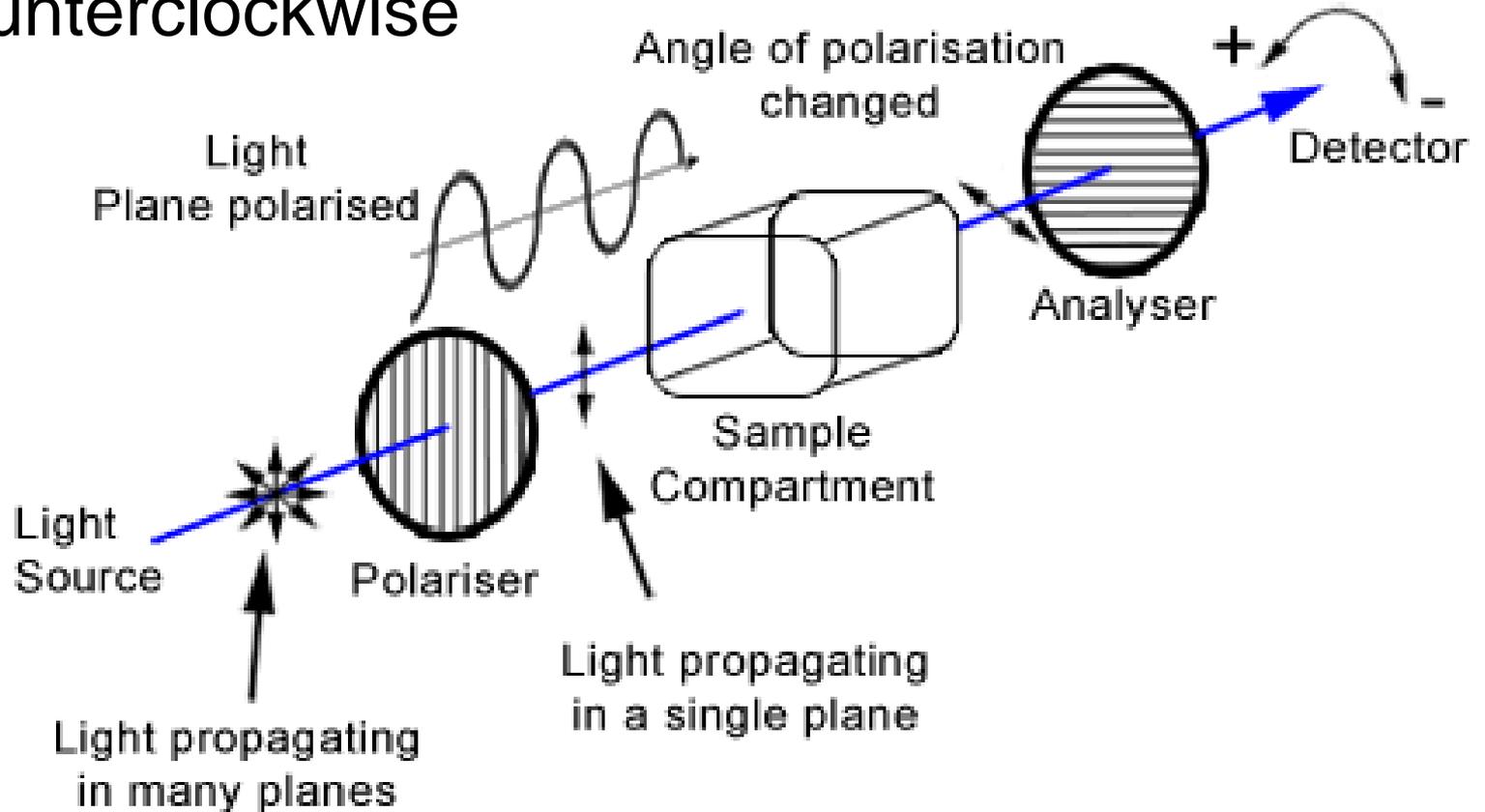


- ❑ Enantiomers: are two stereoisomers that are mirror images to each other but not superimposable
- ❑ **D-** (dexter)/**L-** (laevus) Nomenclature system: commonly used to assign the configurations in sugars and amino acids
 - As a rule of thumb: if the farthest chiral atom from the highest oxidized carbon (i.e. carbonyl group) has -OH group on the right-hand side, the configuration is assigned as **D** but If it is on the left-hand side, the sugar is designated as **L**
- ❑ Most naturally occurring sugars are D-isomers (biologically active form)

Monosaccharides



- Enantiomers are optically active and can rotate the polarized light plane either clockwise or counterclockwise

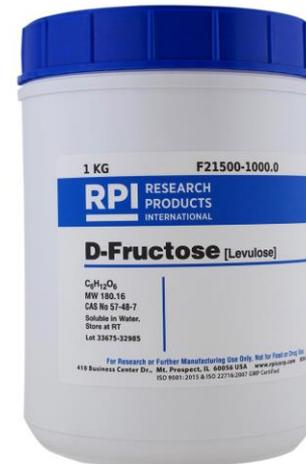


Monosaccharides



- Enantiomers are optically active and can rotate the polarized light plane either clockwise or counterclockwise
 - (+)/(-) nomenclature system: if one enantiomer rotates the light clockwise, it is labeled (+) or (*d*) (dextrorotatory). The second mirror image enantiomer is labeled (-) or (*l*) laevorotatory [(+)D-glucose, (*d*)D-glucose]
 - by chance, it was found that D-glyceraldehyde is in fact the dextrorotatory isomer.
 - D/L system should not be confused with +/- or *d/l* system. For example, D-fructose (laevulose) is levorotatory whereas D-glucose (dextrose) is dextrorotatory.

Monosaccharides

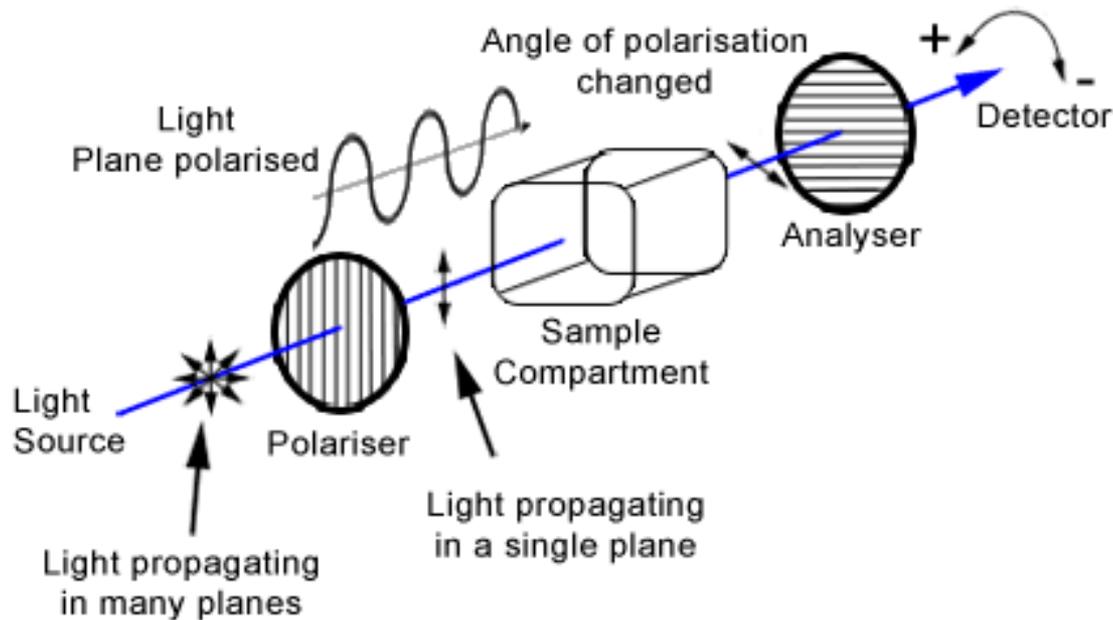


- **Dextrose** is the commercial/trade name of **D-glucose**
- **Laevulose** is the the commercial name of **D-fructose**

Monosaccharides



- Enantiomers are optically active and can rotate the polarized light plane either clockwise or counterclockwise

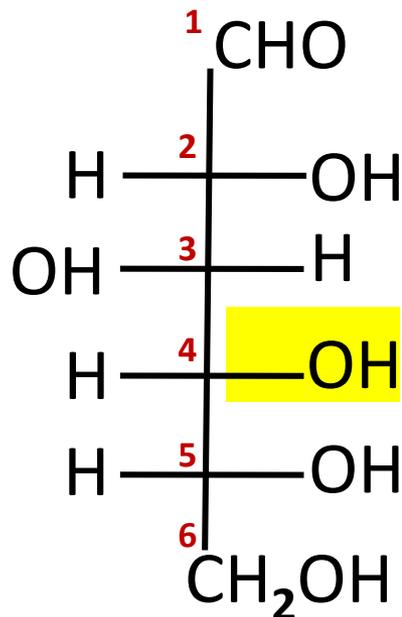


- **Racemic mixture** contains equal amounts of each enantiomer (net rotation is zero)

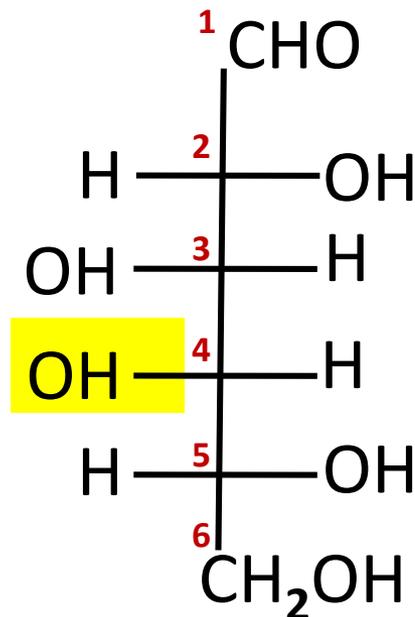
Monosaccharides



- Epimers: are stereoisomers that differ in the configurations of atoms at **only** one chiral center (i.e. chiral carbon in CHO). They are not mirror image isomers.

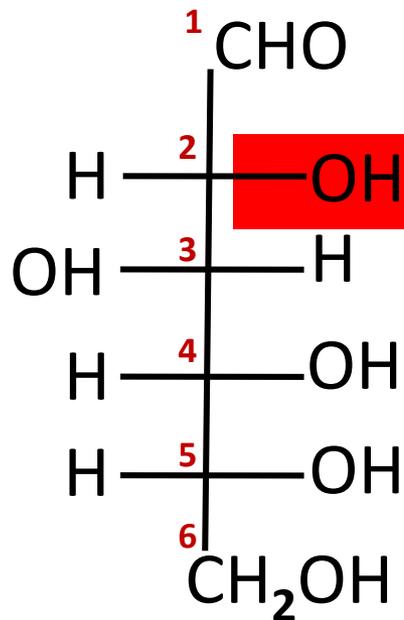


D-glucose

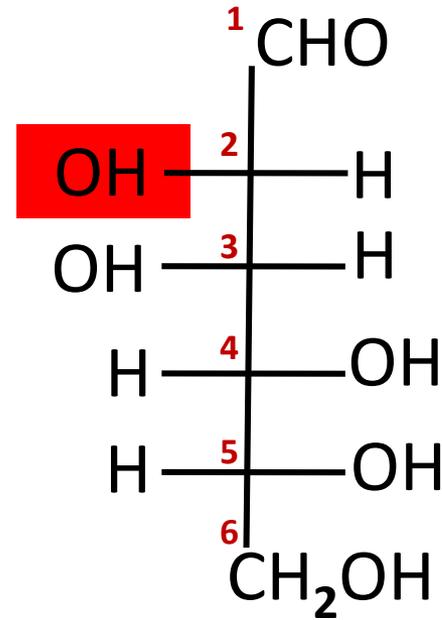


D-galactose

Monosaccharides



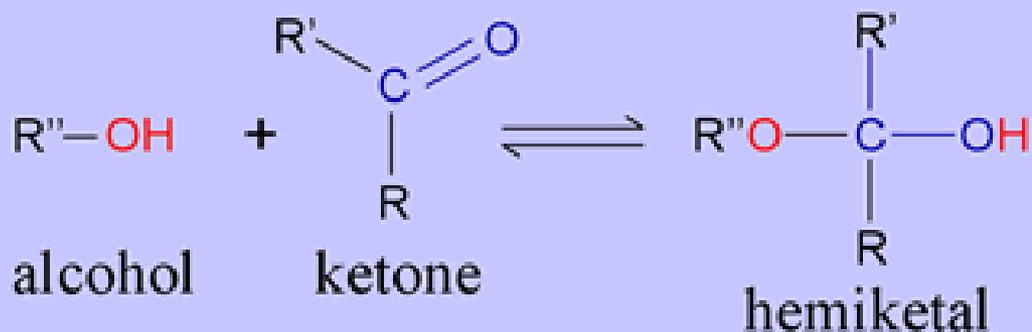
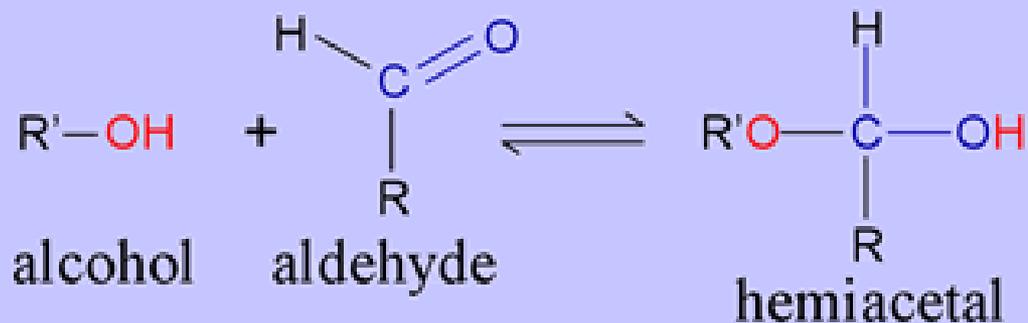
D-glucose



D-mannose

- Glucose and galactose are C4 epimers while glucose and mannose are C2 epimers

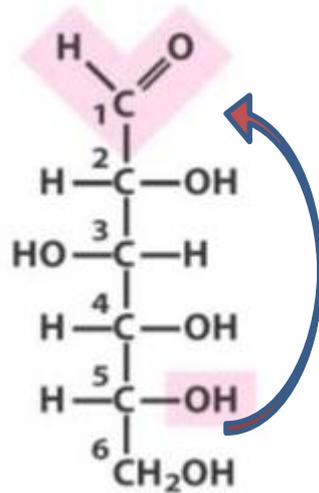
Hemiacetal & Hemiketal



Monosaccharide cyclization

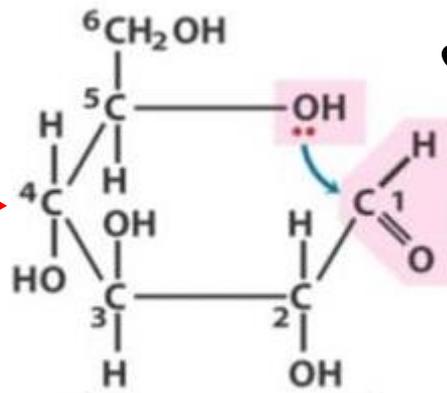


Linear form



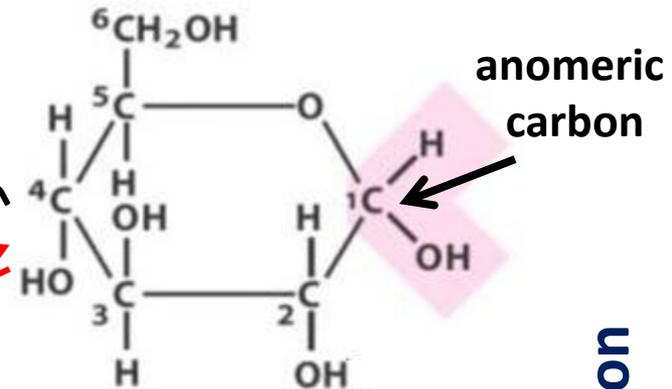
D-glucose

Fisher projection

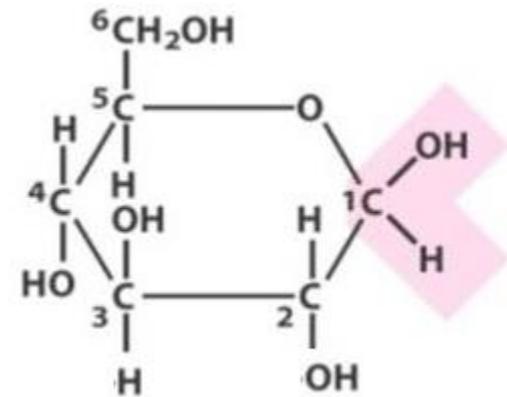


cyclization

cyclization



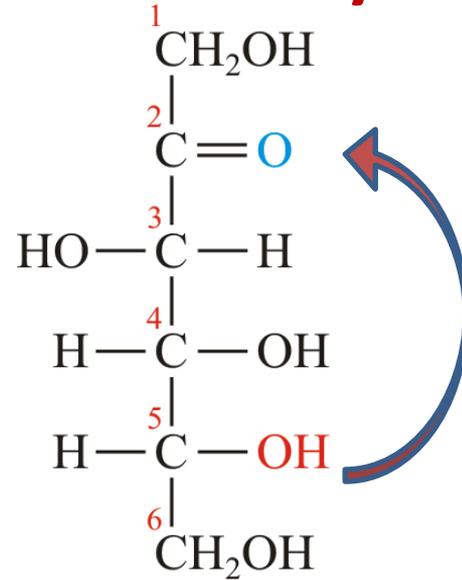
α -D-glucose



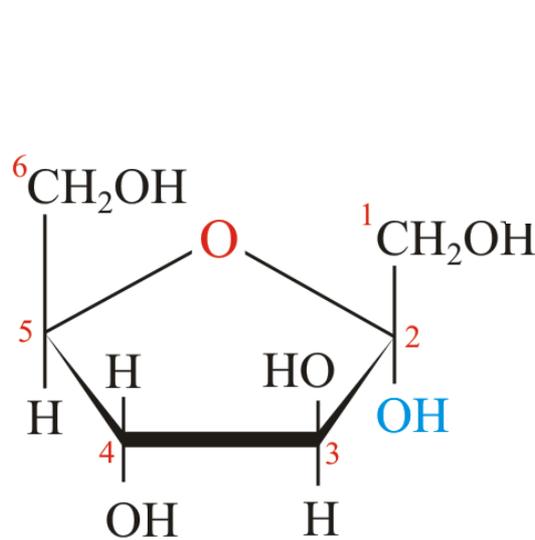
β -D-glucose

Haworth projection

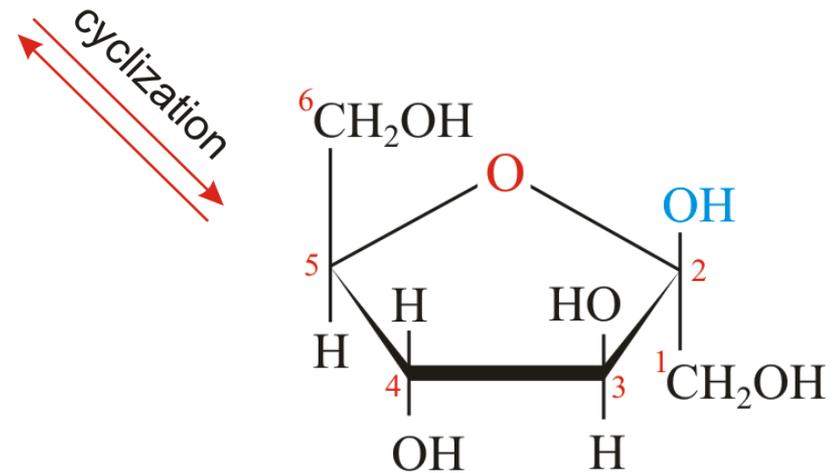
Monosaccharide cyclization



D-fructose
Linear form



α -D-fructose

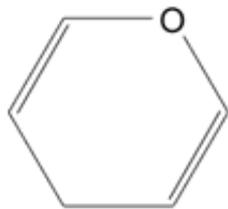


β -D-fructose

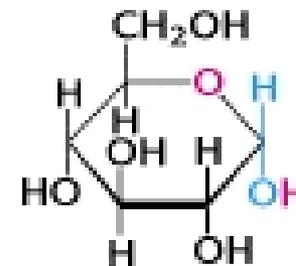
Pyranoses & Furanoses



- ❑ Sugars with six-membered rings are known as pyranoses (e.g. glucopyranose) as they resemble the heterocyclic compound pyran.

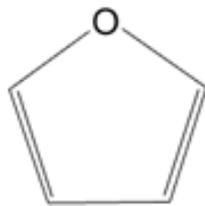


Pyran

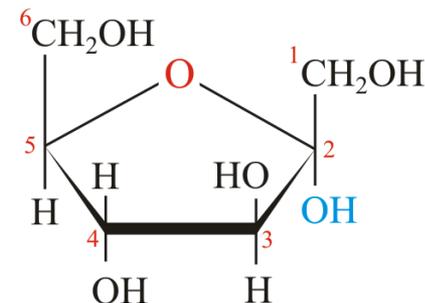


α -D-glucopyranose

- ❑ Sugars with five -membered rings are known as furanoses (e.g. fructofuranose) as they resemble the heterocyclic compound furan.

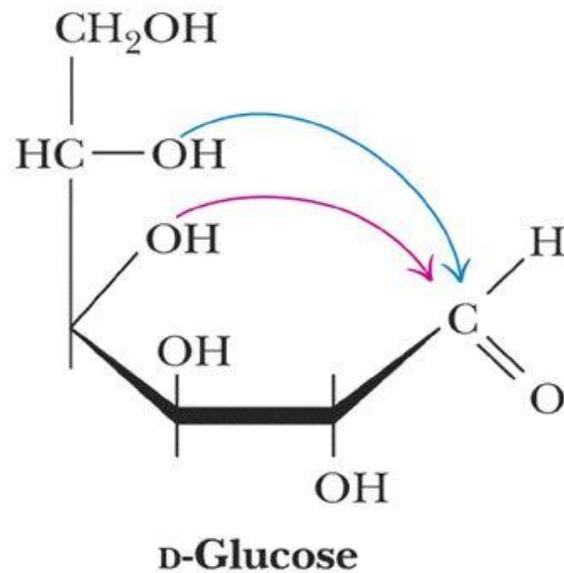


Furan

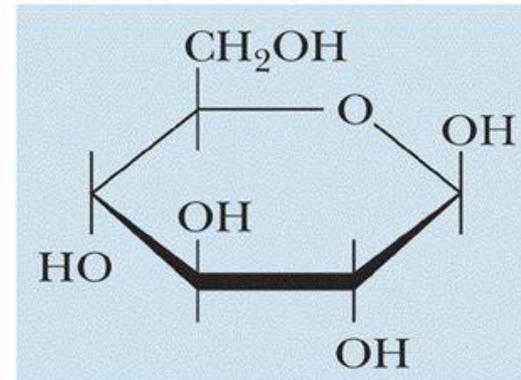


α -D-fructofuranose

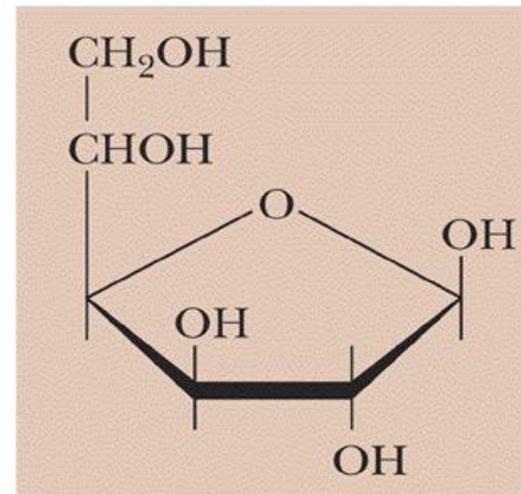
Pyranoses & Furanoses



D-glucose can cyclize in two ways forming either furanose or pyranose structures

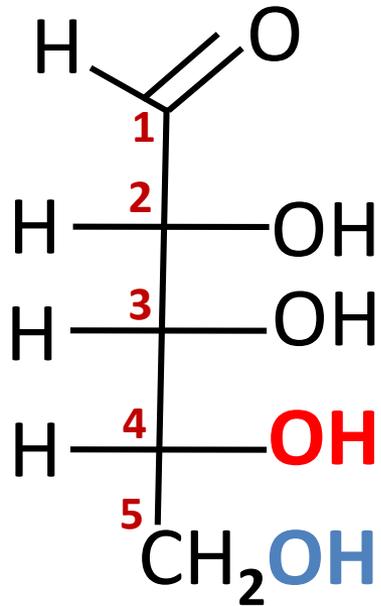


Pyranose form
 β -D-glucopyranose

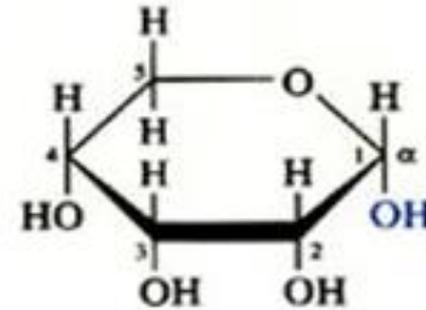


Furanose form
 β -D-glucofuranose

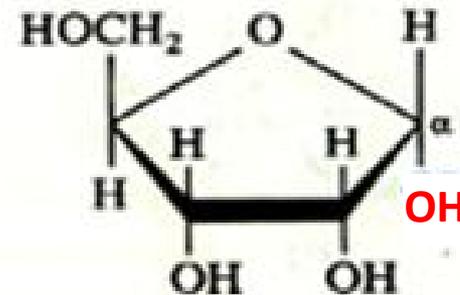
Pyranoses & Furanoses



**D-ribose
Fisher projection**



**α -D-Ribopyranose
(Haworth projection)**

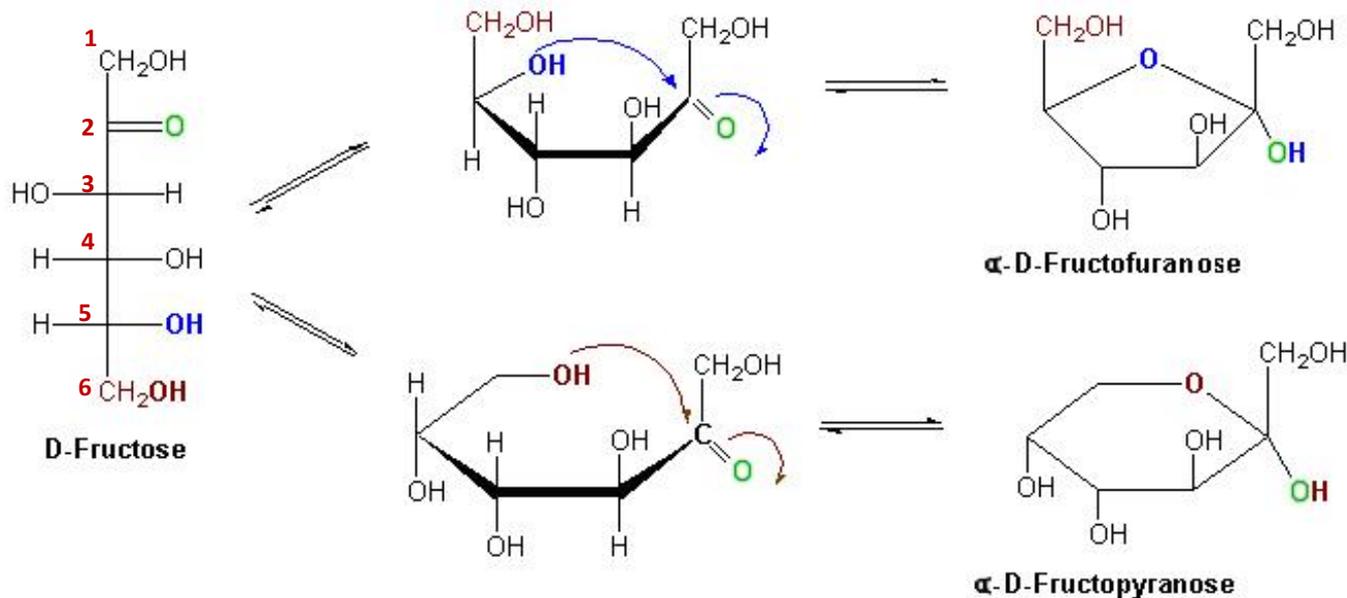


**α -D-Ribofuranose
(Haworth projection)**

Pyranoses & Furanoses



Isomeric Forms of Fructose



- Hexose or pentose can exist in pyranose and furanose forms (the most stable rings).
e.g in solution, glucose and fructose are mostly pyranoses whereas ribose is mostly furanose

Anomers



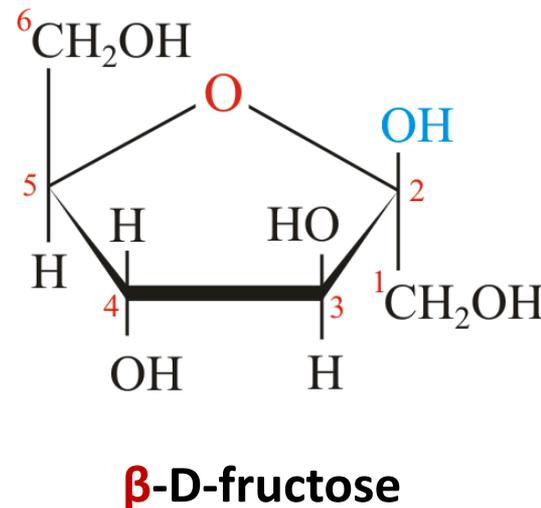
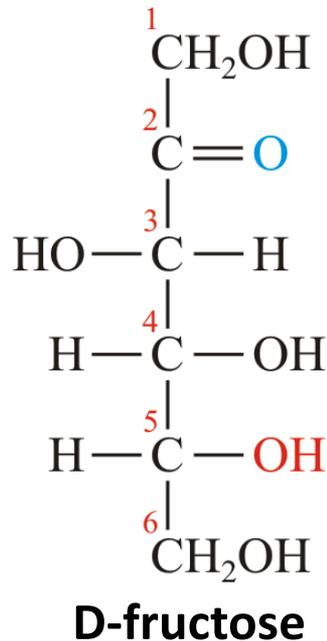
- ❑ In cyclic sugars, the carbonyl carbon becomes a chiral center (asymmetric carbon) with two possible configurations: α and β . This new carbon is called anomeric carbon.
- ❑ Anomers are pair of stereoisomers that differ in spatial arrangement of atoms at the anomeric carbon. In α -anomer, the OH group of the anomeric carbon is projecting down the plane of the ring and on the opposite side of the terminal CH_2OH group (in Fisher projection) and vice versa in β -anomer.
- ❑ The anomers freely interconvert in aqueous solution, e.g. at equilibrium D-glucose is a mixture of β -anomer (63.6%), α -anomer (36.4%) and extremely tiny amounts of the straight chain.

Haworth Projection



- Haworth projection is a simple 3D way to represent the cyclic monosaccharides. The OH groups on the right-hand side of Fisher projection are down in Haworth projection and vice versa. The dark line indicates atoms that are closer to the observer.

Fisher projection



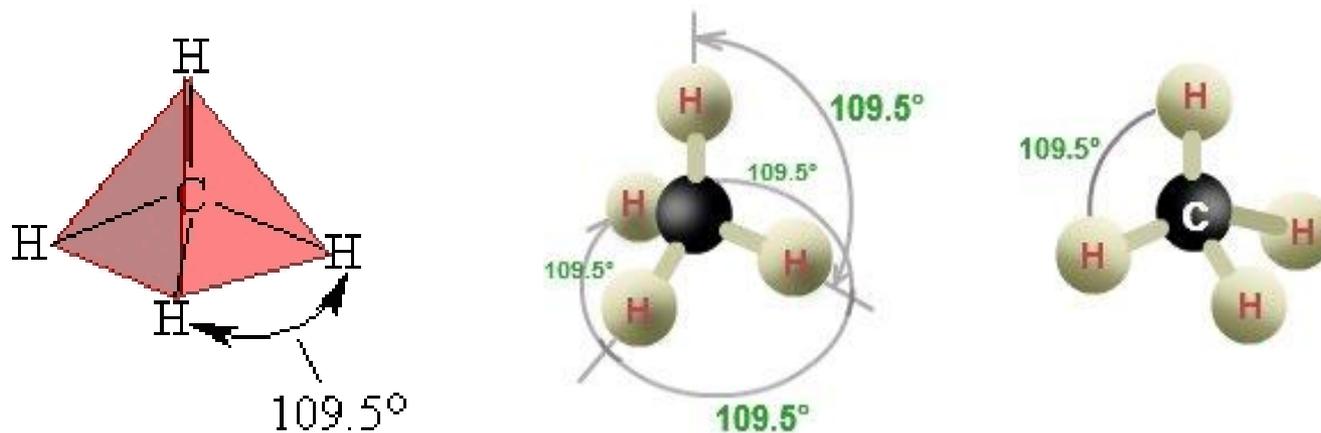
Haworth projection

Conformers

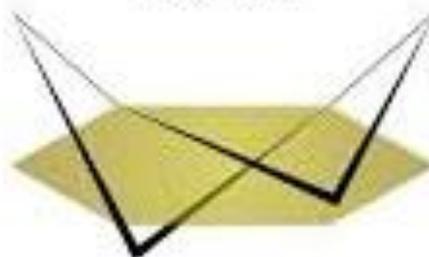
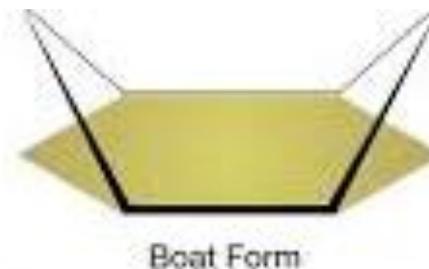
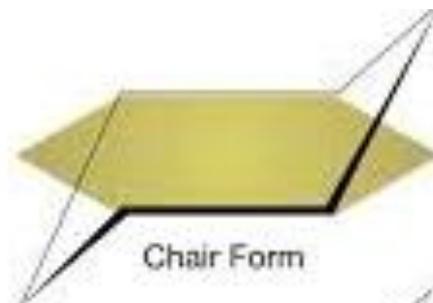


- The geometry of the carbon atoms of monosaccharide ring is tetrahedral (bond angles are close to 109.5°), so sugar rings are not actually planar. For example, pyranoses take on either **Chair** or **Boat** conformations (conformational isomers or conformers).

Conformers



Carbon atoms are tetrahedral

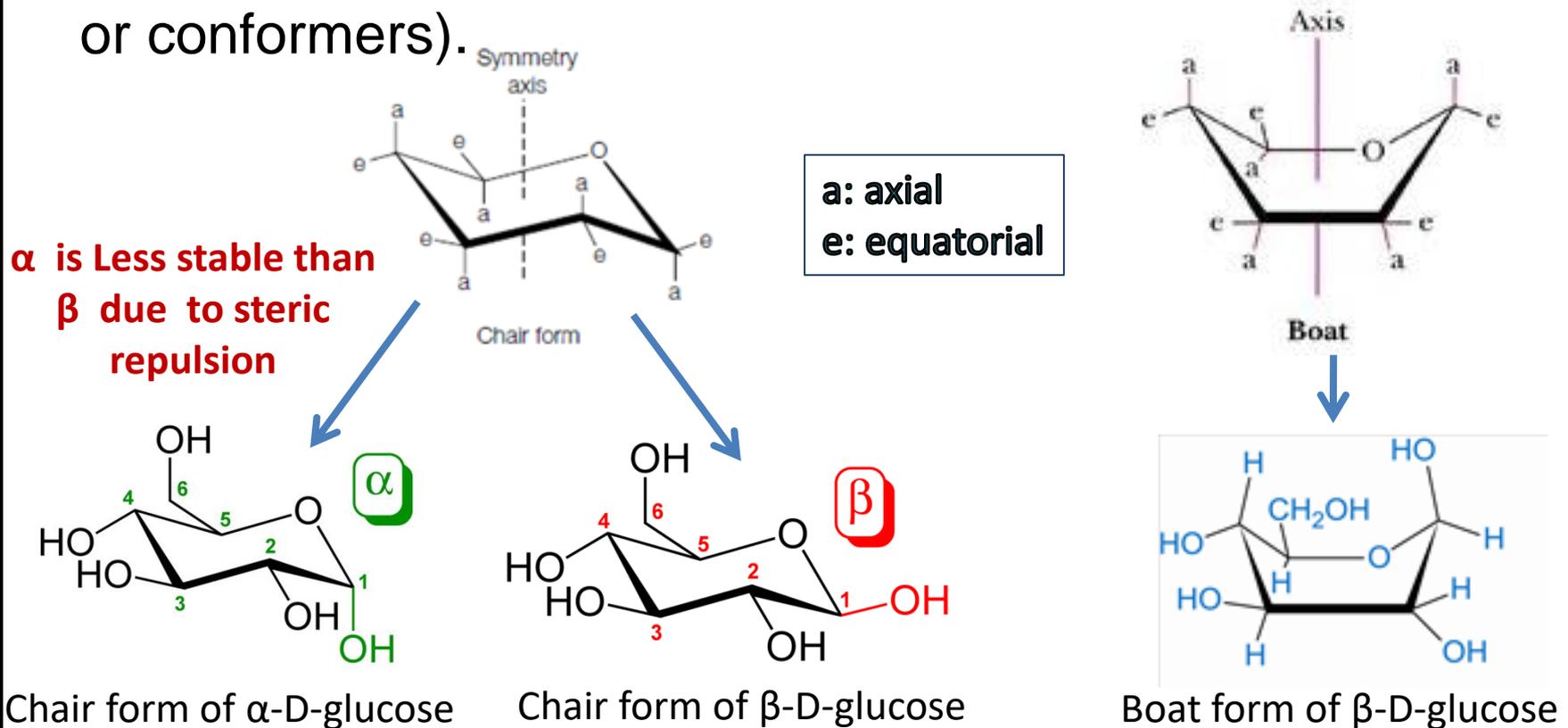


Conformers are stereoisomers with different rotations about single bonds

Conformers



- The geometry of the carbon atoms of monosaccharide ring is tetrahedral (bond angles are close to 109.5°), so sugar rings are not actually planar. For example, pyranoses take on either **Chair** or **Boat** conformations (conformational isomers or conformers).



Sugar Modification

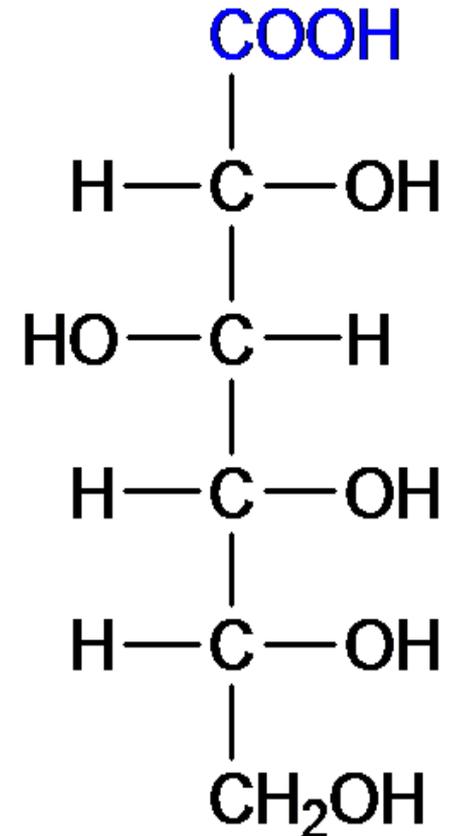


1. **Aldonic acids** : oxidation of aldehyde (C1) to carboxylic acid; e.g. D-gluconic acid

- **Uses:**

- Some drugs are injected in the form Of **gluconate** (the salt of gluconic acid)

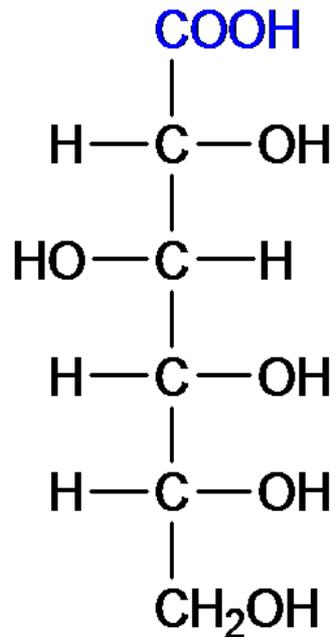
- **Calcium gluconate solution (I.V)** as cardioprotective agent in patients with high blood level of K^+



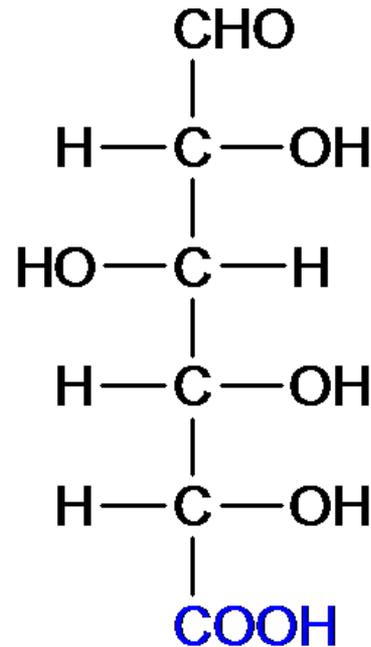
Sugar Modification



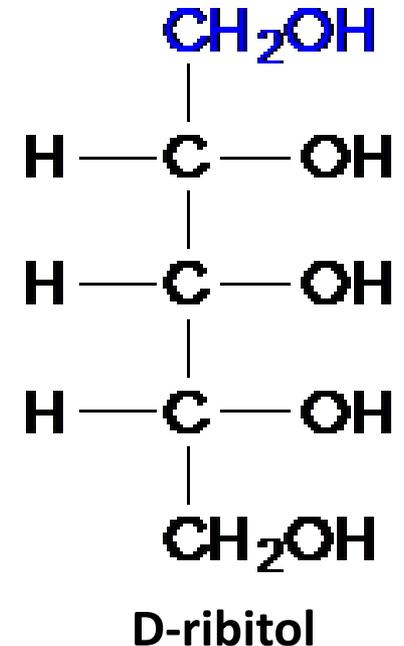
1. Aldonic acids : oxidation of aldehyde (C1) to carboxylic acid; e.g. D-gluconic acid



2. Uronic acids : oxidation of OH at (C6) to carboxylic acid; e.g. D-glucuronic acid



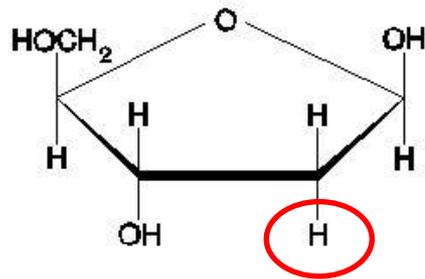
3. Alditols : reduction of carbonyl group to alcohol; e.g. D-ribitol, D-glycerol and D-sorbitol (sweetener)



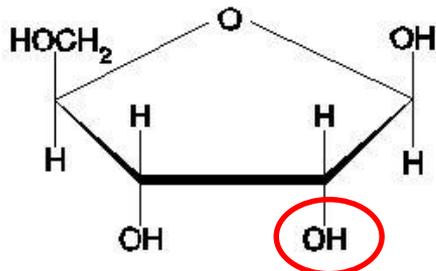
Sugar Modification



4. Deoxy sugars : OH group is replaced by H; e.g. β -D-2-deoxyribose

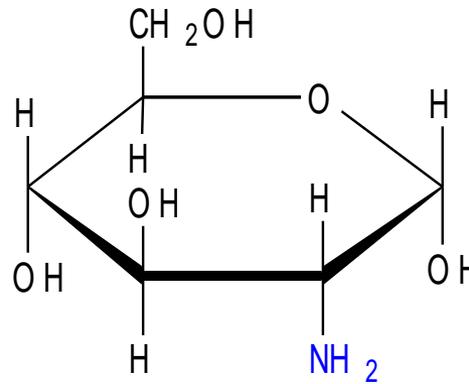


Deoxyribose

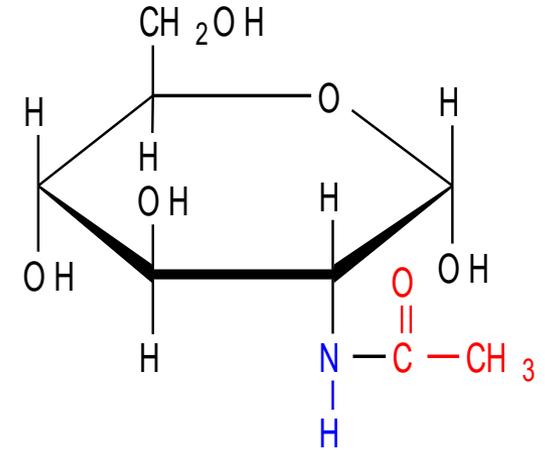


Ribose

4. Amino sugars : one or more OH groups are replaced by **amino group** which is often **acetylated**; e.g. α -D-glucosamine (rebuild cartilage in osteoarthritis & osteoporosis) and α -D-N-acetylglucosamine (both are derivatives of α -D-glucose)



α -D-glucosamine



α -D-N-acetylglucosamine

