Carbohydrates

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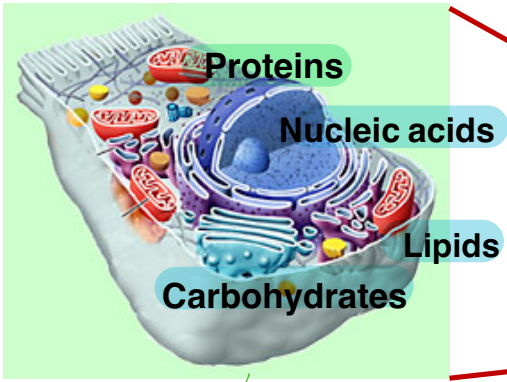
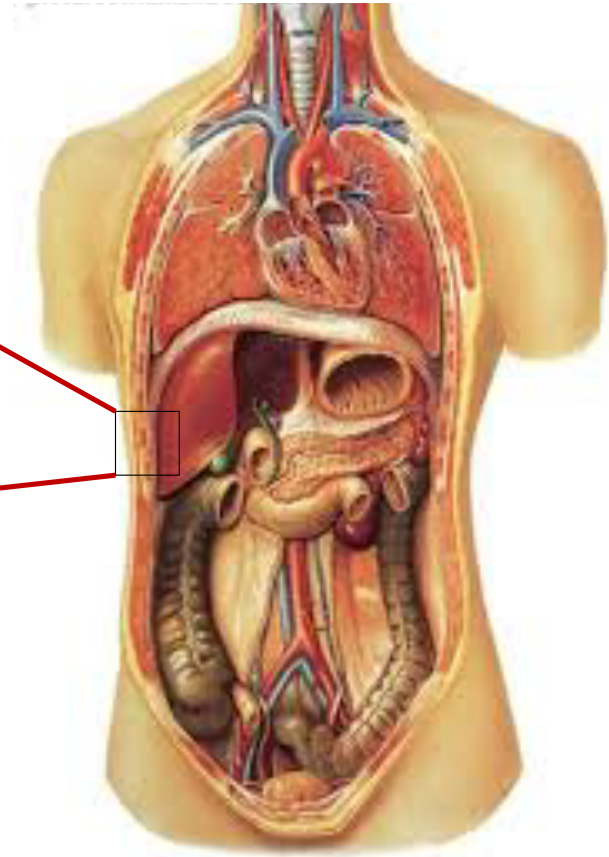
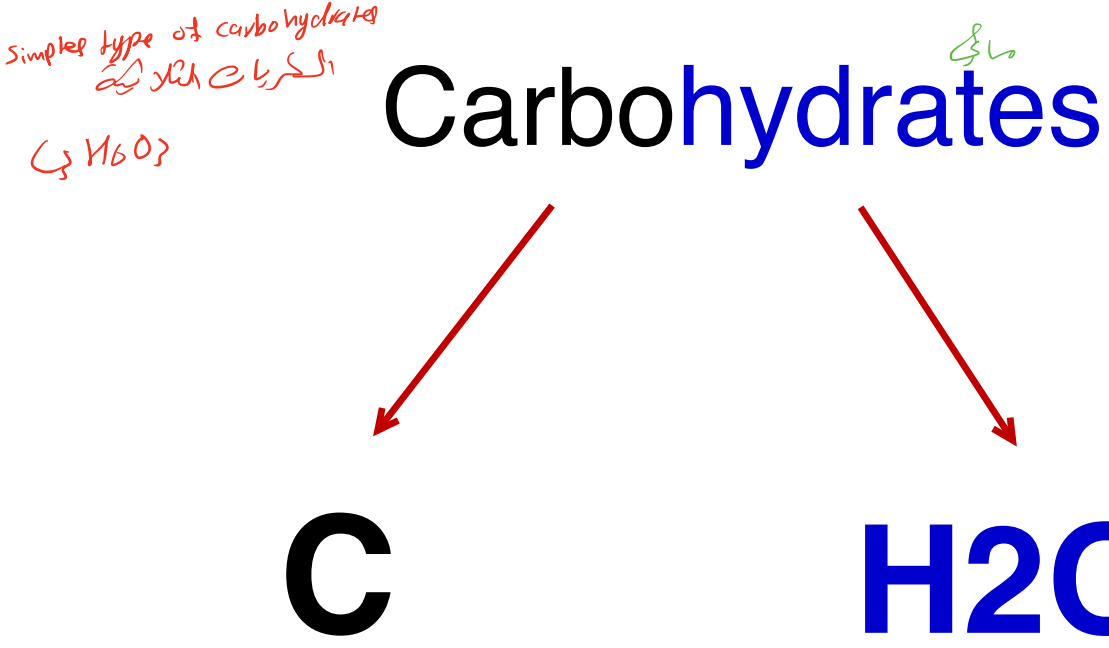
Major Types of Macromolecules





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

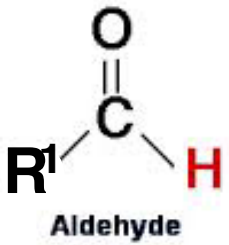


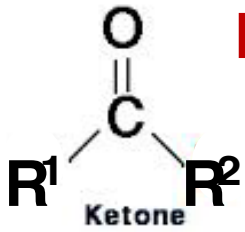
Classification of Carbohydrates

- Carbohydrates are “Sugars” or “Saccharides” consist of the empirical formula $(CH_2O)n$ 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)





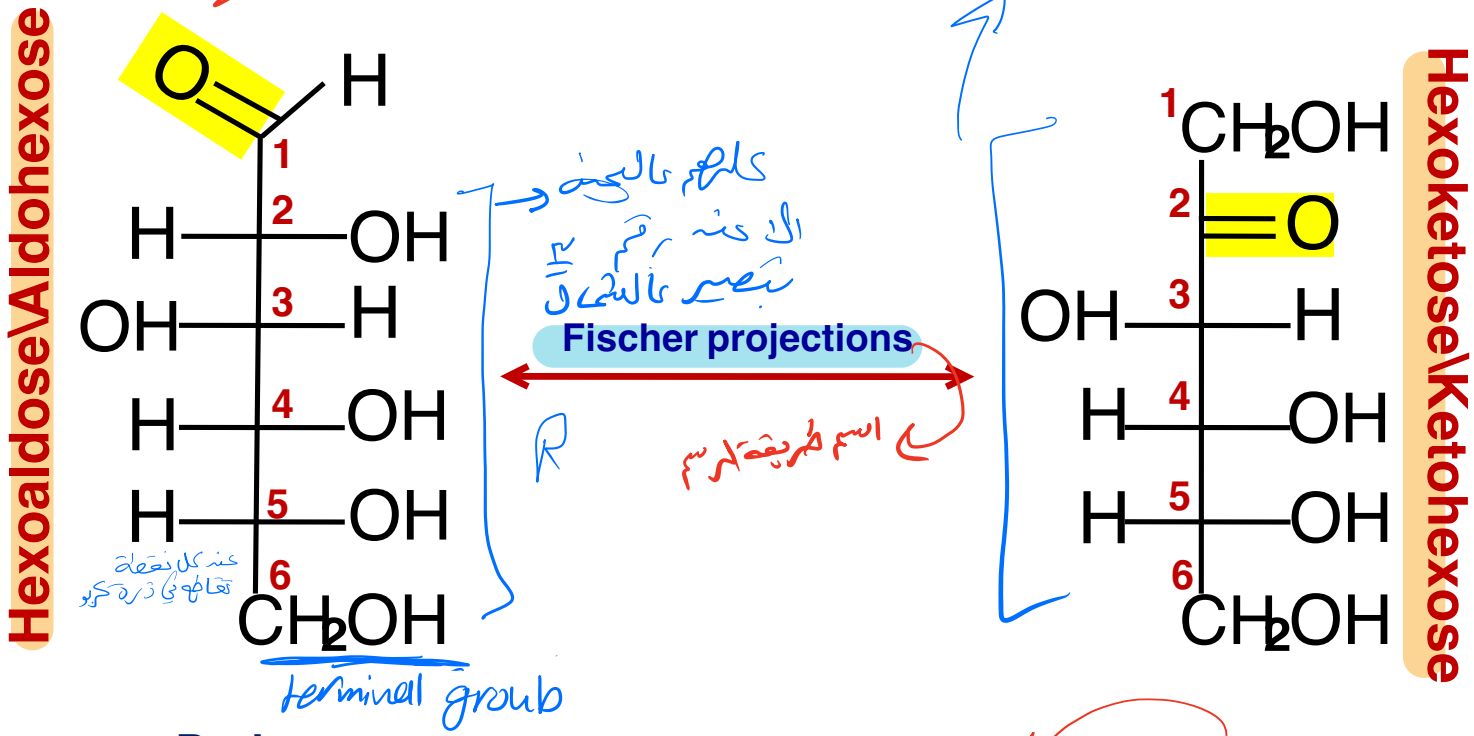
Aldehyde: R^1 = H, alkyl or aryl

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

Monosaccharides

Hexose $C_6H_{12}O_6$

2 terminal group



D-glucose

"grape or blood sugar"

D-fructose

"fruit sugar" + honey

النظائر

Isomerization

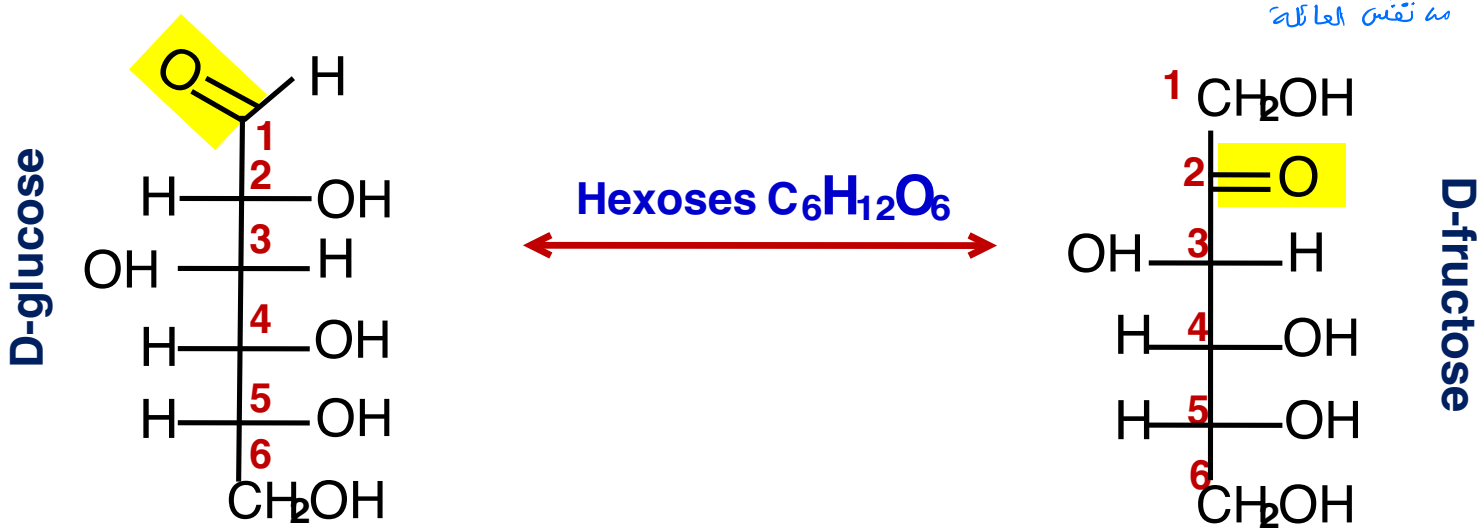
يعني حدول n

- 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)

بنية

ما الهم نلاقة ببعض هالبس من تقنين العائلة



Isomerization

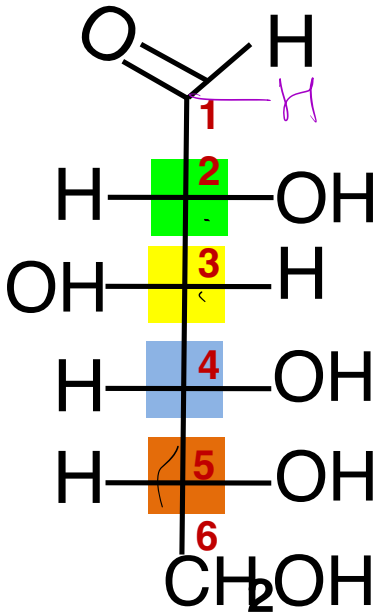
- Isomers: are molecules with same molecular formula but different chemical structures

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

يعني الملخص انه بقدر عدد النظائر
chiral carbon الي بتظهر معنا عدد ال
2^n → n عدد ال chiral Center



D-glucose

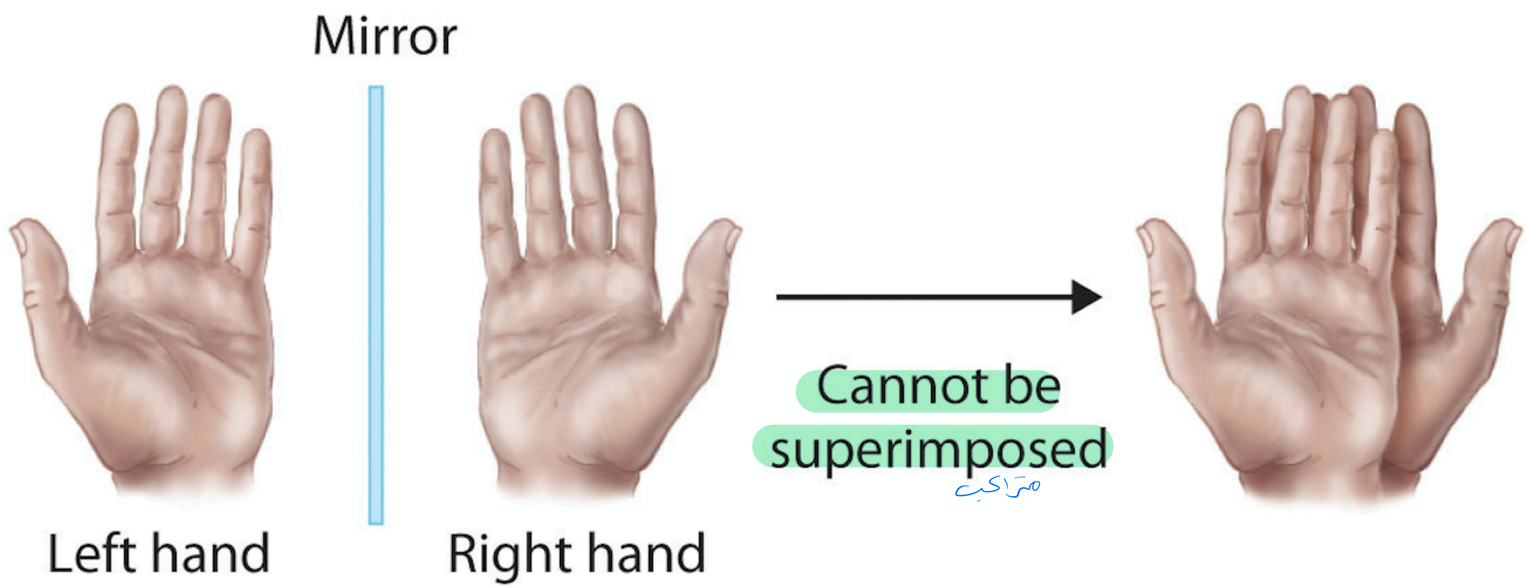
Number of stereoisomers = 2^4

= 16

Hands كلمة يونانية معناها

Chirality & Chiral Object

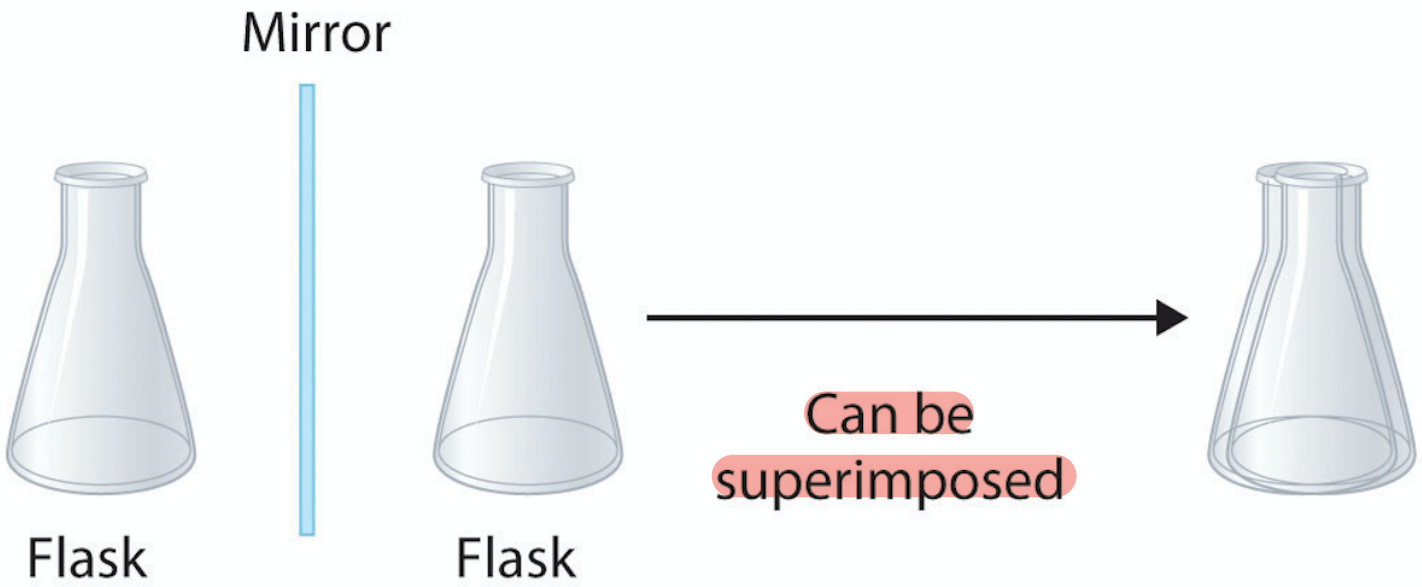
لأنه ايدينا مثال عليها



(a) **Chiral objects**

اي اشي اله صورة مرآة لبعضهم بس مش superimposed بكون 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

glyceraldehyde — Simplest sugar

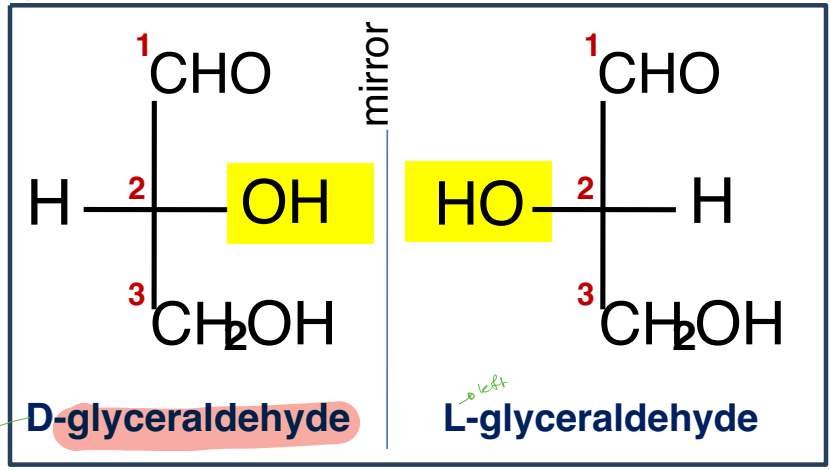
2 stereoisomer

1 chiral center

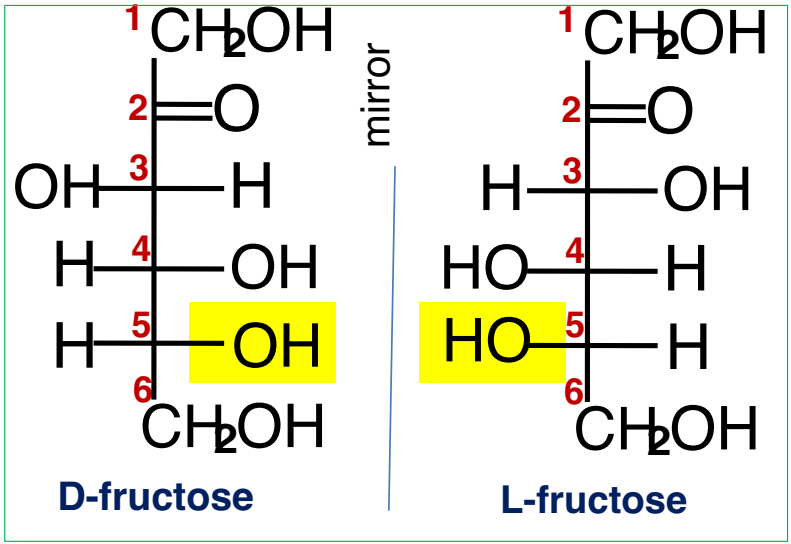
Chiral center

one stereoisomers

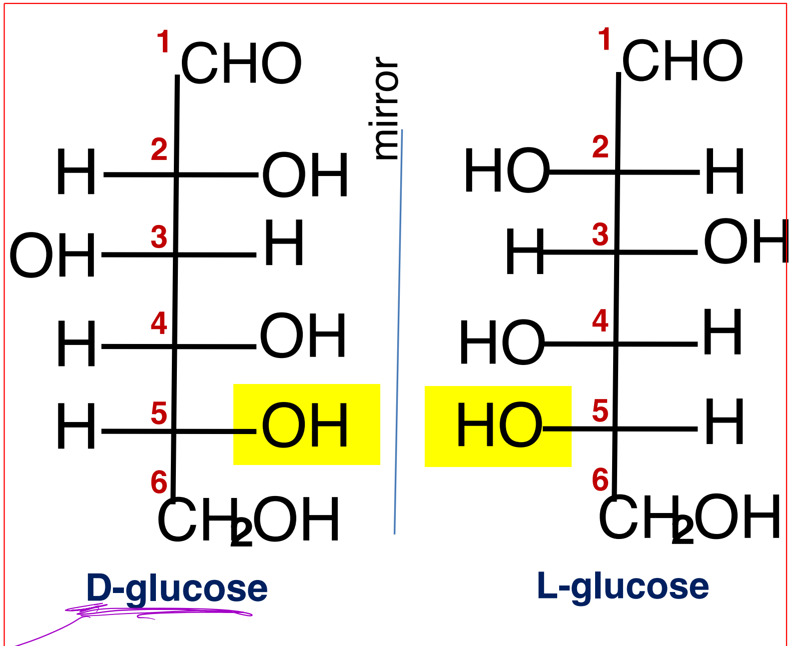
2^0 = 1



$2^3 = 8$ stereoisomers



D/L Monosaccharides



→ biologicly active inside a human body

وهو اللي ح نستعمله بعد بين يحكي بنعرف ليعديش انها D كالك

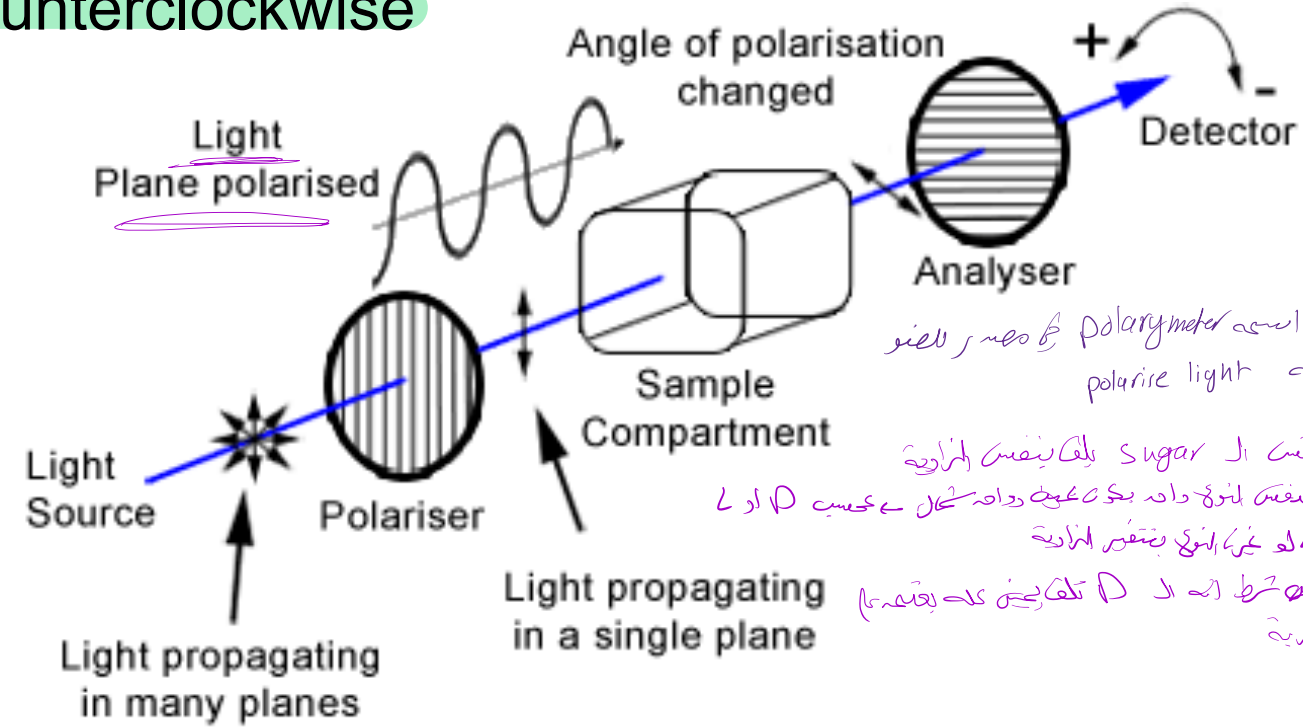
ونستفيد من ال left لاصدار معينة مثل الادوية

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

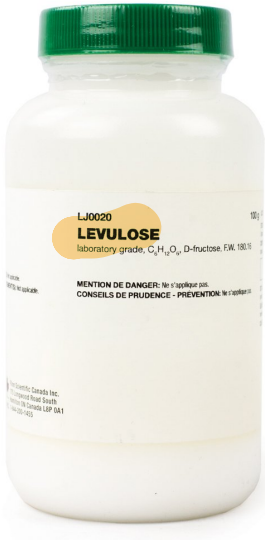
- Enantiomers are optically active and can rotate the polarized light plane either clockwise or counterclockwise



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.

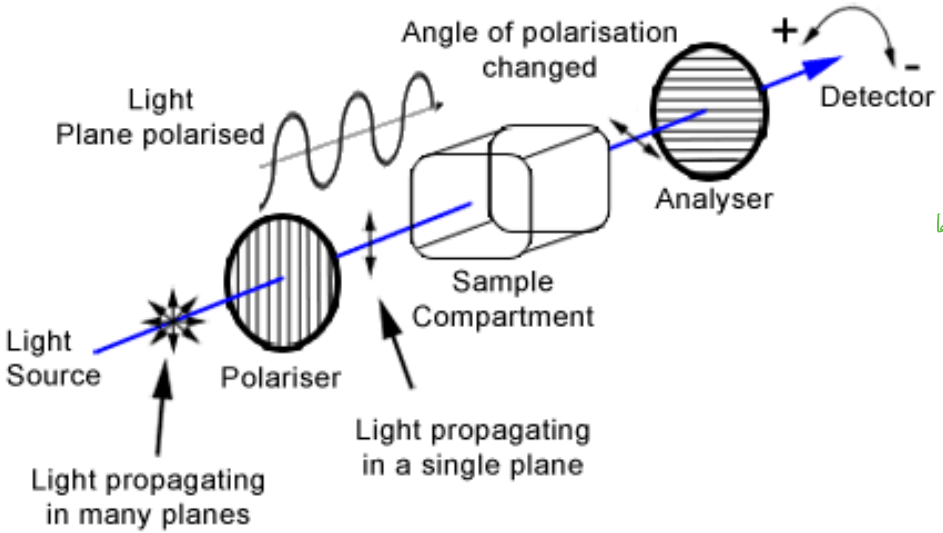
Monosaccharides



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

Monosaccharides

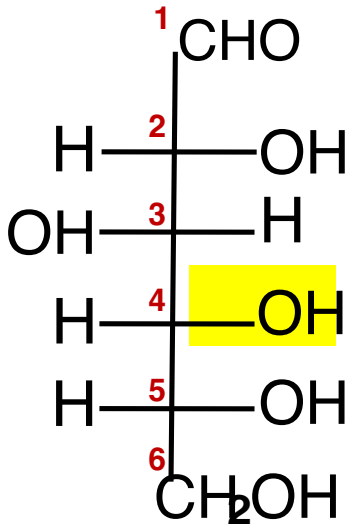
- Enantiomers are optically active and can rotate the polarized light plane either clockwise or counterclockwise



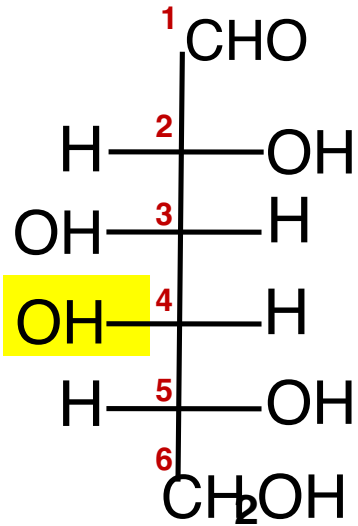
- **Racemic mixture** contains equal amounts of each enantiomer (net rotation is zero)

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.

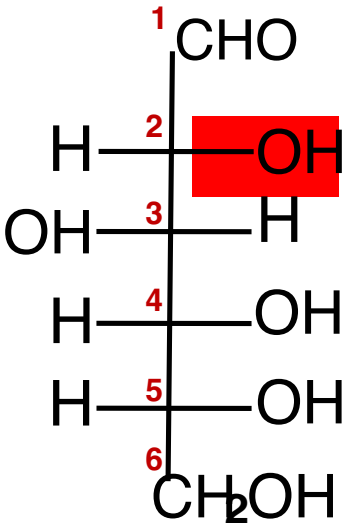


D-glucose

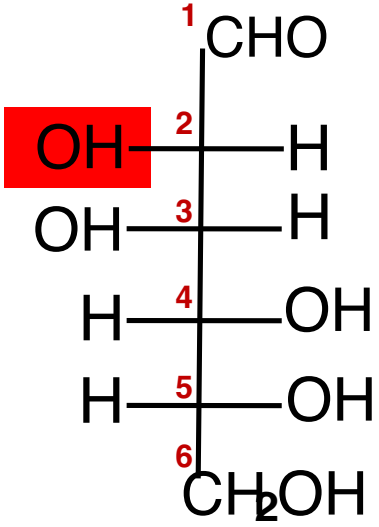


D-galactose

Monosaccharides



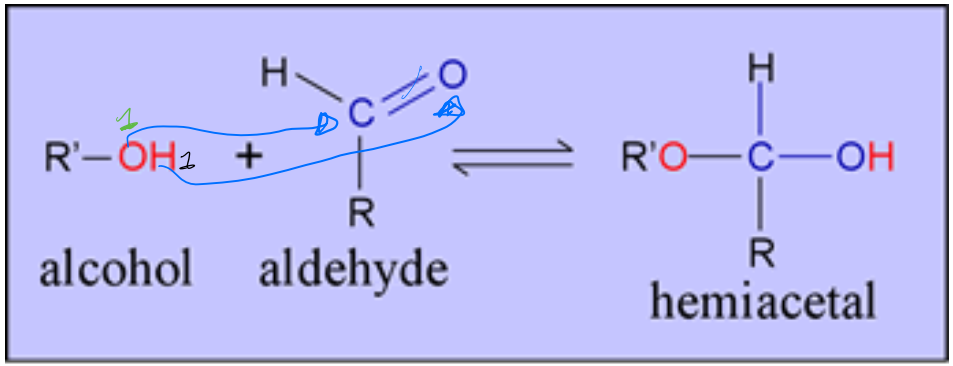
D-glucose

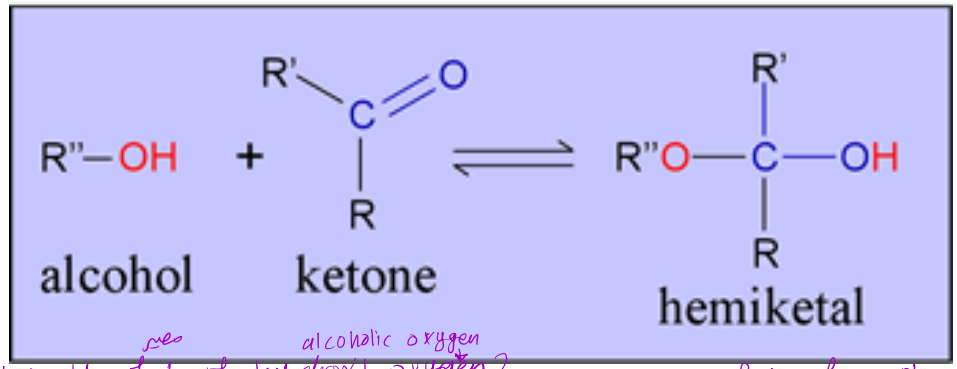


D-mannose

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

Hemiacetal & Hemiketal





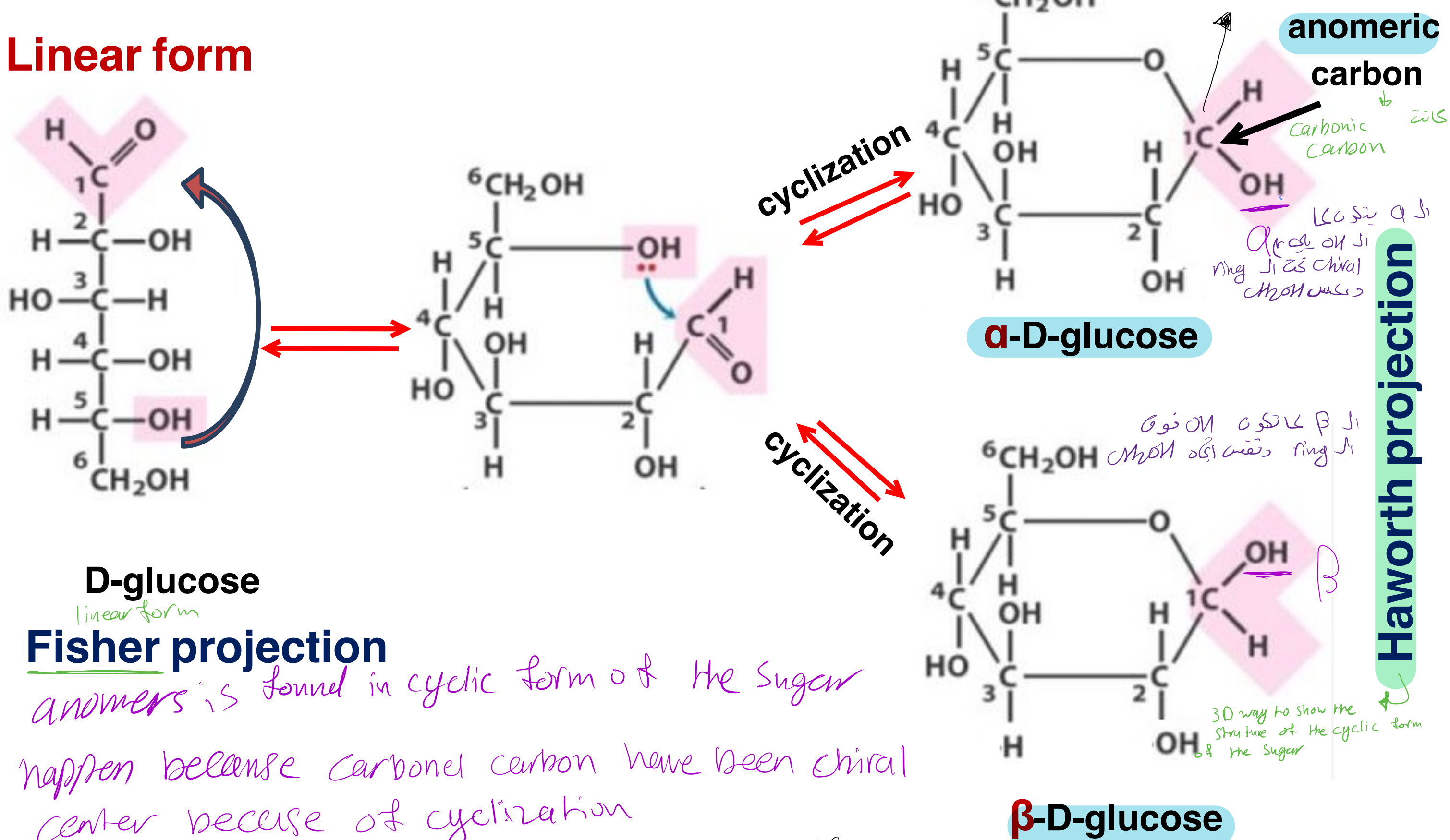
what is the fat of hydroxil oxygen? alcoholic oxygen
it will be ethree group in nemiacital

what is the fat of carbonic carbon?
chiral carbon center

what is the fat of carbonel oxygen?
alcoholic / hydroxel group

Monosaccharide cyclization

intra molecular يصير تفاعل الي فوق نفس بتكون بس هو

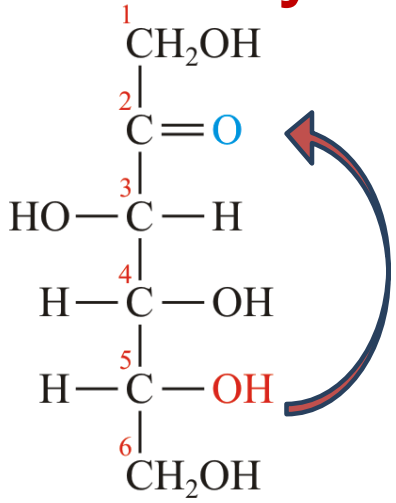


anomers is found in cyclic form of the sugar

happen because carbonel carbon have been chiral center because of cyclization

كيف بدي اعرف اذا الشكل D ولا L؟ من موقع الـ CH2OH اذا فوق تكون D

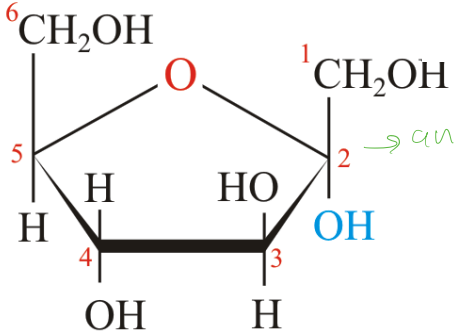
Monosaccharide cyclization



D-fructose
Linear form

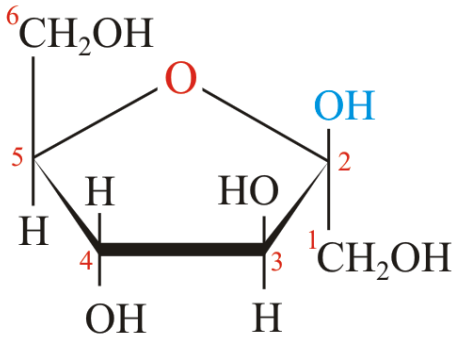
cyclization

cyclization



anomeric

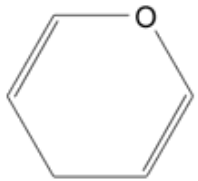
α-D-fructose



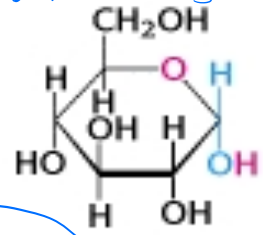
β-D-fructose

Pyranoses & Furanoses

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



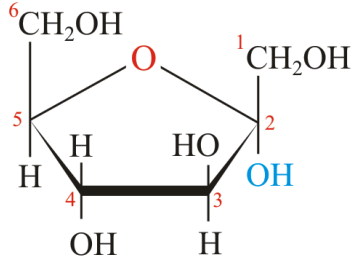
Pyran



α-D-glucopyranose

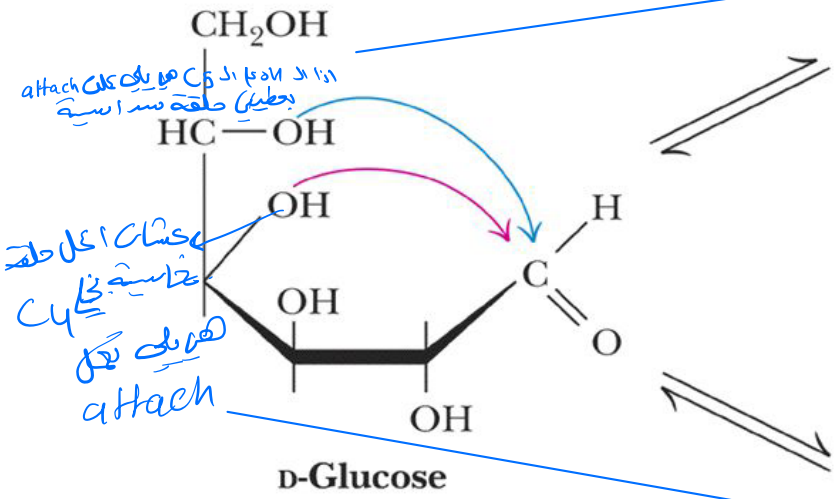
- Sugars with five -membered rings are known as furanoses (e.g. fructofuranose) as they resemble the heterocyclic compound furan.

Furan

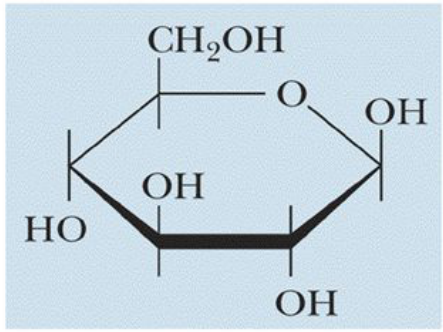


α-D-fructofuranose

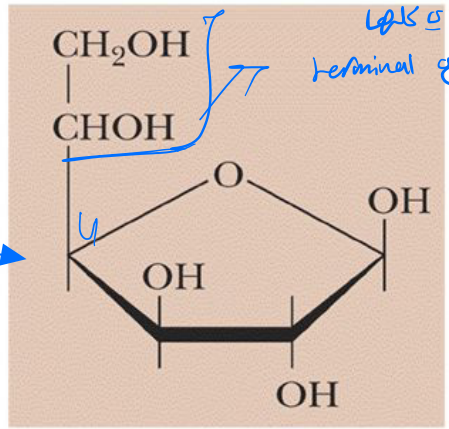
Pyranoses & Furanoses



D-Glucose



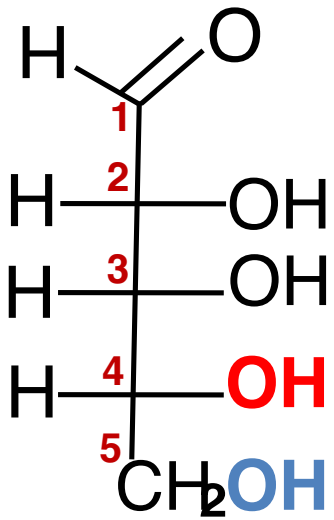
Pyranose form
β-D-glucopyranose



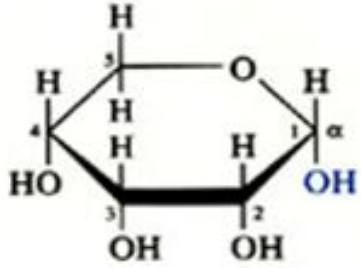
Furanose form
β-D-glucofuranose

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

Pyranoses & Furanoses

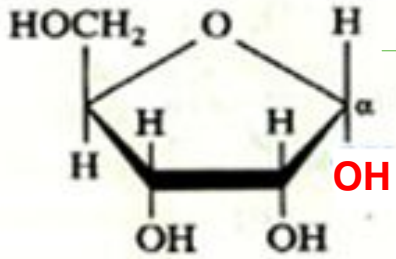


D-ribose
Fisher projection



α-D-Ribopyranose
(Haworth projection)

C5



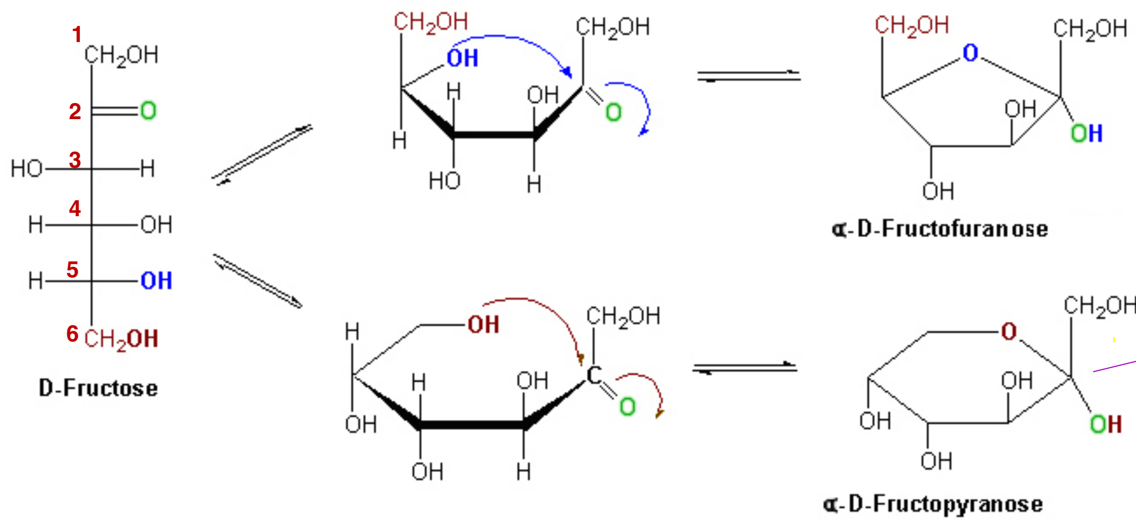
most stabile

α-D-Ribofuranose
(Haworth projection)

C4

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

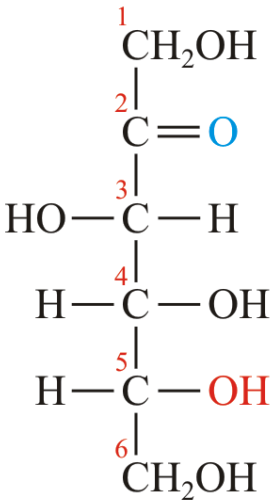
Anomers

- 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_2 OH group (in Fisher projection) and vise 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.

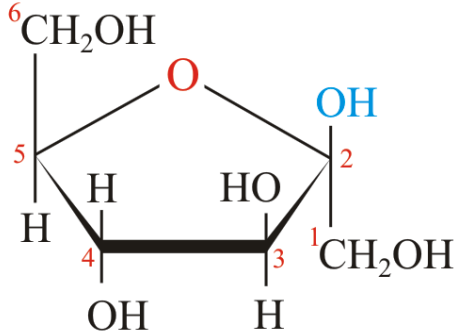
Haworth Projection

- 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 vise versa. The dark line indicates atoms that are closer to the observer.

Fisher projection



D-fructose



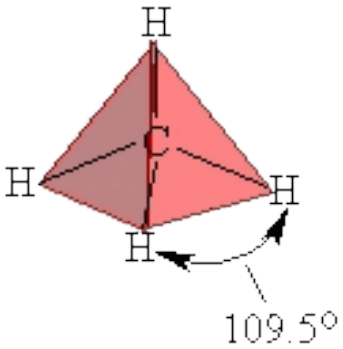
β-D-fructose

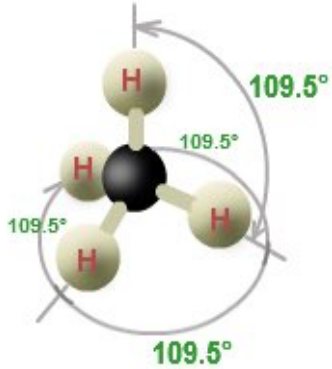
Haworth projection

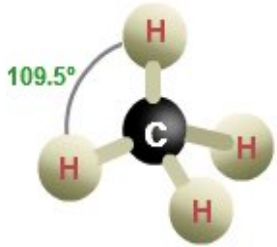
Conformers

- The geometry of the carbon atoms of monosaccharide ring is tetrahedral (bond angles are close to 109.5^0), so sugar rings are not actually planar. For example, pyranoses take on either **Chair** or **Boat** conformations (conformational isomers or conformers).

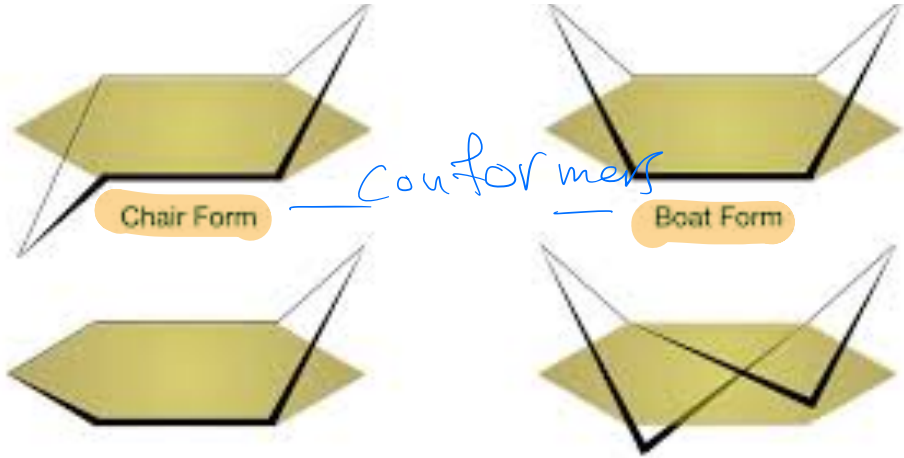
Conformers







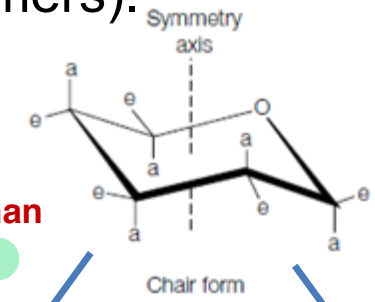
Carbon atoms are tetrahedral



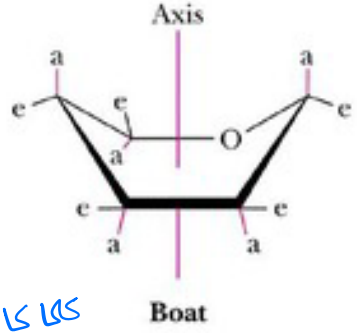
Conformers are stereoisomers with different rotations about single bonds

Conformers

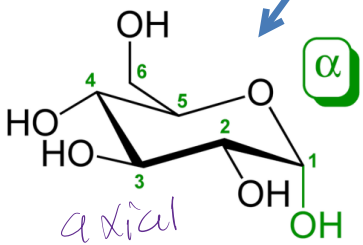
- The geometry of the carbon atoms of monosaccharide ring is tetrahedral (bond angles are close to 109.5⁰), so sugar rings are not actually planar. For example, pyranoses take on either **Chair** or **Boat** conformations (conformational isomers or conformers).



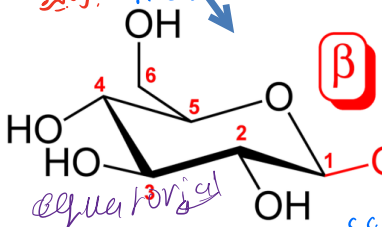
a: axial
e: equatorial



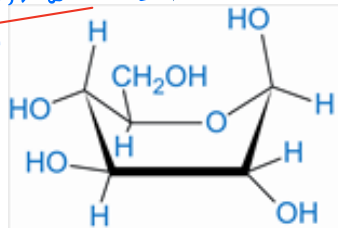
α is Less stable than β due to steric repulsion



Chair form of α-D-glucose



Chair form of β-D-glucose

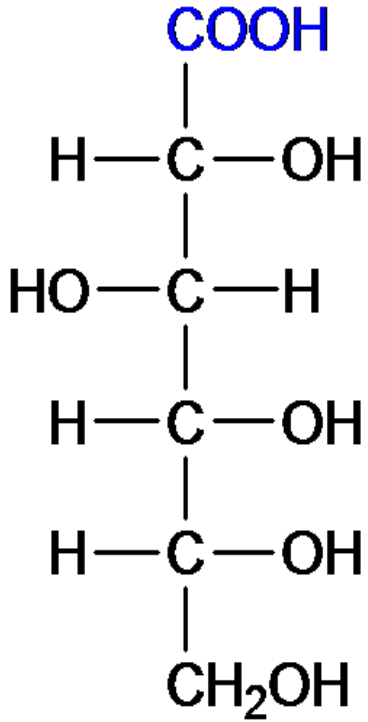


Boat form of β-D-glucose

Sugar Modification

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

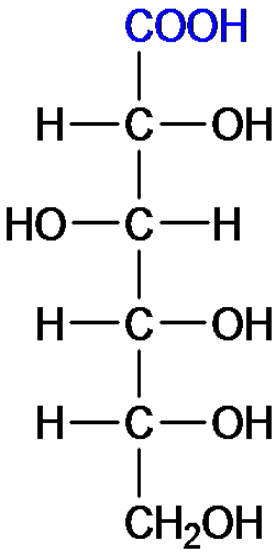
- **Uses:**
  - Some drugs are injected in the form Of **gluconate** (the salt of gluconic acid)
  - **Calcium gluconate solution (I.V)** as cardioprotective agent in patients with high blood level of K^+



Sugar Modification

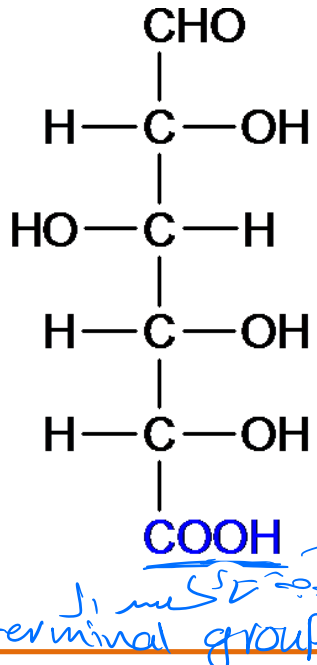
reduction صار الهم

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**

derivative from glucose

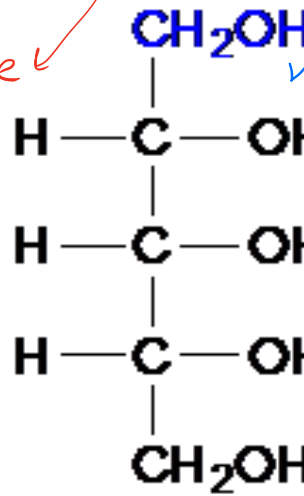


terminal group

D-ribose
D-glyceraldehyde
D-glucose

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

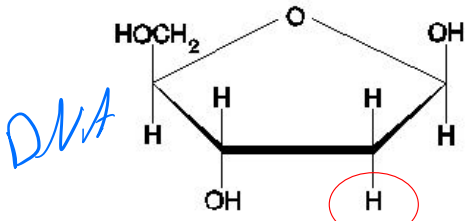
reduction aldehyde



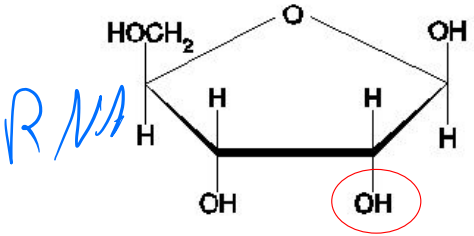
D-ribitol

Sugar Modification

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

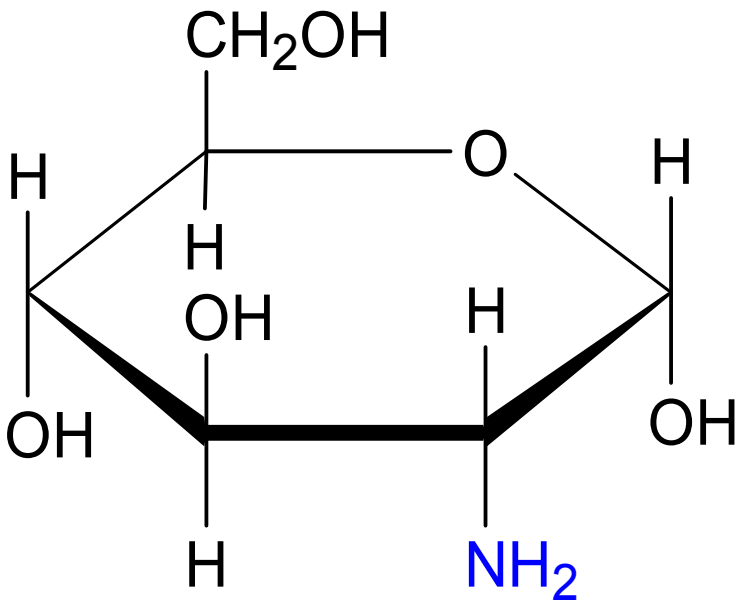


Deoxyribose



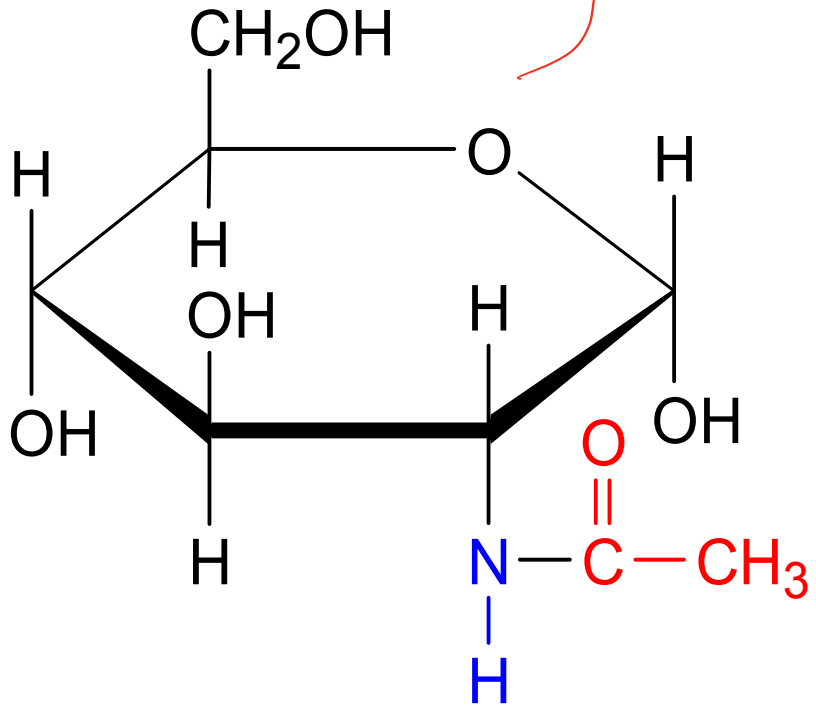
Ribose

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 of α-D-glucose)



acetyle group

α-D-glucosamine



α-D-*N*-acetylglucosamine