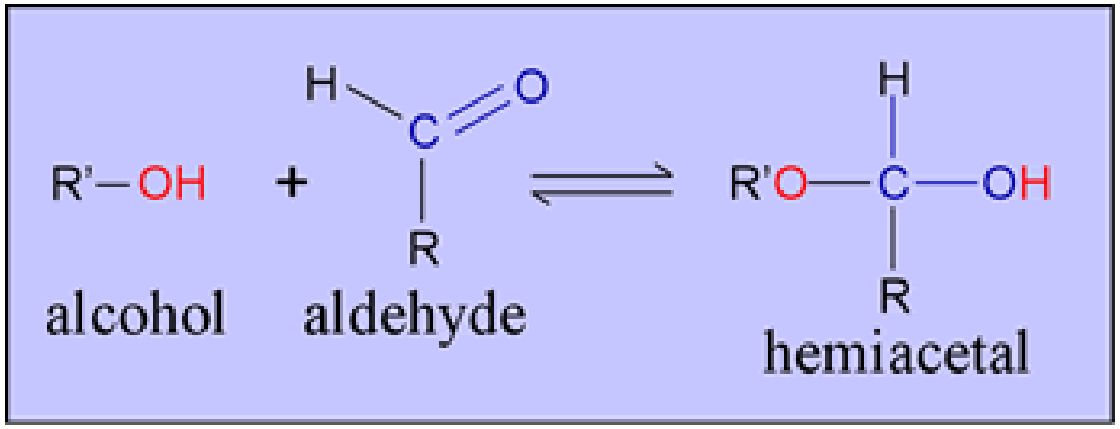
Biochemistry of Carbohydrates II

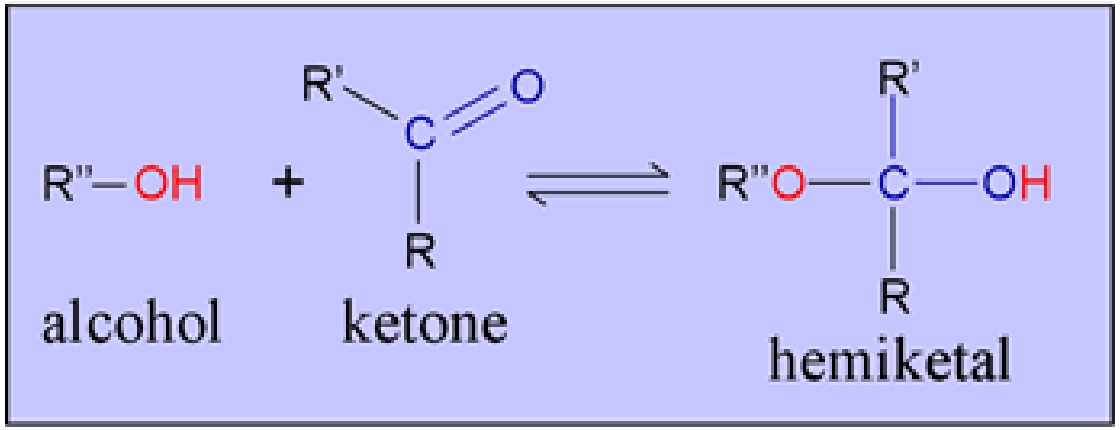
Dr. Nesrin Mwafi

Biochemistry & Molecular Biology Department

Faculty of Medicine, Mutah University

Hemiacetal & Hemiketal

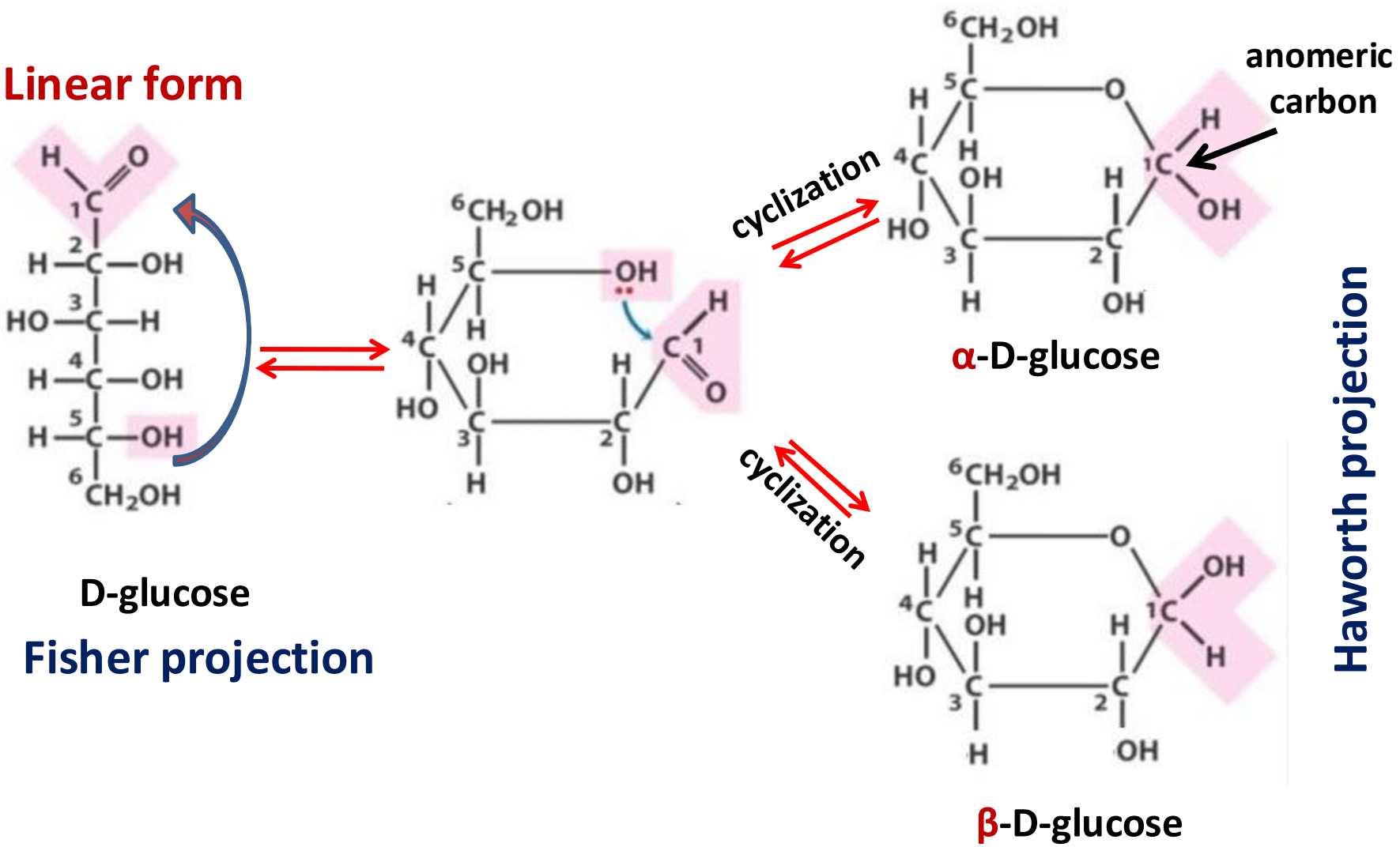




Anomers

- Anomers are pair of stereoisomers that differ in spatial arrangement of atoms at the anomeric carbon

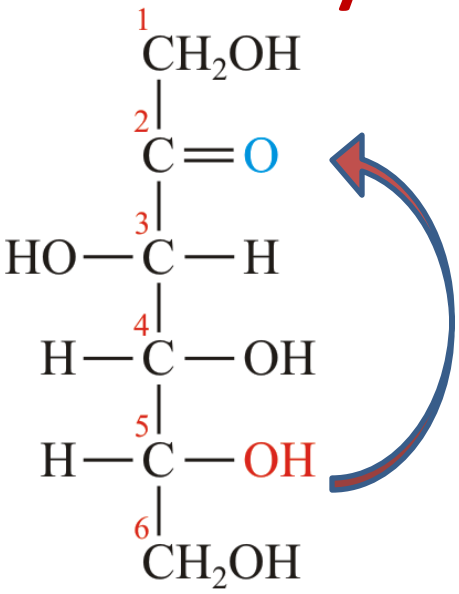
Monosaccharide cyclization



Anomers

- Anomers are pair of stereoisomers that differ in spatial arrangement of atoms at the anomeric carbon
- 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.
- 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 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.

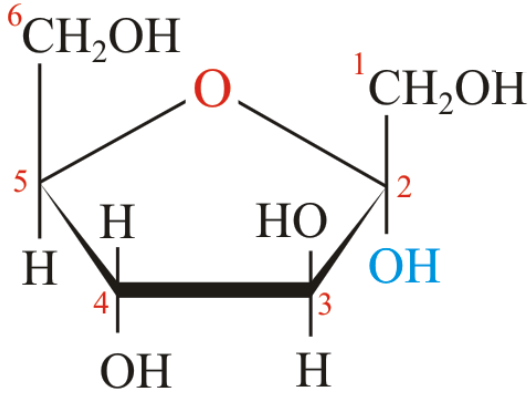
Monosaccharide cyclization



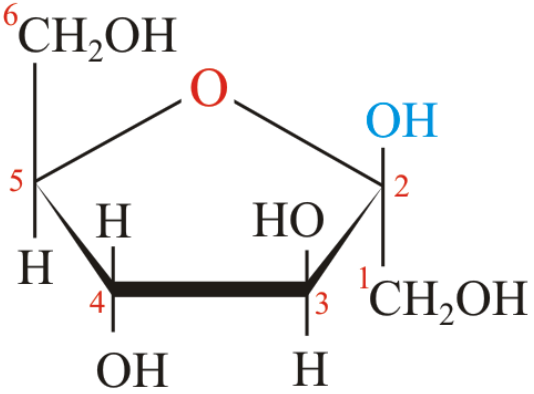
D-fructose
Linear form

cyclization

cyclization



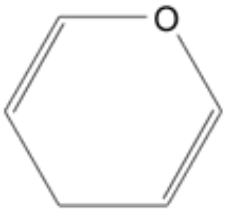
α-D-fructose



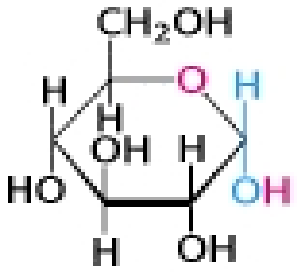
β-D-fructose

Pyranoses & Furanoses

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



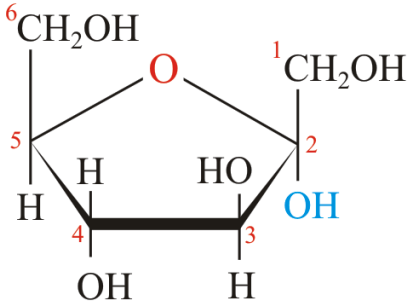
Pyran



α-D-glucopyranose

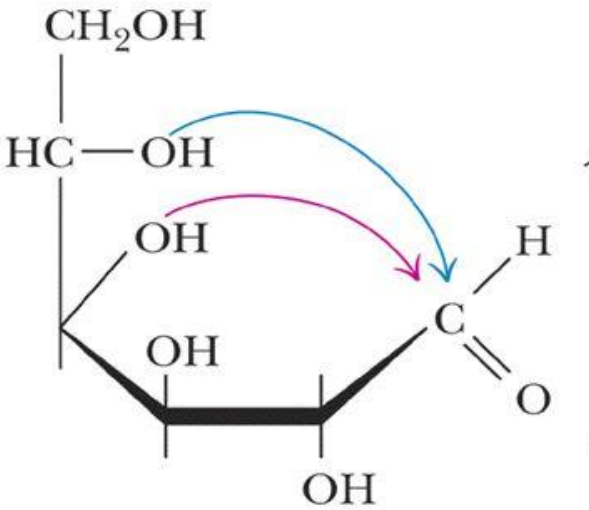
- Sugars with five -membered rings are known as furanoses (e.g. fructofuranose) as they resemble the heterocyclic compound furan.

Furan

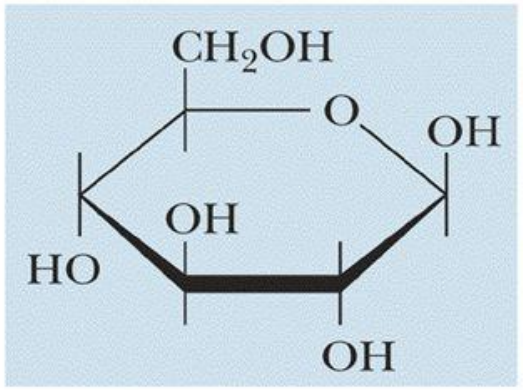


α-D-fructofuranose

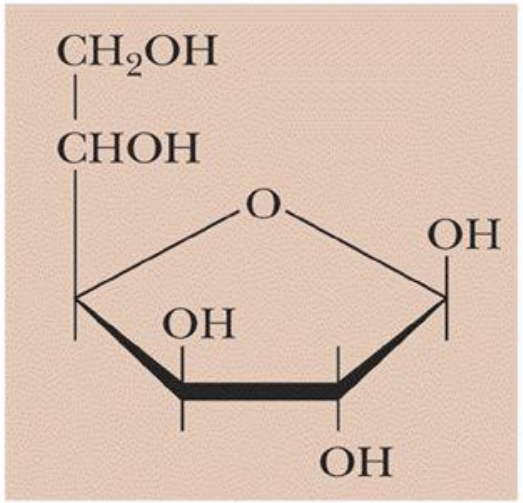
Pyranoses & Furanoses



D-Glucose



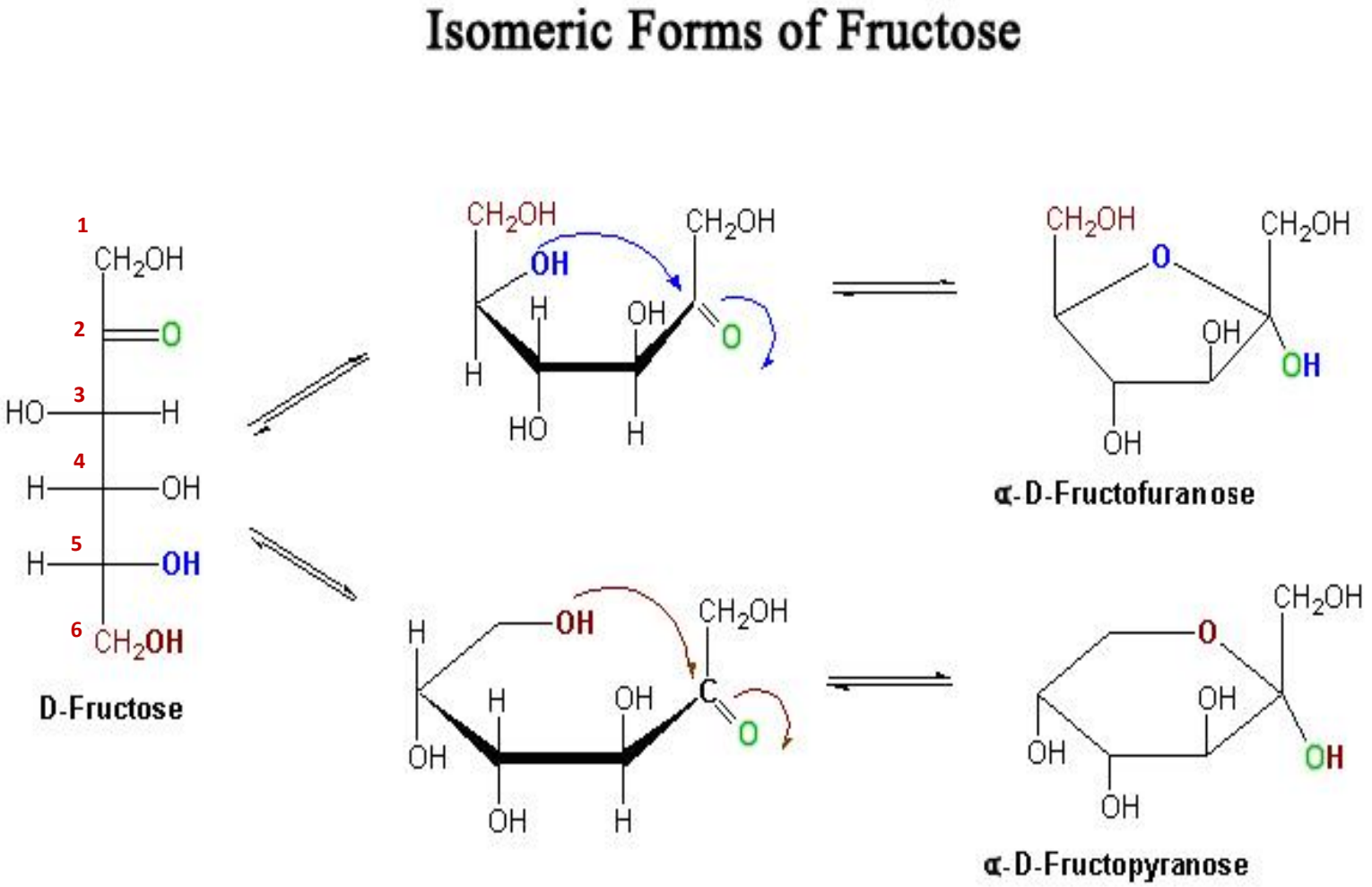
Pyranose form
β-D-glucopyranose



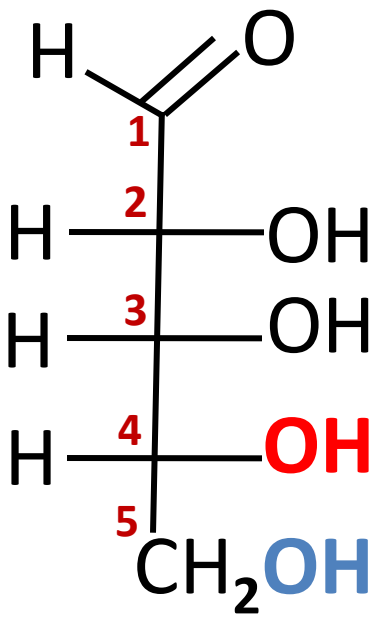
Furanose form
β-D-glucofuranose

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

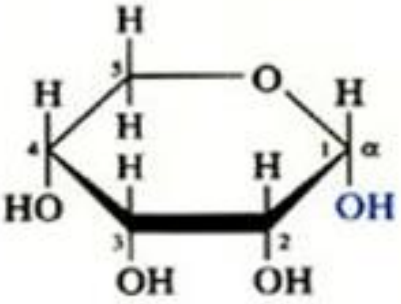
Pyranoses & Furanoses



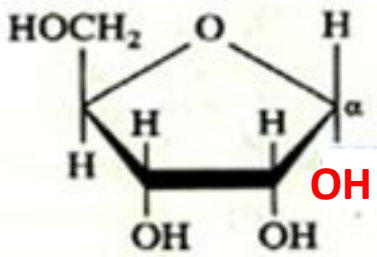
Pyranoses & Furanoses



D-ribose
Fisher projection



α-D-Ribopyranose
(Haworth projection)



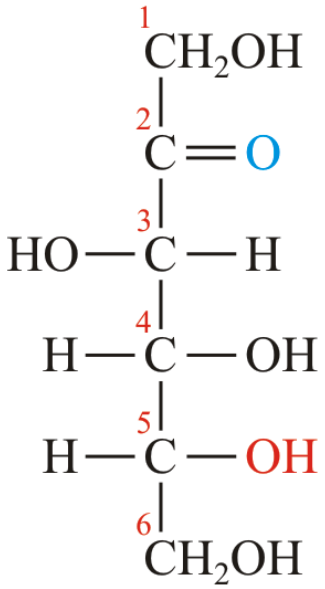
α-D-Ribofuranose
(Haworth projection)

- 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

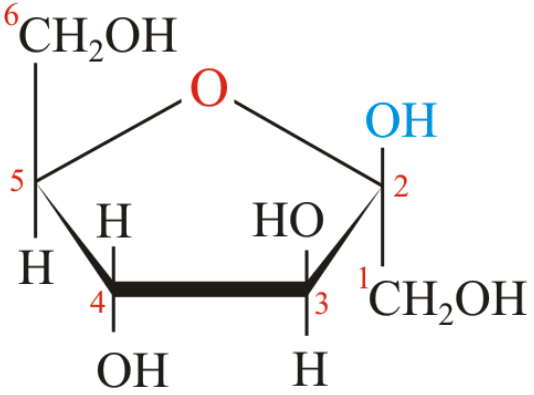
Haworth Projection

- Haworth projection is a simple 3D way to represent the cyclic monosaccharides.

Fisher projection



D-fructose



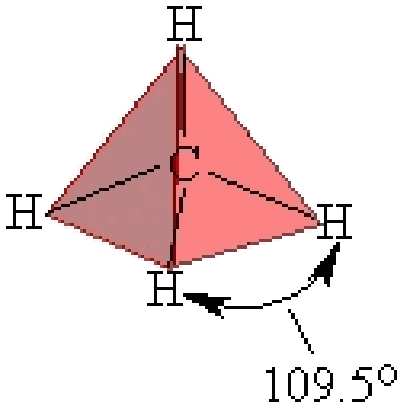
β-D-fructose

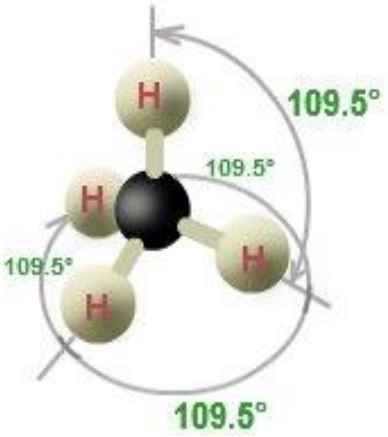
Haworth projection

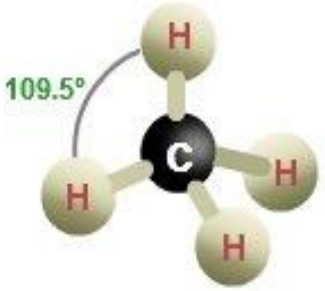
Conformers

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

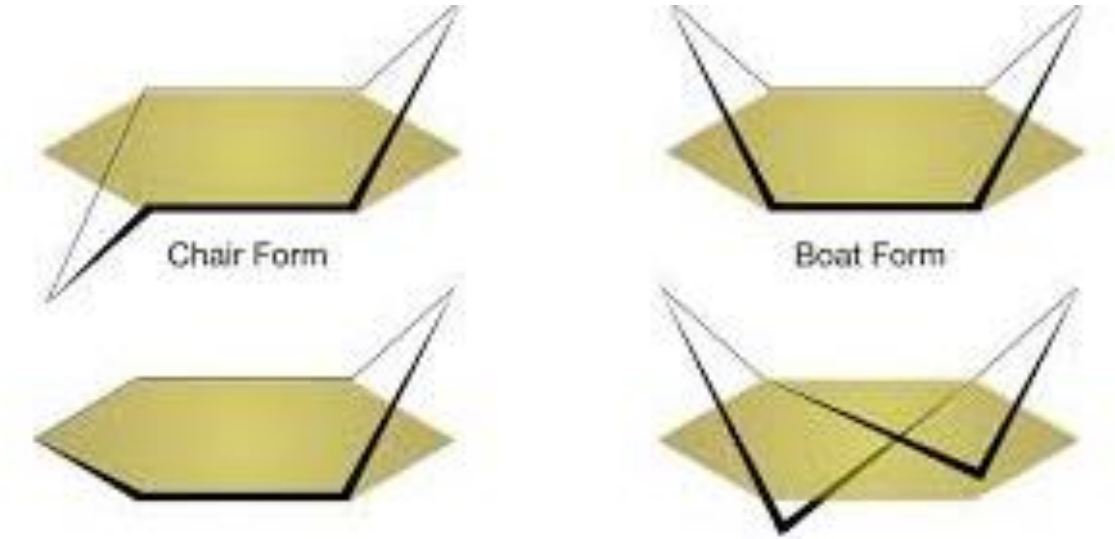
Conformers







Carbon atoms are tetrahedral



Conformers are stereoisomers with different rotations about single bonds

Conformers

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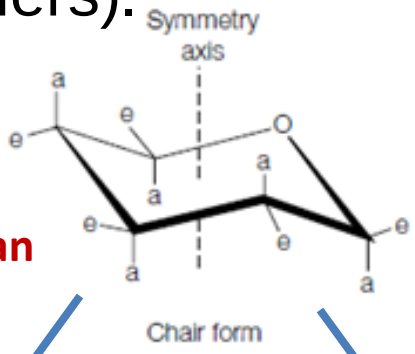
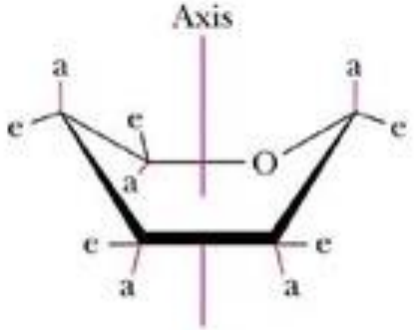
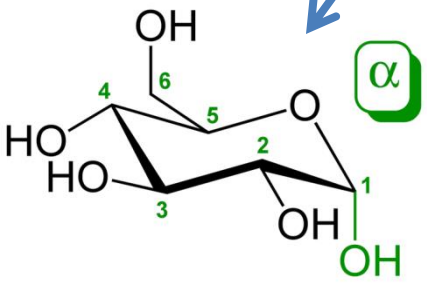


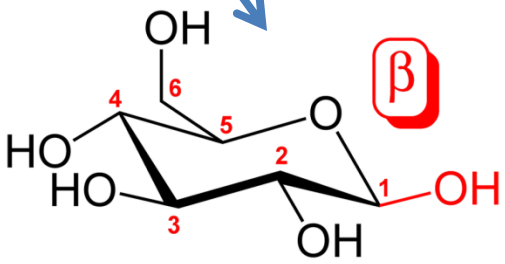
a: axial
e: equatorial



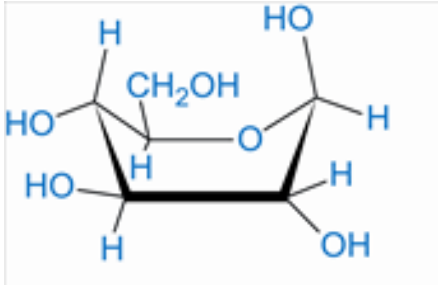
α is Less stable than β due to steric repulsion



Chair form of α-D-glucose



Chair form of β-D-glucose



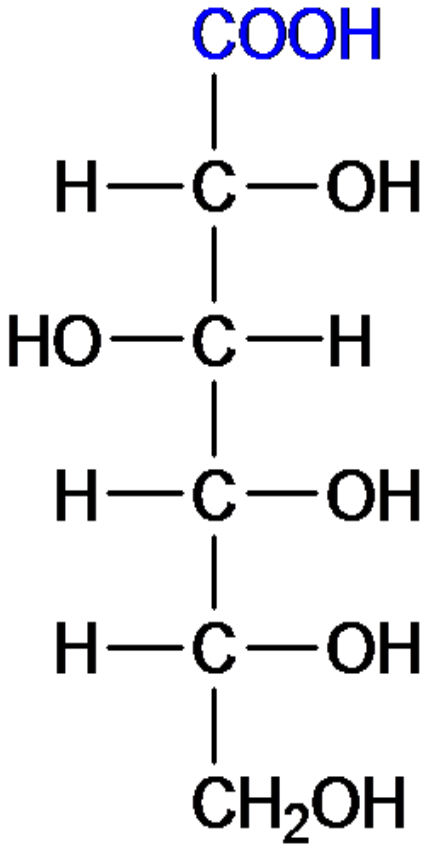
Boat form of β-D-glucose

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^+ (6.5 mmol/L) occurring due to kidney failure



Sugar Modification

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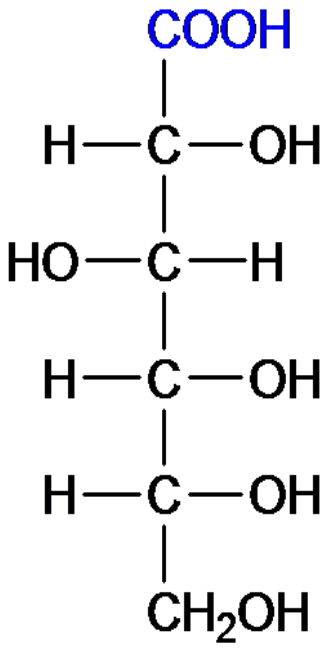
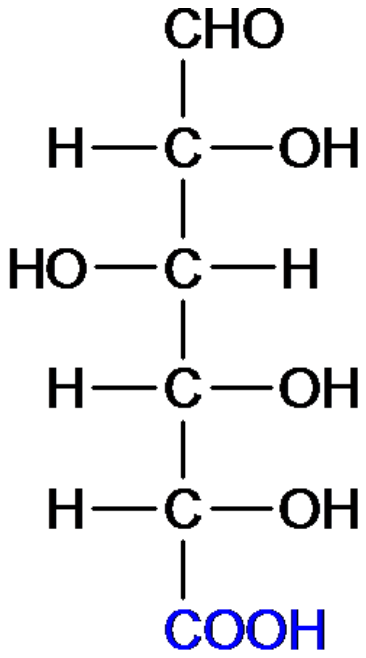
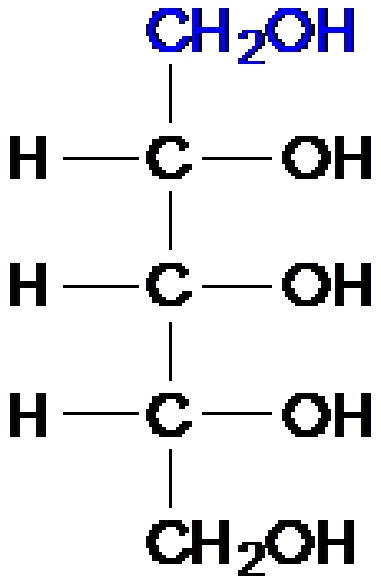


2. **Uronic acids : oxidation of OH at (C6) to carboxylic acid; e.g. D-glucuronic acid**



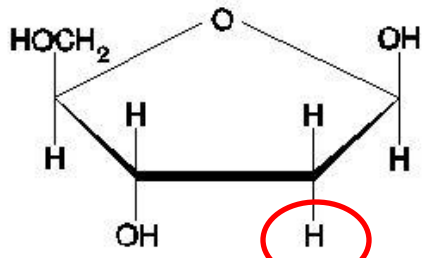
3. **Alditols : reduction of carbonyl group to alcohol; e.g. D-ribitol, D-glycerol and D-sorbitol (sweetener)**



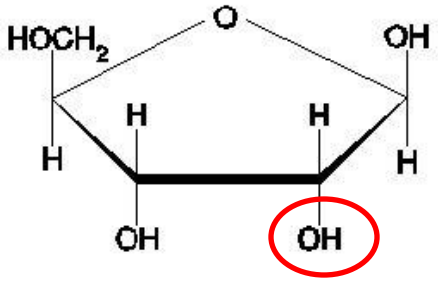
D-ribitol

Sugar Modification

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



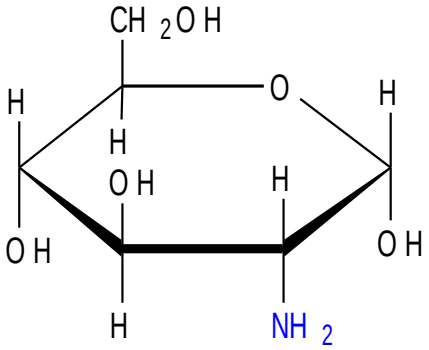
Deoxyribose



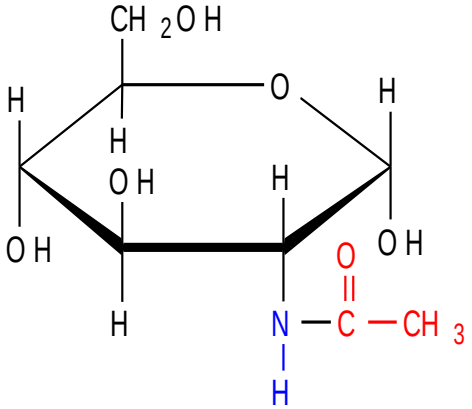
Ribose

4. **Amino sugars : one or more OH groups are replaced by amino group which is often acetylated;**

- **α-D-glucosamine (rebuild cartilage in osteoarthritis & osteoporosis) and α-D-N-acetylglucosamine (both are derivatives of of α-D-glucose)**



α-D-glucosamine



α-D-*N*-acetylglucosamine