Carbohydrates

Carbohydrates

- Carbohydrate is a collective name of polyhydroxy aldehyde or ketones, and their condensational products or derivatives.
- Synthesized by plants using sunlight to convert CO_2 and H_2O to glucose and O_2.
- Most sugars have formula $C_n(H_2O)_n$, “hydrate of carbon.”

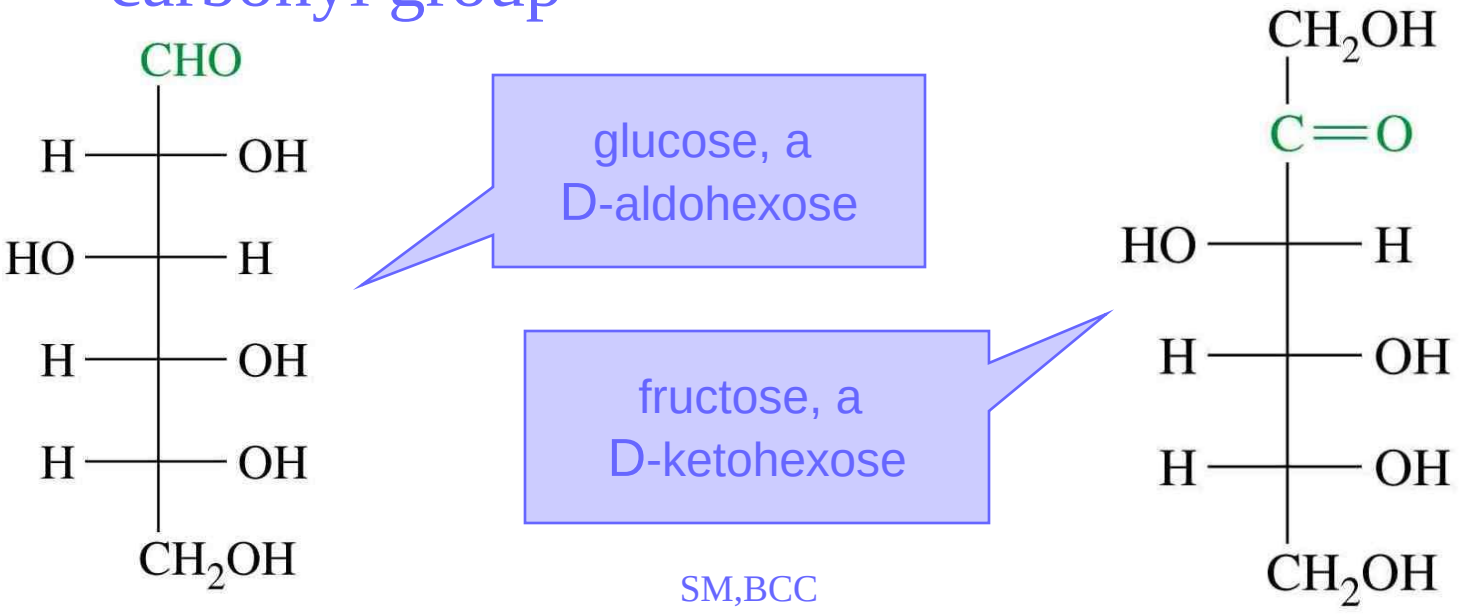
Types of Carbohydrates

Classification based on number of sugar unit

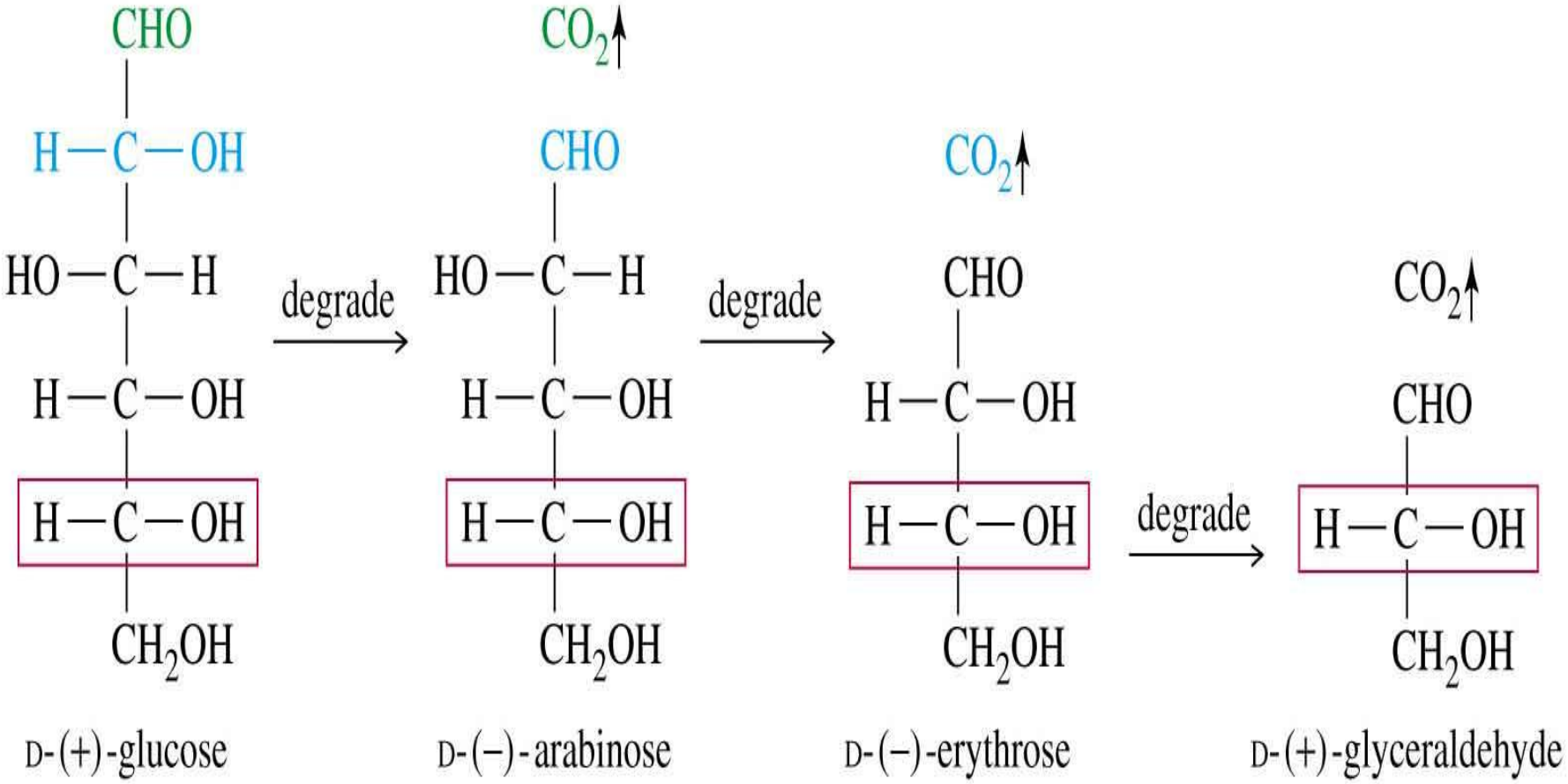
1. Monosaccharides - single sugar unit
   - polyhydroxyaldehydes or aldoses
   - polyhydroxyketones or ketoses
   - can not be broken down by hydrolysis.
2. Disaccharides – Two sugar units
3. Oligosccharides - 2 To 10 sugar units
4. Polysccharides – More than 10 sugar units

Monosaccharides

- Classified by:
  - aldose or ketose
  - number of carbons in chain
  - configuration of chiral carbon farthest from the carbonyl group

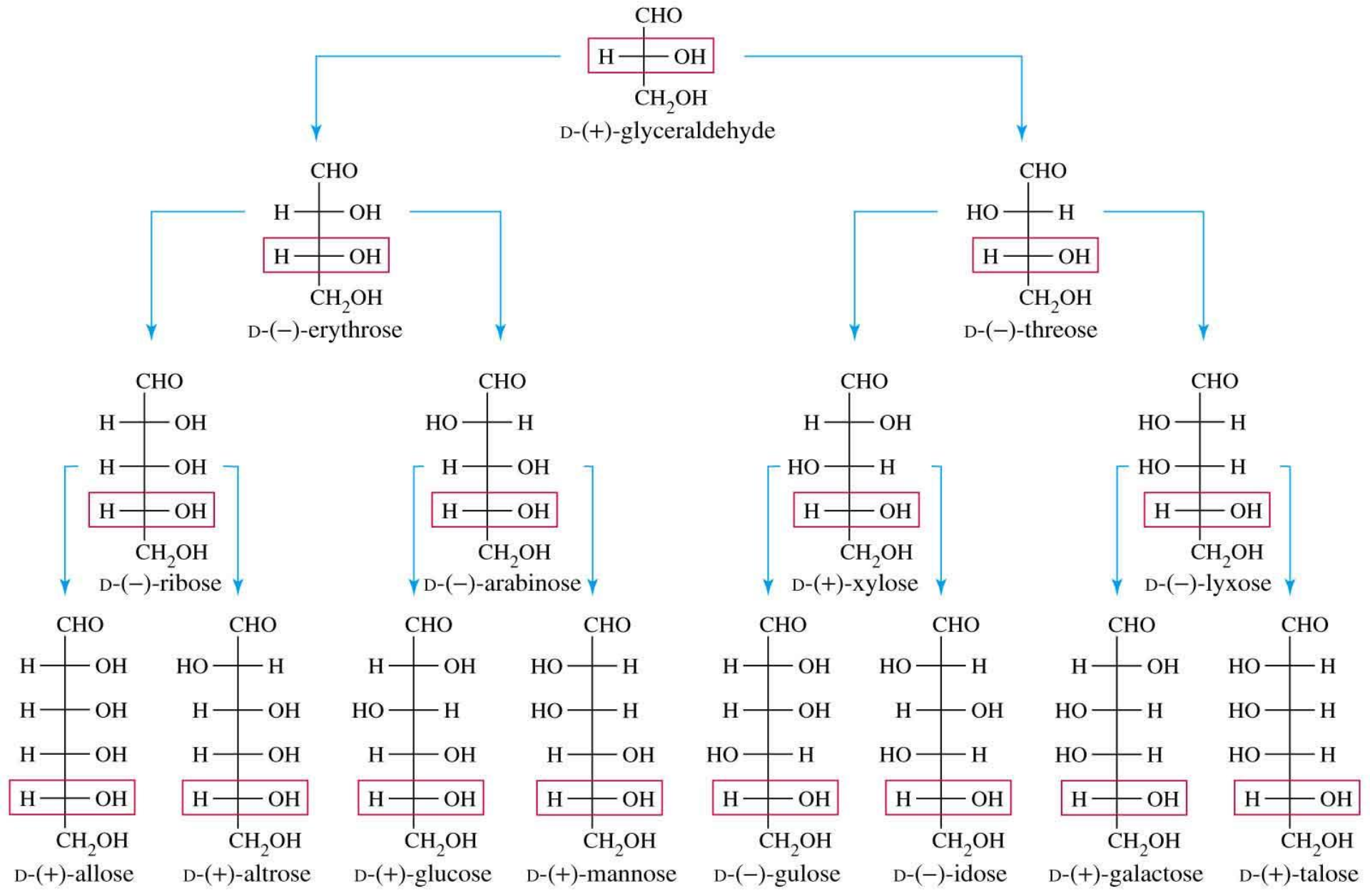


D-Family of Sugars



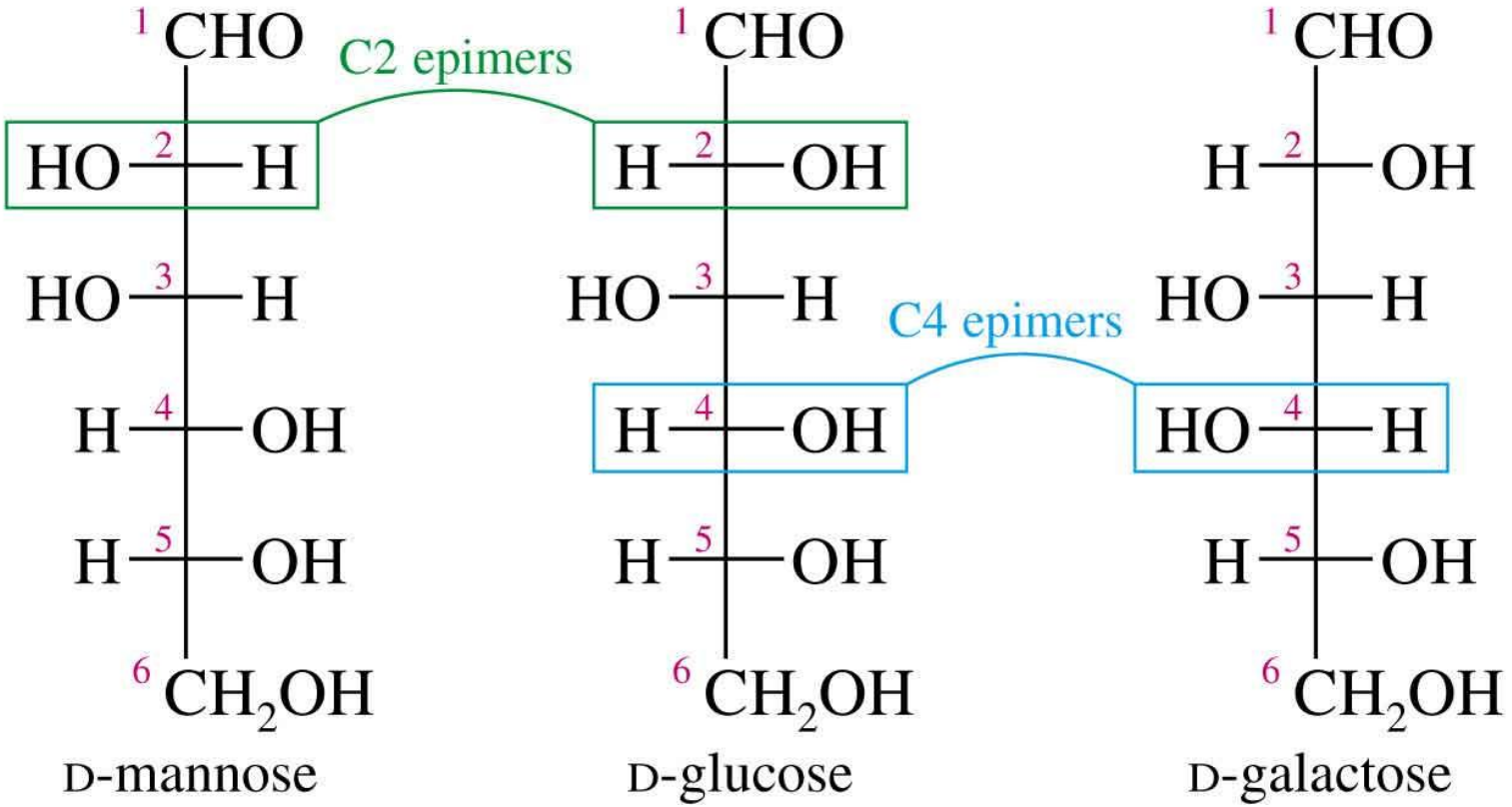
D-(+)-glucose D-(−)-arabinose D-(−)-erythrose D-(+)-glyceraldehyde

The D Aldose Family



Epimers

Sugars that differ only in their stereochemistry at a single carbon.

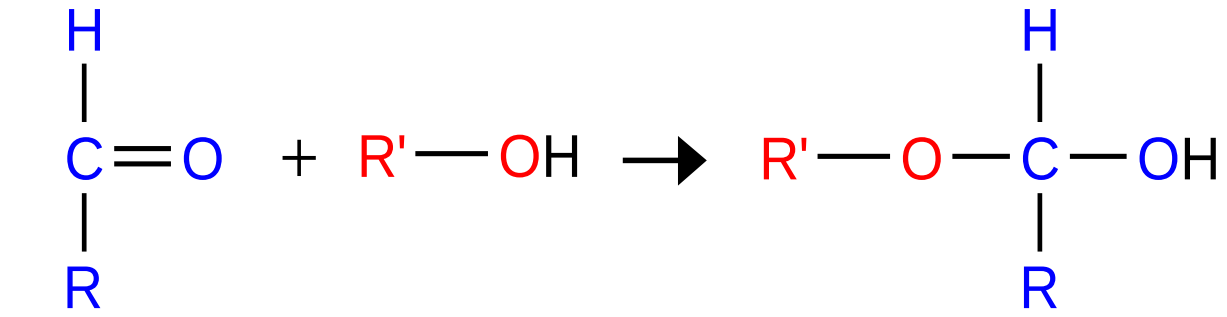


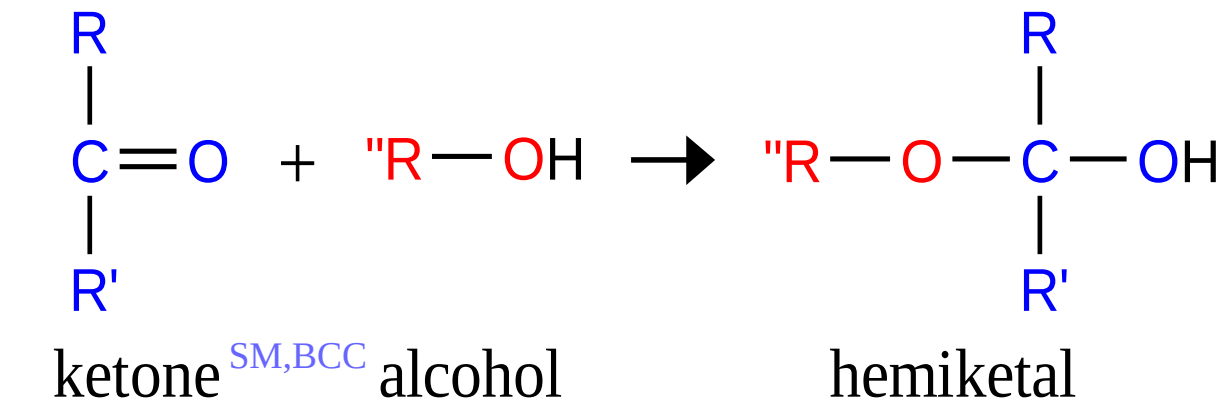
Cyclic Forms of Carbohydrates

Hemiacetal & hemiketal formation

An aldehyde can react with an alcohol to form a **hemiacetal**.

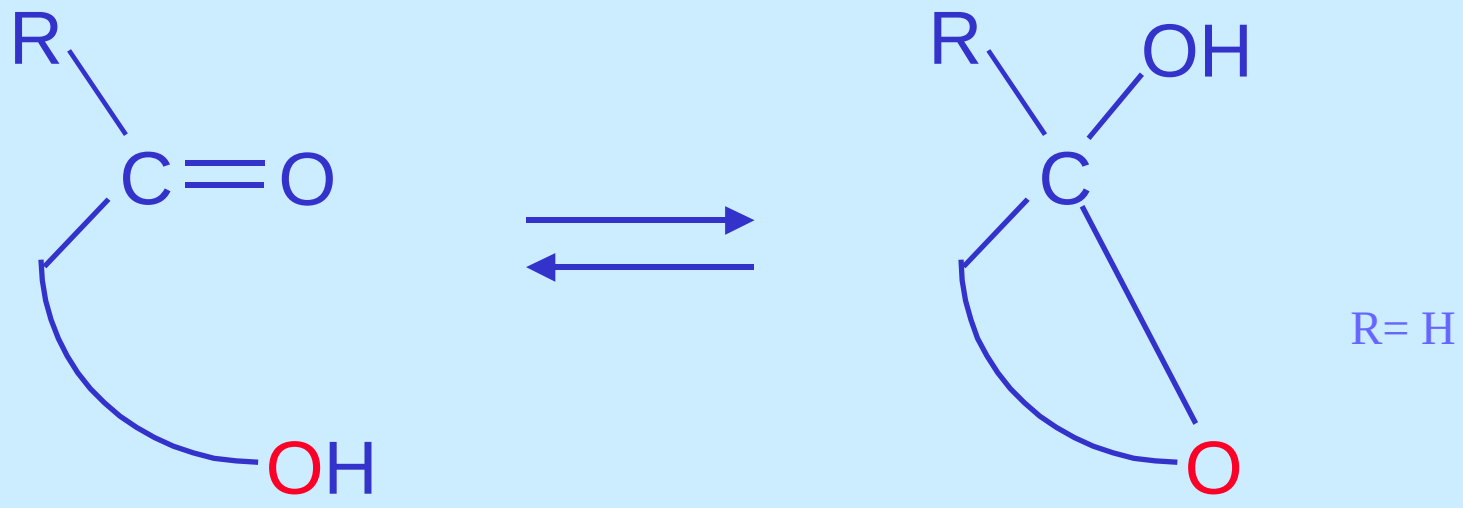
A ketone can react with an alcohol to form a **hemiketal**.





SM,BCC

Cyclic Hemiacetals

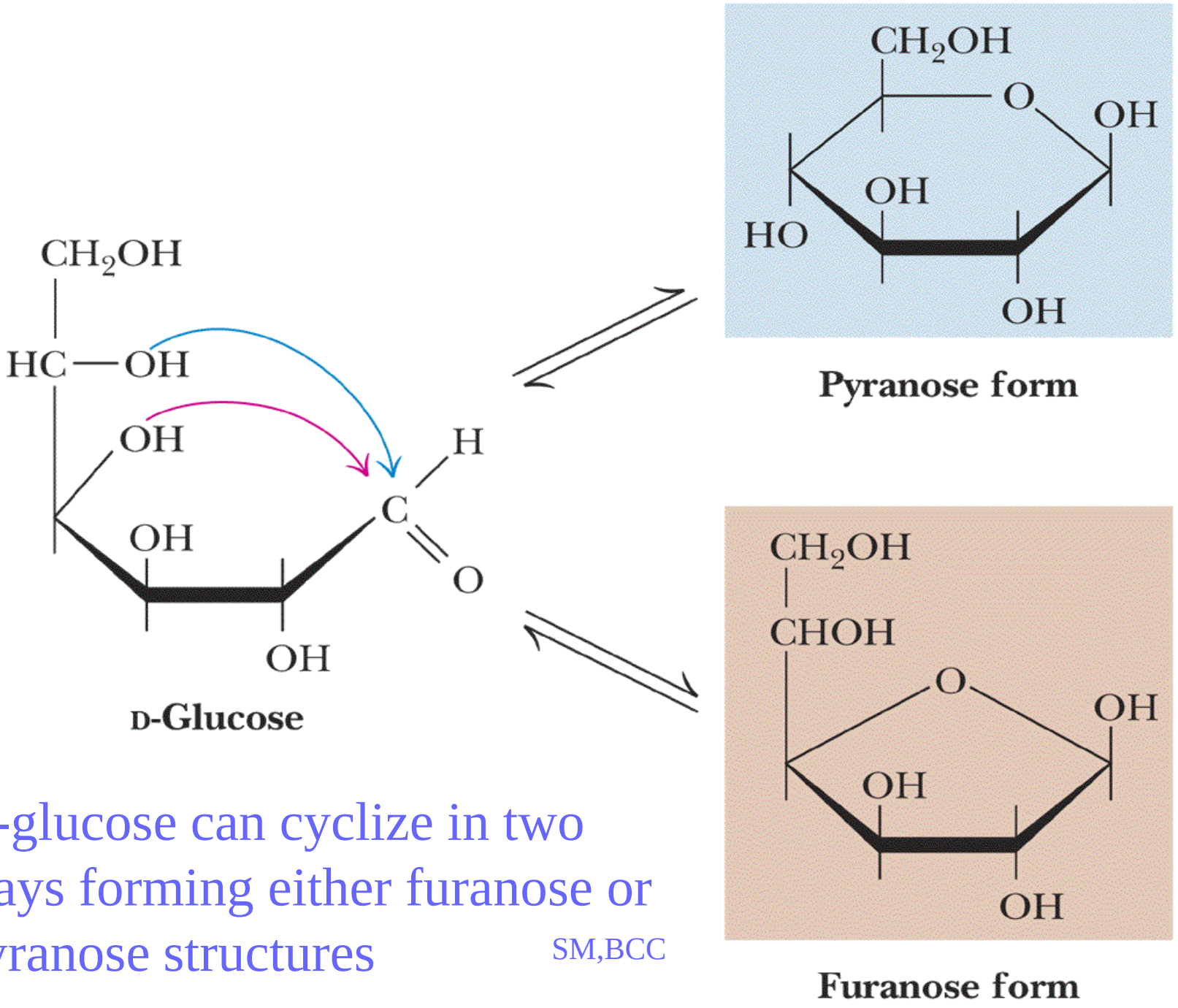


R= H

Aldehydes and ketones that contain an OH group elsewhere in the molecule can undergo intramolecular hemiacetal formation.

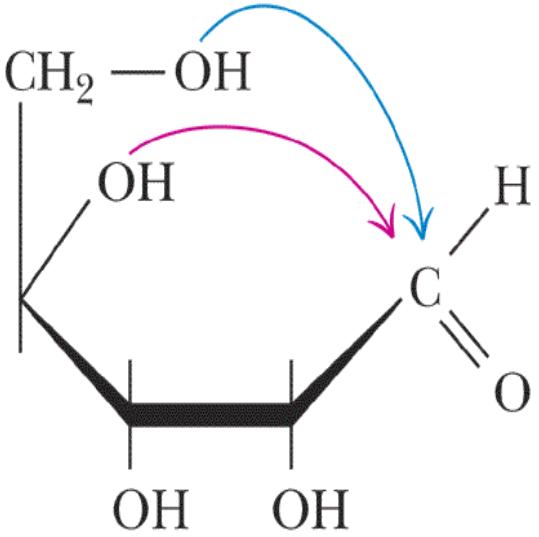
The equilibrium favors the cyclic hemiacetal if the ring is 5- or 6-membered.

SM,BCC

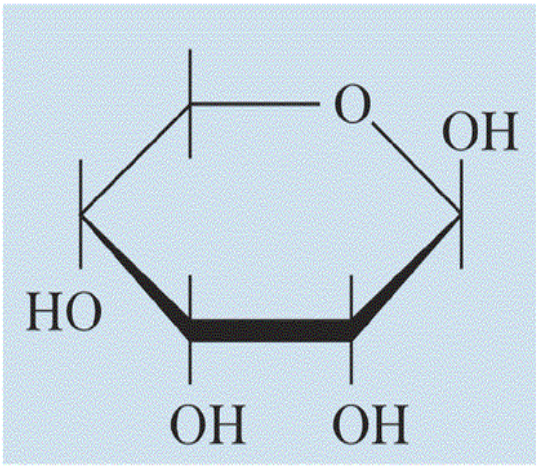


D-glucose can cyclize in two ways forming either furanose or pyranose structures

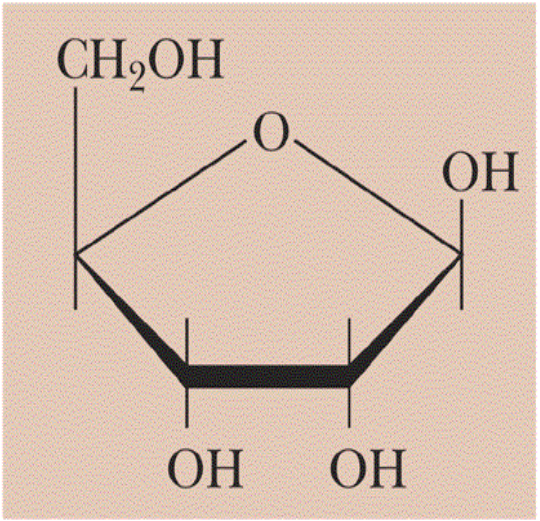
SM,BCC



D-Ribose



Pyranose form



Furanose form

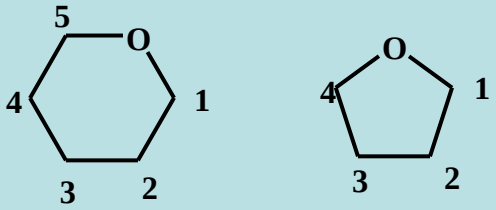
D-ribose and other five-carbon saccharides can form either furanose or pyranose structures

SM,BCC

Rules for drawing Haworth projections

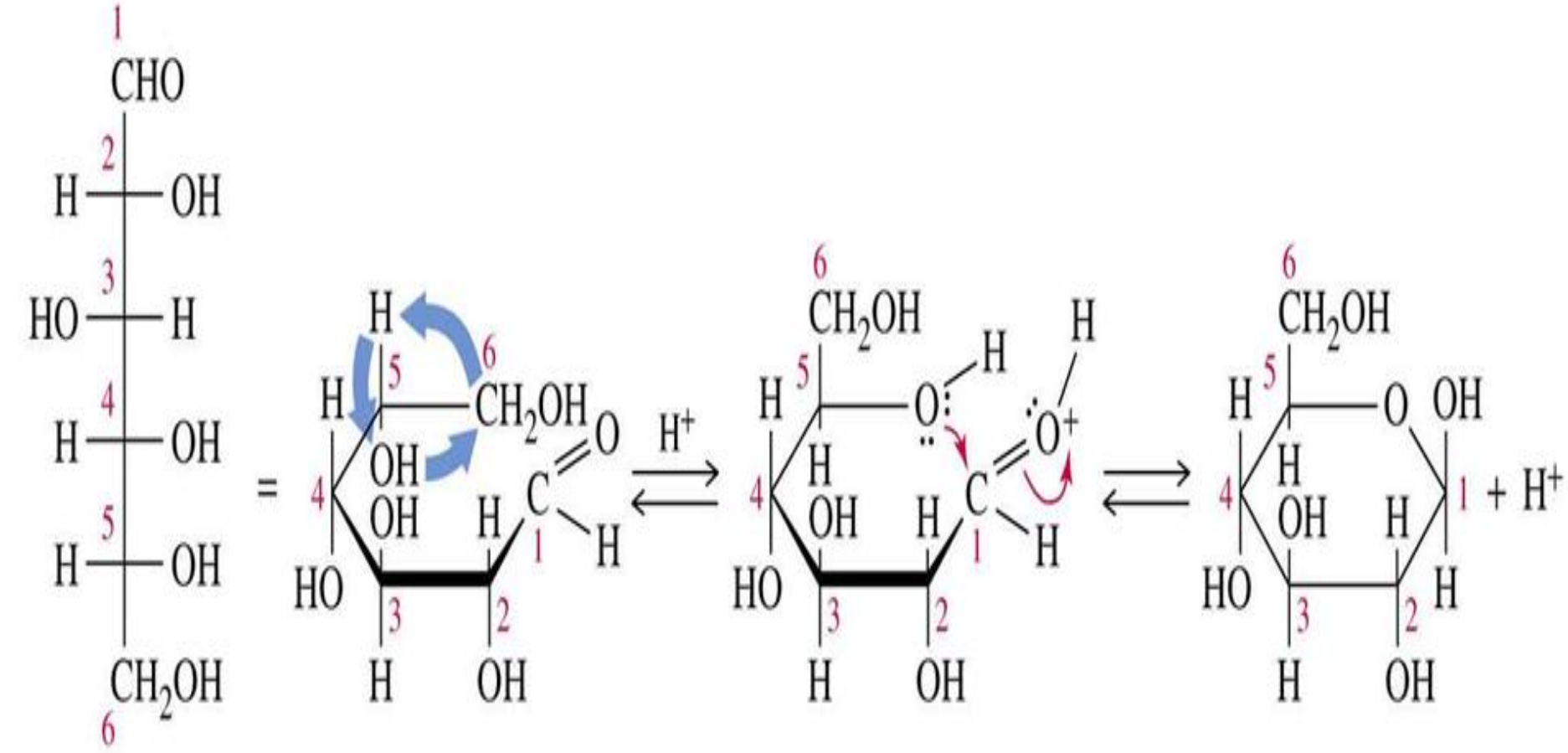
A method to depict ring structures (flat)

- arrange the ring with O in the back or back-right



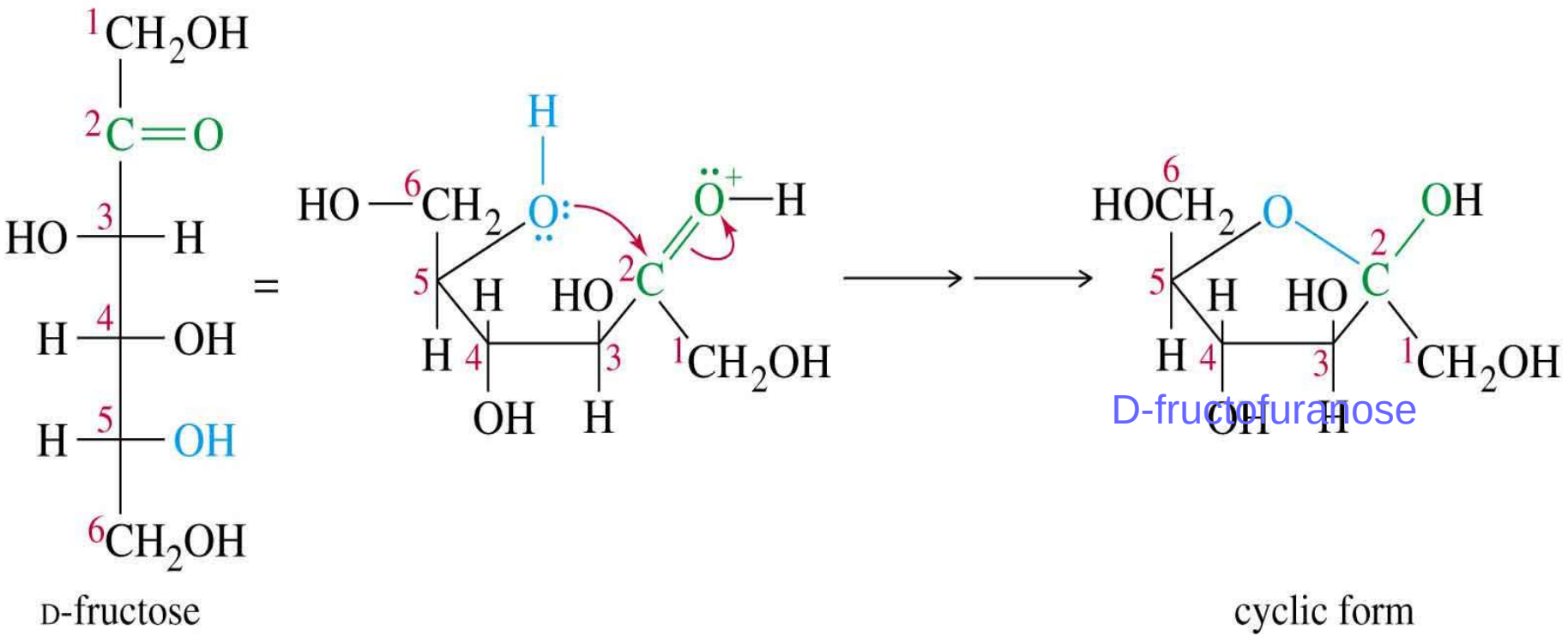
- next number the ring clockwise starting next to the oxygen
- an OH to the right (Fischer) is down (Haworth)
- an OH to the left (Fischer) is up (Haworth)
- D-sugars will have the last CH2OH group up
- the new hemiacetal could have either configuration

Cyclic Structure for Glucose

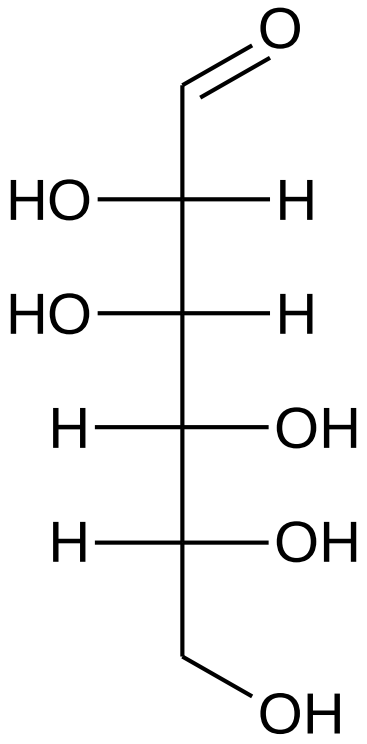


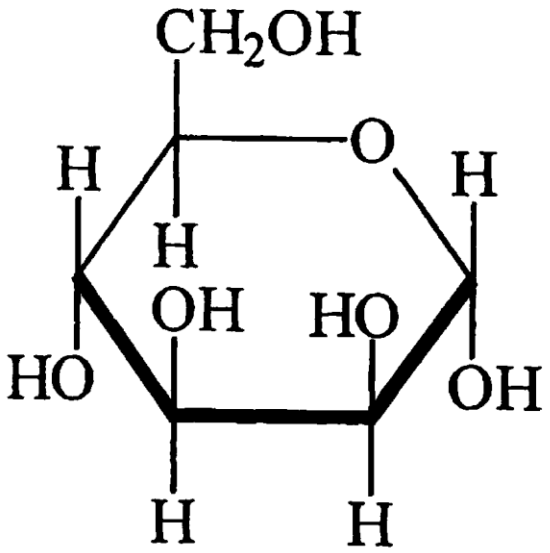
Cyclic Structure for Fructose

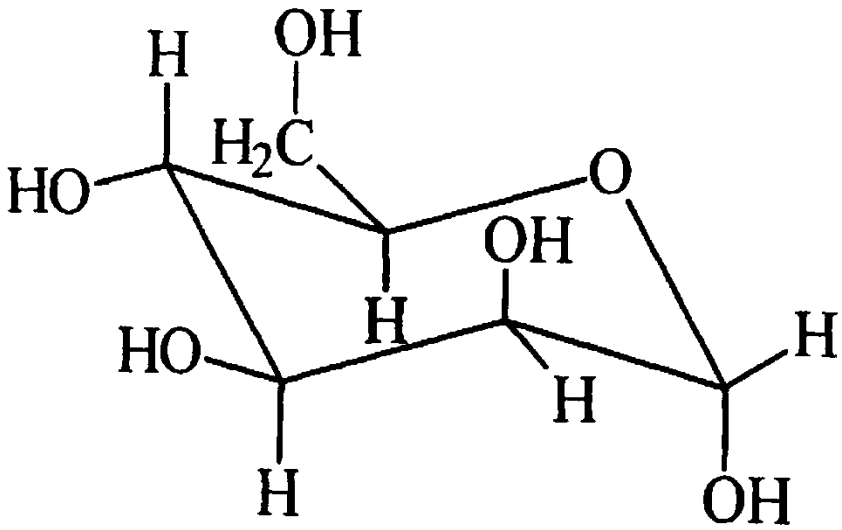
Cyclic hemiacetal formed by reaction of C=O at C2 with -OH at C5.



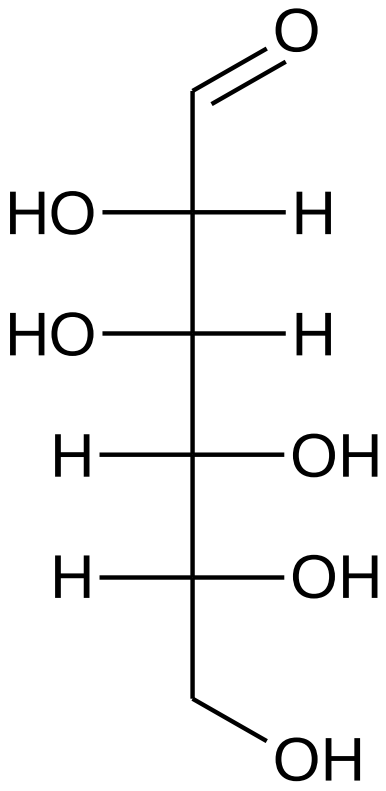
α-D-Mannopyranose

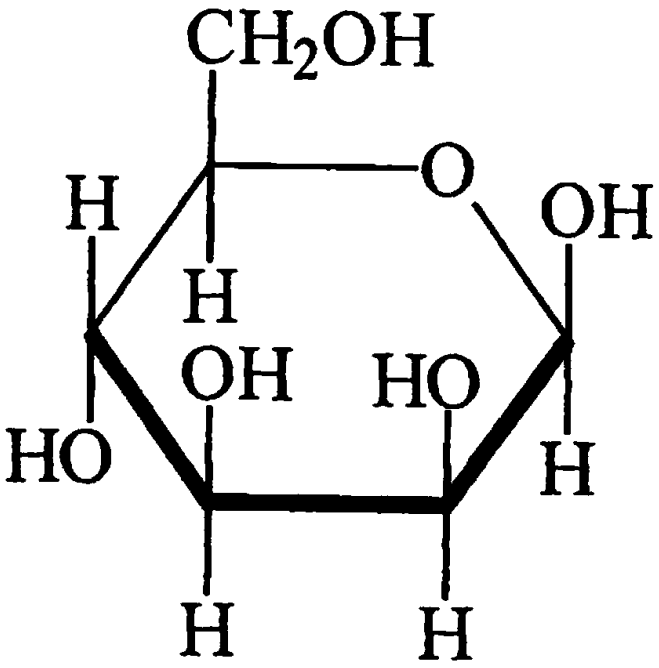


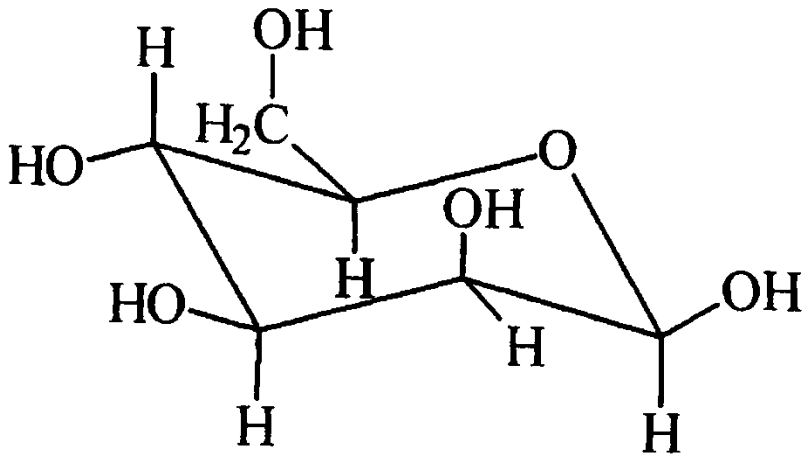




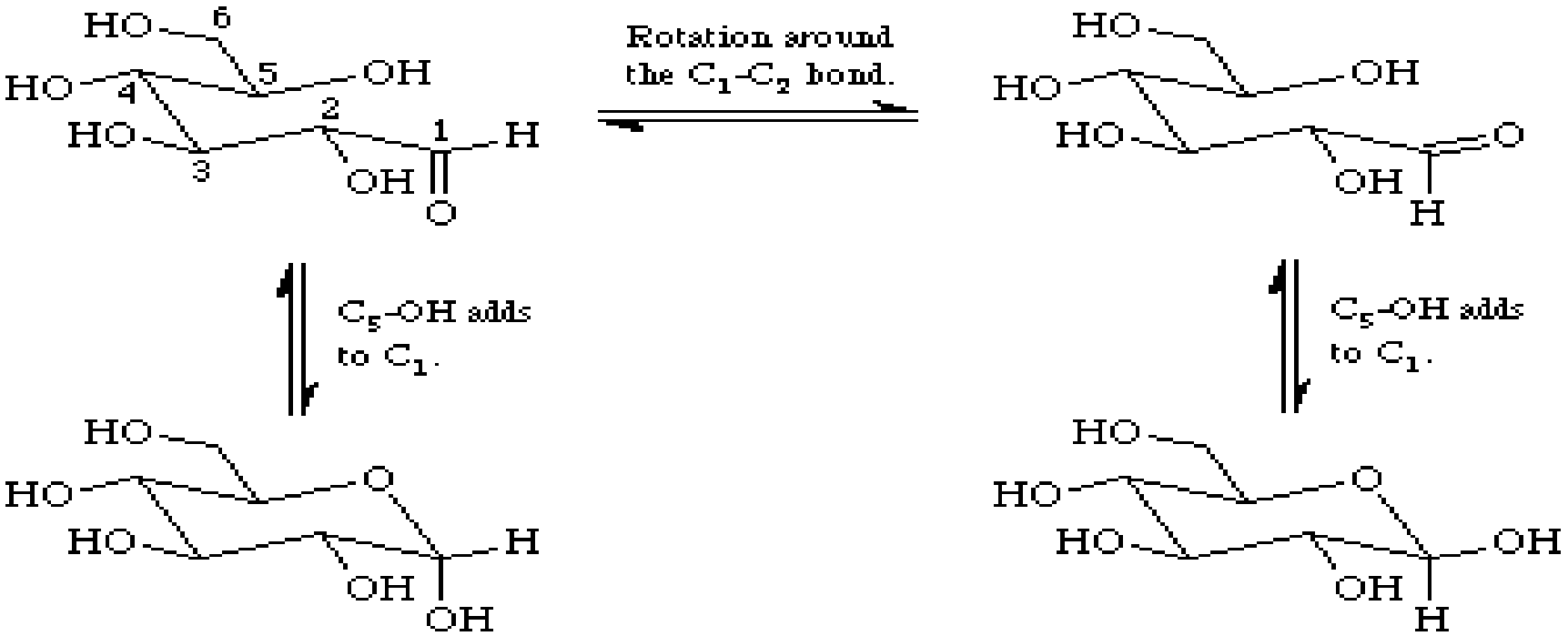
β-D-Mannopyranose



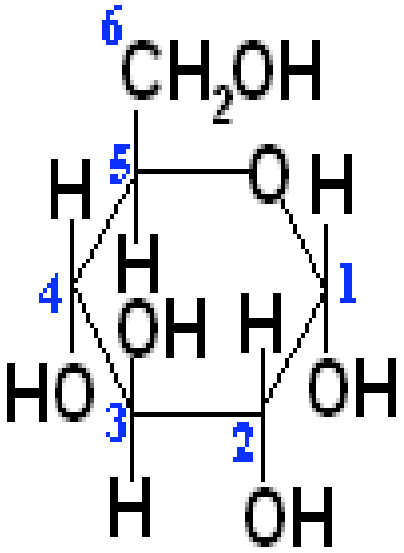




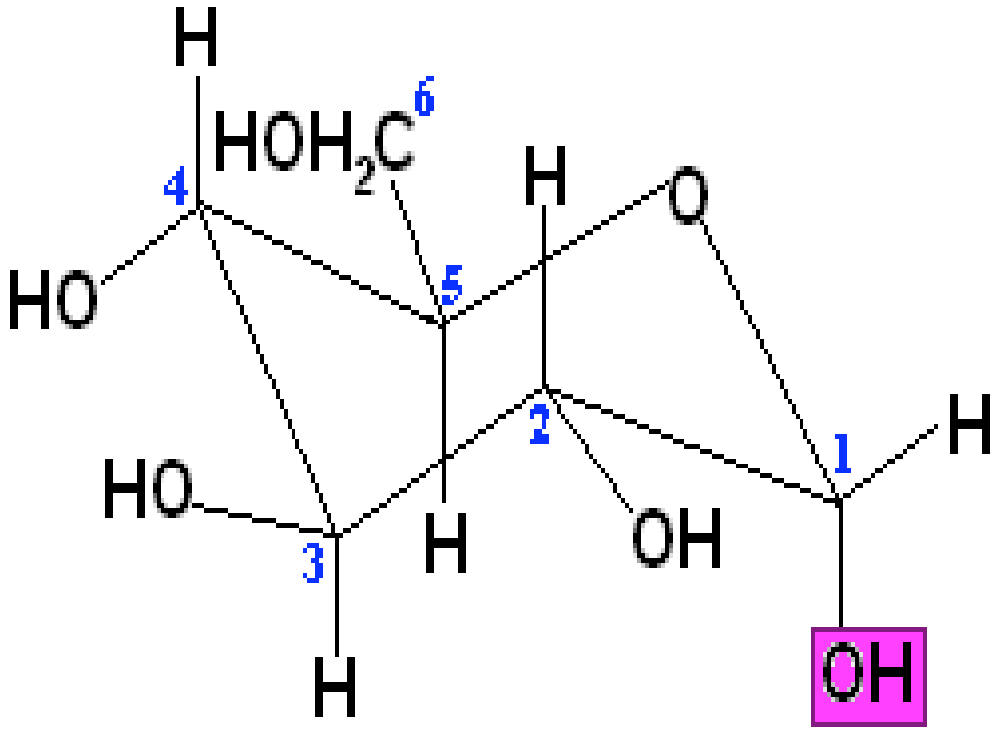
Carbonyl carbon freely rotates



Haworth Projection To Chair Conformation

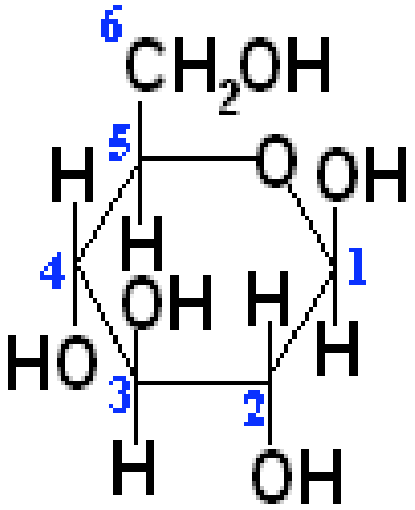


α-D-glucose

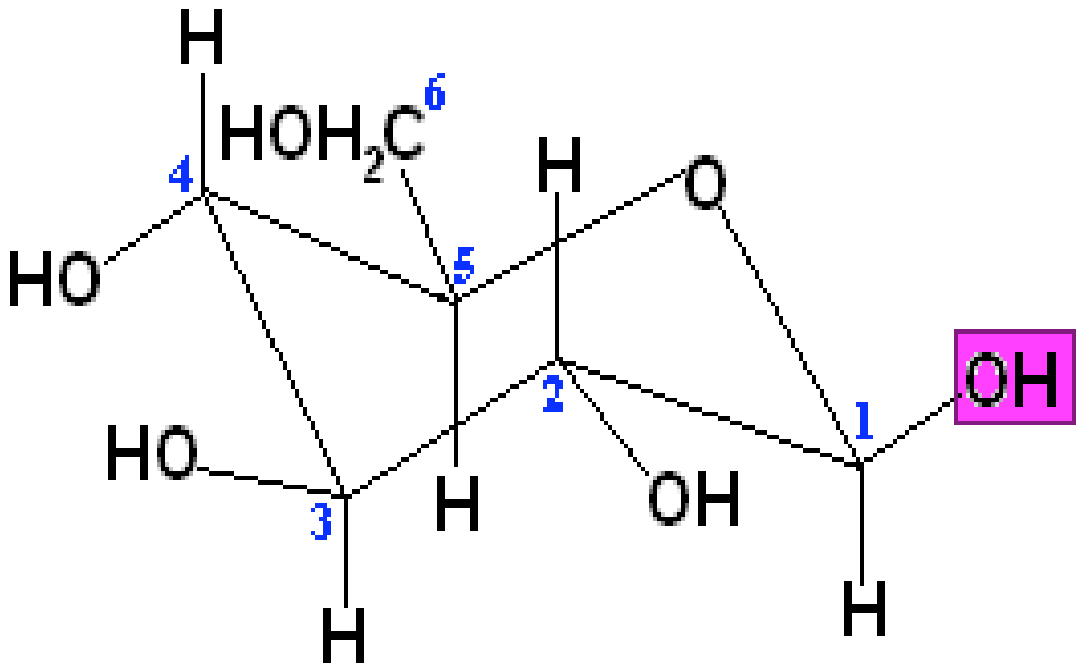


α-D-glucose

Haworth Projection To Chair Conformation

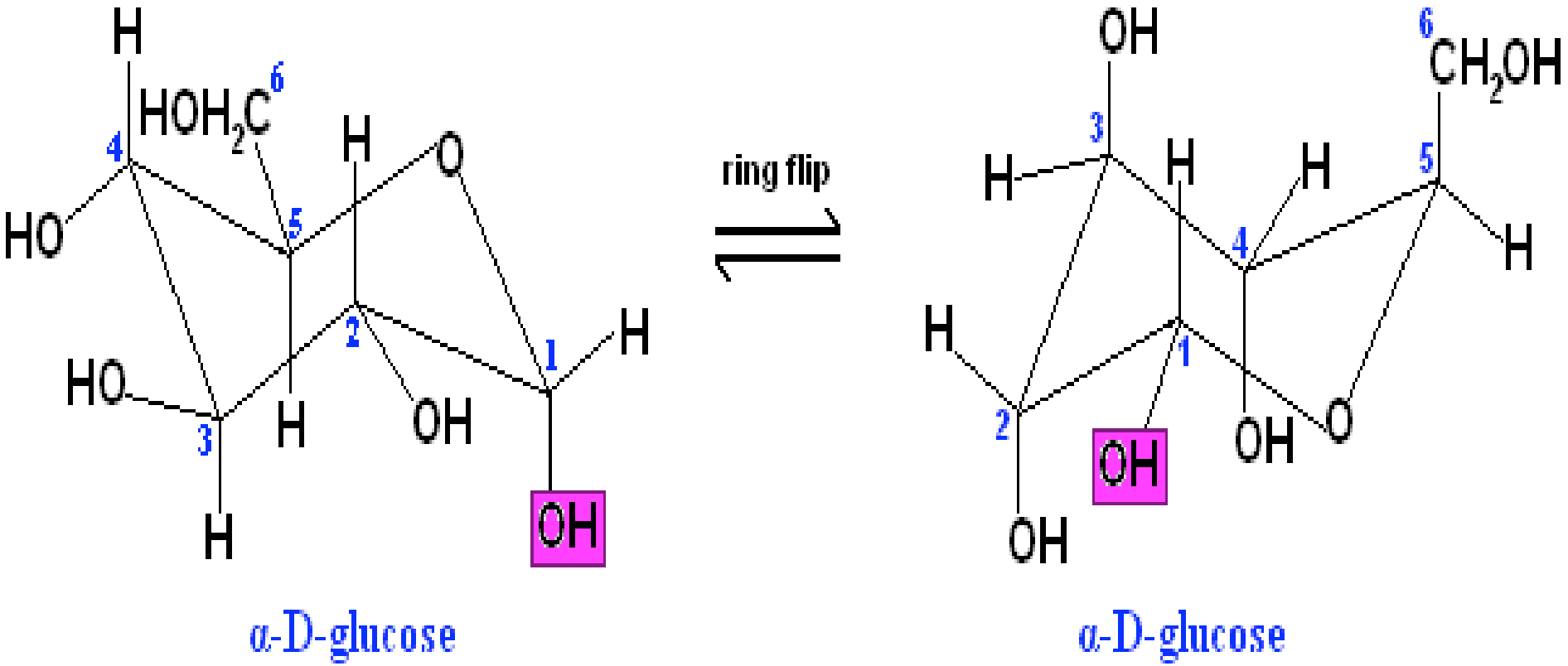


β-D-glucose



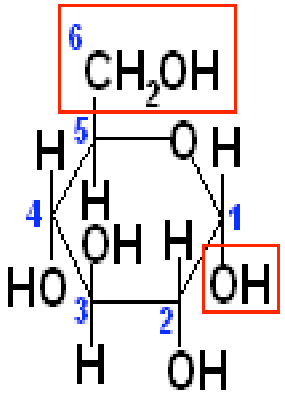
β-D-glucose

Ring Flip in Chair Conformation

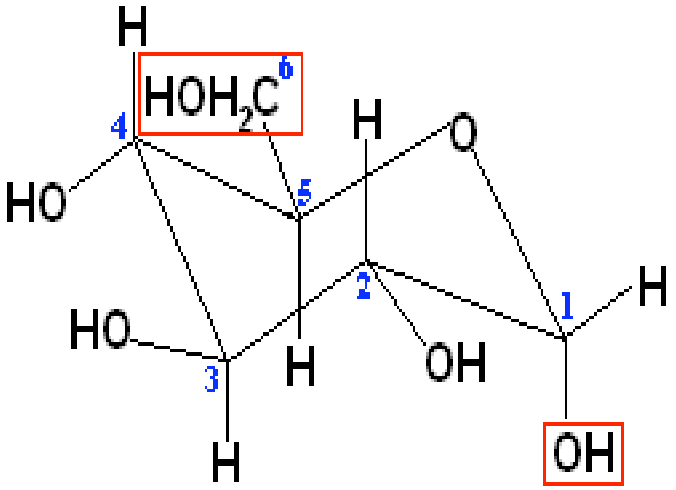


α-D-glucose α-D-glucose

Ring fliping

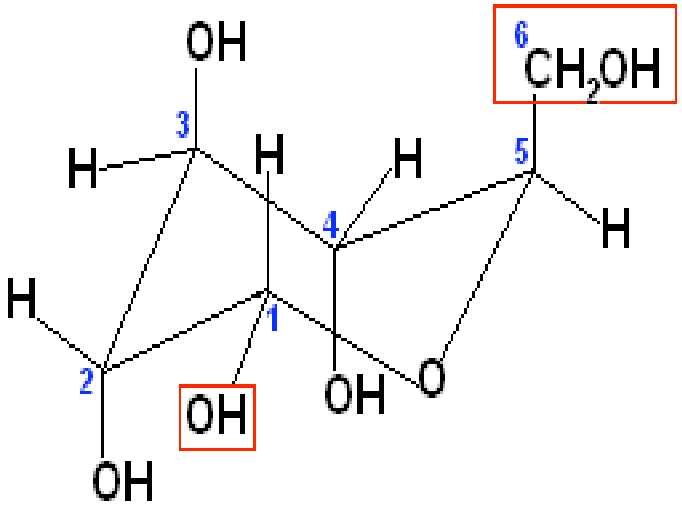


α-D-glucose

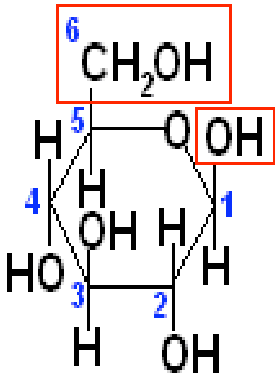


α-D-glucose

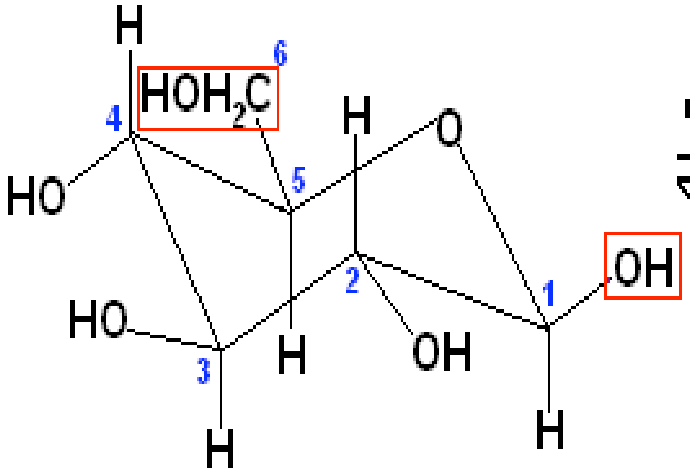
ring flip



α-D-glucose

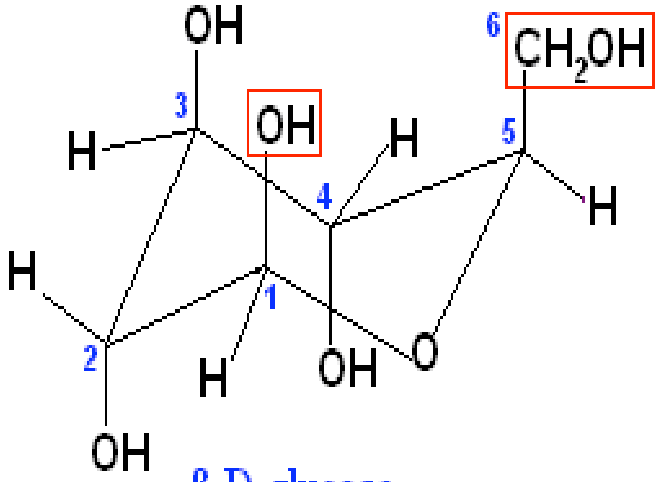


β-D-glucose



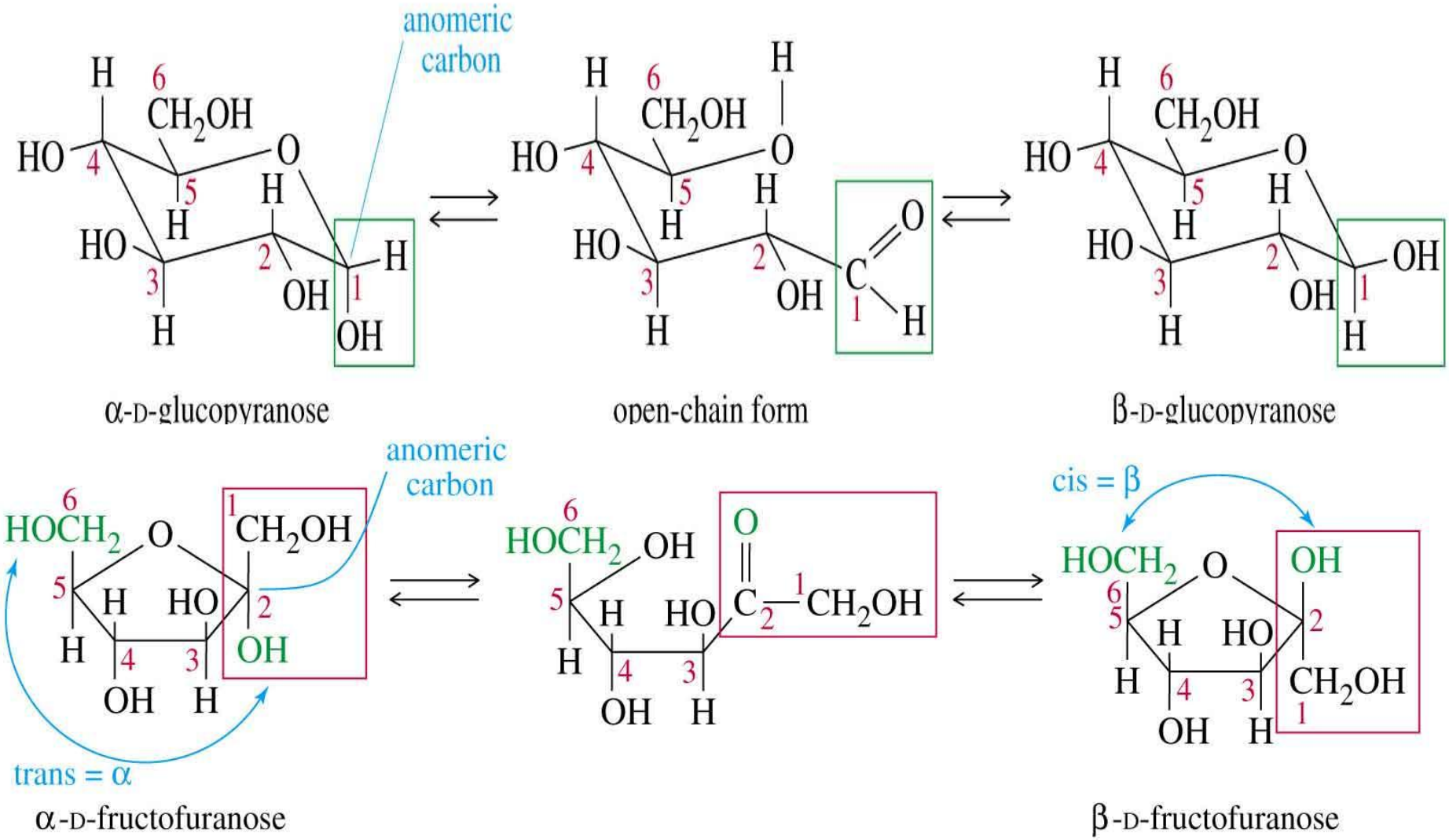
β-D-glucose

ring flip

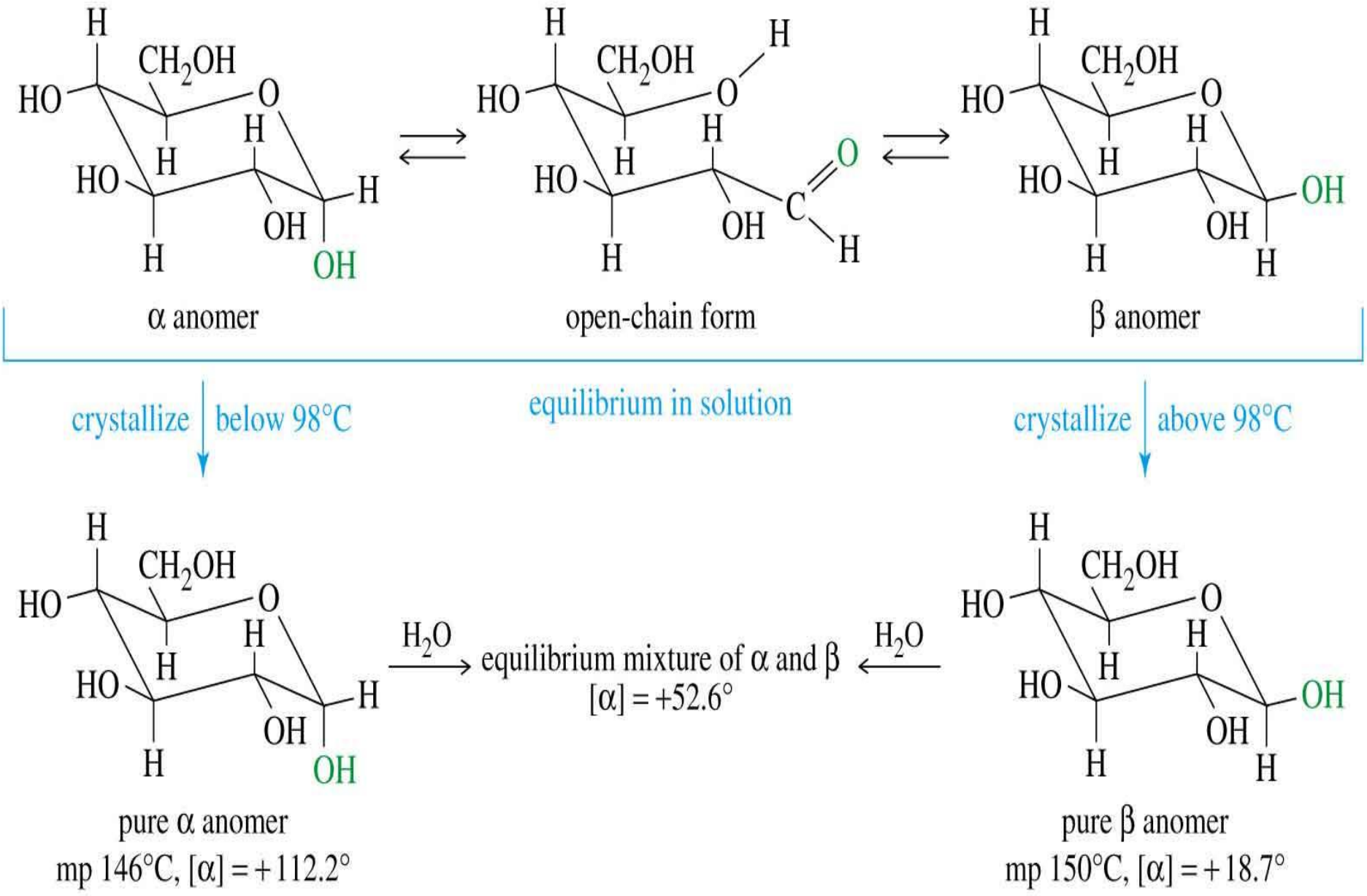


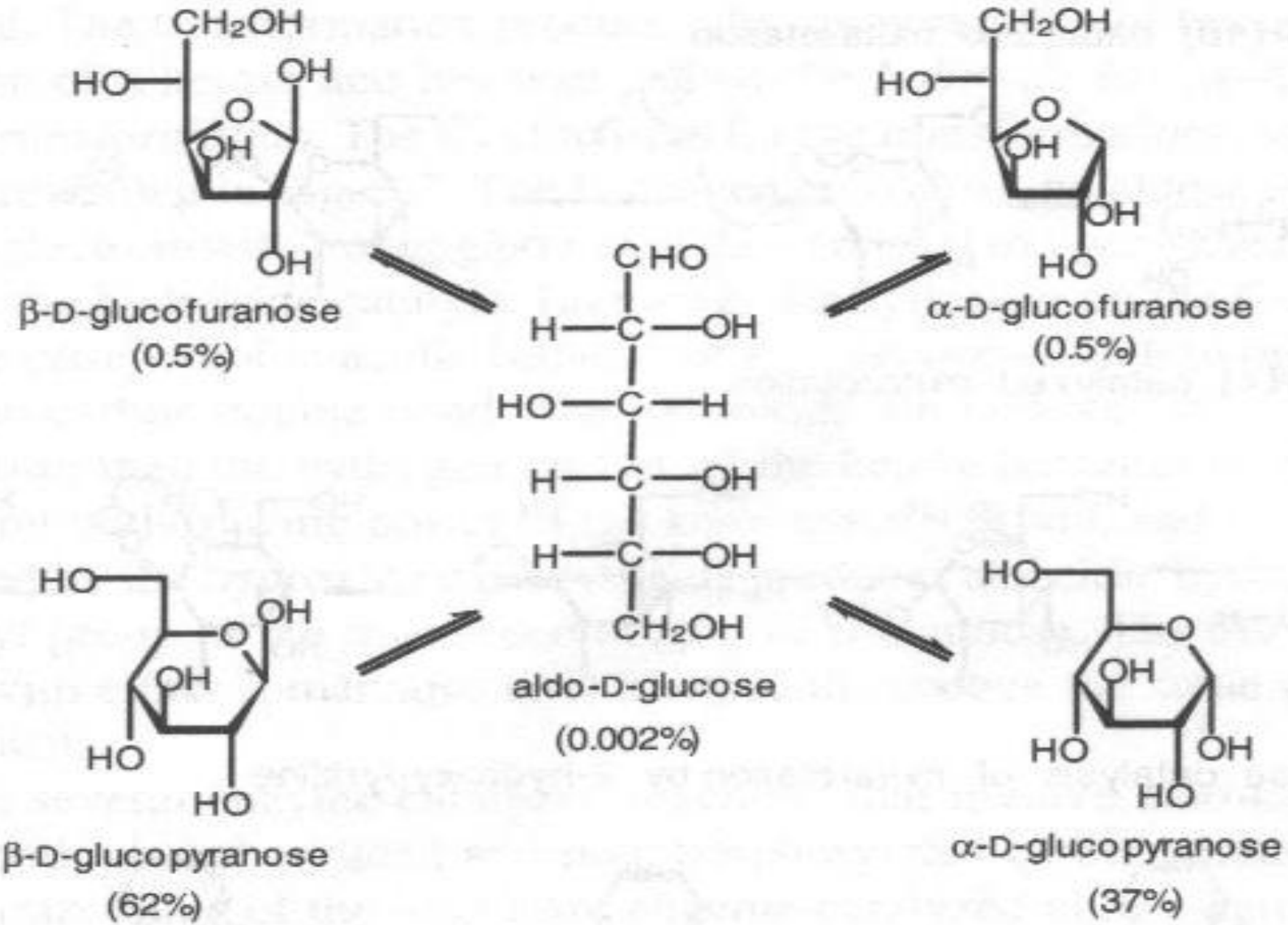
β-D-glucose

Anomers

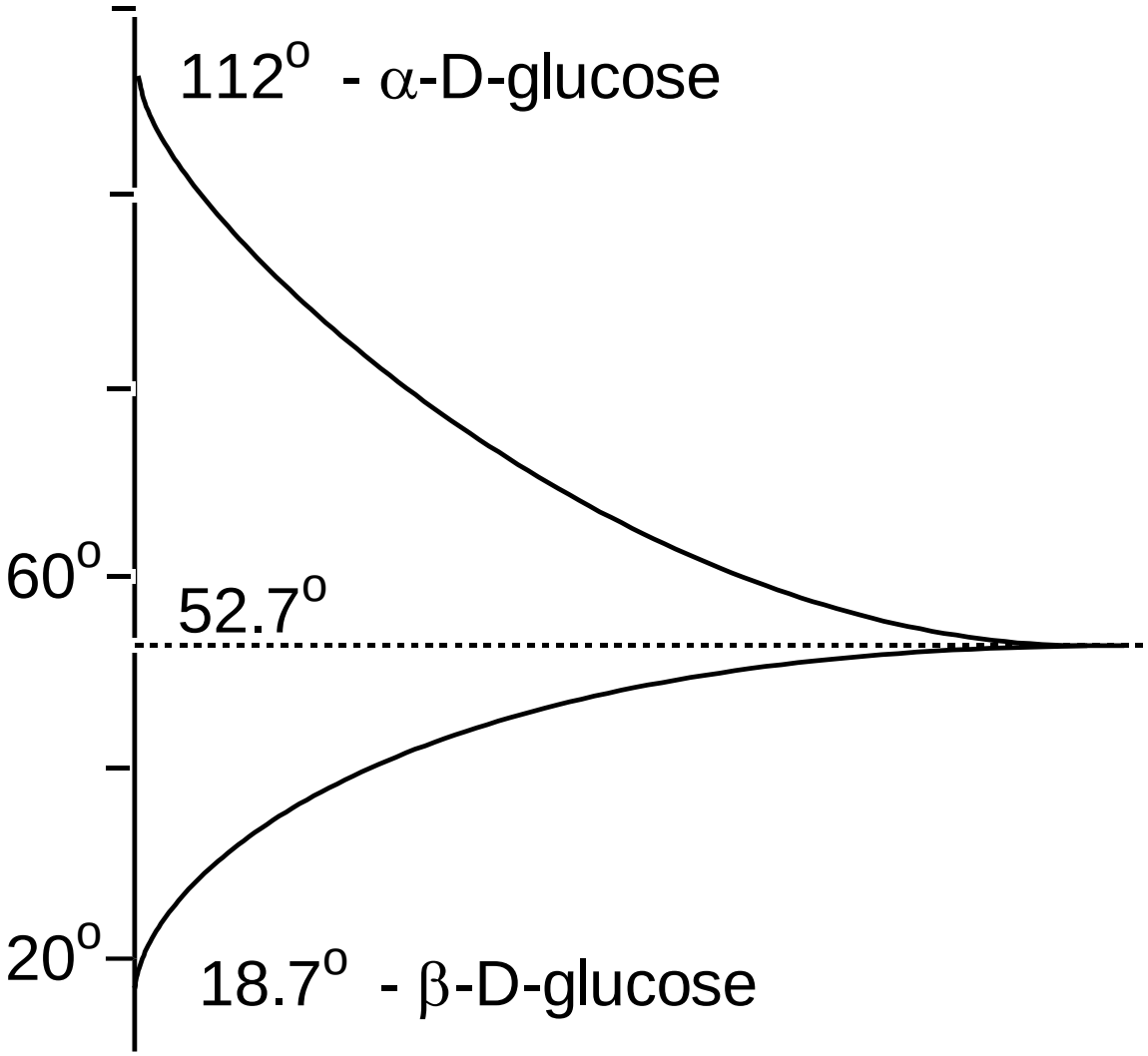

anomeric carbon
α-D-glucopyranose
open-chain form
β-D-glucopyranose
anomeric carbon
cis = β
trans = α
α-D-fructofuranose
β-D-fructofuranose

Mutarotation

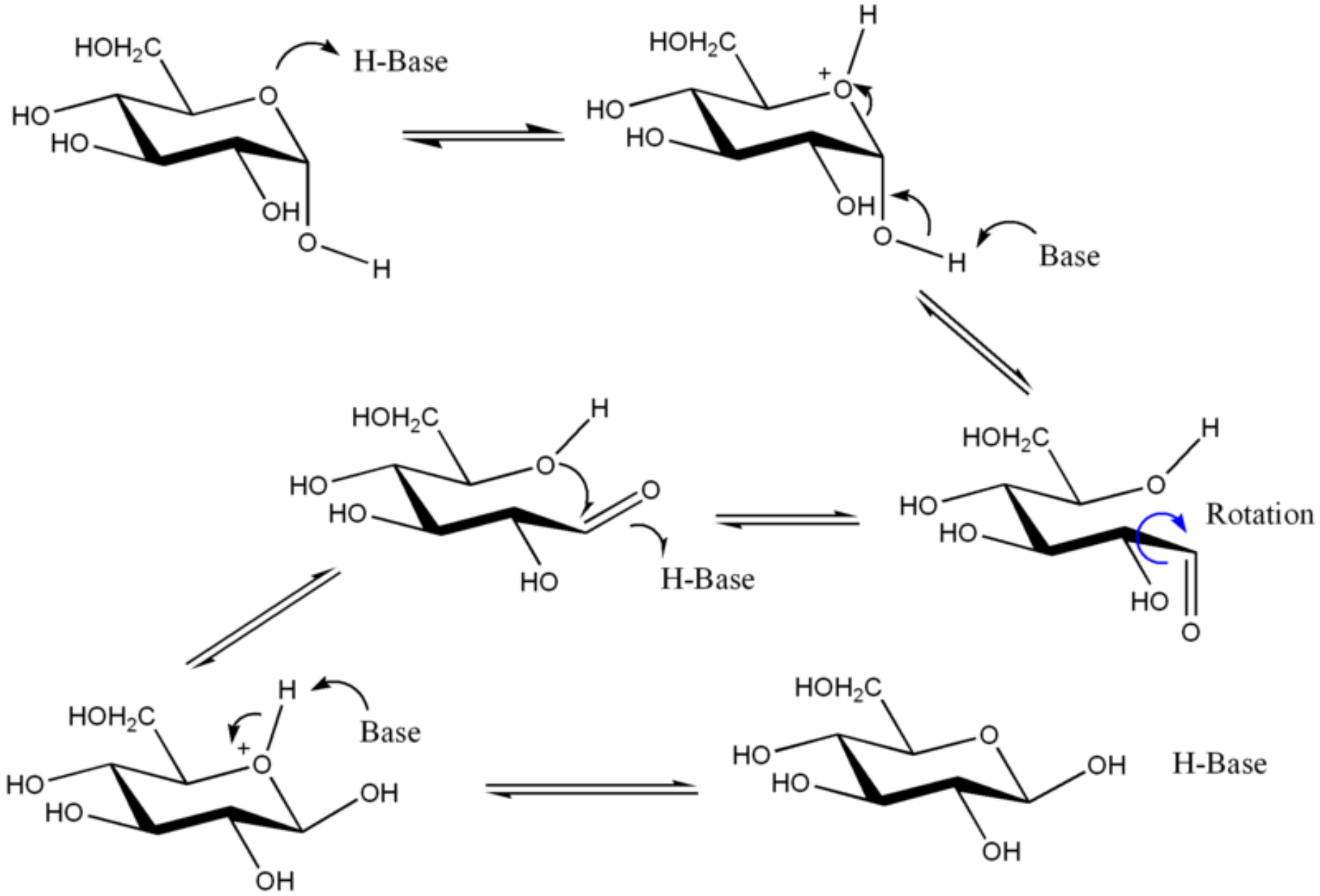



β-D-glucofuranose
(0.5%)
α-D-glucofuranose
(0.5%)
aldo-D-glucose
(0.002%)
β-D-glucopyranose
(62%)
α-D-glucopyranose
(37%)

Mutarotation



Mechanism of Mutarotation



in amphoteric solution such as 2-pyridone, the rate of mutarotation would be much faster