Biochemistry of Carbohydrates I

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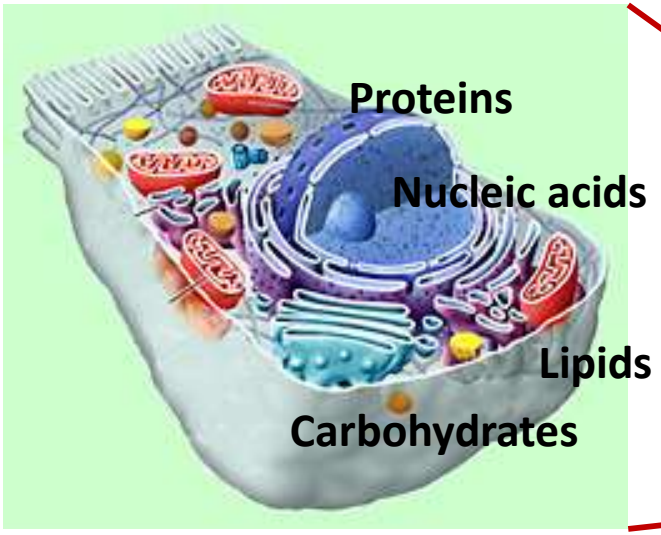
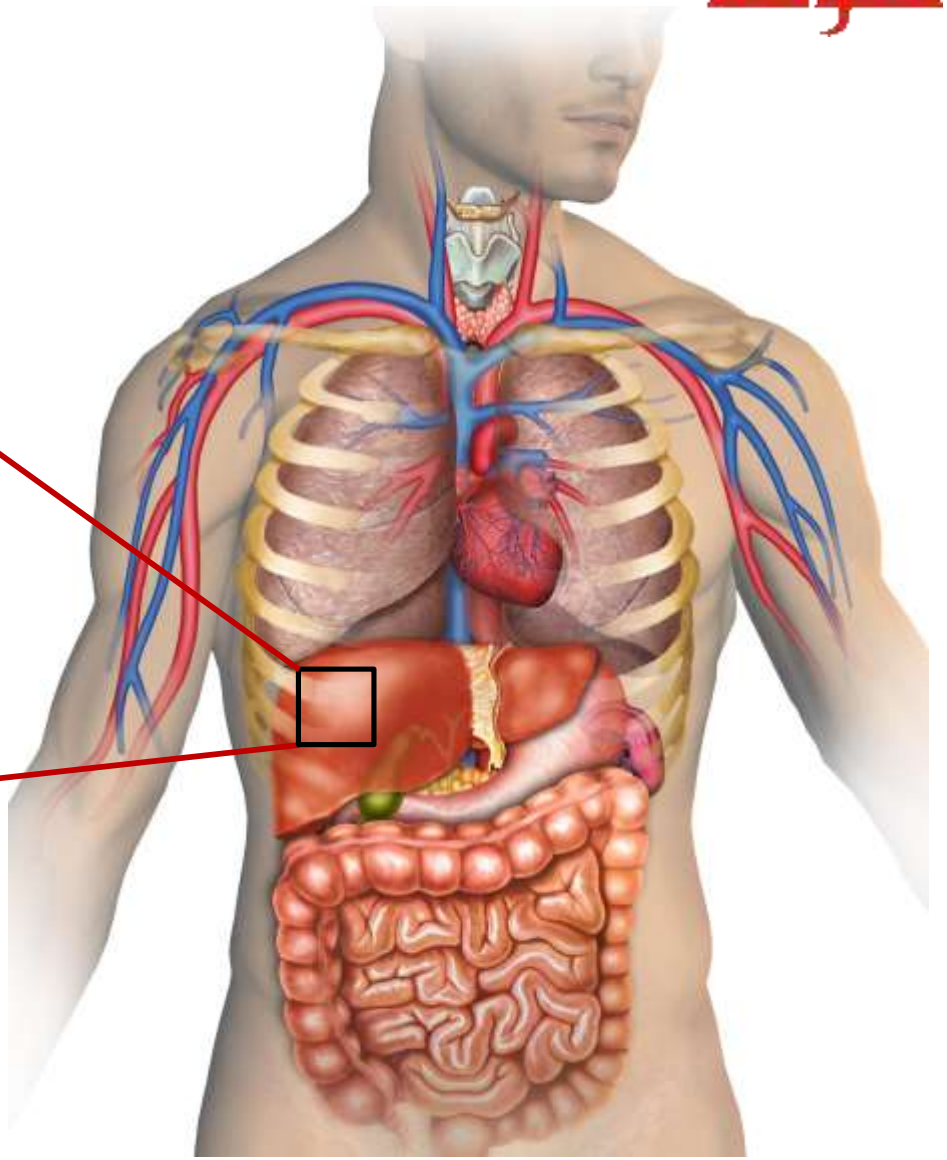
Major Types of Macromolecules





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

Carbohydrates

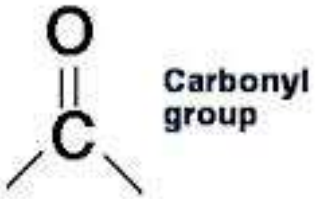
C **H2O**

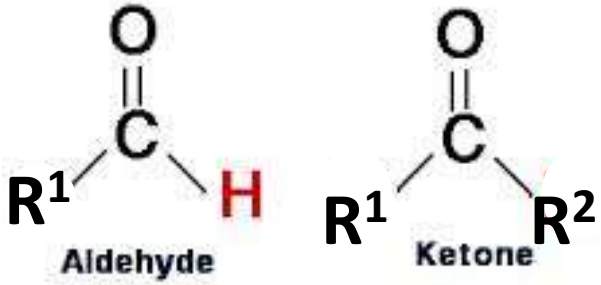
Classification of Carbohydrates

- 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)





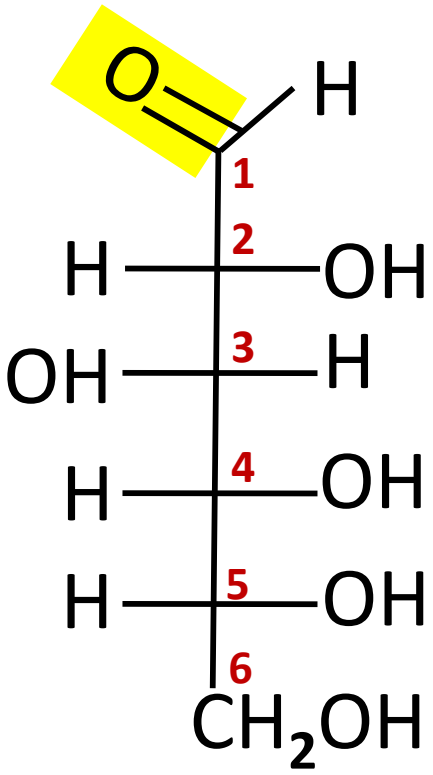
Aldehyde: **R^1 = H, alkyl or aryl**

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

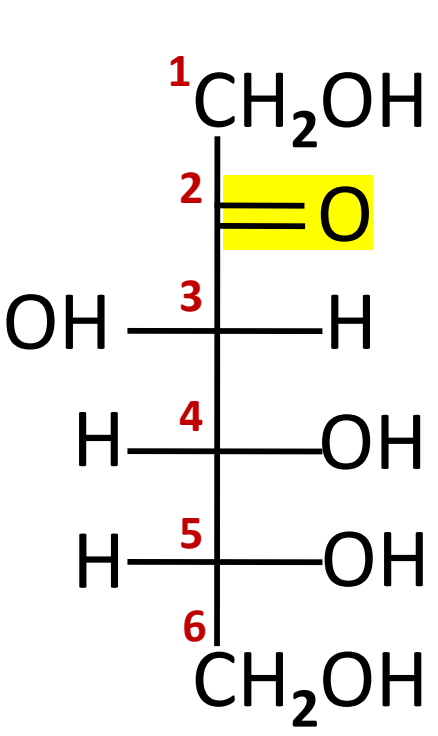
Monosaccharides

Hexose $C_6H_{12}O_6$

Hexoaldose\Aldohexose



Fischer projections



Hexoketose\Ketohexose

D-glucose

"grape or blood sugar"

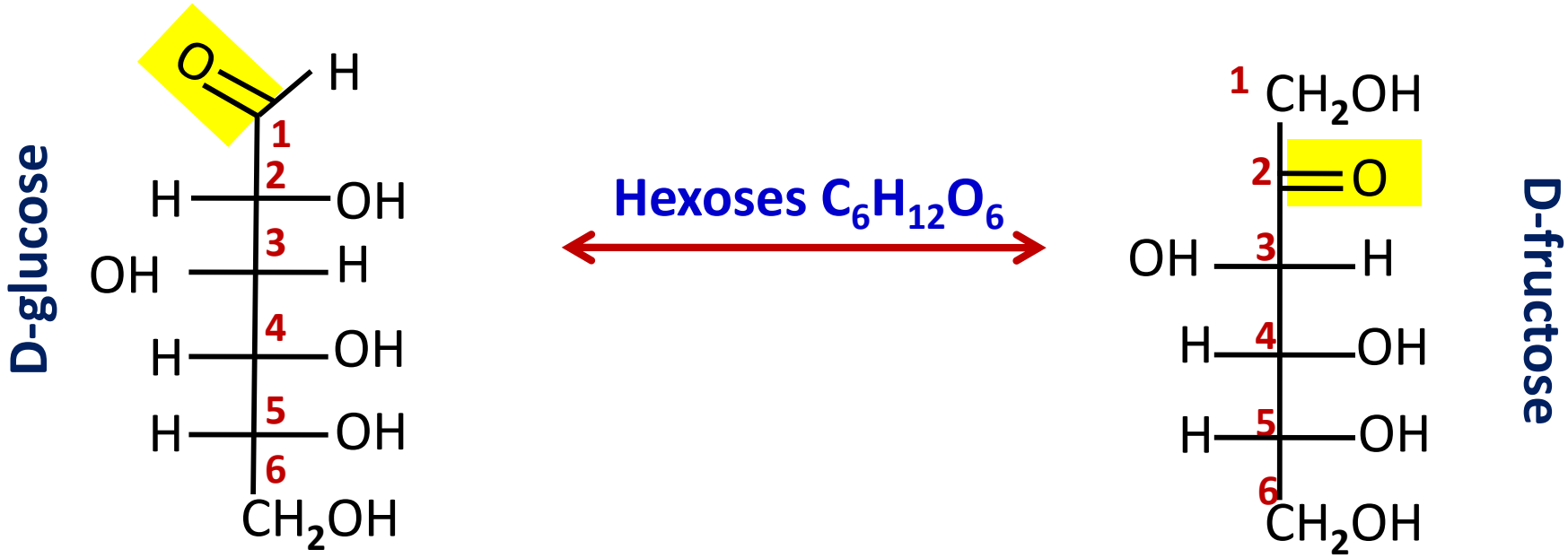
D-fructose

"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)

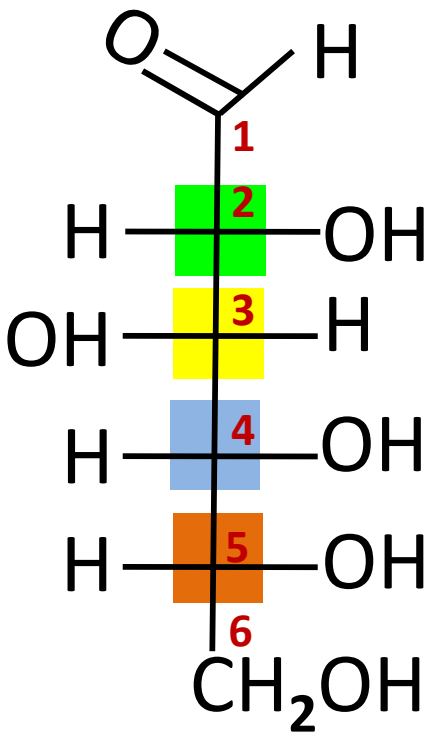


Isomerization

- 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. Stereroisomers (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 = $\mathbf{2^n}$ where n represents the number of chiral centers

Isomerization

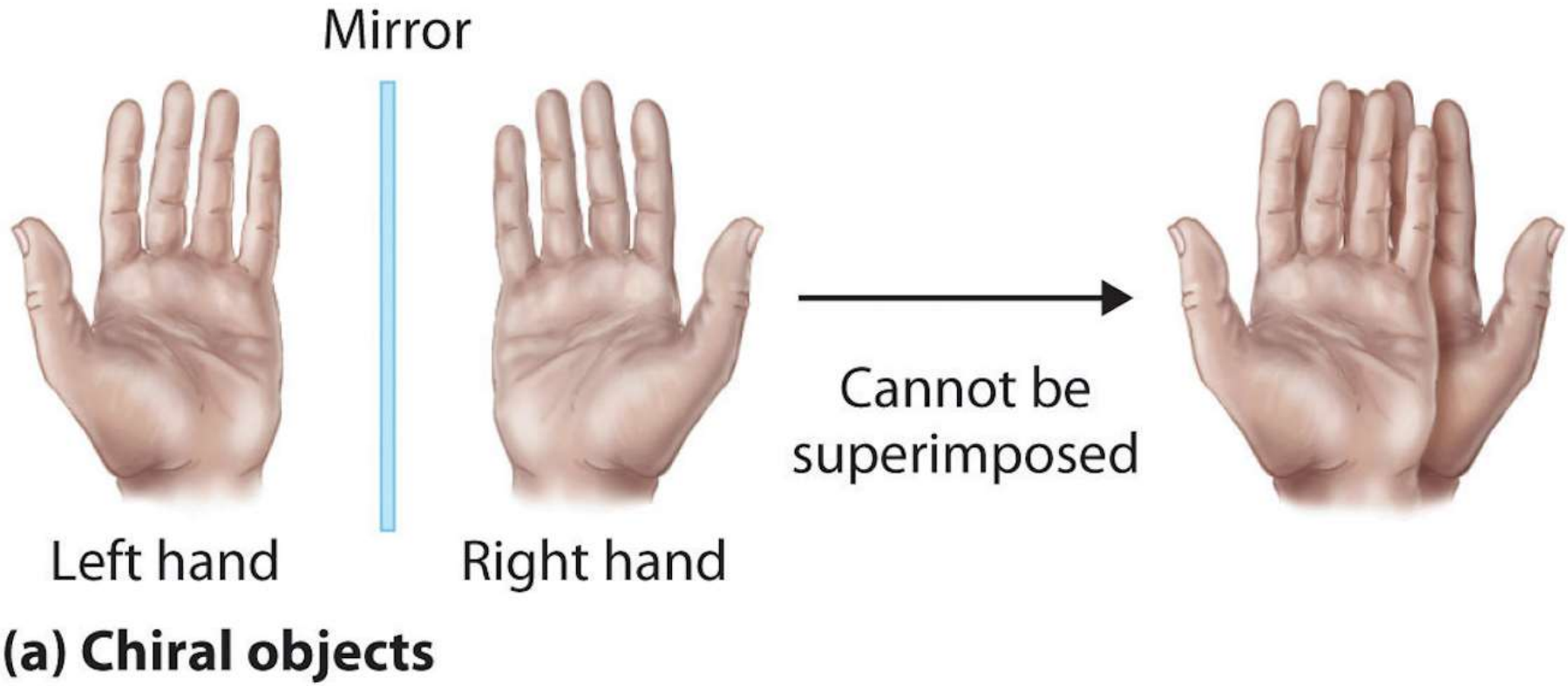


D-glucose

Number of stereoisomers = 2^4

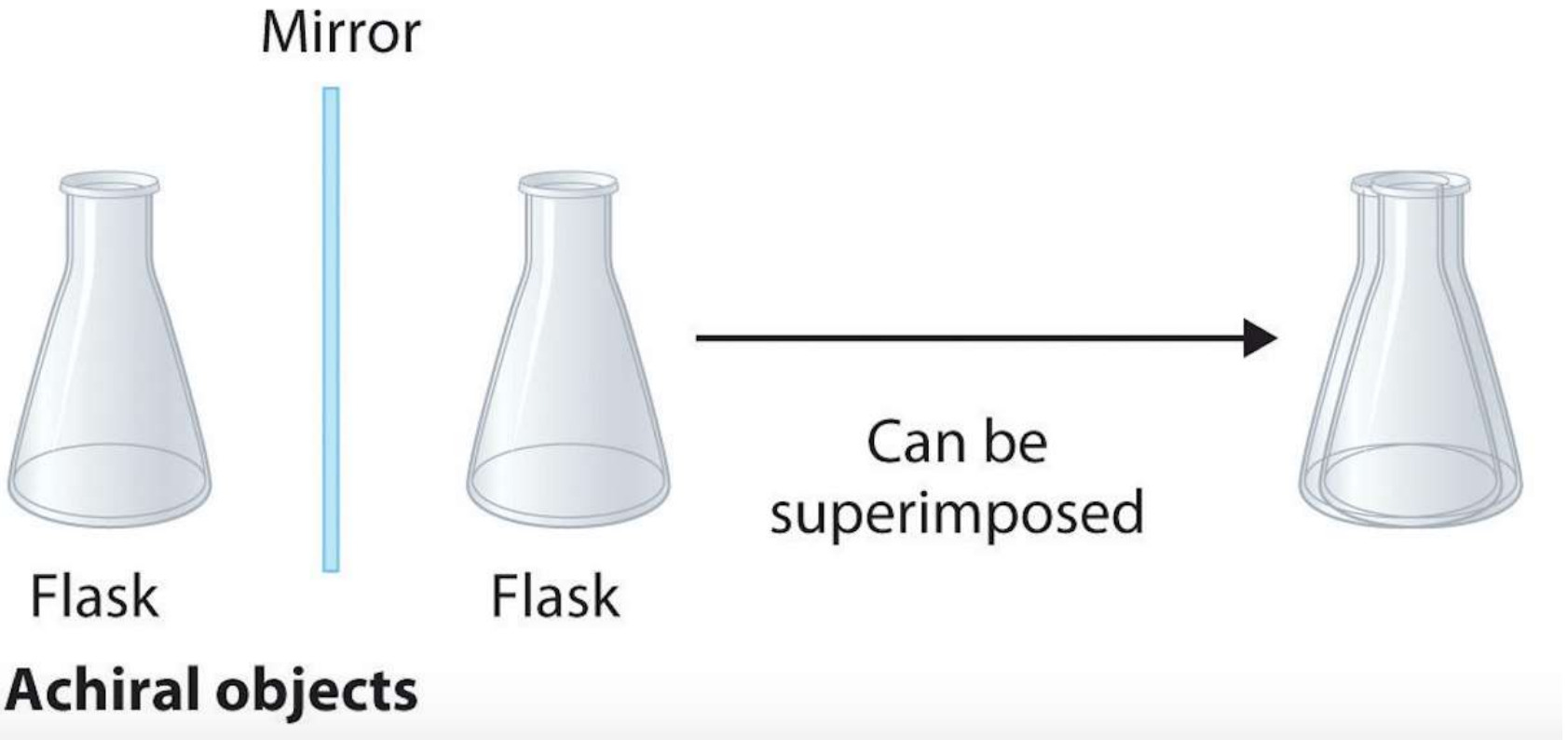
= 16

Chirality & Chiral Object



(a) Chiral objects

Chirality & Chiral Object



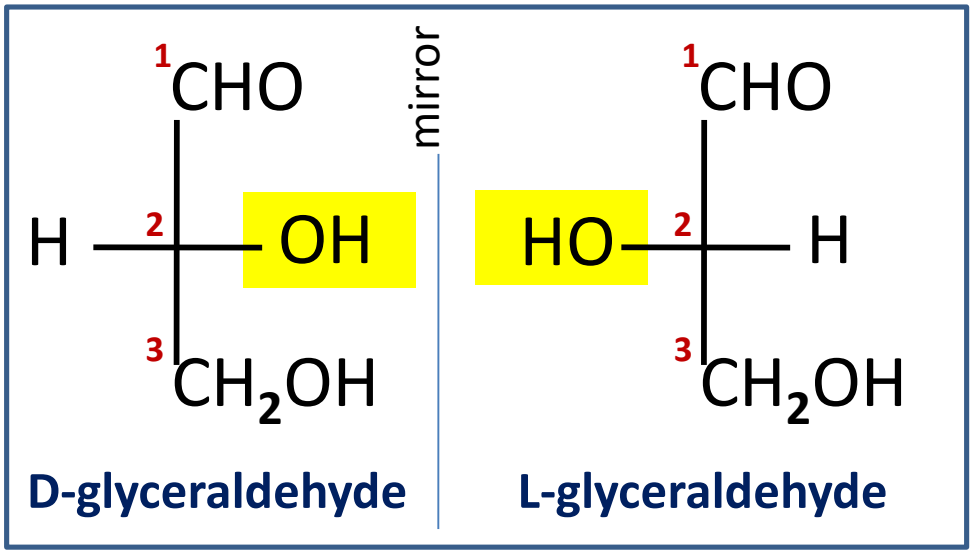
(b) Achiral objects

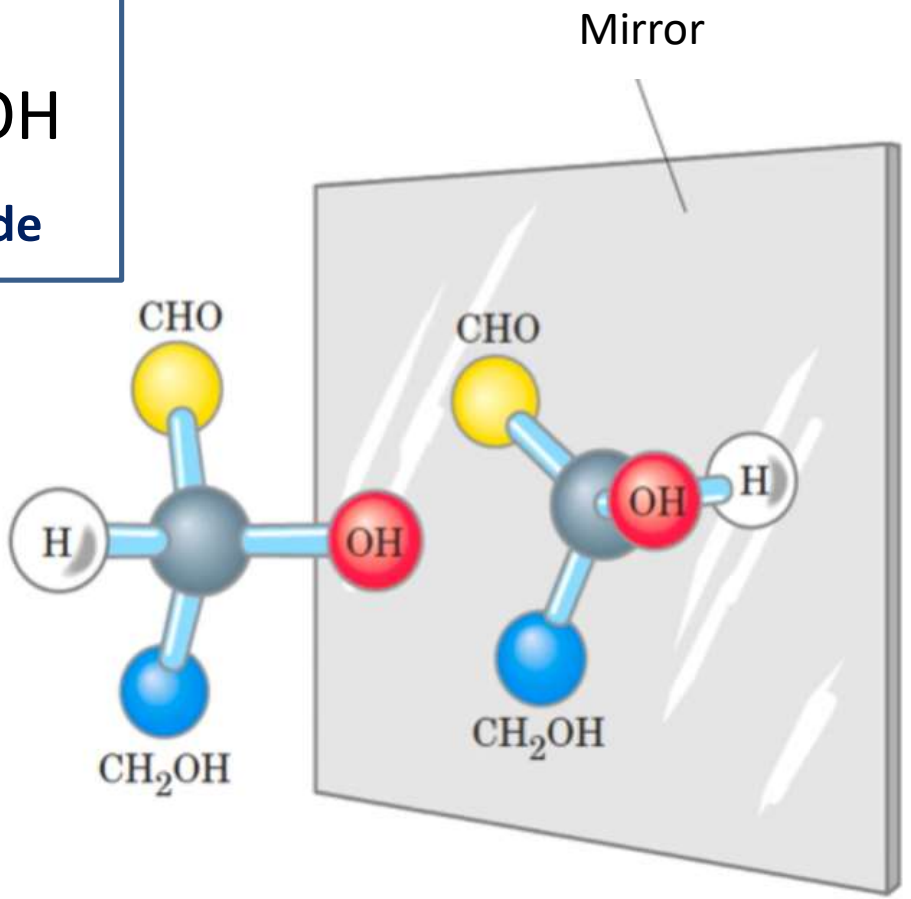
- Chiral molecules should contain at least one chiral center (**usually a carbon atom**)

Stereoisomers

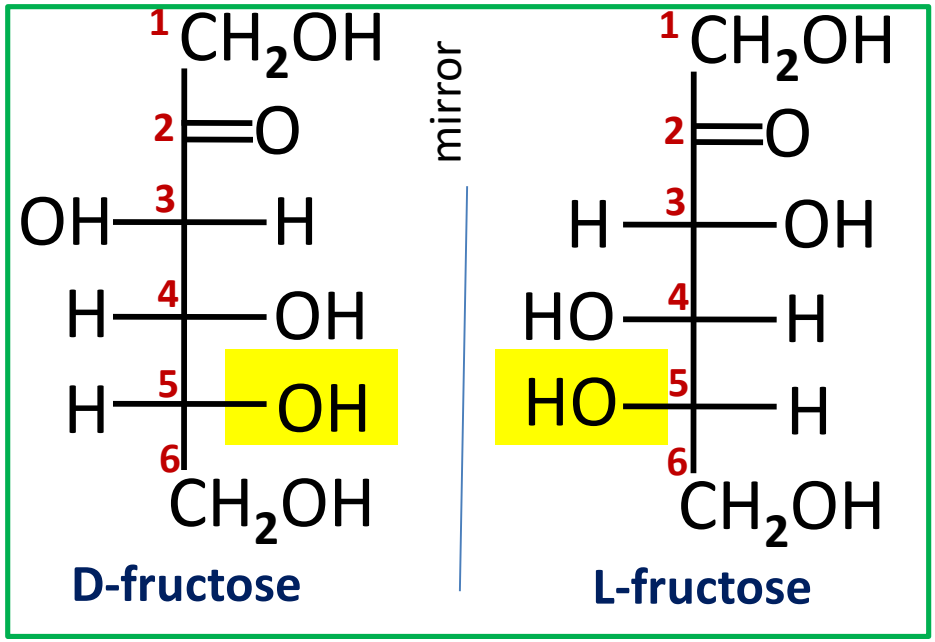
- Enantiomers: are two stereoisomers that are mirror images to each other but not superimposable

D/L Monosaccharides

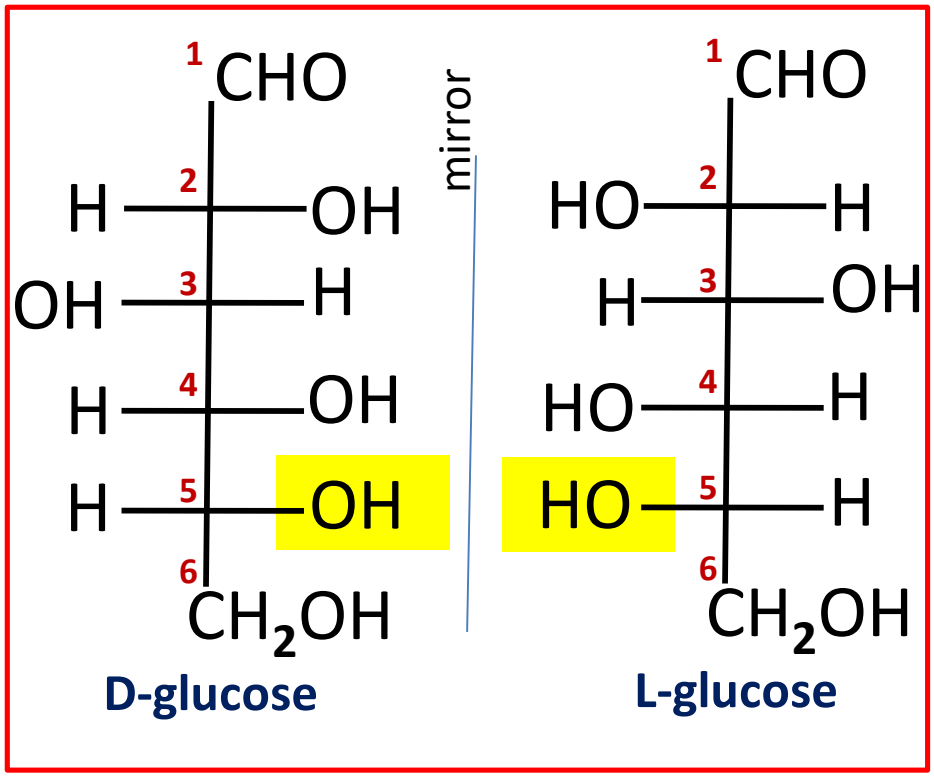




D/L Monosaccharides



D/L Monosaccharides

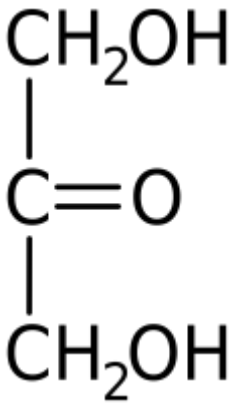


Isomerization

- 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)

D/L Monosaccharides

Ketotriose or Trioketose



Dihydroxyacetone

1. How many stereoisomers do we have for dihydroxyacetone?

Answer: 1

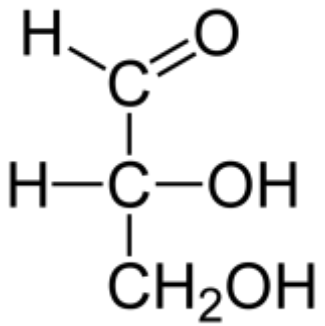
2. Why?

Answer: No chiral carbons ($2^0 = 1$)

3. What is the relation between dihydroxyacetone and glyceraldehyde?

Answer: Structrual isomers

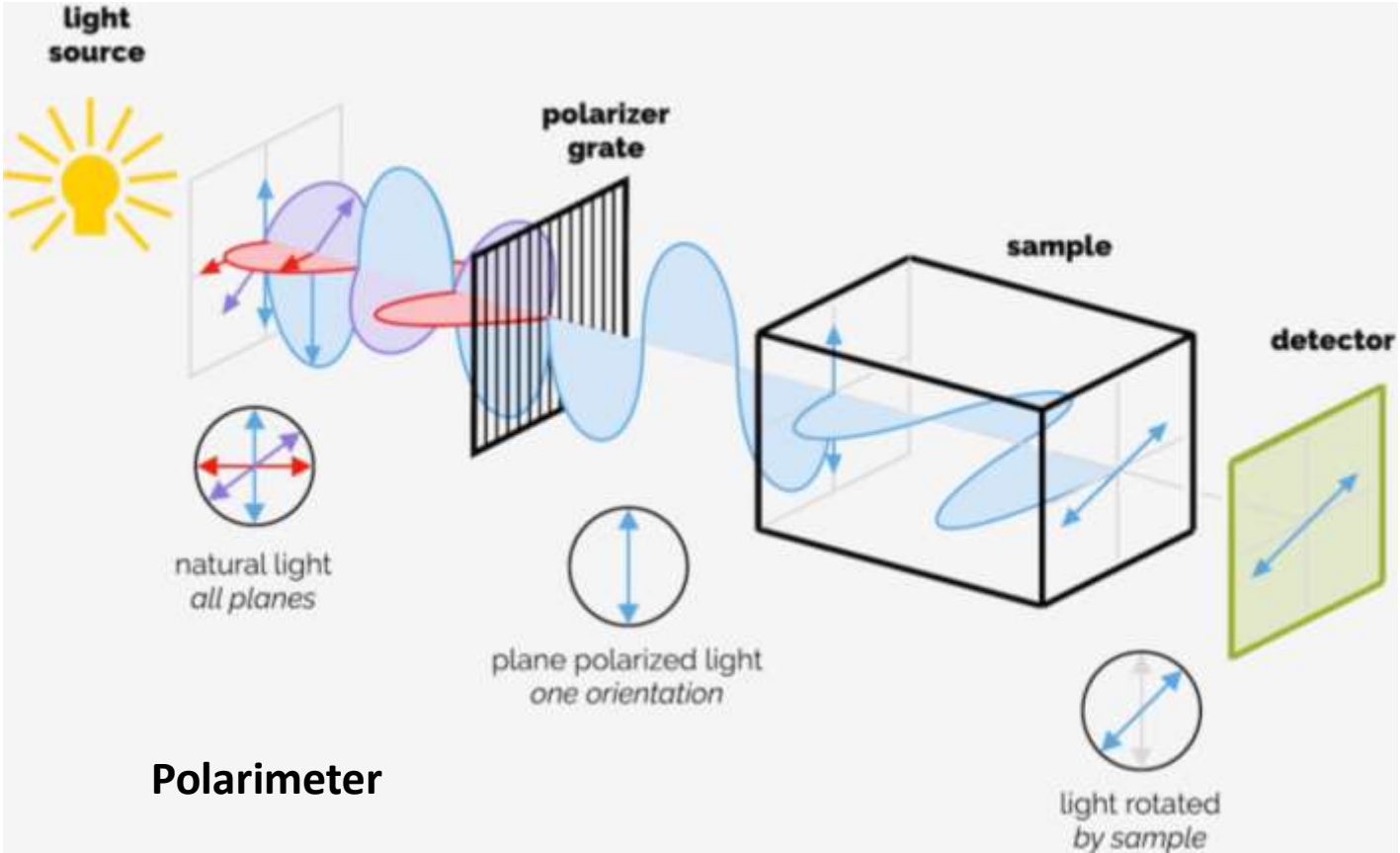
Aldotriose or Trioaldose



Glyceraldehyde

Monosaccharides

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



Monosaccharides

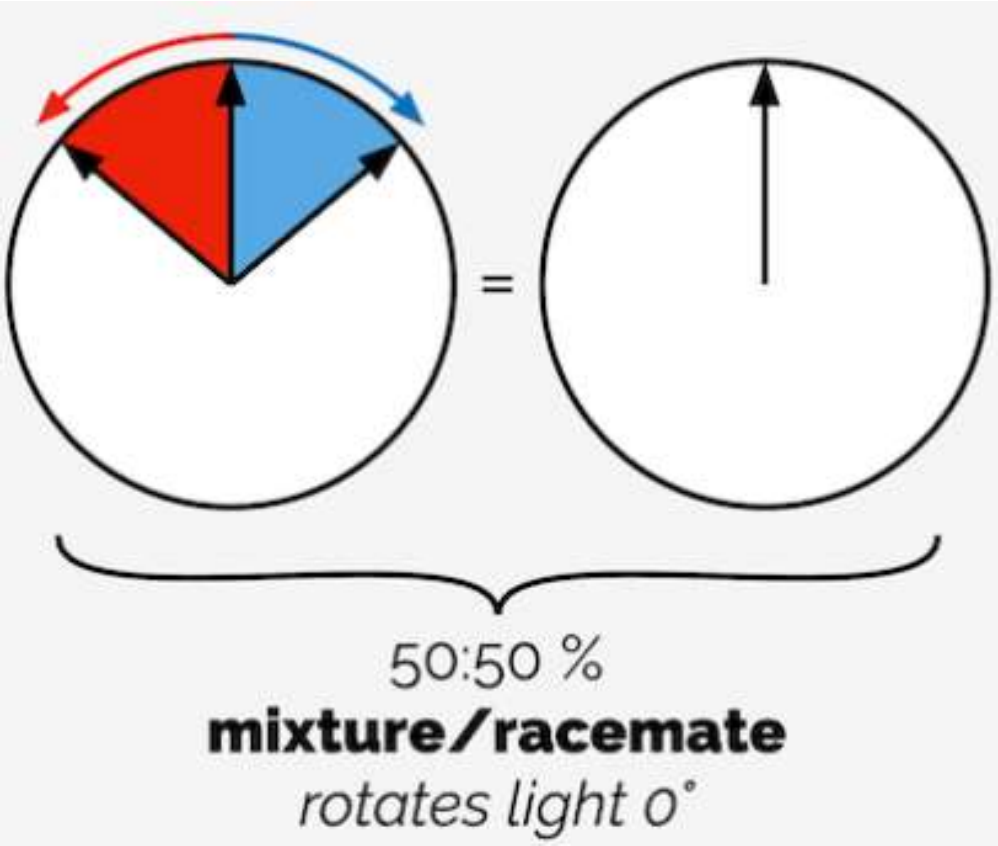
- Enantiomers are optically active and can rotate the polarized light plane either clockwise or counterclockwise
  - (+)/(-) nomenclature system: if one enantiomer rotates the light clockwise, it is labeled (+) or (*d*) (dextrorotatory). The second mirror image enantiomer is labeled (-) or (*l*) laevorotatory [(+)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**

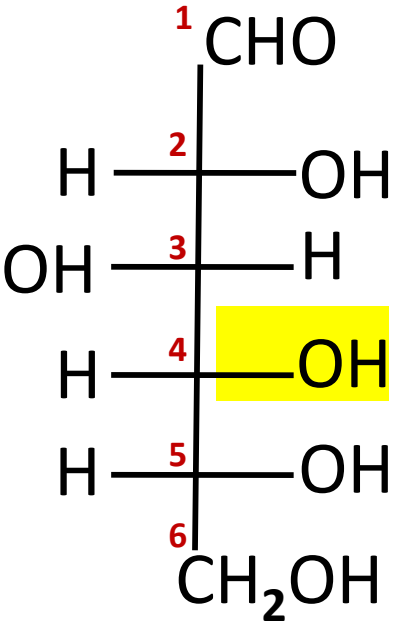
Monosaccharides

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

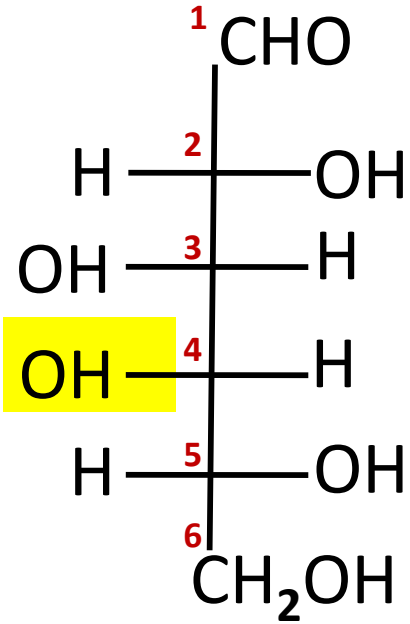


Monosaccharides

- 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.

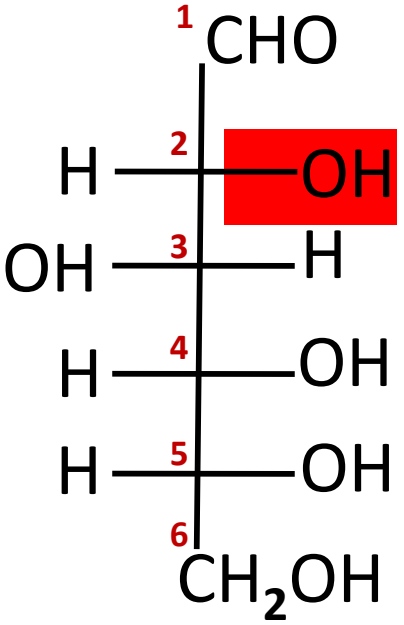


D-glucose

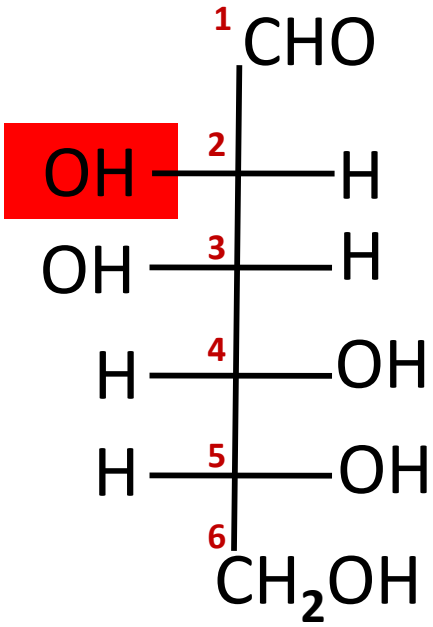


D-galactose

Monosaccharides



D-glucose



D-mannose

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