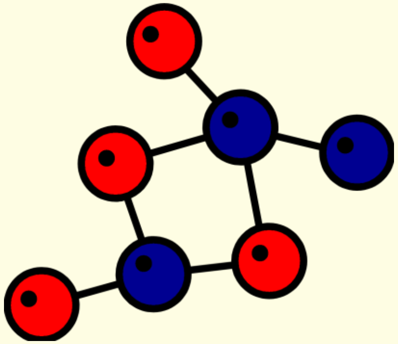

CARBOHYDRATES

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By Dr. Ibtisam. K

Carbohydrates

Carbohydrates are present in humans, animal tissues, plants and in micro-organism. Carbohydrates are also present in tissue fluids, blood, milk, secretions and excretions of animals.

Carbohydrates are organic compounds with C, H and O in the ratio of 1:2:1. ($C_6H_{12}O_6$), Many Carbohydrates also contain Nitrogen and other elements.

Defined as polyhydroxyl aldehyde or ketone derivatives.

Carbohydrate include a large group of compounds commonly known as starches or sugars which are widely distributed in plants and animals

MEDICAL AND BIOLOGICAL IMPORTANCE

1. Carbohydrates are the major source of energy for human . For example, glucose is used in the human body for energy production.

2. Some carbohydrates serve as reserve food material in humans and in plants. For example, glycogen in animal tissue and starch in plants serves as reserve food materials.

3. Carbohydrates are components of several animal structure and plant structures. In animals, carbohydrates are components of skin, connective tissue, tendons, cartilage and bone. In plants, cellulose is a component of wood and fiber.

4. Some carbohydrates are components of cell membrane and nervous tissue.

5. Carbohydrates are components of nucleic acids and blood group substances.

6. Derivative of carbohydrates are drugs. For example, a glycoside ouabain is used in clinical medicine. Streptomycin an antibiotic is a glycoside.

7. Amino sugars, derivatives of carbohydrates are components of antibiotics like erythromycin and carbomycin .

8. Ascorbic acid, a derivative of carbohydrate is a water-soluble vitamin.

9. Bacterial invasion involves hydrolysis of mucopolysaccharides.

Classification of Carbohydrates

Carbohydrates are classified into two major classes based on

1- number of carbon chains present. They are:

1. Monosaccharides 2. Oligosaccharides 3. Polysaccharides

All the three classes contain a saccharose group and hence the name saccharides.

2. Based on the location of C=O

A- Aldoses B- Ketoses

1- Monosaccharide (Simple)

Monosaccharides are those carbohydrates which can not be hydrolyzed to small compounds. Their general formula is **$C_n(H_2O)_n$**. They are also called as simple sugars. Monosaccharide's containing three to nine carbon atoms occur in nature.

Monosaccharides have common names and systematic names. Systematic name

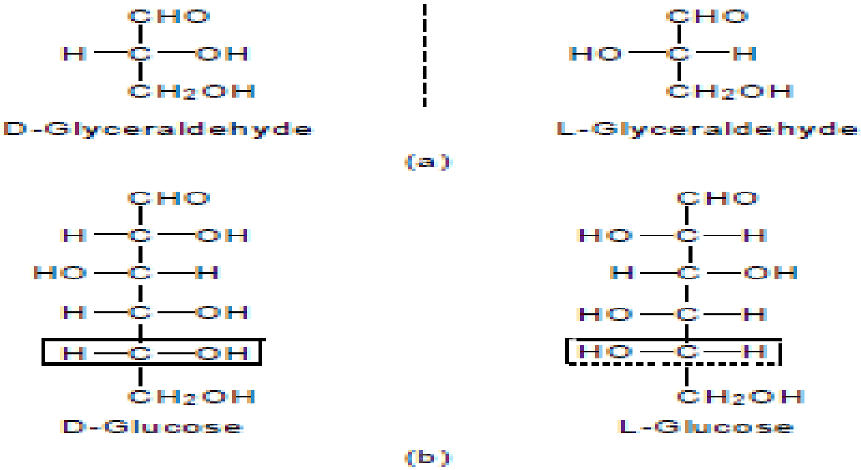
indicates both the number of carbon atoms present and aldehyde or ketone group. For example, glyceraldehyde is a simple sugars containing three carbon atoms and a aldehyde group. Simple sugars containing three carbon atoms are referred as trioses. In addition, sugars containing aldehyde group or keto group are called as aldoses or ketoses, respectively.

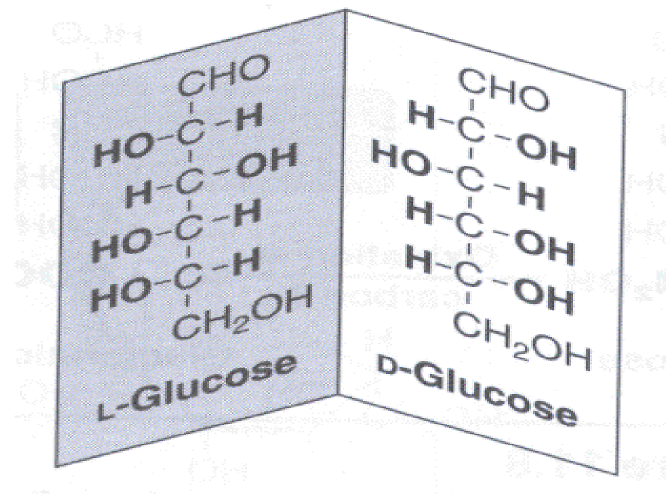
Thus, the systematic name for glyceraldehyde is aldotriose. Similarly, a simple sugar with three carbon atoms and a keto group is called as ketotriose.

PROPERTIES OF MONOSACCHARIDES

1. Optical Isomerism

All the monosaccharides except dihydroxyacetone contain at least one asymmetric carbon atom and hence they exhibit optical isomerism. The two optical isomers of glyceraldehyde containing one asymmetric carbon atom are D-glyceraldehyde and L-glyceraldehyde. The optical isomers are also called as enantiomers. Further D and L-glyceraldehyde are used as parent compounds to designate all other sugars (compounds) as D or L forms. Usually, the hydroxyl group on penultimate carbon atom points to right in ‘D’glucose and D-glyceraldehyde whereas it points to left in L-glucose and L-glyceraldehyde .Further D and L forms of glucose are mirror images like mirror images of glyceraldehyde. Though both forms of sugars are present in nature D-isomer is abundant and sugars present in the body are all D-isomers.



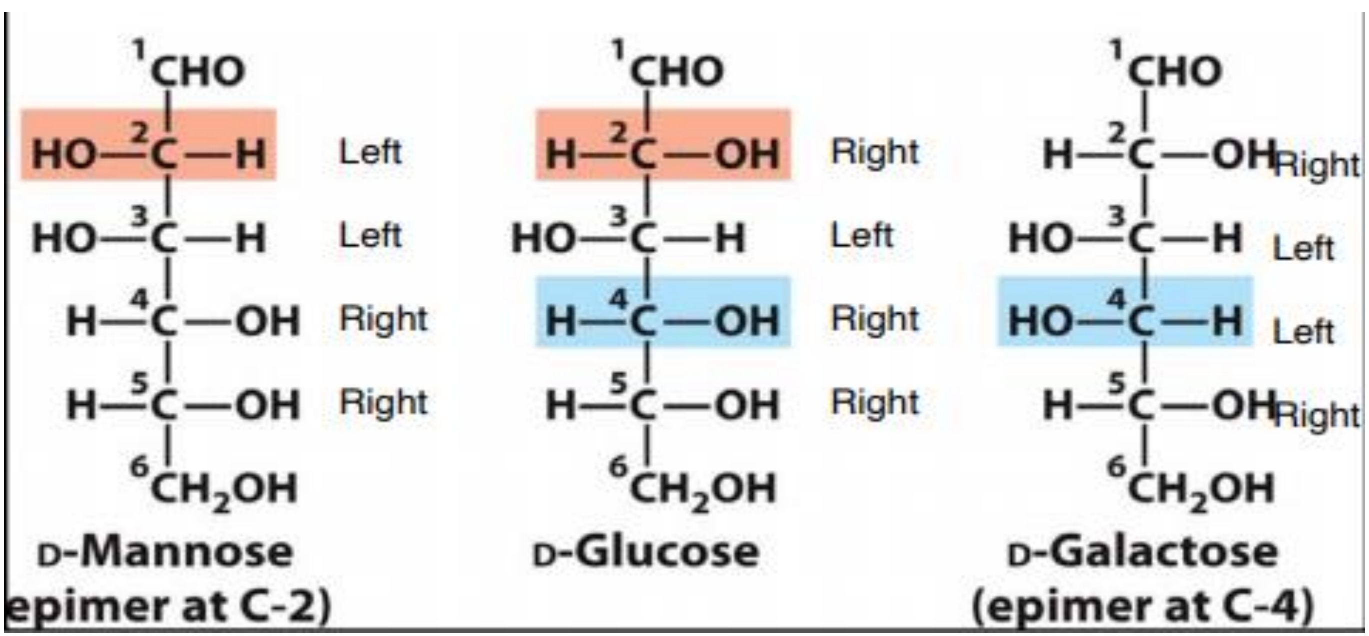


2. Optical Activity

Monosaccharides except dihydroxy acetone exhibit optical activity because of the presence of asymmetric carbon atom. If a sugar rotates plane polarized light to right then it is called as dextrorotatory and if a sugar rotates the plane polarized light to the left then it is called as levorotatory. Usually ‘+’ sign or ‘d’ indicates dextrorotation and ‘–’ sign or I indicates levorotation of a sugar. For example, D-glucose which is dextrorotatory is designated as D(+) glucose and D-fructose, which is levorotatory is designated as D(–) fructose. The letter ‘D’ does not indicate whether a given sugar is dextro or levorotatory.

3. Epimers

Are those monosaccharides that differ in the configuration of –OH group on 2nd, 3rd and 4th carbon atoms. Epimers are also called as diastereoisomers. Glucose, galactose and mannose are examples for epimers. Galactose is an epimer of glucose because, configuration of hydroxyl group on 4th carbon atom of galactose is different from glucose. Similarly, mannose is an epimers of glucose because configuration of hydroxyl group on 2nd carbon atom of mannose is different from glucose . Ribulose and xylulose are also epimers. They differ in the configuration of –OH group on third carbon atom.



2- Oligosaccharides (Complex Carbohydrates)

They consist of 2-10 monosaccharide units. The monosaccharides are joined together by glycoside bonds. Most important oligosaccharides are disaccharides.

Disaccharides

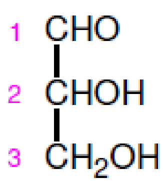
They provide energy to human body. They consist of two monosaccharide units held together by glycosidic bond. So, they are glycosides. Most common disaccharides are maltose, lactose and sucrose.

Based on the location C=O

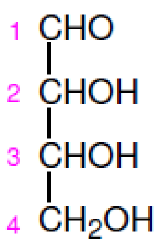
Aldose – polyhydroxyaldehyde, C=O at C1 glucose

Ketose – polyhydroxyketone, C=O at C2 fructose

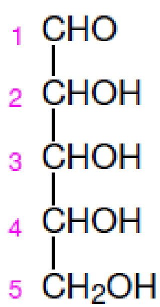
Triose, tetrose, pentose, hexose, etc. – carbohydrates that contain three, four, five, six, etc. carbons per molecule (usually five or six); eg. Aldohexose, ketopentose, etc.



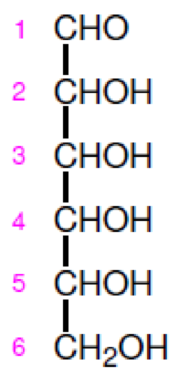
triose
3 carbons



tetrose
4 carbons



pentose
5 carbons

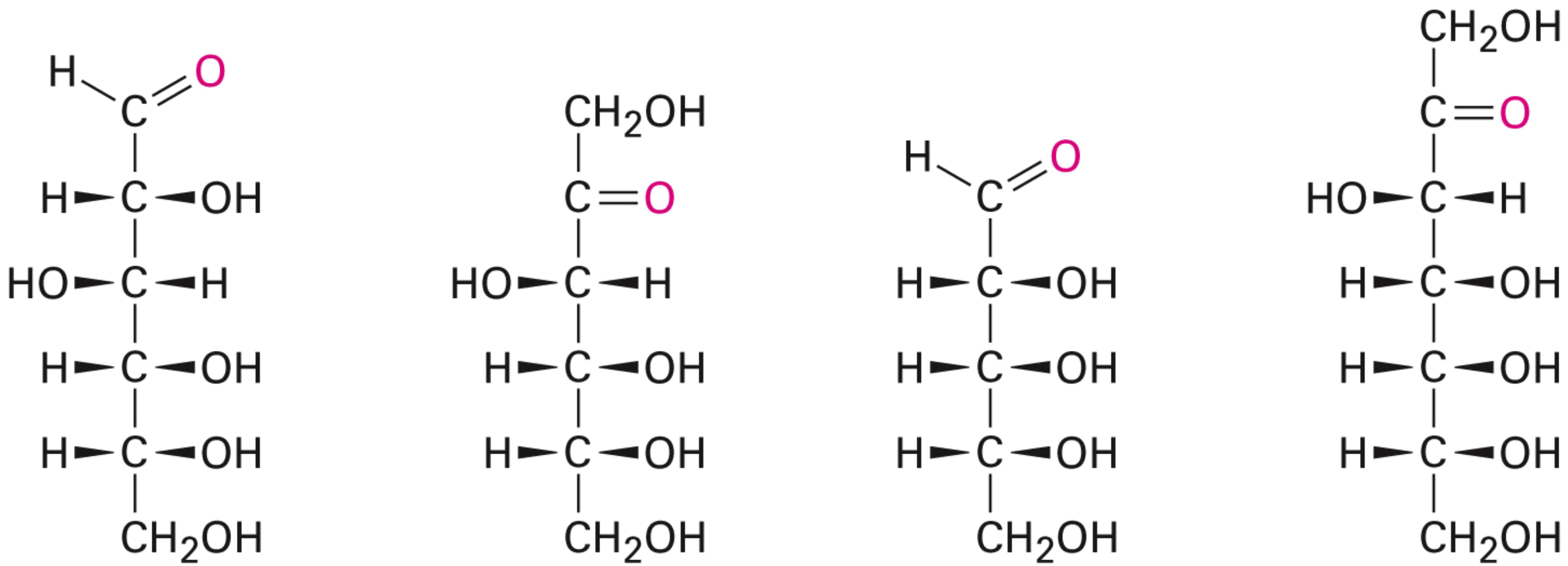


hexose
6 carbons

N. of C	Ketone	Aldehyde
4	Tetrose	Tetrulose
5	Pentose	Pentulose
6	Hexose	Hexulose
7	Heptose	Heptulose
8	Octose	Octulose

Structure of monosaccharide

- *aldo*- and *keto*- prefixes identify the nature of the carbonyl group
- -*ose* suffix designates a carbohydrate
- Number of C's in the monosaccharide indicated by root (tri-, tet-, pent-, hex-)



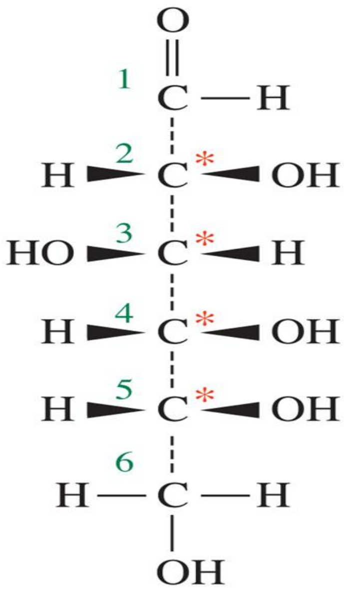
Glucose **(an aldohexose)** — **Fructose** **(a ketohexose)** — **Ribose** **(an aldopentose)** — **Sedoheptulose** **(a ketoheptose)**

Isomerism

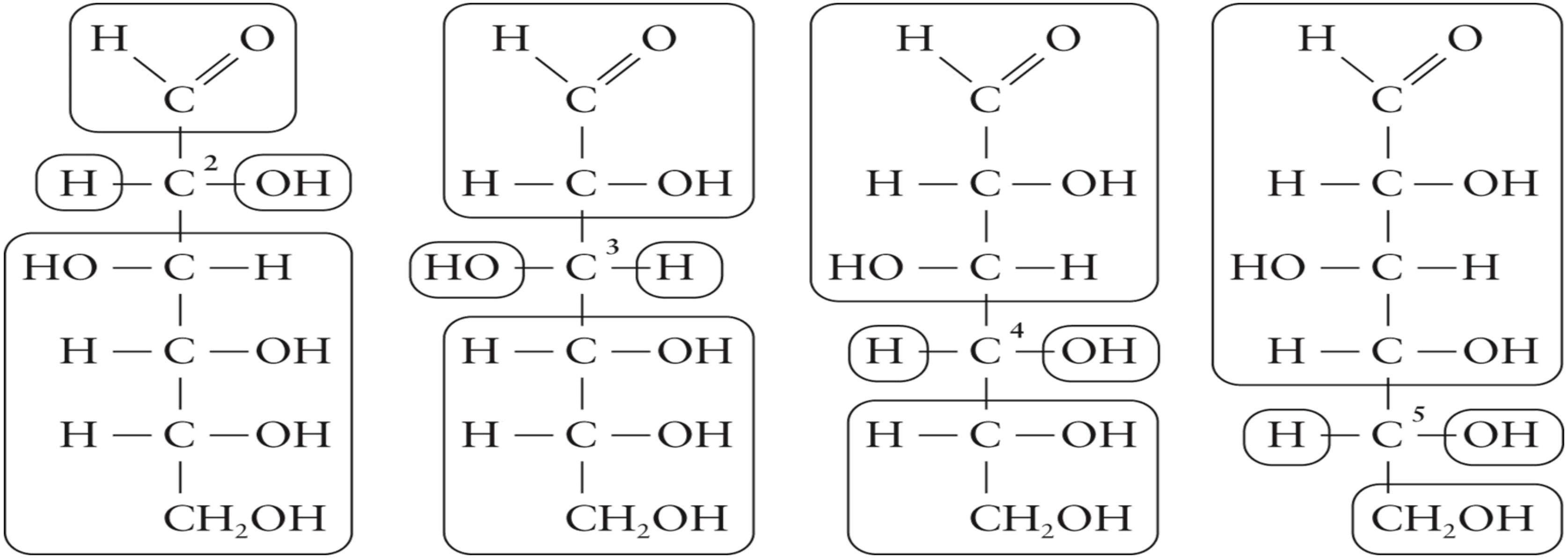
- **Isomers are basically molecules that have the same chemical formula but they differ in their chemical structures.**
- **Asymmetric Carbon is an important determinant of Isomerism.**
- **Asymmetric Carbon is that Carbon which is attached with four different groups.**

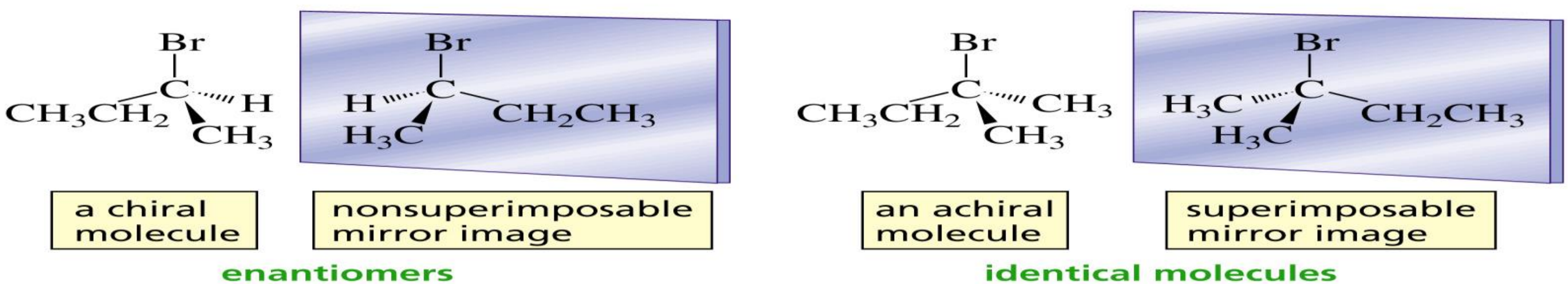
Multiple Chiral Centers

- Recall that a **chiral center** is a carbon atom that have four different atoms or groups of atoms attached to it. Enantiomers are chiral .
- Glucose, a aldohexose, contains four different chiral centers
- Carbons 2 through 5 of glucose are tetrahedral and have four different atoms or groups of atoms attached. Carbons 1 and 6 are not chiral centers. Why?
- Groups bonded to each chiral center have two different arrangements or mirror images, which result in stereoisomers
- The presence of a single **chiral carbon** gives rise to stereoisomerism.
- If a carbon atom is attached to four different groups, **chiral**.
- If any two groups are identical, **Achiral** .
- **Achiral** compounds have superimposable mirror images



* Chiral centers in glucose





a chiral molecule
nonsuperimposable mirror image
enantiomers
an achiral molecule
superimposable mirror image
identical molecules

- The number of stereoisomers for a molecule increases with the number of chiral centers in the molecule
- The general formula for determining the number of stereoisomers is 2^n, where n is the number of chiral centers present in the molecule.
- The number of stereoisomers = 2^n
- Glucose has 4 chiral centers, so there are 16 stereoisomers, $2^4 = 16$.

Physical properties

Optical activity: Optical activity is the capacity of a substance to rotate the plane polarized light passing through it.

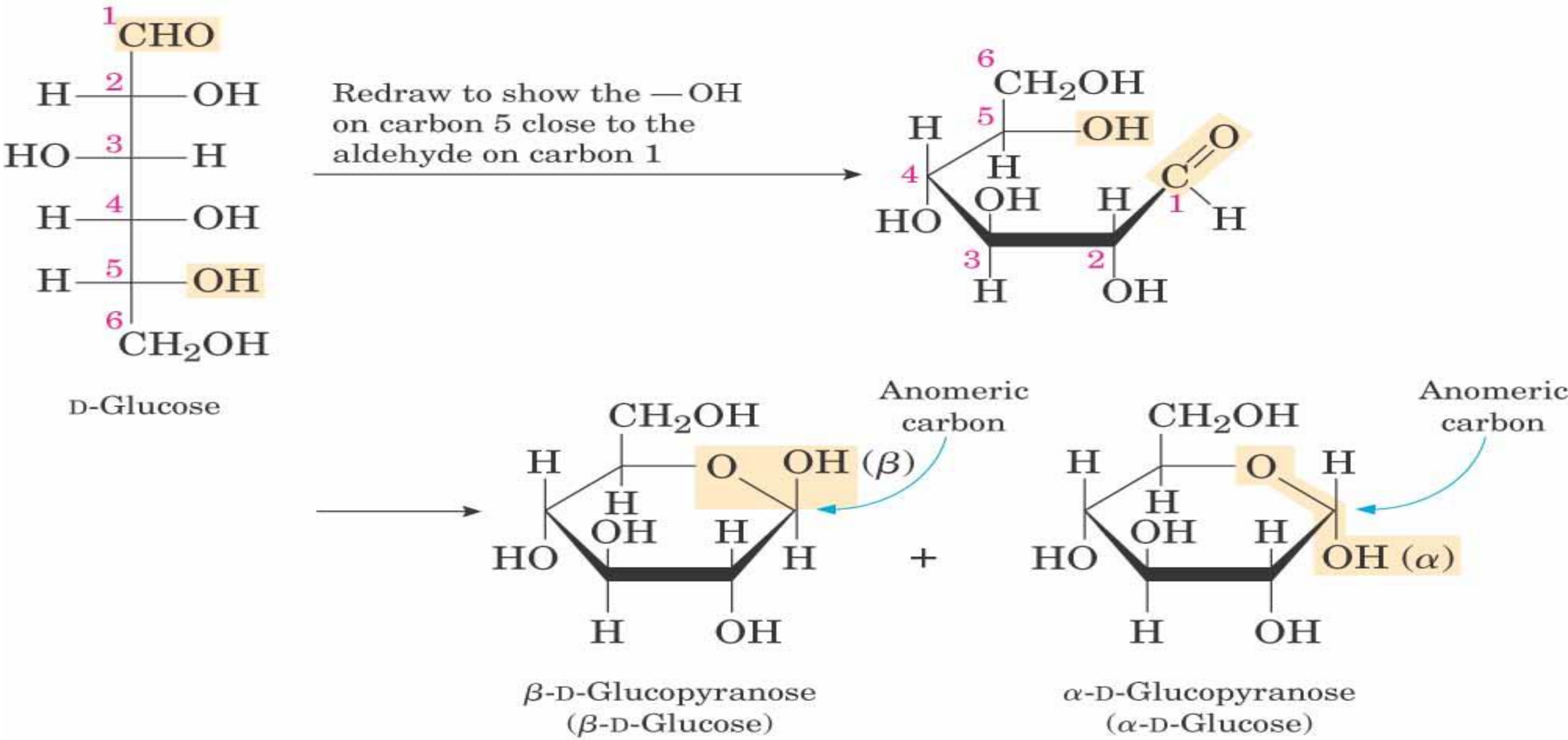
- **Dextrorotatory (+) :If the sugar solution turns the plane of polarized light to right.**
- **Levorotatory (–) :If the sugar solution turns the plane of polarized light to left.**
- **Racemic mixture : Equimolar mixture of optical isomers has no net rotation.**

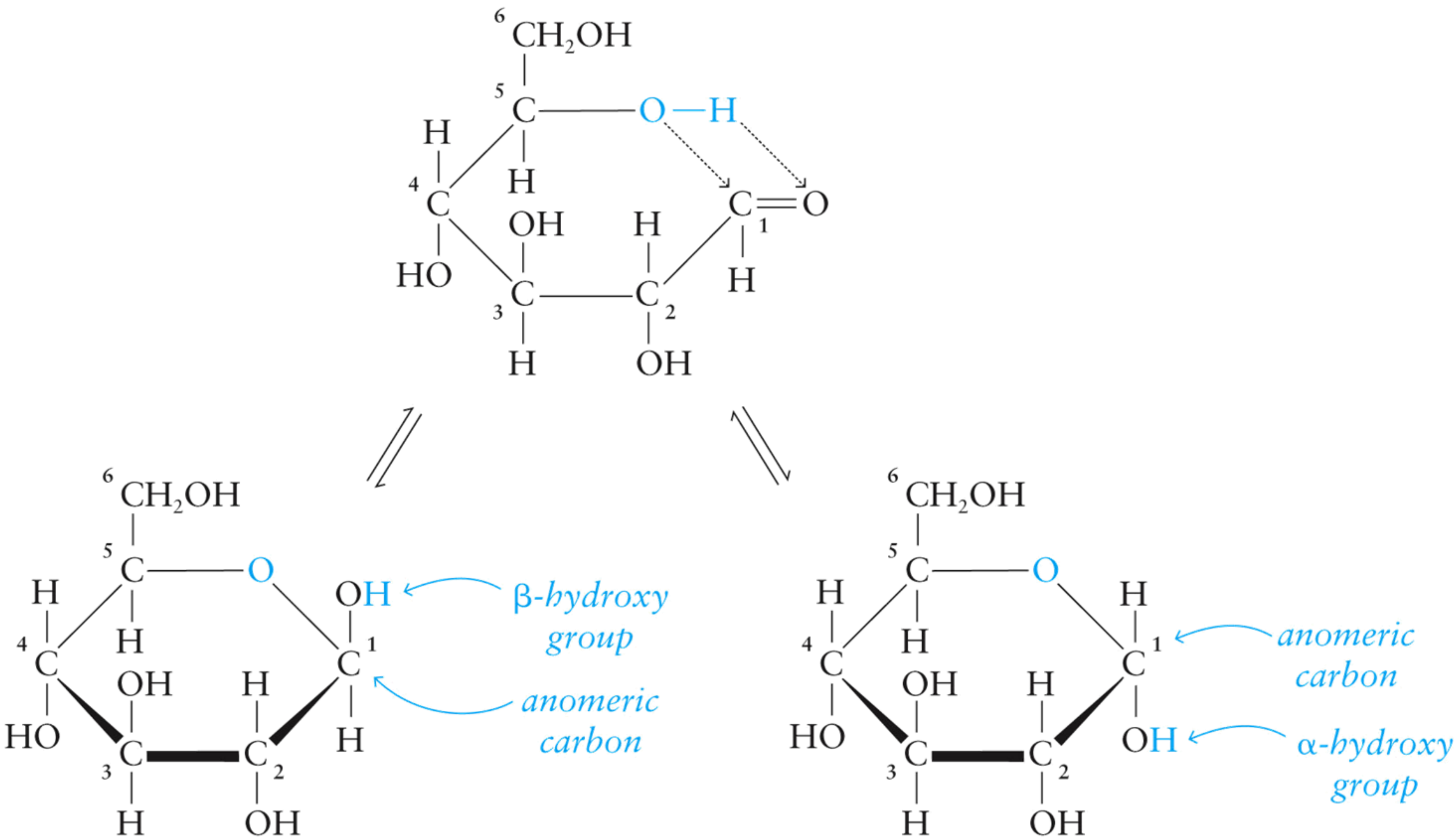
- **Chiral compounds are optically active; they rotate the plane of polarized light.**

- **Achiral compounds do not rotate the plane of polarized light. They are optically inactive.**

Cyclic Structure of monosaccharaide (Haworth formula)

- A **Haworth projection** is a common way of writing a structural formula to represent the cyclic structure of monosaccharides with a simple three-dimensional perspective.
- Monosaccharides have hydroxyl and carbonyl groups in the same molecule and exist almost entirely as five- and six-membered cyclic Hemiacetal An aldehyde can react with an alcohol to form a hemiacetal.
- Hemiaketal A ketone can react with an alcohol to form a hemiketal
  - **anomeric carbon**: the new stereocenter resulting from cyclic hemiacetal or hemiaketal formation
  - **anomers:** carbohydrates that differ in configuration at their anomeric carbons
- **Pentoses and hexoses** can cyclize as the ketone or aldehyde reacts with a distal OH.
- Glucose forms an intra-molecular hemiacetal, as the C1 aldehyde & C5 OH react, to form a 6-member pyranose ring, named after pyran.

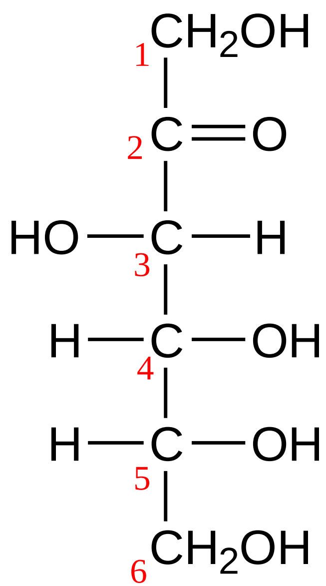

CHO
H OH
HO H
H OH
H OH
CH2OH
D-Glucose
Redraw to show the —OH on carbon 5 close to the aldehyde on carbon 1
CH2OH
OH
Anomeric carbon
OH (β)
OH (α)
β-D-Glucopyranose
(β-D-Glucose)
α-D-Glucopyranose
(α-D-Glucose)



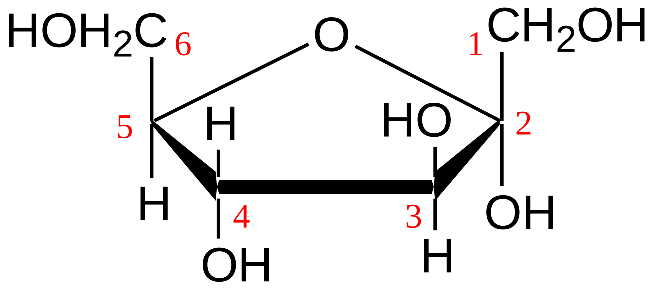
β-D-glucose α-D-glucose

- Because the **anomeric carbon** atom is **chiral**, two possible stereoisomers can be formed during cyclization.
  - An α **anomer** (-OH on the **anomeric carbon** pointing down)
  - A β **anomer** (-OH on the **anomeric carbon** pointing up)
- **Anomers** are stereoisomers that differ in the 3-D arrangement of groups at the **anomeric carbon** of an acetal, ketal, hemiacetal, or hemiketal group

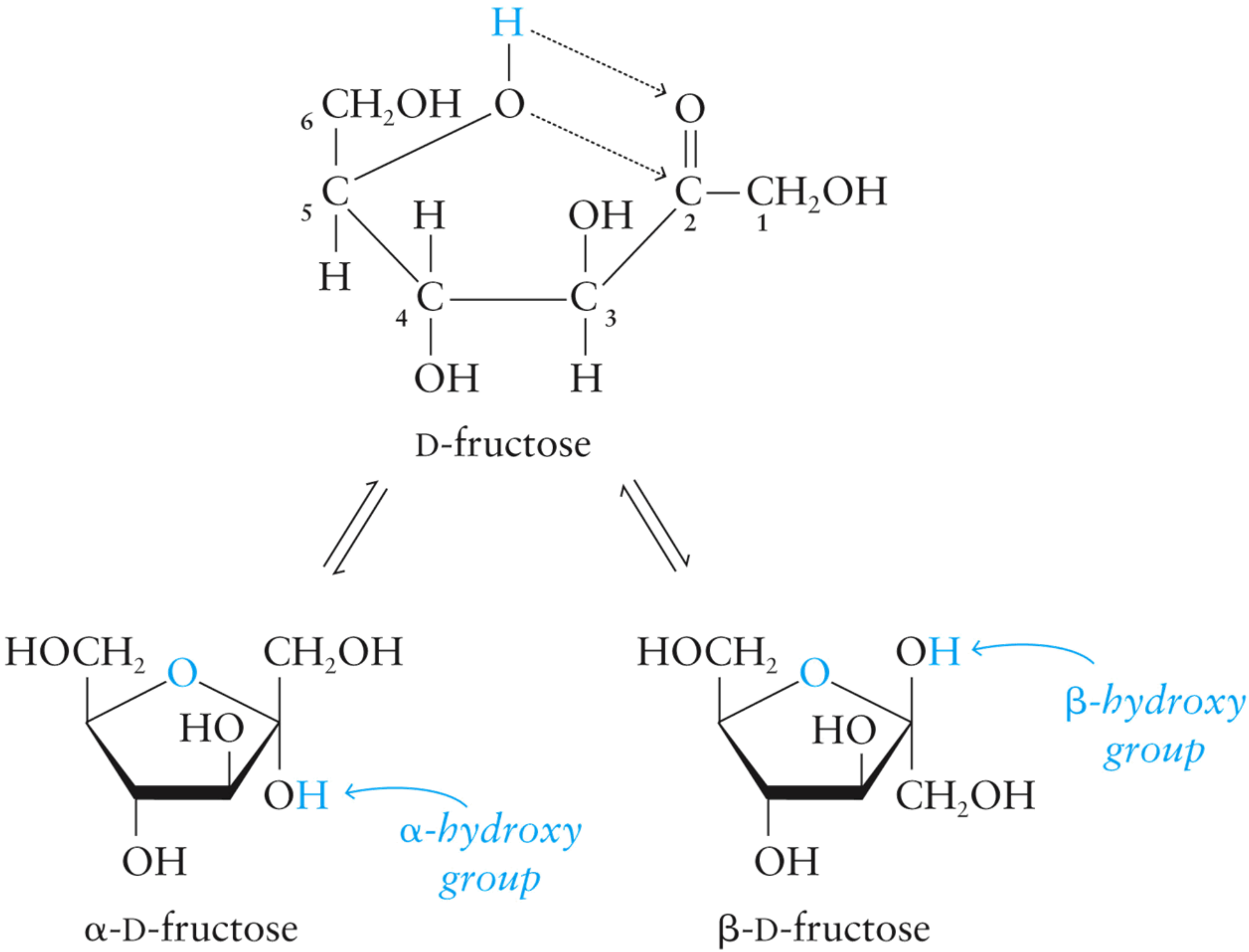
- Fructose forms either a 6-member pyranose ring, by reaction of the C2 keto group with the OH on C6, or a 5-member furanose ring, by reaction of the C2 keto group with the OH on C5.



D-fructose (linear)



α-D-fructofuranose



D-fructose
α-hydroxy group
α-D-fructose
β-hydroxy group
β-D-fructose