Lecture 3

Carbohydrates

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Biochemistry is the study of the chemistry of biomolecules and living organisms.

- In organic chemistry, we organized our study of carbon-containing molecules by functional group (alcohol, alkene, ketone, carboxylic acid, etc.).

Classification of Carbohydrates

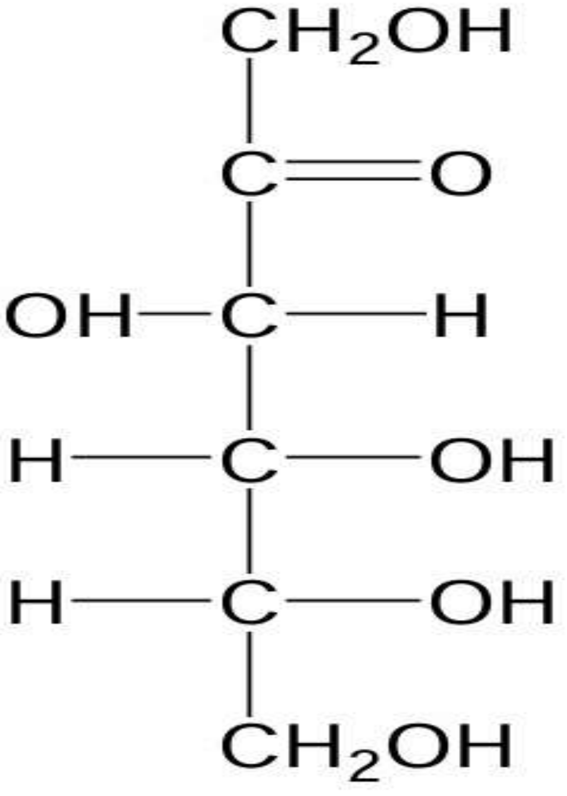
Carbohydrates and Biochemistry

Carbohydrates are compounds of tremendous biological importance:
– they provide energy through oxidation
– they supply carbon for the synthesis of cell components
– they serve as a form of stored chemical energy
– they form part of the structures of some cells and tissues

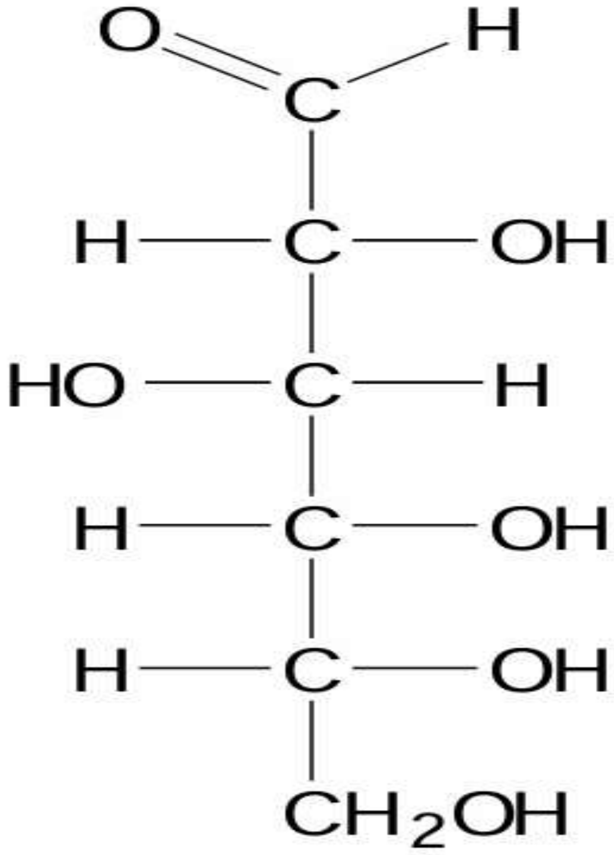
- Carbohydrates, along with lipids, proteins, nucleic acids, and other compounds are known as **biomolecules** because they are closely associated with living organisms.

Carbohydrates

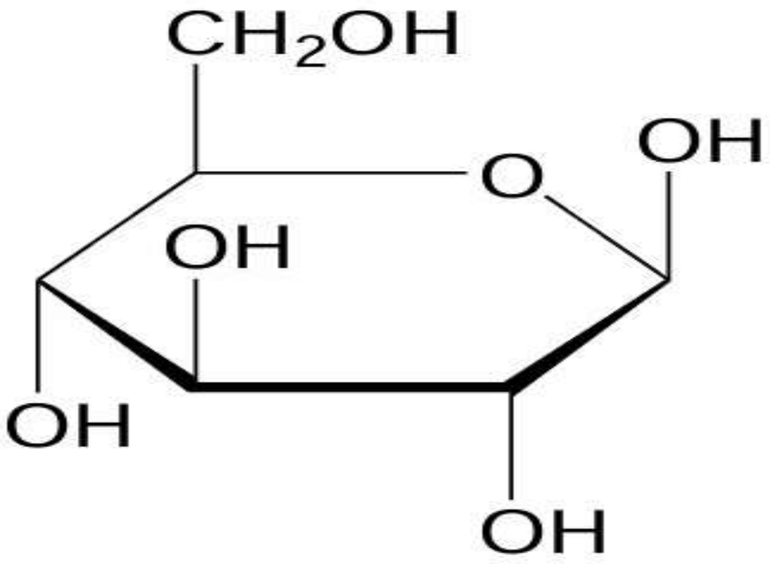
Carbohydrates, or saccharides (saccharo is Greek for “sugar”) are polyhydroxy aldehydes or ketones, or substances that yield such compounds on hydrolysis.



fructose



glucose



β-D-glucose

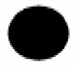
Carbohydrates

- Carbohydrates include not only sugar, but also the starches that we find in foods, such as bread, pasta, and rice

- The term “carbohydrate” comes from the observation that when you heat sugars, you get carbon and water (hence, hydrate of carbon).

Classes of Carbohydrates

Monosaccharides contain a single polyhydroxy aldehyde or ketone unit (e.g., glucose, fructose).

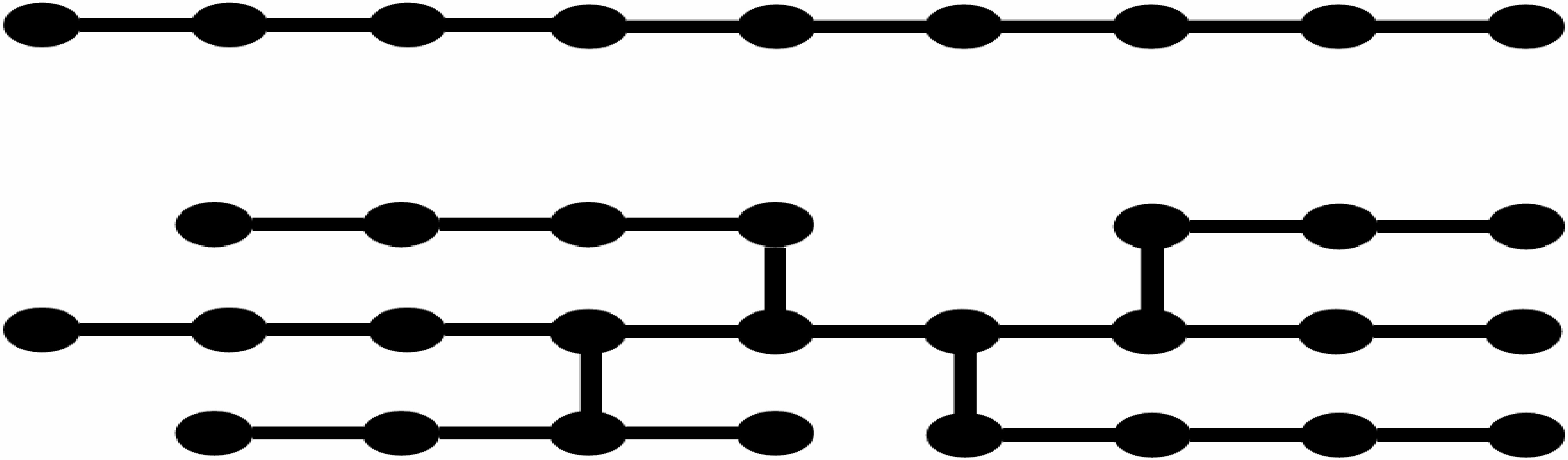


• Disaccharides consist of two monosaccharide units linked to gether by a covalent bond (e.g., sucrose).

• Oligosaccharides contain from 3 to 10 monosaccharide units (e.g., raffinose).

Classes of Carbohydrates

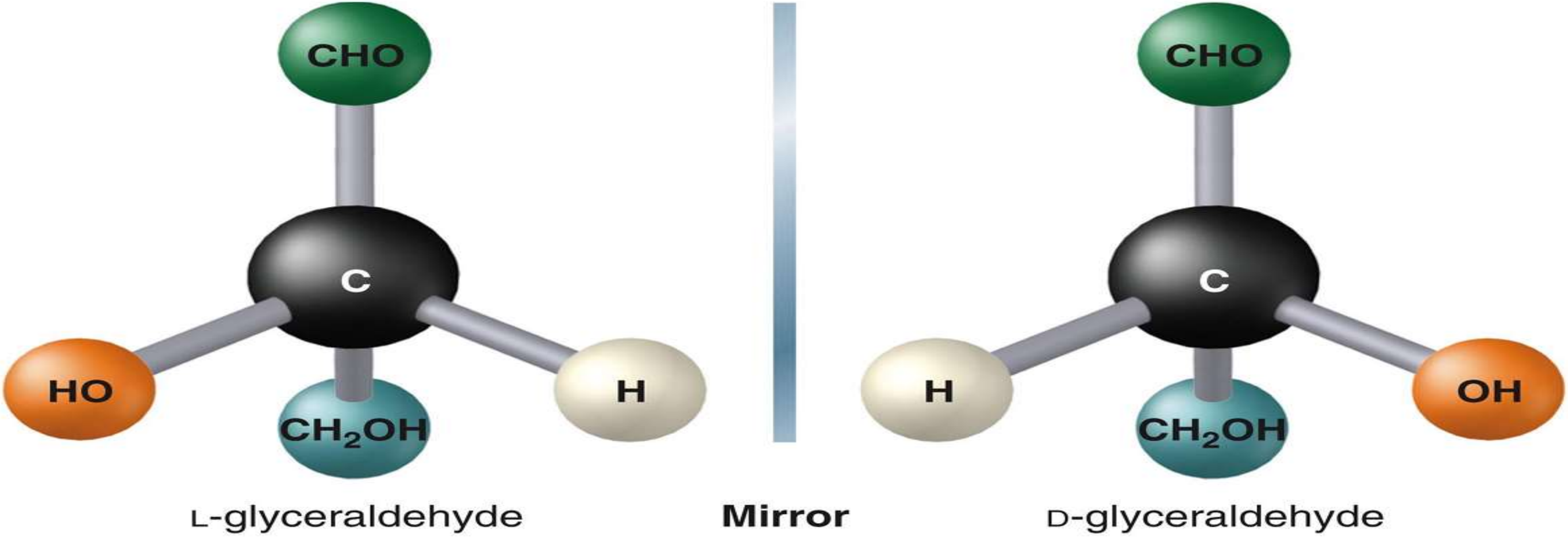
- Polysaccharides contain very long chains of hundreds or thousands of monosaccharide units, which may be either in straight or branched chains (e.g., cellulose, glycogen, starch)



The Stereochemistry of Carbohydrates

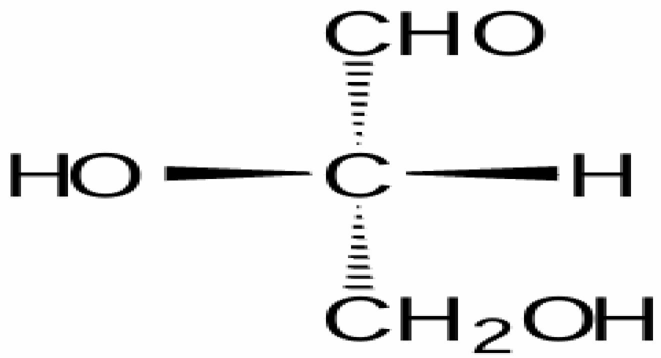
Two Forms of Glyceraldehyde

- Glyceraldehyde, the simplest carbohydrate, exists in two isomeric forms that are mirror images of each other:

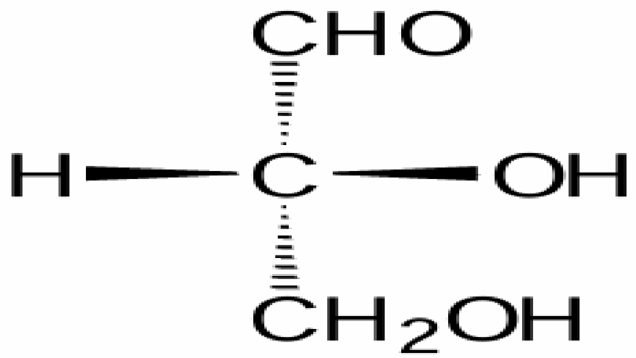


Stereoisomers

- These forms are **stereoisomers** of each other.
- Glyceraldehyde is a **chiral** molecule—it cannot be super imposed on its mirror image. The two mirror Image forms of glyceraldehyde are **enantiomers** of each other.



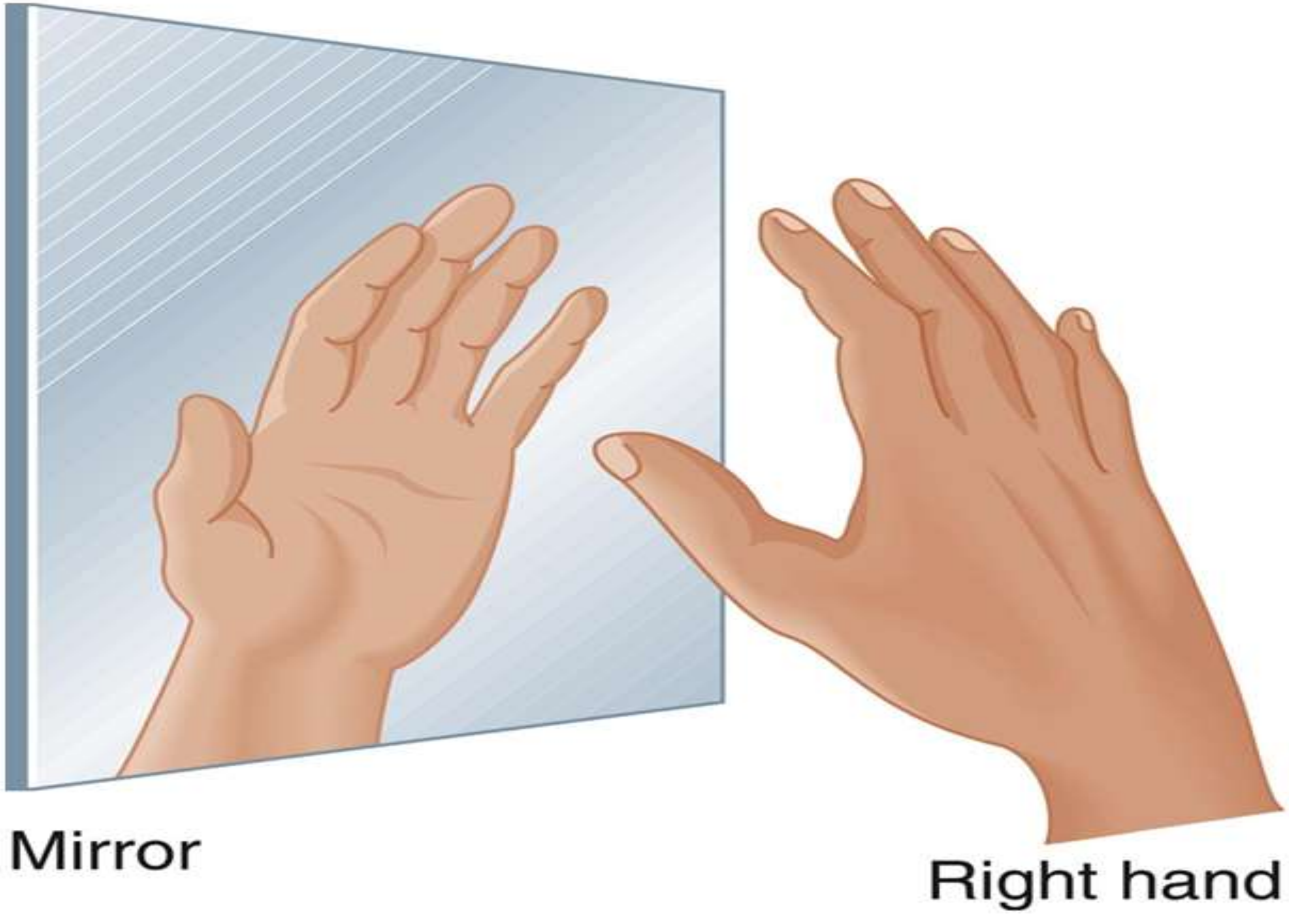
L-glyceraldehyde



D-glyceraldehyde

Chirality and Handedness

• Chiral molecules have the same relationship to each other that your left and right hands have when reflected in a mirror.



Chiral Carbons

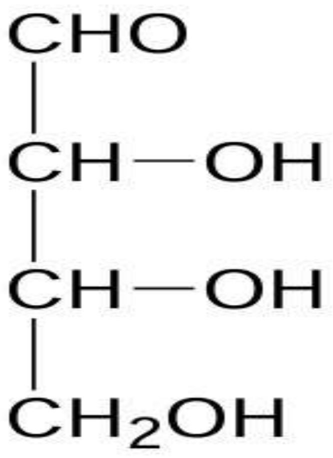
- Chiral objects cannot be superimposed on their mirror images — e.g., hands, gloves, and shoes.

- Achiral objects can be superimposed on the mirror images — e.g., drinking glasses, spheres, and cubes.

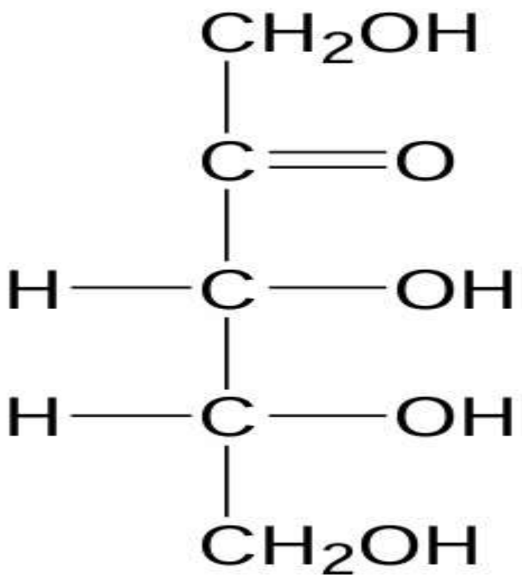
- Any carbon atom which is connected to four different groups will be chiral, and will have two nonsuperimposable mirror images; it is a chiral carbon or a center of chirality.
  – If any of the two groups on the carbon are the same, the carbon atom cannot be chiral.
- Many organic compounds, including carbohydrates, contain more than one chiral carbon.

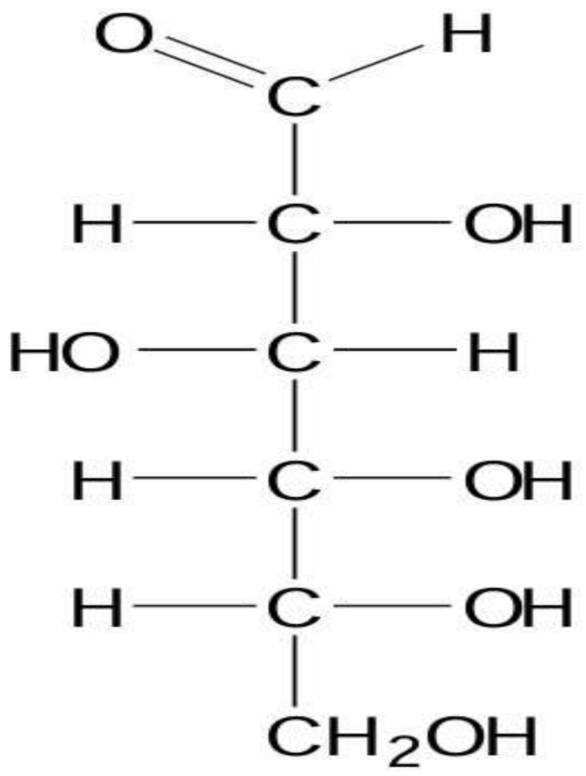
Examples: Chiral Carbons in Carbohydrates

- Identify the chiral carbons (if any) in the following carbohydrates:

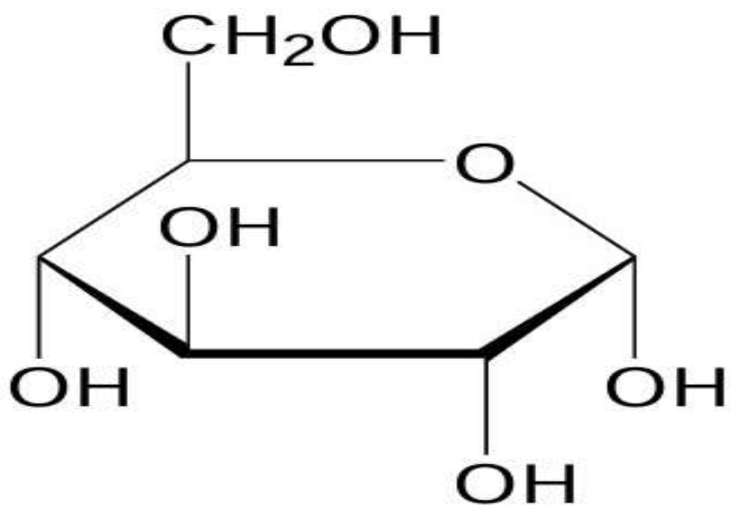


erythrose



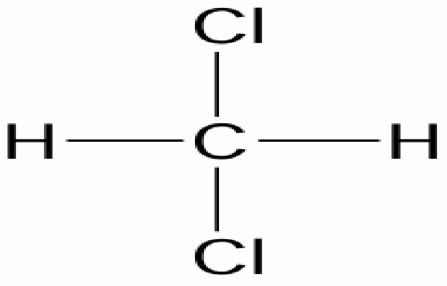


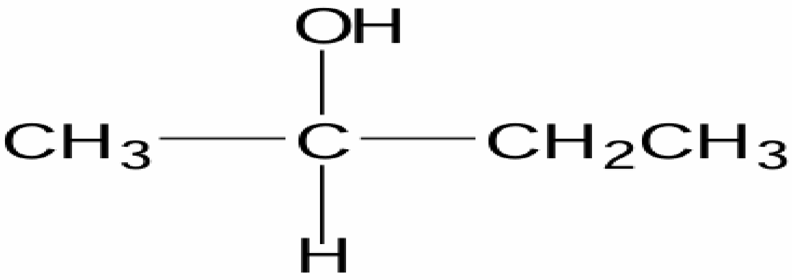
glucose

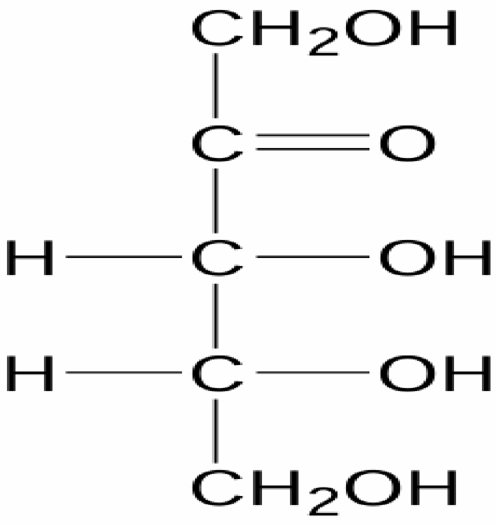


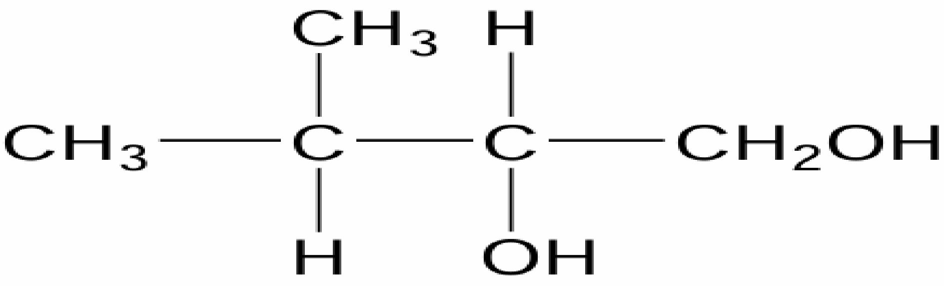
Examples: Number of Stereoisomers

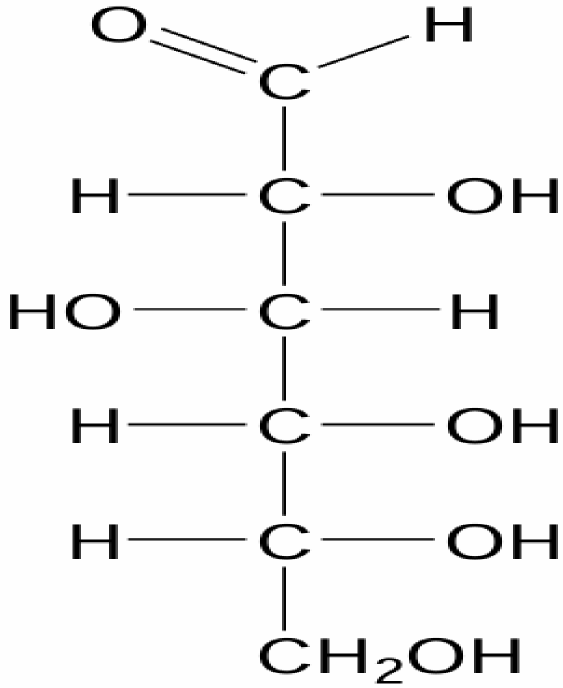
•What is the maximum number of possible stereo isomers of the following compounds?







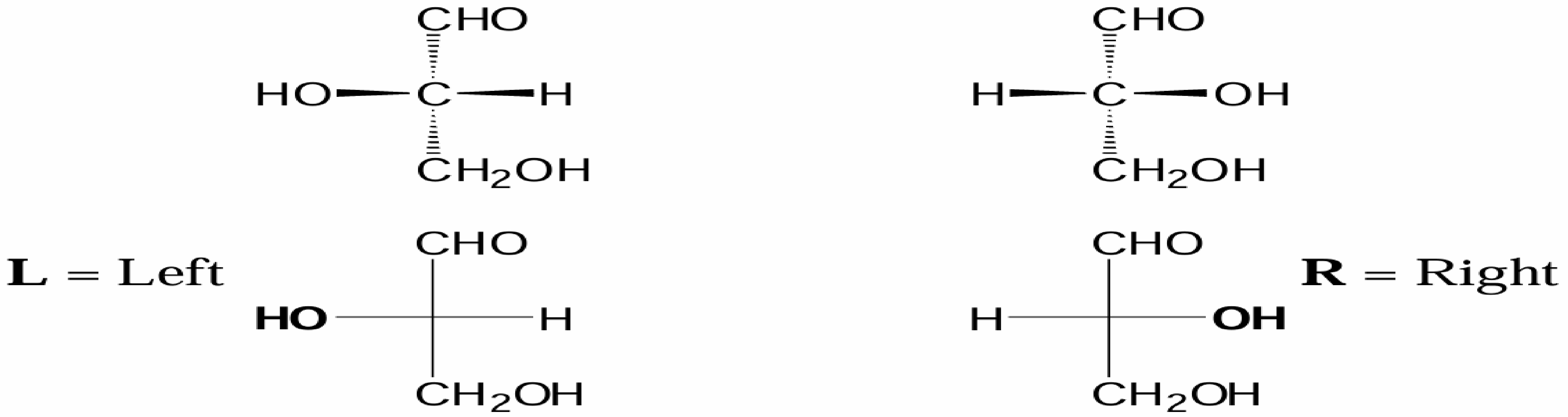




Fischer Projections

• **Fischer projections** are a convenient way to represent mirror images in two dimensions.

• Place the carbonyl group at or near the top and the last achiral CH2OH at the bottom.

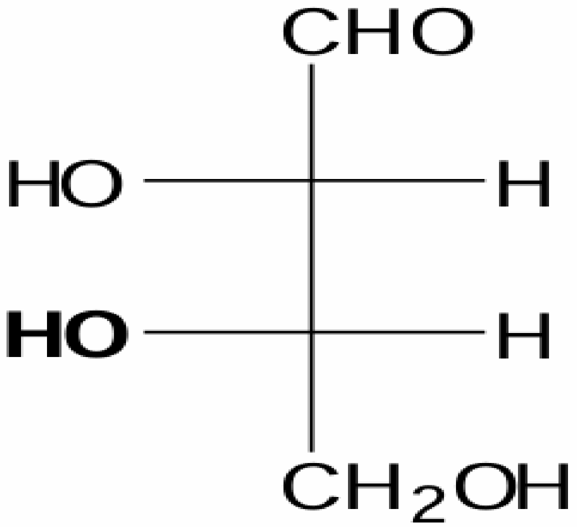


L-glyceraldehyde

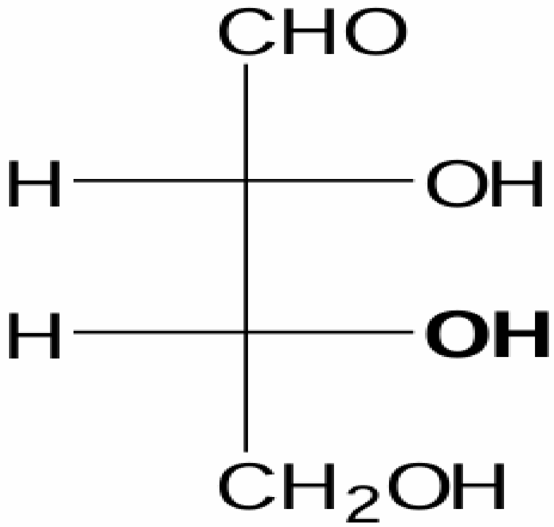
D-glyceraldehyde

Naming Stereoisomers

- When there is more than one chiral center in a carbohydrate, look at the chiral carbon farthest from the carbonyl group: if the hydroxy group points to right when the carbonyl is "up" it is the D-isomer, and when the hydroxy group points to the left, it is the L-isomer.



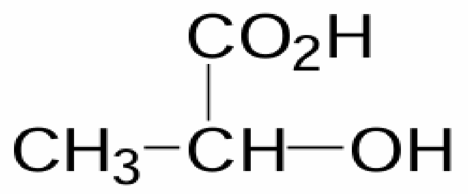
L-erythrose



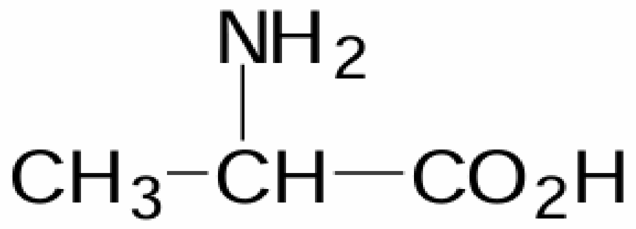
D-erythrose

Examples: Fischer Projections

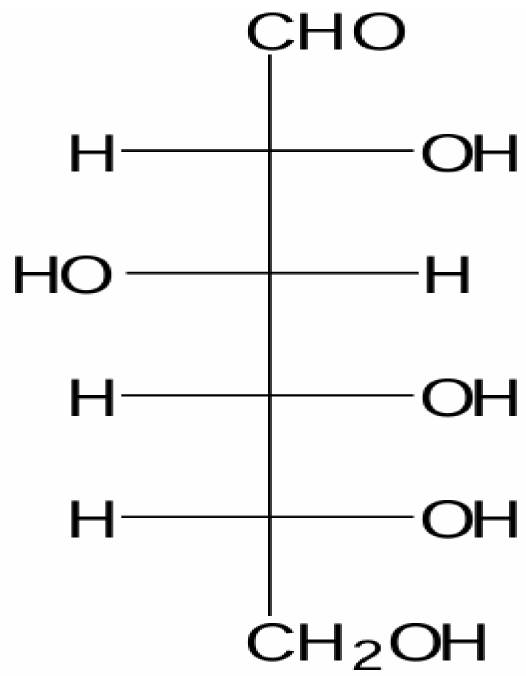
- Draw Fischer projections of D and L lactic acid:



- Draw Fischer projections of D and L alanine:



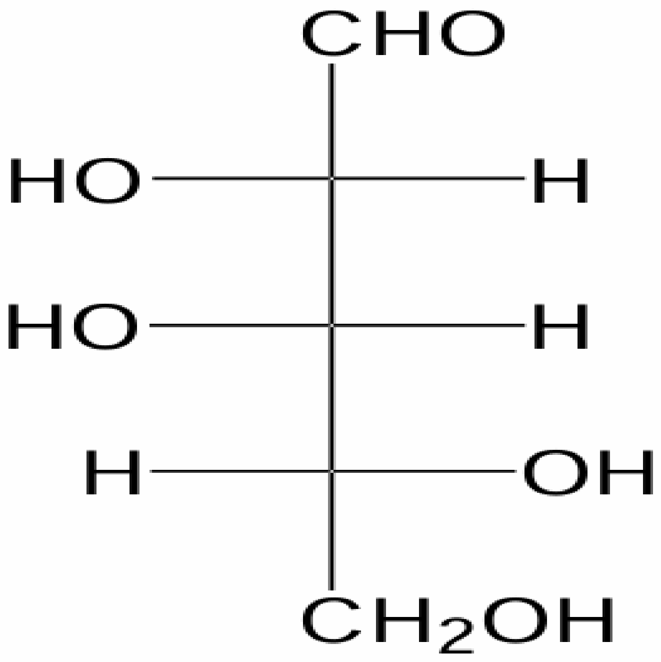
- Given the structure for D-glucose, draw the structure of L glucose:



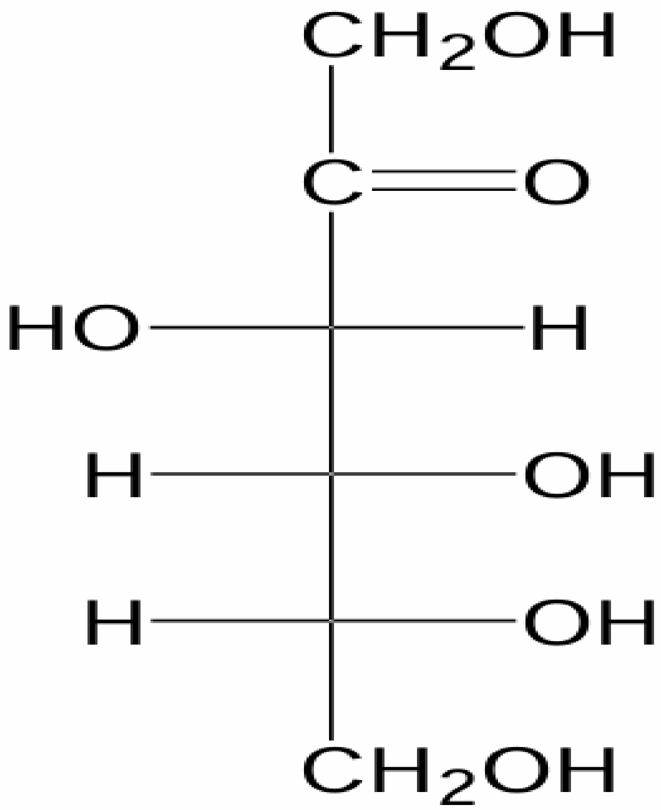
D-glucose

Examples: Fischer Projections

- Identify the following compounds as D or L isomers, and draw their mirror images.



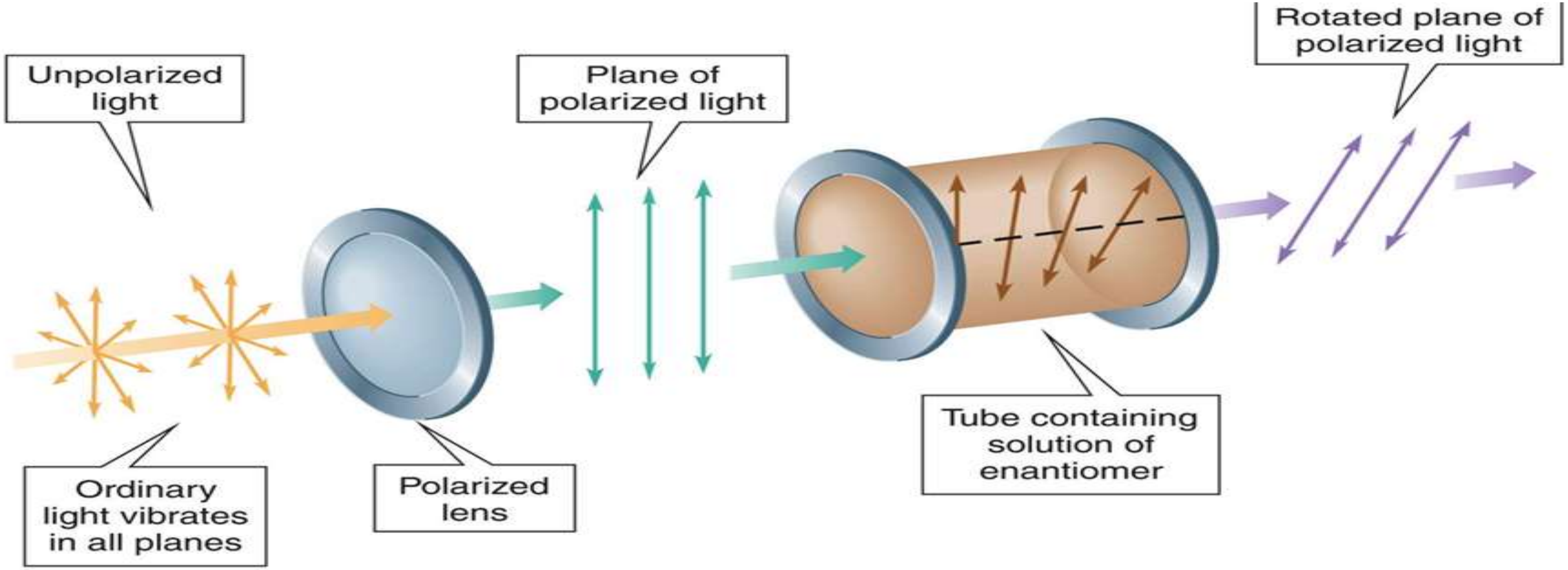
lyxose



fructose

What's So Great About Chiral Molecules?

- Molecules which are enantiomers of each other have exactly the **same** physical properties (melting point, boiling point, index of refraction, etc.) but not their interaction with **polarized light**.
- Polarized light vibrates only in one plane; it results from passing light through a **polarizing filter**.



Optical Activity

- A **levorotatory** (–) substance rotates polarized light to the left [e.g., *l*-glucose; (-)-glucose].
- A **dextrorotatory** (+) substance rotates polarized light to the right [e.g., *d*-glucose; (+)-glucose].
- Molecules which rotate the plane of polarized light are **optically active**.
- Many biologically important molecules are chiral and optically active. Often, living systems contain only one of the possible stereochemical forms of a compound, or they are found in separate systems.
  - L-lactic acid is found in living muscles; D-lactic acid is present in sour milk.
  - In some cases, one form of a molecule is beneficial, and the enantiomer is a poison (e.g., thalidomide).
  - Humans can metabolize D-monosaccharides but not L-isomers; only L-amino acids are used in protein synthesis

Monosaccharides

Classification of Monosaccharides

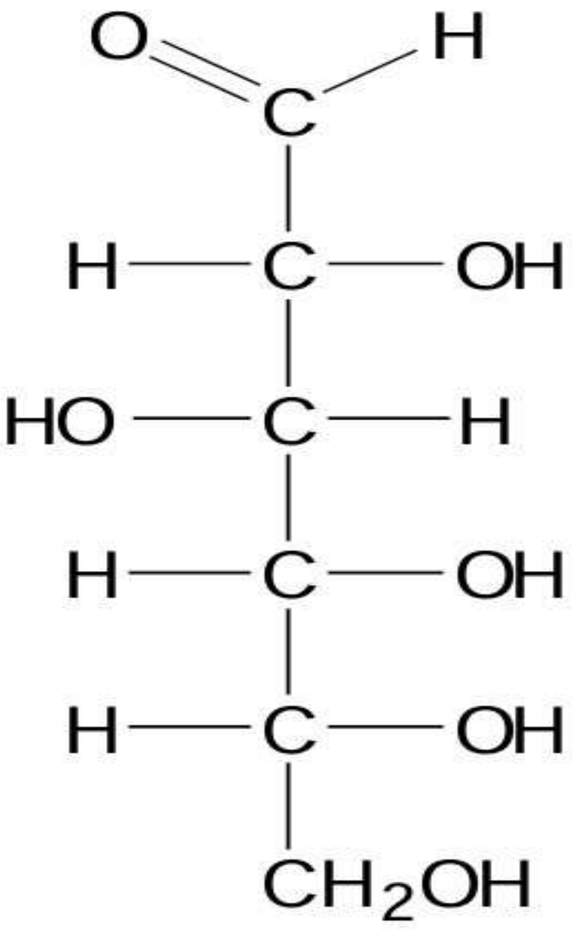
- The monosaccharides are the simplest of the carbohydrates, since they contain only one polyhydroxy aldehyde or ketone unit.
- Monosaccharides are classified according to the number of carbon atoms they contain:

No. of carbons	Class of Monosaccharide
3	triose
4	tetrose
5	pentose
6	hexose

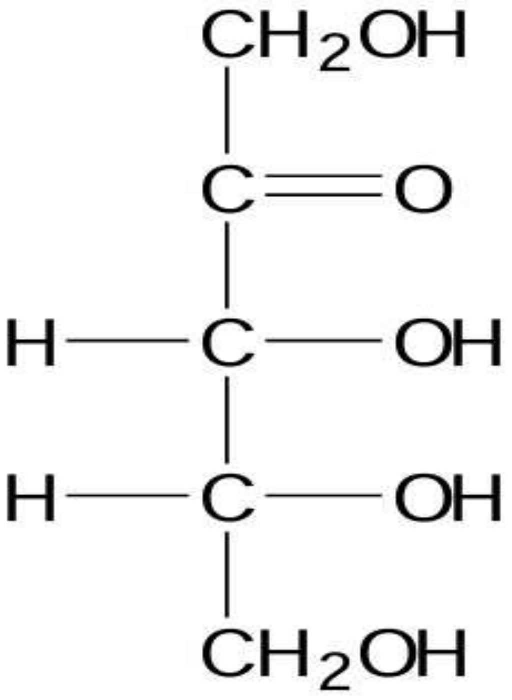
- The presence of an aldehyde is indicated by the prefix **aldo**- and a ketone by the prefix **keto**-.

Classification of Monosaccharides

- Thus, glucose is an **aldohexose** (aldehyde + 6 Cs) and ribulose is a **ketopentose** (ketone + 5 Cs)



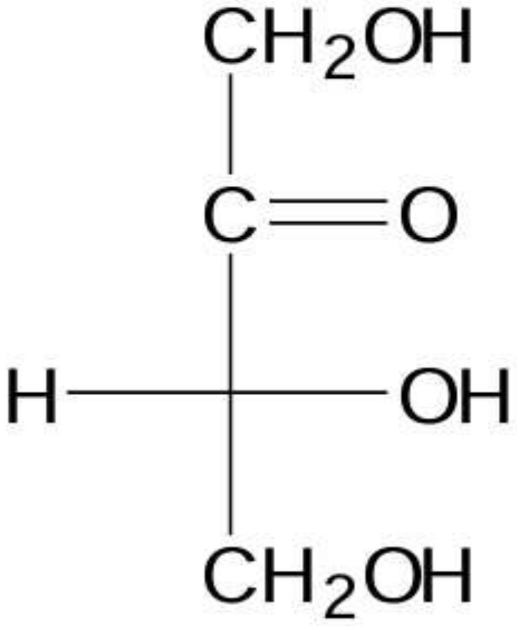
glucose
an **aldohexose**

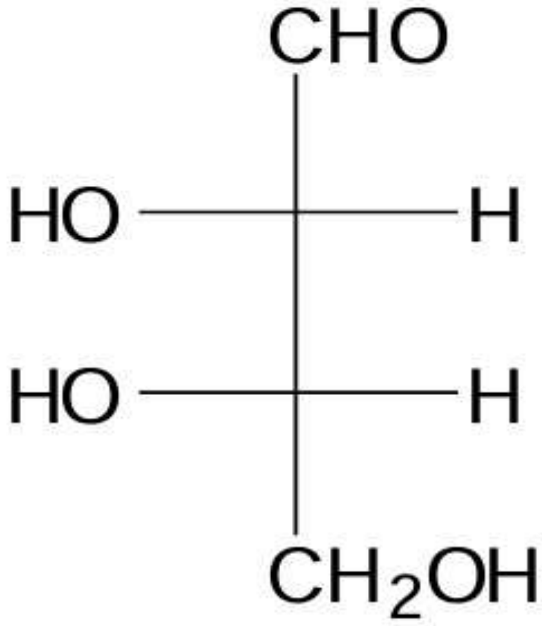


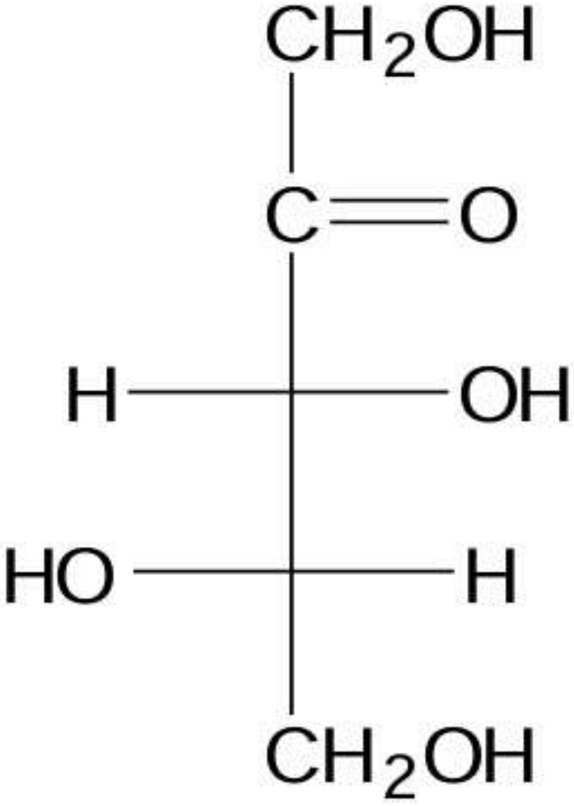
ribulose
a **ketopentose**

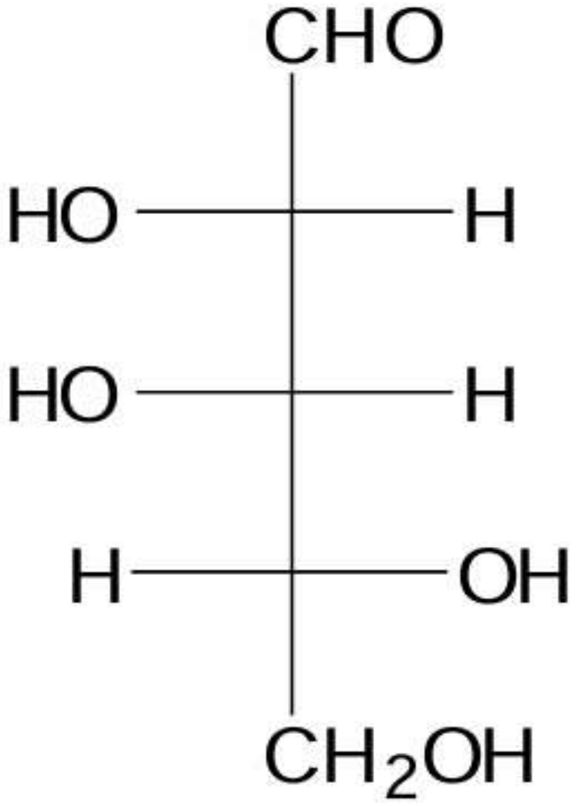
Examples: Classifying Monosaccharides

- Classify the following monosaccharides:



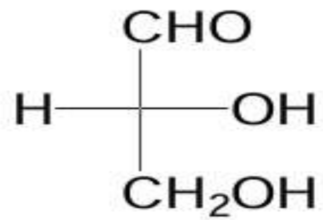






The Family of D-aldoses

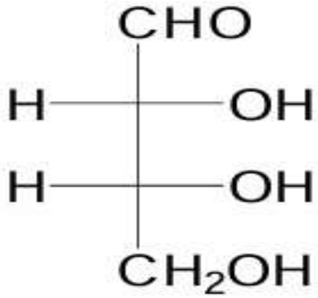
(L-forms not shown)



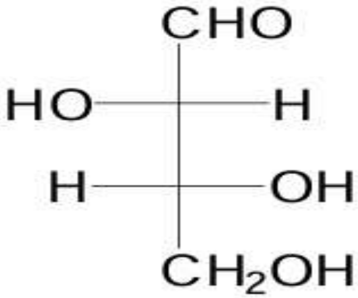
D-glyceraldehyde

Aldotriose

$2^1 = 2$



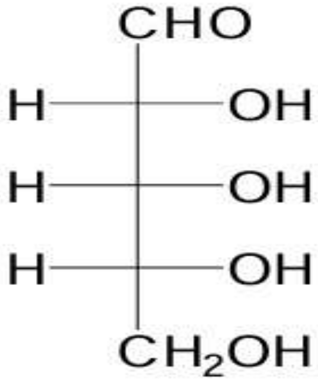
D-erythrose



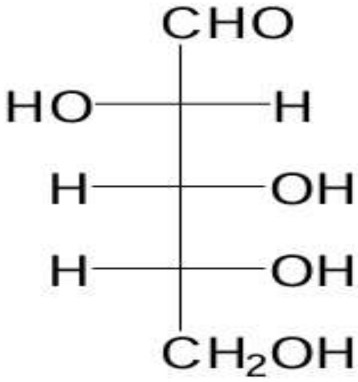
D-threose

Aldotetroses

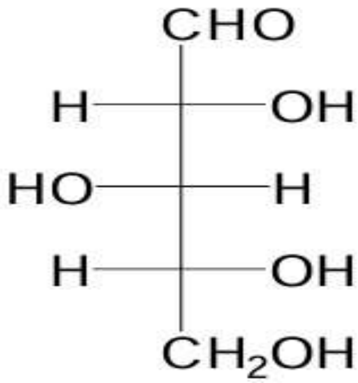
$2^2 = 4$



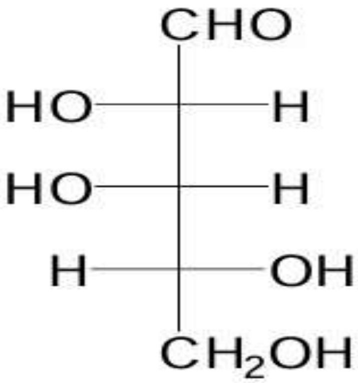
D-ribose



D-arabinose



D-xylose



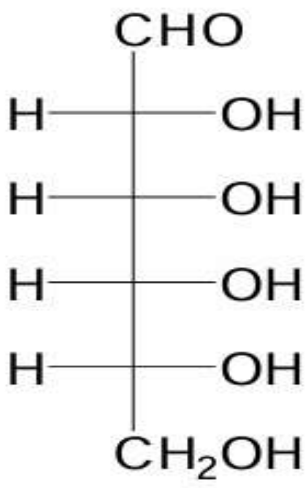
D-lyxose

Aldopentoses

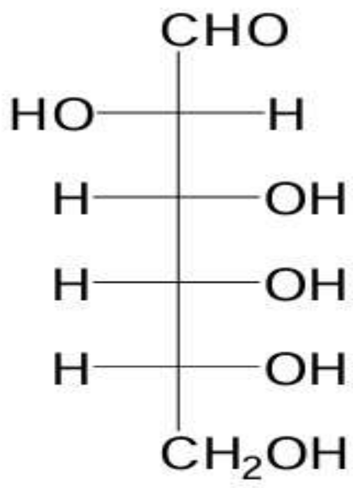
$2^3 = 8$

The Family of D-aldoses

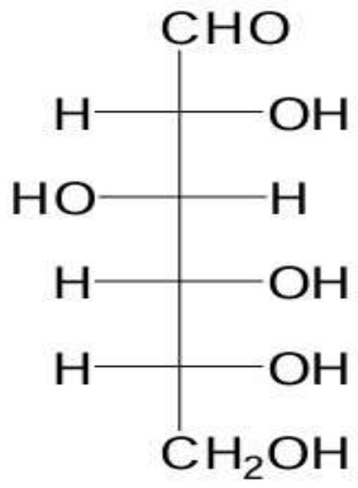
(L-forms not shown)



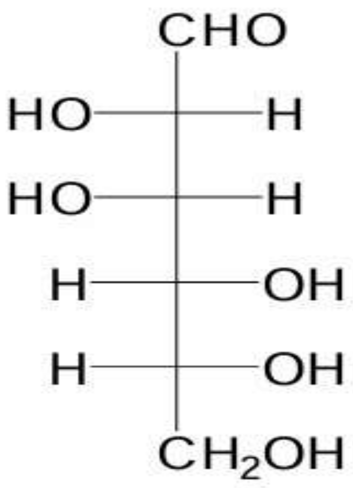
D-allose



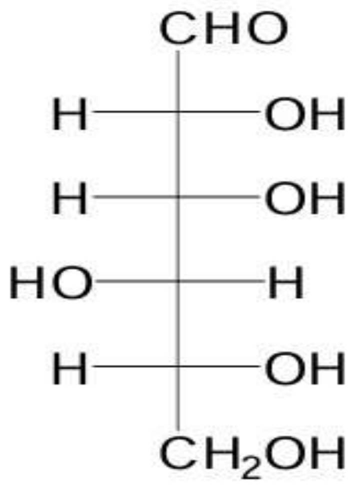
D-altrose



D-glucose

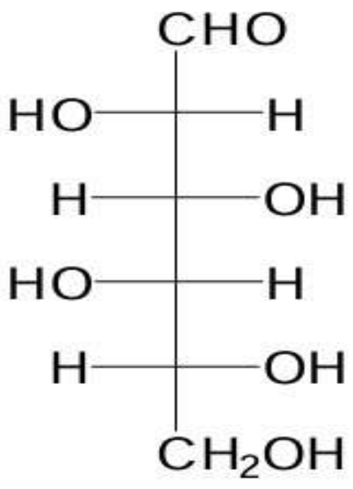


D-mannose

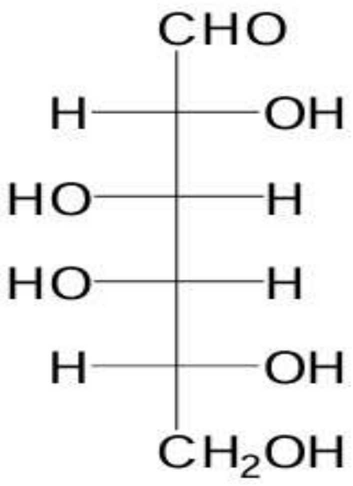


D-gulose

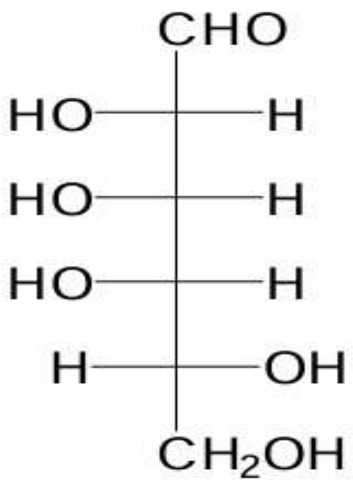
Aldohexoses
$2^4 = 16$



D-idose



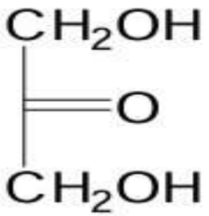
D-galactose



D-talose

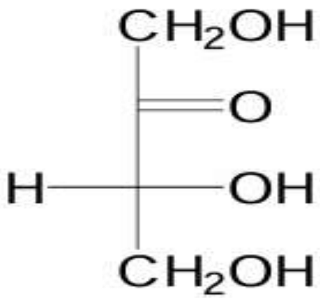
The Family of D-ketoses

(L-forms not shown)



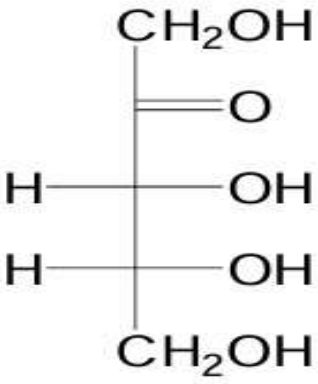
Dihydroxyacetone

Ketotriose
$2^0 = 1$

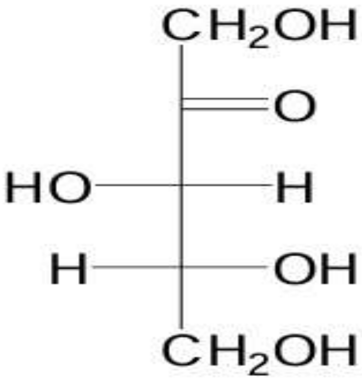


D-erythrulose

Ketotetroses
$2^1 = 2$



D-ribulose

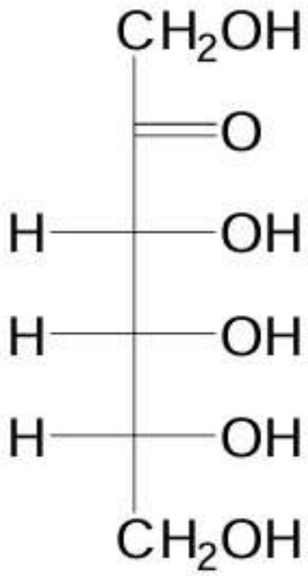


D-xylulose

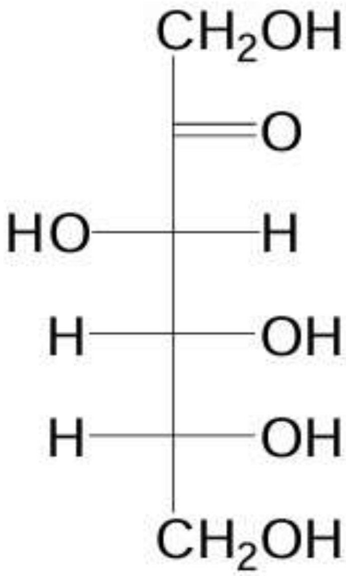
Ketopentoses
$2^2 = 4$

The Family of D-ketoses

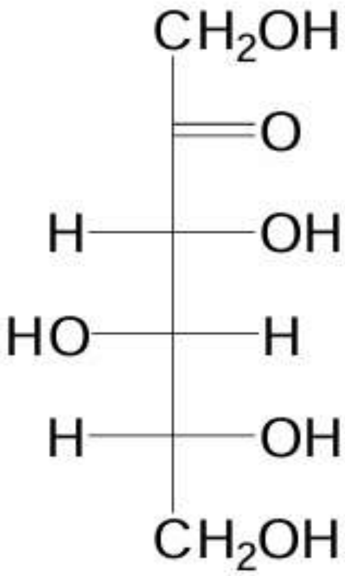
(L-forms not shown)



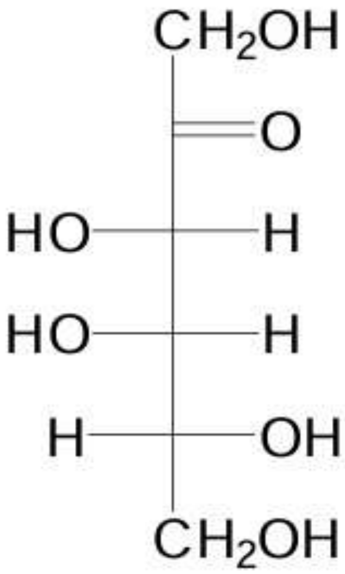
D-Psicose



D-Fructose



D-Sorbose



D-Tagatose

Ketohexoses

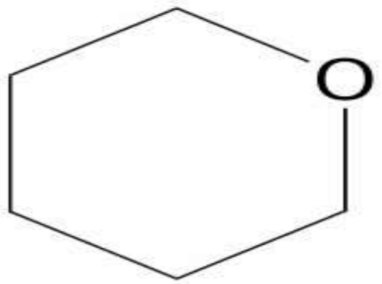
$2^3 = 8$

Physical Properties of Monosaccharides

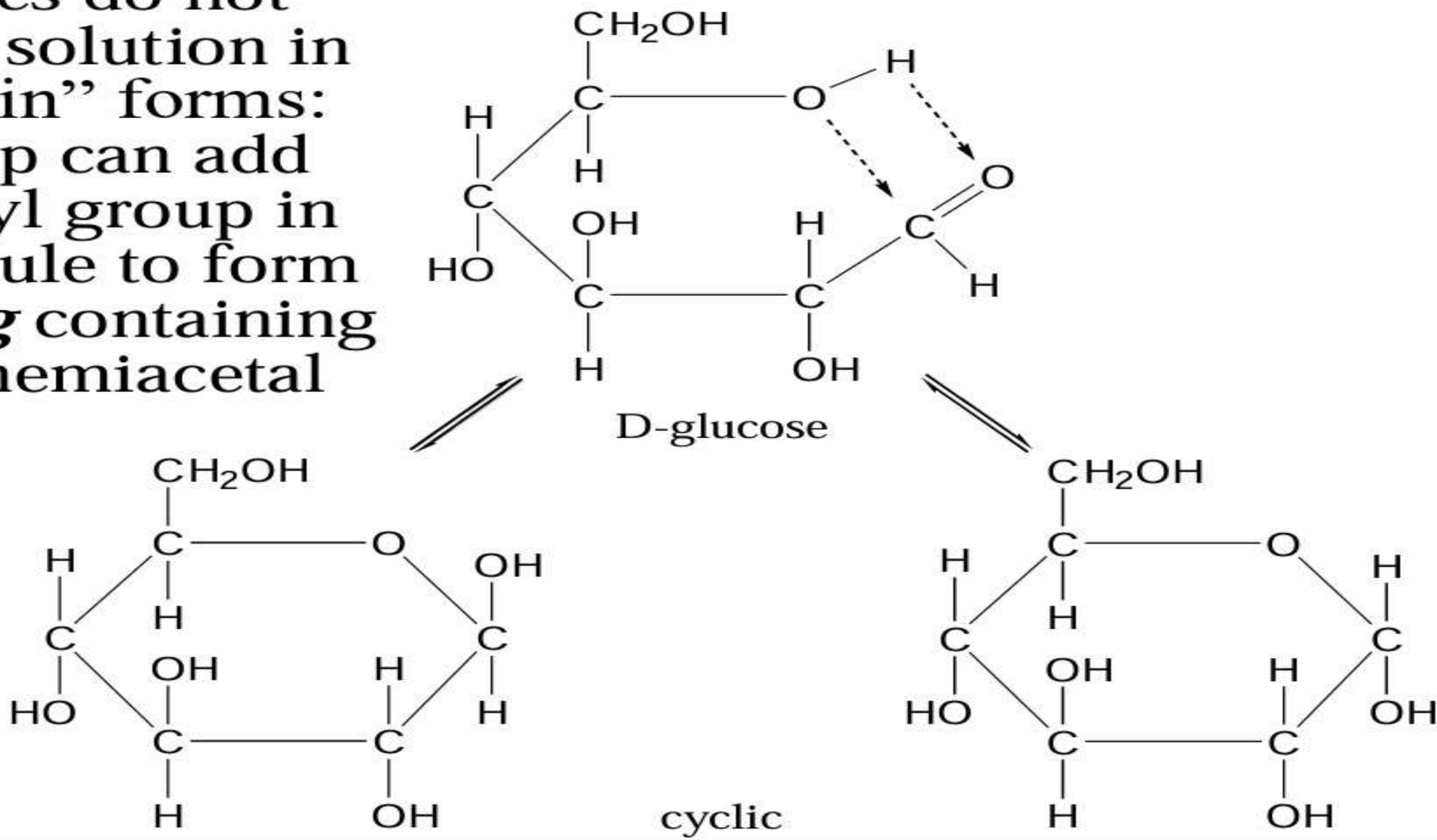
- Most monosaccharides have a sweet taste (fructose is sweetest; 73% sweeter than sucrose).
- They are solids at room temperature.
- They are *extremely* soluble in water:
  - Despite their high molecular weights, the presence of large numbers of OH groups make the monosaccharides much more water soluble than most molecules of similar MW.
  - Glucose can dissolve in minute amounts of water to make a syrup (1 g / 1 ml H2O).

Chemical Properties of Monosaccharides

- Monosaccharides do not usually exist in solution in their “open-chain” forms: an alcohol group can add into the carbonyl group in the same molecule to form a ***pyranose ring*** containing a stable cyclic hemiacetal or hemiketal.



a **pyranose ring**

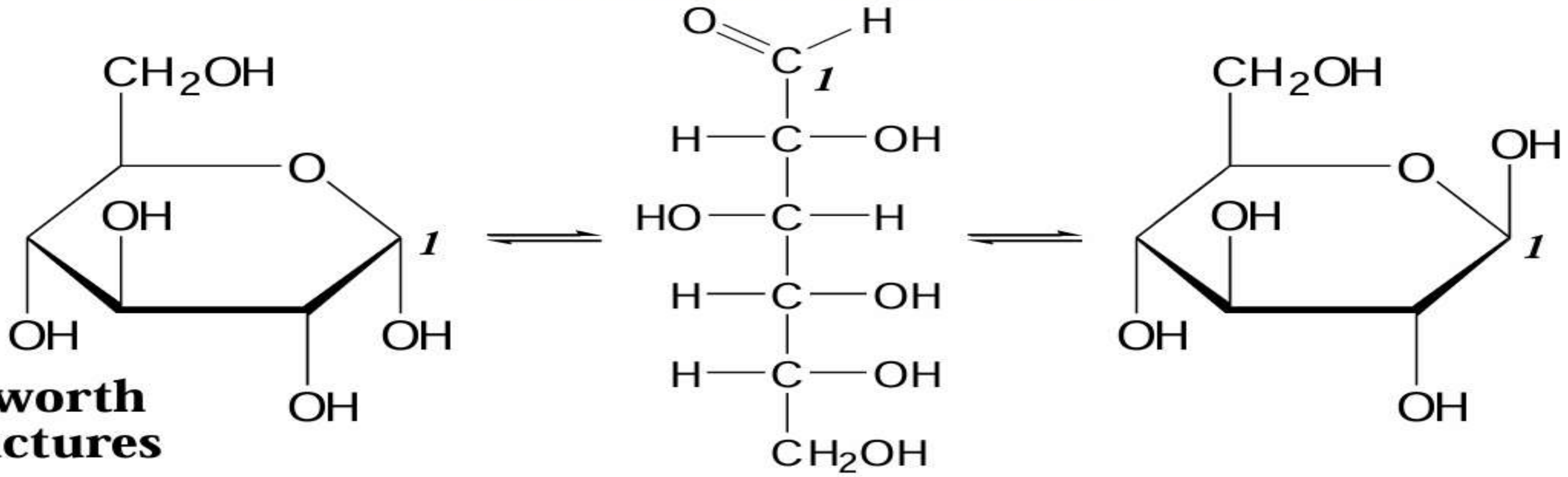


β-D-glucose
β-up

cyclic hemiacetals

α-D-glucose
α-down

Glucose Anomers



Haworth structures

α-D-glucose 36%

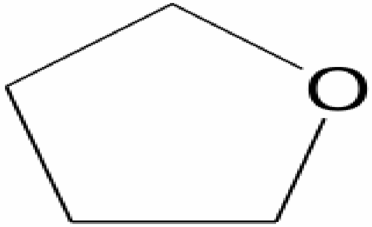
D-glucose 0.02%

β-D-glucose 64%

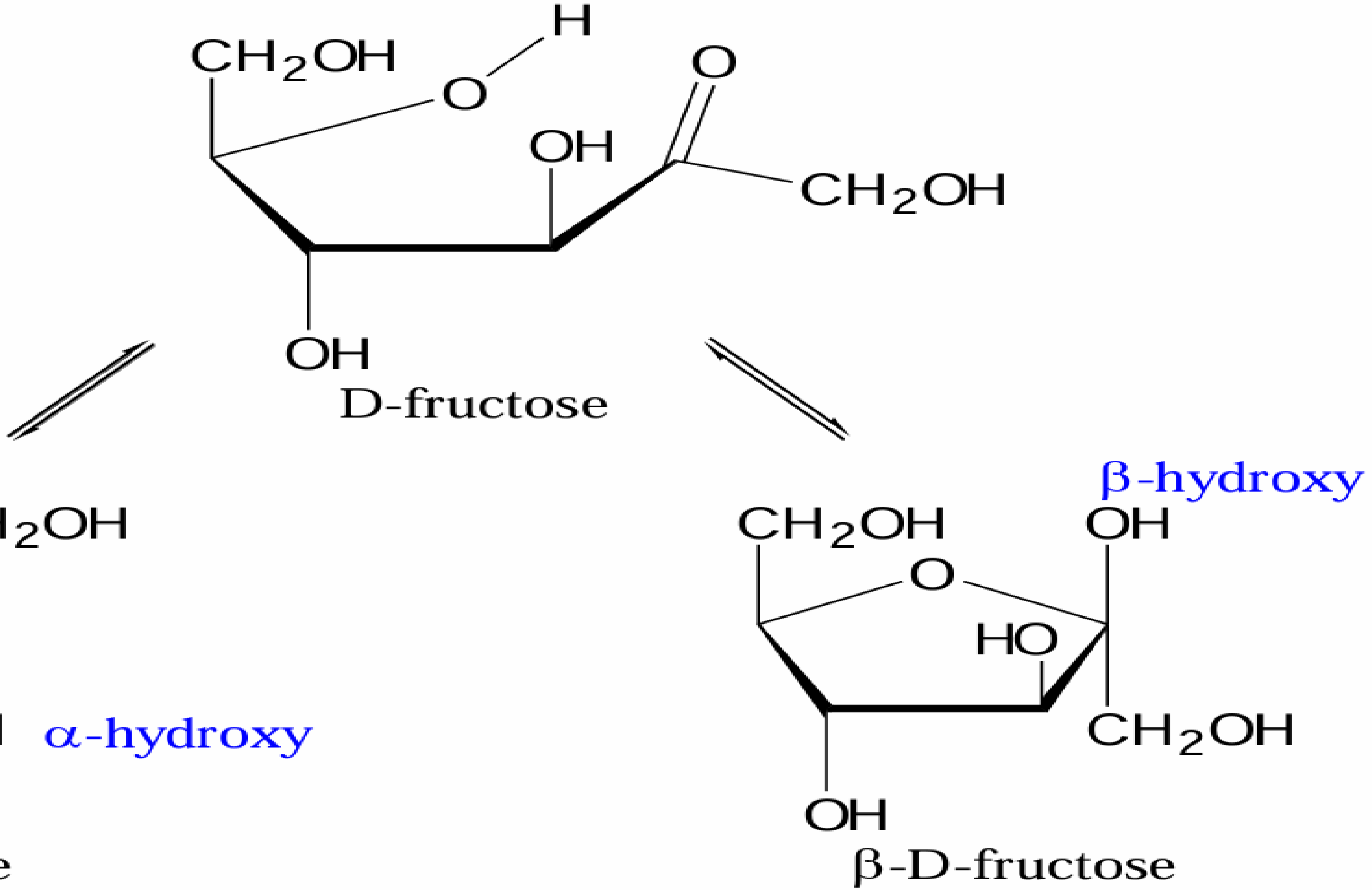
- In the pyranose form of glucose, carbon-1 is chiral, and thus two stereoisomers are possible: one in which the OH group points down (α-hydroxy group) and one in which the OH group points up (β-hydroxy group). These forms are **anomers** of each other, and carbon-1 is called the **anomeric carbon**.

Fructose Anomers

- Fructose closes on itself to form a **furanose ring**:



a **furanose ring**



Drawing Furanose and Pyranose Rings

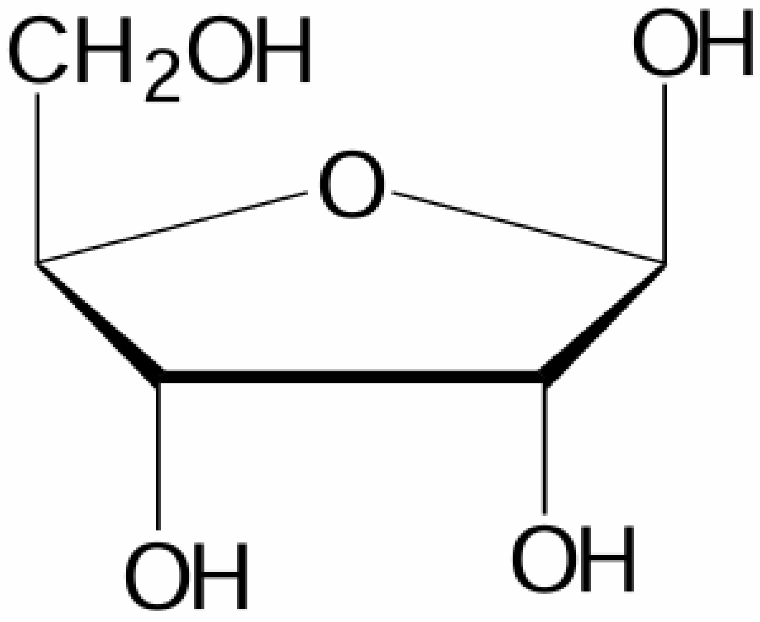
- Monosaccharides are often represented using the Haworth structures shown below for furanose and pyranose rings.
- The remaining OH groups on the ring point up or down depending on the identity of the sugar.

Furanose ring

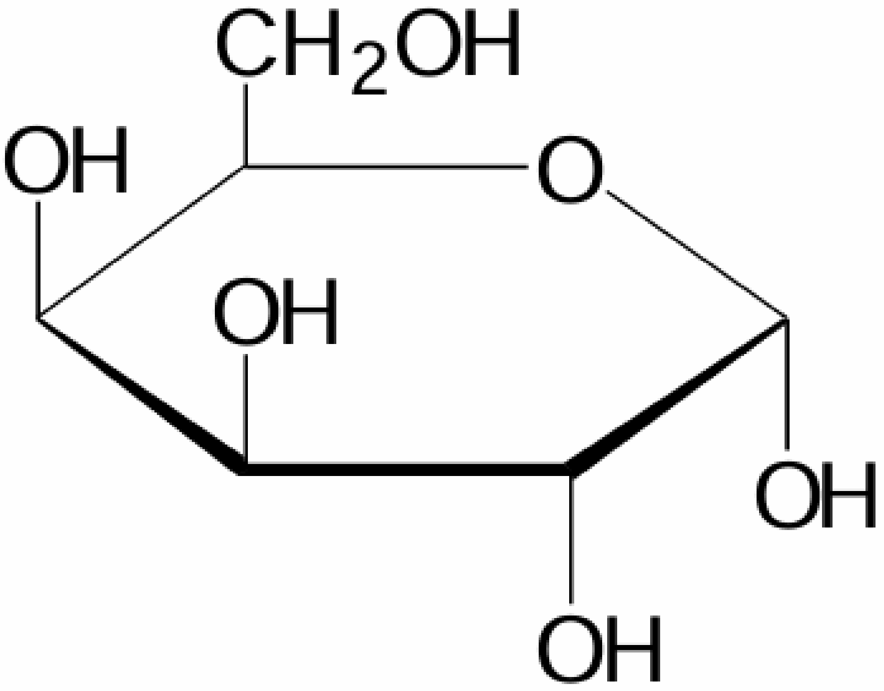
Pyranose ring

Examples: Anomers

- Identify the structures below as being the α- or β-forms, and draw the structure of their anomers:



ribose



galactose

Oxidation of Monosaccharides

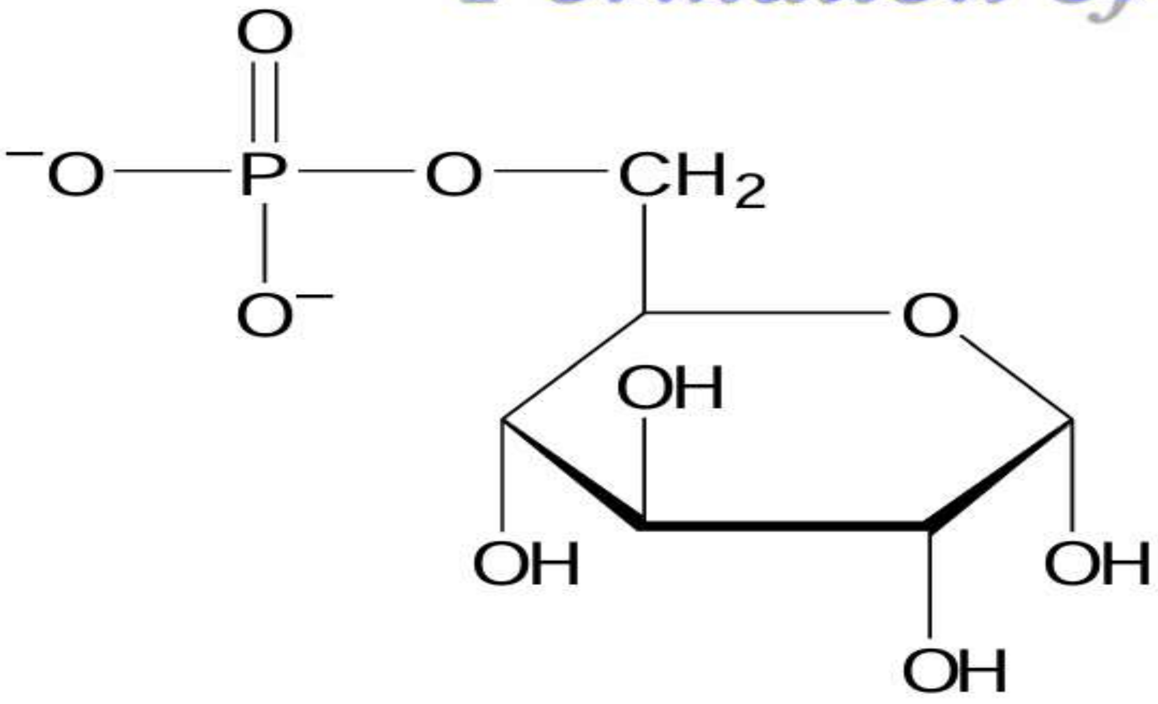
- Aldehydes and ketones that have an OH group on the carbon next to the carbonyl group react with a basic solution of Cu^{2+} (**Benedict's reagent**) to form a red-orange precipitate of copper(I) oxide (Cu_2O).
- Sugars that undergo this reaction are called **reducing sugars**. (All of the monosaccharides are reducing sugars.)

$$\text{Reducing sugar} + \underset{\textit{deep blue solution}}{Cu^{2+}} \longrightarrow \text{oxidation product} + \underset{\textit{red-orange ppt}}{Cu_2O}$$

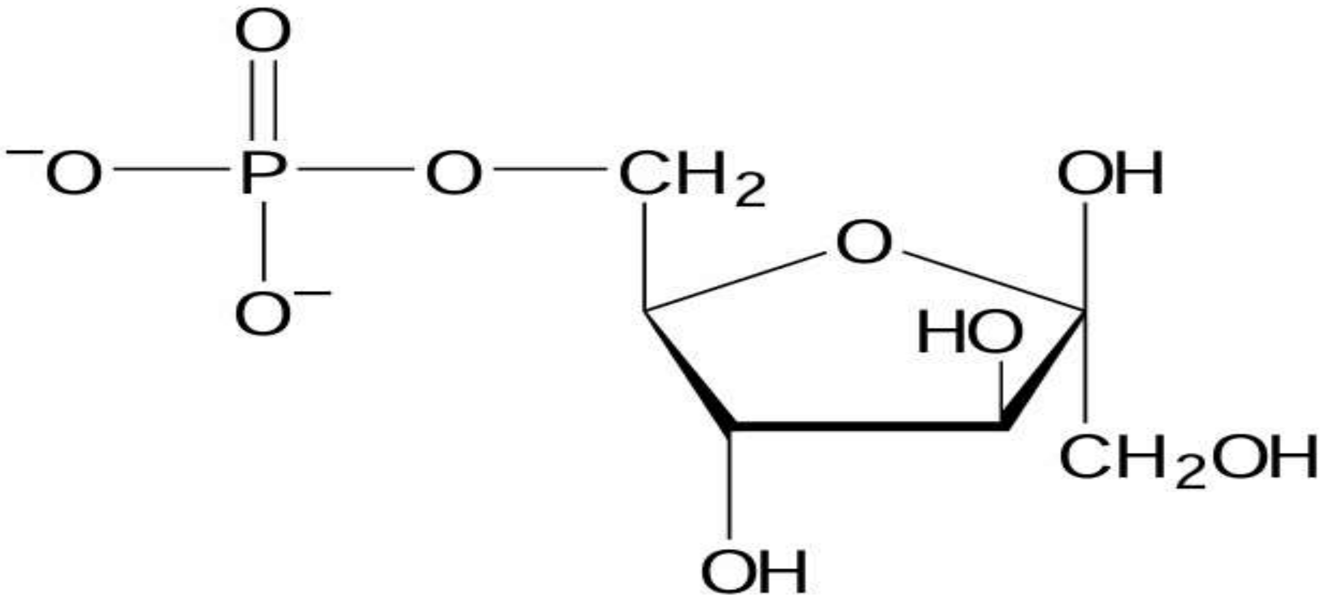
Benedict's Reagent (blue)

Copper(I) oxide (red-orange ppt)

Formation of Phosphate Esters



glucose 6-phosphate

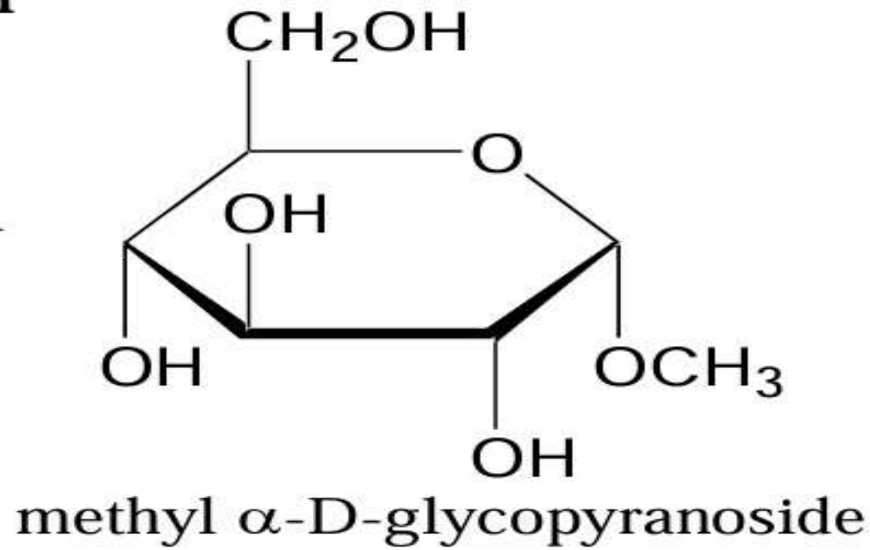


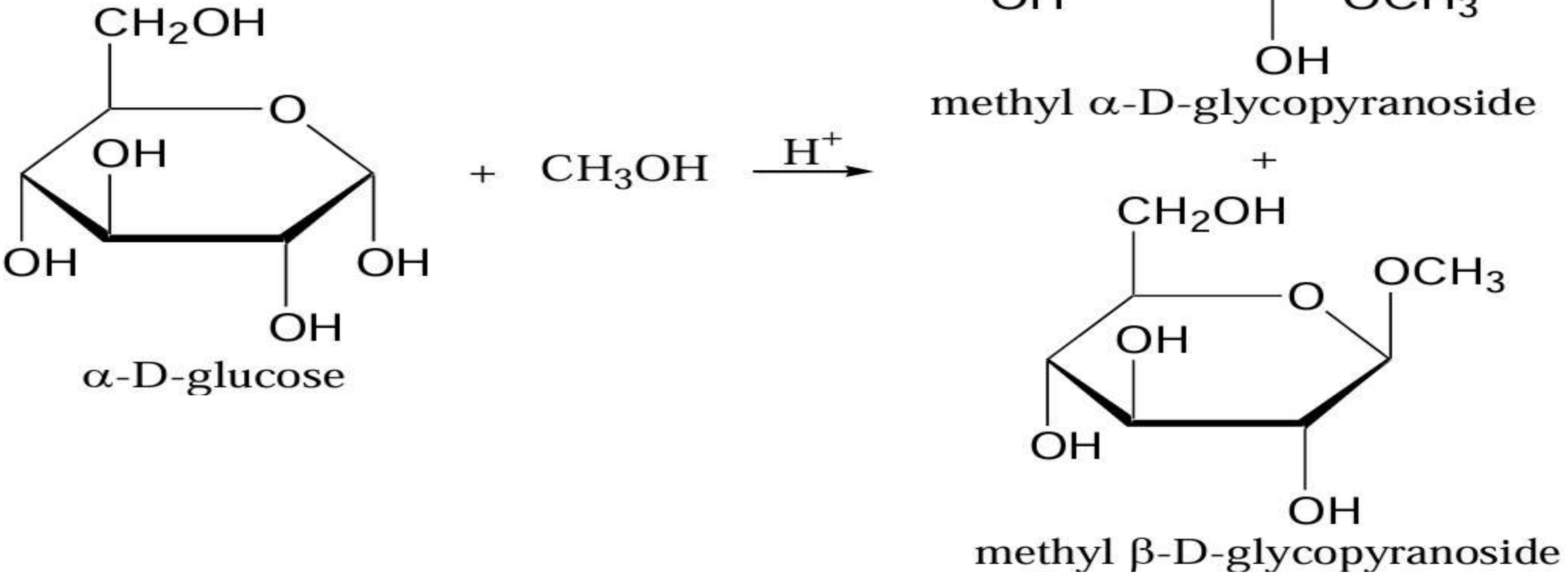
fructose 6-phosphate

- Phosphate esters can form at the 6-carbon of aldohexoses and aldoketoses.
- Phosphate esters of monosaccharides are found in the sugar-phosphate backbone of DNA and RNA, in ATP, and as intermediates in the metabolism of carbohydrates in the body.

Glycoside Formation

- The hemiacetal and hemiketal forms of monosaccharides can react with alcohols to form acetal and ketal structures called **glycosides**. The new carbon-oxygen bond is called the **glycosidic linkage**.





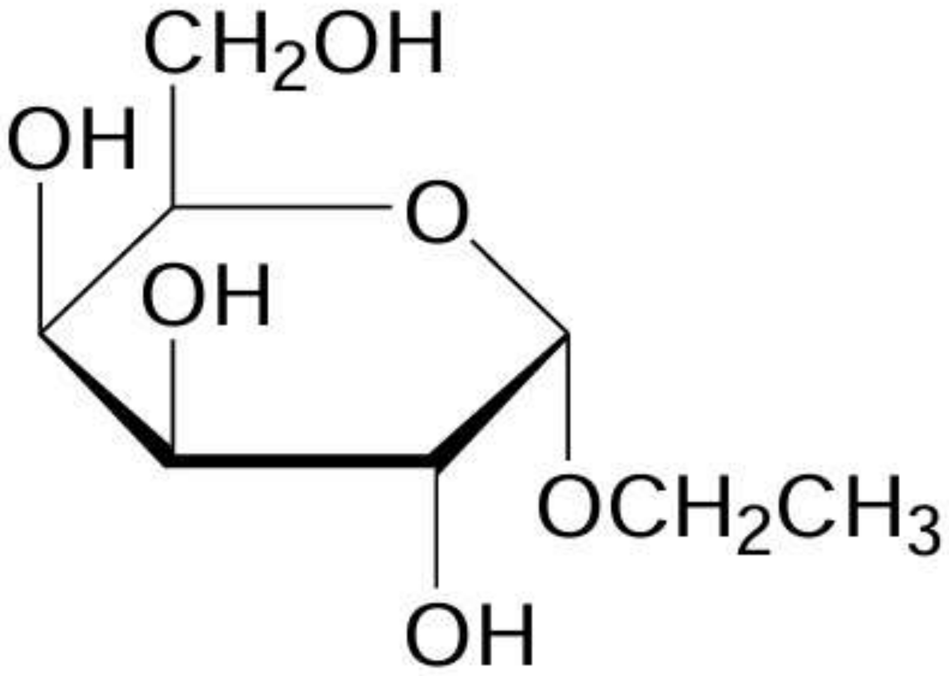
Glycoside Formation

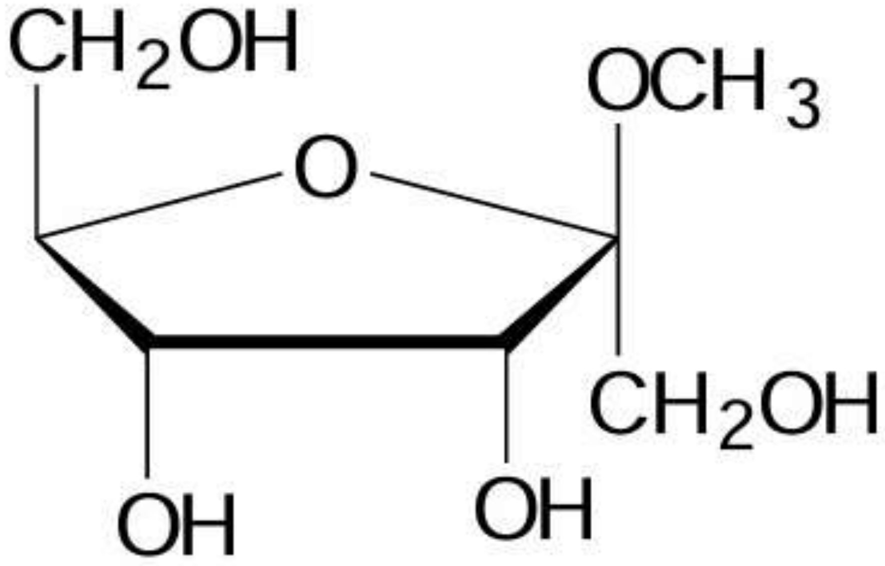
- Once the glycoside is formed, the ring can no longer open up to the open-chain form. Glycosides, therefore, are **not** reducing sugars.

$$\text{Glycoside} + Cu^{2+} \longrightarrow \text{NR}$$

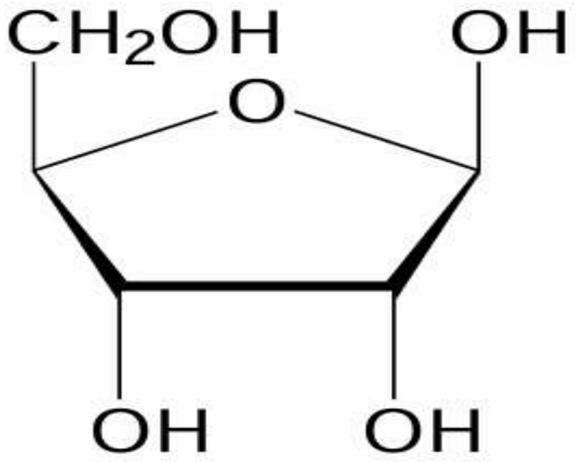
Examples: Glycoside Formation

- Identify the glycosidic linkage in each of the following molecules:

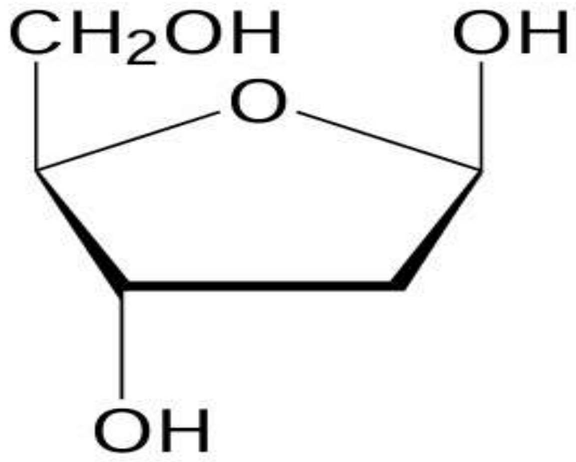




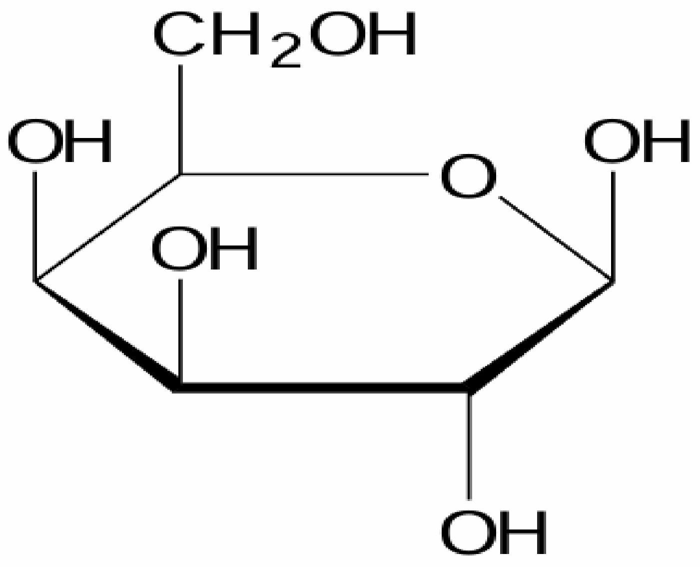
Important Monosaccharides



β-D-ribose
Forms the sugar backbone of
ribonucleic acid (**RNA**)

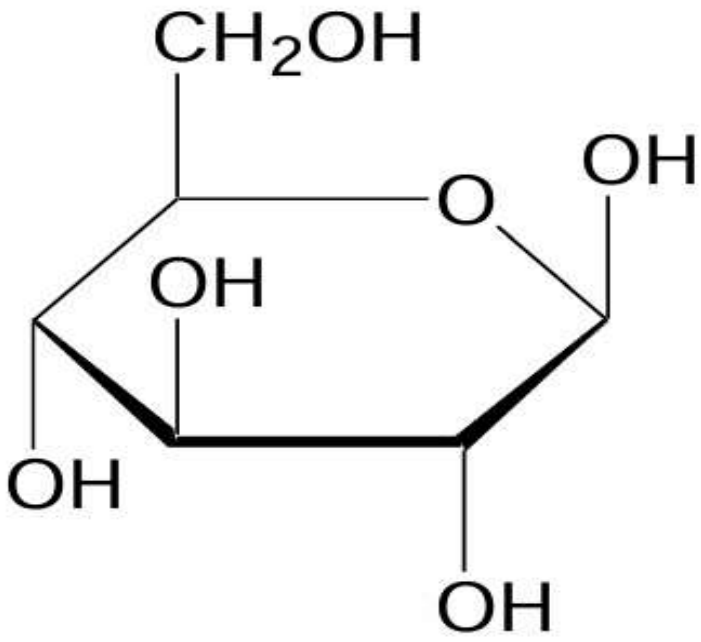


β-D-deoxyribose
Forms the sugar backbone of
deoxyribonucleic acid (**DNA**)



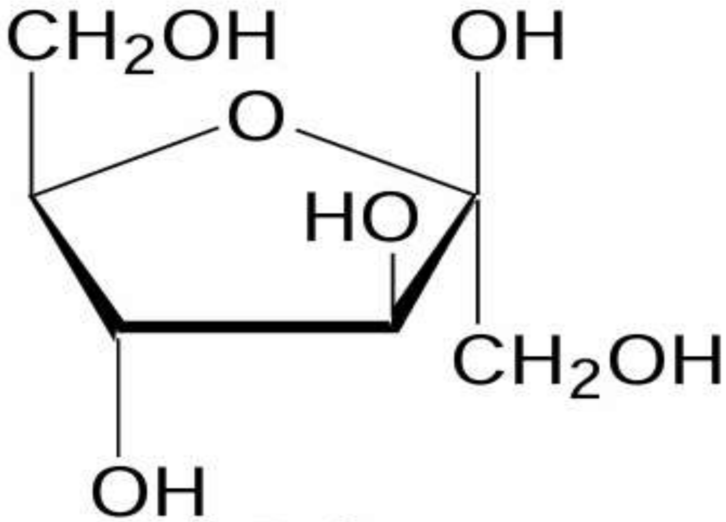
β-D-galactose
Incorporated with glucose
into lactose (milk sugar)

Important Monosaccharides



β-D-glucose

Also known as *dextrose* and *blood sugar*; present in honey and fruits. Glucose is metabolized in the body for energy. Other sugars absorbed into the body must be converted to glucose by the liver.



β-D-fructose

Also known as *levulose* and *fruit sugar*. Fructose is the sweetest of the monosaccharides. It is present in honey (1:1 ratio with glucose), fruits, and corn syrup. It is often used to sweeten foods, since less fructose is needed to achieve the same degree of sweetness.

The End