Carbohydrates

Carbohydrates

Carbohydrates are broadly defined as polyhydroxy aldehydes or ketones and their derivatives or as substances that yields one of these compounds

- Composed of carbon, hydrogen, and oxygen
- Functional groups present include hydroxyl groups
- -ose indicates sugar

Carbohydrates contained in foods such as pasta and bread provide energy for the body.

CARBOHYDRATES

- Carbohydrates are the most abundant organic compounds in the plant world.

- They act as storehouses of chemical energy (glucose, starch, glycogen); are the components of supportive structures in plants (cellulose), crustacean shells (chitin) and connective tissues in animals (acidic polysaccharides) and are essential components of nucleic acids (D-ribose and 2-deoxy-D-ribose).

- Carbohydrates make up about three fourths of the dry weight of plants.

- Animals (including humans) get their carbohydrates by eating plants, but they do not store much, what they consume.

Less than 1% of the body weight of animals is made up of carbohydrates. For a photosynthesis, an endothermic reductive condensation of carbon dioxide requiring light energy and the pigment chlorophyll.

$$nCO_2 + nH_2O + \text{energy} \xrightarrow[\text{chlorophyll}]{\text{sunlight}} C_nH_{2n}O_n + nO_2$$

CLASSIFICATION OF CARBOHYDRATES

- **Simple Sugars**
  - Monosaccharides
  - Disaccharides
- **Complex Carbohydrates**
  - Starch
  - Glycogen
  - Cellulose (a form of fiber)

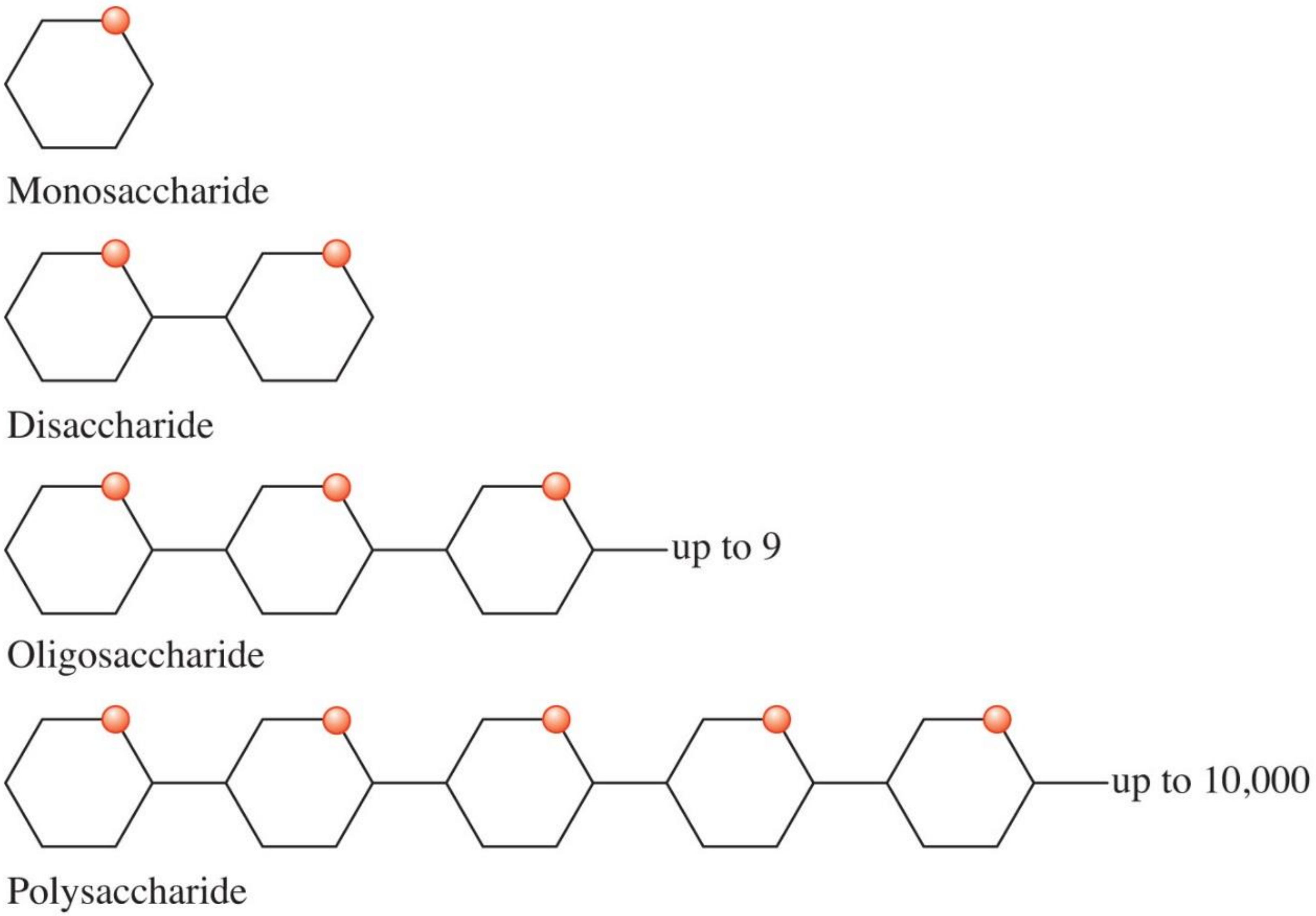
CLASSIFICATION

- There are a variety of interrelated classification schemes. The most useful classification scheme divides the carbohydrates into groups according to the number of individual simple sugar units.

- **Monosaccharides** contain a single unit;eg. glucose

- **disaccharides** contain two sugar units; eg.galactose

- **polysaccharides** contain many sugar units as in polymers - most contain glucose as the monosaccharide unit. eg.starch

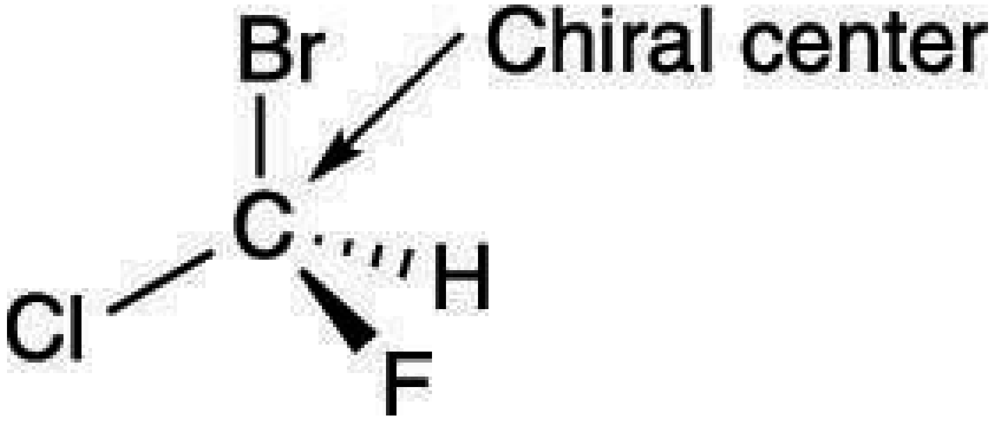

Monosaccharide
Disaccharide
up to 9
Oligosaccharide
up to 10,000
Polysaccharide

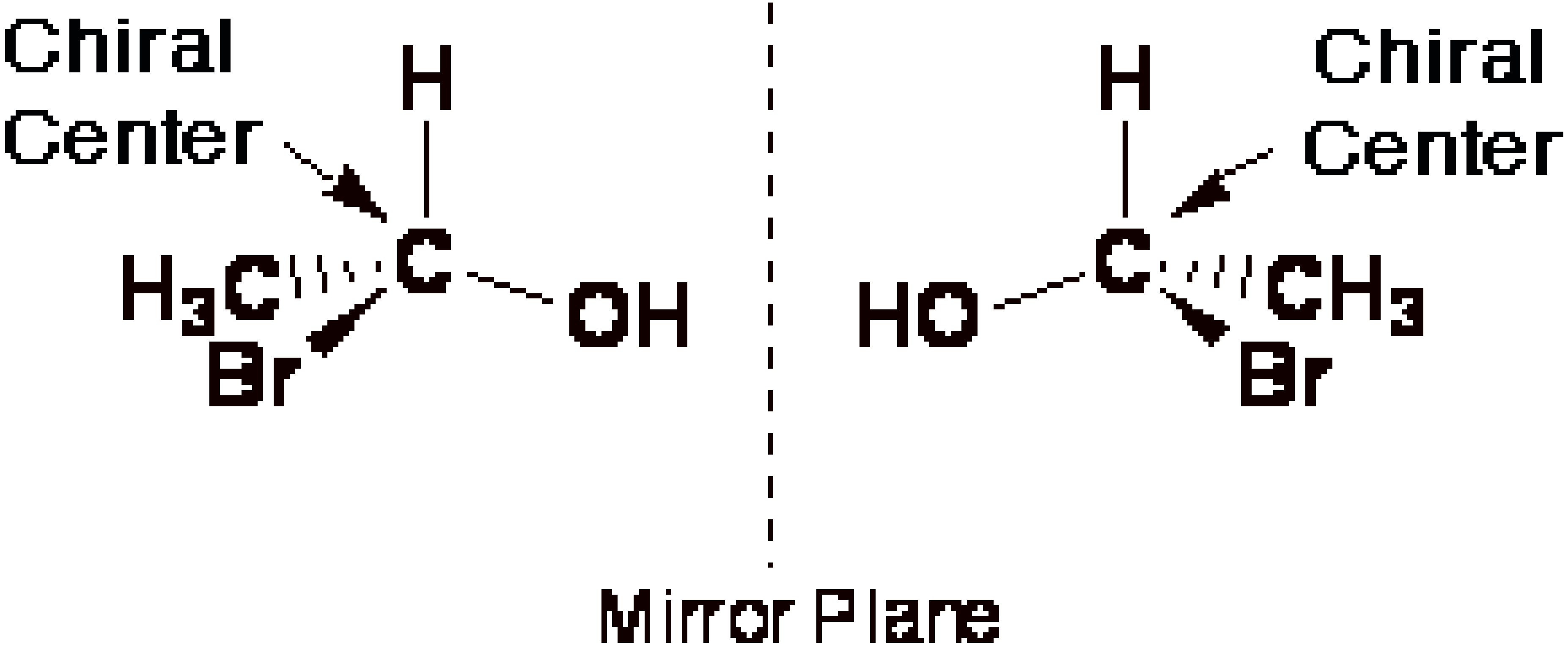
- Another type of classification scheme is based on the hydrolysis of certain carbohydrates to simpler carbohydrates i.e. classifications based on number of sugar units in total chain.
- Monosaccharides: single sugar unit
- Disaccharides: two sugar units
- Oligosaccharides: 3 to 10 sugar units
- Polysaccharides: more than 10 units

Monosaccharides

- **The simplest of the carbohydrates, are either aldehydes or ketones with two or more hydroxyl group.**
- The Six carbon monosaccharides are **glucose and fructose.**

A chiral centre is an atom that has four different groups bonded to it in such a manner that it has a nonsuperimposable mirror image

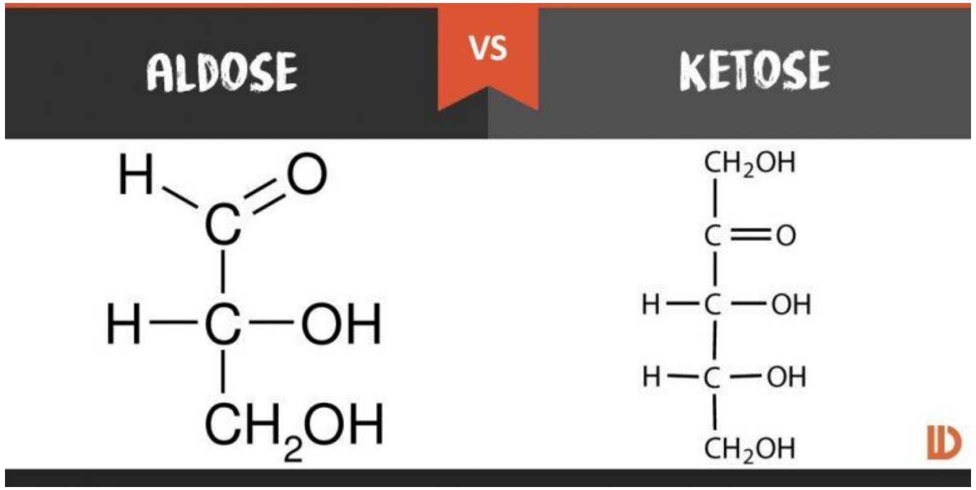



Chiral
Center
H
C
H_3C
Br
OH
H
C
HO
CH_3
Br
Chiral
Center
Mirror Plane

The addition of a hydroxyl group from within same molecule, generates the cyclic forms of five and six carbon sugars
And creates a new Chiral Centre.

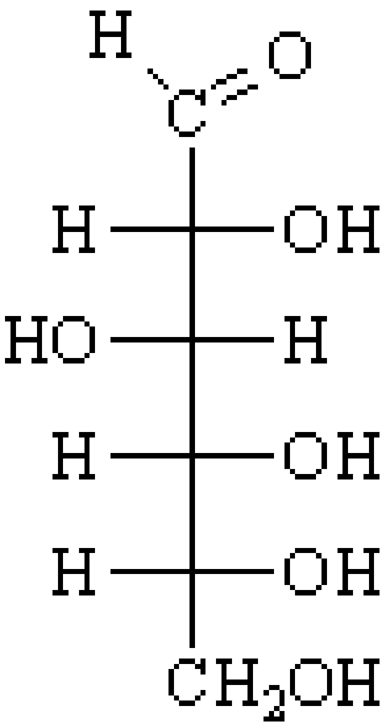
The Carbonyl Group is at end of the carbon chain (that is aldehyde group) , the monosaccharide is an Alodose

The Carbonyl Group is at any other position (in a Ketone Group) The monosaccharide is Ketose.

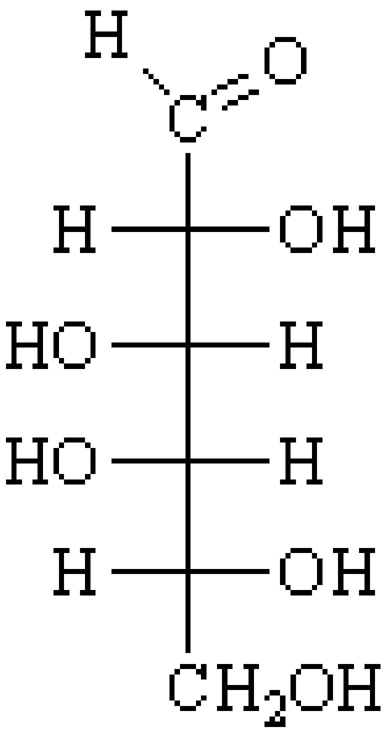


Monosaccharides
Classification by Carbon Atoms

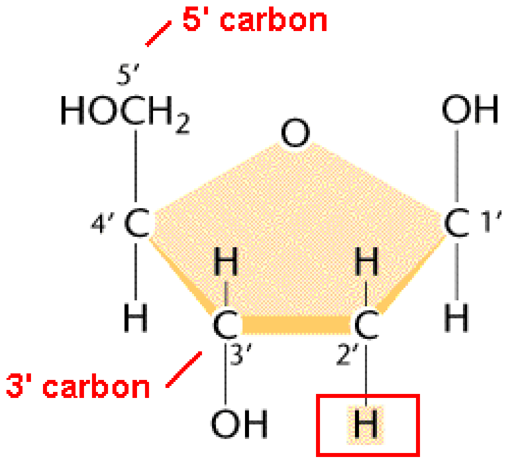
	Sugar	Structure formula	Aldoses	Ketoses
1.	Triose	$C_3H_6O_3$	Glyceraldehydes	Dehydroxy acetone
2.	Tetroses	$C_4H_8O_4$	Erythrose, Threose	Erthrulose
3.	Pentoses	$C_5H_{10}O_5$	Xylose Ribose Arabinose	Ribulose
4.	Hexoses	$C_6H_{12}O_6$	Glucose Galactose Mannose	Fructose



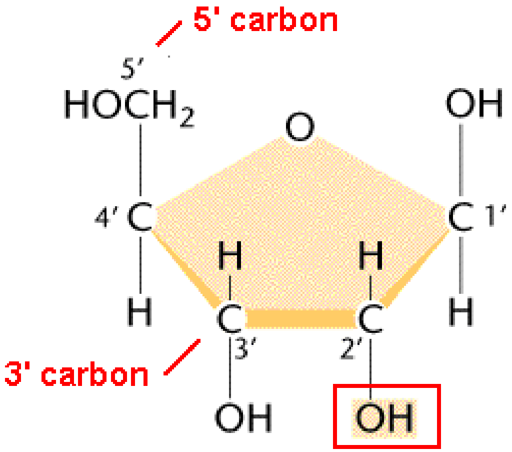
D-glucose



D-galactose



2-Deoxyribose



Ribose

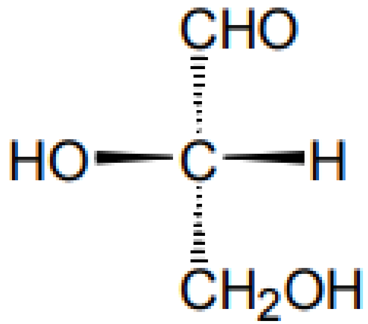
(Klug & Cummings 1997)

Two Common Hexose

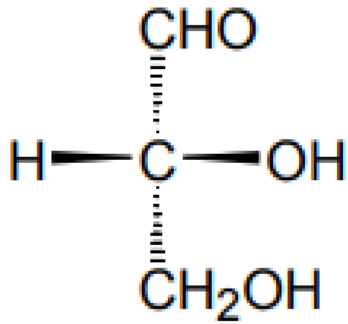
Pentose

Stereoisomers

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



L-glyceraldehyde

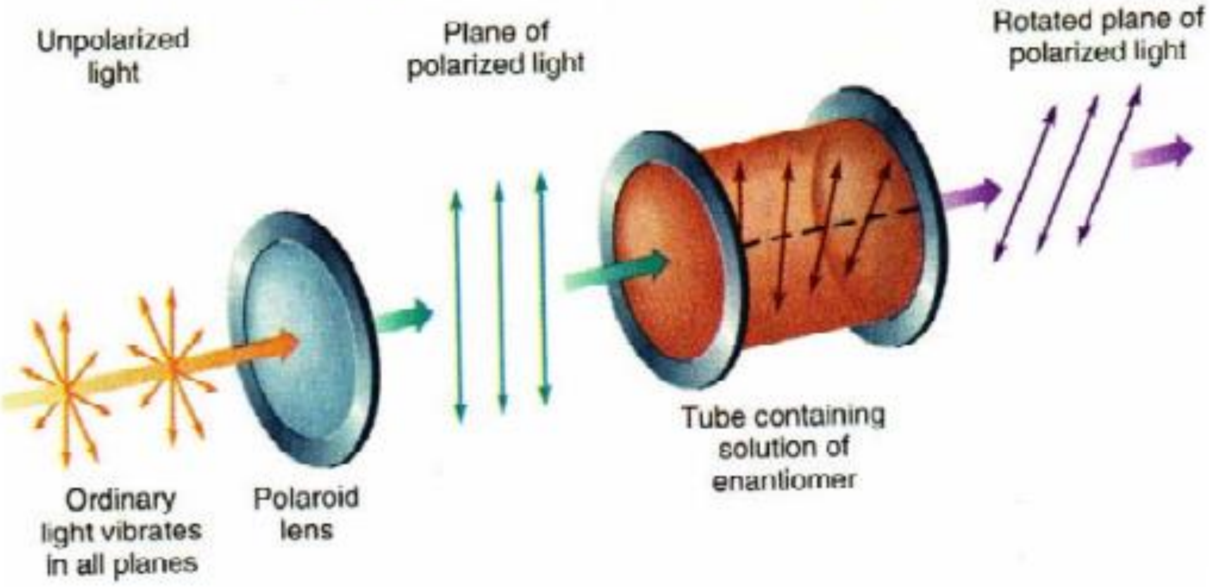


D-glyceraldehyde

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

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**.



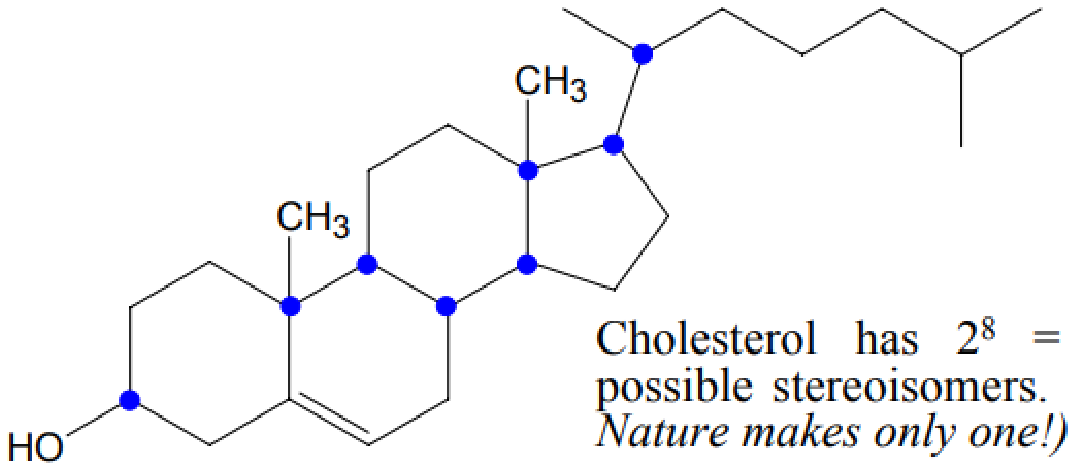
Optical Activity

- 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 of polarized light are **optically active**.
- Most biologically important molecules are chiral, and hence are optically active. Often, living systems contain only one of all of the possible stereochemical forms of a compound. In some cases, one form of a molecule is beneficial, and the enantiomer is a poison (e.g., thalidomide).

2^n Rule

- When a molecule has more than one chiral carbon, each carbon can possibly be arranged in either the right-hand or left-hand form, thus if there are *n* chiral carbons, there are 2^n possible stereoisomers.

Maximum number of possible stereoisomers = 2^n



Cholesterol has 2^8 = 256 possible stereoisomers. *(But Nature makes only one!)*

- <u>Monosaccharides</u> cannot be converted into simpler carbohydrates by hydrolysis. Glucose and fructose are examples of monosacchides is Sucrose, however, is a disaccharide-a compound that can be converted by hydrolysis into two monosaccharides.

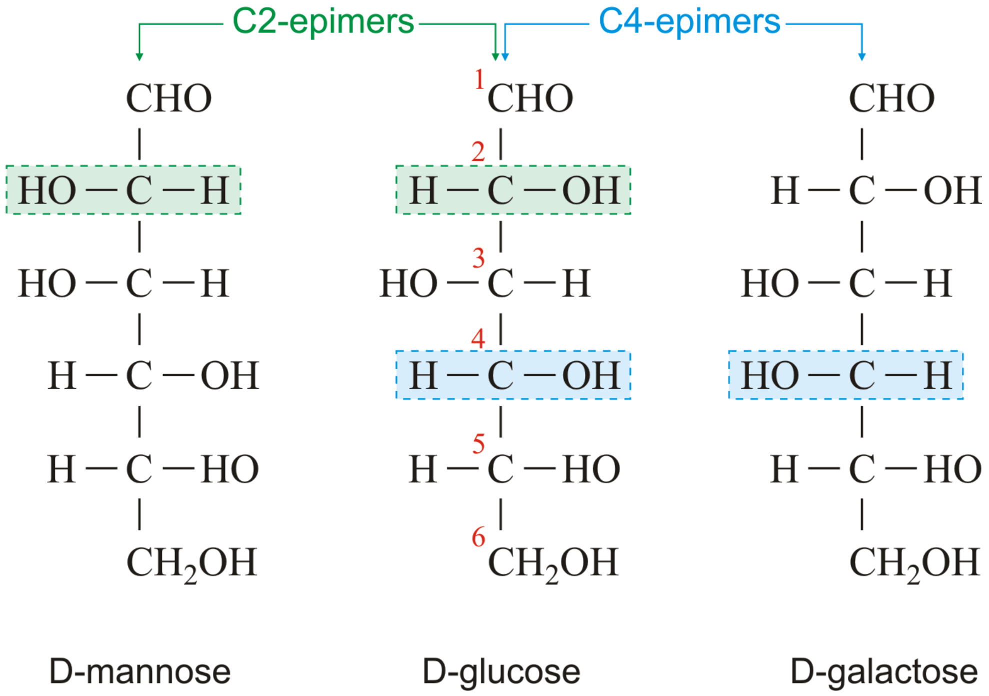
$$\text{Sucrose } (C_{12}H_{22}O_{11}) + H_2O \xrightarrow{\text{acid or certain enzyme}} \text{Glucose } (C_6H_{12}O_6) + \text{Fructose } (C_6H_{12}O_6)$$

Disaccharides **Monosaccharides**

EPIMERS

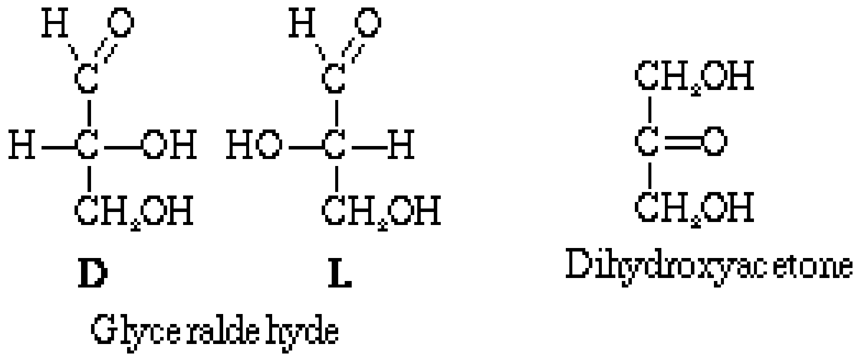
Two Sugars that differ only in the configuration around one carbon atom are called Epimers

D Glucose and D Mannose



Monosaccharides have Asymmetric Centers

- All the monosaccharides expect Dihydroxyacetone contain one or more asymmetric (Chiral) atoms and thus optically active isomeric forms.

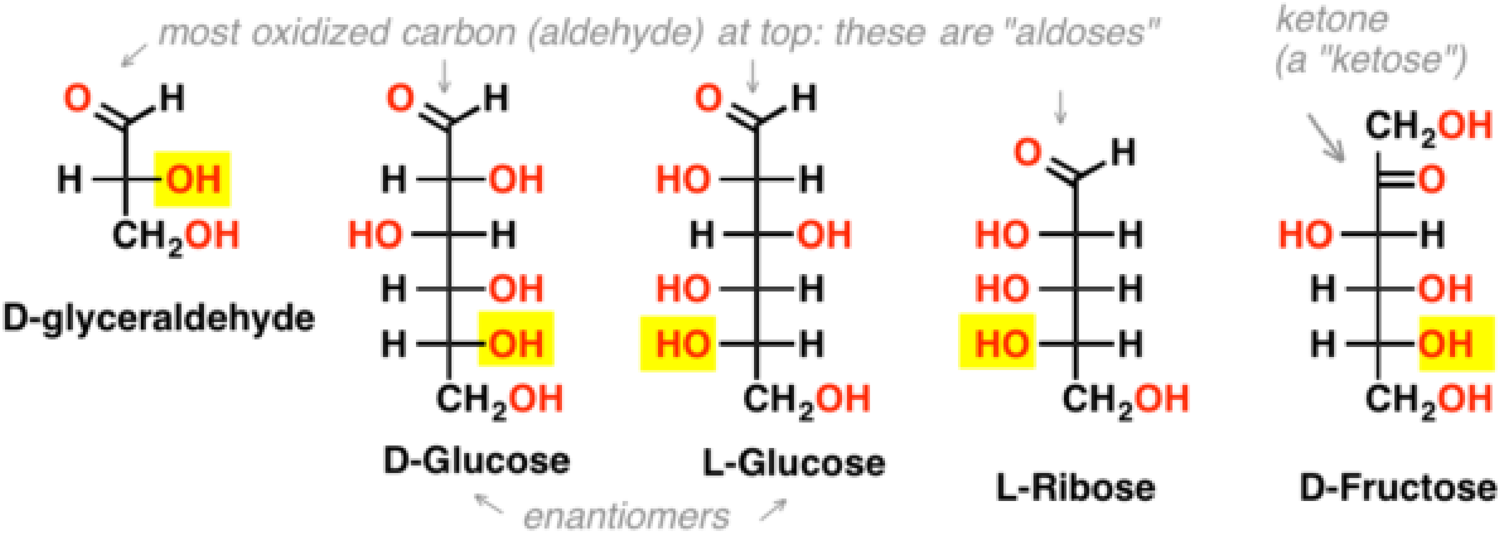


A carbon containing compound commonly exists as Stereoisomers, molecules with same chemical bonds but different Stereochemistry– that is different configuration, the fixed spatial arrangement of atoms.

D- and L- Sugars

For a sugar drawn in the Fischer projection with the most oxidized carbon at the top:

- If the OH on the bottom chiral center points to the **right**, the sugar is **D**
- If the OH on the bottom chiral center points to the **left**, the sugar is **L**

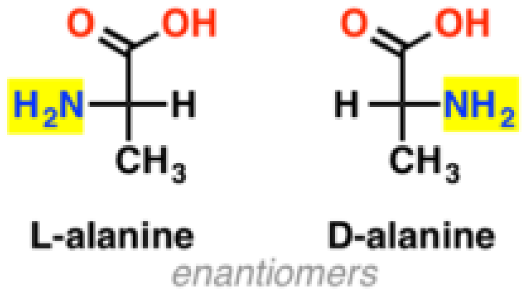


D-glyceraldehyde, D-Glucose, L-Glucose, L-Ribose, D-Fructose

L- and D- is a means of describing the **absolute configuration** of a molecule that pre-dates *R* and *S* but is still used for some biological molecules (sugars, amino acids). It's a quick way of denoting enantiomers: e.g. L-glucose and D-glucose are enantiomers.

L- and D- have no relation to the optical rotation of a molecule.

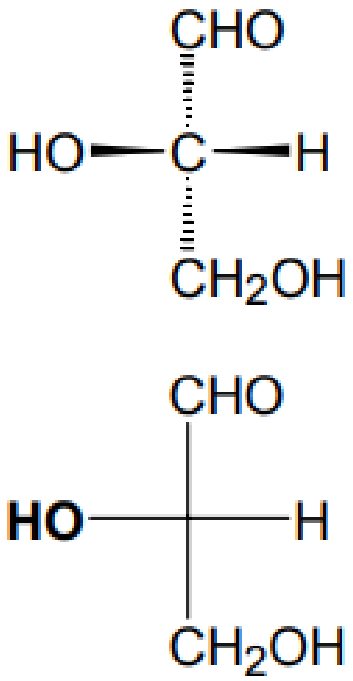
The D- L- system can also be applied to other chiral molecules, e.g. amino acids:



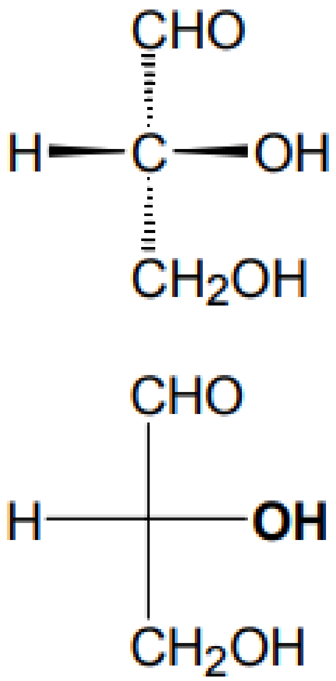
L-alanine, D-alanine

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 CH_2OH at the bottom.



L-glyceraldehyde



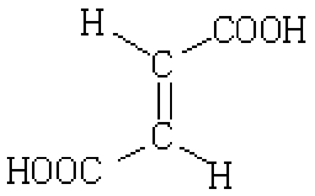
D-glyceraldehyde

Configuration is conferred by the presence of either

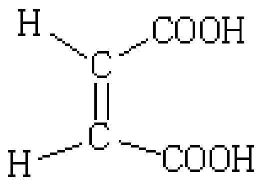
1. Double Bond around which there is no freedom of rotation
2. Chiral Centers around which substituent groups are arranged in a specific sequence

The identifying characteristics of configurational isomers is that they can not be interconverted without temporary breaking one or more covalent bonds

Cis – on the side – groups on the same sides of the double bonds
Trans – Across- Groups on the opposite sides



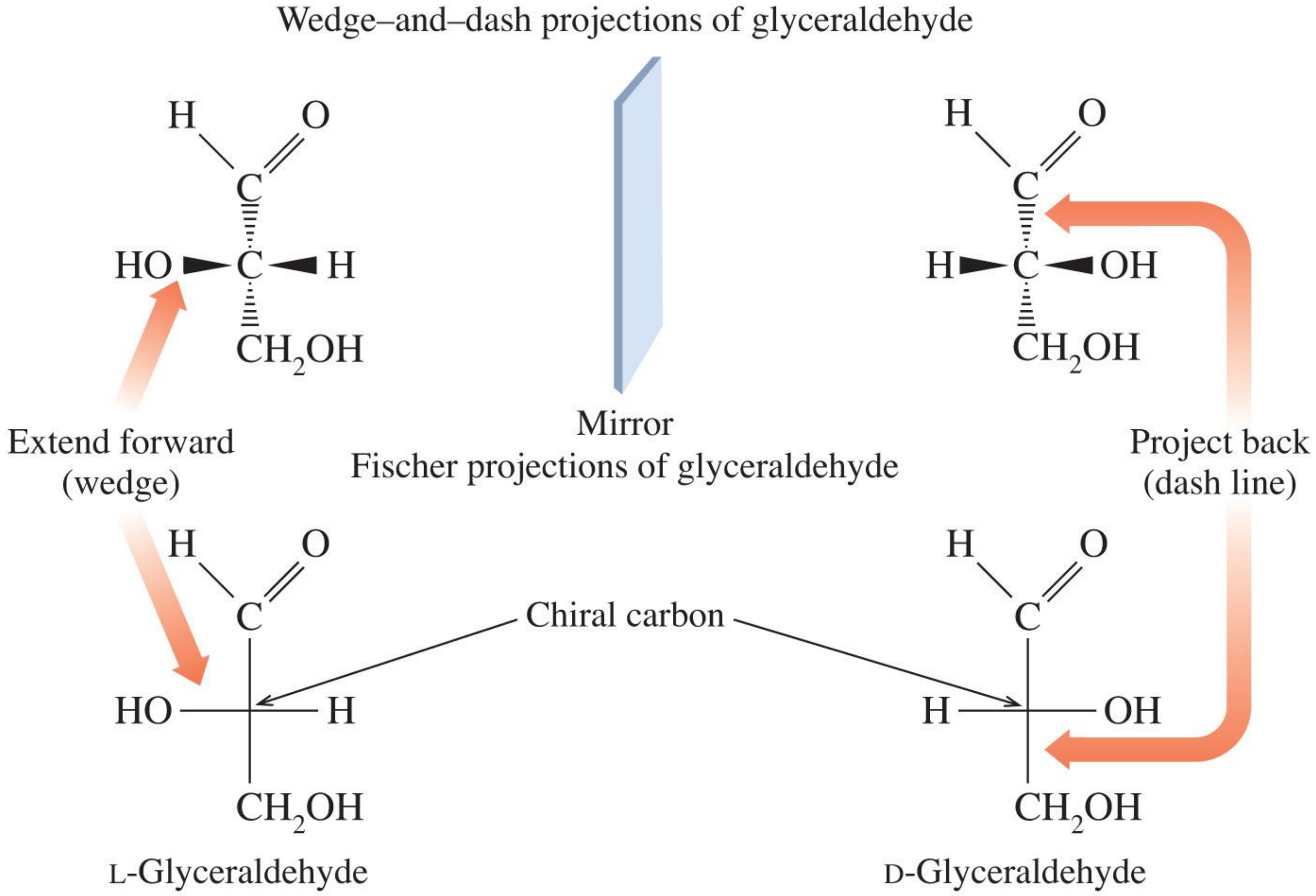
(2*E*)-2,3-dimethylbut-2-enedioic acid
Fumaric Acid M.pt 286°C



(2*Z*)-2,3-dimethylbut-2-enedioic acid
Maleic Acid M.pt 130°C

5.2 Monosaccharides, Continued

Representing stereoisomers—the Fischer projection



Physical Properties of Monosaccharides

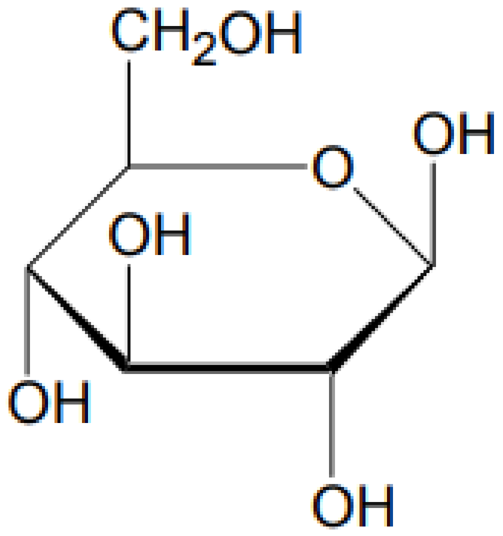
- Most monosaccharides have a sweet taste (fructose is sweetest; 73% sweeter than sucrose).
- They are solids at room temperature.
- They are *extremely* soluble in water:
  - Despite their high molecular weights, the presence of large numbers of OH groups make the monosaccharides much more water soluble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

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.)

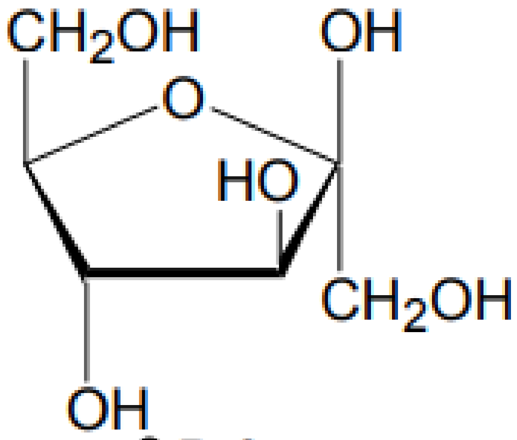
$$\text{Reducing sugar} + \underset{\textit{deep blue solution}}{Cu^{2+}} \longrightarrow \text{oxidation product} + \underset{\textit{red-orange ppt}}{Cu_2O}$$

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.

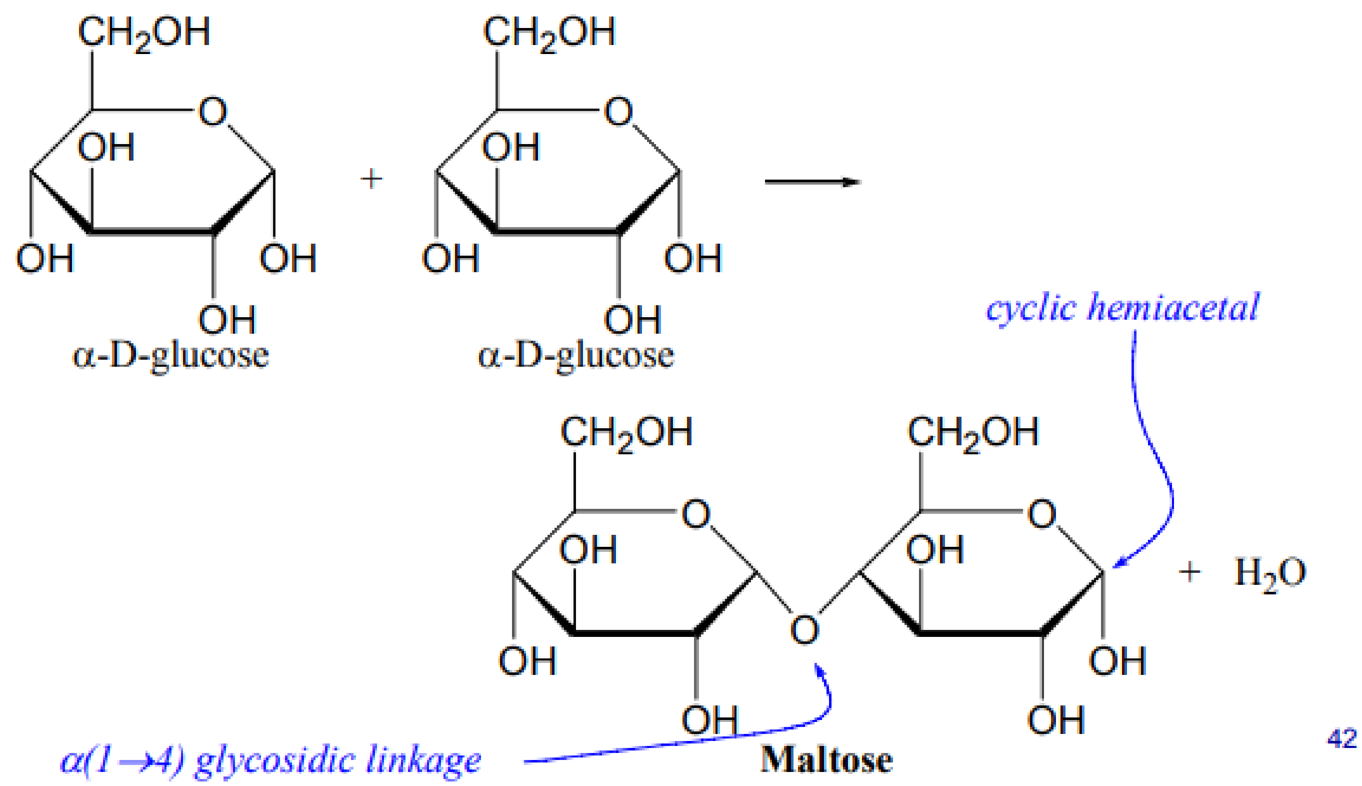


β-D-fructose

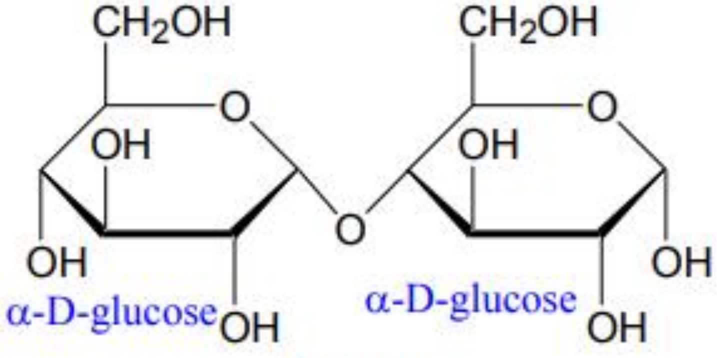
Also known as *levulose* and *fruit sugar*. Fructose is the sweetest of the monosaccharides. It is present in honey (1:1 ratio with glucose), fruits, and corn syrup. It is often used to sweeten foods, since less fructose is needed to achieve the same degree of sweetness.

Disaccharides

- Two monosaccharides can be linked together through a glycosidic linkage to form a **disaccharide**.

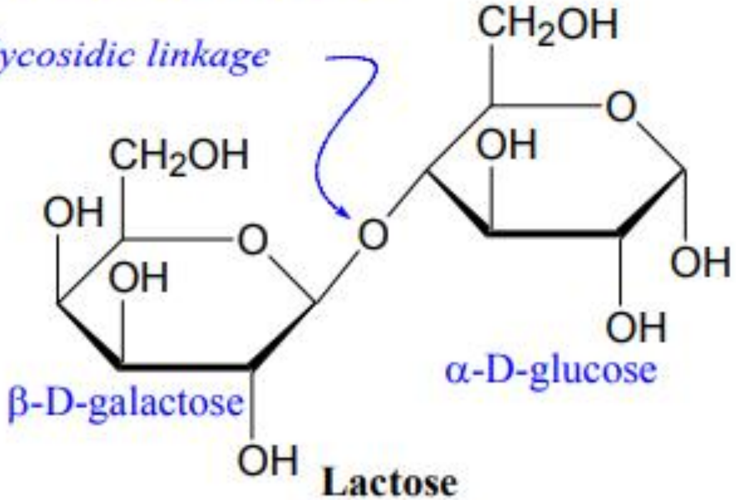


Important Disaccharides



Maltose

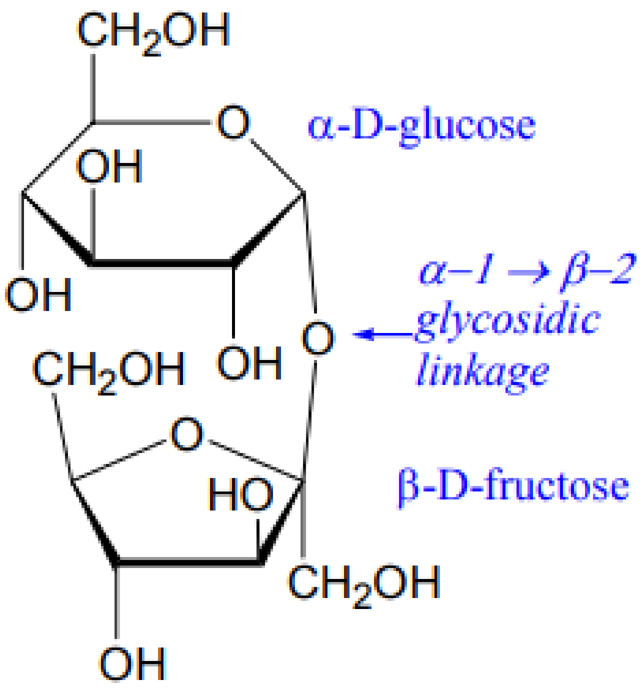
Also known as *malt sugar*. It is found in germinating grain (such as barley), and is formed during the hydrolysis of starch to glucose during digestion. Because it has a hemiacetal group, it is a reducing sugar.

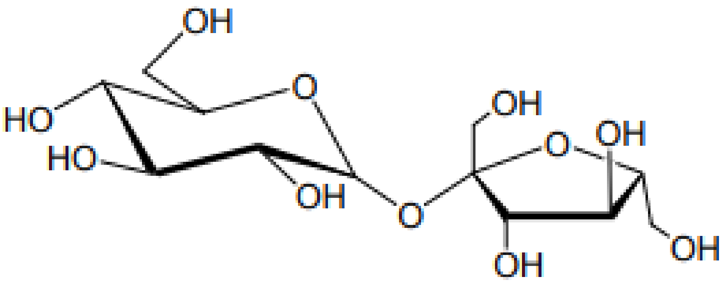


Lactose

Also known as *milk sugar*. Lactose constitutes 5% of cow's milk and 7% of human milk. It is digested by the enzyme *lactase*.

Important Disaccharides



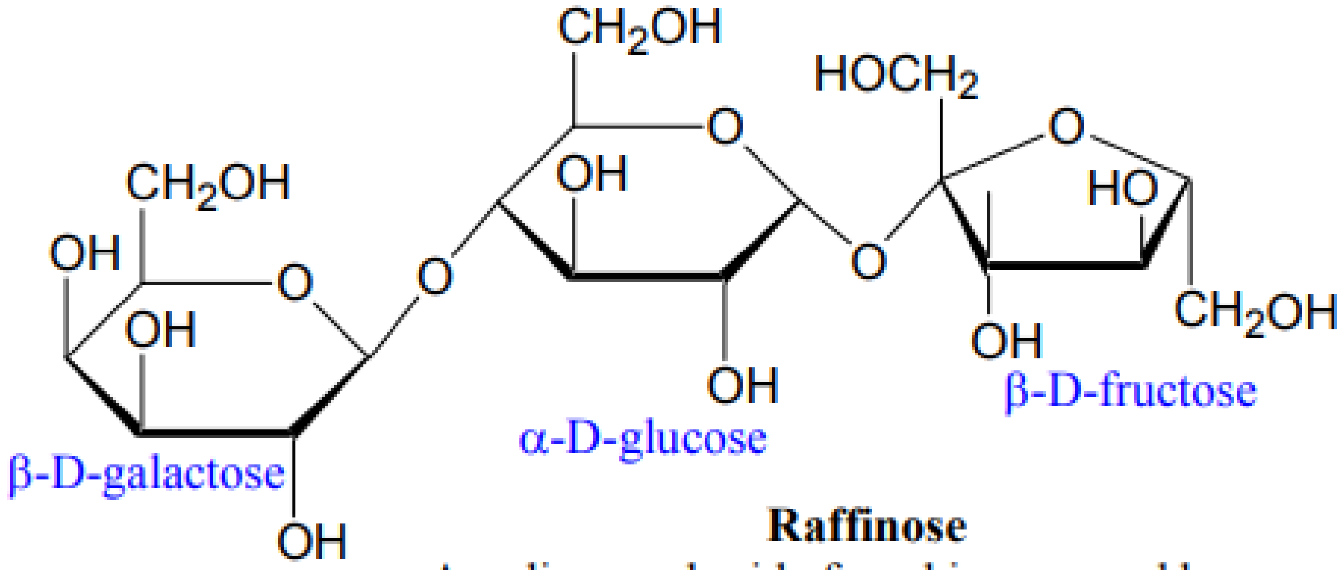


Sucrose

Also known as *table sugar*. Both anomeric carbons of glucose and fructose are tied together in the glycosidic linkage; thus neither ring can open, and sucrose is not a reducing sugar. Sucrose is abundant in sugar cane and sugar beets; maple syrup contains about 65% sucrose, with glucose and fructose present as well; caramel is the solid residue formed from heating sucrose. A flavoring agent called *invert sugar* is produced by the hydrolysis of sucrose under acidic conditions, which breaks it apart into glucose and fructose; invert sugar is sweeter than sucrose because of the fructose. Some of the sugar found in honey is formed in this fashion; invert sugar is also produced in jams and jellies prepared from acid-containing fruits.

Oligosaccharides

- Oligosaccharides contain from 3 to 10 monosaccharide units.



Raffinose

An oligosaccharide found in peas and beans; largely undigested until reaching the intestinal flora in the large intestine, releasing hydrogen, carbon dioxide, and methane)

Polysaccharides

- Polysaccharides contain hundreds or thousands of carbohydrate units.
- Polysaccharides are not reducing sugars, since the anomeric carbons are connected through glycosidic linkages.
- We will consider three kinds of polysaccharides, all of which are polymers of glucose: starch, glycogen, and cellulose.

Starch is a polymer consisting of D-glucose units

Glycogen, also known as animal starch, is structurally similar to amylopectin, containing both α(1→4) glycosidic linkages and α(1→6) branch points.

Cellulose is a polymer consisting of long, unbranched chains of D-glucose connected by β(1→4) glycosidic linkages; it may contain from 300 to 3000 glucose units in one molecule.