CHEM 108

FUNDAMENTALS OF ORGANIC CHEMISTRY

FOR B.Sc. PROGRAMS OF SCIENTIFIC COLLEGES

PRE-REQUISITES COURSE; CHEM 101

CREDIT HOURS; 4 (3+1)

Chemistry Department, College of Science, King Saud University

CHAPTER 9

CARBOHYDRATES

Carbohydrates

- The word *carbohydrate* can be expressed as *hydrates of carbon* because molecular formulas of these compounds.

  Example;

  Glucose has the molecular formula $C_6H_{12}O_6$, which might be written as $C_6(H_2O)_6$.
- *Carbohydrates* are polyhydroxyaldehydes, polyhydroxyketones, or substances that give such compounds on hydrolysis.
- The chemistry of *carbohydrates* is mainly the combined chemistry of two functional groups: the hydroxyl group and the carbonyl group.
- *Carbohydrates* are usually classified according to their structure as monosaccharides, oligosaccharides, or polysaccharides.

  The term *saccharide* comes from Latin (*saccharum,* sugar) and refers to the sweet taste of some simple carbohydrates.

Carbohydrates

- The three classes of carbohydrates are related to each other through hydrolysis.

$$\text{polysaccharide} \xrightarrow[H^+]{H_2O} \text{oligosaccharides} \xrightarrow[H^+]{H_2O} \text{monosaccharides}$$

- *Monosaccharides* (or simple sugars) are carbohydrates that cannot be hydrolyzed to simpler compounds.
- *Oligosaccharides* (from the Greek *oligos,* few) contain at least two and generally no more than a few linked monosaccharide units.

  They may be called disaccharides, trisaccharides, and so on, depending on the number of units, which may be the same or different.

  Example; Maltose is a disaccharide made of two glucose units.

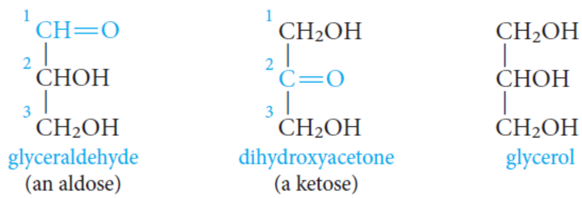
  Sucrose is made of two different monosaccharide units: glucose and fructose.
- *Polysaccharides* contain many monosaccharide units - sometimes hundreds or even thousands. Usually, but not always, the units are identical.

  Example;

  Starch and cellulose, contain linked units of the same monosaccharide, glucose.

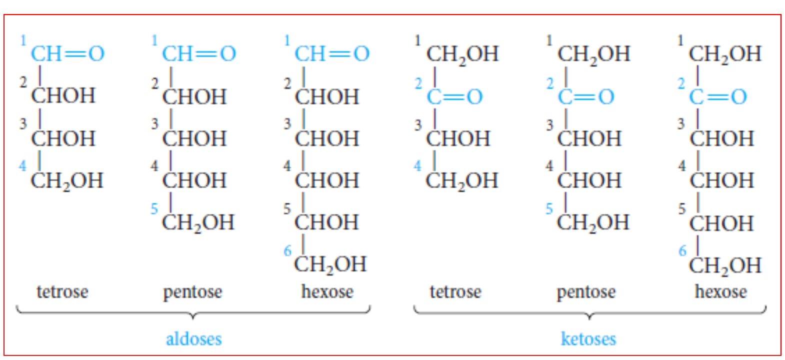
Monosaccharides

- Monosaccharides are classified according to:
  - The number of carbon atoms present (triose, tetrose, pentose, hexose, and so on).
  - Whether the carbonyl group is present as an aldehyde (aldose) or as a ketone (ketose).
- There are only two trioses: glyceraldehyde and dihydroxyacetone.
- Glyceraldehyde is the simplest aldose, and dihydroxyacetone is the simplest ketose.
- Each is related to glycerol in that each has a carbonyl group in place of one of the hydroxyl groups.



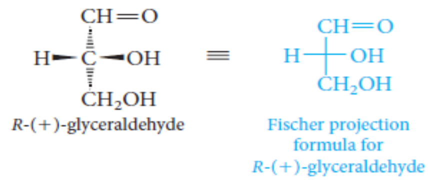
Monosaccharides

- Other aldoses or ketoses can be derived from glyceraldehyde or dihydroxyacetone by adding carbon atoms, each with a hydroxyl group.
- In aldoses, the chain is numbered from the aldehyde carbon.
- In most ketoses, the carbonyl group is located at C-2.

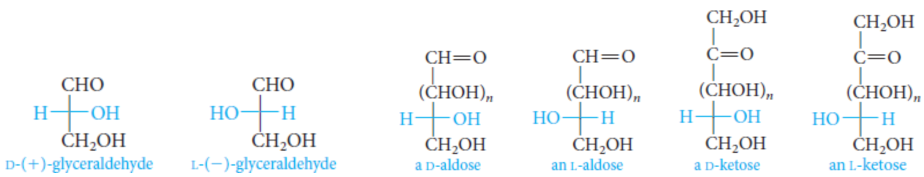


Monosaccharides

Chirality in Monosaccharides; Fischer Projection Formulas and D,L-Sugars

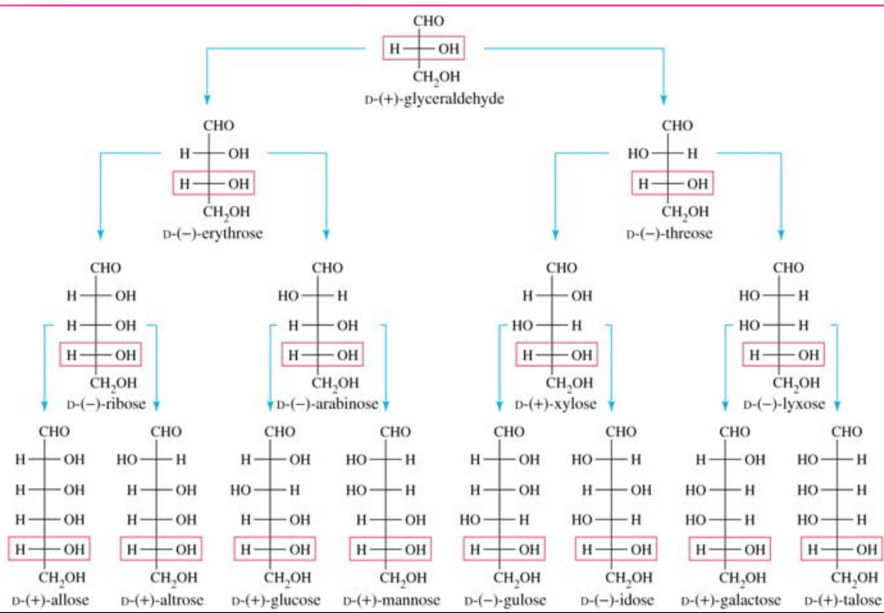


- He used a small capital d to represent the configuration of (+)-glyceraldehyde, with the hydroxyl group on the *right;* its enantiomer, with the hydroxyl group on the *left,* was designated L-(2)-glyceraldehyde.
  The most oxidized carbon (CHO) was placed at the top.



Dr Mohamed El-Newehy

Monosaccharides

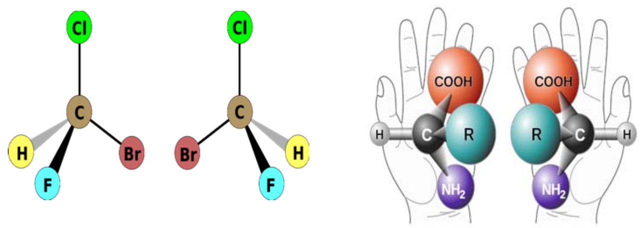


Dr Mohamed El-Newehy

Monosaccharides

The Chiral Center

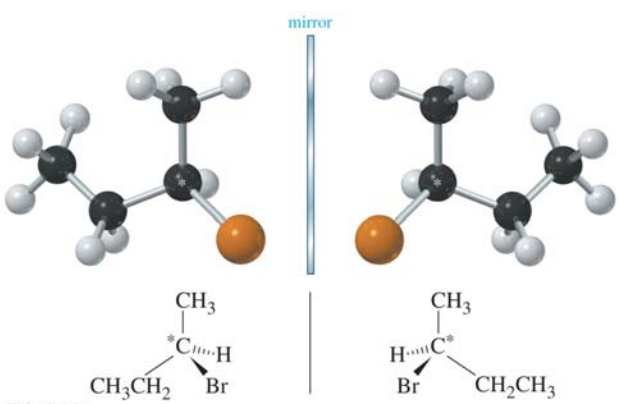
A molecule containing a carbon with four different groups results in a chiral molecule, and the carbon is referred to as a *chiral,* or *asymmetric,* or *stereogenic* center



Its mirror image will be a different compound (enantiomer).

Monosaccharides

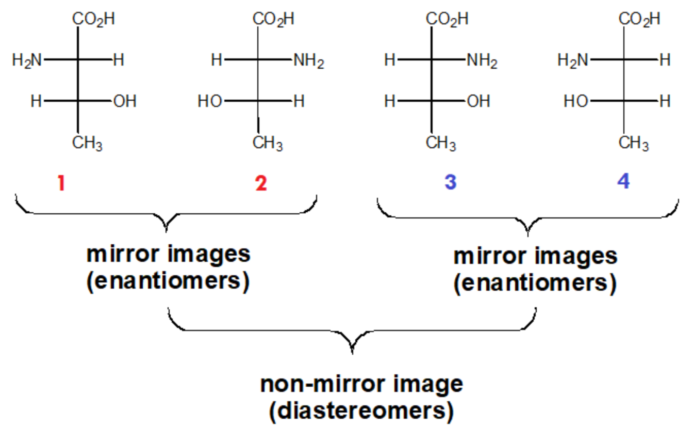
- **Enantiomers:** are chiral molecules that are mirror images of one another and are not superimposable (متطابق). Enantiomers are related to each other much like a right hand is related to a left hand. Enantiomers have identical physical properties, i.e., bp, mp, etc.



Enantiomers have different spatial arrangements of the four groups attached to the asymmetric carbon.
The two possible spatial arrangements are called configurations.

Monosaccharides

- Diastereomers; Diastereomers are the stereomer compounds with molecules that are not mirror images of one another and that are not superimposable.

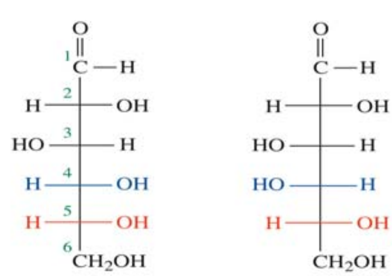


1&3, 1&4 ; 2&3, 2&4 are diastereomers

Dr Mohamed El-Newehy

Monosaccharides

- *Epimers*; A special name is given to diastereomers that differ in configuration *at only one stereogenic center*.
- Each pair has the same configurations at all stereogenic centers except one.
- *Examples;*
  - D-(-)-Erythrose and D-(-)-threose are not only diastereomers, they are epimers.
  - D-glucose and D-mannose are epimers (at C-2).
  - D-glucose and D-galactose are epimers (at C-4).

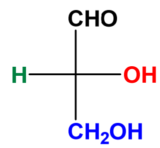


D-Glucose D-Galactose

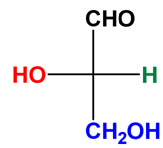
Dr Mohamed El-Newehy

Fischer Projections and the D-L Notation

Fischer Projection: is representation of a three-dimensional molecule as a flat structure



D-glyceraldehyde
R-(+)-glyceraldhyde
(+)-rotation = dextrorotatory = D



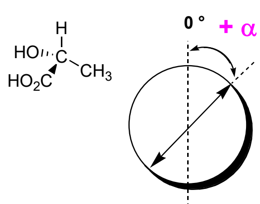
L-glyceraldehyde
S-(-)-glyceraldhyde
(-)-rotation = levorotatory = L

D-carbohydrates have the -OH group of the highest numbered chiral carbon pointing to the right in the Fisher projection as in R-(+)-glyceraldhyde

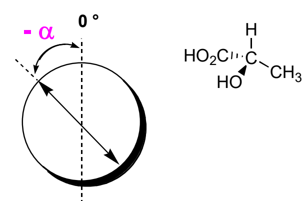
L-carbohydrates have the -OH group of the highest numbered chiral carbon pointing to the right in the Fisher projection as in S-(-)-glyceraldhyde

Dr Mohamed El-Newehy

Fischer Projections and the D-L Notation



dextrorotatory (*d*): rotates light to the right (clockwise)



levororotatory (*l*): rotates light to the left (counterclockwise)

Angle of rotation α (number of degrees) of plane polarized light is rotated by an optically active sample. α is expressed in degrees.

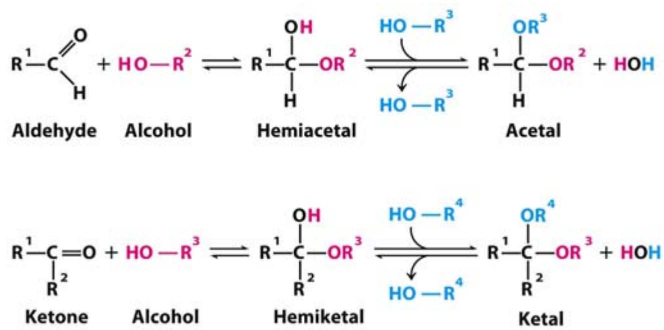
Enantiomers will rotate plane polarized light the same magnitude (α) but in opposite directions (+ or -)

- **Dextrorotation (+)** and **levorotation** (-) are terms describing circular direction of rotating plane-polarized light.
  - **Dextrorotatory (+);** If the light rotates clockwise, (rotation to the right).
  - **Levorotatory (-);** if it rotates counterclockwise, (rotation to the left).

Dr Mohamed El-Newehy

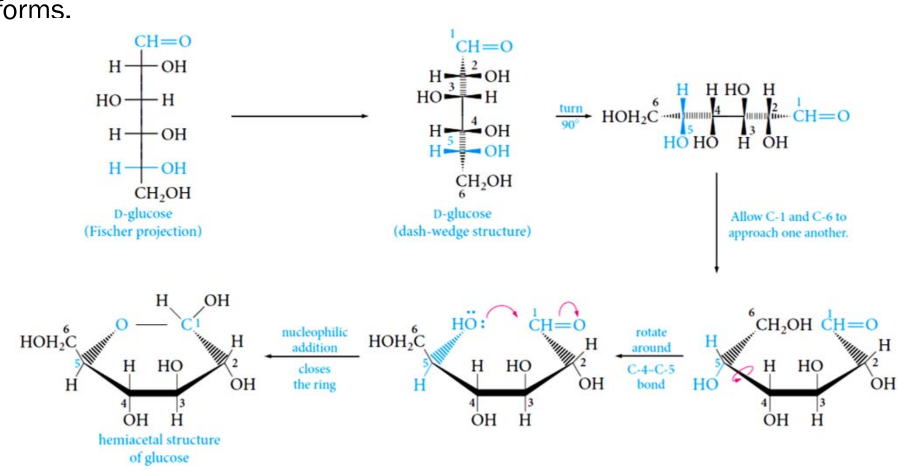
The Cyclic Hemiacetal Structures of Monosaccharides

- Monosaccharides with five or more carbon atoms occur mostly as cyclic ring structures in which the carbonyl group has formed a covalent bond with the oxygen of a hydroxyl group along the chain
- The formation of these ring structures is the result of a general reaction between alcohols and aldehydes or ketones to form derivatives called hemiacetals or hemiketals



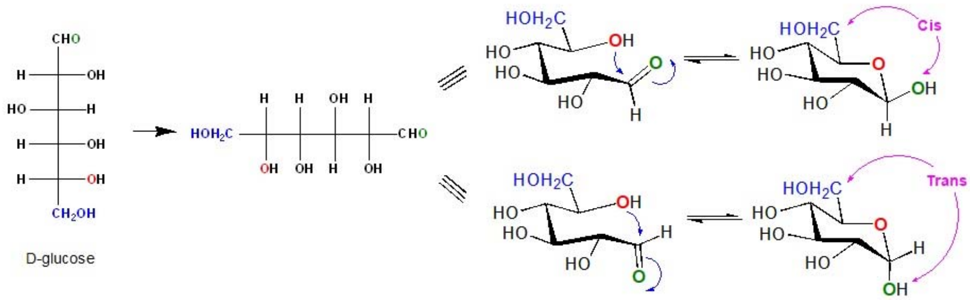
The Cyclic Hemiacetal Structures of Monosaccharides

- *Monosaccharides exist mainly in cyclic, hemiacetal forms* and not in the acyclic aldo- or keto-forms.



Manipulation of the Fischer projection formula of D-glucose to bring the C-5 hydroxyl group in position for cyclization to the hemiacetal form.

The Cyclic Hemiacetal Structures of Monosaccharides

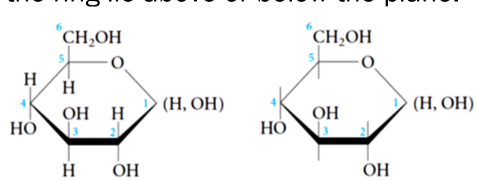


β-D-Glucopyranose (64%)
(β-anomer: C1-OH and CH_2OH are cis)

α-D-Glucopyranose (36%)
(α-anomer: C1-OH and CH_2OH are trans)

Haworth Projection

- The carbons are arranged clockwise numerically, with C-1 at the right.
- Substituents attached to the ring lie above or below the plane.

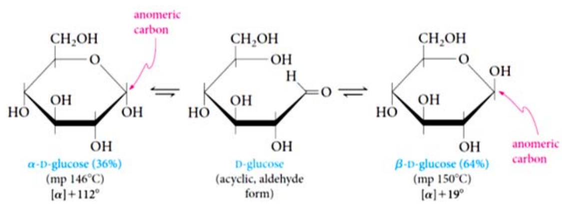


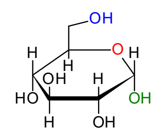
Haworth projection formulas for D-glucose

- Carbons 1 through 5 are part of the ring structure, but carbon 6 (the -CH_2OH group) is a substituent on the ring.
- C-1 is special.
  C-1 is the hemiacetal carbon (it carries a hydroxyl group, and it is also connected to C-5 by an ether linkage).
- C-2, C-3, and C-4 are secondary alcohol carbons.
- C-6 is a primary alcohol carbon.
- Hydroxyl groups on the *right* in the Fischer projection are *down* in the Haworth projection (and conversely.
- hydroxyl groups on the *left* in the Fischer projection are *up* in the Haworth projection).
- For D-sugars, the terminal -CH_2OH group is *up* in the Haworth projection; for L-sugars, it is down.

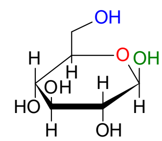
Anomeric Carbons; Mutarotation

- Anomeric carbon; The hemiacetal carbon, the carbon that forms the new stereogenic center.
- Anomers; Two monosaccharides that differ only in configuration at the anomeric center are (a special kind of epimers).
- Anomers are called α or β, depending on the position of the hydroxyl group.
- For monosaccharides in the D-series, the hydroxyl group is "down" in the α anomer and "up" in the β anomer.





α-D-Glucopyranose

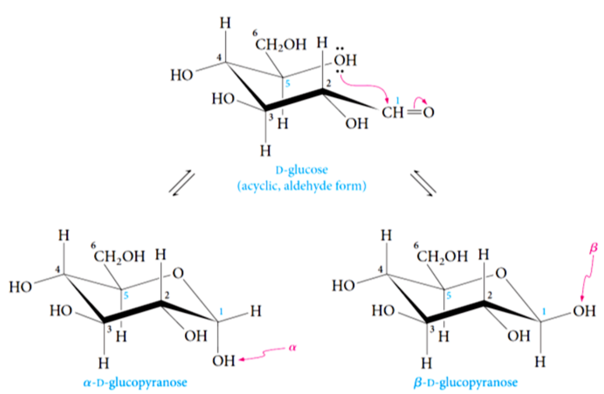


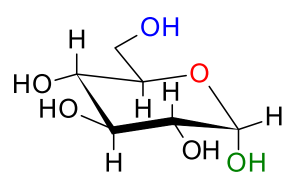
β-D-Glucopyranose

- If D-glucose is crystallized from methanol, the pure α form is obtained.
- Crystallization from acetic acid gives the β form.
- The α and β forms of D-glucose are *diastereomers.*

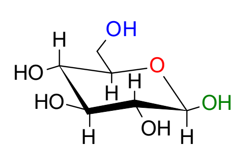
Conformations of Pyranoses; Chair Conformation

- **At the anomeric carbon (C-1), where the hydroxyl group may be axial (in the α anomer) or equatorial (in the β anomer).**





α-D-Glucopyranose



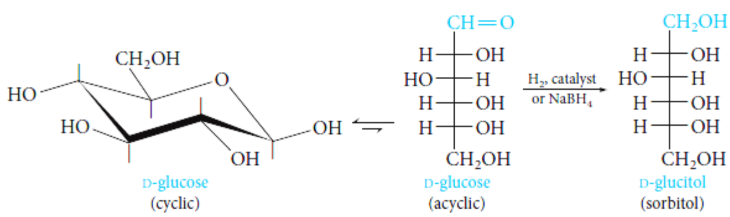
β-D-Glucopyranose

Reactions of Monosaccharides

1) Reduction of Monosaccharides

- The carbonyl group of aldoses and ketoses can be reduced by various reagents to give polyols, called alditols.
- Example;

  Catalytic hydrogenation or reduction with sodium borohydride ($NaBH_4$) converts D-glucose to D-glucitol (sorbitol).
- Sorbitol is used commercially as a sweetener and sugar substitute.



Reactions of Monosaccharides

2) Oxidation of Monosaccharides

2.1. With Mild Oxidizing Agents

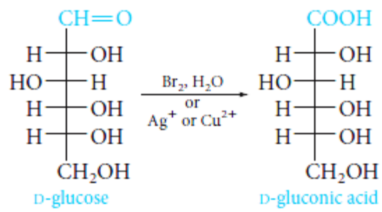
- The oxidation of aldoses is so easy that they react with such mild oxidizing agents as
  - Tollens' reagent (Ag^+ in aqueous ammonia),
  - Fehling's reagent (Cu^{2+} complexed with tartrate ion),
  - Benedict's reagent (Cu^{2+} complexed with citrate ion).
- These aldehyde groups can be easily oxidized to acids which are called aldonic acids.
- A carbohydrate that reacts with Ag^+ or Cu^{2+} is called a reducing sugar

Reactions of Monosaccharides

2) Oxidation of Monosaccharides

2.1. With Mild Oxidizing Agents

- Example; D-glucose is easily oxidized to D-gluconic acid.



- With the copper reagents, the blue solution gives a red precipitate of cuprous oxide, Cu_2O.

$$RCH{=}O + \underset{\text{blue solution}}{2\,Cu^{2+}} + 5\,OH^- \longrightarrow R\overset{O}{\overset{\|}{C}}O^- + \underset{\text{red precipitate}}{Cu_2O} + 3\,H_2O$$

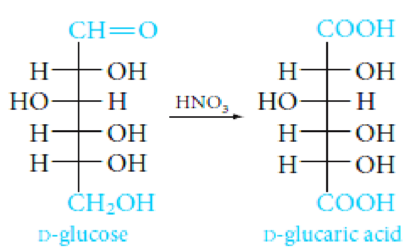
Reactions of Monosaccharides

2) Oxidation of Monosaccharides

2.2. With Strong Oxidizing Agents

- Stronger oxidizing agents, such as aqueous nitric acid.
- The aldehyde group and the primary alcohol group can be oxidized, producing dicarboxylic acids called aldaric acids.
- Example;

D-glucose gives D-glucaric acid.

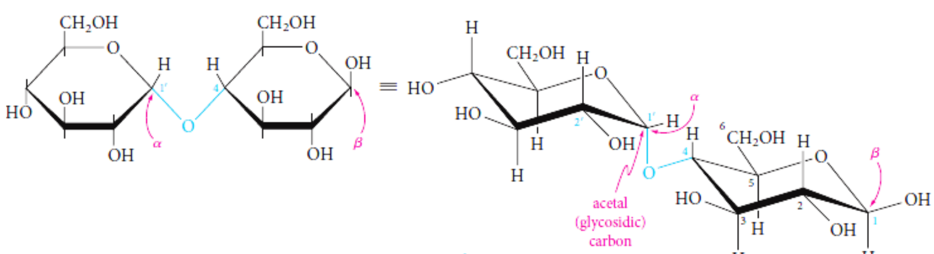


Disaccharides

- The most common oligosaccharides are disaccharides.
- In a disaccharide,

  two monosaccharides are linked by a glycosidic bond between the anomeric carbon of one monosaccharide unit and a hydroxyl group on the other unit.

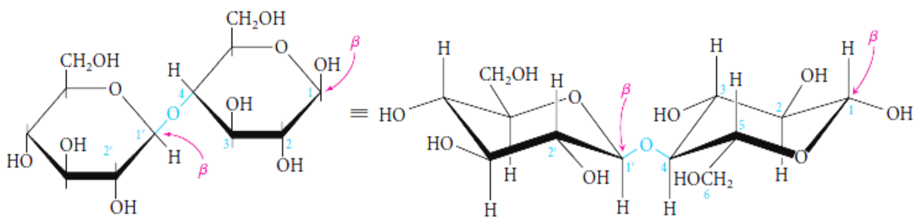
Disaccharides; Maltose



maltose
4-O-(α-D-glucopyranosyl)-β-D-glucopyranose

- Maltose is the disaccharide obtained by the partial hydrolysis of starch.
- Further hydrolysis of maltose gives only D-glucose.
- Maltose must, therefore, consist of two linked glucose units.
- It turns out that the anomeric carbon of the left unit is linked to the C-4 hydroxyl group of the unit at the right as an acetal (glycoside).
- The configuration at the anomeric carbon of the left unit is α.

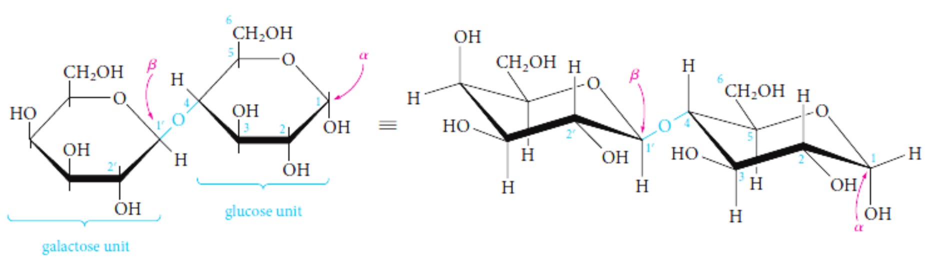
Disaccharides; Cellobiose



- Cellobiose is the disaccharide obtained by the partial hydrolysis of cellulose.
- Further hydrolysis of cellobiose gives only D-glucose.
- Cellobiose must therefore be an isomer of maltose.
- In fact, cellobiose *differs from maltose* only *in having the* β *configuration at C-1 of the left glucose unit.*

Dr Mohamed El-Newehy

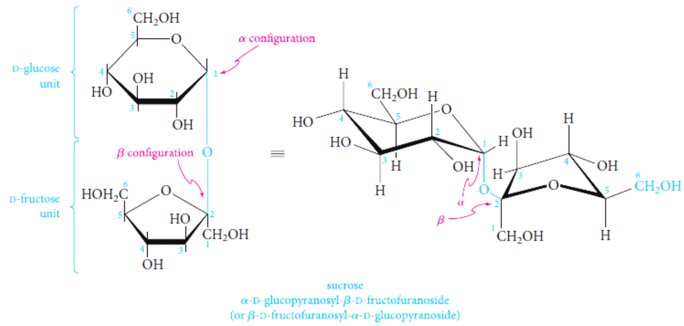
Disaccharides; Lactose



- Lactose is the major sugar in human and cow's milk (4% to 8% lactose).
- Hydrolysis of lactose gives equimolar amounts of D-galactose and D-glucose.
- The anomeric carbon of the galactose unit has the β configuration at C-1 and is linked to the hydroxyl group at C-4 of the glucose unit.

Dr Mohamed El-Newehy

Disaccharides; Sucrose

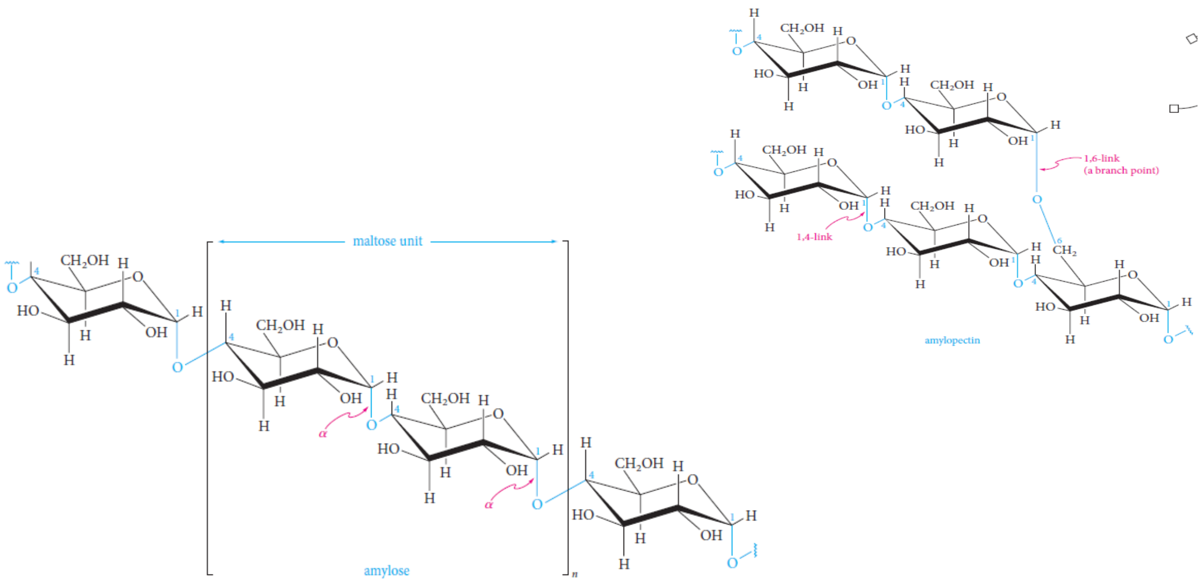


- The most important commercial disaccharide is sucrose, ordinary table sugar.
- Sucrose occurs in all photosynthetic plants, where it functions as an energy source.
- It is obtained commercially from sugar cane and sugar beets, in which it constitutes 14% to 20% of the plant juices.
- Sucrose is very water soluble (2 grams per milliliter at room temperature) because it is polar due to the presence of eight hydroxyl groups on its surface.
- Hydrolysis of sucrose gives equimolar amounts of D-glucose and the ketose D-fructose.

Polysaccharides

- Polysaccharides contain many linked monosaccharides and vary in chain length and molecular weight.
- Most polysaccharides give a single monosaccharide on complete hydrolysis.
- The monosaccharide units may be linked linearly, or the chains may be branched.

Polysaccharides; Starch



Polysaccharides; Starch

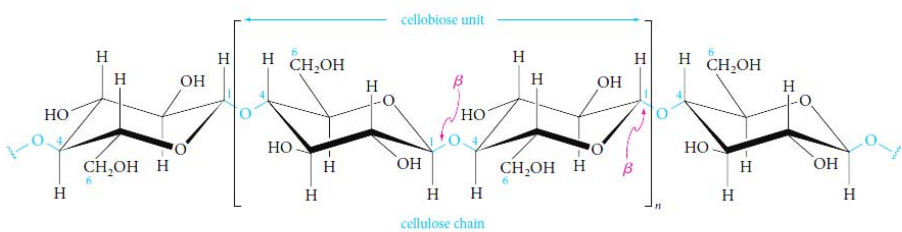
- Starch is the energy-storing carbohydrate of plants.
- It is a major component of cereals, potatoes, corn, and rice.
- Starch is made up of glucose units joined mainly by 1,4-α-glycosidic bonds, although the chains may have a number of branches attached through 1,6- α -glycosidic bonds.
- Partial hydrolysis of starch gives maltose, and complete hydrolysis gives only D-glucose.
- Starch can be separated by various techniques into two fractions: amylose and amylopectin.
- In amylose, which constitutes about 20% of starch, the glucose units (50 to 300) are in a continuous chain, with 1,4 linkages.
- Amylopectin is highly branched. Although each molecule may contain 300 to 5000 glucose units, chains with consecutive 1,4 links average only 25 to 30 units in length.
- These chains are connected at branch points by 1,6 linkages.

Polysaccharides; Glycogen

- Glycogen is the energy-storing carbohydrate of animals.
- Like starch, it is made of 1,4- and 1,6-linked glucose units.
- Glycogen has a higher molecular weight than starch (perhaps 100,000 glucose units), and its structure is even more branched than that of amylopectin, with a branch every 8 to 12 glucose units.
- Glycogen is produced from glucose that is absorbed from the intestines into the blood; transported to the liver, muscles, and elsewhere; and then polymerized enzymatically.
- Glycogen helps maintain the glucose balance in the body by removing and storing excess glucose from ingested food and later supplying it to the blood when various cells need it for energy.

Dr Mohamed El-Newehy

Polysaccharides; Cellulose



- Cellulose is an *unbranched* polymer of glucose joined by 1,4-β-glycosidic bonds.
- It consists of linear chains of cellobiose units.
- These linear molecules, containing an average of 5000 glucose units, aggregate to give fibrils bound together by hydrogen bonds between hydroxyls on adjacent chains.
- Cellulose fibers having considerable physical strength are built up from these fibrils, wound spirally in opposite directions around a central axis.
- Wood, cotton, hemp, linen, straw, and corncobs are mainly cellulose.

Dr Mohamed El-Newehy