108 Chem

Chapter 9

Carbohydrates

Definitions and Classification

- The word carbohydrate arose because molecular formulas of these compounds can be expressed as hydrates of carbon.
- Glucose, for example, 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.

Definitions and Classification

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

$$\text{polysaccharide} \xrightarrow[H^+]{H_2O} \text{oligosaccharide} \xrightarrow[H^+]{H_2O} \text{monosaccharide}$$

$$\underset{\substack{\text{starch} \\ \text{(a polysaccharide)}}}{[C_{12}H_{20}O_{10}]_n} \xrightarrow[H^+]{n\,H_2O} \underset{\substack{\text{maltose} \\ \text{(a disaccharide)}}}{n\,C_{12}H_{22}O_{11}} \xrightarrow[H^+]{n\,H_2O} \underset{\substack{\text{glucose} \\ \text{(a monosaccharide)}}}{2n\,C_6H_{12}O_6}$$

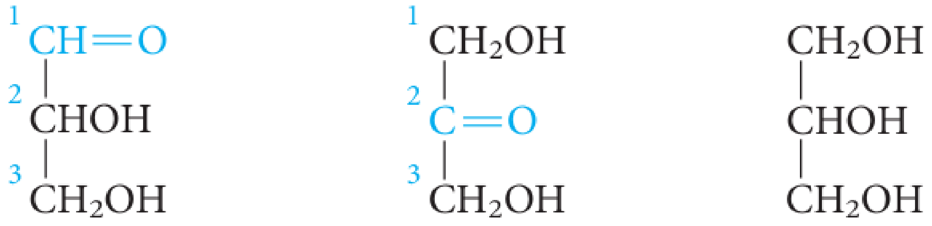
- Monosaccharides (or simple sugars) are carbohydrates that cannot be hydrolyzed to simpler compounds.
- Oligosaccharides (from the Greek oligos, few) contain at least two and generally no more than a few linked monosaccharide units.
- They may be called disaccharides, trisaccharides, and so on, depending 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.
- Two of the most important polysaccharides, 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) and according to whether the carbonyl group is present as an aldehyde (aldose) or as a ketone (ketose).

- There are only two trioses: glyceraldehyde is the simplest aldose and dihydroxyacetone is the simplest ketose.
- Each has two hydroxyl groups, attached to different carbon atoms, and one carbonyl group.
- Each is related to glycerol in that each has a carbonyl group in place of one of the hydroxyl groups.



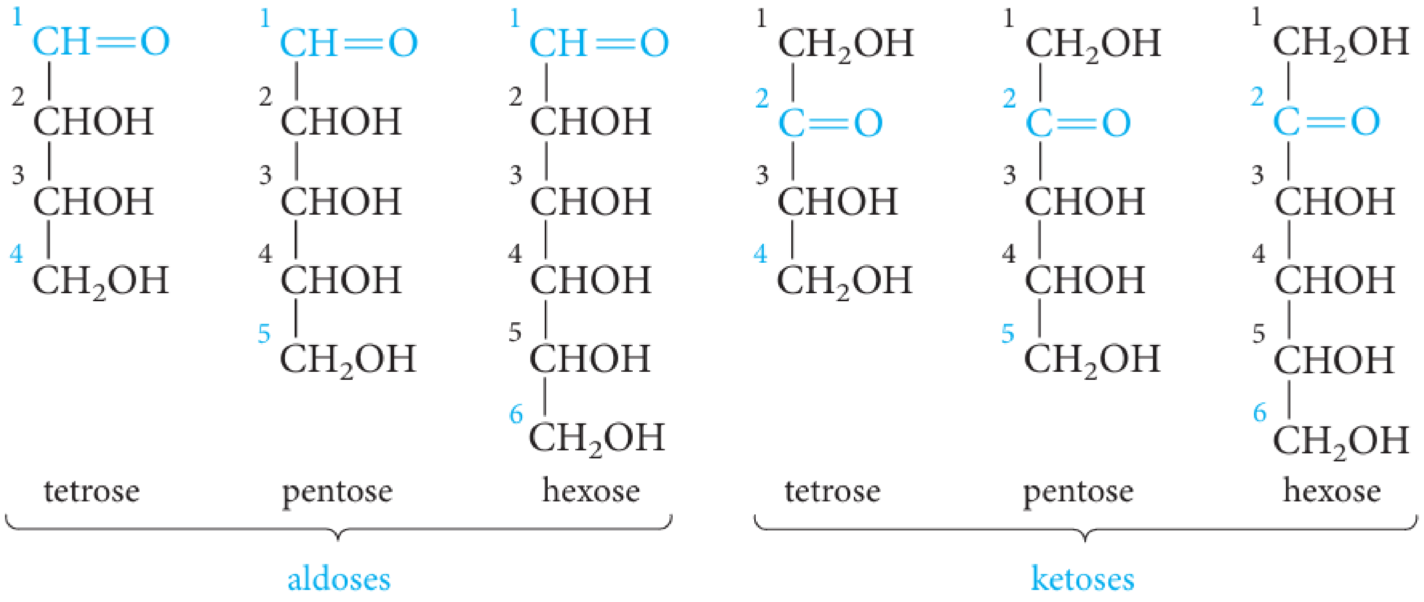
glyceraldehyde (an aldose) Aldotriose

dihydroxyacetone (a ketose) Ketotriose

glycerol

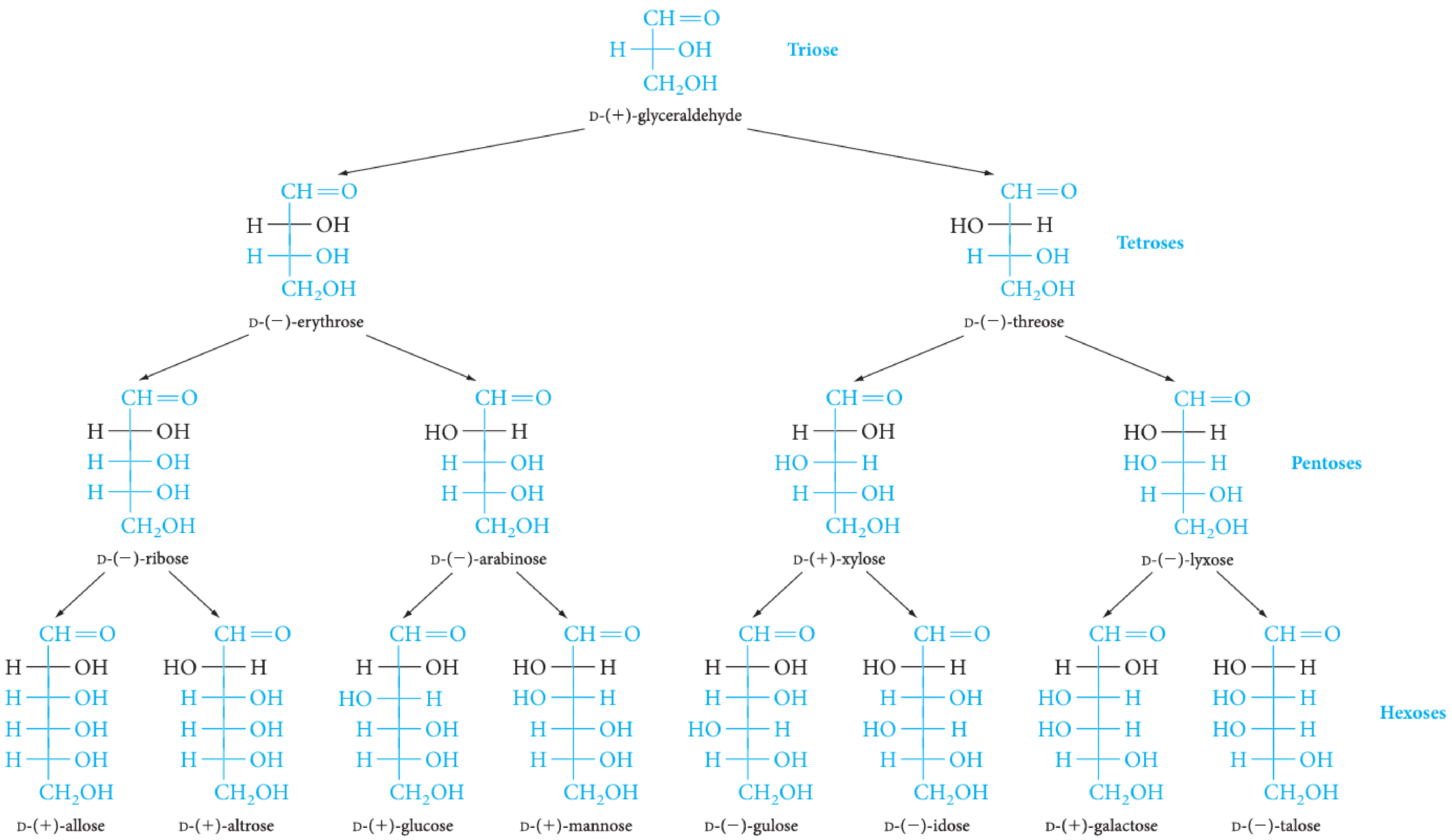
Monosaccharides

- 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.



- The full name of a sugar must has a prefix indicating the nature of the carbonyl group, a Latin word indicating the number of carbons present and a suffix -ose.

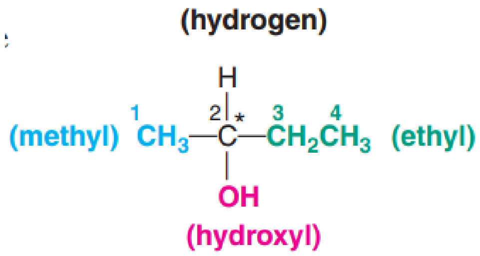
Monosaccharides



Chirality in 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.



Stereogenic centers are often designated with an asterisk (*).

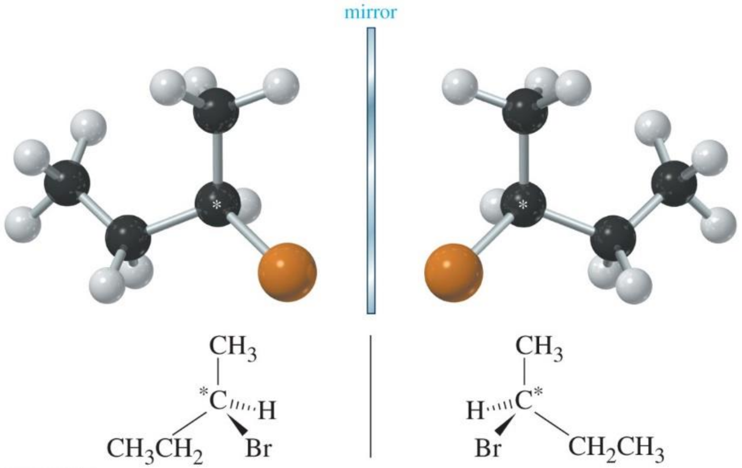
Enantiomers:

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.

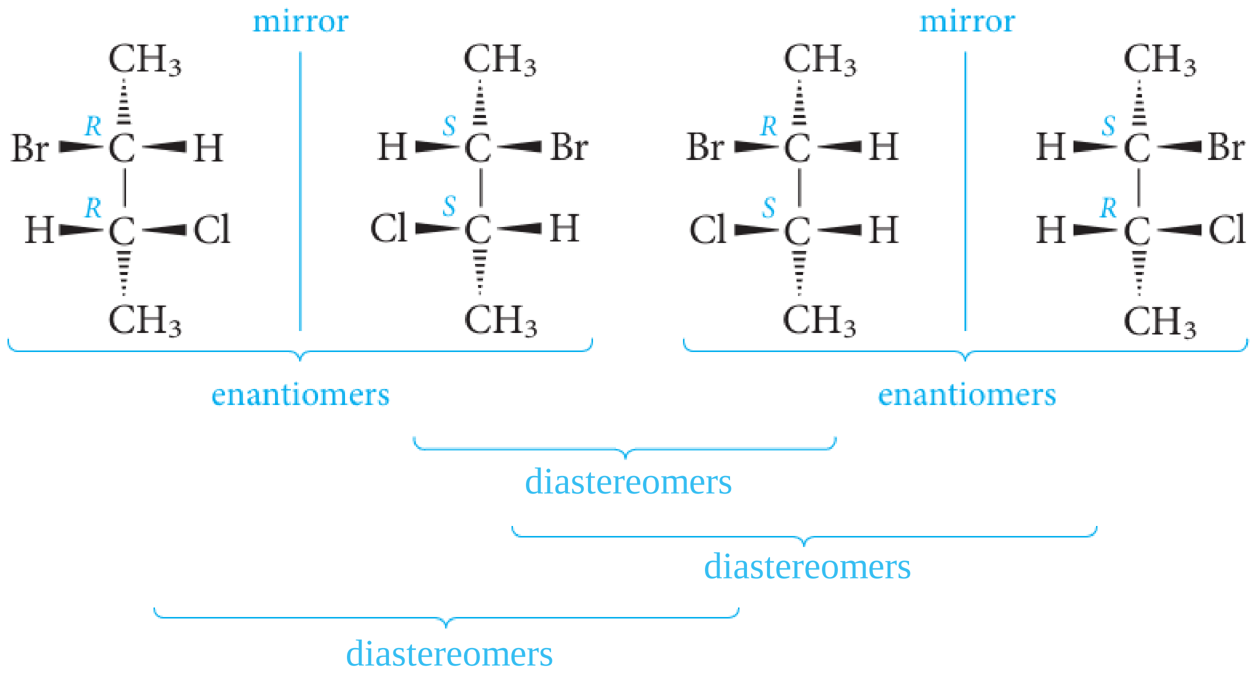
The two possible spatial arrangements are called configurations.



Chirality in Monosaccharides

Diastereomers:

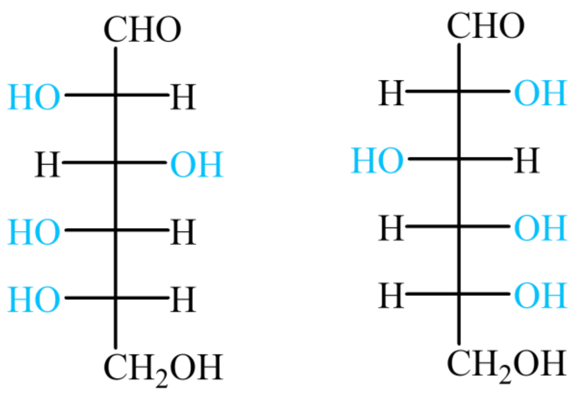
Diastereomers are the stereomer compounds with molecules that are not mirror images of one another and that are not superimposable.



Epimers:

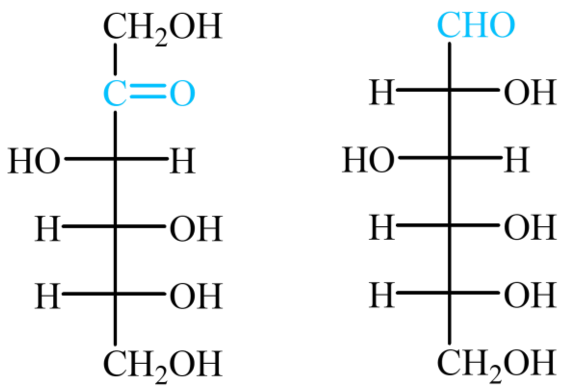
A special name is given to diastereomers that differ in configuration at only one stereogenic center.

Chirality in Monosaccharides



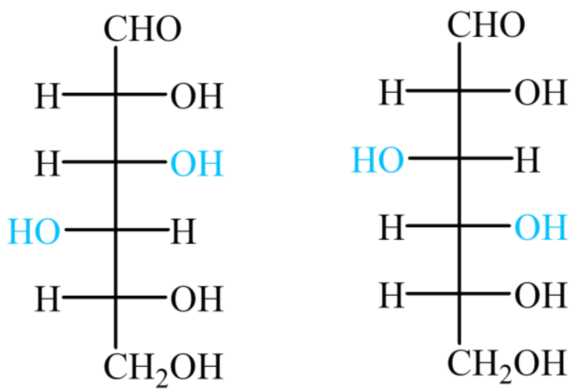
L-glucose D-glucose

Enantiomers



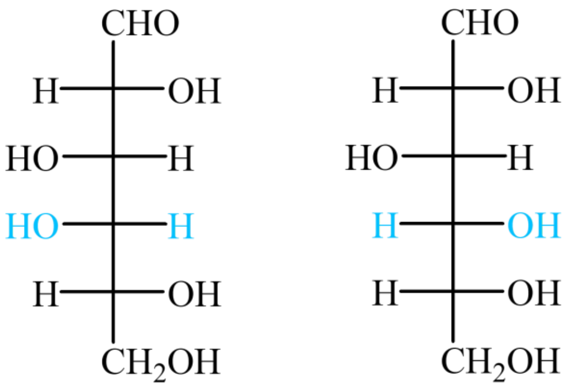
D-fructose D-glucose

Structural Isomers



D-gulose D-glucose

Diastereoisomers



D-galactose D-glucose

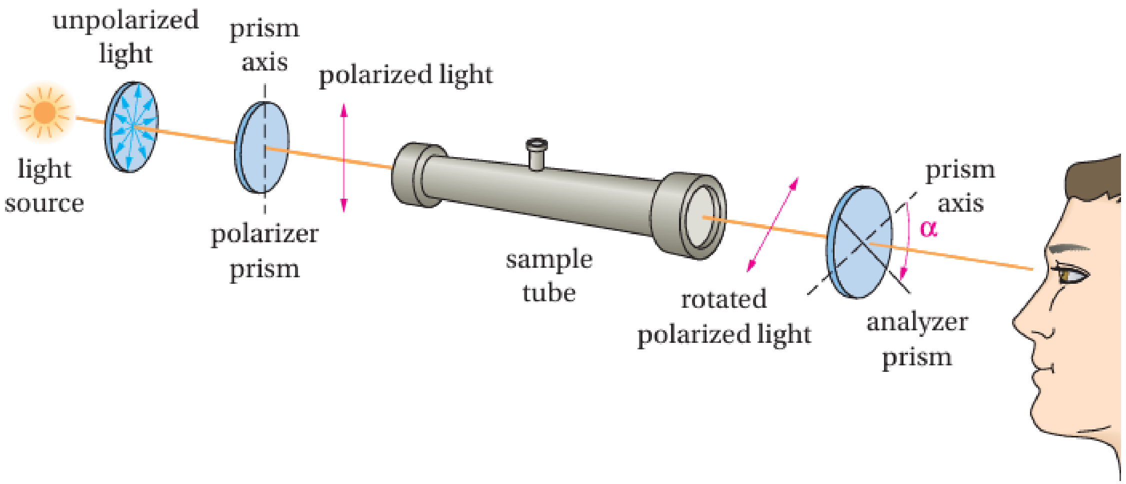
Diastereoisomers

Epimers

Chirality in Monosaccharides

Polarized Light and Optical Activity

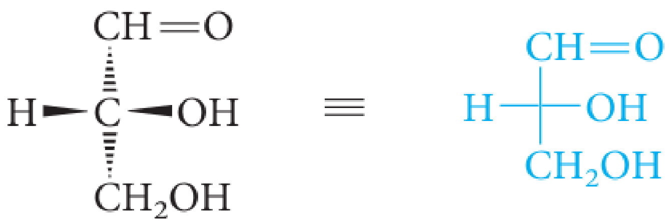
- A polarimeter, or spectropolarimeter, is an instrument used to detect optical activity. An optically active substance rotates plane-polarized light, whereas an optically inactive substance does not.



- The angle through which the analyzer prism must be rotated in experiment is called α, the observed rotation.
- If the analyzer must be rotated to the right (clockwise), substance is dextrorotatory (+); if rotated to the left (counterclockwise), the substance is levorotatory (-).

Chirality in Monosaccharides

Fischer Projection Formulas and D,L-Sugars

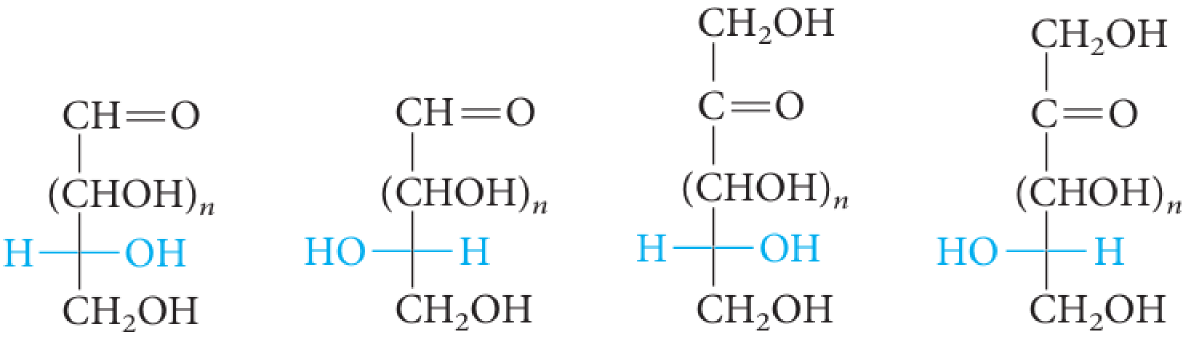


R-(+)-glyceraldehyde

Fischer projection formula for *R*-(+)-glyceraldehyde

- D-glyceraldehyde, with the hydroxyl group on the right.
- L-glyceraldehyde, with the hydroxyl group on the left.

D-(+)-glyceraldehyde L-(−)-glyceraldehyde

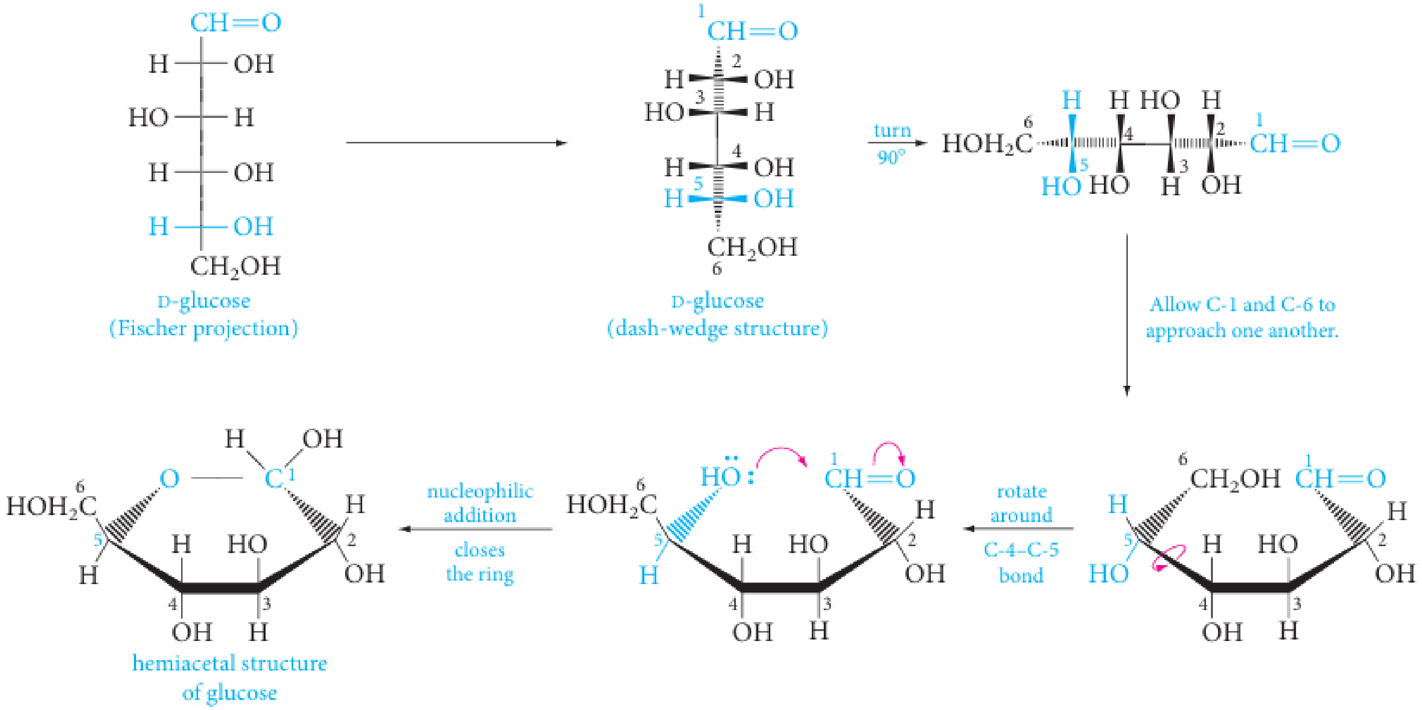


a D-aldose an L-aldose a D-ketose an L-ketose

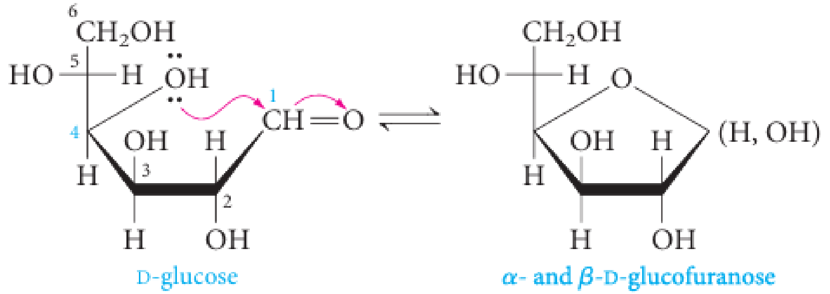
The Cyclic Hemiacetal Structures of Monosaccharides

- Monosaccharides exist mainly in cyclic, hemiacetal forms.
- The cyclization can result in stable 6-memeberd structure resembles pyran ring known as pyranose or 5-memeberd structure resembles furan ring known as furanose.

- Pyranoses are formed by reaction of the hydroxyl group at C-5, with the carbonyl group.

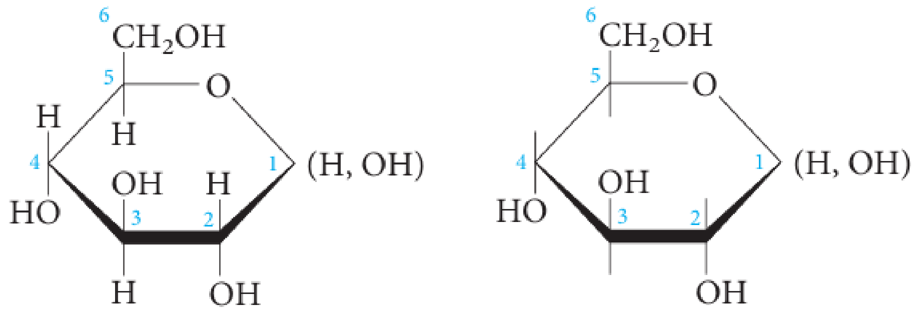


- Furanose are formed by reaction of the hydroxyl group at C-4, with the carbonyl group.



Haworth projections

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

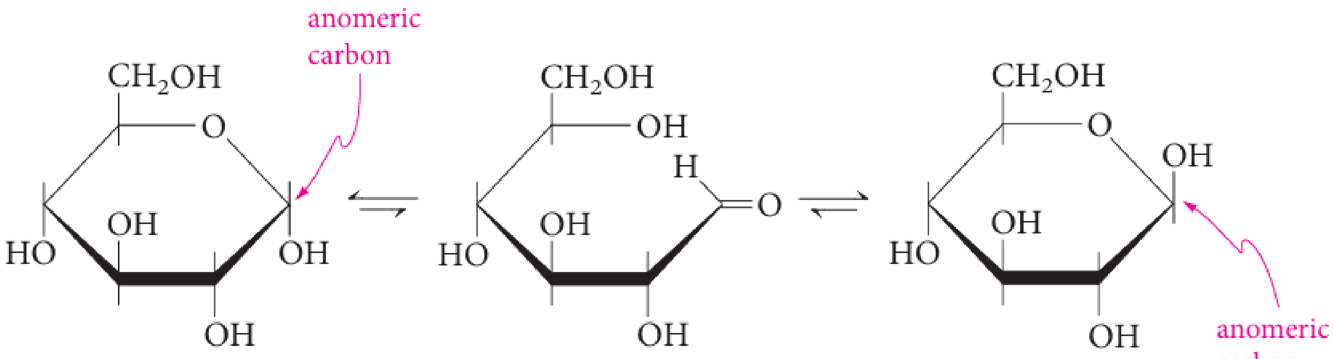


Haworth projection formulas for D-glucose

- The ring is heterocyclic, with five carbons and an oxygen.
- 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 the hemiacetal carbon.
- C-2, C-3, and C-4 are secondary alcohol carbons; C-6 is a primary alcohol carbon; and C-5 is an ether carbon.
- Hydroxyl groups on the right in the Fischer projection are down in the Haworth projection
- 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

- The hemiacetal carbon, the carbon that forms the new stereogenic center, is called the anomeric carbon.
- Two monosaccharides that differ only in configuration at the anomeric center are anomers (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-glucose (36%)
(mp 146°C)
[α]+112°

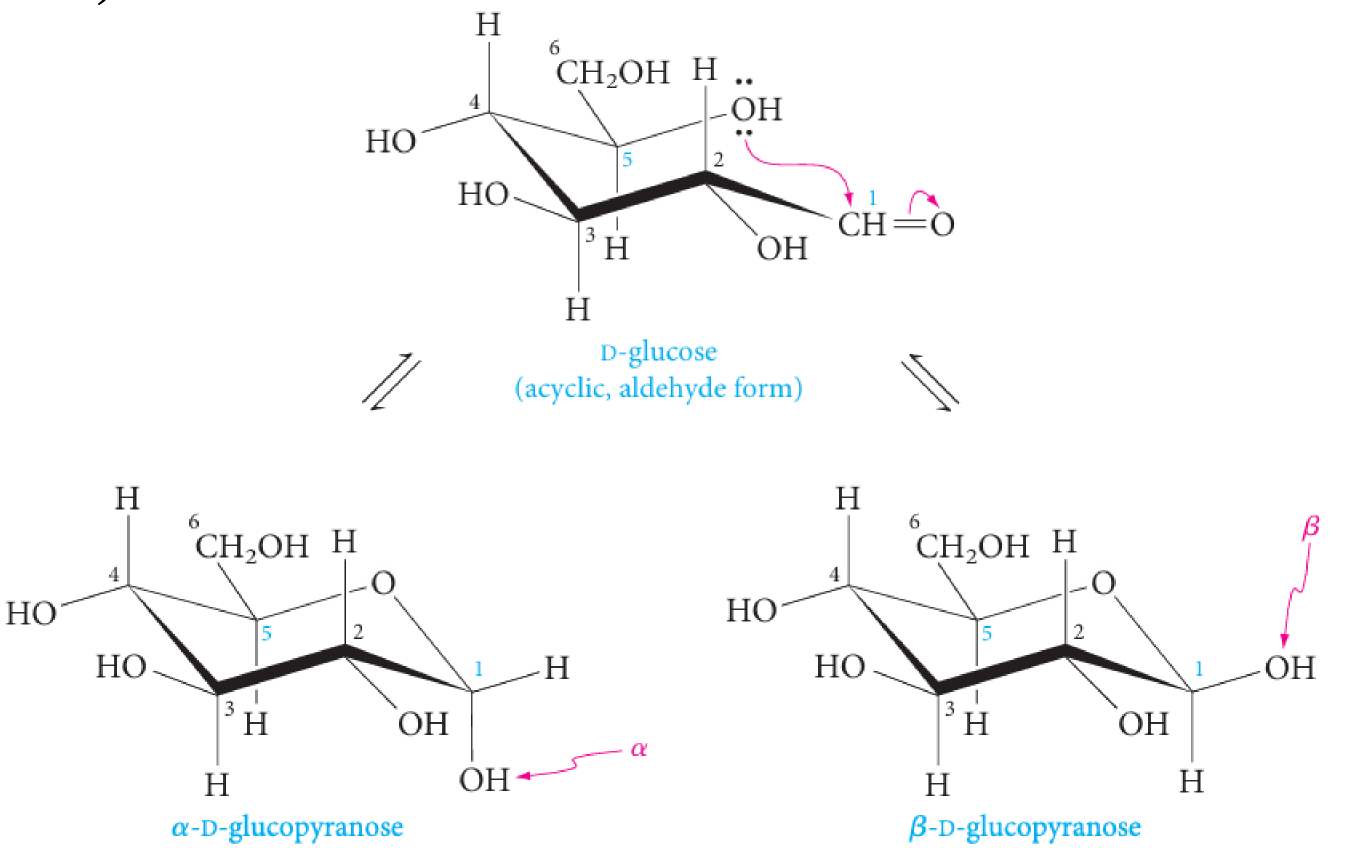
D-glucose
(acyclic, aldehyde
form)

β-D-glucose (64%)
(mp 150°C)
[α]+19°

- There is direct physical evidence. For example, if D-glucose is crystallized from methanol, the pure α form is obtained. On the other hand, crystallization from acetic acid gives the β form.
- The α and β forms of d-glucose are diastereomers.

Conformations of Pyranoses; Chair Conformations

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



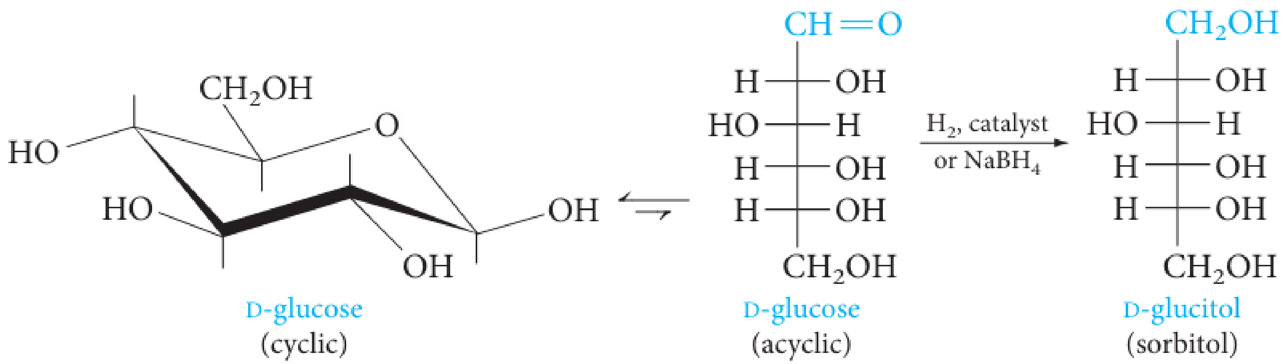
α -D-Glucopyranose (36%)
(*α* -anomer: C1-OH and CH_2OH are *trans*)

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

Reaction of Monosaccharides

Reduction

- The carbonyl group of aldoses and ketoses can be reduced by various reagents.
- The products are polyols, called alditols.



Sorbitol is used commercially as a sweetener and sugar substitute.

Reaction of Monosaccharides

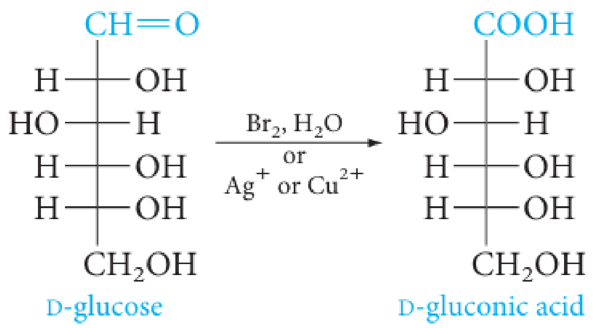
Oxidation

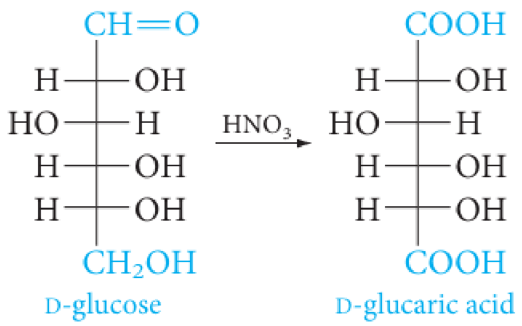
- A carbohydrate that reacts with oxidizing agents is called a reducing sugar.
- With mild oxidizing agents:
    1. Tollens' reagent (Ag^+ in aqueous ammonia).
    2. Fehling's reagent (Cu^{2+} complexed with tartrate ion).
    3. Benedict's reagent (Cu^{2+} complexed with citrate ion).
    4. Br_2, H_2O.

The aldehyde groups can be easily oxidized to acids. The products are called aldonic acids.

- With Stronger oxidizing agents:

  Aqueous nitric acid, oxidize the aldehyde group and the primary alcohol group, producing dicarboxylic acids called aldaric acids.





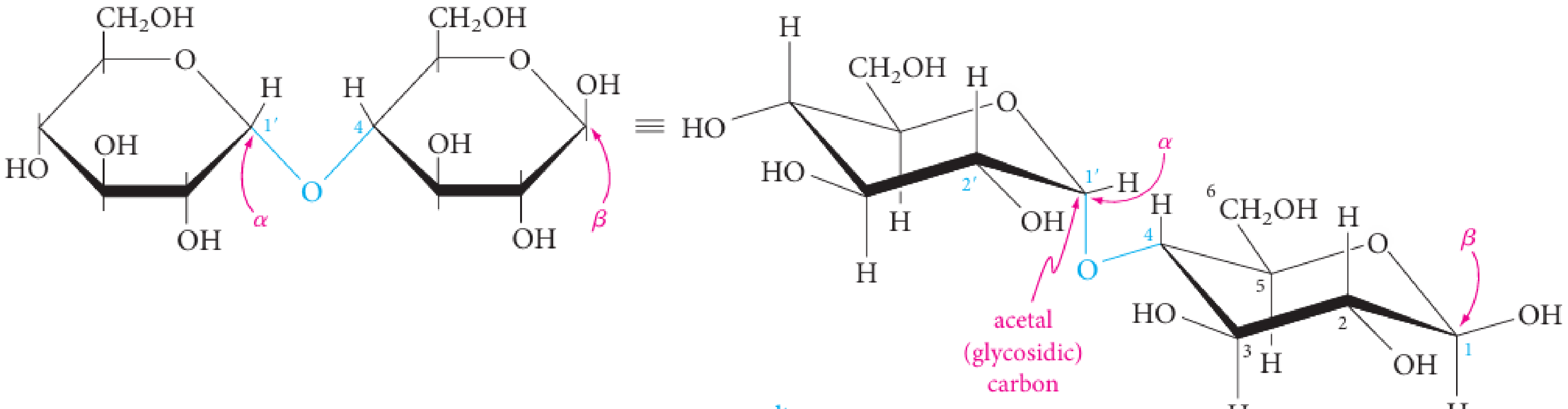
Disaccharides

- The most common oligosaccharides are disaccharides.
- Two monosaccharides are linked by a glycosidic bond between the anomeric carbon of one monosaccharide unit and a hydroxyl group on the other unit, such as : sucrose, lactose, maltose.

Disaccharides

Maltose

- Maltose is the disaccharide obtained by the partial hydrolysis of starch.
- Further hydrolysis of maltose gives only D-glucose.
- Maltose 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. In the crystalline form, the anomeric carbon of the right unit has the β configuration.

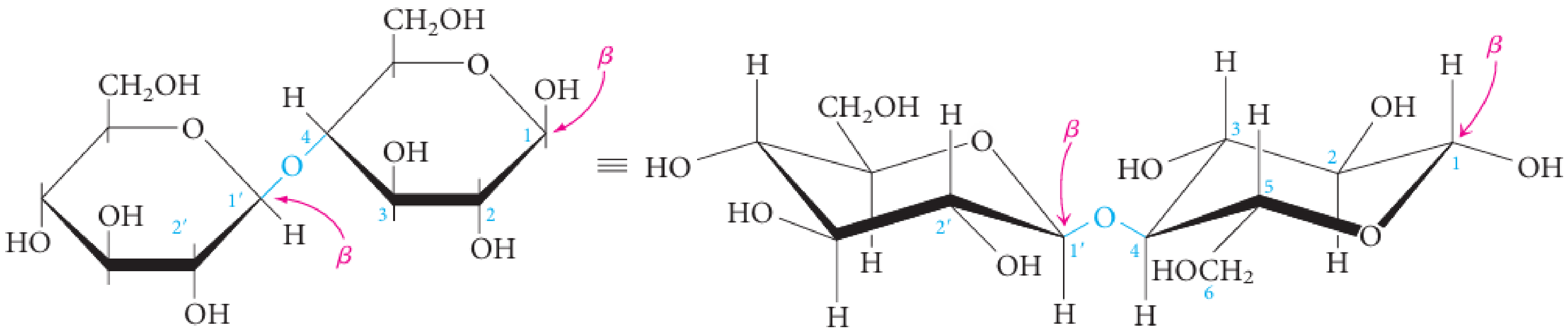


maltose
4-O-(α-D-glucopyranosyl)-β-D-glucopyranose

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.
- Cellobiose differs from maltose only in having the *β* configuration at C-1 of the left glucose unit, including a link from C-1 of the left unit to the hydroxyl group at C-4 in the right unit.



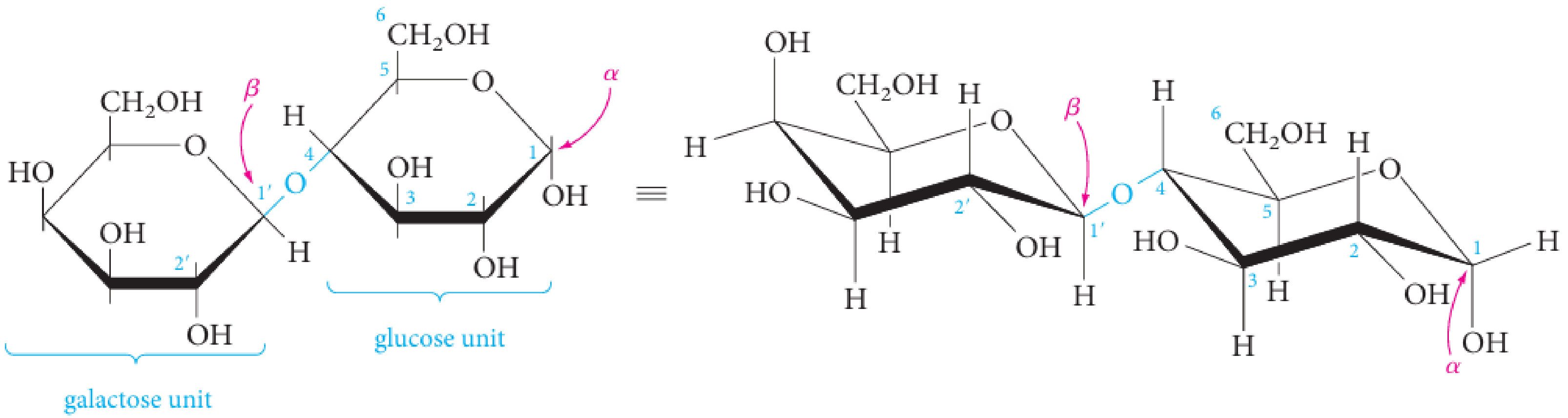
cellobiose

4-O-(*β*-D-glucopyranosyl)-*β*-D-glucopyranose

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.

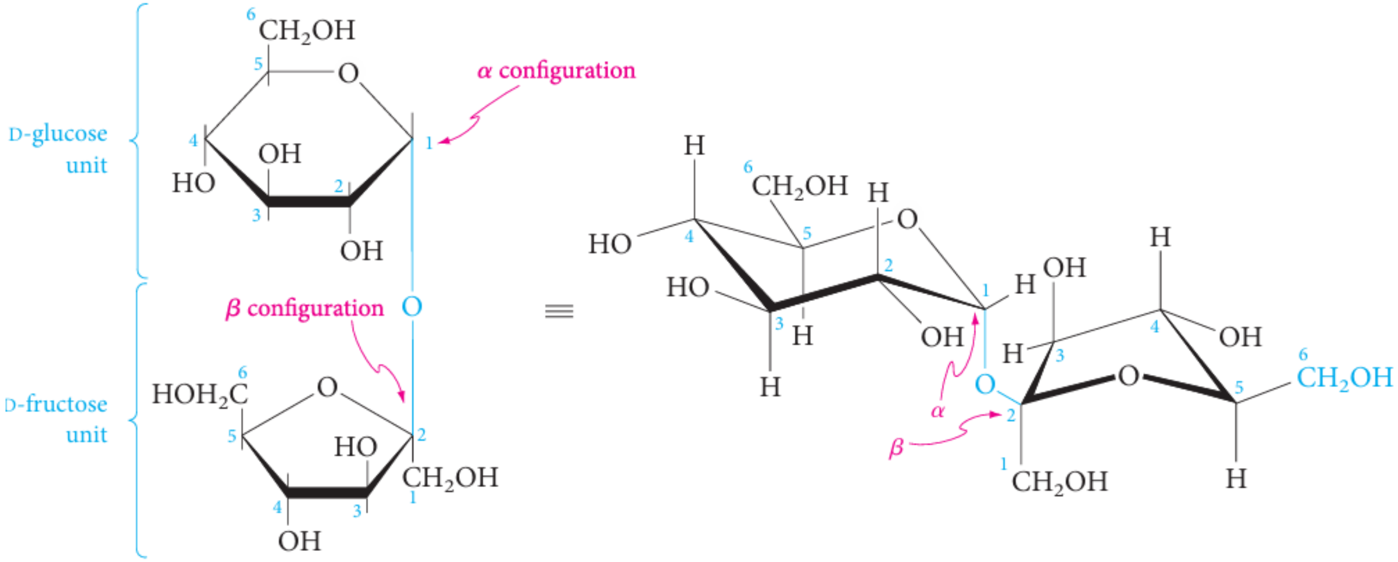


lactose
4-O-(*β*-D-galactopyranosyl)-*α*-D-glucopyranose

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.
- 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.
- It is obtained commercially from sugar cane and sugar beets, in which it constitutes 14% to 20% of the plant juices.
- Hydrolysis of sucrose gives equimolar amounts of D-glucose and D-fructose.



sucrose
α-D-glucopyranosyl-β-D-fructofuranoside
(or β-D-fructofuranosyl-α-D-glucopyranoside)

Polysaccharides

- Polysaccharides contain many linked monosaccharides and vary in chain length and molecular weight, such as : Starch, Glycogen and cellulose
- The monosaccharide units may be linked linearly, or the chains may be branched.

Polysaccharides

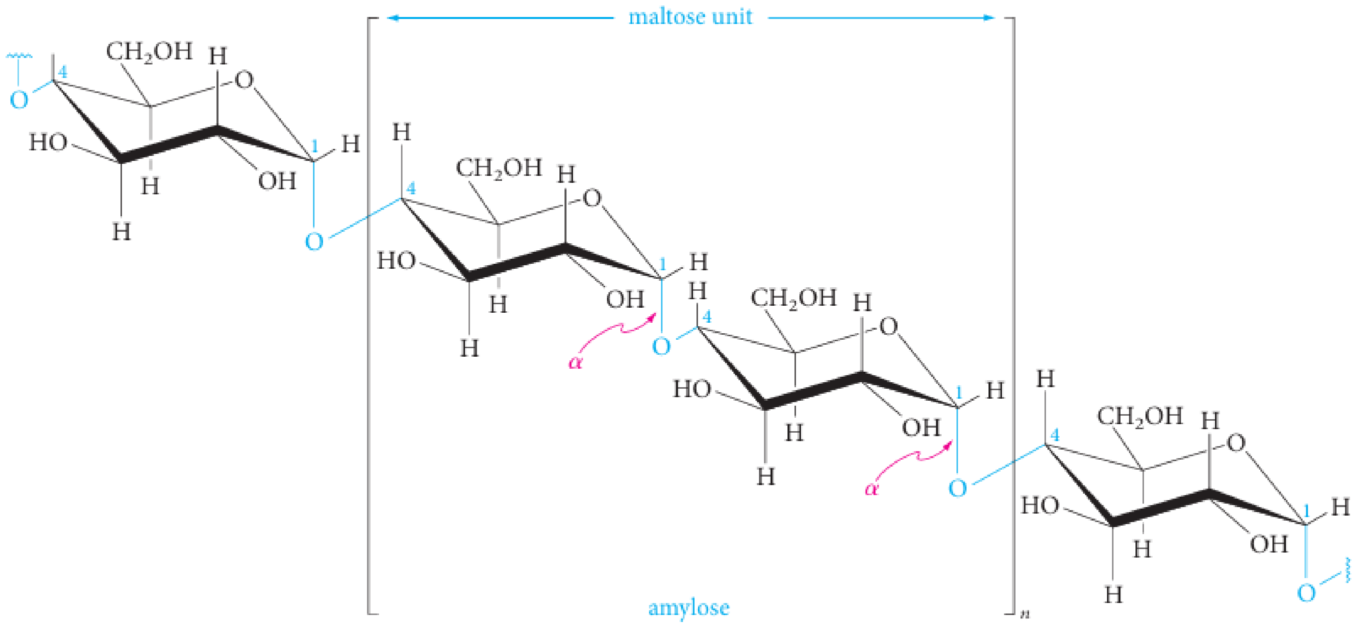
Starch

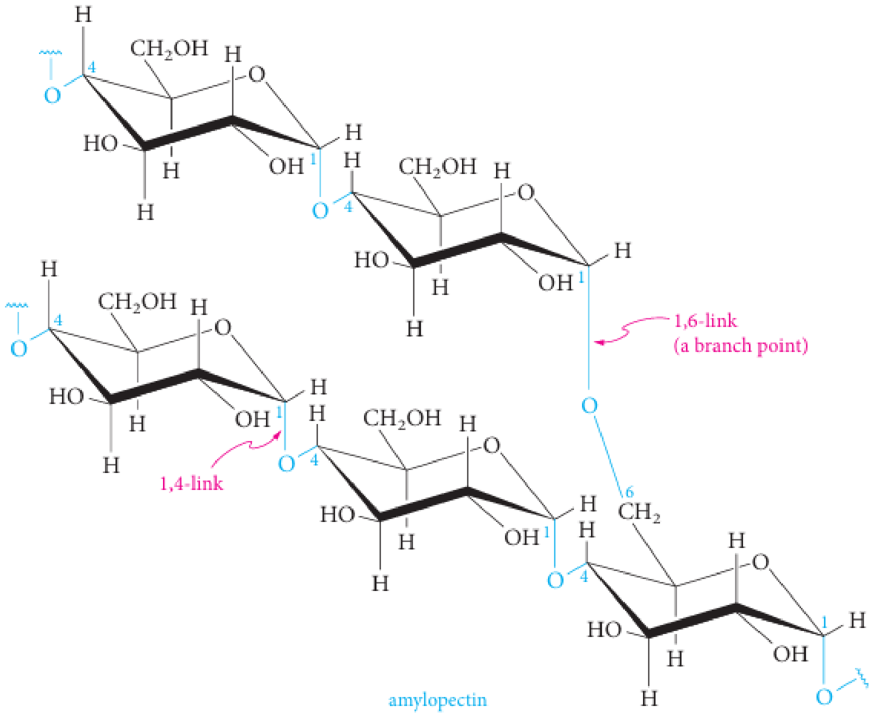
- Starch is the energy-storing carbohydrate of plants. It is a major component of cereals, potatoes, corn, and rice.
- Starch is made up of glucose units joined mainly by 1,4-α-glycosidic bonds, although the chains may have a number of branches attached through 1,6-α-glycosidic bonds.
- Partial hydrolysis of starch gives maltose, and complete hydrolysis gives only D-glucose.
- Starch can be separated by various techniques into two fractions: amylose and amylopectin.

  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.

Starch


maltose unit
α
α
amylose


1,6-link
(a branch point)
1,4-link
amylopectin

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.

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.