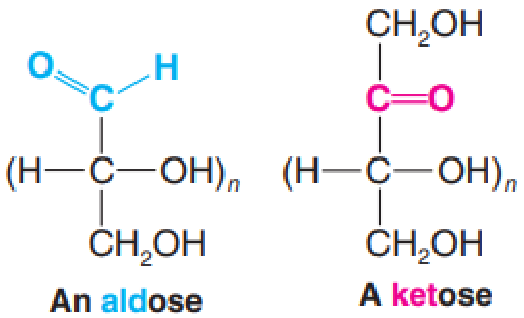
CH-4

Carbohydrates

Definition

- The term carbohydrates stem from the fact that the earliest investigated compounds have the formula $C_n(H_2O)_n$ suggesting that carbohydrates are hydrates of carbon also due to upon heating sugars, water and carbon are produced. However, many carbohydrates are now known that do not correspond to this general formula.
- Also there are compounds which has this formula but they are actually not carbohydrates such as formaldehyde (CH_2O) and acetic acid (CH_3COOH).
- Chemically carbohydrates are polyhydroxy aldehydes (aldoses) or ketones (ketoses) or substances that yield such compounds on hydrolysis



Biological importance

- Carbohydrates are compounds of tremendous biological importance:

  - They provide energy through oxidation in plants, animals and humans.

  - They supply carbon for synthesis of cell components.

  - They serve as a form of stored chemical energy.

  -Structural components of nucleic acids (ribose in RNA and deoxyribise in DNA).

  - They from part of the structures of some cells and tissues

  - Almost all of our food can be traced to carbohydrates such as glucose

  - Clothes are made from various forms of cellulose (e.g. cotton, linen)

  - Cellulose is also the basic component of wood.

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

Classes of carbohydrates

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

Hydrolysis.

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

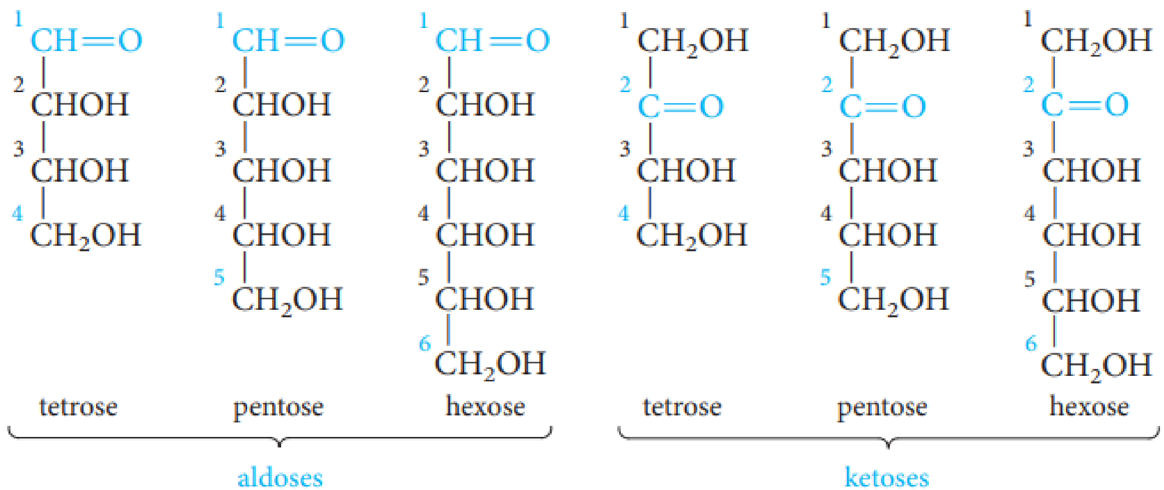
- Monosaccharides (or simple sugars) are carbohydrates that cannot be hydrolyzed to simpler compounds.

- 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.

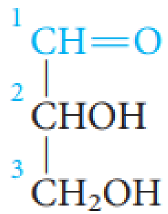
Monosaccharides

- 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).

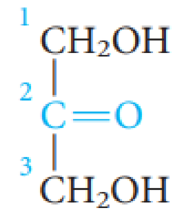


- The full name of a sugar must has a prefix indicating the nature of the carbonyl group, a Latin word indicating the number of carbons present and a suffix -ose.
- There are only two trioses: glyceraldehyde (is the simplest aldose) and dihydroxyacetone (is the simplest ketose).

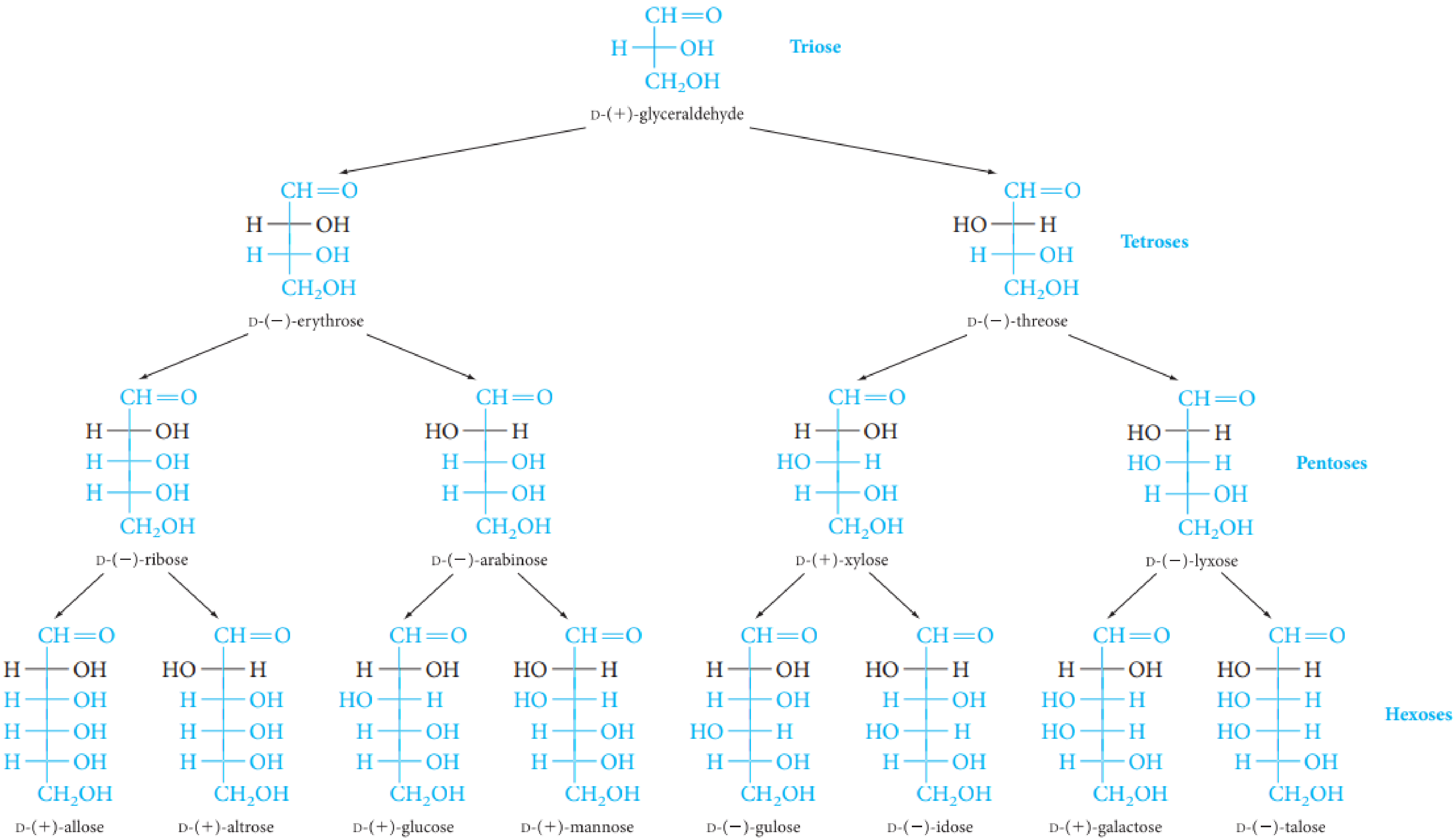
Aldotriose
glyceraldehyde



Ketotriose
dihydroxyacetone

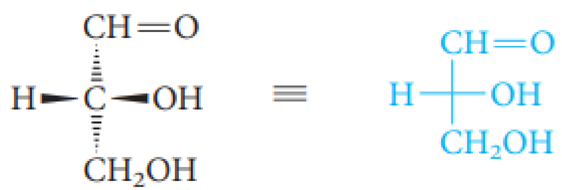


Monosaccharides



Chirality in Monosaccharides

Fischer Projection Formulas and D, L-Sugars



R-(+)-glyceraldehyde

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

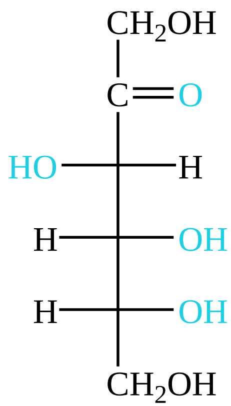
- D-glyceraldehyde, with the hydroxyl group on the right.
- L-glyceraldehyde, with the hydroxyl group on the left.

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

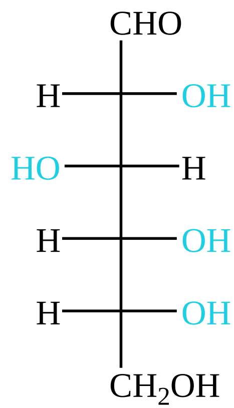
stereoisomers

- Stereogenic centers are mostly carbon atoms (asymmetric carbon) that bind four different groups.
- Stereoisomers = 2^n (n = number of stereogenic centers).
- Each of those stereoisomers has its enantiomer (mirrorimage) (2 pairs of enantiomers).
- Reverting the configuration at more than one stereogenic centre at once will result in two structures known as diasteroisomers.
- While, reverting the configuration at only one stereogenic centre will result in two structures known as Epimers (special class of diastereoisomers).
- Diastereomers differ in their properties.

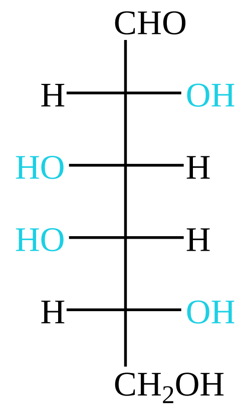
stereoisomers



Fructose



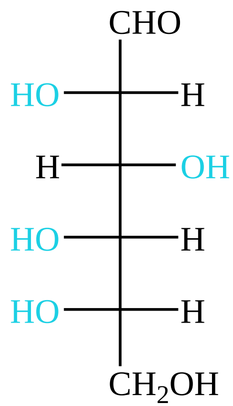
D-glucose



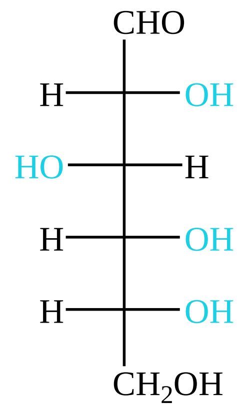
D-galactose

Structural isomers

Diastereomers



L-glucose

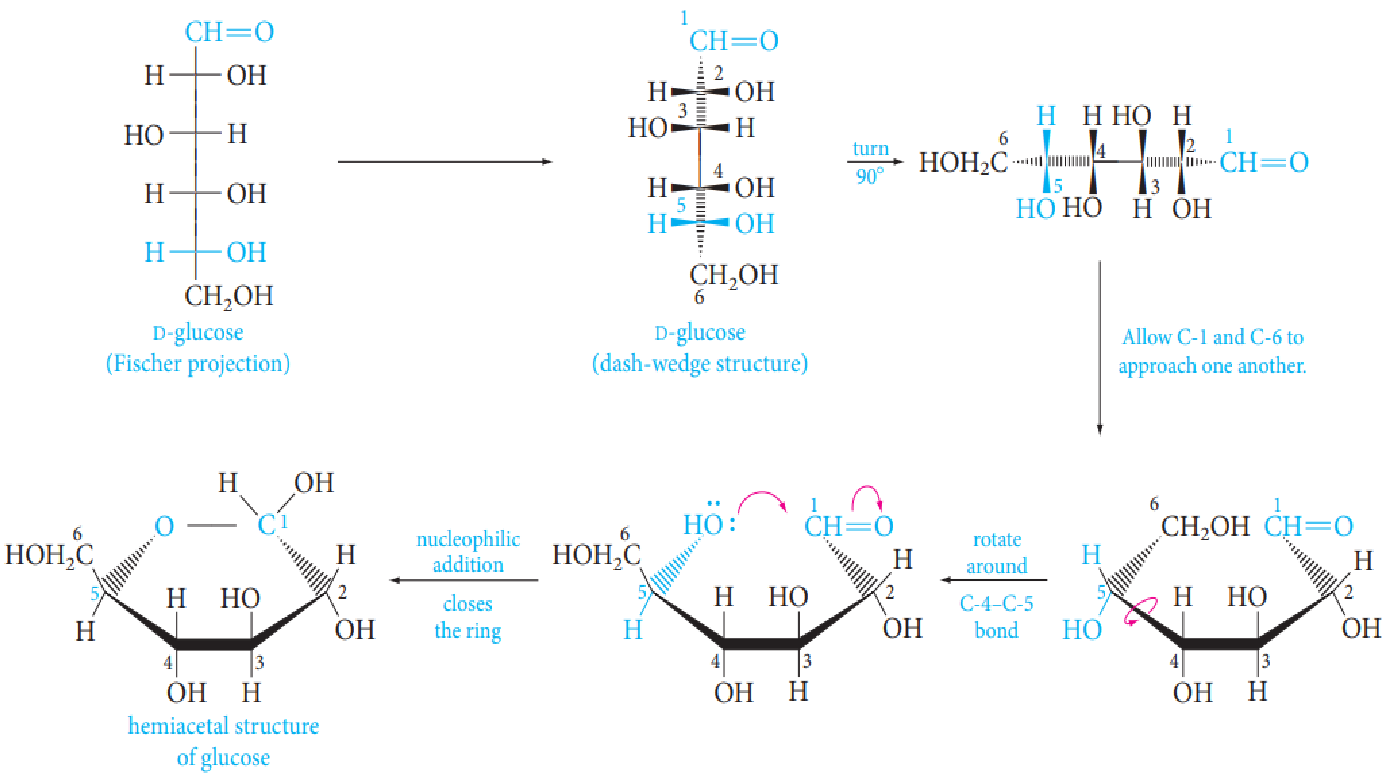


D-glucose

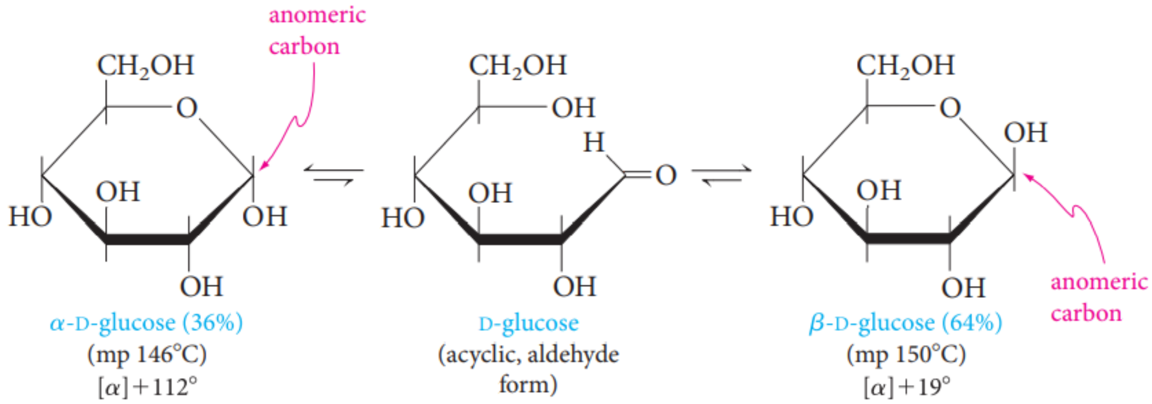
Enantiomers

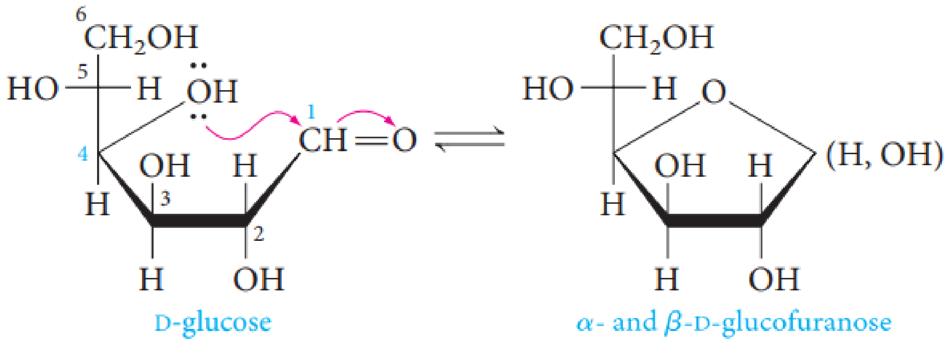
The Cyclic Hemiacetal Structures of Monosaccharides

- Monosaccharides exist mainly in cyclic, hemiacetal forms and not in the acyclic aldo- or keto-forms.
- This cyclization can result in stable 6-memeberd structure resembles pyran ring known as pyranose or 5-memeberd structure resembles furan ring known as furanose.



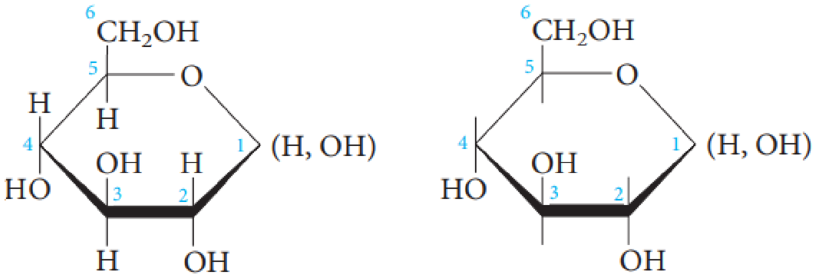
The Cyclic Hemiacetal Structures of Monosaccharides





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.

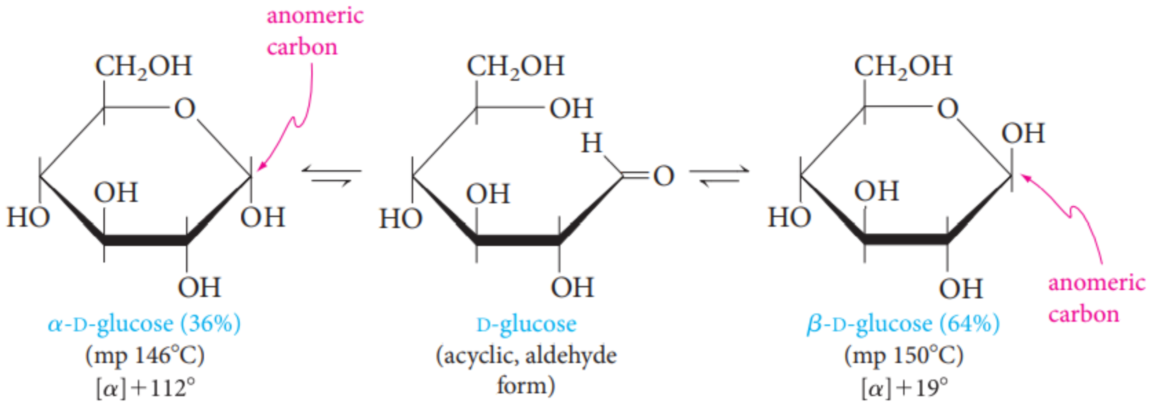


Haworth projection formulas for D-glucose

- 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. Next, 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). In contrast, all of the other carbons are monofunctional.
- 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

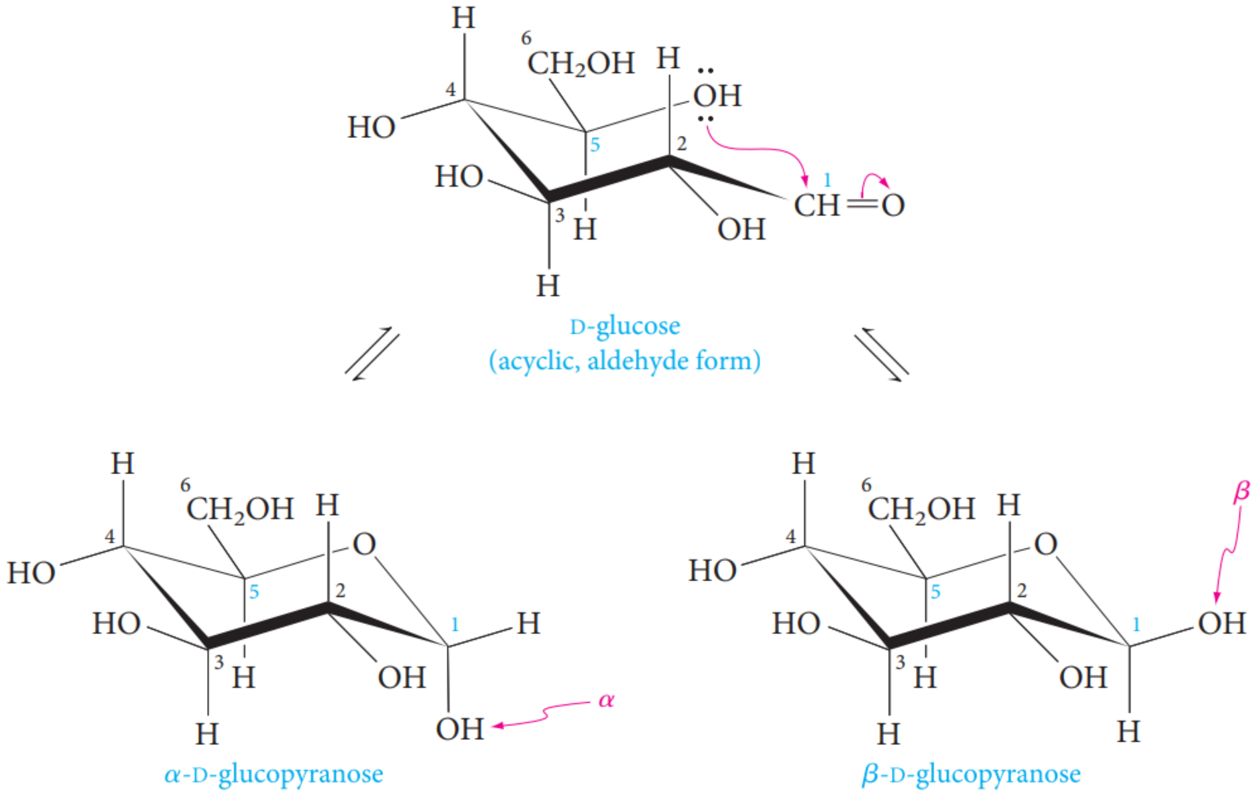
- The hemiacetal carbon, the carbon that forms the new stereogenic center, is called the anomeric carbon.
- Two monosaccharides that differ only in configuration at the anomeric center are anomers (a special kind of epimers).
- Anomers are called α or β, depending on the position of the hydroxyl group.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



- The α and β forms of D-glucose have identical configurations at every stereogenic center except at C-1, the anomeric carbon.
- 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

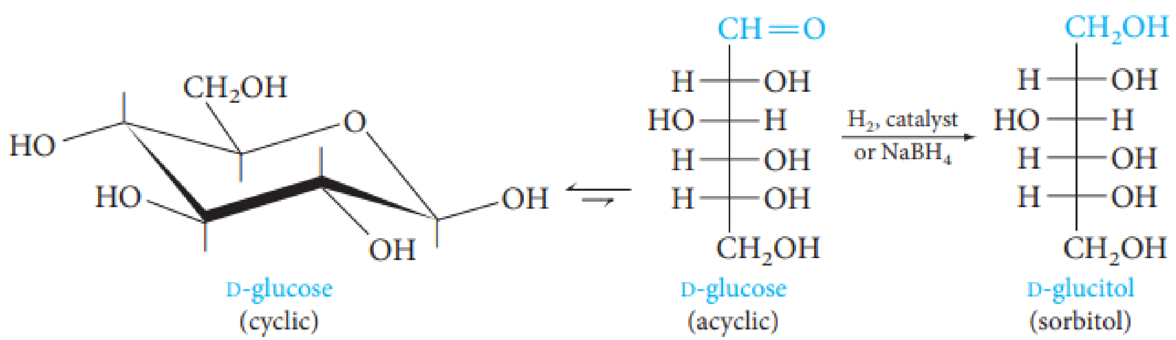
- At the anomeric carbon (C-1), where the hydroxyl group may be axial (in the α anomer) or equatorial (in the β anomer).



Reaction of Monosaccharides

Reduction

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

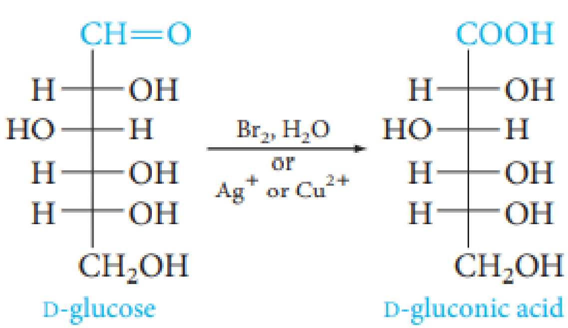


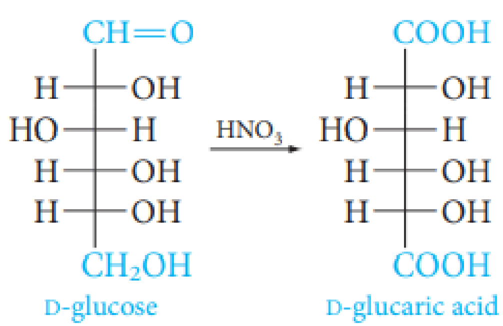
Reaction of Monosaccharides

Oxidation

- A carbohydrate that reacts with oxidizing agents is called a reducing sugar.
- The aldehyde groups can be easily oxidized to acids. The products are called aldonic acids.
- 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.
- With Stronger oxidizing agents:

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





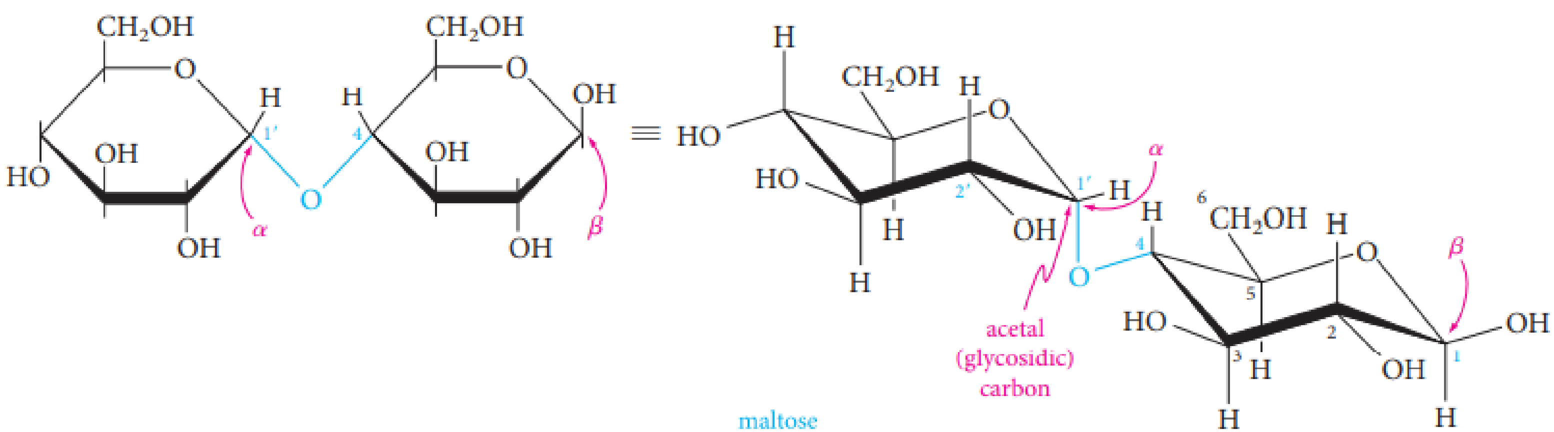
Disaccharides

- 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.

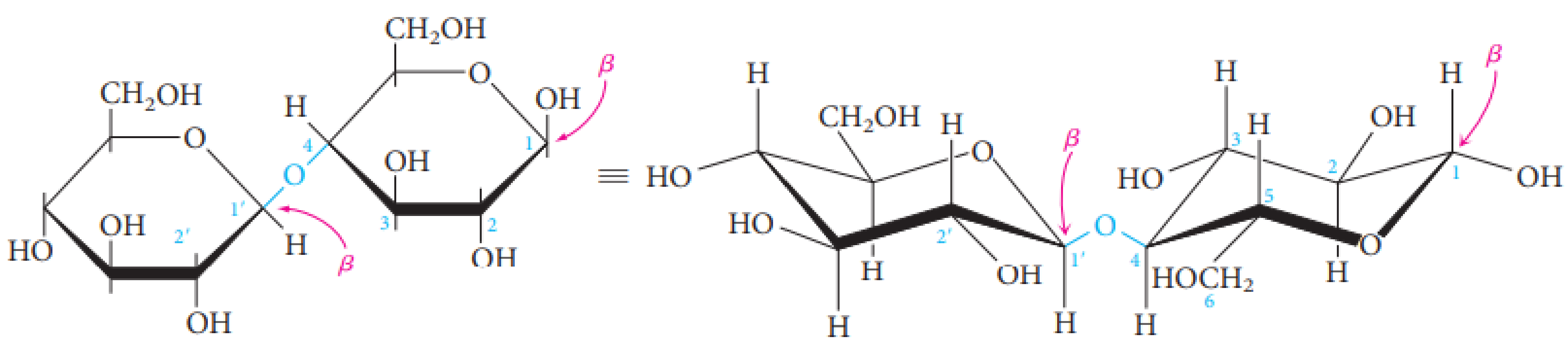


maltose
4-O-(α-D-glucopyranosyl)-β-D-glucopyranose

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.

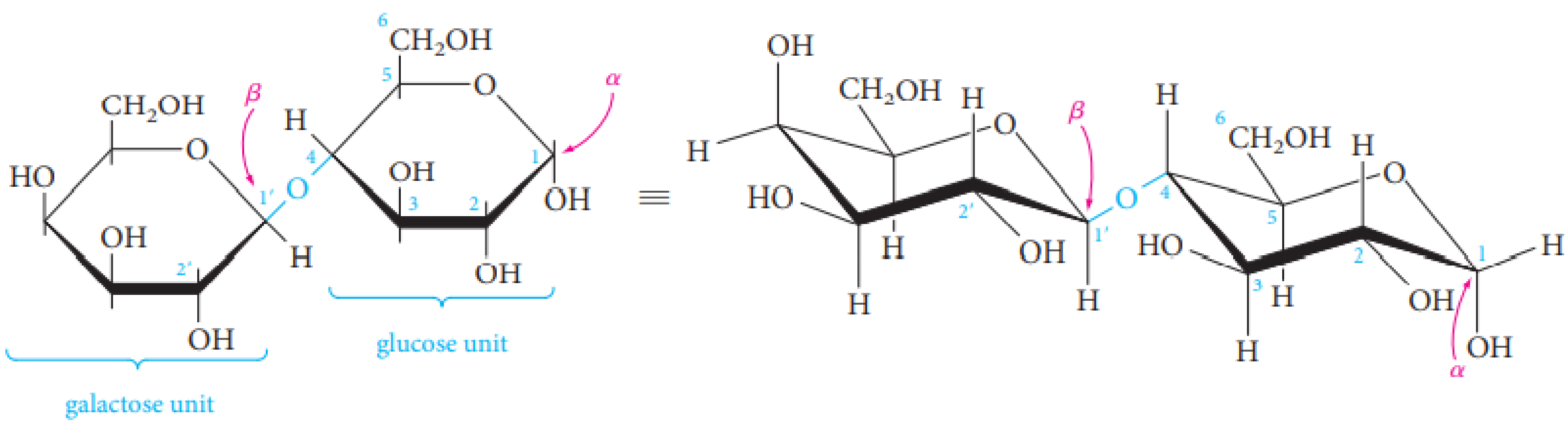


cellobiose
4-O-(β-D-glucopyranosyl)-β-D-glucopyranose

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.

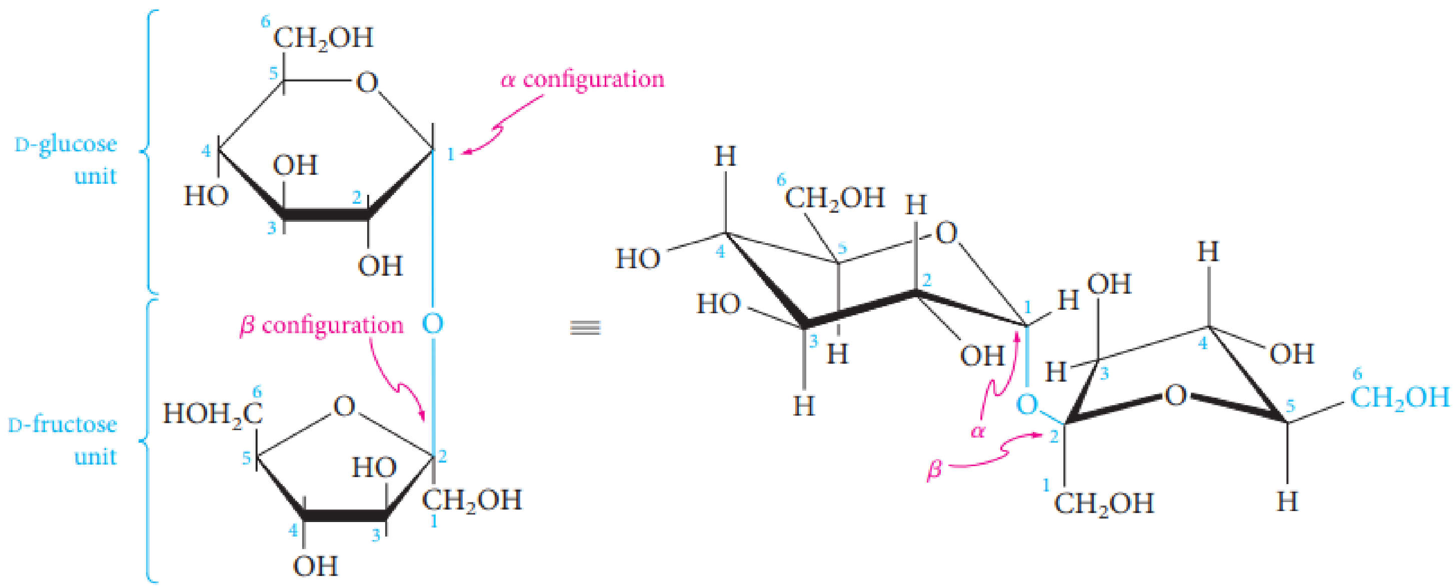


lactose
4-O-(*β*-D-galactopyranosyl)-*α*-D-glucopyranose

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.
- 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

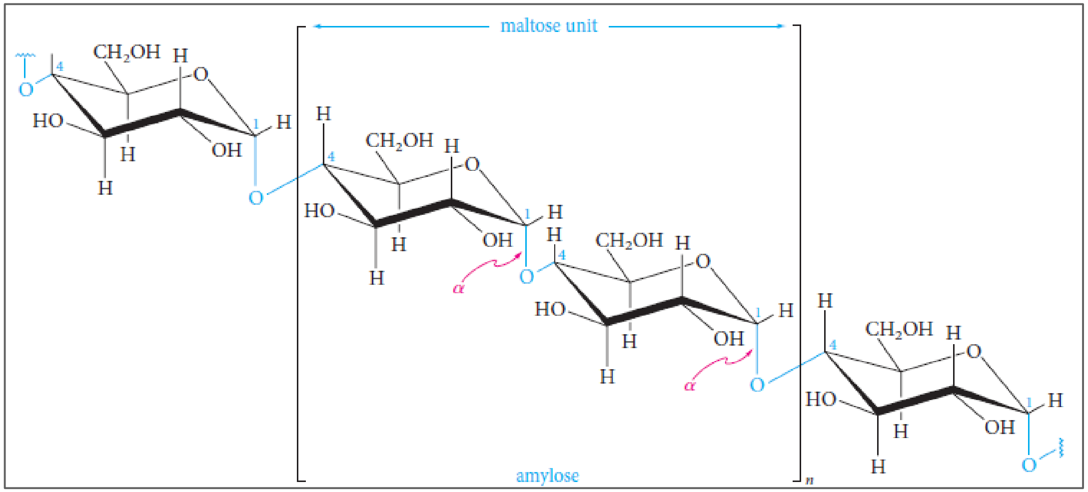
- Starch is the energy-storing carbohydrate of plants. It is a major component of cereals, potatoes, corn, and rice.
- Starch is made up of glucose units joined mainly by 1,4-α-glycosidic bonds, although the chains may have a number of branches attached through 1,6-α-glycosidic bonds.
- Partial hydrolysis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

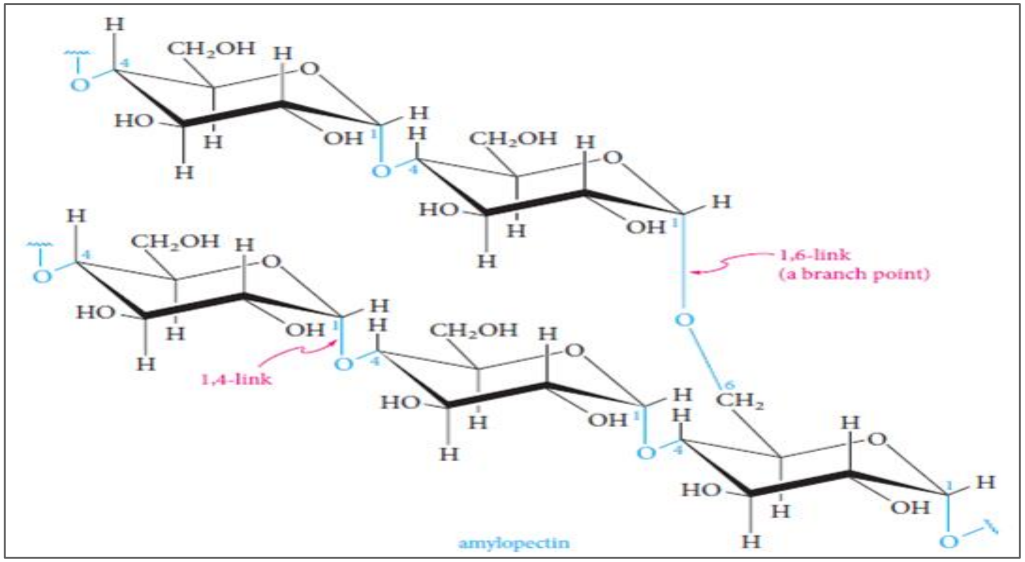
  Amylose, which constitutes about 20% of starch, the glucose units (50 to 300) are in a continuous chain, with 1,4 linkages.

  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.

Polysaccharides

Starch





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.

Polysaccharides

Cellulose