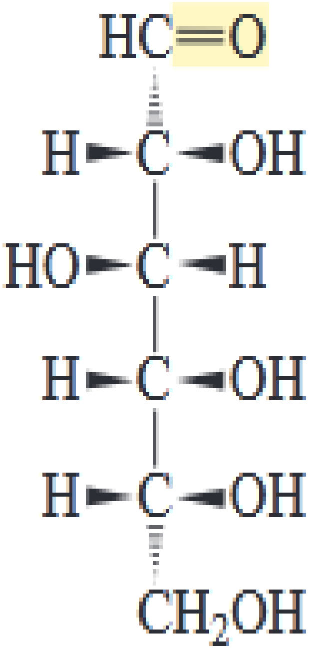
CARBOHYDRATES

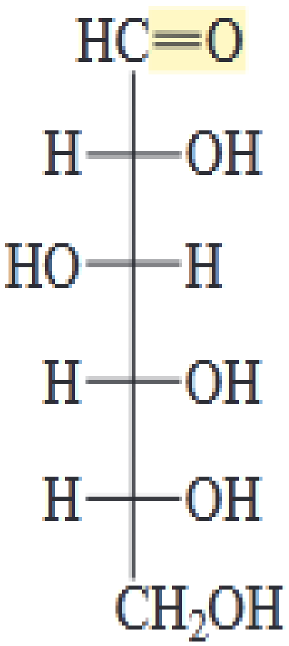
- **Carbohydrates** are polyhydroxy aldehydes such as D-glucose, polyhydroxy ketones such as D-fructose, and compounds such as sucrose that can be hydrolyzed to polyhydroxy aldehydes or polyhydroxy ketones.

- They are naturally occurring organic compounds with the general formula $C_n(H_2O)_n$ where *n* is equal to or greater than three. The chemical structures of carbohydrates are commonly represented by wedge-and-dash structures or by Fischer projections.

- Note that both D-glucose and D-fructose have the molecular formula $C_6H_{12}O_6$, consistent with the general formula $C_6H_{12}O_6$ which made early chemists think that those compounds were hydrates of carbon.



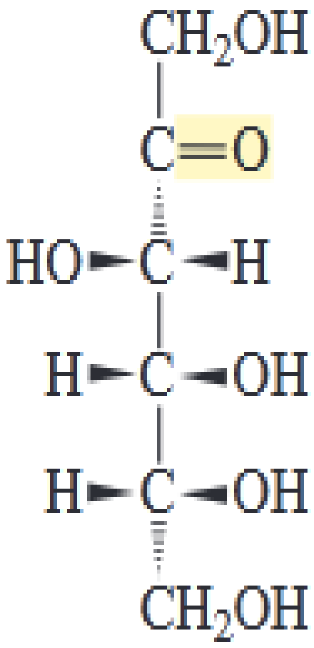
wedge-and-dash structure



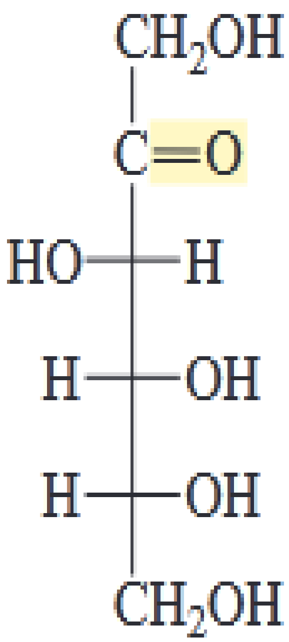
Fischer projection

D-glucose

a polyhydroxy aldehyde



wedge-and-dash structure



Fischer projection

D-fructose

a polyhydroxy ketone

Horizontal bonds point toward the viewer and the vertical bonds point away from the viewer in Fischer projections.

- Though the structures of many carbohydrates appear to be quite complex, the chemistry of these substances usually involves only two functional groups- *ketone* or *aldehyde carbonyls* and *alcohol hydroxyl* groups.

- The carbonyl groups normally do not occur as such, but are combined with hydroxyl groups to form hemiacetal or acetal linkages.

- An understanding of stereochemistry is particularly important to understand the properties of carbohydrates. Configurational and conformational isomerism also play an important role.

- Among the well-known carbohydrates are various sugars, starches, and cellulose, all of which are important for the maintenance of life in both plants and animals.

- The most abundant carbohydrate in nature is D-glucose. Living cells oxidize D-glucose in the first of a series of processes that provide them with energy.

- When animals have more D-glucose than they need for energy, they convert the excess D-glucose into a polymer called glycogen.

- When an animal needs energy, glycogen is broken down into individual D-glucose molecules. Plants convert excess D-glucose into a polymer known as starch.

- Cellulose—the major structural component of plants—is another polymer of D-glucose.

- Chitin, a carbohydrate similar to cellulose, makes up the exoskeletons of crustaceans, insects, and other arthropods and is also the structural material of fungi.

- Animals obtain glucose from food—such as plants—that contains glucose. Plants produce glucose by **photosynthesis**.

$$\underset{\text{glucose}}{C_6H_{12}O_6} + 6\,O_2 \underset{\text{photosynthesis}}{\overset{\text{oxidation}}{\rightleftharpoons}} 6\,CO_2 + 6\,H_2O + \text{energy}$$

Classification of Carbohydrates

The terms “carbohydrate,” “saccharide,” and “sugar” are often used interchangeably.

There are two classes of carbohydrates:

- *simple carbohydrates*
- *complex carbohydrates*.

Simple carbohydrates are **monosaccharides** (single sugars),

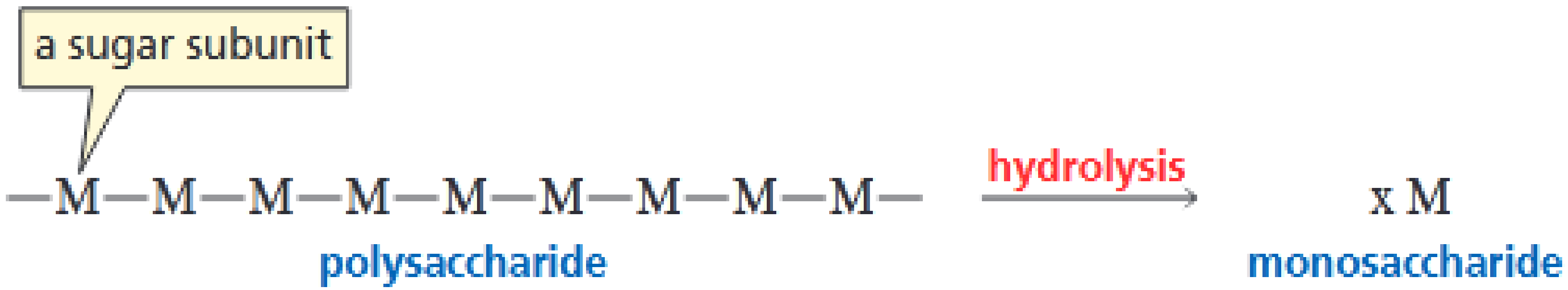
complex carbohydrates contain two or more sugar subunits linked together.

Disaccharides have two sugar subunits linked together,

oligosaccharides have three to 10 sugar subunits linked together, and

polysaccharides have more than 10 sugar subunits linked together.

Disaccharides, oligosaccharides, and polysaccharides can be broken down to monosaccharide subunits by hydrolysis.



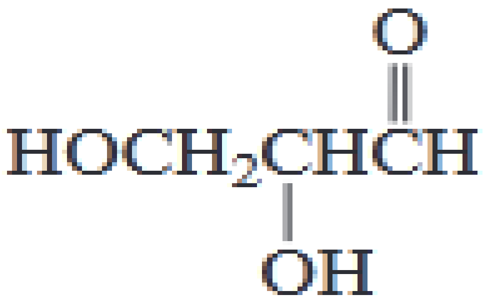
A *monosaccharide* can be a polyhydroxy aldehyde such as D-glucose or a polyhydroxy ketone such as D-fructose.

Polyhydroxy aldehydes are called **aldoses**
polyhydroxy ketones are called **ketoses**.

Monosaccharides are also classified according to the number of carbons they contain:
Monosaccharides with three carbons are **trioses**,
those with four carbons are **tetroses**,
those with five carbons are **pentoses**, and
those with six and seven carbons are **hexoses** and **heptoses**, respectively.
A six-carbon polyhydroxy aldehyde such as D-glucose is an aldohexose,
while a six-carbon polyhydroxy ketone such as D-fructose is a ketohexose.

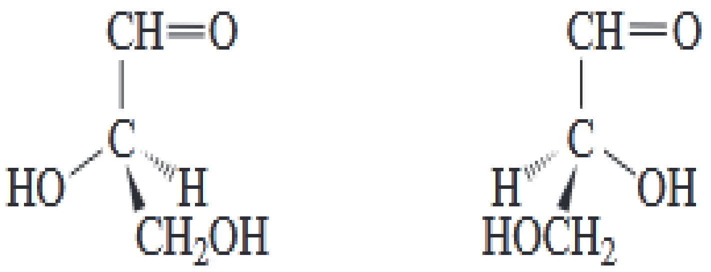
The D and L Notation

The smallest aldose, and the only one whose name does not end in "ose," is glyceraldehyde, an aldotriose.



glyceraldehyde

Glyceraldehyde can exist as a pair of enantiomers because it has an asymmetric carbon.



(*R*)-(+)-glyceraldehyde (*S*)-(−)-glyceraldehyde

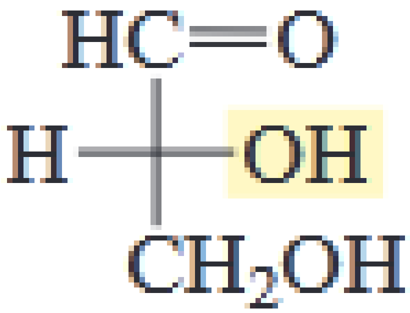
perspective formulas

(*R*)-(+)-glyceraldehyde (*S*)-(−)-glyceraldehyde

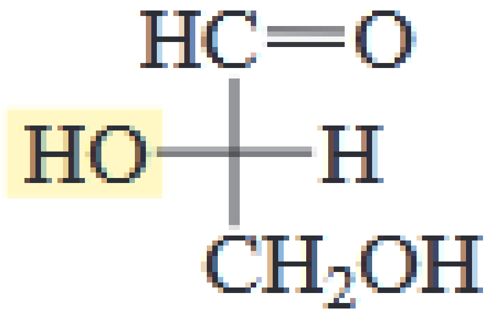
Fischer projections

Fischer arbitrarily assigned the R-configuration to the dextrorotatory isomer of glyceraldehyde known as D-glyceraldehyde.

D-Glyceraldehyde is (R)-(+) -glyceraldehyde, and
L-glyceraldehyde is (S)-(-) -glyceraldehyde.



D-glyceraldehyde



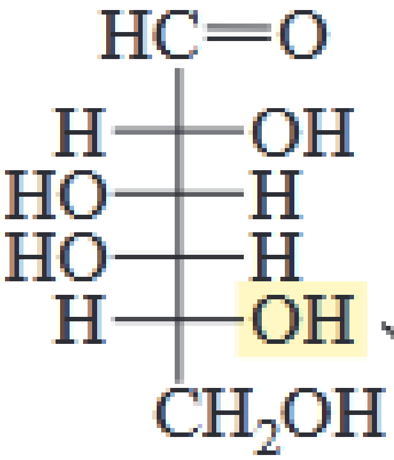
L-glyceraldehyde

- The notations D and L are used to describe the configurations of carbohydrates and amino acids, so the knowledge is important to learn what D and L signify.

- In Fischer projections of monosaccharides, the carbonyl group is always placed on top (in the case of aldoses) or as close to the top as possible (in the case of ketoses).

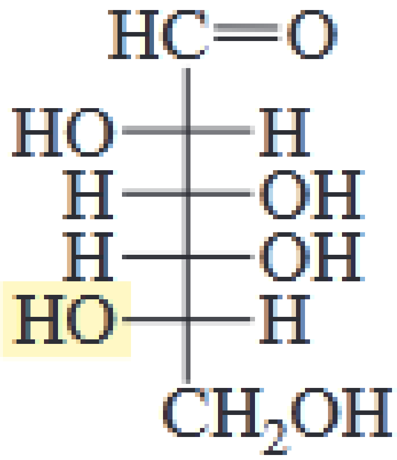
- From its structure, galactose has four asymmetric carbons (C-2, C-3, C-4, and C-5). If the OH group attached to the bottom-most asymmetric carbon (the carbon that is second from the bottom) is on the right, then the compound is a D-sugar.

- If the OH group is on the left, then the compound is an L-sugar.
- Almost all sugars found in nature are D-sugars.



D-galactose

the OH group is on the right



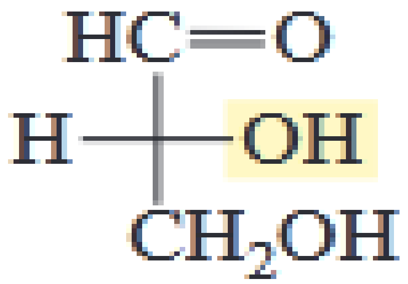
L-galactose

mirror image of D-galactose

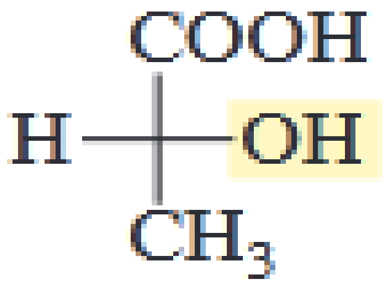
Like R and S, D and L indicate the configuration of an asymmetric carbon, but they do not indicate whether the compound rotates polarized light to the right (+) or to the left (-).

For example, D-glyceraldehyde is dextrorotatory, while D-lactic acid is levorotatory.

In other words, optical rotation, like melting or boiling points, is a physical property of a compound, whereas "R, S, D, and L" are conventions used to indicate the configuration of a molecule.



D-(+)-glyceraldehyde



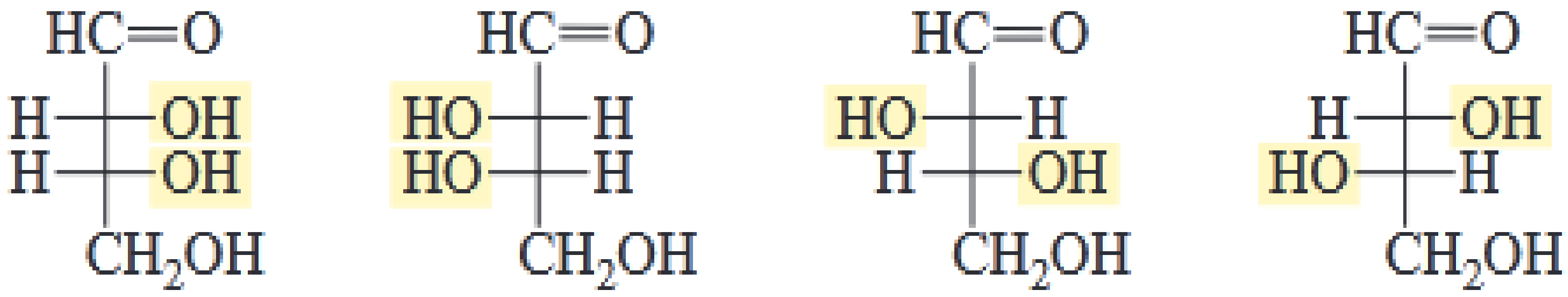
D-(–)-lactic acid

The common name of the monosaccharide, together with the D or L designation, completely defines its structure because the relative configurations of all the asymmetric carbons are implicit in the common name.

Configurations of Aldoses

Aldotetroses have two asymmetric carbons and therefore four stereoisomers. Two of the stereoisomers are D-sugars and two are L-sugars.

The names of the aldotetroses—erythrose and threose—were used to name the erythro and threo pairs of enantiomers



D-erythrose L-erythrose D-threose L-threose

- Aldopentoses have three asymmetric carbons and therefore eight stereoisomers (four pairs of enantiomers), while aldohexoses have four asymmetric carbons and 16 stereoisomers (eight pairs of enantiomers).

- The four D-aldopentoses and the eight D-aldohexoses are shown in Table 1. Diastereomers that differ in configuration at only one asymmetric carbon are called *epimers*. For example, D-ribose and D-arabinose are C-2 epimers (they differ in configuration only at C-2), and D-idose and D-talose are C-3 epimers.

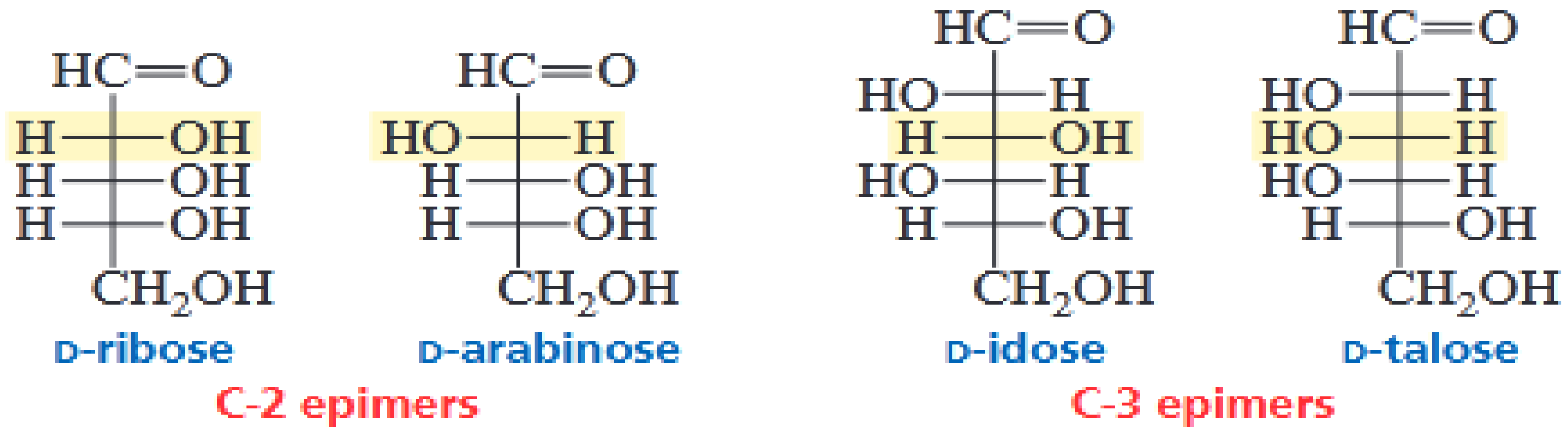
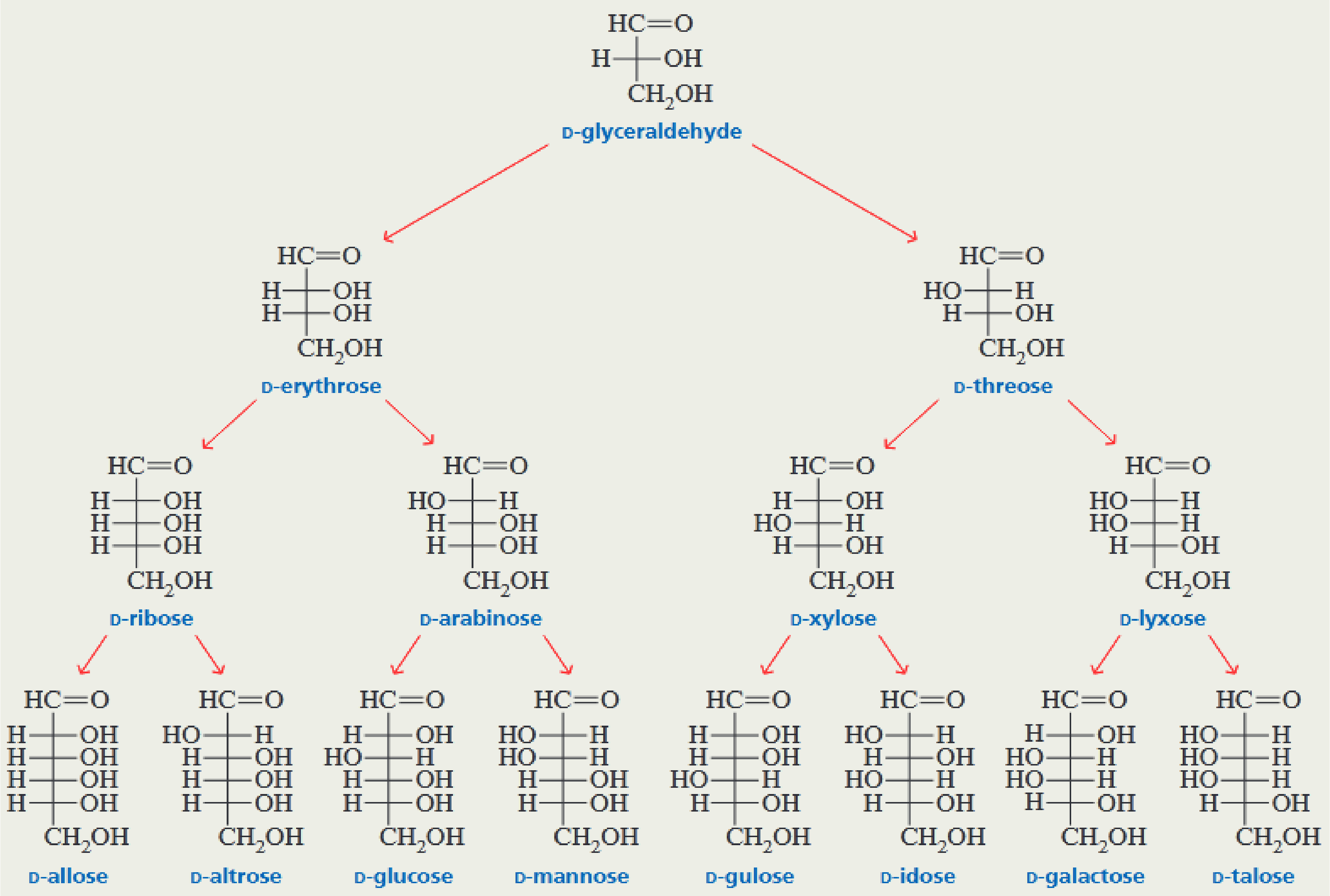


TABLE 1: Configurations of the D-Aldoses



- D-Glucose, D-mannose, and D-galactose are the most common aldohexoses in biological systems.

- An easy way to learn their structures is to memorize the structure of D-glucose and then remember that D-mannose is the C-2 epimer of D-glucose and D-galactose is the C-4 epimer of D-glucose.

- Sugars such as D-glucose and D-galactoseare also diastereomers because they are stereoisomers that are not enantiomers.

- An epimer is a particular kind of diastereomer.

Configurations of Ketoses

- Naturally occurring ketoses have the ketone group in the 2-position. The configurations of the D-2-ketoses are shown in Table 2.

- A ketose has one fewer asymmetric carbon than does an aldose with the same number of carbon atoms.

- Thus, a ketose has only half as many stereoisomers as an aldose with the same number of carbon atoms.

TABLE 2: Configurations of the D-Ketoses