Carbohydrates

Carbohydrates: polyhydroxy aldehydes or polyhydroxy ketones, or substances that give these compounds on hydrolysis.

Carbohydrates or saccharides (Greek: sakcharon, sugar) are polyhydroxy aldehydes or polyhydroxy ketones or substances that give such molecules on hydrolysis. They are essential components of all living organisms and are, in fact, the most abundant class of biological molecules. The name carbohydrate, means "carbon hydrate", is derived from their chemical composition, which is roughly **$(C\text{-}H_2O)_n$**, where $n \geq 3$ (many, but not all, carbohydrates have this general formula, some also contain nitrogen, phosphorus, or sulfur). Many of these compounds are synthesized from simpler substances in a process named gluconeogenesis. Others (and ultimately nearly all biological molecules) are the products of photosynthesis, through which plants and certain bacteria form carbohydrates. Carbohydrates account for approximately three-fourths of the dry weight of plants. Animals (including humans) get their carbohydrates by eating plants, but they do not store much of what they consume. In fact, less than 1% of the body weight of animals is made up of carbohydrates.

Functions of carbohydrates

1. Carbohydrates (like glucose) serve as energy source in the living system. The metabolic breakdown of monosaccharides provides much of the energy used to power biological processes.
2. Carbohydrates serve as energy stores in the living system (like glycogen and starch).
3. Some carbohydrates are also principal components of a number of biomolecules like ribose and deoxy ribose in nucleic acids.
4. Insoluble carbohydrate polymers serve as structural and protective elements in the cell walls of bacteria and plants (like cellulose) and in the connective tissues of animals (acidic polysaccharides).

Depending on the number of sugar units in their molecules, carbohydrates can be divided into three classes:

1. Monosaccharides: consist of a single polyhydroxy aldehyde or ketone unit.
2. Oligosaccharides: consist of short chains of monosaccharide units, or residues, joined by glycosidic bonds. The most abundant are the disaccharides, with two monosaccharide units.
3. Polysaccharides: they are sugar polymers consist of more than 20 monosaccharide units (some have hundreds or thousands of units).

Monosaccharides

Monosaccharides:
Are aldehyde or ketone derivatives of straight-chain alcohols containing at least three carbon atoms and cannot be hydrolyzed to simpler compounds

Monosaccharides are aldehyde or ketone derivatives of straight-chain alcohols containing at least three carbon atoms. They are simple sugars and cannot be hydrolyzed to form simpler saccharides. Monosaccharides are colorless, crystalline solids that are freely soluble in water but insoluble in nonpolar solvents. Most have a sweet taste.

Aldose:
a monosaccharide containing an aldehyde group.

The backbones of common monosaccharide molecules are unbranched carbon chains in which all the carbon atoms are linked by single bonds. In the open-chain form, one of the carbon atoms is double-bonded to an oxygen atom to form a carbonyl group; each of the other carbon atoms has a hydroxyl group.

Ketose:
a monosaccharide containing a ketone group.

Monosaccharides are classified according to the chemical nature of their carbonyl group. If the carbonyl group is an aldehyde, as in glucose, the sugar is an aldose. If the carbonyl group is a ketone, as in fructose, the sugar is a ketose.

Notes:

1. Examples of heptoses include the ketoses mannoheptulose and sedoheptulose.

2. Monosaccharides with eight or more carbons are rarely observed as they are quite unstable.

Monosaccharides can also be classified according to the number of carbon atoms in their backbones, smallest monosaccharides, those with three carbon atoms, are trioses. Those with four, five, six, seven, etc., C atoms are, respectively, tetroses, pentoses, hexoses, heptoses, etc. The two classifications may be combined to describe one sugar so that, for example, glucose is an aldohexose, whereas fructose is a ketopentose.

Stereochemistry of monosaccharides

Any tetrahedral carbon atom that has four different substituents is said to be asymmetric. In stereochemistry, the asymmetric carbons are called chiral centers while the symmetric carbons are called achiral atoms.

There are two facts about the molecule that contains one (or more) chiral center: **(1) it is optically active** and **(2) it occurs in more than one isomeric form**. Consequently, all monosaccharides except dihydroxyacetone (the simplest ketose) are **optically active isomeric forms** because they contain one or more chiral carbon atoms in their structures.

Optical activity

Optical activity: the ability of an asymmetric compound to rotate the plane of polarized light.

All monosaccharides (except dihydroxyacetone) are optically active due to the presence of chiral centers. Thus, they are able to rotate the plane of polarized light either clockwise or counter clockwise.

When a solution of an optically active compound rotates the plane of the polarized light clockwise, we say it is dextrorotatory; if it rotates the plane counter clockwise, we say it is levorotatory. A dextrorotatory compound is indicated by a plus sign (+) before its name, and a levorotatory compound is indicated by a minus sign (–) before its name. For example, D-glucose is dextrorotatory, it is written as (+)D-glucose, while D-Fructose is levorotatory written: (-)D-fructose.

The number of degrees by which an optically active compound rotates the plane of polarized light is called its **specific rotation** and is given the symbol [α] and can only be determined practically. The instrument used to measure the specific rotation is called polarimeter.

Configuration about the chiral center

There are two configurations about each chiral center, in other words, the atoms attached to a chiral center can exist in two spatial arrangements, and hence, the molecule can exist in two isomeric forms.

Configuration:
the spatial relative arrangement of the substituents around the chiral center.

Accordingly, glyceraldehyde (the simplest aldose) has two different stereoisomers because it has one chiral center at the middle carbon atom as in figure (1.1). The two forms are mirror images of each other so they are called enantiomers. By convention, one of these two forms is designated the D isomer, the other the L isomer.

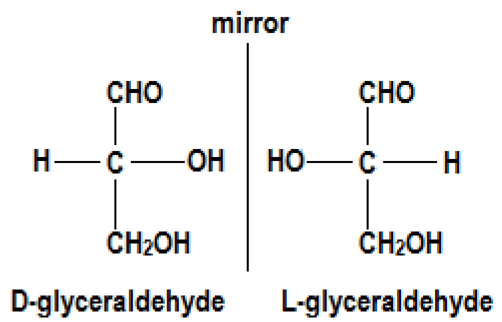

Figure (1.1): The two stereoisomers of glyceraldehyde

Number of stereoisomers= 2^n, where n represents the number of chiral atoms and 2 represents the number of possible configurations about each chiral atom.

In general, a molecule with n chiral centers can have 2^n stereoisomers. Glyceraldehyde has 2^1 = 2 stereoisomers; the aldohexoses, with four chiral centers, have 2^4 = 16 stereoisomers.

D-Monosaccharide:
A monosaccharide that has the OH group at the last chiral atom to the right when drawn in Fischer projection.

L-Monosaccharide:
A monosaccharide in which the OH group at the last chiral atom is to the left when drawn in Fischer projection.

The stereoisomers of monosaccharides (of each carbon-chain length) can be divided into two groups that differ in the configuration about the chiral center most distant from the carbonyl carbon. When the hydroxyl group at this reference carbon is on the right in the projection formula, the sugar is the D isomer; when on the left, it is the L isomer. The L sugars, in accordance with this convention, are mirror images of their D counterparts, as is shown below in Fischer projection for glucose (figure 1.2).

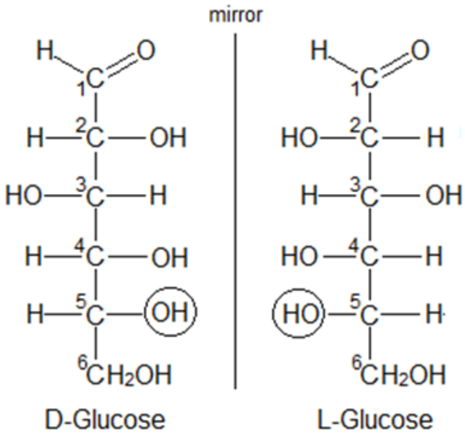

Figure (1.2): Fischer projections for D-glucose and L-glucose, the reference hydroxyl groups are shown in cycles.

Diastereomers: pairs of stereoisomers that are non-superimposable, non-mirror images of one another.

Enantiomers: pairs of stereoisomers that are mirror images of one another.

Epimers: pairs of monosaccharides that have the same molecular formula and bonding but differ in the configuration about one chiral center.

It is important to know that the carbons of a sugar are numbered beginning from the carbonyl group (the functional group). Stereoisomers that are mirror images of each other are called **enantiomers**. Pairs of stereoisomers that are not mirror images of each other are called **diastereomers**. To represent three-dimensional sugar structures on paper, we often use Fischer projection formulas. The stereochemistry and names of the D-aldoses are presented in figure (1.3).

Sugars that differ only by the configuration about one C atom are known as **epimers** of one another. Thus D-glucose and D-mannose are epimers with respect to C2, whereas D-glucose and D-galactose are epimers with respect to C4 .However, D-mannose and D-galactose are not epimers of each other because they differ in configuration about two of their carbon atoms.

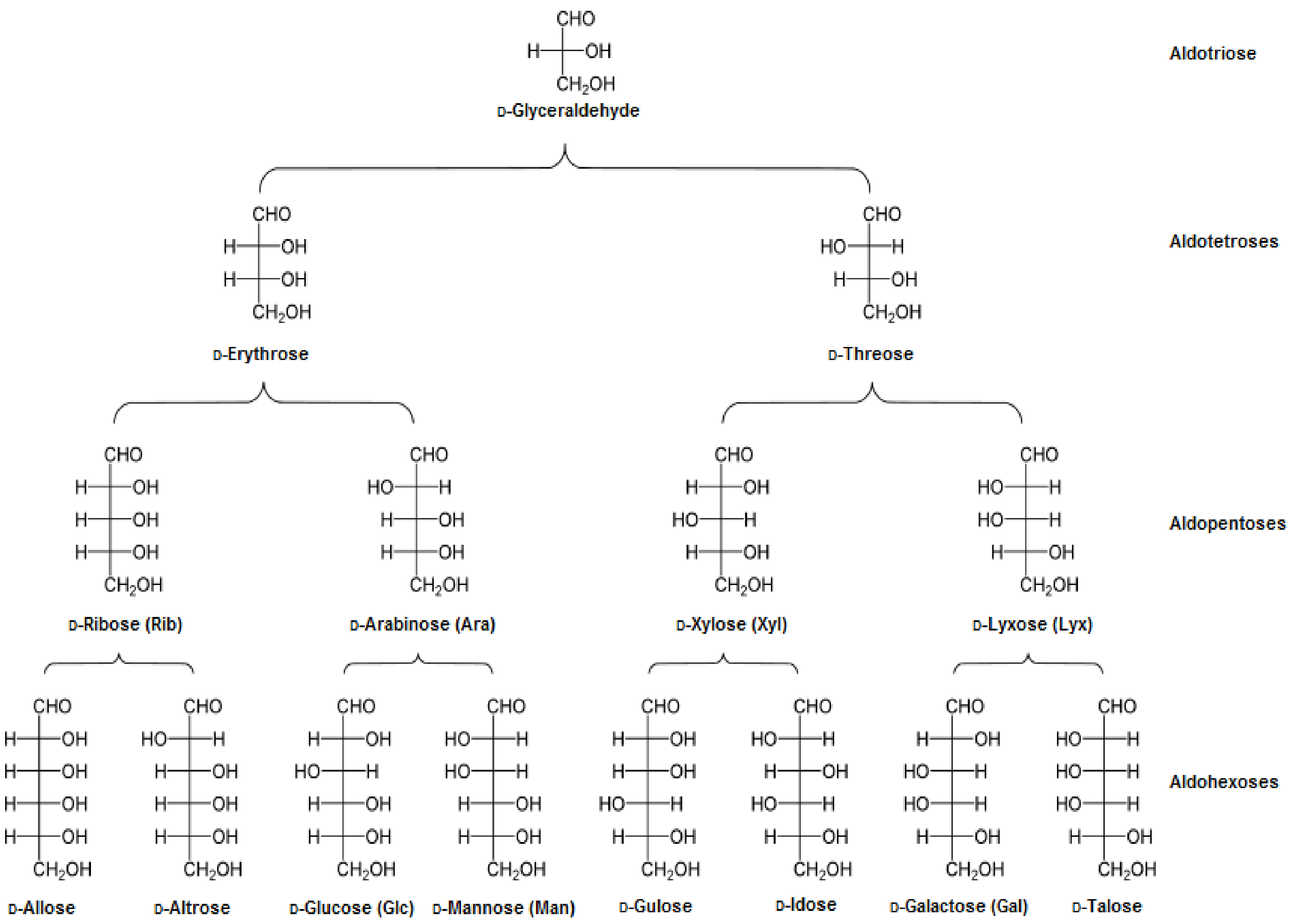

Figure (1.3): Fischer projection formulas and names of the D-aldoses. Note: the L-aldoses are simply the mirror images of these D-aldoses.

D-Glucose is the only aldose that commonly occurs in nature as a monosaccharide; however, it and several other monosaccharides including D-glyceraldehyde, D-ribose, D-mannose, and D-galactose are important components of larger biological molecules. L-sugars are biologically much less abundant than D sugars.

The position of their carbonyl group gives ketoses one less chiral center than their isomeric aldoses (e.g., compare D-fructose and D-glucose).Those with their ketone groups at C2 are the most common forms. Figure (1.4) shows structures and names of the D-ketoses.

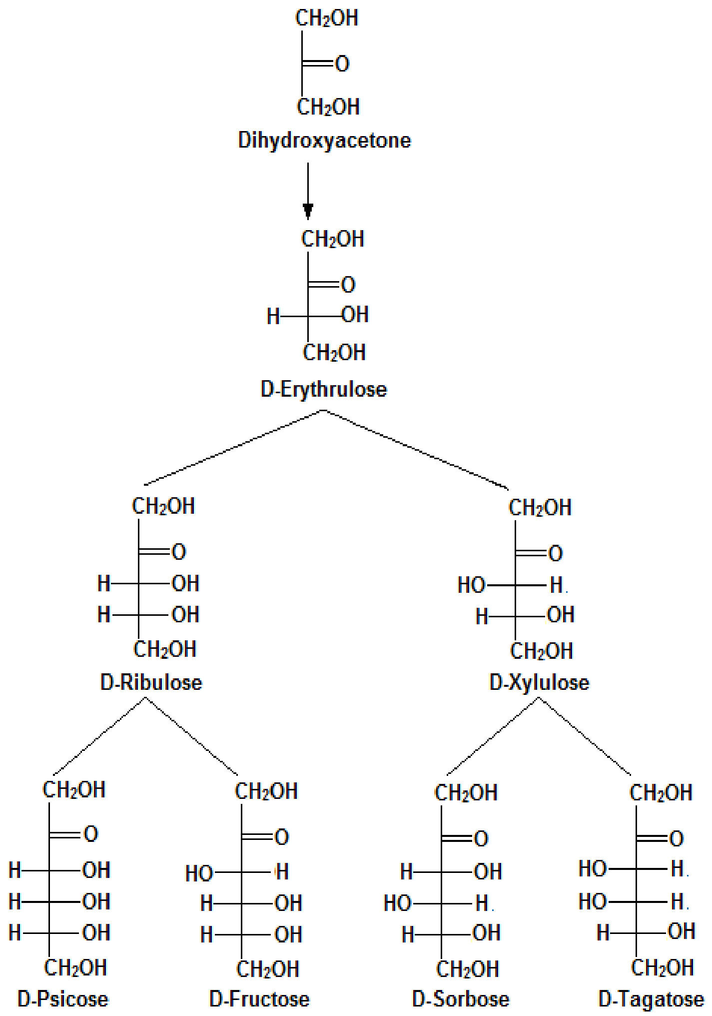

Figure (1.4): Fischer projection formulas and names of the D-ketoses. L-ketoses are the mirror images of them.

Note that some of these ketoses are named by the insertion of -ul- before the suffix -ose in the name of the corresponding aldose; thus D-xylulose is the ketose corresponding to the aldose D-xylose. Dihydroxyacetone, D-fructose, D-ribulose, and D-xylulose are the biologically most prominent ketoses.