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CARBOHYDRATES

Carbohydrates or saccharides (Greek: sakcharon, sugar) are the most abundant biological molecules. They are chemically simpler than nucleotides or amino acids, containing just three elements- carbon, hydrogen and oxygen - combined according to the formula $(C.H_2O)n$, where n is greater than or equal to 3. The basic carbohydrate units are called monosaccharides. There are numerous different types of monosaccharides, which differ in their number of carbon atoms and in the arrangement of the H and O atoms attached to these carbons. Further more monosaccharides can be strung together in almost limitless way to form polysaccharides.

Until the 1960s, carbohydrates were thought to have only passive roles as energy sources(example glucose and starch) and as structural materials (example cellulose). Carbohydrates as we shall see, do not catalyze complex chemical reactions as do proteins, nor do carbohydrates replicate themselves as do nucleic acids. And because polysaccharides are not built according to a genetic ''blueprint'', as are nucleic acids and proteins they tend to be much more heterogeneous - both in size and in composition- than other biological molecules. However, in has become clear that the innate structural variation in carbohydrates is fundamental to their biological activity. The apparently haphazard arrangements of carbohydrates on proteins and on the surfaces of cells are the key to many recognitions events between proteins and between cells. An understanding of carbohydrates structure, from the simplest monosaccharides to the most complex branch polysaccharides, is essential for appreciating the varied functions of carbohydrates in biological system.

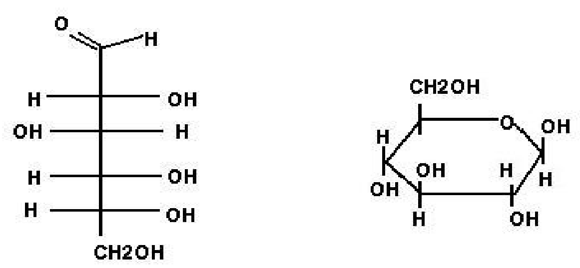
Monosaccharides

Monosaccharides, or simple sugars, are synthesized from smaller precursors that are ultimately derived from CO_2 and H_2O by photosynthesis.

Classification of monosaccharides

Monosaccharides are aldehyde or ketone derivatives of straight chain polyhydroxy alcohol containing at least three carbon atoms. They are classified according to the chemical nature of their carbonyl group and the number of their carbon atoms. If the carbonyl group is an aldehyde, the sugar is an aldose. If the carbonyl a group is a ketone, the sugar is a ketose. The smallest monosaccharides, those with 3 carbon atoms are trioses, those with four, five, six, seven, etc. carbon atoms are, respectively, tetroses, pentoses, hexoses, heptoses, etc.

The aldohexose D- glucose has the formula $(C.H_2O)_6$.

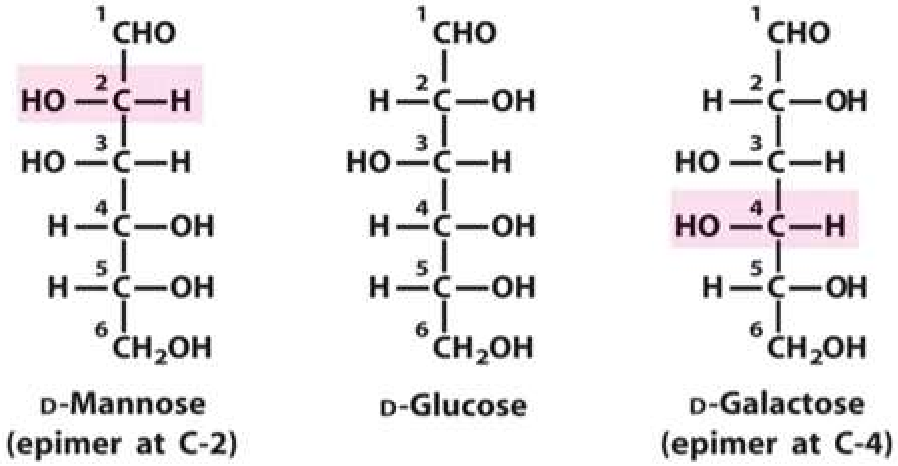


Fischer projection

Haworth Projection

D- Glucose

All but two of its six C atoms, C1 and C6, are chiral centers, so D- glucose is one of 2^4 = 16 possible stereoisomers. D-sugars have the same absolute configuration at the asymmetric center farthest this from their carbonyl group as does D-glyceraldehyde. The L sugars are the mirror images of their D counterparts. Sugars that differ only by the configuration around one C atom are known as epimers of one another. Thus, D- glucose and D-mannose are epimers with respect to C2.

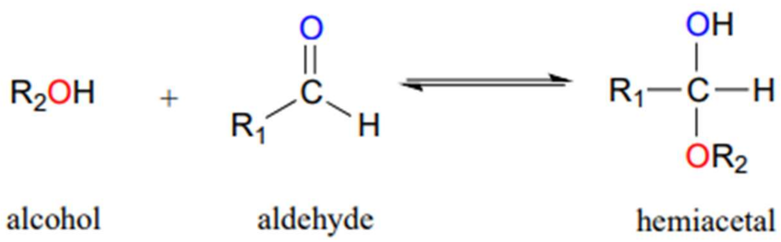


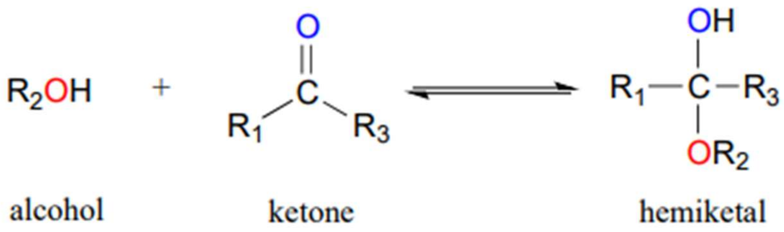
The most common ketoses are those with their ketone function at C_2. The position of their carbonyl group gives ketoses one less as asymmetric center than their isomeric aldoses, so a ketohexose has only 2^3=8 possible stereoisomers (4 D sugars and 4 L sugars).

Because L sugars are biologically much less abundant than D sugars, the D prefix is often omitted. The most important monosaccharides are the aldoses glyceraldehyde, ribose, glucose, mannose and galactose, and the ketoses dihydroxyacetone, ribulose and fructose.

Configuration and conformation

Alcohols react with the carbonyl groups of aldehydes and ketones to form hemiacetals and hemiketal respectively.

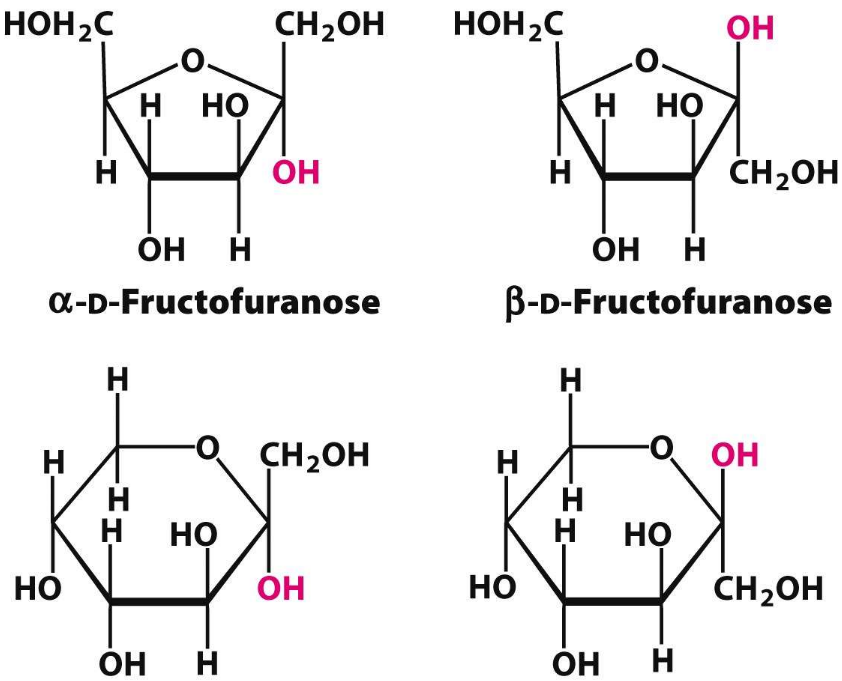




The hydroxyl and either the aldehyde or the ketone functions of monosaccharides can likewise react intramolecularly to form cyclic hemiacetals and hemiketals. The configurations of the substituents of each carbon atom in these sugar rings are conveniently represented by their Haworth projections, in which the darker ring bonds project in front of the plane of the paper and the lighter ring bonds project behind it.

A sugar with a six membered ring is known as a pyranose in analogy with pyran, the simplest compound containing such a ring. Similarly sugars with five membered rings are designated fuel furanoses in analogue with furan.

The cyclic forms of glucose and fructose with 6 and 5 membered rings are therefore known as glucopyranose and fructofuranose respectively.



α-D-Fructofuranose β-D-Fructofuranose

α-D-Fructopyranose β-D-Fructopyranose

Fig
Bio
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Cyclic sugars have two anomeric forms

When a monosaccharide cyclizes, the carbonyl carbon, called the anomeric carbon, becomes a chiral center with two possible configurations. The pair of stereoisomers that differ in configuration at the anomeric carbon are called anomers. In the α anomer, the OH substituent of the anomeric carbon is on the opposite side of the sugar ring from the CH_2OH group at the chiral center that designates the D or L configuration. The other anomer is known as the β form. The two anomers of D-glucose have slightly different physical and chemical properties, including different optical rotations. The anomers freely inter convert in aqueous solution, so at equilibrium, D-glucose is a mixture of the β anomer(63.6%) and the α anomer(36.4%). The linear form is normally present in only minute amounts.

A monosaccharide can readily shift its confirmation, because no bonds are broken in the process. The shift in configuration between the alpha and beta anomeric forms or between the pyranose and furanose forms, which requires breaking and re-forming bonds, occurs slowly in aqueous solution. Other changes in configuration, such as epimerization, do not occur under physiological conditions without appropriate enzymes.

Reference:

Voet,D.Voet,J,D.Pratt,C.W. Fundamentals of Biochemistry.1998.Von Hoffmann Press.