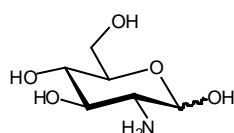


Structure of saccharides

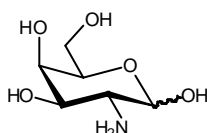
Modified Monosaccharides

Standard monosaccharides are widely distributed in nature and easily obtained by degradation of polysaccharides or isolation from various materials for example plants, microorganisms, yeast, marine sources or milk.

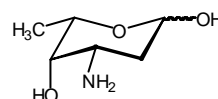
However, the structures of many sugars which are known today are different from the general formula $C_n(H_2O)_n$. They are modified by amino groups or deoxygenation to name but a few. Many of them have been given trivial names as they are frequently found as constituents of different classes of biologically active compounds such as hormones, alkaloids, antibiotics, or cardiac glycosides.



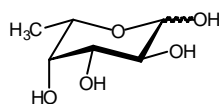
Glucosamine
(2-Amino-2-deoxy-D-glucopyranose)



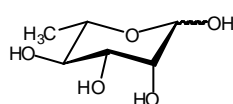
Galactosamine
(2-Amino-2-deoxy-D-galactopyranose)



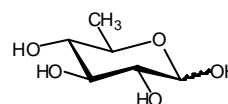
Daunosamine
(3-Amino-2,3,6-trideoxy-
L-lyxo-hexopyranose)



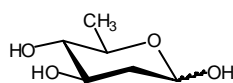
L-Fucose
(6-Deoxy-L-galactopyranose)



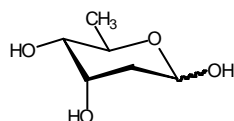
L-Rhamnose
(6-Deoxy-L-mannopyranose)



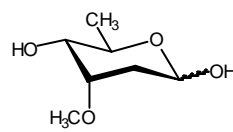
Quinovose
(6-Deoxy-D-glucopyranose)



Olivose
(2,6-Dideoxy-
D-arabino-hexopyranose)



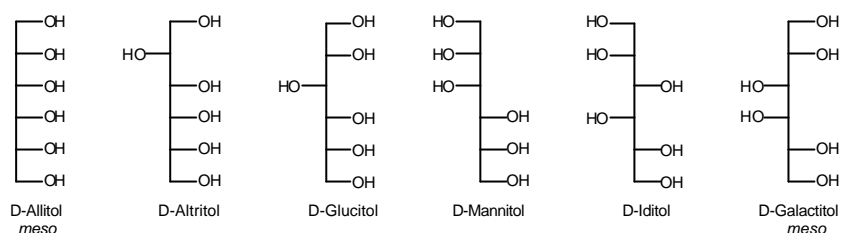
Digitoxose
(2,6-Dideoxy-
D-ribo-hexopyranose)



Cymarose
(2,6-Dideoxy-3-O-methyl-
D-ribo-hexopyranose)

Alditols

Mild reduction of aldoses and ketoses with, for example, sodium boronate leads to sugar alcohols which are called alditols. Like the corresponding monosaccharides they are named according to the number of carbon atoms, as pentitols and hexitols, for example. Whereas in the reduction of aldoses only one product is obtained, reduction of ketoses leads to two diastereomers.

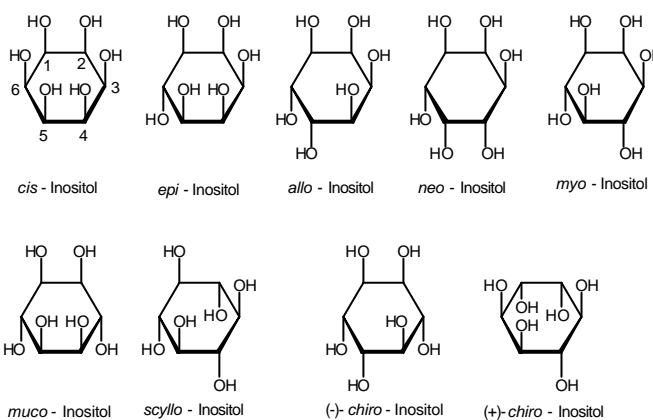


The six diastereomeric D-alditols derived from aldohexoses or aldoketoses, respectively.

Cyclitols

Cyclitols as cyclic polyhydroxyalkanes have a lot in common with monosaccharides and are often used in carbohydrate chemistry. Of the cyclitols the hexahydroxycyclohexanes are called inositols and are best known. All nine possible stereoisomers have been prepared. *myo*-Inositol is often simply referred to as inositol. It occurs widely in nature, particularly as a phosphate ester.

Closely related to the inositols are the carbosugars which were previously known as pseudo-sugars. They differ from normal sugars in the replacement of the ring oxygen atom with a methylene group.



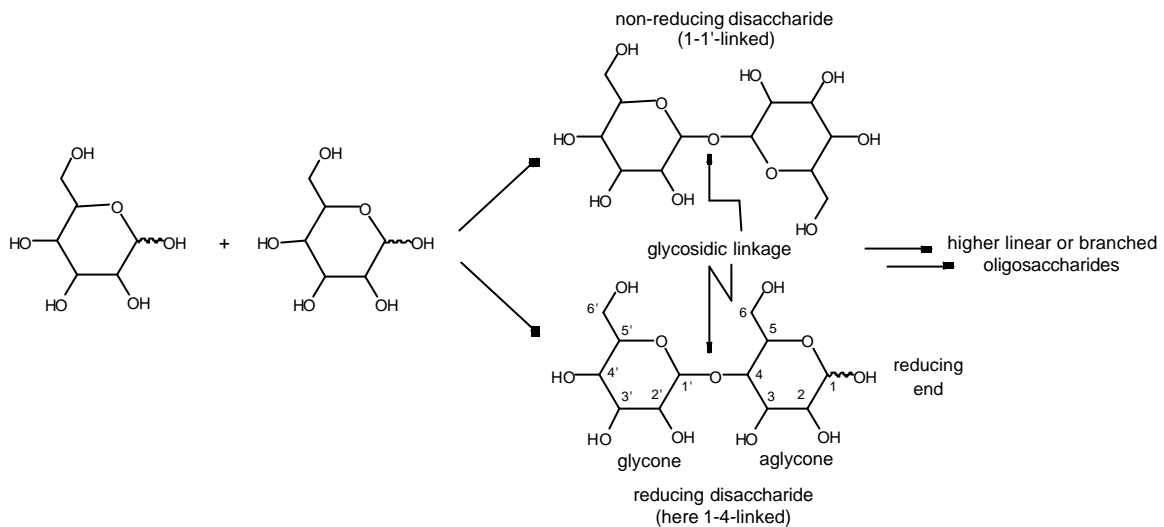
Structures of all nine stereoisomeric inositols; only the *chiro*-inositols are chiral, the other stereoisomers are *meso* forms. All inositols are numbered as indicated for *cis*-inositol.

Modification of a hydroxyl group or its replacement by another function is envisaged as substitution. The stereochemistry at the carbon atom carrying the new substituent is expressed as before with the substituent regarded as equivalent to OH. The substituted position is indicated as 'deoxy-(substituent-prefix)' in the name of the derivative preceded by the position of the modification, e.g. 4-deoxy-4-methyl or 3-bromo-3-deoxy.

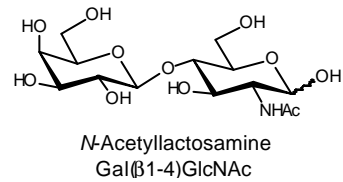
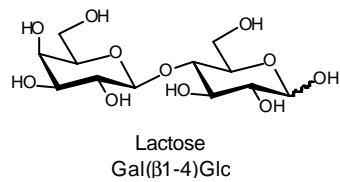
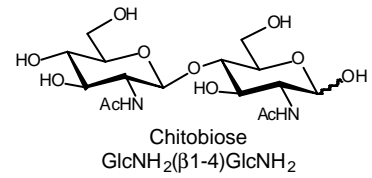
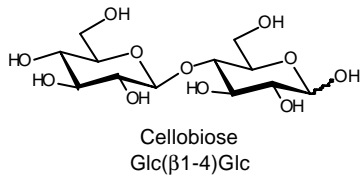
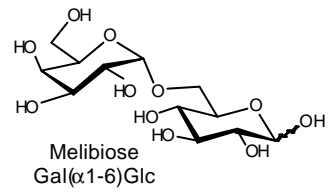
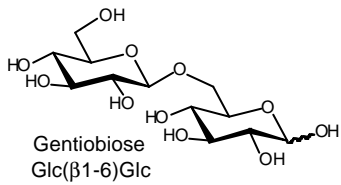
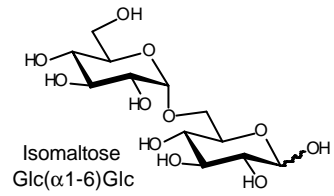
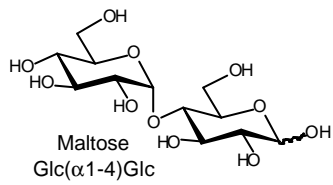
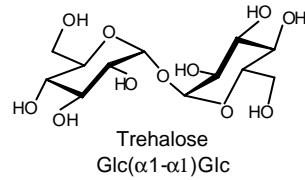
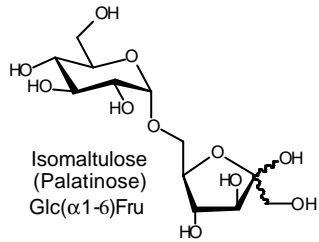
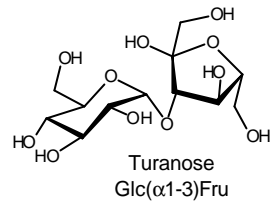
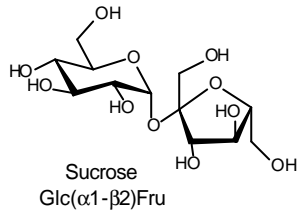
For assigning the configurational symbols D and L, the configuration at the highest-numbered center of chirality is used. This stereogenic carbon atom is called the 'configurational atom'. To specify the anomeric configuration an 'anomeric reference atom' is used.

Structure of simple oligosaccharides

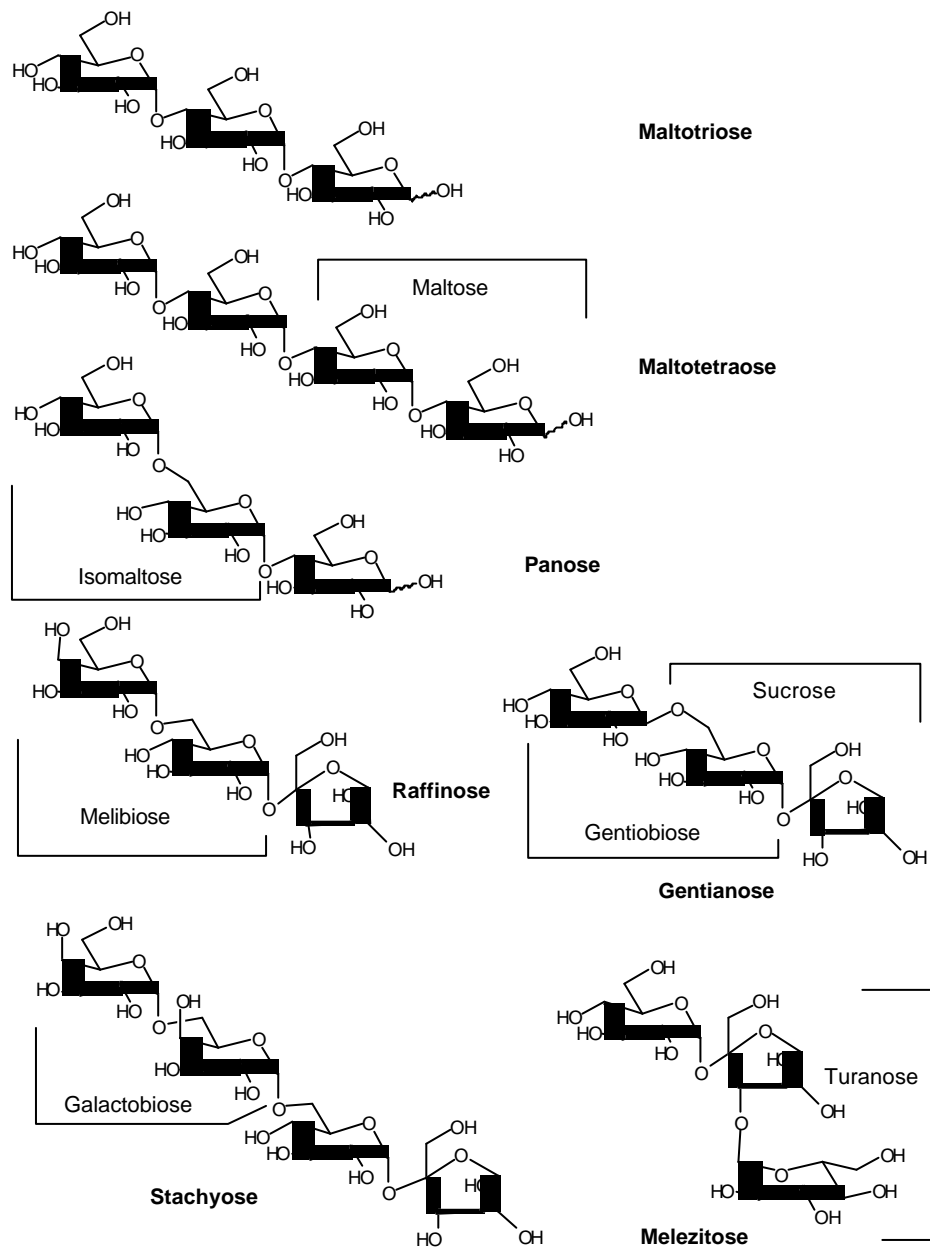
When a free, so-called reducing monosaccharide, which resembles a cyclic hemiacetal in its cyclic form, reacts with another monosaccharide under acid catalysis a mixed acetal is formed, which is generally called a glycoside and named a disaccharide in the simplest case. The bond between the two components of the acetal is called the glycosidic bond. Thus, monosaccharides can react as monomers to form oligo- and polymers, called oligosaccharides and polysaccharides, respectively. Indeed, most carbohydrates do occur as oligo- and polysaccharides, rather than as monosaccharides.



Linking monosaccharides via glycosidic bonds leads to the formation of oligosaccharides, which may be linear or branched, reducing or non-reducing. The moiety at the reducing end is called the aglycone, the remaining oligosaccharide portion the glycone part. Numbering of oligosaccharide carbon atoms use numbers 1 to 6 for the reducing end residues and primed and double-primed numbers, respectively, for the glycone constituents. Though even triple-priming is used for higher oligosaccharides an individual solution is often sought for labeling of the atoms of complex products.



Structures and trivial names of the most common disaccharides.



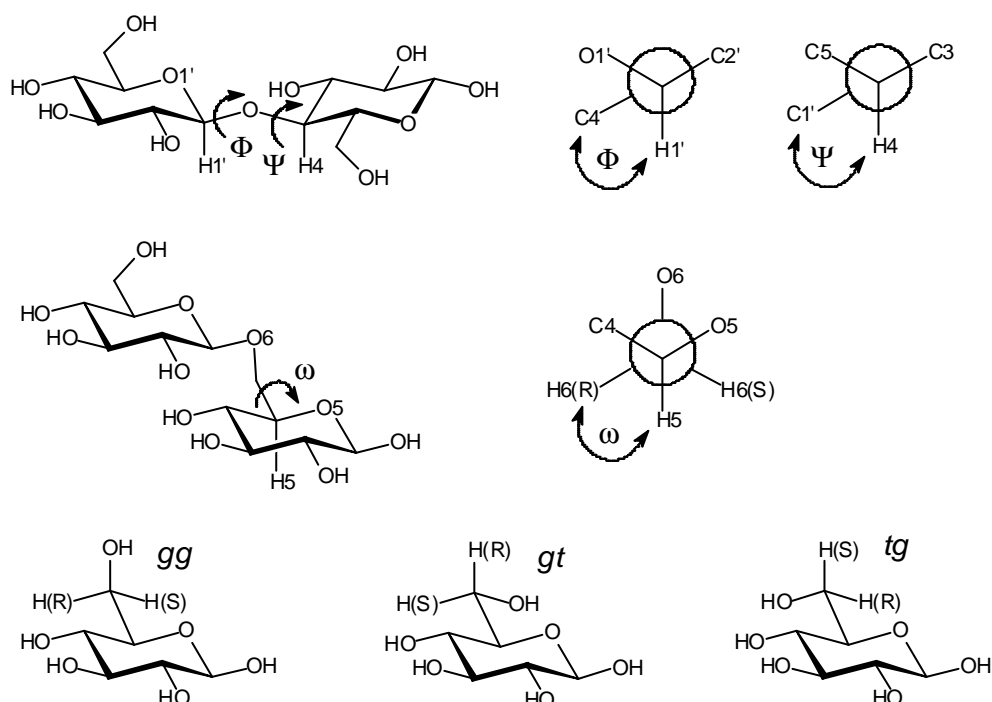
Structures and trivial names of common oligosaccharides found in nature. Names of disaccharide sub-structures are also indicated.

Conformational properties of oligosaccharides

The three-dimensional properties of oligosaccharides are of particular importance in the biochemical context of molecular recognition processes in which carbohydrates are involved. When investigating the shapes of oligosaccharides their energy minimum conformations, both in free and in receptor-bound form have to be addressed, as well as the molecular dynamics of the respective molecules, i.e. are they flexible or rather rigid structures and in which conformational variability do they occur?

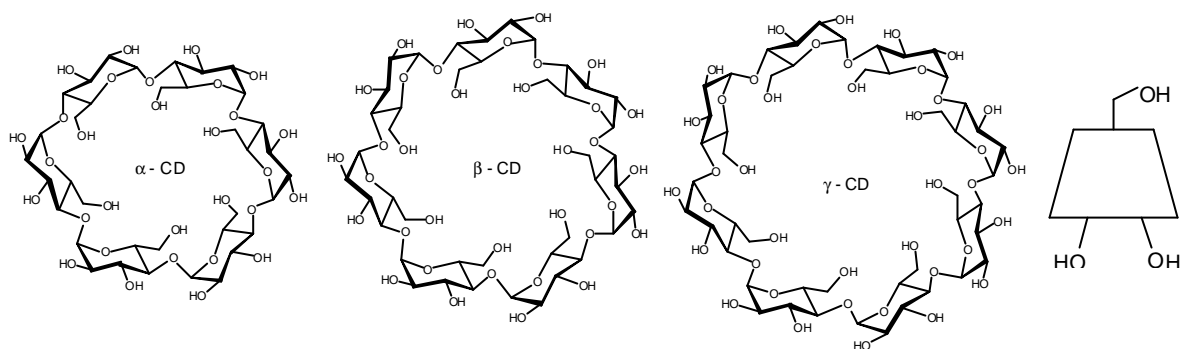
In the case of crystalline carbohydrates their three-dimensional structure can be determined by X-ray analysis; for the study of saccharide conformations in solution, NMR experiments on the one hand and theoretical, computer-assisted methods, called molecular modeling, on the other are valuable tools.

For defining oligosaccharide conformations, which are mainly governed by the spatial disposition of the involved glycosidic linkages, a nomenclature was defined using dihedral angles at or close to the respective glycosidic linkage. The two dihedral angles Φ (phi) and Ψ (psi) are used to assign the stereochemistry of a glycosidic link in cases where two secondary alcohols are encountered, i.e. 1→1, 1→2, 1→3, or 1→4 linkages in hexopyranoses. The Φ angle is defined by the H1'-C1'-O-C(aglycone) fragment, Ψ is given by the arrangement of the C1'-O-C(aglycone)-H(aglycone) fragment. In the case of a 1→6 bond the additional degree of freedom is described by the ω (omega) angle, which is defined by the atoms O6-C6-C5-O5. The three most common conformations of the C5-C6 fragment are the staggered conformations which are termed *gg* (*gauche-gauche*), *gt* (*gauche-trans*), and *tg* (*trans-gauche*).



Cyclodextrins

Cyclodextrins are cyclic oligosaccharides, where monosaccharide units form a ring resulting in intersaccharide α -1,4-glycosidic bonds. They are readily available from starch by large scale preparation using cyclodextrin glucotransferases (CGTases), amylolytic enzymes produced by *Bacillus macerans* and other bacterial microorganisms. By this enzymatic procedure a mixture of cyclodextrins is obtained which can be separated by chromatography or fractionated crystallization. The most common and commercially available cyclodextrins are those consisting of six, seven and eight glucose moieties, which are called α -, β -, and γ -cyclodextrin (also cyclohexaamylose, cycloheptaamylose and cyclooctaamylose) according to a special nomenclature that this rather unique class of molecules has acquired.



Structures of α -, β -, and γ -cyclodextrin together with a common used abbreviation cartoon which also symbolizes the conical shape of cyclodextrin