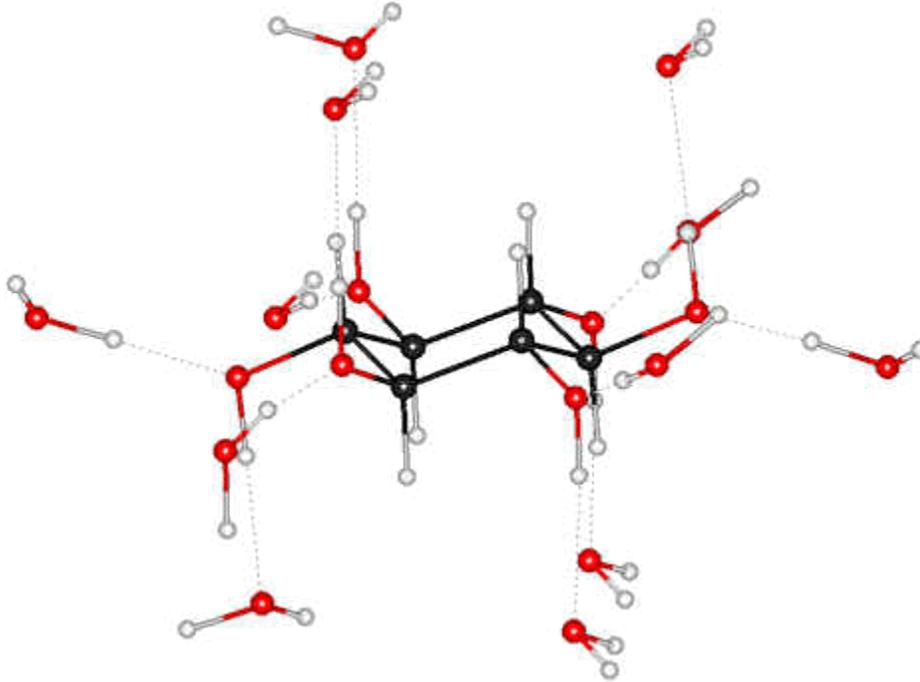


Sugar Hydration

Sugar hydration depends upon the balance between intra-molecular hydrogen bonding and hydrogen bonding to water. This balance involves several layers of hydrating water molecules. A recent modeling study has characterized the hydration around a number of saccharides [1600].



Some sugar molecules can fit into a network structure of [icosahedral water clusters](#), with hydrogen bonding, by replacing a [chair-form water hexamer](#) in a cluster. Equatorial alcoholic oxygen atoms may be placed in similar positions to the oxygen atoms of the water molecules. Thus, in the case of scyllo-inositol^a which has six such oxygen atoms, each hydroxyl group can both donate and accept a hydrogen bond, as shown above where the remaining water molecules have been removed to clarify the image.

More detailed interactive structures are available ([Jmol](#)). These show how the scyllo-inositol fits into the full network of hydrogen bonding within icosahedral water clusters.

¹⁷O Spin lattice relaxation times have confirmed inositol to have the strongest interaction with water compared with a range of monosaccharides and their reduced polyols [307]. Such interactions ensure that no hydrogen bonds are left 'dangling' in the water cluster.

As the [chair-form water hexamers](#) are the least affected part of the [icosahedral water clusters](#) by the $ES \rightleftharpoons CS$ equilibrium [structural changes](#), sugars may stabilize preferentially either the [ES](#) or [CS](#) hydrogen-bonded network, dependent on their conformation. Equatorial hydroxyl groups on chair-form sugars show stronger interactions [307] as the water molecules are optimally positioned for more extensive and stronger hydrogen bonding. This offers explanation over why the beta anomers of D-xylopyranose and D-glucopyranose predominate in solution in contrast to *ab initio* modeling predictions [324]. The tendency for the scyllo-inositol to stretch the water structure towards [ES](#) is at an energetic cost (particularly of entropy of hydration), however, and this is minimized by reducing its solubility.^b A similar effect can be seen in the low solubility of β -glucans, β -xylans and β -mannans, where the fit of their 1-2, 1-3, 1-4, 2-3, 2-4, and 3-4 O-O distances with that of [ES](#) water neighbors (2.82 Å, 4.60 Å, 5.40 Å, 2.82 Å, 4.60 Å, 2.82 Å, respectively) can be seen below (mean square deviations).^c

| Monosaccharide OH fit with water lattice | | | | | | | |
|--|-----------------|----------------|-----------------|----------------|-----------------|----------------|-----------------|
| β -D-Glc | α -D-Glc | β -D-Man | α -D-Man | β -D-Gal | α -D-Gal | β -D-Xyl | α -D-Xyl |
| 0.02 | 0.16 | 0.03 | 0.29 | 0.18 | 0.17 | 0.02 | 0.17 |

Cooperative intramolecular hydrogen bonding in carbohydrates depends on the equatorial/axial orientation of the hydroxyl groups. Such intramolecular hydrogen bonding reduces the hydration of the carbohydrates, increases their non-polar character and is key to their biological recognition [981]. Simulations of β -D-glucose, β -D-mannose, β -D-galactose and β -D-talose using explicit water molecular dynamics gave generally acceptable structural, dynamical, solvation and energetic agreement with the available experimental data [1216]. First-principles molecular dynamics of glucose in water has shown that each hydroxyl group forms about two hydrogen bonds, forming a weaker acceptor and a stronger donor to water which together fit relatively poorly (if compared with scyllo-inositol) into a locally tetrahedral network [1367].

Reducing sugars undergo mutarotation in solution forming an equilibrium mixture of the α - and β -forms. This mutarotation process is catalyzed by water molecules [1009] and although the equilibrium position is reportedly determined partially by the water clustering there appears no differences in molal volume or specific heats between the anomers [1421]. The structure of reduced carbohydrates (polyols) seem more compatible with that of water when they form planar zigzag structures, such as mannitol but not sorbitol, and where their alcohol groups fit in well with water's second neighbor oxygen distances [1421].

The solubility of carbohydrates in water increase with increasing temperature, but reduce with increasing pressure [1892] .

Footnotes

Although scyllo-inositol is not a monosaccharide sugar, it is used as an example of this type of structure.

A highly stabilized crystal structure also contributes to this low solubility.

Favored intramolecular hydrogen bonding also contributes to the relatively poor hydration of the β -linked sugar residues [791] .

Source: <http://www1.lsbu.ac.uk/water/inos.html>