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Methyl 3-*O*-*β*-L-fucopyranosyl *α*-D-glucopyranoside trihydrate

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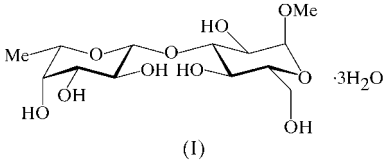
The water content of the title compound, $C_{13}H_{24}O_{10}\cdot 3H_2O$, creates an extensive hydrogen-bonding pattern, with all the hydroxyl groups of the disaccharide acting as hydrogen-bond donors and acceptors. The water molecules are arranged in columns along the crystallographic *b* axis and form, together with one of the hydroxyl groups, infinite hydrogen-bonded chains. The conformation of the disaccharide is described by glycosidic torsion angles of −38 and 18°.

Comment

Carbohydrates are one of the most abundant types of molecules found in nature, and many oligo- and polysaccharides play important roles in biological systems (Varki *et al.*, 1999). To understand the role of carbohydrates better, a detailed knowledge of their three-dimensional structure is required. The X-ray diffraction technique is unsurpassed for studying the three-dimensional structure of molecules, as long as suitable crystals can be grown. However, the growth of such crystals has proven difficult for polyhydroxylated carbohydrates. A recent review (Peréz *et al.*, 2000) states that until the year 2000 only 55 unsubstituted disaccharides had been crystallized and solved by X-ray diffraction, and only two disaccharides containing fucose had been solved (Eriksson *et al.*, 2000; Watt *et al.*, 1996; Allen, 2002). Furthermore, three trisaccharides containing fucose were found in the Cambridge Strutural Database (Allen, 2002).



(I)

The conformation of the title disaccharide, (I), is described by the two torsion angles around the glycosidic linkage, φ_H (defined by H1*f*—C1*f*—O3*g*—C3*g*) and ψ_H (defined by C1*f*—O3*g*—C3*g*—H3*g*), where *f* and *g* denote the fucosyl and glucosyl residues, respectively (Fig. 1). The value of the φ_H torsion angle is governed mainly by the exoanomeric effect, which predicts that a *β*-L sugar should have a φ_H angle of ∼−60°. The ψ_H torsion angle is set by steric interactions and is generally between −60 and 60°. For (I), φ_H is −37.7° and ψ_H is 18.2°, and thus the glycosidic torsion angles are found in the expected regions. Selected torsion angles are given in Table 1. A grid search using a simplified molecular-mechanics potential energy function found the global minimum at angles of $\varphi_H = -55°$ and $\psi_H = -5°$ (Baumann *et al.*, 1991). This conformation differs from that found in the crystalline state by ∼20° at each of the glycosidic torsion angles. The exocyclic torsion angle for the glucose residue has an angle ω_g (defined by O5*g*—C5*g*—C6*g*—O6*g*) of −66.4 (2)°, which describes a *gauche–gauche* conformation. The bond angle at the glycosidic

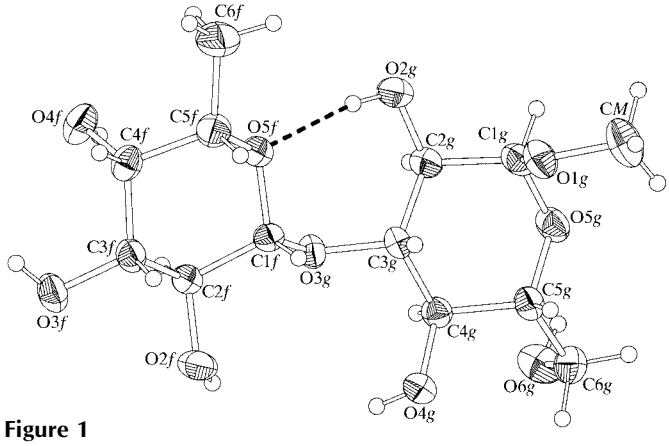


Figure 1
The molecular structure of (I), showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level. H atoms are drawn as small spheres of arbitrary radii. An internal hydrogen bond, O2*g*—HO2*g*···O5*f*, is also shown (dashed line). The water molecules have been omitted.

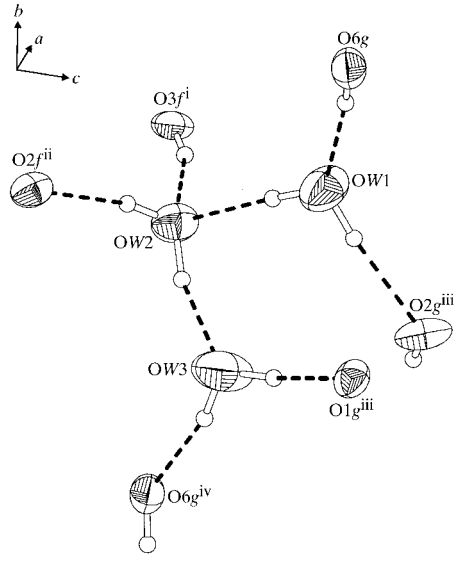


Figure 2
A view of the hydrogen-bond scheme for the three water molecules (dashed lines). Some H atoms have been omitted for clarity. [Symmetry codes: (i) $\frac{3}{2}-x, 1-y, -\frac{1}{2}+z$; (ii) $\frac{5}{2}-x, 1-y, -\frac{1}{2}+z$; (iii) $\frac{1}{2}+x, \frac{3}{2}-y, -z$; (iv) $3-x, \frac{1}{2}+y, -\frac{1}{2}-z$.]

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linkage τ (defined by C1*f*—O3*g*—C3*g*) is 116.2 (2)°. The calculated Cremer & Pople (1975) puckering parameters show that both pyranose rings in (I) are in the expected chair conformations, *i.e.* $^1C_4$ for the fucosyl ring [Q = 0.583 (2) Å, θ = 172.6 (2)° and φ = 145 (2)°] and $^4C_1$ for the glucose ring [Q = 0.578 (2) Å, θ = 4.9 (2)° and φ = 135 (2)°]. The mean C—C bond length is 1.53 Å, which agrees with the average bond length reported for carbohydrates (Peréz *et al.*, 2000). The main packing feature in the structure is the hydrogen-bond network, where the water molecules give rise to a complex hydrogen-bonding scheme (see Table 2). An intramolecular hydrogen bond, O2*g*—HO2*g*···O5*f*, is observed over the glycosidic linkage.

From an NMR study of (I) in water and acetone (85:15), obtained at 265 K, it was concluded that a weak hydrogen bond is present between the two above-mentioned atoms. This conclusion was based on a large negative chemical shift difference, a small value of the J coupling and a high temperature coefficient for HO2*g* (Ivarsson *et al.*, 2000).

There are 11 intermolecular hydrogen bonds in the range 2.68–3.07 Å. All the hydroxyl groups act as hydrogen-bond donors, either to other hydroxyl groups or to water molecules. The water molecules are grouped together in a channel through the structure along the crystallographic *b* axis and form an infinite hydrogen-bonded chain, as depicted in Fig. 2, where the sequence donor → acceptor is O6*g* → O*W*1 → O*W*2 → O*W*3 → O6*g*^{vi} [symmetry code: (vi) $3-x$, $\frac{1}{2}+y$, $-\frac{1}{2}-z$]. Several more hydrogen-bond clusters and chains are also present.

Experimental

The synthesis of (I) was described by Baumann *et al.* (1991). Crystals suitable for single-crystal X-ray diffraction were grown at 295 K using the sitting-drop technique, in which the solvent was allowed to evaporate. Compound (I) was dissolved in water to a concentration of 375 mg ml^{-1} and mixed with an equal amount of 30% PEG-400 in water at ambient temperature. After approximately one week, the crystals were harvested and mounted in capillaries to avoid the loss of crystal water. Data were collected on beamline I711 at the Swedish synchrotron radiation facility, MAXLAB, Lund.

Crystal data

$C_{13}H_{24}O_{10}\cdot 3H_2O$
M_r = 394.37
Orthorhombic, $P2_12_12_1$
a = 6.8638 (16) Å
b = 15.861 (4) Å
c = 17.014 (7) Å
V = 1852.2 (10) Å^3
Z = 4
D_x = 1.414 Mg m^{-3}
Synchrotron radiation
λ = 0.8720 Å
Cell parameters from 882 reflections
θ = 2.0–32.0°
μ = 0.21 mm^{-1}
T = 293 (2) K
Needle, colourless
0.35 × 0.10 × 0.10 mm

Table 1
Selected torsion angles (°).

H1*f*—C1*f*—O3*g*—C3*g*	−38	O5*g*—C1*g*—O1*g*—C*M*	67.9 (3)
C1*f*—O3*g*—C3*g*—C4*g*	137.58 (18)	C1*f*—O3*g*—C3*g*—H3*g*	18
C3*g*—O3*g*—C1*f*—O5*f*	82.7 (2)	C2*g*—C1*g*—O1*g*—C*M*	−170.1 (2)
C*M*—O1*g*—C1*g*—H1*g*	−53	C1*f*—O3*g*—C3*g*—C2*g*	−103.3 (2)
C3*g*—O3*g*—C1*f*—C2*f*	−158.51 (17)	O5*g*—C5*g*—C6*g*—O6*g*	−66.5 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*g*—HO2*g*···O5*f*	0.82	1.954	2.763 (2)	169
O6*g*—HO6*g*···O*W*1	0.82	1.876	2.689 (3)	171
O4*g*—HO4*g*···O3*f*^{i}	0.82	2.261	3.077 (3)	173
O2*f*—HO2*f*···O3*f*^{i}	0.82	1.985	2.794 (3)	169
O3*f*—HO3*f*···O*W*2^{ii}	0.82	1.983	2.769 (3)	160
O4*f*—HO4*f*···O4*g*^{iii}	0.82	2.043	2.804 (3)	154
O*W*1—H1*W*1···O*W*2	0.96 (2)	1.89 (2)	2.850 (3)	175 (3)
O*W*1—H2*W*1···O2*g*^{iv}	0.96 (3)	2.00 (3)	2.938 (3)	168 (5)
O*W*2—H1*W*2···O*W*3	0.95 (3)	1.77 (3)	2.687 (4)	160 (3)
O*W*2—H2*W*2···O2*f*^{v}	0.96 (3)	1.98 (3)	2.918 (3)	166 (3)
O*W*3—H1*W*3···O6*g*^{vi}	0.95 (2)	1.79 (2)	2.719 (3)	162 (3)
O*W*3—H2*W*3···O1*g*^{iv}	0.95 (2)	2.24 (4)	3.054 (4)	143 (4)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, -z$; (ii) $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$; (iii) $x-1, y, z$; (iv) $\frac{1}{2}+x, \frac{3}{2}-y, -z$; (v) $\frac{5}{2}-x, 1-y, z-\frac{1}{2}$; (vi) $3-x, \frac{1}{2}+y, -\frac{1}{2}-z$.

Data collection

MAR CCD area-detector diffractometer
Area-detector φ scans
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1997)
T_{min} = 0.93, T_{max} = 0.98
25 554 measured reflections
2062 independent reflections
1811 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 32.4°
$h = -8 \rightarrow 8$
$k = -19 \rightarrow 19$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.087
S = 1.56
2062 reflections
259 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

The water H atoms were located from difference electron-density maps, while the H atoms of the carbohydrate molecule were positioned geometrically. Restraints were applied to bond lengths and to the distances between the H atoms of the water molecules, to stabilize the structure during refinement. The O—H distance was set at 0.82 Å, while the C—H distances were set at 0.98, 0.97 and 0.96 Å for the CH, CH_2 and CH_3 groups, respectively. All non-H atoms were refined with anisotropic displacement parameters, employing a rigid-bond restraint to U_{ij} of the two bonded atoms (Rollett, 1970). The H atoms were allowed to ride on the coordinates of their parent atoms during the least-squares refinement. The U_{iso}(H) values were taken as 1.5U_{eq}(C,O) for the methyl and hydroxyl groups and as 1.2U_{eq}(C) for all other atoms. The H atoms of the hydroxyl groups were allowed to rotate around the *X*—C—O—H torsion angle during the refinement by means of the AFIX 147 instruction available in *SHELXL*97 (Sheldrick, 1997).

The absolute configuration of (I) is set by the components of the synthesis. As the value of the Flack (1983) parameter that was initially calculated was meaningless, the Friedel equivalents (1497) were included in the merging process (MERG 3 in *SHELXL*97).

Data collection: *MARCCD* (MAR, 2002); cell refinement: *TWINSOLVE* (Svensson, 2002); data reduction: *TWINSOLVE*; program(s) used to solve structure: *SHELXD* (Sheldrick & Schneider, 2001); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1049). Services for accessing these data are described at the back of the journal.

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