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Methyl 2-*O*-β-D-glucopyranosyl-α-L-rhamnopyranoside

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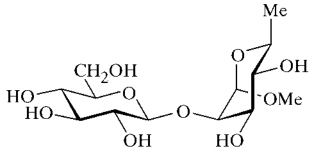
The overall conformation of the title compound, $C_{13}H_{24}O_{10}$, is described by the glycosidic torsion angles φ_H ($H1_g—C1_g—O2_r—C2_r$) and ψ_H ($C1_g—O2_r—C2_r—H2_r$), which have values of 13.6 and 16.1°, respectively. The former is significantly different from the value predicted by consideration of the *exo*-anomeric effect ($\varphi_H \sim 60°$) and from that in solution ($\varphi_H \sim 50°$), as determined previously by NMR spectroscopy. An intramolecular $O3_r—H\cdots O2_g$ hydrogen bond may help to stabilize the conformation in the solid state. The orientation of the hydroxymethyl group of the glucose residue is *gauche–gauche*, with a torsion angle ω ($O5_g—C5_g—C6_g—O6_g$) of $-70.4\,(4)°$. Both pyranose rings are in their expected chair conformations, *i.e.* $^4C_1$ for D-glucose and $^1C_4$ for L-rhamnose.

Comment

Oligo- and polysaccharides have many important roles in biological systems (Varki, 1993). Many of their effects are mediated by interaction with other biomolecules, in particular proteins such as antibodies and lectins. An understanding of these interactions on a molecular level requires a detailed knowledge of the conformational preferences of carbohydrates, as well as those of proteins. At present, most of our knowledge of carbohydrate conformation is derived from NMR spectroscopy, but the information is scarce and often difficult to interpret. It is therefore important to obtain further data using other experimental techniques.

Whilst methyl 2-*O*-β-D-glucopyranosyl-α-L-rhamnopyranoside, (I), does not occur naturally, there are several bacterial polysaccharides and saponins that contain a 2-*O*-β-D-glucopyranosyl-α-L-rhamnopyranosyl fragment (Doubet & Albersheim, 1992), and which are likely to display conformational similarities to (I).

The solution conformation of (I) has been determined from ^1H–^1H NOE (nuclear Overhauser effect) and $^3J_{C,H}$ measurements, and compared with the results of *in vacuo* molecular modelling (Mamyan *et al.*, 1988). The computed lowest-energy conformation differs from the crystal structure and has $\varphi_H \sim 50°$ and $\psi_H \sim 20°$. Thus, the difference in φ_H is more than 30°, despite the fact that this torsion angle is considered to be more restricted than ψ_H because the *exo*-anomeric effect stabilizes the conformation with φ_H at around 60° (Thøgersen *et al.*, 1982). A comparison with the reported $^3J_{C,H}$ and ^1H–^1H NOE values shows that, in solution, (I) is much more similar to the calculated structure than the conformation found here for the solid state.



(I)

The calculated Cremer & Pople (1975) puckering parameters show that both pyranose rings in (I) are in the expected chair conformations, $^1C_4$ for the rhamnose ring [Q = 0.598 (4) Å, θ = 175.7 (4)° and φ = 75 (4)°] and $^4C_1$ for the glucose ring [Q = 0.615 (4) Å, θ = 6.3 (4)° and φ = 98 (3)°].

Four distinct hydrogen-bond systems can be deduced from the structural model. The donor–acceptor sequence for the first infinite chain along the b axis is composed of $O3_r^i—H\cdots O2_g^i—H\cdots O3_r^{ii}—H\cdots O2_g^{ii}—H\cdots O3_r^{iii}—H\cdots$ *etc.* along the b axis, where the subscripts r and g denote the rhamnose and glucose residues, respectively [symmetry codes: (i) x, y, z; (ii) $-x, \frac{1}{2}+y, 1-z$; (iii) $x, 1+y, z$]. This first hydrogen-bonded chain (Fig. 2) contains an intramolecular hydrogen bond, $O3_r—H\cdots O2_g$; otherwise, all the hydrogen bonds are intermolecular. Secondly, there is a ladder-like structure of hydrogen bonds along the b direction made up of two distinct bonds, $O6_g^i—H\cdots O5_r^{iv}$ and $O6_g^{iv}—H\cdots O5_r^{iii}$ *etc.* [symmetry code: (iv) $1-x, \frac{1}{2}+y, 2-z$]. The third hydrogen-bonded chain is a three-edged graph connected to atom $O3_r$ of the first chain and is composed of $O3_g^i—H\cdots O4_r^{ii}—H\cdots O4_g^v—H\cdots O3_r^i—H$ [symmetry code: (v) $1-x, y-\frac{1}{2}, 1-z$]. These hydrogen bonds link molecules of (I) to form sheets in the ab plane. These sheets are further linked to each other through the fourth hydrogen bond connection, $O6_g^i—H\cdots O5_r^{iv}—H$.

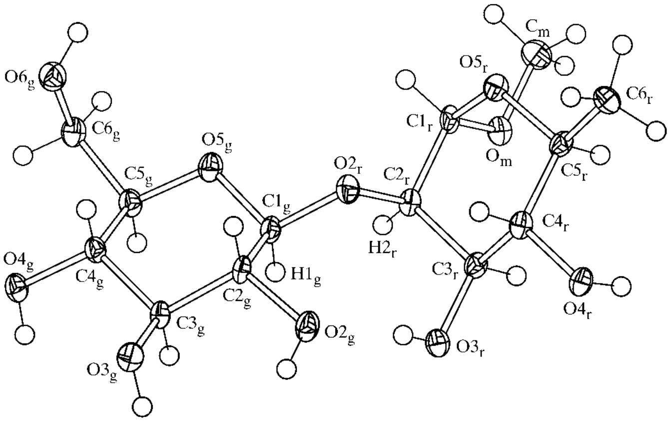


Figure 1
A view of the molecular structure of (I) showing the atom-labelling scheme and 50% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii.

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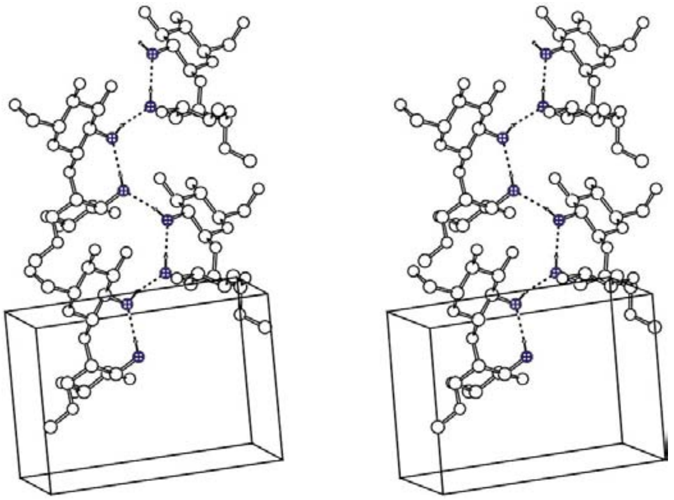

Figure 2
A stereoview of the infinite hydrogen-bond chain along the *b* axis, $\mathrm{O3_r}^{\mathrm{i}}$—H···$\mathrm{O2_g^i}$—H···$\mathrm{O3_r^{ii}}$—H···$\mathrm{O2_g^{ii}}$—H···$\mathrm{O3_r^{iii}}$—H [symmetry codes: (i) *x*, *y*, *z*; (ii) $-x, \frac{1}{2} + y, 1 - z$; (iii) $x, 1 + y, z$].

Table 1
Selected geometric parameters (Å, °).

$\mathrm{C1_r—O_m}$	1.385 (5)	$\mathrm{O2_r—C1_g}$	1.409 (4)
$\mathrm{C2_r—O2_r}$	1.445 (4)		
$\mathrm{C1_g—O2_r—C2_r}$	116.0 (3)	$\mathrm{C3_r—O3_r—HO3_r}$	110 (3)
$\mathrm{C1_r—C2_r—O2_r—C1_g}$	135.4 (3)	$\mathrm{O5_g—C5_g—C6_g—O6_g}$	−70.4 (4)
$\mathrm{C3_r—C2_r—O2_r—C1_g}$	−103.5 (3)	$\mathrm{C2_r—O2_r—C1_g—H1_g}$	13.6
$\mathrm{C2_r—O2_r—C1_g—O5_g}$	−107.0 (3)	$\mathrm{H2_r—C2_r—O2_r—C1_g}$	16.1
$\mathrm{C2_r—O2_r—C1_g—C2_g}$	135.9 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
$\mathrm{O3_r—HO3_r\cdots O2_g}$	0.820 (10)	1.892 (10)	2.700 (4)	168 (4)
$\mathrm{O4_r—HO4_r\cdots O4_g^{i}}$	0.82	1.952	2.768 (4)	173
$\mathrm{O2_g—HO2_g\cdots O3_r^{ii}}$	0.82	2.115	2.772 (4)	137
$\mathrm{O3_g—HO3_g\cdots O4_r^{ii}}$	0.82	2.095	2.840 (4)	151
$\mathrm{O4_g—HO4_g\cdots O3_r^{iii}}$	0.82	2.081	2.806 (4)	147
$\mathrm{O6_g—HO6_g\cdots O5_r^{iv}}$	0.82	2.056	2.862 (4)	168

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

Experimental

The synthesis of (I) has been described by Jansson *et al.* (1990). Crystals of (I) were obtained by slow evaporation at ambient temperature from a solution of the disaccharide in methanol–water.

Crystal data

$C_{13}H_{24}O_{10}$
$M_r = 340.32$
Monoclinic, $P2_1$
$a = 7.180$ (4) Å
$b = 8.430$ (5) Å
$c = 12.688$ (10) Å
$\beta = 101.46$ (8)°
$V = 752.6$ (8) Å^3
$Z = 2$

$D_x = 1.502$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 628 reflections
$\theta = 2.5$–$26.0°$
$\mu = 0.13$ mm^{-1}
$T = 293$ (2) K
Thin prismatic flake, colourless
0.12 × 0.08 × 0.03 mm

Data collection

Stoe IPDS image-plate diffractometer
Area-detector scans
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1997)
$T_{\min} = 0.97$, $T_{\max} = 0.99$
11 346 measured reflections

1542 independent reflections
1251 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.071$
$\theta_{\max} = 25.8°$
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.087$
$S = 1.07$
1542 reflections
219 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.022 (5)

The absolute configuration of the molecule cannot be deduced from the diffraction data collected in this experiment. It can, however, be assigned from the known absolute configuration of the reactants. The O—H distances were set at 0.82 Å, while the C—H distances were set at 0.98, 0.97 and 0.96 Å for CH, CH_2 and CH_3, respectively. One of the H atoms ($\mathrm{HO3_r}$) was refined freely, with an $\mathrm{O3_r—HO3_r}$ distance restraint of 0.82 Å. For methyl and hydroxyl H atoms, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C,O})$, while for other H atoms, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *EXPOSE* in *IPDS* (Stoe & Cie, 1997); cell refinement: *CELL* in *IPDS*; data reduction: *INTEGRATE* in *IPDS*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996) and *SCHAKAL* (Keller, 1992); software used to prepare material for publication: *SHELXL*97 and *PLATON*98 (Spek, 1998).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1489). Services for accessing these data are described at the back of the journal.

References

Bergerhoff, G. (1996). *DIAMOND*. Gerhard-Domagk-Straße 1, 53121 Bonn, Germany.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Doubet, S. & Albersheim, P. (1992). *Glycobiology*, **2**, 505.
Jansson, P. E., Kenne, L. & Ottosson, H. (1990). *J. Chem. Soc. Perkin Trans.* 1, pp. 2011–2018.
Keller, E. (1992). *SCHAKAL*92. University of Freiburg, Germany.
Mamyan, S. S., Lipkind, G. M., Shashkov, A. S., Bairamova, N. E., Nikolaev, A. V. & Kochetkov, N. K. (1988). *Bioorg. Khim.* **14**, 205–215.
Rollett, J. S. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 167–181. Copenhagen: Munksgaard.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1998). *PLATON*98. University of Utrecht, The Netherlands.
Stoe (1997). *IPDS* (Version 2.87) and *X-RED* (Version 1.09). Stoe & Cie, Darmstadt, Germany.
Thøgersen, H., Lemieux, R. U., Bock, K. & Meyer, B. (1982). *Can. J. Chem.* **60**, 44–57.
Varki, A. (1993). *Glycobiology*, **3**, 97–130.