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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1091). Services for accessing these data are described at the back of the journal.

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Methyl 2-*O*-α-D-Mannopyranosyl-β-D-glucopyranoside

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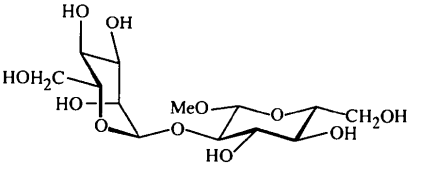
Abstract

The structure of the title compound, $C_{13}H_{24}O_{11}$, has been determined. The torsion angles of the glycosidic linkage connecting the two sugar residues, φ_H (H1′—C1′—O2—C2) and ψ_H (C1′—O2—C2—H2), have values of −62.7 (2)° and −28.6 (2)°, respectively. The conformation in the crystal is similar to that obtained by energy minimization *in vacuo* using the HSEA (hard-sphere *exo*-anomeric) force field. A chain of seven inter-residue hydrogen bonds, involving all possible H-atom donors in the molecule is observed. The chain is terminated by a ring O atom as an acceptor.

Comment

The three-dimensional structure of an oligosaccharide is governed by the glycosidic torsion angles φ_H and ψ_H. Their values determine the overall shape of an oligosaccharide and it is important to have an accurate measurement of these for an understanding of conformational aspects of the glycosidic linkage and for recognition processes between proteins and carbohydrates.

We have determined the crystal structure of methyl 2-*O*-α-D-mannopyranosyl-β-D-glucopyranoside, (I) (Fig. 1). The major degrees of freedom, the glycosidic torsion angles φ_H and ψ_H, and the exocyclic torsion angles for hydroxymethyl groups, ω, show values in the expected regions of conformational space. Thus, for the glycosidic linkage between the two sugar residues, the torsion angles φ_H and ψ_H are −62.7 (2) and −28.6 (2)°, respectively. The φ_H (H1—C1—O1—C7) torsion angle for the glucose residue is 49.7 (2)°. For both φ_H torsion angles, the values are in the conformational region where the *exo*-anomeric effect (Thøgersen, Lemieux, Bock & Meyer, 1982) contributes to energy stabilization.



(I)

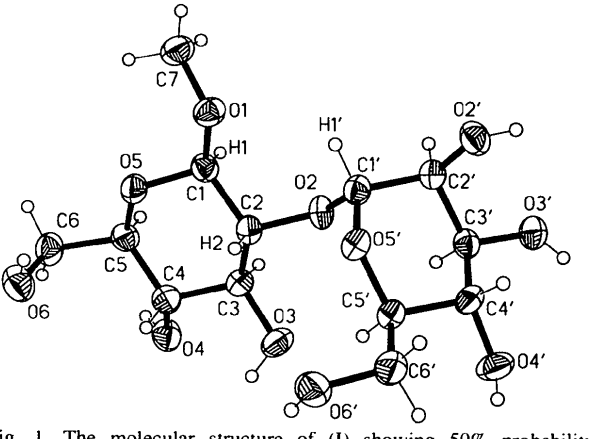


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms are drawn as small circles of arbitrary radii.

The exocyclic torsion angles for the constituent monosaccharides have ω' (O5′—C5′—C6′—O6′) = 63.5 (2)° (*gauche–trans*) for the mannose residue and ω (O5—C5—C6—O6) = −65.2 (2)° (*gauche–gauche*)

for the glucose residue. Both the *gauche* effect (Wolfe, 1972; Wiberg, Murcko, Laidig & MacDougall, 1990) to O5 and the Hassel–Ottar effect (Hassel & Ottar, 1947) to O4 favour the observed conformers.

Energy minimization, using the HSEA force field (Thøgersen *et al.*, 1982), of the disaccharide *in vacuo* on a φ_H/ψ_H grid produced the Ramachandran plot shown in Fig. 2. The geometry of the disaccharide was also optimized using the same force field starting from the crystal structure. The optimized structure *in vacuo* has $\varphi_H = -43$, $\psi_H = -17$ and the φ_H torsion angle for the glucose residue equal to 32°. The difference between these torsion angles in the optimized structure and the corresponding angles in the crystal structure is $\leq 20°$, so we can regard them as being similar, bearing in mind differences between a molecule in a vacuum and the crystalline state. The difference in the potential energy, calculated with the HSEA force field (Thøgersen *et al.*, 1982), of the crystal structure conformation and the global energy minimum is approximately 1.5 kcal mol^{-1}. The conformation of the crystal structure of (I) is marked on the Ramachandran map.

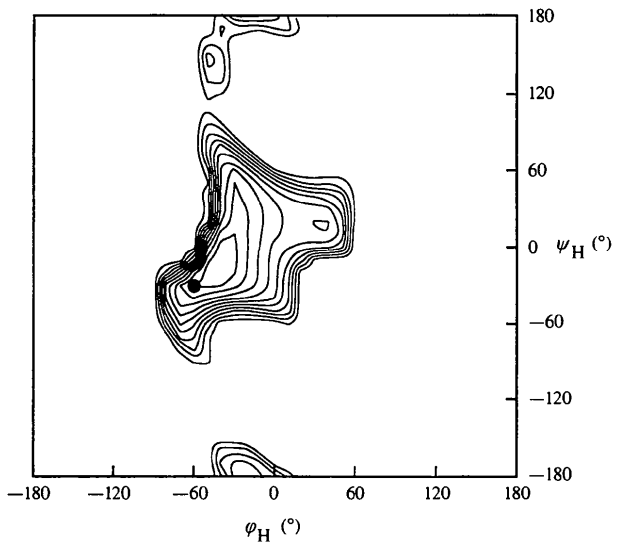


Fig. 2. Ramachandran map of methyl 2-*O*-α-D-mannopyranosyl-β-D-glucopyranoside. Contour lines are drawn in 1 kcal mol^{-1} increments above the global energy minimum. The conformation of the crystal structure is marked.

There are seven inter-residue hydrogen bonds which form a chain with limited extension. The sequence, donor → acceptor, is $O3_g \rightarrow O4_m^{i} \rightarrow O4_g \rightarrow O2_m^{ii} \rightarrow O6_m^{iii} \rightarrow O6_g \rightarrow O3_m^{iv} \rightarrow O5_m^{v}$, in which the subscripts *g* and *m* denote glucose and mannose residues, respectively, in the molecule and the superscript denotes symmetry equivalent molecules [symmetry codes: (i) $x-\frac{1}{2}$, $\frac{3}{2}-y$, $1-z$; (ii) $\frac{1}{2}-x$, $1-y$, $z-\frac{1}{2}$; (iii) $x-\frac{1}{2}$, $\frac{1}{2}-y$, $1-z$; (iv) $x, y-1, z$; (v) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$]. Thus, a glucose residue in one molecule and mannose residues in five other molecules are involved in the chain in which all possible hydrogen bonds are engaged. Intramolecular short O···O contact distances (< 2.9 Å) are not considered to contribute to the stabilization of the conformation due to the fact that all of these contacts make up five-edged graphs with the H atom as one vertex and thereby form angles too acute for hydrogen bonding.

Experimental

The synthesis of methyl 2-*O*-α-D-mannopyranosyl-β-D-glucopyranoside by glycosylation of methyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside with 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside bromide in the presence of silver zeolite has been described previously (Jansson, Kenne, Persson & Widmalm, 1990). The disaccharide was crystallized from methanol/water at ambient temperature.

Crystal data

$C_{13}H_{24}O_{11}$
$M_r = 356.32$
Orthorhombic
$P2_12_12_1$
$a = 9.3767\ (14)$ Å
$b = 10.6508\ (8)$ Å
$c = 15.825\ (2)$ Å
$V = 1580.4\ (3)$ Å^3
$Z = 4$
$D_x = 1.498$ Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 42 reflections
$\theta = 25.4–29.7°$
$\mu = 1.146$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.74 × 0.34 × 0.26 mm
Colourless

Data collection

Stoe AED-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Philips & Mathews, 1968)
$T_{min} = 0.665$, $T_{max} = 0.742$
9628 measured reflections
2807 independent reflections
2629 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 68.51°$
$h = -11 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -19 \rightarrow 15$
4 standard reflections
frequency: 90 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.080$
$S = 1.050$
2807 reflections
246 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0291P)^2 + 0.5793P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.175$ e Å^{-3}
$\Delta\rho_{min} = -0.155$ e Å^{-3}
Extinction correction: *SHELXL93*
Extinction coefficient: 0.0077 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.03 (19)

Table 1. *Selected geometric parameters (Å, °)*

C1′—O2	1.409 (2)	C5—O5	1.440 (2)
C1′—O5′	1.420 (2)	O5—C1	1.421 (2)
O5′—C5′	1.451 (2)	C1—O1	1.394 (2)
O2—C2	1.426 (2)		

O2—C1′—O5′	112.95 (15)	C1—O5—C5	112.48 (15)
C1′—O5′—C5′	115.57 (15)	O1—C1—O5	107.9 (2)
C1′—O2—C2	118.02 (15)	C1—O1—C7	111.9 (2)
O5′—C1′—O2—C2	59.0 (2)	O5—C1—O1—C7	−69.9 (2)
C1′—O2—C2—C1	95.0 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*b*···O4′^{i}	0.95 (4)	1.90 (4)	2.789 (2)	154 (3)
O4′—H4′*b*···O4^{ii}	0.96 (4)	1.99 (4)	2.854 (2)	149 (3)
O4—H4*b*···O2′^{iii}	0.92 (4)	1.85 (4)	2.762 (2)	171 (3)
O2′—H2′*b*···O6′^{iv}	0.89 (4)	1.77 (4)	2.653 (2)	172 (3)
O6′—H6′*c*···O6^{v}	0.86 (5)	1.81 (5)	2.666 (2)	174 (5)
O6—H6*c*···O3′^{vi}	0.91 (4)	2.02 (4)	2.874 (2)	157 (3)
O3′—H3′*b*···O5′^{iv}	0.90 (4)	1.95 (4)	2.840 (2)	172 (3)

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

All non-H atoms were refined with anisotropic displacement parameters using a 'rigid-bond' restraint to U_{ij} of two bonded atoms (Rollett, 1970), implemented as the *DELU* instruction in *SHELXL*93 (Sheldrick, 1993). The H atoms were positioned geometrically and allowed to ride during the least-squares refinements. The torsion angles containing H atoms are calculated with geometrically placed H atoms, thereby the e.s.d.'s of these are of little significance since the e.s.d.'s of the H-atom positions are related to those of the parent atom. The absolute configuration of the title compound was determined by its constituent monosaccharides that have the D configuration. This absolute configuration is in agreement with the obtained value of the Flack parameter which indicates the correct absolute configuration.

Data collection: *DIF*4 (Stoe & Cie, 1991*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1991*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1034). Services for accessing these data are described at the back of the journal.

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(1*RS*,3*SR*,4*RS*,5*RS*,7*SR*,9*SR*)-4,7-Diacetyl-9-hydroxy-1,3,5,9-tetramethyl-2,6,8-trioxatricyclo[3.2.1.1^{3,7}]nonane: a Tricyclic System Formed Under Cathodic Conditions

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Abstract

The title compound, $C_{14}H_{20}O_6$, generated from a bicyclic precursor under electrochemical conditions, crystallizes with six identical molecules in the asymmetric unit. Comparison of equivalent bond lengths and angles reveals no major structural differences between the molecules. However, the intermolecular distances suggest that the molecular packing is due to pairwise attractive interactions between the species, resulting in three different types of dimers. The crystal lattice can be described as a layer structure with strata either perpendicular or parallel to the *ac* plane.

Comment

During our work in the field of the electrochemistry of substituted 4,7,8-trioxabicylo[3.2.1]oct-2-enes [(3), see scheme below] we obtained the title compound (2) as a side product following the method described in the *Experimental* section. Isolation of (2) from the reaction mixture provides evidence that bicyclooctenes like (3) serve as precusors to tricyclic products under cathodic conditions. Evaluation of the reaction mechanism (Thomas, Wellen, Simons & Raabe, 1993; Simons 1992) critically depends on a reliable determination of the structures of the products.

Compound (3) was obtained as a racemate. Moreover, the fact that (2) was also formed as a racemate indicates that the two-electron reduction of (3) is stereoselective in the sense that one enantiomer of (3) yields a single enantiomer of (2). The title compound (2) has six chiral centres (C6, C11, C4, C3, C10 and C13, which are C1, C3, C5, C4, C7 and C9 according to IUPAC numbering). While the chirality of the first five C atoms could be determined by spectroscopic

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