Crystal data

$C_{62}H_{66}N_8O_2Si$	Mo $K\alpha$ radiation
M_r = 983.33	λ = 0.71073 Å
Triclinic	Cell parameters from 15729 reflections
$P\overline{1}$	θ = 1–25°
a = 9.608 (1) Å	μ = 0.098 mm^{-1}
b = 10.742 (1) Å	T = 298 K
c = 14.468 (1) Å	Thin plate
α = 107.121 (1)°	0.6 × 0.4 × 0.2 mm
β = 102.757 (1)°	Dark blue
γ = 104.349 (1)°	
V = 1311.1 (4) Å^3	
Z = 1	
D_x = 1.24 Mg m^{-3}	
D_m = 1.25 Mg m^{-3}	

Data collection

KappaCCD diffractometer	3561 reflections with $I > 2\sigma(I)$
φ scan	θ_{max} = 25.78°
Absorption correction: none	$h = 0 \rightarrow 12$
4809 measured reflections	$k = -13 \rightarrow 11$
4809 independent reflections	$l = -18 \rightarrow 17$

Refinement

Refinement on F	$w = 1/[\sigma^2(F) + 0.03F^2]$
R = 0.062	$(\Delta/\sigma)_{max}$ = 0.007
wR = 0.114	$\Delta\rho_{max}$ = 0.23 e Å^{-3}
S = 1.0181	$\Delta\rho_{min}$ = −0.22 e Å^{-3}
3561 reflections	Extinction correction: none
395 parameters	Scattering factors from Waasmaier & Kirfel (1995)
H-atom parameters not refined	

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

Si1—O1	1.711 (3)	Si1—N5	1.934 (3)
Si1—O2	1.682 (3)	Si1—N7	1.930 (3)
Si1—N1	1.906 (3)	O1—C33	1.416 (5)
Si1—N3	1.912 (3)	O2—C48	1.427 (4)
O1—Si1—O2	175.4 (2)	O2—Si1—N3	92.7 (2)
O1—Si1—N1	89.0 (2)	Si1—O1—C33	148.4 (3)
O1—Si1—N3	83.6 (2)	Si1—O2—C48	148.0 (3)
O2—Si1—N1	93.7 (2)		

The measurements were carried out on a Nonius area detector through a 180° scan (no Friedel pairs were required, so no complete sphere was measured, as there was no use in checking the absolute configuration) in 2° φ steps.

Data collection: *KappaCCD Software* (Nonius, 1997). Data reduction: *maXus* (Mackay *et al.*, 1998). Program(s) used to solve structure: *maXus*. Program(s) used to refine structure: *maXus*. Molecular graphics: *maXus*. Software used to prepare material for publication: *maXus*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1427). Services for accessing these data are described at the back of the journal.

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Methyl β-lactoside (methyl 4-*O*-β-D-galactopyranosyl-β-D-glucopyranoside) methanol solvate

ROLAND STENUTZ, MAOYU SHANG AND ANTHONY S. SERIANNI

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556-5670, USA. E-mail: serianni.1@nd.edu

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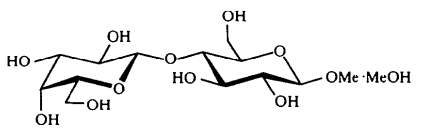
Abstract

The structure of the title compound, $C_{13}H_{24}O_{11}\cdot CH_4O$, has been determined. The glycosidic torsion angles, φ (O5′—C1′—O4—C4) and ψ (C1′—O4—C4—C5), have values of −88.4 (2) and −161.3 (2)°, respectively. The structure closely resembles that of methyl β-cellobioside (methyl 4-*O*-β-D-glucopyranosyl-β-D-glucopyranoside) methanol solvate, the difference being the stereochemistry at a single position (C4′).

Comment

Lactose is a major carbohydrate constituent of mammalian milk and a structural element in many biologically important oligosaccharides. The solution structures of lactose and its glycosides have been the subject of several studies, but no structures of its glycosides have been determined previously in the crystalline state.

The global structure of methyl β-lactoside, (I), is most concisely described by the glycosidic torsion angles, φ (O5′—C1′—O4—C4) and ψ (C1′—O4—C4—C5), and the torsion angles of the exocyclic hydroxymethyl groups, ω (O5—C5—C6—O6) and ω' (O5′—C5′—C6′—O6′) (Table 1). The value of the φ torsion angle [−88.4 (2)°] is similar to those obtained for crystalline lactose (Table 2), but ψ [−161.3 (2)°] differs by nearly 30°, being close to that of the structurally related methyl β-cellobioside, (II) (Ham & Williams, 1970). Closer examination reveals more similarities between (I) and (II); the torsions of the hydroxymethyl groups, the position of the methanol molecule in the crystal lattice, and hydrogen bonding are similar. The hydrogen bond at O4′, which is equatorial in (II) but axial in (I), also involves the same acceptor, *i.e.* the methanol oxygen. A similar relationship has been shown to exist between the crystal structures of β-lactose and β-cellobiose (Hirotsu & Shimada, 1974).



(I)

The main factors determining hydroxymethyl orientation in hexopyranosides are repulsive steric interactions between O4 and O6 (Hassel & Ottar, 1947) and the *gauche* effect (Wolfe, 1975). Both the hydroxymethyl torsion angles, ω [−54.6 (2)°, *gg* conformer] and ω' [57.3 (2)°, *gt* conformer], are in agreement with predictions made by these rules. In most other lactose structures, the conformation of the glucose hydroxymethyl group is *gt*, but *gg* is common in other structures containing *gluco* residues (Marchessault & Pérez, 1979). The hydrogen bonds can be separated into two groups: an infinite chain with hydrogen bonds alternating between O6′ and O3′, and a seven-membered chain starting at HO4′ and ending at O5′ (Table 3). One intramolecular hydrogen bond between HO3 and O5′ is observed and is also found in other lactose structures. All hydrogen donors are involved in hydrogen bonds.

The solution structure of methyl β-lactosides has been the subject of NMR investigations, *inter alia*, by Bose *et al.* (1998), using trans-*O*-glycosidic ^3J values ($\varphi \approx -80°$, $\psi \approx -135°$), and by Fernández & Jiménez-Barbero (1993), using nuclear Overhauser effects ($\varphi = -100\pm40°$, $\psi = -150\pm30°$). These results suggest that the solution conformation of (I) is more similar to the crystal structure of lactose ($\psi = -131$ to $-143°$) than that of (I) ($\psi \approx -161°$), but it is reasonable to assume that all the crystal conformations are sampled to some extent in solution.

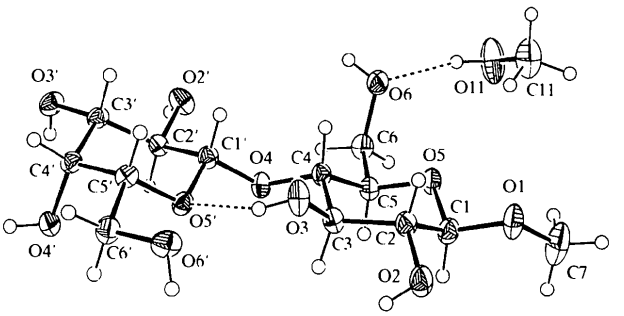


Fig. 1. The structure and atomic numbering in (I). 40% probability displacement ellipsoids are shown for the C and O atoms, and H atoms are shown as spheres of an arbitrary radius.

Experimental

Methyl β-lactoside was prepared by Koenigs–Knorr glycosylation according to Ditmar (1902). Crystals were grown from a methanol solution by slow evaporation at 295 K.

Crystal data

$C_{13}H_{24}O_{11}\cdot CH_4O$
$M_r = 388.36$
Monoclinic
$P2_1$
$a = 4.659\,(1)$ Å
$b = 25.117\,(2)$ Å
$c = 7.758\,(1)$ Å
$\beta = 105.51\,(1)°$
$V = 874.9\,(2)$ Å^3
$Z = 2$
$D_x = 1.474$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 18$–$19°$
$\mu = 0.130$ mm^{-1}
$T = 293\,(2)$ K
Bar
0.55 × 0.20 × 0.12 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical ψ scan (North *et al.*, 1968)
$T_{min} = 0.93$, $T_{max} = 0.99$
3473 measured reflections
1584 independent reflections
1541 reflections with $I > 2\sigma(I)$

$R_{int} = 0.023$
$\theta_{max} = 25.01°$
$h = 0 \rightarrow 5$
$k = -29 \rightarrow 29$
$l = -9 \rightarrow 8$
3 standard reflections every 200 reflections
frequency: 120 min
intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.079$
$S = 1.124$

$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 0.1945P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

1584 reflections
243 parameters
H atoms idealized with riding models

$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C1—O1	1.384 (3)	C4—O4	1.437 (3)
C1—O5	1.413 (3)	O4—C1′	1.387 (3)
O1—C7	1.420 (4)	C1′—O5′	1.425 (3)
C1—O1—C7	113.7 (2)	C1—O5—C5	112.0 (2)
C1′—O4—C4	116.2 (2)	C1′—O5′—C5′	112.3 (2)
O5—C1—O1—C7	−77.4 (3)	O5—C5—C6—O6	−54.6 (2)
C1′—O4—C4—C5	−161.3 (2)	O5′—C1′—O4—C4	−88.4 (2)
C1′—O4—C4—C3	78.4 (2)	O5′—C5′—C6′—O6′	57.3 (2)

Table 2. *Comparison of methyl β-lactoside (I) with related structures (°)*

Compound	φ	ψ	ω	ω'
Methyl β-lactoside·CH_3OH[a]	−88.4	−161.3	−54.6	57.3
Methyl β-cellobioside·CH_3OH[b]	−91.1	−160.7	−55.1	52.4
β-Lactose[c]	−70.9	−131.5	72.6	50.5
α-Lactose·H_2O[d]	−94.2	−142.8	63.2	59.4
α-Lactose·$CaCl_2·7H_2O$[e]	−76.9	−136.7	63.8	59.8
α-Lactose·$CaBr_2·7H_2O$[f]	−76.0	−134.9	61.9	62.4
N-Acetyl α-lactosamine·H_2O[g]	−88.1	−139.5	−56.0	66.8

Notes: (*a*) this work; (*b*) Ham & Williams (1970); (*c*) Hirotsu & Shimada (1974); (*d*) Fries *et al.* (1971); (*e*) Cook & Bugg (1973); (*f*) Bugg (1973); (*g*) Longchambon *et al.* (1981).

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
O4′—H4′O···O11^{i}	1.87	2.686 (3)	171
O11—H11O···O6	1.93	2.727 (3)	164
O6—H6O···O2^{ii}	1.94	2.748 (2)	169
O2—H2O···O2′^{iii}	1.96	2.757 (3)	163
O2′—H2′O···O3^{iv}	1.96	2.775 (3)	175
O3—H3O···O5′	2.08	2.764 (2)	141
O3′—H3′O···O6′^{iv}	1.96	2.740 (2)	160
O6′—H6′O···O3′^{iii}	1.84	2.662 (2)	175

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

Data collection: *CAD*-4 *ARGUS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *ARGUS*. Data reduction: *Chi*90*s* (Boyle, 1997), *XCAD*4 (Harms, 1997) and *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997). Software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1465). Services for accessing these data are described at the back of the journal.

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4-Methylbicyclo[6.3.0]undecane-2,6-dione, (I), 7-bromo-4-methylbicyclo[6.3.0]undecane-2,6-dione, (II), 7-acetonyl-4-methylbicyclo[6.3.0]undecane-2,6-dione, (III), and 8-methyltricyclo[9.3.0.0^{2,6}]tetradec-5-ene-4,10-dione, (IV)

MISAO UMEHARA,[a] HIROYUKI HOSOMI[b] AND SHIGERU OHBA[b]

[a]*Department of Chemistry, Keio University, Hiyoshi 4-1-1, Kohoku-ku, Yokohama 223-8521, Japan, and* [b]*Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223-8522, Japan. E-mail: ohba@chem.keio.ac.jp*

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Abstract

The crystal structures of the four title compounds, $C_{12}H_{18}O_2$, (I), $C_{12}H_{17}BrO_2$, (II), $C_{15}H_{22}O_3$, (III), and $C_{15}H_{20}O_2$, (IV), which were obtained during studies of the preparation of C_5–C_8–C_5 fused-ring compounds,