2,4,6-Tri-*O*-benzyl-*myo*-inositol

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Abstract

The crystal structure of 2,4,6-tri-*O*-benzyl-*myo*-inositol [2,4,6-tris(benzyloxy)-1,3,5-cyclohexanetriol], $C_{27}H_{30}O_6$, has been determined by X-ray diffraction. The structure consists of a cyclohexyl ring having three hydroxy groups alternating with three benzyloxy groups. The cyclohexyl ring adopts a chair conformation with five substituents in equatorial orientations and one in an axial orientation.

Comment

As part of a program of research directed towards the synthesis of 1,3,5-*myo*-inositol triphosphate, we obtained the title compound, (1), in good yield. The structure of (1) is reported as determined by X-ray crystallography.

(1)
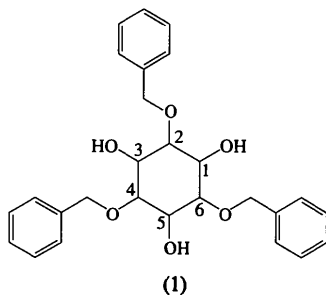
The title molecule consists of a cyclohexyl ring in a chair conformation containing six substituents. The three hydroxy groups on atoms C1, C3 and C5 occupy equatorial positions alternating with three benzyloxy groups, one of which adopts an axial position, *i.e.* the group on atom C2; a perspective view (*ORTEP*II; Johnson, 1976) of the molecule is shown in Fig. 1. This is similar to the positioning of the benzyl groups found in another *O*-benzyl-*myo*-inositol derivative reported recently (Steiner, Hinrichs, Saenger & Gigg, 1992).

The molecule appears to have a flattened form incorporating the inositol ring and the benzyloxy groups on atoms C4 and C6, with no interaction between the phenyl rings. The benzyloxy group on C2 stands upright with respect to this plane. As shown in Fig. 2, O3···O3 and O5···O6 hydrogen bonds connect the molecules in the crystal. The general organization in the network is
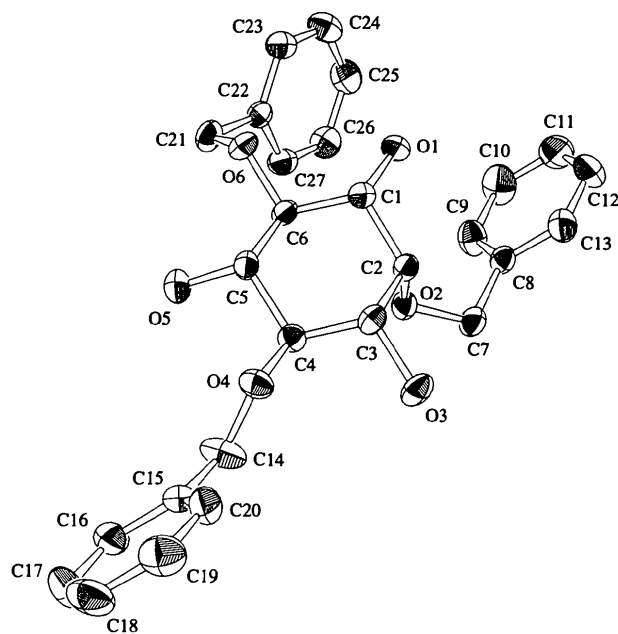

Fig. 1. A perspective *ORTEP*II (Johnson, 1976) view of the title compound showing 33% probability displacement ellipsoids.
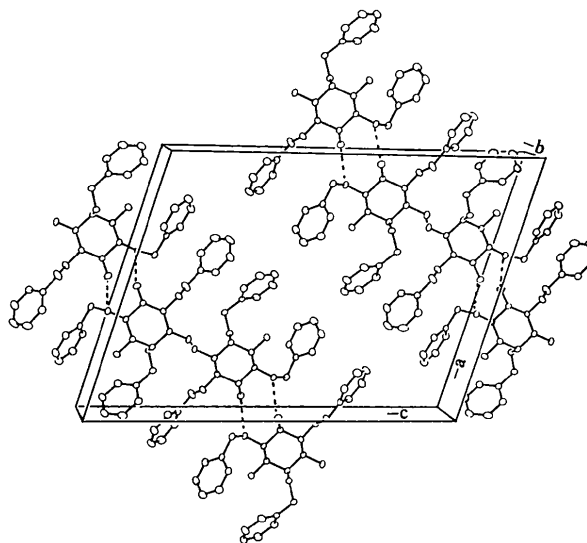

Fig. 2. Packing diagram of the unit cell with hydrogen bonds indicated by dashed lines.

layer-like, with pleated chains of molecules linked pairwise around an inversion centre by O5···O6 hydroxy-to-benzyloxy hydrogen bonds [O5···O6 2.855 (1) Å]. Moreover, a weaker set of hydrogen-bond interactions keeps the O3 hydroxy groups at a close distance [3.004 (2) Å].

Experimental

2,4,6-Tri-*O*-benzyl-*myo*-inositol was prepared by a series of chemical reactions from the parent compound *myo*-inositol

$C_{27}H_{30}O_6$

(Billington *et al.*, 1989). Crystals (m.p. 357–358 K) suitable for X-ray analysis were grown by slow cooling of a hot diethyl ether solution.

Crystal data

$C_{27}H_{30}O_6$	Mo $K\alpha$ radiation
$M_r = 450.5$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 18.244\,(6)$ Å	$\theta = 12\text{–}18°$
$b = 5.403\,(2)$ Å	$\mu = 0.084$ mm^{-1}
$c = 24.480\,(8)$ Å	$T = 293$ K
$\beta = 106.94\,(5)°$	Prism
$V = 2308\,(1)$ Å^3	$0.60 \times 0.55 \times 0.50$ mm
$Z = 4$	Colourless
$D_x = 1.296$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.015$
diffractometer	$\theta_{max} = 24°$
$\theta/2\theta$ scans	$h = 0 \rightarrow 20$
Absorption correction:	$k = 0 \rightarrow 6$
none	$l = -27 \rightarrow 26$
4463 measured reflections	2 standard reflections
3607 independent reflections	frequency: 120 min
2547 observed reflections	intensity decay: 1.6%
$[I > 3\sigma(I)]$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.08$
$R = 0.048$	$\Delta\rho_{max} = 0.256$ e Å^{-3}
$wR = 0.060$	$\Delta\rho_{min} = -0.220$ e Å^{-3}
$S = 2.1$	Extinction correction: none
2547 reflections	Atomic scattering factors
298 parameters	from *International Tables*
H-atom parameters not	*for X-ray Crystallography*
refined	(1974, Vol. IV, Table
$w = 1/(\sigma^2(F)$	2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.27268 (8)	0.0797 (3)	0.54631 (6)	0.0449
O2	0.27213 (8)	-0.2564 (3)	0.63862 (6)	0.0358
O3	0.21960 (9)	-0.0506 (4)	0.72754 (6)	0.0582
O4	0.05973 (8)	-0.1057 (3)	0.66601 (6)	0.0522
O5	0.02867 (9)	-0.2602 (4)	0.55001 (7)	0.0436
O6	0.11353 (9)	0.0008 (3)	0.48747 (6)	0.0501
C1	0.2149 (1)	0.0767 (5)	0.57472 (9)	0.0416
C2	0.2477 (1)	-0.0033 (4)	0.63690 (9)	0.0400
C3	0.1875 (1)	0.0144 (5)	0.66829 (9)	0.0450
C4	0.1183 (1)	-0.1452 (4)	0.63938 (9)	0.0403
C5	0.0860 (1)	-0.0841 (5)	0.57561 (9)	0.0353
C6	0.1471 (1)	-0.0869 (4)	0.54469 (9)	0.0381
C7	0.3509 (1)	-0.3022 (5)	0.6699 (1)	0.0358
C8	0.4050 (1)	-0.2484 (5)	0.63597 (9)	0.0342
C9	0.4063 (1)	-0.3998 (6)	0.5908 (1)	0.0521
C10	0.4565 (2)	-0.3517 (7)	0.5591 (1)	0.0653
C11	0.5063 (2)	-0.1549 (7)	0.5727 (1)	0.0565
C12	0.5055 (2)	-0.0039 (6)	0.6176 (1)	0.0566
C13	0.4548 (2)	-0.0509 (6)	0.6490 (1)	0.0546
C14	0.0317 (2)	-0.3220 (6)	0.6838 (1)	0.0883
C15	-0.0334 (1)	-0.2651 (5)	0.70793 (9)	0.0489
C16	-0.0925 (2)	-0.4306 (6)	0.6988 (1)	0.0701
C17	-0.1519 (2)	-0.3893 (7)	0.7222 (1)	0.0572
C18	-0.1521 (2)	-0.1856 (7)	0.7549 (1)	0.0671
C19	-0.0932 (2)	-0.0185 (6)	0.7642 (1)	0.0828
C20	-0.0340 (1)	-0.0574 (5)	0.7407 (1)	0.0513
C21	0.1053 (1)	-0.1848 (5)	0.4433 (1)	0.0490
C22	0.1802 (1)	-0.2438 (5)	0.43191 (9)	0.0475
C23	0.2092 (1)	-0.0852 (5)	0.3987 (1)	0.0609
C24	0.2781 (2)	-0.1387 (6)	0.3882 (1)	0.0775
C25	0.3181 (2)	-0.3510 (6)	0.4101 (1)	0.0621
C26	0.2891 (2)	-0.5097 (5)	0.4426 (1)	0.0629
C27	0.2203 (1)	-0.4565 (5)	0.4530 (1)	0.0625

Table 2. *Selected geometric parameters (Å, °)*

O1—C1	1.423 (3)	C9—C10	1.385 (5)
O2—C2	1.435 (3)	C10—C11	1.376 (5)
O2—C7	1.440 (2)	C11—C12	1.373 (5)
O3—C3	1.441 (2)	C12—C13	1.388 (5)
O4—C4	1.420 (3)	C14—C15	1.503 (4)
O4—C14	1.396 (4)	C15—C16	1.368 (4)
O5—C5	1.418 (3)	C15—C20	1.381 (4)
O6—C6	1.436 (2)	C16—C17	1.384 (5)
O6—C21	1.449 (3)	C17—C18	1.361 (5)
C1—C2	1.527 (3)	C18—C19	1.371 (5)
C1—C6	1.523 (3)	C19—C20	1.380 (4)
C2—C3	1.515 (4)	C21—C22	1.506 (4)
C3—C4	1.522 (3)	C22—C23	1.388 (4)
C4—C5	1.536 (3)	C22—C27	1.379 (3)
C5—C6	1.520 (3)	C23—C24	1.385 (4)
C7—C8	1.493 (4)	C24—C25	1.381 (4)
C8—C9	1.382 (4)	C25—C26	1.375 (4)
C8—C13	1.377 (4)	C26—C27	1.382 (4)
C2—O2—C7	115.7 (2)	C9—C8—C13	118.7 (3)
C4—O4—C14	114.3 (2)	C8—C9—C10	120.4 (3)
C6—O6—C21	114.9 (2)	C9—C10—C11	120.5 (3)
O1—C1—C2	111.1 (2)	C10—C11—C12	119.5 (3)
O1—C1—C6	112.5 (2)	C11—C12—C13	120.0 (3)
C2—C1—C6	110.1 (2)	C8—C13—C12	120.9 (3)
O2—C2—C1	109.1 (2)	O4—C14—C15	110.8 (2)
O2—C2—C3	108.1 (2)	C14—C15—C16	118.5 (3)
C1—C2—C3	110.9 (2)	C14—C15—C20	122.3 (2)
O3—C3—C2	110.7 (2)	C16—C15—C20	119.2 (3)
O3—C3—C4	111.6 (2)	C15—C16—C17	120.1 (3)
C2—C3—C4	110.7 (2)	C16—C17—C18	120.7 (3)
O4—C4—C3	109.5 (2)	C17—C18—C19	119.6 (3)
O4—C4—C5	108.5 (2)	C18—C19—C20	120.1 (3)
C3—C4—C5	111.8 (2)	C15—C20—C19	120.3 (3)
O5—C5—C4	108.7 (2)	O6—C21—C22	112.5 (2)
O5—C5—C6	109.1 (2)	C21—C22—C23	120.0 (2)
C4—C5—C6	112.6 (2)	C21—C22—C27	121.2 (2)
O6—C6—C1	109.6 (2)	C23—C22—C27	118.8 (2)
O6—C6—C5	108.4 (2)	C22—C23—C24	120.1 (2)
C1—C6—C5	111.3 (2)	C23—C24—C25	120.4 (3)
O2—C7—C8	112.9 (2)	C24—C25—C26	119.6 (3)
C7—C8—C9	120.0 (2)	C25—C26—C27	120.0 (3)
C7—C8—C13	121.3 (2)	C22—C27—C26	121.1 (3)

H atoms were placed in calculated positions. Those attached to atoms O1 and O3 were not included.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BK1230). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl 6-*O*-[(*R*)-1-Carboxyethyl]-α-D-galactopyranoside

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Abstract

The structure of the *O*-methyl glycoside of the naturally occurring 6-*O*-[(*R*)-1-carboxyethyl]-α-D-galacto-pyranose, $C_{10}H_{18}O_8$, has been determined. The absolute configuration was considered as *R* at the 1-carboxyethyl moiety which had previously been assigned by synthesis. This absolute configuration is consistent both with the determined Flack parameter [0.04 (43)] and the previously known configuration of D-galactose. The conformation of the torsion angle ω, O5—C5—C6—O6, is shown to be *gauche–trans*.

Comment

Substituents on sugar residues play an important biological role as modifiers of the parent carbohydrate compound (van Boeckel & Petitou, 1993). These substituents range from acetates, phosphates and sulfates to amino acids, pyruvates and lactates. Lactic acid substituents have been found to have both the (*R*) and (*S*) configuration in nature and can substitute sugar residues at different positions.

The capsular polysaccharide from *Butyrivibrio fibrisolvens* strain X6C61 contains a D-galactose residue with a 1-carboxyethyl group in the 6-position (Andersson, Ratnayake, Kenne, Ericsson & Stack, 1993). The synthesis of 1-carboxyethyl-substituted monosaccharides and their NMR and CD spectroscopy characterizations have recently been described (Andersson, Kenne, Stenutz & Widmalm, 1994), including those of the title compound, (I).

(I)
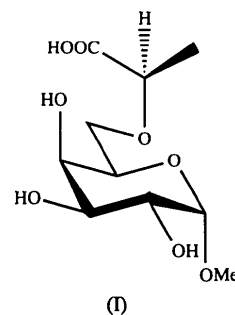
In oligosaccharides the major degrees of freedom are observed at the glycosidic linkage. The available conformational space can be monitored by the torsion angles φ, here defined by H1—C1—O1—C10, and ψ which are also most conveniently used for describing a certain conformer. In the case of 6-substitution an additional torsion angle ω, defined by O5—C5—C6—O6, is of paramount importance for the overall three-dimensional structure.

The title compound (I) is substituted at position 6 by a 1-carboxyethyl group, and three dihedral angles are of major interest. The ω torsion angle [76.4 (5)°] is *gauche–trans* which has been shown to be the preferred conformation in crystal structures having the *galacto* configuration, as in the present molecule.

In the case of the *gluco* configuration, the *gauche–gauche* conformer is the most abundant in the crystal state (Marchessault & Perez, 1979). The torsion angle φ, defined above, has a value of $-45.4 (3)°$, *i.e.* the staggered conformer where the exoanomeric effect contributes to energy stabilization.

The torsion angle φ', defined by H8—C8—O6—C6 [$-34.7 (3)°$], has a *gauche*($-$) conformation and the torsion angle ψ' defined by C8—O6—C6—C5 [170.8 (4)°] has an *anti* conformation. The latter conformation gives an overall extended three-dimensional shape of (I) with