

Data reduction: *ABSMAD* (Karaulov, 1992). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SNOOPI* (Davies, 1983). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1047). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,3,4,5-Tetra-*O*-acetyl-1,6-di-*O*-(triphenylmethyl)-*D*-mannitol

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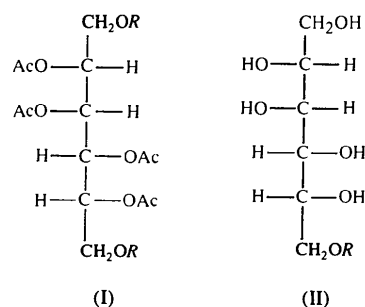
Abstract

The central six-C-atom chain of the title compound, C₅₂H₅₀O₁₀, adopts a nearly planar extended conformation free from C//C, C//O and O//O 1,3-parallel interactions. The three torsion angles formed by these atoms have values of 177.4 (2), 174.2 (2) and –178.0 (2)°. The bulky triphenylmethyl groups, which are oriented *gauche* to their neighboring acetoxy groups with O—

C—C—O torsion angles of –69.8 (2) and –63.0 (2)°, cause no distortion of the bond lengths and bond angles of the sugar moiety.

Comment

The title compound, 2,3,4,5-tetra-*O*-acetyl-1,6-di-*O*-(triphenylmethyl)-*D*-mannitol, (I), is one of the acyclic alditol derivatives which have shown, by crystal structure analyses, to possess some interesting conformational features (Kopf, Morf, Zimmer, Bischoff & Koll 1992). The structure of (I) was determined in order to confirm the identity of the reaction product and to observe to what extent the conformation of its parent compound, *D*-mannitol, (II) (Kim, Jeffrey & Rosenstein 1968; Kanters, Roelofsen & Smiths 1977), might be affected by the presence of the two bulky triphenylmethyl groups.



R = triphenylmethyl

The molecular structure of (I) (Fig. 1) reveals that the molecule does not possess crystallographic twofold symmetry as observed in the parent compound (II). Approximate twofold symmetry is present, however, and the mannitol core has an extended conformation with no 1,3-parallel interactions between the heavy atoms. This conformation is described by the three *anti* torsion angles given in the *Abstract*, as well as O1—C1—C2—C3 and C4—C5—C6—O6 [47.7 (2) and 53.9 (2)°, respectively]. The C—C bond distances in the sugar moiety are in the range 1.514 (3)–1.526 (3) Å while the C—O bonds are in the range 1.411 (2)–1.445 (2) Å, in good agreement with the corresponding values for (II) and other related carbohydrate structures (Jeffrey & French, 1978; Allen, 1986; Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The orientation of the triphenylmethyl groups at the terminal positions (C1 and C6) are *gauche* to their neighbouring acetoxy O atoms, as are the primary hydroxy groups in the parent compound (II), the torsion angles O1—C1—C2—O2 and O6—C6—C5—O5 being –69.8 (2) and –63.0 (2)°, respectively. The four acetoxy groups, on C2, C3, C4, and C5, are oriented in the sequence *trans, gauche, trans*; the torsion angles O2—C2—C3—O3, O3—C3—C4—O4 and O5—C5—C4—O4 are 178.5 (2), 49.9 (2)

and $-177.3(1)^\circ$, respectively. Thus, the presence of the bulky triphenylmethyl groups on O1 and O6 causes no distortion of the bond lengths and bond angles of the sugar moiety, nor any large effect on the conformation of (I) compared with that of (II).

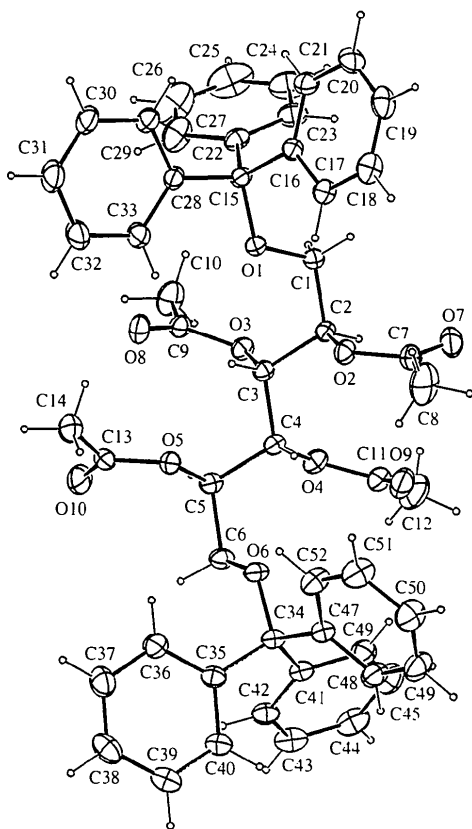


Fig. 1. ORTEP (Johnson, 1976) drawing of the title compound with displacement ellipsoids drawn at the 30% probability level.

Experimental

The title compound was prepared in 95% yield by the treatment of D-mannitol, (II), with 2 molar equivalents of triphenylmethyl chloride followed by acetylation of the resultant 1,6-di-O-(triphenylmethyl)-D-mannitol with acetic anhydride in pyridine.

Crystal data

C₅₂H₅₀O₁₀

$M_r = 835.0$

Orthorhombic

$P2_12_12_1$

$a = 14.542(2) \text{ \AA}$

$b = 16.5650(2) \text{ \AA}$

$c = 19.334(2) \text{ \AA}$

$V = 4658(2) \text{ \AA}^3$

$Z = 4$

$D_x = 1.191 \text{ Mg m}^{-3}$

D_m not measured

Cu $K\alpha$ radiation

$\lambda = 1.54184 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 24\text{--}30^\circ$

$\mu = 0.63 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Irregular fragment

$0.42 \times 0.28 \times 0.20 \text{ mm}$

Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

ψ scan (North, Phillips & Mathews, 1968)

$T_{\min} = 0.961$, $T_{\max} = 0.999$

5213 measured reflections

5213 independent reflections

4672 observed reflections

$[I > 3\sigma(I)]$

$\theta_{\max} = 75^\circ$

$h = 0 \rightarrow 17$

$k = 0 \rightarrow 20$

$l = 0 \rightarrow 24$

3 standard reflections

frequency: 167 min

intensity decay: 2.4%

Refinement

Refinement on F

$R = 0.034$

$wR = 0.046$

$S = 2.273$

4672 reflections

560 parameters

H-atom parameters not refined

$w = 4F_o^2/[\sigma^2(I) + (0.02F_o^2)^2]$

$(\Delta/\sigma)_{\max} = 0.05$

$\Delta\rho_{\max} = 0.13 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.04 \text{ e \AA}^{-3}$

Extinction correction:

$(I + gI_c)^{-1}$ applied to F_c

Extinction coefficient:

$g = 5.2(3) \times 10^{-7}$

Atomic scattering factors

from *International Tables*

for X-ray Crystallography

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
O1	0.68972 (9)	0.52213 (7)	0.42535 (6)	3.61 (3)
O2	0.66838 (9)	0.64906 (8)	0.52795 (6)	4.04 (3)
O3	0.58874 (9)	0.66806 (8)	0.35262 (6)	3.75 (3)
O4	0.5560 (1)	0.80463 (9)	0.42803 (8)	4.50 (3)
O5	0.78880 (9)	0.78794 (8)	0.36540 (6)	3.76 (3)
O6	0.74272 (9)	0.91910 (7)	0.45033 (7)	3.81 (3)
O7	0.5493 (1)	0.6423 (1)	0.60095 (9)	6.87 (4)
O8	0.7098 (1)	0.6364 (1)	0.28480 (7)	5.21 (3)
O9	0.5629 (1)	0.8209 (1)	0.54322 (9)	6.69 (4)
O10	0.7972 (1)	0.8171 (1)	0.25264 (8)	7.05 (5)
C1	0.6031 (1)	0.5451 (1)	0.4536 (1)	3.67 (4)
C2	0.6079 (1)	0.6343 (1)	0.47037 (9)	3.41 (3)
C3	0.6475 (1)	0.6842 (1)	0.41119 (9)	3.22 (3)
C4	0.6492 (1)	0.7744 (1)	0.42535 (9)	3.40 (3)
C5	0.6978 (1)	0.8225 (1)	0.36877 (9)	3.56 (4)
C6	0.7024 (2)	0.9122 (1)	0.3842 (1)	4.13 (4)
C7	0.6287 (2)	0.6542 (1)	0.5912 (1)	5.16 (5)
C8	0.6971 (3)	0.6754 (3)	0.6448 (1)	9.6 (1)
C9	0.6282 (1)	0.6406 (1)	0.2936 (1)	4.05 (4)
C10	0.5571 (2)	0.6169 (2)	0.2429 (1)	6.74 (7)
C11	0.5205 (2)	0.8248 (1)	0.4907 (1)	5.21 (5)
C12	0.4233 (2)	0.8508 (2)	0.4837 (2)	8.76 (9)
C13	0.8289 (2)	0.7848 (1)	0.3025 (1)	4.51 (4)
C14	0.9148 (2)	0.7369 (2)	0.3045 (1)	5.92 (6)
C15	0.7059 (1)	0.4369 (1)	0.41611 (9)	3.45 (4)
C16	0.7136 (1)	0.3957 (1)	0.48717 (9)	3.51 (4)
C17	0.7437 (1)	0.4402 (1)	0.5439 (1)	4.17 (4)
C18	0.7540 (2)	0.4047 (2)	0.6077 (1)	5.50 (6)
C19	0.7355 (2)	0.3242 (2)	0.6168 (1)	5.93 (6)
C20	0.7075 (2)	0.2788 (1)	0.5615 (1)	5.64 (5)
C21	0.6959 (2)	0.3144 (1)	0.4968 (1)	4.60 (5)
C22	0.6301 (2)	0.4019 (1)	0.3702 (1)	4.33 (4)
C23	0.5460 (2)	0.3775 (2)	0.3979 (1)	5.21 (5)
C24	0.4761 (2)	0.3513 (2)	0.3554 (2)	7.71 (7)
C25	0.4867 (2)	0.3498 (2)	0.2861 (2)	10.55 (9)
C26	0.5677 (3)	0.3733 (3)	0.2576 (2)	10.9 (1)
C27	0.6406 (2)	0.4005 (2)	0.2989 (1)	7.45 (8)
C28	0.8007 (1)	0.4311 (1)	0.3806 (1)	3.96 (4)
C29	0.8400 (2)	0.3562 (1)	0.3690 (1)	5.09 (5)

C30	0.9249 (2)	0.3499 (2)	0.3365 (1)	6.49 (6)
C31	0.9700 (2)	0.4167 (2)	0.3153 (2)	7.13 (7)
C32	0.9332 (2)	0.4916 (2)	0.3268 (2)	7.26 (7)
C33	0.8473 (2)	0.4987 (1)	0.3587 (1)	5.38 (5)
C34	0.7563 (2)	0.9988 (1)	0.4792 (1)	3.67 (4)
C35	0.8410 (1)	1.0394 (1)	0.4471 (1)	3.95 (4)
C36	0.8992 (2)	0.9988 (2)	0.4037 (1)	5.05 (5)
C37	0.9753 (2)	1.0378 (2)	0.3756 (2)	6.29 (6)
C38	0.9934 (2)	1.1166 (2)	0.3907 (2)	6.13 (6)
C39	0.9364 (2)	1.1573 (2)	0.4359 (1)	5.62 (6)
C40	0.8614 (2)	1.1191 (1)	0.4642 (1)	4.64 (5)
C41	0.6683 (1)	1.0481 (1)	0.4686 (1)	3.83 (4)
C42	0.6607 (2)	1.1061 (1)	0.4172 (1)	4.44 (4)
C43	0.5790 (2)	1.1473 (1)	0.4060 (1)	5.56 (5)
C44	0.5031 (2)	1.1298 (2)	0.4455 (2)	6.18 (6)
C45	0.5075 (2)	1.0715 (2)	0.4954 (2)	6.12 (6)
C46	0.5903 (2)	1.0297 (1)	0.5069 (1)	5.09 (5)
C47	0.7782 (1)	0.9809 (1)	0.5555 (1)	3.97 (4)
C48	0.7538 (2)	1.0320 (1)	0.6087 (1)	5.39 (5)
C49	0.7758 (2)	1.0135 (2)	0.6764 (1)	6.62 (7)
C50	0.8219 (2)	0.9441 (2)	0.6919 (1)	6.95 (7)
C51	0.8489 (2)	0.8932 (2)	0.6395 (1)	6.71 (6)
C52	0.8266 (2)	0.9114 (2)	0.5719 (1)	5.46 (5)

Table 2. Selected geometric parameters (\AA , $^\circ$)

O1—C1	1.424 (2)	O8—C9	1.201 (3)
O1—C15	1.443 (2)	O9—C11	1.190 (3)
O2—C2	1.439 (2)	O10—C13	1.195 (3)
O2—C7	1.356 (3)	C1—C2	1.514 (3)
O3—C3	1.444 (2)	C2—C3	1.525 (3)
O3—C9	1.357 (2)	C3—C4	1.519 (3)
O4—C4	1.445 (2)	C4—C5	1.526 (3)
O4—C11	1.359 (3)	C5—C6	1.518 (3)
O5—C5	1.443 (2)	C7—C8	1.479 (4)
O5—C13	1.350 (2)	C9—C10	1.477 (3)
O6—C6	1.411 (2)	C11—C12	1.484 (4)
O7—C7	1.185 (3)	C13—C14	1.480 (4)
C1—O1—C15	117.0 (1)	O5—C5—C6	110.9 (2)
C2—O2—C7	116.7 (2)	C4—C5—C6	112.9 (2)
C3—O3—C9	118.2 (1)	O6—C6—C5	106.0 (1)
C4—O4—C11	118.3 (2)	O2—C7—O7	123.2 (2)
C5—O5—C13	116.9 (1)	O2—C7—C8	111.1 (2)
O1—C1—C2	107.6 (1)	O7—C7—C8	125.7 (2)
O2—C2—C1	111.1 (2)	O3—C9—O8	123.8 (2)
O2—C2—C3	104.9 (1)	O3—C9—C10	110.6 (2)
C1—C2—C3	112.7 (2)	O8—C9—C10	125.6 (2)
O3—C3—C2	105.3 (1)	O4—C11—O9	123.4 (2)
O3—C3—C4	109.5 (1)	O4—C11—C12	110.6 (2)
C2—C3—C4	113.9 (1)	O9—C11—C12	126.0 (3)
O4—C4—C3	109.4 (1)	O5—C13—O10	122.9 (2)
O4—C4—C5	106.2 (1)	O5—C13—C14	111.2 (2)
C3—C4—C5	113.0 (1)	O10—C13—C14	125.9 (2)
O5—C5—C4	104.5 (1)		
C15—O1—C1—C2	170.1 (2)	O3—C3—C4—O4	49.9 (2)
C34—O6—C6—C5	179.9 (2)	C2—C3—C4—C5	174.2 (2)
O1—C1—C2—O2	-69.8 (2)	O4—C4—C5—O5	-177.3 (2)
O1—C1—C2—C3	47.7 (2)	C3—C4—C5—C6	-178.0 (2)
O2—C2—C3—O3	178.5 (2)	O5—C5—C6—O6	-63.0 (2)
C1—C2—C3—C4	177.4 (2)	C4—C5—C6—O6	53.9 (2)

H atoms were visible in difference maps, but were placed in idealized positions with $C-H = 0.95 \text{ \AA}$ and $B_{iso} = 1.3B_{eq}$ of the bonded C atom, and were not refined.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Structure solution: *RANTAN* (Yao, 1981). Structure refinement: *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Preparation of material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1015). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cyclo(L-alanyl-L-seryl).H₂O and Cyclo-(glycyl-L-seryl)

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Abstract

We have determined the crystal structures of two diketopiperazines, cyclo(L-alanyl-L-seryl).H₂O (*cis*-6-hydroxymethyl-3-methyl-2,5-piperazinedione hydrate, C₆H₁₀N₂O₃.H₂O) and cyclo(glycyl-L-seryl) (3-hydroxymethyl-2,5-piperazinedione, C₅H₈N₂O₃). The crystal structure of cyclo(L-alanyl-L-seryl).H₂O [cyclo(L-Ala-L-Ser)] consists of a peptide backbone that is hydrogen bonded to two adjacent diketopiperazine rings, forming extended chains through the crystal. The serine hydroxy group of cyclo(L-Ala-L-Ser) is hydrated by two adjacent water molecules in the crystal. In contrast, the crystal structure of cyclo(glycyl-L-seryl) [cyclo(Gly-L-Ser)] is