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Methyl 3,6-di-*O*-pivaloyl-α-D-manno-pyranoside

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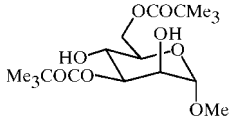
The X-ray crystal structure analysis of the title compound, $C_{17}H_{30}O_8$, revealed a $^4C_1$ conformation of the pyranosyl ring [Cremer–Pople puckering parameters of $Q = 0.568$ (2) Å, $\theta = 5.1$ (2) and $\varphi = 218$ (3)°]. The structure shows no deviations from the geometric parameters of pyranoside carbohydrates. The hydroxyl groups participate in O—H···O hydrogen bonds, forming a two-dimensional pattern [O···O = 2.811 (3) and 2.995 (3) Å].

Comment

The methyl α-glycosides of glucose, mannose and galactose are valuable in the study of hydrogen-bonding patterns and conformational stability in pyranose sugars and their derivatives. Other factors, such as van der Waals and dipole interactions, and the shape and size of the substituents on the sugar residues, also play an important role in the determination of molecular packing.



(I)

Regioselective acylation of sugars is rarely carried out efficiently. Therefore, the selective pivaloylation of methyl α-D-glycosides receives much attention in carbohydrate chemistry, as does the selective enzymatic deacylation of such compounds. Migration of the pivaloyl group has also been observed, and these intramolecular transesterifications in reactions catalysed by esterases from mammalian sera have been studied by Tomić (1999).

The structure determination of the title compound, (I), the major product of the pivaloylation of methyl α-D-manno-pyranoside (Trojko, 1999), was undertaken in order to investigate the conformation of the pyranoside ring and the hydrogen-bonding pattern in the solid state.

The main conformational feature of the pyranosyl ring in (I) (Fig. 1) is the expected $^4C_1$ conformation, with a slightly distorted chair geometry, as shown by the range of the ring torsion angles [53.3 (3)–58.3 (2)°, compared with 60° for an ideal chair conformation and 55.8–61.7° for an ideal pyranose ring; Kim & Jeffrey, 1967]. The Cremer & Pople (1975) puckering parameters [$Q = 0.568$ (2) Å, $\theta = 5.1$ (2) and $\varphi = 218$ (3)°] are analogous to those found for other mannose derivatives in the Cambridge Structural Database (Version 5.23; Allen, 2002).

The Csp^3—Csp^3 bond lengths within the pyranosyl moiety [mean = 1.518 (4) Å; Table 1] agree with the values reported for other carbohydrates (Jeffrey, 1990; Allen *et al.*, 1987). The external C5—C6 bond is short, and the ring C4—C5 distance is long. The Csp^3—O distances, however, show a greater variation [mean = 1.427 (9) Å; Table 1].

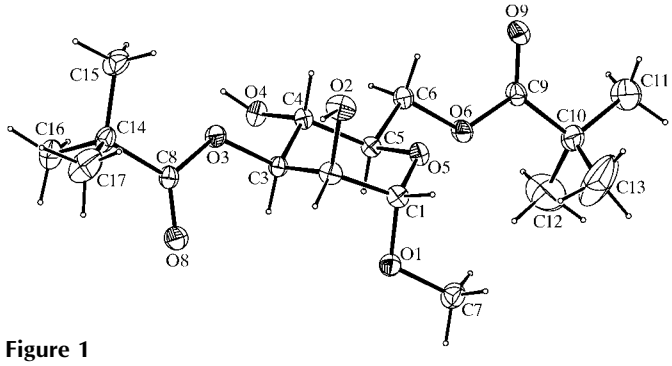


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level.

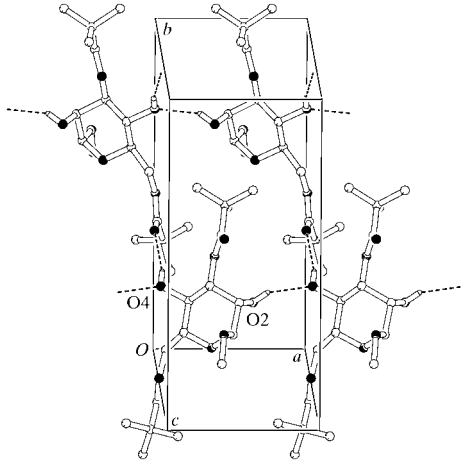


Figure 2
Part of the crystal packing, with the hydrogen-bonding network shown as dashed lines. Only those H atoms involved in the hydrogen-bonding interactions are shown.

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The anomeric C1—O1 bond is slightly shorter than the endocyclic C1—O5 and C5—O5 bonds, as is found in pyranosidic compounds. These bond lengths, which are related to the acetal sequence C5—O5—C1—O1—C7, are ascribed to the anomeric effect and are consistent with observations in many α- and β-pyranoses. A systematic survey of this geometry in α-anomers of hexapyranosides gave the following average values: C1—O1 = 1.398, C1—O5 = 1.419 and C5—O5 = 1.434 Å (Jeffrey, 1990; Jeffrey & Taylor, 1980), or C1—O1 = 1.413(2), C1—O5 = 1.418 (1) and C5—O5 = 1.439 (2) Å (Allen & Fortier, 1993).

The crystal structure is dominated by a two-dimensional network of O—H···O hydrogen bonds and involves free hydroxyl groups. Atom O4 acts both as a donor and as an acceptor, whereas O2 acts only as a donor (Table 2 and Fig. 2). The O4 H atom appears to be hydrogen bonded to O9($2-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$), and the O2 H atom is hydrogen bonded to O4($x-1$, y, z) (Table 2). The resulting motif, in the formalism of graph-set analysis of hydrogen-bond patterns (Etter *et al.*, 1990), is characterized as an $R_4^4(28)$ ring pattern. According to Jeffrey's (1990) investigation, cyclic hydrogen-bonded systems are rare in mono- and disaccharide crystal structures.

In addition, a short intramolecular C—H···O hydrogen bond occurs in (I), with atom C6 as donor and atom O4 as acceptor (Table 2). This C—H···O contact, where H and O are separated by four covalent bonds, is characterized as $S(5)$ according to the classification of Etter *et al.* (1990). These interactions are a structural characteristic of the carbohydrates. Because of the conformational flexibility, the geometric parameters of C—H···O contacts may vary over considerable ranges (the mean values are H···O = 2.60, C···O = 2.92 Å and C—H···O = 96°; Steiner & Saenger, 1992). Several other C—H···O interactions in (I), which include methyl C atoms, exhibit geometric parameters similar to these reported average values (with angles ranging from 93 to 100°), but these interactions are not included in Table 2.

The calculated density is significantly lower than that of carbohydrates with free OH groups, *e.g.* 1.412 Mg m^{-3} in methyl 3-deoxy-α-D-mannopyranoside (Evdokimov & Frolow, 1997), 1.416 Mg m^{-3} in methyl 6-deoxy-α-L-mannopyranoside (Shalaby *et al.*, 1994*a*), 1.461 Mg m^{-3} in methyl α-D-mannopyranoside (Jeffrey *et al.*, 1977) and 1.564 Mg m^{-3} in α-D-mannopyranose (Longchambon *et al.*, 1976), or the values reported for acylated monosaccharides, *e.g.* 1.244 Mg m^{-3} in methyl 6-deoxy-2,3,4-tri-*O*-acetyl-α-L-mannopyranoside (Shalaby *et al.*, 1994*b*) and 1.324 Mg m^{-3} in 1,2,3,4,6,7-hexa-*O*-acetyl-L-*glycero*-D-mannopyranoside (Duda *et al.*, 1986). The density points to a looser packing, probably caused by the bulky pivaloyl groups, which exhibit augmented displacements. Also, the intramolecular C—H···O contacts mentioned above have no significant influence in reducing the thermal vibrations of the pivaloyl C atoms.

Experimental

Compound (I) was synthesized as the major product (yield = 49%) in the acylation of methyl α-D-mannopyranoside (485 mg, 2.5 mmol) with five equivalents of pivaloyl chloride (1.54 ml, 12.5 mmol). The mixture in dry pyridine (1.5 ml) was stirred at room temperature for 50 min, and the products were isolated by column chromatography on silica gel (Trojko, 1999). Colourless single crystals of adequate quality for diffraction analysis were obtained by evaporation from diisopropyl ether (m.p. 362–364 K).

Crystal data

$C_{17}H_{30}O_8$
M_r = 362.41
Orthorhombic, $P2_12_12_1$
a = 6.8711 (11) Å
b = 15.231 (2) Å
c = 19.263 (3) Å
V = 2016.0 (5) Å^3
Z = 4
D_x = 1.194 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 38 reflections
θ = 10.1–17.8°
μ = 0.09 mm^{-1}
T = 293 (2) K
Prism, colourless
0.55 × 0.35 × 0.30 mm

Data collection

Philips PW1100 diffractometer (upgraded by Stoe)
ω scans
4972 measured reflections
2487 independent reflections
2268 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 27.0°
$h = -8 \rightarrow 8$
$k = -19 \rightarrow 19$
$l = -24 \rightarrow 24$
5 standard reflections
frequency: 90 min
intensity decay: 5.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.120
S = 0.93
4343 reflections
242 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0646P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0133 (16)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.405 (3)	O6—C6	1.443 (3)
O1—C7	1.420 (3)	O8—C8	1.206 (3)
O2—C2	1.427 (3)	O9—C9	1.204 (3)
O3—C8	1.331 (3)	C1—C2	1.516 (3)
O3—C3	1.447 (3)	C2—C3	1.522 (4)
O4—C4	1.427 (3)	C3—C4	1.517 (3)
O5—C1	1.414 (3)	C4—C5	1.531 (3)
O5—C5	1.433 (3)	C5—C6	1.505 (3)
O6—C9	1.328 (3)		
C5—O5—C1—C2	−56.3 (3)	C2—C3—C4—C5	58.3 (2)
O1—C1—C2—O2	170.30 (19)	C1—O5—C5—C4	57.8 (2)
O5—C1—C2—C3	53.3 (3)	O4—C4—C5—O5	−178.52 (19)
O2—C2—C3—O3	−54.8 (2)	C3—C4—C5—O5	−57.2 (2)
C1—C2—C3—C4	−55.9 (3)	O4—C4—C5—C6	64.8 (2)
O3—C3—C4—O4	−62.3 (2)	C4—C5—C6—O6	−173.41 (19)

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H22···O4^{i}	0.82 (5)	2.08 (5)	2.811 (3)	149 (5)
O4—H44···O9^{ii}	0.78 (3)	2.23 (3)	2.995 (3)	167 (3)
C6—H6*A*···O4	0.97	2.57	2.924 (3)	102

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

The *tert*-butyl group at C9 displays large displacement parameters, indicating the possible presence of positional disorder. Contoured electron-density Fourier maps were drawn in the final stages of refinement, in order to reveal possible multiple positions for atoms C11, C12 and C13. Note that the observed reflections have very sharp maxima. Since the contour map does not reveal a partial disorder of C11, C12 and C13, and the maximum peak of residual electron density was 0.16 e $Å^{-3}$, the ordered model was used in the final refinement. Most H atoms were visible in the difference maps but were placed at calculated positions and refined as riding atoms [$U_{iso}(H) = 1.5U_{eq}(C)$ for CH_3 and $U_{iso}(H) = 1.2U_{eq}(C)$ for other H atoms]. The positions of the hydroxyl H atoms were determined from difference electron-density maps and were refined freely, with individual U_{iso} parameters. The absolute configuration could not be determined from the diffraction data because of the absence of significant anomalous scatterers in the compound, and an attempt to confirm the absolute structure by refinement of the Flack (1983) parameter led to an inconclusive value (Flack & Bernardinelli, 2000). Therefore, Friedel equivalents were merged in the final refinement, and the absolute structure was set in accordance with the known chirality of the methyl α-D-mannopyranoside precursor.

Data collection: *STADI*4 (Stoe & Cie, 1995); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*98 (Spek, 1998); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1007). Services for accessing these data are described at the back of the journal.

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