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Methyl 4-*O*-benzoyl-2,3-*O*-isopropylidene-α-L-rhamnopyranoside

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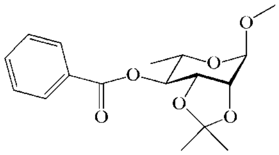
The title compound, $C_{17}H_{22}O_6$, has an exocyclic ester group at the hexopyranosyl sugar residue. The carbonyl group shows a conformation that is eclipsed with respect to the adjacent ring C—H bond. The two ester torsion angles are denoted by *syn* and *cis* conformations. One of these torsion angles is indicated to have a similar conformation in solution, as analyzed by NMR spectroscopy and a Karplus-type relationship.

Comment

The title compound, (I), is an intermediate in the synthesis of rhamnopyranosyl oligosaccharides. The crystal structure of (I) is similar to that of another rhamnose derivative published some time ago (Eriksson *et al.*, 1999). In the light of recent conformational analysis of acetyl esters of cyclic alcohols based on molecular mechanics calculations, NMR criteria and crystal structures (González-Outeiriño *et al.*, 2005), it was of interest to analyze the conformation of the ester group in (I).


(I)

In the study by González-Outeiriño *et al.* (2005), it was concluded that acetyl ester groups without flanking equatorial groups prefer a staggered conformation, whereas when two flanking equatorial substituents were present an eclipsed conformation was preferred. For the θ_1 torsion angle, corresponding to H4—C4—O4—C10 in (I), the *syn* conformation is the one that is usually observed, since the *anti* conformation was calculated to be at least 8 kJ mol^{-1} higher in energy. For the θ_2 torsion angle, corresponding to C4—O4—C10—O10 in (I), analysis of the crystal structures revealed almost exclusive preference for a *cis* conformation, with only a few cases having a *trans* (antiperiplanar) conformation. Furthermore, a Karplus-type relationship was derived for use with NMR data, *viz*. $^3J_{\rm C,H} = 3.1\cos^2\theta - 1.25\cos\theta + 2.35$ (Anderson, 2005).

For (I), the torsion angles are $\theta_1 = -14.2°$ and $\theta_2 = -7.7\ (2)°$. Thus, the conformation at the ester group can be described as eclipsed according to González-Outeiriño *et al.* (2005), with θ_1 as *syn* and θ_2 as *cis*.

To investigate the conformational preference of the θ_1 torsion angle of the monosaccharide in solution, the ^{1}H and ^{13}C chemical shifts, as well as selected $^3J_{\rm H,H}$ coupling constants,

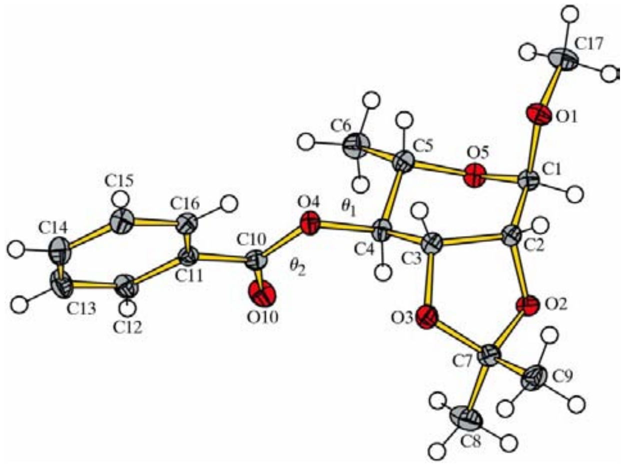


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii. The torsion angles θ_1 (H4—C4—O4—C10) and θ_2 (C4—O4—C10—O10) are indicated.

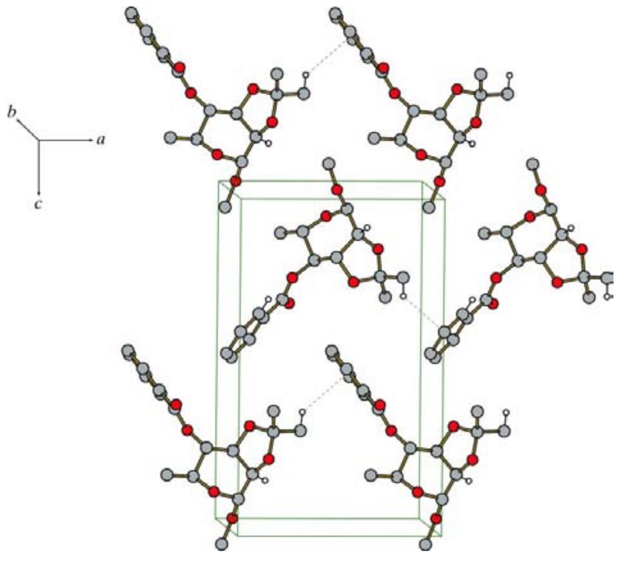


Figure 2
A packing diagram, viewed along the *b* axis, showing one-half of the unit-cell contents in the *b* direction. Note the herring-bone pattern (Desiraju & Steiner, 1999) for the packing of the benzene rings. The C9—H9*B*···*Cg* interaction is shown with a dotted line (*Cg* is the centroid of the C11–C16 benzene ring).

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were determined by one- and two-dimensional NMR spectroscopy (Table 3). Heteronuclear $^3J_{C,H}$ coupling constants can be determined using an NMR technique based on selective excitation of ^{13}C resonances and detection of the anti-phase multiplet pattern in the ^{1}H NMR spectrum, using band-selective proton decoupling during the acquisition period if necessary (Nishida *et al.*, 1996). Analysis of the NMR spectrum obtained with band-selective proton decoupling of the H5 resonance revealed $J_{H4,C10}$ = 4.0 Hz. Employing the Karplus-type relationship, $|\theta_1|$ = 17°, if interpreted as a single *syn* conformer. The θ_1 torsion angle in (I) is therefore anticipated to have a similar conformation in solution to that in the crystal.

A few weak intermolecular hydrogen bonds are listed in Table 2. The phenyl rings are oriented in a pattern resembling the well known herring-bone pattern (Desiraju & Steiner, 1999), as shown in Fig. 2, although it appears that close C—H···π contacts are absent in the title compound. The hexapyranose ring is somewhat distorted from a regular $^1C_4$ chair conformation, with puckering parameters (Cremer & Pople, 1975) q_2 = 0.226 (2) Å, q_3 = −0.489 (2) Å, φ_2 = 122.2 (4)°, Q = 0.538 (2) Å and θ = 155.2 (2) Å. The five-membered ring has an envelope conformation on C2, with puckering parameters q_2 = 0.353 (2) Å and φ_2 = 28.5 (2)°.

Experimental

The synthesis of (I) was performed starting from L-rhamnose using the methodology described by Rainer *et al.* (1992) and Norberg *et al.* (1986). Compound (I) has previously been prepared *via* a different route (Byramova *et al.*, 1985). The synthesis product was analyzed with MALDI–MS; $[M + Na]^+$ m/z, calculated for $C_{17}H_{22}NaO_6$: 345.13; found: 345.26. ^{1}H and ^{13}C NMR data for (I), referenced to internal TMS (δ = 0.0) in CDCl$_3$ solution at 298 K, were assigned by one- and two-dimensional NMR spectroscopy techniques using a Varian Inova spectrometer operating at a proton frequency of 600 MHz. The monosaccharide was dissolved in hot ethanol and an excess of *n*-pentane was added at ambient temperature. Crystals suitable for X-ray crystallographic analysis were formed at 253 K. The scattering power of the crystals was weak. Thus, it was decided to collect data with synchrotron radiation on beamline I711 at the Swedish synchrotron radiation facility, MAXLAB, Lund, Sweden.

Crystal data

$C_{17}H_{22}O_6$
M_r = 322.35
Orthorhombic, $P2_12_12_1$
a = 9.720 (8) Å
b = 10.654 (11) Å
c = 16.127 (14) Å
V = 1670 (3) Å^3
Z = 4
D_x = 1.282 Mg m^{-3}
Synchrotron radiation
λ = 1.350 Å
μ = 0.52 mm^{-1}
T = 100 (2) K
Prism, colourless
0.15 × 0.10 × 0.08 mm

Data collection

Bruker SMART 1K area-detector diffractometer
ω scan at different φ and 2θ
Absorption correction: part of the refinement model (ΔF) (*SADABS*; Sheldrick, 2002)
T_{min} = 0.98, T_{max} = 1.00
18820 measured reflections
2244 independent reflections
2133 reflections with $I > 2\sigma(I)$
R_{int} = 0.095
θ_{max} = 63.4°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.088
S = 1.08
2244 reflections
212 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 0.241P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Selected torsion angles (°).

O5—C1—C2—C3	−34.55 (19)	C2—C1—O5—C5	54.17 (17)
C1—C2—C3—C4	32.16 (19)	C4—C5—O5—C1	−68.33 (16)
C2—C3—C4—C5	−46.56 (18)	O10—C10—O4—C4	−7.7 (2)
C3—C4—C5—O5	63.04 (17)	C10—O4—C4—H4	−14.2

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

Cg is the centroid of the C11–C16 benzene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O10^{i}	1.00	2.53	3.334 (4)	137
C16—H16···O2^{i}	0.95	2.60	3.285 (4)	129
C9—H9*B*···*Cg*^{ii}	0.98	2.88	3.585 (4)	130

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

Table 3
^{1}H and ^{13}C NMR chemical shifts of compound (I) in CDCl$_3$ solution at 298 K; selected $^3J_{H,H}$ are given in parentheses.

H atom	δ_H ($^3J_{H,H+1}$)	C atom	δ_C
H1	4.95 (0.8)	C1	98.2
H2	4.19 (5.5)	C2	76.1
H3	4.33 (7.8)	C3	75.9
H4	5.12 (10.1)	C4	75.1
H5	3.87 (6.2)	C5	64.0
H6	1.23	C6	17.2
		C7	109.8
H8	1.62	C8	27.8
H9	1.35	C9	26.4
		C10	165.8
		C11	129.9
H12,H16	8.05	C12,C16	129.8
H13,H15	7.44	C13,C15	128.4
H14	7.56	C14	133.2
H17	3.42	C17	55.0

H atoms were positioned geometrically and allowed to ride on their parent atoms, with CH, CH$_3$ and aromatic C—H bonds of 1.00, 0.98 and 0.95 Å, respectively, and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C). The Flack (1983) parameter derived from the refinement using unmerged data [x = 0.43 (15)] was inconclusive. Thus, the reflection data were merged in the final refinement. The absolute configuration was set by the *a priori* knowledge of the absolute configuration of the components of the synthesis.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3012). Services for accessing these data are described at the back of the journal.

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