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Methyl 2,3,4-tri-*O*-pivaloyl-β-D-xylopyranoside

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.039
wR factor = 0.094
Data-to-parameter ratio = 8.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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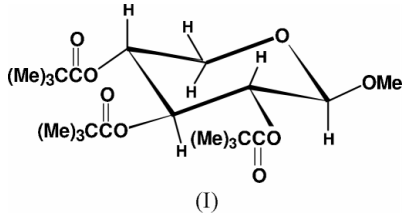
The crystal structure of the title compound, $C_{21}H_{36}O_8$, has been determined by X-ray analysis at 100 K. The six-membered pyranosyl ring adopts a chair conformation.

Comment

Several series of acylated monosaccharides, the acyl groups being pivaloyls, acetyls or a combination of the two, have been synthesized (Ljevaković *et al.*, 1992; Tomić *et al.*, 1991; Petrović *et al.*, 2002). One of the series of acylated monosaccharides previously prepared was that of methyl β-D-xylopyranoside, of which methyl 2,3,4-tri-*O*-pivaloyl-β-D-xylopyranoside, (I), is the completely acylated analog (Petrović *et al.*, 1997). In carbohydrates, the hydroxyl groups are of comparable reactivity. Therefore, continued interest exists in investigating the characteristics of protective groups such as acyls in order to find suitable conditions to transform these molecules in a selective manner. The pivaloyl group is of special interest since it can be introduced into carbohydrates regioselectively, making further transformations selective as well. It can also be removed selectively by enzymes isolated from mammalian sera (Petrović *et al.*, 1997; Tomić *et al.*, 1991). Therefore, hydroxyl-group protection by pivaloyls leads to interesting new substrates in the investigation of enzymes as catalysts in organic synthesis.



(I)

The structure of methyl β-D-xylopyranoside was determined by X-ray analysis (Brown *et al.*, 1996) and by neutron diffraction methods (Takagi & Jeffrey, 1977). Several crystal structures of methyl β-D-*xylo*pyranoside substituted at positions 2, 3 and 4 have been published, *e.g.* methyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranoside (Vangehr *et al.*, 1980) and methyl 2,3,4-tri-*O*-acetyl-β-methyl-D-xylopyranoside (James & Stevens, 1981). We have previously reported the crystal structure of the 3,4-substituted compound methyl 3,4-di-*O*-pivaloyl-β-D-xylopyranoside (Prugovečki *et al.*, 2004). It is interesting to compare the geometrical parameters of (I) with those in the crystal structures of methyl β-D-xylopyranosides with substituents at positions 2, 3 and 4. The bond lengths within the pyranoside moiety agree with the values reported by Vangehr *et al.* (1980) and James & Stevens (1981). The

anomeric effect can be seen, with the anomeric C1—O1 bond length slightly shorter than the endocyclic C1—O5 and C5—O5 bonds. The six-membered ring in (I) adopts the β-$^4C_1$ conformation with a slightly distorted chair geometry. The puckering parameters are q_2 = 0.016 (2) Å, q_3 = 0.615 (2) Å, φ_2 = 79 (6)°, Q = 0.616 (2) Å and Θ = 1.4 (2)° (Cremer & Pople, 1975). The same conformation is found in methyl 2,3,4-tri-*O*-acetyl-β-methyl-D-xylopyranoside (James & Stevens, 1981); however, in methyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranoside (Vangehr *et al.*, 1980), the pyranosyl ring adopts a twist-boat conformation due to the large benzoyl groups. The molecules are connected only by van der Waals contacts.

Experimental

The title compound was synthesized according to the method of Petrovic *et al.* (1997).

Crystal data

$C_{21}H_{36}O_8$
M_r = 416.50
Monoclinic, $P2_1$
a = 9.828 (1) Å
b = 6.849 (1) Å
c = 17.634 (1) Å
β = 96.36 (1)°
V = 1179.7 (2) Å^3
Z = 2
D_x = 1.173 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1573 reflections
θ = 15.0–25.0°
μ = 0.09 mm^{-1}
T = 100 (2) K
Prism, colorless
0.3 × 0.3 × 0.2 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
ω scans
Absorption correction: none
38147 measured reflections
3376 independent reflections
3234 reflections with $I > 2\sigma(I)$
R_{int} = 0.088
θ_{max} = 29.0°
$h = -13 \rightarrow 13$
$k = -9 \rightarrow 9$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.094
S = 1.14
3376 reflections
406 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.2141P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.3881 (19)	O5—C5	1.431 (2)
O2—C2	1.4352 (18)	C1—C2	1.524 (2)
O3—C3	1.443 (2)	C2—C3	1.527 (2)
O4—C4	1.4421 (19)	C3—C4	1.515 (2)
O5—C1	1.4278 (19)	C4—C5	1.527 (2)
C1—O5—C5	110.88 (12)	O3—C3—C4	109.13 (13)
O1—C1—O5	108.55 (12)	O3—C3—C2	108.55 (14)
O1—C1—C2	108.35 (14)	C4—C3—C2	107.77 (12)
O5—C1—C2	108.59 (12)	O4—C4—C3	108.50 (12)
O2—C2—C1	108.51 (12)	O4—C4—C5	108.97 (15)
O2—C2—C3	108.88 (12)	C3—C4—C5	109.00 (13)
C1—C2—C3	108.82 (13)	O5—C5—C4	109.61 (14)

H atoms were found in a difference Fourier map and refined isotropically, giving C—H distances in the range 0.918 (2)–1.03 (3) Å. The absolute configuration could not be determined from the diffraction data because of the absence of significant anomalous scatterers; Friedel equivalents were merged in the final refinement and the absolute configuration was assigned in accordance with the known chirality of the methyl β-D-*xylo*pyranoside precursor.

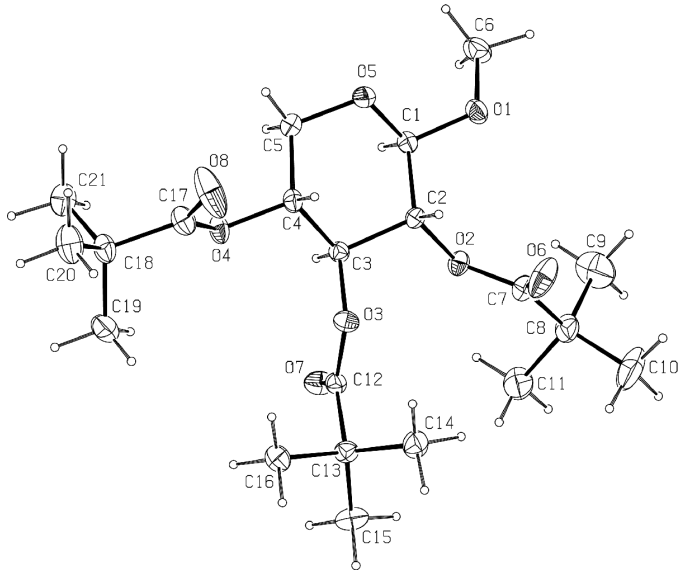


Figure 1
View of methyl 2,3,4-tri-*O*-pivaloyl-β-D-*xylo*pyranoside with the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*98 (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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