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Methyl 4-*O*-pivaloyl-β-D-xylopyranoside

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
R factor = 0.051
wR factor = 0.159
Data-to-parameter ratio = 10.3

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

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The six-membered ring of the title compound, $C_{11}H_{20}O_6$, adopts the chair conformation, with the 4-*O*-pivaloyl group in an equatorial position. Two vicinal hydroxyl groups of each molecule form four hydrogen bonds of the O—H···O type in a one-dimensional chain running along the *b* axis.

Comment

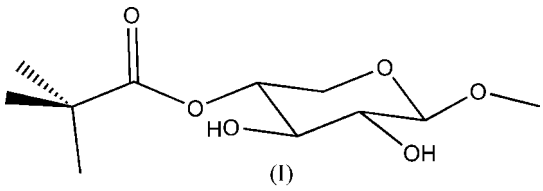
The introduction and/or removal of protecting groups represent some of the most challenging transformations in sugar chemistry. In our previous work we described the synthesis and the hydrolysis of several series of acylated monosaccharides, acyl being acetyl, pivaloyl or a combination of both (Ljevaković *et al.*, 1992; Tomić *et al.*, 1993; Ljevaković *et al.*, 1995; Petrović *et al.*, 1997). Selective acylations and deacylations can be achieved with enzymes as regio- and chemoselective catalysts. We demonstrated that mammalian sera, which are a rich source of different enzymes, contain esterases specific for acylated monosaccharides and can be used for the selective hydrolysis of *O*-acyl derivatives of different monosaccharides (Tomić *et al.*, 1993; Ljevaković *et al.*, 1995; Petrović *et al.*, 1997).

Intramolecular migrations of acyls are well known in carbohydrate chemistry. Especially prone to migration are acetyls, which spontaneously migrate around the sugar ring even under neutral conditions, in organic solvents. The pivaloyl group was generally regarded as not prone to migrations, but we reported that intramolecular migrations of the pivaloyl group were occasionally observed during enzymic hydrolysis (Tomić *et al.*, 2003) or in neutral buffered conditions (Petrović *et al.*, 2002).

Even though it is possible in most cases to determine the position of protecting groups on the sugar ring on the basis of chemical shifts and the splitting pattern of ring protons in ^{1}H NMR spectra, in some cases such determinations were shown to be ambiguous, requiring crystal structure analysis to provide reliable data about the position of the specific protecting group on the sugar ring. Selective pivaloylations of methyl β-D-xylopyranoside have been studied using different equivalents of pivaloyl chloride as the acyl donor (Petrović *et al.*, 1997). On the basis of synthetic studies and ^{1}H NMR data, we concluded that the reactivity of secondary hydroxyl groups follows the order 2-OH < 3-OH < 4-OH. Further proof that the most readily formed derivative is indeed the 4-pivalate was obtained by crystal structure analysis, as described here.

Among the series of pivaloyl-protected xylopyranosides (Prugovečki *et al.*, 2004*a*,*b*), the title compound, (I), has only one hydroxyl group protected, in position 4. It has two vicinal hydroxyl groups which can form hydrogen bonds. The complexity of the hydrogen-bonding network is reduced on

going from unprotected to fully pivaloyl-protected methyl β-D-xylopyranoside. The network of hydrogen bonds of the O—H···O-type is two-dimensional in the unprotected compound (Takagi & Jeffrey, 1978). In methyl 3,4-di-*O*-pivaloyl-β-D-xylopyranoside molecules are connected by two hydrogen bonds, forming distinct dimers in the crystal structure (Prugovečki *et al.* 2004*a*), while fully protected methyl β-D-xylopyranoside forms only van der Waals contacts (Prugovečki *et al.*, 2004*b*).



(I)

Along the *b* axis, molecules of (I) are connected by four O—H···O hydrogen bonds (Table 1) and form zigzag chains in which each molecule acts twice as donor and twice as acceptor. The network of hydrogen bonds is shown in Fig. 2.

In the unprotected methyl β-D-xylopyranoside, a similar one-dimensional chain of hydrogen bonds along the *b* axis is formed. The remaining third, unprotected, OH group connects these chains into layers parallel to the (001) plane. Instead of the methoxy O atom as in (I), the anomeric O atom acts as the acceptor in a hydrogen bond in methyl β-D-xylopyranoside.

Experimental

Compound (I) was synthesized as described previously (Petrović *et al.*, 1997).

Crystal data

$C_{11}H_{20}O_6$
M_r = 248.27
Orthorhombic, $P2_12_12_1$
a = 6.1419 (12) Å
b = 7.0145 (13) Å
c = 31.244 (4) Å
V = 1346.1 (4) Å^3
Z = 4
D_x = 1.225 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 295 (2) K
Prism, colourless
0.75 × 0.40 × 0.40 mm

Data collection

Oxford Diffraction Xcalibur3 CCD diffractometer
ω scans
Absorption correction: none
5650 measured reflections
1728 independent reflections
1254 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 27.1°

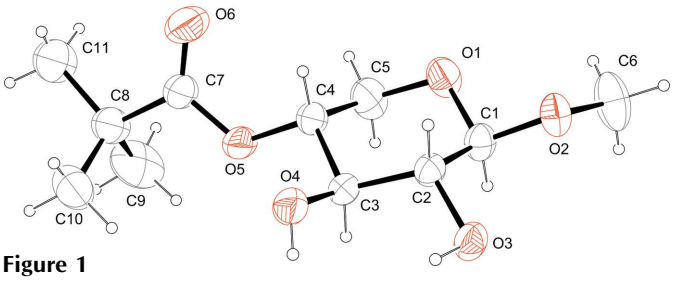


Figure 1
The molecular structure, with the atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

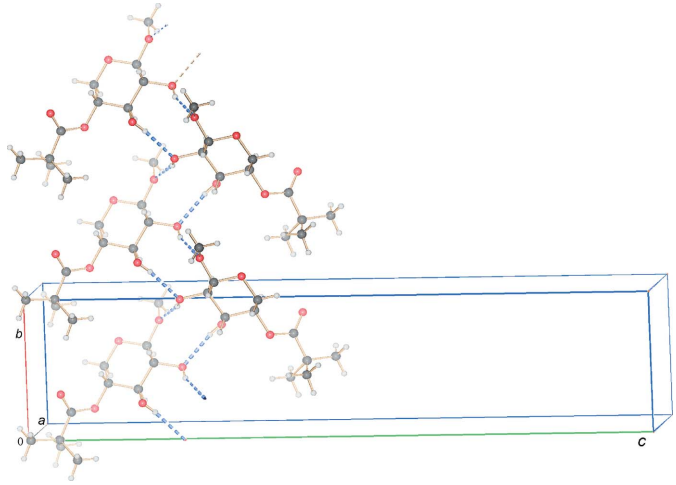


Figure 2
One-dimensional network of hydrogen bonds (dashed lines), extending along the *b* axis.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.159
S = 1.09
1728 reflections
167 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0991P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.093 (16)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H21···O2^{i}	0.93 (4)	1.89 (5)	2.784 (3)	159 (3)
O4—H22···O3^{i}	0.78 (4)	2.11 (4)	2.874 (3)	166 (4)

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

Hydroxyl H atoms were found in a difference map and were refined isotropically. All other H atoms were positioned geometrically, with C—H bond distances of 0.96 Å for methyl H atoms, 0.97 Å for methylene H atoms and 0.98 Å for methine H atoms, and refined as riding, with U_{iso}(H) = 1.2U_{eq}(C) [1.5U_{eq}(C) for methyl groups]. In the absence of significant anomalous scattering, Friedel pairs were merged. The absolute configuration of (I) is known from that of methyl β-D-xylopyranoside, which was used as a starting material.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *SCHAKAL99* (Keller, 1999); software used to prepare material for publication: *SHELXL97*.

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