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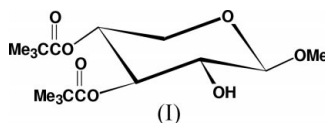
## Key indicators

Single-crystal X-ray study  
 $T = 100$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.043  
 $wR$  factor = 0.108  
Data-to-parameter ratio = 11.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Methyl 3,4-di-*O*-pivaloyl- $\beta$ -D-xylopyranoside

The crystal and molecular structure of the title compound,  $\text{C}_{16}\text{H}_{28}\text{O}_7$ , has been determined by X-ray analysis at 100 K. The six-membered ring adopts the chair conformation. Molecules are connected in pairs around twofold rotation axes *via* two  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds with 2.852 (2) Å.

## Comment

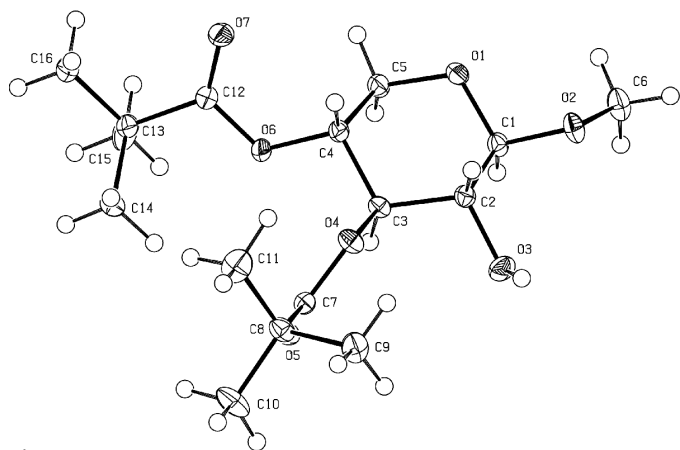
Saccharides contain a multitude of hydroxyl groups which have to be manipulated selectively in the directed synthesis of carbohydrate derivatives. In our investigations of mono-saccharides, *O*-acyl groups were used as protective groups and it was shown that pivaloyl groups, in contrast to acetyl groups, can be introduced into a molecule with a satisfactory degree of selectivity using standard chemical methods. It was also shown that they can be removed selectively using enzymes. Thus, selective pivaloylations of methyl  $\beta$ -D-xylopyranoside led, among other products, to methyl 3,4-di-*O*-pivaloyl- $\beta$ -D-xylopyranoside, (I) (Petrović *et al.*, 1997). In the case of partially pivaloylated products, such as (I), intramolecular migrations of pivaloyl groups were occasionally observed during enzymic hydrolyses (Petrović *et al.*, 2002). Therefore, determination of the exact position of the pivaloyl groups in the starting compounds and final products in such reactions is of particular importance.



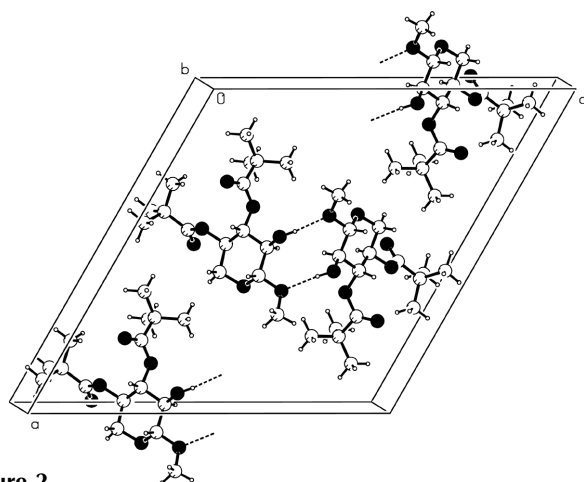
The bulky pivaloyl groups, which are on positions 3 and 4, have little influence on the ring structure as was found by comparison with the structure of methyl  $\beta$ -D-xylopyranoside, which was determined by X-ray (Brown *et al.*, 1966) and neutron diffraction methods (Takagi & Jeffrey, 1978). In the structure of (I), the six-membered ring also adopts the chair conformation. The puckering parameters  $q_2 = 0.072$  (2),  $q_3 = 0.574$  (2) Å,  $\varphi_2 = 341$  (2)°,  $Q = 0.578$  (2) Å and  $\theta = 7.0$  (2)° (Cremer & Pople, 1975) do not differ much from those in methyl  $\beta$ -D-xylopyranoside.

Several crystal structures of substituted methyl  $\beta$ -D-xylopyranosides have also been published, all of them with substituents on positions 2, 3 and 4, *e.g.* methyl 2,3,4-tris(*O*-benzoyl)- $\beta$ -D-xylopyranoside (Vangehr *et al.*, 1980) and 2,3,4-tri-*O*-acetyl- $\beta$ -methyl-D-xylopyranoside (Vorontsova *et al.*, 1985). The ring geometry in these is similar to that in (I). Since there are no hydroxyl groups in these substituted xylopyranosides, no hydrogen bonds are found. It is therefore inter-

Received 28 January 2004  
Accepted 6 February 2004  
Online 14 February 2004



**Figure 1**  
A view of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.



**Figure 2**  
Packing of the molecules in the unit cell. Hydrogen bonds are indicated by dashed lines.

esting to compare the hydrogen bonds found in (I) with those in unsubstituted methyl  $\beta$ -D-xylopyranoside. The large pivaloyl groups seem to play an important role in the determination of exposed and available O atoms as hydrogen-bond acceptors. The non-polar methyl group regions orient themselves toward the same region in the neighbouring molecule, leaving ring atom O1 and anomeric atom O2 as the possible hydrogen-bond acceptors. However, it was found that, in (I), the ring O atom is not involved in hydrogen bonding. The molecules are connected in pairs by two O—H...O hydrogen bonds (Table 2), which are related by the twofold axis (Fig. 2). In unsubstituted methyl  $\beta$ -D-xylopyranoside, a complex hydrogen-bonding network is established. All three hydroxyl groups are hydrogen-bond donors and two of them (in positions 2 and 3) and the ring O atom are acceptors, with O...O distances ranging from 2.728 (2) to 3.040 (3) Å (Takagi & Jeffrey, 1977).

## Experimental

The title compound was synthesized by our group according to the method of Petrović *et al.* (1997).

## Crystal data

$C_{16}H_{28}O_7$   
 $M_r = 332.38$   
Monoclinic,  $C2$   
 $a = 19.111$  (3) Å  
 $b = 5.9619$  (11) Å  
 $c = 18.726$  (2) Å  
 $\beta = 119.337$  (12)°  
 $V = 1860.0$  (5) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.187$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 6732 reflections  
 $\theta = 8.3$ – $28.2^\circ$   
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 100$  (2) K  
Needle, colourless  
 $0.59 \times 0.23 \times 0.16$  mm

## Data collection

Oxford Diffraction Xcalibur CCD diffractometer  
 $\omega$  scans  
Absorption correction: none  
19022 measured reflections  
2829 independent reflections

2507 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.094$   
 $\theta_{max} = 30.0^\circ$   
 $h = -26 \rightarrow 26$   
 $k = -8 \rightarrow 7$   
 $l = -26 \rightarrow 26$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.043$   
 $wR(F^2) = 0.108$   
 $S = 1.03$   
2829 reflections  
240 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0726P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.37$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.22$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

O1—C1	1.431 (2)	O6—C12	1.348 (2)
O1—C5	1.440 (2)	O6—C4	1.4500 (19)
O2—C1	1.402 (2)	O7—C12	1.217 (2)
O2—C6	1.434 (2)	C1—C2	1.536 (2)
O3—C2	1.425 (2)	C2—C3	1.521 (2)
O4—C7	1.3591 (19)	C3—C4	1.522 (3)
O4—C3	1.4479 (18)	C4—C5	1.528 (2)
O5—C7	1.207 (2)		
C1—O1—C5	110.89 (13)	O4—C3—C4	108.50 (15)
O2—C1—O1	107.30 (14)	C2—C3—C4	111.60 (13)
O2—C1—C2	108.16 (12)	O6—C4—C3	105.91 (13)
O1—C1—C2	110.36 (16)	O6—C4—C5	110.01 (12)
C3—C2—C1	110.50 (12)	C3—C4—C5	109.85 (16)
O4—C3—C2	106.29 (12)	O1—C5—C4	109.34 (12)

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O3—H3...O2 <sup>i</sup>	0.82	2.04	2.852 (2)	174

Symmetry code: (i)  $-x, y, 1-z$ .

Although all H atoms were found in a difference Fourier map, the geometry of the hydroxyl and methyl groups was not ideal, so their geometry was fixed. Only the ring H atoms were refined, isotropically, giving C—H distances in the range 0.91 (3)–1.04 (2) Å. The absolute configuration could not be determined from the diffraction data, because of the lack of significant anomalous scattering, so Friedel pairs were merged before the final refinement. The absolute configuration is known from the synthesis.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON98*

(Spek, 1990); software used to prepare material for publication: *SHELXL97*.

The authors thank the Ministry of Science and Technology of the Republic of Croatia for financial support (grants No. 119632 and 119610).

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