

## 1,4-Anhydro-2-C-benzoyloxymethyl-2,3:5,6-di-O-isopropylidene-D-tallitol

David J. Watkin,<sup>a\*</sup> Loren L. Parry,<sup>a</sup> Raquel Soengas<sup>b</sup> and George W. J. Fleet<sup>b</sup><sup>a</sup>Chemical Crystallography, Chemistry Research Laboratory, University of Oxford, Oxford OX1 3TA, England, and <sup>b</sup>Department of Organic Chemistry, Chemical Research Laboratory, Oxford University, Mansfield Road, Oxford OX1 3TA, England

Correspondence e-mail: david.watkin@chem.ox.ac.uk

## Key indicators

Single-crystal X-ray study  
T = 170 K  
Mean  $\sigma(C-C) = 0.003 \text{ \AA}$   
Disorder in main residue  
R factor = 0.047  
wR factor = 0.075  
Data-to-parameter ratio = 9.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.The crystal structure of the title compound, C<sub>20</sub>H<sub>28</sub>O<sub>6</sub>, allows a firm assignment of the stereochemistry at C-4 of formation of the tetrahydrofuran (THF) ring.

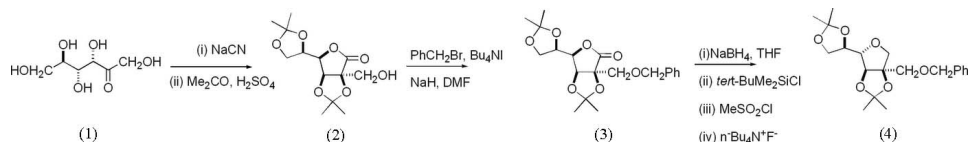
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## Comment

Hitherto, most carbohydrate building blocks have linear carbon chains (Lichtenthaler & Peters, 2004). However, the Kiliani reaction on each of the four keto-hexoses provides branched sugar lactones which are readily crystallized as a new family of chiral carbohydrate building blocks (Soengas *et al.*, 2005). Such materials have been used to make novel sugar amino acids as potential dipeptide isosteres (Simone *et al.*, 2005). In further studies on the potential of such intermediates to form complex chiral targets, further investigations into the synthesis of branched THF rings have been carried out. Thus reaction of D-fructose (1) with sodium cyanide, followed by acetonation of the crude mixture of the resulting lactones, gave the crystalline diacetone (2) (Hotchkiss *et al.*, 2004). Reaction of (2) with benzyl bromide and sodium hydride in the presence of tetra-*n*-butyl ammonium iodide in dimethylformamide afforded the corresponding benzyl ether (3). The lactone (3) was subjected to a sequence of reactions to construct the THF ring: reduction of (3) to the corresponding diol, followed by protection of one of the hydroxy groups as a silyl ether, activation of the remaining hydroxy group by mesylation and ring closure of the resulting silyl ether by treatment with tetrabutylammonium fluoride gave a crystalline ether (4). As silyl ethers are particularly prone to migrate under basic conditions, there were a number of stages in the sequence that could have given rise to alternative stereochemistry at C-4; the crystal structure of the title compound (Fig. 1) firmly establishes that the closure of the THF ring proceeded by nucleophilic displacement of a C-4 mesylate by the C-1 hydroxy function of the polyol (Soengas & Fleet, 2005).



The crystal structure of (4) (Fig. 2) contains a close contact, H231...O70 = 2.49 Å, which, if it were a weak C—H...O interaction, would link molecules along 2<sub>1</sub> screw axes to form extended chains in the *b* axis direction. However, this interaction is too weak to prevent the O70/O71 disorder.

## Experimental

The benzyl ether (4) was crystallized from 60–80° petroleum spirit (m.p. 317–318 K,  $[\alpha]_D^{23} -13.2$ ,  $c$  1.0 in chloroform) (Soengas & Fleet, 2005).

## Crystal data

$C_{20}H_{28}O_6$	Mo $K\alpha$ radiation
$M_r = 364.44$	Cell parameters from 2296 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 5-27^\circ$
$a = 5.9504$ (2) Å	$\mu = 0.09$ mm $^{-1}$
$b = 14.5676$ (4) Å	$T = 170$ K
$c = 22.0403$ (8) Å	Lath, colourless
$V = 1910.52$ (11) Å $^3$	$0.90 \times 0.15 \times 0.10$ mm
$Z = 4$	
$D_x = 1.267$ Mg m $^{-3}$	

## Data collection

Bruker–Nonius KappaCCD diffractometer	2486 independent reflections
$\omega$ scans	2305 reflections with $I > -3\sigma(I)$
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)	$R_{int} = 0.037$
$T_{min} = 0.84$ , $T_{max} = 0.99$	$\theta_{max} = 27.5^\circ$
10188 measured reflections	$h = -7 \rightarrow 7$
	$k = -18 \rightarrow 18$
	$l = -28 \rightarrow 28$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F^2) + (0.03P)^2 + 0.2P]$
$R[F^2 > 2\sigma(F^2)] = 0.047$	where $P = (\max(F_o^2, 0) + 2F_c^2)/3$
$wR(F^2) = 0.075$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.99$	$\Delta\rho_{max} = 0.21$ e Å $^{-3}$
2305 reflections	$\Delta\rho_{min} = -0.20$ e Å $^{-3}$
245 parameters	Extinction correction: Larson (1970), equation 22
H-atom parameters constrained	Extinction coefficient: $7.9(11) \times 10^2$

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C23-H231 \cdots O70^i$	0.95	2.49	3.372 (2)	155

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

In the absence of significant anomalous scattering, Friedel pairs were merged, and the absolute configuration was arbitrarily assigned. Changes in illuminated volume were kept to a minimum, and were taken into account (Görlitz, 1999) by multi-scan inter-frame scaling (DENZO/SCALEPACK; Otwinowski & Minor, 1997). H atoms were all located in a difference map, but those attached to C atoms were repositioned geometrically. H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C–H in the range 0.93–0.98 Å) and displacement parameters [ $U_{iso}(H)$  in the range 1.2–1.5 times  $U_{eq}$  of the parent atom], after which they were refined with riding constraints. The crystal structure shows disorder in the C4–C8 ring. One of the O atoms was modelled as split (O70 and O71, with site-occupancy factors of 0.44 and 0.56, respectively). The consequential alternative sites for C9 and C10 were adequately accommodated by their anisotropic displacement parameters. No attempt was made to model disordered H atoms on C8, C9 and C10; stable positions were found for ‘average’ atoms during the restrained least-squares refinement.

Data collection: COLLECT (Nonius, 2001); cell refinement: DENZO/SCALEPACK (Otwinowski & Minor, 1997; data reduction:

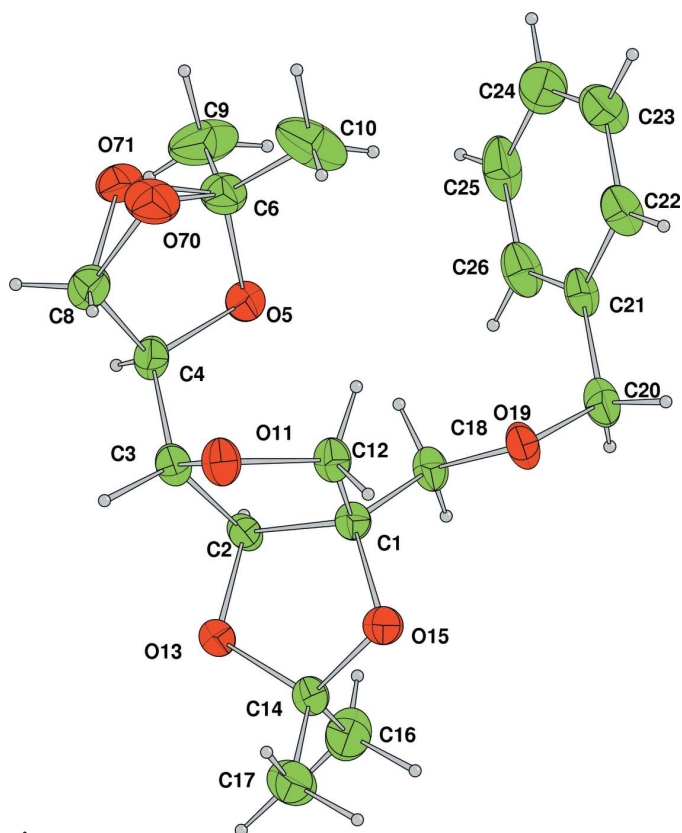


Figure 1

The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii. Both disorder components are shown.

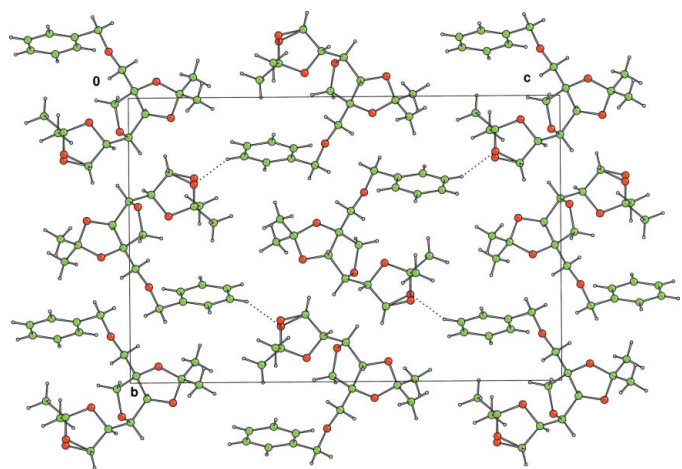


Figure 2

A projection of the crystal structure of the title compound along the  $a$  axis. Putative hydrogen bonding is shown by dotted lines.

DENZO/SCALEPACK; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: CRYSTALS (Betteridge *et al.*, 2003); molecular graphics: CAMERON (Watkin *et al.*, 1996); software used to prepare material for publication: CRYSTALS.

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