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

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Key indicators

Single-crystal X-ray study
T = 170 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.047
wR factor = 0.075
Data-to-parameter ratio = 9.4

For 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, $C_{20}H_{28}O_6$, allows a firm assignment of the stereochemistry at C-4 of formation of the tetrahydrofuran (THF) ring.

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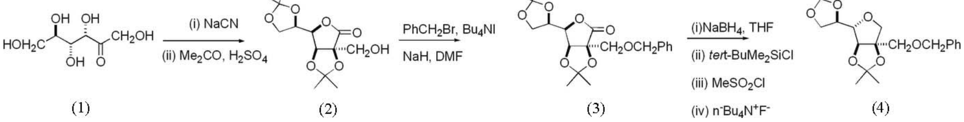
Comment

Hitherto, most carbohydrate building blocks have linear carbon chains (Lichtenthaler & Peters, 2004). However, the Kiliani reaction on each of the four ketohexoses 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 diacetonide (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 mesyl chloride 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_1 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

$C_{20}H_{28}O_6$
$M_r = 364.44$
Orthorhombic, $P2_12_12_1$
$a = 5.9504$ (2) Å
$b = 14.5676$ (4) Å
$c = 22.0403$ (8) Å
$V = 1910.52$ (11) Å^3
$Z = 4$
$D_x = 1.267$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 2296 reflections
$\theta = 5$–27°
$\mu = 0.09$ mm^{-1}
$T = 170$ K
Lath, colourless
0.90 × 0.15 × 0.10 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.84$, $T_{max} = 0.99$
10188 measured reflections

2486 independent reflections
2305 reflections with $I > -3\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 27.5°$
$h = -7 \rightarrow 7$
$k = -18 \rightarrow 18$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.075$
$S = 0.99$
2305 reflections
245 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F^2) + (0.03P)^2 + 0.2P]$
where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: Larson (1970), equation 22
Extinction coefficient: 7.9 (11) × 10^2

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

D—H···A	D—H	H···A	D···A	D—H···A
C23—H231···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 (Görbitz, 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: *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*.

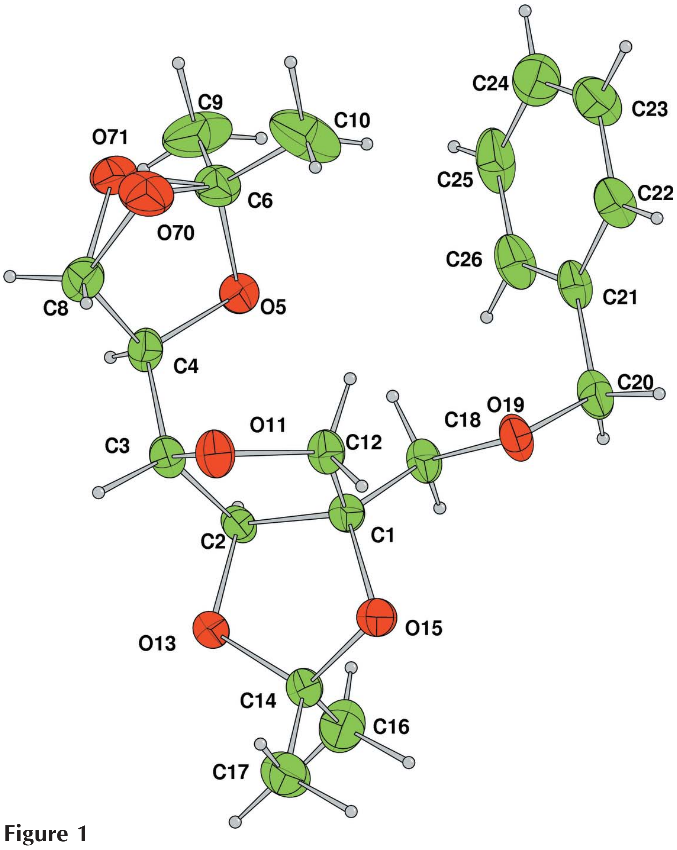


Figure 1
The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii. Both disorder components are shown.

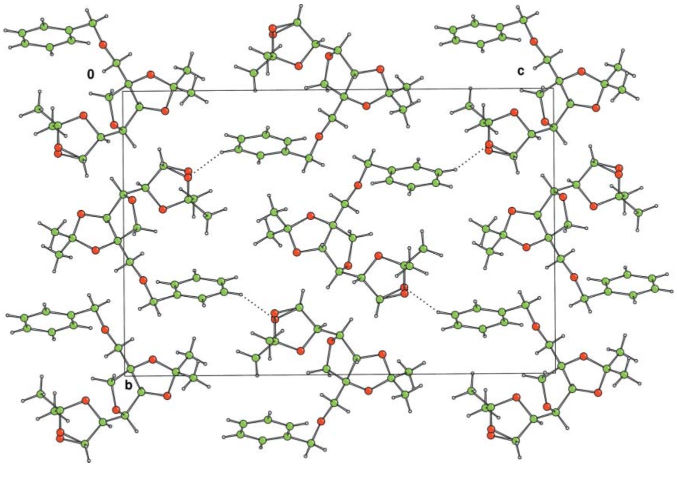


Figure 2
A projection of the crystal structure of the title compound along the *a* axis. Putative hydrogen bonding is shown by dotted lines.

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