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2,3:6,7-Di-*O*-diethylidene-D-*glycero*-L-*talo*-heptono-1,4-lactone

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The title compound, $C_{17}H_{28}O_7$, was prepared from protected D-*glycero*-D-*gulo*-heptono-1,4-lactone by tandem S_N2 displacements. The relative configuration of the crystal structure establishes that two stereocentres have been inverted; the absolute configuration was determined by the use of D-glucose as the starting material. There are three independent molecules in the asymmetric unit (Z'=3).

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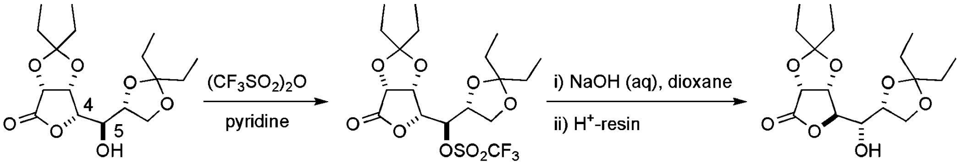
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.006 Å
R factor = 0.052
wR factor = 0.113
Data-to-parameter ratio = 7.4

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

Comment

Although carbohydrates are the most widely used chiral scaffolds (Lichtenthaler & Peters, 2004; Bols, 1996), D-*glycero*-D-*gulo*-heptono-1,4-lactone – prepared industrially from D-glucose – is the only seven-carbon sugar that is cheaply available. The value of this carbohydrate lactone as a starting material has been illustrated by the syntheses of the antibiotic gonifurfuranone (Shing *et al.*, 1992; Shing & Tsui, 1992) and a number of imino sugars (Watson *et al.*, 2001; Asano *et al.*, 2000; Fairbanks *et al.*, 1991; Myerscough *et al.*, 1992). Otherwise the use of protected seven-carbon sugars is rare (Choi *et al.*, 1991; Beacham *et al.*, 1991).



(1) (2) (3)

This paper reports the structure of the protected D-*glycero*-L-*talo*-heptono-1,4-lactone (3) which is likely to be another easily available and valuable seven-carbon sugar chiron for the enantiospecific synthesis of complex bioactive compounds. D-*glycero*-D-*gulo*-Heptono-1,4-lactone was treated with 3-pentanone to give the diketal (1) in which only the hydroxyl atom C5 is unprotected (Burke *et al.*, 1994; Burke *et al.*, 2000). Esterification of the alcohol group in (1) with triflic anhydride in the presence of pyridine gave the trifluoromethanesulfonate ester (2), which on treatment with hydroxide gives an open chain epoxide, which upon neutralization gives the title lactone (3). The X-ray crystal analysis of (3) shows that there has been an overall inversion of configuration at atoms C4 and C5 from the starting lactone (1); the absolute configuration of (3) arises from the use of D-glucose as the starting material for the synthesis of the protected lactone (1). The technique of double inversion of the stereochemistry at atoms C4 and C5 of sugar lactones used in this paper appears to be general (Hotchkiss *et al.*, 2004; van Ameijde *et al.*, 2004) and may allow

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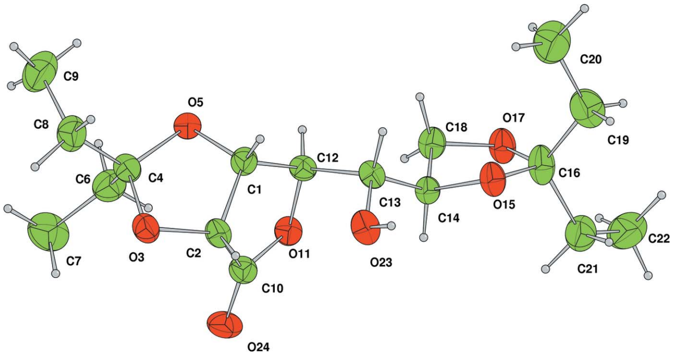

Figure 1
Molecule *A* of the title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.

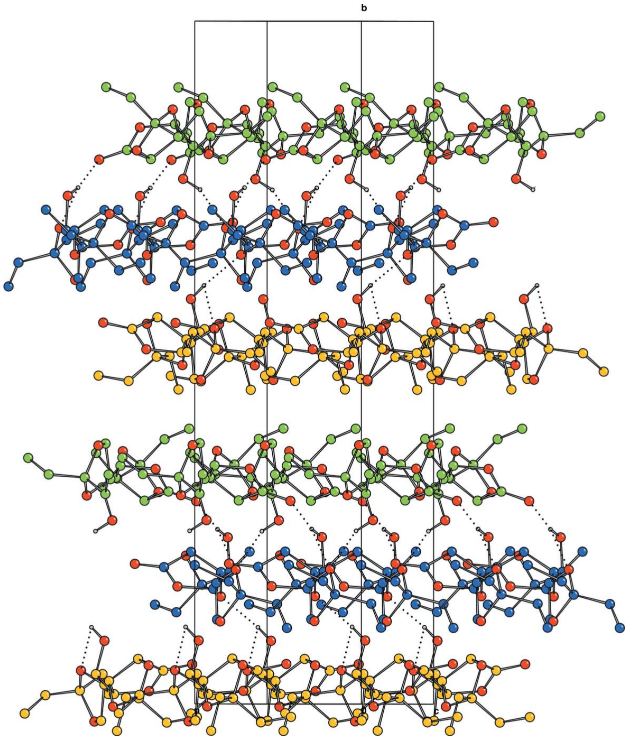

Figure 2
Layers of molecules perpendicular to the *b*-axis direction. The layers are linked by hydrogen bonds in the order molecule *B* (green C atoms) to molecule *C* (blue C atoms) to molecule *A* (orange C atoms). Layers of molecules *A* are not hydrogen-bonded to layers of molecules *B*. Hydrogen bonds are shown as dotted lines.

a considerable increase in the number of carbohydrate lactones available as synthetic intermediates.

There are three independent molecules in the asymmetric unit. The molecules C1–O24 (molecule *A*) and C201–O224 (molecule *B*) are related by an approximately pseudo twofold axis, with a pseudo-symmetry operator of form: 0.17 + *x*, 0.36 − *y*, 1.76 − *z*. On molecular superposition, the r.m.s. positional deviation is 0.90 Å, the r.m.s. bond-length deviation is 0.019 Å, and the r.m.s. torsion-angle deviation is 48.06°. Molecule C101–O124 (molecule *C*) has no rational relationship with the other molecules. The crystal structure consists of layers perpendicular to the *b* axis, with each layer composed solely of one type of molecule (Fig. 2). The layers form a type of sandwich, with the filling (molecule *C*) hydrogen-bonded to molecules *A* and *B* below and above it (Fig. 3). There is no hydrogen bonding between the layers *A* and *B*.

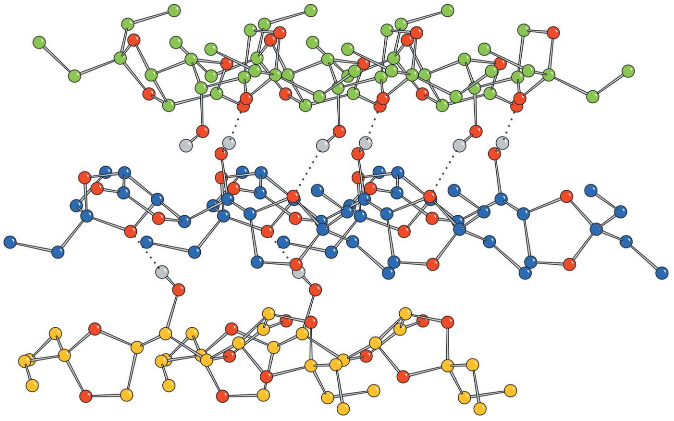

Figure 3
The asymmetric hydrogen-bonding network. Layers of molecules *B* and *C* are bonded by one donor and one acceptor hydrogen bond; layers of molecules *C* and *A* are only linked by one type of bond. H atoms not involved in hydrogen bonding have been omitted. Blue, green and yellow C atoms are as in Fig. 2 and hydrogen bonds are shown as dotted lines.

Experimental

Diketal (1)(Burke *et al.*, 2000) was converted into (2) by treatment with trifluoromethanesulfonic anhydride (1.3 eq) in the presence of pyridine (2.5 eq). Crude (2) was stirred under basic conditions (KOH, 3 eq) followed by a careful acidic work-up (Amberlyst 15) to produce (3) (Håkansson *et al.*, 2006). The title material was crystallized from heptane to yield fine colourless lath-like crystals with m.p. 366–367 K and $[\alpha]_D^{21} = -28.4$ (c=1.93, CHCl$_3$).

Crystal data

$C_{17}H_{28}O_7$
$M_r = 344.41$
Monoclinic, $P2_1$
$a = 6.7757$ (2) Å
$b = 27.7655$ (6) Å
$c = 14.8433$ (3) Å
$\beta = 101.4341$ (8)°
$V = 2737.06$ (11) Å^3
$Z = 6$
$D_x = 1.254$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 150$ K
Lath, colourless
0.40 × 0.20 × 0.06 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan
DENZO/*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.37$, $T_{\max} = 0.99$
16244 measured reflections
4828 independent reflections
4828 reflections with $I > -3\sigma(I)$
$R_{\rm int} = 0.039$
$\theta_{\max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.113$
$S = 0.97$
4828 reflections
649 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F^2) + (0.05P)^2 + 1.81P]$,
where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O223—H2225···O115^{i}	0.82	1.92	2.696 (2)	157
O123—H123···O224	0.83	1.90	2.719 (2)	166
O23—H23···O105^{i}	0.80	1.96	2.738 (2)	162

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

In the absence of significant anomalous scattering, Friedel pairs were merged and the absolute configuration was assigned from the known configuration of the starting materials.

The H atoms were all located in a difference map, but those attached to C atoms were repositioned geometrically. The 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, O—H = 0.82 Å) and U_{iso}(H) in the range 1.2–1.5 times U_{eq} of the parent atom], after which the positions were refined with riding constraints.

Data collection: *COLLECT* (Nonius, 1997-2001).; 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*.

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