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6-Deoxy-1,2:3,4-di-*O*-isopropylidene-*α*-D-*galacto*-heptodialdo-1,5-pyranose diphenyl dithioacetal

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The structure of the title compound, $C_{25}H_{30}O_5S_2$, was determined by single-crystal X-ray diffraction at 100 K. The bond angles of the dithiane unit as well as the bond lengths of the whole molecule are within the expected ranges.

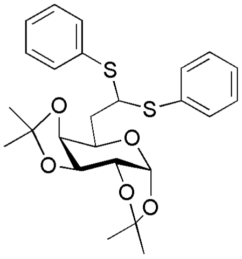
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
R factor = 0.045
wR factor = 0.107
Data-to-parameter ratio = 17.6

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

Comment

The search for carbohydrate mimics which are both functional and stable can be tackled in several ways. One possibility, for example, involves C-glycosides in which the easily hydrolysable oxygen linkages are replaced by stable carbon bridges (Meo & Osborn, 2003). These compounds are often synthesized using Umpolung chemistry, such as the dithiane method. As part of this approach, dithioacetal-functionalized sugars have been prepared that are then deprotonated and added to sugar lactones to create the key carbon bridge (McCartney *et al.*, 2003). In this report, we present the crystal structure of one such dithiane-functionalized saccharide, derived from substitution at C-6 of 1,2;3,4-di-*O*-isopropylidene-D-galactopyranose by the reaction with $LiCH(SPh)_2$.



(I)

The title compound, (I), crystallizes in the non-centrosymmetric orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. The fusion of the two dioxolane rings prevents the pyranose ring from assuming its preferred chair conformation. Instead it exhibits a distorted twist-boat geometry (Fig. 1). The bonds C1—C2 and C3—C4, each part of one of the fused five-membered rings, have close to eclipsed geometry. Their average dihedral angles are 19.5 (2) and 14.8 (2)°, respectively. All other bonds of the pyranose ring are closer to a staggered arrangement, but the deviations from the ideal angle of 60° varies greatly [from a 6.2 (2)° deviation for O4—C3—C2—O3 to a 20.1 (3)° deviation for C5—O1—C1—C2], pointing towards significant strain of the ring due to the fusion of the dioxolane rings. The two dioxolane rings themselves exhibit a slightly distorted envelope conformation, and the isopropyl groups are each slightly bent towards the less crowded side of the molecule, away from the six-membered ring.

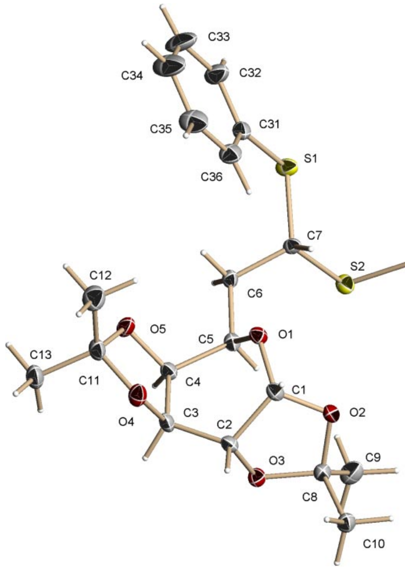


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids.

The flexible methylene spacer connecting the sugar and dithiane moieties allows the two groups to avoid each other and no unusual crowding or close contacts are observed here, a prerequisite for the dithiane to act as an effective nucleophile after deprotonation. The bond angles of the dithiane unit, as well as the bond lengths of the whole molecule are unexceptional and within the expected ranges.

Experimental

Dry pyridine (1.0 ml) was added to dry CH_2Cl_2 (40 ml) and the solution cooled to 263 K while $(CF_3SO_2)_2O$ (1.5 ml) was added dropwise. After stirring for 10 min at 263 K, a solution of 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (1.1 g) in CH_2Cl_2 (10 ml) was added dropwise; the resultant solution was stirred at room temperature for 1.5 h and then poured over ice–water (30 ml). Extraction with CH_2Cl_2 (3 × 10 ml), drying ($MgSO_4$) and evaporation gave the corresponding trifluoromethanesulfonate (1.54 g), which was used without further purification to produce the dithiane. To a solution of bis(phenylthio)methane (2.0 g) dissolved in dry tetrahydrofuran (THF, 20 ml) and cooled to 195 K was added a solution of *n*-BuLi (4.0 ml, 1.6 *M* in hexane). After stirring at low temperature for 20 min, a solution of the trifluoromethanesulfonate (1.54 g) in THF (15 ml) was added dropwise and the resulting solution stirred overnight. Quenching with saturated NH_4Cl, followed by extraction with CH_2Cl_2 (3 × 10 ml) and drying ($MgSO_4$), gave a syrup that was purified by flash chromatography on silica gel (hexane–ethyl acetate, 15:1 as eluant). The dithiane was isolated as a heavy syrup and was crystallized from methanol. ^{1}H NMR: δ 1.31 (*s*, 3H, CH_3), 1.34 (*s*, 3H, CH_3), 1.40 (*s*, 3H, CH_3), 1.60 (*s*, 3H, CH_3), 1.80 (*ddd*, 1H, H-6, J = 2.9, 10.0, 10.8 Hz), 2.3 (*ddd*, 1H, H-6′, J = 3.8, 10.0, 10.9 Hz), 4.10 (*dd*, 1H, H-4, J = 1.8, 7.7 Hz), 4.30 (*m*, 2H, H-2, H-5, J = 2.6, 5.0 Hz), 4.60 (*dd*, 1H, H-3, J = 2.6, 7.9 Hz), 4.72 (*dd*, 1H, H-7, J = 3.7, 10.6 Hz), 5.51 (*d*, 1H, H-1, J = 5.1 Hz), 7.20 (*m*, 10H, Ar-H); ^{13}C NMR: δ 25.9, 26.4, 27.2, 27.3, 37.4, 55.7, 66.3, 71.7, 72.2, 74.2, 97.6, 109.9, 110.4, 128.2, 128.8, 129.7 (double intensity), 129.8 (double intensity), 130.0, 133.0 (double intensity), 134.3, 134.5 (double intensity); MS (APCI): calculated for $C_{25}H_{30}O_5S_2$, 474.15 (M^+); found 475.2 (M^+ + H).

Crystal data

$C_{25}H_{30}O_5S_2$
M_r = 474.61
Orthorhombic, $P2_12_12_1$
a = 9.0880 (4) Å
b = 10.2194 (5) Å
c = 26.5100 (13) Å
V = 2462.1 (2) Å^3
Z = 4
D_x = 1.280 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11023 reflections
θ = 2.7–31.7°
μ = 0.25 mm^{-1}
T = 100 (2) K
Block, colourless
0.43 × 0.25 × 0.13 mm

Data collection

Bruker SMART APEX CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS* in *SAINT-Plus*; Bruker, 2003)
T_{min} = 0.702, T_{max} = 0.97
29848 measured reflections
6099 independent reflections
6072 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 28.3°
$h = -12 \rightarrow 12$
$k = -13 \rightarrow 10$
$l = -35 \rightarrow 34$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.107
S = 1.37
6099 reflections
347 parameters
H-atom parameters treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.106P)^2 + 0.6861P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Absolute structure: (Flack, 1983), 2639 Friedel pairs
Flack parameter = 0.04 (7)

Methyl H atoms were placed in calculated positions, with a C—H bond distance of 0.98 Å, and were refined as riding, with U_{iso}(H) = 1.5U_{eq}(H); all other H atoms were located in a difference density Fourier map and their positions were refined with U_{iso}(H) = 1.2U_{eq}(H); refined C—H distances are in the range 0.87–0.97 Å. The s.u. values of the cell parameters are taken from the software, recognizing that the values are unreasonably small (Herbstein, 2000).

Data collection: *SMART* (Bruker, 1997–2002); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT–Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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