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Note

Crystal and molecular structure of 1,6:3,4-dianhydro-2-*O*-*p*-tolylsulfonyl-β-D-galactopyranose

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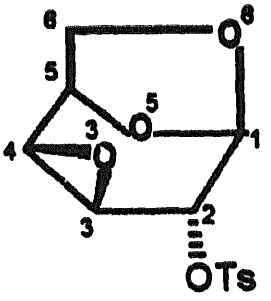
The opening of oxirane rings of dianhydro sugars with high regioselectivity can afford many chiral intermediates for controlling asymmetric syntheses [1–5]. Here, we report the crystal structure of 1,6:3,4-dianhydro-2-*O*-*p*-tolylsulfonyl-β-D-galactopyranose (**1**) which may provide helpful information for the study of the relationship between the structure and NMR spectroscopic data [6].



1

Data collection and crystallographic parameters for **1** are given in Table 1 and the positional and isotropic thermal parameters for the non-hydrogen atoms in Table 2. The

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Table 1
Data collection and crystallographic parameters for 1,6:3,4-dianhydro-2-*O*-*p*-tolylsulfonyl-β-D-galactopyranose

Empirical formula	$C_{13}H_{14}O_6S_1$
Formula weight	298.31
Crystal system	Orthorhombic
Cell dimensions (Å)	
a	6.281
b	13.467
c	15.751
V (Å^3)	1319.0(5)
Space group	$P2_12_12_1$
Z	4
Calculated density (g/cm^3)	1.50
F(000)	624
μ(MoK α) (cm^{-1})	2.56
Diffractometer	Enraf-Nonius CAD4
Radiation	MoK α (λ = 0.71069) Graphite-Monochromated
Temperature (°C)	23
Scan mode	$\omega/2\theta$
ω-Scan width (deg)	0.45 + 0.35 tan θ
2-Theta(max) (deg)	53.9
No. observations [I > 3.00sig(I)]	1481
No. variables	224
Residuals: *R*; *Rw*	0.048; 0.050
S	1.43
Maximum shift in final cycle	0.12
Largest peak in final diff. map (e/Å^3)	0.22

molecular structure is shown in Fig. 1, and the molecular packing diagram in Fig. 2. The mean C–O distance 1.432(6) Å and C–C bond length in the phenyl ring is 1.383(5) Å. The mean double S–O bond length is 1.418(3) Å, and the single S–O bond length 1.580(3) Å. The S–C distance is 1.747(3) Å. In the oxirane ring, all angles are close to 60°. The bond lengths and bond angles in the 1,6:3,4-dianhydro-β-D-galactopyranose moiety are normal except for the C-1–C-2 bond length 1.537(4) Å which is rather longer than the other C–C bond lengths, and the C-1–O-1 bond length 1.384(4) Å which is shorter than a normal C–O single bond. O-6 and O-3 reside on the same side of the pyranose ring, and the O-6 · · · O-3 interdistance is 3.411(4) Å.

Most derivatives of 1,6-anhydro-β-D-glucopyranose adopt the $^1C_4$ or $B_{3,0}$ conformation for the pyranose ring [7]. However, the pyranose ring of **1** is in a half-chair conformation. C-1, C-2, C-3, C-4 and C-5 form a plane and the mean deviation from the least squares plane is 0.0176(2) Å with O-5 at 0.8187 Å from the plane. Obviously, the 3,4-oxirane ring prevents the pyranose ring from adopting an $^1C_4$ or $B_{3,0}$ conformation. The 1,6-anhydro ring is nearly in an envelope conformation, with C-5 out of the O-5, O-6, C-1, C-6 plane. The angles between planes are: 1,6-anhydro ring–pyranose 94.7°; 3,4-oxirane–pyranose 103.7°; phenyl–pyranose 119.4°; 3,4-oxirane–1,6-anhydro ring 154.4°; phenyl–1,6 anhydro ring 78.2°, and 3,4-oxirane–phenyl 107.0°.

Table 2
Atomic coordinates and thermal parameters for **1**

Atom	x	y	z	B_{eq} (Å^2) [a]
S-1	0.3966(1)	0.15939(6)	0.74145(5)	3.75(3)
O-5	0.3135(5)	0.4518(2)	0.8305(1)	4.3(1)
O-6	0.5436(4)	0.4038(2)	0.9321(2)	4.9(1)
O-3	0.1353(5)	0.3325(2)	0.9988(2)	5.7(1)
O-2	0.2567(4)	0.2440(2)	0.7838(1)	3.61(9)
O-4	0.6183(4)	0.1798(2)	0.7557(2)	4.9(1)
O-7	0.3156(5)	0.1547(2)	0.6579(1)	5.4(1)
C-1	0.4495(6)	0.3749(3)	0.8548(2)	3.6(1)
C-2	0.3182(6)	0.2795(2)	0.8679(2)	3.2(1)
C-3	0.1137(7)	0.2997(3)	0.9136(2)	4.5(2)
C-4	0.0627(6)	0.4018(3)	0.9360(3)	4.7(2)
C-5	0.2200(6)	0.4796(2)	0.9101(2)	4.0(2)
C-6	0.4153(6)	0.4827(3)	0.9661(2)	4.4(2)
C-11	0.3252(5)	0.0519(2)	0.7968(2)	3.0(1)
C-12	0.1229(6)	0.0109(3)	0.7843(2)	3.9(1)
C-13	0.0718(4)	0.0776(3)	0.8243(2)	4.1(1)
C-14	0.2164(6)	0.1245(2)	0.8777(2)	3.6(1)
C-15	0.4171(6)	0.0812(2)	0.8890(2)	4.0(1)
C-16	0.4710(6)	0.0068(2)	0.8494(2)	3.6(1)
C-17	0.159(1)	0.2196(3)	0.9215(2)	5.1(2)

[a] $B_{eq} = 4/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + 2ab\cos\gamma\ B(1,2) + 2ac\cos\beta\ B(1,3) + 2bc\cos\alpha\ B(2,3)]$.

The endocyclic torsion angles are O-5–C-1–C-2–C-3 −42.6(4)°, C-1–C-2–C-3–C-4 2.3(5)°, C-2–C-3–C-4–C-5 0.8(6)°, O-5–C-5–C-4–C-3 34.1(5)°, C-2–C-1–O-5–C-5 78.4°, and C-1–O-5–C-5–C-4 −73.0(3)°. The torsion angles between vicinal hydrogens

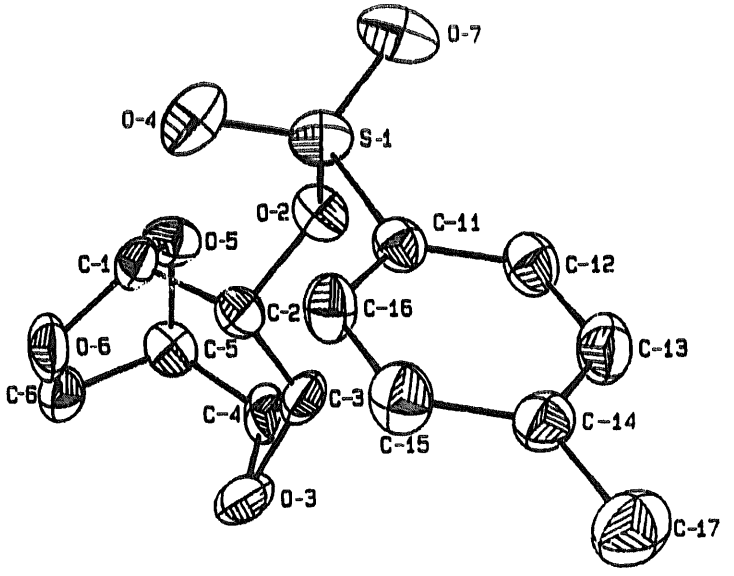

Fig. 1. Molecular conformation and atom numbering for 1,6:3,4-dianhydro-2-*O*-*p*-tolylsulfonyl-β-D-galacto-pyranose. The 40% probability thermal ellipsoids are shown for carbon and oxygen atoms.

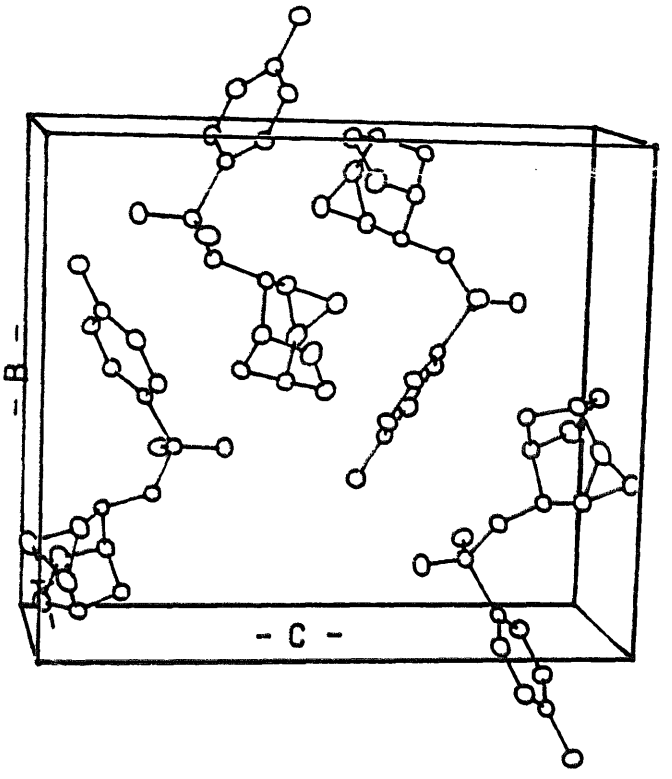

Fig. 2. The molecular packing diagram for 1,6:3,4-dianhydro-2-*O*-*p*-tolylsulfonyl-β-D-galactopyranose.

are H-1–C-1–C-2–H-2 70(3)°, H-2–C-2–C-3–H-3 −76(4)°, H-3–C-3–C-4–H-4 −8(5)°, H-4–C-4–C-5–H-5 −1(4)°, H-5–C-5–C-6–H-6 (*exo*) −33(3)°, and H-5–C-5–C-6–H-6 (*endo*) 96(4)°. Torsion angles for O-6–C-1–C-2–O-2 and O-3–C-3–C-2–O-2 are *anti* [170.3(3) and 178.1(3)°, respectively].

1. Experimental

Crystals of 1,6:3,4-dianhydro-2-*O*-*p*-tolylsulfonyl-β-D-galactopyranose (**1**), prepared according to [8], were dissolved in $CHCl_3$ and allowed to evaporate for several days to give single crystals of **1** with approximate dimensions 0.75 × 0.65 × 0.35 mm which were used for X-ray analysis. The structure was solved by direct methods (MITHRIL) using the program TEXSAN [9–11]. All non-hydrogen atoms were refined anisotropically with the full matrix least squares method. Hydrogen atoms were included by difference Fourier synthesis and refined with isotropic thermal parameters.

Refinement was based on F (structure amplitudes) to minimize the function $\Sigma w(|Fo| - |Fc|)^2$ with $w = 1/\sigma^2(Fo)$, and 224 parameters were refined. The refinement led to a final convergence with $R = 0.041$ and $Rw = 0.050$. The maximum $\Delta/\sigma = 0.12$, and the goodness of fit parameter $S = 1.43$. Max and min heights in the final difference Fourier synthesis were 0.22 and 0.26 e/Å^3.

Acknowledgements

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