Data collection

Stoe Imaging Plate Diffraction System (IPDS) diffractometer
IPDS scans
Absorption correction: Gaussian (*HABITUS*; Herrendorf, 1993)
$T_{\min} = 0.715$, $T_{\max} = 0.931$

6577 measured reflections
1959 independent reflections
1726 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$
$\theta_{\max} = 25.95°$
$h = -11 \rightarrow 11$
$k = -21 \rightarrow 21$
$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.110$
$S = 1.063$
1959 reflections
113 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 0.6557P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.352$ e Å^{-3}
$\Delta\rho_{\min} = -0.406$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—C1	1.747 (2)	C11—C12	1.480 (5)
S1—S2	2.069 (1)	C1—N2	1.366 (3)
S2—C2	1.735 (3)	N2—C2	1.382 (3)
S3—C2	1.624 (3)	N2—C21	1.486 (3)
N1—C1	1.292 (3)	C21—C22	1.505 (4)
N1—C11	1.466 (3)		
C1—S1—S2	93.55 (9)	C1—N2—C2	118.7 (2)
C2—S2—S1	96.17 (9)	N2—C2—S2	114.6 (2)
N2—C1—S1	116.8 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl$^{\rm i}$	0.81 (3)	2.35 (3)	3.140 (3)	166 (3)

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

Atom positions were obtained by direct methods as well as from Patterson maps. All non-H atoms were refined anisotropically. The H atom attached to the N atom was located from a $\Delta\rho$ map and refined isotropically. All other H atoms were treated as riding atoms.

Data collection: *IPDS* (Stoe & Cie, 1995). Cell refinement: *IPDS*. Data reduction: *IPDS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1288). Services for accessing these data are described at the back of the journal.

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1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranosyl (*S*)-cyclohexanesulfinate

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Abstract

The first crystal structure of a chiral diacetone-D-glucose (DAG) sulfinate, $C_{18}H_{30}O_7S$, is reported. The absolute configuration (*S*) of the S atom is assigned. Previous assignments of the stereochemistry of analogous DAG sulfinates were only made indirectly by their transformation into known sulfoxides *via* an S_N2 process.

Comment

Sulfoxides are very useful tools as chiral inductors in asymmetric synthesis. One of the major methods of obtaining such molecules involves the reaction of a chiral sulfinate with a Grignard reagent. This transformation, called the Andersen synthesis (Andersen, 1962, 1964), proceeds with inversion of configuration at sulfur. It

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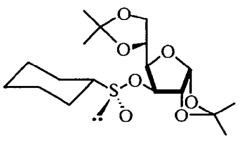
was mostly exploited with menthyl *p*-toluenesulfinate (Mioskowski & Solladié, 1980), giving access to various chiral aromatic sulfoxides.

Fernandez *et al.* (1992) recently developed a very efficient and cheap preparation of chiral sulfinates using diacetone-D-glucose (DAG) as the sole source of chirality. Guerrero-de la Rosa *et al.* (1995) improved the method for large-scale preparations. The reaction is diastereoselective and leads to either diastereomer by changing the nature of the base. Diisopropylethylamine and pyridine lead to sulfinates with an *S* and *R* configuration at sulfur, respectively. The transformation of the chiral DAG sulfinates into known sulfoxides allowed the authors to assign their stereochemistry. We recently reported a new asymmetric version of the thio-Claisen rearrangement, stereo-controlled by a racemic alkylsulfinyl group (Alayrac *et al.*, 1997). In order to extend our methodology to the enantiopure series, we needed to prepare chiral dialkyl sulfoxides. Thus, we applied the method described by Fernandez *et al.* (1992) and were able to prepare the previously unreported DAG cyclohexanesulfinate, (I), by reaction of racemic cyclohexanesulfinyl chloride with DAG in the presence of diisopropylethylamine. Crystallization was carried out from hot petroleum ether.



(I)

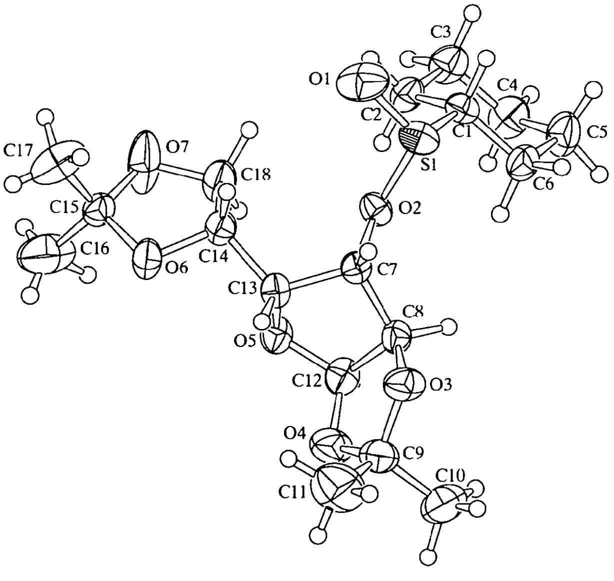


Fig. 1. *ORTEP*II drawing (Johnson, 1976) of the title compound with 45% probability displacement ellipsoids.

The title molecule (Fig. 1) possesses six asymmetric centres, *i.e.* the C atoms C7, C8, C12, C13 and C14, and the S atom S1. The absolute crystal structure is determined with respect to the known configuration of the C atoms of the sugar moiety. As expected from the choice of the base, the configuration at sulfur is (*S*). This is the first direct assignment of the stereochemistry of a chiral DAG sulfinate.

Bond distances and angles (Table 1) do not show any large deviations from expected values (Kojic-Prodic *et al.*, 1984). A sterically favourable conformation where the cyclohexyl and glucose moieties stand away from each other occurs in the crystalline state, as indicated by the torsion angle about the S1—O2 bond [C1—S1—O2—C7 = 157.2 (1)°].

The lone pair on sulfur could not be located in the difference Fourier syntheses.

Experimental

The title compound was prepared according to the method of Fernandez *et al.* (1992). To a cooled (233 K) solution of cyclohexanesulfinyl chloride (5 g, 30 mmol, 1.4 equivalents), prepared according to the method of Youn & Herrmann (1986), in anhydrous THF (40 ml) was added dropwise, under vigorous stirring, a mixture of diacetone-D-glucose (5.57 g, 21.4 mmol, 1 equivalent) and $^{i}\mathrm{Pr_2EtN}$ (4.5 ml, 3.32 g, 25.7 mmol, 1.2 equivalents) in dry THF (40 ml). The reaction mixture was stirred at 233 K for 1 h and was then quenched with water (25 ml) and diluted with CH_2Cl_2 (50 ml). The aqueous layer was extracted with CH_2Cl_2 (25 ml). The combined organic extracts were washed successively with 5% aqueous HCl (25 ml), 2% aqueous $NaHCO_3$ (25 ml) and brine (25 ml), then dried on Na_2SO_4 and concentrated to dryness to afford the crude sulfinate (9.15 g, 78% yield) as a white solid. The diastereomeric ratio was determined by ^{1}H NMR analysis; *R*/*S* = <5/>95. This ratio was similar when the reaction was performed at 195 K. The compound was isolated as colourless needles (5.4 g, 46% yield) by recrystallization from hot petroleum ether [m.p. 387 K, $[\alpha]_D^{22} = -60°$ (*c* = 4, acetone)]. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.32, 1.35, 1.44 and 1.52 [4 *s*, 12H, $OC(CH_3)_2O$], 1.20–2.05 (*m*, 10H, CH_2), 2.62 (*m*, 1H, CHSO), 3.96–4.15 (*m*, 2H, H-6), 4.26–4.35 (*m*, 2H, H-4 and H-5), 4.59 (*d*, *J* = 3.6 Hz, 1H, H-2), 4.72 (*d*, *J* = 2.1 Hz, 1H, H-3), 5.90 (*d*, *J* = 3.6 Hz, 1H, H-1); ^{13}C NMR ($CDCl_3$, 62 MHz): δ 24.4, 24.6, 25.1 and 25.21 (4 CH_2), 25.25 [1 $OC(CH_3)_2O$], 25.6 (1 CH_2), 26.3, 26.7 and 26.8 [3 $OC(CH_3)_2O$], 64.1 (CHSO), 66.7 (C-6), 72.6 (C-5), 79.9 (C-3), 80.5 (C-4), 83.6 (C-2), 105.0 (C-1), 109.2 and 112.5 [2 $OC(CH_3)_2O$]; MS [CI, isobutane, *m*/*z* (%)]: 391 (MH^+, 100), 333 (23), 261 (32), 131 (13), 89 (12); HRMS: *m*/*z* = 391.1802, $C_{18}H_{31}O_7S$ (MH^+) requires 391.1790; elemental analysis calculated for $C_{18}H_{30}O_7S$: C 55.36, H 7.74, O 28.68, S 8.21%; found: C 55.24, H 7.73, O 28.75, S 8.25%.

Crystal data

$C_{18}H_{30}O_7S$

$M_r = 390.49$

Mo $K\alpha$ radiation

$\lambda = 0.7107$ Å

Orthorhombic
$P2_12_12_1$
$a = 8.792$ (2) Å
$b = 12.481$ (2) Å
$c = 18.440$ (4) Å
$V = 2023.5$ (6) Å^3
$Z = 4$
$D_x = 1.282$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 10.1-11.9°$
$\mu = 0.195$ mm^{-1}
$T = 293$ K
Cubic fragment from a prism
0.40 × 0.38 × 0.32 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
3346 measured reflections
3346 independent reflections
2449 reflections with $I > 2\sigma(I)$

$\theta_{max} = 29.96°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 25$
2 standard reflections every 120 reflections intensity decay: −4.61%

Refinement

Refinement on F
$R = 0.040$
$wR = 0.045$
$S = 1.854$
2449 reflections
236 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o) + 0.00022|F_o|^2]$
$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: Zachariasen (1967, 1968)
Extinction coefficient: 1.3 (1) × 10^{-6}
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—O1	1.460 (2)	C2—C3	1.525 (3)
S1—O2	1.640 (1)	C3—C4	1.512 (3)
S1—C1	1.803 (2)	C4—C5	1.504 (3)
O2—C7	1.448 (2)	C5—C6	1.538 (3)
C1—C2	1.513 (3)	C7—C8	1.519 (3)
C1—C6	1.517 (3)	C7—C13	1.521 (3)
O1—S1—O2	107.3 (1)	C2—C3—C4	111.3 (2)
O1—S1—C1	106.56 (9)	C3—C4—C5	111.8 (2)
O2—S1—C1	94.89 (8)	C4—C5—C6	111.8 (2)
S1—O2—C7	114.8 (1)	C1—C6—C5	110.0 (2)
S1—C1—C2	113.5 (1)	O2—C7—C8	107.5 (1)
S1—C1—C6	110.6 (1)	O2—C7—C13	110.6 (1)
C2—C1—C6	111.9 (2)	C8—C7—C13	101.4 (2)
C1—C2—C3	109.4 (2)		

H atoms were located from difference Fourier syntheses but were not refined.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1019). Services for accessing these data are described at the back of the journal.

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A 2:1 co-crystal of 5-(2-pyridyl)-1*H*-1,2,4-triazole and 1,4-dihydroxybenzene

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Abstract

In the 2:1 co-crystal of 5-(2-pyridyl)-1*H*-1,2,4-triazole (pyt) and 1,4-dihydroxybenzene (dhb), $2C_7H_6N_4\cdot C_6H_6O_2$, the pyt molecules form two independent N—H···N hydrogen-bonded chains. The dhb molecules act as hydrogen-bonding bridges between the two pyt chains *via* two O—H···N hydrogen bonds. The complex is further stabilized by a number of weaker interactions, including C—H···N, C—H···O and C—H···π interactions.

Comment

Recently, the crystal structure of a co-crystal between 1,4-dihydroxybenzene (dhb; hydroquinone) and

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