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(−)-(3*S*)-4-(2-{[4,4-Dimethoxy-6-(benzyloxymethyl)perhydropyran-2-yl]methyl}-1,3-dithian-2-yl)-4-methyl-3-(1,1,2,2-tetramethyl-1-silapropoxy)-pentan-1-ol

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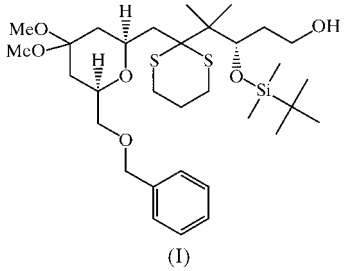
The absolute configuration was determined for the title compound, (−)-$C_{32}H_{56}O_6S_2Si$, (I), which was prepared in a synthetic study on the natural products bryostatins. Two independent molecules show similar conformations, except for the orientation of the methoxy groups.

Comment

The absolute configuration was determined for the title compound, which was prepared in a synthetic study on the natural products bryostatins. A synthetic study on bryostatin 3 has been reported (Obitsu *et al.*, 1998).



(I)

Experimental

The optically active title compound was prepared by the authors in a synthetic study on bryostatins (Ohmori *et al.*, 2000). The angle of rotation $[\alpha]_D^{22}$ is −6.24° (*c* 1.0, $CHCl_3$). Crystals were grown from a hexane/ethyl acetate solution.

Crystal data

$C_{32}H_{56}O_6S_2Si$	D_x = 1.167 Mg m^{-3}
M_r = 629.00	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 25 reflections
a = 6.878 (3) Å	θ = 14.3–15.0°
b = 19.658 (3) Å	μ = 0.220 mm^{-1}
c = 26.493 (2) Å	T = 298 (1) K
β = 91.33 (2)°	Plate-like, colourless
V = 3581.1 (17) Å^3	0.7 × 0.6 × 0.1 mm
Z = 4	

Data collection

Rigaku AFC-5 diffractometer	R_{int} = 0.030
ω scans	θ_{max} = 25°
Absorption correction: by integration (Coppens *et al.*, 1965)	$h = 0 \rightarrow 8$
T_{min} = 0.881, T_{max} = 0.977	$k = 0 \rightarrow 23$
7078 measured reflections	$l = -31 \rightarrow 31$
6497 independent reflections	3 standard reflections every 100 reflections
4622 reflections with $I > 2\sigma(I)$	intensity decay: 1.0%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2 + 1.2827P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R(F)$ = 0.051	$(\Delta/\sigma)_{max}$ = 0.017
$wR(F^2)$ = 0.130	$\Delta\rho_{max}$ = 1.00 e Å^{-3}
S = 1.02	$\Delta\rho_{min}$ = −0.29 e Å^{-3}
6497 reflections	Absolute structure: Flack (1983), no Friedel pairs
745 parameters	Flack parameter = 0.0 (1)
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

S1—C10	1.805 (7)	Si3—O8	1.648 (4)
S1—C13	1.859 (5)	Si3—C36	1.856 (8)
S2—C12	1.807 (7)	Si3—C37	1.864 (10)
S2—C13	1.843 (6)	Si3—C38	1.878 (8)
S51—C60	1.807 (7)	Si53—O58	1.663 (5)
S51—C63	1.861 (5)	Si53—C86	1.845 (8)
S52—C62	1.829 (7)	Si53—C87	1.853 (9)
S52—C63	1.836 (5)	Si53—C88	1.876 (8)
Si3—O8—C33	128.8 (4)	Si53—O58—C83	128.8 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
O9—H9···O4^{i}	0.97 (5)	2.17 (6)	3.035 (6)	147 (5)
O9—H9···O7^{i}	0.97 (5)	2.41 (4)	3.188 (7)	136 (5)
O59—H59···O54^{ii}	0.98 (5)	2.30 (6)	3.096 (6)	138 (5)
O59—H59···O57^{ii}	0.98 (5)	2.28 (5)	3.082 (7)	139 (5)

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

Hydroxyl H atoms were located from a difference synthesis and their positional parameters were refined with a restraint of O—H = 0.98 Å (s.u. 0.01 Å) and with U_{iso}(H) = 1.2U_{eq}(parent atom). The other H-atom positional parameters were calculated geometrically and fixed with U_{iso}(H) = 1.2U_{eq}(parent atom). A maximum residual density of 1.00 e Å^{-3} was located 1.11 Å from the C88 atom, suggesting an orientational disorder of the tetramethylsilapropoxy

group. The absolute structure was determined based on a Flack parameter value of 0.0 (1), which is consistent with the expected absolute configuration of 3*S* produced by Sharpless asymmetric epoxidation protcol. The two independent molecules are related approximately by a translation of (0.47, −0.05, 0.50), except for the methoxy O atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: SiR92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *TEXSAN*.

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