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1-(5-Methanesulfinyl-2,2,6-trimethyl-3a,3b,4,5,6,8a-hexahydro-1,3,8-trioxacyclopenta[*a*]inden-5-yl)hexan-1-ol

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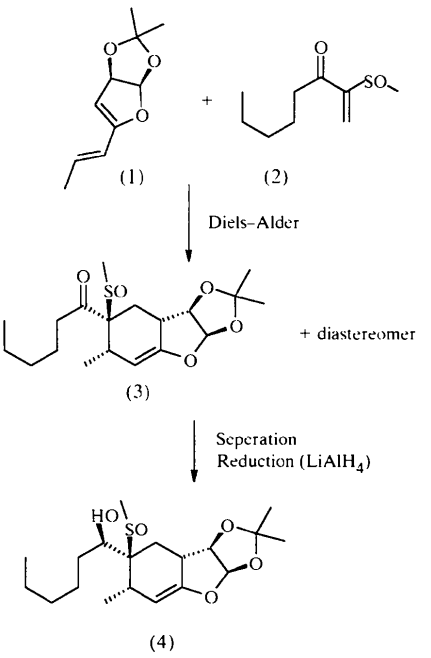
Abstract

The title compound, $C_{19}H_{32}O_5S$, is obtained by selective reduction of the keto group of an adduct which results from a Diels–Alder reaction between a dienic lactone and an ethylenic keto-sulfoxide. The absolute configuration of the stereocentres is established.

Comment

The Diels–Alder reaction of 3,5,6-trideoxy-1,2-*O*-isopropylidene-α-D-glycerohepta-3,5-dienofuranose, (1), obtained from D-(+)-glucose, with 2-methylsulfinyl-oct-1-en-3-one, (2), gives a 64/36 diastereomeric mixture [1-(5-methanesulfinyl-2,2,6-trimethyl-3a,3b,4,5,6,-8a-hexahydro-1,3,8-trioxacyclopenta[*a*]inden-5-yl)hexan-1-ol, (3); see reaction scheme below]. The main product can be separated by liquid chromatography on silica gel and reduced selectively by $LiAlH_4$ to give the title compound, 1-(5-methanesulfinyl-2,2,6-trimethyl-3a,3b,4,5,6,8a-hexahydro-1,3,8-trioxacyclopenta[*a*]inden-5-yl)hexan-1-ol, (4). The synthesis does not affect the configuration of the glucosidic part of the molecule and, consequently, the known configuration of C2 and C3 was used to determine the absolute configuration of the crystal. The configuration of the five other stereocentres is shown to be 1*S*,4*R*,5*S*,6*S*,7*S* (SO, C4, C7, C8 and C10, respectively). This configuration results from selective reduction at C10 and from an exclusive *exo* approach during the Diels–Alder reaction. Atoms C4, C5, C6, C7 and O5 are located in a plane due to the double bond between C5 and C6; the deviations (Å) from the mean plane are −0.005, 0.021, −0.005, −0.002 and −0.009, respectively. Selected bond distances are given in Table 1. This compound will be used as an intermediate in the total synthesis of ivanguline.



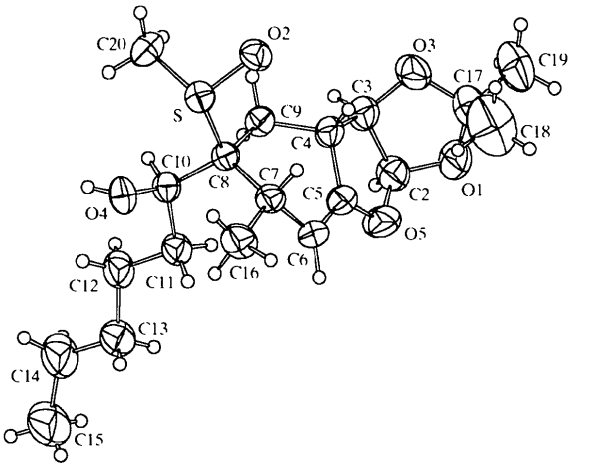


Fig. 1. *ORTEP* plot (Johnson, 1965) of (4). For the sake of clarity, the values of the displacement parameters of the H atoms have been divided by ten. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

Recrystallization from ether gave the title compound as colourless crystals. A parallelepipedic crystal [(100)(010)(001)] was chosen for X-ray analysis.

Crystal data

$C_{19}H_{32}O_5S$
M_r = 372.51
Orthorhombic
$P2_12_12_1$
a = 7.150 (2) Å
b = 10.284 (2) Å
c = 27.726 (2) Å
V = 2038.8 (7) Å^3
Z = 4
D_x = 1.214 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 32 reflections
θ = 30–32°
μ = 0.183 mm^{-1}
T = 293 (2) K
Prism
0.68 × 0.47 × 0.32 mm
Colourless

Data collection

Stoe Siemens AED-2 diffractometer
ω–θ/2 scans
Absorption correction: none
3093 measured reflections
2706 independent reflections
2038 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 27.51°
$h = -1 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = 0 \rightarrow 36$
3 standard reflections
frequency: 60 min
intensity decay: 10.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.117
S = 1.042
2706 reflections
279 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 2.0P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.011$
$\Delta\rho_{max}$ = 0.158 e Å^{-3}
$\Delta\rho_{min}$ = −0.162 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0004 (12)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.13 (13)

Table 1. *Selected bond lengths (Å)*

S—O2	1.513 (2)	C5—C6	1.327 (4)
S—C20	1.793 (3)	C6—C7	1.518 (4)
S—C8	1.869 (3)	C7—C16	1.536 (4)
O1—C2	1.379 (4)	C7—C8	1.570 (4)
O1—C17	1.422 (4)	C8—C9	1.541 (4)
O3—C3	1.403 (4)	C8—C10	1.549 (4)
O3—C17	1.427 (4)	C10—C11	1.525 (4)
O4—C10	1.438 (3)	C11—C12	1.528 (4)
O5—C5	1.381 (3)	C12—C13	1.510 (5)
O5—C2	1.442 (4)	C13—C14	1.519 (5)
C2—C3	1.539 (4)	C14—C15	1.483 (7)
C3—C4	1.544 (4)	C17—C19	1.479 (5)
C4—C5	1.494 (4)	C17—C18	1.489 (6)
C4—C9	1.520 (4)		

An ω–θ/2 step-scan mode in N steps of 0.035° was used, with N_{min} = 37, time per step t_{min} = 1.0 s and t_{max} = 4.0 s, aperture D = 4.0 mm, and standard reflections 228, $\bar{2}28$ and $22\bar{8}$. A solution with all non-H atoms was found with the multi-solution tangent direct methods of *SHELXS*86 (Sheldrick, 1990). Successive refinements and difference Fourier maps allowed the S, O and C atoms to be distinguished (R = 0.160). H atoms were refined as rigid groups associated with their neighbours (R = 0.039) and their displacement parameters were restrained to be equal in order to decrease the number of refined parameters.

Data collection: *DIF*4 (Stoe & Cie, 1987). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1985). Program(s) used to solve structure: *SHELXS*86. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1011). Services for accessing these data are described at the back of the journal.

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N^4,5-Dimethyl-2′-deoxycytidine

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Abstract

In the title molecule ($C_{11}H_{17}N_3O_4$) the pyrimidine ring adopts the anticlinal ($-ac$) conformation [χ = 245.10 (18)°]. The deoxyribose sugar ring has the C2′-*endo* (^2E) envelope conformation. The pseudorotational parameters of the deoxyribose sugar ring are P = 168.92 (2)° and τ_m = 33.86 (2)°. The exocyclic side chain at C5′ has the g^+ conformation [γ = 55.0 (2)°].