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(3a*S*,4*S*,5*R*,7a*S*,1′*R*,2a′*S*,6′*S*,6a′*S*)-5-(2′,5′-Dioxo-2a′-methyl-6′,6a′-epoxyperhydro-inden-1′-yl)-3a,4-epoxy-5-hydroxy-7a-methylperhydro-1*H*-inden-1-one

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.060
wR factor = 0.141
Data-to-parameter ratio = 8.3

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

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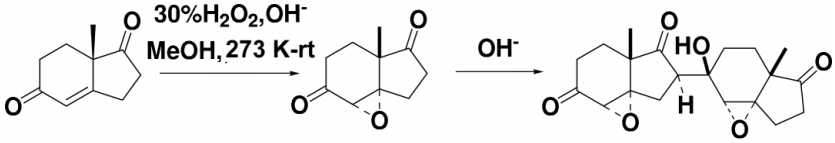
In the molecular structure of the title compound, $C_{20}H_{24}O_6$, there are eight chiral C atoms. Since an enantiomerically pure starting material was used, it can be confirmed that the synthesis of the title compound is stereoselective. There is an intermolecular hydrogen bond in the structure, leading to the formation of two-dimensional molecular layers.

Comment

Hajos' ketone, (1) (Hajos & Parrish, 1985), is one of the most useful building blocks for the synthesis of many natural products of biological importance (Lajunen & Koskinen, 2000). During our research on the epoxidation of (1) (Enev *et al.*, 1997), we accidentally found that, besides the product (2), a new compound (3) was produced by one-pot condensation in the presence of alkali. The title compound, (3), has not been reported in the literature.



(1) (2) (3)

The reaction position of the intermolecular condensation and the structure of (3) were confirmed by ^{1}H NMR, ^{13}C NMR and X-ray single-crystal diffraction analysis. Since enantiomerically pure (7a*S*)-(1) was used as the starting material, the epoxidation of (1) afforded a single epoxy ketone (3a*S*,4*S*,7a*S*)-(2) (Trost & Salzmann, 1975). The nucleophilic addition of enantiomerically pure compound (2) is stereofacially selectively added to the *anti* position of the carbonyl group in the cyclohexane ring to give the enantiomerically pure compound (3) [compound (3) could also be purified by column chromatograph on silica gel, with petroleum ether–

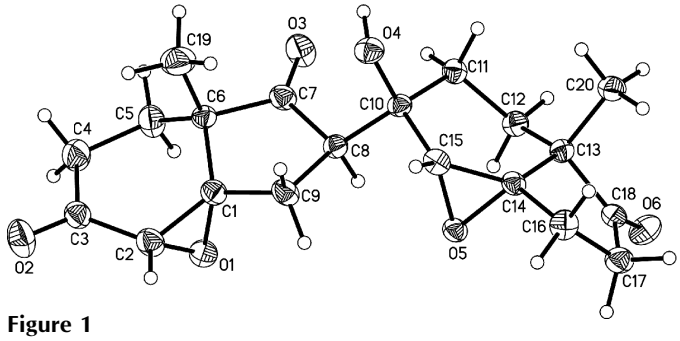


Figure 1
The molecular structure of (3), with 30% probability displacement ellipsoids.

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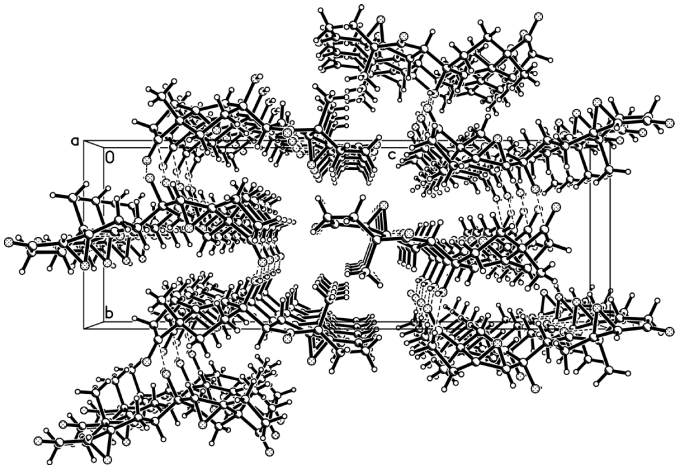

Figure 2
The packing of (3), viewed down the *a* axis.

ethyl acetate (5:1) as eluant. The optical rotation of (3) is $[a]$ = +21.90° (c = 0.092 g ml^{-1}, $CHCl_3$). Therefore, it is confirmed that the intermolecular condensation of (2), forming the title compound (3a*S*,4*S*,5*R*,7a*S*,1′*R*,2a′*S*,6′*S*,6a′*S*)-(3), is stereoselective (see scheme). The molecule of (3) is rigid and its configuration cannot be inverted. It is expected that (3) could be used as an important synthetic intermediate. The molecular structure of the title compound, (3), is shown in Fig. 1. There are eight chiral C atoms, *viz*. C1, C2, C6, C8, C10, C13, C14 and C15. All the bond lengths and angles have normal values. There is an intermolecular hydrogen bond [O4—H4···O6^{i}; symmetry code: (i) $-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$] in the structure, which plays an important role in the packing of the crystal structure. The molecules of (3) are linked as a two-dimensional plane by the hydrogen bonds (Fig. 2). The neighboring molecular layers lie parallel to each other and lead to an extended three-dimensional framework.

Experimental

Sodium hydroxide (10%, 1.5 ml) and hydrogen peroxide (30%, 50 ml) were added to a solution of compound (1) (6 g, 37 mmol) in methanol (60 ml) at 273 K. The mixture was then allowed to warm to ambient temperature and stirring was continued for 4 h (monitored by thin-layer chromatography). At the end of the reaction, the resulting mixture was neutralized with 10% HCl. The mixture was diluted with water (30 ml) and extracted with diethyl ether (3 × 20 ml). The organic layer was washed with brine, dried with Na_2SO_4 and the solvent was evaporated. The crude product was purified by recrystallization (diethyl ether) to give compound (3) as a white powder. White single crystals of (3) suitable for X-ray crystallographic analysis were obtained by recrystallization from dichloromethane. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.65 (*s*, H15), 3.32 (*s*, H2), 3.22–3.14 (*t*, *J*1 = 12.23, *J*2 = 13.03 Hz, H8), 3.07–3.00 (*m*, H9*B*), 2.66–2.34 (*m*, H9*A*, H17*A*, H17*B*, H4*A*, H4*B*), 2.23–1.97 (*m*, H4, H16*A*, H16*B*), 1.79–1.48 (*m*, H11*A*, H11*B*, H12*A*, H12*B*, H5*A*, H5*B*), 1.72 (*s*, H20*A*, H20*B*, H20*C*), 1.23 (*s*, H19*A*, H19*B*, H19*C*). ^{13}C NMR (300 MHz, $CDCl_3$): δ 219.0, 216.1, 205.0, 71.5, 70.5, 69.5, 61.3, 60.4, 58.2, 48.2, 46.6, 34.6, 32.0, 27.9, 25.7, 22.1, 21.8, 18.6, 17.7.

Crystal data

$C_{20}H_{24}O_6$	Mo $K\alpha$ radiation
M_r = 360.39	Cell parameters from 685 reflections
Orthorhombic, $P2_12_12_1$	θ = 2.6–19.3°
a = 6.8847 (12) Å	μ = 0.10 mm^{-1}
b = 9.4841 (17) Å	T = 293 (2) K
c = 26.480 (5) Å	Prism, white
V = 1729.0 (5) Å^3	0.32 × 0.23 × 0.20 mm
Z = 4	
D_x = 1.384 Mg m^{-3}	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	1989 independent reflections
φ and ω scans	1455 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	R_{int} = 0.096
T_{min} = 0.96, T_{max} = 0.97	θ_{max} = 26.0°
9425 measured reflections	$h = -8 \rightarrow 8$
	$k = -11 \rightarrow 6$
	$l = -32 \rightarrow 31$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.060	$w = 1/[\sigma^2(F_o^2) + (0.07P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.141	$(\Delta/\sigma)_{max} < 0.001$
S = 1.06	$\Delta\rho_{max}$ = 0.46 e Å^{-3}
1989 reflections	$\Delta\rho_{min}$ = −0.55 e Å^{-3}
239 parameters	

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O6^{i}	0.82	2.24	3.005 (4)	156
C4—H4A···O6^{ii}	0.97	2.68	3.600 (6)	159

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

C-bound H atoms were refined as riding atoms. The H atom on O4 was located in a difference map. The C—H distances were set at 0.96–0.98 Å. The U_{iso} values for the H atoms were set at 1.2 or 1.5 times U_{eq} of the parent atom. In the absence of significant anomalous dispersion effects, Friedel pairs were merged and the absolute configuration is assigned on the basis of the synthesis.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); 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* and *MERCURY* (Version 1.2.1; Bruno *et al.*, 2002).

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