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12,12-Ethylenedioxy-8α,9α-epoxy-podocarpan-19-oic Acid†

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Abstract

The stereochemistry of the epoxide ring of the title compound, 12,12-ethylenedioxy-8α,9α-epoxypodocarpan-19-oic acid, $C_{19}H_{28}O_5$, prepared during studies aimed at converting podocarpic acid into precursors for the synthesis of biologically active quassinoids, has been confirmed by X-ray structure determination.

Comment

During studies aimed at converting the natural product podocarpic acid into chiral precursors for the synthesis of biologically active quassinoids, we prepared an epoxide which was assigned the structure 12,12-ethylenedioxy-8α,9α-podocarpan-19-oic acid, (I) (Cambie *et al.*, 1998). While products obtained from opening of the epoxide ring supported the assigned stereochemistry, a structural analysis was carried out on the epoxide in order to confirm the stereochemical assignment.

(I)
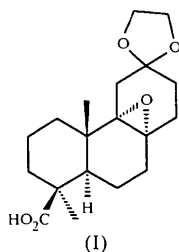
The structure confirms that the epoxide has 8α,9α stereochemistry. The formation of the three-membered ring introduces some strain around C8 and C9, ev-

idenced by the bond angles, which are up to 12.5° greater than the tetrahedral angle. The C8—C9 bond at 1.477 (3) Å is long compared with the C—C bond in other epoxides, where the mean is 1.466 Å (Allen *et al.*, 1987). The increased distance is presumably due to the constraint imposed by the two fused six-membered rings where the epoxide lies across the ring junction. Other distances and angles are unexceptional. There is a hydrogen bond between the proton of the carboxylic acid group and an O atom of the dioxolane ring of an adjacent molecule [O4—O3ⁱ 2.720 (2) Å; symmetry code: (i) $1 - x$, $\frac{1}{2} + y$, $1 - z$]. The absolute stereochemistry could not be determined and Fig. 1 shows the same stereochemistry as that of the parent podocarpic acid.
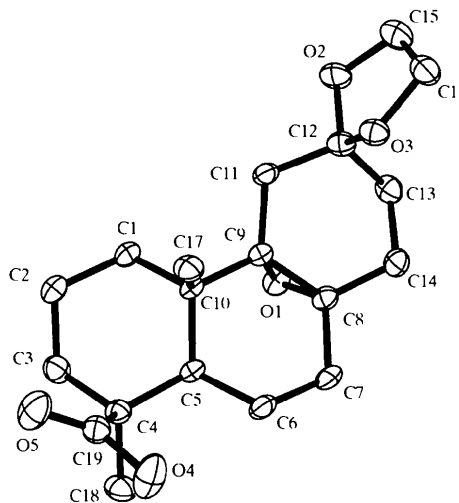

Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

The title compound was obtained by epoxidation of 12,12-ethylenedioxypodocarp-8-en-19-oic acid with *m*-chloroperbenzoic acid in a two-phase system of dichloromethane and 0.5 *M* aqueous sodium hydrogencarbonate. Chromatography on silica gel and elution with dichloromethane–ether (3:1) yielded the crystals of (I) (m.p. 455–458 K).

Crystal data

$C_{19}H_{28}O_5$	Mo $K\alpha$ radiation
$M_r = 336.41$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 4922
$P2_1$	reflections
$a = 10.8912 (6)$ Å	$\theta = 2.0–27.5°$
$b = 7.4907 (4)$ Å	$\mu = 0.093$ mm⁻¹
$c = 11.2879 (6)$ Å	$T = 203 (2)$ K
$\beta = 111.214 (1)°$	Prism
$V = 858.49 (8)$ Å³	$0.60 \times 0.45 \times 0.40$ mm
$Z = 2$	Colourless
$D_x = 1.301$ Mg m⁻³	
D_m not measured	

† Systematic name: 6,6-ethylenedioxy-1,4a-dimethyl-4bα,8aα-epoxy-perhydrophenanthrene-1-carboxylic acid.

Data collection

Siemens SMART diffrac-	2778 reflections with
tometer with area detector	$I > 2\sigma(I)$
ω scans	$R_{int} = 0.036$
Absorption correction:	$\theta_{max} = 27.49°$
multi-scan (Blessing,	$h = -14 \rightarrow 13$
1995)	$k = -9 \rightarrow 8$
$T_{min} = 0.946$, $T_{max} = 0.964$	$l = 0 \rightarrow 14$
5329 measured reflections	Intensity decay: none
2979 independent reflections	

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.451$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.048$	$\Delta\rho_{min} = -0.292$ e Å^{-3}
$wR(F^2) = 0.126$	Extinction correction: none
$S = 1.030$	Scattering factors from
2979 reflections	*International Tables for*
219 parameters	*Crystallography* (Vol. C)
H atoms: see below	Absolute structure:
$w = 1/[\sigma^2(F_o^2) + (0.0904P)^2]$	Flack (1983)
where $P = (F_o^2 + 2F_c^2)/3$	Flack parameter = 0.7 (10)
$(\Delta/\sigma)_{max} = 0.002$	

Table 1. Selected geometric parameters (Å, °)

O1—C9	1.450 (2)	C8—C14	1.515 (3)
O1—C8	1.453 (2)	C9—C11	1.522 (3)
C7—C8	1.514 (3)	C9—C10	1.542 (2)
C8—C9	1.477 (3)		
O1—C8—C9	59.29 (12)	O1—C9—C8	59.54 (12)
O1—C8—C7	114.03 (16)	O1—C9—C11	111.76 (15)
C9—C8—C7	122.02 (16)	C8—C9—C11	120.44 (15)
O1—C8—C14	113.35 (15)	O1—C9—C10	114.43 (14)
C9—C8—C14	119.63 (17)	C8—C9—C10	120.40 (16)
C7—C8—C14	114.94 (17)	C11—C9—C10	115.96 (16)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H4$\cdots$O3^i	0.83	1.96	2.720 (2)	151.1

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

The data collection nominally covered a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 4.94 cm. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds for methyl groups) and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom.

Data collection: *SMART* (Siemens 1994a). Cell refinement: *SAINT* (Siemens 1994a). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL* (Siemens 1994b). Software used to prepare material for publication: *SHELXL97*.

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Intermediates in the Synthesis of (+)-Grandisol. III.† (1S,5R)-2,5-Dimethyl-1-(phenylsulfonyl)bicyclo[3.2.0]hept-2-ene

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Abstract

In the title compound, $C_{15}H_{18}O_2S$, the cyclopentene ring is in an envelope conformation and the cyclobutane ring is puckered. The phenylsulfonyl and the junction methyl groups are *cis* with respect to each other.

Comment

The terpene (+)-*cis*-2-isopropenyl-1-methylcyclobutane-ethanol, (2), *i.e.* (+)-grandisol (Tumlinson *et al.*, 1971), is the principal component in the aggregation pheromone produced by the male cotton boll weevil, *Anthonomus grandis* Boheman (Franke *et al.*, 1989), which is a serious pest in Brazilian cotton fields. The potential use of this terpene in traps for monitoring crop infestation in integrated pest management makes it a target for synthetic organic chemists, especially the

† Part II: Zukerman-Schpector & Monteiro (1998).