

9 β -Hydroxy-1 β ,10 α -epoxyparthenolideMohamed Moumou,^a Mohamed Akssira,^a Lahcen El Ammari,^b Ahmed Benharref^{c*} and Moha Berraho^c^aLaboratoire de Chimie Bioorganique et Analytique, URAC 22, BP 146, FSTM, Université Hassan II, Mohammedia-Casablanca 20810 Mohammedia, Morocco,^bLaboratoire de Chimie du Solide Appliquée, Faculté des Sciences, Avenue Ibn Battouta, BP 1014 Rabat, Morocco, and ^cLaboratoire de Chimie des Substances Naturelles, URAC16, Faculté des Sciences Semlalia, BP 2390 Bd My Abdellah, 40000 Marrakech, Morocco

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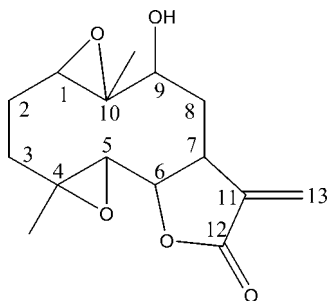
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.033; wR factor = 0.090; data-to-parameter ratio = 8.8.

The title compound, $\text{C}_{15}\text{H}_{20}\text{O}_5$ (systematic name: 5-hydroxy-1 α ,4 α -dimethyl-7-methylenepiperhydrodioxireno[5,6:9,10]cyclo-deca[1,2-*b*]furan-8-one), was obtained by the reaction of 3-chloroperbenzoic acid with 9 β -hydroxyparthenolide. The five-membered ring adopts a twist conformation, whereas the ten-membered ring displays an approximate chair–chair conformation. In the crystal structure, molecules are linked into chains propagating along the b axis by intermolecular O–H \cdots O hydrogen bonds.

Related literature

For background to the medicinal uses of the plant *Anvillea radiata*, see: Abdel Sattar *et al.* (1996); Bellakhdar (1997); El Hassany *et al.* (2004); Qureshi *et al.* (1990). For ring puckering parameters, see: Cremer & Pople (1975). For conformations of ten-membered rings, see: Castaneda-Acosta *et al.* (1997); Watson & Zabel (1982).



Experimental

Crystal data

$\text{C}_{15}\text{H}_{20}\text{O}_5$	$V = 724.84$ (4) Å ³
$M_r = 280.31$	$Z = 2$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 9.2295$ (3) Å	$\mu = 0.10$ mm ⁻¹
$b = 9.5431$ (3) Å	$T = 298$ K
$c = 9.3787$ (3) Å	$0.27 \times 0.18 \times 0.12$ mm
$\beta = 118.662$ (2)°	

Data collection

Bruker X8 APEXII CCD area-detector diffractometer	1617 independent reflections
8090 measured reflections	1378 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$	1 restraint
$wR(F^2) = 0.090$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.13$ e Å ⁻³
1617 reflections	$\Delta\rho_{\text{min}} = -0.13$ e Å ⁻³
184 parameters	

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O}2-H2\cdots\text{O}4^i$	0.82	2.02	2.787 (3)	155

Symmetry code: (i) $x, y - 1, z$.

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and PLATON (Spek, 2009); software used to prepare material for publication: WinGX (Farrugia, 1999).

The authors thank the Unit of Support for Technical and Scientific Research (UATRS, CNRST) for the X-ray diffraction measurements.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5157).

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supplementary materials

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9 β -Hydroxy-1 β ,10 α -epoxyparthenolide

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Comment

Anvillea radiata Coss. & Dur. (Asteraceae) is a wild plant predominantly distributed in steppes of North Africa (Morocco and Algeria). The plant is used in the folk medicine for the treatment of dysentery, gastric-intestinal disorders (Bellakhdar, 1997), hypoglycemic activity (Qureshi *et al.*, 1990), and has been reported to have antitumoral activity (Abdel Sattar *et al.*, 1996). In our study of different Moroccan endemic plants, we have demonstrated that the aerial parts of *Anvillea radiata* Coss and Dur could be used as a renewable source of 9-hydroxyparthenolide (El Hassany, *et al.*, 2004). This work focuses on the preparation of 1 β -10 α -epoxy-9 β -hydroxyparthenolide from the epoxydation of 9 β -hydroxy parthenolide.

The molecular structure of the title compound is shown in Fig. 1. The five-membered ring adopts a twist conformation, as indicated by Cremer & Pople (1975) puckering parameters $Q = 0.186$ (3) Å and $\varphi = 61.5$ (8)°. The ten-membered ring displays an approximate chair-chair conformation. This is the typical conformation found in other sesquiterpenes lactones (Watson & Zabel, 1982; Castaneda-Acosta *et al.*, 1997).

In the crystal structure, molecules are linked into chains (Fig. 2) running along the *b* axis by intermolecular O—H \cdots O hydrogen bonds (Table 1) involving the O2 and O4 atoms.

Experimental

The title compound was obtained by treatment of 9 β -Hydroxyparthenolide (500 mg) by *m*-chloroperbenzoic acid (250 mg) in CH₂Cl₂ (75 ml). The mixture was stirred for 30 min at room temperature and treated with aqueous solution of Na₂CO₃ (10%), then extracted by CH₂Cl₂. The residue obtained after evaporation of CH₂Cl₂, was chromatographed on a silica gel column with hexane-ethylacetate (50/50) as an eluent, to isolate 350 mg of the title compound in 75% yield. It was recrystallized from CH₂Cl₂ (m.p. 363–365 K). The structure of the compound was analyzed by ¹H and ¹³C-NMR and confirmed by X-ray analysis.

Refinement

All H atoms were positioned geometrically [C—H = 0.96 Å (methyl), 0.97 Å (methylene) and 0.98 Å (methine)] and treated as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{methylene/methine C and O})$ or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{methyl C})$. In the absence of significant anomalous scattering, the absolute configuration could not be reliably determined and thus 1278 Friedel pairs were merged.

Figures

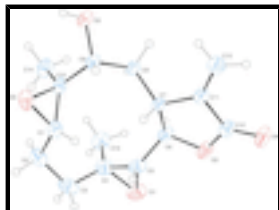


Fig. 1. Molecular structure of the title compound, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.

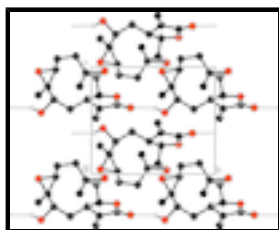


Fig. 2. Partial packing view, showing C—H...O hydrogen-bonded chains parallel to the *b* axis. H atoms not involved in hydrogen bonding (dashed lines) have been omitted for clarity.

5-hydroxy-1a,4a-dimethyl-7- methyleneperhydrodioxireno[5,6:9,10]cyclodeca[1,2-*b*]furan-8-one

Crystal data

$C_{15}H_{20}O_5$

$M_r = 280.31$

Monoclinic, $P2_1$

Hall symbol: P 2yb

$a = 9.2295$ (3) Å

$b = 9.5431$ (3) Å

$c = 9.3787$ (3) Å

$\beta = 118.662$ (2)°

$V = 724.84$ (4) Å³

$Z = 2$

$F(000) = 300$

$D_x = 1.284$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 8090 reflections

$\theta = 2.5$ – 26.5 °

$\mu = 0.10$ mm⁻¹

$T = 298$ K

Prism, colourless

$0.27 \times 0.18 \times 0.12$ mm

Data collection

Bruker X8 APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

φ and ω scans

8090 measured reflections

1617 independent reflections

1378 reflections with $I > 2\sigma(I)$

$R_{int} = 0.031$

$\theta_{max} = 26.7$ °, $\theta_{min} = 2.5$ °

$h = -11 \rightarrow 11$

$k = -10 \rightarrow 12$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

$wR(F^2) = 0.090$

$S = 1.05$

1617 reflections

184 parameters

1 restraint

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 0.0327P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.13 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.13 \text{ e } \text{\AA}^{-3}$$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	-0.1569 (3)	0.2114 (3)	0.0240 (3)	0.0445 (5)
H1	-0.0953	0.2863	0.0055	0.053*
C2	-0.3412 (3)	0.2235 (3)	-0.0757 (3)	0.0567 (7)
H2A	-0.3919	0.1709	-0.0227	0.068*
H2B	-0.3757	0.1811	-0.1811	0.068*
C3	-0.4043 (3)	0.3738 (4)	-0.1004 (3)	0.0638 (8)
H3A	-0.3743	0.4211	-0.1741	0.077*
H3B	-0.5238	0.3729	-0.1505	0.077*
C4	-0.3354 (3)	0.4546 (3)	0.0564 (3)	0.0522 (6)
C5	-0.1856 (3)	0.5389 (3)	0.0973 (3)	0.0493 (6)
H5	-0.1470	0.5325	0.0167	0.059*
C6	-0.0511 (2)	0.5623 (2)	0.2665 (3)	0.0421 (5)
H6	-0.0915	0.5477	0.3448	0.051*
C7	0.0972 (3)	0.4660 (2)	0.3050 (3)	0.0367 (5)
H7	0.0907	0.4403	0.2009	0.044*
C8	0.1049 (3)	0.3287 (2)	0.3942 (3)	0.0423 (5)
H8A	0.2046	0.3294	0.4986	0.051*
H8B	0.0116	0.3261	0.4149	0.051*
C9	0.1036 (3)	0.1953 (2)	0.3041 (3)	0.0395 (5)
H9	0.1641	0.2126	0.2439	0.047*
C10	-0.0689 (3)	0.1455 (2)	0.1862 (3)	0.0407 (5)
C11	0.2419 (3)	0.5625 (2)	0.3892 (3)	0.0399 (5)
C12	0.1773 (3)	0.7075 (2)	0.3533 (3)	0.0465 (5)
C13	0.3997 (3)	0.5360 (3)	0.4776 (3)	0.0601 (7)
H13A	0.4749	0.6094	0.5198	0.072*
H13B	0.4367	0.4438	0.4980	0.072*
C14	-0.1584 (3)	0.0708 (3)	0.2633 (3)	0.0589 (7)
H14A	-0.1411	0.1202	0.3593	0.088*
H14B	-0.1164	-0.0229	0.2917	0.088*
H14C	-0.2744	0.0675	0.1877	0.088*
C15	-0.3799 (3)	0.4050 (3)	0.1816 (3)	0.0599 (7)
H15A	-0.3367	0.4691	0.2715	0.090*
H15B	-0.3336	0.3137	0.2190	0.090*
H15C	-0.4979	0.4004	0.1347	0.090*
O1	-0.3421 (2)	0.6072 (2)	0.0388 (3)	0.0650 (5)
O2	0.1910 (2)	0.09367 (17)	0.4267 (2)	0.0569 (5)
H2	0.1973	0.0204	0.3843	0.085*

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O3	0.0115 (2)	0.70565 (16)	0.2779 (2)	0.0539 (4)
O4	0.2528 (2)	0.81591 (19)	0.3811 (2)	0.0653 (5)
O5	-0.0845 (2)	0.07350 (19)	0.0434 (2)	0.0549 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0426 (11)	0.0524 (14)	0.0442 (11)	-0.0061 (10)	0.0254 (9)	-0.0082 (11)
C2	0.0443 (13)	0.077 (2)	0.0458 (13)	-0.0123 (12)	0.0194 (10)	-0.0122 (13)
C3	0.0351 (12)	0.091 (2)	0.0544 (15)	0.0047 (12)	0.0123 (11)	0.0073 (14)
C4	0.0341 (11)	0.0619 (16)	0.0599 (15)	0.0111 (10)	0.0221 (10)	0.0078 (12)
C5	0.0391 (11)	0.0543 (14)	0.0561 (13)	0.0127 (10)	0.0241 (10)	0.0159 (11)
C6	0.0454 (11)	0.0330 (12)	0.0557 (13)	0.0072 (9)	0.0306 (10)	0.0073 (10)
C7	0.0431 (12)	0.0284 (10)	0.0398 (11)	0.0044 (8)	0.0210 (9)	0.0030 (8)
C8	0.0550 (12)	0.0300 (11)	0.0416 (11)	0.0007 (10)	0.0228 (9)	0.0020 (9)
C9	0.0446 (11)	0.0293 (10)	0.0465 (12)	0.0023 (9)	0.0232 (10)	0.0002 (9)
C10	0.0484 (12)	0.0347 (11)	0.0488 (12)	-0.0043 (9)	0.0311 (10)	-0.0063 (9)
C11	0.0450 (11)	0.0321 (11)	0.0442 (11)	0.0009 (9)	0.0227 (9)	0.0015 (9)
C12	0.0569 (13)	0.0331 (12)	0.0544 (13)	0.0020 (11)	0.0306 (11)	-0.0006 (11)
C13	0.0461 (13)	0.0519 (15)	0.0699 (16)	0.0010 (11)	0.0178 (11)	0.0071 (13)
C14	0.0654 (15)	0.0529 (16)	0.0695 (16)	-0.0123 (13)	0.0413 (13)	0.0045 (13)
C15	0.0536 (14)	0.0636 (17)	0.0754 (18)	0.0038 (13)	0.0413 (13)	0.0003 (13)
O1	0.0441 (10)	0.0637 (13)	0.0835 (12)	0.0202 (8)	0.0276 (9)	0.0214 (10)
O2	0.0673 (11)	0.0297 (8)	0.0630 (10)	0.0118 (8)	0.0226 (9)	0.0057 (8)
O3	0.0574 (10)	0.0299 (8)	0.0780 (11)	0.0121 (8)	0.0355 (9)	0.0071 (9)
O4	0.0786 (13)	0.0307 (8)	0.0896 (13)	-0.0083 (8)	0.0429 (10)	-0.0048 (9)
O5	0.0596 (9)	0.0517 (10)	0.0604 (10)	-0.0073 (8)	0.0342 (8)	-0.0212 (8)

Geometric parameters (\AA , $^\circ$)

C1—O5	1.447 (3)	C8—C9	1.525 (3)
C1—C10	1.477 (3)	C8—H8A	0.97
C1—C2	1.502 (3)	C8—H8B	0.97
C1—H1	0.98	C9—O2	1.422 (3)
C2—C3	1.524 (4)	C9—C10	1.515 (3)
C2—H2A	0.97	C9—H9	0.98
C2—H2B	0.97	C10—O5	1.449 (3)
C3—C4	1.505 (4)	C10—C14	1.512 (3)
C3—H3A	0.97	C11—C13	1.310 (3)
C3—H3B	0.97	C11—C12	1.480 (3)
C4—O1	1.463 (3)	C12—O4	1.204 (3)
C4—C5	1.482 (4)	C12—O3	1.343 (3)
C4—C15	1.495 (4)	C13—H13A	0.93
C5—O1	1.432 (3)	C13—H13B	0.93
C5—C6	1.490 (3)	C14—H14A	0.96
C5—H5	0.98	C14—H14B	0.96
C6—O3	1.469 (3)	C14—H14C	0.96
C6—C7	1.541 (3)	C15—H15A	0.96
C6—H6	0.98	C15—H15B	0.96

C7—C11	1.498 (3)	C15—H15C	0.96
C7—C8	1.537 (3)	O2—H2	0.82
C7—H7	0.98		
O5—C1—C10	59.41 (15)	C9—C8—H8A	108.5
O5—C1—C2	117.7 (2)	C7—C8—H8A	108.5
C10—C1—C2	124.9 (2)	C9—C8—H8B	108.5
O5—C1—H1	114.4	C7—C8—H8B	108.5
C10—C1—H1	114.4	H8A—C8—H8B	107.5
C2—C1—H1	114.4	O2—C9—C10	111.51 (18)
C1—C2—C3	113.8 (2)	O2—C9—C8	105.69 (16)
C1—C2—H2A	108.8	C10—C9—C8	113.10 (17)
C3—C2—H2A	108.8	O2—C9—H9	108.8
C1—C2—H2B	108.8	C10—C9—H9	108.8
C3—C2—H2B	108.8	C8—C9—H9	108.8
H2A—C2—H2B	107.7	O5—C10—C1	59.26 (15)
C4—C3—C2	112.5 (2)	O5—C10—C14	112.5 (2)
C4—C3—H3A	109.1	C1—C10—C14	122.4 (2)
C2—C3—H3A	109.1	O5—C10—C9	115.25 (17)
C4—C3—H3B	109.1	C1—C10—C9	119.00 (18)
C2—C3—H3B	109.1	C14—C10—C9	115.0 (2)
H3A—C3—H3B	107.8	C13—C11—C12	121.9 (2)
O1—C4—C5	58.19 (16)	C13—C11—C7	130.9 (2)
O1—C4—C15	113.1 (2)	C12—C11—C7	107.19 (18)
C5—C4—C15	122.8 (2)	O4—C12—O3	121.4 (2)
O1—C4—C3	115.1 (2)	O4—C12—C11	128.7 (2)
C5—C4—C3	115.8 (2)	O3—C12—C11	109.87 (19)
C15—C4—C3	117.3 (2)	C11—C13—H13A	120.0
O1—C5—C4	60.23 (15)	C11—C13—H13B	120.0
O1—C5—C6	120.8 (2)	H13A—C13—H13B	120.0
C4—C5—C6	123.7 (2)	C10—C14—H14A	109.5
O1—C5—H5	113.9	C10—C14—H14B	109.5
C4—C5—H5	113.9	H14A—C14—H14B	109.5
C6—C5—H5	113.9	C10—C14—H14C	109.5
O3—C6—C5	108.32 (18)	H14A—C14—H14C	109.5
O3—C6—C7	105.30 (16)	H14B—C14—H14C	109.5
C5—C6—C7	110.70 (18)	C4—C15—H15A	109.5
O3—C6—H6	110.8	C4—C15—H15B	109.5
C5—C6—H6	110.8	H15A—C15—H15B	109.5
C7—C6—H6	110.8	C4—C15—H15C	109.5
C11—C7—C8	116.15 (18)	H15A—C15—H15C	109.5
C11—C7—C6	102.94 (17)	H15B—C15—H15C	109.5
C8—C7—C6	116.07 (17)	C5—O1—C4	61.57 (16)
C11—C7—H7	107.0	C9—O2—H2	109.5
C8—C7—H7	107.0	C12—O3—C6	111.09 (16)
C6—C7—H7	107.0	C1—O5—C10	61.33 (14)
C9—C8—C7	115.12 (17)		

supplementary materials

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O2-H2\cdots O4^i$	0.82	2.02	2.787 (3)	155

Symmetry codes: (i) $x, y-1, z$.

Fig. 1

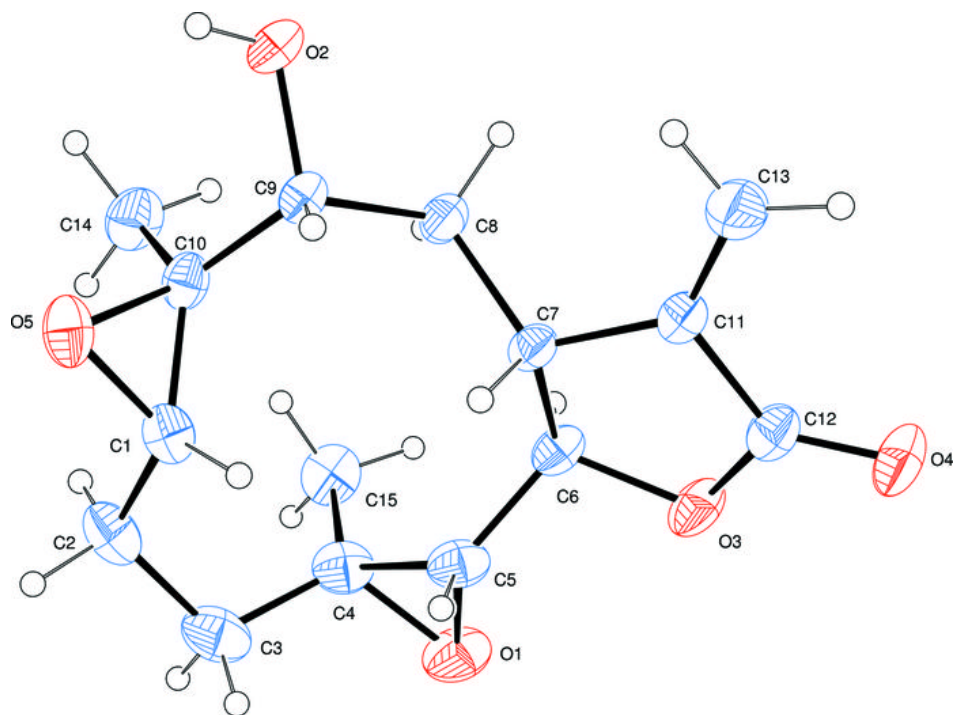


Fig. 2

