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[1a(1aα,5β,9aα)]-1,1a,4,5,7,8,9,9a-Octahydro-3-hydroxy-1,1,2,5-tetramethyl-7-methylene-6*H*-cyclopropa[3,4]cyclohept[1,2-e]inden-6-one

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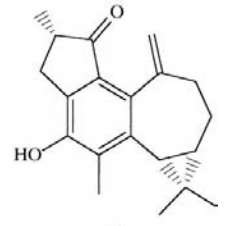
Interest in the title structure, $C_{20}H_{24}O_2$, lies in the novel *cis* ring junction between the three- and seven-membered rings. This stereochemical arrangement causes the methylene moiety and the cycloheptane ring to be twisted out of the plane of the aromatic ring. The cyclopropane ring is also twisted out of the plane of the aromatic system. The molecules are linked by an O—H$\cdots$O hydrogen bond [O$\cdots$O 2.741 (3) Å].

Comment

Jatropholone (JOH), a natural phorbol-related mixture of diterpenes (JOH-A and JOH-B), was isolated from the hexane extract of *Jatropha elliptica* (Goulart *et al.*, 1993). Its acetate was characterized previously by X-ray diffraction (Purushothaman *et al.*, 1979). The tetracyclic array, consisting of fused five-, six-, seven- and three-membered rings with two potentially electroactive functionalities, suggests the possibility of interesting chemical transformations. However, apart from the total synthesis (Smith *et al.*, 1986), little chemical information concerning the reactivity has been available. Recently, the diastereomeric mixture was investigated by electroanalysis (De Azevedo *et al.*, 1999) and subjected to electrochemical and chemical reductions. Electrolysis (Hg cathode, dimethylformamide/tetrabutylammonium perchlorate) and catalytic hydrogenation (H_2/PtO_2) lead, in both processes, to high chemo- and stereoselectivities (De Azevedo *et al.*, 1999). The phenolic proton and the positioning of the seven- and three-membered rings appear to play a very important role in the process. To understand the selectivities, structural information on the non-derivatized substrate is a fundamental requirement. Jatropholone A (JOH-A), (I), was therefore purified and its three-dimensional structure determined by crystallographic analysis.

The five-membered ring has an envelope conformation in which C5 is 0.259 (5) Å out of the plane formed by the remaining four atoms. The Cremer & Pople (1975) ring puckering parameters are $q_2 = 0.167$ (3) Å and $\varphi_2 = 85.0$ (10)°.



(I)

The dihedral angle between the five-membered ring and six-membered aromatic ring is 5.6 (1)°. Atoms C1*A* and C7 are nearly coplanar with the aromatic ring, with distances of 0.068 (5) and 0.158 (5) Å, respectively, out of that plane. Atom C14 of the methylene group is located above the average plane of the aromatic ring, whereas atom C1 of the cyclopropane ring is below the plane. The distances of atoms C14 and C1 from this plane are 1.308 (6) and −1.016 (6) Å, respectively.

The absolute stereochemistry could not be determined from the present data. The coordinates reflect only relative stereochemistry at the chiral centres. The stereochemistry of the H atoms of C1*A* and C9*A*, where the cyclopropane ring is fused to the cycloheptane ring, is *cis*. As measured by the C6*A*—C6*B*—C7—C14 torsion angle, the methylene moiety of the cycloheptane ring is twisted out of the plane of the aromatic ring system by 73.1 (1)°. The cyclopropane ring is twisted out of the plane of the aromatic system by 48.8 (2)°. The structure therefore demonstrates that, in the formation of the hydrogenated product JOHH-2, the reaction has occurred on the least sterically hindered side of the molecule.

The molecules are linked by hydrogen bonding; O2$\cdots$O1^{i} 2.741 (3), HO2$\cdots$O1^{i} 1.96, O2—HO2 0.82 Å and O2—HO2$\cdots$O1^{i} 159° [symmetry code: (i) $-\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{4}-z$]. In addition, the shortest C$\cdots$O contact may also represent a

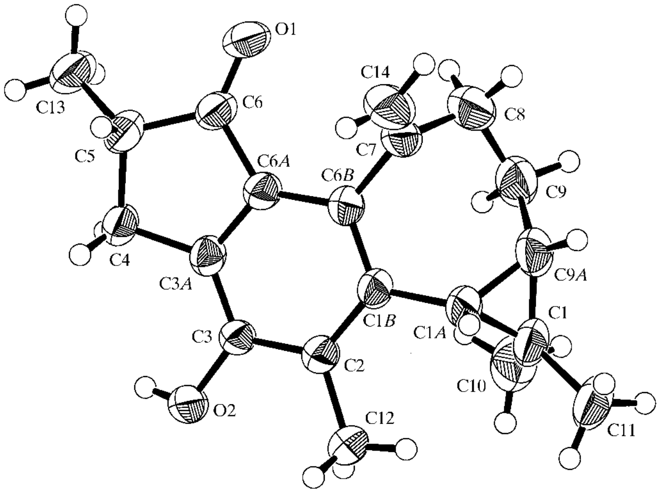


Figure 1
Projection of the title compound, showing the relative stereochemistry, atom labelling and 50% probability displacement ellipsoids for non-H atoms. H atoms are of arbitrary size.

hydrogen bond; C13···O2^{ii} 3.335 (4), H13*A*···O2^{ii} 2.52 Å and C13*A*—H13*A*···O2^{ii} 143° [symmetry code: (ii) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{4}-z$].

A *ZORTEP* (Zsolnai, 1995) illustration of the formula unit is presented in Fig. 1.

Experimental

After isolation from the hexane extract of the plant named *Jatropha elliptica* (Goulart *et al.*, 1993), following the Muell (Arg) classification system, the diastereomeric mixture of jatropholones (0.100 g) was submitted to flash chromatography on a silica-gel (230–400 mesh, Merck) column (internal diameter 2 cm, silica height 31 cm) using a mixture of hexane/ethyl acetate (9:1 *v*/*v*) as eluent, collecting fractions of 10 ml. The column chromatography was followed by thin-layer chromatography (TLC) on silica-gel 60 F_{254} plates (layer thickness 0.2 mm, Riedel–deHaën) using the same eluent and two consecutive runs. TLC spots were visualized by ultraviolet irradiation and were developed using a phosphomolybdic acid solution in ethanol (10%). The less polar compound (JOH-A) eluted first and was left to crystallize in the same solvent system.

Crystal data

$C_{20}H_{24}O_2$
$M_r = 296.39$
Tetragonal, $P4_32_12$
$a = 13.378$ (2) Å
$c = 18.803$ (6) Å
$V = 3365.2$ (13) Å^3
$Z = 8$
$D_x = 1.170$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 25 reflections
$\theta = 9.05$–25.00°
$\mu = 0.074$ mm^{-1}
$T = 293$ (2) K
Irregular, colourless
0.45 × 0.35 × 0.30 mm

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
6369 measured reflections
2975 independent reflections
2357 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\rm max} = 25.04°$
$h = 0 \rightarrow 15$
$k = -15 \rightarrow 15$
$l = 0 \rightarrow 22$
3 standard reflections
frequency: 120 min
intensity decay: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0573$
$wR(F^2) = 0.1249$
$S = 1.157$
2975 reflections
204 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0773P)^2 + 0.0458P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.16$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.021 (2)

All the H atoms were located on difference Fourier maps. The H-atom positions were fixed and an overall isotropic displacement parameter was refined to $U = 0.093$ (4) Å^2. The absolute stereochemistry could not be determined from refinement of the present data. No reflections related by Friedel symmetry were included in the final refinement, which otherwise included all of the independent intensities measured to $\theta = 25°$.

Table 1
Selected geometric parameters (Å, °).

O2—C3	1.358 (3)	C7—C8	1.505 (5)
C6*A*—C3*A*	1.390 (4)	C1*A*—C9*A*	1.502 (4)
C6*A*—C6	1.473 (4)	C1*A*—C1	1.513 (5)
O1—C6	1.219 (4)	C9*A*—C9	1.496 (4)
C1*B*—C1*A*	1.498 (4)	C9*A*—C1	1.497 (5)
C4—C3*A*	1.504 (4)	C10—C1	1.502 (5)
C4—C5	1.530 (4)	C1—C11	1.524 (4)
C6—C5	1.507 (4)	C9—C8	1.523 (5)
C6*B*—C7	1.490 (4)		
C6*B*—C1*B*—C1*A*	118.7 (2)	C9*A*—C1*A*—C1	59.5 (2)
C2—C1*B*—C1*A*	120.6 (2)	C9—C9*A*—C1	122.0 (3)
C3*A*—C4—C5	103.5 (2)	C9—C9*A*—C1*A*	119.6 (3)
C6*A*—C3*A*—C4	112.3 (2)	C1—C9*A*—C1*A*	60.6 (2)
O1—C6—C6*A*	126.3 (3)	C9*A*—C1—C10	119.7 (3)
C6*A*—C6—C5	107.4 (2)	C9*A*—C1—C1*A*	59.9 (2)
C1*B*—C6*B*—C7	120.3 (2)	C10—C1—C1*A*	121.9 (3)
C14—C7—C6*B*	120.3 (3)	C9*A*—C1—C11	116.6 (3)
C14—C7—C8	122.4 (3)	C10—C1—C11	113.4 (3)
C6*B*—C7—C8	117.3 (3)	C1*A*—C1—C11	115.4 (3)
C6—C5—C4	105.7 (2)	C9*A*—C9—C8	112.3 (3)
C1*B*—C1*A*—C9*A*	120.4 (2)	C7—C8—C9	112.1 (3)
C1*B*—C1*A*—C1	124.7 (3)		

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1081). Services for accessing these data are described at the back of the journal.

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