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A clerodane diterpenoid from *Pulicaria wightiana*

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.120
Data-to-parameter ratio = 10.6

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

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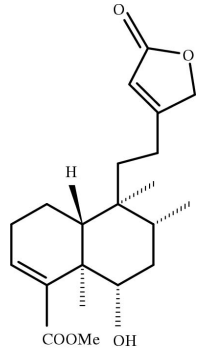
The structure of the clerodane diterpene $C_{21}H_{30}O_5$, with modest antibacterial activity and isolated from the plant *Pulicaria wightiana*, was established to be methyl 6α-hydroxy-3,13-clerodadien-15,16-olid-18-oate. The fused six-membered rings of the decalin system have sofa and chair conformations. The furanone side chain is in an antiperiplanar conformation. The molecules in the crystal structure are stabilized by an intramolecular O—H···O hydrogen bond and a chain of intermolecular C—H···O interactions.

Comment

Various species of *Pulicaria* are distributed in different parts of India and are well known for their medicinal properties. The title compound, (I), was one of the five new clerodane diterpenoids recently isolated from the aerial part of the plant *Pulicaria wightiana*, which shows moderate activity against Gram-positive organisms, *Bacillus subtilis*, *Bacillus sphaerius* and *Staphylococeus* (Das *et al.*, 2005). A large number of diterpenoids with the clerodane skeleton have been isolated from plants in recent years (Merritt & Ley, 1992). Clerodane diterpenoids are a family of secondary metabolites found to possess considerable biological activity, *viz*. antitumoral, antimicrobial, antibacterial and particularly antifeedant (Merritt & Ley, 1992; Simmonds & Blaney, 1992). As a result of this biological potential, the present study was undertaken to obtain the three-dimensional structure of (I).



(I)

All bond lengths and angles are normal and are in good agreement with related structures reported in the literature (Spek *et al.*, 1987; Linden *et al.*, 1996; Soundarya Devi *et al.*, 2003). The molecular structure of (I) consists of a bicyclic, *viz*. cyclohexene and cyclohexane, *trans*-fused decalin ring system. It was observed that the majority of isolated clerodanes have *trans*-ring fusion (Hanson, 1999). The methyl groups at C8 and C9 are *cis* to each other [C21—C8—C9—C17 = 54.1 (2)°]. In

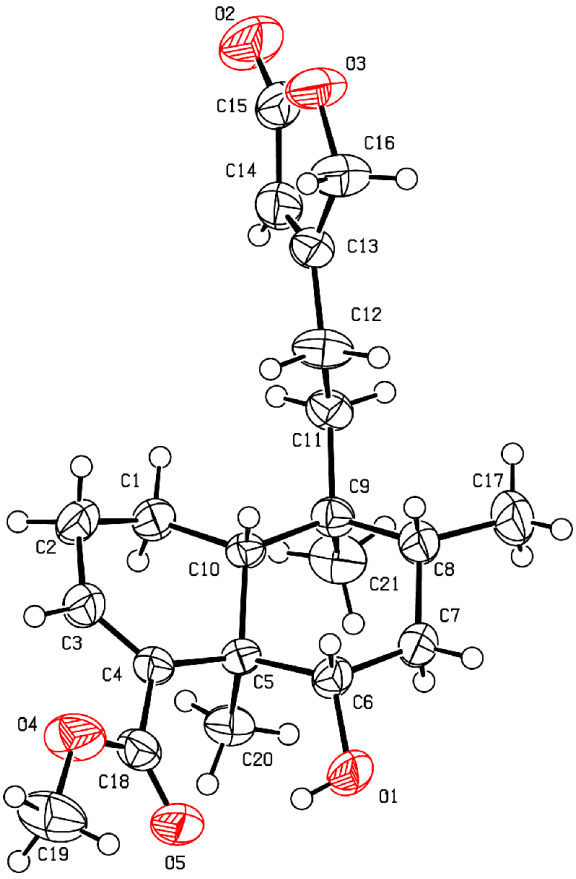


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

addition, the methyl group and the hydroxy group at C5 and C6 are also *cis* to each other [C20—C5—C6—O1 = −44.7 (2)°]. In this respect, our results support earlier spectroscopic assignments (Das *et al.*, 2005).

As expected, the cyclohexane ring exists in a chair conformation [q_2 = 0.019 (2), q_3 = 0.560 (2), Q_T = 0.560 (2) Å, φ_2 = −123 (5) and θ_2 = 2.0 (2)°; Cremer & Pople, 1975], whereas the cyclohexene ring adopts a sofa conformation with C10 lying 0.710 (2) Å out of the plane [q_2 = 0.416 (2), q_3 = 0.343 (2), Q_T = 0.540 (2) Å, φ_2 = −45.8 (3) and θ_2 = 50.6 (3)°]. A similar conformation of the decalin ring system was observed in the crystal structure of 19-acetoxy-*cis*-clerodan-3-en-15-oic acid (Kolocouris *et al.*, 2001). This conformational preference of the bicyclic decalin ring system in the present structure facilitates an intramolecular O—H···O hydrogen bonding (Table 2) between the hydroxy group at C6 and the neighboring methyl ester group at C4. The methyl ester group at C4, in an extended conformation [C19—O4—C18—C4 = 177.0 (2)°], is not coplanar with the endocyclic C=C double bond [C3—C4—C18—O4 = −21.9 (3)°].

It is interesting to note that in some of the clerodane diterpenoids, the presence of the furan ring in the side chain appears to be one of the determinants of antifeedant activity (Enriz *et al.*, 2000).

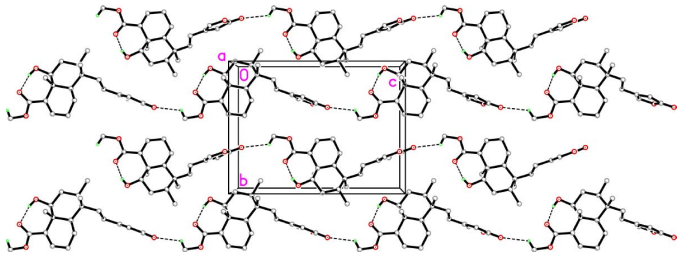


Figure 2
Packing diagram viewed down the *a* axis. Dashed lines indicate intramolecular O—H···O hydrogen bond and intermolecular C—H···O interactions. H atoms not involved in hydrogen bonding have been omitted for clarity.

The methyl ester and furanone ring are involved in an intermolecular C—H···O interaction. This links the molecules into infinite one-dimensional chains, which run parallel to the crystallographic *c* axis.

Experimental

The title compound was isolated from the aerial parts of *Pulicaria wightiana* (Das *et al.*, 2005). Needle-shaped crystals suitable for X-ray study were obtained from a methanol solution.

Crystal data

$C_{21}H_{30}O_5$
M_r = 362.45
Orthorhombic, $P2_12_12_1$
a = 10.3572 (5) Å
b = 11.6812 (5) Å
c = 15.5784 (7) Å
V = 1884.75 (15) Å^3
Z = 4
D_x = 1.277 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9796 reflections
θ = 2.2–28.0°
μ = 0.09 mm^{-1}
T = 273 (2) K
Cut needle, colorless
0.30 × 0.14 × 0.09 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
16247 measured reflections
2549 independent reflections
2386 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 28.0°
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 15$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.120
S = 1.04
2549 reflections
240 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0837P)^2 + 0.187P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O2—C15	1.199 (3)	C3—C4	1.332 (3)
O3—C15	1.365 (4)	C13—C14	1.324 (3)
O5—C18	1.214 (2)		
C4—C5—C10	105.34 (13)	C7—C8—C9	110.86 (15)
C7—C6—C5	112.95 (14)	C8—C9—C10	107.19 (13)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O5	0.82	1.87	2.662 (2)	164
C20—H20A···O5	0.96	2.56	3.222 (3)	126
C19—H19C···O2^{i}	0.96	2.52	3.162 (3)	124

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

The absolute configuration could not be established in this analysis and was assigned on the basis of the spectroscopically found configuration of the title compound (Das *et al.*, 2005). In the absence of anomalous scattering effects, Friedel pairs were merged. H atoms were included in calculated positions (C—H = 0.93–0.98 Å) using a riding model, with U_{iso}(H) values set at 1.2 (O and CH H atoms) and 1.5 (CH3) times the U_{eq} values of the parent atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1990) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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