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Bharangin triacetate

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.005 Å
R factor = 0.053
wR factor = 0.128
Data-to-parameter ratio = 8.0

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

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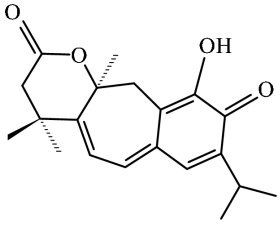
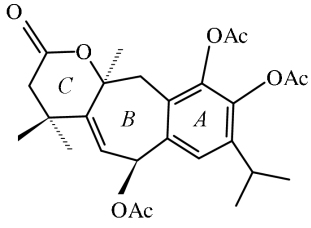
The structure of bharangin triacetate [systematic name: 6,10-bis(acetyloxy)-8-isopropyl-4,4,11*a*-trimethyl-2-oxo-2,3,-4,6,11,11*a*-hexahydrobenzo[5,6]cyclohepta[1,2-*b*]pyran-9-yl acetate], $C_{26}H_{32}O_8$, a tricyclic diterpenoid, contains a seven-membered cycloheptadiene ring forming two planar parts, a six-membered δ-lactone ring in a boat conformation and a planar benzene ring. The structure is stabilized by intra- and intermolecular C—H···O interactions.

Comment

Bharangin, (I), isolated from the root nodules of *Pygmaco-premna herbace (Roxb.) Moldenke* is used locally as a folk medicine in traditional Indian medicine. Different parts of the plant, either alone or as an ingredient in compound preparations, are claimed to be useful in treatments of bronchitis, asthma, blood pressure, epilepsy, *etc*. (Nayar *et al.*, 1976). The chemical structure of bharangin, (I), has already been reported from our laboratory (Sankaram *et al.*, 1988). As part of an effort to explore the structure–activity relationships of natural products isolated from medicinal plants that are used as alternative medicines in Indian society, we report here the crystal structure of bharangin triacetate, (II).



(I)



(II)

The molecular structure of (II) is shown in Fig. 1. It is clear from the structure that acetylation of (I) resulted in the aromatization of the quinone unit with concerted migration of exocyclic double bonds of the molecule, thereby facilitating C1 to bear an additional acetoxy group. It therefore seems likely that the aromatization process has been initiated by nucleophilic attack of the acetoxy group at C1.

The bond distances and angles observed are very similar to those in related compounds (Oddon *et al.*, 1984; Birknes, 1977; Parvez *et al.*, 2004).

The tricyclic system present in the title compound may be described as consisting of two parts folded along the C1···C5 axis. The part containing the benzene ring is planar, while the other with the δ-lactone ring is not. The seven-membered cycloheptadiene ring consists of two planar halves [C1/C7/C6/C5, with a maximum deviation from planarity of 0.001 (3) Å

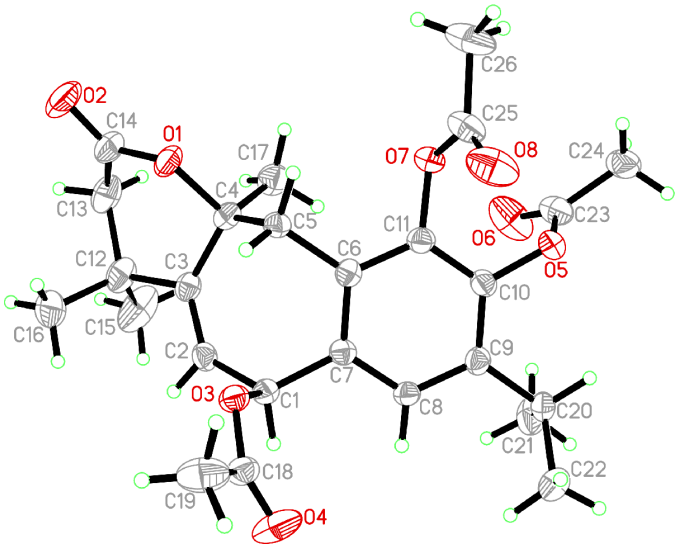


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

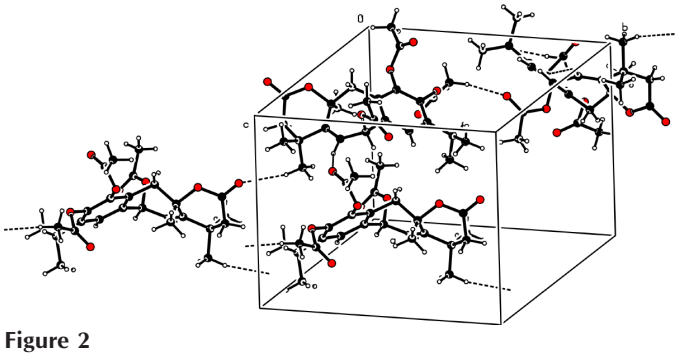


Figure 2
A partial packing diagram for (I), viewed down the *a* axis. Dashed lines indicate intermolecular C—H···O interactions.

for C7, and C1/C2/C3/C4/C5, with a maximum deviation from planarity of 0.151 (3) Å for C4]; the dihedral angle between the two halves is 51.5 (1)°. The attached acetate group is in an axial orientation [C7—C1—O3—C18 = −99.4 (3)°], perhaps to facilitate a possible intramolecular C—H···O interaction (Table 2).

The C13—C14(=O2)—O1—C4 lactone group is essentially planar, with a maximum deviation of 0.034 (4) Å for atom C14. The δ-lactone ring is in a boat conformation [asymmetry parameter ΔC_s(C4) = 0.013 (2) (Nardelli, 1983)], with atoms C4 and C13 displaced by 0.583 (3) and 0.533 (5) Å, respectively, from the mean plane defined by atoms O1/C3/C12/C14. The C17 methyl group is in an axial position with respect to that plane.

The three acetate groups are in extended conformations [C—O—C—C torsion angles of −177.9 (3), −179.7 (3) and 170.7 (3)°]. Furthermore, the two acetate groups attached to the benzene ring are in a perpendicular orientation [C10—C11—O7—C25 = −80.3 (4)° and C9—C10—O5—C23 = 99.0 (4)°]. The dihedral angle between the isopropyl group and the benzene ring is 82.1 (3)°.

In the crystal structure (Fig. 2), there are weak intra- and intermolecular C—H···O (Table 2) and normal van der Waals interactions.

Experimental

Bharangin (70 mg), dissolved in acetic anhydride (2.5 ml), was cooled to 273 K and shaken with perchloric acid (0.1 ml). The reaction mixture was immediately poured into crushed ice with stirring. The separated solid (75 mg) was filtered off and washed with water several times and was purified by column chromatography [silica gel (20 g), column prepared using hexane–ethyl acetate (8:2); eluant: hexane–ethyl acetate (8:2)], resulting in bharangin triacetate as colourless crystalline blocks (58 mg, methanol). Block crystals [m.p. 489–491 K; $[\alpha]_D^{25}$ −8.8° ($CHCl_3$, *c*, 0.0817)] suitable for X-ray structure analysis were obtained by slow evaporation of a solution in methanol at room temperature. ESI–MS *m*/*z*: 472 [M^+]; ^{1}H NMR (C_6D_6, 300 MHz): δ 0.73, 0.93, 1.13 (*s*, CH_3-18,19,20), 1.09, 1.10 (*d*, *J* = 6.9 Hz, CH_3-16,17), 1.52, 1.76, 1.80 (*s*, $OCOCH_3$-7,11,12), 2.04, 2.18 (*d*, *J* = 16.3 Hz, CH_2-3), 2.95 (septet, *J* = 6.9 Hz, H-15), 3.24, 3.88 (*d*, *J* = 14 Hz, CH_2-10), 5.87 (*d*, *J* = 7.4 Hz, H-7), 6.43 (*d*, *J* = 7.4 Hz, H-6), 7.3 (*s*, H-14); ^{13}C NMR (C_6 D_6, 75 MHz): 19.69, 19.63, 20.49, 22.55, 22.80, 25.65, 28.07, 30.92, 32.51, 35.28, 39.14, 43.22, 72.58, 81.65, 121.84, 125.01, 128.75, 136.41, 140.89, 141.59, 142.88, 151.60, 167.50, 169.18, 169.69.

Crystal data

$C_{26}H_{32}O_8$
M_r = 472.52
Orthorhombic, $P2_12_12_1$
a = 10.4278 (5) Å
b = 13.3828 (6) Å
c = 18.0857 (9) Å
V = 2523.9 (2) Å^3
Z = 4
D_x = 1.244 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 5917 reflections
θ = 2.3–24.8°
μ = 0.09 mm^{-1}
T = 273 (2) K
Block, colourless
0.20 × 0.15 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: none
18 391 measured reflections
2528 independent reflections
2435 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 25.0°
h = −12 → 12
k = −15 → 15
l = −21 → 21

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.129
S = 1.25
2528 reflections
315 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0582P)^2 + 0.6697P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C2—C3	1.320 (5)	C14—O2	1.190 (5)
C4—O1	1.474 (4)	C14—O1	1.344 (5)
C6—C7	1.397 (4)		
C3—C4—C5	113.8 (3)	O2—C14—O1	118.7 (4)
C16—C12—C3	109.4 (3)	O2—C14—C13	125.1 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5B···O3	0.97	2.49	3.127 (4)	123
C2—H2···O8^{i}	0.93	2.59	3.288 (5)	133
C15—H15A···O2^{ii}	0.96	2.55	3.490 (6)	166
C24—H24B···O4^{iii}	0.96	2.36	3.304 (6)	167

Symmetry codes: (i) $x-\frac{1}{2},\frac{3}{2}-y,2-z$; (ii) $x-\frac{1}{2},\frac{5}{2}-y,2-z$; (iii) $\frac{1}{2}-x,1-y,z-\frac{1}{2}$.

The absolute configuration could not be established in this analysis and was assigned according to the configuration of bharangin (Sankaram *et al.*, 1988). In the absence of significant anomalous scattering effects, the Friedel pairs were merged. H atoms were included in calculated positions (C—H = 0.93–0.98 Å; riding model) with U_{iso} values set at 1.2 (CH) and 1.5 (CH_3) times the U_{eq} values of the parent atoms. The methyl groups were allowed to rotate but not to tip.

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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