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A stereoisomer of bharangin triacetate

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.060
wR factor = 0.158
Data-to-parameter ratio = 8.8

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

A stereoisomer of bharangin triacetate [systematic name: 6,10-bis(acetyloxy)-8-isopropyl-4,4,11*a*-trimethyl-2-oxo-2,3,-4,6,11,11a-hexahydrobenzo[5,6]cyclohepta[1,2-*b*]pyran-9-yl acetate], $C_{26}H_{32}O_8$, a tricyclic diterpenoid, is reported. There is a 0.56 (3):0.44 (3) disorder in the terminal isopropyl side chain. The title compound and a previously reported stereoisomer, crystallizing in the same space group, exhibit very similar molecular conformations, but differ in the orientation of one of the acetate groups, resulting in a different configuration at the atom to which the acetate group is attached. Consequently, different C—H···O interactions are observed.

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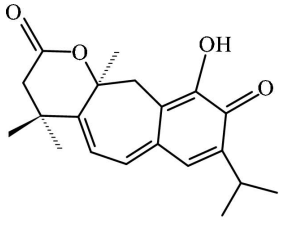
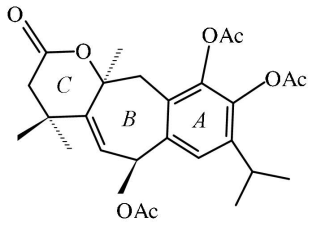
Comment

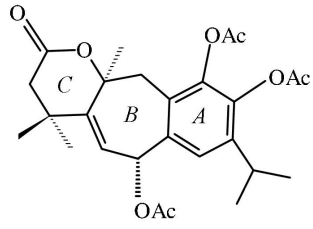
Bharangin, (I), isolated from the root nodules of *Pygmaco-premna herbace (Roxb.) Moldenke*, has been reported to be useful in the treatment of bronchitis, asthma, blood pressure, epilepsy, *etc*. (Nayar *et al.*, 1976). The chemical structure of bharangin (Sankaram *et al.*, 1988) and the crystal structure of its triacetate derivative, (II) (axial; Ravikumar *et al.*, 2005), have been reported from our laboratory. In this paper, the molecular structure of bharangin triacetate, (III) (equatorial), is reported.



(I)



(II) (axial)



(III) (equatorial)

(III) was found to crystallize in the same orthorhombic space group as (II), *viz*. $P2_12_12_1$. All geometric parameters show normal values (Allen *et al.*, 1987) and agree well with the corresponding values observed in (II). The molecular structure of (III) (Fig. 1) exhibits disorder. The isopropyl group is disordered over two sites with occupancies of 0.56 (3) and 0.44 (3).

In both isomers, the heptadiene ring consists of two planar halves. From a molecular perspective, the isomers differ primarily in the orientation of the acetate group attached to the heptadiene ring. In (II), it is in an axial orientation, but it is equatorial in (III), resulting in a different configuration of the ring C atom. A least-squares fit (C1–C11) of (III) with (II) gives an r.m.s. deviation of 0.063 Å (Fig. 2).

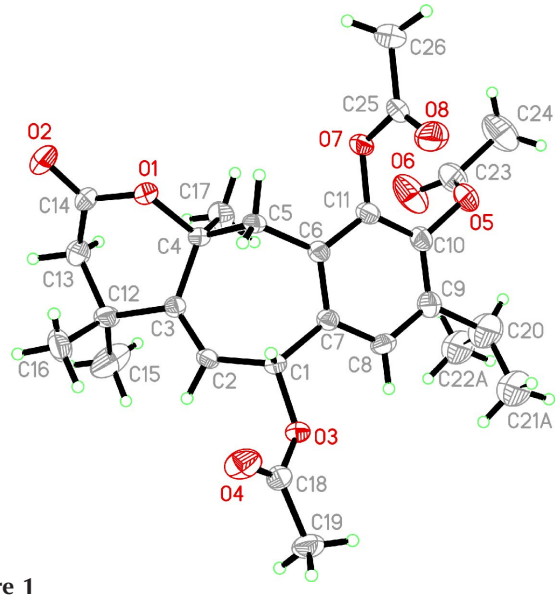


Figure 1
A view of (III), showing 30% probability displacement ellipsoids and the atom-numbering scheme. The disordered atoms of the minor component (C21*B* and C22*B*) have been omitted for clarity. H atoms are shown as small spheres of arbitrary radii.

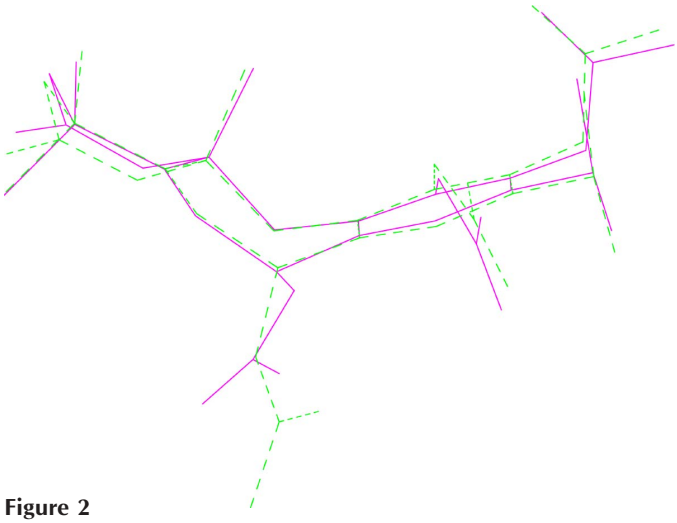


Figure 2
Least-squares fit of (III) (solid lines) with (II) (dashed lines), showing the equatorial and axial orientation of the acetate group.

The δ-lactone ring in both isomers is in a boat conformation [asymmetry parameter ΔC_s(C4) = 0.029 (2) (Nardelli, 1983)], with atoms C4 and C13 displaced by 0.553 (3) and 0.540 (4) 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 the above-mentioned plane in both isomers.

The three acetate groups are in an extended conformation in (III), as was also observed in (II) [torsion angles C—O—C—C = −177.9 (4), 176.3 (3) and 175.9 (5)°]. Furthermore, the two acetate groups substituted on the benzene ring are in perpendicular orientations [C10—C11—O7—C25 = −80.8 (5)° in (III) and −80.3 (4)° in (II); C9—C10—O5—23 = 95.3 (5)° in (III) and 99.0 (4)° in (II)].

Interestingly, the equatorial orientation of the acetate group in (III) facilitates a possible weak intramolecular C—H···O interaction with an adjacent C atom of the benzene ring (Table 2). On the other hand, in (II) the acetate group, being in an axial orientation, also participates in a similar C—H···O interaction, but involving the heptadiene ring. In the absence of hydrogen-bond-donating groups, the molecules are arranged together *via* weak intermolecular C—H···O and normal van der Waals interactions.

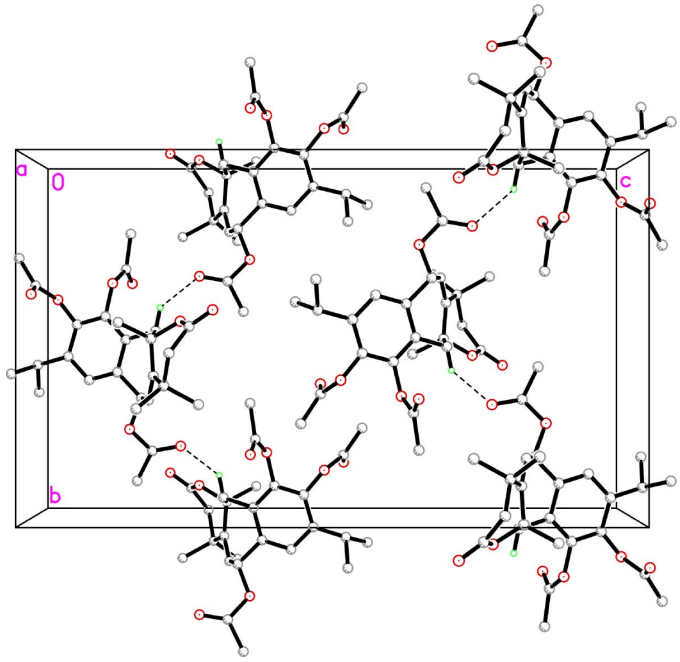


Figure 3
A partial packing diagram for (III), viewed down the *a* axis. Dashed lines indicate the intermolecular C—H···O interactions. The disordered atoms of the minor component (C21*B* and C22*B*) and other H atoms have been omitted for clarity.

Experimental

A solution of lithium borohydride (20 mg) in anhydrous tetrahydrofuran (5 ml) was added to bharangin (45 mg) in anhydrous tetrahydrofuran (10 ml) and warmed for a minute at 313 K. The solution was acidified with dilute hydrochloric acid and extracted with chloroform. The chloroform extract was concentrated and refluxed with acetic anhydride (2 ml) and pyridine (0.5 ml) for an hour. The product (40 mg) was worked up and subjected to column chromatography [silica gel (20 g), column prepared using hexane–ethyl acetate (8:2); eluent: hexane–ethyl acetate (8:2)] giving the title compound as a colorless crystalline material. Needle-shaped crystals suitably cut for X-ray structure analysis were obtained by slow evaporation of a solution in methanol at room temperature.

Crystal data

$C_{26}H_{32}O_8$
M_r = 472.52
Orthorhombic, $P2_12_12_1$
a = 8.1986 (5) Å
b = 14.0252 (9) Å
c = 23.482 (1) Å
V = 2700.1 (3) Å^3
Z = 4
D_x = 1.162 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5772 reflections
θ = 2.5–21.6°
μ = 0.09 mm^{-1}
T = 273 (2) K
Cut needle, colorless
0.27 × 0.15 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	2554 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.032$
ω scans	$\theta_{max} = 25.0^\circ$
Absorption correction: none	$h = -9 \rightarrow 9$
19633 measured reflections	$k = -16 \rightarrow 16$
2719 independent reflections	$l = -27 \rightarrow 27$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0888P)^2 + 1.0606P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.060$	
$wR(F^2) = 0.158$	
$S = 1.10$	$(\Delta/\sigma)_{max} < 0.001$
2719 reflections	$\Delta\rho_{max} = 0.29$ e Å^{-3}
308 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1—C14	1.346 (5)	C2—C3	1.318 (5)
O1—C4	1.469 (4)	C6—C7	1.399 (5)
O2—C14	1.205 (5)		
C3—C4—C5	113.5 (3)	O2—C14—O1	117.7 (4)
C3—C12—C16	109.0 (4)	O2—C14—C13	125.5 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8···O3	0.93	2.35	2.714 (5)	103
C5—H5A···O7	0.97	2.43	2.879 (4)	108
C5—H5A···O4^{i}	0.97	2.51	3.265 (4)	134

Symmetry code: (i) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$.

The absolute configuration could not be established in this analysis and was assigned the same as bharangin (Sankaram *et al.*, 1988). In the absence of significant anomalous scattering effects, Friedel pairs were merged. H atoms were included in calculated positions (C—H = 0.93–0.98 Å) and refined using a 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 site-occupation factors of the disordered atoms refined to 0.56 (3) and 0.44 (3), but were kept fixed in the final cycles of refinement. In addition, distance restraints were applied to the disordered 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); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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