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Epoxyazadiradione

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.052
wR factor = 0.152
Data-to-parameter ratio = 9.1

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

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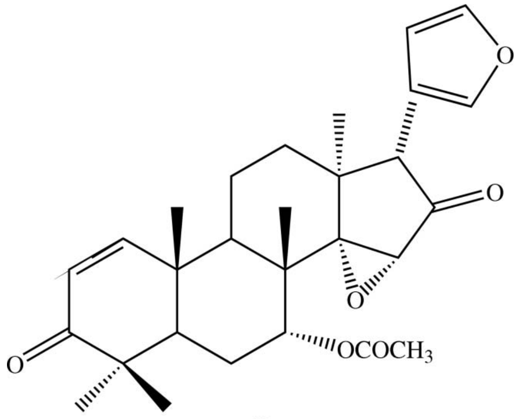
The title compound, epoxyazadiradione or 17-(3-furyl)-4,4,10,13-tetramethyl-3,16-dioxo-3,4,5,6,7,8,9,10,11,12,13,15,-16,17-tetradecahydro-20-oxacyclopropa[14,15]cyclopenta[*a*]-phenathren-7-yl acetate, $C_{28}H_{34}O_6$, was isolated from the fruit of *Azadirachta indica* (neem) and found to have antifeedant activity. The three fused six-membered rings adopt half-chair, chair and boat conformations, with the cyclopentane ring in an envelope conformation. In the crystal structure, C—H···O hydrogen bonds generate an $R_1^2(7)$ ring motif and link the molecules into chains along the *b* axis.

Comment

As a continuation of our work on the structures of neem *Azadirachta indica* constituents (Kabaleeswaran *et al.*,1999, 2000; Anand Solomon *et al.*, 2005), a tree possessing a wide range of biological activities, in particular, antifeedant activity (Jacobson, 1989; Schmutterer *et al.*, 1980), we present here the crystal structure of epoxyazadiradione, (I) (Fig. 1; Lavie & Levy, 1971; Narayanan *et al.*, 1967) isolated from an acetone extract of freshly riped neem fruits. This has been found to show antifeedant activity against larvae of *Spodoptera litura.* Chemically (I) differs from nimonol, isolated from neem leaves (Kabaleeswaran *et al.*, 1999), by the presence of a keto group at C16 instead of a methylene; nonetheless, the level of antifeedant activity is similar to that of (I) (Suresh *et al.*, 2002).



(I)

In (I) (Fig. 1), the furan ring (E) is in an *ap* conformation. Its orientation with respect to ring D (Klyne & Prelog, 1960) is defined by the dihedral angles C16—C17—C20—C22, which are −166.3 (3) and −158.6 (5)° in (I) and nimonol, respectively. The acetoxy group attached to C7 is (−)*sc* with respect to ring B [C6—C7—O7—C24 = −86.1 (2)°], while it is (−)*ac* in nimonol [−108.9 (3)°].

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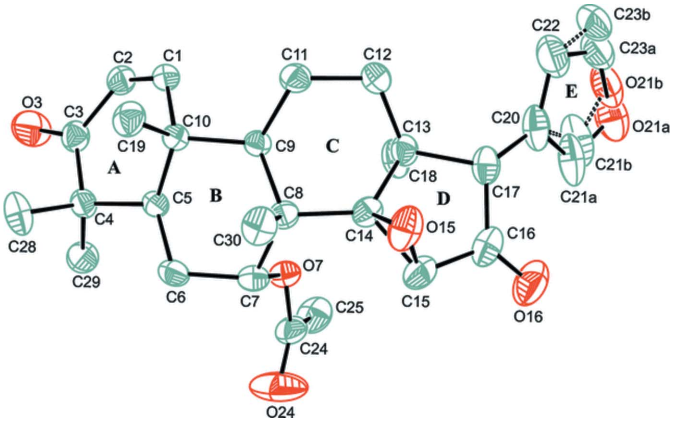

Figure 1
Molecular structure of (I) with 30% probability displacement ellipsoids and the atom numbering scheme. Bonds to atoms of the minor disorder component of the furan ring are drawn as dashed lines. H atoms have been omitted.

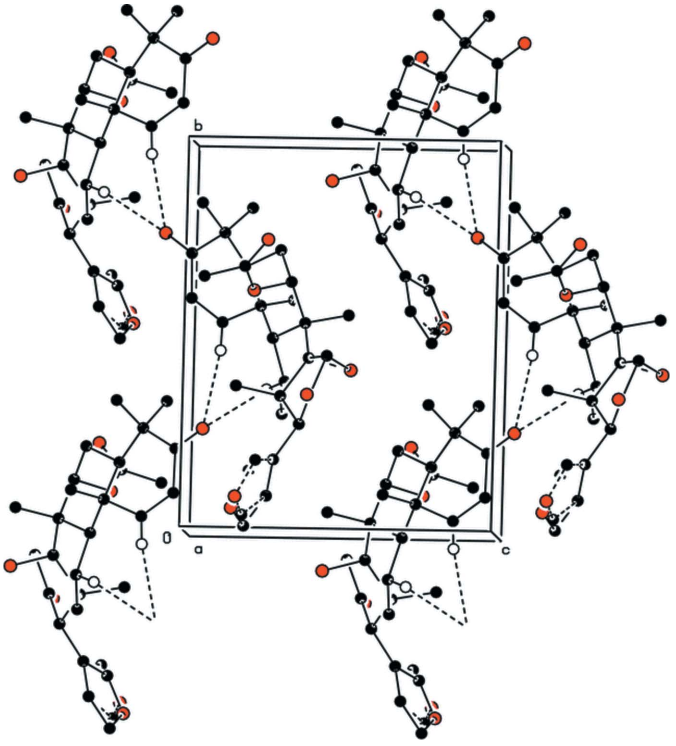

Figure 2
Packing of (I) with hydrogen bonds drawn as dashed lines. Hydrogen atoms not involved in hydrogen bonds have been omitted for clarity. Bonds to atoms of the minor disorder component of the furan ring are drawn as dashed lines.

Ring *A* is in a distorted half-chair conformation [Q_T = 0.468 (2) Å, θ = 59.8 (4)°, φ_2 = −106.6 (4)°] (Cremer & Pople, 1975) and C5 deviates by 0.519 (2) Å from the plane involving the other atoms of the ring. Ring *B* is in a chair conformation with puckering at C5 and C8 [Q_T = 0.576 (2) Å, θ = 5.9 (2)°, φ_2 = 10.1 (1)°]. Atoms C5 and C8 deviate from the plane of the other four atoms by −0.700 (2) and 0.631 (2) Å, respectively. Ring *C* adopts a boat conformation [Q_T = 0.744 (2) Å, θ = 84.4 (2)°, φ_2 = 68.7 (2)°]. Atoms C9 and C13 deviate from the plane formed by atoms C8, C11, C12 and C14 by 0.688 (2) and 0.616 (2) Å, respectively. Ring *D* is in an envelope conformation [q_2 = 0.391 (3) Å, φ = −33.5 (4)°] with C17 as flap, which lies 0.611 (3) Å from the plane of the remaining four atoms. Both disorder components of the furan ring are planar, with a maximum deviation of 0.031 (2) Å for atom C21a from the plane formed by the atoms C20, C21a, C22, C23a and O21a and 0.028 (3) Å for atom C23b from the plane formed by atoms C20, C21b, C22, C23b and O21b. Rings *A*/*B* and *B*/*C* are *trans* fused while the *C*/*D* rings are quasi-*trans* fused, as seen from the endocyclic dihedral angles of the ring junction atoms [C1—C10—C5—C4 = −54.3 (2)°, C9—C10—C5—C6 = 57.3 (2)°, C10—C9—C8—C7 = 51.9 (2)°, C11—C9—C8—C14 = −51.2 (2)°, C12—C13—C14—C8 = 51.2 (3)°, C17—C13—C14—C15 = −24.4 (3)°].

Molecules in the crystal structure are stabilized by C—H···O hydrogen bonds (Table 1). The enone carbonyl O3($-2-x, \frac{1}{2}+y, -z$) accepts two H atoms, one each from C11 and C1, to generate an $R_1^2(7)$ ring-set motif (Bernstein *et al.*, 1995) which runs along the *b* axis.

Experimental

Ripe fresh fruits (2 kg) of *Azadirachta indica* were soaked in acetone and the extract was concentrated to dryness *in vacuo* (14 g). The extract was repeatedly washed with hexane and was chromatographed on silica gel, eluting with ethyl acetate/hexane of increasing polarity, to yield epoxyazadiradione (700 mg). Good diffraction quality crystals were obtained from ethyl acetate/hexane (1:1) by slow evaporation.

Crystal data

$C_{28}H_{34}O_6$
M_r = 466.55
Monoclinic, $P2_1$
a = 9.6532 (7) Å
b = 12.6550 (9) Å
c = 10.5710 (8) Å
β = 105.096 (1)°
V = 1246.80 (16) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 293 (2) K
0.25 × 0.18 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.979, T_{max} = 0.991
14353 measured reflections
3064 independent reflections
2854 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.152
S = 1.13
3064 reflections
336 parameters
66 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11*A*···O3^{i}	0.97	2.52	3.374 (3)	147
C1—H1···O3^{i}	0.93	2.60	3.509 (4)	166

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

In the absence of significant anomalous dispersion effects, 2661 Freidel pairs were merged. The enantiomer employed in the refined model was chosen to agree with the accepted configuration of limonoids (Henderson *et al.*, 1968; Harris *et al.*, 1968). All H-atoms bound to carbon were positioned geometrically and refined using a riding model with C—H = 0.93 Å for aromatic, 0.98 Å for CH, 0.97 Å for CH_2 and 0.96 Å for CH_3 atoms; $U_{iso}(H) = 1.5U_{eq}(C)$ for CH_3 and $1.2U_{eq}(C)$ for all other H atoms. Atoms C21 and C23, with attached H atoms, and O21 of the furan ring are disordered over two positions each with occupancy 0.50 (4).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997) and *PARST97* (Nardelli, 1995).

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