organic compounds

A new clerodane diterpene with antifeedant activity from *Teucrium tomentosum*

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A new diterpene, *viz.* 3β-acetoxy-4α,18:15,16-diepoxy-6β,12-dihydroxyneocleroda-13(16),14-dien-19,20-olide, $C_{22}H_{28}O_8$, exhibiting antifeedant activity against *Spodoptera litura* was isolated from the aerial parts of *Teucrium tomentosum* and its structure is reported. One of the two fused rings has a distorted-chair conformation and the other has a chair conformation. The molecules in the crystal are stabilized *via* O—H···O and C—H···O hydrogen bonds.

Comment

A large number of diterpenoids with the clerodane skeleton have been isolated from plants belonging to the genus *Teucrium* of the family Labiatae, from which a large number of clerodanes have been isolated in the past few years (Merrit & Ley, 1992; Rodriguez *et al.*, 1994; Piozzi *et al.*, 1998). The present study was carried out as part of our ongoing research on the structures of ecofriendly bioinsecticides. Interest in these compounds has been stimulated by their biological activity, particularly as antifeedant agents against lepidopterous pests (Merrit & Ley, 1992; De la Torre *et al.*, 1994). The chemical structure of the title compound, (I), was obtained from ^{13}C and ^{1}H NMR data and HMBC (heteronuclear multiple-bond correlation), and the three-dimensional structure was obtained *via* single-crystal X-ray diffraction.

Rings *A* and *B* have distorted-chair and chair conformations, respectively [Q_T = 0.553 (2) Å, φ_2 = −89.7 (7)° and q_2 = 0.126 (1) Å for ring *A*, and Q_T = 0.610 (1) Å, φ_2 = 0.3 (1.5)° and q_2 = 0.056 (2) Å for ring *B*; Cremer & Pople, 1975]. The lactone ring, *C*, adopts a sofa conformation [Q_T = 0.502 (1) Å, φ_2 = 8.94 (2)° and q_2 = 0.367 (1) Å], whereas ring *D* is planar (Nardelli, 1995). All interatomic distances and angles have normal values. Ring systems *A/B* and *B/C* are *trans* fused and ring system *A/C* is *cis* fused. The

furan ring, *D*, is in a synclinal conformation with respect to ring *B* [C11—C12—C13—C16 = −9.3 (3)°], and the acetyl group on atom C3 is in an anticlinal conformation, as described by the C21—O3—C3—C2 dihedral angle [131.5 (2)°]. The methyl group on atom C8 is in an α configuration, whereas the hydroxy group on atom C6 is in a β configuration.

(I)
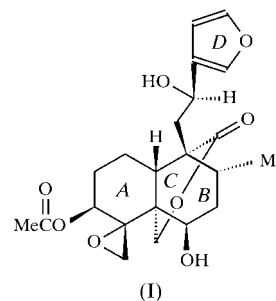
An *ORTEP*III (Burnett & Johnson, 1996) diagram of the molecule (Fig. 1) shows that the displacement parameters are normal; however, the furan ring is highly distorted, which can be attributed to rotational disorder about the C9—C11 bond, as demonstrated by the steady increase in the value of the thermal parameters from atoms C9 to C15. Similar behaviour is observed in many of the limonoids (Narayanan *et al.*, 1980; Kabaleeswaran *et al.*, 1997, 2000; Malathi *et al.*, 2002).

The packing of the molecules (Fig. 2) reveals that the crystal lattice is stabilized by a two-dimensional network (in the *ab* plane) of hydrogen bonds. The O6—H6*A*···O12 hydrogen bond forms an infinite chain along the [100] direction, with a graph-set motif (Bernstein *et al.*, 1995) of *C*(9), and the O12—
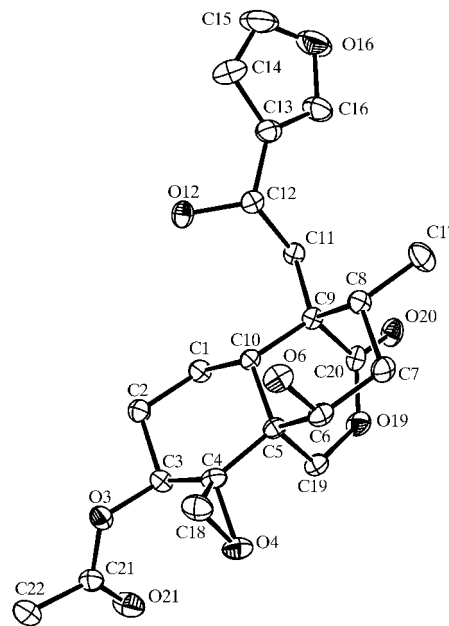

Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 30% probability level and the atomic numbering scheme.
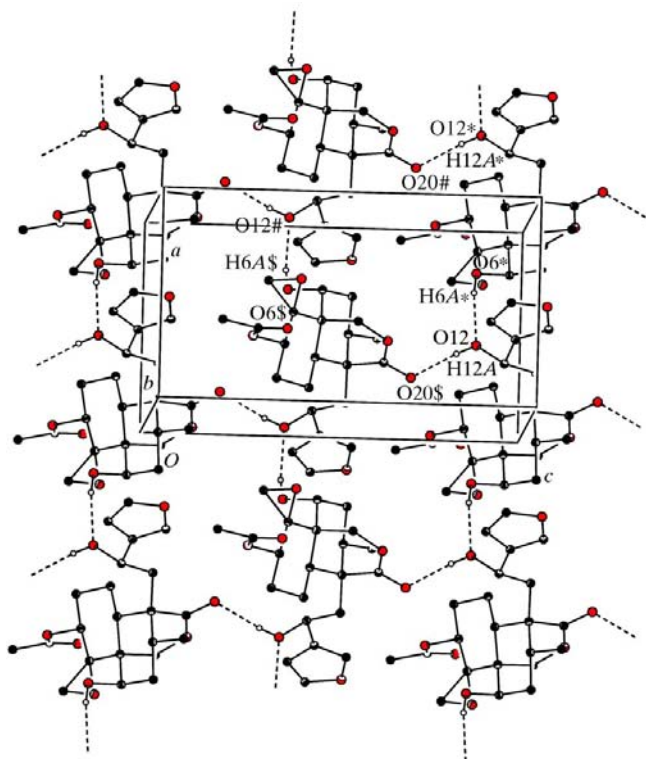
Figure 2
A view of the crystal packing of (I), showing the $R_4^4(26)$ ring. Molecules labelled with an asterisk (*), dollar sign ($) or hash (#) correspond to symmetry positions $(x + 1,\ y,\ z)$, $(-x + \frac{1}{2},\ -y,\ z - 1)$ and $(-x + \frac{3}{2},\ -y,\ z - \frac{1}{2})$, respectively.

H12A···O20 bond forms a graph-set motif of $C(7)$. In addition, there is a C—H···O hydrogen bond between atoms C19 and O21 (Table 1). The two O—H···O hydrogen bonds in the crystal lattice together form an $R_4^4(26)$ ring motif.

Experimental

The shade-dried powdered aerial parts (8.4 kg) of *Teucrium tomentosum* were exhaustively percolated with acetone (3 × 35 l). The extract was then dried in a rotary evaporator to yield a residue (146 g), 55 g of which was subjected to column chromatography using silica gel (70–325) and eluted with chloroform–methanol (1:100), thus yielding 69 fractions in total. Fractions 28–38 were further chromatographed over silica gel (70–325) and eluted with *n*-hexane–ethyl acetate (1:100) to yield teuctosin (75 mg). Needle-shaped crystals of (I) were obtained from a mixture of methanol and chloroform at room temperature (293 K).

Crystal data

$C_{22}H_{28}O_8$	Mo $K\alpha$ radiation
$M_r = 420.44$	Cell parameters from 5722
Orthorhombic, $P2_12_12_1$	reflections
$a = 7.7235\ (5)$ Å	$\theta = 2.6$–$27.8°$
$b = 19.0625\ (9)$ Å	$\mu = 0.10$ mm^{-1}
$c = 13.8907\ (13)$ Å	$T = 293\ (2)$ K
$V = 2045.1\ (3)$ Å^3	Needle, colourless
$Z = 4$	$0.25 \times 0.19 \times 0.15$ mm
$D_x = 1.366$ Mg m^{-3}	

Data collection

Bruker SMART APEX CCD	$R_{int} = 0.022$
area-detector diffractometer	$\theta_{max} = 28.0°$
ω scans	$h = -9 \rightarrow 10$
12 937 measured reflections	$k = -25 \rightarrow 14$
2759 independent reflections	$l = -18 \rightarrow 17$
2526 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0779P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$+ 0.2384P]$
$wR(F^2) = 0.115$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
2759 reflections	$\Delta\rho_{max} = 0.32$ e Å^{-3}
273 parameters	$\Delta\rho_{min} = -0.15$ e Å^{-3}
H-atom parameters constrained	

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6A···O12[i]	0.82	2.07	2.875 (2)	166
O12—H12A···O20[ii]	0.82	1.91	2.727 (2)	171
C19—H19A···O21[iii]	0.97	2.49	3.407 (3)	157

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

In the absence of suitable anomalous scatters, Friedel equivalents could not be used to determine the absolute structure. Refinement of the Flack (1983) parameter led to inconclusive values (Flack & Bernadinelli, 2000) for this parameter [0.1 (8)]. Therefore, the 1990 Friedel equivalents were merged before the final refinement. The enantiomer employed in the refined model was chosen to agree with the accepted configuration of diterpenes (Rogers *et al.*, 1979; De la Torre *et al.*, 1994; Rodriguez *et al.*, 1994). The CH, CH$_2$ and OH H atoms were constrained to an ideal geometry [0.98, 0.97 and 0.82 Å, respectively, with $U_{iso}(H) = 1.5U_{eq}$(parent atom)] but were allowed to rotate freely about the C—C or C—O bonds. All remaining H atoms were placed in idealized positions (C—H = 0.97–0.98 Å) and constrained to ride on their parent atoms, with $U_{iso}(H)$ values of $1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97 and *PARST*97 (Nardelli, 1995).

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