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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: NA1274). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Dolabrane-type Diterpenoids

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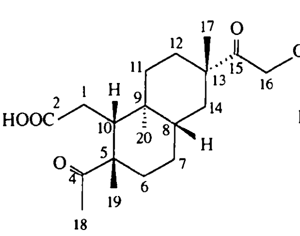
Abstract

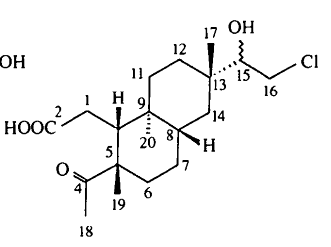
The crystal structures of two dolabrane diterpenes, *ent*-2-seco-3-nor-5α,4,15-dioxo-16-hydroxydolabran-2-oic acid, $C_{19}H_{30}O_5$, (I), and *ent*-2-seco-3-nor-5α,16-chloro-15-hydroxydolabran-2-oic acid, $C_{19}H_{31}ClO_4$, (II), have been determined at room temperature. They revealed the presence of two *trans*-fused rings having a chair conformation and they confirmed previous NMR studies showing that the C9 substituent is *trans* with respect to those at C8 and C10. Furthermore, we observed that the longer C_{sp^3}—C_{sp^3} distances occur for C9—C10 and C5—C10, which is in agreement with the values found in other diterpenes. These are the first reported crystal structures of dolabrane molecules.

Comment

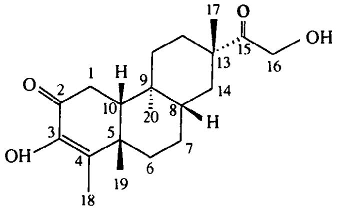
The present work is part of a study concerning the structure and pharmacological activity of diterpene derivatives (Kijjoa *et al.*, 1994; Kijjoa, Pinto, Anantachoke, Gedris & Herz, 1995; Paya *et al.*, 1997). Compounds (I) and (II) belong to a series of dolabrane-type diterpenoids, isolated from *Endospermum diadenum* Airy Shaw (Euphorbiaceae), the only representative of this genus found in Thailand (Kijjoa *et al.*, 1994). They are natural products with potential pharmacological interest since the plant from which they were isolated is used in folk medicine for the relief of fever and skin infections.



(I)



(II)



(III)

Compounds (I) and (II) are similar to the tricyclic diterpene (III), in which C3 is substituted for O3, opening the ring structure. X-ray diffraction studies were performed in order to confirm the NMR studies and to obtain more detailed information about the three-dimensional structure of the molecules.

The compounds both present a bicyclic system with a chair conformation, as shown by the torsion angles around each of the rings. In both compounds, the C20 atom is in a *trans* position relative to the H8 and H10 atoms. The longest C_{sp^3}—C_{sp^3} distances occur in both compounds at bonds C5—C10 and C10—C9, which have respective values of 1.559 (2) and 1.564 (2) Å for compound (I), and 1.563 (2) and 1.563 (2) Å for compound (II). These elongated bonds have been

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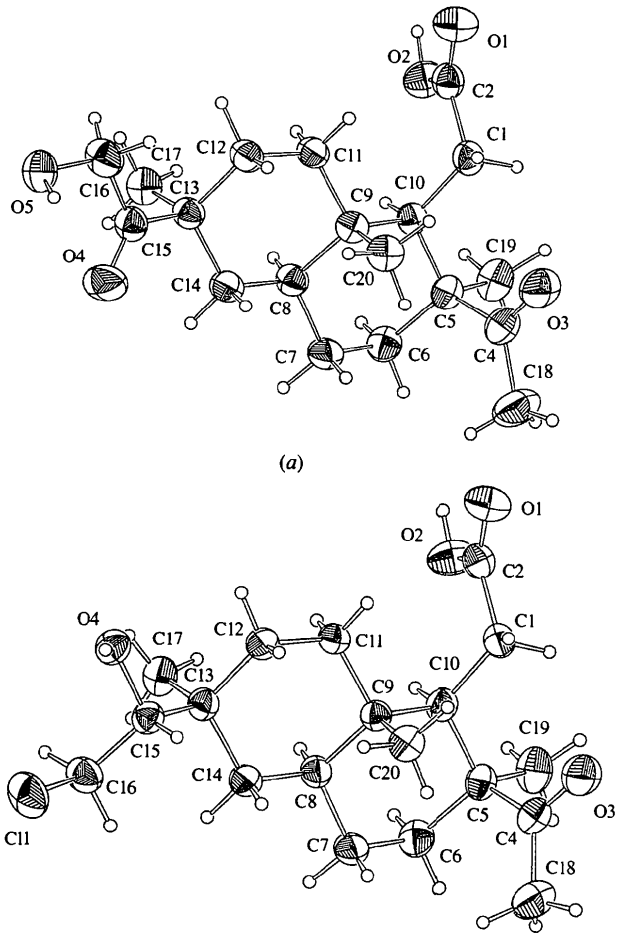
found in other diterpene molecules (Mosquera, Rivera, Gil & Bahsas, 1985). The Cl1—C16 bond length is 1.791 (2) Å, which is within the range of expected values (1.79–1.74 Å; Glusker, Lewis & Rossi, 1994). There are two intermolecular hydrogen bonds in each structure: $O1\cdots O5'(-x+2,\ y-\frac{1}{2},\ -z+\frac{3}{2})$ 2.812 (2) and $O5\cdots O2'(-x+1,\ y+\frac{1}{2},\ -z+\frac{3}{2})$ 2.773 (2) Å for compound (I), and $O1\cdots O4'(-x+1,\ y-\frac{1}{2},\ -z+2)$ 2.889 (2) and $O4\cdots O2'(-x,\ y+\frac{1}{2},\ -z+2)$ 2.765 (2) Å for compound (II).

Comparison of bond lengths and angles between the two compounds shows close agreement.



(a)

(b)

Fig. 1. The molecular structures of (*a*) compound (I) and (*b*) compound (II) showing the atom-labelling schemes. H atoms are depicted as spheres of arbitrary radii. Displacement ellipsoids are shown at the 50% probability level.

Experimental

The title compounds were isolated from *Endospermum diadenum* Airy Shaw as described by Kijjoa *et al.* (1994) and crystals suitable for X-ray work were obtained by slow evaporation of saturated chloroform solutions.

Compound (I)

Crystal data

$C_{19}H_{30}O_5$
$M_r = 338.43$
Orthorhombic
$P2_12_12_1$
$a = 6.2120\ (10)$ Å
$b = 10.162\ (5)$ Å
$c = 27.589\ (6)$ Å
$V = 1741.6\ (10)$ Å^3
$Z = 4$
$D_x = 1.291$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 1242 reflections
$\theta = 4.8\text{–}23.1°$
$\mu = 0.092$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.50 × 0.15 × 0.15 mm
Colourless

Data collection

Stoe IPDS diffractometer
Image plate scans
Absorption correction: none
16 068 measured reflections
4083 independent reflections (94% of theoretical)
3594 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.1135$
$\theta_{\rm max} = 28.13°$
$h = -7 \rightarrow 7$
$k = -13 \rightarrow 13$
$l = -36 \rightarrow 35$
100 standard reflections
frequency: 6 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0366$
$wR(F^2) = 0.1156$
$S = 1.047$
3728 reflections
337 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0345P)^2 + 0.1922P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.092$
$\Delta\rho_{\rm max} = 0.153$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.167$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Bond lengths (Å) for (I)*

O1—C2	1.222 (2)	C7—C8	1.526 (2)
O2—C2	1.317 (2)	C8—C14	1.531 (2)
O3—C4	1.204 (2)	C8—C9	1.544 (2)
O4—C15	1.204 (2)	C9—C20	1.540 (2)
O5—C16	1.414 (2)	C9—C11	1.544 (2)
C1—C2	1.502 (2)	C9—C10	1.564 (2)
C1—C10	1.548 (2)	C11—C12	1.535 (2)
C4—C18	1.497 (3)	C12—C13	1.542 (2)
C4—C5	1.532 (2)	C13—C15	1.531 (2)
C5—C6	1.546 (2)	C13—C14	1.536 (2)
C5—C19	1.547 (2)	C13—C17	1.543 (2)
C5—C10	1.559 (2)	C15—C16	1.511 (2)
C6—C7	1.518 (2)		

Compound (II)

Crystal data

$C_{19}H_{31}ClO_4$
$M_r = 358.89$
Monoclinic
$P2_1$
$a = 6.2570\ (10)$ Å
$b = 15.137\ (3)$ Å
$c = 9.819\ (2)$ Å
$\beta = 96.56\ (2)°$
$V = 923.9\ (3)$ Å^3
$Z = 2$
$D_x = 1.290$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 1404 reflections
$\theta = 4.8\text{–}23.1°$
$\mu = 0.226$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.45 × 0.28 × 0.20 mm
Colourless

Data collection

Stoe IPDS diffractometer
Image plate scans
Absorption correction: none
10 929 measured reflections
4086 independent reflections (91% of theoretical)
3934 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0356$
$\theta_{\rm max} = 28.13°$
$h = -7 \rightarrow 7$
$k = -19 \rightarrow 20$
$l = -13 \rightarrow 13$
100 standard reflections
frequency: 4 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0316$
$wR(F^2) = 0.0801$
$S = 1.057$
4083 reflections
341 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2 + 0.1319P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.117$
$\Delta\rho_{\rm max} = 0.140$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.196$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.04 (5)

Table 2. *Bond lengths (Å) for (II)*

Cl1—C16	1.791 (2)	C7—C8	1.525 (2)
O1—C2	1.208 (2)	C8—C14	1.533 (2)
O2—C2	1.324 (2)	C8—C9	1.551 (2)
O3—C4	1.209 (2)	C9—C20	1.531 (2)
O4—C15	1.434 (2)	C9—C11	1.541 (2)
C1—C2	1.503 (2)	C9—C10	1.563 (2)
C1—C10	1.551 (2)	C11—C12	1.536 (2)
C4—C18	1.502 (2)	C12—C13	1.541 (2)
C4—C5	1.539 (2)	C13—C17	1.526 (2)
C5—C6	1.543 (2)	C13—C14	1.546 (2)
C5—C19	1.553 (2)	C13—C15	1.549 (2)
C5—C10	1.563 (2)	C15—C16	1.521 (2)
C6—C7	1.522 (2)		

For both compounds, data collection: Stoe IPDS software package; cell refinement: Stoe IPDS software package; data reduction: Stoe IPDS software package; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP* (Zsolnai & Pritzkow, 1995) and *XPMA* (Zsolnai, 1996); software used to prepare material for publication: *SHELXL*93 and *ORTEP*.

This work has received partial support from JNICT (I&D n/226/94 and I&D n/316/94) and grant PRAXIS/2/2.1/QUI/17/94.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: HA1184). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5-Methylthiophene-2-carboxaldehyde 4-Nitrophenylhydrazone–Water (1/1)

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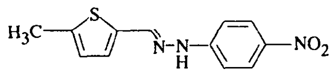
Abstract

The title compound, $C_{12}H_{11}N_3O_2S.H_2O$, is a practically planar organic hyperpolarizable molecule. The non-centrosymmetric packing of its monohydrate crystals and its relationships to non-linear optical properties are discussed.

Comment

Optimal second-order non-linear optical organic materials which contain stable molecules with large molecular hyperpolarizabilities in a non-centrosymmetric packing are of great interest for device applications (Bosshard, Sutter, Schlesser & Günter, 1993), but according to a statistical study, an overwhelming majority of achiral molecules crystallize centrosymmetrically (Jacques, Collet & Wilen, 1981).

In the course of our studies of materials exhibiting high second harmonic signals, the title compound, MTNPH, was synthesized. Due to its large hyperpolarizability and non-centrosymmetric packing, MTNPH is an organic non-linear optical molecule exhibiting a large second harmonic signal (Wong, Meier *et al.*, 1996).



MTNPH

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