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Acta Cryst. (1999). C**55**, 1835–1837

Filic-3-ene, a pentacyclic triterpene from *Davallia canariensis*

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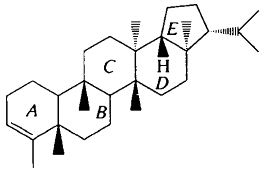
(*Received 24 May 1999; accepted 15 July 1999*)

Abstract

The triterpene filic-3-ene, 3-isopropyl-3a,5a,7a,8,11b,13a-hexamethyl-2,3,3a,4,5,5a,5b,6,7,7a,10,11,11a,11b,12,13,13a,13b-octadecahydro-1*H*-cyclopenta[α]chrysene, $C_{30}H_{50}$, was isolated from *Davallia canariensis*, a fern from Tenerife (Canary Islands), and its structure was elucidated. It was confirmed to be a pentacyclic molecule, with four six-membered rings and one five-membered ring. The two independent molecules in the asymmetric unit do not differ significantly.

Comment

This paper, part of a systematic study of bioactive metabolites from Canary Island ferns, presents the results of a structural study of filic-3-ene, (I), a triterpene hydrocarbon isolated from *Davallia canariensis* as a minor component (Bermejo, 1998). This fern is called 'batatilla' locally and features in traditional medicine as having emollient, aperient, restorative and expectorant properties (Pérez de Paz & Medina, 1988). Xanthones are known to occur frequently in the *Davallia* genus (Soeder, 1985).



(I)

Filic-3-ene (or 3-filicene) was isolated from *Adiantum monochlamys* (Ageta *et al.*, 1964) and from *Adiantum pedatum* (Ageta & Iwata, 1966). The structural model was established by these authors by means of chemical and spectroscopic investigations and is now confirmed by our X-ray analysis. We were not able to determine the absolute stereochemistry by X-ray methods and the configuration shown here was chosen to be in accord with that reported in previous chemical studies (Ageta *et al.*, 1964; Ageta & Iwata, 1966).

After extraction followed by chromatography on silica gel to afford filic-3-ene as a colourless oil, crystals were grown from a benzene/acetone mixture; there are two molecules, *A* and *B*, in the asymmetric unit with remarkably similar conformations overall, including the substituents. A quantitative measure of the similarity of the two molecules (*A* and *B*) was obtained using a least-squares fit. The weighted r.m.s. deviation was 0.0663 Å with 0.202 Å for maximum deviation in 30 C atoms. All bond lengths and angles are in the expected ranges and need no further discussion.

In the molecules (see Fig. 1) which involve the pentacyclic ring system *A*–*E*, one endocyclic double bond C3═C4 was identified, indicated by the bond length of 1.307 (8) in molecule *A* and 1.323 (7) Å in molecule *B*.

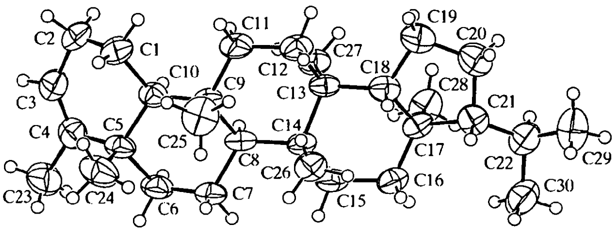


Fig. 1. A perspective view of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

In both molecules, rings *B*, *C* and *D* are in the chair form and C26 and C27 in the *trans* conformation. Atoms C26, C13, C14 and C27 are coplanar. In ring *A*, atoms C2, C3, C4 and C5 are also coplanar. The relevant torsion angles for molecules *A* and *B* are given in Table 1.

Also in both molecules, ring *E* assumes a half-chair conformation, whereas in molecules containing fused five- and six-membered ring systems the usual form of the five-membered ring is the envelope conformation [see 2α-bromoarborinone (Kennard *et al.*, 1967) and giberellic acid (Hartsuch & Lipscomb, 1963)]. Torsion angles in ring *E* for molecules *A* and *B* are given in Table 1.

The packing of the molecules is assumed to be dictated mainly by van der Waals forces. The closest intermolecular contact between H atoms is 2.35 Å for molecule *A* and 2.27 Å for molecule *B*, while the closest intermolecular contact H···C between molecules *A* and *B* is 3.04 Å.

Experimental

Compound (I) was isolated from the *Devalliaceae* by solvent extraction, followed by chromatography of the crude extract on silica gel to afford filic-3-ene as a colourless oil. The crystals were grown from a benzene and acetone mixture.

Crystal data

$C_{30}H_{50}$
$M_r = 410.70$
Monoclinic
$P2_1$
$a = 11.015$ (2) Å
$b = 7.678$ (3) Å
$c = 30.045$ (4) Å
$\beta = 99.02$ (1)°
$V = 2509.6$ (11) Å^3
$Z = 4$
$D_x = 1.087$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.08–18.56°$
$\mu = 0.060$ mm^{-1}
$T = 293$ (2) K
Prism
0.42 × 0.21 × 0.11 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
9325 measured reflections
6197 independent reflections
3020 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.047$
$\theta_{\rm max} = 27.50°$
$h = -14 \rightarrow 14$
$k = -9 \rightarrow 9$
$l = -38 \rightarrow 38$
1 standard reflection frequency: 120 min intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.060$
$wR(F^2) = 0.197$
$S = 0.884$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.21$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}
Extinction correction: none

6197 reflections
557 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.1246P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected torsion angles (°)*

C10*A*—C1*A*—C2*A*—C3*A*	42.7 (6)
C2*A*—C1*A*—C10*A*—C5*A*	−64.8 (6)
C1*A*—C2*A*—C3*A*—C4*A*	−12.7 (9)
C2*A*—C3*A*—C4*A*—C5*A*	2.8 (9)
C3*A*—C4*A*—C5*A*—C10*A*	22.7 (7)
C4*A*—C5*A*—C10*A*—C1*A*	52.4 (5)
C27*A*—C13*A*—C14*A*—C26*A*	−178.6 (4)
C21*A*—C17*A*—C18*A*—C19*A*	49.0 (4)
C18*A*—C17*A*—C21*A*—C20*A*	−39.9 (4)
C17*A*—C18*A*—C19*A*—C20*A*	−38.1 (5)
C18*A*—C19*A*—C20*A*—C21*A*	11.7 (6)
C19*A*—C20*A*—C21*A*—C17*A*	17.9 (6)
C10*B*—C1*B*—C2*B*—C3*B*	42.8 (6)
C2*B*—C1*B*—C10*B*—C5*B*	−65.7 (5)
C1*B*—C2*B*—C3*B*—C4*B*	−11.2 (8)
C2*B*—C3*B*—C4*B*—C5*B*	0.7 (8)
C3*B*—C4*B*—C5*B*—C10*B*	−22.3 (6)
C4*B*—C5*B*—C10*B*—C1*B*	53.4 (5)
C27*B*—C13*B*—C14*B*—C26*B*	−179.7 (4)
C21*B*—C17*B*—C18*B*—C19*B*	49.4 (4)
C18*B*—C17*B*—C21*B*—C20*B*	−42.3 (5)
C17*B*—C18*B*—C19*B*—C20*B*	−36.8 (5)
C18*B*—C19*B*—C20*B*—C21*B*	9.2 (6)
C19*B*—C20*B*—C21*B*—C17*B*	21.7 (6)

Though data were collected to a 2θ maximum of 61.9°, only reflections having 2θ less than 55° were used for structure refinement, as only a few reflections were found to be observed at higher angles. Reflections and Friedel opposites were combined and merged before refinement. All H atoms were placed in geometrically calculated positions. The methyl-H atoms were refined as rigid groups, which were allowed to rotate but not to tip, with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$. All other H atoms were allowed to ride on their parent atoms with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. The absolute configuration of the structure of the crystal could not be determined reliably; refinement of the Flack parameter (Flack, 1983) gave an ambiguous result. Friedel opposite reflections were therefore merged.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *HELENA* (Spek, 1997). Program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1998). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *PLATON*.

This work has been partly subsidized by grant No. PETRY 95.0178.OP (CICYT). JBB is indebted to Industrial Farmacéutica Cantabria, Madrid (Spain).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1362). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1837–1839

4β,15-Dihydro-3-dehydrosolstitialin A†

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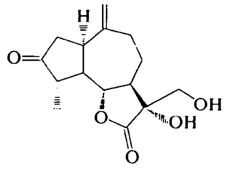
(*Received 24 May 1999; accepted 5 July 1999*)

Abstract

The sesquiterpene lactone 4β,15-dihydro-3-dehydrosolstitialin A, $C_{15}H_{20}O_5$, was isolated from *Centaurea musimomum*, a composite collected in the Souk-Ahra area in the east of Algeria. The fused-ring system contains a seven-membered ring in a twisted-boat and two five-membered rings with envelope conformations. The crystal structure is stabilized by intermolecular hydrogen bonds, with O···O separations of 2.709 (3) and 3.007 (2) Å.

Comment

In connection with a systematic investigation of the genus *Centaurea*, this paper presents the results of a structural study of 4β,15-dihydro-3-dehydrosolstitialin A, (I), a sesquiterpene lactone isolated from aerial parts of *Centaurea musimomum* (Bermejo, 1998), which could only be isolated as the diacetate from *C. behen* and *C. solstitialin* (Rustaiyan *et al.*, 1981; Öksüz *et al.*, 1993). Compound (I), m.p. 427–428 K, was obtained as colourless crystals by repeated silicic acid chromatography; IR bands at ν 3400, 1770, 1730 and 1640 cm^{-1} indicated the presence, respectively, of a hydroxy, a γ-lactone, a cyclopentanone and a double bond function. The spectroscopic properties (IR and ^{1}H and ^{13}C NMR) of this lactone are closely related to those of solstitialin A, the absolute configuration of which was established by Thiessen & Hope (1970). This structural information suggests that (I) is a guayanolide-type sesquiterpene containing two hydroxy groups, a γ-lactone, a cyclopentanone and a methylene double bond.



(I)

The structure and stereochemistry of (I) were established by our analysis; the absolute configuration was not determined by this X-ray analysis and that shown was chosen to be the same as that for solstitialin A The ground state of molecule (I) is non-planar. Bond lengths and angles are generally as expected. The molecule (Fig. 1) involves a seven-membered ring in a twisted-boat conformation. Deviations of atoms in this ring from the Cremer & Pople (1975) plane were less than 0.1 Å for atoms C5, C8 and C9 and more than 0.4 Å for the remaining atoms of the ring. Using the same definition for the two five-membered rings, the lactone is present in an

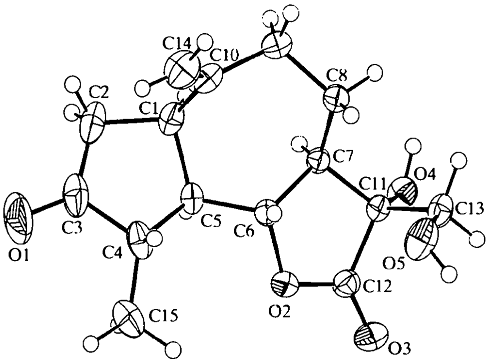


Fig. 1. A perspective view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

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† Alternative nomenclature: 11α-acetoxy-13-hydroxy-4α-methyl-3-oxo-1α*H*,5α*H*,6β*H*,7α*H*-guai-10(14)-en-6,12-olide or 3-hydroxy-3-hydroxymethyl-9-methyl-6-methyleneperhydroazuleno[4,5-*b*]furan-2,8-dione.