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Fern-9(11)-en-6*α*-ol–methanol (1/1)

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The title compound, $C_{30}H_{50}O{\cdot}CH_4O$, is a triterpenoid. It consists of four six-membered rings and one five-membered ring. Of the four six-membered rings, two adopt the chair conformation, one is in the twist-boat conformation and the one containing a double bond is in a distorted chair conformation with distortion towards the boat conformation. The five-membered ring adopts the pure envelope conformation. There is a hydrogen bond between the O atom of the hydroxyl group at C6 and the O atom of the solvent molecule, but no other intermolecular hydrogen bonds exist in the structure, so it is stabilized by van der Waals interactions only.

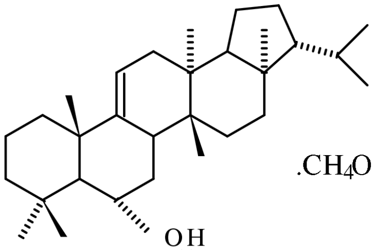
Key indicators

Single-crystal X-ray study
T = 293 K
Mean *σ*(C–C) = 0.004 Å
R factor = 0.052
wR factor = 0.158
Data-to-parameter ratio = 9.2

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

Comment

The title compound, (I), has been isolated from the whole plant of *Adiantum lunuatum* L. (Adiantaceae) which is a common fern and used as an ornamental plant in Japan, Europe and widely distributed in India. The dried whole plant has been used as a medicine for bronchitis and cough (Hashimoto & Nishimoto, 1996). Isolation of this compound has also been reported by another group (Sunder *et al.*, 1976). Spectroscopic analysis suggests that the compound is closely related to a derivative of fern-9(11)-ene, but there is an ambiguity regarding the position of the hydroxyl group which is located at C6. So to establish the structure unequivocally the present X-ray structural analysis of the title compound has been undertaken, which confirms the structure obtained by chemical and spectroscopic studies.



(I)

The data set does not contain any Friedel opposites, and the value of the Flack (1983) parameter obtained is inadequate to indicate the absolute configuration. However, the absolute stereochemistry of a related triterpenoid has been established by Oh & Maslen (1966) by a direct method of anomalous dispersion phasing and the present structure is in accord with this. Hence the present enantiomer has been retained.

The molecule is composed of five fused rings, four of which are six-membered and one is five-membered. Rings *A* (C1–C5/C10) and *D* (C13–C18) adopt a chair conformation (see

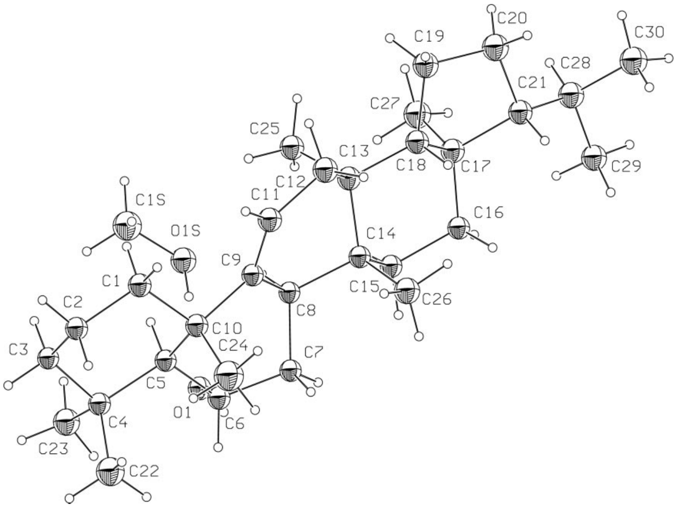


Figure 1
The structure of the title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme.

Table 2), ring *B* (C5–C9/C10) is in a twist boat conformation, ring *C* (C8–C14) containing a double bond is in a distorted chair conformation and the five-membered ring *E* (C17–C21) adopts an envelope conformation. The conformation of a chair in ring *A* followed by a boat in ring *B* is unusual but also observed in the pentacyclo triterpenoid (Parvez *et al.*, 1999). This configuration seems to have arisen from the coplanarity of atoms C8–C12 due to the double bond at C9═C11. The relevant torsion angles are C8—C9—C11—C12 −0.3 (5)° and C10—C9—C11—C12 177.4 (3)°. In ring C, atoms C8, C9, C13 and C14 are only approximately coplanar, with deviations of up to 0.238 (3) Å from their mean plane. Atom C8 is 0.526 (3) Å above this plane and atom C12 is 0.481 (3) Å below it. Hence it is inferred that the conformation of ring *C* is intermediate between a chair and a twist boat, with a ring puckering parameter φ = 95.1 (4)°. The ring-puckering parameters (Table 2) were calculated using the method of Cremer & Pople (1975). The hydroxyl group at C6 is twisted from the plane of the ring *B*. The associated torsion angles are C10—C5—C6—O1 −143.6 (2)° and C8—C7—C6—O1 81.4 (3)°.

The Csp^3—Csp^3 bond lengths lie between 1.519 (6) and 1.571 (4) Å. The variation in bond length indicates that the structure is subject to certain strain which mainly arises from the repulsion of the methyl groups at C25 and C27 and also from the constraint placed on C8–C12 to lie in one plane due to the presence of a double bond at C9═C11. Repulsion between two methyl groups C25 and C27 is evident in that the angles C18—C13—C25 112.3 (2)° and C18—C17—C27 115.3 (2)° are much larger than the normal tetrahedral value of 109.5° formed by pairs of Csp^3—Csp^3 bonds. Csp^3—Csp^2 bond lengths lie between 1.502 (5) and 1.546 (3) Å. In the molecule (Fig. 1), there is one endocyclic double bond C9═C11 and one Csp^3—O bond, indicated by the bond lengths 1.331 (4) and 1.451 (3) Å, respectively. All these values are within expected ranges.

The O1*S* atom of the methanol solvent molecule is connected to the main molecule through a hydrogen bond with the O atom of the hydroxyl group: O1*S*—H1O*S*···O1, with O1*S*···O1 2.781 (4) Å and O1*S*—H1O*S*···O1 173.2 (2)°. There are no other intermolecular hydrogen bonds and the structure is stabilized by van der Waals interactions.

Experimental

The shade-dried and powdered whole plant (1.25 kg) of *Adiantum lunulatum* was extracted with hexane (3 × 5 l) followed by CH_2Cl_2–MeOH (1:1) (3 × 5 l) at room temperature. The combined hexane extract was filtered and concentrated under pressure to obtain a greenish gummy residue (16.41 g). Silica gel column chromatography by gradient elution using hexane through hexane/benzene mixtures to benzene afforded the compound fern-9(11)-en-6α-ol (120 mg). Crystals of the title compound were then obtained from a solution in methanol by slow evaporation at room temperature. The extraction procedure is described by Niranjan Reddy *et al.* (2001).

Crystal data

$C_{30}H_{49}OH\cdot CH_4O$
$M_r = 458.74$
Monoclinic, $P2_1$
$a = 11.505$ (3) Å
$b = 8.484$ (2) Å
$c = 14.616$ (4) Å
$\beta = 99.42$ (3)°
$V = 1407.4$ (6) Å^3
$Z = 2$
$D_x = 1.083$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 39 reflections
$\theta = 11.1$–36.7°
$\mu = 0.49$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.19 × 0.14 × 0.11 mm

Data collection

Siemens AED single-crystal diffractometer
ω–2θ scans
Absorption correction: refdelf *DIFABS* (Walker & Stuart, 1983) and Gluzinski (1989)
$T_{min} = 0.92$, $T_{max} = 0.95$
5337 measured reflections
2865 independent reflections
2600 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 70.0°$
$h = -14 \rightarrow 13$
$k = -10 \rightarrow 2$
$l = 0 \rightarrow 17$
2 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.158$
$S = 1.12$
2865 reflections
310 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1072P)^2 + 0.1153P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.007$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0116 (17)
Absolute structure: Flack (1983)
Flack parameter = 0.0 (4)

Table 1
Selected geometric parameters (Å, °).

C6—O1	1.451 (3)		
C9—C11	1.331 (4)		
O1—C6—C7	108.8 (2)	C8—C9—C10	116.9 (2)
O1—C6—C5	107.0 (2)	C9—C11—C12	125.5 (2)
C11—C9—C8	120.7 (2)	C18—C13—C25	112.3 (2)
C11—C9—C10	122.4 (2)	C27—C17—C18	115.3 (2)
C10—C5—C6—O1	−143.6 (2)	C8—C9—C11—C12	−0.2 (5)
O1—C6—C7—C8	81.4 (3)	C10—C9—C11—C12	177.4 (3)

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Table 2
Ring-puckering parameters (Å, °).

Ring	q_2	q_3	Q_T	θ
A	0.037 (4)	0.562 (4)	0.563 (4)	3.7 (4)
B	0.758 (3)	−0.027 (3)	0.758 (3)	92.0 (2)
C	0.417 (3)	−0.355 (3)	0.548 (3)	130.4 (3)
D	0.038 (3)	0.563 (3)	0.564 (3)	3.9 (3)
E	0.490 (3)			

Methyl and hydroxy H atoms were placed in ideal positions according to difference-map calculations and were allowed torsional freedom, with $U(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C\ or\ O})$. The remaining H atoms were included at geometrically calculated positions and allowed to ride on their parent atoms with $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$.

Data collection: local program (Belletti *et al.*, 1992); cell refinement: local program; data reduction: local program; program(s) used to solve structure: *SIR*97 (Cascarano *et al.*, 1996); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai & Huttner, 1994); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardeli, 1983).

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