C6—C7	1.384 (2)	C16—C17	1.411 (2)
C7—C8	1.393 (2)	C18—C19	1.5465 (15)
O4—C18	1.4162 (13)	C19—C20	1.5424 (15)
O5—C12	1.3614 (15)	C20—C21	1.537 (2)
O5—C28	1.4290 (15)	C21—C22	1.530 (2)
N1—C16	1.316 (2)	C21—C25	1.541 (2)
N1—C15	1.370 (2)	C22—C23	1.533 (2)
N2—C24	1.5005 (15)	C24—C25	1.544 (2)
N2—C23	1.5060 (14)	C25—C26	1.498 (2)
N2—C19	1.5065 (13)	C26—C27	1.317 (2)
C1—O1—O3	68.49 (7)	O5—C12—C11	125.67 (10)
C2—O3—O1	65.38 (6)	O5—C12—C13	113.37 (11)
O2—C1—O1	126.86 (11)	C11—C12—C13	120.96 (11)
O2—C1—C2	117.08 (11)	C14—C13—C12	120.00 (11)
O1—C1—C2	116.06 (10)	C13—C14—C15	121.13 (11)
O3—C2—C3	112.05 (10)	N1—C15—C14	117.54 (10)
O3—C2—C1	109.89 (10)	N1—C15—C10	123.36 (11)
C3—C2—C1	110.28 (9)	C14—C15—C10	119.11 (11)
C8—C3—C4	119.19 (12)	N1—C16—C17	124.19 (11)
C8—C3—C2	120.95 (12)	C9—C17—C16	119.79 (11)
C4—C3—C2	119.86 (11)	O4—C18—C9	111.27 (9)
C5—C4—C3	120.70 (12)	O4—C18—C19	109.95 (9)
C4—C5—C6	119.83 (14)	C9—C18—C19	107.44 (8)
C7—C6—C5	119.80 (13)	N2—C19—C20	107.73 (9)
C6—C7—C8	120.54 (13)	N2—C19—C18	111.80 (8)
C7—C8—C3	119.93 (13)	C20—C19—C18	114.50 (9)
C12—O5—C28	116.98 (9)	C21—C20—C19	110.02 (9)
C16—N1—C15	116.95 (10)	C22—C21—C20	109.38 (9)
C24—N2—C23	109.30 (9)	C22—C21—C25	107.53 (10)
C24—N2—C19	108.85 (8)	C20—C21—C25	110.43 (9)
C23—N2—C19	113.06 (9)	C21—C22—C23	109.09 (9)
C17—C9—C10	118.36 (10)	N2—C23—C22	108.89 (9)
C17—C9—C18	120.09 (10)	N2—C24—C25	110.00 (9)
C10—C9—C18	121.50 (10)	C26—C25—C21	113.58 (11)
C15—C10—C9	117.30 (10)	C26—C25—C24	111.66 (10)
C15—C10—C11	119.04 (10)	C21—C25—C24	107.24 (9)
C9—C10—C11	123.67 (10)	C27—C26—C25	124.2 (2)
C12—C11—C10	119.73 (10)		
O1—C1—C2—O3	−5.13 (15)	C25—C21—N2—C24	7.11 (8)
O1—C1—C2—C3	118.87 (12)	C25—C21—N2—C19	125.10 (8)
C1—C2—C3—C4	70.32 (14)	C25—C21—N2—C23	−112.06 (8)
O3—C2—C3—C4	−166.93 (10)	C20—C21—N2—C19	3.54 (7)
C10—C9—C18—O4	159.14 (10)	C20—C21—N2—C23	126.38 (9)
C17—C9—C18—O4	−23.61 (14)	C20—C21—N2—C24	−114.45 (9)
C17—C9—C18—C19	96.79 (12)	C22—C21—N2—C23	5.67 (8)
C10—C9—C18—C19	−80.45 (12)	C22—C21—N2—C24	124.84 (9)
C9—C18—C19—N2	154.64 (9)	C22—C21—N2—C19	−117.17 (9)
C9—C18—C19—C20	−82.49 (11)	C24—C25—C26—C27	114.2 (2)
O4—C18—C19—C20	38.75 (11)	C11—C12—O5—C28	−3.1 (2)
O4—C18—C19—N2	−84.12 (11)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	H···A	D···A	D—H···A
O4—H4O···O1^i	1.72 (2)	2.6711 (12)	174 (1)
N2—H2N···O2^{ii}	1.70 (2)	2.6239 (13)	167 (2)
O3—H3O···O1	1.94 (2)	2.5857 (12)	129 (1)

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

All H atoms were located in difference Fourier calculations after refinement of the non-H atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *DREADD* (Blessing, 1987). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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6α-Hydroxyvouacapan-7β,17β-lactone†

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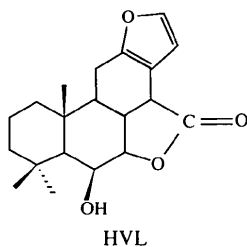
Abstract

In the crystal structure of the title compound, $C_{20}H_{26}O_4$, adjacent molecules are linked through hydrogen bonds in an infinite chain structure in the [100] direction.

† Alternative name: 4b,6a,7,7a,8,9,10,11,11a,11b,11c,12-dodecahydro-7-hydroxy-8,8,11a-trimethylphenanthro[3,2-*b*:10.10a,1-*bc*]difuran-5(5*H*)-one.

Comment

6α-Hydroxyvouacapan-7β,17β-lactone (HVL) is a synthetic derivative of 6α,7β-dihydroxyvouacapan-17β-oic acid (ADV), which was isolated from the fruits of *Pterodon polygalaeflorus* Benth, as reported by Mahajan & Monteiro (1973). Both compounds showed anti-

inflammatory and analgesic activities (Nunan, Pilo-Veloso, Turchetti & Alves, 1982; Ferreira Alves *et al.*, 1990); more recently it was reported that they also present a remarkable selectivity effect on the radial growth of mono- and dicotyledones (Demuner, Barbosa, Pilo-Veloso, Alves & Howarth, 1997). The title compound, HVL, was synthesized as described by Rubinger *et al.* (1991).

HVL

A *ZORTEP* (Zsolnai, Pritzkow & Huttner, 1996) drawing of HVL is shown in Fig. 1. According to Cremer–Pople parameters (Cremer & Pople, 1975; Iulek & Zuckerman-Schpector, 1997), the ring fused to furan [$\theta = 51.8\,(9)$ and $\varphi = 5\,(1)°$] is in a half-boat conformation, while rings C1—C2—C3—C4—C5—C10 [$\theta = 169.1\,(7)$ and $\varphi = 157\,(4)°$] and C5—C6—C7—C8—C9—C10 [$\theta = 8.4\,(7)$ and $\varphi = 286\,(5)°$] adopt chair conformations like ADV (Ruggiero, Rodrigues, Fernandes, Stefani & Pilo-Veloso, 1997). The lactone ring O3—C7—C8—C14—C17 [$\varphi = 74\,(8)°$] is in an envelope conformation.
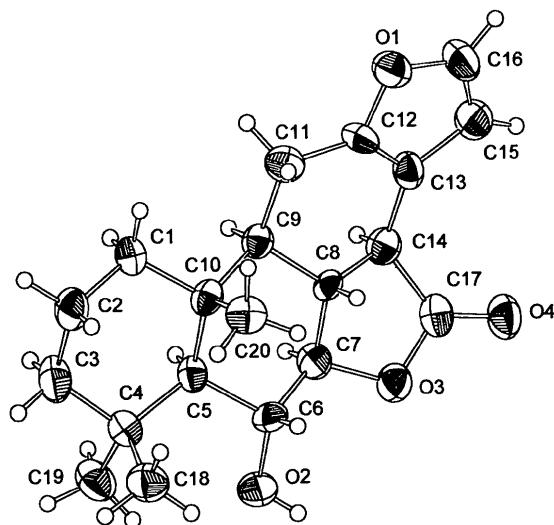

Fig. 1. The structure of HVL with atom labels. The displacement ellipsoids are plotted at the 50% probability level.

The crystal packing involves O2—HO2···O4^i intermolecular hydrogen bonds [O2—HO2 0.889 (10), O2···O4^i 2.879 (8), HO2···O4^i 2.068 (5) Å and O2—HO2···O4^i 151.1 (4)°; symmetry code: (i) $\frac{1}{2} + x$, $\frac{3}{2} - y$, $-z$].

Experimental

Single crystals of HVL suitable for X-ray analysis were obtained by slow evaporation of ethanol. The absolute structure could not be determined.

Crystal data

$C_{20}H_{26}O_4$	Mo $K\alpha$ radiation
$M_r = 330.41$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 25
$P2_12_12_1$	reflections
$a = 7.8937\,(6)$ Å	$\theta = 8.12–18.13°$
$b = 10.808\,(2)$ Å	$\mu = 0.090$ mm^{-1}
$c = 19.523\,(2)$ Å	$T = 298\,(2)$ K
$V = 1665.7\,(3)$ Å^3	Prism
$Z = 4$	$0.15 \times 0.08 \times 0.03$ mm
$D_x = 1.318$ Mg m^{-3}	Colourless
D_m not measured	

Data collection

Enraf–Nonius CAD-4	$\theta_{max} = 26.30°$
diffractometer	$h = -9 \rightarrow 0$
$\omega/2\theta$ scans	$k = -13 \rightarrow 0$
Absorption correction: none	$l = 0 \rightarrow 24$
1954 measured reflections	3 standard reflections
1954 independent reflections	frequency: 120 min
911 reflections with	intensity decay: none
$I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = -0.001$
$R[F^2 > 2\sigma(F^2)] = 0.057$	$\Delta\rho_{max} = 0.307$ e Å^{-3}
$wR(F^2) = 0.180$	$\Delta\rho_{min} = -0.347$ e Å^{-3}
$S = 1.169$	Extinction correction: none
1953 reflections	Scattering factors from
218 parameters	*International Tables for*
H atoms not refined	*Crystallography* (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2$	Absolute configuration:
$+ 1.7436P]$	Flack (1983)
where $P = (F_o^2 + 2F_c^2)/3$	Flack parameter = 3 (5)

Table 1. *Selected geometric parameters (Å, °)*

O2—C6	1.427 (9)	C7—C8	1.495 (10)
O3—C17	1.368 (9)	C8—C14	1.504 (9)
O3—C7	1.487 (8)	C14—C17	1.523 (10)
O4—C17	1.203 (8)		
C17—O3—C7	108.2 (6)	O4—C17—O3	121.5 (8)
O3—C7—C8	100.2 (6)	O4—C17—C14	129.8 (8)
C7—C8—C14	101.3 (6)	O3—C17—C14	108.6 (6)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Frenz, 1978). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XPMA* (Zsolnai, 1994) and *ZORTEP* (Zsolnai, Pritzkow & Huttner, 1996). Software used to prepare material for publication: *SHELXL93*.

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Relative and Absolute Configuration of Aloperine

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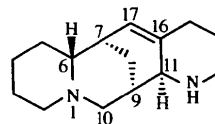
Abstract

The relative and absolute configuration of the title compound, (6*R*,7*R*,9*R*,11*S*)-16,17-didehydro-9-de-2-piperidinylormosanine, $C_{15}H_{24}N_2$, has been elucidated. Two

X-ray structures, one of the free base of the alkaloid and the second of its dihydrochloride monohydrate salt, $C_{15}H_{26}N_2^{2+}.2Cl^-.H_2O$, have been determined to unequivocally establish the stereochemistry of aloperine, the parent member of a rare family of lupinine alkaloids.

Comment

Aloperine, (1), is the parent member of a small family of C_{15} lupinine alkaloids that includes the *N*-methyl and *N*-allyl derivatives. Aloperine was first isolated in 1935 from the seeds and leaves of *Sophora alopecuroides* L. (Orechoff, Proskurnina & Konowalowa, 1935) and was later isolated from *Leptorhabdos parviflor* Benth. (Bocharnikova & Massagetov, 1964). In 1975, a bridged tetracyclic structure was proposed on the basis of chemical degradation, low-field NMR and mass spectrometric data (Tokachev *et al.*, 1975). However, the stereochemistry of aloperine had not been rigorously established and the absolute configuration was unknown. We report here the full stereostructure of aloperine.

(1)
(2) (1).2HCl.H₂O

The structurally related *Ormosia* alkaloids, in general, possess the aloperine skeleton in addition to a 2-piperidinyl substituent at C9, and are typically fully saturated at the C16—C17 juncture. Several diastereomers of this family have been isolated, and furthermore, have been isolated as single enantiomers, racemates or partial racemates, depending on the specific alkaloid and/or its plant source. Although absolute configurations have been determined for several compounds in the *Ormosia* family, both enantiomeric forms have been found (McLean, Misra, Kumar & Lamberton, 1981). Therefore, the *Ormosia* alkaloids cannot pro-
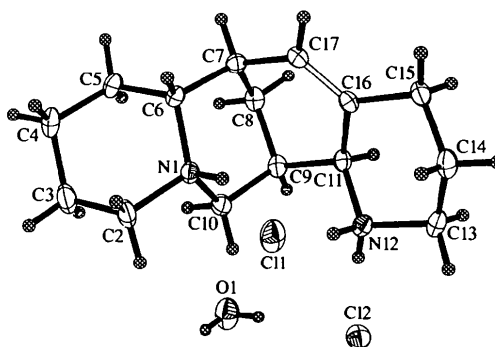

Fig. 1. Molecular structure of aloperine dihydrochloride monohydrate, (2), indicating its relative and absolute stereochemistry. Displacement ellipsoids are drawn at the 50% probability level.