Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1155). Services for accessing these data are described at the back of the journal.

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Relative and Absolute Configuration of Aloperine

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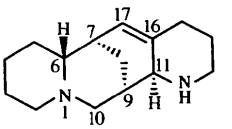
Abstract

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.H_2O

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-

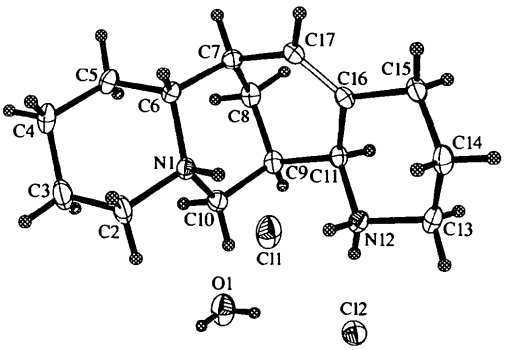


Fig. 1. Molecular structure of aloperine dihydrochloride monohydrate, (2), indicating its relative and absolute stereochemistry. Displacement ellipsoids are drawn at the 50% probability level.

vide a stereochemical reference for the aloperine family, members of which have been reported only as single enantiomers.

The structure of aloperine dihydrochloride monohydrate, (2), reveals an *anti* relationship between the angular methine H atom at C6 and the methano bridge (C8), and a *syn* relationship between the H atom at C11 and the methano bridge. The quinolizidine portion of the molecule is in an all-chair conformation and possesses a *cis* relationship between the H atom at C6 and the lone pair on N1. This finding agrees with earlier suggestions about the stereochemistry of this ring fusion (Tokachev *et al.*, 1975). The cyclohexene ring adopts a sofa conformation, while the piperidine ring has a chair conformation.

The structure of the free base of aloperine, (1), is substantially similar to that of the salt, (2), in that the conformations of all four rings are the same. However, the C—N bonds are somewhat longer in (2) than in (1). This variation in C—N bond lengths can also be seen within the *Ormosia* family. In general, structures of the *Ormosia* alkaloids reveal longer C—N bond lengths for salts than for free bases (Cheng, McLean, Misra & Nyburg, 1976; Mackay, McCall & Poppleton, 1976; Mackay & Poppleton, 1980; Mackay, Satzke & Matheison, 1975).

The absolute configuration of aloperine, as depicted in the scheme above for (1), was determined by refinement of the Flack (1983) parameter for (2). Thus, the aloperine family possesses the 6*R*,7*R*,9*R*,11*S* stereochemistry.

Experimental

Natural aloperine, (1), as supplied to us by Professors Chongchu Zhou and Qiming Zhang, was suitable for X-ray analysis. No recrystallization was required. Aloperine dihydrochloride monohydrate, (2), was prepared by treatment of a solution of aloperine in EtOH with excess HCl in Et_2O, followed by precipitation of the salt by the addition of EtOAc. The resulting solid was recrystallized from ^{i}PrOH and THF (1:2), affording colorless prisms in 82% yield.

Compound (1)

Crystal data

$C_{15}H_{24}N_2$
M_r = 232.27
Monoclinic
$P2_1$
a = 9.006 (2) Å
b = 6.6905 (13) Å
c = 10.963 (2) Å
β = 97.415 (14)°
V = 655.0 (2) Å^3
Z = 2
D_x = 1.178 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 31 reflections
θ = 3.76–13.85°
μ = 0.069 mm^{-1}
T = 158 K
Plate
0.24 × 0.17 × 0.07 mm
Colorless

Data collection

Siemens $P4$ diffractometer
$2\theta/\omega$ scans
Absorption correction: none
1747 measured reflections
1641 independent reflections
1335 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

θ_{max} = 27.49°
$h = -9 \rightarrow 11$
$k = -7 \rightarrow 8$
$l = -14 \rightarrow 14$
3 standard reflections
every 97 reflections
intensity decay: <1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.102
S = 1.076
1641 reflections
251 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2 + 0.1282P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.227 e Å^{-3}
$\Delta\rho_{min}$ = −0.160 e Å^{-3}

Extinction correction: *SHELXTL* (Sheldrick, 1994)
Extinction coefficient: 0.012 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0 (4)

Compound (2)

Crystal data

$C_{15}H_{26}N_2^{2+}.2Cl^-.H_2O$
M_r = 323.29
Orthorhombic
$P2_12_12_1$
a = 9.6442 (12) Å
b = 11.2487 (12) Å
c = 15.097 (2) Å
V = 1637.8 (4) Å^3
Z = 4
D_x = 1.311 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 28 reflections
θ = 4.99–13.59°
μ = 0.395 mm^{-1}
T = 158 K
Prism
0.30 × 0.30 × 0.26 mm
Colorless

Data collection

Siemens $P4$ diffractometer
$2\theta/\omega$ scans
Absorption correction: none
5777 measured reflections
4784 independent reflections
4277 reflections with $I > 2\sigma(I)$
R_{int} = 0.011

θ_{max} = 30.00°
$h = -13 \rightarrow 13$
$k = -15 \rightarrow 15$
$l = -21 \rightarrow 21$
2 standard reflections
every 98 reflections
intensity decay: <1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.073
S = 1.040
4784 reflections

Extinction correction: *SHELXTL* (Sheldrick, 1994)
Extinction coefficient: 0.0007 (6)

294 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0347P)^2 + 0.4519P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.358$ e Å^{-3}
$\Delta\rho_{min} = -0.205$ e Å^{-3}
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.02 (4)

For both compounds, data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *CARESS* (Broach, 1978); program(s) used to solve structures: *SHELXTL* (Sheldrick 1994); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1032). Services for accessing these data are described at the back of the journal.

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3,3,6,6-Tetramethyl-9-(2-phenylethyl)-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione

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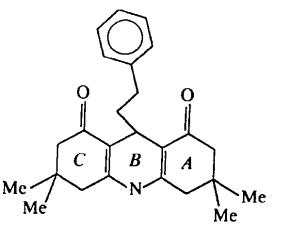
Abstract

In the title compound, $C_{25}H_{31}NO_2$, the phenyl ring is approximately perpendicular to the acridine moiety, whose planarity is lost as a consequence of lack of π-conjugation along the ring system. Intermolecular hydrogen bonding and van der Waals interactions stabilize the molecules in the crystal.

Comment

The fluorescence nature and the DNA binding tendency of acridinediones drew our attention towards the crystallographic study of these compounds (Sivaraman, Subramanian, Velmurugan, Subramanian & Shanmugasundaram, 1996). This work is part of our study to correlate their DNA binding ability with their structure. The observed bond angles around the N atom in



(I)

the heterocyclic ring of the title compound, (I), sum to 360° indicating sp^2 hybridization. Due to the N-atom lone pair delocalization, the bond lengths N10—C1a and N10—C8a are shorter than the C—N single bond, in agreement with the value of 1.355 (14) Å given by Allen *et al.* (1987) for the average C_{sp^2}—N_{sp^2} planar bond. Atoms C9 and C17 are completely staggered to one another about the C15—C16 bond. The substitution at C9 is in an axial position. Mean-plane calculations show that the compound is folded by

† DCB contribution No. 856.