

(-)-Argemonine hemihydrate

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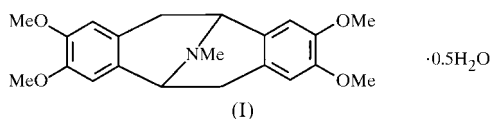
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(-)-Argemonine hemihydrate [systematic name: (6*S*,12*S*)-2,3,8,9-tetramethoxy-13-methyl-13-azabenzob[*b,f*]bicyclo[3.3.1]nona-2,6-diene hemihydrate], C₂₁H₂₅NO₄·0.5H₂O, is a tertiary pavinane alkaloid. Both partially saturated nitrogen heterocycles adopt twisted half-chair conformations. The angle between the two aromatic rings is 86.90 (5)°.

Comment

(-)-Argemonine hemihydrate, (I), is a member of a relatively small group of pavinane alkaloids occurring in some plant species of the genera *Argemone* (Papaveraceae), *Thalictrum* (Ranunculaceae) and *Berberis*, and some *Leontice* (Berberidaceae) (Gözler *et al.*, 1983). In the *Leontice* species, argemonine occurs as the dextrorotatory enantiomer (Gözler *et al.*, 1983). (-)-Argemonine has been isolated for the first time from *Argemone hispida* Gray (Soine & Gisvold, 1944; Schermerhorn & Soine, 1951) and later found in some other *Argemone* species which occur naturally in the southern regions of North America. The structure of argemonine was determined by Martell *et al.* (1963) and Stermitz *et al.* (1963), and the identity with *N*-methylpavine, a semisynthetic derivative of papaverine, was proved (Schöpf, 1949; Battersby & Binks, 1955). The absolute configuration was established as 6*S*,12*S* (Červinka *et al.*, 1966) and confirmed by the X-ray study of (-)-argemonine methiodide (Kaneda *et al.*, 1976).



Argemonine possesses an azabicyclo[3.3.1]nonadiene system fused with two benzene rings, each of them bearing two methoxy groups (Fig. 1). All bond lengths and angles are within normal ranges. The bond lengths involving trivalent nitrogen, *i.e.* N1—C6, N1—C12 and N1—C17, are 1.4610 (18), 1.4648 (18) and 1.4582 (18) Å, respectively. These are shorter than the corresponding distances involving tetravalent nitro-

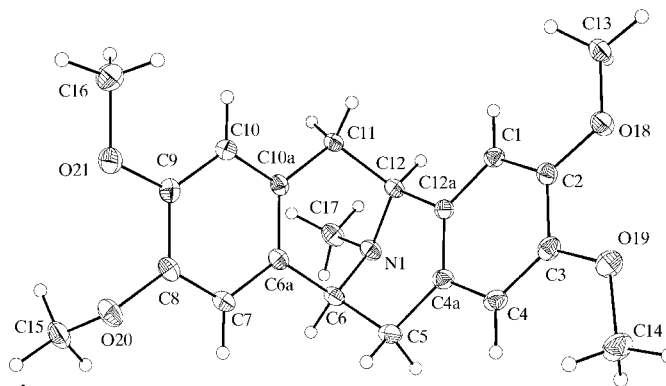


Figure 1
A perspective view of the (-)-argemonine molecule with the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level.

gen in argemonine methiodide (Kaneda *et al.*, 1976). The bond angles C12—N1—C17 [113.24 (12)°] and C6—N1—C17 [113.32 (12)°] are somewhat enlarged probably due to sterical repulsion of the *N*-methyl group within the rigid azabicyclic nonadiene system. The bond angles around the O atoms O18, O19 and O21 are enlarged [average value 116.2 (5)°] compared with the C8—O20—C15 angle [112.41 (12)°]. Similar findings were made for (-)-argemonine methiodide (Kaneda *et al.*, 1976). The three methoxy groups C2—OMe, C3—OMe and C9—OMe essentially lie in the planes of the adjacent aromatic rings [*cis* torsion angles of -0.9 (2), -0.8 (2) and 5.6 (2)°, respectively]. The remaining methoxy group (C8—OMe) is almost perpendicular to the aromatic plane [torsion angle C15—O20—C8—C7 -75.56 (18)°]. The angle between the two aromatic rings is 86.90 (5)° (Fig. 2). Both partially saturated nitrogen heterocycles adopt twisted half-chair conformations, with atoms N1, C6 and C12 deviating significantly from the planes of the aromatic rings.

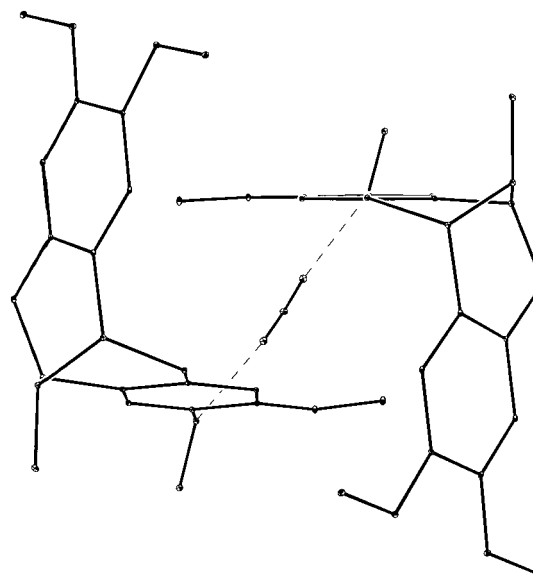


Figure 2
A view of two molecules of (-)-argemonine linked by O—H...O hydrogen bonds, with the water molecule on a twofold axis.

Both the last mentioned methoxy and the *N*-methyl group deviate most from molecular twofold symmetry. As they rotate freely, their position can be most easily affected by packing interactions, including hydrogen-bonding interactions. The conformation is nearly identical to the structure of argemonine methiodide, with the r.m.s. deviation of the superimposition being only 0.08 Å.

The water O atom of this hemihydrate lies on a twofold axis and takes part in O—H...O hydrogen bonding to symmetry-related argemonine molecules (Table 1). Their mutual orientation can be described as two crossed 'L' letters (Fig. 2). This finding is in contrast with the previously published structure of (–)-argemonine methiodide (Kaneda *et al.*, 1976), where the crystal packing revealed molecules aligned in a sandwich-like arrangement.

Experimental

(–)-Argemonine was isolated from *Argemone platyceras* Link et Otto (Slavík & Slavíková, 1963), crystallized from ether and recrystallized from aqueous methanol (m.p. 427–428 K), $[\alpha]_D^{21} = -208^\circ$ (0.5 M in CHCl₃).

Crystal data

C ₂₁ H ₂₅ NO ₄ ·0.5H ₂ O	$D_x = 1.337 \text{ Mg m}^{-3}$
$M_r = 364.43$	Mo $K\alpha$ radiation
Monoclinic, C2	Cell parameters from 50 reflections
$a = 18.169 (4) \text{ \AA}$	$\theta = 11.01\text{--}20.84^\circ$
$b = 9.801 (2) \text{ \AA}$	$\mu = 0.094 \text{ mm}^{-1}$
$c = 12.726 (3) \text{ \AA}$	$T = 130 (2) \text{ K}$
$\beta = 126.96 (3)^\circ$	Trigonal bipyramid, colourless
$V = 1810.8 (7) \text{ \AA}^3$	$0.70 \times 0.50 \times 0.50 \text{ mm}$
$Z = 4$	

Data collection

Kuma KM-4 CCD diffractometer	$\theta_{\max} = 28.48^\circ$
ω scans	$h = -23 \rightarrow 23$
6415 measured reflections	$k = -12 \rightarrow 13$
2254 independent reflections	$l = -16 \rightarrow 15$
2201 reflections with $I > 2\sigma(I)$	Intensity decay: none
$R_{\text{int}} = 0.021$	

Table 1

Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O30—H30A...O20	0.90 (4)	2.23 (3)	3.0997 (15)	164 (3)

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0540P)^2 + 0.4286P]$
$R[F^2 > 2\sigma(F^2)] = 0.028$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.077$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.057$	$\Delta\rho_{\max} = 0.23 \text{ e \AA}^{-3}$
2254 reflections	$\Delta\rho_{\min} = -0.21 \text{ e \AA}^{-3}$
249 parameters	
H atoms: see below	

The absolute structure could not be established from the present data (Flack, 1983) because of the weak anomalous scattering signal. Friedel reflections were merged for the final refinement. The absolute configuration shown, *i.e.* the 6*S*,12*S* isomer, is based on the absolute stereochemistry established previously (Červinka *et al.*, 1966; Kaneda *et al.*, 1976). All argemonine H atoms were treated as riding, with C—H = 0.93–0.98 Å. The H atom (H30A) of the water molecule was positioned from a difference map and allowed to refine isotropically.

Data collection: *KM-4 Software* (Kuma, 1992); cell refinement: *KM-4 Software*; data reduction: *KM-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Johnson & Burnett, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1108). Services for accessing these data are described at the back of the journal.

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