C7	0.85508 (11)	0.4782 (2)	0.15986 (14)	0.0408 (3)
O7	0.87533 (8)	0.4285 (2)	0.28766 (10)	0.0486 (3)
N8	0.89618 (10)	0.3890 (2)	0.05777 (13)	0.0458 (3)
O9	0.95877 (9)	0.2264 (2)	0.08540 (13)	0.0545 (3)

Table 2. *Selected geometric parameters* (Å, °)

C1—C2	1.512 (3)	C4—C5	1.497 (3)
C1—C6	1.526 (2)	C5—C6	1.517 (3)
C1—C7	1.502 (2)	C7—O7	1.247 (2)
C2—C3	1.517 (3)	C7—N8	1.322 (2)
C3—C4	1.504 (3)	N8—O9	1.383 (2)
C1—C2—C3	111.6 (2)	C2—C1—C7	112.14 (13)
C1—C6—C5	111.0 (2)	C3—C4—C5	112.1 (2)
C1—C7—O7	122.27 (13)	C4—C5—C6	111.6 (2)
C1—C7—N8	115.56 (12)	C6—C1—C7	109.39 (14)
C2—C3—C4	111.6 (2)	C7—N8—O9	121.71 (12)
C2—C1—C6	110.4 (2)	O7—C7—N8	122.16 (15)
C1—C2—C3—C4	54.6 (3)	C6—C1—C2—C3	−55.4 (2)
C2—C3—C4—C5	−54.0 (3)	C1—C7—N8—O9	−174.40 (12)
C3—C4—C5—C6	54.7 (3)	C3—C2—C1—C7	−177.6 (2)
C4—C5—C6—C1	−55.5 (3)	C5—C6—C1—C7	179.6 (2)
C5—C6—C1—C2	55.7 (2)	O7—C7—N8—O9	4.5 (2)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
N8—H8···O7^{i}	1.973 (2)	2.822 (2)	169.17 (5)
O9—H9···O7^{ii}	1.917 (2)	2.697 (2)	158.87 (4)

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

Data reduction: *DREADD* (Blessing, 1987, 1989). Program(s) used to solve structure: *SHELXS*90 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1191). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Securinine, an Alkaloid from *Fluggea virosa*

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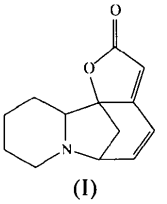
Abstract

Securinine, $C_{13}H_{15}NO_2$, is an alkaloid obtained from the leaves of the Vietnamese plant *Fluggea virosa* (*Roxb. ex Willd.*) Voigt. Its molecular structure differs markedly from the previously determined structure of its hydrobromide in that the piperidine ring has a regular chair conformation in the title compound but has a boat conformation in the protonated form.

Comment

Securinine (I) was isolated in 1.07% yield from the leaves of the Vietnamese plant *Fluggea virosa* (*Roxb. ex Willd.*) Voigt. The biological activity of securinine is well known. It stimulates the central nervous system in a manner similar to strychnine but is less toxic. It is useful in the treatment of paralysis following infectious disease and also in the treatment of psychological disorder (Do Tat Loi, 1986). So far, only the crystal structure of the hydrobromide dihydrate of securinine is known (Imado, Shiro & Horii, 1965).



(I)

A sample of the free base was isolated as mentioned above and recrystallized from chloroform (m.p. 414–416 K, molecular peak at m/z = 217). Its structure was examined by X-ray analysis to establish its spatial structure and to allow comparison with its protonated form.

The molecular structure of securinine (free base) is shown in Fig. 1 along with the atom-numbering scheme. The absolute configuration was chosen in accordance with that of the hydrobromide. Bond lengths and angles are in the expected ranges. The N—C bonds (average 1.460 Å) are considerably shorter than the corresponding bonds in the hydrobromide (average 1.52 Å) due to the protonation of the nitrogen in the latter. The two dienic double bonds C3═C4 [1.333 (6) Å] and C5═C6 [1.337 (6) Å] are comparable in the present structure but are different in the hydrobromide (1.32 and 1.40 Å). There is a major conformational difference in the oligocyclic ring system between the free base and the protonated form. As indicated by the Cremer–Pople puckering parameters (Cremer & Pople, 1975; Luger & Bülow, 1983), the piperidine ring in the title compound has a normal almost undistorted chair conformation, while the piperidine ring of the protonated form has an unusual boat conformation (Table 3), obviously caused by an N—H···Br hydrogen bond involving the protonated N atom. It was thought that in the free base the nitrogen lone pair would be directed in the same way as the N→H vector in the protonated form so as to approach close to the diene part of the molecule; however, the molecular structure of the title compound shows that this is not the case. There is little conformational difference in the five-membered (N7, C7, C14, C13, C12) and six-membered (C7, C6, C5, C4, C13, C14) rings for both structures (Table 3). While the five-membered ring has a twist form with a tendency towards an envelope conformation (C7 as the out-of-plane atom), the six-membered ring is intermediate between an envelope (C14 as the out-of-plane atom) and a half-chair form. The lactone ring is planar (average deviation of the contributing atoms from the least-squares plane σ = 0.009 Å); however, the diene part is not, as was already observed in the protonated molecule. The least-squares plane through the lactone ring is inclined to the plane through atoms C13, C4, C5, C6 and C7 by an angle of 13.3 (2)° (this angle was 10° in the hydrobromide). There are no short contact distances in the crystal lattice of the title compound so no special intermolecular interactions are observed.

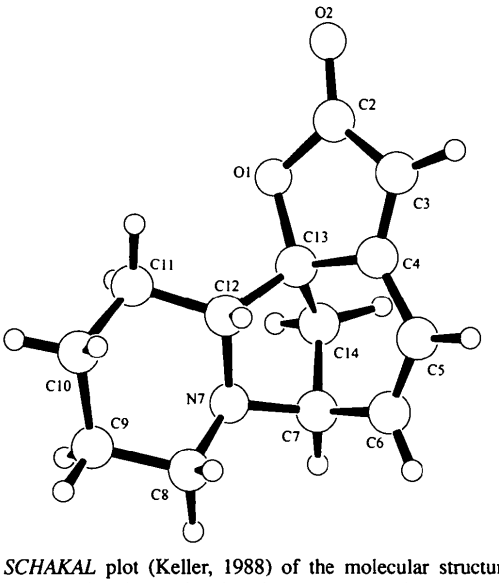


Fig. 1. *SCHAKAL* plot (Keller, 1988) of the molecular structure of securinine (free base) showing the atom-numbering scheme.

Experimental

Crystal data

$C_{13}H_{15}NO_2$	Cu $K\alpha$ radiation
M_r = 217.27	λ = 1.5418 Å
Orthorhombic	Cell parameters from 86 reflections
$P2_12_12_1$	θ = 20–40°
a = 16.492 (4) Å	μ = 0.724 mm^{-1}
b = 9.483 (3) Å	T = 293 K
c = 7.025 (2) Å	Plate
V = 1098.7 (5) $Å^3$	0.44 × 0.10 × 0.06 mm
Z = 4	Yellow
D_x = 1.313 Mg m^{-3}	

Data collection

Stoe four-circle MicroVAX-controlled diffractometer	θ_{max} = 63.99°
$\omega/2\theta$ scans	$h = 0 \rightarrow 19$
Absorption correction: none	$k = 0 \rightarrow 11$
1081 measured reflections	$l = 0 \rightarrow 8$
1081 independent reflections	3 standard reflections
816 observed reflections [$F_o > 2\sigma(F_o)$]	frequency: 90 min
	intensity variation: statistical

Refinement

Refinement on F	$\Delta\rho_{max}$ = 0.259 e $Å^{-3}$
R = 0.036	$\Delta\rho_{min}$ = −0.264 e $Å^{-3}$
wR = 0.026	Extinction correction: Zachariasen
S = 1.717	Extinction coefficient: 925 (42)
816 reflections	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)
206 parameters	
All H-atom parameters refined	
Weighting scheme based on measured e.s.d.'s	
$(\Delta/\sigma)_{max}$ = 0.722	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.3985 (2)	0.2371 (3)	0.2235 (4)	0.046 (2)
C2	0.3345 (3)	0.1609 (5)	0.1494 (6)	0.049 (3)
O2	0.3017 (2)	0.2008 (4)	0.0058 (4)	0.067 (2)

C3	0.3192 (2)	0.0400 (5)	0.2710 (6)	0.044 (3)
C4	0.3701 (2)	0.0462 (4)	0.4183 (6)	0.039 (2)
C5	0.3813 (2)	−0.0346 (5)	0.5921 (7)	0.049 (3)
C6	0.4274 (3)	0.0222 (6)	0.7284 (6)	0.051 (3)
C7	0.4682 (3)	0.1633 (5)	0.7039 (6)	0.048 (3)
N7	0.5418 (2)	0.1597 (4)	0.5867 (5)	0.041 (2)
C8	0.6156 (3)	0.0866 (6)	0.6401 (7)	0.051 (3)
C9	0.6822 (3)	0.1389 (7)	0.5077 (8)	0.060 (3)
C10	0.6582 (3)	0.1219 (7)	0.2989 (7)	0.057 (3)
C11	0.5745 (3)	0.1846 (6)	0.2549 (7)	0.049 (3)
C12	0.5148 (2)	0.1231 (4)	0.3948 (6)	0.035 (2)
C13	0.4254 (2)	0.1701 (4)	0.3964 (6)	0.037 (2)
C14	0.4162 (3)	0.2583 (5)	0.5768 (7)	0.047 (3)

Table 2. *Selected geometric parameters* (Å, °)

O1—C2^{i}	1.381 (5)	C7—C14^{i}	1.530 (6)
O1—C13^{i}	1.441 (5)	N7—C8^{i}	1.451 (6)
C2—O2^{i}	1.205 (5)	N7—C12^{i}	1.462 (5)
C2—C3^{i}	1.452 (6)	C8—C9^{i}	1.522 (7)
C3—C4^{i}	1.333 (6)	C9—C10^{i}	1.528 (7)
C4—C5^{i}	1.453 (6)	C10—C11^{i}	1.534 (7)
C4—C13^{i}	1.495 (5)	C11—C12^{i}	1.509 (6)
C5—C6^{i}	1.337 (6)	C12—C13^{i}	1.541 (5)
C6—C7^{i}	1.507 (7)	C13—C14^{i}	1.526 (6)
C7—N7^{i}	1.467 (5)		
C2^{i}—O1—C13^{i}	108.8 (3)	C8^{i}—N7—C12^{i}	112.4 (3)
O1^{i}—C2—O2^{i}	119.6 (4)	N7^{i}—C8—C9^{i}	107.0 (4)
O1^{i}—C2—C3^{i}	108.9 (3)	C8^{i}—C9—C10^{i}	111.4 (4)
O2^{i}—C2—C3^{i}	131.5 (4)	C9^{i}—C10—C11^{i}	112.7 (4)
C2^{i}—C3—C4^{i}	108.2 (4)	C10^{i}—C11—C12^{i}	107.8 (4)
C3^{i}—C4—C5^{i}	135.1 (4)	N7^{i}—C12—C11^{i}	108.1 (3)
C3^{i}—C4—C13^{i}	109.8 (4)	N7^{i}—C12—C13^{i}	102.5 (3)
C5^{i}—C4—C13^{i}	115.1 (3)	C11^{i}—C12—C13^{i}	121.2 (4)
C4^{i}—C5—C6^{i}	117.5 (4)	O1^{i}—C13—C4^{i}	104.2 (3)
C5^{i}—C6—C7^{i}	122.0 (4)	O1^{i}—C13—C12^{i}	114.6 (3)
C6^{i}—C7—N7^{i}	114.4 (4)	O1^{i}—C13—C14^{i}	115.4 (3)
C6^{i}—C7—C14^{i}	109.8 (4)	C4^{i}—C13—C12^{i}	110.9 (3)
N7^{i}—C7—C14^{i}	98.6 (3)	C4^{i}—C13—C14^{i}	106.5 (3)
C7^{i}—N7—C8^{i}	124.1 (3)	C12^{i}—C13—C14^{i}	105.0 (3)
C7^{i}—N7—C12^{i}	105.7 (3)	C7^{i}—C14—C13^{i}	96.1 (3)

Symmetry code: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Table 3. *Cremer–Pople puckering parameters in the oligocyclic ring system of securinine*

The first line of data represents the free base and the second the hydrobromide dihydrate (Imado, Shiro & Horii, 1965). Ring *A* is the piperidine ring, ring *B* is N7, C7, C14, C13 and C12, and ring *C* is C7, C6, C5, C4, C13 and C14. C = chair, B = boat, H = half-chair, T = twist, E = envelope.

Ring	Size	Q, q_2 (Å)	Φ, ϕ_2 (°)	θ (°)	Type
A	6	0.598 (5)	156 (3)	171.4 (4)	C
		0.770	49	91.6	B
B	5	0.544 (4)	48.9 (4)		T⟝E
		0.513	59.9		T⟝E
C	6	0.675 (4)	105.9 (5)	129.3 (4)	E↔H
		0.600	112.5	132.1	E↔H

Data collection: Stoe software. Cell refinement: Stoe software. Data reduction: *Xtal ADDREF SORTRF* (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *Xtal CRYLSQ* (Hall, Flack & Stewart, 1992). Molecular graphics: *SCHAKAL*88 (Keller, 1988). Software used to prepare material for publication: *Xtal BONDLA CIFIO* (Hall, Flack & Stewart, 1992).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including H-atom geometry, and torsion angles have been deposited with the IUCr (Reference: SE1067). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4,5-Dicyclohexyl-1,3,2-dioxathiolane 2-Oxide, $C_{14}H_{24}O_3S$

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Abstract

The title compound, 4,5-dicyclohexyl-1,3,2-dioxathiolane 2-oxide (1), adopts a half-chair (envelope) conformation with the S=O bond taking up a pseudo-axial position. The cyclohexyl groups occupy *trans* positions.

Comment

The conformations of phenyl-1,3,2-dioxathiolane 2-oxides (five-membered cyclic sulfites) have been studied by several physical methods, including X-ray crystallography (Hellier & Motevalli, 1995), from which it is evident that the envelope conformation is adopted with a strong preference for the S=O bond to take up a pseudo-axial position. As a part of our extensive investigation of the structures of a wide variety of cyclic sulfites, we were interested in the