C5′	0.9173 (4)	0.4498 (2)	−0.628 (1)	4.7 (1)
C6′	0.9172 (3)	0.4131 (2)	−0.484 (1)	4.5 (1)
OM†	0	0	1/2	9.8 (8)
*OM*1†	0.476 (2)	0.4881 (9)	0.784 (7)	8.2 (7)
*OM*2†	0.518 (2)	0.5084 (8)	0.748 (7)	7.7 (7)
CM†	−0.021 (3)	0.024 (1)	0.53 (1)	9 (1)
*CM*1†	−0.024 (2)	0.0083 (9)	0.017 (9)	8.6 (7)

† Partially occupied (see below).

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

S5—C12	1.758 (4)	N3—C3	1.394 (5)
S5—C13	1.762 (4)	N4′—C4′	1.482 (5)
O3—N4′	1.205 (5)	C1—C2	1.370 (6)
O4—N4′	1.221 (6)	C2—C3	1.384 (5)
N10—C11	1.385 (5)	C3—C4	1.410 (5)
N10—C14	1.426 (5)	C4—C12	1.369 (5)
N10—C15	1.465 (5)	C1—C11	1.400 (5)
N1′—N3	1.258 (4)		
C12—S5—C13	99.1 (2)	O1—N2′—C2′	118.2 (4)
C11—N10—C14	120.4 (4)	N10—C11—C1	122.1 (3)
N10—C11—C12	120.0 (3)	S5—C12—C4	119.1 (3)
S5—C12—C11	119.4 (3)	N1′—C1′—C6′	124.9 (4)
C11—N10—C15	118.8 (3)	N1′—C1′—C2′	117.4 (3)
N1′—N3—C3	114.8 (3)	N2′—C2′—C3′	116.6 (4)
O1—N2′—O2	123.4 (4)	N2′—C2′—C1′	119.7 (4)

The methanol molecule had a site-occupation factor of 0.5. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares techniques. H atoms were located by difference Fourier synthesis. During refinement, a disordered region consisting of partially occupied methanol molecules was identified. This region contains molecules in orientations which would be mutually incompatible were they to be fully occupied. The disordered C and O atoms of methanol were labelled *OM*, *OM*1, *OM*2, *CM* and *CM*1, and their occupation factors refined to be 0.14, 0.18, 0.18, 0.20 and 0.30, respectively. The atoms were refined with isotropic displacement parameters. All calculations were performed with the *SDP-Plus* program system (Frenz, 1985) on a DEC PDP11/44 computer system.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP-Plus*. Program(s) used to solve structure: *SDP-Plus*. Program(s) used to refine structure: *SDP-Plus*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM0002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 2791-2793

A Pyridine-2,6(1*H*,3*H*)-dione Alkaloid

Ying Zhu,[a]* Zhong-Jian Jia,[a] Jian-Gong Shi[b] and Han-Qing Wang[b]

[a]*National Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China, and* [b]*Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China*

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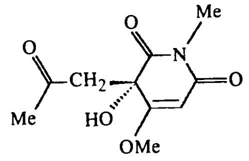
Abstract

The crystal structure of the pyridine-2,6(1*H*,3*H*)-dione alkaloid 3-acetonyl-3-hydroxy-4-methoxy-1-methyl-pyridine-2,6(1*H*,3*H*)-dione, $C_{10}H_{13}NO_5$, has been determined. The tetrahydropyridine ring possesses a distorted half-chair conformation. The unit-cell molecular packing appears to be stabilized by hydrogen bonding.

Comment

Speranskia tuberculata (Bge.) *Baill* (Chinese name: Tou Gu Cao) is a Chinese herb which is widely distributed in the Gansu, Jiling, Hebai, Shandong and Anhui Provinces of China. It has been used for the treatment of rheumatic arthritis, contracture, sores, swelling, pain and inflammatory diseases (Jiangsu Xingyi Xueyuan, 1977). No work has been published previously on this genus. We isolated a novel pyridine-2,6(1*H*,3*H*)-dione alkaloid, (I), from the the dried whole plant of *S. tuberculata*, which grows in Beizai, Gansu Province of China, and report here its structure.



(I)

The C(4)—C(5) bond length exhibits double-bond character. The torsion angles of the tetrahydropyridine ring possess approximate local C_2 symmetry about an axis bisecting the C(2)—C(3) and C(5)—C(6) bonds. The asymmetry parameter ΔC_2 is 2.7 indicating that the ring preferably adopts a distorted half-chair conformation (Duax, Weeks & Rohrer, 1976) similar to most 1,2,3,6- and 1,2,5,6-tetrahydropyridine rings that exist in half-chair conformations (Bandoli, Dolmella, Moos, Nicolini & Ongaro, 1991).

The molecules are linked through intermolecular hydrogen bonds; O(2)—HO(2) 0.90 (5), HO(2)···O(1^{i}) 1.90 (5), O(2)···O(1^{i}) 2.764 (3) Å and O(2)—HO(2)···O(1^{i}) 161 (4)° [symmetry code: (i) $x, \frac{1}{2}-y, z-\frac{1}{2}$].

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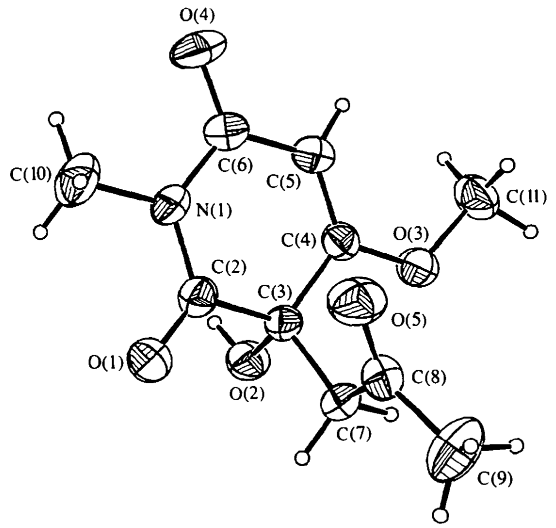

Fig. 1. View of the title molecule shown with 50% probability displacement ellipsoids.

Experimental

The title alkaloid, (I), was isolated from the acetone extract of the dried whole plant of *S. tuberculata*, which grows in Beizai, Gansu Province of China.

Crystal data

$C_{10}H_{13}NO_5$
$M_r = 227.22$
Monoclinic
$P2_1/c$
$a = 8.5879\,(7)$ Å
$b = 17.4610\,(8)$ Å
$c = 7.893\,(1)$ Å
$\beta = 113.82\,(1)°$
$V = 1082.8\,(3)$ Å^3
$Z = 4$
$D_x = 1.394$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 20$–39°
$\mu = 0.961$ mm^{-1}
$T = 293$ K
Prismatic
$0.25 \times 0.18 \times 0.08$ mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.78$, $T_{\max} = 0.93$
1886 measured reflections
1638 independent reflections

1514 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.040$
$\theta_{\max} = 62°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 19$
$l = -9 \rightarrow 9$
3 standard reflections
frequency: 60 min
intensity decay: insignificant

Refinement

Refinement on F
$R = 0.054$
$wR = 0.055$
$S = 0.801$
1690 reflections
145 parameters
H atoms: see below
Unit weights applied

$(\Delta/\sigma)_{\max} = 0.16$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
O(1)	0.8422 (2)	0.2663 (1)	0.9489 (3)	3.78 (5)
O(2)	0.6251 (2)	0.1862 (1)	0.6082 (2)	3.18 (4)
O(3)	0.6757 (2)	0.0228 (1)	0.6788 (3)	3.45 (5)
O(4)	1.2283 (2)	0.1216 (1)	0.8429 (3)	5.08 (6)
O(5)	0.8699 (2)	0.1052 (1)	1.1448 (3)	4.25 (5)
N(1)	1.0340 (3)	0.1964 (1)	0.8893 (3)	2.89 (5)
C(2)	0.8750 (3)	0.2082 (2)	0.8846 (3)	2.67 (6)
C(3)	0.7317 (3)	0.1506 (2)	0.7807 (3)	2.38 (5)
C(4)	0.7992 (3)	0.0762 (2)	0.7416 (4)	2.63 (6)
C(5)	0.9594 (3)	0.0673 (2)	0.7605 (4)	3.10 (6)
C(6)	1.0827 (3)	0.1281 (2)	0.8306 (4)	3.19 (6)
C(7)	0.6196 (3)	0.1391 (2)	0.8859 (4)	2.66 (6)
C(8)	0.7152 (3)	0.1093 (2)	1.0794 (4)	3.07 (6)
C(9)	0.6152 (4)	0.0865 (2)	1.1862 (4)	4.98 (8)
C(10)	1.1618 (4)	0.2571 (2)	0.9660 (5)	4.42 (8)
C(11)	0.7226 (4)	−0.0516 (2)	0.6326 (5)	4.09 (8)

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

O(1)—C(2)	1.217 (4)	N(1)—C(10)	1.470 (3)
O(2)—C(3)	1.441 (3)	C(2)—C(3)	1.544 (3)
O(3)—C(4)	1.348 (4)	C(3)—C(4)	1.504 (4)
O(3)—C(11)	1.449 (4)	C(3)—C(7)	1.517 (4)
O(4)—C(6)	1.220 (4)	C(4)—C(5)	1.332 (5)
O(5)—C(8)	1.218 (3)	C(5)—C(6)	1.442 (4)
N(1)—C(2)	1.366 (4)	C(7)—C(8)	1.505 (4)
N(1)—C(6)	1.403 (4)	C(8)—C(9)	1.480 (5)
C(4)—O(3)—C(11)	117.1 (2)	C(4)—C(3)—C(7)	112.4 (2)
C(2)—N(1)—C(6)	123.2 (2)	O(3)—C(4)—C(3)	111.2 (2)
C(2)—N(1)—C(10)	118.3 (2)	O(3)—C(4)—C(5)	125.8 (3)
C(6)—N(1)—C(10)	118.5 (2)	C(3)—C(4)—C(5)	122.9 (2)
O(1)—C(2)—N(1)	120.8 (2)	C(4)—C(5)—C(6)	121.5 (3)
O(1)—C(2)—C(3)	119.7 (2)	O(4)—C(6)—N(1)	119.0 (3)
N(1)—C(2)—C(3)	119.3 (2)	O(4)—C(6)—C(5)	122.2 (3)
O(2)—C(3)—C(2)	106.6 (3)	N(1)—C(6)—C(5)	118.9 (3)
O(2)—C(3)—C(4)	109.3 (3)	C(3)—C(7)—C(8)	113.2 (3)
O(2)—C(3)—C(7)	105.8 (2)	O(5)—C(8)—C(7)	120.4 (3)
C(2)—C(3)—C(4)	112.5 (3)	O(5)—C(8)—C(9)	121.8 (3)
C(2)—C(3)—C(7)	110.0 (2)	C(7)—C(8)—C(9)	117.8 (2)
C(6)—N(1)—C(2)—C(3)	−10.7 (4)	C(2)—C(3)—C(4)—C(5)	−12.8 (4)
C(2)—N(1)—C(6)—C(5)	0.4 (4)	C(3)—C(4)—C(5)—C(6)	3.6 (4)
N(1)—C(2)—C(3)—C(4)	16.0 (3)	C(4)—C(5)—C(6)—N(1)	3.5 (4)

The title structure was solved by direct and Fourier methods and refined by full-matrix least squares. Non-H atoms were refined with anisotropic displacement parameters. The positions of the H atoms were located from difference Fourier maps and were included in the structure-factor calculations and not refined. Data collection and cell refinement were carried out using *CAD-4 Software* (Enraf–Nonius, 1989). Structure determination and refinement were performed using *SDP-Plus* (B. A. Frenz & Associates Inc., 1985) running on a DEC PDP11/44 computer. The diagram was produced using *ORTEP*II (Johnson, 1976).

The authors thank the National Laboratory of Applied Organic Chemistry for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: TA1075). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,7-Dimethyl-5-phenyl-2-(3-thenoylaminomethyl)-2,3-dihydro-1*H*-1,4-benzodiazepin-4-ium Chloride

NORBERT M. BLATON, OSWALD M. PEETERS AND CAMIEL J. DE RANTER

Laboratorium voor Analytische Chemie en Medicinale Fysicochemie, Faculteit Farmaceutische Wetenschappen, Katholieke Universiteit Leuven, Van Evenstraat 4, B-3000 Leuven, Belgium. E-mail: maurice.peeters@farm.kuleuven.ac.be

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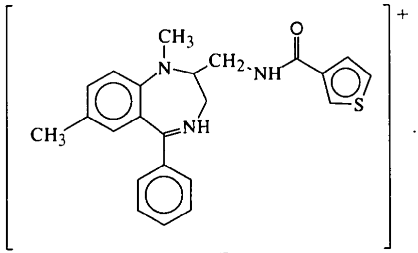
Abstract

The seven-membered ring of $C_{23}H_{24}N_3OS^+.Cl^-$ has a conformation halfway between a distorted boat and a distorted sofa. The 3-thenoylaminomethyl moiety is in an extended conformation. This conformation is stabilized by two hydrogen bonds with the chloride anion, one from the protonated basic N atom of the heptadiene ring and another from the amidic N atom. The thienyl ring shows 180° rotational disorder.

Comment

The title compound, (I), belongs to a series of 2-acylaminomethylbenzodiazepine derivatives with opioid activity. This single-crystal structure analysis is part of a structure–activity study on κ-opioid agonists related to tifluadom. Fig. 1 shows the molecule. Bond lengths and angles show small deviations from values found in other compounds of the series (Blaton, Peeters, Meurisse & De Ranter, 1996, and references therein). The puckering parameters [sequence N1, C2, C3, N4, C5, C5a, C9a: $q_2 = 0.678(3)$, $q_3 = 0.299(3)$ Å, $\varphi_2 = -36.0(2)$, $\varphi_3 = -142.8(5)°$] and asymmetry parameters [$\Delta C_s(C_3) = 0.071(1)$] indicate a conformation halfway between a distorted boat and a distorted sofa. The 3-thenoylaminomethyl side chain has the extended conformation and substitutes the diazepine ring axially at position 2. This side chain is stabilized by two N—H···Cl hydrogen bonds [N4···Cl = 3.052(2), H4···Cl = 2.28 Å, N4—H4···Cl = 150.4°; N12···Cl = 3.213(2), H12···Cl = 2.40, N12—H12···Cl = 158°].



(I)

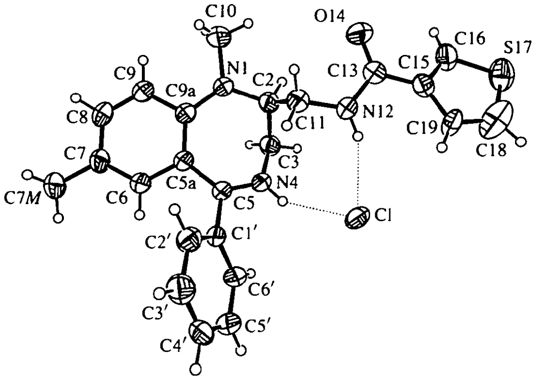


Fig. 1. Perspective view of the title compound with the thienyl ring in the *A* conformation showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

Experimental

Crystals of the title compound were obtained by slow evaporation at room temperature from a solution in methanol/amyl acetate.

Crystal data

$C_{23}H_{24}N_3OS^+.Cl^-$
$M_r = 425.96$
Monoclinic
$P2_1/n$
$a = 10.319(2)$ Å
$b = 8.933(2)$ Å
$c = 23.976(2)$ Å
$\beta = 94.92(2)°$

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 24 reflections
$\theta = 15–23°$
$\mu = 2.560$ mm^{-1}
$T = 293$ K
Prism

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