Acta Cryst. (1996). **C52**, 1491–1493

7-Methoxyvasicinone Hydrate

Dharminder K. Magotra,[a] Vivek K. Gupta,[a] Rajnikant,[a] Kaidar N. Goswami,[a] Rajinder K. Thappa[b] and Shri G. Agarwal[b]

[a]*Department of Physics, University of Jammu, Jammu Tawi 180004, India, and* [b]*Regional Research Laboratory, Jammu Tawi 180001, India*

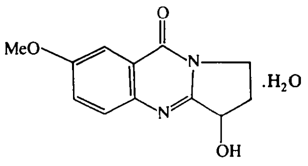
(*Received 15 March 1995; accepted 4 August 1995*)

Abstract

The phenyl ring in the title compound, 3β-hydroxy-7-methoxy-2,3-dihydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one hydrate, $C_{12}H_{12}N_2O_3.H_2O$, is perfectly planar. The pyrimidine ring deviates slightly from planarity and the five-membered ring has a conformation intermediate between a half-chair and an envelope. Molecules are held together in the crystal by hydrogen bonds.

Comment

The title compound, (I), has been isolated from the leaves of *Adhatoda vasica* (Nees), a highly reputed ayurvedic medicinal plant used for the treatment of asthma, bronchitis and tuberculosis (Mehta, Naravane & Desai, 1963). The plant is a rich source of quinazoline alkaloids (Atal, 1981; Pandita *et al.*, 1983; Dhar, Jain, Kaul & Atal, 1981). The present study is part of a program of crystal-structure analyses of these alkaloids.



(I)

A drawing of the title compound with the atomic numbering scheme is shown in Fig. 1. The C3a—N4 bond [1.288 (4) Å] displays typical double-bond character (Allen *et al.*, 1987). The N—C—N angle in the present structure is 125.2 (3)°. Generally, this bond angle has been found to be greater than 120° in most pyrimidine and quinazoline compounds (Wheatley, 1960; Stroud, 1973).

The least-squares planes and torsion-angle calculations indicate strict planarity for the phenyl ring with the methoxy group coplanar with it. The pyrimidine ring deviates slightly from planarity [with a maximum deviation from the plane of 0.023 (4) Å for C9]. The five-membered ring has an intermediate half-chair/envelope conformation with a phase angle of pseudorotation δ = 53.95° and a maximum angle of torsion φ_m = 27.72° (Altona, Geise & Romers, 1968). The asymmetry parameters are $\Delta C_s(\mathrm{C2}) = 5.32$ and $\Delta C_2(\mathrm{C2—C3}) = 6.87$ (Duax, Weeks & Rohrer, 1976). Atom O3 attached to C3 is 1.472 (3) Å above the plane defined by the atoms of the fused ring system.

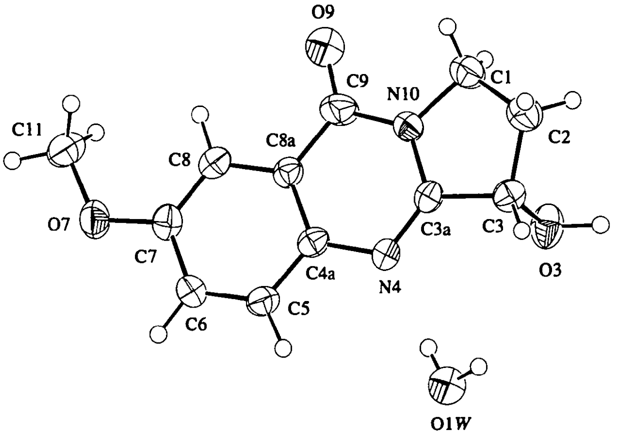


Fig. 1. A general view of the title compound indicating the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

The crystal structure of 7-methoxyvasicinone (Fig. 2) is stabilized by two O—H···O-type intermolecular contacts involving water molecules of crystallization. The packing view of the molecules in the unit cell along the *b* axis shows extended molecular stacking.

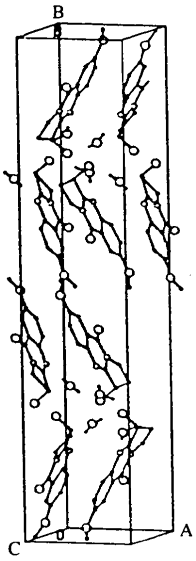


Fig. 2. A view of the unit-cell packing along the *b* axis.

Experimental

Leaves of *Adhatoda vasica* (Nees) (2000 kg) were collected in August–September and extracted with ethanol at room temperature. The major alkaloids, vasicine and vasicinone,

Acta Crystallographica Section C
ISSN 0108-2701 © 1996

were isolated by the usual acid–alkali treatment. The mother liquor was subjected to repeated chromatography over silica gel and alumina. The pooled chloroform fractions on further purification on an alumina column gave a solid which gave 7-methoxyvasicinone (m.p. 475–476 K) on crystallization from methanol.

Crystal data

$C_{12}H_{12}N_2O_3.H_2O$
$M_r = 250.3$
Orthorhombic
Pbca
$a = 7.630\,(1)$ Å
$b = 35.156\,(5)$ Å
$c = 8.505\,(1)$ Å
$V = 2281.4$ Å^3
$Z = 8$
$D_x = 1.457$ Mg m^{-3}
$D_m = 1.449$ Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12$–$16°$
$\mu = 0.104$ mm^{-1}
$T = 293$ K
Rectangular
0.31 × 0.22 × 0.19 mm
Red–brown

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
3145 measured reflections
1800 independent reflections
1294 observed reflections [$F > 4\sigma(F)$]

$R_{\rm int} = 0.019$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 40$
$l = 0 \rightarrow 10$
2 standard reflections monitored every 100 reflections
intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.049$
$wR(F^2) = 0.149$
$S = 0.703$
1800 reflections
218 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o)^2 + (0.1402P)^2 + 7.37P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = -0.107$ (for *y* of H22)
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

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

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

	x	*y*	*z*	$U_{\rm eq}$
C1	−0.1567 (7)	0.6637 (1)	−0.1388 (5)	0.0445 (15)
C2	−0.2734 (7)	0.6964 (1)	−0.0797 (5)	0.0474 (16)
C3	−0.2135 (5)	0.7039 (1)	0.0872 (5)	0.0351 (12)
O3	−0.0721 (4)	0.7304 (1)	0.0978 (4)	0.0487 (10)
C3a	−0.1423 (5)	0.6660 (1)	0.1384 (4)	0.0298 (11)
N4	−0.1164 (4)	0.6552 (1)	0.2813 (3)	0.0322 (9)
C4a	−0.0436 (5)	0.6189 (1)	0.3002 (4)	0.0303 (11)
C5	−0.0192 (6)	0.6047 (1)	0.4527 (4)	0.0366 (13)
C6	0.0512 (6)	0.5694 (1)	0.4751 (4)	0.0380 (14)
C7	0.1003 (5)	0.5469 (1)	0.3476 (5)	0.0356 (13)
O7	0.1676 (4)	0.5123 (1)	0.3860 (3)	0.0471 (10)
C8	0.0764 (5)	0.5598 (1)	0.1968 (4)	0.0337 (12)
C8a	0.0047 (5)	0.5959 (1)	0.1726 (4)	0.0315 (12)
C9	−0.0244 (5)	0.6097 (1)	0.0123 (4)	0.0344 (12)
O9	0.0143 (4)	0.5929 (1)	−0.1093 (3)	0.0523 (11)
N10	−0.1050 (4)	0.6449 (1)	0.0071 (3)	0.0332 (10)
C11	0.2168 (7)	0.4874 (1)	0.2597 (6)	0.0456 (14)
O1*W*	−0.2436 (5)	0.7047 (1)	0.5193 (4)	0.0478 (11)

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

C1—C2	1.538 (6)	C5—C6	1.366 (5)
C1—N10	1.460 (5)	C6—C7	1.393 (5)
C2—C3	1.514 (6)	C7—O7	1.360 (5)
C3—O3	1.428 (5)	C7—C8	1.372 (5)
C3—C3a	1.503 (5)	O7—C11	1.436 (5)
C3a—N4	1.288 (4)	C8—C8a	1.397 (5)
C3a—N10	1.370 (4)	C8a—C9	1.464 (5)
N4—C4a	1.401 (5)	C9—O9	1.227 (4)
C4a—C5	1.402 (5)	C9—N10	1.383 (5)
C4a—C8a	1.403 (5)		
C3—C3a—N10	108.6 (3)	O7—C7—C8	124.7 (3)
C3—C3a—N4	126.1 (3)	C3a—N10—C9	123.4 (3)
N4—C3a—N10	125.2 (3)	C1—N10—C9	123.5 (3)
C6—C7—C8	120.3 (3)	C1—N10—C3a	113.0 (3)
C6—C7—O7	115.0 (3)		
C2—C1—N10—C3a	−12.9 (4)	C2—C3—C3a—N10	20.0 (4)
N10—C1—C2—C3	24.7 (4)	C3—C3a—N10—C1	−4.4 (4)
C1—C2—C3—C3a	−27.2 (4)		

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

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H10*W*···O3$^{\rm i}$	1.90 (6)	2.844 (5)	170 (5)
O3—H3O···O1*W*$^{\rm ii}$	1.68 (7)	2.714 (5)	178 (6)

Symmetry codes: (i) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (ii) $x, \frac{3}{2} - y, z - \frac{1}{2}$.

Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985). Isotropic refinement of the structure by least-squares methods using *SHELXL*93 (Sheldrick, 1993) was followed by anisotropic refinement of all the non-H atoms. All H atoms were located from a difference Fourier map and their positions and isotropic displacement parameters refined (except $U_{\rm iso}$ of H8). All calculations were performed on a PC/AT computer.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: local program. Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

The authors are thankful to the Head, Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras, for extending the use of the data collection facility. One of the authors (KNG) is thankful to the University Grants Commission, New Delhi, for financial support.

Lists of structure factors, anisotropic displacement parameters, torsion angles, H-atom coordinates, least-squares-planes data and complete geometry have been deposited with the IUCr (Reference: DE1008). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.
Altona, C., Geise, H. J. & Romers, C. (1968). *Tetrahedron*, **24**, 13–32.

Atal, C. K. (1981). *Chemistry and Pharmacology of Vasicine – A New Oxytocic and Abortifacient.* Regional Research Laboratory, Jammu, India.
Dhar, K. L., Jain, M. P., Kaul, S. K. & Atal, C. K. (1981). *Phytochemistry*, **20**, 319–321.
Duax, W. L., Weeks, C. M. & Rohrer, D. C. (1976). *Stereochemistry*, Vol. 9, edited by N. L. Allinger & E. L. Eliel, pp. 271–383. New York: John Wiley.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Mehta, D. R., Naravane, J. S. & Desai, R. M. (1963). *J. Org. Chem.* **28**, 445–448.
Motherwell, W. D. S. & Clegg, W. (1976). *PLUTO. Program for Plotting Molecular and Crystal Structures.* University of Cambridge, England.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Pandita, K., Bhatia, M. S., Thappa, R. K., Agarwal, S. G., Dhar, K. L. & Atal, C. K. (1983). *Planta Med.* **48**, 81–82.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Stroud, R. M. (1973). *Acta Cryst.* B**29**, 690–696.
Wheatley, P. J. (1960). *Acta Cryst.* **13**, 80–85.

Acta Cryst. (1996). C**52**, 1493–1496

Bis(*p*-nitrobenzoate) Ester of *cis*-1,1-Dimethylsilacyclohexane-3,4-diol

JONATHAN M. WHITE,* WAI-YING THAM AND ALISON J. GREEN

School of Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia. E-mail: u6105322@ucsvc.ucs.unimelb.edu.au

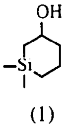
(*Received 27 September 1995; accepted 5 December 1995*)

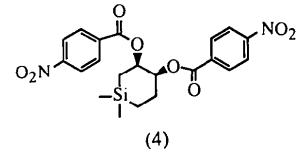
Abstract

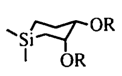
The asymmetric unit of the title structure, 1,1-dimethyl-1-silacyclohexane-3,4-diyl bis(4-nitrobenzoate), consists of four independent $C_{21}H_{22}N_2O_8Si$ molecules which show only minor differences in conformation. The silacyclohexane ring adopts a distorted chair conformation, with the C4 substituent axial and the C3 substituent equatorial.

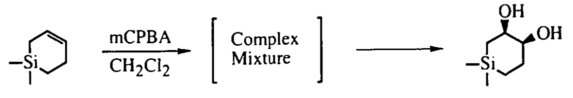
Comment

As part of our structural studies on silicon-substituted alcohols and esters (White & Robertson, 1992; White, Green & Kuan, 1995), we attempted to prepare 1,1-dimethylsilacyclohexan-3-ol, (1), by the method outlined below. Unfortunately, treatment of alkene (2) with *m*-chloroperoxybenzoic acid (mCPBA) in dichloromethane gave a complex mixture, which after reduction with lithium aluminium hydride gave the *cis*-diol (3) as the major product. The present structural study was carried out on the bis(*p*-nitrobenzoate) derivative (4) in order to verify the unexpected *cis* stereochemical relationship between the two hydroxy substituents of compound (3).


(1)


(4)


(5)


(2) (3)

The asymmetric unit of (4) consists of four independent molecules having similar conformations (Figs. 1–4), although small differences in the orientations of the nitro and carboxyl substituents with respect to the phenyl ring are apparent from the list of selected torsion angles (Table 2). The conformations of the silacyclohexane rings are best described as chair, with distortions from idealized cyclohexane geometry resulting from the longer C—Si bond lengths. The *p*-nitrobenzoate substituent at C3 is in an equatorial position and that at C4 is axial, a conformation that is also observed in solution, as shown by 1D and 2D proton NMR experiments. It is interesting to note that the alternative conformation, (5), having the C3 substituent axial and the C4 substituent equatorial, is predicted by molecular-mechanics calculations to be more stable. The observation that the diester

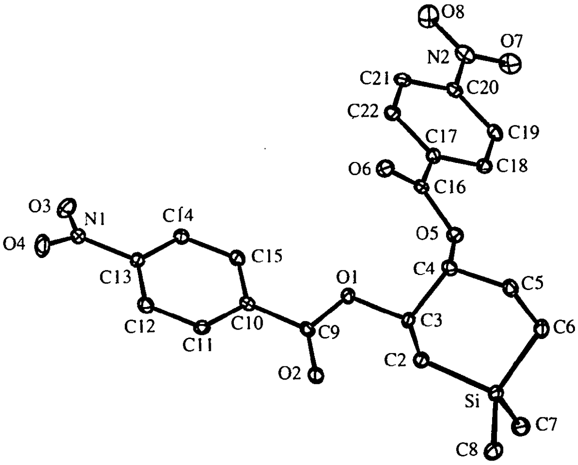


Fig. 1. *ORTEP*II (Johnson, 1976) diagram of molecule 1 of compound (4). Displacement ellipsoids are at the 50% probability level.