

Fig. 2. Projection of the crystal structure along *b*. Hydrogen bonds are shown by broken lines.

The state of ionization of the phosphate group and the protonation of the guanidino group indicate that the charge distribution of the present compound can be written as  $(\text{NH}_2)_2^+\text{CNHCH}_2\text{PO}_3\text{H}^-$ .

The conformation of the molecule is described by torsion angles  $\chi^1$ ,  $\chi^2$ ,  $\chi^{21}$  and  $\tau$  (IUPAC-IUB Commission on Biochemical Nomenclature, 1970). The conformation of the guanidino group is defined by the torsion angles  $\chi^2$  and  $\chi^{21}$  describing the conformation about C(2)–N(1). The values of  $\chi^2$  and  $\chi^{21}$  are  $171.8(2)$  and  $-12.1(3)^\circ$  respectively (Table 2);  $\chi^1$  is  $-95.9(3)^\circ$  and  $\tau [-58.4(2)^\circ]$  is similar to that observed in  $\beta$ -AMPH (Darriet *et al.*, 1975).

The crystal structure contains a network of hydrogen bonds\* which plays an important role in stabilization. The only H atom not participating in a hydrogen bond is H(6) of the guanidino group. The molecules are linked together through the hydrogen bonds O(1)–H(1)...

\* See deposition footnote.

O(3)( $\frac{1}{2}-x$ ,  $\frac{1}{2}+y$ ,  $\frac{1}{2}-z$ ), N(2)–H(5)···O(3)( $-x$ ,  $-y$ ,  $-z$ ), N(3)–H(7)···O(3)( $-x$ ,  $-y$ ,  $-z$ ) to form a chain, running along the diagonal of the *ac* plane. The donor···acceptor (*D*···*A*) lengths are 2.582 (2), 2.994 (3) and 2.915 (3) Å, respectively. Neighbouring chains are linked by N(1)–H(4)···O(5)<sub>w</sub>( $-1-x$ ,  $-y$ ,  $-z$ ), N(3)–H(8)···O(2)( $\frac{1}{2}-x$ ,  $\frac{1}{2}-y$ ,  $-z$ ), O(4)<sub>w</sub>–H(9)<sub>w</sub>···O(2)( $-\frac{1}{2}+x$ ,  $-\frac{1}{2}+y$ ,  $z$ ) and O(5)<sub>w</sub>–H(10)<sub>w</sub>···O(2) hydrogen bonds. Apart from the O(5)<sub>w</sub>–H(10)<sub>w</sub>···O(2) hydrogen bond the others are nonlinear, as shown by the *D*–H···*A* angles, which range from 145 (4) to 167 (4)°.

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## Structure of Cataline, $\text{C}_{21}\text{H}_{25}\text{NO}_5$ , a Non-phenolic Aporphine Alkaloid

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**Abstract.**  $M_r = 371.4$ , orthorhombic,  $P2_12_12_1$ ,  $a = 7.3558(9)$ ,  $b = 14.869(3)$ ,  $c = 17.410(4)$  Å,  $V = 1904.2(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.295$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha)$

$= 1.54178$  Å,  $\mu = 0.8026$  mm<sup>-1</sup>,  $F(000) = 792$ , room temperature; block-diagonal-matrix least-squares refinement based on 1822 Friedel pairs led to final *R* and *R<sub>w</sub>*

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values of 0.036 and 0.045 respectively. Ring *B* has a half-chair conformation and ring *C* a diplanar one. The O(4) and H(6a) atoms are in *trans* positions.

**Introduction.** 4-Hydroxyaporphines present an interesting problem concerning the biological origin of the benzylic hydroxy group. Cataline (Fig. 1) is a non-phenolic aporphine alkaloid, hydroxylated at C(4), isolated from *Glaucium flavum* Cr. var. *vestitum*. The structure was postulated on the basis of spectroscopic properties (Ribas, Sueiras & Castedo, 1972), but the assignment of the configuration at the C(4) atom has been questioned (Urzúa & Cassel, 1978). This work has been undertaken in order to establish the configuration of these alkaloids at the hydroxylated center.

**Experimental.**  $D_m$  not determined. Orthorhombic symmetry proved by single-crystal X-ray techniques. Unit cell: 59 reflections, least-squares refinement. Crystal: prismatic fragment approximately  $0.32 \times 0.16 \times 0.14$  mm. Philips PW 1100 automatic four-circle diffractometer. Cu  $K\alpha$  radiation monochromatized by a graphite plate. 1989 independent Friedel pairs collected between 8 and  $80^\circ$  ( $2\theta$ ),  $\omega-2\theta$  scan. Two standard intensity and orientation reflections measured every 90 min: no significant variation. 1822 pairs with  $I > 2\sigma(I)$  used. Data not corrected for absorption. Structure solved by direct methods with *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). H atoms (isotropic) located on a  $\Delta\rho$  map.  $\sum w(\Delta F)^2$  minimized;  $w = 1/\sigma^2(F)$ ,  $F$  being the e.s.d. in the observed amplitudes based on counting statistics. Anomalous effect of the O atoms (*International Tables for X-ray Crystallography*, 1974) used to confirm the absolute configuration. No correction for secondary extinction. All calculations performed with the XRAY system (Stewart, Kundell & Baldwin, 1970). Final difference map featureless (within  $-0.44$  and  $0.37$  e  $\text{\AA}^{-3}$ ).  $(\Delta/\sigma)_{\max} = 1.3$ .

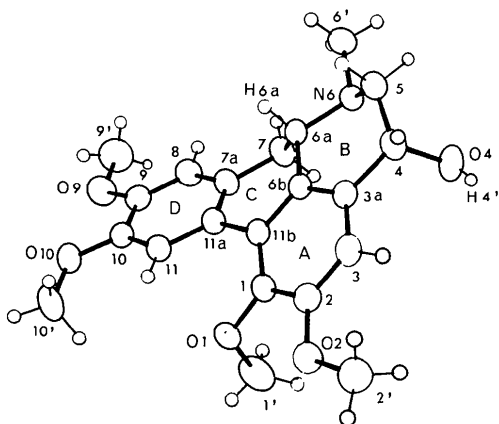


Fig. 1. An ORTEP view (Johnson, 1965) of the molecule with the atomic numbering.

**Discussion.** Atomic coordinates are given in Table 1.\* Intramolecular bond distances and bond angles are given in Table 2 according to the atomic numbering scheme of Fig. 1; they are in good agreement with their expected values (standard deviations being considered). Ring *B* has a half-chair conformation at C(3a)–C(6b) and ring *C* a diplanar one at C(6b)–C(11b) and C(7a)–C(11a), as can be seen from least-squares-planes' calculations, the Cremer & Pople (1975) parameters, and the torsion angles. The O(4) and H(6a) atoms are placed in *trans* positions, the torsion angle through the ideal bond C(4)···C(6a) being  $-161(2)^\circ$ . The absolute configurations, determined by the program *CONFAB* (Martínez-Ripoll & Fayos, 1979), give  $R = 0.029$  (0.030) and  $R_1 = 0.978$  (1.103) (figures in parentheses for the enantiomer), which confirms the  $4R$  configuration established by Ribas, Sueiras & Castedo.

The molecules are linked partially by van der Waals forces and partially by the intermolecular hydrogen bond (Fig. 2) established between N(6') and O(4): N(6')···H(4')–O(4) =  $2.836(2)$   $\text{\AA}$ , O(4)–H(4')···N(6') =  $168(3)^\circ$  [(i)  $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$ ].

\* Lists of anisotropic thermal parameters, structure factors, H-atom parameters, least-squares-planes' data and conformational parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38880 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters ( $\times 10^5$ ) and equivalent isotropic thermal parameters ( $\times 10^4$ )

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}(\text{\AA}^2)$
C(1)	3856 (21)	5608 (10)	27767 (8)	367 (4)
O(1)	6227 (16)	–1921 (7)	23231 (6)	434 (3)
C(1')	15964 (36)	–8801 (15)	27012 (14)	668 (7)
C(2)	–10265 (22)	5478 (10)	33199 (9)	394 (4)
O(2)	–20676 (19)	–2141 (9)	33045 (7)	544 (4)
C(2')	–34258 (33)	–3010 (18)	38756 (13)	672 (7)
C(3)	–12430 (21)	12630 (11)	38120 (8)	397 (4)
C(3a)	–530 (19)	19937 (10)	37807 (7)	342 (4)
C(4)	–2744 (21)	27438 (11)	43604 (8)	377 (4)
O(4)	2932 (18)	24527 (10)	51047 (6)	470 (3)
C(5)	8219 (23)	35589 (10)	41382 (8)	404 (4)
N(6)	26789 (18)	33282 (8)	39009 (6)	355 (3)
C(6')	36933 (32)	41669 (12)	37858 (11)	514 (6)
C(6a)	26500 (21)	27941 (10)	31842 (7)	344 (4)
C(6b)	13149 (19)	20245 (10)	32320 (7)	331 (4)
C(7)	45368 (23)	24058 (12)	30172 (9)	439 (5)
C(7a)	44631 (21)	19078 (11)	22617 (9)	397 (4)
C(8)	58519 (23)	19857 (11)	17188 (10)	440 (4)
C(9)	57288 (22)	15566 (11)	10145 (9)	415 (4)
O(9)	70238 (19)	15943 (9)	4518 (7)	565 (4)
C(9')	85886 (31)	21298 (17)	5978 (14)	693 (7)
C(10)	41821 (23)	10504 (10)	8429 (8)	372 (4)
O(10)	41672 (17)	6717 (8)	1216 (6)	452 (3)
C(10')	26998 (28)	811 (15)	–538 (10)	560 (6)
C(11)	28242 (23)	9495 (10)	13811 (8)	371 (4)
C(11a)	29543 (21)	13745 (10)	21053 (8)	353 (4)
C(11b)	15177 (20)	13074 (10)	27000 (7)	339 (4)

Table 2. Intramolecular bond lengths (Å), bond angles (°) and torsion angles (°)

C(1)—O(1)	1.381 (2)	C(6a)—C(6b)	1.510 (2)
C(1)—C(2)	1.405 (2)	C(6a)—C(7)	1.531 (2)
C(1)—C(11b)	1.394 (2)	C(6b)—C(11b)	1.420 (2)
O(1)—C(1')	1.412 (3)	C(7)—C(7a)	1.510 (2)
C(2)—O(2)	1.368 (2)	C(7a)—C(8)	1.397 (2)
C(2)—C(3)	1.375 (2)	C(7a)—C(11a)	1.391 (2)
O(2)—C(2')	1.415 (3)	C(8)—C(9)	1.385 (2)
C(3)—C(3a)	1.396 (2)	C(9)—O(9)	1.368 (2)
C(3a)—C(4)	1.513 (2)	C(9)—C(10)	1.396 (2)
C(3a)—C(6b)	1.388 (2)	O(9)—C(9')	1.422 (3)
C(4)—O(4)	1.428 (2)	C(10)—O(10)	1.376 (2)
C(4)—C(5)	1.506 (2)	C(10)—C(11)	1.378 (2)
C(5)—N(6)	1.468 (2)	O(10)—C(10')	1.425 (2)
N(6)—C(6')	1.467 (2)	C(11)—C(11a)	1.414 (2)
N(6)—C(6a)	1.479 (2)	C(11a)—C(11b)	1.483 (2)

C(2)—C(1)—C(11b)	121.1 (1)	C(6a)—C(6b)—C(11b)	117.7 (1)
O(1)—C(1)—C(11b)	121.0 (1)	C(3a)—C(6b)—C(11b)	120.0 (1)
O(1)—C(1)—C(2)	117.8 (1)	C(6a)—C(7)—C(7a)	108.5 (1)
C(1)—O(1)—C(1')	112.6 (1)	C(7)—C(7a)—C(11a)	118.6 (1)
C(1)—C(2)—C(3)	119.6 (2)	C(7)—C(7a)—C(8)	121.5 (2)
C(1)—C(2)—O(2)	114.3 (1)	C(8)—C(7a)—C(11a)	119.9 (2)
O(2)—C(2)—C(3)	126.0 (2)	C(7a)—C(8)—C(9)	120.9 (2)
C(2)—O(2)—C(2')	117.2 (2)	C(8)—C(9)—C(10)	119.4 (1)
C(2)—C(3)—C(3a)	120.3 (2)	C(8)—C(9)—O(9)	124.7 (1)
C(3)—C(3a)—C(6b)	120.4 (2)	O(9)—C(9)—C(10)	115.9 (1)
C(3)—C(3a)—C(4)	118.7 (1)	C(9)—O(9)—C(9')	117.3 (2)
C(4)—C(3a)—C(6b)	120.8 (1)	C(9)—C(10)—C(11)	120.2 (1)
C(3a)—C(4)—C(5)	111.4 (1)	C(9)—C(10)—O(10)	115.0 (1)
C(3a)—C(4)—O(4)	110.5 (1)	O(10)—C(10)—C(11)	124.8 (1)
O(4)—C(4)—C(5)	108.7 (2)	C(10)—O(10)—C(10')	117.0 (1)
C(4)—C(5)—N(6)	112.5 (1)	C(10)—C(11)—C(11a)	120.6 (1)
C(5)—N(6)—C(6a)	110.5 (1)	C(7a)—C(11a)—C(11)	118.9 (1)
C(5)—N(6)—C(6')	108.2 (1)	C(11)—C(11a)—C(11b)	123.0 (1)
C(6')—N(6)—C(6a)	110.4 (1)	C(7a)—C(11a)—C(11b)	118.0 (1)
N(6)—C(6a)—C(7)	110.5 (1)	C(6b)—C(11b)—C(11a)	118.7 (1)
N(6)—C(6a)—C(6b)	111.7 (1)	C(1)—C(11b)—C(11a)	123.1 (1)
C(6b)—C(6a)—C(7)	108.3 (1)	C(1)—C(11b)—C(6b)	118.2 (1)
C(3a)—C(6b)—C(6a)	122.3 (1)		

Torsion angles (°) for rings B and C

C(4)—C(3a)—C(6b)—C(6a)	0.3 (2)
C(6b)—C(3a)—C(4)—C(5)	13.3 (2)
C(3a)—C(4)—C(5)—N(6)	-45.8 (2)
C(4)—C(5)—N(6)—C(6a)	65.7 (2)
C(5)—N(6)—C(6a)—C(6b)	-48.9 (2)
N(6)—C(6a)—C(6b)—C(3a)	17.3 (2)
N(6)—C(6a)—C(7)—C(7a)	-177.1 (1)
C(6a)—C(6b)—C(11b)—C(11a)	-3.2 (2)
C(6a)—C(7)—C(7a)—C(11a)	-41.5 (2)
C(7)—C(7a)—C(11a)—C(11b)	-1.5 (2)
C(7a)—C(11a)—C(11b)—C(6b)	25.7 (2)

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## Structures of *trans*-6,7-Dibromo-8-oxabicyclo[3.2.1]octan-3-one, C<sub>7</sub>H<sub>8</sub>Br<sub>2</sub>O<sub>2</sub>, and 6-Bromo-8-oxabicyclo[3.2.1]oct-6-en-3-one, C<sub>7</sub>H<sub>7</sub>BrO<sub>2</sub>

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**Abstract.** C<sub>7</sub>H<sub>8</sub>Br<sub>2</sub>O<sub>2</sub> (1):  $M_r = 283.96$ ,  $C2/c$ ,  $T = 140$  K,  $a = 16.244$  (10),  $b = 12.500$  (8),  $c = 12.134$  (7) Å,  $\beta = 137.24$  (3)°,  $Z = 8$ ,  $V = 1673$  (2) Å<sup>3</sup>,  $D_x(140$  K) = 2.25 g cm<sup>-3</sup>,  $Mo K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu$

= 95.5 cm<sup>-1</sup>,  $R = 0.051$ , 1245 unique observed reflections,  $F(000) = 1088$ , recrystallized from dichloromethane/diethyl ether. C<sub>7</sub>H<sub>7</sub>BrO<sub>2</sub> (2):  $M_r = 203.04$ ,  $P2_1/c$ ,  $T = 140$  K,  $a = 7.900$  (2),  $b =$

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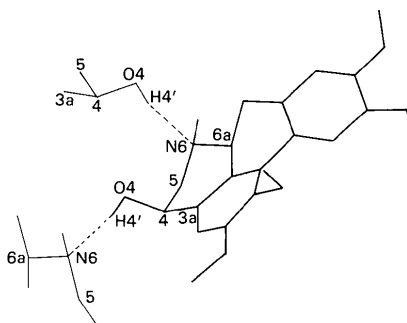


Fig. 2. A scheme of the molecule with the hydrogen bond.

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