

Fig. 2. Packing of the molecules viewed down *a*.

disorder has also been proposed to account for both bond-length anomaly and space-group ambiguity in the structure of 1,1-cyclopropanedicarboxamide (Usha & Venkatesan, 1979). The molecules are arranged in infinite chains with intermolecular hydrogen bonds of length 2.637 (3) Å [O(3)···O(1)'] and 2.675 Å [O(4)···O(2)'] almost parallel to *b* (Fig. 2).

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## Structure of Verticinone Hydrochloride

BY VIKTOR KETTMANN

*Department of Analytical Chemistry, Faculty of Pharmacy, Comenius University, Odbojárov 10,  
880 34 Bratislava, Czechoslovakia*

AND IRENA MAŠTEROVÁ AND JOZEF TOMKO

*Department of Pharmacognosy and Botany, Faculty of Pharmacy, Comenius University, Odbojárov 10,  
880 34 Bratislava, Czechoslovakia*

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**Abstract.**  $C_{27}H_{44}NO_3^+ \cdot Cl^-$ ,  $M_r = 466.1$ ,  $F(000) = 1016$ , orthorhombic, space group  $P2_12_12_1$ ,  $a = 10.311$  (1),  $b = 10.869$  (1),  $c = 23.564$  (6) Å,  $U = 2640.8$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.10$ ,  $D_c = 1.09$  Mg m<sup>-3</sup>,  $Cu K\alpha$  ( $\lambda = 1.54178$  Å),  $\mu = 0.55$  mm<sup>-1</sup>. The final  $R$  is

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0.050 for 1231 independent observed reflections. All the six-membered rings in this compound are in the chair conformation and the five-membered ring is in the envelope conformation. Ring fusions are *A/B trans*, *B/C trans*, *C/D cis*, *D/E trans* and *E/F trans*.

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**Introduction.** The alkaloid verticinone was isolated as a minor *C-nor-D-homo* steroidal alkaloid from *Fritillaria imperialis* L.c.v. *rubra* in the form of the hydrochloride. In the preliminary report on the structure of verticinone methobromide (Itô, Fukazawa & Okuda, 1968) it was proposed that configurational change of the ring juncture *E/F* from *trans* to *cis* takes place upon quaternization with methyl bromide. To confirm this and to give a complete description of the structure of this alkaloid we have examined verticinone hydrochloride by X-ray crystallography.

A crystal 0.4 × 0.2 × 0.15 mm was used for crystal-data and intensity measurements on a Syntex P2<sub>1</sub> diffractometer. The unit cell was measured by automatically centring 12 independent reflections and refining the orientation matrix and unit-cell parameters by least squares. Intensities were collected with Cu K $\alpha$  radiation using the  $\theta$ -2 $\theta$  scan technique and a scan interval of -1.0 to 1.0°. 1584 independent reflections were measured within the range  $1 < \theta \leq 50^\circ$ ; 1231 of these were treated as observed according to the condition  $I \geq 1.96\sigma(I)$ . Lorentz-polarization corrections were applied.

Table 1. Final atomic coordinates ( $\times 10^4$ ) with e.s.d.'s in parentheses and equivalent isotropic thermal parameters  $B_{eq}$  defined as  $B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}$ (Å <sup>2</sup> )
C(1)	-2321 (7)	5372 (8)	2965 (3)	4.83
C(2)	-2312 (8)	4963 (9)	2338 (3)	5.64
C(3)	-1451 (8)	5773 (8)	1977 (3)	5.14
C(4)	-81 (7)	5827 (7)	2207 (3)	4.53
C(5)	-141 (7)	6292 (7)	2823 (3)	4.33
C(6)	1174 (8)	6563 (9)	3082 (3)	5.41
C(7)	1189 (9)	7104 (9)	3671 (4)	5.96
C(8)	344 (7)	6273 (7)	4062 (3)	4.26
C(9)	-991 (7)	6055 (7)	3796 (3)	4.10
C(10)	-936 (8)	5436 (7)	3217 (3)	4.10
C(11)	-1749 (7)	5427 (8)	4283 (3)	4.57
C(12)	-1032 (7)	5803 (8)	4838 (3)	4.35
C(13)	-417 (7)	4709 (7)	5146 (3)	3.80
C(14)	-56 (8)	6795 (7)	4650 (3)	4.93
C(15)	1032 (10)	7061 (9)	5076 (4)	6.80
C(16)	1592 (9)	5901 (9)	5357 (3)	5.91
C(17)	522 (7)	5147 (8)	5620 (3)	4.75
C(18)	-1459 (7)	3881 (7)	5366 (3)	3.42
C(19)	-336 (9)	4131 (7)	3252 (3)	5.17
C(20)	1010 (7)	4063 (8)	5972 (3)	5.07
C(21)	1853 (9)	4476 (10)	6474 (4)	6.79
C(22)	-118 (7)	3237 (8)	6192 (3)	4.67
C(23)	332 (9)	2168 (9)	6563 (3)	6.33
C(24)	-783 (9)	1290 (9)	6708 (3)	5.80
C(25)	-1475 (8)	808 (9)	6189 (3)	5.62
C(26)	-1942 (7)	1903 (8)	5835 (3)	4.55
C(27)	-630 (9)	-81 (8)	5851 (4)	6.22
N(1)	-875 (5)	2780 (6)	5677 (2)	4.07
O(1)	-1462 (6)	5227 (6)	1412 (2)	6.51
O(2)	2196 (5)	6388 (7)	2827 (2)	7.19
O(3)	1765 (5)	3248 (5)	5613 (2)	5.14
Cl(1)	4746 (2)	3411 (2)	5529 (1)	5.50

The structure was solved by direct methods. The starting set of seven phases (defining the origin and enantiomorph) and symbols was extended with a local version of the tangent-formula program TANFOR (Drew & Larson, 1968) for the 156 reflections having  $|E_h| > 1.55$ . The best of 16 sets ( $R_{Karle} = 0.24$ ) was refined and further extended by the program NRC 005 (Huber & Brisse, 1970) and the *E* map based on 281 phases revealed the positions of all non-H atoms. The structure was isotropically and anisotropically refined by means of block-diagonal least squares, the function minimized being  $\sum w(\Delta F)^2$ .

Table 2. Interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses

C(1)-C(2)	1.54 (1)	C(12)-C(14)	1.54 (1)
C(1)-C(10)	1.55 (1)	C(13)-C(17)	1.55 (1)
C(2)-C(3)	1.51 (1)	C(13)-C(18)	1.49 (1)
C(3)-C(4)	1.51 (1)	C(14)-C(15)	1.53 (1)
C(3)-O(1)	1.46 (1)	C(15)-C(16)	1.54 (1)
C(4)-C(5)	1.54 (1)	C(16)-C(17)	1.51 (1)
C(5)-C(6)	1.52 (1)	C(17)-C(20)	1.53 (1)
C(5)-C(10)	1.55 (1)	C(18)-N(1)	1.53 (1)
C(6)-C(7)	1.51 (1)	C(20)-C(21)	1.53 (1)
C(6)-O(2)	1.23 (1)	C(20)-C(22)	1.56 (1)
C(7)-C(8)	1.56 (1)	C(20)-O(3)	1.45 (1)
C(8)-C(9)	1.53 (1)	C(22)-C(23)	1.53 (1)
C(8)-C(14)	1.55 (1)	C(22)-N(1)	1.53 (1)
C(9)-C(10)	1.52 (1)	C(23)-C(24)	1.53 (1)
C(9)-C(11)	1.55 (1)	C(24)-C(25)	1.51 (1)
C(10)-C(19)	1.55 (1)	C(25)-C(26)	1.53 (1)
C(11)-C(12)	1.56 (1)	C(25)-C(27)	1.53 (1)
C(12)-C(13)	1.53 (1)	C(26)-N(1)	1.50 (1)
C(2)-C(1)-C(10)	112.0 (7)	C(12)-C(13)-C(18)	109.5 (6)
C(1)-C(2)-C(3)	112.0 (7)	C(17)-C(13)-C(18)	112.6 (6)
C(2)-C(3)-C(4)	111.6 (7)	C(8)-C(14)-C(12)	100.0 (6)
C(2)-C(3)-O(1)	105.8 (7)	C(8)-C(14)-C(15)	117.3 (7)
C(4)-C(3)-O(1)	110.5 (7)	C(12)-C(14)-C(15)	114.9 (7)
C(3)-C(4)-C(5)	108.3 (6)	C(14)-C(15)-C(16)	113.7 (8)
C(4)-C(5)-C(6)	114.1 (7)	C(15)-C(16)-C(17)	110.4 (7)
C(4)-C(5)-C(10)	112.9 (6)	C(13)-C(17)-C(16)	109.1 (7)
C(6)-C(5)-C(10)	110.4 (6)	C(13)-C(17)-C(20)	111.1 (7)
C(5)-C(6)-C(7)	117.1 (7)	C(16)-C(17)-C(20)	113.7 (7)
C(5)-C(6)-O(2)	122.7 (8)	C(13)-C(18)-N(1)	110.8 (6)
C(7)-C(6)-O(2)	120.1 (8)	C(17)-C(20)-C(21)	112.4 (7)
C(6)-C(7)-C(8)	108.2 (7)	C(17)-C(20)-C(22)	112.3 (7)
C(7)-C(8)-C(9)	110.6 (7)	C(17)-C(20)-O(3)	109.3 (6)
C(7)-C(8)-C(14)	117.7 (7)	C(21)-C(20)-C(22)	109.6 (7)
C(9)-C(8)-C(14)	100.6 (6)	C(21)-C(20)-O(3)	108.9 (7)
C(8)-C(9)-C(10)	113.8 (6)	C(22)-C(20)-O(3)	104.0 (6)
C(8)-C(9)-C(11)	102.6 (6)	C(20)-C(22)-C(23)	113.7 (7)
C(10)-C(9)-C(11)	119.3 (7)	C(20)-C(22)-N(1)	107.9 (6)
C(1)-C(10)-C(5)	106.6 (6)	C(23)-C(22)-N(1)	111.3 (7)
C(1)-C(10)-C(9)	109.3 (6)	C(22)-C(23)-C(24)	111.9 (8)
C(1)-C(10)-C(19)	110.3 (7)	C(23)-C(24)-C(25)	112.9 (8)
C(5)-C(10)-C(9)	107.0 (6)	C(24)-C(25)-C(26)	108.7 (7)
C(5)-C(10)-C(19)	111.7 (6)	C(24)-C(25)-C(27)	111.9 (8)
C(9)-C(10)-C(19)	111.9 (7)	C(26)-C(25)-C(27)	112.8 (7)
C(9)-C(11)-C(12)	105.5 (6)	C(25)-C(26)-N(1)	113.5 (7)
C(11)-C(12)-C(13)	113.1 (6)	C(18)-N(1)-C(22)	109.1 (6)
C(11)-C(12)-C(14)	104.6 (6)	C(18)-N(1)-C(26)	109.1 (6)
C(13)-C(12)-C(14)	114.2 (7)	C(22)-N(1)-C(26)	112.7 (6)
C(12)-C(13)-C(17)	111.2 (6)		

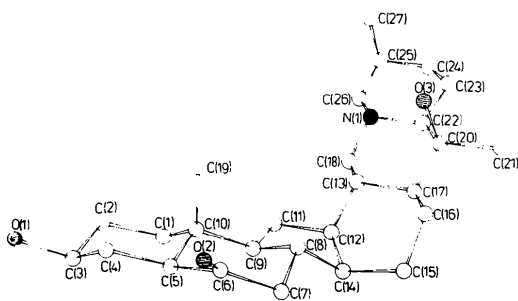


Fig. 1. View of the molecule showing atom numbering.

with the weights  $w = 1$  if  $|F_o| \leq 100$  and  $w = 100/|F_o|$  if  $|F_o| > 100$ . A difference synthesis revealed positions for the H atoms, which were refined isotropically together with the non-H atoms (anisotropically). The refinement was terminated at  $R_1 = 0.050$  and  $R_2 = 0.049$  for all observed reflections, where  $R_1 = \sum |\Delta F| / \sum |F_o|$  and  $R_2 = [\sum w(\Delta F)^2 / \sum w|F_o|^2]^{1/2}$ . The final cycle of refinement showed little dependence on  $|F_o|$  or on  $\sin \theta$ , which indicates that the relative weighting scheme is reasonable. The scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All crystallographic calculations were performed with the NRC program package (Ahmed, 1970). The final atomic coordinates of non-H atoms and equivalent isotropic  $B$ 's are listed in Table 1, bond distances and angles in Table 2.\* Fig. 1 shows a view of the molecule, and the numbering of the atoms.

**Discussion.** The X-ray examination confirmed the original proposal (Itô *et al.*, 1968) that rings *E* and *F* in the cevanine skeleton of verticinone should be *trans*-fused. Thus the stereochemistry of the ring junctures is: *A/B trans*, *B/C trans*, *C/D cis*, *D/E trans* and *E/F trans*. The configurations at other chiral centres have been settled as: C(3)—OH equatorial, C(10)—Me axial,

\* Lists of structure factors, anisotropic thermal parameters, H-atom positions, mean planes and torsion angles of the ring system have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36412 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C(20)—OH axial, C(25)—Me axial; all these groups are in  $\beta$  positions. All bond lengths and angles in Table 2 have values close to those generally expected. All the six-membered rings except for the *D* ring have almost ideal chair conformations. This is reflected in the mean values of the torsion angles:  $57.1$  (9),  $55.5$  (9),  $56.7$  (8) and  $53.7$  (9) $^\circ$  for rings *A*, *B*, *E* and *F* respectively ( $56^\circ$  in cyclohexane). Ring *D* adopts a conformation markedly different from that of a normal chair owing to the *cis* fusion with ring *C*. This is indicated by the small torsion angles C(13)—C(12)—C(14)—C(15) =  $-39.3$  (10) and C(12)—C(14)—C(15)—C(16) =  $41.4$  (10) $^\circ$ . The five-membered ring *C* has an envelope conformation with C(8)  $0.745$  (8) Å from the mean plane of the remaining four atoms. The crystal structure consists of discrete ions held together by ionic and van der Waals forces. The chloride ion is situated so as to form a system of three hydrogen bonds to three different ions of verticinone:  $N^+ \cdots H \cdots Cl^-$ ,  $O(1) \cdots H \cdots Cl^-$  and  $O(3) \cdots H \cdots Cl^-$ , with  $H \cdots Cl^- = 2.37$ ,  $1.99$  and  $2.14$  Å respectively.

All calculations were performed on a Siemens 4004/150 computer at the Research Computing Centre of Comenius University. We are grateful to Dr F. R. Ahmed for kindly supplying us with the NRC program package, and Dr J. Soldánová for measurements of X-ray diffraction intensities on a Syntex  $P2_1$  diffractometer.

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