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Isobaimonidine, $C_{27}H_{45}NO_3$: A New Alkaloid from *Fritillaria imperialis* L.

BY V. KETTMANN AND F. PAVELČÍK

Department of Analytical Chemistry, Faculty of Pharmacy, Comenius University, Odbojárov 10, 83232 *Bratislava, Czechoslovakia*

AND I. MAŠTEROVÁ AND J. TOMKO

Department of Pharmacognosy and Botany, Faculty of Pharmacy, Comenius University, Odbojárov 10, 83232 *Bratislava, Czechoslovakia*

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Abstract. $M_r = 431{\cdot}7$, monoclinic, $P2_1$, $a = 12{\cdot}048\ (2)$, $b = 7{\cdot}292\ (1)$, $c = 14{\cdot}408\ (3)$ Å, $\beta = 101{\cdot}54\ (4)°$, $V = 1240{\cdot}2$ Å^3, $Z = 2$, $D_m = 1{\cdot}15$, $D_x = 1{\cdot}16$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54178$ Å, $\mu = 0{\cdot}57$ mm^{-1}, $F(000) = 476$, $T = 293$ K, $R = 0{\cdot}042$ for 1195 unique observed reflections. The cyclohexane rings were found to have normal chair conformations except for ring *D*, which exists in a distorted boat form. There is a considerable amount of flexibility in the cevanine skeleton and this flexibility may be characterized by rotation about the C(14)—C(15) bond.

Introduction. Imperialine, verticine, verticinone and a new alkaloid have been isolated from *Fritillaria imperialis* L. (Mašterová, Kettmann, Majer & Tomko, 1982). On the basis of chemical properties, spectral evidence and preliminary X-ray examination the structure of this new compound was assumed as 3α,6α,-20β-trihydroxy-5α-cevanine. In this paper a full description of the structural and stereochemical properties of the alkaloid is given.

Experimental. Crystallization from chloroform/acetone solution, colourless plate-like crystal, $0{\cdot}40 \times 0{\cdot}30 \times 0{\cdot}05$ mm, D_m by flotation in aqueous KI solution; Syntex $P2_1$ diffractometer; unit-cell parameters by least-squares refinement of 18 reflections, $15 < \theta < 35°$; intensity data (h 0 to 11, k 0 to 7, l −14 to 13) collected with Cu $K\alpha$ radiation using θ–2θ scanning mode, each reflection scanned 1° (in 2θ) above and below $K\alpha$ doublet, background to scan time ratio 1·0; two standard reflections measured every 98 reflections, no significant systematic fluctuation; intensities not corrected for absorption; 1406 unique reflections, $3 < \theta < 55°$, 1195 with $I \geq 1{\cdot}96\sigma(I)$ considered observed and included in refinement; structure solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by Fourier and block-diagonal least-squares methods; difference electron density map showed positions of all H atoms, refinement then continued on all positional parameters, anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H; in final cycle $R = 0{\cdot}042$, $R_w = 0{\cdot}044$ for all observed reflections, max. Δ/σ 0·25, function minimized $\sum w(\Delta F)^2$, where $w = 1$ if $|F_o| < 35$ and $w = 35/|F_o|$ if $|F_o| \geq 35$; final difference map showed no maxima greater than 0·3 e Å^{-3}; scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974); all calculations except *MULTAN* carried out with NRC program package (Ahmed, 1970).

Discussion. Refined positional parameters of non-H atoms and equivalent isotropic B's are listed in Table 1.* Numbering of the atoms is shown in Fig. 1, which also displays configurational and conformational

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles of the ring system have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39728 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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aspects of the molecule. The X-ray examination confirmed the original assumption (Mašterová *et al.*, 1982) that the structure of the new minor alkaloid from *Fritillaria imperialis* L. should be 3α,6α,20β-trihydroxy-5α-cevanine. The stereochemistry of the ring junctions in the *C*-nor-*D*-homo steroidal skeleton is thus *A*/*B trans*, *B*/*C trans*, *C*/*D cis*, *D*/*E trans* and *E*/*F trans*. The alkaloid was trivially named as isobaimonidine since it differs from the known alkaloid baimonidine only in the configuration of the hydroxyl at C(6) (Kaneko, Tanaka, Haruki, Naruse & Mitsuhashi, 1979).

Table 1. *Final atomic coordinates* ($\times 10^4$) *with e.s.d.'s in parentheses and equivalent isotropic thermal parameters*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
C(1)	10051 (5)	5931 (11)	2146 (4)	4·24
C(2)	11139 (5)	6476 (11)	2838 (4)	4·75
C(3)	11167 (5)	5715 (11)	3822 (4)	4·61
C(4)	10948 (6)	3637 (11)	3799 (4)	4·92
C(5)	9852 (5)	3116 (10)	3097 (4)	3·49
C(6)	9595 (6)	1060 (10)	3053 (4)	4·45
C(7)	8409 (6)	653 (10)	2457 (4)	4·44
C(8)	8341 (5)	1430 (10)	1467 (4)	3·49
C(9)	8677 (5)	3461 (10)	1489 (4)	3·36
C(10)	9869 (5)	3866 (10)	2061 (4)	3·41
C(11)	8362 (5)	3963 (9)	430 (4)	3·46
C(12)	7189 (5)	3085 (9)	128 (4)	3·24
C(13)	6811 (5)	2691 (9)	−933 (4)	3·30
C(14)	7193 (5)	1311 (10)	766 (4)	3·49
C(15)	7026 (6)	−414 (10)	168 (4)	4·22
C(16)	5939 (6)	−340 (10)	−612 (5)	4·95
C(17)	5717 (5)	1549 (10)	−1085 (4)	3·77
C(18)	6625 (5)	4480 (9)	−1473 (4)	3·97
C(19)	10790 (6)	2959 (12)	1628 (4)	4·98
C(20)	5154 (5)	1447 (10)	−2151 (4)	3·70
C(21)	4029 (6)	423 (12)	−2282 (5)	5·19
C(22)	5000 (5)	3388 (11)	−2565 (4)	3·71
C(23)	4379 (5)	3319 (12)	−3629 (5)	4·72
C(24)	4418 (6)	5138 (12)	−4130 (5)	5·45
C(25)	5621 (6)	5821 (10)	−4031 (4)	4·97
C(26)	6140 (6)	5963 (10)	−2966 (5)	5·00
C(27)	6348 (6)	4621 (13)	−4535 (5)	6·09
N(1)	6145 (4)	4174 (8)	−2487 (3)	3·81
O(1)	10299 (4)	6669 (7)	4183 (3)	4·96
O(2)	9625 (4)	364 (8)	4014 (3)	5·82
O(3)	5894 (4)	430 (7)	−2648 (3)	4·34

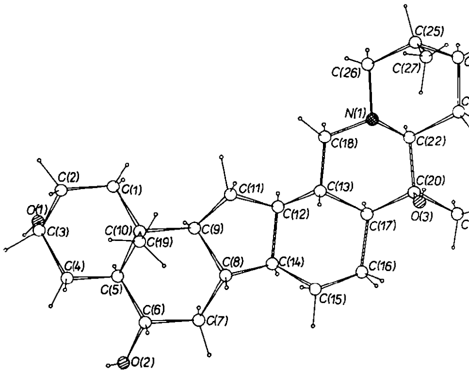

Fig. 1. A perspective view of isobaimonidine showing atom numbering. H atoms are not labelled for clarity.

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

C(1)–C(2)	1·53 (1)	C(12)–C(14)	1·59 (1)
C(1)–C(10)	1·52 (1)	C(13)–C(17)	1·54 (1)
C(2)–C(3)	1·52 (1)	C(13)–C(18)	1·51 (1)
C(3)–C(4)	1·54 (1)	C(14)–C(15)	1·52 (1)
C(3)–O(1)	1·44 (1)	C(15)–C(16)	1·55 (1)
C(4)–C(5)	1·54 (1)	C(16)–C(17)	1·54 (1)
C(5)–C(6)	1·53 (1)	C(17)–C(20)	1·55 (1)
C(5)–C(10)	1·59 (1)	C(18)–N(1)	1·48 (1)
C(6)–C(7)	1·54 (1)	C(20)–C(21)	1·53 (1)
C(6)–O(2)	1·47 (1)	C(20)–C(22)	1·53 (1)
C(7)–C(8)	1·52 (1)	C(20)–O(3)	1·45 (1)
C(8)–C(9)	1·53 (1)	C(22)–C(23)	1·57 (1)
C(8)–C(14)	1·54 (1)	C(22)–N(1)	1·48 (1)
C(9)–C(10)	1·54 (1)	C(23)–C(24)	1·52 (1)
C(9)–C(11)	1·54 (1)	C(24)–C(25)	1·51 (1)
C(10)–C(19)	1·53 (1)	C(25)–C(26)	1·54 (1)
C(11)–C(12)	1·53 (1)	C(25)–C(27)	1·52 (1)
C(12)–C(13)	1·53 (1)	C(26)–N(1)	1·48 (1)

C(2)–C(1)–C(10)	113·5 (5)	C(12)–C(13)–C(18)	109·6 (5)
C(1)–C(2)–C(3)	111·7 (6)	C(17)–C(13)–C(18)	111·1 (5)
C(2)–C(3)–C(4)	111·7 (6)	C(8)–C(14)–C(12)	103·4 (5)
C(2)–C(3)–O(1)	106·2 (5)	C(8)–C(14)–C(15)	114·7 (5)
C(4)–C(3)–O(1)	110·5 (5)	C(12)–C(14)–C(15)	111·2 (5)
C(3)–C(4)–C(5)	112·2 (6)	C(14)–C(15)–C(16)	112·4 (5)
C(4)–C(5)–C(6)	114·1 (5)	C(15)–C(16)–C(17)	113·6 (6)
C(4)–C(5)–C(10)	111·2 (5)	C(13)–C(17)–C(16)	110·7 (5)
C(6)–C(5)–C(10)	109·8 (5)	C(13)–C(17)–C(20)	111·1 (5)
C(5)–C(6)–C(7)	111·7 (6)	C(16)–C(17)–C(20)	113·5 (5)
C(5)–C(6)–O(2)	109·5 (5)	C(13)–C(18)–N(1)	111·5 (5)
C(7)–C(6)–O(2)	107·8 (5)	C(17)–C(20)–C(21)	110·4 (5)
C(6)–C(7)–C(8)	108·7 (5)	C(17)–C(20)–C(22)	109·6 (5)
C(7)–C(8)–C(9)	112·1 (5)	C(17)–C(20)–O(3)	108·8 (5)
C(7)–C(8)–C(14)	117·8 (5)	C(21)–C(20)–C(22)	111·7 (6)
C(9)–C(8)–C(14)	105·4 (5)	C(21)–C(20)–O(3)	107·9 (5)
C(8)–C(9)–C(10)	114·3 (5)	C(22)–C(20)–O(3)	108·6 (5)
C(8)–C(9)–C(11)	101·4 (5)	C(20)–C(22)–C(23)	110·3 (5)
C(10)–C(9)–C(11)	120·3 (5)	C(20)–C(22)–N(1)	106·9 (5)
C(1)–C(10)–C(5)	107·0 (5)	C(23)–C(22)–N(1)	110·0 (5)
C(1)–C(10)–C(9)	109·7 (5)	C(22)–C(23)–C(24)	112·6 (6)
C(1)–C(10)–C(19)	110·9 (5)	C(23)–C(24)–C(25)	111·3 (6)
C(5)–C(10)–C(9)	104·5 (5)	C(24)–C(25)–C(26)	107·9 (6)
C(5)–C(10)–C(19)	112·4 (5)	C(24)–C(25)–C(27)	113·4 (6)
C(9)–C(10)–C(19)	112·0 (5)	C(26)–C(25)–C(27)	110·9 (6)
C(9)–C(11)–C(12)	102·3 (5)	C(25)–C(26)–N(1)	111·7 (6)
C(11)–C(12)–C(13)	115·8 (5)	C(18)–N(1)–C(22)	108·0 (5)
C(11)–C(12)–C(14)	106·2 (5)	C(18)–N(1)–C(26)	107·0 (5)
C(13)–C(12)–C(14)	113·0 (5)	C(22)–N(1)–C(26)	113·0 (5)
C(12)–C(13)–C(17)	109·6 (5)		

All bond lengths in Table 2 have values close to those generally expected except for two bond lengths C(5)–C(10) and C(12)–C(14) at the ring junctions *A*/*B* and *C*/*D* respectively. Deviations of these bond lengths from an expected value of 1·533 ±0·033 Å for C–C bond lengths in *n*-hydrocarbons (Bartell, 1959) by more than 2·6 standard deviations are considered significant (Cruickshank & Robertson, 1953). Flexibility of the five-membered *C* ring and the strain inherent in the *B*/*C* ring junction are responsible for the valency angles C(10)–C(9)–C(11) = 120·3 (5)° and C(7)–C(8)–C(14) = 117·8 (5)° being greater than those normally observed for tertiary (110·5°) substituted C atoms (Geise, Altona & Romers, 1967). The relative strain in the *C*/*D* ring junction is much less pronounced as reflected in the valency angles C(11)–C(12)–C(13) = 115·8 (5)° and C(8)–C(14)–C(15) = 114·7 (5)°, which are both closer to the standard value (110·5°).

The conformations of individual rings have been deduced from the torsion angles and least-squares planes. All the six-membered rings except for the *D* ring are fixed in the chair conformation with small but significant departures from the ideal chair form. Nevertheless, the mean values of the torsion angles: 55·4 (7), 58·1 (7), 58·6 (7) and 55·7 (8)° for rings *A*, *B*, *E* and *F*, respectively, are all comparable with the value of 55·1° found in chair-shaped cyclohexane (Kahn, Fourme, André & Renaud, 1973). Ring *D* adopts a flexible boat form, which is asymmetrically distorted towards the skew boat. This is seen from the values of the torsion angles C(13)—C(12)—C(14)—C(15) = 10·3 (7)° and C(15)—C(16)—C(17)—C(13) = 20·3 (7)° (0° for ideal boat). The three-dimensional conformation of a cyclopentane ring may be described by the parameters Δ and φ_m (Altona, Geise & Romers, 1968; Duax & Norton, 1975). The overall ring conformation is defined by the phase-angle parameter, Δ ($\Delta = \pm 36°$, envelope; $\Delta = 0°$, half-chair), while φ_m is the maximum torsion angle attainable for the conformation described by Δ. Thus, if C(9)—C(11) is taken as the reference bond, the *C* ring of the isobaimonidine can be described as a distorted C(9) envelope conformation with $\Delta = -22{\cdot}2°$ and $\varphi_m = 46{\cdot}1°$. The distance of C(9) from the mean plane of the remaining four atoms is 0·677 (6) Å.

Stereochemically, it is interesting to compare the overall molecular shape of the *C*-nor-*D*-homo steroidal skeleton in isobaimonidine with that in verticinone hydrochloride (Kettmann, Mašterová & Tomko, 1982). The superposition of these two conformations on the *A* side of the molecules (Fig. 2) shows the great flexibility of the cevanine skeleton; the general bend of the molecules is quite different. The stereochemical behaviour of the cevanine skeleton in other derivatives so far studied by X-ray crystallography (Brisse, 1970; Itô, Fukazawa & Miyashita, 1976; Pavelčík & Tomko, 1979) is essentially the same as that observed in verticinone hydrochloride. The principal source of this flexibility is the rotation about the C(15)—C(14) bond: the torsion angle C(16)—C(15)—C(14)—C(12) takes the value of 41·2° in verticinone hydrochloride and −55·2 (7)° in isobaimonidine (Fig. 3). The conformation observed for the C(15)—C(14) bond in the isobaimonidine compels the cyclohexane *D* ring to have an energetically unfavourable boat conformation (this energy loss is, of course, balanced by other intramolecular interactions).

Examination of the three-dimensional packing of the molecules within the crystalline lattice reveals that O(1)—H and O(2)—H hydroxyl substituents are involved in hydrogen bonding with both serving in a proton-donor and a proton-acceptor capacity. These hydrogen bonds, O(1)—H···O(2)($2-x$, $\frac{1}{2}+y$, $1-z$) 2·75 (1) Å and O(2)—H···O(1)(x, $-1+y$, z) 2·81 (1) Å, connect the 'ends' of the molecules into spirals, which run along a screw axis (at 0, y, $\frac{1}{2}$). The third hydroxyl O(3)—H is oriented so that it forms an intramolecular hydrogen bond O(3)—H···N(1) 2·75 (1) Å.

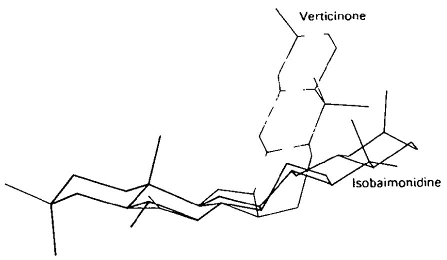

Fig. 2. Comparison of conformations of the cevanine skeleton in isobaimonidine and verticinone hydrochloride.

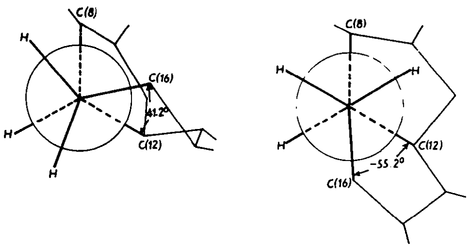

Fig. 3. Newman projections of verticinone (left) and isobaimonidine (right) about the C(15)—C(14) bond.

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