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Alkaloids of *Veratrum album* subspecies *lobelianum* (Bernh.) Suessenguth. XXX.* Structure of *O*-Acetylveramarine

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Abstract

$C_{29}H_{45}NO_4$, $M_r = 471 \cdot 7$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 6 \cdot 342$ (2), $b = 20 \cdot 961$ (11), $c = 19 \cdot 809$ (6) Å, $U = 2633 \cdot 3$ Å^3, $D_m = 1 \cdot 14$ (8), $D_x = 1 \cdot 19$ Mg m^{-3}, μ(Cu $K\alpha$, $\lambda = 1 \cdot 5418$ Å) $= 0 \cdot 62$ mm^{-1}. The structure was solved by direct methods and refined by least squares to an R of $0 \cdot 044$ on the basis of 1501 independent counter intensities. The three O substituents on the cevanine skeleton are on the β side, and the rings are *trans*-fused in pairs, except for the middle five- and six-membered rings which are *cis*-fused. There is strong evidence for intramolecular O–H···O–H···N hydrogen bonds with H···O = $2 \cdot 02$ and H···N = $2 \cdot 19$ Å.

Introduction

The alkaloid veramarine, a minor alkaloid from *Veratrum album* subspecies *lobelianum* (Bernh.), was isolated by Tomko & Vassová (1965). Its chemical configuration was established (Tomko, Votický, Budzikiewicz & Durham, 1965) and its stereochemistry proposed (Itô, Ogino & Tomko, 1968) on the basis of its chemical reactivity, physico-chemical measurements and a consideration of the biogenesis of the *C*-nor-*D*-homo steroidal skeleton. Feeling the need for more substantial proof of this proposal we have examined *O*-acetylveramarine by X-ray crystallography (since veramarine is amorphous).

Experimental

The crystal used for structure determination was of prismatic form {100}, {010}, {011} with approximate dimensions $0 \cdot 25 \times 0 \cdot 15 \times 0 \cdot 05$ mm. The density was measured by flotation in aqueous KI solution. The space group and unit-cell data were obtained from rotation and Weissenberg photographs. Unit-cell parameters were refined by a least-squares fit of seven independent reflections measured on the diffractometer. The intensities of 2085 reflections (up to $2\theta = 115°$) were collected on a four-circle fully automated

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* Part XXIX: *Chem. Zvesti* (1978), **32**, 120.

Syntex $P2_1$ diffractometer with graphite-monochromated Cu $K\alpha$ radiation and the θ–2θ scan technique. The background was measured at each end of the scan for one half of the reflection scan time. To check stability, two standard reflections were measured after every 98 reflections. The net count of these reflections did not change significantly during data collection. The 1501 reflections with $I > 1.96\,\sigma(I)$ were considered observed. The intensities were corrected for Lorentz and polarization factors. No correction for absorption was made.

Structure determination and refinement

The structure was determined by direct methods. The starting set of 10 phases obtained from origin and enantiomorph defining, cos φ and cos$(\varphi_1 + \varphi_2)$ seminvariants (Hauptman, 1972) and symbolic addition (Karle & Karle, 1966), and symbols for two general reflections was extended with a local version of the tangent formula program TANFOR (Drew & Larson, 1968) for the 198 reflections having $|E_h| > 1.55$. The

Table 1. *Final atomic coordinates* $(\times 10^4)$ *for nonhydrogen atoms with e.s.d.'s in parentheses*

	x	y	z
C(1)	3866 (7)	−2653 (2)	6011 (2)
C(2)	2441 (8)	−3150 (2)	5684 (2)
C(3)	855 (7)	−3380 (2)	6194 (2)
C(4)	−435 (7)	−2837 (2)	6478 (2)
C(5)	939 (7)	−2309 (2)	6765 (2)
C(6)	549 (8)	−2085 (2)	7376 (2)
C(7)	1743 (9)	−1551 (2)	7707 (2)
C(8)	3129 (7)	−1203 (2)	7206 (2)
C(9)	4226 (7)	−1676 (2)	6739 (2)
C(10)	2683 (7)	−2073 (2)	6303 (2)
C(11)	5966 (7)	−1292 (2)	6390 (2)
C(12)	6368 (7)	−705 (2)	6863 (2)
C(13)	5901 (7)	−72 (2)	6515 (2)
C(14)	4980 (8)	−834 (2)	7484 (2)
C(15)	4495 (10)	−260 (2)	7930 (2)
C(16)	4027 (9)	357 (2)	7549 (2)
C(17)	5726 (8)	490 (2)	7012 (2)
C(18)	7551 (8)	70 (2)	5988 (2)
C(19)	1708 (8)	−1669 (2)	5725 (2)
C(20)	5481 (7)	1123 (2)	6625 (2)
C(21)	5256 (10)	1684 (2)	7105 (3)
C(22)	7346 (8)	1212 (2)	6142 (2)
C(23)	7293 (9)	1859 (2)	5789 (2)
C(24)	8919 (10)	1919 (2)	5235 (3)
C(25)	8764 (10)	1376 (2)	4727 (2)
C(26)	8882 (8)	743 (2)	5111 (2)
C(27)	6751 (12)	1418 (3)	4289 (3)
C(28)	−109 (8)	−4416 (2)	5805 (2)
C(29)	−1729 (10)	−4811 (2)	5438 (3)
N(1)	7244 (6)	687 (2)	5645 (2)
O(1)	−639 (5)	−3812 (1)	5874 (1)
O(2)	1964 (6)	319 (2)	7256 (2)
O(3)	3566 (5)	1106 (1)	6231 (1)
O(4)	1573 (8)	−4621 (2)	6006 (2)

best of 16 sets ($R_{Karle} = 0.21$) was refined and further extended by the program NRC005 (Huber & Brisse, 1970), and the E map based on 350 coefficients revealed the positions of all nonhydrogen atoms. Isotropic block-diagonal least-squares refinement decreased R_1 to 0.15. A difference Fourier synthesis showed positions for all H atoms. At this stage, anisotropic temperature factors for heavy atoms and isotropic temperature factors for H atoms were introduced and R_1 dropped to 0.047. Since the discrepancies in $|F_o|$ were indicative of extinction, a correction (Stout & Jensen, 1968) was made. Although this procedure is not fully satisfactory, the agreement between F_o and F_c for 12 affected reflections improved markedly. Five more cycles of refinement gave a final $R_1 = 0.044$ and $R_2 = 0.048$ for observed reflections. R_1 for all reflections was 0.069; $R_2 = 0.058$. The function $\sum w(|F_o| - |F_c|)^2$ was minimized; the weighting scheme $w^{-1} = \sigma^2(F) + (0.03|F_o|)^2$, where $\sigma(F)$ is derived from counting statistics, was employed. $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/ \sum w|F_o|^2]^{1/2}$. The final cycle of refinement showed little dependence on $|F_o|$ or on sin θ, which indicates that the relative weighting scheme is reasonable. A final difference map was featureless. 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 are given in Table 1, together with standard deviations.* The absolute configuration of veramarine (Fig. 1) was taken to be the same as that in the similar alkaloid verticinone methobromide (Itô, Fukazawa & Okuda, 1968) which was determined by the anomalous-dispersion effect. Fig. 2 shows a projection of the molecule and the labelling of the atoms.

Discussion

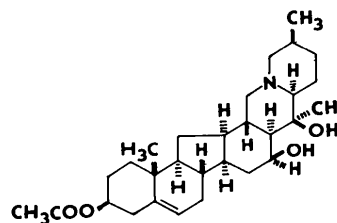The X-ray examination confirmed the previously assigned molecular configuration based on a cevanine-

Fig. 1. Absolute configuration of veramarine.

type skeleton (Tomko, Votický, Budzikiewicz & Durham, 1965). All bond lengths and angles in Table 2 have values close to those generally expected and clearly establish that the molecule has the double bond at the 5,6 position [C(5)—C(6) = 1·320 Å]. The stereochemistry of the ring junctions is described as: *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)—O equatorial, C(10)—Me axial,

C(16)—OH axial, C(20)—OH axial, C(25)—Me axial, lone pair on N atom axial; all these groups are in β positions. The axial–equatorial character of C(16)—OH is different from that originally proposed by Itô, Ogino & Tomko (1968). Torsion angles for the ring system are given in Table 3. The C(5)—C(6) double bond causes ring *A* to have a non-ideal chair conformation. The reduced torsion angle C(4)—C(5)—C(10)—C(1) of −47·6° indicates that ring *A* is some-

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

C(1)—C(2)	1·524 (6)	C(8)—C(9)	1·524 (6)	C(14)—C(15)	1·523 (7)	C(22)—N(1)	1·478 (5)
C(1)—C(10)	1·542 (6)	C(8)—C(14)	1·510 (7)	C(15)—C(16)	1·528 (7)	C(23)—C(24)	1·511 (8)
C(2)—C(3)	1·505 (6)	C(9)—C(10)	1·547 (6)	C(16)—C(17)	1·540 (7)	C(24)—C(25)	1·523 (7)
C(3)—C(4)	1·511 (6)	C(9)—C(11)	1·531 (6)	C(16)—O(2)	1·434 (7)	C(25)—C(26)	1·531 (7)
C(3)—O(1)	1·455 (5)	C(10)—C(19)	1·553 (6)	C(17)—C(20)	1·540 (6)	C(25)—C(27)	1·546 (9)
C(4)—C(5)	1·519 (6)	C(11)—C(12)	1·567 (6)	C(18)—N(1)	1·476 (5)	C(26)—N(1)	1·487 (6)
C(5)—C(6)	1·320 (6)	C(12)—C(13)	1·526 (6)	C(20)—C(21)	1·519 (6)	C(28)—C(29)	1·506 (8)
C(5)—C(10)	1·518 (6)	C(12)—C(14)	1·536 (6)	C(20)—C(22)	1·532 (6)	C(28)—O(1)	1·317 (6)
C(6)—C(7)	1·501 (6)	C(13)—C(17)	1·540 (6)	C(20)—O(3)	1·444 (5)	C(28)—O(4)	1·216 (7)
C(7)—C(8)	1·515 (7)	C(13)—C(18)	1·507 (6)	C(22)—C(23)	1·527 (6)		

C(2)—C(1)—C(10)	114·2 (3)	C(10)—C(9)—C(11)	119·1 (3)	C(12)—C(14)—C(15)	116·2 (4)	C(20)—C(22)—N(1)	107·0 (3)
C(1)—C(2)—C(3)	109·4 (4)	C(1)—C(10)—C(5)	108·9 (3)	C(14)—C(15)—C(16)	114·9 (4)	C(23)—C(22)—N(1)	110·8 (4)
C(2)—C(3)—C(4)	111·7 (4)	C(1)—C(10)—C(9)	109·0 (3)	C(15)—C(16)—C(17)	111·0 (4)	C(22)—C(23)—C(24)	113·1 (4)
C(2)—C(3)—O(1)	110·0 (3)	C(1)—C(10)—C(19)	110·3 (3)	C(15)—C(16)—O(2)	109·2 (4)	C(23)—C(24)—C(25)	112·0 (4)
C(4)—C(3)—O(1)	106·2 (3)	C(5)—C(10)—C(9)	107·4 (3)	C(17)—C(16)—O(2)	111·6 (4)	C(24)—C(25)—C(26)	108·4 (4)
C(3)—C(4)—C(5)	112·2 (4)	C(5)—C(10)—C(19)	109·4 (3)	C(13)—C(17)—C(16)	110·8 (4)	C(24)—C(25)—C(27)	112·5 (5)
C(4)—C(5)—C(6)	119·6 (4)	C(9)—C(10)—C(19)	111·7 (3)	C(13)—C(17)—C(20)	110·3 (4)	C(26)—C(25)—C(27)	111·6 (4)
C(4)—C(5)—C(10)	115·5 (3)	C(9)—C(11)—C(12)	105·0 (3)	C(16)—C(17)—C(20)	115·5 (4)	C(25)—C(26)—N(1)	112·8 (4)
C(6)—C(5)—C(10)	124·9 (4)	C(11)—C(12)—C(13)	112·4 (3)	C(13)—C(18)—N(1)	113·6 (3)	C(29)—C(28)—O(1)	113·8 (4)
C(5)—C(6)—C(7)	124·8 (4)	C(11)—C(12)—C(14)	104·4 (3)	C(17)—C(20)—C(21)	111·4 (4)	C(29)—C(28)—O(4)	124·2 (5)
C(6)—C(7)—C(8)	111·4 (4)	C(13)—C(12)—C(14)	113·8 (4)	C(17)—C(20)—C(22)	109·8 (3)	O(1)—C(28)—O(4)	122·0 (5)
C(7)—C(8)—C(9)	110·4 (4)	C(12)—C(13)—C(17)	113·0 (3)	C(17)—C(20)—O(3)	109·4 (3)	C(18)—N(1)—C(22)	109·8 (3)
C(7)—C(8)—C(14)	117·3 (4)	C(12)—C(13)—C(18)	110·5 (3)	C(21)—C(20)—C(22)	111·7 (4)	C(18)—N(1)—C(26)	107·8 (3)
C(9)—C(8)—C(14)	101·6 (3)	C(17)—C(13)—C(18)	110·0 (3)	C(21)—C(20)—O(3)	106·1 (4)	C(22)—N(1)—C(26)	112·6 (3)
C(8)—C(9)—C(10)	113·6 (3)	C(8)—C(14)—C(12)	104·0 (4)	C(22)—C(20)—O(3)	108·4 (3)	C(3)—O(1)—C(28)	118·5 (3)
C(8)—C(9)—C(11)	105·1 (3)	C(8)—C(14)—C(15)	117·3 (4)	C(20)—C(22)—C(23)	112·2 (4)		

Table 3. *Selected torsion angles* (°)

|					
C(10)—C(1)—C(2)—C(3)	−57·7	C(9)—C(8)—C(14)—C(15)	174·1	C(8)—C(14)—C(15)—C(16)	−83·5
C(2)—C(1)—C(10)—C(5)	51·9	C(8)—C(9)—C(10)—C(1)	−164·1	C(12)—C(14)—C(15)—C(16)	40·5
C(2)—C(1)—C(10)—C(9)	168·8	C(8)—C(9)—C(10)—C(5)	−46·2	C(14)—C(15)—C(16)—C(17)	−49·4
C(1)—C(2)—C(3)—C(4)	57·2	C(11)—C(9)—C(10)—C(1)	71·3	C(15)—C(16)—C(17)—C(13)	57·1
C(2)—C(3)—C(4)—C(5)	−53·9	C(11)—C(9)—C(10)—C(5)	−170·8	C(15)—C(16)—C(17)—C(20)	−176·6
C(3)—C(4)—C(5)—C(6)	−130·6	C(8)—C(9)—C(11)—C(12)	21·6	C(13)—C(17)—C(20)—C(22)	−57·1
C(3)—C(4)—C(5)—C(10)	50·1	C(10)—C(9)—C(11)—C(12)	150·2	C(16)—C(17)—C(20)—C(22)	176·4
C(4)—C(5)—C(6)—C(7)	−178·0	C(9)—C(11)—C(12)—C(13)	−118·3	C(13)—C(18)—N(1)—C(22)	60·8
C(10)—C(5)—C(6)—C(7)	1·3	C(9)—C(11)—C(12)—C(14)	5·5	C(13)—C(18)—N(1)—C(26)	−176·2
C(4)—C(5)—C(10)—C(1)	−47·6	C(11)—C(12)—C(13)—C(17)	165·1	C(17)—C(20)—C(22)—C(23)	−174·9
C(4)—C(5)—C(10)—C(9)	−165·6	C(11)—C(12)—C(13)—C(18)	−71·2	C(17)—C(20)—C(22)—N(1)	63·4
C(6)—C(5)—C(10)—C(1)	133·1	C(14)—C(12)—C(13)—C(17)	46·7	C(20)—C(22)—C(23)—C(24)	−171·3
C(6)—C(5)—C(10)—C(9)	15·1	C(14)—C(12)—C(13)—C(18)	170·5	N(1)—C(22)—C(23)—C(24)	−51·8
C(5)—C(6)—C(7)—C(8)	12·5	C(11)—C(12)—C(14)—C(8)	−30·8	C(20)—C(22)—N(1)—C(18)	−64·2
C(6)—C(7)—C(8)—C(9)	−42·1	C(11)—C(12)—C(14)—C(15)	−161·4	C(20)—C(22)—N(1)—C(26)	175·7
C(6)—C(7)—C(8)—C(14)	−157·7	C(13)—C(12)—C(14)—C(8)	92·0	C(23)—C(22)—N(1)—C(18)	173·3
C(7)—C(8)—C(9)—C(10)	62·3	C(13)—C(12)—C(14)—C(15)	−38·6	C(23)—C(22)—N(1)—C(26)	53·2
C(7)—C(8)—C(9)—C(11)	−165·9	C(12)—C(13)—C(17)—C(16)	−56·7	C(22)—C(23)—C(24)—C(25)	53·5
C(14)—C(8)—C(9)—C(10)	−172·6	C(12)—C(13)—C(17)—C(20)	174·2	C(23)—C(24)—C(25)—C(26)	−54·0
C(14)—C(8)—C(9)—C(11)	−40·8	C(18)—C(13)—C(17)—C(16)	179·4	C(24)—C(25)—C(26)—N(1)	56·1
C(7)—C(8)—C(14)—C(12)	164·6	C(18)—C(13)—C(17)—C(20)	50·3	C(25)—C(26)—N(1)—C(18)	−178·5
C(7)—C(8)—C(14)—C(15)	−65·5	C(12)—C(13)—C(18)—N(1)	−178·1	C(25)—C(26)—N(1)—C(22)	−57·2
C(9)—C(8)—C(14)—C(12)	44·2	C(17)—C(13)—C(18)—N(1)	−52·7		
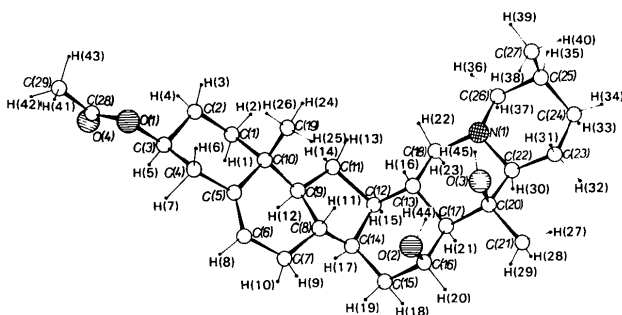
Fig. 2. A perspective drawing of O-acetylveramarine and the numbering scheme of the atoms.

what flattened. Ring B has a regular cyclohexene half-chair conformation. The five-membered ring C has an envelope conformation with C(8) 0·65 Å from the mean plane of the remaining four atoms. Ring D adopts a conformation markedly different from that of a normal chair owing to cis fusion with ring C. This is reflected in the small torsion angles C(13)—C(12)—C(14)—C(15) = −38·6° and C(12)—C(14)—C(15)—C(16) = 40·5°, compared with the value of 56° in cyclohexane. H atoms on the C(16)—OH and C(20)—OH hydroxyl groups are oriented so that they form intramolecular hydrogen bonds: $O(2)$—H···$O(3)$ and $O(3)$—H···$N(1)$, with H···$O = 2·02$ and H···$N = 2·19$ Å. The crystal structure consists of discrete molecules separated by normal van der Waals contacts.

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 system of programs, and Dr J. Soldánová for measurements of intensities on a Syntex $P2_1$ diffractometer.

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Accurate Structure Determination of trans-2,5-Dimethyl-3-hexene-2,5-diol Hemihydrate, C₈H₁₆O₂.½H₂O, at 86 K.

I. Results of High-Order and Multipole Refinements

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Abstract

The title compound is orthorhombic, space group Pbcn, $Z = 8$, $a = 9·678$ (5), $b = 10·419$ (8), $c = 18·290$ (10) Å at 86 K. Accurate X-ray diffraction intensities were obtained for 9618 independent reflections up to $\sin \theta/\lambda = 1·08$ Å^{-1}, from the intensities measured on a CAD-4F diffractometer for a complete hemisphere with monochromatized Mo radiation and the step-scan method. Multiple diffraction was avoided on line. A spherical high-order refinement ($\sin \theta/\lambda > 0·7$ Å^{-1}) with scale and overall thermal motion from full-angle data decreased $R_w(I)$ to 0·108 for the 8255 full-angle and to 0·078 for the 5716 high-order reflections with