Veratrum alkaloids
XXXI. Crystal and molecular structure of dihydroveracintine

[a]F. PAVELČÍK and [b]J. TOMKO

[a]*Department of Analytical Chemistry, Faculty of Pharmacy, Komenský University, CS-832 32 Bratislava*

[b]*Department of Pharmacognosy and Botany, Faculty of Pharmacy, Komenský University, CS-832 32 Bratislava*

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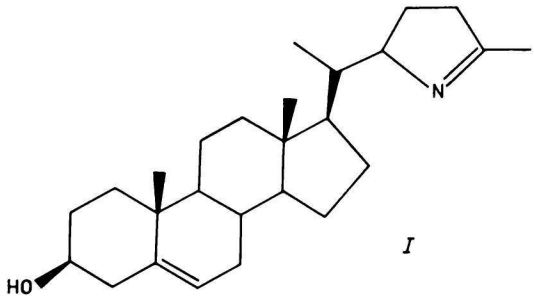
The structure of steroidal alkaloid veracintine, monoclinic symmetry, space group $P2_1$, a = 1.3650 nm, b = 1.3332 nm, c = 1.5298 nm, β = 97.38°, has been solved by direct methods and refined by the least-squares to an $R = 0.077$ using 1841 independent observed reflections. Two molecules occur in the symmetrically independent part of the unit cell which differ in conformation of the pyrrolidine ring. The absolute configuration is (S) at the asymmetric carbon atom C(20) and (R) at C(25).

Структура стероидного алкалоида верацинтина (моноклинная кристаллическая система, пространственная группа $P2_1$, $a = 1{,}3650$ нм, $b = 1{,}3332$ нм, $c = 1{,}5298$ нм, $\beta = 97{,}38°$) была определена прямыми методами и, затем, уточнена методом наименьших квадратов при $R = 0{,}077$ на основе 1841 независимых наблюдаемых рефлексий. В симметрически независимой части находятся две молекулы, отличающиеся конформацией пирролидинового кольца. Абсолютная конфигурация асимметрического атома углерода C(20) – (S), а C(25) – (R).

Alkaloid veracintine, 20-(2-methyl-1-pyrrolin-5-yl)pregn-5-ene-3-β-ol) (*I*), was isolated from the aboveground part of *Veratrum album* subsp. *Lobelianum* [1]. Its structure was proposed on the basis of infrared, mass, and ^{1}H-n.m.r. spectra [1] and later confirmed by the ^{13}C-n.m.r. spectrometry. Since we suggested as necessary to verify our proposal, we performed X-ray structure analysis of dihydroveracintine (veracintine itself is not stable in X-ray radiation).

Two stereoisomers were obtained by sodium borohydride reduction of the azomethine double bond of veracintine (*Va* and *Vb*, Ref. [2]) differing in



I

configuration at C(25); *Vb* (m.p. 165—168 °C, $[\alpha]_D^{23} = -40°$ (*c* 0.9, EtOH)) was found to be suitable for X-ray structure analysis. The absolute configuration at chiral centres and a detailed molecular stereochemistry have been found.

Experimental

The rod-like crystal used in the structure analysis had dimensions 0.5 × 0.1 × 0.075 mm. The quality of the arbitrarily oriented crystal was controlled with help of Weissenberg photographs oscillated in a 30° range. The lattice parameters were determined on a Syntex $P2_1$ diffractometer of the setting angles of 15 centred reflections. The monoclinic unit cell of the following crystallographic parameters was selected with help of an automatic self-indexing program

$a = 1.3650\ (15)$ nm	$V = 2.3467(30)$ nm^3
$b = 1.3332(4)$ nm	$C_{26}H_{34}NO$
$c = 1.5298(34)$ nm	$M_r = 371.61$
$D_o = 1.09$ g cm^{-3}	$\mu(\mathrm{CuK}\alpha) = 0.49$ mm^{-1}
$\beta = 97.38(7)°$	$Z = 4$

Systematic absences among $(0k0)$ reflections for $k = 2n + 1$ and a requirement of the noncentrosymmetry corresponding to chiral molecules gave the unique space group $P2_1$.

Integral intensities were measured on a four-circle diffractometer using a graphite monochromator and CuKα radiation. The intensities were collected by a Θ—2Θ scan technique in a 2Θ interval ⟨0°, 114°⟩. The scan speed was changing in the interval 4.88—29.3 (° 2Θ) min^{-1} for the scan range starting at 1 (° 2Θ) below the calculated peak centre of $K\alpha_1$ and ending at 1 (° 2Θ) above the calculated peak centre of $K\alpha_2$. The background was recorded for half the scan period, at the end of each scan. The intensities of two standard reflections did not change significantly during the experiment. Of the 3371 independent reflections measured, 1841 reflections were regarded as observed if $I > 1.96\ \sigma(I)$. The intensities of all reflections were corrected for Lorentz and polarization factors. No absorption and extinction corrections were made.

Structure solution

Two molecules of dihydroveracintine, *i.e.* 56 equally heavy atoms, occur in the symmetrically independent part of the unit cell. The structure solution was relatively difficult. Neither application of the MULTAN 78 [3] program nor symbolic addition procedure using calculated cos Φ and cos $(\Phi_1 + \Phi_2)$ of structure semiinvariants [4] gave direct structure solution. Detailed analysis of the E-map evaluated with help of MULTAN 78 enabled us to localize, in a cluster of maxima, two linked six-membered rings which were overlapped by an

Table 1

Final atomic coordinates (x 10^4) with e.s.d.'s in parentheses and equivalent isotropic thermal parameters B_{eq} ($10^{-20}m^2$) defined as $B_{eq} = 4/3 \sum_i \sum_j B_{ij} \vec{a}_i \cdot \vec{a}_j$

C(1)	5619(9)	3539(12)	5797(9)	7.77	C(101)	3013(8)	6249(11)	7917(7)	6.09
C(2)	6606(10)	3868(14)	5453(9)	8.99	C(102)	2002(8)	6024(11)	8276(8)	6.34
C(3)	7452(7)	3483(11)	6106(8)	6.48	C(103)	1993(7)	4729(11)	8568(8)	5.92
C(4)	7410(8)	2196(11)	6255(8)	6.67	C(104)	2819(8)	4461(11)	9296(7)	5.68
C(5)	6467(8)	1871(9)	6639(7)	5.26	C(105)	3813(8)	4792(10)	9017(6)	5.38
C(6)	6486(9)	1280(12)	7359(8)	7.47	C(106)	4562(8)	4023(10)	9172(7)	5.52
C(7)	5573(7)	910(11)	7781(8)	6.86	C(107)	5591(7)	4235(10)	8973(7)	5.78
C(8)	4633(7)	1040(10)	7201(7)	5.39	C(108)	5774(7)	5519(10)	8696(7)	5.10
C(9)	4628(8)	2229(10)	6674(7)	5.47	C(109)	4882(7)	6003(11)	8108(7)	5.85
C(10)	5516(8)	2240(10)	6094(7)	5.54	C(110)	3912(7)	5958(9)	8610(6)	4.53
C(11)	3631(7)	2435(12)	6080(8)	6.84	C(111)	5076(7)	7209(10)	7730(7)	5.74
C(12)	2720(8)	2421(12)	6668(7)	6.97	C(112)	5998(8)	7207(10)	7218(7)	6.12
C(13)	2720(7)	1231(10)	7196(6)	4.50	C(113)	6912(7)	6794(10)	7848(6)	4.74
C(14)	3755(8)	1125(10)	7708(7)	5.65	C(114)	6689(7)	5549(9)	8203(6)	4.64
C(15)	3623(8)	79(11)	8367(9)	7.66	C(115)	7686(9)	5050(12)	8639(8)	7.67
C(16)	2521(8)	240(12)	8554(8)	7.05	C(116)	8457(8)	5576(11)	8039(7)	6.32
C(17)	2061(7)	1254(10)	7940(6)	4.69	C(117)	7845(8)	6427(10)	7383(7)	5.67
C(18)	2422(9)	193(13)	6592(8)	8.42	C(118)	7195(9)	7674(11)	8562(7)	6.59
C(19)	5344(10)	1493(16)	5259(8)	9.91	C(119)	3989(8)	6942(10)	9362(7)	6.01
C(20)	924(7)	1138(11)	7717(6)	5.10	C(120)	8516(8)	7477(11)	7102(8)	6.71
C(21)	479(8)	2135(12)	7143(7)	7.06	C(121)	7914(10)	8248(13)	6373(9)	8.58
C(22)	444(8)	981(11)	8575(8)	6.56	C(122)	9433(8)	6900(11)	6776(7)	6.37
C(23)	- 650(8)	639(12)	8429(7)	7.18	C(123)	10226(9)	7836(13)	6586(9)	7.80
C(24)	- 1111(8)	1286(13)	9164(8)	7.57	C(124)	10811(9)	7168(13)	5971(10)	9.14
C(25)	- 513(8)	2397(11)	9248(8)	7.37	C(125)	10108(9)	6094(16)	5476(9)	10.73
C(26)	- 525(10)	3046(14)	10129(9)	8.99	C(126)	10630(11)	4972(16)	5653(12)	12.73
N(1)	495(6)	2131(8)	9129(6)	6.64	N(101)	9135(7)	6225(11)	5927(7)	9.33
O(1)	8391(6)	3770(7)	5811(6)	8.05	O(101)	1009(6)	4530(8)	8838(5)	8.00

Table 2

Coefficients of anisotropic temperature factors (x 10^4) with e.s.d.'s in parentheses

Temperature factor is of the form $\tau = \exp[-(B_{11}h^2+\ldots+B_{12}hk+\ldots)]$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	93(10)	146(16)	96(9)	17(22)	18(16)	82(21)
C(2)	117(11)	208(21)	92(9)	12(26)	98(17)	50(23)
C(3)	55(8)	117(14)	101(9)	- 52(17)	13(13)	- 22(18)
C(4)	63(8)	157(16)	82(8)	0(20)	44(13)	29(19)
C(5)	97(9)	71(10)	59(6)	13(16)	51(12)	- 28(14)
C(6)	108(10)	134(15)	84(8)	44(23)	38(15)	35(20)
C(7)	47(7)	136(15)	114(9)	38(17)	59(13)	87(21)
C(8)	73(8)	110(12)	62(6)	2(18)	63(11)	- 18(16)
C(9)	89(9)	90(12)	64(6)	- 4(17)	78(13)	28(15)
C(10)	85(8)	117(13)	52(6)	2(18)	48(12)	- 27(15)
C(11)	50(7)	203(19)	70(7)	- 31(19)	24(12)	49(19)
C(12)	94(9)	174(17)	56(7)	16(21)	18(13)	87(18)
C(13)	76(7)	92(11)	37(5)	- 8(16)	39(10)	- 18(14)
C(14)	94(8)	95(12)	60(6)	11(18)	53(12)	39(16)
C(15)	70(8)	125(14)	129(10)	58(18)	70(15)	142(21)
C(16)	75(9)	153(16)	88(8)	7(20)	55(14)	56(20)
C(17)	68(7)	99(11)	47(6)	- 9(16)	38(10)	27(15)
C(18)	118(11)	196(18)	76(8)	- 84(24)	69(15)	- 149(21)
C(19)	140(13)	250(25)	78(9)	- 114(30)	75(17)	- 85(25)
C(20)	51(6)	116(13)	63(6)	- 20(17)	36(10)	- 37(17)
C(21)	54(7)	202(18)	74(7)	55(20)	12(12)	88(20)
C(22)	72(8)	133(15)	85(8)	- 29(19)	45(12)	- 15(18)
C(23)	89(9)	174(18)	70(7)	- 102(21)	58(14)	- 60(18)
C(24)	77(9)	183(18)	87(8)	- 48(22)	52(14)	- 10(22)
C(25)	78(9)	158(17)	97(8)	33(21)	86(14)	- 32(20)
C(26)	153(14)	170(18)	85(9)	17(26)	105(18)	- 46(22)
N(1)	76(7)	113(11)	100(7)	- 7(15)	84(12)	- 34(16)
O(1)	101(7)	133(10)	119(7)	- 79(14)	123(11)	- 38(14)
C(101)	93(9)	113(13)	63(7)	11(20)	32(12)	37(17)
C(102)	73(8)	114(13)	89(8)	38(19)	56(13)	15(19)
C(103)	49(7)	113(14)	96(8)	- 14(16)	61(12)	- 32(18)
C(104)	73(8)	113(13)	67(7)	- 4(17)	44(13)	28(17)
C(105)	96(9)	104(13)	46(6)	8(18)	59(12)	18(15)
C(106)	91(9)	91(12)	60(7)	32(17)	46(13)	31(15)
C(107)	61(8)	99(12)	86(8)	45(16)	30(13)	55(17)
C(108)	58(7)	105(12)	62(6)	33(16)	21(11)	15(15)

Table 2 (Continued)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(109)	74(8)	103(12)	77(7)	8(17)	43(12)	- 1(16)
C(110)	75(7)	78(10)	46(5)	11(15)	28(10)	- 8(13)
C(111)	77(8)	98(12)	73(7)	8(17)	44(12)	58(16)
C(112)	94(9)	95(13)	75(7)	23(18)	54(13)	89(16)
C(113)	82(8)	91(11)	38(5)	- 5(16)	14(11)	33(13)
C(114)	58(7)	108(12)	45(6)	- 7(15)	13(10)	35(14)
C(115)	103(10)	141(16)	91(9)	38(23)	40(15)	42(21)
C(116)	102(9)	129(14)	52(6)	5(19)	21(13)	69(16)
C(117)	85(8)	96(12)	71(7)	26(17)	78(12)	52(15)
C(118)	104(10)	139(15)	59(7)	- 42(20)	56(14)	- 64(17)
C(119)	113(10)	97(12)	55(6)	- 25(18)	52(13)	- 6(15)
C(120)	82(9)	146(15)	80(8)	3(19)	82(14)	37(18)
C(121)	130(12)	161(17)	92(9)	- 1(24)	81(17)	81(22)
C(122)	94(9)	118(14)	69(7)	- 51(19)	43(13)	21(18)
C(123)	96(10)	154(17)	100(9)	- 52(21)	99(16)	- 36(21)
C(124)	111(11)	141(17)	138(11)	- 75(22)	94(19)	70(24)
C(125)	100(11)	289(26)	119(11)	8(31)	121(19)	90(31)
C(126)	128(13)	206(23)	208(16)	- 50(31)	135(24)	- 210(36)
N(101)	122(9)	181(15)	116(8)	- 118(21)	124(14)	- 122(21)
O(101)	107(7)	148(11)	103(6)	- 7(14)	110(11)	- 52(14)

inversion image of one of them. A fragment consisting of 11 atoms allowed us to evaluate quasinormalized structure factors and advantage of this partial phase information was taken in a multisolution procedure. The structure solution was not found in phase sets with high values of combined FIGURE OF MERIT but in a set with a relatively low PSI ZERO criterion. The E-map corresponding to this set gave two fragments including 31 atoms from which 29 were later confirmed as correct. The structure solution was completed with repeated weighted Fourier syntheses of electron density.

The positional and isotropic temperature parameters of 56 atoms were refined to an $R = 15.4$ %. A part of the hydrogen atoms were found in the difference Fourier synthesis and the remaining hydrogen atoms were located by calculation of ideal positions assuming sp^3 hybridization and a C—H bond length of 109 pm. The final refinement was performed by block-diagonal least-square method. The positional parameters of all atoms as well as the isotropic temperature parameters of hydrogen atoms and anisotropic temperature parameters of remaining atoms were refined. The function minimized was $M = \Sigma\, w(|F_o| - |F_c|)^2$; a weighting scheme $w^{-1} = \sigma^2(F_o) + (C|F_o|)^2$ was introduced, where $\sigma(F_o)$ is taken from counting statistics and $C = 0.04$. The C value was adjusted to make the $\Sigma\, w(|F_o| - |F_c|)^2$ summation uniform for different intervals of $|F_o|$. The final R value, where $R = \Sigma\, |\Delta F|/\Sigma\, |F_o|$, was 0.077 and the value of weighted R_w factor, where $R_w = [\Sigma\, w|\Delta F|^2/ /\Sigma\, w|F_o|^2]^{1/2}$, was 0.086 for the observed reflections. Atomic scattering curves were taken for

neutral atoms [5]. The maximum residual electron density in the final difference Fourier map was 270 e nm^{-3}. The positions of hydrogen atoms attached to O and N atoms could not be located. The absolute molecular configuration was determined from the known absolute configurations at the C(10) and C(13) atoms [6].

The refined positional parameters of the heavy atoms are given in Table 1, the corresponding coefficients of anisotropic thermal parameters are in Table 2. The observed and calculated structure factors are available from the authors.

All calculations were carried out on a Siemens 4004/150 computer at the Institute of Computing Technique of the Komenský University in Bratislava using NRC and MULTAN 78 program systems [3, 7].

Discussion

Two symmetrically independent molecules of dihydroveracintine form dimers in the crystal through two intermolecular hydrogen bonds O(1) ... N(101) and O(101) ... N(1). The O ... N distances are 299(2) and 285(2) pm, respectively. Dimers are bonded to each other through the van der Waals interactions. Both molecules, *II* and *III*, and atomic numbering are shown in Figs. 1 and 2. The

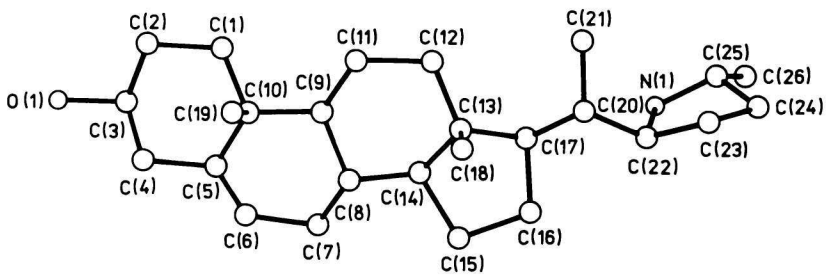


Fig. 1. Perspective projection of dihydroveracintine (molecule *II*) and the atomic numbering scheme.

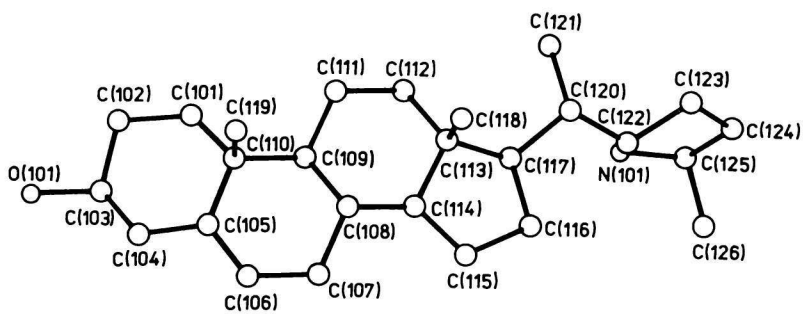


Fig. 2. Perspective projection of dihydroveracintine (molecule *III*) and the atomic numbering scheme.

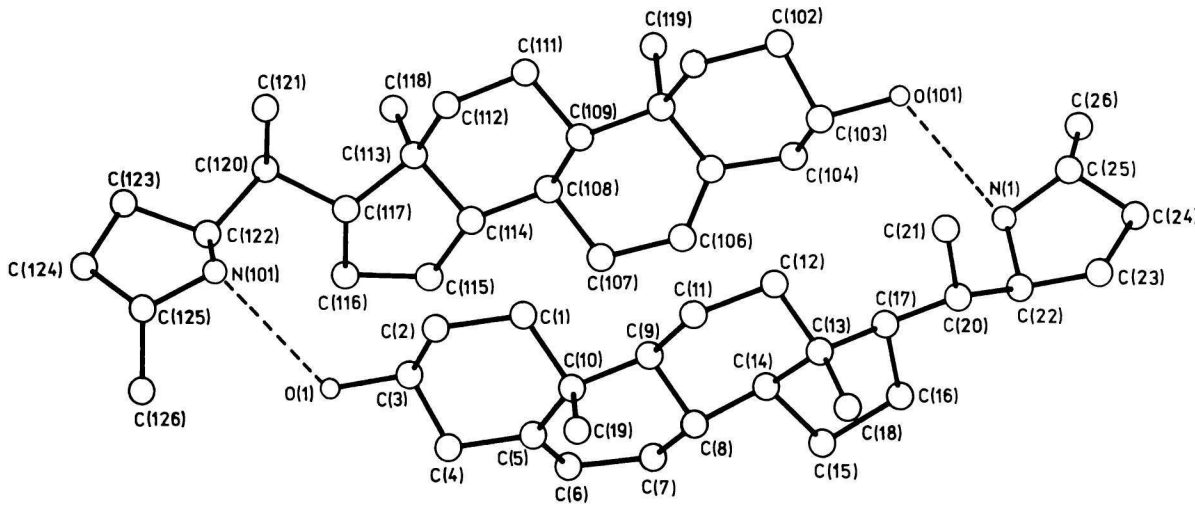


Fig. 3. Perspective projection of the dihydroveracintine dimer showing the hydrogen-bonding system.

numbering for molecule *III* is a standard one except by adding a number 100. Perspective drawing of the dimer can be seen in Fig. 3.

Bond distances and angles in Table 3 are consistent with the data for 5-pregnene skeleton [6], although the accuracy of the parameters is relatively low due to a small number of the measured intensities per one refined parameter.

The stereochemistry of the 5-pregnene skeleton is a standard one with a *C/B* and *C/D trans*-fusion. The O(1) and C(20) substituents are equatorial. The absolute configuration at C(20) is (S) as it was predicted [2], while the absolute configuration at C(25) is (R). Both *A* and *C* rings have a chair conformation. The *B* ring shows some conformational flexibility in the 5-ene steroids [6]. Conformation of the *B* ring in dihydroveracintine may be described in the most proper way as the 8β, 9α half-chair deformed towards the 9α sofa, with the asymmetry parameters [6] $\Delta C_s(6)$ and $\Delta C_2(5\text{-}6)$ equal to 15.40° and 6.15° for molecule *II* and 14.50° and 8.92° for molecule *III*. Conformation of both *D* rings may be described as an intermediate conformation between 13β, 14α half-chair and 13β envelope. Since this geometric description has no essential physical meaning with respect to pseudorotation, the pseudorotation Δ and φ_{max} parameters were calculated using a procedure of *Altona et al.* [8] (relation *3*). These parameters were calculated for all five combinations of torsion angles and the phase shifts were evaluated for φ_0 [C(17)—C(13)—C(14)—C(15)] and the inconsistency between separate calculations was characterized by standard deviation σ_{n-1}. Both *D* rings possess nearly identical conformations with φ_{max} equal to 49.2(4)° and 47.4(5)° and Δ equal to 21.4(8)° and 21.6(1.2)°.

Table 3

Bond distances, bond angles, and torsion angles with standard deviation in parentheses

Bond distances/pm					
C(1)-C(2)	154(2)	C(9)-C(10)	160(2)	C(20)-C(21)	150(2)
C(1)-C(10)	155(2)	C(9)-C(11)	155(2)	C(20)-C(22)	154(2)
C(2)-C(3)	148(2)	C(10)-C(19)	153(2)	C(22)-C(23)	153(2)
C(3)-C(4)	148(2)	C(11)-C(12)	159(2)	C(22)-N(1)	156(2)
C(3)-O(1)	146(2)	C(12)-C(13)	157(2)	C(23)-C(24)	154(2)
C(4)-C(5)	152(2)	C(13)-C(14)	154(2)	C(24)-C(25)	150(2)
C(5)-C(6)	128(2)	C(13)-C(17)	155(2)	C(25)-C(26)	152(2)
C(5)-C(10)	151(2)	C(13)-C(18)	153(2)	C(25)-N(1)	145(2)
C(6)-C(7)	156(2)	C(14)-C(15)	158(2)	C(101)-C(102)	159(2)
C(7)-C(8)	148(2)	C(15)-C(16)	160(2)	C(101)-C(110)	154(2)
C(8)-C(9)	157(2)	C(16)-C(17)	157(2)	C(102)-C(103)	154(2)
C(8)-C(14)	150(2)	C(17)-C(20)	155(2)	C(103)-C(104)	151(2)

Table 3 (Continued)

Bond distances/pm					
C(103)-O(101)	146(2)	C(110)-C(119)	160(2)	C(117)-C(120)	160(2)
C(104)-C(105)	152(2)	C(111)-C(112)	160(2)	C(120)-C(121)	157(2)
C(105)-C(106)	134(2)	C(112)-C(113)	155(2)	C(120)-C(122)	157(2)
C(105)-C(110)	148(2)	C(113)-C(114)	156(2)	C(122)-C(123)	156(2)
C(106)-C(107)	149(2)	C(113)-C(117)	157(2)	C(122)-N(101)	150(2)
C(107)-C(108)	155(2)	C(113)-C(118)	150(2)	C(123)-C(124)	153(2)
C(108)-C(109)	152(2)	C(114)-C(115)	155(2)	C(124)-C(125)	166(3)
C(108)-C(114)	155(2)	C(115)-C(116)	157(2)	C(125)-C(126)	148(3)
C(109)-C(110)	160(2)	C(116)-C(117)	155(2)	C(125)-N(101)	149(2)
C(109)-C(111)	152(2)				

Bond angles/°			
C(2)-C(1)-C(10)	116.3(1.2)	C(102)-C(101)-C(110)	112.4(1.0)
C(1)-C(2)-C(3)	110.1(1.3)	C(101)-C(102)-C(103)	107.0(1.0)
C(2)-C(3)-C(4)	110.3(1.2)	C(102)-C(103)-C(104)	111.6(1.1)
C(2)-C(3)-O(1)	111.8(1.1)	C(102)-C(103)-O(101)	105.5(1.1)
C(4)-C(3)-O(1)	108.8(1.1)	C(104)-C(103)-O(101)	112.8(1.1)
C(3)-C(4)-C(5)	110.7(1.1)	C(103)-C(104)-C(105)	110.8(1.0)
C(4)-C(5)-C(6)	121.5(1.2)	C(104)-C(105)-C(106)	118.7(1.1)
C(4)-C(5)-C(10)	115.2(1.0)	C(104)-C(105)-C(110)	118.3(1.0)
C(6)-C(5)-C(10)	123.3(1.2)	C(106)-C(105)-C(110)	123.0(1.1)
C(5)-C(6)-C(7)	124.7(1.3)	C(105)-C(106)-C(107)	125.3(1.2)
C(6)-C(7)-C(8)	113.9(1.1)	C(106)-C(107)-C(108)	113.1(1.0)
C(7)-C(8)-C(9)	110.2(1.0)	C(107)-C(108)-C(109)	110.8(1.0)
C(7)-C(8)-C(14)	112.1(1.0)	C(107)-C(108)-C(114)	108.8(1.0)
C(9)-C(8)-C(14)	105.2(1.0)	C(109)-C(108)-C(114)	110.0(1.0)
C(8)-C(9)-C(10)	110.1(1.0)	C(108)-C(109)-C(110)	110.6(1.0)
C(8)-C(9)-C(11)	112.0(1.0)	C(108)-C(109)-C(111)	112.6(1.0)
C(10)-C(9)-C(11)	110.9(1.0)	C(110)-C(109)-C(111)	113.1(1.0)
C(1)-C(10)-C(5)	109.0(1.1)	C(101)-C(110)-C(105)	111.8(1.0)
C(1)-C(10)-C(9)	106.3(1.0)	C(101)-C(110)-C(109)	107.1(0.9)
C(1)-C(10)-C(19)	106.7(1.1)	C(101)-C(110)-C(119)	108.6(1.0)
C(5)-C(10)-C(9)	110.6(1.0)	C(105)-C(110)-C(109)	110.7(1.0)
C(5)-C(10)-C(19)	110.1(1.1)	C(105)-C(110)-C(119)	108.4(1.0)
C(9)-C(10)-C(19)	113.8(1.0)	C(109)-C(110)-C(119)	110.3(0.9)
C(9)-C(11)-C(12)	111.2(1.1)	C(109)-C(111)-C(112)	111.6(1.0)
C(11)-C(12)-C(13)	110.6(1.0)	C(111)-C(112)-C(113)	109.0(1.0)
C(12)-C(13)-C(14)	105.6(1.0)	C(112)-C(113)-C(114)	108.3(0.9)
C(12)-C(13)-C(17)	114.4(1.0)	C(112)-C(113)-C(117)	115.6(1.0)
C(12)-C(13)-C(18)	111.4(1.0)	C(112)-C(113)-C(118)	111.0(1.0)

Table 3 (Continued)

Bond angles/°			
C(14)-C(13)-C(17)	102.3(1.0)	C(114)-C(113)-C(117)	97.2(0.9)
C(14)-C(13)-C(18)	113.6(1.0)	C(114)-C(113)-C(118)	113.0(1.0)
C(17)-C(13)-C(18)	109.4(1.0)	C(117)-C(113)-C(118)	111.1(1.0)
C(8)-C(14)-C(13)	118.5(1.0)	C(108)-C(114)-C(113)	113.9(0.9)
C(8)-C(14)-C(15)	116.3(1.1)	C(108)-C(114)-C(115)	121.0(1.0)
C(13)-C(14)-C(15)	102.3(1.0)	C(113)-C(114)-C(115)	105.9(1.0)
C(14)-C(15)-C(16)	103.0(1.1)	C(114)-C(115)-C(116)	103.1(1.1)
C(15)-C(16)-C(17)	106.6(1.1)	C(115)-C(116)-C(117)	105.6(1.0)
C(13)-C(17)-C(16)	101.9(0.9)	C(113)-C(117)-C(116)	105.8(1.0)
C(13)-C(17)-C(20)	120.1(1.0)	C(113)-C(117)-C(120)	116.2(1.0)
C(16)-C(17)-C(20)	112.4(1.0)	C(116)-C(117)-C(120)	110.9(1.0)
C(17)-C(20)-C(21)	112.5(1.0)	C(117)-C(120)-C(121)	109.7(1.1)
C(17)-C(20)-C(22)	110.0(1.0)	C(117)-C(120)-C(122)	106.7(1.0)
C(21)-C(20)-C(22)	113.6(1.1)	C(121)-C(120)-C(122)	111.8(1.1)
C(20)-C(22)-C(23)	115.1(1.1)	C(120)-C(122)-C(123)	111.6(1.1)
C(20)-C(22)-N(1)	111.8(1.0)	C(120)-C(122)-N(101)	113.6(1.1)
C(23)-C(22)-N(1)	104.9(1.0)	C(123)-C(122)-N(101)	106.1(1.1)
C(22)-C(23)-C(24)	105.2(1.1)	C(122)-C(123)-C(124)	101.3(1.2)
C(23)-C(24)-C(25)	101.3(1.2)	C(123)-C(124)-C(125)	108.8(1.3)
C(24)-C(25)-C(26)	114.5(1.3)	C(124)-C(125)-C(126)	107.9(1.4)
C(24)-C(25)-N(1)	109.1(1.2)	C(124)-C(125)-N(101)	101.2(1.2)
C(26)-C(25)-N(1)	109.2(1.2)	C(126)-C(125)-N(101)	114.1(1.5)
C(22)-N(1)-C(25)	105.8(1.0)	C(122)-N(101)-C(125)	109.7(1.2)
Torsion angles/°			
C(10)-C(1)-C(2)-C(3)	- 51(2)	C(110)-C(101)-C(102)-C(103)	- 57(2)
C(2)-C(1)-C(10)-C(5)	43(2)	C(102)-C(101)-C(110)-C(105)	49(2)
C(2)-C(1)-C(10)-C(9)	163(1)	C(102)-C(101)-C(110)-C(109)	170(1)
C(2)-C(1)-C(10)-C(19)	- 75(2)	C(102)-C(101)-C(110)-C(119)	- 71(1)
C(1)-C(2)-C(3)-C(4)	58(2)	C(101)-C(102)-C(103)-C(104)	61(2)
C(1)-C(2)-C(3)-O(1)	179(1)	C(101)-C(102)-C(103)-O(101)	- 176(1)
C(2)-C(3)-C(4)-C(5)	- 62(2)	C(102)-C(103)-C(104)-C(105)	- 56(2)
O(1)-C(3)-C(4)-C(5)	175(1)	O(101)-C(103)-C(104)-C(105)	- 175(1)
C(3)-C(4)-C(5)-C(6)	- 126(2)	C(103)-C(104)-C(105)-C(106)	- 134(1)
C(3)-C(4)-C(5)-C(10)	57(2)	C(103)-C(104)-C(105)-C(110)	48(2)
C(4)-C(5)-C(6)-C(7)	- 180(1)	C(104)-C(105)-C(106)-C(107)	- 177(1)
C(10)-C(5)-C(6)-C(7)	- 3(2)	C(110)-C(105)-C(106)-C(107)	1(2)
C(4)-C(5)-C(10)-C(1)	- 46(2)	C(104)-C(105)-C(110)-C(101)	- 44(2)

Table 3 (Continued)

Torsion angles/°			
C(4)-C(5)-C(10)-C(9)	- 163(2)	C(104)-C(105)-C(110)-C(109)	- 163(1)
C(4)-C(5)-C(10)-C(19)	71(2)	C(104)-C(105)-C(110)-C(119)	75(1)
C(6)-C(5)-C(10)-C(1)	137(2)	C(106)-C(105)-C(110)-C(101)	138(1)
C(6)-C(5)-C(10)-C(9)	20(2)	C(106)-C(105)-C(110)-C(109)	18(2)
C(6)-C(5)-C(10)-C(19)	- 106(2)	C(106)-C(105)-C(110)-C(119)	- 103(1)
C(5)-C(6)-C(7)-C(8)	14(2)	C(105)-C(106)-C(107)-C(108)	9(2)
C(6)-C(7)-C(8)-C(9)	- 42(2)	C(106)-C(107)-C(108)-C(109)	- 39(2)
C(6)-C(7)-C(8)-C(14)	- 158(1)	C(106)-C(107)-C(108)-C(114)	- 160(1)
C(23)-C(22)-N(1)-C(25)	- 2(2)	C(123)-C(122)-N(101)-C(125)	35(2)
C(22)-C(23)-C(24)-C(25)	34(2)	C(122)-C(123)-C(124)-C(125)	24(2)
C(23)-C(24)-C(25)-C(26)	- 160(1)	C(123)-C(124)-C(125)-C(126)	- 124(2)
C(23)-C(24)-C(25)-N(1)	- 37(2)	C(123)-C(124)-C(125)-N(101)	- 4(2)
C(24)-C(25)-N(1)-C(22)	24(2)	C(124)-C(125)-N(101)-C(122)	- 19(2)
C(26)-C(25)-N(1)-C(22)	150(1)	C(126)-C(125)-N(101)-C(122)	97(2)
C(18)-C(13)-C(14)-C(8)	61(2)	C(118)-C(113)-C(114)-C(108)	65(1)
C(18)-C(13)-C(14)-C(15)	- 69(1)	C(118)-C(113)-C(114)-C(115)	- 70(1)
C(12)-C(13)-C(17)-C(16)	- 158(1)	C(112)-C(113)-C(117)-C(116)	- 156(1)
C(12)-C(13)-C(17)-C(20)	77(2)	C(112)-C(113)-C(117)-C(120)	80(1)
C(14)-C(13)-C(17)-C(16)	- 44(1)	C(114)-C(113)-C(117)-C(116)	- 42(1)
C(14)-C(13)-C(17)-C(20)	- 169(1)	C(114)-C(113)-C(117)-C(120)	- 166(1)
C(18)-C(13)-C(17)-C(16)	76(1)	C(118)-C(113)-C(117)-C(116)	76(1)
C(18)-C(13)-C(17)-C(20)	- 49(2)	C(118)-C(113)-C(117)-C(120)	- 47(2)
C(13)-C(14)-C(15)-C(16)	- 33(1)	C(113)-C(114)-C(115)-C(116)	- 33(1)
C(8)-C(14)-C(15)-C(16)	- 164(1)	C(108)-C(114)-C(115)-C(116)	- 165(1)
C(14)-C(15)-C(16)-C(17)	6(1)	C(114)-C(115)-C(116)-C(117)	6(1)
C(15)-C(16)-C(17)-C(13)	23(1)	C(115)-C(116)-C(117)-C(113)	24(1)
C(15)-C(16)-C(17)-C(20)	153(1)	C(115)-C(116)-C(117)-C(120)	150(1)
C(13)-C(17)-C(20)-C(21)	- 62(2)	C(113)-C(117)-C(120)-C(121)	- 65(2)
C(13)-C(17)-C(20)-C(22)	171(1)	C(113)-C(117)-C(120)-C(122)	174(1)
C(16)-C(17)-C(20)-C(21)	179(1)	C(116)-C(117)-C(120)-C(121)	174(1)
C(16)-C(17)-C(20)-C(22)	51(2)	C(116)-C(117)-C(120)-C(122)	53(1)
C(17)-C(20)-C(22)-C(23)	- 170(1)	C(117)-C(120)-C(122)-C(123)	- 173(1)
C(17)-C(20)-C(22)-N(1)	71(1)	C(117)-C(120)-C(122)-N(101)	68(2)
C(21)-C(20)-C(22)-C(23)	63(2)	C(121)-C(120)-C(122)-C(123)	68(2)
C(21)-C(20)-C(22)-N(1)	- 56(1)	C(121)-C(120)-C(122)-N(101)	- 52(2)
C(20)-C(22)-C(23)-C(24)	- 144(1)	C(120)-C(122)-C(123)-C(124)	- 159(1)
N(1)-C(22)-C(23)-C(24)	- 21(2)	N(101)-C(122)-C(123)-C(124)	- 35(2)
C(20)-C(22)-N(1)-C(25)	124(1)	C(120)-C(122)-N(101)-C(125)	158(1)
C(7)-C(8)-C(9)-C(10)	59(1)	C(107)-C(108)-C(109)-C(110)	59(2)

Table 3 (Continued)

Torsion angles/°			
C(7)-C(8)-C(9)-C(11)	- 177(1)	C(107)-C(108)-C(109)-C(111)	- 173(1)
C(14)-C(8)-C(9)-C(10)	- 180(1)	C(114)-C(108)-C(109)-C(110)	179(1)
C(14)-C(8)-C(9)-C(11)	- 56(2)	C(114)-C(108)-C(109)-C(111)	- 53(2)
C(7)-C(8)-C(14)-C(13)	- 178(1)	C(107)-C(108)-C(114)-C(113)	177(1)
C(7)-C(8)-C(14)-C(15)	- 56(2)	C(107)-C(108)-C(114)-C(115)	- 55(2)
C(9)-C(8)-C(14)-C(13)	62(2)	C(109)-C(108)-C(114)-C(113)	55(2)
C(9)-C(8)-C(14)-C(15)	- 176(1)	C(109)-C(108)-C(114)-C(115)	- 177(1)
C(8)-C(9)-C(10)-C(1)	- 166(1)	C(108)-C(109)-C(110)-C(101)	- 170(1)
C(8)-C(9)-C(10)-C(5)	- 48(2)	C(108)-C(109)-C(110)-C(105)	- 48(2)
C(8)-C(9)-C(10)-C(19)	77(2)	C(108)-C(109)-C(110)-C(119)	72(1)
C(11)-C(9)-C(10)-C(1)	70(1)	C(111)-C(109)-C(110)-C(101)	63(1)
C(11)-C(9)-C(10)-C(5)	- 172(1)	C(111)-C(109)-C(110)-C(105)	- 175(1)
C(11)-C(9)-C(10)-C(19)	- 47(2)	C(111)-C(109)-C(110)-C(119)	- 55(1)
C(8)-C(9)-C(11)-C(12)	57(2)	C(108)-C(109)-C(111)-C(112)	56(2)
C(10)-C(9)-C(11)-C(12)	- 180(1)	C(110)-C(109)-C(111)-C(112)	- 178(1)
C(9)-C(11)-C(12)-C(13)	- 56(2)	C(109)-C(111)-C(112)-C(113)	- 58(1)
C(11)-C(12)-C(13)-C(14)	54(1)	C(111)-C(112)-C(113)-C(114)	57(1)
C(11)-C(12)-C(13)-C(17)	165(1)	C(111)-C(112)-C(113)-C(117)	165(1)
C(11)-C(12)-C(13)-C(18)	- 70(1)	C(111)-C(112)-C(113)-C(118)	- 67(1)
C(12)-C(13)-C(14)-C(8)	- 62(2)	C(112)-C(113)-C(114)-C(108)	- 58(1)
C(12)-C(13)-C(14)-C(15)	169(1)	C(112)-C(113)-C(114)-C(115)	166(1)
C(17)-C(13)-C(14)-C(8)	178(1)	C(117)-C(113)-C(114)-C(108)	- 178(1)
C(17)-C(13)-C(14)-C(15)	49(2)	C(117)-C(113)-C(114)-C(115)	46(1)

Conformations of the pyrrolidine rings are in both molecules different. In the molecule *II*, the phase shift Δ is 42.5(1.3)°, but −97.5(2.0)° in the molecule *III* (related to the angle C(22)—C(23)—C(24)—C(25)). The maximum torsion angles, φ_{max}, are equal within standard deviation: 37.8(5)° and 36.9(8)°, respectively. Conformation of the *E* ring in *II* is close to the C(24) envelope conformation with an asymmetry parameter $\Delta C_s(24) = 3.2°$. The C(26) atom is in a pseudoequatorial position with respect to the five-membered ring, while C(20) has no outstanding ax-eq character. The *E* ring in *III* possesses an approximate C(22) envelope conformation with the asymmetry parameter $\Delta C_s(22) = 3.6°$. The C(20) atom is a pseudoequatorial and the C(26) atom is a pseudoaxial substituent.

References

1. Tomko, J., Brázdová, V., and Votický, Z., *Tetrahedron Lett. 1971,* 3041.
2. Vassová, A., Votický, Z., Tomko, J., and Ahond, A., *Collect. Czech. Chem. Commun. 41,* 2964 (1976).
3. Main, P., *Program MULTAN 78.* University of York, England, 1978.
4. Hauptman, H. A., *Crystal Structure Determination. The Role of the Cosine Semiinvariants,* pp. 207 and 327. Plenum Press, New York, 1972.
5. *International Tables for X-ray Crystallography,* Vol. *IV.* Kynoch Press, Birmingham, 1974.
6. Duax, W. L., Weeks, C. M., and Rohrer, D. C., *Topics in Stereochemistry 9,* 271 (1976).
7. Ahmed, F. R., *Crystallographic Computing,* pp. 55—57. Munksgaard, Copenhagen, 1970.
8. Altona, C., Geise, H. J., and Romers, C., *Tetrahedron 24,* 13 (1968).

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