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Acta Cryst. (1977). B33, 1988–1990

18(17 → 16)abeo-Yohimbine Acetate Methanol Solvate

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(Received 13 January 1977; accepted 7 February 1977)

Abstract. C₂₃H₂₈N₂O₄.CH₄O, monoclinic, *P*2₁, *a* = 6.734 (5), *b* = 14.465 (9), *c* = 12.114 (10) Å, β = 105.2 (2)°, *Z* = 2, final *R* value 0.07. The *C/D* ring junction is *trans*-quinolizidine; the *D/E* ring junction is *trans*. The six-membered rings *C* and *D* have half-chair and chair conformations, the five-membered ring *E* has a half-chair conformation.

Introduction. In a study of ring closure by mercury oxidation, demethylcorynantheine led mostly to a new derivative of the 18(17 → 16)abeo-yohimbine type (Djakouré, Jarreau & Goutarel, 1975). Recently, the reaction mechanism has been established (Boivin, Païs & Goutarel, 1976). The present X-ray structure determination was undertaken to ascertain the stereochemistry at C(20).

Data were collected from a crystal 0.3 × 0.3 × 0.6 mm on a Philips PW 1100 diffractometer with graphite-monochromated Cu *K*α radiation (λ = 1.5418 Å), for θ between 3 and 68°. 2266 independent reflexions were measured, of which 1972 were considered observed with *I* > 3σ(*I*), σ(*I*) being derived from counting statistics.

The structure was solved by straightforward application of *MULTAN* (Germain, Main & Woolfson,

Table 1. Final coordinates (× 10⁴) and their e.s.d.'s

	<i>x</i>	<i>y</i>	<i>z</i>
N(1)	7051 (5)	506 (0)	2066 (3)
C(2)	5242 (6)	952 (3)	1495 (4)
C(3)	5071 (6)	1965 (3)	1319 (4)
N(4)	2823 (5)	2205 (3)	1022 (3)
C(5)	1661 (8)	1610 (4)	97 (4)
C(6)	1599 (7)	610 (4)	479 (4)
C(7)	3709 (7)	326 (3)	1162 (4)
C(8)	4553 (7)	-565 (3)	1532 (4)
C(9)	3710 (9)	-1458 (4)	1485 (5)
C(10)	4995 (11)	-2189 (4)	1964 (5)
C(11)	7056 (11)	-2034 (4)	2477 (5)
C(12)	7923 (8)	-1154 (4)	2546 (4)
C(13)	6652 (7)	-430 (3)	2086 (4)
C(14)	6248 (6)	2540 (3)	2335 (4)
C(15)	5969 (6)	3544 (3)	2032 (4)
C(16)	6896 (6)	4314 (3)	2901 (4)
C(17)	9196 (7)	4416 (4)	2987 (4)
C(18)	5636 (7)	5178 (3)	2372 (4)
C(19)	3802 (7)	4842 (3)	1401 (4)
C(20)	3675 (6)	3805 (3)	1636 (3)
C(21)	2539 (7)	3189 (3)	681 (4)
O(22)	10114 (5)	5098 (3)	3844 (3)
C(23)	10842 (7)	5876 (4)	3504 (5)
O(24)	10665 (6)	6071 (3)	2531 (4)
C(25)	11889 (11)	6476 (5)	4479 (7)
C(26)	6696 (8)	4035 (3)	4068 (4)
O(27)	7942 (6)	3618 (3)	4765 (3)
O(28)	4874 (5)	4303 (3)	4243 (3)
C(29)	4452 (12)	3957 (6)	5301 (5)
O(30)	11023 (5)	1604 (3)	2838 (4)
C(31)	12360 (11)	1256 (9)	3789 (7)

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1971) and refined by full-matrix least-squares methods. In the refinement, the quantity $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/\sigma^2(F)$. Scattering factors for the non-hydrogen atoms were taken from Doyle & Turner (1968) while those for H were from Stewart, Davidson & Simpson (1965). 22 H atoms, bonded directly to the skeleton, were included in their idealized positions (C—H = 1.00 Å). They were assigned the equivalent isotropic thermal factors of the bonded carbons. Those of the methyl groups and of the methanol molecule could not be located. The final

Table 4. *Principal least-squares planes and atomic deviations (Å) from the planes*

Atoms marked with an asterisk are included in the plane calculation. The general equation for the plane is $lX + mY + nZ + p = 0$, where X , Y and Z are the coordinates in Å with respect to the orthogonal axes a , b and c^* , and p is the origin-to-plane distance.

Plane A:	$0.4815X - 0.1188Y - 0.8684Z + 0.2121 = 0$
Plane B:	$0.4638X - 0.1493Y - 0.8733Z + 0.2564 = 0$
Plane A + B:	$0.4727X - 0.1333Y - 0.8711Z + 0.2540 = 0$
Plane C:	$-0.8886X + 0.4571Y - 0.0377Z + 1.7654 = 0$
Plane D:	$-0.3273X - 0.8641Y - 0.3824Z + 7.9084 = 0$

Planes A, B and A + B (mean e.s.d. 0.005 Å)

	A	B	A + B
N(1)	0.002*	0.064	0.013*
C(2)	-0.002*	0.058	0.008*
C(7)	-0.001*	0.013	-0.014*
C(8)	0.005*	-0.010*	-0.021*
C(13)	-0.006*	0.010*	-0.017*
C(9)	0.069	0.005*	0.019*
C(10)	0.087	0.005*	0.029*
C(11)	0.044	-0.006*	0.002*
C(12)	-0.004	-0.005*	-0.023*
C(3)	0.022	0.125	0.051*
C(6)	-0.066	-0.064	-0.085*
Plane C			
O(22)	0.000*	C(17)	-0.105
C(23)	-0.002*	C(16)	1.183
O(24)	0.000*	C(18)	2.382
C(25)	0.001*		
Plane D			
O(27)	0.001*	O(28)	0.001*
C(26)	-0.005	C(16)	0.001*

Table 2. *Bond lengths (Å)*

N(1)—C(2)	1.391 (6)	C(14)—C(15)	1.498 (6)
N(1)—C(13)	1.381 (5)	C(15)—C(16)	1.547 (6)
C(2)—C(3)	1.481 (6)	C(15)—C(20)	1.539 (6)
C(2)—C(7)	1.352 (6)	C(16)—C(17)	1.532 (6)
C(3)—N(4)	1.502 (6)	C(16)—C(18)	1.552 (6)
C(3)—C(14)	1.524 (6)	C(16)—C(26)	1.509 (6)
N(4)—C(5)	1.466 (6)	C(17)—O(22)	1.448 (6)
N(4)—C(21)	1.480 (6)	C(18)—C(19)	1.543 (7)
C(5)—C(6)	1.524 (8)	C(19)—C(20)	1.534 (7)
C(6)—C(7)	1.501 (7)	C(20)—C(21)	1.501 (6)
C(7)—C(8)	1.433 (7)	O(22)—C(23)	1.335 (7)
C(8)—C(9)	1.406 (8)	C(23)—O(24)	1.188 (8)
C(8)—C(13)	1.410 (7)	C(23)—C(25)	1.486 (10)
C(9)—C(10)	1.394 (8)	C(26)—O(27)	1.187 (6)
C(10)—C(11)	1.382 (10)	C(26)—O(28)	1.356 (6)
C(11)—C(12)	1.394 (8)	O(28)—C(29)	1.471 (8)
C(12)—C(13)	1.375 (7)	O(30)—C(31)	1.359 (10)

Table 3. *Bond angles (°)*

C(2)—N(1)—C(13)	108.3 (3)	C(3)—C(14)—C(15)	109.1 (4)
N(1)—C(2)—C(3)	123.7 (4)	C(14)—C(15)—C(16)	122.0 (4)
N(1)—C(2)—C(7)	109.8 (4)	C(14)—C(15)—C(20)	111.4 (4)
C(3)—C(2)—C(7)	126.5 (4)	C(16)—C(15)—C(20)	103.2 (3)
C(2)—C(3)—N(4)	107.4 (4)	C(15)—C(16)—C(17)	109.6 (4)
C(2)—C(3)—C(14)	114.8 (4)	C(15)—C(16)—C(18)	102.7 (3)
N(4)—C(3)—C(14)	110.1 (4)	C(15)—C(16)—C(26)	109.0 (4)
C(3)—N(4)—C(5)	110.4 (4)	C(17)—C(16)—C(18)	112.6 (4)
C(3)—N(4)—C(21)	109.7 (3)	C(17)—C(16)—C(26)	107.4 (4)
C(5)—N(4)—C(21)	110.3 (4)	C(18)—C(16)—C(26)	115.4 (4)
N(4)—C(5)—C(6)	112.1 (4)	C(16)—C(17)—O(22)	110.4 (4)
C(5)—C(6)—C(7)	109.2 (4)	C(16)—C(18)—C(19)	107.6 (4)
C(2)—C(7)—C(8)	121.3 (4)	C(18)—C(19)—C(20)	103.9 (4)
C(2)—C(7)—C(8)	107.4 (4)	C(15)—C(20)—C(19)	101.4 (4)
C(6)—C(7)—C(8)	131.2 (4)	C(15)—C(20)—C(21)	111.2 (4)
C(7)—C(8)—C(9)	133.7 (5)	C(19)—C(20)—C(21)	118.7 (4)
C(7)—C(8)—C(13)	106.9 (4)	N(4)—C(21)—C(20)	110.7 (4)
C(9)—C(8)—C(13)	119.4 (4)	C(17)—O(22)—C(23)	118.3 (4)
C(8)—C(9)—C(10)	118.7 (5)	O(22)—C(23)—O(24)	123.9 (5)
C(9)—C(10)—C(11)	120.3 (6)	O(22)—C(23)—C(25)	112.5 (5)
C(10)—C(11)—C(12)	122.0 (6)	O(24)—C(23)—C(25)	123.6 (6)
C(11)—C(12)—C(13)	117.7 (5)	C(16)—C(26)—O(27)	125.6 (4)
N(1)—C(13)—C(8)	107.6 (4)	C(16)—C(26)—O(28)	112.1 (4)
N(1)—C(13)—C(2)	130.6 (4)	O(27)—C(26)—O(28)	122.2 (5)
C(8)—C(13)—C(2)	121.8 (4)	C(26)—O(28)—C(29)	115.4 (4)

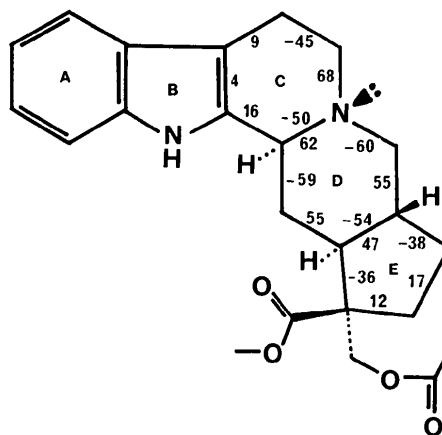


Fig. 1. Chemical formula and torsional angles (°).

conventional R value was 7%.* The atomic coordinates are listed in Table 1, bond lengths and angles in Tables 2 and 3. Deviations from the principal mean planes are listed in Table 4.

Discussion. The result of the structure determination is illustrated in Fig. 2. Torsional angles are shown in Fig. 1. Ring C has a half-chair conformation, where C(6), C(7), C(2) and C(3) are slightly displaced from their mean plane (Table 4). Ring D is chair shaped. For ring E we calculate a pseudorotation phase angle ϕ (Altona,

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32492 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

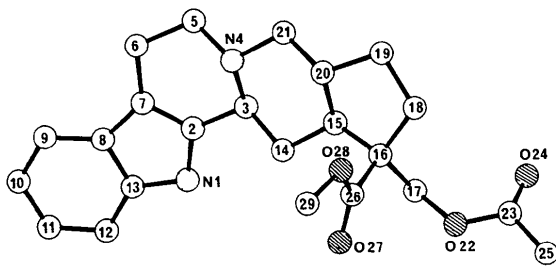


Fig. 2. A perspective view of the molecule.

Geise & Romers, 1968) of 6.3° and a maximum torsional angle ϕ_m of 46.7° , corresponding to a $C_2(18)$ half-chair form. The six- and five-membered rings A and B are planar within ± 0.01 and ± 0.06 Å respectively. The angle between the normals to these planes is 2.1° . The C/D ring junction is *trans*. C(17) is slightly out of the mean plane of the acetate group (0.10 Å) and the torsional angle C(16)–C(17)–O(22)–C(22) is -114° .

The methanol molecule is involved in two hydrogen bonds linking two different molecules (translated along a): N(1)H...O(30) (3.03 Å) and O(30)H...N(4) (2.90 Å).

The authors thank Dr Mary Païs for suggesting the problem.

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Acta Cryst. (1977). **B33**, 1990–1992

Pandine

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(Received 24 January 1977; accepted 21 February 1977)

Abstract. $C_{21}H_{24}O_3N_2$, $M_r = 352$, triclinic, $P1$, $a = 6.918$ (4), $b = 12.634$ (5), $c = 13.008$ (5) Å, $\alpha = 94.00$ (2), $\beta = 93.73$ (2), $\gamma = 100.61$ (2)°, $Z = 2$. The unit cell contains two independent molecules of pandine, one molecule of methanol and two molecules of water. The two molecules of the alkaloid are in the same conformation, and the configuration at C(20) is R .

Introduction. 4031 intensities were collected on a Philips PW 1100 diffractometer (with Cu $K\alpha$ radiation and a graphite monochromator) up to $2\theta = 68^\circ$. 3403 were above the background (2σ), and were corrected for the L_p factor, but not for absorption.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971), and refined by least-squares methods with isotropic temperature factors to a final R