$C_{33}H_{50}O_5$

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The Structure of 20-Epiheyneanine Acetone Solvate

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Abstract. Methyl 1,2,3,4,4a,6,7,12b-octahydro-4-(1-hydroxyethyl)-2,5-methano-$5H$,$12H$-[1]benzazepino-[4,5-b]indol-12b-acetate acetone solvate. $C_{21}H_{26}N_2O_3.C_3H_6O$, $M_r = 412\cdot6$, orthorhombic, $P2_12_12_1$, $a = 8\cdot626$ (1), $b = 13\cdot490$ (4), $c = 19\cdot181$ (3) Å, $V = 2232$ (1) Å^3, $Z = 4$, $D_m = 1\cdot16$ (flotation), $D_x = 1\cdot22$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0\cdot71069$ Å, $\mu = 0\cdot048$ mm^{-1}, $F(000) = 888$, room temperature, final $R = 0\cdot056$ for 907 observed reflections. An indole ring system is fused with a seven-membered nitrogen-containing ring with two sides fused to a bicyclic isoquinuclidine ring system. The bond lengths and angles are normal. The indole rings are planar. The seven-membered tetrahydro-$1H$-azepine ring and the isoquinuclidine rings have distorted boat conformations. The isoquinuclidine cage is twisted.

Introduction. The indole alkaloid 20-epiheyneanine (Fig. 1) is the major alkaloid (Fonteles, Jerram, Matos & Alquist, 1974) isolated from the crude extract of the root bark of *Peschiera affinis* (Muell Arg.) Miers, a characteristic shrub of the sandy plateaus around Fortaleza, Brazil. The molecular formula was determined by high-resolution mass spectrometry. The structure was elucidated by UV, IR and ^{1}H NMR spectra (Matos, Braz Fº, Gottlieb, Machado & Madruga, 1976) and defined as an epimer of heyneanine (Govindachari, Joshi, Saksema, Sathe & Viswanathan, 1965; Kupchan, Cassady & Telang, 1966). The ^{13}C NMR spectra of these two compounds confirmed the different stereochemistry of the C(20) atom and furnished its relative configuration (Wenkert *et al.*, 1976). An intramolecular hydrogen bond between the hydroxyl group and N(4) was also inferred from the invariance of the IR 3470 cm^{-1} band upon dilution in CHCl$_3$ and by ^{13}C NMR, measured in CDCl$_3$. The crystallographic analysis was undertaken to clarify the stereochemistry of the hydroxyl group and the relative position of H(C20) in the crystal.

Experimental. Transparent single crystal, obtained by slow evaporation of an acetone solution, with dimensions $0\cdot20 \times 0\cdot43 \times 0\cdot48$ mm; all data collected using an Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation; 18 reflections used for a least-squares determination of cell constants in the range $10 < \theta < 19°$; systematic absences ($h = 2n + 1$ for $h00$, $k = 2n + 1$ for $0k0$, $l = 2n + 1$ for $00l$) consistent with space group $P2_12_12_1$; 1664 unique measured reflections, $1 \le \theta \le 22°$, $0 \le$

$h \leq 9$, $0 \leq k \leq 14$, $0 \leq l \leq 20$; two standard reflections (420, 222) recorded every hour, intensity variation $<3\%$; $R_{int} = 0.019$; 907 reflections with $I > 3\sigma(I)$ for $\theta \leq 22°$; θ–2θ scan mode, scan range $(1.0 + 0.35\tan\theta)°$, scan speed varied from 7 to $20°$ min^{-1}; corrections applied for Lp effects but not for absorption or extinction. Structure solved by *MULTAN*80 (Main *et al.*, 1980) using $E \geq 1.4$, and refined by full-matrix least squares with *SHELX*76 (Sheldrick, 1976) by minimization of $\sum w(k \mid F_o \mid - \mid F_c \mid)^2$, where $w = \mid \sigma(F_o) + (0.016 F_o)^2 \mid^{-1}$ for observed reflections and $w = 0$ for unobserved reflections; scattering factors from *International Tables for X-ray Crystallography* (1974). All the H-atom positions were inferred from difference Fourier syntheses and placed at their theoretical positions except those attached to the N(1), O(3) and C(20) atoms. Each H atom was assigned an isotropic temperature factor equal to that of the atom to which it is attached. The final refinement cycle gave $R = 0.056$, $wR = 0.059$; $R(wR) = 0.136$ (0.085) for all reflections. Two reflections, 020 and 002, were not included in the least-squares refinement owing to strong secondary extinction. 271 parameters were refined; max. shift/e.s.d. <0.3; max. difference peak 0.12, min. -0.19 e Å^{-3}. The projection shown in Fig. 1 was calculated with the program *ORTEP* (Johnson, 1965) incorporated in the Enraf–Nonius (1979) *Structure Determination Package*.*

Discussion. The atomic numbering is shown in Fig. 1. Final coordinates and equivalent isotropic temperature factors are given in Table 1. The bond lengths and angles are not significantly different from the expected range. Their large e.s.d.'s may be due to the low value of the data/variable parameter ratio which reflects the poor diffracting quality of the crystal.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, interatomic distances and angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43596 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
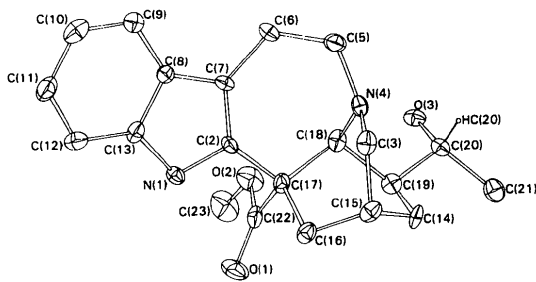

Fig. 1. Molecule with atom numbering and 20% probability ellipsoids (*ORTEP*: Johnson, 1965).

Table 1. *Final positional parameters and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

	x	y	z	B_{eq}*
N(1)	0.1636 (6)	−0.0058 (4)	1.0345 (3)	2.6 (2)
C(2)	0.3199 (8)	−0.0313 (5)	1.0349 (4)	2.6 (2)
C(3)	0.502 (1)	−0.2219 (6)	0.9708 (5)	4.0 (3)
N(4)	0.6006 (8)	−0.1496 (5)	1.0066 (3)	3.3 (2)
C(5)	0.610 (1)	−0.1616 (6)	1.0836 (4)	3.8 (3)
C(6)	0.522 (1)	−0.0865 (7)	1.1262 (5)	4.9 (4)
C(7)	0.3619 (8)	−0.0617 (6)	1.1000 (4)	3.0 (3)
C(8)	0.2242 (9)	−0.0595 (6)	1.1421 (4)	3.1 (3)
C(9)	0.191 (1)	−0.0830 (7)	1.2124 (4)	4.0 (3)
C(10)	0.042 (1)	−0.0719 (7)	1.2358 (5)	5.2 (4)
C(11)	−0.076 (1)	−0.0332 (8)	1.1934 (5)	5.0 (4)
C(12)	−0.048 (1)	−0.0088 (7)	1.1243 (4)	4.0 (3)
C(13)	0.1034 (9)	−0.0232 (6)	1.1000 (4)	3.1 (3)
C(14)	0.606 (1)	−0.1395 (6)	0.8659 (4)	3.7 (3)
C(15)	0.462 (1)	−0.1786 (6)	0.8993 (4)	3.7 (3)
C(16)	0.3461 (9)	−0.0918 (6)	0.9095 (4)	3.7 (3)
C(17)	0.4121 (9)	−0.0208 (6)	0.9678 (4)	2.9 (3)
C(18)	0.5845 (9)	−0.0486 (5)	0.9793 (4)	2.8 (3)
C(19)	0.6669 (9)	−0.0479 (6)	• 0.9066 (4)	3.1 (3)
C(20)	0.8421 (9)	−0.0472 (6)	0.9140 (4)	3.5 (3)
C(21)	0.921 (1)	−0.0476 (9)	0.8418 (5)	5.3 (4)
C(22)	0.393 (1)	0.0863 (6)	0.9431 (5)	3.4 (3)
C(23)	0.475 (1)	0.2502 (6)	0.9606 (6)	6.6 (5)
O(1)	0.2962 (8)	0.1139 (5)	0.9018 (3)	5.8 (3)
O(2)	0.4847 (8)	0.1478 (4)	0.9785 (3)	5.0 (2)
O(3)	0.8939 (6)	0.0409 (4)	0.9509 (3)	3.4 (2)
O(1')	0.288 (1)	0.3055 (7)	1.1352 (6)	10.5 (5)
C(1')	0.340 (2)	0.2409 (9)	1.1722 (7)	6.4 (5)
C(2')	0.249 (2)	0.192 (1)	1.2248 (6)	9.0 (6)
C(3')	0.501 (2)	0.209 (1)	1.1623 (8)	10.8 (8)

* $B_{eq} = \frac{4}{3} \sum_i \sum_j T_{ij} B_{ij}$ and $\sigma(B_{eq}) = T_{ij}\, \sigma(B_{ij})$.

The asymmetric unit consists of an epiheyneanine molecule and a solvent acetone molecule hydrogen bonded to the hydroxyl function; the angle O(3)—H(O3)⋯O(1') ($\frac{1}{2}+x$, $\frac{1}{2}-y$, $2-z$) is 146.0 (8)° and O—H and H⋯O distances are 1.085 and 1.837 (5) Å. The epiheyneanine molecules are bonded together through hydrogen bonds with an N(1)—H(N1)⋯O(3) (1+x, y, z) angle of 143.0 (8)° and N—H and N⋯O distances of 1.057 and 1.980 (5) Å.

The least-squares equation of the plane of the indole rings, referred to the crystallographic axis system, is $-0.2278x - 0.9347y - 0.2728z - 5.6673 = 0$. The atoms in the indole rings are coplanar within twice their e.s.d.'s.

The seven-membered ring has a distorted boat conformation. Two other alkaloids, ibogaine (Arai, Coppola & Jeffrey, 1960) and andrangenine (Riche & Pascard-Billy, 1979) show seven-membered rings with distorted chair and half-chair conformations, respectively.

The puckering coordinates Q, θ, φ, calculated following Cremer & Pople (1975) and Norrestam (1981) for the isoquinuclidine ring system are: [C(15), C(14), C(19), C(18), C(17), C(16)] 0.887 (8) Å, -88.8 (5), 14.3 (5)°; [C(15), C(16), C(17), C(18), N(4), C(3)] 0.836 (8) Å, 87.5 (6), 17.4 (6)°; [C(15), C(3), N(4), C(18), C(19), C(14)] 0.839 (8) Å, -89.0 (6), 165.8 (6)°, respectively; thus the three
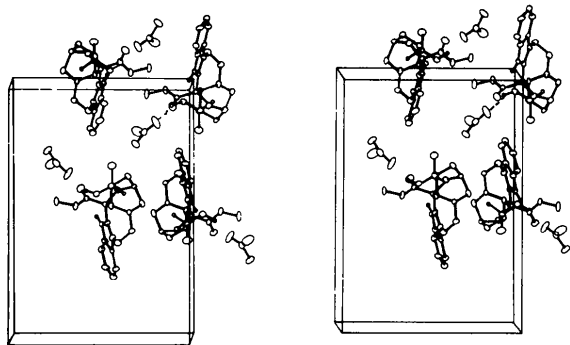
Fig. 2. Stereoscopic view of the molecular packing. The z axis is vertical, the y axis horizontal, and the origin is in the lower right-hand front corner.

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isoquinuclidine rings are in a slightly distorted boat conformation. The top of the isoquinuclidine cage [atoms C(3), C(14) and C(16)] is twisted by 10·5° (mean value) relative to the bottom [atoms N(4), C(19) and C(17)]. The similar alkaloid ibogaine (Arai *et al.*, 1960) shows a less-twisted cage, with mean value 5·5°. As can be seen in the stereoscopic view of the molecular packing shown in Fig. 2, the greater twist of the isoquinuclidine cage in epiheyneanine is possibly due to the hydrogen bond between O(3) and the solvated acetone molecule.

The present X-ray analysis confirmed the relative configuration at C(20) but did not reveal the presence of the intramolecular hydrogen bond between O(3) and N(4) [distance $N \cdots O = 3 \cdot 761$ Å] proposed by Wenkert *et al.* (1976).

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Structure of the 1:1 π-Molecular Complex of Tetracene with 1,2:4,5-Pyromellitic Dianhydride*

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Abstract. $C_{18}H_{12}.C_{10}H_2O_6$, $M_r = 446 \cdot 42$, triclinic, $P\bar{1}$, $a = 6 \cdot 719$ (1), $b = 7 \cdot 342$ (2), $c = 10 \cdot 734$ (2) Å, $\alpha = 82 \cdot 52$ (2), $\beta = 79 \cdot 51$ (2), $\gamma = 104 \cdot 06$ (2)°, $V = 496 \cdot 6$ (2) Å³, $Z = 1$, $D_x = 1 \cdot 49$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å, $\mu(\text{Mo}) = 0 \cdot 99$ cm⁻¹, $F(000) = 230$, $T = 295$ K, $R = 0 \cdot 029$ for 1375 observed reflections [$I > 3\sigma(I)$]. Centrosymmetric planar component molecules are stacked alternately in columns parallel to **a**. Both molecular planes are perpendicular to **a**, the interplanar separation being $3 \cdot 36$ Å.

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* Tetracene = naphthacene; 1,2:4,5-pyromellitic dianhydride = 1*H*,3*H*-benzo[1,2-*c*:4,5-*c'*]difuran-1,3,5,7-tetrone.