

Fig. 2. Packing of the molecules projected on (001). (Distances in Å.)

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Hemanthamine, C₁₇H₁₉NO₄

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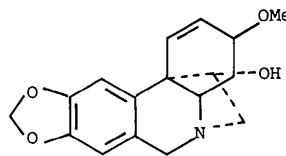
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Abstract. (3*S*,11*S*)-3,4,4a,6-Tetrahydro-11-hydroxy-3-methoxy-5,10b-ethano-8,9-methylenedioxyphenanthridine, $M_r = 301.34$, orthorhombic, $P2_12_12_1$, $a = 11.006$ (2), $b = 14.022$ (2), $c = 9.582$ (2) Å, $V = 1478.8$ (4) Å³, $Z = 4$, $D_x = 1.35$ Mg m⁻³, $\text{Cu } K\alpha$, $\lambda = 1.54178$ Å, $\mu = 0.781$ mm⁻¹, $F(000) = 640$, room temperature, $R = 0.070$ for 1486 unique reflections with $I > 3\sigma(I)$. The cyclohexene ring and the six-membered ring containing the N atom exist as 1,2-diplanar conformations while the five-membered methylenedioxy ring is a flattened envelope. The N-containing five-membered ring exhibits a slightly flattened half-chair conformation. The molecules are held together by hydrogen bonds between the hydroxyl of one molecule and the N of another, $\text{O}\cdots\text{N} = 2.693$ (16) Å.

Introduction. Extracts of *Hippeastrum bicolor* (Amaryllidaceae) upon chromatography yielded several alkaloids including a few milligrams of a poorly crystalline material melting at 478 K with UV maxima at 240 and 296 nm. An X-ray diffraction study of an

opaque crystal revealed the compound to be hemanthamine (1). Hemanthamine is a crinine-type alkaloid which has been isolated from other Amaryllidaceae. The absolute configuration was originally assigned through CD studies (Wildman & Bailey, 1969); however, further CD and ORD work brought the assignment into question (DeAngelis & Wildman, 1969; Kuriyama, Iwata, Moriyama, Kotera, Hameda, Mitsui & Takeda, 1967). A structural investigation of the *p*-bromobenzoate of hemanthamine confirmed the original assignment of configuration (Clardy, Hauser, Dahm, Jacobson & Wildman, 1970). The structure of crinamine, the C(3) epimer of hemanthamine, has also been reported (Roques, Declercq & Germain, 1977).



(1)

Experimental. Crystal dimensions $0.41 \times 0.33 \times 0.26$ mm. Syntex $P2_1$ diffractometer. $\theta:2\theta$ scan, $2\theta_{\max} = 140^\circ$, graphite-monochromated $\text{Cu } K\alpha$. Lattice parameters from least-squares refinement of 15 medium-angle reflections. Angles measured by a center-

ing routine associated with the diffractometer system. Systematic absences $h = 2n + 1$ for $h00$, $k = 2n + 1$ for $0k0$, $l = 2n + 1$ for $00l$. 1575 independent reflections measured ($h \leq 13$, $k \leq 16$, $l \leq 11$), 1486 with $I > 3\sigma(I)$. Monitored reflections showed no significant changes in intensities. Lorentz and polarization corrections, no absorption correction. Direct methods (*MULTAN78*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). All H atoms from difference Fourier map. Full-matrix least-squares anisotropic refinement (H atoms isotropic), $R = 0.070$, $R_w = 0.065$, $S = 0.80$, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$. Largest peak in final difference Fourier $0.3 \text{ e } \text{Å}^{-3}$. Average and maximum Δ/σ 0.05 and 0.03. Atomic scattering factors from XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). No correction for secondary extinction. Locally written programs used for data reduction and initial block-diagonal least-squares refinement. *MULTAN78* used for the direct-methods calculations and XRAY76 for all other computations.*

Table 1. Atomic positional parameters ($\times 10^4$) and U_{eq} values (Å^2)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$

	x	y	z	U_{eq}
C(1)	6306 (5)	1673 (5)	2958 (7)	35
C(2)	6272 (6)	803 (5)	3510 (7)	42
C(3)	7302 (7)	327 (5)	4253 (7)	43
C(4)	8404 (6)	985 (5)	4521 (7)	41
C(4a)	8602 (6)	1710 (5)	3336 (7)	35
N(5)	9503 (4)	2462 (4)	3725 (5)	35
C(6)	9893 (5)	2905 (4)	2433 (7)	35
C(6a)	8907 (5)	3163 (4)	1421 (6)	31
C(7)	9194 (6)	3709 (5)	275 (7)	36
C(8)	8293 (7)	3988 (5)	-578 (7)	41
C(9)	7087 (7)	3782 (5)	-279 (7)	40
C(10)	6741 (6)	3229 (5)	874 (7)	38
C(10a)	7702 (6)	2896 (4)	1722 (6)	31
C(10b)	7418 (5)	2298 (4)	3047 (6)	28
C(11)	7401 (6)	3010 (4)	4302 (7)	31
C(12)	8795 (6)	3158 (5)	4588 (7)	38
O(13)	8315 (5)	4548 (4)	-1759 (5)	54
C(14)	7090 (8)	4502 (5)	-2336 (7)	61
O(15)	6289 (4)	4196 (4)	-1233 (5)	56
O(16)	7738 (4)	-478 (3)	3460 (5)	52
C(17)	6919 (7)	-1261 (5)	3532 (8)	62
O(18)	6856 (4)	2667 (3)	5528 (4)	38

Table 2. Interatomic distances (Å) and torsion angles ($^\circ$)

C(1)–C(2)	1.330 (9)	C(7)–C(8)	1.34 (1)
C(1)–C(10b)	1.508 (8)	C(8)–C(9)	1.39 (1)
C(2)–C(3)	1.50 (1)	C(8)–O(13)	1.377 (8)
C(3)–C(4)	1.55 (1)	C(9)–C(10)	1.403 (9)
C(3)–O(16)	1.443 (8)	C(9)–O(15)	1.394 (9)
C(4)–C(4a)	1.54 (1)	C(10)–C(10a)	1.413 (9)
C(4a)–N(5)	1.494 (8)	C(10a)–C(10b)	1.553 (8)
C(4a)–C(10b)	1.567 (9)	C(10b)–C(11)	1.564 (9)
N(5)–C(6)	1.450 (8)	C(11)–C(12)	1.572 (9)
N(5)–C(12)	1.498 (9)	C(11)–O(18)	1.404 (8)
C(6)–C(6a)	1.500 (9)	O(13)–C(14)	1.46 (1)
C(6a)–C(7)	1.376 (9)	C(14)–O(15)	1.442 (9)
C(6a)–C(10a)	1.407 (8)	O(16)–C(17)	1.422 (9)

C(10b)–C(1)–C(2)–C(3)	-1 (1)
C(1)–C(2)–C(3)–C(4)	8 (1)
C(2)–C(3)–C(4)–C(4a)	-34.7 (8)
C(3)–C(4)–C(4a)–C(10b)	54.1 (7)
C(4)–C(4a)–C(10b)–C(1)	-46.5 (7)
C(4a)–C(10b)–C(1)–C(2)	20.7 (9)
C(4a)–C(10b)–C(11)–C(12)	31.4 (6)
C(10b)–C(11)–C(12)–N(5)	-8.7 (6)
C(11)–C(12)–N(5)–C(4a)	-18.9 (6)
C(12)–N(5)–C(4a)–C(10b)	38.9 (6)
N(5)–C(4a)–C(10b)–C(11)	-44.3 (6)
C(4a)–N(5)–C(6)–C(6a)	46.0 (7)
N(5)–C(6)–C(6a)–C(10a)	-5.2 (8)
C(6)–C(6a)–C(10a)–C(10b)	-3.1 (8)
C(6a)–C(10a)–C(10b)–C(4a)	-28.0 (7)
C(10a)–C(10b)–C(4a)–N(5)	66.8 (5)
C(10b)–C(4a)–N(5)–C(6)	-77.9 (6)
C(9)–C(8)–O(13)–C(14)	-12.0 (7)
C(8)–O(13)–C(14)–O(15)	19.9 (7)
O(13)–C(14)–O(15)–C(9)	-19.3 (6)
C(14)–O(15)–C(9)–C(8)	12.4 (7)
O(15)–C(9)–C(8)–O(13)	-0.3 (7)

Discussion. Table 1 lists atomic positional parameters and U_{eq} values while Table 2 gives interatomic distances and selected torsion angles.

Fig. 1 is an *ORTEP* drawing (Johnson, 1971) of hemanthamine. The phenyl ring and C(10b) and O(13) form a planar system, but C(6) and O(15) are 0.07 and 0.09 Å out of the plane. The five-membered methylenedioxy ring is folded by $20.2 (3)^\circ$ along the O(13)··O(15) line. The six-membered cyclohexene ring and the six-membered heterocyclic ring are in slightly distorted 1,2-diplanar conformations (Bucourt, 1974). The N-containing five-membered ring displays a distorted half-chair conformation. The molecule can be described

* Lists of structure factors, anisotropic thermal parameters H-atom coordinates, bond distances involving H atoms, and valence angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38891 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

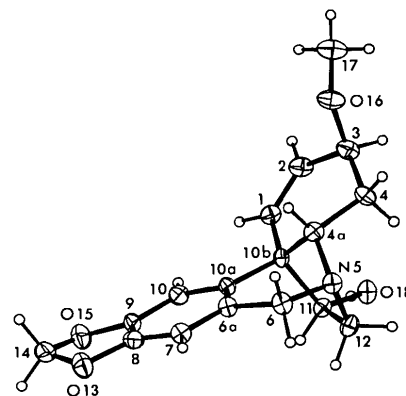


Fig. 1. *ORTEP* drawing of hemanthamine (thermal ellipsoids drawn at the 50% probability level).

roughly as composed of two perpendicular halves. The function-group O atoms are readily accessible to reactant molecules or receptor sites.

There is an intermolecular hydrogen bond formed between the basic N of one molecule and the O(18) hydroxyl of another at $(0.25 + x, 0.25 - y, 0.5 - z)$: O(18)—H(18) = 1.01 (4), H(18)···N(5) = 1.84 (4), O(18)···N(5) = 2.693 (6) Å and O(18)—H(18)···N(5) = 139.4 (5)°.

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Structure of 3 α ,7 α -Bis(2-hydroxy-2-propyl)bicyclo[3.3.1]nonane,* C₁₅H₂₈O₂

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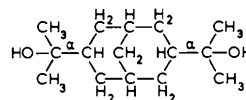
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Abstract. $M_r = 240.39$, orthorhombic, $P2_12_12_1$, $a = 12.700$ (3), $b = 10.474$ (3), $c = 10.771$ (2) Å, $V = 1432.7$ Å³, $Z = 4$, $D_x = 1.12$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.077$ mm⁻¹, $F(000) = 536$, $T = 293$ K. Final $R = 0.043$ for 1559 observed data. The molecule exhibits the double twist-boat conformation. The hydroxypropyl groups have different orientations with respect to the ring system. The molecules are packed by hydrogen bonds of 2.811 and 2.769 Å.

Introduction. For bicyclo[3.3.1]nonane derivatives three groups of conformations must be envisaged: the double-chair, the chair-boats and the double twist-boats. The conformational preference strongly depends on the substituents present on the bicyclic skeleton (Peters, Baas, van de Graaf, van der Toorn & van Bekkum, 1978). Several bicyclo[3.3.1]nonane derivatives occurring in the the double-chair and in the chair-boat conformation have been studied by X-ray

diffraction (Bhattacharjee & Chacko, 1980; van Koningsveld & Peters, 1981; van Koningsveld, 1981), but up till now no such studies have been reported on bicyclo[3.3.1]nonane derivatives existing in the double twist-boat conformation. From ¹H and ¹³C NMR data it was concluded that 3 α ,7 α -bis(2-hydroxy-2-propyl)bicyclo[3.3.1]nonane (HYNONA) exists, at least in solution, predominantly in the double twist-boat conformation (Peters, van der Toorn & van Bekkum, 1975). The structure of HYNONA as determined by X-ray diffraction is reported here.



Experimental. HYNONA (Peters *et al.*, 1975) recrystallized from dimethyl ether at 278 K. A small fragment (approximate size 0.2 × 0.3 × 0.3 mm) mounted on an Enraf–Nonius CAD-4 diffractometer.

* 2,2'-(Bicyclo[3.3.1]nonan-3 α ,7 α -ylene)di-2-propanol.