Crystal Structures and Absolute Stereochemistry of Tecomanine Methoperchlorate and 'Alkaloid C' Methiodide: Two Monoterpene Alkaloids from *Tecoma stans*

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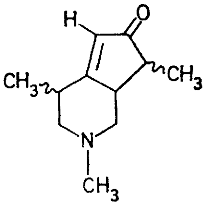
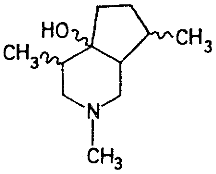
Crystals of tecomanine methoperchlorate are monoclinic, $a = 8.032(1)$, $b = 10.019(1)$, $c = 8.900(2)$ Å, $\beta = 91.44(1)$°, $Z = 2$, space group $P2_1$; crystals of 'alkaloid C' methiodide are orthorhombic, $a = 8.874(1)$, $b = 9.361(1)$, $c = 16.861(2)$, $Z = 4$, space group $P2_12_12_1$. Both structures were determined from Patterson and Fourier syntheses, and refined by full-matrix and block-diagonal least-squares to R 0.047 (1305 observed reflexions, tecomanine methoperchlorate) and 0.049 (1412 observed reflexions, 'alkaloid C' methiodide). The two structures have identical absolute stereochemistry at their common asymmetric centres, and in each case the six-membered ring is in the chair, and the five-membered ring in the envelope conformation.

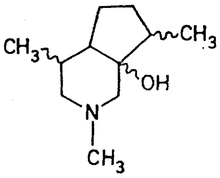
A NUMBER of alkaloids have been isolated from various samples of *Tecoma stans*[1,2] including the principal alkaloid tecomanine and an oxygenated skytanthine, 'alkaloid C'. Structure (I) was suggested for tecomanine, and for 'alkaloid C' structure (II) was considered most likely, although (III) could not be ruled out.[2] No assignment of stereochemistry was possible. Accordingly, crystal structure analyses of suitable derivatives, tecomanine methoperchlorate and 'alkaloid C' methiodide were undertaken to establish the structures, stereochemistry, and absolute configuration of these monoterpene alkaloids.[3]



(I)



(II)



(III)

EXPERIMENTAL

Both compounds crystallized as colourless needles: tecomanine methoperchlorate was elongated along b with {101} well developed and smaller {010}; and 'alkaloid C' methiodide was elongated along a with {011} well developed and smaller {100}. In each case unit-cell and space-group data were determined from various rotation, Weissenberg, and precession photographs; accurate cell parameters were obtained by a least-squares procedure applied to 12 general reflexions measured on a Hilger and Watts diffractometer.

Crystal Data.—(*a*) *Tecomanine methoperchlorate*. $C_{12}H_{20}ClNO_5$, $M = 293.8$, Monoclinic, $a = 8.032(1)$, $b = 10.019(1)$, $c = 8.900(2)$ Å, $\beta = 91.44(1)°$, $U = 716$ Å^3, $D_c = 1.36$ g cm^{-3}, $Z = 2$, $F(000) = 312$. $\lambda(\text{Cu-}K_\alpha) = 1.5418$ Å, $\mu(\text{Cu-}K_\alpha) = 25.3$ cm^{-1}. Systematic absences: $0k0$ when k is odd. Space group $P2_1$ (C_2^2) or $P2_1/m$ (C_{2h}^2); $P2_1$ from structure analysis.

(*b*) '*Alkaloid C*' *methiodide*. $C_{12}H_{24}INO$, $M = 325.2$, Orthorhombic, $a = 8.874(1)$, $b = 9.361(1)$, $c = 16.861(2)$, $U = 1\,401$ Å^3, $D_c = 1.54$ g cm^{-3}, $Z = 4$, $F(000) = 656$. $\mu(\text{Cu-}K_\alpha) = 181.2$ cm^{-1}. Systematic absences: $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd. Space group $P2_12_12_1$ (D_2^4).

The procedure followed in the data collection was the same for each compound. The intensities of all reflexions with 2θ (Cu-K_α) $< 140°$ (minimum interplanar spacing 0.82 Å) were measured on a PDP8 I controlled Hilger and Watts four-circle diffractometer with a scintillation counter, approximately monochromatic Cu-K_α radiation (Ni filter and pulse-height analyser), and a θ—ω step scan with 0.01° steps and a counting time of 1 s per step. A scan width of 0.8° in θ was used. Background counts for 20 s were made at the beginning and end of each scan.

Lorentz and polarization factors were applied and the structure amplitudes derived in the usual manner. Reflexions having $I < 3\sigma(I)$ were considered unobserved, where $\sigma(I)$ is defined by $\sigma^2(I) = S + 4(B_1 + B_2) + (0.05S)^2$, S is the scan count, and B_1 and B_2 the background counts. These reflexions, which were assigned structure amplitudes equal to the measured values, were excluded from the refinement. For tecomanine methoperchlorate 1 305 of the 1 624 independent reflexions (80.4%), and for 'alkaloid C' methiodide 1 412 of the 1 543 independent reflexions were classified as observed.

Structure Analyses.—(*a*) *Tecomanine methoperchlorate*.

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[1] G. Jones, H. M. Fales, and W. C. Wildman, *Tetrahedron Letters*, 1963, 397.

[2] G. Jones and E. M. Dickinson, *Tetrahedron*, 1969, **25**, 1523.

[3] G. Jones, G. Ferguson, and W. Marsh, *Chem. Comm.*, 1971, 994.

Although two space groups ($P2_1$ and $P2_1/m$) are possible from a consideration of the systematic absences alone, the fact that the compound was known to be optically active eliminated space group $P2_1/m$. The co-ordinates of the chlorine and oxygen atoms of the perchlorate ion were deduced from a three-dimensional Patterson function. The first electron-density map phased by the perchlorate ion showed almost complete pseudomirror symmetry; nevertheless a careful examination of the map allowed the atoms of the five-membered ring to be located unambiguously. When these additional atoms were included in a second round of structure factor and electron-density calculations, the pseudomirror symmetry was completely destroyed and all remaining non-hydrogen atoms were located.

The positional and isotropic thermal parameters were refined by full-matrix least-squares methods, with the scattering factors of ref. 4, the function minimized being $\Sigma w(F_o - F_c)^2$, with w taken as the reciprocal of the variance in F as determined from the counting statistics. Convergence was reached at R 0.134 for the observed reflexions. Subsequent anisotropic refinement was by block-diagonal least-squares methods, convergence being reached at R 0.075 after six cycles. At this stage a three-dimensional difference synthesis clearly revealed all 20 hydrogen atom positions. The hydrogen atoms were included in the refinement with the scattering curve of ref. 5, and isotropic thermal parameters. Refinement was continued until convergence at R 0.047 for the 1 305 observed reflexions. The maximum ratio of shift-to-σ in the final cycle was 0.5. Final positional parameters are given in Tables 1 and 2, bond lengths and valency angles in Table 3, and intermolecular contacts <4.0 Å in Table 4.

TABLE 1

Final positional parameters for non-hydrogen atoms, with standard deviations in parentheses, for tecomanine methoperchlorate

Atom	*x*	*y*	*z*
Cl	0.1866(1)	1/4	0.1784(1)
O(1)	0.2235(6)	0.2196(11)	0.0271(5)
O(2)	0.3325(5)	0.2839(6)	0.2620(7)
O(3)	0.1166(5)	0.1331(5)	0.2431(5)
O(4)	0.0675(6)	0.3536(5)	0.1800(5)
O(5)	0.5754(4)	0.0136(4)	0.3140(3)
C(1)	0.6124(5)	0.0677(5)	0.4329(3)
C(2)	0.4969(4)	0.0896(4)	0.5637(3)
C(3)	0.6184(4)	0.1147(4)	0.6969(3)
C(4)	0.7805(4)	0.1481(4)	0.6234(4)
C(5)	0.7774(5)	0.1216(5)	0.4760(4)
C(6)	0.9211(4)	0.2008(4)	0.7200(4)
C(7)	0.8538(4)	0.3075(4)	0.8275(4)
C(8)	0.5652(4)	0.2251(4)	0.7995(3)
N(1)	0.7016(3)	0.2653(4)	0.9105(3)
Me(1)	0.3695(5)	−0.0207(5)	0.5803(5)
Me(2)	0.0607(5)	0.2691(7)	0.6295(5)
Me(3)	0.6423(6)	0.3850(6)	0.9967(5)
Me(4)	0.7408(5)	0.1535(5)	0.0194(4)

As a final step in the analysis the absolute configuration of the molecule was determined by the anomalous dispersion method.[6] Structure factors were calculated for all the hkl and $\bar{h}\bar{k}\bar{l}$ reflexions including the real and imaginary parts of the chlorine scattering curve.[4] Thirty pairs of reflexions with large differences between $F_c(hkl)$ and $F_c(\bar{h}\bar{k}\bar{l})$ were chosen and the intensities measured with Cu-K_α radiation. The results unambiguously indicated that the co-ordinates in Tables 1 and 2, when referred to a

TABLE 2

Final positional and isotropic thermal parameters for hydrogen atoms, with standard deviations in parentheses

Atom	Bonded to	*x*	*y*	*z*	$B/\text{Å}^2$
H(1)	C(2)	0.438(5)	0.171(7)	0.542(5)	6.7(14)
H(2)	C(3)	0.630(5)	0.027(6)	0.757(4)	4.3(10)
H(3)	C(5)	0.871(5)	0.137(6)	0.404(5)	5.5(11)
H(4)	C(6)	0.989(5)	0.123(7)	0.791(5)	6.9(14)
H(5)	C(7)	0.794(6)	0.392(7)	0.758(5)	6.2(13)
H(6)	C(7)	0.933(6)	0.340(7)	0.902(5)	6.1(11)
H(7)	C(8)	0.528(5)	0.309(7)	0.741(5)	6.6(13)
H(8)	C(8)	0.464(7)	0.199(8)	0.863(6)	7.2(13)
H(9)	Me(1)	0.293(7)	−0.038(8)	0.490(6)	8.9(16)
H(10)	Me(1)	0.294(5)	−0.002(7)	0.660(5)	6.4(12)
H(11)	Me(1)	0.407(6)	−0.090(7)	0.620(5)	7.1(13)
H(12)	Me(2)	0.090(6)	0.205(7)	0.569(5)	6.7(13)
H(13)	Me(2)	0.084(7)	0.256(9)	0.694(5)	8.6(15)
H(14)	Me(2)	−0.009(6)	0.363(7)	0.548(4)	6.0(12)
H(15)	Me(3)	0.601(6)	0.462(8)	0.908(6)	8.7(15)
H(16)	Me(3)	0.710(6)	0.416(7)	0.059(5)	7.0(13)
H(17)	Me(3)	0.547(6)	0.345(7)	0.057(5)	6.1(12)
H(18)	Me(4)	0.783(5)	0.075(6)	0.956(4)	4.5(9)
H(19)	Me(4)	0.592(6)	0.149(7)	0.082(6)	7.7(14)
H(20)	Me(4)	0.844(6)	0.175(8)	0.092(5)	7.3(14)

TABLE 3

Bond distances (Å), valency and torsion angles (deg.) for tecomanine methoperchlorate, with estimated standard deviations in parentheses

(*a*) Bond distances			
Cl–O(1)	1.419(5)	C(4)–C(5)	1.338(5)
Cl–O(2)	1.414(5)	C(4)–C(6)	1.498(5)
Cl–O(3)	1.426(5)	C(6)–C(7)	1.541(6)
Cl–O(4)	1.412(5)		
		N(1)–C(7)	1.504(5)
C(1)–O(5)	1.220(5)	N(1)–C(8)	1.511(4)
C(1)–C(2)	1.522(5)	N(1)–Me(3)	1.507(6)
C(1)–C(5)	1.472(6)	N(1)–Me(4)	1.509(6)
C(2)–C(3)	1.538(4)		
C(3)–C(4)	1.509(5)	C(2)–Me(1)	1.516(6)
C(3)–C(8)	1.503(5)	C(6)–Me(2)	1.555(6)
(*b*) Valency angles			
O(1)–Cl–O(2)	111.1(3)	C(3)–C(4)–C(5)	112.7(3)
O(1)–Cl–O(3)	107.5(5)	C(6)–C(4)–C(5)	128.9(3)
O(1)–Cl–O(4)	108.9(4)	C(4)–C(5)–C(1)	108.8(3)
O(2)–Cl–O(3)	108.3(3)	C(4)–C(6)–C(7)	109.2(3)
O(2)–Cl–O(4)	111.8(3)	C(4)–C(6)–Me(2)	113.6(3)
O(3)–Cl–O(4)	109.0(3)	C(7)–C(6)–Me(2)	106.6(4)
		C(6)–C(7)–N(1)	114.3(3)
C(2)–C(1)–C(5)	108.0(3)	C(3)–C(8)–N(1)	112.4(3)
C(2)–C(1)–O(5)	126.0(4)		
C(5)–C(1)–O(5)	126.0(4)	C(7)–N(1)–C(8)	109.8(2)
C(1)–C(2)–C(3)	103.1(3)	C(7)–N(1)–Me(3)	107.3(3)
C(1)–C(2)–Me(1)	113.3(4)	C(7)–N(1)–Me(4)	111.4(3)
C(3)–C(2)–Me(1)	117.5(3)	C(8)–N(1)–Me(3)	108.2(3)
C(2)–C(3)–C(4)	103.9(3)	C(8)–N(1)–Me(4)	110.9(3)
C(2)–C(3)–C(8)	113.9(3)	Me(3)–N(1)–Me(4)	109.1(3)
C(4)–C(3)–C(8)	111.2(3)		
C(3)–C(4)–C(6)	118.4(3)		
(*c*) Torsion angles			
C(5)–C(1)–C(2)–C(3)	−18.1(4)	C(3)–C(4)–C(6)–C(7)	−44.6(4)
C(1)–C(2)–C(3)–C(4)	17.4(3)	C(4)–C(6)–C(7)–N(1)	49.1(4)
C(2)–C(3)–C(4)–C(5)	−11.7(4)	C(6)–C(7)–N(1)–C(8)	−56.8(4)
C(3)–C(4)–C(5)–C(1)	0.2(4)	C(3)–C(8)–N(1)–C(7)	57.5(4)
C(2)–C(1)–C(5)–C(4)	11.7(4)	C(4)–C(3)–C(8)–N(1)	−51.8(4)
C(8)–C(3)–C(4)–C(6)	47.1(4)		

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[4] 'International Tables for *X*-Ray Crystallography,' vol. III, 1962, Kynoch Press, Birmingham.

[5] R. F. Stewart, F. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[6] J. M. Bijvoet, *Proc. k. ned. Akad. Wetenschap.*, 1949, **52**, 313.

right-handed set of axes, represent the true absolute configuration.

(*b*) *' Alkaloid C ' methiodide*. The co-ordinates of the iodide ion were determined from a three-dimensional Patterson function and a three-dimensional electron-density map phased by the iodide ion alone gave the positions of all the remaining non-hydrogen atoms. Atomic positions corresponding to the same absolute configuration as the tecomanine methoperchlorate were chosen as a working co-ordinate system.

TABLE 4

Intermolecular contacts <4.0 Å for tecomanine methoperchlorate

Cl ··· Me(4^{I})	3.938	O(3) ··· Me(3^{III})	3.833
O(1) ··· C(8^{II})	3.453	O(4) ··· C(7^{IV})	3.568
O(1) ··· Me(3^{III})	3.530	O(4) ··· Me(4^{I})	3.572
O(1) ··· C(7^{IV})	3.533	O(4) ··· C(6^{V})	3.592
O(1) ··· C(6^{IV})	3.615	O(4) ··· C(4^{V})	3.627
O(1) ··· Me(2^{II})	3.774	O(4) ··· Me(3^{IV})	3.761
O(1) ··· Me(4^{I})	3.932	O(4) ··· C(3^{V})	3.778
O(2) ··· C(3^{V})	3.357	O(4) ··· Me(4^{VI})	3.832
O(2) ··· Me(1^{V})	3.371	O(4) ··· N(1^{IV})	3.849
O(2) ··· Me(3^{II})	3.617	O(5) ··· C(8^{III})	3.255
O(2) ··· C(2^{V})	3.682	O(5) ··· Me(3^{III})	3.481
O(2) ··· C(4^{V})	3.902	O(5) ··· Me(2^{III})	3.837
O(2) ··· C(1^{V})	3.949	O(5) ··· N(1^{III})	3.861
O(3) ··· C(7^{III})	3.332	C(4) ··· Me(1^{V})	3.954
O(3) ··· C(5^{I})	3.467	C(5) ··· Me(1^{V})	3.802
O(3) ··· Me(4^{I})	3.580	Me(1) ··· Me(3^{III})	3.885

Roman numerals as superscripts refer to the equivalent positions:

I $-1 + x, y, z$
II $x, y, z - 1$
III $1 - x, -\frac{1}{2} + y, 1 - z$
IV $-1 + x, y, -1 + z$
V $1 - x, \frac{1}{2} + y, 1 - z$
VI $1 - x, \frac{1}{2} + y, -z$

The refinement was carried out as before, with the same weighting scheme. Initial isotropic refinement converged at R 0.095, and subsequent anisotropic refinement at R 0.080. At this point the large value of the absorption coefficient suggested the data be corrected for absorption. The procedure followed was that of Coppens [7] modified for the Hilger and Watts diffractometer. Two further anisotropic cycles on the corrected data reduced R to 0.054. At this stage a difference synthesis revealed the positions of 23 of the 24 hydrogens, the hydroxy-hydrogen being the only one not located. One further anisotropic cycle, with the hydrogens included in the structure-factor calculation with an isotropic B of 5.0 Å^2 but not in the refinement, gave a final value of R 0.049. The maximum ratio of shift-to-σ in the final cycle was 0.5.

TABLE 5

Final positional parameters, with standard deviations in parentheses, for ' alkaloid C ' methiodide

Atom	x	y	z
I	0.2324(1)	0.0965(1)	0.1299(1)
O(1)	0.4438(7)	0.4286(7)	0.2867(3)
C(1)	0.1776(15)	0.3171(11)	0.3667(6)
C(2)	0.2593(11)	0.3961(9)	0.4348(5)
C(3)	0.3138(10)	0.5384(8)	0.3978(4)
C(4)	0.3123(10)	0.5118(8)	0.3078(4)
C(5)	0.1757(11)	0.4157(9)	0.2952(5)
C(6)	0.3171(10)	0.6499(9)	0.2584(4)
C(7)	0.2044(10)	0.7595(9)	0.2893(4)
C(8)	0.2057(9)	0.6561(8)	0.4230(4)
N(1)	0.2261(8)	0.7931(6)	0.3763(4)
Me(1)	0.3867(13)	0.3054(12)	0.4712(6)
Me(2)	0.2863(13)	0.6235(12)	0.1700(5)
Me(3)	0.3765(11)	0.8597(9)	0.3922(5)
Me(4)	0.1054(12)	0.8967(10)	0.4016(6)

TABLE 6

Bond distances (Å), valency and torsion angles (deg), for ' alkaloid C ' methiodide, with estimated standard deviations in parentheses

(*a*) Bond distances			
C(2)–Me(1)	1.540(16)	C(1)–C(2)	1.547(15)
C(6)–Me(2)	1.535(12)	C(1)–C(5)	1.519(15)
		C(2)–C(3)	1.548(12)
N(1)–C(7)	1.512(10)	C(3)–C(4)	1.539(11)
N(1)–C(8)	1.516(10)	C(3)–C(8)	1.522(12)
N(1)–Me(3)	1.497(13)	C(4)–C(5)	1.525(11)
N(1)–Me(4)	1.506(13)	C(4)–C(6)	1.539(12)
		C(6)–C(7)	1.524(13)
C(4)–O(1)	1.447(11)		
(*b*) Valency angles			
C(2)–C(1)–C(5)	107.8(9)	C(1)–C(5)–C(4)	103.8(8)
C(1)–C(2)–C(3)	105.0(7)	C(4)–C(6)–C(7)	111.2(7)
C(1)–C(2)–Me(1)	112.1(9)	C(4)–C(6)–Me(2)	112.7(7)
C(3)–C(2)–Me(1)	113.9(9)	C(7)–C(6)–Me(2)	108.9(8)
C(2)–C(3)–C(4)	104.9(7)	C(6)–C(7)–N(1)	112.9(7)
C(2)–C(3)–C(8)	108.3(7)	C(3)–C(8)–N(1)	113.1(7)
C(4)–C(3)–C(8)	108.3(7)		
C(3)–C(4)–C(5)	103.9(7)	C(7)–N(1)–C(8)	108.2(6)
C(3)–C(4)–C(6)	113.5(7)	C(7)–N(1)–Me(3)	111.9(7)
C(5)–C(4)–C(6)	116.2(7)	C(7)–N(1)–Me(4)	108.6(7)
C(3)–C(4)–O(1)	108.8(7)	C(8)–N(1)–Me(3)	111.5(7)
C(5)–C(4)–O(1)	106.8(7)	C(8)–N(1)–Me(4)	108.2(7)
C(6)–C(4)–O(1)	107.3(7)	Me(3)–N(1)–Me(4)	108.4(7)
(*c*) Torsion angles			
C(5)–C(1)–C(2)–C(3)	−4.0(9)	C(3)–C(4)–C(6)–C(7)	−46.9(9)
C(1)–C(2)–C(3)–C(4)	−19.5(9)	C(4)–C(6)–C(7)–N(1)	55.4(9)
C(2)–C(3)–C(4)–C(5)	35.8(8)	C(6)–C(7)–N(1)–C(8)	−60.2(8)
C(3)–C(4)–C(5)–C(1)	−38.0(8)	C(3)–C(8)–N(1)–C(7)	57.9(8)
C(2)–C(1)–C(5)–C(4)	26.0(9)	C(4)–C(3)–C(8)–N(1)	−51.6(8)
C(8)–C(3)–C(4)–C(6)	45.4(9)		

TABLE 7

Intermolecular contacts <4.0 Å for 'alkaloid C ' methiodide

C(2) ··· C(7^{I})	3.942	C(8) ··· O(1^{IV})	3.447
C(3) ··· C(10^{II})	3.931	C(9) ··· C(10^{V})	3.746
C(4) ··· C(9^{III})	3.989	C(9) ··· O(1^{IV})	3.799
C(7) ··· O(1^{IV})	3.728	I ··· O(1^{VI})	3.564

Roman numerals as superscripts refer to the equivalent positions:

I $-x, -\frac{1}{2} + y, \frac{1}{2} - z$
II $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$
III $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$
IV $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
V $\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$
VI $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$

Final positional parameters are listed in Table 5, bond lengths and valency angles in Table 6, and intermolecular contacts <4.0 Å in Table 7.

Finally the absolute configuration was determined as outlined earlier using the iodide as the anomalous scatterer. The results clearly indicate that the co-ordinates in Table 5, when referred to a right-handed set of axes, represent the true absolute configuration.

General views [8] of the two molecules are shown in Figures 1 and 2. The molecular packing arrangement for tecomanine methoperchlorate viewed along b is shown in

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[7] P. Coppens, ' Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970.

[8] C. K. Johnson, ORTEP: A FORTRAN Thermal Ellipsoid Plot Program, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Figure 3 and that for ' alkaloid C ' methiodide viewed along *a* in Figure 4.

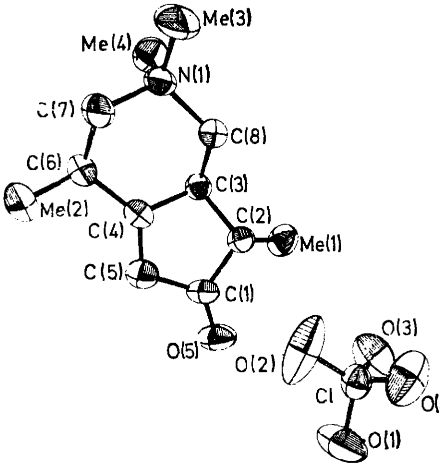

FIGURE 1 View of tecomanine methoperchlorate; thermal ellipsoids are drawn at the 50% level

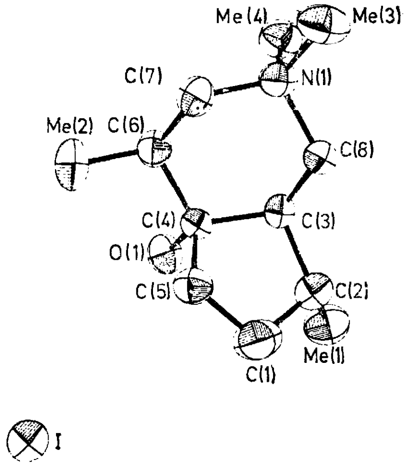

FIGURE 2 View of ' alkaloid C ' methiodide; thermal ellipsoids are drawn at the 50% level

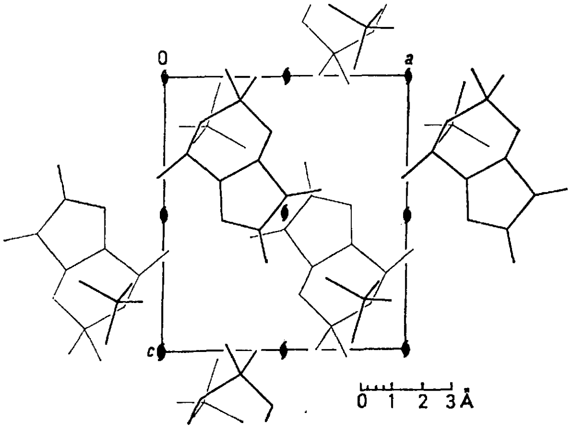

FIGURE 3 Crystal structure of tecomanine methoperchlorate viewed along *a*

Measured and calculated structure factors, anisotropic thermal parameters, details of some least-squares planes, and Bijvoet pairs used in the anomalous-dispersion calculation for both structures, are listed in Supplementary Publication No. SUP 21390 (8 pp., 1 microfiche).*

DISCUSSION

The results of the *X*-ray analyses establish that tecomanine methoperchlorate and ' alkaloid C ' methiodide have the structure and absolute setereochemistry shown in Figures 1 and 2 respectively, and identical stereochemistry at their common asymmetric centres.

The conformations of the five- and six-membered rings in the tecomanine cation are established by the torsion angles (Table 3) and deviations from least-squares planes. The six-membered ring adopts a chair conformation which is slightly flattened at the junction to the cyclopentene ring. C(4) and N(1) are displaced from the C(6)—(8), C(3), plane by 0.52 and −0.67 Å respectively. The five-membered ring has the envelope conformation with C(2) at the ' flap ', 0.30 Å above the plane containing C(1) and C(3)—C(5). The valency angles (Table 3) reflect the strains imposed by the unsaturated five-membered ring. The endocyclic angle at C(1) is reduced to 108° from the nominal value of 120° for an sp^2 hybridized carbon atom whilst the exocyclic angles are increased to 126°. A similar effect is found at C(5) where the internal angle is reduced to 108.8° and at C(4) where the C(3)–C(4)–C(5) angle is 112.7° while C(5)–C(4)–C(6) has increased to 128.9°. The bond distances in the tecomanine cation do not differ significantly from the literature values [9] for similar bond types except for C(3)–C(8) [1.503(5) Å] and C(2)–Me(1) [1.516(6) Å] which are somewhat shorter than expected. There is no apparent reason why this should be so. The bond lengths and angles in the perchlorate anion are normal, mean Cl–O 1.418(5) Å, mean O–Cl–O 109.4(4)°.

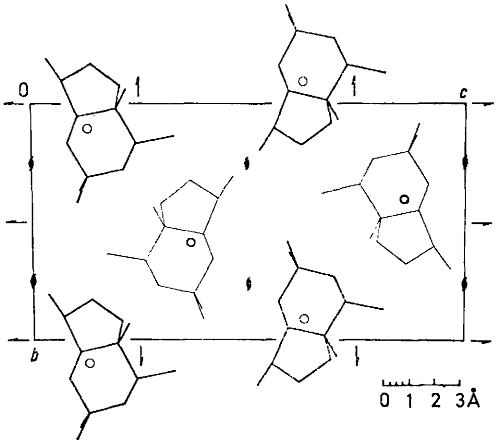

FIGURE 4 Crystal structure of ' alkaloid C ' methiodide viewed along *a*

The shorter interionic distances, omitting the hydrogen atoms, involve contacts between carbon and oxygen

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* For details see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

[9] *Chem. Soc. Special Publ.*, No. 18, 1965.

atoms and correspond to van der Waals interactions (Table 4).

The stereochemistry of the ' alkaloid C ' cation is similar *to that* found for the tecomanine cation, differences being attributable to the removal of the C(4)-C(5) unsaturation. The torsion angles (Table 6) and deviations from least-squares planes establish the conformation of the six-membered ring as a chair [C(4) and N(1) displaced from the C(6)—(8) and C(3) plane by 0.56 and −0.70 Å respectively] which is also slightly flattened at the junction to the *cis*-fused five-membered ring. The conformation of the five-membered ring here is distorted away from a C(4) envelope towards a half-chair with C(4) 0.50 above and C(5) 0.10 Å below the C(1)—(3) plane. There are no significant deviations of the bond distances or valency angles from accepted values.[9] The shorter interionic distances involve contacts between carbon and oxygen atoms and correspond to van der Waals interactions (Table 7).

We thank Dr. G. Jones for the crystals and the National Research Council of Canada for financial support. The computer programs used were supplied by N.R.C., the University of British Columbia, and the University of Canterbury, New Zealand.

[4/2085 *Received, 8th October*, 1974]