

Fig. 3. Stereoscopic drawing of the unit cell viewed down the *c* axis.

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Diacetyltlyphorinidine Methiodide*

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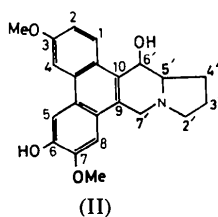
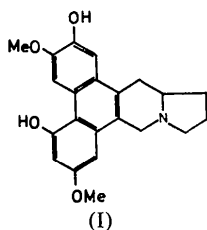
Abstract. $C_{27}H_{30}NO_6I$, $M = 591.4$, monoclinic, $C2$, $a = 26.89$ (1), $b = 12.35$ (1), $c = 16.62$ (1) Å, $\beta = 109$ (1)°, $Z = 8$, $D_m = 1.52$ (1), $D_x = 1.51$ (1) g cm⁻³, $F(000) = 2400$, $\mu(Cu K\alpha) = 102.3$ cm⁻¹. Tylophorinidine, a potential anti-cancer phenolic alkaloid isolated from the plant *Tylophora asthmatica*, is shown to be 6,6'-di-

hydroxy-3,7-dimethoxyphenanthro[9,10:6',7']indolizidine. Its absolute configuration was also determined.

Introduction. Tylophorinidine was first isolated by Mulchandani, Iyer & Badheka (1971) from *Tylophora asthmatica*, a plant used indigenously in the treatment of allergic rhinitis and bronchial asthma. Structure (I) was assigned to it by these authors. However, this could not be considered unambiguous (Wadhawan,

* A preliminary report of this study has already been published (Wadhawan, Sikka & Mulchandani, 1973).

Sikka & Mulchandani, 1973; Saxton, 1972). The present study was undertaken to verify the structure and to determine its absolute configuration.



Weissenberg photographs were taken up to the ninth layer with a cylindrical crystal ($\mu R=0.95$), mounted along *c*, and Ni-filtered $\text{Cu K}\alpha$ radiation. Reflexions with $h+k$ odd were absent and, in general, $I(hkl)$ was not equal to $I(h\bar{k}l)$. No measurable intensities could be recorded beyond $\theta=45^\circ$. Intensities of 1387 independent reflexions (23% of the number present in the Cu sphere) were measured by visual estimation; 934 of these were above background.

The two I^- ions in the asymmetric unit were located from a Patterson synthesis and their coordinates refined by least squares to an R of 0.28. The remaining 68 atoms were located by successive Fourier syntheses, least-squares fitting and model building. A computer program developed for interpreting the poor resolution Fourier maps was of help. With this program, approximate expected coordinates of an atom in the rigid part of the molecule could be calculated once the corresponding atom in the other molecule in the asymmetric unit had been located.

An F -based least-squares refinement of the atomic parameters was then carried out. Zero weights were assigned to unobserved reflexions. Owing to the large number of parameters, the refinement was done in three batches, keeping the two I^- ions common to all the batches. With isotropic temperature factors, R fell to 0.13 for 934 observed reflexions. However, temperature factors for many of the atoms refined to negative values. To increase the observations-to-parameters ratio, an alternative refinement was then carried out. In

Table 1. Fractional coordinates and thermal parameters

For iodine ions the thermal parameters are defined by $T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$. For all other non-hydrogen atoms, a common isotropic temperature factor refined to a value of 4.2 \AA^2 . All entries are multiplied by 10^4 .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>b</i> ₁₁	<i>b</i> ₂₂	<i>b</i> ₃₃	<i>b</i> ₁₂	<i>b</i> ₁₃	<i>b</i> ₂₃
I(1)	1758 (2)	5000 (-)	3810 (4)	17 (2)	161 (11)	83 (8)	-7 (3)	19 (2)	-59 (6)
I(2)	2063 (2)	2714 (7)	127 (4)	16 (2)	65 (8)	89 (7)	3 (3)	17 (2)	-10 (5)
	Molecule 1			Molecule 2					
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>			
C(1)	286 (32)	8193 (79)	-755 (52)	5252 (31)	5309 (70)	4190 (51)			
C(2)	-311 (30)	8715 (71)	-1458 (53)	4889 (33)	5657 (68)	3468 (54)			
C(3)	-526 (30)	7983 (71)	-2057 (51)	4481 (31)	5153 (78)	2950 (50)			
C(4)	-501 (33)	6878 (71)	-2088 (54)	4502 (32)	4150 (71)	2857 (52)			
C(5)	-348 (32)	4506 (74)	-1934 (53)	4580 (32)	1771 (68)	2959 (52)			
C(6)	-298 (33)	3429 (76)	-1746 (54)	4564 (31)	553 (72)	3119 (50)			
C(7)	161 (33)	3032 (72)	-1078 (55)	5010 (30)	110 (74)	3777 (50)			
C(8)	445 (35)	3552 (72)	-619 (58)	5429 (31)	650 (68)	4428 (50)			
C(9)	828 (30)	5600 (69)	-76 (48)	5785 (31)	2358 (64)	4792 (49)			
C(10)	735 (32)	6675 (70)	-188 (49)	5703 (32)	3558 (74)	4769 (51)			
C(11)	233 (36)	7103 (92)	-904 (55)	5271 (33)	4116 (72)	4217 (54)			
C(12)	-108 (36)	6415 (74)	-1424 (57)	4941 (32)	3572 (71)	3590 (51)			
C(13)	-43 (32)	5288 (74)	-1297 (52)	4981 (30)	2418 (61)	3659 (49)			
C(14)	444 (31)	4840 (72)	-720 (51)	5342 (31)	1672 (64)	4238 (51)			
C(15)	-1080 (30)	9272 (70)	-3065 (49)	4096 (30)	6664 (67)	2347 (47)			
C(16)	-969 (32)	2612 (74)	-2054 (53)	3850 (31)	-410 (66)	2770 (62)			
C(17)	-1371 (33)	1973 (70)	-2603 (50)	3439 (28)	-1037 (69)	2079 (47)			
C(18)	479 (36)	1482 (71)	-516 (56)	5436 (31)	-1489 (69)	4354 (51)			
O(3)	-988 (19)	8147 (41)	-2762 (31)	4125 (19)	5513 (45)	2309 (30)			
O(6)	-638 (19)	2935 (45)	-2473 (31)	4230 (19)	-116 (44)	2562 (29)			
O(7)	109 (22)	1957 (48)	-1121 (35)	5016 (19)	-1038 (42)	3705 (32)			
O(16)	-1164 (19)	2931 (45)	-1661 (32)	3820 (19)	-330 (40)	3564 (39)			
N	1679 (24)	5758 (53)	829 (38)	6659 (23)	2536 (52)	5807 (37)			
C(2')	2084 (30)	5171 (77)	1579 (50)	7004 (33)	2170 (68)	6579 (54)			
C(3')	2267 (30)	6111 (72)	1941 (51)	7310 (30)	3174 (64)	7287 (49)			
C(4')	1981 (31)	7240 (67)	1666 (49)	6971 (31)	3997 (74)	6847 (50)			
C(5')	1471 (32)	6689 (66)	1212 (50)	6416 (32)	3670 (70)	6118 (51)			
C(6')	1130 (32)	7308 (65)	481 (52)	6113 (32)	4388 (69)	5569 (52)			
C(7')	1228 (29)	4996 (72)	641 (47)	6189 (31)	1751 (67)	5424 (50)			
C(8')	1919 (31)	5882 (67)	198 (49)	6971 (28)	2934 (68)	5250 (49)			
C(9')	1452 (30)	8877 (82)	115 (55)	6448 (33)	5990 (80)	5272 (57)			
C(10')	1753 (30)	9558 (66)	-423 (49)	6873 (32)	6436 (69)	5177 (48)			
O(6')	1354 (18)	7866 (55)	-87 (30)	6419 (18)	4917 (50)	5093 (32)			
O(9')	1345 (19)	9355 (45)	744 (36)	6366 (19)	6166 (44)	5900 (36)			

this, all the 68 non-iodine atoms were assigned a common isotropic temperature factor, and anisotropic temperature factors were taken for the two I^- ions. The weighting scheme, based on an analysis of the residuals, was $w^{-1/2} = 5.0 + 0.0634F_o$ for $F_o \leq 284.0$, $w^{-1/2} = 23.0 + 0.588(F_o - 284.0)$ for $F_o > 284.0$. The refinement resulted in an R of 0.12, and R_w of 0.14.* The calculated values are for the correct absolute configuration, which was determined by the anomalous-dispersion method. Seven Bijvoet pairs were chosen for comparison. The choice was such that the observed ratio of raw intensities was at least 1.5. Atomic coordinates and temperature factors are given in Table 1.

Discussion. This study leads to structure (II) for tylophorinidine. An independent chemical and spectroscopic investigation by Govindachari, Viswanathan, Radhakrishnan, Pai, Natarajan & Subramaniam (1973) also arrived at the same result. The absolute configuration of diacetyltylophorinidine methiodide is as indicated in Fig. 1. (The two molecules in the asymmetric unit have quite similar conformations. Fig. 1 shows the average conformation.) ORD studies by Govindachari, Viswanathan & Pai (1974) have further confirmed this assignment of absolute configuration.

The e.s.d.'s of the bond lengths range between 0.09 and 0.15 Å and those of the bond angles between 5 and 9°. These high values are attributed to: (i) the limited amount of low-resolution data, (ii) domination of X-ray

scattering by the I^- ions* ($\sum Z_{\text{iodine}}^2 / \sum Z_{\text{light}}^2 = 1.96$), and (iii) low accuracy of the visually estimated intensities; visual estimation was made difficult by the fact that the diffraction spots tended to be very diffuse at the edges.† But since the principal aim of the study was to determine the structural formula and the stereochemistry, the low accuracy did not present any problems. Some average bond lengths are: $C_{sp^2}-C_{sp^2} = 1.42$, $O-C_{sp^2} = 1.38$, and $O-C_{sp^3} = 1.40$ Å. Mean angle in the aromatic six-membered rings is 119.4°. The five-membered ring has a half-chair conformation.

* Somewhat similar loss of accuracy because of this occurs in cleavamine methiodide (Camerman & Trotter, 1964), cryptostyline I methiodide (Westin, 1972), and DL-isocryptopleurine methiodide (Fridrichsons & Mathieson, 1955).

† A small amount of damage to the crystal due to exposure to X-rays, air and/or light is also possible. However, this aspect was not investigated.

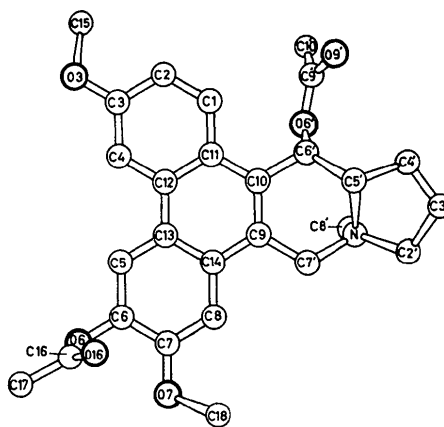


Fig. 1. Atom labels and absolute configuration.

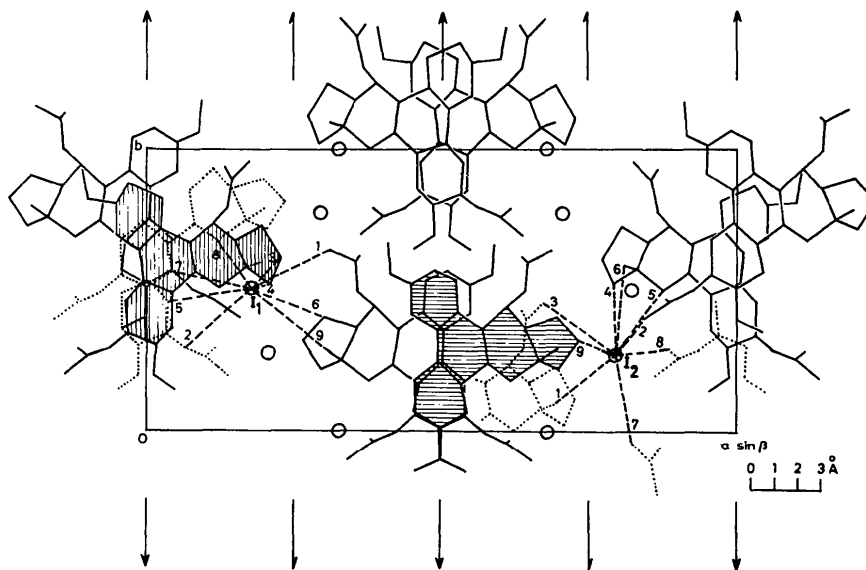


Fig. 2. Projection of the unit-cell contents along the c axis. Skeletons of the crystallographically independent molecules, designated 1 and 2 in Table 1, have been distinguished by vertical and horizontal hatching respectively. For clarity, not all the atoms generated by lattice translations are shown.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31911 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Fig. 2 shows a view of the crystal structure along *c*. I(1) has nine nearest neighbours, all at the expected distance of about 4 Å. These comprise eight C and one O, belonging to four different molecules. I(2) also has nine nearest neighbours, at distances below 4 Å. These also consist of eight C and one O, belonging to six different molecules. These are indicated in Fig. 2 by broken lines. The coordination around both types of I⁻ ions seems to be determined by the requirements of close packing of nearly flat molecules. The shortest I⁻-N⁺ distances are: I(1)-N=4.64 (7) and I(2)-N=4.17 (7) Å, the two N atoms being from molecule 2 and molecule 1 respectively. The crystal structure consists of columns of molecules stacked along *c* (Fig. 2). The two shortest intermolecular distances [both 3.1 (1) Å] are rather short for normal van der Waals contacts. Both of these are between atoms of the same type: the first between O(16) of molecule 1 and C(7') of a neighbouring molecule 1, and the second between O(16) of molecule 2 and C(7') of another molecule 2.

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1-(2-Ethoxy-1-naphthyl)ethyl Methyl Ether

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Abstract. C₁₅O₂H₁₈, orthorhombic, *Pna*2₁; *a*=15.66 (2), *b*=11.25 (2), *c*=7.24 (1) Å; *Z*=4, *D*_m=1.20, *D*_c=1.21 g cm⁻³; μ(Cu Kα)=6.28 cm⁻¹; *R*=0.081. The central aromatic ring in the molecule is planar and the ethoxy group atoms are nearly coplanar with it. C(13), C(14), O(2) of the ethyl methyl ether group are in a plane nearly normal to the ring atoms.

Introduction. 580 independent X-ray reflexions were collected by single-crystal Weissenberg photography

around [001] and [010] with Cu K radiation; their intensities were estimated visually and brought to an absolute scale by statistical methods.

From the systematic absences (*0kl*, *k+l=2n+1*, *h0l*, *h=2n+1*) two space groups were possible: *Pna*2₁ and *Pnam*. Intensity statistics (Howells, Phillips & Rogers, 1950) indicated the non-centrosymmetric *Pna*2₁. Moreover, only four molecules are present in the unit cell and as there is no symmetry in the molecule, *Pnam* is ruled out.

The structure was solved from a [001] Patterson projection and packing considerations. Full-matrix least-squares analysis with *ORFLS* (Busing, Martin & Levy, 1962) with weights Δ*F*=*a*+*bF*_o, where *a* and *b* are constants for the observed reflexions, and anisotropic temperature factors for the heavy atoms reduced *R* to 0.102. An extinction correction was also applied in the last stages of refinement (Zachariasen, 1967). Fourteen H atoms were located from a difference map; the positions of the remaining four (marked by asterisks in Table 1) were assumed to have their theoretically expected values. The final *R* was 0.081.*

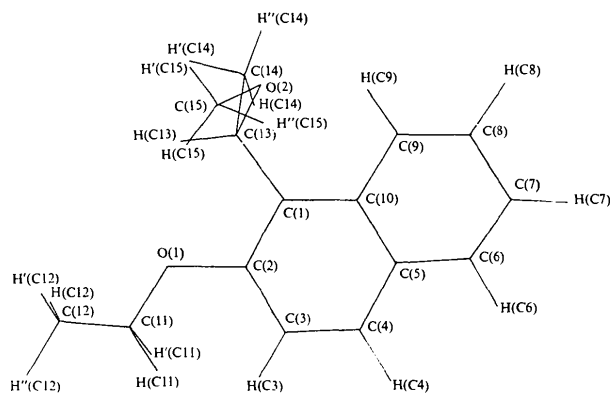


Fig. 1. Numbering scheme for C₁₅O₂H₁₈.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31923 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.