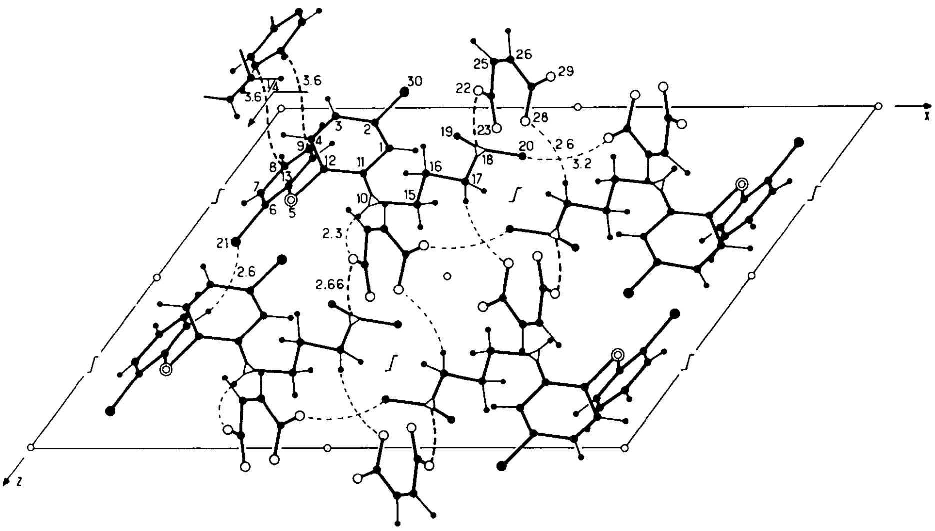

Fig. 3. Projection de la structure le long de l'axe *Oy*.

homologues par inversion ainsi qu'entre atomes de chlore Cl(21) et cycles *B* (molécules homologues par glissement *c*).

Du même que dans le CB57 l'anion maléate prend une configuration non plane due aux multiples liaisons échangées (rotation d'un groupement COOH).

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1,6-Dimethyl-8β-[(benzyloxycarbonyl)aminomethyl]-10α-ergoline, 'Lyserdol'

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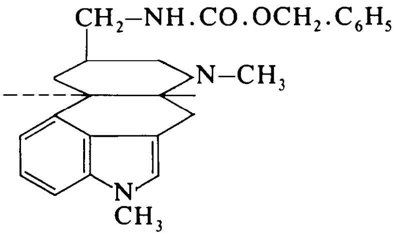
Abstract. $C_{25}H_{29}N_3O_2$, triclinic, $P1$, $a = 9{\cdot}753\ (1)$, $b = 10{\cdot}751\ (2)$, $c = 5{\cdot}225\ (1)$ Å, $\alpha = 94{\cdot}04\ (2)$, $\beta = 97{\cdot}51\ (2)$, $\gamma = 77{\cdot}12\ (2)°$, $Z = 1$, $d_c = 1{\cdot}27$ g cm^{-3}. The final R for 1434 reflexions was 0·069. The side chain is extended and its orientation with respect to the main bulk of the molecule is novel.

Introduction. Numerous pharmacological investigations by a research group active in Farmitalia Research Institute, Milano, have ascertained the efficacy of Lyserdol, or MCE, (I) as having inhibitory effect on platelet aggregation and specifically as an anti-5-hydroxytryptamine agent (Baldratti, Arcari & Suchowski, 1965; Arcamone, Glässer, Minghetti & Nicolella, 1971; Fregnan, 1972).

Within a large collaborative programme the X-ray structural investigation of (I) was required to determine both overall conformation and exact molecular



(I)

parameters, with the aim of comparing molecular structure with biological activity and steric arrangement at the receptor site. To the authors' knowledge only one related structure has been reported (Baker, Chothia, Pauling & Weber, 1972) in addition to that of nicergoline (Sabatino, Foresti Serantoni, Krajewski, Mongiorgi & Riva di Sanseverino, 1975) which we are currently refining further.

An extremely tiny crystal was isolated from a batch recrystallized from acetone and used throughout data collection on a Philips PW 1100 diffractometer. 1800 unique reflexions were collected with Cu $K\alpha$ radiation of which 366 having $F_o < 5\sigma(F_o)$ were not included in the final refinement. A partial structure was obtained by multisolution tangent refinement followed by a negative-quartet test (De Titta, Edmonds, Langs & Hauptman, 1975); it was extended to the complete structure (except for H) by tangent phase expansion (Karle, 1968).

Successive difference maps calculated during the isotropic least-squares refinement indicated positions

Table 1. *Heavy-atom coordinates* (×10⁴) *and isotropic temperature factors* (Å² ×10³)

	x	y	z	U
N(1)	707 (6)	2090 (5)	6700 (10)	57 (1)
C(2)	1487 (7)	2521 (6)	5024 (13)	55 (1)
C(3)	2670 (6)	1620 (6)	4673 (11)	47 (1)
C(4)	2636 (6)	570 (5)	6236 (11)	43 (1)
C(5)	3637 (6)	−547 (5)	6574 (11)	43 (1)
C(6)	3341 (6)	−1384 (6)	8238 (11)	47 (1)
C(7)	2132 (7)	−1058 (6)	9536 (13)	56 (2)
C(8)	1143 (7)	72 (6)	9163 (13)	54 (1)
C(9)	1406 (6)	905 (6)	7463 (12)	50 (1)
C(10)	3919 (6)	1490 (6)	3203 (11)	48 (1)
C(11)	5229 (6)	616 (6)	4616 (11)	47 (1)
N(12)	6450 (5)	366 (5)	3133 (10)	48 (1)
C(13)	7718 (7)	−358 (6)	4593 (12)	52 (1)
C(14)	7536 (6)	−1660 (6)	5193 (12)	48 (1)
C(15)	6258 (6)	−1532 (5)	6625 (11)	43 (11)
C(16)	4932 (6)	−709 (5)	5154 (10)	40 (1)
C(17)	−536 (8)	2871 (7)	7756 (15)	70 (2)
C(18)	6727 (8)	1572 (7)	2306 (14)	63 (2)
C(19)	8837 (7)	−2411 (7)	6734 (13)	59 (2)
N(20)	10118 (5)	−2684 (5)	5410 (12)	
C(21)	10420 (7)	−3673 (6)	3707 (12)	53 (1)
O(22)	9664 (5)	−4438 (4)	3061 (11)	
O(23)	11630 (4)	−3706 (4)	2807 (10)	
C(24)	12056 (7)	−4699 (7)	934 (13)	61 (2)
C(25)	13602	−4798	669	
C(26)	14155	−5497	−1456	
C(27)	15585	−5639	−1741	
C(28)	16462	−5082	98	
C(29)	15909	−4383	2223	
C(30)	14479	−4241	2509	

Table 2. *Hydrogen-atom coordinates* (×10⁴) *and isotropic temperature factors* (Å² ×10³)

	x	y	z	U
H(2)	1328 (54)	3371 (49)	4393 (78)	49 (9)
H(6)	4004 (60)	−2163 (55)	8833 (86)	62 (10)
H(7)	1971 (57)	−1654 (51)	10809 (83)	54 (9)
H(8)	391 (63)	456 (56)	10340 (86)	70 (10)
H(10*a*)	4105 (56)	2436 (53)	3111 (79)	55 (10)
H(10*b*)	3818 (50)	1102 (45)	1588 (76)	39 (9)
H(11)	5405 (44)	1037 (40)	6429 (70)	21 (8)
H(13*a*)	7925 (52)	29 (49)	6415 (78)	43 (9)
H(13*b*)	8463 (75)	−453 (70)	3513 (96)	106 (11)
H(14)	7357 (51)	−2036 (46)	3617 (76)	39 (9)
H(15*a*)	6638 (54)	−1245 (51)	8573 (79)	53 (9)
H(15*b*)	5927 (47)	−2418 (44)	6820 (73)	34 (9)
H(16)	4622 (65)	−1168 (61)	3036 (91)	85 (10)
H(17*a*)	−860	3752	6749	107 (9)
H(17*b*)	−277	3081	9790	107 (9)
H(17*c*)	−1390	2368	7493	107 (9)
H(18*a*)	6003 (49)	1843 (43)	1214 (74)	38 (9)
H(18*b*)	6908 (50)	2019 (45)	3554 (77)	39 (9)
H(18*c*)	7616 (74)	1201 (69)	1283 (96)	107 (9)
H(19*a*)	9016 (50)	−1966 (46)	8354 (75)	38 (9)
H(19*b*)	8797 (56)	−3159 (50)	7146 (80)	57 (10)
H(20)	10740 (76)	−2311 (70)	5864 (97)	107 (9)
H(24*a*)	11533 (62)	−4609 (58)	−661 (87)	74 (10)
H(24*b*)	11846 (58)	−5443 (53)	1414 (84)	63 (10)
H(26)	13476	−5928	−2880	104 (11)
H(27)	16013	−6180	−3386	90 (10)
H(28)	17568	−5191	−123	88 (10)
H(29)	16588	−3952	3647	117 (11)
H(30)	14051	−3700	4154	109 (11)

Table 3. *Bond lengths* (Å)

N(1)–C(2)	1·396 (11)	N(1)–C(9)	1·364 (9)
N(1)–C(17)	1·461 (10)	C(2)–C(3)	1·355 (9)
C(3)–C(4)	1·448 (10)	C(3)–C(10)	1·498 (10)
C(4)–C(5)	1·374 (8)	C(4)–C(9)	1·398 (10)
C(5)–C(6)	1·393 (10)	C(5)–C(16)	1·518 (10)
C(6)–C(7)	1·402 (10)	C(7)–C(8)	1·381 (9)
C(8)–C(9)	1·389 (11)	C(10)–C(11)	1·542 (10)
C(11)–N(12)	1·470 (9)	C(11)–C(16)	1·566 (11)
N(12)–C(13)	1·458 (8)	N(12)–C(18)	1·486 (11)
C(13)–C(14)	1·509 (11)	C(14)–C(15)	1·511 (11)
C(14)–C(19)	1·510 (10)	C(15)–C(16)	1·540 (9)
C(19)–N(20)	1·470 (10)	N(20)–C(21)	1·344 (9)
C(21)–O(22)	1·225 (10)	C(21)–O(23)	1·319 (9)
O(23)–C(24)	1·425 (9)	C(24)–C(25)	1·512 (10)
C(2)–H(2)	0·97 (5)	C(6)–H(6)	0·98 (5)
C(7)–H(7)	1·00 (6)	C(8)–H(8)	1·02 (6)
C(10)–H(10*a*)	1·08 (6)	C(10)–H(10*b*)	0·92 (4)
C(11)–H(11)	1·03 (4)	C(13)–H(13*a*)	1·02 (4)
C(13)–H(13*b*)	0·96 (7)	C(14)–H(14)	0·90 (4)
C(15)–H(15*a*)	1·08 (4)	C(15)–H(15*b*)	1·09 (5)
C(16)–H(16)	1·21 (5)	C(18)–H(18*a*)	0·86 (4)
C(18)–H(18*b*)	0·81 (4)	C(18)–H(18*c*)	1·06 (7)
C(19)–H(19*a*)	0·96 (4)	C(19)–H(19*b*)	0·86 (6)
N(20)–H(20)	0·80 (8)	C(24)–H(24*a*)	0·92 (5)
C(24)–H(24*b*)	0·93 (6)		

Table 4. *Bond angles* (°)

C(2)–N(1)–C(9)	109·0 (6)	C(2)–N(1)–C(17)	124·6 (7)
C(9)–N(1)–C(17)	125·8 (7)	N(1)–C(2)–C(3)	109·8 (7)
C(2)–C(3)–C(4)	106·0 (7)	C(2)–C(3)–C(10)	136·5 (5)
C(4)–C(3)–C(10)	117·5 (6)	C(3)–C(4)–C(5)	127·5 (7)
C(3)–C(4)–C(9)	107·7 (6)	C(5)–C(4)–C(9)	124·7 (7)
C(4)–C(5)–C(6)	115·2 (6)	C(4)–C(5)–C(16)	116·8 (5)
C(6)–C(5)–C(16)	128·0 (6)	C(5)–C(6)–C(7)	121·1 (5)
C(5)–C(7)–C(8)	122·5 (8)	C(7)–C(8)–C(9)	117·0 (7)
N(1)–C(9)–C(4)	107·5 (7)	N(1)–C(9)–C(8)	133·1 (6)
C(4)–C(9)–C(8)	119·4 (6)	C(3)–C(10)–C(11)	110·1 (6)
C(10)–C(11)–N(12)	112·1 (6)	C(10)–C(11)–C(16)	112·0 (6)
N(12)–C(11)–C(16)	107·3 (5)	C(11)–N(12)–C(13)	111·6 (6)
C(11)–N(12)–C(18)	111·3 (6)	C(13)–N(12)–C(18)	110·1 (6)
N(12)–C(13)–C(14)	111·7 (6)	C(13)–C(14)–C(15)	110·1 (6)
C(13)–C(14)–C(19)	112·1 (6)	C(15)–C(14)–C(19)	110·1 (6)
C(14)–C(15)–C(16)	111·0 (6)	C(5)–C(16)–C(11)	111·2 (5)
C(5)–C(16)–C(15)	112·1 (6)	C(11)–C(16)–C(15)	110·0 (6)
C(14)–C(19)–N(20)	114·4 (7)	C(19)–N(20)–C(21)	123·2 (7)
N(20)–C(21)–O(22)	124·4 (7)	N(20)–C(21)–O(23)	111·2 (7)
O(22)–C(21)–O(23)	124·5 (7)	C(21)–O(23)–C(24)	116·7 (6)
O(23)–C(24)–C(25)	108·7	C(24)–C(25)–C(26)	118·1
C(24)–C(25)–C(30)	121·9		

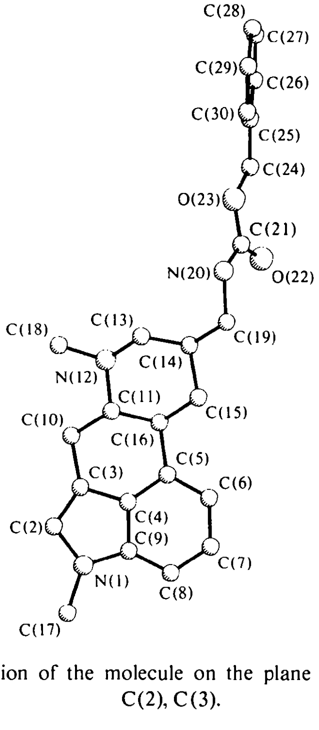


Fig. 1. Projection of the molecule on the plane formed by C(1), C(2), C(3).

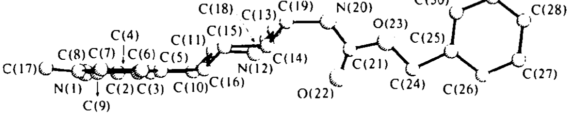


Fig. 2. Projection of the molecule on the plane formed by C(25), C(26), C(27).

for the majority of H atoms and remarkable anisotropic thermal vibration for the phenyl ring, N(20), O(22) and O(23). Therefore: (*a*) the phenyl ring was treated as a rigid body (C–C distances 1·395 Å, C–C–C angles 120°), but the individual atoms N(20), ring O(22) and O(23) were allowed to refine with anisotropic temperature factors; (*b*) the five H atoms attached to the phenyl ring and those belonging to methyl C(17) were geometrically positioned (C–H distance 1·08 Å) and constrained to refine riding on their respective C atoms; (*c*) the H atoms H(20) and H(18*c*) were also positioned geometrically, but left to refine independently. The final agreement factor is 0·069 for 1434 reflexions. Complex neutral-atom scattering factors were employed but no attempt was made to confirm the absolute configuration. The weighting scheme was $w = 1/[\sigma^2(F_o) + 0{\cdot}004F_o^2]$.

Positional and isotropic thermal parameters are listed in Tables 1 and 2* and bond distances and angles in Tables 3 and 4.† The *SHELX* system of programs (Sheldrick, 1976) was used throughout the calculations; the drawings were made with *PLUTO* (Motherwell, 1976). The literature search was performed with the Cambridge Crystallographic Data Centre system of programs.

Discussion. The main structural feature of MCE revealed by Figs. 1 and 2 is the orientation of the phenyl ring with respect to the planar bulk of the molecule, quite different from that we observed in the parent compound, nicergoline (Sabatino *et al.*, 1975); the two compounds play different pharmaceutical roles (Arcari, Bernardi, Bosisio, Coda, Fregnan & Glässer, 1972). Table 5 quotes some relevant torsion angles describing the molecular conformation. The extended side chain follows this change in orientation: there is little reason to attribute this effect to crystal-packing forces. There is no intermolecular contact under 3·4 Å. In view of the anisotropy of thermal motion of the

Table 5. *Relevant torsion angles* (°)

C(30)–C(25)–C(24)–O(23)	16·1
C(26)–C(25)–C(24)–O(23)	−165·6
C(25)–C(24)–O(23)–C(21)	−165·3
C(24)–O(23)–C(21)–N(20)	−178·7
O(23)–C(21)–N(20)–C(19)	180·0
C(21)–N(20)–C(19)–C(14)	−83·6
N(20)–C(19)–C(14)–C(15)	175·1
N(20)–C(19)–C(14)–C(13)	−61·9

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32674 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† In Tables 1–4 some distances and/or e.s.d.'s are omitted because they were under constraint during the least-squares refinement.

$-NHCOOCH_2C_6H_5$ moiety, the torsional barrier may well be low in solution.

Related molecules both with much greater and with no anti-5-HT activity are now under X-ray structural investigation.

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2-Amino-5-methylpyridine*

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Abstract. $C_6H_8N_2$, monoclinic, $P2_1/c$, $a = 10{\cdot}413$ (5), $b = 5{\cdot}908$ (3), $c = 10{\cdot}828$ (5) Å, $\beta = 116{\cdot}69$ (3)°, $M_r = 108{\cdot}144$, $Z = 4$, $D_x = 1{\cdot}207$ g cm^{-3}. The structure has been determined from four-circle X-ray diffractometer single-crystal data. The H atoms have been located and full-matrix least-squares refinement gave a final $R(F)$ value of 0·048. The molecules are linked together by a very weak N—H···N bond (N···N, 3·113 Å) to produce cyclic dimers which, in turn, pack in a herringbone formation.

Introduction. Commercial 2-amino-5-methylpyridine was recrystallized several times from chloroform. A crystal with dimensions 0·18 × 0·18 × 0·23 mm was selected for data collection and was mounted in a glass capillary to prevent sublimation during the experiment. A preliminary film investigation indicated diffraction symmetry and systematic absences uniquely consistent with the monoclinic space group $P2_1/c$ (No. 14, *International Tables for X-ray Crystallography*, 1952).

Cell parameters were refined from 18 θ values measured on a Guinier–Hägg powder camera at +24 °C with monochromatized Cr $K\alpha_1$ radiation ($\lambda = 2{\cdot}28962$ Å). CoP_3 ($a = 7{\cdot}7073$ Å) was used as an internal standard. Intensity data were collected on a Stoe–Philips four-circle X-ray diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). An ω–2θ scan technique was used to obtain the intensities. Only small random fluctuations were observed in the intensities of the three standard reflexions measured every 50 reflexions. In all, 2708 reflexions were measured out to $\sin\theta/\lambda = 0{\cdot}703$ Å^{-1}. An absorption correction ($\mu = 0{\cdot}825$ cm^{-1}) was made, with the Gaussian integration method with a grid of 216 points. After removal of systematic absences and averaging of *hkl* and *hkl* reflexions, 2118 reflexions remained of which 1112 were greater than $2\sigma(I)$ and were used in the refinement.

The structure was solved by direct methods following the iterative procedure programmed by Long (1965). The H atoms were located unambiguously in a difference Fourier synthesis, calculated after several cycles of full-matrix least-squares refinement of non-hydrogen atomic parameters with isotropic thermal

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* Hydrogen Bond Studies. CXXIV.

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