Crystal Structure and Absolute Configuration of Lycopodine Hydrochloride

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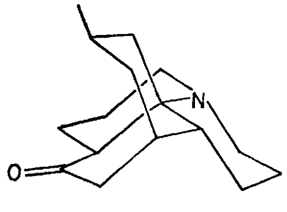
Crystals of the title compound are orthorhombic, space group $P2_12_12_1$, a = 7·606(1), b = 9·540(1), c = 21·371(1) Å, Z = 4. The structure was solved from diffractometer data by Patterson and heavy-atom methods and refined by full-matrix least-squares to R 0·050 for 1687 independent reflexions. The results confirm the chirality (I) earlier deduced from chemical work and a positive Cotton effect.

LYCOPODINE, one of the numerous alkaloidal constituents of *Lycopodium lucidulum* Michx, has been assigned the structure and chirality (I) on the basis of extensive chemical work and a positive Cotton effect.[1-5] Recently, Ayer *et al.*[6] have re-examined the o.r.d. evidence for several members of this group of alkaloids, their salts, and derivatives. They found that lycopodine salts, epilycopodine and its salts, and the alkaloid L23 all have negative Cotton effects and that the structure of the o.r.d. curves is more complex than was realised when Wiesner *et al.*[4] first assigned the chirality of congeneric annotinine and lycopodine. As the octant diagrams are not altered by protonation and are generally similar for all these compounds, they concluded that it was not safe to apply octant rules in this context until the large and obviously different contributions of N: and N$^+$ were properly understood, and they specifically queried whether (I) correctly depicted lycopodine. They adduced other items of indirect evidence and concluded, but with less confidence than before that (I) was probably correct after all. We have recently completed the determination of the crystal structure of lycopodine hydrochloride, and have confirmed that (I) is correct.[7]



(I)

EXPERIMENTAL

A crystal *ca.* 0·20 × 0·33 × 0·86 mm^3 was used for intensity measurements. Accurate cell dimensions were obtained by least-squares from fifteen high-θ values measured with Cu-$K_{\alpha 1}$ radiation (λ = 1·54050 Å) on a diffractometer.

Crystal Data.—$C_{16}H_{26}ClNO$, M = 283·8. Orthorhombic, a = 7·606(1), b = 9·540(1), c = 21·371(1) Å, U = 1550·6 Å^3, D_m = 1·20(2), Z = 4, D_c = 1·21 g cm^{-3}, $F(000)$ = 616. Space group $P2_12_12_1$ uniquely from systematic absences; Cu-K_α radiation, $\bar{\lambda}$ = 1·5418 Å, μ(Cu-K_α) = 21·1 cm^{-1}.

The intensities of 1716 reflexions were measured with filtered Cu-K_α radiation to θ 70° on a Siemens off-line four-circle diffractometer by the θ—2θ scan technique with the 'five-value' measuring procedure.[8] A total of 1695 reflexions was considered observable, having a net count $N > 2{\cdot}58\sigma(N)$ (*i.e.* 99% confidence level). The 045 reflexion, which was used as reference reflexion and measured every 50 reflexions, showed no significant change during the period of data collection (*ca.* 4 days). It was used to adjust the observed intensities to a common arbitrary scale. Lorentz and polarisation corrections were applied. Atomic scattering factors were taken from ref. 9, except those for hydrogen which were taken from ref. 10.

Structure Determination and Refinement.—The structure was determined and refined mostly by use of the crystal-structure computing system '*X*-RAY 70'.[11]

The position of the chloride ion was deduced from the Harker sections of the three-dimensional Patterson, and the whole structure emerged from the first three $\Delta\rho$ maps. Three cycles of full-matrix least-squares isotropic refinement of all nonhydrogen atoms brought R to 0·149, and four further cycles of anisotropic refinement gave R 0·088.

At this stage the data were corrected for absorption according to the procedure of Busing and Levy[12] using a grid of 10 × 10 × 14 with path-lengths determined by the method of Coppens *et al.*[13] A weighting scheme of the type suggested by Hughes[14] was applied, where $w = 1$ for $|F_0| < 12$ and $w = 12/|F_0|$ for $|F_0| \geqslant 12$. Four cycles of anisotropic full-matrix least-squares refinement reduced R to 0·078, at which stage all 26 hydrogen atoms were discernible in the $\Delta\rho$ map. In the next four cycles of refinement hydrogen atoms were allowed for as fixed-atom contributions with isotropic temperature factors 0·5 Å^2 higher than their parent atoms, and R fell to 0·052. Refinement of hydrogen atoms was attempted but led to some unacceptable bond lengths, angles, and temperature factors and no improvement in R. Evidently the accuracy of the data did not justify such refinement. Finally, eight zonal reflexions, affected by extinction, were excluded from refinement to give a final unweighted R of 0·050 for

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[1] R. H. F. Manske and L. Marion, *Canad. J. Res. B*, 1946, **24**, 57.

[2] W. A. Harrison and D. B. Maclean, *Chem. and Ind.*, 1960, 261, and references therein.

[3] F. A. L. Anet, *Tetrahedron Letters*, 1960, **20**, 13.

[4] K. Wiesner, J. E. Francis, A. J. Findlay, and Z. Valente, *Tetrahedron Letters*, 1961, **5**, 187.

[5] R. H. Burnell and D. R. Taylor, *Tetrahedron*, 1961, **15**, 173.

[6] W. A. Ayer, B. Altenkirk, R. H. Burnell, and M. Moinas, *Canad. J. Chem.* 1969, **47**, 449.

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[8] F. H. Allen, D. Rogers, and P. G. H. Troughton, *Acta Cryst.*, 1971, **B27**, 1325.

[9] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

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

[11] '*X*-RAY 70' Computing System, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin, University of Maryland.

[12] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[13] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

[14] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

the 1687 reflexions. At the end of refinement all shift/error ratios were $<0{\cdot}01$, and there was nothing unexplained in the difference map.

The absolute configuration was deduced to be (I) from a comparison of R factors for the nonzonal reflexions in which the anomalous scattering component $\Delta f''$ for chlorine was given both signs. Details have been reported elsewhere[7] in the form of a warning to crystallographers because a flaw was discovered in certain well-known crystallographic programs which had the effect of assigning wrong chiralities.

Final atomic co-ordinates and their standard deviations are listed in Tables 1 and 2. Thermal parameters have been deposited with the F lists in Supplementary Publication No. SUP 21163 (8 pp.).* Bond lengths and valence and torsion angles are listed in Tables 3—5 respectively, and least-squares planes in Table 6.

TABLE 1

Fractional co-ordinates ($\times 10^4$) for the non-hydrogen atoms, with standard deviations in parentheses

Atom	x	y	z
Cl	−1479(1)	5372(1)	4674(0)
C(1)	2305(7)	7324(4)	3969(2)
C(2)	4095(8)	7698(4)	3702(2)
C(3)	4845(7)	6528(4)	3288(2)
C(4)	4831(4)	5129(4)	3640(1)
C(5)	5706(5)	3965(5)	3288(2)
C(6)	5555(6)	2541(5)	3594(2)
C(7)	3740(7)	2196(4)	3842(2)
C(8)	2399(7)	1957(5)	3314(2)
N(9)	2347(4)	5928(3)	4299(1)
C(10)	3292(5)	6054(4)	4913(1)
C(11)	3228(6)	4689(4)	5272(1)
C(12)	4030(6)	3504(4)	4881(2)
C(13)	3039(5)	3379(3)	4268(2)
C(14)	2987(4)	4732(3)	3878(1)
C(15)	1651(5)	4537(4)	3348(2)
C(16)	2081(5)	3274(5)	2926(2)
C(17)	628(7)	3062(7)	2443(2)
O(18)	6576(4)	4152(4)	2827(1)

TABLE 2

Fractional co-ordinates ($\times 10^3$) for hydrogen atoms (derived from a $\Delta\rho$ map and unrefined)

Atom	Attached to	x	y	z
H(11)	C(1)	130	747	370
H(12)	C(1)	175	800	428
H(21)	C(2)	400	847	340
H(22)	C(2)	520	800	410
H(31)	C(3)	400	650	280
H(32)	C(3)	630	720	330
H(41)	C(4)	580	527	408
H(61)	C(6)	620	167	332
H(62)	C(6)	630	240	396
H(71)	C(7)	360	133	412
H(81)	C(8)	290	117	310
H(82)	C(8)	140	167	352
H(91)	N(9)	130	567	440
H(101)	C(10)	250	687	520
H(102)	C(10)	480	620	488
H(111)	C(11)	180	453	544
H(112)	C(11)	400	477	568
H(121)	C(12)	530	380	480
H(122)	C(12)	400	247	499
H(131)	C(13)	175	307	444
H(151)	C(15)	50	430	352
H(152)	C(15)	150	540	308
H(161)	C(16)	330	347	268
H(171)	C(17)	30	400	212
H(172)	C(17)	100	217	220
H(173)	C(17)	0	233	270

TABLE 3

Bond lengths (Å), with standard deviations in parentheses

$C(sp^3)$–$C(sp^3)$		$C(sp^3)$–$C(sp^2)$	
C(1)–C(2)	1·519(8)	C(4)–C(5)	1·497(5)
C(2)–C(3)	1·534(6)	C(5)–C(6)	1·511(6)
C(3)–C(4)	1·533(5)		
C(4)–C(14)	1·540(4)	C=O	
C(6)–C(7)	1·515(7)	C(5)–O(18)	1·200(5)
C(7)–C(8)	1·537(7)		
C(7)–C(13)	1·545(5)	C–N	
C(8)–C(16)	1·525(6)	C(1)–N(9)	1·507(4)
C(10)–C(11)	1·513(5)	C(10)–N(9)	1·500(4)
C(11)–C(12)	1·531(5)	C(14)–N(9)	1·532(4)
C(12)–C(13)	1·516(5)		
C(13)–C(14)	1·537(4)		
C(14)–C(15)	1·533(5)	NH · · · Cl	3·065
C(15)–C(16)	1·541(6)		
C(16)–C(17)	1·526(6)		

TABLE 4

Valence angles (deg.), with standard deviations in parentheses

C(2)–C(1)–N(9)	111·4(4)	C(12)–C(13)–C(7)	113·3(3)
C(1)–C(2)–C(3)	112·3(4)	C(12)–C(13)–C(14)	114·5(3)
C(2)–C(3)–C(4)	110·3(3)	C(14)–C(13)–C(7)	107·6(3)
C(3)–C(4)–C(5)	113·4(3)	C(13)–C(14)–C(4)	111·2(3)
C(3)–C(4)–C(14)	112·5(3)	C(13)–C(14)–N(9)	108·4(2)
C(5)–C(4)–C(14)	112·9(3)	C(13)–C(14)–C(15)	108·5(3)
C(5)–C(6)–C(7)	114·5(3)	N(9)–C(14)–C(4)	107·5(3)
C(6)–C(7)–C(8)	112·4(3)	N(9)–C(14)–C(15)	108·3(3)
C(6)–C(7)–C(13)	111·2(3)	C(15)–C(14)–C(4)	112·9(3)
C(8)–C(7)–C(13)	108·2(4)	C(14)–C(15)–C(16)	112·8(3)
C(7)–C(8)–C(16)	112·5(4)	C(15)–C(16)–C(8)	111·0(3)
C(1)–N(9)–C(10)	110·4(3)	C(15)–C(16)–C(17)	110·2(4)
C(1)–N(9)–C(14)	113·0(2)	C(17)–C(16)–C(8)	112·0(4)
C(10)–N(9)–C(14)	114·9(2)		
N(9)–C(10)–C(11)	111·1(3)	C(4)–C(5)–C(6)	114·6(3)
C(10)–C(11)–C(12)	110·2(3)	C(4)–C(5)–O(18)	123·1(4)
C(11)–C(12)–C(13)	109·4(3)	C(6)–C(5)–O(18)	122·0(4)

TABLE 5

Torsion angles (degrees), grouped to emphasise the near-symmetry of the rings and their substituents

		Mean
(*a*) Ring A		
C(1)–C(2)–C(3)–C(4)	−52·5	
C(2)–C(3)–C(4)–C(14)	56·1	
C(3)–C(4)–C(14)–N(9)	−57·5	55·5
C(4)–C(14)–N(9)–C(1)	57·7	
C(14)–N(9)–C(1)–C(2)	−56·6	
N(9)–C(1)–C(2)–C(3)	52·9	
(*b*) Ring B		
C(4)–C(5)–C(6)–C(7)	44·3	
C(5)–C(6)–C(7)–C(13)	−51·7	
C(6)–C(7)–C(13)–C(14)	59·0	52·4
C(7)–C(13)–C(14)–C(4)	−60·3	
C(13)–C(14)–C(4)–C(5)	54·1	
C(14)–C(4)–C(5)–C(6)	−44·8	
(*c*) Ring C		
N(9)–C(14)–C(13)–C(12)	−51·3	
C(14)–C(13)–C(12)–C(11)	56·6	
C(13)–C(12)–C(11)–C(10)	−58·0	56·5
C(12)–C(11)–C(10)–N(9)	57·6	
C(11)–C(10)–N(9)–C(14)	−55·1	
C(10)–N(9)–C(14)–C(13)	50·1	

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue.

TABLE 5 (*Continued*)

(*d*) Ring D

		Mean
C(7)–C(13)–C(14)–C(15)	64·3	
C(13)–C(14)–C(15)–C(16)	−57·7	
C(14)–C(15)–C(16)–C(8)	50·5	57·9
C(15)–C(16)–C(8)–C(7)	−51·1	
C(16)–C(8)–C(7)–C(13)	58·9	
C(8)–C(7)–C(13)–C(14)	−64·9	
C(17)–C(16)–C(15)–C(14)	175·2	
C(17)–C(16)–C(8)–C(7)	−174·8	
C(2)–C(3)–C(4)–C(5)	−174·4	
C(3)–C(4)–C(5)–C(6)	−174·2	
C(1)–N(9)–C(14)–C(13)	178·0	
N(9)–C(14)–C(13)–C(7)	−178·3	
C(3)–C(4)–C(14)–C(13)	−176·1	
C(5)–C(4)–C(14)–N(9)	172·7	
C(12)–C(13)–C(7)–C(8)	167·5	
C(12)–C(13)–C(14)–C(15)	−168·7	
C(10)–N(9)–C(14)–C(15)	167·6	
C(1)–N(9)–C(10)–C(11)	175·7	
C(7)–C(13)–C(12)–C(11)	−179·7	
C(16)–C(15)–C(14)–C(4)	66·0	
C(16)–C(8)–C(7)–C(6)	−64·3	
C(1)–N(9)–C(14)–C(15)	−64·0	
C(7)–C(13)–C(14)–C(15)	64·3	
N(9)–C(14)–C(15)–C(16)	−175·1	
C(10)–N(9)–C(1)–C(2)	73·7	
C(10)–N(9)–C(14)–C(4)	−70·2	
C(12)–C(13)–C(14)–C(4)	66·6	
C(12)–C(13)–C(7)–C(6)	−68·7	
C(15)–C(14)–C(4)–C(3)	61·8	
C(15)–C(14)–C(4)–C(5)	−68·0	
C(8)–C(7)–C(6)–C(5)	69·7	
O(18)–C(5)–C(4)–C(14)	140·8	
O(18)–C(5)–C(6)–C(7)	−141·2	
O(18)–C(5)–C(4)–C(3)	11·4	

DISCUSSION

Figure 1, which is derived from the co-ordinates of Table 1 referred to right-handed axes, depicts the conformation and absolute configuration of the molecule and its relation to the nearest chloride ion. It also shows the numbering scheme used. The stereochemistry and chirality are exactly as forecast in the earlier mentioned studies.[1-6] Apart from the presence of sp^2 hybridisation at C(5) and a nitrogen atom, the skeleton corresponds to a fairly large tract of the diamond structure, and this fact seems to influence some of the geometrical details described below.

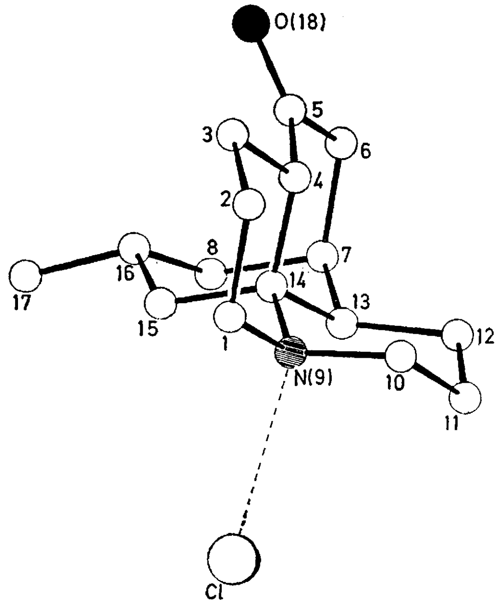

FIGURE 1 Molecular of lycopodine hydrochloride, showing the numbering scheme used

TABLE 6

The planes are of the form $Px + Qy + Rz = S$, with x, y, z in fractional co-ordinates and P, Q, R, S in Å. Deviations of atoms from the plane are in Å $\times$ 10^{-3}; those in parentheses do not define the plane

Plane:	(1)	(2)	(3)	(4)	(5)	(6)	(7)
C(1)	17	33	(−598)		(−1148)	(41)	
C(2)	(1193)	−7		0	(−143)	(−1382)	
C(3)	(1253)	(−667)		0	(−191)		
C(4)	(1206)	−9		0	(−171)	(−1411)	
C(5)	(1395)	(−511)		(134)	(−90)		
C(6)	(1217)	16		0	(−198)	(−1407)	
C(7)	16	10	(−665)		(−1230)	−4	(1105)
C(8)	(−1313)	(−1412)	(−312)			4	0
N(9)	−3	(660)	−8		(−1109)	(744)	
C(10)	(1077)		8		0		
C(11)	(1005)		(691)		0		
C(12)	(1114)		−8		0		
C(13)	1	(709)	8		(−1138)	(781)	
C(14)	−31	−43	(−631)		(−1238)	4	(1092)
C(15)	(−1350)	(−1469)	(−294)			−4	0
C(16)	(−1541)					(−621)	0
C(17)	(−2917)					(−493)	(−1177)
O(18)	(1760)			(429)	(140)		
P	−7·123	−2·699	6·433	−6·973	−6·420	5·420	−7·402
Q	−1·841	−0·303	1·933	−1·819	−1·762	1·789	−2·131
R	6·260	19·969	10·547	7·500	7·828	14·449	1·166
S	3·185	17·069	12·309	5·476	5·968	14·858	−2·670

Angles between planes are indicated in Figure 3.

The fifteen C(sp^3)–C(sp^3) bonds have a mean of 1·530 Å, σ 0·010 Å. The mean of the calculated σ for these bonds is 0·006 Å, so none is significantly discordant. The mean value is appreciably (2σ) lower than the 'paraffinic' value [1·541(3) Å], quoted in ref. 15. However, this latter value seems to be based on a large number of studies, not all of them of good accuracy. With the aid of ref. 15, ten structures were selected, all of which had $R \leqslant 0{\cdot}10$, had no atoms heavier than fluorine, had accurate cell parameters, and made explicit allowance for hydrogen atoms. These gave a total of sixty C(sp^3)–C(sp^3) bonds with a mean of 1·524 Å, and σ 0·011 Å. Our mean is, therefore, in good agreement with the better published values.

The mean of the three C(sp^3)–N(sp^3) bonds is 1·513(14) Å which is very much longer than that [1·479(5) Å] quoted[15] for quadricovalent nitrogen. The elongation seems to be due to the regularity and strength of the diamond-like skeleton. Evidently the nitrogen is abnormally loosely bound. It is worth noting that the mean C–N distance in vincamine is 1·486 Å, whereas in vincamine hydrobromide methanolate it is 1·515 Å,[16] in good agreement with our result.

The mean of the C–C bonds adjacent to the carbonyl group is 1·504(7) Å, which, though barely significantly shorter than 1·516(5) Å quoted in ref. 15 has contracted by the same fraction as the mean C(sp^3)–C(sp^3) bond length.

The mean of the thirty valence angles at tetrahedral atoms is 111·3(21)°, which is closer to the ideal value of 109·5° than is usual in cyclohexane systems, presumably in this case because of the multiple stiffening constraints exerted on each ring by its neighbours. For the same reason, the sp^2 ring-angle at C(5) is reduced to 114·6°.

The torsion and dihedral angles are listed in Table 5, and Figure 2 depicts details of the four rings A–D. Ring D, which is the least constrained, has the highest mean torsion angle (57·9°). Rings A and C have means of 55·5 and 56·5° respectively which are more typical of cyclohexane rings that have been somewhat flattened by interaxial non-bonded repulsions. In this case much of the flattening comes from interactions between C(10)–H and both C(2)–H and C(4)–H. Ring B is even flatter (mean 52·4°), partly from the C(sp^2) constraints and partly from nonbonded interactions between C(12)–H and both C(4)–H and C(6)–H. All these nonbonded C · · · C distances in an ideal diamond structure, of bond length 1·525 Å, would be 2·93 Å, whereas the observed distances [C(10) · · · C(2) 3·09, C(10) · · · C(4) 3·09, C(12) · · · C(4) 3·13, and C(12 · · · C(6) 3·12 Å] indicate appreciable splaying between ring C and rings A and B. This is also borne out by the planes data in Table 6 from which the dihedral angle between the planes of atoms N(9), C(10), C(12), C(13) and C(1); C(2), C(4), C(6), C(7), C(14) is calculated as 81·2° instead of the ideal 70·5°. However, the mean of the eight valence angles under the arch of the double *cis*-decalin is 111·8°, which is not significantly different from the overall mean (111·3°), so the splaying is achieved principally by deformations of torsion angles.

A further source of nonbonded strain occurs between C(16)–H and the carbonyl group, C(5)=O(18). The distance between C(5) and C(16) is 2·94 Å (*cf.* 2·49 Å in the diamond skeleton). Figure 3 shows that this interaction has enlarged the three dihedral angles between the planes C(2)—(4); C(14), C(4), C(6), and C(7); C(14), C(7), C(8), C(15); and C(8), C(15), C(16) to 134·3, 111·8, and 131·4° instead of the ideal values of 125·3, 109·5, and 125·3°. In addition, the plane C(4)—(6) has been splayed a further 12·2°, and the carbonyl bond is bent out of this plane by yet another

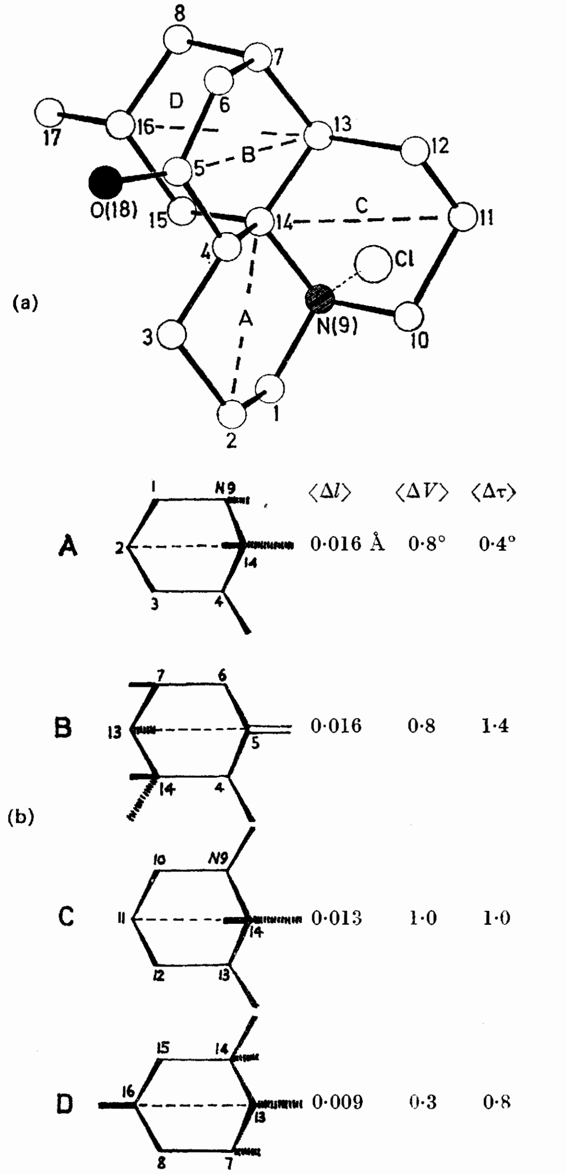

FIGURE 2 (a) The rings A—D and their pseudosymmetry diameters. (b) The approximate symmetry in each ring

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[15] 'Molecular Structures and Dimensions,' vol. A1, eds. O. Kennard *et al.*, 1972, Oesthoek, Utrecht, p. S2.

[16] H. P. Weber and T. J. Petcher, *J.C.S. Perkin II*, 1973, 2001.

9°. As a corollary to this, the mean of the six angles in the ring C(4)—(8), C(14)—(16) [excluding those at C(5) and C(16)] is **113·0(7)**°, which is fairly significantly larger than the overall mean (111·3°).

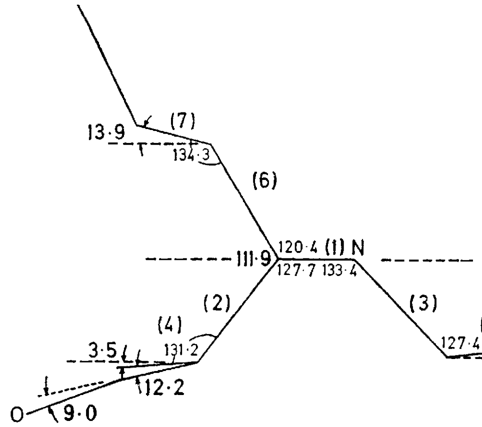

FIGURE 3 Angles between various best planes. Plane numbers are indicated by parentheses, and are defined in Table 5

Figure 2(b) gives details of the four rings. In each case there is marked symmetry about one diameter. It is most easily seen in the torsion angles, but is least obvious in the bond lengths. Each diagram shows the substituent bonds and the symmetry of these is most obvious in rings C and D. Ring D is also the most symmetrical if one considers all the criteria given with the diagram. Ring C, however, incorporates a nitrogen atom asymmetrically into the ring. Ring A, which also incorporates a nitrogen and has unbalanced substituents, nevertheless contrives to be the most symmetrical as far as torsion angles are concerned. Ring B is on almost all counts the least symmetrical. The diameter about which strain 'symmetry' exists is in every ring exactly that which one might expect as a result of the nonbonded interactions (see Figure 2).

Table 6 summarises the results of calculations on best planes and some of these are shown in Figure 3. This shows that the splaying has tilted the plane C(10)—(12) upwards, but a similar tendency for the plane C(2)—(6) has been more than counterbalanced by the pressure from ring D so that this plane tilts downward. Table 6 also shows that the splaying has had little effect on the coplanarity of the bridge atoms, C(1), N(9), C(14), C(13), C(7).

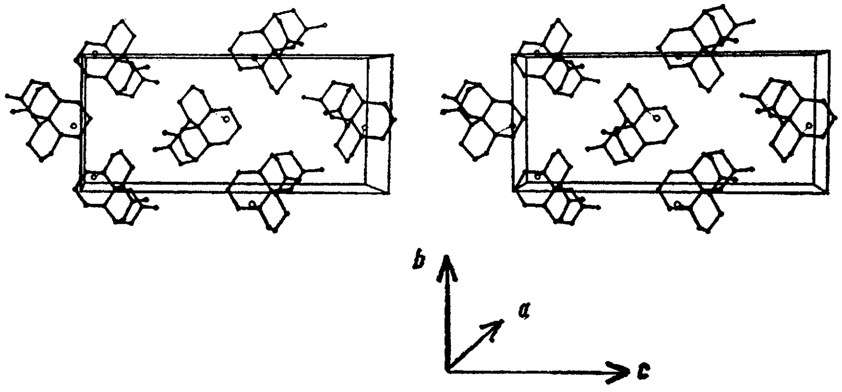

FIGURE 4 Stereopair showing the packing of the molecules

The conversion of lycopodine by means of $LiAlH_4$ into dihydrolycopodine (with OH axial to ring B) introduces extremely severe steric strain between H(16) and the new position of O(18), so the easy *trans*-elimination of the hydroxy-group [5] is explicable.

The packing of these molecules is depicted in the ORTEP [17] stereodiagram (Figure 4). The chloride ion lies **3·065** Å from the nitrogen atom and the N · · · Cl vector is nearly tetrahedrally related to the three N–C bonds. This is clearly a hydrogen bond: the N–H distance is **0·86** Å. A similar situation is found in DL-α-prodine hydrochloride [18] where N · · · Cl is **3·03** Å. The only other intermolecular contact $<$**3·5** Å is one of **3·36** Å between C(17) and O(18) in the molecule lying next up the *a* axis. This value is quite normal. The shortest other contact to chlorine is **3·53** Å to C(10) at $[x - \frac{1}{2}, \frac{3}{2} - y, 1 - z]$.

The chirality of this molecule, which is now set on a firm footing, matches that of three other lycopodium alkaloids (annopodine,[19] alopecurine,[20] and lycopecurine [21]) which have been reported without details as having been determined by *X*-ray anomalous dispersion by Masaki. This agreement obviously provides a firm basis for the chiralities of this whole group of alkaloids.

Crystallographic data for lycopodine are: $C_{16}H_{25}NO$, $M = 247$, space group $P2_12_12_1$, $a = 9{\cdot}0_7$, $b = 11{\cdot}1_5$, $c = 29{\cdot}4_5$ Å, $Z = 8$.

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