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The Structure of 5,6-Cyclopentenopyrido[3,2-α]carbazole, Lys-P-1, a Potent Mutagenic Product from the Dry Distillation of L-Lysine

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Abstract. $C_{18}H_{14}N_2$, monoclinic, $P2_1/a$, a = 13·388 (6), b = 18·273 (7), c = 5·216 (3) Å, β = 95·72 (2)°, Z = 4. The final R value was 0·04 including H atoms. The present study established the chemical structure of Lys-P-1 to be a derivative of pyridocarbazole.

Introduction. It has been shown that the pyrolysate of proteinous foods, proteins and amino acids exhibits high mutagenic activity (Nagao, Honda, Seino, Yahagi, Kawachi & Sugimura, 1977; Sugimura, Nagao, Kawachi, Honda, Yahagi, Seino, Matsushima, Shirai, Sawamura, Sato, Matsumoto & Matsukura, 1977). Since then, certain mutagenic principles have been extracted from the pyrolysis products of D,L-tryptophan, D,L-phenylalanine and L-glutamic acid (Sugimura, Kawachi, Nagao, Yahagi, Seino, Okamoto, Shudo, Kosuge, Tsuji, Wakabayashi, Iitaka & Itai, 1977; Kosuge *et al.*, 1978; Yamamoto *et al.*, 1978). A new potent mutagenic principle (Lys-P-1) has recently been isolated from the L-lysine pyrolysate. A preliminary paper describing the extraction, purification and the structure of this compound has been published (Wakabayashi *et al.*, 1978).

To elucidate the structure of Lys-P-1 and to obtain precise structural information, necessary for studying the mechanism of induction of mutation, we have undertaken the present X-ray crystallographic analysis.

The lattice constants and intensity data were obtained with a Philips PW 1100 diffractometer using Cu $K\alpha$ radiation monochromated by a graphite plate.

The θ–2θ scan technique was employed for the whole angular range up to $2\theta = 130°$. Background was measured at each end of the scan range for half the total scan time. 1556 reflexions were measured as being above the $2\sigma(I)$ level. Lorentz and polarization corrections were applied.

The crystal structure was determined by the direct method using *MULTAN* (Main, Woolfson & Germain, 1971) and refined by the block-diagonal least-squares method using the *HBLS* IV program (Okaya & Ashida, 1967).

The final R value was 0·043 including H atoms. Positional parameters are listed in Table 1.*

Discussion. The chemical structure of Lys-P-1 was determined as 5,6-cyclopentenopyrido[3,2-*a*]-carbazole (Fig. 1). The bond lengths and valency angles are shown in Fig. 2. The standard deviations are estimated as σ(C–C) = 0·004, σ(C–H) = 0·03 Å, and σ(C–C–C) = 0·2, σ(C–C–H) = 1·4 and σ(H–C–H) = 2·0°. In Table 2 the range of the bond lengths and their average values are listed for each kind of bond. The bond lengths and angles are compatible with the chemical structure.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34753 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates of Lys-P-1* ($\times 10^4$ *for non-hydrogen atoms and* $\times 10^3$ *for hydrogen atoms*)

Estimated standard deviations are given in parentheses.

	x	*y*	*z*
C(1)	1958 (2)	4852 (2)	12737 (5)
C(2)	2849 (2)	5237 (2)	13097 (6)
C(3)	3635 (2)	5092 (2)	11639 (6)
C(4)	3580 (2)	4547 (2)	9793 (6)
C(5)	2691 (2)	4145 (1)	9462 (5)
C(6)	1475 (2)	3350 (1)	8093 (5)
C(7)	912 (2)	2783 (1)	6762 (5)
C(8)	1259 (2)	2342 (2)	4836 (5)
C(9)	646 (2)	1815 (2)	3694 (5)
C(10)	−321 (2)	1732 (2)	4474 (5)
C(11)	−92 (2)	2678 (1)	7414 (5)
C(12)	−475 (2)	3136 (1)	9289 (5)
C(13)	−1515 (2)	3107 (2)	10162 (5)
C(14)	−1498 (2)	3710 (2)	12251 (5)
C(15)	−466 (2)	4087 (1)	12404 (5)
C(16)	93 (2)	3675 (1)	10509 (5)
C(17)	1092 (2)	3789 (1)	9953 (5)
C(18)	1872 (2)	4297 (1)	10863 (5)
N(1)	2445 (1)	3573 (1)	7777 (4)
N(2)	−692 (2)	2140 (1)	6259 (4)
H(C1)	134 (2)	497 (1)	1405 (5)
H(C2)	301 (2)	556 (1)	1478 (5)
H(C3)	429 (2)	542 (2)	1192 (5)
H(C4)	418 (2)	441 (1)	872 (5)
H(C8)	201 (2)	245 (1)	436 (5)
H(C9)	89 (2)	147 (1)	220 (4)
H(C10)	−80 (2)	132 (1)	370 (5)
H(C13)	−167 (2)	259 (1)	1084 (5)
H′(C13)	−202 (2)	320 (1)	856 (5)
H(C14)	−205 (2)	410 (1)	1183 (5)
H′(C14)	−166 (2)	348 (1)	1404 (5)
H(C15)	−52 (2)	462 (1)	1197 (5)
H′(C15)	−10 (2)	406 (1)	1434 (5)
H(N1)	290 (2)	329 (1)	701 (5)

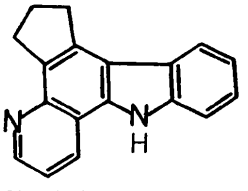

Fig. 1. Chemical structure of Lys-P-1.

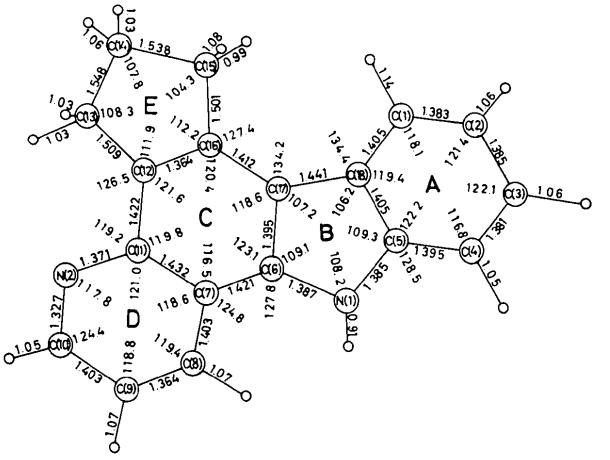

Fig. 2. Bond lengths (Å) and valency angles (°) in Lys-P-1.

Table 2. *The range of the bond lengths and their average values*

	Ring	Maximum	Minimum	Average	Mean deviation
$C(sp^2)$⋯$C(sp^2)$	*A*	1·405 Å	1·381 Å	1·392 Å	0·009 Å
	B	1·441	1·395	1·403	0·016
	C	1·432	1·364	1·408	0·019
	D	1·423	1·364	1·401	0·018
	E	1·364			
$C(sp^3)$–$C(sp^2)$	*E*	1·509	1·501	1·505	0·004
$C(sp^3)$–$C(sp^3)$	*E*	1·548	1·538	1·543	0·005
C⋯N	*B*	1·387	1·385	1·386	0·001
	D	1·371	1·327	1·349	0·022

Table 3. *Deviations of the atoms* (Å) *from the least-squares planes*

A ring		*B* ring		*C* ring	
C(1)	−0·001	C(18)	0·004	C(17)	0·008
C(2)	0·009	C(5)	−0·000	C(16)	−0·007
C(3)	−0·006	N(1)	−0·004	C(12)	−0·000
C(4)	−0·006	C(6)	0·006	C(11)	0·005
C(5)	0·014	C(17)	−0·006	C(7)	−0·003
C(18)	−0·011			C(6)	−0·004

D ring		*E* ring	
C(11)	−0·014	C(12)	0·004
N(2)	0·003	C(13)	−0·002
C(10)	0·005	C(15)	0·002
C(9)	−0·004	C(16)	−0·004
C(8)	−0·005	C(14)*	0·043
C(7)	0·012		

* Atoms not included in the least-squares calculation.

As in the mutagenic compounds Trp-P-1 (Itai & Iitaka, 1978) and Glu-P-1 (Yamaguchi, Iitaka, Shudo & Okamoto, 1979), which were found respectively in the pyrolysates of L-tryptophan and L-glutamic acid, the main part of the present molecule consists of a planar fused heterocyclic ring system. Unlike the previous structures, the present compound has two additional rings, *D* and *E*, fused to the *C* ring. Furthermore, the number of N atoms and their locations as well as the substituent groups indicate that the present structure may be classified as a different type of compound from Trp-P-1 and Glu-P-1. Recognition that Lys-P-1 is an isomer of ellipticine may be quite important, as the latter is also a pyridocarbazole and is known to act as an anticancer agent (Courseille, Busetta & Hospital, 1974).

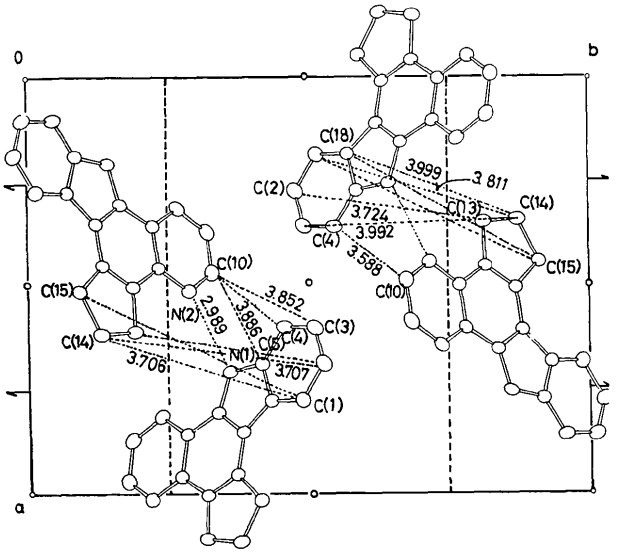

Fig. 3. Projection of the crystal structure of Lys-P-1 along the *c* axis.

The planarity of the molecule can be seen from Table 3, which lists the deviations of atoms from the least-squares plane. The atoms in ring *E* do not deviate significantly from the plane even though the ring contains three saturated methylenic C atoms; only a slight puckering of the *E* ring occurs.

The crystal structure is illustrated in Fig. 3 by the *c*-axis projection. The molecules are stacked along the *c* axis with a perpendicular separation of 3·541 Å. The inclination of the normal of the molecular plane to the *c* axis is 47·21°.

One type of hydrogen bond occurs which connects the N(1)—H group of ring *B* to the N(2) atom of ring *D*, binding the molecules along the *a* glide plane. The N(1)···N(2) distance is 2·989 (3) Å and H(N1)···N(2) is 2·12 (3) Å.

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Refinement of the Structure of Dopamine Hydrochloride

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Abstract. $C_8H_{12}NO_2^+.Cl^-$, orthorhombic, $Pbc2_1$, a = 10·421 (2), b = 11·105 (2), c = 7·936 (2) Å, Z = 4, D_m = 1·356 (2), D_c = 1·355 (1) Mg m^{-3}, μ(Mo $K\alpha$) = 0·325 mm^{-1}. The structure, which has already been solved, was refined by counter-measured data to R = 0·032. All H atoms were located and the average e.s.d. of the refined parameters decreased by two thirds compared to the previous investigation.

Introduction. In recent years a number of dopaminergic substances have been studied by X-ray diffraction at our department. The aim of this project is to elucidate

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