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THE ISOLATION OF SPERMIDINE BY DEGRADATION OF LUNARINE*

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RECENTLY, we have reported the formation of an amine by alkaline degradation,[1] and by acid hydrolysis[2] of the alkaloid lunarine ($C_{25}H_{31}O_4N_3$). We ascribed to this amine the molecular formula $C_5H_{14}N_2$ on the basis of the analysis of the hydrochloride. Further studies have shown that this formula is incorrect and have proved the identity of the amine with spermidine (I).

A B A A B B A

$$H_2N.CH_2.CH_2.CH_2.NH.CH_2.CH_2.CH_2.CH_2.NH_2$$

I

It was found that the gas chromatographic behaviour of the amine was similar to that of spermidine. The melting point of the amine hydrochloride was identical with that of, and showed no depression on admixture with, an authentic sample of spermidine trihydrochloride. Furthermore the infrared spectra of the hydrochloride, picrate, and chloraurate of the amine were

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* This letter should be regarded as the fourth paper in the series "Alcaloides du Lunaria biennis Moench" and the second part in the series "The Chemistry of Lunaria Alkaloids".

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1 P. Potier and J. Le Men, Bull. Soc. Chim. Fr. 456 (1959).

2 P. Bladon, R. Ikan, F. S. Spring and A. D. Tait, Tetrahedron Letters No. 9, 18 (1959).

TABLE 1

Salts of Amine Derived from Lunarine and of Spermidine

	Spermidine	Amine from lunarine	
	m.p.	m.p.	Analysis
Trihydrochloride	255-257° cf. 256-258° [4]	258°	Found: C, 32.8; H, 8.7; N, 16.4; Cl, 41.2. Calc. for $C_7H_{22}N_3Cl_3$: C, 33.0; H, 8.7; N, 16.5; Cl, 41.8%
Picrate	210-212° cf. 210-212° [3,4]	210-212°	Found: C, 35.9; H, 3.45; N, 19.8. Calc. for $C_{25}H_{28}N_{12}O_{21}$: C, 36.1; H, 3.4; N, 20.2%
Chloroaurate	207-212° dec. cf. 220-222° [3] 219-220.5° [4]	207-212° dec.	Found: Au, 50.2. Calc. for $C_7H_{22}N_3Cl_{12}Au_3$: Au, 50.7%.

[3] H. W. Dudley, O. Rosenheim and W. W. Starling, Biochem. J. 21, 97 (1927).

[4] M. Danzig and H. P. Schultz, J. Amer. Chem. Soc. 74, 1836 (1952).

identical with those of the corresponding salts of spermidine. (See Table 1). The molecular weight of the amine determined by mass spectrometry was 145 (Calc. for $C_7H_{19}N_3$:145).

Difficulty has been encountered in reconciling the proton magnetic resonance spectrum of the amine hydrochloride with any structure based on $C_5H_{14}N_2$. The chief features of this spectrum (obtained at 60 mc/s in D_2O) are two groups of signals centred at 100 (A) and 180 c/s (B) (relative to the HDO peak); the ratio of the areas of these two groups (A:B) is 4:3, which indicates that the total number of hydrogens bonded to carbon is a multiple of 4 + 3. The structure of spermidine agrees well with these results: the signal at 100 c/s (relative area 4) arises from the hydrogens of the four CH_2 groups attached to nitrogen atoms, while the signal at 180 c/s (area 3) is due to the hydrogens of the three CH_2 groups attached only to carbon. (These assignments are indicated in the formula of spermidine, I.)

This is the second isolation of the typical animal base, spermidine, by degradation of a plant alkaloid: in the last few months, Baumann et al.[5] have encountered spermidine as a degradation product of the alkaloid palustrine, for which they suggest a macrocyclic structure. It seems probable that also in lunarine, which is a monoacidic secondary amine, there is present a macrocyclic system, the two terminal nitrogens of the spermidine moiety being attached by amide links to the rest of the molecule.

We are indebted to Dr. LeRoy Johnson of Varian Associates, Palo Alto, California, for the n.m.r. spectrum of the amine hydrochloride, and to Dr. R.I. Reed and Mr. J.M. Wilson of Glasgow University for the mass spectrum of the amine.

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[5] C.G. Baumann, W. Dietsche and C.H. Eugster, Chimia 14, 85 (1960); cf. Angew. Chem. 72, 270 (1960).