The Aconite Alkaloids. XXXIV[1]*. On Lucidusculine. Part IV*[2]

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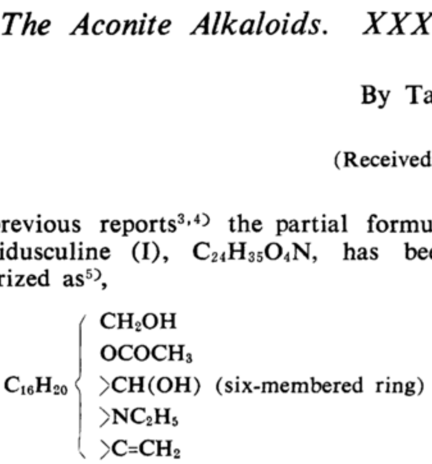
In previous reports[3,4] the partial formula of lucidusculine (I), $C_{24}H_{35}O_4N$, has been summarized as[5],



$$C_{16}H_{20}\begin{cases} CH_2OH \\ OCOCH_3 \\ >CH(OH)\ \text{(six-membered ring)} \\ >NC_2H_5 \\ >C{=}CH_2 \end{cases}$$

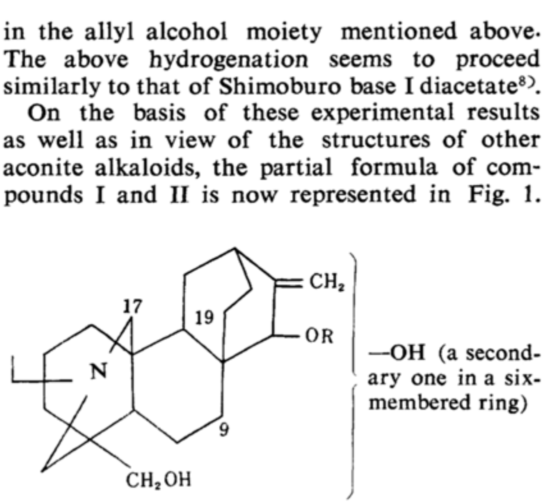
(I)

Moreover, luciculine (II), $C_{22}H_{33}O_3N\cdot H_2O$, which is yielded from compound I by hydrolysis and hence is a sort of trihydric amino alcohol, has been shown to possess an allyl alcohol moiety in its six-membered ring[6].

On the other hand, on dehydrogenation of compound I, phenanthrene and its homologues were obtained by Suginome and Kakimoto[7] in this laboratory.

Under the same conditions as in the case of isomerization of compound II to isoluciculine (III)[6], compound I was found not to isomerize. Instead, a certain compound IV was formed. This compound did not crystallize. It seemed to be a dihydro compound. In the infrared spectrum, compound IV gave no band characteristic of a ketone carbonyl group in a six-membered ring near 5.8 μ but it did give a band characteristic of an ester carbonyl group. No absorption band near 11 μ, indicative of a terminal methylene group, was observed in the spectrum. On hydrolysis of compound IV by alcoholic potassium hydroxide, an amorphous base V was obtained. In the infrared region, this base showed no band near 5.7~5.8 μ, indicating that carbonyl group, either ester or ketone, was quite absent. The spectrum also showed that no band characteristic of a terminal methylene group near 11 μ existed. This fact may show that the acetylated hydroxyl group in compound I is the secondary one involved in the allyl alcohol moiety mentioned above. The above hydrogenation seems to proceed similarly to that of Shimoburo base I diacetate[8].

On the basis of these experimental results as well as in view of the structures of other aconite alkaloids, the partial formula of compounds I and II is now represented in Fig. 1.



(I) R=Ac
(II) R=H

Fig. 1.

Lucidusculine has been assumed to have a hexacyclic structure[9]. Considering the structures of hypogenavine[10], kobusine[11], ignavine[12], hetisine[13] and songorine[14], the existence of the C-17—C-19 or C-17—C-9 bond seems to be reasonable. Moreover, to complete the structure of compound I, it is necessary to confirm the position of an indefinite secondary hydroxyl group (see Fig. 1).

Experimental

Hydrogenation of Lucidusculine (I) with Pd-C. —Lucidusculine (0.3 g.) was dissolved in 15 cc. of methanol and hydrogenated with 10% palladium-carbon (0.2 g.) at room temperature for 4.5 hr. After removal of palladium-carbon, the solution was evaporated to dryness. On treatment with methanol, the residue was not crystallized. The infrared absorption spectrum in nujol had no peak attributable to a terminal methylene group but

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[1] This constitues a part of a series entitled "The Aconite Alkaloids" by H. Suginome. Part XXXIII: cf. Ref. 4).

[2] XXXIII of this series corresponds to part III of "On Lucidusculine".

[3] T. Amiya, This Bulletin, **30**, 677 (1957).

[4] T. Amiya, ibid., **33**, 644 (1960)..

[5] The partial formula of I was presented in a previous report[3], as $C_{17}H_{20}$ erroneously, but this should be corrected.

[6] T. Amiya, This Bulletin, **32**, 421 (1959).

[7] H. Suginome and S. Kakimoto, ibid., **32**, 352 (1959).

[8] T. Sugasawa, *Pharm. Bull.*, **4**, 6 (1956).

[9] H. Suginome, T. Amiya and T. Shima, This Bulletin, **32**, 824 (1959).

[10] S. Sakai, *Chem. Pharm. Bull.*, **6**, 448 (1958).

[11] M. Natsume, ibid., **7**, 539 (1959).

[12] E. Ochiai and T. Okamoto, ibid., **7**, 556 (1959).

[13] A. J. Solo and S. W. Pelletier, *J. Am. Chem. Soc.*, **81**, 4439 (1959).

[14] E. Ochiai, T. Okamoto, S. Sakai, T. Sugasawa and T. Onouchi, *Chem. Pharm. Bull.*, **7**, 542 (1959).

showed the presence of hydroxyl groups (2.92~2.94 μ) and an acetoxyl group (5.80 and 8.10 μ).

Hydrolysis of Compound IV. — A solution of compound IV (0.05 g.) and potassium hydroxide (0.15 g.), dissolved in 2 cc. of ethanol and a drop of water, was heated for 1.5 hr. After removal of the solvents, the residue was washed with water. On treatment with methanol, it was not crystallized. The infrared absorption spectrum in nujol had no peak attributable to a terminal methylene group but showed the presence of hydroxyl groups (2.97 μ).

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