The Aconite Alkaloids. XXXV[1]. *On Lucidusculine. V*[2]

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Lucidusculine (I) ($C_{24}H_{35}O_4N$) is a monoacetate, and gives on hydrolysis[5,6], a trihydric amino alcohol, luciculine (II) ($C_{22}H_{33}O_3N \cdot H_2O$). In contact with Pd-carbon in the presence of hydrogen and methanol, compound II isomerized to a ketone base, isoluciculine (III) ($C_{22}H_{33}O_3N \cdot 1/2H_2O$), m. p. 131～136°C. The infrared spectrum of compound III shows a band at $1716\,cm^{-1}$ due to a ketone carbonyl group in a six-membered ring, but lacks the bands characteristic of a terminal methylene group, corresponding to the bands (1642 and $907\,cm^{-1}$) of compound II[6,7]. It has already been shown that a terminal methylene group exists in compound II[5]. The ultraviolet absorption spectrum of compound III has a maximum (λ_{max} 302 mμ, log ε 1.4), indicating the presence of a ketone carbonyl group and, therefore, is apparently distinguishable from the ultraviolet spectra[6] of compounds I and II, which show only end absorption (Fig. 1). From these considerations regarding the spectra it may be reasonably concluded that in this isomerization a ketone carbonyl group is newly formed with simultaneous disappearance of a terminal methylene group. Therefore, this reaction seems to proceed similarly to those of Shimoburo base I[8], hypognavine[9], kobusine[10] and napellonine[11,*] as follows:

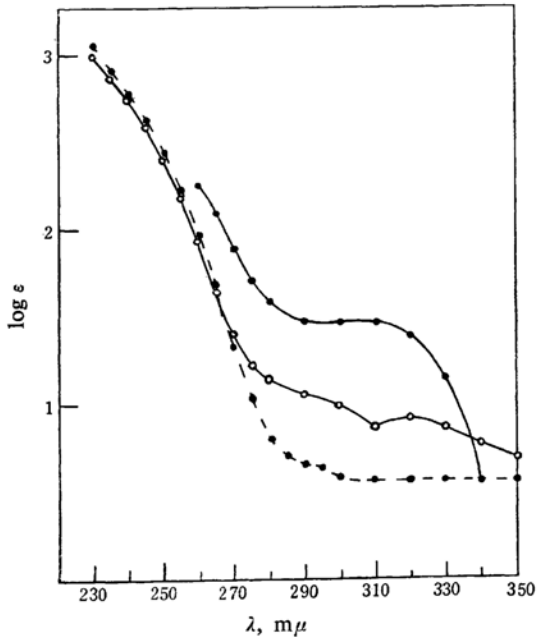
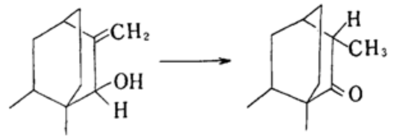


Fig. 1

—○—○— Lucidusculine (I)
--●--●-- Luciculine (II)
—●—●— Isoluciculine (III)



(II) (III)

Fig. 2

On the basis of the observation of this process, the presence of an allyl alcohol moiety constituting a six-membered ring may be claimed in the structure of compound II as shown in Fig. 2.

A report regarding bromoanhydrolucidusculine hydrobromide (IV) has been published[7]. Recently, it has been found that compound IV decomposed spontaneously on standing for about two years. Hence, a freshly prepared sample, m. p. 195°C (decomp.)**, was analyzed once more, and found to have composition $C_{24}H_{37}O_8NBr_2$. The infrared spectrum is nearly identical with that previously described[7]. The detailed data of this compound may be reported latter. The determinations of bromine and

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[1] The present paper constitutes Part XXXV of the series entitled "The Aconite Alkaloids" by H. Suginome and Part XXXIV[3] corresponds to "On Lucidusculine. IV".

[2] A preliminary note partly describing the matter of the present paper appeared in this Bulletin[4].

[3] T. Amiya, This Bulletin, 33, 1175 (1960).

[4] T. Amiya, ibid., 32, 421 (1959).

[5] H. Suginome, T. Amiya and T. Shima, ibid., 32, 824 (1959).

[6] T. Amiya, ibid., 32, 1133 (1959).

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

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

[9] S. Sakai, ibid., 5, 1 (1957).

[10] T. Okamoto, ibid., 7, 44 (1959).

[11] K. Wiesner, Z. Valenta, J. F. King, R. K. Maudgal, L. G. Hamber and S. Itō, *Chemistry & Industry*, **1957**, 173.

* It has been shown that napellonine is identical with Shimoburo base I[12].

[12] K. Wiesner, S. Itō and Z. Valenta, *Experientia*, 14, 167 (1958).

** The melting point given in the previous paper[7] should be revised to this.

specific rotation reported in the previous paper⁷⁾ were made by using a sample, freshly prepared then, and the ultraviolet absorption spectrum was measured with the same material once dried at 110°C in vacuo.

Experimental

Isoluciculine (III).—To luciculine (300 mg.) dissolved in 15 cc. of methanol, 10% Pd-C (200 mg.) was added. The mixture was shaken under H_2-atmosphere for 2.5 hr. The absorption of H_2 proceeded rapidly and practically stopped within 15 min.; in total about 30 cc. of H_2 was absorbed. After elimination of the catalyst the solvent was removed, and the residue was crystallized from methanol. The substance melted at 131∼136°C. The ultraviolet absorption spectrum of the base in methanol showed $\lambda_{\max}$ 302 mμ, log ε 1.4 (Fig. 1). The infrared absorption spectrum in Nujol had no peak attributable to a terminal methylene group but showed the presence of hydroxyl groups (3375 cm^{-1}) and a ketone carbonyl group (1716 cm^{-1}).

Found: C, 71.22; H, 9.33; N, 3.32; H_2O, 2.33. Calcd. for $C_{22}H_{33}O_3N\cdot 1/2H_2O$: C, 71.72; H, 9.30; N, 3.80; H_2O, 2.44%.

Bromoanhydroluciducsuline Hydrobromide (IV).—A freshly prepared sample showed m. p. 195°C (decomp.). The infrared absorption spectrum in Nujol showed the presence of hydroxyl groups (3410∼3360 cm^{-1}), and acetoxyl group (1724 and 1235 cm^{-1}) and water (1628 cm^{-1}). It showed no peak attributable to a terminal methylene group.

Found: C, 45.57, 45.57; H, 5.85, 6.08. Calcd. for $C_{24}H_{37}O_8NBr$: C, 45.92; H, 5.94%.

Summary

Luciculine (II) was isomerized to a ketone base, isoluciculine (III), and this fact shows the presence of an allyl alcohol system in the structure of compound II. The previous report concerning bromoanhydroluciducsuline hydrobromide (IV) was in part revised.

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