Some Kinds of Reaction Behavior of Lucidusculine

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Some reactions concerning lucidusculine¹⁾ (I), an alkaloid from Aconitum lucidusculum Nakai, have been investigated in this Laboratory. The methods are here communicated. Oxidation of I by 3% hydrogen peroxide gave lucidusculine N-oxide (II) d. p. 191°C (Found: C, 65.94; H, 8.37; H_2O_1 , 3.31. Calcd. for $C_{24}H_{35}O_5N\cdot H_2O: C_1$ 66.18; H, 8.56; H₂O, 4.13%). Also oxidation of I by perbenzoic acid yielded a compound (III), d. p. 200°C, $[\alpha]_{D}^{15}$ -101° (CH₃OH) (Found: C, 65.30; H, 8.53%), identical (analysis, d.p. and methods of formation) with compound II. Reduction of III with zinc and hydrochloric acid regenerated substance I. Compound III afforded anhydrous compound (IV), when reserved in a desiccator, d. p. 205°C(Found; C, 69.32; H, 8.27. Calcd. for $C_{24}H_{35}O_5N$: C, 69.03; H, 8.45). Dehydration of III with 1% potassium chromate gave dehydrolucidusculine (V), m. p. 173-175°C (Found: C, 72.38; H, 8.75. Calcd. for $C_{24}H_{33}O_4N$: C, 72.15; H, 8.33%). Oxidation of I with N-bromosuccinimide gave a compound(VI), m. p. 175-180°C (Found: C, 71.51; H, 8.41%), identical (analysis and mixed m. p.) with compound V. Bromination of I with bromine in methanol gave bromoanhydrolucidusculine (VII), d.p. 210°C (Found: C, 50.02; H, 6.74; Br, 29.70; H₂O, 5.5. Calcd. for $C_{24}H_{32}O_3NBr \cdot HBr \cdot 2H_2O$: C, 49.73; H, 6.43; Br, 27.57; H_2O , 6.2%). The u.v. absorption of compound VII showed no λ max. at wavelengths 210-340 m μ . Oxidation of I with chromic anhydride in pyridine gave monocarboxylic acid (VIII), which showed neither definite m, p. nor definite d. p. (Found: C, 54.22, 54.60; H, 7.88, 7.69; N, 3.05. Calcd. for $C_{24}H_{31}O_5N\cdot 6H_2O$: C, 55.26; H, 8.31; N, 2.68%). In the infrared region the compound VIII showed a strong absorption near 5.85 μ , indicating the presence of the keto group. Methylation of VIII with diazomethan gave methyl ester (IX), which showed neither definite m.p. nor definite d.p. (Found: C, 57.01; H, 7.70. Calcd. for $C_{25}H_{33}O_5N \cdot 5H_2O$: C, 58.00; H, 8.37%). Because of its low yield and difficult purification, the analysis of IX led to only

an approximate agreement. Since the presence of the terminal methylene group has already been confirmed²⁾ in I, the partformula of I may be tentatively summarized as,

$$\begin{array}{c} CH_{2}OH \\ OCOCH_{3} \\ > CH(OH) \\ > N-C_{2}H_{5} \\ > C=CH_{2} \end{array}$$

Further work is in progress and will be published later. The author is grateful to Professor Harusada Suginome, President of Hokkaido University, for his unfailing kindness in encouraging this work, and to Professor Shinichiro Fujise, Tohoku University, for his kindness in making the material available.

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¹⁾ R. H. F. Manske and H. L. Holmes, "The Alkaloids", Vol. IV, Academic Press Inc., New York, (1954), p. 287.

²⁾ T. Amiya and T. Shima, read before the 7th Annual Meeting of the Chemical Society of Japan held in Tokyo, April, 1954.