*On Lucaconine**

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An alkaloid, lucaconine (I) ($C_{24}H_{39}O_7N$), was first isolated from the roots of *Aconitum luciduscul*um, Nakai by Suginome et al.[1,2] in this Laboratory. Moreover, Furusawa[3] has studied the degradation reactions of compound I. The present authors have further investigated the degradation reactions.

Oxidation of compound I with chromium trioxide-pyridine complex yielded neutral products, oxolucaconine (II)[3] ($C_{24}H_{37}O_8N.\ 1^3/_4H_2O$), oxolucaconinone-II (III), m. p. 218°, λ_{max} 298 mμ, log ε 1.9 (*Anal.* Found: C, 62.31; H, 7.64; OCH_3, 18.22. Calcd. for $C_{24}\ H_{35}O_8N$: C, 61.92; H, 7.58; OCH_3, 19.99%) and oxolucaconinedione (IV)[3] ($C_{24}H_{33}O_8N$). Compound III showed a lactam carbonyl band at 6.15 μ and a six-membered ketone carbonyl band at 5.83 μ in the infrared spectrum**.

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1) H. Suginome, S. Kakimoto, J. Sonoda and S. Noguchi, *Rroc. Japan Acad.*, **22**, 122 (1946).

2) H. Suginome and S. Furusawa, in preparation.

3) S. Furusawa, in preparation.

** All infrared spectra were measured in nujol mulls.

To the previously obtained experimental results[3] and the observations so far recorded, the partial formula of I may be extended as follows:

$$C_{15}H_{19}\begin{cases}(OCH_3)_3\\(>COH)_2\\>CHOH\ \text{(five-membered ring)}\\>CHOH\ \text{(six-membered ring)}\\>NC_2H_5\end{cases}$$

Lucaconine.

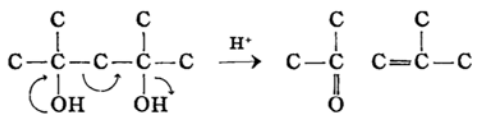
Next, oxidation of a naturally occurring base, monoacetyllucaconine (V)[2] ($C_{26}H_{41}O_8N$), with chromium trioxide-pyridine complex, followed by hydrolysis, afforded compound III. This fact shows that an acetylated hydroxyl group in compound V is the secondary one attached to a carbon atom in a five-membered ring.

It was reported that on treatment of each of compound I or its derivatives, except compound IV, with acetyl chloride, one molecule of water was lost and an anhydro-compound was produced[3].

Anhydrodiacetyllucaconine (VI)[3] ($C_{28}H_{41}O_8N$), obtained by the treatment of lucaconine (I) with acetyl chloride, showed carbonyl bands at 5.77 and 5.81 μ due to ester carbonyl groups and a ketone carbonyl group newly formed by dehydration, but no hydroxyl band in the infrared spectrum.

On hydrogenation over platinum in acetic acid, compound VI absorbed one mole of hydrogen and yielded anhydrodihydrodiacetyllucaconine (VII), m. p. 175° (*Anal.* Found: C, 64.42; H, 8.03; OCH_3, 17.54. Calcd. for $C_{28}H_{43}O_8N$: C, 64.47; H, 8.31; OCH_3, 17.85%), showing carbonyl bands at 5.77 and 5.93 μ due to the ester carbonyl groups and the ketone carbonyl group; no hydroxyl band appeared in the infrared spectrum. On hydrolysis, compound VII splits off two moles of acetic acid to give anhyrodihydrolucaconine (VIII), m.p. 210° (*Anal.* Found: C, 65.98; H, 9.11. Calcd, for $C_{24}H_{39}O_6N$: C, 65.87; H, 8.98%). The infrared spectrum of compound VIII showed a band at 5.92 μ characteristic of a ketone carbonyl group. On reduction of compound VIII by lithium aluminum hydride, followed by acetylation with acetic anhydride in pyridine, anhydrodihydrotriacetyllucaconinol (IX) yielded, m. p. 130~133° (*Anal.* Found: C, 64.19; H, 8.62; OCH_3, 19.66; $COCH_3$, 20.18. Calcd. for $C_{30}H_{47}O_9N$: C, 63.69; H, 8.38; OCH_3, 18.23; $COCH_3$, 22.83%) showing neither keton carbonyl band near 5.92 μ nor hydroxyl band in the infrared spectrum. On reduction of compound VI with lithium aluminum hydride, anhydrolucaconinol (X), m.p. 185~190° (*Anal.* Found: C, 66.22; H, 8.74; OCH_3, 20.31. Calcd. for $C_{24}H_{39}O_6N$: C, 65.87; H, 8.98; OCH_3, 21.25%) was given, showing no ketone carbonyl band in the infrared spectrum. On treatment of compound III with acetyl chloride, followed by hydrolysis and further oxidation by chromium trioxide-pyridine complex, anhydrooxolucaconinedione (XI) ($C_{24}H_{31}O_7N$) was produced. This had previously been obtained from VI through two steps[3].

These experiments indicate that in each compound, VI and XI, obtained by treatment with acetyl chloride both a ketone carbonyl group and a double bond were formed with elimination of one mole of water, and, moreover, that this dehydration took place between the two tertiary hydroxyl groups. This dehydration reaction seems to be one of 1—3 cleavages[4] and the following mechanism may be shown.



Wolf-Kishner reduction of lucaconinone-I (XII) ($C_{24}H_{37}O_7N$), which was previously prepared[3] and showed a five-membered ketone carbonyl band at 5.72 μ, gave deoxylucaconinone-I (XIII), m. p. 165° (*Anal.* Found: C, 66.16; H, 8.96; OCH_3, 19.25. Calcd. for $C_{24}H_{39}O_6N$: C, 65.87; H, 8.98; OCH_3, 21.27%), showing no band characteristic of the ketone carbonyl group in the infrared spectrum. Treatment of compound XIII with acetyl chloride, followed by hydrogenation over platinum in acetic acid, gave anhydrodihydromonoacetyldeoxylucaconinone-I (XIV), m. p. 84~90° (*Anal.* Found: C, 67.41; H, 9.26; OCH_3, 21.58; $COCH_3$, 10.36. Calcd. for $C_{26}H_{41}O_6N$: C, 67.36; H, 8.91; OCH_3, 20.08; $COCH_3$, 9.28%), showing carbonyl bands at 5.79 and 5.93 μ due to an ester carbonyl and a ketone carbonyl group formed by dehydration but no hydroxyl band in the infrared spectrum.

On the other hand, it was previously shown that treatment of compound I with acetyl chloride gave the anhydro-compound VI with loss of a mole of water, and that, on the contrary, the same treatment of compound IV, gave monoacetyloxolucaconinedione (XV) [$C_{24}H_{32}O_8N(COCH_3)$] without elimination of water[3].

On the basis of the above-mentioned experimental results, it may be shown that whilst on treatment of each of compounds I, III and XIII, which contained no five-membered ketone carbonyl group, with acetyl chloride, a mole of water was lost, on the same treatment of compound IV water was not lost. Accordingly, it may be reasonably concluded that dehydration by acetyl chloride occurs in such a case that a secondary hydroxyl group attached to the carbon atom in the five-membered ring is present or substituted for hydrogen atom, and that dehydration does not occur on

4) S. Archer, T. R. Lewis and B. Zenitz, *J. Am. Chem. Soc.*, **80**, 958 (1958).

the contrary in such a case that the above hydroxyl group is converted into a ketone carbonyl group.

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