methylthio-5-pyrrolealdehyde (m.p. 105–106°, τ_{CHO} = 0.69, τ_3 = 3.78, τ_4 = 3.12, τ_{SCH} = 7.59 p.p.m., J_{34} = 3.8 c/s. *Anal.* Calcd. for C_6H_7NOS C, 51.04; H, 4.99; N, 9.92; S, 22.71: Found: C, 51.41; H, 5.15; N, 10.08; S, 22.56), thus giving further evidence that the original methylthiopyrrole is the 2- isomer. Additional evidence against preferential β-thiocyanation in pyrroles is obtained from the fact that 2-methylpyrrole yields 5-thiocyano-2-methylpyrrole (m.p. 65.5–66°, τ_3 = 4.13, τ_4 = 3.56 p.p.m., $J_{CH_3\text{-}3}$ = 0.80, $J_{CH_3\text{-}4}$ = 0.35, J_{34} = 3.55 c/s. *Anal.* Calcd. for $C_6H_6N_2S$: C, 52.15; H, 4.38; N, 20.28; S, 23.19: Found: C, 52.22; H, 4.39; N, 20.21; S, 22.86:) upon thiocyanation with cupric thiocyanate, the NMR evidence for its structure being based on the values of the chemical shifts and ring-coupling constants, in addition to the side-chain couplings.[3]

Since the structure of III is proved beyond any doubt by Snyder *et al.*[1,9] and since it is very improbable that any rearrangement occurred in the transformation of the thiocyanopyrrole to methylthiopyrrole or (pyrrolylthio)acetic acid, the discrepancy between our results and those of Matteson and Snyder regarding the structure of the thiocyanopyrrole must be ascribed to a rearrangement during the cyclization of (2-pyrrolylthio)acetic acid with polyphosphoric acid to III. Rearrangements during treatment with polyphosphoric acid, although not analogous to that found here, have been observed by others.[10,11]

A detailed account of the observations reported here will be published in *Arkiv Kemi*.

Acknowledgments. Financial support from the Swedish Natural Science Research Council and from the Swedish Technical Research Council is acknowledged.

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Received April 17, 1961

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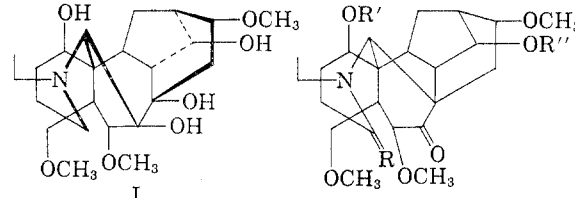
On Anhydrodiacetyllucaconine (Diacetyldelcosine,[1] M.P. 159–161°) and Its Derivatives

Sir:

Previously, it was shown that an aconite alkaloid, lucaconine (I) ($C_{24}H_{39}O_7N$), gave anhydrodiacetyllucaconine (II) ($C_{28}H_{41}O_8N$) on treatment with acetyl chloride.[4] Compound II has been found to have a ketone carbonyl group formed with elimination of one mole of water, and to absorb one mole of hydrogen without reduction of the carbonyl group.[5] Moreover, it has been shown that this dehydration takes place between two tertiary hydroxyl groups of compound I.[5]

On the other hand, on the basis of the biogenetical viewpoint as well as experimental results, Marion and his co-workers[6–8] have pointed out that delcosine[1] (lucaconine) (I) probably possesses the same carbon-nitrogen nucleus as lycoctonine, and also that this base is represented by the structure I shown below. In the belief that their conclusions



I

II. R = H_2, R′ = R″ = Ac
III. R = O, R′ = R″ = H

are quite reasonable, the present authors now would like to propose structures II and III for anhydrodiacetyllucaconine[4] and anhydrooxolucaconine (III),[4] respectively. Compound III has previously been obtained from both compound II and oxolucaconine through two steps.[4] The mechanism of the above dehydration is considered to be analogous to that of the dehydration of oxolycoctonine or demethyleneoxodelpheline.[9]

The ultraviolet absorption spectrum of compound III in methanol shows a maximum at 301 mμ (log ϵ 2.01) while compound II manifests a maximum at 237 mμ (log ϵ 3.20). The limiting structure IIa of compound II seems to give a good explanation of the marked difference between these two absorption bands. A similar phenomenon was observed and interpreted in the case of some delphinine and neoline derivatives.[10]

(1) It has been shown that lucaconine is identical with delcosine,[2] and therefore anhydrodiacetyllucaconine is identical with diacetyldelcosine (m.p. 159–161°) obtained by Marion *et al.*.[3] The name "lucaconine" should be revised to "delcosine."

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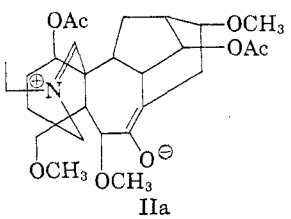
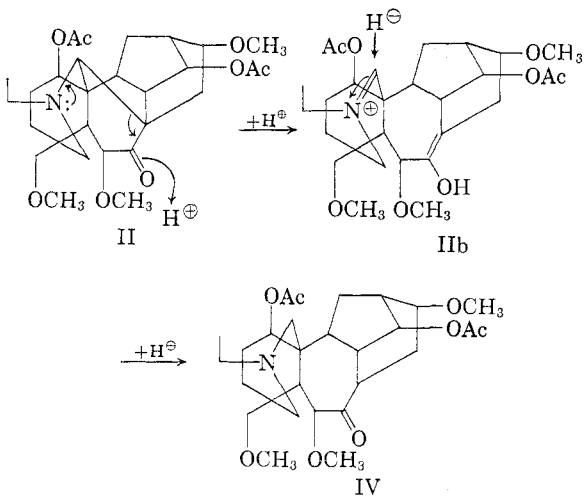


IIa

Furthermore, the formation of anhydrodihydrodiacetyllucaconine (IV) ($C_{28}H_{43}O_8N$)[5] from compound II by hydrogenation, may be expressed in the following way (II → IIb → IV) (Scheme A). The ultraviolet absorption spectrum of compound IV shows only end absorption. Compound III was recovered unchanged after being subjected to the conditions leading to the hydrogenation of compound II.



Scheme A

Acknowledgment. The authors are grateful to Professor Harusada Suginome, President of Hokkaido University, for his unfailing kindness in encouraging this work.

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Preparation of α-Diazo Ketones

Sir:

The preparation of α-diazo ketones by the oxidation of the monohydrazones of α-keto aldehydes or α-diketones has long been known.[1] The oxidizing agent most frequently used has been mercuric oxide,[1] often in the presence of bases[2]; silver oxide,[3] "mercuric acetamide,"[4] and mercuric trifluoroacetate[5] have also been used. An excellent variant of this method has been developed by Cava, Litle and Napier,[6] who prepared α-diazo ketones by the action of sodium hydroxide on the monotosylhydrazones of α-diketones. We now report on two new methods for the oxidation of the monohydrazones of α-diones which appear to have considerable general utility.

(i) "Activated" manganese dioxide[7] rapidly oxidizes the hydrazones in chloform solution to the corresponding α-diazo ketones in high yield. In a typical experiment 1.00 g. of 1-mesitylglyoxal 2-hydrazone[8] was dissolved in 15 ml. of chloroform (reagent grade) and to the solution was added 1.5 g. of "activated" manganese dioxide; the mixture was stirred for 1 hr. at room temperature, with initial cooling to abate the exothermic reaction. It was then filtered and the solvent was evaporated to give a quantitative yield of 2-diazo-2′,4′,6′-trimethylacetophenone, m.p. 59–61° dec. The infrared spectrum of this product was indistinguishable from that of a recrystallized sample, m.p. 59–61° dec., of the authentic diazo ketone prepared by oxidation of the hydrazone with mercuric oxide.[8] The latter method gives a less pure crude product in 75% yield. Manganese dioxide has also been used for the preparation of 2-diazopropiophenone, 2-diazo-2′,4′,6′-trimethylpropiophenone, 2-diazo-2-phenylacetophenone (azibenzil), 3-diazo-2-butanone, 3-diazo-D-camphor, and 2-diazo-1,5,5-trimethylbicyclo[2.2.1]heptan-3-one from the corresponding hydrazones; the scale varied from 0.060 g. to 10 g. of hydrazone and the weight of manganese dioxide used was *ca.* 1.5 times that of the hydrazone. In every case the diazo ketone was obtained directly from the reaction mixture in 90–100% yield and was free from significant amounts of impurities as vouchsafed by its infrared spectrum.[9]

(ii) α-Diazo ketones may also be prepared by oxidation of the corresponding hydrazones in methanolic solution containing sodium hydroxide with calcium hypochlorite. In a typical experiment, 0.100 g. of D-camphorquinone monohydrazone[4] was dissolved in 5 ml. of methanol and 1 ml. of 0.05*M* aqueous sodium hydroxide was added, the solution was stirred with 0.250 g. of calcium hypo-

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