208. The Alkaloids of Ergot. Part IV. A Complex Group common to Ergotoxine and Ergotamine.

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VERY little is known of the relationship between ergotoxine, the specific alkaloid of ergot of rye, and ergotamine, an alkaloid possessing the same pharmacological action, found in certain grass ergots. The identity of pharmacological action, the similarity of the absorption spectra, and the general chemical properties of the two alkaloids suggest that the relationship is probably very close. Evidence based upon the formation of complex degradation products has hitherto been lacking, but it has now been found that both alkaloids when treated with alcoholic potassium hydroxide undergo degradation to the same crystalline base, ergine. This base, which was first prepared from ergotoxine and ergotinine (Part III; this vol., p. 763), has the formula $C_{17}H_{21}ON_3$ and constitutes approximately half the parent molecule. Both alkaloids must therefore be similar in respect of this portion of the molecule and the differences which exist between them are to be sought for in the remaining moiety. Ergotaminine, the isomeride of ergotamine, also gives ergine when treated in the same way and the yield of the base is the same in each instance. Evolution of ammonia during the course of the reaction also occurs with all four alkaloids.

EXPERIMENTAL.

Ergotamine or ergotaminine (5 g.) was treated with N-methylalcoholic potassium hydroxide as previously described (*loc. cit.*). The yield of ergine, crystallised from methyl alcohol, was the same as that from ergotoxine and ergotinine, viz., 0.5 g. The gaseous product of the reaction was absorbed in hydrochloric acid and converted into the chloroplatinate in each case [Found : Pt, 43.9, 44.0. Calc. for $(NH_4)_2PtCl_6$: Pt, 43.9%]. The crystallised base from each alkaloid frothed at about 135° and decomposed with blackening and evolution of gas at about 230° in the same way as ergine, and when mixed with the latter the mixture behaved similarly on heating. The base was recrystallised from dilute acetone and the identity with ergine was confirmed by determination of the specific optical rotation and by analysis. Ergine from ergotamine had $[\alpha]_{5461}^{90°}$ $+511^{\circ}; [\alpha]_{Hg \,yellow}^{90°} + 430^{\circ}$ (c in acetone, 1.29), the previously recorded values being $+514^{\circ}$ and $+432^{\circ}$ respectively (Found : C, 72.0; H, 6.7; N, 15.3. Calc. for $C_{17}H_{21}ON_3: C, 72.0;$ H, 7.5; N, 14.8; NMe, 10.2%). Ergine from ergotaminine had $[\alpha]_{5661}^{90°} + 513^{\circ};$ $[\alpha]_{Hg \,yellow}^{900} + 431^{\circ}$ (c in acetone, 1.17) (Found : C, 71.9; H, 6.9; N, 15.1; OMe, nil; NMe, 10.0%).

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