On Reduction of Agroclavine and Elymoclavine with Sodium and *n*-Butanol

Sir:

It is believed that agroclavine (I) gives two isomeric dihydro-derivatives by reduction of the double bond between carbon atoms 8 and 9 as in the case of elymoclavine¹⁾. However, as a matter of fact, the catalytic hydrogenation of this substance^{2,3)} merely yields one dihydro-derivative, which is identical with festuclavine (alkaloid "Y") (II).

Recently, we have studied the reduction of agroclavine with sodium and *n*-butanol in the hope that the supposed derivative would result. The reduction gave a reaction mixture from which a number of substances, viz., pyroclavine (III), costaclavine (IV) and a basic substance (V), not to speak of festuclavine (II), were isolated. The basic substance was crystallized from ethyl acetate, methanol or ethanol in prisms; m.p. 265–7° (uncorr. decomp.), $[\alpha]_D^{30} = +67^\circ$, $[\alpha]_{5461}^{30} = +99^\circ$ (c. 0.2 in pyridine), $[\alpha]_D^{30} = +112^\circ$, $[\alpha]_{5461}^{30} = +149^\circ$ (c. 0.2 in CHCl_3). *Anal.* Found: C, 80.90; H, 7.73; N, 11.70; N-CH_3 , 12.23. *Calcd.* for $\text{C}_{16}\text{H}_{18}\text{N}_2$: C, 80.62; H, 7.62; N, 11.76; N-CH_3 , 12.19%. It gave the color reactions of agroclavine and showed the UV.-spectrum typical of lysergic acid. It was insoluble in petroleum ether, sparingly soluble in ether, benzene, ethyl acetate, acetone, methanol and ethanol, but moderately soluble in chloroform and pyridine. Its solutions in organic solvents exhibited a marked fluorescence. It dissolved slightly in water, and readily in dilute acids. This basic substance exclusively yielded festuclavine (II) on catalytic hydrogenation, whereas, it afforded the same substance to-

gether with a considerable amount of costaclavine (IV) on the reduction with sodium and *n*-butanol. Moreover, the basic substance itself was obtained in excellent yield by treatment of agroclavine with hot sodium butylate. These facts indicate that the substance corresponds to 6,8-dimethyl-ergolene-(9) (V). We have therefore adopted the designation lysergine for this product.

It is naturally presumed that elymoclavine (VI), on reduction with sodium and alcohols, gives a certain lysergol as a product corresponding to lysergine, besides different dihydrolysergols. However, when elymoclavine was reduced with sodium and *n*-butanol by a similar procedure as in the case of agroclavine, an unexpected result was obtained. That is, the reduction gave agroclavine (I), festuclavine (II), pyroclavine (III), costaclavine (IV) and lysergine (V), as well as α - and β -dihydrolysergols (VII and VIII, respectively). In the meantime, it was ascertained that both α - and β -dihydrolysergols once occurred, could never suffer reduction of their alcohol groups to the methyls during the procedure. From this fact and from the result obtained in the reduction of agroclavine, it is evident that in the above reduction the following reactions have proceeded, thus giving the conclusion that the stereochemical constitutions of agroclavine (I), festuclavine (II), pyroclavine (III), costaclavine (IV), lysergine (V) and elymoclavine (VI) must be those as shown here.

At any rate, the present results give support to the previous presumption^{3,4)} that agroclavine must be produced by ergot fungus

1) S. Yamatodani and M. Abe, *This Bulletin (Communication)*, **19**, 94 (1955).

2) M. Abe, *Ann. Rep. Takeda Res. Lab.*, **10**, 145 (1951).

3) M. Abe and S. Yamatodani, *J. Agr. Chem. Soc. Japan (Communication)*, **28**, 501 (1954).

4) M. Abe, T. Yamano, Y. Kōzu and M. Kusumoto, Report at the Annual Meeting of Agr. Chem. Soc. Japan held at the University of Tokyo (April 5, 1952).

through elymoclavine, as well as our view⁵⁾ that like festuclavine, both pyroclavine and costaclavine are produced through agroclavine by the fungus.

5) M. Abe, S. Yamatodani, T. Yamano and M. Kusumoto, This Bulletin (Communication), **20**, 59 (1956).

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