Furoquinolines. VI. Establishment of the Linear Tricyclic Structures for Dictamine and Skimmiane.

The structures for dictamine (I) and skimmiane (II) were elucidated by Asahina, Ohta, and Inubuse, and by Asahina and Inubuse. In these investigations, the difference in the properties of dictannic acid (III) with the synthetic 2-methoxy-4-hydroxyquinoline-3-carboxylic acid (IV) led to the conclusion that the methoxyl group in the pyridine ring of (I) is situated in the 4-position, i.e. the linear tricyclic structure (I), but the accepted structure for (II) was based only on analogy. The structure of (II), therefore, has not been rigidly established as yet.

In the first paper of this series, it was shown that (I) and (II) are catalytically degraded with PtO₂ and hydrogen to yield 3-ethyl-carbostyril derivatives, (V) and (VI), respectively, the hydrogenolysis of the fused furan ring occurring in the 1,2-position. In Part IV, it was further concluded that the most appropriate structures for (V) and (VI) are 3-ethyl-4-methoxy and 3-ethyl-4,7,8-trimethoxy-α-quino-lone, respectively.

We made an attempt to synthesize (V) and (VI) from 3-ethyl-4-hydroxy-(VII) and 7,8-dimethoxy-3-ethyl-4-hydroxy-carbostyril (VIII) by methylation. When (VII) was methylated with diazomethane in ether, it gave a compound, m.p. 186°, corresponding to C₉H₉O₂N, which proved to be a monomethyl ether. It is insoluble in alkali solutions and gave no color with ferric chloride. From the experimental results on the methylation of 4-hydroxy-carbostyril with diazomethane, which was elaborated by Arndt et al., the compound thus obtained must be 3-ethyl-4-methoxy-carbostyril. This compound showed no depression in melting point on admixture with the specimen of the catalytic reduction product of (I).

Similarly, methylation of (VIII) with diazomethane yielded a monomethyl ether, m.p. 184°, which was quite identical with (VII) derived from (II). Consequently, it was established that the structures for dictamine and skimmiane are 4-methoxy- (I) and 4,7,8-trimethoxy-furo[2,3-b]quinoline (II), respectively, and not the angular structures indicated as (IX) and (X).

The details of these experiments will be published in the near future.

Tokyo College of Pharmacy
Kashiwa 2-Chome
Shinjuku-ku, Tokyo.

September 6, 1955.

2) Y. Asahina, T. Ohta, M. Inubuse : Ber., 63, 2045(1930).
3) Y. Asahina, M. Inubuse : Ber., 63, 2052(1930).