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Comments on the papers "The Synthesis of Samane (desoxysamanine) and 17ß-hydroxy-samane"[1] and "The total synthesis of Samanine"[2]

G.Habermehl and A.Haaf

Institut für Organische Chemie der Technischen Hochschule Darmstadt

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K.Oka und S.Hara recently reported the synthesis of the oxygen-free reduction product of cycloneosamandione, samane (= neosamane[3]), and in the subsequent paper, the synthesis of the salamandra alkaloid samanine[4]. Both papers cause us to make some remarks.

1. Samane is not (as mentioned) a "degradation product of samandarine" but of cycloneosamandione. Numerous attempts to get samane form samandarine via samanone or samanole failed[3].

2. We reported in a short communication already in 1968 the stereospecific synthesis of samane[5].
   We also reported in an earlier paper[5] that cycloneosamandione has the structure of 16.19-Dioxo-3-aza-A-homo-5ß.10ß-androstane. In the same paper we dealt with the total synthesis of cycloneosamandione.
   Thus the reports of Oka and Hara concerning the configuration of cycloneosamandione and samane are confirming only our results.

3. We also published the total synthesis of samanine[6].

4. Our suspicion that the sample of samanine, sent to us by Oka and Hara, was contaminated with small amounts of the 4-aza-isomere[7] was based on a comparison of its IR spectrum with the spectra of the 3-aza- und the 4-aza-compounds prepared by us. The sample of Oka und Hara furthermore was s slightly brownish but crystalline material. The natural samanine as well as the samples synthetized by us are colourless, crystalline materials which show no tendency to decompose even after a long period of storage. Nevertheless the mass spectrum of the compound prepared by Oka and Hara is identical with that of our samanine.

5. The statement that the separation "by chromatographic methods" of the 3-aza- and 4-aza-lactames was "so difficult that it was not applicable to the specific synthesis of samanine" is in this case cleary incorrect. It is true that the separation of both of the isomers mentioned above cannot be achieved on silica gel, but is possible by using Al_2O_3 "Merck", Type T[6,8], as we did in gram amounts.

REFERENCES

1) K.Oka and S.Hara, Tetrahedron Letters, No. 15, p.1189 (1969).

2) K.Oka and S.Hara, Tetrahedron Letters, No. 15, p.1193 (1969).

3) C.Schöpf und O.W.Müller, Liebigs Ann.Chem. 633, 127 (1960).

4) G.Habermehl in R.H.F.Manske "The Alkaloids", Vol.IX, p.427, Academic Press, New York, 1967.
G.Habermehl in "Progress in Organic Chemistry", Vol.VII, p.35, Butterworth, London, 1968.

5) G.Habermehl and A.Haaf, Z.Naturforsch. 23b, 1551 (1968).

6) G.Habermehl and A.Haaf, Liebigs Ann.Chem. 722, 155 (1969).

7) private communication to Prof.Hara.

8) G.Habermehl and A.Haaf, Liebigs Ann.Chem. 723, 181 (1969).