A NEW DIDEHYDRO DERIVATIVE OF THE MATRINE ALKALOIDS

Kh. A. Aslanov, U. N. Zainutdinov, Yu. K. Kushmuradov, and A. S. Sadykov

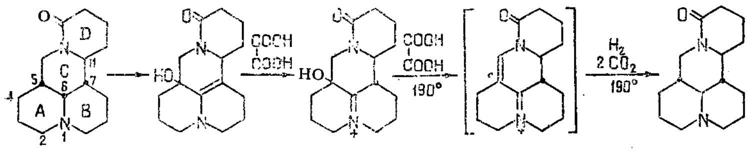
Khimiya Prirodnykh Soedinenii, Vol. 6, No. 3, p. 381, 1970

UDC 547.944/954

Two didehydro derivatives of the matrine alkaloids are known: sophoramine (11, 13-didehydromatrine) and isosophoramine (11, 13-didehydroallomatrine). The double bond in these substances involves one optical center and on hydrogenation they form matrine and allomatrine, respectively [1–3].

It was of interest to synthesize didehydro compounds of the matrine series with double bonds which involved three or four optical centers. The hydrogenation of such a compound could possibly form a series of isomers, as in the hydrogenation of 5-hydroxy-6, 7-dehydromatrine [4]. We obtained such a compound from matrine (I) via 5-hydroxy-6, 7-dehydromatrine (II). The dehydration of 5-hydroxy-6, 7-dehydromatrine with P_2O_5 by Bohlmann's method [4] led to a complex mixture of substances, while dehydration in p-xylene solution led to a didehydro derivative of matrine with a yield of 40%. When the latter was hydrogenated without isolation over Raney nickel, matrine was formed, and when it was hydrogenated by Adams' method matrine and allomatrine were formed. It is possible that in this case thermodynamically unstable isomers are obtained which are reconverted into the stable isomer under the conditions of the experiment.

The formation of matrine in this reaction is probably due to the fact that in the hydrogenation of the didehydro derivative of matrine hydrogen adds from the most favorable side of the reaction center. In Adams' hydrogenation, apparently, the matrine formed isomerizes into allomatrine [5]. The dehydration of 5-hydroxy-6, 7-dehydromatrine with oxalic acid gives allomatrine (V) with a yield of 25%. Apparently, in this reaction in addition to the formation of the dehydro product (IV), the oxalic acid decomposes into hydrogen and carbon dioxide and IV undergoes hydrogenation.



I II III IV V

As a result of this investigation, we assume that by selecting the conditions for the hydrogenation of the didehydro product a series of new stereoisomers of matrine can be obtained.

REFERENCES

1. A. P. Orekhov, Khimfarmprom., 5, 10, 1934.
2. Yu. K. Kushmuradov and A. S. Sadykov, ZhOKh, 32, 1699, 1962.
3. F. Rulko and N. F. Proskurnina, ZhOKh, 32, 1690, 1962.
4. F. Bohlmann, D. Rautz, and C. Arndt, Ber., 91, 2189, 1958.
5. E. Ochiai, S. Okuda, and H. Minato, J. Pharm. Soc. Jap., 72, 781, 1952.

26 December 1969

Lenin Tashkent State University