ERGOVALIDE – A NEW ALKALOID FROM ERGOT

A. N. Ban'kovskaya, V. I. Sheichenko,
A. I. Ban'kovskii, L. D. Vechkanova,
and V. S. Kabanov

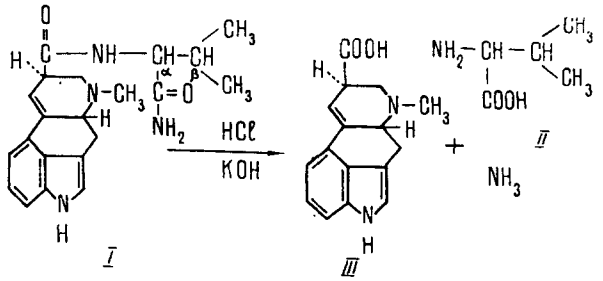
UDC 547.944/945

By preparative chromatography on Whatman No. 3 paper in the chloroform system we have isolated from ergot of the ergotoxine strain a new alkaloid with the composition $C_{21}H_{26}O_2N_4$, mp 152.5-154°C (from methanol), $[\alpha]_D^{20}$ −80.8° (c 0.47; chloroform), mol. wt. 366 (mass spectrometry) which we have called ergovalide (I). The base forms a hydrochloride with mp 273-275°C (decomp.).

The UV spectrum of ergovalide($\lambda_{max}^{CH_3OH}$ 315 nm; log ε 4.02; λ_{min} 270 nm, log ε 3.30) is identical with that of lysergic acid [1]; in the IR spectrum there are absorption bands at (cm^{-1}): 3430, 3330, 3230 (> NH), a broad band at 1670 (–C(=O)–N–), and bands at 1550 and 1475 cm^{-1} (–C=C– of an aromatic ring).

In the NMR spectrum ($CDCl_3$ solution) of ergovalide the signals of aromatic protons, of an olefinic proton, and of the protons of a methyl group attached to nitrogen appear in the same positions as in the spectrum of ergometrine. This shows the closeness of the structure of ergovalide to that of ergometrine. In addition to this, in ergovalide there are signals characteristic for a valine residue: $2CH_3$ – 0.80 and 0.90 ppm; CαH – 2.25 ppm; CβH – 4.43 ppm; NH – 7.7 ppm; $J_{C\alpha H=C\beta H}$ 5.1, J_{NHCH} 8.3 Hz.

In the mass spectra of ergovalide and of ergometrine there are intense molecular peaks: M^+ 366 and M^+ 325 (respectively), and a number of peaks of medium intensity with the same m/e values – 223, 221, 207, 196, 192, 167, 154, 111 – which shows the similarity of their structures and the presence in the mass spectra of both of them of a common fragment having the same structure as in lysergic acid. Peaks with m/e 223 in the spectra of both compounds show that the splitting out of a radical with 143 amu from ergovalide and with 102 amu from ergometrine took place. The even-numbered molecular weight of ergovalide and the elimination of an odd-numbered fragment with 143 amu shows that the number of nitrogen atoms in ergovalide is even and that a fragment containing two nitrogen atoms is eliminated, while in ergometrine the molecular weight is odd and an even-numbered fragment with one nitrogen atom is eliminated. After the acid hydrolysis of ergovalide, we identified valine (II) (paper chromatography) and ammonia (Nessler's reagent); and after alkaline hydrolysis we found lysergic acid (III) (paper chromatography).



The results obtained permit the structure of N-lysergylvalylamide to be proposed as the most probable for ergovalide.

The amount of ergovalide in the combined alkaloids of the ergotoxine strain of ergot is about 10%, and in the ergometrine strain 10-20%.

All-Union Scientific-Research Institute of Medicinal Plants. Translated from Khimiya Prirodnykh Soedinenii, No. 1, p. 134, January-February, 1973. Original article submitted August 4, 1972.

LITERATURE CITED

1. A. Hofmann, Die Mutterkornalkaloide, Enke, Stuttgart (1964).