HAPLAMINE – A NEW ALKALOID FROM Haplophyllum perforatum

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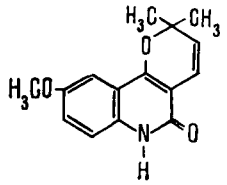
We have investigated the epigeal part of the plant H. perforatum collected in the flowering period in the Dzhungarian Ala-Tau. From the mixture of bases obtained by the methanolic extraction of the plant we have isolated a new, optically inactive, alkaloid (I) with mp 201-202°C (ethanol) having the composition $C_{15}H_{15}NO_3$, which we have called haplamine. The substance contains a methoxy group (by the method of Viebock and Brecher).

In the IR spectrum of haplamine there are absorption bands at 3155 and 1660 cm^{-1} (−NHCO−), and its UV spectrum is typical for pyranodihydroquinolin-2-one alkaloids of the flindersine type [1]. The main peaks in the mass spectrum of haplamine are those of ions with m/e 257 (M^+, 47%) and 242 (M−15, 100%), which are also characteristic for this group of alkaloids [2].

The NMR spectrum of haplamine (taken in CCl_4, τ scale) clearly shows the signals from the 15 protons of the base: at 8.50 ppm (6 H, singlet, gem-dimethyl group), at 6.20 ppm (3 H, singlet, OCH_3), at 4.57 ppm (J = 10 Hz), and 3.28 ppm (J = 10 Hz) (two one-proton doublets from a −C−CH = CH−C− group).

In the region of aromatic protons there are three signals: a doublet at 2.64 ppm (J_{ortho} = 8.5 Hz, a quartet with its center at 2.99 ppm (J_{ortho} = 8.5 Hz, J_{meta} = 3 Hz), and a broadened signal at 2.95 ppm characteristic of a 1,2,4-substituted benzene ring [3]. The signal of the NH group is in the very weak field at −3.23 ppm. The facts given above permit the assumption that haplamine differs from flindersine by the presence of a methoxy group in position 6 or 7 of the benzene ring. To confirm this, haplamine was distilled with a 30% solution of alkali. A phenolic substance (II) was obtained with bp 317-320°C, mol. wt. 191 (mass spectrometry), the physicochemical properties of which were close to those of 4-hydroxy-6- and 7-methoxydihydroquinoline-2-ones (bps of 4-hydroxy-5- and 8-methoxydihydroquinolin-2-ones 255-256°C and 245-246°C, respectively) [4].

The methylation of (II) with dimethyl sulfate gave an N,O-dimethyl derivative (III) with mp 142-143°C, mol. wt. 219 (mass spectrometry) which was shown by direct comparison not to be identical with 4,7-dimethoxy-1-methyldihydroquinolin-2-one. The NMR spectrum of (III) agreed with a 4,6-dimethoxy-1-methyldihydroquinolin-2-one structure.



Consequently, haplamine has the structure of 6-methoxyflindersine.

LITERATURE CITED

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