THE STRUCTURE OF INDICAININE

S. Khakimdzhanov, A. Abdusamatov, and S. Yu. Yunusov

UDC 547.944/945

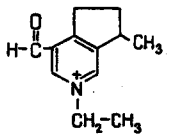
From the acid ethereal fraction of the combined alkaloids of Pedicularis olgae Rgl. [1] the picrate of a base with mp 125-127°C (water) has been obtained. We chromatographed the picrate of the base on alumina. A liquid quaternary [2] base with the composition $C_{12}H_{16}N^{+}O$, $[\alpha]_D^{30}$ +14.2° (c 1.9; chloroform), M^{+} 190 (mass spectrometry), R_f 0.85 [TLC on silica gel in the ethyl acetate–methanol (4:1) system] was obtained. The UV spectrum of the base had two maxima at λ_{max} 261 and 268 nm (log ε 3.52, 3.48) which are characteristic for alkaloids of the pyridine type. The IR spectrum of the substance had absorption bands at (cm^{-1}): 3600-3200 (OH), 2980-2940 (C–CH_3), 2800-2700 (N–C_2H_5), 1700 (Ar–C(=O)H), 1580 (pyridine ring) and 910, 855 (1,2,3,5-tetrasubstituted benzene ring). The base proved to be new and we have called it indicainine.

The NMR spectrum of indicainine (JNM-4H-100/100 MHz in $CDCl_3$ with HMDS as internal standard, δ scale) clearly shows a one-proton singlet at 10.13 ppm corresponding to the hydrogen atom of an aldehyde group and two one-proton singlets at 8.75 and 8.55 ppm due to two atoms of hydrogen present in the α,α' positions with respect to the nitrogen atom of a pyridine ring. In the strong-field region of the spectrum there is a two-proton quartet at 3.49 ppm (methylene group attached to a nitrogen atom), two one-proton multiplets at 2.34 and 1.70 ppm (two nonequivalent protons at C-2), and a six-proton multiplet at 1.25 ppm (protons of two methyl groups).

The mass spectrum of indicainine (MKh-1303, 100°C, energy of the ionizing electrons of 40 eV) has the peaks of the ions (m/e: M^{+} 190, 162, 161, 146, 133, 132, 118, 117, 91, and 77). The splitting out of an ethyl radical from the molecular ion leads to the formation of an ion with m/e 161. The further fragmentation of the latter is similar to that of indicaine [3].

The oxidation of indicainine with silver oxide gave plantagonine, which was identified by a mixed melting point with an authentic sample and by their IR spectra.

On the basis of these facts, we propose the following structure for indicainine:



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Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 126-127, January, 1971. Original article submitted November 9, 1970.