UDC 547.944/945

THE STRUCTURE OF PEDICULARINE

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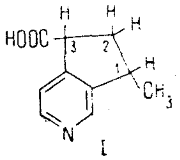
Khimiya Prirodnykh Soedinenii, Vol. 5, No. 5, pp. 457–458, 1969

The isolation of pedicularine from Pedicularis olgae Rgl. has been reported previously [1]. When pedicularine was subjected to TLC in the ethanol–chloroform–butyl acetate (3 : 2 : 1) system we found two spots with R_f 0.19 and 0.52. By repeated recrystallization we obtained a base showing on TLC a single spot with R_f 0.19, $C_{10}H_{11}NO_2$, mp 208–209° C decomp., methanol), $[\alpha]_D^{20}$ −15.3° (c 0.78; methanol), mol. wt. 177 (mass spectrum); UV spectrum: λ_{max} 272 mμ (log ε 2.89). The IR spectrum of the base had absorption bands at 2960 cm^{-1} ($C-CH_3$), 1710 cm^{-1} (>CO), and 1600 cm^{-1} (pyridine ring).

The NMR spectrum of pedicularine (taken on a JNM-4-H-100/100 MHz instrument in CF_3COOH with HMDS as internal standard, τ scale), clearly showed a one-proton singlet at 1.08 ppm and two two-proton doublets at 1.53 and 1.93 ppm, corresponding to three hydrogen atoms in the α, α', β' positions with respect to the nitrogen atom of a pyridine ring. The absence of other signals from the weak-field region shows that the remaining two positions of the pyridine ring are substituted. The three-proton doublet at 8.93 ppm (J = 6.0 Hz) is due to the protons of a methyl group at $C_{(1)}$. The signals of the methine protons at $C_{(1)}$ and $C_{(3)}$ appear at 6.92 ppm in the form of a two-proton multiplet. The two one-proton multiplets at 7.82 and 8.34 ppm relate to the two nonequivalent protons at $C_{(2)}$.

The mass spectrum of pedicularine (taken on a MKh-1303 instrument with an energy of the ionizing electrons of 32 eV at a temperature of 220° C) has the peaks of the ions (m/e) M^+ 177 (52%), 162 (100%) 133 (40%), 118 (68%), 91 (34%), and 77 (14%). This route of fragmentation is characteristic for the alkaloid plantagonine [2, 3].

When pedicularine was oxidized with $KMnO_4$ in an alkaline medium, 12 g-atoms of oxygen were consumed and we obtained an acid with mp 261–262° C (decomp.), identical according to a mixed melting point and in respect of its IR spectrum with pyridine-3, 4-dicarboxylic acid [4].



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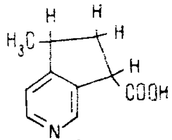

II

Consequently, either of structures I or II is possible for pedicularine. On the basis of biogenetic considerations, we consider structure I more likely.

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23 April 1969

Institute of Chemistry of Plant Substances AS UzSSR

UDC 547.944/945

A NEW SYNTHETIC ISOMER OF THE MATRINE ALKALOIDS

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Khimiya Prirodnykh Soedinenii, Vol. 5, No. 5, pp. 458–450, 1969

When epilupinoylpiperidine (I), which we have obtained previously [1], was heated in acetic acid solution with mercuric acetate at 70–80° C for 22 hr [2, 3], a mixture of dehydro products was formed which contained three com-