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THE STRUCTURE OF PEDICULARINE

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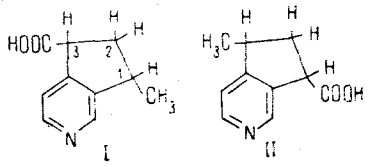
The isolation of pedicularine from Pedicularis olgae Rgl. has been reported previously [1]. When pedicularine was subjected to TLC in the ethanol-chloroform-butyl acetate (3:2:1) system we found two spots with R_f 0.19 and 0.52. By repeated recrystallization we obtained a base showing on TLC a single 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].



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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A NEW SYNTHETIC ISOMER OF THE MATRINE ALKALOIDS

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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-

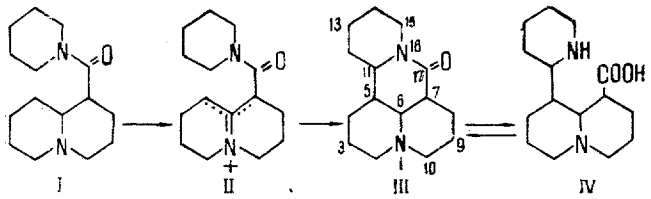
ponents with R_f 0.26, 0.78, and 0.35 (in a thin layer of alumina with acetone as the solvent and iodine vapor as the revealing agent). The mixture of dehydro products was hydrogenated with sodium borohydride in methanol.

By means of adsorption chromatography on alumina and elution with acetone, two individual substances were isolated from the hydrogenation products. One of them (yield 3.4%; R_f 0.24; $[\alpha]_D$ +18.1°; c 2.1; ethanol) had the composition $C_{15}H_{24}ON_2$ (III). The IR spectrum of the base III exhibits bands at 1630 cm^{-1} (>N—CO group) and 2763 cm^{-1} (trans-quinolizidine).

By heating the base III with 18% hydrochloric acid in a sealed tube at 160–180° C for 20 hr we obtained an amino acid (IV) giving an ethyl ester (picrate mp 70–72° C) and a N-benzoyl derivative (hydrochloride, mp 220–222° C).

The cyclization of IV by heating at 240–250° C regenerated the base III.

The reduction of the base III with lithium aluminum hydride gave allomatridine. Consequently, the base that we obtained is a new structural isomer of allomatrine and the lactam carbonyl in it is present at $C_{(17)}$ (III).



I II III IV

The second base (yield 85%, R_f 0.78) is optically inactive. When it was boiled with 20% sulfuric acid for 18 hr, piperidine and the racemate of epilupinic acid was obtained.

The second base is a racemate of epilupinoylpiperidine (I) which is probably formed by the hydrogenation of an intermediate product, 6,7-dehydroepilupinoylpiperidine (II).

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LYCORINE FROM UNGERNIA TRISPHAERA

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Lycorine is used in the treatment of acute and chronic bronchitis, bronchiectatic diseases, and bronchial asthma.

Table 1

Time of gathering	Height of the leaves, cm	Percentage of the weight of the dry leaves	
		combined alkaloids	lycorine
25 March	3—6	1.3	0.61
8 April	6—10	1.25	0.55
15 April	10—14	1.09	0.52
21 April	20—25	1	0.5
5 May	25—30	0.77	0.45
15 May	30—32	0.30	0.1
5 June	30—32	0,15	0.02