PEDICULININE – A NEW ALKALOID FROM Pedicularis olgae

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Continuing the separation of the chloroform fraction from P. olgae [1] (from the surroundings of Burchmulla), we have extracted a base with the composition $C_{10}H_{13}NO$, mp 133-134°C (acetone), mol. wt. 163 (mass spectrometrically). The same substance was isolated from fractions 6-8 on separating the chloroform fraction of the total alkaloids (obtained after the separation of N-methylcytisine) according to their basicities. It is optically inactive and dissolves readily in chloroform, ethanol, and methanol, and moderately in acetone. The base proved to be new, and we have called it pediculinine (I).

The UV spectrum of the alkaloid [λ_{max} 262, 269 nm (log ε 3.33, 3.23)] is characteristic for pyridine bases [2, 3]. In the IR spectrum there are absorption bands at 3400-3200 cm^{-1} (OH) and 1595 cm^{-1} (pyridine ring). The NMR spectrum of (I) (Fig. 1) shows six groups of signals with an intensity ratio of 2 : 1 : 2 : 4 : 2 : 2 corresponding to the 13 hydrogen atoms.

In the weak-field region there is a two-proton singlet at τ 1.81 ppm corresponding to two hydrogen atoms at C-2 and C-6 and a one-proton doublet at 3.07 ppm, J=5.0 Hz, due to a proton at C-5 of the pyridine ring. The absence of other signals in this region shows that the other two positions of the pyridine ring of (I) are substituted. The signal of the methine proton at C-9 is shifted downfield and is superposed

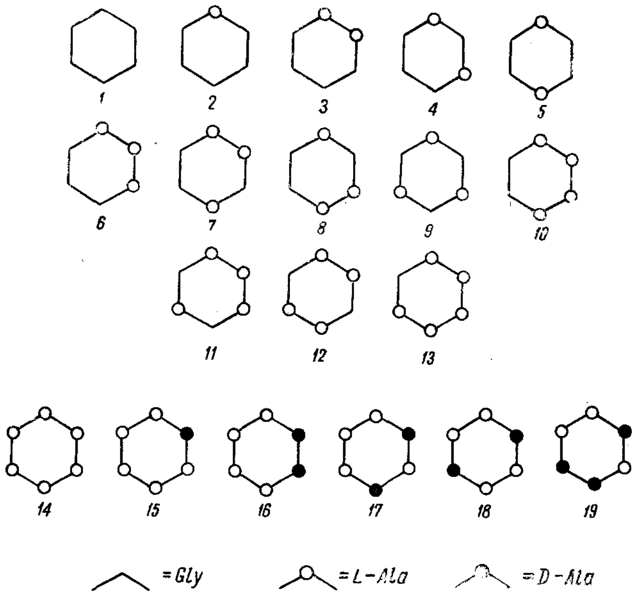

Fig. 1. NMR spectra of pediculinine (a) and acetylpediculinine (b).

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on the signal of the proton of a hydroxy group. There is a two-proton singlet at 5.99 ppm. In the 6.95-7.60 ppm region there are signals of four proton units corresponding to methylene protons at C-7 and C-11. Two two-proton triplets at 8.02 and 8.43 ppm obviously relate to methylene protons at C-8 and C-10.

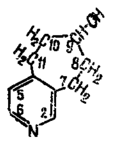
In the NMR spectrum of acetyl-(I), the signal of the methine proton at C-9 is shifted downfield, a one-proton multiplet appears at 4.92 ppm, and the signal of the methyl of the acetyl group appears at 7.95 ppm in the form of a singlet.

In the mass spectrum of the base there are peaks of ions with m/e 163 (M^+), 161, 146 (M−17), 145 (M−18), 131, 130, 119, 118, 117, 91, 77.

The presence of peaks of the fragments M−17 (M^+−OH), and M−18 (M^+−H_2O) is characteristic for hydroxyl-containing compounds.

On the oxidation of (I) with potassium permanganate in an alkaline medium with the consumption of 13 atoms of oxygen, an acid was obtained with mp 258-260°C (decomp.), identified as pyridine-3,4-dicarboxylic acid. This acid confirms the structure of (I) as a 3,4-disubstituted pyridine.

On the basis of the above facts, the following structure may be proposed for pediculinine:



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EXPERIMENTAL

The UV spectra were taken on an SF-4 instrument (in ethanol), the IR spectra on a UR-10 spectrometer (molded tablets with KBr), the NMR spectra on JNM-4H-100/100 MHz (pediculinine) and JNM-C-6OH (acetylpediculinine) instruments, and the mass spectra on an MKh-1303 instrument with a glass inlet system at an ionizing voltage of 40 eV.

Isolation of Pediculinine. A solution of 40.5 g of the chloroformic fraction of the alkaloids (after the isolation of N-methylcytisine) in 200 ml of 1 N sulfuric acid was treated successively with 20-ml portions of 1 N caustic soda solution and extracted with ether. A total of ten fractions was obtained: 1 − 0.35 g; 2 − 0.35 g; 3 − 0.69 g; 4 − 0.81 g; 5 − 0.45 g; 6 − 1.25 g; 7 − 1.56 g; 8 − 1.94 g; 9 − 0.74 g; 10 − 0.45 g. Then the alkaloids were exhaustively extracted with chloroform. On concentration, 25.8 g of combined chloroform alkaloids was obtained.

When the ethereal solutions of fractions 6-8 were concentrated, crystals deposited with mp 129-132°C. Yield 0.36 g. After recrystallization from acetone, the base had mp 133-134°C, and on a plate with a fixed layer of silica gel it gave a single spot with R_f 0.24 in the butan-1-ol−acetic acid−water (20 : 1 : 20) system.

Acetylation. A mixture of 0.039 g of the base, 2 ml of acetic anhydride, and 2 ml of pyridine was heated at 40-50°C for 6 h. After complete evaporation under vacuum, the residue was dissolved in a small amount of water, made alkaline with $NaHCO_3$, and extracted with ether, and the extract was dried with anhydrous sodium sulfate. Elimination of the ether gave a colorless oily substance with R_f 0.52 in the ethyl acetate−methanol (4 : 1) system; melting point of the picrate 160-161°C.

Oxidation. With constant stirring, an aqueous solution of 1.26 g of potassium permanganate was added to a solution of 0.15 g of the base in 20 ml of 1% caustic soda solution, and the mixture was heated on the water bath for 5 h. The manganese dioxide that deposited was separated off, the filtrate was evaporated to dryness, and the residue was treated with an ethanolic solution of hydrochloric acid. This gave an acid with mp 240-246°C (decomp.). Yield 0.072 g. After recrystallization from water, the melting point of the acid was 258-260°C (decomp.). A mixture with pyridine-3,4-dicarboxylic acid gave no depression of the melting point; the IR spectra of the samples were also identical. On chromatography on paper in the pyridine−acetic acid−butan-1-ol−water (20 : 6 : 30 : 24) system, the acid isolated and pyridine-3,4-dicarboxylic acid gave identical spots with R_f 0.49. The revealing agent was a 0.05% ethanolic solution of bromphenol blue.

SUMMARY

A new substance – pediculinine, $C_{10}H_{13}NO$, mp 133-134°C – has been isolated from the chloroformic fraction of the combined alkaloids of P. olgae.

Structure (I) has been proposed for the new alkaloid on the basis of UV, IR, NMR, and mass spectra and chemical characteristics.

LITERATURE CITED

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3. A. Abdusamatov, S. Khakimdzhanov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 5, 457 (1969).