THE STRUCTURE OF PEDICULIDINE

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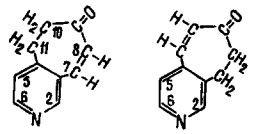
From the epigeal part of Pedicularis olgae collected on June 18, 1968 (region of the village of Sagyrdasht, TadzhSSR), 0.59% of total bases have been isolated by chloroform extraction. The ethereal fraction of the combined alkaloids yielded the picrate of a base with mp 211-212°C (ethanol), which was chromatographed on alumina. A base was isolated with the composition $C_{10}H_9NO$, mp 74-75°C, M^+ 159 (mass spectrometrically), R_f 0.51. The IR spectrum of the base had the three maxima at λ_{max} 268, 273 and 293 nm (log ε 3.97, 39.6, and 3.36) that are characteristic for alkaloids of the pyridine type [1, 2]. The IR spectrum of the alkaloid had absorption bands at (cm^{-1}) 1695-1640 $\left(-C\overset{O}{\diagup\!\!\diagdown}-CH=CH-\right)$, 1620, 1590, 1595 (pyridine ring), and 810, 855 (1,3,4-trisubstituted benzene ring) [3]. The base proved to be new, and we have called it pediculidine (I).

In the NMR spectrum of (I) (δ scale) (Fig. 1), a one-proton singlet appears clearly in the weak-field region at 8.51 ppm, corresponding to the hydrogen atom at C-2, and there are two one-proton doublets at 8.41 and 7.15 ppm, J=5.0 Hz, corresponding to two atoms of hydrogen at C-5 and C-6 of a pyridine ring. The absence of other signals in this region shows that positions 3 and 4 of the pyridine ring of (I) are substituted.

Two olefinic protons of C-7 and C-8 are observed in the form of two symmetrical one-proton doublets with centers at 7.12 and 6.34 ppm, J=12.2 Hz. The magnitude of the spin–spin coupling constant of the olefinic protons shows that the latter are in the cis position in a seven-membered ring [4-7]. Signals in the 2.45-3.15 ppm region correspond to two methylene protons at C-10 and C-11.

The mass spectrum of the base has peaks of the ions M^+ (159) and 158, 132, 131, 130, 118, 117, 104, 103, 102, 91, 89, 77 m/e. This manner of fragmentation is characteristic for alkaloids of the pyridine type [8].

On the basis of the facts presented, two structural formulas may be proposed for pediculidine: (I) or (II). Biogenetic considerations [9] permit the choice of formula (I) as the more likely.



I II

EXPERIMENTAL

The NMR spectra were taken on a JNM-4-H-100/100 MHz instrument (in $CDCl_3$), and the mass spectra on an MKh-1303 instrument with a glass inlet system at an ionizing voltage of 40 eV.

Isolation of Pediculidine (I). The comminuted epigeal part of P. olgae (30 kg) was moistened with 10% ammonia solution (1:1) and charged into an extractor. After it had stood for 2 hours, it was covered with chloroform and extraction was carried out overnight. A total of 12 overflows took place. The con-

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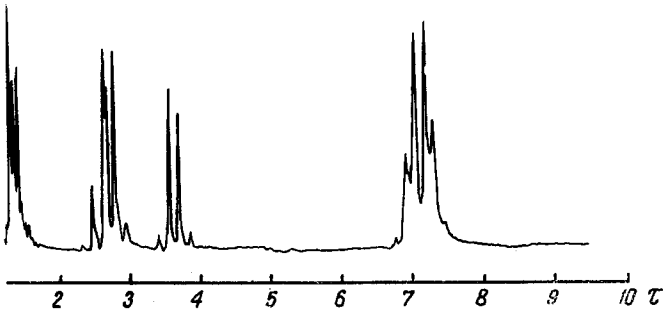

Fig. 1. NMR spectrum of pediculidine.

centrated chloroform extract was treated with 10% sulfuric acid. The combined acid solution was washed with ether and filtered and, with cooling, it was made alkaline with 25% ammonia solution. The alkaloids were extracted first with ether and then with chloroform. Distillation of the ether yielded 125.3 g of combined ether alkaloids and the chloroform solution gave 51.7 g of combined chloroform alkaloids. The total weight of the alkaloids was 177 g (0.59% of the weight of the dry plant).

The ether alkaloids (15 g) were treated with petroleum ether. Into this passed 6 g of the ether alkaloids, which was dissolved in 40 ml of acetone and treated with a saturated ethanolic solution of picric acid.

This gave 1.8 g of the picrate of an alkaloid with mp 204-208°C; after recrystallization from ethanol, mp 211-212°C. Yield 1.25 g. The picrate (1.25 g) was converted into the base by chromatography on a column of alumina (50 g; activity grade II). From the chloroform eluate 0.45 g of crystals with mp 70-74°C was isolated; after sublimation, mp 74-75°C; R_f 0.51 on TLC in silica gel in the methanol–chloroform–butyl acetate (1:2:1) system.

SUMMARY

A new alkaloid pediculidine, $C_{10}H_9NO$, mp 74-75°C, has been isolated from the ethereal fraction of the combined alkaloids of P. olgae.

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

LITERATURE CITED

1. A. Abdusamatov, M. R. Yagudaev, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 4, 265 (1968).
2. A. Abdusamatov, S. Khakimdzhanov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 5, 457 (1969).
3. K. Nakanishi, Infrared Absorption Spectroscopy. Practical, Holden-Day, San Francisco (1962).
4. O. L. Chapman, J. Amer. Chem. Soc., 85, 2014 (1963).
5. G. V. Smith and H. Kriloff, J. Amer. Chem. Soc., 85, 2016 (1963).
6. P. Laszlo and P. V. R. Schleyer, J. Amer. Chem. Soc., 85, 2017 (1963).
7. M. Karplus, J. Amer. Chem. Soc., 85, 2017 (1963).
8. S. Khakimdzhanov, A. Abdusamatov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 6, 142 (1970).
9. D. Gross, Fortschr. Bot., 32, 93 (1970).