The IR spectrum of the base $C_{15}H_{26}N_2O$ contains bands at 1623 cm^{-1} (>N–CO group) and 2800–2700 cm^{-1} (trans-quinolizidine system). Its saponification with 20% sulfuric acid gave lupininic acid and piperidine. Consequently, the substance $C_{15}H_{26}N_2O$ is lupininoylpiperidine. In order definitively to establish which of the epimers this substance was, we reduced it with lithium aluminum hydride. An oxygen-free base $C_{15}H_{28}N_2$ corresponding in composition to piperidinolupinane was obtained.

For a direct comparison of piperidinolupinanes, we synthesized them by published methods [2–4]. The results of a direct comparison of the substances showed that the oxygen-free base $C_{15}H_{28}N_2$ is piperidino-d-epilupinane. Thus, the compound $C_{15}H_{26}N_2O$ has the structure d-epilupininoylpiperidine.

REFERENCES

1. A. S. Sadykov, Kh. A. Aslanov, and T. Tursunbaev, ZhOKh, 30, 3496, 1960.
2. F. Bohlmann, E. Winterfeld, and U. Frise, Ber., 96, 2251, 1963.
3. German patent nos. 386936, C. I 2636, 1924; 481285, C. II 2505, 1929.
4. P. Karrer and A. Vogt, Helv. Chim. Acta, 13, 1073, 1930.

21 February 1967

Lenin Tashkent State University

UDC 547.944.3

STRUCTURE AND CONFIGURATION OF PEIMISINE

R. N. Nuriddinov, R. Shakirov, and S. Yu. Yunusov

Khimiya Prirodnykh Soedinenii, Vol. 3, No. 6, pp. 413–414, 1967

Peimisine has the composition $C_{27}H_{41}O_3N$, $[\alpha]_D$ –44.62° (c 0.98; ethanol) [1], R_f 0.25 on alumina [ethyl acetate–ligroin–methanol (50:90:8)]. IR spectrum of peimisine: ν_{max} 3520 cm^{-1} (OH), 1665 (=), 1700 (C=O), 2930, 1470 (C–CH_3) and 3260 cm^{-1} (>N–H), and of O, N-diacetylpeimisine: ν_{max} 1735, 1245 cm^{-1} (–OCOCH_3), 1670 (>N–CO–CH_3), 1718 cm^{-1} (C = O). One oxygen atom in peimisine is inert. UV spectrum of peimisine: λ_{max} 290 mμ (log ε 1.74). The reduction of the alkaloid (C_2H_5OH, H_2, Pt) gave an amino alcohol with mp 199–201° C (from methanol), the IR spectrum of which lacked the absorption band of a carbonyl group. The mass spectra of peimisine and jervine are very similar [2].

Substance	Chemical shifts, τ						
	C–19CH_3	C–18CH_3	C–21CH_3	C–26CH_3	O–CO–CH_3	N–CO–CH_3	C–3αH
(I)	9.38	8.44	9.15	9.10	—	—	—
(II)	9.12	8.44	9.15	9.15	—	—	—
(III)	9.36	8.35	9.21	9.03	8.04	7.96	5.36

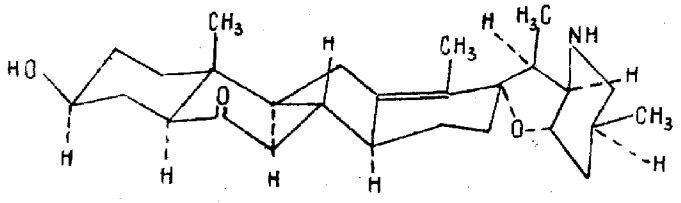
Thus, peimisine is based on the heterocyclic skeleton of jervine. The results of the NMR spectra of peimisine (I), the amino alcohol (II), and O, N-diacetylpeimisine (III) are given in Table 1.

The presence in the spectra of singlets at 8.44τ and 9.36τ and of peaks with m/e 110, 124, and 125 show that the double bond in peimisine is between C-12 and C-13, as in jervine [3]. According to the NMR spectrum, the substance investigated has a C-3β OH and a carbonyl group in position 6 [4]. In addition, the signal from the C-19 methyl group in deoxypeimisine must be observed in a strong field and correspond to the 5α-H, 19β-CH_3 configuration. Consequently, in peimisine the tertiary hydrogen atoms and the methyl groups on the carbon atoms of rings A, B, C, and D are in the same positions as in 11-deoxy-5α, 6-dihydrojervine [4].

The mass spectra of jervine and peimisine differ not only in the mass numbers of the molecular ions but also in the intensities of the peaks with m/e 110 and 125. In the spectrum of peimisine, the peak with m/e 125 is more intense (100%) than the 110 peak (46%), and in jervine the 110 peak is more intense (100%) than the 125 peak (50%). This shows that in jervine the hydrogen atom at C-20 is oriented in the β-position and in peimisine in the α-position.

In the NMR spectrum of peimisine the signal from the protons of the C-26 CH_3 group are subject to considerable screening, which shows its axial position.

On the basis of what has been said above, the following may be considered the most probable configuration for peimisine:



REFERENCES

1. R. Shakirov, R. N. Nuriddinov, and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], 1, 384, 1965.
2. H. Budzikiewicz, Tetrah., 20, 2267, 1964.
3. T. Masamune, N. Sato, K. Kabayashi, and J. Yamazaki, Tetrah., 23, 1591, 1967.
4. R. F. Zürcher, Helv. Chim. Acta, 46, 2054, 1963.

16 June 1967

Institute of the Chemistry of Plant Substances, AS UzSSR