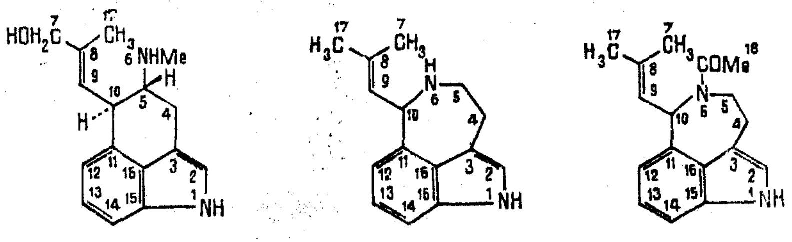
CONFORMATIONS OF THE ERGOT ALKALOIDS CHANOCLAVINE-1, AURANTIOCLAVINE, AND N-ACETYLAURANTIOCLAVINE

V. G. Sakharovskii, A. V. Aripovskii,
M. B. Baru, and A. G. Kozlovskii

UDC 547.94:541.63:543.422.23

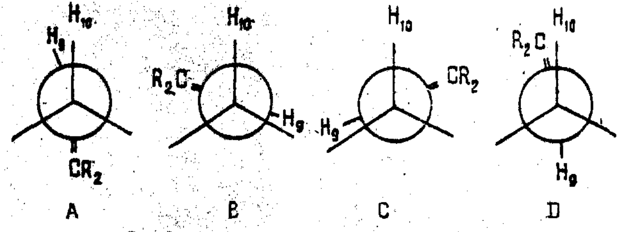
In order to study the conformational states of the ergot alkaloids containing an exocyclic 2',2'-dialkylvinyl grouping, we have performed a comparative study of the ^{1}H NMR spectra of chanoclavine-1 (I) [1], aurantioclavine (II) [2] and N-acetylaurantioclavine (III), obtained by the acetylation of aurantioclavine with acetic anhydride at room temperature.



I II III

(I) — chanoclavine; (II) — aurantioclavine; (III) — N-acetylaurantioclavine.

The values of $^3J_{9,10}$ calculated from the angular dependence of $^3J_{H,H}$ in the allyl fragment [3] for conformations A, B, C, and D are 6.6, 4.9, 4.9, and 11.5 Hz, respectively. Compounds (I) and (II) possess high values of $<^3J_{9,10}>$ (9.8 and 9.2 Hz, respectively), and can therefore be represented in the form of an equilibrium mixtures of conformers A–D with a predominance of conformer D. The complete absence of homoallyl interaction of H_{10} with the protons of the methyl groups in (I) and (II) also shows the predominance of conformer D [4]. From the condition $<^3J> = \sum_{\varphi} {}^3J_{\varphi} \cdot N_{\varphi}$, where $^3J_{\varphi}$ is the spin-spin coupling constant corresponding to this conformer and N_{φ} is its molar fraction, it is easy to estimate the amount of D in the mixture of conformers ($D \geqslant 70\%$). When the orientation influence of the nitrogen atom on $^3J_{9,10}$ in (II) is taken into account [3], the calculated proportion of D becomes even higher.



Conformation of compounds (I) - (III) ($R = CH_3$) at the $C_9 - C_{10}$ bond.

The passage from (II) to (III) is accompanied by a marked decrease in $^4J_{10,12}$: thus, for (II), $^4J_{10,12} = 1.3$ Hz, and for (III) $^4J_{10,12} = 0.2$ Hz. This fact can be explained by a change in the conformation of the seven-membered heterocycle with the passage of the $Me_2C{=}CH$ substituent from the pseudoequatorial to the pseudoaxial conformation [4]. This conclusion is also confirmed by the screening of the H_9 proton observed in the passage from (II) to (III) ($\Delta\delta = +0.30$ ppm) with a simultaneous decreasing of H_{10} ($\Delta\delta = -0.98$ ppm).

Institute of the Biochemistry and Physiology of Microorganisms, Academy of Sciences of the USSR, Pushchino-on-Oka. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 656-657, September-October, 1983. Original article submitted February 22, 1983.

An analysis of the $<{}^3J_{9,10}>$ values for (III) — 8.1 and 7.5 Hz, respectively, for the Z and E form of the acetamide grouping (the E form was identified from its NOE value of H_{17}—$\{H_{10}\} \approx 4\%$) shows that, in the first place, in contrast to (I) and (II), in (III) the D conformer is no longer predominant and, in the second place, the E form contains an appreciably lower proportion of the D conformer than Z form. The influence of the state of acetamide fragment on the proportion of the D conformer in (III) can be explained in terms of the Van der Waals interaction of the 7-Me group with the 18-Me group (E) and the oxygen atom (Z) of the acetyl residue. An analysis of the calculated values of the energies of these interactions ("6-exp" potential) with Dashevskii's parameters [5]) shows that the D conformation of the side chain of (III) is destabilized by the E conformation of the acetamide grouping by ≈ 0,5 kcal/mole more strongly than the Z conformation.

LITERATURE CITED

1. A. G. Kozlovskii, M. U. Arinbasarov, T. F. Solov'eva, and V. M. Adanin, Prikl. Biokhim. Mikrobiol., 16, No. 4, 569 (1980).
2. A. G. Kozlovskii, T. F. Solov'eva, V. G. Sakharovskii, and V. M. Adanin, Dokl. Akad. Nauk SSSR, 260, 230 (1981).
3. V. F. Bystrov, Usp. Khim., 46, 532 (1972).
4. M. Barfield, Chem. Rev. 69, 757 (1969).
5. V. G. Dashevskii, Conformations of Organic Molecules [in Russian], Moscow (1974), p. 111.

ALKALOIDS OF *Delphinium ternatum*

V. M. Matveev, A. S. Narzullaev,
and S. S. Sabirov

UDC 547.944/945

Continuing a study of the alkaloid composition of *Delphinium ternatum* [1], we have investigated the epigeal part and roots of the plant collected in the flowering phase on June 18, 1979 in the basin of R. Varzob. The customary chloroform extraction of the epigeal part yielded 0.15% of combined bases, which was separated into phenolic and nonphenolic fractions. Crystals isolated from the ether-soluble nonphenolic fraction proved, on TLC, to be a mixture of two substances. Chromatography on a column of alumina [eluent: hexane—ethyl acetate (1:1)] yielded delcorine [2] and a base (I) with mp 215-217°C (acetone). From the mother liquor after the separation of the crystals, an additional amount of base (I) was isolated by chromatography on a column of alumina [eluent: ether—chloroform (1:25)].

The IR spectrum of (I) is characteristic for diterpene alkaloids of the lycoctonine type, having absorption bands at 1100 cm^{-1} (ether C—O bonds) and 3475 cm^{-1} (hydroxy groups). The NMR spectra ($CDCl_3$, ppm, δ scale, HMDS = 0) revealed signals in the form of a three-proton singlet at 0.86 from a $-\overset{|}{\underset{|}{C}}-CH_3$ group; a three-proton triplet at 0.98 from a $>N-CH_2-CH_3$ group; three-proton singlets at 3.16, 3.25, and 3.33 from three methoxy groups; a one-proton triplet at 3.59 from β-H at C-14; a one-proton singlet at 4.11 from α-H at C-6; and two one-proton singlets at 4.92 and 5.02 from a CH_2O_2 group.

Analysis of the results that we had obtained and their comparison with information in the literature enabled base (I) to be identified as delpheline [3-5]. This is the first time that delpheline has been isolated from plants of the family *Ranunculaceae* growing in the territory of the USSR.

Abu Ali Ibn Sina Tadzhik State Medical Institute, Dushanbe. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 657-658, September-October, 1983. Original article submitted March 14, 1983.

0009-3130/83/1905-0627$07.50