In the spectrum of the aporphine-benzyltetrahydroisoquinoline alkaloid foetidine (V) [3], the signals of the two N–CH_3 groups give singlets at 7.70 and 7.63 ppm, and the six OCH_3 groups form five signals with a total intensity of 18 proton units. The one-proton signal in the weak field at 1.93 ppm corresponds to the aromatic proton in position 4 of the aporphine moiety of the molecule and the other six protons of the ring resonate in the 3.95–3.27 ppm region.

The relationship between the resonance position of the substituting groups and the chemical structure of the alkaloids (I)–(IV) agrees in the main with the literature data given for the bisbenzylisoquinoline bases [4].

These spectra were obtained on a JNM-4H-100/100 MHz instrument in deuterochloroform with HMDS as the internal standard (τ scale).

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STRUCTURE OF UNGMINORIDINE

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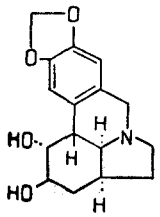
In the separation of the alkaloids from the leaves of Ungernia minor by the acetone treatment of the combined chloroformic alkaloids, in addition to lycorine, ungminorine, and ungeremine [1], an alkaloid with mp 193–194° C (from methanol) with the composition $C_{16}H_{19}O_4N$ was isolated and was given the name ungminoridine. The IR spectrum of the latter has absorption bands at 3400 cm^{-1} (hydroxy group) and at 931 and 1040 cm^{-1} which are characteristic for a benzene ring with a methylenedioxy group.

From a comparison of the UV absorption spectrum of ungminoridine [λ_{max} 240, 290 mμ (log ε 3.50, 3.54)] with that of dihydrolycorine it can be seen that ungminoridine belongs to the alkaloids of the lycorine type.

In the NMR spectrum of ungminoridine taken in deuterochloroform there are well-defined signals of the protons of an aromatic ring at τ = 3.08 and 3.40 ppm, each with an intensity of one proton unit. A signal located in the weak-field region (3.08) evidently relates to proton 8 [2, 3]. A signal at τ = 4.13 (intensity 2 proton units) corresponds to an $-OCH_2O-$ group and one at τ = 6.16 ppm to the protons of OH groups. The assignment of the signal at τ = 6.16 ppm to OH is confirmed by the fact that in the NMR spectrum of ungminoridine taken in CD_3OD it completely disappeared. The absence from the NMR spectrum of ungminoridine of a signal at τ = 4.50 shows the absence of a 3a–4 double bond [2]. The mass spectrum of ungminoridine has six characteristic peaks—M^+ 289, 288, 271, 254, 252, 250 m/e—which are analogous to the spectrum of dihydrolycorine [4, 5].

Thus, the information given permits us to put forward the following structural formula for ungminoridine:



Ungminoridine is an optically inactive alkaloid and therefore the possibility is excluded that it is the racemate of zephyranthine [6]. The NMR spectrum was recorded on a JNM-4H-100/100 MHz instrument in deuterochloroform solution.

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STRUCTURE OF BUCHARAINE

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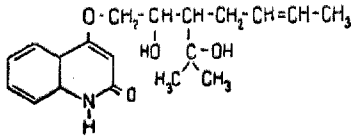
We have previously [1] established that the basic skeleton of bucharaine is 2, 4-dihydroxyquinoline. The structure of the side chain, which, according to our hypothesis, must be attached in the γ-position, remained undetermined.

The IR spectrum of chloroacetylbucharaine lacks the absorption band of a hydroxy group but has bands at 1740 and 1240 cm^{-1} which are characteristic for alcohol esters.

The production of chloroacetylbucharaine shows the presence of two hydroxy groups in bucharaine. The Kuhn-Roth oxidation of the latter gave acetone. The formation of acetone and the replacement of a hydroxy group by chlorine under the action of acetyl chloride in bucharaine confirms the presence in bucharaine of a $CH_3-C(OH)-CH_3$ grouping.

In view of the presence of one double bond, we ozonized bucharaine and isolated a bucharainic acid with the composition $C_{17}H_{21}O_6N$, mp 288-289° C, together with acetaldehyde. This shows that the double bond is located at the end of the chain in the form of the $CH=CH-CH_3$ grouping. The nitrogen-free substance obtained by the hydrogenation of bucharaine [1] was oxidized by Percheron's method [2, 3]. Of the oxidation products, acetic and valeric acids were identified by paper chromatography. The formation of valeric acid shows that the hydroxyisopropyl grouping is located on the fifth carbon atom of the side chain of bucharaine. The NMR spectrum of the substance has a doublet at δ = 4.6, J = 6 Hz, with an intensity of two proton units and a quadruplet (δ = 3.59) with an intensity of one proton unit, which may be due [4] to a $-CH_2-CH(OH)$ grouping. The position of the signal of the methylene group is characteristic for groups located next to an atom of oxygen which, in its turn, is attached to the nucleus [5].

On the basis of what has been said above, it may be concluded that bucharaine has the structure



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