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ALKALOIDS OF Liriodendron tulipifera

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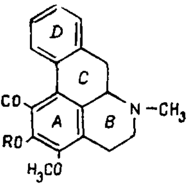
UDC 547.944.945

Continuing the separation of the ether-soluble fraction of the combined alkaloids of the leaves of L. tulipifera L., family Magnoliaceae, gathered on September 2, 1974 in Tashkent (Botanical Garden of the Academy of Sciences of the Uzbek SSR), on a column of silica gel, we have isolated, in addition to the alkaloids obtained previously [1, 2], N-methylcrotsparine [4], lanuginosine [5, 6], and a new base with the composition $C_{19}H_{21}NO_3$, mp. 142-144°C (acetone), $[\alpha]_D^{20} -38°$ (c 0.095; chloroform), M^+ 311, which we have called liridinine (I).

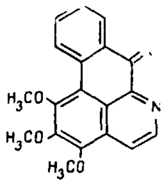
UV spectrum of (I): $\lambda_{max}^{C_2H_5OH}$ 221, 281 nm (log ε 4.41, 4.16). IR spectrum (KBr) (cm^{-1}): 3200-3400 (−OH), 2830, 1290 ($-OCH_3$), 1595, 760 (1,2-disubstituted benzene ring). The NMR spectrum of (I) (δ scale, ppm, $CDCl_3$) shows singlets at 2.50 (3H, $> N-CH_3$), 3.65 and 3.94 (3H each, $2-OCH_3$), and multiplets at 7.16 (3H, Ar−H) and 8.10 ppm (1H, Ar−H). The acetylation of liridinine with acetic anhydride in pyridine yielded its O-acetate (II), the IR spectrum of which showed an absorption band at 1760 cm^{-1} $\left(-O-\overset{O}{\overset{\|}{C}}-CH_3\right)$. On the basis of the facts given, the alkaloid (I) can be assigned to the aporphine series with one hydroxy group and two methoxy groups.

The methylation of liridinine with diazomethane yielded the O-methyl ether of (I) (III); oxidation of the latter with chromium trioxide in pyridine led to the formation of a compound (IV) with mp 162-164°C which, in a direct comparison, proved to be identical with liridine (O-methylmoschatoline) [2, 3, 7]. Consequently, in liridinine the substituting groups are present in ring A at C_5, C_6 and C_7.

In the NMR spectrum of O-acetylliridinine (II) there is no influence of the carbonyl group on the chemical shift of the aromatic proton at C_4 (multiplet at 8.14 ppm). This shows that one methoxy group in it is present at C_5 and the second $-OCH_3$ group (or −OH group) is at C_6 or C_7. On comparing the resonance of the signal from the methyl group at C_7 in (I) (3.94 ppm and in cassythine, cassythidine [8], and thalicmine [9, 10], we consider the most probable position of the second methoxy group in liridinine to be at C_7, and for liridinine we propose the structure of 6-hydroxy-5,7-dimethoxyaporphine (I).



I. R = H
II. R = COCH₃
III. R = CH₃



IV

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THE STRUCTURE OF ACONORINE

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From the total alkaloids of the roots of Aconitum orientale Mill. [1] collected in the flowering period in the environs of Lake Gek-Gel (Kirovabad region, AzerbSSR), we have isolated a new amorphous base which we have called aconorine, composition $C_{32}H_{44}N_2O_7$ (I), mol. wt. 568. The perchlorate of the base has mp 237°C (with effervescence).

The IR spectrum of (I) has absorption bands at 1695 cm^{-1} (ester carbonyl) and 1595 cm^{-1} (aromatic ring). The NMR spectrum of the alkaloid, (JNM-4H-100/100 MHz, $CDCl_3$, internal standard HMDS, δ scale) contains the signals of an ethyl group (1.03 ppm, 3H, triplet), and acetyl group (2.19 ppm 3H, singlet), and two methoxy groups (3.24 and 3.31 ppm, two three-proton singlets). In the weak-field region there are the signals from four aromatic protons at 6.9-8.7 ppm.

The alkaline hydrolysis of aconorine in a 10% solution of caustic soda in aqueous ethanol gave the amino alcohol of the base, $C_{23}H_{37}NO_5$ (III) with mp 140-141°C (hexane–acetone) and an acid $C_9H_9NO_3$ with mp 172°C which was identified as acetylanthranilic acid. The amino alcohol contains an ethyl group, two methoxy groups, and three hydroxy groups. The mass spectrum of (II) is characteristic for alkaloids with the lycoctonine skeleton [2]. The results of the pyrolysis of diacetylaconorine (III) are in harmony with this.

The NMR spectrum of the pyrolysis product contains signals from only two acetyl groups and has retained the signals of the aromatic protons. In the region of olefinic protons (6.06-5.59 ppm) there is an unresolved two-proton signal the nature of the splitting of which coincides with that in the spectrum of isopyroacetylthalatisamine [3]. Thus, the pyrolysis product that we isolated is isopyroacetylaconorine (IV), and, consequently, in aconorine there is a hydroxy group at C_8 and a methoxy group at C_{15} [4].

In the NMR spectrum of (II) at 4.11 ppm there is a poorly resolved triplet with an intensity of one proton unit, J = 5 Hz, shifting in the spectra of the acetyl derivatives of (I) and (II) to 4.76 ppm, which shows the presence of a hydroxy group at C_{10} in aconorine [5].

In the mass spectrum of (II), the maximum peak is that of the ion M − 31, due to the detachment of the methoxy group at C_1 [2]. The results of a comparison of the relative intensities of the peaks M^+(4.3%), M − 15 (3.2%), and M − 31 (100%) permits the methoxy group at C_1 to be assigned the α orientation [6].

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