PERFAMINE – A NEW ALKALOID FROM THE SEEDS OF Haplophyllum perforatum

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Continuing an investigation of the neutral fraction of a chloroform extract of the seeds of H. perforatum collected in the "Gallya-Aral" sovkhoz, Samarkand oblast, we chromatographed the mother liquors remaining after the separation of eudesmine and haplamine, which are the main components of the neutral fraction [1]. From ethereal eluates we obtained a new optically active base (I) with the composition $C_{18}H_{19}NO_4$, mp 164-165°C (ether–acetone), $[\alpha]_D$ + 53.4°, mol. wt., 313 (mass spectrometry), which we have called perfamine.

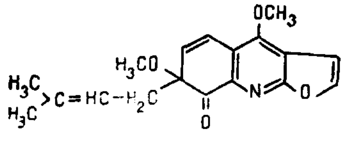
Perfamine (I) is readily soluble in chloroform, less readily in ethanol, methanol, acetone, and ether, and insoluble in water, dilute acids, and alkalis, and it gives one spot with R_f 0.60 in the toluene–ethyl acetate–formic acid (5 : 4 : 1) system on TLC (silica gel). It fluoresces dull green in UV light and is revealed by means of the Dragendorff reagent.

The IR spectrum of perfamine shows absorption bands at 3145, and 3165 cm^{-1} (furan ring) and 1670 cm^{-1} (conjugated carbonyl group).

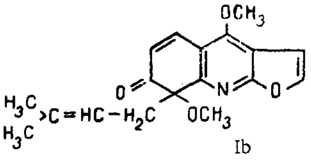
The UV spectrum of (I) [λ_{max} 215, 264.5, 272.5, 345 nm (log ε 4.30, 4.43, 4.43, 3.91); λ_{min} 238, 290 (log ε 3.90, 3.69)] differs from those of the 4-methoxyfuranoquinoline [2] and 4-methoxy-5,6,7,8-tetrahydrofuranoquinoline alkaloids [3]. The maximum at 345 nm, which is absent from the spectra of the latter, is due to the presence of a dienone chromophore in the alkaloid [4].

In the NMR spectrum of the base (I) ($CDCl_3$) there are the signals of 19 protons at the following values of τ (ppm): 2.10 and 3.88 (two doublets, 1 H each, J = 9 Hz, olefinic protons of the dienonic ring A [4], 2.36 and 2.96 (two doublets, 1 H each, J = 3 Hz, protons of a furan ring), 5.24, 7.27, 8.52, and 8.72 (1H, triplet; 2H, doublet, J = 6.5 Hz, and two three-proton singlets corresponding to the protons of an isopentenyl side chain attached to the dienonic ring A), and at 5.66 and 6.96 (two three-proton singlets corresponding to two methoxy groups, one of which is located in the pyridine ring [5] and the other in the dienonic ring).

The facts given above, and also that all the 4-methoxyfuranoquinoline alkaloids found in the seeds of H. perforatum have substituents in positions 7 and 8 have permitted structure (Ia) or (Ib) to be suggested for perfamine.



Ia



Ib

The action on perfamine of concentrated sulfuric acid yielded a phenolic base isomeric with haplopine [6], the methylation of which with diazomethane gave skimmianine [7], identified by comparison with an authentic sample. Consequently, perfamine has the structure (Ia).

LITERATURE CITED

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ALKALOIDS OF Liriodendron tulipifera

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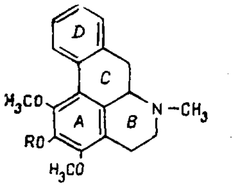
Continuing the separation of the ether-soluble fraction of the combined alkaloids of the leaves of L. tulipifera L., family Magnoliaceae, gathered on September 2, 1974 in Tashkent (Botanical Garden of the Academy of Sciences of the Uzbek SSR), on a column of silica gel, we have isolated, in addition 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).

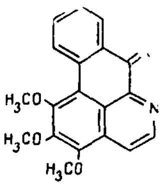
UV spectrum of (I): $\lambda_{max}^{C_2H_5OH}$ 221, 281 nm (log ε 4.41, 4.16). IR spectrum (KBr) (cm^{-1}): 3200-3400 (−OH), 2830, 1290 ($-OCH_3$), 1595, 760 (1,2-disubstituted benzene ring). The NMR spectrum of (I) (δ scale, ppm, $CDCl_3$) shows singlets at 2.50 (3H, $>N-CH_3$), 3.65 and 3.94 (3H each, $2-OCH_3$), 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} $\left(-O-C\overset{O}{/\!/}-CH_3\right)$. 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=$COCH_3$
III. R=CH_3



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