ALKALOIDS OF Liriodendron tulipifera

R. Ziyaev, M. S. Yunusov,
and S. Yu. Yunusov

UDC 547.944/945

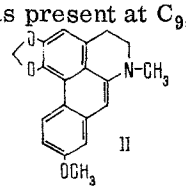
Continuing a study of the alkaloid composition of various organs of the plant Liriodendron tulipifera L., family Magnoliaceae [1-3], we have investigated young branches of the plant collected on May 10, 1974 in the Botanical Garden of the Academy of Sciences of the Uzbek SSR (Tashkent) in the flowering period. Chloroform extraction yielded 0.12% of combined alkaloids, which were separated into phenolic and nonphenolic fractions.

The separation of the nonphenolic ether-soluble fraction of the combined alkaloids on a column of silica gel led to the isolation of liriodenine, glaucine, base I, and a new base II, and from the phenolic fraction three bases were obtained which identified by comparison of UV, NMR, and mass spectra, and also by the preparation of salts, as d-caaverine [1], asimilobine [4, 5], and predicentrine [6, 7].

Base I had the composition $C_{18}H_{15}NO_2$, mp 88-90°C (benzene). UV spectrum of I: λ_{max}^{EtOH} 254, 262, 332 nm (log ε 4.61; 4.76; 4.12). The mass spectrum of the base showed the peaks of ions with m/e 277 (M^+, 100%), 262, 246, 232, 218, 138.5 (M^{++}). In the NMR spectrum of I (JNM-4H-100/100 MHz, internal standard HMDS, δ scale, CCl_4) signals appeared from a N-methyl group (2.95 ppm) and a methylenedioxy group (6.07 ppm) and from six aromatic protons (one-proton signals at 6.34 and 6.71 ppm, three-proton multiplet at 7.02-7.40 ppmand a one-proton multiplet at 8.69 ppm). The properties of (I) that have been described are identical with those of dehydroremerine which has been isolated previously from the plant Colubrina faraleotra ssp. faralaotra (family Rhamnaceae) [8].

Base (II), $C_{19}H_{17}NO_3$, mp 143-145°C (benzene), optically inactive, dissolved readily in the usual organic solvents. The UV spectrum [λ_{max}^{EtOH} 264, 334 nm (log ε 4.75, 4.08)] is characteristic for dehydroaporphine alkaloids [9, 10]. NMR spectrum (CCl_4, δ scale) showed three-proton singlets at 2.96 ppm (>N−CH_3) and 3.81 ppm (−OCH_3), a two-proton singlet at 6.08 ppm (O_2CH_2), and the signals of five aromatic protons. The characteristic downfield shift of the protons of the N-methyl group and of one of the aromatic protons confirms the dehydroaporphine structure of (II) [9-11]).

One-proton singlets at 6.29 and 6.70 ppm are similar to the signals observed in the NMR spectrum of dehydroremerine and correspond to the aromatic protons at C_7 and C_3. One-proton doublets at 8.59 and 6.77 ppm (J = 8 Hz) are due to two ortho aromatic protons in positions C_{11} and C_{10}, respectively, and a singlet at 6.83 ppm (1H−C_8) shows that the methoxy group is present at C_9, consequently, (II) is dehydroisolaureline:



II

LITERATURE CITED

1. R. Ziyaev, A. Abdusamatov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 760 (1973).
2. A. Abdusamatov, R. Ziyaev, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 112 (1974).
3. R. Ziyaev, A. Abdusamatov, S. Yu. Yunusov, Khim. Prirodn. Soedin., 478 (1975).
4. H. Guinaudeau, M. Leboeuf, and A. Gave, Lloydia, 38, 275 (1975).
5. E. Gellert and R. Rudzats, Aus. J. Chem., 25, 2477 (1972).
6. S. R. Johns, J. A. Lamberton, A. A. Sioumis, and H. J. Tweeddale, Aust. J. Chem. 22, 1277 (1969).
7. C. Chen, H. Chang, E. B. Cowling, G. H. Hsu, and R. P. Gates, Phytochem., 15, 1161 (1976).
8. H. Guinaudeau, M. Leboeuf, M. M. Debray, A. Gave, and R. R. Paris, Planta Medica, 27, 304 (1975).

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 715-716, September-October, 1977. Original article submitted May 10, 1977.

 0009-3130/77/1305-0602$07.50

9. S. Kh. Maekh. V. G. Khodzhaev, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 381 (1971).
10. M. P. Cava, V. Watanabe, K. Bessho, M. L. Mitchell, Tetrahedron Lett., 2427 (1968).
11. H. G. Kiryakov and P. Panov, Dokl. Bolg. Akad. Nauk, 222, 1019 (1969).

O-ACETYLDELECTINE – A NEW ALKALOID FROM Delphinium dictyocarpum

B. T. Salimov, M. S. Yunusov, and S. Yu. Yunusov

UDC 547.944/945

Continuing the separation of the combined alkaloids of the epigeal part of Delphinium dictyocarpum DC., collected in the flowering phase in the environs of the village of Topolevsky (Dzhungarian Ala-tau) [1-3], we have isolated a new base (I), $C_{33}H_{46}O_9N_2$, mp 118-120°C (methanol), M^+ 614.

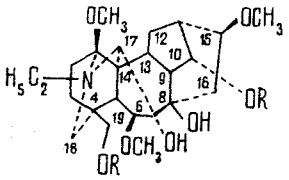
The IR spectrum of (I) shows absorption bands at (cm^{-1}) 3460 (hydroxy groups), 1690, 1740 (carbonyl groups), 1593 (aromatic ring), and 1090 (ether C–O bonds). The NMR spectra has the signals corresponding to a N-ethyl group (three-proton triplet at 1.04 ppm), an acetyl group (three-proton singlet at 2.02 ppm), three methoxy groups (three-proton singlets at 3.18, 3.26, and 3.29 ppm), and four aromatic protons (multiplets at 6.61 and 7.76 ppm). The composition and spectral characteristics permit (I) to be assigned to the diterpene alkaloids with a lycoctonine skeleton.

Identity of the signals of the aromatic protons in the NMR spectrum of (I) with those in the spectrum of delectine (II) and the presence of intense peak of an ion with m/e 120 in the mass spectrum of (I) due to an anthranilic acid residue show that the amino alcohol in (I) is acylated with anthranilic and acetic acids.

In the NMR spectrum of (I) at 4.73 ppm there is a one-proton triplet with $J \approx 5$ Hz. The splitting constant and the chemical shift are characteristic for a β proton at C_{10} geminal to an acetoxy group [4].

According to the mass spectrum (in which the maximum peak is that of the ion M – 31), there is a β-methoxy group at C_1 [5].

On the basis of what has been said, it may be assumed that (I) is 10-O-acetyldelectine. To confirm this, we acetylated (I) with acetic anhydride in pyridine and obtained the monoacetate (III), $C_{35}H_{48}O_{10}N_2$, mp 128-130°C (hexane–ether), which was identical with the N,O-diacetate of delectine. Consequently, the new base that we have isolated has the structure (I):



I

I. R = anthranoyl $R_1 = COCH_3$
II. R = anthranoyl $R_1 = H$
III. R = acetylanthoranoyl $R_1 = COCH_3$

LITERATURE CITED

1. A. S. Narzullaev, M. S. Yunusov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 498 (1972).
2. B. T. Salimov, M. S. Yunusov, S. Yu. Yunusov, and A. S. Narzullaev, Khim. Prirodn. Soedin., 665 (1975).
3. B. T. Salimov, M. S. Yunusov, and S. Yu. Yunusov, Khim. Prirodn., Soedin., 128 (1977).
4. S. W. Pelletier, L. H. Keith, and P. C. Parthasarathy, J. Am. Chem. Soc., 89, 4146 (1967).
5. M. S. Yunusov, Ya. V. Rashkes, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 85 (1972).

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent.
Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 716-717, September-October, 1977. Original article submitted May 10, 1977.

0009-3130/77/1305-0603$07.50