ALKALOIDS OF Liriodendron tulipifera

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Continuing the separation of the nonphenolic fraction of the combined alkaloids of the leaves of L. tulipifera L. [1] on a column of silica gel we have isolated two individual alkaloids from a benzene-methanol (99 : 1) eluate.

Base (I) had the composition $C_{18}H_{17}NO_2$ (M^+ 279, mass spectrometrically), $[\alpha]_D^{22}$ + 68° (c 0.27; ethanol) and formed a crystalline hydrochloride with mp 263-265°C (decomp.).

All its physicochemical properties were close to those of d-isoremerine [3-5]. A mixture of the alkaloid (I) with an authentic sample of d-isoremerine gave no depression of the melting point.

Base (II) had the composition $C_{18}H_{19}NO_2$ (M^+ 281, mass spectrometrically), $[\alpha]_D^{22}$ + 140° (c 0.18; ethanol) R_f 0.46 in the benzene–ethanol (8 : 2) system on TLC in silica gel. Its UV spectrum [$\lambda_{max}^{ethanol}$ 232, 272, 311 nm (log ε 4.29, 4.12, 3.62)] is similar to those of nuciferine and caaverine [2, 6]. The IR spectrum of (II) has an absorption band showing the presence of a secondary nitrogen atom in the substance. In actual fact, the acetylation of the alkaloid (II) with acetic anhydride in pyridine gave the N-acetyl derivative of (II) with mp 229-232°C (from acetone). The IR spectrum of the latter had an absorption band at 1630 cm^{-1} (N-acetyl group).

The mass spectrum of (II) showed the intense peaks of ions with m/e M^+ 281, 280 $(M-1)^+$ (100%), 266 $(M-15)^+$, 252 $(M-29)^+$, 250 $(M-31)^+$, 221, 165, 152, which are characteristic for the noraporphine bases [7]. The NMR spectrum of the alkaloid (II) showed the signals from two methoxy groups at 6.17 and 6.36 ppm (two three-proton singlets). In the weak-field region there were signals at 3.41 ppm (1 H, singlet), 2.67-2.90 ppm (3 H, multiplet), and 1.71 ppm (1 H, multiplet) due to aromatic protons. The UV, IR, and NMR spectra of (II) and of d-caaverine are very similar but the base differs from d-caaverine by the presence of a methoxy group instead of a hydroxy group. To confirm this, d-caaverine (isolated previously from the same plant) was methylated in an excess of diazomethane, giving the O-methyl ether of d-caaverine, which was identical with the alkaloid (II). The facts given above show that the base (II) is the dextrorotatory form of l-nornuciferine [8, 9].

Thus, d-isoremerine and d-nornuciferine have been isolated from L. tulipifera for the first time.

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