ALKALOIDS OF Liriodendron tulipifera

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From the leaves of L. tulipifera L. (tulip tree) we have isolated the new aporphine alkaloid lirinine [1]. Continuing the separation of the phenolic part of the combined alkaloids from the leaves of L. tulipifera, from a benzene–methanol eluate we have obtained an amorphous base with mp 162-164°C (decomp.), composition $C_{19}H_{21}O_4N$, M^+ 327 (mass spectrometrically), optically active, sparingly soluble in the usual solvents, and readily soluble in water.

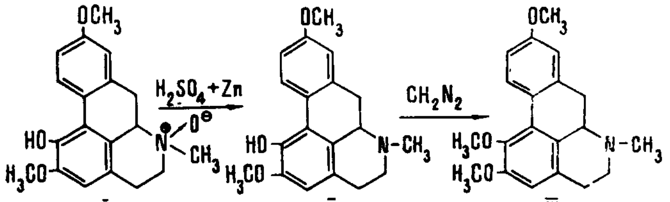
The UV spectrum of the alkaloid has absorption maxima $\lambda_{max}^{ethanol}$ 218, 284 nm (log ε 4.40, 4.03), which are characteristic for the aporphine alkaloids [2]. The IR spectrum of the base shows absorption bands at 3200-3500 cm^{-1} (hydroxy group), 2855 and 1245 cm^{-1} (methoxy group), and 1590 cm^{-1} (benzene ring). In its mass spectrum, the molecular peak with m/e 327 is the weakest, the peaks of ions with m/e 311 $(M-16)^+$ 310 $(M-17)^+$, 309 $(M-18)^+$ are fairly strong and the peaks of ions with m/e 296 $(M-31)^+$, 294 $(M-33)^+$, 280 $(M-47)^{+\cdot}$, 268 $(M-59)^+$ (100%), 253 $(M-74)^+$ are strong.

The solubility of the alkaloid in water and the presence in its mass spectrum of the peak of an ion with m/e 311 $(M-16)^+$ [3, 4] permitted the assumption that the base is lirinine N-oxide (I). The reduction of the alkaloid (I) gave a base with R_f 0.62 (system 1) identical with lirinine (II) [1].

By separating the nonphenolic fraction of the combined alkaloids from the leaves on a column of silica gel, we isolated an optically active amorphous base (III) with the composition $C_{20}H_{23}O_3N$, M^+ 325 (mass spectrometrically).

The UV spectrum of this base [$\lambda_{max}^{ethanol}$ 222, 283 nm (log ε 4.46, 4.22)] is similar to that of lirinine. The IR spectrum of the alkaloid shows absorption bands at 2855, 1270 cm^{-1} (methoxy group) and 1590 cm^{-1} (aromatic ring). The mass spectrum of the base has the peaks of ions with m/e M^+ 325 (100%), 324 $(M-1)^+$, 310 $(M-15)^+$, 394 $(M-31)^+$, 282 $(M-43)^+$, 267 $(M-58)^+$, 251 $(M-74)^+$, which are characteristic for the aporphine alkaloids [5]. The results of a comparative study of the UV, IR, and mass spectra of the alkaloids showed that this base and lirinine are structurally similar; they differ by only 14 m/e. The methylation of lirinine with diazomethane gave its O-methyl ether, which proved to be identical with the new alkaloid (III).

Thus, the facts given above show that (I) with mp 162-164°C (decomp.) is lirinine N-oxide and (III) is lirinine O-methyl ether.



I II III

EXPERIMENTAL

The UV spectra were taken on a Hitachi EPS-3T instrument (in ethanol), the IR spectra on a UR-10 spectrometer (molded tablets with KBr), and the mass spectra on an MKh-1303 instrument with a glass in-

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let to the admission system at an ionizing voltage of 40 eV. Thin-layer chromatography (TLC) was performed with type KSK silica gel containing 5% of gypsum and the following systems: 1) benzene–ethanol (4:1); 2) butan-1-ol–acetic acid–water (4:1:5); and 3) ethanol–chloroform–ethyl acetate (3:2:1).

Lirinine N-Oxide (I). Continuing the separation of the phenolic fraction of the combined alkaloids on a column of silica gel, from a benzene–methanol (9:1) eluate by treatment with acetone we isolated 0.045 g of a base with mp 162-164°C (decomp.), $[\alpha]_D^{22} -49.9°$ (c 0.15; methanol), R_f 0.14 (system 1), 0.55 (system 2), and 0.59 (system 3).

Lirinine (II). A solution of 0.030 g of lirinine N-oxide in 10% sulfuric acid was treated with granules of zinc and left for 17 h. Then it was filtered and the filtrate was made alkaline with ammonia and extracted with ether. The ether was driven off to give a base with mp 152-154°C showing no depression of the melting point with lirinine. Their IR spectra were identical.

O-Methyllirinine (III). The nonphenolic fraction of the bases (0.74 g) was passed through a column of silica gel. Elution was performed with benzene–methanol (99:1) with the collection of 50-ml fractions. Fractions 23-30 yielded 0.037 g of a base with R_f 0.65 (system 1), $[\alpha]_D^{25} -52.9°$ (c 0.17; chloroform).

Methylation of Lirinine. An ethereal solution of diazomethane was added to 30 mg of lirinine and the mixture was left for four days. Then the ether was distilled off and the residue was dissolved in water, made alkaline with 10% ammonia, and extracted with ether. Elimination of the ether gave a mixture of bases with R_f 0.62 and 0.65. By chromatography on a column of silica gel the base with R_f 0.65 was isolated, this R_f value coinciding with that of O-methyllirinine. Their IR spectra were also identical.

SUMMARY

1. The leaves of L. tulipifera L. have yielded lirinine N-oxide and a new amorphous base with the composition $C_{20}H_{23}O_3N$, $[\alpha]_D^{25} -52.9°$ (c 0.171; chloroform), M^+ 325 (mass spectrometrically).

2. On the basis of its UV, IR, and mass spectra and chemical transformations, the structure of 2,5,6-trimethoxyaporphine has been established for the new alkaloid.

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