# LIRININE — A NEW ALKALOID FROM Liriodendron tulipifera

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The aporphine alkaloids glaucine and liriodenine have been isolated from the plant L. tulipifera L. (family Magnoliaceae) [1-3].

We have studied the leaves of L. tulipifera L. collected on September 27, 1971 in the town of Tashkent. Chloroform extraction gave 0.134% of combined ethereal and 0.086% of combined chloroform alkaloids (on the weight of the dry plant). The ethereal fraction of the combined alkaloids was separated into phenolic and nonphenolic fractions.

By chromatographing the phenolic fraction of the combined alkaloids on a column of silica gel [eluent: benzene–methanol (99 : 1)] we isolated a crystalline base with the composition $C_{19}H_{21}O_3N$, mp 152-154°C (ethanol), $[\alpha]_D^{22}$ −55° (c 0.089; chloroform), $M^+$ 311 (mass spectroscopically). UV spectrum: $\lambda_{max}^{ethanol}$ 223, 284 nm (log ε 4.42, 417). From its spectrum and specific rotation, the base can be assigned to the aporphine series with an unsubstituted $C_4$ position [4, 5].

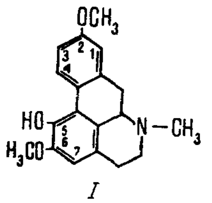
The IR spectrum of the base shows absorption bands in the following regions ($cm^{-1}$): 3100-3400 (hydroxy group), 2850, 1290 (methoxy group), and 1590 (aromatic ring). The presence of a hydroxy group was confirmed by the production of an O-acetyl derivative. The IR spectrum of the latter exhibited an absorption band at 1770 $cm^{-1}$ $(-\mathrm{C}\overset{\mathrm{O}}{/\!\!/}\ -\mathrm{O}-\mathrm{Ar}$ of a phenolic ester group). The alkaloid proved to be new, and we have called it lirinine.

In the NMR spectrum of lirinine (Fig. 1), in the strong-field region there is a three-proton singlet at τ 7.55 ppm, relating to a > N–methyl group, and two three-proton singlets: at τ 6.37 and 6.14 ppm, due to two aromatic methoxyls. In the weak-field region a two-proton singlet appeared in the spectrum at τ 2.78 ppm corresponding to two aromatic protons in the $C_7$ and $C_1$ positions and two one-proton doublets at τ 1.85 and 2.72 ppm (J 7.5 Hz), corresponding to aromatic protons at $C_4$ and $C_3$ [6, 8].

It follows from the above that the substituting groups in lirinine are located in the $C_2$, $C_5$, and $C_6$ positions. It can be seen from the NMR spectrum that the chemical shift from the fourth aromatic proton is shifted in the downfield direction. This shift of the signal is characteristic for this proton when a hydroxy group occupies the $C_5$ position [8, 9].

To check the position of the hydroxy group in lirinine we attempted to perform deuteration [10, 11]. When the mass spectrum of the deuterated derivative of the alkaloid was recorded, a molecular ion with m/e 311 was observed, which shows that no deuteration had taken place. Consequently, the hydroxy group in lirinine is located in the $C_5$ position.

On the basis of these facts, we propose the structure (I) for lirinine.



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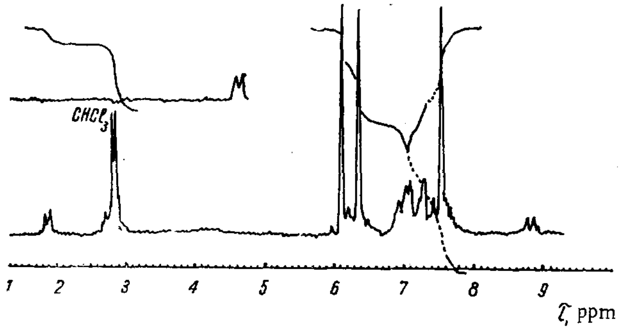

Fig. 1. NMR spectrum of lirinine.

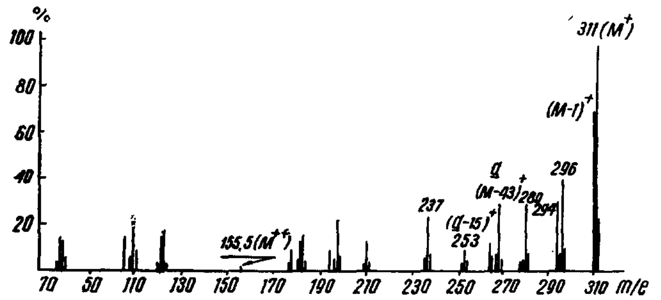

Fig. 2. Mass spectrum of lirinine.

The mass spectrum of the alkaloid also confirms the proposed structure. In this spectrum (Fig. 2), the maximum peak is that of the molecular ion with m/e 311 $M^+$ (100%), and the intensities of the peaks of the ions $(M-1)^+$ and $(M-43)^+$ are characteristic for aporphine alkaloids [12, 13].

The ions with m/e 296, 294, and 280 are formed by the loss of methyl, hydroxy, and methoxy groups from the molecular ion. The result of α and β cleavages of the molecular ion is the appearance of the ions $H_2C=\overset{+}{N}-CH_3$ with m/e 43 and fragment *a* $(M-43)^+$. The ion *a*, losing methyl and methoxy groups, gives ions with m/e 253 and 237. In addition, the mass spectrum has the peak of the doubly charged molecular ion with m/e 155.5.

## EXPERIMENTAL

Thin-layer chromatography (TLC) was performed with KSK silica gel (10 nm) and the following solvent system: 1) benzene–ethanol (8 : 2); and 2) butan-1-ol–acetic acid–water (40 : 10 : 50). The chromogenic agent was Dragendorff's reagent. The mass spectra were taken on an MKh-1303 instrument fitted with a system for the direct introduction of the substance into the ion source at an ionizing potential of 40 eV, and the NMR spectra on an M-4-H-100/100 MHz spectrophotometer ($CDCl_3$, with HMDS as internal standard).

Isolation of the Alkaloids. Comminuted air-dry leaves of Liriodendron tulipifera L. (2 kg) were wetted with 10% ammonia (2 : 1) and extracted with chloroform in a continuous apparatus. The chloroform extract was concentrated and treated with 10% sulfuric acid. The combined acid solution was washed with ether and, with cooling, alkalized with 25% ammonia. The alkaloids were exhaustively extracted first with ether and then with chloroform. This gave 2.68 g of ethereal and 1.72 g of chloroform alkaloids (the total amount of alkaloids was 0.22% on the weight of the dry plant).

Lirinine. The combined ethereal bases (2.68 g) were treated with 10% sulfuric acid. The acid solution was alkalized with 25% ammonia, and the free bases were exhaustively extracted with ether. The concentrated ethereal extract was treated three times with 5% caustic soda solution (20, 15, and 15 ml) and was washed with water. After the ethereal solution had been dried with anhydrous potassium carbonate, it was filtered and it then yielded 0.74 g of the nonphenolic fraction of the combined ethereal bases. The alkaline solution containing the phenolic bases was acidified with hydrochloric acid and was then again made alkaline with 25% ammonia and was extracted with ether. The yield of phenolic bases was 1.70 g. The phenolic fraction consisted of substances with $R_f$ 0.11, 0.14, 0.23, 0.33, 0.52, 0.63, and 0.78, and the nonphenolic fraction contained bases with $R_f$ 0.25, 0.43, 0.52, and 0.65 (TLC, system 1). The mixture of bases from the phenolic fraction (1.70 g) was passed through a column of silica gel and was eluted with a mixture of benzene and methanol (99 : 1). The first 200 ml of eluate gave 0.16 g of a crystalline base with mp 152-154°C (ethanol), $[\alpha]_D^{22}-55°$ (c 0.089; chloroform). $R_f$ 0.62 (system 1) and 0.34 (system 2).

Acetylation of Lirinine. A mixture of 20 mg of lirinine, 0.5 ml of acetic anhydride, and one drop of pyridine was left to stand for four days. Then the acetic anhydride and the pyridine were evaporated off, the residue was dissolved in a small amount of water, the solution was made alkaline with 10% ammonia and extracted with ether, and the extract was dried with anhydrous potassium carbonate. Evaporation of the ether gave a base with $R_f$ 0.68 (system 1).

## SUMMARY

1. The leaves of Liriodendron tulipifera have yielded a new alkaloid, lirinine. On the basis of a study of the UV, IR, NMR and mass spectra of lirinine the structure of 5-hydroxy-2,6-dimethoxyaporphine has been proposed for it.

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