THE DYNAMICS OF THE ACCUMULATION AND MUTUAL TRANSFORMATION OF ALKALOIDS IN *Liriodendron tulipifera*

R. Ziyaev, A. Abdusamatov, and S. Yu. Yunusov

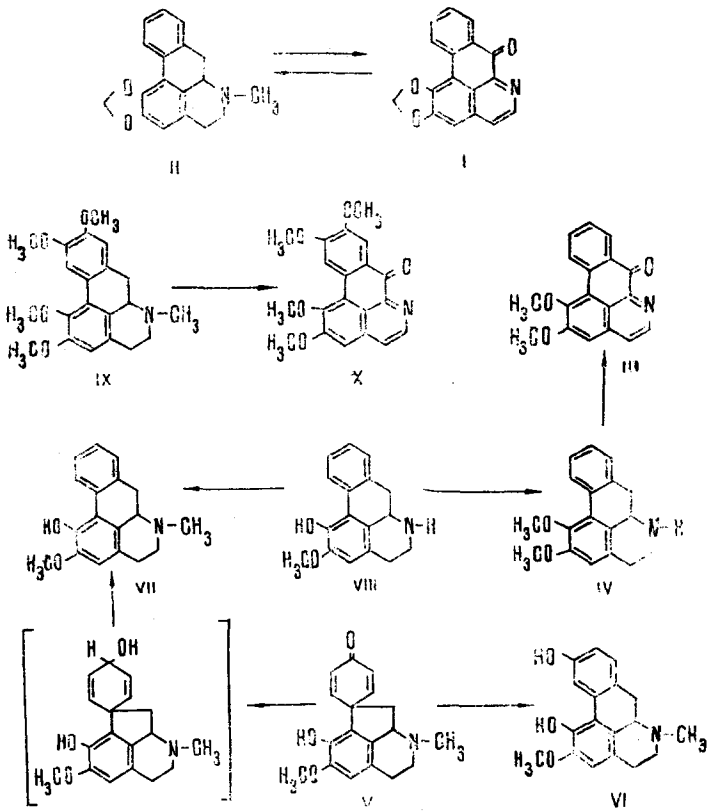
UDC 547.944/945

From the plant *Liriodendron tulipifera* L. (tulip tree) we have previously isolated alkaloids of the aporphine [1-3], oxoaporphine [4, 5], and proaporphine series (see scheme).

L. tulipifera L., cultivated in the botanical garden of the Academy of Sciences of the Uzbek SSR, Tashkent, was investigated at various vegetation periods, each organ separately (Table 1). The results of our study with respect to the periods of vegetation of the combined alkaloids of the leaves of the tulip tree have shown that the maximum amount of alkaloid is present in them in the spring and early vegetation period (0.32%), and the minimum amount is present in the yellow autumn leaves (0.11%).

From green leaves of this tree collected in the fruit-bearing stage we have isolated eight bases belonging to the aporphine alkaloids, and from the yellowed leaves together with aporphine alkaloids we have isolated oxoaporphine alkaloids — liriodenine (I), lysicamine (III) — and a proaporphine alkaloid — N-methylcrotsparine (V). From the wood and bark we isolated oxoaporphine alkaloids (see Table 1). In the green leaves, the main alkaloid is

Scheme 1



Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 478-481, July-August, 1975. Original article submitted May 7, 1974.

TABLE 1. Alkaloid Content in *L. tulipifera* L.

Plant organ	Vegetation period and date of collection	Total alkaloids	Alkaloids isolated
Leaves	Fruit-bearing September 28, 1971	0.22	d-Isoremerine, d-nornuciferine, lirinine, d-caaverine, lirinidine, O-methyllirinine, N-oxide of lirinine, base A
Wood	End of vegetation May 25, 1972	0.15	Liriodenine, lysicamine
Bark		0.105	O-methylatheroline, liridine Liriodenine, lysicamine
Yellowed leaves	October 28, 1972	0.11	d-Isoremerine, liriodenine, lirinine, lysicamine, d-caaverine, lirinidine, d-isolaureline, N-methylcrotsparine
Leaves	Beginning of flowering May 10, 1972	0.32	
	End of flowering May 25, 1972	0.30	
	Fruit-bearing September 20, 1972	0.23	
	Fading October 12, 1972	0.14	
Young branches	The same	0.13	
Petals	End of flowering May 25, 1972	0.10	
Seeds	Period of dying off October 28, 1972	0.087	

d-isoremerine (II) (30% of the combined bases), and in the yellowed leaves its amount is smaller (6%) than that of liriodenine (23%).

Thus, *L. tulipifera* is one more example of the fact that each organ of a plant may contain qualitatively and quantitatively different alkaloids, depending on the growth site and the vegetation period, and may also be considered an independent object of investigation [6].

The absence from the yellowed leaves of the aporphine alkaloid d-nornuciferine (IV) and from the wood of d-nornuciferine and d-isoremerine, and the presence in them of the oxoaporphine alkaloids lysicamine and liriodenine permit the assumption that aporphine is converted into oxoaporphine and that they possibly serve as intermediate links in a single biogenetic process [7-8].

The oxidation of d-nornuciferine (IV) and of glaucine (IX) with chromium trioxide in pyridine gave lysicamine (III) and O-methylatheroline (X). The reduction of lysicamine by zinc in hydrochloric acid gave an optically inactive nornuciferine.

Then passage from the proaporphine alkaloid N-methylcrotsparine (V) to 3,5-dihydroxy-6-methoxyaporphine (VI) and lirinidine (VII) and from d-caaverine (VIII) into d-nornuciferine (IV) and lirinidine takes place (see scheme).

EXPERIMENTAL METHOD

The conditions for the isolation and separation of the alkaloids and for recording their spectra are given in our previous papers [1, 2]. For thin-layer chromatography (TLC) we used KSK silica gel and the following solvent systems: 1) benzene—ethanol (4:1) and 2) ethyl acetate—methanol (9:1).

Oxidation of d-Nornuciferine (IV). At 0°C, 0.38 g of anhydrous chromium trioxide was added over 10 min to 4 ml of absolute pyridine. The mixture was stirred at room temperature (22°C) for 20 min, and then 0.055 g of d-nornuciferine in 2 ml of pyridine was added and the mixture was left for 44 h. Then 3 ml of ethanol was added and it was stirred for 20 min. The precipitate was filtered off and washed with chloroform. The filtrate and the wash

solution were evaporated to dryness, the residue was dissolved in chloroform, and the reaction product was extracted with 5% hydrochloric acid. The acid solution was made alkaline with 25% ammonia solution, and the base was extracted with chloroform. The residue after the elimination of the solvent was chromatographed on a column of silica gel. Elution with a mixture of benzene and methanol (95:5) and crystallization from ethanol yielded 10 mg of a base with mp 208-210°C. A mixture of the oxidized product with lysicamine (III) gave no depression of the melting point. Their IR spectra were also identical.

Reduction of Lysicamine (III). A solution of 0.1 g of lysicamine in 15 ml of dilute acetic acid (1:1) was treated with 1.2 g of zinc dust and 5 ml of concentrated hydrochloric acid, and the mixture was stirred on the boiling-water bath for 2 h. The solution was filtered, the precipitate was washed with hot water, the filtrate was made alkaline with 25% ammonia solution, and the base was extracted with ether. After evaporation of the ether, 0.020 g was obtained of a base with R_f 0.43 (system 1), $[\alpha]_D^{24} \pm 0°$ (c 0.12; chloroform).

The IR and UV spectra of the reduction product were identical with those of d-nornuciferine.

Reduction of N-Methylcrotsparine (V). Over a period of 30 min, 0.13 g of sodium tetrahydroborate ($NaBH_4$) in 12 ml of methanol was added to a solution of 0.065 g of N-methylcrotsparine in 8 ml of methanol, and the mixture was heated on the water bath for 2 h. The methanol was evaporated off and the residue was diluted with water and was acidified with dilute hydrochloric acid (1:1). Then it was made alkaline with 10% ammonia solution and extracted with ether. The ether was distilled off and the residue was chromatographed in a column of silica gel. Elution was performed with benzene–methanol (99:1); the first 60 ml of eluate yielded a base with R_f 0.52 (system 1) giving a hydrochloride with mp 237-239°C (decomp.).

The UV and IR spectra of the reduced product were identical with the spectra of lirinidine (VII).

Isomerization of N-Methylcrotsparine (V). A solution of 0.055 g of N-methylcrotsparine in 10 ml of 4 N hydrochloric acid was heated in the water bath for 1 h. Then it was cooled, made alkaline with 25% ammonia solution, and extracted with ether. The ether was distilled off and the residue was dissolved in 4 ml of ethanol and this solution was made weakly acid by the addition of an ethanolic solution of hydrochloric acid. This led to the precipitation of the hydrochloride of 3,5-dihydroxy-6-methoxyaporphine (VI), mp 249-252°C (decomp), M^+ 297, R_f 0.42 (system 1), 0.47 (system 2). UV spectrum: λ_{max} 220, 267, 275, 311 nm (log ε 4.40; 4.15; 4.22; 3.70).

SUMMARY

As the result of a study of the leaves of *Liriodendron tulipifera* L. according to the vegetation periods, it has been established that they contain the maximum amount of alkaloids in the spring and early vegetation period of the plant (0.32%) and the minimum amount when they are in the yellowed state in the autumn (0.11%).

Transitions from N-methylcrotsparine to lirinidine, from d-caaverine to lirinidine and d-nornuciferine, and from the latter to lysicamine have been established.

LITERATURE CITED

1. R. Ziyaev, A. Abdusamatov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 67 (1973).
2. R. Ziyaev, A. Abdusamatov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 760 (1973).
3. R. Ziyaev, A. Abdusamatov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 108 (1974).
4. A. Abdusamatov, R. Ziyaev, and S. Yu. Yunusov, Khim. Prirodn.Soedin., 112 (1974).
5. A. Abdusamatov, R. Ziyaev, and S. Yu. Yunusov, Abstracts of Lectures at the third Indo-Soviet Symposium on the Chemistry of Natural Compounds [in Russian], Tashkent (1973), p. 3.
6. S. Yu. Yunusov, Izv. Akad. Nauk UzSSR, No. 4, 11 (1948); Khim. Prirodn. Soedin., 104 (1966).
7. M. S. Yunusov, S. T. Akramov, and S. Yu. Yunusov, Dokl. Akad. Nauk UzSSR, No. 5, 38 (1966).
8. Kh. G. Pulatova, Z. F. Ismailov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 426 (1966).