ALKALOIDS OF THE WOOD OF Liriodendron tulipifera

A. Abdusamatov, R. Ziyaev, and S. Yu. Yunusov UDC 547.944/945

We have previously reported the isolation from the leaves of L. tulipifera L. of the new aporphine alkaloids lirinine and O-methyllirinine [1, 2].

We have investigated the wood of this tree collected in May, 1972, in the Tashkent Botanical Garden. Ordinary chloroform extraction gave 0.09% of combined ether-soluble and 0.06% of combined chloroformsoluble alkaloids. The ethereal fraction of the mixture of bases was separated into nonphenolic and phenolic fractions. The nonphenolic fraction of the combined alkaloids was chromatographed on silica gel.

A benzene-methanol (99:1) eluate yielded dark-yellow crystals of a base with the composition $C_{19}H_{15}$ NO₄, mol. wt. 321 (mass spectrometry) with mp 162-164°C (from chloroform), Rf 0.59 in the benzene-methanol (4:1) system. The alkaloid proved to be new, and we have called it liridine. On elution with a mixture of benzene and methanol (95:5), a base with the composition $C_{17}H_9NO_3$, mp 271-273°C (from chloroform) was obtained. Its Rf value was 0.35, and by its IR spectrum and a mixed melting point it was identified as liriodenine.

The UV spectrum of liridine has absorption maxima at 238, 276, and 440 nm (log ε 4.32, 4.36, 3.80) undergoing bathochromic shifts on acidification: $\lambda_{max}^{ethanol + HCl}$ 243, 282, 450 nm (log ε 4.31, 4.35, 3.62).

The IR spectrum showed absorption bands at 1655 cm⁻¹ for a conjugated carbonyl group and at 760 cm⁻¹ due to the deformation vibrations of the C-H groups of four adjacent aromatic protons. Consequently, liridine belongs to alkaloids of the dibenzo[de,g]quinolin-F-one type [3] in which ring D contains no substituents. On studying the NMR spectrum of liridine and comparing it with the spectrum of liridenine (Table 1), we found that the nature of the signals of the aromatic protons was the same, but only in liridine was there no signal of an aromatic proton at C₃. Consequently, there must be a methoxy group in this position.

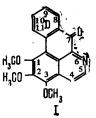


TABLE 1

Compound	CH _s O _s		-OCH3			Aromatic protons						
	$c-\overline{1}$	c-2	c−İ	c-2	c-3	C-3	c-8	c-9	C- 10	c-11	c-4	c-5
Liriodenine Liridine	3,78 (2H) s.		6,1 (9H) s.		2,89 s.		2,65 — 1,22 (6H) m 2,71 — 1,13 (6H) m					

<u>Note.</u> JNM-4H-100/100 MHz instrument (in CF₃COOH with HMDS as internal standard, τ scale, s - singlet; m - multiplet).

Order of the Red Banner of Labor Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 112-113, January-February, 1974. Original article submitted July 4, 1973.

© 1975 Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.

On the basis of the facts given, liridine has the structure of 1,2,3-trimethoxydibenzo [de, g]quinolin-F-one (I).

It must be mentioned that substance (I) has been synthesized previously [4] but we are the first to have found it in a plant.

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., 505 (1973).
- 3. M. A. Buchanan and E. E. Dickey, J. Org. Chem., 25, 1389 (1960).
- 4. I. R. C. Bick and G. K. Douglas, Tetrahedron Lett., 4655 (1965).

.