

Active Principles of the Trunk-bark of *Michelia Champaca* Linn.

P. L. Majumder and (Mrs.) A. Chatterjee

A yellow base, m.p. 272° (decomp.), isolated from *Michelia champaca* Linn., has been proved to be an aporphine alkaloid, identical with liriodenine, a pigment of yellow poplar tree¹.

*Michelia champaca*² Linn. (Family, Magnoliaceae) is widely distributed in the eastern sub-Himalayan tracts and is cultivated in various parts of India. It produces golden yellow and highly scented flowers. Though a considerable amount of work has been done on the essential oil of the flowers³, chemical investigation on other parts of this plant has not been reported so far. Since several of *Michelia* species, such as, *Michelia compressa*^{4,5}, *Michelia alba*⁶, *Michelia fuscata*⁷, have been found to produce alkaloids belonging to bis-benzylisoquinoline and aporphine series, it has been thought desirable to investigate *Michelia champaca* with a view to isolating its alkaloidal principles, if any. This plant grows luxuriantly in this country. At present the bark of the species has been selected for the purpose.

The powdered plant material was defatted with petroleum (b.p. 60-80°) and then extracted with chloroform. The light petroleum extract furnished a white crystalline substance, m.p. 136-37°, which was identified as β -sitosterol. From the chloroform extract, an alkaloid, C₁₇H₂₃O₃N, m.p. 272° (decomp.), was isolated in a small quantity (0.0005%). The main bulk of the alkaloid was, however, extracted from the ethanolic extract (0.0015%). The base crystallises from chloroform in fine needles. It is moderately soluble in ethanol and acetone and sparingly soluble in ether. The base is optically inactive.

The homogeneity of the base was confirmed from a single yellow spot on a uni-dimensional paper chromatogram ($R_f=0.78$; BuOH:AcOH:H₂O=4:1:1).

The alkaloid exhibits light absorption in the ultraviolet region and the absorption spectrum is typical of an aporphine base. This was further substantiated by the following colour reactions exhibited by the alkaloid: HCl (conc.), orange; HNO₃ (conc.), deep orange; H₂SO₄ (conc.), reddish yellow; Fröhde, reddish violet-dirty red; Hopkin-Cole, orange.

The base is free from methoxyl, -N-methyl and terminal methyl groups, and active hydrogen atom, but contains a methylenedioxy group. The presence of the latter could

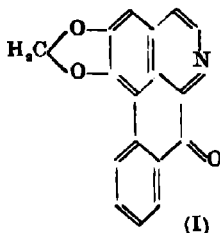
1. Buchanan and Dickey, *J. Org. Chem.*, 1960, 25, 1389.
2. Chopra, Nayar & Chopra, "Glossary of Indian Medicinal Plants", p.166, published by the C.S.I.R., 1956.
3. Girard, *Ind. Perfume*, 1947, 2, 183, 217, 267.
4. Tsang-Hsiung Yang, *J. Pharm. Soc., Japan*, 1962, 82, 794.
5. Kazuo Ito (Univ. Kyoto), *ibid.*, 1960, 80, 705.
6. Tsang-Hsiung Yang, *ibid.*, 1962, 82, 811.
7. Kazuo Ito and Uchida (Univ. Kyoto), *ibid.*, 1959, 79, 1108.

only be indicated from the IR spectrum of the alkaloid ($\lambda_{\max}$ 7.92, 8.14, 9.5, and 10.3 μ). Chemical evidence for methylenedioxy group, viz., green colour with gallic acid- H_2SO_4 or red precipitate with phloroglucinol-HCl (Clowes & Tollen's method) was not obtained. Presence of a conjugated $\text{C}=\text{O}$ group in the yellow base was indicated by the characteristic peak, 6.0 μ , in the IR spectrum, which was further confirmed by formation of a monoxime, m.p. 262° (decomp.).

The low proportion of hydrogen to carbon in the base suggests a highly unsaturated condensed ring system. The intense yellow colour of the base is in conformity with its unsaturated nature.

The alkaloid forms a red pierate, which crystallises in prisms from methanol, m.p. 280° (decomp.) and an orange perchlorate which separates from methanol in needles, m.p. 308-10° (decomp.).

Our preliminary investigation of the base suggests its identity with liriodenine, the structure of which has been established recently by an unambiguous synthesis by Taylor⁸ as (I).



The identity of our base with liriodenine has been confirmed from a comparison of these two bases by UV and IR spectra and by mixed m.p. The authentic sample of liriodenine was obtained through the courtesy of Dr. M. A. Buchanan. Liriodenine under different names has been isolated independently by the Formosan⁹ and Japanese¹⁰ workers. The former called it Micheline-B and the latter, oxoushinsunine (liriodenine).^{*}

EXPERIMENTAL

Isolation.—The dried and pulverised bark (1 kg.) of *M. champaca* was successively soxhletted with petroleum (b.p. 60-80°) and chloroform. The petroleum extract was concentrated and its chromatographic resolution over Brockmann alumina furnished a white substance (15 mg.). It was eluted with benzene-chloroform mixture (4:1) and crystallised from methanol, m.p. 136-37°. The substance gave a positive Burchard-Lieberman test for sterol and showed no depression in m.p. with an authentic sample of β -sitosterol.

8. Taylor, *Tetrahedron*, 1961, 14, No. 42.

9. Shu-Shu Yang *et al.*, *Chemistry* (Taipei), p. 144, 1961.

10. Tseng-Hsiung Yang, *J. Pharm. Soc., Japan*, 1962, 82, 798.

* Recently attention of the authors has been drawn to isolation of Oxoushinsunine from *M. Champaca* (*J. Pharm. Soc., Japan*, 1963, 83, 210).

The concentrated chloroform extract on similar chromatographic resolution over a column (30cm $\times$ 1.5 cm) of Brockmann alumina furnished liriodenine, migrated as a sharp yellow band with benzene-chloroform mixture (1:1) (5 mg.). The eluates were collected in 25-ml fractions each. Liriodenine was obtained from 32-35 fractions.

The marc left after extraction with light petroleum and chloroform was percolated with ethanol containing 0.01% acetic acid for 3 weeks. The solvent was distilled under reduced pressure and the concentrated syrupy mass was treated with 2*N* acetic acid. The aqueous acetic acid solution was filtered, basified with ammonia, and extracted with chloroform. The chloroform extract was dried over anhydrous Na_2SO_4 and concentrated. The concentrated extract on chromatographic resolution over Brockmann alumina furnished a further quantity of liriodenine (15 mg.). Several recrystallisations from chloroform yielded yellow needles of pure liriodenine, m.p. 272° (decomp.); $[\alpha]_D^{20} \pm 0^\circ$. (Found: C, 73.89; H, 3.34; N, 5.44. Calc. for $\text{C}_{17}\text{H}_{10}\text{O}_3\text{N}$: C, 74.18; H, 3.27; N, 5.10%). Mass number, 275; $\lambda_{\text{max}}^{\text{EtOH}}$ 246 m μ (log ϵ , 4.45), 267 m μ (log ϵ , 4.4), 306 m μ (log ϵ , 4.3). λ_{max} (nujol): 6.0, 7.92, 8.14, 9.5, and 10.3 μ .

Orime.—The base (50 mg.) was refluxed for 45 minutes with pyridine (2 ml) and hydroxylamine hydrochloride (51 mg.). The reaction product was cooled and stirred into 20 ml of 2*N* acetic acid. The yellow precipitate (30 mg.) was filtered, washed with water, and recrystallised twice from butanol¹² to furnish a yellow crystalline substance, m.p. 262° (decomp.). (Found: C, 69.57; H, 3.25; N, 9.39. Calc. for $\text{C}_{17}\text{H}_{10}\text{O}_3\text{N}_2$: C, 70.34; H, 3.47; N, 9.65%).

The authors acknowledge their grateful thanks to Dr. A. Bernhardt, Mikro-laboratory, Max Planck Institute for Köhlen Forschung, Mullheim, West Germany, for micro-analysis and to Dr. M. A. Buchanan, Institute of Paper Chemistry, Appleton, Wisconsin, U.S.A., for a generous gift of liriodenine.