

MINOR ALKALOIDS OF *BOEHMERIA PLATYPHYLLA* DON.
(FAMILY URTICACEAE)*

II.† ISOLATION OF CRYPTOPLEURINE AND A NEW SECO-PHENANTHRO-
QUINOLIZIDINE ALKALOID

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Although available in only very small quantities, two minor alkaloids from the shrub *Boehmeria platyphylla* Don. are of special interest because so little is known of alkaloids from the family Urticaceae, and because of their biosynthetic relationship to the phenanthroindolizidine alkaloids of *Tylophora* and *Ficus* species¹ and even closer relationship to the alkaloids of the botanically unrelated tree *Cryptocarya pleurosperma* White & Francis (family Lauraceae).²⁻⁴ Consideration of the structures of the three *Boehmeria* alkaloids provides further evidence for the postulated biosynthetic scheme^{1,5} whereby cryptopleurine and the *Tylophora* bases are derived from two equivalents of dihydroxyphenylalanine and one equivalent of lysine or ornithine respectively. Each of the three alkaloids corresponds to a different stage of the biosynthetic scheme.

It was shown in Part I⁶ that the major *B. platyphylla* alkaloid is 3,4-dimethoxy- ω -(2'-piperidyl)acetophenone (Ia), and its structure was established from its preparation by *O*-methylation of pleurospermine (Ib), an alkaloid from the leaves of *Cryptocarya pleurosperma*.² One of the minor *B. platyphylla* alkaloids, C₂₄H₂₇NO₃, m.p. 197–198°, $[\alpha]_D -64^\circ$ in chloroform, can also be directly related to a *C. pleurosperma* alkaloid, as, apart from a difference in the magnitude of $[\alpha]_D$, it is identical with cryptopleurine (II), the highly vesicant alkaloid from the bark of *C. pleurosperma*.³ Purified (–)-cryptopleurine was found to have $[\alpha]_D -109^\circ$ in chloroform, in agreement with the previously reported value of $[\alpha]_D -106^\circ$,³ so that it is evident that cryptopleurine is obtained from *B. platyphylla* as a partial racemate.

The second minor base, C₂₄H₂₉NO₃, m.p. 134.5–135.5°, $[\alpha]_D +4.6^\circ$ in chloroform, has a strong molecular ion peak at *m/e* 379 (89% of base peak), two mass units higher than that observed in the mass spectrum of cryptopleurine. As there was

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¹ Govindachari, T. R., "The Alkaloids." (Ed. R. H. F. Manske.) Vol. IX, p. 517. (Academic Press: New York 1967.)

² Loder, J. W., *Aust. J. Chem.*, 1962, **15**, 296.

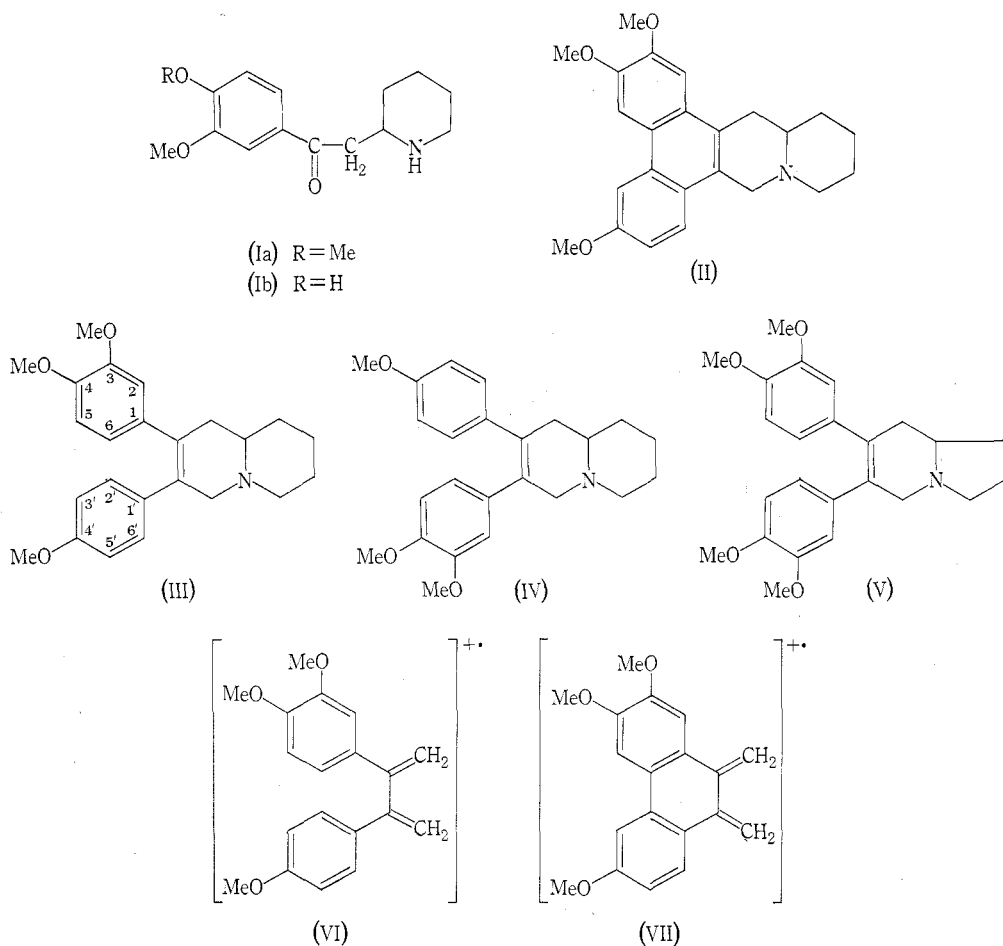
³ Gellert, E., and Riggs, N. V., *Aust. J. Chem.*, 1954, **7**, 113.

⁴ Fridrichsons, J., and Mathieson, A. McL., *Nature*, 1954, **173**, 732.

⁵ Wenkert, E., *Experientia*, 1959, **15**, 165.

⁶ Hart, N. K., Johns, S. R., and Lambertson, J. A., *Aust. J. Chem.*, 1968, **21**, 1397.

only a very limited amount of the purified alkaloid available, microanalyses were not obtained and the molecular formula was shown to be $C_{24}H_{29}NO_3$ by a high-resolution mass spectrum which indicated a molecular weight of 379.2141 (calc. mol. wt. 379.2147). This alkaloid, which is considered to be (III) or (IV), probably bears a



relationship to cryptopleurine like that of the alkaloid septicine (V) to tylocrebrine in *Ficus septicus*,⁷ and accordingly (III) is preferred, although chemical evidence does not enable a distinction to be drawn between (III) and (IV). The ultraviolet absorption spectrum of (III) in ethanol (λ_{\max} 230 m μ ($\log \epsilon$ 4.34), 280 ($\log \epsilon$ 4.07)) is different from that of cryptopleurine and resembles the spectra reported for *cis*-stilbenes.⁸ The 100-Mc/s n.m.r. spectrum of the alkaloid in $CDCl_3$ solution (TMS δ 0.00) shows signals from three methoxyl groups at δ 3.47, δ 3.66, and δ 3.74, and signals from

⁷ Russel, J. H., *Naturwissenschaften*, 1963, 50, 443.

⁸ Scott, A. I., "Interpretation of the Ultraviolet Spectra of Natural Products," p. 99. (Pergamon Press: Oxford 1964.)

seven aromatic protons. On the basis of structure (III), the aromatic proton signals can be interpreted as a one-proton signal at δ 6.43 showing only a small *meta* (2–3 c/s) coupling (H 2), an A_2B_2 system of four protons (δ_A 6.64, δ_B 6.95, J_{AB} 9.0 c/s) assigned respectively to H 3', H 5' and H 2', H 6' on the methoxyphenyl substituent, and a two-proton signal at δ 6.63 assigned to H 5 and H 6, which coincide in chemical shift and show only a small *meta*-coupling.

The mass spectrum of (III) shows a base peak at m/e 265, and an intense peak at m/e 296 (58% of base peak) which can be explained by fragmentation to (VI), whereas cryptopleurine (II) shows a base peak at m/e 294 which can be attributed to (VII). This fragmentation for cryptopleurine is completely analogous to that suggested for the alkaloid tylophorine.¹

Experimental

The isolation of the major alkaloid from 17 kg of dried *B. platyphylla* has already been described in Part I. The major base (Ia) was eluted from a column of neutral alumina by a mixture of benzene and chloroform (10 : 1), and both minor bases were obtained from a small crystalline fraction (39 mg) eluted from the column by benzene in front of the fractions containing the major base (Ia). This small crystalline fraction was shown by thin-layer chromatography to be essentially a mixture of two components, and a separation was achieved by preparative thin-layer chromatography on plates of Kieselgel G developed in the solvent system acetone–chloroform (1 : 1). In this solvent system cryptopleurine had R_F 0.63 and the minor seco-phenanthroquinolizidine base R_F 0.75. The alkaloids recovered from the thin-layer plates were each further purified by chromatography on a small column of alumina and eventually 15 mg of cryptopleurine and 10 mg of the seco-base were obtained.

Cryptopleurine, m.p. 197–198°, $[\alpha]_D -64^\circ$ (c , 0.5 in $CHCl_3$), crystallized from acetone in colourless needles, and was identified by a mixed melting point determination and by comparison of the i.r. and mass spectra with those of authentic cryptopleurine.

The seco-phenanthroquinolizidine base (III) crystallized from acetone in colourless needles, m.p. 134.5–135.5°, $[\alpha]_D +4.6^\circ$ (c , 0.5 in $CHCl_3$). Spectroscopic data for this alkaloid has already been set out in the discussion, and the high-resolution mass spectrum was obtained on an MS9 instrument. The accurate molecular weight determination was made with perfluorotributylamine as a reference standard.

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