

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* species<sup>1</sup> and even closer relationship to the alkaloids of the botanically unrelated tree *Cryptocarya pleurosperma* White & Francis (family Lauraceae).<sup>2-4</sup> Consideration of the structures of the three *Boehmeria* alkaloids provides further evidence for the postulated biosynthetic scheme<sup>1,5</sup> 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 I<sup>6</sup> that the major *B. platyphylla* alkaloid is 3,4-dimethoxy- $\omega$ -(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*.<sup>2</sup> One of the minor *B. platyphylla* alkaloids, C<sub>24</sub>H<sub>27</sub>NO<sub>3</sub>, m.p. 197–198°, [ $\alpha$ ]<sub>D</sub> –64° in chloroform, can also be directly related to a *C. pleurosperma* alkaloid, as, apart from a difference in the magnitude of [ $\alpha$ ]<sub>D</sub>, it is identical with cryptopleurine (II), the highly vesicant alkaloid from the bark of *C. pleurosperma*.<sup>3</sup> Purified (–)-cryptopleurine was found to have [ $\alpha$ ]<sub>D</sub> –109° in chloroform, in agreement with the previously reported value of [ $\alpha$ ]<sub>D</sub> –106°,<sup>3</sup> so that it is evident that cryptopleurine is obtained from *B. platyphylla* as a partial racemate.

The second minor base, C<sub>24</sub>H<sub>29</sub>NO<sub>3</sub>, m.p. 134.5–135.5°, [ $\alpha$ ]<sub>D</sub> +4.6° 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

\* Manuscript received June 19, 1968.

† Part I, *Aust. J. Chem.*, 1968, **21**, 1397.

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

<sup>2</sup> Loder, J. W., *Aust. J. Chem.*, 1962, **15**, 296.

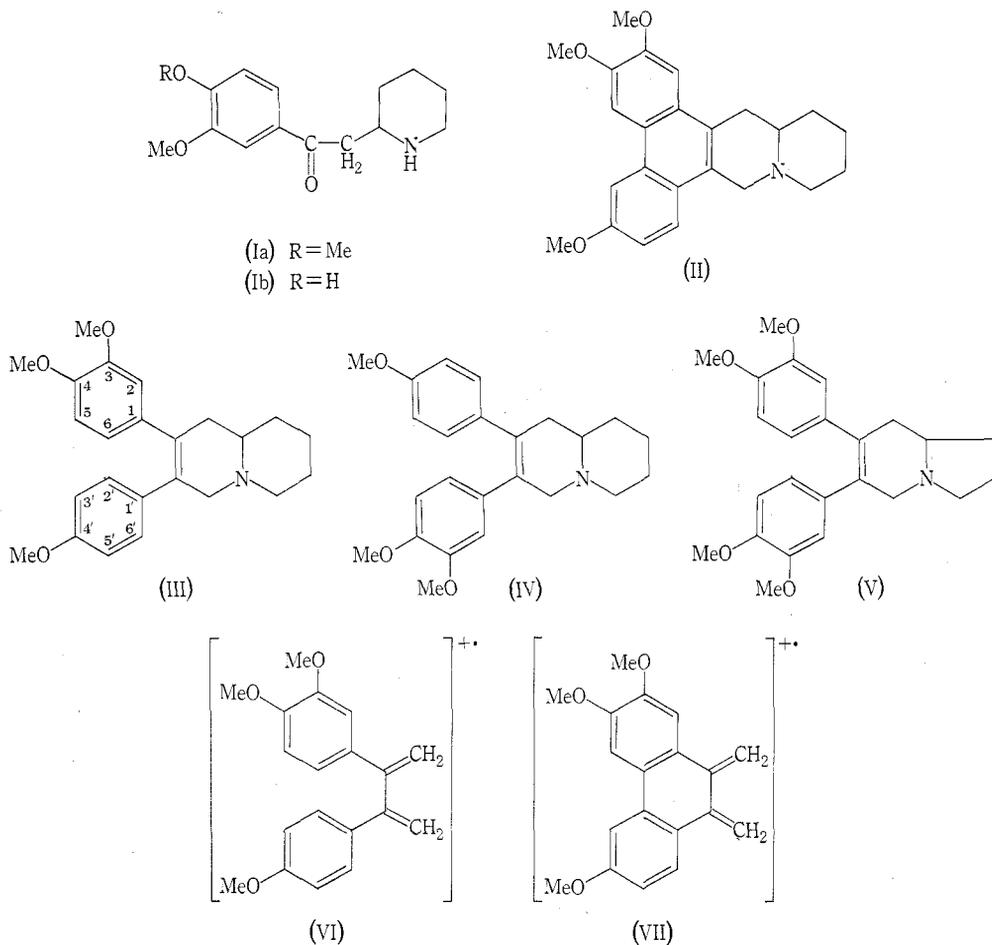
<sup>3</sup> Gellert, E., and Riggs, N. V., *Aust. J. Chem.*, 1954, **7**, 113.

<sup>4</sup> Fridrichsons, J., and Mathieson, A. McL., *Nature*, 1954, **173**, 732.

<sup>5</sup> Wenkert, E., *Experientia*, 1959, **15**, 165.

<sup>6</sup> 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 septica*,<sup>7</sup> 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 ( $\lambda_{max}$  230  $m\mu$  ( $\log \epsilon$  4.34), 280 ( $\log \epsilon$  4.07)) is different from that of cryptopleurine and resembles the spectra reported for *cis*-stilbenes.<sup>8</sup> The 100-Mc/s n.m.r. spectrum of the alkaloid in  $CDCl_3$  solution (TMS  $\delta$  0.00) shows signals from three methoxyl groups at  $\delta$  3.47,  $\delta$  3.66, and  $\delta$  3.74, and signals from

<sup>7</sup> Russel, J. H., *Naturwissenschaften*, 1963, 50, 443.

<sup>8</sup> 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  $\delta$  6.43 showing only a small *meta* (2–3 c/s) coupling (H 2), an  $A_2B_2$  system of four protons ( $\delta_A$  6.64,  $\delta_B$  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  $\delta$  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.<sup>1</sup>

### 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.

### Acknowledgments

The authors are indebted to Dr Q. N. Porter (University of Melbourne) for an accurate molecular weight determination from a high-resolution mass spectrum, and to Mr W. T. Jones for the collection of *B. platyphylla*.