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 scheme4,5 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-\(\omega\)-(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. One of the minor B. platyphylla alkaloids, \(C_{24}H_{27}NO_3\), m.p. 197-198°, \([\alpha]_D -64°\) 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.6 Purified (−)-cryptopleurine was found to have \([\alpha]_D -109°\) in chloroform, in agreement with the previously reported value of \([\alpha]_D -106°,3\) so that it is evident that cryptopleurine is obtained from B. platyphylla as a partial racemate.

The second minor base, \(C_{23}H_{28}NO_8\), m.p. 134.5-135.5°, \([\alpha]_D -4.6°\) 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

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5 Wenkert, E., Experientia, 1959, 15, 166.

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, 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 ($\lambda_{\text{max}}$ 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. The 100-Mc/s n.m.r. spectrum of the alkaloid in CDCl$_3$ solution (TMS 6 0.00) shows signals from three methoxyl groups at 6 3.47, 6 3.66, and 6 3.74, and signals from

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 (H2), an A2B2 system of four protons (δA 6·64, δB 6·95, JAB 9·0 c/s)
assigned respectively to H3', H5' and H2', H6' on the methoxyphenyl substituent,
and a two-proton signal at δ 6·63 assigned to H5 and H6, 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 chromato-
graphy on plates of Kieselgel G developed in the solvent system acetone–chloroform (1 : 1). In this
solvent system cryptopleurine had RF 0·63 and the minor seco-phenanthroquinolizidine base
RF 0·75. The alkaloids recovered from the thin-layer plates were each further purified by chroma-
tography 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°, [α]D −64° (c, 0·5 in CHCl3), 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°, [α]D +4·6° (c, 0·5 in CHCl3). 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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