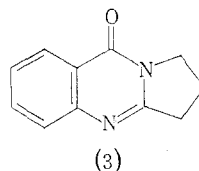
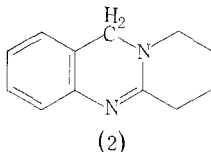
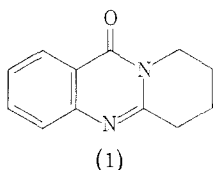


# THE IDENTIFICATION OF A MINOR ALKALOID OF *MACKINLAYA MACROSCIADIA* (ARALIACEAE) AS DEOXYVASICINONE

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Two *Mackinlaya* species, *M. macrosciadia* (F. Muell.) F. Muell. from Queensland and a New Guinea species, the name of which was previously recorded as *M. subulata* Philipson but has now been revised to *Mackinlaya* cf. *klossii* Philipson (T. G. Hartley, personal communication), are of interest as the first plants of the family Araliaceae to yield significant amounts of alkaloids.<sup>1,2</sup> The major tetrahydropyridoquinazoline alkaloids (1) and (2) and anabasine were previously isolated from both species. A minor alkaloid of *M. macrosciadia* has now been identified as deoxyvasicinone (3), an alkaloid previously obtained from *Peganum harmala* Linn. (family Zygophyllaceae).<sup>3</sup> The isolation of deoxyvasicinone is of biosynthetic interest as it lends support to the suggestion<sup>2</sup> that the alkaloids (1) and (2) are derived from anthranilic acid and lysine in a manner analogous to the formation of vasicine from anthranilic acid and ornithine. Another alkaloid, C<sub>12</sub>H<sub>16</sub>N<sub>2</sub>O, has been isolated from *M. macrosciadia* in amounts too small for detailed study.



## Experimental

Examination of the total alkaloids of *M. macrosciadia* by thin-layer chromatography on plates of Kieselgel G in the solvent system chloroform-methanol (9:1) indicated the presence of constituents with  $R_F$  values (0.71 and 0.69) close to that of alkaloid (1) ( $R_F$  0.77). The crude alkaloids were chromatographed on a column of neutral alumina (Spence Type H deactivated with ethyl acetate). The first fractions eluted from the column by benzene consisted essentially of alkaloid (1), and these fractions were followed by fractions which contained alkaloid (1), and the alkaloids with  $R_F$  values 0.71 and 0.69.

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<sup>1</sup> Johns, S. R., and Lambertson, J. A., *Chem. Commun.*, 1965, 267.

<sup>2</sup> Fitzgerald, J. S., Johns, S. R., Lambertson, J. A., and Redcliffe, A. H., *Aust. J. Chem.*, 1966, **19**, 151.

<sup>3</sup> Chatterjee, A., and Ganguly, M., *Phytochemistry*, 1968, **7**, 307.

The alkaloid of  $R_F$  0.71 was isolated by preparative thin-layer chromatography on plates of Kieselgel G in the system chloroform-methanol (93:7). The *alkaloid* recovered from the t.l.c. plates crystallized from benzene-hexane (1:4) in colourless prisms (12 mg), m.p. 92.5–93.5°,  $[\alpha]_D \pm 0^\circ$  (c, 0.78 in  $\text{CHCl}_3$ );  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 1627  $\text{cm}^{-1}$  (very strong), 3270, 3380, and 3500  $\text{cm}^{-1}$ ;  $\nu_{\text{max}}$  (ethanol) 242 nm ( $\log \epsilon$  3.78), 294 ( $\log \epsilon$  3.36) (Found: C, 70.8; H, 7.8; N, 13.3.  $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}$  requires C, 70.6; H, 7.9; N, 13.7%). The mass spectrum showed peaks at  $m/e$  204 (molecular ion base peak, 100%), 185 (17), 159 (22), 147 (43), 133 (14), 120 (22), 119 (13), 107 (32), 106 (97), 104 (16), 98 (38), 78 (17), 77 (26), 70 (22), and 55 (14). After exchange with  $\text{D}_2\text{O}$  the molecular ion peak shifted to  $m/e$  206.

The alkaloid of  $R_F$  0.69 was also isolated by preparative t.l.c. and it separated from benzene as colourless crystals (10 mg), m.p. 109–110°,  $[\alpha]_D \pm 0^\circ$  (c, 0.78 in  $\text{CHCl}_3$ ). The n.m.r. spectrum indicated that this alkaloid was deoxyvasicinone (3) and the infrared and mass spectra were identical with those of authentic deoxyvasicinone. A mixed m.p. determination showed no depression of m.p.

### *Acknowledgment*

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