was identified as agathic acid 19-monomethyl ester[4] m.p. 87–88° (evac. cap. corr.), (lit.[4] 81–86°); $[\alpha]_D^{25}$ +61·1° (*c* 0·6, $CHCl_3$), (lit.[4] +57°); and NMR ($CDCl_3$) δ 0·52 (*s*, Me at C-10), 1·18 (*s*, Me at C-4), 2·17 (*s*, Me, C-16), 3·63 (*s*, COOMe), 4·51 and 4·90 (=CH_2), 5·66 (*br s*, H at C-14) and 11·33 (COOH), cf. data of Thomas.[4]

Imbricataloic acid was identified by the GLC retention characteristics of the methyl ester and by the NMR spectrum of the ester as isolated by preparative GLC. Imbricataloic acid was first found in the needles of *P. elliottii*[5] and has since been found to occur in the needles of a large number of pines.[6]

From these data, it appears that there are at least two chemically different variants of *P. massoniana*.

Cortex. All of the trees contain the common pine resin acids with levopimaric/palustric and neoabietic acids predominating. The resin acid fractions for trees of the Ma-14 type do not contain any of the agathic acid monomethyl ester; trees of the Ma-55 type have 10–20% imbricataloic acid in the resin acids.

Acknowledgements—We thank Dr D. R. Roberts, SE Forest Experiment Station, Forest Service, for samples of *P. massoniana* from the Olustee Arboretum

[4] Found in *Agathis australis* resin, THOMAS, B. R. (1966) *Acta Chem. Scand.* **20**, 1074. Agathic acid 16-monomethyl ester has been isolated from *Agathis microstachya* oleoresin, CARMAN, R. M. and MARTY, R. A. (1966) *Australian J. Chem.* **19**, 2403. Dehydropimfolic acid (the C-4 epimer of agathic acid) has been found in the needles of *P. sylvestris*, NORIN, T., SUNDIN, S. and THEANDER, O. (1971) *Acta Chem. Scand.* **25**, 607.

[5] SPALDING, B. P., ZINKEL, D. F. and ROBERTS, D. R. (1971) *Phytochemistry* **10**, 3289. The C-4 epimer of imbricataloic acid has been found in the needles of some *P. nigra* samples.[6]

[6] ZINKEL, D. F., unpublished.

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CYANIDIN-3-NEOHESPERIDOSIDE, A NOVEL ANTHOCYANIN FROM *PODOCARPUS LAWRENCII*

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An earlier study of anthocyanins in *Podocarpus lawrencii*[1] had failed to identify a cyanidin glycoside which appeared as a minor constituent in extracts of female cones. On paper chromatography this compound, PC3, had unusually high R_f values in both BAW and 5% AcOH solvents (0·42, 0·63, compared with cyanidin-3-glucoside 0·30, 0·24 and cyanidin-3-rutinoside 0·30, 0·36, respectively). PC3 has since been obtained in high yield (in fact it appears as the major component in the extract) by using a procedure for extraction of fresh cones and primary pigment purification, in which contact with mineral acid is

[1] CROWDEN, R. K. and GRUBB, M. J. (1971) *Phytochemistry* **10**, 2821.

virtually eliminated [2] This suggested that PC3 contained an unusually labile type of glycoside

Hydrolysis with 2N HCl gave equimolar quantites of cyanidin, glucose and rhamnose, and spectral examination showed the 5-hydroxyl was unsubstituted Partial hydrolysis yielded cyanidin 3-glucoside as the only intermediate, and all of the original PC3 had disappeared within 2 min. The extreme lability of PC3 to acid conditions was shown further in attempts to prepare purified samples by paper electrophoresis in formate buffer, pH 2 2, and by PC using the solvent H_2O AcOH–conc HCl (82·15 3) In each case PC3 ran as a bioside, but was degraded to cyanidin 3-glucoside as the paper dried out The most likely structure for PC3 was considered to be a 3-bioside of cyanidin, containing glucose and rhamnose, other than rutinose That it was the 3-neohesperidoside (1,2-α-rhamnosylglucose) was shown by hydrogen peroxide oxidation of PC3[3] and comparison of the resultant disaccharide with an authentic sample of neohesperidose obtained from naringin in the same way PC data published by Williams *et al* [4] show a corresponding differentiation of the 3-neohesperidoside and 3-rutinoside of quercetin

Lowry[5] has previously reported two anthocyanins from *Podocarpus* species (podocarpins A and B, substituted 3-glucosides of cyanidin and pelargonidin, respectively) with unusual chromatographic behaviour similar to that reported here for PC3 Lowry remarks also on the inherent instability of his compounds, and that they may not have resisted storage as "dried films" prior to working up In view of these properties and the distribution of podocarpins A and B in other species of the subfamily Podocarpoideae, to which *P lawrencii* also belongs, it is probable that podocarpin A is in fact cyanidin-3-neohesperidoside and podocarpin B the pelargonidin analogue It is of interest to note also that the cones of another endemic Tasmanian species *Microcachrys tetragyna* Hook contains an unidentified pelargonidin derivative showing chromatographic behaviour corresponding to podocarpin B. However, this material has not yet been collected in sufficient quantity to confirm its identity as pelargonidin 3-neohesperidoside

EXPERIMENTAL

Extraction and isolation was carried out using a column of the weak carboxylic acid ion-exchange resin Bio Rex 70 H^+ (Bio-Rad Laboratories) followed by PC procedures as described by Jarman and Crowden [2] Hydrogen peroxide oxidation to detach the 3-bioside was basically the method of Chandler and Harper,[3] but allowing oxidation to proceed for only 4 hr and omitting the treatment with Pd

[2] JARMAN, S J and CROWDEN, R K (1973) *Phytochemistry* **12**, 171
[3] CHANDLER, B V and HARPER, K A (1962) *Australian J Chem* **15**, 114
[4] WILLIAMS, C A, HARBORNE, J B and CLIFFORD H T (1971) *Phytochemistry* **10**, 1059
[5] LOWRY, J B (1972) *Phytochemistry* **11**, 725