

DITERPENE RESIN ACIDS IN *PINUS MASSONIANA* NEEDLES AND CORTEX

DUANE F. ZINKEL

Forest Products Laboratory,* Forest Service, U S Department of Agriculture, Madison, WI 53705, U S A
and

WILLIAM B CRITCHFIELD

Pacific Southwest Forest and Range Experiment Station, Forest Service, U S Department of Agriculture,
Berkeley, CA 94701 U S A

(Received 28 April 1974)

Key Word Index—*Pinus massoniana*, Pinaceae, agathic acid monomethyl ester, imbricataloic acid, resin acids

Plant. *Pinus massoniana* Lamb (Masson pine), IFGP (trees Ma-14 and Ma-55) *Source.* All trees except Ma-14-0 growing at the Institute of Forest Genetics, Placerville, Calif. Taxonomic identity of Ma-14 and Ma-55 was verified by cone morphology and leaf structure. *Previous work.* Oleoresin ¹ *Needles.* The methylated (CH₂N₂) acids from ether extracts of needles from trees of different origin were determined by GLC on DEGS and SE-30/EGiP ²

TABLE 1 PRINCIPAL RESIN ACIDS IN *Pinus massoniana* NEEDLES*

Tree	Per cent of total resin acid fraction			Seed source
	Imbricataloic	Mono-Me agathic	Other	
Ma-14	—	80	—	Purple Mt., Nanking, China
Ma-14-0	—	79	—	As Ma-14 but grown in Olustee, Fla. Arboretum
Ma-39	—	25	48 pimaric	Taiwan
Ma-42	—	36	28 pimaric	Lun-ian, Fukien Prov. China
Ma-63	—	83	—	Tsiang-Tsiang, Chiangsi (Kiangsi?) Prov., China
Ma-V8	—	71	—	Nanking, Kiangsu Prov., China
Ma-55	60	—	—	Ta Shan region, central Taiwan
Ma-62	45	—	—	Nanhsing, Kwangsi Prov., China

* Small amounts of pimaric, sandaracopimaric, levopimaric/palustic, isopimaric, abietic, dehydroabietic and neoabietic acids are also present

The ether extract of the needles of Ma-14 was extracted with 1 N NaOH and an acids fraction isolated in the usual manner. The remaining neutrals were removed from this fraction using a DEAE-Sephadex column.³ The CO₂ eluate of the DEAE-Sephadex column was collected in two fractions, the second of which readily crystallized from pentane and

* Maintained at Madison, Wis., in cooperation with the University of Wisconsin

¹ BARDYSHIV, I. I., CHERCHIS, Kh. A. and KOKHANSKAYA, Zh. F. (1960) *Z. Prikl. Khim.* **33**, 884

² NESTLER, F. H. M. and ZINKEL, D. F. (1967) *Analyt. Chem.* **39**, 1118. Dimethyl agathate has retention values (r_{pm}) at cited GC operating conditions of about 6.0 for DEGS and 2.7 for SE-30/EGiP, the exact values are highly dependent upon liquid phase loading, support activity, and column history

³ ZINKEL, D. F. and ROWL, J. W. (1964) *Analyt. Chem.* **36**, 1160

was identified as agathic acid 19-monomethyl ester⁴ m.p. 87–88° (evac. cap. corr.), (lit.⁴ 81–86°); $[\alpha]_D^{25} + 61.1^\circ$ (*c* 0.6, CHCl₃), (lit.⁴ + 57°); and NMR (CDCl₃) 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 (=CH₂), 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. elliotii*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 Dehydropinifolic 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* samples⁶

⁶ ZINKEL, D F, unpublished

Phytochemistry, 1974, Vol 13 pp 2877 to 2878 Pergamon Press Printed in England

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

R K CROWDEN

Botany Department, University of Tasmania, Box 252C Hobart, Tasmania, 7001, Australia

(Received 2 April 1974)

Key Word Index—*Podocarpus lawrencii*, Podocarpaceae, cyanidin-3-neohesperidoside, anthocyanin, podocarpins A & B

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