

THE DITERPENE ACIDS IN THE BLEED RESINS OF THREE PACIFIC KAURI, *AGATHIS VITIENSIS*, *A. LANCEOLATA* AND *A. MACROPHYLLA*

ROGER M. SMITH†, ROBERT A. MARTY* and CHRISTOPHER F. PETERS*

School of Natural Resources, University of the South Pacific, Box 1168, Suva, Fiji; * Chemistry Department, Ballarat College of Advanced Education, Gear Avenue, Mt. Helen, Victoria 3350, Australia

(Received 28 February 1981)

Key Word Index—*Agathis vitiensis*; *A. lanceolata*; *A. macrophylla*; Araucariaceae; kauri pine; bled resin; diterpene acids.

Abstract—The composition of the diterpene acids in the bled resins of three kauri pines, *Agathis vitiensis* from Fiji, *A. lanceolata* from New Caledonia, and *A. macrophylla* from the Solomon Islands has been determined by extraction, methylation and chromatography. The results are compared with *Agathis* species from Australia and New Zealand.

INTRODUCTION

The kauri pines are the native important commercial timbers of S.E. Asia, the western Pacific Islands, Australia and New Zealand [1]. They are members of the *Agathis* genus (Araucariaceae) and when punctured their bark exudes a thick milky bled resin [2, 3]. On standing, this solidified to a gum which is used as a glaze on native pottery in Malaysia and Fiji. Fossilized gum is exploited commercially in New Zealand for the manufacture of varnishes and lineoleum. A number of species have been described [4] and their taxonomy has been confused but has recently been revised on the basis of the morphology [5, 6]. For this study the currently accepted local names were used.

The compositions of the bled resin diterpene acids were used in a chemotaxonomic study of *A. robusta*, *A. palmerstonii*, *A. microstachya* and Bull and Black kauri of Queensland, Australia, and a number of characteristic differences were observed [7]. The composition of the resin of *A. australis* from New Zealand has also been studied in detail [8] and a preliminary survey of *A. dammara* from Malaysia, *A. lanceolata*, *A. ovata* and *A. moorei* from New Caledonia and *A. vitiensis* from Fiji was noted in a review [3] but no details have been reported.

In this paper we report our detailed studies on three resins from the South Pacific, dakua resin (*A. vitiensis*) from Fiji, *A. macrophylla* from Santa Cruz, Solomon Islands, and *A. lanceolata* from New Caledonia, and compare the results with the previous studies and the recent taxonomic revision.

RESULTS AND DISCUSSION

Although other components, including phenolic compounds, have been isolated from *Agathis* species [9] the present work concentrated on the diterpene resin acids as they had been used in previous chemotaxonomic studies [7]. The resin samples of *A. vitiensis*, *A.*

macrophylla and *A. lanceolata* were initially examined in a similar way to previous reports, by separating a hexane–acetone-soluble mixture of free acids, diazo-methylation and examination by GC.

Two columns, OV 101 and OV 210, were used to aid in identification and the results for typical samples of the three species are given in Table 1. Replicate analysis on the same resin sample gave reproducible results and comparison of separate samples of the same species showed that the principal difference was in the proportion of communic acids. These acids are particularly susceptible to polymerization and their composition is reported to vary with the age of the resin [8]. Methyl dehydroabietate was used as a reference compound.

The individual methyl esters were identified by spectral comparison with reported values after isolation by TLC [7, 10–14]. Methyl agathalate could not be isolated free of agathate but NMR spectroscopy indicated the presence of aldehyde groups. Neoabietate was identified by retention time only. The TLC separation also yielded a mixture of *cis*- and *trans*-communol and sandaracopimaradienol from *A. vitiensis* but only the last compound from *A. lanceolata* as minor constituents. These three alcohols were identified by NMR spectroscopy; however, their relative proportion in the resins could not be determined accurately by GLC as they were not resolved from methyl abietate.

Although in an unpublished and unconfirmed study the resins from *A. ovata* from New Caledonia were found to contain components with an enantiomeric configuration at C-10, it was expected that the present acids would have the normal configuration [3]. This was confirmed by the isolation and examination of larger samples of communic, sandaracopimaric, abietic and agathic acids as the free acids or esters from *A. macrophylla* resins. Attempts were made to also identify a number of the minor components but these seemed to be particularly unstable although there were indications of the presence of aldehydic groups.

The major components of *A. vitiensis* and *A. macrophylla* were very similar in proportion. This would agree with the recent botanical revision in which *A. vitiensis* and *A. obtusa* from New Caledonia are regarded as synonyms for *A. macrophylla* [5].

† Present address for correspondence: Department of Chemistry, University of Technology, Loughborough, Leics. LE11 3TU, U.K.

Table 1. Composition of bled resin acids from *Agathis* species on GLC analysis as methyl esters

Ester	RR _i Columns		% Peak areas on OV 101		
	OV 101*	OV 210†	<i>A. vitiensis</i>	<i>A. macrophylla</i>	<i>A. lanceolata</i>
	50			1	
	52		} 3	2	
	56			1	1
Methyl <i>cis</i> -communate	61	52	26	16	4
Methyl <i>trans</i> -communate	67	59	34	42	9
Methyl sandaracopimarate	69		trace		
	73		1		6
	78		1	2	trace
Methyl dehydroabietate	85	89	trace	trace	trace
	93		trace	trace	trace
Methyl abietate	100	100	9‡	10	17§
	112				trace
Methyl neoabietate	117		13	12	4
	132		1	2	trace
Methyl agathalate	140		2	2	13
Dimethyl agathate	156	225	9	10	41
	184				5
	232				1

* 220° Methyl abietate R_i 11.5 min.† 170° Methyl abietate R_i 13.7 min.‡ Includes traces of *cis*- and *trans*-communol and sandaracopimaradienol.

§ Includes traces of sandaracopimaradienol.

The other species examined, *A. lanceolata*, was significantly different and in particular contained a very low proportion of communic acids and no corresponding alcohols and a high proportion of agathic acid. This result is similar to the earlier brief report which found agathic type 35%, abietic type 10%, sandaracopimaric 35%, and communic type 0% [3]. Taxonomically *A. lanceolata* is regarded as a distinct species although in the same botanical group as *A. macrophylla* (group B) [5].

The present results were compared with the compositions determined by Carman and Marty for Queensland kauri pines [7]. The black kauri, now identified as *A. atropurpurea* [15], contained a high proportion of agathic acid (56%) similar to the level found in *A. lanceolata* and in the botanical revision this species was also placed in group B [5]. The remaining four pines now identified as *A. robusta* and *A. microstachya* had similar compositions, with low (1–3%) proportions of agathic acid and higher proportions of abietic (35–37%) and neoabietic acid (26–49%). These species were placed in two further botanical groups from their morphology [5]. The other species which has been reported in detail *A. australis* from New Zealand [8] contains medium proportions of abietic acid (20%) and agathic acid (30%) largely as the monomethyl ester) as well as *cis*- and *trans*-communic acid, sandaracopimaric acid and the corresponding alcohols and is thus similar to *A. vitiensis*. Again it has been placed in the botanical B group and it appears that medium to high proportions of agathic acid constituents may be characteristic of this morphological group.

EXPERIMENTAL

Resins. Fresh resin of *A. vitiensis* (Seeman) Benth and Hook was collected at Colo-i-Suva, Forestry Station, Suva, Viti Levu, Fiji. Fresh and old resin of *A. macrophylla* (Lindley) Masters was obtained from the Forestry Station, Santa Cruz, Solomon Islands, and samples of *A. lanceolata* Lindley ex Warbury were obtained from New Caledonia.

Extraction of acids and esterification. Resin samples were dissolved in Me₂CO (25 ml/g of resin) and an equal vol. of hexane was added. After standing for 2 hr the mixture was filtered to remove polymeric material and the filtrate was evapd to give a mixture of acids. For GLC analysis ethereal solns of the acids were treated with ethereal diazomethane at 0°.

Isolation of acids. Polymer-free *A. macrophylla* resin was extracted as reported previously to give abietic acid [11] and agathic acid [7] which were identified by NMR, IR, MS and optical rotation comparison with authentic samples.

Isolation of esters. Individual esters were isolated from the methylated resin by TLC on Si gel (toluene) and AgNO₃-Si gel (1:9) (80–100° petrol) and identified by NMR, IR, MS comparison with authentic samples and literature values.

Acknowledgements—We thank Mr. K. Yabaki of the Forestry Department, Ministry of Agriculture, Fisheries and Forestry, Fiji, Mr. Debray, CNRS Laboratories, Noumea, New Caledonia and Mr. K. D. Marten, Forestry Division, Ministry of Natural Resources, Honiara, Solomon Islands for samples of resins, Mr. R. W. Rickards, Australian National University for NMR and MS, and Professor Guthrie, Griffith University, for laboratory facilities.

REFERENCES

1. Whitmore, T. C. (1980) *Econ. Botany* **34**, 1.
2. Thomas, B. R. (1970) *Phytochemical Phylogeny* (Harborne, J. B., ed.) Chapter 4. Academic Press, London.
3. Thomas, B. R. (1969) *Organic Geochemistry* (Eglinton, G. and Murphy, M., eds.) Chapter 25. Springer, Heidelberg.
4. Dallimore, W. and Jackson, A. B. (revised by Harrison, S. G.) (1966) *Handbook of Coniferae and Ginkgoaceae*, 4th edn. Arnold, London.
5. Whitmore, T. C. (1980) *Plant System. Evol.* **135**, 41.
6. Page, C. N. (1980) *Plant System. Evol.* **135**, 71.
7. Carman, R. M. and Marty, R. A. (1970) *Aust. J. Chem.* **23**, 1457.
8. Thomas, B. R. (1966) *Acta Chem. Scand.* **20**, 1074.
9. Enzell, C. R. and Thomas, B. R. (1966) *Tetrahedron Letters* 2395.
10. Chien, J. C. W. (1960) *J. Am. Chem. Soc.* **82**, 4762.
11. Harris, G. C. and Sanderson, T. F. (1948) *J. Am. Chem. Soc.* **70**, 334.
12. Carman, R. M. and Marty, R. A. (1966) *Aust. J. Chem.* **19**, 2403.
13. Carman, R. M. and Dennis, N. (1964) *Aust. J. Chem.* **17**, 390.
14. Carman, R. M. (1964) *Aust. J. Chem.* **17**, 393.
15. Hyland, B. P. M. (1978) *Brunonia* **1**, 103.
16. Arya, V. P., Erdtman, H. and Kubota, T. (1961) *Tetrahedron* **16**, 255.