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FATTY ACIDS, RESIN ACIDS AND PHENOLS IN *PINUS MURICATA*

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Abstract—Acetone-soluble extractives of "blue" and "green" strain *Pinus muricata* D. Don were found to consist of free and "combined" fatty acids, resin acids, and phenols. The composition of the extractives from the two strains was similar though "green" strain *P. muricata* contained more $\Delta^{8(9),15}$ isopimaric acid than "blue" strain. This difference may be used to identify these muricata strains if the age of the wood precludes a monoterpene examination.

INTRODUCTION

Pinus muricata D. Don is native to California, where it belongs with *P. radiata* D. Don and *P. attenuata* Lemm. to a well-defined subgroup of pines. *P. muricata* has been divided into four varieties [1] on the basis of tree size, foliage, bark, and cone characteristics. One of these varieties, the "blue" strain, is being considered as a useful timber and pulp source in New Zealand because of its high growth rate.

Conflicting results on the monoterpene composition of *P. muricata* wood were obtained in early work [2,3] and these led to further detailed studies [4] of samples from many areas along the Californian coast. As a result *P. muricata* was subdivided into three distinct "races" based on chemical constituents: (i) a northern race with turpentine consisting almost entirely of (±)-α-pinene; (ii) a central race containing mainly Δ3-carene; (iii) a southern race containing mainly (−) sabinene and terpinolene.

The present work describes the analysis of nonvolatile extractives of groups (i) and (ii) termed "blue" and "green" strain respectively.

RESULTS AND DISCUSSION

The methanol extractives content of *P. muricata* breast-height samples was similar to that of other *Pinus* species of the same age (45 years) [5]. The "blue" strain heartwood and sapwood contained 10·2% and 2·2% extractives respectively, while the corresponding contents of "green" strain samples were 8·7 and 2·5%.

Extractives composition

The relative proportions of free acids, phenols, "combined" fatty acids, and unsaponifiables in both strains were similar (Table 1) and resemble those of other *Pinus* species [5]. No notable differences between the two strains were evident.

Table 1. Composition of *Pinus muricata* extractives

	Acetone extractives (%)			
	Blue strain		Green strain	
	Heart	Sap	Heart	Sap
Free acids	67·2	41·5	66·2	33·4
Phenols	12·8	—	12·2	—
Combined fatty acids	10·5	44·6	10·9	51·9
Unsaponifiables	9·2	13·5	10·7	14·7
Free fatty acids*	3·9	0·6	2·9	0·6

* Expressed as per cent of free acids.

Free acids were most abundant in heartwood and consisted mainly of resin acids. The small amounts of fatty acids probably resulted from hydrolysis of fatty acid esters, especially during the process of heartwood formation. Palmitic, oleic, and linoleic acids were the most abundant free fatty acids.

The two strains differed in their resin acid compositions (Table 2). There was a much higher proportion of $\Delta^{8(9),15}$ isopimaric acid in heartwood

Table 2. Composition of resin acid fraction from GLC

Acid	Free acids (average %)				Maximum and minimum values (%) (5 samples)			
	Blue strain		Green strain		Blue strain		Green strain	
	Heart	Sap	Heart	Sap	Heart	Sap	Heart	Sap
Unidentified				2·6	Trace in 3 trees	Trace in 2 trees	Trace in 2 trees	1·0–4·0
$\Delta^{7,15}$ Isopimaric	0·4			2·2	0·2–0·5	Trace in 2 trees	Trace in 3 trees	0·5–4·3
Pimaric	5·3	6·1	7·9	7·5	4·4–6·9	4·6–8·4	6·0–9·7	6·1–9·8
Sandaracopimaric	1·0	0·5	0·5	0·4	0·5–1·9	0·2–1·0	0·2–1·0	0·0–0·5
Levopimaric palustric	28·9	49·4	22·3	34·1	20·4–39·4	45·6–52·8	19·9–24·0	30·2–38·2
$\Delta^{8(9),15}$ Isopimaric	7·6	9·8	20·1	20·5	6·4–9·1	7·9–12·8	18·5–22·6	17·9–24·3
Abietic	26·4	12·8	28·8	14·6	24·0–29·5	10·0–15·8	25·4–30·2	11·9–18·4
Dehydroabietic	10·3	9·1	5·8	7·2	6·5–18·0	7·4–10·6	2·8–8·1	4·0–9·7
Neoabietic	16·5	10·3	12·6	8·8	12·7–21·1	8·1–12·5	8·1–17·3	9·2–12·7

and sapwood samples of "green" strain *P. muricata* than in corresponding "blue" strain samples. Thus the free acids of "green" strain heartwood contained 20·1% of this constituent while "blue" strain heartwood contained only 7·6%. Similar differences were observed for sapwood samples from the two strains. This difference was apparent in all samples examined and thus may be useful in identifying these *P. muricata* strains if the age of the sample precludes a monoterpene analysis.

Heartwood of both strains contained more abietic acid than sapwood, and sapwood contained more levopimaric and palustric acids than did heartwood. The ratio of levopimaric to palustric acid was determined by forming the maleic anhydride Diels Alder adduct with the levopimaric methyl ester. Subsequent GLC analysis gave the ratio of levopimaric:palustric acid as (7:3) for both strains.

"Combined" fatty acids, relative to the other extractives, were more abundant in sapwood, especially in the "green" strain, than in heartwood (Table 1). Oleic and linoleic acids comprised approximately 80% of the fatty acids present as esters (Table 3). Both *P. muricata* strains had very similar fatty acid compositions though heartwood and sapwood compositions were different. The oleic: linoleic ratio was considerably lower in heartwood, as has been observed in other conifers [6].

Table 3. Composition of "combined acids" from GLC

Acid*	"Combined" acids (%)			
	Blue strain		Green strain	
	Heart	Sap	Heart	Sap
16:0	5·4	5·7	6·8	5·8
18:1	38·1	50·1	40·1	50·3
18:2	42·6	33·4	40·9	31·0
18:3	3·0	3·9	3·6	3·3
20:0	5·3	5·2	3·9	3·0

* The number before the colon indicates the number of carbon atoms in the chain, and the number after the colon the number of double bonds.

Heartwood phenolic compounds comprised 12·8 and 12·2% respectively of "blue" and "green" acetone extractives (Table 1). The four phenols which characterize the Diploxylon subgroup [7], pinobanksin, pinocembrin, pinosylvin, and its methyl ether, were all present in both strains. Small amounts of an unidentified flavonoid were also detected in both strains.

Both strains contained more unsaponifiables in sapwood than in heartwood, though the composition of these fractions was not examined.

EXPERIMENTAL

Samples were collected in December from trees growing in Compartment 1217, Kaingaroa Forest, North Island, New Zealand. Increment cores from 45-yr-old *P. muricata* trees at breast height (1·4 m up the stem) were separated into heartwood and sapwood portions. Extractives contents were determined for 30 trees by Soxhlet extraction with MeOH. C_3H_6O extractives composition was then determined using 5 trees of each strain.

Cores were chipped to matchstick size soon after collection and extracted with C_3H_6O for 3 days at 3°. The extract was dried and cone under mild conditions and a phenolic fraction was then obtained from the heartwood extract by treatment with petrol. ether which left the phenolics as undissolved residue. Extracts were separated into acids and neutrals on DEAE sephadex columns [8] and acids analysed by GLC after methylation with CH_2N_2. Neutral fractions were hydrolysed by refluxing in methanolic KOH followed by separation into acidic and unsaponifiable fractions.

A Pye 104 gas chromatograph was used to analyse the various fractions. Methyl esters were separated on 10% DEGS

in a 152 cm glass column at 190° and 165° for free and "combined" acids respectively. Phenols were analysed as their silyl ethers on 3% SE-30 in a 152 cm glass column at 190°.

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