DISTRIBUTION OF EXTRACTIVES IN *PINUS RADIATA* EARLYWOOD AND LATEWOOD

J. A. LLOYD
New Zealand Forest Service, Rotorua

(Received for publication 3 March 1978)

ABSTRACT

Earlywood and latewood of both a 19-year-old and a 45-year-old **Pinus radiata** tree had similar extractives content and composition. However latewood in the heartwood had more extractives than earlywood in the same annual growth ring. The additional extractives are resin acids which probably arise from enrichment of this latewood tissue with resin acids long after the heartwood is formed. No significant differences were detected in the compositions of the fatty and resin acids present in the earlywood and latewood.

INTRODUCTION

The composition and distribution of *Pinus radiata* wood extractives have been studied extensively. The resin content is low in comparison with most other *Pinus* species, the main resin components being diterpene resin acids, fats, fatty acids, sterols and phenols (Porter, 1969). Hemingway and Hillis (1971) studied the distribution of these components across the stem, and found that resin acids are concentrated in the inner heartwood while the sapwood contains a higher proportion of fatty acid esters. The resin acid composition throughout the tree is remarkably constant but the fatty acids in heartwood differ from those in sapwood.

In addition to these broad changes across the stem, differences might also be expected to occur across various sub-sections of the heartwood and sapwood. For example seasonal variations in the amount of extractives arise as secondary compounds synthesis is governed by metabolic processes in the tree. Also it would be expected that extractives such as fats or starch would show the greatest seasonal variation as they are formed during periods of growth and consumed during winter.

Nylinder and Haglund (1954) carried out a study on a population of spruce including an analysis of earlywood and latewood extractives content. It was found that latewood had a lower resin content than earlywood and also that extractives content varied with latitude, height above sea level and width of the annual ring. Pensar (1967) also carried out a study of spruce extractives distribution with age and examined earlywood and latewood tissues. He found that age of the wood was the most important factor, and generally the trends in distribution and composition were the same for both earlywood and latewood. In *Pinus sylvestris* the situation was similar to that in spruce (Pensar, 1967).

This paper describes the radial variation of earlywood and latewood extractives in two *P. radiata* trees

N.Z. J. For. Sci. (2): 288-94 (1978).

EXPERIMENTAL

The two trees sampled were 19 and 45-year-old trees grown in Kaingaroa State Forest.

The 19-year-old tree was analysed for earlywood and latewood extractives by taking the disc which had 15 annual growth rings, and then separating every 3rd ring into earlywood and latewood fractions. A disc with 40 growth rings was cut from the 45-year-old tree and the earlywood and latewood of every 5th ring across the disc separated.

The separate samples of earlywood and latewood tissue were finely chipped and extracted by soaking in acetone at 3°C for three days. The extracts were concentrated to dryness *in vacuo* and the extractives content determined. The extracts were dissolved in diethyl ether: methanol: water (89 : 10 : 1) and separated into acidic and neutral components on DEAE Sephadex according to the method of Zinkel and Rowe (1964). The neutral fraction was hydrolysed by refluxing with 3M methanolic KOH for four hours. The alkaline solution was diluted with water and unsaponifiable material removed by ether extraction. The acids which were released on saponification were obtained by ether extraction of the acidified solution. The weight of each fraction was determined by gas liquid chromatography using hydrocarbon internal standards.

Acids were methylated with diazomethane and separated on 10% diethylene glycol succinate on gas chrom P; fatty acid methyl esters were eluted at 165°C and resin acid methyl esters at 190°C. The unsaponifiable fraction was silylated and separated on a 3% SE-30 column, temperature programmed from 70-250°C at 4°C/minute.

RESULTS AND DISCUSSION

The distribution of the total acetone-soluble extractives across the stems of the 19- and 45-year-old trees is shown in Fig. 1. The acetone extractives content in sapwood was approximately constant in both trees and was about 1% of O.D. weight in both earlywood and latewood though it may have been marginally higher in earlywood.

This result suggests a fairly even apportionment of vertical resin canals between the earlywood and latewood samples. Microscopic examination of several annual rings confirmed this although the majority of the canals are in the region of transition from earlywood to latewood. Since this is so, the position where the earlywood and latewood is separated may have more bearing than any other factor on the extractives content actually measured in practice. In many of the annual rings in the sapwood it was very difficult to define the exact earlywood-latewood transition.

The extractives distribution in heartwood was markedly different to that in sapwood (Fig. 1). This difference was most pronounced in the inner heartwood of the 45-year-old tree where the earlywood surrounding the pith contained 6.8% acetone solubles and the latewood of the same annual ring had 17.2% extractives. The difference between the amount of extractives in earlywood and latewood decreased across the heartwood with ring number from the pith until at 15 rings from the pith in the 45-year-old tree the earlywood actually had a higher extractives content than the latewood. The transition from earlywood to latewood shows up more in the heartwood and this may also have helped to accentuate the difference in the measured earlywood and latewood extractives contents.

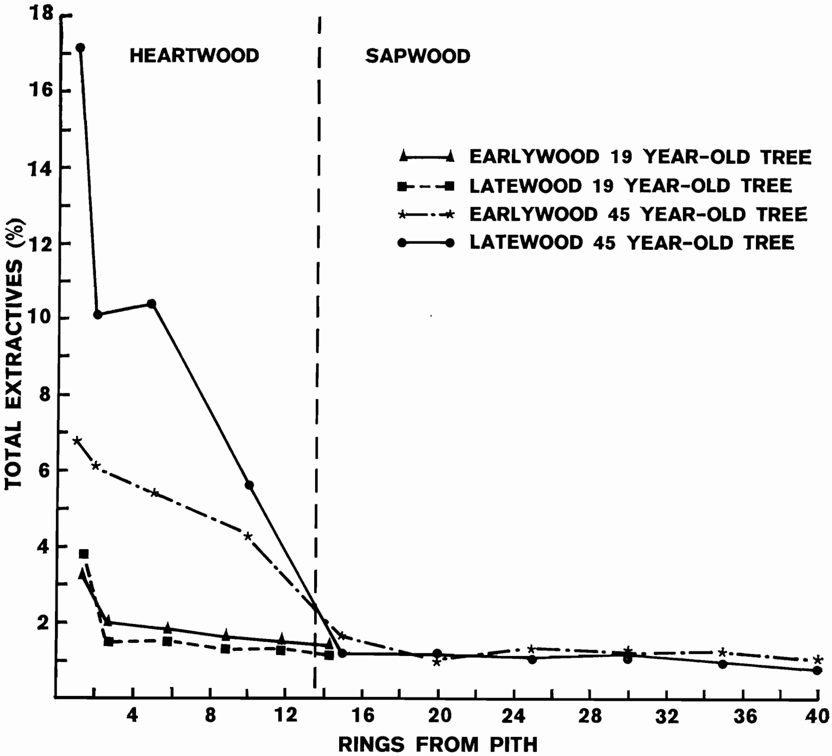

FIG. 1—Distribution of total extractives across disc.

The increased resin content of the heartwood probably arises, not because of more or larger resin canals in the latewood, but because of so-called enrichment of heartwood with extractives long after the original heartwood has been formed (Harris, 1965). This type of extractive enrichment is believed to take place by resin flow through the transverse resin canals into the heartwood. It was postulated by Harris that if the epithelial cells rupture, resin was more likely to flow into a latewood tracheid than an earlywood one as the pits in latewood do not aspirate on forming heartwood but those of earlywood do (Harris, 1965). Harris also suggested that the pith was likely to be enriched in a similar manner. This was indeed the case in the two trees examined as the pith in the 19-year-old and the 45-year-old trees were found to contain 12.2% and 19.9% acetone solubles in the discs examined.

The extractives contents measured are expressed as a percentage of O.D. weight of wood. A much different figure would be obtained if volume of wood was considered as the much denser population of resin canals in the latewood material gives this tissue a much higher resin content based on volume, something which is commonly overlooked.

Composition of Extractives

The percentage of free acids, fatty acid esters and unsaponifiables in the two discs examined are shown in Fig. 2. The components present were the same as previously reported for *P. radiata* wood (Porter, 1969).

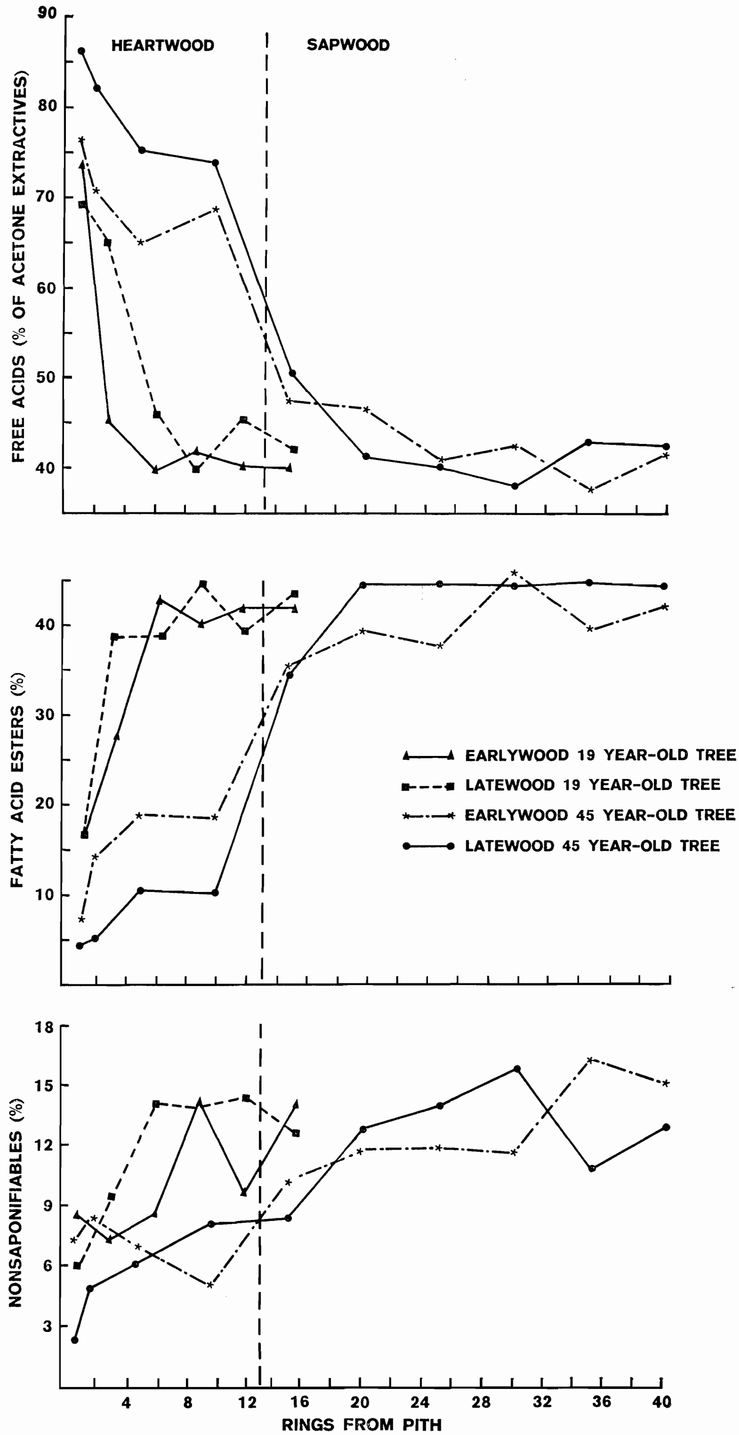

FIG. 2—Distribution of free acids, fatty acid esters and nonsaponifiables (as % of acetone extract) in cross-section of **Pinus radiata** stem.

These results show that there is very little difference in the composition of earlywood and latewood extractives apart from those of inner heartwood. The free acids and fatty acid esters each comprised approximately 40% of both the earlywoods and latewood extractives throughout the sapwood; unsaponifiables were also constant at around 12%.

The latewood in heartwood, especially the inner heartwood, was much richer in free acids than the earlywood (Fig. 2). These free acids consisted of about 98% resin acids and 2% fatty acids. This result provides more evidence for heartwood enrichment with extractives as the transverse resin canals are believed to be occupied principally with resin acids (Mutton, 1962), and thus the latewood would be expected to have a higher resin acid content if the epithelial cells were ruptured as described earlier in this paper. The latewood in the inner heartwood had a lower proportion of fatty acid esters and unsaponifiables but this is only a relative reduction as it is brought about by the greatly increased resin acid content in this tissue.

The actual amounts of fatty acid esters and unsaponifiables in heartwood, earlywood and latewood are in fact fairly similar.

The composition of the resin acids from earlywood and latewood samples was similar. In the 19-year-old tree, the latewood appeared to contain marginally more pimaric acid while the earlywood had more isopimaric acid. However, this difference was not noted in the 45-year-old tree (Table 1). Table 1 also indicates that the resin

TABLE 1—Composition of resin acid fraction in earlywood and latewood from 45-year-old **P. radiata** tree

	% of Resin Acids Rings from Pith								
LATEWOOD	1	5	10	15	20	25	30	35	40
Levopimaric/Palustric	42.6	44.0	47.8	49.4	48.6	50.1	53.6	49.6	54.1
Neoabietic	19.9	18.9	19.4	22.4	22.4	20.2	20.0	19.7	14.6
Abietic	16.6	8.9	9.1	6.9	6.0	5.9	3.6	5.1	4.5
Dehydroabietic	4.3	4.6	6.9	6.9	8.7	8.4	7.2	8.6	10.8
Pimaric	7.6	7.1	8.3	6.4	7.2	8.1	9.0	7.6	8.7
$\Delta^{7,15}$ Isopimaric	5.1	4.9	2.8	3.6	4.1	4.0	3.4	4.4	4.6
$\Delta^{8(9),15}$ Isopimaric	1.0	1.4	1.8	2.0	1.2	1.8	2.0	3.6	2.7
Sandaracopimaric	0.8	0.7	1.2	0.8	1.2	1.3	1.0	0.8	0.7
EARLYWOOD									
Levopimaric/Palustric	43.4	44.0	46.4	49.6	50.5	48.6	49.8	52.1	52.3
Neoabietic	18.9	20.2	19.9	23.1	21.9	24.9	21.2	21.9	19.4
Abietic	17.8	13.4	8.4	5.0	4.0	5.8	5.8	4.2	4.8
Dehydroabietic	4.0	4.6	5.4	9.1	7.2	7.6	8.1	7.9	9.6
Pimaric	7.9	8.2	7.6	6.4	9.8	8.6	8.4	8.9	9.4
$\Delta^{7,15}$ Isopimaric	5.0	4.6	3.6	4.1	4.2	2.9	4.1	4.9	3.6
$\Delta^{8(9),15}$ Isopimaric	1.2	0.9	0.8	0.6	1.2	0.9	0.7	0.6	0.5
Sandaracopimaric	1.1	1.2	1.6	0.4	1.4	0.6	1.4	0.8	1.3

acid composition changes little from pith to bark, a slight drop in the levopimaric/palustric acid content being the only significant change. This change is a result of isomerisation of levopimaric to other abietane acids.

The composition of the fatty acids released on hydrolysis of the esters changes from pith to outer sapwood but no significant differences in earlywood and latewood composition were evident (Table 2). The ratio of oleic to linoleic increases from pith to bark.

TABLE 2—Composition of fatty acid esters (percentage for each fatty acid type) in earlywood and latewood from 45-year-old **P. radiata** tree

ACID*	1	5	10	15	20	25	30	35	40
LATEWOOD									
18 : 1	32.7	38.4	39.4	35.6	40.0	47.2	41.6	45.0	50.0
18 : 2	37.6	29.9	38.1	36.2	34.6	32.1	37.1	37.4	33.7
16 : 0	12.8	12.8	9.1	8.3	7.6	10.1	9.4	8.3	9.4
20 : 3	6.8	4.5	3.4	2.8	3.0	2.6	3.4	2.7	2.1
18 : 3	4.8	2.6	4.5	3.1	2.7	1.9	4.1	2.7	3.1
18 : 0	2.1	2.0	1.8	1.8	1.0	0.9	1.2	1.2	0.5
EARLYWOOD									
18 : 1	38.4	33.6	36.3	44.8	39.4	41.8	46.1	48.0	46.4
18 : 2	37.6	34.6	33.2	31.3	35.1	33.7	34.7	36.9	35.4
16 : 0	13.1	13.6	11.4	7.2	10.4	9.4	8.6	9.7	8.6
20 : 3	5.4	4.6	3.6	2.1	2.9	4.0	2.2	2.5	3.2
18 : 3	4.5	4.4	4.9	2.3	2.8	3.8	4.4	3.6	2.8
18 : 0	1.8	1.8	1.7	1.2	1.0	0.9	1.4	0.8	0.6

* 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.

CONCLUSION

Apart from the inner heartwood, the earlywood and latewood in *P. radiata* appear to have similar extractives content and composition. The latewood in the heartwood, especially the inner heartwood, has a higher extractives content than the earlywood and this is because of increased amounts of resin acids in these latewood bands. This increase in resin acid content in the heartwood latewood can be explained by the postulate that enrichment of the heartwood latewood takes place long after it is formed. The actual composition of the fatty and resin acids was similar in earlywood and latewood.

ACKNOWLEDGMENTS

The author wishes to thank Dr J. M. Uprichard for suggesting the study and Miss H. Bristow for her technical assistance.

REFERENCES

HARRIS, J. M. 1965: Enrichment of radiata pine heartwood with extractives. Paper presented IUFRO, Section 41, October 1965. **N.Z. For. Serv., Reprint 334.**

HEMINGWAY, R. W. and HILLIS, W. E. 1971: Changes in fats and resins of **Pinus radiata** associated with heartwood formation. **Appita 24(6):** 439.

MUTTON, O. B. 1962: "Wood Extractives and their Significance to the Pulp and Paper Industry." Ed. W. E. HILLIS. Academic Press, New York.

NYLINDER, P. and HÄGLUND, E. 1954: **Memoranda from the State Forestry Institute**, Stockholm, 44(1).

PENSAR, G. 1967: Distribution and composition of extractives in wood. 1. Ether extractives of earlywood and latewood in spruce (**Picea abies**) **Transln from Abo Akademi Institutet för Trakemi Medd. No. 211. Australia CSIRO Transln No. 9110.**

——— 1967: A micro method for study of the extractives in structural elements of wood. Earlywood and latewood of pine (**Pinus sylvestris**). **Acta. Acad. Abo. Math. Phys. 26 (10). Chem. Abs. 67,** 74608j, (1967).

PORTER, L. J. 1969: The resin and fatty acid content of living **Pinus radiata** wood. **N.Z. J. Sci. 12(4):** 687-93.