

INFLUENCE OF TREE AGE ON THE CHEMICAL COMPOSITION OF RADIATA PINE

J. M. UPRICHARD and J. A. LLOYD

Forest Research Institute, New Zealand Forest Service,
Private Bag, Rotorua, New Zealand

The distribution of extractives, lignin, and carbohydrates in radiata pine and their variation with tree age are reviewed.

Extractives, their nature, and amount depend on the heartwood content of the tree, and thus upon wood age. Lignin decreases in the pith-to-bark sequence; pentosans content decreases over the first 10-15 growth rings from the pith, after which it is approximately constant.

Cellulose content of radiata pine increases over the first 10-15 growth rings from the pith, after which it is approximately constant. The carbohydrates in radiata pine are also briefly described.

INTRODUCTION

Most chemical pulping studies involve characterisation of the raw material, the properties of interest being wood density, fibre length, and chemical composition. Although resin content as extractive content is the property of most direct interest to the pulpwood users, it is apparent that cellulose and lignin content of wood will influence pulp yield and rate of delignification. Extractive content is of most importance because acidic or phenolic extractives will consume alkali required for lignin cleavage and removal, and also because the quantity and nature of extractives will be reflected in yields of by-products such as turpentine and tall oil.

Over the years numerous studies have been made on the chemical composition of radiata pine samples used for pulping. These and related studies are reviewed in this paper. With the data available, the effects of changing from mature 50-year-old radiata pine trees to trees of 25 years of age or less are assessed and evaluated, and the effect of such changes on pulpmill and sawmill operations are described.

EXTRACTIVES: THEIR COMPOSITION AND DISTRIBUTION

Volatile constituents

The volatile constituents of radiata pine are about 0.4% oven-dry wood weight, the major constituents being β -pinene (70%) and α -pinene (25%) as was shown by Blight *et al.* (1964). These compounds, because they can be used for the production of perfumery intermediates, are technically important products, despite the small amounts present.

Extractives distribution within the tree

Buckland *et al.* (1953) examined resin distribution in 24-, 30-, 35-, and 40-year-old trees, and showed that: "No definite trend of extractive content with increase in age of tree was observed although the mean extractive content for trees in the higher age group was substantially greater than those for the other age groups examined. The resin content of wood surrounding the pith showed some decrease with overall tree height, this being very marked between the butt and breast height levels. In the case of sapwood* the amount of other extractives appeared to be independent of height in tree." These early data provide an excellent picture of radiata pine as it is today, although much more is now known about the nature of heartwood and sapwood extractives.

The quantity and composition of radiata pine extractives are dependent upon the percentage of heartwood present and thus on tree age. More extractives are present in heartwood than sapwood, and the extractives in heartwood differ from those in sapwood (Hillis 1962). Heartwood forms when trees are from 12 to 15 years old (Harris 1954).

Heartwood extractives occur in greatest amount in inner growth rings surrounding the pith (Uprichard 1971; Lloyd 1972). As mature trees age there is a gradual increase in the resin content of inner heartwood, especially in the lower portions of the tree stem. The extractive distribution within 40-year-old trees is given in Table 1. Harris (1965) considered that the high resin content of inner heartwood arose from a process of enrichment with sapwood extractives via the transverse resin canals. Extractive content of sapwood is low, about 1.5% of wood weight.

TABLE 1—Acetone extractives % in oven-dry wood from 40-year-old radiata pine

No. of growth rings in sample	Ring-group from pith							
	1-5	6-10	11-15	16-20	21-25	26-30	31-35	36-40
15	3.5 H/S	1.8	1.5					
25	5.4	1.5 H/S	0.8	0.7	1.0			
35	7.4	2.0 H/S	1.1	1.0	0.9	1.1	1.2	
40	9.7	2.8 H/S	1.0	1.0	0.9	0.9	0.8	0.9

H/S — the approximate heartwood/sapwood boundary

As is shown in Fig. 1, heartwood in the inner growth rings of 50-year-old trees has higher extractive content than younger material, and the older trees contain more heartwood than 25-year-old trees.

The major constituents of both heartwood and sapwood extractives are resin acids, fatty acid esters, and neutral compounds (Table 2). Resin acids predominate in heartwood, making up between 70 and 80% of total extractives. There are approximately equal amounts of resin acids and fatty acid esters in sapwood. The composition of the resin and fatty acids present in heartwood and sapwood extractives has been studied by numerous investigators (Hemingway & Hillis 1971; McDonald & Porter 1969; Porter 1969; Lloyd 1972). One of us (Lloyd, unpubl. data) studied the distribution of extractives

* The term sapwood replaces "outer lower resin content wood".

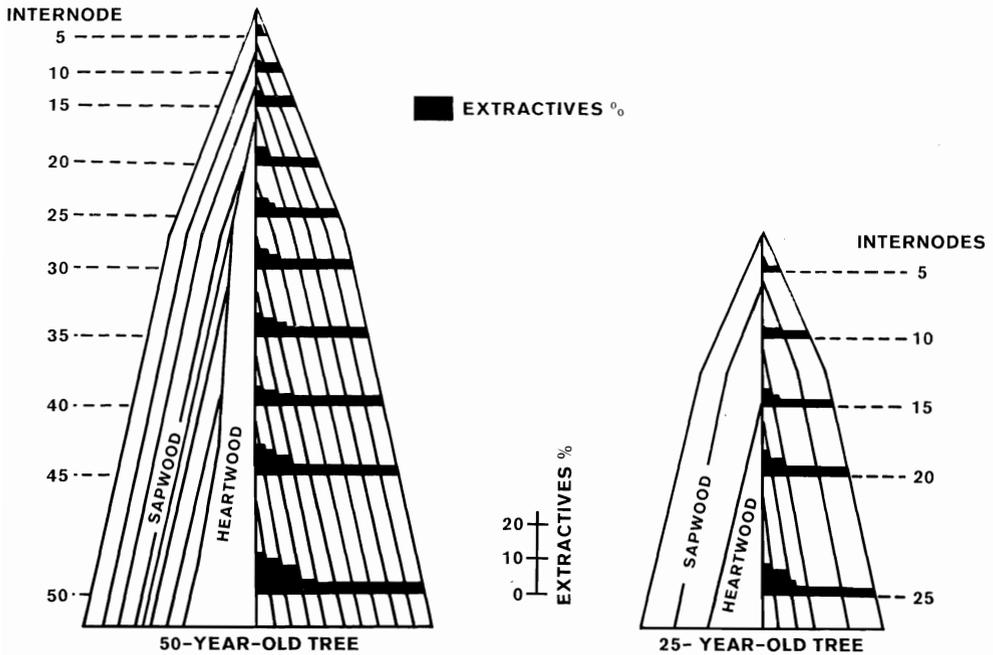


FIG. 1—Extractive distribution in radiata pine.

in 2 trees of radiata pine, one 19 years old and the other 45 years old, and concluded that the extractives composition in these 2 trees was similar except for the higher extractive content of heartwood near the pith at the base of the 45-year-old tree.

Extractive content

Most of the fatty acids are present as glycerides, the predominant acids being oleic and linoleic. The relative amounts of these two acids present changes on transition from sapwood to heartwood. The resin acids present are pimaric, isopimaric, levopimaric, sandaracopimaric, neoabietic, abietic, and dehydroubietic acids. Abietic acid is the major component in tall oil and is produced by isomerisation during pulping (McDonald & Porter 1968). About 10% of the total extractive is unsaponifiable material consisting largely of sterols, alcohols, and hydrocarbons.

TABLE 2—Compounds (as % of total extractives) in heartwood and sapwood of radiata pine

Compounds	Heartwood	Sapwood
Fatty acids (free)	2	1
Fatty acid esters	11	41
Resin acids	71	41
Phenols	6	3
Unsaponifiables (neutrals)	10	14

The extractives in earlywood and latewood have been shown to have similar composition (Lloyd 1978).

The effect of changes in tree age

The data available for extractive composition and distribution show that as tree age decreases and less heartwood reaches the kraft pulpmill digesters, there will be decreases in tall oil production and in the resin acid content of tall oil. Data discussed by Kerr & Swann (1980) confirm that this is so.

The reduction in sawlog "age" means that the quantity of heartwood will also be reduced: there will therefore be less heartwood in residues. A beneficial effect of this reduction in heartwood to the pulpmill will be a small but significant drop in effective alkali requirement for kraft pulping.

The reduction in heartwood content of logs, or chips, to refiner pulpmills means also that the quantity of resin acids to effluent will be slightly reduced, a small but distinct advantage (Corson & Lloyd 1978), since resin acids are toxic to fish (Rogers 1973). The lowering of tree age will also mean less heartwood in the timber produced in the sawmill. Since sapwood has higher moisture content than heartwood, the energy requirements of drying will increase, and the timber will also need some form of treatment, so there will be an increase in processing costs.

The effects of tree age on extractive content are significant, but in comparison with the major changes in the wood properties — density and fibre length — which will result from a reduction in the age of trees to the pulpmill, the impact of the change in extractives with tree age on processing will be small.

CELLULOSE AND LIGNIN DISTRIBUTION

Because of its importance as a pulpwood species, the carbohydrates of radiata pine have received particular attention at the Forest Research Institute (Uprichard 1971; Harwood 1971; Kibblewhite 1981).

Studies on five 35-year-old trees of radiata which were sampled at internodes 5, 10, 15, 25, and 30 from the tree apex by means of 5-ring groups numbered from the pith, showed that cellulose content increased with growth ring number from the pith over the first 10 or 15 growth rings, after which cellulose content was approximately constant (Uprichard 1971); 3 other trees used by Harwood in his studies of radiata pine carbohydrates showed similar behaviour (Harwood 1971). Earlier, Dadswell *et al.* (1959), who used a different analytical procedure, had also recorded an increase in cellulose content with growth ring number from the pith in the inner growth rings of young radiata pine trees. This same general trend (Table 3) has been observed in trees ranging from 15 to 35 years of age.

In studies on lignin and pentosans distribution in radiata pine, it was shown that the lignin content of inner wood near the pith was greater than that of outer wood, and that pentosans content decreased with ring number from the pith in the first 10 or 15 growth rings, after which it remained approximately constant (Uprichard 1971).

The variation in lignin, cellulose, and pentosans content is shown schematically in Fig. 2, where the distribution of these components in a 50-year-old and a 25-year-old tree is compared. Based on the analytical data available, the trees of the older age class contain more cellulose than those of the young age class, and Harwood's (1971) data on wood carbohydrates confirm this.

TABLE 3—Carbohydrate composition of *P. radiata* and its variation with wood age

Ring-group from pith	Sugars % in wood hydrolysate				
	Galactose	Glucose	Mannose	Arabinose	Xylose
1-5	8.7	62.3	16.4	2.3	10.3
6-10	5.9	64.4	17.7	2.3	9.7
11-15	4.2	66.9	18.2	1.8	8.9
16-20	4.0	67.5	18.8	1.7	8.1
21-25	4.9	69.6	16.9	1.3	7.3

Source: Harwood & Uprichard (1968).

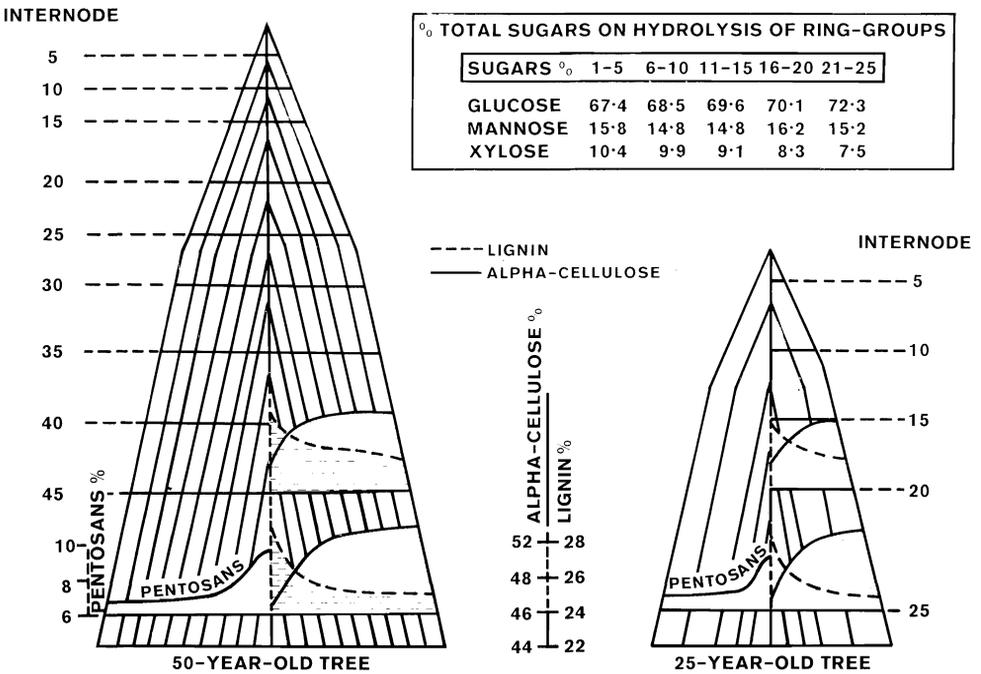


FIG. 2—Lignin and alpha-cellulose in radiata pine.

Wood carbohydrates and acid hydrolysis

Harwood (1971) studied the variation in radiata pine carbohydrates by taking 5-ring group samples from 35-year-old trees and subjecting these samples, or their derived holocelluloses (Uprichard 1965) to acid hydrolysis by the Klason lignin procedure (Tappi Standard T13-54). Sugars in hydrolysates were determined by paper chromatography; some typical data are shown in Table 3 and also in Fig. 2.

Harwood's data show clearly that there is an increase in glucan (cellulose) content with rings from the pith over the first 10 or 15 growth rings, after which glucan content increases only slowly. Mannan content shows essentially similar behaviour. Arabinan is virtually constant within the tree, but xylan decreases from pith to bark. Overall the data obtained by acid hydrolysis procedures resemble very closely those obtained by other methods.

The studies by Harwood on radiata pine carbohydrates are summarised here since they proved a most valuable foundation for pulping studies and also for the more recent studies on the production of ethanol from wood sugars.

From radiata pine chlorite holocellulose, Harwood obtained by extraction with 24% w/v potassium hydroxide a xylan, or more specifically an arabinoglucuronoxylan, which was further purified (Harwood 1972) and which was structurally identified by conventional procedures. The xylan is made up of 4-0-methyl-D-glucuronic acid, D-xylose, and L-arabinose units in the ratio 1:5.8:1.1. Harwood (1973) also isolated a galactoglucomannan, the structure of which was also identified.

On the basis of these data, radiata pine has the following approximate composition:

<i>Component</i>	<i>% composition</i>
Lignin	26
Cellulose	42
Galactoglucomannan	15
Arabinoglucuronoxylan	10
Arabinogalactan	4
Uronic acids, etc.	(3)
Total	100

Chemical composition effects

The low cellulose content of the inner wood of mature trees, which is also apparent in younger trees, is not unexpected. The cells of inner wood have thin walls and will have a thinner S₂ cellulose layer than the fibres of outer mature wood — which are thick-walled (Kibblewhite 1973). There is also a higher latewood content in outer wood than in inner wood, and it is essentially the changes in fibre morphology and cell wall thickness that account for the observed variation in chemical composition. In terms of pulping, the changes in fibre structure which affect pulp quality and yield per digester charge are probably more important than chemical composition changes which affect yield of pulp on the basis of wood weight (Harwood & Uprichard 1969).

On the basis of analytical data, lower pulp yields would be expected from young trees than from old ones, yet Kerr & Swann (1980) report the opposite.

The changes in cell wall composition appear well established, but only indirectly are they of importance in pulping or papermaking quality.

CONCLUSIONS

The effects of tree age on chemical composition of radiata pine are small. If tree age is reduced from 50 years to 25 years then the effect on the mill supply will be as follows:

- (1) There will be less heartwood in the mill.
- (2) The increase in sapwood content will mean higher moisture content (and higher timber drying costs).
- (3) The extractive content (and resin acid content) of the wood will be reduced, and therefore tall oil yield and resin acid content of tall oil will be reduced.
- (4) There will be an increase in the lignin content and a decrease in the cellulose content of pulpwood.

ACKNOWLEDGMENT

The authors wish to thank Dr K. L. Mackie for his assistance in the preparation of this paper.

REFERENCES

- BLIGHT, M. M.; BREWERTON, H. W.; McDONALD, I. R. C.; BANNISTER, M. H. 1964: α - and β -pinene content of the *Pinus radiata* population of Kaingaroa Forest. **New Zealand Journal of Science** 457.
- BUCKLAND, N. J.; DALLEY, O. T.; MATHIESON, C. J. 1953: The distribution and nature of resinous material in *Pinus radiata*. **Appita Proceedings** 7: 165.
- CORSON, S. R.; LLOYD, J. A. 1978: Refiner pulp mill effluent. **Paperi ja Puu (Papper och Tra)** 8: 435.
- DADSWELL, H. E.; WATSON, A. J.; NICHOLLS, J. W. P. 1959: What are the properties required by the paper industry in the trees of the future. **Tappi** 42: 521.
- HARRIS, J. M. 1954: Heartwood formation in *Pinus radiata*. Forest Research Institute, New Zealand Forest Service, Technical Paper No. 1.
- 1965: Enrichment of radiata pine heartwood with extractives. IUFRO Meeting, Section 41. October 1965.
- HARWOOD, V. D. 1971: Variation in carbohydrate analysis in relation to wood age in *Pinus radiata*. **Holzforschung** 25: 74.
- 1972: Studies on the cell wall polysaccharides of *Pinus radiata*; I. Isolation and structure of a xylan. **Svensk Papperstidn.** 75: 207.
- Studies on the cell wall polysaccharides of *Pinus radiata*; II. Structure of a glucomannan. **Svensk Papperstidn.** 76: 377.
- HARWOOD, V. D.; UPRICHARD, J. M. 1969: Pulp quality and chemical composition of *Pinus radiata* pulps. **Appita** 22: 153.
- HEMINGWAY, R. W.; HILLIS, W. E. 1971: Changes in fats and resins of *P. radiata* associated with heartwood formation. **Appita** 24: 439.
- HILLIS, W. E. 1962: In "Wood Extractives and their Significance to the Pulp and Paper Industry", W. E. Hillis (Ed.), Academic Press, New York.
- KERR, A. J.; SWANN, D. A. 1980: Effects of tree age on kraft pulping of *Pinus radiata*. Symposium on "The pulping and papermaking properties of radiata pine corewood (juvenile wood)" Rotorua, New Zealand.
- KIBBLEWHITE, R. P. 1973: Effects of beating and wood quality on radiata pine kraft paper properties. **New Zealand Journal of Forestry Science** 3: 220.
- 1981: The qualities of radiata pine papermaking fibres. Paper presented at the 35th Appita General Conference, Rotorua, New Zealand, 6-10 April 1981.
- LLOYD, J. A. 1978: Distribution of extractives in *Pinus radiata* earlywood and latewood. **New Zealand Journal of Forestry Science** 8: 288.
- McDONALD, I. R. C.; PORTER, L. J. 1979: The resin and fatty acid composition of *Pinus radiata* D. Don whole wood, and its relation to the yield and composition of New Zealand tall oil. **New Zealand Journal of Science** 12: 352.
- PORTER, L. J. 1969: The resin and fatty acid content of living *Pinus radiata* wood. **New Zealand Journal of Science** 12: 687.
- ROGERS, I. H. 1973: Isolation and chemical identification of toxic components of kraft mill wastes. **Pulp Paper Magazine Canada** 74: 111.
- UPRICHARD, J. M. 1965: The alpha-cellulose content of wood by the chlorite procedure. **Appita** 19: 36.
- 1971: Cellulose and lignin content in *Pinus radiata* D. Don. Within-tree variation in chemical composition, density, and tracheid length. **Holzforschung** 25: 97.
- ZOBEL, B. J.; McELWEE, R. L. 1958: Variation of cellulose in loblolly pine. **Tappi** 41: 167.