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The extractives in *Pinus pinaster* wood

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SUMMARY: The extractives in *Pinus pinaster* wood grown in South Australia were examined as part of an assessment of the suitability of this wood for manufacture of absorbent tissues from bisulphite pulps. The average petroleum solubility of the wood was 2.0% but the amount and composition of the petroleum extract varied widely depending upon the age of the tree, growth rate and height position in the tree. The resin acids were dominated by levopimaric + palustric acids but large proportions of abietic and neoabietic acids were present along with small proportions of dehydroabietic, isopimaric, pimaric and sandaracopimaric acids. The fatty acids and their esters were made up primarily of oleic and linoleic acids while small proportions of palmitic, palmitoleic, stearic, linolenic and other acids were also present. The average amount of ethanol soluble material in petroleum extracted heartwood was 2.8% and was highest in slowly grown trees which also contained the smallest amounts of petroleum soluble materials. The main phenolic heartwood constituents were pinocembrin, pinobanksin, and pinosylvin monomethyl ether while small proportions of pinosylvin, dihydrokaempferol and dihydroquercetin were present. The amounts and compositions of the extractives in *P. pinaster* wood were compared with the results of previous studies on *P. radiata* wood. It was concluded that trees from 15 year-old plantations and suppressed trees and the tops of trees from 35 year-old plantations of the former species could be used without substantially increasing the amount of petroleum soluble material in the wood supply.

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P. pinaster of the Mediterranean region is being planted in the States of South and Western Australia particularly on low quality, sandy sites which are less suited to *P. radiata*. Thinnings from plantations of both species are used for groundwood pulp in paper board production and bisulphite pulps from *P. radiata* thinnings are being used for absorbent tissue manufacture. It would be desirable if *P. pinaster* thinnings could also be used for the latter purpose. The amount of fat and resin in wood is very important for the acceptability of a wood as a source of bisulphite pulp for tissues. The accumulation of fats and resins causes "pitch troubles" in paper mills (1, 2) and also the fatty compounds are related to the instability of water absorbency of the paper (3, 4, 5). An examination of the fats and resins in *P. pinaster* wood was undertaken because of the absence of any published information which could indicate whether the thinnings of this species are suitable for absorbent tissue manufacture. The phenolic heartwood extractives were also studied because of their influence on pulp colour.

Materials and methods

Eight trees were selected from plantations near Mount Gambier, South Australia, which were close to an absorbent tissue mill. Four trees were taken from a 15 year-old plantation of site quality III—IV (site quality I is the highest and VII is the lowest), two of which were 25 cm DBH (diameter breast height outside bark) and two were 12 cm DBH. The 25 cm trees represented the maximum growth rate on this site. Four trees were taken from a 35 year-old plantation of site quality IV—V, two of which were 25 cm and two were 12 cm DBH. The 12 cm trees represented the minimum growth rate on this site. Billets about 1 m in length were cut from the base, middle and top portions of the merchantable stems, transported to the laboratory and frozen within 30 hours of felling the trees. The diameter inside the bark and percentage area of heartwood in each billet were determined after staining the disks with diazotized tolidine reagent (6).

Freeze dried groundwood was extracted with 40—60° petroleum, the extracts separated into acidic and neutral components using DEAE-Sephadex A-25 columns and the constituent fatty or resin acid methyl esters examined by gas-liquid chromatography as described previously (7). As levopimaric and palustric acids were not separated, the total GLC peak area was measured and referred to as levopimaric + palustric acids.

Selected heartwood samples were extracted with 40—60° petroleum followed by ethanol and the materials soluble in ethanol were separated using Kieselgel G-254 thin layer plates or silica gel columns. The thin layer plates were examined under ultra-violet light and after spraying with a saturated solution of diazotized *p*-nitroaniline in 20% sodium acetate. The UV spectra of isolated compounds were determined in methanol alone or with addition of aluminium chloride or sodium ethylate. The trimethylsilyl ether derivatives of the compounds were prepared with a mixture of hexamethyldisilazane, trimethylchlorosilane and bis- N,O,trimethylsilylacetamide in pyridine (2/1/4/10 parts by volume). These derivatives were examined by gas chromatography on 2 m by 3 mm ID glass columns packed with either 2% OV-17 or 3% SE-30 liquid phases on DMCS treated 80—100 mesh Chromosorb W. The oven was programmed from 140° increasing at 2° a minute to 220° and the upper limit was maintained until significant peaks were no longer eluted.

Results and discussion

The amount and composition of the petroleum soluble material in the wood was variable and dependent upon the age of the tree, growth rate and height in the tree (*Table 1*). The amount of petroleum soluble material in the wood of 15 year-old trees which contained no heartwood was lower at the base than in the upper portions of the stem. The proportion of resin acids to fatty acid esters was low at all positions in the 15 year-old trees examined. There was more petroleum soluble material in the wood from rapidly growing trees than from the trees of average growth rate in the 15 year-old plantation.

In the 35 year-old trees which contained heartwood, there was much more petroleum soluble material in wood from the base of the tree than in the upper portion of the stem and this was associated with high proportions of resin acids. There were significantly higher proportions of resin acids compared with fatty

Table 1. Amount and composition of extractives in Pinus pinaster wood

Sample			Heartwood	Petroleum solubility*	Ethanol solubility*	Resin acids**	Fatty acids**	Fatty acid esters**
Age Years	DBH cm	Position in tree	% Total area	Per cent of dried wood		Per cent of total GLC Peak area		
15	12	Top	—	1.86	—	21.8	3.09	74.4
		Mid	—	1.84	—	20.3	1.90	77.8
		Base	—	1.39	—	25.1	2.05	71.6
	Average			1.70		22.4	2.35	74.6
15	25	Top	—	1.95	—	28.1	3.80	68.1
		Mid	—	2.36	—	22.3	3.60	74.5
		Base	—	1.58	—	26.9	3.12	70.0
	Average			1.96		25.8	3.51	70.9
35	12	Top	< 15	1.08	2.90	44.3	1.76	53.4
		Mid	22.5	1.21	3.48	48.0	2.56	49.3
		Base	21.2	2.47	5.37	68.3	4.09	27.6
	Average			1.59	3.92	53.5	2.80	43.4
35	25	Top	< 14	2.70	1.56	33.2	0.94	65.4
		Mid	28.9	1.81	1.85	41.4	1.48	57.2
		Base	33.0	3.99	1.54	66.7	1.34	32.0
	Average			2.83	1.65	47.1	1.25	51.5

* Figures represent the average of duplicate determinations on each of 2 trees.
** Figures represent the average of 4 determinations on each of 2 trees.

acid esters in the 35 year-old trees than in the 15 year-old trees even at the tops of the trees where there was little heartwood. The wood of the suppressed trees contained much lower amounts of petroleum soluble materials than wood from the trees of average growth rate in the 35 year-old plantation. The proportions of fatty acids were small in all samples of wood examined. The above results are in accord with those obtained in an examination of the radial distribution of these compounds in *P. radiata* trees (7).

Some interpretation of the data in Table 1 is necessary to estimate the amount of fat and resin in *P. pinaster* wood which might be used for bisulphite pulps. The figures in Table 1 were weighted according to the cross-sectional area of the billets and various combinations of trees or portions of trees were then averaged according to their weighted volume basis to estimate the average petroleum solubility of wood chips which could be supplied to the mill (*Table 2*). A previous examination of the amount of petroleum soluble material in *P. radiata* wood being used for absorbent tissue manufacture indicated that a range of 1.6 to 2.0% petroleum solubility was presently being accepted in the chips from *P. radiata* thinnings.

The weighted average petroleum solubility of all the trees sampled from the 15 year-old plantation was 1.8%. The 15 year-old trees that were 25 cm DBH were exceptionally fast grown and represent a minor proportion of the plantation. Consequently, an estimate of

Table 2. Weighted volume average petroleum solubility

Sample	% Petroleum solubility
1. 15 year old—12 cm trees	1.63
2. 15 year old—25 cm trees	1.88
3. All 15 year old trees	1.81
4. 35 year old—12 cm trees	1.82
5. 35 year old—25 cm trees	3.26
6. All 35 year old trees	2.88
7. All 35 year old trees except resin soaked one	2.65
8. Tops of 35 year old trees	2.06
9. 50% of 15 year old trees, 25% of suppressed 35 year old and 25% of tops of 35 year old trees	1.78

Example:

15 year old—12 cm diameter trees

	Radius	Petroleum sol.	Radius²	Petrol. × Radius²
Top	4.7	1.86	22.1	41.2
Middle	6.1	1.84	33.3	68.6
Bottom	7.4	1.39	54.8	76.2
			114.2	186.0

$$\frac{186.0}{114.2} = 1.63$$

the average petroleum solubility of wood from the whole 15 year-old plantation would more closely approximate that found for the 12 cm DBH trees or 1.6% petroleum solubility. Therefore, all trees from the 15 year-old plantation could be used without increasing the level of petroleum soluble material in the wood chips significantly beyond the lower limit of the range found in *P. radiata* chips that have been used for tissue manufacture.

The wood from trees in the 35 year-old plantation contained much more petroleum soluble material. One of the trees contained 4.9% petroleum solubles at the base of the tree and this extract contained 75% of the measured GLC peak area as resin acids. Small patches of resin soaking were observed in the heartwood. This has been observed in other *P. pinaster* trees in the Mount Gambier area. The colour reactions given by the heartwood of this tree with diazotized tolidine suggested that some decay may have been present and the high resin acid content may have been associated with it. The weighted average for all of the trees selected from the 35 year-old plantation was 2.9% petroleum solubility but only 2.4% when the tree with exceptionally high resin acid content was omitted from the sample. In either case, trees from the 35 year-old plantation contain too much fat and resin to be acceptable unless only certain trees are selected. If only the suppressed trees from this plantation were selected, the weighted average petroleum solubility would be about 1.8% which is within the apparent tolerable range. If the suppressed trees and only the tops of trees of average growth rate from the 35 year-old plantation were mixed with trees from the 15 year-old plantation the average petroleum solubility of the chips would be expected to be about 1.8%.

The proportion of resin acids in the petroleum extract is of considerable significance to the effect of the wood resin on the incidence of pitch troubles in the paper mill. With sulphite pulps, there is a low incidence of pitch troubles if the resin acids comprise less than 25% or more than 75% of the petroleum solubles and a high incidence of pitch troubles when the proportion of resin acids is between 50 and 75% of the petroleum solubles (8—10). The least troublesome pitch deposit collected from a mill using *P. radiata* bisulphite pulps also contained low proportions of resin acids (11). Wood from all the trees in the 15 year-old plantations and from the tops of trees from the 35 year-old plantation contained low proportions of resin acids in the petroleum soluble material (Table 1). Therefore the viscosity of the pitch would be expected to decrease if *P. pinaster* wood were to be used.

The composition of the resin acids in *P. pinaster* wood (*Table 3*) was similar to that found in *P. radiata* wood (7, 11). There was a higher proportion of abietic acid and a lower proportion of neoabietic acid in the *P. pinaster* wood than in the *P. radiata* wood examined so far. The 15 year-old trees contained more levopimaric + palustric acids and less pimaric and dehydroabietic acids than did the 35 year-old trees. Within the 35 year-old trees (which contained heartwood) there was significantly more levopimaric + palustric acids at the top of the tree than at the base, indicating some autoxidation of the labile resin acids in the older heartwood at the base of the tree. The effect was small, however, considering the rate of autoxidation of the

*Table 3. Composition of resin acids in P. pinaster wood**

Sample			Per cent of total resin acid GLC peak area**						
Age Years	DBH cm	Position in tree	Pim	San	Levo/Pal	Isop	Abie	Dehyd	Neo
15	12	Top	9.4	1.2	51	3.8	16	4.4	13
		Mid	10	1.2	51	3.4	14	5.8	14
		Base	10	1.6	51	2.8	16	4.8	14
15	25	Top	10	0.81	51	4.0	14	2.4	17
		Mid	9.5	0.90	49	4.4	15	3.7	17
		Base	8.5	0.84	47	6.5	16	3.8	17
	Average		10	1.0	50	4.1	15	4.2	16
35	12	Top	12	1.4	42	3.6	17	7.8	17
		Mid	12	1.0	44	4.2	16	4.9	18
		Base	12	1.3	38	2.4	19	7.5	18
	25	Top	10	1.3	49	3.5	15	3.8	17
		Mid	11	1.3	41	3.9	17	9.2	15
		Base	11	1.2	41	3.7	16	10	15
	Average		11.4						

*Table 4. Composition of fatty acids in P. pinaster wood**

Sample			Per cent of total fatty acid GLC peak area**						
Age Years	DBH cm	Position in tree	C16	C16-1	C17	C18	C18-1	C18-2	C18-3
15	12	Top	12	.24	1.2	1.9	38	43	2.3
		Mid	11	.30	1.3	2.1	40	43	2.2
		Base	14	.42	1.1	2.4	38	42	2.1
15	25	Top	15	.16	1.2	1.3	40	40	2.1
		Mid	13	.26	1.0	1.4	43	39	2.0
		Base	12	.13	1.0	1.2	40	43	2.2
	Average		13	.25	1.1	1.7	40	42	2.1
35	12	Top	15	.54	5.2	3.4	27	46	2.9
		Mid	14	.30	2.4	2.8	32	46	2.8
		Base	9	.20	1.7	1.6	40	45	2.9
35	25	Top	11	.33	1.6	2.1	40	42	2.0
		Mid	10	.33	1.7	2.1	39	43	2.4
		Base	9	.28	1.3	1.5	37	49	2.1
	Average		11	.33	2.3	2.2	36	45	2.5

* Figures represent the average of 4 determinations on each of 2 trees.
** Methyl esters of the fatty acids: — C16 = Palmitic, C16-1 = Palmitoleic, C17 = a saturated fatty acid, C18 = Stearic, C18-1 = Oleic, C18-2 = Linoleic, C18-3 = Linolenic acids.

*Table 5. Composition of fatty acid esters in P. pinaster wood**

Age Years	Dia. cm	Position in tree	Per cent of total fatty acid GLC peak area**						
			C16	C16-1	C17	C18	C18-1	C18-2	C18-3
15	12	Top	8.6	0.14	0.70	1.2	45	42	1.8
		Mid	8.3	0.13	0.64	1.0	44	44	1.7
		Base	9.5	0.10	0.59	1.1	46	41	1.5
15	25	Top	8.1	0.06	0.54	0.72	49	40	1.8
		Mid	8.7	0.06	0.56	0.74	49	39	1.6
		Base	9.7	0.08	0.52	0.98	50	38	1.4
	Average		8.8	0.09	0.59	0.94	47	41	1.6
35	12	Top	5.8	0.34	2.0	0.90	33	56	2.1
		Mid	5.9	0.15	1.7	0.84	34	55	1.9
		Base	6.6	0.18	1.1	0.90	39	50	1.9
35	25	Top	6.0	0.12	1.2	1.0	47	41	3.5
		Mid	5.6	0.15	1.0	1.1	44	46	2.5
		Base	7.5	0.25	0.7	0.9	47	42	1.2
	Average		6.2	0.15	1.3	0.9	41	48	2.2

* Figures represent the average of 4 determinations on each of 2 trees.
** Methyl esters of the fatty acids: — C16 = Palmitic, C16-1 = Palmitoleic, C17 = a saturated fatty acid, C18 = Stearic, C18-1 = Oleic, C18-2 = Linoleic, C18-3 = Linolenic acids.

resin acids in dry wood exposed to air (9). There does not appear to be sufficient difference in the composition of the resin acids between *P. pinaster* and *P. radiata* woods to cause a different response during pulp and paper making.

Oleic and linoleic acids were the predominant fatty acids either free (*Table 4*) or esterified (*Table 5*). The *P. pinaster* samples analysed contained less palmitic acid, more linoleic acid and more of a saturated C-17 fatty acid in the fatty acid fraction than did *P. radiata* wood (7). The fatty acid fraction contained a higher proportion of saturated fatty acids than did the fatty acid ester fraction, as was found in *P. radiata* wood (7). In the 35 year-old trees, the proportion of saturated fatty acids increased with increasing height particularly in the suppressed trees. This was probably a reflection of the greater proportions of saturated fatty acids in the sapwood than in the heartwood as was found in *P. radiata* wood (7). The fatty acid ester fraction of *P. pinaster* wood contained a higher proportion of linoleate and C-17 esters than the corresponding esters in *P. radiata* wood. The fatty acid ester fraction of the 15 year-old trees contained higher proportions of palmitate esters than the 35 year-old trees. The suppressed 35 year-old trees (12 cm DBH) contained significantly higher proportions of linoleic acid and lower proportions of oleic acid than did the other trees in both the fatty acid and fatty acid ester fractions. The difference in composition of fatty acids and fatty acid esters in *P. pinaster* and *P. radiata* woods observed so far do not appear large enough or of a type to cause differences in behaviour during bisulphite pulping and absorbent tissue manufacture.

The wood from 15 year-old *P. pinaster* trees contained relatively large amounts of unsaturated fatty acid esters compared with the *P. radiata* wood that was being used for absorbent tissues. Examination of the fatty acid esters in *P. radiata* wood and pulps at various stages of manufacture (1) indicated that the esters were only partially hydrolysed during the cook and the remaining esters were not removed from the pulp much during washing and screening. Therefore, it could be expected that the amount of fatty acid ester in *P. pinaster* pulps from 15 year-old trees would be higher than in the present *P. radiata* pulps. An important effect of increased fatty acid ester content in the pulp would be an adverse effect on the long term water absorbency of the tissues, particularly those made from chlorine bleached pulps. The relationship of fatty acids and esters on the wettability of papers after storage has been well documented by Swanson and coworkers (3, 4) and Buchanan (5). Leopold and Mutton (12) have shown that the unsaturated fatty acids are readily chlorinated in the first bleach stage and these products are extremely hydrophobic and difficult to remove from the pulp. Some consideration should be given to the water absorbency of tissues after storage if substantial proportions of 15 year-old *P. pinaster* thinnings were to be used.

The petroleum extracted heartwood contained about 2.8% ethanol soluble material. The suppressed trees contained more than double the amount of these materials in the heartwood than did the heartwood from trees of average growth rate in the 35 year-old stand (Table 1). The heartwood at the base of the suppressed trees contained very high concentrations of ethanol soluble materials compared with wood from the top of the tree and this distribution with height in the tree was not found in the trees of average growth rate. Similar relationships have been reported previously (13).

Table 6. Chromatographic properties of phenolic extractives in P. pinaster heartwood

Compound	TLC				GLC	
	R_f values with				RRT*	
	MCP**		CEF***			
	1/2/7	2/4/7	7/4/1	5/4/1	SE-30 3%	OV-17 2%
Pinosylvin monomethyl ether	0.24	0.44	0.91	—	0.662	0.610
Pinosylvin	0.09	0.33	0.69	—	0.758	0.600
Pinocembrin	0.21	0.41	0.88	0.90	1.000	1.000
Pinobanksin	—	0.36	0.76	0.81	1.12	1.05
Dihydrokaempferol	—	—	0.56	0.63	1.53	1.42
Dihydroquercetin	—	—	0.37	0.54	1.67	1.54

* Relative retention time of trimethylsilyl derivates separated on SE-30 and OV-17 columns at an oven temperature programmed from 140° increasing 2°/min to 220°C.
** MCP = methanol, chloroform, 100—120° petroleum; 1/2/7 and 2/4/7 parts by volume.
*** CEF = chloroform, ethyl acetate, formic acid; 7/4/1 and 5/4/1 parts by volume.

The monomeric phenolic extractives that were identified from their chromatographic and spectral properties after isolation by thin layer or column chromatography included pinocembrin, pinobanksin, pinosylvin and pinosylvin monomethyl ether all of which have been found in all pine species of the Diploxylon subgenus (14) and were previously reported in *P. pinaster* heartwood (15). In addition to these compounds, both thin layer and gas chromatography of ethanol extracts indicated that there were many more phenolic materials present in small quantities and two of these were identical with authentic dihydrokaempferol and dihydroquercetin.

A comparison of the relative proportion of GLC peak areas obtained for the above compounds from the analysis of the ethanol extracts indicated that there was appreciable variation in the composition of the phenolic heartwood constituents between the trees (*Table 7*). This was especially evident in the proportions of pinobanksin and pinocembrin. The ratio of pinosylvin monomethyl ether to pinosylvin varied between 8 to 1 and 3 to 1, which is similar to the range reported by Erdtman (14). The heartwood samples that may have contained some incipient decay also contained low proportions of

*Table 7. Composition of phenolic extractives in P. pinaster heartwood**

Sample			Per cent of total GLC peak area**					
Age Years	DBH cm	Position Height	TMS—phenolic derivatives of					
			PSME	PS	PC	PB	DHK	DHQ
35	12	Top	23	8.9	50	12	1.1	5.8
		Mid	23	5.5	54	12	1.5	2.6
		Base	24	7.8	50	13	1.6	2.9
35	12	Top	16	4.0	31	36	5.4	8.6
		Mid	20	2.6	40	32	1.9	3.7
		Base	25	6.3	35	28	1.3	3.5
	Average		22	5.8	43	22	2.1	4.5
35	25	Top	23	6.8	51	14	1.7	3.5
		Mid***	10	2.0	55	24	1.8	6.7
		Base***	7	—	46	30	3.5	7.2
35	25	Top	16	3.7	38	34	3.8	4.7
		Mid	15	3.0	34	37	3.8	4.0
		Base	18	3.3	34	38	2.2	4.5
	Average		—	3.7	43	30	2.8	5.1

* Figures represent the average of duplicate determinations.
** PSME = pinosylvin monomethyl ether, PS = pinosylvin, PC = pinocembrin, PB = pinobanksin, DHK = dihydrokaempferol, DHQ = dihydroquercetin.
*** These samples contained some incipient decay.

stilbenes. The phenolic extractives in *P. pinaster* heartwood are not substantially different from those in *P. radiata*. As the polyphenols in jack pine (*P. banksia*) contribute considerably to the coloration of groundwood on ageing (16) and in bisulphite pulps (17), the increased amounts of polyphenols in the heartwood of suppressed *P. pinaster* trees could affect the color of pulp. The most significant components in this regard could be the stilbenes (18, 19) as well as pinobanksin (17). However, the polyphenols would not be expected to be troublesome provided that the percentage of heartwood in each digester charge is kept low.

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