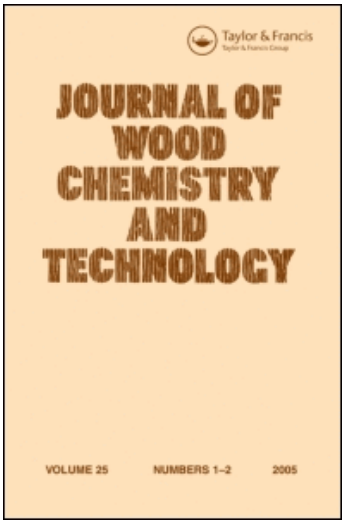

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VACUUM PYROLYSIS OF BARK FROM PINUS PONDEROSA

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ABSTRACT

The inner and outer barks of ponderosa pine (P. ponderosa) have been pyrolysed at 350°C in vacuum and the tars analyzed by gas chromatography after tri-O-methylsilylation. The nine major peaks in the gas chromatogram have been identified and quantified and it is concluded that all (except pinitol) originate predominantly from polysaccharide components of the barks. They account for up to 53% of the total tar. Removal of most of the metal ions from the barks by ion exchange with dilute acid has a dramatic influence on the tar constituents, e.g. increasing the yield of levoglucanosan from inner bark from 0.8% to 13%, which represents 31% of the original glucan content of the bark. The polyphenol and lignin components of the bark are predominantly converted directly to char at 350°C.

INTRODUCTION

Bark remains a major high-volume low-value "waste" product of the forest products industry especially from softwood, despite extensive research into its constituents and uses (e.g., more than 500 papers and patents since 1967). However, one avenue of utilization which has been less extensively investigated than others is the thermal conversion of bark, either with a view to isolation of high-value products by pyrolysis or for gasification.

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This is despite the very extensive literature on such thermal treatments of wood and cellulose. This paper represents our first report of an attempt to use a new concept of ion control (including total removal of metal ions) to influence the pyrolysis of barks. The concept is based on recent work carried out in this laboratory on cellulose and wood (e.g. [1-3]) and seemed likely to be even more effective with bark because of the greater proportion of acidic and phenolic groups available in bark which will bind metal ions in nature. The ultimate targets are to obtain high-value products by pre-extraction and ion-controlled pyrolysis. A complementary study of gasification of chars from the barks to produce gases either for combustion or (preferably) conversion to products such as methanol will be reported separately.

The major differences between bark and wood for a given species in terms of gross chemical content are generally that "bark contains more polyphenols, inorganic constituents and uronic acid (pectin) than the wood, but less glucose (cellulose) and mannose residues".[4] A large proportion of the polyphenols is readily extracted from bark and may have potential commercial value, e.g. as adhesives.[5] The higher content of indigenous cations in the polyphenols of bark (compared with wood) will certainly have a major influence on any thermal treatment of whole bark and hence bark was expected to be especially sensitive to our procedures for ion control in thermal treatments.

The thermal treatment of extracted barks (which could be carried out after removal of polyphenols for other uses) involves the reaction of several species of polysaccharides which (with suberin and lignin) make up the bulk of the non-extractable part of the bark. These polysaccharides have been very extensively studied, especially by Timell and coworkers,[6-9] who have shown e.g. that Amabilis Fir bark contains 50%[6] and White Birch bark 54%.[7] Several softwood barks have been shown to contain 30-38% α-cellulose.[8] Pectins[6] and galactoglucomannans[9] are also major bark constituents. The uronic acid content of polysaccharides in

bark is much higher than in wood[4] and hence the polysaccharide fraction, like the polyphenol fraction, will also contain more indigenous cations than comparable wood and will be more sensitive to our ion-control thermal treatments.

Several authors have carried out thermal analysis on barks, (e.g. [10-15]), but there is need for more extensive identification of major volatile products. In particular, McGinnis and coworkers[10] have carried out thermal analysis of barks with and without alkaline pre-extraction, and have identified some of the volatile products of flash pyrolysis,[16-18] but without the ion control which is the central feature of the present investigation. Ross and coworkers[11,12] have carried out thermal analysis of bark with many inorganic additives, but have not identified any products from pyrolysis. Furthermore, we have shown with wood that such an additive approach will yield completely different results from the ion-control procedures which we propose, which will disperse individual metal ions within the bark morphology in accordance with the distribution of naturally-occurring carboxylic and phenolic groups. For example, DeGroot and Shafizadeh[1] state "potassium carbonate absorbed on cellulose significantly increases its decomposition temperature, although it has the opposite effect when added to wood through ion exchange". The profile of pyrolysis products from cellulose[20,21] and also from another neutral polysaccharide (β-1,3-glucan) have been shown to be completely changed by presence of less than 0.2% sodium chloride.[22]

Ponderosa Pine (Pinus ponderosa) was selected for initial study because it is an abundant commercialized species in Northwestern America and has a relatively heavy bark in which the outer bark is preponderant.

EXPERIMENTAL

Preparation of Barks

Bark was collected from a 120 cm length of bole from a healthy 49 year old tree (12 m x 20 cm diameter at base) at

Lubrecht Experimental Forest at the University of Montana in June. The inner bark (thickness ca. 2 mm) was immediately stripped manually from the outer bark (thickness 10-30 mm). Both barks were air dried overnight in the dark, Wiley milled to pass a 1 mm screen and then stored in sealed plastic bags at -20°C. The respective air dry yields were 249 g (inner) and 2297 g (outer) and removal of inner bark from outer was 50-70% complete. I.e. the inner bark sample was free from outer bark and all subsequent results are regarded as representative of "pure" phloem. The outer bark sample was tenfold greater in weight than the inner bark and therefore the 30-50% of total inner bark left with the outer bark will have only a small influence on the subsequent results obtained with the latter fraction. Samples (20 g) of ground bark were washed as follows. The bark was covered with the wash liquid, degassed at 15 mm Hg and transferred to a glass column. Water-washed barks were then eluted with water (2 L) over a period of ca. 10 hr at room temperature. Acid-washed barks were washed with 0.05 N hydrochloric acid (1.5 L) followed by water (2 L). Strong acid-washed barks were washed with 1 N hydrochloric acid (5 L) followed by water (2 L). EDTA-washed outer bark was eluted with 0.07 M EDTA (3 L) followed by 0.05 N hydrochloric acid (2 L) and then water (3 L). All washed barks were filtered, vacuum dried at 40°C and stored at -20°C.

Pyrolysis Conditions

Batch vacuum pyrolyses were conducted on 0.5-2.0 g samples under a flow of nitrogen at approximately 1.5 mm Hg.[23] The material condensing at room temperature is described as "tar" and was almost entirely soluble in methanol. The material which subsequently condensed at -40°C is described as "distillate" and contained a large proportion of water. Trace amounts of waxes were present in both tar and distillate from 350°C pyrolyses, these were not soluble in methanol or water and were not included in subsequent analyses. In some limited pyrolysis experiments at higher temperatures, increased yields of waxes were observed.

Gas Chromatography

Packed nickel columns, nitrogen carrier gas, flame ionization detection and digital integration were used with the following columns: (a) 3% SE52 on GasChrom Q (100-120 mesh) (2.2 mm o.d. x 2.4 m) programmed from 130° to 250°C at 6°/ min for TMS ethers and (b) 3% ECNSS on GasChrom Q (100-120 mesh) (2.2 mm o.d. x 1 m) programmed from 160° to 190°C at 2°/min for alditol acetates.

The tar was derivatized for gas chromatography on column (a) with bis-(trimethylsilyl)trifluoro-acetamide (BSTFA, Pierce Chemical Co.) in pyridine at 90° for 10 min after addition of D-glucitol as internal standard.

Glycan content was determined by hydrolysis with 72% sulfuric acid followed by reduction, acetylation and gas chromatography on column (b) using myo-inositol as the internal standard and corrected for acid degradation of glycoses.[24] Uronic acid contents were determined on aliquot portions of the acid hydrolysates by reaction with 3-phenylphenol, using galacturonic acid standards and corrected for losses due to acid degradation.[24]

NMR Analysis

Distillates were diluted with deuterium oxide containing 2,2-dimethyl-propan-1-ol as internal standard and ^{1}H-n.m.r. recorded with a Jeol FX-90Q instrument at 90 MHz. Yields of individual products were then determined by integration of peak areas as described earlier.[25]

RESULTS AND DISCUSSION

Carbohydrate Components of Barks

The glycan content of the barks is shown in Table 1. These values represent absolute contents of anhydroglycose units, corrected for acid degradation, and they indicate total carbohydrate contents of 45% in the outer bark and 66% in the

inner bark. The major non-carbohydrate components are polyphenols (especially proanthocyanidins), lignin, suberin and low molecular weight extractives.[16,26] Among the carbohydrate components, in the outer bark the glucose is likely to occur predominantly as cellulose and the other major type of polysaccharide is pectic substance, as indicated by the high content of galacturonic acid and by the fact that pectins have previously been isolated from barks (e.g. Abies amabilis[6]). The arabinose is probably present partly as a component of the pectin[6] and partly as an arabinan, similar to that reported from Pinus sylvestris bark.[27] In the phloem (inner bark) glucose is the major carbohydrate constituent. This will occur partly as cellulose, but also as starch (20% starch content was found in P. sylvestris phloem[28]) and as callose, a 1,3-β-glucan, occurring particularly in the sieve tubes.[28] Some glucose will also occur as monomer and as sucrose. The content of pectic substances and arabinan is rather higher in the phloem than in the outer bark and a galactomannan is present in small amount in both parts of the bark (cf. the galactomannan from P. sylvestris[29]).

Neither the accuracy nor the precision of the carbohydrate analyses in Table 1 is high, but some general conclusions are possible. The total carbohydrate content is increased by acid-washing, both with outer and inner barks. This is due to removal of non-carbohydrate constituents, both metal ions and also water-soluble extractives such as some of the polyphenols, cyclohexitols, etc. The fall in arabinose content of the outer bark on acid-washing suggests that some such components contain arabinose units. The increase in uronic acid content with acid-washing indicates that the pectic substances of the barks are not water or acid soluble at room temperature. The increase in glucose content with mild acid-washing is due to the fact that the major glucan components (cellulose, starch and callose) are insoluble in room temperature water, but the fall in glucose content between mild and strong acid-washing is unexplained and may indicate some selective extraction of a glucan by the

TABLE 1

Glycan Content of Ponderosa Pine Barks (% dry weight).

Bark	Rhamnose	Arabinose	Xylose	Mannose	Galactose	Glucose	Uronic Acids	Total Carbohydr.
OUTER BARK								
Untreated	0.6	6.0	1.9	2.9	2.3	17.3	13.6	44.6
Mild acid-washed	0.5	5.0	2.6	4.2	3.0	21.1	16.5	52.9
Strong acid-washed	0.5	5.0	2.3	3.3	2.3	17.9	16.5	47.8
INNER BARK								
Untreated	0.5	7.2	1.5	2.2	2.8	35.7	16.1	66.0
Mild acid-washed	0.5	9.5	2.4	2.5	3.3	41.5	26.5	86.2
Strong acid-washed	0.9	9.5	1.9	2.0	2.2	35.2	24.0	76.0

stronger acid. Acid hydrolysis of glycan bonds by the stronger acid does not appear to be significant because the arabinose content after strong acid-washing is the same as with mild acid-washing and the arabinose component would be expected to be the most sensitive marker of hydrolysis because it is most probably present predominantly in the furanoside form.[30]

Metal Ion Constituents of Barks

Table 2 shows the metal ion content of the barks as determined by argon plasma spectrometry. In the outer bark, the major metal ion is calcium. The phloem contains a similar amount of calcium, but even more potassium and also a high content of magnesium and phosphorus. This difference is probably associated with the fact that, unlike the outer bark, the phloem contains living cells. The latter cells therefore contain cytoplasm, which is probably the major source of the potassium, magnesium and phosphorus, whereas the calcium appears to be predominantly a cell-wall constituent, present as the counter-ion to the uronic acids.[2] Accordingly, the potassium is readily removed by water-washing (e.g. as potassium salts of organic acids), while the calcium is strongly bound by ion exchange in the cell wall, resists removal by water-washing and even increases as a result of removal of water-soluble organic extractives. About three-quarters of the calcium is removed by ion exchange as the result of washing with 0.05 M hydrochloric acid at room temperature, but the balance is remarkably resistant even to extraction with Molar hydrochloric acid and with EDTA. The basis of this resistance of part of the calcium to ion exchange will be further investigated. In the meantime however, the results described below show that even the partial removal of metal ions has a major influence on the products of subsequent pyrolysis.

Components of Pyrolysis Tars

In the pyrolysis of the barks, relatively low temperature vacuum conditions were used in order to gain maximum information

TABLE 2

Cation Content of Ponderosa Pine Barks (ppm).

Bark	Al	Ca	Co	Cu	Fe	Mg	Mn	P	K	Si	Na	Zn	Ti	Total M%
OUTER BARK														
Untreated	85	4762	0	6	112	249	41	134	634	112	16	19	3.96	0.62
Water-washed	68	5165	0	18	182	175	38	78	48	110	11	32	3.04	0.59
EDTA-washed	60	1617	2	3	55	12	6	75	13	96	13	4	4	0.20
Mild acid-washed	55	1135	0	10	155	20	6	84	41	123	29	17	4.32	0.17
Strong acid-washed	63	818	0.1	3.5	53.5	16	3	73	214	98	26	2	4	0.14
INNER BARK														
Untreated	52	4524	0.1	6.8	30.7	1250	122.2	902	5009	55	16	37.3	1.0	1.20
Water-washed	39	6349	0	8.7	41.1	899	119.3	399	-8	14	-1	44.9	0.8	0.79
Mild acid-washed	24	1480	0.1	5.3	32.1	7	8.5	497	87	40	18	3.1	1.4	0.22
Strong acid-washed	16	1067	2.7	2.1	18.5	8	6.3	316	196	27	56	2	4	0.17

on the mechanisms of pyrolysis of the various components. The yields of char were accordingly high and these types of conditions might be appropriate for process design which incorporated subsequent economic benefit from gasification of char. In any process designed to maximize yield of pyrolysis oils, it would be logical to use higher temperatures (and possibly flash pyrolysis). The yields of pyrolysis fractions are shown in Table 3. The influences of water- and acid-washing on tar yields were greater with inner than with outer bark, presumably because the metal ion content and extractives removed by the washing were greater in the former. Some major effects of the washing procedures were found in the GC analyses of the TMS ethers prepared from the tars after addition of D-glucitol as internal standard (Tables 4 and 5). The products listed in these tables correspond to all of the major peaks detected in the gas chromatography. Retention times and relative response factors are shown in Table 6. The identifications were by comparison with authentic compounds and by mass spectrometry. All of the peaks were completely resolved from each other except for 5-(hydroxymethyl)-2-furaldehyde and 1,2-dihydroxybenzene, which coincided. In this case the mass spectrometry was compatible with a mixture of these two components and the combined yields are expressed as the total for that peak, using a response factor (Table 6) which was the average of the two pure components.

It is notable that there are some major components of the tars which are not detected by GC of TMS ethers. Thus the highest "recovery" in Tables 4 and 5 is 53% of the tar from strong acid-washed inner bark, while the lowest is 16% of the tar from untreated outer bark. Evidently some major components of the tars are not determined by GC of the TMS ethers, presumably because they do not pass through the GC column. It seems probable that the unidentified components are of higher molecular weight than those shown in Tables 4 and 5. The same discrepancies occur in the earlier studies of tar from pyrolysis of cellulose using similar techniques and in such cases the tar components which are

TABLE 3

Vacuum Pyrolysis of Ponderosa Pine Barks, 350°C, 30 min.

Bark	% Tar	% Distillate	% Char	Total Recovery
OUTER BARK				
Untreated[a]	21	18	46	85
EDTA-washed	23	15	47	85
Untreated	25	18	43	86
Water-washed	22	ND	41	ND
Mild acid-washed	26	17	40	83
Strong acid-washed	25	ND	45	ND
Cork	21	22	27	70
INNER BARK				
Untreated	19	24	31	74
Water-washed	33	26	28	87
Mild acid-washed	38	22	29	89
Strong acid-washed	30	ND	32	ND

[a]Pyrolyzed 15 min. only.

ND, not determined.

TABLE 4

Major Peaks from G.C. of TMS Ethers of Tars from Inner Bark as % of dry bark.*
Pyrolysis Conditions: 350°/30 minutes.

Bark Pretreatment	Untreated	Water-washed	Mild acid-washed	Strong acid-washed
Tar yield	19	33	38	30
1,5-Anhydroarabinose	1.03(4.6)	2.4(7.2)	2.4(6.5)	2.2(7.3)
Levoglucosan pyranose	0.8(3.5)	10.3(30.9)	12.0(32.7)	11.7(38.8)
Levoglucosan furanose	- (-)	0.7(2.1)	1.3(3.5)	1.2(4.0)
Metasaccharinolactone	0.4(1.8)	0.1(0.3)	- (-)	- (-)
Pinitol	0.5(2.2)	- (-)	- (-)	- (-)
1,2-Dihydroxybenzene[a]	0.7(3.1)	0.1(0.3)	0.1(0.3)	0.2(0.7)
1,4-Dihydroxybenzene	0.1(0.5)	0.1(0.3)	0.1(0.3)	0.1(0.3)
1,2,3-Trihydroxybenzene	0.2(1.0)	0.1(0.3)	0.1(0.3)	0.1(0.3)
1,2,4-Trihydroxybenzene	0.3(1.3)	0.4(1.2)	0.6(1.6)	0.4(1.3)
Total "recovery" of tar (%)	18	42	45	53

*Figures in parenthesis are % content in tar.

[a]Includes 5-(hydroxymethyl)-2-furaldehyde.

TABLE 5

Major Peaks from G.C. of TMS Ethers of Tars from Outer Bark as % of Dry Bark.*
Pyrolysis Conditions: 350°/30 minutes

Bark Pretreatment	Untreated	Water-washed	Mild acid-washed	Strong acid-washed	EDTA-washed
Tar yield	29	22	26	25	23
1,5-Anhydroarabinose	1.2(4.2)	1.2(5.5)	0.8(3.2)	1.4(5.4)	1.3(5.7)
Levoglucosan pyranose	2.5(8.5)	3.2(14.5)	3.5(13.3)	6.0(23.5)	4.8(20.9)
Levoglucosan furanose	0.1(0.3)	0.2(0.9)	0.2(0.8)	0.4(1.6)	0.3(1.3)
Metasaccharinolactone	0.1(0.3)	- (-)	- (-)	- (-)	- (-)
Pinitol	0.2(0.7)	0.05(0.2)	- (-)	0.1(0.4)	0.05(0.2)
1,2-Dihydroxybenzene[a]	0.4(1.4)	0.1(0.5)	0.1(0.4)	0.5(2.0)	0.2(0.9)
1,4-Dihydroxybenzene	0.1(0.3)	0.1(0.5)	0.1(0.4)	0.2(0.8)	0.1(0.4)
1,2,3-Trihydroxybenzene	0.1(0.3)	0.1(0.5)	0.05(0.2)	0.1(0.4)	0.05(0.2)
1,2,4-Trihydroxybenzene	0.2(0.7)	0.1(0.5)	0.1(0.4)	0.3(1.2)	0.2(0.9)
Total "recovery" of tar (%)	16	23	19	35	30

*Figures in parenthesis are % content in tar.

[a]Includes 5-(hydroxymethyl)-2-furaldehyde.

TABLE 6

Gas Chromotography of Tri-O-Methyl Silyl Ethers.

Tar Component	Retention Time (min)	Relative F.I.D. Response
5-(Hydroxymethyl)-2-furaldehyde	4.6	0.30
1,2-Dihydroxybenzene	4.6	0.94
1,4-Dihydroxybenzene	5.7	0.92
1,5-Anhydro-β-L-Arabinose	5.9	0.44
1,2,3-Trihydroxybenzene	8.1	0.98
1,2,4-Trihydroxybenzene	9.1	0.98
Levoglucosan (pyranose)	11.0	0.72
Levoglucosan (furanose)	11.7	0.72
Metasaccharino-1,4-gluconolactone	12.3	0.53
Pinitol	13.4	0.97
D-Glucitol (Internal Standard)	15.2	1.00

not accounted for by GC are partly polysaccharide in nature and are derived from post-pyrolysis polymerization of levoglucosan.[31] In the case of barks, we have the additional possibility of high molecular weight aromatic components derived from polyphenols. In considering the tar components which are identified in Tables 4 and 5 however, we conclude that in almost all cases the most probable source is pyrolysis of a polysaccharide consitutent of the bark. These products will now be discussed separately.

Origins of Tar Components

The anhydroarabinose is no doubt derived by pyrolytic scission of pendant L-arabinofuranoside units contained in pectins and hemicelluloses, followed by ring closure of the primary

pyrolytic product (possibly an arabinosyl cation) as described earlier for several types of biomass.[30] In accordance with the earlier studies,[30] the yield is increased by removal of metal ions before pyrolysis and is higher from inner bark, which has the higher arabinose content. The levoglucosan (both pyranose and furanose) is no doubt derived from pyrolysis of cellulose in accordance with the abundant previous studies of pyrolysis of cellulose (e.g.[31]), although some will also be derived from starch, especially in inner bark. The yield of levoglucosan is dramatically increased by reduction in salts (by water-washing) and in metal ions (by acid-washing). Thus the untreated inner bark yields only 0.8%, whereas after acid-washing the yield of levoglucosan is increased to 13% of the bark, which represents 31% of the original glucan content. Previous studies on acid-washing of cellulose[31] suggest that this yield might be doubled by complete removal of the metal ions. As would be expected, the outer bark, with lower glucan content, gave lower yields of levoglucosan.

The metasaccharinolactone is derived from callose, the 1,3-β-glucan found in the sieve tubes of barks. We have previously identified this product from pyrolysis of such a glucan (curdlan).[22] In the previous work also it was found that presence of salts favored pyrolysis to metasaccharinolactone, while removal of the salt before pyrolysis favored levoglucosan formation. The pinitol in the tar is almost certainly derived directly from the same compound in bark since this compound is a common component of gymnosperms.[32] The yield is lowered by washing before pyrolysis, because the pinitol is water-soluble.

The phenol constituents of the tars are the same in identity and similar in yield to those given by pyrolysis of cellulose in presence of salts.[20] In particular, the absence of 1,3-dihydroxybenzene and 1,3,5-trihydroxybenzene is notable. It is concluded that the most probable source of these phenols in the tar is the polysaccharides of the bark. There appear to be no significant components in the tar therefore which are derived from

the aromatic constituents of the bark (at least as indicated by GC of TMS ethers). Except for the methanol found in the distillate (see below), in general we conclude that under our conditions of pyrolysis, the aromatic constituents of bark (i.e. polyphenols and lignin) are predominantly converted to char and contribute little to the formation of volatile products.

The earlier studies of Fang and McGinnis[16] on pyrolysis of isolated polyphenols from bark confirm that temperatures higher than 350° (e.g. 500°C) are required for generation of volatile phenols from these components. In their work the polyphenols were isolated by alkaline extraction of the bark and then pyrolyzed. The authors note that their polyphenol products contain carbohydrates, the content of the latter in the polyphenol extracted under nitrogen was stated as 12% by an unspecified method. It should be noted however that there are major uncertainties in the analysis of carbohydrates by acidic colorimetric methods in the presence of proanthocyanidins (probably the major components of the polyphenols).[33] In fact, the elemental analysis of the isolated polyphenol was intermediate between that of a hexosan and that of a polymeric procyanidin and it is possible that the carbohydrate content was much higher than that reported. The major carbohydrate components of the alkali extracted polyphenols would be hemicelluloses and callose. It is probable that these polysaccharides would yield several polyhydroxybenzenes on pyrolysis (cf.[20]), but likely that this would be a relatively minor source of the phenols obtained by Fang and McGinnis; their yield of catechol especially (up to 2.5% from polyphenol) was by far the highest of the phenols in the tar and there is no doubt that catechol is a major product of polyphenol pyrolysis while only a relatively minor product of polysaccharide pyrolysis.[20]

Components of Pyrolysis Distillates

In a previous study of cellulose pyrolysis[25] the addition of sodium chloride before pyrolysis was found to favor the production

TABLE 7

Products from Distillates of Inner Barks, Vacuum Pyrolysis, 350°/30 min.

	Yield (% of dry bark)*					
Bark	Distillate Yield	Acetic acid	Hydroxyacetone	Glycolaldehyde	Formic acid	Methanol
Untreated	24	1.4(5.9)	1.3(5.4)	4.3(17.8)	0.9(3.8)	0.1 (0.7)
Water-washed	26	1.0(3.8)	0.4(1.6)	2.3(9.1)	0.2(0.6)	0.3 (1.0)
Acid-washed	22	0.2(0.9)	- (-)	0.4(1.7)	- (-)	0.02(0.1)

*Values in parenthesis represent % content in distillate.

of several low molecular weight products which collect not in the tar, but in the distillate. This type of effect has been investigated in the bark samples and is shown in Table 7, where the identifications and analyses are by proton magnetic resonance.[25] All of the products shown, except methanol, were found in pyrolysis of cellulose containing sodium chloride and their formation is favored by presence of salts at the expense of levoglucosan. When the non-ion-exchanged salts are removed by water-washing, the yield of these products is reduced and levoglucosan is increased (Table 4) and both effects are further influenced by removal of most of the ion-exchanged metal ions by acid-washing. The acetic acid is only partly derived from pyrolysis of polysaccharides such as cellulose and mostly originates from pyrolysis of acetyl groups in hemicelluloses, while the methanol is derived from pyrolysis of lignin. Both of these effects have recently been investigated for pyrolysis of wood.[31] The other products shown in Table 7 can be obtained by pyrolysis of cellulose containing sodium chloride and are presumably derived therefore from cellulose and other glycans in the bark.

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