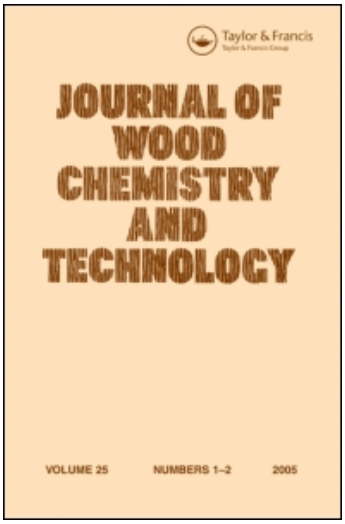

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Iiyama, Kenji and Wallis, Adrian F. A.(1990) 'Dissolution of Wood with Acetyl Bromide Solutions-Reactions of Lignin Model Compounds', Journal of Wood Chemistry and Technology, 10: 1, 39 — 58
To link to this Article: DOI: 10.1080/02773819008050226
URL: http://dx.doi.org/10.1080/02773819008050226

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 10(1), 39-58 (1990)

DISSOLUTION OF WOOD WITH ACETYL BROMIDE SOLUTIONS - REACTIONS OF LIGNIN MODEL COMPOUNDS

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ABSTRACT

A *Pinus radiata* refiner mechanical pulp (RMP) sample and a range of lignin model compounds were treated with a solution of 25% w/w acetyl bromide (AcBr) in acetic acid to assess the reactions which take place during the dissolution of wood with the AcBr solution. The lignin model reactions were also carried out in solutions to which 4% w/w perchloric acid was added. The RMP sample gave a product which contained 9.2% bromine, and was severely degraded to low molecular weight products, the polysaccharides more so than the lignin fraction. The reactions of the lignin model compounds with AcBr included O-acetylation of phenolic and aliphatic hydroxyl groups, cleavage of β-ether bonds, C-acetylation of aromatic rings, particularly in positions *para* to methoxyl groups, demethylation of aromatic methoxyl groups and probable replacement of benzyl alcohol groups by bromine functions. The reactions were accelerated by perchloric acid, and the rates appeared to decrease in the order O-acetylation ≈ bromine substitution >> β-ether cleavage ≈ C-acetylation > demethylation. It is concluded that dissolution of wood in the AcBr solution is a consequence of depolymerisation of the polysaccharides and lignin, and acetylation to give products which would be soluble in the reaction medium.

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INTRODUCTION

Karrer and Widmer observed in 1921 that both softwood and hardwood meals dissolved in acetyl bromide (AcBr) at ambient temperatures.[1] Dissolution took place in a few hours, although if moisture was rigorously excluded from the woodmeals, or if glacial acetic acid was added to the digestion medium,[2] the reaction was considerably slower. Both cotton cellulose[1] and Willstätter lignin[2] dissolved on treatment with AcBr at ambient temperatures.

Johnson *et al.*[3] used the AcBr reaction to determine the lignin content of wood samples. The woodmeals were digested with a solution of 25% AcBr in acetic acid at 70°C, and the ultraviolet (UV) absorbances at 280 nm of the digests were proportional to the lignin contents. We have recently proposed an improved method for the AcBr lignin determination, wherein perchloric acid ($HClO_4$) was added to the digestion medium,[4] and we have applied this procedure to the analysis of lignin in polyphenol-containing *Eucalyptus* woods[5] and in grasses.[6] We have also shown that the change in UV absorbance at 280 nm of lignin model compounds after AcBr treatment is dependent on the type of aromatic nucleus.[7]

The dissolution of wood with AcBr is catalysed by acids; small amounts of water generate hydrogen bromide on reaction with AcBr which accelerates the digestion,[2] and we have observed a similar accelerating effect with perchloric acid.[4] The AcBr treatment effects the depolymerisation of the wood polysaccharides, and "acetobromoglucose" was found as a product of the reaction of AcBr with cellulose.[1] Treatment of monosaccharides with AcBr or hydrogen bromide in acetic acid is known to give bromo-compounds by displacement of the anomeric hydroxyl group by a bromide ion.[8] In addition, the AcBr reaction causes acetylation of other aliphatic hydroxyl groups.

Although the reactions of AcBr with cellulose are generally understood, little is known about the reaction of AcBr with lignins. Karrer and Bodding-Wiger[2] found that AcBr-treated Willstätter lignin contained acetyl and bromide functions. On the basis of the methoxyl content of the AcBr-treated lignin (7-8%), Brauns later inferred that methoxyl groups in the lignin had been cleaved.[9] In spite of the dearth of information on the lignin reactions, clues to the reactions which may occur can be obtained by reviewing the known reactions of AcBr with compounds which have stuctures similar to those which occur in lignin.

Acetyl bromide is known to acetylate aliphatic hydroxyl groups and to replace certain hydroxyl functions with bromine. Although products from acetylation alone and from dehydration are common, the reagent is little used for preparative purposes.[8] However, it has been used with trifluoroacetic acid to good effect for selective acetylation of the phenolic hydroxyl groups of the alkaloid apomorphine.[10] Reaction of a series of methylolphenols with AcBr at 0°C has given products in which the phenolic hydroxyl groups were acetylated and the benzylic hydroxyls were substituted by bromine.[11] Mathur *et al.*[12] found that sodium perchlorate-catalysed reaction of acetyl chloride with various phenolic ethers gave products in which acetyl groups were introduced onto the aromatic ring in the position *para* to the phenolic ether function. Later, Corriu and Dabosi[13] showed that a similar reaction, catalysed by $HClO_4$, took place between AcBr and anisole. Anisole also reacts with hydrogen bromide to give the ether-cleaved product, phenol.[14] Hydrogen bromide is liberated when AcBr reacts with groups containing active hydrogens, and would thus be liberated in small amounts from the digestion of wood with the AcBr solution.

Thus O- and C-acetylation and C-α bromination reactions and possibly ether cleavage reactions would be expected to take place

when lignin is treated with AcBr. In order to assess the importance of these reactions, a refiner mechanical pulp (RMP) and various lignin model compounds were treated with the AcBr reagent both with and without the addition of a perchloric acid catalyst.

RESULTS AND DISCUSSION

Reaction of *Pinus radiata* RMP with AcBr

For the AcBr reactions, the same conditions as those that prevail during the lignin determinations were used, *viz.* reaction with 25% (w/w) solutions of AcBr in acetic acid at 70°C for 30 min (as is used in the "conventional" method[3]). In the "modified" method,[4] the digesting medium also contained 4% w/w $HClO_4$. A *P. radiata* RMP sample treated with AcBr without the $HClO_4$ catalyst gave a product which had a bromine content of 9.2%. The presence of bromine in the product would result from reaction of both the polysaccharide and lignin components of the pulp with AcBr.[1,2]

The high performance size exclusion chromatography (HPSEC) elution traces of the AcBr-treated RMP with both UV and refractive index (RI) detection are shown in Figure 1. The RI-detected trace measures the entire sample, both lignin and carbohydrates, and the contribution of lignin to the chromatogram was estimated from the UV-detected trace, after correcting for the relative sensitivities of the detectors to an acetylated *P. radiata* milled wood lignin sample. The contribution of the carbohydrate to the RI trace was obtained by difference. From Figure 1, it is clear that the polysaccharide-derived fraction of the AcBr-treated RMP was more severely degraded than the lignin fraction. The chromatogram of the carbohydrate fraction showed partial resolution of peaks in the lower molecular weight (MW) region, which were indicative of cellulose oligomers. The column system appeared to separate

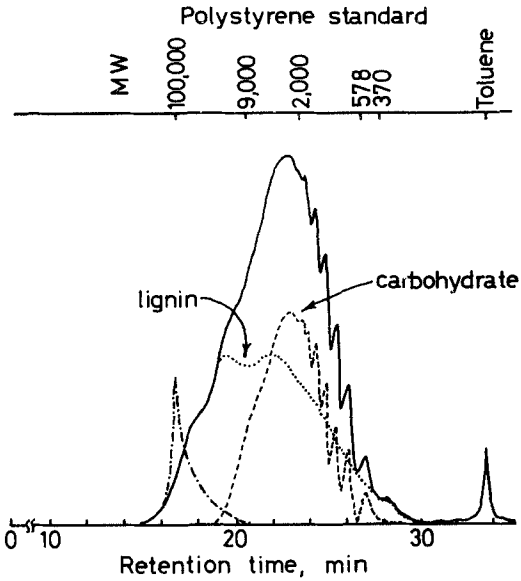
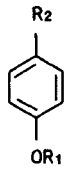


FIGURE 1. HPSEC traces for the reaction product of *P. radiata* RMP with AcBr. ——: RI detection (curve A); ·····: UV detection (curve B); - - - - -: difference (curve A - curve B); —·—·: low viscosity cellulose acetate (RI detection). Columns: 3 x Shodex KF-series with crosslinked polystyrenes. Eluant: THF, 1 mL/min.

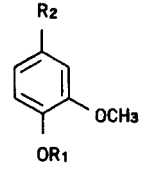
oligomers with a degree of polymerisation (DP) up to 8, and the peak of the curve occurred at DP≈10, corresponding to a polystyrene MW of *ca.* 3,000. The chromatogram of a low DP commercial cellulose acetate sample (Figure 1) showed that a large fraction was excluded from the columns (exclusion limit 7×10^4 daltons for polystyrene), and it had a higher MW than the AcBr-treated wood sample. Thus the polysaccharide fraction of the RMP sample was severely depolymerised, and the low DP acetylated fragments are soluble in the digesting medium.

Reaction of monomeric lignin model compounds with AcBr

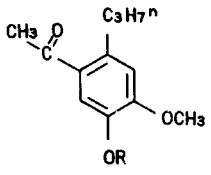
Reactants and products of the AcBr treatments were generally



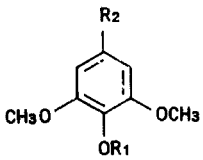
	R_1	R_2
1a	H	CH_3
b	$COCH_3$	CH_3
c	CH_3	H
d	$COCH_3$	H
e	CH_3	$COCH_3$
f	CH_3	CH_3



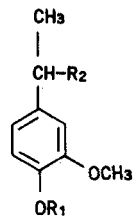
	R_1	R_2
2a	H	$C_3H_7^n$
b	$COCH_3$	$C_3H_7^n$
c	CH_3	H
d	H	H
e	$COCH_3$	H
f	H	$COCH_3$
g	CH_3	$COCH_3$
h	CH_3	$C_3H_7^n$



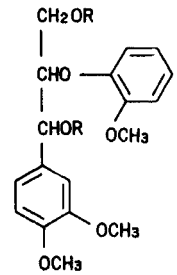
3a R = H
b R = $COCH_3$
c R = CH_3



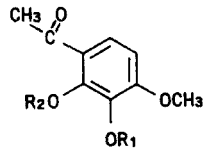
	R_1	R_2
4a	H	H
b	$COCH_3$	H
c	H	$COCH_3$
d	$COCH_3$	$COCH_3$
e	CH_3	H
f	CH_3	$COCH_3$



	R_1	R_2
6a	H	OH
b	$COCH_3$	$OCOCH_3$
c	$COCH_3$	Br
d	CH_3	OH
e	CH_3	$OCOCH_3$
f	CH_3	Br



7a R = H
b R = $COCH_3$



	R_1	R_2
5a	$COCH_3$	CH_3
b	H	H
c	$COCH_3$	$COCH_3$
d	CH_3	CH_3

obtained by known methods. The 5-acetylguaiacol derivative **3a**, a reaction product of AcBr treatment of the phenol **2a**, was prepared by the Fries reaction of the guaiacol acetate **2b**. The structure of **3a** was supported by its PMR spectrum; the C-3 and C-6 protons were singlets at 6.70 δ and 7.30 δ respectively, and the benzylic protons of **3a** (2.85 δ) were deshielded by the adjacent acetyl group compared to those of **2a** (2.57 δ). An analogous Fries reaction of creosol acetate has been reported by Munavalli.[15]

Various phenols and phenol ethers which contain the essential structural features of lignin were reacted with the AcBr and AcBr-$HClO_4$ solutions, and the reaction products were analysed by high performance liquid chromatography (HPLC) (Table 1). *p*-Cresol (**1a**) gave the O-acetyl compound **1b** as the only identified product from both $HClO_4$-catalysed and non-catalysed reactions, and small amounts of the phenol remained. For anisole (**1c**), the products from reaction with AcBr were 4-acetylanisole (**1e**) and smaller amounts of phenyl acetate (**1d**), formed by C-acetylation and demethylation, respectively. The yields of **1e** and **1d** were higher, and the amount of anisole was lower, for the $HClO_4$-catalysed reaction. Corriu and Dabosi[13] have already reported that a C-acetylated product is obtained from reaction of anisole with AcBr. Reaction of 4-methylanisole (**1f**) with AcBr gave the demethylated products *p*-cresol and its acetate (**1a** and **1b**). Four additional minor peaks present in the chromatograms of the reaction products could not be identified. Although C-acetylation is favoured at the *para* position to the methoxyl group, in this case some C-acetylation could occur in the *ortho* positions. Mathur *et al.*[12] found that *ortho* C-acetylation occurred on reaction of **1f** with a sodium perchlorate-acetyl chloride mixture.

4-*n*-Propylguaiacol (**2a**) gave the O-acetate **2b** as the major product of reaction with AcBr (Table 1). Small amounts of starting material and 5-acetyl products **3a** and **3b** were also formed, more from the $HClO_4$-catalysed reaction. The etherified phenol veratrole

TABLE 1

Reaction Products from Treatment of Lignin Model Compounds with 25% AcBr and AcBr–$HClO_4$ in Acetic Acid at 70°C for 30 min.

Compound	Reagent[a]	Products (% yield)			
		Starting material	O-acetylated	C-acetylated	ether cleaved
1a	A	(1.2)	1b(62)		
1a	B	(4.0)	1b(58)		
1c	A	(94)		1e(2.3)	1d(tr[b])
1c	B	(63)		1e(36)	1d(4.6)
1f	A	(96)			1a(tr) 1b(tr)
1f	B	(71)			1a(tr) 1b(22)
2a	A	(1.5)	2b(96)	3b(0.6)	
2a	B	(3.2)	2b(77)	3b(7.5) 3a(tr)	
2c	A	(91)		2g(7.7)	2e(3.7) 2f(tr)
2c	B	(17)		2g(69)	2e(14) 2f(1.4) 2d(tr)
2h	A	(73)		3c(5.2)	2b(11) 3b(tr) 3a(tr)
2h	B	(2.7)		3c(20)	2b(27) 3b(8.3) 3a(2.8)
4a	A	(1.6)	4b(78)		
4a	B	(2.3)	4b(44)	4c(tr)	
4e	A	(56)		5d(12)	4a(tr) 4b(3.6) 4c(tr)
4e	B	(6.4)		5d(88)	4a(2.3) 4b(5.3) 4c(tr)
6a	A	--	6b(29)		
6a	B	--	6b(19)		
6d	A	(9.4)	6e(12)		
6d	B	(3.2)	6e(1.5)		
7a	A	--	7b(10)		2e(17)
7a	B	--	7b(3.6)		2e(8.5)

[a]A: 25% w/w AcBr in acetic acid, B: 25% w/w AcBr in acetic acid containing 4% $HClO_4$ [b]tr ≡ trace

(**2c**) was largely unreactive to AcBr, but in the presence of $HClO_4$ it gave the C-acetylated compound acetoveratrone (**2g**) as the major product, and demethylated compounds guaiacol acetate (**2e**), guaiacol (**2d**) and acetoguaiacone (**2f**). A similar suite of products was obtained from reaction of 4-*n*-propylveratrole (**2h**) with AcBr, although there was less C-acetylation, more demethylation, and less remaining starting material than from reaction of the unsubstituted compound, veratrole. Thus the 5-acetylveratrole **3c** was the C-acetylated product, and products of demethylation included the acetates **2b** and **3b**, and the phenol **3a**. A further peak in the HPLC trace may be due to a product analogous to **2b**, formed by demethylation of the other methoxyl group.

Syringol (**4a**) was converted to its O-acetate (**4b**) on reaction with AcBr (Table 1). There was a large peak in the HPLC traces, particularly that from the $HClO_4$-catalysed reaction, which was not attributable to acetosyringone (**4c**), nor its acetate **4d**. Mauthner[16] found that the acetophenone **5b** was a product of the Fries reaction of syringol acetate (**4b**), but neither **5b** nor its diacetate **5c** corresponded to the large HPLC peak. The peak is most likely to be due to the C-acetylated compound **5a**. A trace amount of acetosyringone was noted as a product of the $HClO_4$-catalysed reaction. Pyrogallol trimethyl ether (**4e**) was converted to the C-acetylated product **5d** as the major product of reaction with AcBr, although there was no trace of the isomeric acetophenone **4f** in the reaction mixture. Mathur *et al.*[12] identified **5d** as the product of reaction of **4e** with sodium perchlorate-acetyl chloride. Demethylation reactions of **4e** also took place during AcBr treatment, and syringol (**4a**), its acetate **4b**, and acetosyringone (**4c**) were identified as reaction products.

The compounds with benzylic hydroxyl functions, apocynol (**6a**) and its methyl ether **6d**, on treatment with AcBr gave their respective acetates (**6b** and **6e**) as products (Table 1). There were several additional peaks which were not identified, although the

α-bromo compounds **6c** and **6f** were expected products. Zawadowski[11] has shown that benzylic hydroxyl groups are rapidly replaced by bromo functions during reaction with AcBr. Other workers[17] have shown that benzyl acetates are converted to benzyl bromides by hydrogen bromide in acetic acid. Hydrogen bromide is formed from acetyl bromide during acetylation reactions, and it is likely to be the active reagent for the generation of α-bromo compounds.

Thus the reactions which take place between monomeric lignin models and AcBr are O-acetylation of phenolic and aliphatic hydroxyl groups, C-acetylation of aromatic rings, probable bromine substitution of benzylic hydroxyl groups and demethylation of aromatic methoxyl groups. The relative importance of these reactions is dependent on the nature of the substituents. This is particularly so for the reactions involving electrophilic substitution of acetyl groups onto the aromatic ring and cleavage of methoxyl groups, which are sensitive to electron densities at the reaction sites.

Reaction of the dimeric lignin model veratrylglycerol-β-guaiacol ether with AcBr

The HPLC traces obtained after treating *erythro*-veratrylglycerol-β-guaiacol ether (**7a**) at 70°C for 30 min with AcBr, AcBr-water and AcBr-$HClO_4$ are given in Figure 2. In all cases, no starting material remained, and the diacetate **7b**, guaiacol (**2d**) and guaiacol acetate (**2e**) were among the products. The AcBr reaction with no additives gave more diacetate **7b** than the reactions in which water and $HClO_4$ were added, and there was a large peak (A) in the chromatogram of the uncatalysed AcBr reaction mixture which was not present in the other chromatograms. The $HClO_4$-catalysed reaction gave more guaiacol acetate than the reaction in which water was present, whereas in the latter reaction there were more C-acetylated products (UV examination).

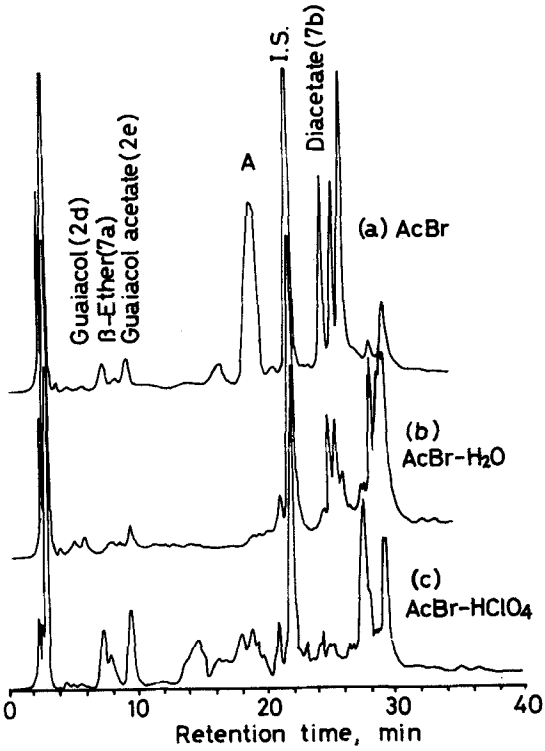


FIGURE 2. HPLC traces of products from reaction of β-ether **7a** at 70°C for 30 min with 25% AcBr in acetic acid. (a) no additive, (b) 4% water added, (c) 4% $HClO_4$ added. Column: Waters C-18 Radial-PAK. Solvent: methanol:water, gradient elution at 1 mL/min.

Water reacts vigorously with AcBr to give hydrogen bromide and acetic acid, and the hydrogen bromide is probably the reactive species which catalyses the further reactions of **7b** and the compounds represented in peak "A". Guaiacol and guaiacol acetate are examples of products formed in further reactions; in this case by β-ether cleavage.

The chromatogram of the product mixture after reaction of the β-ether **7a** with AcBr-$HClO_4$ at 20°C for 1 min are given in Figure 3

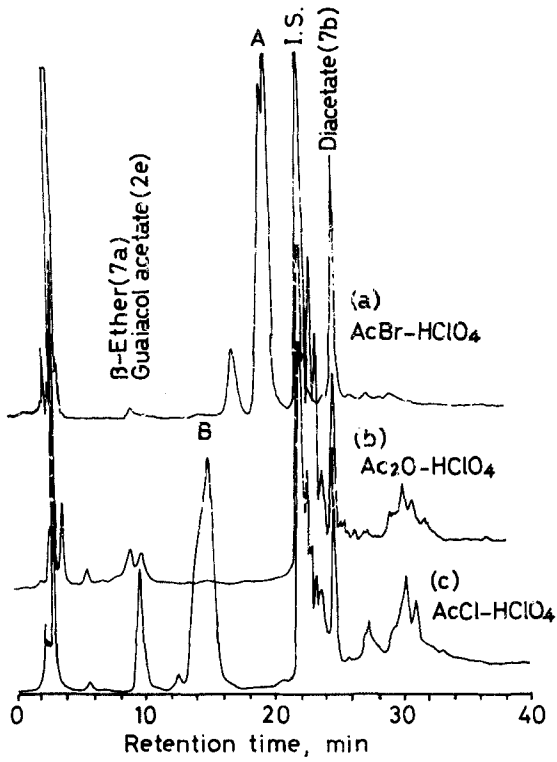


FIGURE 3. HPLC traces of reaction mixtures of β-ether **7a** with (a) 25% AcBr in acetic acid containing 4% $HClO_4$ at 20°C for 1 min, (b) acetic anhydride containing 3.3% $HClO_4$ at 20°C for 1 min, (c) 50% acetyl chloride in acetic acid containing 4% $HClO_4$ at 70°C for 30 min. Column: Waters C-18 Radial-PAK. Solvent: methanol: water, gradient elution at 1 mL/min.

[trace (a)]. Even under these conditions, the starting material was consumed and there were two large peaks corresponding to "A" (see Figure 2), and a peak assigned to the diacetate **7b**. The amounts of the diacetate **7b** and guaiacol acetate (**2e**) formed from both uncatalysed and $HClO_4$-catalysed reactions at 70°C for periods up to 40 min are shown in Figure 4. For both reactions series, there was a reduction of the diacetate **7b** and an increase of guaiacol acetate with time, and the rates were faster for the

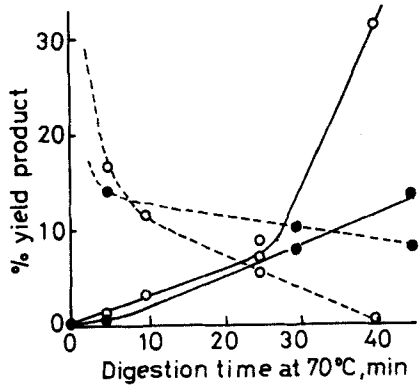


FIGURE 4. Yield of guaiacol acetate (**2e**) (——) and diacetate **7b** (– – –) after treatment of β-ether **7a** with 25% AcBr in acetic acid, both with (—○—) and without (—●—) 4% $HClO_4$, at 70°C for varying periods of time.

$HClO_4$-catalysed reactions than for the non-catalysed reactions. There was also a gradual reduction in the peaks corresponding to "A" in the catalysed reaction, and after 30 min at 70°C, they were only minor components of the chromatogram (Figure 2). When the diacetate **7b** was substituted for compound **7a** as the starting material in the AcBr reactions, identical chromatograms were obtained.

The β-ether **7a** was reacted with acetic anhydride-$HClO_4$ at 20°C for 1 min, and with acetyl chloride-$HClO_4$ at 70°C for 30 min, and the chromatograms of the reaction mixtures are depicted in Figure 3. As before, the starting material was entirely consumed, and the diacetate **7b** was among the products. However, there was no peak corresponding to "A", although the acetyl chloride reaction had a similar peak (B) with a lower retention time which was absent in the chromatograms of the AcBr and acetic anhydride reactions. The double peak "A" is probably due to the *threo* and *erythro* forms of a bromo compound formed by replacement of the benzylic hydroxyl function with bromine, and the peak "B"

(Figure 3) is probably due to corresponding chloro compounds. The diacetate **7b** and the compounds due to peak "B" are evidently more stable in the acetyl chloride-$HClO_4$ medium than the analogous compounds in the AcBr-$HClO_4$ reaction. The diacetate **7b** and bromo compounds undergo further reactions in the AcBr media such as those leading to β-ether cleavage and formation of guaiacol acetate as well as C-acetylation and demethylation reactions described in the previous section.

Thus reaction of a lignin model β-ether compound with AcBr reveals that O-acetylation and probably bromine subsitution are fast reactions, but that the initially-formed compounds are further transformed to other products. The cleavage of the β-ether linkage indicates that the AcBr reaction causes a reduction in molecular weight of the lignin, which would aid the dissolution of wood.

Concluding remarks

The results described in the previous sections indicate that the reasons for the solubilising action of AcBr on lignocellulosic materials is that the AcBr depolymerises the lignocellulose components, particularly the polysaccharides, and acetylates the hydroxyl functions. Both of these processes would render the lignocellulosic fragments soluble in the AcBr-acetic acid medium.

It has been known since the early work of Karrer *et al.*[1,2] and recently reinforced by van Zyl[18] that if moisture was rigorously excluded from the digesting medium, the dissolution is considerably slower. The effect of small amounts of water would be to release hydrogen bromide which would act as a catalyst for the reaction. We have found that $HClO_4$ also catalyses the dissolution reaction.[4] Corriu and Dabosi[13] have suggested that in the AcBr-$HClO_4$ system, hydrogen bromide is formed, and protonated acetyl perchlorate is the active acetylating agent. $HClO_4$ has long

been recognized as a superior acylation catalyst.[19] Acetyl chloride catalysed by $HClO_4$ is not as reactive to the β-ether **7a** as AcBr, which probably reflects the different reactivities of hydrogen chloride compared with hydrogen bromide.

The reaction of AcBr with lignin models is characterised by fast acetylation of phenolic and aliphatic hydroxyl groups, and probable rapid introduction of bromine at the benzylic carbon atom. Slower reactions include cleavage of β-ether linkages, C-acetylation of the aromatic ring, especially in positions *para* to methoxyl groups, and demethylation reactions. The reactions are catalysed by $HClO_4$, and are generally analogous to known reactions of phenols and phenol ethers with AcBr and hydrogen bromide. The rates of reactions of AcBr with lignin appeared to decrease in the order O-acetylation ≈ bromine substitution >> β-ether cleavage ≈ C-acetylation > demethylation, and bromine substitution is a probable fast reaction.

EXPERIMENTAL

Chemicals

The lignin model compounds **1a**, **1c**, **1d**, **2c**, **2d**, **2f**, **4a**, **4c** and **4e** were obtained from commercial sources.

Compounds **1b**, **2b**, **3b**, **2e**, **4b**, **4d**, **5c** and *erythro*-**7b** were obtained from the acetylation of **1a**, **2a**, **3a**, **2d**, **4a**, **4c**, **5b** and *erythro*-**7a** respectively.

The model compounds **1e**, **1f**, **2g**, **2h**, **3c**, **4f**, **5d** and **6d** were prepared by methylation of 4-hydroxyacetophenone, **1a**, **2f**, **2a**, **3a**, **4c**, **5b** and **6a**, respectively.

4-*n*-Propylguaiacol (**2a**) was the product of catalytic hydrogenation of eugenol.

The acetophenone (**5b**) was obtained from the reaction of the boron trifluoride–acetic acid complex on 1-methylpyrogallol.[20]

Apocynol (**6a**) was prepared by sodium borohydride reduction of acetoguaiacone (**2f**).

erythro-Veratrylglycerol-β-guaiacol ether (**7a**) was prepared by established methods.[21,22]

The *P. radiata* milled wood lignin sample was prepared by the method of Bland and Menshun,[23] and it was acetylated with acetic anhydride–pyridine at ambient temperature.

The low DP cellulose acetate sample was an Eastman-Kodak product, with an acetyl content of 39.8±0.5%, and an ASTM viscosity of 3±1 sec.

2-*n*-Propyl-4-methoxy-5-hydroxyacetophenone (**3a**)

A solution of 4-*n*-propylguaiacyl acetate (**2b**) (5.0 g) in nitrobenzene (10 mL) was added slowly to a stirred solution of anhydrous aluminium chloride (6.4 g) in nitrobenzene (20 mL) in a 100 mL Erlenmeyer flask. After stirring for a further 18 h at 20°C, water (20 mL) was carefully added, followed by 10M hydrochloric acid (2 mL). The nitrobenzene was removed by steam distillation, and the reaction products, isolated by extraction with ether, were treated with 0.1M sodium hydroxide in methanol (50 mL) at 20°C for 4 h. The methanol was removed by rotary evaporation, and the residue was acidified and the products, isolated again with ether, were adsorbed on a column of silica gel. Elution with light petroleum–ether (95:5) gave 4-*n*-propylguaiacol (**2a**) (350 mg), followed by compound **3a** (890 mg). The acetophenone (**3a**) crystallized from light petroleum as *plates*, m.p. 85–6°C. Found: C, 69.4; H, 7.7; $C_{12}H_{16}O_3$ requires C, 69.2;

H, 7.7%. PMR δ ($CDCl_3$) 0.95 (t, 3, CH_2CH_3), 1.2-1.9 (m, 2, CH_2CH_3), 2.51 (s, 3, $COCH_3$), 2.7-3.0 (m, 2, $ArCH_2$), 3.92 (s, 3, OCH_3), 5.74 (s, 1, OH), 6.70 (s, 1, H-3) and 7.30 (s, 1, H-6).

Treatment of *P. radiata* RMP with the AcBr solution

Oven-dried *P. radiata* RMP (1.0 g) was stirred with 25% (w/w) AcBr in acetic acid (200 mL) at 70°C for 30 min. After cooling, the mixture was added to a stirred solution of water (1 L), and solid sodium carbonate was added to the solution until the pH was 5.5. The solution was concentrated to *ca.* 100 mL on a rotary evaporator at 40°C, and dioxane (100 mL) was added. The inorganic salts which precipitated were removed by filtration, and the concentration-precipitation cycle was repeated until no further inorganic salts precipitated from the solution. The concentrated dioxane solution was added dropwise into a ten-fold excess of ether, and after washing successively with ether and 40-70 light petroleum, and drying *in vacuo*, a light-brown powder (1.1 g) was obtained. The bromine content of the powder was 9.2%.

Treatment of lignin models with AcBr

The lignin model compound (50 mg) was placed in a 15 mL glass reaction bottle with a solution of 25% (w/w) AcBr in acetic acid (2.5 mL). In some cases, 70% perchloric acid (0.1 mL) was also included in the reaction mixture. The bottle was sealed with a PTFE-coated silicone cap, placed in an oven at 70±0.2°C for 30 min, and was shaken at 10 min intervals. After digestion, the solution was transferred to a 50 mL volumetric flask containing 2M sodium hydroxide (10 mL) and acetic acid (12 mL). The bottle was rinsed, and the solution made up to 50 mL, with acetic acid. A solution of an appropriate internal standard in methanol was added to an aliquot of the reaction product solution, and the mixture was analysed by HPLC. The internal standard used for reactions of the β-ether **7a** was 4-*n*-propylguaiacol (**2a**).

Catalysed reactions of *erythro*-veratrylglycerol-ß-guaiacol ether (7a) with AcBr, acetyl chloride and acetic anhydride

A reaction of the ß-ether was carried out as above, except that water (0.1 mL) was added instead of the 70% $HClO_4$.

For the acetyl chloride reaction, the procedure was as above, except that a 50% (w/w) solution of acetyl chloride in acetic acid was used instead of the 25% AcBr solution.

The acetic anhydride reaction utilised the ß-ether (50 mg), acetic anhydride (3.0 mL) and 70% $HClO_4$ (0.1 mL). After 1 min at 20°C, the reaction mixture was treated as above.

HPLC and HPSEC analyses

HPLC and HPSEC was carried out on a system comprising a Waters WISP 710B autosampler and Model 481 variable wavelength detector, a Spectra-Physics SP8700 solvent delivery system and SP4100 computing integrator, and an Erma ERC7510 refractive index detector.

The columns used for HPLC were a Spherisorb S5 ODS1 (250 mm x 4.5 mm) and two Waters Radial-PAK cartridges (100 mm x 8 mm), one containing 10µ C-18 packing, and the other RESOLVE 5µ C-18 packing. The HPLC conditions were as follows: injection vol., 30 µL; solvent, methanol:water 80:20-50:50 delivered at 1.0 mL/min; detection, UV at 280 nm (other wavelengths were also used for identification of products). A gradient elution was used for some product mixtures. The reaction products were examined on more than one column.

For HPSEC, the column set contained crosslinked polystyrene packings and was a series of Shodex columns KF-803, -802.5, and

-802, and a KF-800P guard column. Stabilised HPLC-grade THF was delivered to the columns at a rate of 1.0 mL/min. Solutions (0.1%) of the samples in THF containing 0.05% toluene as a reference were used. Detection was by UV at 280 nm, and by refractive index. The relative sensitivities of the UV and RI detectors to an acetylated lignin sample were assessed, and the appropriate detector settings were used to generate the curves A and B in Figure 1. The carbohydrate curve was obtained by manual subtraction of curve B from curve A.

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