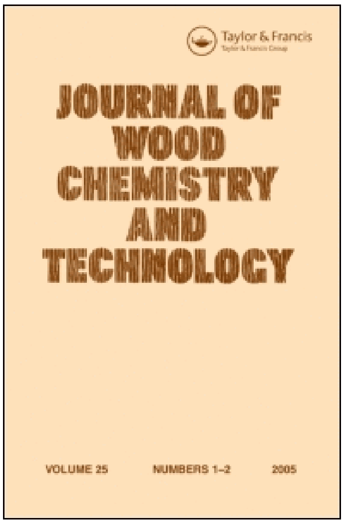

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CONTRIBUTION OF LIGNIN SUB-STRUCTURES TO NITROBENZENE OXIDATION PRODUCTS

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ABSTRACT

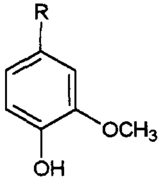
Nitrobenzene oxidation of a series of lignin model compounds with varying aromatic nuclei and sidechain structures, including diphenylmethane compounds, gave benzaldehydes and benzoic acids in a range of yields. The yields were dependent on the structure of the aromatic nucleus, and were in the order syringyl > guaiacyl > 4-hydroxyphenyl. The yields were also dependent on the benzylic group, in the order C=O > CHOH > CH_2. Veratryl compounds afforded low yields of oxidation products. Lignin model 1-1'-, 1,5'- and 5,5'-diphenylmethanes gave rise to moderate yields of nitrobenzene oxidation products. However, 1,6'-diphenylmethanes gave only low yields of oxidation products, and no oxidation products were obtained from a non-phenolic 1,1'-diphenylmethane. This suggests that the assumption in the nucleus exchange-nitrobenzene oxidation method for determining lignin structures, that diphenylmethanes do not give rise to oxidation products, should be reappraised. It is proposed that a key influence on the yield of nitrobenzene oxidation products is the ability of the aromatic ring to supply electrons to the benzylic carbon atoms. Alternatively, condensations at the *ortho* positions of the guaiacyl and 4-hydroxyphenyl compounds could affect the yield of oxidation products.

INTRODUCTION

Degradation of lignin by oxidation with nitrobenzene in alkaline solutions at elevated temperatures is a useful technique for investigating lignin structure.[1] Softwood lignins give vanillin (**1a**) with smaller amounts of vanillic acid (**1b**) as the main oxidation products, whereas hardwood lignins yield, in addition, syringaldehyde (**2a**) and syringic acid (**2b**). Besides these four products, grass lignins give rise to 4-hydroxybenzaldehyde (**3a**) and the corresponding acid **3b**. Nitrobenzene oxidation thus gives an indication of the types of lignin under investigation, and the yields of the oxidation products provide information on the structure of the lignin. For example, as most lignin aromatic units which are linked by bonds stable to alkaline hydrolysis (condensed structures) do not give monomeric aldehyde products, lignins with a higher content of these structures afford lower yields of oxidation products. The yield of products is also dependent on the structure of the lignin sidechain.[2]

Nitrobenzene oxidation of lignin was considered by Chang and Allan to involve two-electron transfer and to proceed *via* quinonemethide intermediates.[2] However, in later studies Schultz *et al.* concluded that the oxidation was a free radical process (involving one electron transfer), and they proposed that homolysis of the O-H bond of the benzylic hydroxyl group was a central feature of the mechanism.[3-5] This proposal was partly predicated on their observation that model compounds containing α-carbonyl groups did not give nitrobenzene oxidation products at temperatures lower than those normally used (*ca* 170°C) for the oxidation.[3] However, other studies showed that at 170°C the α-carbonyl compounds did give rise to oxidation products,[6,7] which led Iiyama and Lam[7] to suggest that at higher temperatures the oxidation mechanism was a two-electron (heterolytic) process.

Nitrobenzene oxidation has been used extensively for studying structural changes in lignins during various chemical and heat treatments. A recent application of the technique, in combination with the nucleus exchange reaction, has been to determine the relative proportions of condensed, non-condensed and diphenylmethane structures in modified lignins.[8] This has given information on



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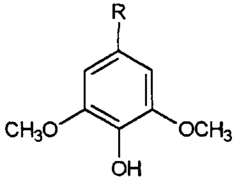

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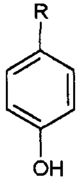

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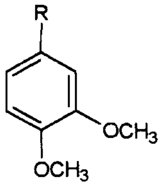
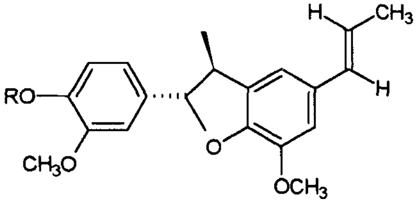


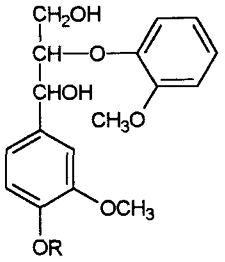
4

a R = CHO **b** R = COOH **c** R = $COCH_3$ **d** R = $CHOHCH_3$

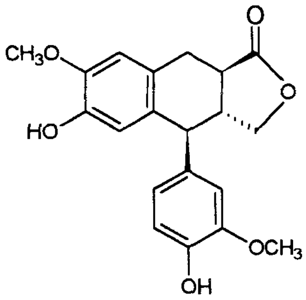
e R = $CH_2CH_2CH_3$ **f** R = H **g** R = CH_3



5 a R = H
b R = CH_3



6 a R = H
b R = CH_3



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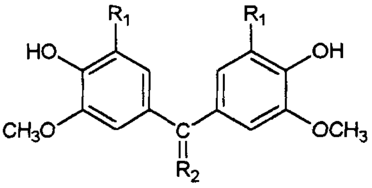

	R_1	R_2
8 a	OCH_3	H_2
b	OCH_3	O
c	OCH_3	H, OH
d	H	H_2
e	H	O

softwood[9-11] and hardwood[11,12] kraft lignins, and softwood lignins after acid[13] and heat[14] treatment of wood. One of the assumptions made in devising the method was that diphenylmethane structures in lignin do not give rise to nitrobenzene oxidation products.[9] Although Leopold and Malmström reported that conidendrin (7), a diphenylmethane lignin model 1,6'-linked* through a methylene group, gave vanillin in only 1% yield after nitrobenzene oxidation,[15] the product of condensation of vanillyl alcohol with resorcinol, a 1,5'-linked diphenylmethane, afforded vanillin in *ca* 30% yield.[16] Furthermore, Kratzl *et al.*[17] found that diguaiacylmethane and dicreosylmethane gave vanillin on nitrobenzene oxidation in 22% and 4% yield, respectively. The present study seeks to further the understanding of the contribution of lignin sub-structures to nitrobenzene oxidation products and the oxidation reaction mechanisms, through oxidation of a range of lignin models with guaiacyl, syringyl and 4-hydroxyphenyl nuclei, including those in which the phenolic hydroxyl groups were methylated, and also diphenylmethane structures.

RESULTS AND DISCUSSION

Nitrobenzene oxidation of lignin models

Several monomeric guaiacyl, syringyl and 4-hydroxyphenyl lignin model compounds with different sidechains were oxidised with alkaline nitrobenzene for 2 h at 170°C, and the products were analysed by gas chromatography-mass spectrometry (GC-MS) (Table 1). Acetoguaiacone (**1c**) and apocynol (**1d**) gave *ca* 65% yields of oxidation products, whereas 4-*n*-propylguaiacol (**1e**) yielded only 21% products and 65% of unreacted starting material remained. The syringyl compounds **2c**-**2e** gave higher yields of oxidation products than the guaiacyl compounds, in particular acetosyringone (**2c**), which afforded products in 93% yield (Table 1). However, although benzyl alcohols were reactive to nitrobenzene oxidation at 135°C, α-carbonyl compounds did not give oxidation products at that temperature.[3] In contrast, the 4-hydroxyphenyl compounds **3c**-**3e** gave lower yields of oxidation products than the guaiacyl compounds. The

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* numbering of carbon atoms follows the convention used for lignin

TABLE 1

Nitrobenzene oxidation of lignin model compounds[a]

Compound	Aldehyde		Acid		% total oxidation products	% starting material
	product	% yield	product	% yield		
1c	**1a**	66.3	**1b**	n.d.[b]	66.3	5.9
1d	**1a**	65.2	**1b**	n.d.	65.2[c]	n.d.
1e	**1a**	17.7	**1b**	3.6	21.3	64.6
2c	**2a**	89.8	**2b**	3.5	93.3	3.4
2d	**2a**	71.7	**2b**	n.d.	71.7	n.d.
2e	**2a**	33.1	**2b**	n.d.	33.1	4.3
3c	**3a**	14.7	**3b**	trace	14.7	15.7
3d	**3a**	4.4	**3b**	n.d.	4.4[d]	n.d.
3e	**3a**	n.d.	**3b**	n.d.	0.0	87.4
4c	**4a**	n.d.	**4b**	8.5	8.5[c]	27.2
	1a	trace	**1b**	n.d.		
4d	**4a**	n.d.	**4b**	1.2	1.2[e]	79.2
4e	**4a**	n.d.	**4b**	1.3	1.3	77.5
5a	**1a**	86.0	**1b**	7.8	93.8	n.d.
5b	**4a**	n.d.	**4b**	n.d.		14.8
6a	**1a**	90.0	**1b**	trace	90.0	n.d.
6b	**1a**	1.6	**1b**	n.d.	12.7	58.3
	4a	8.7	**4b**	2.4		

[a] yields are mol % [b] not detected [c] trace acetoguaiacone

[d] trace 4-hydroxyacetophenone [e] trace acetoveratrone

propensity of the phenols to give nitrobenzene oxidation products follows the order of the ability of the aromatic rings to supply electrons to the benzylic carbon atoms, *viz.* syringyl > guaiacyl > 4-hydroxyphenyl. This is consistent with the studies of Schultz *et al.*, who previously demonstrated that vanillyl alcohol oxidises faster than 4-hydroxybenzyl alcohol,[4] and electron donating groups in the *para* position of 4-hydroxystilbenes enhance their rate of nitrobenzene oxidation.[5]

An alternative explanation for the difference in yields of oxidation products is that condensation reactions may occur in the position *ortho* to the phenolic hydroxyl group when there is no substitution at that position. Possible condensation reactions include reaction of the phenolate with a quinonemethide generated from a *para*-hydroxybenzyl alcohol to form a diarylmethane, or with an aldehyde or ketone to form a diarylcarbinol. These condensation reactions could occur in the 4-hydroxyphenyl and guaiacyl compounds with two and one vacant *ortho* positions respectively, whereas with syringyl compounds, only oxidation would occur. Thus the order of reactivity of the aromatic nuclei towards condensation reactions would be 4-hydroxyphenyl > guaiacyl > syringyl, which is in the reverse order of yields of oxidation products. However, no evidence for the formation of condensation products in the form of higher molecular mass compounds among the reaction products.

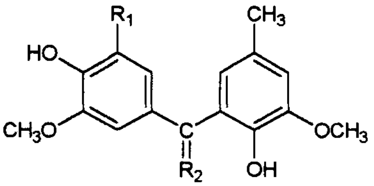
In line with earlier work,[2] sidechains with C-α substituents gave higher yields of oxidation products, in the order C=O > CHOH > CH_2 (Table 1). It is evident that oxidation of compounds already oxygenated at C-α to aldehydes is easier than oxidation of compounds with alkyl sidechains, which will presumably require conversion to oxygenated intermediates prior to generation of aldehydes.

A series of veratryl compounds was subjected to nitrobenzene oxidation to ascertain whether free phenolic hydroxyl groups are a prerequisite for the oxidation. Compounds **4c**-**4e** gave veratric acid (**4b**) in low yields and no veratraldehyde (**4a**) (Table 1), probably due to the disproportionation of veratraldehyde to the acid and veratryl alcohol in a Cannizzaro reaction.[2] A trace amount of vanillin was detected in the product mixture from acetoveratrone (**4c**), evidently arising from demethylation of the C-4 methoxyl group prior to the oxidation. The low yields of reaction products from the veratryl compounds could either be due to their low solubilities in the aqueous alkali, or to the absence of a *para* phenolic hydroxyl group. The formation of nitrobenzene oxidation products from non-phenolic lignin model compounds, albeit in low yield, reaffirms the conclusion of Schultz and Templeton[3] that phenolic hydroxyl groups which are able to participate in the formation of quinonemethides are not prerequisites for oxidation to occur.

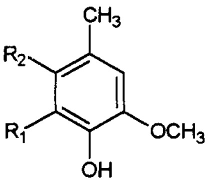
The ß-5' dimeric compound dehydrodiisoeugenol (**5a**) on nitrobenzene oxidation gave a 94% yield of products, whereas its methyl ether (**5b**) did not give rise to oxidation products, and only 14.8% starting material remained. Guaiacylglycerol-ß-guaiacyl ether (**6a**) also gave a high yield of oxidation products (90%), but its methyl ether **6b** afforded oxidation products in only 13% yield. Products from reaction of **6b** include veratraldehyde and veratric acid, as well as vanillin. Lee *et al.*[6] reported vanillin, vanillic acid and trace amounts of veratric acid as products from nitrobenzene oxidation of **6b**, whereas Iiyama and Lam[7] found no products from the same reaction. The failure of these workers to detect veratraldehyde as a reaction product could be because they extracted the alkaline mixture before acidification to remove excess nitrobenzene and its reduction products, a procedure which would also remove the neutral veratraldehyde. Alternatively, the veratraldehyde could be converted to veratric acid in the Cannizzaro reaction.

Nitrobenzene oxidation of diphenylmethane structures

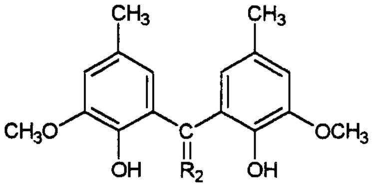
In line with an earlier study,[15] conidendrin (**7**) gave only trace amounts of oxidation products (Table 2). However, the 1,1'-substituted lignin model diphenylmethane, disyringylmethane (**8a**), afforded syringaldehyde in 64% yield. Additional reaction products were disyringylketone (**8b**) (18% yield) and a trace amount of syringol (**2f**), identified by GC-MS comparison with authentic samples. Disyringylcarbinol (**8c**) on nitrobenzene oxidation gave rise to syringaldehyde (45% yield), but disyringylketone (**8b**) and syringol were not detected. This suggests that **8c** could be an intermediate in the formation of syringaldehyde from disyringylmethane, but not in the formation of disyringyl ketone. The latter probably derives from disyringylmethane by direct oxidation. Reaction of disyringylcarbinol under the alkaline conditions of nitrobenzene oxidation, but omitting the nitrobenzene oxidant, gave syringaldehyde (40% yield) and trace amounts of syringol. The conversion is thus not an oxidation, and the α-1 bond of **8c** is cleaved in an alkali-catalysed retrograde type Aldol reaction as shown in Figure 1. A similar mechanism is probably operative in the nitrobenzene oxidation. This suggests that the oxidation mechanism of diphenylcarbinols to aldehydes could be different from that operative for lignin model benzyl alcohols, for which radical cleavage processes have been proposed.[3-5]



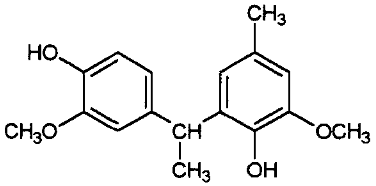
	R_1	R_2
9 a	H	H_2
b	H	O
c	H	H, OH
d	OCH_3	H_2
e	OCH_3	O



	R_1	R_2
10 a	CHO	H
b	H	CHO



11 a R = H_2
b R = O



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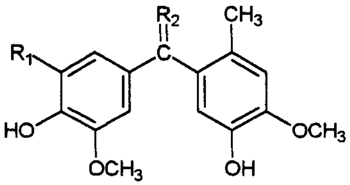
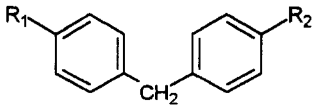


	R_1	R_2
13 a	H	H_2
b	H	O
c	OCH_3	H_2
d	OCH_3	O



	R_1	R_2
14 a	OH	CH_3
b	OCH_3	CH_3
c	OH	OH
d	OH	OCH_3
e	OCH_3	OCH_3

TABLE 2

Nitrobenzene oxidation of diphenylmethane structures related to lignin[a]

Compound	Aldehyde %	Acid %	Oxidation products %	Starting material %	Phenol %	Formyl creosol %	Diphenyl ketone %
7	**1a**, trace	**1b**, trace	trace	-	**1f**, n.d.[b]		
8a	**2a**, 64.0	**2b**, trace	64.0	2.2	**2f**, trace	-	**8b**, 18.2
8c	**2a**, 45.2	**2b**, n.d.	45.2	n.d.	**2f**, n.d.	-	**8b**, n.d.
8c[c]	**2a**, 40.3	**2b**, n.d.	40.3	n.d.	**2f**, trace	-	-
8d	**1a**, 46.0	**1b**, 3.6	49.6	36.0	**1f**, 6.4	-	**8e**, 21[d]
9a	**1a**, 21.0	**1b**, trace	21.0	17.8	**1f**, 4.0 **1g**, 1.5	**10a**, 13.0	**9b**, 10[d]
9d	**2a**, 18.8	**2b**, 4.1	22.9	19.2	**2f**, 15.9 **2g**, 3.3	**10a**, 27.1	**9e**, 5[d]
11a	**1a**, n.d.	**1b**, n.d.	0.0	21.0	**1g**, 10.0	**10a**, 14.6	**11b**, 24[d]
12	**1a**, 11.0	**1b**, n.d.	11.0	30.9	**1f**, n.d.	**10a**, n.d.	-
13a	**1a**, 5.5	**1b**, n.d.	5.5	46.1	**1f**, n.d.	**10b**, trace	**13b**, n.d.
13c	**2a**, 1.5	**2b**, n.d.	1.5	15.6	**2f**, n.d.	**10b**, trace	**13d**, 4[d]
14c	**3a**, 6.9	**3b**, n.d.	6.9	33.1	**3f**, n.d.	-	-
14d	**3a**, n.d.	**3b**, n.d.	n.d.	42.0	**3f**, n.d.	-	-
14e	**3a**, n.d.	**3b**, n.d.	n.d.	68.8	**3f**, n.d.	-	-

[a] yields are mol % [b] not detected [c] no nitrobenzene [d] approximate values based on response factors of starting materials

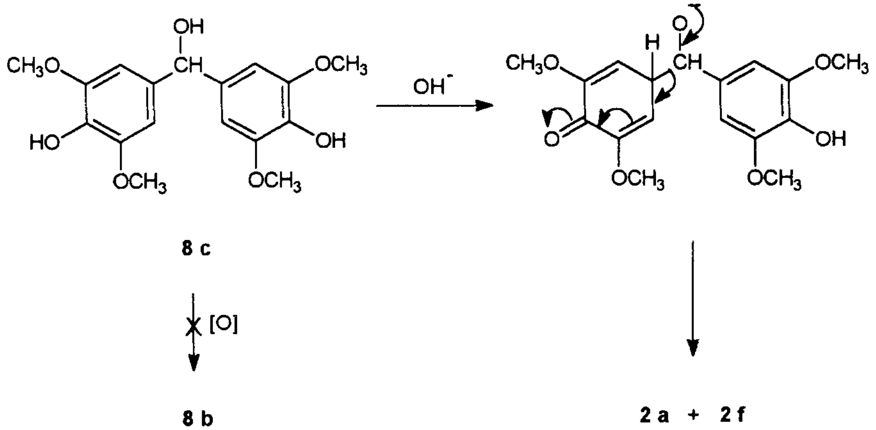


FIGURE 1. Reactions of disyringylcarbinol (**8c**) with alkali

Diguaiacylmethane (**8d**) on nitrobenzene oxidation gave similar products to its syringyl analogue **8a** but the yield of oxidation products was lower, that of the phenol (guaiacol) was higher, and a greater amount of starting material was retained. An additional product was identified as diguaiacylketone (**8e**) by GC-MS of its trimethylsilyl ether, $[M^+]$ *m/z* 418. Because no authentic sample was available, compound **8e** was estimated by using the same GC response factor as the starting material **8d**.

The guaiacyl 1,5'-substituted diphenylmethane **9a** on oxidation with nitrobenzene gave 21% vanillin and a trace of vanillic acid as the oxidation products and approximately the same yield of starting material remained (Table 2). Additional products identified were guaiacol (**1f**), creosol (**1g**) and 6-formylcreosol (**10a**) by GC-MS comparison with authentic samples, and the diphenylketone **9b**, identified by GC-MS of its trimethylsilyl ether, $[M^+]$ *m/z* 432. The products formed from oxidation of **9a** are those arising from scission of the α-1 or α-5' bond, and the oxidation to monomeric products probably involves the intermediacy of the diphenylcarbinol **9c**. Oxidation of the syringyl 1-5'-substituted diphenylmethane **9d** gave analogous products to those from **9a**, although the yields of syringol and 6-formylcreosol were higher than the yields of corresponding products from the guaiacyl compound (Table 2). This indicates that α-1 bond splitting is more prevalent in the syringyl than in the guaiacyl compound.

The 5,5'-diphenylmethane **11a** on oxidation gave rise to creosol, 6-formylcreosol and the diphenyl ketone **11b** (GC-MS examination) (Table 2). The absence of vanillin as an oxidation product can be explained by the resistance of the methyl sidechain of the model **11a** and creosol to oxidation; a model with an oxygenated sidechain would be expected to yield vanillin.

Diphenylmethane structures in modified lignins would usually be expected to have α-alkyl substituents.[18] To test whether these structures would give rise to nitrobenzene oxidation products, the α-methyl guaiacyl 1,5'-diphenylmethane **12** was subjected to nitrobenzene oxidation. The compound gave rise to 11% vanillin as the only product identified, and 31% starting material remained (Table 2). Thus the substituted structure **12** also gives nitrobenzene oxidation products, but in lower yield than the unsubstituted compound **9a**.

As conidendrin (**7**), a lignin model 1,6'-diphenylmethane, gave only trace amounts of nitrobenzene oxidation products, additional compounds were oxidised to ascertain whether this is a general feature of 1,6'-diphenylmethanes. Oxidation of the guaiacyl 1,6'-diphenylmethane **13a** afforded vanillin in 5.5% yield, considerably lower than that from the 1,5'-diphenylmethane **9a** (21%) (Table 2). A further product of the reaction was 5-formylcreosol (**10b**), detected in trace amounts (GC-MS identification). No trace of the diphenyl ketone **13b** was found. The syringyl 1,6'-diphenylmethane **13c** also gave rise to an oxidation product, syringaldehyde (1.5%), in a lower yield than that obtained from the 1,5'-diphenylmethane **9d** (Table 2). Additional products from the oxidation were trace amounts of 5-formylcreosol and the diphenyl ketone **13d**, identified by GC-MS. Thus the 1,6'-diphenylmethanes are less reactive to nitrobenzene oxidation than the 1,5'-diphenylmethanes. It is recognised that compounds with *meta*-hydroxyl groups give considerably lower yields of nitrobenzene oxidation products than those with *para*-hydroxyl groups.[3] The reason for the lower reactivity of 1,6'-diphenylmethanes could be because, unlike the 1,5'-diphenylmethanes, they cannot form a quinonemethide through the creosol ring. Alternatively, the lower reactivity could be due to the lower electron density on the C-5' carbon located in the *meta* position of the powerful electron donating phenoxy group of the creosol.

Kratzl *et al.*[17] reported that both phenolic and non-phenolic 4-hydroxyphenyldiphenylmethanes **14a-c** gave rise to nitrobenzene oxidation products. In this study, although the di-4-hydroxyphenylmethane **14c** gave 4-hydroxybenzaldehyde in 7% yield, both the monomethyl and dimethyl ether of **14c** (**14d** and **14e**) did not give rise to nitrobenzene oxidation products (Table 2). This is surprising, in view of the oxidation of the similar compounds **14a** and **14b**, which gave moderate yields of products.[17] The low yield of product from the 4-hydroxyphenyl compound **14c** is consistent with the earlier observation that these nuclei give rise to low product yields (Table 1).

Schultz *et al.*[3-5] have presented cogent arguments in favour of nitrobenzene oxidations proceeding *via* free radical intermediates. The mechanisms they propose involve homolytic cleavage of the O-H bond of benzyl alcohols as the initial step. However, this does not explain the oxidation of structures with α-carbonyl groups and α-methylene groups, which also give rise to nitrobenzene oxidation products. The α-methylene compounds require oxidation to an oxygenated intermediate, probably a benzyl alcohol, before conversion to the final oxidation products. This process is likely to be rate determining, which would account for the lower yields of oxidation products from α-methylene compounds.

The above results show that diphenylmethane compounds, models of lignin transformation structures, do give rise to nitrobenzene oxidation products, contrary to the assumptions made earlier by Chiang and Funaoka.[9] Furthermore, the yields of oxidation products from lignin models are influenced by the nature of the aromatic nucleus and the structure of the sidechain. Thus the method recently used for determining the relative proportions of structures in modified lignins involving both nitrobenzene oxidation and nucleus exchange[9-14] should be reassessed, and the results should be treated with caution.

Conclusions

Nitrobenzene oxidation of a series of lignin model compounds to benzaldehydes and their corresponding acids showed that:

- There was a range of product yields, depending on the structure of the aromatic nucleus and the sidechain.
- The yield of oxidation products from the models was in the order syringyl > guaiacyl > 4-hydroxyphenyl groups.
- Sidechains affect the yield of oxidation products, with benzylic groups giving yields in the order C=O > CHOH > CH_2.
- The non-phenolic veratryl lignin models gave low yields of oxidation products.
- Diphenylmethane lignin model structures with phenolic hydroxyl groups also gave rise to nitrobenzene oxidation products, although a non-phenolic diphenylmethane gave no products.
- The combined nucleus exchange-nitrobenzene oxidation method for determining the proportions of diphenylmethane structures in modified lignins requires reassessment.
- It is proposed that a key influence on the yield of nitrobenzene oxidation products from lignin model compounds is the ability of the aromatic ring to donate electrons to the benzylic carbon atoms.

EXPERIMENTAL

NMR spectra were obtained at 100 MHz for protons and 25 mHz for carbons for deuterochloroform solutions (unless otherwise specified), and chemical shifts are given in ppm from tetramethylsilane (δ 0.00). GC-MS analyses were carried out on a Hewlett Packard HP5890 series II chromatograph fitted with an autoinjector and an HP5971 mass selective detector. Elemental analyses were carried out by the University of Otago, Dunedin, New Zealand.

Chemicals

Unless otherwise stated, the lignin models or starting materials for synthesis were obtained from commerical sources. Apocynol (**1d**) was prepared by the reduction of acetoguaiacone (**1c**) with sodium borohydride.[19] Similarly, **3d** and **4d** were prepared from 4-hydroxyacetophenone and acetoveratrone, respectively. 1-Guaiacylpropane (**1e**), 1-syringylpropane (**2e**) and 1-veratrylpropane (**4e**) were the products of Pd-C-catalysed hydrogenation of eugenol, 4-allylsyringol and methyleugenol, respectively, in ethanol. Dehydrodiisoeugenol (**5a**) was prepared by the oxidative coupling of isoeugenol with ferric chloride,[20] and the methyl ether **5b** was obtained by the diazomethane methylation of **5a**. The ß-ethers **6a** and **6b** were obtained by multistep syntheses from acetoguaiacone[21] and acetoveratrone,[22] respectively. Disyringylmethane (**8a**) was obtained by reaction of an alkaline solution of 2,6-dimethoxyphenol with formaldehyde,[23] and diguaiacylmethane (**8d**) was prepared by heating an alkaline solution of vanillyl alcohol.[24] Disyringylketone (**8b**) and disyringylcarbinol (**8c**) were prepared by oxidation of **8a** with 2 and 1 equivalents, respectively, of hydrogen peroxide catalysed by peroxidase.[25] 6-Formylcreosol (**10a**) was obtained by heating an acidic solution of creosol with hexamethylenetetramine.[26] Di(2-hydroxy-3-methoxy-5-methylphenyl)methane (**11a**) was the product of heating an alkaline solution of creosol with formaldehyde.[27] Guaiacyl(5-hydroxy-4-methoxy-2-methylphenyl)methane (**13a**) and syringyl-(5-hydroxy-4-methoxy-2-methylphenyl)methane (**13c**) were prepared by heating an acidic solution of creosol with vanillyl alcohol and syringyl alcohol,[28] respectively. Di(4-methoxyphenyl)methane (**14e**) was prepared by methylation of **14c** with dimethyl sulfate.

α-Methylsyringyl alcohol (**2d**)

Sodium borohydride (4.25 g) was added to a stirred solution of acetosyringone (10.0 g) in 50% aqueous ethanol (300 mL) at 20°C. After 24 h at 20°C, a further amount of sodium borohydride (1.4 g) was added, and the mixture was stirred for an additional 24 h. The reaction mixture was saturated with carbon dioxide to give a solution pH 7.8, water (300 mL) was added and the organic material was extracted with diethyl ether (ether) (3 x 150 mL) and dried. Evaporation of the ether *in vacuo* gave a solid (5.62 g) which was recrystallised from dichloromethane-hexane to give *α-methylsyringyl alcohol* (**2d**), m.p. 98-9°C (Found: C, 60.66; H, 7.30. $C_{10}H_{14}O_4$ requires C, 60.59; H, 7.12%) ^1H NMR δ 1.44 (3H, d, J=6.4 Hz, CH_3), 2.16 (1H, bs, OH), 3.84

(6H, s, OCH_3), 4.77 (1H, q, $J=13.1$, 6.4 Hz, CHOH), 5.58 (1H, bs, OH) and 6.56 (2H, s, ArH) ^{13}C NMR δ 25.2, 56.3, 70.6, 102.2, 103.1, 133.9, 137.5, and 147.0. Di(trimethylsilyl) ether, MS *m/z* [M^+] 342.

Guaiacyl(2-hydroxy-3-methoxy-5-methylphenyl)methane (9a)

A solution of vanillyl alcohol (1.0 g) and creosol (4.5 g, 5 equiv.) in 2M sodium hydroxide (100 mL) was heated under reflux under nitrogen for 10 h. After cooling, the solution was acidified to pH 2 with sulfuric acid, extracted with ethyl acetate and the extracts were dried and evaporated *in vacuo*. The resulting oil was adsorbed onto a column of silica gel, and eluted with 7:3 dichloromethane (DCM):hexane to give creosol as a colourless liquid, MS [M^+] *m/z* 138. Elution with 1:1 DCM:hexane gave a solid (1.26 g) which on recrystallisation from hexane-ether gave compound **9a** as *needles*, m.p. 103-4°C (lit.[29] m.p. 114-5°C) (Found: C, 70.06; H, 6.61. $C_{16}H_{18}O_4$ requires C, 70.07; H, 6.57%) ^1H NMR δ 2.22 (3H, s, CH_3), 3.80 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 3.88 (2H, s, CH_2), 5.36 (2H, bs, OH) and 6.49-6.87 (5H, m, ArH) ^{13}C NMR δ 21.0, 35.0, 55.8, 55.9, 109.5, 111.5, 114.1, 121.4, 122.7, 126.9, 128.7, 132.8, 140.9, 143.7, 146.1 and 146.3. Di(trimethylsilyl) ether MS *m/z* [M^+] 418. Elution with 1:1 DCM:hexane gave a solid (150 mg) which on recrystallisation afforded 1,1'-diguaiacylmethane (**8d**), m.p. 105-6°C (lit.[24] m.p. 107-8°C) ^1H NMR δ 3.80 (6H, s, OCH_3), 3.91 (2H, s, CH_2), 5.59 (2H, bs, OH) and 6.54-6.88 (6H, m, ArH) ^{13}C NMR δ 41.2, 55.9, 110.0, 111.5, 115.3, 121.6, 133.4, 144.0 and 146.5. Di(trimethylsilyl) ether MS *m/z* [M^+] 404.

Syringyl(2-hydroxy-3-methoxy-5-methylphenyl)methane (9d)

A solution of syringyl alcohol (1.0 g) and creosol (3.75 g, 5 equiv.) in 2M sodium hydroxide (100 mL) was heated under reflux under nitrogen for 10 h. The organic material was isolated as above for compound **9a**, and was adsorbed on silica gel. Elution with 1:4 DCM:hexane afforded creosol. Elution with 3:2 DCM:hexane yielded a solid (400 mg), which after recrystallisation from hexane-ether gave *compound* ***9d***, m.p. 108-9°C (Found: C, 67.38; H, 6.52. $C_{17}H_{20}O_5$ requires C, 67.09; H, 6.62%) ^1H NMR δ 2.25 (3H, s, CH_3), 3.83 (9H, s, OCH_3), 3.90 (2H, s, CH_2), 5.72 (2H, bs, OH) and 6.45-6.60 (4H, m, ArH) ^{13}C NMR δ 21.1, 35.6, 56.0, 56.3, 105.9, 109.8, 122.8, 126.9, 128.8, 132.1, 133.1, 141.1, 146.3 and 147.0. Di(trimethylsilyl) ether MS *m/z* [M^+] 448. Elution with 1:1 DCM:hexane gave a solid (120 mg) which on recrystallisation afforded disyringylmethane (**8a**), m.p. 112-3°C (lit.[23] m.p. 111-111.5°C) ^1H NMR δ 3.74 (14H, s, OCH_3 and CH_2), 5.41 (2H, bs, OH) and 6.32 (4H, s, ArH) ^{13}C NMR δ 41.9, 56.3, 105.8, 132.2, 133.2 and 147.1. Di(trimethylsilyl) ether MS *m/z* [M^+] 464.

1-Guaiacyl-1'-(2-hydroxy-3-methoxy-5-methylphenyl)ethane (12)

A solution of apocynol (2.0 g) and creosol (4.9 g) in 2M sodium hydroxide (200 mL) was heated under reflux under nitrogen for 8 h. The organic material was isolated as above for compound **9a**, and was adsorbed on silica gel. Elution with 1:4 DCM:hexane afforded creosol. Elution with 2:3 DCM:hexane yielded a solid (480 mg), which after recrystallisation from hexane-ether gave *compound **12***, m.p. 86-7°C (Found: C, 70.91; H, 7.30. $C_{17}H_{20}O_4$ requires C, 70.83; H, 6.94%) ^1H NMR δ 1.63 (3H, d, J=7.3 Hz, $CHCH_3$), 2.31 (3H, s, $ArCH_3$), 3.86 (6H, d, OCH_3), 4.54 (1H, q, J=14.4, 7.3 Hz, $CHCH_3$), 5.72 (2H, bs, OH), 6.60 (2H, s, ArH) and 6.87 (3H, s, ArH) ^{13}C NMR δ 20.8, 37.1, 55.7, 55.8, 109.3, 110.7, 114.0, 119.9, 120.0, 128.6, 132.0, 138.0, 140.4, 143.6, 146.0 and 146.2. Di(trimethylsilyl) ether MS *m/z* [M^+] 432.

(4-Hydroxyphenyl)(4'-methoxyphenyl)methane (14d)

Dimethyl sulfate (1.5 mL) was added dropwise to a stirred solution of di(4-hydroxyphenyl)methane (1.0 g) in 2M sodium hydroxide (9 mL) at 0°C. After heating under reflux for 2 h and subsequent cooling, the mixture was extracted with ether and the extracts were dried with sodium sulfate and evaporated. The resulting solid (350 mg) was recrystallised from hexane-ether to give *compound **14d***, m.p. 84-5°C (Found: C, 78.57; H, 6.34. $C_{14}H_{14}O_2$ requires C, 78.48; H, 6.59%) ^1H NMR δ 3.75 (3H, s, OCH_3), 3.82 (2H, s, CH_2), 5.18 (1H, bs, OH) and 6.6-7.2 (8H, m, ArH) ^{13}C NMR δ 40.1, 55.3, 114.0, 115.3, 129.8, 129.9, 133.8, 153.8 and 157.8. Trimethylsilyl ether MS *m/z* [M^+] 286.

Nitrobenzene oxidation of lignin model compounds

A mixture of the lignin model (0.1 mmol), 2M sodium hydroxide (6 mL) and nitrobenzene (0.5 mL) were placed in a 20 mL teflon-lined steel pressure vessel, and the vessels were heated, four at a time, in a rocking hot air bath at 170°C for 2 h. After cooling, the contents of the vessels were transferred to a separating funnel with a small amount of water and extracted with DCM (2 x 25 mL) and the extracts discarded. The aqueous phase was acidified to pH 2, and 1 mL of a solution of DCM containing 15 mg 3-ethoxy-4-hydroxybenzaldehyde was added as the internal standard. The mixture was extracted with dichloromethane (3 x 25 mL) and the combined extracts were dried with sodium sulfate. For non-phenolic model compounds, the initial extraction of the alkaline solution was not carried out. After evaporation of the solvent, the residue was transferred to a septum vial with DCM, and the DCM was removed in a stream of nitrogen. The residue was silylated with *N*,*O*-bis(trimethylsilyl)-trifluoroacetamide (100 μL) for 1 h at 100°C. The excess silylating reagent was removed under nitrogen, and the sample was dissolved in 4.0 mL DCM and was analysed by GC. The samples were oxidised in duplicate.

GC and GC-MS analyses of nitrobenzene oxidation products

The column used for GC-MS analyses was a J&W bonded phase DB5 fused silica column (30 m x 0.25 mm ID) with a phase thickness 0.25 μm. Purified helium was the carrier gas with a linear velocity 30 cm/sec. The injector temperature was 250°C and the transfer line was at 280°C. The column temperature program was: initial temperature 100°C, 5°C/min to 200°C, 10°C/min to 250°C, 30°C/min to 280°C, and 15 min at 280°C. Splitless injections of 1 μL with a 0.3 min purge delay were used and full-scan (*m/z* 30-550) electron impact (70 eV) mass spectra were collected. The yields of products were expressed on a mol. % basis.

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