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REACTIVITIES OF GUAIACYL AND SYRINGYL LIGNIN MODEL
PHENOLS TOWARDS OXIDATION WITH OXYGEN-ALKALI

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Dedicated to the memory of Professor Kyösti V. Sarkanen.

ABSTRACT

A range of guaiacyl and syringyl lignin model phenols was treated with oxygen in 1M potassium hydroxide solution at 70°C. The reactions were monitored by high performance liquid chromatography and gas chromatography-mass spectrometry. The reactions of the phenols, which followed pseudo-first-order kinetics, were faster for syringyl than for guaiacyl phenols. For the various 4-substituted syringols the reactivities were in decreasing order $\text{CH}_2\text{-syringyl} > \text{CHOH-CH}_3 \approx \text{C}_3\text{H}_7 > \text{CH}_2\text{OH} > \text{COOH} > \text{CHO} > \text{CO-CH}_3$. Reaction of 1-guaiacylpropane in 1M potassium hydroxide with oxygen gave products of oxidative scission of the aromatic ring and no dehydrodimer, whereas at pH 11.5 some dehydrodimer was among the reaction products. Vanillyl alcohol and syringyl alcohol yielded vanillin and syringaldehyde, respectively, as minor oxidation products. However, the reaction sites for the series of phenols were generally the aromatic rings rather than the side-chains. Oxidation of alkaline solutions of the phenols with oxygen at 1.0 MPa pressure and 110 and 150°C gave similar mixtures of acids and hydroxyacids.

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INTRODUCTION

The application of oxygen in alkali media to wood pulps is assuming an increasingly important rôle in commercial delignification processes.¹ Under alkaline conditions, oxygen reacts with both the aromatic rings and side-chain structures in lignin.² In the former case, reaction of lignin phenolic units can give products from oxidative coupling,³ side-chain displacement⁴ and ring scission,⁵ whereas non-phenolic aromatic units are relatively stable to oxygen-alkali conditions.⁶ The side-chain structures in lignin are also reactive to oxygen-alkali especially when there are carbon-carbon double bonds present, *e.g.* in stilbene structures.⁷ The initial products formed by reaction of oxygen with lignin models are hydroperoxides,² and the course of further transformations of these intermediates is pH dependent.^{8,9}

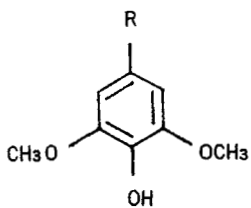
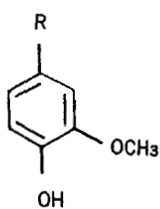
Although the mechanism of oxidation of lignin models with oxygen-alkali is generally understood, less is known about the comparative reactivities of lignin structures, particularly those pertaining to hardwood lignins. Kratzl *et al.*³ showed that the rate of oxygen uptake for alkaline solutions of various lignin models at 70°C decreased in the order catechol > syringyl > guaiacyl > biguaiacyl units. In addition, the presence of an alkyl substituent *para* to the phenolic hydroxyl group accelerated the oxygen uptake. Gierer *et al.*¹⁰ found that syringyl β -aryl ethers were more reactive to oxygen than were the corresponding guaiacyl models. The structure of side-chains in lignin model phenols affects their reactivity towards oxygen; for guaiacyl models, oxygen uptake was found to be in decreasing order vanillyl alcohol (1f) > apocynol (1e) > vanillin (1d) > acetoguaiacone (1c).⁴ Ljunggren and Johansson¹¹ have recently shown that for guaiacyl structures, which are considered to be important in residual kraft pulp lignins, the order of reactivity with oxygen-alkali was stilbene > vinyl ether > β -aryl ether.

Results from lignin model compound studies have been reinforced by studies of oxidation of isolated lignins. Kratzl *et al.*³ found that an alkaline solution of a hardwood kraft lignin at 70°C absorbed more oxygen at a greater rate than did a pine kraft lignin. In a related study, Lai and Sarkanen¹² noted that hardwood lignins were more reactive to peroxyacetic acid than were softwood lignins; this they attributed to the oxidation reactivity of syringyl groups being greater than that of guaiacyl groups.

Despite the general recognition that syringyl compounds are more reactive to alkaline oxygen oxidation than are guaiacyl compounds, there is little comparative information about the reactivities of structures with different side-chains. In the present study, we have reacted a range of lignin models with oxygen under alkaline conditions and have analysed the products by high performance liquid chromatography (HPLC) and by gas chromatography-mass spectrometry (GC-MS).

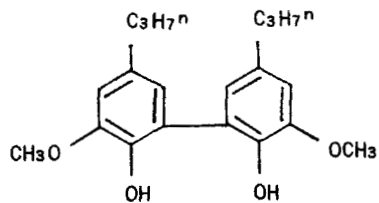
RESULTS AND DISCUSSION

A range of guaiacyl and syringyl models characteristic of lignin structures in wood and pulps was studied. Reaction of the lignin model phenols with oxygen was carried out at 70°C by maintaining a constant flow of the gas through the alkaline solutions. This allowed the phenols to react with solutions saturated with oxygen at atmospheric pressure. Because of the insolubility of some phenols in sodium hydroxide, *e.g.* 1-syringylpropane (2a), solutions of 1M potassium hydroxide were used for the series of reactions rather than the more widely used sodium hydroxide. The course of the reactions was monitored by measuring the amounts of starting phenols remaining and the amounts of certain products formed. In every case, the

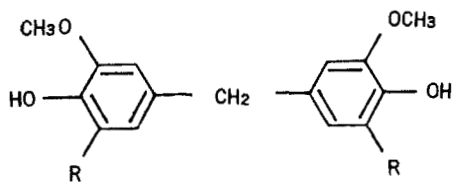


	R
1a	C ₃ H ₇ ⁿ
b	COOH
c	COCH ₃
d	CHO
e	CH(OH)CH ₃
f	CH ₂ OH
g	CH ₂ OCH ₃

	R
2a	C ₃ H ₇ ⁿ
b	COOH
c	COCH ₃
d	CHO
e	CH(OH)CH ₃
f	CH ₂ OH
g	CH ₂ OCH ₃



3



4a R = H
b R = OCH₃

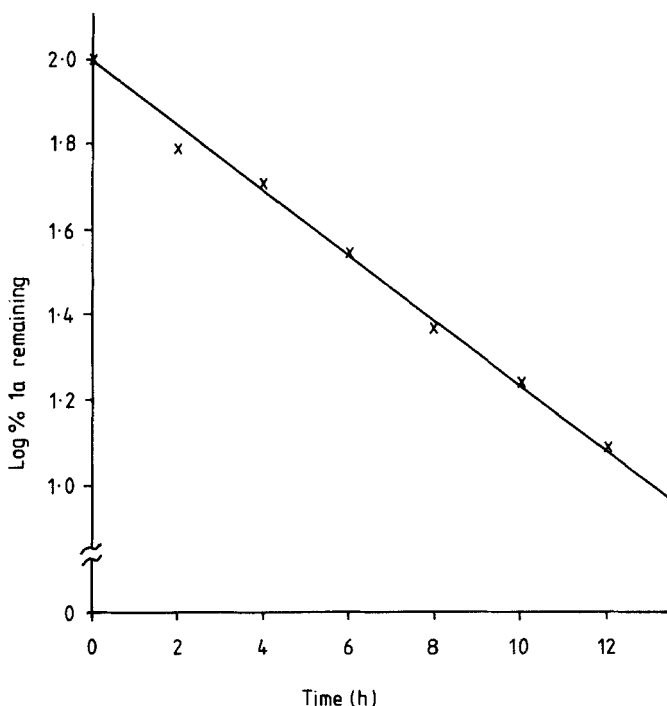


FIGURE 1. First-order rate plot of the reaction of 1-guaiacylpropane (1a) in 1M KOH with oxygen at 70°C.

disappearance of the phenols followed pseudo-first-order kinetics, as shown for 4-*n*-propylguaiacol in Figure 1. Lunggren found that reactions of phenolic stilbene,^{11,13} enol ether,¹¹ β -aryl ether¹¹ and alkyl¹⁴ structures with oxygen-alkali also followed pseudo-first-order kinetics.

1-Syringylpropane (2a) reacted rapidly with oxygen at 70°C; after 3 h there was only a small amount of the phenol remaining. Reaction of 1-guaiacylpropane (1a) was less rapid, and the guaiacyl dimer 3 in 35% aqueous ethanol reacted only slowly with oxygen (Figure 2, Table 1). The inclusion of ethanol in the

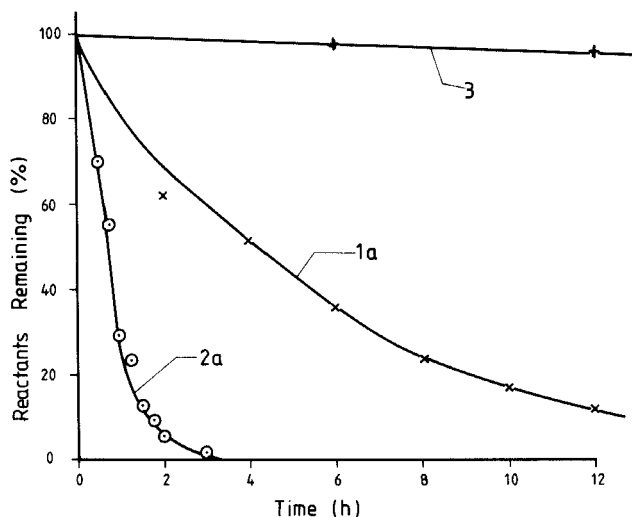


FIGURE 2. Reaction of lignin model phenols in 1M KOH with oxygen at 70°C. Phenols remaining (%): — + — dimer 3 (in 35% aq. ethanol); — x — 1-guaiacylpropane (1a); — o — 1-syringylpropane (2a).

TABLE 1

Observed Pseudo-First-Order Rate Constants for Oxidation of Lignin Model Phenols in 1M Potassium Hydroxide with Oxygen at 70°C.

Guaiacyl compound	$10^3 k_{obs}$ (min^{-1})	Syringyl compound	$10^3 k_{obs}$ (min^{-1})
1-guaiacylpropane (1a)	1.28	1-syringylpropane (2a)	9.95
dimer (3)**	0.793*	—	—
diguaiacylmethane (4a)	3.17	disyringylmethane (4b)	57.5
vanillic acid (1b)	*	syringic acid (2b)	0.690
acetoguaiacone (1c)	*	acetosyringone (2c)	0.0470
vanillin (1d)	*	syringaldehyde (2d)	0.445
apocynol (1e)	1.04	1-syringylpropanol (2e)	11.5
vanillyl alcohol (1f)	0.642	syringyl alcohol (2f)	7.40

*Reaction in 50% aq. acetonitrile at 60°C and pH 11.5 according to Ljunggren**18

**Reaction in 35% aq. ethanol

*No reaction after 32 h

reaction mixture of dimer 3 was necessary for its dissolution. Reaction of 1-guaiacylalkanes with oxygen-alkali has previously been shown to be slower in the presence of organic solvents.^{14,15} Oxidation of phenols 1a and 2a gave in each case, after HPLC on a reversed phase column, a single peak with a short retention time, indicative of hydrophilic material, e.g. organic acids, formed by oxidative scission of the aromatic ring. This was confirmed after GC-MS examination of the reaction mixtures, which were shown to contain a large number of components, chiefly a range of dibasic acids and hydroxyacids similar to those isolated from creosol¹⁶ (see Experimental).

There was a notable absence of the dehydrodimer 3 among the oxidation products of 1-guaiacylpropane (1a). Although compound 3 was reported to be the primary product of oxidation of 1a in 0.2M sodium hydroxide at 70°C,^{3,4} later work¹⁷ showed that dimerisation to 3 did not take place under those conditions. San Clemente *et al.*⁸ found that the dehydrodimer of 1-guaiacylethane was formed in alkaline oxygen oxidations only at pH values below 13. This they attributed to the instability of the initially-formed hydroperoxide at lower alkalinities, producing peroxy-radicals which subsequently gave the dehydrodimer by *ortho-ortho* coupling.

When treated with oxygen in 50% aqueous acetonitrile at pH 11.5 and 60°C according to the procedure of Ljunggren,¹⁸ 1-guaiacylpropane (1a) gave the dimer 3 as one of the products (Figure 3). The rates of oxidation of the phenol and formation of the dimer were greater when the experiment was carried out in a polyethylene bottle than when in a glass flask. However, the rates were considerably slower than those reported earlier.^{14,18} The pseudo-first-order rate constant for the reaction carried out at pH 11.5 was less than that obtained when the reaction was performed in 1M potassium hydroxide (Table 1).

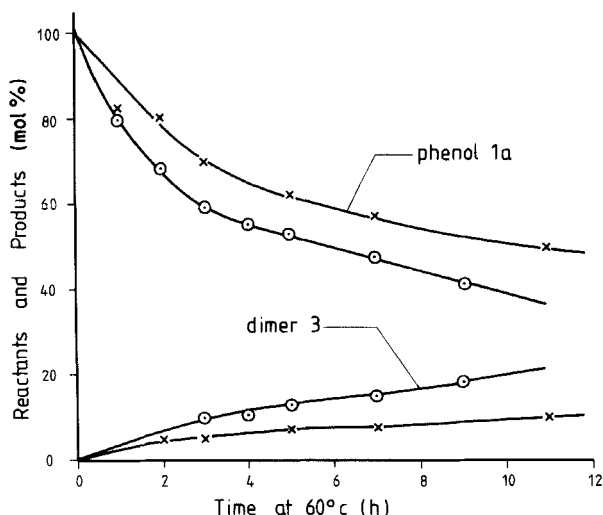


FIGURE 3. Reaction of 1-guaiacylpropane (1a) in 50% aq. acetonitrile at pH 11.5 and 60°C in — x — glass, and — o — polyethylene vessels.

Of the lignin model phenols tested, disyringylmethane (4b) reacted with oxygen-alkali most rapidly, and considerably faster than diguaiacylmethane (4a) (Table 1). In both cases, the phenols were converted to hydrophilic material which had a short retention time on the reversed phase HPLC column. There was no indication that diarylethanols or dibenzophenones were among the products.

Vanillic acid (1b), acetoguaiacone (1c) and vanillin (1d) were stable to the alkaline oxygen conditions, and in each case no reaction occurred after 32 h (HPLC and GC-MS examination). Kratzl *et al.*⁴ have reported that compounds 1c and 1d in 0.2M sodium hydroxide solution absorbed oxygen over a 24 h period at 70°C. However, in a kinetic study of the autoxidation of vanillin, Wallick and Sarkanen⁹ found that relatively high temperatures (130 to 170°C) were required for reaction with alkaline oxygen to occur.

Syringic acid (2b) was reactive to alkaline oxygen (Table 1), giving products which were more hydrophilic than was the starting material. GC-MS examination showed the products to be mixtures of aliphatic acids and hydroxy-acids. Acetosyringone (2c) reacted very slowly with oxygen, whereas syringaldehyde (2d) had a reaction rate closer to that of syringic acid (Table 1). In both cases, syringic acid was not among the reaction products, and the mixtures had HPLC peaks with short retention times, indicative of ring-opened oxidised material.

The models with α -hydroxy substituents, apocynol (1e) and its syringyl analogue 2e, had similar reaction rates to the 4-alkylphenols 1a and 2a respectively, and the syringyl compound was significantly more reactive. Gierer *et al.*¹⁰ have previously shown a syringyl α -hydroxy- β -ether model to be more reactive to oxygen-alkali than its guaiacyl counterpart. Neither acetoguaiacone (1c) nor acetosyringone (2c) were found as reaction products of 1e and 2e, respectively; the products were acids arising from oxidative ring cleavage.

Vanillyl alcohol (1f) and syringyl alcohol (2f) were less reactive to oxygen-alkali than their α -methyl analogues 1e and 2e (Table 1). For these models, side-chain oxidation to the aldehydes vanillin (1d) and syringaldehyde (2d) occurred as minor reactions (Figure 4), although the corresponding acids 1b and 2b were not among the reaction products. After acidification, HPLC analyses of the reaction mixtures were carried out without delay, as the phenols 1e and 2e reacted slowly with acidified methanol to give the methyl ethers 1f and 2f respectively.^{19,20}

Alkaline solutions of the phenols were also treated with oxygen under pressure and at elevated temperatures (110 and 150°C). The products, identified by GC-MS after conversion to their TMS derivatives, were similar for all oxidation conditions and for all the compounds examined. These products were aliphatic acids resulting from severe oxidation of the phenols.

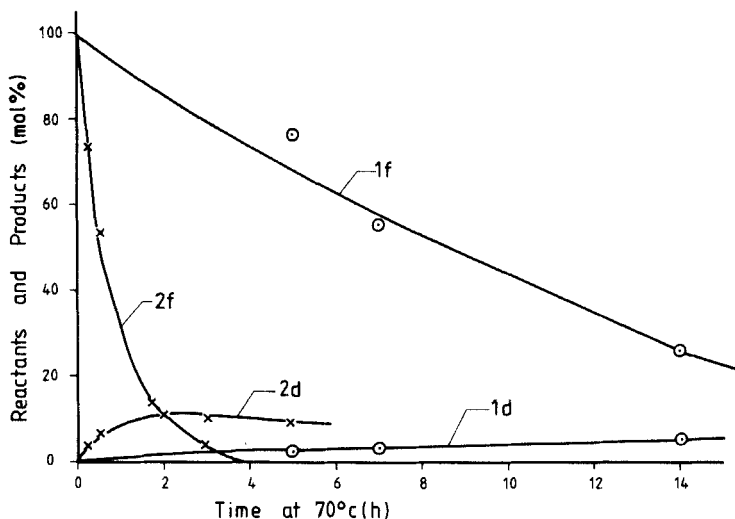


FIGURE 4. Reactions of lignin model phenols in 1M KOH with oxygen at 70°C and formation of aldehydes.
 — o — 1f and 1d, — x — 2f and 2d.

Concluding remarks

From Table 1 it follows that 4-substituted syringols show reactivities to oxygen-alkali at 70°C in the decreasing order $\text{CH}_2\text{-syringyl} > \text{CHOH-CH}_3 \approx \text{C}_3\text{H}_7^n > \text{CH}_2\text{OH} > \text{COOH} > \text{CHO} > \text{CO-CH}_3$. Guaiacyl phenols are less reactive to oxygen-alkali than are syringyl phenols. The reactivities of the phenols can be correlated with their electron donating powers; greater electron densities in the aromatic rings renders them more susceptible to oxidative cleavage between the two carbon atoms bearing oxygenated substituents. Under the reaction conditions used in the present study, oxidative cleavage of the aromatic rings appears to be a more favoured reaction pathway than is oxidation of the side-chains. A better indication of the reactivities of the models to oxygen-alkali is obtained by monitoring the disappearance of starting materials (as in the present study) rather than by measurement of the oxygen absorbed (common in earlier work).

EXPERIMENTAL

Lignin model compounds

Unless otherwise specified, the lignin models 1-4 were obtained from commercial sources, and were checked for purity by melting points, GC and HPLC, and by spectroscopic means. 1-Guaiacylpropane and 1-syringylpropane (1a and 2a) were the products of hydrogenation of eugenol and 4-allylsyringol respectively in ethanol with Pd-C as a catalyst. Apocynol and 1-syringylethanol (1e and 2e) were prepared by sodium borohydride reduction of 1c and 2c respectively. 4,4'-Di-*n*-propyl-6,6'-biguaiacol (3) was obtained by oxidation of 1-guaiacylpropane (1a) with hydrogen peroxide-peroxidase according to Pew's procedure.²¹ Disyringylmethane (4b) was prepared by reaction of 2,6-dimethoxyphenol with formaldehyde in alkali by the method of Steelink.²²

Diguaiacylmethane (4a)

Attempted preparation of diguaiacylmethane (4a) from vanillyl alcohol by heating with 2.5M sodium hydroxide according to the method of Pearl²³ gave mostly unreacted starting material (HPLC examination). A better result was obtained by refluxing the mixture for 1 h in a flask to which an air condenser was attached to allow the liberation of formaldehyde.

A solution of vanillyl alcohol (4.0 g) in 2.5M sodium hydroxide (100 mL) was refluxed under nitrogen for 1 h in a flask fitted with an air condenser. After cooling, the solution was saturated with carbon dioxide and extracted with ether. The extract was dried and the ether was evaporated to give an oil (3.6 g), which displayed three major TLC spots. Adsorption of the oil onto a column of silica gel and elution with hexane:chloroform

3:1 gave a solid, which crystallised from hexane-ether as needles of diguaiacylmethane (710 mg) m.p. 107–8°C. (Lit.²³ m.p. 108–9°C). PMR δ (CDCl₃) 3.62 (s, 8, 2 x OCH₃, ArCH₂Ar), 5.4 (s, 2, 2 x OH) and 6.6–7.3 (m, 6, ArH).

Oxidation of lignin models with alkaline oxygen

(a) *At atmospheric pressure* Oxygen was slowly bubbled through a solution of a lignin model compound (30 mmol) in 1M potassium hydroxide solution (10 mL) in a pear-shaped flask immersed in a thermostatted water bath at 70°C. Aliquots (1.0 mL) were taken at intervals, and the solution was acidified to pH \approx 3 with 10M hydrochloric acid and made up to 5 mL with methanol prior to HPLC analysis. Estimation of the starting materials and reaction products was accomplished with the use of external standards. Alternatively, the entire reaction mixture was acidified with 10M hydrochloric acid to pH \approx 3, freeze-dried, and extracted successively with methyl ethyl ketone and acetone. After evaporation of the extracts, the residue was silylated with a mixture of N,O-bis(trimethylsilyl)-trifluoroacetamide (200 μ L), chlorotrimethylsilane (10 μ L) and pyridine (500 μ L) at 70°C for 1 h before analysis by GC.

A solution of dimer 3 (5 mg) in ethanol (3.5 mL) and 1M potassium hydroxide (6.5 mL) was treated with a slow stream of oxygen at 70°C, and the reaction was monitored as above.

Oxidation of 1-guaiacylpropane in 50% aqueous acetonitrile with oxygen at pH 11.5 and 60°C was carried out according to the procedure of Ljunggren.¹⁷ Aliquots (1.0 mL) were periodically removed, acidified to pH \approx 3, and analysed by HPLC.

The logarithm of the percentage of the phenol reactants remaining was plotted against reaction time, and gave in every

case a straight line. From the slope of this line, the pseudo-first-order rate constant was determined.

(b) In pressure vessels Solutions of the phenols in 1.25M sodium hydroxide were placed in 180 mL steel vessels and charged with 1.0 MPa oxygen. The vessels were placed in a cradle in an air bath and were rotated at temperatures of 110 and 150°C for periods of up to 3 h. The reaction mixtures were acidified with 10M hydrochloric acid to pH \approx 3 and were analysed as above.

HPLC Analyses

HPLC was carried out on a system comprising a Waters WISP 710B autosampler and Model 481 variable wavelength detector, and a Spectra-Physics SP8700 solvent delivery system and SP4100 computing integrator. The column used was a Waters Radial-PAK cartridge (100 mm x 8 mm) containing a RESOLVE 5 μ C-18 packing. The HPLC conditions were as follows: injection vol., 20 μ L; 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).

GC and GC-MS Analyses

GC and GC-MS data were obtained with Hewlett-Packard 5830A and 5995 instruments, respectively, with vitreous silica capillary columns, an SE-30 wall-coated open tubular column (25 m x 0.33 mm ID) and a BP1 bonded phase column (25 m x 0.2 mm ID) (Scientific Glass Engineering, Melbourne) and flame ionisation detection for the 5830A instrument. Split ratio: 100:1; carrier gas: helium; injector and detector temperatures: 250°C; column temperature: 80°C for 5 min, then 3°C min⁻¹ to 240°C. Acids identified as their

TMS esters/ethers were (retention time, min.): lactic (11.6), glycolic (12.1), levulinic (13.7), 2-hydroxybutanoic (14.3), oxalic (14.3), 3-hydroxypropanoic (14.8), 3-hydroxybutanoic (15.6), 2-hydroxypentanoic (17.0), malonic (17.3), maleic (21.7), succinic (22.4), methylsuccinic (23.0), glyceric (23.6), fumaric (24.0), tartronic (26.4), malic (31.1) and 2,3-dihydroxysuccinic (37.2).

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