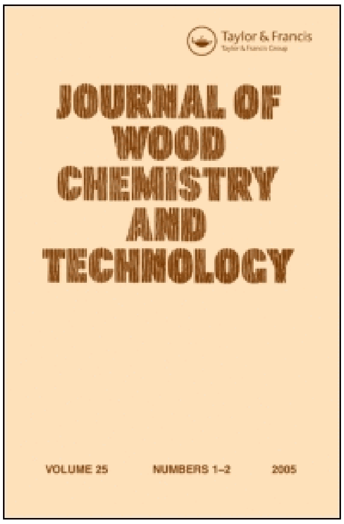

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Sun, Yan-Ping , Wallis, Adrian F. A. and Nguyen, Kien Loi(1997) 'Aromatic Products from Reaction of Lignin Model Compounds with UV-Alkaline Peroxide', Journal of Wood Chemistry and Technology, 17: 3, 209 — 222
To link to this Article: DOI: 10.1080/02773819708003128
URL: http://dx.doi.org/10.1080/02773819708003128

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 17(3), 209-222 (1997)

AROMATIC PRODUCTS FROM REACTION OF LIGNIN MODEL COMPOUNDS WITH UV-ALKALINE PEROXIDE

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ABSTRACT

A series of guaiacyl and syringyl lignin model compounds and their methylated analogues were reacted with alkaline hydrogen peroxide while irradiating with UV light at 254 nm. The aromatic products obtained were investigated by gas chromatography-mass spectrometry (GC-MS). Guaiacol, syringol and veratrol gave no detectable aromatic products. However, syringol methyl ether gave small amounts of aromatic products, resulting from ring substitution and methoxyl displacement by hydroxyl radicals. Reaction of vanillin and syringaldehyde gave the Dakin reaction products, methoxy-1,4-hydroquinones, while reaction of their methyl ethers yielded benzoic acids. Acetoguaiacone, acetosyringone and their methyl ethers afforded several hydroxylated aromatic products, but no aromatic products were identified in the reaction mixtures from guaiacylpropane and syringylpropane. In contrast, veratrylpropane gave a mixture from which 17 aromatic hydroxylated compounds were identified. It is concluded that for phenolic lignin model compounds, particularly those possessing electron-donating aromatic ring substituents, ring-cleavage reactions involving superoxide radical anions are dominant, whereas for non-phenolic lignin models, hydroxylation reactions through attack of hydroxyl radicals prevail.

INTRODUCTION

Many studies of the reaction of lignin model compounds with alkaline hydrogen peroxide have been carried out with the objective of elucidating the mechanism of the bleaching of mechanical pulps with peroxide. Early work showed that reaction of creosol and apocynol[1] and their syringyl analogues[2] with alkaline peroxide gave aliphatic acid products involving cleavage of aromatic rings. However, Agnemo and Gellerstedt[3] found that if oxygen was excluded and a peroxide stabiliser was present, α-methyl syringyl alcohol was stable to alkaline peroxide. The ring-opened products were found to be formed through the intermediacy of radicals from the decomposition of peroxide, whereas in the absence of peroxide decomposition, the perhydroxyl anion is the major reactive species[3]. The major reactions of stabilised peroxide with lignin were found to be conversion of phenols containing α-carbonyl groups to hydro-quinones[4-7] (the Dakin reaction) and cleavage of the α-ß double bond in cinnamaldehyde structures[4,5]. Other reactions include degradation of quinones[8,9], ß-ethers[10], ß-1 dimers[11] and stilbenes[12] with alkaline peroxide.

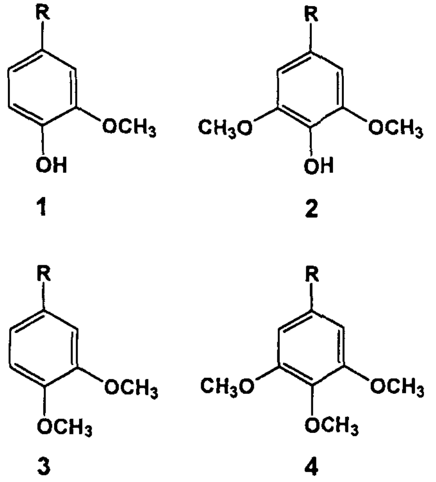
Peroxide bleaching of kraft[13-16] and organosolv[17,18] pulps has been found to be enhanced by UV light. UV irradiation of alkaline hydrogen peroxide gives rise to hydroxyl radicals and superoxide radical anions[19,20], and the mechanism of action of these radicals with residual lignin in pulps has been ascertained by studies of lignin model compound reactions. Hydroxyl radicals are very powerful oxidants, and they were found to attack aromatic rings of lignin through hydroxylation, demethoxylation, dealkoxylation and sidechain displacement reactions, and to oxidise lignin sidechains[21]. Hydroxyl radicals can also generate phenoxyl radicals which undergo coupling reactions, although these phenoxyl radicals are not able to cause opening of the lignin aromatic rings[21]. In contrast, the major reaction of superoxide radical anions in alkaline solution with lignin is the scission of aromatic rings with the formation of aliphatic acids, although in acidic media, the major attack by perhydroxyl radicals is through demethoxylation reactions[22]. Singlet oxygen has also been implicated as a reaction intermediate in the reaction of lignin with UV-peroxide[23], and both singlet oxygen and superoxide anion radicals have been detected in UV-irradiated alkaline peroxide solutions used for bleaching of pulps[24].

Tatsumi and Terashima have made extensive investigations of the effects of UV irradiation on the reactions of lignin model compounds under acidic conditions. Their results show that the comparative reactivities of lignin models with UV-peroxide at pH 4.5 differed from those with alkaline peroxide at pH 9 without UV irradiation[25]. Veratric acid, when reacted at pH 4.5 with UV-peroxide, underwent hydroxylation reactions to give a large number of reaction products through aromatic ring substitution, and displacement of ring-substituted methoxyl and carboxyl groups by hydroxyl groups[26,27]. Oxidation reactions leading to ring-opened products were minor pathways under acidic conditions, and the rate of degradation of vanillic acid with UV-peroxide was found to be greater at pH 9 than at pH 6[28]. Irradiation with UV alone gave dimeric products formed by oxidative coupling, whereas in the presence of peroxide no dimeric compounds resulted[28]. UV-peroxide conditions were also able to cleave ß-ether[29] and biphenyl[30] bonds in lignin model compounds.

Our own studies have shown that lignin models react with UV-peroxide faster under alkaline than acidic conditions and that substituents which donate electrons to the aromatic rings promote the reactions[31,32]. Thus phenols reacted faster than their methyl ethers, and a methoxyl group *ortho* to the phenolic hydroxyl or its methyl ether enhanced reactivity. The aliphatic acid products arising from opening of the aromatic rings of the lignin models with UV peroxide were described, and it was shown that phenols also gave more ring-opened products than did phenol ethers[33]. The present report discusses the reaction of some lignin model compounds with UV-alkaline peroxide, with emphasis on the aromatic products.

RESULTS AND DISCUSSION

Aqueous alkaline solutions of several guaiacyl, syringyl, veratryl and 3,4,5-trimethoxyphenyl lignin model compounds (**1-4,a-d**, Figure 1) were reacted at pH 11 and 40°C with hydrogen peroxide in the presence of UV irradiation at 254 nm for periods of time up to 120 min. A substrate:peroxide ratio of 1:10 was used, to ensure availability of peroxide throughout the reaction. Water was chosen as the solvent for the models, because organic solvents can interfere with the radical processes and thus complicate the interpretation of the results[34]. The extracts were



	R
a	H
b	CHO
c	CO-CH3
d	CH2-CH2-CH3

FIGURE 1. Lignin model compounds used for reaction with UV-peroxide

analysed after silylation by gas chromatography-mass spectrometry (GC-MS). Identification of the products was by GC-MS comparison with authentic compounds where available, or by examination of the mass spectra (Tables 1 and 2) in conjunction with known reactivities of the substrates and relative GC retention times of the products. Structural assignments of products by the latter methods remain tentative in the absence of authentic compounds. The yields of products were calculated from comparison of the GC peaks with those of the internal standard (salicylic acid), assuming unit detector response with the products.

Reaction of the unsubstituted phenols guaiacol and syringol (**1a** and **2a**) and guaiacol methyl ether (veratrol) (**3a**) with alkaline hydrogen peroxide for periods up to 120 min gave mixtures in which no aromatic products were detected by GC-MS, although ring-opened aliphatic acids have been identified previously[33]. Similar treatment of 1,2,3-trimethoxybenzene (**4a**) afforded small amounts of the phenols **5**, **6a** and **6b** (< 1% yield of each) (Table 1, Figure 2). The formation of these products can be understood by attack of hydroxyl radicals on the aromatic ring, resulting in replacement of a methoxyl group by hydroxyl, and in hydroxyl

TABLE 1

GC-MS data on trimethylsilylated reaction products of lignin model compounds with UV-peroxide

Substrate	Product	Yield (%)	GC RT* (min)	MS data *m/z* (% of base peak)
4a	**5**	0.7	24.53	226(M, 27), 210(19), 196(100), 181(13), 153(12)
	6a	0.3	28.06	256(M, 76), 241(37), 226(100), 211(43), 100(22), 73(71)
	6b	0.6	29.48	314(M, 50), 284(71), 254(29), 201(60), 73(100)
1b	**7a**	83	29.18	284(M, 50), 269(10), 254(100), 239(8), 112(6), 89(4), 73(20)
2b	**7b**	79	32.69	314(M, 52), 284(100),254(4), 135(4), 89(5), 73(21)
3b	**8a**	36	33.47	254(M, 47), 239(78), 195(100), 165(93), 137(9), 107(7), 79(15), 73(8)
4b	**8b**	59	35.16	284(M, 88), 269(85), 225(100), 195(98), 151(14), 137(17), 73(32)
1c	**7a**	15	29.18	284(M, 51), 269(11), 254(100), 73(22)
	10	1.3	33.11	296(M, 50), 281(100), 193(17), 165(4), 73(100)
	11a	0.9	35.33	326(M, 44), 311(100), 223(12), 73(88)
2c	**11a**	tr.**	35.33	326(M, 31), 311(85), 223(15), 73(100)
	12a	0.6	35.89	356(M, 5), 341(100), 311(25), 281(6), 207(4), 73(31)
3c	**1c**	tr.	31.05	238(M, 39), 223(98), 208(49), 193(100), 180(37), 165(85), 77(80), 73(61)
	13a	3.6	33.58	372(M, 91), 342(100), 254(41), 165(11), 73(93)
	13b	tr.	32.31	314(M, 100), 298(33), 284(47), 254(27), 165(25), 77(76), 73(62)
4c	**3c**	8.6	34.50	268(M, 37), 253(51), 238(93), 223(100), 195(17), 137(10), 73(24)
	11b	4.5	33.81	268(M, 53), 253(48), 238(100), 223(94), 195(60), 137(21), 77(51), 73(49)
	12a	0.6	35.88	341(M-15, 100), 281(20), 207(47), 77(39), 73(34)
	14	1.1	32.92	344(M, 100), 314(72), 195(43), 75(84), 73(72)

* retention time ** trace

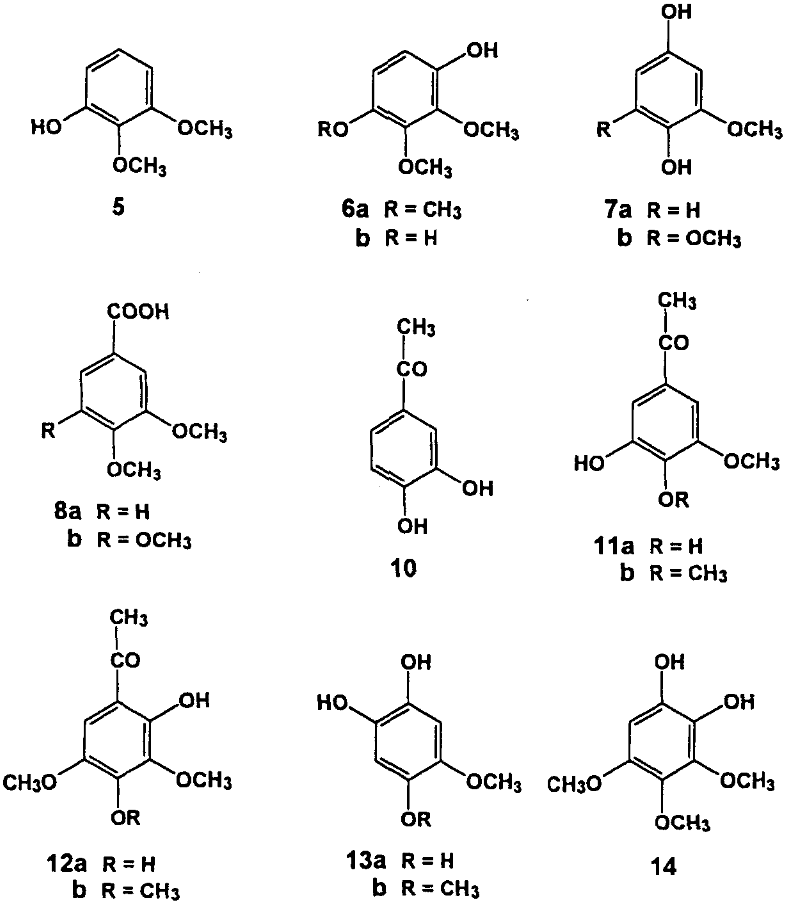


FIGURE 2. Products from reaction of compounds **4a**, **1b-4b**, and **1c-4c** with UV-peroxide

substitution onto the ring. The structure of **5** follows from its similar mass spectrum but different GC retention time to that of syringol (**2a**), while assignment of structure to **6a** is made on the basis of the expected electrophilic attack at the C-4 position of the aromatic ring. Compound **6b** may be formed by replacement of the methoxyl group of **6a** by hydroxyl, or from **5** by hydroxyl substitution at the strongly activated *para* position to the phenol under alkaline conditions[35]. The absence of aromatic compounds in the product mixtures from compounds **1a-1c** is probably a result of their strong propensity to give aliphatic acid products by ring opening.

The aldehydes vanillin (**1b**) and syringaldehyde (**2b**) reacted for 20 min under the UV-peroxide conditions gave the quinols **7a** and **7b**, in 83% and 79% yield, respectively, as the sole products (Table 1). This rapid reaction is well-documented as the Dakin reaction[1,4,36], and the formation of the quinols follows from reaction of the hydroperoxide anion through the intermediacy of a quinhydrol[4]. The non-phenolic aldehydes veratraldehyde (**3b**) and 3,4,5-trimethoxybenzaldehyde (**4b**) also reacted rapidly under UV-peroxide conditions, giving veratric acid (**8a**) and 3,4,5-trimethoxybenzoic acid (**8b**) in 36% and 59% yield, respectively. The acids **8a** and **8b** were also the sole oxidation products from peroxide reaction of the aldehydes in the absence of UV light. The oxidation of veratraldehyde can be understood in terms of attack of hydroperoxide anion on the carbon atom of the carbonyl group to give a peroxy-intermediate **9** (Figure 3). Removal of the benzyl proton in **9** with alkali and subsequent electron shifts with the displacement of the hydroxyl group gives veratric acid as the product.

Reaction of acetoguaiacone (**1c**) with UV-peroxide gave the hydroquinol **7a**, and smaller amounts of the acetophenones **10** and **11a** (Table 1). Compound **7a** is formed as a result of the Dakin reaction, whereas **10** results from replacement of the methoxyl group in **1c** by hydroxyl, and **11a** by substitution of hydroxyl in the aromatic ring *ortho* to the hydroxyl group (*cf* chlorination of acetoguaiacone[36]). However, no hydroquinone was identified among the products of oxidation of acetosyringone (**2c**) with UV-peroxide - only small amounts of the demethoxylation product **11a** and the hydroxylation product **12a** resulted (Table 1).

Acetoveratrone (**3c**) on reaction with UV-peroxide gave trace amounts of acetoguaiacone (**1c**) by replacement of the methoxyl group with hydroxyl, and compounds **13a** and **13b**, in which the acetyl group was displaced by hydroxyl (Table 1). Formation of the quinol **13a** could occur through a Dakin reaction after demethoxylation, or by direct displacement of the acetyl group by a hydroxyl radical. The displacement of the acetyl group in acetoveratrone by hydroxyl to form **13b** would probably occur by the latter mechanism. The ring-substitution by

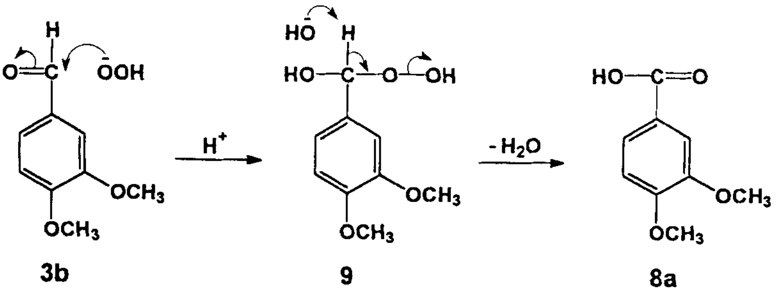


FIGURE 3. Mechanism for oxidation of veratraldehyde to veratric acid with hydrogen peroxide

hydroxyl to give **13a** and **13b** is considered to occur at the position *para* to the methoxyl group. Oxidation of 3,4,5-trimethoxyacetophenone (**4c**) with UV-peroxide gave products analogous to those for acetoveratrone. Compounds formed included **3c** and **11b**, resulting from demethoxylation, compound **14**, resulting from displacement of the acetyl group by hydroxyl, and compound **12a**, in which hydroxyl substitution occurred (Table 1).

Reaction of guaiacylpropane (**1d**) and syringylpropane (**2d**) with UV-peroxide gave mixtures which contained aliphatic acids[33] but no aromatic products were identified. However, the non-phenolic compound veratrylpropane (**3d**) yielded a mixture from which 17 products were tentatively identified, in addition to the starting material (Table 2, Figure 4). The propensity of the propylphenols to form ring-opened products is probably due to the activating effect of the propyl group towards electrophilic attack of superoxide anion radicals on the mesomeric phenoxyl radical at the carbon atom bearing the methoxyl group. In contrast, the non-phenolic compound **3d** would undergo substitution and displacement reactions with hydroxyl radicals.

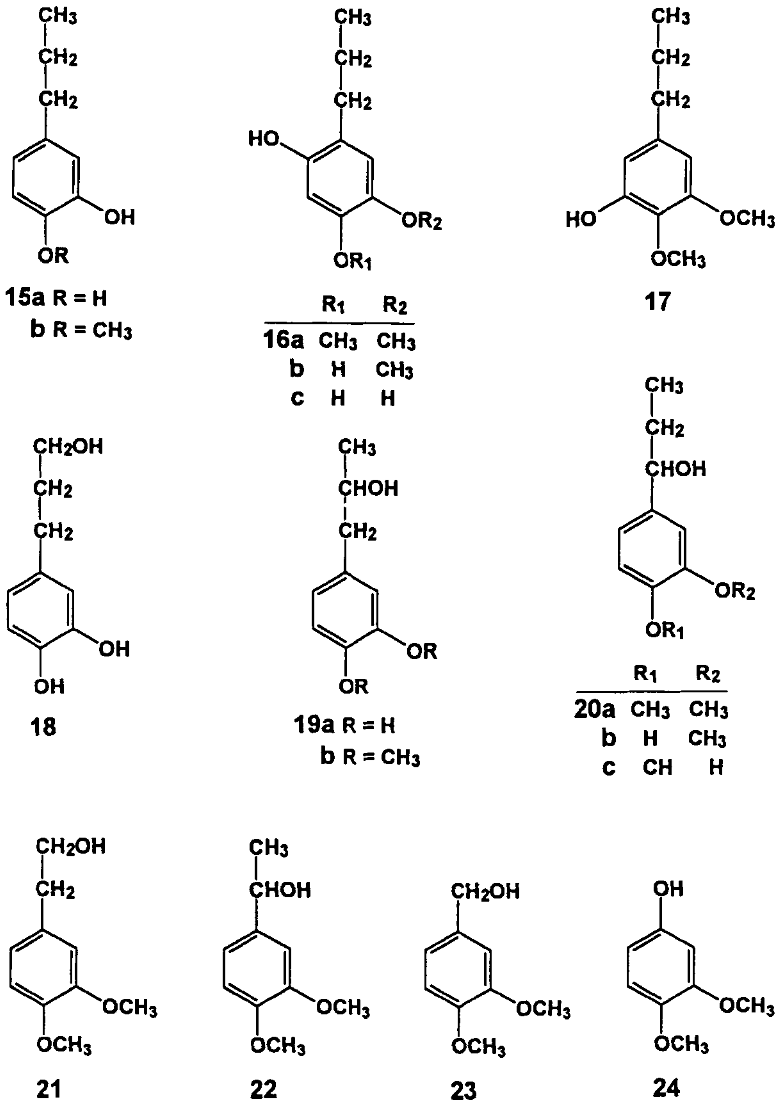
Use was made of the following rules for structural assignment, based on elution times from the GC column: (i) compounds with 3-hydroxy-4-methoxy aromatic substitution elute earlier than those with 4-hydroxy-3-methoxy substitution[27], (ii) compounds with hydroxyl aromatic substitution *ortho* to the

TABLE 2

GC-MS data on trimethylsilylated reaction products of veratrylpropane (**3d**) with UV-peroxide

Product	Yield (%)	GC RT* (min)	MS data *m/z* (% of base peak)
15b	tr.**	27.05	238(M, 34), 223(12), 82), 179(100), 149(16), 73(21)
24	tr.	27.17	226(M, 86), 211(88), 199(11), 153(10), 73(100)
1d	2.1	27.28	238(M, 33), 223(17), 209(100), 179(61), 149(16), 73(24)
ISTD^{+}		28.30	
15a	5.3	29.00	296(M, 80), 267(84), 179(71), 149(16), 73(100)
21	1.2	29.15	254(M, 32), 239(100), 227(71), 211(30), 181(31), 111(21), 73(84)
16a	2.3	29.65	268(M, 48), 253(23), 239(80), 209(100), 194(16), 73(36)
22	2.4	29.75	254(M, 10), 227(100), 137(99), 109(19), 73(54)
23	1.5	29.90	240(M, 21), 225(7), 209(15), 151(100), 73(20)
17	8.3	30.26	268(M, 68), 253(16), 238(100), 209(88), 73(28)
20a	23	30.57	268(M, 5), 253(2), 239(100), 73(26)
19b	10	31.56	268(M, 59), 253(21), 239(100), 209(10), 179(10), 151(10), 117(32), 73(54)
20c	3.2	31.82	326(M, 9), 297(100), 73(43)
16b	tr.	32.51	326(M, 60), 297(40), 267(15), 237(11), 209(41), 151(9), 73(100)
20b	1.5	32.91	326(M, 68), 297(100), 267(13), 238(5), 223(9), 73(71)
19a	tr.	33.14	384(M, 9),355(10),326(10), 211(25), 179(32), 154(55), 117(93), 73(100)
16c	1.7	34.05	384(M, 6), 356(12), 327(100), 297(10), 224(11), 73(53)
18	tr.	36.04	384(M, 7), 356(5), 327(20), 267(30), 209(18), 179(8), 147(19), 117(31), 73(100)

* retention time ** trace $^{+}$ internal standard



15a R = H
b R = CH_3

	R_1	R_2
16a	CH_3	CH_3
b	H	CH_3
c	H	H

17

18

19a R = H
b R = CH_3

	R_1	R_2
20a	CH_3	CH_3
b	H	CH_3
c	CH	H

21 **22** **23** **24**

FIGURE 4. Products from reaction of compound **3d** with UV-peroxide

sidechain elute earlier than those with *meta* substitution[27], and (iii) hydroxyl aromatic substitution will occur in positions *para* to methoxyl groups rather than in *ortho* positions[35]. Products from reaction of **3d** include those in which methoxyl groups were replaced by hydroxyl groups (**1d**, **15a** and **15b**), and the analogous compounds hydroxylated in the position *ortho* (**16a-c**) and *meta* to the propyl sidechain (**17**) (Table 2). Other products were those in which the sidechain was hydroxylated (**18-20**), and those in which the sidechain was also diminished in length (**21-24**). The structures of the sidechains follow from the mass fragments in their mass spectra (Table 2). Thus hydroxyl radicals react with sidechains of lignin models, resulting in both hydroxylation and cleavage of carbon-carbon bonds.

Concluding remarks

The study has shown that lignin model compounds react with alkaline hydrogen peroxide irradiated with UV light at 254 nm to give a variety of products resulting from substitution and replacement reactions on the aromatic ring and on the sidechain by hydroxyl groups, and oxidative cleavage of sidechains and aromatic rings. These products are similar to those found in reaction mixtures of lignin models with UV-peroxide at pH 5. Lignin model phenols are susceptible to ring-opening reactions by reaction with superoxide radical anions, and ring opening is promoted by electron-donating substituents on the aromatic rings. Non-phenolic lignin models react preferentially by hydroxylation on the aromatic rings and the sidechains. The diverse nature of the products from the lignin model compounds are indicative of the complexity of the reactions taking place during the UV-peroxide decomposition of lignin.

EXPERIMENTAL

Chemicals

Unless otherwise stated, the lignin model compounds were obtained from commercial sources. Catalytic hydrogenation of eugenol, 4-allylsyringol and 4-allylveratrole gave compounds **1d**, **2d** and **3d**, respectively.

UV-peroxide treatment of model compounds

A solution of a lignin model compound (0.3 mmol) in aqueous sodium hydroxide adjusted to pH 11 (45 mL) in an 80 mL quartz tube was heated to 40°C.

Hydrogen peroxide (30%, 3 mmol) was added, and the tube was placed in the centre of a Rayonet photochemical reactor (Southern New England Ultraviolet Co., Middletown, CT, USA) with 10 mercury lamps emitting UV light at 254 nm, and the reaction was maintained at 40°C for 60 min. Portions of the reaction mixtures (5 mL) were acidified to pH 2 with 0.1M sulfuric acid, and an aliquot of a solution of salicylic acid in acetone was added as an internal gas chromatography standard. The mixture was freeze dried, the residue was extracted with acetone (10 x 2 mL), and the combined extracts were dried over sodium sulfate. The solvent was removed *in vacuo*, and the residue was silylated with *N,O*-bis-(trimethylsilyl)trifluoroacetamide for 1 h at 60°C. The silylated product was analysed by gas chromatography-mass spectrometry (GC-MS).

GC-MS analysis

The GC-MS system consisted of a Hewlett Packard HP5890 series II gas chromatograph fitted with an autoinjector and an HP5971 mass selective detector. The column was a J & W bonded phase DB5 fused silica column (30 m x 0.25 mm ID) with a film thickness 0.25 μm. GC conditions were: injector temp. 250°C, detector temp. 320°C, oven temp. 40°C for 3 min, programmed at the rate of 5°C/min to 180°C, 2 min at 180°C, 30°C/min to 300°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 products were analysed by comparison of the peak areas with that of silylated salicylic acid, the internal standard, assuming unit response.

ACKNOWLEDGEMENTS

The authors are grateful to Mr Ross Wearne for his skilful assistance with the GC-MS experiments, and to the Cooperative Research Centre for Hardwood Fibre and Paper Science for providing a PhD Scholarship to Y.-P. Sun.

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