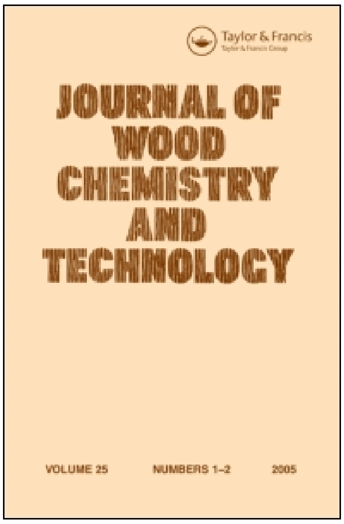

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DISCOLORATION OF α-CARBONYL-FREE LIGNIN MODEL COMPOUNDS UNDER UV LIGHT EXPOSURE

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ABSTRACT

A series of α-carbonyl-free lignin model compounds was prepared and adsorbed onto bleached chemical pulp. The rates of discoloration of these materials, under simulated solar light exposure, were established and compared to that of peroxide bleached methylated (alkali and dimethyl sulfate) and non-methylated chemithermomechanical pulps. Phenolic phenylcoumarone and phenolic stilbenes were found to be the most sensitive chromophores under UV irradiation, both inducing a strong yellowing. Also, monophenolic biphenyl and biphenylmethane entities were shown to be prone to discolouration in contrast to the biphenolic and dimethylated ones. Moreover, the catechol structures which are known to be easily oxidizable into ortho quinones, display significant yellowing only when their absorption spectra are shifted above 300 nm where the light source emits. The behaviour of the phenolic stilbenes and the biphenyl catechol is reminiscent of the behaviour of CTMP. This indicates the possible involvement of such stuctures as being mainly responsible for the discoloration of lignocellulosic materials under UV irradiation. A mechanism is proposed to account for the photoyellowing of the models involving a cyclohexadienone hydroperoxide as intermediate, which is formed by UV irradiation from a complex between the phenol and ground state oxygen.

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INTRODUCTION

The mechanism of discoloration of high yield pulps under UV light exposure is still a topic of interest, extensive research activity and debate[1-13], even if the predominant role of lignin is beyond question since the work of Nolan et al.[14] Among the lignin chromophores able to absorb the UV portion of sunlight (300-400 nm), α-carbonyl entities have been put forward as being the main sensitizers of the photoyellowing process[15], although some biphenyls and ring conjugated double bonds were invoked.[15,16]

The main action of α-carbonyl groups, outlined in the following scheme, is considered to be the abstraction of hydrogen from phenolic groups giving phenoxyl radicals, which are oxidized by ground state oxygen in colored ortho and para quinones.[12,13] Also, quinones appear to be able to generate singlet oxygen which might contribute to the oxidation process.[12]

$$^{3}({>}C{=}O)^{*} + ArOH \longrightarrow \bullet{>}C\text{-}OH + ArO\bullet$$

$$ArO\bullet + {}^{3}O_{2} \longrightarrow \text{Quinones}$$

$$\left\{\begin{matrix} ^{3}({>}C{=}O)^{*} \\ \\ ^{3}(ArCH{=}CH\text{-}Z)^{*} \end{matrix}\right. + {}^{3}O_{2} \longrightarrow \left\{\begin{matrix} {>}C{=}O \\ \\ ArCH{=}CH\text{-}Z \end{matrix}\right. + {}^{1}O_{2}{}^{*}$$

$$^{1}O_{2}{}^{*} + ArOH \longrightarrow \text{Quinones}$$

$$\text{Quinones} + h\nu \longrightarrow \text{Photoproducts}$$

Intramolecular ß-bond cleavage in the α-carbonyl ß-O-4 structures, also produces phenoxyl radicals, and this has been claimed as probably being responsible for the yellowing process in

In another respect, the discoloration of high yield pulps has been correlated with the number of phenolic groups present in the lignin polymer.[17] Also, blocking the phenolic groups by etherification or esterification has improved the light stability of the material to a greater extent than the use of reductive treatments.[17] Considering i) these results on the pulp ii) the facile autoxidation of phenols to colored derivatives[18-20] and iii) because the photophysical and photochemical studies on phenols, mainly by flash photolysis[21-25], have shown the direct generation of phenoxy radicals by light, it may be concluded that one of the main causes of the discoloration process is due to the photoreactivity of the absorbing phenolic part of the lignin which is oxidized to colored materials under UV light.

The present article describes an approach for determining the role of phenols in the discoloration process of high yield pulps by measuring the rate of photoyellowing, in simulated solar light, of selected α-carbonyl-free phenolic lignin models (depicted in Figure 1) themselves and when adsorbed on lignin-free paper. In addition, the yellowing of methylated and non-methylated bleached CTMP were measured for comparison. Also, the yellowing of some models in degassed and non-degassed aqueous ethanolic solution (10^{-3} M) have been measured to assess the role of oxygen.

EXPERIMENTAL

GENERAL

Melting points were measured with a Kofler block. The NMR spectra were recorded on a Perkin-Elmer R-24B (60 MHz) spectrometer and/or a Bruker AC 250 FT spectrometer. The IR and UV spectra were recorded on Perkin-Elmer 1420 and Cary 219 spectrometers, respectively. Mass spectra were obtained using a VG Micromass type 16F instrument. Elemental analyses were carried out at the CNRS Microanalysis Centre (Lyon). All synthesized compounds were purified by column chromatography on silica gel using the appropriate eluents. The solid products were crystallized

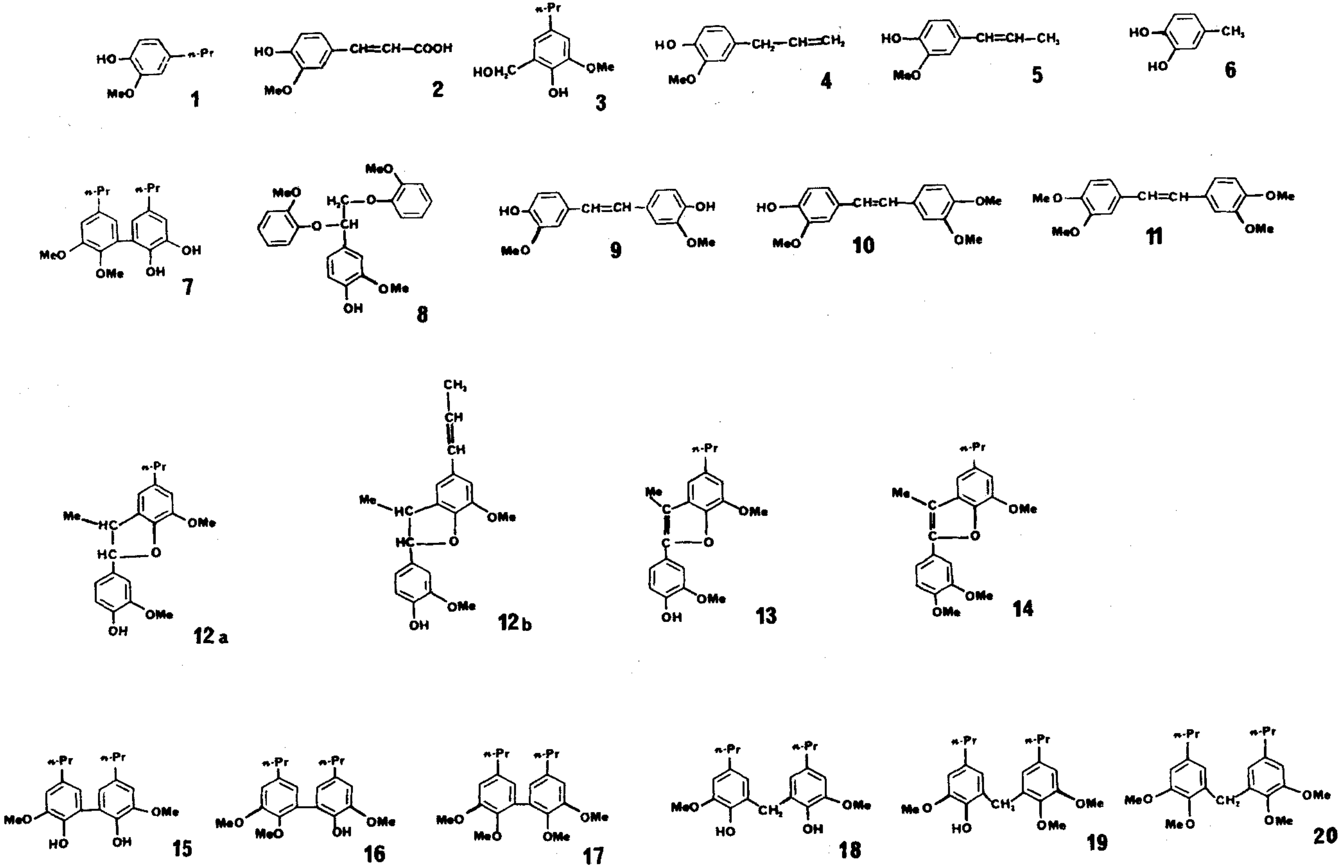


Figure 1. Formulae of compounds used in study.

after chromatography. The purity of the compounds was confirmed by HPLC (NH_2 column, eluent dichloromethane/heptane mixtures).

MATERIALS

Ferulic acid, (2), eugenol, (4), isoeugenol, (5), and 4-methylcatechol, (6), were purchassed from Aldrich Chemical Company. Compound, (1), was obtained by hydrogenation of eugenol using a Pd/C catalyst.

3,3'-Dimethoxy-4,4'- dihydroxystilbene (9)

This compound was synthesized via a spirocyclohexadienone intermediate according to the procedure described by Sieber.[26] Yield:20% ; m.p.215°C (lit. 213-215°C[27]).
^1H NMR (CD_3COCD_3) δ ppm 6.5-6.7 (m, ArH, 8H); 6.4 (s, OH, 2H); 3.3 (s, OCH_3, 6H).
IR νmax (KBr) 3500-3200, 3010, 2960, 2920, 1585, 1500, 1450, 1420, 1370, 1320, 1270, 1245, 1220, 1150, 1110, 1020, 935, 840, 815, 790 cm^{-1}.
MS (70 ev) e/z (rel. int.) 272 (100, $M^{+}\cdot$).
UV (methanol) λmax nm (ϵ $Lmol^{-1}cm^{-1}$) 295 (11100); 306 (12660); 333 (19660).

3,3',4-Trimethoxy-4'-hydroxystilbene (10)

Compound, (10), was synthesized in 4 steps from 3,4-dimethoxybenzyl alcohol which is converted successively to 3,4-dimethoxybenzyl chloride, 3,4-dimethoxybenzyl triphenylphosphonium chloride and then condensed with vanillin acetate.

3,4-DIMETHOXYBENZYL CHLORIDE

Thionyl chloride (6.5 mL, 0.9 mol) and 3,4-dimethoxybenzyl alcohol (15 g, 0.89 mol) in anhydrous benzene were refluxed for 10 h. After cooling to room temperature, the solvent was evaporated under vacuum at room temperature giving an oily residue (14.1 g) which was used without further purification. Yield:85% .
^1H NMR ($CDCl_3$) δ ppm 6.5-6.8 (m, ArH, 3H); 4.5 (s, CH_2, 2H); 3.7 (s, OCH_3, 6H).

3,4-DIMETHOXYBENZYL TRIPHENYLPHOSPHONIUM CHLORIDE

As described by Miller[28], the chloride derivative (13.5 g, 72.6 mmol) and triphenylphosphine (19 g, 72.6 mmol) in benzene (100 mL) were stirred first for 24 h at room temperature, then refluxed for another 24 h giving a white precipitate which was filtered. Yield:68%, m.p.230-234°C.

^{1}H NMR ($CDCl_3$) δ ppm 7.3-7.9 (m, ArH, 15H); 7.1-7.2 (m, ArH, 3H); 5.25 (d, CH_2, 2H, J_{HP}=13Hz); 3.7 (s, OCH_3, 3H).

3,3',4-TRIMETHOXY-4'-ACETOXYSTILBENE

The stilbene derivative was obtained by reaction of phosphonium chloride with vanillin acetate[11] as described by Lonsky[27]. The product, isolated as a cis/trans mixture, was purified by column chromatography on silica gel and crystallized in ethanol. Yield:75%, m.p.142°C.

^{1}H NMR ($CDCl_3$) δ ppm 6.2-7.4 (m, ArH, 6H and vinylic, 2H); 3.8 (s, OCH_3, 6H); 3.6 (s, OCH_3, 3H); 2.2 (s, $OCOCH_3$, 3H).

IR νmax (KBr) 3020, 2995, 2950, 2920, 2820, 1750, 1680, 1590, 1505, 1460, 1420, 1360, 1270, 1195, 1150, 1120, 900, 870 cm^{-1}.

3,3',4-TRIMETHOXY-4'-HYDROXYSTILBENE (**10**)

The preceding acetate was saponified with an methanolic solution of potassium carbonate by heating under reflux for 3 h. After usual work-up and chromatography the trans isomer was isolated in pure form. Yield:70%, m.p.100-102°C.

^{1}H NMR ($CDCl_3$) δ ppm 6.6-7.4 (m, ArH, 6H and vinylic, 2H); 5.55 (s, OH, 1H); 3.9 (s, OCH_3, 6H); 3.8 (s, OCH_3, 3H).

IR νmax (KBr) 3500-3300, 3020, 2990, 2940, 2920, 1660, 1585, 1505, 1460, 1425, 1290, 1265, 1250, 1160, 1150, 1130, 1040, 960, 850, 820 cm^{-1}.

MS (70 ev) e/z (rel. int.) 286 (3.1, $M^{+\cdot}$), 152 (100), 151 (99), 123 (15), 109 (20), 81 (28).

UV (methanol) λmax nm (ϵ $Lmol^{-1}cm^{-1}$) 220 (16420); 294 (12550), 305 (14230); 330 (18100).

Anal. calc. for $C_{17}H_{18}O_4$: C, 71.33; H, 6.29; O, 22.38. Found: C, 70.57; H, 6.21; O, 22.92.

3,3',4,4-Tetramethoxystilbene (11)

This derivative previously prepared by Sieber[26] was synthesized by the method used for compound, (10). 3,4-Dimethoxybenzaldehyde was used instead of vanillin acetate. Yield:50% of a 50/50 cis-trans mixture, m.p.118-120°C. The cis isomer was isolated by crystallization from ethanol. m.p.120°C.

^{1}H NMR ($CDCl_3$) δ ppm 6.2-6.7 (m, ArH, 6H and vinylic, 2H); 3.7 (s, OCH_3, 6H); 3.6 (s, OCH_3, 6H).

IR νmax (KBr) 3080, 3000, 2960,2840, 1600, 1580, 1510, 1470, 1450, 1420, 1320, 1260, 1240, 1160, 1140, 1020, 860, 810, 780, 760 cm^{-1}.

MS (70 ev) e/z (rel. int.) 300 (100, $M^{+}\cdot$); 285 (32); 271 (3.2).

UV (methanol) λmax nm (ϵ $Lmol^{-1}cm^{-1}$) 267 (9960); 275 (10600).

Anal. calc. for $C_{18}H_{20}O_4$: C, 72.00; H, 6.67; O, 21.33. Found: C, 71.94; H, 6.49; O, 21.19.

2,2'-Dihydroxy-3,3'-dimethoxy-5,5'-di-n-propyldiphenyl (15)

This compound was prepared via oxidative coupling of 2-methoxy-4-n-propylphenol, (1),[29] following the procedure described by Haynes[30] for analogous derivatives. Yield: 50%, m.p.152°C (lit. 152°C[31]).

^{1}H NMR ($CDCl_3$) δ ppm 6.7 (s, ArH, 4H); 5.9 (s, OH, 2H); 3.85 (s, OCH_3, 6H); 2.55 (t, CH_2, 4H); 1.7 (m, CH_2, 4H); 1 (t, CH_3, 6H).

IR νmax (KBr) 3300-3200, 3000, 2940, 2920, 2900, 2840,2820, 1580, 1480, 1450, 1440, 1410, 1360, 1300, 1250, 1220, 1175, 1145, 1080, 1040, 1020, 910, 840, 795, 730 cm^{-1}.

MS (70 ev) e/z (rel. int.) 33O (100, $M^{+}\cdot$); 302 (16); 301 (77); 227 (10); 136 (17); 43 (19).

UV (methanol) λmax nm (ϵ $Lmol^{-1}cm^{-1}$) 218 (41070); 248 (9810); 288 (5780).

Anal. calc. for $C_{20}H_{26}O_4$: C, 72.73; H, 7.88; O, 19.39. Found: C, 72.84; H, 7.93; O, 18.59.

2-Hydroxy-,2',3,3'-trimethoxy-5,5'-di-n-propyldiphenyl (16)

This compound was synthesized by refluxing, under nitrogen for 12 h, compound, (15) (4g, 12.1 mmol), KOH (0.67 g, 12.1 mmol), and dimethyl sulfate (3.82 g, 30.3 mmol) in a water-THF mixture (10 mL/150 mL). After work-up and column chromatography, 2.8 g of (16) were isolated as a white solid. Yield: 50%, m.p.50°C.

^1H NMR ($CDCl_3$) δ ppm 6.6 (s, ArH, 4H); 6.3 (s, OH, 1H); 3.75 (s, OCH_3, 6H); 3.5 (s, OCH_3, 3H); 2.4 (t, CH_2, 4H); 1.5 (m, CH_2, 4H); 0.7 (t, CH_3, 6H).

IR νmax (KBr) 3500-3400, 3020, 2940, 2920, 2830, 1570, 1480, 1450, 1410, 1345, 1255, 1225, 1170, 1140, 1095, 1050, 1010, 900, 830, 730 cm^{-1}.

MS (70 ev) e/z (rel. int.) 344 (100, $M^{+\cdot}$); 316 (16); 315 (72); 297 (9); 283 (11); 143 (23).

UV (methanol) λmax nm (ϵ $Lmol^{-1}cm^{-1}$) 213 (44600); 284 (4580).

Anal. calc. for $C_{21}H_{28}O_4$: C, 73.26; H, 8.14; O, 18.60. Found: C, 73.36; H, 7.89; O, 18.37.

2,2',3,3'-Tetramethoxy-5,5'-di-n-propyldiphenyl (17)

This derivative was obtained by methylation of (16) with diazomethane using a procedure described by Dence[17] for alkylation of high yield pulps. After chromatography, compound, (17) was obtained pure as an oil. Yield: 62 %

^1H NMR ($CDCl_3$) δ ppm 6.9 (s, ArH, 4H); 3.7 (s, OCH_3, 6H); 3.5 (s, OCH_3, 6H); 2.4 (t, CH_2, 4H); 1.5 (m, CH_2, 4H); 0.8 (t, CH_3, 6H).

IR νmax (NaCl film) 3000, 2940, 2915, 2840, 1570, 1470, 1450, 1400, 1350, 1260, 1220, 1180, 1130, 1100, 1050, 1010, 900, 830, 780 cm^{-1}.

MS (70 ev) e/z (rel. int.) 358 (100, $M^{+\cdot}$); 329 (46); 283 (13.4); 181 (30); 150 (13.5); 84(24).

UV (methanol) λmax nm (ϵ $Lmol^{-1}cm^{-1}$) 212 (44600); 278 (4860).

Anal. calc. for $C_{22}H_{30}O_4$: C, 73.74; H, 8.38; O, 17.89. Found: C, 73.63; H, 8.71; O, 17.59.

2,2'-Dihydroxy-3,3'-dimethoxy-5,5'-di-n-propyldiphenylmethane (18) and 2-hydroxymethyl-3-methoxy-4-n-propylphenol (3)

Compound, (18), was prepared, as described by Smith[32] for similar derivatives, by refluxing a mixture of phenol, (1) (10.8 g, 65 mmol), formaldehyde (10 g, 0.1 mol) and sodium hydroxide (5.2 g, 0.130 mol) in water (150 mL). After the usual work-up and column chromatography on silica gel, compound, (18), was isolated as a white solid (5 g). Yield: 50%, m.p.106°C. In addition, 2-hydroxymethyl-3-methoxy-4-n-propylphenol, (3), was obtained as a byproduct (0.74 g). Yield: 5.8%, m.p.58°C.

COMPOUND (18)

^{1}H NMR ($CDCl_3$) δ ppm 6.5 (d, ArH, 4H); 5.9 (s, OH, 2H); 3.9 (s, CH_2, 2H); 3.8 (s, OCH_3, 6H); 2.5 (t, CH_2, 4H); 1.5 (m, CH_2, 4H); 0.9 (t, CH_3, 6H).

IR νmax (KBr) 3320-3220, 3020, 2980, 2920, 2890, 2830, 1580, 1480, 1450, 1430, 1415, 1350, 1280, 1230, 1220, 1210, 1130, 1070, 1050, 960, 910, 825, 780, 760 cm^{-1}.

MS (70 ev) e/z (rel. int.) 344 (100, $M^{+\cdot}$); 315 (28); 179 (51); 178 (51); 166 (97); 149 (43); 143 (62); 137 (34).

UV (methanol) λmax nm (ε $Lmol^{-1}cm^{-1}$) 226 (21490); 280 (6120).

Anal. calc. for $C_{21}H_{28}O_4$: C, 73.26; H, 8.14; O, 18.60. Found: C, 73.46; H, 8.14; O, 18.60.

COMPOUND (3)

^{1}H NMR ($CDCl_3$) δ ppm 6.5 (s, ArH, 2H); 4.6 (s, CH_2OH, 2H); 3.6 (s, OCH_3,3H); 2.4 (t, CH_2, 2H); 1.5 (m, CH_2, 2H); 0.9 (t, CH_3, 3H).

2-Dihydroxy-,2',3,3'-trimethoxy-5,5'-di-n-propyldiphenylmethane (19)

This derivative was synthesized by monoalkylation of (18) as described for the preparation of (16). Yield: 70%, Oil.

^{1}H NMR ($CDCl_3$) δ ppm 6.5 (d, ArH, 4H); 5.85 (s, OH, 1H); 3.9 (s, CH_2, 2H); 3.4 (s, OCH_3, 6H); 3.35 (s, OCH_3, 3H); 2.4 (t, CH_2, 4H); 1.5 (m, CH_2, 4H); 0.9 (t, CH_3, 6H).

IR νmax (NaCl film) 3500-3300, 3020, 2930, 2900, 2840, 1590, 1570, 1480, 1450, 1420, 1330, 1280, 1220, 1180, 1140, 1090, 1070, 1005, 940, 830, 780, 750 cm^{-1}.

MS (70 ev) e/z (rel. int.) 358 (100, $M^{+\cdot}$); 329 (41); 283 (14), 180 (82); 165 (14); 151 (30); 150 (30); 83 (31).

UV (methanol) λmax nm (ϵ $Lmol^{-1}cm^{-1}$) 224 (22000); 278 (3960).

Anal. calc. for $C_{22}H_{30}O_4$: C, 73.74; H, 8.38; O, 17.88. Found: C, 74.09; H, 8.42; O, 17.86.

2,2',3,3'-Tetramethoxy-5,5'-di-n-propyldiphenylmethane (20)

Methylation of (18) with an excess of sodium hydroxide and dimethyl sulfate in a THF-water mixture gave compound, (20), as an oil. Yield: 65% .

^1H NMR ($CDCl_3$) δ ppm 6.4 (d, ArH, 4H); 3.85 (s, CH_2, 2H); 3.7 (s, OCH_3,6H); 3.6 (s, OCH_3, 6H); 2.35 (t, CH_2, 4H); 1.5 (m, CH_2, 4H); 0.85 (t, CH_3, 6H).

IR νmax (NaCl film) 3020, 2980, 2960, 2950, 2920, 2900, 1570, 1475, 1450, 1410, 1340, 1290, 1220, 1170, 1140, 1090, 1070, 1000, 825, 790, 760 cm^{-1}

MS (70 ev) e/z (rel. int.) 372 (100, $M^{+\cdot}$); 343 (30); 179 (35); 163 (28).

UV (methanol) λmax nm (ϵ $Lmol^{-1}cm^{-1}$) 222 (22030); 278 (2730).

Anal. calc. for $C_{23}H_{32}O_4$: C, 74.19; H, 8.60; O, 17.21. Found: C, 74.01; H, 8.89; O, 17.44.

2-(4'-Hydroxy-3'-methoxyphenyl)-3-methyl-5-n-propyl-7-methoxyphenylcoumarone (13)

The phenylcoumarone, (13), was obtained by sulfur dehydrogenation of dihydrodehydrodiisoeugenol ,(12), (phenyl coumaran) which was prepared in two steps from isoeugenol (5) via dehydrodiisoeugenol (12b). The numbering of the atoms of the different coumarans and coumarones is indicated in Figure 2.

DEHYDRODIISOEUGENOL (12b)

Compound, (12b), was prepared by oxidative coupling of (5) according the procedure described by Leopold.[33] Yield: 20%.

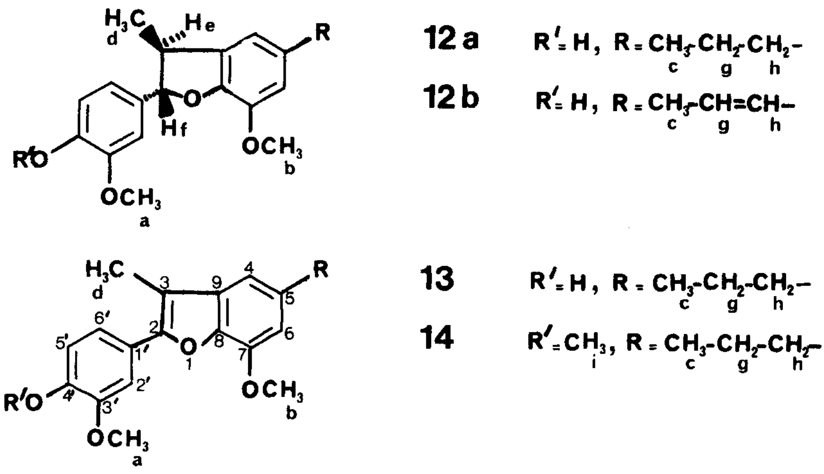


Figure 2. Coumaran and coumarone formulae.

m.p.134°C (lit 132-133[33]). Of note, is the stereochemistry of the C2-C3 bond found to be trans.[34]

^{1}H NMR (250 MHz, $CDCl_3$) δ ppm J Hz: ArH: 6.8-7 (m, 5H); H_h: 6.35, J_{hg}= 15.9, J_{hc}=1.5 (1H); H_g: 6.1, J_{hg}= 15.9, J_{gc}=6.5 (1H); HO: 5.65 (s, 1H); H_f: 5.1, J_{ef}= 9.5, (1H); H_a and H_b: 3.93 (s, 3H), 3.93 (s, 3H); H_e: 3.45, J_{ef}= 9.5, J_{ed}= 6.6 (1H); H_c: 1.92, J_{cg}= 6.5, J_{ch}= 1.5 (3H); H_d: 1.4, J_{de}= 6.6 (3H).

DIHYDRODEHYDRODIISOEUGENOL (12a)

Compound, (12a), could not be obtained in significant yield by the procedure described by Ralph.[35] The hydrogenation at atmospheric pressure was performed in acetic acid containing 7% of water with Pd/C as catalyst instead of $PdCl_2/BaSO_4$ used by Adler.[36] Compound, (12a), was obtained after the usual work-up and crystallization from ligroin (b.p. 50-60°C). Yield:75%, m. p.90-92°C (lit. 94°C[37], 89-91°C[36]). The choice of the solvent and the hydrogenation conditions were of the utmost importance for the obtainment of (12a). Methanol or ethanol gave mainly the hydrogenolysis product.

^{1}H NMR (250 MHz, CDCl$_3$) δ ppm J Hz: ArH: 6.6-7.15 (m, 5H); HO: 6 (s, 1H); H$_f$: 5.15, J$_{ef}$= 9.8, (1H); H$_a$ and H$_b$: 3.85 (s, 3H),3.95 (s, 3H);); H$_e$: 3.5, J$_{ef}$= 9.8, J$_{ed}$= 6.7 (1H); H$_h$: 2.5, J$_{hg}$= 7.2 (2H); H$_g$: 1.7, J$_{gc}$= J$_{gh}$= 7.2 (2H); H$_d$: 1.45, J$_{de}$= 6.7 (3H); H$_c$: 1.05, J$_{cg}$= 7.2 (3H).
IR νmax (KBr) 3600-3300, 3020, 2920, 2900, 2840, 1630, 1610, 1600, 1585, 1500, 1480, 1450, 1440, 1420, 1320, 1260, 1210, 1200, 1160, 1140, 1120, 1025, 940, 850, 800 cm^{-1}.
UV (methanol) λmax nm (ε Lmol^{-1}cm^{-1}) 228 (16000); 280 (5700).

PHENYLCOUMARONE (13)

This derivative was prepared following the procedure described by Spetz.[38] After column chromatography on silicagel (13), was isolated as a white solid. Yield: 50%, m.p.85°C (lit. 86.5-87.5°C[38]). The assigments of the ^{13}C NMR spectrum were made using DEPT sequences.
^{1}H NMR (250 MHz, CDCl$_3$) δ ppm J Hz: ArH: 6.7-7.6 (m, 5H); HO: 6.15 (s, 1H); H$_a$ and H$_b$: 4.05 (s, 3H), 4.25 (s, 3H);); H$_h$: 2.85, J$_{hg}$= 7.2 (2H); H$_d$: 2.6 (s, 3H); H$_g$: 1.95, J$_{gc}$= J$_{gh}$= 7.2 (2H); H$_c$: 1.15, J$_{cg}$= 7.2 (3H).
^{13}C NMR (CDCl$_3$) δ ppm 9.7 (C$_c$); 14.9 (C$_d$); 25.3 (C$_g$); 38.5 (C$_h$); 56.1 (C$_a$ and C$_b$); 107.6 (C$_{2'}$); 109.6 (C$_{5'}$);110.1 (C$_9$); 110.9 (C$_{6'}$); 114.8 (C$_6$); 120.6 (C$_4$); 124.1 (C$_3$); 135.1 (C$_5$); 138.0 (C$_{1'}$); 141.4 (C$_2$); 144.7 (C$_{4'}$); 145.9 (C$_8$); 146.9 (C$_{3'}$), 151.9 (C$_7$).
IR νmax (KBr) 3600-3300, 3020, 2990, 2940, 2910, 2840, 1585, 1500, 1475, 1450, 1440, 1415, 1380, 1360, 1300, 1260, 1215, 1140, 1080, 1050, 1030, 780, 755 cm^{-1}.
MS (70 ev) e/z (rel. int.) 326 (100, M$^{+\cdot}$); 298 (18), 297 (35), 327 (22).
UV (methanol) λmax nm (ε Lmol^{-1}cm^{-1}) 214 (33300); 304 (24400).

2-(3,4'-Dimethoxyphenyl)-3-methyl-5-n-propyl-7-methoxyphenylcoumarone (14)

Compound, (14), was synthesized by methylation of (13) using the procedure described for the preparation of (19) . Yield: 50%, m.p.90°C (lit. 91.5-92°C[38]). The assignments for the ^{13}C NMR spectrum were done using DEPT sequences.

^{1}H NMR (250 MHz, $CDCl_3$) δ ppm J Hz: ArH: 6.5-7.3 (m, 5H); H_a, H_b and H_i: 4.02 (s, 3H), 3.98 (s, 3H), 3.92 (s, 3H); H_h: 2.70, J_{hg}= 7.3 (2H); H_d: 2.4 (s, 3H); H_g: 1.68, J_{gc}= J_{gh}= 7.3 (2H); H_c: 1.00, J_{cg}= 7.3 (3H).

^{13}C NMR ($CDCl_3$) δ ppm 9.6 (C_c); 14.0 (C_d); 25.2 (C_g); 38.6 (C_h); 55.8 (C_i); 55.9 (C_a and C_b); 107.5 ($C_{2'}$); 109.9 ($C_{5'}$); 110.2 (C_9); 110.7 ($C_{6'}$); 111.1 (C_6); 119.7 (C_4); 124.4 (C_3); 132.9 (C_5); 137.9 ($C_{1'}$); 141.3 (C_2); 144.6 ($C_{4'}$); 148.9 (C_8); 149.0 ($C_{3'}$); 151.0 (C_7).

IR νmax (KBr) 3040, 2990, 2950, 2920, 2860, 2840, 1620, 1600, 1520, 1490, 1465, 1450, 1370, 1310, 1265, 1240, 1150, 1105, 1060, 1030, 870, 840, 800, 760 cm^{-1}.

MS (70 ev) e/z (rel. int.) 340 (100, $M^{+\cdot}$).

UV (methanol) λmax nm (ε $Lmol^{-1}cm^{-1}$) 215 (33000); 305 (24800).

2,3-Dimethoxy,-2',3'-dihydroxy-5,5'-di-n-propyldiphenyl (7)

Catechol, (7), was made by reduction of the corresponding orthoquinone which has been obtained by periodate oxidation[40,41] of the monophenol, (16).

To 1.85 g (5.16 mmol) of substrate, (16), dissolved in 50 mL of dichloromethane, was added 1 mL of acetic acid and a solution of $NaIO_4$ (1.22 g, 5.68 mmol) in 10 ml of water. Benzyltriethylammonium chloride (50 mg) was added to the mixture and the reaction mixture was stirred for 24 h. The organic layer was washed with water, dried over sodium sulfate and evaporated to dryness leaving 1.5 g of a dark red residue. This material, without purification, was dissolved in ethanol (50 mL) and reacted with a mixture of 1.5 g (37.5 mmol) of sodium hydroxide and 2 g (11.49 mmol) of sodium dithionite in 50 ml of water for 1 h. After acidification with sodium bisulfite, extraction with dichloromethane and work-up 1.3 g a yellow oil was obtained. A 300 mg sample of the preceding mixture, separated by preparative thin layer chromatography yielded 150 mg of pure catechol (7) as a solid.

Overall yield from (16): 38%, m.p.54-56 °C.
^{1}H NMR ($CDCl_3$) δ ppm 7.3 (s, OH, 1H); 6.5-6.9 (m, ArH, 4H); 5.9 (s, OH, 1H); 3.9 (s, OCH_3, 3H); 3.6 (s, OCH_3, 3H); 2.5 (t, CH_2, 4H); 1.5 (m, CH_2, 4H); 0.95 (t, CH_3, 6H).
IR νmax (NaCl film) 3520, 3500-3100, 3020, 3000, 2960, 2920, 2860, 1590, 1490, 1465, 1450, 1420, 1380, 1340, 1270, 1250, 1230, 1180, 1140, 1070, 1000, 980, 830, 785 cm^{-1}.
MS (70 ev) e/z (rel. int.) 330 (100, $M^{+\cdot}$); 301 (52); 259 (9); 136 (19).
UV (methanol) λmax nm (ϵ $Lmol^{-1}cm^{-1}$) 283 (2870); 219 (6000, shoulder).

1-(4'-Hydroxy-3'-methoxyphenyl)-1-(2"-methoxyphenoxy)-2-(2'''-methoxyphenoxy)-ethanol (8)

The trimer, (8), was synthesized by reacting guaiacol with the quinone methide generated from 1-(4'-hydroxy-3'-methoxyphenyl)-2-(2'-methoxyphenoxy)ethanol[39] following the procedure described by Ralph.[42]

To a solution of the above named benzyl alcohol (1.45 g, 5 mmol) in dichloromethane (100 mL), under nitrogen, was slowly added trimethylbromosilane (1.53 g, 10 mmol) in dichloromethane (20 mL). After 10 min of stirring at room temperature, 125 mL of a saturated bicarbonate solution was added, the organic layer was washed with water, and dried with sodium sulfate.

To the preceding organic phase, under nitrogen, was added 1.8 g (15 mmol) of guaiacol. The mixture was magnetically stirred at room temperature for 1 h, then 1 mL of tetra-n-butylammonium hydroxide (1 M in methanol) was added and the mixture stirred 5 more min. After the usual work-up and column chromatography, the trimer, (8) (0.3 g), was isolated as a white solid. Yield: 15%, m.p.89-91°C.
^{1}H NMR ($CDCl_3$) δ ppm 6.9-7.4 (broad s, ArH, 11H); 5.4 (m, $C_\alpha H$, 1H); 4.23 (m, $C_\beta H_2$, 2H); 3.8 (broad s, OCH_3, 9H).
IR νmax (KBr) 3600-3200, 29OO, 2810, 1560, 1500, 1490, 1440, 1360, 1320, 1240, 1240, 1170, 1150, 1110, 1020, 740 cm^{-1}.

MS (70 ev) e/z (rel. int.) 396 (5, $M^{+\cdot}$); 272 (100); 246 (19); 211 (27); 181 (27); 151 (16); 149 (24); 137 (26); 124 (47); 109 (46); 77 (16).
UV (methanol) λmax nm (ϵ $Lmol^{-1}cm^{-1}$) 227 (23600); 278 (8950).
Anal. calc. for $C_{23}H_{24}O_6$: C, 69.70; H, 6.06; O, 24.24. Found: C, 69.10; H, 6.00; O, 23.80.

RATE OF BRIGHTNESS LOSS

The procedure for the adsorption of the lignin model on lignin-free paper has been described elsewhere[39]; the weight percents of the model on the dry paper were estimated to be around 2% .

Brightness reversion was induced by exposing the sheets to a medium pressure mercury lamp (Mazda 400W), surrounded with a borosilicate glass filter to eliminate light with wavelengths below 300 nm. The sheets were placed on a merry-go-round in order to ensure uniform irradiation. The temperature of the apparatus was maintained near 30°C by fans.[43] The procedure for irradiation in solution has been reported elsewhere.[44]

Brightness indices of the sheet were determined with a Zeiss-Elrepho reflectometer. The yellowing of the papers was indicated with post-colour number P.C.N., according to the equation:

$$P.C.N. = [(K/S)_t - (K/S)_{t=0}] \times 100$$

K and S are, respectively, the absorption and scattered coefficients.[12]

Methylated pulp was prepared by reacting peroxide-bleached chemithermomechanical pulp (6 g) with dimethyl sulfate (20 mL) in a basic medium (6 g of NaOH in 60 mL of distilled water) for 12 h, the resulting pulp was washed thoroughly with distilled water and dried at 45°C.

RESULTS AND DISCUSSION

1- Electronic absorption spectra

Several α-carbonyl-free lignin model compounds were studied and their UV spectra in methanolic solutions are shown in Figure 3.

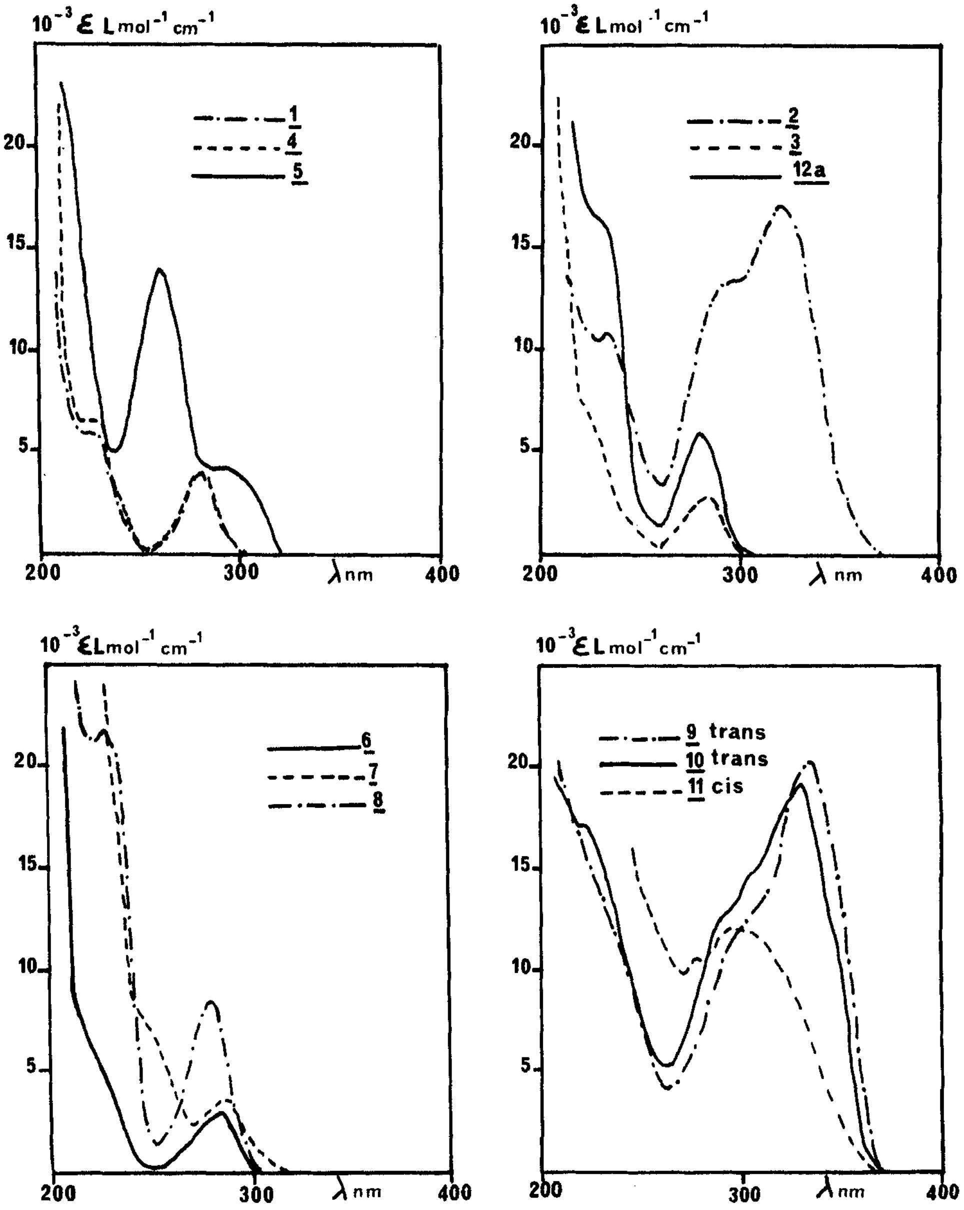


Figure 3. UV absorption spectra in methanol of the lignin models compounds under study.

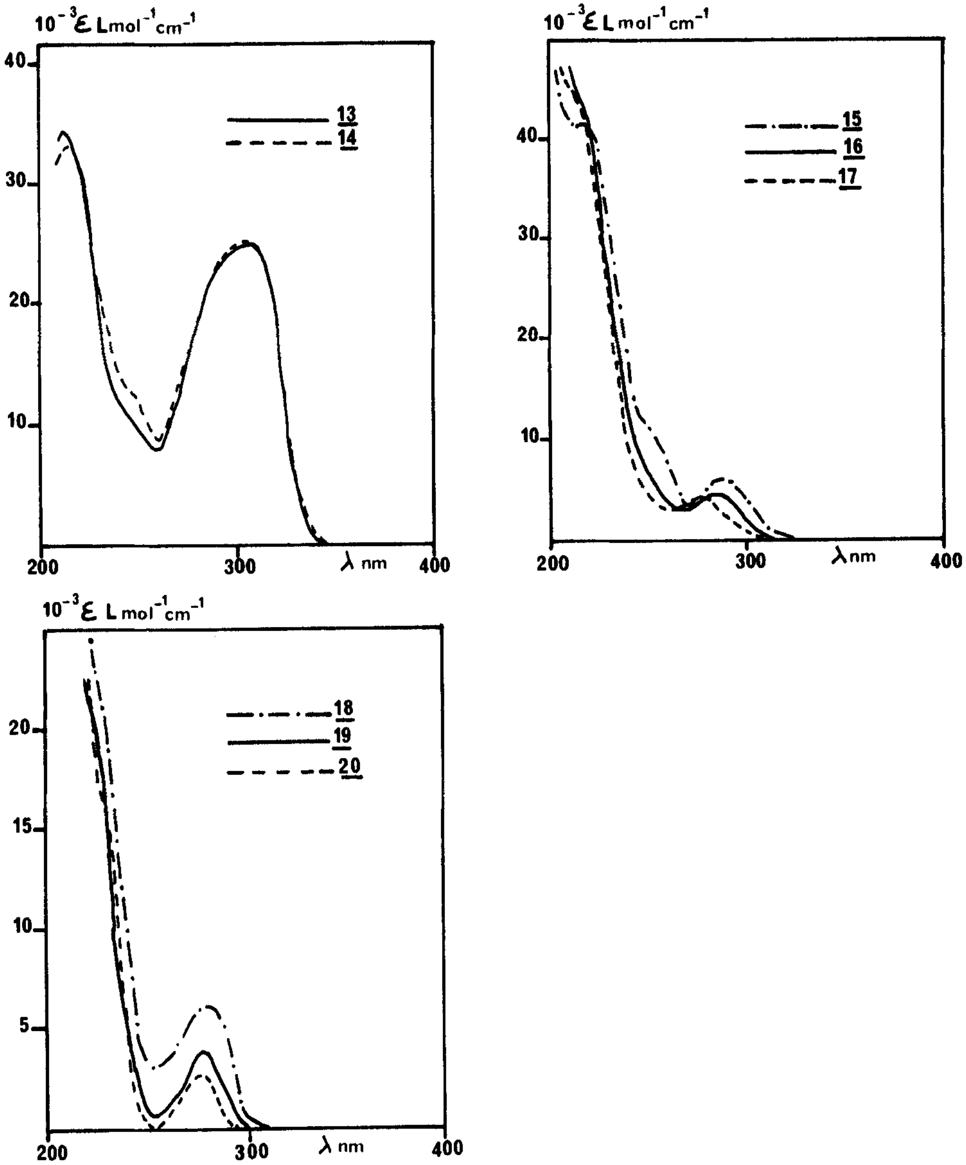


FIG. 3 CONTINUED

From this figure, one may estimate the relative contribution of each chromophore to the absorption above 300 nm where the sunlight is more intense. The relative absorption was found in the decreasing order : stilbenes, ferulic acid, phenylcoumarones, biphenyls, isoeugenol and non-conjugated benzene derivatives. These results are in accordance with those found in previous studies[15,45] and with what would be expected considering the substituent pattern of the aromatic ring.

2- Photodiscoloration of the models in the solid state

The rate of yellowing, indicated with post color number, under simulated solar light exposure of a series of α-carbonyl-free lignin model compounds, adsorbed on lignin free paper (bleached bisulfite softwood pulp) are presented in Figures 4-7 and compared to those of peroxide-bleached chemithermomechanical pulps, methylated with dimethyl sulfate and alkali and the corresponding unmethylated pulps. The absence of photoyellowing of the chemical pulp was noted under the same experimental conditions

MONOMERS

The non-conjugated monophenolic monomers, (1), (3), (4) and the 4-methylcatechol, (6), which are characterized by very little or no absorption above 300 nm, do not undergo significant discoloration within the investigated irradiation period. The behaviour of (6) is quite surprising owing to the easy oxidation of catechols to ortho quinones.[46]

Peroxides are considered to be very important species in the photodegradation of synthetic polymers[47] and their photolysis contributes to the formation of absorbing entities.[47] Irradiation of (1) and (6) in the presence of di-t-butylperoxide and t-butylhydroperoxide was performed to assess the role of peroxides in the brightness reversion of high yield pulps. The rates of discoloration are depicted in Figure 5. A slight increase in the color formation was noted but not as much as we might expect considering

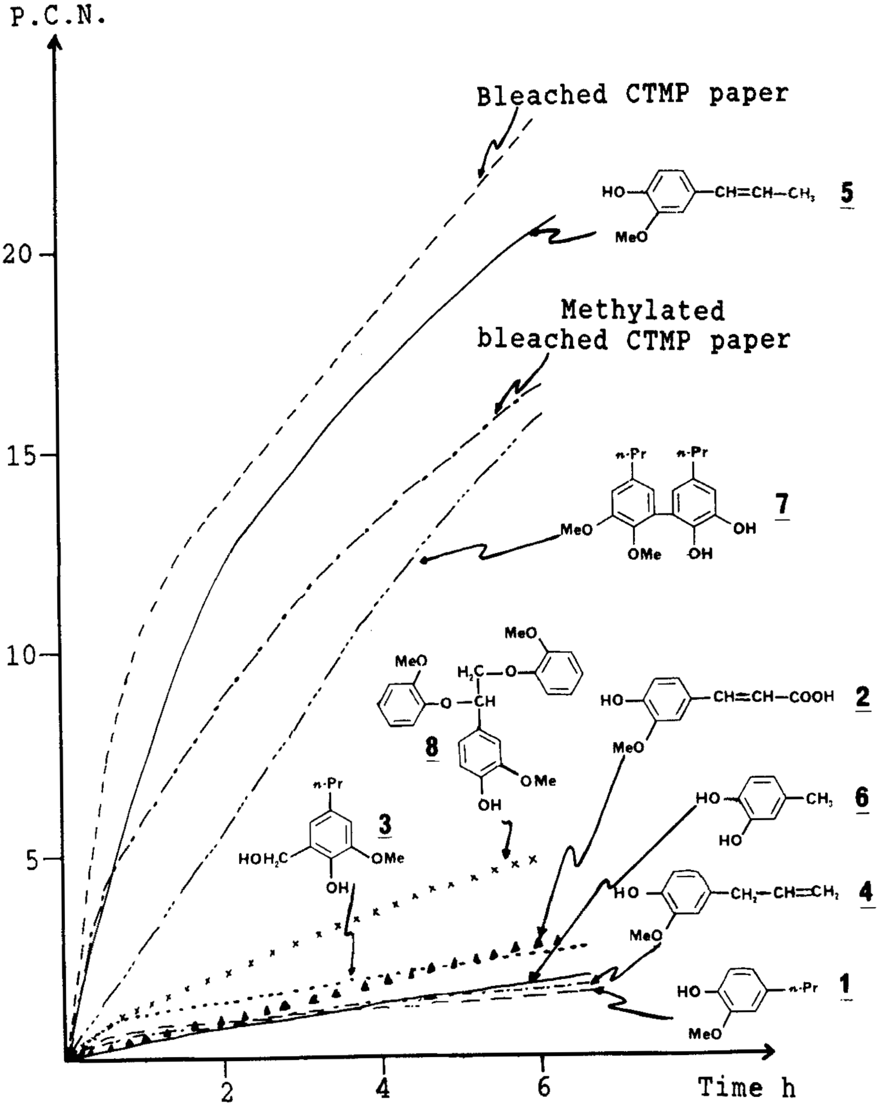


Figure 4. Rate of yellowing under simulated solar light of adsorbed lignin model compounds adsorbed on bleached softwood chemical pulp. Peroxide bleached non-methylated CTMP (70 g m^{-2}) and bleached methylated CTMP (70 g m^{-2}) are reported for comparison. The percent ages of the models based on dry paper are (1): 1.8; (2): 1.6; (3): 1.9; (4): 1.7; (5): 1.9; (6): 1.4; (7): 1.7; (8): 1.7.

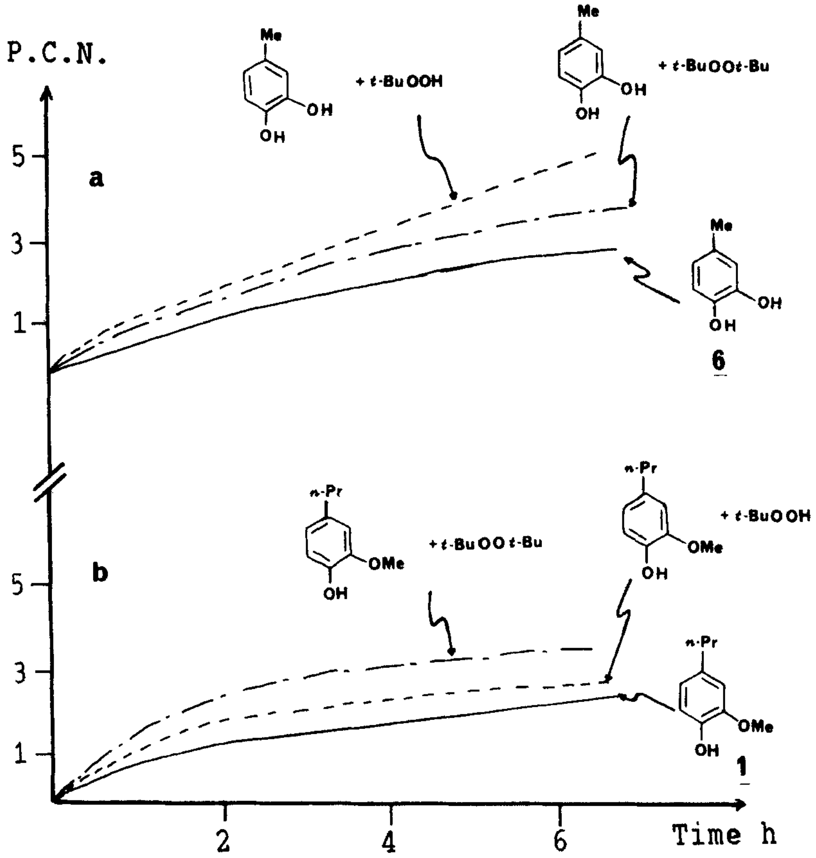


Figure 5. Rate of yellowing under simulated solar light of adsorbed lignin model molecules on bleached softwood chemical paper. The percentages of the models over dry paper are a) (1): 1.9; $(t\text{-}Bu\text{-}O)_2$: 3; t-BuOOH: 2.4 b) (6): 1.4; $(t\text{-}Bu\text{-}O)_2$: 2.8; t-BuOOH: 2.7.

the large amount of peroxide used (peroxide 2-3%). This observation seems to indicate that direct photolysis of the peroxidic bonds, in the presence of phenolic stuctures, is not a major contributor to the color formation of lignocellulosic materials.

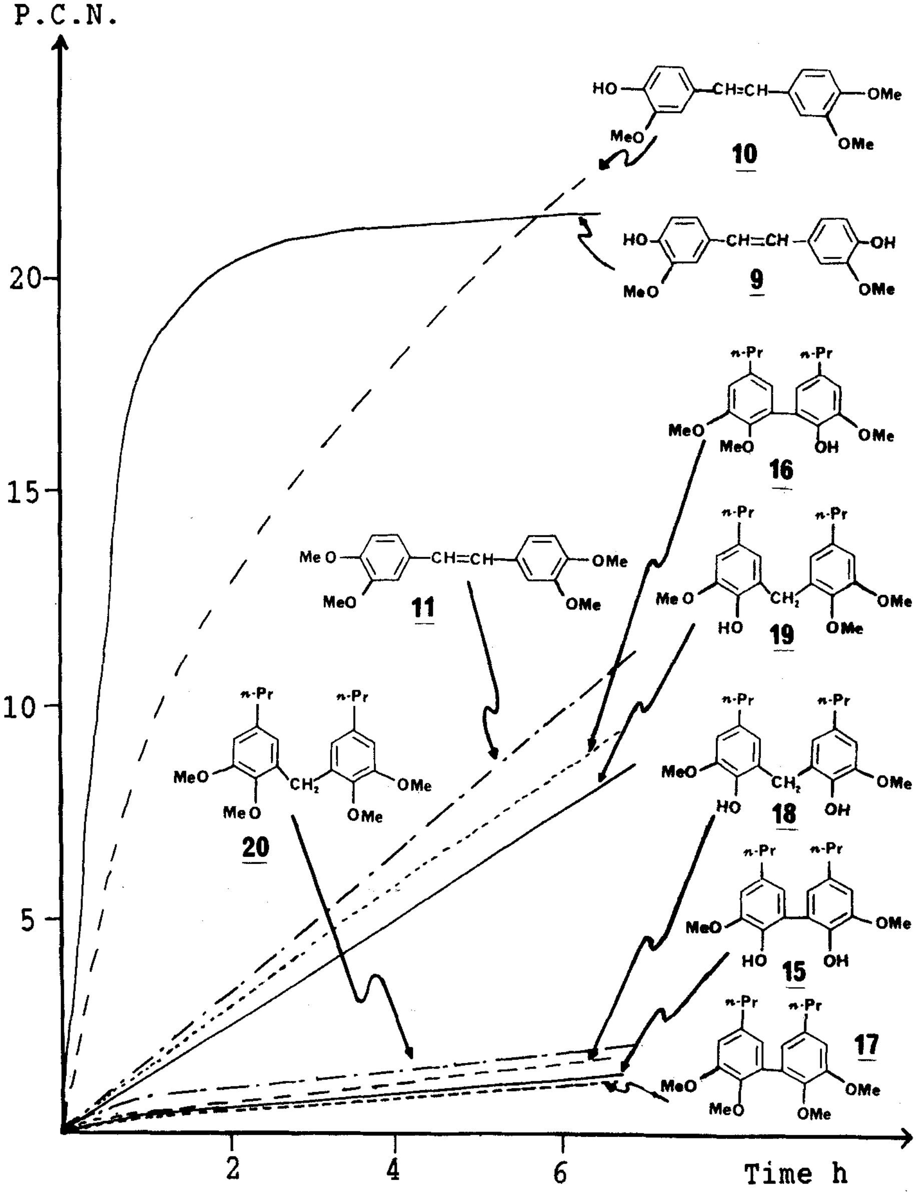


Figure 6. Same caption as Figure 5. The percentages of the models based on dry paper are (9): 1.5; (10): 2; (11): 2.2; (15): 2; (16): 2; (17): 2.5; (18): 16; (19): 2.3; (20): 3.

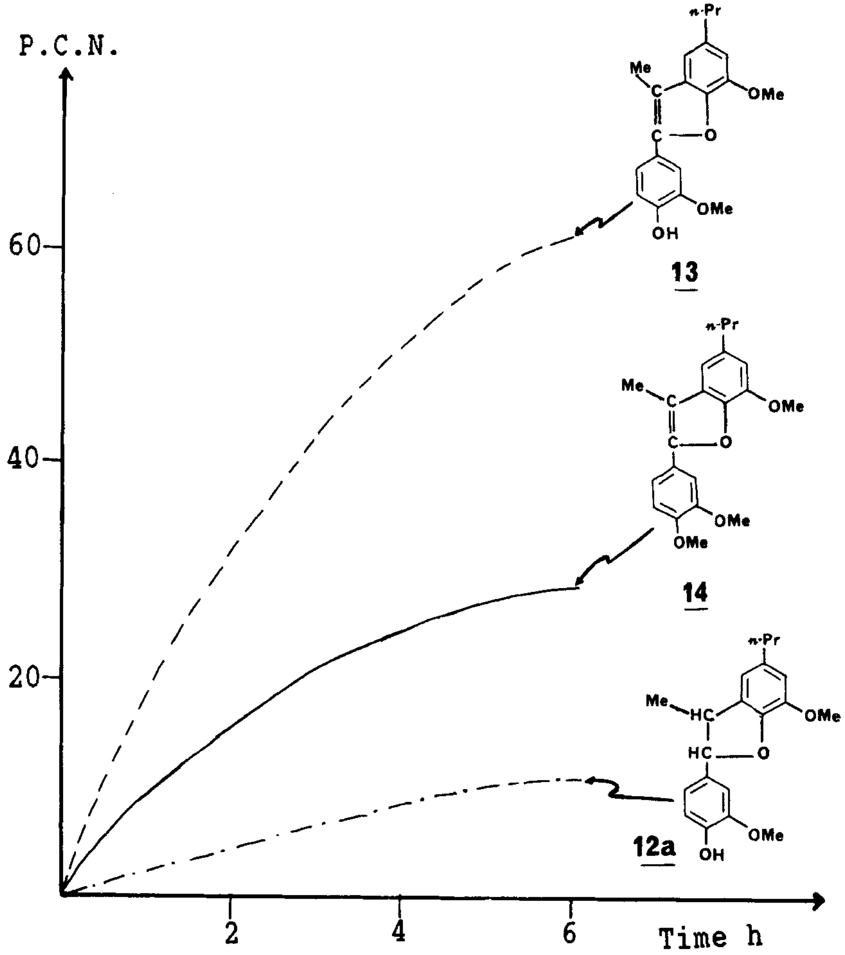


Figure 7. Same caption as Figure 5. The percentages of the models based on dry paper are (12a): 2.2; (13): 1.6; (14): 2.1.

The rate of discoloration of ferulic acid, (2), is low compared to that of isoeugenol, (5), despite the fact that (2) absorbs more intensively above 300 nm and that cis-ferulic acid, (2), has been identified as a possible chromophore responsible for the color of the irradiated pulp.^{5}

DIMERS AND TRIMER

The curves recorded for the diphenyls, (15), (16), (17), and diphenylmethanes, (18), (19), (20), show a parallel behaviour even though the biphenyls absorbed more light above 300 nm. It was quite surprising to find the monomethylated phenols being the most active models in the solid state. This contrasts with the results obtained in aqueous ethanol and may be due to some conformational effects in the solid which cause interactions between the two OH groups. The ease of yellowing of the phenolic diphenylmethane chromophore is probably ascribable to the susceptibility of the benzylic hydrogen to oxidation.

The diguaiacylstilbenes, (9), (10), and (11), are easily phototodiscolored in the following expected order: diphenol> monophenol> O-methylated derivative. Noteworthy is the yellowing of compound, (11). The phenylcoumarones, (13) and (14), which belong to the stilbene structures were found to be much more light sensitive than the non-cyclic structures. Of note is the observation that the phenylcoumaran (12a) displays a discoloration comparable to that of the biphenyl, (7), despite its lower absorption.

The biphenylcatechol (7) whose absorption spectrum is shifted to wavelengths higher than that of (6), displays a more intense photodiscoloration. This indicates the aptitude of catechol structures to be converted into colored quinones when they absorb light.

Finally, the trimer, (8) displays more intense photoyellowing than ferulic acid. Homolytic cleavage of the benzylaryl ether bond generating a pair of benzyl and phenoxy radicals is probably involved in the discoloration of (8), due to the sensitivity of the α-O-4 bond to light, as was shown previously for related compounds.[48]

3- Photodiscoloration of several models in solution

The effect of oxygen was assessed by irradiating (merry-go-round, medium pressure mercury lamp, pyrex vessel ($\lambda > 300$ nm)) several lignin models in aerated and degassed (freeze and thaw), buffered (pH 6.8) aqueous ethanolic solutions.[44] Oxygenation of the irradiated degassed solutions in the dark was also performed to see if some thermal discoloration was occuring. Some after-yellowing of degassed solutions has already been observed with lignin model compounds[44], and was attributed to the oxidation of radicals in equilibrium with diamagnetic molecules called "radical reservoir" species.[44] The results are depicted in Figures 8-11.

The yellowing observed in the solid state, occurs also in solution. Degassing reduced but did not eliminate the yellowing . This behavior was previously observed for CTMP[2] and for other lignin model compounds.[44] The reactivity of the dihydroxybiphenyls and diphenylmethanes is comparable and even superior to that of monohydroxy derivatives. Also, as noted for the solid state measurements, complete methylation of the phenols decreases discoloration in aqueous ethanol. In contrast to similar preceeding studies[44], is the finding that no noticeable after-yellowing due to "radical reservoir" species, was observed for the above models.

4- Mechanism of photodiscoloration

The rate of photoyellowing of the models adsorbed on lignin-free paper indicate unambiguously the ability of the phenolic models to undergo significant discoloration, comparable to that found for CTMP, without the need of α-carbonyl groups as sensitizers.

We have seen in the introduction that phenoxy radicals are considered to be the main responsible of the discoloration of high-yield pulps. Direct photolysis of the phenolic structures, where light above 300 nm is absorbed and phenoxy radicals are generated, might be also one important primary photochemical step. The generation of phenoxyl radicals, in the presence or absence of ground state oxygen, has been demonstrated using flash photolysis.[21-22]

$$\mathrm{ArOH} + h\nu \text{ --------> } \mathrm{ArO.} + e^- + H^+$$

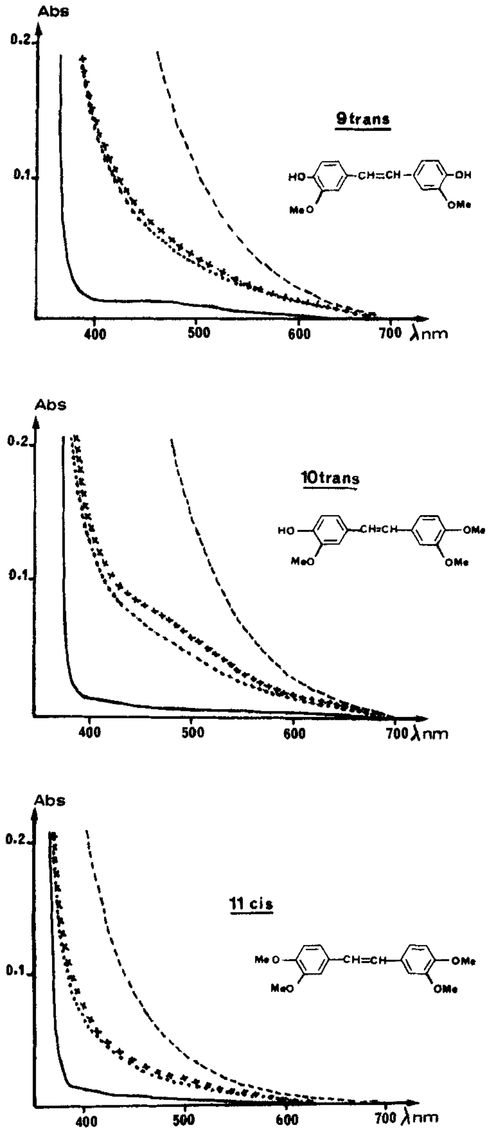


Figure 8. Electronic absorption spectra of lignin model molecules (10^{-3}M) in buffered (pH≈7) aqueous ethanol solution (EtOH, H_2O, KH_2PO_4, (0.1N): 6/3/1). (———): before irradiation; (- - -): irradiated 24 h, aerated medium; (·····): irradiated 24 h, degassed medium; (xxxxx): irradiated 24 h, degassed medium followed by 4 h aeration and 1 min bubling oxygen.

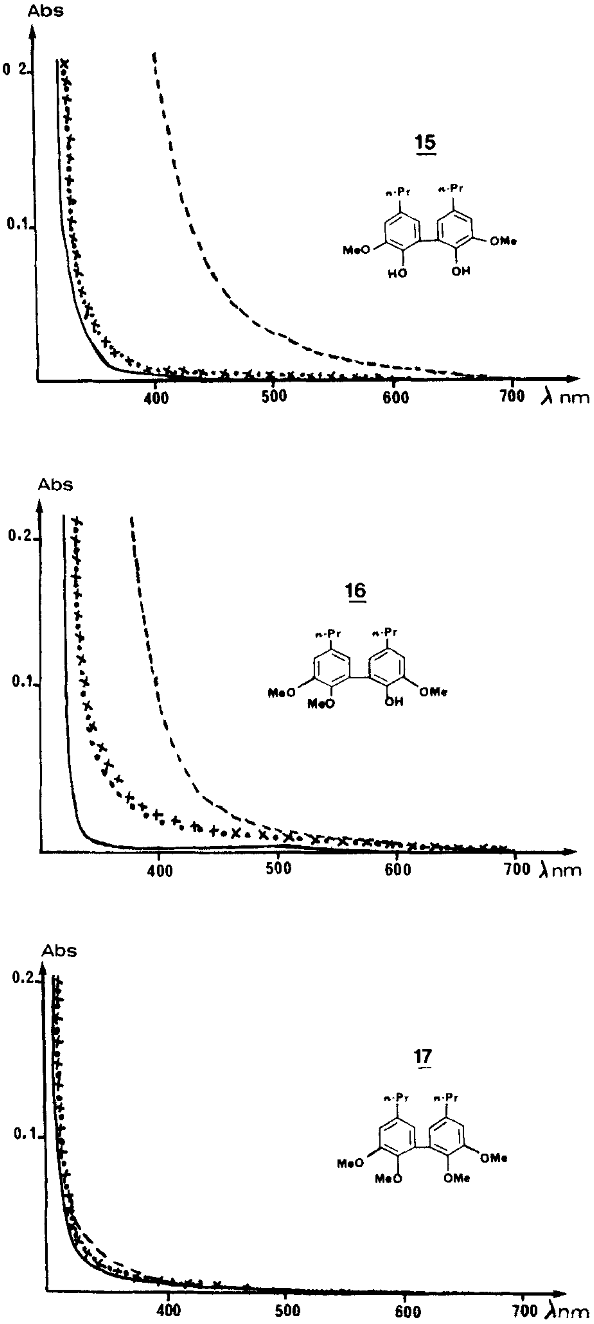


Figure 9. Same caption as Figure 8.

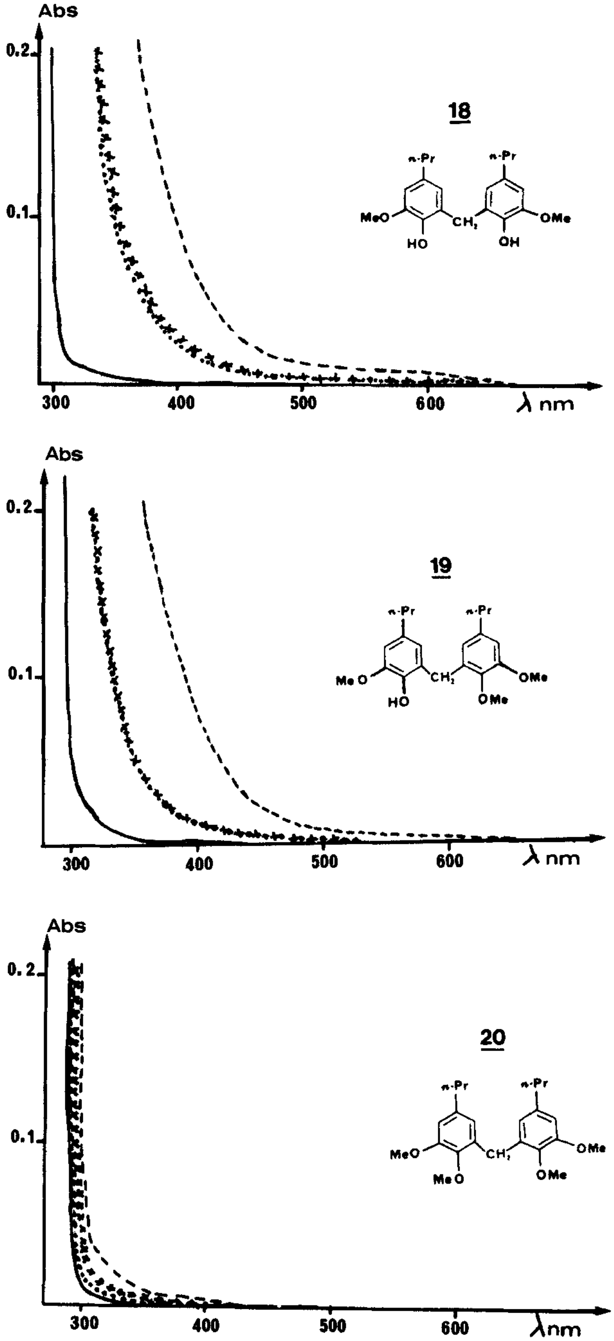
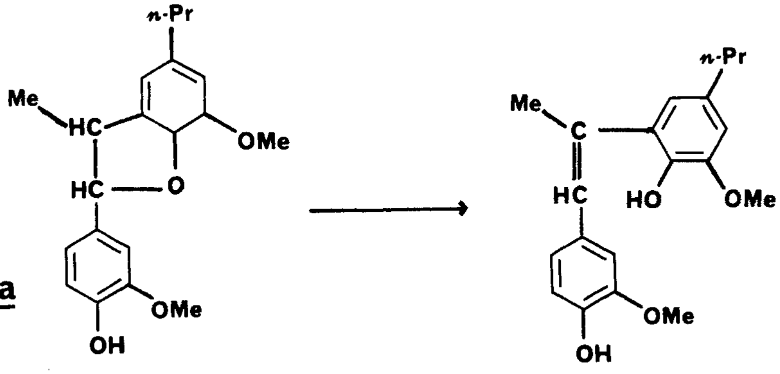


Figure 10. Same caption as Figure 8.



12a

Figure 11. Benzylic ether cleavage in phenylcoumaran **12a**.

However, in the presence of oxygen, as for example in the oxidation of polystyrene[49], ground state complexes of the phenol and ground state oxygen might be postulated. Such complexes could, by irradiation, generate phenoxy and hydroperoxy radicals which might couple to form very unstable cyclohexadienone hydroperoxide and thence ultimately colored derivatives.

$$\mathrm{ArOH} + \mathrm{O_2} \longrightarrow (\mathrm{ArOH,O_2}) + h\nu \longrightarrow (\mathrm{ArO.} + \mathrm{HOO.})$$

$$\text{(cyclohexadienone hydroperoxide)}\ \mathrm{HOO\text{-}Ar{=}O} \longleftarrow$$

In addition to the above mechanism which probably is applicable mainly to the phenolic models, sensitized singlet oxygen formation via an exciplex[50] and oxidation by this species has to be considered relevent for stilbene-type derivatives, whether they be phenolic or not. This mechanism might account partly for the residual discoloration of the O-methylated stilbenes.

The unexpected high level of yellowing of the phenylcoumaran, (12a), might be due to α-cleavage of the benzylic ether bond leading to benzyl and phenoxy radicals which might rearrange into light-sensitive phenolic stilbene structures as proposed in Figure 11.

CONCLUSION

The present study provides additional important data for understanding the photodegradation of lignocellulosic materials. It was established that phenols absorbing light above 300 nm are able, in condensed media, to induce discoloration by direct photolysis without the presence of α-carbonyl groups as sensitizers. Stilbene-type structures appear to be among the most sensitive, especially when the double bond is incorporated in a phenylcoumaran entity. Moreover, non-conjugated chromophores, such as (12a) and (19) which absorb very little above 300 nm, were found to be quite prone to undergo discoloration. A complex between ground state oxygen and the phenol which absorbs the UV light and generates cyclohexadienone hydroperoxide, has been put forward to explain the discoloration of the phenols. The results found for the carbonyl-free models adsorbed on lignin-free paper mimic quite well the behavior of bleached high yield papers. Further studies are being pursued to obtain a better understanding of the complex photoyellowing mechanism of lignocellulosic materials.

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