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L. C. Harvey; A. J. Ragauskas

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MECHANISTIC INVESTIGATIONS INTO THE BRIGHTNESS STABILIZATION  
EFFECTS OF HEXADIENOL

L.C. HARVEY AND A.J. RAGAUSKAS\*

Chemical and Biological Sciences Division  
Institute of Paper Science and Technology  
Atlanta, GA 30318

ABSTRACT

The total amounts of 3,4,5-trimethoxyacetophenone and 2,6-dimethoxyphenol formed via the photocleavage of 3,4,5-trimethoxy- $\alpha$ -(2',6'-dimethoxyphenoxy)-acetophenone (**1**) in benzene and 3:2 ethanol/benzene, have been quantified in the presence and absence of 2,4-hexadienol, a potential photostabilizing agent for mechanical pulps. Photodegradation of **1** in ethanol/benzene solutions was shown to be reduced by the addition of hexadienol. Photolysis of bleached chemithermomechanical pulp (BCTMP) treated with *trans,trans*-2,4-hexadienol was shown to yield all four possible geometric isomers of the hexadienol. These results suggest that a potential mode of stabilization of mechanical pulps by the hexadienol is triplet quenching of the excited state of lignin chromophores such as the  $\alpha$ -carbonyl groups of phenacyl aryl ethers.

INTRODUCTION

Advances in mechanical pulping and bleaching technology have substantially improved the overall quality of these grades of paper. In principle, mechanical pulps could be utilized for a variety of high grade paper products. Unfortunately, these pulps are known to suffer from photo- and thermally induced yellowing processes. This yellowing phenomenon, occurs minimally via thermal discoloration but primarily from

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\*To whom correspondence should be addressed

exposure to indoor and outdoor light and is attributable to photooxidation of lignin<sup>1</sup>. Rapid photo-yellowing properties of these pulps limits the use of mechanical pulps to short-life paper products.

Due to the efforts of many researchers, key features of the photoinitiated deterioration have been resolved. The primary photochemical processes are known to involve a variety of sub-units of lignin such as  $\alpha$ -keto- $\beta$ -O-4-aryl ether units, stilbene, conferyl alcohol, and some phenolic structures. Several pathways for phenoxy radical formation have been proposed including abstraction of hydrogen atoms from neighboring phenolic groups by the excited state of carbonyls, and photocleavage of phenacyl-O-aryl ethers<sup>2-5</sup>. Recently, formation of phenoxy free radicals has been postulated to occur by the photoinduced breakdown of arylglycerol- $\beta$ -aryl ether structures via the corresponding ketyl radical<sup>6</sup>. In many of these studies, lignin model compounds, such as  $\alpha$ -guaiacoxycetoveratrone, have been instrumental in the investigation of the photochemical pathways that result in yellowing<sup>3-10</sup>.

As our understanding of the fundamental mechanisms of brightness reversion improve, so also has our ability to design new photostabilizers for mechanical pulp.

Two classes of additives that have shown the most promising results are the UV-absorbers and free-radical scavengers (hydrogen atom donors)<sup>11-17</sup>. Although the application of UV-absorbers decreases light-induced yellowing, the amounts required to substantially reduce the rates of photoyellowing makes this class of stabilizers economically unfeasible. Previously investigated free radical scavengers include thiols, thioethers, ascorbates, and formates. These radical scavengers also decrease photoyellowing, but they do not prevent the primary photochemical processes that lead to initial radical formation.

Recently, we have demonstrated that 2,4-hexadienol and related unsaturated systems were effective additives for retarding photoyellowing in hardwood BCTMP pulps<sup>18</sup>. Although significant reductions in the rates of photoyellowing were observed, further improvements will be required prior to any potential commercial considerations. To guide our research efforts at improving the brightness stabilization effects of these and related additives we have begun to investigate the chemical mechanisms by which these photostabilizers operate. General chemical considerations suggested that hexadienol could act either as a radical scavenger agent or as a triplet quencher for the excited of lignin chromophores<sup>19</sup>. Hexadienol's  $\lambda_{\text{max}}$  is centered at 254 nm, hence this additive is not expected to photostabilize mechanical pulps via absorption of 300-400 nm light the frequencies which are most commonly attributed to initiating brightness

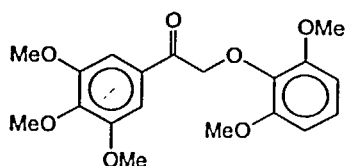


FIGURE 1. 3,4,5-Trimethoxy- $\alpha$ -(2',6'-dimethoxyphenoxy)-acetophenone

reversion. To explore the potential mechanism(s) of photostabilization we initiated a research program to examine the fundamental interactions of 2,4-hexadienol with compounds containing chromophores that play a major role in lignin photodegradation, such as that present in 3,4,5-trimethoxy- $\alpha$ -(2'-6'-dimethoxyphenoxy)-acetophenone **1** (Figure 1).

Since solution studies may not be indicative of the preferred reaction pathways in the solid state, the effect of 2,4-hexadienol was also investigated on two solid supports: bleached chemithermomechanical pulp (BCTMP) and cellulose.

## EXPERIMENTAL

### Materials and General Methods

Trans, trans-2,4-hexadienol was purchased from a commercial source and used as received. All solvents used in solution photolyses were spectrophotometric grade and used as received. Commercial sources of hardwood BCTMP and cotton linter fluff were employed for the solid state photolysis experiments. Routine  $^1\text{H}$  NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer, typically in deuteriochloroform with tetramethylsilane as internal standard. High resolution spectra were recorded with a Varian 400 MHz spectrometer. Quantification of photoproducts was accomplished on a Hewlett Packard 5890 Gas Chromatograph equipped with an HP-17 capillary column and flame ionization detector. Routine GC-MS data were obtained with an HP-5890 Series 2 gas chromatograph coupled to an HP-5971A Mass Selective Detector.

### Synthesis of Lignin Model Dimer 1

Compound **1** was synthesized via bromination of 3,4,5-trimethoxyacetophenone in chloroform followed by condensation with 2,6-dimethoxyphenol in the presence of NaH in anhydrous THF. Bromine (4.34g, .0272 mol) was added dropwise via an addition funnel to a solution of 3,4,5-trimethoxyacetophenone (5.25g, .0250 mol) in chloroform. The reaction mixture was stirred for an additional 2 hours after complete addition of bromine (and fading of color), at which time it was washed with saturated NaHCO<sub>3</sub> (3 x 30 mL) and water (2 x 30 mL), followed by drying over MgSO<sub>4</sub> and evaporation of solvent. The crude  $\alpha$ -bromo derivative was dissolved in anhydrous THF along with 2,6-dimethoxyphenol (4.24g, .0275 mol) followed by addition of NaH (1.21g, .0504 mol). The reaction mixture was stirred and maintained under an inert atmosphere overnight. Excess NaH was quenched by careful addition of water and the product extracted with methylene chloride (3 x 50 mL). **1** was isolated by crystallization from hot MeOH to yield 6.06 g (.0168 mol) in 67% yield. The melting point was 114.0° C. The spectral data were: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.83 (s, 6), 3.92 (s, 9), 5.14 (s, 2), 6.59 (d, 2, J = 8.4), 7.01 (t, 1), 7.39 (s, 2). Anal. Calcd. for C<sub>19</sub>H<sub>22</sub>O<sub>7</sub>: C, 62.98; H, 6.08. Found: C, 63.09; H, 6.06.

### Solution Photolysis Studies

Solutions of **1** (.004 M) were prepared in benzene and 3:2 ethanol/benzene (the low solubility of **1** precluded the use of neat ethanol). Solutions of **1** (.004 M) containing 2,4-hexadienol (0.004 M) were also prepared in benzene and ethanol/benzene. All solutions were deoxygenated by purging with solvent saturated nitrogen for 20 minutes prior to photolysis. Irradiations were performed at 30° C in Pyrex tubes using a Rayonet reactor (The Southern New England U.V. Company) equipped with RPR-3500Å lamps. Samples were uniformly and simultaneously photolyzed on a merry-go-round apparatus. For studies where products were monitored over specific time intervals, aliquots were removed at .5 h, 1 h, 2 h, and 4 h intervals. After the prescribed irradiation period, the solvent was removed and the photolysis products redissolved in methylene chloride and spiked with O-benzyl vanillone as internal standard. Quantification of lignin model dimer remaining post photolysis as well as the major products formed as a result of the initial homolytic rupture of the  $\beta$ -O-aryl ether

bond, 3,4,5-trimethoxyacetophenone (TMAP) and 3,4-dimethoxyphenol (DMP) was accomplished via gas chromatography. The results of the ethanol/benzene and benzene experiments are summarized in Tables 1 and 2, respectively.

Photoisomers of hexadienol were obtained in the following manner: trans, trans 2,4-hexadienol (.288 g, 2.93 mmol) in .20 L benzene was photolyzed in the Rayonet reactor in the presence of 1 (.311 g, .860 mmol) for 45 minutes. The isomerized hexadienols were separated from the reaction mixture by chromatography on silica gel with methylene chloride as eluent. The total recovered hexadienols totaled .0776 g ( $7.91 \times 10^{-4}$  mol, 27% recovery, based on initial amount). The ratio of the four isomers present (3.4:1:1:1 trans,trans to other isomers) was determined by  $^1\text{H}$  NMR (Note: attempts to separate the four hexadienol isomers were not successful with standard column chromatography or preparative TLC methods). Capillary GC techniques provided, at best, the opportunity to separate the four isomers into two different fractions.  $^1\text{H}$  NMR analysis of the purified hexadienol mixture allowed for the determination of the ratio of isomers present due to the well resolved hydroxymethyl "methylene" proton signals ( $\delta$  4.14-4.34) for each isomer. The presence of the four isomers was confirmed by a  $^{13}\text{C}$  NMR APT experiment, which revealed the presence of the four methylene carbons of the isomeric mixture:  $\delta$  58.67, 58.77, 63.49, and 63.55, as well as the 16 methine carbon signals:  $\delta$  123.69, 125.47, 126.22, 126.58, 126.86, 127.06, 128.50, 128.59, 129.01, 129.11 (trans, trans), 130.13 (trans, trans), 130.69 (trans, trans), 131.15, 131.42, 131.90, and 131.94 (trans, trans).

### Solid State Photolysis Studies

Trans, trans-2,4-hexadienol was irradiated on two solid supports: BCTMP pulp and cellulose. The BCTMP pulp employed in these studies was initially extracted with methanol for 24 hours in order to remove any extraneous, extractable materials remaining in the pulp. The hexadienol was applied to the BCTMP fibers (28.72 g.) by immersing the fibers in a methanolic hexadienol solution (0.0303 M, 587.46 ml) for 45 minutes followed by evaporation of the solvent with a roto-evaporator under reduced pressure. The impregnated BCTMP fibers were then placed on a sample pan and air-dried overnight to remove residual methanol from the pulp sample. Exhaustive soxhlet extraction of the treated BCTMP pulp (30.00 g) with methylene chloride (2 x 12 h) afforded a 94% recovery of trans,trans-2,4-hexadienol (1.20 g., 0.0122 mol).

Hexadienol-treated fibers were irradiated for a period of two hours with the RPR-3500 Å lamps. The hexadienol was recovered by exhaustive soxhlet extraction of the irradiated fibers with methylene chloride (2 x 12 h). The recovered hexadienol from the combined solvent extractions was separated from other extracted materials by chromatography on silica gel with 2% ethyl acetate/methylene chloride as eluent. The structure of the isolated hexadienols (.0114 mol, 92% recovery) was verified by proton NMR, which revealed a 14:1:1:1 (trans, trans to three other isomers) mixture.

Application of 2,4-hexadienol to cellulose was accomplished in an identical manner. A methanolic solution of trans, trans-2,4-hexadienol (0.0298 M, 250.33 ml) was added to cellulose (12.65 g) and the pulp slurry was vigorously mixed for 30 min. The slurry was then concentrated under reduced pressure and air-dried overnight following the same procedure described above. Photolysis of the cellulose followed by methylene chloride soxhlet extraction and isolation afforded a 90% recovery of pure trans,trans starting material.

## RESULTS AND DISCUSSION

The major photolysis products quantified in this study, 3,4-dimethoxyphenol (DMP) and 3, 4, 5-trimethoxyacetophenone (TMAP), result from the well-known cleavage of the  $\beta$  aryl ether bond in **1** to yield substituted phenacyl and phenoxy radicals (Figure 2). The initially formed radicals can recombine to form starting material or further degrade to low molecular weight products. The phenoxy radicals further react to form higher molecular weight oligomeric materials. Hydrogen atom abstraction from solvent or other H-atom donors leads to acetophenone and phenol derivatives.

Quantification of **1** remaining after various photolysis periods can provide information about the primary photochemical process, photocleavage of the aryl ether, and whether added hexadienol can affect this process, and if so, to what extent. Quantification of TMAP and DMP formed in solutions containing hexadienol and in solutions containing no hexadienol can provide useful information about secondary processes (such as H atom abstraction) occurring after initial cleavage.

### Solution Photolysis Studies

The lignin model dimer (**1**) remaining after irradiation in degassed solutions of

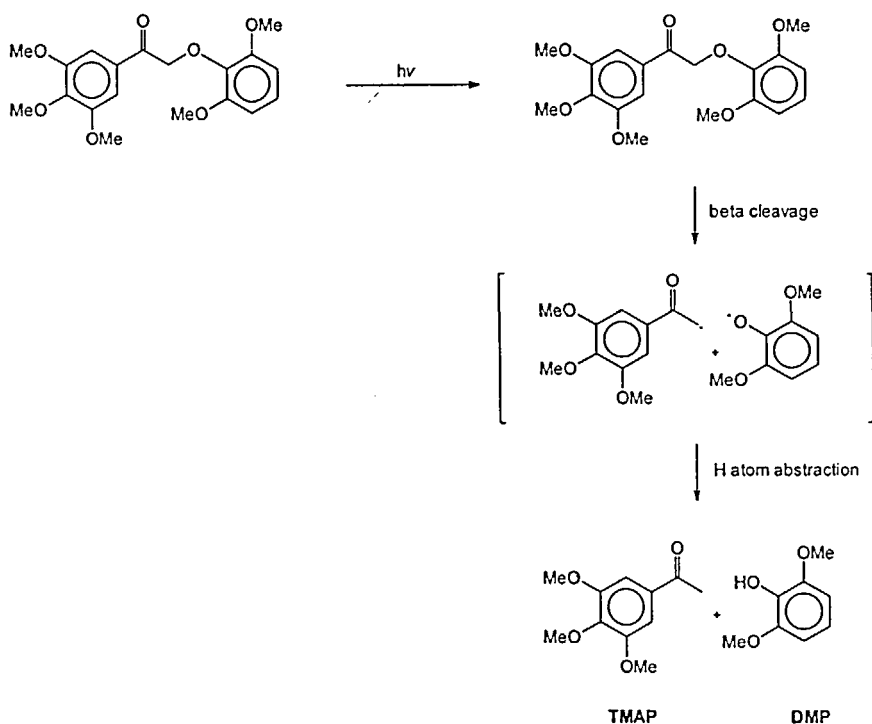


FIGURE 2

ethanol/benzene (3:2), as well as the amounts of TMAP and DMP formed during the corresponding photolysis periods, are reported in Table 1. The analogous results for the photolysis of **1** in benzene are reported in Table 2. The effect of added hexadienol on the photodecomposition of **1** (or the formation of DMP and TMAP) are also reported for both solvent systems.

Inspection of the amounts of **1** remaining after photolysis in ethanol/benzene indicates that the addition of hexadienol deters photocleavage as manifested in greater amounts of **1** detected after each photolysis period (Figure 3). These results suggest that the addition of hexadienol retards one of the initial photochemical reactions that contributes photodegradation of compound **1**. Since hexadienol does not absorb in the 300-400 nm frequency range and is a known triplet quencher the reduced rates of photodegradation of lignin model compound **1** in the presence of the diene are most



TABLE 1.  
Decomposition Products<sup>a</sup> of  $\alpha$ -Carbonyl  $\beta$ -O-4 Lignin Model Dimer (1) With and Without 2,4-Hexadienol in Ethanol/Benzene.

Photolysis time	Lignin dimer (1) <sup>b</sup>	DMP <sup>c</sup>	IMAP <sup>d</sup>
.5 H (no hexadienol)	$2.58 \times 10^{-5}$ (.60 $\pm$ .02)	$1.37 \times 10^{-5}$ (.32 $\pm$ .02)	$1.09 \times 10^{-5}$ (.25 $\pm$ .07)
.5 H (with hexadienol)	$3.06 \times 10^{-5}$ (.81 $\pm$ .02)	$9.12 \times 10^{-6}$ (.24 $\pm$ .02)	$3.85 \times 10^{-6}$ (.10 $\pm$ .02)
1 H (no hexadienol)	$1.02 \times 10^{-5}$ (.24 $\pm$ .04)	$1.45 \times 10^{-5}$ (.34 $\pm$ .003)	$1.22 \times 10^{-5}$ (.28 $\pm$ .02)
1 H (with hexadienol)	$1.48 \times 10^{-5}$ (.39 $\pm$ .11)	$9.86 \times 10^{-6}$ (.26 $\pm$ .10)	$4.83 \times 10^{-6}$ (.13 $\pm$ .09)
2 H (no hexadienol)	$2.09 \times 10^{-6}$ (.05 $\pm$ .08)	$1.05 \times 10^{-5}$ (.24 $\pm$ .02)	$1.28 \times 10^{-5}$ (.30 $\pm$ .02)
2 H (with hexadienol)	$2.84 \times 10^{-6}$ (.08 $\pm$ .07)	$7.72 \times 10^{-6}$ (.20 $\pm$ .002)	$4.99 \times 10^{-6}$ (.13 $\pm$ .004)
4 H (no hexadienol)	-----	$8.69 \times 10^{-7}$ (.02 $\pm$ .05)	$9.86 \times 10^{-7}$ (.02 $\pm$ .03)
4 H (with hexadienol)	-----	$3.92 \times 10^{-6}$ (.10 $\pm$ .06)	$8.15 \times 10^{-6}$ (.22 $\pm$ .03)

<sup>a</sup> moles; <sup>b</sup> lignin dimer remaining after the indicated photolysis time. Number in parentheses refers to ratio of product (or remaining starting material) to initial quantity (moles) of 1; <sup>c</sup> 2,6-dimethoxyphenol;

<sup>d</sup> 3, 4, 5-trimethoxyphenol.

TABLE 2.  
Decomposition products<sup>a</sup> of  $\alpha$ -carbonyl  $\beta$ -O-4 lignin model dimer (1) with and without 2,4-hexadienol in benzene.

Photolysis time:	Lignin dimer (1) <sup>b</sup>	DMP <sup>c</sup>	• TMAP <sup>d</sup>
.5 H (no hexadienol)	$2.05 \times 10^{-5}$	$5.29 \times 10^{-6}$	$1.87 \times 10^{-6}$
.5 H (with hexadienol)	$2.03 \times 10^{-5}$	$7.33 \times 10^{-6}$	$1.41 \times 10^{-6}$
1 H (no hexadienol)	$1.62 \times 10^{-5}$	$7.75 \times 10^{-6}$	$5.03 \times 10^{-6}$
1 H (with hexadienol)	$1.86 \times 10^{-5}$	$8.87 \times 10^{-6}$	$3.56 \times 10^{-6}$
2 H (no hexadienol)	$1.07 \times 10^{-5}$	$5.09 \times 10^{-6}$	$7.88 \times 10^{-6}$
2 H (with hexadienol)	$1.33 \times 10^{-5}$	$1.11 \times 10^{-5}$	$7.93 \times 10^{-6}$ y
4 H (no hexadienol)	$9.61 \times 10^{-6}$	$5.85 \times 10^{-6}$	$1.06 \times 10^{-5}$
4 H (with hexadienol)	$8.27 \times 10^{-6}$	$8.32 \times 10^{-6}$	$8.38 \times 10^{-6}$

<sup>a</sup> moles; <sup>b</sup> lignin dimer remaining after the indicated photolysis period; <sup>c</sup> 2,6-dimethoxyphenol  
<sup>d</sup> 3, 4, 5-trimethoxyacetophenone.

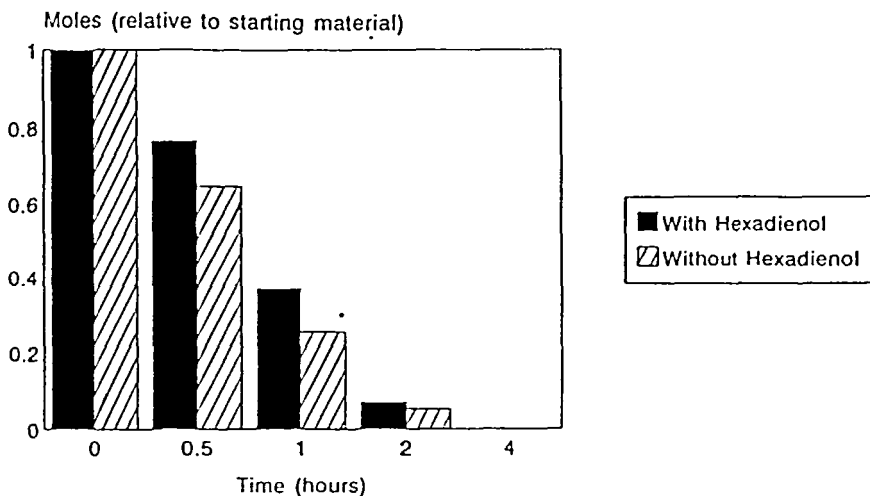


FIGURE 3. Photodegradation of Lignin Model in Ethanol/Benzene

likely to be due to quenching of the ketone excited state. These results suggest that the addition of hexadienol can retard one of the initiation steps in brightness reversion phenomena (i.e.,  $\beta$ -cleavage of photoexcited **1** in Figure 2).

Examination of the amounts of **1** remaining after photolysis in benzene reveals that the addition of hexadienol does not affect its photodecomposition in a manner analogous to the ethanol/benzene photolysis experiments. In the benzene system, the addition of hexadienol appears to have diminished effect on the decomposition of keto compound **1**. As summarized in Figure 4, after 1/2 h of irradiation samples photolyzed in the absence of hexadienol exhibited comparable amounts of starting lignin dimer than samples photolyzed in the presence of the diene. Samples irradiated for prolonged periods of 1 and 2 hours exhibited greater amounts of compound **1** in the presence of hexadienol. Furthermore, whereas some lignin model dimer remained after 4 hours of photolysis in benzene, none was detected after the same period in ethanol/benzene (Fig. 4).

Presumably some of the differences observed in the photochemistry of keto compound **1** with and without hexadienol in the two solvent systems can be attributed to differences in the reactivity of the singlet and triplet excited states. Vanucci and co-workers have observed that the disappearance quantum yield of  $\alpha$ -guaiacoxy-

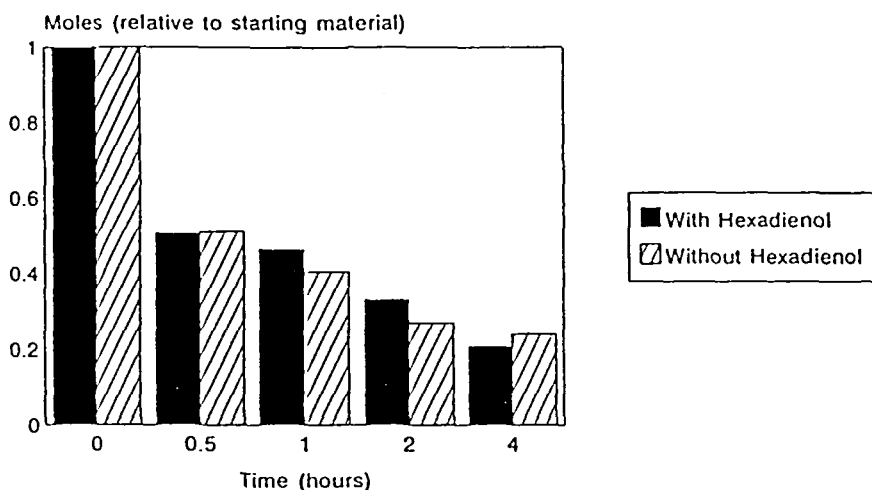


FIGURE 4. Photodegradation of Lignin Model in Benzene

acetoveratrone (GAV) is greater in ethanol than benzene, and that although the same photoproducts are isolated in both solvents, the distribution of these is sensitive to the nature of the solvent<sup>3</sup>. These results are compatible with recent findings by several authors of the occurrence of photochemical processes originating from the singlet excited state of guaiacoxycetoveratrone and related lignin model compounds<sup>8, 20-21</sup>. Schmidt et al. have reported that guaiacoxycetoveratrone exhibits singlet state reactivity in aprotic solvents but the addition of a protic solvents induces reactivity from the triplet state<sup>4,7</sup>. The authors suggested that for GAV  $\beta$ -O-4 bond cleavage becomes a viable reaction pathway from the triplet state because hydrogen bonding provides steric hindrance to  $\beta$ -phenyl quenching, a competing excited state deactivation process. The added bulk of the hydrogen bonded groups was proposed to decrease  $\beta$ -phenyl quenching by increasing the barrier to the necessary rotation about the C-O bond, thereby leading to greater bond cleavage.

Depew and co-workers have studied the photochemical processes of GAV through time-resolved CIDEP (chemically induced dynamic electron polarization)<sup>5</sup>. These authors found that the primary photochemical process of GAV in 3:1 benzene/ethanol is photoreduction by solvent to yield ketyl radical prior to cleavage of the  $\beta$ -ether linkage. Solution and solid state studies provided indirect evidence for  $\beta$ -

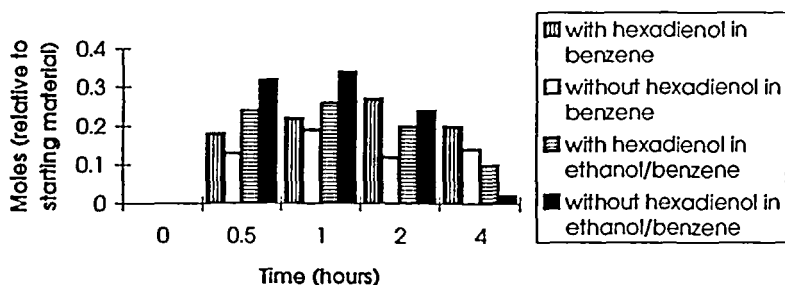


FIGURE 5. Formation of 2,6-Dimethoxyphenol

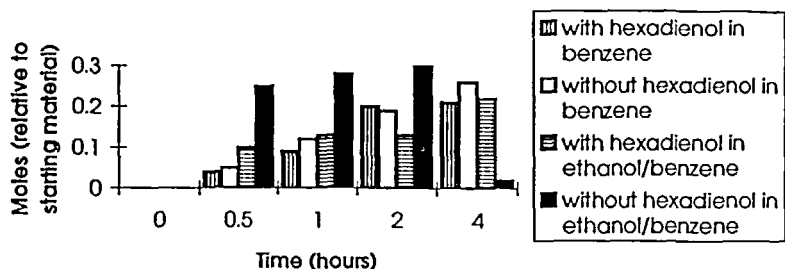


FIGURE 6. Formation of 3,4,5-Trimethoxyacetophenone

ether cleavage from the singlet state. Hence, if singlet reactivity is prominent in apolar solvents, the effect of an added triplet quencher will have minimal effect on the photodegradation of GAV. Similar behavior was observed for **1** in the present study.

Interesting trends exist in the amounts of DMP and TMAP products formed via photocleavage of **1** in benzene (Figure 5). If the addition of hexadienol influenced only the initial photodecomposition of **1**, then the amounts of DMP and TMAP would be expected to be comparable in solutions photolyzed with and without hexadienol. Instead, we detected more DMP product when **1** was photolyzed in the presence of hexadienol. We attribute this increase in DMP to participation by the hexadienol as a hydrogen atom donor, a favorable role for the hexadienol since the resulting hexadienyl radical is resonance stabilized. The observed amounts of TMAP product were not noticeably affected by addition of hexadienol. In ethanolic solvent, greater formation of both DMP and TMAP are observed in the absence of hexadienol (Figure 6). As was

expected, less DMP and TMAP were observed in the presence of hexadienol, due to the previously observed deterrence to photocleavage of **1** in ethanol with hexadienol present. Lack of triplet state quenching (and therefore increased photocleavage of **1**) by the hexadienol after four hours of photolysis (Figure 6) was manifested in the increased detection of DMP and TMAP relative to the amounts formed in the absence of hexadienol.

### Solid State Photolysis Studies

As previously noted, the application of hexadienol to BCTMP has been shown to retard photoyellowing of mechanical pulps. The results of our model compound studies, with and without hexadienol, suggest that one of the mechanisms by which this additive retards photo-yellowing is triplet quenching of the excited-state of carbonyls in lignin-like structures. The differences in reactivity of chromophores in model compound studies in solution and those in wood fibers could be significant and may impact on the overall mechanism(s) of stabilization. To explore this issue, we applied *trans,trans*-2,4-hexadienol to BCTMP fibers and irradiated these samples for 2 hours under comparable photolysis conditions as employed with the model compound studies. Following photolysis, the pulp fibers were extracted and the extracts were studied by GC/MS and NMR. Analysis of these extracts indicated that *trans,trans*-2,4-hexadienol had been photo-isomerized to yield all four geometric isomers in a manner analogous to the model compound studies. Furthermore, control experiments clearly demonstrated that the isomerization process was not due to mere application of 2,4-hexadienol onto BCTMP fibers but resulted only from photolysis of BCTMP pulp fibers containing the hexadienol.

To further examine this photoisomerization process we applied *trans-trans*-2,4-hexadienol onto cellulose fibers and photolyzed the mixture for an extended time period. The irradiated fibers were extracted with methylene chloride and the extracts were analyzed by GC/MS,  $^1\text{H}$  and  $^{13}\text{C}$  NMR. These studies indicated that photolysis of *trans,trans*-2,4-hexadienol adsorbed onto cellulose fibers afforded only the starting *trans, trans* isomer. These results clearly suggest that the observed photo-isomerization of 2,4-hexadienol on BCTMP fibers is due to the presence of lignin chromophores in mechanical pulp.

### CONCLUSIONS

The data presented in this paper suggest that one of the principal mechanisms of action of 2,4-hexadienol is triplet quenching of excited lignin chromophores both in model compound 1 and BCTMP pulp. Although there are potentially significant differences between the photochemical pathways available to carbonyl groups of phenacyl aryl ethers in solution and lignin chromophores those in wood fibers, we have observed that photolysis of hexadienol in both matrices results in its photo-sensitized isomerization. Other pathways of stabilization for hexadienol applied to BCTMP may include termination of free-radical propagation by hydrogen atom donation, and experiments to clarify such a role of the hexadienol are currently being investigated.

### Acknowledgements

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