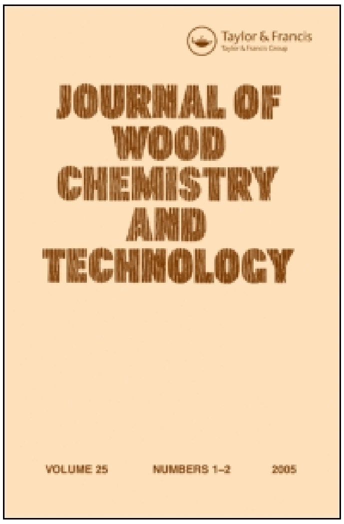


Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Modification of High-Yield Pulps with Polyethylene Glycols. I. Model Compound and Isolated Lignin Studies

Barbara J. W. Cole[a]; Stacey P. Huth[a]; Pamela S. Runnels[a]
[a] Department of Chemistry, University of Maine Orono, Maine, USA

To cite this Article Cole, Barbara J. W. , Huth, Stacey P. and Runnels, Pamela S.(1993) 'Modification of High-Yield Pulps with Polyethylene Glycols. I. Model Compound and Isolated Lignin Studies', Journal of Wood Chemistry and Technology, 13: 1, 59 — 72

To link to this Article: DOI: 10.1080/02773819308020507

URL: http://dx.doi.org/10.1080/02773819308020507

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 13(1), 59-72 (1993)

MODIFICATION OF HIGH-YIELD PULPS WITH POLYETHYLENE GLYCOLS. I. MODEL COMPOUND AND ISOLATED LIGNIN STUDIES

Barbara J.W. Cole, Stacey P. Huth, and Pamela S. Runnels
Department of Chemistry, University of Maine
Orono, Maine 04469 USA

Dedicated to the memory of Kyosti V. Sarkanen

ABSTRACT

Phenolic hydroxyl groups in three lignin model compounds, guaiacol, acetoguaiacone, and dehydrodiisoeugenol, and in organosolv lignin were blocked by etherification with polyethylene glycol (PEG). Polyethylene glycol modification, even at a low degree of substitution, greatly enhanced the hydrophilicity of the substrate, producing water-soluble substances. When etherified by reaction with PEG-mesylate, the lignin dimer model compound, dehydrodiisoeugenol, was stabilized considerably against light-induced yellowing.

INTRODUCTION

One of the primary uses of our forest resources is in the production of pulp for paper manufacture. Much of this pulp is produced by chemical pulping methods that utilize less than one-half of the fiber raw material. Hence, there is growing interest in replacing these low-yield (40-50% yield) chemical pulps with high-yield pulps, such as thermo- and chemi-mechanical pulps, that have yields of 85-96%, based on raw material. It was estimated that in 1992, high-yield pulps will account for only 10-11% of the total pulp production in the United States[1]. Therefore, there is tremendous potential for increasing the relative amount of high-yield pulps utilized. Because of the huge difference in yield between chemical and high-yield pulps, partial substitution of high-yield pulp for chemical pulp would result in significant improvement in wood fiber utilization. Furthermore, considerable environmental benefits and reduced capital costs will result when high-yield pulps are used more widely.

Currently, high-yield pulps are used for newsprint and magazine papers, but they cannot be used in higher quality papers for two major reasons: (1) high-yield pulps undergo photo-induced discoloration (yellowing), and (2) papers produced from high-yield pulps are not as strong as those made from chemical pulps. Unfortunately, today's market demands pulps and papers of increasingly high strength and long-lasting brightness which severely limits the use of high-yield pulps.

For over fifty years, researchers have attempted to elucidate the mechanisms responsible for photo-induced color reversion of papers. Although complete and indisputable mechanisms remain elusive, it is generally accepted that photooxidation of lignin, resulting in the formation of phenoxyl free radicals, is primarily responsible for yellowing. The role of free phenolic hydroxyl groups has been demonstrated in numerous studies [2-12]. When free phenolic hydroxyl groups are eliminated by methylation with dimethyl sulfate and alkali[11,13,14], acetylation[11,13,15] or benzoylation[11], intermediate phenoxy radicals cannot be formed and the rate of photo-induced yellowing is inhibited significantly. The problem is that these treatments do not selectively modify the lignin phenolic positions. Thus, large amounts of chemicals are required and the pulps produced have reduced strength properties because hydrogen-bonding hydroxyl groups in cellulose are derivatized also. Selective reaction of phenolic hydroxyl groups is possible, however, since careful control of pH allows ionization of the relatively acidic phenolic hydroxyl groups (pK_a ~10-11) to form phenoxide ions, while aliphatic hydroxyls (pK_a ~12-13) are not ionized[16]. Selective modification of lignin phenolic hydroxyl groups has been demonstrated in several studies[16-19].

The strength of a particular pulp, or the paper produced from it, depends largely on the chemical and physical characteristics of the fibers making up that pulp. High-yield fibers are stiff, rod-like structures that do not collapse to give large bonding areas[20]. In addition, the fibers produced in high-yield processes tend to be coated with lignin, and contain large amounts of lignin internally[21]. Because lignin is comparatively hydrophobic, interfiber hydrogen bonding is greatly diminished. Therefore, the strength of high-yield pulps is much lower than that of chemical pulps. Based on these known characteristics, it can be postulated that selective derivatization of phenolic hydroxyl groups in lignin with hydrophilic materials will increase brightness stabilization as well as improve strength properties in high-yield pulps.

Modified polyethylene glycols (PEG) or oligoethylene glycols (OEG) are compounds potentially capable of providing both effects. Polyethylene glycol (I) is an inexpensive material produced commercially in a wide range of molecular weights. PEG is remarkably hydrophilic and even at relatively high molecular weights is water-soluble. PEG is easily derivatized since the alcohol end groups are much more reactive than the polyoxyethylene chain[22]. These characteristics make PEG an ideal material to react with lignin in high-yield pulps. In a brief investigation, Fredholm and coworkers[17,18] treated the mesyl and epoxide derivatives of oligoethylene glycols with lignin model compounds, ball-milled lignin, and TMP. With the latter, moderate increases in pulp strength were observed.

$$HO\text{-}CH_2CH_2\text{-}O\text{-}(CH_2CH_2O)_n\text{-}CH_2CH_2\text{-}OH$$

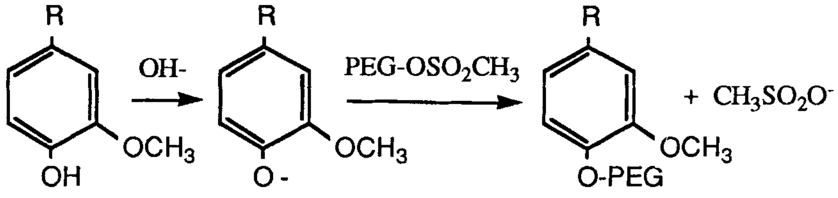
(I) - Polyethylene glycol

The work reported in this paper includes the modification of lignin model compounds and organosolv lignin with a polyethylene glycol mesylate.

RESULTS AND DISCUSSION

Proposed Reactions

Under alkaline conditions, etherification of phenolic hydroxyl groups proceeds via an S_N2 mechanism. The phenoxide ion is a strong nucleophile that compounds possessing good leaving groups. This reaction sequence, written specifically for the compounds used in this study, is shown in Figure 1.



R = H, CH_3CO, dimer fragment, or lignin

Figure 1. The reaction of PEG-mesylate with lignin and lignin model compounds.

Polyethylene Glycol Derivatives

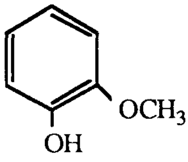
To react with phenolic groups in models or in lignin, polyethylene glycol must be derivatized to provide reactive functional sites. In this study, the mesyl derivative of PEG methyl ether (II) was used. PEG methyl ether, in which one hydroxyl group is blocked by a methyl group, was chosen as the starting material to facilitate product separation and analysis and to avoid crosslinking reactions. PEG-mesylate is known to be exceptionally stable and the mesylate group has high reactivity in S_N2 reactions[23]. In addition, low molecular weight PEG-mesylates are soluble in water and in various organic solvents. In this study, yields of approximately 90% were obtained when PEG methyl ether (MW 350) was reacted with methanesulfonyl chloride using triethylamine as catalyst.

$$H_3CO\text{-}CH_2CH_2\text{-}O\text{-}(CH_2CH_2O)_n\text{-}CH_2CH_2\text{-}OSO_2CH_3$$

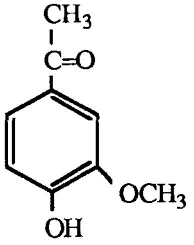
(II) - PEG-Mesylate

Model Compound Studies

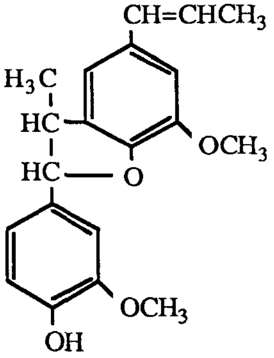
To optimize reaction conditions and gain information to aid in the interpretation of modified lignin and pulp results, it is essential to conduct model compound studies. PEG-mesylate (II) was reacted with guaiacol (III), acetoguaiacone (IV), and dehydrodiisoeugenol (V). Dehydrodiisoeugenol, which contains a phenylcoumaran structure, was selected as the dimer model because it is easily prepared in large quantities and the NMR spectra are well resolved and easily interpreted. Phenylcoumaran units are important structural segments of lignin that are believed to play a major role in yellowing of high-yield pulps[14, 24].



III



IV



V

Initial studies with guaiacol indicated that a minimum pH of 12.6 was required to form an acceptable yield of PEG-modified product at ambient pressure and 80°C. At lower pH and temperatures, little product was obtained. Etherification of guaiacol, acetoguaiacone, and dehydrodiisoeugenol with II at pH=12.6 gave yields of 80%, 64%, and 82%, respectively. The etherification products were identified using ^{1}H-nmr and ^{13}C-nmr. Characteristic peaks at 3.1 and 4.4 ppm in the ^{1}H-nmr spectrum of PEG-mesylate disappeared in the modified model, while a new signal appeared at 4.2 ppm, verifying the formation of the ether. In addition to the appearance and disappearance of signals, shifts of the ring carbon signals were clearly evident in the ^{13}C-nmr spectrum following modification of the model. Details of the NMR spectra are provided in the Experimental section of this paper.

We also verified PEG etherification of all three model compounds using simple solubility tests. Guaiacol, acetoguaiacone, and dehydrodiisoeugenol were all insoluble in water while the PEG-modified products were completely water-soluble. This observation not only confirms the existence of a chemical bond between PEG and the models, but it also gives support to the concept that attachment of PEG to lignin in pulp will increase its hydrophilicity.

Lignin Studies

The chloroform-soluble fraction of an organosolv lignin obtained by methanol-water pulping of black cottonwood was utilized in this study. Lignin was reacted with PEG-mesylate under conditions similar to those used in the model compound studies. After purification, the PEG-modified lignin was characterized using ^{1}H-nmr, ^{13}C-nmr, solubility properties, and phenolic hydroxyl content measurement. In the ^{1}H-nmr spectrum of the product, signals at 3.36 ppm ($-OC\underline{H}_3$ endcap in PEG), 3.5 ppm (ethylene hydrogens in PEG) and 3.73 ppm ($-OC\underline{H}_3$ in lignin), and the lack of a signal at 3.08 ppm ($-OSO_2C\underline{H}_3$), provided evidence for the presence of a PEG-modified lignin. Similarly, in the ^{13}C-nmr spectrum, signals derived from PEG (57.9 ppm, $O\underline{C}H_3$ endcap; 69.7, ethylene carbons) and lignin (55.8 ppm, $O\underline{C}H_3$) were observed and the peak at 36.7 ppm for the mesylate methyl carbon was not present.

Further indication of etherification of lignin with PEG was provided by the observed differences in solubilities between lignin and lignin-PEG. While the chloroform-soluble fraction of the organosolv lignin was completely insoluble in water, the PEG-modified lignin was fully water-soluble. Phenolic hydroxyl (phOH) content also was determined by the periodate method to confirm the blockage of free phenolic groups in lignin. This method is based on the oxidation of simple phenolic guaiacyl compounds to ortho-quinone structures with release of methanol. The periodate method has been applied extensively to isolated lignins and to pulps and has been found to give results comparable to those obtained using the more tedious aminolysis procedure[25]. Phenolic hydroxyl content determinations for lignin and lignin-PEG suggested the elimination of some of the free phenolic hydroxyl groups. The phOH content in lignin was 19.3 phOH/100 C_9, whereas lignin-PEG had a phenolic hydroxyl content of 15.8 phOH/100 C_9. These results indicate that about 20% of the free phenolic positions were blocked with PEG. Although this relatively low substitution level significantly affected the solubility of lignin, we believe that a greater degree of etherification will be required to improve the strength and brightness retention of pulps.

The Effect of PEG on Brightness Stabilization

Using the dimer model compound, dehydrodiisoeugenol, we investigated the effects of PEG modification on brightness and brightness stabilization. Solutions of known concentration (0.03 M) of dehydrodiisoeugenol (dimer) and dehydrodiisoeugenol-PEG (dimer-PEG) were adsorbed onto lignin-free filter papers. ISO brightness was determined for the treated sheets which were subjected subsequently to ultraviolet irradiation in a Rayonet photoreactor for 8 hours. Brightness was determined several times during the irradiation period. The results of these experiments are shown in Figure 2. For reasons we cannot explain yet, the brightness of the dimer-PEG treated sheet was lower than that of the dimer treated sheet. It is possible that the alkaline conditions used in the preparation of dimer-PEG generated chromophoric groups that were not removed during purification. It can be seen, however, that PEG-modification inhibited brightness reversion of the dimer significantly. The brightness of the sheet treated with dimer alone dropped very quickly from 77.6 to 53.6 in the first two hours of irradiation and then continued to drop more slowly until a final brightness of 50.9 was obtained after 8 hours. The brightness of the dimer-PEG treated sheet lost only 4 units of brightness, 72.8 to 66.8, in the first two hours and then stabilized at a brightness of 65.7 for the remainder of the 8 hour irradiation period. Thus, while the unmodified dimer lost 26.7 units of brightness overall, dimer that had been modified with PEG lost only 7.1 units. We are now applying these procedures to other dimer model compounds and pulps to verify the effects of PEG modification on brightness reversion.

EXPERIMENTAL

General Experimental Procedures

^{1}H-nmr and ^{13}C-nmr spectra were recorded on a Varian XL-200 spectrometer. ^{1}H-nmr spectra were obtained in $CDCl_3$, and ^{13}C-nmr spectra in DMSO-d_6. Gas

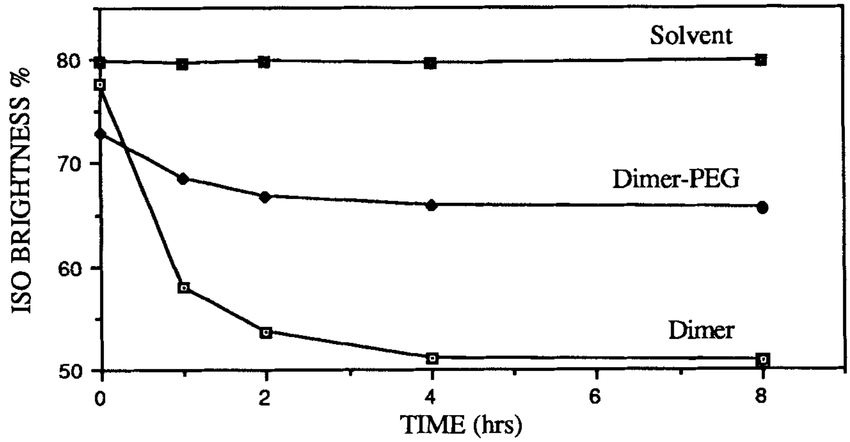


Figure 2. The effect of PEG-modification on the lignin model compound, dehydrodiisoeugenol (dimer). Solvent = acetonitrile, t =0 is the brightness recorded immediately after adsorption of compound on filter paper. The brightness of untreated filter paper is 80.1%.

chromatographic data were obtained using a Hewlett Packard 5890 GC, equipped with an FID detector.

Lignin & Lignin Model Compounds

Compound III (guaiacol) was purchased from Aldrich Chemical Company, Inc. ^{1}H-nmr: 3.89 (-OC$\underline{H}_3$), 5.59 (-O$\underline{H}$); ^{13}C-nmr: 145.85 ($\underline{C}$-OH), 146.94 ($\underline{C}$-OCH$_3$).

Compound IV (acetoguaiacone) was purchased from Aldrich. ^{1}H-nmr: 3.96 (-OC$\underline{H}_3$), 6.08 (-O$\underline{H}$); ^{13}C-nmr: 146.72 ($\underline{C}$-OH), 150.94 ($\underline{C}$-OCH$_3$).

Compound V (dehydrodiisoeugenol) was synthesized according to the method of Leopold[26]. Isoeugenol (5.0 g, purchased from Aldrich) was dissolved in 45 mL of ethanol (95%) and 20 mL of water. To this solution was added 7.0 g of ferric chloride in 20 mL of water. The solution, which turned dark green and cloudy, was refrigerated for at least 24 hours. The reddish white crystalline solid which formed was collected by vacuum filtration and washed with 45% ethanol. The resulting product (yield = 30%) had a melting point of 132-133 °C which is in agreement with that reported in the literature[26]. The ^{1}H-nmr spectrum was identical to that reported in The Handbook of Proton-NMR Spectra and Data[27]. The phenolic hydroxyl proton was observed at 5.62 ppm. ^{13}C-nmr spectral data coincided with that in the literature[28]. The carbon adjacent to the phenolic hydroxyl was observed at 145.5 ppm.

Organolsolv lignin was isolated from black cottonwood (*P. trichocarpa*) which had been pulped using a methanol/water (70/30) solvent system with $NaHSO_4$ as a catalyst [29]. The chloroform-soluble fraction of this lignin was utilized in this study. ^{1}H-nmr: broad peaks were observed at 3.7 and 6.7 ppm; ^{13}C-nmr: 55.9 ($-O\underline{C}H_3$), and other typical lignin peaks were observed from 103 ppm to 152 ppm. Periodate oxidation of organosolv lignin, followed by GC analysis, showed 19.3 phOH/100 C_9 units.

PEG Compounds

Compound I (PEG methyl ether, MW 350) was purchased from Aldrich Chemical Company. ^{1}H-nmr: 3.38 ($-OC\underline{H}_3$), 3.65 ($-OC\underline{H}_2C\underline{H}_2O-$); ^{13}C-nmr: 59.47 ($-O\underline{C}H_3$), 69.04 ($-O\underline{C}H_2\underline{C}H_2O-$).

Compound II (PEG-mesylate) was synthesized according to the method of Harris and coworkers[23]. Methanesulfonyl chloride (0.39 mL, 5 mmol), in 60 mL of methylene chloride was mixed at 0°C with 0.35 g (1 mmol) of PEG methyl ether (MW 350) and 0.28 mL (2 mmol) of triethylamine dissolved in 60 mL of methylene chloride. The reaction was stirred for 2 hrs at 0°C. Excess ammonium salt was precipitated by the addition of ether (twice) and ethyl acetate (once), and removed by filtration. The viscous liquid which remained was purified by passage through a cation exchange column (Dowex 50W-X8, 20-50 mesh, hydrogen form). The sample was dissolved in a small amount of water or methanol and passed through the column using water as the solvent. The PEG-mesylate was extracted from the water phase with methylene chloride at least twice, and evaporated. An anion exchange column (Dowex 2-X8, 20-50 mesh, chloride form), converted to the hydroxide form with NaOH, was used for further purification. The sample was again dissolved in water and passed through the anion column using water as the solvent. The purified PEG-mesylate was extracted from the water phase with methylene chloride and evaporated. ^{1}H-nmr: 3.08 ($-OSO_2C\underline{H}_3$), 3.38 ($-OC\underline{H}_3$), 3.65 ($-OC\underline{H}_2C\underline{H}_2O-$), 4.38 ($-CH_2C\underline{H}_2OSO_2CH_3$); ^{13}C-nmr: 36.7 ($-OSO_2\underline{C}H_3$), 57.93 ($-O\underline{C}H_3$), 69.63 ($-O\underline{C}H_2\underline{C}H_2O-$).

Guaiacol-PEG was synthesized using a method similar to that of Fredholm and coworkers[17]. A 20% aqueous dioxane solution of 0.4 M NaOH was prepared. To 4 mL of this solution, guaiacol (0.154 mL) and PEG-mesylate (0.3424 g) were added. NaOH (0.4 M) was added dropwise until a pH = 12.6 was obtained. The solution was stirred at 80°C for 24 hrs. The product was extracted from the aqueous phase with methylene chloride and the organic phase evaporated. The NMR spectrum of the viscous liquid showed a mixture of guaiacol and guaiacol-PEG. Column chromatography with silica gel (230-400 mesh) and an ethyl acetate/methanol gradient, was used for the separation. Pure guaiacol-PEG was obtained in 80% yield. ^{1}H-nmr: 3.35 ($-OC\underline{H}_3$ from PEG), 3.63 ($-OC\underline{H}_2C\underline{H}_2O-$ from PEG), 3.83 ($-OC\underline{H}_3$ from guaiacol), 4.2 ($-CH_2C\underline{H}_2-O-\varnothing$); ^{13}C-nmr: 59.46 ($-O\underline{C}H_3$ from PEG), 69.17 ($-O\underline{C}H_2\underline{C}H_2O-$ from PEG), 147.26 ($\underline{C}-OPEG$), 148.34 ($\underline{C}-OCH_3$ from guaiacol).

Acetoguaiacone-PEG was prepared according to the procedure described for guaiacol-PEG except that 0.231 g of acetoguaiacone was treated in a 20% dioxane solution of 0.25 M NaOH with a pH of 10.4. A silica gel column, as described above, was used for isolation of acetoguaiacone-PEG. Pure acetoguaiacone-PEG was obtained in 64% yield. ^{1}H-nmr: 3.38 ($-OC\underline{H}_3$ from PEG), 3.65 ($-OC\underline{H}_2C\underline{H}_2O-$ from PEG), 3.91 ($-OC\underline{H}_3$ from acetoguaiacone), 4.25 ($-CH_2C\underline{H}_2-O-\varnothing$); ^{13}C-nmr: 59.47 ($-O\underline{C}H_3$ from PEG), 69.04 ($-O\underline{C}H_2\underline{C}H_2O-$ from PEG),147.88 ($\underline{C}-OPEG$), 151.55 ($\underline{C}-OCH_3$ from acetoguaiacone).

Dehydrodiisoeugenol-PEG was prepared as described above for guaiacol-PEG. Dehydrodiisoeugenol (0.457 g) was used in the reaction. Column chromatography with silica gel (230-400 mesh) and a methylene chloride/ethyl acetate/methanol gradient was used for the isolation of the product. Pure dehydrodiisoeugenol-PEG was obtained in 82% yield. ^{1}H-nmr: 3.37 (-$OC\underline{H}_3$ from PEG), 3.65 (-$OC\underline{H}_2C\underline{H}_2O$- from PEG), 4.2 (-$CH_2C\underline{H}_2$-O-Ø): ^{13}C-nmr: 68.8 (-$O\underline{C}H_2\underline{C}H_2O$- from PEG), 145.32 ($\underline{C}$-OPEG).

Organosolv lignin-PEG was synthesized using a procedure similar to that used for the lignin model compounds. A 20% dioxane solution of 0.4 M NaOH was prepared. To 6 mL of this solution, 0.6 g of the chloroform soluble fraction of organosolv lignin and 0.488 g of PEG-mesylate were added. NaOH (0.4 M) was added dropwise until pH=12.6 was reached. The solution was stirred at 80°C for 24 hrs. Extraction with methylene chloride gave a viscous black material. The product was washed with several portions of ether, to remove excess PEG-mesylate, and filtered through a sintered glass funnel. The remaining light brown powder weighed 0.370 g. ^{1}H-nmr: 3.36 (-$OC\underline{H}_3$ from PEG), 3.5 (-$OC\underline{H}_2C\underline{H}_2O$- from PEG), 3.73 (-$OC\underline{H}_3$ from lignin); ^{13}C-nmr: in addition to the typical peaks observed for lignin, such as -$O\underline{C}H_3$ at 55.8 ppm, PEG peaks were seen at 57.9 (-$O\underline{C}H_3$) and 69.72 (-$O\underline{C}H_2\underline{C}H_2O$-). Periodate oxidation of this lignin-PEG, followed by GC analysis, gave 15.8 phOH/mole lignin-PEG. In calculating the phOH content in lignin and lignin-PEG, a C_9 molecular weight of 220 was used.

Periodate Oxidation

The procedure used was similar to that of Francis et al.[25]. A sample (41 mg) of material to be analyzed was treated with 400 mg of $NaIO_4$ dissolved in 4 mL of H_2O in a centrifuge tube. An internal standard (1.5 mg acetonitrile in 1 mL of H_2O) was added. The mixture was shaken vigorously and was kept in the dark in a refrigerator at 4°C with frequent shaking throughout the reaction period. The mixture was centrifuged prior to drawing a 1-μL aliquot of the mixture which was analyzed by GC. The mixture was shaken again and the reaction period of the sample was continued. The rate of methanol formation was measured daily for six days.

GC Method

Methanol and acetonitrile (internal standard) were determined using a J&W Scientific DB-Wax high speed GC column (20M, ID 0.18 mm, 0.3 μ film thickness). The column was operated with an injection port temperature of 200°C, detector temperature of 220°C and a column head pressure of 14 psi. The split ratio was 50:1 and the injection volume was 1 μL. Gas flow rates were: He-40 psi; H_2-14 psi; air-40 psi; N_2-42.5 psi. An initial oven temperature of 45°C was held for 7.5 minutes. A 40°C/minute gradient was then initiated for 2 minutes, followed by 1.5 minutes at 125°C. Retention times for methanol and acetonitrile were ≈ 4 and 6.8 minutes, respectively.

Brightness Reversion Study

Solutions of dehydrodiisoeugenol (0.033 M) and dehydrodiisoeugenol-PEG (0.036 M) were prepared using acetonitrile as the solvent. A 100-μL aliquot of each solution was carefully adsorbed onto a 4.25 cm Whatman filter paper. The sheets were air dried and brightness values were measured using a Technibrite brightness meter. The sheets were irradiated in a Rayonet RPR-100 merry-go-round photochemical reactor (Southern New England Ultraviolet Co., Branford, CT). Sunlight phosphor lamps providing 21 W of energy and a maximum output of ≈ 300 nm were used. The brightness of each handsheet was determined after 1, 2, 4, and 8 hours of irradiation.

ACKNOWLEDGMENTS

This paper is dedicated to Professor Kyosti V. Sarkanen who through his knowledge and enthusiasm inspired the senior author of this paper and many other students to pursue careers in wood chemistry research and teaching. Kyosti, perhaps more than any other individual, influenced the field of wood chemistry by instilling in others a sense of curiosity and excitement. We are deeply indebted to him for this.

The collaboration of Dr. A. Ragauskas at the Institute of Paper Science and Technology who provided 400 MHz NMR spectra and Mr. L.N. Lester who provided assistance in obtaining 200 MHz NMR spectra is gratefully acknowleged. This project has been supported by USDA grant 90-37291-5766.

REFERENCES

1. N. Deking, Pulp and Paper, 64, 176 (1990).
2. S. Y. Lin and K.P. Kringstad, Tappi J., 53, 658 (1970).
3. S. Y. Lin and K.P. Kringstad, Norsk Skogind., 25, 252 (1971).
4. I. J. Forsskåhl, Photochem., 25, 197 (1984).
5. I. J. Forsskåhl, I., Photosensitized reactions of lignin model compounds and the role of singlet oxygen in lignin photochemistry. Ph.D. Dissertation, University of Helsinki, Helsinki, Finland (1985).
6. G. Gellerstedt and I. Pettersson, Acta Chem. Scand., B29, 1005 (1975).
7. G. Gellerstedt and I. Pettersson, Svensk Papperstidn., 80, 15 (1977).
8. J. Gierer and S. Lin, Svensk Papperstidn., 75, 233 (1972).
9. K.P. Kringstad and S.Y. Lin, Tappi J., 53, 2296 (1970).
10. G. Brunow and M. Sivonen, Pap. Puu., 57, 215 (1975).
11. G.J. Leary, Tappi J., 51, 257 (1968).
12. G. Brunow, I. Forsskåhl, A. Gronlund, G. Lindstrom and K. Nyberg, In Singlet Oxygen: Reactions with Organic Compounds and Polymers, B.Ranby, and J.F. Rabek (eds), John Wiley & Sons, New York (1978).
13. V. Lorås, Pulp Paper Mag. Can., 69, 57 (1968).
14. J. Schmidt and C. Heitner, J. Wood Chem. Technol., 11, 397 (1991).
15. D.F. Manchester, J. McKinney and A.A. Pataky, Svensk Papperstidn., 63, 699 (1960).
16. F.A. Wallis and R. H. Wearne, Appita, 36, 192 (1982).
17. B. Fredholm, B. Samuelsson, A. Wallis, A. Westfelt and L. Westfelt, Cellulose Chem. Technol., 17, 245 (1983).
18. B.Fredholm, B. Samuelsson, A. Wallis, A. Westfelt and L. Westfelt, Cellulose Chem. Technol., 17, 255 (1983).

19. U. Tschirner and C.W. Dence, Pap. Puu., 36, 338 (1988).
20. D.C. McIntosh, In Handbook of Pulp and Paper Technology, 2nd Edition, K.W. Britt (ed), Van Nostrand Reinhold Co., New York (1970).
21. G.A. Smook, Handbook for Pulp and Paper Technologists, Joint Textbook Committee of the Paper Industry of the U.S. and Canada, Montreal, p. 56 (1982).
22. J.M. Harris, Rev. Macromol. Chem. Phys., C25, 325 (1985).
23. J.M. Harris, E.C. Struck, M.G. Case, M.S. Paley, M. Yalpani, J.M. Van Alstine and D. Brooks, J. Polym. Sci., 22, 341 (1984).
24. D.Y. Lee and M. Sumimoto, Holzforschung, 45(suppl.), 15 (1991).
25. R.C. Francis, Y. Lai, C.W. Dence and T.C. Alexander, Tappi J., 73, 219 (1991).
26. B. Leopold, Acta Chem. Scand., 4, 1523 (1950).
27. Handbook of Proton-NMR Spectra and Data, Vol. 5, p. 314, Asahi Research Center (eds), Academic Press, Tokyo, (1985).
28. K.P. Kringstad and R. Mörck, Holzforschung, 37, 237 (1983).
29. B.J.W. Cole, Black Cottonwood (*Populus trichocarpa*): Organosolv Pulping and Chemical Composition, M.S. Thesis, University of Washington, Seattle, WA (1983).