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### Photoyellowing of Milled Wood Lignin and Peroxide-Bleached Milled Wood Lignin in Solid 2-Hydroxypropylcellulose Films After Sodium Borohydride Reduction and Catalytic Hydrogenation in Solution: an Uv/Vis Absorption Spectroscopic Study

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**PHOTOYELLOWING OF MILLED WOOD LIGNIN AND PEROXIDE-BLEACHED  
MILLED WOOD LIGNIN IN SOLID 2-HYDROXYPROPYLCELLULOSE FILMS  
AFTER SODIUM BOROHYDRIDE REDUCTION AND CATALYTIC  
HYDROGENATION IN SOLUTION : AN UV/VIS ABSORPTION  
SPECTROSCOPIC STUDY**

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**SUMMARY**

UV absorption spectroscopy was used to determine the chromophore composition of tetrahydrofuran/water-soluble milled wood lignin (MWL) and peroxide-bleached lignin (LHO) using ionization difference UV spectroscopy. MWL and LHO were treated in solution with sodium borohydride to reduce the carbonyl chromophores which were shown to be prone to induce photoyellowing. Furthermore, the reduced solutions were hydrogenated in solution over Pd/C catalyst to eliminate the aromatic-conjugated double bonds that also induce photodiscoloration. The lignins were incorporated into 2-hydroxypropylcellulose (HPC) at a concentration near 0.5% and then irradiated with filtered light ( $\lambda > 300$  nm) in the form of solid, transparent films. The photochemistry of the different samples was followed by UV/Vis absorption spectroscopy and the kinetics of discoloration and aromatic ring destruction were established. The peroxide-bleached, reduced, and hydrogenated lignin was found to be almost completely stable in the solid carbohydrate matrix under irradiation. Furthermore, the kinetics show the importance of phenolic biphenyl chromophores and probably also of phenolic phenylcoumaran structures in the photoyellowing process.

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## INTRODUCTION

The mechanism of discoloration of high-yield pulps, attributed to a large extent to the photoreactivity of lignin<sup>1</sup>, is not completely understood<sup>2,3</sup>. Experiments conducted in our laboratory on model molecules have shown that homolytic  $\beta$ -C-O bond cleavage is the major pathway in the discoloration process involving  $\beta$ -O-4  $\alpha$ -carbonyl structures which were found to give *inter-alla*  $\alpha$ -carbonyl  $\beta$ -1 derivatives<sup>4,5</sup>. The latter chromophores were shown to display photoyellowing when adsorbed on a solid carbohydrate matrix<sup>6</sup> and their photoreactivity, studied on deoxyveratrolin, is accounted for by Norrish type 1 cleavage and formation of ketyl and desyl radicals which are further oxidized by ground state oxygen<sup>7</sup>.

The importance of phenolic groups has been recognized for a long time<sup>2</sup>. The mechanisms involved are phenolic hydrogen abstraction by excited carbonyl groups, hydroxyl radicals<sup>2</sup> and/or by singlet oxygen<sup>2,3</sup>. Direct photolysis of phenols, that absorb light above 290 nm where sunlight is effective<sup>8</sup>, has been postulated to account for the low increase in the UV stability of bleached high-yield pulps after reduction with sodium borohydride<sup>9</sup>.

The present article deals with an attempt to assess the role of conjugated chromophores (e.g. carbonyl and non-carbonyl phenols, biphenyls and conjugated double bonds) in the discoloration of high-yield pulps. For this purpose, a photochemical study on milled wood lignin (maritime pine, MWL) and peroxide-bleached MWL (LHO) incorporated into transparent hydroxypropylcellulose (HPC) films, is described. Although the irradiations were performed in the solid state, MWL and LHO, owing to their solubility in organic solvents, allow easier spectroscopic characterization and more complete chemical reaction than does lignin in pulps.

## EXPERIMENTAL

### *Preparation of milled wood lignin (MWL)*

Milled wood lignin was prepared as described by Lapiere<sup>10</sup> using the Björkman procedure<sup>11</sup>. Maritime pine sawdust was successively pre-extracted in a Kumagawa apparatus with an ethanol-toluene mixture (3/2 V/V), ethanol, and water. The material was dried at 35°C for 24 h.

Ultragrinding of the wood meal was performed in a vibratory porcelain ball mill (vibratom grinder type SN06 Siebtechnik) in the dry state at room temperature for 50 h.

The extraction of the ball-milled pre-extracted wood (30g) was done with 600 mL of a dioxane-water mixture (9/1 V/V) at 25°C under nitrogen. The solid was separated by centrifugation, the solution concentrated to 80 mL under vacuum

(aspirator) at 35 °C and poured into 2L of aqueous sodium sulfate solution (4%). The precipitated solid was isolated by centrifugation and washed twice with distilled water, centrifuged, and freeze-dried leaving 1.4 g of a yellow material. This solid, soluble in a THF/water mixture (9/1 V/V), was analyzed by the acetyl bromide method<sup>12</sup> which indicated that it contained 80% lignin.

#### *Preparation of peroxide bleached milled wood lignin (LHO)*

The bleaching of MWL was performed without chelating agent and silicate. One charge of the bleaching mixture (1 g of H<sub>2</sub>O<sub>2</sub> (30%) and 1 mL of NaOH (1N)) was added to 500 mg of unbleached MWL in 150 mL of THF under magnetic stirring at 50 °C. After 2 h of reaction, another charge of the bleaching solution was added and the reaction continued for 2 hours more. The THF was then evaporated under vacuum (aspirator) at 25 °C and 10 mL of distilled water was added to the residual solution. After acidification to pH 5 with sulfuric acid, a white solid precipitated which was isolated by centrifugation, washed twice with 5 mL of water and freeze-dried leaving 350 mg of a white material containing 74% lignin (acetyl bromide method).

#### *Acetylation of MWL and LHO*

A 50 mg sample was stirred at room temperature, under nitrogen, for 44 h with 2 mL of triethylamine, 2 mL of acetic anhydride and 1.5 mg of N,N-dimethyl-4-aminopyridine in 15 mL of an anhydrous THF-CH<sub>2</sub>Cl<sub>2</sub> mixture (2/1 V/V). The solution was evaporated under vacuum (aspirator) and washed with water, centrifuged, freeze-dried, and kept at -30 °C before analysis.

#### *Preparation of MWL in hydroxypropylcellulose films (MWL)*

Five mg of unbleached MWL was dissolved in 13 mL of THF and 1.5 mL of water, then 850 mg of hydroxypropylcellulose (HPC, Hercules Klucel E 60,000) were added and the mixture sonicated until the HPC was completely dissolved. After concentration to 8 mL under vacuum (aspirator), the solution was spread out in a polished Teflon dish and evaporated to dryness (3 h) in a circulating air oven at 35 °C, giving a transparent film which was used for the different studies.

#### *Preparation of LHO in hydroxypropylcellulose films (LHO)*

The procedure used to prepare the MWL film was employed, the 5 mg of MWL being replaced by 7 mg of LHO.

### *Preparation of sodium borohydride-reduced MWL films (BL)*

Five mg of MWL in 10 mL of THF and 0.5 mL of distilled water were reduced with 70 mg of sodium borohydride in 0.5 mL of NaOH (1N) at room temperature for 42 h. After acidification with sulfuric acid to pH 4, the solution was centrifuged to eliminate the insoluble boric salts, the latter being washed with 2 mL of THF. The THF solutions were mixed and combined with 850 mg of HPC to prepare a film as described above for MWL.

### *Preparation of sodium borohydride-reduced and hydrogenated (Pd/C) MWL films (PBL)*

This preparation used the same procedure described above for the preparation of BL, but prior to making the film, 5 mg of Pd/C (5%) was added to the THF solution, and the mixture was hydrogenated at atmospheric pressure for 4h. After centrifuging the solution to eliminate the catalyst, 850 mg of HPC was added to prepare the film as described for MWL.

### *Preparation of sodium borohydride-reduced, peroxide-bleached MWL films (HOBL)*

The procedure used to prepare the BL film was employed, the 5 mg of MWL being replaced by 7 mg of LHO.

### *Preparation of sodium borohydride-reduced and hydrogenated (Pd/C), peroxide-bleached MWL films (HOPBL)*

The procedure used to prepare the PBL film was employed, the 5 mg of MWL being replaced by 7 mg of LHO.

### *General methods*

Gel permeation chromatography of acetylated MWL and LHO (1% THF solutions) was performed on a Varian HPLC 5560 apparatus equipped with 4 TSK columns (1000H, 2000H, 3000H and 5000H) and with UV detection using THF as eluent (1 mL/mn). The elution time was calibrated with polystyrene standards.

UV spectra were measured on a Cary 219 connected to a PC to analyze the data. Rigorously reproducible positioning of the films in the optical compartment, was essential for a good comparison of the spectra. Before irradiation, except for MWL,

the different studied lignins in the films do not present significant absorption in the visible region. This observation indicates that hydrogen peroxide and sodium borohydride treatments are efficient in bleaching the colored MWL.

Irradiation of the films was performed with the set-up described previously<sup>9</sup> using a medium-pressure mercury lamp and a borosilicate glass filter to eliminate wavelengths below 300 nm.

IR spectrometry (Perkin-Elmer 983 dispersive apparatus equipped with a data station) was not found sensitive enough to follow the photochemical reaction due to the low concentration of the lignin used (0.5%) in the HPC films.

### *Chromophore analysis of MWL and LHO by ionization difference UV spectroscopy in solution*

The evaluation of the different chromophores in the soluble lignins (MWL and LHO) was done using the Aulin-Erdtman method<sup>13</sup>. The ionization spectra were recorded for MWL and LHO (concentration: 0.055 g/L) in 2-methoxyethanol/ethanol (2/3 V/V), with the basic solution placed in the sample beam and the neutral one in the reference beam. The ionization spectra were also recorded for MWL and LHO after reduction with sodium borohydride (10 mg/ mg of lignin) in the same solvent mixture for 50 h at room temperature. The concentrations of the solutions were adjusted to provide 0.055 g /L of lignin after the NaBH<sub>4</sub> reduction to evaluate the reduction quantitatively. In addition, catalytic hydrogenation (H<sub>2</sub>) over Pd/C (5%; 1 mg/ mg of lignin) of the sodium borohydride-reduced solutions (MWL and LHO) was performed at room temperature for 4 h and the ionization spectra recorded.

The reaction time was chosen to be long enough, so that no further change was observed in the UV spectra of the sodium borohydride-treated and hydrogenated solutions. The evaluation of the chromophore content was thus done assuming complete reduction of the  $\alpha$ -carbonyl and coniferaldehyde groups by NaBH<sub>4</sub>, and complete hydrogenation of the conjugated double bonds by H<sub>2</sub> (Pd/C).

The total phenolic content was evaluated from the ionization difference curve of the sodium borohydride-reduced MWL and LHO at 300 nm ( $\epsilon_1=4100$  <sup>14</sup>). The content of phenolic  $\alpha$ -carbonyl groups and phenolic coniferaldehyde chromophores was estimated using the ionization curves before and after NaBH<sub>4</sub> reduction, respectively, at 350 nm ( $\epsilon_1=25000$  <sup>13g</sup>) and 420 nm ( $\epsilon_1=35000$  <sup>13d</sup>). The total  $\alpha$ -carbonyl content was determined by comparison of the absorption curves at 304 nm ( $\epsilon=8700$  <sup>4</sup>) in a neutral medium before and after NaBH<sub>4</sub> reduction of the MWL and LHO. The same method was applied to determine the total amount of etherified and non-etherified coniferaldehyde groups at 340 nm ( $\epsilon=23500$  <sup>13c</sup>). The content of phenolic stilbene groups and the hydroxyphenylcoumarone chromophore were

determined using the ionization curves before and after hydrogenation respectively at 356 nm using 4-hydroxy-3,3',4'-trimethoxystilbene as a model<sup>8</sup> ( $\epsilon_i=28000$ ) and at 330 nm by comparison with a phenolic phenylcoumarone model<sup>8</sup> ( $\epsilon_i=29000$ ). In the same way, the amount of phenolic isoeugenol type chromophore was determined at 310 nm using isoeugenol as a model ( $\epsilon_i=11700$ ). The phenolic biphenyl content was evaluated with the ionization curve at 316 nm of the hydrogenated MWL and LHO using 2-hydroxy-2',3,3'-trimethoxy-5,5'-di-n-propylbiphenyl<sup>8</sup> ( $\epsilon_i=5000$ ) as a model.

## RESULTS AND DISCUSSION

### *Isolation and chromophore characterization of soluble lignin MWL and LHO*

Tetrahydrofuran /water (9/1 V/V) soluble lignin was prepared from maritime pine according to Björkman<sup>11</sup>. The isolated material contained 80% lignin, the remaining 20% being probably carbohydrates linked to the lignin polymer. Calculated from the starting wood (29% lignin), the yield of soluble lignin was 13%. The material was not further purified because our objective was to obtain a soluble substrate to perform i) chromophore characterization by ionization difference UV spectroscopy which is a very sensitive technique and ii) sodium borohydride reduction and catalyzed hydrogenation in a medium where steric hinderance by the solid carbohydrate matrix cannot be invoked as a cause of incomplete reaction.

Bleaching of MWL was performed in THF solution with a  $H_2O_2/NaOH$  mixture. The yield based on lignin was 65%.

The measurement of molecular weight distribution using gel permeation chromatography (GPC) was performed on acetylated MWL and LHO to increase the solubility of the material in dry THF and also to minimize solute-solute, solute-solvent, and solute-column interactions<sup>15</sup>. The results are reported in Figure 1.

The values observed compare well with those obtained by Himmel et al. on ball-milled aspen lignin<sup>15</sup>. Of note are the lower mass numbers found in the bleached material. This indicates a slight depolymerisation of MWL during bleaching involving the action of powerful oxidizing species such as the peroxy radicals ( $ROO\cdot$ ), the hydroxyl radical ( $HO\cdot$ ) and the superoxide anion ( $O_2^{\cdot-}$ )<sup>16</sup>. The low-molecular weight phenolic fractions of LHO, which are more soluble, are probably eliminated during the washing of the solid material with water.

The results of the analysis by ionization difference UV spectroscopy on MWL and LHO are reported in Table 1.

The total number of phenolic hydroxyl groups measured in MWL is of the same order as that found by Månsson<sup>17</sup> by aminolysis for spruce MWL (33/100G<sub>9</sub>) and

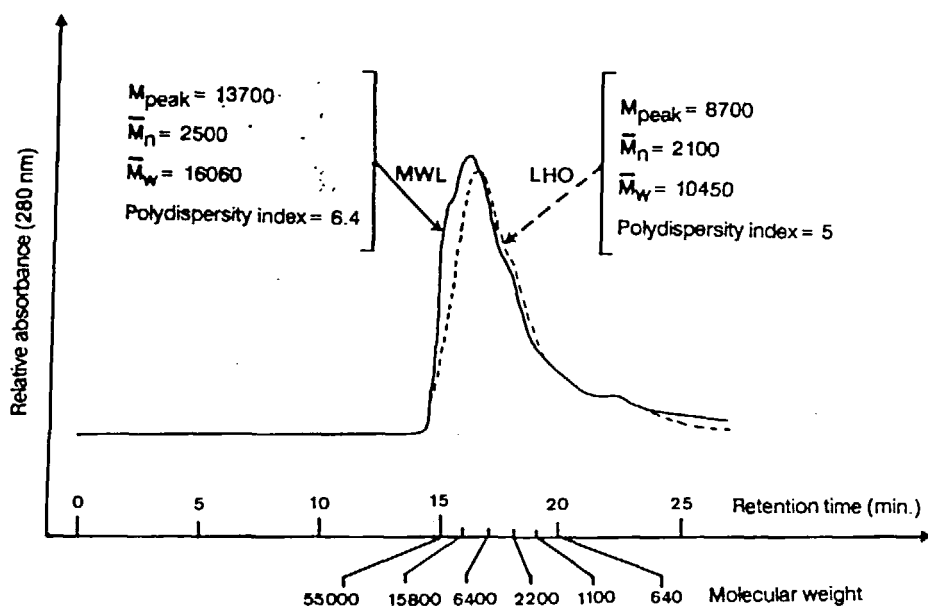


Figure 1: Gel permeation chromatograms of MWL and LHO

higher than that observed by Sjöström for pine (28.2/100C<sub>g</sub>)<sup>18</sup>. The lower total phenolic content obtained for LHO compared to MWL is unexpected, because among the chemical reactions involved in the peroxide bleaching process, extensively studied by Dence<sup>19</sup>, it was shown that guaiacylglycerol- $\beta$ -guaiacyl ether structures, the most abundant linkage in lignin, undergo Dakin-like reactions giving *inter-alia* methoxy-p-hydroquinone and guaiacol<sup>19c</sup> and so increase the amount of phenols. The low value observed, is thus probably ascribable to the isolation procedure of the material.

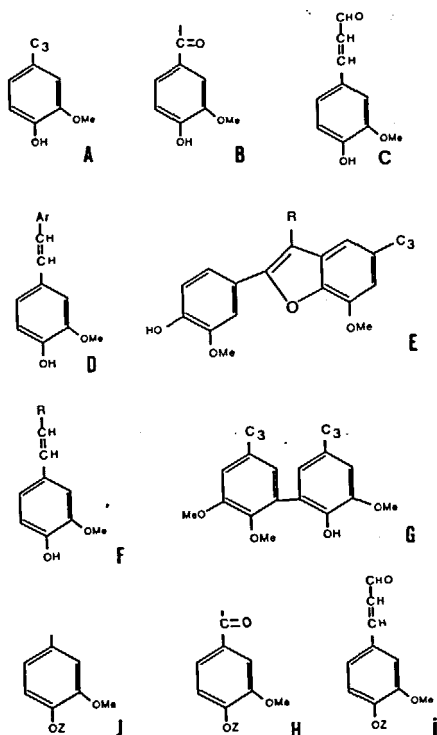
The content of the different chromophores determined for MWL compare well with those found by others, for softwood MWL, for phenolic  $\alpha$ -carbonyl, coniferaldehyde, and 5,5'-biphenyl units and for total (phenolic and O-etherified) coniferaldehyde structures<sup>20,13g</sup>. Higher values were obtained for phenolic isoeugenol<sup>13g</sup> and  $\alpha$ -ketone (etherified and non-etherified)<sup>20</sup> type chromophores. This increase might be due to different experimental conditions in the ball-milling procedure which is known to produce  $\alpha$ -carbonyl groups by mechanochemistry<sup>21</sup> or to some conjugated species (a phenolic  $\beta$ -carbonyl tautomer and/or quinones)



Table 1: Chromophore analysis of MWL and LHO by ionization difference UV Spectroscopy<sup>a</sup>

CHROMO- PHORE TYPE				(d)	(e)	(e)	(f)		(f)
	A	B	C	D	E	F	G	H	I
MWL (b)	35.9	1.7	1	0.6	0.9	4.7	6.8	13.5	4.5
MWL (c)		(g) 1	(g) 1			(h) 2	(h) 6	(g) 7	(g) 4
LHO (b)	13.8	2.3	1	0.2	0.5	2.3	3.6	7.2	1.1

(a) see experimental section; (b) mol / 100 C<sub>9</sub> assuming the molecular weight of the C<sub>9</sub> unit = 180, (c) Literature values; (d) Ar = J; (e) R = CH<sub>2</sub>O-Z; (f) Z = H or lignin; (g) Ref [20]; (h) Ref [13g]



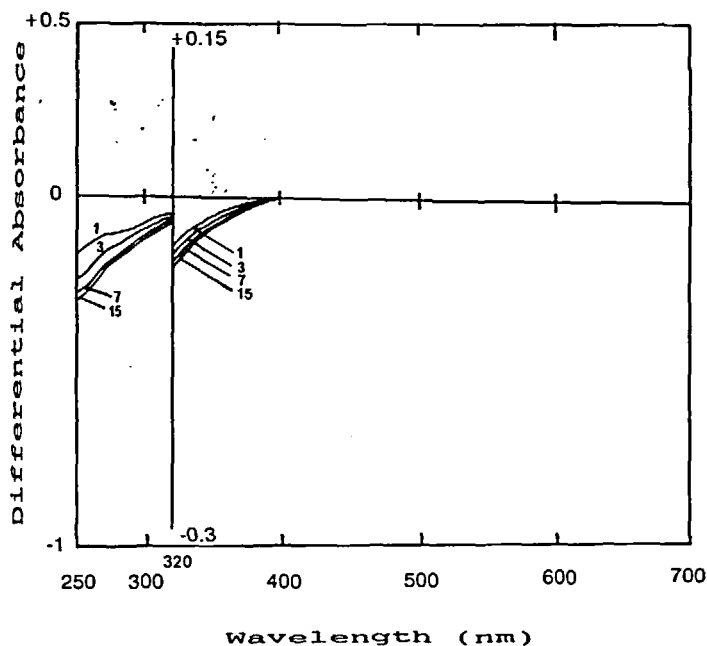


Figure 2: Differential absorbance spectra of HPC film before and after irradiation. Numbers indicate the irradiation time in hours

contributing to the absorption at 310 nm in the neutral medium and which are reduced by the  $\text{NaBH}_4$  treatment. Because of their great ability to induce photoyellowing<sup>8</sup>, an important result is that we have detected a small amount of phenolic stilbenes (open and cyclic forms) by the ionization procedure after hydrogenation; this contrasts with Marton's observations<sup>22</sup> which indicated that no stilbenes were present in MWL.

The chromophore analysis of the LHO fraction shows a net decrease of the O-etherified  $\alpha$ -carbonyl and coniferaldehyde groups, phenolic biphenyl, isoeugenol and stilbenoid chromophores, in accordance with Dence's model studies<sup>19</sup>. Compared to MWL, it is however quite surprising to find the same amount of phenolic coniferaldehyde structures and a slight increase in the content of the phenolic  $\alpha$ -keto units; we have no simple explanation for this result.

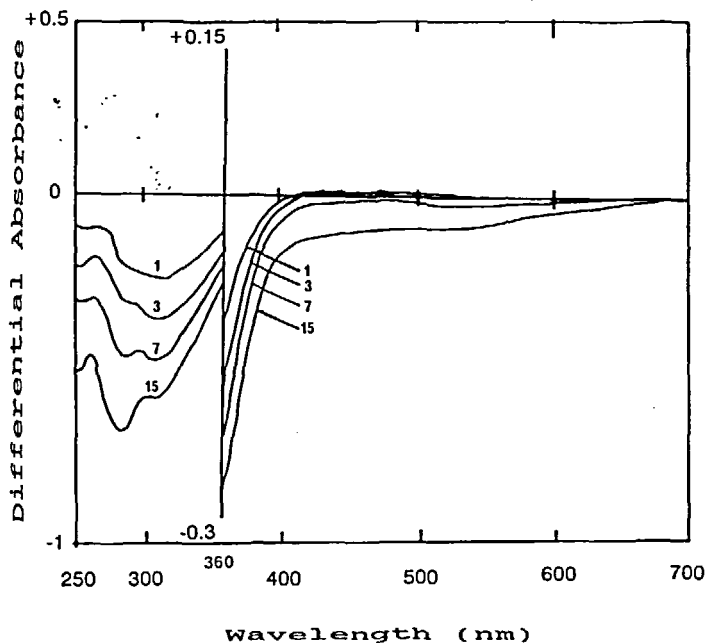


Figure 3: Differential absorbance spectra of unbleached milled wood lignin (MWL) in an HPC film before and after irradiation. Numbers indicate the irradiation time in hours. (See experimental section)

#### *Irradiation kinetics of HPC, MWL, LHO, BL, PBL, HOBL, HOPBL*

The differential UV/Vis absorbance spectra before and after irradiation for 1, 3, 7 and 15 h with light from a medium-pressure mercury lamp filtered with borosilicate glass (which eliminates the wavelengths below 300 nm) are presented in Figures 2-8 for an HPC film and for soluble lignins (MWL and LHO) incorporated at a concentration near 0.5% in HPC films after sodium borohydride and hydrogenation treatments in homogeneous media.

The photodegradation of cellulose has been extensively investigated<sup>23</sup>. The absorption of UV light induces the formation of various radicals and chain scissions leading to a depolymerization of the material. The irradiation of HPC in the solid state (Fig. 2) causes the disappearance of chromophores, probably ketones or

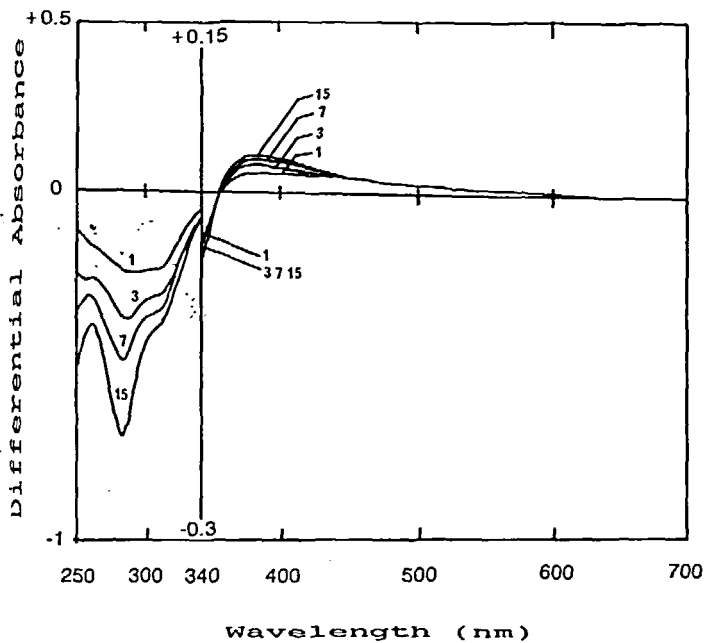


Figure 4: Differential absorbance spectra of peroxide-bleached milled wood lignin (LHO) in an HPC film before and after irradiation

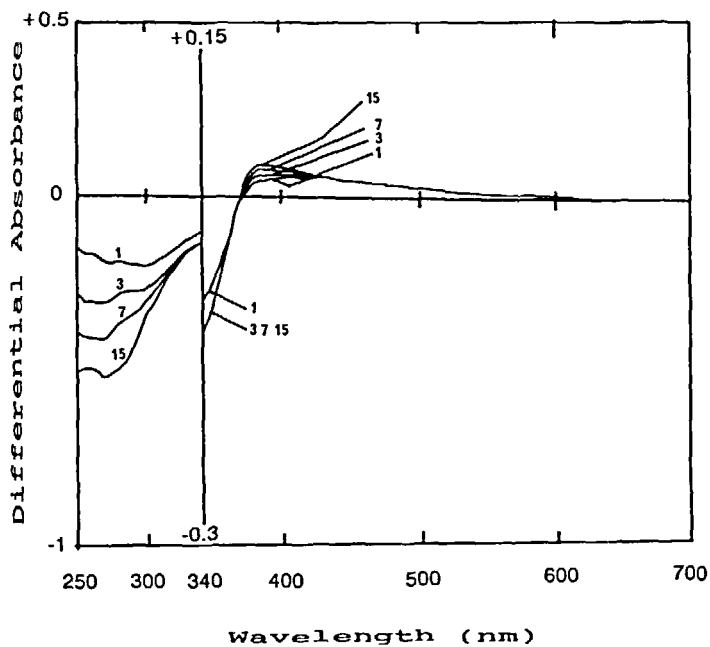


Figure 5: Differential absorbance spectra of sodium borohydride-reduced MWL (BL) in an HPC film before and after irradiation

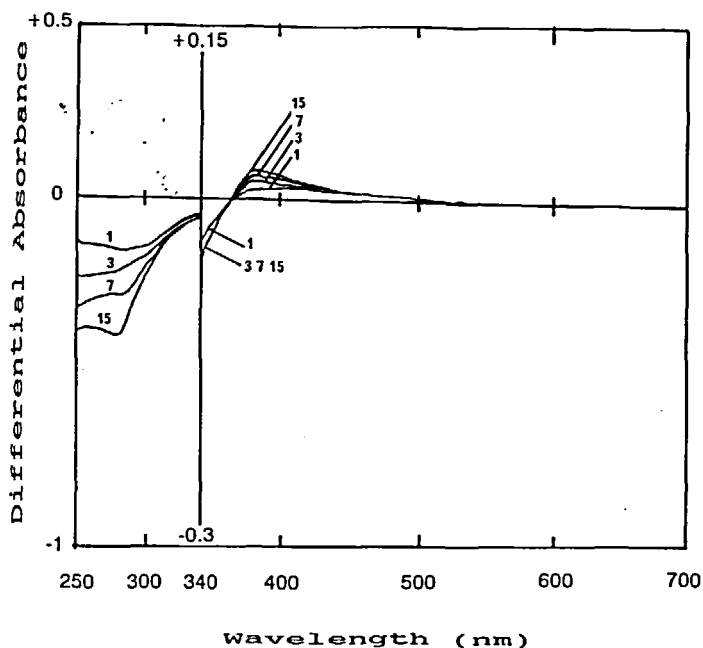


Figure 6: Differential absorbance spectra of sodium borohydride-reduced and hydrogenated (Pd/C) MWL (PBL) in an HPC film before and after irradiation

aldehydes<sup>24</sup>, which absorb in the UV part of the spectra. No absorption above 400 nm is observed.

Irradiation of the colored MWL induces an increase of the yellowing during the first 3 hours and then an intense bleaching of the film is observed (Fig. 3). Noticeable is the loss of aromatic structure observed at 285 nm during the irradiation. These results are in accordance with previous studies on high-yield pulps<sup>25</sup> where it was shown that UV light at wavelengths between 290 nm and 390 nm produced a photoyellowing effect whereas light in the range 420-470 nm produced a photobleaching effect.

In contrast to MWL, LHO displays a strong yellowing and a loss of the aromatic structure under light exposure (Fig. 4). This behavior parallels that of bleached high-yield pulps<sup>9, 26, 27</sup>.

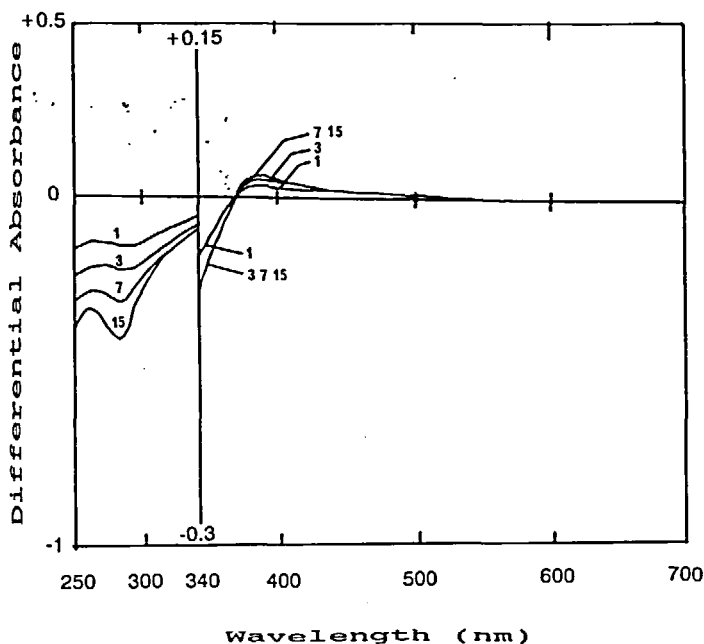


Figure 7: Differential absorbance spectra of sodium borohydride-reduced, peroxide-bleached milled wood lignin (HOBL) in an HPC film before and after irradiation

The reduction treatments of MWL by  $\text{NaBH}_4$  and hydrogenation ( $\text{Pd/C}$ ) by  $\text{H}_2$  (BL and PBL samples) decrease, but do not stop the photodiscoloration and the breakdown of aromatic structure (Fig. 5 and 6). With LHO, such treatments (HOBL and HOPBL samples) appear more efficient, particularly the hydrogenation, where the photoyellowing is almost completely stopped (Fig 7 and 8). Noticeable is the disappearance, for MWL and LHO, of species absorbing at 310 nm during the irradiation. This effect is probably caused by the photoreactivity of  $\alpha$ -carbonyl groups because they absorb at this wavelength and since the effect is much less when the lignin is reduced by  $\text{NaBH}_4$ .

For MWL, BL, PBL, LHO, HOBL, and HOPBL, the kinetics of photoyellowing (expressed by the differential absorbance measured at 390 nm except for MWL which was measured at 425 nm) and the kinetics of the breakdown of aromatic structure (expressed by the differential absorbance measured at 285 nm) are reported in

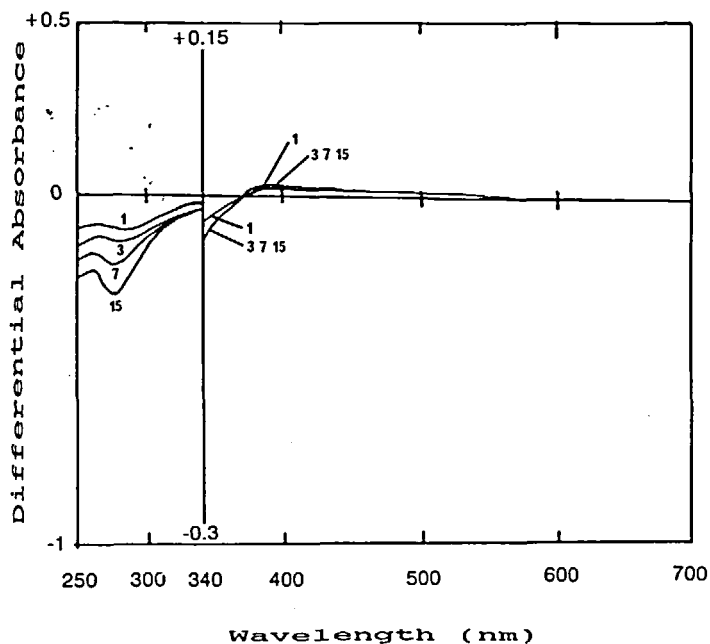


Figure 8: Differential absorbance spectra of sodium borohydride-reduced and hydrogenated (Pd/C), peroxide-bleached milled wood lignin (HOPBL) in an HPC film before and after irradiation

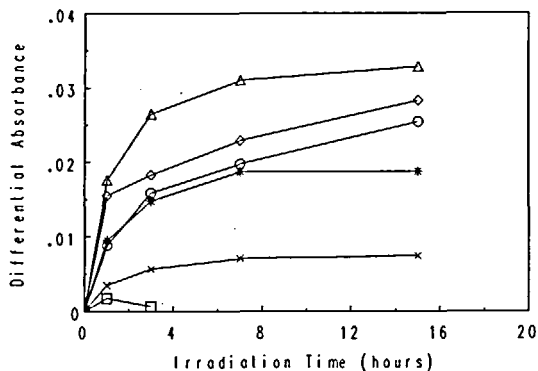


Figure 9: Kinetics of photoyellowing expressed by the differential absorbance measured at 390 nm as a function of irradiation time except for MWL which was measured at 425 nm. (□): MWL; (Δ): LHO; (◇): BL; (O): PBL; (\*): HOBL; (X): HOPBL

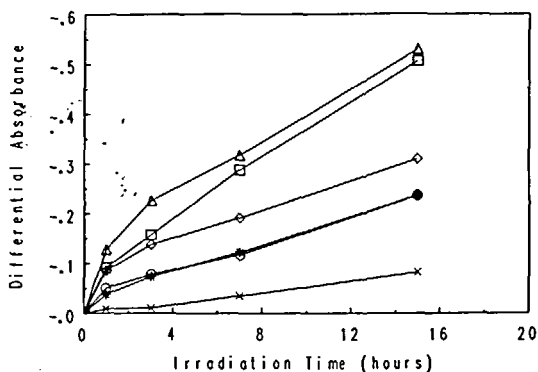


Figure 10: Kinetics of aromatic breakdown expressed by the differential absorbance measured at 285 nm as a function of irradiation time. (□): MWL; (△): LHO; (◇): BL; (○): PBL; (✱): HOBL; (X): HOPBL.

Figures 9 and 10. In contrast with what has been observed for bleached high-yield pulps<sup>9,28</sup>, sodium borohydride treatment affords some stabilization against discoloration. This may have resulted from an incomplete lignin carbonyl reduction of the pulp by the hydride in the solid state or, more probably, to an increase in carbonyl content ascribable to ball-milling in the isolation procedure (mechanochemistry) of the soluble lignin compared to that of the pulp (see Table 1). The response of LHO to hydrogenation (Pd/C) after the hydride reduction, where almost complete stabilization is observed, is different from that of MWL. This observation and examination of Table 1 show that chromophores without carbonyl groups and conjugated double bonds are responsible for the difference. They might be hydroxybiphenyls, which directly absorb light above 300 nm<sup>8</sup>, or other phenolic structure types such as phenylcoumaran<sup>8</sup>, catechols, and hydroquinones which are excited probably partly *via* energy transfer from other absorbing, extended aromatic non-phenolic chromophores.

The kinetics of aromatic loss measured at 285 nm follows the same trend as that of discoloration measured at 390 nm, except for MWL where the photobleaching of already yellow materials masks the photoyellowing. This indicates that the same types of chromophores are responsible for the appearance of the color and for the destruction of the lignin. A discrepancy is noted when we compare our results on MWL included in HPC to those of Lin and Kringstad<sup>29</sup>. These authors observed an



almost complete stabilization of spruce MWL solutions with respect to irradiation when reduced with sodium borohydride and hydrogenated ( $\text{PdCl}_2/\text{BaSO}_4$ ). Nevertheless, Lin and Kringstad's experiments have to be compared with the kinetics measured at 285 nm (Fig. 10). The difference noted might be ascribable to the different lignin preparations or more likely to different irradiation conditions (lamps, hydroxypropylcellulose instead of methyl cellosolve, and solid state in contrast to liquid state).

## CONCLUSION

The use of milled wood lignin and peroxide-treated milled wood lignin, which were submitted to extensive hydride reduction and catalytic hydrogenation treatments ( $\text{Pd/C}$ ) in homogeneous solution, and then incorporated into 2-hydroxypropylcellulose (0.5%) before irradiation in the solid state, was shown to be useful for the understanding of the photochemical brightness reversion of high-yield pulps. UV/Vis absorption spectroscopy was shown to be a very sensitive technique for the analysis of the different chromophores present in MWL and LHO and also for following the behavior of the films during UV irradiation. The almost complete stabilization of the bleached, reduced, and hydrogenated lignin (HOPBL) in comparison with the behavior of unbleached, reduced, and hydrogenated lignin (PBL) underlined the role played by biphenyl phenolic structures<sup>8</sup>, and other phenolic structure types such as phenylcoumaran<sup>8</sup> in the photoyellowing process. Fluorescence has also been used to investigate the photochemical reaction as will be presented in a forthcoming paper. Further work is being pursued in this laboratory to understand the complex mechanism of photoyellowing of high yield pulps.

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