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LIGNIN STRUCTURES IN WHITE SPRUCE REFINER MECHANICAL PULP**

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**THE OCCURRENCE AND LIGHT INDUCED FORMATION OF  
ortho-QUINONOID LIGNIN STRUCTURES IN WHITE SPRUCE  
REFINER MECHANICAL PULP**

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**ABSTRACT**

A sensitive method, based on reaction with trimethyl phosphite, was developed for the determination of ortho-quinonoid structures in pulp. It was used to show that structures of this type are responsible for most of the color of white spruce mechanical pulp and for most of the increase in color associated with light induced yellowing. The untreated pulp contained 5-6 quinone units per 100 lignin C<sub>9</sub> units, which were responsible for about 75% of its color. Upon irradiation with simulated sunlight for 20 hr, the number increased to about 10 and the increase accounted for about 75% of the increase in color. The quantum efficiency of quinone formation was 0.08 moles per mole of photons absorbed.

**INTRODUCTION**

Increasing wood costs and predicted shortages in future wood supplies have continued to stimulate interest in the production and use of high yield pulps. However, a major problem associated with the use of such pulps, both bleached and unbleached, is that they "yellow" upon exposure to sunlight. This light induced yellowing (or reversion) increases the absorbance of these pulps in the visible region of the spectrum, and hence, decreases pulp brightness. This, in turn, limits their use as substitutes for fully bleached chemical pulps.

The photochemical and chemical reactions involved, while of economic significance, are not fully understood. Results obtained with model compounds (1-6), isolated lignins (7,8), and ground-wood pulps (9-10), have led to theories suggesting that ortho-quinonoid lignin structures are formed during the photoyellowing process (Fig. 1). It is well known that such structures are highly colored, and their formation would account for at least a part of the color developed when mechanical pulps are exposed to light. In addition, it has been suggested that such structures may account for the natural color of wood and wood pulps (9-10).

The extent of the contribution of these structures to the color of wood pulps, however, has not been quantitatively evaluated. In this work, a method was developed to study both the occurrence and the light induced formation of ortho-quinonoid lignin structures in situ. The method was then used to estimate their contribution to the color of

unirradiated and sunlight irradiated white spruce mechanical pulp. It was also used to estimate the quantum efficiency of 312 nm UV light induced ortho-quinone formation.

**Method of ortho-quinone Analysis**

Since ortho-quinonoid structures in lignin are likely to be strongly colored, the occurrence of only a few of them could account for the color of yellowed high yield pulps. To detect such small amounts in the chemically complex pulp fibers, we sought a method that was both sensitive and specific for these structures.

The method we developed to fill this need is based on the known reaction between ortho-quinones and trivalent phosphorus compounds (11-13). For example, we reacted trimethyl phosphite with 3-methoxy-1,2-ortho-benzoquinone to form, in quantitative yield, the colorless oxyphosphorane adduct, I, as shown in Fig. 2 (13). Upon addition of water, I was quantitatively converted to the corresponding cyclic phosphate triester, II (also colorless). These reactions are significant because the ortho-quinone becomes "tagged" with phosphorus, an element foreign to the fiber wall, and one for which sensitive microanalytical techniques are available.

A further advantage of the phosphorus tag is that it allows one to check the assumption that the reagent is specific for ortho-quinonoid structures. This is possible because the phosphorus-31 nucleus is paramagnetic, and its structural environment can, therefore, be characterized by nuclear magnetic resonance (NMR). Thus, the <sup>31</sup>P NMR spectrum of the oxyphosphorane adduct, I, displayed a single signal at a chemical shift (relative to 85% H<sub>3</sub>PO<sub>4</sub>) of -45.8 ppm, and the corresponding value for the cyclic phosphate triester, II, was 11.1 ppm. These chemical shifts are characteristic (14); a second reaction with 3,5-di-tert-butyl-1,2-ortho-benzoquinone, for example, gave products with corresponding values of -46.5 and 12.1 ppm.

To further test this method, we oxidized a sample of white spruce mechanical pulp with Fremy's salt (potassium nitrosodisulfonate), which is known to introduce ortho-quinonoid structures into lignin (15,16). When the oxidized pulp was reacted with trimethyl phosphite, it was rapidly bleached, and the resulting pulp produced a single, strong <sup>31</sup>P NMR signal at 13.2 ppm, characteristic of a cyclic phosphate triester structure.

**Occurrence of ortho-Quinonoid Lignin Structures**

We investigated the occurrence of ortho-quinonoid lignin structures by reacting a white spruce mechanical pulp (WSMP) with trimethyl phosphite. As shown in Table 1, the Kubelka-Munk light absorption coefficients of the pulp decreased significantly upon exposure to this reagent. Its <sup>31</sup>P NMR spectrum had a strong signal at 12.4 ppm (71.5% of the total signal). A second, weaker signal was observed at 4.2 ppm (28.5% of the total signal). On the basis of the results described above, the signal at 12.4 ppm was attributed to cyclic phosphate triester formation. The origin of the second signal is not known. It appears to be

\*Now with Reed Lignin, Inc., 100 Highway 51 South, Rothschild, WI 54474.

\*\*Now with Kimberly-Clark, B400-4, Roswell, GA 30076.

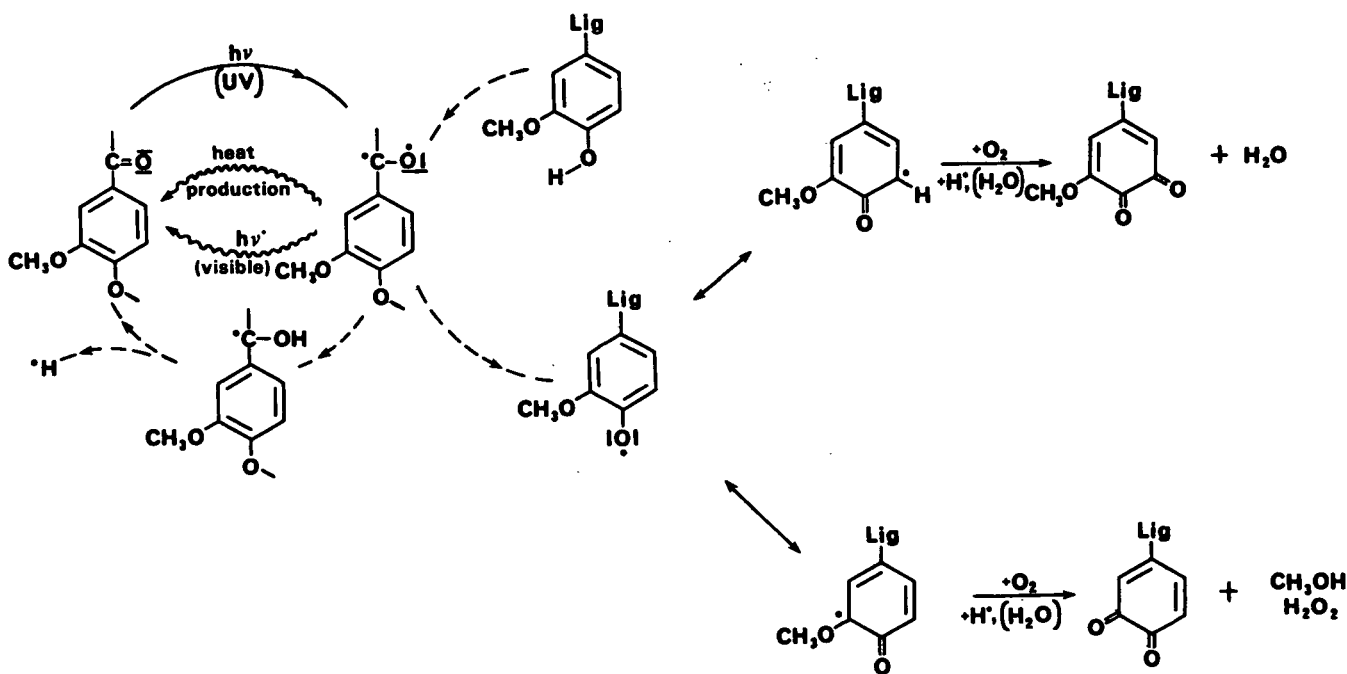


Fig. 1 Proposed mechanism for the light induced formation of ortho-quinonoid lignin structures (10).

lignin related, however, since a similarly reacted holocellulose sample produced no clear signals.

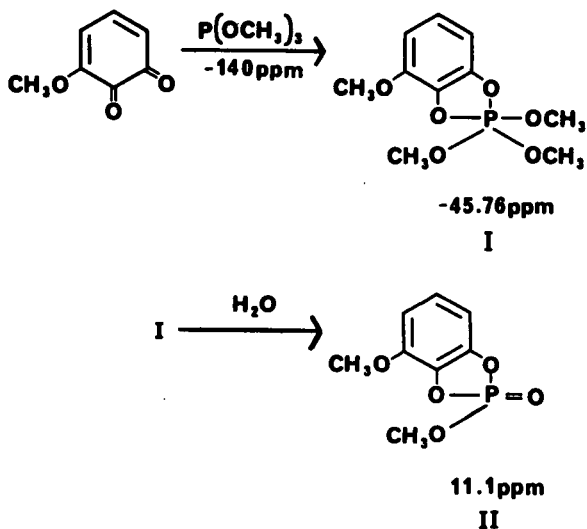


Fig. 2 Reaction of trimethyl phosphite with 3-methoxy-1,2-ortho-benzoquinone (13).

Phosphorus microanalysis of three separate samples yielded a value of  $0.39 \pm 0.056$  gram of phosphorus per 100 grams of dry pulp. From the NMR data, the amount of phosphorus associated with naturally occurring ortho-quinonoid structures was calculated to be 0.27%, or 71.5% of the total phosphorus present in the pulp. From this and the Klason lignin content (26.9%) the number of moles of ortho-quinonoid structures per gram of lignin

was calculated to be  $3.3 \times 10^{-4}$ . Assuming a unit weight for spruce lignin of 185 g lignin/mole of C<sub>9</sub> units (17), we then estimated that the pulp contained 5-6 ortho-quinonoid lignin structures per 100 C<sub>9</sub> lignin units.

Table 1. Kubelka-Munk absorption coefficients of WSMP before and after reaction with trimethyl phosphite.

Sample	Kubelka-Munk Absorption Coefficient (cm <sup>2</sup> /g)		
	415 nm	457 nm	520 nm
Unreacted WSMP	141	48.9	20.2
Trimethyl phosphite reacted WSMP	74.8	13.2	5.01

The light absorption measurements of Table 1 indicate that these ortho-quinonoid structures contribute significantly to the "natural" color of the pulp. From these measurements, we estimate that their contribution to the absorbance was about 50% at 415 nm, and about 75% at 457 and 520 nm. The formula used in these estimations was

$$\text{contribution to absorbance} = \frac{k - k_b}{k}$$

where  $k$  is the absorption coefficient of the pulp before reaction and  $k_b$  is the absorption coefficient of the pulp after reaction (i.e., bleaching with trimethyl phosphite). Detailed UV-visible spectroscopic analysis (18) indicated that the majority of the reduction in pulp color resulted

from the reaction of trimethyl phosphite with ortho-quinonoid structures and not from the reaction of trimethyl phosphite with the structure giving rise to the signal at 4.7 ppm. This was particularly true for the two longer wavelengths examined.

#### Sunlight Induced Formation of ortho-quinonoid Lignin Structures

Upon exposure to simulated sunlight for 20 hours the WSMP underwent severe yellowing (reversion). The results presented in Table 2 show that the associated increases in visible light absorption were partially reversed when the exposed pulp was reacted with trimethyl phosphite. The  $^{31}\text{P}$  NMR spectrum of the exposed and reacted pulp had a strong signal at 12.6 ppm (95% of the total signal) and a weak signal at 2.1 ppm (5% of the total signal). As in the two earlier pulps, we attributed the signal at 12.6 ppm to the formation of cyclic phosphate triesters. The origin of the second signal is not known; it may have originated from the same structure found in the unirradiated and reacted pulp.

Table 2. Kubelka-Munk absorption coefficients of sunlight irradiated WSMP before and after reaction with trimethyl phosphite.

Sample	Kubelka-Munk Absorption Coefficient ( $\text{cm}^2/\text{g}$ )		
	415 nm	457 nm	520 nm
Irradiated WSMP	442	186	68.4
Irradiated and reacted WSMP	170	42.3	15.0

The increased formation of cyclic phosphate triester structures after irradiation shows that the formation of ortho-quinonoid structures is an important component of the photoyellowing mechanism. To confirm that the increased phosphorus incorporation was a direct result of irradiation, we used x-ray microanalysis (scanning electron microscopy with energy dispersive spectrometry, SEM-EDS) to see how phosphorus incorporation varied with distance from the irradiated surface of the sheet. The results (Fig. 3) showed clearly that the surface layers, where most of the radiation is absorbed, contained most of the cyclic phosphate triester structures. This shows, in turn, that ortho-quinonoid structures are formed in an amount that increases with the amount of UV radiation absorbed.

Phosphorus microanalysis of the above pulp yielded a value of  $0.47 \pm 0.025$  gram of phosphorus per 100 grams of dry pulp. From the NMR data, the amount of phosphorus associated with the ortho-quinonoid lignin structures present in the pulp was calculated to be 0.45%, or 95% of the total phosphorus present in the pulp. Calculations similar to those described above yielded a value for this pulp of 10-11 ortho-quinonoid lignin structures per 100 C<sub>9</sub> lignin units. Thus, we estimate that upon exposure to 20 hours of simulated sunlight, 4-6 additional ortho-quinonoid structures were formed per 100 C<sub>9</sub> lignin units. From the absorption data in Tables 1 and 2, we estimated the contribution of

these additional structures to the increase in absorbance of this pulp to be 70-80% when measured at wavelengths of 415, 457, and 520 nm. The formula used in these estimations was

contribution to reversion =

$$\frac{(k_r - k_{rb}) - (k - k_b)}{(k_r - k)}$$

where

- $k$  = absorption coefficient of unreverted and unreacted pulp
- $k_r$  = absorption coefficient of irradiated (reverted) pulp
- $k_b$  = absorption coefficient of reacted (bleached) pulp
- $k_{rb}$  = absorption coefficient of irradiated and reacted pulp.

Thus, ortho-quinonoid structures are responsible for most of the color formed when white spruce mechanical pulp is exposed to simulated sunlight.

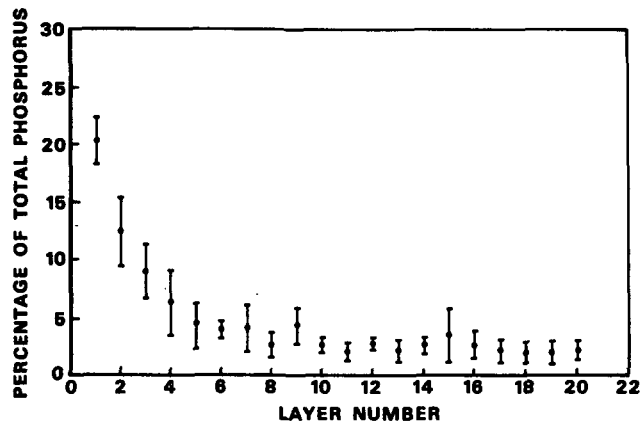


Fig. 3 Z-direction phosphorus distribution in a  $160 \text{ g/m}^2$  sheet irradiated for 20 hours with simulated sunlight and reacted with trimethyl phosphite. 1 layer = 40  $\mu\text{m}$ .

#### Quantum Efficiency

The quantum efficiency of ortho-quinone formation, defined here as the number of moles of ortho-quinonoid lignin structures formed per mole of photons absorbed, is a quantity of both theoretical and practical interest. If exposure conditions are known, quantum efficiency values at various wavelengths allow one to predict the extent of yellowing. Such values would also be useful in the design of optical brighteners for high yield pulps.

In an attempt to determine this value, we irradiated sheet samples with known amounts of nearly monochromatic UV light. We then determined the number of moles of ortho-quinonoid lignin structures generated in each sample by reaction with trimethyl phosphite. It has been shown that the UV component of sunlight (i.e., light in the 290-400 nm wavelength range) induces yellowing, and the wavelength range 310-315 nm is most effective

(18). Accordingly, we used light within this range in these experiments. The optical system used also allowed incident light flux to be measured and controlled (18).

From the results obtained (Table 3), the quantum efficiency of ortho-quinone formation at this wavelength was calculated to be 0.08 mole of ortho-quinonoid lignin structures per mole of photons absorbed.

Table 3. Effect of irradiation with 312 nm light on the amount of ortho-quinonoid structures in a sample of white spruce mechanical pulp.

Number of Photons Absorbed $\times 10^{-18}$	Moles of Quinone Present $\times 10^6$
0	1.5
7.27	2.1
10.7	3.1

### CONCLUSIONS

Most of the color of white spruce mechanical pulp can be attributed to ortho-quinonoid lignin structures. When the pulp is exposed to sunlight, additional ortho-quinonoid lignin structures are formed. At an incident wavelength of 312 nm, 0.08 mole of ortho-quinonoid lignin structures are formed per mole of photons absorbed. They are responsible for most of the increase in color associated with the light-induced yellowing of the pulp.

### EXPERIMENTAL PROCEDURES

The white spruce mechanical pulp used was prepared in a 12-inch Sprout-Waldron laboratory refiner from fresh chips. It was EDTA treated for 24 hours, ethanol/benzene extracted, and washed with distilled water. Handsheets were then formed according to the procedures described in TAPPI test method T 218 om-83 (basis weight = 160 g/m<sup>2</sup>) or T 205 Om-81 (basis weight = 30 g/m<sup>2</sup>).

Kubelka-Munk absorption coefficients were determined using the method of "black backing" described by Polcin and Rapson (19). Measurements of  $R_{\infty}$  and  $R_0$  were made on a Perkin-Elmer Model 320 spectrophotometer equipped with a Hitachi integrating sphere accessory. Pressed BaSO<sub>4</sub> pellets were used as a reference.

Irradiations were conducted with an ORIEL 1000 watt solar simulator (distance from source = 50 cm, total irradiance 85 mw/cm<sup>2</sup>, roughly equivalent to natural sunlight) or with light from optical equipment designed to provide nearly monochromatic light (18). Both units were located in humidity (50%) and temperature (21°C) controlled labs. "Thick" handsheet samples (basis weight = 160 g/m<sup>2</sup>) were used in these experiments.

The reaction of trimethyl phosphite with irradiated or unirradiated pulp was performed in anhydrous dichloromethane. Sheet samples were

Wiley milled to 20 mesh and dried under vacuum over P<sub>2</sub>O<sub>5</sub> for 48 hours. While under dry nitrogen, 0.25-0.30 g of each sample was added to 10 mL of a 10% solution of trimethyl phosphite in anhydrous dichloromethane. The resulting samples were sealed and allowed to react for one week at 20°C. While still under nitrogen, the samples were washed separately with two 500 mL portions of anhydrous dichloromethane and one 1.0 L portion of anhydrous ether. The washed samples were then dried under vacuum and stored under dry nitrogen.

Solid state <sup>31</sup>P NMR analyses were performed by Spectral Data Services, Inc. (818 Pioneer, Champaign, IL 61820). An inert environment was maintained during sample preparation and analysis. Microanalyses were conducted by Micro-Tech Labs, Inc. (4117 Oakton St., Skokie, IL 60076). SEM-EDS analyses were conducted by the EM lab at The Institute of Paper Chemistry (P.O. Box 1039, Appleton, WI 54912).

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