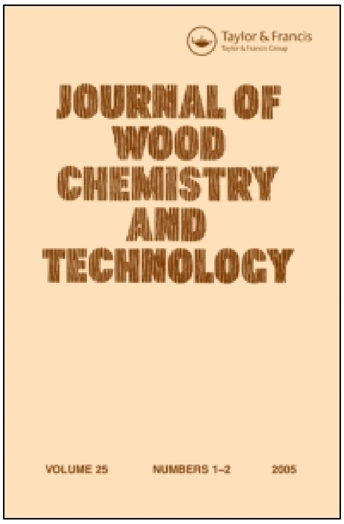

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Formation and Identification of Cis/Trans Ferulic Acid in Photoyellowed White Spruce Mechanical Pulp

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FORMATION AND IDENTIFICATION OF CIS/TRANS FERULIC ACID IN PHOTOYELLOWED WHITE SPRUCE MECHANICAL PULP

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ABSTRACT

Direct studies of photoyellowed unbleached white spruce refiner mechanical pulp have been carried out using laser Raman spectroscopy, gas chromatography/mass spectrometry (GC/MS) and Fourier transform infrared spectroscopy (FTIR) techniques. A new chromophore, namely, cis-ferulic acid has been detected. The experimental results indicate the presence of both cis and trans isomers of ferulic acid. The former, because of its yellow color, is considered to be a contributor in the yellowing process.

INTRODUCTION

The topic of photoinduced brightness reversion of high-yield pulps is of great interest to the pulp and paper industry. Brightness reversion refers to the yellowish appearance which is developed in these pulps upon exposure to light in the presence of molecular oxygen. Unknown photochemical reactions involving the pulp components and O_2 cause yellowing and are responsible for the pulp's lower brightness. Pulp which may decline in

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*Present address: USDA Forest Products Laboratory, One Gifford Pinchot Drive, Madison, WI 53705-2398 brightness is undesirable for a wide range of applications. Furthermore, in several applications, substitution of high-yield pulps for chemical pulps is limited for the same reason.

Although numerous studies, carried out in the past, have enhanced our understanding of the color reversion phenomenon, the causes and mechanisms of yellowing are not well understood. It has been known for a long time[1-6] that lignin in the pulp is the primary factor in the photoinduced color reversion. On the basis of earlier work, quinonoid structures were thought to be responsible[4,7-9]. More recently, o-quinonoid structures have been found to exist in the yellowed pulp[10]. A review of the literature on the topic reveals that the understanding of the process remains incomplete. For example, the identities of many chromophores are not known, nor are the various pathways that the system moves through after initial ultraviolet excitation. Because of the complexity of the lignocellulosics, direct studies of lignin photochemistry are very few. Nevertheless, detailed studies of lignin model compounds abound[6,11-14]. Such investigations have enhanced our knowledge with regard to what may take place in pulp. However, in view of the fact that the photochemistry of aromatic compounds is sensitive to changes in their physical and chemical surroundings[15,16], it is not always clear under what experimental conditions the models will best simulate lignin photochemistry. This view is underscored by a recent study of lignin model compounds by Castellan et al.[14], who have shown that a change in the environment/medium could lead to modified photochemical behaviour.

In this report, we describe the results of our in situ studies of unbleached white spruce refiner mechanical pulp (RMP) handsheets. The objective was to identify various chromophores that contribute to photoyellowing of pulp sheets. A number of analytical techniques including Raman spectroscopy, GC/MS, and FTIR were used. In the Raman spectral studies, a unique sampling procedure has paved the way for obtaining novel results.

EXPERIMENTAL

Both yellowed and nonyellowed white spruce hand sheets were used in this work. Handsheets were made from unbleached white spruce refiner mechanical pulp in accordance with TAPPI standard 205 om-81. This pulp had earlier been treated with ethylenediaminetetraacetic acid (EDTA), extracted in ethanol/benzene and washed in distilled water. The treatments with EDTA and ethanol/benzene were, respectively, to remove metal ions and extractives from the pulp. Photoirradiation of handsheets was carried out by using an ORIEL 1000 W solar simulator fitted with an "air mass one" filter. The sheets were exposed on one side at a chosen irradiance level for 20 hr under controlled conditions (RH 50%, temperature 21°C). When not in use, pulp handsheets were stored in a freezer that was maintained at -15°C. Additional details are provided in reference 17. Although the sheets were studied directly using Raman and FTIR spectroscopy, only their extracts were used during GC/MS measurements.

Raman spectra were obtained on an Instruments SA Ramanor HG2S system using the 514.5 nm line of an Ar ion laser for excitation. Samples were mounted in homemade cells through which oxygen could be flushed. Oxygen flushing was used in order to reduce the background fluroscence contribution to the total signal. This sampling technique was developed by us, and has proven effective towards quenching fluorescence in lignocellulosics[18].

The GC/mass spectrometric analyses of samples were carried out using a Hewlett-Packard GC MS 5985B system. The silicone stationary phase OV-17 (3% adsorbed on Gaochrom Q) was used in a 2 mm inner diameter GC glass column. The heating program consisted of maintaining the column oven at 90 degree for 2 minutes and then heating it at the rate of 10°/min until the final temperature of 300°C was achieved. In some instances, however, the initial 2 minute scan delay was not carried out. Helium at the flow rate of 30 cc/min was used as a carrier gas. The GC/MS interface temperature was maintained at 275°C. The mass spectrometer was a quadrupole instrument, and the detector was used in the electon impact mode with electron energy at 70 ev. In selective ion monitoring, when looking for small quantities of compounds, increased sensitivity was achieved by increasing the electron multiplier voltage to 2200-2600 volts.

The compounds investigated were isolated from handsheets either by a laser desorption technique or by direct extraction in methanol. The 514.5 nm line of a continuous wave (CW) argon ion laser was used for laser desorption purposes. In laser-induced thermal desoption, which is generally carried out using a pulsed laser, the adsorbed molecules on a surface are electronically excited and thus are subjected to a rapid temperature jump, during which they are vaporized from the surface[19]. These desorbed molecules are in turn solvated by the surrounding solvent molecules. In a CW laser mode, we envision occurance of a similar process. The laser excited molecules desorb as a result of thermalization of the excited energy. Laser desorption was carried out by immersing handsheets in methanol in pyrex glass containers and irradiating them with laser light in numerous spots. Surfaces of both yellowed and nonyellowed handsheets were irradiated in this manner. Methanol extracts produced in this fashion were concentrated by bubbling pure dry nitrogen gas, and silated using standard procedures[20]. The concentrated extract obtained from the yellowed sheet was visibly yellow. Sample preparations were carried out in the dark in order to avoid any photochemically induced reactions.

The FTIR work was carried out on a Nicolet 7199 spectrometer. Spectra were obtained in one or more of the following sampling modes: diffuse reflectance infrared Fourier transform (DRIFT), thin film, and KBr pellet.

Brightness measurements were made in accordance with TAPPI standard T 452 om-83 at an effective wavelength of 457 nm. The data were obtained using a common backing pad for all samples studied.

Ferulic acid was obtained from Aldrich Chemical Company, and was recrystallized from methanol before use. A mixture of cis/trans ferulic acid was produced by exposing the methanol solution of predominantly trans-ferulic acid in the solar simulator. In the case of ferulic acid, the photostationary cis/trans ratio of isomers depends upon the solution concentration[21]. However, for qualitative GC analyses solutions were prepared by arbitrarily choosing the concentration of trans-ferulic acid in methanol.

RESULTS AND DISCUSSION

The Raman spectrum of a yellowed unbleached sheet recorded under oxygen flushing conditions is shown in Fig. 1(a). As oxygen flushing was continued for an additional 24 hr, no evidence for temporal changes in the Raman features was detected. However, the background fluorescence, as expected, showed a steady decline. Such a reduction in background fluorescence is generally exhibited by lignocellulosic materials[18], and is indeed desirable for better signal-to-background ratio. Temporal invariance of Raman spectral features was interpreted to mean that the spectrum did not arise as a result of laser and/or oxygen induced chemical changes in the substrate. Further evidence in support of this conclusion, based on GC/mass spec. and FTIR studies is presented below.

The spectrum of a nonyellowed unbleached sheet sample, obtained under identical experimental conditions, is shown in Fig. 1(b). This sample, used as a control, possesses spectral features which are typical of lignocellulosics[22] and quite different from the spectrum of the yellowed specimen. The spectral region between 1050 and 1650 cm^{-1} is particularly different. This suggests that the photoyellowed surface contains species that are substaintially different from their precursors.

In order to assign the features in the spectrum of Fig. 1(a), Raman spectra of a number of compounds that could be responsible for yellowing were compared. These included o and p-benzoquinones and disubstituted biphenyls. These efforts were unsuccessful, so a Raman study of lignin model compounds was undertaken. This was suggested by the strong aromatic ring stretching band at ~1600 cm^{-1}. Raman data on a number of lignin models were acquired. A simple comparison of the spectrum of ferulic acid [Fig. 2(b)] with that of the yellowed sample [Fig. 2(a)] resulted in the suggestion that this compound is most likely present in the sheet sample. Figure 2 shows these spectra, along with that of the control, plotted in the 1050-1750 cm^{-1} interval. Table 1 lists various peak positions for this set of spectra.

In light of the fact that only small amount of chromophores are expected to be present on the surface of the sheet, the intensity of peaks in the spectrum in Fig. 1(a) needs an interpretation. Considering the structure of ferulic acid, both resonance Raman and conjugation effects[23] are expected to be important, and would result in enhanced peak intensities for certain vibrational transitions. This aspect of Raman technique makes it particularily sensitive to ferulic acid detection.

In order to address the question of sample alteration under Raman sampling conditions, infrared spectra of the yellowed sample were recorded both before and after the Raman studies [Fig. 3(a) and (b)]. Since it was not possible to locate precisely the region from which Raman spectra were obtained, four IR spectra in the general area of Raman measurements were

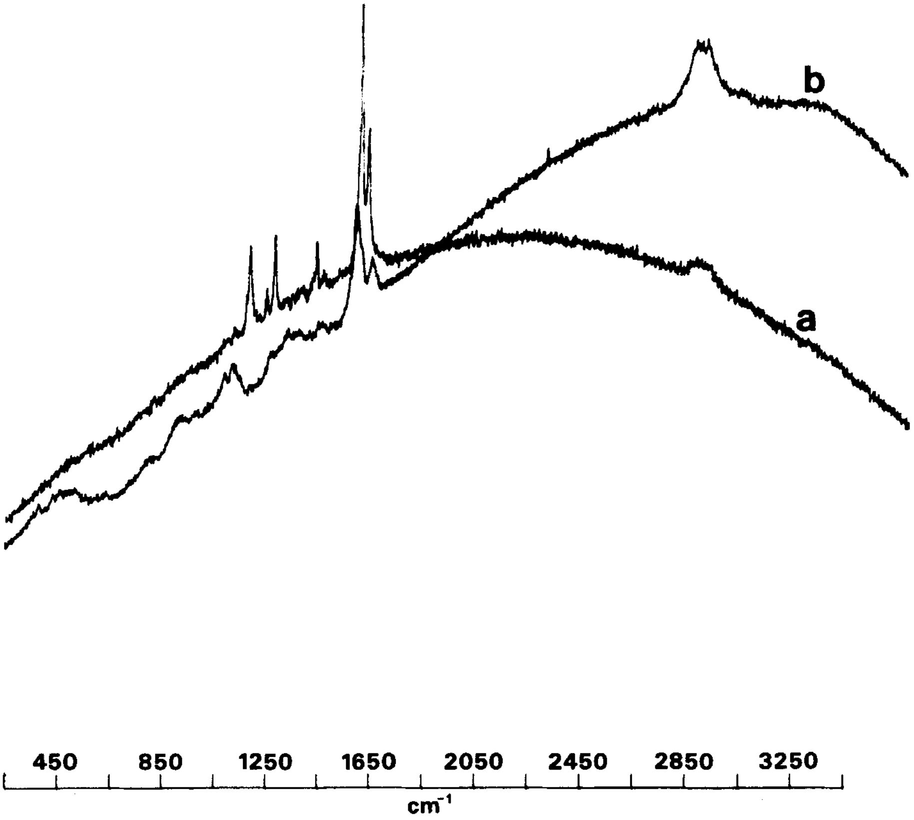


FIGURE 1 Raman spectra of yellowed (a) and nonyellowed (b) white spruce handsheet samples obtained under molecular oxygen atmosphere.

acquired. These four spectra were identical, and no significant differences between this set and the one recorded before laser exposure could be discerned. This supports our earlier thinking that the 514.5 nm laser line, in the presence of molecular oxygen, did not produce changes in the sample.

Having shown the presence of ferulic acid in the yellowed sample, its role in color reversion phenomena needed to be

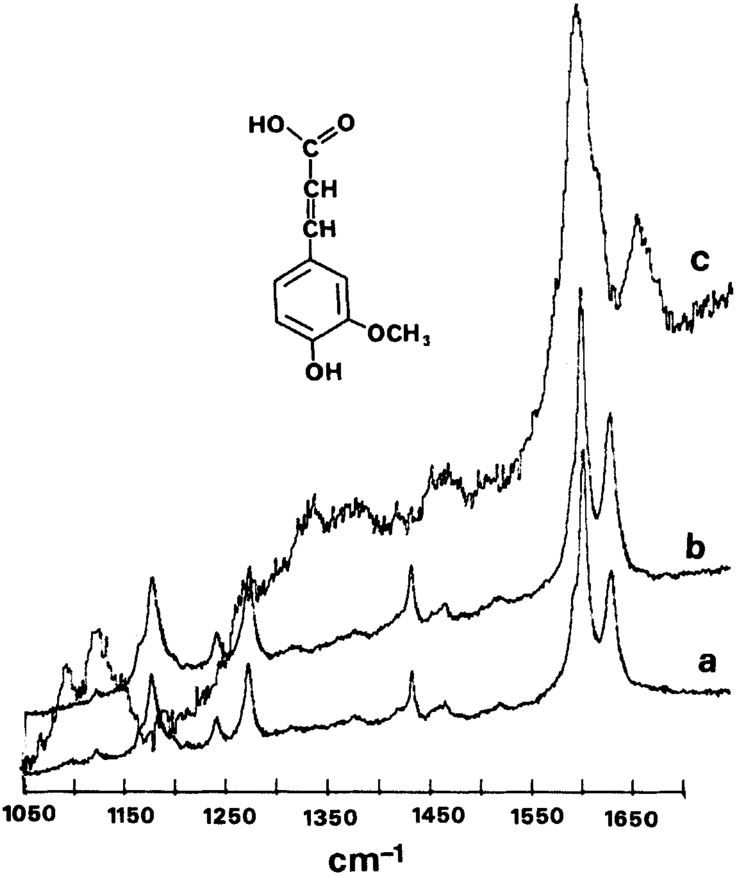


FIGURE 2 Raman spectra in the region 1050-1750 cm^{-1} shown on expanded frequency scale; (a) yellowed sheet; (b) ferulic acid; (c) nonyellowed sheet. Ferulic acid molecular structure is also shown.

established. Ferulic acid is known to exhibit UV light induced cis/trans isomerization[24] and the cis form is yellow in color[25]. In view of this, we hypothesized that a portion of the yellowing that occurs on exposure to light may arise from the cis isomer.

TABLE 1

A Comparision of Raman Band Frequencies (cm^{-1}) of Samples Whose Spectra are Shown in Fig. 2

Figure 2(a) Yellowed sheet	Figure 2(b) Ferulic acid	Figure 2(c) Nonyellowed sheet
		1094 w
1120 w	1122 w	1120 m, br
		1150 w, sh
1165 sh	1163 sh	
1175 s	1175 s	
1240 m	1240 m	
1271 s	1270 s	1275 w, br
		1335 w, br
1375 w	1375 w	1380 w, br
1420 sh	1420 sh	1420 w, br
1432 s	1430 s	
1465 w	1465 w	1460 w, br
1590 sh	1590 sh	1595 s
1600 vs	1600 vs	
1628 s	1628 s	1620 sh
		1660 m

In order to test this hypothesis, efforts were focused on detecting cis and trans ferulic acids in the yellowed sheet. GC/mass spectrometry was considered ideally suited because of its high specificity and great sensitivity. Extracts, which were obtained by laser desorption of material from both yellowed and nonyellowed sheets in methanol, were concentrated and silated using N,O-bis(trimethylsilyl)acetamide (BSA) in pyridine[20]. Such samples were then analysed by GC/MS. In addition, similar measurements on specimens obtained without laser desorption were carried out.

Figure 4 shows a number of chromatograms. These include chromatogram of trans-ferulic acid (a), that of a mixture of cis/trans ferulic acid (b), a laser desorbed yellowed sheet extract (c), and a laser desorbed nonyellowed sheet extract (d,

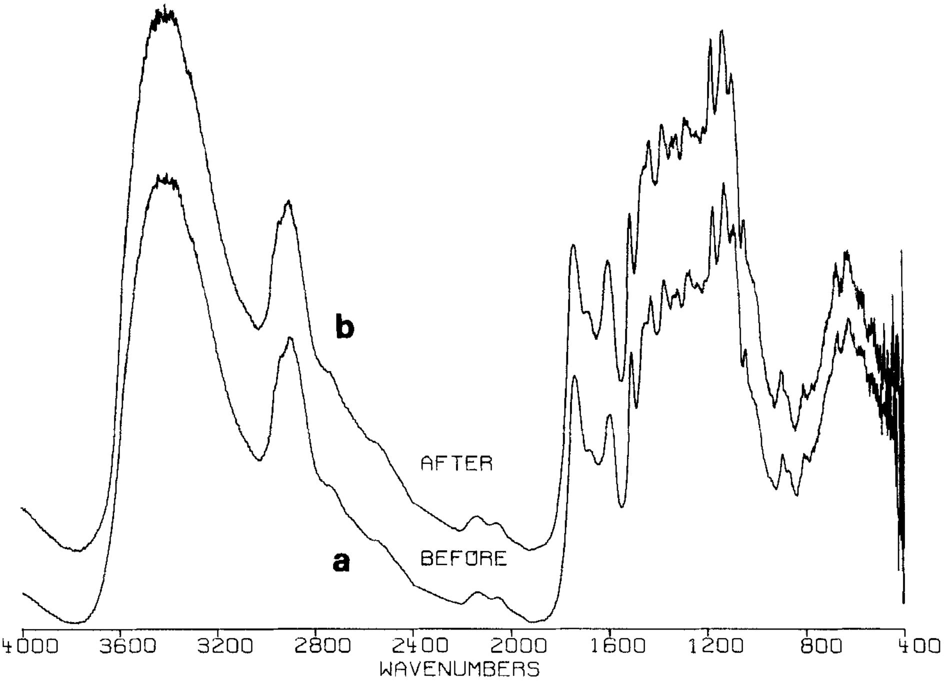


FIGURE 3 Typical infrared spectra obtained from yellowed sample (a) before and (b) after Raman experiment.

used as a control). Upon comparison of Fig. 4(b), (c), and (d) one finds peaks for both cis and trans isomers in the yellowed sample chromatogram [Fig. 4(c) and Table 2]. On the other hand, peaks present in the control are found not to be due to ferulic acid as is evident from Table 2. Table 2 lists characteristic ions found in mass spectra of separated chromatogram peaks of silated samples.

With regard to the finding of cis-ferulic acid in the extract of the yellowed sample, it should be noted that laser irradiation of trans-ferulic acid at 514.5 nm wavelength does not result in its photoisomerization to the cis isomer. It is well known that visible light does not play any part in the trans/cis photoconversion[21,24].

In the initial phase of GC/MS studies, as described above, we have used laser induced thermal desorption in order to dissolve the substance from the surface of the handsheets. In later work, however, it was thought that perhaps sufficient sample for GC/MS analysis could be obtained by simply using a larger amount of solvent. In view of this, the yellowed and control sheets were immersed in excess methanol for a week. The resulting solutions were concentrated by bubbling pure nitrogen gas. The concentrated extract corresponding to the yellowed sheet did not appear yellow. These samples were analysed for ferulic acid using selective-ion monitoring [Fig. 5(a) & (b)]. In addition, Fig. 5(c) shows a gas chromatogram of a mixture of cis/trans ferulic acid. This chromatogram shows somewhat lower retention times for both ferulic acid isomers as compared to that obtained in Fig. 4(b). This is due to the fact that in these sample runs the column was not held for two minutes at 90°C. The peaks at 11.5 and 13 minutes were found to be, respectively, due to cis and trans-ferulic acid. Confirmation of trans-ferulic acid in the yellowed sheet extract was made by comparing the observed relative ion abundances [Fig. 5(b) or 6(a)] to those of authentic trans-ferulic acid [Fig. 6(b)]. In Fig. 6(a), abundances corresponding to isotope and other molecular fragments are not seen as only displayed ion peaks were monitored. In the case of the cis isomer, however, the ratios were not the same. Nonetheless, characteristic mass spectral peaks corresponding to this isomer were seen [Fig. 5(b)]. There could be several reasons for this. The primary reasons, we feel, are its low concentration and the presence of an impurity that has some common mass peaks.

In order to compare the laser desorption and direct methanol extraction modes, TAPPI brightness measurements on handsheets were made. These measurements were made on

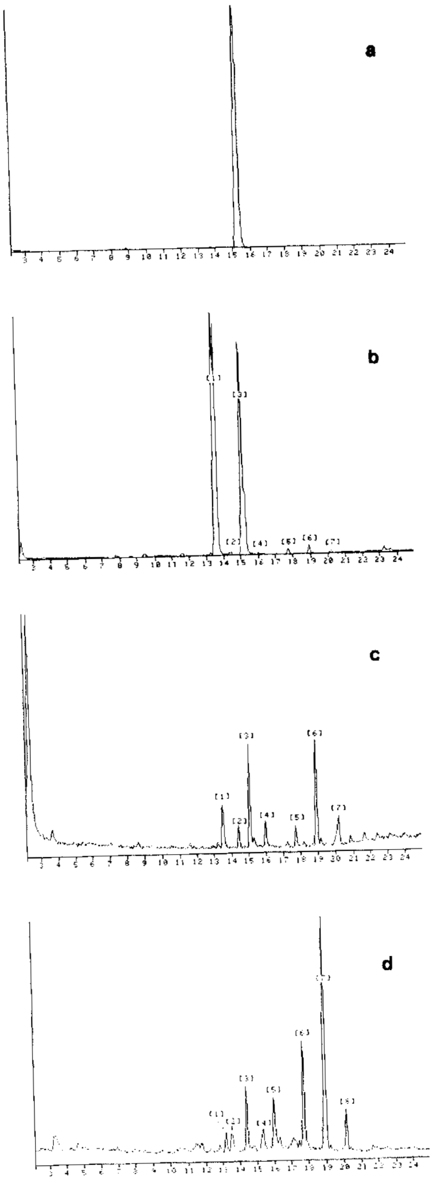

a
3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
b
[1]
[3]
[2]
[4]
[5]
[6]
[7]
3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 23 23 24
c
[3]
[6]
[1]
[2]
[4]
[5]
[7]
3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
d
[7]
[6]
[3]
[5]
[1]
[2]
[4]
[8]
3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24

TABLE 2

Mass Spectra of Silated Samples Separated in Chromatograms a, b, c, d of Fig. 4

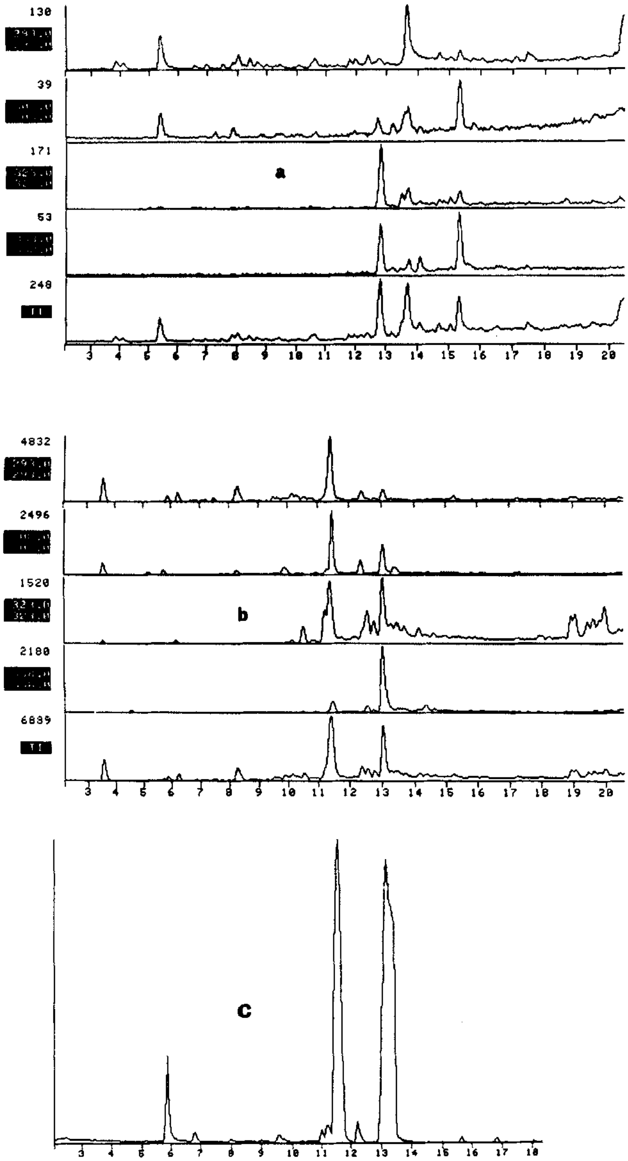
Chromatogram	Peak No.	Sample Identification	Base Peak	Other Characteristic Ions
a		t-ferulic acid	338	323, 308, 293, 249, 73
b	1	c-ferulic acid	73	338, 323, 308, 293, 249
	3	t-ferulic acid	73	338, 323, 308, 293, 249
	2,4,5	under analysis[e]	--	--------------------
	6,7	under analysis[e]	--	--------------------
c	1	c-ferulic acid	73	338, 323, 308, 293, 249
	3	t-ferulic acid	338	323, 308, 293, 249, 73
	2,4,5	under analysis[e]	--	--------------------
	6,7	under analysis[e]	--	--------------------
d	2	palmitic acid	73	328, 313, 145, 132, 117
	4	stearic + oleic acid	73	356, 341, 263, 145, 129
	1,3,5	under analysis[e]	--	--------------------
	6,7,8	under analysis[e]	--	--------------------

[e] perhaps impurity peaks; also seen in solvent run.

photoyellowed handsheets both before and after a particular extraction method. In addition, brightness of a nonyellowed sheet was measured. Such results are shown in Table 3.

In Table 3, the partially laser desorbed sheet shows higher TAPPI brightness as compared to one directly extracted in methanol. This suggests the usefulness of the former procedure in

FIGURE 4 Chromatograms of silated samples; (a) t-ferulic acid; (b) cis/trans ferulic acid mixture; (c) yellowed hand sheet extract; (d) control or nonyellowed hand sheet extract. Both (c) and (d) were obtained using laser desorption technique.


130
39
171
a
53
248
TI
3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
4832
2496
1520
b
2180
6889
TI
3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
c
3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18

removing chromophores from the sheet surface. Direct methanol extraction of the yellowed sheet, on the other hand, does not seem to have removed any significant amount of color causing material.

The low amount of cis-ferulic acid in the sample extract obtained by direct methanol extraction is supported by the brightness data in Table 3, where this extraction procedure did not result in any significant change in the sheet's brightness value. The lower concentration of cis isomer could be a direct reflection of its stronger adsorption in the pulp as compared to acid's trans counterpart. This is likely in view of the effect of the structure on chemical reactivity[26]. In this regard it must be noted that molecules containing phonolic and carboxylic groups are known to be strongly adsorbed on cellulosic substrates[27]. Moreover, the photostationary state concentration of cis ferulic acid could be lower to begin with.

Thus analyses of sheet sample extracts by GC/mass spectrometry support our findings obtained by using the laser Raman technique. Therefore, on the basis of the above work, it can be concluded that photoyellowed handsheets made from unbleached white spruce pulp contain both cis and trans-ferulic acid.

Finally, we carried out infrared spectroscopic analyses of our samples. The initial IR studies made it clear that the spectral changes resulting from yellowing were subtle and that, at best, interpretation of the infrared data would be supportive in nature rather than confiramatory[28].

FIGURE 5 Ferulic acid detection by selective-ion monitoring; (a) nonyellowed handsheet extract, (b) yellowed handsheet extract. Both (a) and (b) were obtained with out using a laser. Shown in (c) is a gas chromatogram of silated cis/trans mixture of ferulic acid.

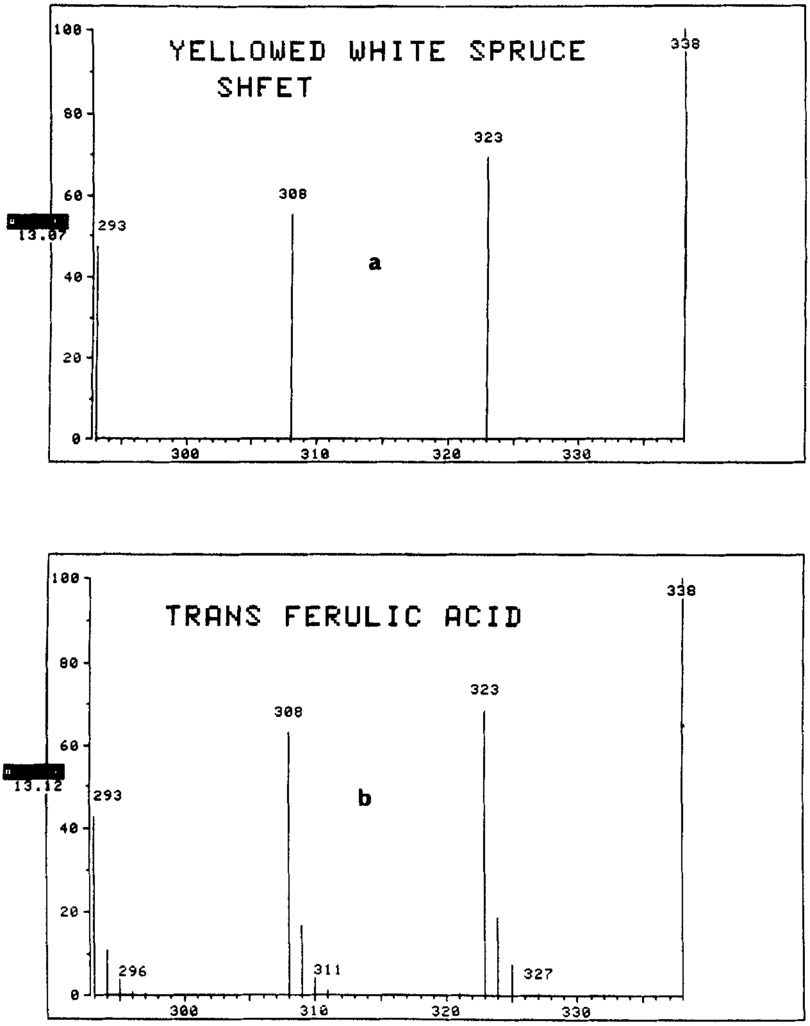


FIGURE 6 Relative ion abundances of several ferulic acid ions in (a) yellowed handsheet extract obtained by direct extraction in methanol, and (b) authentic trans-ferulic acid. Ion abundances in (a) were obtained by using selective-ion monitoring technique.

TABLE 3

Brightness Data on Handsheets.

Handsheet Identification	Tappi Brightness(%)
Nonyellowed	55.30
Photoyellowed	30.90
Photoyellowed and directly methanol extracted	31.05
Photoyellowed and partially laser desorbed	37.30

Deepicted in Figure 7 are spectra of (A) a yellowed sheet, (B) t-ferulic acid adsorbed on a nonyellowed sheet, (C) a nonyellowed sheet, (D) a cis/trans ferulic acid mixture, and (E) t-ferulic acid. A comparison of various features, in the region 1500-1800 cm^{-1}, is presented in Table 4. Upon photoyellowing, the only noticeable changes are reduction in the 1662 cm^{-1} band intensity and appearance of a new feature at 1680 cm^{-1} [Fig. 7(A) and (C)]. The new feature at 1680 cm^{-1} can be accounted for in terms of a ferulic acid band at the same frequency. It appears in the IR spectra of all ferulic acid containing samples, i.e., Fig. 7(B), (D), and (E). Infrared spectra of trans as well as cis/trans mixtures of ferulic acid show many features that are also seen in the IR spectra of spruce handsheets. This is not totally unexpected in view of the structural similiarity between ferulic acid and the molecular structure of lignin[29].

The FTIR studies lend support to the other experimental evidence for ferulic acid. Although only limited information is available through IR analysis, the fact that it supports our findings is noteworthy.

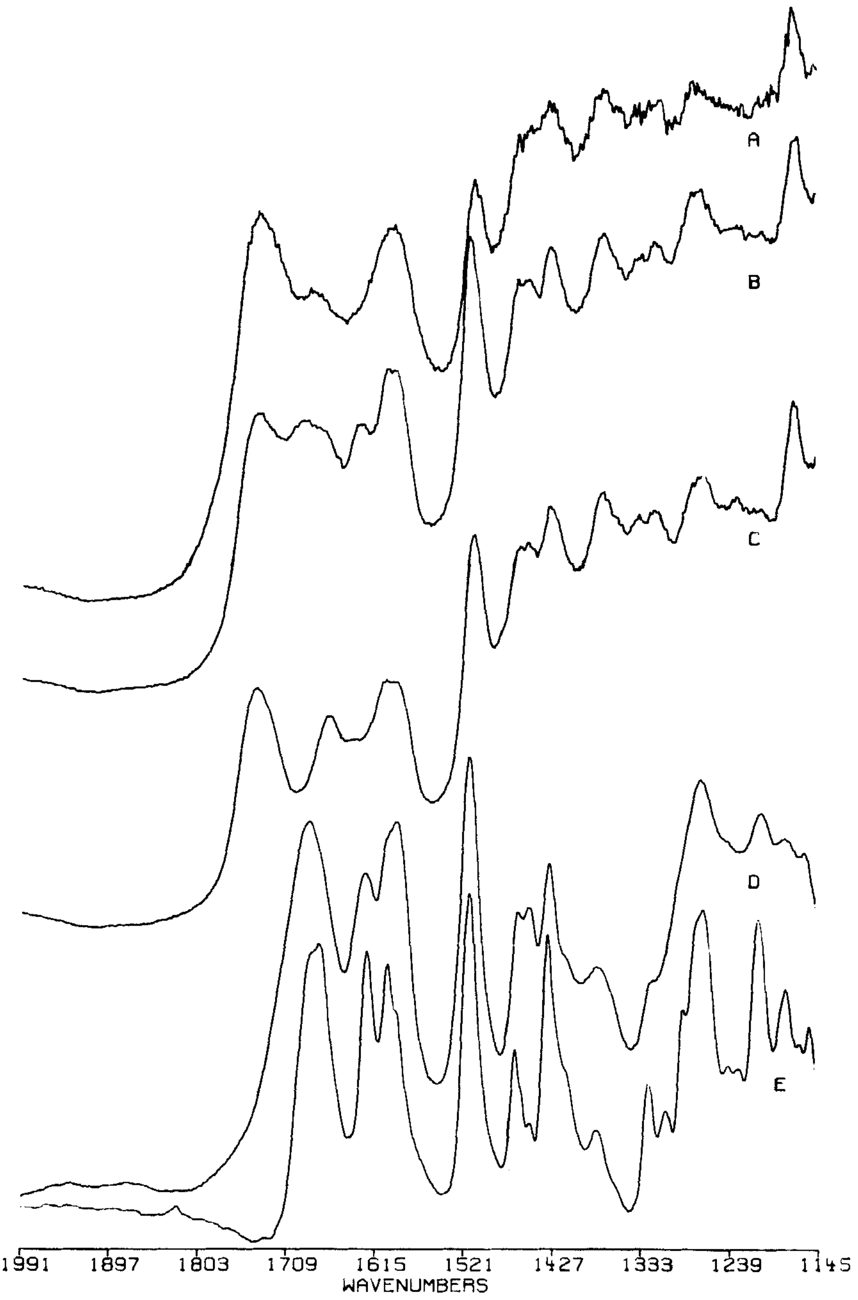


FIGURE 7 Infrared spectra of (A) yellowed sheet; (B) nonyellowed sheet + (trans-ferulic acid); (C) nonyellowed sheet; (D) cis/trans ferulic acid mixture; (E) trans-ferulic acid.

TABLE 4

IR Peak Positions in the Region 1800-1500 cm^{-1} for Spectra Shown in Fig. 7

A	B	C	D	E
1738	1738	1738		
1680	1687		1684	1681
	1670	1662		
	1631		1625	1625
1593	1599	1599	1594	1599
				1593
1510	1510	1510	1517	1517

In the end, an explanation is in order for the absence of evidence for quinone type structures in our experimental work. Recently, such structures have been shown to be relevant in photoinduced brightness reversion phenomena[10]. Moreover, in the past, researchers have suggested that they might play an important role in such processes[4,7-9]. In view of the phtoreactivity of quinones[30], however, it is possible that these structures, if initially formed, may have been transformed to other products either during the process of photoyellowing or when exposed to laser light in the Raman experiment. In the latter case, thermal effects due to laser irradiation may also be important. This implies that the procedures and techniques used here may not have been the best suited for detection of quinones. In light of these observations, it appears that more than one class of structures may be responsible for yellowing. In any event, further studies to deal with these questions are needed.

CONCLUSIONS

A number of physical methods have been used to study photoyellowed and nonyellowed unbleached white spruce pulps. In the yellowed pulp, a new chromophore, namely cis-ferulic acid, has been detected. Both cis and trans isomers have been found to occur as would be expected on the basis of the photochemistry of ferulic acid. In view of the yellow color of cis-ferulic acid, its role in color reversion processes needs to be evaluated further.

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