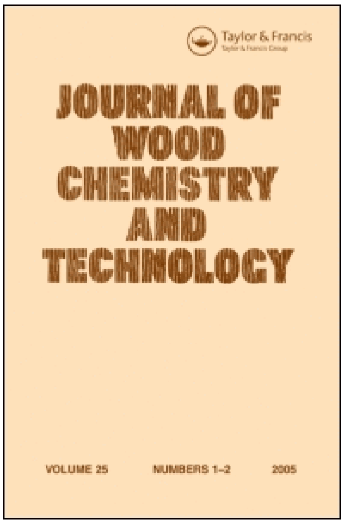


Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Structure and Reactivity of Spruce Mechanical Pulp Lignins Part III. Bleaching and Photoyellowing of Isolated Lignin Fractions

Xiaoqi Pan[a][b]; Dominique Lachenal[a][b]
[a] Ecole Française de Papeterie, Institut National Polytechnique de Grenoble, Saint Martin d' Héres, Cedex, France [b] Catherine Lapierre and Bernard Monties Laboratoire de Chimie Biologique, Thiverval-Grignon, France

To cite this Article Pan, Xiaoqi and Lachenal, Dominique(1993) 'Structure and Reactivity of Spruce Mechanical Pulp Lignins Part III. Bleaching and Photoyellowing of Isolated Lignin Fractions', Journal of Wood Chemistry and Technology, 13: 2, 145 — 165
To link to this Article: DOI: 10.1080/02773819308020512
URL: http://dx.doi.org/10.1080/02773819308020512

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 13(2), 145-165 (1993)

STRUCTURE AND REACTIVITY OF SPRUCE MECHANICAL PULP LIGNINS

PART III. BLEACHING AND PHOTOYELLOWING OF ISOLATED LIGNIN FRACTIONS

Xiaoqi Pan and Dominique Lachenal*
Ecole Française de Papeterie, Institut National Polytechnique de
Grenoble, BP 65, 38402 Saint Martin d' Hères Cedex, France

Catherine Lapierre and Bernard Monties
Laboratoire de Chimie Biologique, INRA / CBAI,
INA Paris-Grignon, 78850 Thiverval-Grignon, France

ABSTRACT

Organosolv lignin fractions were used as substrate for further investigations on the effect of bleaching and photoyellowing on lignin. These lignins were extracted from spruce TMP, bleached TMP (BTMP) and bleached and yellowed TMP (YBTMP). Furthermore, lignin fractions from TMP were also directly submitted to bleaching conditions and lignin fractions from BTMP to irradiation in the solid state. These lignin samples were all analyzed by thioacidolysis and FT-IR spectroscopy. The bleaching did not substantially change the lignin polymer but considerably destroyed some chromophoric structures such as coniferaldehyde end-groups. On the other hand, the photoyellowing resulted in marked degradations of lignin, shown by a decrease in the amount of β-O-4 and β-1 interunit bonds and a substantial increase in vanillin and vanillic acid end-groups and in catechol units.

---

* To whom correspondences should be addressed

INTRODUCTION

In Part I of this series,[1] the structural changes of *in situ* spruce TMP lignins during bleaching and photoyellowing were examined by analysis of the thioacidolysis degradation products of original, bleached and yellowed TMP samples. It was shown that the lignin structure was not changed to an appreciable extent by the bleaching but that the photoyellowing caused lignin degradation. In a continuation of this work, isolated lignin samples were prepared for further study by a variety of different analytical methods.

In the present work, organosolv lignin fractions isolated from spruce TMP sample and the corresponding bleached (BTMP) and photoyellowed (YBTMP) ones were investigated. As previously reported,[2] such lignins were obtained in quite high yields and without severe modification. The comparative structural evaluations of these series of lignin fractions, performed by analysis of thioacidolysis products and FT-IR, provided support and complement for what had been observed for the *in situ* lignins.

Furthermore, attempts have been made to confirm the above-obtained results by treatment of an isolated TMP lignin sample under the conditions simulating those encountered during bleaching and by irradiation experiment performed, in the solid state, on an isolated BTMP lignin sample and on a lignin model compound of guaiacylglycerol-β-guaiacyl ether type.

EXPERIMENTAL

Materials

The preparation of spruce (*picea abies*) pulps[1] and isolation of lignin fractions [2] were described in detail in the previous papers of this series. The brightness levels of TMP and BTMP were 50 % and 76 % (ISO), respectively. Two yellowed pulps were prepared by irradiation of BTMP handsheets (YBTMP-1) and pulps (YBTMP-4) in an original

Hanau suntest apparatus using a Xenon lamp for 2 hrs with an UV filter which eliminates the light of wavelength below 290 nm. The brightness values were 59 % and 65 % (ISO), for YBTMP-1 and YBTMP-4, respectively.

Bleaching Experiment of Isolated Lignins

300 mg of TMP L_2 sample (Fraction 2 of the ethanol-water lignins extracted from TMP)[2] were dissolved in 7 ml of bleaching solution containing 50 mg of hydrogen peroxide, 25 mg of sodium hydroxide, 30 mg of sodium silicate and 4 mg of DTPA (Diethylenetriaminepentaacetic acid). The initial pH of the solution was 11. The mixture was then placed in a bath at 70 °C and allowed to react for 4.5 hrs. At the end of this period, the reaction mixture was removed from the bath. After cooling, the final pH was 9.5. The solution was then acidified to pH 3 by addition of 1 N hydrochloric acid. The precipitated lignins were recovered by centrifugation and freeze-drying. These resulting lignins represented 50 % of the starting samples by weight.

Irradiation of Isolated Lignins or Model Compounds

After dissolution in acetone-water (8 : 2, v/v), the BTMP L_2 sample [2] was absorbed on a filter paper disc (Whatman No 1) and the solvent was evaporated. The disc was then irradiated in the suntest apparatus for 24 hrs, with (**I-1**) or without (**I-2**) the UV filter. After this treatment, the resulting lignins were divided into two parts: a soluble part (**SP**) and an insoluble part (**IP**) remaining on the paper disc after solvent extraction of the **SP** sample. This **SP** fraction was recovered by exhaustive extraction of the disc with acetone-water. Then most of the acetone in the solution was removed by vacuum evaporation. An aqueous lignin suspension was obtained and freeze-dried. The **IP** sample together with the paper was freeze-dried for analysis. Ethanol was used as solvent for the absorption on paper of the model compounds. After irradiation, the whole sample (paper together with photoproducts and residual model compounds) was ground and then freeze-dried before thioacidolysis.

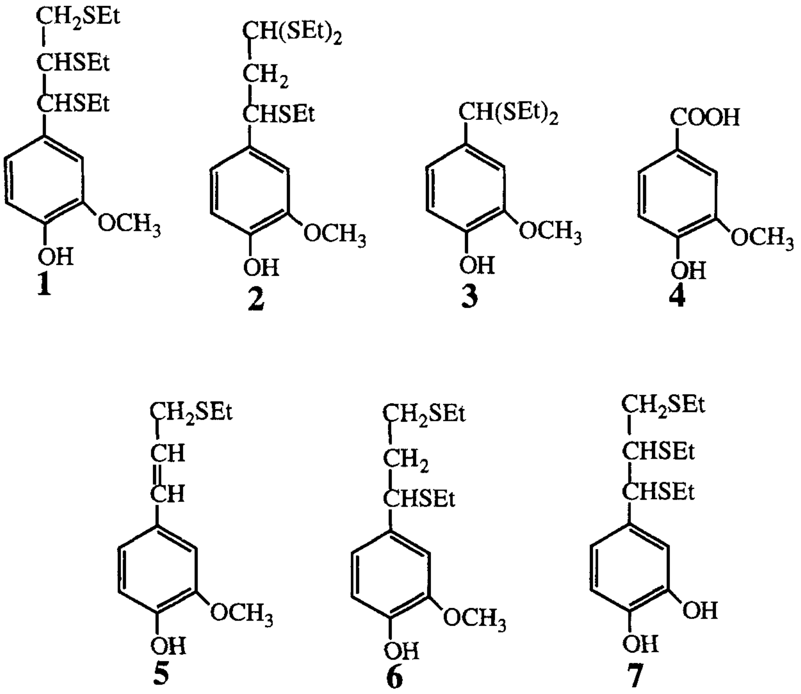
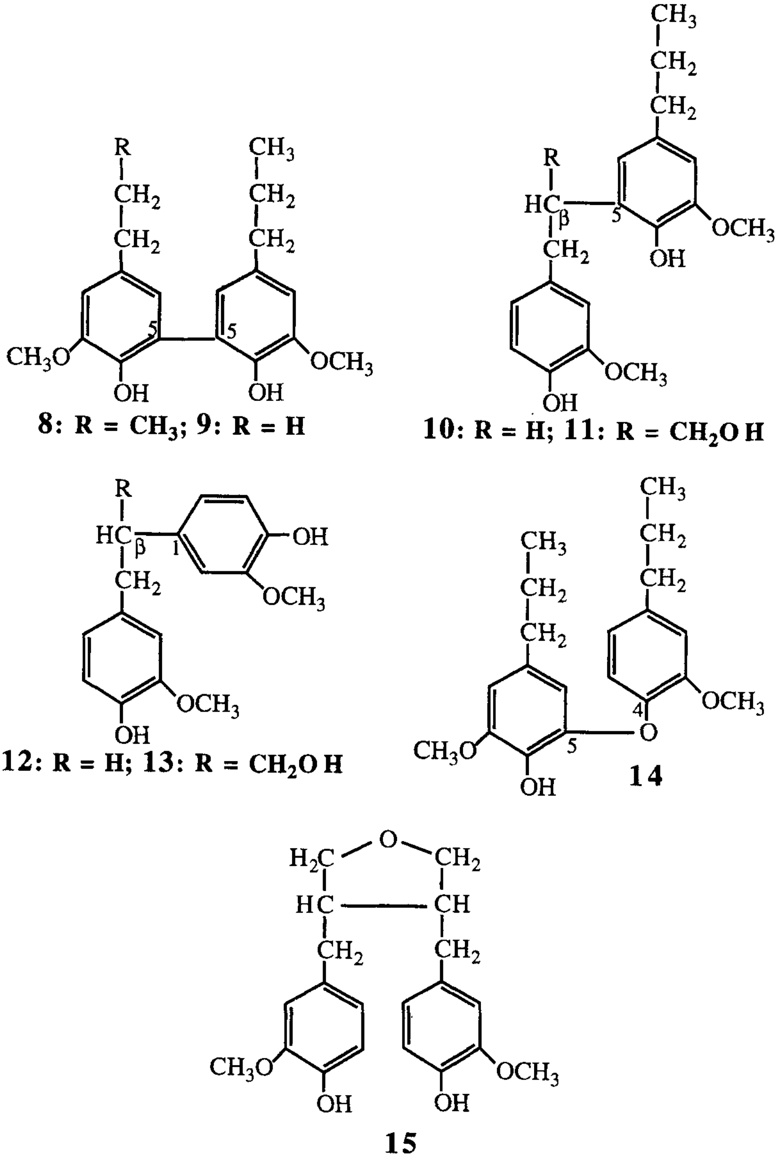


FIGURE 1. Monomeric degradation products recovered from thioacidolysis of β-O-4 linked guaiacyl structure (**1**), coniferaldehyde end-group (**2**), vanillin end-group (**3**), vanillic acid end-group (**4**), coniferyl alcohol end-group (**5**, **6**) and β-O-4 linked catechol unit (**7**).

Thioacidolysis

Analysis of the monomeric [3] and dimeric [4] degradation products recovered from thioacidolysis of the aforementioned samples was performed as previously described. The monomers and dimers are illustrated in Figures 1 and 2. Standard errors between duplicate experiments were 5 % and 10 %, for the monomeric and dimeric products, respectively.



8: R = CH_3; 9: R = H

10: R = H; 11: R = CH_2OH

12: R = H; 13: R = CH_2OH

14

15

FIGURE 2. Main dimers recovered from thioacidolysis and Raney nickel desulfuration of spruce lignins

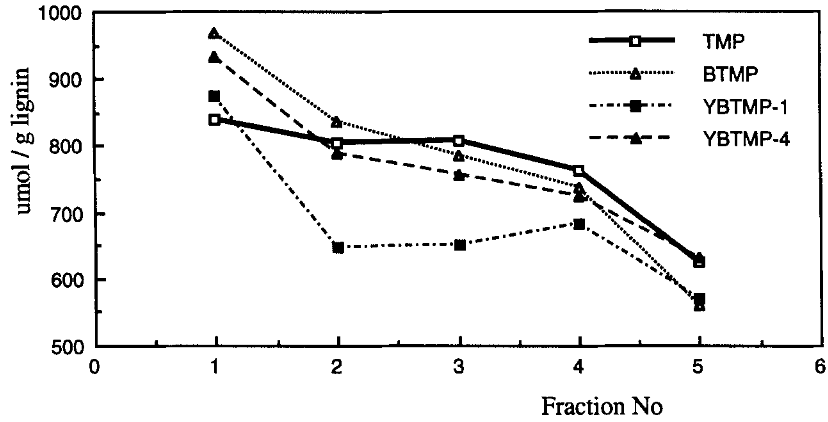


FIGURE 3. Changes in the amount of non-condensed β-O-4 structures obtained from thioacidolysis of lignin fractions extracted from four pulp samples in a flow-through reactor using ethanol-water.

FT-IR Spectrometric Analysis

The FT-IR spectra of the lignin samples were recorded on a Bruker IFS 45 Fourier Transform infrared spectrometer using the KBr pellet method.

RESULTS AND DISCUSSION

1. Characterization of Organosolv Lignin Fractions

The amount of arylglycerol-β-aryl ether (β-O-4) structures was essentially reflected by the yield of compound **1**. The results obtained for the five lignin fractions extracted from the four pulp samples are shown in Figure 3.

It appeared that trends were similar in all these series of fractions. Generally, the number of non-condensed β-O-4 structures decreased when the delignification proceeded but was not significantly different in TMP, BTMP and YBTMP-4 lignins. However, the YBTMP-1

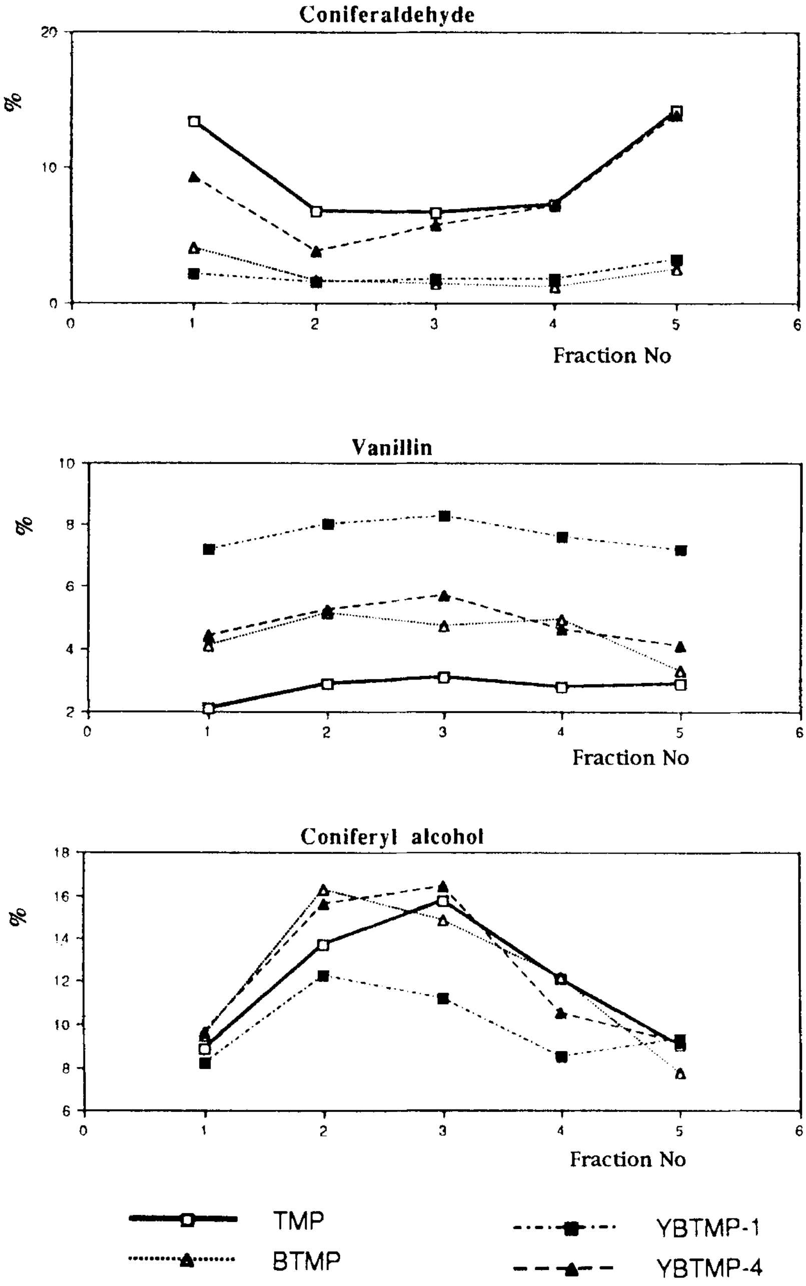


FIGURE 4. Variations in the relative proportion of some thioacidolysis monomeric products (molar % based on the main monomeric product 1 from non-condensed β-O-4 structures)

TABLE 1. Weight-Average Values of Some Thioacidolysis Monomeric Products Obtained from Five Successive Lignin Fractions Extracted from the Four Pulp Samples (μmol/g lignin).

Compound	TMP	BTMP	YBTMP-1	YBTMP-4
1. β-O-4 linked guaiacyl	742	712	638	722
2. coniferaldehyde e.g.	70	14	15	61
3. vanillin e.g.	21	31	48	34
5, 6 coniferyl alcohol e.g.	89	90	63	92

e.g.: end-group

sample appeared to have less non-condensed β-O-4 structures, which had to be related to the more severe yellowing treatment.

In addition, changes in the thioacidolysis monomeric products originating from coniferaldehyde (**2**), vanillin (**3**) and coniferyl alcohol (**5**, **6**) end-groups are represented in Figure 4. According to the previous investigation on the *in situ* lignins,[1] the variations in these structures were indicative of the lignin reactions involved in bleaching and photoyellowing.

For the sake of comparison, the weight-average values of the above-mentioned structures together with the main monomer (compound **1**) were calculated for each series of lignin fractions on the basis of the weight proportion of different fractions, and reported in Table 1.

The number of non-condensed β-O-4 structures was similar in TMP and BTMP lignins, which was in agreement with what was found for the *in situ* lignins.[1] The main bleaching effect, shown by the data of Figure 4 and Table 1, was a decrease in coniferaldehyde end-groups and a simultaneous increase in vanillin end-groups.

The non-condensed β-O-4 structures were not changed either by the yellowing treatment of YBTMP-4, indicating that lignin degradation must be very limited. In contrast the more severe treatment (YBTMP-1) induced structural changes in lignin to a certain extent. The major observations were the following:

- the number of non-condensed β-O-4 structures was reduced;

- the yield of vanillin end-groups increased whereas that of coniferyl alcohol end-groups decreased.

The former could be assigned to the homolytic cleavage of β-O-4 bonds [5 - 8] and to condensation reactions leading to new cross-linked lignin structures. The latter could be related to the light-induced cleavage of C_α-C_β linkages.[9 - 11] These results coincide with those previously reported on the *in situ* lignins.[1]

On the other hand, it is interesting to note the behaviour of coniferaldehyde end-group towards the bleaching and photoyellowing treatments. The coniferaldehyde structure is known as one of the major coloured species present in lignin.[12, 13] Here, it is obvious that the bleaching substantially brought about destruction of this group. According to Reeves and Pearl,[14] the mechanism involves an oxidative cleavage of the ring-conjugated double bonds by alkaline hydrogen peroxide.

On the contrary, the behaviour of coniferaldehyde structure towards the yellowing is not well understood. As shown in Figure 4 and Table 1, the content of coniferaldehyde end-groups was high and close to that of the TMP lignin in the YBTMP-4 lignin whereas it was considerably reduced in the YBTMP-1 lignin. These variations are, at present, difficult to interpret. It is assumed that under mild treatment conditions (YBTMP-4) coniferaldehyde end-groups reappeared as chromophoric photoproducts. Whereas when conditions were more severe (YBTMP-1), such formed coniferaldehyde structures might be oxidized to vanillin and vanillic acids via oxidative cleavage of α, β double bonds.[11] In addition, the coniferaldehyde structures could be extended to give yellow polyenealdehyde type compounds, not analyzed by the method used herein, as proposed by Hirashima and Sumimoto.[15]

Apart from the monomeric degradation products representative of the lignin structures which are only linked by alkyl aryl ether bonds,

TABLE 2. Total Yield and Relative Percentage of Main Dimeric Products Recovered from Thioacidolysis of Various Lignin Fractions.

Sample	Total yield (μmol/g lignin)	Relative molar percentage (%) 5-5 (8, 9)	β-5 (10, 11)	β-1 (12, 13)	4-O-5 (14)	THF (15)
TMP L_1	264	21.2	29.9	37.8	5.3	5.7
BTMP L_1	291	21.3	32.3	37.1	4.5	4.8
YBTMP-1 L_1	267	24.3	38.7	25.3	6.1	5.6
TMP L_2	287	21.2	34.4	33.4	4.9	5.9
BTMP L_2	287	24.4	33.4	32.0	4.9	5.2
YBTMP-1 L_2	269	21.4	42.2	24.5	6.5	5.3

the thioacidolysis mixture contains dimeric degradation products. These dimers represent the so-called 5-5 (**8** and **9**), β-5 (**10** and **11**), β-1 (**12** and **13**), 4-O-5 (**14**) and THF ring (**15**) lignin interunit bonds, which are referred to as condensed bonds and outlined in Figure 2. The absolute and relative amounts of these dimers obtained for the first two lignin fractions are reported in Table 2.

It can be seen that the total yields of dimers are of the same order in these lignin fractions. The main carbon-carbon interunit linkage patterns are 5-5, β-5 and β-1. It is confirmed that the bleaching did not cause any substantial change in the lignin polymer. In analogy to the case of the *in situ* lignins,[1] a noticeable effect of the photoyellowing was the decrease in the amount of β-1 structures. As discussed previously,[1] the photodegradation of these lignin units could be related to the formation of coloured products upon irradiation.

Infrared absorption characteristics were also examined. Table 3 presents a systematic comparison among these lignin samples. In the present work, we concentrated on the C=O stretching region of the IR spectra which is assigned to groups likely related to colour. The bands at 1670 and 1720 cm^{-1} originate from the absorption of conjugated

TABLE 3. Relative Absorptivities of the Maxima in the C=O Stretching Region of IR Spectra of Three Series of Lignin Fractions.

	L_1	L_2	L_3	L_4	L_5
			A_{1670} / A_{1510}		
TMP	0.33	0.23	0.19	0.19	0.19
BTMP	0.19	0.15	0.16	0.13	0.18
YBTMP-1	0.29	0.26	0.24	0.26	0.30
			A_{1720} / A_{1510}		
TMP	0.17	0.13	0.14	0.14	0.17
BTMP	0.17	0.15	0.12	0.13	0.16
YBTMP-1	0.25	0.22	0.20	0.18	0.21

carbonyl and unconjugated carbonyl (and carboxyl) groups, respectively.[16] Polcin and Rapson [17] pointed out that the colour of pulp varied proportionally with absorptivity at 1670 cm^{-1}. For comparison, the intensities of these two absorption bands were measured relatively to the reference band at 1510 cm^{-1} (aromatic ring vibration) according to the baseline method of Sarkanen and coworkers.[18]

As shown in Table 3, the absorptivities of lignin at 1670 cm^{-1} were decreased after bleaching. Based on literature data,[19] this observation can be attributed to the degradation of coniferaldehyde and quinone structures to colourless products upon alkaline hydrogen peroxide bleaching. On the contrary, the yellowing increased the amount of carbonyl and carboxyl groups in lignin. According to previous results[10, 20, 21] and to what was found in this study, quinone, vanillin and vanillic acid are observed as photoproducts in the irradiated lignocellulosic materials.

TABLE 4. Yields of Main Monomeric Products Obtained from Thioacidolysis of TMP L_2 Lignin Sample Before and After H_2O_2 Treatment (µmol/g lignin).

Compound	Before treatment	After treatment
1. β-O-4 linked guaiacyl unit	847	902
2. coniferaldehyde end-group	30	n.d.

n.d.: not detectable

2. Treatment of a TMP Lignin Sample by Hydrogen Peroxide

The TMP L_2 lignin sample underwent direct bleaching treatment under the conditions simulating those encountered in the bleaching of TMP (see experimental section). The effect of this bleaching treatment on the lignin structure was thus further investigated. Analyses of the main thioacidolysis products of the H_2O_2-treated sample together with the original TMP L_2 sample are reported in Tables 4 and 5.

It can be seen that the β-O-4 structure was not affected by this direct bleaching treatment, as reflected by the similar yield of compound **1**. However, this treatment almost totally destroyed the coniferaldehyde end-groups, which was not the case for the *in situ* lignins. This indicates that the residual coniferaldehyde groups found in pulp after bleaching were likely of low accessibility and could be due to incomplete bleaching action. Furthermore, the total yield of dimers was not changed. These results further confirm the conclusion obtained for the *in situ* lignins [1] and isolated lignins.

However, the relative importance of various dimers was slightly changed by the direct bleaching treatment. Table 5 shows that the amount of β-1 structures decreased and that of β-5 structures increased, which might be an artefact due to incomplete recovery of the bleached lignin sample (50 % of the starting lignin sample). As pointed out

TABLE 5. Total Yields and Relative Molar Percentages of Various Dimeric Products Obtained from Thioacidolysis of TMP L_2 Lignin Sample Before and After H_2O_2 Treatment.

	Total yield (μmol/g lignin)	Relative molar percentage (%)				
		5-5 (8, 9)	β-5 (10, 11)	β-1 (12, 13)	4-O-5 (14)	THF (15)
Before treatment	287	21.2	34.4	33.4	4.9	5.9
After treatment	276	19.5	40.1	29.2	4.3	6.7

previously,[2] the β-1 structures are more closely associated with easily solubilized lignin fragments.

Table 6 shows once again that conjugated carbonyl groups disappeared after bleaching. The increase in IR absorption at 1720 cm^{-1} could be assigned to the formation of carboxyl compounds, which are important degradation products formed during hydrogen peroxide bleaching.[19]

3. Photodegradation of Isolated Lignin Samples

Upon irradiation in the solid state, a soluble lignin sample, BTMP L2, became partly insoluble. As shown in Table 7, 20 to 30 % of the starting sample proved to be non-extractible and tightly attached to the paper. The higher value of this percentage was observed for the more drastic irradiation conditions. Since complete recovery was possible for a control experiment, it is very likely that the photodegradation caused condensation reactions which made lignins partly insoluble due to the increase in cross-linking and molecular weight or even to linkage with the cellulosic matrix.

Variations in the yield of the thioacidolysis monomers were obvious and significant for the aforementioned samples. For

TABLE 6. Relative Absorptivities of the Maxima in the C=O Stretching Region of IR Spectra of TMP L_2 Lignin Sample Before and After H_2O_2 Treatment.

	A_{1670} / A_{1510}	A_{1720} / A_{1510}
Before treatment	0.23	0.13
After treatment	0.13	0.17

TABLE 7. Relative Recoveries of Soluble (**SP**) and Insoluble (**IP**) Parts of lignin, According to the Irradiation Conditions (BTMP L_2 sample was absorbed on a filter paper disc before irradiation).

Irradiation		**I-1**	**I-2**	Control
Duration (hrs)		24 (12 each side)	24 (12 each side)	0
UV filter		yes	no	
Recovery yield	**SP**	82	66	100
(%)	**IP**	18	34	0

comparison, their relative importances were expressed as molar percentages of the main product **1** in Table 8.

Similarly to the case of the *in situ* lignins,[1] the analysis of thioacidolysis monomeric degradation products revealed that the content of non-condensed β-O-4 structures was substantially decreased by the irradiation, as demonstrated by the lower yield of compound **1**. Other effects of the irradiation on such lignin structures were:

- a slight increase of coniferaldehyde end-groups, particularly in the insoluble fraction (**IP**);
- a pronounced increase of vanillin and vanillic acid end-groups;
- a decrease of coniferyl alcohol end-groups.

TABLE 8. Absolute and Relative Yields of Main Monomeric Products Obtained from Thioacidolysis of BTMP L_2 Lignin Sample Before and After Irradiation.

Compound	Control	I-1		I-2	
		SP	IP	SP	IP
1. β-O-4 linked guaiacyl (μmol/g lignin)	890	487	407	456	326
Molar percentages based on compound 1					
2. Coniferaldehyde e.g.	2	3	7	3	6
3. Vanillin e.g.	6	23	8	26	12
4. Vanillic acid e.g.	traces	16	22	18	17
5, 6. Coniferyl alcohol e.g.	14	3	5	3	6
7. Catechol unit	traces	8	9	6	9

e.g.: end-group

The second effect could be related to oxidative cleavage of C_α-C_β bonds upon the irradiation. The formation of vanillin and vanillic acid was repeatedly reported as a typical feature of irradiated lignocellulosic materials.[9, 10, 21] The disappearance of coniferyl alcohol end-groups could be explained by the mechanism of ring-conjugated double bond cleavage proposed by Gellerstedt and Pettersson.[11]

In addition, compound 7, resulting from the thioacidolysis of β-O-4 linked catechol units, could be observed in substantial quantities after the irradiation, whereas it was present only as traces in the thioacidolysate of the starting lignin sample. In accordance with literature data,[5, 20, 22, 23] this result unambigously confirms that demethylation reactions occurred during yellowing.

TABLE 9. Total Yields and Relative Molar Percentages of Main Dimeric Products Obtained from Thioacidolysis of BTMP L_2 Lignin Sample Before and After Irradiation.

		Total yield (μmol/g lignin)	Relative molar percentage (%)			
			5-5 (**8, 9**)	β-5 (**10, 11**)	β-1 (**12, 13**)	4-O-5 (**14**)
Control		287	25.7	35.3	33.8	5.1
I-1	**SP**	134	25.8	38.5	30.1	5.5
	IP	98	37.1	31.9	19.2	11.8
I-2	**SP**	132	25.4	40.0	29.9	4.7
	IP	82	35.8	32.0	20.0	12.2

Within all the irradiated lignin samples analysed so far by thioacidolysis (either *in situ* or after isolation), it was not possible to detect any significant formation of ferulic acid end-groups, although this method allowed characterization of ferulic acid ethers or esters.[24] Our data do not confirm the occurrence of cis-ferulic acid as a coloured photoproduct, reported by Agarwall and Attalla in the case of photoyellowing of spruce mechanical pulp.[25]

The total yields and relative frequencies of various condensed bonds are given in Table 9. After the irradiation, the THF ring pattern could not be detected, indicating that this structure was damaged and / or suffered condensation. As a whole, the irradiation brought about a substantial decrease in the yield of dimers. This implies that the lignins might be so cross-linked that thioacidolysis gave large quantities of trimers and oligomers not analyzed here. The presence (**I-1**) or absence (**I-2**) of the UV filter had little effect on the results reported in Table 9.

TABLE 10. Relative Absorptivities of the Maxima in the C=O Stretching Region of IR Spectra of BTMP L_2 Lignin Sample Before and After Irradiation.

	Control	**I-1 SP**	**I-2 SP**
A1670 / A1510	0.15	0.64	0.70
A1720 / A1510	0.15	0.67	0.78

As shown in Table 9, the main effect of the irradiation treatment, particularly in the case of insoluble lignin fraction (**IP**), was a marked decrease in relative importance of β-1 bonding pattern. The variation of β-5 structure was not significant upon this treatment. Furthermore, the relative proportion of 5-5 and 4-O-5 dimers increased, particularly for the **IP** lignins. Coupling and rearrangement reactions of radicals arised from light-induced hydrogen abstraction and β-O-4 bond cleavage were possible pathways to the formation of 5-5 structures.[5, 7, 26] 4-O-5 structures could also be formed in the similar way.

From the data of Tables 8 and 9, it can be seen that the more extensively modified lignins were those strongly attached to the paper after the irradiation. Lower yields in both monomers and dimers were obtained in the case of these lignin fractions as compared with their counterparts. Thus, we can conclude that the lignin remaining on the paper was more highly condensed. Moreover, some chromophoric components like coniferaldehyde, catechol and 5-5 biphenyl were abundant in this part of lignin.

Infrared absorption was recorded on the **SP** samples. Table 10 shows that the light exposure considerably increased the amount of carbonyl and carboxyl groups, which was in agreement with the thioacidolysis results.

TABLE 11. Relative Yields (%) of Compound **1** from Thioacidolysis of a β-O-4 Model Compound (GGE) Before and After Irradiation.

Untreated (Control)	24 hrs (12 each side) With UV filter	24 hrs (12 each side) Without UV filter
100	47	33

4. Photolysis of a β-O-4 Model Compound

The monomeric product **1** obtained from the thioacidolysis of guaiacylglycerol-β-guaiacyl ether (GGE) absorbed on a filter paper disc and irradiated was measured. GGE was taken as a model of β-O-4 structure to verify the photodegradation of this structure reproted for both the *in situ* and isolated lignins. Results are given in Table 11.

It is shown that the β-O-4 structure was extensively destroyed by the irradiation treatment. The presence of UV filter, which cuts off the near UV portion of wavelength below 290 nm, afforded a moderate protection. Unfortunately, the method used here has not allowed characterization of any coloured products from the photodegradation of β-O-4 structures. However, the β-O-4 compound impregnated paper apparently yellowed upon the light exposure; and exhaustive extraction by dioxane failed to afford any visible bleaching effect on the paper. It is thus speculated that coloured materials formed and might be partially attached to the cellulosic matrix.

CONCLUSION

In summary, the results presented above are in good agreement with those reported on the *in situ* lignins.

Alkaline hydrogen peroxide bleaching does not substantially modify the structure of lignin. The major reaction which takes place during the bleaching is the destruction of chromophoric groups, which is demonstrated by the decrease in the amount of coniferaldehyde end-groups and in the IR absorptivity at 1670 cm^{-1}. This result has been confirmed by our further study using ^1H and ^{13}C-NMR spectrometric methods, which will be included in the following paper of this series.

On the other hand, a pronounced degradation of lignin occurs upon light exposure. The substantial decrease in the amount of β-O-4 structure is related to the breakdown of β-O-4 bonds and to condensation reactions. The occurrence of the latter has also been demonstrated by the decrease in the yield of thioacidolysis monomeric and dimeric products as well as in the solubility of lignin. The increase of vanillin and vanillic acid end-groups results from oxidative cleavage of Cα-Cβ bonds. The other effects of photoyellowing are an increase in catechol units and a decrease in β-1 structures, which may likely lead to yellow products.

ACKNOWLEDGEMENT

Financial support and a thesis grant to X.P. from the Centre Technique du Papier (CTP Grenoble) is gratefully acknowledged.

REFERENCES

1. X. Pan, D. Lachenal, C. Lapierre and B. Monties, J. Wood Chem. Technol., 12 (2), 135 (1992).

2. X. Pan, F. Pla, D. Lachenal, C. Lapierre and B. Monties, J. Wood Chem. Technol., 12 (3), (1992).

3. C. Lapierre, B. Monties and C. Rolando, 4th Int. Symp. Wood & Pulping Chem., Paris, France, Proceedings Vol. 2, 431 (1987).

4. C. Lapierre, B. Pollet, B. Monties and C. Rolando, Holzforschung, 45 (1), 61 (1991).

5. J. Gierer and S. Y. Lin, Svensk Papperstid., 75 (7), 233 (1972).

6. C. Vanucci, P. Fornier de Violet, H. Bouas-Laurent and A. Castellan, J. Photochem. Photobiol. A: Chemistry, 41, 251 (1988).

7. A. Castellan, N. Colombo, C. Cucuphat and P. Fornier de Violet, Holzforschung, 43 (3), 179 (1989).

8. J. C. Scaiano, J. C. Netto-Ferreira and V. Wintgens, J. Photochem. Photobiol. A: Chemistry, 59, 265 (1991).

9. J. A. Hemmingson and H. Wong, Holzforschung, 43 (2), 141 (1989).

10. J. A. Hemmingson and H. Wong, Holzforschung, 44 (4), 297 (1990).

11. G. Gellerstedt and E.L. Pettersson, Acta. Chem. Scand., B 29, 1005 (1975).

12. J. C. Pew and W. J. Connors, Tappi, 54 (2), 245 (1971).

13. F. Imsgard, S. I. Falkehag and K. P. Kringstad, Tappi, 54 (10), 1680 (1971).

14. R. H. Reeves and I. A. Pearl, Tappi, 48 (2), 121 (1965).

15. H. Hirashima and M. Sumimoto, Mokuzai Gakkaishi, 33 (1), 31 (1987).

16. H. L. Hergert, pp. 267 - 297, In: Lignins: Occurrence, Formation, Structure and Reactions (Sarkanen, K. V. and Ludwig, C. H. Eds.), Wiley Intersci., New York, 1971.

17. J. Polcin and W. H. Rapson, Pulp Paper Mag. Can., 72 (3), T103 (1971).

18. K. V. Sarkanen, H. M. Chang and G. G. Allan, Tappi, 50, 583 (1967).

19. J. Gierer, Wood Sci. Technol., 20, 1 (1986).

20. S. E. Lebo, W. F. W. Lonsky, T. J. McDonough, P. J. Medvecz and D. R. Dimmel, J. Pulp Paper Science, 16 (5), 139 (1990).

21. B. Holmbom, R. Ekman and C. Eckerman, 5th Int. Symp. Wood & Pulping Chem., Raleigh, USA, Proceedings Vol. 1, 445 (1989).

22. G. J. Leary, Nature, 217, 672 (1968).

23. G. J. Leary, Tappi, 50 (1), 17 (1967).

24. C. Lapierre, D. Jouin and B. Monties, pp. 118 - 130, In: Physico-Chemical Characterization of Plant Residues for Industrial and Feed Use (Chesson, A. and Orskov, E. R. Eds.), Elsevier Applied Science, London, New York, 1989.

25. P. Agarwall and R. H. Atalla, J. Wood Chem. Technol., 10 (2), 169 (1990).

26. G. Gellerstedt and E. L. Pettersson, Svensk Papperstid., 80 (1), 15 (1977).