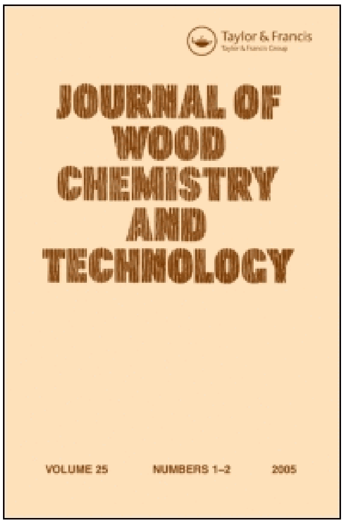

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Xiaoqi Pan; Dominique Lachenal; Catherine Lapierre; Bernard Monties

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STRUCTURE AND REACTIVITY OF SPRUCE MECHANICAL PULP LIGNINS
PART I. BLEACHING AND PHOTOYELLOWING OF *IN SITU* LIGNINS

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

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

ABSTRACT

This paper reports the structural investigation of a series of *in situ* spruce lignins in wood, thermomechanical pulp (TMP) and the corresponding bleached (BTMP) and photoyellowed (YBTMP) samples. This was achieved by using an original two-step degradative technique, thioacidolysis followed by Raney nickel desulfuration. The determination of thioacidolysis monomeric and dimeric products allowed an estimate of various lignin building units and interunit bonds, respectively. It was observed that the thermomechanical and bleaching treatments did not affect spruce lignin structure to an appreciable extent. On the contrary, the photoyellowing treatment caused marked structural changes in lignin, particularly when run in severe conditions. These changes were essentially a decrease in the amount of β-O-4 and β-1 interunit bonds and a relative increase in catechol units and in vanillin end-groups.

INTRODUCTION

Interest in high yield pulps, such as thermomechanical pulp (TMP), is growing because these pulps can be produced with a low capital investment and without pollution problems associated with the manufacture of chemical pulps.

However, their widespread use as substitutes for chemical pulps is hampered by their rapid colour reversion upon light exposure. Although the detailed mechanism of this photoyellowing is not yet clearly understood, a number of studies have shown that lignin is primarily involved in this process , according to the following sequence [1, 2] : i) absorption of the near ultraviolet portion of sunlight by photosensitizers like α-carbonyl groups in lignin, [3, 4] and ii) light-induced oxidation leading to coloured products from lignin. [1, 2, 5, 6]

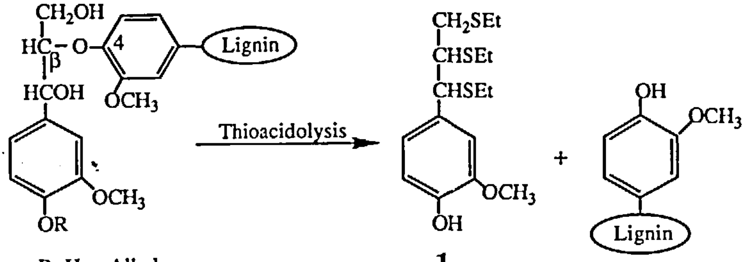
The present study, together with forthcoming papers of series, aims at obtaining a better knowledge of the structure of TMP lignins and of their chemical changes during bleaching and photoyellowing processes.

Despite the complexity of a whole lignocellulosic sample, we chose to examine *in situ* TMP lignins, because isolated lignin preparations, which are often used when soluble samples without analytical interferences from polysaccharides are looked for, may not adequately reflect the behaviour of *in situ* lignins towards bleaching and photoyellowing. Accordingly, a spruce wood was successively subjected to thermomechanical defibration, bleaching treatment and photoyellowing experiments of variable duration. We thus recovered one TMP sample together with one bleached TMP (BTMP) and three photoyellowed BTMP (YBTMP) samples.

The comparative structural evaluations of the *in situ* spruce TMP, BTMP and YBTMP lignins were achieved by a chemical degradation method -thioacidolysis, which leads to lignin depolymerization by selective cleavage of alkyl aryl ether bonds (except methyl aryl ether). The monomeric and dimeric degradation products analyzed are representative of lignin building units and interunit bonds, respectively. [7 - 10]

The thioacidolysis technique first allows an estimate of the amount of the most frequent lignin structures, i.e. arylglycerol-β-aryl ether (β-O-4), through the determination of the main monomeric product **1**. As shown in Figure 1, the compound **1** represents the non condensed β-O-4 linked structure in lignin.

In addition, analysis of other thioacidolysis monomeric products makes it possible to quantitate the amount of some minor structural constituents of lignin which may play a key role in the bleaching and photoyellowing processes. These structures are coniferaldehyde, vanillin and coniferyl alcohol end-groups and also the β-O-4 linked catechol units, which lead to the specific thioacidolysis products **2** - **6**, respectively, as outlined in Figure 2.



R: H or Alkyl

1

FIGURE 1. Main monomeric product **1** formed from the thioacidolysis of guaiacyl β-O-4 structures.

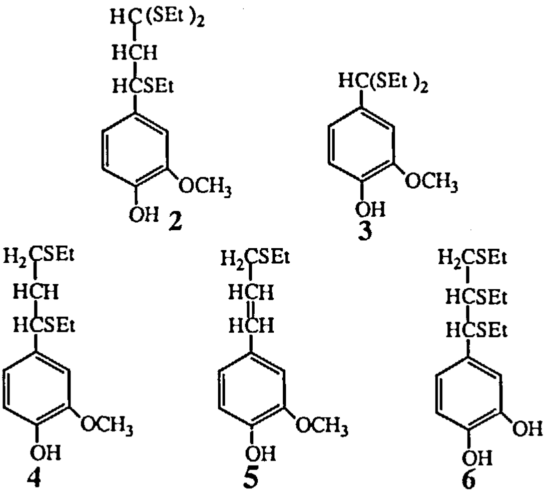
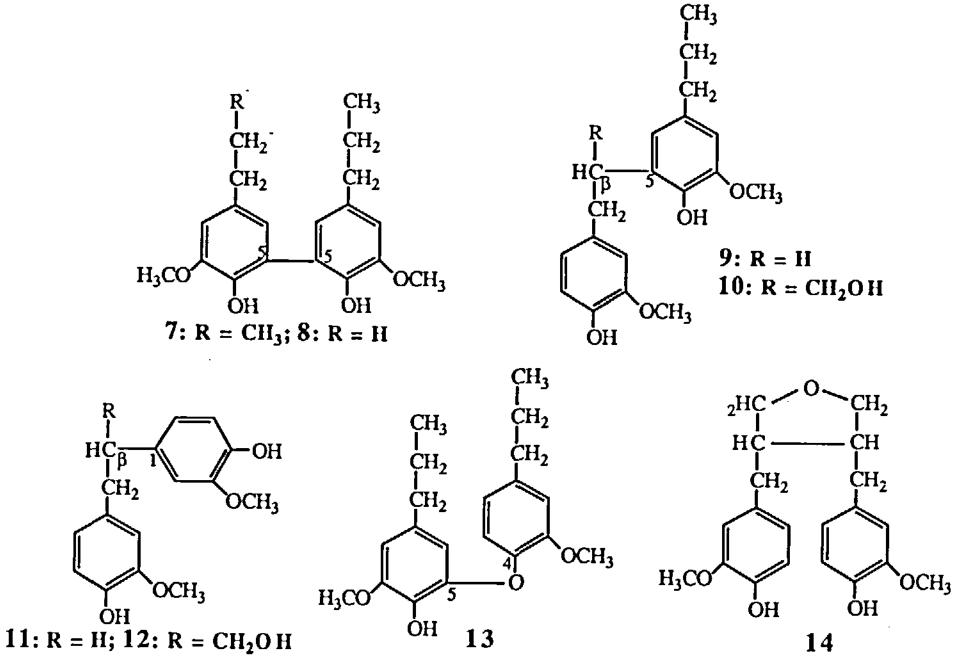


FIGURE 2. Monomeric degradation products issued from the thioacidolysis of coniferaldehyde (**2**), vanillin (**3**), coniferyl alcohol (**4** and **5**) end-groups and β-O-4 linked catechol units (**6**).

Finally, a recent extension of the thioacidolysis method, namely thioacidolysis followed by Raney nickel desulfuration, allows an estimate of the amount of various carbon-carbon and diaryl ether interunit linkages, through the quantitative determination of the dimeric degradation products illustrated in Figure



7: R = CH_3; 8: R = H

9: R = H
10: R = CH_2OH

11: R = H; 12: R = CH_2OH

13

14

FIGURE 3. Main dimers recovered from the thioacidolysis, then desulfuration of guaiacyl lignins.

3. These dimers represent so-called 5-5 (compounds 7 and 8), β-5 (compounds 9 and 10), β-1 (compounds 11 and 12), 4-O-5 (compound 13) and tetrahydrofuran ring (THF compound 14) lignin interunit linkages. In the degradative method used herein, dimer 11 may originate from 1,2-diguaiacylpropane structures and / or p,p'-diguaiacylstilbene ones.

RESULTS AND DISCUSSION

The lignin content and the brightness value of the various samples investigated are reported in Table 1.

TABLE 1. Lignin Content and Brightness Value of Spruce Wood and Pulp Samples

	Wood	TMP	BTMP	YBTMP-1	YBTMP-2	YBTMP-3
Brightness (% ISO)	n. d.	50	76	59	56	41
Klason lignin (%)	28.5	29.0	28.4	26.2	26.1	24.8
Acid-soluble lignin (%)	0.3	0.4	0.4	0.5	0.8	2.0

n.d. : not determined

It can be seen that the lignin content is not affected by the thermomechanical and bleaching treatments, indicating that lignin removal is not significant in these processes. The photodegradation does not cause any substantial variations in this lignin content either. Only the more severe yellowing experiment (YBTMP-3) induces a small decrease in Klason lignin content and simultaneously a slight increase in the acid-soluble lignin fraction. This result supports the hypothesis that UV irradiation might increase solubility of lignin in sulfuric acid.[2] This phenomenon could be linked to the formation of small acid-soluble chromophoric fragments from the lignin polymer.

The absolute and relative yields of the thioacidolysis monomers **1** - **6** recovered from the spruce wood meal and pulp samples are reported in Table 2. It can be observed that the number of non condensed β-O-4 structures, essentially reflected by the yield of compound **1**, is similar in wood, TMP and BTMP, which indicates that the thermomechanical and bleaching treatments do not affect these prominent structures to any large extent. The only bleaching effect revealed by the data of Table 2 is the decrease in coniferaldehyde end-group and the concomitant increase in vanillin one. According to Gierer [11], alkaline hydrogen peroxide leads to oxidative cleavage of the ring-conjugated double bond of coniferaldehyde. This mechanism may be of significance to the bleaching process since coniferaldehyde is known as one of the major coloured species present in lignin. [12, 13]

TABLE 2. Absolute (*) and Relative (**) Yields of Monomeric Products Recovered from the Thioacidolysis of *in situ* Lignins in Spruce Wood and Various TMP Samples.

Compound	Origin in Lignin	Wood	TMP	BTMP	YBTMP-1	YBTMP-2	YBTMP-3
* **1**	β-O-4 linked guaiacyl unit	1232	1081	1003	1043	859	149
** **2**	coniferaldehyde	2	3	1	2	2	3
** **3**	vanillin	n.d.	1	3	4	4	14
** **4** and **5**	coniferyl alcohol	10	11	13	11	12	8
** **6**	catechol unit	n.d.	2	4	3	5	15

* and **: The values are expressed as μmol / g lignin and as relative molar percentages based on compound **1**, respectively.

n.d.: not determined because of small amount

On the other hand, the photoyellowing treatments induce more pronounced structural changes in lignin, particularly in the case of the more drastic YBTMP-3 one. According to Table 2, main observations are the following:

i) The number of non condensed β-O-4 structures is considerably reduced, as demonstrated by the decrease in the yield of compound **1**, after a drastic yellowing treatment. Based on literature data, [14 - 16] this could involve the homolytic cleavage of β-O-4 linkages and the formation of phenoxy and phenacyl radicals which could be further degraded or condensed to coloured photoproducts. The extent of this lignin degradation is dependent on the treatment conditions such as irradiation time and spectral distribution of the light source. On the other hand, lignin condensation reaction upon light exposure may be, to a larger extent, responsible for the reduction in the yield of compound **1** because of formation of cross-linked structures. This point will also be discussed below.

ii) The amount of vanillin end-groups increases whereas that of coniferyl alcohol ones slightly decreases, as shown by the relative determinations of compounds **3** and **4**, **5**, respectively. The former change could be related to the C_α-C_β bond oxidative cleavage occurring during lignin photodegradation, which is consistent with the repeated observations of vanillin and vanilllic acid in irradiated lignocellulosic materials. [6, 17 - 19] Besides, the destruction of coniferyl alcohol end-groups could be explained by the mechanism of ring-conjugated double bond cleavage proposed by Gellerstedt and Pettersson. [20]

iii) The relative amount of the catechol compound **6** increases, especially for the more severe YBTMP-3 treatment. This change suggests that demethylation reactions occur during photoyellowing and convert β-O-4 linked guaiacyl units to the corresponding catechol ones. This is also in accordance with previously reported studies which stressed the role of ortho-quinonoid and catechol structures in lignin photodegradation. [5, 13, 14, 21 - 23]

As discussed above, the analysis of the thioacidolysis monomers essentially leads to results that are in agreement with previously reported literature data. However, analysis of the thioacidolysis dimers may provide original structural information which could not be obtained for *in situ* lignins by other degradative or spectrometric techniques for lack of specificity and / or sensitivity. The absolute and relative amounts of dimers **7 - 14** recovered after thioacidolysis and Raney nickel desulfuration of the various samples are shown in Table 3.

TABLE 3. Total Yield and Relative Molar Percentage of Main Dimeric Products Obtained from the Thioacidolysis of *in situ* Lignins in Spruce Wood and Various TMP Samples.

Sample	Total yield (μmol / g lignin)	Relative molar percentages (%) 5-5 (7,8)	β-5 (9,10)	β-1 (11,12)	4-O-5 (13)	THF (14)
Wood	352	30.9	32.3	26.0	6.7	4.2
TMP	380	29.5	34.1	25.6	7.7	3.1
BTMP	337	31.6	33.7	25.1	6.1	3.6
YBTMP-1	280	33.1	35.8	19.8	6.6	4.8
YBTMP-2	264	33.4	36.1	18.0	8.9	3.6
YBTMP-3	24	36.4	40.5	17.4	5.8	n.d.

n.d. : not determined (too small amount)

In this Table, it can be seen that the 5-5, β-5 and β-1 bonds are the main carbon-carbon interunit linkages in spruce lignin. The values obtained for the wood, TMP and BTMP *in situ* lignins are very similar. This result once again indicates that the thermomechanical treatment and the bleaching process do not cause any significant changes in the lignin polymer. According to model compound experiments,[24, 25] however, the phenolic 1,2-diguaiacylpropane structures may undergo alkali-promoted conversion to the corresponding stilbenes under bleaching experimental conditions. As stated in Introduction, the β-1 dimer **11** may originate from 1,2-diguaiacylpropane and / or p,p'-diguaiacylstilbene structures. Hence, the method used herein is not able to detect any structural variation corresponding to the formation of p,p'-stilbenes in lignin.

In contrast, the yellowing treatments cause marked changes, summarized as follows.

i) Similarly to the case of thioacidolysis monomers, the yield of the dimers **7 - 14** is reduced after the yellowing experiments, particularly in the case of the drastic YBTMP-3 treatment. This markedly low yield is indicative of the high cross-linked degree of the YBTMP-3 lignin, since the total lignin contents are similar within the whole series of samples studied (Table 1). Condensation reactions might increase the yields of trimers and other oligomers, not analyzed herein, in the thioacidolysis product mixture. Such highly condensed lignins might contain coloured structures.

ii) The results reported in Table 3 shows that the major modification of the dimers brought about by the photoyellowing appears to be the relative decrease in β-1 interunit bond. This observation indicates that the β-1 structure is targetted by the photodegradation process. To our knowledge, this is the first direct experimental evidence of the role of β-1 structures in the photodegradation of *in situ* lignins. Actually, this role is indirectly supported by some model compound experiments performed by Castellan and coworkers.[26,27] They demonstrated that β-1 structure was prone to photodegradation leading to coloured products. According to Nimz,[28] this β-1 structure is potential precursors of leucochromophoric and chromophoric systems. Upon bleaching, the β-1 structures may be converted to stilbene intermediates via alkali-promoted reaction.[24,25] The latter can readily be oxidized to strongly chromophoric stilbenequinones and / or phenanthrenes in the presence of oxygen, particularly under the influence of light.[28] Our results suggest that the mechanism proposed might be a possible way leading to formation of chromophores.

CONCLUSION

The results presented in this paper provide evidence about the structural changes occurring to *in situ* spruce TMP lignins during bleaching and photoyellowing.

The bleaching treatment does not substantially change the structure of the lignin polymer. The main reaction which can be detected is the destruction of the chromophoric coniferaldehyde end-groups. This conclusion supports the hypothesis that bleaching can be performed without degrading lignin to an appreciable extent.

On the contrary, a marked degradation of lignin occurs upon light exposure of the lignocellulosic samples under conditions simulating solar irradiation. This degradation is demonstrated by the following structural changes: a substantial decrease in the amount of non condensed β-O-4 structures, a higher condensation degree reflected by the low yield of the thioacidolysis monomeric and dimeric degradation products, a relative increase in vanillin end-groups as well as in catechol units and a noticeable relative decrease in β-1 lignin bonding patterns.

All these detailed structural informations have been quantitatively obtained by means of an original two-step degradative technique, thioacidolysis followed by Raney nickel desulfuration, applied to a microanalytical scale amount of spruce wood and TMP samples.

EXPERIMENTAL

1.Pulp Sample Preparation

The TMP samples were prepared from spruce (*picea abies*) in a Sprout-Waldron pilot installation at the Centre Technique du Papier in Grenoble. The following conditions were used: temperature 120 °C, pressure 1.4 bar, retention time 15 min. The pulps were then refined in a Sprout-Bauer refiner to a freeness of 45 °SR. The pulp brightness was 50 % (ISO).

Bleaching treatments were performed in polyethylene bags under the following conditions: pulp consistency 15 % , H_2O_2 5 % , NaOH 2.5 % , Na_2SiO_3 (39° Be') 3 % , DTPA (commercial solution) 0.4 % (all chemicals being charged on the basis of oven-dried pulp), temperature 70 °C, time 4.5 hours. The brightness of the resulting bleached TMP (BTMP) was 76 % (ISO).

BTMP handsheets (about 50 g / m^2) were irradiated in an Original Hanau suntest apparatus using a Xenon lamp and with or without an UV filter which eliminates the light of wavelength below 290 nm. Three yellowed pulp samples were prepared:

- **YBTMP-1**: 2 hours irradiation (1 hr. each side), with UV filter, final brightness 59 % (ISO);
- **YBTMP-2**: 2 hours irradiation (1 hr. each side), without UV filter, final brightness 56 % (ISO);
- **YBTMP-3**: 24 hours irradiation (12 hrs. each side), with UV filter, final brightness 41 % (ISO).

Brightness measurements were conducted using an Elrepho 2000 instrument at the wavelength of 457 nm. Brightness data reported herein are average values of the measurements performed on both sides of ten different pulp handsheets.

2. Lignin Content Determination

Both acid-insoluble and acid-soluble lignin contents in the wood meal and aforementioned pulp samples were determined according to the TAPPI standard methods (T 222 os-74 and Useful method 250, respectively).

3. Thioacidolysis

The analyses of the monomeric [7, 8] and dimeric [9, 10] degradation products recovered from the thioacidolysis of the wood meal and various pulp samples were performed as previously described. Standard errors between duplicate experiments were 5 % and 10 %, for the monomeric and dimeric products, respectively.

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