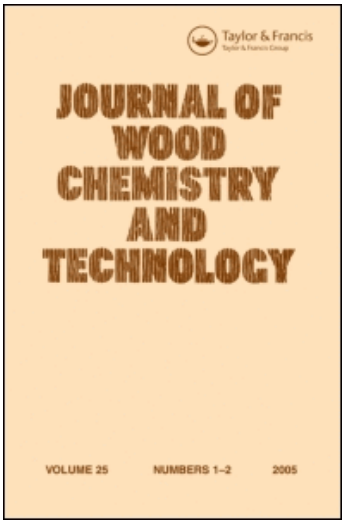

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FORMATION AND REACTIONS OF LEUCOCHROMOPHORIC STRUCTURES IN HIGH YIELD PULPING

To the memory of Kyosti V. Sarkanen

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ABSTRACT

Low molecular weight lignols with intact side chains were produced by mild hydrolysis of spruce wood, of unbleached and hydrogen peroxide bleached spruce groundwood and of chemithermomechanical pulp (CTMP). The major monomeric, dimeric and trimeric lignin products derived were isolated by HPLC and characterized by GC-MS and NMR. The behaviour of these products towards photo-oxidation in the solid state on filter paper was studied. Coniferaldehyde structures, the major leucochromophores originally present in spruce wood lignin, were reduced during the CTMP process and eliminated after bleaching with hydrogen peroxide. Diguaiacyl stilbene originating from diarylpropane structures and produced during hydrogen peroxide bleaching were found to be the predominant leucochromophoric structure present in the hydrogen peroxide bleached pulps and these were found to be responsible for the fast photoyellowing of these pulps.

INTRODUCTION

The rapid discoloration of high yield pulps on exposure to sunlight is one of the major drawbacks to their widespread use in long-life paper products. Numerous attempts have been made to stabilize the brightness of bleached high-yield pulps but so far without success, partly due to the fact that neither the mechanism of this photochemical reaction nor the nature of responsible leucochromophoric groups has been known in detail.

Recent studies carried out by irradiating low molecular weight lignin model compounds in the solid state have shown that diguaiacyl stilbenes and phenylcoumarones bearing free phenolic hydroxyl groups are among the most sensitive leucochromophoric structures [1-3]. By model experiments it has also been demonstrated that stilbenes and phenylcoumarones can be produced from two of the major lignin structural units, viz. phenylcoumaran (β-5) structures [4, 5] and diarylpropane (β-1) structures [6] during simulated disc refining treatment. The conversion of a diarylpropane structure to a stilbene was also observed by alkaline hydrogen peroxide treatment of a β-1 model compound at a pH above 12 [7]. It is not clear, however, to what extent these reactions take place inside the wood fiber during commercial pulping and bleaching processes. In other reports it has been suggested that para-quinones [8] and ortho-quinones [9] are the chromophores primarily associated with the light-induced yellowing of high yield pulps. Further detailed molecular information seems, however, to be needed before the major leucochromophores of high yield pulps can be clearly identified.

Various analytical degradation techniques, like pyrolysis GC-MS [10], permanganate oxidation [11] and thioacidolysis [12] have previously been used in studies of lignin photo-yellowing in order to identify chemical changes. The formation of vanillin and vanillic acid, the cleavage of β-O-4 structures and

demethylation reactions were commonly observed as reaction products or reaction types. In addition to these degradative reactions, photo-induced condensation was also found to take place [11] and this reaction may be of importance in the photo-yellowing processes [3]. In all these analytical degradation studies, important information on lignin inter-aromatic linkages has, however, been lost since the side-chain structures of the products after degradation have been drastically changed.

Mild hydrolysis is the only known technique for obtaining low molecular weight lignols bearing intact side chains from a polymeric lignin [13-17]. The liberation of 20% of the lignin from spruce wood and 40% of the lignin from beech wood was achieved by percolation of finely ground wood meal with water at 100 °C for several weeks [17]. The removal of 75% of the lignin was reported by treatment of oak wood 250 successive times with water for 4 hr. at 100 °C [18]. After such treatment, the aqueous solution contains carbohydrates and polymeric lignin compounds, and also low molecular weight lignin products. The isolation and characterization of these low molecular weight lignin products can provide valuable information about lignin side chains and inter-aromatic linkages, which may play important roles in the photo-yellowing of high yield pulps.

In the present work, spruce wood as well as commercial unbleached and bleached high yield pulps were subjected to mild hydrolysis to release low molecular weight lignin end-groups. HPLC techniques combined with GC-MS and 2D-NMR permitted the isolation and unambiguous characterization of the major monomeric, dimeric and trimeric products. Subsequently, these lignols were impregnated on filter paper sheets and irradiated with simulated sunlight to evaluate the effects of different lignin structure units on photo-discolouration in the solid state. The behaviour of leucochromophoric groups present in native spruce wood lignin as well as of those formed in the residual pulp lignin after refining and hydrogen peroxide bleaching is discussed.

RESULTS AND DISCUSSION

Isolation and Analysis

Commercial bleached and unbleached groundwood (GW) and chemithermo-mechanical (CTMP) pulp samples of Swedish origin were selected for investigation with spruce wood shavings as a reference. All the samples were exhaustively extracted with acetone to eliminate the extractives. Subsequently they were subjected to mild hydrolysis by refluxing the sample with water for 19 hours at a pH value of 4.0.

Mild hydrolysis has previously been used successfully [13-17] to degrade lignin into its dimeric and oligomeric cleavage products bearing intact side chains. In the present work, it was found that buffering of the aqueous solution at a pH of 4 accelerates the release of lignols with no danger of changing the side chain structures. No positive effects were obtained, however, by increasing the treatment temperature. The yield of low molecular weight lignols was not increased by increasing the treatment temperature to 140 °C, probably because of condensation reactions [19]. On the other hand, the yield of some of the identified structures (such as the detached side-chain structures, see below) decreased due to hydrolytic degradation reactions.

About 2% of the lignin was liberated as low molecular weight products by refluxing either spruce wood, GW or CTMP in water at a pH of 4 for 19 hrs. These low molecular weight lignin hydrolysis products were probably originally present in the wood or pulp lignin as end units, since they were liberated at a very early stage of delignification. Figure 1 shows the analytical HPLC profiles of monomeric and dimeric lignols liberated from spruce wood. Semi-preparative HPLC separations were also conducted in order to produce the major lignols on a miligram scale, thus enabling the 2D NMR analyses.

Structural assignments of the major low molecular weight lignols were mainly based on NMR analysis. In addition to ^{1}H and ^{13}C spectra, modern NMR

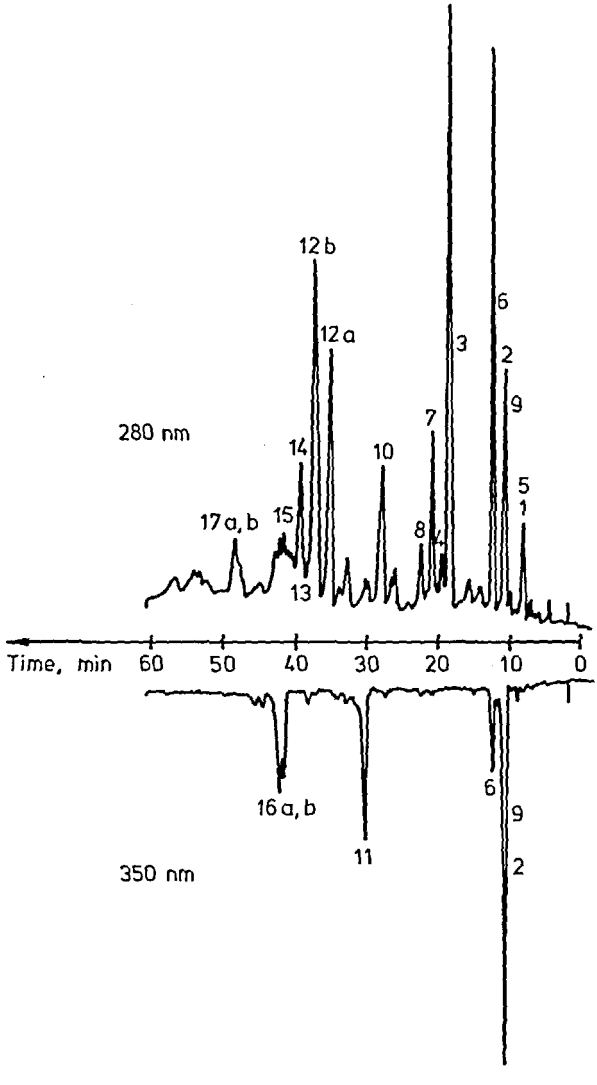

FIGURE 1. HPLC analysis of monomeric and dimeric lignin hydrolytic products from spruce wood (detector response at 280 nm, positive curve, and at 350 nm, negative curve).

techniques including DEPT, H-H COSY, TOCSY(HOHAHA), short range and long range C-H chemical shift correlation experiments were employed when necessary. DEPT provides information for distinguishing between methyl, methylene, methine and quaternary carbon atoms in ^{13}C spectra. H-H COSY gives H-H connections within three bonds. TOCSY shows consecutive H-H correlation on the same carbon chain. Direct C-H linkages can be established by short range C-H chemical shift correlation experiments, whereas information on C-H connections within three bonds is provided by long range C-H chemical shift correlation experiments. Unambiguous structural characterization of the major monomeric, dimeric and trimeric lignin products was acheived by using these NMR techniques. GC-MS analyses provided further structural confirmation with molecular weights and reasonable fragmentation patterns. The structures of the major low molecular weight lignin-related products liberated from spruce wood, GW and CTMP after hydrolysis are shown in Figure 2. Detailed 2D NMR analysis of the low molecular weight lignols will be addressed in a forthcoming paper.

Quantitative information concerning these products can be estimated from their peak heights in the HPLC chromatograms. (Table 1). Dual channel UV detection was used during HPLC analysis, with one channel set at 280 nm to detect all the lignin-related products. The other channel was set at a wavelength of 350 nm to monitor the possible leucochromophoric structures present, since it has been shown in a recent study that irradiation with monochromatic UV light at 350 nm results in the discoloration of unbleached and peroxide bleached spruce CMP [20].

Structures in Wood Lignin

Compounds derived from coniferyl alcohol (**3, 7, 14** and **17**) and coniferaldehyde (**2, 6, 11** and **16**) were isolated as the major products,

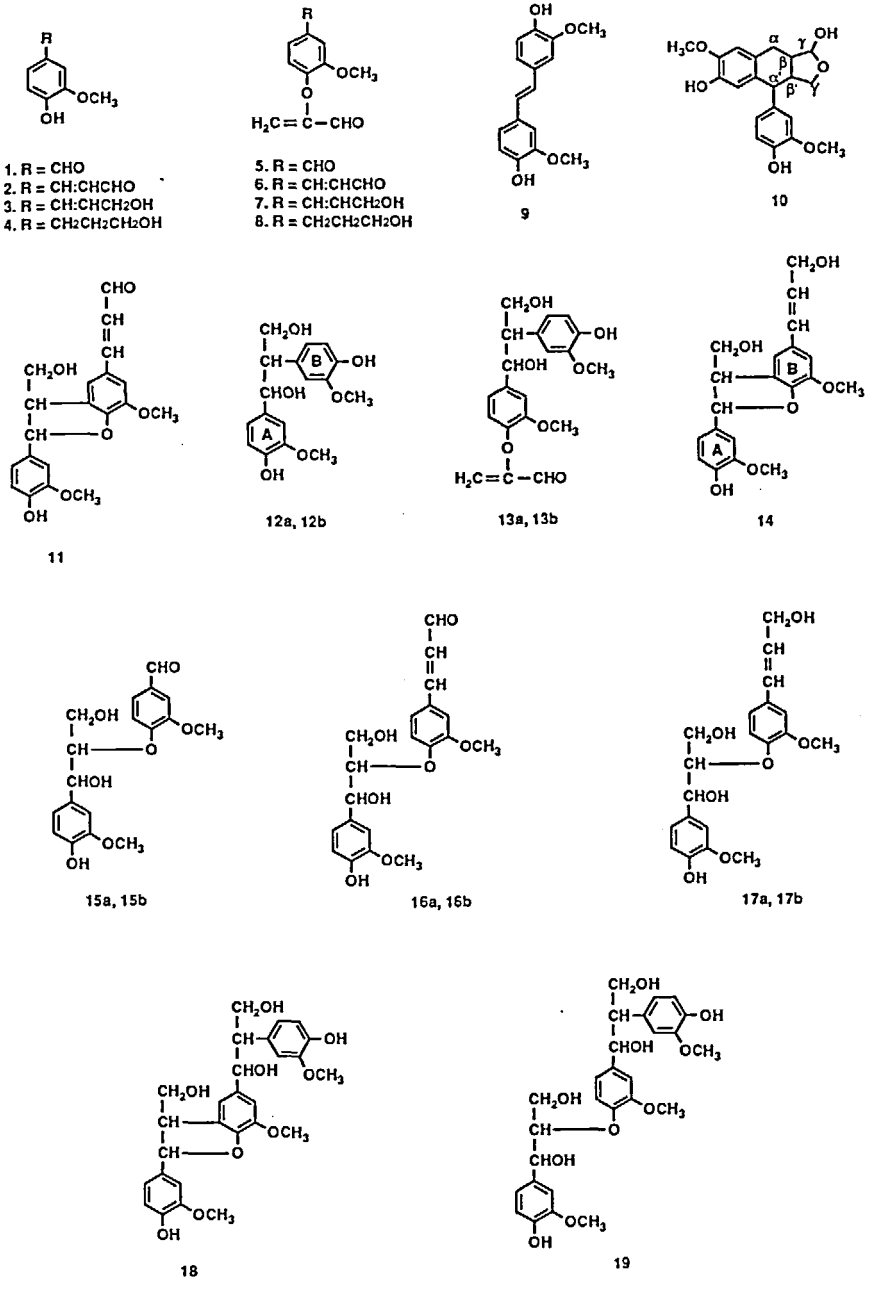

FIGURE 2. Major low molecular lignin products isolated and identified after mild acid hydrolysis of spruce wood and various high yield pulps.

Table 1 Relative yields of the major low molecular weight lignin hydrolysis products from different samples (peak heights).

Sample	Compounds									
	Monitored at 350 nm					Monitored at 280 nm				
	2	**6**	**9**	**11**	**16**	**3**	**7**	**12**	**14**	**17**
Wood	70	19	18	35	43	140	37	118	30	13
GW [1)]	74	13	63	25	19	118	28	86	29	6
BGW [1)]	39	3	129	tr	tr	124	22	66	30	5
CTMP [1)]	42	5	71	9	18	63	31	84	19	8
BCTMP[1)]	23	tr	175	tr	tr	110	13	10	31	8

1) GW = Stone groundwood

BGW = Bleached stone groundwood

CTMP = Chemithermomechanical pulp

BCTMP = Bleached chemithermomechanical pulp

demonstrating the roles of these two structures as predominant spruce lignin end-groups. They are linked to the lignin polymer through their phenolic oxygen atoms (**6, 7, 16** and **17**) or aromatic 5-carbon atoms (**11** and **14**). As can be seen in Figure 1, compounds derived from coniferaldehyde (**2, 6, 11** and **16**) are the only structures with a strong UV-absorption at 350 nm. Apart from coniferaldehyde, a significant UV absorption by coniferyl alcohol structures can be observed when the HPLC separation is monitored at 315 nm. Compared with these two major ring conjugated structures, UV absorption at wavelengths above 315 nm by other types of structures is negligible.

Structures with a detached side chain (**5, 6, 7, 8** and **13**) constitute another type of major lignin end-group and it should be noted that the relative yields of compounds **5, 6** and **8** were higher than those of the correspondent monomers (**1, 2** and **4**, Table 1). The linkage between the detached side-chain structures and the lignin polymer is not known but it is assumed to be of the acetal or γ-ether type[21]. The behaviour of these types of structure during the chemical pretreatment of wood with sulfite, simulating CTMP production, has been studied earlier [21, 22].

Diarylpropane (β-1) structures (**12, 13, 18** and **19**) were present in the hydrolysis mixture from spruce wood as predominant dimeric and trimeric constituents. It has been shown previously [23] that most of the end-groups of the β-1 type carry free phenolic hydroxyl groups on ring A while the ring B phenolic oxygen participates in linkages which are stable towards mild alkali but sensitive to acid. During the mechanochemical conversion of β-1 structures to stilbenes, free phenolic hydroxyl groups on ring A have been proven to play a key role[6].

Structures of the β-O-4 type (**15, 16, 17** and **19**) and of the β-5 type (**11, 14** and **18**) were also isolated as major constituents. All the isolated β-1 and β-O-4 structures were found to consist of similar amounts of threo and erythro isomers, whereas β-5 structures were obtained in only one configuration. Compounds

containing the β-β linkage as in (**10**) seem to be less abundant and biphenyl (5-5) structures were not detected at all. Compound **10** was isolated as colourless crystals and was found to be identical to todolactol B [24]. The latter compound has been isolated before from a Brauns' lignin preparation of the Japanese spruce wood todomatsu and is considered to be a component of a polymeric lignan fraction because of its optical activity. In Norwegian spruce, however, this structure is assumed to be chemically linked to the wood polymer since it has survived the exhaustive acetone extraction.

A very small amount of diguaiacyl stilbene (**9**) was also found to be released from spruce wood. This compound has a strong absorption of UV light at 350 nm, but it can not be considered to be a main leucochromophore in native spruce wood because of its low natural abundance (Table 1). Diguaiacyl stilbene is eluted together with coniferaldehyde (**2**) under a common peak (Figure 1) from an adsoption HPLC column. To determine the respective yields of stilbene and coniferaldehyde (Table 1), the eluent corresponding to this peak was therefore collected and separated again on a reversed phase column.

Structures in Unbleached and Bleached GW and CTMP

Commercial unbleached and bleached spruce GW and CTMP samples were treated under mild acidic conditions as described above. Chemical changes taking place in the fiber lignin during the defibration and bleaching processes were reflected in the low molecular weight lignin products which were formed. The yields of the major lignols from the different samples are summarized in Table 1. The changes of important leucochromophoric structures are shown in Figure 3.

Much less coniferaldehyde was liberated from unbleached CTMP than from spruce wood (Table 1), indicating that the commercial CTMP process, i.e. sodium sulfite impregnation of the wood chips followed by refining, was quite effective in reducing the content of coniferaldehyde end-groups in the lignin. This observation

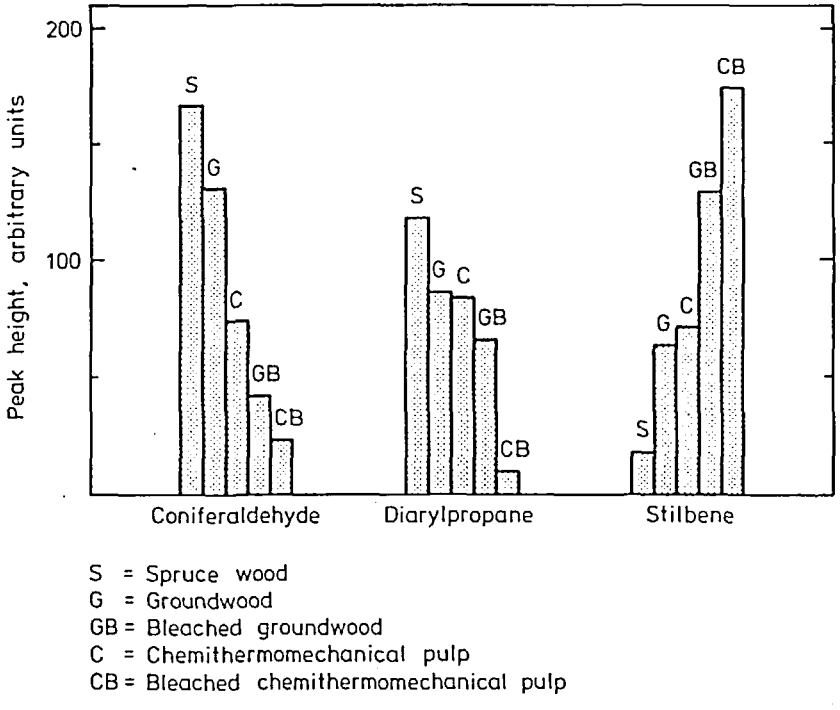

FIGURE 3. Formations of major leucochromophoric structures after mild acid hydrolysis of spruce wood and various high-yield pulps.

is in agreement with previous results from us [21, 22] and others [25] showing that coniferaldehyde structures are sulfonated very quickly. Unbleached GW, on the other hand, still contains significant amounts of coniferaldehyde structures. After bleaching with hydrogen peroxide, the content of coniferaldehyde groups in the pulps decreased to lower levels, as shown in Table 1 and Figure 3. Coniferaldehyde structures are not, however, completely eliminated after hydrogen peroxide bleaching of high yield pulps; a result which is somewhat surprising in view of the high reactivity of such structures to oxidation with hydrogen peroxide [26].

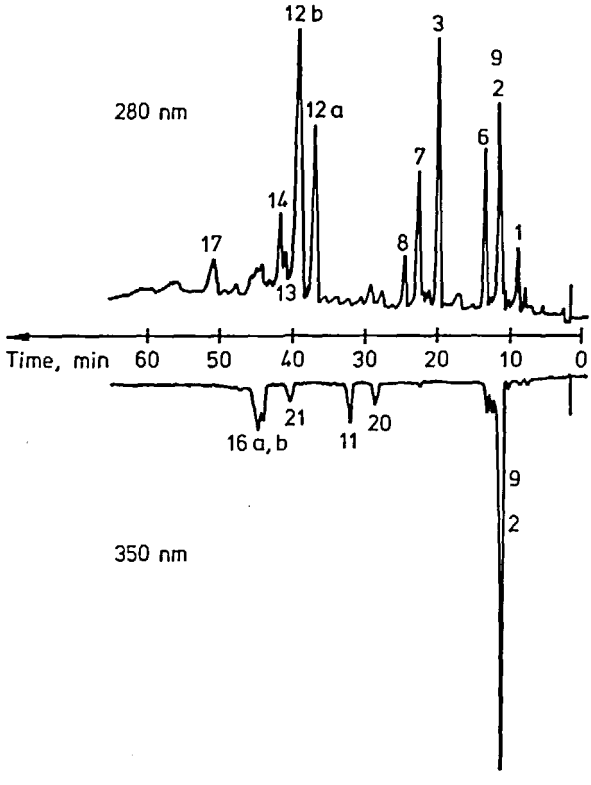

FIGURE 4. HPLC analysis of monomeric and dimeric lignin hydrolytic products from CTMP.

The conversion of β-1 structures (**12**) to stilbenes (**9**) was found to be one of the major chemical changes taking place in the pulp lignin during high yield pulping and bleaching processes. It was also found that both the unbleached GW and the CTMP samples had a higher content of stilbenes and less β-1 structures than the spruce wood, indicating that a small part of the β-1 structures can be converted into stilbenes during wood grinding or refining, in accordance with a recent model compound study [6]. However, the most intensive conversion of β-1

structures to stilbenes was found to take place during bleaching with hydrogen peroxide. The bleaching conditions seem to influence the formation of stilbenes and, as shown in Figure 3, more β-1 structures were converted into stilbenes in bleached CTMP than in bleached GW. Such a conversion has been observed previously in a model compound study and the pH was found to play a key role [7].

Small amounts of new chromophores were formed in the lignins of CTMP and GW (Figure 4, peak **20** and **21**). Although the structures of these new chromophores have not yet been characterized, their optical properties, i.e. a strong absorption of UV light at 350 nm, and their chromatographic behaviour suggest that they may be derived from the stilbene or phenylcoumarone type of compounds produced from β-5 structures (e.g. **11** or **14**) by mechanochemical reactions as described in a recent report [4]. After bleaching with hydrogen peroxide, the content of these new chromophores was reduced to trace amounts, as shown in Figure 5. The contribution of phenylcoumaran structures to the formation of leucochromophores in hydrogen peroxide bleached high yield pulps does not, therefore, seem to be important. In fact, the β-5 structure (**14**) was found to be one of the most stable structures present and it survived in the residual pulp lignin as a major dimeric structure after CTMP pulping and hydrogen peroxide bleaching (Figure 5).

Coniferyl alcohol end groups (**3, 7, 14, 17**) seem to be rather resistent towards all kinds of high yield pulping and bleaching treatments. In bleached GW and bleached CTMP, coniferyl alcohol end-groups were still present to a major extent (Table 1 and Figure 5).

It is not clearly known whether the detached side-chain structures in native spruce wood lignin are present as propenal, as is shown in Figure 2 (compounds **5, 6, 7, 8** and **13**), or as glyceraldehyde structures. Compounds containing detached side chains were exclusively isolated as propenal structures in this work. It was also found that these structures were somewhat reduced during pulping and bleaching (Table 1). If the detached side-chain units are originally present as

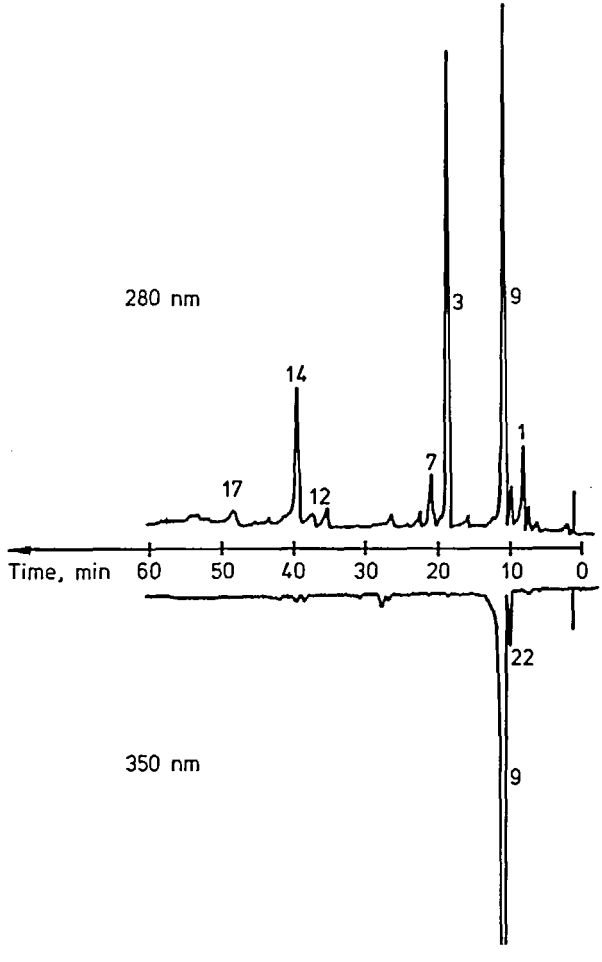

FIGURE 5. HPLC analysis of monomeric and dimeric lignin hydrolytic products from CTMP bleached with hydrogen peroxide.

glyceraldehyde structures in spruce wood lignin, they are obviously very unstable and are quickly converted into propenal type structures when heated in water under mild acidic conditions. In such a case it can be assumed that the detached side-chain end-groups are mainly present as propenal structures in the residual

lignin of mechanical pulps, such as TMP, a process carried out under mild acidic conditions.

Apart from diguaiacyl stilbene (9), an unknown leucochromophoric structure (Figure 5, 22) was also formed in the pulp lignin during hydrogen peroxide bleaching. The characterization of this structure is under investigation.

Contribution of Isolated Lignin Structures to Photoyellowing

Extracts of low molecular weight lignin compounds obtained after hydrolysis of spruce wood (S), unbleached GW (GW), unbleached CTMP (CTMP), bleached GW (GWB) and bleached CTMP (CTMPB) were impregnated onto filter paper sheets. The loss in brightness of the paper sheets after 30 min. of simulated sunlight irradiation is shown in Figure 6. The strongest discoloration (over 8 ISO-units) was obtained with the filter paper sheet impregnated with the CTMPB extract.

The most sensitive extract (CTMPB) was then fractionated into three fractions by preparative HPLC (Figure 7). Fraction 1 (F 1) contained mainly the stilbene (9) and monomeric products, compound 17 and other dimeric products were the major components of fraction 2 (F 2), and fraction 3 (F 3) included compounds 18 and 19 together with other trimeric lignols. After irradiation, fraction 1 exhibited the greatest yellowing on filter paper sheets, as shown in Figure 8. The components present in fraction 1 were further divided into nine subfractions by HPLC, as shown in Figure 7 (fractions a - i). Among these the subfraction e, consisting mainly of diguaiacyl stilbene (9), showed the strongest discoloration on the paper sheet (Figure 9), whereas other monomeric components yielded lower brightness reversion values.

These observations demonstrate that diguaiacyl stilbenes, formed mainly from diarylpropane (β-1) structures during peroxide bleaching, seem to be the major leucochromophoric structure responsible for the light-induced yellowing of

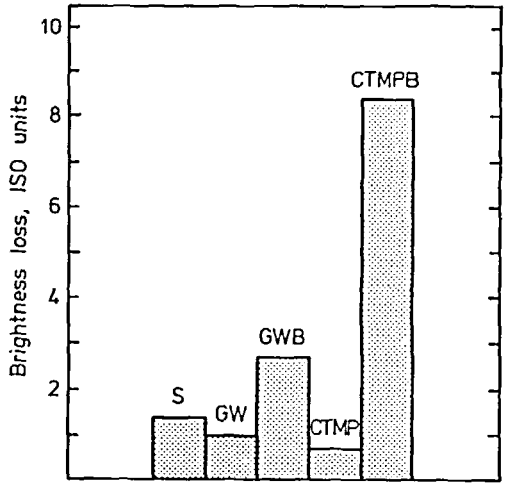

FIGURE 6. Yellowing of filter paper sheets impregnated with extracts from spruce wood (S), GW (GW), peroxide bleached GW (GWB), CTMP (CTMP) and peroxide bleached CTMP (CTMPB).

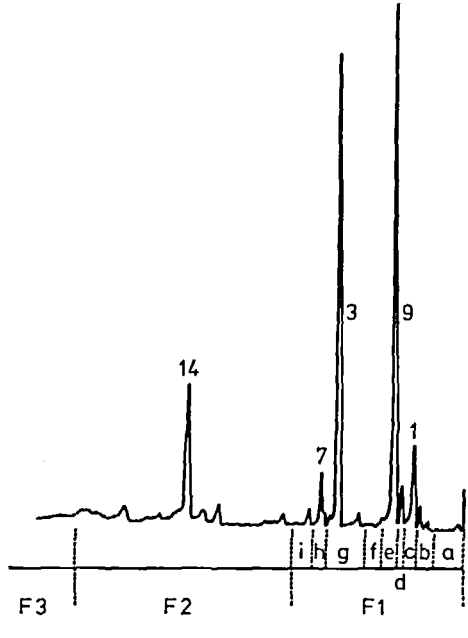

FIGURE 7. Fractionation of the low molecular weight lignin extract after hydrolysis of bleached CTMP.

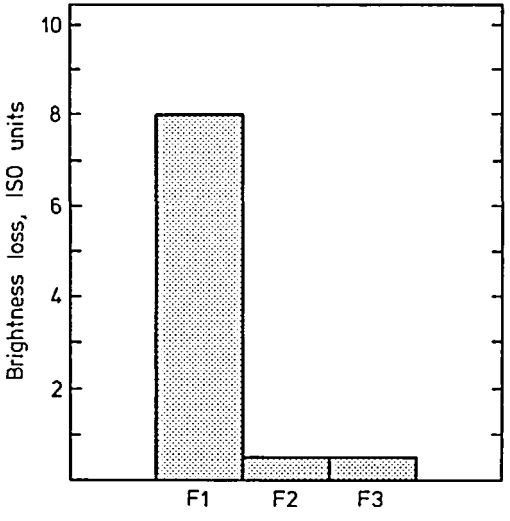

FIGURE 8. Effect of **F 1**, **F 2** and **F 3** (see Figure 7) on the photodiscoloration of filter paper sheets.

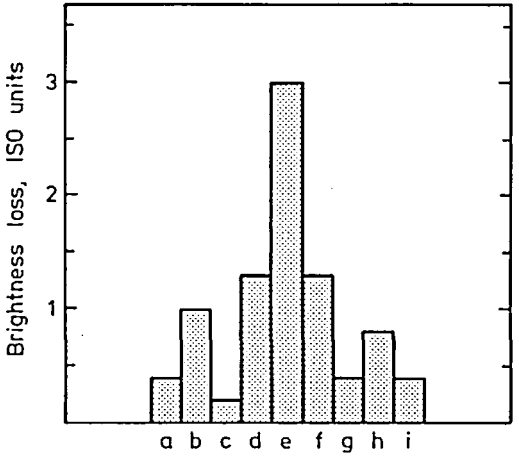

FIGURE 9. Effect of individual subfractions from **F 1** on the photodiscoloration of impregnated filter paper sheets.

peroxide bleached high yield pulps. However, a comparison of the brightness loss values obtained from the various extracts (Figure 6) reveals that other leucochromophores must also be contributing since the wood extract (S) exhibited a higher loss in brightness than either GW or CTMP despite a much lower content of stilbenes. These differences will be addressed in forthcoming papers.

CONCLUSIONS

Mild hydrolytic treatment of spruce wood and high yield pulps produced low molecular weight lignin derived compounds bearing intact side-chains, thus providing valuable information about the chemical changes taking place in the lignin during pulping and bleaching processes.

Coniferaldehyde end-groups seem to be the major original leucochromophoric structures present in spruce wood, having a strong absorption of UV radiation at wavelengths around 350 nm. Most of the coniferaldehyde end-groups are eliminated from the pulps during bleaching with hydrogen peroxide. Diarylpropane structures are present in spruce wood lignin as major dimeric end groups. They are reactive towards both mechanical and peroxide bleaching treatments. Diguaiacylstilbenes, mostly produced from diarylpropane structures during peroxide bleaching, are the predominant leucochromophores present in the lignin of peroxide bleached high yield pulps, and such structures seem to be responsible for a major portion of the fast photo-yellowing of these pulps. Phenylcoumaran structures, on the other hand, are stable towards both mechanical and peroxide bleaching treatments and they do not seem to contribute to the formation of leucochromophores in high yield pulps. Coniferyl alcohol end groups are also very stable during high-yield pulping and bleaching processes, and such structures remain to a large extent in the residual pulp lignin.

EXPERIMENTAL

Materials

All pulp samples were commercial pulps made from Norwegian spruce. Diguaiacyl stilbene (9) was a synthetic compound provided by N-O. Nilvebrant [27]. Distilled solvents were used for all working up procedures and HPLC separations. Other chemicals used were of analytical grade.

Hydrolysis and Working-up Procedure

An extractive-free wood or pulp sample (2.0 g) was treated with 100 ml deionized water at refluxing temperature for 19 hours in a 250-ml round-bottomed flask equipped with a cooling condenser. The aqueous solution was buffered with 0.2% sodium acetate and drops of diluted sulfuric acid to provide an initial pH of 4. After hydrolysis, the aqueous phase was filtered and extracted with ethyl acetate (3 × 100 ml). The extract was dried over anhydrous sodium sulfate, filtered and evaporated to a volumn of less than 1 ml. The concentrated solution was put on 0.4 ml of silica gel (silica gel 60, 70 - 230 mesh, Merck) placed in a small pipette. Monomeric and dimeric lignin hydrolysis products were obtained by eluting the pipet with 5 ml of ethyl acetate. Subsequently, this solution was evaporated and adjusted to a volumn of 1.0 ml and immediately analysed by HPLC. Trimeric lignin hydrolysis products were then eluted from the pipet by a mobile phase containing 5% methanol in ethyl acetate.

A larger scale hydrolysis with 500 grams of spruce wood shavings was carried out for preparative purposes in order to obtain enough material for NMR analysis. The working up procedure in this case included evaporation of the resulting aqueous phase at 40 °C under reduced pressure before ethyl acetate extraction.

The work-up procedure was similar to that described above. Acetylation of isolated products was carried out as mentioned before [21].

Analytical Procedures

HPLC analyses and separations were performed on a Beckman system with the UV detection wavelength set at 280 nm and 350 nm. A NUCLEOSIL 50-5 (5μ, 4.6 × 250mm) column was used in the analytical analyses and a POLYGOSIL 60-5 (5μ, 10×250mm) column was used for preparative separations; mobile phase: petroleum ether (40-60°C) / ethyl acetate, linear gradient between 10 and 100% of ethyl acetate. The flow rate was 1.5 ml/min for the analytical column and 3 - 4 ml/min for the preparative column. Reversed-phase HPLC analyses for separation and quantification of coniferaldehyde and diguaiacyl stilbene were performed on a Waters system using a NUCLEOSIL C_{18} column (5μ, 4.6 × 150 mm). The mobile phase consisted of water and acetonitrile, with a linear gradient from 30% to 100% of acetonitrile during 30 min and a flow rate of 1 ml/min. The UV detector was set at a wavelength of 350 nm. Coniferaldehyde had a retention time of about 6.4 min whereas stilbene was eluted at about 14.6 min.

GC-MS analyses were run on a Finnigan 4000 mass spectrometer interfaced with a Finnigan 9610 gas chromatograph. MS spectra of trimeric lignols were obtained by the solid inlet technique. ^1H NMR spectra were collected on a Bruker AC250 instrument. Two-D (H-H COSY, TOCSY, short range C-H chemical shift correlation experiment and long range C-H chemical shift correlation experiment) and ^{13}C NMR (including DEPT135 and DEPT90) spectra were recordeded on Bruker AMX360 and AM400 instruments.

Impregnation and Irradiation of Filter Paper

Low molecular weight lignin hydrolysis products (5 mg) were dissolved in ethyl acetate, impregnated onto filter paper sheets (5.5 cm, 200 mg) and air dried. Fractions **F 1 - F 3** and subfractions **a - i** (see text) were obtained from 5 mg of **CTMPB. F 3** was dissolved in methanol while the others were dissolved in ethyl acetate and impregnated onto filter paper sheets of the same type as above. Irradiation was carried out for 30 min. in the same way as described before[28].

Compound Identification

Analytical data of monomeric products and diarylpropane (β-1) structures (**1 - 8, 12, 13, 18, 19**) have been published elsewhere [21, 23]. Diguaiacyl stilbene (9) was identified by comparing its HPLC and GC retention times and MS spectrum with a synthetic sample[27].

Diguaiacyl stilbene (**9**)

MS m/e: 272 (M^+, 100%).

Diguaiacyl stilbene diacetate (**9** - diacetate)

MS m/e: 356 (M^+, 20%), 314 (25%), 272 (100%).

Tetrahydro-7-methoxy-6,α^2-dihydroxy-4-(4-hydroxy-3-methoxyphenyl)-2,3-pentacyclo [3,0]-naphtalene (**10**)

^{13}C NMR (400 MHz, acetone-d6) δ: 32.15 (Cα, another signal of epimers hide under solvent signal), 46.51 (Cβ'), 47.20(Cβ), 50.15 and 51.35 (Cα'), 56.23 and

56.31 (OMe), 71,15 and 72.32 (Cγ), 99.00 and 104.20 (Cγ), 112.55, 113.06, 115.80, 116.40, 116.50, 122.00, 128.17, 128.60, 133.80, 137.00, 137.50, 145.38, 146.10, 146.91 and 148.50 (ArC). ^{1}H NMR (300 MHz, acetone-d6) δ: 1.96 (1H, m, Hβ), 2.28 and 2.55 (1H, m each, Hβ'), 2.83(1H, m, HαA), 3.0 (1H, m, HαB), 3.47 (1H, m, HγA),3.64 (1H, m, Hα'), 3.77 (1H, m, HγB), 3.78 and 3.79 (3H, s each, OMe), 3.81 (3H, s, OMe), 5.19 and 5.40 (1H, Hγ), 6.22 (1H, s ArH), 6.61-6.80 (4H, m, ArH), 7.31, 7.35, 7.58 and 8.02 (s, ArOH). MS (**10** - triacetate) m/e: 484 (M$^+$, 6%), 442 (6%), 424 (11%), 382 (100%), 340 (58%), 309 (11%), 293 (19%), 279 (15%), 216 (21%), 187 (11%), 137(25%).

Aldehyde corresponding to dehydroconiferyl alcohol diacetate (**11** - diacetate)

^{1}H NMR (250 MHz, CDCl3) δ: 2.08 (3H, s, OAc), 2.3 (3H, s, OAc), 3.80 (1H, m, Hβ), 3.82 (3H, s, OMe), 3.95 (3H, s, OMe), 4.40 (2H, m, Hγ), 5.60 (1H, d, J = 7.0, Hα), 6.60 (1H, dd, Jα',β' = 15.4, Jβ',γ = 7.4, H β'), 6.95 - 7.10 (5H, m, ArH), 7.4 (1H, d, J = 15.4, H α'), 9.66 (1H, d, J = 7.4, CHO). MS m/e: 440 (M$^+$, 30%), 380 (11%), 338 (100%), 323 (30%), 306 (18%), 195 (12%), 186 (11%), 177 (10%), 165 (11%), 153 (12%), 137 (12%).

Dehydroconiferyl alcohol triacetate (**14** - triacetate)

^{1}H NMR (250 MHz, CDCl3) δ: 2.06 (3H, s, OAc), 2.10 (3H, s, OAc), 2.31 (3H, s, ArOAc), 3.78 (1H, m, Hβ), 3.81 (3H, s, OMe), 3.92 (3H, s, OMe), 4.30 (1H, dd, JγA,γB = 11.2, Jβ,γA = 7.6, HγA), 4.45 (1H, dd, JγA,γB = 11.2, Jβ,γB = 5.3, HγB), 4.71 (2H, dd, Jβ',γ = 6.5, Jα',γ = 0.73, Hγ), 5.54 (1H, d, J = 6.8, Hα), 6.16 (1H, m, Hβ'), 6.60 (1H, d, Jα',β' = 15.8, Hα'), 6.88 - 7.03 (5H, m, ArH). MS m/e: 484 (M$^+$, 85%), 424 (47%), 382 (100%), 322 (47%), 291 (47%), 162 (35%), 137 (37%).

Guaiacylglycerol-β-vanillyl ether triacetate *erythro* (**15 a** - triacetate)

^{1}H NMR (250 MHz, CDCl3) δ: 2.00 (3H, s, OAc), 2.09 (3H, s, OAC), 2.30

(3H, s, ArOAc), 3.81 (3H, s, OMe), 3.86 (3H, s, OMe), 4.25 (1H, dd, $J_{\gamma A,\gamma B}$ = 11.3, $J_{\beta,\gamma A}$ = 4.9, $H_{\gamma A}$), 4.45 (1H, dd, $J_{\gamma A,\gamma B}$ = 11.3, $J_{\beta,\gamma B}$ = 6.0, $H_{\gamma B}$), 4.88 (1H, m, Hβ), 6.07 (1H, d, J = 5.3, Hα), 6.95 - 7.10 (6H, m, ArH), 9.85 (1H, s, CHO). MS m/e: 474 (M^+, 8%), 432 (11%), 323 (32%), 280 (10%), 237 (32%), 221 (48%), 195 (91%), 179 (65%), 178 (65%), 153 (100%), 151 (31%).

Guaiacylglycerol-β-vanillyl ether triacetate *threo* (**15 b** - triacetate)

^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.98 (3H, s, OAc), 2.06 (3H, s, OAC), 2.32 (3H, s, ArOAc), 3.86 (6H, 2 × s, OMe), 4.13 (1H, dd, $J_{\gamma A,\gamma B}$ = 11.4, $J_{\beta,\gamma A}$ = 6.8, $H_{\gamma A}$), 4.32 (1H, dd, $J_{\gamma A,\gamma B}$ = 11.4, $J_{\beta,\gamma B}$ = 4.5, $H_{\gamma B}$), 4.82 (1H, m, Hβ), 6.11 (1H, d, J = 6.3, Hα), 6.90 - 7.05 (6H, m, ArH), 9.87 (1H, s, CHO). MS m/e: 474 (M^+, 12%), 432 (30%), 323 (20%), 280 (8%), 237 (50%), 221 (25%), 195 (92%), 179 (74%), 178 (60%), 153 (100%), 151 (35%).

Guaiacylglycerol-β-coniferaldehyde ether triacetate *erythro* (**16 a** - triacetate)

^{1}H NMR (250 MHz, $CDCl_3$) δ: 2.04 (3H, s, OAc), 2.09 (3H, s, OAC), 2.31 (3H, s, ArOAc), 3.82 (3H, s, OMe), 3.83 (3H, s, OMe), 4.26 (1H, dd, $J_{\gamma A,\gamma B}$ = 12.0, $J_{\beta,\gamma A}$ = 4.3, $H_{\gamma A}$), 4.45 (1H, dd, $J_{\gamma A,\gamma B}$ = 12.0, $J_{\beta,\gamma B}$ = 5.8, $H_{\gamma B}$), 4.78 (1H, m, Hβ), 6.06 (1H, d, J = 5.5, Hα), 6.61 (1H, dd, $J_{\alpha',\beta'}$ = 15.8, $J_{\beta',\gamma}$ = 7.7, Hβ'), 6.86 - 7.10 (6H, m, ArH), 7.39 (1H, d, J = 15.8, Hα'), 9.67 (1H, d, J = 7.7, CHO). MS m/e: 500 (M^+, 10%), 323 (50%), 281 (11%), 263 (15%), 221 (80%), 179 (80%), 178 (100%), 161 (18%), 153 (20%), 147 (35%).

Guaiacylglycerol-β-coniferaldehyde ether triacetate *threo* (**16 b** - triacetate)

^{1}H NMR (250 MHz, $CDCl_3$) δ: 2.01 (3H, s, OAc), 2.06 (3H, s, OAC), 2.31 (3H, s, ArOAc), 3.83 (3H, s, OMe), 3.88 (3H, s, OMe), 4.11 (1H, dd, $J_{\gamma A,\gamma B}$ =

12.0, $J_{\beta,\gamma A}$ = 6.1, $H_{\gamma A}$), 4.31 (1H, dd, $J_{\gamma A,\gamma B}$ = 12.0, $J_{\beta,\gamma B}$ = 4.5, $H_{\gamma B}$), 4.74 (1H, m, Hβ), 6.11 (1H, d, J = 6.3, Hα), 6.62 (1H, dd, $J_{\alpha',\beta'}$ = 15.8, $J_{\beta',\gamma}$ = 7.7, Hβ'), 6.99 - 7.13 (6H, m, ArH), 7.40 (1H, d, J = 15.8, Hα'), 9.68 (1H, d, J = 7.7, CHO). MS m/e: 500 (M^+, 19%), 323 (20%), 281 (13%), 263 (20%), 221 (60%), 179 (70%), 178 (100%), 161 (13%), 153 (21%), 147 (25%).

Guaiacylglycerol-β-coniferyl ether triacetate *erythro* (**17 a** - tetraacetate)

^{1}H NMR (250 MHz, $CDCl_3$) δ: 2.03 (3H, s, OAc), 2.10 (6H, 2 × s, OAC), 2.31 (3H, s, ArOAc), 3.80 (3H, s, OMe), 3.82 (3H, s, OMe), 4.24 (1H, dd, $J_{\gamma A,\gamma B}$ = 11.9, $J_{\beta,\gamma A}$ = 3.9, $H_{\gamma A}$), 4.45 (1H, dd, $J_{\gamma A,\gamma B}$ = 11.9, $J_{\beta,\gamma B}$ = 5.8, $H_{\gamma B}$), 4.66 (1H, m, Hβ), 4.71 (2H, d, J = 6.3, Hγ), 6.06 (1H, d, J = 5.3, Hα), 6.18 (1H, m, Hβ'), 6.57 (1H, d, J = 15.9, Hα'), 6.76 - 7.06 (6H, m, ArH).

Guaiacylglycerol-β-coniferyl ether triacetate *threo* (**17 b** - tetraacetate)

^{1}H NMR (250 MHz, $CDCl_3$) δ: 2.00 (3H, s, OAc), 2.05 (3H, s, OAc), 2.10 (3H, s, OAC), 2.31 (3H, s, ArOAc), 3.82 (3H, s, OMe), 3.83 (3H, s, OMe), 4.06 (1H, dd, $J_{\gamma A,\gamma B}$ = 11.9, $J_{\beta,\gamma A}$ = 5.8, $H_{\gamma A}$), 4.31 (1H, dd, $J_{\gamma A,\gamma B}$ = 11.9, $J_{\beta,\gamma B}$ = 4.4, $H_{\gamma B}$), 4.62 (1H, m, Hβ), 4.71 (2H, d, J = 6.4, Hγ), 6.11 (1H, d, J = 6.4, Hα), 6.19 (1H, m, Hβ'), 6.59 (1H, d, J = 15.8, Hα'), 6.90 - 7.02 (6H, m, ArH). MS m/e: 544 (M^+, 14%), 323 (21%), 281 (12%), 222 (100%), 221 (65%), 179 (87%), 161 (23%), 147 (25%).

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