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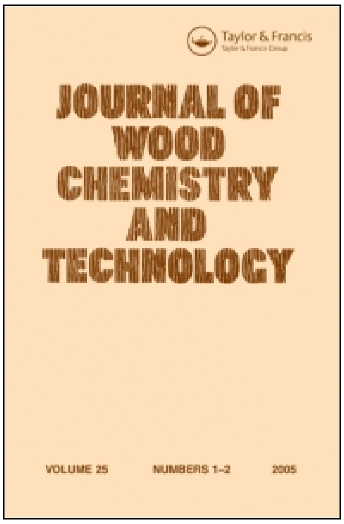

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STUDIES OF THE PHOTODEGRADATION OF SPRUCE LIGNIN BY NMR SPECTROSCOPY

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ABSTRACT

The light-induced degradation of lignin was studied using spruce MWL impregnated on handsheets prepared from cotton linters. The sheets were irradiated with simulated sunlight and the lignin was extracted. Solutions of untreated and irradiated lignin were studied by ^{1}H and ^{13}C NMR spectroscopy. The results showed that α- and β- ether and α–β bond cleavage were the main reactions. The main degradation products were vanillin and vanillic acid. The amount of terminal groups containing aromatic aldehyde and carboxyl groups also increased on irradiation. The existing α- C=O groups were transformed mainly to carboxyl groups. However, the results indicate that new α- C=O groups were generated on irradiation. The methoxyl content decreased and some degradation of aromatic rings took place. However, no formation of quinoid structures was observed. Degradation of phenylcoumaran units was evident. α- Ether cleavage in phenylcoumarans could possibly lead to formation of stilbenes and stilbene derived chromophores.

INTRODUCTION

Light-induced brightness reversion (yellowing) and loss of fiber strength of mechanical pulps limit their use to short-life products.

The yellowing of mechanical pulp has been attributed primarily to chemical changes in lignin. Therefore wood, wood-meal, high-yield pulps, newsprint, isolated lignins and lignin model compounds have been subjected to numerous studies during the last 50 years in order to elucidate the chemical processes behind the light-induced brightness reversion of mechanical pulps.[1] Understanding of the formation and the structures of the coloured products will help to develop methods for the prevention of the photochemical degradation and yellowing of pulp-based materials of high lignin content.

Today it seems obvious that the excitation of aromatic α- carbonyl groups by light is one of the primary stages in the degradation and yellowing process. The excitation of the carbonyl group could then be followed by formation of phenoxy free-radicals which by reaction with ambient oxygen would form coloured products. Several routes for the formation of phenoxy radicals have been suggested. One is based on abstraction of a hydrogen atom from a free phenolic hydroxyl group by the excited carbonyl group. This would result in the formation of a ketyl-phenoxy radical pair.[2] This direct route has been disputed, since it is difficult to visualize interaction between the excited carbonyl groups and phenolic groups in a solid matrix like a paper.[3] It has instead been proposed that hydroxyl radicals may abstract a hydrogen atom from a phenolic hydroxyl group.[3] Hydroxyl radicals may be formed by photolysis of hydrogen peroxide and hydroperoxide intermediates.[4] In fact, hydroxyl radicals are known to be generated on irradiation of sheets of TMP and CTMP.[5] Furthermore, addition of hydrogen peroxide accelerated the yellowing process.[5] A third route to phenoxy radicals would be cleavage of β- aryl ether bonds adjacent to exited carbonyl groups.[6] Phenoxy radical formation as a result of hydrogen abstraction from a phenolic hydroxyl group by singlet oxygen formed by energy transfer from the excited carbonyl group, has been rejected as exposure of lignin-rich paper sheets to singlet oxygen did not cause yellowing.[7] Part of the formed radicals would then undergo bond forming as well as bond breaking reactions besides oxidations. The phenoxy radicals would mainly be oxidized to quinoid chromophores part of which are probably rapidly oxidized further.[8] The mechanisms of the suggested reaction paths are shown in Fig. 1.

Recently, Castellan *et al.*[9], basing their arguments on studies of lignin model dimers lacking an α- carbonyl group, showed that the presence of α- carbonyls is not a prerequisite for the formation of coloured compounds in lignin on irradiation.

Among the methods used for studies of the chemical changes in lignin occuring on irradiation, ^{13}C NMR (Nuclear Magnetic Resonance) spectroscopy has gained increasing attention lately.[10-13] The main advantage of NMR spectroscopy compared with other analytical methods is the large amount of detailed qualitative as well as quantitative structural information obtained. The main disadvantages are the large amounts of sample (often > 100 mg) needed and the

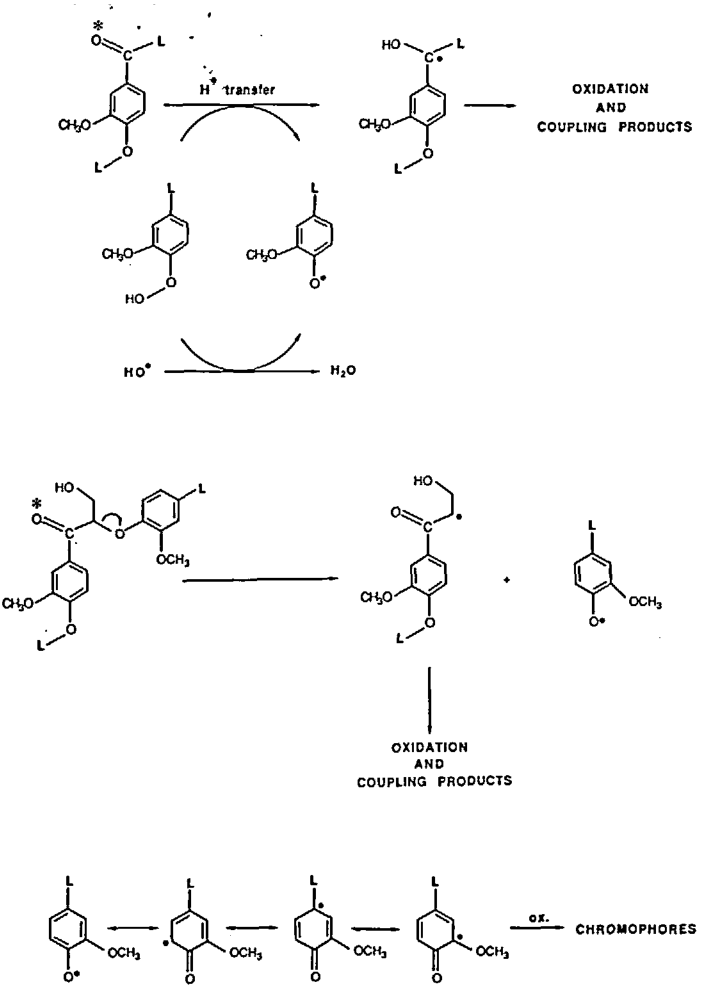

FIGURE 1. *Suggested reaction mechanisms for the initial steps in the photodegradation of lignin.*[2-6,8] The capital L stands for the lignin matrix and the asterisk marks the excited state of the carbonyl group.

necessity of reasonable sample solubility (> 100 mg/2.5 mL) in suitable solvents. NMR studies of chemical changes in the lignin of mechanical pulps on exposure to direct sunlight have been performed on the acetone-water extractable part of the lignin.[10,11] This restricted the studies to the degraded part of the lignin (c. 9 %) and most of the lignin - and probably also the colour - was left in the pulp. Solid state NMR studies have been performed on mechanical pulps exposed to sunlight for various periods[12] However, although some obvious trends in the degradation of the lignin could be seen in the spectra, detailed information was hard to get due to the low resolution of the solid state NMR technique. To our knowledge, no NMR studies on irradiated soluble lignin preparates have been published.

The present paper reports the results of our studies by NMR spectroscopy of light induced structural changes in MWL from Norway spruce (*Picea abies*).

RESULTS AND DISCUSSION

Handsheets were prepared from cotton linters and and their brightness was measured. The brightness was 83 % (ISO). The sheets were impregnated with an acetone-water (85:15 v/v) solution of MWL from spruce. The sheets were dried and their brightness measured. The impregnation lowered the brightness to 52 %. One half of the sheets were extracted with dimethylsulfoxide (DMSO) to give the reference sample (MWL). The resulting pulp was washed with water and new sheets were made and their brightness measured. The brightness rose to the original value, showing that all the coloured lignin had been extracted from the sheets. The rest of the impregnated sheets were irradiated with simulated sunlight for three hours on each side and their brightness values were measured. Irradiation lowered the brightness of the sheets to 46 %. The impregnated and irradiated sheets were extracted with warm (≈50 °C) DMSO under sonication to yield c. 90 % of the lignin in solution (irradiated MWL). The pulp was washed with water, new sheets were prepared and their brightness measured. The brightness was 68 %, which shows that most of the chromophores (c. 80 %) were recovered.

NMR samples were prepared of the "native" lignin (MWL) and the DMSO soluble irradiated lignin (irradiated MWL) and the samples were analyzed by ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectroscopy.

^1H NMR spectra.

The ^1H NMR spectra of MWL and irradiated MWL are shown in Fig. 2. The interpretations of the spectra are based on data presented by Lundquist.[14]

The spectrum of MWL displayed broad and poorly resolved signals, as expected for a macromolecule like lignin. The ^1H NMR spectrum of the irradiated lignin, however, displayed several sharp peaks in the aldehyde proton region (δ=9.7–9.9 ppm) and on the broad signal in the aromatic proton region (δ=6.5–8.0 ppm). The peaks were probably due to monomeric aromatic aldehydes and carboxylic acids resulting from the light-induced degradation of the lignin. Vanillin and vanillic acid were identified as the main monomeric components. The presence of acids, other than vanillic, is also probable. Vanillin and vanillic acid have been found to be the main low-molecular degradation products formed on irradiation of lignin-rich paper.[15] Besides the aldehyde signal of vanillin, at least three other aldehyde signals could be observed in the region δ=9.7–9.9 ppm of the spectrum of the irradiated sample. The signals all appear to be singlets, which excludes cinnamaldehyde type groups, and are probably due to different benzaldehyde type units and/or monomers.

By integration of the signal areas it was found that irradiation resulted in a relative intensity increase, within the aromatic part of the spectrum, of the signals at δ=7.4–8.5 ppm. In this region mainly H-2 and H-6 in aromatic rings with an α- carbonyl group as well as H-α in cinnamaldhyde-cinnamic acid type units absorb. The largest contribution to this intensity increase then probably comes from the signals of H_2 and H_6 in benzaldehyde and benzoic acid type units besides other α- carbonyl group containing species.

A decrease of the intensities of signals at δ=5.2–5.8 ppm, assigned to H-α in β–5/α–O–4 (phenylcoumaran) units, was observed. The decrease is probably a result of α–O–4 ether cleavage which could be followed by formation of stilbenes. This would also result in an increase of intensities of signals in the aromatic region. However, no definitive proof of the presence of stilbenes could be found in the ^1H NMR spectra.

A decrease of the intensities of the signals of H-α in β–O–4 units at δ=4.5–4.9 ppm was also observed. This indicates that α- CH–OH groups are transformed, probably by oxidation to carbonyl groups. This is supported by the intensity increase of the low-field part of the aromatic signal.

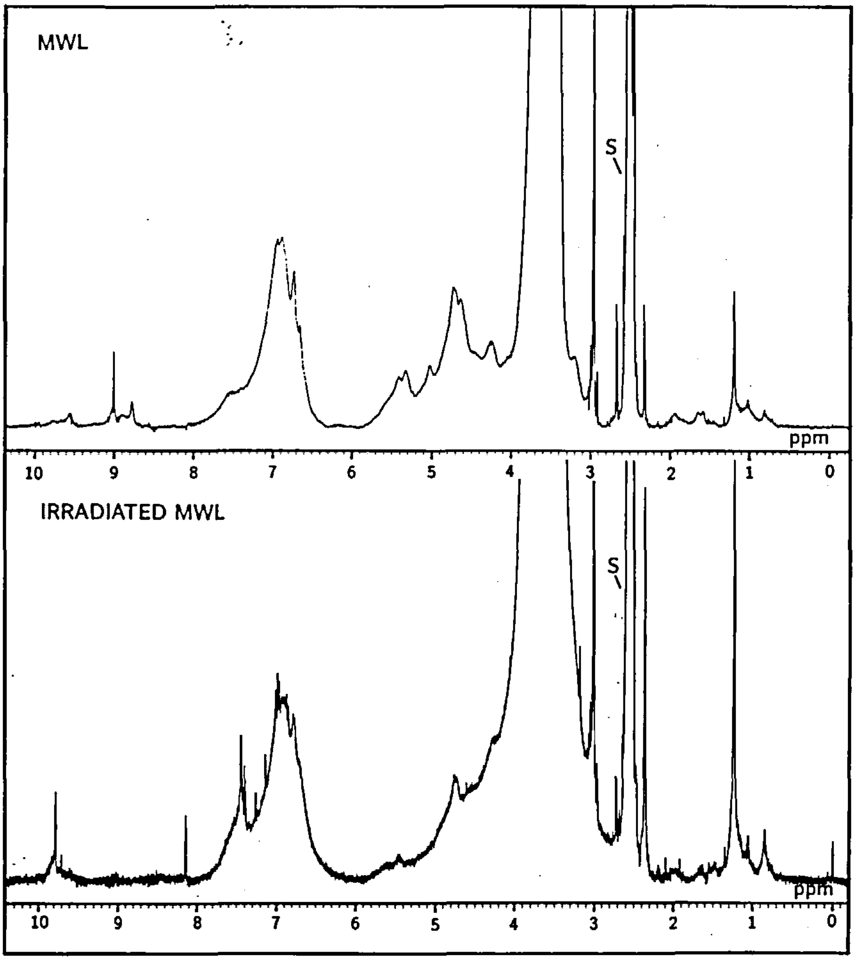

FIGURE 2. ^1H NMR spectra (400 MHz, DMSO-D_6) of MWL, and irradiated MWL. S=solvent signal.

Thus, the yellowing and degradation of MWL, is accompanied by a decrease in the intensity of a part of the aliphatic proton NMR resonances. At the same time new signals appear in the aromatic–olefinic and the aldehyde region. This indicates that probably α–β bond cleavage accompanied by oxidation of the α-carbons to carboxyl groups is a dominating reaction in the light-induced degradation of lignin. Oxidation of α- CH–OH groups to C=O groups and formation of stilbenes *via* α- ether cleavage in phenylcoumaran units, may also be important steps in the light-induced degradation and discolouration of lignin.

^{13}C NMR spectra.

The spectra of the lignin samples are shown in Fig. 3. The spectra were registered in "quantitative" mode according to Robert *et al.*,[16] the signal assignments were based on data in Ref. 17, and the signals were numbered according to Robert *et al.*[17d] The recorded chemical shifts and signal assignments are given in Table 1.

The fact that some signal numbers are missing is due to the absence of some of the signals assigned in ref. 17 d.

The signals were divided, according to their origin, into seven groups, the assignments and chemical shift ranges of which are given in Table 2, together with the normalised (in % of total carbon) integrated intensities of signals within each shift range.

The relative signal intensities in ^{13}C NMR spectra of MWL and irradiated MWL are shown graphically in Fig. 4.

The quantitative character of the ^{13}C NMR spectra is apparent from the fact that calculation gives c. 1 MeO group/aromatic ring for MWL, which is close to the values found in the literature for spruce MWL.[17d,18] The number was calculated assuming that spruce MWL contains 6 conjugated olefinic double bonds per 100 phenylpropane units.[17d] The same way of calculation gives c. 0.2 carbonyl groups and 2.4 C–O units/aromatic ring.

The spectra show that the two samples have structural differences. The largest differences can be found in the amount of carbonyl and especially carboxyl groups. The amount of aldehyde/ketone carbonyls rises from c. 1 % (corresponding to c. 0.1/aromatic ring) in MWL to > 3 % in the irradiated sample. The change in the amount of carboxyl groups is still more dramatic, increasing

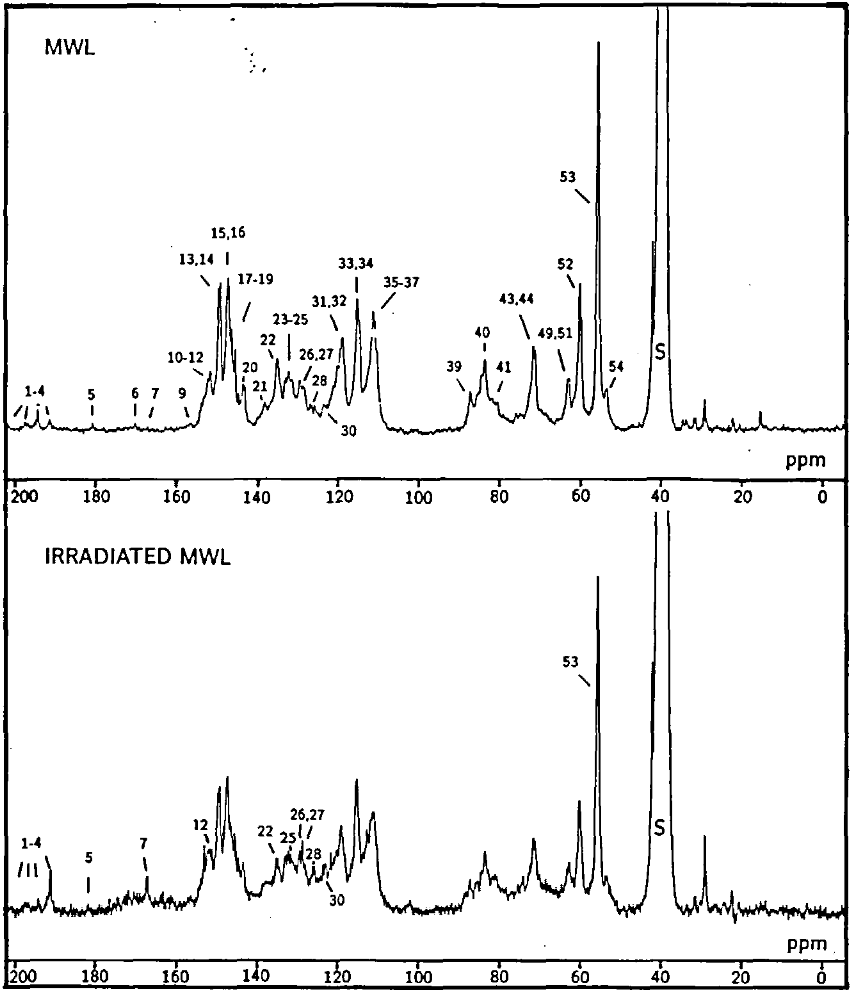

FIGURE 3. ^{13}C NMR spectra (100 MHz, DMSO-D_6) of MWL, and irradiated MWL. S=solvent signal.

TABLE 1.

^{13}C NMR (100 MHz, DMSO-D_6) chemical shifts and signal assignments for spruce MWL (internal std., center peak of DMSO, δ=39.5 ppm). Numbering and assignments (no. 7–54) are from Ref. 17 d.

Signal nr.	Chemical shift (δ, ppm)	Assignments*
1	201.6	C=O in aldehydes, ketones; non-conjugated
2	197.5	C=O in ketones; conjugated
3	194.3	C=O in Ar-CH=CH-CHO
4	191.4	C=O in Ar-CHO
5	180.4	C=O in quinones?
6	170.3	C=O in non-conjugated COOH
7	167.2	C=O in Ar-COOH
9	156.3	C-4 in H-units
10	153.0	C-3/C-3' in etherified 5-5 units, C-α in Ar-CH=CH-CHO units
11	152.3	C-3/C-5 in 4-O-5 units
12	151.6	C-4 in etherified G-units with α-CO
13, 14	149.7, 149.2	C-3 in etherified G-units
15	147.6	C-4 in etherified G-units
16	147.3	C-3 in non-etherified G-units
17	146.5	C-4 in non-etherified G-units
18	145.5	C-4/C-4' in etherified 5-5 units
19	144.3	C-4 in ring B of β-5 units
20	143.3	C-4/C-4' in non-etherified 5-5 units
21	138.2	C-1 in α-Ar, G-units
22	135.2	C-1 in etherified G-units
23	133.3	C-5/C-5' in etherified 5-5 units
24	132.3	?
25	131.4	C-1 in non-etherified G-units
26	129.6	C-β in Ar-CH=CH-CHO units
27	128.6	C-α and C-β in Ar-CH=CH-CH_2OH units
28	125.8	C-5/C-5' in non-etherified 5-5 units, C-α in stilbenes?
30	123.5	C-6 in G-units with α-CO
31, 32	120.1, 119.0	C-6 in G-units
33, 34	115.4, 114.8	C-5 in G-units
35-37	113.4-111.1	C-2 in G-units
39	87.2	C-β in β-O-4 units (*threo*), C-β in β-β units
40	83.7	C-β in β-O-4 units (*erythro*)
41	80.4	C-β in β-O-4 with α-CO
43	71.7	C-α in β-O-4 units (*erythro*)
44	71.1	C-α in β-O-4 units (*threo*)
49	63.2	C-γ in β-O-4 units with α-CO
51	62.8	C-γ in β-5 and β-1 units
52	60.1	C-γ in β-O-4 units
53	55.7	C-Me in Ar-OMe
54	53.4	C-β in β-β and β-5 units

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* H = p-Hydroxyphenylpropane; G= Guaiacylpropane

TABLE 2.

Chemical Shift Ranges and Normalised Signal Intensities of Different Types of Carbon Atoms in ^{13}C NMR Spectra of MWL and Irradiated MWL.

Spectral region	Shift range (δ, ppm)	Rel. int.		Types of carbons
		MWL	irr. MWL	
1	204-184	1.2	3.3	C=O in aldehydes and ketones
2	184-159	1.0	5.2	C=O in carboxylic acids
3	159-125	37.7	36.9	Ar. quat. carbons
4	125-107	24.3	24.3	Ar. tert. carbons
5	92- 58	24.1	19.9	Aliph. C-O carbons
6	57- 55	10.2	8.7	Ar. methoxyl carbons
7	55- 51	1.5	1.7	Aliph. tert. β-carbons in β-5 and β-β-units

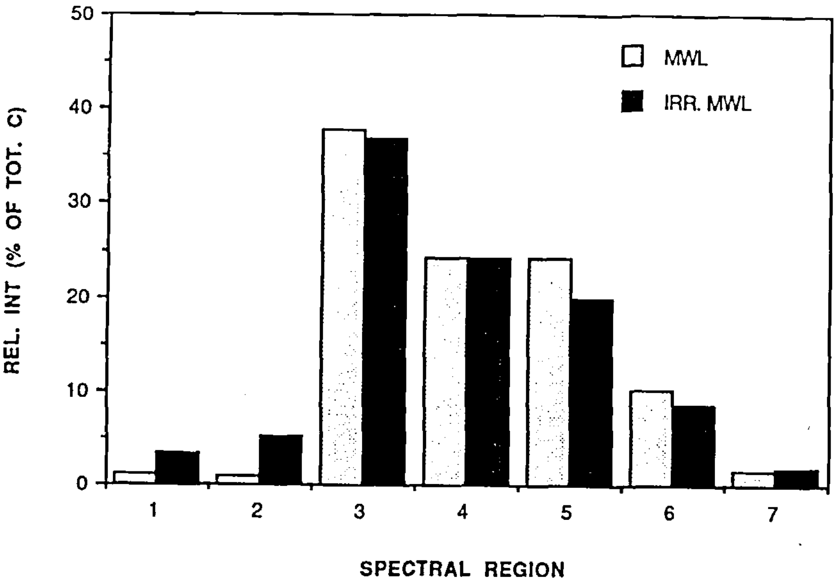

FIGURE 4. Relative ^{13}C NMR signal intensities within the spectral regions defined in Table 2., of MWL and irradiated MWL.

from c. 1 % to c. 5 %. The exact number of carbonyl carbons per aromatic ring in the irradiated lignin cannot be calculated as the proportion of aromatic to olefinic carbons is probably not the same as in "native" MWL and not known. However, assuming that the aromatic signals represent 6.12 C-atoms (aromatic and olefinic) as in MWL,[17d] the irradiated lignin would contain c. 0.5 carboxyl groups per aromatic ring. The high amount can be explained by the fact that the signals in spectral region 2 can be assigned to carboxyl groups formed by oxidation of α- as well as β- and γ- carbons of the side chain. Also, part of the carboxyl groups can be due to acids formed by degradation of the aromatic rings. One of the sharp peaks in spectral region 2 is that of the carboxyl group of vanillic acid and other benzoic acid type units at δ=167.6 ppm (peak 7, Fig. 3).

The signal of γ- C=O in cinnamaldehyde type units at δ=194 ppm dominates spectral region 1 in the spectrum of MWL while the carbonyl signal of vanillin and benzaldehyde type units at δ=191.5 ppm dominates the same region in the spectrum of the irradiated lignin.

A weak signal at δ=197.5 ppm (signal 2) assigned to α- C=O groups in phenylpropane units is seen in both spectra. The fact that the intensity of this signal does not decrease indicates that new α- carbonyls in phenylpropane units are formed, probably by oxidation of α- CH–OH groups.

The formation of vanillin and vanillic acid shows that α–β bond cleavage is a dominating reaction in the photodegradation of lignin. The reaction is probably preceded by β–O–4 ether cleavage in units containing α- C=O groups. However, the original amount of α- C=O groups in MWL is not high enough to explain the extent of formation of vanillin and vanillic acid and corresponding end-groups on irradiation. Part can be explained by the oxidation of α- olefinic double bonds but most of the new α- carbonyl groups have to form from benzyl alcohol groups by oxidative processes. A mechanism of this transformation is suggested later in Fig. 7.

Lebo *et al.*[13] claimed that *o*- quinoid structures are responsible for most of the colour of mechanical pulp and most of the increase of colour on light- induced yellowing of the same pulp. They say that untreated pulp contains 5–6 quinoid units per 100 C_9-units and that treatment with simulated sunlight would raise the amount to about 10. Our results do not support the presence of large amounts of quinoid structures, neither in MWL nor in irradiated MWL. On the ^{13}C NMR scale *o*- quinone carbonyls should absorb at $\delta \approx 180$ ppm.[19] Figure 3 shows that in both spectra a weak signal can be observed at $\delta = 180.5$ ppm (signal 5). Integration showed that the signal intensity was less than 0.3 % of the total carbon signal intensity. In the spectrum of MWL the intensity would roughly correspond to c. 1.5 quinoid units/100 C_9-units. In the spectrum of irradiated MWL the intensity of the signal at $\delta = 180.5$ ppm is still lower, corresponding to ca 1 unit. The peak at $\delta = 180.5$ ppm could not be definitively identified.

The signals in the low-field part of the aromatic spectrum (spectral region 3) assigned mainly to quaternary aromatic carbons show a relative intensity decrease on irradiation. This could be ascribed to the oxidative cleavage of the aromatic 3–4 bond which would turn the quaternary carbons C-3 and C-4 into carboxyl carbons. Within the low-field part of region 3 the signal 12, assigned to C-4 in guajacyl units with α- C=O shows, as expected, a relative increase on irradiation. The intensity of signal 22, assigned mainly to C-1 in etherified guajacyl units, is reduced by irradiation. This is expected as ether cleavage will move the signal to higher field (signal 25). The weak signal at $\delta = 125.8$ ppm (signal 28) shows an increase of intensity on irradiation. This signal has been assigned to C-5 in non-etherified 5–5 units and the increase could be due to ether cleavage in 5–5 units but also to the presence of stilbenes, the α- carbons of which absorb near $\delta = 126$ ppm.[20] Stilbenes could be formed from phenylcoumaran units containing free phenolic hydroxyl groups by a mechanism outlined in Fig. 5.

The intensity increase of signal 30 on irradiation is probably mainly a consequence of the formation of α- C=O groups.

The signals in the high-field part of the aromatic spectrum (spectral region 4), mainly due to tertiary aromatic and olefinic carbons, showed no significant change in intensity. A slight decrease of the signal intensity in this area could have been expected due to condensations (mainly 5–5) of aromatic rings. However, this decrease could be compensated by the intensity increase observed for signal 30.

A weak signal at $\delta \approx 102$ ppm in the spectrum of irradiated MWL was assigned to the anomeric carbons in carbohydrates. The signal could be due to degraded cellulose. The signal could also be explained by the formation of chemical bonds between lignin and carbohydrates, which is supported by the fact that extraction of the irradiated lignin from the paper sheets was very difficult and was not complete even with warm DMSO.

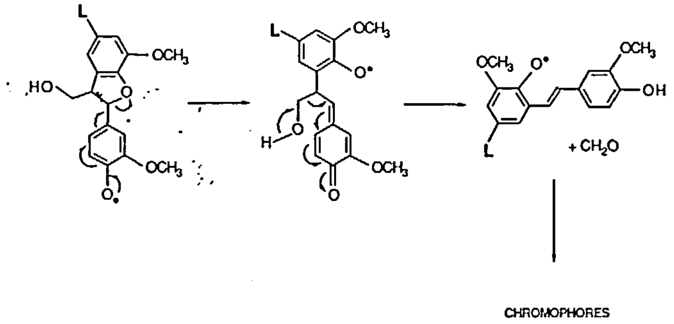

FIGURE 5. Proposed mechanism of α- aryl ether cleavage in phenylcoumaran derived phenoxy radicals, leading to stilbenes.

The signals in the spectral region of oxygenated aliphatic carbons (region 5) show an intensity decrease on irradiation. This region also contains the signals of the rest of the carbohydrate carbons. The contribution of these to the total signal intensity was aproximatively calculated from the intensity of the signal at $\delta \approx 102$ ppm. The intensities of all signals in region 5 decreased. Most of the intensity decrease of the signals in region 5 is probably due to oxidative α–β cleavage which transforms α- carbons to carbonyl groups in vanillin, vanillic acid and related structures in monomers as well as in polymer end-groups. At the same time the β- carbons are transformed to carbonyl groups. Oxidation of γ-carbons probably also takes place. These processes can be preceded by β–O–4 ether cleavage in α- C=O/β–O–4 units as well as α–O–4 ether cleavage.

The β–O–4 ether cleavage produces two resonance-stabilized radicals as shown previously in Fig. 1. The stabilisation of the phenacyl type radical involves an enolic structure as one of the canonical forms, and a keto-enol mixture can be formed by hydrogen transfer (Fig. 6, *cf.* Fig. 7 and 8). Enols are known to form peroxides in the presence of oxygen.[21] The peroxides are easily decomposed to carbonyl compounds by cleavage of the carbon-carbon double bond of the enol. In MWL this would result in formation of low-molecular aliphatic aldehydes and acids besides the aromatic ones (Fig. 6). As a matter of fact, oxalic acid was detected in the irradiated sample by GC/MS. The occurrence of β- ether cleavage in α- C=O containing lignin units as well as the occurrence

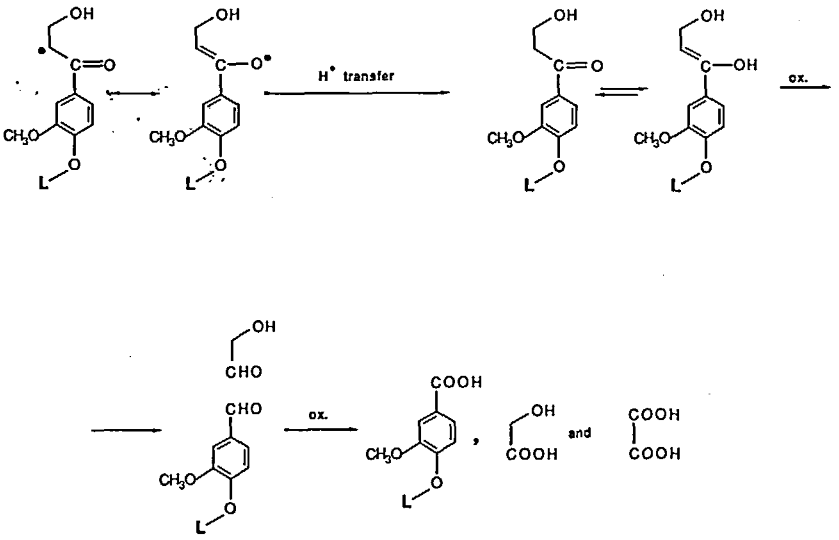

FIGURE 6. Proposed reaction of the phenacyl free-radical (*cf.* Fig. 1) resulting in α–β bond cleavage and the formation of low-molecular carbonyl compounds.

of hydrogen transfer processes in papers under irradiation is supported by the formation of γ- hydroxy propiovanillone, previously detected in acetone/water extracts of irradiated mechanical pulp.[15]

The signals 39–41 (mainly β- carbons) and the signals 43,44 (mainly α-carbons) showed almost the same decrease of intensity on irradiation. This indicates that, if the degradation starts by β- aryl ether cleavage in α- C=O/β–O–4 units, at the same time processes start which lead to the transformation of α- CH–OH groups to carbonyl groups. Part of the intensity decrease can be due to α-ether cleavage in phenylcoumaran units followed by stilbene formation. The transformation of α- carbons, which bind a hydroxyl group, into carbonyl carbons could be initiated by hydrogen abstraction from the α- carbon, followed by internal proton rearrangements as described in Fig. 7.

In a unit containing a phenoxy radical an other reaction route is possible, which could lead to quinone methide-like intermediates, as shown in Fig. 8. The signal in region 6 assigned to aromatic methoxyl groups shows an intensity decre-

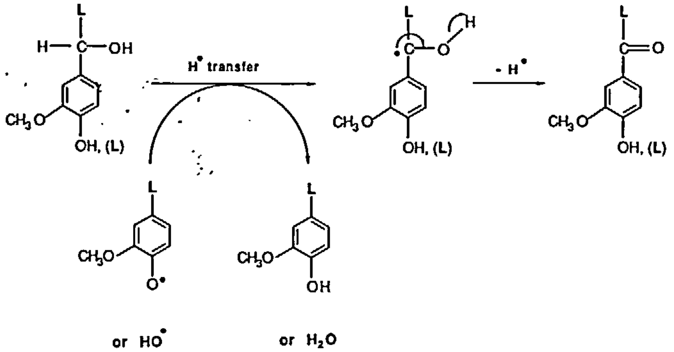

FIGURE 7. Formation of α- carbonyl groups from α- hydroxymethine groups.

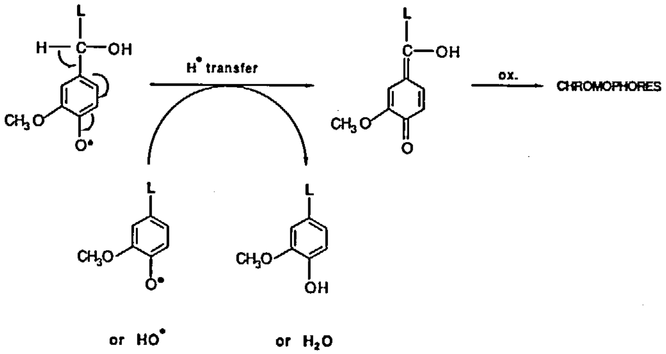

FIGURE 8. Formation of quinone methide by α- hydrogen abstraction from a phenoxy radical.

ase on irradiation. The decrease is a result of demethylation leading to catechols which can be further oxidized to quinones, which in turn can be important intermediates in the formation of ring-opened products and chromophores. The formation of catechols on irradiation of sheets has recently been demonstrated by a method based on oxidative degradation combined with GC.[22]

A slight increase in the intensity of the signals in region 7 assigned to the β-carbons in β–β and β–5 units can be observed in the spectra of the irradiated lignins, indicating that radical centers at C-β and C-5 are formed on irradiation (*cf.* Fig. 1). The intensity increase of the signals can probably be ascribed mainly to β–β coupling as the proton spectra indicated that the number of β–5 bonds, at least of those in phenylcoumarans, is reduced on irradiation.

CONCLUSIONS

The results show that cleavage of α- and β- aryl ether bonds is the main reaction taking place on irradiation of spruce MWL. These reactions are probably followed by the cleavage of α–β bonds. The mechanism presented in Fig. 6 seems probable for the reactions of units containing α- C=O groups and β- aryl ether bonds. However, the amount of α- C=O groups originally present is not high enough to account for all the formed aldehyde and carboxyl groups. New α- C=O groups could be formed from the α- CH–OH groups by the mechanism presented in Fig. 7. The formation of stilbenes is likely as α- ether cleavage in phenylcoumaran units is evident and could lead to stilbenes by a reaction route described in Fig. 5. Some cleavage of aromatic rings apparently took place. However, the decrease in aromaticity was quite small (c. 1.3 %) which could be due to the formation of unsaturated structures by reactions in the side chains. Demethylation decreased the methoxyl signal intensity by c. 15 %. Although weak signals (rel. int.< 0.3 %) at $\delta \approx 180$ ppm were observed, no conclusive evidence for the formation of quinones or quinoid units on irradiation of MWL could be presented. This does, however, not exclude the presence of quinoid structural units as reactive intermediates in the degradation process.

EXPERIMENTAL

Materials

Milled-wood lignin (MWL) was prepared[23] from fresh (stored at -20 °C in the dark) unbleached SGW pulp from a Finnish pulp mill using Norway spruce (*Picea abies*) and was stored at -20 °C in the dark before use. Handsheets (20g/m^2) were prepared from pure cotton linters. The sheets were impregnated with an acetone-water (85:15 v/v) solution of MWL to a lignin concentration of c. 30 % and freeze-dried. Part of the impregnated sheets were stored at-20 °C in the dark, for reference, while the rest of the sheets were subjected to accelerated light-induced yellowing for 3 h on each side in a HERAEUS 150 S XENOTEST "sunlight behind windowpane" simulator. The brightness of the reference and irradiated sheets was measured using a Zeiss-Elrepho Instrument in accordance with ISO standard method. The reported values are averages of measurements at several points of 8-10 sheets. The sheets were extracted with warm (c. 50 °C) dimethyl sulfoxide (DMSO). The solvent was evaporated in a freeze-drier and the samples were dissolved in DMSO-D_6 and the solutions were analyzed by NMR spectroscopy.

NMR analyses

All ^1H and ^{13}C NMR spectra were obtained at ambient temperature with a JEOL GX-400 FT NMR spectrometer at 400 and 100 MHz respectively. Solutions of c. 200 mg of sample in 2.5 mL of DMSO-D_6 were used for the analyses. The central peak in DMSO-D_6 (δ=39.5 ppm from TMS) was used as internal standard. The ^{13}C NMR spectra were recorded using a 90 ° pulse with an anti gated pulse sequence (SGNNE) suppressing the Nuclear Overhauser Effect (NOE) and a pulse delay of 12 s. An acceptable S/N ratio was obtained with c. 20000 pulses.

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