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The reaction of phloroglucinol in the presence of acid with lignin-containing materials

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Abstract

UV-visible diffuse reflectance spectrometry has been used to monitor the reaction of phloroglucinol (in the presence of hydrochloric acid) with high yield pulps. When papers made from such pulps are irradiated, coniferaldehyde residues are generated as judged by their reaction with phloroglucinol/HCl. Treatment of such papers with sodium borohydride reduces the coniferaldehyde residues and consequently no colour reaction with phloroglucinol/HCl is observed. Irradiation of these borohydride-reduced papers leads to the generation of coniferaldehyde entities as detected by phloroglucinol/HCl. Similar results were obtained using a thin section of abies wood. Irradiation of papers made from high yield pulps destroys coniferaldehyde residues on the one hand and generates them from other sources on the other hand. Examination of papers made from the morphological components of poplar showed that it is impossible to quantify the amount of lignin present by this colour test method. Thioacidolysis analysis of the fractions shows for all of them a higher proportion of syringyl than guaiacyl β-O-4 aryl ether linkages. In contrast, photocleavage of the β-O-4 aryl ether linkages is more important for the guaiacyl structures. This is in accordance with the observed higher sensitivity to UV light of softwood pulps compared with hardwood pulps. Also, the thioacidolysis experiments indicate that UV irradiation of the fractions maintains a stationary concentration of the coniferaldehyde structures.

Keywords: Phloroglucinol; Irradiation

1. Introduction

Currently there is much interest in using high yield pulps [1]. The presence of lignin in the pulps leads to them possessing an off-white colour [2]; consequently, if they are to be used for the production of high yield quality papers, they have to be bleached [2,3]. The bleaching process [4-6] exacerbates the tendency of such papers to exhibit colour reversion and the occurrence of photoyellowing is a particularly undesirable feature [7]. Pure cellulose undergoes photoyellowing [8,9], but when lignin is present, the colour change is more marked and ascribable in the main to reactions of lignin [7,10-15]. There appear to be many potential chromophores in lignin which can lead to yellowing, e.g. the presence of carbonyl groups (such as derivatives of acetophenones [16] and quinones [17-20]), phenols [21], stilbene derivatives [21a,22-24], etc. A component of some importance is coniferaldehyde which is still present after bleaching of thermomechanical pulp (TMP) [25]. Some coniferaldehyde chromophore appears to be formed by UV irradiation of bleached TMP [25] probably by oxidation of coniferyl alcohol residues. However, photochemical studies on coniferyl alcohol models adsorbed on a carbohydrate matrix indicate no formation of coniferaldehyde but the production of coloured products many of which become grafted to cellulose and hemicelluloses [21c]. A well known colour test for lignin relies upon the reaction of coniferaldehyde residues with phloroglucinol in the presence of acid (Wiesner reaction) [26-28]. This reaction is supposedly specific to coniferaldehyde moieties [29] (Scheme 1). This requires confirmation since in principle any compound that can, upon protonation, produce a benzylic carbocation will attack phloroglucinol, ultimately, giving a quinone methide, which is likely to be highly coloured.

2. Results and discussion

When phloroglucinol in tetrahydrofuran solution was applied to paper made from high yield pulp (stone ground wood pulp SGWP) a very faint yellow colour developed (Fig. 1). By way of contrast, application of an acidified

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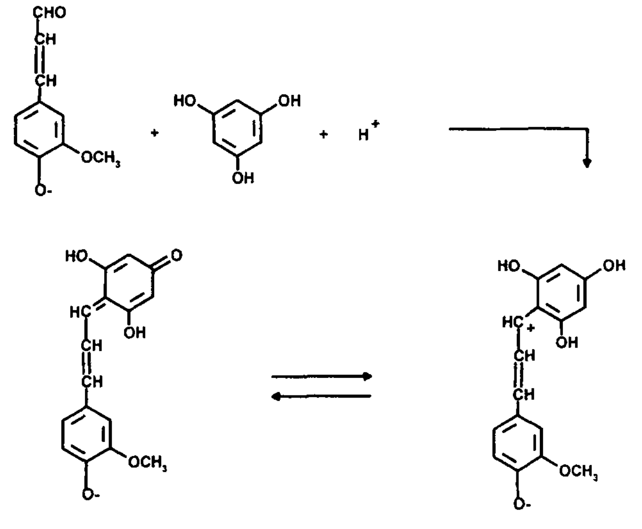


Scheme 1. Wiesner reaction between coniferaldehyde residue and phloroglucinol [28].

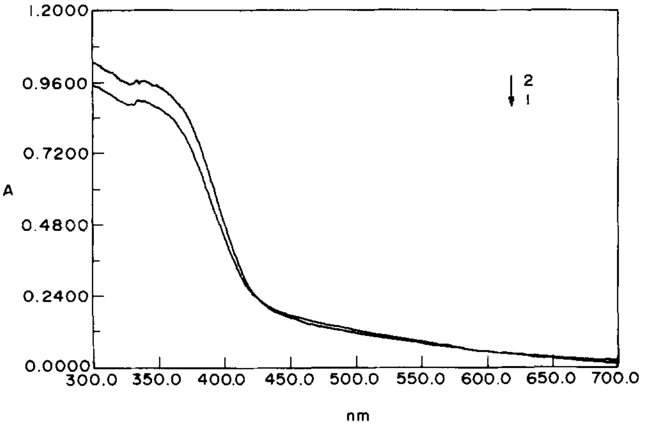


Fig. 1. Diffuse reflectance spectra of SGWP (1) and SGWP with phloroglucinol (2).

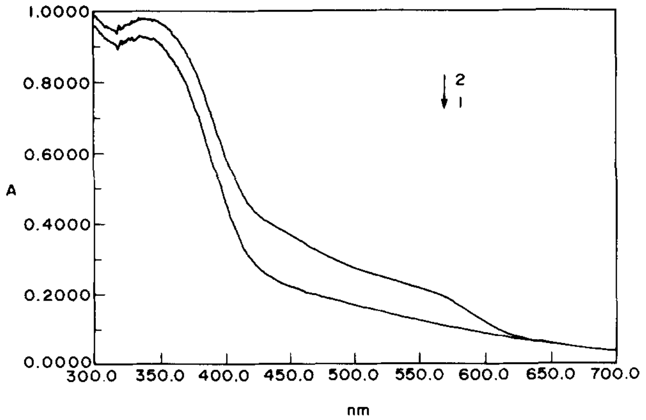


Fig. 2. Diffuse reflectance spectra of SGWP (1) and SGWP with phloroglucinol/HCl (2).

solution of phloroglucinol to the paper led to the production of the expected pink colour. A diffuse reflectance spectrum of the paper (Fig. 2) showed the presence of two absorption bands at 450 nm and 560 nm. In order to be certain that the observed absorption bands were due to lignin–phloroglucinol reaction, acidified phloroglucinol was added to pure cellulose (filter paper and cotton). In both cases a new absorption band was observed at 450 nm (Figs. 3 and 4). The origin of the 450 nm absorption band appears to be phloroglucinol and it is probably related to an oxidation product. Further oxidation is likely to occur on the paper surface. When a freshly made solution of phloroglucinol in acid is used, this band does not appear.

From the experiments it is clear that the absorption band at 560 nm which is shown in Fig. 2 is definitely related to the lignin–phloroglucinol reaction.

When paper made from SGWP is weathered by exposure to light (simulated daylight), it acquires a yellow colour which is due to increased absorption in the 400–600 nm region (Fig. 5, spectrum 1). Addition of acidified phloroglucinol to this paper led to the production of a pink colour and a strong absorption band at 560 nm (Fig. 5, spectrum 2). Within this broad envelope an absorption band at 560 nm is likely to be present, which in turn suggests that coniferaldehyde residues are present in the paper.

If phloroglucinol in acid solution is added to paper made from SGWP, spectrum 2 shown in Fig. 6 is obtained. Irradiation of the paper leads to growth of the absorption at 560

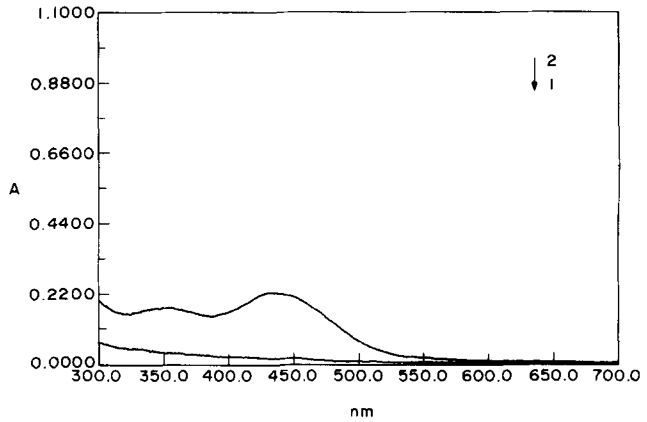


Fig. 3. Diffuse reflectance spectra of filter paper (1) and filter paper with phloroglucinol/HCl (2).

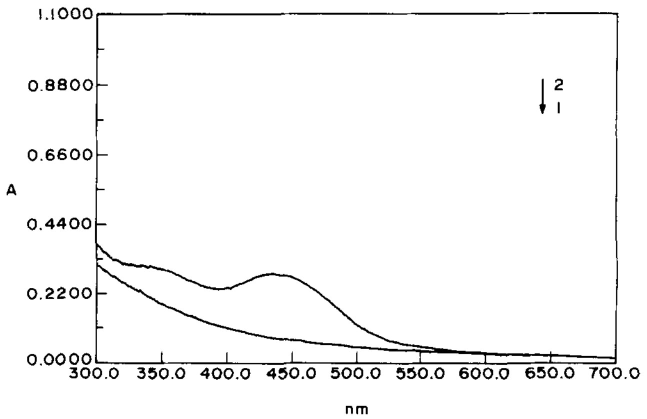


Fig. 4. Diffuse reflectance spectra of cotton (1) and cotton with phloroglucinol/HCl (2).

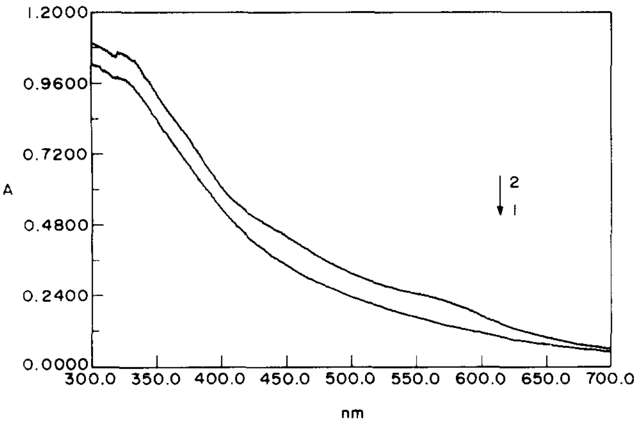


Fig. 5. Diffuse reflectance spectra of weathered SGWP (1) and weathered SGWP with phloroglucinol/HCl (2).

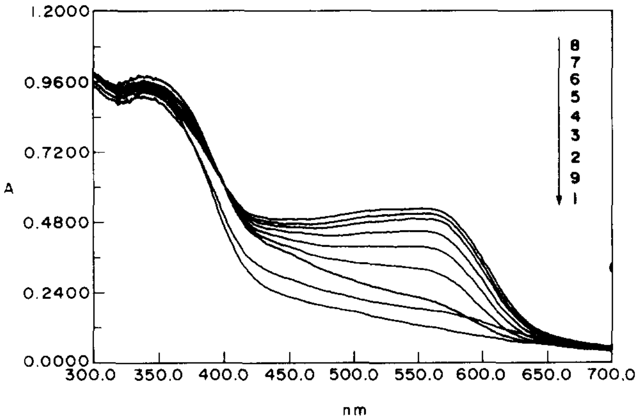


Fig. 6. Diffuse reflectance spectra of SGWP thick (1), SGWP with phloroglucinol/HCl unirradiated (2), SGWP with phloroglucinol/HCl irradiated for 1 min (3), SGWP with phloroglucinol/HCl irradiated for 3 min (4), irradiated for 5 min (5), irradiated for 10 min (6), irradiated for 15 min (7), irradiated for 20 min (8) and unirradiated face after 25 min (9).

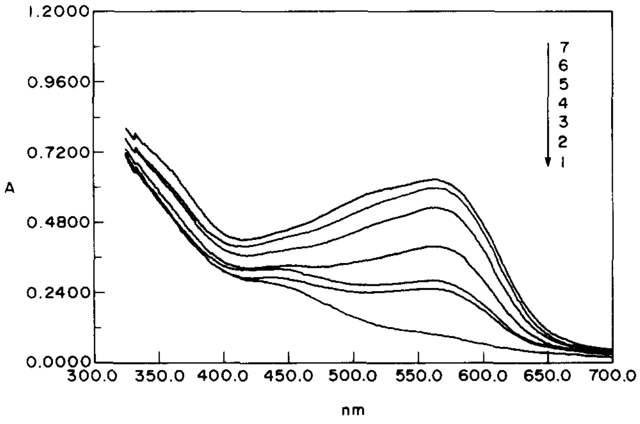


Fig. 7. Diffuse reflectance spectra of sodium-borohydride-reduced SGWP after addition of phloroglucinol/HCl (unirradiated) (1), 75 min after addition of phloroglucinol/HCl (unirradiated) (2), irradiated for 4 min (3), irradiated for 8 min (4), irradiated for 11 min (5), irradiated for 15 min (6) and irradiated for 25 min (7).

nm, but the complexity of the spectra suggests that more than one absorbing species is present. When the experiment was carried out using a thick sheet of paper, the light did not penetrate to the bottom of the paper (Fig. 6, spectrum 9). The results shown in Figs. 5 and 6 can be interpreted as providing evidence for the production of coniferaldehyde upon irradiation of the paper. This could arise by oxidation of coniferyl alcohol residues. To this end, paper made from SGWP was reduced with sodium borohydride and then washed with water until the pH was about 6, to remove any remaining borohydride.

Phloroglucinol in acid was added to the paper and the spectra displayed in Fig. 7 were recorded. The initial spectrum (Fig. 7, spectrum 1) shows a maximum at 450 nm which is due to phloroglucinol oxidation. If the borohydride-reduced paper is left in the dark for 75 min and the spectrum recorded (Fig. 7, spectrum 2), an absorption band corresponding to the reaction of coniferaldehyde residues is observed ($\lambda_{max} = 560$ nm).

Alternatively, if the borohydride-treated paper is irradiated, an absorption maximum at 560 nm develops quickly and increases rapidly in intensity. There is also some evidence for the production of a species (unknown) with an absorption maximum at 520 nm.

These observations may be explained as follows.

Treatment of the paper with sodium borohydride should reduce any coniferaldehyde residues to coniferyl alcohol and similarly other acetophenone residues should be reduced. Reoxidation of these residues occurs slowly in the absence of light, but the process becomes rapid in the presence of light. These observations are in accord with those obtained by previous workers, who showed that "reduced" papers made from high yield pulps undergo photoyellowing. We have speculated that these reactions are triggered by light-absorbing phenols such as biphenols, dihydroxystilbenes, phenylcoumarones, etc. [21a]. In accordance with the above, it has been shown using the thioacidolysis technique that some coniferaldehyde is produced on weathering bleached TMP [25]. Previously we have found it useful to compare the chemistry of the paper with that of the wood from which it was derived [30]. When a section of abies wood was treated with phloroglucinol in acid, an intense pink–purple colour developed, indicating the presence of coniferaldehyde. Further, a thin section of abies wood was reduced with sodium borohydride and, after washing, treated with phloroglucinol in acid solution. Spectra were recorded (Fig. 8) and these showed that upon irradiation the absorption band with a maximum at 560 nm grew in intensity as did the band with a maximum at 450 nm. It is clear that what we observe with the paper is not caused by an artefact introduced during pulping, since the wood sample behaved in a similar way to the paper.

Given that the colour reaction between phloroglucinol and coniferaldehyde in acidified medium is sensitive, it seemed sensible to use the reaction to investigate the lignin residues present in the morphological components of wood. Paper made from poplar pulp showed the typical colour reaction (Fig. 9).

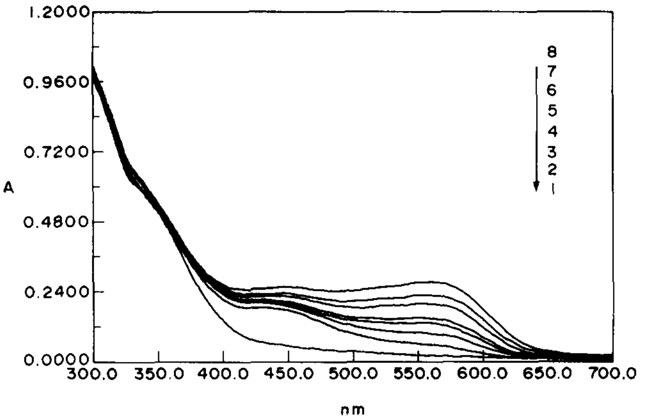


Fig. 8. Diffuse reflectance spectra of sodium-borohydride-reduced *Picea Abies* wood (1), sodium-borohydride-reduced *Picea Abies* with phloroglucinol/HCl unirradiated (2), irradiated for 1 min (3), irradiated for 3 min (4), irradiated for 5 min (5), irradiated for 10 min (6) and irradiated for 15 min (7), irradiated for 25 min (8).

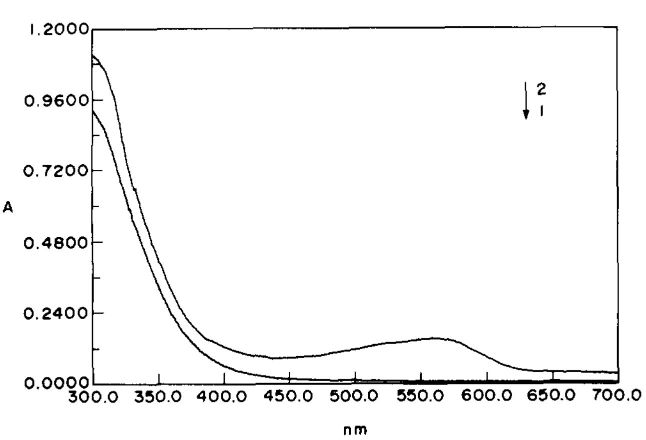


Fig. 9. Diffuse reflectance spectra of pulp from poplar (1) and pulp with phloroglucinol/HCl (2).

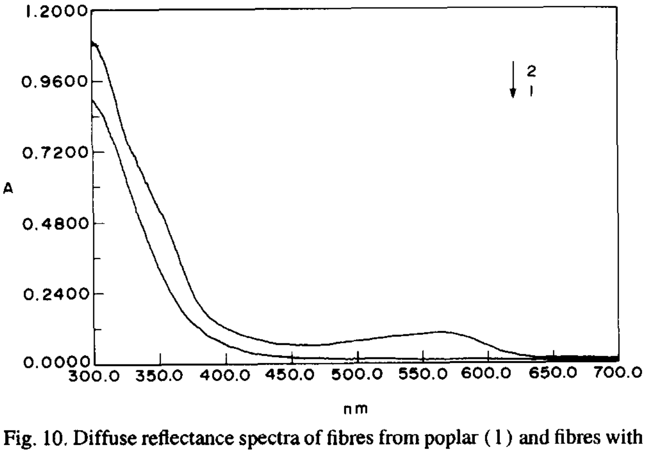


Fig. 10. Diffuse reflectance spectra of fibres from poplar (1) and fibres with phloroglucinol/HCl (2).

A comparison was then made of the reaction of acidified phloroglucinol with papers made from fibres, middle lamella and ray cells. The spectra are shown in Figs. 10–12 respectively.

What is most striking is the intense colouration which is produced by the paper made from ray cells. This may be confirmation of an earlier finding that the lignin content (33.5%) [31] is high. However, middle lamella also contains a high lignin content (33.7%), but the acidified phloroglucinol reaction indicates a much lower lignin content. Paper made from fibres (lignin content 19.8%) also developed little colour. These findings show that the phloroglucinol colour test is far from being quantitative. It has been previously recognized that a factor which influences the reaction is the ratio of guaiacyl to syringyl residues.

The ratio between syringyl and guaiacyl of uncondensed structures in the lignin of the morphological fractions can be determined by the thioacidolysis technique developed by Lapierre et al. [32]. This was done on the morphological fractions before and after UV irradiation and the results are presented in Table 1.

The levels of uncondensed guaiacyl and syringyl β-O-4 aryl ethers were respectively calculated from the levels of compounds **3** and **4** in the thioacidolysis products (Scheme 2). It was also possible to detect and measure the amount of coniferaldehyde **1** residues. Titration of the sinapaldehyde **2** residues has not been possible under our experimental conditions. The assumptions made in the analyses were the following: (i) an efficiency of formation of compounds **3** and **4** from all uncondensed β-ethers in the lignin of the fractions,

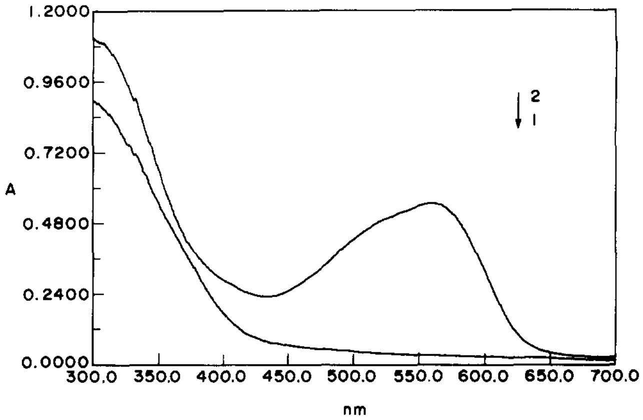


Fig. 11. Diffuse reflectance spectra of middle lamella from poplar (1) and middle lamella with phloroglucinol (2).

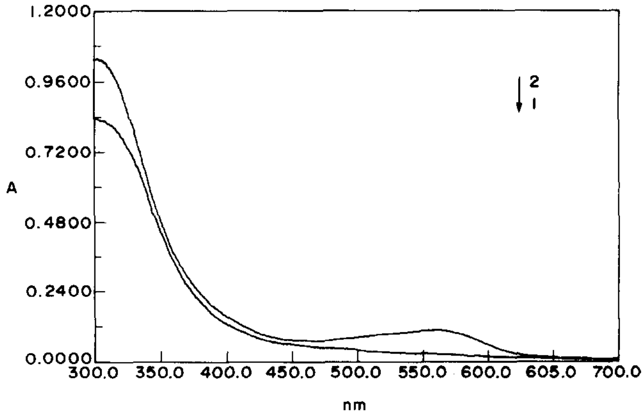
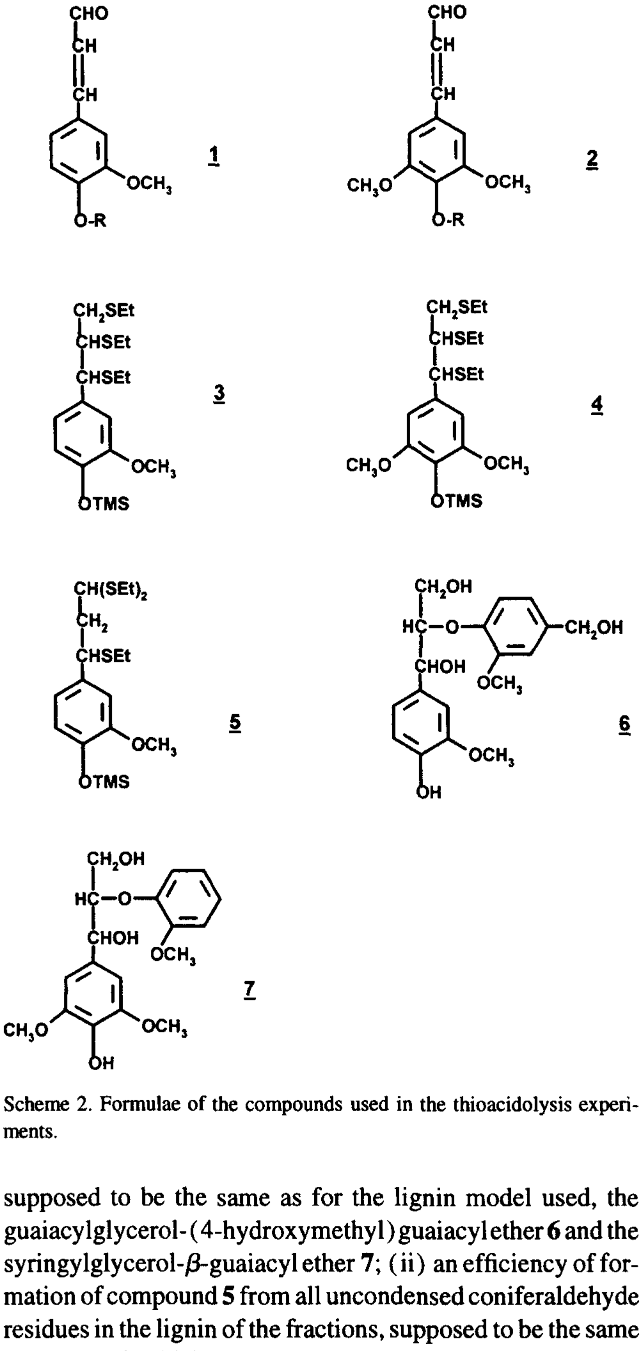


Fig. 12. Diffuse reflectance spectra of ray cells from poplar (1) and ray cells with phloroglucinol (2).

Table 1
Estimation in morphological components of poplar pulps of the content of β-O-4 aryl ether linkages (guaiacyl, G; syringyl, S) and of coniferaldehyde **1** residues determined by thioacidolysis according to the procedure developed by Lapierre et al. [32]

Sample	Lignin content (%) [21]	Unirradiated sample				Irradiated sample			
		β-O-4 G ^{a,d} (μmol (g pulp)$^{-1}$)	β-O-4 S ^{b,d} (μmol (g pulp)$^{-1}$)	S/G	Coniferaldehyde ^{c,d} (μmol (g pulp)$^{-1}$)	β-O-4 G ^{a,d} (μmol (g pulp)$^{-1}$)	β-O-4 S ^{b,d} (μmol (g pulp)$^{-1}$)	S/G	Coniferaldehyde ^{c,d} (μmol (g pulp)$^{-1}$)
Pulp	23.2	240	370	1.54	6.5	160	285	1.78	5.5
Fibres	19.8	255	410	1.6	7.5		380	1.77	6.5
Middle lamella	33.7	300	440	1.47	8	250	435	1.74	8
Ray cells	33.5	300	475	1.58	6	235	445	1.89	5.5

[a] Based on titration by GC–MS of the silylated mixture after thioacidolysis of compound **3** G–CHR–CHR–CH_2R erythro + threo (R ≡ –S–Et; G ≡ TMS guaiacyl).
[b] Based on titration by GC–MS of the silylated mixture after thioacidolysis of compound **4** S–CHR–CHR–CH_2R erythro + threo (R ≡ –S–Et; S ≡ TMS syringyl).
[c] Based on titration by GC–MS of the silylated mixture after thioacidolysis of compound **5** G–CHR–CH_2–CHR_2 (R ≡ –S–Et; G ≡ TMS guaiacyl).
[d] ±0.5%.



Scheme 2. Formulae of the compounds used in the thioacidolysis experiments.

supposed to be the same as for the lignin model used, the guaiacylglycerol-(4-hydroxymethyl)guaiacyl ether **6** and the syringylglycerol-β-guaiacyl ether **7**; (ii) an efficiency of formation of compound **5** from all uncondensed coniferaldehyde residues in the lignin of the fractions, supposed to be the same as for coniferaldehyde (**1**, R ≡ H). Examination of Table 1 indicates that the syringyl/guaiacyl (S/G) β-ether ratio varies very little, the syringyl structures being the most abundant. Moreover, the coniferaldehyde residues are present in all morphological fractions. The intensity of the colouration band in the phloroglucinol test (ray cells > pulp > fibres > middle lamella) does not correlate with the total amount of uncondensed coniferaldehyde residues (middle lamella > fibres > pulp ≈ ray cells). The fact that the colour test is not quantitative is probably ascribable to other lignin reactive structures which give positive reaction with phloroglucinol/HCl and contribute to the band near 560 nm. Alternatively, or in addition, the colour reaction may be affected by the accessibility of the phloroglucinol to uncondensed coniferaldehyde chromophores in the morphological fractions. By way of contrast, the thioacidolysis procedure gives the total amount of coniferaldehyde residues. After acidolysis with $BF_3/Et_2O/EtSH$ almost all the sample is dissolved and consequently all the coniferaldehyde residues will have been transformed into the appropriate species. Thus, following silylation, gas chromatography of the components gives a lower estimate of the concentration of the components of lignin.

Irradiation of morphological fractions with UV light induces a strong cleavage of the guaiacyl β-O-4 ether linkages compared with the syringyl ones (the ratio S/G increases when the fractions are exposed to light). This is in accordance with the well-known greater sensitivity to light of softwoods compared with hardwoods. Examination of Table 1 indicates that during irradiation a steady state concentration of coniferaldehyde is maintained, i.e. the coniferaldehyde residues may be formed and destroyed at the same rate. Another possibility is that coniferaldehyde is relatively photostable, as was previously observed when the aldehyde was irradiated in solution [21c]. All these observations show that the test with phloroglucinol is very sensitive and allows the detection of minute amounts of conjugated propenal residues.

3. Conclusions

Examination of papers made from the morphological components of poplar showed that it is impossible to quantify the amount of lignin present by the phloroglucinol colour test method. Whilst the colour reaction of acidified phloroglucinol may be used to show the presence of coniferaldehyde and related residues, it is not a reliable test for lignin.

The colour reaction can be used to show that coniferaldehyde and related residues are generated upon UV irradiation, because the test is very sensitive but not quantitative. In contrast, the thioacidolysis method allows a quantitative estimation of the uncondensed coniferaldehyde structures even if it is less sensitive. It was observed that upon UV irradiation the fractions display a stationary concentration of the coniferaldehyde residues. Thus it would appear that there is a reservoir of species which can generate some coniferaldehyde structures upon irradiation, thereby maintaining a measurable concentration of coniferaldehyde chromophores in the paper.

4. Experimental details

4.1. Phloroglucinol experiments

Phloroglucinol solution, purchased from BDH, contains phloroglucinol (2.67%), 85% ethanol (methylated spirit) and 10% hydrochloric acid. This was further eluted by THF and applied to the paper by means of a graduated syringe to a concentration of 0.2% on the weight of paper or wood.

Phloroglucinol stain. A solution of 1.00 g phloroglucinol (Aldrich) in 23.5 ml of ethanol (methylated spirit) and 12.25 ml of dilute hydrochloric acid was applied to the paper by means of a graduated syringe to a concentration of 7% of the weight of the paper [33].

For the paper made from the morphological components the solution was applied to 0.4% on a paper weight basis.

4.2. Weathering

Unless otherwise stated, the samples were weathered for 24 h with three black light fluorescent tubes (Philips TLD 18W/08).

4.3. Pulp preparation, pulp fractionation and sheet preparation

Paper made from stone-ground wood pulp (softwood, mainly spruce) was kindly supplied by Dr. D. Lachenal (Centre Technique du Papier, Grenoble).

The bleached CTMP poplar pulp used to separate the morphological fractions was produced in the pilot plant at the Centre Technique du Papier. The chips were pressure impregnated with a solution of 70 g l^{-1} sodium dithionite and 25 g l^{-1} sodium hydroxide and then steamed for 15 min at 125 °C. The chips were defibrated under pressure and refined at atmospheric pressure to 42 °SR. Bleaching was carried out at 17% consistency for 3.5 h at 65 °C in a solution containing 5% hydrogen peroxide, 3.5% sodium hydroxide, 3% sodium silicate, 0.1% magnesium sulphate and 0.3% diethylenetriamine-pentaacetic acid.

The pulp was fractionated according to a method described previously [34]. The fraction passing a 20 μm sieve contained most of the middle lamella and was further purified by suspending it in water, collecting the material in suspension and rejecting the sediment. A fraction enriched in ray cells was obtained by the procedure described earlier. The fibre fraction was collected by filtering the pulp on an 80 μm sieve to remove the fines and on a 200 μm sieve to eliminate shives and fibre bundles. Nylon sieves and deionized water were used in order to avoid contamination with metals in the separation process. Thin sheets with a basis weight of about 10 g m^{-2} were prepared by filtering a suspension of the sample of known concentration onto a 0.45 μm Teflon membrane placed over a glass holder. The membrane, along with the sheet still attached, was dried in a desiccator under vacuum. After drying, the sheets were carefully separated from the membrane and stored in a dark place at low temperature.

4.4. Thioacidolysis studies

Dry pulp (5–10 mg) was heated in an oil bath at 100 °C for 12 h with 5–10 ml of ethanethiol–dry dioxane mixture (9:1, v/v) and 0.2 M BF_3 etherate. The solution was magnetically stirred for a better homogeneity of the reaction mixture. The cooled reaction mixture, together with a few millilitres of water used to rinse the vessel, was poured over dichloromethane (20 ml). Then 3 ml of docosane (C_{22}, gas chromatography (GC) internal standard, 3.8×10^{-4} M) solution in CH_2Cl_2 was added to the mixture. The pH of the aqueous phase was adjusted to 3–4 with 0.4 M $NaHCO_3$ aqueous solution and the whole mixture was extracted with CH_2Cl_2. The combined organic extracts, dried over magnesium sulphate, were evaporated under reduced pressure at 40 °C. The thioacidolysis residue in a "Reactivial" vessel was silylated at room temperature with bis(trimethylsilyl)-trifluoroacetamide (50 l) in tetrahydrofuran (50 l) and pyridine (10 l). The TMS derivatives were analysed by gas chromatography.

Gas chromatography was carried out in a Shimadzu GC14A instrument equipped with a Shimadzu CR4A integrator. The GC used the split mode for injection, a flame ionization detector and a capillary column (DB1, 40 m × 0.32 mm, 1 m film thickness) flowed with helium. The oven was programmed from 180 °C (1 min) to 300 °C at 4 °C min^{-1} and then held at 300 °C for 35 min. The injector and detector were set at 280 and 300 °C respectively. The response factors of compounds **3**–**5** relative to docosane were determined using authentic sample **1** (R ≡ H), **6** and **7** prior analysis.

The attribution of the peaks was established by gas chromatography–mass spectrometry (GC–MS) on the thioacidolysis mixture of the pulp and with appropriate reference compounds. The mass spectra were obtained on a VG Autopec Q spectrometer.

Coniferaldehyde (**1**, R ≡ H) was prepared by Jaeger et al. [21c] and sinapaldehyde (**2**, R ≡ H) was synthesized according to Nakamura et al.'s procedure [35]. The guaiacyl β-O-4 lignin model dimer **7** was kindly provided by Dr. M. Hauteville (Laboratoire de Chimie Biologique, Université Lyon 1, Villeurbanne). The syringyl β-O-4 lignin model dimer **8** was prepared according to the procedure described by Hauteville and Duclos-Jordan [36].

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References

[1] R.A. Cokram, *Proc. Int. Mechanical Pulping Conf., Helsinki, 1989.*

[2] R.P. Singh, in R.P. Singh (ed.), *The Bleaching of Pulp,* Tappi, Atlanta, GA, 1979, p. 1.

[3] D. Lachenal, C. De Choudens and L. Bourson, *Tappi J., 70* (3) (1987) 119.

[4] A. Michell, C.W.J. Chin and P.J. Nelson, *Proc. 6th Int. Symp. on Wood and Pulping Chemistry, Melbourne, 1989,* Vol. 2, p. 333.

[5] J. Gierer, *Holzforschung, 43* (1989) 391.

[6] M. Ek, J. Gierer and K. Jansbo, *Holzforschung, 43* (1989) 391.

[7] (a) R.S. Davidson and A. Castellan, *Paper, 10* (1991) 24; (b) A. Castellan, *L'Actualité Chimique, 6 Suppl.* (1994) 148; (c) G. Gellerstedt, I. Pettersson and S. Sundin, *Svensk Papperstidn., 86* (1983) R157; (d) C. Heitner, *ACS Symp. Ser., 531* (1993) 1.

[8] J.F. Lenest, J. Silvy and A. Gandini, *J. Photochem., 31* (1985) 359.

[9] G. Buschle-Diller and S.H. Zeronian, *ACS Symp. Ser., 531* (1993) 177.

[10] D.N.S. Hon and N. Minemura, in D.N.S. Hon and N. Shiraishi (eds.), *Wood and Cellulosic Chemistry,* Marcel Dekker, New York, 1991, pp. 395, 525.

[11] I.H. Spinner, *Tappi J., 45* (1962) 495.

[12] S.Y. Lin and K.P. Kringstad, *Tappi J., 53* (1970) 658.

[13] U. Tschirner and C.W. Dence, *Pap. Puu, 36* (1988) 338.

[14] A. Castellan, N. Colombo, P. Fornier de Violet, A. Nourmamode and H. Bouas-Laurent, *Proc. 5th Int. Symp. on Wood and Pulping Chemistry, Raleigh, NC, 1989,* Vol. 1, p. 421.

[15] C. Vanucci, P. Fornier de Violet, H. Bouas-Laurent and A. Castellan, *J. Photochem. Photobiol. A: Chem., 41* (1988) 251.

[16] K.P. Kringstad and S.Y. Lin, *Tappi J., 53* (1970) 2296.

[17] S.Y. Lin and K.P. Kringstad, *Norsk Skogsindustri, 25* (1971) 252.

[18] S.E. Lebo, W.F. Lonski, T.J. McDonough, P.J. Medvecz and D.R. Dimmel, *J. Pulp Pap. Sci., 16* (1990) J139.

[19] D.S. Argyropoulos and C. Heitner, *Holzforschung, 48 Suppl.* (1994) 112.

[20] A. Castellan, A. Nourmamode, C. Jaeger and I. Forsskåhl, *ACS Symp. Ser., 531* (1993) 60.

[21] (a) A. Castellan, A. Nourmamode, J.H. Zhu, D. Lachenal, R.S. Davidson and L. Dunn, *J. Wood Chem. Technol., 10* (1990) 461; (b) P. Fornier de Violet, A. Nourmamode, N. Colombo and A. Castellan, *Cell. Chem. Technol., 23* (1989) 535; (c) C. Jaeger, A. Nourmamode and A. Castellan, *Holzforschung, 47* (1993) 375.

[22] D.Y. Lee, M. Matsuka and M. Sumimoto, *Holzforschung, 44* (1990) 415.

[23] C. Noutary, P. Fornier de Violet, J. Vercauteren and A. Castellan, *Res. Chem. Intermed.,* in press.

[24] L. Zhang and G. Gellerstedt, *Acta Chem. Scand., 48* (1994) 490.

[25] X. Pan, D. Lachenal, C. Lapierre and B. Monties, *J. Wood Chem. Technol., 12* (1992) 135.

[26] L.M. Srivastava, *Tappi J., 49* (1966) 173.

[27] E.D. Bland, *Holzforschung, 20* (1966) 12.

[28] G.G. Allan, in K.V. Sarkanen and C.H. Ludwig (eds.), *Modification Reactions in Lignins, Occurrence and Formation, Structure and Reactions,* Wiley–Interscience, New York, 1971, p. 511.

[29] E. Adler, K.J. Bjorkquist and S. Haggaroth, *Acta Chem. Scand., 2* (1948) 93.

[30] A. Castellan, H. Choudhury, R.S. Davidson and S. Grelier, *J. Photochem. Photobiol. A: Chem., 81* (1994) 117–123.

[31] G. Capretti and R. Maiocchi, unpublished results.

[32] (a) C. Lapierre, B. Monties and C. Rolando, *Holzforschung, 40* (1986) 113; (b) C. Lapierre, B. Monties and C. Rolando, *Proc. 4th Int. Symp. on Wood and Pulping Chemistry, Paris, 1987,* Vol. 2, p. 431.

[33] J. Grant, *A Laboratory Handbook of Pulp and Paper Manufacture,* Arnold, London, 2nd edn., 1961.

[34] (a) U. Westermark, *Wood Sci. Technol., 19* (1985) 223; (b) U. Westermark and G. Capretti, *Nordic Pulp Pap. Res. J., 3* (1988) 95.

[35] Y. Nakamura, F. Nakatsubo and T. Higuchi, *Wood Res., 56* (1974) 1.

[36] M. Hauteville and M.C. Duclos-Jordan, *Holzforschung, 40* (1986) 293.