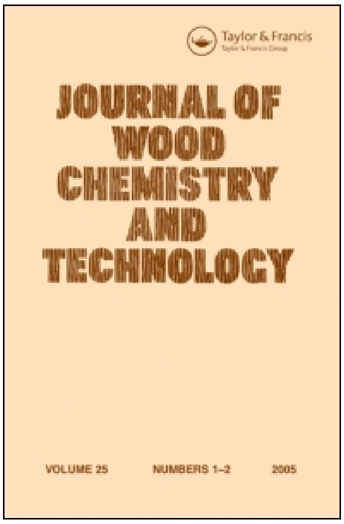
This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Wood Chemistry and Technology

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

Characterization of the Lignin Isolated From Birch Woo After Capbohydrate Extraction with Hydrogen Fluoride

John Fapauopoulos[a]; Jacques Defaye[a]
[a] Centre elf Recheiches sur les Macromolécules Végétales C.N.R.S., France

To cite this Article Fapauopoulos, John and Defaye, Jacques(1986) 'Characterization of the Lignin Isolated From Birch Woo After Capbohydrate Extraction with Hydrogen Fluoride', Journal of Wood Chemistry and Technology, 6: 2, 203 — 218
To link to this Article: DOI: 10.1080/02773818608085224
URL: http://dx.doi.org/10.1080/02773818608085224

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 6(2), 203-218 (1986)

CHARACTERIZATION OF THE LIGNIN ISOLATED FROM BIRCH WOOD AFTER CARBOHYDRATE EXTRACTION WITH HYDROGEN FLUORIDE[1]

John Papadopoulos and Jacques Defaye
Centre de Recherches sur les Macromolécules Végétales
C.N.R.S. Grenoble, B.P. 68, F-38402 Saint Martin d'Hères, France.

ABSTRACT

High yields of D-glucose and D-xylose water soluble oligosaccharides were obtained by extraction of birch wood with anhydrous hydrogen fluoride at sub-ambient or ambient temperature. A small amount of carbohydrates remained in the resulting insoluble lignin. Investigation by infrared spectroscopy as well as phenolic group analyses indicated a probable low level of aryl alkyl ether linkage cleavage, at least in the range of the reaction conditions studied. Alkaline nitrobenzene oxidation of lignin showed that condensation occurred, as measured by the decrease in yield of total p-hydroxybenzaldehydes, during the hydrogen fluoride treatment.

INTRODUCTION

Hydrogen fluoride (HF) is now a well-recognized reagent for the conversion of polysaccharides into water-soluble, small oligomers. The course and mechanism of the fluorolysis reaction has been established for cellulose, starch, xylan[2], inulin[3], chitin, and chitosan[4]. One of the main features of this reagent is that it dissolves and depolymerizes polysaccharides more rapidly and at lower temperatures than any other acid that has been studied for this purpose. Furthermore, the low boiling point of HF is an attractive characteristic for technological applications as it may enable an easy recovery of the reagent [5,6,7].

0277-3813/86/0602-0203$3.50/0

These unique properties have attracted interest in its possible use for the extraction of carbohydrate components from lignocellulosic materials, and several patents[8] were issued for this purpose as early as in the 1930's. Technological improvements, involving the use of hydrogen fluoride in a continuous process, appeared more recently in the patent literature[9]. Although it is generally recognized[10] that the economical potential of any wood hydrolysis process would be considerably enhanced by taking into account, as far as possible, added values for components other than saccharides, lignin has received little attention in this respect.

Partial characterization of lignins resulting from hydrochloric and sulfuric acid hydrolysis of wood has been previously attempted[11-13]. It seemed therefore appropriate to investigate the structural characteristics of lignins resulting from wood hydrolysis with hydrogen fluoride under various conditions, and compare them with the lignin resulting from other acid hydrolysis processes.

EXPERIMENTAL

The birch (Betula verucosa L.) wood meal was extracted for 48 h with benzene-ethanol (2:1, v/v), then dried at 60°C under vacuum to constant weight. In a typical experiment, ten grams of dried wood meal were placed in a polyethylene flask immersed in liquid nitrogen, and pre-cooled hydrogen fluoride (40 mL) was poured into the flask which was then closed. The temperature was allowed to rise within a few min, to the desired level (0°C or 23°C), at which it was maintained for the indicated period of time. The reaction flask was then cooled again in liquid nitrogen, and cold diethyl ether (500 mL) was slowly added. The insoluble fraction was separated by filtration and washed several times with diethyl ether (3 x 50 mL). It was then suspended in water (400 mL), stirred for 2 h, and finally centrifuged to separate the water-soluble carbohydrate fraction from the insoluble lignin residue. This step was repeated twice. The combined aqueous fractions, thus collected, were neutralized with calcium carbonate, and filtered, to obtain a carbohydrate solution free of solids. The total volume was reduced to about 100 mL by evaporation under reduced pressure, and then freeze-dried, as was also the lignin residue.

Carbohydrate analysis was carried out on the corresponding alditol acetates. These were prepared as follows : The insoluble fractions (0.3 g samples) were treated in a test tube with sulfuric acid (72 %, 3 mL) for 1 h at 30°C, with continuous stirring with a glass rod. The resulting hydrolysates were diluted with water (84 mL), sealed in a serum bottle and placed in an autoclave at 120°C for 1 h, then eventually filtered. Aliquots of the filtrate were used for the determination of the carbohydrate composition according to the method of Borchardt and Piper,[14] as well as for the determination of the acid soluble lignin. For the carbohydrate analysis of the water soluble fractions, the initial hydrolysis step with 72 % sulfuric acid was omitted. The column calibration constants were 0.99 and 1.04 for xylitol pentaacetate and glucitol hexaacetate, respectively, and hydrolysis survival factors of 0.912 for D-xylose and 0.975 for D-glucose were used[15]. Percent yields for both D-xylose and D-glucose are reported on a weight basis of the original amount of sugars present in the wood. Acid-soluble lignin was recorded on a Beckman model Acta III spectrophotometer assuming absorptivity of 110 L g^{-1} cm^{-1} [16]. Alkaline degradation of the HF-lignin samples was performed in a 12.5-mL Prolabo (Paris) autoclave, by allowing the sample (0.5 g) to react with 2 N sodium hydroxide (5 mL) at 170°. The suspension of the resulting lignin degradation products was acidified with N hydrochloric acid to a pH of about 2-3. The solids, separated by centrifugation, were washed three times with small amounts of water (10 mL), and freeze-dried from aqueous suspension. Alkaline depolymerisation, in the presence of anthraquinone (AQ) as catalyst, was carried out under the same conditions, with addition of AQ (0.1% of the weight of lignin). Since very small amounts of catalyst were used, no attempt was made to remove the catalyst from the lignin degradation products. Methylation with diazomethane was performed as usual[17] on a suspension of lignin in ether. In order to ensure complete methylation, the process was repeated five times.

Reduction of lignin samples (200 mg) was carried by stirring them with sodium borohydride (30 mg) in 0.1 N sodium hydroxide for 12 h. The lignin was precipitated by acidification to pH 2, and the insoluble part was then separated by centrifugation, washed three times with small portions of distilled water to pH 4, dispersed in water, and freeze-dried. Buffering was carried out by stirring lignin (5 mg) with sodium hydrogencarbonate (0.05 N, 2 mL) for 12 h, centrifuging out the solids, and freeze-drying them from water suspension. Mild alkaline hydrolysis was carried out according to the procedure described by Sarkanen et al.[18]. Infrared spectra were recorded from lignin samples (5 mg) on KBr disks, using a Perkin-Elmer model 598 spectrophotometer.

Alkaline nitrobenzene oxidation of lignin was carried out in Prolabo (Paris) stainless steel autoclaves, as described[19]. The quantitative determination of vanillin, syringaldehyde, and syringic acid was performed using a Waters M 6000 high-pressure chromatograph fitted with a UK 6 high-pressure injector and a C-18 Radialpack column with acetonitrile--water (1:2, v/v) as eluent. The yields were calculated as molar percentage, assuming the average C-9 unit molar weight of lignin as 200, and using calibration factors of 0.4603 for vanillin, 0.7615 for syringaldehyde, and 0.6053 for syringic acid.

RESULTS AND DISCUSSION

Treatment of birch wood-meal with anhydrous hydrogen fluoride at 0°C for 60 min resulted in 75-80% yield of D-glucose and D-glucose oligosaccharides, and a 85% yield of D-xylose and D-xylose oligosaccharides, as estimated by sulfuric acid post-hydrolysis and conversion into the corresponding alditol acetates. This overall yield reached 90% for both carbohydrate components after 180 min (Fig. 1A). At 23°C, such optimal yield was obtained after 30 min, and further exposure to the reagent resulted in a lower yield of the extracted glucan, although unexpectedly the amounts of xylan extracted appeared to remain unchanged (Fig. 1B). Carbohydrate analysis of the corresponding lignin residue showed that a small proportion of the carbohydrate part remained associated, even after prolonged acidic treatment at both reaction temperatures (Table 1). Use of an excess of HF did not increase the amounts of carbohydrates removed (Table 1). This implies that reasons other than incomplete hydrolysis may be responsible for the portion of

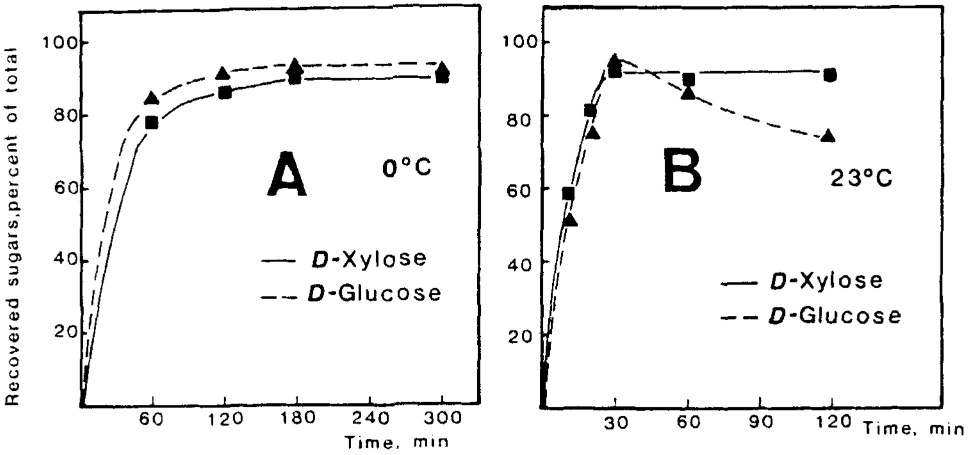


Figure 1.- Respective yields in D-glucose and D-xylose oligosaccharides after extraction of birch wood with HF (1 : 4 w/w) : (A) at 0°C ; (b) at 28°C.

carbohydrates remaining in the lignin residue. Furthermore, prolonged exposure (60 and 120 min) of the wood samples to HF, at ambient temperature, caused an increase in the residual carbohydrate content. This indicates that reassociation of some carbohydrate components with lignin may occur. Such reaction may, in fact, be expected in view of the known reactivity of carbohydrates with aromatic hydrocarbons as well as with lignin in HF, shown to result in acid-stable condensation products that presumably arise through Friedel-Crafts electrophilic alkylations[20]. A small amount of residual fluorine (less than 1%) appears to be present in the lignin residues, suggesting that glycosyl fluoride[2] may account for part of the residual carbohydrate.

Depolymerisation of lignin is known to occur under conditions of acid-catalysed solvolysis, through hydrolysis of alkyl aryl ether linkages, leading to the formation of Hibbert-type ketones and phenols[21,22]. Such reactivity was found in the ethanolysis of alkyl aryl ether linkages, where carbonyl and phenolic hydroxyl groups were formed

Table 1. Residual carbohydrate, Klason lignin and fluorine content of lignin samples resulting from time-correlated extraction of birch wood-meal with hydrogen fluoride.

Hydrolysis time (min)	Insoluble residue (%)	Total Klason lignin in residue (%)	D-xylose in residue (%)	D-glucose in residue (%)	Total D-xylose and D-glucose (%)	Fluorine (%)
At 23°C (HF/Wood, 4:1 w/w)						
10	34.5	68.3	12.7	16.3	29.0	0.83
20	31.1	75.9	8.3	14.5	22.8	0.55
30	28.8	81.7	8.4	9.0	17.4	0.40
60	30.5	79.8	8.4	10.5	18.9	0.56
120	32.5	73.1	11.0	14.8	25.8	0.63
At 0°C (HF/Wood, 4:1, w/w)						
60	40.2	63.1	14.2	21.7	35.9	0.76
120	36.7	67.2	12.9	18.9	21.8	0.62
180	31.9	73.9	8.6	15.3	23.9	0.32
300	29.1	81.2	8.4	9.0	17.4	0.22
At 20°C (HF/Wood, 10:1, w/w)						
30	30.9	74.4	8.2	14.3	22.5	
60	28.6	81.4	8.3	9.5	17.8	

in an approximately equal ratio[23]. The formation of carbonyl groups was also reported in lignin resulting from wood autohydrolysis[24,25], with a simultaneous increase in the carbonyl infrared absorption frequencies as the autohydrolysis time was prolonged. In order to investigate possible changes of this kind in the molecular structure of lignin under the influence of HF, infrared spectra of lignin samples were measured as a function of the residence time of wood in HF. An evaluation of the possible variations in the content of phenolic hydroxyl groups was simultaneously undertaken in order to correlate these results.

The IR spectra of lignins that resulted from HF treatment of wood under varying conditions of residence time and temperature (Figure 2) do not show significant differences. In particular, no difference in the intensity of the carbonyl absorption band at 1730 cm^{-1} was observed. This can be considered as an indication that, at least in the range of conditions studied, no significant formation of keto groups such as would be expected in Hibbert-type processes occurs.

In order to evaluate more precisely the nature of the absorption band at 1730 cm^{-1}, the lignin sample with the lowest carbohydrate content (30 min HF treatment at 23°C) was subjected to the reagents illustrated in Figure 3. Treatment with a buffer solution of pH 7 showed neither a change of the intensity, nor a shift in the position of this absorption band, suggesting the absence of any significant proportion of carboxyl groups in the sample. Moreover, mild alkaline hydrolysis eliminated the 1730 cm^{-1} absorption band, exposing a small shoulder at 1720 cm^{-1}. Identical results were also obtained when the lignin residues were reduced with sodium borohydride under mild alkaline conditions. It is therefore likely that this carbonyl absorption band originates mainly from ester linkages present in wood, and to a lesser extent from residual non conjugated carbonyl groups (residual small shoulder at 1720 cm^{-1}). Esters are known to be usually stable in anhydrous hydrogen fluoride[26].

The absence of any detectable cleavage of alkyl aryl ether linkages in HF-lignin was further confirmed by diazomethane methylation of a series of samples resulting from gradually prolonged exposure of wood to HF, either at 0°C or 23°C. From previous results[23], an increase in the

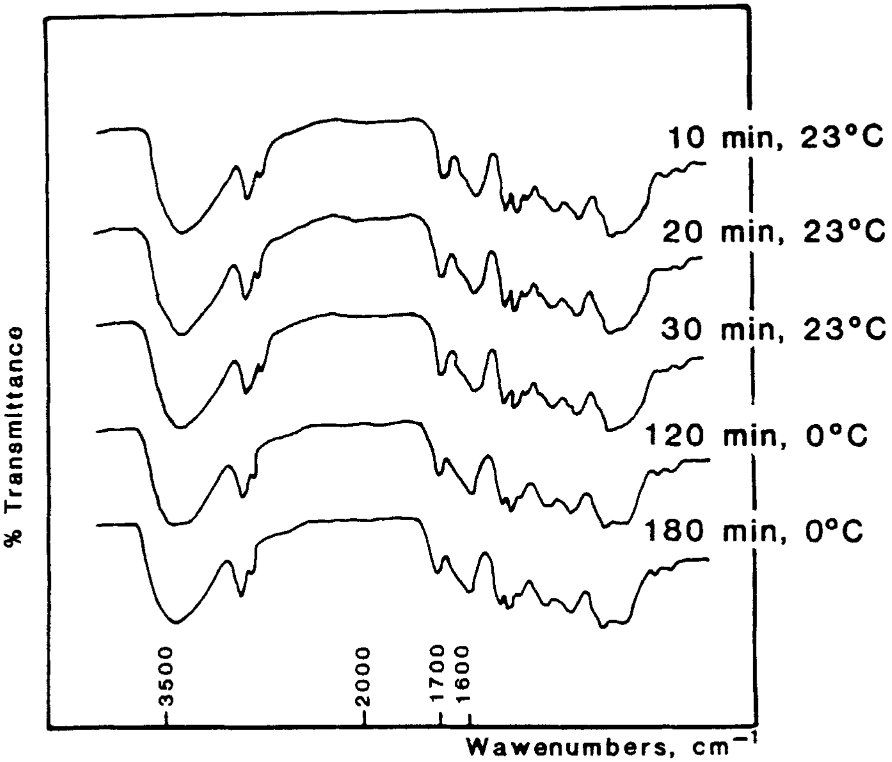


Figure 2.- Comparative infrared spectra (KBr) of lignin samples resulting from the action of HF on birch wood according to time of contact (min) and temperature.

methoxyl group content would be expected owing to the newly generated, phenolic hydroxyl groups. This was in fact not observed to any significant extent (Table 2), in agreement with the aforementionned infrared studies. Because of the possibility that a time-correlated variation of the phenolic hydroxyl-group content during the HF treatment of wood may not have been observable because of a very fast alkyl aryl ether cleavage in the early phase of the treatment, some alkaline depolymerizations were attempted. Lignin is known to depolymerize in alkali at high temperature, with cleavage of the aryl ether linkages between phenylpropane units and the simultaneous formation of phenolic

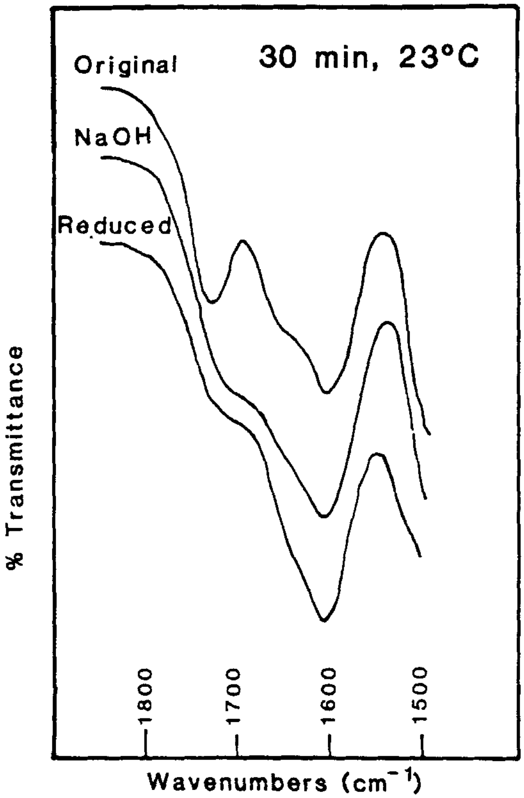


Figure 3.- Investigation of the nature of the IR-carbonyl band in HF-lignin.

hydroxyl groups[27]. The cleavage of α-aryl ether linkages is known to occur relatively easily under certain conditions[27], when the cleavage of β-aryl-ethers is better achieved in the presence of hydrosulfide ions[27] or redox systems like anthraquinone[28]. Both types of linkage are known to be cleaved under the usual acidic solvolytic conditions[21,23].

Alkaline treatments were performed with lignin preparations low in residual carbohydrate, i.e. samples obtained from meal wood treated with HF for 30 min at 23°C, in order to minimize any side effect which might be due to that component. In a first series of experiments, 2 N sodium

Table 2. Estimation of the increase in phenolic hydroxyl group content of birch wood lignin samples isolated after various hydrolysis times at 23° and 0°C in HF as determined by subsequent diazomethane etherification.

Reaction time with HF (Min)	Methoxyl group Content	Methoxyl content (after diazomethane methylation)	Increase in methoxyl Content
Lignin extracted at 23°C			
10	22.6	30.6	8.1
20	20.7	30.3	9.6
30	18.9	28.6	9.7
60	19.2	28.5	9.3
120	20.0	31.3	11.3
Lignin extracted at 0°C			
60	20.2	29.2	9.7
120	19.7	29.5	9.8
180	20.0	29.6	9.6
300	20.1	29.8	9.7

hydroxide was used, at 170°C and with increasing reaction times. In two further experiments, anthraquinone was added (Table 3). The formation of new phenolic hydroxyl groups was followed by the increase in methoxyl content after treatment with diazomethane. The action of base alone resulted in a small increase in methoxyl content, signifying the formation of small amounts of new phenolic hydroxyl groups, in direct

Table 3. Estimation of the increase in phenolic hydroxyl group content of HF-birch wood lignin after respective alkaline and alkaline-anthraquinone treatments.

Reaction time (min)	Methoxyl content after diazomethane methylation
in 2 N NaOH at 170°C	
0	28.6
10	32.0
20	32.5
30	33.0
60	33.3
120	33.9
in 2 N NaOH and anthraquinone at 170°C	
60	38.3
120	40.9

proportion with the length of the base treatment. This small increase has probably to be related to hydrolysis of ester groups as well as to hydrolysis of α-O-4 alkyl aryl ether linkages, the former being perceptible in the net methoxyl increase within the first 10 min of alkaline treatment. Alkaline depolymerization with anthraquinone catalysis led to an even greater methoxyl group incorporation and, therefore, liberation of additional phenolic groups (Table 3), in agreement with a probable additional cleavage of β-O-4 alkyl aryl ether linkages. These results are thus in further support of the hypothesis that α- and β-alkyl aryl ether linkages should still be present in HF-lignins, at least for the range of reaction conditions studied.

Condensation of lignin is known to occur under the usual conditions of acidolysis[29], and this structural change is reflected, among other things, in the time-dependent decrease in the yield of aromatic aldehydes obtainable by alkaline nitrobenzene oxidation[30]. A similar reactivity is noticeable for lignin resulting from HF wood extraction. The data in Table 4 show an important decrease in the yield of vanillin and syringaldehyde that is obviously related to the time of contact with HF and temperature used in the experiment. A slow decrease in the molar ratio of syringaldehyde to vanillin is also noticed as the reaction time increases. In order to obtain a general estimate of the extent of condensation of lignin in HF, a comparison was attempted with birch wood lignin samples derived from acidolysis with other mineral acids, namely sulfuric and hydrochloric acids. As regards the HF-lignin samples, they were obtained under the conditions of extraction (30 min at 23°C) required for optimum recovery of carbohydrates. For dilute sulfuric acid, prehydrolysis was carried out with 0.5% acid at 140°C for 1 h followed by hydrolysis at 180°C for 2 h[30]. The hydrochloric acid-treated sample was isolated after prehydrolysis of birch wood-meal with 30% acid, followed by hydrolysis with 43% acid at 50°C for 2 h[31]. The respective residual carbohydrate contents were 5.2 and 8.4%.

Comparative, alkaline nitrobenzene oxidation of these acidolysis lignin samples, and determination of total aldehydes produced shows (Table 5) that HCl-lignin gave the highest yield. The yields from HF and H_2SO_4-lignins were lower, but comparable to each other. Although it is understood that lignin may suffer different structural changes upon different acid treatments, which may account for variations in the yield of aromatic aldehydes upon nitrobenzene oxidation, this result may indicate that HF-lignin has suffered extensive condensation, correlated with the residence time of wood in HF. Such reactivity may be related to the known propensity of hydrogen fluoride to stabilize carbonium ions[32], species which are known to account for lignin as well as the previously discussed lignin carbohydrate[2,29] condensation reactions. It correlates with the known reactivity of lignin in hydrochloric acid where the

Table 4. Effect of time and temperature of exposure to HF on the yields of vanillin and syringaldehyde derivable from birch wood lignin after HF extraction and alkaline nitrobenzene oxidation.

Time (min)	Vanillin (Mole %)	Syringaldehyde (Mole %)	Total aldehydes (Mole %)	SYR/VAN
Lignin extracted at 23°C				
0	20.3	22.3	42.6	1.1
10	14.3	14.3	28.6	1.0
20	12.0	12.0	24.0	1.0
30	10.4	9.4	19.8	0.9
60	8.7	6.9	15.6	0.8
120	7.2	5.7	12.9	0.8
Lignin extracted at 0°C				
0	20.3	22.3	42.6	1.1
60	12.3	12.3	24.6	1.0
120	9.0	10.0	19.0	0.9
180	8.9	7.1	16.0	0.8
300	6.8	5.4	12.2	0.8

extent of condensation is known to be lower as compared to sulfuric acid solvolysis[29], in agreement with such concepts, although this must be tempered by relative conditions including hydronium ion concentration. The enhanced reactivity of dialkoxy-aryl residues of lignin in HF, as experienced from the comparative decrease in the molar ratio of syringaldehyde to vanillin after nitrobenzene oxidation of lignin resulting from increased time of contact with HF is a further point in support of this hypothesis.

Table 5. Comparative yields in aromatic aldehydes and syringic acid resulting from alkaline nitrobenzene oxidation of various acidolysis lignins.

	Vanillin (Mole %)	Syringaldehyde (Mole %)	Total aldehydes (Mole %)	SYR/VAN	Syringic acid (Mole %)
Total birch Wood	20.3	22.3	42.6	1.1	0
HF-lignin	10.4	9.4	19.8	0.9	~8
HCl-lignin	9.1	16.4	25.5	1.8	0.5
H_2SO_4-lignin	8.4	10.9	19.3	1.3	1.5

In the prehydrolysate and hydrolysate of both hydrochloric and sulfuric acid treatment of wood, an important proportion of the original wood lignin, amounting to 15 and 10% respectively, was detected (Table 5). Treatment with HF yielded no acid soluble lignin. This result, too, may be associated with the previously discussed condensation scheme, as well as the low extent of hydrolysis of aryl ether and ester bonds. Of further interest in this connection is the syringaldehyde/vanillin ratio obtained after nitrobenzene oxidation of lignins originating from different acidolysis methods, and the proportion of syringic acid simultaneously produced. The HF-lignin is seen (Table 5) to yield considerable proportions (7-8%) of this acid, whereas very small amounts of it arose from the HCl- and H_2SO_4-lignins.

ACKNOWLEDGMENTS

This research was supported by a Grant from the Action Thématique Programmée of the C.N.R.S. "Valorisation de la Matière Végétale par voie Chimique". J.P. present address : Forest Research Institute, Terma Alkamanos, Athenes, 11528, Greece), thanks the C.N.R.S. for a research fellowship.

REFERENCES

1. Presented in part at the 9th Cellulose Conference, Syracuse (N.Y.), May 24--27, 1982. For a preliminary report, see : J. Defaye, A. Gadelle, J. Papadopoulos and C. Pedersen, J. Appl. Polym. Sci. : Appl. Polym. Symp., 37, 653 (1983).

2. J. Defaye, A. Gadelle and C. Pedersen, Carbohydr. Res., 110, 217 (1982).

3. J. Defaye, A. Gadelle and C. Pedersen, Carbohydr. Res., 136, (1985).

4. J. Defaye, A, Domard, A. Gadelle and C. Pedersen, 9th Intern. Symp. Carbohydr. Utrecht (July 1-7, 1984), abstract A 2.35, p. 96.

5. Th. Bentsen, in Energy from Biomass, 2nd E.C. Conference, A. Strub, P. Chartier and G. Schlesser, (ed.), Applied Science Pub., London, 1982, p. 1103-1105.

6. R. Franz, R. Erckel, Th. Riehm, R. Woernle and H.M. Deger, ibid., p. 873-878.

7. S.M. Selke, M.C. Hawley and D.T.A. Lamport, in Wood and Agricultural Residues, E. J. Soltes (ed.), Academic Press, New-York 1983, p. 329-349.

8. G. Pfleiderer and E. Koch, I.G. Farbenindustrie A.G., Fr. Pat. 711, 393 (Feb. 17, 1931) ; I.G. Farbenindustrie A.G., Ger. Pat. 585, 318 (June 21, 1930) ; H. Bohunek, H. Hoch and G. Mayrhofer, Fr. Pat., 809, 208 (Feb. 26, 1937) ; Br. Pat. 476, 191 (Dec. 3, 1937).

9. R. Erckel, R. Franz, R. Woernle and R. Riehm, Hoechst Aktiengesellschaft, Fr. Pat. 2515209 (Oct. 21, 1982) and 2515210.

10. I.S. Goldstein, in Organic Chemicals from Biomass, I.S. Goldstein, (ed.), CRC Press, Inc.: Boca Raton, Fla., 1981, p. 281-286.

11. Y.Z. Lai and K.V. Sarkanen, in Lignins, Occurence, Formation, Structure and Reactions, K.V. Sarkanen and C.H. Ludwig (ed.), Wiley-Interscience, New York, 1971, p. 165-230.

12. M.H. Winston, C.L. Chen, J.S. Gratzl and I.S. Goldstein, 181th ACS Meeting, Atlanta, Ga, March 1981.

13. I.S. Goldstein, R.J. Preto, J.L. Pittman and T.P. Schultz, The Ekman-Days 1981, Proc. Int. Symp. Wood Pulp. Chem., Stockholm June 9-12, 1981, vol. 4, p. 9-13.

14. L.G. Borchardt and C.V. Piper, Tappi, 53, 257 (1970).

15. J.F. Saeman, W.F. Moore, P.L. Mitchell and M.A. Millet, Tappi, 37, 336 (1954).

16. I.A. Pearl and L.R. Busche, Tappi, 43, 961 (1960).

17. A.I. Vogel, Practical Organic Chemistry, Longmans, London, 3rd ed. 1961, p. 973.

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

19. J. Papadopoulos, C.L. Chen and I.S. Goldstein, Holzforschung, 35, 283 (1981).

20. G. Louis, C. Knauel, F. Micheel and M. Pesenacker, ACS Symp. Ser., 39, 227 (1977).

21. L. Mitchell and H. Hibbert, J. Am. Chem. Soc., 66, 602 (1944).

22. E. Adler, J.M. Pepper and E. Erikson, Ind. Eng. Chem., 49, 1391 (1957).

23. K. Sarkanen and C. Schuerch, ibid, 77, 4203 (1957).

24. M.G.S. Chua and M. Wayman, Can. J. Chem., 57, 2603 (1979).

25. M. Wayman and M.G.S. Chua, ibid, 57, 2612 (1979).

26. H. Paulsen, Adv. Carbohydr. Chem. Biochem., 26, 127 (1971).

27. J. Gierer, Wood Sci. Technol., 14, 241 (1981).

28. J. Gierer, O. Lindeberg and I. Noren, Holzforschung, 33, 213 (1979) ; L.L. Landucci, J. Wood Chem. Technol., 1, 61 (1981).

29. Y.Z. Lai and K.V. Sarkanen, in Lignins, Occurence, Formation, Structure and Reactions, K.V. Sarkanen and C.H. Ludwig, (ed.), Wiley Interscience, New-York 1971, p. 165-240.

30. M. Oshima, Wood Chemistry Process Engineering Aspects (Chemical Process Monograph n° 11), Pearl River, N.Y. Noyes Development Corp. 1965.

31. J. Papadopoulos, Ph.D. Thesis, North Carolina State University, Raleigh NC (1981).

32. M. Kilpatrick and J.G. Jones, in The Chemistry of Non-Aqueous Solvents, J.J. Lagowski (ed.), Academic Press, New-York, 1967, p. 43-99.