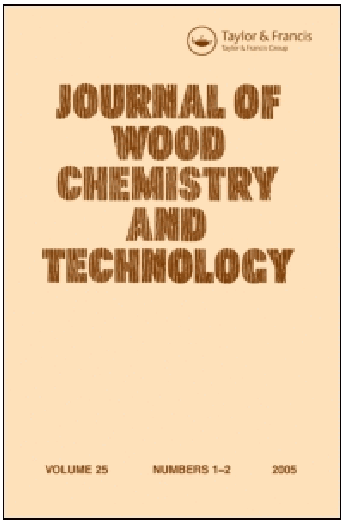

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ANALYSIS OF LIGNIN AND CHLOROLIGNIN RESIDUES IN A BEECH XYLAN FRACTION BY PYROLYSIS GAS CHROMATOGRAPHY MASS SPECTROMETRY

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ABSTRACT

The xylan fraction of Beech wood was analysed by Curie point pyrolysis gas chromatography mass spectrometry. Chlorinated methoxyphenols were detected among the pyrolysis products. These compounds are released from chlorolignin residues present in the xylan preparation. The chlorination must have occurred during delignification of the holocellulose with sodium chlorite.

INTRODUCTION

A standard procedure for xylan isolation starts from a highly delignified pulp, the so-called holocellulose[1,2]. Holocellulose is defined as the water-insoluble carbohydrate portion including cellulose and hemicelluloses[3]. It is usually prepared by removal of lignin with sodium chlorite[4], or by several treatments with chlorine in ice-water, followed by exhaustive extraction of the oxidation products of the chlorinated lignin with alcoholic ethanolamine[5]. An ideal delignification should result in a total removal of lignin without chemical attack on the polysaccharides, but probably no delignification procedure will satisfy this requirement.

The pyrolysis gcms data of total Beech wood show marker compounds for xylanes, celluloses and lignin[6]. The presence of several guaiacyl and syringyl derivatives in the flash pyrolysate of the holocellulose[7] and xylan of Beech wood points to residual lignin-like material in these fractions.

Surprisingly, a number of chlorinated methoxyphenols was also identified in the pygcms data of both fractions. This suggests the presence of chlorolignin as residues in the polysaccharide preparations. This paper reports on the pygcms analysis of lignin and chlorolignin residues in a Beech xylan preparation.

EXPERIMENTAL

Xylan Fraction

The xylan fraction was a gift from Dr. J. Puls and Dr. O. Faix (Bundesforschungsanstalt fur Forst und Holzwirtschaft, Hamburg, BRD), which was isolated using the procedure as described by Dietrichs and Zschirnt[4]. This procedure consists of repeated treatment of the wood chips with sodium chlorite (0.5 *M*) at pH 4. The xylan fraction was obtained by extraction of the holocellulose with 4.5% sodium hydroxide solution.

Pyrolysis Unit

Figure 1 shows a schematic diagram of the pyrolysis unit designed by our group, which is used for the analysis of plant materials. The sample is applied

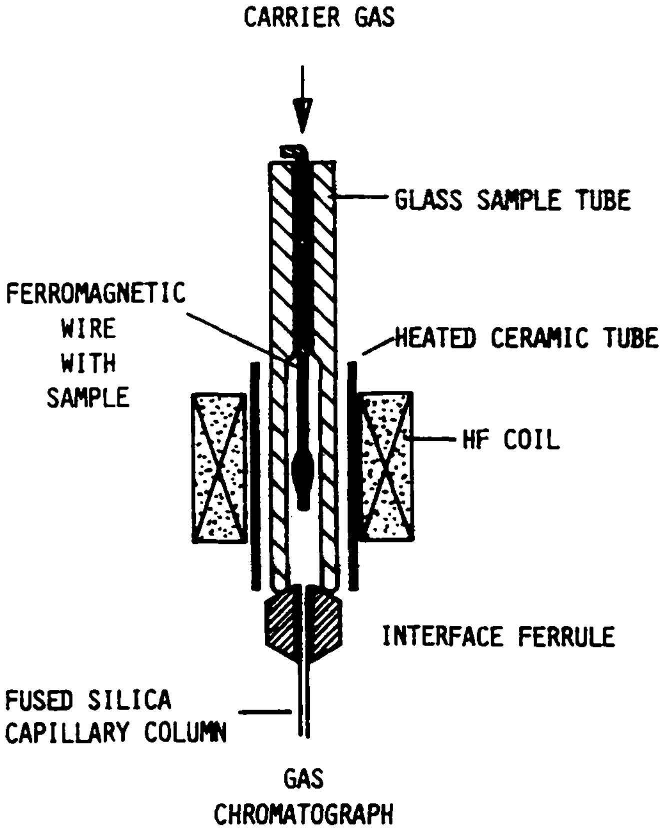

Figure 1 Schematic diagram of the FOM-3LX Curie point pyrolysis unit for splitless injection of pyrolysate on capillary columns.

from a suspension in water or from solution onto a ferromagnetic wire, which is inserted into a glass liner. The liner is placed into the pyrolysis unit (FOM 3-LX) and rests on a Kalrez interface directly above the entrance of the capillary column. The glass liner is surrounded by a ceramic tube kept at 180°C, which in turn is surrounded by a high frequency coil. The unit is flushed with helium, which is also used as the carrier gas. The ferromagnetic wire is inductively heated to its Curie point within 0.1 s. Thermal energy is transferred to the sample, which evaporates and/or is pyrolysed. The volatile products are swept to the beginning of the capillary column.

Chromatographic Conditions and Mass Spectrometry

The xylan fraction from Beech wood was analyzed at a Curie point temperature of 610°C (sample size about $3 \cdot 10^{-6}$ gram). Pygcms was performed with a Packard 438-S GC and a JEOL DX-300/DA-5000 double focussing mass spectrometer with data system. The column used was a 50 meter CP Sil 5 CB fused silica capillary column (ID. 0.32 mm, film thickness 1 μm). The column ended directly into the ion source. The gc oven was kept at 30°C during pyrolysis and was subsequently programmed to 300°C at a rate of 4°C/min. Compounds were ionised at 70 eV electron impact voltage. The acceleration voltage was 3 kV. The scan speed was 0.5 s/dec. Chemical ionization was performed in isobutane.

The sofware package in the JEOL data system was used without modifications.

RESULTS

Apart from pyrolysis products indicative of the acetylglucurono-xylan backbone, the pyrolysis gcms data show the presence of guaiacyl and syringyl

TABLE 1

Identified Guaiacol and Syringol Derivatives in the pyrolysate of the Xylan Fraction Isolated from Beech (*Fagus sylvatica*)

Peaknr.:	Identity:	Scannr.:	Peak area:	Structure:
1	guaiacol	1680	46	G-H
2	methylguaiacol	1960	7	G-C
3	hydroxyguaiacol	2140	5	G-OH
4	vinylguaiacol	2250	11	G-C=C
5	syringol	2320	17	S-H
6	guaiacylaldehyde	2430	2	G-CHO
7	methylsyringol	2540	7	S-C
8	guaiacylethanal	2555	2	G-C-CHO
9	guaiacylprop-2-ene (*trans*)	2570	3	G-C=C-C
10	guaiacylethanone	2640	6	G-CO-C
11	vanillic acid methyl ester	2680	1	G-CO-O-C
12	guaiacylpropan-2-one	2720	10	G-C-CO-C
13	vinylsyringol	2780	4	S-C=C
14	syringylaldehyde	2950	2	S-CHO
15	acetylsyringol	3100	2	S-CO-C
16	syringylpropan-2-one	3160	4	S-C-CO-C

TABLE 2

Identified Chloromethoxyphenol Derivatives in the pyrolysate of the Xylan Fraction Isolated from Beech (*Fagus sylvatica*)

Peak nr.:	Identity:	Scan nr.:	Peak area:	Structure:
1	6-chloroguaiacol	2200	2	Cl-G-H
2	3-chlorosyringol	2630	41	Cl-S-H
3	6-chlorovinylguaiacol	2680	2	Cl-G-C=C
4	3-chloromethylsyringol	2850	3	Cl-S-C
5	6-chloroguaiacylpropan-2-one	2980	1	Cl-G-C-CO-C
6	3-chlorovinylsyringol	3050	27	Cl-S-C=C
7	3-chlorosyringylethanal	3280	3	Cl-S-C-CHO
8	3-chlorosyringylprop-2-ene (*cis*)	3290	6	Cl-S-C=C-C
9	3-chlorosyringylpropan-2-one	3380	18	Cl-S-C-CO-C
10	3-chlorosyringylpropanal	3750	3	Cl-S-C-C-CHO

derivatives as lignin marker compounds (table 1) as well as chlorinated methoxyphenol derivatives (table 2).

The partial total ion current trace (scan range 1600-3800) of pygcms data of the xylan fraction isolated from Beech wood is shown in figures 2a and 3a. Figures 2b and 3b show a partial total ion current trace of the methoxyphenols and of the chlorinated methoxyphenols respectively. The mass scale was set to m/z 110-250 to delete all peaks with m/z values below m/z 110. This eliminates contributions of many polysaccharide marker peaks to the total ion current. All methoxyphenols and chlorinated methoxyphenols have major peaks above m/z 110. Peak numbers in figures 2b and 3b refer to the compounds listed in tables 1 and 2 respectively.

The identification of the guaiacyl and syringyl derivatives listed in table 1, is based on the available data on methoxyphenol derivatives, which are supported by high resolution gcms data[6]. Identification of the spectra of chlorinated methoxyphenols is based on isotope ratio and on comparison with the fragmentation patterns of guaiacol and syringol derivatives. Figure 4 shows the mass spectra of syringol, vinylsyringol and syringylpropan-2-one together with their chlorinated analogues.

It is interesting that the order of elution from this capillary column is almost identical for methoxyphenols and their analogous monochloroderivatives. The only exception is 3-chlorosyringol which elutes before 6-chlorovinylguaiacol (table 2). The relatively high abundance of 3-chlorosyringol, 3-chlorovinylsyringol and 3-chlorosyringylpropan-2-one is also striking (table 2).

DISCUSSION

The principle aim of pulp bleaching is to increase brightness, which is related to the presence of light-absorbing chromophoric components. These

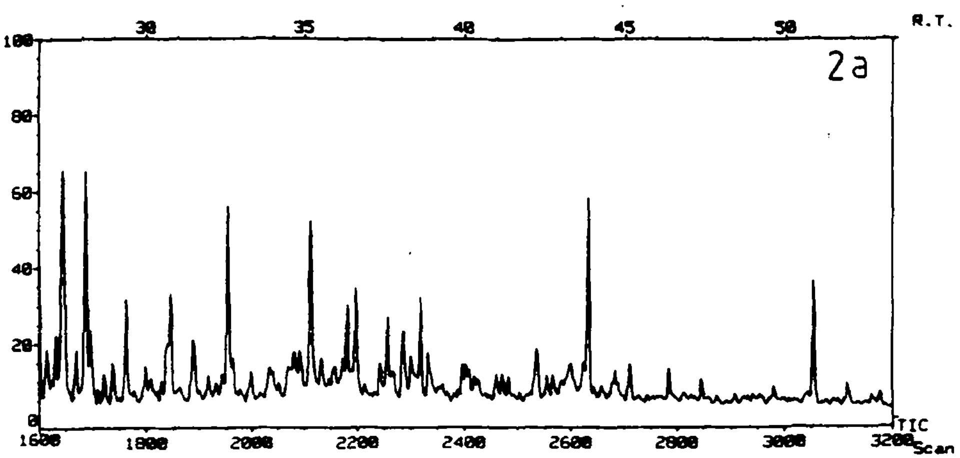

Figure 2a Partial total ion current trace of pygcms data of the xylan fraction isolated from Beech wood.

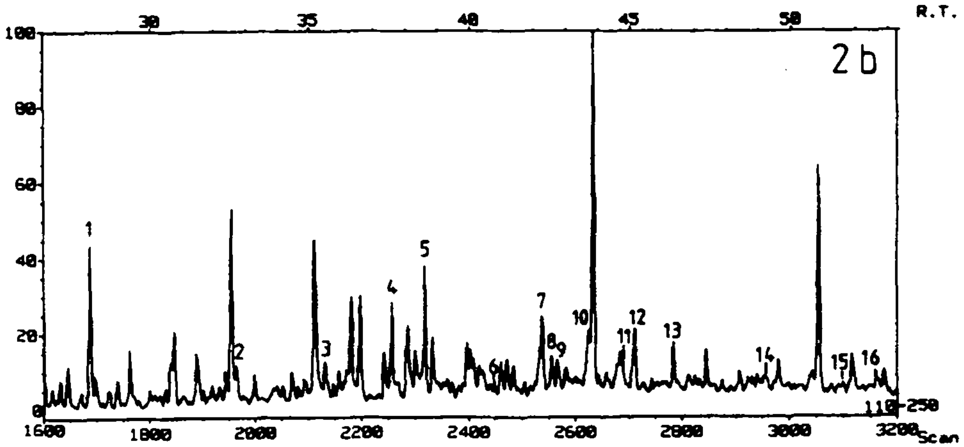

Figure 2b Partial total ion current trace of the xylan fraction isolated from Beech wood. Mass scale is set to m/z 110-250. Peak numbers refer to the compounds listed in table 1.

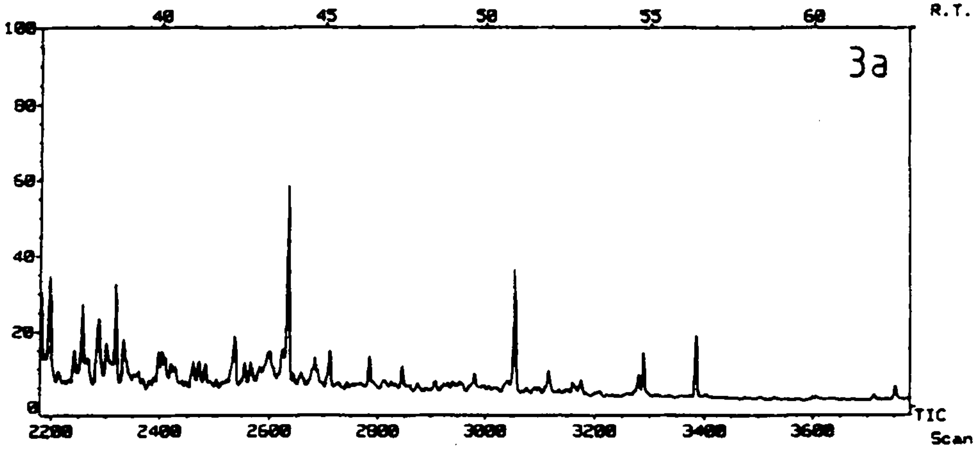

Figure 3a Partial total ion current trace of pygcms data of the xylan fraction isolated from Beech wood.

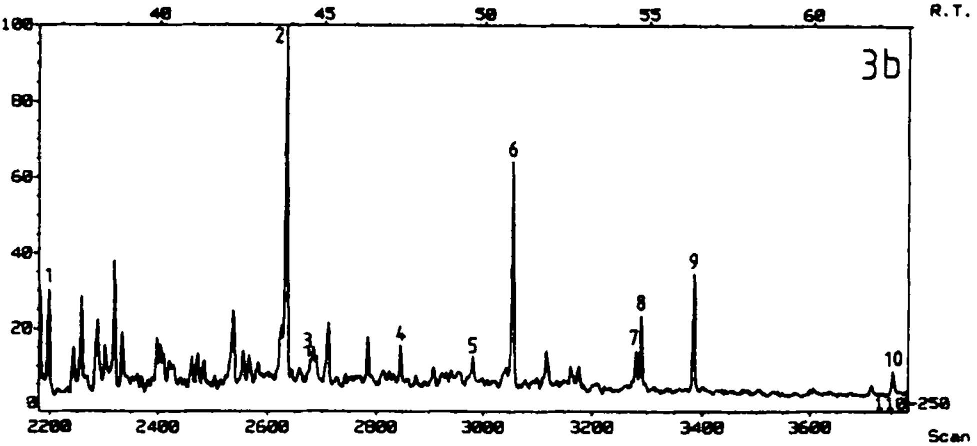

Figure 3b Partial total ion current trace of the xylan fraction isolated from Beech wood. Mass scale is set to m/z 110-250. Peak numbers refer to the compounds listed in table 2

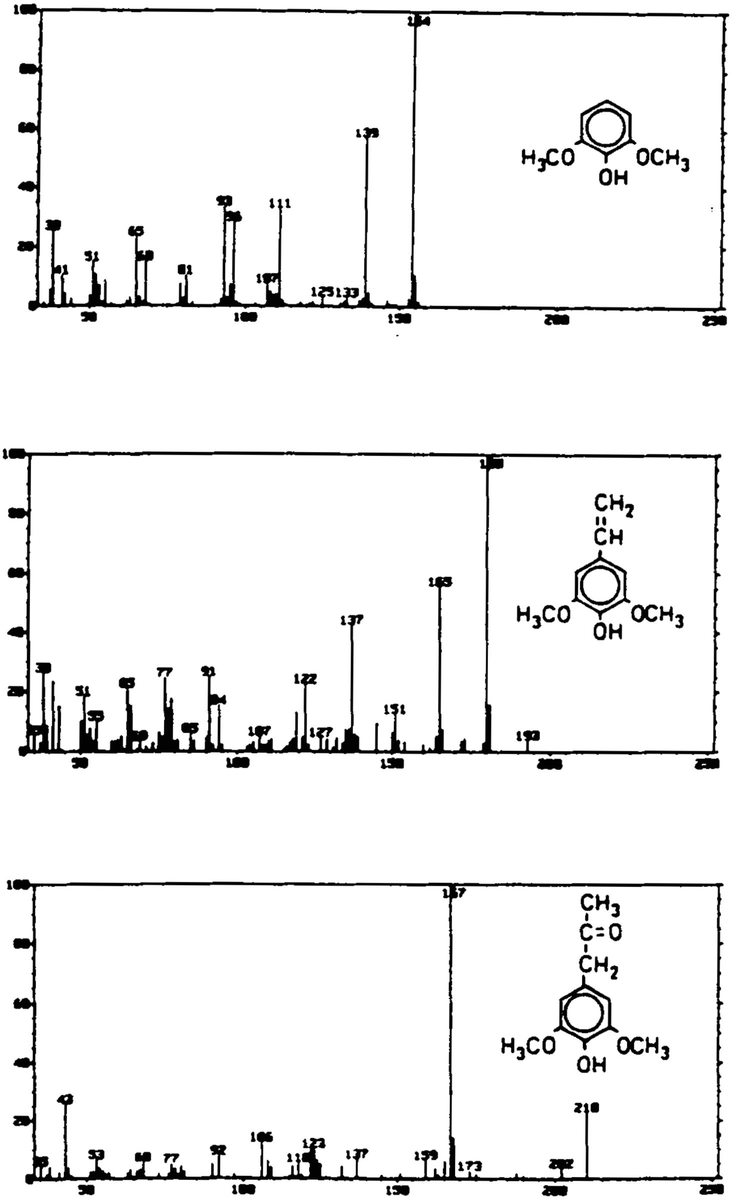

Figure 4 Mass spectra of syringol and 3-chlorosyringol, vinylsyringol and 3-chloro-vinylsyringol, syringylpropane-2-one and 3-chlorosyringylpropan-2-one.

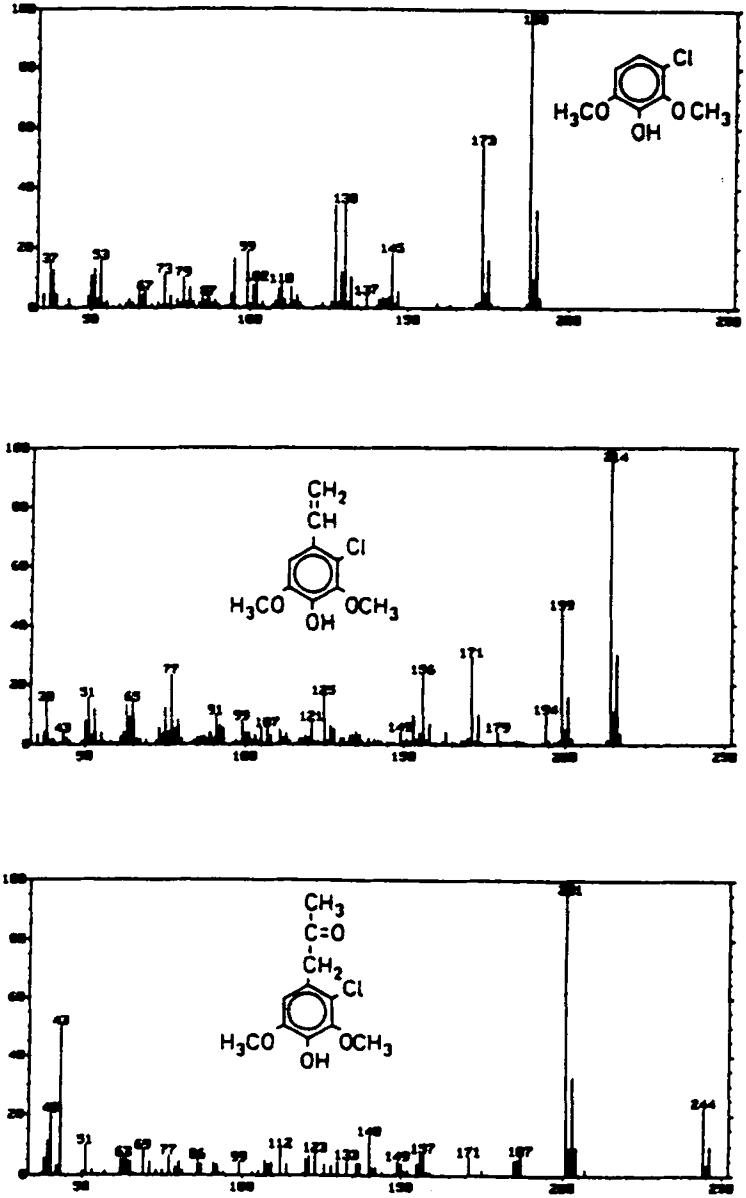

Figure 4 Continued

are predominantly functional groups of degraded and altered residual lignin. Generally, the process of bleaching can be devided into two main groups, namely lignin-preserving bleaching (converting and stabilizing chromophoric groups without loss of substance) and lignin-removing bleaching. In the latter process other compounds (extractives and ash components, polyoses) and insufficiently delignified particles (shives, bark specks) may also be removed along with the lignin[4,5]. Therefore, bleaching can be regarded additionally as a purification process.

The oxidation of lignin by chlorine dioxide or chlorite is much more complicated than degradation by hypochlorite. In alkaline media chlorine dioxide is reduced to chlorite. A similar reaction can occur in the presence of hydroxyl ions, in which two chlorine dioxide molecules disproportionate to form chlorite and chlorate ions[8].

In acidic media chlorine dioxide is completely reduced. Chlorite, on the other hand, is stable under neutral as well as alkaline conditions and hence has to be acidified to be an effective oxidizing agent. Obviously, chlorous acid rather than the chlorite anion is the reactive species in acidic media. Hypochlorous acid is formed as an intermediate in the reduction of chlorous acid and since it has a higher oxidation potential than chlorous acid, it can oxidize the latter to chlorine dioxide[8]. It is therefore evident that in acidic media not only both chlorine dioxide and chlorous acid, but also hypochlorous acid and molecular chlorine are involved in the reaction, no matter whether chlorine dioxide or chlorite was used initially as an oxidizing agent.

In acidic solutions elemental chlorine is one of the reaction intermediates and will give rise to reactions characteristic for this species, such as ring substitutions and hydrolysis of alkyl-aryl ether bonds[8]. This partly might account for the formation of monochlorinated methoxyphenolics, depending on the reaction conditions during bleaching.

Model compound studies have shown that oxidation of the methoxy-phenol nucleus is preceded by chlorination, and experimental evidence supports the hypothesis that the reactive species in the chlorination reaction is hypochlorous acid or even perhaps the hypochlorite anion and chlorous acid in chlorite and chlorine dioxide bleaching respectively[9,10]. In alkaline solutions almost no molecular chlorine is present. In monomethoxyphenols the *ortho*-position is preferentially chlorinated[8], in dimethoxyphenols only the *meta*-position is available for chlorination.

It should be emphasized that the presence of mono- and dimethoxyphenols in the Beech wood xylan pyrolysate is due to incomplete delignification. In the chlorite holocellulose method, a considerable loss of polysaccharides occurs if delignification is carried to completion. Therefore, it is necessary to halt the treatment while the holocellulose still contains 2-4% lignin[11]. Part of this residual lignin is co-extracted with the xylan in the extraction of the holocellulose with sodium hydroxide solution. The presence of lignin linked to the acidic side chains of the xylan possibly also accounts for part of the residual lignin-like material in the xylan fraction[12].

During the delignification with sodium chlorite part of the lignin can be chlorinated. Chlorinated methoxyphenols as well as other chlorinated compounds have been identified earlier in spent liquors from pulp bleaching plants[13]. The chlorinated methoxyphenols identified in the Beech wood xylan fraction are formed on pyrolysis of the partly chlorinated residual lignin. The presence of these compounds is probably an artefact due to the use of sodium chlorite in one of the stages of the isolation procedure.

When we compare the ratio of guaiacyl and syringyl derivatives (G/S ratio) in the pygcms data of Beech wood with the G/S ratio in the Beech wood xylan fraction, the difference is striking. The abundance of syringyl derivatives in Beech wood pyrolysate[7] is much higher than the abundance of guaiacyl derivatives. Syringylprop-3-en-1-ol (*trans*) and syringylethanal are the only dimethoxy compounds with a lower abundance than their monomethoxy analogues.

If we consider the G/S ratio in the pygcms data from the xylan fraction, the abundance of guaiacyl derivatives is much higher than the abundance of syringyl derivatives and the range of methoxyphenol compounds is much smaller. Here, only syringaldehyde has a slightly higher abundance than its monomethoxy analogue (table 1). A possible explanation for this reversed distribution ratio is the stability of the compounds involved. During the isolation procedure demethoxylation of syringyl units in the lignin polymer may occur. This is not improbable, since it is generally accepted that monomethoxyphenolics are more stable than their dimethoxy analogues. The oxidising effect of the bleaching procedure may account for the smaller range of methoxyphenols, all of which have highly oxidised side chains in comparison with the methoxyphenols found in the pygcms data of Beech wood.

The G/S ratio in the chlorinated methoxyphenols differs from the non-chlorinated phenols. The chlorinated dimethoxyphenols are more abundant than the chlorinated monomethoxyphenols. The higher abundance of chlorinated dimethoxyphenols is possibly accounted for by the reactivity of methoxy-phenols towards chlorination with sodium chlorite and its intermediate products like chlorine dioxide, molecular chlorine and hypochloric acid. The presence or absence of a free hydroxyl group (activating, *ortho-para* directing) should also be taken into account. Furthermore, the stability of chlorinated methoxyphenols may have some influence. With the data now available it is not possible to state with certainty which explanation(s) is (are) applicable here.

The high abundance of 3-chlorosyringolpropan-2-one, 3-chlorovinylsyringol and 3-chlorosyringol (table 2) indicates that there must be structural elements in the Beech lignin which resist further oxidation although initial oxidation can take place. It is tempting to speculate that β-1 linkages are involved here. As mentioned earlier, the oxidative degradation rate of phenolic ethers by hypochlorite is greatly favored by the presence of a free hydroxyl group. The abundance of the three above mentioned chlorinated syringols might have no free hydroxyl groups in the lignin polymer structure, thus only chlorination can occur, since oxidative break-down is hampered. This is in agreement with the statement that chlorination is the first step in the oxidative degradation by hypochlorite[8].

Another point of interest is that a number of depolymerisation products found in total Beech wood pyrolysate is not recovered in the pyrolysis products from the Beech wood xylan fraction. This phenomenon is probably correlated with the relatively high abundance of higher oxidized methoxyphenols. The oxidation of methoxyphenols with unsaturated alkyl side chains to methoxyphenols with an C_α- or C_β-oxygenated side chain position (e.g hydroxyl, carbonyl or keto group), is greatly favored by the reaction conditions under which bleaching is carried out.

In oxidation studies of lignin with sodium chlorite[9] as well as in the analysis of the high molecular weight fractions from the effluent of pulp and paper industries[13,14], a variety of chlorinated organic compounds such as chlorinated methoxyphenols and chlorinated methoxyphenol degradation products have been identified. In contrast with these results, we did not find any chlorinated methoxyphenol degradation products, nor di- or tri-chlorinated methoxyphenols, nor methoxyphenols with chlorinated side chains. The chlorination of side chains normally requires different reaction conditions (radical mechanism catalyzed by UV-light). Nuclear substitution requires a Lewis acid for catalysis, e.g $FeCl_3$[15]. Fe^{3+} ions are undoubtedly present in small amounts in Beech wood, so this catalysis is possible. The formation of di- and trisubstituted chloromethoxyphenols probably requires special reaction conditions, since introduction of a chlorine atom on the aromatic ring deactivates the ring towards further substitution, and chlorination is also competitive with rapid nuclear oxidation, the latter usually takes place immediately after chlorination[8].

Considering the amount of residual lignin, the data on the determination of the carbohydrate and lignin content of woods should be presented with due reserve. The isolation procedures should also be taken into account because of the strong influence of the isolation methods used on the chemical composition of the wood samples thus analyzed.

CONCLUSIONS

Summarizing the results of this study, it can be stated that the bleaching process is far from being an ideal delignification procedure. First, lignin removal is very incomplete in order to prevent severe polysaccharide degradation, consequently, the obtained polysaccharide fractions contain a considerable amount of residual lignin, and second, part of the residual lignin is chlorinated.

It is well known that wood is a very heterogeneous material. This survey shows that a number of pyrolysis products can be correlated with known chemical units in hardwood. At the present state of the investigation, the impurity of the "purified" fractions as well as the presence of artefacts due to the isolation procedure used cause severe problems and preclude a more detailled correlation.

Combined Curie point pyrolysis capillary gcms is an usefull microanalytical characterisation method for identification of plant materials and purified polysaccharide and lignin fractions. The pygcms data can provide structural information on the chemical nature of complex polymeric systems. This makes pyrolysis gcms a widely applicable identification method.

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