

# On the reactions and degradation of the lignin during steam hydrolysis of aspen wood

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**SUMMARY:** Acetone extracts of aspen wood subjected to steam hydrolysis according to the Iotech process have been investigated with special reference to lignin degradation products. The extracted materials included the major part of the lignin moiety of the wood. Fractions of "monomers" and "dimers" have been isolated from the acetone extract by procedures involving gel permeation chromatography. The yields of monomers were comparatively low and *p*-hydroxybenzoic acid was the main constituent of the monomer fractions. A series of *p,p'*-dihydroxystilbenes has been detected in the dimer fractions. Syringaresinol and related compounds were prominent constituents of the dimer fractions. More drastic steam hydrolysis resulted in a moderate increase of the amounts of low molecular mass compounds, in part due to formation of 5-hydroxymethyl-2-furaldehyde from hexoses.

The reactions of lignin during steam hydrolysis are discussed on the basis of the results from the studies of degradation products.

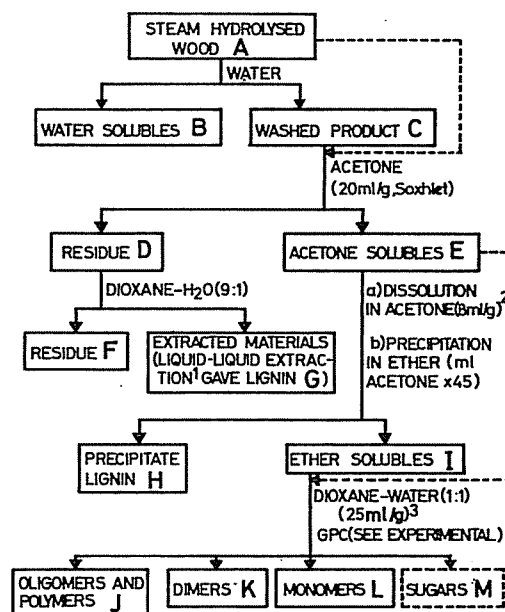
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In order to find in biomass an inexpensive and large supply of chemicals and organic materials (cf. 1) some technical procedures like steam hydrolysis of wood (1-8, cf. also 9) have recently been reconsidered.

One of the main advantages of this kind of process is to make readily available from the wood the three major components: a cellulose residue, a lignin fraction, and a hemicellulose fraction. The fractionation proceeds through selective extraction with different solvents. Steam hydrolysis according to the Iotech process (2, 3) has been shown to be a suitable pretreatment for the separation of the wood components along these lines (4). This paper describes the degradation of the lignin component of aspen wood with formation of low molecular mass compounds under the conditions for the Iotech procedure. It has previously been found in preliminary HPLC studies (6) that ether extracts of aspen wood treated according to this procedure contain a series of mononuclear aromatic compounds, *p*-hydroxybenzoic acid (*I*)<sup>1</sup> being a major constituent.

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<sup>1</sup>Italicized numbers designate compounds.



<sup>1</sup> To remove carbohydrates (10).

<sup>2</sup> A small amount of insoluble material was removed by centrifugation.

<sup>3</sup> Some materials (essentially fatty substances) did not dissolve and could be at least in part released by centrifugation before GPC.

Fig. 1. Fractionation of products extracted from steam hydrolysed wood (dashed lines show fractionation sequences performed in some experiments; when precipitation in ether is omitted, a sugar fraction (M) is obtained from the GPC column).

## Extraction and fractionation of lignin products

The steam hydrolysed wood was subjected to extractions followed by fractionations according to the scheme in fig. 1. Yields of various fractions obtained from aspen wood treated 45 sec (sample 45) and 205

Table 1. Yields of various fractions in per cent of the original wood from experiments 45 and 205 (see Experimental).

Fraction <sup>1</sup>	Sample 45 (45 bar/45 sec)	Sample 205 (45 bar/205 sec)
Crude product (A), %	92 <sup>2</sup>	78 <sup>2</sup>
Water solubles (B), %	18	4
Washed product (C), %	74	74
Acetone solubles (E), %	18	27
Residue (D), %	56	47
Lignin (G), %	3	1.5
Residue (F), %	50	44

<sup>1</sup> See the fractionation scheme in fig. 1.

<sup>2</sup> Does not include volatile products; the yield is to some extent lowered by mechanical losses.

Table 2. Yield of fractions in per cent of the original wood obtained from the acetone soluble materials (see table 1) of steam hydrolysed aspen wood (experiments 45 and 205).

Fraction <sup>1</sup>	Sample 45 (45 bar/45 sec)	Sample 205 (45 bar/205 sec)
Lignin (H), %	10.5 (OCH <sub>3</sub> , 18.6%)	15.7 (OCH <sub>3</sub> , 17.0%)
Ether solubles (I), %	6.3	10.5
"Polymers and oligomers" (J), %	2.3	4.5
"Dimers" (K), %	2.3 <sup>2</sup>	4.0 <sup>2</sup>
"Monomers" (L), %	0.8	1.2

<sup>1</sup> See the fractionation scheme in fig. 1.

<sup>2</sup> GPC analyses showed that substantial amounts of oligomers were present in this fraction.

sec (sample 205) with steam at 45 bar are given in tables 1 and 2. The major part of the lignin degradation products is found in the acetone-soluble fraction (E). Some lignin (lignin G) is obtained by a subsequent extraction with dioxane-water (9:1); this lignin was found to have a high molecular mass [GPC (Sephadex LH 60/DMF-HAc (100:1) showed that the molecular mass was >10,000]. An IR examination indicated that the proportion of lignin left in the residue (F) was very small [the band at 1510 cm<sup>-1</sup> (aromatic C-C skeletal vibrations) was practically absent and the spectrum resembled that of cellulose].

Analytical GPC experiments (fig. 2) showed that monomeric and dimeric material accumulated in the ether-soluble fraction I (small amounts of low molecular mass compounds were, however, found in fraction B, see below).

Polysaccharides and lignin carbohydrate complexes are not soluble in acetone. Xylose, however, was found to be present in fraction E. When this fraction was subjected directly to GPC (the precipitation in ether was omitted; i.e. the route indicated by the dashed line starting from fraction E in fig. 1 was followed), a sugar fraction (primarily xylose) could be isolated (cf. 11), which constituted 1-2% of fraction E. In one steam hydrolysis experiment (40 bar, 165 sec) water washings as well as precipitation in ether were omitted (the separation sequence including the steps indicated by dashed lines in fig. 1 was followed); in this case, the sugar fraction obtained by GPC was found to constitute 10% of the acetone extract.

In this experiment, it was also found that the monomer fraction contained comparatively large amounts of the sugar degradation product 5-hydroxymethyl-2-furaldehyde (2). Thus, the washing with water releases the major part of the water-soluble carbohydrates and part of the 5-hydroxymethyl-2-furaldehyde. Low molecular mass phenols were also found to be present in the water washings (fraction B); the amount was, however, rather small. The amount of *p*-hydroxybenzoic acid (1) which seemed to have accumulated was <10% of the

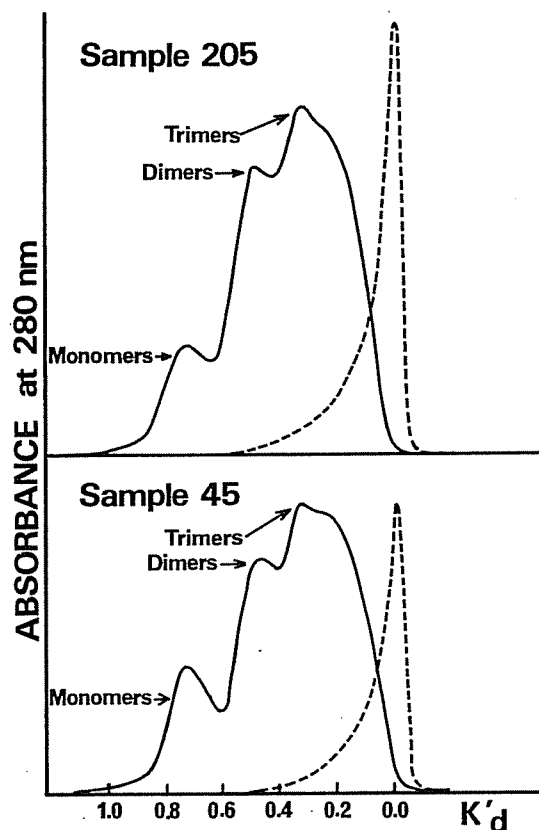
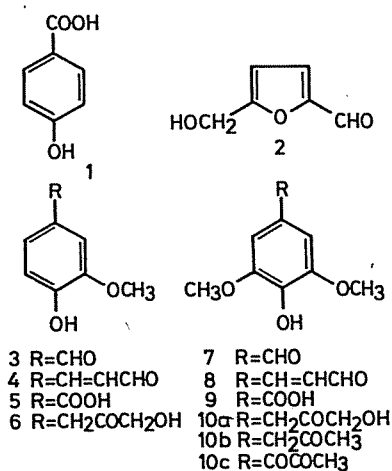


Fig. 2. GPC [Sephadex LH-20/DMF-HAc (100:1)] of the ether soluble (I) (—) and ether insoluble (H) (---) fractions of acetone extracts (E, fig. 1), from samples of steam hydrolysed aspen wood.  $K'_d = 1$  corresponds to the elution volume of a small molecule (acetone) and  $K'_d = 0$  corresponds to the elution volume of a polymer (milled wood lignin). (The amount applied to the column is four times larger in the case of ether solubles; the difference in peak areas of fractions from Sample 45 and Sample 205 is explained by the higher absorptivity of Sample 205).



amount present in the acetone extract (TLC). However, as a control, the composition of a monomer fraction from wood which had not been washed with water (step A-E directly, dashed line starting from fraction A in fig. 1) was examined. It was found that a somewhat higher proportion of aryl propanones (6 and 10) was present in this case. To summarize, fraction E contains the major part of the lignin and lignin degradation products, a small amount of low molecular mass carbohydrates, reaction products of carbohydrates [the only compound of this type identified is 5-hydroxymethyl-2-furaldehyde (2)], and a least part of what usually is referred to as "extractives" [e.g. fatty substances insoluble in dioxane-water (1:1), see fig. 1]. Fractions of monomers (L) and dimers (K) separated from the ether-soluble portion of fraction E (fig. 1) have been examined for individual components.

### Composition of the monomer (L) and dimer (K) fractions

Examination of the monomer fractions (L) of sample 45 and sample 205 (fig. 1 and table 2) by TLC and GC-MS of trimethyl silyl derivatives (12) revealed the presence of compounds 1-10 (traces of 2,6-dimethoxyphenol were also present in the monomer fractions). Both fractions had a similar composition; *p*-hydroxybenzoic acid was a major constituent. Arylpropanones (6 and 10) were present only in small amounts. Sample 205 contained comparatively large amounts of the carbohydrate degradation product 5-hydroxymethyl-2-furaldehyde (2).

Syringaresinol (26) and episyringaresinol (27) could be isolated by column chromatography from the dimer fractions (K, see fig. 1 and table 2) and were found to be prominent constituents of these fractions (chromatography of a dimer fraction from sample 45 gave crude syringaresinol (26) and episyringaresinol (27) in an amount which constituted 12% of the fraction).

GC-MS of the dimer fractions provided evidence for the presence of an additional compound of the "resinol" type, namely compound 28.

It could be concluded by means of TLC and GC-MS examinations that stilbene 22 was present in the dimer fractions. The same techniques also provided very strong arguments for the occurrence of the analogous stilbenes 23 and 24 in these fractions.

### Discussion

It is well known that substantial amounts of *p*-hydroxybenzoic acid are attached to aspen lignin, primarily by ester linkages (13, 14, 12), and thus the presence of *p*-hydroxybenzoic acid (1) in fraction L can be explained by hydrolysis of such linkages. The liberation of acid 1 from the lignin and acetic acid from the xylan increases the acidity of the wood which in turn promotes acid catalysed reactions.

Previous studies (5, 7, 15) have shown that steam hydrolysis results in an extensive liberation of phenolic groups, and undoubtedly this is primarily due to cleavage of the aryl ether bonds in  $\beta$ -O-4 structures (11). The  $^{13}\text{C}$  NMR spectrum of fraction H from sample 45 (fig. 3, cf. ref. 5 and 7) as well as the  $^1\text{H}$  NMR spectrum of the acetate derivative of the same sample [fig. 4; the peak corresponding to phenolic acetate ( $\delta$  2.31) is relatively large, cf. ref. 14] is consistent with a substantial cleavage of  $\beta$ -aryl ether bonds. As expected, the spectra of the corresponding fraction from sample 205 evidenced the same structural changes in a more pronounced way. Fig. 5 shows conceivable reaction routes (*a*, *b* and *c*) for the cleavage of the  $\beta$ -O-4 linkages. As judged from the very low yield of aryl propanones (6 and 10) reaction route *a* (16, 17) is of limited importance. Studies on the acidolytic degradation of severely treated wood samples such as sample 205 suggest the presence of minor amounts of enol ethers of type 15 (15). This constitutes support for reaction route *b* (16, 17). Reaction route *c* has been suggested for the formation of  $\beta$ - $\beta$ ,  $\beta$ -1, and other lignols from  $\beta$ -O-4 model compounds on brief heating (20 min) at 180°C in dioxane-water (1:1) solution (18). Some more or less indirect evidence for the occurrence of reaction route *c* during steam hydrolysis is given below in connection with the discussion of results from the investiga-

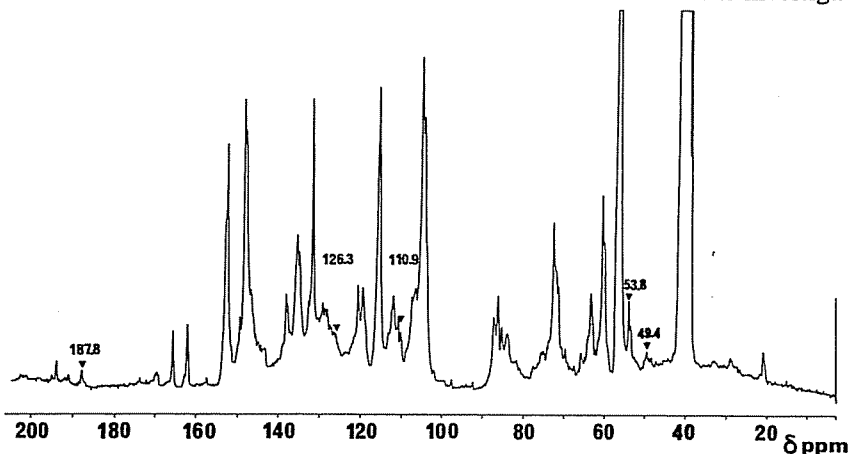


Fig. 3.  $^{13}\text{C}$  NMR spectrum of lignin H (fig. 1) from Sample 45.

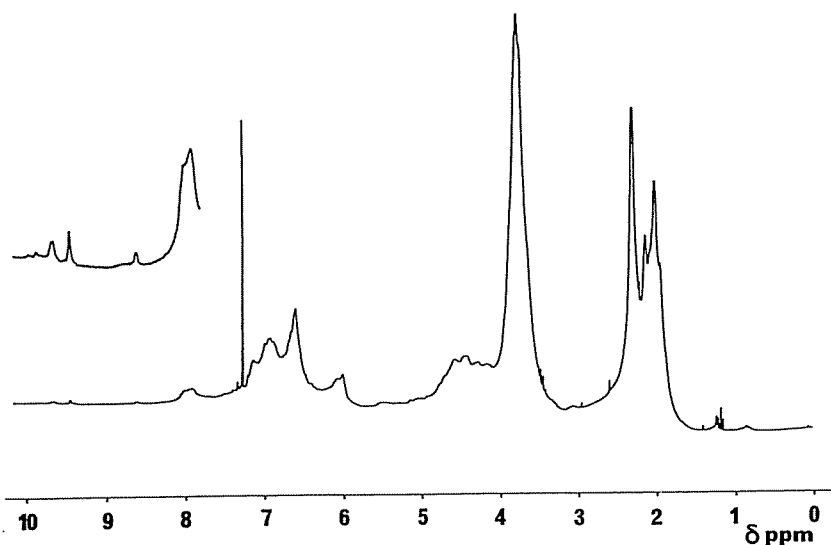


Fig. 4.  $^1\text{H}$  NMR spectrum of acetylated lignin H (fig. 1) from Sample 45.

tion of the dimer fractions. For the moment, we are unable to estimate the relative importance of reaction routes *a*, *b*, and *c* and it cannot be excluded that some other reactions are responsible for the cleavage of the  $\beta$ -ether linkages.

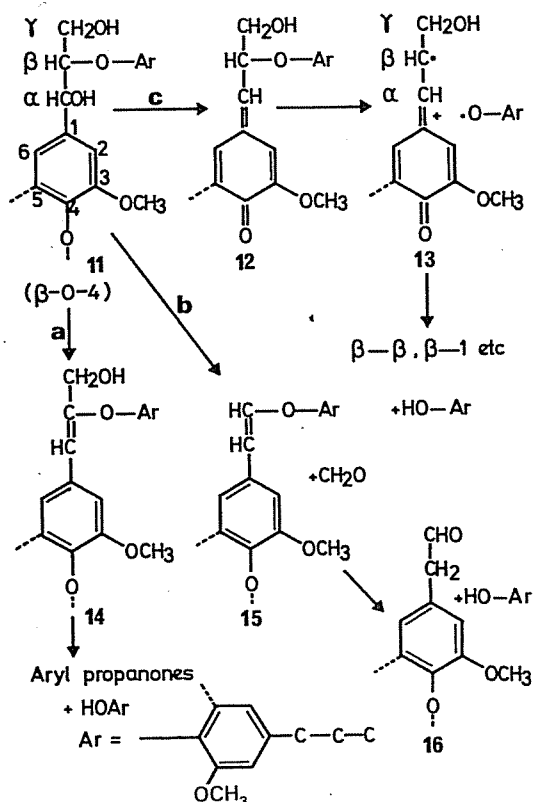


Fig. 5. Conceivable reaction routes (*a*, *b*, and *c*) for the cleavage of  $\beta$ -0-4 linkages during steam hydrolysis.

It has been shown that coniferaldehyde (4) is formed on aqueous hydrolysis ( $175^\circ\text{C}$ , pH 3) of a  $\beta$ -0-4 model compound (19). Therefore the cinnamaldehydes in fraction L (4 and 8) might originate from  $\beta$ -0-4 structures (11). Compounds 4 and 8 could, however, also originate from cinnamaldehyde end groups present in the original lignin. It is, in this respect, of interest to note that the size of the signal due to formyl protons in cinnamaldehyde units ( $\delta$  9.65, fig. 4) is of the same order in treated and non-treated lignin.

One would expect that extensive cleavage of aryl ether linkages would be accompanied by the formation of rather large amounts of lignin monomers. This is, however, not the case (table 2) and a likely explanation for this is the occurrence of reactions which counteract the formation of low molecular mass products: radical reactions (cf. reaction route *c*, fig. 5), condensation reactions with liberated formaldehyde (cf. reaction route *b*, fig. 5), reactions with carbohydrates or their conversion products, etc.

Since  $\beta$ -1 compounds (18-21) have been shown to form in connection with hydrolytic treatments of lignins (20) and acid treatment of such compounds results in formation of stilbenes of the type present in the dimer fraction (16), it is obvious that these compounds originate from  $\beta$ -1 compounds or  $\beta$ -1 structures (17) (i.e.  $\beta$ -1 compounds attached to the lignin) (fig. 6). The  $\beta$ -1 compounds or structures are either constituents of the original lignin or formed from  $\beta$ -0-4 structures according to reaction route *c* (cf. ref. 21) during the steam hydrolysis.

It has been suggested that  $\beta$ -1 linkages are formed in connection with formation of glyceraldehyde-2-aryl ethers (21). Interestingly, the  $^1\text{H}$  NMR spectrum of acetylated sample 45 exhibited a peak at  $\delta$  9.44 which can be attributed to  $\alpha$ -aryloxyacroleins (22) and the  $^{13}\text{C}$  NMR spectrum of sample 45 showed a peak at  $\delta$  187.8 (fig. 3) which could be due to the

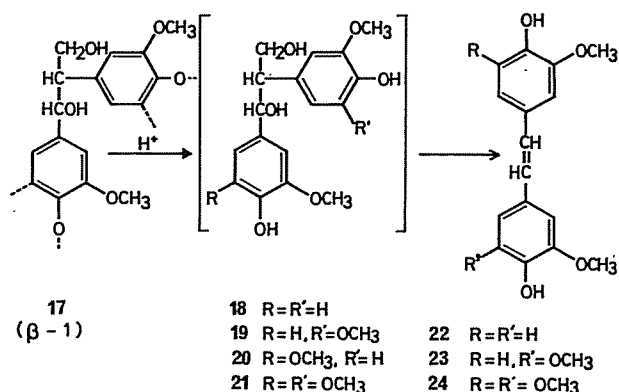


Fig. 6. Formation of stilbenes from  $\beta-1$  structures during steam hydrolysis of aspen wood.

formyl carbon in the same type of structure; such structures could form on dehydration of glyceraldehyde-2-aryl ethers.

Since syringaresinol structures (25) have been shown to be constituents of aspen lignin, the presence of syringaresinol and, analogously, of compound 28 can be explained as a result of the cleavage of ether bonds during the treatment (14, cf. also 20). These compounds might, however, also be formed from  $\beta-0-4$  structures via reaction route *c* (fig. 5). The presence of episyringaresinol in the dimer fraction is most likely a result of an acid catalyzed isomerization of syringaresinol (fig. 7).

It is noteworthy that signals which could be attributed to stilbenes ( $C_\alpha=126.3$  ppm,  $C-2=110.9$  ppm) and episyringaresinol [ $C_{\beta'}=49.4$  ppm; the signal from  $C_\beta$  is located at 53.8 ppm, in treated as well as nontreated lignin, the peak appearing at this position is primarily due to  $C_\beta$  in syringaresinol structures (53.7 ppm)] appear in the  $^{13}\text{C}$  NMR spectrum of fraction H from sample 45 (fig. 3). It could be demonstrated by a special pulse sequence technique (DEPT) that the above-mentioned signals are due to methine groups (23).

The formation of conjugated systems (stilbenes and enol ethers) during the steam hydrolysis is in accordance with the increase in UV absorbance which was observed. (Lignin H from sample 45 showed a maximum at 272 nm and  $E_{1\text{cm}}^{1\%}$  was found to be 230, and the corresponding fraction from sample 205 showed a maximum at the same wavelength and  $E_{1\text{cm}}^{1\%}$  was determined as 290.) The UV spectra also exhibited an inflexion at about 330 nm. This provides support for the occurrence of stilbene structures (stilbene 22 has a UV maximum at 333 nm).

Stilbenes 22-24 are readily oxidized to orange-colored stilbene quinones (e.g. on storage of TLC chromatograms the stilbenes became visible as orange spots due to autoxidation). Solutions of steam hydrolysed lignin exhibit a rather vivid reddish orange color, and we think that oxidation products of stilbenes (or stilbene structures in the lignin polymer) contribute to this coloration.

Finally it should be pointed out that the amount of low molecular mass phenols in extractives from untreated wood constituted only 0.1% of the wood; *p*-hydroxybenzoic acid was a major constituent while the amount of dimers was negligible.

## Experimental

### Analyses

$^{13}\text{C}$  NMR spectra (solvent, DMSO- $d_6$ ; temperature, 323 K) and  $^1\text{H}$  NMR spectra (solvent,  $\text{CDCl}_3$ ) were recorded on a Bruker WM-200 instrument (internal reference, TMS). UV spectra were run with dioxane-water (4:1) as solvent. Analytical gel permeation chromatography (GPC) experiments were performed with the system Sephadex LH-20 or Sephadex LH-60/DMF-HAc (100:1), using stainless steel columns (length 65 cm, inner diameter 0.75 cm) and HPLC equipment (pump, Waters M-6000 A; injector, Rheodyne 71-25; UV detector, UVISCO 1840). Flow rate: 6 ml/h. Gas chromatography-mass spectrometry (GC-MS) was performed with the system

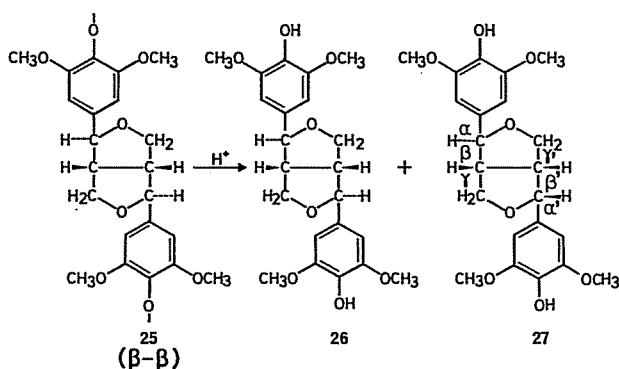
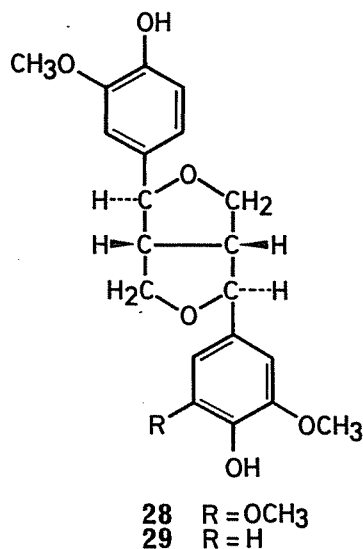


Fig. 7. Formation of syringaresinol (26) and episyringaresinol (27) from syringaresinol structures (25) during steam hydrolysis of aspen wood.



Varian 3700 (gas chromatograph)/MAT 212 (mass spectrometer), using a capillary column (stationary phase, CP SIL5). Thin layer chromatography (TLC) was performed with silica gel plates (Kieselgel 60 F 254, Merck), using toluene-dioxane-acetic acid (90:25:4) ( $R_F$  values: syringaresinol (26), 0.20; episyngaresinol (27), 0.23; 5-hydroxymethyl-2-furaldehyde (2), 0.28; *p*-hydroxybenzoic acid (1), 0.32; stilbene 24, 0.32; stilbene 23, 0.40; sinapaldehyde (8), 0.41; coniferaldehyde (4), 0.45; stilbene 22, 0.46) and water saturated butanone (this eluent was used for the detection of sugars).

*p*-Hydroxybenzoic acid (1) was detected by UV light. Other compounds could be made visible by spraying with  $H_2SO_4$ -formalin (9:1) and subsequent heating at 140°C. The stilbenes gave strong brownish orange spots on exposure to iodine vapor. 2-Methylindol in hydrochloric acid/ethanol was used for the detection of 5-hydroxymethyl-2-furaldehyde (2) (yellow spot). Coniferaldehyde (4) (red violet spot) and sinapaldehyde (8) (purple spot) could be made visible by spraying with 0.1 mole/l phloroglucinol in 60% ethanol and 4 mole/l hydrochloric acid in water-ethanol (1:2).

#### Samples

Wood chips from aspen (*Populus tremuloides*) were treated with steam (45 bar) for 45 sec according to the lotech process; the steam hydrolysed product is in this paper referred to as Sample 45. In a second experiment, the time of treatment was extended to 205 sec; the obtained product is in this paper referred to as Sample 205. The steam hydrolysis was performed at Centre Technique de l'Industrie des Papiers, Cartons et Celluloses, Grenoble, France.

#### Extraction of lignin from the treated wood and fractionation of the extracted material

The scheme in fig. 1 describes most of the steps in the extraction and fractionation procedures used. Ether soluble fractions (I) were subjected to gel permeation chromatography on 150 g Sephadex G-25 (fine), using dioxane-water (1:1) as eluent. Column size: 35 × 4.5 cm. The samples (1-2 g) dissolved in dioxane-water (1:1) were applied to the column and the effluent divided into fractions of polymers/oligomers, dimers and monomers, on the basis of TLC examinations (the presence of the easily detected stilbenes 22-24 was particularly useful for the recognition of the eluate with dimeric compounds). Solvents were removed by film evaporation, and the residue dried in vacuo over  $P_2O_5$ . Monomers and dimers were alternatively extracted from the eluate with chloroform. The extracts were dried over  $Na_2SO_4$ , solvents removed by film evaporation, and the residues dried in vacuo over  $P_2O_5$ .

#### Identification of individual components in the monomer and dimer fractions

*p*-Hydroxybenzoic acid (1), coniferaldehyde (4), sinapaldehyde (8), and 5-hydroxymethyl-2-furaldehyde

(2), were identified by TLC in the monomer fractions. The presence of these compounds could be confirmed by gas chromatography-mass spectroscopy (GC-MS) of their trimethyl silyl derivatives (12). GC-MS in addition revealed the presence of vanillin (3), vanillic acid (5), syringaldehyde (7), syringic acid (9) and small amounts of aryl propanones 6 and 10 (primarily 10).

The monomer fractions from samples 45 and 205 had a similar composition; in both cases, *p*-hydroxybenzoic acid was the major constituent. The monomer fraction from samples 205 contained more 5-hydroxymethyl-2-furaldehyde than the one from sample 45.

TLC provided evidence for the presence of diguaiaicylstilbene (22), syringaresinol (26), and episyngaresinol (27) in the dimer fractions. Column chromatography [50 g  $SiO_2$ ; eluent, toluene-ethyl acetate (3:2)] of the dimer fraction of sample 45 gave fractions of syringaresinol (identified by  $^{13}C$  NMR and  $^1H$  NMR of the acetate derivative) and episyngaresinol (identified by  $^1H$  NMR of the acetate derivative (24) and  $^{13}C$  NMR; the acidolysis mixture of syringaresinol (25) served as a reference).  $^1H$  NMR of episyngaresinol (acetate derivative):  $\delta$  2.35 (6H, s;  $CH_3CO$ ), 2.93 (1H, m;  $H_{\beta'}$ ), 3.35 (1H, m;  $H_{\beta}$ ), 3.84 (12H, s;  $OCH_3$ ), ~4 (4H, m;  $H_{\gamma}$ ), 4.47 (1H, d,  $J=6.8$  Hz;  $H_{\alpha'}$ ), 4.87 (1H, d,  $J=5.5$  Hz;  $H_{\alpha}$ ), 6.62 (4H, s; aromatic protons).

$^{13}C$  NMR of episyngaresinol:  $\delta$  49.4 ( $C_{\beta}$ ), 53.8 ( $C_{\beta'}$ ), 56.2 ( $OCH_3$ ), 68.9 and 70.5 ( $C_{\gamma}$ ), 81.5 ( $C_{\alpha}$ ), 87.1 ( $C_{\alpha'}$ ), 103.6 and 104.0 (C-2, C-6), ~130 (C-1, C-4), 148 (C-3, C-5). (The interpretation of the  $^{13}C$  spectrum is correlated to the proton spectrum by selective irradiation experiments, the assignments of primed and unprimed carbons and hydrogens are interchangeable.)

The fractions of syringaresinol and episyngaresinol constituted 12% of the dimer fraction of Sample 25.

TLC chromatograms of the dimer fractions indicated the presence of stilbenes 23 and 24 (color reaction with iodine vapor, lower  $R_F$  values are in agreement with the introduction of syringyl groups).

GC-MS of the dimer fraction and stilbene 22 (before and after acetylation) corroborated that this compound was present in the dimer fraction. GC-MS also provided more direct evidence for the occurrence of stilbenes 23 and 24 in the dimer fraction. As in the case with stilbene 22, the molecular ions strongly dominate the MS. The analogy of the MS also holds true for the acetylated products; the ions corresponding to the non-derivatized products constituting the base peaks and peaks of moderate intensity corresponding to the molecular ions and M-42.

The presence of compound 28 in the dimer fraction was shown by GC-MS investigations. The MS exhibited a strong peak at  $m/z$  388 which corresponds to the molecular ion and comparisons with the MS of pinosresinol (29) and syringaresinol (26) (before and

after acetylation) strongly supported structure 28. This compound has previously been identified among lignin hydrolysis products obtained from *Fraxinus mandshurica* (26) and the MS given in ref. 26 is in accordance with that of our product.

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