Holzforschung
33 (1979) 210—212

Short Note

Pyrolysis—Gas Chromatography—Mass Spectrometry of Lignins

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Keywords
Pyrolysis of lignins
Pyrolysis — gas chromatography — mass spectrometry
Pyrolysis products

Schlüsselwörter (Sachgebiete)
Pyrolyse von Ligninen
Pyrolyse — Gaschromatographie — Massenspektrometrie
Pyrolyseprodukte

Pyrolysis in combination with gas chromatography is currently used to characterize biopolymers, supplying reliable information about its chemical structure (Martin et al. 1977, 1979; Saiz-Jimenez et al. 1979). This method has barely been applied to lignins. Kratzl et al. (1965) studied the pyrolysis — gas chromatography of lignins, identifying 15 compounds and stating that method can be used for rapid identification of lignins. Watanabe et al. (1966) using the same technique were able to differentiate softwood from hardwood lignins in terms of pyrolysis products. Furthermore, they found that the mole ratio of pyrolysis products had analogy with the ratio of alkaline nitrobenzene oxidation products. Recently, Faix and Schweers (1975) pyrolysing lignin model polymers (DHP's) found that the yields of guaiacol, methylguaiacol, ethylguaiacol, syringol and methylsyringol, the main components of the pyrolysates, showed a systematic dependence from the amounts of the guaiacyl and syringyl units in the DHP's.

In this note, pyrolysis — gas chromatography — mass spectrometry-computer (py-gc-ms-c) is used in attempts to evaluate the possibility to draw chemical information on the lignin units.

Three MWL lignins were used in this investigation. The samples and its analytical data, kindly provided by Dr. O. Faix, Hamburg, are listed in Table 1. The pyrolysis and analytical procedures have been extensively described in previous papers (Martin et al. 1977, 1979; Saiz-Jimenez et al. 1979).

The pyrolysates of lignins were separated into low and high boiling point compounds by use of appropriate columns. Among the low boiling point compounds (Chromosorb 102 column) a diversity of products were identified, namely, CO, CO_2, H_2O, methane, ethane, propane, methanol, acetone, acetic acid and some furan derivatives. These most probably arise from the side-chains and associated carbohydrates, which were not completely removed during the extraction and subsequent purification of lignins. A few aromatics, such as benzene and toluene could also be discerned. All the above referred compounds are common to other biopolymers (Martin et al. 1977; Saiz-Jimenez et al. 1979) and do not shed much light about the lignin chemistry.

Figure 1 shows the pyrograms of the three studied lignins and Table 2 the identified pyrolysis products using a column of Chromosorb AW DMCS 80-100 mesh, coated with 10% FFAP, for resolution of the high boiling point compounds.

Spruce lignin pyrogram (Fig. 1a) shows lesser peak intensity when compared to the other two lignins. This may be due to the absence of condensed structures among syringyl units in beech and bamboo lignins, which made more easily pyrolysable these lignins. This has also been substantiated by the nitrobenzene oxidation results, where it was demonstrated that only 30% of guaiacyl units are recoverable as vanillin, while the conversion of syringyl moieties to syringaldehyde may well be at the 90% level (Sarkanen and Hergert 1971). Pyrolysis products of spruce lignin are mainly guaiacyl derivatives, with major peaks from methylguaiacol (10), vinylguaiacol (22), trans-isoeugenol (26) and vanillin (34). C_3-alkylphenol (19) and vinylphenols (27, 28, 29) may originate from the p-hydroxyphenyl units, which are found in minor amounts in this lignin. After peak 39, a few peaks with mass spectra similar to dihydroxybenzene, two of its alkylderivatives and coniferylaldehyde were tentatively identified. However, due to the low peak/background ratio and bleed of the column, a positive identification could not be obtained, therefore, they are not listed in Table 2.

Table 1

Analytical data of MWL's

Lignins	C	H	O	OCH_3
Spruce (*Picea abies*)	62,59	6,07	31,34	15,80
Beech (*Fagus silvatica*)	60,12	6,42	33,46	21,50
Bamboo (*Bambusa* sp.)	61,96	5,67	32,37	17,90

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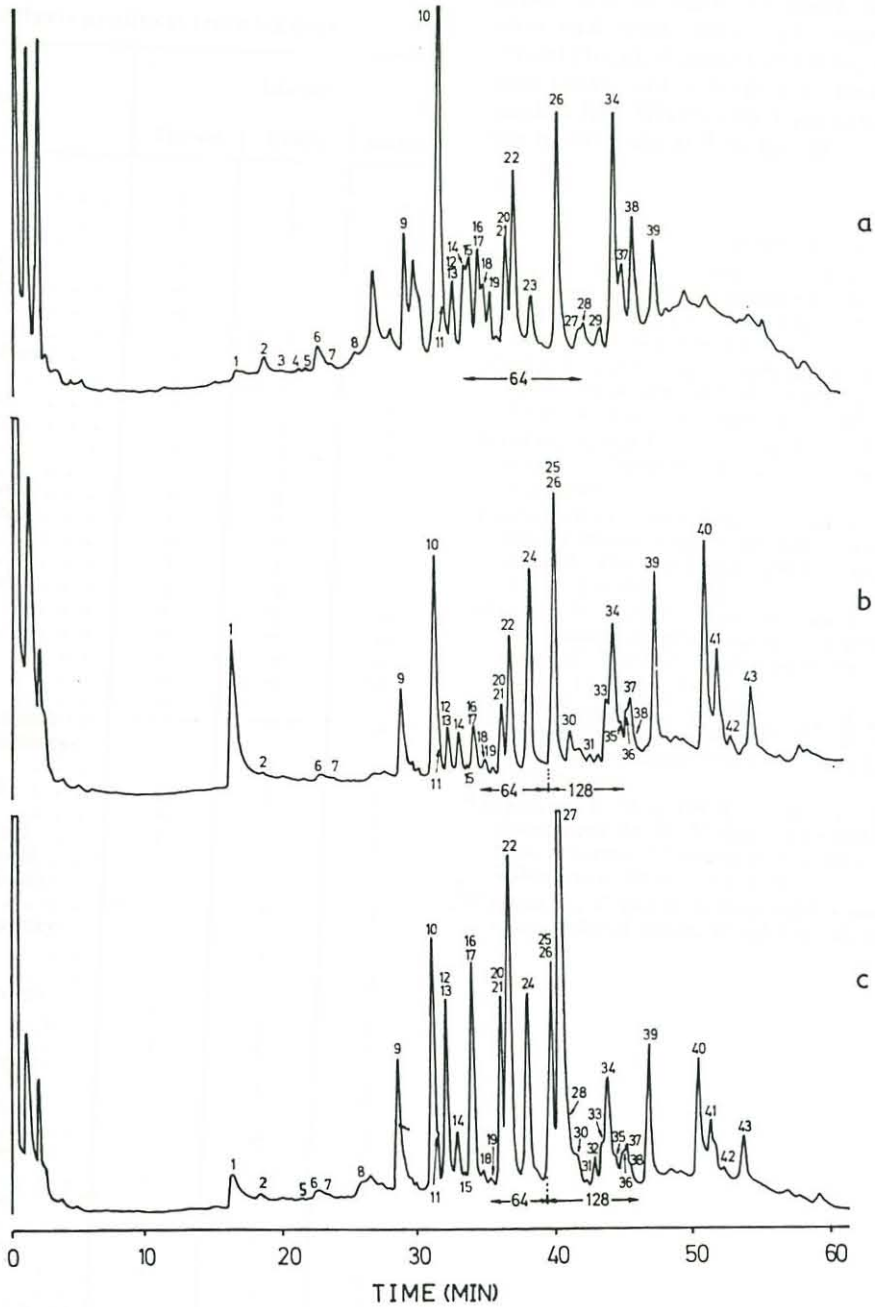

Fig. 1. Pyrograms of lignins. a: spruce lignin; b: beech lignin; c: bamboo lignin

Main thermal fragments of beech lignin (Fig. 1b) are guaiacyl and syringyl units, with major peaks from methylguaiacol (10), 3,5-dimethoxyphenol (24), methyl-3,5-dimethoxyphenol (25), trans-isoeugenol (26), vanillin (34), a possible vanillin derivative (39), syringaldehyde (40) and a possible syringaldehyde derivative (41). Other important peak, unlike spruce and bamboo lignins, is acetic acid (1).

Bamboo lignin pyrogram (Fig. 1c) shows as prominent peaks those of methylguaiacol (10), phenol (12), o-cresol (13), xylenol (16), p-cresol (17), eugenol (20), xylenol (21), vinylguaiacol (22), 3,5-dimethoxyphenol (24), methyl-3,5-dimethoxyphenol (25), trans-isoeugenol (26), vinylphenol (27), vanillin (34), a possible vanillin derivative (39) and syringaldehyde (40), being majors vinylguaiacol, methyl-3,5-dimethoxyphenol and vinylphenol, which correspond to the guaiacyl, syringyl and p-hydroxyphenyl units, respectively. It is remarkable that peaks from phenol, xylenols and cresols are three times higher than in beech lignin and two times higher than in spruce lignin. These compounds may arise, in part, from the p-hydroxyphenyl units, which confirmate that these units are more extensively represented in bamboo lignin.

The results of this study show that there is a high correlation between pyrolysis products and lignin units from which they arise. This indicate that py-gc-ms-c is a valuable method to differentiate distinct lignin

Table 2

Pyrolysis products from lignins

Compounds	Lignins		
	Spruce	Beech	Bamboo
1 Acetic acid	+	+	+
2 Furfural	+	+	+
3 Indene	+		
4 Methylindene	+		
5 Methylbenzofuran	+		+
6 Butyric acid	+	+	+
7 Ethylenglycol	+	+	+
8 C_2-alkylbenzofuran	+		+
9 Guaiacol	+	+	+
10 Methylguaiacol	+	+	+
11 C_2-alkylguaiacol	+	+	+
12 Phenol	+	+	+
13 o-cresol	+	+	+
14 C_2-alkylguaiacol	+	+	+
15 C_3-alkylguaiacol	+	+	+
16 Xylenol	+	+	+
17 p-cresol	+	+	+
18 C_3-alkylguaiacol	+	+	+
19 C_3-alkylphenol	+	+	+
20 Eugenol	+	+	+
21 Xylenol	+	+	+
22 Vinylguaiacol	+	+	+
23 cis-isoeugenol	+		
24 3,5-dimethoxyphenol		+	+
25 Methyl-3,5-dimethoxyphenol		+	+
26 trans-isoeugenol	+	+	+
27 Vinylphenol	+		+
28 Methylvinylphenol	+		+
29 C_2-alkylvinylphenol	+		
30 Ethyl-3,5-dimethoxyphenol		+	+
31 Propyl-3,5-dimethoxyphenol		+	+
32 Propenylphenol			+
33 Allyl-3,5-dimethoxyphenol		+	+
34 Vanillin	+	+	+
35 Vinyl-3,5-dimethoxyphenol		+	+
36 Propenyl-3,5-dimethoxyphenol		+	+
37 $C_9H_{10}O_3$ (vanillin derivative?)	+	+	+
38 $C_{10}H_{12}O_3$ (vanillin derivative?)	+	+	+
39 $C_{11}H_{14}O_3$ (vanillin derivative?	+	+	+
40 Syringaldehyde		+	+
41 $C_9H_{12}O_4$ (syringaldehyde derivative?)		+	+
42 Sinapylalcohol		+	+
43 Coniferylaldehyde		+	+

types and to draw chemical information about its structural units, unlike the statement of Karig and Stahl (1974). A more deep study of some of the uncertain peaks and a further comparison with synthetic models like DHP's could provide interesting clues on the lignin units and its linkages.

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