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Pyrolysis-Mass Spectrometry Analysis of Dehydrogenation Lignin Polymers with Various Syringyl/Guaiacyl Ratios

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The present paper describes the application of pyrolysis-mass spectrometry (PYMS) to the analyses of lignocellulosic materials. Dehydrogenation lignin polymers (DHPs) with various syringyl/guaiacyl (S/G) ratios, and a standard, milled wood lignin from *Aesculus turbinata* Blume, were pyrolyzed at 500 °C for 4 s and the volatile products were ionized by low-voltage (20 eV) electron impact. The PYMS spectra of the lignins are shown with identification of most mass peaks. Of the observed mass peaks, the intensities of the monomeric peaks corresponding to monomethoxyphenols (*m/z* 124, 137, 138 and 180) and dimethoxyphenols (*m/z* 154, 167, 182 and 210) were sensitive to the S/G ratio shifts of the DHPs. Changes in the monomeric mass peak intensities reflected those in the yields of the corresponding products determined by pyrolysis-gas chromatography (PYGC). The S/G pyrolytic ratios, calculated from the summed mass peak intensities of syringyl and guaiacyl monomeric products, showed a linear correlation with syringaldehyde/vanillin (S/V) ratios determined by nitrobenzene oxidation. This finding suggested that the S/V ratios of lignocellulosic materials are predicted from the S/G pyrolytic ratios obtained by PYMS. Similar linear correlations were observed also between the S/G pyrolytic ratios determined by PYGC and the S/V ratios, for the DHPs and for Japanese hardwoods. Unlike the PYGC method, however, the PYMS method does not need time-consuming determinations of the response factor of each product to a flame ionization detector. This advantage may outweigh the inherent problems of PYMS, such as the ambiguous structural assignment of the mass peaks in the quantitative PYMS analyses of lignocellulosic materials. The dimeric mass peaks, which were hardly detected in an analytical system with a gas chromatograph, also contributed to the mass spectra. © 1997 by John Wiley & Sons, Ltd.

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Analytical pyrolysis has achieved wide acceptance as an effective polymer analysis method. Pyrolysis-mass spectrometry (PYMS) is an analytical pyrolysis technique combining a pyrolyzer directly with a mass spectrometer. Interest has grown in the application of PYMS to analyses of lignocellulosic materials[1–19] due to the high sensitivity and speed of analysis compared to pyrolysis-gas chromatography(/mass spectrometry) (PYGC/MS), a popular analytical pyrolysis technique. In an analytical pyrolysis system with a gas chromatograph, we have often noticed that high-molecular weight products and polar products disappear from the PYGC(/MS) spectra. These unfavorable findings are mainly due to the GC column preventing high-molecular weight products and polar products from being easily eluted. Furthermore, by contact with the long, hot column, thermally labile products often undergo condensation and rearrangement reactions to yield pyrolysis products which no longer carry structural information on the original polymers. Therefore, PYMS is capable of delivering a large proportion of the GC-intractable pyrolysis products to the detector due to the absence of the column. Detailed descriptions are given by Boon[13,17] and by Boon's group.[14]

PYMS provides structural information on polymers from microgram samples by relating chemical components to mass peaks. Therefore, differences in chemical composition of the samples can be visualized qualitatively from the mass spectra directly. High degrees of reproducibility are reported for in-source PYMS of lignins and humic acids.[6,10,11] However, PYMS is often reputed to be unsuitable for obtaining quantitative results,[6,7,10,17] suggesting that quantitative PYMS is still a relatively unexplored field.

In this work, we pyrolyzed hardwood-type dehydrogenation lignin polymers (DHPs) with various syringyl/guaiacyl (S/G) ratios to correlate the PYMS data with information on the relative abundances of chemical components of lignocellulosic materials. The PYMS spectra of the DHPs, and of a reference milled wood lignin isolated from *Aesculus turbinata* Blume, up to **m/z** 580, are reported with identification of most mass peaks. A linear correlation was obtained between the S/G pyrolytic ratios, calculated from the summed intensities of syringyl mass peaks and those of guaiacyl mass peaks, and the syringaldehyde/vanillin (S/V) ratios determined by nitrobenzene oxidation, a representative chemical degradation method of lignin analysis.

MATERIALS AND METHODS

Materials

Five hardwood-type synthetic lignin polymers (DHPs 1–5) pyrolyzed here were the same as those used in previous PYGC/MS experiments.[20] The DHPs were prepared by dehydrogenating a mixture of coniferyl

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and sinapyl alcohols according to the dialysis method of Tanahashi and Higuchi.[21] The mixing ratios of sinapyl alcohol/coniferyl alcohol (S/C), used to prepare DHPs 1–5, were 0.2, 0.33, 1, 3 and 5, respectively (Table 1). A hardwood milled wood lignin (MWL) was prepared from *Aesculus turbinata* Blume according to Björkman's method.[22] Table 1 shows the S/C mixing ratios and the syringaldehyde/vanillin (S/V) ratios of the DHPs 1–5. The table also shows the S/V ratio of the *A. turbinata* Blume MWL sample.

Pyrolysis-mass spectrometry

The PYMS system was a combination of a model JDI-800 Curie-point direct injection probe (Japan Analytical Industry, Tokyo, Japan) and a model QP-2000 quadrupole mass spectrometer (Shimadzu, Kyoto, Japan). The Curie-point direct injection probe used is described in detail by Oguri *et al.*[23,24] Briefly, it consisted of an injection probe and a radio frequency power supply. Samples (about 1 μg) wrapped with a 500 °C pyrofoil were placed in a quartz sample cell (9 mm length × 2 mm i.d.). The sample-loaded cell was held inside the radio frequency induction coil by a ceramic bobbin. A small silver tube was put on the tip of the cell in order to provide closer contact of the cell with the entrance aperture of the ion source as a thermal conductor, preventing condensation of thermally labile products. After the probe assembly had been inserted in the mass spectrometer up to the position where the sample cell at the tip of the probe is connected to the ion source, the samples were pyrolyzed at 500 °C for 4 s by induction heat. The volatile products were ionized at 20 eV in an ion chamber heated at 250 °C, and then mass analyzed. The mass range used was *m/z* 80–580. The scan speed was 10 scans/s with a total data acquisition time of 50 s. The PYMS spectra obtained were summarized as the average spectrum for the total pyrolysis period. The ions appearing in the PYMS spectrum were identified by the PYGC/MS analyses of DHPs and by comparing with published data.[3,4,8,11,15,18] Analyses were routinely performed in triplicate.

Nitrobenzene oxidation

Nitrobenzene oxidation was carried out according to the method of Iiyama and Lam.[25] Vanillin and syringaldehyde were determined as the major oxidation products.

Table 1. S/C ratios and S/V ratios of DHPs 1–5 and MWL

Samples	S/C[a]	S/V[b]
DHP **1**	0.20	0.33
DHP **2**	0.33	0.53
DHP **3**	1.0	0.99
DHP **4**	3.0	2.94
DHP **5**	5.0	4.03
MWL[c]	—	1.09

[a] Molar mixing ratios of sinapyl alcohol/coniferyl alcohol.
[b] Syringaldehyde/vanillin molar ratios determined by nitrobenzene oxidation.
[c] From *Aesculus turbinata* Blume.

RESULTS AND DISCUSSION

PYMS spectra of the DHP and MWL samples

Figure 1(a)–(c) shows the PYMS spectra of DHPs 1, 3 and 5 after pyrolysis at 500 °C for 4 s. On the basis of the complementary PYGC/MS data obtained using comparable pyrolysis conditions,[20] Table 2 lists the probable compounds for the major mass peaks, observed in the PYMS spectra of DHPs 1, 3 and 5, together with relative peak intensities. The structures of the pyrolysis products are shown in Fig. 2. Low-voltage electron impact ionization at 20 eV was employed to obtain molecular weight distributions of the pyrolysate with a minimum of ion fragmentation. The PYMS spectra of polymers contain both fragment and molecular ions. Moreover, a mass peak may represent several structurally different ions which also may differ in origin. For example, the molecular ions of dihydroconiferyl alcohol (**14**), syringaldehyde (**18**), and 4-ethylsyringol (**19**) all appear at *m/z* 182. The PYGC/MS data of the DHPs showed that peak *m/z* 182 is dominated by the molecular ion of syringaldehyde (**18**) for the DHPs with large S/C mixing ratios such as DHP 5, but in the DHPs with small S/C mixing ratios such as DHP 1 the peak is mainly attributed to dihydroconiferyl alcohol (**14**). This conclusion is supported by the observation that the relative intensity of *m/z* 182 increased, even though the fractional abundance of guaiacyl moieties in the DHPs lessened with increasing S/C mixing ratios. 4-Ethylsyringol (**19**) showed a small contribution for all of the DHPs. The ion at *m/z* 210, derived from sinapyl alcohol (**27**) and propiosyringone (**26**), is mainly attributed to the molecular ion of sinapyl alcohol (**27**) for all of the DHPs because the contribution of **26** was very small compared to that of **27**. Therefore, the assignment of the mass peaks is ambiguous. However, many of these mass peaks, either alone or in combination, are specific for certain polymers or molecules. We obtained standard deviations within the triplicate runs of about 10% for the relative intensities of peaks above 5% of that of the base peak. These values are inferior to those ($< 5\%$)[6,10] observed with in-source PYMS of lignosulfonic acids and humic acids. Consequently, DHPs 1–5 were characterized by only monomeric pyrolysis products such as *m/z* 124, 137, 138, 150, 151, 152, 164, 166, 178, 180, 182 (G-type), and *m/z* 154, 167, 168, 180, 181, 182, 194, 196, 208, 210, 212 (S-type). Large differences in the relative intensities of mass peaks were observed among the PYMS spectra of the DHPs due to the S/C mixing ratio shifts. The PYMS spectrum of DHP 1 shows a large abundance of guaiacyl-derived mass peaks, including the prominent peaks for guaiacol (**1**) (*m/z* 124, 72.5%), a fragment ion of coniferyl alcohol (**13**) (*m/z* 137, 100%), 4-methylguaiacol (**2**) (*m/z* 138, 34.1%), and coniferyl alcohol (**13**) (*m/z* 180, 78.7%). In contrast, enrichment in the syringyl equivalents (*m/z* 154 (**15**, 59.7%), *m/z* 167 (fragment ion of **27**, 100%), *m/z* 168 (**16**, 42%), *m/z* 210 (**27**, 77.8%)) were observed in the PYMS spectrum of DHP 5. As expected from a S/C mixing ratio of 1.0, DHP 3 displayed mixed guaiacyl–syringyl derived mass spectra, the prominent peaks being the fragment ions of coniferyl and sinapyl alochols (*m/z* 137 (100%) and *m/z* 167 (99.5%), respectively), and the molecular ions of

guaiacol (**1**) (*m/z* 124, 62.5%), syringol (**15**) (*m/z* 154, 42.1%), 4-methylsyringol (**16**) (*m/z* 168, 49.8%), coniferyl alcohol (**13**) (*m/z* 180, 78.3%), dihydroconiferyl alcohol (**14**) and syringaldehyde (**18**) (*m/z* 182, 31.2%), sinapaldehyde (**25**) (*m/z* 208, 34.4), sinapyl alcohol (**27**) (*m/z* 210, 82.4%), and dihydrosinapyl alcohol (**28**) (*m/z* 212, 30.9%).

Guaiacylglycerol-β-guaiacyl ether (β-O-4 type lignin model compound) and coniferyl alcohol benzyl ether (coniferyl alcohol end-group type) produced coniferyl alcohol (**13**) as the major monomeric products upon analytical pyrolysis.[26] Therefore, the high sensitivity of mass peaks arising from cinnamyl alcohols easily provides information on the relative abundances of either cinnamyl alcohol end-groups or phenolic arylglycerol moieties involved in β-aryl ether substructures. A direct comparison of the relative intensities of *m/z* 180 and 210, or of *m/z* 137 and 167, suggests that DHP 5 contains large amounts of sinapyl alcohol end-groups and/or phenolic syringylglycerol moieties involved in β-aryl ether substructures, and small amounts of the corresponding guaiacyl lignin units.

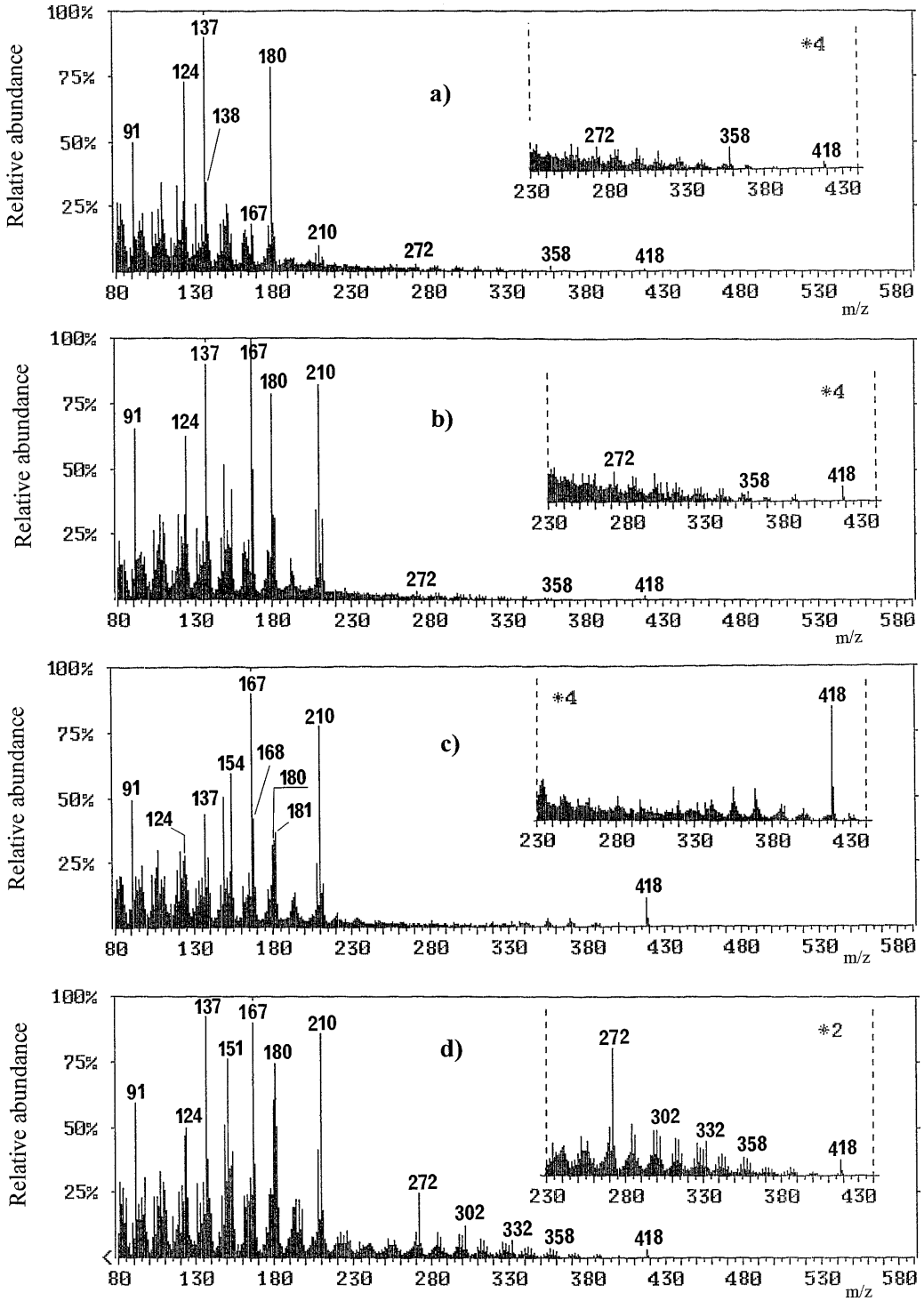


Figure 1. PYMS spectrum of DHPs and *Aesculus turbinata* Blume MWL at 500 °C for 4 s: (a) DHP 1, (b) DHP 3, (c) DHP 5 and (d) MWL.

The PYMS spectra of DHPs 1, 3 and 5 also displayed the molecular ions of what are probably dimeric pyrolysis products in the mass range above *m/z* 250. Attention is drawn to peaks at *m/z* 272 (G-G), 302 (G-S), 332 (S-S), 340 (G-G), 358 (G-G), 370 (G-S), 388 (G-S), 400 (S-S) and 418 (S-S) (see Table 2), which were not observed in the analytical pyrolysis system with the gas chromatograph column. Of these dimeric markers, the peak at *m/z* 358 is attributed to the molecular ions of dehydrodiconiferyl alcohol (**32**) and pinoresinol (**33**). Haider and Schulten[19] observed a base peak at *m/z* 358 in the PYMS spectrum of a bulk dehydrogenation polymer of coniferyl alcohol. The peak at *m/z* 418 is believed to be the molecular ion of syringaresinol (**34**). The intensities of dimeric mass peaks at *m/z* 358 and 418 also reflected the S/C mixing ratio shifts. The PYMS spectrum of DHP 1 shows 2.1% and <1% peak intensities at *m/z* 358 and 418, respectively. DHP 3 gave <1% and 1.4% peak intensities at *m/z* 358 and 418, respectively. A peak at *m/z* 418 was observed at appreciable intensities (10.2%) in the PYMS spectrum of DHP 5. In contrast, the intensity of the peak at *m/z* 358 in the PYMS spectrum of DHP 5 was <1%. These data suggest that DHP 5 contains large abundances of syringaresinol substructures and lower abundances of pinoresinol and phenylcoumaran substructures, compared to DHPs 1 and 3.

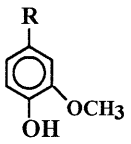
As a reference, the PYMS spectrum of the MWL sample is shown in Fig. 1(d). The MWL showed a S/V ratio (1.09), similar to that (1.0) of DHP 3, on nitrobenzene oxidation. Therefore, the MWL was expected to display a PYMS spectrum similar to that of DHP 3. The pattern of the mass peak distribution up to *m/z* 250 in the PYMS spectrum of the MWL was indeed similar to that of DHP 3, although the relative intensities of the peaks attributed to α-carbonyl compounds (*m/z* 151, 152, 166, 181, 182 and 196) in the PYMS spectrum of the MWL were larger than those in the PYMS spectrum of DHP 3. Large differences in abundances of dimeric mass peak (*m/z* 272–418) were also observed between the two PYMS spectra. The more complicated distribution pattern and stronger intensities of dimeric mass peaks in the PYMS spectrum of the MWL indicate that it consists of various and many more substructures compared to DHP 3. In particular, a series of mass peaks with a regular increment of 30 Da (methoxyl group substitution for H-atom), at *m/z* 272 (24.4%, G-G), 302 (12%, G-S) and 332 (6.5%, S-S), was noted in the PYMS spectrum of the MWL. These peaks were observed at only 2.9, 1.9 and 0.8% relative intensities in the DHP 3 spectrum. Boon and coworkers[11] detected peaks at *m/z* 272 and 332 as base peaks in the PYMS analyses of commercial kraft and organosolv lignins, respectively. A peak at *m/z* 272 (G-G) was assigned to 4,4'-dihydroxy-3,3'-dimethoxystilbene (**29**)[3,4,8,11] (β-1 type substructure), of which a pyrolytic origin is 1,2-bis(4-hydroxy-3-methoxyphenyl) propane-1,3-diol. On this basis, the ions at *m/z* 302 (G-S) and 332 (S-S) incorporate either one (**30**, *m/z* 302)[3,8,11] or two (**31**, *m/z* 332)[3,4,8,11] additional methoxyl

Table 2. Proposed chemical identity of mass peaks

		Peak intensities (%)			
m/z	Compounds	DHP **1**	DHP **3**	DHP **5**	MWL
124	Guaiacol (**1**)	72.5	62.5	27.3	49.6
137	Fragment ions of 4-ethylguaiacol (**5**), homovanillin (**9**), 4-propylguaiacol (**10**), coniferyl alcohol (**13**) and dihydroconiferyl alcohol (**14**)	100.0	100.0	43.7	92.5
138	4-Methylguaiacol (**2**)	34.1	31.9	15.4	37.9
150	4-Vinylguaiacol (**3**)	17.5	19.3	15.0	29.6
151	Fragment ions of vanillin (**4**), acetoguaiacone (**8**) and propioguaiacone (**12**)	25.6	26.7	18.7	76.0
152	Vanillin (**4**) and 4-ethylguaiacol (**5**)	22.0	21.3	13.2	34.1
154	Syringol (**15**)	14.4	42.1	59.7	40.8
164	Eugenol (**6**) and isoeugenol (**7**)	13.1	15.4	12.8	21.7
166	Acetoguaiacone (**8**), homovanillin (**9**) and 4-propylguaiacol (**10**)	6.9	10.9	11.7	23.9
167	Fragment ions of 4-ethylsyringol (**19**), homosyringaldehyde (**23**), 4-propylsyringol (**24**), sinapyl alcohol (**27**) and dihydrosinapyl alcohol (**28**)	18.3	99.5	100.0	100.0
168	4-Methylsyringol (**16**) and fragment ion of dihydrosinapyl alcohol (**28**)	13.9	49.8	42.0	36.1
178	Coniferaldehyde (**11**)	17.2	18.3	11.0	26.4
180	Propioguaiacone (**12**), coniferyl alcohol (**13**) and 4-vinylsyringol (**17**)	78.7	78.3	31.6	60.6
181	Fragment ions of syringaldehyde (**18**), acetosyringone (**22**) and propiosyringone (**26**)	18.6	32.3	38.4	74.6
182	Dihydroconiferyl alcohol (**14**), syringaldehyde (**18**) and 4-ethylsyringol (**19**)	13.2	31.2	36.7	50.5
194	4-Allylsyringol (**20**) and 4-(prop-1-enyl)syringol (**21**)	4.7	8.8	13.2	22.3
196	Acetosyringone (**22**), homosyringaldehyde (**23**) and 4-propylsyringol (**24**)	3.2	5.1	5.7	22.5
208	Sinapaldehyde (**25**)	6.5	34.4	23.2	41.4
210	Propiosyringone (**26**) and sinapyl alcohol (**27**)	9.9	82.4	77.8	85.9
212	Dihydrosinapyl alcohol (**28**)	5.5	30.9	17.2	7.3
272	**29** (G–G dimer)[a]	2.3	2.9	0.9	24.4
302	**30** (G–S dimer)	1.1	1.9	1.3	12.0
332	**31** (S–S dimer)	0.3	0.8	1.6	6.5
340	(G–G dimer)	0.9	1.2	1.3	3.6
358	Dehydrodiconiferyl alcohol (**32**) and pinoresinol (**33**) (G–G dimer)	2.1	0.9	0.8	3.3
370	(G–G dimer)	0.3	0.4	1.9	1.4
388	(G–S dimer)	0.2	0.6	1.4	1.1
400	(S–S dimer)	0.1	0.2	1.0	0.6
418	Syringaresinol (**34**) (S–S dimer)	0.6	1.4	10.2	3.1

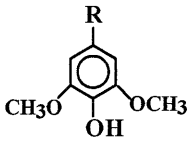
[a] G; guaiacyl, S; syringyl. Note: The structures of the compounds are shown in Fig. 2.

Guaiacyl monomeric products (1-14)



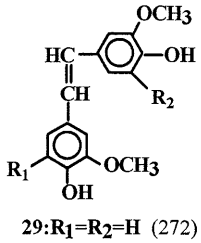
1: R = -H (124)
2: R = -CH_3 (138)
3: R = -CH=CH_2 (150)
4: R = -CHO (152)
5: R = -CH_2CH_3 (152)
6: R = -CH_2CH=CH_2 (164)
7: R = -CH=CHCH_3 (164)
8: R = -$COCH_3$ (166)
9: R = -CH_2CHO (166)
10: R = -$CH_2CH_2CH_3$ (166)
11: R = -CH=CHCHO (178)
12: R = -$COCH_2CH_3$ (180)
13: R = -CH=CHCH_2OH (180)
14: R = -$CH_2CH_2CH_2$OH (182)

Syringyl monomeric products (15-28)

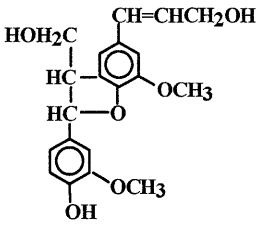


15: R = -H (154)
16: R = -CH_3 (168)
17: R = -CH=CH_2 (180)
18: R = -CHO (182)
19: R = -CH_2CH_3 (182)
20: R = -CH_2CH=CH_2 (194)
21: R = -CH=CHCH_3 (194)
22: R = -$COCH_3$ (196)
23: R = -CH_2CHO (196)
24: R = -$CH_2CH_2CH_3$ (196)
25: R = -CH=CHCHO (208)
26: R = -$COCH_2CH_3$ (210)
27: R = -CH=CHCH_2OH (210)
28: R = -$CH_2CH_2CH_2$OH (212)

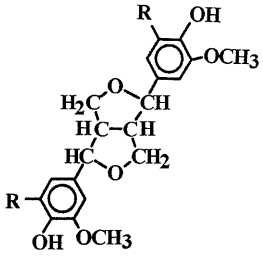
Dimeric products (29-35)



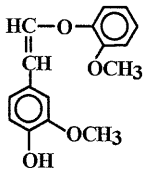
29: R_1=R_2=H (272)
30: R_1=OCH_3, R_2=H (302)
31: R_1=R_2=OCH_3 (332)



32 (358)



33: R=H (358)
34: R=OCH_3 (418)



35 (272)

Figure 2. Pyrolysis products **1–35** of DHPs and *A. turbinata* Blume MWL. The values in parentheses are molecular weights of the products. Note: **29**, 4,4'-dihydroxy-3,3'-dimethoxystilbene; **30**, 4,4'-dihydroxy-3,3',5-trimethoxystilbene; **31**, 4,4'-dihydroxy-3,3',5,5'-tetramethoxystilbene; **32**, dehydrodiconiferyl alcohol; **33**, pinoresinol; **34**, syringaresinol; **35**, 4-hydroxy-3-methoxy-β-(2-methoxyphenoxy)styrene.

groups in **29**. β-1 substructures account for approximately 7% of the total substructures on both soft and hardwood lignins.[27] Another candidate for the origins of the ion at *m/z* 272 is 4-hydroxy-3-methoxy-β-(2-methoxyphenoxy)styrene (**35**),[18] which retains a β-O-4 linkage. β-O-4 linkages are the most predominant linkages, accounting for 60% of the total in hardwood lignins.[27] For the ion at *m/z* 272, Evans *et al.*[18] also proposed a third candidate retaining a phenylcoumaran linkage. The dimeric mass peaks may be invaluable for the analysis of the lignins, in particular so-called residual lignins remaining in lignocellulosic materials after chemical treatments such as pulping and bleaching processes. The residual lignins are very intractable samples for presently available analytical methods.

Quantification of the PYMS peaks

To assess the mass peak intensities in the PYMS spectra, we calculated the percentage contributions of the intensities of the molecular ions representing monomethoxyphenols (*m/z* 124, 138, 150, 152, 164, 166, 178, 180 and 182) and dimethoxyphenols (*m/z* 154, 168, 182, 194, 196, 208, 210 and 212) to the summed intensities of these mass peaks. The ion at *m/z* 180 was included as the molecular ion of coniferyl alcohol (**13**); the molecular ions of propioguaiacone (**12**) and 4-vinylsyringol (**17**) both also appear at *m/z* 180, but the PYGC/MS data of the DHPs showed rather small contributions of propioguaiacone (**12**) and 4-vinylsyringol (**17**) compared to that of coniferyl alcohol (**13**). The peak intensity at *m/z* 182, combined ions derived from dihydroconiferyl alcohol (**14**), syringaldehyde (**18**) and 4-ethylsyringol (**19**), was tentatively assigned to the syringyl mass peaks and the guaiacyl mass peaks on the basis of the intensity ratio of *m/z* 167 to that of *m/z* 137 because the intense peaks at *m/z* 137 and 167, the fragment ions of coniferyl (137) and sinapyl (167) alcohols, are indicative of guaiacyl- and syringyl-derived products. Figure 3 shows that the monomeric peaks corresponding to monomethoxyphenols (*m/z* 124, 138 and 180) and dimethoxyphenols (*m/z* 154, 182 and 210) are sensitive to the S/C mixing ratio shifts of the DHPs. Similar results were obtained for the intensities of the fragment ions, *m/z* 137 and 167. With increasing S/C mixing ratios, the relative contributions of the syringyl mass peaks (*m/z* 168, 208 and 212) increased and those of the guaiacyl mass peaks (*m/z* 150, 152 and 178) reduced. The relative intensities of all of these six mass peaks appeared to level off after reaching a 3.0 S/C mixing ratio. The other mass peaks were insensitive to the shift in the S/C mixing ratios. We observed similar trends previously in the product yields of the DHPs determined by PYGC.[20] With increasing

S/C mixing ratios the yields of guaiacol (**1**), 4-methylguaiacol (**2**) and coniferyl alcohol (**13**) decreased and those of the syringyl equivalents (syringol (**15**), 4-methylsyringol (**16**) and sinapyl alcohol (**27**)) increased, whereas changes in the other product yields were small. This suggests that the changes in the mass peak intensities reflect those in the corresponding PYGC product yields.

Establishment of correlations between the PYMS results and the nitrobenzene oxidation results is of importance from the viewpoint of development of PYMS for routine analysis of lignocellulosic materials. However, to our knowledge no samples with a wide range of S/V ratios have been analyzed in this way. Figure 4 shows the S/G pyrolytic ratios plotted against the S/V ratios measured by the nitrobenzene oxidation method. The pyrolytic ratios were calculated from the summed intensities of the monomeric syringyl and

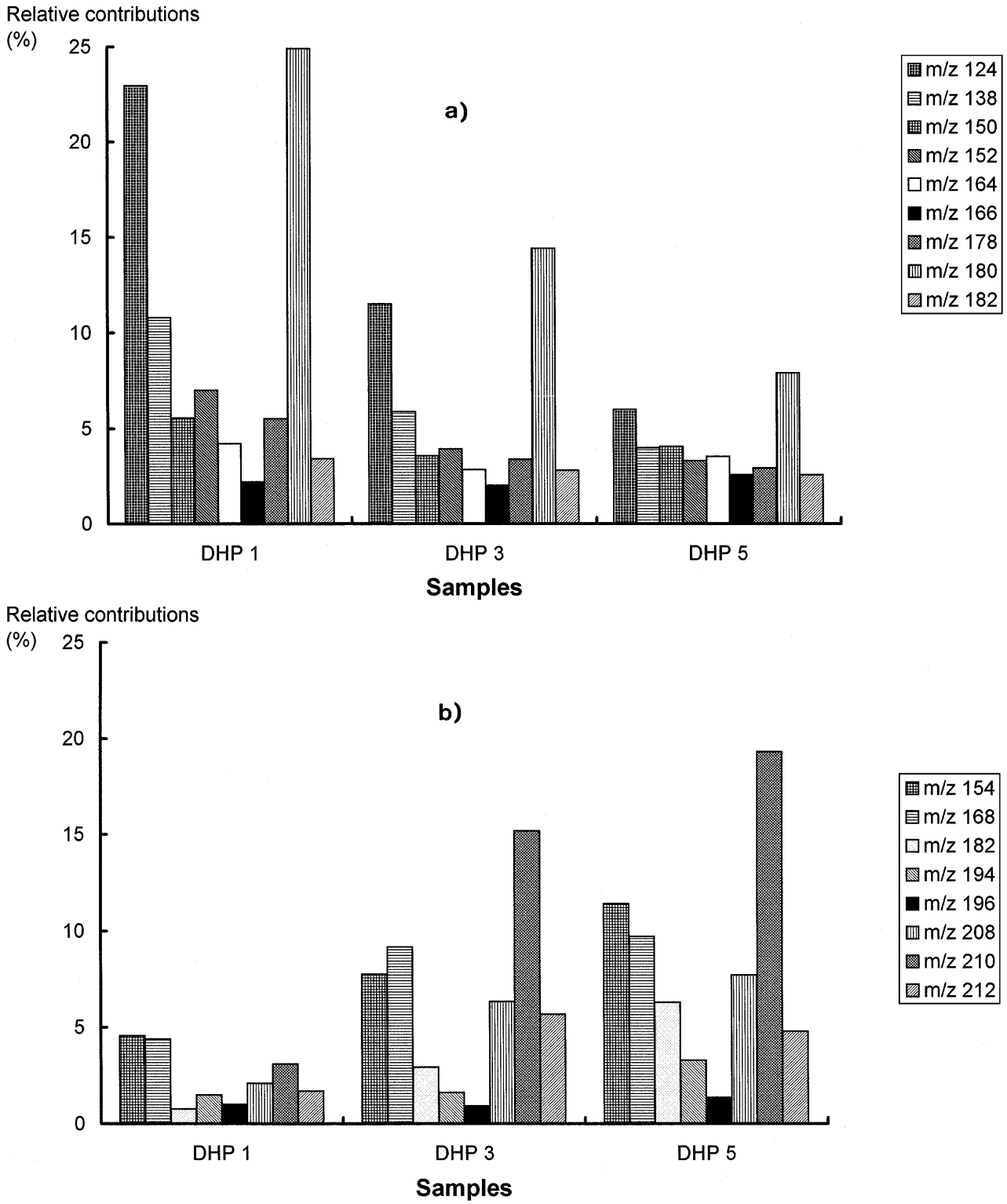


Figure 3. Relative contributions of the mass peak intensities of (a) monomethoxyphenols and (b) dimethoxyphenols to the summed mass peak intensities of monomeric lignin pyrolysis products.

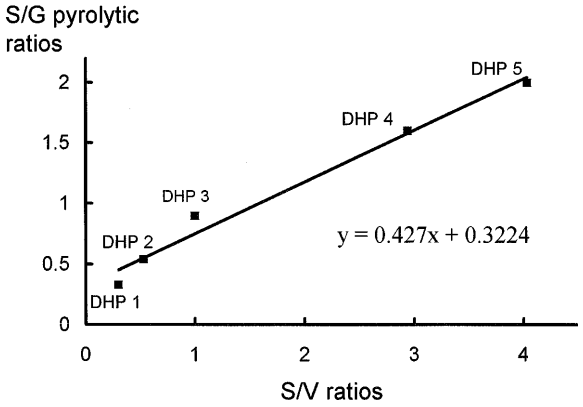


Figure 4. Correlation of the S/G pyrolytic ratios* by PYMS with the S/V ratios by nitrobenzene oxidation. * The ratios of the summed intensities of the syringyl mass peaks (*m/z* 154, 168, 182, 194, 196, 208, 210 and 212)-to-those of the guaiacyl peaks (*m/z* 124, 138, 150, 152, 164, 166, 178, 180 and 182).

guaiacyl mass peaks. As shown in Fig. 4, the S/G pyrolytic ratios and the S/V ratios are well correlated, with a significant linear regression (R^2 = 0.9802). Thus, the close correspondence between the PYMS and nitrobenzene oxidation methods is shown by the excellent linear correlation of Fig. 4. Therefore, we can predict the S/V ratios of lignocellulosic materials from the S/G pyrolytic ratios obtained by PYMS. For example, the MWL sample is predicted to have a calculated S/G pyrolytic ratio of 0.98 from its S/V ratio (1.09). This value agrees reasonably well with an experimental S/G pyrolytic ratio of 0.86 obtained by using PYMS. Linear correlations were observed also between the S/G pyrolytic ratios determined by PYGC and the S/V ratios, for the DHPs and for Japanese hardwoods, the R^2 values being 0.9990 for the DHPs[20] and 0.9063 for the hardwoods.[28] Therefore, the PYGC method also provides information on the S/G ratios of lignocellulosic materials as well as the PYMS method. Unlike the PYGC method, however, the PYMS method does not need time-consuming determinations of the response factor of each product to a flame ionization detector. This advantage may outweigh the inherent problems of PYMS, such as the ambiguous structural assignment of the mass peaks in the quantitative PYMS analyses of lignocellulosic materials. The results obtained in this study demonstrate that PYMS will play an increasing role in the rapid characterization of microgram or nanogram samples, because this method offers qualitative fingerprints of samples plus semiquantitative information.

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