

SURVIVAL OF LIGNIN-DERIVED STRUCTURAL UNITS IN ANCIENT COALIFIED WOOD SAMPLES

Patrick G. Hatcher and Harry E. Lerch, III

U. S. Geological Survey, Reston, VA 22092

ABSTRACT

Analysis of five Cretaceous-age and one Carboniferous-age fossil wood samples of lignite rank by pyrolysis-gas chromatography-mass spectrometry has revealed the presence of lignin-derived compounds such as phenols and methoxyphenols. In Cretaceous lignitic wood, the various methoxyphenols were of the same suite as those produced from pyrolysis of modern lignin and degraded wood. Indications are that the lignin structural units of Cretaceous lignitic wood samples are preserved to varying degrees. In Carboniferous lignitic wood only traces of methoxyphenols were detected, but phenols were abundant. This is the first indication that lignin-derived methoxyphenols can survive in geological materials as old as the Carboniferous.

INTRODUCTION

Lignin is a major biochemical component of woody tissue; however, it rarely survives early stages of coalification. Biochemical and chemical alteration during burial limit the extent to which lignin biomarkers can be preserved and recognized in the geologic record. Lignin-derived compounds have been observed in pyrolysis products of low rank coals and associated woody tissue[1-5]. Mycke and Michaelis[6] isolated lignin-derived methoxyphenols from a Miocene coal by catalytic hydrogenolysis. Sigleo[7,8] reported the presence of phenolic compounds derived from alteration of lignin in pyrolysis products of silicified woody tissue as old as Triassic age. However, no trace of methoxyphenols, that would clearly relate back to lignin structures, could be identified in Sigleo's samples. Hayatsu *et al.*[9] similarly reported the presence of lignin-derived products from copper-oxide oxidation of several coal samples. They, too, were unable to identify methoxylated phenols in their products. Recently, Nip *et al.*[2] subjected two lignite samples, one of Paleocene age and the other of Eocene age, to Curie-point pyrolysis-mass spectrometry. The data indicated only traces of methoxyphenols. They were puzzled by the low abundance of phenols in general, because the petrographic data indicated large amounts of huminite derived from woody tissue.

The most definitive identification of lignin-derived pyrolysis products in coalified wood samples as old as Paleocene age was reported in a study of coalified wood by Stout *et al.*[4]. They identified numerous lignin-derived methoxyphenols in angiospermous and gymnospermous wood samples from various lignites by Curie-point pyrolysis-gas chromatography-mass spectrometry. In a study of lignitic gymnospermous wood samples of Cretaceous and younger ages by analytical pyrolysis[5], we reported the presence of methoxyphenols in the pyrolyzates. Many of these methoxyphenols had associated propenyl side chains indicative of the presence of well-preserved lignin residues.

In an attempt to delineate the degree of preservation of lignin in coal, we examined numerous coalified wood samples ranging from Carboniferous to Holocene age. The samples were initially screened by solid-state C-13 nuclear magnetic resonance to detect the possible presence of methoxyl carbon. Once such carbons were detected, the samples were subjected to analytical pyrolysis to determine the content of methoxyphenols which would provide an indication of the state of preservation of the lignin-derived structural units. We report here on the

identification of lignin-derived methoxyphenols in the coalified wood samples selected for analytical pyrolysis.

SAMPLES AND METHODS

Samples of coalified wood (xylem) were obtained from Carboniferous and younger strata in various locales. A sample of coalified wood was collected by D. Gottfried (U. S. Geological Survey) from the Magothy Formation (Upper Cretaceous) at the C&O canal near Bethel, Maryland. Byrd Stadium lignitic wood was collected by the late I. A. Breger (U. S. Geological Survey) from an excavation for Byrd Stadium on the campus of the University of Maryland. The coalified logs at this site were buried in an upright position in sediments of the Potomac Group (Lower Cretaceous). Wayne Newell (U. S. Geological Survey) graciously provided a sample (Stafford lignite) of coalified wood buried in sediments of the Potomac Group (Lower Cretaceous) near Stafford, Virginia. Another sample was obtained by Roger Thomas (U. S. Geological Survey) from the Patapsco Formation of the Potomac Group (Lower Cretaceous) near the intersection of I-95 and I-695 in Landsdowne, Maryland. Another sample (Long Island lignite) was obtained by Byron Stone (U. S. Geological Survey) from probable Pleistocene clay in the Nassau Brick Co. clay pit on Long Island, New York; the sample probably was reworked from the Magothy Formation (Upper Cretaceous). Finally, a sample of coalified wood was obtained from the collection of the late I. A. Breger, and this sample was from the Carboniferous lignite deposits of the Moscow Basin, USSR, Kurovskaya mine No. 1. All samples were essentially of lignite rank as partially demonstrated by the elemental data in Table 1.

Table 1. Elemental compositions (dry mineral-matter free) for coalified wood samples.

Lignite Sample	Wood type	%C	%H	%N	%O
Stafford	G	74.9	4.98	0.58	18.9
Long Island	NA	61.1	4.57	0.33	34.0
Patapsco	G	65.7	5.00	0.27	29.3
Byrd Stadium	G	59.2	3.17	0.21	36.3
Magothy	G	72.2	4.43	0.21	22.0
Moscow Basin	NA	NA	NA	NA	NA

G- gymnospermous wood

NA-data not available

Pyrolysis-gas chromatography-mass spectrometry was performed on a Dupont 490B gas chromatograph-mass spectrometer system interfaced with a Technivent Vector 1 data system and a Chemical Data Systems model 120 pyroprobe. Pyrolysis-gas chromatography was performed with a Perkin-Elmer Sigma 2B gas chromatograph interfaced to the pyroprobe. The fused silica column was a 50% phenylmethylsilicone phase available from Hewlett-Packard. Operating conditions and specific methodologies have been given in a previous report[5].

The presence of lignin structural units was confirmed by pyrolysis-gas chromatography-mass spectrometry using comparisons of mass spectra to library spectra, to spectra of authentic standards, and to published mass spectra of lignin phenols[10].

RESULTS AND DISCUSSION

Pyrolysis of Cretaceous lignitic xylem has been shown in a previous report[5] to yield abundant quantities of methoxyphenols derived from the lignin residues preserved in the lignitic woods. The state of preservation can be determined by the abundance of methoxyphenols relative to other altered lignin byproducts such as the phenols and catechols. Figure 1 shows the pyrograms for two samples representative of most of the Cretaceous age lignitic wood in which the state of preservation of lignin varies widely. Peaks for guaiacol, 4-methylguaiacol, 4-vinylguaiacol, 4-ethylguaiacol, eugenol, *cis*- and *trans*-isoeugenol, vanillin, and acetoguaiaconone are clearly the major products in the Long Island lignite, the one representative of lignitic wood samples in which lignin-derived structures are believed to be the least altered. These specific methoxyphenols are clearly derived from lignin precursors or partially altered lignin that has survived in the lignitic wood samples. Extensively altered lignin products such as phenol, the cresol isomers, catechol isomers, and the alkylphenols are also major components of the pyrogram, but they are subordinate to the methoxyphenols in the Long Island lignite. In the Magothy lignite, the phenols and cresols are dominant over the methoxyphenols, indicating that the lignin residues in this sample are significantly more altered than in the Long Island lignite. The degree of lignin preservation varies widely among the lignitic wood samples. In wood samples of subbituminous rank, methoxyphenols have not been detected; the dominant pyrolysis products are phenols and cresols[5].

Analytical pyrolysis of gymnospermous lignin that is minimally altered has been shown to yield the same products as those mentioned above for the least coalified wood samples, although the relative peak intensities may be different[10,12,13]. Figure 2 shows a pyrogram for a gymnospermous log (Atlantic White Cedar, *Chamaecyparis thyoides*) buried in peat from the Great Dismal Swamp, Virginia. Previous studies have shown that most of the cellulosic components of this sample have been degraded microbiologically, leaving lignin relatively unaltered[14]. The pyrogram confirms this by showing a product distribution that is typical of lignin[12], although the broad peak for levoglucosan indicates a small amount of cellulosic material is present. The four largest peaks are for 4-methylguaiacol, 4-vinylguaiacol, guaiacol, and *trans*-isoeugenol in decreasing order of intensity. The relatively high abundance of methoxyphenols having the 3-carbon side chain (eugenol, the isoeugenols, coniferaldehyde, and guaiacylpropan-2-one) and the low abundance of methylvanillate, vanilloyl methyl ketone, and vanillic acid is evidence that the lignin is not altered extensively[12]. Also, the presence of only trace levels of phenols, cresols, and catechols in the buried log is evidence for unaltered lignin.

The lesser quantities of methoxyphenols having the 3-carbon side chain, relative to the other methoxyphenols, in the Cretaceous lignitic wood samples, compared to the modern buried cedar, are an indication that the lignin in the Cretaceous samples has been altered significantly. For example, the ratio of peak intensities, for guaiacol/*trans*-isoeugenol, is 1.3 for the modern buried cedar, whereas the Cretaceous lignitic samples have values that range from 4.8 to 11. This more than five-fold increase in the ratio is indicative of the fact that the lignin molecules in the lignitic woods are altered at the side-chain sites.

Although the lignin-derived methoxyphenols are important components of the pyrolysis of Cretaceous lignitic wood samples, phenols, catechols, and methylated phenols are equally important. The ratio of phenols+catechols to methoxyphenols ranges from 1.0 to 4.9 in the lignitic woods. In the buried cedar, this ratio is 0.10, indicative of the fact that lignin-derived methoxyphenols are the principal constituents and the phenols and catechols, the products of altered lignin, are subordinate. Sigleo[7] suggested that phenols, cresols, and catechols in pyrolysis products of 200-million-year-old petrified wood are derived from altered lignin. We support this conclusion, primarily because lignin is the most likely source of phenols in the lignitic

woods and because of the abundance of lignin-derived methoxyphenols which are co-produced during pyrolysis.

The pyrolysis data for the lignitic wood from the Moscow Basin are shown in Figure 3. The major pyrolysis products are alkylbenzenes, but phenol and alkylphenols comprise major peaks in the pyrogram (Figure 3a). Only a trace of methoxyphenol (Figure 3b) and methylmethoxyphenol (Figure 3c) could be detected in the sample. However, the trace presence of these two methoxyphenols is clear indication that lignin-like material was present in the wood and that only a trace of it remains, albeit in a highly altered form. Thus, the presence of the methoxyphenols in pyrolysis products indicates that lignin-derived components have survived for approximately 300 million years. It is interesting that three isomers of methoxyphenol can be detected in the selected ion trace of m/z 124 (Figure 3b). That these specific peaks were indeed methoxyphenols was determined by retention times and by examination of the fragment ions at m/z 109 and 81. Similarly, the verification of the presence of methylmethoxyphenol was made by retention time and by examination of fragment ions at m/z 123 and 95. Only one isomer of methylmethoxyphenol was detected (Figure 3c) and its retention time on the column corresponds to that of 4-methylguaiacol. Direct comparison of mass spectra to library spectra of authentic methoxyphenols was not possible due to the trace quantities and the complexity of the pyrolysis mixture in the retention-time windows for elution of the methoxyphenols.

Phenol, the cresol isomers, and the dimethylphenols, major pyrolysis products in the Moscow wood sample, are probably also derived from lignin precursors that have been altered through coalification reactions. Hatcher *et al.*[5] have shown that an increase is observed in the relative proportion of phenols and cresols as rank of coalified wood samples increases to subbituminous coal. Comparing the pyrolysis products from the Moscow wood to other coalified wood samples of Hatcher *et al.*[5] allows us to deduce that the Moscow wood is more similar to coalified wood of subbituminous rank than it is of coalified wood of lignite rank, assuming that its lignin was originally similar to lignin in Cretaceous or younger woods.

CONCLUSIONS

The analysis of lignitic woods by analytical pyrolysis has shown that lignin structural units can be preserved as biomarkers in samples as old as Carboniferous age, or approximately 300 million years. At least half or more of the pyrolysis products in lignitic wood of Cretaceous age are methoxyphenols characteristic of lignin. The product distributions in these Cretaceous samples indicate that the lignin is mainly altered in the side chains. Phenols, cresols, catechols, and other methylated phenols account for the remainder of the pyrolysis products. It is likely that these products are also derived from lignin, especially lignin that has been altered by coalification reactions.

ACKNOWLEDGMENTS

We thank our colleagues at the U. S. Geological Survey, Roger Thomas, David Gottfried, Byron Stone, and Wayne Newell, for providing samples for this study.

REFERENCES

1. Philp, R. P., Russell, N. J., Gilbert, T. D., and Friedrich, J. M., *J. Anal. Appl. Pyrol.*, **4**, 143-161, (1982).
2. Nip, M., de Leeuw, J. W., Schenck, P. A., Meuzelaar, H. L. C., Stout, S. A., Given, P. H., and Boon, J. J., *J. Anal. Appl. Pyrol.*, **8**, 221-239, (1985).

3. Chaffee, A. L., Johns, R. B., Baerken, N. J., de Leeuw, J. W., Schenck, P. P., and Boon, J. J., *Org. Geochem.*, **6**, 409-416, (1984).
4. Stout, S. A., Boon, J. J., and Spackman, W., *Geochim. Cosmochim. Acta*, **52**, 405-414, (1988).
5. Hatcher, P. G., Lerch, H. E., III, Kotra, R. K., and Verheyen, T. V., *Fuel*, **67**, 1069-1075, (1988).
6. Mycke, B., and Michaelis, W., *Naturwissenschaften*, **73**, 731-734, (1986).
7. Sigleo, A. C., *Geochim. Cosmochim. Acta*, **42**, 1397-1405, (1978).
8. Sigleo, A. C., *Science*, **200**, 1054-1056, (1978).
9. Hayatsu, R., Winans, R. E., McBeth, R. L., Scott, R. G., Moore, L. P., and Studier, N. H., *Nature*, **278**, 41-43, (1979).
10. Obst, J. R., *J. Wood Chem. Technol.*, **3**, 377-397, (1983).
11. van de Meent, D., Brown, S. C., Philp, R. P., and Simoneit, B. R. T., *Geochim. Cosmochim. Acta*, **44**, 999-1013, (1980).
12. Saiz-Jimenez, C., and de Leeuw, J. W., *Org. Geochem.*, **6**, 417-422, (1984).
13. Saiz-Jimenez, C., Boon, J. J., Hedges, J. I., Hessels, J. K. C., and de Leeuw, J. J., *J. Anal. Appl. Pyrol.*, **11**, 437-450, (1987).
14. Hatcher, P. G., Romankiw, L. A., and Evans, J. R., *Proc. 1985 Int. Conf. Coal Science*, 616-617, (1985).

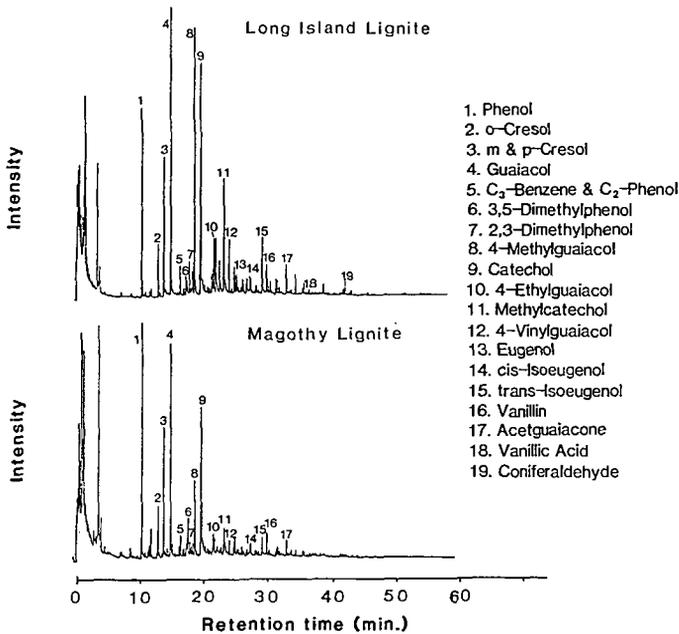


Figure 1. Pyrolysis-gas chromatography of two Cretaceous lignitic wood samples. Numbers above the peaks refer to identified pyrolysis products listed to the right.

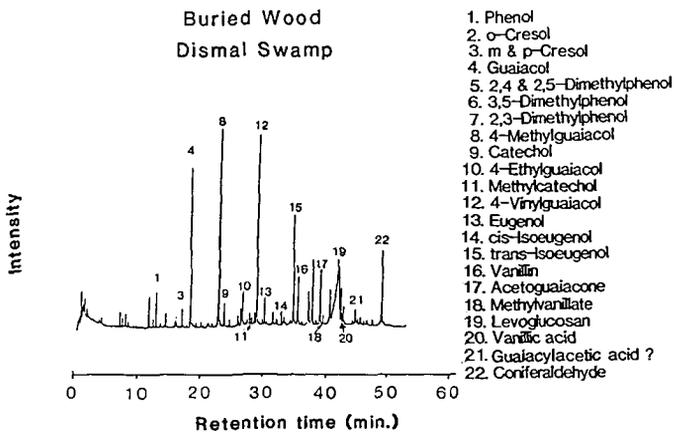


Figure 2. Pyrolysis-gas chromatography of Atlantic White Cedar from the Dismal Swamp, VA. Numbers above the peaks refer to identified pyrolysis products listed to the right.

Moscow Coalified Wood

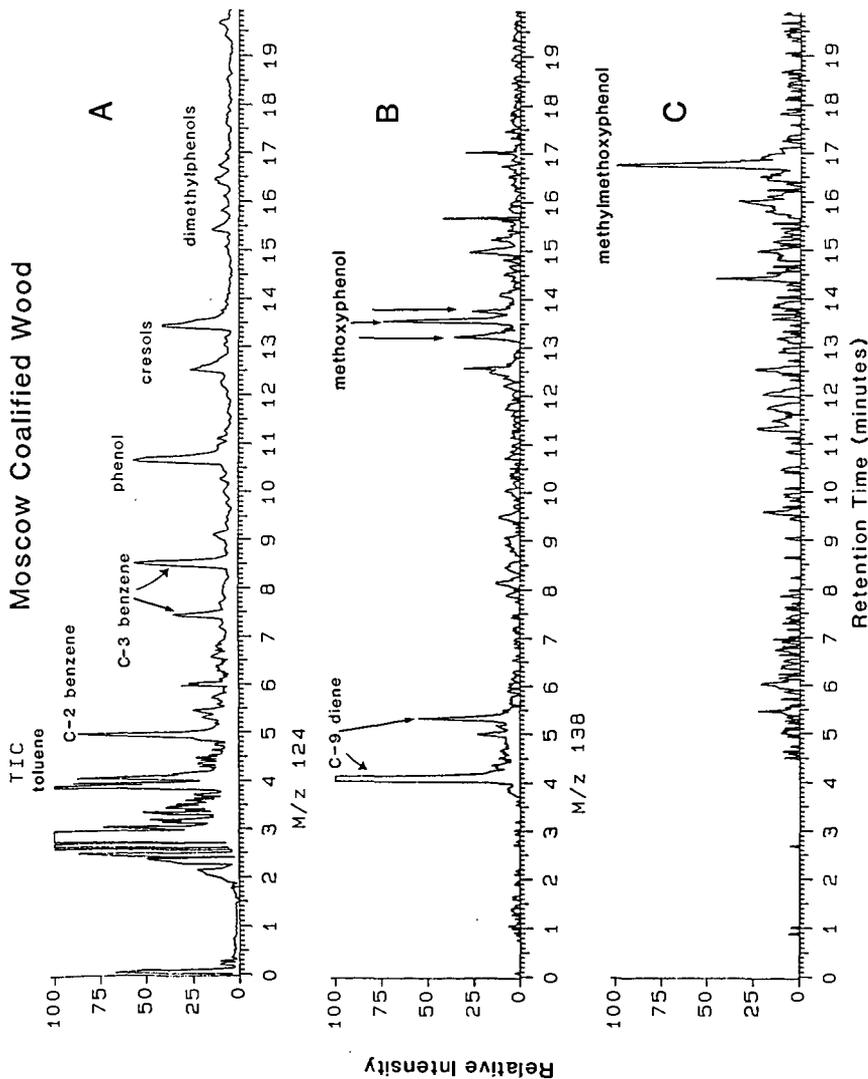


Figure 3. Pyrolysis-gas chromatography-mass spectrometry of the coalified wood from the Moscow Basin lignite. Trace A represents the total ion chromatogram (TIC), B represents the mass chromatogram for m/z 124, and C represents the mass chromatogram for m/z 138. Peak assignments are listed.