



Characterization of humic acids from low-rank coals by ^{13}C -NMR and pyrolysis-methylation. Formation of benzenecarboxylic acid moieties during the coalification process

J. C. DEL RÍO, F. J. GONZÁLEZ-VILA, F. MARTÍN and T. VERDEJO

Instituto de Recursos Naturales y Agrobiología de Sevilla, C.S.I.C., P.O. Box 1052, 41080-Seville, Spain

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Abstract—Humic acid (HA) fractions isolated from a peat and lignite deposit were studied by CP/MAS ^{13}C -NMR and pyrolysis-methylation. Loss of carbohydrates, removal of methoxyls and formation of catechols during the coalification process was evident. Pyrolysis-methylation released a great variety of components, the lignin-derived monomers being the most prominent. A very striking feature was the release of benzenecarboxylic moieties after pyrolysis-methylation which have not been observed previously by pyrolytic techniques. These moieties were released in higher amounts from the lignite HA, suggesting that the content in carboxylic groups increase with coalification, at least up to the lignite stage. Oxidation of the C-3 side chain of the lignin structure would produce these benzenecarboxylic acids and benzylic ketones.

Key words—peat, lignite, coalification, pyrolysis, tetramethylammonium hydroxide (TMAH), CP/MAS ^{13}C -NMR, benzenecarboxylic acids

INTRODUCTION

The characterization of the humic acid (HA) fractions from low-rank coals has been shown to be useful for obtaining information about organic source materials, depositional environments and for the elucidation of diagenetic pathways during the coalification process (Hatcher *et al.*, 1980, 1981, 1982; Verheyen and Johns, 1981; Verheyen *et al.*, 1982; Ibarra and Juan, 1985; González-Vila *et al.*, 1994). Since peat is considered to be one of the materials from which coal is derived, the chemical characterization of peat and its humic matter are essential for delineating the chemical transformation of peat in the early stages of coal formation.

In recent years, numerous techniques have been applied in the study of coalification of wood polymers and have provided new insights into the chemical origin of coal. By examining modern wood, wood buried in peat swamps, and ancient wood coalified to different ranks, with combined NMR and pyrolysis techniques, a detailed understanding has been obtained on the early stages of coalification. Wood transformation to coalified wood begins at the peat stage, where cellulose is degraded and removed while the lignin is selectively preserved (Philp *et al.*, 1982; Stout *et al.*, 1988; Hatcher *et al.*, 1988, 1989; Hatcher, 1990; Bates *et al.*, 1991).

Pyrolysis techniques have proved to be particularly useful in studying the coalification process, due to the detailed information obtained at the molecular level

and the ease of sample preparation. However, pyrolysis seems to underestimate the potential presence of carboxylic bearing units among the structural 'building blocks'. In fact, flash pyrolysis of polymers containing benzenecarboxylic acid moieties (such as fulvic and humic acids) leads to biased structural interpretation since it has been shown that these units undergo decarboxylation under these conditions (Martín *et al.*, 1994a). In the case of humic acids from low-rank coals, only a few carboxylic pyrolysis products have usually been reported, although the presence of carboxylic groups in these materials has been determined by spectroscopic and wet chemical methods to be around 5% (Martín, 1975; Hatcher, 1990; Stefanova *et al.*, 1993; González-Vila *et al.*, 1994).

In a previous paper (Martín *et al.*, 1994a), we proposed pyrolysis in the presence of tetramethylammonium hydroxide (TMAH) for the detection of benzenecarboxylic acids, which otherwise undergo decarboxylation under conventional pyrolysis. This technique, also called simultaneous pyrolysis methylation (SPM), was introduced by Challinor (1989), and produces methyl esters of carboxylic acids and methyl ethers of hydroxy compounds. This technique has already been successfully applied to assess the structure of different natural and artificial polymers such as cutins, alkyd resins, polyester fibres and humic substances (Challinor, 1989, 1991a, b; Anderson and Winans, 1991; de Leeuw and Baas, 1993; Martín *et al.*, 1994a, b). It has been demonstrated that the

reaction that takes place consists of thermally assisted chemolysis rather than the methylation of released pyrolysis products (de Leeuw and Baas, 1993; Martín *et al.*, 1994a).

In this paper, the structural characteristics of the HA fractions isolated from a peat, and a lignite deposit, have been approached both by solid-state ^{13}C -NMR and pyrolysis-methylation. We mainly focused our attention on the release of carboxylic moieties.

MATERIAL AND METHODS

A sapric peat from the Padul deposit (Granada, south Spain) and a lignite sample from the Pontes de Garcia Rodriguez (PGR) deposit (La Coruña, north Spain) were selected for this study. Various chemical, geochemical and geological data of the selected samples have been published elsewhere (González-Vila *et al.*, 1994; Martín, 1975; del Rio *et al.*, 1992). The peat and lignite samples were ground to less than $53\ \mu\text{m}$ and Soxhlet extracted with toluene for 48 h. The bitumen free samples were then extracted three times with 0.1 M NaOH solutions. The extracts obtained after centrifugation were precipitated with 0.1 M HCl. The humic acids (HA) were then centrifuged, dialysed against distilled water and freeze-dried. The content on humic acids was as follows: Padul peat, 78% dry, ash-free; PGR lignite, 56% dry, ash-free. Analytical characteristics of the HAs are listed in Table 1.

Pyrolysis-gas chromatography-mass spectrometry

For pyrolysis in the presence of TMAH, the HA samples were first dissolved in the minimum amount of TMAH (25% aqueous solution) and dried in a desiccator overnight. The syrups were placed on the ribbon foil of the CDS pyroprobe and heated to 500°C for 10 s. Separation of the pyrolysis products was achieved on a fused silica column (SE-52; J&W Scientific) of 25 m length and 0.2 mm i.d. The gas chromatograph (Hewlett Packard HP-5890) was programmed from 40 to 300°C at a rate of $6^\circ\text{C}/\text{min}$. Helium (1 ml/min flow rate) was used as a carrier gas. The mass spectrometer (HP 5988 A) was set at 70 eV. Identification was achieved by mass fragmentography, library search and comparison with literature data. When possible, the identifications were accomplished by comparison with authentic standards. The substitution patterns of the different positional isomers were established by comparison of relative retention times with literature data and, when possible, confirmed by co-injection with authentic standards.

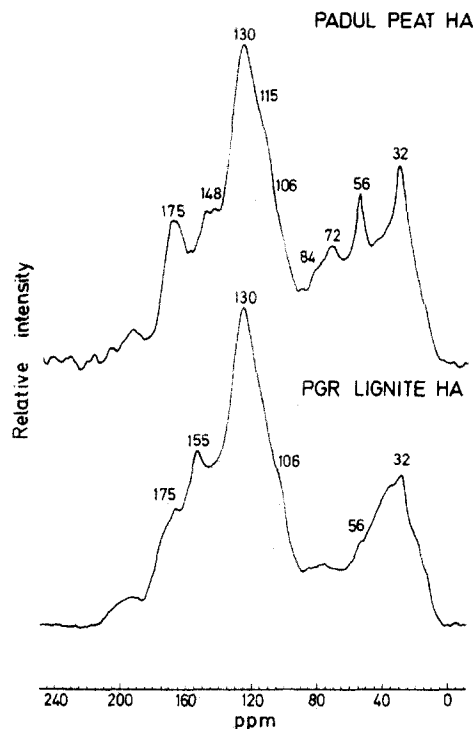


Fig. 1. (CP/MAS) ^{13}C -NMR spectra of the Padul peat and Pontes Garcia Rodriguez lignite HAs.

^{13}C -nuclear magnetic resonance

High resolution solid-state ^{13}C -NMR spectra of the HA samples were collected at 25.2 MHz under cross polarization-magic angle spinning conditions (CP/MAS) using the quantitation condition described elsewhere (Fründ and Lüdemann, 1991).

RESULTS AND DISCUSSION

Figure 1 shows the solid-state ^{13}C -NMR spectra of the Padul peat and the PGR lignite HAs. Both spectra are characterized by prominent bands at 32 and 130 ppm corresponding to aliphatic and aromatic carbons respectively. The total ion chromatograms (TIC) of the thermal degradation products, obtained after pyrolysis of the peat and lignite humic acids in the presence of TMAH, are shown in Fig. 2. The identification of the different chromatographic peaks are listed in Table 2. The major peaks corresponded to lignin derived units and aliphatic moieties (fatty acids and alkene/alkane pairs).

Table 1. Elemental composition (wt%) and functional group content (% of coal dry ash-free) of the selected HA

	C	H	N	O + S	H:C	O:C	Ash	Total acidity	Carboxyl	Phenolic OH
HA Padul peat	53.0	4.9	1.3	38.7	1.10	0.55	3.5	8.3	3.0	5.3
HA PGR lignite	63.9	4.7	1.0	30.4	0.88	0.36	3.8	9.3	3.4	5.9

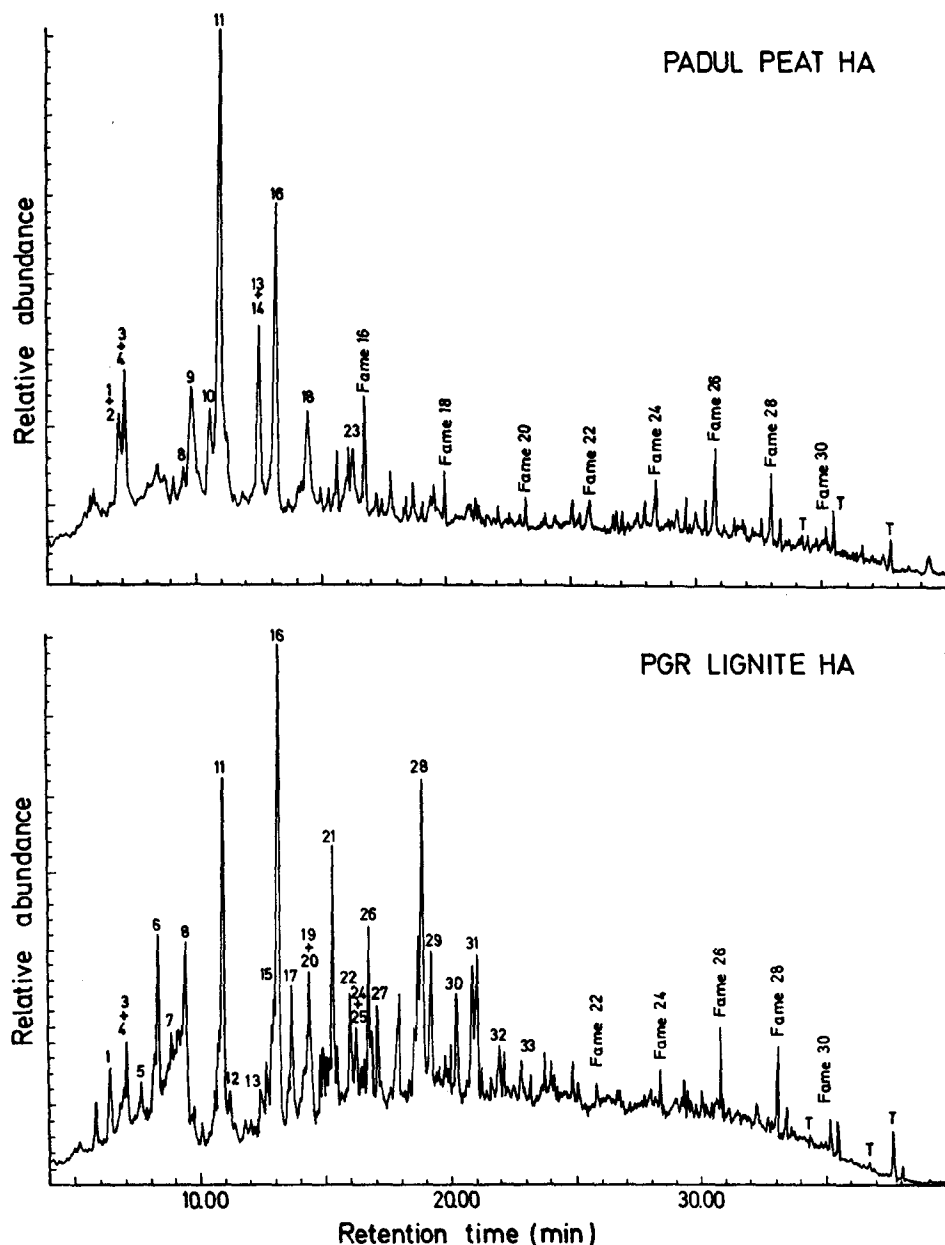


Fig. 2. Total ion chromatogram of the thermal degradation products obtained after pyrolysis of the HA fractions from Padul peat and Pontes Garcia Rodriguez lignite, in the presence of TMAH. For peak identification refer to Table 2. T: triterpenoids.

Noticeable qualitative and quantitative differences between the pyrolytic and NMR patterns are observed. The ^{13}C -NMR spectrum of the peat HA shows signals at 72 and 106 ppm (for the anomeric carbon) and a small band at 84 ppm due to cellulosic carbon. Although the band at 106 ppm is clearly present in the lignite spectrum, the others are practically absent indicating the loss of carbohydrates during the coalification process (Stout *et al.*, 1988; Hatcher *et al.*, 1988). The only compound derived from polysaccharides detected in the pyrograms of both samples was furan-2,5-dicarboxylic acid

dimethyl ester (peak No. 3). However, in the PGR lignite HA, only trace amounts of this compound were detected indicating that polysaccharides are progressively lost with increasing coalification. The related thiophene-2,5-dicarboxylic acid (peak No. 8) was identified in both samples suggesting that the incorporation of sulphur into the HA structure has taken part in the early stages of the coalification process.

Signals corresponding to lignin were also observed in the ^{13}C -NMR spectrum of the Padul peat HA. Thus, the spectrum showed a prominent band at

Table 2. Identification and relative abundance of the compounds released after pyrolysis-methylation of the Padul peat and PGR lignite HAs

No.	Compound	<i>m/z</i>	Padul peat HA	PGR lignite HA
1	3-methoxybenzenecarboxylic acid, methyl ester	135,166	+	+
2	4-methoxyacetophenone	135,150	+	-
3	furan, 2,5-dicarboxylic acid, dimethyl ester	153,184	+	+
4	4-methoxybenzenecarboxylic acid, methyl ester	135,166	+	+
5	4-methoxybenzeneacetic acid, methyl ester	149,180	-	+
6	1,2-benzenedicarboxylic acid, dimethyl ester	163,194	-	++
7	1,3-benzenedicarboxylic acid, dimethyl ester	163,194	-	+
8	2,5-thiophenedicarboxylic acid, dimethyl ester	169,200	+	++
9	3,4-dimethoxybenzenemethanol, methyl ether	151,182	++	-
10	3,4-demethoxyacetophenone	165,180	+	-
11	3,4-dimethoxybenzoic acid methyl ester	165,196	++	+++
12	3,4-dimethoxybenzeneacetic acid, methyl ester	179,210	-	+
13	2-propenoic acid, 3-(4-methoxyphenyl), methyl ester	161,192	++	+
14	3,4,5-trimethoxyacetophenone	195,210	++	-
15	3-methoxybenzene-1,2-dicarboxylic acid, dimethyl ester (t)	193,224	-	+
16	3,4,5-trimethoxybenzoic acid, methyl ester	211,226	+++	+++
17	4-methoxybenzene-1,3-dicarboxylic acid, dimethyl ester (t)	193,224	-	++
18	3,4,5-trimethoxybenzenemethanol, methyl ether	181,212	++	-
19	2,3,4-trimethoxybenzenecarboxylic acid, methyl ester	195,226	-	+
20	2-methoxybenzene-1,5-dicarboxylic acid, dimethyl ester (t)	193,224	-	++
21	1,2,4-benzenetricarboxylic acid, trimethyl ester (t)	221,252	-	++
22	3,4-dimethoxybenzene-1,2-dicarboxylic acid, dimethyl ester (t)	223,254	-	++
23	2-propenoic acid-3-(3,4-dimethoxyphenyl) methyl ester	191,222	+	-
24	1,3,5-benzenetricarboxylic acid, trimethyl ester (t)	221,252	-	+
25	4,5-dimethoxybenzene-1,3-dicarboxylic acid, dimethyl ester (t)	223,254	-	+
26	4,5-dimethoxybenzene-1,2-dicarboxylic acid, dimethyl ester (t)	223,254	-	++
27	3-methoxybenzene-1,2,4-tricarboxylic acid, trimethyl ester (t)	251,282	-	++
28	2-methoxybenzene-1,3,5-tricarboxylic acid, trimethyl ester (t)	251,282	-	+++
29	5-methoxybenzene-1,3,5-tricarboxylic acid, trimethyl ester (t)	251,282	-	++
30	1,2,3,4-benzenetetracarboxylic acid, tetramethyl ester (t)	279,310	-	++
31	1,2,4,5-benzenetetracarboxylic acid, tetramethyl ester (t)	279,310	-	++
32	5-methoxybenzene-1,2,3,4-tetracarboxylic acid, tetramethyl ester (t)	309,340	-	+
33	2-methoxybenzene-1,3,4,5-tetracarboxylic acid, tetramethyl ester (t)	309,340	-	+

+, ++, +++: low, medium, high relative abundances.
-: not detected.

(t) the positional isomers were tentatively assigned according to the relative retention times given by Schnitzer (1974), Schnitzer and Skinner (1974) and Spittler (1981).

56 ppm due to methoxyl carbons, at 115 ppm from the combined signals of C-2, C-5 and C-6 in guaiacyl units, and at 148 ppm from the oxygen-substituted aromatic carbons (C-3 and C-4) in guaiacyl units. These bands disappear in the spectrum of the lignite HA. At the same time, a band at 155 ppm due to hydroxyls attached to aromatic rings (catechols) appears in the lignite HA spectrum, which is absent in the peat HA spectrum. This indicates the demethylation of the methoxyl groups in the lignin macromolecule, during the coalification process, and their gradual transformation into catechol structures, in agreement with Hatcher *et al.* (1988). Other peaks of significance in both spectra are those assigned to carbonyl carbons in carboxyl groups (175 ppm) and aldehyde/ketone groups (200 ppm). These peaks are broad and comprise around 10% of the total carbon. It is likely that a greater part of these carbonyl carbons originate from oxidized lignin residues, especially those oxidized at the α -carbon in the 3-carbon side chain. Their relative abundance in the spectra of the peat and lignite HAs is greater than in the published spectra for lignins.

Lignin-derived units with carboxyl groups have, however, not been detected previously by conventional pyrolysis. Tegelaar *et al.* (1989) noted that esterified *p*-coumaric acid generates *p*-coumaric acid

as a primary pyrolysis product that subsequently undergoes decarboxylation giving rise to *p*-vinylphenol. More recently, it has been shown with standard compounds that benzenecarboxylic moieties undergo decarboxylation under conventional pyrolysis (Martin *et al.*, 1994a) and this could be the reason why the presence of carboxyl groups, in lignin-derived units, have been overlooked in the past. Pyrolysis in the presence of TMAH, however, avoids decarboxylation and produces methyl esters of carboxylic acids and methyl ethers of hydroxyl groups, as has been demonstrated with standard compounds (Martin *et al.*, 1994a) and with aliphatic polyesters (de Leeuw and Baas, 1993). The mechanism of pyrolysis in the presence of TMAH has also been described in detail in these papers (de Leeuw and Baas, 1993; Martin *et al.*, 1994a).

In agreement with NMR data, the main diagnostic groups among the pyrolysis products of the peat and lignite HAs were the methyl derivatives of the phenolic compounds, characteristic of lignins. The methylated carboxylic groups, released in the pyrolysate, arise from both free carboxyl groups and ester moieties present in the HA macromolecule. Also, the methoxyl groups at C-4 in the lignin moieties arise from both free -OH groups, which become methylated, and by TMAH-assisted cleavage of the

alkyl-aryl ether bond leading to the formation of a methoxyl group. The three main structural units (*p*-coumaryl, guaiacyl and syringyl) were identified. It is interesting to note the absence of the methyl derivatives of coniferyl and synapyl alcohols in the pyrolysates of both samples. Stout *et al.* (1988) also noticed a rapid decrease in intensity of the coniferyl and synapyl alcohol during early coalification. However, the most striking feature of the pyrograms was the release of high concentrations of benzenecarboxylic acid moieties from both samples which have not been released previously from HAs by conventional pyrolysis. It is known that peat accumulations require anaerobic conditions to preserve sufficient organic matter for coal formation. Under such circumstances, it is likely that lignin in peat HA remains relatively unaltered. The release, by pyrolysis-methylation, of higher amounts of benzenecarboxylic acids from the lignite HA suggests that oxidation of lignin occurs with increasing coalification. The lignin molecule is thus gradually transformed to an oxidized framework. The placement of the carboxyl and carbonyl groups in the lignin-derived compounds identified in Table 2 indicates that such oxidative alteration affects the 3-carbon side-chain of the lignin. The presence of carbonyl and carboxyl groups, located at the α -carbon of lignin monomeric units, was previously presupposed in the structural model for low-rank coals proposed by Hatcher (1990) and based solely on lignin as the only component, due to the propensity that these carbon units have for oxidation. Several other compounds, with the carboxyl group located at the β and γ carbons, such as benzeneacetic acids (peak Nos 5 and 12) and benzenepropionic acids (peak Nos 13 and 23) respectively, were also identified among the pyrolysis products. The benzenepropionic acids were mainly released from the peat HA and in very low amounts from the lignite HA, indicating that they are produced in the early stage of the coalification process but are subsequently oxidized and disappear with increasing coalification. The benzeneacetic acids, on the contrary, are not present in the peat HA but appear in the lignite HA suggesting their formation at this later stage.

The results presented here suggest that the content of carboxyl groups in the lignin macromolecule increase during the first steps of the coalification process from peat to lignite in agreement with the model proposed by Hatcher (1990) for the transformation of lignin up to low-rank coal levels. According to this model, the content of carboxylic groups in the lignin macromolecule increases during the first stages of the coalification process, and reaches the maximum at the lignite stage. After that, the content of carboxyl groups decreases with increasing maturation. The low amounts of carbonyl and carboxyl groups present in this model was equated with the low amounts detected by NMR. However, measurements of carboxyl and carbonyl carbons are not precise due to the broadness of the NMR peaks. The

increase of the carboxyl groups in the lignin macromolecule during coalification seems also to be related to the increase of the carboxyl content in the HA fractions from peat to lignite, as determined by wet chemical methods. According to the results presented in this paper it seems that the HA from PGR lignite is highly oxidized while the HA from Padul peat is only partly oxidized. Ibarra and Juan (1985) also observed the same trend in the analysis of HAs extracted from a series of coals of different rank. This trend has only been observed by wet chemical and spectroscopic methods and now has been confirmed by pyrolytic techniques.

Finally, a series of fatty acids (mono- and dicarboxylic acids) from C_{12} to C_{30} , as well as some methoxylated counterparts, were also produced. These series might derive from the ester bound fatty acids in the HA macromolecular network. The distribution of fatty acids, with a strong even over odd predominance and maxima at C_{16} and C_{26} , reflects the contribution of higher plant waxes. The α,ω -alkanedioic acids may act as bridges in the macromolecular network, their content being related to the degree of cross-linking of the macromolecular structure. A bacterial contribution was evidenced by the release of the *iso*- and *anteiso*- C_{15} and C_{17} fatty acids. Minor amounts of triterpenoid acids were also released by pyrolysis-methylation. They arise either from higher plants (oleanane and ursane skeletons) or bacteria (hopane skeletons). Since the HAs were exhaustively extracted with organic solvents before pyrolysis, these triterpenoids must be covalently bound to the HA structure, possibly by ester bonds. Additional aliphatic series identified in the pyrograms were *n*-alkanes and *n*-alkenes, with chain lengths up to C_{30} . These aliphatic hydrocarbons have been observed in other peat and coal pyrolysates and indicate the presence of significant amounts of polyalkyl components (Kotra and Hatcher, 1988). As previously suggested for similar materials, the major contributors to the alkyl components in peat and lignite might be the new types of non-saponifiable, highly aliphatic biopolymers similar to those recently identified in present-day and fossil plant cuticles, and in the cell walls of some species of algae (Nip *et al.*, 1986; Largeau *et al.*, 1986). Such biopolymers yield, by conventional pyrolysis, a series of *n*-alkanes/*n*-alkenes with a distribution similar to that found in our HA samples. Although the above biopolymers are minor constituents of the original biomass, they are more refractory than other major vegetable components, including lignin, and could concentrate in the sediment during diagenesis. They are also responsible for the sharp, narrow signal at about 32 ppm in the ^{13}C -NMR spectra of the HA samples.

CONCLUSIONS

Attempts to describe structural models for low-rank coals have often overlooked the presence of

carboxyl groups in their structure. This has been due to the limitations of the techniques used (pyrolysis and oxidative degradation mainly). The first steps of the coalification process are characterized by the progressive decrease of polysaccharides, demethylation of methoxyl groups and the formation of catechols and also by a progressive oxidation and enrichment in carboxylic groups in the lignin macromolecule. Such oxidative alteration affects the 3-carbon side-chain of the lignin giving rise mainly to benzenecarboxylic acids and benzylic ketones. A more complete knowledge of the role of carboxylic groups during the coalification process will arise from the analysis by pyrolysis-methylation of a wider set of coals of increasing rank.

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