Humic acids from lignite. 2. Alkaline permanganate oxidation

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The potassium permanganate oxidation of methylated humic acid from a Spanish lignite yielded mainly straight-chain alkanes together with a mixture of fatty acids, methyl straight-chain alkyl ketones, aliphatic dicarboxylic, phenolic and benzenecarboxylic acids. Furthermore, some unusual compounds such as dehydroabietic and bromohydroxybenzoic acids and bis(2-ethylhexyl)phthalate were also identified. Although the analytical characteristics permit them to be included within the concept of humic acids, the oxidation products are closer to those from organic geochemical substances such as kerogen.

The term humic acids (HA) has been in recent years extensively used, arising from the imprecise definition 'those yellow to brown amorphous acidic substances extracted in alkaline media that precipitate upon acidification'. According to this definition, HA from various origins have been isolated.

The problem increases with the use of the parameters commonly applied to characterize them, like C and H contents, E_4/E_6 ratio, functional groups, i.r. and u.v. spectra etc., since with the same or similar values many natural and artificial substances extracted with alkali and precipitated in acid media are found.

Therefore other methods have been used to investigate the differences between HA from various origins or extracted by diverse agents. These methods have been mainly degradative, oxidative being in general more successful than reductive. Khan and Schnitzer¹ have used the oxidation of methylated soil HA with potassium permanganate, making possible the isolation and identification of amounts of phenolic, benzenecarboxylic and fatty acids as well as alkanes and phthalates. Maximov *et al.*² also applied this method to HA isolated from peats and lignites, and found among the degradation products basically benzenecarboxylic and aliphatic dicarboxylic acids. Ishiwatari³ by alkaline permanganate oxidation of sedimentary HA found straight-chain and branched aliphatic and benzenecarboxylic acids, the yield of these latter being relatively high. Schnitzer *et al.*⁴ also applied this method to the characterization of fungal HA. The major oxidation products were aliphatic mono- and dicarboxylic acids, being in this case similar to those from an arctic-soil HA, where the ratio benzenecarboxylic:aliphatic acids is less than 1, whereas in temperate soil HA (where the method has been extensively employed) the ratio ranged between 30 to 60 and higher.

In a first paper⁵ we reported the analytical characteristics and thermal degradation behaviour of HA extracted from a Spanish lignite. It was proved that there was no significant difference between HIA extracted by two alkaline agents and shown that the analytical data allowed them to be included within the concept of HA. In the present paper, to continue the characterization of lignite HA, we have carried out the alkaline permanganate oxidation of one of the

samples (HA-L-N) after methylation. In order to secure identification of the degradation products, these were studied in a combined system, gas chromatography-mass spectrometry-computer.

EXPERIMENTAL

The extraction procedure and characteristics of the HA have been previously reported⁵. Methylation of the sample was carried out with diazomethane. 1 g of the sample was suspended in 5 ml of methanol and an excess of diazomethane was added. After standing for 24 h the ethereal solution was evaporated. This procedure was repeated three times.

Oxidation procedure was as follows: 0.5 g of the methylated sample was suspended in 40 ml of a 2.5% solution of sodium carbonate and, under stirring and N_2 atmosphere, 60 ml of 4% potassium permanganate were added, keeping the reaction mixture at 90°C for 4 h. After this time the reaction mixture was cooled, acidified with 2 N HCl, and the MnO_2 residue was eliminated with sodium disulphite. The resulting yellow solution was exhaustively extracted (about 12% of total methylated) with ethyl acetate.

The ethyl acetate extract (after re-methylation) was separated by tlc on alumina (activated at 150°C for 18 h) using a solvent system toluene:ethyl acetate (3:1). Four fractions were scraped out after visualization under u.v. light, but only that with R_f between 0.55 and 0.80 gave a response in the gas chromatograph.

The gas chromatograph was a 5750 G dual FID Hewlett-Packard instrument, fitted with a 3.05 m $\times$ 3.2 mm (1/8 in) s.s. column packed with 3% OV-17 on Chromosorb W HMDS 80-100 mesh, programmed from 90 to 300°C at a rate of 8°C/min. The mass spectrometer was an AEI MS 30 double-focusing instrument, coupled to a DS computer system. In this case the gas chromatograph was a Pye 104 with the same conditions as stated above.

Fractionation with solvent system was made according to Schnitzer and Khan⁶.

Air oxidation was made according to Wright and Schnitzer⁷ (170°C, 500 h).

Figure 1 Gas chromatographic separation of oxidation products of methylated lignite HA. 2 μ l from a 0.5 ml solution

Table 1 Compounds produced by potassium permanganate oxidation of lignite HA (see Figures 1 and 3). (Alkanes and alkyls and fatty acids are straight-chain)

1: benzoic acid
2: C ₁₄ alkane
3: C ₁₅ alkane + C ₁₂ methyl alkyl ketone
4: <i>o</i> -hydroxybenzoic acid
5: <i>m</i> -hydroxybenzoic acid
6: <i>p</i> -hydroxybenzoic acid + pimelic acid
7: C ₁₆ alkane + C ₁₃ methyl alkyl ketone
8: suberic acid
9: C ₁₇ alkane + C ₁₄ methyl alkyl ketone
10: 1, 2 phthalic acid + C ₁₃ fatty acid
11: 1, 3 phthalic acid
12: 1, 4 phthalic acid + azelaic acid
13: C ₁₈ alkane + C ₁₅ methyl alkyl ketone
14: C ₁₄ fatty acid
15: C ₁₉ alkane + sebacic acid
16: dihydroxybenzoic acid
17: C ₁₆ methyl alkyl ketone
18: C ₁₅ fatty acid + undecanedioic acid + bromo-hydroxybenzoic acid
19: C ₂₀ alkane + C ₁₇ methyl alkyl ketone
20: C ₁₆ fatty acid
21: hydroxybenzenedicarboxylic acid
22: C ₂₁ alkane + dodecanedioic acid
23: C ₁₇ fatty acid
24: hydroxybenzene dicarboxylic acid
25: benzenetricarboxylic acid
26: C ₂₂ alkane + C ₁₈ fatty acid + benzenetricarboxylic acid
27: dihydroxybenzenedicarboxylic acid
28: C ₂₃ alkane + C ₁₉ fatty acid
29: dihydroxybenzenedicarboxylic acid + trihydroxybenzoic acid
30: C ₂₄ alkane + C ₂₀ fatty acid + hydroxybenzenetricarboxylic acid
31: hydroxybenzenetricarboxylic acid
32: C ₂₅ alkane + C ₂₁ fatty acid
33: C ₂₆ alkane
34: dehydroabiatic acid
35–43: C ₂₇ –C ₃₅ alkanes

RESULTS

Figure 1 shows a chromatogram of the oxidized sample. It can be seen that the major peaks belong to a series. Table 1 shows the identified compounds. As the oxidation products have been methylated and the methoxyl content of the original sample is very low, they have been referred to as compounds with COOH and OH rather than esters and ethers. The isomers are listed without detailed substitution patterns, except for hydroxybenzoic and phthalic acids as the three isomers of each have been found.

The most abundant compounds belong to the straight-chain alkane series from C₁₄ to C₃₅ representing between C₂₂ and C₃₃ 90% of the total oxidation products. The relative yields of the major alkanes were C₂₇ $\geq$ C₂₆ $>$ C₂₅ $>$ C₂₈ $>$ C₂₄ $>$ C₂₉.

Palmitic acid (as ester) is the most abundant fatty acid and the yield is three times as great as that of stearic, the second in abundance. Phenolic and benzenecarboxylic acids (also as esters and ethers) represent less than 5% of the total compounds. Aliphatic dicarboxylic acids and methyl alkyl ketones are the minor compounds produced by permanganate oxidation.

In view of the high straight-chain alkanes content, the HIA was extracted with hexane, benzene and ethyl acetate according to Schnitzer and Khan⁶. The results are shown in Table 2. Ethyl acetate extracts the greatest amount before and after methylation whereas hexane and benzene extract almost the same quantity *in toto*.

After extraction the residual HA was oxidized. The yield of oxidation products was very poor. The chromatogram is shown in Figure 2 and the identified compounds are listed in Table 3. In this case the identification was focused only on the major peaks. These correspond to the most prominent fatty acids and to three other compounds, two of them not found among the oxidation products before extraction.

Figure 3 shows the chromatogram of the oxidation products obtained after air oxidation. The identified compounds are the same as those found before this treatment with the exception that dicarboxylic acids are not present.

DISCUSSION

The alkaline potassium permanganate oxidation of methylated HA from soil of diverse origin yields mainly benzenecarboxylic and phenolic acids (Griffith and Schnitzer⁸). As far as we know the oxidation of methylated lignites HA has been reported only by Maximov *et al.*² indicating also a predominance of aromatic over aliphatic compounds. Although the lignite under study was exhaustively extracted with a mixture ethanol:benzene (1:1) before extracting the HA⁵ to remove bitumen, the oxidation products are mainly

Table 2 Extraction of lignite HA with different solvents, as % of original material (see Figure 2)

	Before methylation	After methylation
Hexane	0.12	1.34
Benzene	0.41	1.25
Ethyl acetate	18.88	11.43

Figure 2 Gas chromatographic separation of oxidation products of methylated lignite HA after extraction with hexane, benzene and ethyl acetate. 2 μ l from a 0.1 ml solution

Table 3 Compounds produced by potassium permanganate oxidation of lignite HA after solvents extraction (see Figure 2)

- 1: benzaldehyde oxime
- 2: C₁₆ fatty acid
- 3: C₁₈ fatty acid
- 4: dehydroabietic acid
- 5: N-phenyl- β -naphthylamine
- 6: bis(2-ethyl hexyl)phthalate

constituted by aliphatic compounds and within these by straight-chain alkanes.

These last have been reported to occur in soil HA⁹ in amounts between 0.01 and 0.37% and have also been found among the oxidation products of HA in minute amounts. In the HA under study, they constitute about 90% of the total oxidation products with a C-odd to C-even ratio of 1.07 which indicates a plant origin for the bulk of the alkanes.

Fatty acids occur in HA⁹ in a range within 0.14–9.8% and have also been found among the oxidation products, namely straight-chain C₁₆ and C₁₈. These were major fatty acids identified in lignite HA, which suggest a biological origin. As Schnitzer and Neyroud⁹ pointed out fatty acids may be tightly retained as proved by the fact that after exhaustive extraction the above two are the prominent compounds found among the oxidation products.

Besides fatty acids, aliphatic dicarboxylic acids from pimelic to dodecanedioic have been identified. These acids are also found among the oxidation products of soil HA¹⁰ and lignites HA² and possibly derive from long chains attached to an aromatic core¹¹ since they disappear after prolonged air oxidation.

Methyl alkyl ketones from C₁₁ to C₂₀ were produced in small amounts. Morrison and Bick¹² have isolated long-chain

members from a garden soil and a peat ranging from C₁₇ to C₃₃. In our case these could be detected till C₂₀ though the presence of higher ketones is highly probable. The GC–MS system, owing to the high alkane content (with an intense MS response), and the small amounts of methyl ketones (with very similar fragmentation pattern to alkanes) did not permit a conclusive identification of members higher than C₂₀.

Abietic acid and various isomers constitute the main component of pine resins, resins that have been found in association with coal deposits¹³. Abietic acid after heating gives dehydroabietic acid, which is more stable and resistant to oxidation. Although this compound has been reported to be soluble in organic solvents, it is however one of those remaining after solvent extraction, which indicates, as for fatty acids, that it is tightly retained or that it is incorporated in the HA nucleus.

Benzenecarboxylic and phenolic acids are in this lignite HA minor compounds among the oxidation products. As happened with methyl alkyl ketones and probably straight-chain fatty acids, higher substituted benzenecarboxylic and phenolic acids could not be detected by GC–MS. However in the gas chromatogram (Figure 1) peaks whose *R_f* values correspond to these series of compounds have been detected.

Bis(2-ethylhexyl)phthalate has been found in the lignite HA after solvent extraction, and though Khan and Schnitzer¹⁴ have reported the presence of alkyl phthalates, we think that in our case this phthalate arises from the solvents, being firmly retained by the HA matrix.

Bromo-hydroxybenzoic acid (bromine from typical MS fragmentation pattern) is an uncommon compound the presence of which cannot be explained, though Ogner¹¹ found bromo derivatives among the oxidation products of non-hydrolysable humic residue from podzolic soil. Martín

Figure 3 Gas chromatographic separation of oxidation products of lignite HA after 600 h air oxidation. 2 μ l from a 0.5 ml solution. Peak 15 no sebaccic acid; peak 18 no undecanedioic acid; peak 22 no dodecanedioic acid; peak 26' a better separation of C₁₈ fatty acid

et al.¹⁵ have also found bromomethane among the pyrolysis compounds of FA and HA from podzols.

Taking into account the yield of identified compounds, the aromaticity of this lignite HA calculated as

$$\frac{\text{benzenecarboxylic} + \text{phenolic}}{\text{total oxidation products}} \times 100$$

must be very low. The aromaticity calculated according to Wright and Schnitzer⁷ was 68%, in the same range as for HA from Chernozem, Solod and Solonetz soils⁶. Ishiwatari¹⁶ also by air oxidation found an aromaticity of 36% for a lake-sediment HA and this value, according to this author, appears to be related to the nature of the material from which this HA may have originated.

However the above author found that the yield of benzenecarboxylic acids in the oxidation products is relatively high, assuming that the aliphatic compounds are considered to be less stable than aromatic ones. That depends on the nature of the aliphatic compounds and on the bond between them and the aromatics, since after 600 h of air oxidation of this lignite HA, the oxidation products were constituted by the same compounds as before with the exception of dicarboxylic acids, which suggests that these acids may arise from methylene bridges or alicyclic hydrocarbons that are removed by air oxidation, while the other aliphatic compounds such as straight-chain alkanes, fatty acids, and methyl alkyl ketones are more stable, giving a value for aromaticity higher than that which is really correct.

CONCLUSIONS

According to the data presented in the first paper⁵ the HA extracted from this lignite has characteristics which permit

it to be included within the concept of HA. This is indicated by i.r. and u.v. spectra, functional group content, E_4/E_6 ratio, Sephadex distribution, pyrolysis gas chromatography, etc. However the study of the potassium permanganate oxidation products of the methylated sample shows that the bulk of this HA is constituted by straight-chain alkanes together with a mixture of fatty acids, methyl alkyl ketones, aliphatic dicarboxylic, phenolic and benzenecarboxylic acids, which is in agreement not with the constitution reported for other humic acids but with that for organic geochemical substances such as kerogen.

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