

CHARACTERISATION OF HUMIC ACIDS BY MASS SPECTROMETRY

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ABSTRACT

Humic acids from peat, soils and an estuarine sediment have been rendered soluble in organic solvents and mildly oxidised. The products have been characterised by GC-MS and it has been found that despite their different origins, the humic acids gave similar products most of which derived from a limited number of phenolic structures which are described.

INTRODUCTION

Humic acids are formed by the degradation of naturally occurring materials under aerobic conditions. Their formation and assimilation by living material, or their consolidation to fossil fuels forms an important part of the carbon biogeo-cycle.¹ Humic acids are also of interest as they control the passage of trace metals through the environment.² Previous work has indicated that terrestrial humic acids contain similar chemical structures to those detected in lignites.³ An account of the structures detected in lignite has been produced by Dogru et al.⁴ These included aromatic compounds containing carboxyl,

phenolic and alkyl substituents linked together through aliphatic, alicyclic and ether linkages. Such humic acids may be leached from the soil and reach the sea via the river system. However, marine humic acids are presumed to be derived from zoo-plankton and phytoplankton which possess no lignin so they might be expected to contain different structures from those found in terrestrial humic acids. A hemicellulose component has been reported.⁵

This work discusses the fragmentation products of five humic acids analysed by GS-MS. One, F is available commercially from Fluka and is obtained from peat, K and T were obtained from organic rich soils in the South of Turkey (G was extracted from sediment in the mouth of a river and the fifth D was from sediment two hundred metres below the surface of the Mediterranean from a location which appeared not to be influenced by river water.

Experimental.

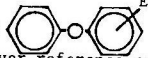
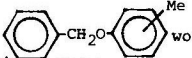
1. Isolation and purification of humic acids from soil and sediment samples.
2. Each humic acid was subjected to two methods of degradation:
 - i) a mild oxidation using alkaline nitrobenzene and
 - ii) a reduction procedure employing sodium hydroxide and ethanol⁹ followed by a mild oxidation.

The products were analysed with a VG Micromass 12-12 quadrupole mass spectrometer coupled to a Pye 304 gas chromatograph.

Discussion.

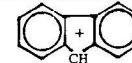
The elemental analyses and ranges of relative molar mass of each humic acid have been determined previously.⁶ Oxidation of humic acid using alkaline nitrobenzene has resulted in the isolation of vanillin, syringaldehyde and p-hydroxybenzaldehyde⁸.

THF extracts of F,T,K and G Humic acids. The total ion current (TIC) traces obtained from each of these terrestrial humic acids were comparable. A typical TIC is shown in Figure 1. As shown in Figure 1, the TIC traces were dominated by four peaks. These peaks corresponded to material of relative molar mass of less than 300. Chromatograms obtained from oxidised samples were similar to those obtained from reduced then oxidised samples. Some reduction products of nitrobenzene were detected in the samples. It was observed that the major peaks in each TIC corresponded to material having parent ions of m/e 198, 220 or 270. Compounds of relative molar mass (R.M.M) 198 have mass spectra which are characterised by m/e 91, 105 and frequently m/e 169 (M-29) and m/e 182 (M-16).

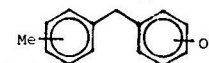
Compounds such as  and  would appear to be indicated. However reference spectra of these compounds do not agree with those obtained and therefore further work is required to elucidate the mass spectra obtained. Eight compounds appeared to have a molecular ion of m/e 220. These mass spectra were similar to each other and to that recorded for 2,6-di-tert-butyl-4-methylphenol, a known commercial anti-oxidant, and 3,5-di-tert-butyl-4-methylphenol. These compounds are only slightly oxidised by alkaline nitrobenzene⁷. It also appears that when a t-butyl group is ortho to the phenolic hydroxy group little silylation occurs as the mass spectra of both silylated and non-silylated samples were very similar. The

majority of the mass spectra acquired may be explained in terms of a di-tert-butylmethyl phenol. The ready loss of CH_3 gave a base peak of m/e 205, the prominent m/e 57 peak and m/e 41 - more intense than m/e 55 - indicate the presence of at least one t-butyl group. In three samples; CF5TS scan 251, ROK5TS scan 261, and ROG5TS scan 148, the peak due to m/e 55 was more intense than m/e 41 which suggests that in this case the peak may be due to a n-butyl group or even $\text{C}_2\text{H}_5\text{OCO}^+$ or $\text{CH}_3\text{COCH}_2^+$ ions. It is of interest that oxygenated ions are suggested in the humic acid obtained from an estuarine sediment.

Compounds of mass 270 were detected only in silylated samples. An M-15 peak was observed as was a large peak at m/e 73 and it may be suggested that this is a silylated form of a molecule of m/e 198. The mass spectra were also characterised by having fragments of m/e 77 91 and m/e 165. It is possible that a silylated hydroxyazobenzene is present, m/e 165 may be due to



but in this case $\text{C}_6\text{H}_4\text{OSi}(\text{CH}_3)_3$ appears more likely, thus these compounds may be derived from a molecule such as



However further work is needed to elucidate such structures. Ether extracts of F,T,K and G Humic acids.

These extracts, derived from water soluble material, showed more peaks in the TIC trace than those obtained from the THF extracts. The samples analysed were all silylated and showed a large m/e 73, a parent peak and a M-15 peak. A series of unsilylated compounds having m/e 139 were present.

Marine Humic acids

THF extract. This humic acid was treated in the same way as the terrestrial samples. The TIC trace did not show the same pattern as the other traces. The most significant compound present in the fraction had a structure similar to those compounds having a parent ion of m/e 198 obtained from terrestrial humic acids. However, in this case it contained nitrogen and had a parent ion of m/e 199.

Ether extract. Far more compounds were present in this extract than in the extracts previously examined. It might be expected therefore that this extract contains a wider range of compounds. The separation of the THF and ether extracts is not as clear in this case as it was in the terrestrial humic