NATURE OF PLANT COMPONENTS IDENTIFIED IN SOIL HUMIC ACIDS

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SUMMARY

The chemical structure of two acid hydrolysed soil humic acids was investigated using analytical pyrolysis. A large part of the pyrolysis mixture consisted of a homologous series of straight chain alkanes, alk-1-enes and α, ω -alkadienes probably derived from plant cuticles. The origin of other major components in the pyrolysate, phenols and aromatic hydrocarbons, is less clear.

INTRODUCTION

The origin of the humic acid fraction of soils is still unclear in spite of extensive investigations accomplished over the last years (ref. 1). Different origins have been proposed, based on the most recent theory or on the application of the latest analytical method. Thus, it has been proposed that soil humic acids are derived from lignins, microbial activity and synthesis of melanins, reaction between sugars and amino acids, etc. (ref. 1). Although there is no doubt that the components mentioned are involved in the formation of humus, recent investigations have demonstrated that lignin, sugar and protein moieties are peripheral or loosely attached to the so-called core of soil humic acid and can easily be removed by acid hydrolysis (ref. 2). The question arises what the structure and origin of the more resistant part is. This core is not or hardly affected by acid hydrolysis or mild oxidations but is extensively degraded upon drastic oxidation with permanganate (ref. 3).

This paper describes the chemical nature of the most resistant part of soil humic acids based on Curie-point pyrolysis-gas chromatography-mass spectrometric analyses. This technique has proved to be useful in the characterization of biopolymers and geopolymers (ref. 2, 4, 5).

METHODS

Two soil samples from the South of Spain were used in this study. One of them was a Typic Rendoll and the other a Typic Rhodoxeralf. The preparation of the humic acid fractions has been described previously (ref. 6). Elemental analyses and NMR spectra of the humic acid fractions have also been reported (ref. 7). The

analytical pyrolysis method as well as the acid hydrolysis have been described elsewhere (ref. 2, 4).

RESULTS AND DISCUSSION

The pyrolysis behaviour of unhydrolysed humic acids have been extensively reported (ref. 2, 4). Briefly, humic acid fractions yield upon flash pyrolysis/evaporation products derived from polysaccharides, proteins, lignins, lipids and pollutants.

Figure 1 shows the pyrograms of the humic acids after hydrolysis with 6 N HCl and extraction with hexane (sonication, 2 x 10 min.). The main difference with comparison to the unhydrolysed samples is the disappearance of characteristic pyrolysis products derived from polysaccharides, proteins and, to some extent, lignins. Also fatty acid concentrations decreased drastically, probably due to the extraction process.

The pyrolysis mixture of the humic acids shows a homologous series of straight chain alkanes, alk-1-enes and α , ω -alkadienes ranging from C_5 to C_{31} . In addition, aromatic hydrocarbons such as homologous series of alkylbenzenes and alkylnaphthalenes and some polycyclic aromatic hydrocarbons are present. Phe nol and alkylphenols are also major pyrolysis products. Similar pyrograms have been obtained for hydrolysed fulvic acids, although in that case the homologous series of the aliphatic components were less prominent (unpublished data).

Recently, the occurrence of a new, non saponifiable, highly aliphatic, biopolymer in modern and fossil plant cuticles has been reported (ref. 8). The pyrograms of this cuticle biopolymers consist of series of n-alkanes, n-alkenes and α , ω -alkadienes and the pattern is similar to the aliphatic hydrocarbon pattern encountered in the soil humic acids after hydrolysis. Since unhydrolysed soil humic acids yield upon pyrolysis compounds derived from plant components, such as lignins, tocopherols, chlorophylls, terpenoids, etc. (ref. 4) it is speculated that the new biopolymer present in cuticles make up a part of the so-called core of humic acids.

The short and long chain aliphatic mono- and dicarboxylic acids obtained upon alkaline permanganate oxidation of humic acids (ref. 3) might be derived from this biopolymer. The phenolic acids and benzenecarboxylic acids identified upon permanganate oxidation of humic acids might originate from substances in the humic acid core which on flash pyrolysis yield the aromatic hydrocarbons and phe nols. However, the origin and nature of these substances is as yet unclear.

Figure 1. Flash pyrolysis-gas chromatography-mass spectrometric analysis of 6 N HCl hydrolysed and hexane extracted humic acids. A: Typic Rendoll humic acid, B: Typic Rhodoxera lft humic acid. Curie-point temperature 770°C. Peak identifications are given in Table 1. Owing to the vast number of identified compounds in each pyrolysate only major peaks are indicated in the figures.

GC conditions: Fused silica column (28 m x 0.5 mm I.D.) coated with CP-sil 5 held at 0°C for 5 min. and subsequently programmed to 300°C at a rate of 50°C/min. The chromatograph (Varian 3200) was coupled to a Varian MAT 44 quadrupole mass spectrometer operated in the EI mode at 80 eV.

TABLE 1

Pyrolysis products of 6 N HCl hydrolysed and hexane extracted soil humic acids

1	Carbon monoxide	57	Methylindene
2	Carbon dioxide	58	Methylindene
3	Methane	59	C ₄ -alkylbenzene
4	Ethene	60	C ₅ -alkylbenzene
5	Ethane	61	Naphthalene
6	Propene	62	C ₅ :1-alkylbenzene
7	Propane	63	Methylguaiaicol
8	Sulphur dioxide	64	α , ω -dodecadiene
9	But-1-ene	65	Dodec-1-ene
10	Butane	66	Dodecane
11	Acetone	67	Methylnaphthalene
12	Pent-1-ene	68	Branched tridecane
13	Furan	69	Vinylphenol
14	Pentane	70	C ₆ -alkylbenzene
15	Hex-1-ene	71	C ₆ -alkylbenzene
16	2-Methylfuran	72	Methylnaphthalene
17	Hexane	73	Ethylguaiaicol
18	3-Methylfuran	74	Methylnaphthalene
19	Benzene	75	α , ω -tridecadiene
20	Cyclohexene	76	Tridec-1-ene
21	Hept-1-ene	77	Methylnaphthalene
22	Heptane	78	Tridecane
23	Methylcyclohexane	79	C ₇ -alkylbenzene
24	Toluene	80	C ₇ -alkylbenzene
25	Acetic acid	81	Acenaphthene
26	Oct-1-ene	82	C ₂ -alkylnaphthalene
27	Octane	83	Methylbiphenyl
28	Ethylbenzene	84	α , ω -tetradecadiene
29	m- and/or p-xylene	85	Tetradec-1-ene
30	Styrene	86	C ₂ -alkylnaphthalene
31	o-xylene	87	Tetradecane
32	Non-1-ene	88	C ₂ -alkylnaphthalene
33	Nonane	89	C ₂ -alkylnaphthalene
34	C ₃ -alkylbenzene	90	trans-isoeugenol
35	C ₃ -alkylbenzene	91	C ₂ -alkylnaphthalene
36	C ₃ -alkylbenzene	92	C ₈ -alkylbenzene
37	Phenol	93	α , ω -pentadecadiene
38	Dec-1-ene	94	Pentadec-1-ene
39	Decane	95	Pentadecane
40	C ₃ -alkylbenzene	96	C ₃ -alkylnaphthalene
41	Indane	97	C ₃ -alkylnaphthalene
42	Indene	98	C ₉ -alkylbenzene
43	C ₄ -alkylbenzene	99	Fluorene
44	p-cresol	100	C ₁₂ fatty acid
45	C ₄ -alkylbenzene	101	C ₃ -alkylnaphthalene
46	C ₄ :1-alkylbenzene	102	α , ω -hexadecadiene
47	Guaiaicol	103	Hexadec-1-ene
48	o-cresol	104	Hexadecane
49	C ₄ :1-alkylbenzene	105	Xanthene
50	α , ω -undecadiene	106	C ₁₀ -alkylbenzene
51	Undec-1-ene	107	C ₄ -alkylnaphthalene
52	Undecane	108	α , ω -heptadecadiene
53	C ₄ :1-alkylbenzene	109	Heptadec-1-ene
54	C ₄ -alkylbenzene	110	Heptadecane
55	C ₄ :1-alkylbenzene	111	Prist-1-ene
56	C ₄ :1-alkylbenzene	112	Prist-2-ene

TABLE 1 (continued)

113 C ₁₄ fatty acid	133 Docosane
114 Anthracene	134 Tricos-1-ene
115 α,ω -octadecadiene	135 Tricosane
116 Octadec-1-ene	136 Tetracos-1-ene
117 Octadecane	137 Tetracosane
118 C ₁₅ fatty acid	138 Pentacos-1-ene
119 Phytadiene	139 Pentacosane
120 α,ω -nonadecadiene	140 Dialkyl phthalate
121 Nonadec-1-ene	141 Hexacos-1-ene
122 Nonadecane	142 Hexacosane
123 Methylanthracene	143 Heptacos-1-ene
124 Dialkyl phthalate	144 Heptacosane
125 C ₁₆ fatty acid	145 Octacos-1-ene
126 α,ω -eicosadiene	146 Octacosane
127 Eicos-1-ene	147 Nonacos-1-ene
128 Eicosane	148 Nonacosane
129 α,ω -heneicosadiene	149 Triacot-1-ene
130 Heneicos-1-ene	150 Triacotane
131 Heneicosane	151 Hentriacont-1-ene
132 Docos-1-ene	152 Hentriacontane

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