

Naturwissenschaften 78, 311 – 312 (1991) © Springer-Verlag 1991
002810429100136W

A Chemical Structure for Humic Substances

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Dedicated to Prof. Dr. H. D. Beckey on the occasion of his 70th birthday.

The chemical structure of humic substances has been subject of much speculation and research over the past 200 years. In spite of the availability of abundant experimental data in the literature, soil and environmental scientists as yet have not been able to propose a valid concept of the chemical structure of these materials. The purpose of this communication is to report results of recent, extensive Curie-point pyrolysis-mass spectrometric analyses, which indicate that much of the structural network of humic substances consists of aromatic rings which are joined by long-chain alkyl structures to form a flexible network.

The humic acids (HAs) were extracted from air-dry samples taken from the surface horizon of the Bainsville soil, an Aquoll, and from the Bh horizon of the Armadale soil, a Spodosol. Methods of extraction and purification were those recommended by the International Humic Substances Society. The purified Bainsville HA contained 54.2% C, 6.0% H, 6.0% N, and 33.8% O. The Armadale HA contained 58.2% C, 5.4% H, 3.1% N, and 33.3% O.

The HA samples were pyrolyzed in a Fischer Curie-point pyrolyzer 0316. The pyrolysis temperature employed was 500 °C. The GC was equipped by a 45-m DB5 column. The temperature was programmed to rise from 40 to 280 °C with heating rates of 3, respectively 5 °C min⁻¹. The mass spectra of

the chromatographically separated compounds were recorded with the double-focusing Finnigan MAT 212 mass spectrometer in the mass range from 46 to 400 Da and evaluated by the Finnigan SS 200 data system. The thermal degradation products were identified by GC/MS using the NBS and Wiley libraries.

As shown in Table 1, the major thermal products resulting from the two HAs were benzene and alkylbenzenes. Of special interest is the series of C₁–C₁₃ n-alkylbenzenes. In addition, ethylmethylbenzene, methyl-propylbenzene, methyl-heptylbenzene, methyl-octylbenzene, methyl-nonylbenzene, methyl-decylbenzene, methyl-undecylbenzene are essentially branched members of the same series of alkylbenzenes that have important functions for the three-dimensional (sponge-like) structure of humic substances. Other compounds of interest are trimethylbenzenes, tetramethylbenzenes, alkylnaphthalenes, and alkylphenanthrenes. The alkyl substitution on naphthalene ranges from one to five methyls, while on phenanthrene it extends from one to four methyls. It is noteworthy that the Armadale HA is richer in most compounds listed in Table 1 than the Bainsville HA. This may be due to the differ-

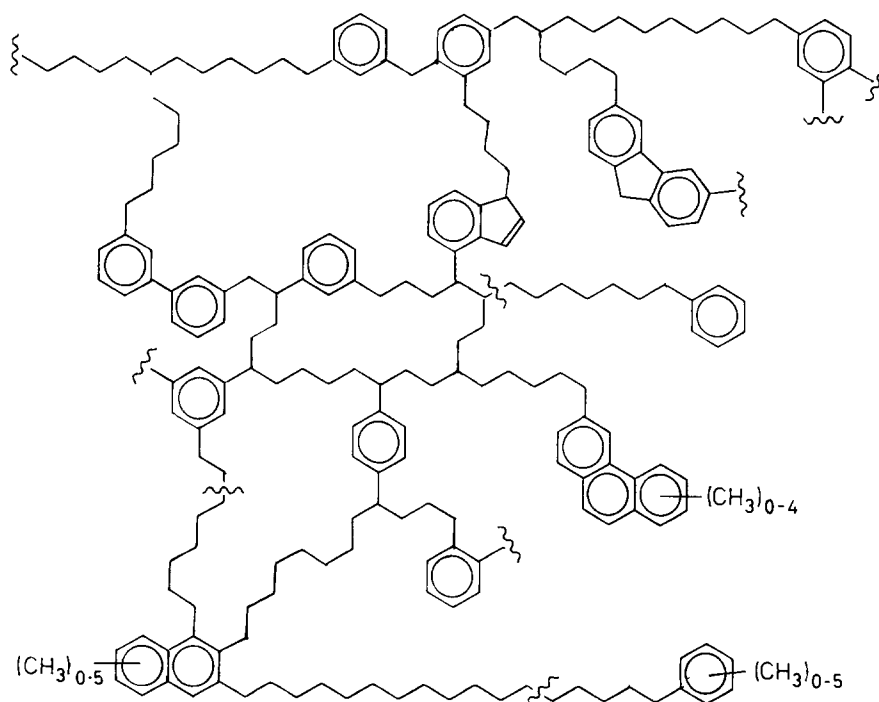


Fig. 1. The tentatively proposed chemical network structure of humic substances is visualized with its voids and flexible covalent links [4]

ent origins of the two HAs. The Armadale HA was extracted from the Bh horizon, about 25 cm below the surface, while the Bainsville HA was extracted from an agricultural surface soil. One of the most striking features of the Armadale Bh horizon is its very low microbial activity which may have led to a better preservation of the compounds listed in Table 1.

The alkyl-aryl compounds detected consist of isolated aromatic rings which are linked covalently to aliphatic chains. We propose that these "building blocks" are released during low-temperature thermal degradation from an alkylaromatic structural network which is made up of the constituents listed in Table 1. This leaves voids of various dimensions in the structure which could trap and bind other organic components such as carbohydrates, proteins, lipids, biocides, as well as inorganics such as clay minerals and hydrous oxides. The structure would be expected to be flexible in line with observations from surface pressure and viscosity measurements [2] and from electron microscopy [1]. Also, the oxidative degradation of this structure would produce the benzene-carboxylic acids which have been isolated repeatedly as major oxidation products of humic substances [3].

From the data presented herein it appears that alkylaromatics are significant structures in HAs. In the past these compounds have been largely overlooked because of the unavailability of adequate and sensitive analytical methods. A chemical structure for the basic skeleton of HA based on alkylbenzenes, -naphthalenes, and -phenanthrenes is tentatively proposed in Fig. 1.

Table 1. Building blocks of Bainsville and Armadale humic acids as identified by Curie-point pyrolysis-gas chromatography/mass spectrometry (***** 80–100, **** 60–80, *** 40–60, ** 20–40 % intensity of peak height, * observed)

Intensity		Compounds
Armadale	Bainsville	
*****	***	benzene
*****	*****	toluene
****	****	ethylbenzene, xylenes
*	*	ethyl-methyl-benzene
**	**	propylbenzene
**	**	trimethylbenzenes
*		butylbenzene
*		methyl-propyl-benzene
*	*	tetramethylbenzene
**	*	pentylbenzene
*	*	hexylbenzene
**	*	heptylbenzene
**	*	octylbenzene
*		methyl-heptyl-benzene
*	*	nonylbenzene
**		methyl-octyl-benzene
**	*	decylbenzene
*		methyl-nonyl-benzene
*	*	undecylbenzene
*		methyl-decyl-benzene
**		dodecylbenzene
*		methyl-undecyl-benzene
*		tridecylbenzene
*		tetradecylbenzene
*		pentadecylbenzene
*		hexadecylbenzene
*		heptadecylbenzene
*		octadecylbenzene
*		nonadecylbenzene
*		eicosylbenzene
*		hemicosylbenzene
*		docosylbenzene
***	***	styrene
*	*	methylstyrene
**	*	indene
***	**	indane
*		fluorene
**	*	naphthalene
**	*	methylnaphthalenes
**	*	dimethylnaphthalenes
**	*	trimethylnaphthalenes
*	*	tetramethylnaphthalenes
*		pentamethylnaphthalene
*		phenanthrene
*		methylphenanthrene
*		dimethylphenanthrene
*		trimethylphenanthrene
*		tetramethylphenanthrene

Received April 4, 1991

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