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A State of the Art Structural Concept for Humic Substances

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In a recent communication [1] we presented a carbon skeleton for humic acid (HA) based on extensive mass spectrometric data in which alkylbenzene structures played a dominant role. We now show a more complete version of this structure in which we have inserted oxygen, hydrogen, and nitrogen atoms in conformity with analytical data obtained on many naturally occurring soil HAs. Oxygen is present in the form of carboxyls, phenolic and alcoholic hydroxyls, carboxylic esters and ethers, and nitrogen in heterocyclic structures and as nitriles.

The elemental composition of the HA structure (Fig. 1) is $C_{308}H_{328}O_{90}N_5$, with a molecular weight of 5540 Da, and an elemental analysis of 66.8 % C, 6.0 % H, 26.0 % O, 1.3 % N. There are different views in the literature on soil organic matter as to whether carbohydrates and proteinaceous materials are adsorbed on or loosely retained by HA or whether they are bonded covalently to HA [2–5]. But regardless of which mechanism is considered, carbohydrates and proteinaceous materials are HA components for analytical purposes; their presence affects the elemental analysis and functional group content of HAs. Carbohydrates have been reported to account for about 10 % of the HA weight [6]; a similar value has been suggested for proteinaceous materials in HA [5]. Thus, let us assume that one molecular weight of HA interacts with 10 % carbohydrates and 10 % proteinaceous materials. The resulting HA has then an elemental composition of $C_{342}H_{388}O_{124}N_{12}$, with a molecular weight of 6651 Da, and an elemental analysis of 61.8 % C, 5.9 % H, 29.8 % O, and 2.5 % N. If more carbohydrates and proteinaceous materials are added, the C content of the HA decreases and the O content increases.

The elemental composition and functional group content of HAs extracted from soils belonging to three different Geat Soil Groups as well as similar data for the proposed HA structure (after inclusion of carbohydrates and proteinaceous materials) are shown in Table 1. A comparison of the data indicates that the analytical features of the proposed HA structure are in general agreement with those of HAs extracted from soils.

The HA structure shown in Fig. 1 is the result of extensive pyrolysis-GC/MS [7] and pyrolysis-FIMS [8], ^{13}C NMR [9], chemical [10], oxidative and reductive degradation [11, 12], colloid-chemical [13] and electron microscope [14] investigations done on HAs over many

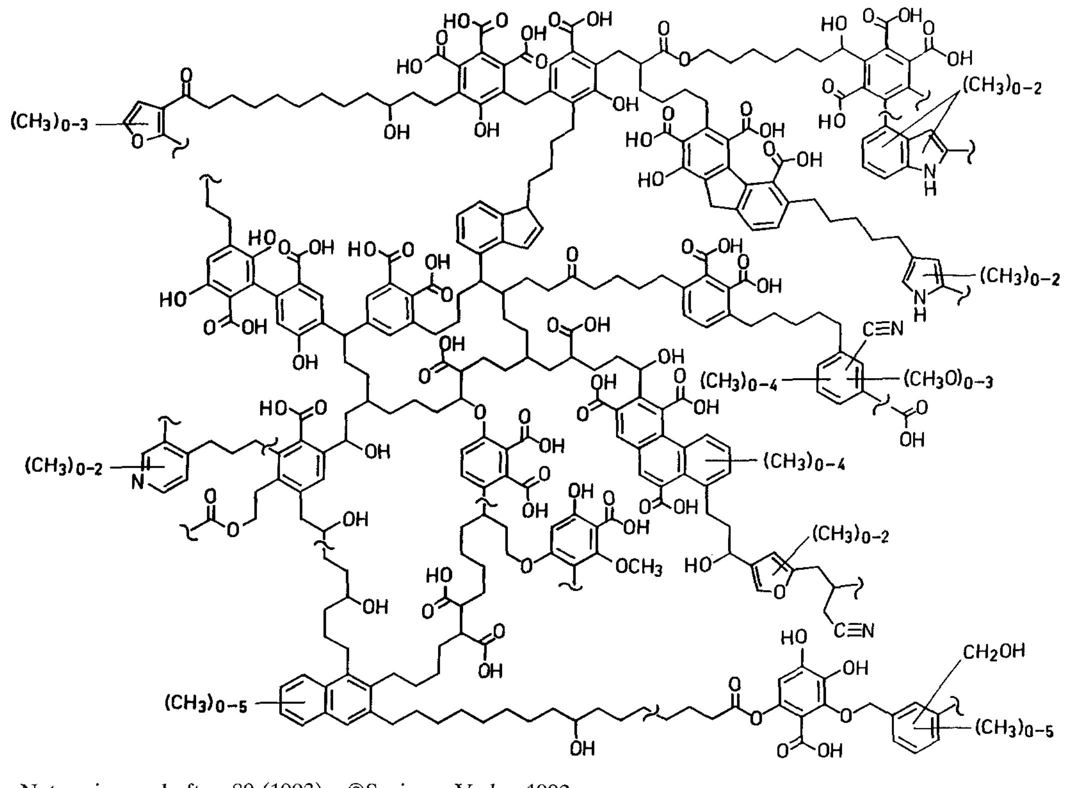

Fig. 1. Schematic, biomacromolecular HA structure developed from the tentatively proposed chemical network of humic substances [1,8] on the basis of analytical pyrolysis; spectroscopic, chemical, oxidative/reductive degradation, and colloid-chemical and electron microscope results

Table 1. Analytical characteristics of HAs extracted from soils belonging to three different Great Soil Groups and of the proposed HA structure

	Udic Boroll	Haplaquod	Haplaquoll	Proposed[a]
C [%]	56.4	58.2	54.2	61.8
H [%]	5.5	5.4	6.0	5.9
N [%]	4.1	3.1	6.0	2.5
S [%]	1.1	0.7	0.9	–
O [%]	32.9	32.6	32.9	29.8
Total acidity [meq/g]	6.6	5.7	6.4	5.8
CO_2H [meq/g]	4.5	3.2	3.5	4.4
Phenolic OH [meq/g]	2.1	2.5	2.9	1.4
Alcoholic OH [meq/g]	2.8	3.2	3.0	1.4
OCH_3[meq/g]	0.3	0.4	0.4	0.3

[a]MW = 6651 Da

years, and exhaustive consultations on the voluminous literature on this subject. More detailed experimental support for the proposed structure will be published elsewhere.

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Identification of the Sex Pheromone of an Ant, *Formica lugubris* (Hymenoptera, Formicidae)

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Pheromones play a cardinal role in mediating intraspecific communication in animals [1], especially in insects where they are involved in a number of processes including attraction of the sexes and social interactions. Although sex pheromones have been identified in a variety of insect species which include a number of Hymenoptera [2], none has yet been identified in ants (Formicidae). This is in contrast to the dozens of pheromones serving a social function, e.g., trail and alarm pheromones, that have been identified from among this group [3]. Evidence has been previously obtained in several species that females attract males using sex pheromones [4], but characterization of the active components has so far proven elusive. We have identified what appears to be the major and two minor components of the sex pheromone of the red wood ant, *Formica lugubris* Zett., by testing in a natural field situation the principal volatile compounds emitted by sexually attractive females collected from the field. The major component, undecane, also acts as an alarm pheromone in workers of this and other species. Thus, undecane serves different functions in the two castes of *F. lugubris*.

The ants used in this study belong to a supercolony of *F. lugubris* located in the Swiss Jura [5]. Winged males and females (sexuals) fly from their nests to