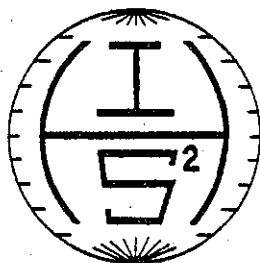


# IHSS COMMUNICATIONS

VOLUME 1 NUMBER 4

OCTOBER 1985



INTERNATIONAL HUMIC  
SUBSTANCES SOCIETY

**EDITORS:**

**MICHAEL A. MIKITA**  
DEPARTMENT OF CHEMISTRY-BOX 171  
UNIVERSITY OF COLORADO AT DENVER  
DENVER, COLORADO 80202 USA

**KEVIN A. THORN**  
U.S. GEOLOGICAL SURVEY  
5293 WARD RD.  
ARVADA, COLORADO 80002 USA

## CONTENTS

|  | <u>Page</u> |
|--|-------------|
| Announcements . . . . .  | ii          |
| Tentative program for symposium session,<br>Problems and Solutions to the Application<br>of Magnetic Resonance in the Study of<br>Humic Substances and Other Complex<br>Geological Materials . . . . . | iii         |
| Program, Advances in Humic Substances<br>Research Related to Soil and Crop Sciences . . . . .  | iv          |
| <b>Abstracts</b>   |             |
| Incorporation of water dissolved chlorophenoxyalkanoic<br>herbicides by humic acids of various origin and nature . . . . .   | 1           |
| Intrinsic copper, iron and vanadyl complexes in<br>humic acid-type polymers (melanins) from soil<br>fungi: An ESR study . . . . .  | 2           |
| Infrared spectra of melanoidins . . . . .  | 3           |
| Heterocyclics as building blocks of the polymeric<br>matrix of humic substances and melanoidins . . . . .  | 4           |
| The role of humic substances in the environmental chemistry<br>of chlorinated phenoxyalkanoic acids and esters . . . . .   | 6           |
| Complexation of some transition metal ions in<br>soil humic acids: An ESR study . . . . .  | 7           |
| Pyrolysis-mass spectrometry/pattern recognition<br>on a well-characterized suite of humic samples . . . . .  | 8           |
| Removal of paraquat, diquat, and amitrole from<br>aqueous solution by chemically modified peat . . . . .   | 9           |
| Use of C-13 depleted DMSO-d6 in C-13 NMR<br>spectra of fulvic acids . . . . .  | 10          |

## IHSS INTERNATIONAL MEETING (1986)

August 4-8, 1986, Oslo, Norway

Chairman of Meeting: Egil T. Gjessing, Norwegian Institute for Water Research, Oslo.

Vice Chairman: Georg Becher, National Institute of Public Health, Oslo.

Members of Organizing Committee:

Stale Johnsen, Center for Industrial Research, Oslo.

Britt Salbu, University of Oslo.

Hallvard Odegaard, University of Trondheim.

General Secretary:

Oddny Falck  
Norwegian Institute for Water Research  
P.O. Box 333, Blindern  
0314 Oslo 3, Norway

The three main topics of the meeting will be:

- \*Marine Humic Substances.
- \*Biochemical-Biological Aspects of Humic Substances.
- \*Practical Applications of Basic Research on Humic Substances.

The titles and speakers for invited papers will be announced in the next IHSS Newsletter.

### Call for Papers

A major part of the IHSS meeting will consist of volunteered papers and poster sessions on all aspects of humic substances, with an emphasis on the themes of the meeting. Abstracts of two or three double-spaced typewritten pages should be submitted to the secretariat (see address above) no later than February 15, 1986.

## SYMPOSIUM ANNOUNCEMENT (1986)

A symposium will be jointly sponsored by the International Humic Substances Society and the International Society of Soil Science during the ISSS Congress in Hamburg, Germany, August 1986.

Cochairmen of Symposium: R. S. Swift and D. S. Jenkinson

### SYMPOSIUM ANNOUNCEMENT (1987)

SYMPOSIUM: "Influence of Aquatic Humic Substances on Fate and Treatment of Pollutants"

Sponsored jointly by the International Humic Substances Society and the Environmental Chemistry Division of the American Chemical Society.

April 5-10, 1987, Denver, Colorado.

Cochairmen of Symposium: P. MacCarthy and I. H. Suffet.

A symposium entitled "Structural and Chemical Analysis of Humic Substances" has been scheduled for the 8th Rocky Mountain Regional Meeting of the American Chemical Society. The regional meeting will take place June 8-12, 1986, at the Denver Convention Complex, Denver, Colorado. One of the major sessions of this symposium will be "Problems and solutions to the application of magnetic resonance in the study of humic substances and other complex geological materials". The tentative list of invited speakers and topics for this session follows.

Those interested in presenting papers at the general session of the symposium on humic substances should contact the chairmen:

Dr. Michael A. Mikita  
Assistant Professor of Chemistry  
University of Colorado at Denver  
Department of Chemistry, Box 171  
Denver, CO 80202 U.S.A.  
Phone 303-556-3202

Dr. Robert L. Wershaw  
Research Hydrologist  
U.S. Geological Survey  
5293 Ward Road  
Arvada, CO 80002 U.S.A.  
Phone 303-236-3613

Problems and solutions to the application of magnetic resonance in the study of humic substances and other complex geological materials.

Introduction and scope of the problems (R. L. Wershaw, USGS, and M. A. Mikita, University of Colorado).

Review of solution NMR spectroscopy of humic substances (Caroline Preston, Agriculture Canada).

Review of solid state NMR spectroscopy of humic substances (Gary Maciel and James Frye, NSF Regional NMR Center, Colorado State University).

Review of electron spin resonance spectroscopy of humic substances (Cornelius Steelink, University of Arizona).

Techniques employed in the measurement of wide-line NMR spectra (Eiichi Fukushima, Lovelace Research Foundation).

Design and limitations of liquid-state NMR spectrometers (Stephen Smallcomb, Varian Instrument Division).

Design and limitations of solid-state NMR spectrometers (Victor Bartuska, Magnachem, Inc.).

NMR evidence for the membrane model of humic substances (Robert L. Wershaw, USGS).

Polarization transfer and 2-D experiments in solution spectroscopy of humic materials and synthetic fuel liquids (Larry Dennis, Exxon Research and Engineering Co.).

The chemistry and spectral applications of derivatization techniques for humic substances (Michael A. Mikita, University of Colorado).

Detection of mobile phases in the solid-state NMR spectra of model systems (William Earl, Los Alamos National Laboratory).

Detection of mobile phases in the solid-state NMR of coals (D. E. Axelson, Energy, Mines and Resources Canada).

Quantitative reliability in the solid-state NMR spectra of model systems (D. E. Grant, University of Utah).

Quantitative reliability in the solid-state NMR spectra of humic substances (Tony Vassalla, Commonwealth Scientific and Industrial Research Organization).

Summary and recommendation (M. A. Mikita and R. L. Wershaw).

Chicago, Dec. 2, 1985, during annual meeting of American Society of Agronomy (Dec. 1-6, 1985).

Joint International Humic Substances Society/American Society of Agronomy Society Symposium.

"Advances In Humic Substances Research Related to Soil and Crop Sciences"

Cochairmen of Symposium: R. L. Malcolm and C. E. Clapp.

Program

PRESIDING: W. E. Larson, University of Minnesota

- 8:15 Introductory remarks.  
R. L. Malcolm, IHSS  
E. C. A. Runge, SSSA
- 8:30 New Methods for the Characterization of Soil Organic Matter.  
M. Schnitzer, Agric. Canada, Ottawa, Canada
- 9:00 Analytical Pyrolysis Applied to Soil Productivity and Classification.  
J. M. Bracewell and G. W. Robertson, The Macaulay Inst.  
for Soil Research, Aberdeen, Scotland.
- 9:30 Ecological Aspects of Humic Substances: Influences of Cropping Practices and Acid Rain.  
W. Zech, University of Bayreuth, Germany
- 10:00 Whole Soil NMR Applications to Soil Productivity and Classification.  
M. Wilson, CSIRO, Sidney, Australia
- 10:30 Discussion.
- 10:45 Adjourn.

PRESIDING: C. E. Clapp, USDA-ARS, University of Minnesota

SYMPOSIUM -- "Advances in Humic Substances Research Related to Soil and Crop Sciences: II"

- 1:25 (p.m.) Introductory remarks.
- 1:30 Biochemistry of Natural and Synthetic Polymers in Soils.  
D. E. Stott and J. P. Martin\*, USDA-ARS, Purdue University  
and University of California, Riverside
- 2:00 The Roles of Soil Organic Matter and Minerals in Sorption of Nonionic Organic Compounds from Aqueous and Vapor Phases.  
C. Chiou, USGS, Denver, CO
- 2:30 Effect of Humic Substances on Plant Growth.  
Y. Chen and T. Solovitch, The Hebrew University of Jerusalem,  
Rehovot, Israel
- 3:00 Determination of an Average Structural Model of the Suwannee Standard Fulvic Acid by Convergent Independent Analyses.  
J. A. Leenheer, USGS, Denver, CO
- 3:30 Recess.
- 3:45 Nitrogen in Humic Substances Related to Soil Productivity.  
F. J. Stevenson and H. Xin-Tao, University of Illinois
- 4:15 Characterization of Humic Substances Isolated from Sewage Wastes.  
S. A. Boyd\* and L. E. Sommers, Michigan State University and  
Colorado State University
- 4:45 Variation Between Humic Substances Isolated from Soils, Stream Waters, and Ground Waters.  
R. L. Malcolm, USGS, Denver, CO
- 5:15 Discussion.

INCORPORATION OF WATER DISSOLVED CHLOROPHENOXYALKANOIC HERBICIDES BY  
HUMIC ACIDS OF VARIOUS ORIGIN AND NATURE

N. SENESI, T. MIANO, and C. TESTINI

Istituto di Chimica Agraria, Università degli Studi di Bari, Bari, Italy.

ABSTRACT

Humic acids (HA) of coal, peat, compost and synthetic origin were singly reacted with a number of chlorophenoxyalkanoic compounds showing herbicidal activity, in aqueous medium, in air and under the effect of natural light. The products of interaction were analyzed for their chlorine content and by infrared (IR) and electron spin resonance (ESR) spectrometries. The apparent increase of chlorine content in the obtained products indicated the incorporation of partially chlorinated units of the herbicide into humic molecules. Infrared analysis suggested a very limited, secondary involvement of weak bonds, i.e. hydrogen bonds and Vander Waals forces, in the interaction processes. ESR results, and in particular the definite quenching of free radical concentrations measured in the interaction products, in comparison with the original concentrations in unreacted humic acids, suggested as the main interaction mechanism the omolytic coupling between humic, indigenous free radicals and herbicide-derived aryloxy of phenoxy radicals. This reaction would therefore lead to the firm incorporation, through stable covalent bonds, into the humic polymer of partially dechlorinated and degraded herbicidal residues. The order of reactivity determined for examined HA's towards any type of chlorophenoxyalkanoic herbicide was generally: synthetic > peat > coal > compost. The higher the COOH group content and the COOH/OH ratio of HA, the lower resulted the ability of its indigenous free radicals in coupling with herbicide-derived free radicals. The beneficial, immediate effect and the unknown, long-term fate of the addition of HA's of various sources to environments which are receiving for various reasons chlorophenoxy compounds is briefly discussed.

INTRINSIC COPPER, IRON AND VANADYL COMPLEXES IN HUMIC ACID-TYPE  
POLYMERS (MELANINS) FROM SOIL FUNGI : AN ESR STUDY

N.SENESI\*, G.SPOSITO° and J.P.MARTIN°

\*Istituto di Chimica Agraria.Università di Bari.70125-BARI.ITALIA.

° Department of Soil and Environmental Sciences.University of Calif-  
ornia, Riverside, CA-92521, U.S.A.

ABSTRACT

Humic acid-type polymers synthesized by five soil fungi in culture medium (fungal melanins) were analyzed for their elemental composition, functional groups content and electron spin resonance (ESR) properties. The fungal polymers showed significative differences in their COOH and nitrogen contents, which were reflected in their complexation properties towards intrinsic paramagnetic metal ions. ESR spectra gave evidence of the presence of intrinsic  $Fe^{3+}$  ions, strongly bound and protected in inner-sphere complexes in all the fungal melanins, while only some of them displayed an anisotropic spectrum consisting of one or more components originating from intrinsic  $Cu^{2+}$  ions immobilized in inner-sphere, equatorial coordination with fungal polymer-ligands of different types. ESR parameters of the latter features were consistent with prevalently nitrogenated sites for  $Cu^{2+}$  ions, thus indicating the high participation of proteinaceous components in the ligation of copper in the fungal melanins. Evidence of the presence of intrinsic  $VO^{2+}$  ions complexed in these materials was also indicated by the ESR spectra. In conclusion, our results suggested that humic acid-type polymers of soil fungal origin would play an important role in all the equilibria and reactions involving trace metal ions in soils and related environments, including complexation and solubility, transport and accumulation, bioavailability, etc.

## INFRARED SPECTRA OF MELANOIDINS

Rubinsztain<sup>1</sup>, Y., Yariv<sup>2</sup>, S., Ioselis<sup>1</sup>, P., Aizenshtat<sup>1</sup>, Z. and Ikan<sup>1</sup>, R.

<sup>1</sup>Department of Organic Chemistry, Laboratory of Natural Products and Energy Research Center, Hebrew University, Jerusalem, Israel.

<sup>2</sup>Department of Inorganic Chemistry, Hebrew University, Jerusalem, Israel.

It is well known that infrared spectrum provides valuable information on the nature and the arrangement of functional groups of humic acids (1).

Several attempts were made to correlate the structural features of humic substances and melanoidins (2,3).

An extensive study of infrared spectra of melanoidins (which were prepared from various ratios of amino acids: glycine, lysine, isoleucine, valine and arginine, and sugars: glucose and galactose) led to the following conclusions:

1. Absence of peptide linkages in synthetic melanoidins (absence of amide peaks at  $1660\text{ cm}^{-1}$  and  $1540\text{ cm}^{-1}$ ; absence of absorptions at  $600\text{--}750\text{ cm}^{-1}$ , which is characteristic of polyamino acids).
2. The skeletal structure of melanoidins is based on sugar moieties.
3. The exact location of nitrogen atoms could not be determined.
4. Treatment of melanoidins at various pH values revealed the nitrogen atoms as tertiary amines.
5. The acidity of melanoidins depends on the structural features of amino acids.
6. Most carboxyl groups of melanoidins originate from sugars.
7. A remarkable similarity of the infrared spectra exists in humics and melanoidins which were prepared from high ratios of sugars.
8. A pronounced imprint on IR of the carbon skeleton of amino acids and of the "extra" amino groups (arginine, lysine) was observed.

### References

1. Stevenson, F.J. Humus Chemistry: genesis, composition, reactions, John Wiley, 1982.
2. Hoering, T.C. Carnegie Institution Washington Year Book, 72, 682 (1973).
3. Ertel, U.R. and Hedges, J.I. Aquatic and Terrestrial Humic Materials, (Christman and Gjessing, eds.), Ann Arbor Science, 143-163 (1983).



# HETEROCYCLICS AS BUILDING BLOCKS OF THE POLYMERIC MATRIX OF HUMIC

## SUBSTANCES AND MELANOIDINS

Ikan<sup>1</sup>, R., Ioselis<sup>1</sup>, P., Rubinsztain<sup>1</sup>, Y., Aizenshtat<sup>1</sup>, Z., Pugmire<sup>2</sup>, R., Anderson<sup>2</sup>, L.L., Woolfenden<sup>3</sup>, W.R. and Ishiwatari<sup>4</sup>, R.

<sup>1</sup>Department of Organic Chemistry, Laboratory of Natural Products and Energy Research Center, Hebrew University, Jerusalem, Israel.

<sup>2</sup>Department of Fuels Engineering, University of Utah, Salt Lake City, Utah, USA.

<sup>3</sup>Department of Chemistry, University of Utah, Salt Lake City, Utah, USA.

<sup>4</sup>Department of Chemistry, Tokyo Metropolitan University, Tokyo, Japan.

It has been assumed that the aromatic structures are the dominant building blocks of the polymeric core of humic substances. This was mainly due to the historic linkage of humics with lignin (1). The aromatic (benzenoid) structures were detected in humics by means of chemical degradation methods, such as potassium permanganate oxidation (2) and pyrolytic (3) methods. These techniques, however, did not furnish quantitative structural information.

We suggest a non-benzenoid structure of humic substances. Our assumption is supported by various chemical and spectroscopic methods. The infrared absorption spectra of most humics lacks the aromatic bands at  $3030\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$ . The <sup>1</sup>H-NMR at 7.4-8.8 ppm might be due to aromatic as well as protonated heterocyclic and other systems (4).

The electron spin resonance (ESR) data (5) may also be due to heterocyclic systems (6).

A close resemblance was observed in the <sup>13</sup>C-CP/MASS NMR spectra between melanoidins (synthesized from amino acids and sugars in molar ratio 1:1 and 1:9).

The <sup>13</sup>C-NMR studies support the presence of aliphatic, furanoid, hydroxy-alkyl-furanoid, hydroxy-alkyl-cyclopentenoid and related heterocyclics as the major building blocks of humics and melanoidins.

These observations were also supported by thermal (7) and spectroscopic data (8). We believe that the contribution of the melanoidin pathway is more significant in the formation of the skeletal structure of humic substances than previously thought.

#### References

1. Flaig, W., Beutelspacher, H. and Rietz, E. in: Soil Components (Gieseking, ed.), 1-211, Springer, New York (1975).
2. Hansen, E.H. and Schnitzer, M., Soil Sci. Soc. Amer. Proc. 30, 745 (1966).
3. Meuzelaar, H.L.C., Haider, K., Nagar, B., and Martin, J.P., Geoderma, 17, 239 (19-7).
4. Wilson, M.A. and Goh, K.M., J. Soil Sci., 34, 305 (1983).
5. Steelink, C., Geochim. Cosmochim. Acta 28, 1615 (1964).
6. Rubinsztain, Y. Ph.D. Thesis, Hebrew University, 1985.
7. Boon, J.J., de Leeuw, J.W., Rubinsztain, Y., Aizenshtat, Z., Ioselis, P., and Ikan, R. Org. Geochem. 6, 805 (1984).
8. Rubinsztain, Y., Yariv, S., Ioselis, P., Aizenshtat, Z. and Ikan, R. Org. Geochem. (1985), submitted for publication.

THE ROLE OF HUMIC SUBSTANCES IN THE ENVIRONMENTAL CHEMISTRY OF  
CHLORINATED PHENOXYALKANOIC ACIDS AND ESTERS

N.SENESI - †.MIANO - C.TESTINI

Istituto di Chimica Agraria, Università di Bari, Bari - 70125, Italia.

ABSTRACT

Products of interaction obtained in aqueous medium between three humic acids of synthetic, peat and coal origin and nine chlorophenoxyalkanoic acids and esters of different chemical structure and properties (type of alkanolic chain and number of chlorine ring-atoms) were investigated by electron spin resonance and infrared spectrometries and chlorine analysis in order to obtain information on the occurring interaction mechanisms and type of bonding. The increased chlorine content and decreased free radical concentration generally measured in the interaction products, in comparison with values of the original humic acids, confirmed the already suggested incorporation of xenobiotic units by stable covalent bonds into humic polymers, through cross-coupling, homolytic reactions between indigenous humic free radicals and chlorophenoxy-radical intermediates generated by a previous chemical, photochemical and/or enzymatic degradation of the original xenobiotic molecule. For comparative purposes, the study was also extended to the products obtained by interaction of the same chlorophenoxy compounds with seven more humic acids of different sources, including soil and compost. The various humic acids considered showed a definite, different interacting power in coupling with the xenobiotics, in the order: synthetic > peat > soil > coal > compost. The reactivity of humic acids was found to be indirectly correlated with their carboxyl content and carboxyl/phenolic hydroxyl ratio. The different molecular structure of chlorophenoxyalkanoic compounds did not apparently influence their reactivity towards humic acids. An approximate trend was shown as a function of the number of chlorine ring-atoms, which appeared to affect the reactivity according to the order: monochlorinated > dichlorinated > trichlorinated.

COMPLEXATION OF SOME TRANSITION METAL IONS IN SOIL HUMIC ACIDS

AN ESR STUDY

Nicola Senesi<sup>o</sup>, Garrison Sposito\*, and James P. Martin\*

<sup>o</sup> Istituto di Chimica Agraria, Università di Bari, Bari, Italia.

\* Dept. of Soil and Environ Science, Unive. of California, Riverside-CA, U.S.A.

ABSTRACT

Electron spin resonance (ESR) spectra here presented for naturally-occurring, unfractionated soil humic acid (HA)<sub>3+</sub> are the first experimental evidence of the simultaneous detection of Fe<sup>3+</sup>, Cu<sup>2+</sup> and VO<sup>2+</sup> ions naturally complexed in humic materials. The ESR rigid-limit spectra and related parameters suggest that the three metal ions are bound to HA in inner-sphere complexes of various stability. Fe<sup>3+</sup> appears strongly bound to HA in sites with high rhombic character, Cu<sup>2+</sup> ions are strongly immobilized by 3,0,1 N or 2,0,2 N humic ligand atoms arranged in a square planar environment and VO<sup>2+</sup> appear coordinated in a fully oxygenated, relatively labile site to surface carboxylate groups of solid HA, probably involving also H<sub>2</sub>O molecules.

P. MacCarthy, S. J. DeLuca and K. J. Voorhees

Department of Chemistry and Geochemistry

Colorado School of Mines

Golden, Colorado 80401

R. L. Malcolm and E. M. Thurman

U. S. Geological Survey, Box 25046

Denver Federal Center

Denver, Colorado 80225

PYROLYSIS-MASS SPECTROMETRY/PATTERN RECOGNITION ON

A WELL-CHARACTERIZED SUITE OF HUMIC SAMPLES

A suite of well-characterized humic and fulvic acids of freshwater, soil and plant origin was subjected to pyrolysis-mass spectrometry and the resulting data were analyzed by pattern recognition and factor analysis. A factor analysis plot of the data shows that the humic acids and fulvic acids can be segregated into two distinct classes. Carbohydrate and phenolic components are more pronounced in the pyrolysis products of the fulvic acids, and saturated and unsaturated hydrocarbons contribute more to the humic acid pyrolysis products. A second factor analysis plot shows a separation which appears to be based primarily on whether the samples are of aquatic or soil origin.

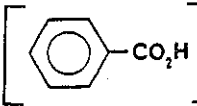
Removal of Paraquat, Diquat, and Amitrole  
from Aqueous Solution by Chemically Modified Peat<sup>1</sup>

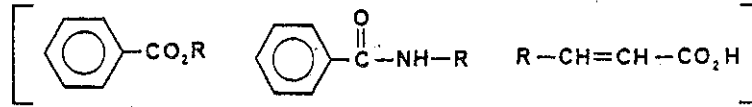
The presence of organic pesticides in aquatic systems has been reported for more than forty years. Various methods, such as sorption by clays, activated carbon or synthetic resins, have been used to remove these pesticides from water. Certain pesticides, such as the cationic species paraquat and diquat and the basic species amitrole, are sorbed by peat. However, the use of raw peat as a sorption medium for the removal of pesticides is hampered by the relative impermeability of peat, the leaching of organic matter from peat into the effluent, and by the disaggregation of peat at pH values greater than ca. 6.0. Treatment of peat with concentrated sulfuric acid at elevated temperatures yields a granular product that has an enhanced cation exchange capacity, that is resistant to leaching, and is permeable to water flow. The objective of this research was to evaluate the use of such chemically-modified peat for removing paraquat, diquat and amitrole from aqueous solution under a variety of experimental conditions. Using isotherm and column experiments, it was shown that the treated peat is very effective in removing these pesticides from aqueous solution. Treated peat has a capacity of about 1 mol(+)kg<sup>-1</sup> for these three pesticides. The effects of pH, ionic strength and flow rate on the efficiency of pesticide removal were found to be relatively small. Peats from two different localities behaved similarly in these experiments.

Kevin A. Thorn  
 U.S. Geological Survey  
 Water Quality Lab  
 Water Resources Division  
 5293 Ward Road  
 Arvada, Colorado 80002

### Use of C-13 Depleted DMSO-d<sub>6</sub> in C-13 NMR of Fulvic Acids

Liquid state C-13 NMR spectra of fulvic acids dissolved in <sup>13</sup>C depleted DMSO-d<sub>6</sub> show improved resolution and S/N compared to spectra of samples dissolved in aqueous solution. Spectra of the Suwannee River fulvic acid are shown in Figures 1 and 2. Figure 1 is the spectrum of 200 mg of the fulvic acid adjusted to pH 6 in 1.5 ml H<sub>2</sub>O/0.5 ml D<sub>2</sub>O; Figure 2 is the spectrum of 200 mg of the H-saturated fulvic acid dissolved in 2 ml of <sup>13</sup>C depleted DMSO-d<sub>6</sub>. The acquisition parameters were identical for both spectra: 45° flip angle, 30 KHz sweep width, 0.2 second acquisition time, 1.0 second pulse delay, continuous broad band decoupling, 20 Hz line broadening, 66,000 transients. <sup>13</sup>C-depleted DMSO-d<sub>6</sub> is necessary because severe dynamic range problems which arise with the use of undepleted DMSO-d<sub>6</sub> prohibit meaningful phasing of spectra.

Figure 2 exhibits discrete resonances in the aromatic region at 134.1, 131.8, 129.7, and 128.7 ppm, and a resonance in the aliphatic region at 62.2 ppm, which are not discernible in the aqueous solution spectrum. The carbonyl region is also more clearly resolved in Figure 2. The peak centered at 167.7 ppm represents primarily carbonyl carbons of aromatic carboxylic acids.  Carbonyl carbons of aromatic esters, aromatic amides, and α, β-unsaturated carboxylic acids may also contribute to this peak.

 The peak centered at 173.8 ppm represents primarily carbonyl carbons of aliphatic and benzylic carboxylic acids.

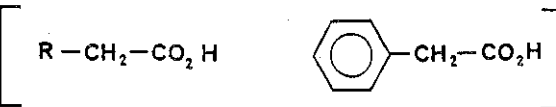
 The ketone peak, centered at 195.8 ppm, extends out to approximately 217 ppm and encompasses aryl-aryl, aryl-alkyl, and alky-alkyl ketones.

FIGURE 1.  
C-13 NMR  
SUWANNEE FULVIC ACID  
AQUEOUS SOLUTION

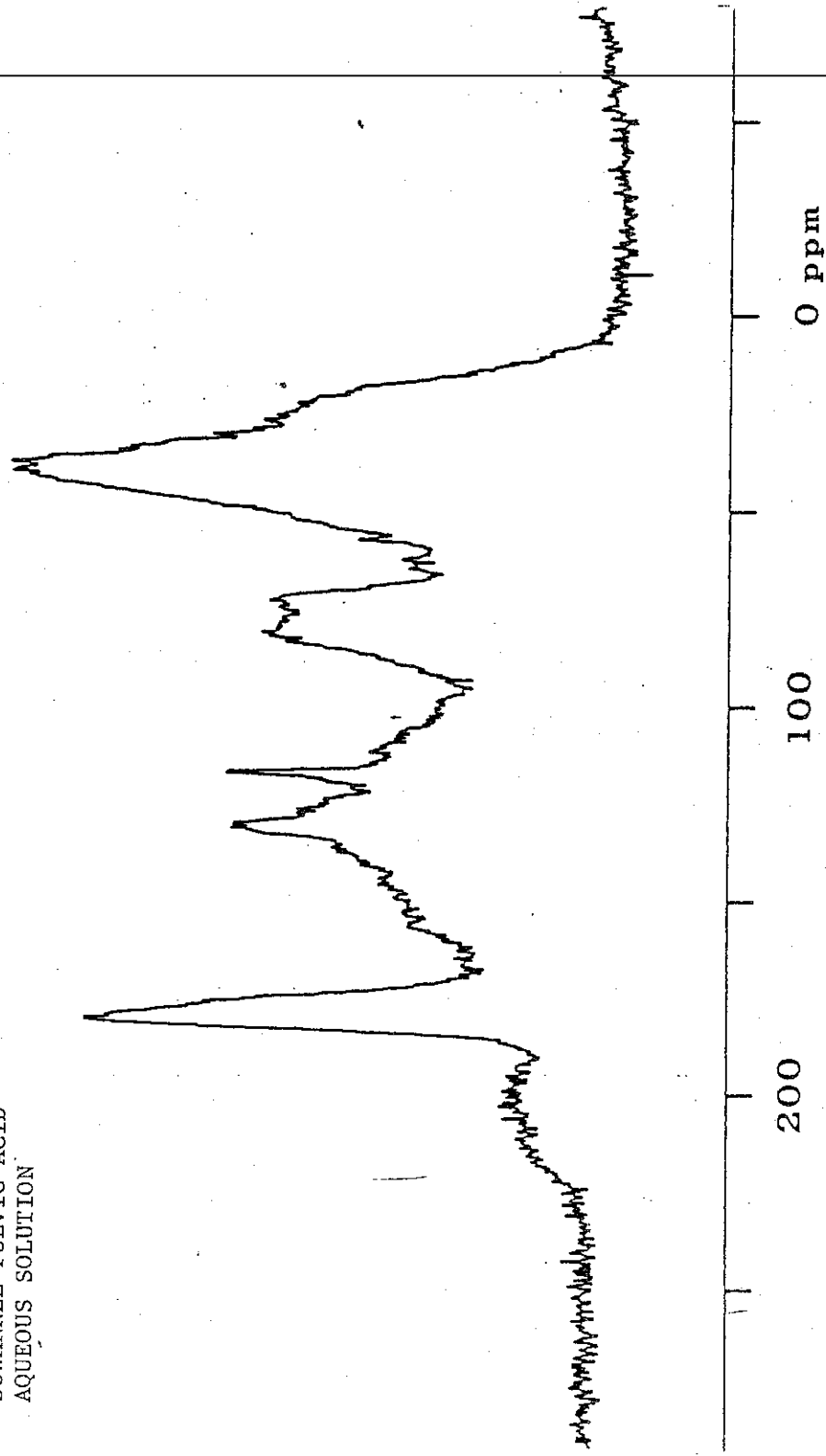




FIGURE 2.  
C-13 NMR  
SUWANNEE FULVIC ACID  
C-13 Depleted DMSO-d<sub>6</sub>

