ORGANIC MASS SPECTROMETRY, VOL. 23, 622–623 (1988)

OMS Letters

Dear Sir

A Mass Spectrometric Investigation on Humic Acid Structure: Some Preliminary Results

The structural characterization of humic materials is one of the more open and debated arguments in the field of agronomy.[1] Leaving aside the problem connected with the separation of pure fractions from the complex matrix,[2] the further structural determinations have, until now, led only to proposed structures.[1] Some encouraging results have been obtained in preliminary attempts for a total synthesis of this kind of compound.[3]

Mass spectrometry is usually successfully employed in the structural characterization of complex molecules[4] and can now be considered an essential tool in the field of natural products. We report here some highly encouraging results obtained with this technique in the characterization of humic acids. The sample of humic acid was obtained as described in the literature.[5]

The mass spectrometric measurements were performed with different ionization methods in order to determine the best ionizing conditions for this type of molecule. The approach until now has been pyrolysis, which has established the presence of some small functional groups and/or parts of the molecule with fragment ions not higher than $m/z = 200$.[6] Similar results in the low mass region can be easily obtained by the direct introduction of the sample into the electron impact ion source and heated to 320 °C.[7]

More recently, an attempt has been made with positive fast atom bombardment (FAB) which is generally considered a satisfactory method for high mass molecules. However, in this case no relative molecular mass higher than $m/z = 260$ was obtained.[8]

We performed the mass spectrometric analysis of humic acid using two different methods, i.e. by employing FAB, both positive and negative with different matrices (glycerol, acidified and basified glycerol, etc.) and by field desorption ionization techniques.

Using the different experimental procedures mentioned above on a VG 7070 instrument, FAB did not lead to a clear characterization of the molecule, the reason being the low molecular species produced ($m/z = 250$) or the irreproducibility of the FAB spectra.[9]

However, field desorption produced well-reproducible mass spectra reported in Fig. 1. The FD measurements were performed on a MAT instrument with an emitter current of 20 mA. The highest m/z value obtained is at $m/z = 670$, followed by intense peaks at $m/z = 549$, 522, 509, 494, 480 and 431.

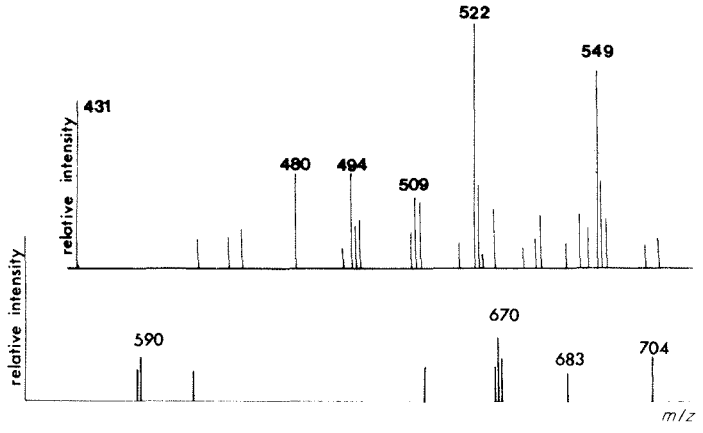

Figure 1. Field desorption mass spectrum of the humic acid.

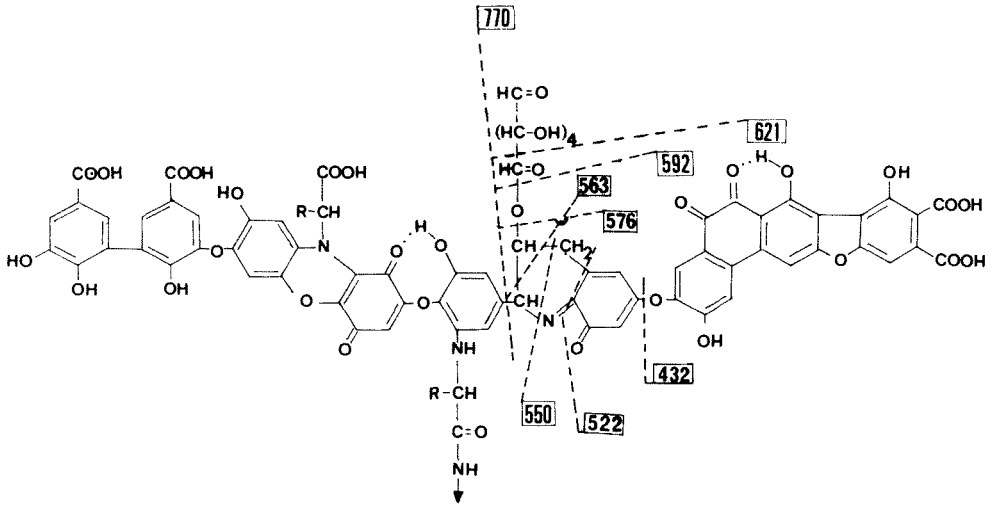

Figure 2. Possible origin of the fragment ions.

© 1988 by John Wiley & Sons, Ltd.

Received 24 May 1988
Accepted 27 May 1988

These ionic species, arising directly from the pyrolysis process occurring on the FD emitter are well related to the structure proposed in the literature,[1] and shown in Fig. 2. The pyrolysis induced decomposition processes occur generally in the weakest part of the molecular skeleton. So the abundant ionic species at m/z = 522, 549 and 431 as well as m/z 590 are easily explained by the indicated cleavages in Fig. 2. Ions m/z 494, 670 and 684 have probably the atomic composition indicated below. Peaks m/z = 684 and 704 are not present in all the mass spectra.

$$m/z\ 522 \xrightarrow[28]{} m/z\ 494$$

$$m/z\ 670 = 621 + \mathrm{CHOH} + \mathrm{OH} + 2\mathrm{H}$$

$$m/z\ 684 = 621 + (\mathrm{CHOH})_2 + 2\mathrm{H}$$

Thus field desorption appears to be a very promising ionization technique in the field of research of humic acids and work is in progress along this line.

Yours

F. ANDREUX
CNRS, Centre de Pédologie Biologique,
54501 Vandoeuvre les Nancy Cedex,
France

E. CONSTANTIN
Institut de Chimie,
1 rue Blaise Pascal, 67000 Strasbourg,
France

B. GIOIA
Farmitalia, Carlo Elba,
Via dei Gracchi, Milano,
Italy

P. TRALDI
Istituto di Polarografia ed Eletrochimica Preparative,
Corso Stati Uniti 4, Padova,
Italy

References

1. F. J. Stevenson, *Bioscience*, **22**, 643 (1972).
2. M. Schnitzer and S. U. Khan, *Soil Organic Matter*, Elsevier, Amsterdam (1978).
3. F. Andreux, D. Golebiowska, T. Chone, F. Jacquin and M. Metche, *Soil Organic Matter Studies*, Vol. II, Int. Atomic Energy Agency, Vienna (1977), p. 43 and references therein.
4. H. Budzikiewicz, C. Djerassi and D. Williams, *Interpretation of Mass Spectra of Organic Compounds*, Holden-Day, San Francisco (1965).
5. E. Barriuso, J. M. Portal and F. Andreux, Communication at the International Humic Substances Soc. Meeting, Estes Park, Colorado, August 1983.
6. H. L. C. Meuzelaar, J. Haverkamp and F. D. Hileman, *Pyrolysis Mass Spectrometry of Recent and Fossil Biomaterials*, Elsevier, Amsterdam (1982).
7. E. Constantin, to be published.
8. F. Y. Saleh, D. Chanz and J. S. Frye, *Anal. Chem.* **55**, 826 (1983).
9. G. Moneti, unpublished results.