

## CHAPTER 67

### Formation of Aryl-Chlorinated Aromatic Acids and Precursors for Chloroform in Chlorination of Humic Acid

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The formation of chloroform when humic substances are chlorinated is well known.<sup>1</sup> Other chlorinated products that may be formed are chloral, di- and trichloroacetic acid, chlorinated C-4 diacids, and  $\alpha$ -chlorinated aliphatic acids.<sup>2-5</sup> Several of these compounds are formed in molar yields comparable to chloroform.<sup>5-7</sup>

The mechanism for the formation of these products is still largely unknown, due to the complex structure of humic material. Humic materials are geopolymers formed from lignin, carbohydrates, proteins, and fatty acids by microbial degradation and enzymatic or autooxidative coupling reactions. Although humic materials are not well defined organic compounds, several structures have been proposed<sup>8</sup> which contain moieties that may be converted into chloroform by chlorine in aqueous medium.

For example, 1,3-dihydroxybenzenes,<sup>2,9,10</sup> 1,3-diketo compounds,<sup>11</sup> natural acids such as citric acid,<sup>12</sup> and compounds with activated C-H bonds such as indoles<sup>13</sup> or methylketones<sup>14</sup> can form chloroform in high yield on chlorination in aqueous medium. For humic substances, 1,3-dihydroxybenzenes appear to be likely chloroform precursor candidates as suggested by the fact that 3,5-dihydroxybenzoic acid is formed in the degradation of humic material with  $\text{CuSO}_4\text{-NaOH}$  at 175 to 180°C.<sup>15</sup> However, the products of KOH fusion may be of no diagnostic value for the structure of humic substances.<sup>16</sup> In recent  $\text{KMnO}_4$  degradation studies of humic and fulvic acids no 1,3-dihydroxybenzene structures were detected,<sup>17,18</sup> probably because of complete oxidation of these structures.<sup>19</sup>

Although the possibility of 1,3-dihydroxybenzene structures as the precursor fragments for chloroform remains to be proven, Rook proposed a mechanism based on the chemistry of the reaction between chlorine and resorcinol.<sup>2,20</sup> The identification of reaction intermediates is necessary to achieve a better understanding of this mechanism and to assist in the identification of

the structural fragments in humic material that are converted into chloroform and chlorinated acids.<sup>21</sup>

In this study we describe (1) the identification and structural assignment of such intermediates in the reaction between terrestrial humic acid and chlorine in aqueous medium at pH 7.2, and (2) the attempts to demonstrate the presence of 1,3-dihydroxybenzene structures in humic acids by means of Curie-point pyrolysis/gas chromatography/mass spectrometry (Py/GC/MS) and nuclear magnetic resonance (NMR) before and after the chlorination reaction.

## EXPERIMENTAL

### Isolation and Chlorination of Humic Acid

The humic acid (HA) used in this research was extracted from a peat soil in the Liesselse Peel. The elementary composition of the final HA was C, 50.7%; H, 5.1%; N, 1.5%; O, 39.4%; ash, 1.5%. The HA was chlorinated under the following experimental conditions: HA, 0.83 g/L; pH, 7.2 (0.5 M  $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4$  buffer);  $\text{Cl}_2/\text{C}$  molar ratio, 0.39 to 3.35; total volume, 300 mL; reaction time, 24 h.

After completion of the reaction, a possible excess of chlorine was removed by adding solid sodium arsenite and the pH was lowered to 1 with concentrated HCl. The solution was extracted with 50 mL freshly distilled diethyl ether and 50 mL freshly distilled ethyl acetate. Both extracts were dried with anhydrous sodium sulfate, concentrated in a Kuderna-Danish evaporator to about 5 mL, methylated by passing diazomethane gas through the solution, and finally concentrated to 100  $\mu\text{L}$  by a gentle stream of nitrogen.

### Isolation of Humic Acid after Chlorination

In the experiment with an initial  $\text{Cl}_2/\text{C}$  molar ratio of 0.39, a precipitate was formed on acidification to pH 1. This product was removed by filtration, redissolved in 0.1 M NaOH, and reprecipitated with concentrated HCl. After dissolution in water, the product (yield, 140 mg) was freeze-dried. This product will be referred to as chlorinated humic acid (CHA).

## Instrumental Analysis

### *Gas Chromatography*

For a fingerprint analysis of the reaction products, a Varian 3700 capillary gas chromatograph equipped with a flame ionization detector (FID) and a 63 Ni electron capture detector (ECD) was used. The GC conditions were; column, fused silica CP-SIL-5 (Chrompack, Middelburg), 0.23 mm by 25 m; injector, 280°C; detector, 300°C; oven temp., 35°C (5 min) programmed to 300°C (15 min) with a program rate 6°/min; carrier gas, N<sub>2</sub>, flow rate, 0.8 mL/min.

### *Gas Chromatography/Mass Spectrometry*

The gas chromatograph/mass spectrometer (GC/MS) was a Varian MAT 44, capillary GC-quadrupole MS, with a computerized data system of our own design. The capillary column was the same type as above and was connected to the MS by an open atmospheric split. GC conditions were as above, except that helium was used as the carrier gas. Electron impact (EI) spectra were obtained at 80 eV and chemical ionization (CI) spectra at 160 eV with isobutane as the reagent gas. The ionization current was 700 and 200  $\mu$ A, respectively. Cyclic scanning from  $m/z = 50$  to 500 was used with a cycle time of 2 s.

### *Curie-Point Pyrolysis—Gas Chromatography/Mass Spectrometry*

Py/GC/MS was carried out with a Curie-point pyrolysis system as described by Meuzelaar et al.<sup>22</sup> and modified according to van de Meent et al.<sup>23</sup> HA and CHA samples (100–200  $\mu$ g) were brought onto a ferromagnetic Ni/Fe wire (Curie temperature 610°) in the form of a suspension (20 mg/mL) in methanol. After evaporation of the methanol, the wire was heated to the Curie-temperature in 0.15 s. The pyrolysis products were separated and identified in the capillary GC/MS system as described above.

### *Nuclear Magnetic Resonance Spectroscopy*

About 100 mg HA or CHA was dissolved in 1-mL DMSO-d<sub>6</sub>. <sup>1</sup>H-NMR spectra were measured at 200 MHz with a Nicolet NT 200 WB spectrometer using the FT-technique.

## RESULTS AND DISCUSSION

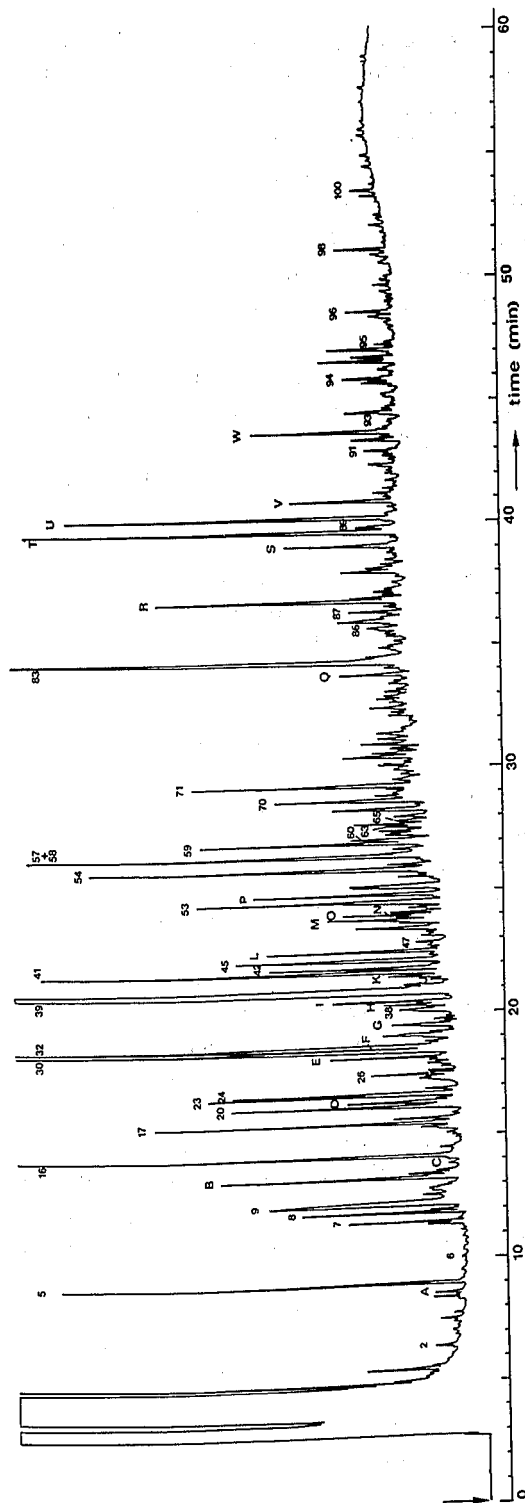
## Chlorination Products

Figure 1 shows the chromatograms of the GC/FID analysis of the methylated ethyl acetate extract of HA chlorinated at a  $\text{Cl}_2/\text{C}$  molar ratio of 3.35. Ethyl acetate was shown to be more effective in extracting polar chlorination products than diethyl ether. Notably, the aromatic polycarboxylic acids and the cyano-substituted alkanolic acids were found mainly in the ethyl acetate extract.

The chlorine dose used strongly influenced the composition of the product mixture. With a high chlorine dose more products were found which appeared early in the chromatogram, whereas at low chlorine dose most products were found to elute late in the chromatogram. Structures were assigned to more than 100 different reaction products by the combined use of GC/MS with EI and CI. The principal products for the different classes of organic compounds are given in Table I.

Table I. Principal Reaction Products for Different Classes of Organic Compounds in the Chlorination of Terrestrial Humic Acid

Compounds Class	Compounds Identified (No.)	Principal Compound
Nonchlorinated products		
Aliphatic monobasic acids	25	Hexacosanoic acid
Aliphatic dibasic acids	8	Butanedioic acid
Cyano-substituted acids	2	3-Cyanopropanoic acid
Aromatic carboxylic acids	13	1,2,4-Benzenetricarboxylic acid
Heterocyclic acids	2	Methylfuranedicarboxylic acid
Miscellaneous	6	Indole
Chlorinated Products		
Aliphatic monobasic acids		
$\alpha$ -Monochlorinated	6	2-Chloropentanoic acid
$\alpha,\alpha$ -Dichlorinated	6	Dichloroethanoic acid
Other substitution	9	Trichloroethanoic acid
Unsaturated	7	2,3-Dichloropropenoic acid
Aliphatic dibasic acids		
$\alpha$ -Monochlorinated	4	Chlorobutanedioic acid
$\alpha,\alpha$ -Dichlorinated	5	2,2-Dichlorobutanedioic acid
Other substitution	5	Tetrachlorohexanedioic acid
Unsaturated	10	Dichlorobutenedioic acid
Aromatic carboxylic acids	6	2-Chlorophenylacetic acid
Chloroform precursors	11	See Table II
Miscellaneous	6	Chloral



**Figure 1.** Capillary gas chromatogram of HA chlorination products. Methylated ethyl acetate extract. Chlorine dose 3.35 mol Cl<sub>2</sub> per mol C. The numbers refer to a full list of identified products (see Reference 26). Letters denote products that were found in the ethyl acetate extract and not in the preceding diethyl ether extract.

At the high chlorine dose, the products identified agreed very well with the compounds identified by Christman and co-workers after chlorination of aquatic humic and fulvic acid.<sup>4,5</sup> We used terrestrial HA with a H:C molar ratio of 1.20 and an O:C of 0.58, which placed our HA in the normal position in the van Krevelen diagram for a peat HA.<sup>24</sup> Lake or river fulvic acids show different H:C and O:C ratios, depending on the molecular weight fraction isolated.<sup>25</sup> Despite the apparent differences in overall structure, aquatic and terrestrial humic materials produced corresponding chlorination products, which indicates that the precursor structures in both materials must be similar and that differences (e.g., in product yield) must be explained by differences in the concentration of the precursor structure in the humic material.

In the identification study three new classes of chlorination products were found: (1) cyano substituted aliphatic monobasic acids at high chlorine dose, (2) chlorinated aromatic carboxylic acids at high chlorine doses, and (3) a group of compounds that can be characterized as chloroform precursors at low chlorine dose.

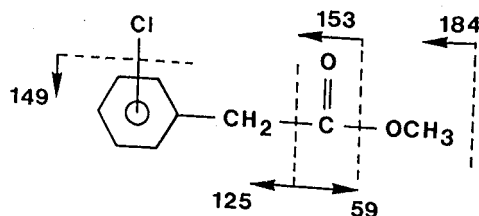
The identification and mode of formation for the chlorinated aromatic acids and some chloroform precursors will be described here in detail. Most other compounds will be described elsewhere.<sup>26</sup>

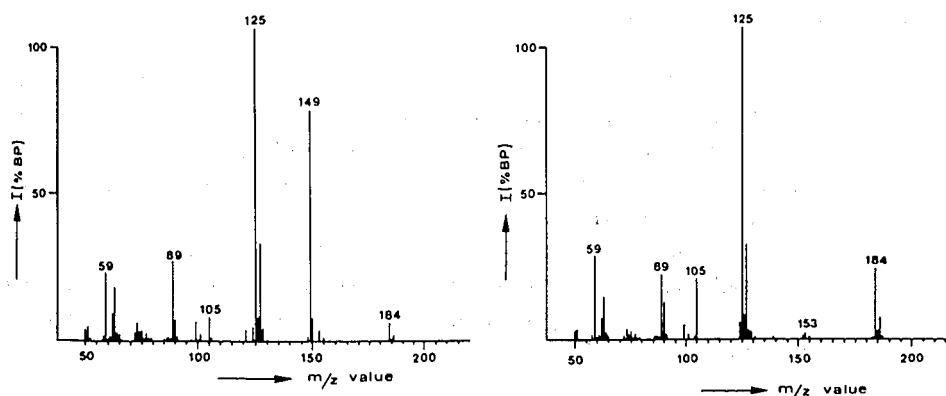
### Aryl-Chlorinated Aromatic Carboxylic Acids

The aryl chlorinated aromatic carboxylic acids comprised 2- and 4-chlorobenzoic acid, 2- and 4-chlorophenylacetic acid, and 2,4- and 2,6-dichlorophenylacetic acid. The identification of the first four compounds was confirmed by comparison of the chromatographic behavior and the mass spectra with those of authentic samples.

In the case of the phenylacetic acids we also expected the presence of phenylchloroacetic acid. Although the the mass spectra of the methyl esters of phenylchloroacetic acid and 4-chlorophenylacetic acid showed much similarity, they could be distinguished on the basis of their GC retention. Therefore, we concluded that phenylchloroacetic acid was not present.

Chlorophenylacetic acids with a chlorine atom in the ortho position could be characterized quite easily on the basis of the unexpected loss of the ortho-chlorine atom as exemplified in the mass spectra of the methyl esters of 2- and 4-chlorophenylacetic acid (Figure 2). The major fragments can be explained as simple primary fission products:

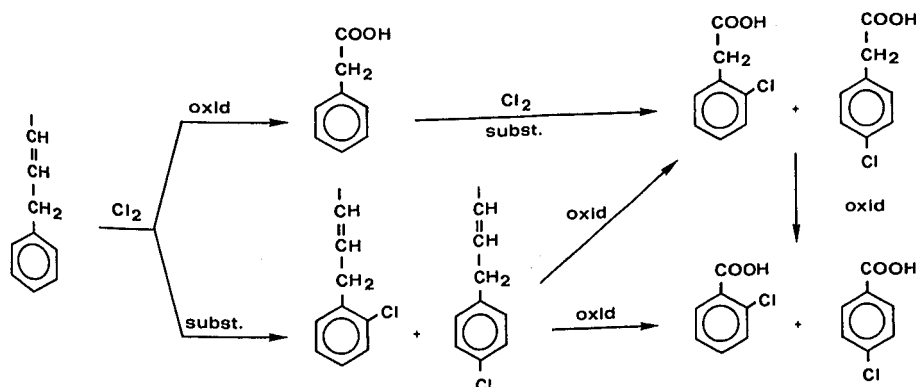




**Figure 2.** EI mass spectra for 2-chlorophenylacetic acid (left) and 4-chlorophenylacetic acid (right). Note the intense fragment at  $m/z = 149$  corresponding with the loss of a chlorine atom from the molecular ion in the spectrum of 2-chlorophenylacetic acid.

The formation of the aryl-chlorinated phenylacetic acid derivatives seems possible through the direct chlorination of phenylacetic acid, which was found as one of the products after chlorination of HA.<sup>12,26</sup> The ortho/para substitution pattern is in accordance with this assumption. For benzoic acid, which was also found after chlorination of HA,<sup>26</sup> direct chlorination would yield 3-chlorobenzoic acid and not the 2- and 4-chlorobenzoic acid found in this study. This direct chlorination is also very improbable because of the deactivating effect of the carboxyl group.

An explanation for the occurrence of both chlorinated benzoic acids and phenylacetic acids may be given by the assumption that first an alkenyl substituted aromatic ring in the humic acid core is chlorinated, followed by an oxidative breakdown of the alkenyl side chain as shown in Scheme I.

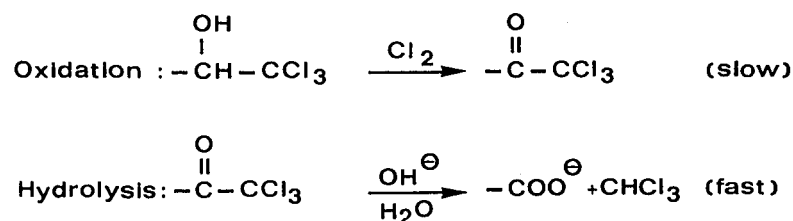


**Scheme I.** The formation of aryl-substituted benzoic and phenylacetic acid derivatives.

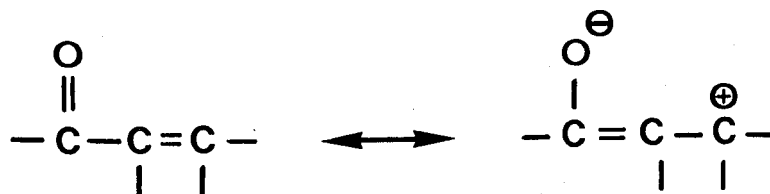




ing to the classical haloform reaction. The first step is expected to be slow and the second step may need further activation if it is to be achieved at neutral pH and normal temperatures.<sup>14</sup>

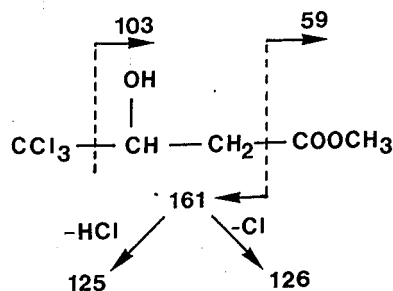


The second group of chloroform precursors already contains a trichloroacetyl group, but in these cases hydrolysis to chloroform is hampered by resonance stabilization of the carbonyl group with a carbon-carbon double bond.



The structural assignments for all chloroform precursors are based on a priori interpretation of the EI and CI spectra. The application of CI mass spectrometry was essential, because the molecular ion was missing in all cases, and the presence of a trichloromethyl group ( $\text{CCl}_3$ ) could be deduced from the combined use of both techniques only.

For example, two isomers were found with CI-mass spectrometry at  $M + 1 = 221$  (Figure 3). From the isotope distribution pattern of the quasi molecular ion the presence of three chlorine atoms could be deduced. From the EI spectra, the presence of the  $\text{CCl}_3$  group could not be deduced directly from a peak at  $m/z = 117$  but only indirectly from the loss of a  $\text{CCl}_3$  group ( $-117$ )



from the molecule, which gives the fragment at  $m/z = 103$ . The presence of a  $\text{COOCH}_3$  group ( $m/z = 59$ ) leaves a mass of 44 or a  $-\text{C}_2\text{H}_4\text{O}$ -group for the rest of the molecule.

Several isomers seem possible, but in view of the stability of the  $m/z = 103$  ion ( $\alpha$ -cleavage next to a hydroxyl group), a  $\text{CCl}_3\text{-C-OH}$  group is to be prefer-

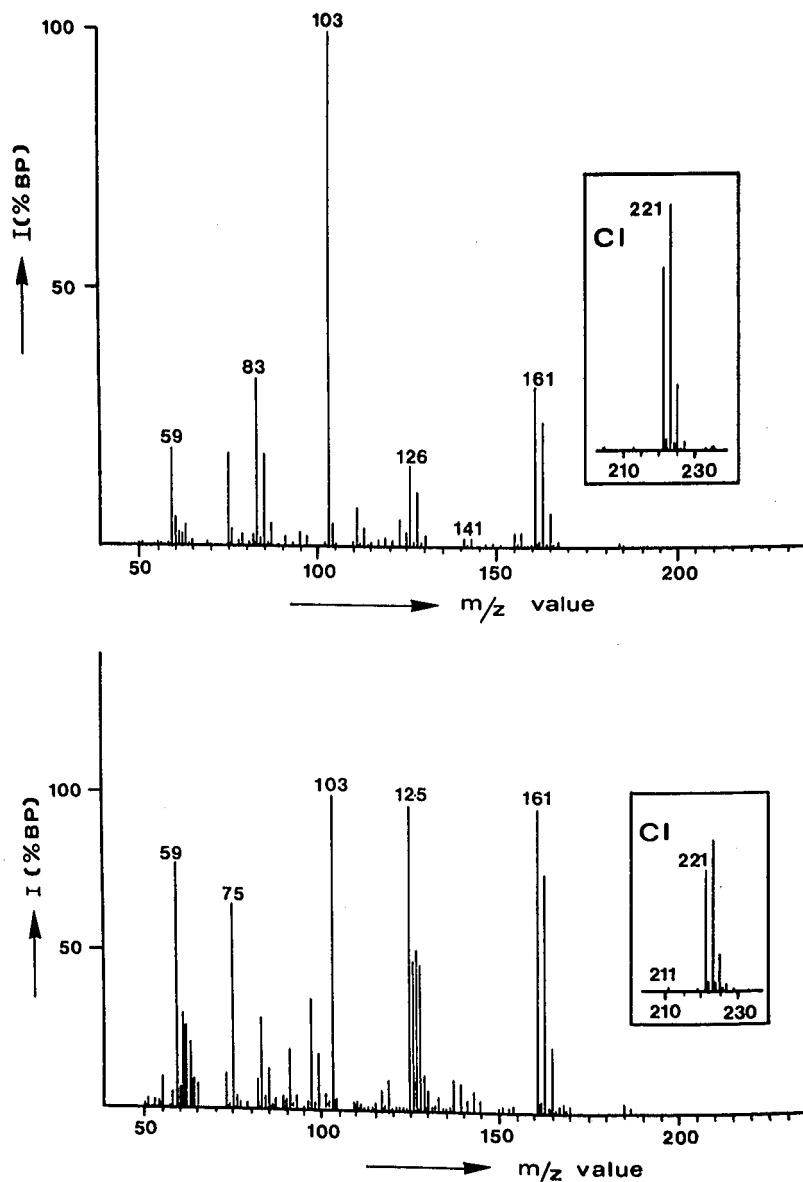


Figure 3. EI and CI mass spectra of two  $\text{C}_5\text{H}_7\text{O}_3\text{Cl}_3$  isomers. The assigned structures are 3,3,3-trichloro-2-hydroxy-2-methylpropanoic acid methyl ester (lower) and 4,4,4-trichloro-3-hydroxybutanoic acid methyl ester (upper).

red. The final decision between 3,3,3-trichloro-2-hydroxy-2-methylpropanoic acid methyl ester (Figure 3, left) and 4,4,4-trichloro-3-hydroxy-butanoic acid methyl ester (Figure 3, right) is based on the intensity of the  $m/z = 103$  ion (tertiary or secondary C) and the loss of Cl or HCl from the  $m/z = 161$  ion.

The structure of many chloroform precursors was confirmed independently from the isolation of identical products in the chlorination of substituted resorcinol derivatives.<sup>26</sup> The formation of those compounds can be explained on the ground of the mechanism proposed by Rook<sup>2</sup> and extended by Boyce and Hornig<sup>10</sup> and points to the important role of 1,3-dihydroxybenzene structures in the formation of chloroform in the chlorination of HA.

The formation of chloroform precursors also explains the difference in chloroform yield as found by extraction with pentane followed by GC-analysis and the direct aqueous injection (DAI) method.<sup>10</sup> Trichloromethyl-substituted products will be decomposed into chloroform in the heated injection port on DAI, whereas these products are not extracted from the reaction mixture with pentane.

With the HA used in this study 1.3% of the carbon content could be converted into chloroform. When we consider that resorcinol gives a yield of 14.2% mol per mol  $\text{CHCl}_3$  per mol C according to Rook,<sup>2</sup> this yield is quite high. Indeed, if only resorcinol structures are responsible for the chloroform production in the chlorination of HA, about 10% of the organic carbon must be present as free or fused 1,3-dihydroxybenzene structures.

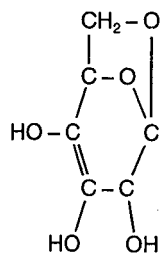
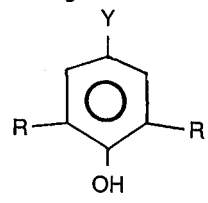
### Pyrolysis – GC/MS and NMR Investigation of HA and CHA

We tried to detect the presence of 1,3-dihydroxybenzene structure in HA by applying Curie-point pyrolysis–GC/MS and 200 MHz NMR. After Py/GC/MS about 160 pyrolysis products could be identified, which are summarized in Table III.

Py/GC/MS showed the presence of proteins, carbohydrates, lignin, and lipids which give characteristic pyrolysis products.<sup>28</sup> There was no indication of the presence of 1,3-dihydroxybenzene structures. This could be due to the destruction of these structures during pyrolysis at 610°C. Indeed in the pyrolysis of several model compounds like hesperitin, florhizin, and rutin, only one 1,3-dihydroxybenzene product could be identified. However, because no structure could be assigned for many compounds, no definitive answers can be given.

Comparison of the pyrolysis products of HA and CHA showed that in CHA the number of aromatic structures was drastically reduced. For example, the intensity ratio between 4-vinylguaiacol, an aromatic lignin pyrolysis product, and 1-tridecene, the decarboxylation product of tetradecanoic acid, changed from 10:1 for HA to 1:5 for CHA.

Table III. Typical Curie-Point Pyrolysis Products of Humic Acid

<i>Carbohydrate Origin</i>		<i>Lipid Origin</i>	
Acetic acid		Alkanes	$\text{CH}_3 - (\text{CH}_2)_n - \text{CH}$ $n = 4 - 29$
2-Methylfuran		Alkenes	$\text{CH}_3 - (\text{CH}_2)_n - \text{CH} = \text{CH}_2$ $n = 4 - 26$
Furfural		1-Pristene	
Levoglucosan			
<i>Lignin Origin</i>		<i>Protein Origin</i>	
Y = H, -CH <sub>3</sub> , -CH <sub>2</sub> -CH <sub>3</sub> ,		Toluene, C-2-benzenes	
-CH=CH <sub>2</sub> , -CHO		Phenol	
R = H or OCH <sub>3</sub>		Benzonitrile	
		Phenylacetonitrile	
		Pyrrole	

Py/GC/MS of CHA showed chloroform as the only chlorinated product. Chloroform may be formed during pyrolysis from trichloromethyl substituted products that are still bound to the HA frame in an analogous way as the formation of chloroform in the heated injection port of a gas chromatograph on DAI.

The disappearance of aromatic structure from HA on chlorination was also confirmed from the 200 MHz NMR spectra of HA and CHA, which show a strong reduction of the aromatic signal from 6.5 to 8.5 ppm as compared with the aliphatic part of the spectrum for CHA (Figure 4).

## CONCLUSION

Chlorination of terrestrial HA, at a chlorine-to-carbon ratio commonly used in the production of drinking water, produces several compounds that can be regarded as precursors for chloroform. Whether these precursors form the

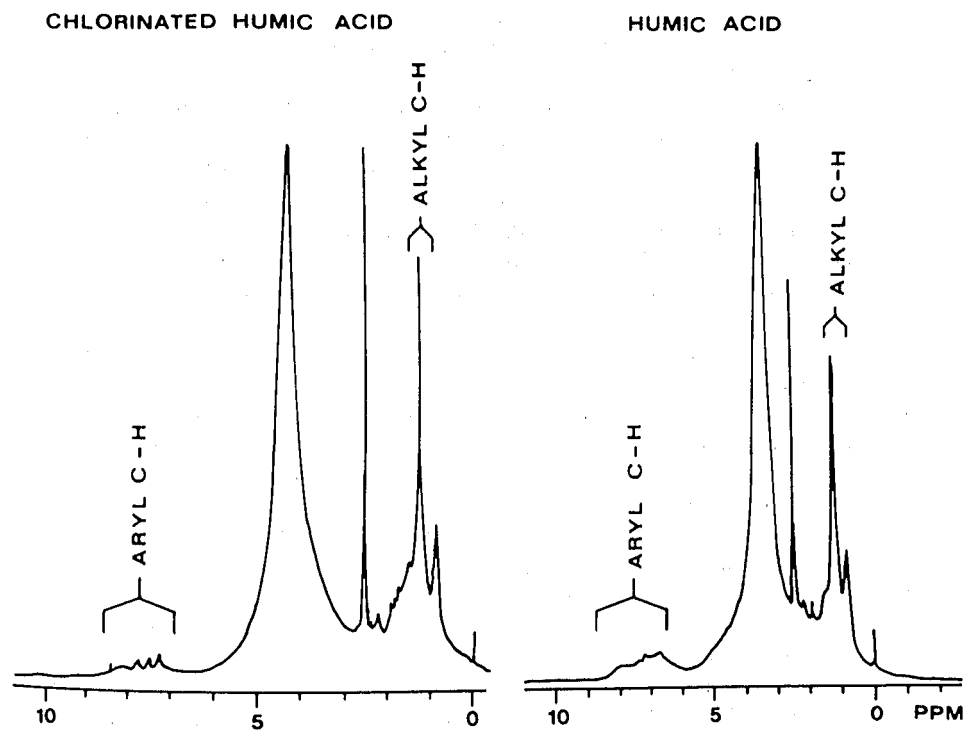


Figure 4. 200-MHz NMR spectra of CHA and HA.

only source of chloroform cannot be concluded, but they point strongly to the important role of 1,3-dihydroxybenzene structures as the primary source. However, it remains to be demonstrated that these structures form a significant part of the HA frame.

It was demonstrated by Py/GC/MS and 200-MHz NMR that chlorination destroys the aromatic part of the HA-structure.

## REFERENCES

1. Rook, J. J. "Formation of Haloforms During Chlorination of Natural Waters," *Water Treat. Exam.* 23(2):234-243 (1974).
2. Rook, J. J. "Chlorination of Fulvic Acids in Natural Waters," *Environ. Sci. Technol.* 11(5):478-482 (1977).
3. Quimby, B. D., M. F. Delaney, P. C. Uden, and R. M. Barnes. "Determination of the Aqueous Chlorination Products of Humic Substances by Gas Chromatography with Microwave Emission Detection," *Anal. Chem.* 52(2):259-263 (1980).

4. Johnson, J. D., R. F. Christman, D. L. Norwood, and D. S. Millington. "Reaction Products of Aquatic Humic Substances with Chlorine," *Environ. Health Perspect.* 46(1):63-71 (1982).
5. Christman, R. F., D. L. Norwood, D. S. Millington, J. D. Johnson, and A. A. Stevens. "Identity and Yields of Major Halogenated Products of Aquatic Fulvic Acid Chlorination," *Environ. Sci. Technol.* 17(10):625-628 (1983).
6. Uden, P. C., and J. W. Miller. "Chlorinated Acids and Chloral in Drinking Water," *J. Am. Water Works Assoc.* 75(10):524-527 (1983).
7. Miller, J. W., and P. C. Uden. "Characterization of Nonvolatile Aqueous Chlorination Products of Humic Substances," *Environ. Sci. Technol.* 17(3):150-157 (1983).
8. Schnitzer, M., and S. U. Khan. *Humic Substances in the Environment*, (New York: Marcel Dekker, Inc., 1972).
9. Norwood, D. L., J. D. Johnson, R. F. Christman, J. R. Hass, and M. J. Bobenrieth. "Reactions of Chlorine with Selected Aromatic Models of Aquatic Humic Material," *Environ. Sci. Technol.* 14(2):187-190 (1980).
10. Boyce, S. D., and J. F. Hornig. "Reaction Pathways of Trihalomethane Formation from the Halogenation of Dihydroxy-Aromatic Model Compounds for Humic Acid," *Environ. Sci. Technol.* 17(4):202-211 (1983).
11. De Laat, J., N. Merlet, and M. Dore. "Chlorination of Organic Compounds: Chlorine Demand and Reactivity in Relationship to the Trihalomethane Formation," *Water Res.* 16(10):1437-1450 (1982).
12. Larson, R. A., and A. L. Rockwell. "Chloroform and Chlorophenol Production by Decarboxylation of Natural Acids during Aqueous Chlorination," *Environ. Sci. Technol.* 13(3):325-329 (1979).
13. Morris, J. C., and B. Baum. "Precursors and Mechanisms of Haloform Formation in the Chlorination of Water Supplies," in *Water Chlorination: Environmental Impact and Health Effects, Vol. 2*, R. L. Jolley, H. Gorchev, and D. H. Hamilton, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1978), pp. 29-48.
14. Gurol, M. D., A. Wowk, S. Myers, and I. H. Suffet. "Kinetics and Mechanism of Haloform Formation: Chloroform Formation from Trichloroacetone," in *Water Chlorination: Environmental Impact and Health Effects, Vol. 4*, R. L. Jolley, W. A. Brungs, J. A. Cotruvo, R. B. Cumming, J. S. Mattice, and V. A. Jacobs, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), pp. 269-284.
15. Christman, R. F., and M. Ghassemi. "Chemical Nature of Organic Color in Water," *J. Am. Water Works Assoc.* 58(6):723-741 (1966).
16. Cheshire, M. V., P. A. Cranwell, and R. D. Haworth. "Humic Acid-III," *Tetrahedron* 24(14):5155-5167 (1968).
17. Liao, W., R. F. Christman, J. D. Johnson, D. S. Millington, and J. R. Hass. "Structural Characterization of Aquatic Humic Material," *Environ. Sci. Technol.* 16(7):403-410 (1982).
18. Reuter, J. H., M. Ghosal, E. S. K. Chian, and M. Giabbi. "Oxidative Degradation Studies on Aquatic Humic Substances," in *Aquatic and Terrestrial Humic Materials*, R. F. Christman and E. Gjessing, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), pp. 107-125.
19. Randall, R. B., M. Benger, and C. M. Grocock. "The Alkaline Permanganate Oxidation of Organic Substances Selected for Their Bearing Upon the Chemical Constitution of Coal," *Proc. Roy. Soc.* 165(A1):432-452 (1938).

20. Rook, J. J. "Possible Pathways for the Formation of Chlorinated Degradation Products During Chlorination of Humic Acids and Resorcinol," in *Water Chlorination: Environmental Impact and Health Effects, Vol. 3*, R. L. Jolley, W. A. Brungs, and R. B. Cumming, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1980), pp. 85-98.
21. Christman, R. F., and E. Gjessing. "Priorities in Humic Research," in *Aquatic and Terrestrial Humic Materials*, R. F. Christman, and E. Gjessing, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), pp. 517-528.
22. Meuzelaar, H. L. C., H. G. Ficke, and H. C. den Harrinck. "Fully Automated Curie-Point Pyrolysis Gas Liquid Chromatography," *J. Chromatogr. Sci.* 13(1):12-17 (1975).
23. Meent, D. van de, S. C. Brown, R. P. Philip, and B. R. T. Simoneit. "Pyrolysis-High Resolution Gas Chromatography and Pyrolysis Gas Chromatography-Mass Spectrometry of Kerogens and Kerogen Precursors," *Geochim. Cosmochim. Acta* 44(7):999-1013 (1980).
24. Van Krevelen, D. W. "Graphical-Statistical Method for the Study of Structure and Reaction Processes of Coal," *Fuel* 29(12):269-284 (1950).
25. Visser, S. A. "Application of Van Krevelen's Graphical Statistical Method for the Study of Aquatic Humic Material," *Environ. Sci. Technol.* 17(7):412-417 (1983).
26. De Leer, E. W. B., J. S. Sinninghe Damsté, C. Erkelens, and L. de Galan. "The Identification of Intermediates Leading to Chloroform and C-4 Diacids in the Chlorination of Humic Acid," *Environ. Sci. Technol.* (in press).
27. Peters, C. J., R. J. Young, and R. Perry. "Factors Influencing the Formation of Haloforms in the Chlorination of Humic Materials," *Environ. Sci. Technol.* 14(11):1391-1395 (1980).
28. Meent, D. van de, J. W. de Leeuw, and P. A. Schenck. "Chemical Characterization of Non-Volatile Organics in Suspended Matter and Sediments of the River Rhine Delta," *J. Anal. Appl. Pyr.* 2:249-263 (1980).