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Received for review April 23, 1984. Revised manuscript received September 28, 1984. Accepted December 11, 1984. This work was partially supported by a NSERC Visiting Fellowship (to S.R.).

Identification of Intermediates Leading to Chloroform and C-4 Diacids in the Chlorination of Humic Acid

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■ The chlorination of terrestrial humic acid was studied at pH 7.2 with varying chlorine to carbon ratios. The principal products are chloroform, di- and trichloroacetic acid, and chlorinated C-4 diacids. At a high chlorine dose many new chlorination products were detected, among them chlorinated aromatic acids. At a low chlorine dose a class of chlorinated compounds was found, which contained a trichloromethyl group. These compounds may be converted into chloroform and in most cases C-4 diacids by oxidation and hydrolysis reactions. Because these compounds are found mainly at low chlorine dosage, they may be regarded as intermediates in the reactions that give chloroform. The intermediates support the hypothesis of Rook that *m*-dihydroxybenzene moieties in humic acid are responsible for the formation of chloroform. A reaction scheme is proposed that explains the formation of the intermediates.

Introduction

In 1974 Rook (1) described that superchlorination of water from the rivers Rhine and Meuse produced trihalomethanes as undesirable side products. Because a good correlation was found between the chloroform formation and the color intensity of the water, he suggested that humic substances are the precursors for the trihalomethanes. This hypothesis was supported by the observation that an aqueous extract of peat gave the four trihalomethanes CHCl_3 , CHBrCl_2 , CHBr_2Cl , and CHBr_3 upon chlorination in the presence of bromide ions. Since then, the presence of trihalomethanes has been demonstrated in many drinking waters (2, 3), and generally, the reaction between chlorine and humic material is regarded as the main source for these products (4).

Detailed investigations of the reaction between chlorine and humic material have clearly established that chloroform is the major volatile chlorination product but that a large number of other halogenated and nonhalogenated products are also formed. The formation of volatile chlorination products like chloral and chlorinated acetones (5), 2-chloropropenal (6), and chlorinated isoprenoid alcohols (7) was demonstrated by gas chromatography/mass spectrometry (GC/MS). However, total organic halogen formed in the chlorination of water or solutions of humic materials is much greater than can be accounted for by the amount of volatile products (8, 9). Many nonvolatile products can be converted into volatile products by methylation with diazomethane, which makes them amenable to analysis by GC/MS or other special techniques.

Quimby et al. (10) found by gas chromatography with microwave emission detection that trichloroacetic acid was a major product and identified several chlorinated acids

and phenols on the basis of their retention times. Later, Uden and Miller (11, 12) and Christman et al. (13) showed that trichloroacetic acid is formed in a molar yield comparable to that of chloroform. More systematic studies, aimed at the identification of a large number of nonvolatile products, were conducted by Christman and co-workers (13-15). Over 100 products were identified and many structures were assigned by GC/MS. Di- and trichloroacetic acid and 2,2-dichlorobutanedioic acid were the main products, which, together with chloroform, accounted for 53% of the total organic halogen. Other chlorinated products included 2,2-dichloropropanoic acid, 2-chlorobutanedioic acid, 2-chlorobutenedioic acid, 2,3-dichlorobutenedioic acid, dichloropropanedioic acid, and various other less abundant compounds.

No chlorinated aromatics were found. Most of the nonchlorinated products are aliphatic and aromatic carboxylic acids, demonstrating that chlorine acted not only through substitution and addition but also through oxidation reactions.

To establish a reaction pathway for the production of chloroform and the chlorinated acids, knowledge of the structure of humic material is necessary. Humic materials are geopolymers formed from lignin, carbohydrates, proteins, and fatty acids by microbiological degradation and enzymatic or autooxidative coupling reactions (16). Although humic materials obviously are not well-defined organic compounds, several structures (17-20) have been proposed, which contain fragments that may be converted into chloroform by chlorine in aqueous medium at pH 7-8. 1,3-Dihydroxybenzenes (1, 5, 21), 1,3-diketo compounds (22), natural acids like citric acid (23), and compounds with activated C-H bonds like indoles (24) were shown to give chloroform in high yield on chlorination in aqueous medium. For humic acid, 1,3-dihydroxybenzenes seem to be the more likely candidates as 3,5-dihydroxybenzoic acid is formed in the degradation of humic material with $\text{CuSO}_4\text{-NaOH}$ at 175-180 °C (20). From the work of Cheshire et al. (25) it appears, however, that the products of KOH fusion may be of no diagnostic value for the structure of humic substances, and in recent KMnO_4 degradation studies of humic and fulvic acids (26, 27) no 1,3-dihydroxybenzene structures were detected, possibly as a result of complete oxidation of these structures (28).

Although the possibility of 1,3-dihydroxybenzene structures as the precursor fragment for chloroform formation from humic material remains to be proven, Rook (5, 21) proposed a mechanism based on the chemistry of the reaction between chlorine and resorcinol. For a better understanding of this mechanism and for the identification of the structural fragments in humic material that are converted into chloroform and chlorinated acids, the

identification of intermediates is necessary (29).

We report here the identification and structural assignment of such intermediates in the reaction between terrestrial humic acid and chlorine in aqueous medium at pH 7.2. We propose structural assignments for a large number of products analyzed by gas chromatography/mass spectrometry and compared the products with the chlorination products of 3,5-dihydroxybenzoic acid. Suggestions are given for the mechanism of the reactions leading to chloroform and chlorinated acids.

Experimental Section

Separation of Humic Acid. Humic acid was isolated from peat (Liesselse Peel, O-Brabant) following the procedure described by Stevenson (30). This involved treatment with 0.1 M HCl, extraction with 0.5 M NaOH, removal of residual solids, acidification to pH 1 with precipitation of humic acid, purification by redissolution/precipitation, washing with deionized water, and freeze-drying. To minimize chemical changes caused by oxidation, all steps (if possible) were carried out in an atmosphere of nitrogen.

The elementary composition of the final humic acid was the following: C, 50.7%; H, 5.1%; N, 1.5%; O, 39.4%; ash, 1.5%.

Chlorination Procedure. For the *identification studies*, 250 mg of humic acid was dissolved in 40 mL of 0.1 M NaOH. A total of 100 mL of 1 M KH_2PO_4 buffer (pH 7.2) and aqueous hypochlorite was added, and the volume was adjusted to 200 mL with deionized water. Two chlorine concentrations were chosen with Cl_2/C molar ratios of 0.39 and 3.35, respectively. After 24 h the possible excess of chlorine was removed by adding solid sodium arsenite, and the pH was lowered to 1 with HCl. The solution was then extracted with 50 mL of freshly distilled diethyl ether and 50 mL of freshly distilled ethyl acetate. The extracts were dried with sodium sulfate, concentrated in a Kuderna Danish apparatus to about 5 mL, methylated by passing a stream of diazomethane gas through the solution, and finally concentrated to 100 μL by passing a gentle stream of nitrogen.

For the *quantitation studies* this procedure was slightly modified. To 25 mL of humic acid solution (960 mg/L in 0.01 M NaOH) was added 25 mL of KH_2PO_4 buffer (1 M, pH 7.2) and aqueous hypochlorite to various Cl_2/C molar ratios (0.12–2.96). After adjustment of the volume to 100 mL, the bottle was capped head space free and allowed to react for 24 h.

The chlorination of 3,5-dihydroxybenzoic acid was carried out at pH 7.2 in a 0.16 M phosphate buffer. A total of 250 mL of a solution of 3,5-dihydroxybenzoic acid (2×10^{-3} mol/L) and sodium hypochlorite (20×10^{-3} mol/L) was allowed to react in the dark without head space for 2 h. After the given reaction times the excess of chlorine was removed by adding solid sodium arsenite. The solution was acidified to pH 1 with concentrated sulfuric acid and extracted 3 times with 25 mL of freshly distilled diethyl ether.

The concentration and methylation procedure was as described above.

Chlorine Consumption. Chlorine concentrations before and after chlorination were measured iodometrically (31).

Quantitation of Chloroform Production. A total of 25 mL of the reaction mixture was extracted with 25 mL of pentane after destruction of the excess of chlorine with solid sodium arsenite.

The extraction yield was >95%. After proper dilution the extract was analyzed by gas chromatography using a

glass column (ϕ 2.5 mm \times 1.8 m) packed with 13% OV-101 on Chromosorb W HP (100–200 mesh) and an electron capture detector: injector 120 °C; column 70 °C; detector 300 °C; carrier gas N_2 ; flow 30 mL/min. The quantitation was carried out with external standards.

Quantitation of Dichloroacetic Acid (DCA) and Trichloroacetic Acid (TCA) Production. The extraction procedure described by Quimby et al. (10) was used. To 25 mL of reaction mixture were added some solid sodium arsenite and 5 g of sodium chloride. After acidification to pH 0.5 with concentrated H_2SO_4 the solution was extracted with 25 mL of diethyl ether. The extract was methylated with diazomethane gas, and the volume was adjusted to 50 mL. The final solutions were analyzed by gas chromatography with a glass column (ϕ 2.5 mm \times 1.8 m) packed with 15% OV-225 on Chromosorb W-HP (100–200 mesh) and an electron capture detector: injector 200 °C; column 120 °C; detector 300 °C; carrier gas N_2 ; flow 30 mL/min. The quantitation was carried out with external standards: calibration range for DCA, 38–66 $\mu\text{g}/\text{L}$, and TCA, 14–24 $\mu\text{g}/\text{L}$. If necessary, the sample solutions were diluted to an appropriate volume, to obtain a signal in the linear range of the detector.

Determination of Extraction Yields. (1) Chloroform. A total of 25 mL of the type of water under investigation was equilibrated with 25 mL of a series of standard solutions of chloroform in pentane (147–588 $\mu\text{g}/\text{L}$). The extraction yield was calculated from the slope of a graph of the chloroform concentrations in pentane before and after the equilibration. The yield was >95%. Experiments with a 10/1 volume ratio of water to pentane gave a distribution coefficient $K = 56$ (extraction yield = 82%), from which an extraction yield of 98% for a 1/1 volume ratio can be calculated.

(2) DCA and TCA. A solution of 5 g of NaCl in 25 mL of water acidified to pH 0.5 was equilibrated with 25 mL of a solution of DCA and TCA in diethyl ether (66 and 24 $\mu\text{g}/\text{L}$, respectively). DCA and TCA concentrations before and after equilibration were determined as described above. Duplicate experiments gave yields of 98 and 100% for DCA and TCA, respectively.

The quantitative extraction was also checked on actual reaction mixtures, by spiking with known amounts of DCA and TCA.

Retention Index Determination. The retention indexes were measured by mixing a portion of the methylated extract with an *n*-alkane standard (*n*- C_6 –*n*- C_{27}) and analyzing on a fused silica capillary column (ϕ 0.23 mm \times 25 m), CP-SIL-5 (Chrompack, Middelburg): injector 280 °C; column 35 °C (5 min) programmed to 300 °C (15 min), program rate 6 °C/min; detector FID 300 °C; carrier gas N_2 ; flow rate 0.8 mL/min. The retention indexes were calculated by linear interpolation of the retention time of the compound of interest with the retention times of the two neighboring *n*-alkanes.

The same GC conditions were used for the analysis of the chlorination products of humic acid and 3,5-dihydroxybenzoic acid.

Apparatus. The gas chromatograph was a Varian 3700, equipped with a packed and a capillary column, a flame ionization detector, and a ^{63}Ni electron capture detector.

The GC/MS combination was a Varian MAT 44 capillary GC–quadrupole MS with a computerized data system of own design.

The fused silica capillary column (CP-SIL-5) was connected to the mass spectrometer by an open atmospheric split. GC conditions used were as above, except that helium was used as the carrier gas. Electron impact spectra

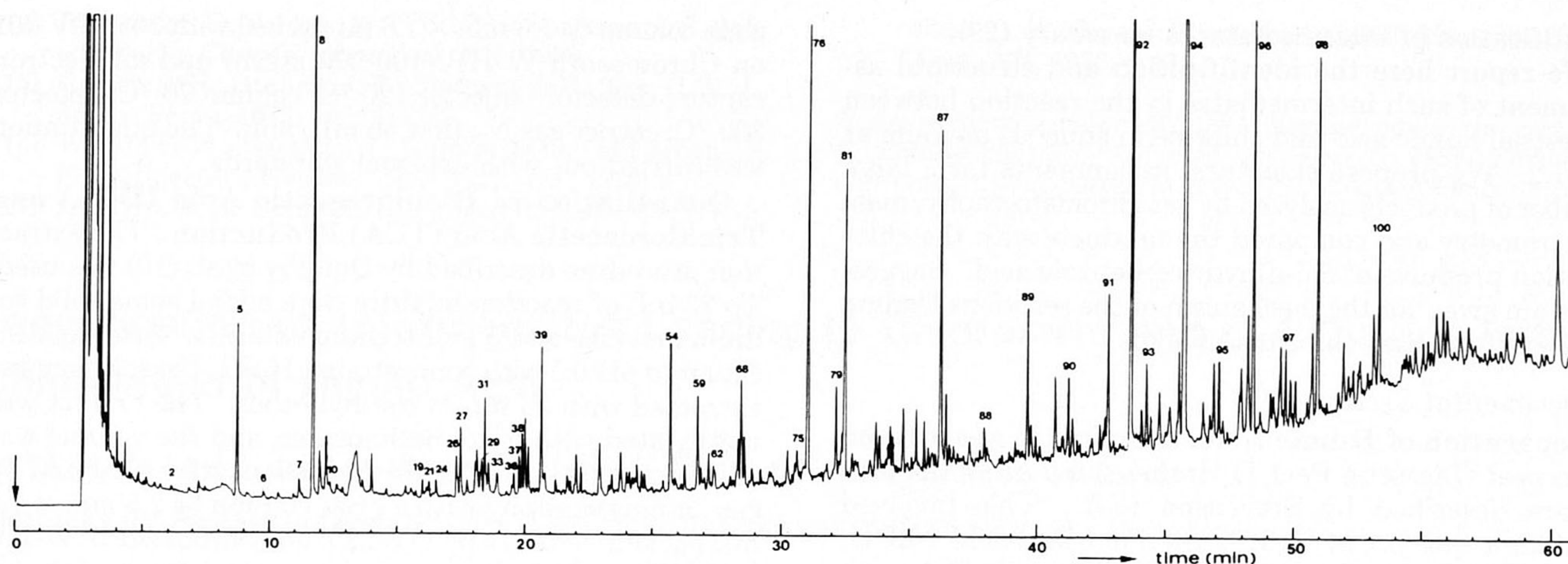


Figure 1. Humic acid chlorination products at a chlorine to carbon ratio of 0.39. Methylated ether extract on a capillary CP-Sil-5 column (FID). Peak numbers refer to the numbers given in Table I.

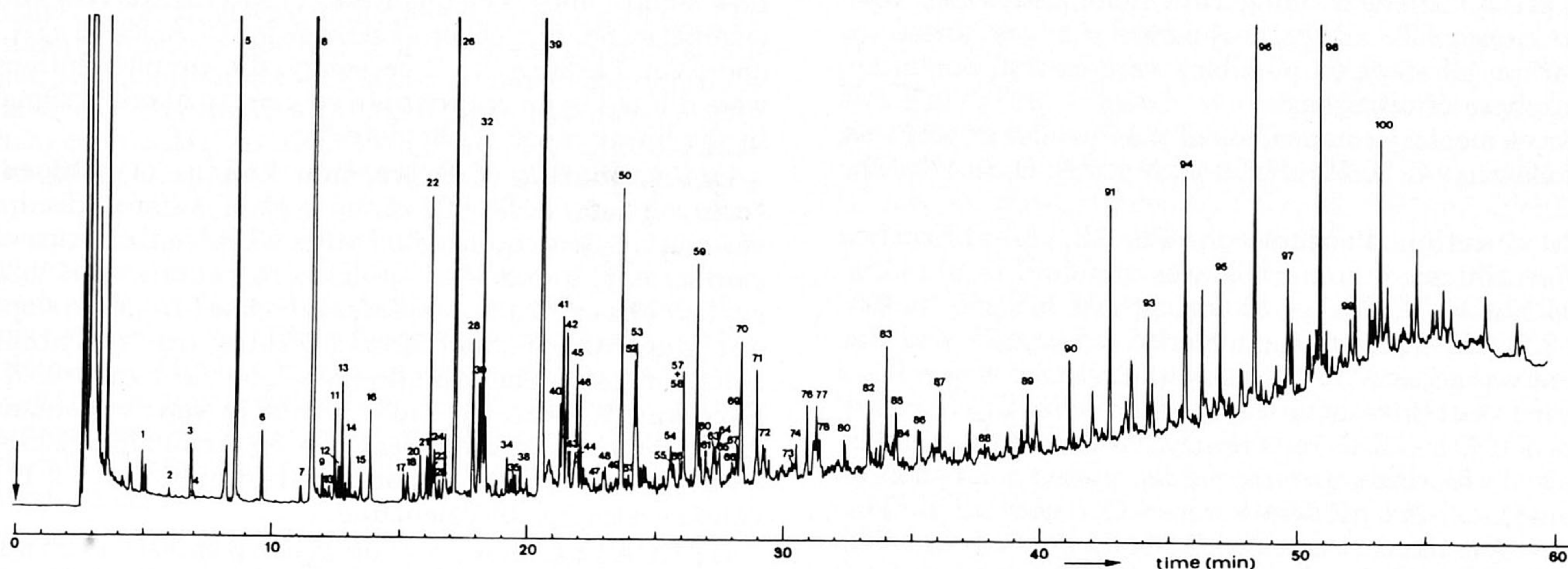


Figure 2. Humic acid chlorination products at a chlorine to carbon ratio of 3.35. Methylated ether extract on a capillary CP-Sil-5 column. The high chlorine dose produces more low molecular weight compounds, while at a low chlorine dose (Figure 1) more high molecular weight compounds are detected.

were obtained at 80 eV and chemical ionization spectra at 160 eV with isobutane as the reagent gas. Ionization current was 700 and 200 μA , respectively. Cyclic scanning from m/z 50 up to 500 was used with a cycle time of 2 s.

Structural Assignments. The confidence level of the structural assignments is given as confirmed (level 3), confident (level 2), tentative (level 1), and very tentative according to Christman (32-34).

For level 3 and level 2 identifications we strictly followed the proposed definitions (34). All level 1 identifications are based on a priori interpretation of the EI spectrum and are supported by the CI spectrum. An identification is given as very tentative if based on the a priori interpretation of the EI spectrum only.

Reference spectra were taken from the literature as indicated or from a mass spectra data base from the Mass Spectrometry Data Centre (England).

Results and Discussion

The chlorination of humic acid was carried out at two chlorine to carbon molar ratios of 0.39 and 3.35, respectively, in a pH 7.2 buffer system. A ratio of 0.39 represents the normal chlorination practice for drinking water, and the 3.35 ratio is used to obtain a high yield of chlorination products. As shown by the chromatograms for the ether extracts (Figures 1 and 2), the composition of the product mixture was quite different in the two experiments. The ether and ethyl acetate extracts differed mainly in the fact that ethyl acetate is more effective in extracting aromatic acids. The identified products are presented in Table I.

With the low chlorine dose more high molecular weight chlorinated products are formed, while at a high chlorine dose more low molecular weight chlorinated products and aromatic acids are formed.

The structural assignments for more than 100 different reaction products was accomplished by the combined use of GC/MS with electron impact and chemical ionization. At the high chlorine dose, the products identified agree very well with the compounds identified by Christman et al. (13, 14) after chlorination of aquatic humic and fulvic acid. This shows that the differences in the nature of the chlorination products from terrestrial or aquatic humic material are small and that differences may be reflected only in the product distribution and product yield.

The main products were identified as chloroform and trichloroacetic acid (TCA), which were quantified together with dichloroacetic acid (DCA) and the chlorine consumption as a function of the chlorine to carbon ratio. The results are presented in Figure 3.

The analytical procedure for the quantitation of DCA and TCA used a simple packed GC column and an electron capture detector. This compares favorably in speed and/or simplicity with the microwave plasma emission detection used by Miller et al. (35) and the isotope dilution GC/MS method with trichloro[^{13}C]acetic acid used by Christman et al. (13). The extraction/methylation procedure proceeded quantitatively, as demonstrated by external calibration and spiking of the reaction mixture. Drying of the ether extract on Na_2SO_4 was omitted in this procedure, because then losses of 10-15% were observed. The water

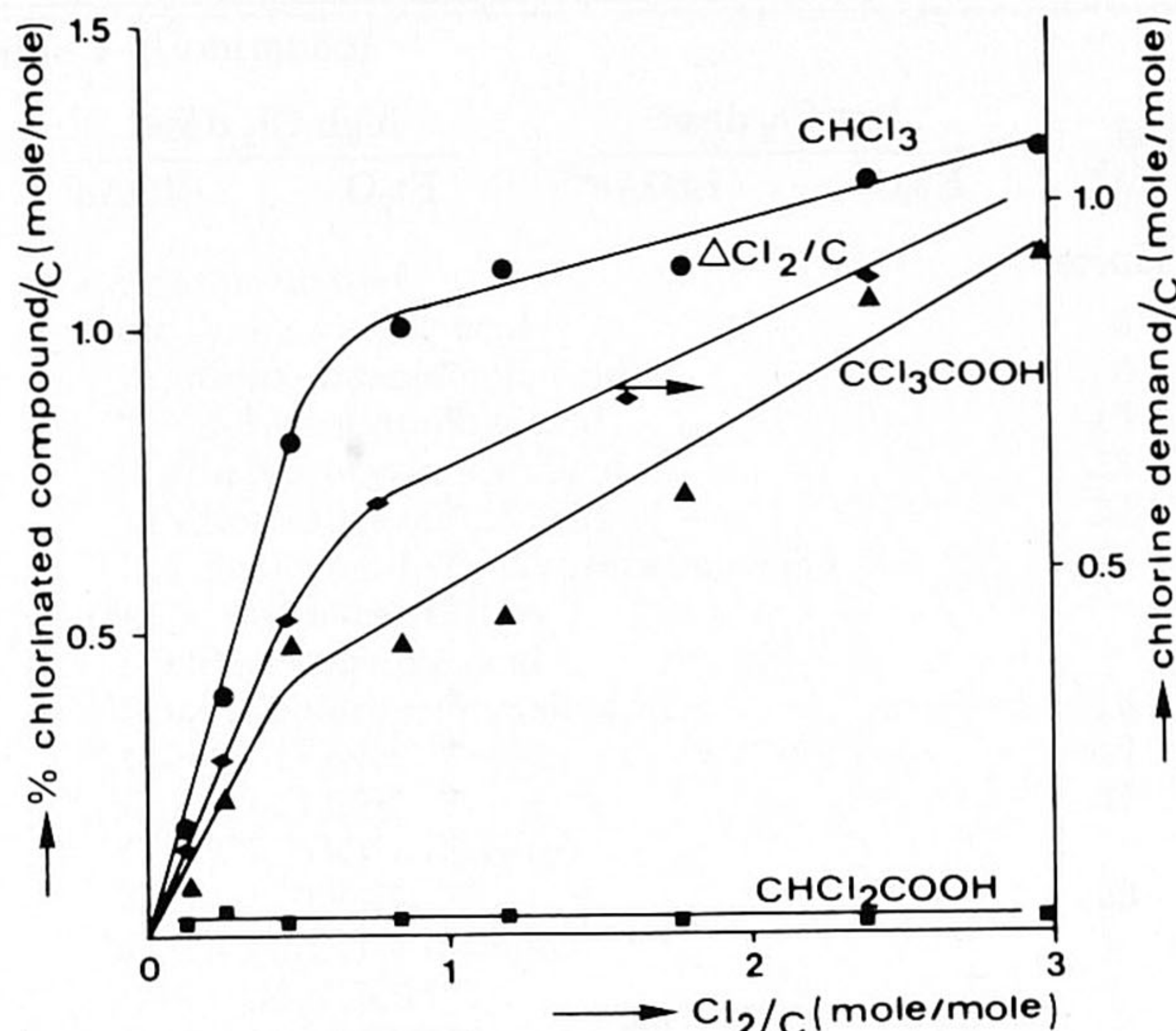


Figure 3. Production of chloroform, dichloroacetic acid, and trichloroacetic acid and chlorine consumption as a function of chlorine dose in humic acid chlorination.

content of the extract apparently did not influence the methylation step.

At the highest chlorine dose, 1.3% of the carbon content is converted into chloroform, 2.2% into TCA, and 0.1% in DCA. These values for terrestrial humic acid agree with results obtained in the chlorination of other humic materials, for which yields of 0.3–1.6% for chloroform (5, 9, 11–13, 36), 1.8–3.0% for TCA (12, 13), and 0.4–0.7% for DCA (12, 13) have been reported.

When we consider that a very favorable chloroform precursor like resorcinol gives a yield of 14.2% mol of CHCl_3 /mol of C (5), the yields for chloroform and TCA are quite high. Indeed, if only resorcinol structures are responsible for the chloroform production in the chlorination of humic acid, about 10% of the organic carbon must be present as free or fused 1,3-dihydroxybenzene structures. This is within the possibilities for Suwannee River fulvic acid, which was shown (37) to have a molecular formula of approximately $\text{C}_{74}\text{H}_{72}\text{N}_{0.7}\text{O}_{46}$ and a total of 20 aromatic plus phenolic carbon atoms (28% aromatic carbon).

Apart from the three quantified products, many other compounds were detected which are discussed below in two groups: nonchlorinated and chlorinated compounds.

Nonchlorinated Compounds. The nonchlorinated reaction products were similar to the KMnO_4 oxidation products of humic and fulvic acid (26, 27). Aliphatic carboxylic acids were observed from *n*-heptanoic acid up to *n*-octacosanoic acid. The strong even predominance is typical for the terrestrial origin of the humic acid (38). It indicates that the aliphatic carboxylic acids are formed by hydrolysis of ester groups, and in this case not by oxidation of alkylarenes (26). Aliphatic dicarboxylic acids and aromatic carboxylic acids were found mainly at the high chlorine dose, indicating that they are end products in the oxidation process.

Two cyano-substituted carboxylic acids were detected for the first time and identified as 3-cyanopropanoic acid (level 2) and 4-cyanobutanoic acid (level 1). The EI and CI spectra for the methyl esters of both compounds are given in Figures 4 and 5.

The spectrum assigned to methyl 3-cyanopropanoate showed a good match with a reference spectrum (39), while the possibility of methyl 2-cyanopropanoate could be ruled out as this compound shows fragments at m/z 59 and 68 as the dominant peaks.

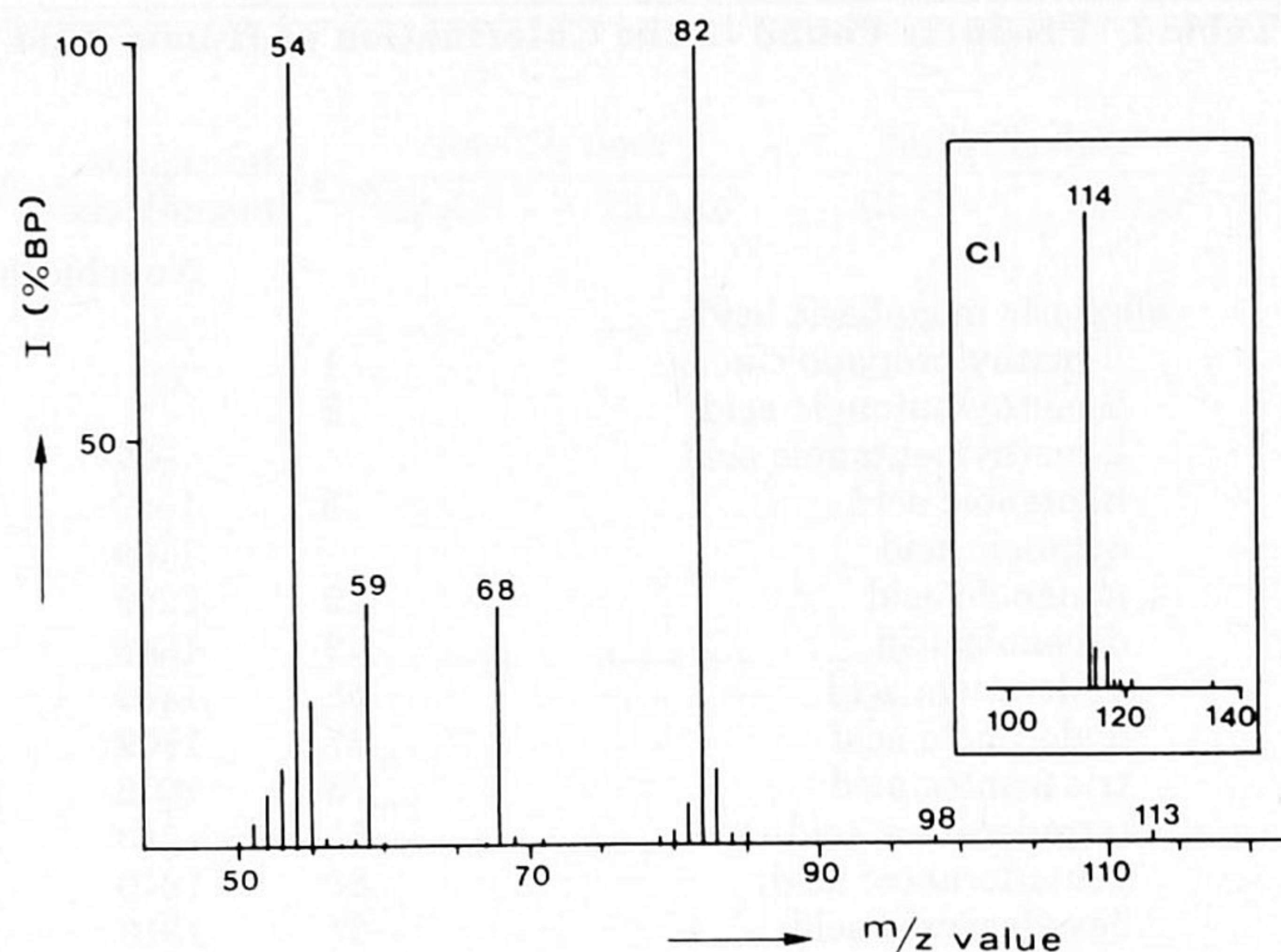


Figure 4. EI and CI mass spectrum of the methyl ester of 3-cyanopropanoic acid. m/z 82 ($-\text{OCH}_3$); m/z 54 ($-\text{COOCH}_3$); m/z 59 ($=\text{COOCH}_3^+$).

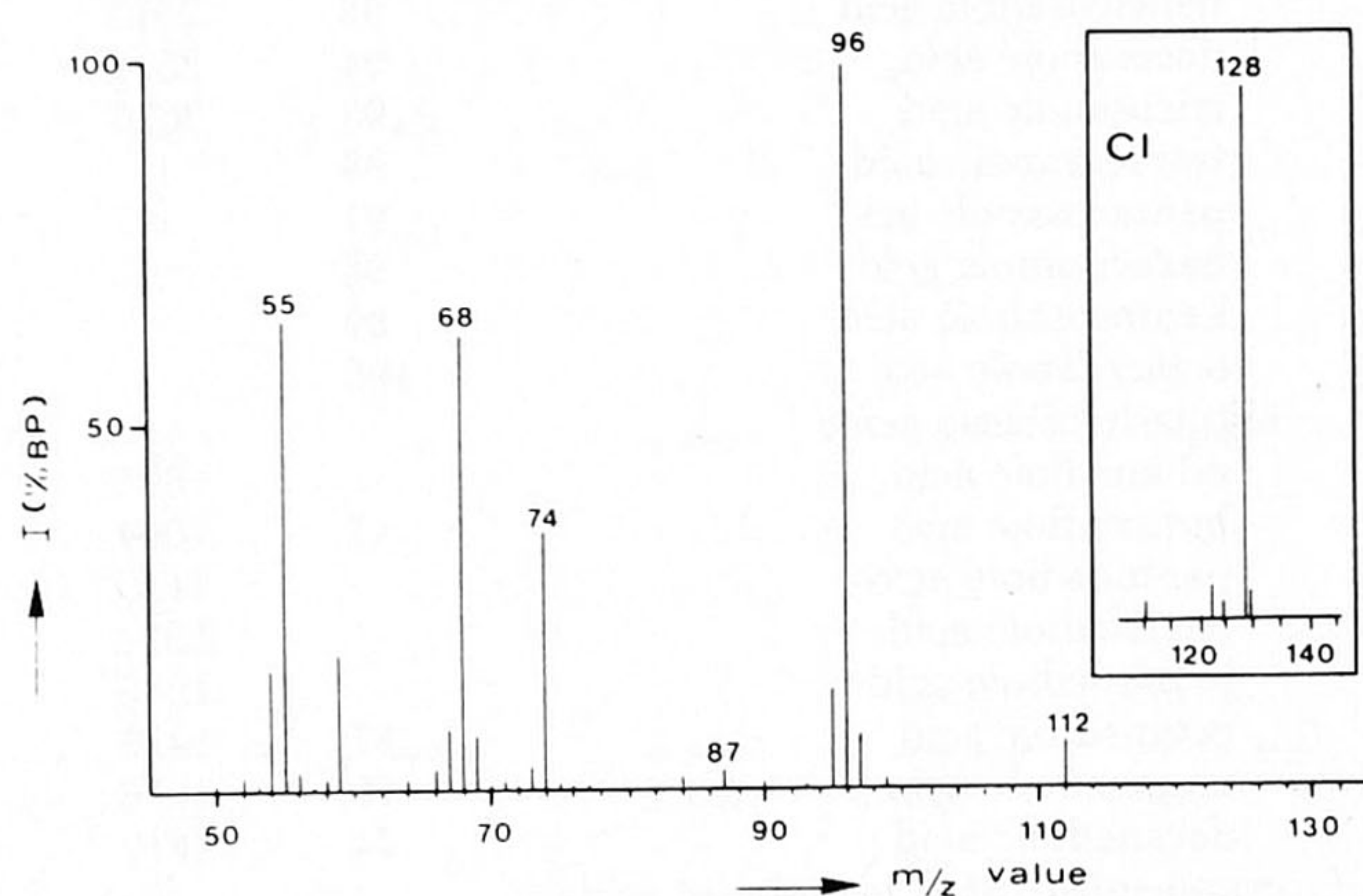
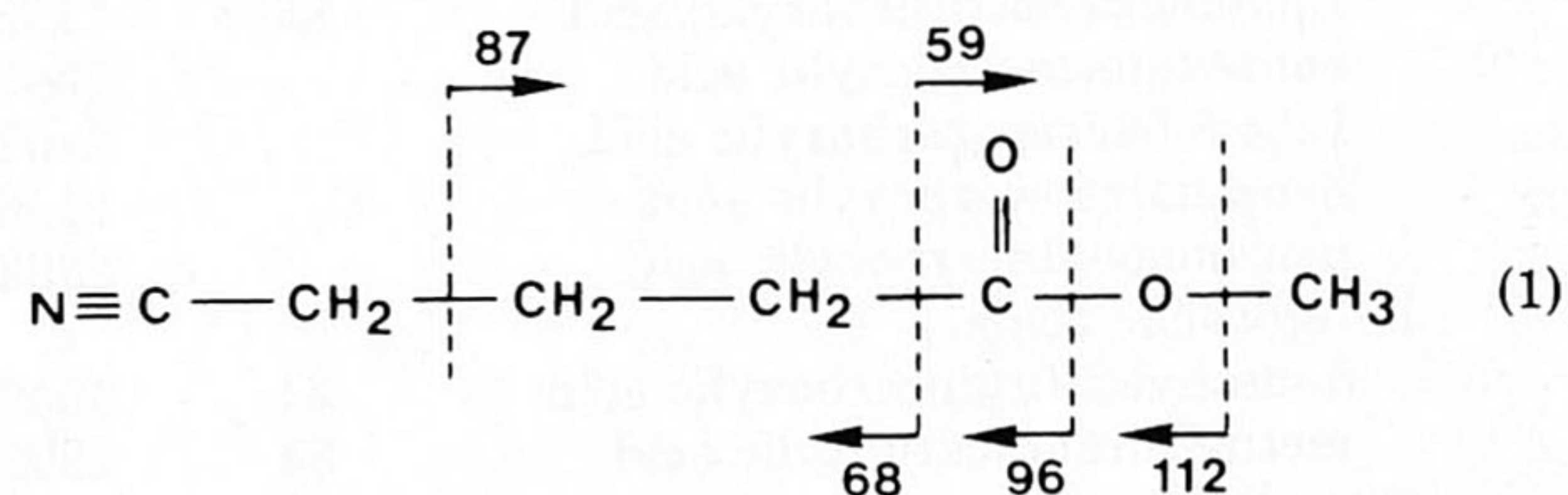
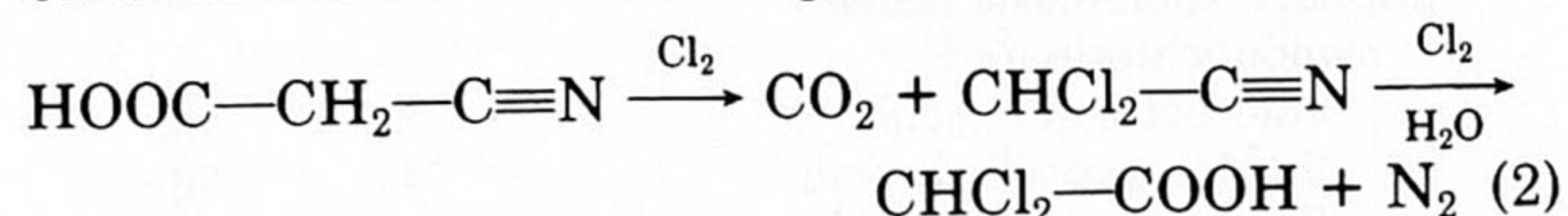


Figure 5. EI and CI mass spectrum of the methyl ester of 4-cyanobutanoic acid. m/z 112 ($-\text{CH}_3$); m/z 96 ($-\text{OCH}_3$); m/z 74, McLafferty rearrangement product; m/z 68 ($-\text{COOCH}_3$).

The spectrum of the cyanobutanoic acid is assigned to methyl 4-cyanobutanoate on the basis of the formation of the m/z 74 ion, which is the normal McLafferty rearrangement product for unbranched methyl alkananoates with γ -H atoms, and the m/z 87 ion, which indicates the 4-position of the cyano group (eq 1).



Cyano acids are of interest in the formation of dihaloacetonitriles after chlorination of water. The two cyano-substituted acids may be formed from some protein material containing glutamic acid and 2-aminoadipic acid, according to a mechanism proposed by Bieber and Trehy (40). No cyanoethanoic acid was detected, possibly because of a rapid conversion into dichloroacetonitrile followed by oxidation to DCA and nitrogen (eq 2).



Chlorinated Compounds. Chloroform, chloral, and tetrachloromethane were the only volatile chlorinated products detected. Chloral appeared at different places in the chromatogram due to artifact formation by reaction

Table I. Products Found in the Chlorination of Humic Acid

| | no. ^a | RI | structural assignment ^b | low Cl ₂ dose ^c | | high Cl ₂ dose ^c | |
|-----------------------------------|------------------|------|------------------------------------|---------------------------------------|--------------------|--|-------|
| | | | | Et ₂ O ^d | EtOAc ^e | Et ₂ O | EtOAc |
| Nonchlorinated Products | | | | | | | |
| aliphatic monobasic acids | | | | | | | |
| 2-methylpropanoic acid | 1 | | C | | | + | |
| 2-methylbutanoic acid | 3 | | C | | | + | |
| 2-methylpentanoic acid | | 962 | C | | | | + |
| heptanoic acid | 18 | 1009 | C | | | + | |
| octanoic acid | | 1109 | C | | | + | |
| nonanoic acid | 40 | 1209 | C | | | + | |
| decanoic acid | 49 | 1309 | C | | | + | |
| undecanoic acid | 56 | 1409 | C | | | + | |
| dodecanoic acid | 67 | 1509 | SC | | | + | |
| tridecanoic acid | 73 | 1608 | SC | | | + | |
| tetradecanoic acid | 80 | 1710 | SC | | | + | |
| pentadecanoic acid | 84 | 1810 | SC | | | + | |
| hexadecanoic acid | 87 | 1910 | SC | ++++ | +++ | + | + |
| heptadecanoic acid | 88 | 2011 | SC | + | | + | |
| octadecanoic acid | 89 | 2111 | SC | +++ | +++ | ++ | + |
| nonadecanoic acid | 90 | 2212 | SC | ++ | + | ++ | |
| eicosanoic acid | 91 | 2312 | C | +++ | ++ | +++ | + |
| heneicosanoic acid | 93 | 2414 | C | +++ | ++ | ++ | + |
| docosanoic acid | 94 | 2514 | C | ++++ | +++ | +++ | + |
| tricosanoic acid | 95 | 2614 | C | +++ | + | ++ | + |
| tetracosanoic acid | 96 | | C | ++++ | +++ | +++ | + |
| pentacosanoic acid | 97 | | C | +++ | + | ++ | |
| hexacosanoic acid | 98 | | C | ++++ | ++ | +++ | + |
| heptacosanoic acid | 99 | | C | ++ | | ++ | |
| octacosanoic acid | 100 | | C | +++ | ++ | ++ | + |
| aliphatic dibasic acids | | | | | | | |
| ethanedioic acid | | 804 | SC | | | | + |
| butanedioic acid | 17 | 1004 | SC | + | ++ | + | ++ |
| pentanedioic acid | | 1110 | SC | | | | + |
| hexanedioic acid | | 1214 | SC | | | | + |
| heptanedioic acid | | 1315 | SC | | | | + |
| octanedioic acid | 57 | 1416 | SC | | | + | ++ |
| nonanedioic acid | 70 | 1516 | SC | | | ++ | + |
| decanedioic acid | 74 | 1617 | SC | | | + | |
| cyano-substituted monobasic acids | | | | | | | |
| 3-cyanopropanoic acid | | 940 | C | | | | ++ |
| 4-cyanobutanoic acid | | 1036 | T | | | | + |
| aromatic carboxylic acids | | | | | | | |
| benzoic acid | 26 | 1070 | SC | ++ | | ++++ | + |
| phenylacetic acid | 36 | 1149 | SC | ++ | | | |
| 1,2-benzenedicarboxylic acid | 58 | 1416 | SC | | +++ | ++ | ++ |
| 1,4-benzenedicarboxylic acid | 63 | 1471 | SC | | | + | + |
| 1,3-benzenedicarboxylic acid | 65 | 1478 | SC | | | + | + |
| toluenedicarboxylic acid | | | T | | | | + |
| 1,2,3-benzenetricarboxylic acid | | 1772 | SC | | | | + |
| 1,2,4-benzenetricarboxylic acid | 83 | 1797 | SC | | | ++ | +++ |
| 1,3,5-benzenetricarboxylic acid | 86 | 1872 | SC | | | + | + |
| benzenetetracarboxylic acid | | 2068 | C | | | | + |
| 1,2,4,5-benzenecarboxylic acid | | 2102 | SC | | | | +++ |
| benzenetetracarboxylic acid | | 2136 | C | | | | ++ |
| benzenepentacarboxylic acid | | 2363 | C | | | | + |
| heterocyclic acids | | | | | | | |
| 5-methyl-2-furancarboxylic acid | 24 | 1045 | C | + | | + | ++ |
| methylfurandicarboxylic acid | 54 | 1393 | T | +++ | ++ | + | ++ |
| miscellaneous | | | | | | | |
| trimethyl phosphate | 9 | 911 | C | + | ++ | + | +++ |
| benzaldehyde | 12 | 930 | SC | | | + | |
| indole | 28 | 1094 | C | | | ++ | |
| unknown (M _r 242) | 81 | 1711 | VT | ++++ | | | |
| branched fatty acid | 82 | 1759 | VT | | | ++ | |
| unknown (M _r 398) | 92 | 2371 | VT | ++++ | | | |
| unknown (M _r 278) | | | VT | | | | + |
| Chlorinated Products | | | | | | | |
| aliphatic monobasic acids | | | | | | | |
| α-monochlorinated | | | | | | | |
| chloroethanoic acid | 2 | 733 | SC | + | + | + | + |
| 2-chloropropanoic acid | 4 | 765 | SC | | | + | |
| 2-chlorobutanoic acid | | | T | | | + | |
| 2-chloropentanoic acid | 11 | 924 | T | | | ++ | |
| 2-chlorohexanoic acid | 25 | 1051 | T | | | + | |
| 2-chloroheptanoic acid | 35 | 1149 | T | | | + | |

Table I (Continued)

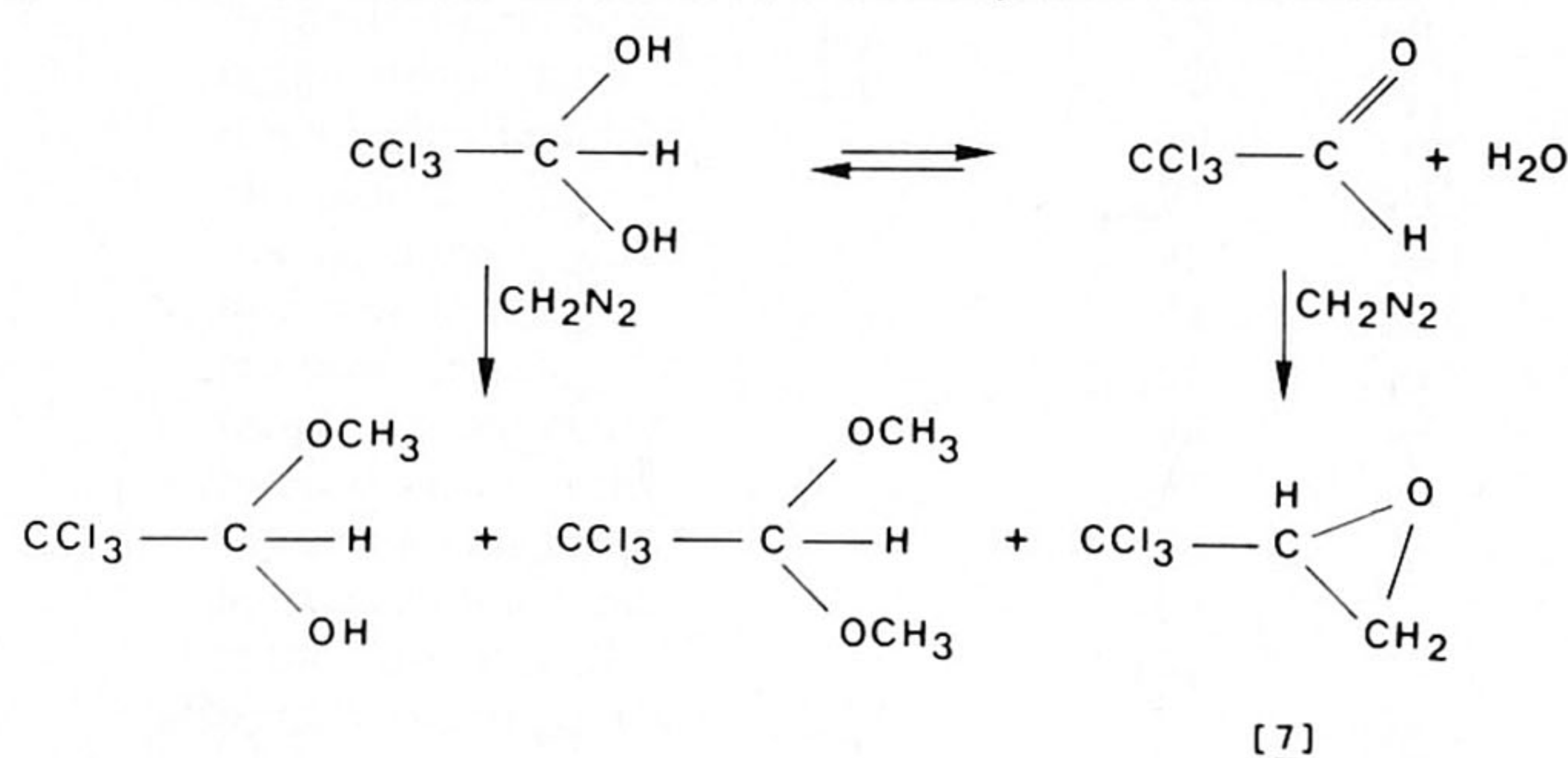
| | no. ^a | RI | structural assignment ^b | low Cl ₂ dose ^c | | high Cl ₂ dose ^c | |
|---|------------------|------|------------------------------------|---------------------------------------|--------------------|--|-------|
| | | | | Et ₂ O ^d | EtOAc ^e | Et ₂ O | EtOAc |
| <i>α,α</i> -dichlorinated | | | | | | | |
| dichloroethanoic acid | 5 | 816 | SC | +++ | ++++ | ++++ | ++ |
| 2,2-dichloropropanoic acid | 6 | 838 | SC | + | | ++ | + |
| 2,2-dichlorobutanoic acid | 15 | 955 | C | | | + | |
| 2,2-dichloropentanoic acid | 22 | 1039 | T | | | +++ | |
| 2,2-dichlorohexanoic acid | 34 | 1142 | T | | | + | |
| 2,2-dichloro-3-hydroxypropanoic acid | 20 | 1027 | T | | | + | ++ |
| unspecified substitution | | | | | | | |
| trichloroethanoic acid | 8 | 898 | SC | +++++ | +++++ | +++++ | ++ |
| 3,3,3-trichloropropanoic acid | 16 | 965 | T | | | ++ | +++ |
| C ₂ H ₂ Cl ₃ COOH | 19 | 1027 | T | + | | | |
| C ₄ H ₇ Cl ₂ COOH | 27 | 1075 | T | ++ | | | |
| C ₄ H ₇ Cl ₂ COOH (isomer) | | 1093 | T | | ++ | | + |
| C ₅ H ₉ Cl ₂ COOH | 29 | 1100 | T | + | | | |
| C ₅ H ₉ Cl ₂ COOH (isomer) | | 1175 | T | | | | ++ |
| CCl ₃ C ₃ H ₆ COOH | | 1209 | T | | ++ | | + |
| C ₆ H ₁₁ C ₁₂ COOH | | 1255 | T | | ++ | | ++ |
| unsaturated | | | | | | | |
| 3,3-dichloropropenoic acid | 10 | 918 | T | ++ | | + | |
| 2,3-dichloropropenoic acid | 13 | 933 | T | | | ++ | |
| 2,3-dichloropropenoic acid | 14 | 942 | SC | | | + | |
| 2,3,3-trichloropropenoic acid | 21 | 1034 | SC | ++ | | + | |
| C ₃ H ₄ ClCOOH | | | T | | + | | + |
| C ₃ H ₂ Cl ₃ COOH | 33 | 1126 | T | ++ | | | |
| C ₃ HCl ₄ COOH | 46 | 1248 | T | | | ++ | |
| aliphatic dibasic acids | | | | | | | |
| <i>α</i> -monochlorinated | | | | | | | |
| chlorobutanedioic acid | 30 | 1104 | SC | | +++ | ++ | +++ |
| 2-chloroheptanedioic acid | 61 | 1453 | T | | | + | |
| 2-chlorooctanedioic acid | 72 | 1557 | T | | | + | |
| 2-chlorononanedioic acid | 78 | 1662 | T | | | + | |
| <i>α,α</i> -dichlorinated | | | | | | | |
| 2,2-dichloropropanedioic acid | 32 | 1108 | T | | | +++ | +++ |
| 2,2-dichlorobutanedioic acid | 39 | 1190 | T | +++ | ++++ | ++++ | +++++ |
| 2,2-dichloropentanedioic acid | 53 | 1336 | T | | +++ | ++ | ++ |
| 2,2-dichlorohexanedioic acid | 60 | 1442 | T | | | + | + |
| 2,2-dichlorooctanedioic acid | 77 | 1655 | T | | | ++ | |
| unspecified substitution | | | | | | | |
| HOCC ₂ H ₃ ClCOOH | 23 | 1045 | T | | | + | ++ |
| HOCC ₃ H ₄ Cl ₂ COOH | 47 | 1271 | T | | | + | + |
| trichlorobutanedioic acid | 48 | 1286 | T | | | + | |
| HOCC ₄ H ₇ ClCOOH | | 1311 | T | | | | + |
| HOCC ₄ H ₄ Cl ₄ COOH | 71 | 1545 | T | | | ++ | ++ |
| HOCC ₃ H ₄ OCl ₂ COOH | | | VT | | | | ++ |
| unsaturated | | | | | | | |
| chlorobutenedioic acid | | 1170 | SC | | | | + |
| dichlorobutenedioic acid | 41 | 1221 | SC | | ++++ | +++ | ++ |
| dichlorobutenedioic acid | 42 | 1227 | SC | | +++ | ++ | ++ |
| HOCC ₃ H ₃ ClCOOH | | | T | | ++ | | |
| HOCC ₃ H ₃ ClCOOH | | | T | | | + | |
| HOCC ₃ H ₃ ClCOOH | | | T | | | + | |
| HOCC ₃ H ₃ ClCOOH | | | T | | + | | + |
| HOCC ₃ H ₂ Cl ₂ COOH | 51 | 1324 | T | | ++ | + | + |
| HOCC ₃ HCl ₃ COOH | 59 | 1439 | T | +++ | +++ | +++ | ++ |
| tetrachloropentenedioic acid | 69 | 1516 | T | | | ++ | |
| aromatic carboxylic acids | | | | | | | |
| 4-chlorobenzoic acid | 43 | 1228 | SC | | | + | |
| 2-chlorobenzoic acid | 44 | 1239 | SC | | | + | |
| 2-chlorophenylacetic acid | 50 | 1312 | SC | | | +++ | |
| 4-chlorophenylacetic acid | 52 | 1333 | SC | | | ++ | |
| 2,6-dichlorophenylacetic acid | 64 | 1476 | T | | | + | |
| 2,4-dichlorophenylacetic acid | 66 | 1500 | T | | | + | |
| chloroform precursors | | | | | | | |
| 3,3,3-trichloro-2-hydroxypropanoic acid | 31 | 1107 | T | +++ | +++ | | |
| 2,4-dichloro-3-hydroxybutanoic acid | | 1142 | T | | | | + |
| 3,3,3-trichloro-2-methyl-2-hydroxypropanoic acid | 37 | 1157 | T | ++ | | + | + |
| 4,4,4-trichloro-3-hydroxybutanoic acid | 38 | 1160 | T | ++ | | | |
| 3,5,5,5-tetrachloro-4-oxopentenoic acid | | 1420 | VT | | | + | |
| 3,5,5,5-tetrachloro-4-oxo-2-methylpentenoic acid | 62 | 1466 | T | ++ | | + | |
| 3,5,5,5-tetrachloro-4-oxo-2-methylpentenoic acid | | 1475 | T | | | + | |
| 3,3,5,5,5-pentachloro-4-hydroxypentanoic acid | 68 | 1514 | T | +++ | | | |
| 2-chloro-3-(trichloroacetyl)butenedioic acid | 75 | 1618 | T | ++ | ++ | | |
| 2,3,3,5,5,5-hexachloro-4-hydroxypentanoic acid | 76 | 1639 | T | ++++ | +++ | ++ | |
| 2-carboxy-3,5,5,5-tetrachloro-4-oxopentenoic acid | 79 | 1693 | T | ++ | ++ | + | |
| heptachloro-5-oxohexenoic acid | 85 | 1816 | VT | | | ++ | |

Table I (Continued)

| | no. ^a | RI | structural assignment ^b | low Cl ₂ dose ^c | | high Cl ₂ dose ^c | |
|--|------------------|------|------------------------------------|---------------------------------------|--------------------|--|-------|
| | | | | Et ₂ O ^d | EtOAc ^e | Et ₂ O | EtOAc |
| miscellaneous | | | | | | | |
| tetrachloromethane | | | C | | | + | |
| chloral | | | T | + | | + | |
| 1,1,1-trichloro-2,3-epoxypropane | 7 | 887 | T | + | | + | + |
| dichlorinated acid (M _r 196) | 45 | 1241 | VT | | | ++ | ++ |
| C ₃ H ₅ O ₃ CCl ₂ COOH | | 1307 | T | | | | + |
| chloroethenetetracarboxylic acid | 55 | 1398 | T | | | + | |
| trichlorinated acid (M _r 374) | | | VT | | | | ++ |

^aNo numbers are given if the product was detected in the ethyl acetate extracts only. ^bSC = standard confirmed; C = confident; T = tentative; VT = very tentative. ^c(+++++) most abundant peak (MAP); (++++) 30–100% MAP; (++++) 10–30% MAP; (++) 3–10% MAP; (+) <3% MAP. ^dEt₂O = diethyl ether extract. ^eEtOAc = ethyl acetate extract.

Scheme I. Artifact Formation in the Methylation of Chloral



with diazomethane in the methylation step (41–44) (Scheme I).

The monomethyl and dimethyl acetal, resulting from methylation of one or two hydroxyl groups in the hydrate, and 1,1,1-trichloro-2,3-epoxypropane (7), resulting from methylene insertion into the carbonyl group, were repeatedly found in chlorination experiments with humic acid and model compounds. The EI spectrum of 7 which shows an interesting fragmentation pattern is given in Figure 6. Other volatile chlorinated products such as chlorinated acetones or 3-chloropropenal were not detected.

The principal nonvolatile reaction products were chlorinated aliphatic monobasic and dibasic acids and one tribasic acid. At a low chlorine dose in particular, a large number of chlorinated acids containing a trichloromethyl group were detected. Because these compounds may be converted into chloroform by further chlorination and/or hydrolysis, they will be denoted as "chloroform precursors". At a high chlorine dose several chlorine-substituted benzoic acids and phenylacetic acids were detected for the first time.

The chlorinated saturated aliphatic acids comprised a series of α -chlorinated acids from 2-chloroethanoic acid up to 2-chloroheptanoic acid and a series of α,α -dichlorinated acids from 2,2-dichloroethanoic acid up to 2,2-dichlorohexanoic acid.

The identification of the unsaturated 3,3-dichloropropenoic acid has been reported earlier by Christman (13, 14), but at a high chlorine dose we found larger amounts of the two *Z/E* isomers of 2,3-dichloropropenoic acid.

2,2-Dichlorobutanedioic acid was the major representative of the class of chlorinated aliphatic dibasic acids. Saturated and unsaturated C-4 diacids were the dominant products, but C-3, C-5, C-6, and C-7 diacids were also found. C-4 diacids are also formed in the chlorination of resorcinol and resorcinol derivatives, where 2-chlorobutanedioic acid has been detected with a yield of 60% (22, 45). The C-4 diacids found in this study, therefore,

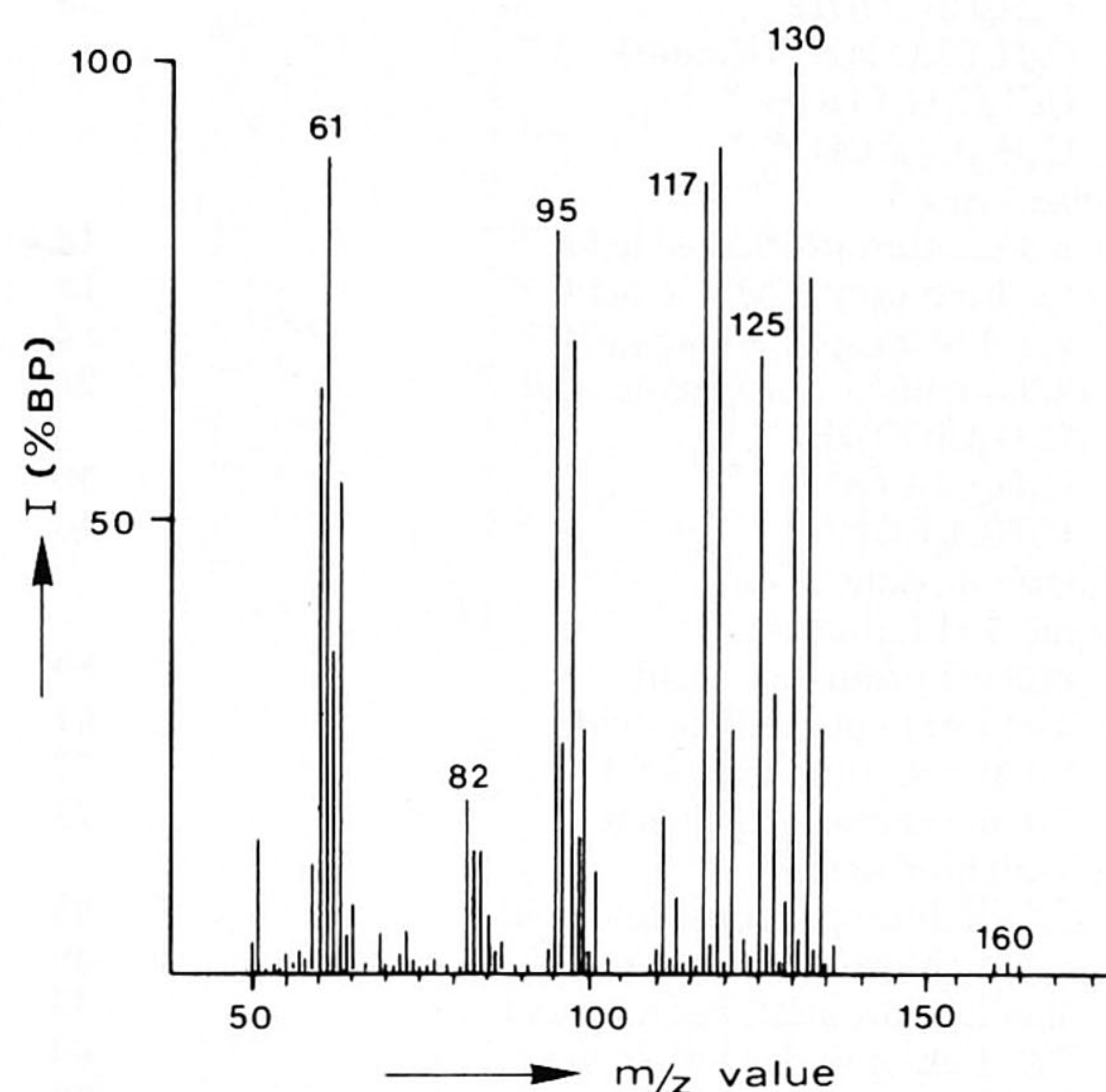


Figure 6. EI mass spectrum of 1,1,1-trichloro-2,3-epoxypropane (7). *m/z* 130 ($-\text{CH}_2=\text{O}$), 125 ($-\text{Cl}$), 117 ($-\text{CCl}_3^+$), and 95 ($130 - \text{Cl}$).

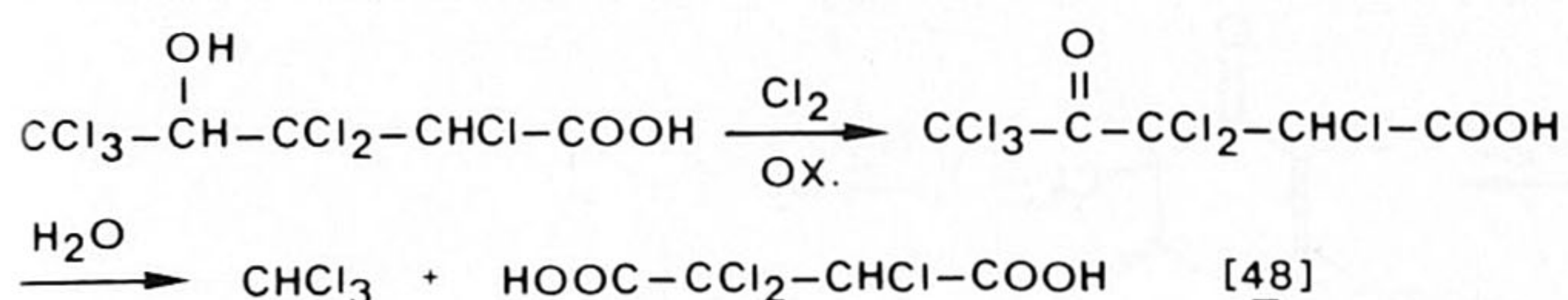
may reflect 1,3-dihydroxybenzene structures as a part of the humic acid structure.

Several aryl-chlorinated aromatic acids were detected and standard confirmed, although only at high chlorine dose and most of them in low yield. Direct chlorination of the aryl group in the phenylacetic acid derivatives seems possible, and the substitution pattern found follows the normal substitution rules. Direct chlorination of benzoic acid does not seem very likely and would yield meta-substituted products. A better explanation for the formation of chlorinated benzoic acids may be given by the assumption that first an alkyl-substituted aromatic ring is chlorinated, followed by an oxidative breakdown of the alkyl side chain. The 2,4-substitution pattern is in accordance with this explanation.

Chloroform Precursors. From a mechanistic point of view, the identification of a large number of compounds containing a trichloromethyl group is the most important result of this study. Upon further chlorination, decarboxylation, oxidation, and/or substitution, these compounds may be converted into chloroform and, in most cases, C-4 diacids. These chloroform precursors were detected mainly in the low chlorine dose experiment, which demonstrates that they are converted into other products at the high chlorine dose.

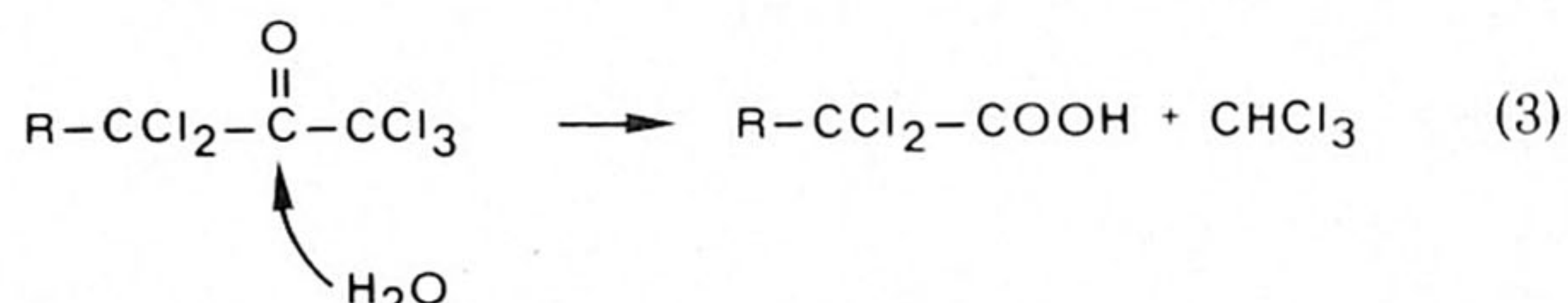
Not all products containing a trichloromethyl group may be converted into chloroform in aqueous medium at pH 7–8. For example, chloral could be converted into chloroform by a simple hydrolysis, and this reaction has been

Scheme II. Conversion of HCHPA into Chloroform and TCBD A



observed on injection of aqueous solutions in the heated injection port of a gas chromatograph (46). However, at neutral pH and room temperature the conversion is very slow, and chloral is detected as an important product, even at a high chlorine dose when oxidation to trichloroacetic acids seems a more plausible reaction.

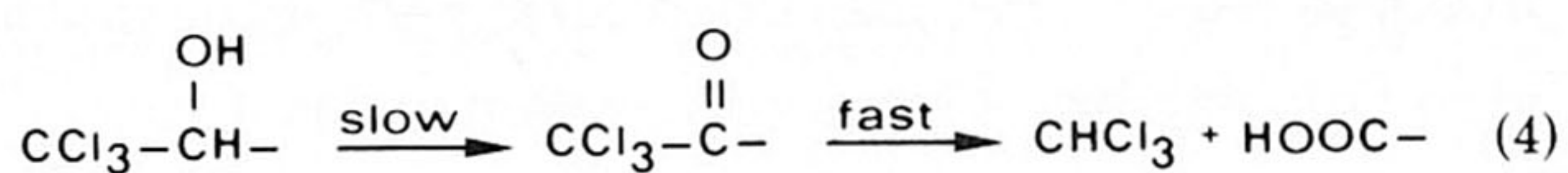
If conversion of a trichloroacetyl group into chloroform is to be achieved at neutral pH and normal temperatures (eq 3), further activation of the carbonyl group for nu-



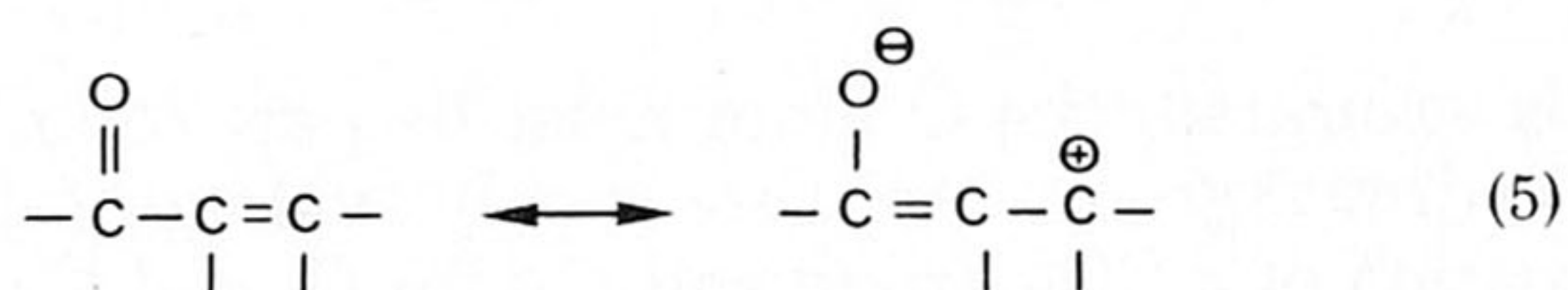
cleophilic substitution is required (22, 47). This may be accomplished by chlorine substitution on the carbon adjacent to the trichloroacetyl group. The most abundant chloroform precursor identified after chlorination of humic acid at a low chlorine dose fulfills this requirement. The hydroxy group in 2,3,3,5,5,5-hexachloro-4-hydroxypentanoic acid (HCHPA) (76) may be oxidized to a carbonyl group by the action of chlorine, which makes the compound susceptible to hydrolysis, which gives chloroform and trichlorobutanedioic acid (TCBDA) (48) (Scheme II).

In a similar way, the 3,3,5,5,5-pentachloro-4-hydroxypentanoic acid (68) may be converted into chloroform and the most abundant C-4 diacid, 2,2-dichlorobutanedioic acid (39).

Six of the 12 chloroform precursors listed in Table I contain a hydroxyl group, presumably adjacent to the trichloromethyl group, indicating that oxidation of the hydroxyl group may become the rate-determining step in the conversion to chloroform (eq 4). The other six chlo-



roform precursors contain a trichloroacetyl group, bound to a carbon-carbon double bond. In these cases the carbonyl group is part of a conjugated double bond system (eq 5). Hydrolysis to chloroform is hampered now by

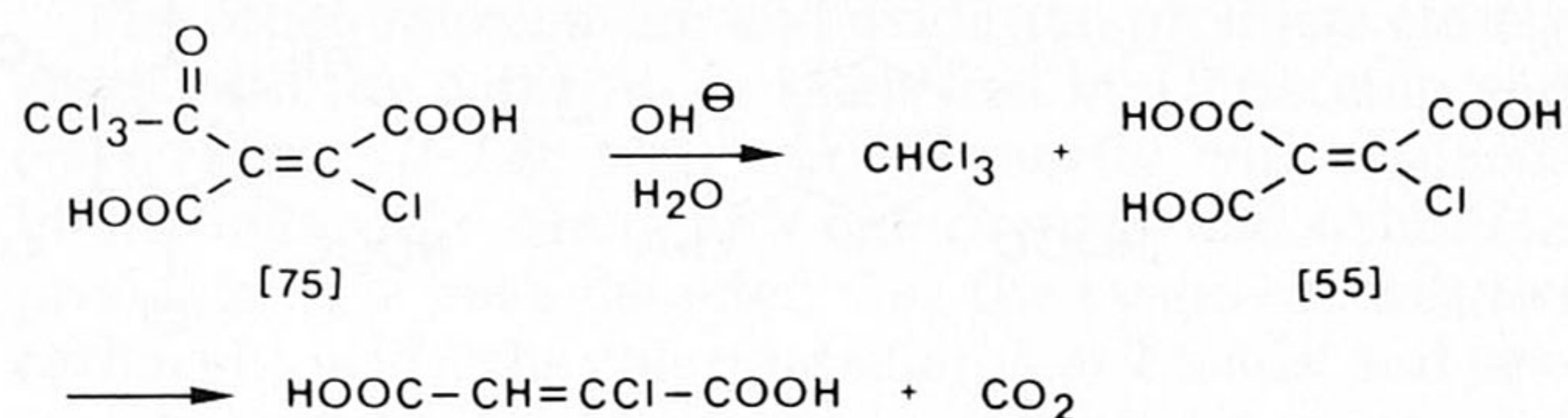


resonance stabilization which makes these compounds rather stable under the chlorination conditions applied.

The two unsaturated diacids found in this group (75 and 79) are very interesting because 79 was found as the major reaction product in the chlorination of 3,5-dihydroxybenzoic acid. Hydrolysis of both compounds produces chloroform and the only tricarboxylic acid (55) detected. The tricarboxylic acid may be converted into 2-chlorobutanedioic acid by a decarboxylation reaction (Scheme III).

Model Studies. An explanation for the formation of the chloroform precursors on the basis of the structure of humic acid is still speculative, but resorcinol structures play an important role. Chlorination of 3,5-dihydroxybenzoic acid gave chloroform in a yield of 74%, but after extraction and methylation, GC/MS revealed the presence of a large number of other chlorinated compounds. The

Scheme III. Conversion of 2-Chloro-3-(trichloroacetyl)butenedioic Acid into Chloroform and 2-Chlorobutanedioic Acid

Table II. Identical Products Found in the Chlorination of Humic Acid and 3,5-Dihydroxybenzoic Acid^a

| |
|--|
| CHCl ₃ |
| CCl ₃ CHO |
| CHCl ₂ COOH (5) |
| CCl ₃ COOH (8) |
| CHCl=CClCOOH (14) |
| CCl ₃ CH ₂ COOH (16) |
| CCl ₃ CHOHCOOH (31) |
| C ₃ H ₂ Cl ₃ COOH (33) |
| HOCCCl=CClCOOH (41, 42) |
| C ₃ HCl ₄ COOH (46) |
| HOCC ₃ H ₂ Cl ₂ COOH (51) |
| HOCCCl=C(COOH) ₂ (55) |
| CCl ₃ CHOHCCl ₂ CHClCOOH (76) |
| CCl ₃ COCCl=C(COOH) ₂ (79) |

^a Numbers in parentheses indicate the peak numbers in Figures 1 and 2 and numbers in Table I.

major product was 2-carboxy-3,5,5,5-tetrachloro-4-oxo-2-pentenoic acid (79), indicating that humic acid and 3,5-dihydroxybenzoic acid may give identical products on chlorination. Other identical products are summarized in Table II, which includes three chloroform precursors (31, 76, and 79 in Table I).

The two isomers of 3,5,5,5-tetrachloro-4-oxo-2-methyl-2-pentenoic acid (62) have also been found in the chlorination of 3,5-dihydroxytoluene, which again indicates the crucial role of resorcinol structures in the formation of chloroform and chloroform precursors on chlorination of humic acid.

Boyce and Hornig (48) studied the chlorination of various resorcinol derivatives and tentatively identified several trichloromethyl-substituted products. In all cases the trichloromethyl group was part of a trichloroacetyl group conjugated with a C=C bond, in accordance with our proposal of a retardation of the hydrolysis reaction.

The mechanism for the chlorination of resorcinol was proposed originally by Rook (5, 21) and later extended by Boyce and Hornig (48). This mechanism may explain the formation of the precursor (79) when additional hydrolysis and decarboxylation reactions are included and is given in Scheme IV. Supporting evidence for these steps was found in the identification of the intermediate dicarboxylic acid and in the formation of 1 mol of CO₂/mol of 3,5-dihydroxybenzoic acid.

Structural Assignments. The identification of the chloroform precursors is based on a priori interpretations of the EI and CI spectra. In those cases, where the spectra did not provide sufficient information to allow a complete structural assignment, the proposed structures are also based on the information that identical products are formed in the chlorination of resorcinol and resorcinol derivatives.

The structural assignments will be exemplified by the identification of two hydroxyl-type precursors, 31 and 76, and one acetyl-type precursor, 79.

The EI and CI spectra of 31 are given in Figure 7. The CI spectrum shows the protonated molecular ion (M + 1)⁺ at *m/z* 207, and the chlorine isotope distribution pattern

Scheme IV. Formation of 79 in the Chlorination of Humic Acid and 3,5-Dihydroxybenzoic Acid

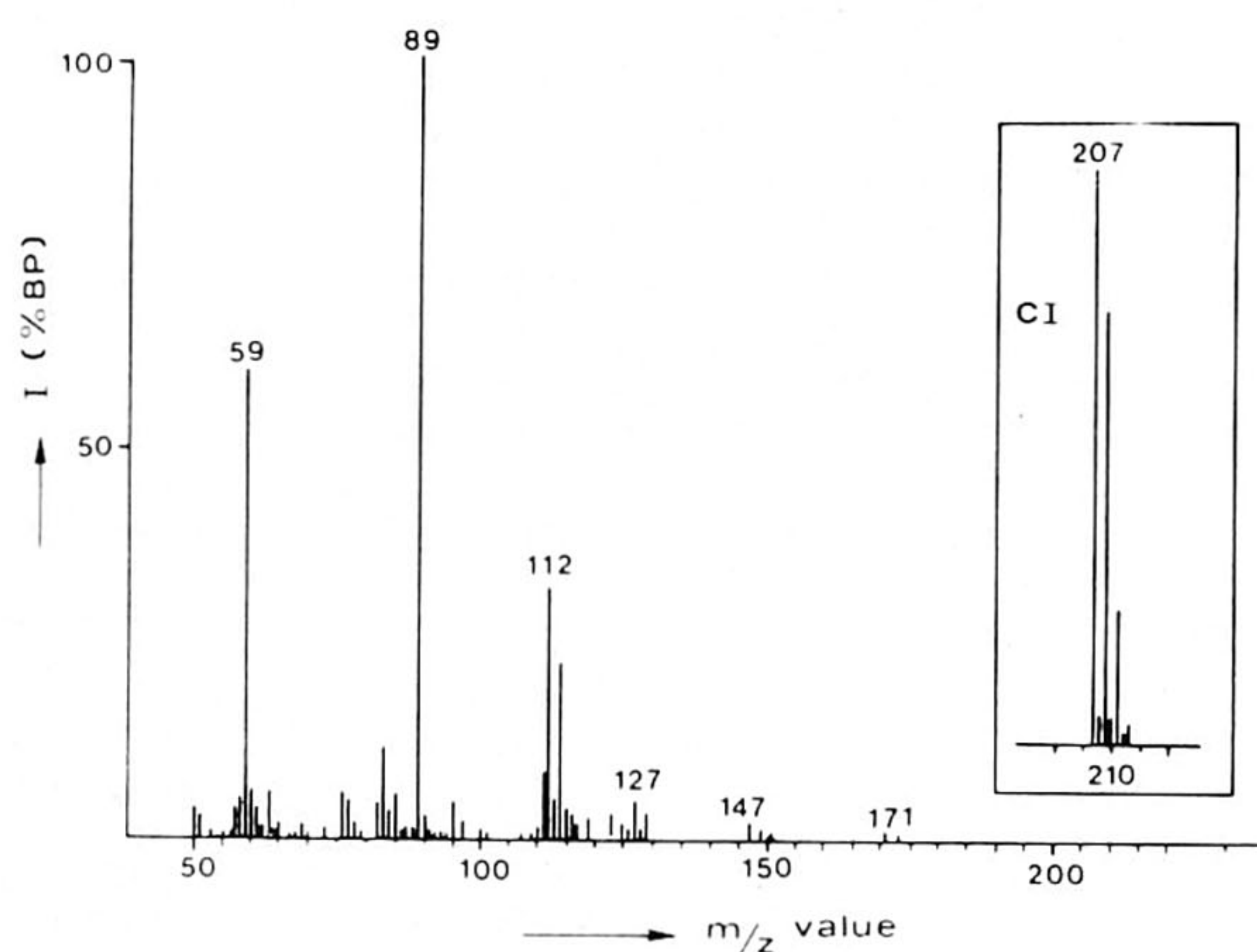
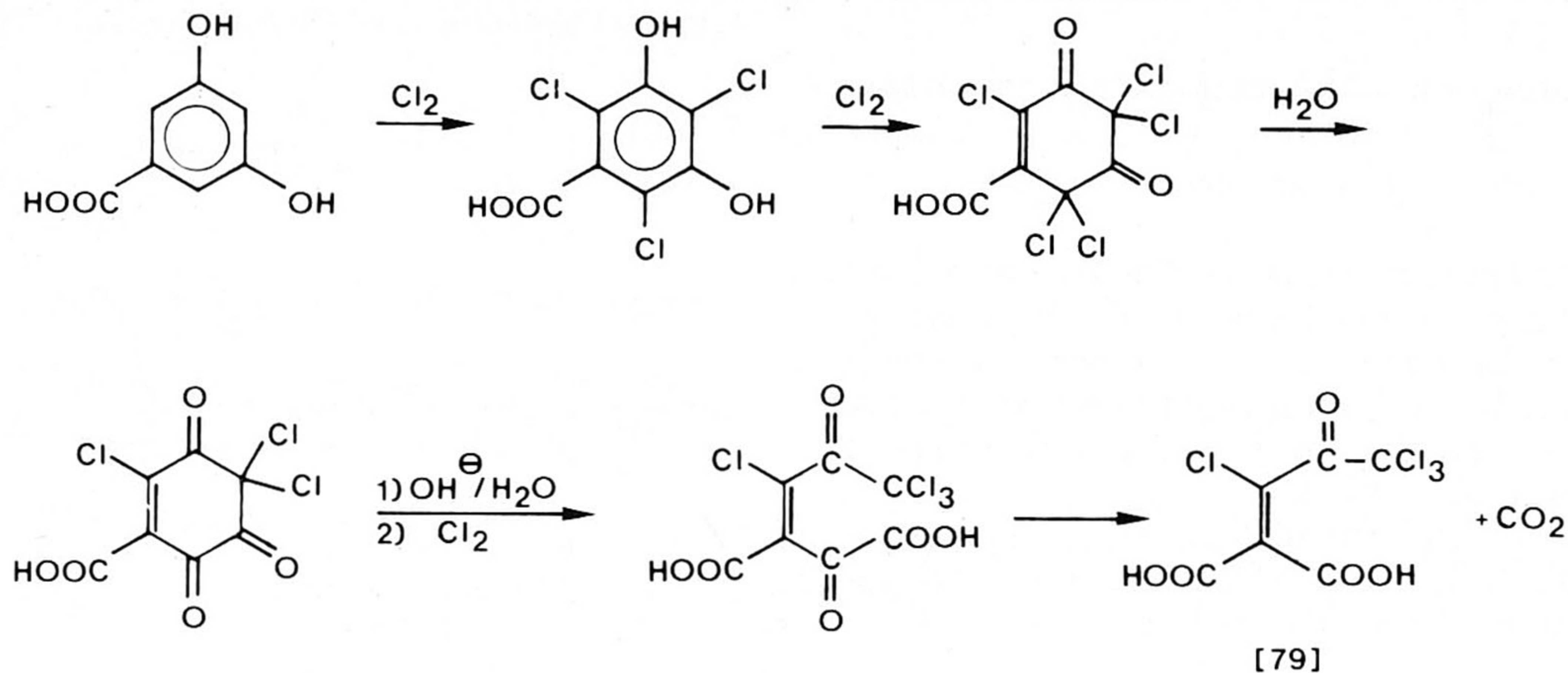


Figure 7. EI and CI mass spectrum of the methyl ester of 3,3,3-trichloro-2-hydroxypropanoic acid (3).

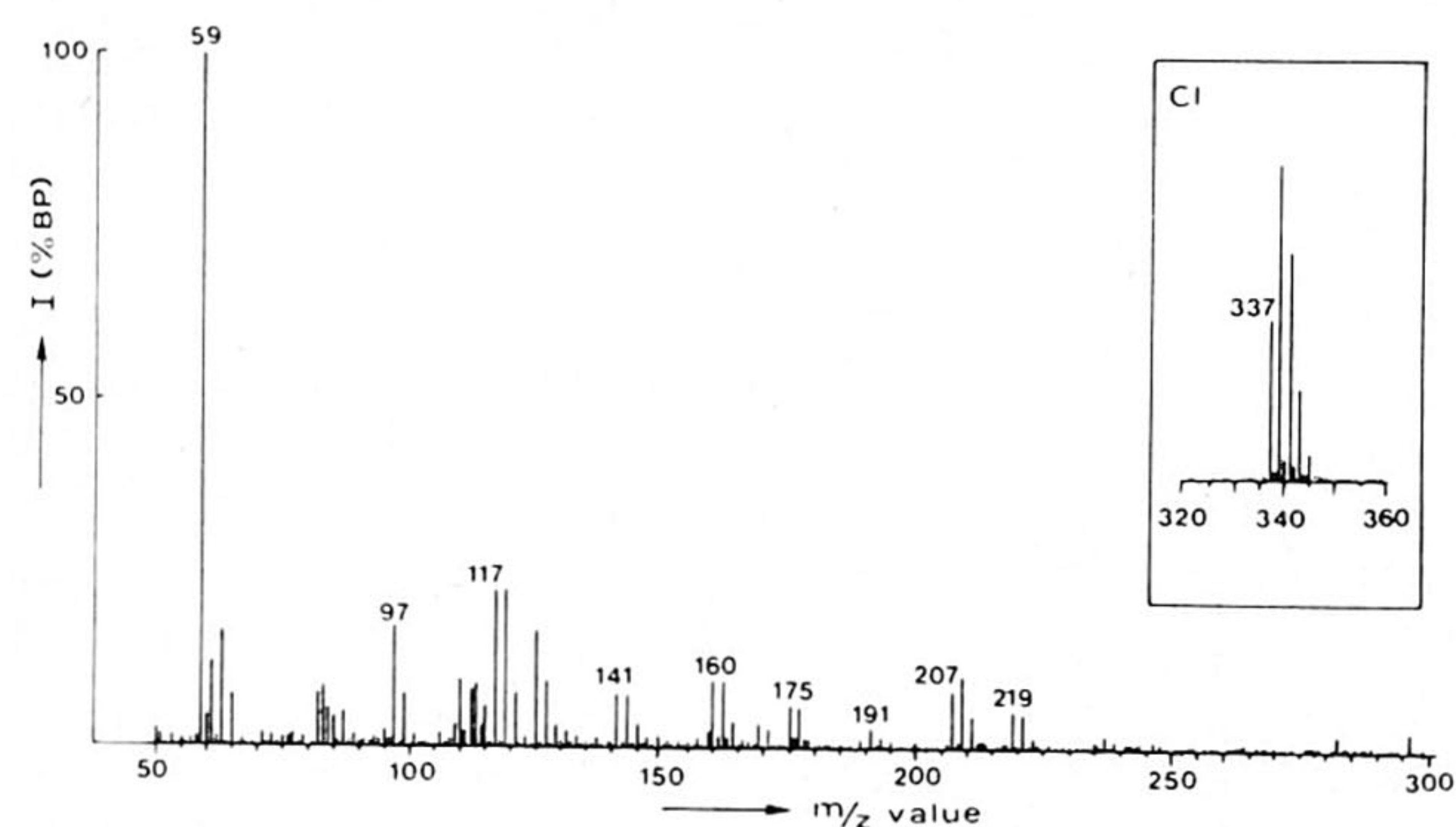


Figure 8. EI and CI mass spectrum of the methyl ester of 2,3,3,5,5,5-hexachloro-4-hydroxypentanoic acid (76).

indicates the presence of three chlorine atoms. The three chlorine atoms must be bound to the same carbon atom, as the fragment at m/z 89 in the EI spectrum does not contain chlorine and therefore must be formed by elimination of a CCl_3 group ($206 - 117 = 89$). The presence of a COOCH_3 group is evident from the m/z 59 ion, which leaves $-\text{CH}_2\text{O}-$ for the rest of the molecule.

Methyl 3,3,3-trichloro-2-hydroxypropanoate is the only plausible structure, which explains the fragments at $m/z = 89$ and 147 by a simple α -cleavage mechanism (eq 6).

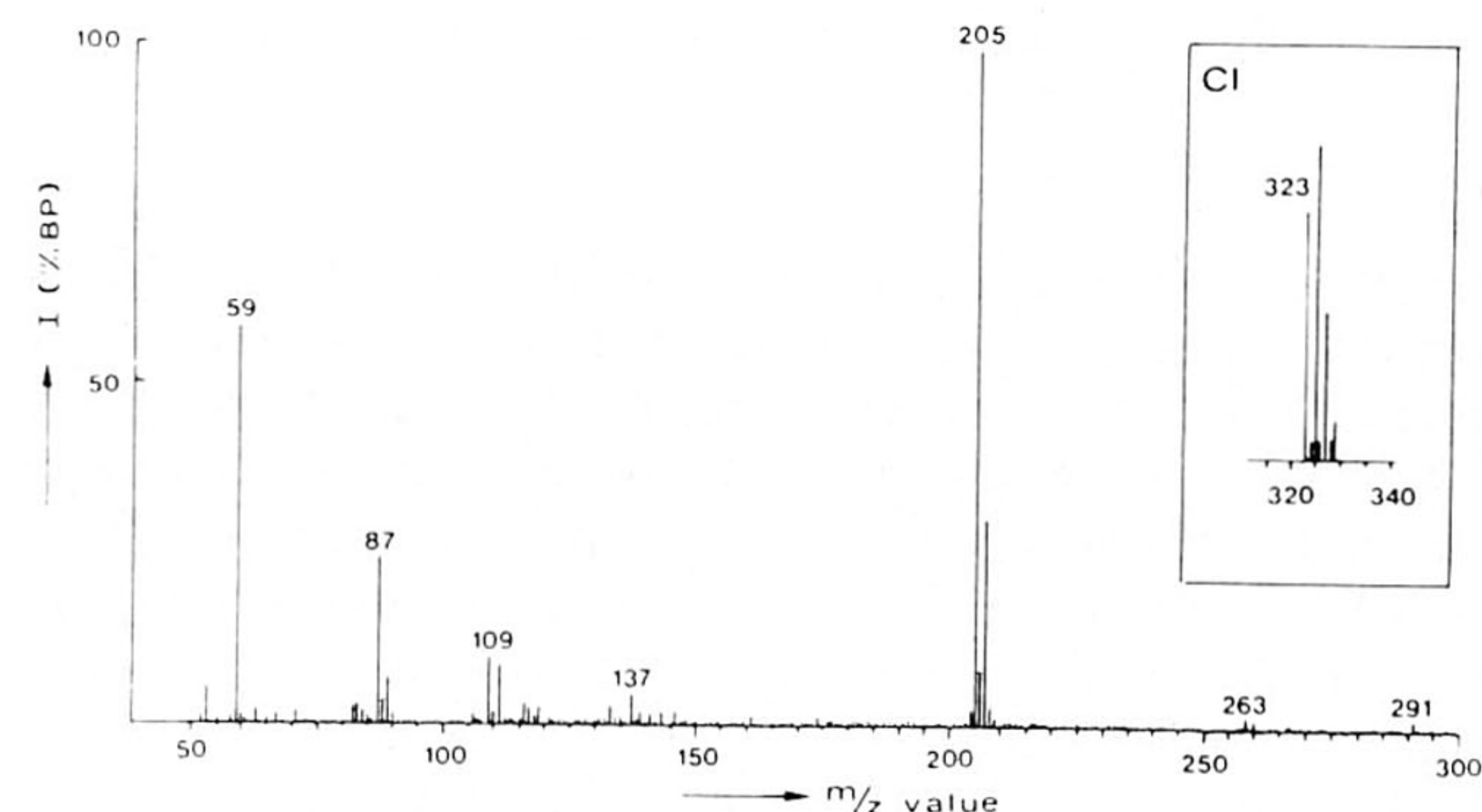
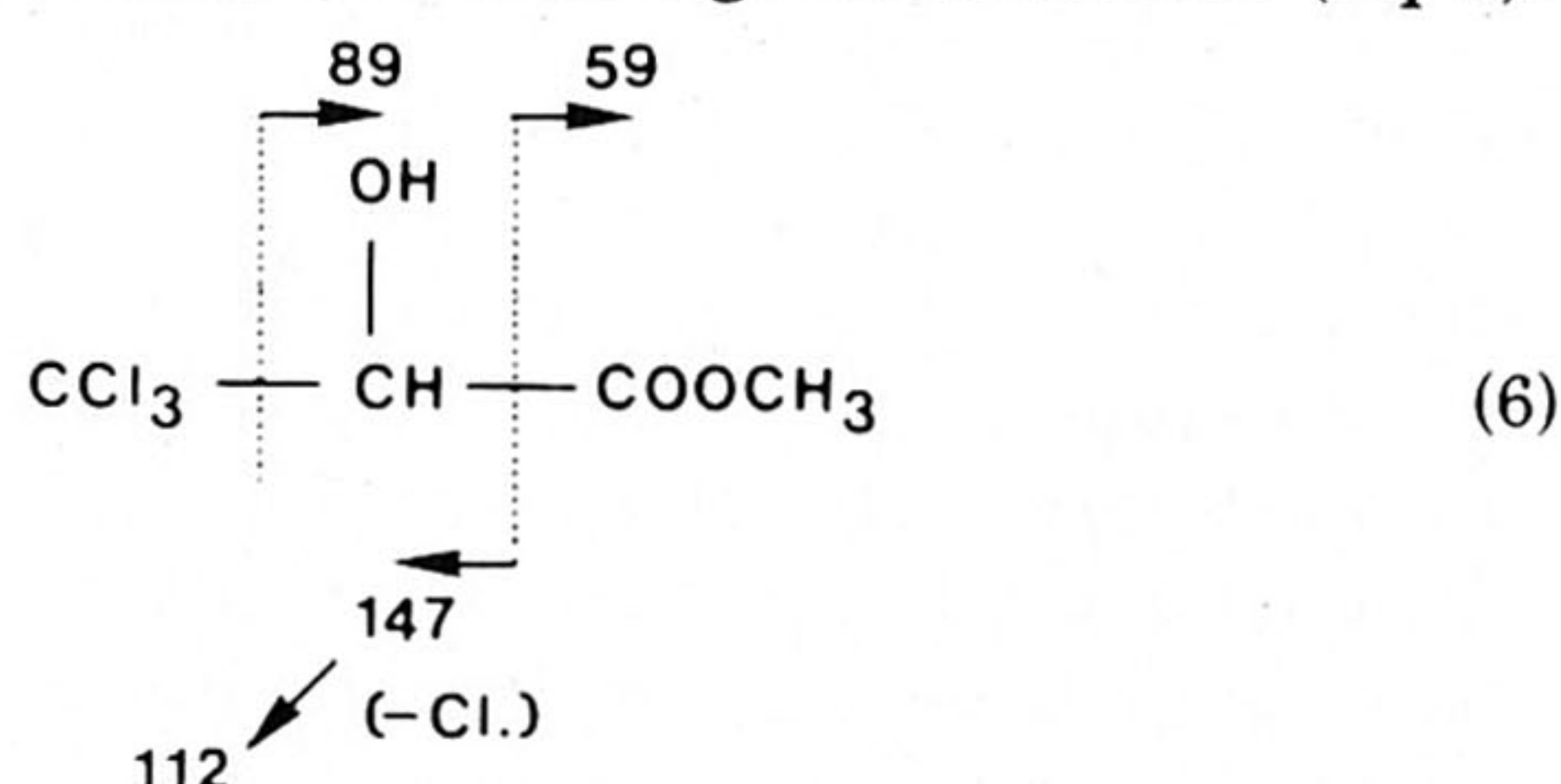
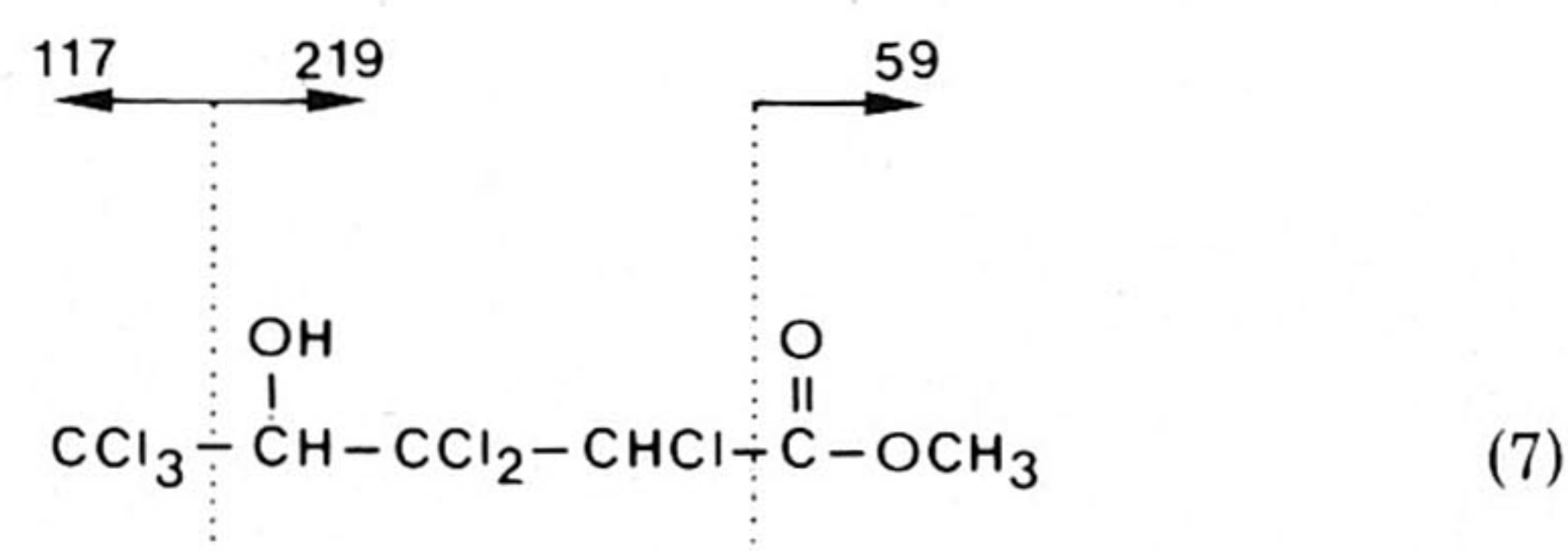


Figure 9. EI and CI mass spectrum of the dimethyl ester of 2-carboxy-3,5,5,5-tetrachloro-4-oxo-2-pentenoic acid (79).

The structure of the more complicated precursor 76 cannot be deduced conclusively from the EI and CI spectrum (Figure 8) alone. The CI spectrum gives the protonated molecular ion at m/z 337 and indicates the presence of six chlorine atoms.

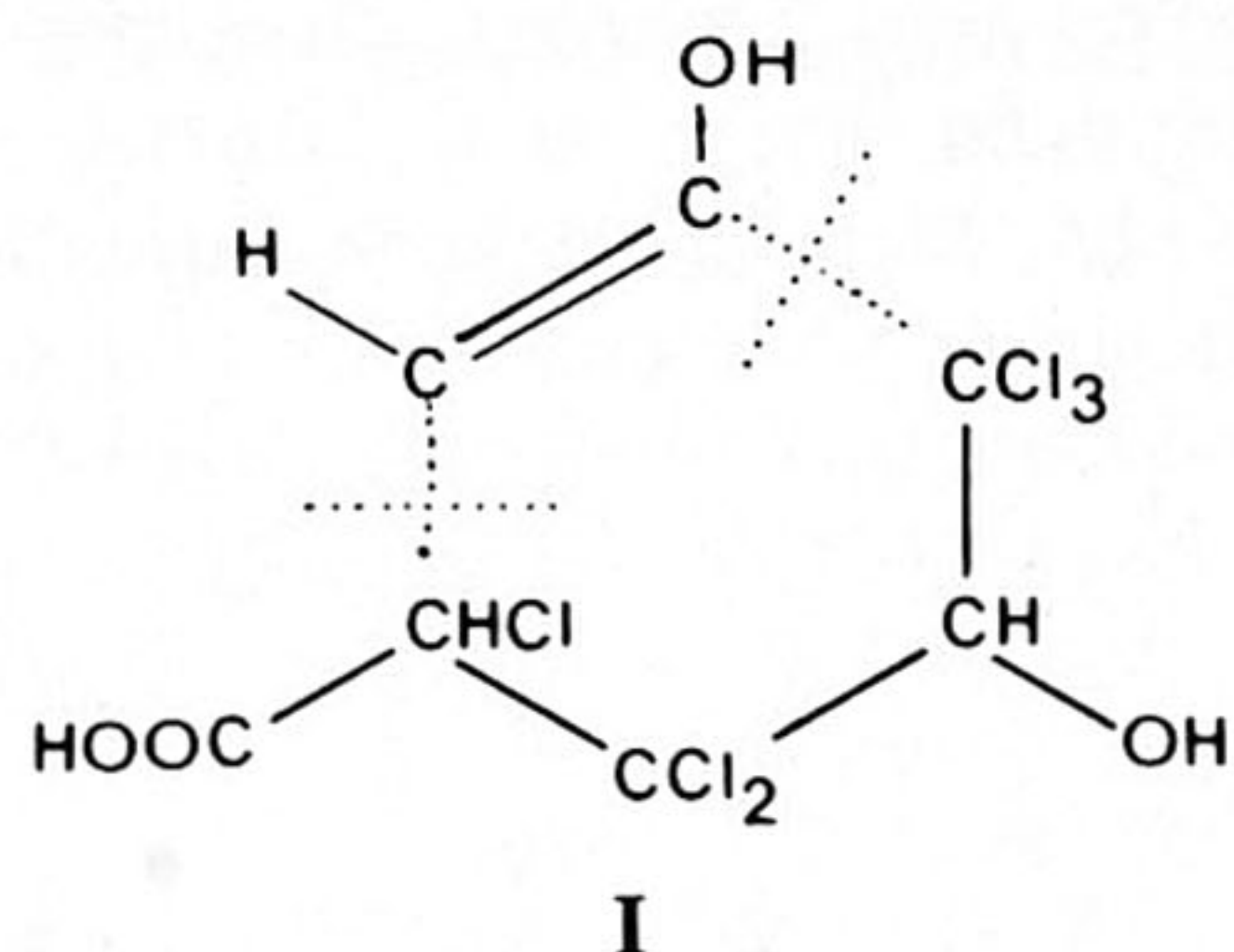
The EI spectrum shows many fragments up to m/z 235, most of which contain chlorine. The fragments at m/z 59, 117, and 219 can be explained by simple bond fission processes (eq 7). Because the central part of the molecule



is saturated, the O atom must be part of an ether or a hydroxyl group. As there is only evidence for the elimination of a CCl_3 group and not for C_2 and C_3 fragments, we propose that the CCl_3 group is bound to a $-\text{CHOH}-$ group. The formation and stability of the m/z 219 ion are then explained by the α -type cleavage of alcohols.

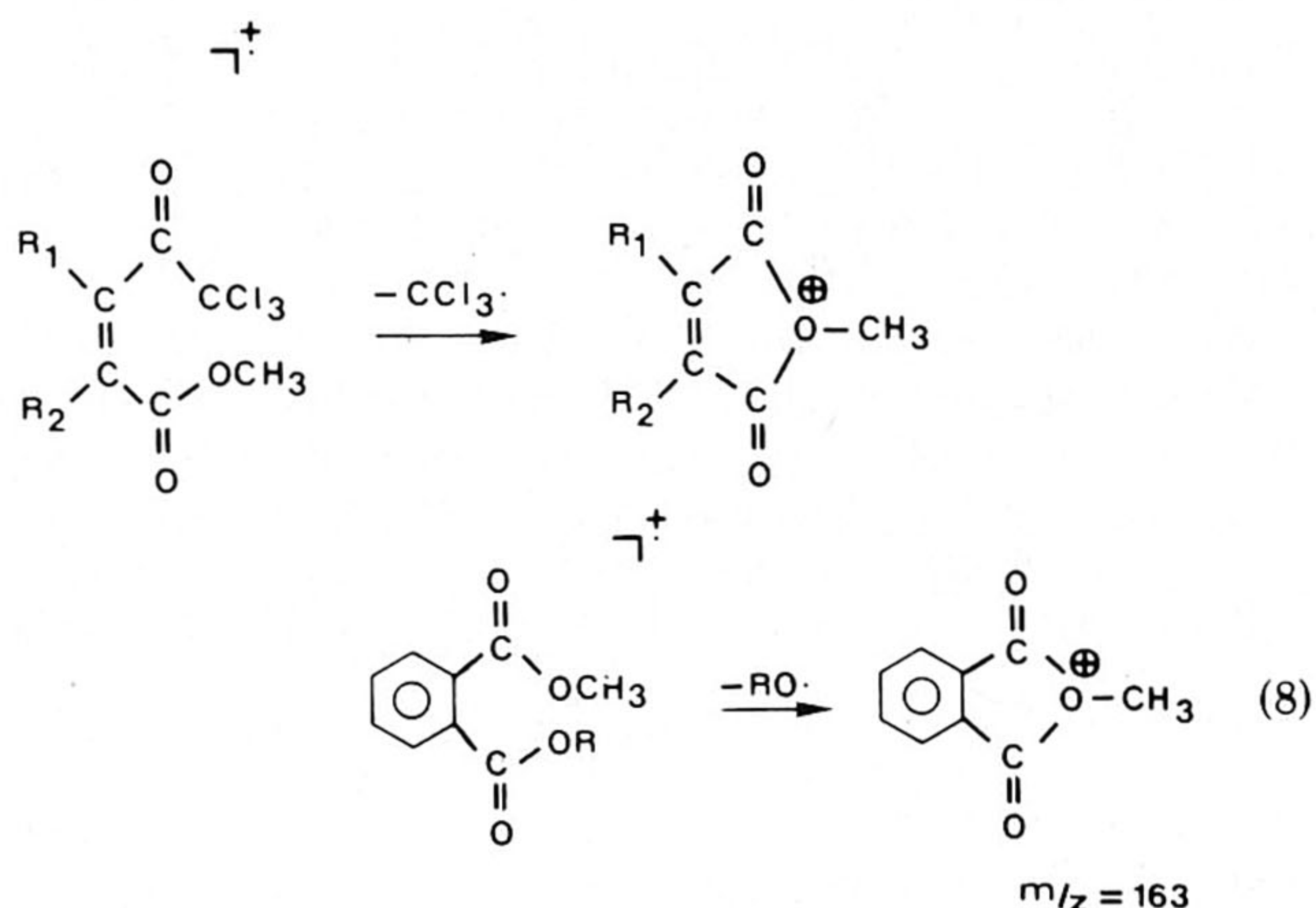
Most of the other fragments in the EI spectrum can be explained by successive eliminations of CO , CO_2 , Cl_2 , etc., which, however, do not provide information about the structure of the central part of the molecule. We propose methyl 2,3,3,5,5,5-hexachloro-4-hydroxypentanoate to be the final structure because the same product was found in the chlorination of 3,5-dihydroxybenzoic acid. This structure gives relevance to the structure of the starting compound and the possible mechanism of the chlorination of resorcinol derivatives (I).

All chloroform precursors of the acetyl type show only one important fragment which is caused by the loss of a CCl_3 group from the molecule. As further fragmentations are observed only to a minor extent (Figure 9), the ion



formed apparently must have a very stable structure.

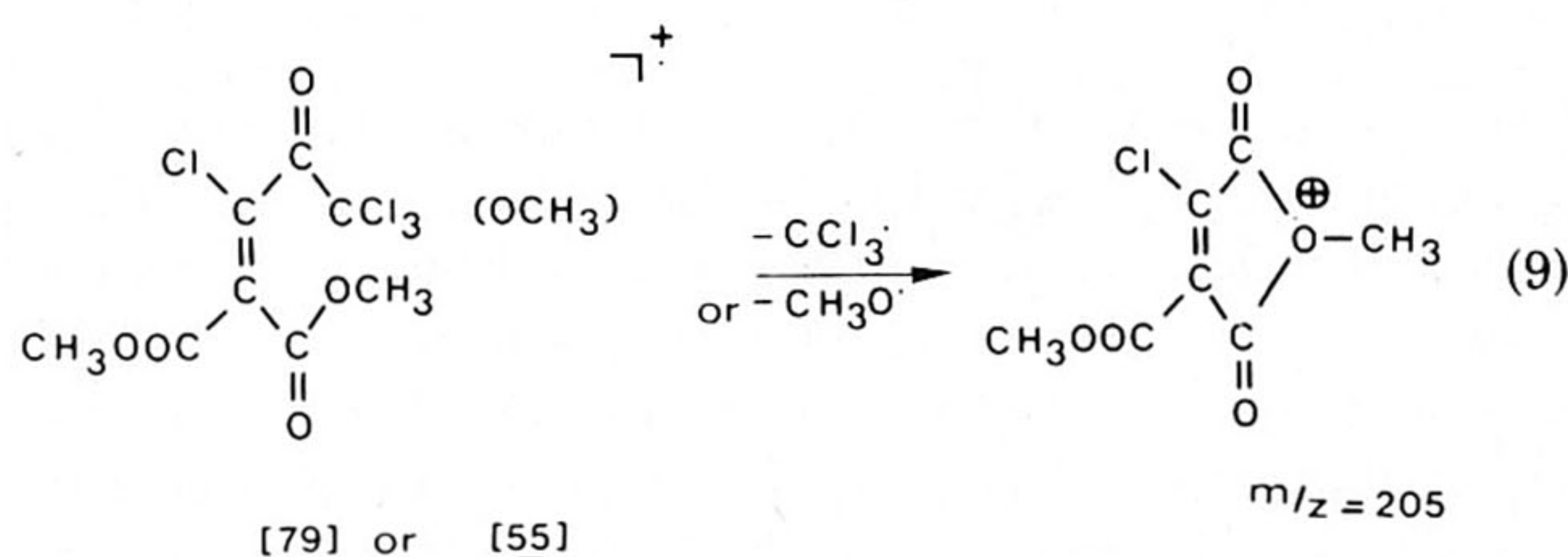
We propose a methylated cyclic anhydride structure for this ion, in analogy with the m/z 163 ion which is the most abundant fragment in the mass spectra of methyl phthalates (eq 8). We observed this ion for $R_1 = \text{Cl}$ and $R_2 =$



H (m/z 147), CH_3 (m/z 161), and COOCH_3 (m/z 205). With $R_2 = \text{CH}_3$ or COOCH_3 , structural isomers with identical EI/CI spectra were found, which may be caused by the reversal of R_1 and R_2 or by Z/E isomerism.

It must be noted that the spectrum of the dimethyl ester of 2-carboxy-3,5,5,5-tetrachloro-4-oxo-2-pentenoic acid (**79**) showed a very strong resemblance with the spectrum of the trimethyl ester of chloroethenetetracarboxylic acid (**55**) (15).

In the last case the ion at m/z 205 is formed by the elimination of a CH_3O group instead of a CCl_3 group (eq 9). The difference between **55** and **79** was detected only



by the combined use of EI and CI mass spectrometry.

Conclusion

It has been shown that chlorination of terrestrial humic acid 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 and C-4 diacids. Whether these precursors form the only source of chloroform cannot be concluded, but they point strongly to the important role of 1,3-dihydroxybenzene structures as the primary source. It remains to be demonstrated, however, that these structures form a significant part of the humic acid frame.

Because conversion of the precursors into chloroform is slow, they may account for the slow formation of chloroform at high chlorine to carbon doses and long reaction times (49). The fast initial formation of chloroform may proceed through other mechanisms starting with the same

1,3-dihydroxybenzene structures.

The other chlorination and oxidation products closely agree with the compounds identified by Christman and co-workers (13-15), who worked mostly with aqueous humic material. Many new chlorination and oxidation products have been detected, i.e., the cyano-substituted carboxylic acids, the chlorinated aromatic acids, and several α -monochloro and α,α -dichloroaliphatic mono- and dibasic acids.

Registry No. 1, 79-31-2; 2, 79-11-8; 3, 116-53-0; 4, 598-78-7; 6, 75-99-0; 9, 512-56-1; 12, 100-52-7; 14, 13167-36-7; 15, 13023-00-2; 17, 110-15-6; 18, 111-14-8; 21, 2257-35-4; 24, 1917-15-3; 26, 65-85-0; 28, 120-72-9; 30, 16045-92-4; 36, 103-82-2; 40, 112-05-0; 43, 74-11-3; 44, 118-91-2; 49, 334-48-5; 50, 2444-36-2; 52, 1878-66-6; 56, 112-37-8; 57, 505-48-6; 58, 88-99-3; 63, 100-21-0; 65, 121-91-5; 67, 143-07-7; 70, 123-99-9; 73, 638-53-9; 74, 111-20-6; 80, 544-63-8; 83, 528-44-9; 84, 1002-84-2; 86, 554-95-0; 87, 57-10-3; 88, 506-12-7; 89, 57-11-4; 90, 646-30-0; 91, 506-30-9; 93, 2363-71-5; 94, 112-85-6; 95, 2433-96-7; 96, 557-59-5; 97, 506-38-7; 98, 506-46-7; 99, 7138-40-1; 100, 506-48-9; TCA, 76-03-9; DCA, 79-43-6; chloroform, 67-66-3; 2-methylpentanoic acid, 97-61-0; octanoic acid, 124-07-2; ethanedioic acid, 144-62-7; pentanedioic acid, 110-94-1; hexanedioic acid, 124-04-9; heptanedioic acid, 111-16-0; 3-cyanopropanoic acid, 16051-87-9; 1,2,3-benzenetricarboxylic acid, 569-51-7; 1,2,4,5-benzenetetracarboxylic acid, 89-05-4; benzenepentacarboxylic acid, 1585-40-6; 2-chlorobutenedioic acid, 19071-21-7; (*E*)-2,3-dichlorobutenedioic acid, 25144-43-8; (*Z*)-2,3-dichlorobutenedioic acid, 608-42-4; tetrachloromethane, 56-23-5.

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Received for review May 22, 1984. Revised manuscript received November 14, 1984. Accepted January 8, 1985.

Relationships between Octanol-Water Partition Coefficient and Aqueous Solubility

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■ The thermodynamic relationship between octanol-water partition coefficient and aqueous solubility is discussed in the light of recently measured data for highly hydrophobic chemicals. Experimental data indicate that the presence of dissolved octanol in water has little effect on the solubility of chemicals in water and that the presence of dissolved water in octanol has little effect on the solubility of chemicals in octanol. The activity coefficients of hydrophobic chemicals in aqueous solution and in octanol solution both increase with increased chemical molar volume. An approximately linear relationship between log activity coefficient and molar volume is suggested in both phases, a consequence of which is that a plot of log octanol-water partition coefficient vs. log liquid or subcooled liquid solubility has a slope of approximately -0.8. A molecular thermodynamic interpretation of the data is presented, and some environmental implications are discussed.

Introduction

Two physical chemical properties, aqueous solubility (C^S , mol/m³) and octanol-water partition coefficient (K_{OW}),

play an important role in determining the partitioning behavior of chemicals in the environment, especially bio-concentration factor and organic carbon partition coefficients. Of particular concern are stable, hydrophobic chemicals such as benzene, the polynuclear aromatic hydrocarbons, biphenyl, dibenzodioxin, and dibenzofuran, and their chlorinated and brominated congeners which have low solubilities and high K_{OW} values and thus partition appreciably into biota and organic matter in soils and sediments. It is experimentally difficult to measure very low solubilities and high K_{OW} values; thus, few accurate measurements are available for chemicals with K_{OW} values exceeding 10⁶ or, correspondingly, solubilities below 50 mg/m³ (i.e., 50 µg/L). It is clear that reliable assessment of environmental fate requires accurate values for both properties; thus, there is an incentive to ensure that reported values are accurate and, since the properties are related, consistent.

Hansch et al. (1) first proposed a linear relationship between aqueous solubility and K_{OW} . Later Chiou et al. (2) developed this relationship more quantitatively for environmental chemicals, and several subsequent correlations have been proposed, notably by Yalkowsky and Valvani (3), Mackay et al. (4), Amidon et al. (5), Chiou et al. (6), Tewari et al. (7), Banerjee et al. (8), and Bowman

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