23. FURTHER PRELIMINARY RESULTS ON THE HIGHER WEIGHT HYDROCARBONS AND FATTY ACIDS IN THE DSDP CORES, LEGS 5-8[1]

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ABSTRACT

Studies of the organic geochemistry of the DSDP cores are revealing new concepts regarding the diagenesis and preservation of biological matter in oceanic floor sediments. Various cores from Legs 5 to 8 have been analyzed in two phases dependent on the amount of sample available.

First, one gram samples were exhaustively extracted with benzene and methanol (3:1) and these extracts were subjected to high resolution mass spectrometry. These results permitted an evaluation survey of the major homologous compound series present as well as their relative concentrations. The heptane solubles from these exhaustive extracts were quite diverse; in all cases, the most predominant compounds were hydrocarbons, having the most commonly encountered degrees of unsaturation of 0, 1 and 4, less of 2, 3 and 5. Minor amounts of mono and dioxygenated species were present, with trace amounts of polyoxygenated compounds. No nitrogen or sulfur containing species were detected above background in these total extracts.

Secondly, larger samples (50 to 100 grams) were subjected to more detailed analyses (consisting of high resolution mass spectrometry, GC-MS and GLC techniques) for the major compound classes indicated to be present in the preliminary survey. They were again exhaustively extracted with benzene and methanol (3:1), and these exhaustive extracts were separated by wet chemical methods into: acids, usually 2 to 20 per cent of the extracts; alkanes, usually 80 to 95 per cent of the extracts; and bases, usually less than 1 per cent of the extracts. The acid fractions consisted mainly of saturated acids, $C_nH_{2n}O_2$ for n = 5-21 with minor amounts of $C_nH_{2n-2}O_2$ (n = 5-20), $C_nH_{2n-4}O_2$ (n = 5-19), and some dicarboxylic acids. The alkanes were found to be mainly hydrocarbons with minor amounts of oxygenated species. The compositional series C_nH_{2n+2}, C_nH_{2n} and C_nH_{2n-2} for n = 1-22 were usually the major constituents.

Exhaustively extracted samples, which contained significant amounts of carbonates, were then partially demineralized with hydrochloric acid in order to liberate any fatty acids from salts. After this treatment the samples were reextracted and an acidic fraction was isolated. These extracts consisted mainly of fatty acids of the series $C_nH_{2n}O_2$ for n = 5-22 and $C_nH_{2n-2}O_2$ and $C_nH_{2n-4}O_2$ in minor amounts to n of approximately 20.

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[2]John Simon Guggenheim Memorial Fellow, 1970-1971.

The remarkable state of preservation of the organic matter in these cores over their geologic history (recent to early Cretaceous) is resulting in new insights into the diagenesis of biological matter in such sediments.

INTRODUCTION

The Deep Sea Drilling Project is for the first time providing cored samples taken through the sedimentary layers of the deep ocean basins and the continental rises. Studies of the organic geochemistry of such samples are revealing new concepts regarding the diagenesis and preservation of biological matter in oceanic floor sediments. The following report describes further preliminary organic analyses performed on the DSDP Cores at the Space Sciences Laboratory, University of California, Berkeley (cf. Simoneit and Burlingame, (1971) for previous report).

Selected core samples from Legs 5 to 8 have been analyzed in two phases dependent on the amount of sample available. The small (approximately 1 to 2 grams) samples remaining from the organic carbon analysis of Leg 8 were solvent extracted and the extract residues subjected to high resolution mass spectrometry. Based on the findings from this initial survey the experimental procedures for the larger (approximately 100 grams) samples were modified and applied as discussed later in this report. The results presented will be correlated to the ages and to the fossil fauna and flora in the sediments.

EXPERIMENTAL

The small (approximately 1 to 2 grams) samples remaining from the organic carbon analyses of Leg 8 were solvent (3:1 benzene and methanol) extracted, as was the case for the samples from previous legs (Simoneit and Burlingame, 1971). The bulk of the organics were removed from the extract residue by solution in heptane and weighed after solvent removal (see Table 1). The residue was then treated with acetone to dissolve the more polar organics and of course large amounts of inorganic salts (see Table 1). It should be noted that in samples where the acetone solubles are high, a large salt residue remained insoluble. All the heptane extracts and some of the acetone extracts were subjected to high (and some low) resolution mass spectrometry. These analyses were carried out on a GEC-AEI MS-902 mass spectrometer online to an XDS Sigma 7 Computer (described by Burlingame, 1968 and 1970, and Burlingame *et al.*, 1970). The samples were introduced *via* a direct inlet probe into the ion source, operated at the following conditions: resolution 10,000 to 12,000; ionizing current 500 μA; ionizing voltage 50 eV; and temperature 200 to 220°C. The scan rate was 16 seconds per decade with a clock rate of 24 KHz. Multiple scans were taken during each analysis and then sum averaged together during data reduction. Selected high resolution mass spectral data are presented as heteroatomic plots (Burlingame and Smith, 1968) in various figures in the text.

Gas chromatography was carried out using a Perkin-Elmer Model 900 gas chromatograph with a flame ionization detector and operating conditions as stated

TABLE 1
DSDP Small Core Sample Extracts, Leg 8

Sample	Organic Carbon (Per Cent)	Heptane Extract (ppm)	Acetone Extract (ppm)	Approximate Age	Type
8-72-4-6 (60-150)	0.08	216	1560	Upper Miocene	Carbonate ooze
8-73-13-6 (60-120)	0.30 0.09	30	62	Upper Miocene	Carbonate ooze
8-73-19-5 (65-100)	0.08	173	1860	Upper Miocene	Carbonate ooze
8-74-9-2 (60-150)	0.19	7	–	Lower Oligocene	Nannofossil ooze
8-74-12-2 (50-150)	0.38 0.05	566	113	Lower Miocene	Carbonate ooze
8-75-9-4 (60-150)	0.11	–	350	Lower Oligocene	Clay & nannofossil ooze

in the respective figure legends. Analyses using gas chromatography-mass spectrometry were carried out on a modified Perkin-Elmer Model 270 GC-MS linked online to an XDS Sigma-2 Computer (Smith *et al.*, 1971).

The larger samples packed and frozen in Kapak pouches were defrosted and extracted under a nitrogen atmosphere with 3:1 benzene/methanol in a Soxhlet extractor. The procedures used for extraction and functional group separations were essentially the same as described by Burlingame *et al.* (1969), except all operations were carried out under nitrogen wherever possible and the isolated fractions were stored in solution under refrigeration. Any modifications to the procedures described (Simoneit and Burlingame, 1971, and Burlingame *et al.*, 1969) are discussed in the Results section of this report.

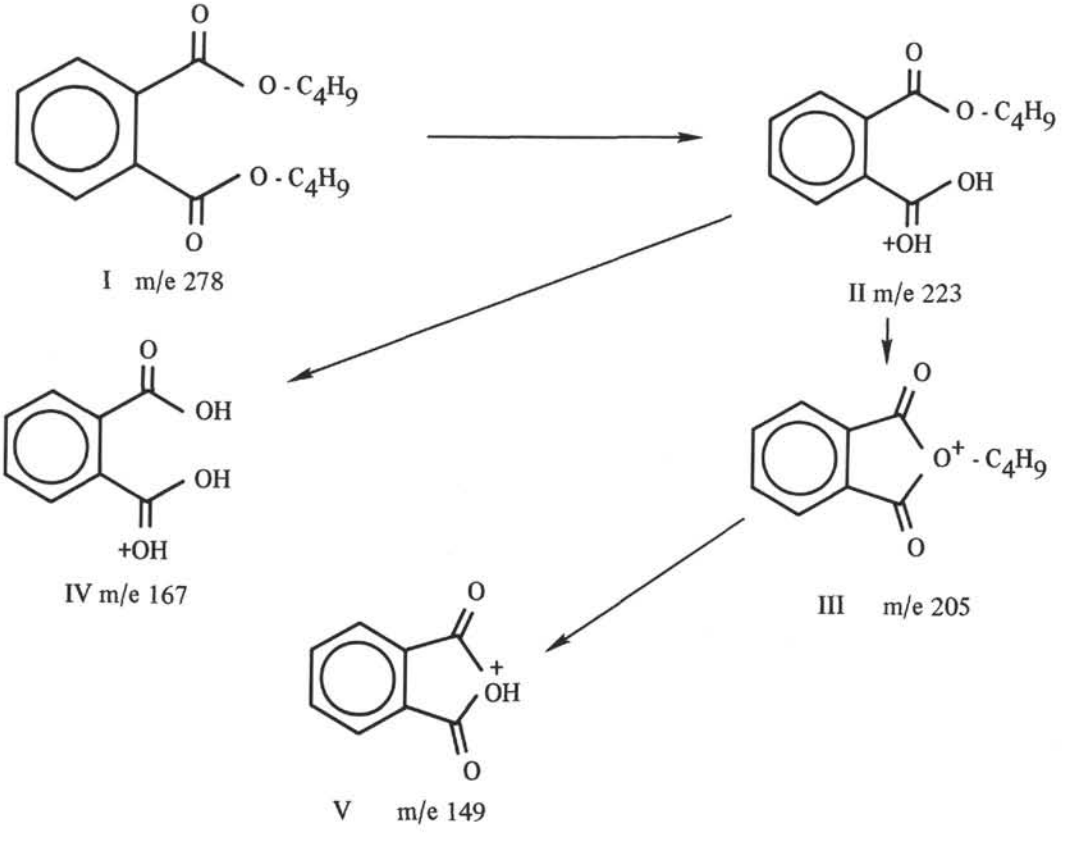
RESULTS

Small Core Samples, Legs 5 to 7

Some further data from the small core samples from Legs 5 to 7 will be discussed first.

Sample 5-40-15-5:
The heptane extract (10 ppm) of this sample was only analyzed by low resolution mass spectrometry. A representative scan is shown in Figure 1. Since this fraction represents the heptane solubles, it is assumed from solubility properties that the bulk of the constituents present are hydrocarbons. The fragmentation pattern at low mass fits with such an assumption. The main homologous series present are the saturated alkane fragments of composition C_nH_{2n+1} for n = 3-23, 27-31, 40 and 42, and the fragments of composition C_nH_{2n-11} for n = 14-42. The fragment ion series C_nH_{2n-9} for n = 21-28 and 36-42 is present in minor amounts.

Sample 5-42-10-2:
The heptane extract (534 ppm) of this sample was again analyzed only by low resolution mass spectrometry. A representative scan is shown in Figure 2. The major constituents were butyl phthalate (deduced from the peaks at m/e 278-Structure I, the molecular ion, m/e 223-Structure II, m/e 205-Structure III, m/e 167-Structure IV, and m/e 149-Structure V) and a group of peaks which appear to be cyclic alkanes of the series C_nH_{2n}. The fragment ion series C_nH_{2n-1} is present for n = 16-22 and the cyclohexyl and cyclopentyl ions at m/e 83 and 69, respectively, are significantly intense. The dibutyl phthalate is most likely a contaminant such as plasticizer from polyethylene, for example.



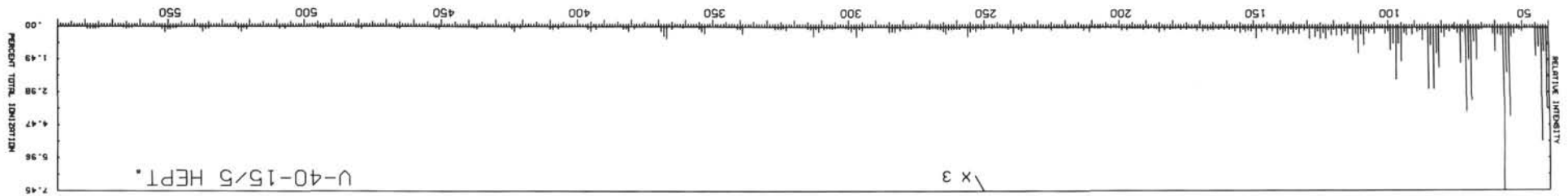


Figure 1. *Low resolution mass spectrum of the heptane extract residue from Sample 5-40-15-5.*

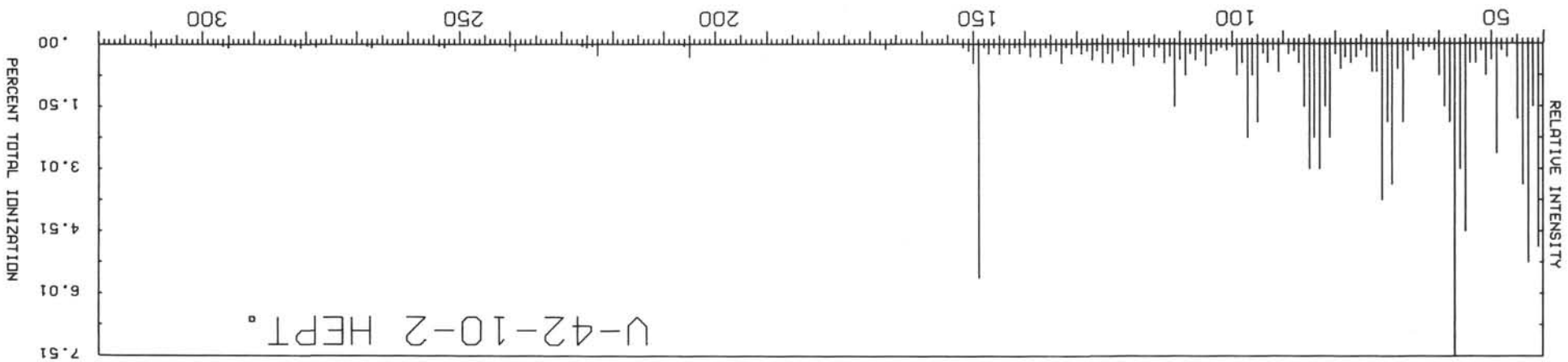


Figure 2. *Low resolution mass spectrum of the heptane extract residue from Sample 5-42-10-2.*

Sample 6-56.2-10-6:
The heptane extract (150 ppm) of this sample was subjected to low resolution mass spectrometry. A representative scan is shown in Figure 3. Based on the M + 1 and M + 2 (molecular ion, M) peak intensities of the high weight constituents and the heptane solubility of the extract, it is concluded that the bulk of the peaks have hydrocarbon compositions. A series of alkyl fragment ions, C_nH_{2n+1}, is present for n = 3 to 22. The ions at m/e 175, 189, 321, 347, 349 and 375 belong to various series of unknown compositions. The peaks above m/e 494 belong to probably two hydrocarbon series: C_nH_{2n-8} for n = 36, 38 and 40 (possibly the carotene, Structure VI in Simoneit and Burlingame, 1971) and C_nH_{2n-10} for n = 36 to 60. Only the even-numbered homologs are present.

Sample 7-65.0-9-6:
The heptane extract (118 ppm) of this sample was subjected to low resolution mass spectrometry. A representative spectrum is shown in Figure 4. A series of alkyl fragment ions, C_nH_{2n+1}, is indicated for n = 13-20. The peaks at m/e 498, 526, 554 and 582 fit into the series C_nH_{2n-6} for n = 36, 38, 40 and 42. The peaks at m/e 576 and 578 possibly correspond to the compositions $C_{42}H_{72}$ and $C_{42}H_{74}$, respectively.

Small Core Samples, Leg 8

The results from the analyses of the small core samples from Leg 8 will be discussed next. Referring to Table 1, it should be noted that in general the heptane and acetone soluble fractions are smaller than was the case with most of the samples from Legs 5 to 7 (Table 1 in Simoneit and Burlingame, 1971).

Acetone Background

Some of these samples were Soxhlet extracted with acetone instead of the 3:1 benzene and methanol mixture in order to alleviate some of the solubility and toxicity problems associated with the use of that solvent mixture. The nanograde quality acetone was used as received. The residue from the evaporation of 400 milliliters of acetone, amounting to 40 μg was subjected to high resolution mass spectrometry and the data is shown in Figure 5. The hydrocarbon contamination is very low. Phthalate ester contamination was not detected. The major constituents of the residue are ketones such as $C_5H_{10}O$, C_6H_8O and $C_6H_{10}O$, and several higher weight homologs in minor amounts (see Figure 5).[3] A series of substituted benzoic acids, $C_nH_{2n-8}O_2$, are present in minor amounts for the values of n = 7-10 and 12, as well as carboxylic acids of the series $C_nH_{2n}O_2$ for n = 1-7.

Sample 8-72-4-6:
The heptane extract residue (see Table 1) of this sample was subjected to both low and high resolution mass spectometry and a representative low resolution scan is shown in Figure 6. The major higher molecular weight homologs belong to the series C_nH_{2n-10} for n = 21-42 and C_nH_{2n-8} for n = 21-23, 26-28, and 38-42 with minor amounts of C_nH_{2n-12} for n = 21, 22, 25-31, 33 and 39-42. The fragment ions derived from the homologs of these series are also present (mainly the M-CH_3 types). The acetone extract residue was subjected to high resolution mass spectrometry and the data is shown in Figure 7. The whole spectrum is suppressed by the fragmentation pattern of a nitrogenous compound of composition $C_6H_{15}N$. The best fit of a known pattern appears to be diisopropylamine (Structure VI).

There are only trace amounts of oxygenated material. The hydrocarbon fragmentation pattern indicates low amounts of the more saturated alkanes with the more aromatic series such as C_nH_{2n-6} for n = 6 to approximately 17 predominating. The ion $C_{16}H_{25}$

[3] In this report, all high resolution mass spectra are presented as heteroatomic plots (Burlingame and Smith, 1968) with the masses plotted in methylene units. On the abscissa, each principal division marker corresponds to the saturated alkyl fragment (even-electron ion), for example, C_nH_{2n+1}, with the number of carbon and hydrogen atoms given subsequently. Each principal division of the abscissa is further divided into seven units. The number of hydrogen atoms of an unsaturated or cyclic-fragment ion is obtained by subtracting the number of units (two hydrogen atoms) or half units from the 2n+1 hydrogen atoms of the respective saturated principal division, C_nH_{2n+1}. Fragments which have more than seven degrees of unsaturation are plotted as heteroatomic plots where each principal division marker on the abscissa corresponds to the fragment ion C_nH_{2n-14}. Each principal division is again further divided into seven units and the number of hydrogen atoms of a fragment ion is derived as discussed above. The origin of the abscissas is the same m/e ratio for each plot, thus the nominal masses from plot to plot lie directly above one another and a superposition of the plots would yield a "low" resolution mass spectrum of the sample. The nominal masses are indicated in 50 mass unit intervals below the carbon/hydrogen ratio scale. All plots are normalized to a base peak (usually the base peak of the entire spectrum, unless otherwise specified) on the relative intensity scale. In order to make high mass, low intensity features of the spectrum observable, the whole spectrum or any region thereof can be multiplied by a scale factor. This factor is indicated by\X*00* at the point of scale expansion.

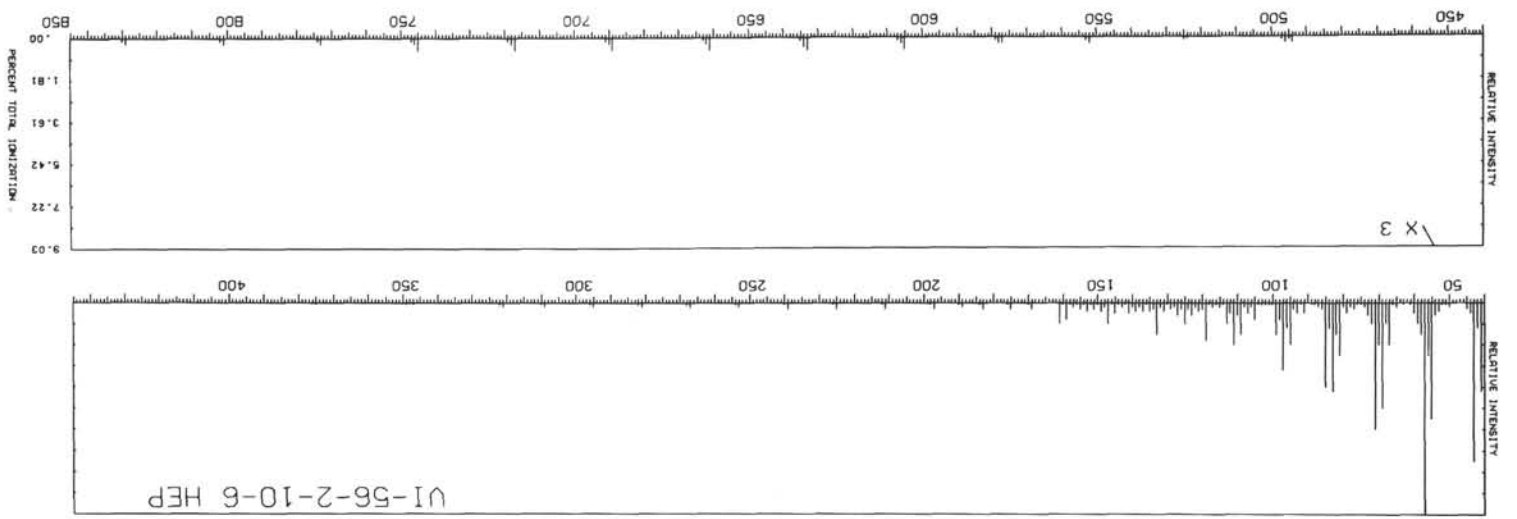


Figure 3. *Low resolution mass spectrum of the heptane extract residue from Sample 6-56.2-10-6.*

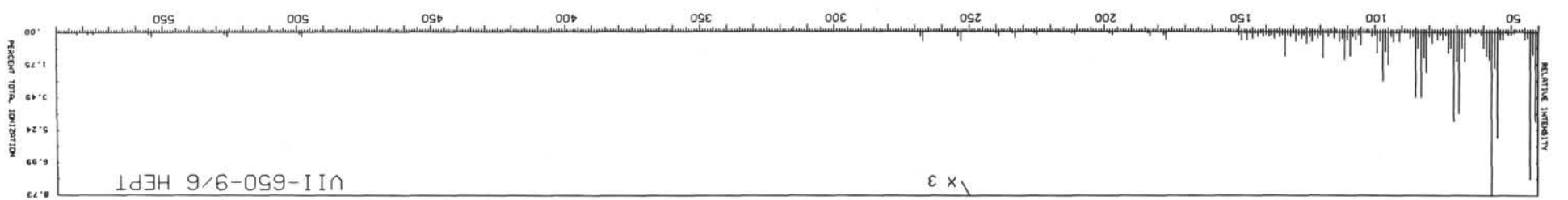


Figure 4. *Low resolution mass spectrum for the heptane extract residue from Sample 7-65.0-9-6.*

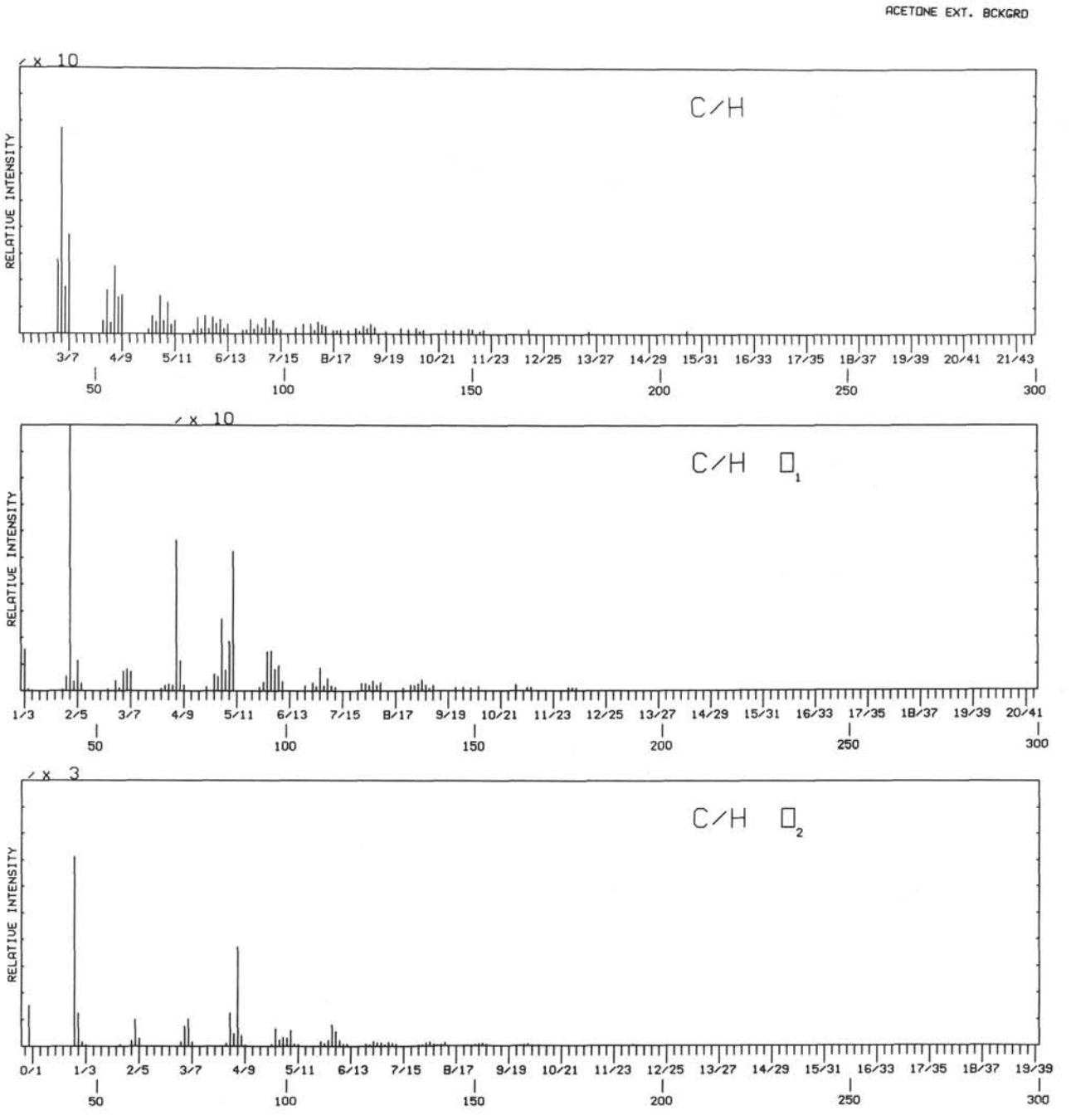
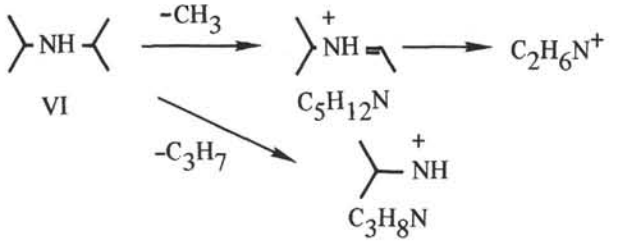
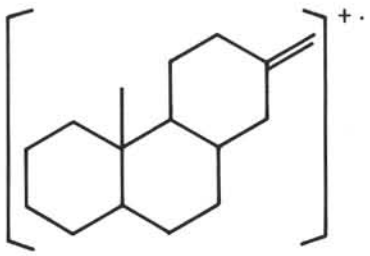


Figure 5. *Partial high resolution mass spectral data for the nanograde acetone background residue.*



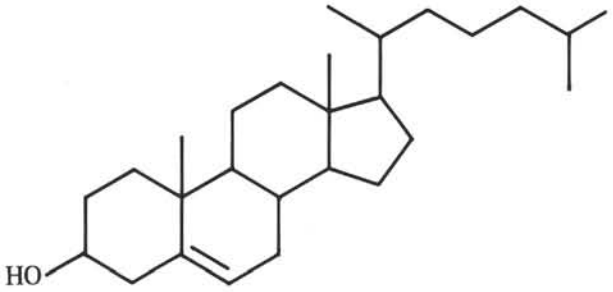
(Structure VII) is significantly above background. The fragment ion series C_nH_{2n-13} for n = 10-19 is present with a maximum at $C_{19}H_{25}$.

The high resolution mass spectral data for the heptane extract residue in Figure 8 exhibits similar hydrocarbon species, as was the case for the acetone extract.

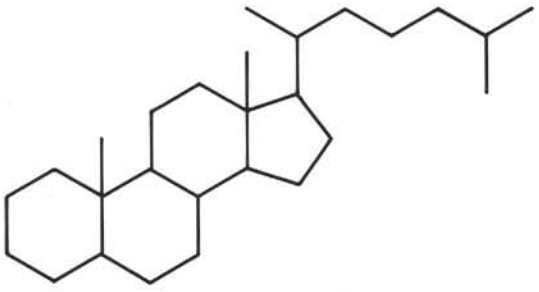


VII m/e 217, $C_{16}H_{25}$

The range extends to about C_{30} for most of the series. The fragment ion $C_{16}H_{25}$ (Structure VII), $C_{18}H_{38}$, and ions of compositions $C_{27}H_{44}$ (possibly cholestadiene derived from cholesterol-Structure VIII), $C_{27}H_{48}$ (possibly cholestane-Structure IX), and $C_{28}H_{42}$ are quite intense. In the C/H O plot of Figure 8, there appear possible molecular ions of cholesterol (Structure VIII), $C_{27}H_{46}O$ and a higher weight sterol,



VIII



IX

$C_{29}H_{48}O$. The dioxygenated species are also quite diverse. The predominant higher weight series is $C_nH_{2n}O_2$ for n = 14-18. The C/H O_3 data is dominated by the peak at m/e 149 of composition $C_8H_5O_3$ (Structure V) derived from phthalate contamination and the fragment ion series $C_nH_{2n-1}O_3$ for n = 15-21. The phthalate appears to be mainly dihexyl phthalate and dioctyl phthalate deduced from the

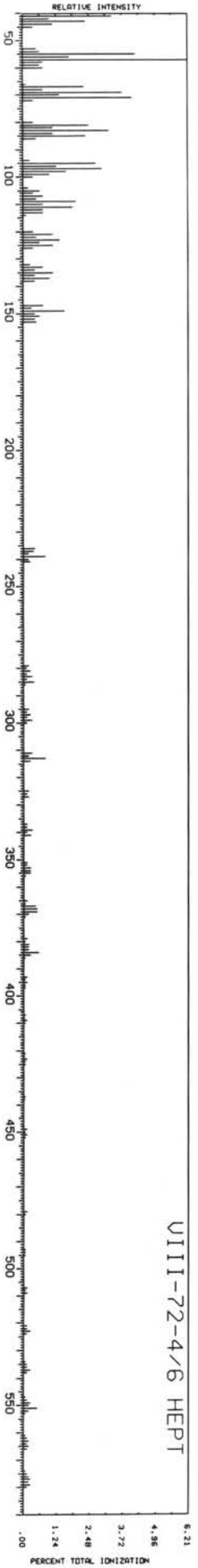


Figure 6. *Low resolution mass spectrum of the heptane extract residue from Sample 8-72-4-6.*

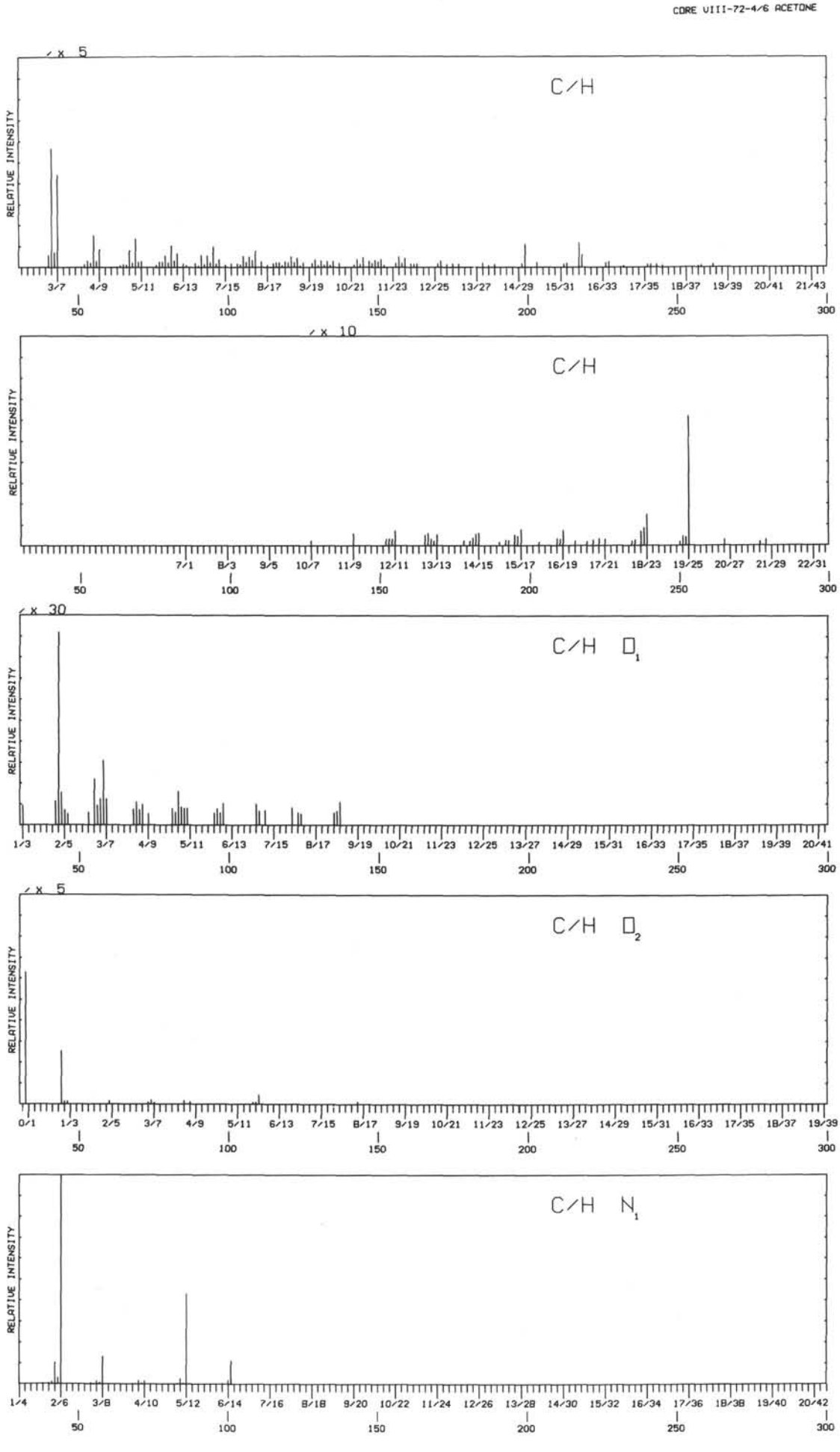


Figure 7. *Partial high resolution mass spectral data for the acetone extract residue from Sample 8-72-4-6.*

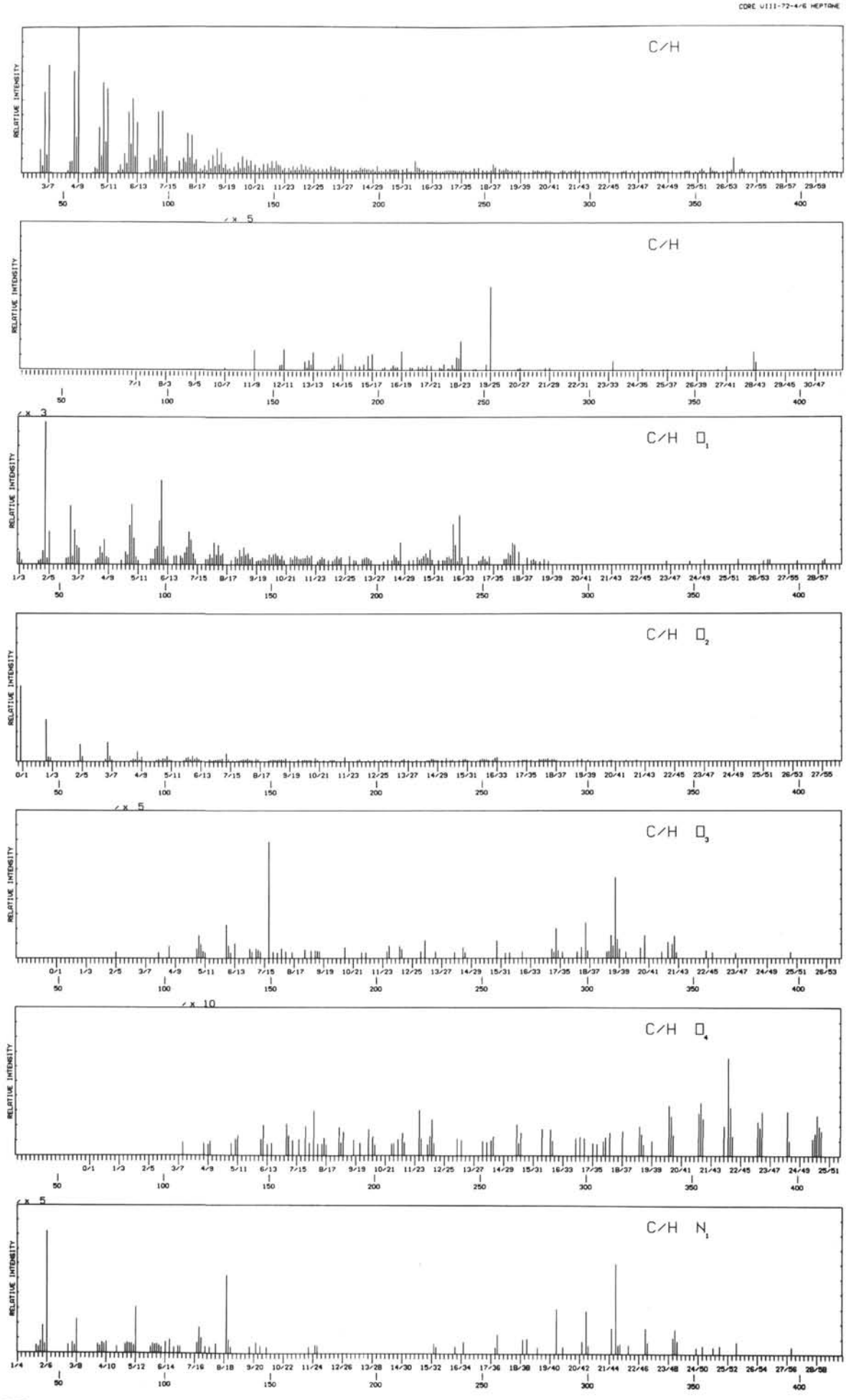
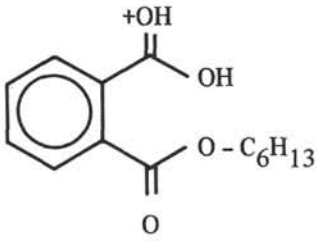
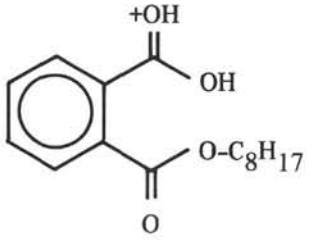


Figure 8. *Partial high resolution mass spectral data for the heptane extract residue from Sample 8-72-4-6.*

peaks of compositions $C_{14}H_{19}O_4$ (Structure X) at m/e 251 and $C_{16}H_{23}O_4$ (Structure XI) at m/e 279 in the C/H O_4 plot of Figure 8.



X



XI

There also is a group of homologs clustered about the composition $C_nH_{2n-5}O_4$ from n = 7-25 present. The peaks from the fragmentation of the diisopropyl-amine (Structure VI) are present in minor amounts with an additional peak of composition $C_8H_{19}N$, another amine. The peaks at higher mass in the C/H N plot of Figure 8 are redundancies with the O_3 species.

Sample 8-73-13-6:
The heptane extract residue (see Table 1) of this sample was analyzed by GLC only. The major amount of the extract consists of low weight volatile compounds (GLC retention times less than a C_{16} alkane).

Sample 8-73-19-5:
The acetone extract residue from this sample was analyzed by GLC only, and the resulting trace is shown in Figure 9. The bulk of the GLC peaks have retention times less than a C_{18} alkane.

The heptane extract residue was analyzed by both low and high resolution mass spectrometry and a typical low resolution scan is shown in Figure 10. The major homologous series indicated are C_nH_{2n-10} for n = 16, 18, 20-44, and C_nH_{2n-12} for n = 16, 18, 20-44, and C_nH_{2n-14} in lower amounts for n = 16, 18, 20-27, 29-31, 35, 38-42 and 44. In minor amounts are found the series $C_nH_{2n}O_3$ (cross-correlated from the high resolution mass spectral data) for n = 17-38 and $C_nH_{2n-4}O$ for n = 16 and 18. The partial high resolution mass spectral data is shown in Figure 11 and corroborates the hydrocarbon series indicated in the low resolution data. No phthalate contamination is evident. The oxygenated species $C_{16}H_{28}O$ and $C_{18}H_{32}O$ are the most intense high mass ions in the C/H O plot, whereas the peak of composition C_2H_3O appears to be acetone solvent residue. In the C/H O_2 plot of Figure 11 the molecular ion of probably palmitic acid ($C_{16}H_{32}O_2$) is found in minor intensity; the remaining peaks are mainly trace component fragments.

Sample 8-74-9-2:
The heptane extract of this sample (see Table 1) was analyzed by both low and high resolution mass spectrometry. The low resolution mass spectrum is shown in Figure 12. The low mass end of the spectrum is characteristic of hydrocarbon fragmentation and at higher masses the following series are apparent: C_nH_{2n+2} for n = 18-26, C_nH_{2n} for n = 18 and 20, C_nH_{2n-10} for n = 19-32 and possibly 36, 38-42, and C_nH_{2n-8} for n = 19-29, 31 and possibly 36-40. The peaks at m/e 256, 284, 286 and 300 are significantly higher than the general hydrocarbon pattern and are found to be O_2 species by high resolution mass spectrometry. That data is shown in Figure 13. The C/H plot essentially corroborates the alkane fragmentation pattern; mainly the fragment ion series C_nH_{2n+1} for n = 3-23 is indicated. The fragment ion series C_nH_{2n-13} for n = 9-19 is also evident in minor amounts. The C/H O_2 data show peaks of probably palmitic and stearic acids ($C_{16}H_{32}O_2$ and $C_{18}H_{36}O_2$, respectively), which are substantiated by the peaks of composition $C_{16}H_{31}O$ and $C_{18}H_{35}O$ (M-OH radical) in the C/H O plot. The peaks fitting phthalate esters are $C_8H_5O_3$ (Structure V), $C_8H_7O_4$ (Structure IV), and $C_{12}H_{15}O_4$ (Structure II).

Sample 8-74-12-2:
The heptane extract residue from this sample (see Table 1) was analyzed by GC-MS, and a few representative scans are shown in Figure 14. Scan 34 appears to be a mixture of hydrocarbons of molecular ion composition $C_{11}H_{20}$ at m/e 152 and $C_{12}H_{24}$ at m/e 168. Scans 68 and 69 are mixtures of probably hydrocarbons with molecular ion compositions fitting $C_{15}H_{30}$ at m/e 210, $C_{14}H_{24}$ at m/e 192, and $C_{14}H_{22}$ at m/e 190. Scan 83 fits the fragmentation pattern of diethyl phthalate (Structure XII), which loses an ethoxy radical to yield the peak at m/e 177 (Structure XIII), which loses ethylene to yield the peak at m/e 149 (Structure V). Scan 118 fits the fragmentation pattern of dibutyl phthalate (Structures I to V). Scan 141 is another mixture of hydrocarbons, probably fitting the compositions $C_{24}H_{50}$ at m/e 338, $C_{24}H_{48}$ at m/e 336, and $C_{22}H_{44}$ at m/e 308.

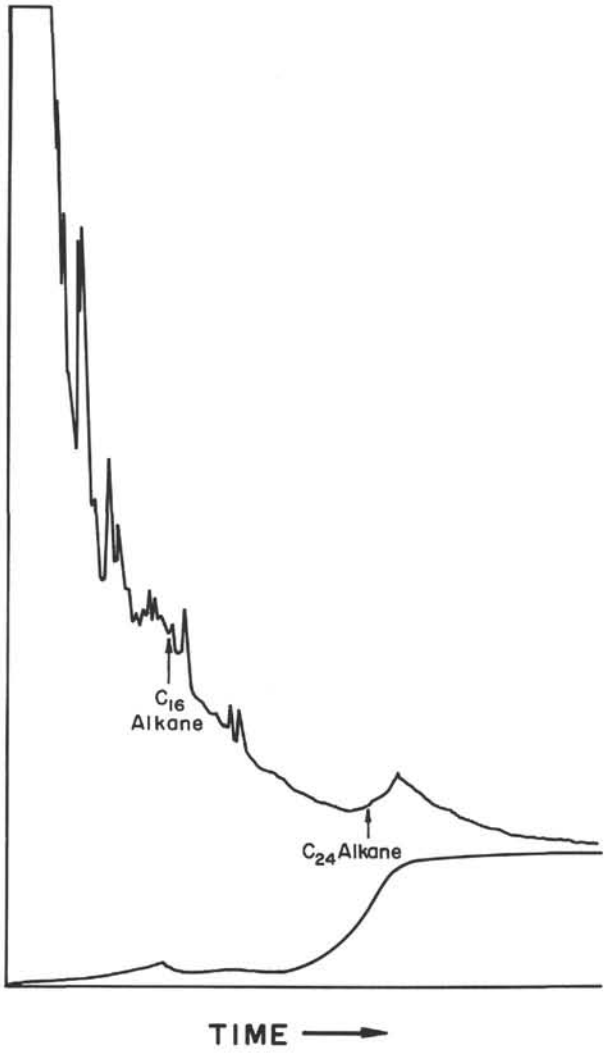
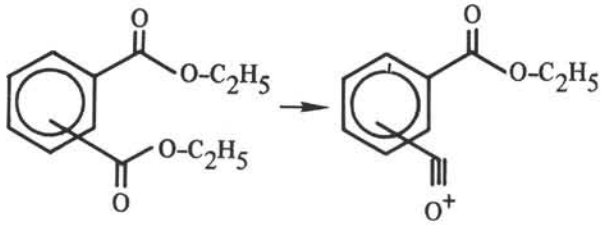


Figure 9. *Gas chromatogram of the acetone extract residue from Sample 8-73-19-5. (Conditions: 10 ft. X 1/8 inch stainless steel column, packed with 3 per cent OV-1 on 100-120 mesh Gaschrom Q, programmed from 100-250°C at 8°/min. and using He at 40 ml/min.).*



XII m/e 222 XIII m/e 177

Sample 8-75-9-4:
The total benzene and methanol (3:1) extract of this sample was subjected to both low and high resolution mass spectrometry. Two selected low resolution mass

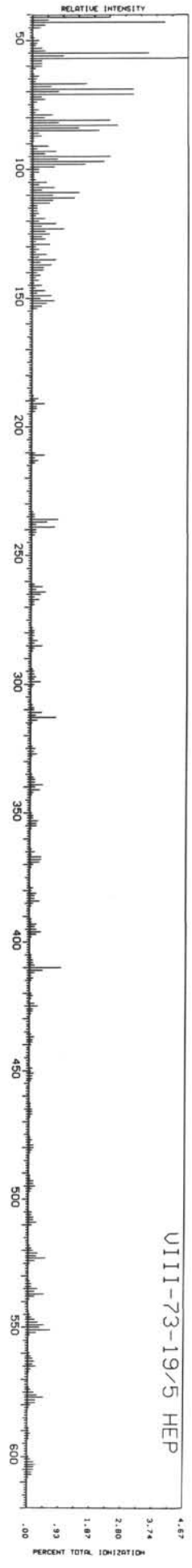


Figure 10. *Low resolution mass spectrum of the heptane extract residue from Sample 8-73-19-5.*

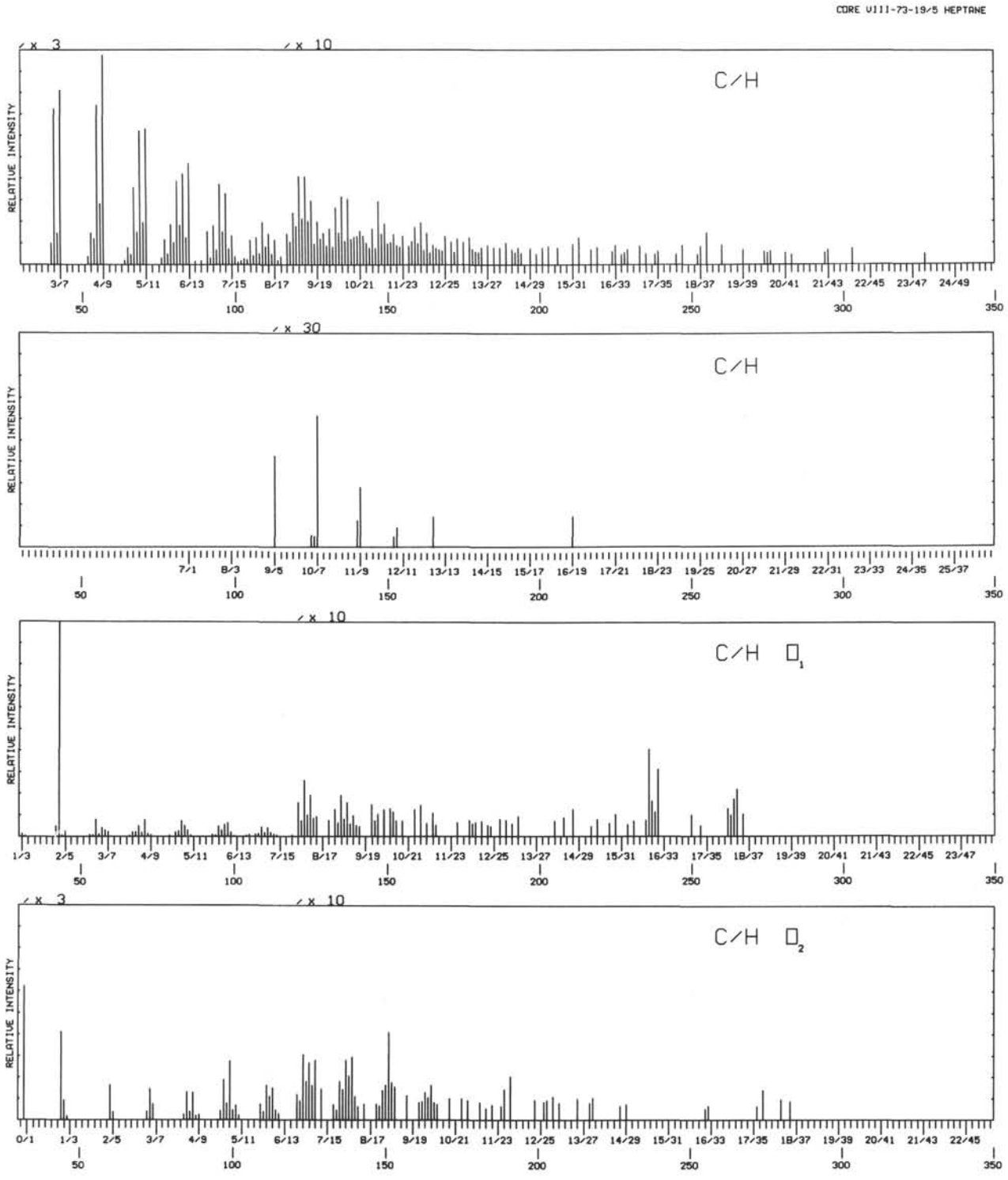


Figure 11. *Partial high resolution mass spectral data for the heptane extract residue from Sample 8-73-19-5.*

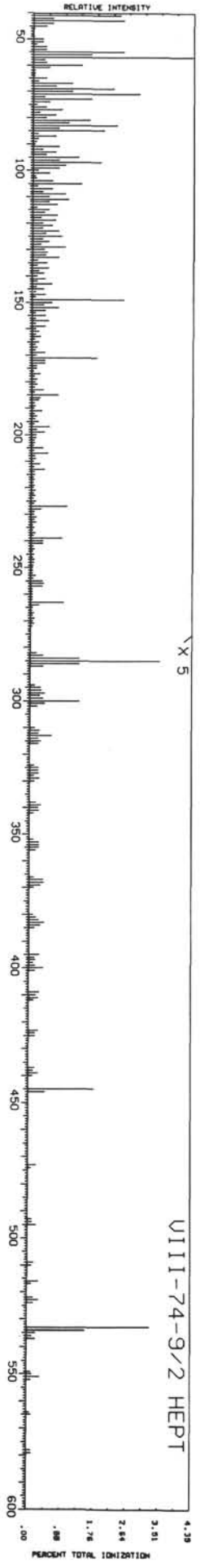


Figure 12. *Low resolution mass spectrum of the heptane extract residue from Sample 8-74-9-2.*

spectra are shown in Figure 15. In the first spectrum the peak at m/e 217 is probably derived from steroidal compounds and can be assigned Structure VII. The peak at m/e 239 in both spectra probably has the composition $C_{18}H_{23}$. The higher mass homologous series in the second spectrum are identical for the most part to the series found in the Sample 8-73-19-5 (see Figure 10) extract. The main series, C_nH_{2n-10}, is found for n = 20-42 with lower amounts of C_nH_{2n-12} for n = 20-42 and C_nH_{2n-8} for n = 18-40. The partial high resolution mass spectral data is shown in Figure 16. The hydrocarbon fragmentation pattern can be corroborated with the low weight fragments in the low resolution mass spectra (see Figure 15). The peak of composition $C_{27}H_{44}$ is possibly cholestadiene derived from the peaks of compositions $C_{27}H_{44}O$ and $C_{27}H_{46}O$ (possibly cholesterol-Structure VIII). The fragment ion series C_nH_{2n-13} for n = 11-19 is present in minor amounts. The phthalate ester, as well as polyoxygenated material, level is quite low.

Large Core Samples

Some further data on larger core samples analyses will be discussed next.

Sample 5-35-6-3:
The solvent extractable organic matter from this large core sample has been discussed (Simoneit and Burlingame, 1971). The exhaustively extracted core residue was then further treated with hydrochloric acid (HCl) and re-extracted. A general flow sheet for this demineralization is shown in Figure 17. The esters derived by the sonication method were found to be the same as the esters derived by subsequent Soxhlet extraction. The neutrals, which are predominantly alkanes, were also found to be the same from both extraction methods.

The following overall yields of acids versus alkanes are noteworthy and indicate that a significant amount of adipocere is present in this sample:

	Exhaustive Extract	Demineralization Extract
Acids	0.005%*	0.021%
Alkanes	0.032%	0.022%

*Per cent by weight of the original wet core.

The total alkanes from the exhaustive extract were further analyzed by low resolution mass spectrometry and by GLC-high resolution mass spectrometry. A low resolution scan is shown in Figure 18 and the major peaks present at high mass are groups in the m/e ranges of mid-500, 600, 700 and 800. The series C_nH_{2n-10} can, for example, be fitted to the m/e values of 564,

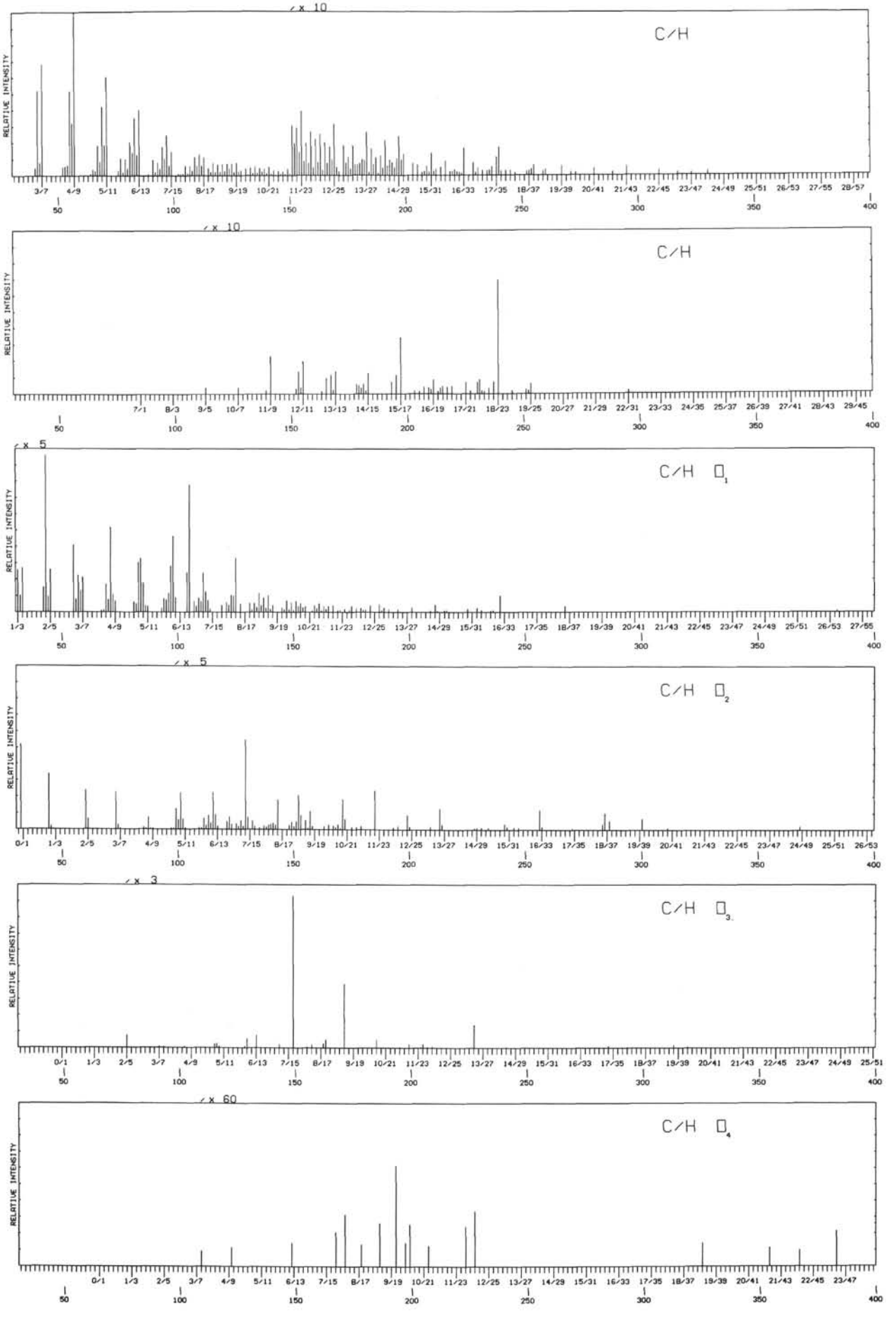


Figure 13. *Partial high resolution mass spectral data for the heptane extract residue from Sample 8-74-9-2.*

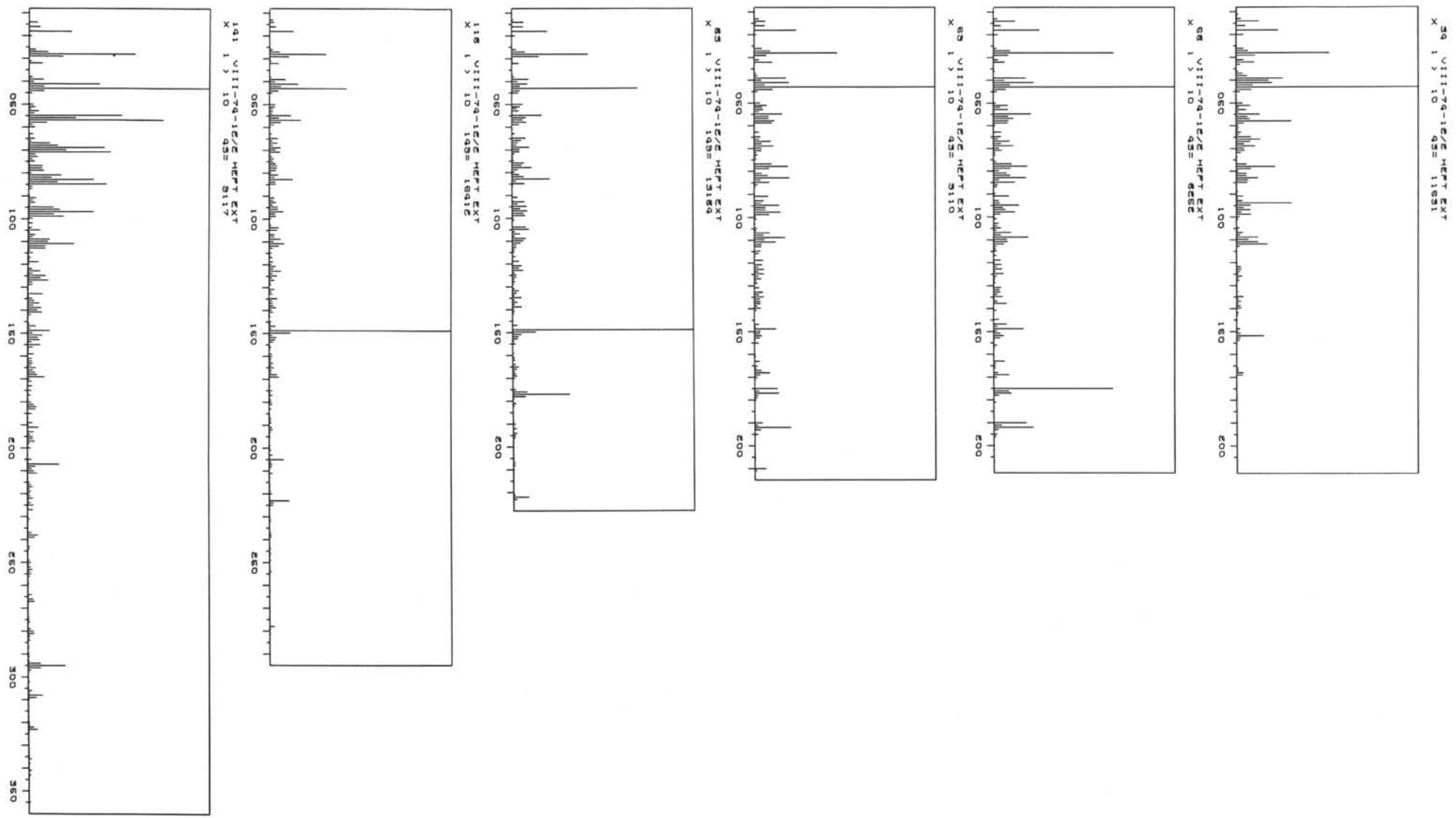


Figure 14. *Selected GC-MS data for the total heptane extract isolated from Sample 8-74-12-2 (GC-MS column conditions as in Figure 9).*

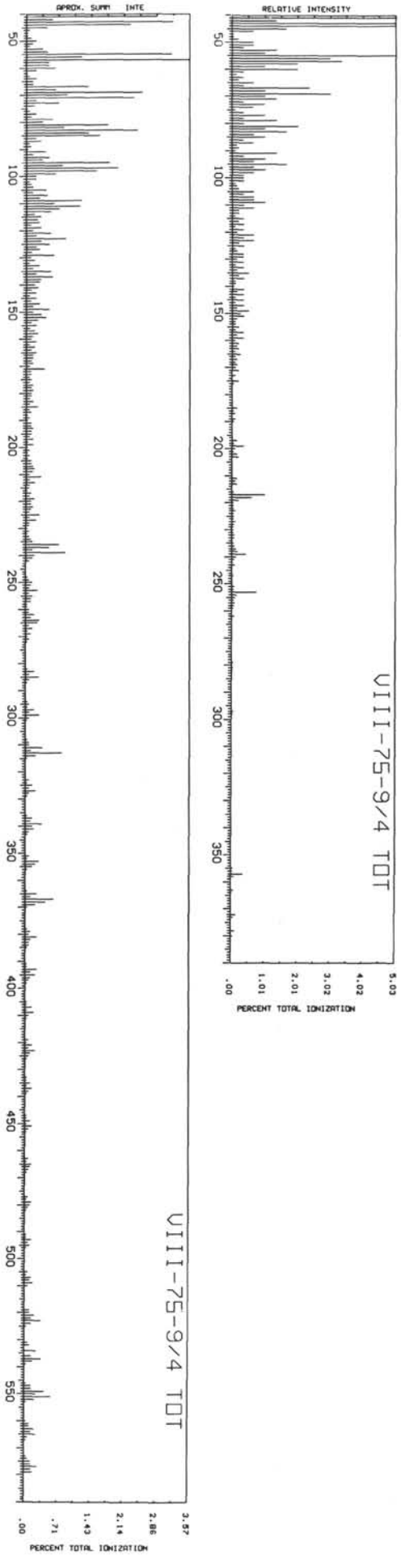
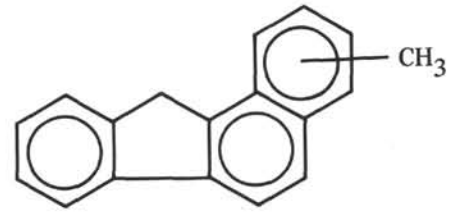
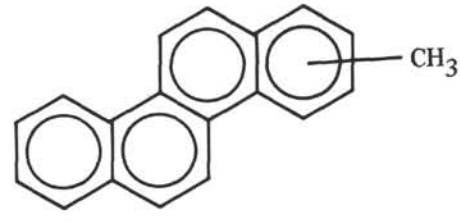


Figure 15. *Low resolution mass spectra of the heptane extract residue from Sample 8-75-9-4.*

578, 676, 732, 774, 816, 830, 858 and 872, but the m/e 858 peak would correspond to $C_{62}H_{114}$, which should be confirmed by accurate mass measurements. The salient features of the GLC-high resolution mass spectrometric analysis of these alkanes are presented in Figures 19 and 20. Scan 5 of Figure 19 consists mainly of heneicosane and a minor amount of an aromatic hydrocarbon of composition $C_{18}H_{14}$, which exhibits the loss of a methyl radical. Structure XIV would be a possibility fitting this composition. Scan 7 of Figure 19 consists mainly of docosane and another minor amount of an aromatic hydrocarbon of composition $C_{19}H_{14}$, which exhibits the loss of a methyl radical. Structure XV is a possible carbon skeleton fitting this composition.

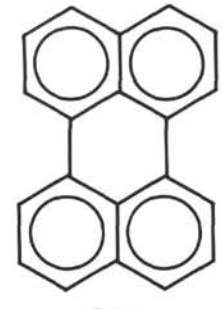


XIV



XV

Scan 9 of Figure 20 indicates mainly the fragmentation pattern of tricosane. Scan 10 of Figure 20 exhibits peaks characteristic of perylene, $C_{20}H_{12}$ (Structure XVI). Scan 11 of Figure 20 shows the hydrocarbon fragmentation pattern of octacosane, and in minor amount peaks due to a methylperylene (Structure XVII) of composition $C_{21}H_{14}$ and perylene (Structure XVI). Later scans showed indications of alkyl benzene hydrocarbons such as, for example, the composition $C_{16}H_{26}$ (possibly Structure XVIII), substantiated by



XVI

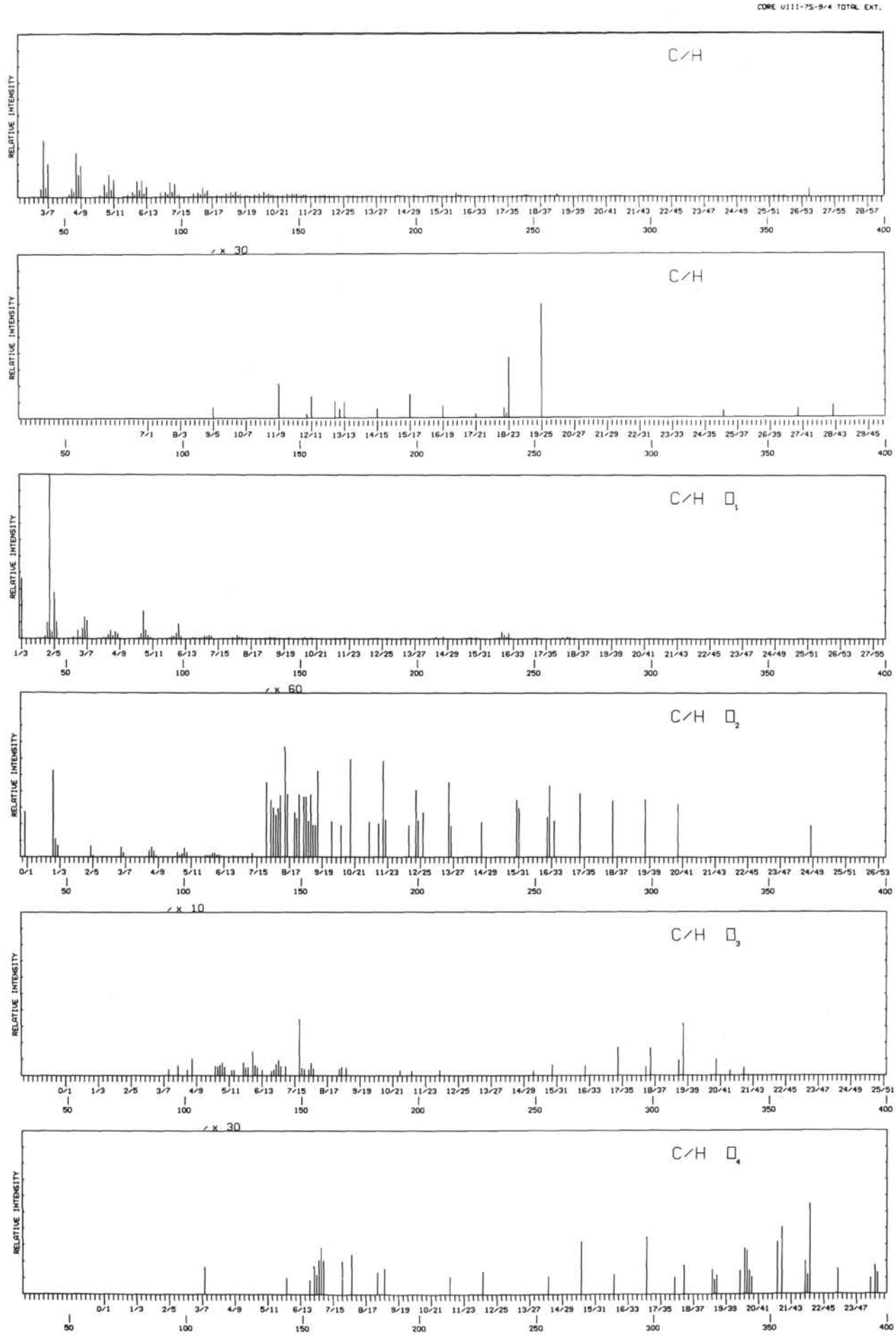


Figure 16. *Partial high resolution mass spectral data for the total benzene and methanol extract residue from Sample 8-75-9-4.*

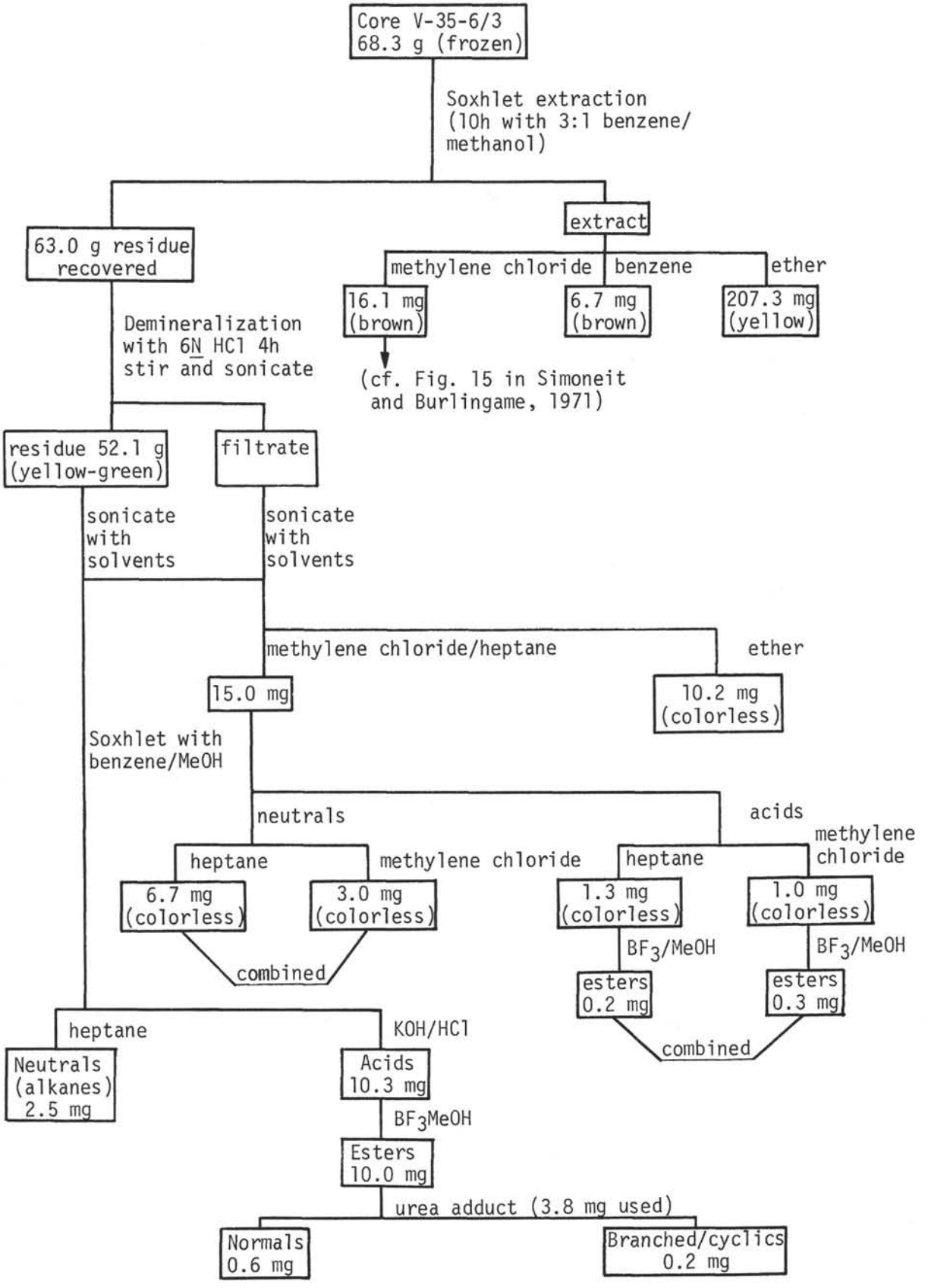


Figure 17. *Flow sheet for the various extractions of Sample 5-35-6-3.*

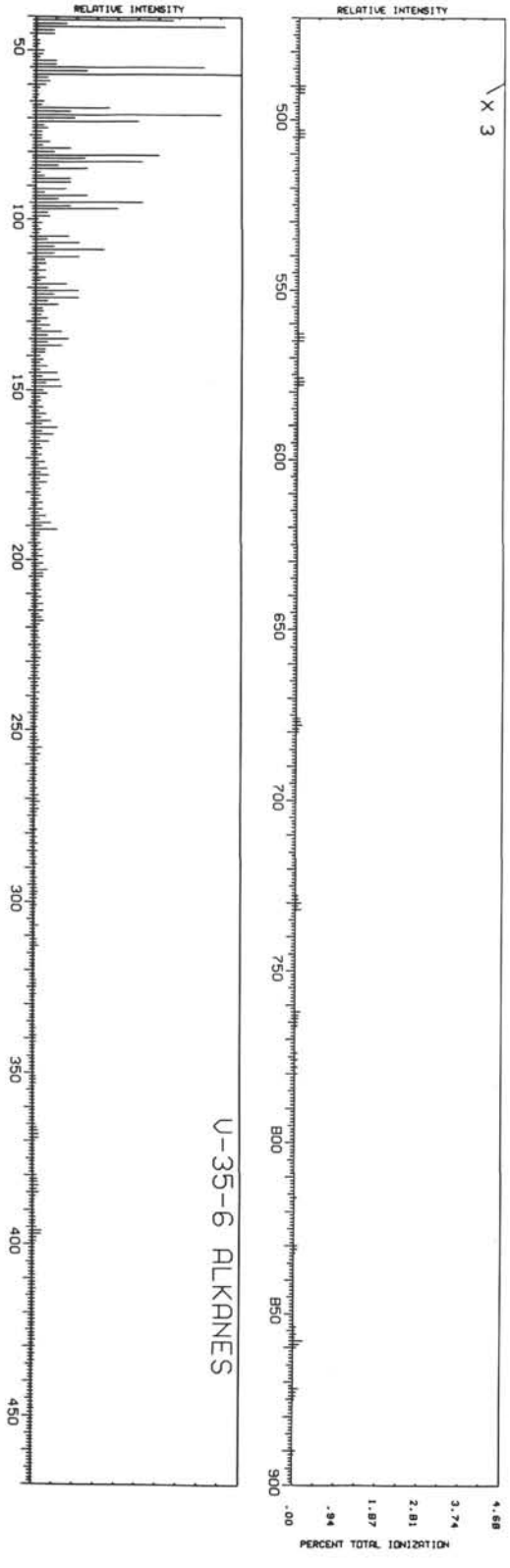
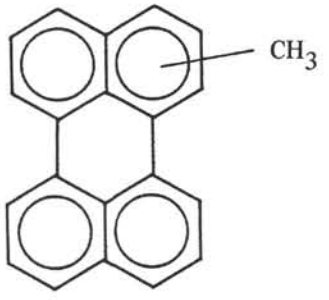
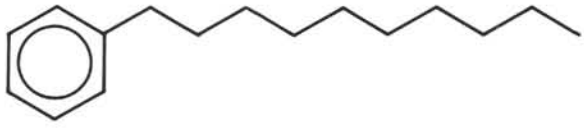


Figure 18. *Low resolution mass spectrum of the total alkanes from the extract of Sample 5-35-6-3.*

the presence of the typical hydrocarbon fragmentation to C_{10} and strong C_6H_5 and C_7H_7 ions.

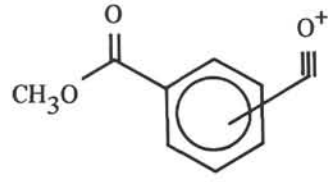


XVII

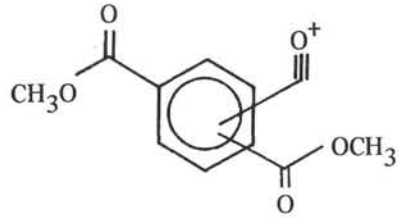


XVIII

Selected GC-MS data for the diethyl ether extract residue from the demineralization is shown in Figure 21. The GLC peak shapes tail, probably due to the polarity of the extract components. Scan 163 of Figure 21 fits the fragmentation pattern of dibutyl phthalate (Structure I). The peaks at m/e 169 and 207 are derived from GLC column bleed. Scan 176 appears to be a mixture of a phthalic acid dimethyl ester (peak at m/e 163-Structure XIX), a methylated benzene tricarboxylic acid (peak at m/e 221-Structure XX), and probably other phthalates. Scan 198, which is the best spectrum of the major peak in the GLC of the extract, fits the fragmentation pattern of butyl phthalyl butyl glycolate (Structure XXI). The molecular ion loses a



XIX m/e 163



XX m/e 221

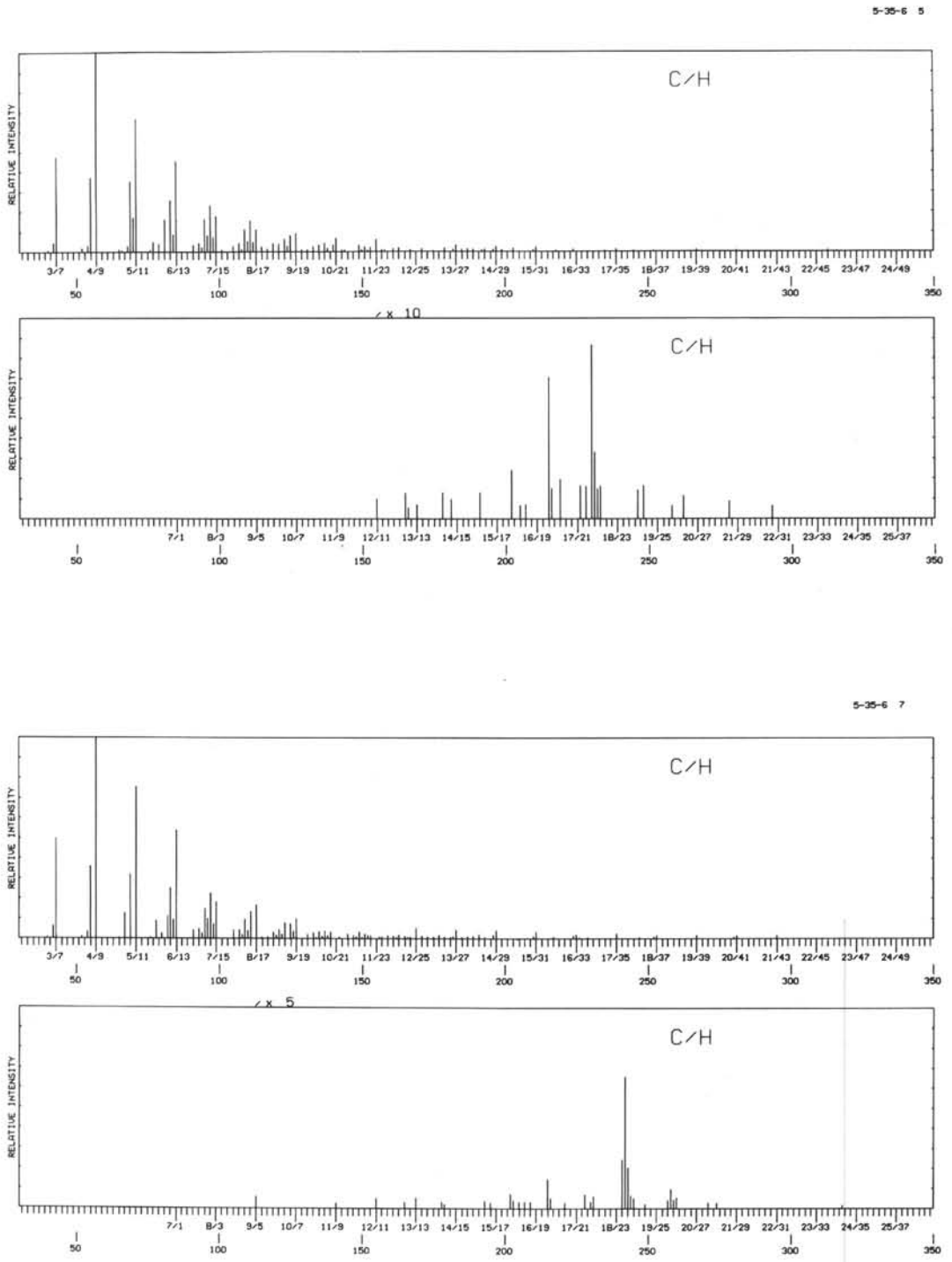


Figure 19. *Partial GLC-high resolution mass spectral data for the alkanes from the exhaustive extract of Sample 5-35-6-3.*

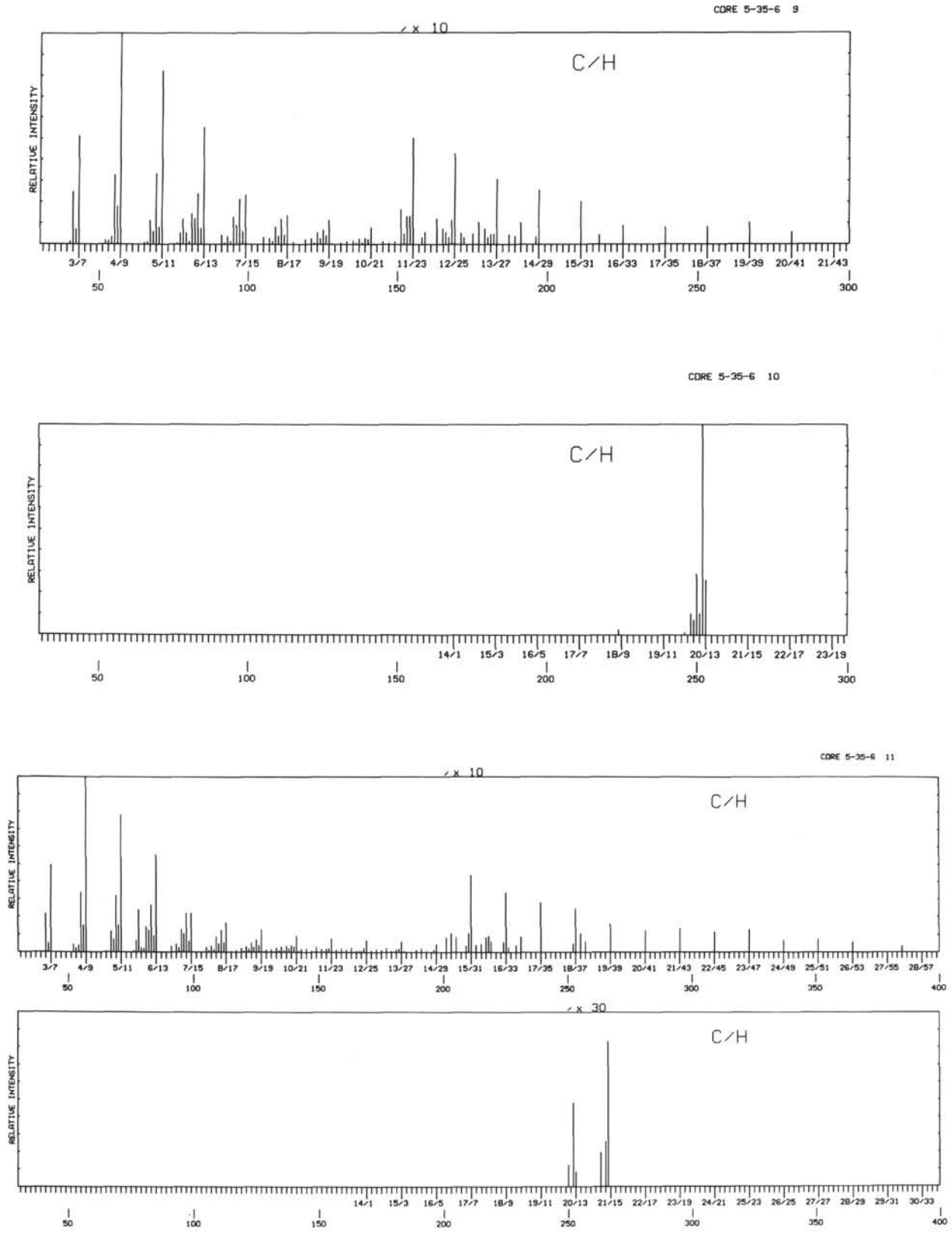


Figure 20. *Partial GLC-high resolution mass spectral data for the alkanes from the exhaustive extract of Sample 5-35-6-3.*

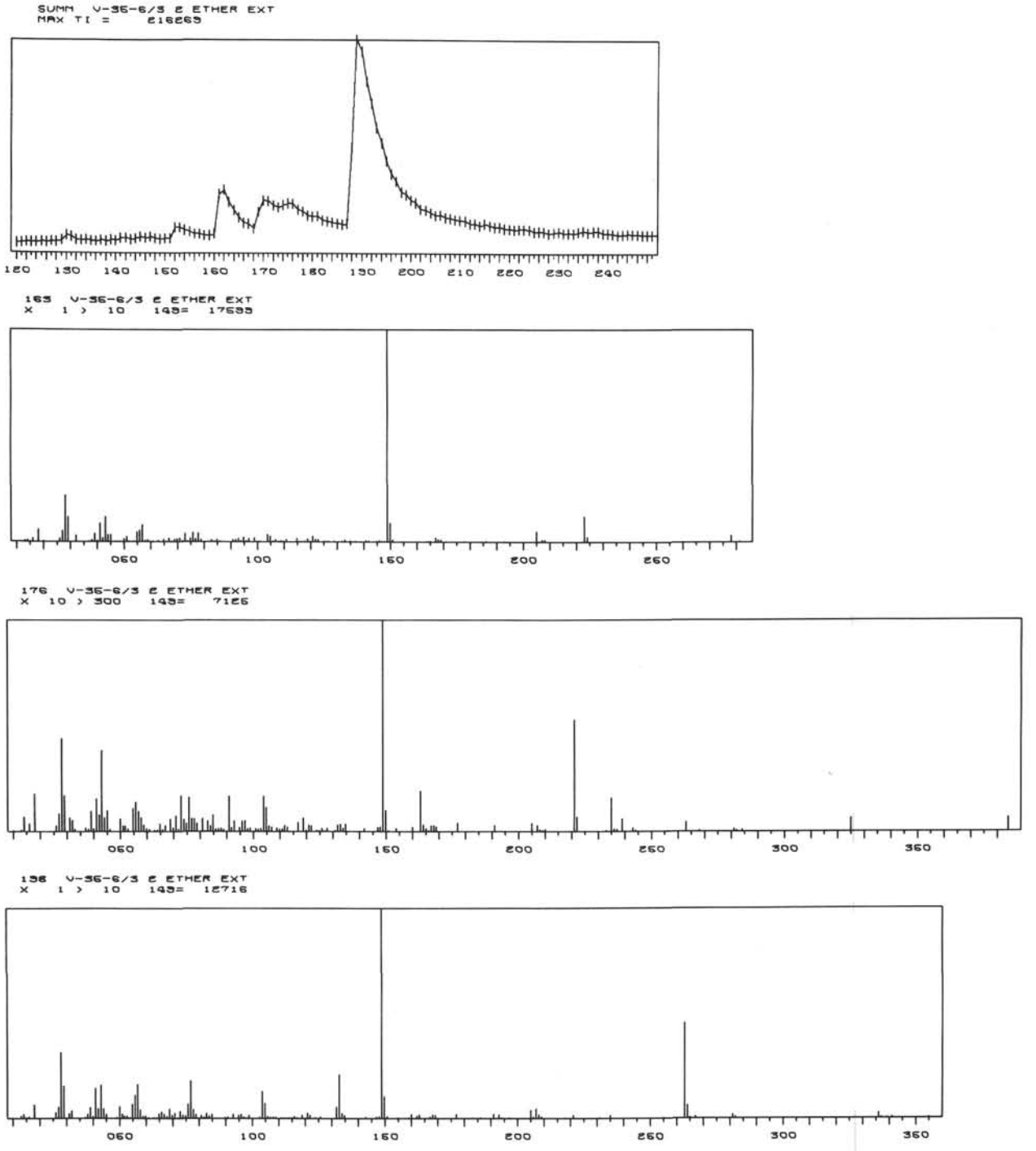
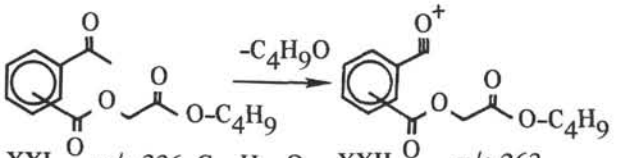


Figure 21. *Selected GC-MS data for the diethyl ether extract from the demineralization residue of Sample 5-35-6-3 (GC-MS column conditions as in Figure 9).*

butyoxy fragment to yield the peak at m/e 263 (Structure XXII), which in turn loses the fragment $C_6H_{10}O_2$ to yield the peak at m/e 149 (probably Structure V). It is suspected that these large amounts of phthalates are contaminants from the core tube which is made of cellulose acetate butyrate polymer. Samples of this material as well as the polyethylene tube caps are being analyzed at this laboratory.



XXI m/e 336, $C_{18}H_{24}O_6$ XXII m/e 263

A portion of the total acid esters isolated from the demineralization residue by heptane extraction was adducted with urea, yielding 0.6 milligram of normal and 0.2 milligram of branched-cyclic esters. The total, normal and branched-cyclic fractions were then analyzed by GLC (Figures 22a, b and c), and the total fraction was subjected to GC-MS analysis.

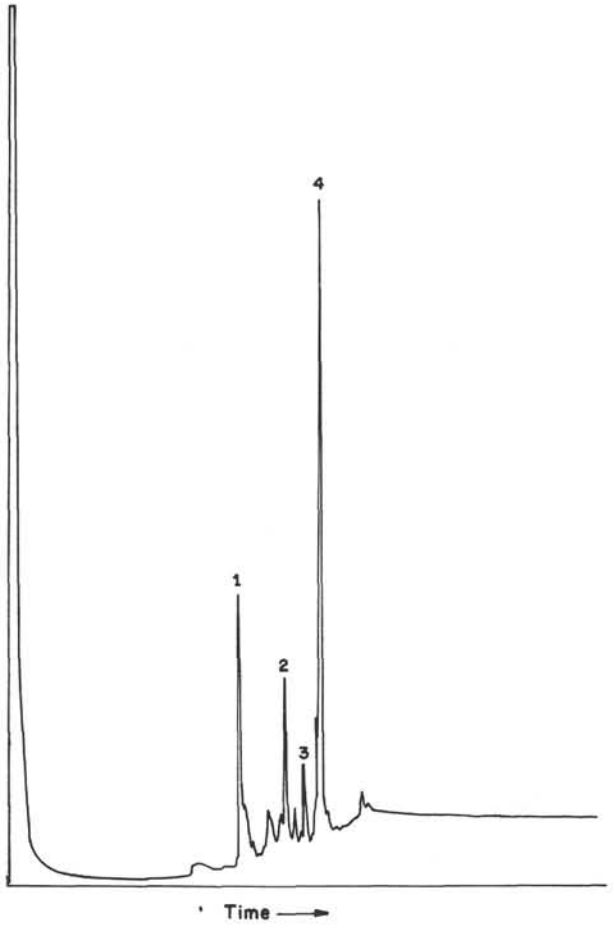


Figure 22a. *Gas chromatogram of the total acid esters isolated from the demineralized residue of Sample 5-35-6-3 (conditions as in Figure 9).*

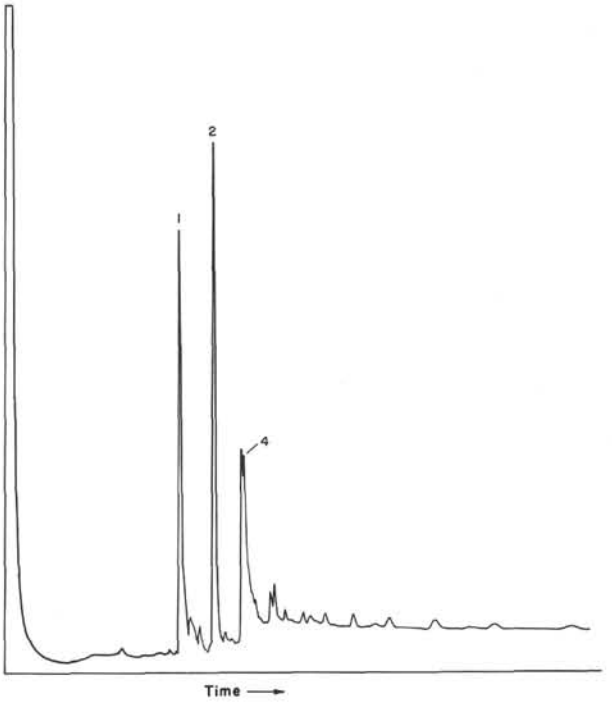


Figure 22b. *Gas chromatogram of the normal acid esters isolated by urea adductination of the total acid esters from the demineralization of Sample 5-35-6-3 (conditions as in Figure 9).*

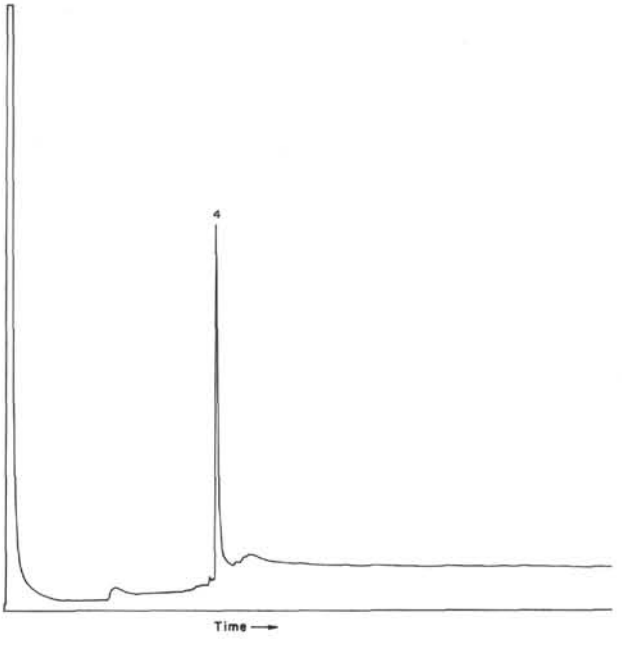
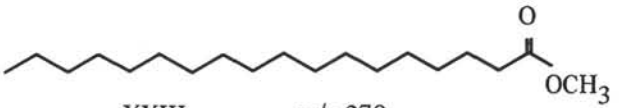


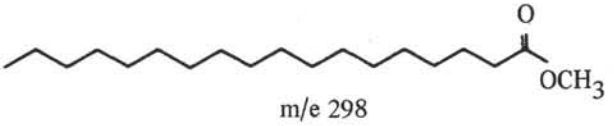
Figure 22c. *Gas chromatogram of the branched/cyclic acid esters isolated by urea adduction of the total acid esters from the demineralization of Sample 5-35-6-3 (conditions as in Figure 9).*

Selected GC-MS data for the total ester fraction from the demineralization is shown in Figure 23. The sum plot (Smith *et al.*, 1971) corresponds well with the GLC in Figure 22a. Scan 100 of Figure 23, which corresponds to the GLC peak labeled 1 in Figure 22a, fits the fragmentation pattern of methyl patmitate (Structure XXIII). Scan 109 appears to be a mixture of



XXIII m/e 270

phthalates (Structure V) and a benzene tricarboxylic acid ester (Structure XX) as was found in scan 176 of Figure 23. Scan 118 (GLC peak 2 in Figure 22a) fits the fragmentation pattern of methyl stearate (Structure XXIV). Scan 126 (GLC peak 3 in Figure 22a)



m/e 298

appears to be the fragmentation pattern of a cyclic ester belonging to the series $C_nH_{2n-10}O_2$ for n = 20 (molecular weight of 316). Scan 132 is a mixture of several components, namely phthalate esters and cyclic acid esters. Scan 136 (GLC peak 4 in Figures 22a and c) fits the fragmentation pattern of an oxygenated polycyclic compound encountered in other background and sample data. The compositions were determined to be $C_{21}H_{30}O_2$ for the peak at m/e 314, $C_{20}H_{27}O_2$ for m/e 299 and $C_{18}H_{23}$ for m/e 239. A structure assignment is not possible at this time.

The heptane soluble alkanes liberated after demineralization of the sample were analyzed by GLC and the trace is shown in Figure 24. The major peaks are a homologous series of normal alkanes ranging from C_{17} to C_{30}.

Sample 8-74-9-2:
This sample was extracted by ultrasonication with distilled water to remove water soluble salts and lower weight organic compounds. This water extract is under further analysis. The sample was then dried and extracted ultrasonically with benzene and methanol (3:1). The total extract yield was 1.1 per cent of the original sample weight. This extract was treated with a heptane and ether mixture to remove the less polar organic compounds and yielded 0.0007 per cent (based on original sample) of extractables. A GLC of this residue is shown in Figure 25, and the major peak appears to have the same retention time as peak 4 in Figure 22a. This fraction is under further analysis. The remaining benzene and methanol extract residue does not give a good GLC analysis.

The exhaustively extracted residue was then treated with hydrochloric acid (HCl) and the reaction mixture extracted with heptane and ether, followed by benzene and methanol mixtures using ultrasonication to aid the process. The heptane and ether extract residue amounted to 0.0013 per cent (based on the original sample weight) and the benzene and methanol extract residue was 1.42 per cent. A GLC of the heptane and ether extract residue is shown in Figure 26 and indicates mainly a series of probably alkanes ranging from C_{22} to C_{30}. Again, the benzene and methanol extract residue does not yield any GLC data. Both of these extracts are undergoing further analyses.

CONCLUSIONS

The more detailed examination of Sample 5-35-6-3 and the general survey data of samples from Legs 5, 6 and 7 (Simoneit and Burlingame, 1971) seem to indicate that the terpenoidal compounds and some of the steroidal compounds may be terrigenous in origin. The presence of terpenoidal compounds was assumed by the appearance of strong m/e 191 and sometimes m/e 177 peaks in both the high and low resolution mass spectral data, as well as molecular ion compositions fitting such carbon skeletons as, for example, Structure VI reported then (Simoneit and Burlingame, 1971). The Leg 8 core samples discussed in this report do not indicate the presence of any terpenoidal compounds. These samples originate from the Central Pacific Ocean. They do contain sterols and steranes, which can be derived from marine or terrigenous sources. The geologic age of these Leg 8 samples ranges from 11 to 40 million years. The excellent state of preservation of the organic matter with regard to structural and functional features is noteworthy in comparison to terrestrial samples of similar age (for example, Burlingame *et al.*, 1969).

These Leg 8 samples contain comparatively low amounts of extractable organic material (see Table 1 and Simoneit and Burlingame, 1971). Thus the problem of organic contamination is becoming very obvious. The suite of phthalates isolated from these samples are quite unambiguously contaminants, the suspected source being the cellulose acetate butyrate core tubes. Hydrolysis products of these esters are, however, more difficult to tag as contaminants, as for example benzene dicarboxylic acid (derived from any phthalate by hydrolysis) would be carried through the carboxylic acid separation scheme and finally be detected as a benzene dicarboxylic acid dimethyl ester. In order to avoid such ambiguity in the future and to possibly reduce the overall organic contamination, more detailed analytical studies of the organic materials involved in the sampling program will be carried out at this laboratory. The analytical methods used are analogous to those reported (Simoneit, 1971 and Simoneit and Flory, 1971).

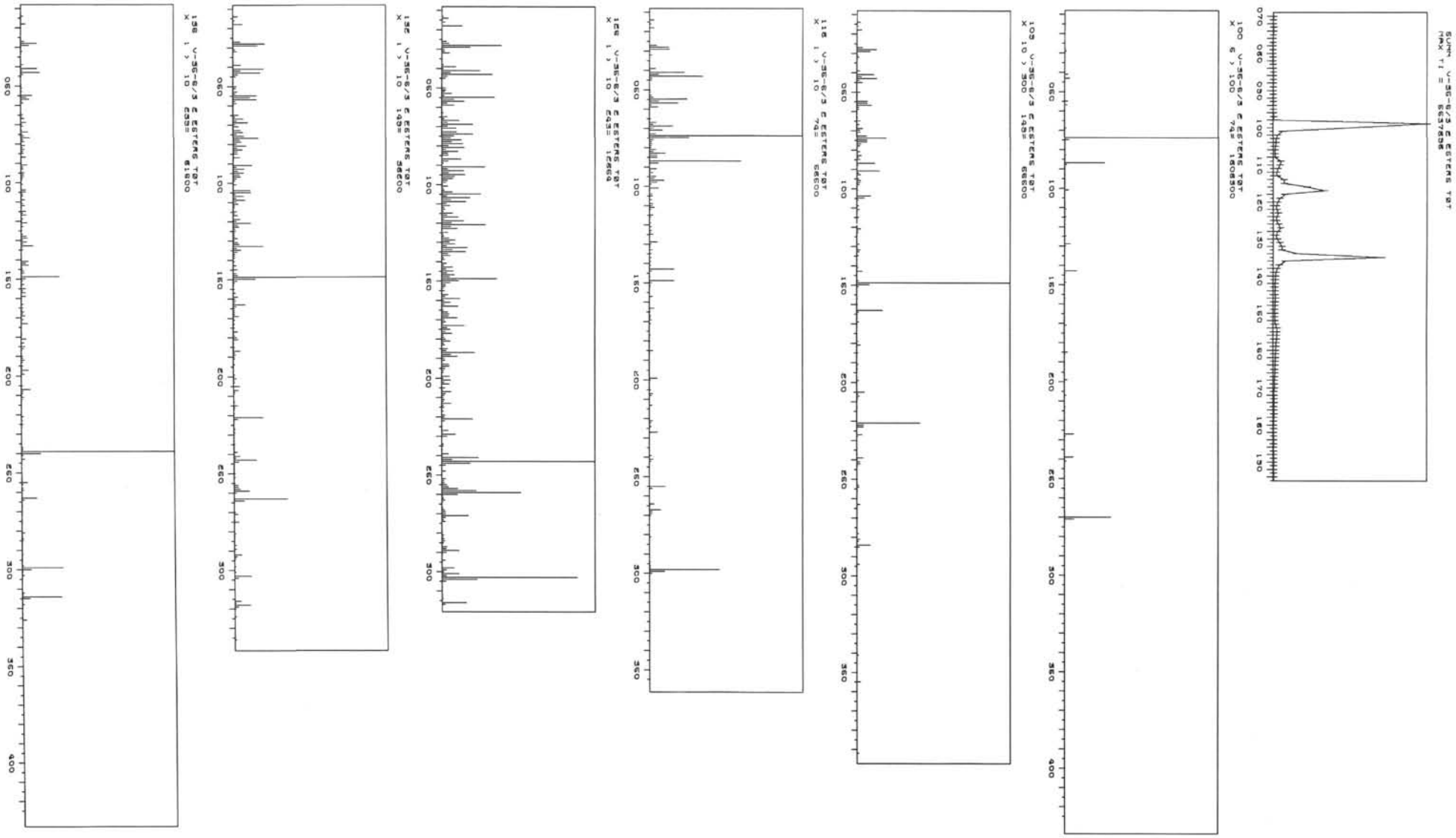


Figure 23. *Selected GC-MS data for the total acid ester fraction isolated from the demineralization residue of Sample 5-35-6-3 (GC-MS column conditions as in Figure 9).*

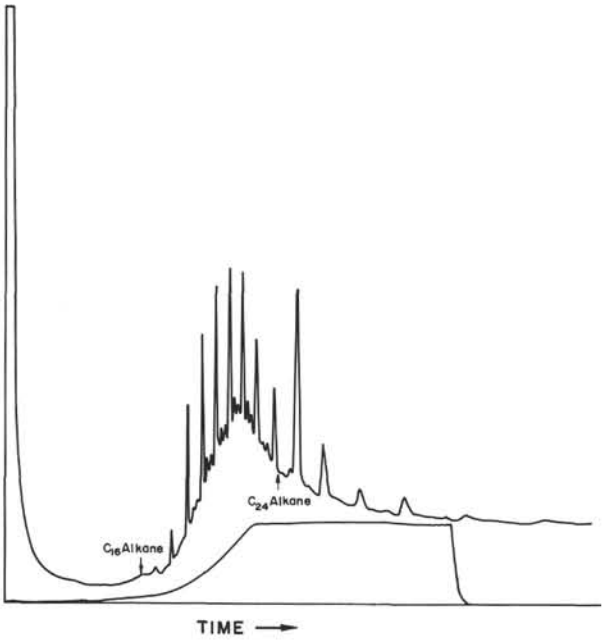


Figure 24. *Gas chromatogram of the heptane soluble alkanes isolated from the demineralization residue of Sample 5-35-6-3 (conditions as in Figure 9).*

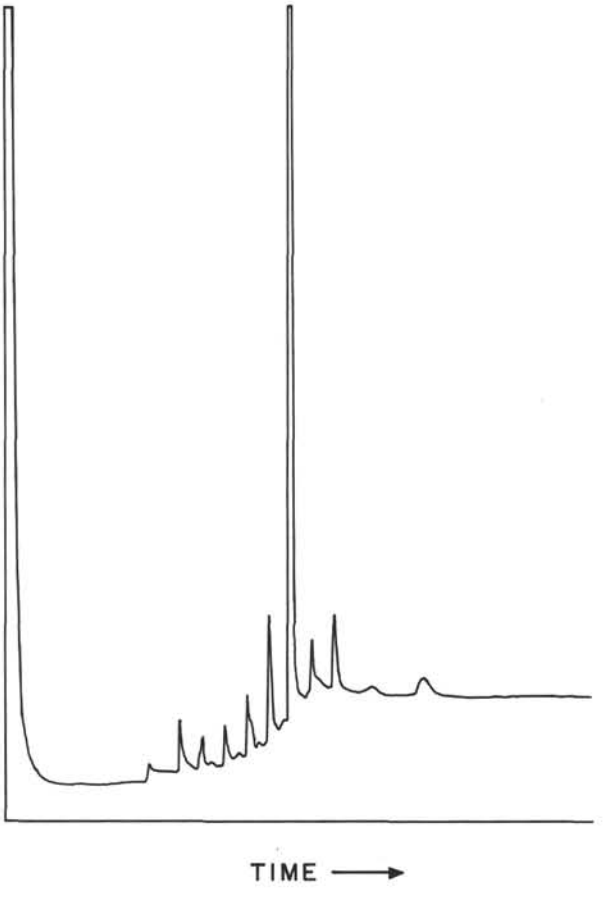


Figure 25. *Gas chromatogram of the heptane and ether extract of Sample 8-74-9-2 (conditions as in Figure 9).*

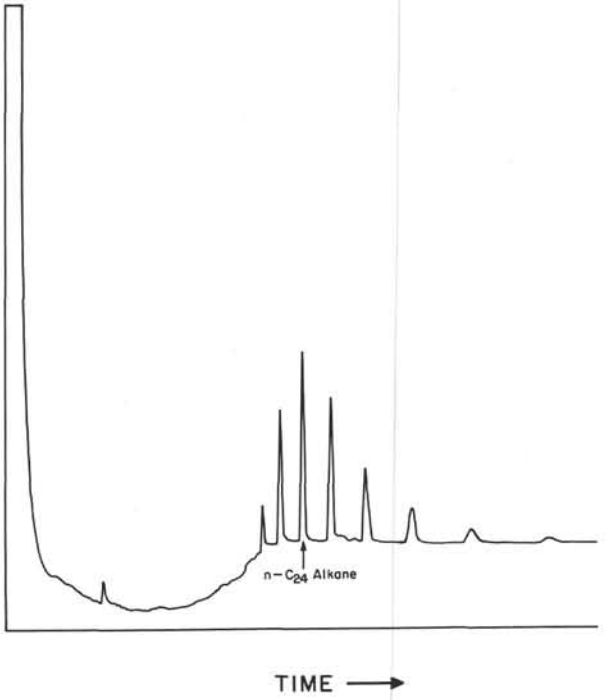


Figure 26. *Gas chromatogram of the heptane and ether extract residue from the demineralized Sample 8-74-9-2 (conditions as in Figure 9).*

ACKNOWLEDGMENTS

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