19. FURTHER PRELIMINARY RESULTS ON THE HIGHER WEIGHT HYDROCARBONS AND FATTY ACIDS IN THE DSDP CORES, LEG 9[1]

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ABSTRACT

The core samples analyzed from DSDP Leg 9 range in age from Pliocene to lower Miocene and consist mainly of chalk or ooze containing foraminifera, Radiolaria and nannoplankton fossils. The analytical procedure consisted essentially of solvent extraction followed by high resolution mass spectrometry, GLC and GLC-MS analyses on total or separated extract fractions. Although several samples were contaminated with extraneous organic material, the indigenous solvent extractable organic matter consisted mainly of normal alkanes with minor amounts of carboxylic acids and some sterols and their diagenetic products. The alkanes, C_nH_{2n+2}, are found for approximately n = 16-32 in some samples, and the carboxylic acids consist mainly of palmitic and stearic acids. The sterols and their derivatives are found in the C_{27} to C_{29} carbon range. Again, the remarkable state of preservation of the organic matter in these cores is quite noteworthy.

INTRODUCTION

The core samples analyzed from DSDP Leg 9 range in age from Pliocene to lower Miocene (2 to 20 X 10^6 years) and consist mainly of chalk or ooze containing foraminifera, Radiolaria and nannoplankton fossils. All the samples were cored at 3000 to 4500 meters water depth in the equatorial Pacific. The following preliminary study of the organic geochemistry of these samples will further supplement the previous reports (see Simoneit and Burlingame, 1971a and b). The analytical procedures were kept the same, as much as possible, making correlations with the previous data more feasible.

EXPERIMENTAL

The small (approximately 1 to 2 grams) samples remaining from the carbon analyses of Leg 9 were solvent (3:1 benzene and methanol or acetone) extracted as was the case for the samples from previous legs (Simoneit and Burlingame, 1971a and b). The bulk of the organics was 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 (Table 1). It should be noted that in samples where the acetone solubles are high, a large salt residue remained insoluble. Some of the heptane extracts, as well as some of the acetone extracts, were subjected to high resolution mass spectrometry. These analyses were carried out on a GEC-AEI MS-902 mass spectrometer on-line to an XDS Sigma-7 Computer (described by Burlingame, 1968 and 1970 and Burlingame *et al.*, 1970). The samples were introduced via a ceramic direct inlet probe into the ion source, operated at the following conditions: resolution 10,000 to 12,000; ionizing current 500μA; 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 in the respective figure legends. Analyses using gas chromatography-mass spectrometry were carried out on a modified Perkin-Elmer Model 270 GC-MS linked on-line to an XDS Sigma-2 Computer (Smith *et al.*, 1971).

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TABLE 1
DSDP Small Core Sample Extracts, Leg 9

Sample	Organic Carbon (Per Cent)	Heptane Extract (ppm)	Acetone Extract (ppm)	Approximate Age	Type
9-77B-19-1 (25-150 cm)	0.040	22.4	392	Upper Miocene	Foraminiferal-nannoplankton-radiolarian ooze
9-77B-25-2 (13-97 cm)	0.060	–	290	Pliocene	Foraminiferal-nannoplankton-radiolarian ooze
9-78-29-6 (75-150 cm)	0.500	9.7	874	Upper Oligocene	Foraminiferal-nannoplankton chalk
9-79-13-3 (79-150 cm)	0.065	18.0	493	Upper Miocene	Foraminiferal-nannoplankton-radiolarian ooze
9-79A-2-6 (79-150 cm)	0.510 0.110	412.0	1440	Upper Miocene	Foraminiferal-nannoplankton-radiolarian ooze
9-80A-5-5 (60-150 cm)	0.530	139.0	1315	Lower Miocene	Foraminiferal-nannoplankton-radiolarian chalk
9-82A-3-5 (82-150 cm)	0.160	64.0	1300	Pliocene	Foraminiferal-nannoplankton-radiolarian ooze
9-83A-10-4 (52-150 cm)	1.400 0.240	344.0	1583	Pliocene	Foraminiferal-nannoplankton-radiolarian ooze
9-83A-13-4 (92-150 cm)	0.950 0.200	256.0	2360	Upper Miocene	Nannoplankton-radiolarian ooze
9-84-16-6 (70-150 cm)	1.770 0.440	105.0	116	Pliocene	Foraminiferal-nannoplankton-radiolarian chalk

The larger samples packed and frozen in Kapak pouches were defrosted and extracted under a nitrogen atmosphere with 3:1 benzene and methanol in a Soxhlet extractor. These Kapak pouches were leached with benzene and methanol (3:1), and the extract concentrate was analyzed for organic contaminants (see Simoneit and Burlingame, 1971a). The procedures used for extraction and functional group separations were essentially the same as described by Burlingame and others (1969), except that 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, 1971a and b, and Burlingame *et al.*, 1969) are discussed in the Results section of this report.

In order to assess further possible sources of organic contamination in the DSDP samples, the core tube material and the core tube caps were leached with benzene and methanol (3:1), and the extract concentrates were analyzed as usual.

RESULTS

The small samples remaining from the carbon analysis were extracted with acetone or benzene and methanol, and the extract yields are listed in Table 1. The data obtained on these samples will be discussed first.

Core 9-77B-19-1

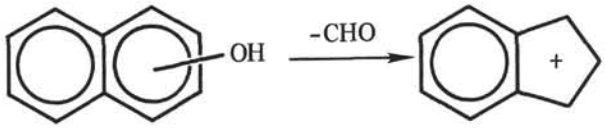
The acetone soluble portion of the total extract of this sample was analyzed by GLC and high resolution mass spectrometry, and the data are shown in Figures 1 and 2. The GLC indicates compounds with retention times mainly less than that of a C_{24} alkane. The high resolution mass spectral data indicate this extract consists mainly of oxygenated polar compounds. The major compound classes present are possibly phenols of the series $C_nH_{2n-6}O$ for n = 6, 7 and 8, $C_nH_{2n-6}O_2$ for n = 6, 7 and 8 and $C_nH_{2n-6}O_3$ for n = 6 and 7. Low molecular weight carboxylic acids are present in minor amounts ($C_nH_{2n}O_2$ for n = 2 to 6). Alkanes are at background levels. Phthalate ester contamination is also very low (see peak of composition $C_8H_5O_3$[3] in the C/H O_3 plot of Figure 2.

Core 9-77B-25-2

The total acetone extract residue was subjected to GLC and high resolution mass spectral analyses, and the data are shown in Figures 3 and 4. During the Soxhlet extraction the receiver flask had gone dry (the flask-to-extractor seal was not tight), and the extract represents the soluble residue remaining in the extractor (see Table 1). The major constituents appear to be hydrocarbons and some oxygenated species. The alkanes are present mainly as the series C_nH_{2n+2} for n = 3 to 12 and C_nH_{2n} for n = 3 to 11. Minor amounts of phthalates are present. The strong peak of composition $C_6H_8O_2$ (see C/H O_2 plot of Figure 4) is probably derived by pyrolytic dimerization of acetone. Residual ethanol solvent is indicated by the peaks of compositions C_2H_6O, C_2H_5O, C_2H_4O and C_2H_3O; the latter can also be derived from acetone. Possible phenolic compounds are indicated to be present ($C_nH_{2n-6}O$ for n = 6, 7 and 8).

Core 9-78-29-6

The heptane extract residue of this sample (Table 1) was analyzed by high resolution mass spectrometry only, and the data are shown in Figure 5. The alkane concentration in the extract is very low, and the major constituents appear to be contaminants. Naphthol is indicated to be present in large amounts by the peaks of compositions $C_{10}H_8O$ (Structure I), $C_{10}H_7O$ and C_9H_7 (Structure II). Dibutyl phthalate is found in



I II

significant concentration (see peaks of compositions $C_8H_5O_3$, $C_8H_7O_4$ and $C_{12}H_{15}O_4$ in Figure 5). A group of peaks of unknown derivation belonging to the series $C_{19}H_{15}O_2$ for n = 2 to 5 are present in the data. Carboxylic acids, $C_nH_{2n}O_2$ for n = 3 to 8, 11, 13 and 16, are present as minor constituents, and

[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 subsequently given. 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.

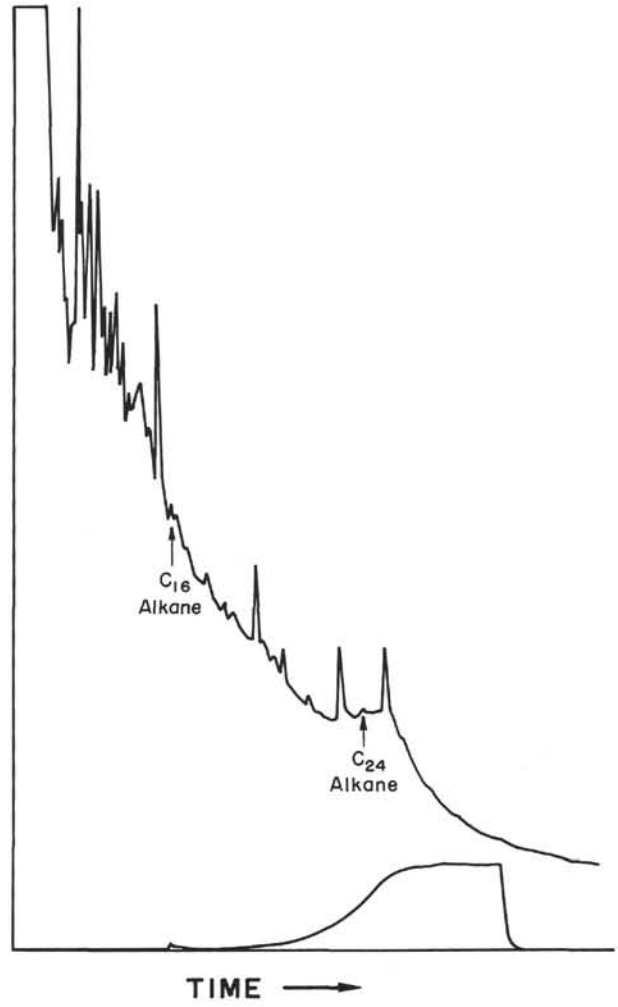


Figure 1. *Gas chromatogram of the acetone solution extract from Core 9-77B-19-1. (Conditions: 10 foot by 1/8 inch stainless steel columne, packed with 3 per cent OV-1 on 100 to 120 mesh Gaschrom Q, programmed from 100 to 250° at 8°/min and using He at 40 m1/min. The arrows indicate the relative retention times of a C_{16} and C_{24} normal alkane, and the lower trace is the background.)*

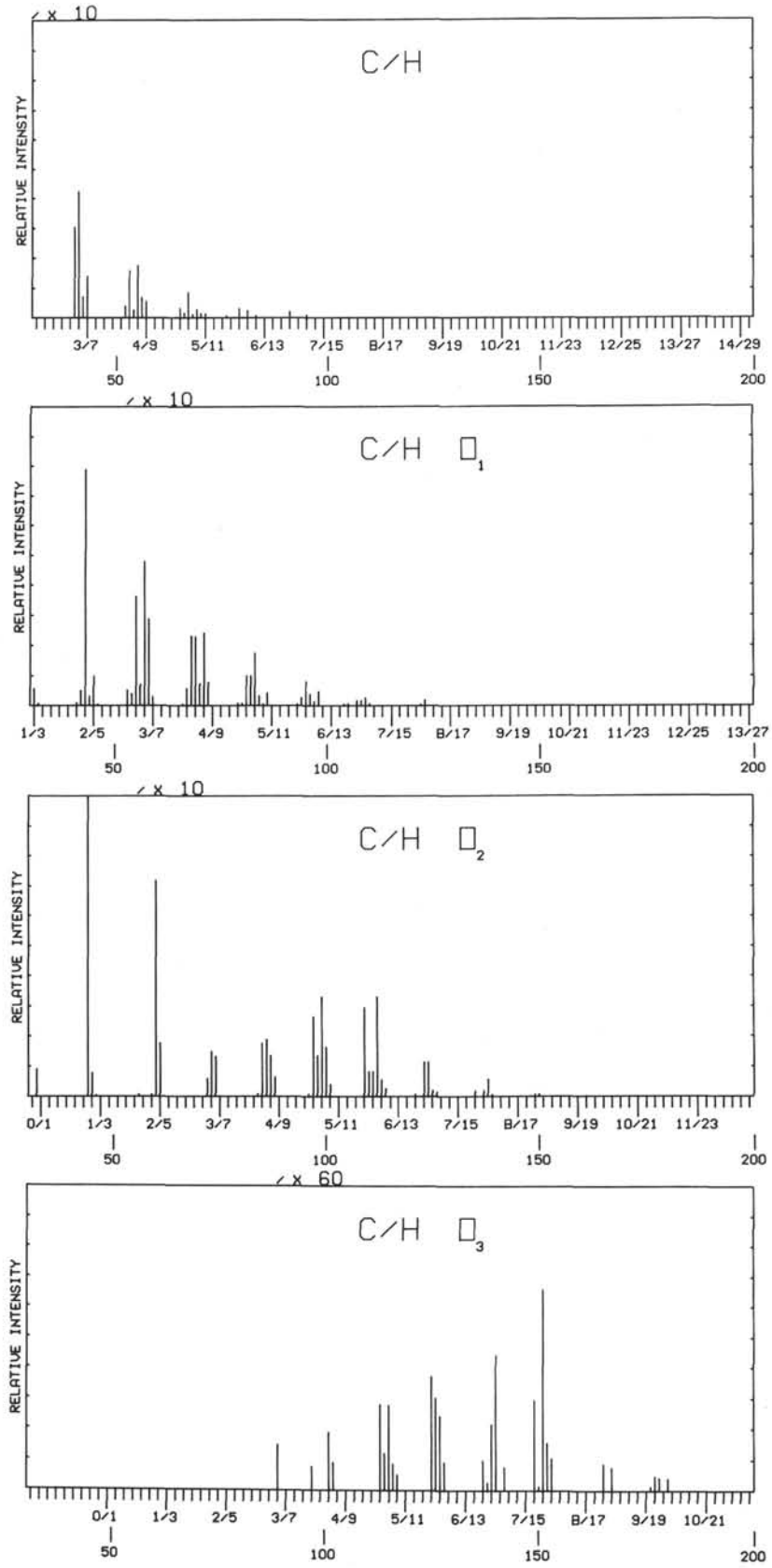


Figure 2. *Partial high resolution mass spectral data for the acetone soluble extract residue from Core 9-77B-19-1.*

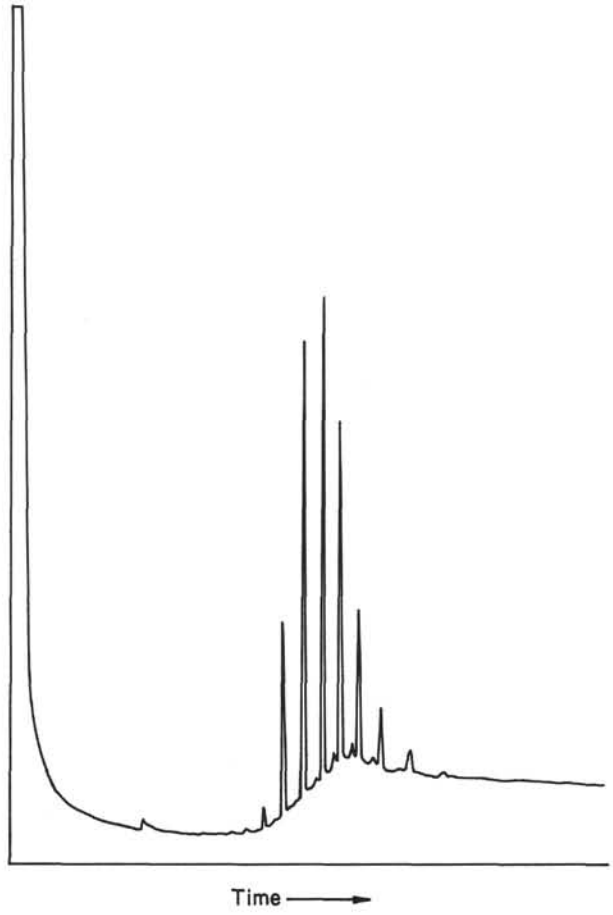


Figure 3. *Gas chromatogram of the total acetone extract residue from Core 9-77B-2. (Conditions as in Figure 1.)*

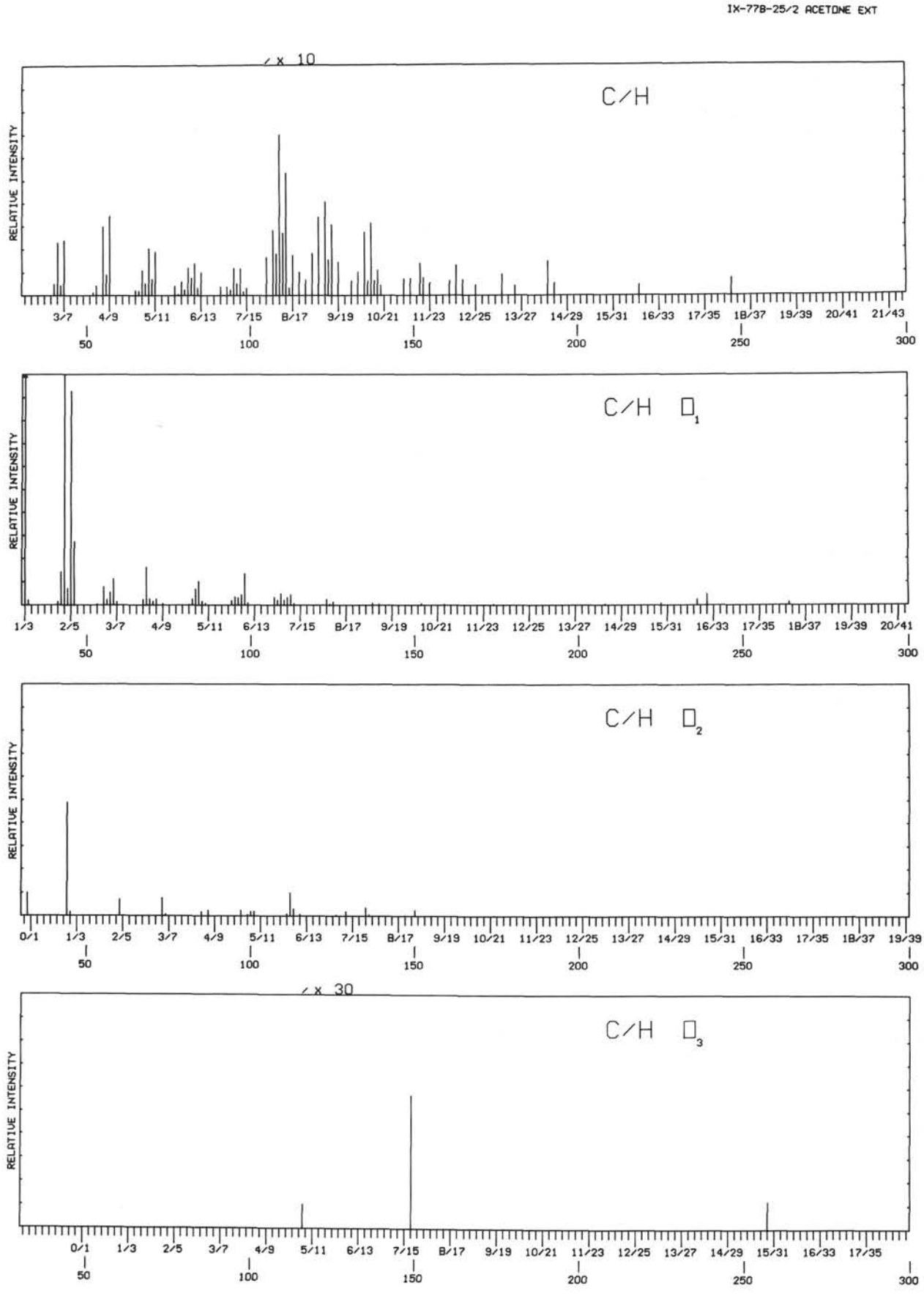


Figure 4. *Partial high resolution mass spectral data for the acetone residue from Core 9X-77B-25-2.*

alkanes of the series C_nH_{2n} to C_nH_{2n-8} for n = 3 to 11 (not each homolog is found) are also indicated.

Core 9-79-13-3

The heptane extract residue of this sample was subjected to GLC analysis, and the trace is shown in Figure 6. Sample size did not allow further analysis to date, but the GLC pattern indicates the major peaks are probably due to alkanes. The relative retention times (established by coinjection of standards) range from approximately n-C_{24} to C_{34} alkanes. The high resolution mass spectral data for the acetone extract residue are shown in Figure 7. The major constituents are alkanes of the series C_nH_{2n+2} to C_nH_{2n-8} for n = 3 to 11, not every homolog being present, and carboxylic acids, $C_nH_{2n}O_2$ for n = 2 to 7, 10, 11 and 16 (palmitic acid $C_{16}H_{32}O_2$ is the most abundant). Phthalate esters (see peak of composition $C_8H_5O_3$ in the C/H O_3 plot of Figure 7), phenols ($C_nH_{2n-6}O$ for n = 6, 7 and 8) and cyclohexanone are present in minor amounts.

Core 9-79A-2-6

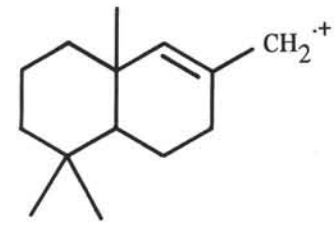
The heptane extract residue from this sample was analyzed by low resolution mass spectrometry, and the data are shown in Figure 8. The peaks at m/e 382, 384, 386, 396, 398, 400, 410, 412 and 414 probably represent a group of sterols or sterones with carbon skeletons ranging from C_{27} to C_{29} and containing probably one oxygen atom per molecule. A general hydrocarbon fragmentation pattern is evident in the lower weight range, extending to m/e 212 and 210, which fit molecular ions of possibly pentadecane and pentadecene, respectively.

Core 9-80A-5-5

This sample was exhaustively extracted with benzene and methanol (3:1), and the extract residue was analyzed by high resolution mass spectrometry (see Figure 9) and then divided into heptane and acetone soluble fractions. The major components of the total exhaustive extract are alkanes of the series C_nH_{2n+2} for n = 3 to 23 (see C_nH_{2n+1} fragment ion series in the C/H plot of Figure 9). The hydrocarbon series C_nH_{2n} to C_nH_{2n-10} for n = 4 to 18 with not every homolog present are found in minor amounts, and oxygenated material (for example, C_6H_6O–possibly phenol) is present in traces. The GLC traces of the acetone and heptane soluble fractions are shown in Figure 10a and b, respectively. The major peak in both GLC traces has not been identified yet, but the remaining peaks in the heptane trace resemble an alkane pattern.

Core 9-82A-3-5

The acetone extract residue of this sample was analyzed by GLC and both low and high resolution mass spectrometry. The GLC trace exhibited a group of skew peaks of relative retention times of less than that of n-eicosane. The low resolution mass spectrum, shown in Figure 11, indicates peaks at m/e 298 and 256, which fit the molecular weights of stearic and palmitic acids, respectively. These acids are also indicated to be present as signfiicant constituents in the high resolution mass spectral data shown in Figure 12. There are also peaks at m/e 254 (see Figure 11), fitting the molecular weight of a C_{18} alkane, and m/e 266, 252, 238, 224 and 210, fitting possible cyclic or unsaturated alkanes ranging from C_{15}-C_{19}. The high resolution data (see Figure 12) further indicate phthalate esters (see peak of composition $C_8H_5O_3$ in the C/H O_3 plot of Figure 12) and probably phenols of the series $C_nH_{2n-6}O$ for n = 6 to 9. It should also be noted that the peak of composition $C_{14}H_{23}$ at m/e 191 (Structure III) is significantly above background. The heptane extract residue of this sample was analyzed by



III $C_{14}H_{23}$, m/e 191

GLC and high resolution mass spectrometry. The GLC trace (Figure 13) is virtually identical to the trace of the heptane extract from Core 9-79-13-3 (Figure 6). The higher weight compounds have retention times corresponding to n-C_{22}-C_{32} alkanes (indicated by coinjection of standards). The high resolution mass spectrometric data are shown in Figure 14 and indicate mainly hydrocarbons, probably phytosterols and carboxylic acids with minor amounts of phenols and octoil. The hydrocarbons found belong to the series C_nH_{2n+2} to C_nH_{2n-14} for n = 3 to 20, not every homolog being present and the groups being more unsaturated, that is, the normal alkanes are not found as the major constituents of the hydrocarbons. Peaks of compositions fitting possibly phytosterols are found in the C/H O and C/H O_2 plots of Figure 14. For example, the peaks of compositions $C_{29}H_{48}O$ and $C_{29}H_{46}O$ can be represented by the possible Structures IV and V, stigmastenones; and $C_{27}H_{44}O$ can be drawn as possible Structure VI, a cholestenone. It should again be noted that the peak of composition $C_{14}H_{23}$ at m/e 191 (Structure III) is significantly above background, and no peaks derived by fragmentation of compounds such as Structures IV-VI, for example, are significantly intense. More detailed work on the actual structures and sources of these preliminary indicated

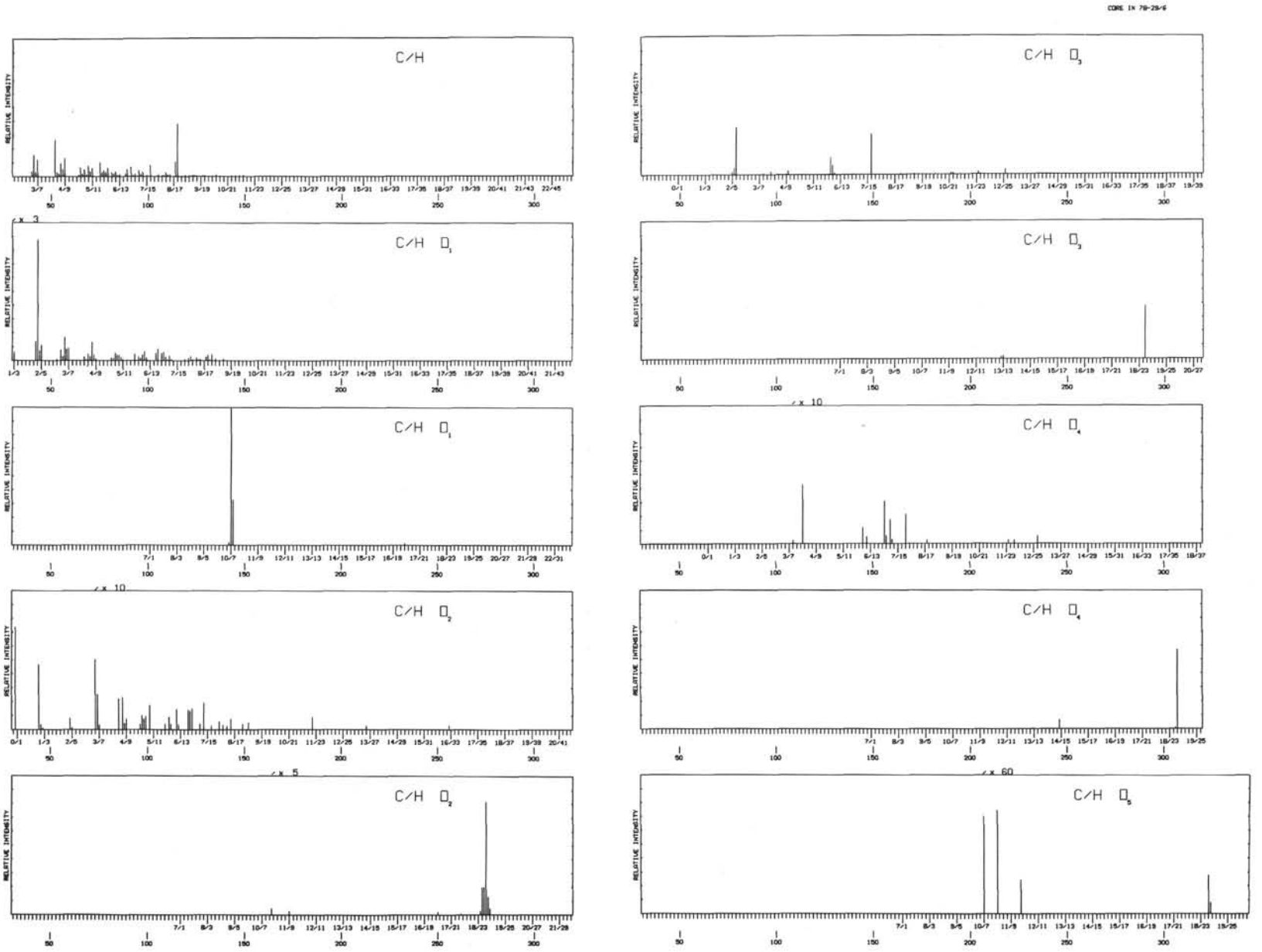


Figure 5. *Partial high resolution mass spectral data for the heptane extract residue from Core 9X-78-29-6.*

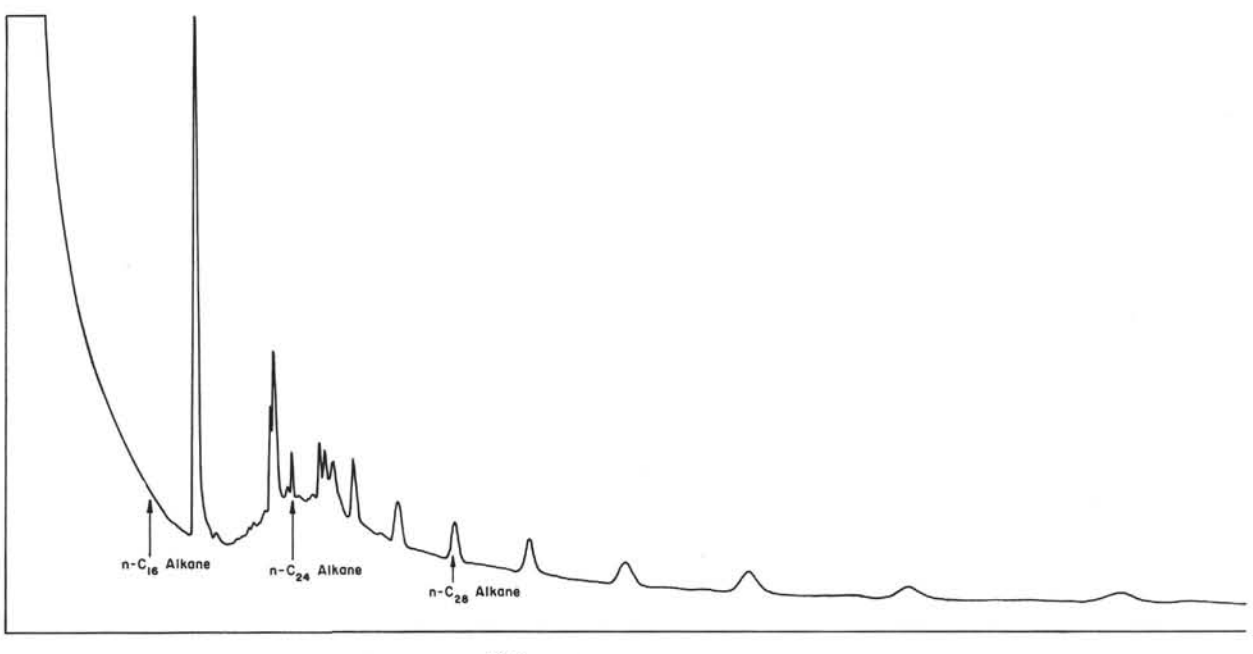


Figure 6. *Gas chromatogram of the heptane extract residue from Core 9X-79-13-3. (Conditions as indicated in Figure 1.)*

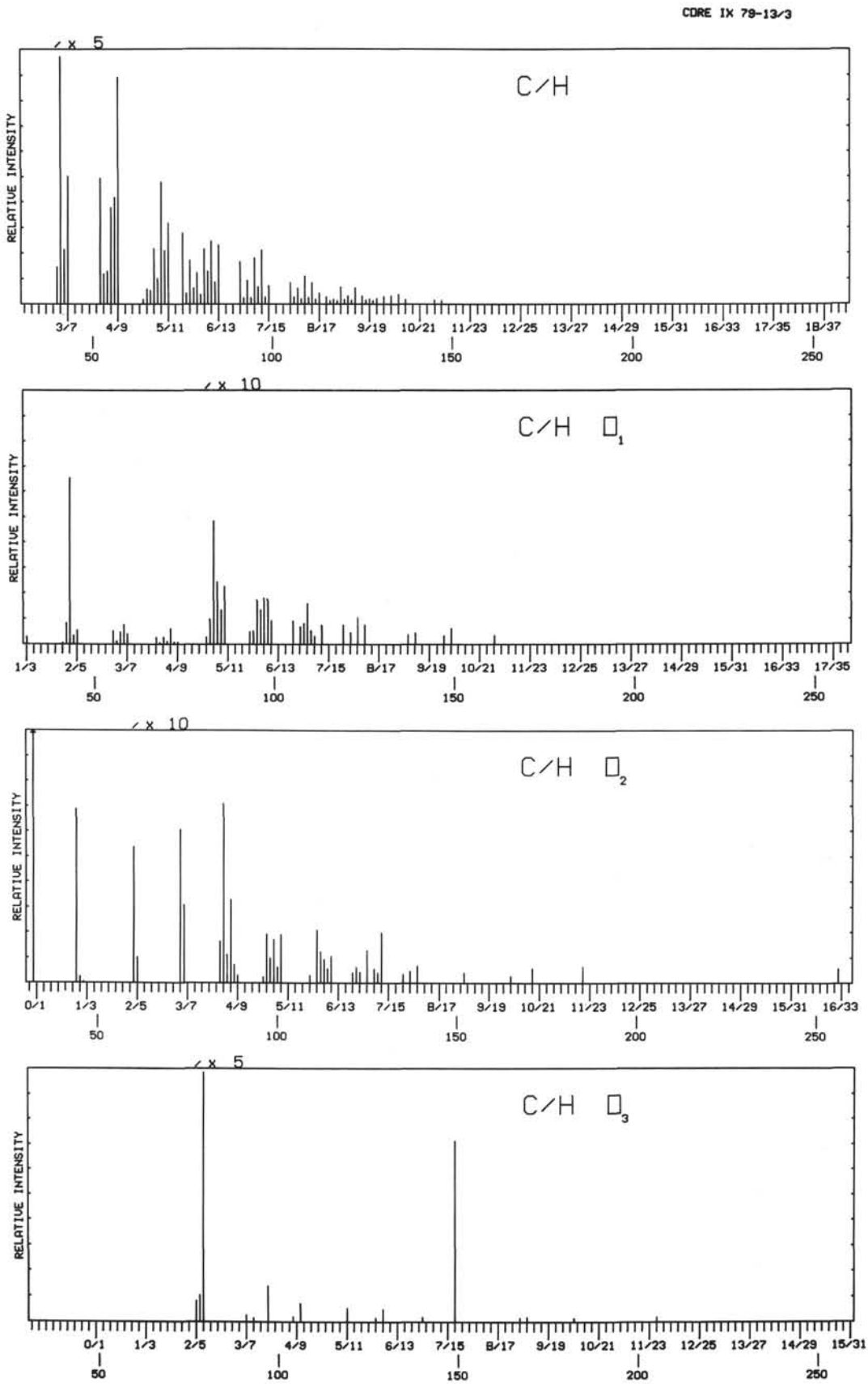


Figure 7. *Partial high resolution mass spectral data for the acetone extract residue from Core 9X-79-13-3.*

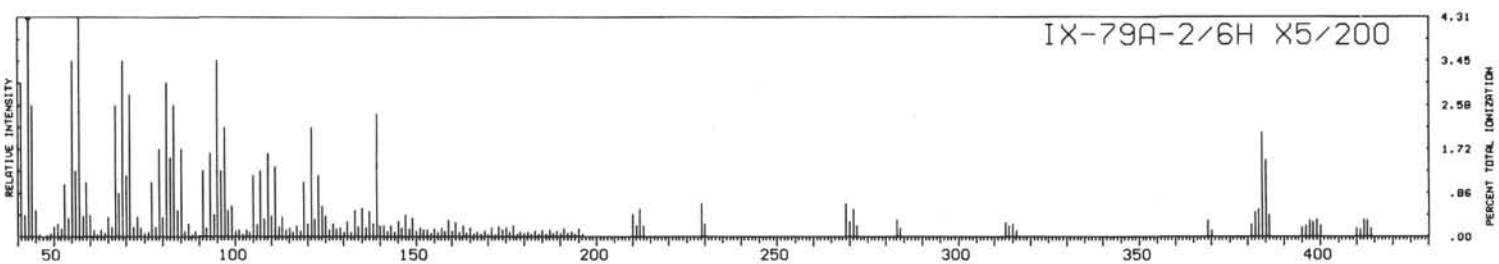


Figure 8. *Low resolution mass spectrum of the heptane extract residue from Core 9X-79A-2-6.*

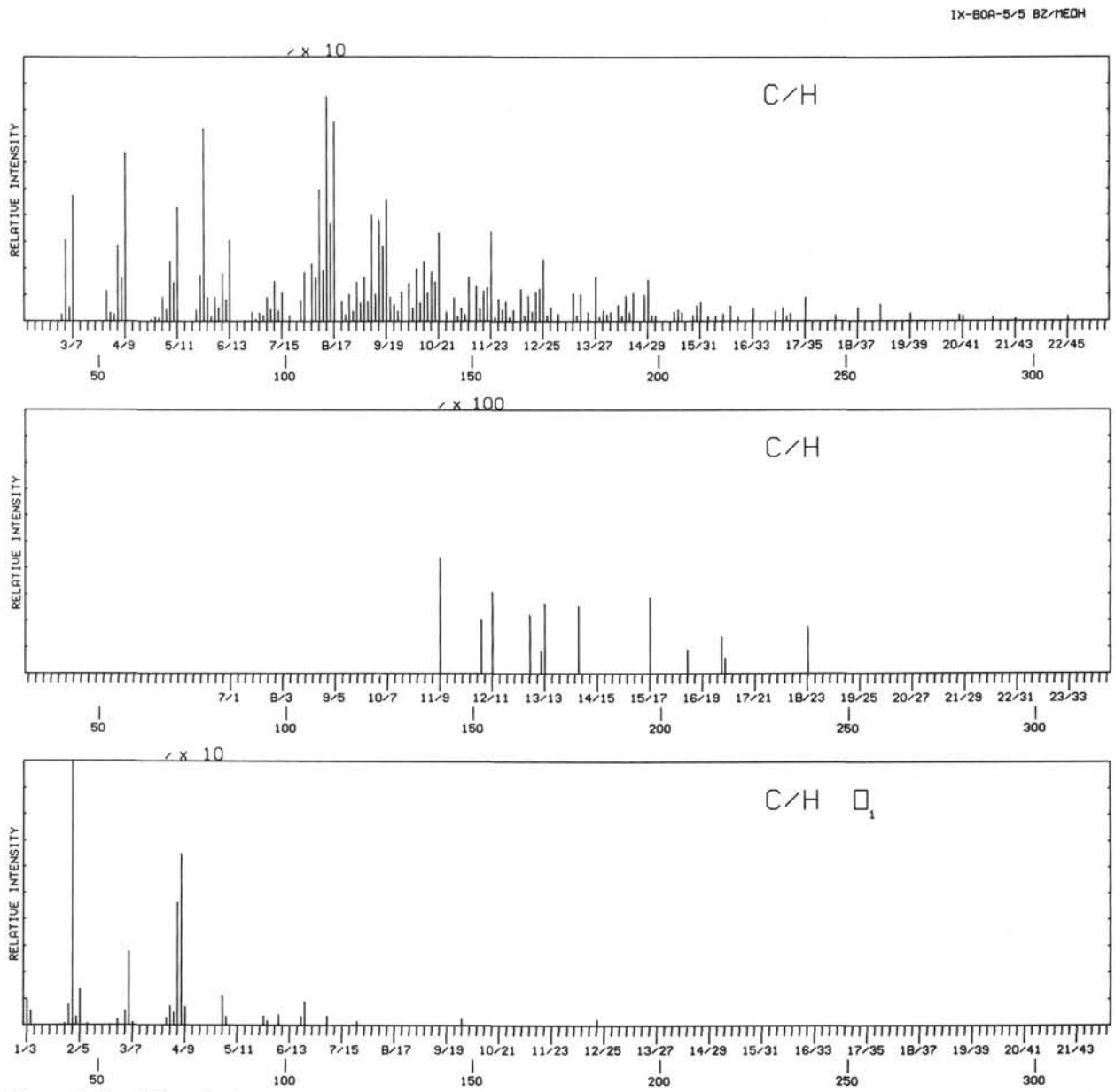


Figure 9. *Partial resolution mass spectral data of the benzene and methanol extract residue from Core 9X-80A-5-5.*

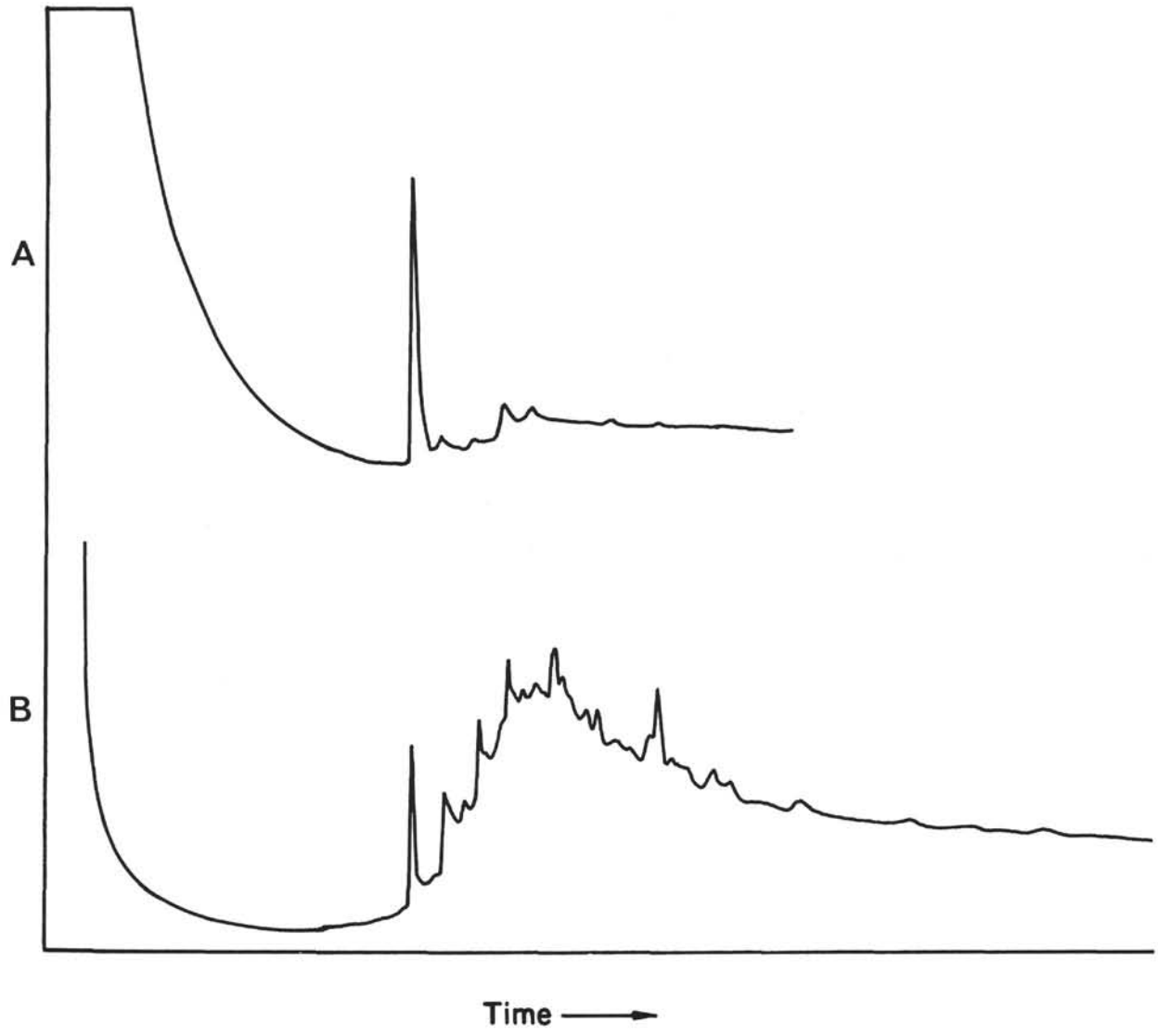


Figure 10a. *Gas chromatogram of the acetone extract residue from Core 9X-80A-5-5. (Conditions as cited in Figure 1.)*

Figure 10b. *Gas chromatogram of the heptane extract residue from Core 9X-80A-5-5. (Conditions as cited in Figure 1.)*

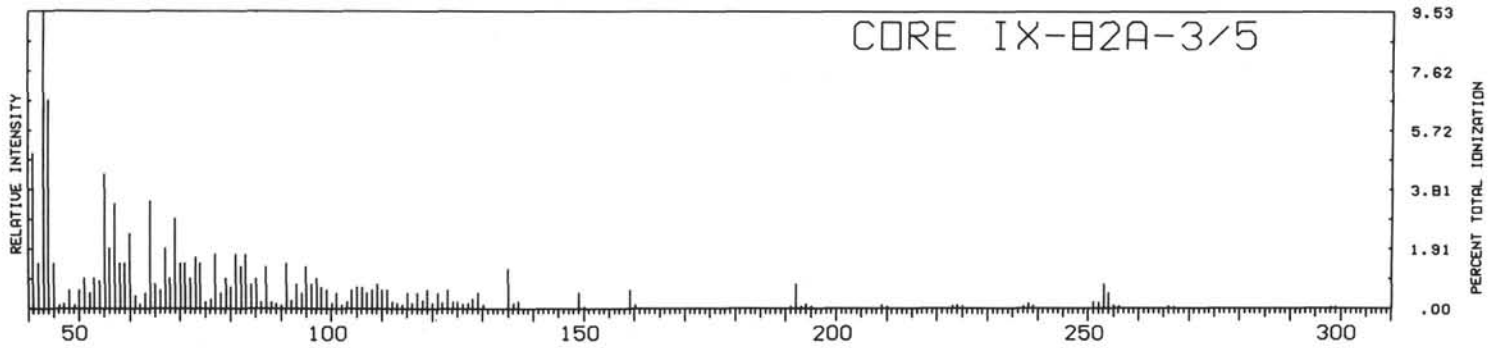


Figure 11. *Low resolution mass spectrum of the acetone extract residue from Core 9X-82A-3-5.*

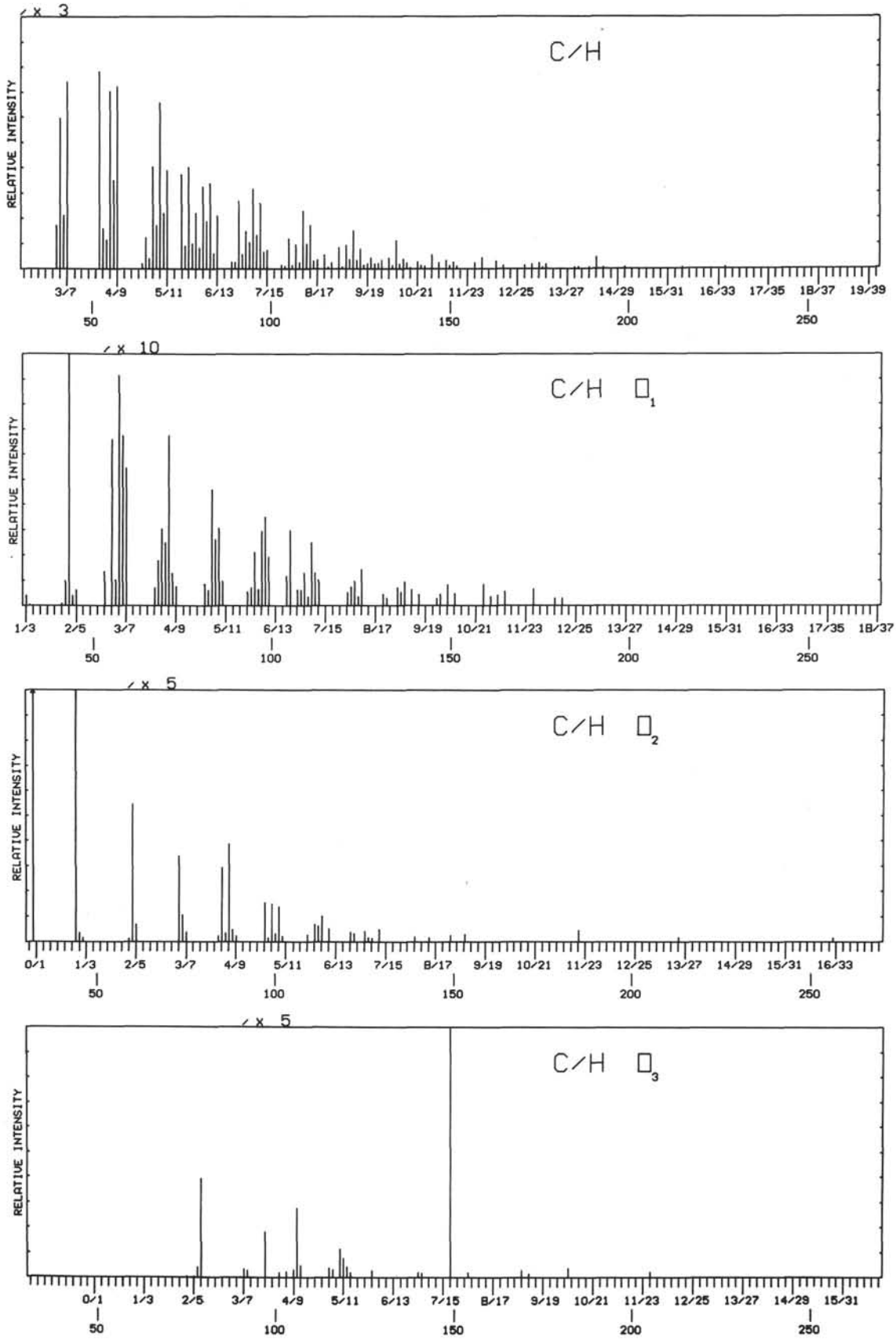


Figure 12. *Partial high resolution mass spectral data for the acetone extract residue from Core 9X-82A-3-5.*

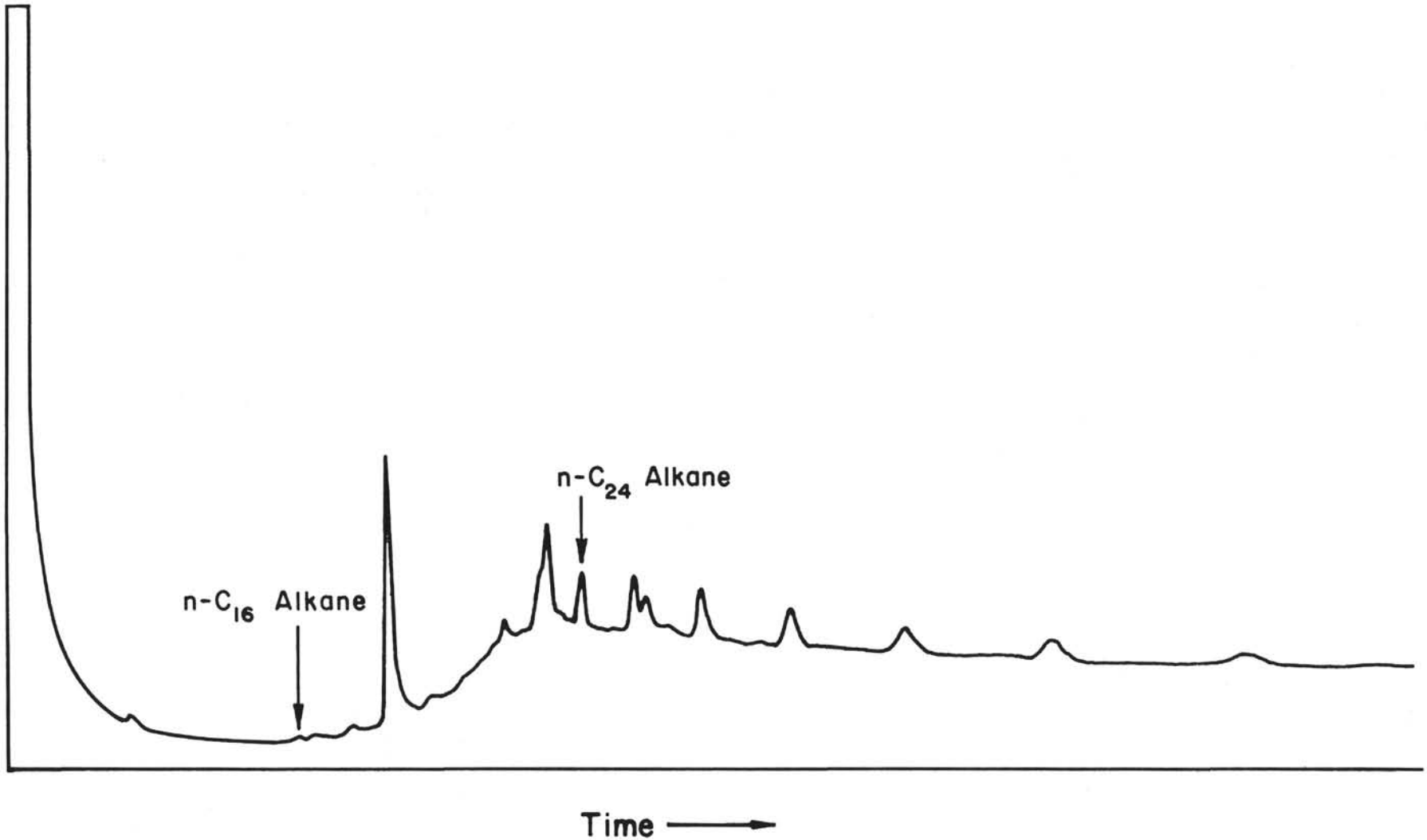


Figure 13. *Gas chromatogram of the heptane extract residue from Core 9X-82A-3-5. (Conditions as cited in Figure 1; the relative retention times of two alkanes are indicated by arrows.)*

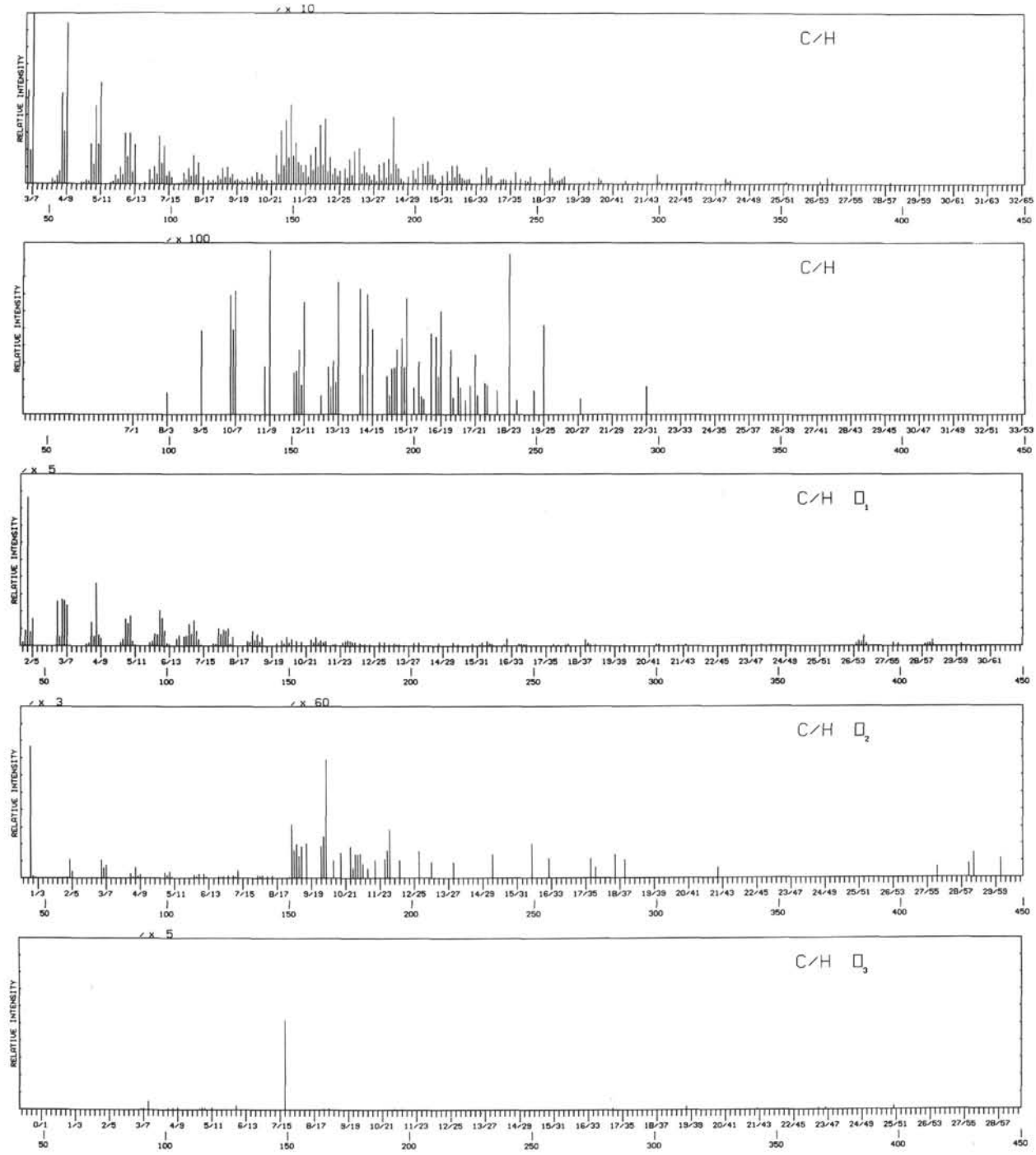


Figure 14. *Partial high resolution mass spectral data for the heptane extract residue from Core 9X-82A-3-5.*

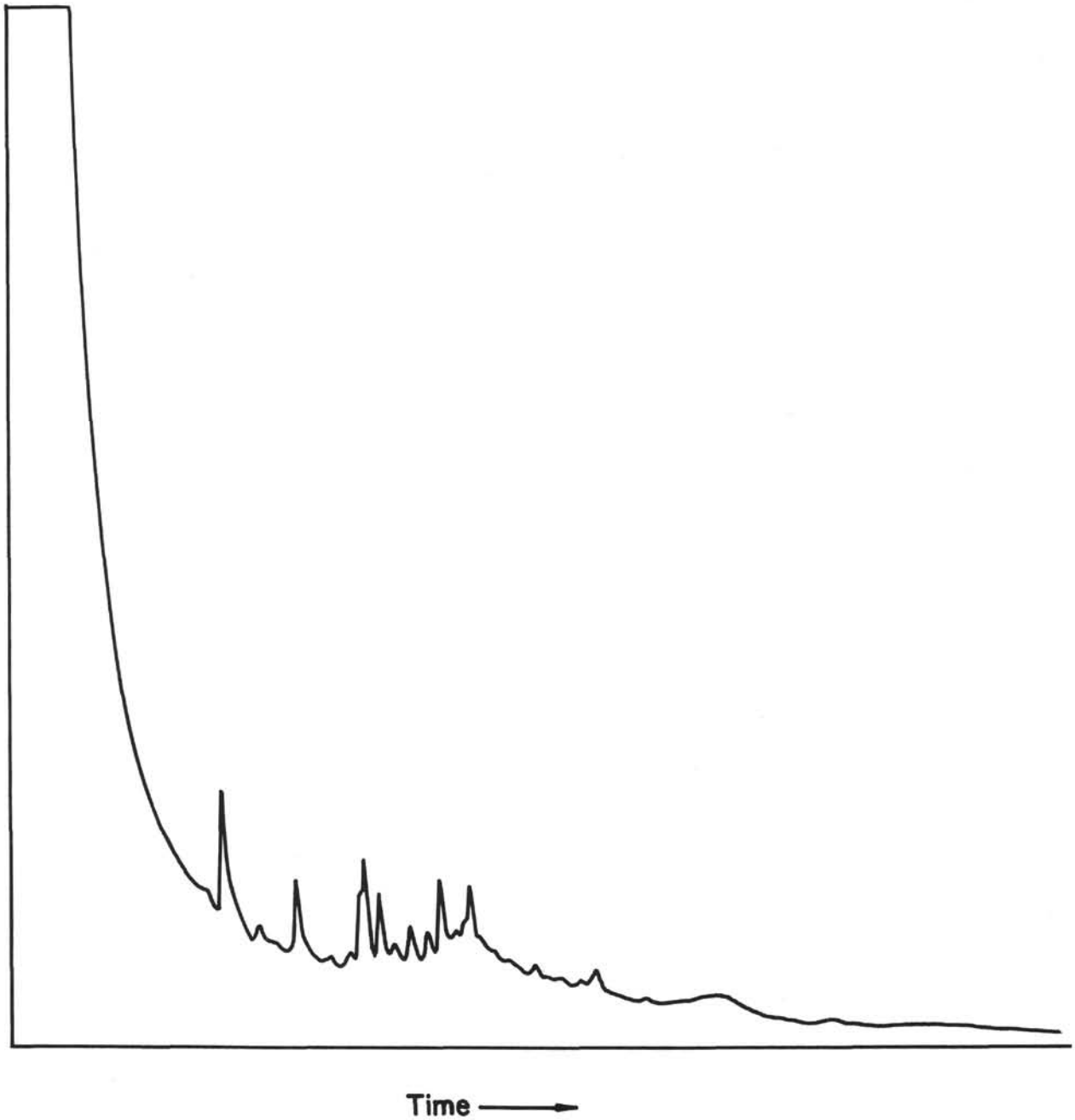


Figure 15. *Gas chromatogram of the acetone extract residue from Core 9X-83A-10-4. (Conditions as cited in Figure 1.)*

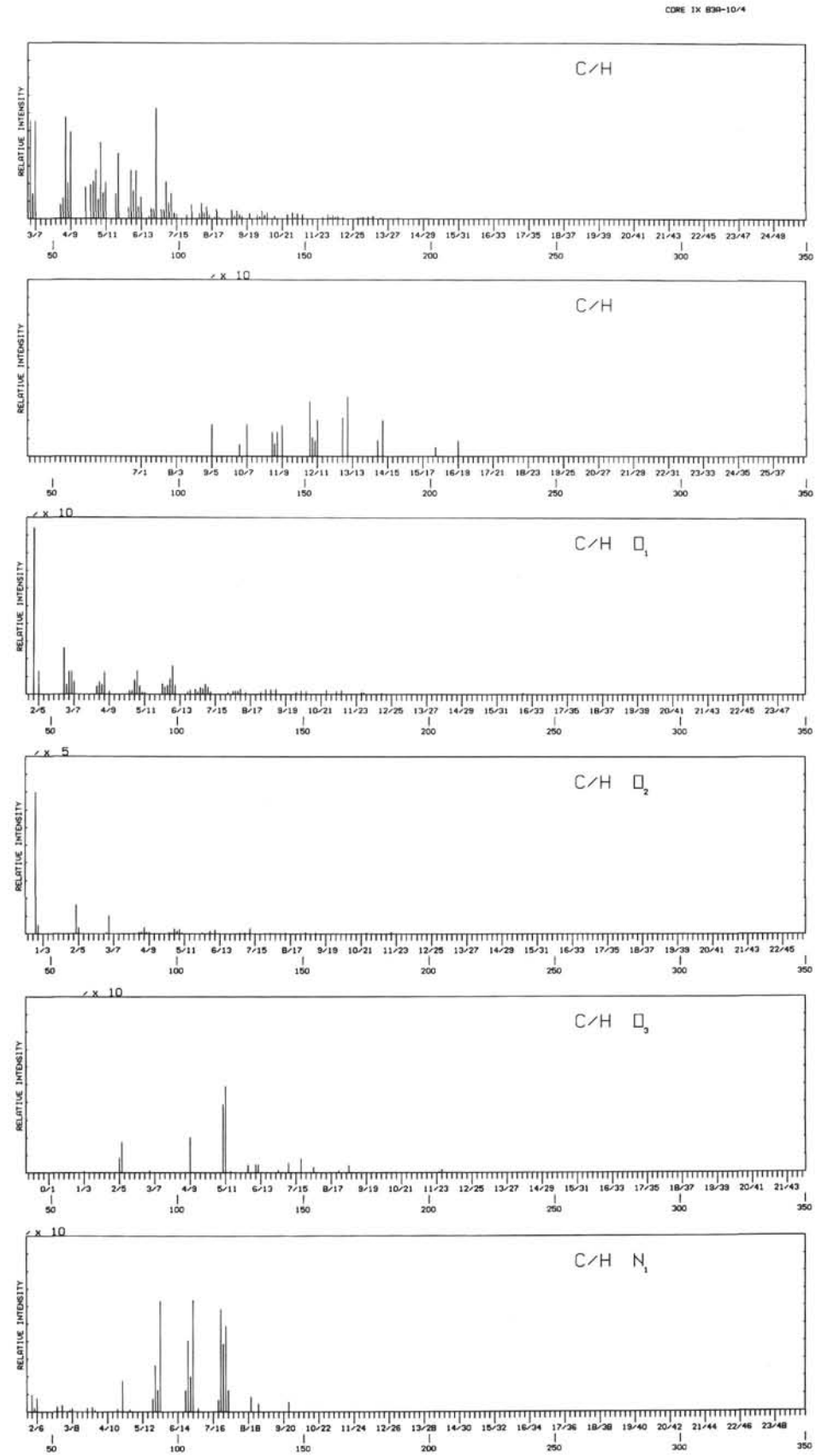
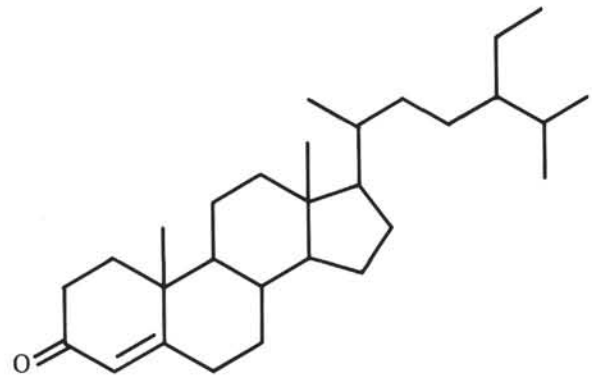
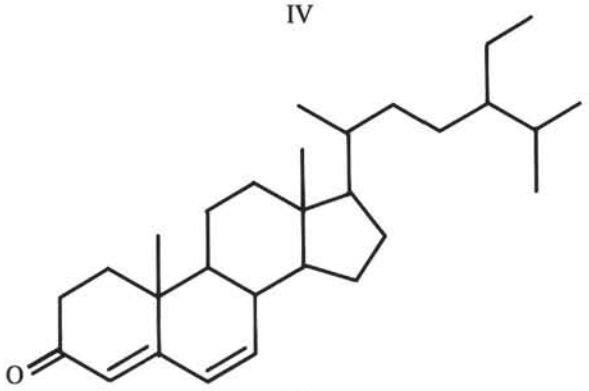


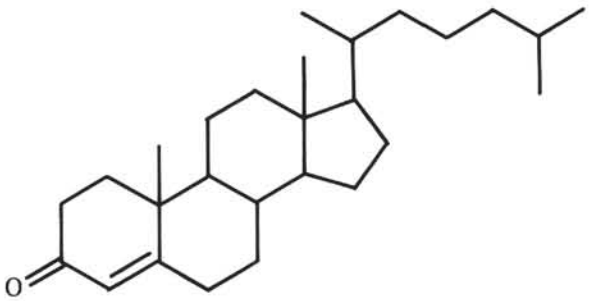
Figure 16. *Partial high resolution mass spectral data for the acetone extract residue from Core 9X083A-10-4.*



IV



V



VI

peaks from similar core samples is in progress. The carboxylic acids consist mainly of the series $C_nH_{2n}O_2$ for n = 3 to 11, 16 and 18, the latter two homologs being the most abundant. Possible phenols are indicated by peaks of the series $C_nH_{2n-6}O$ for n = 6 to 13. A small amount of phthalate esters are indicated to be present by the peak of composition $C_8H_5O_3$ in the C/H O_3 plot of Figure 14.

Core 9-83A-10-4

The acetone extract residue of this sample was subjected to GLC and high resolution mass spectrometric analyses. The GLC trace (Figure 15) indicates mainly compounds with relative retention times less than that of n-octadecane. The high resolution data are shown in Figure 16 and indicate mainly hydrocarbons, possibly (Structure XVI). Scan 43 fits the fragmentation pattern of a dibutyl phthalate, and scan 49 (Figure 20d) fits the pattern of the ortho isomer (Structure XVII). Scan 71 (Figure 20e) appears to indicate yet another phthalate ester. The peak at m/e 264 appears to be a molecular ion (probable composition: $C_{15}H_{20}O_4$) fitting a phthalic acid monoheptyl ester (Structure XVIII). The absence of a large peak at m/e 265 instead of m/e 264 and no peak at m/e 167 eliminate the fit of the diheptyl ester to this spectrum. Only trace indications of alkanes above column bleed background were found in this GLC-MS analysis.

Core 9-84-16-6

The heptane extract residue from this sample was subjected to low resolution mass spectrometry, and a representative scan is shown in Figure 21. The major components appear to be alkanes of the series C_nH_{2n+2} for n = 17 to 34, indicated by the molecular ion peaks at m/e 240 to 492 in 14 mass unit increments. The respective alkane or cyclic series appear to be present in minor amounts for the series C_nH_{2n} for n = 17, 18, 19, 22, 23 and 24, and for the series C_nH_{2n-2} for n = 19 to 26. The peaks in the m/e region 370 to 414 are possibly derived from steroidal compounds. The following compositions fit to the m/e values: $C_{26}H_{42}O$ for m/e 370; $C_{27}H_{44}O$ (Structure VI) and $C_{27}H_{46}O$ for m/e 384 and 386, respectively; $C_{28}H_{44}O$, $C_{28}H_{46}O$ and $C_{28}H_{48}O$ for m/e 396, 398 and 400, respectively; and $C_{29}H_{48}O$ (Structure IV) and $C_{29}H_{50}O$ (Structure XIX) for m/e 412 and 414, respectively. The peaks above m/e 500 appear to fit the hydrocarbon series C_nH_{2n-2} for n = 37 to 40. These compounds are possibly perhydrocartanes as, for example, the peak at m/e 558 of composition $C_{40}H_{78}$ could fit Structure XX. There appear to be no peaks present which indicate carboxylic acids.

Larger core samples and coring aids were anlayzed by the same technique just described.

Core 9-80A-5-5

This sample (88.4 grams) was pale brown in color and had the following carbon contents: total–6.76 per cent, and organic–0.53 per cent. It was Soxhlet extracted with 3:1 benzene and methanol, and the extract concentrate was divided into heptane and ether (3:1) soluble and benzene and methanol (3:1) soluble fractions. The extract yields were somewhat lower than was the case for the small sample. The heptane-ether extract amounted to 85 ppm (Table 1), and the benzene and methanol solubles amounted to 1250 ppm (Table 1). The heptane-ether extract fraction was divided into a neutral and acidic fraction (ratio 5:2). The neutral (that is, alkane) fraction was analyzed by gas chromatography and GLC-MS. The GLC trace (Figure 22) indicates five major peaks with relative retention times

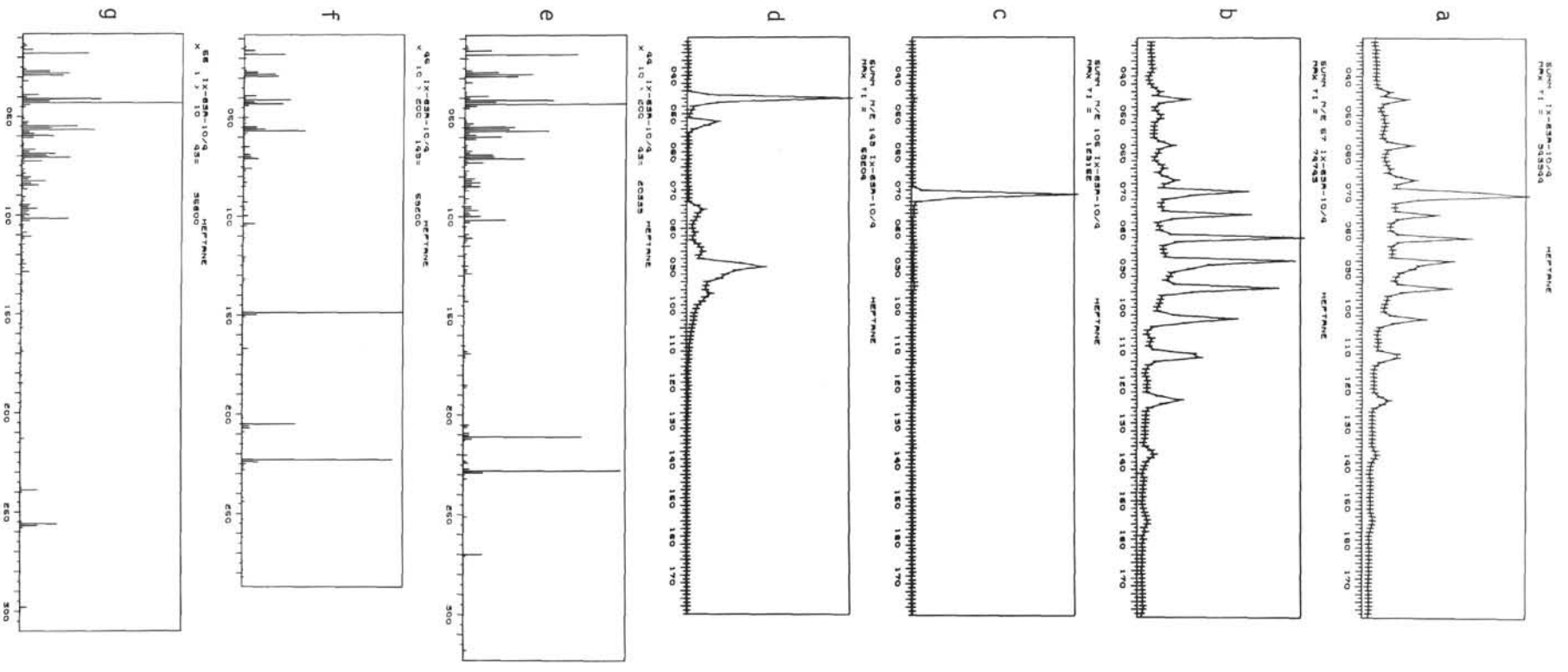


Figure 17. *GLC-MS data for the heptane extract residue from Core 9X-83A-10-4. (GLC conditions as cited in Figure 1.)*

a) total ionization sum plot
b) m/e 57 sum plot
c) m/e 105 sum plot
d) m/e 149 sum plot
e) mass spectrum scan 44
f) mass spectrum scan 46
g) mass spectrum scan 58

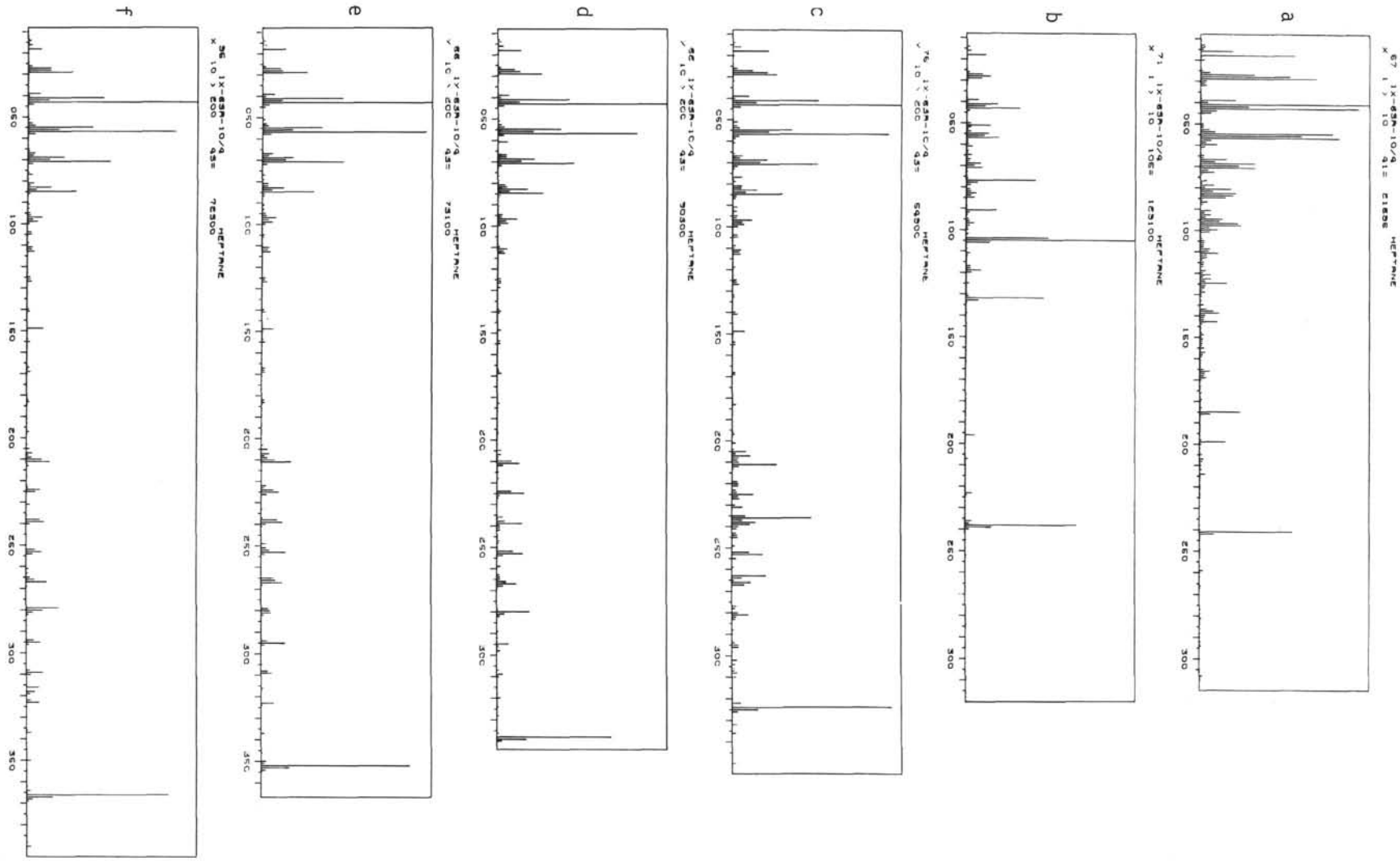


Figure 18. *GLC-MS data for the heptane extract residue from Core 9X-83A-10-4. (GLC conditions as cited in Figure 1.)*
a) mass spectrum scan 67 d) mass spectrum scan 82
b) mass spectrum scan 71 e) mass spectrum scan 88
c) mass psectrum scan 76 f) mass spectrum scan 95

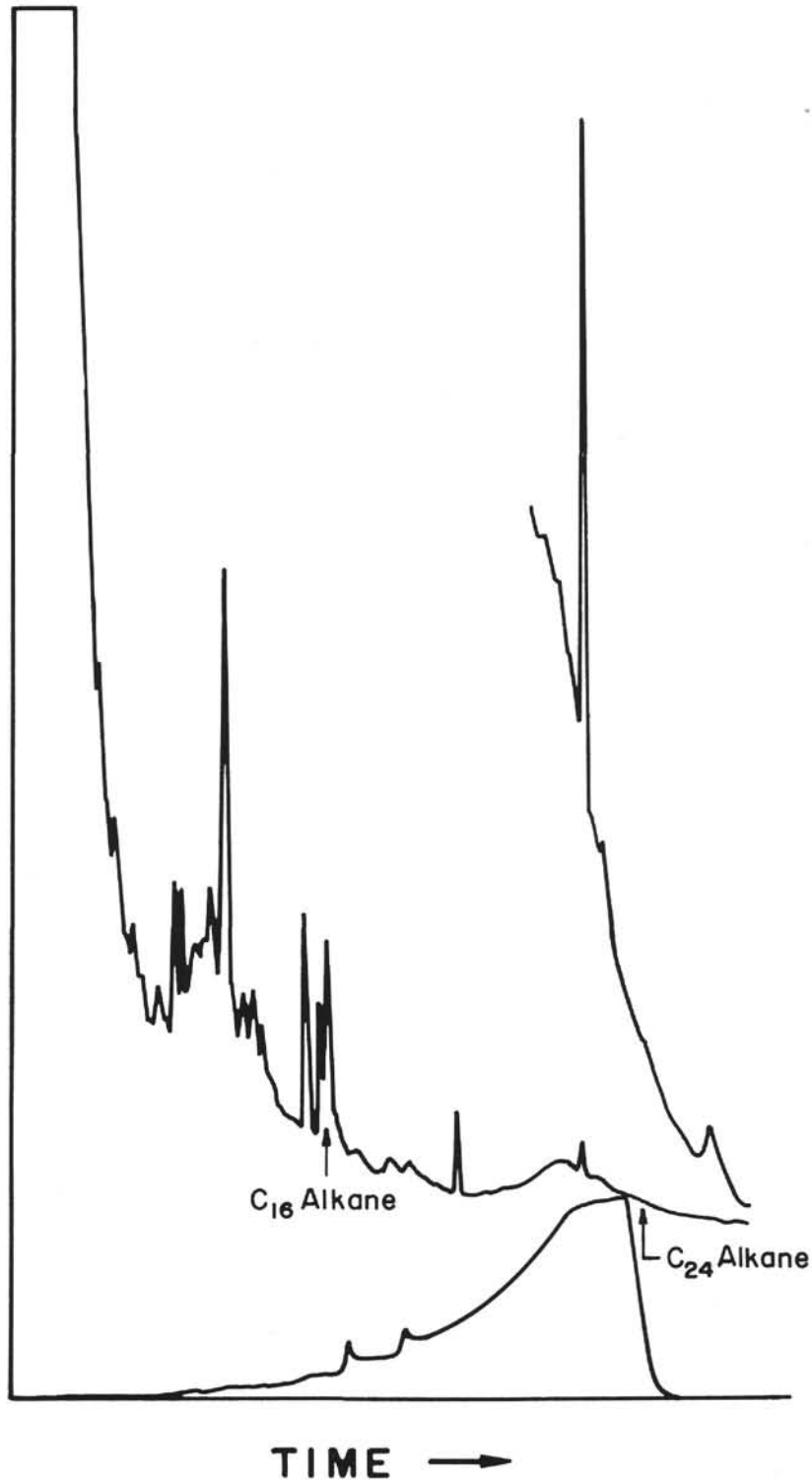


Figure 19. *Gas chromatogram of the acetone extract residue from Core 9X-83A-13-4. (Conditions as indicated in Figure 1. Center trace–sample, top trace–sensitivity increased by x60, and lower trace–back ground; the relative retention times of two alkanes are indicated by arrows.)*

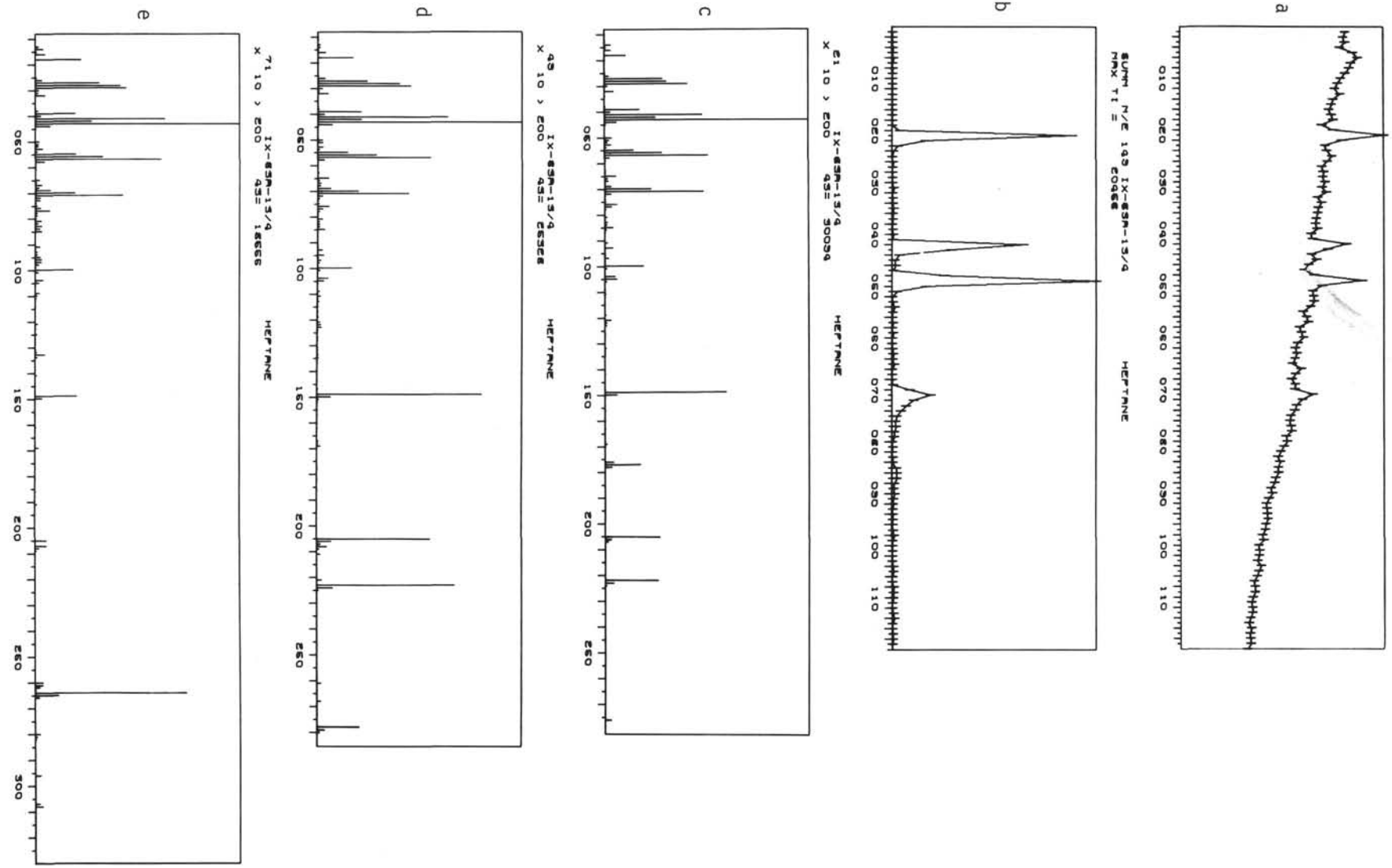


Figure 20. *GLC-MS data for the heptane extract residue from Core 9X-83A-13-4. (GLC conditions as cited in Figure 1.)*
a) total ionization sum plot
b) m/e 149 sum plot
c) mass spectrum scan 21
d) mass spectrum scan 49
e) mass spectrum scan 71

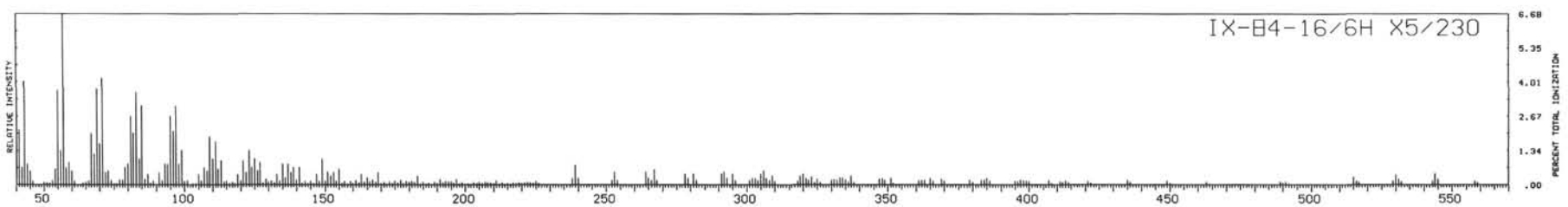


Figure 21. *Low resolution mass spectrum of the heptane extract residue from Core 9X-84-16-6.*

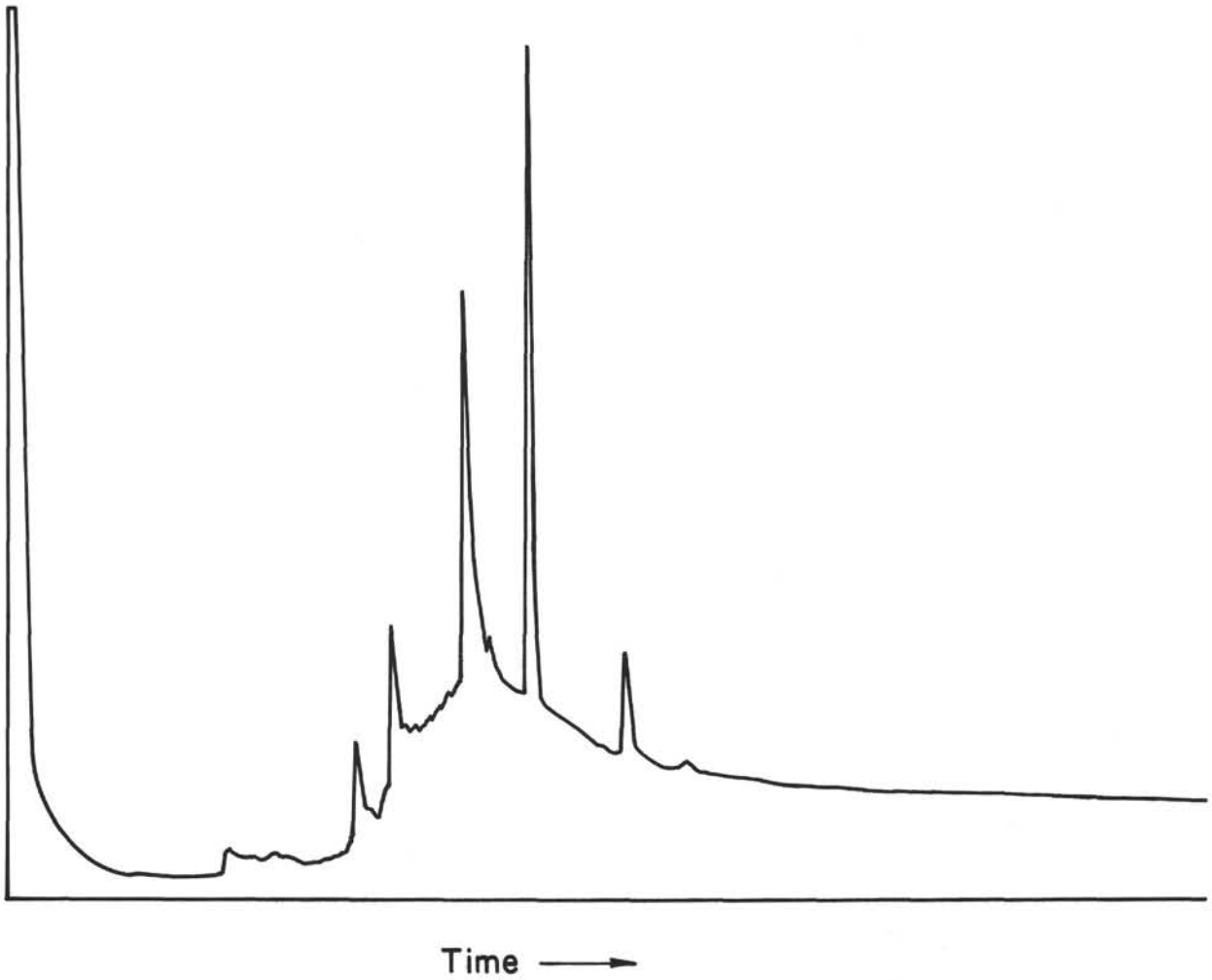
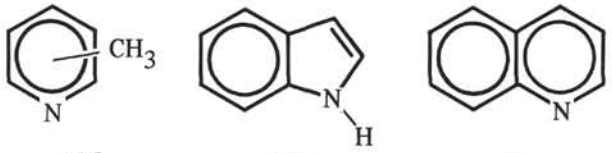


Figure 22. *Gas chromatogram of the alkane fraction from the exhaustive extract of Core 9X-80A-5-5. (Conditions as cited in Figure 1.)*

TABLE 2
Major Components of the Heptane Extract from Core 9-83A-10-4 (determined by GLC-MS)

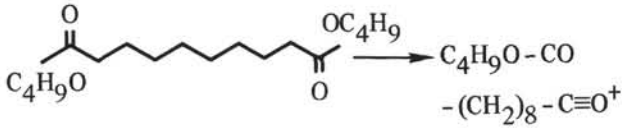
Peak at Scan Number (see Figure 17)	Compound Name	Molecular Weight and Composition		Figure References
44	Tetradecanoic acid	228	$C_{14}H_{28}O_2$	17e
46	Dibutyl phthalate	278	$C_{16}H_{22}O_4$	17f
52	Dibutyl phthalate	278	$C_{16}H_{22}O_4$	–
58	Palmitic acid	256	$C_{16}H_{32}O_2$	17g
67	Dibutyl sebacate	314	$C_{18}H_{34}O_4$	18a
70	n-Docosane	310	$C_{22}H_{46}O$	–
71	1,5-Diphenyl-3-pentanone	238	$C_{17}H_{18}O$	18b
72	Stearic acid	284	$C_{18}H_{36}O_2$	–
76	n-Tricosane	324	$C_{23}H_{48}$	18c
82	n-Tetracosane	338	$C_{24}H_{50}$	18d
88	n-Pentacosane	352	$C_{25}H_{52}$	18e
90-91	Dioctyl phthalate	390	$C_{24}H_{38}O_4$	–
95	n-Hexacosane	366	$C_{26}H_{54}$	18f
103	n-Heptacosane	380	$C_{27}H_{56}$	–
112	n-Octacosane	394	$C_{28}H_{58}$	–
124	n-Nonacosane	408	$C_{29}H_{60}$	–
138	n-Triacontane	422	$C_{30}H_{62}$	–
155	n-Hentriacontane	436	$C_{31}H_{64}$	–

phenols and nitrogen compounds. The hydrocarbons of the series C_nH_{2n+2} to C_nH_{2n-8} for n = 3 to 13 are found, but not all homologs are represented. The peak of composition C_7H_7, tropylium ion, is quite intense and is probably derived from fragmentation of the nitrogenous bases in this sample. The series $C_nH_{2n-6}O$ for n = 6, 7 and 8 is present and possibly indicates phenols. Carboxylic acids were not detected above background levels. Octoil is also at background levels, as indicated by the peak of composition $C_8H_5O_3$ (see C/H O_3 plot of Figure 16). The C/H N data indicate molecular ions of low molecular weight bases analagous to the base fraction from Core 5-35-6/3 (Simoneit and Burlingame, 1971a). Here the lower members of the various base series (see Simoneit *et al.*, 1970 and 1971) are present, namely $C_nH_{2n-5}N$ for n = 6 (Structure VII); $C_nH_{2n-7}N$ for n = 7 and 8 (Structure VIII); $C_nH_{2n-9}N$ for n = 7, 8 and 9 (Structure IX); and $C_nH_{2n-11}N$ for n = 9. Contamination should not, however, be ruled out as a source for these compounds.



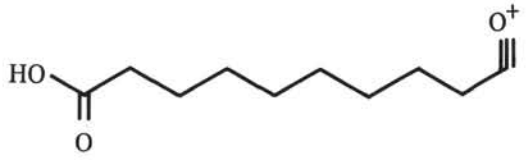
VII VIII IX

The heptane extract residue was analyzed by GLC-MS, and the salient data are shown in Figures 17 and 18 (Smith *et al.*, 1971). The major components of this extract are alkanes, free carboxylic acids and minor amounts of octoil. The total ion beam summarization plot appears in Figure 17a, and the m/e sum plot is shown below (Figure 17b) to indicate the scans where significant amounts of alkyl chains are fragmented (that is, an indication of alkane content). Figure 17d indicates the m/e 149 sum plot, the characteristic ion peak (composition $C_8H_5O_3$) of phthalate esters. The major GLC peaks were identified by their spectra and are listed in Table 2. The normal alkanes range from C_{22} to C_{31}. The carboxylic acids of the series $C_nH_{2n}O_2$ are present for n = 14, 16 and 18. Octoil contamination is mainly due to dibutyl and dioctyl phthalates. The scan 67 spectrum fits the fragmentation pattern of



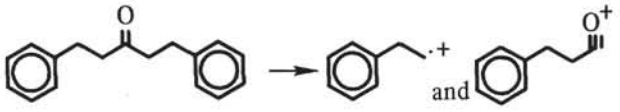
X

dibutyl sebacate (Structure X). The peak at m/e 241 (Structure XI) is due to loss of butoxy radical from the molecular ion. Subsequent loss of the elements of butylene yields the ion at m/e 185 (Structure XII). The



XII m/e 185

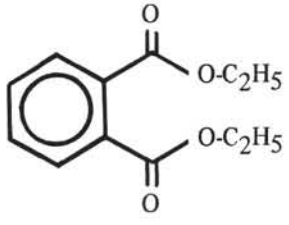
scan 71 spectrum (see also the m/e 105 sum plot–Figure 17c) fits the fragmentation pattern of 1,5-diphenyl-3-pentanone (Structure XIII), which exhibits a molecular ion at m/e 238 and cleaves the C-C bond alpha to the carbonyl, with charge retention on either fragment (Structures XIV and XV).



XIII m/e 238 XIV m/e 105 XV m/e 132

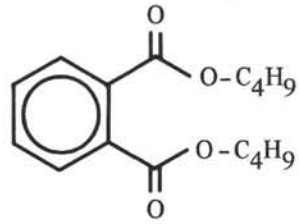
Core 9-83A-13-4

The acetone extract residue of this sample was subjected to GLC analysis, and the trace is shown in Figure 19. The major components appear to have retention times of less than that of a C_{16} alkane. The heptane extract residue was subjected to GLC-MS analysis, and the salient results are shown in Figure 20 (Smith *et al.*, 1971). The major constituents of the extract are phthalate ester contaminants. The total ion intensity plot is shown in Figure 20a, and the m/e 149 sum plot appears just below (Figure 20b) to indicate where the major octoil contaminants are. Scan 21 (Figure 20c) fits the fragmentation pattern of diethyl phthalate



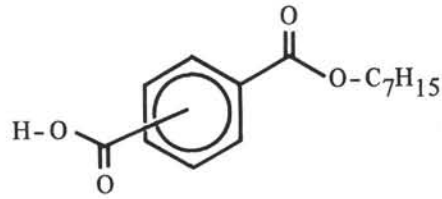
XVI m/e 222

(Structure XVI) scan 43 fits the fragmentation pattern of a dibutyl phthalate, and scan 49 (Figure 20d) fits the pattern of the ortho isomer (Structure XVII). Scan



XVII m/e 278

71 (Figure 20e) appears to indicate yet another phythlate ester. The peak at m/e 264 appears to be a molecular ion (probable composition: $C_{15}H_{20}O_4$) fitting a phthalic acid monoheptyl ester (Structure XVIII). The

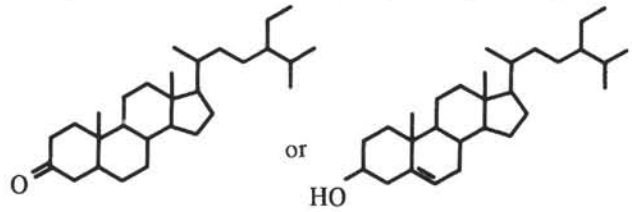


XVIII m/e 264

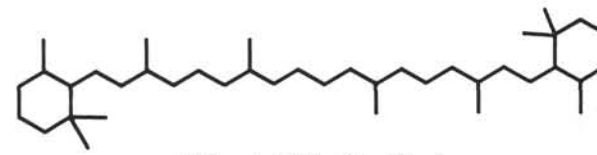
absence of a large peak at m/e 265 instead of m/e and no peak at m/e 167 eliminate the fit of the diheptyl ester to this spectrum. Only trace indications of alkanes above column bleed background were found in this GLC-MS analysis.

Core 9-84-16-6

The heptane extract residue from this sample was subjected to low resolution mass spectrometry, and a representative scan is shown in Figure 21. The major components appear to be alkanes of the series C_nH_{2n+2} for n = 17 to 34, indicated by the molecular ion peaks at m/e 240 to 492 in 14 mass unit increments. The respective alkane or cyclic series appear to be present in minor amounts for the series C_nH_{2n} for n = 17, 18, 19, 22, 23 and 24, and for the series C_nH_{2n-2} for n = 19 to 26. The peaks in the m/e region 370 to 414 are possibly derived from steriodal compounds. The following compositions fit to the m/e values: $C_{26}H_{42}O$ for m/e 370; $C_{27}H_{44}O$ (Structrue VI) and $C_{27}H_{46}O$ for m/e 384 and 386, respectively; $C_{28}H_{44}O$, $C_{28}H_{46}O$ and $C_{28}H_{48}O$ for m/e 396, 398 and 400, respectively; and $C_{29}H_{48}O$ (Structure IV) and $C_{29}H_{50}O$ (Structure XIX) for m/e 412 and 414, respectively. The peaks above m/e 500 appear to fit the hydrocarbon series C_nH_{2n-2} for n = 37 to 40. These compounds are possibly perhydrocartanes as, for example, the peak at m/e 558 of composition $C_{40}H_{78}$ could fit Structure XX. There appear to be no peaks present which indicate carboxylic acids.



XIX m/e 414 ($C_{29}H_{50}O$)

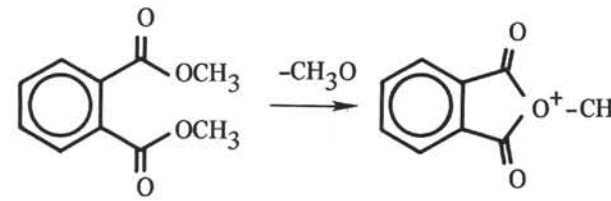


XX m/e 558 ($C_{40}H_{78}$)

Larger core samplse and coring aids were analyzed by the same technique just described.

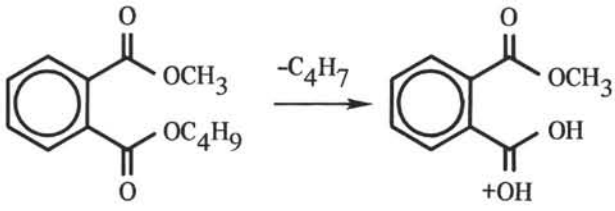
Core 9-80A-5-5

This sample (88.4 grams) was pale brown in color and had the following carbon contents: total–6.76 per cent, and organic–0.53 per cent. It was Soxhlet extracted with 3:1 benzene and methanol, and the extract concentrate was divided into heptane and ether (3:1) soluble and benzene and methanol (3:1) soluble fractions. The extract yields were somewhat lower than was the case for the small sample. The heptane-ether extract amounted to 85 ppm (Table 1), and the benzene and methanol solubles amounted to 1250 ppm (Table 1). The heptane-ether extract fraction was divided into a neutral and acidic fraction (ration5:2). The neutral (that is, alkane) fraction was analyzed by gas chromatography and GLC-MS. The GLC trace (Figure 22) indicates five major peaks with relative retention times of less than that of a C_{28} alkane. The salient features of the GLC-MS data are shown in Figure 23a and b. The m/e 57 sum plot is shown below the total ionization sum plot and indicates an alkane pattern in scan 72 and scan 107 (the octyl groups on dioctyl phthalate exhibit an m/e 57 fragment). The m/e 149 sum plot is also shown, indicating that the bulk of the extract consists of phthalate esters. The scan 30 spectrum fits the fragmentation pattern of dimethyl phthalate (Structure XXI), which loses a methoxy radical to yield the peak at m/e 163 (Structure XXII) and the subsequent



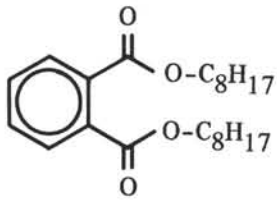
XXI m/e 194 XXII m/e 163

loss of CO yields the peak at m/e 135. The scan 46 spectrum fits the fragmentation pattern of butyl methyl phthalate (Structure XXIII), which loses a C_4H_7 fragment to yield the peak at m/e 181 (Structure XXIV), and subsequent loss of H_2O yields the ion at m/e 163 (Structure XXII). The scan 64 spectrum fits



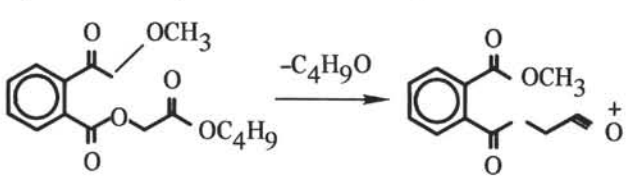
XXIII m/e 236 XXIV m/e 181

the fragmentation pattern of dibutyl phthalate (Structure XVII). The scan 70 spectrum fits the fragmentation pattern of another phthalate ester. The scan 72 spectrum appears to be a mixture of the previous phthalate ester and possibly hexadecane. The scan 107 spectrum fits the fragmentation pattern of dioctyl phthalate (Structure XXV).



XXV m/e 390

The acid fraction was esterified with BF_3 in methanol and then subjected to GLC and GLC-MS analyses. The GLC trace is shown in Figure 24 and indicates three major peaks. The salient features of the GLC-MS analysis are shown in Figures 25 and 26. The major GLC peaks were identified from their mass spectra and are listed in Table 3. The scan 50 mass spectrum fits the fragmentation pattern of methyl myristate, and the scan 65 mass spectrum fits the fragmentation pattern of methyl palmitate. The scan 72 spectrum probably fits the fragmentation pattern of methyl phthalyl butyl glycolate (Structure XXVI), which loses a butoxy radical to yield the peak at m/e 221 (Structure XXVII), and by subsequent fragmentation yields the peaks at m/e 163 and m/e 149. The scan 76 spectrum fits the



XXVI XXVII

fragmentation pattern of a methyl octadecenoate (molecular ion $[M^+]$ at m/e 296, $M^+ - CH_3\cdot$ at m/e 281, and $M^+ - CH_3O\cdot$ at m/e 265). The scan 78 spectrum fits the fragmentation pattern of methyl stearate. The scan 91 spectrum consists of a mixture. The major constituents are methyl arachidate (M^+ at m/e 326) and a compound of molecular weight 314 (see scan 92 in Figure 26d). Methyl nonadecanoate (M^+ at m/e 312) is found as a minor component. The scan 92 spectrum indicates a compound of molecular weight 314 (composition $C_{21}H_{30}O_2$) which loses a methyl radical to yield the peak at m/e 299, the subsequent loss of 60 mass units yields the peak at m/e 239. This compound is possibly a steroidal carboxylic acid methyl ester. The scan 99 spectrum also consists of a mixture of compounds. The major molecular ion peaks are at m/e 328 (unknown structure), m/e 326 (methyl arachidate), and 312 (methyl nonadecanoate). The scan 105 spectrum indicates another probable steroidal carboxylic acid methyl ester with a molecular ion at m/e 320 (composition $C_{21}H_{36}O_2$). The scan 113 spectrum indicates the next higher homolog of the steroidal compound in scan 92. The molecular ion appears at m/e 328, with loss of methyl radical at m/e 313 and subsequent loss of 60 mass units at m/e 253. The scan 147 spectrum fits the fragmentation pattern of methyl lignocerate. In summary, the major carboxylic acids in this extract are of the series $C_nH_{2n}O_2$ for n = 14, 16, 18 and traces of n = 19, 20 and 24, and $C_nH_{2n-12}O_2$ for n = 20 and 21.

Core Tube Contamination

The polymer making up the core tubes is cellulose acetate butyrate. A partial solution of the plastic was made in 3:1 benzene and methanol, and the "extract syrup" was analyzed by GLC and mass spectrometry. The GLC trace is shown in Figure 27, and indicates one major peak with a minor group of homologous compounds in the retention time range equivalent to methyl tetradecanoate to methyl eicosanoate. The high resolution mass spectral data are shown in Figure 28. The major homologous series present is $C_nH_{2n-2}O_3$ for n = 6 to 15 and the respective fragment ion series $C_nH_{2n-3}O_3$ for n = 4 to 15 (with n = 9 and 13 most intense). There are minor amounts of carboxylic acids of the series $C_nH_{2n}O_2$ for n = 2 to 13 and $C_nH_{2n-8}O_2$ for n = 7, 8 and 9. Phthalate esters are extremely low in concentration as indicated by the small peaks of compositions $C_8H_5O_3$ in the C/H O_3 plot and $C_8H_7O_4$ in the C/H O_4 plot of Figure 28. The extract residue is under further investigation to identify the individual GLC peaks, but preliminarily it appears that the core tubes are not the major source of the phthalate contamination in the samples.

Core Tube Cap Contamination

The benzene and methanol (3:1) extract residue (light yellow) of the red polypropylene core tube caps was

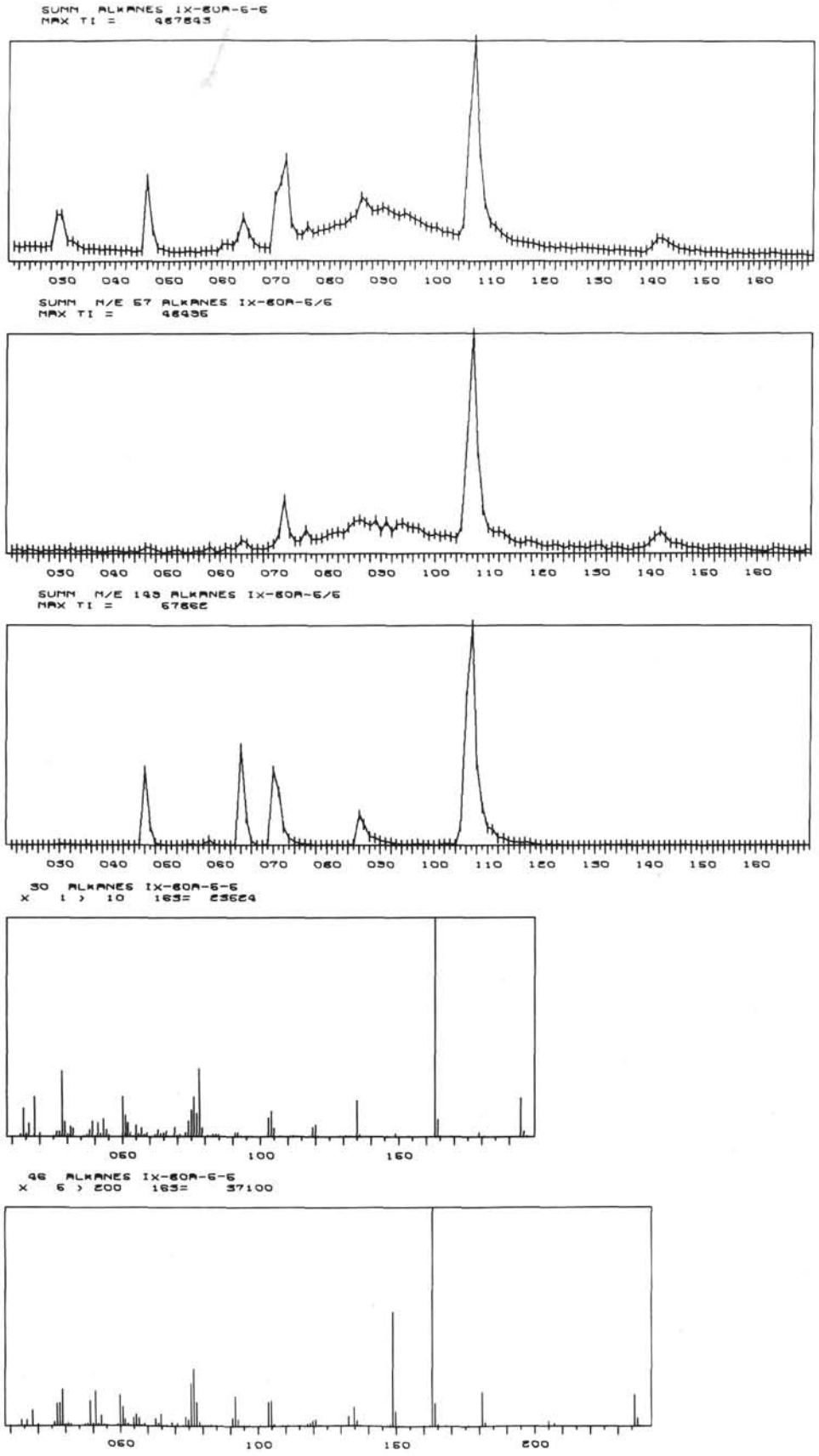


Figure 23a. *GLC-MS data for the alkane fraction from the exhaustive extract of Core 9X-80A-5-5. (GLC conditions as indicated in Figure 1.)*

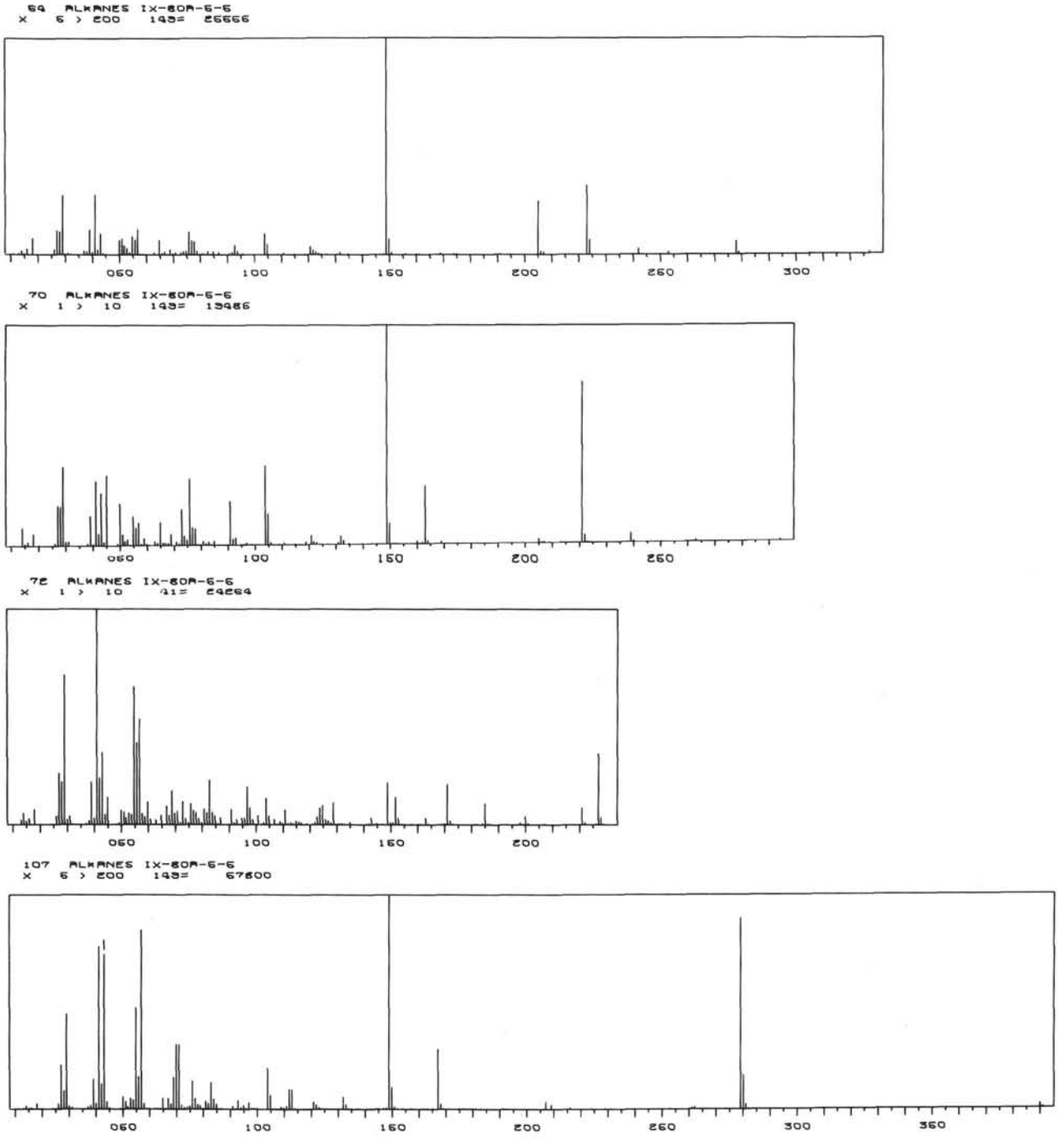


Figure 23b. *GLC-MS data for the alkane fraction from the exhaustive extract of Core 9X-80A-5-5. (GLC conditions as indicated in Figure 1.)*

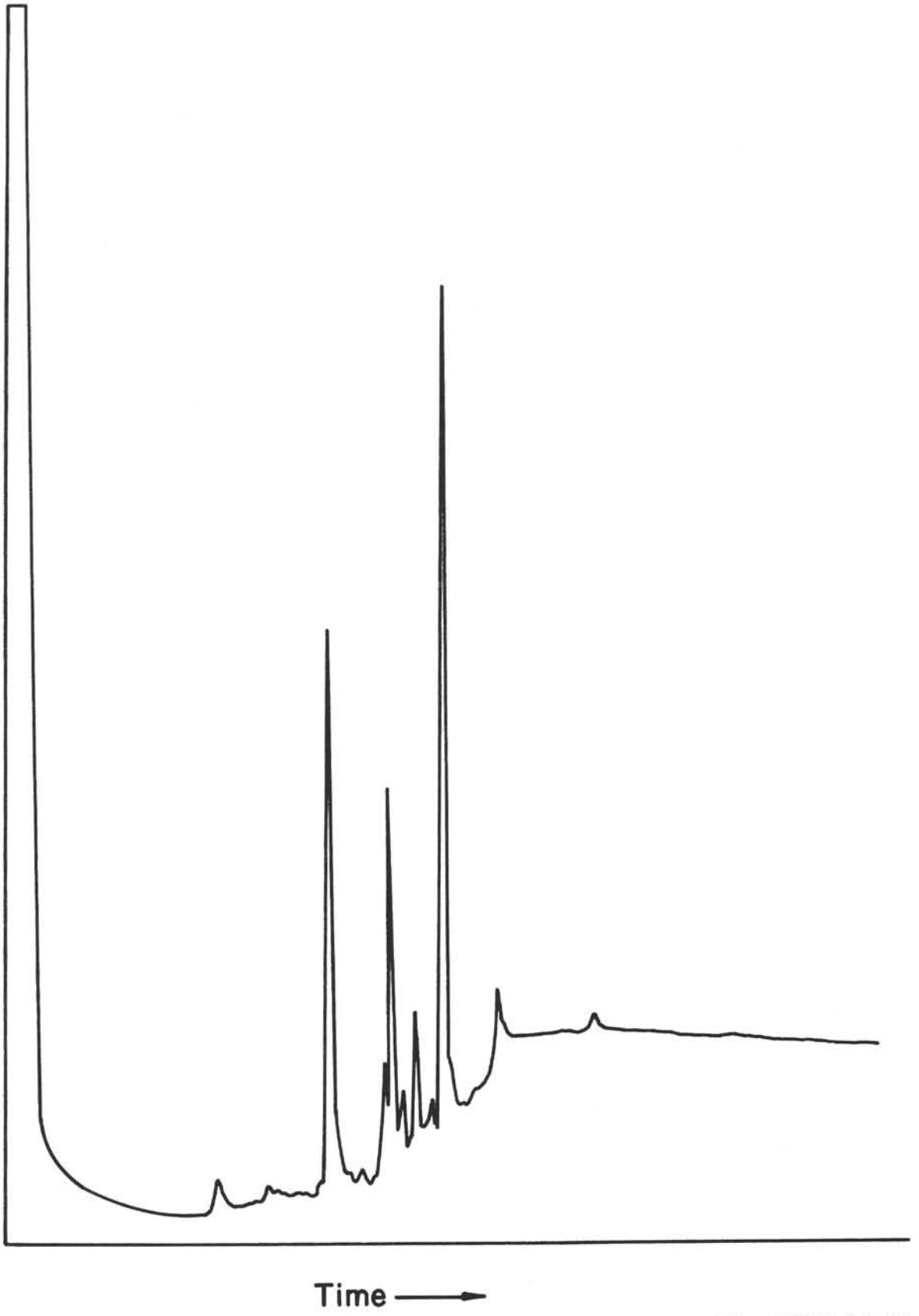


Figure 24. *Gas chromatogram of the ester fraction from the exhaustive extract of Core 9X-80A-5-5. (Conditions as cited in Figure 1.)*

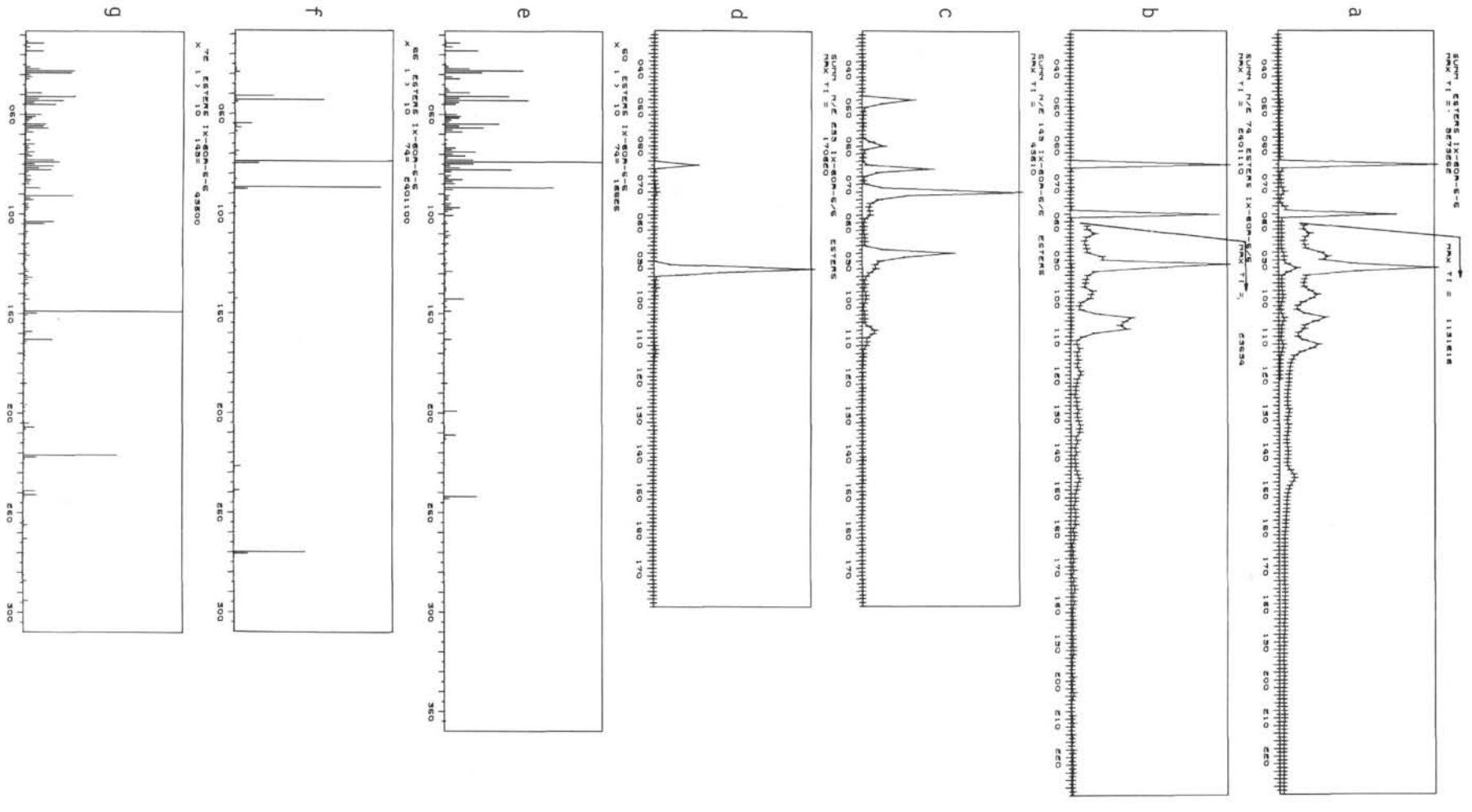


Figure 25. *GLC-MS data for the ester fraction from the exhaustive extract of Core 9X-80A-5-5. (GLC conditions as indicated in Figure 1.)*

a) total ionization sum plot (scans 80-230 are expanded by a factor of 10)
b) m/e 74 sum plot (scans 80-230 are expanded by a factor of 10)
c) m/e 149 sum plot
d) m/e 239 sum plot
e) mass spectrum scan 50
f) mass spectrum scan 65
g) mass spectrum scan 72

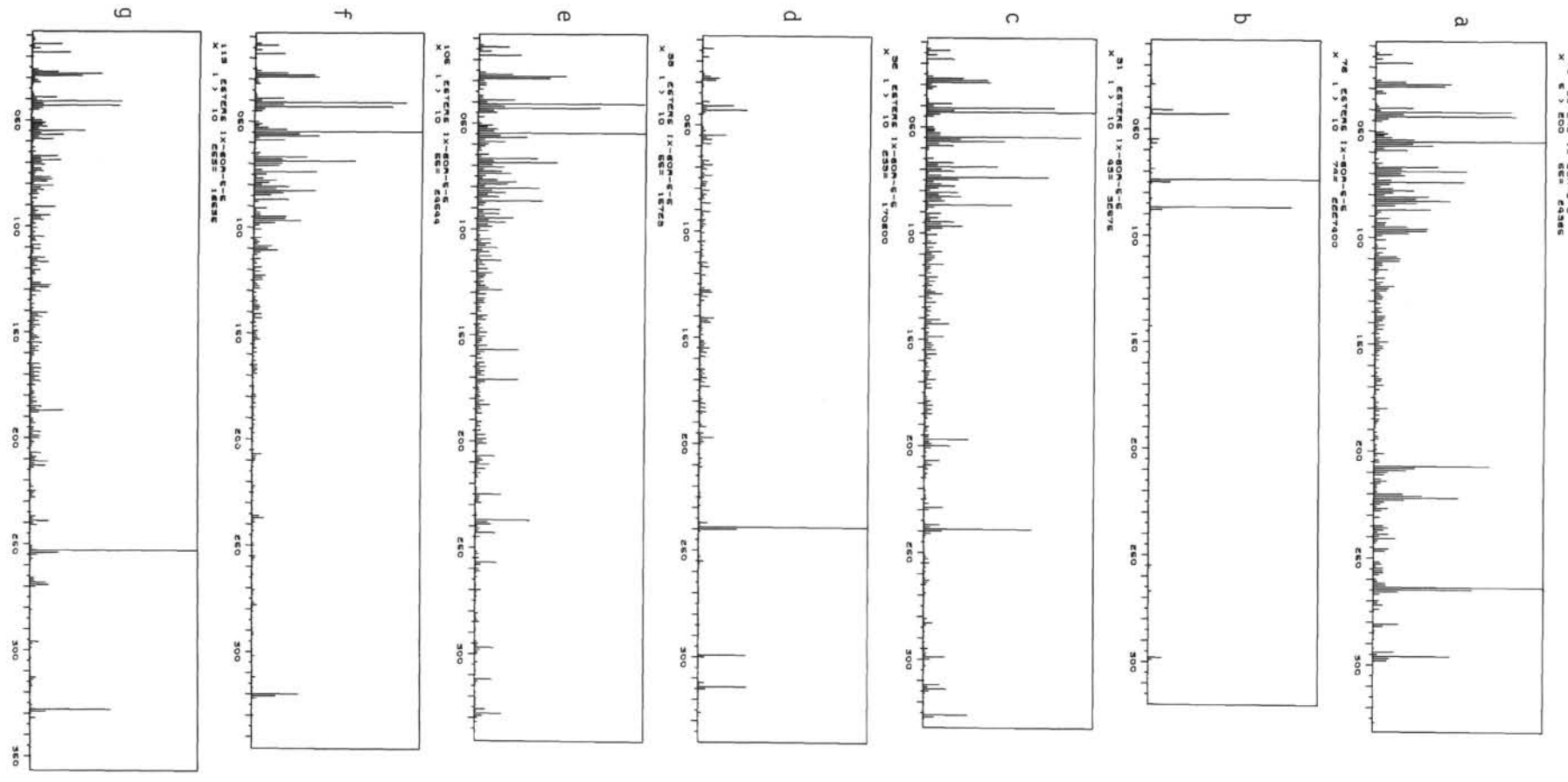


Figure 26. *GLC-MS data for the ester fraction from the exhaustive extract of Core 9X-80A-5-5. (GLC conditions as indicated in Figure 1.)*

a) mass spectrum scan 76
b) mass spectrum scan 78
c) mass spectrum scan 91
d) mass spectrum scan 92
e) mass spectrum scan 99
f) mass spectrum scan 105
g) mass spectrum scan 113

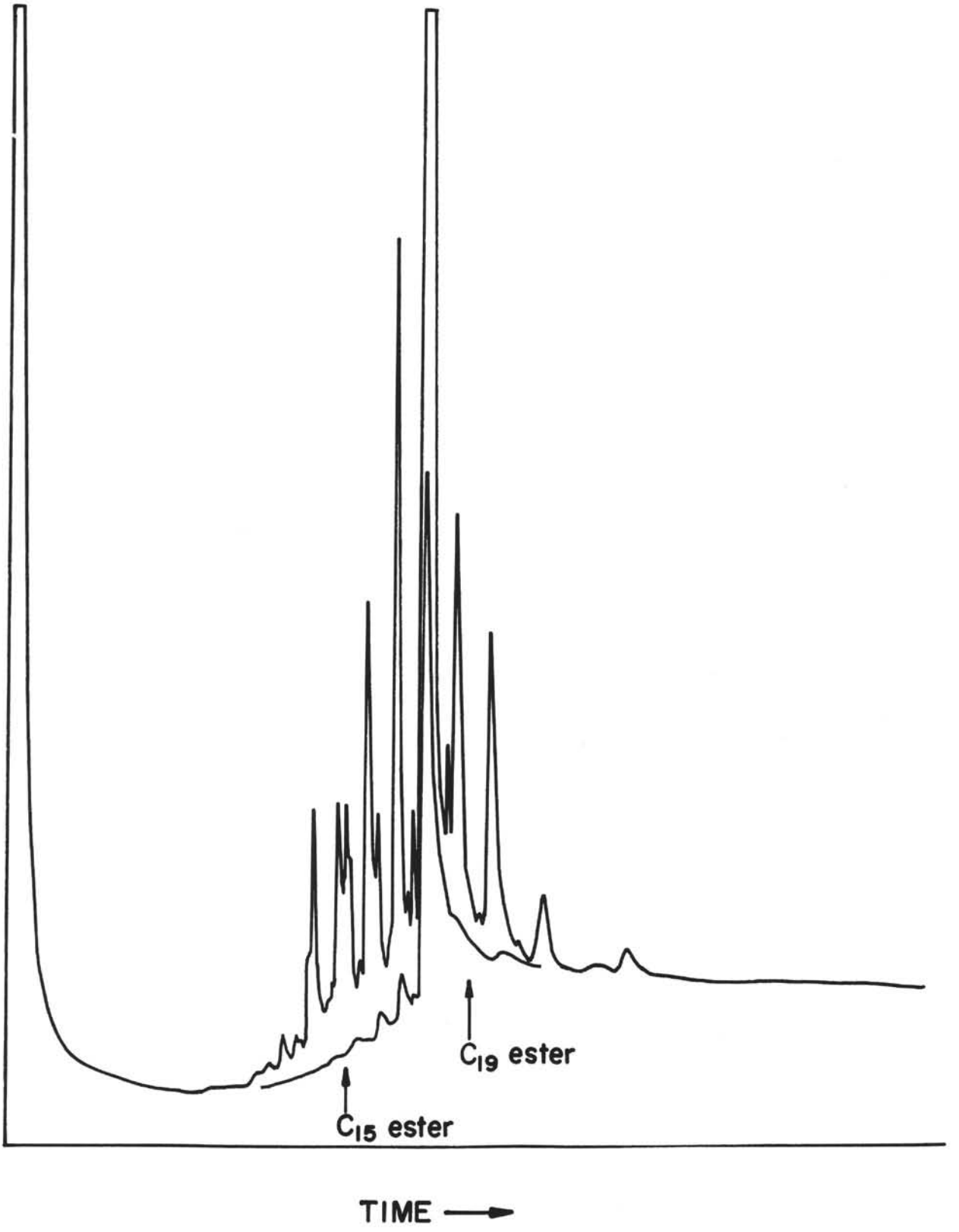


Figure 27. *Gas chromatogram of the extract concentrate from the core tube polymer. (Conditions as cited in Figure 1: lower trace–sample run at lower sensitivity; the relative retention times of two normal esters are indicated by arrows.)*

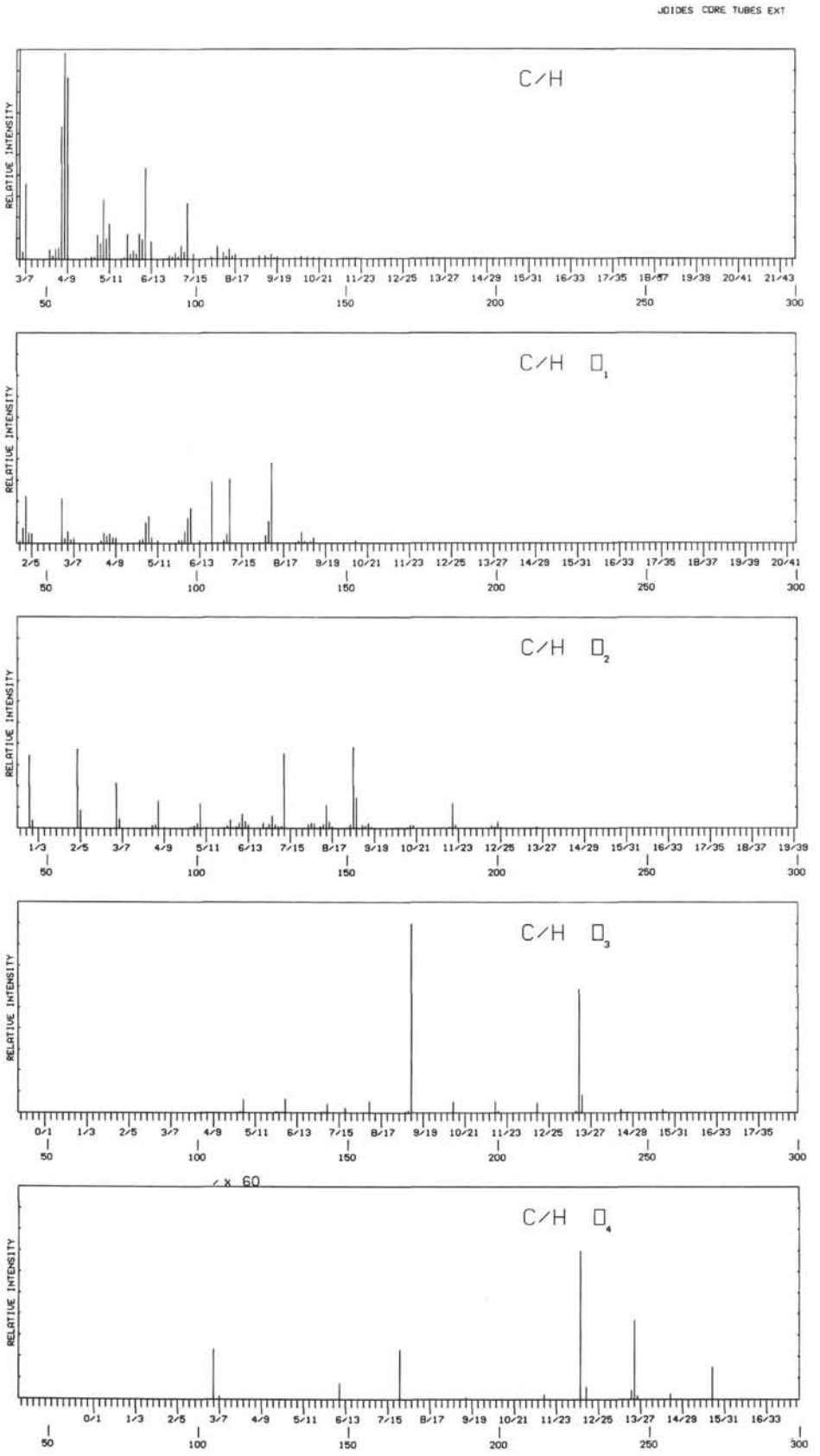


Figure 28. *Partial high resolution mass spectral data for the extract residue from the core tube polymer.*

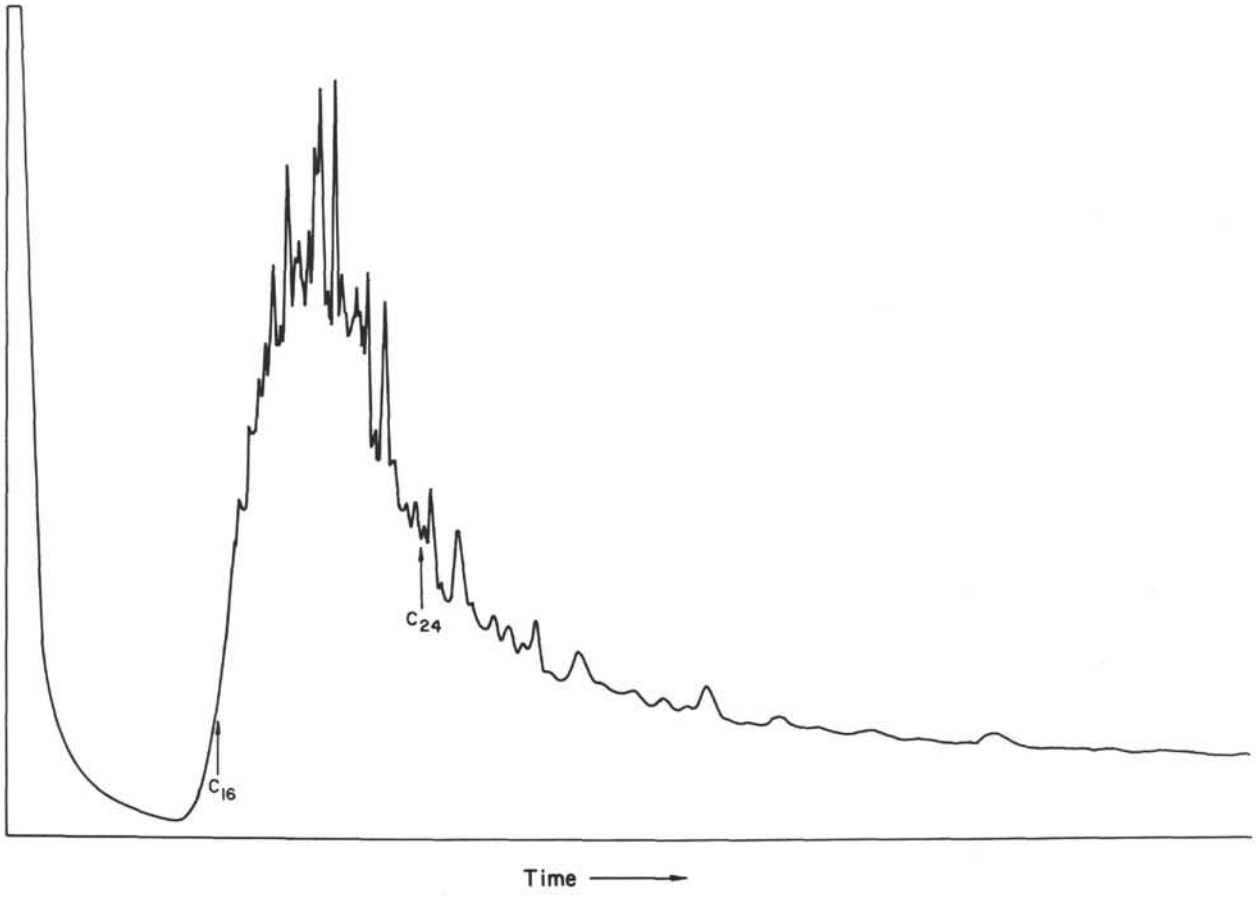


Figure 29. *Gas chromatogram of the benzene and methanol extract residue from the core tube caps. (Conditions as cited in Figure 1. The relative retention times of two normal alkanes are indicated by arrows.)*

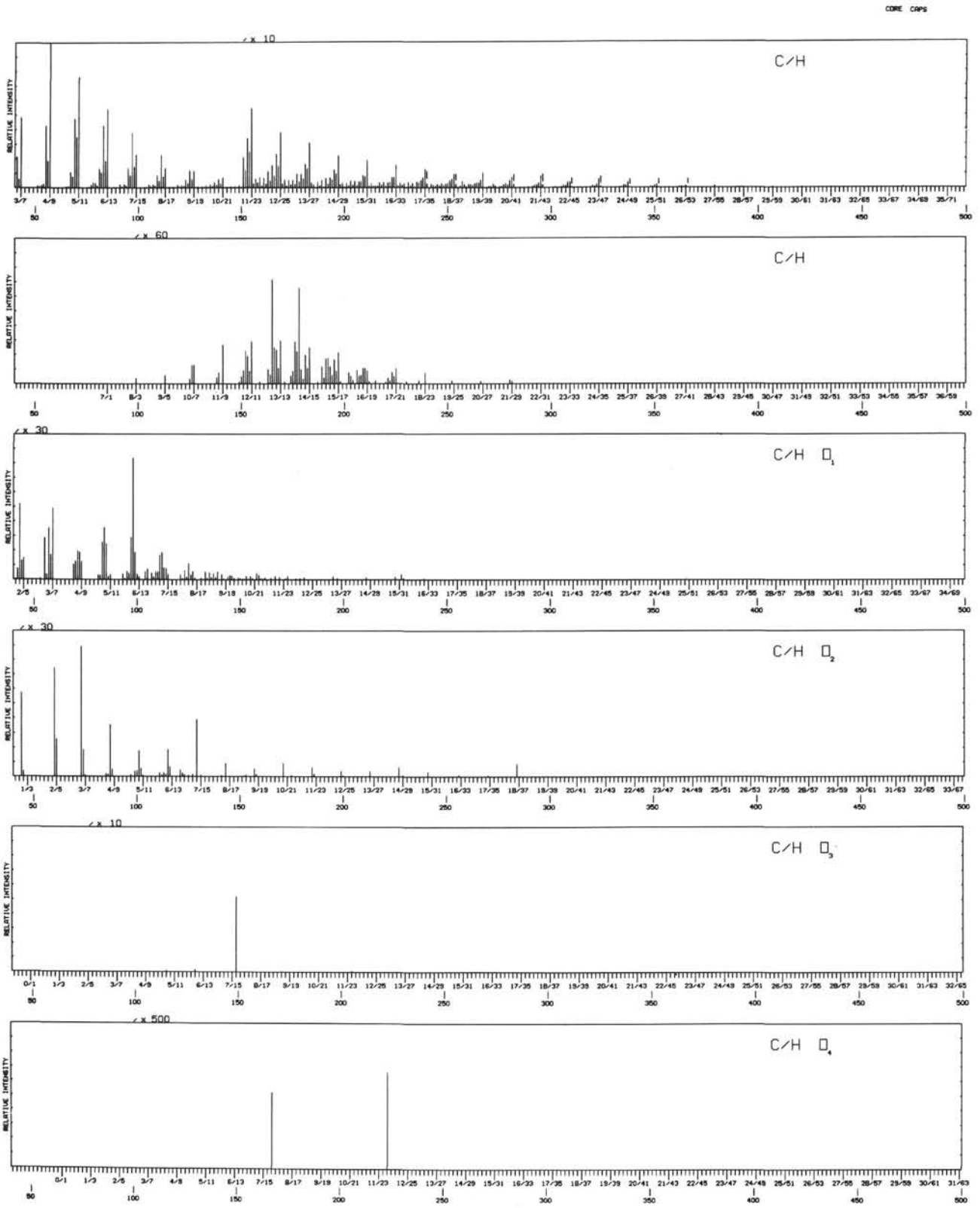


Figure 30. *Partial high resolution mass spectral data for the benzene and methanol extract residue from the core tube caps.*

TABLE 3
Major Components of the Ester Fraction from the Exhaustive Extract of Core 9-80A-5-5 (Determined by GLC-MS)

Peak at Scan Number (see Figure 25a)	Compound Name	Molecular Weight and Composition		Figure Reference
50	Methyl myristate	242	$C_{15}H_{30}O_2$	25e
65	Methyl palmitate	270	$C_{17}H_{34}O_2$	25f
72	Methyl phthalyl butyl glycolate	294	$C_{15}H_{18}O_6$	25g
76	Methyl octadecenoate	296	$C_{19}H_{36}O_2$	26a
78	Methyl stearate	298	$C_{19}H_{38}O_2$	26b
91	Mixture			
	Methyl arachidate	326	$C_{21}H_{42}O_2$	26c
	Unknown	314	$C_{21}H_{30}O_2$	
	Methyl nonadecanoate (trace)	312	$C_{20}H_{40}O_2$	
92	Unknown	314	$C_{21}H_{30}O_2$	26d
99	Mixture			
	Methyl arachidate (trace)	326	$C_{21}H_{42}O_2$	26e
	Methyl nonadecanoate (trace)	312	$C_{20}H_{40}O_2$	
	Unknown	328	$C_{22}H_{32}O_2$	
105	Unknown	320	$C_{21}H_{36}O_2$	26f
113	Unknown	328	$C_{22}H_{32}O_2$	26g
147	Methyl lignocerate	382	$C_{25}H_{50}O_2$	–

analyzed by GLC and high resolution mass spectrometry. The GLC trace, shown in Figure 29, indicates the typical pattern of a hydrocarbon oil or grease. The major constituents appear to have a retention time range equivalent to C_{16} to C_{26} alkanes. The high resolution mass spectral data are shown in Figure 30 and indicate mainly hydrocarbons with minor amounts of carboxylic acids and octoil. The hydrocarbons consist of the alkane series C_nH_{2n+2} to C_nH_{2n-2} for n = 3 to 35. The more unsaturated and/or cyclic hydrocarbon series C_nH_{2n-4} to C_nH_{2n-22} for n = 8 to 21 (not each homolog being present) are present in lesser amounts. The carboxylic acids consist mainly of the series $C_nH_{2n}O_2$ for n = 2 to 18. The octoil consist of dibutyl phthalate as indicated by the peaks of compositions $C_8H_5O_3$, $C_8H_7O_4$ and $C_{12}H_{15}O_4$ in the C/H O_3 and C/H O_4 plots of Figure 30.

CONCLUSIONS

These samples from Leg 9 contain comparatively low amounts of solvent extractable organic material (see Table 1). The problem of organic contamination was quite serious and obvious in some samples. The major contaminants were a suite of phthalate esters, probably derived mainly from plasticizers in the various sampling containers. Other occasional contaminants were found (for example, naphthol in 9-78-20-6), and, also, compounds which could possibly be derived from contamination or be indigenous to the samples were detected (for example, nitrogen heterocycles in 9-83A-10-4).

In order to avoid such ambiguity and to possibly implement a reduction of the overall organic contamination, more detailed analytical studies of the organic materials involved in the sampling program have been, and are still being, carried out at this laboratory. The analytical methods used are analogous to those reported (Simoneit, 1971, and Simoneit and Flory, 1971). The core tube caps, consisting of polypropylene, were analyzed and found to exude a hydrocarbon oil, where for example the alkanes range mainly from C_{16} to C_{26}. The core tubes, consisting of cellulose acetate butyrate, do not appear to be the major source of phthalate ester contaminants, but do leach out polyoxygenated organic material by solvent treatment.

In most heptane extracts the normal alkanes, ranging from usually C_{22} to C_{32}, are the major constituents, and in all cases exhibit no specific odd/even or even/odd predominance (for example, 9-83A-10-4).

The fatty acid content of blue-green algae consists mainly of $C_{14:0}$, $C_{14:1}$, $C_{16:0}$, $C_{16:1}$, $C_{18:0}$ and $C_{18:1-3}$ for most species; and, marine bacteria contain mainly $C_{16:0}$, $C_{16:1}$, $C_{18:0}$ and $C_{18:1}$ acids (Parker, van Baalen and Maurer, 1967). The major fatty acids present in these sediments are palmitic and stearic acids, with minor amounts of myristic acid. In Core 9-80A-5-5, where a larger sample was analyzed, there is an indication of olefinic acids (mainly 16:1 and 18:1) eluting in the GLC-MS data. These results are corroborated by the data presented by Farrington and Quinn (1971) on recent sediments from Narragansett Bay. Further work is in progress to establish the presence of the unsaturated fatty acids and to assess a diagenetic boundary for their reduction in deep-sea sediments. It should also be noted that in some of the acetone extracts from the carbonate-rich samples (usually pure white), the alkane content is low, but significant amounts of fatty acids and minor amounts of other polar compounds were isolated (for example, 9-82A-3-5).

These samples appear to contain sterones, sterols and some steranes in the carbon skeleton range of C_{27} to C_{29}. There were no terpenoidal compounds with a 30 or 40 carbon skeleton detected. The peak at m/e 191 ($C_{14}H_{23}$), however, was significantly above background. This peak was previously thought to be characteristic only of terrigenous terpenoids (Simoneit and Burlingame, 1971a), but the possibility of the C_{27} to C_{29} steroids fragmenting to such an ion is under further investigation. Again the excellent state of preservation of the organic matter with regard to structural and functional features in these samples is noteworthy as compared to terrestrial samples of similar age (Burlingame *et al.*, 1969).

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REFERENCES

Burlingame, A. L., 1968. Data acquisition, processing and interpretation *via* coupled high-speed real-time digital computer and high resolution mass spectrometer systems. *Advances in Mass Spectrometry.* E. Kendrick (Ed.), London (The Institute of Petroleum), **4**, 15.

———, 1970. Developments and applications of real-time high resolution mass spectrometry. Intern. Conf. on Mass Spectroscopy, Kyoto. **In** *Recent Developments in Mass Spectroscopy.* K. Ogata and T. Hayakawa (Eds.), Tokyo (University of Tokyo Press), 104.

Burlingame, A. L., Haug, P. A., Schnoes, H. K. and Simoneit, B. R., 1969. Fatty acids derived from the Green River Formation oil shale by extractions and oxidations–a review. *Advances in Organic Geo-*

chemistry 1968. P. A. Schenck and I. Havenaar (Eds.) Braunschweig (Pergamon-Viewig), 85.

Burlingame, A. L., Smith, D. H., Merren, T. O. and Olsen, R. W., 1970. Real-time high resolution mass spectrometry. *Computers in Analytical Chemistry* (Vol. 4 in Progress in Analytical Chemistry series). C. H. Orr and J. Norris (Eds.), New York (Plenum Press), 17.

Burlingame, A. L. and Smith, D. H., 1968. Automated heteroatomic plotting as an aid to the presentation and interpretation of high resolution mass spectral data. *Tetrahedron.* **24**, 5749.

Farrington, J. W. and Quinn, J. G., 1971. Fatty acid diagenesis in recent sediment from Narragansett Bay, Rhode Island. *Nature. (Physical Science).* **230**, 67.

Parker, P. L., Van Baalen, C. and Maurer, L., 1967. Fatty acids in eleven species of blue-green algae: geochemical significance. *Science.* **155**, 707.

Simoneit, B. R., 1971. *Apollo 14 Organic Contamination Monitoring History.* NASA-Manned Spacecraft Center report (in press).

Simoneit, B. R. and Burlingame, A. L., 1971a. Some preliminary results on the higher weight hydrocarbons and fatty acids in the DSDP Cores, Legs 5-7. **In** E. L. Winterer *et al.,* 1971, *Initial Reports of the Deep Sea Drilling Project, Volume VII.* Washington (U. S. Government Printing Office) (in press).

———, 1971b. Further preliminary results on the higher weight hydrocarbons and fatty acids in the DSDP cores, Legs 5-8. **In** A. Kaneps *et al.,* 1971, *Initial Reports of the Deep Sea Drilling Project, Volume VIII.* Washington (U. S. Government Printing Office) (in press).

Simoneit, B. R. and Flory, D. A., 1971. *Apollo 11, 12 and 13 Organic Contamination Monitoring History.* NASA-Manned Spacecraft Center, Division Internal Note, MSC 04350.

Simoneit, B. R., Schnoes, H. K., Haug, P. and Burlingame, A. L., 1970. Nitrogenous compounds of the Colorado Green River Formation oil shale: a preliminary analysis by mass spectrometry. *Nature.* **226**, 75.

———, 1971. High resolution mass spectrometry of nitrogenous compounds of the Colorado Green River Formation oil shale. *Chem. Geol.* **7**, 123.

Smith, D. H., Olsen, R. W., Walls, F. C. and Burlingame, A. L., 1971. Real-time organic mass spectrometry: LOGOS—a generalized laboratory system for high and low resolution, GC/MS and closed-loop applications. *Anal. Chem.* (in press).