

APPENDIX

IV. COMPLEX TRITERPANOIDAL ACIDS AND HYDROCARBONS IN DSDP CORE SAMPLES AND THEIR GEOCHEMICAL SIGNIFICANCE¹

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ABSTRACT

Various DSDP core samples from Legs 5 to 15 were reexamined for the presence of triterpanoidal compounds. C₃₀ triterpanes were found in samples associated with terrigenous organic detritus or a lacustrine sedimentation environment. Samples 10-92-5-4, 50-150 cm and 11-105-11-2, 10-138 cm also contained triterpanoidal acids, C_nH_{2n-10}O₂, for n = 32-35 and a pentacyclic ketone, besides triterpanes. These compounds are potential markers for source correlations of the organic matter.

INTRODUCTION

Reexamination of the preliminary data for the DSDP core samples indicated the presence of significant amounts of triterpanoidal acids and hydrocarbons in the total extract fractions of a sample from the Gulf of Mexico (10-92-5-4, 50-150 cm, Simoneit et al., 1973a) and one from the North Atlantic Basin (11-105-11-2, 10-138 cm, Simoneit et al., 1972). Sample 10-92-5-4, 50-150 cm is from the site at 25°50.7'N and 91°49.3'W in 2573 meters of water and was sampled 178 meters below the sea bed. It is a gray silty clay with 14% carbonate of upper Pleistocene age. The total carbon content is 2.5%, 0.8% organic carbon, and the heptane-soluble matter is 320 ppm (Simoneit et al., 1973a). Sample 11-105-11-2, 10-138 cm is from the site at 34°53.7'N and 69°10.4'W in 5251 meters of water and was sampled 306 meters below the sea bed. It is a black calcareous (18% carbonate) clay ooze of lower Cretaceous age. The total carbon content is 5.7%, with 3.6% organic carbon, and the heptane-soluble matter amounts to 440 ppm (Simoneit et al., 1972).

¹Research supported by the Oceanographic Section, National Science Foundation, NSF Grant GA-24214.

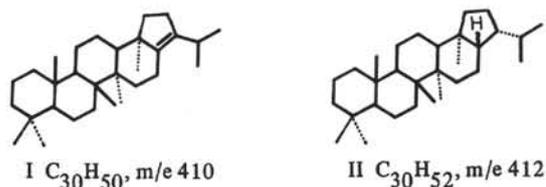
²In this report, the high resolution mass spectra are presented as heteroatomic plots (Burlingame and Smith, 1968) with the masses plotted in methylene units. On the abscissa, each principal division marker corresponds to the saturated alkyl fragment (even-electron ion), for example, C_nH_{2n+1}, with 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}. 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 yields a "low" resolution mass spectrum of the sample (presented at the bottom of the figure). The nominal masses are indicated in 50 mass unit intervals below the carbon/hydrogen ratio scale. In order to make high mass, low intensity features of the spectrum observable, the whole spectrum or any region thereof is multiplied by a scale factor, which is indicated by /x 00 at the point of scale expansion.

EXPERIMENTAL

The analytical procedures and preliminary data evaluations of the DSDP core samples discussed here have been presented (Simoneit et al., 1972, 1973a; Simoneit and Burlingame, 1973a, 1973b). The GC/MS data of the samples from all legs (Simoneit and Burlingame, 1971, 1973a, 1973b) were reexamined using computer techniques, and the compounds of interest were detected mainly in the samples from Leg 10, Site 92 and Leg 11, Site 105. The extracts from these samples were further examined using high resolution mass spectrometry² and supplementary GC/MS analysis.

RESULTS AND DISCUSSION

Triterpanoidal compounds, mainly C₃₀ species, were found in many DSDP samples associated with terrigenous organic detritus or a lacustrine history, and thus they were considered potential markers for source correlations of the organic matter (Simoneit and Burlingame, 1973a, 1973b). Triterpanes of the compositions C₃₀H₄₈, C₃₀H₅₀, C₃₀H₅₂, and C₃₁H₅₄ were detected in the samples from Leg 14, Site 138 drilled in the Canary Basin, Atlantic Ocean (Simoneit et al., 1973b). The mass spectrometric data indicated possibly 17(21)-hopene (Structure I) for the C₃₀H₅₀ species and hopane (Structure II) for the C₃₀H₅₂ species (Simoneit and Burlingame, 1973a, 1973b).



In the case of Sample 10-92-5-4, 50-150 cm the major C₃₀ triterpanoidal species present in the total alkane fraction is possibly 17(21)-hopene (Structure I). The salient features of the GC/MS data for these polycyclic compounds are shown in Figure 1. The complete data have appeared elsewhere (Simoneit et al., 1973a). The scan 230-233 spectra (cf. Figure 1) are all mixtures of compounds,

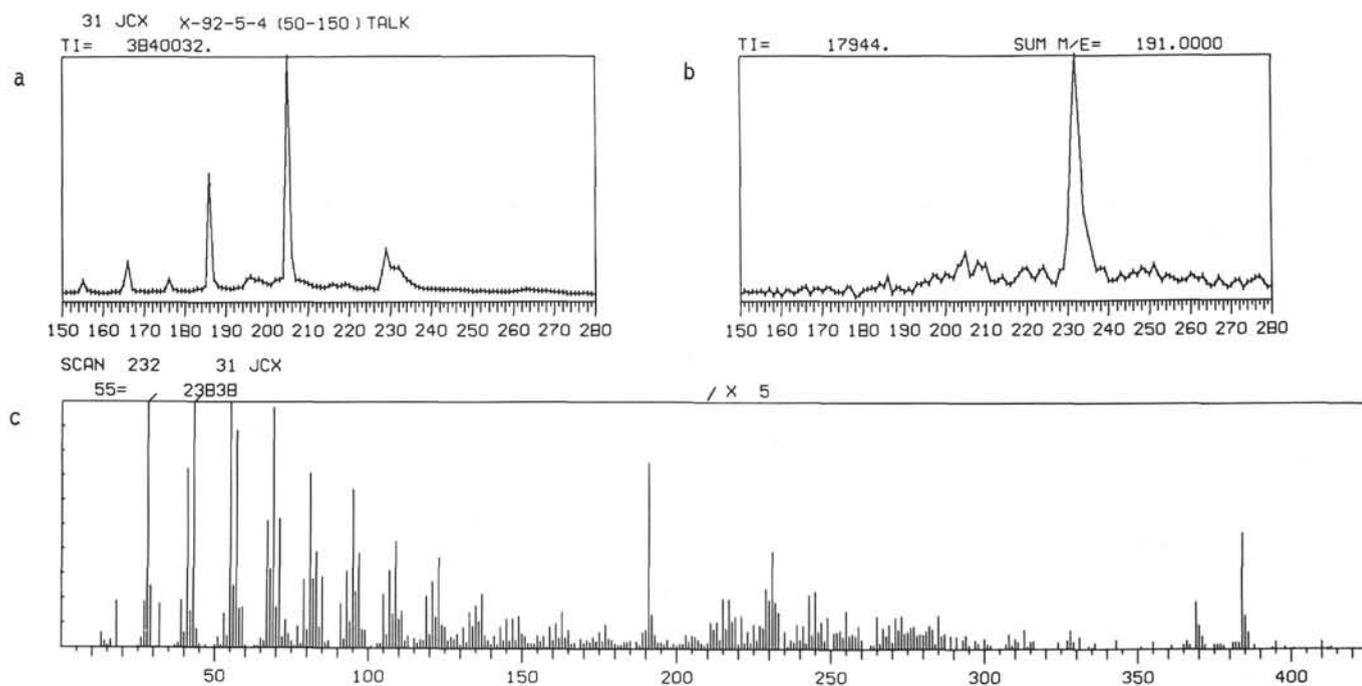
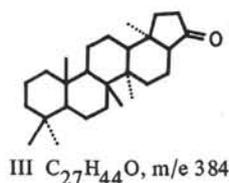
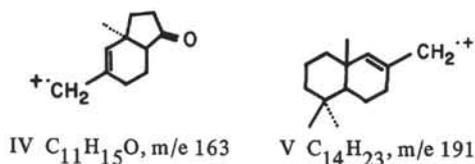


Figure 1. GC/MS data for the total alkane fraction from Sample 10-92-5-4, 50-150 cm (isothermal temperature program region shown only; GC conditions as in Simoneit et al., 1973a). (a) total ionization sum plot, (b) m/e 191 sum plot, (c) mass spectrum scan 232 (mixture of probably trinorhopanone-21, MW 384 and 17(21)-hopene, MW 410).

consisting mainly of the triterpane with MW 410 and a pentacyclic ketone—probably trinorhopanone-21 (Structure III). This ketone is indicated by the peaks at m/e 163



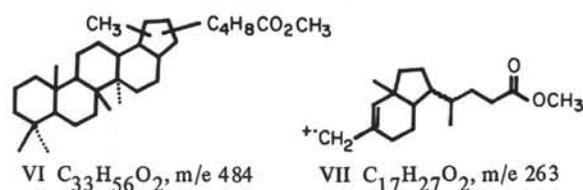
(Structure IV) and m/e 191 (Structure V) in the mass spectrum of Figure 1c. Both compounds also exhibit the loss of methyl radical from their molecular ion.



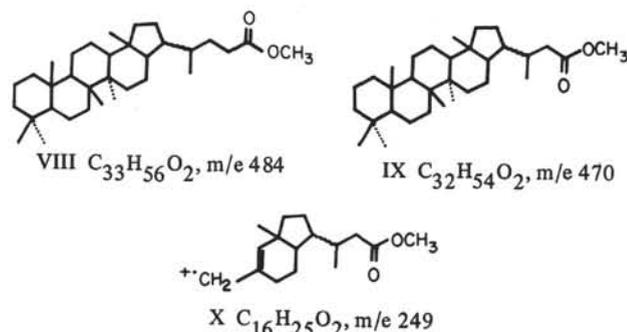
These triterpanes and a triterpanoidal ketone were identified in a terrestrial lacustrine oil shale (Bouxwiller shale) by Arpino, 1973.

Triterpanoic acids were present in the acid fractions from core Samples 10-92-5-4, 50-150 cm (the total methyl esters) and 11-105-11-2, 10-138 cm (the branched/cyclic methyl esters). The salient features of the GC/MS data for Sample 10-92-5-4, 50-150 cm are shown in Figure 2. The major homolog of the series $C_nH_{2n-10}O_2$ in both DSDP samples is $n = 32$ (as the methyl ester) and has the Structure VI. Structure VI exhibits a loss of methyl radical to yield the peak at m/e 469 (cf. Figure 2d) and loss of

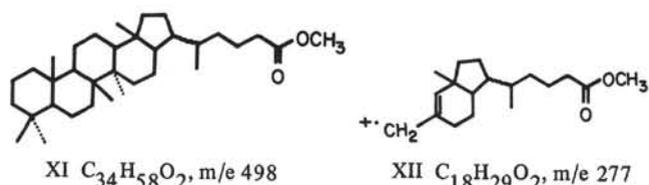
$C_4H_8CO_2CH_3$ to yield the peak at m/e 369 of composition $C_{27}H_{45}$. The base peak is m/e 263 (Structure VII) and m/e 191 (Structure V) is also intense. The strong loss of



$C_6H_{11}O_2$ to yield m/e 369, the hydrocarbon fragment, indicates that the configuration of ring E probably is as shown in Structure VIII, a higher homolog of homohopanoic acid (Albrecht, private communication, 1973; Arpino, 1973). The other homologs of the series $C_nH_{2n-10}O_2$ are $n = 31$ and 33 (cf. Figure 2). The scan 368-371 spectra fit the fragmentation pattern of the methyl ester of homohopanoic acid (Structure IX) with a base peak at m/e 249 (Structure X, cf. Figure 2c). The scan

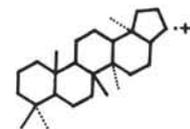


483-491 spectra (cf. Figure 2) fit the fragmentation pattern of the methyl ester of bishomohopanoic acid (Structure XI) with a base peak at m/e 277 (Structure XII).



The compositions of the major fragment ions of these acids were confirmed by high resolution mass spectrometry. The HRMS data for the branched/cyclic acid fraction from Sample 11-105-11-2, 10-138 cm are shown in Figure 3. The

C/H data (Figure 3a) indicate the compositions $C_{14}H_{23}$ for the ion at m/e 191 (Structure V) and $C_{27}H_{45}$ for the ion at m/e 369 (Structure XIII). In the C/HO₂ data (cf. Figure



XIII $C_{27}H_{45}$, m/e 369

3b) the major fragment ion series $C_nH_{2n-7}O_2$ ranges mainly from $n = 15-20$, with a maximum intensity at $n = 17$ (Structure VII). The molecular ion series, $C_nH_{2n-10}O_2$, ranging from $n = 32-35$ and the $M - CH_3$ ion series, $C_nH_{2n-11}O_2$, ranging from $n = 30-34$ are also evident (cf.

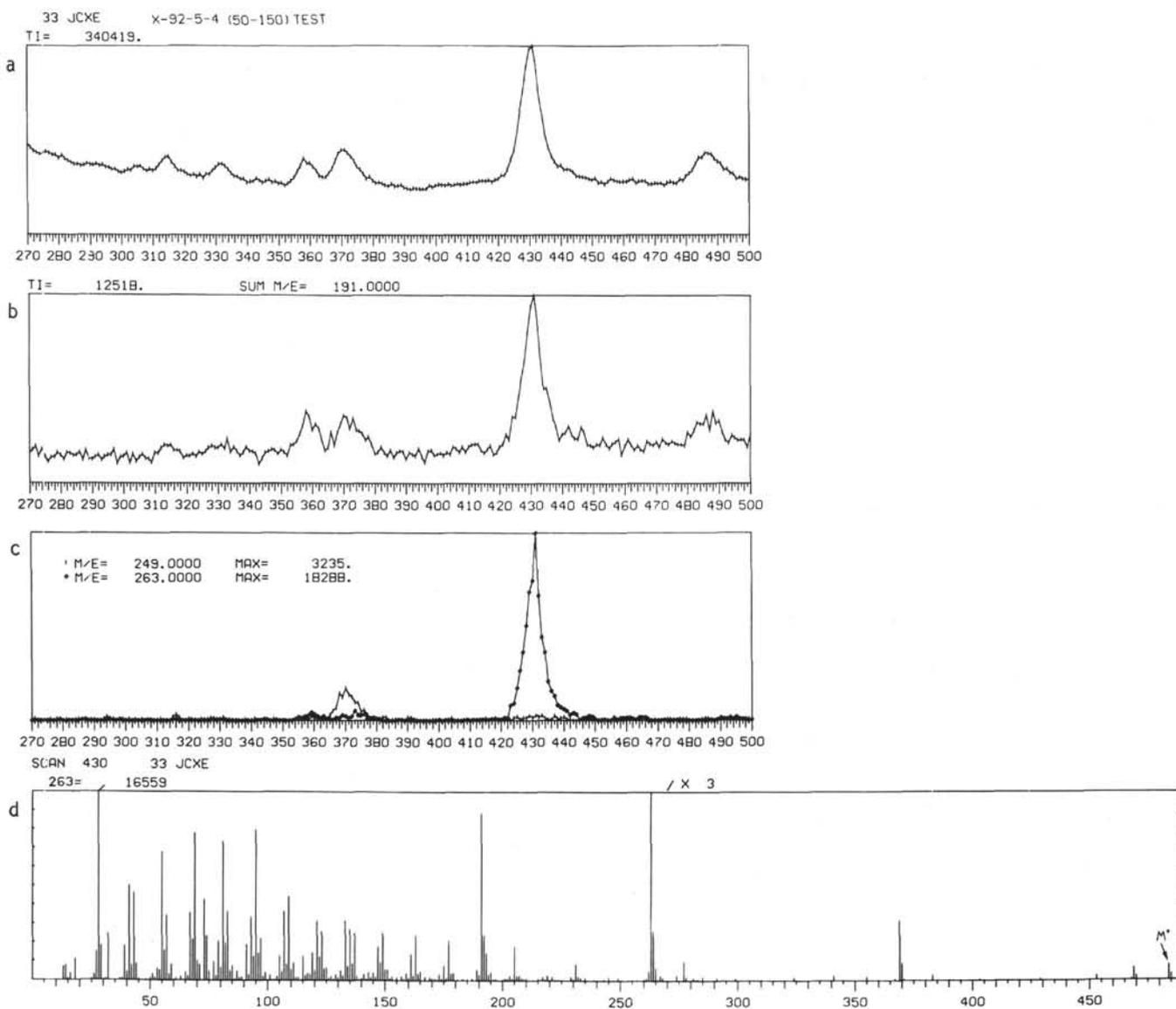


Figure 2. GC/MS data for the total acid ester fraction from Sample 10-92-5-4, 50-150 cm (isothermal temperature program region shown only; GC conditions as in Simoneit et al., 1973a). (a) total ionization sum plot, (b) m/e 191 sum plot, (c) m/e 249 and 263 sum plot, (d) mass spectrum scan 430 (methyl bishomohopanoate, MW 484).

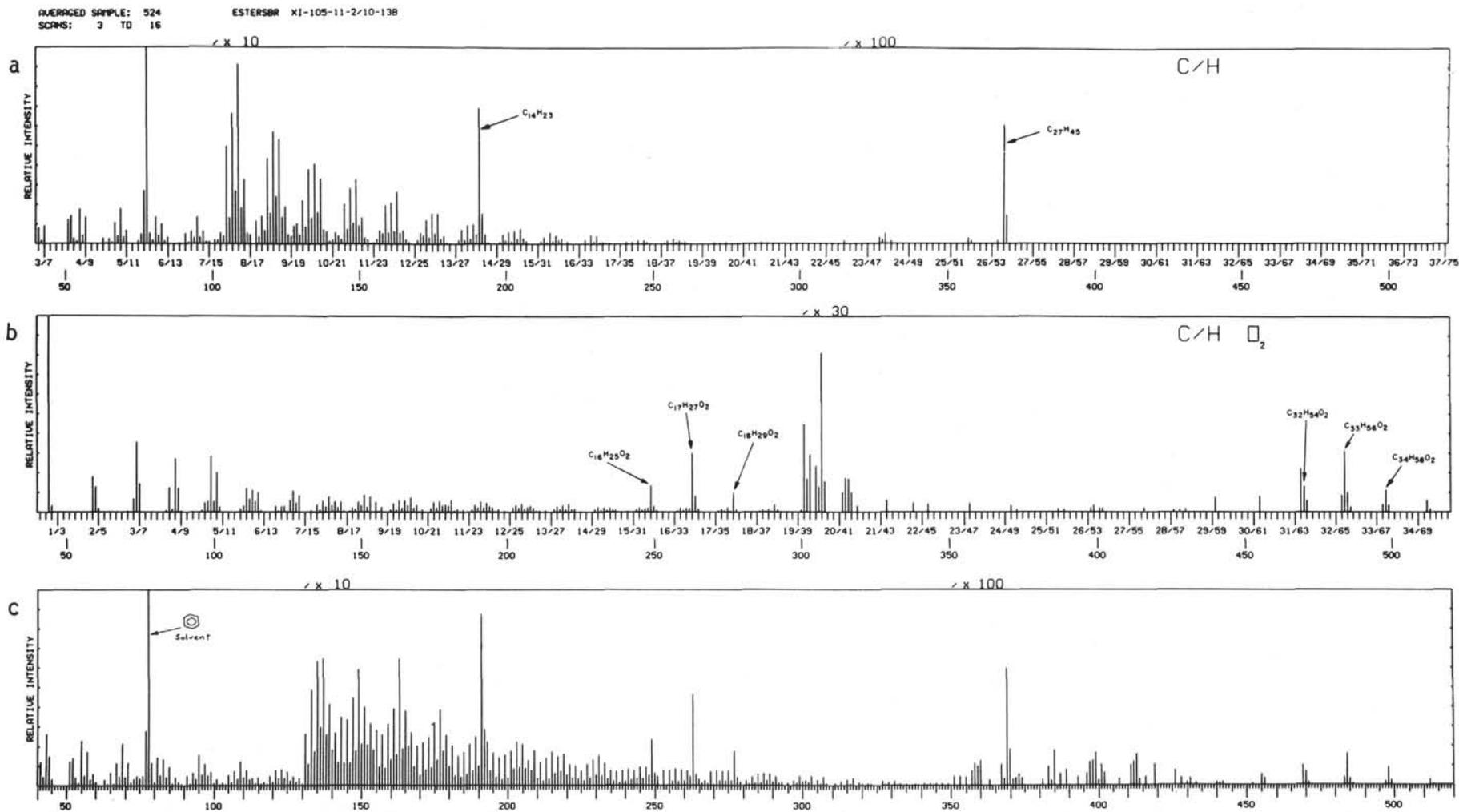


Figure 3. High resolution mass spectrometric data for the branched/cyclic acid esters from Sample 11-105-11-2, 10-138 cm. (a) C/H data, (b) C/H O_2 data, (c) composite data.

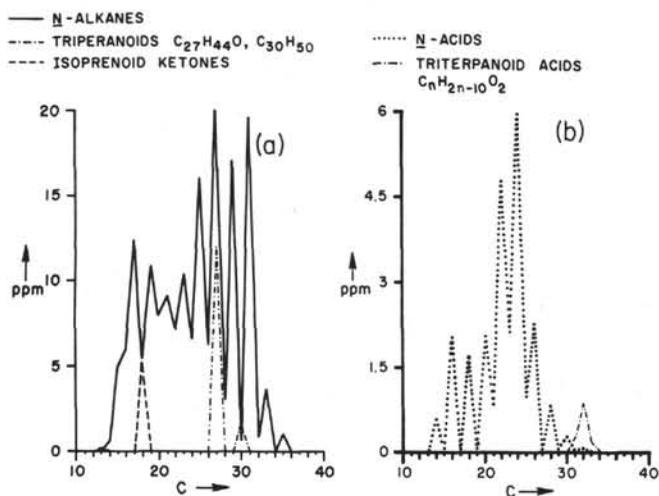


Figure 4. Histograms for the various compound distributions in Sample 10-92-5-4, (50-150 cm). (a) n-alkanes, isoprenoid ketones, and triterpenoidal compounds, (b) n-acids and triterpanoid acids.

Figure 3b). The relative intensities of these acid fragment ions versus other compound fragmentation can be discerned in the composite plot of all the HRMS data (cf. Figure 3c).

These triterpanoic acids were identified in lacustrine oil shales (Bouxwiller shale by Arpino, 1973; and Messel shale by Albrecht, private communication, 1973). The major fragment ions of this acid series and the low resolution mass spectrum of the C_{32} acid (Figure 2d) present in the DSDP samples match the patterns observed by Arpino (1973).

The relative concentrations of these acids versus the normal fatty acids and the polycyclic hydrocarbons and ketones versus the normal alkanes are found in the distribution histograms of Figure 4.

CONCLUSIONS

Triterpanes and triterpanoic acids were identified in several DSDP sediment samples. They are attributable to a terrigenous and/or lacustrine derivation. Terrestrial oil shales of lacustrine origin (Eocene age) also contain these compounds (Albrecht, personal communication, 1973; Arpino et al., 1972; Arpino, 1973). The presence of triterpanoic acids in the Pleistocene sample from the Gulf of Mexico indicates a Recent biogenic source for these compounds. The presence of these acids in Sample 11-105-11-2, 10-138 cm indicates that these compounds are stable over longer geologic times (in this case to Lower Cretaceous—140 m.y.). It also corroborates the evolution of the North Atlantic Ocean from an enclosed sea by continental drift over this time span (Dietz and Holden, 1970; Tarling, 1971). At the time of sedimentation of this sample, the Atlantic Sea was probably a lacustrine environment.

ACKNOWLEDGMENTS

I thank Dr. A. L. Burlingame for his encouragement and use of the laboratory facilities, Mrs. E. Roitman and Mrs. E. Scott for technical assistance, and Dr. R. Cox and Dr. J. J. Chang for mass spectrometric data. The financial support from the Oceanographic Section of the National Science Foundation (NSF Grant GA-24214) is gratefully acknowledged.

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