

27. ORGANIC GEOCHEMISTRY OF MESOZOIC SEDIMENTS FROM DEEP SEA DRILLING PROJECT SITE 330, FALKLAND PLATEAU¹

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ABSTRACT

Sources of organic matter in Mesozoic sediments from the DSDP Site 330, Falkland Plateau, have been examined. The lipids of a Cretaceous sample are mixed terrigenous and marine, and those of a Jurassic sample are predominantly marine. Kerogens are predominantly oxidized terrigenous detritus, except from an autochthonous marine sample from the middle Jurassic.

INTRODUCTION

The organic matter of various Mesozoic sediments from the Atlantic Ocean has been analyzed (e.g., Simoneit, 1978a, 1978b, 1979, in press[a], Stuermer and Simoneit, 1978; Deroo et al., 1978). These data have resulted in detailed assessments of the conditions of sedimentation, of the catagenetic maturity of the organic matter, and of the biogenic origins of the organic matter (Simoneit, in press[a]; Deroo et al., 1978). Similar data for the South Atlantic Ocean are sparse; thus it was of interest to examine the samples from DSDP Leg 36 (e.g., Simoneit, in press [a].)

The samples analyzed here are from Site 330 (50°55.19'S, 46°53.00'W; water depth 2626 m), at the western end of an elongate rise, the Maurice Ewing Bank (Barker et al., 1974), forming the eastern end of the Falkland Plateau.

ANALYTICAL METHODS

The core samples were freeze-dried and then extracted with toluene and methanol (4:1), using ultrasonication. The extracts for each sample were concentrated on a rotary evaporator and subjected to gas chromatography (GC). The extracts were then treated with diazomethane in ether and subjected to silica-gel thin-layer chromatography (TLC), using methylene chloride as eluent. The bands corresponding to hydrocarbons, esters, and ketones were scraped off the TLC plate after development with iodine vapor, and eluted with ether or ethyl acetate. The hydrocarbon and combined ester and ketone fractions were subjected to GC and combined GC and mass spectrometric (MS) analyses.

The GC analyses were carried out on a Hewlett-Packard model 5830 gas chromatograph, using a 16 meter by 0.25 mm stainless steel Scott column coated with OV-101, programmed from 110 to 280°C at 4°C per minute, using He carrier gas at a flow rate of 3 ml/min.

The GC/MS analyses were carried out on a Finnigan model 4000 quadrupole mass spectrometer interfaced directly to a Finnigan model 9610 gas chromatograph equipped with a 30 meter by 0.25 mm glass capillary column coated with OV-101. The GC conditions for the GC/MS analyses were like those for the analytical GC system. Mass-spectrometry data were recorded and processed by a Finnigan-Incos model 2300 data system.

Analyses of stable carbon isotopes were carried out by the methodology described by Kaplan et al. (1970), using the Chicago PDB as reference standard.

RESULTS AND INTERPRETATION

Sample descriptions and results of the carbon, lipid, and kerogen analyses are in Table 1. The organic-carbon content of the sapropelic claystones is high, and the lipid yield is low. An evaluation of the petroleum potential of these sediments has been presented (Comer and Littlejohn, 1976), in which hydrocarbons and kerogens were analyzed.

Concentrations of various homologous-compound series in the lipid fractions are given in Figure 1. The *n*-alkanes for Sample 330-4-2, 120–126 cm (Neocomian) exhibit a bimodal distribution, ranging from *n*-C₁₃ to *n*-C₃₅, with maxima at C₁₉ and C₃₁ and a strong odd-carbon-number predominance (Figure 1A). The homologs *>n*-C₂₅ are derived from higher-plant wax, and those *<n*-C₂₁ are indicative of a bacterial origin (Simoneit, 1979c). The presence of significant amounts of *n*-alkylcyclohexanes, C_{*n*}H_{2*n*}, with carbon numbers ranging from 13 to 25, and a maximum at 19 (Figure 1C), is further evidence for bacterial lipid residues. The pristane/phytane ratio is 0.5, and the presence of elemental sulfur indicates euxinic conditions of sedimentation (Didyk et al., 1978), in agreement with preliminary findings (Barker et al., 1974). The *n*-fatty acids exhibit a bimodal distribution over the range from *n*-C₁₂ to *n*-C₃₂, and a strong even-carbon-number predominance, with maxima at *n*-C₁₆ and *n*-C₂₈ (Figure 1E). The maximum at *n*-C₂₈ fatty acid, when considered with the maximum at *n*-C₃₁ for the *n*-alkanes, indicates a higher-plant-wax origin (Simoneit, in press[b]). The *n*-fatty acids *<n*-C₂₀

¹ Contribution No. 1919 from the Institute of Geophysics and Planetary Physics, University of California, Los Angeles. (This chapter was included in this volume for publication convenience.)

TABLE 1
Sample Descriptions and Results of Carbon, Lipid, and Kerogen Analyses

Sample (Interval in cm)	Sub-Depth (m)	Geologic Age	Lithology	Carbon ^a			<i>n</i> -alkanes			Lipid Yields			<i>n</i> -methylketones			Kerogen			
				Total (%)	Org. (%)	CaCO ₃ (%)	Total (μg/g)	CPI ^b	Max. ^c	Total (μg/g)	CPI ^b	Max. ^c	Total (μg/g)	CPI ^b	Max. ^c	Pr/Ph ^d	Perylene	H/C ^a	δ ¹³ C (‰) ^e
330-4-2, 120-126	274.2	Cret. (Neocom.)	Gray sapropelic claystone	3.64	3.25	3	3.5	1.86	19,31	4.0	7.3	16,28	0.4	0.7	16	0.5	0	1.17	-26.7
330-5-2, 57-61	302.1	L. Jur. (Oxf.-Kimm.)	Gray sapropelic claystone	4.4	4.0	3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.11	-25.5
330-5-3, 29-34	303.3	L. Jur. (Oxf.-Kimm.)	Gray sapropelic claystone	3.5	3.2	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.05	-25.6
330-6-6, 77-82	317.8	L. Jur. (Oxf.-Kimm.)	Gray sapropelic claystone	4.6	4.4	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.15	-25.1
330-10-1, 98-102	405.5	L. Jur.	Olive sapropelic claystone	3.12	3.1	0	25	1.56	17,22, 29	8	3.10	16,24	1.0	0.9	11,16	0.8	0	1.20	-27.3
330-14-4, 127-136	524.3	M. Jur.	Olive gray clayey silt	1.87	1.8	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.18	-24.1

^a Determined and calculated from data by Galbraith Laboratories, Knoxville, Tennessee; Deep Sea Drilling Project; and UCLA.

^b Carbon preference index, summed from C₁₀ to C₃₅.

^c The dominant homolog is underscored.

^d Pristine-phytane ratio.

^e Compared to Chicago PDB standard.

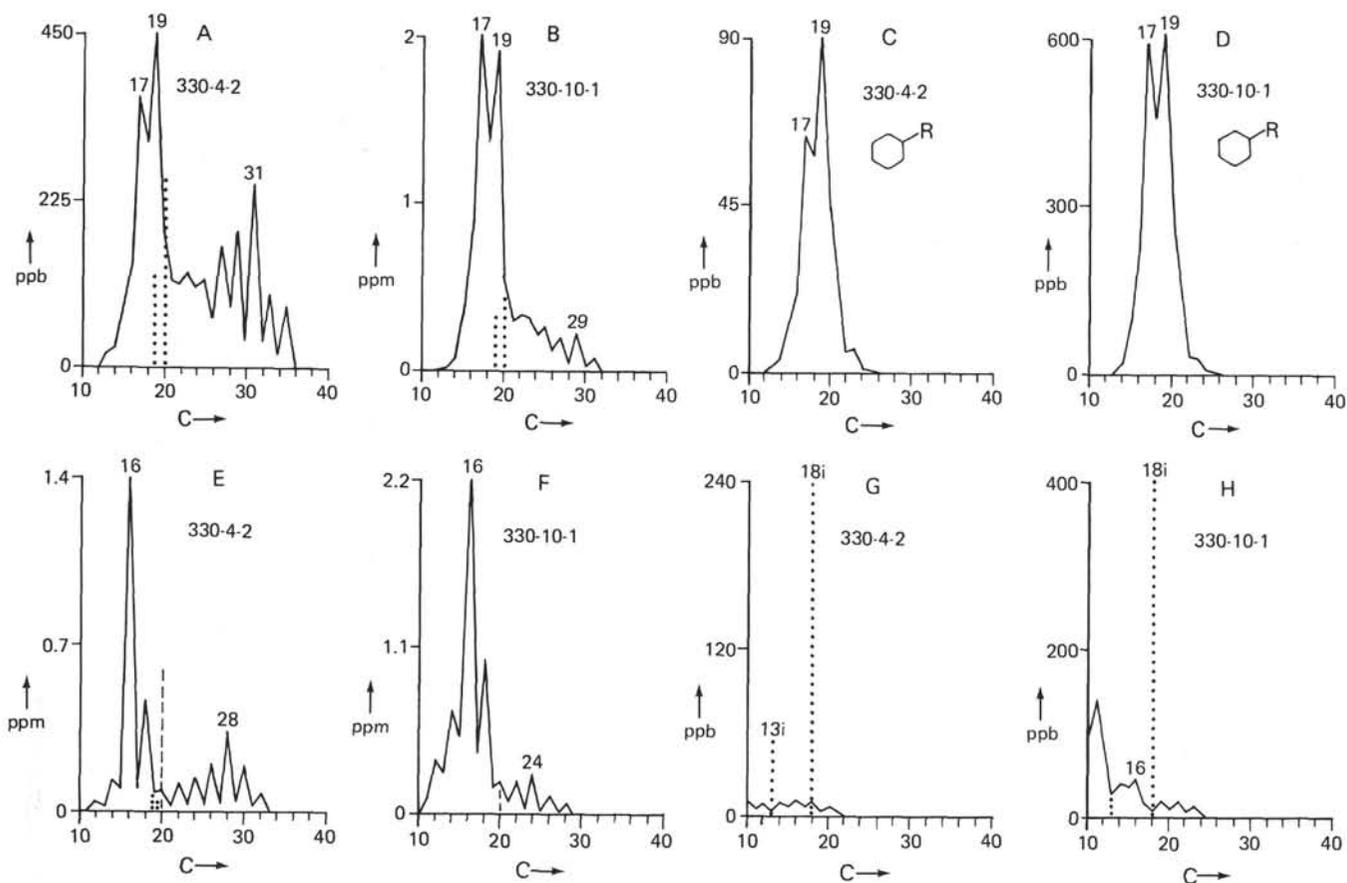


Figure 1. Concentrations of various lipid components: (A) and (B), *n*-alkanes; (C) and (D), *n*-alkylcyclohexanes; (E) and (F), *n*-fatty acids; (G) and (H), *n*-alkane-2-ones. Isoprenoids shown by dotted lines, dehydroabietic acid by dashed lines.

are most likely marine and autochthonous (Simoneit, in press[b]). A significant amount of dehydroabietic acid (structure I) is also present, indicating an allochthonous influx from resinous higher plants (Simoneit, 1977).

The ketones consist predominantly of 6,10,14-trimethylpentadecan-2-one, 6,10-dimethylundecan-2-one and *n*-alkane-2-ones ranging from C₁₀ to C₂₁ with an even-carbon-number predominance (Figure 1G). These

compounds are probably products of microbial degradation of phytol and microbial lipids (Simoneit, 1973, in press[b]).

The *n*-alkanes in Sample 330-10-1, 98–102 cm (Upper Jurassic) exhibit an essentially unimodal distribution, ranging from *n*-C₁₃ to *n*-C₃₁, with *n*-C₁₇ and *n*-C₁₉ dominant (and minor dominance > *n*-C₂₅ showing a strong odd-carbon-number predominance) (Figure 1B). This indicates a minor influx of higher-plant wax and a predominantly bacterial lipid residue, which is further substantiated by the presence of the alkylcyclohexanes (Figure 1D). The pristane/phytane ratio is 0.8; this and the presence of elemental sulfur may indicate partially euxinic conditions of sedimentation (Didyk et al., 1978). The *n*-fatty acids exhibit a bimodal distribution, with a maximum at *n*-C₁₆ and a lesser one at *n*-C₂₄, and show a strong even-carbon-number predominance (Figure 1F). These acids are primarily autochthonous microbial products, with a minor allochthonous influx from higher-plant wax. The presence of dehydroabietic acid (I) indicates a contribution from resinous plants (Simoneit, 1977b). The ketones consist of mainly 6,10,14-trimethylpentadecan-2-one; 6,10-dimethylundecan-2-one; and *n*-alkan-2-ones ranging from C₁₀ to C₂₅ with a strong odd-carbon-number predominance (Figure 1H). These compounds are probably products of microbial degradation of phytol and microbial lipids (Simoneit, 1973, in press[b]).

Perylene, a possible terrigenous marker preserved under anaerobic conditions of sedimentation (Didyk et al., 1978; Aizenshtat, 1973), was not detected in either sample.

The polycyclic components of the hydrocarbon fractions consist of sesquiterpenoidal, diterpenoidal, triterpenoidal, and steroidal compounds. The sesquiterpenoids comprise cadalene (II), tetrahydrocadalene (probably 5,6,7,8-tetrahydro, III), and a trace of cadinane (IV) in both Samples 330-4-2, 120–126 cm and 330-10-1, 98–102 cm. These compounds may have originated from resinous plants or from autochthonous algae. The diterpenoidal compounds of both samples consist of dehydroabietane (V), retene (VI), dehydroabietin (VII) with another isomer, and simonellite (VIII). These diterpenoids are derived from terrestrial resinous plants (Simoneit, 1977b). The relative concentrations of diterpenoids and triterpenoids (based on the *m/z* 191 peak intensity in the GC/MS data and on GC response) are plotted in Figure 2.

The triterpenoids are composed mainly of the hopane series, with minor amounts of the moretanenes. The 17β(H),21β(H) stereoisomers are predominant over the 17α(H), 21β(H) isomers, and 17β(H), 21β(H)-homohopane (IX, R = CH₃) is the major homolog. The hopane series comprises the trisnorhopanes (X, R = H), norhopanes (X, R = C₂H₅), hopanes (X, R = C₃H₇), homohopanes (IX, R = CH₃), and bishomohopanes (IX, R = C₂H₅). The moretane series probably consists of the 17β(H), 21α(H) stereoisomers and ranges from C₃₀ to C₃₂. No triterpenes were detected. These triterpanes are probably autochthonous, derived from the diagenetic products of bacteriohopanepolyols (Rohmer,

1975). The dominance of the 17β(H) stereochemistry (cf. ratios <1.0 in Table 2), indicates the geologic immaturity of these triterpenoids (Dastillung and Albrecht, 1976; Simoneit and Kaplan, in press). Similar triterpane distributions were found for Cretaceous shales from the North Atlantic Ocean (e.g., Simoneit, 1979a,d). Triterpenoidal acids were identified in Sample 330-10-1, 98–102 cm only and consisted of the extended hopanoic acids (XI) ranging from C₃₁ to C₃₃. The 17β(H) stereoisomers are predominant over the 17α(H) stereoisomers (cf. ratios <1.0 in Table 2), indicating that they are also geologically immature.

Significant amounts of steranes are present, and their concentrations are plotted in Figure 3. The 5α(H) isomers (XII) are predominant over the 5β(H) series (XIII) (i.e., cholestane > coprostanene) for both samples. The ratios of the *cis* (5β) to *trans* (5α) stereoisomers are given in Table 2; all are less than 0.6. Ratios for mature source rocks and petroleum have been observed in the range 0.6 to 0.8 (e.g., Seifert and Moldowan, 1978). Cholestane (XII, R = H) is the predominant sterane in Sample 330-4-2, 120–126 cm and 24-ethylcholestane (XII, R = C₂H₅) is the major sterane in Sample 330-10-1, 95–102 cm. The distribution of the steranes in Sample 330-4-2, 120–126 cm appears to indicate that they are terrigenous; the steranes of Sample 330-10-1, 95–102 cm appear to be autochthonous (Gaskell, 1974; Goad et al., 1972; Rubinstein, 1973); however, the distinction is not very clear.

Contamination from various plasticizers and lubricants is minor and consists primarily of dibutyl and dioctyl phthalates, and dibutyl esters of dicarboxylic acids from the core tubes (Simoneit, 1975).

The kerogen was isolated from the sediments using the procedure of Stuermer et al. (1978) and the ratio H/C ranges from 1.05 to 1.20 (Table 1; rather aromatic). The δ¹³C values are found in Table 1. The data for Samples 330-4-2, 120–126 cm; 330-5-3, 29–34 cm; and 330-10-1, 98–102 cm are in the range typical of terrigenous material. The material in Sample 330-14-4, 127–136 cm is marine. If both the H/C and δ¹³C data are considered, this kerogen appears to be oxidized terrigenous detritus which was redeposited at Site 330. This is corroborated by the content of terrestrial pollen and spores (Hedlund and Beju, 1976).

CONCLUSIONS

The lipids of Sample 330-4-2, 120–126 cm (Cretaceous) are of mixed origin (predominantly marine, with some terrigenous influx), whereas the lipids of Sample 330-10-1, 98–102 cm (Jurassic) are predominantly marine. This is indicated by the distributions of the *n*-fatty acids, alkylcyclohexanes, *n*-alkan-2-ones, and molecular markers such as diterpenoids, sesquiterpenoids, triterpenoids, and steroids.

The kerogens appear to be composed primarily of oxidized terrigenous detritus (low H/C values and δ¹³C < -25‰), except for Sample 330-14-4, 127–136 cm, which is autochthonous marine. The conditions of sedimentation were anaerobic; there probably was an influx of oxidized kerogen from terrestrial areas, coupled with

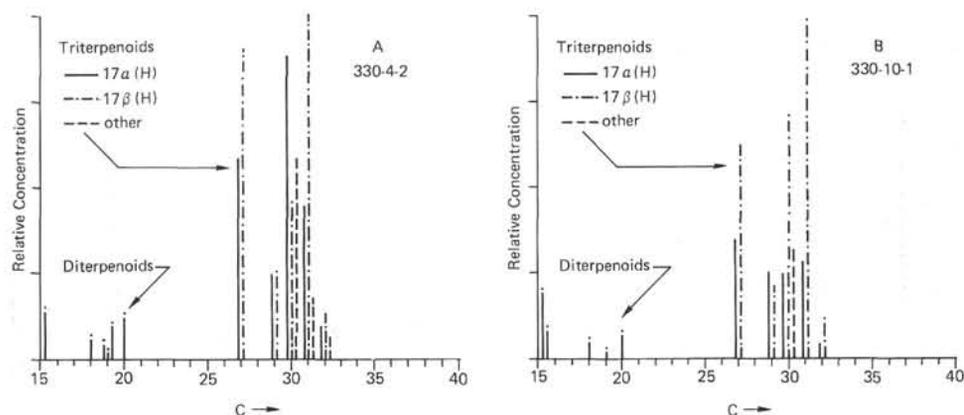


Figure 2. Relative concentrations of diterpenoids and triterpenoids.

TABLE 2
Stereoisomeric Ratios for Triterpanes and Steranes^a

Sample (Interval in cm)	C ₂₇	C ₂₈	C ₂₉	C ₃₀	C ₃₁	C ₃₂	C ₃₃
Triterpanes: 17 α (H)/17 β (H)							
330-4-2, 120-126	0.66	—	0.96	1.90	0.44	0.83	—
330-10-1, 98-102	0.55	—	1.25	0.36	0.28	0.33	—
Triterpenoid Acids: 17 α (H)/17 β (H)							
330-10-1, 95-102	—	—	—	—	0.50	0.55	0.67
Steranes: 5 β (H)/5 α (H)							
330-4-2, 120-126	0.56	0.56	0.56	0.58	—	—	—
330-10-1, 95-102	0.40	0.45	0.42	—	—	—	—

^aDetermined by integration of peaks in the respective m/z 191 and m/z 217 mass chromatograms.

some influx of terrigenous lipids for Sample 330-4-2, 120-126 cm, and autochthonous production of lipids. These inferences are in agreement with the description of the sedimentary record at this site (Barker et al., 1974) and other areas (Thiede and van Andel, 1977; Schlanger and Jenkyns, 1976).

ACKNOWLEDGMENTS

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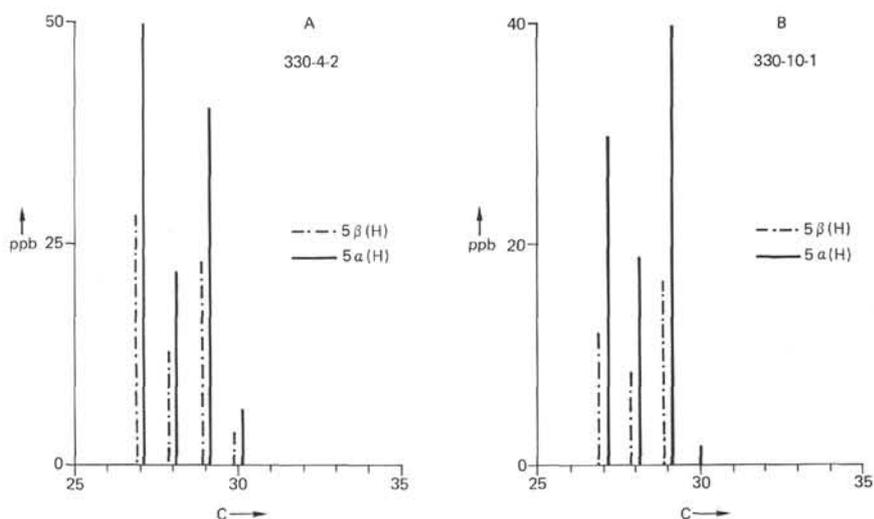
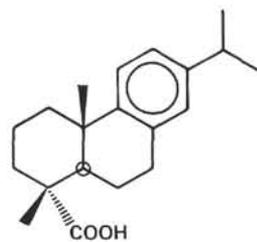


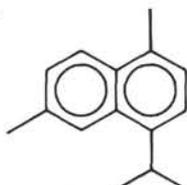
Figure 3. Concentrations of steranes.

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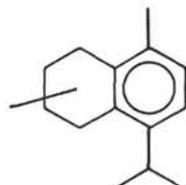
APPENDIX



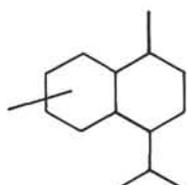
I. Dehydroabietic acid



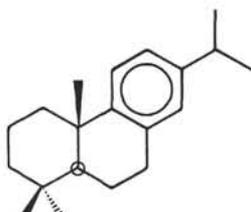
II. Cadalene



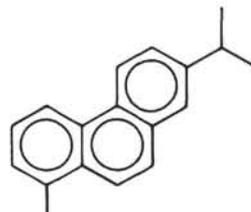
III. Tetrahydrocadalene



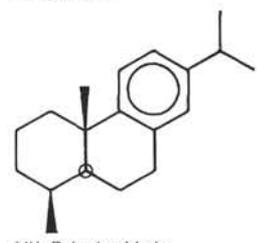
IV. Cadinane



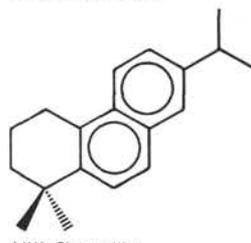
V. Dehydrobietane



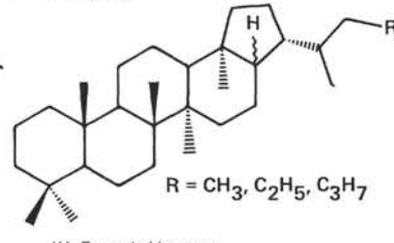
VI. Retene



VII. Dehydrobietin

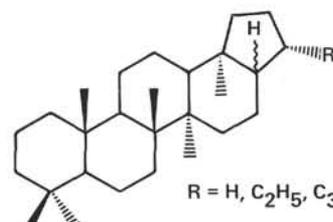


VIII. Simonellite



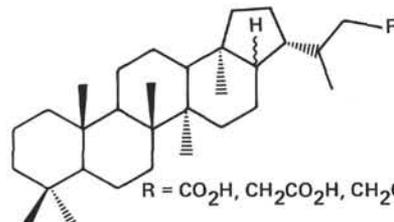
IX. Extended hopanes

R = CH₃, C₂H₅, C₃H₇



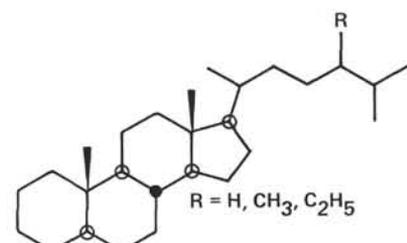
X. Hopanes

R = H, C₂H₅, C₃H₇



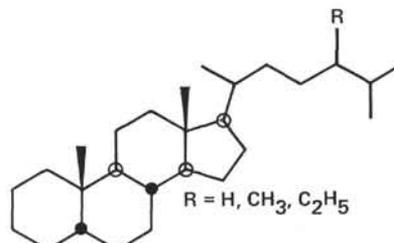
XI. Extended hopanoic acids

R = CO₂H, CH₂CO₂H, CH₂CH₂CO₂H



XII. 5α(H)-Steranes

R = H, CH₃, C₂H₅



XIII. 5β(H)-Steranes

R = H, CH₃, C₂H₅