15. OLEANENE, URSENE, AND OTHER TERRIGENOUS TRITERPENOID BIOLOGICAL-MARKER HYDROCARBONS IN BAFFIN BAY SEDIMENTS

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ABSTRACT

The aliphatic hydrocarbon fractions of eight early Miocene to Pliocene sediment samples from Hole 645E (Baffin Bay; ODP Leg 105) were investigated by gas chromatography and gas chromatography/mass spectrometry. Long, straight-chain alkanes of terrigenous origin are often present as major compounds. Other terrigenous biological markers include three oleananes with a double bond at positions 12, 13(18), or 18, and taraxer-14-ene. Urs-12-ene is identified tentatively. In the three deepest samples, 17α(H), 18α(H), and 21β(H)-28, 30-bisnorhopane is the most abundant compound. Several new compounds were detected, some of which are tentatively identified. The identification and possible significance of 23-norhopane, three A/B-ring nuclear demethylated (or A-nor-) oleanenes, and an A/B-ring nuclear demethylated (or A-nor-) urs-12-ene are discussed. The authors postulate that taraxer-14-ene isomerizes to olean-12-ene with increasing burial depth.

INTRODUCTION

The continental shelf areas of Baffin Bay and Davis Strait were important areas for oil exploration in the mid-1970s. However, drilling was unsuccessful, although some source rocks having a potential mainly for gas were encountered (Rolle, 1985). Site 645 is located on the continental slope off southern Baffin Island in a water depth of 2020 m (Fig. 1). The sediments recovered while drilling seven holes are considered to represent almost a continuous record well into the early Miocene. This sediment sequence shows a pronounced terrigenous fraction almost devoid of fossils (Shipboard Scientific Party, 1987). Organic matter is predominantly of kerogen type III (Stein et al., this volume). Standard laboratory procedures are described elsewhere (e.g., Rullkötter et al., 1987). Gas chromatography of the aliphatic hydrocarbon fractions was performed using a Hewlett-Packard 5710A gas chromatograph equipped with a Gerstel programmed temperature-injector system (KAS, Gerstel, Mülheim/Ruhr) and a fused silica capillary column (length = 25 m; inside diameter = 0.32 mm) coated with CP Sil 8. Helium was used as carrier gas, and the temperature was programmed from 80° to 300°C at 4°C/min. Gas chromatography/mass spectrometry was conducted using a Carlo Erba Fractovap 4160 gas chromatograph coupled to a VG 7070E mass spectrometer operating at 70 eV. Samples were injected, using the on-column mode, onto a fused silica capillary column (length = 25 m; inside diameter = 0.32 mm) coated with SE 54. Helium was used as carrier gas, and the temperature was programmed from 110° to 320°C at 3°C/min.

METHODS AND PROCEDURES

Eight samples from Hole 645E were investigated (Table 1). All are from lithologic Unit III (Shipboard Scientific Party, 1987) and were selected on the basis of organic-petrographic differences as reported by Stein et al. (this volume). Standard laboratory procedures are described elsewhere (e.g., Rullkötter et al., 1987). Gas chromatography of the aliphatic hydrocarbon fractions was performed using a Hewlett-Packard 5710A gas chromatograph equipped with a Gerstel programmed temperature-injector system (KAS, Gerstel, Mülheim/Ruhr) and a fused silica capillary column (length = 25 m; inside diameter = 0.32 mm) coated with CP Sil 8. Helium was used as carrier gas, and the temperature was programmed from 80° to 300°C at 4°C/min. Gas chromatography/mass spectrometry was conducted using a Carlo Erba Fractovap 4160 gas chromatograph coupled to a VG 7070E mass spectrometer operating at 70 eV. Samples were injected, using the on-column mode, onto a fused silica capillary column (length = 25 m; inside diameter = 0.32 mm) coated with SE 54. Helium was used as carrier gas, and the temperature was programmed from 110° to 320°C at 3°C/min.
olean-12-ene points to an oleanene/ursene skeleton. However, their molecular ions are shifted to m/z 396. The base peak of olean-12-ene points to an oleanene/ursene skeleton. Thus, we tentatively identified compounds 9 and 12 of olean-12-ene and urs-12-ene, respectively (Karliner and Djerassi, 1966). Thus, we tentatively identified compounds 9 and 12 the lack the typical m/z 191 fragment, which indicates that a methylene unit (CH₂) is missing from the A/B ring part of the molecule. The mass spectrum of compound 9 shows a more intense m/z 203 fragment (35%) than the mass spectrum of compound 12 (16%), a phenomenon also observed in the mass spectra of olean-12-ene and urs-12-ene, respectively (Karliner and Djerassi, 1966). Thus, we tentatively identified compounds 9 and 12 as A/B-ring nuclear demethylated olean-12-ene and urs-12-ene, respectively, or as the corresponding A-nor species. Compounds 8 and 10 have mass spectra similar to those of olean-13(18)-ene and olean-18-ene, respectively, but their molecular ions are shifted 14 daltons to m/z 396. By analogy with the above discussion of compounds 9 and 12, we tentatively identified compound 8 as an A/B-ring nuclear demethylated olean-13(18)-ene and compound 10 as an A/B-ring nuclear demethylated olean-18-ene (or as the corresponding A-nor compounds). The elution sequence of these tentatively identified nor-oleanenes (8, 9, 10) is thus similar to that of the regular oleanenes (14a, 15, 16). Brassell (1980) also tentatively identified a Δ¹²C₂₃ triterpane in sediments from the Japan Trench. The mass spectroscopic characteristics [M⁺ 396(10), 381(5), 218(100), 203(30)] suggest that this may be identical to our component 9. Brassell postulated that the compound has a photochemically or bacterially degraded A-ring, i.e., the former six-membered ring was transformed into a five-membered ring (A-nor triterpane; see Corbet et al., 1980).

The mass spectrum of the third most abundant compound (14b) is shown in Figure 5. The molecular ion at m/z 398 points to an elemental composition of C₃₀H₅₀, and the (M-43)⁺ fragment indicates the presence of an intact isopropyl side-chain. The fragment at m/z 206 seems characteristic of the lupane series (Budzikiewicz et al., 1963), and the base peak at m/z 177 points to the loss of a methylene unit from the A- or B-ring. By comparison with mass spectra of 23, 28-bisnor-, and 28-norlupanes (Rullkötter et al., 1982), we identified compound 14b as a 23-norlupane.

Three more compounds with unknown structures (3a, 7, 11a) occur in the Hole 645E samples. Compound 11a is characterized by a molecular ion at m/z 382 (10%), a base peak at m/z 163, and a rearrangement ion at m/z 190 (30%). The mass spectrum of compound 3a is shown in Figure 6. Compound 7 exhibits a similar spectrum. The mass spectra of these compounds indicate that the structures are remarkably stable under electron impact, as the molecular ions are intense peaks (base peak in 7). We can only speculate about their structures, but note that their mass spectra show similarities with a dehydration product of β-amyrin, with double bonds at positions 12 and 14 and a molecular ion (base peak) at m/z 408 (Elgamal et al., 1969). The molecular ions of compounds 3a and 7 are 14 daltons less, but the relatively important fragment at m/z 255, which results from cleavage across ring B (Elgamal et al., 1969), does not shift to lower values. This implies loss of a methylene unit from ring A, analogous to what we interpreted for compounds 8, 9, 10, and 12.

The sample from a depth of 778.1 m (Fig. 3E) is similar to the samples from depths of 499.9 m and 626.9 m (Figs. 3A and 3B), but it lacks taraxer-14-ene (13) and contains the unknown compound 11a. In addition, a compound having similar characteristics as compound 11a but with a molecular ion at m/z 326
was detected in the \( n-C_{23}H_{46}/n-C_{24}H_{50} \) range (Fig. 2). In this sample, two compounds were identified as des-A-ursanes, (VI) and des-A-lupanes (VII), the mass spectra of which were reported by Corbet (1980).

The geologically oldest samples (Figs. 3F to 3H) are characterized by a number of compounds not observed in the other samples. The major compound (11b) is identified as 17\( \alpha \)-H, 18\( \alpha \)-H(28,30)-bisnorhopane. The fragment at m/z 163 is somewhat enhanced (49%), compared to literature data (Seifert et al., 1978). However, careful scanning of the front and rear sides of this peak revealed the presence of the unknown compound 11a, with its base peak at m/z 163. Compounds 1, 2, and 3b are unknowns, and the mass spectra are shown in Figure 6. Compound 3b is most probably a homologue of compound 2, because the major fragments have shifted 14 daltons (m/z 229 to m/z 243; m/z 367 to m/z 381; m/z 382 to m/z 396). In the mass spectrum of compound 3b, some fragments can be assigned to the unknown compound 3a.

Diasterenes were identified in small amounts only in the three oldest samples (not indicated in Fig. 3). The 24-ethyl diasterene (17\( \alpha \)-H) is more abundant than the C27 and C28 homologues. The 20R isomers (e.g., X) are present in higher concentrations than the 20S isomers (e.g., XI), although there is some resolution between the 20R-C28 diasterene and the 20S-C29 diasterene (see Brassell et al., 1984).

**DISCUSSION**

**Biological Markers**

The \( n \)-alkanes in the higher molecular weight range all have a similar distribution pattern (Figs. 3A to 3H) and show a strong odd-over-even carbon number predominance. Nonacosane \( n-C_{29}H_{60} \) is the most abundant alkane. The distribution of the earlier eluting alkanes varies little. This kind of distribution pattern indicates an origin from higher plants (Eglinton and Hamilton, 1963). Carbon-preference-index (CPI) values were not calculated because of coelution of compound 5 with \( n-C_{29}H_{60} \) and compound 13 with \( n-C_{30}H_{66} \) in some samples. Nevertheless, Figures 2 and 3 indicate that CPI values are very high for Baffin Bay sediments.

As stated previously, the selection of samples for this study of biological markers was based on data derived from kerogen microscopy (Stein et al., this volume). A high alginite content (30%-50%), together with an increased Hydrogen Index (from Rock-Eval pyrolysis) of the organic material that was interpreted as the result of an enhanced marine influx, was observed in samples from depths of 562.9 m, 760.0 m, and 766.5 m, respectively, while the alginite content of the other samples was low (0%-10%). These petrographic differences are clearly not corroborated here.

A possible explanation for this discrepancy is that at the stage of diagenesis encountered in the Hole 645E sediments, marine biological markers still occur as functionalized components (e.g., sterols), whereas part of the terrigenous precursors are defunctionalized at an earlier stage and thus can already be identified in the aliphatic hydrocarbon fraction. McEvoy and Maxwell (1983), among others, showed that sterols in deep-sea sediments can survive at greater depths even in areas of high heat flow (offshore California). Future investigations of the alcohol, ketone, and fatty acid fractions of the Hole 645E sediments will evaluate our hypothesis.

The composition of the aliphatic biological-marker hydrocarbons is unusual in many aspects. An origin from terrigenous higher plants for most compounds (if not all) seems irrefutable. A variety of pentacyclic triterpenoids with oleanane, ursane, taraxerane, lupane, and friedelane skeletons have been identified in higher plants, but not in marine organisms. In sediments, the most frequently encountered members of these terrigenous biological markers are those having \( \beta \)-amyrin (oleanane) and \( \alpha \)-amyrin (ursane) skeletons (Brassell and Eglinton, 1986). However, a dominance of these compounds, as observed in sediments from Baffin Bay, has not yet been reported for deep-sea sediments. Oleananes have been detected in some deltaic sequences, such as the Niger Delta (Ekweozor et al., 1979a) and the Mahakam Delta (Hoffmann et al., 1984). These deltaic environments also characterize the occurrence of ring-A-degraded triterpenes (see Baas, 1985, for an overview); these compounds (e.g., VI, VII) are present in relatively low amounts in Baffin Bay sediments. Ring-A-degraded triterpenes are thought to be products of microbial breakdown of seco-A-triterpenoids, which, in turn, may originate from unchanged seco-A-triterpenoids (Baas, 1985), or may be the result of photochemical or photomimetic degradation of triterpenoids (Corbet et al., 1980; Schmitter et al., 1981). However, Baas (1985) suggested that at least part of the degradation of the A-ring may also occur in the plant prior to sedimentation. Apparently, many mechanisms seem to play an active role in the A-ring degradation of triterpenoids, but a functional group at C-3 seems to be a prerequisite. To our knowledge, precursors for the tentatively identified nuclear demethylated compounds (8, 9, 10, 12) have not been reported in the geochemical literature, but the corresponding geochemical reactions are known for diterpenoids (e.g., degradation of abietic acid; Simonet, 1975). We believe that the triterpenoid precursors are functionalized at C-23 (or C-24), but not at C-3. A similar reason can be given for the precursor of the tentatively identified 23-norlupane.

In Tertiary sediments from adjacent land sections in West Greenland, Rullkötter et al. (1982) identified a pair of isomeric nuclear demethylated triterpanes having a lupane skeleton. The absence of any specific precursor led them to suggest that a specific reaction sequence with probable microbial intervention under restricted environmental conditions might be responsible for the formation of the 23,28-bisnorlupanes. These compounds were also detected in sediments from the Beaufort-Mackenzie Delta (Brooks, 1986) and the Gulf of Suez (Rullkötter et al., 1982). Restricted environmental conditions cannot be invoked for sediments investigated here and, therefore, may not be responsible for the formation of the nuclear demethylated triterpanes in Baffin Bay. Investigations of the heterocompound fractions may provide the crucial information necessary for conclusions about precursors and their diagenetic pathways.

**Diagenetic Transformations**

Lipid transformation processes in sediments have been the subject of many studies. In particular, the diagenetic fate of steroids was studied in detail (Mackenzie et al., 1982; Brassell et al., 1984). Steroidal hydrocarbons were virtually absent in Baffin Bay sediments, but some traces of 20R and 20S diasterenes were detected in the three deepest samples, using mass fragmentography of m/z 257. An increase in the relative concentration of the 20S isomer was observed with increasing burial depth, similar to results obtained by Brassell et al. (1984) for deep-sea sediments from other locations. The diasterene isomerization ends with a 1:1 mixture of 20R and 20S isomers, but this end point was not reached at a depth of 1076.9 m in Hole 645E. Concomitant with the occurrence of diasterenes is the first appearance of 17\( \alpha \)-H, 18\( \beta \)-H(28,30)-bisnorhopane (Fig. 3F; compound 11b). Note that the relative concentration of this bisnorhopane increases with burial depth (Figs. 3F to 3H), a behavior similar to that of the 20S diasterenes.

The relative concentration of taraxer-14-enes decreases with depth, while in the same interval the relative concentration of...
Figure 3. Partial gas chromatograms of aliphatic hydrocarbon fractions of sediment samples from Hole 645E (A-H). $n$-Alkanes are indicated in black. The first eluting black peak is $n$-C$_{27}$H$_{56}$; the last eluting black peak is $n$-C$_{35}$H$_{72}$. The coelution effect of $n$-C$_{30}$ with compound 13 is indicated symbolically.
oils with a pronounced terrigenous molecular signal and why triterpanes with a taraxerane skeleton are found in sediments or involving taraxerene to oleanene conversion can explain why no Philp and Gilbert, 1986; Riva et al., 1986; Talukdar et al., 1986; sediments (e.g., Ekweozor et al. 1979b; Hoffmann et al., 1984; Zumberge, 1987 and references therein). A diagenetic pathway and 18/3(H)-oleananes (Ekweozor et al., 1979a; Riva et al., in though we favor the transformation reaction hypothesis, an ulti­able.

ter 8 hr yields a mixture of olean-12-ene and olean-13(18)-ene, catalyzed rearrangement leading directly from taraxerene to olean-12-ene was demonstrated by Courtney et al. (1958). Beaton et al. (1955) argued that Clemmensen reduction of taraxerone after 8 hr yields a mixture of olean-12-ene and olean-13(18)-ene, while a continued acid treatment yields only pure olean-13(18)-ene; Brownlie et al. (1956) managed to convert olean-12-ene into olean-13(18)-ene. Although these transformation reactions are chemically feasible, alternative explanations for the change in relative concentrations cannot be completely disregarded. Taraxerene may be preferentially lost or the sedimentation rate of taraxerene (or its precursor) relative to that of the oleananes (or their precursors) may have changed with geological time. Although we favor the transformation reaction hypothesis, an ultimate conclusion cannot be made at present with the data available.

Hydrogenation of olean-13(18)-ene would lead to 18α(H)- and 18β(H)-oleananes (Ekweozor et al., 1979a; Riva et al., in press). 18β(H)-oleanane has been identified in deltaic sediments (e.g., Ekweozor et al., 1979a; Hoffmann et al., 1984; Riva et al., 1986) and in a number of crude oils mostly related to deltaic sediments (e.g., Ekweozor et al. 1979b; Hoffmann et al., 1984; Philip and Gilbert, 1986; Riva et al., 1986; Talukdar et al., 1986; Zumberge, 1987 and references therein). A diagenetic pathway involving taraxerene to oleanane conversion can explain why triptenes with a taraxerane skeleton are found in sediments or oils with a pronounced terrigenous molecular signal and why oleananes are encountered.

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Figure 4. Mass spectra of biological-marker compounds in the hydrocarbon fraction of Site 645 samples. Compound 9 = A/B-ring nuclear demethylated (or A-nor-) olean-12-ene. Compound 12 = A/B-ring nuclear demethylated (or A-nor-) urs-12-ene. Compound 15 = olean-12-ene.
Figure 5. Mass spectrum of compound 14b, tentatively identified as a 23-norlupane.
Figure 6. Mass spectra of some selected unknown compounds in the aliphatic hydrocarbon fraction of Site 645 samples.

APPENDIX

Chemical Compound Structures