APPENDIX I. IDENTIFICATION OF ISOPRENOIDAL KETONES IN DEEP SEA DRILLING PROJECT CORE SAMPLES AND THEIR GEOCHEMICAL SIGNIFICANCE

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ABSTRACT

DSDP core samples from Legs 5 to 15, Black Sea, Lake Kivu, and Mangrove Lake core samples were all examined for the presence of isoprenoidal ketones. The calcareous Pacific Ocean sediments (DSDP Legs 5 to 9) did not contain detectable amounts of isoprenoid ketones. These compounds were present in the DSDP samples from Legs 10 to 15 and the core samples from the Black Sea and Lake Kivu. The Mangrove Lake sample had a ketone concentration comparable to the detection limit. The major ketone present was 6,10,14-trimethylpentadecanone-2 in all cases, with minor amounts of 6,10-dimethylundecanone-2. No C23 homolog was detected. The C13 and C18 compounds are possible microbial degradation products from phytol which were thus sedimented.

INTRODUCTION

The isoprenoid ketones C_nH_{2n}O with n = 13, 18, and 23 are the major nonacidic products obtained from the chemical degradation of the Green River Formation oil shale kerogen (Burlingame and Simoneit, 1969; Burlingame et al., 1969; Simoneit and Burlingame, in press). This kerogen is thought to have had a large phytol input during its formation. The presence in anoxic deep-sea sediments of large amounts of phytadienes probably derived from phytol (Simoneit, in preparation) raises a question regarding the fate of phytol in oxic systems prior to the incorporation of the isoprenoid moiety into kerogenic matter. Chemical oxidation of phytol yields mainly isoprenoid acids and the C13 and C18 isoprenoid ketones (Cox, 1971). Thus, a search for these isoprenoid ketones in marine samples was initiated.

The samples discussed in this report are derived from several sources. The DSDP core samples are from Legs 5 to 15. The samples which were examined from Legs 5 to 9 are all from the Pacific Ocean (Simoneit and Burlingame, 1972b); the Leg 10 samples are from the Gulf of Mexico (Simoneit et al., 1973a); the Leg 11, 12, and 14 samples are from the Atlantic Ocean (Simoneit et al., 1972 and 1973b; Simoneit and Burlingame, 1973); the Leg 13 samples are from the Mediterranean Sea (Simoneit et al., in press); and the Leg 15 samples are from the Cariaco Trench on the continental shelf off Venezuela (Simoneit et al., in press). The Black Sea core samples were recovered on a cruise of the R.V. Atlantis II in 1971 (Station 1798 at 10°39'N and 65°3'W). The sample from Mangrove Lake (Bermuda) is derived from 5.87 meters below sea level (ML69-14). The geologic ages of the samples containing isoprenoidal ketones range from Recent (<500 years) to middle Cretaceous (about 108 years).

EXPERIMENTAL

The analytical procedures and preliminary data evaluation of the DSDP core samples discussed here have been presented (Simoneit and Burlingame, 1971a and 1971b; 1972a and 1972b; 1973; Simoneit et al., 1972 and 1973a, 1973b, in press). Similar data have been presented for the core samples from the Black Sea (Simoneit, in press). The samples from Lake Kivu, the Cariaco Trench, and Mangrove Lake were extracted and analyzed analogously to those listed above. The GC/MS data of this sample suite were reexamined using computer techniques (Smith et al., 1971; Smith, 1972; Chang et al., in preparation) and the suite of isoprenoidal ketones was identified. The GC retention times of these compounds were then rechecked with authentic standards.

RESULTS

The reexamination of the GC/MS data for various ocean and lake sediments revealed the presence of isoprenoidal ketones. The most predominant member is 6,10,14-trimethylpentadecanone-2 (Structure I), with minor amounts...
of 6,10-dimethylundecanone-2 (Structure II). The C_{23} homolog was not detected in any sample. The mass spectrum of authentic 6,10,14-trimethylpentadecanone-2 (Cox, 1971) is shown in Figure 1. The major peaks are C_{22}H_{34}O at m/e 43; C_{33}H_{36}O—the base peak at m/e 58; m/e 124; m/e 268—the molecular ion with the loss of H_{2}O to yield m/e 250 and the loss of C_{3}H_{6}O to yield m/e 210.

The GC/MS analyses of the DSDP samples from Legs 5 to 9 did not reveal the presence of any isoprenoidal ketone. All these samples were derived from the Pacific Ocean and were highly calcareous, with a low yield of extractable organic matter (Simoneit and Burlingame, 1972b). The data for the DSDP Leg 10 samples are shown in Figures 2 and 3. The ketone yields are listed in Table 1. The C_{18} ketone is present admixed with some hydrocarbons at scan 105 for Sample 10-90-7-2 (cf. Figure 2) and scans 82-83 for Sample 10-92-5-4 (cf. Figure 3); the C_{15} ketone is found at scans 40 and 29, respectively. The data for Sample 11-105-11-2 are shown in Figure 4. Only the C_{18} ketone is present and is the major component of the total extract.

The ketone yields for the samples from Legs 12 to 14 are found in Table 1, and the GC/MS data have been published (Simoneit and Burlingame, 1973; Simoneit et al., in press).

Six samples from the Cariaco Trench were analyzed and the ketone yields are listed in Table 1. The GC traces of the branched-cyclic fraction of the heptane-soluble material from Samples 15-147B-1-4 (6 m), 14-147B-7-4 (67 m), and 14-147C-3-1 (138 m) (Simoneit et al., in press) are shown in Figure 5. The major peak in all three GC traces is the C_{18} isoprenoid ketone (Structure I). The total ionization and m/e 58 sum plots for these samples are found in Figure 6, and the mass spectra of the individual ketones are presented in Figure 7. The GC retention times of the C_{18} ketone in the samples are in close agreement with that of the standard compound. Due to other minor oxygenated impurities, the m/e 43 peak is the base peak in these mass spectra unlike the m/e 58 base peak in the standard spectrum (cf. Figure 1).

The mass spectrum 53 (cf. Figure 7c) fits the fragmentation pattern of 6,10-dimethylundecanone-2 (Structure II). The major peaks are C_{22}H_{34}O at m/e 43, C_{33}H_{36}O at m/e 58, and the molecular ion at m/e 198, with the loss of H_{2}O to yield the peak at m/e 180 and the loss of C_{3}H_{6}O to yield m/e 140.

Three of the samples analyzed from the Black Sea (Simoneit, in press) contained isoprenoidal ketones. The GC traces of their total extracts are shown in Figure 8, and the corresponding GC/MS data are found in Figure 9. Only the C_{18} homolog (Structure I) was found and in minor amounts (cf. Table 1). The mass spectra (cf. Figure 9c, f, i) are all derived from an unresolved peak of a binary sample mixture of 6,10,14-trimethylpentadecanone-2 and neo-phytadiene (Structure III) (Simoneit, in preparation). These two compounds coelute under the GC conditions utilized.

The heptane extract fraction of the sample from Lake Kivu (0-10 cm) was also examined for isoprenoid ketones, and the GC trace of the total mixture is shown in Figure 10. The GC/MS data are found in Figure 11. The major constituent of the Scan 46 spectrum (cf. Figure 11e) is neo-phytadiene with a minor amount of the C_{18} ketone (Structure I). The Mangrove Lake sample (ML69-14) contains what appears to be the C_{18} isoprenoid ketone (Structure I) at a concentration comparable to the detection limit of the analytical technique.

The distribution histograms for the normal alkanes (in some cases, the fatty acids) and the isoprenoid ketones are shown in Figures 12 and 13.

DISCUSSION

These isoprenoid ketones have not been found endogenous previously in any terrestrial sediment, nor have they been reported present in any marine sediment. They have also not been identified in any microorganisms or plankton.

These ketones were not detected in the calcareous sediments examined from the Pacific Ocean. However, in the clay-rich sediments from the Atlantic Ocean, Gulf of Mexico, Mediterranean Sea, and Black Sea these ketones were detected in significant amounts (2 to 740 ppm). These samples had both oxic and anoxic sedimentation conditions, and some had a large terrigenous influx. This indicates a prerequisite high precursor concentration, probably of phytol. The absence of a C_{23} homolog indicates that probably only phytol is the major precursor and not some higher weight isoprenoidal compound as, for example, a lycopene. The isoprenoid ketone yields from the sapropelic algal and bacterial sediments of Mangrove Lake and Lake Kivu are low, probably due to the low precursor content in the source organisms.

Phytol can be chemically oxidized to yield these same ketones and isoprenoidal acids (Cox, 1971). In the case of the sediment samples, this oxidative degradation of phytol appears to be microbial prior to sedimentation, since these ketones are found in both oxic (DSDP Legs 10 to 14) and anoxic (DSDP Leg 15 and Black Sea) sediment samples. Subsequent reduction of the C_{18} ketone in the sediment would yield the C_{18} isoprenoid hydrocarbon (C_{18}H_{38}). This compound increases in concentration relative to phytane with depth of burial in the Green River Formation oil shale (Robinson et al., 1965). It is also the major
Figure 1. Low resolution mass spectrum of authentic 6,10,14-trimethylpentadecanone-2.

Figure 2. GC/MS data for the total heptane soluble extract from Sample 10-90-7-2. (a) total ionization sum plot; (b) m/e 58 sum plot; (c) mass spectrum scan 105.

Figure 3. GC/MS data for the total heptane-soluble extract from Sample 10-92-5-4. (a) total ionization sum plot; (b) m/e 58 sum plot; (c) summed mass spectra scans 82-83.
TABLE 1

Description of Samples and Concentration of Isoprenoid Ketones

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth Below Sea Bed (m)</th>
<th>Geologic Age (or yrs B.P.)</th>
<th>Total Hydrocarbons (ppm dry weight)</th>
<th>Isoprenoid Ketones (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-90-7-2, 40-140 cm</td>
<td>353.0</td>
<td>U. Miocene</td>
<td>90</td>
<td>0.2 3.2</td>
</tr>
<tr>
<td>10-92-5-4, 50-150 cm</td>
<td>178.0</td>
<td>L. Pleistocene</td>
<td>300</td>
<td>0.3 5.0</td>
</tr>
<tr>
<td>11-105-11-2, 10-138 cm</td>
<td>310.0</td>
<td>L. Cretaceous</td>
<td>360</td>
<td>- 50.0</td>
</tr>
<tr>
<td>12-112-11-4, 10-99 cm</td>
<td>329.0</td>
<td>M. Oligocene</td>
<td>50</td>
<td>- 12.0</td>
</tr>
<tr>
<td>12-114-5-5, 80-140 cm</td>
<td>507.0</td>
<td>M. Pliocene</td>
<td>700</td>
<td>- 132.0</td>
</tr>
<tr>
<td>13-128-3-4, 34-124 cm</td>
<td>84.8</td>
<td>Pleistocene</td>
<td>1300</td>
<td>46.0 740.0</td>
</tr>
<tr>
<td>13-128-3-5, 38-40 cm</td>
<td>85.4</td>
<td>Pleistocene</td>
<td>1600</td>
<td>32.0 420.0</td>
</tr>
<tr>
<td>13-130-1-2, 123-125 cm</td>
<td>15.6</td>
<td>Pleistocene</td>
<td>1200</td>
<td>- 240.0</td>
</tr>
<tr>
<td>14-138-2-6, 12-13 cm</td>
<td>117.6</td>
<td>Oligocene</td>
<td>1200</td>
<td>- 100.0</td>
</tr>
<tr>
<td>14-138-6-3, 49-50 cm</td>
<td>428.5</td>
<td>M. Cretaceous</td>
<td>4200</td>
<td>103.0 420.0</td>
</tr>
<tr>
<td>14-144A-5-1, 114-116 cm</td>
<td>181.0</td>
<td>U. Cretaceous</td>
<td>400</td>
<td>5.0 49.0</td>
</tr>
<tr>
<td>14-144A-6-1, 100-101 cm</td>
<td>190.1</td>
<td>U. Cretaceous</td>
<td>3000</td>
<td>4.0 80.0</td>
</tr>
<tr>
<td>14-144A-3-1, 14-15 cm</td>
<td>216.1</td>
<td>U. Cretaceous</td>
<td>1900</td>
<td>- 152.0</td>
</tr>
<tr>
<td>15-147B-1-4, 0-18 cm</td>
<td>6.0</td>
<td>10,000</td>
<td>432</td>
<td>20.0 70.0</td>
</tr>
<tr>
<td>15-147B-5-0, 0-18 cm</td>
<td>40.1</td>
<td>80,000</td>
<td>400</td>
<td>5.0 95.0</td>
</tr>
<tr>
<td>15-147B-7-4, 0-18 cm</td>
<td>67.0</td>
<td>130,000</td>
<td>427</td>
<td>13.0 220.0</td>
</tr>
<tr>
<td>15-147C-3-1, 015 cm</td>
<td>138.0</td>
<td>270,000</td>
<td>660</td>
<td>28.0 300.0</td>
</tr>
<tr>
<td>AI60-1798G, 015 cm</td>
<td>0 to &lt;500</td>
<td></td>
<td>200</td>
<td>- 15.0</td>
</tr>
<tr>
<td>AI60-1798G, 108-118 cm</td>
<td>1.1</td>
<td>2200</td>
<td>656</td>
<td>10.0 105.0</td>
</tr>
<tr>
<td>AI49-1461, 0.4 m</td>
<td>0.4</td>
<td>Pleistocene</td>
<td>800</td>
<td>- 72.0</td>
</tr>
<tr>
<td>AI49-1474, 5.5 m</td>
<td>8.6</td>
<td>Pleistocene</td>
<td>100</td>
<td>- 7.0</td>
</tr>
<tr>
<td>AI49-1474, 11.55 m</td>
<td>11.6</td>
<td>Pleistocene</td>
<td>160</td>
<td>- 8.0</td>
</tr>
<tr>
<td>Lake Kivu, 0.10 cm</td>
<td>0 to 1000</td>
<td>Pleistocene</td>
<td>1700</td>
<td>- 15.0</td>
</tr>
<tr>
<td>ML-69-14, 5.9 cm</td>
<td>&lt;1000</td>
<td>5000</td>
<td>- 0.5</td>
<td></td>
</tr>
</tbody>
</table>

*Dash indicates not detected.

Chemical degradation of Green River Formation oil shale kerogen yields isoprenoidal acids and these same ketones (Burlingame and Simoneit, 1969; Burlingame et al., 1969; Simoneit and Burlingame, in press). The oxidation of phytol (probably derived from the phytyl side chain of chlorophyll) to these ketones may be one pathway for the introduction of isoprenoidal moieties into kerogenic material. Such a mechanism has been proposed (Arpino et al., 1972) for the incorporation of an alcohol into kerogen.

A mass balance for the concentrations of phytol, phytadienes, and isoprenoid ketones is in the process of being established. The uniformly deposited Pleistocene
sequence in the anoxic Cariaco Trench (DSDP Leg 15, Site 147) is under further investigation to establish the interrelations of these compounds and their concentrations.

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REFERENCES


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Figure 5. GC traces of the branched-cyclic fractions (nonadducted) from the heptane-soluble material of (a) Sample 15-147B-1-4 (6 m) (1.3 µl of 10 wt % solution in CHCl₃); (b) Sample 15-147B-7-4 (67 m) (1.2 µl of 11 wt % solution in CHCl₃); (c) Sample 15-147C-3-1+ (138 m) (1.7 µl of 10 wt % solution in CHCl₃). GC conditions: 10 ft X 1/8 in. stainless steel column, packed with 3% OV-1 on gaschrom Q, programmed from 100°C-275°C at 8°C/min, using He carrier gas at 40 ml/min.
Figure 6. GC/MS data for the Cariaco Trench samples. Sample AII60-1798G 108-118 cm total extract: (a) total ionization sum plot, (b) m/e 58 sum plot, (c) m/e 68 sum plot (base peak for phytadiene); Sample 15-147B-1-4 (6 m) branched-cyclics of heptane extract: (d) total ionization sum plot, (e) m/e 58 sum plot; Sample 15-147B-7-4 (67 m) branched-cyclics of heptane extract: (f) total ionization sum plot, (g) m/e 58 sum plot; Sample 15-147C-3-1+ (178 m) branched-cyclics of heptane extract: (h) total ionization sum plot, (i) m/e 58 sum plot.
Figure 7. Mass spectra (G/6MS) of the isoprenoid ketones in the Cariaco Trench samples: (a) 15-160-1798G 108-118 cm – 6,10,14-trimethylpentadecanone-2; (b) 15-147B-1-4 (6 m) – 6,10,14-trimethylpentadecanone-2; (c) 15-147B-7-4 (67 m) – 6,10-dimethylundecanone-2; (d) 15-147B-7-4 (67 m) – 6,10,14-trimethylpentadecanone-2; (e) 15-147C-3-1+ (138 m) – 6,10,14-trimethylpentadecanone-2.
Figure 8. GC traces of the total heptane extract fractions from the Black Sea samples: (a) Sample AII49-1461 (0.40 m); (b) Sample AII49-1474 (8.55 m); (c) Sample AII49-1474 (11.55 m). GC conditions as cited in Figure 5, except the temperature program was 100°C-150°C only.
Figure 9. GC/MS data for the total heptane-extract fractions from the Black Sea samples. Sample AII49-1461 (0.40 m): (a) total ionization sum plot, (b) m/e 58 sum plot, (c) mass spectrum scan 94; Sample AII49-1471 (8.55 m): (d) total ionization sum plot, (e) m/e 58 sum plot (the maxima < scan 70 are due to the $^{13}$C isotope peaks of m/e 57 from alkanes), (f) summed mass spectra scans 64-65; Sample AII49-1474 (11.55 m): (g) total ionization sum plot, (h) m/e 58 sum plot (the maxima < scan 50 are due to the $^{13}$C isotope peaks of m/e 57 from alkanes), (i) mass spectrum scan 43.
Figure 10. GC trace for the total heptane-extract fraction from the Lake Kivu (0-10 cm) sample. GC conditions as cited in Figure 5.
Figure 11. GC/MS data for the heptane extract fraction from the Lake Kivu sample (Station 5, 0-10 cm): (a) total ionization sum plot, (b) m/e 58 sum plot, (c) m/e 68 sum plot, (d) m/e 82 sum plot, (e) mass spectrum scan 46.
Figure 12. Homologous series distribution histograms (alkanes and isoprenoid ketones) for various DSDP core samples: (a) 10-90-7-2, 40-140 cm; (b) 10-92-5-4, 50-150 cm; (c) 11-105-11-2, 10-138 cm; (d) 12-112-11-4, 10-99 cm; (e) 12-114-5-5, 80-140 cm; (f) 13-130-1-2, 123-125 cm; (g) 13-128-3-4, 122-124 cm; (h) 13-128-3-5, 38-40 cm; (i) 14-144-4-3, 14-15 cm.
Figure 13. Homologous series distribution histograms (alkanes and isoprenoid ketones) for various DSDP and Black Sea core samples. DSDP: (a) 14-138-6-3, 49-50 cm; (b) 14-144A-5-1, 114-116 cm; (c) 14-144A-6-1, 100-101 cm; (d) 15-147B-7-4 (67 m); (e) 15-147B-7-4 (67 m); (f) 15-147C-3-1* (138 m); Black Sea: (g) AII49-1461 (0.40 m); (h) AII49-1461 (0.40 m); (i) AII49-1471 (8.55 m); (j) AII49-1474 (11.55 m).