Identification of Bicyclic Sesquiterpanes in Oils from the Niger Delta, Nigeria

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Abstract: Two series of bicyclic sesquiterpanes have been identified in the crude oil from the Niger delta by Gas chromatography-Mass spectrometry. The mass spectra of the sesquiterpanes were compared with those of previously reported compounds. The first series with base peak at m/z 193 or 123 had mass spectra that corresponded with C_{17}H_{28} (M+: 208) and C_{18}H_{30} (M+: 222). The second series was distinguished by base peak, m/z 123 and corresponded to C_{18}H_{26} (M+: 292), that is bicyclic terpanes having branched chain. The presence of these compounds in the Niger delta oil suggests a significant terrigenous input into the source-rock of the oils.

Key words: Biomarkers, molecular ion, fragmentation, source-rock, diagnostic ions

INTRODUCTION

Biomarkers of which bicyclic sesquiterpanes belong are organic compounds with well preserved basic skeleton which can be unambiguously linked to the structure of precursor compounds occurring in original source material. Restriction of occurrence of some biomarkers mainly to certain environment and the stereoechemical changes at some carbon centres during maturation makes such compounds useful as paleoenvironmental and thermal maturity indicators. The compounds can also provide information on post generative effects, such as migration, thermal alteration and biodegradation on the oil. The occurrence of biomarkers in both rock extracts and crude oil forms the basis for oil-oil and oil-source rock correlation studies. The development of gas chromatography-mass spectrometry has made the identification of such compounds in rock extracts and crude oils very easy.

Bicyclic sesquiterpanes comprises the largest of terpenoid classes. The compounds have been detected in crude oils and sediments from many part of the world but their sources have not been unequivocally established. Degradation of steroid and triterpanes precursor, thermal degradation of higher plants triterpanes during maturation processes and microbial degradation of hopancoids in petroleum source-rocks during diagenesis are among the possible origins that have been proposed for these compounds. Philip et al. have suggested that tricyclic diterpanes of higher plants origin could be the source of the bicyclic terpanes through the opening of ring C during maturation. Two C_{16} and C_{14} bicyclic alkanes have also been detected in a tertiary crude oil of terrestrial origin. However, one thing that stands out clearly is the fact that the compounds have been widely reported for crude oils derived mostly from source-rock with significant terrestrial contributions, suggesting their possible utility as terrestrial source indicators.

A wide range of cyclic alkanes namely; tricyclic, tetracyclic and pentacyclic triterpanes have been reported in oils and sediments from the Niger delta. In this study, we reported the occurrence of bicyclic sesquiterpanoid hydrocarbons in the Niger delta crude oil and it’s significant in determining the origin of Niger delta source rock.

Petroleum geology of the Niger delta: The Niger delta basin has an estimated reserve of about 25 billion barrels of oil and 160 trillion cubic feet of natural gas. The basin covers an area of about 75,000 km² with a clastic sequence which reaches a maximum thickness of 9,000 to 12,000 of sediments. It is bound in the west and east by, the Benin flank and Calabar flank respectively, in the south by Gulf of Guinea and in the north by Anambra basin, Abakaliki anticlinorium and Afikpo basin. Stratigraphically, the thick sedimentary sequence basically consists of three principal lithostratigraphic units, namely; the Akata, Agbada and Benin Formation. Akata Formation consists mainly of overpressure marine shale. This Formation has not been drilled in most parts of the delta, except at the continental margin. Overlaying the Akata Formation is the Agbada Formation which composed of paralic sequence of

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RESULTS AND DISCUSSION

The partial m/z 123 and 191 mass chromatograms of typical oil that was studied are shown in Fig. 1. The distribution of the bicyclic sesquiterpanes in the oil is similar to that of other oils from many regions of the world[10]. The compound corresponding to each of the peaks labeled A to K were identified by comparing their mass spectra with those already reported in the literature and the fragmentation patterns on the spectra. The peak identities of the bicyclic compounds identified on the mass chromatogram of the oils are listed in Table 1. Structures for the compounds are shown in Appendix A.

MATERIALS AND METHODS

Twenty-two crude oil samples from the Niger delta were used. The crude oils were fractionated in a 1 m long and 1.5 cm diameter column packed with 8 g of silica gel (70-230 mesh, Merck). The saturated and aromatic hydrocarbon fractions were eluted with hexane and hexane/dichloromethane (90:10 v/v), respectively. The saturated fractions were separated into n-alkanes and branched/cyclic alkanes using 5 A molecular sieves. GC-MS analysis of the branched/cyclic alkanes fractions was performed on an HP 5890 GC interface to an HP 5970 Mass Selective Detector. GC was carried out on a fused silica capillary column (30x0.25 mm i.d coated with 0.25 m thick SE-54). The oven temperature was programmed from 50 to 300°C at 4°C/min, isothermal for 30 min. Helium was used as carrier gas. The Mass spectrometer was operated at electron energy of 70 eV, an ion source temperature of 250°C and transfer line temperature of 300°C. The oven temperature was programmed from 50 to 300°C at 4°C/min, isothermal for 30 min. The main ions monitored were m/z 123 and 191 representing the diagnostic ions for terpanes.

Appendix A: Structures of bicyclic sesquiterpanes (I-VII)

Table 1: Bicyclic terpanes in crude oil from Niger delta

<table>
<thead>
<tr>
<th>Peak</th>
<th>Molecular formula</th>
<th>Structure</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>C₁₃H₂₂</td>
<td>I</td>
<td>Bicyclic sesquiterpane</td>
</tr>
<tr>
<td>B</td>
<td>C₁₃H₂₃</td>
<td>II</td>
<td>Bicyclic sesquiterpane</td>
</tr>
<tr>
<td>C</td>
<td>C₁₃H₂₄</td>
<td>III</td>
<td>Bicyclic sesquiterpane</td>
</tr>
<tr>
<td>D</td>
<td>C₁₃H₂₅</td>
<td>IV</td>
<td>Bicyclic sesquiterpane</td>
</tr>
<tr>
<td>E</td>
<td>C₁₃H₂₆</td>
<td>V</td>
<td>Bicyclic sesquiterpane</td>
</tr>
<tr>
<td>F</td>
<td>C₁₃H₂₇</td>
<td>VI</td>
<td>Bicyclic sesquiterpane</td>
</tr>
<tr>
<td>G</td>
<td>C₁₃H₂₈</td>
<td>VII</td>
<td>Bicyclic sesquiterpane</td>
</tr>
<tr>
<td>H</td>
<td>C₁₃H₂₉</td>
<td>VIII</td>
<td>Bicyclic sesquiterpane</td>
</tr>
<tr>
<td>I</td>
<td>C₁₃H₁₀</td>
<td>IX</td>
<td>Bicyclic sesquiterpane</td>
</tr>
<tr>
<td>J</td>
<td>C₁₃H₁₁</td>
<td>X</td>
<td>Bicyclic sesquiterpane</td>
</tr>
<tr>
<td>K</td>
<td>C₁₃H₁₂</td>
<td>XI</td>
<td>Bicyclic sesquiterpane</td>
</tr>
</tbody>
</table>

C₁₃ Bicyclic sesquiterpanes: The mass spectra of the peaks A, B, C, F and G (Fig. 2) are similar to those of the C₁₅ bicyclic sesquiterpanes alkanes already reported[9].
Fig. 1: Partial m/z 123 and 191 mass chromatogram of crude oil from Niger delta.

The mass spectra are characterized by molecular ion at m/z 208 and base peak at m/z 123 or 193 and correspond to a molecular formula C_{12}H_{26}. Structures I, II and III have been tentatively assigned to peaks A, B and C having base peak at m/z 193. Peaks F and G having base peak at m/z 123 have spectra similar to that of 8β(H) drimane with structure IV.

Prominent ions on the mass spectra of these peaks (A, B, C, F and G), such as m/z 208, 193, 137, 123 and 109 could be accounted for in terms of fragmentation of structure III. The M⁺ ion is at m/z 208 while m/z 193 resulted from loss of methyl group from the parent ion (M⁺-15). Fragmentation by cleavage of the C₇-C₇ and C₇-C₈ bonds will give m/z 137 (M⁺-71). The loss of 85 daltons from the molecular ion arising from the cleavage of the C₅-C₆ and C₅-C₇ bonds will give m/z 123 (M⁺-99). Cleavage of A and B ring at C₁₂ and C₁₈ position can result to m/z 109.

C_{18} Bicyclic sesquiterpanes: Peaks D, E, H, I and J have mass spectra that are similar to those of previously reported C_{18} bicyclic sesquiterpanes. The mass spectra of peaks D, E, H and I feature M⁺ ion at m/z 222 corresponding to C_{18}H_{36} (Fig. 3). The spectra show base peak at m/z 193. A possible structure is V. The mass spectrum of peak J features base peak at m/z 123 and very low abundance of ion at m/z 193. This feature is typical of 8β(H) homodrimate VI. The absence or low abundance of ion at m/z 193 corresponding to M⁺-29 fragmentations has been attributed to unfavourable cleavage of ethyl group at C-9 position. There are prominent ions on the mass spectra of these peaks at m/z 222, 207, 193, 137, 123 and 109. The fragmentation pattern is similar to that of C_{18} member. The Molecular ion (M⁺) is at m/z 222 while m/z 207 and m/z 193 resulted from loss of methyl and ethyl groups, respectively.

C_{21} Bicyclic sesquiterpanes: The mass spectra of peak K (Fig. 4) is similar to that of C_{21} already reported. The molecular ions (M⁺) at 292 corresponded to molecular formula C_{21}H_{38}. These compounds have basic structure of C_{18} bicyclic terpanes and a long branched chain attached to C-8 (structure VII).

The fragmentation resulting in the prominent ions such as m/z 137 and 109 is similar to that of C_{18} bicyclic terpanes. The m/z 277, 263, 233 and 193 resulted from successive loss of 14 daltons from the parent ion by the cleavage of the alkyl side chain on C-8 position.

Bicyclic sesquiterpanes have been reported to be widely distributed in oils derived mostly from source-rock...
Fig. 3: Mass spectra of C_{18} bicyclic terpanes of crude oils from Niger delta: (a) peaks D, E, H and I (b) peak J and (c) mass spectra of C_{16} bicyclic terpanes reported by Alexander et al.\textsuperscript{91}

Fig. 4: Mass spectra of C_{20} bicyclic terpanes of crude oils from Niger delta (peak J) with significant terrestrial contributions, suggesting their possible utility as terrestrial source indicators\textsuperscript{1,2,90}. The presence of these compounds in crude oil from the Niger delta tends to support significant terrestrial contributions to Niger delta source rock.

ACKNOWLEDGMENTS

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REFERENCES


