

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 C₁₅H₂₈ (M⁺: 208) and C₁₆H₃₀ (M⁺: 222). The second series was distinguished by base peak, m/z 123 and corresponded to C₂₁H₄₀ (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 stereochemical changes at some carbon centres during maturation makes such compounds useful as paleoenvironmental and thermal maturity indicators^[1-5]. 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^[4,6]. 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^[7], thermal degradation of higher plants triterpanes during maturation processes^[8] and microbial degradation of hopanoids in petroleum source-rocks during diagenesis^[9] are among the possible origins that have been proposed for these compounds. Philip *et al.*^[10] 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 C₁₅ and C₁₆ bicyclic alkanes have also been detected in a tertiary crude oil of terrestrial origin^[11]. 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 indicator^[11-13].

A wide range of cyclic alkanes namely; tricyclic, tetracyclic and pentacyclic triterpanes have been reported in oils and sediments from the Niger delta^[2,14-16]. In this study, we reported the occurrence of bicyclic sesquiterpenoid 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 oils 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^[17]. 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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interbedded sands and shales up to 4000 m thick in the central parts, thinning seawards and towards the delta margin. The youngest of the sequence, Benin Formation composed of mainly fluvial gravels and sands which thickens to 2000 m in the delta centre and thins towards the margin.

The basin is partitioned into six to seven east-west bound blocks corresponding to depositional belts or depobelts. These depobelts correspond to discrete periods of the delta's evolutionary history starting from the oldest in the north, Northern delta (50-60 million years) to the youngest, Offshore (1-2 million years) in the south^[18,19]. Each depobelt was assumed to constitute more or less independent unit with respect to sedimentation, structural deformation and hydrocarbon generation and accumulation^[20].

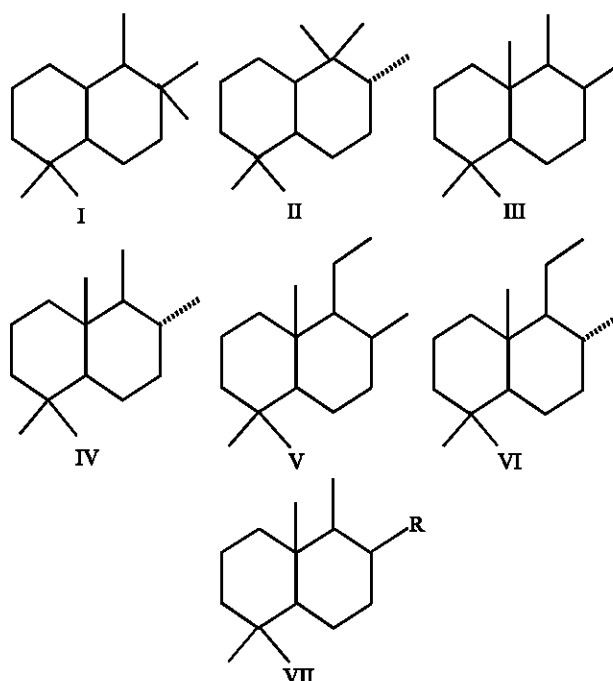
The hydrocarbon habitat of the Niger delta is mostly within the sandstone reservoir of the Agbada Formation where they are usually trapped in rollover anticlines associated with growth faults. The age of the reservoir sands with average thickness between 10 and 20 m ranges from Eocene to Pliocene^[21]. Niger delta produces mainly medium to light oil with API gravities ranging from 30 to 45°. The lighter crude oils are volatile with GORs ranging from 180 to 1600 ft³/bbl. The Niger delta source rock contains predominantly mixture of oil- and gas-prone type IIB and IIIA kerogen.

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 Å molecular sieves. GC-MS analysis of the branched/cyclic alkanes fractions was performed on 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 µm 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.

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^[9,10]. 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.



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

Table 1: Bicyclic terpanes in crude oil from Niger delta

Peak	Molecular formula	Structure	Name
A	C ₁₅ H ₂₈	I	Bicyclic sesquiterpane
B	C ₁₅ H ₂₈	II	Bicyclic sesquiterpane
C	C ₁₅ H ₂₈	III	Bicyclic sesquiterpane
D	C ₁₆ H ₃₀	V	Bicyclic sesquiterpane
E	C ₁₆ H ₃₀	V	Bicyclic sesquiterpane
F	C ₁₅ H ₃₀	IV	8β(H) drimane
G	C ₁₅ H ₃₀	IV	8β(H) drimane
H	C ₁₆ H ₃₀	V	Bicyclic sesquiterpane
I	C ₁₆ H ₃₀	V	Bicyclic sesquiterpane
J	C ₁₆ H ₃₀	VI	8β(H) drimane
K	C ₂₁ H ₄₀	VII	Bicyclic sesquiterpane

C₁₅ 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].

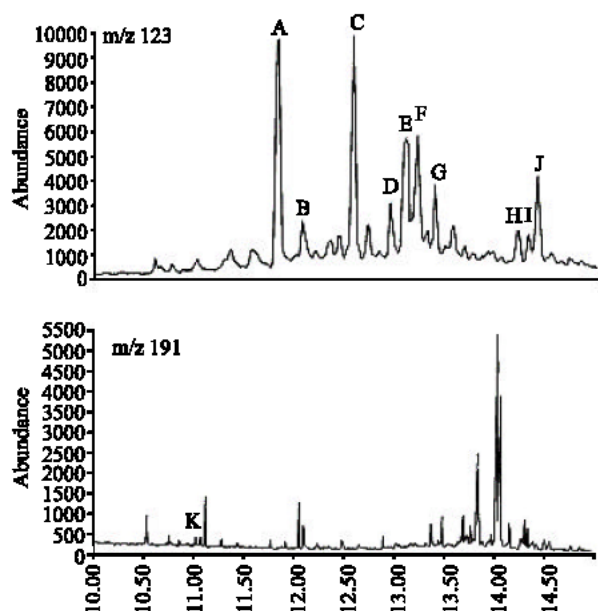


Fig. 1: Partial m/z 123 and 191 mass chromatogram of crude oil from Niger delta

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 $C_{15}H_{28}$. Structures I, II and III have been tentatively assigned to peaks A, B and C having base peak at m/z 193^[8]. Peaks F and G having base peak at m/z 123 have spectra similar to that of $\delta\beta(H)$ drimane with structure IV^[9].

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 C_6-C_7 and C_9-C_{10} bonds will give m/z 137 (M^+-71). The loss of 85 daltons from the molecular ion arising from the cleavage of the C_5-C_6 and C_9-C_{10} bonds will give m/z 123 (M^+-99). Cleavage of A and B ring at C_5 and C_{10} position can result to m/z 109.

C_{16} Bicyclic sesquiterpanes: Peaks D, E, H, I and J have mass spectra that are similar to those of previously reported C_{16} bicyclic sesquiterpanes^[9,22]. The mass spectra of peaks D, E, H and I feature M^+ ion at m/z 222 corresponding to $C_{16}H_{30}$ (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 $\delta\beta(H)$ homodrimane VI^[9]. The absence or low abundance of ion at m/z 193 corresponding to M^+-29 fragmentations has been attributed to unfavourable cleavage of ethyl

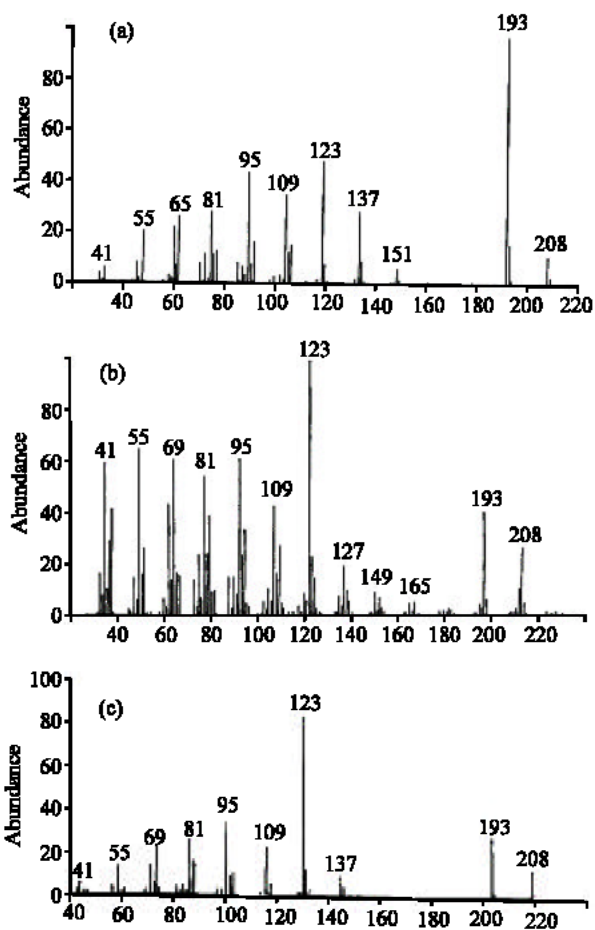


Fig. 2: Mass spectra of C_{15} bicyclic terpanes of crude oils from Niger delta: (a) peaks A, B and C (b) peaks F and G (c) mass spectra of C_{15} bicyclic terpanes^[9]

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_{15} 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^[22]. The molecular ions (M^+) at 292 corresponded to molecular formula $C_{21}H_{40}$. These compounds have basic structure of C_{15} 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_{15} 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

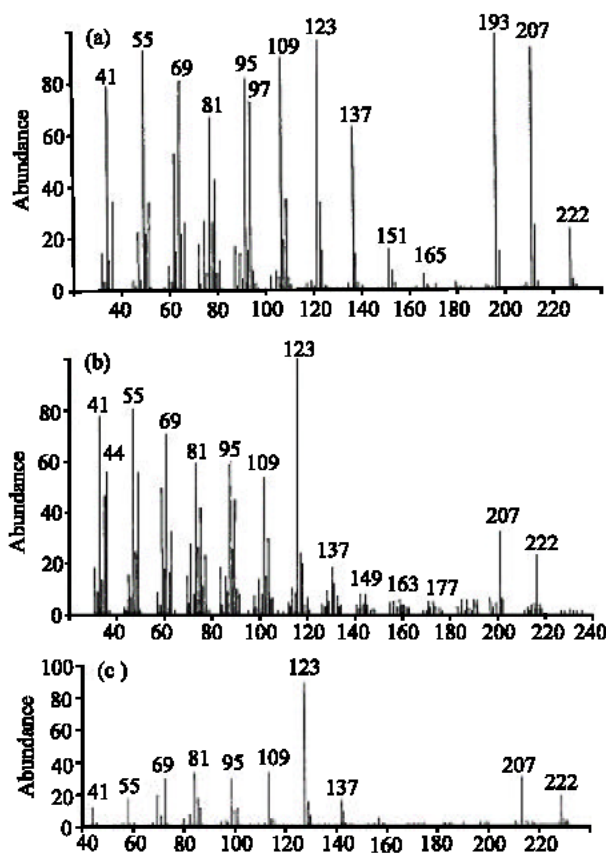


Fig. 3: Mass spectra of C₁₆ bicyclic terpanes of crude oils from Niger delta: (a) peaks D, E, H and I (b) peak J and (c) mass spectra of C₁₆ bicyclic terpanes reported by Alexander *et al.*^[9]

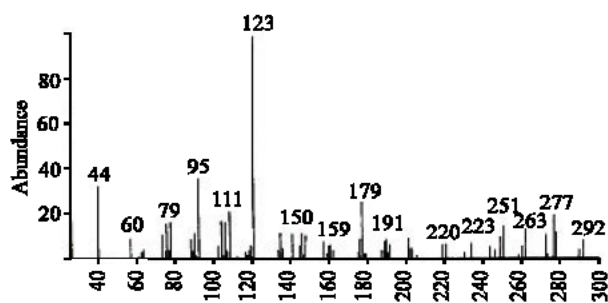


Fig. 4: Mass spectra of C₂₁ bicyclic terpanes of crude oils from Niger delta (peak J)

with significant terrestrial contributions, suggesting their possible utility as terrestrial source indicator^[11,13]. The presence of these compounds in crude oil from the Niger delta tends to support significant terrestrial contributions to Niger delta source rock.

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