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Tricyclic Terpane Fingerprint of Crude Oils from Niger Delta, Nigeria

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Abstract

Tricyclic terpanes identified in two representative crude oils from the Central and Western Niger Delta (oil- RVAG and oil-DTIR, respectively) ranged from C_{19} to C_{29}, including C_{24} tetracyclic terpane. Plot of the abundances of tricyclic terpanes show similarity in the distribution profile of the oil samples, characterized by the uncommon distribution of C_{20} and C_{21} tricyclic terpanes indicating both Niger Delta crude oils are derived from similar source organic matter. Ratios of C_{22}/C_{21} and C_{24}/C_{23} tricyclic terpanes indicate source rocks of the crude oil samples were deposited in a deltaic environment and derived from mixed marine/terrestrial organic matter. Additional, C_{26}/C_{25} tricyclic terpanes, C_{24} tetracyclic/C_{23} tricyclic terpanes and C_{24} tetracyclic/C_{26} tricyclic terpanes indicate the crude oil samples are generated from shale source rocks derived from terrestrial organic matter, with oil-DTIR receiving a more terrestrial contribution, and marine facies, with oil-RVAG receiving a more marine contribution. Thermal maturity, determined from ratios of low to high molecular weight tricyclic terpanes, indicate the crude oil samples are mature with oil-RVAG more mature than oil-DTIR. The ratios of C_{19}/C_{23} and C_{20}/C_{23} tricyclic terpanes, which indicate high maturity of the crude oils, suggested terrestrial and marine source for oil-RVAG and oil-DTIR, respectively, contrasting with the relative abundances of tricyclic and tetracyclic terpanes. This implies the abundances of C_{19} and C_{20} tricyclic terpanes, particularly in crude oils at high maturity, as in the Niger Delta, has interfering effect on source interpretation and its ratios be used in combination with other parameters for evaluating Niger Delta crude oils.

Keywords: Tricyclic terpane, distribution, crude oil, abundance, diagnostic ratio, maturity, Niger Delta.

INTRODUCTION

Tricyclic terpanes in crude oils are a class of hydrocarbons that consist of three fused 6-carbon rings with an isoprenoid side chain (Peters, 2000). The most prominent tricyclic terpanes are the cheilanthanes (13-methyl, 14- alkylpodocarpanes) which are derived from a natural product, cheilanthatriol, of the plant Cheilanthes farinose (Khan *et al.,* 1971). Other sources of tricyclic terpanes include bacteria, tasmanite algae and thermally broken down triterpanes (Tissot and Welte, 1984; Simoneit *et al.,* 1993; Revill *et al.,* 1994; Greenwood *et al.,* 2000). The distribution and composition of tricyclic terpanes are characteristic and are employed as fingerprints to evaluate source-rock properties, depositional environments, extent of thermal maturity and biodegradation as well as correlate crude oils and source-rock extracts (Walters and Cassa, 1985; Zumberge, 1987; Peters and Moldowan, 1993).

In Nigeria's Niger Delta region, characterization and correlation of crude oils have been undertaken using trace metals, whole oil bulk properties, saturates and aromatic biological markers fingerprints; C_7 Light hydrocarbons, alkylated polycyclic aromatic hydrocarbons and aromatic steranes (Eneogwe, 2004; Akinlua *et al.,* 2007; Sonibare *et al.,* 2008; Onyema and Osuji, 2015 Okoroh *et al.,* 2020). However, there is inadequate data on the use of tricyclic terpanes in the characterization of crude oils in the Niger Delta. This study investigates the distribution, composition and characterization of tricyclic terpanes in crude oils from the Niger Delta region of Nigeria, with a view to providing another geochemical means for correlation studies of crude oils from the region.

EXPERIMENTAL

Description of Study Site

The Niger Delta region of Nigeria is located in the southern part of the country between longitudes 5°

and 8° E and latitudes 3° and 6° N, at the apex of the Gulf of Guinea. The region is an extremely prolific hydrocarbon province that consists of three stratigraphic sequences namely: the marine shale Akata formation, the shale interbedded with paralic sandstone of the Agbada formation and the Benin formation, which consist of coastal plain sands (Turtle *et al.,* 1999).

Sample Collection

Two crude oil samples (one each) were obtained from oil flow stations (onshore) in Rivers State (4°39' N, 7°16' E) and Delta State (5°28' N, 6°12' E) located in Central and Western Niger Delta sub-regions, respectively. Each crude oil is a mixture of several oil producing wells flowing into the flow station and serve as a representative crude oil sample of the sub-region. The crude oil samples were labelled appropriately as oil-RVAG and oil-DTIR, respectively.

Crude Oil Fractionation

50 mg of each crude oil sample was weighed into a labelled centrifuge tube. Excess pentane was poured into each tube with the oil sample and the mixture was allowed to stand for three hours to precipitate the asphaltenes, then centrifuged for 30 minutes to coalesce the precipitated asphaltenes. The pentane soluble fraction was decanted, concentrated with nitrogen gas at 40°C, and placed on top a glass column (30 cm x 1 cm) stuffed with glass wool at the bottom and packed with activated silica (mesh 100 - 200). *n*-hexane was poured into the packed column to elute the saturates, which contains the tricyclic terpanes. The eluent (*n*-hexane and saturates) was collected into a pre-weighed vial and the solvent evaporated to dryness under a gentle stream of nitrogen at 40°C.

Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

Agilent 7890A gas chromatograph (GC) system with an HP-5 silica capillary column (50 m x 320 m i.d. and 0.25 m film thickness) and an Agilent 5975 mass selective detector (MSD) was used to analyzed the saturate fractions of the crude oil samples. An automatic liquid sampler, G4513A, was used to inject 1 microliter of the saturate fraction into the GC capillary column in splitless mode. The GC oven was set to an initial temperature of 80°C for 5 min., then ramped to 300°C at a rate of 4°C /min. and held at this temperature for 30 min. The GC analyses of the samples were monitored at the mass to charge (m/z) 191 fragment ion. Quantification of each peak was obtained by area integration which was processed by Chemstation OPEN LAB CDS software.

RESULTS AND DISCUSSION

Profile of Tricyclic Terpanes

Analyses of both crude oil samples, monitored at m/z 191 identified C_{19} to C_{29} tricyclic terpanes which elute from the GC between 20 and 40 minutes. In addition to tricyclic terpanes, C_{24} tetracyclic terpane was also identified in the m/z 191 mass chromatograms of the studied crude oils. The GC-MS analyses showed four peaks each for C_{20} (TR20a-d) and C_{21} (TR21a-d) tricyclic terpanes, which were nearly equal in heights (fig. 1). The mass chromatograms of tricyclic terpanes usually show a single peak for each of C_{19} to C_{24} and a pair of peaks (R and S isomers) for C_{25} and higher homologues due to the presence of a chiral centre at C-22 (Younes, 2001; Wang *et al.,* 2006). This indicates the distribution of the C_{20} and C_{21} tricyclic terpanes in the Niger Delta crude oils is uncommon (Ajie and Onyema, 2022). Figure 1 shows the distribution and abundances of tricyclic terpanes in oil samples -RVAG and -DTIR.

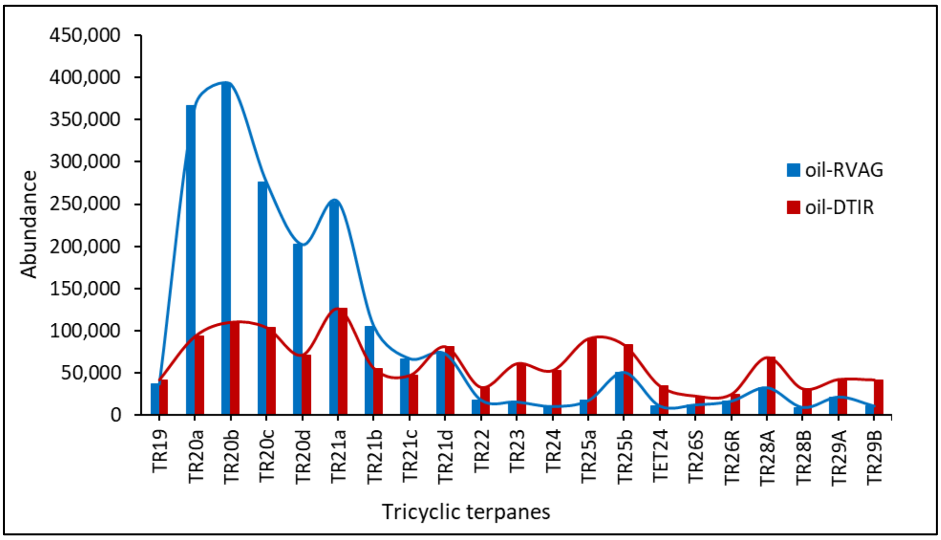

Figure 1: Distribution and abundances of C_{19} to C_{29} tricyclic terpanes, including C_{24} tetracyclic terpane, in oil samples -RVAG and -DTIR from Central and Western Niger Delta, respectively. TR19: C_{19} tricyclic terpane, ... etc., TET24: C_{24} tetracyclic terpane.

From fig.1, the distribution profile of tricyclic terpanes in both oil samples generally followed similar pattern. Terpanes derived from different sources have distinct profiles which are employed as fingerprints for crude oil correlation and/or differentiation (Peters *et al.*, 2005). The similarity in the distribution profile of tricyclic terpanes indicate the Niger Delta crude oils are not distinct, but derived from similar source organic matter.

The total abundance of TR20 and TR21 is more than from TR22 to TR29, considerably in oil-RVAG (7.98) and slightly in oil-DTIR (1.25). This indicates the Niger Delta crude oils are characterized by abundance of C_{20} and C_{21} tricyclic terpanes. In both oil samples, the high abundances of C_{20} and C_{21} tricyclic terpanes, common for terrestrial oils (Aquino Neto *et al.*, 1983), and the presence of C_{24} tetracyclic terpane (TET24), a biomarker that is believed to originate from higher plants (Disnar and Harouna, 1994) suggest the Niger Delta crude oil samples are derived from terrestrial organic matter. The total abundance of TR20 and TR21 is more in oil-RVAG, whereas the total abundance from TR22 to TR29 is more in oil-DTIR (fig. 1). This increased abundance of the low molecular weight tricyclic terpanes generated from thermal cracking of the high molecular weight homologues, which decreases during crude oil maturation (Farrimond *et al.*, 1999), indicate oil-RVAG is more mature than oil-DTIR.

Source and Depositional Environment of Tricyclic Terpanes

The relative abundances (ratios) of tricyclic terpanes in crude oils are utilized to geochemically characterize their organic matter source and depositional environment (Tao *et al.*, 2015). Diagnostic ratios were calculated from the abundances of tricyclic and tetracyclic terpanes obtained from GC-MS analyses of the oil samples (Elfadly *et al.*, 2017). Table 1 shows the diagnostic ratios of tricyclic and tetracyclic terpanes commonly used for geochemical characterization of crude oil samples.

Table 1: Diagnostic ratios of tricyclic and tetracyclic terpanes in oils -RVAG and -DTIR from Niger Delta, Nigeria

Tricyclic terpane ratios	oil-RV-AG	oil-DTIR
TR19/TR23	2.32	0.69
TR20/TR23	77.55	6.20
TR21/TR23	31.27	5.08
TR22/TR21	0.04	0.11
TR24/TR23	0.66	0.87
TeT24/TR23	0.69	0.57
TeT24/TR26	0.38	0.73
TR26/TR25	0.43	0.27

Tricyclic terpane ratios commonly used for assessment of the organic matter type from which source rocks and crude oils were derived are C_{19}/C_{23} (TR19/TR23) and C_{20}/C_{23} (TR20/TR23). The C_{19} and C_{20} tricyclic terpanes are more abundant in terrestrial oils while the C_{23} tricyclic terpane, are often the dominant in crude oils from marine sources (Peters and Moldowan, 1993). Ratio of TR19/TR23 in oil-RVAG is 2.32 and in oil-DTIR is 0.69, while ratio of TR20/TR23 is 77.55 and 6.20, respectively (Table 1). The TR19/TR23 ratio in oil-RVAG (> 1) suggest a terrestrial organic matter source and in oil-DTIR (< 1) suggest a marine source, whereas the TR20/TR23 ratio indicate high abundance of C_{20} tricyclic terpanes suggesting terrestrial organic matter source in both oil samples (Volk *et al.*, 2005), with oil-RVAG having a greater input than oil-DTIR.

The ratios of C_{22}/C_{21} (TR22/TR21a-d) and C_{24}/C_{23} (TR24/TR23) tricyclic terpanes are generally used to identify the depositional environment and organic matter source of crude oils, respectively. For oils -RVAG and -DTIR, TR22/TR21a-d ratio values are significantly low; 0.04 and 0.11, while TR24/TR23 ratio values are lower than 1; 0.66 and 0.87, respectively (table 1). This indicate the values of TR22/TR21a-d and TR24/TR23 ratios for both oil samples were close and consistent with source rocks deposited in a deltaic environment and derived from mixed marine/terrestrial organic matter.

C_{24} tetracyclic terpane (TET24) detected in both oils-RVAG and -DTIR have relative abundances of 0.55% and 2.64% of the total tricyclic and tetracyclic terpane abundances, respectively (calculated from fig. 1). Ratios of C_{24} tetracyclic/C_{23} tricyclic terpane (TeT24/TR23) and C_{24} tetracyclic/C_{26} tricyclic terpane (TeT24/TR26) are commonly used to assess crude oils source of deposition as well as indicating the input of terrestrially (higher plant) derived organic matter (Philip and Gilbert 1986). High abundance of C_{24} tetracyclic terpane (i.e. TeT24/TR26 >1) have been found in carbonate samples, while low to medium values suggest shale source (Peters *et al.*, 2005). Both TeT24/TR23 and TeT24/TR26 ratios for oils-RVAG and -DTIR are less than 1 (<1; table 1) suggesting shale source for the Niger Delta crude oil samples. The TeT24/TR26 ratio (0.38 and 0.73) together with the relative abundances of TeT24 (0.55% and 2.64%) indicate the Niger Delta crude oil samples were derived from terrestrial organic matter with oil-RVAG receiving a lesser terrestrial contribution than oil-DTIR, respectively. The C_{26}/C_{25} tricyclic terpane ratio (TR26[S,R]/TR25[a,b]) is useful, in combination with other parameters, for distinguishing lacustrine from marine oils. Higher carbon number tricyclic terpanes are often the dominant in crude oils from saline lacustrine and marine sources (Aquino Neto *et al.*, 1983). Values of TR26/TR25 ratio which is moderate in oil-RVAG (0.43) and low in oil-DTIR (0.27) show the C_{26} tricyclic terpanes are lower in abundance than the C_{25} tricyclic terpanes (Table 1). This abundance of C_{26} and C_{25} tricyclic terpanes is diagnostic for sourcing from marine facies with oil-RVAG receiving a more marine source input than oil- DTIR.

Thermal Maturity of Tricyclic Terpanes

The abundances of tricyclic terpanes in crude oils are used as an indicator of thermal maturity (Van Graas, 1990). With increasing maturity of crude oil, thermal cleavage of the high molecular weight tricyclic terpanes occurs and the abundances of lower-carbon number homologues are favoured, regardless of source-rock organic matter (Walples and Machihara, 1991). Tricyclic terpanes used for assessment of the thermal maturities of oils -RVAG and -DTIR compared low to high molecular weight homologues (table 2).

Table 2: Ratios of tricyclic terpanes used for assessment of the thermal maturities of oils -RVAG and -DTIR from Niger Delta, Nigeria

Ratios	RV-AG	DT-IR
TR19/TR24	3.52	0.79
TR20/TR21	2.48	1.22
TR20/TR23	77.55	6.20
TR21/TR25	7.27	1.79
TR21/TR29	15.19	3.67
TR23/TR24	1.52	1.15

Ratio values of tricyclic terpanes employed for assessment of the thermal maturities of both oil samples show the low molecular weight tricyclic terpanes are more abundant than the high molecular weight homologues in both oils- RVAG and -DTIR (Table 2). This higher abundance of the low molecular weight tricyclic terpanes over the high molecular weight homologues indicates the Niger Delta crude oils are mature. From table 2, oil-RVAG had higher values for all the thermal maturity ratios indicating this oil sample is more mature than oil-DTIR.

Tricyclic terpane maturity ratios TR19/TR24, TR20/TR21, TR21/TR25, TR21/TR29 and TR23/TR24 indicate oil-RVAG is more mature than oil-DTIR, however TR20/TR23 indicate oil-RVAG is significantly more mature than oil- DTIR. Ratios of TR19/TR23 and TR20/TR23 are commonly used for assessment of the organic matter type from which source rocks and crude oils were derived. The TR19/TR23 ratio suggested a terrestrial organic matter source for oil- RVAG (> 1) and a marine source for oil-DTIR (< 1) in variance with TET24 abundance and ratios (table 1) as well as previous studies by Sonibare (2008) and Onyema *et al.,* (2018). This suggest the abundance of the C_{19} and C_{20} tricyclic terpanes, particularly at high maturity has interfering effects on source interpretation and the C_{19}/C_{23} and C_{20}/C_{23} tricyclic terpane ratios be used in combination with other parameters for determining/distinguishing organic matter source for crude oils.

CONCLUSIONS

Distribution and abundances of tricyclic terpanes in two representative crude oil samples from the Central and Western Niger Delta (oil-RVAG and oil-DTIR, respectively) show similarity in their profile characterized by an unusual abundance of C_{20} and C_{21} tricyclic terpanes indicating both Niger Delta crude oils are derived from similar source organic matter. The ratios of C_{22}/C_{21}, C_{24}/C_{23} and C_{26}/C_{25} tricyclic terpanes as well as C_{24} tetracyclic/C_{23} tricyclic terpanes and C_{24} tetracyclic/C_{26} tricyclic terpanes indicate both Niger Delta crude oils were generated from shale source rocks derived from terrestrial organic matter and marine facies which were deposited in a deltaic environment, with oil-RVAG receiving a more marine contribution and oil-DTIR receiving a more terrestrial contribution. In addition, abundances of low to high molecular weight tricyclic terpanes, used as an indicator of thermal maturity, indicate the Niger Delta crude oils are mature with oil-RVAG being more mature than oil-DTIR. The maturity ratios of C_{19}/C_{23} and C_{20}/C_{23} tricyclic terpanes, commonly used for evaluation of organic matter source, suggested terrestrial and marine organic matter source for oil-RVAG and oil-DTIR, respectively, contrasting with the distribution profile and relative abundances of tricyclic and tetracyclic terpanes. This implies that the abundance of C_{19} and C_{20} tricyclic terpanes, particularly in crude oils at high maturity, such as in the Niger Delta, has interfering effect on source interpretation and its ratios be used in combination with other parameters for evaluating Niger Delta crude oils.

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