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Research Paper

C_{20} and C_{21} Tricyclic Terpanes in Niger Delta Crude Oils 1: Unusual Distribution and Characterization

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ABSTRACT: *C_{20} and C_{21} tricyclic terpanes in Niger Delta crude oils were investigated and characterized. From comparison of the partial m/z 191 mass chromatograms of two crude oil samples (RV-35 and DT-80) to that of related literatures, 12 peaks which eluted from the gas chromatography (GC) at a given retention time, were designated as C_{20} (TR20a-e) and C_{21} (TR21a-g) tricyclic terpane isomers. This reveal an unusual distribution of the C_{20} and C_{21} tricyclic terpanes in Niger Delta crude oils. Total abundance of the C_{20} and C_{21} tricyclic terpanes suggest RV-35, with considerably higher abundance, was more mature than DT-80 and that the C_{20} tricyclic terpanes were generated more than C_{21} tricyclic terpanes with increase in crude oil maturity. Individual C_{20} and C_{21} tricyclic terpane abundances were mostly higher in RV-35, except TR20c and TR21g which were slightly higher in DT-80. Similarities in the profiles of abundance, composition and ratios of C_{20} and C_{21} tricyclic terpanes indicate that the Niger Delta crude oils are derived from terrigenous Tertiary deltaic petroleum system. However, some C_{20} and C_{21} tricyclic terpane ratios permitted differentiation of the oil samples and are suggestive as indicator of maturity and source/depositional environment. Multivariate plot showed moderate similarities in paths followed by both oil samples suggesting the Niger Delta crude oils were derived from the same terrestrial source, with input from a different source/depositional environment, marine, to one of the crude oils.*
KEYWORDS: *Tricyclic terpane, characterization, Niger Delta, correlation, crude oil*

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I. INTRODUCTION

Tricyclic terpanes are hydrocarbon compounds made up of three fused 6-carbon rings with an alkyl side chain. The most common tricyclic terpanes are cheilanthanes (13-methyl, 14-alkylpodocarpanes), which are generated from cheilanthatriol, a natural product of the plant Cheilanthes farinose [1]. Other sources of tricyclic terpanes include bacteria, tasmanite algae which they have been discovered to occur frequently with, and the thermal breakdown of triterpanes in kerogen, where they are cogenerated with related monoaromatic to triaromatic tricyclic hydrocarbons [2], [3] and [4].

Tricyclic terpanes are frequently found in the saturated hydrocarbon fraction of petroleum oils and source rock extracts. They are determined using gas chromatography-mass spectrometry (GC-MS) by utilizing the mass to charge (m/z) 191 fragment ion. The C_{19} to C_{29} homologous series are often observed in the m/z 191 mass chromatogram, with the higher members up to C_{54} obscured by the abundance of hopanes [5] and [6]. C_{19} to C_{24} tricyclic terpanes usually show a single peak on the mass chromatogram and a pair of peaks for C_{25} and higher [7], [8] and [9]. This is due to the presence of a chiral centre at C-22 in C_{25} and higher tricyclic terpanes, resulting in two peaks, R and S isomers [10].

Tricyclic terpanes have been used to successfully correlate crude oils and source-rock extracts, predict source-rock characteristics, and assess thermal maturity and biodegradationb [11], [12] and [13]. Crude oils from the Niger Delta region of southern Nigeria have been characterized and correlated using their bulk properties, light hydrocarbons, aliphatic hydrocarbons, triterpanes, alkylated polycyclic aromatic hydrocarbons (Alkyl-PAHs) and aromatic steranes [14], [15], [16], [17], [18] and [19]. This study investigates the occurrence and distribution of C_{20} and C_{21} tricyclic terpanes in Niger Delta crude oils. Furthermore, the C_{20} and C_{21} tricyclic terpanes will be characterized with a view to providing another geochemical means for crude oil correlation studies.

II. MATERIAL AND METHODS

2.1 Sample collection

The Niger Delta region is located in southern Nigeria at the apex of the Gulf of Guinea between longitudes 5°- 8° E and latitudes 3° - 6° N. The region covers an area of about 75,000 km^2 and was formed from the late Cretaceous to Recent age with depositions of sediments south westward into the Gulf of Guinea [20]. Crude oil samples (one each) were obtained from oil producing fields (onshore) in Rivers and Delta states, both located in the Niger Delta region. The crude oil samples were obtained with the assistance of field technicians, labelled appropriately (RV-35 and DT-80, respectively) and taken to the laboratory for analysis.

2.2 Crude oil fractionation

50 mg of each crude oil sample was weighed into a labelled centrifuge tube and excess pentane added. The mixture was allowed to stand for three hours to precipitate the asphaltenes, and centrifuged for 30 minutes to coalesce the precipitated asphaltenes. The pentane soluble fraction was decanted, concentrated with nitrogen gas at 40°C, and put on top a glass column (30 cm x 1 cm) packed with silica and stuffed with glass wool at the bottom. n-hexane was poured into the packed column to elute the saturates. The eluent (n-hexane and saturates) was concentrated using nitrogen gas at 40°C.

2.3 Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

The saturate fraction of the crude oil samples were analyzed on an Agilent 7890A gas chromatograph (GC) system equipped with a HP-5 silica capillary column (50 m x 320 µm i.d and 0.25µm film thickness) and an Agilent 5975 mass selective detector (MSD). 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 fragmentation ion. Quantification of each peak was obtained by area integration which was processed by Chemstation OPEN LAB CDS software.

III. RESULTS AND DISCUSSION

3.1 Distribution of C_{20} and C_{21} Tricyclic Terpanes

Comparing the mass chromatograms (m/z 191) of the oil samples to that of related literatures, twelve (12) peaks were selected as C_{20} and C_{21} tricyclic terpanes (figs 1 and 2). The 12 peaks selected were well-resolved and eluted from the GC between 21 and 25 minutes.

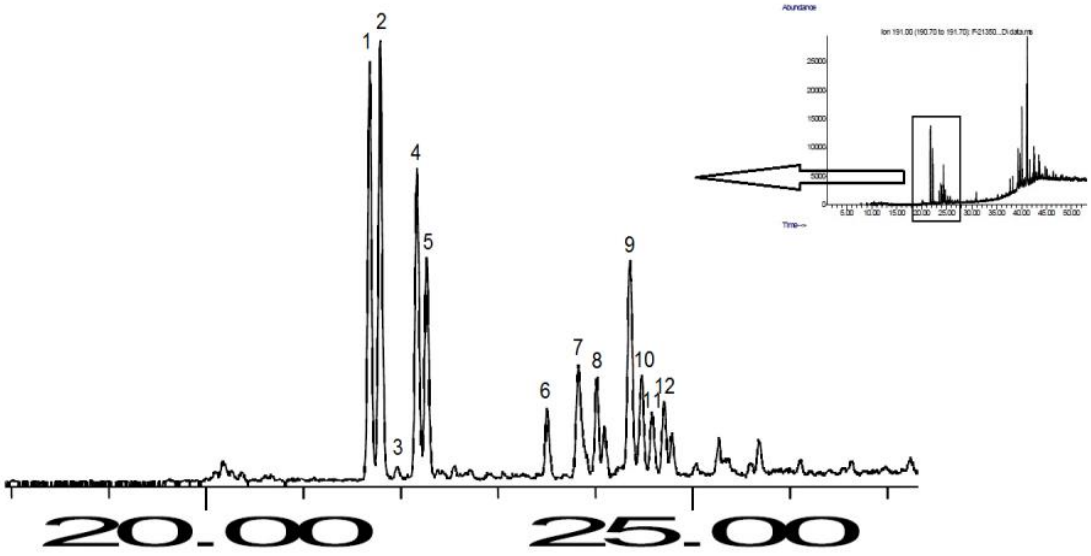

Figure 1: Partial m/z 191 mass chromatogram of Niger Delta crude oil sample RV-35 showing the selected C_{20} and C_{21} tricyclic terpane peaks

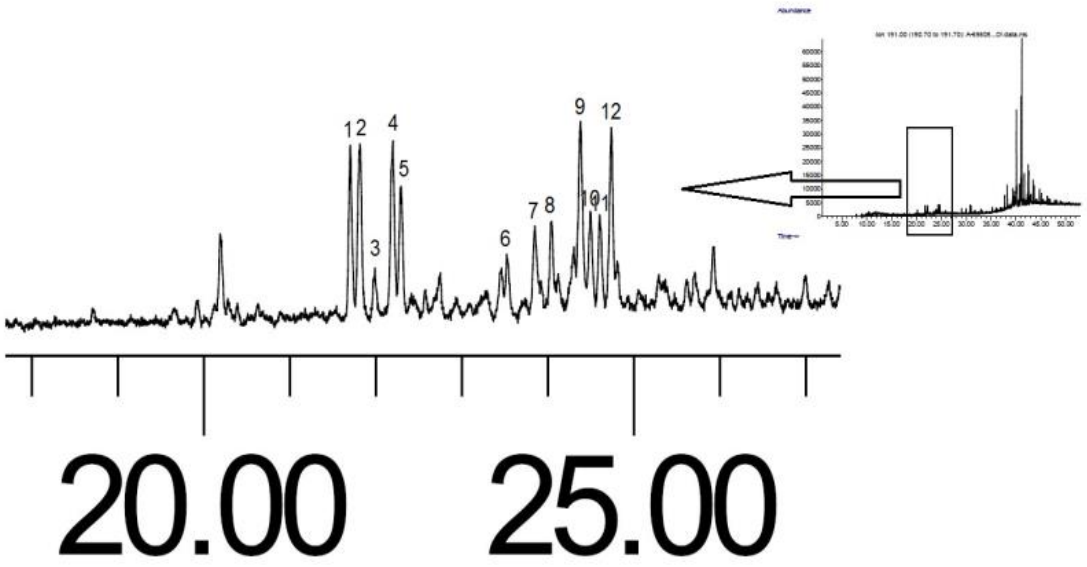

Figure 2: Partial m/z 191 mass chromatogram of Niger Delta crude oil sample DT-80 showing the selected C_{20} and C_{21} tricyclic terpane peaks

The 12 selected peaks of C_{20} and C_{21} tricyclic terpanes occurred in both crude oil samples (figures 1 and 2). Generally, the mass chromatograms of tricyclic terpanes show a single peak each for C_{20} and C_{21} [7] and [21]. From the comparisons to related literatures, this C_{20} and C_{21} tricyclic terpane distribution is uncommon in crude oils and the distribution in the Niger Delta crude oils is unusual. From figures. 1 and 2, the 12 peaks separated into two groups. Peaks 1 - 5 were tightly clustered and eluted from the GC about 22 minutes, whereas peaks 6 - 12 were loosely clustered and eluted from the GC about 24 minutes. The mass chromatogram of an ion (m/z) at a given GC retention time is often indicative of a class of homologous compounds with similar carbon numbers but different structures and isomerism [9]. This suggest peaks 1 - 5 as C_{20} tricyclic terpane isomers and peaks 6 - 12 as C_{21} tricyclic terpane isomers.

C_{20} tricyclic terpane peaks 1, 2, 4 and 5 were more prominent than peak 3 in both mass chromatograms, and also were more prominent in RV-35 (figure 1) than in DT-80 (figure 2). Peaks 1, 2 and 4, 5 were also tightly clustered and nearly equal in height. C_{21} tricyclic terpane peaks 7, 8 and 10, 11 in both oil samples and 9, 12 in DT-80, were closely clustered and nearly equal in heights. The most common C_{20} and C_{21} tricyclic terpanes discovered in crude oil and source rock samples include 13α(H), 14α(H) and 13β(H), 14α(H) isomers, as well as the ββ and αβ isomers [21]. These isomers often occur in almost equal abundance [10]. This suggest C_{20} tricyclic terpane peaks 1, 2 and 4, 5 as well as C_{21} tricyclic terpane peaks 7, 8 and 10, 11 are isomers with different isomerism possibly derived from similar source/depositional environment. Peak 3 was considerable diminished in height compared to peaks 1, 2, 4 and 5, with which it is clustered (figures 1 and 2), suggesting isomers possibly derived from different source/depositional environment. Peaks 9 and 12 in DT-80 have nearly equal heights, but differ in RV-35, suggesting they are C_{21} tricyclic terpane isomers possibly derived from different source/depositional environment.

3.2 Abundance and Composition Profiles

Abundances of the C_{20} and C_{21} tricyclic terpane isomers were calculated by area integration of the selected peaks. Table 1 shows the selected peaks for the C_{20} and C_{21} tricyclic terpane isomers, labels and abundances. The total abundance of C_{20} and C_{21} tricyclic terpanes in RV-35 was 2.43 times more than the total abundance in DT-80 (table 1).

Table 1: Peak labels and abundances of C_{20} and C_{21} tricyclic terpane isomers in crude oil samples from Niger Delta, Nigeria

Peak No.	Tricyclic Terpanes (TR)	Code	Abundance	
			RV-35	DT-80
1	C_{20} tricyclic terpane (a)	TR20a	366,124	93,621
2	C_{20} tricyclic terpane (b)	TR20b	391,817	110,218
3	C_{20} tricyclic terpane (c)	TR20c	16,020	28,941
4	C_{20} tricyclic terpane (d)	TR20d	275,646	103,863
5	C_{20} tricyclic terpane (e)	TR20e	202,053	71,337

6	C_{21} tricyclic terpane (a)	TR21a	69,523	38,008
7	C_{21} tricyclic terpane (b)	TR21b	150,939	42,236
8	C_{21} tricyclic terpane (c)	TR21c	93,007	51,410
9	C_{21} tricyclic terpane (d)	TR21d	252,643	126,261
10	C_{21} tricyclic terpane (e)	TR21e	105,559	55,733
11	C_{21} tricyclic terpane (f)	TR21f	67,180	47,132
12	C_{21} tricyclic terpane (g)	TR21g	72,831	81,286
	Total C_{20} tricyclic terpanes		1,251,660	407,980
	Total C_{21} tricyclic terpanes		811,682	442,066
	Total Tricyclic Terpanes		2,063,342	850,046

During the transformation of organic matter to crude oil, high molecular weight hydrocarbons are thermally cracked to low molecular weight hydrocarbons [22]. As a result, sesterterpanes and triterpanes in kerogen are thermally cracked to tricyclic terpanes, which are always abundant in high maturity crude oils regardless of the organic matter source [23]. This suggest oil sample RV-35 was significantly more mature than DT-80. From table 1, the total abundance of C_{20} and C_{21} tricyclic terpanes is 3.07 and 1.84 times more in RV-35 than DT-80, respectively. Furthermore, the total abundance of C_{20} tricyclic terpane isomers (TR20a - TR20e; see peak labels in table 1) was 1.54 times more than total abundance of C_{21} tricyclic terpane isomers (TR21a - TR21g; see peak labels in table 1) in RV-35, but was slightly lower (0.92 times) in DT-80. This suggests that the C_{20} tricyclic terpanes are generated more than the C_{21} tricyclic terpanes as crude oils mature.

Individual C_{20} and C_{21} tricyclic terpanes were generally more abundant in RV-35 than DT-80, except TR20c and TR21g which were slightly more abundant in DT-80 than RV-35. TR20a, TR20b, TR20d and TR21d were the most abundant C_{20} and C_{21} tricyclic terpanes in both oil samples. TR20b, TR20a, TR20d, and TR21d were the most abundant in RV-35, constituting 18.99%, 17.74%, 13.36% and 12.24% of total C_{20} and C_{21} tricyclic terpane abundances, while TR21d, TR20b, TR20d, and TR20a were the most abundant in DT-80, constituting 14.85%, 12.97%, 12.22% and 11.01% of total C_{20} and C_{21} tricyclic terpane abundances, respectively. TR20c was the least abundant in RV-35 and DT-80 constituting 0.78% and 3.40%, respectively (table 1). Terpanes derived from different sources have distinct compositions and their characteristic profiles are employed as fingerprints for crude oil correlation and/or differentiation [24]. The degree of similarity in the abundance profile and compositions of C_{20} and C_{21} tricyclic terpanes indicates that the Niger Delta crude oils are not distinct but rather are predominantly derived from the same source organic matter/depositional environment. The slightly more abundance of TR20c and TR21g in DT-80 than RV-35 suggest contribution from a different source/depositional environment to the DT-80 crude oil.

3.3 Correlation of Niger Delta Crude oils

From the abundances of C_{20} and C_{21} tricyclic terpanes in RV-35 and DT-80, 66 ratios were derived and calculated. Majority of the derived ratios exhibited little/no difference in their calculated values which did not allow for clear differentiation of the crude oil samples. Crude oils which show little variation in tricyclic terpane distributions and derivable ratios are mostly from terrigenous Tertiary deltaic petroleum systems [25]. The little/no difference in the values of majority of the calculated C_{20} and C_{21} tricyclic terpane ratios indicate the Niger Delta crude oil samples are from terrigenous Tertiary deltaic petroleum systems. However, some of the calculated C_{20} and C_{21} tricyclic terpane ratios gave values that permit differentiation of the oil samples (table 2).

Table 2: C_{20} and C_{21} tricyclic terpanes ratios that permit differentiation of the crude oil samples, Niger Delta, Nigeria

Ratios	RV-35	DT-80
TR20a/TR20c	22.85	3.23
TR20a/TR21g	5.03	1.15
TR20b/TR20c	24.46	3.81
TR20b/TR21g	5.38	1.36
TR20c/TR20d	0.06	0.28
TR20c/TR20e	0.08	0.41
TR20c/TR21b	0.11	0.69
TR20c/TR21d	0.06	0.23
TR21b/TR21g	2.07	0.52

* see peak labels in table 1

Table 2 shows nine (9) ratios with values that differentiated the Niger Delta crude oil samples. TR20a/TR20c and TR20b/TR20c ratios had considerably high values of 22.85 and 24.46 for RV-35 and low values of 3.23 and 3.81 for DT-80, respectively. Inversely, TR20c/TR20d, TR20c/TR20e, and TR20c/TR21d ratios had relatively low values of 0.06, 0.08 and 0.06 for RV-35 compared to values of 0.28, 0.41, and 0.23 for DT-80, respectively. These ratios indicate that TR20a, TR20b, TR20d, TR20e and TR21d were predominant in RV-35 (which is more mature) than DT-80, suggesting these ratios for use as maturity indicators. Ratios of TR20a/TR21g, TR20b/TR21g, TR20c/TR21b and TR21b/TR21g also showed values that differentiated the crude oil samples. TR20a/TR21g, TR20b/TR21g and TR21b/TR21g ratios had high values of 5.03, 5.38 and 2.07 for RV-35 and low values of 1.15, 1.36 and 0.52 for DT-80, respectively. Inversely, TR20c/TR21b ratio had a low value of 0.11 for RV-35 and a high value of 0.69 for DT-80. These ratios indicate TR20a, TR20b and TR21b were more abundant in RV-35, whereas TR20c and TR21g were more abundant in DT-80, suggesting these ratios for use as for source/depositional environment indicators.

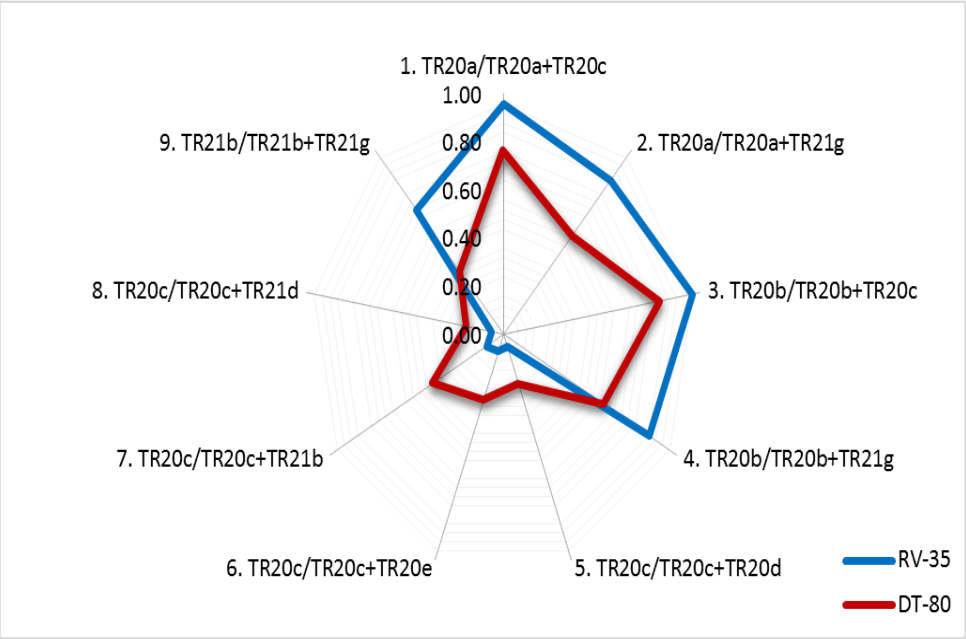

Figure 3: Plot of C_{20} and C_{21} tricyclic terpane ratios used for multivariate correlation of the Niger Delta crude oil samples

The C_{20} and C_{21} tricyclic terpane ratios that differentiated the oil samples (table 2) were normalized and put in a multivariate plot with nine (9) axis for comparison (figure 3). Multivariate plots are based on recognition of hydrocarbon compositional similarities that discriminate a homologous suit of oils from a different source [26] and [27]. They are used to complement correlation studies of crude oils [28] and [29]. From figure 3, the multivariate plot showed that the shapes formed from the paths followed, from axis-1 to -9, by both oil samples were not completely different. The crude oil samples followed similar paths on axis-1, -3, -5, -6, -7 and -8. Axis-1 and -3 of RV-35 were enhanced, while axis-5, -6, -7 and -8 of DT-80 were amplified. Differences were observed in the paths followed on axis-2, -4 and -9, with RV-35 more enhanced than DT-80. This showed that the paths followed by both crude oil samples on their multivariate plots were mostly similar and reveal a strong genetic relationship between the oils with minor differences in the paths followed suggesting input from a different source/depositional environment. The multivariate plots of both samples suggest that the Niger Delta crude oils are predominantly derived from the same source, terrestrial organic matter [30] and [31], with input from a different source organic matter/depositional environment, marine.

IV. CONCLUSION

12 peaks which eluted from the GC, at a given retention time, were selected from the mass chromatogram (m/z 191) of two Niger Delta crude oils and identified as C_{20} and C_{21} tricyclic terpane isomers. Total abundance suggest that the C_{20} tricyclic terpanes were generated more than the C_{21} tricyclic terpanes as the crude oils mature. Individual C_{20} and C_{21} tricyclic terpanes were generally more abundant in RV-35, except TR20c and TR21g which were slightly more abundant in DT-80. Similarities in the abundances and compositions of the C_{20} and C_{21} tricyclic terpanes indicate that the Niger Delta crude oils are not distinct, but derived from terrigenous Tertiary deltaic petroleum source. Multivariate plot of the normalized ratios showed reasonable similarity in paths followed by

both oil samples suggesting the Niger Delta crude oils are predominantly derived from terrestrial organic matter source. Minor differences observed on the multivariate plot suggest one of the Niger Delta crude oil received input from a different source/depositional environment, marine.

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