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Chemical Fingerprinting of Tricyclic Terpanes in Two Niger Delta Crude Oils and their Mixtures

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Abstract: **Gas chromatography system equipped with a mass selective detector was employed for chemical fingerprinting of two Niger Delta crude oils (samples A-001 and F-100) and their mixtures (samples B-208, C-406, D-604 and E-802) at different proportion. Total and individual abundances of C_{19} to C_{29} tricyclic terpanes, including C_{24} tetracyclic terpane, detected in the six oil samples followed similar patterns, A-001 < E-802 < F-100 < B-208 < C-406 < D-604, indicating the abundances did not mix correspondingly with the proportion of the two Niger Delta crude oils. Pearson correlation suggested sample A-001 was genetically related to sample F-100 (76.03%), and the four mixtures were significantly similar to each other (99.00% - 99.90%) and sample F-100 (99.00% - 99.81%), and similar to sample A-001 (76.02% - 81.60%). Hierarchical cluster analysis (HCA) separated the tricyclic and tetracyclic terpanes detected into 2 main groups, which distinctly differed (strong negative correlation) in the variations of their compositions in the six crude oil samples. Plots show the compositions of HCA group-A and -B tricyclic terpanes decrease as the proportion of sample A-001 decrease, and increase as the proportion of sample F-100 increase in the six crude oil samples, respectively. Values of the coefficient of determination (R^2) for the tricyclic terpane plots, range from 0.1406 to 0.9113 for group-A and 0.1226 to 0.6081 for group-B, with the compositions of C_{21} tricyclic terpane(d) being most suitable for use to estimate (91.13%) the proportion(s) of the two Niger Delta crude oils in their mixtures.**

Keywords: **Abundance, Correlation, Crude oil mixtures, Distribution, Niger Delta, Tricyclic terpane.**

I. INTRODUCTION

Crude oil is derived from the chemical and geological transformation of organic matter buried deep under the earth during sedimentary processes over geological time scale. The changing conditions during the transformation processes transmit geochemical compounds with characteristic distribution and composition (fingerprint) to crude oil which varies from one field to another (Tissot and Welte, 1984; Hunt, 1996). Consequently, within the carbon-carbon skeletons of some geochemical compounds are embodied essential information on the source organic matter, depositional environment, thermal history, lithology of the source rock and geological condition of the crude oil or source rock extract in which they occur (Peters and Moldowan, 1993; Osuji and Antia, 2005). Geochemical compounds whose characteristic fingerprints have been utilized for crude oil studies include C_7 light hydrocarbons, C_8 to C_{40} *n*-alkanes including pristane and phytane, steranes, terpanes, and polycyclic aromatic hydrocarbons (Mango, 1997; Kolonic et al., 2002; Volk et al., 2005; Sonibare et al., 2008). They have been utilized as diagnostic tool for interpreting geochemical data for crude oils as well as for correlation and/or differentiation between oil-oil and oil-source rock, unravel oil migration pathway, assessment of reservoir continuity/compartmentalization and commingled crude oil allocation (Pasadakis, 2002; Peters et al., 2005; Pomerantz et al., 2010; Al-Ameri et al., 2016; He et al., 2018; Kanshio, S. 2019).

Tricyclic terpanes are a group of terpanes with three fused 6-carbon rings and an alkyl side chain. They are commonly detected in crude oils and source rock extracts in a mixture of other types of geochemical compounds by gas chromatography-mass spectrometry (GC-MS) by monitoring the mass to charge (m/z) 191, the characteristic fragmentation ion of the terpanes (Wang al., 2006; Killops and Killops, 2013). The C_{19} to C_{29} are commonly observed with the higher members (up to C_{54}) obscured by the abundance of the pentacyclic terpanes (de Grande et al., 1993; Greenwood et al., 2000). The relative compositions of tricyclic terpanes such as C_{19}/C_{23}, C_{23}/C_{24}, and C_{26}/C_{25} have been employed as diagnostic parameters for interpreting source-rock properties, source organic matter (marine or terrestrial), depositional environment (oxic and anoxic), thermal maturity and biodegradation as well as well as correlation and/or differentiation of crude oils and source rock extracts (Walters and Cassa, 1985; Zumberge, 1987; Peters and Moldowan, 1993). Characterization of tricyclic terpanes in crude oils from the Niger Delta region of Nigeria showed an uncommon distribution of the C_{20} and C_{21} homologs (Ajie and Onyema, 2022). In addition, the relative compositions indicated that crude oils from the region were predominantly derived from terrigenous Tertiary deltaic petroleum systems with minor input from a different source and/or depositional environment and were mature. This research investigates the distribution and composition fingerprints of tricyclic terpanes in two crude oils from Niger Delta, Nigeria and their mixtures. This is aimed at characterizing, correlating and resolving the tricyclic terpanes that correspond to the proportion(s) of the two Niger Delta crude oils in their mixtures.

II. EXPERIMENTAL

SAMPLING

The Niger Delta region, situated in Southern Nigeria, is a prolific petroleum-producing Tertiary delta basin located between longitudes 5°- 8° E and latitudes 3° - 6° N (Tuttle et al., 1999). Two crude oils (one each) were obtained, with the assistance of field technicians, from oil flow stations located in Western and Central Niger Delta sub-regions, respectively. The crude oils were labelled appropriately as samples A-001 and F-100, respectively. Four mixtures of the two crude oils were made at different proportions of 20:80, 40:60, 60:40 and 80:20, and labelled appropriately as samples B-208, C-406, D-604 and E-802, respectively. All six oil samples were placed in pre-cleaned glass jars and stored in the refrigerator at a temperature of less 4 °C until analysis.

CRUDE OIL FRACTIONATION

Centrifuge tubes were labelled and 50 mg of each oil sample was weighed into each tube. Excess pentane was added into each tube with the oil sample and the mixture was allowed to stand for three hours to precipitate the asphaltenes. The mixture was then centrifuged for 30 minutes to coalesce the precipitated asphaltenes, the content decanted and concentrated under a gentle stream of nitrogen gas at 40°C. The pentane soluble fractions of each oil sample was transferred to the top a glass column (30 cm x 1 cm) stuffed with glass wool at the bottom and packed with activated silica gel. *n*-hexane was poured into the packed column to elute the saturates, which contains the tricyclic terpanes. The eluent was concentrated under a gentle stream of nitrogen gas at 40°C.

GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS) ANALYSES

The saturate fractions of the six oil samples were put in sample vials and packed on a tray fitted to 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). With the aid of a G4513A automatic liquid sampler, 1µL of the saturate fraction of each sample was injected into the GC 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^{-1} and held at this temperature for 30 min. Quantification was acquired by area integration of each identified compound peak, which was processed by Chemstation OPEN LAB CDS software.

III. RESULTS AND DISCUSSION

DISTRIBUTION OF TRICYCLIC TERPANES

GC-MS (m/z 191) analysis of the two Niger Delta crude oils (samples A-001 and F-100) and their mixtures at different proportions (samples B-208, C-406, D-604 and E-802) detected twenty-one (21) tricyclic terpanes that range from C_{19} to C_{29}, including C_{24} tetracyclic terpane. Total abundances of the tricyclic terpanes in the six oil samples are shown in Figure

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1 (insert). The total abundances of tricyclic terpanes in the oil samples increased in the order A-001 < E-802 < F-100 < B-208 < C-406 < D-604 (Fig. 1 insert). This show the total abundance of tricyclic terpanes in the oil samples did not mix correspondingly with the proportion of the two Niger Delta crude oils in their mixtures.

Plots of the abundances of tricyclic terpanes in the six oil samples generally followed similar distribution patterns (figure 1). From the plots, the abundances of individual tricyclic terpanes were different in the six oil samples, but followed similar profile as the total abundances (figure 1). This indicate that the abundances of the individual tricyclic terpanes did not mix correspondingly and so cannot directly be used to evaluate the proportion of the two Niger Delta crude oils in the mixtures.

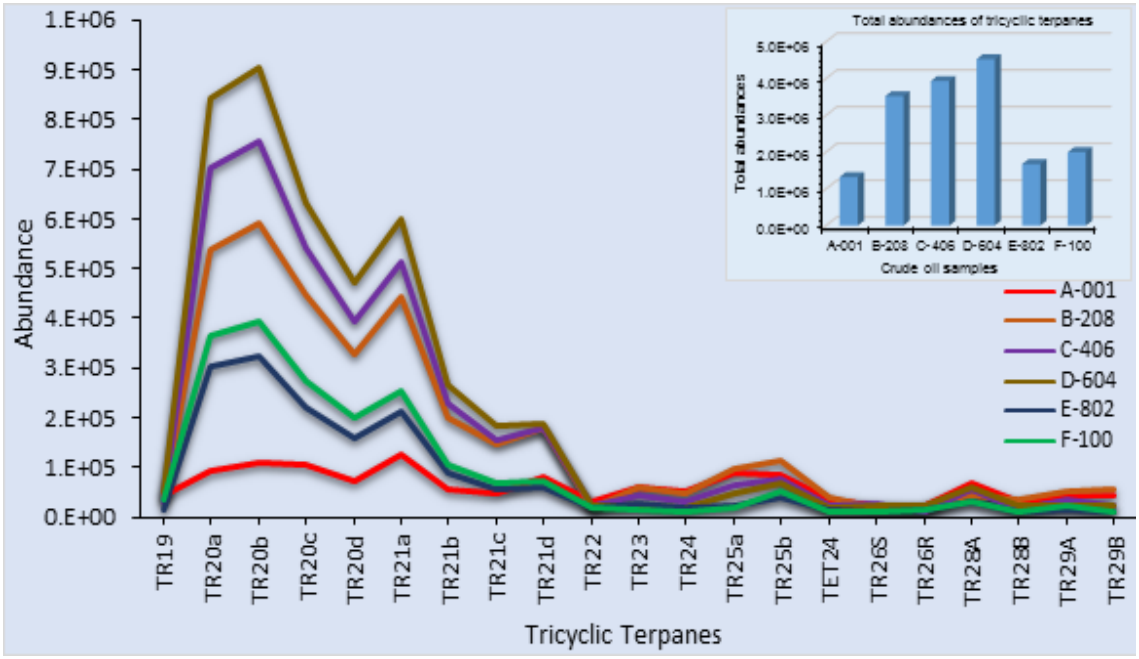

Figure 1. Distribution of C_{19} to C_{29} tricyclic terpanes, including C_{24} tetracyclic terpane, in the two Niger Delta crude oils (A-001 and F-100) and their mixtures (samples B-208, C-406, D-604 and E-802). *Insert*: Total abundances of tricyclic terpanes in the six oil samples. TR19: C_{19} tricyclic terpane, ... etc., TET24: C_{24} tetracyclic terpane.

The distribution of tricyclic terpanes detected by GC-MS (m/z 191) showed four peaks each for C_{20} (TR20a-d) and C_{21} (TR21a-d), a single peak each for C_{19}, C_{22} to C_{24}, and a pair of peaks for the C_{25} to C_{29} (figure 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 for C_{25} and higher homologues due to the presence of a chiral centre at C-22 (Ekweozor and Strausz, 1983; Wang et al., 2006). This indicate the two Niger Delta crude oil samples are characterized by an unusual distribution of the C_{20} and C_{21} tricyclic terpanes (Ajie and Onyema, 2022). Total abundances of C_{20} (TR20a-d) and C_{21} (TR21a-d) tricyclic terpanes constituted 52.25% of the total tricyclic terpane abundance in sample A-001, and constituted 81.58%, 88.23%, 90.35%, 84.70% and 86.72% in samples B-208, C-406, D-604, E-802 and F-100, respectively. Also, the total abundances of C_{22} to C_{29} tricyclic terpanes constituted 44.57% of total terpane abundance in sample A-001, and constituted 17.23%, 10.99%, 8.46%, 14.45% and 11.42% in samples B-208, C-406, D-604, E-802 and F-100, respectively. This distribution result show the total abundances of C_{20} and C_{21} tricyclic terpanes are more than TR22 to TR29 slightly in sample A-001 (1.17) and considerably in samples B-208, C-406, D-604, E-802 and F-100 (4.73 - 10.69) and indicate the distribution of tricyclic terpanes in the proportional mixtures are more similar to each other and sample F-100, and similar to sample A-001.

The similarities between the distributions of tricyclic terpanes in the oil samples were evaluated by Pearson correlation (r). Pearson correlation is a linear correlation tool commonly used in statistics to measure the extent to which two sets of variables are related. Results of Pearson's correlation of the abundance distributions of C_{19} to C_{29} tricyclic terpanes between the oil sample pairs are presented in table I.

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Table I. Pearson correlation (*r*) of the abundance distributions of C_{19} to C_{29} tricyclic terpanes between the oil samples

	A-001	B-208	C-406	D-604	E-802	F-100
A-001	1	0.8160	0.7805	0.7602	0.7684	0.7603
B-208	0.8160	1	0.9961	0.9931	0.9900	0.9900
C-406	0.7805	0.9961	1	0.9990	0.9970	0.9968
D-604	0.7602	0.9931	0.9990	1	0.9970	0.9981
E-802	0.7684	0.9900	0.9970	0.9970	1	0.9979
F-100	0.7603	0.9900	0.9968	0.9981	0.9979	1

Pearson correlation results usually have values between −1 and +1. The larger the number, the stronger the relationship between the variables and the smaller the number, the less of a relationship between the variables, while a value of zero (0) indicate that the two sets of variables are dissimilar. From table I, samples A-001 and F-100 show a strong positive correlation of 0.7603 indicating that the abundance distributions of the tricyclic terpanes in the two crude oils are 76.03% similar. Samples B-208, C-406, D-604 and E-802 show very strong positive correlations (0.9900 - 0.9990) with each other, strong positive correlations with sample A-001 (0.7602 - 0.8160) and very strong positive correlation with sample F-100 (0.9900 - 0.9981). The correlation results indicate the abundance distributions of tricyclic terpanes in the four proportional mixtures are significantly similar to each other (99.00% - 99.90%) and sample F-100 (99.00% - 99.81%), and similar to sample A-001 (76.02% - 81.60%). Hydrocarbons derived from distinct sources have different distribution profiles which are employed as geochemical fingerprints for crude oil correlation and/or differentiation (Peters et al., 2005). The relationships in the distribution profiles of the tricyclic terpanes indicate the two Niger Delta crude oils (samples A-001 and F-100) are derived from genetically related source and their geochemical characteristics were preserved in the four proportional mixtures (Onyema et al., 2018). The correlation results also indicate that the abundance distributions of the tricyclic terpanes are strongly similar to unambiguously differentiate the two Niger Delta crude oils and the four proportional mixtures.

MULTIVARIATE CORRELATION

GC-MS (m/z 191) analysis detected 21 tricyclic and tetracyclic terpanes in the six oil samples. In chemical fingerprinting crude oils with a large number of data, the use of multivariate statistical methods are beneficial (Peters et al., 2005). Hierarchical cluster analysis (HCA) is a multivariate statistical method that sorts out similarities in sets of variables and uses it to construct a hierarchy of clusters (Pavon et al., 2006). HCA was employed to test the normalized compositions of the 21 tricyclic and tetracyclic terpanes detected in the 6 oil samples for correlations. The compositions of phenanthrenes have been observed to correlate more than their abundances and better explain the pattern of mixing of two crude oils in their mixtures (Okoroh et al., 2018). The result of HCA, which shows the similarities (correlation) among the tricyclic and tetracyclic terpanes is displayed graphically as a dendrogram (figure 2).

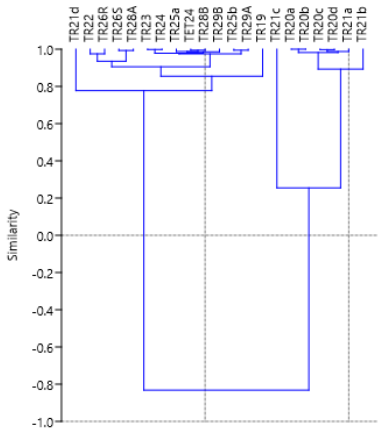

Figure 2. Hierarchical cluster analysis (HCA) dendrogram showing the groupings of C_{19} to C_{29} tricyclic and C_{24} tetracyclic terpanes according to similarities in the variation of their compositions in the crude oil samples

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HCA sorts out similarities in sets of variables and uses it to construct clusters, so that elements in the same cluster show similar variation to each other than those from different clusters. From the dendogram (fig. 2), HCA separated the individual tricyclic and tetracyclic terpanes into 2 main groups, according to similarities in the variation of their compositions in the six crude oil samples. The two main groups (-A and -B) show a similarity of -0.8331 on the HCA dendrogram indicating they strongly correlate negatively. This correlation suggest group-A and group-B tricyclic terpanes distinctly differed in the variations of their compositions in the six crude oil samples and their contribution from two different sources.

Group-A consist of 14 tricyclic terpanes, which include TR19, TR21d, TR22, TR23, TR24, TR25a, TR25b, TET24, TR26S, TR26R, TR28A, TR28B, TR29A and TR29B. Similarities among group-A tricyclic terpanes were ≥ 0.7674 on the HCA dendrogram indicating they strongly correlate positively. This correlation suggest similarities in the variation of the compositions of group-A tricyclic terpanes in the six crude oil samples and their contribution from a similar source. Group-B consist of 7 tricyclic terpanes, which include TR20a TR20b TR20c TR20d TR21a TR21b TR21c. Similarities of group-B tricyclic terpanes were ≥ 0.8471 on the HCA dendrogram, except for TR21c with similarity of 0.3218 with other elements of the group. This correlation result indicate the group-B tricyclic terpanes strongly correlate positively, except for TR21c which poorly correlates with other elements of the group. This correlation suggest similarities in the variation of the compositions of group-B tricyclic terpanes in the six crude oil samples and their contribution from a similar source.

COEFFICIENT OF DETERMINATION (R^2)

The variations in the compositions of group-A and group-B tricyclic terpanes were determined from plots of their individual normalized compositions against the oil samples (figures 3 and 4).

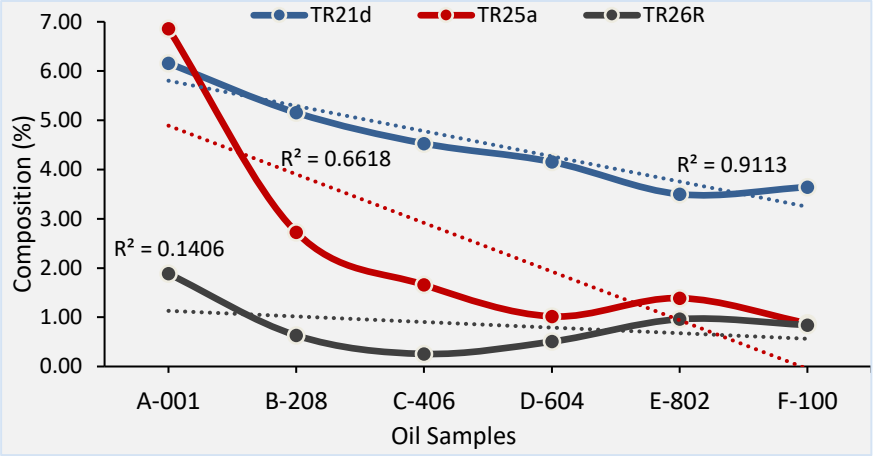

Figure 3: Plots of the compositions of TR21d, TR25a, and TR26R (group-A) showing their variation in the crude oil samples

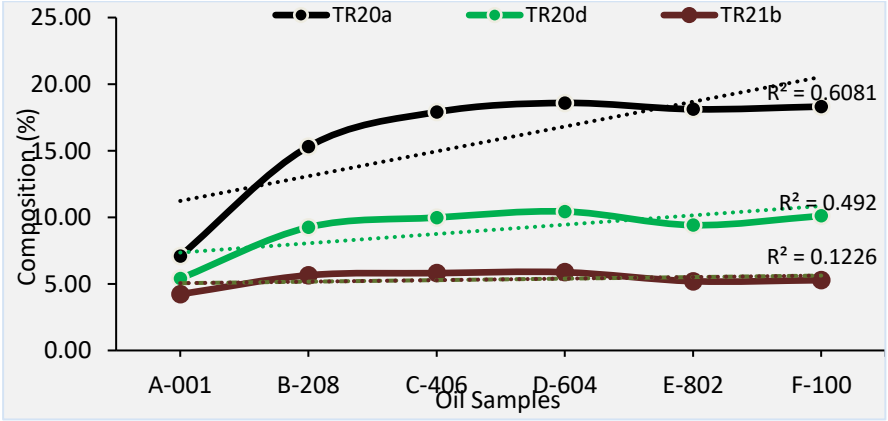

Figure 4: Plots of the compositions of TR20a, TR20d, and TR21b (group-B) showing their variation in the crude oil samples

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From the plots, the line of best fit drawn depicted the variation pattern of the compositions of tricyclic terpane in the six oil samples. Figure 3 shows the compositions of TR21d, TR25a, and TR26R (Group-A) decrease as the proportion of oil sample A-001 decrease, and oil sample F-100 increase, in the two Niger Delta crude oil samples and their mixtures, respectively. Figure 4 shows the compositions of TR20a, TR20d, and TR21b (Group-B) increase as the proportion of oil sample A-001 decrease, and oil sample F-100 increase, in the two Niger Delta crude oil samples and their mixtures, respectively.

The coefficient of determination (R^2) was also determined from the line of best fit. R^2 is a correlation coefficient for relationships (between 0 and 1) that measures of how correctly a variable can be estimated from a set of other variables. Values of R^2 for group-A tricyclic terpanes range from 0.1406 to 0.9113 and group-B range from 0.1226 to 0.6081 (table II).

Table II: Coefficient of determination (R^2) values for group-A and group-B tricyclic terpanes

Group-A		
Tricyclic terpane	**Code**	R^2
C_{19} tricyclic terpane	TR19	0.1826
C_{21} tricyclic terpane (d)	TR21d	0.9113
C_{22} tricyclic terpane	TR22	0.1813
C_{23} tricyclic terpane	TR23	0.5256
C_{24} tricyclic terpane	TR24	0.5223
C_{25} tricyclic terpane (a)	TR25a	0.6618
C_{25} tricyclic terpane (b)	TR25b	0.4377
C_{24} tetracyclic terpane	TET24	0.5686
C_{26} S tricyclic terpane (S)	TR26S	0.3518
C_{26} tricyclic terpane (R)	TR26R	0.1406
C_{28} tricyclic terpane (a)	TR28A	0.3253
C_{28} tricyclic terpane (b)	TR28B	0.5574
C_{29} tricyclic terpane (a)	TR29A	0.4899
C_{29} tricyclic terpane (b)	TR29B	0.6621
Group-B		
Tricyclic terpane	**Code**	R^2
C_{20} tricyclic terpane (a)	TR20a	0.6081
C_{20} tricyclic terpane (b)	TR20b	0.5964
C_{20} tricyclic terpane (c)	TR20c	0.5068
C_{20} tricyclic terpane (d)	TR20d	0.492
C_{21} tricyclic terpane (a)	TR21a	0.3725
C_{21} tricyclic terpane (b)	TR21b	0.1226
C_{21} tricyclic terpane (c)	TR21c	0.2614

The closer the R^2 value is to 1 the stronger the relationship between the variables, while a value of zero (0) indicate the variables are unrelated. From table 2, the R^2 values of Group-A tricyclic terpanes range from 0.1406 - 0.9113 and Group-B tricyclic terpanes range from 0.1226 - 0.6081. The R^2 results imply that the compositions of Group-A tricyclic terpanes show poor to very good relationships with the two Niger Delta crude oils and their mixtures and the compositions of Group-B tricyclic terpanes show poor to moderate relationships with the two Niger Delta crude oils and their mixtures. Consequently, the compositions of C_{21} tricyclic terpane (d), with the highest R^2 value, will be most suitable for use to estimate (91.13%) the proportion(s) of the two Niger Delta crude oils in their mixtures.

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IV. CONCLUSION

Total and individual abundances of the tricyclic terpanes in two Niger Delta crude oils (samples A-001 and F-100) and their proportional mixtures (samples B-208, C-406, D-604 and E-802) suggest the abundances did not mix correspondingly with the mixing proportion of the two Niger Delta crude oils. Pearson correlation suggested sample A-001 was genetically related F-100 (76.03%), while the four proportional oil mixtures were significantly similar to each other and sample F-100, and similar to sample A-001. The compositions of tricyclic terpanes in the six crude oil samples were separated into 2 main groups: tricyclic terpane compositions that decrease as the proportion of sample A-001 decrease (group-A) and increase as the proportion of sample F-100 increase (group-B). R^2 values from plots of individual tricyclic terpane compositions suggest the compositions of C_{21} tricyclic terpane(d) as the most suitable for use to estimate (91.13%) the proportion(s) of the two Niger Delta crude oils in their mixtures.

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