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Research Paper

C_{20} and C_{21} Tricyclic Terpanes in Niger Delta Crude Oils II: Geochemical Correlation and Allocation of their Binary mixtures

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ABSTRACT: *The C_{20} and C_{21} tricyclic terpanes were characterized in two Niger Delta crude oils (samples A-100:0 and F-0:100), denoted as end-members, and their binary mixtures of different proportions (samples B-80:20, C-60:40, D-40:60 and E-20:80). Total and individual abundances of the C_{20} and C_{21} tricyclic terpanes decreased in the order C-60:40 > D-40:60 > E-20:80 > A-100:0 > B-80:20 > F-0:100, indicating the tricyclic terpanes did not mix correspondingly. Plots and correlation of the abundances of C_{20} and C_{21} tricyclic terpanes indicate all the crude oil samples were significantly similar to permit meaningful geochemical differentiation. Hierarchical cluster analysis (HCA) grouped the C_{20} and C_{21} tricyclic terpanes into two distinct clusters according to similarities in the variation of their compositions in the crude oil samples. Cluster-1 consist of TR20c, TR21a, TR21c, TR21d, TR21e, TR21f and TR21g, which increased with increase in the proportion of sample F-0:100 and cluster-2 consist of TR20a, TR20b, TR20d, TR20e and TR21b, which increased with increase in the proportion of sample A-100:0. Plots of the most and least variant compositions of C_{20} and C_{21} tricyclic terpanes in each cluster, produced R^2 values which indicate TR20a/TR20d and TR21a/TR21g ratios show moderate and very strong predictability (66.29% and 98.28%) of the proportion of the two end-member Niger Delta crude oils in their binary mixtures, respectively*

KEYWORDS: *Correlation, Allocation, Crude Oil Mixture, Niger Delta, Tricyclic Terpane, Ratio*

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I. INTRODUCTION

Crude oil is a naturally occurring liquid mixture of hydrocarbons derived from the chemical and geological transformation of organic matter in the depositional environment under the influence of heat and pressure over geological time scale [1]. These conditions transmit compositionally distinct geochemical hydrocarbons to crude oils, which varies from one field to another. Consequently, within the compositionally distinct geochemical hydrocarbons are embodied essential information on the organic matter source (marine or terrestrial), depositional environment (oxic or anoxic), lithology of the source rock, thermal maturation and/or biodegradation level [2] and [3]. Some of the compositionally distinct geochemical hydrocarbons are C_7 light hydrocarbons, aliphatic hydrocarbons (C_8 to C_{40} *n*-alkanes, pristane and phytane), steranes, terpanes, alkylated polycyclic aromatic hydrocarbons and aromatic steranes [4], [5], [6] and [7]. They have been utilized for correlation and/or differentiation between oil-oil and oil-source rocks, unravel oil migration pathway, assessment of reservoir continuity/compartmentalization and determination of proportions of commingled crude oil production [8], [9], [10] and [11].

Commingling of crude oil production is the mixing of crude oils from two or more different producing wells, zones or reservoirs to make a single stream through a shared production or transportation facility. The proportion of each crude oil to the commingled oil received at the shared facility, are usually allocated to detect change in injection rate, detect poor production from one zone, supplement/detect variation in flowmeter measurements or aid taxation of production from different zones [12]. Geochemical hydrocarbons have been reviewed for evaluating crude oil mixtures and providing information on the allocation of proportion of all the contributing (end-member) crude oils to monitor commingled production [13], [14], [15] and [16]. Kaufman et al. (1987) used three distinct peak ratios, measured from precise laboratory mixes of two end-member oils, to

construct a calibration curve and identify the composition of end-member oils in an unknown mix [17]. Oil fingerprinting technology was used by Hwang et al. (2000) to correctly back allocate commingled pipeline crude oil production from six contributing fields in an offshore South East Asia basin, while plots of some ratios of aliphatic hydrocarbons have shown strong correlations (R^2 = 99.4%, 99.3% and 99.2%) that could be useful for estimating the compositions of two Niger Delta crude oils in their mixtures [18] and [19]. The end-members and commingled oils are usually analyzed by whole oil high-resolution gas chromatography (GC) which separates the various hydrocarbons present in the crude oils and a flame ionization detector (FID) which detects the hydrocarbons as they elute from the GC column and shows the distribution and abundance (fingerprint).

Tricyclic terpanes are a class of hydrocarbons with three fused 6-carbon rings and an alkyl side chain. The C_{19} to C_{29} tricyclic terpanes are commonly observed in crude oils and source rock extracts, with the higher members (up to C_{54}) obscured by the abundance of hopanes in the m/z 191 mass chromatogram [20] and [21]. They have been used to evaluate source-rock characteristics, thermal maturity, biodegradation and correlation of crude oils and source-rock extracts [22], [23] and [24]. This research appraises the C_{20} and C_{21} tricyclic terpanes in two Niger Delta crude oils and their mixtures with a view to characterize, correlate and ascertain their applicability to providing another geochemical means for allocation of the proportion of two crude oils to monitor commingled production

II. MATERIAL AND METHODS

2.1 Sample collection

Two crude oil samples were obtained from oil producing onshore fields in Rivers and Delta states, both located in Niger Delta region of southern Nigeria between longitudes 5°- 8° E and latitudes 3° - 6° N [25]. The two crude oils represent the end-member oils and labelled appropriately as samples A-100:0 and F-0:100, respectively. Binary mixtures of the two end-member oils were made at different proportions of 80:20, 60:40, 40:60 and 20:80, and labelled appropriately as samples B-80:20, C-60:40, D-40:60 and E-20:80, respectively. All six samples were placed in pre-cleaned glass jars and stored until analyses.

2.2 Crude oil fractionation

50 mg of each oil sample was weighed into a labelled centrifuge tube and excess pentane added. The mixture was allowed to stand for three hours and then centrifuged at 1,500 rpm for 30 minutes to coalesce the precipitated asphaltenes. The oil sample and excess pentane mixture was decanted, concentrated under a gentle stream of nitrogen gas at 40°C and transferred onto the top a glass chromatographic 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 terpanes. The eluent was concentrated under a gentle stream of nitrogen gas at 40°C

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

The saturate fractions of all six oil samples were put in sample vials and packed on a tray for gas chromatography-mass spectrometry (GC-MS) analyses. With the aid of a G4513A automatic liquid sampler (ALS), 1 microliter (µL) of the saturate fraction of each sample was inject into the HP-5 silica capillary column (50 m x 320 µm i.d and 0.25µm film thickness) of an Agilent 7890A gas chromatograph (GC) system equipped an Agilent 5975 mass selective detector (MSD) which was operated in splitless mode. The analyses were monitored at the mass to charge (m/z) 191, the characteristic fragment ion of terpanes (Wang et al., 2006). Abundance of each peak was quantified by area integration which was processed by Chemstation OPEN LAB CDS software.

2.4. Statistical analyses

Pearson correlation (*r*) and hierarchical cluster analysis (HCA) were performed to assess the statistically relationships (correlations) between samples and similarities among tricyclic terpanes using PAST software version 4.11 [26].

III. RESULTS AND DISCUSSION

3.1. Geochemical characterization of oil samples

The GC-MS analyses of the two end-member Niger Delta crude oils (samples A-100:0 and F-0:100) and their binary mixtures at different proportions (samples B-80:20, C-60:40, D-40:60 and E-20:80) showed peaks at m/z 191, the characteristic fragment ion of terpanes. 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 (isomers) but different structures and isomerism [27]. Comparing the partial m/z 191 mass chromatograms of all the oil samples

to that of related literatures, twelve (12) peaks, with retention time between 21 and 25 minutes, were designated as C_{20} and C_{21} tricyclic terpanes (fig. 1).

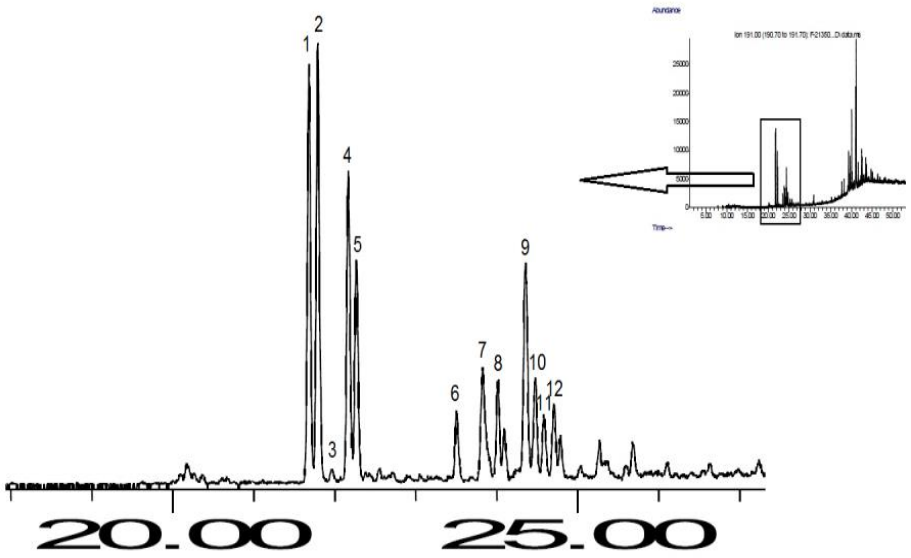


Figure 1: Partial m/z 191 mass chromatogram of sample A-100:0 one of the end-member Niger Delta crude oil, showing the 12 peaks of C_{20} and C_{21} tricyclic terpanes

The 12 peaks of C_{20} and C_{21} tricyclic terpanes appeared in the partial m/z 191 mass chromatograms of all the crude oil samples, A-100:0, B-80:20, C-60:40, D-40:60, E-20:80 and F-0:100. From fig. 1, peaks 1-5 were designated C_{20} tricyclic terpane isomers; TR20a - TR20e, and peaks 6-12 designated C_{21} tricyclic terpane isomers; TR21a - TR21g, respectively. Figure 2 shows the abundances of the C_{20} and C_{21} tricyclic terpane isomers in the oil samples.

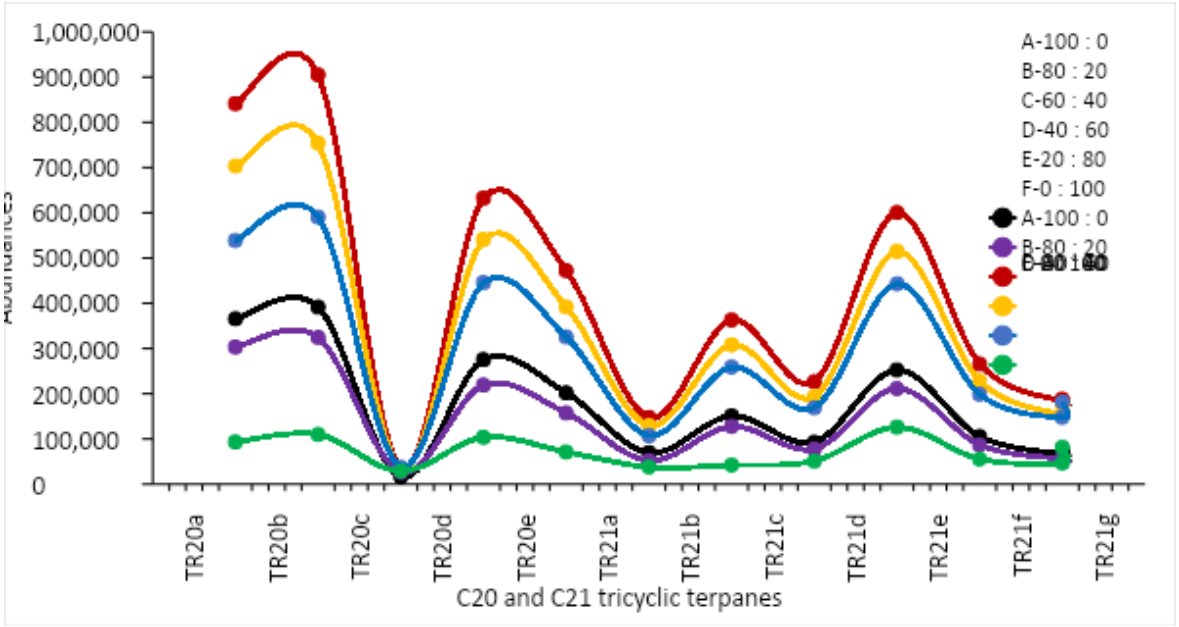


Figure 2: Plots of the abundances of C_{20} and C_{21} tricyclic terpanes in the two end-member crude oils and their four binary mixtures.

Total abundance of the tricyclic terpanes in the crude oil samples decreased in the order C-60:40 > D-40:60 > E-20:80 > A-100:0 > B-80:20 > F-0:100. From fig. 2, it was observed that the abundances of individual C_{20} and C_{21} tricyclic terpanes generally followed similar trend as the total abundance. It was also observed that the abundances followed similar distribution patterns in the oil samples. This indicate the individual and total abundances of the C_{20} and C_{21} tricyclic terpanes did not mix linearly and therefore cannot directly be used to allocate the proportion of the two end-member Niger Delta crude oils in their binary mixtures. The similarities in the distribution patterns followed suggest that the two end-member Niger Delta crude oils (A-100:0 and F-0:100) are not distinct, but related (derived from a similar source) and their geochemical characteristics were preserved in their binary mixtures (B-80:20, C-60:40, D-40:60 and E-20:80).

3.2. Geochemical correlations

Crude oil correlation studies require geochemical comparisons that reveal similarities and/or differentiate oils from one another [28]. Correlations between the two end-member oils and the four binary mixtures were evaluated by Pearson correlation (*r*). Pearson's correlation is a linear correlation tool commonly used in statistics to measure the extent to which two sets of variables are related. Table 1 shows the Pearson correlation results of the abundances of C_{20} and C_{21} tricyclic terpanes between the crude oil samples.

Table 1. Pearson correlation (*r*) of the abundances of C_{20} and C_{21} tricyclic terpanes in crude oil samples.

	A-100:0	**B-80:20**	**C-60:40**	**D-40:60**	**E-20:80**	**F-0:100**
A-100:0	1.0000					
B-80:20	0.9985	1.0000				
C-60:40	0.9991	0.9977	1.0000			
D-40:60	0.9985	0.9970	0.9996	1.0000		
E-20:80	0.9916	0.9892	0.9950	0.9968	1.0000	
F-0:100	0.8123	0.8070	0.8215	0.8337	0.8682	1.0000

Results of Pearson's correlation usually have coefficients between □1 and +1 indicating a perfect negative and positive relationship (correlation), respectively, while a value of zero **(**0) indicate that the two sets of variables are independent and unrelated. The larger the number, the stronger the relationship between the variables and the smaller the number, the less of a relationship there is between the variables. From table 1, correlation between the abundances of the C_{20} and C_{21} tricyclic terpanes in the two end-member oils samples, A-100:0 and F-0:100, show a strong positive relationship of 0.8123. This indicate the two end-member oils are genetically similar (81.23%). Correlation results of the binary mixtures (table 1) show samples B-80:20, C-60:40, D-40:60 and E-20:80 have a very strong positive relationship with each other (98.92% - 99.96%) and with sample A-100:0 (99.16% - 99.91%) and a strong positive relationship with sample F-0:100 (80.70% - 86.82%). The correlation results indicate the abundance distributions of C_{20} and C_{21} tricyclic terpanes are strongly similar to permit meaningful differentiation of the two end-member Niger Delta crude oils and the four binary mixtures.

Okoroh et al. (2018) observed that the compositions of C_0 - C_4 phenanthrenes better explained the mixing pattern of two end-member Niger Delta crude oils than their abundance [29]. Normalized compositions of individual C_{20} and C_{21} tricyclic terpanes in the crude oil samples were determined and evaluated with a multivariate correlation tool, hierarchical cluster analysis (HCA). HCA sorted out the similarities in the varying compositions of individual C_{20} and C_{21} tricyclic terpanes and used it to construct a hierarchy of clusters, so that components in the same cluster show similar variation (in compositions) to each other than those from different clusters [30]. Figure 3 shows the result of HCA displayed graphically as a dendrogram.

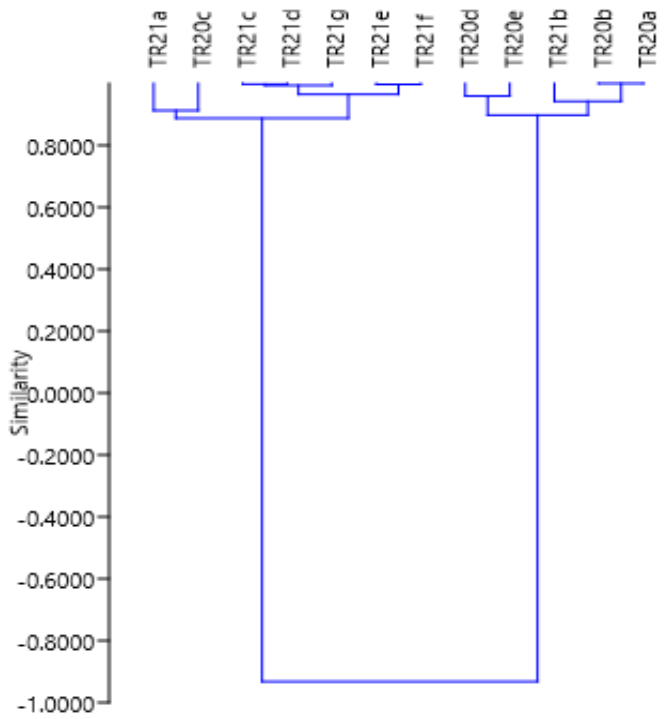
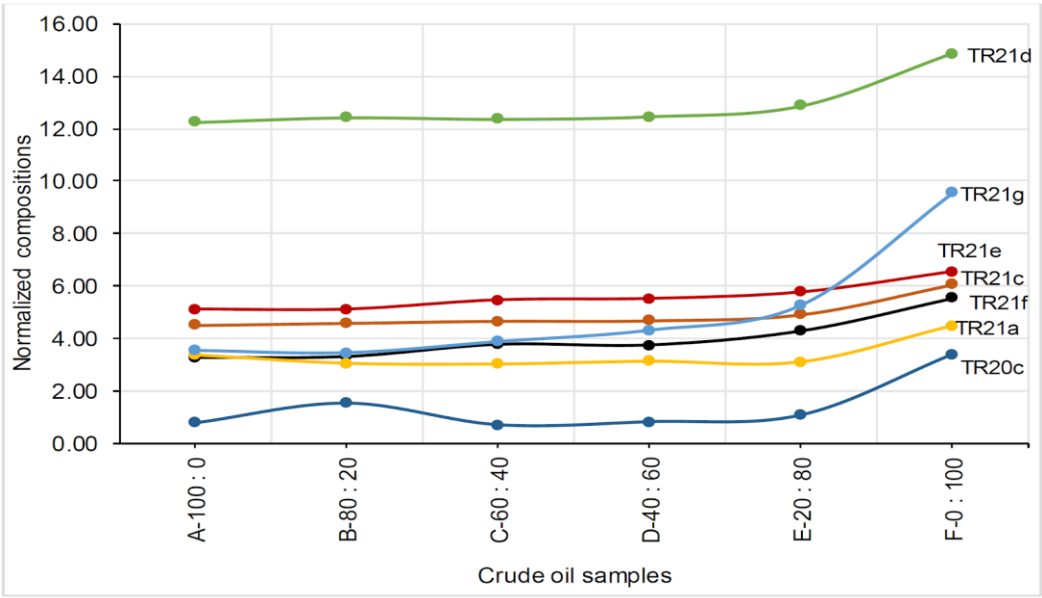


Figure 3: Hierarchical cluster analysis (HCA) dendrogram showing the C_{20} and C_{21} tricyclic terpanes grouped according to similarities in their varying compositions.

HCA grouped the C_{20} and C_{21} tricyclic terpanes, according to similarities in their varying compositions in the crude oil samples, into two main clusters (fig. 3). Cluster-1 consist of TR20c, TR21a, TR21c, TR21d, TR21e, TR21f and TR21g. They are mostly C_{21} tricyclic terpane isomers (6 of 7). Similarities of cluster-1 tricyclic terpanes ($\geq$ 0.9124) indicate that their compositions very strongly (positive) correlated and suggest they are all from the same crude oil. Cluster-2 consist of TR20a, TR20b, TR20d, TR20e and TR21b. They are mostly C_{20} tricyclic terpane isomers (4 of 5). Similarities of cluster-2 tricyclic terpanes ($\geq$ 0.9424) indicate that their compositions very strongly (positive) correlated and suggest they are all from the same crude oil. From the HCA dendrogram, the 2 main clusters showed a similarity of □0.9437. This indicate the compositions of cluster-1 and cluster-2 C_{20} and C_{21} tricyclic terpanes negatively (strong) correlated, distinctly differ and suggest they are from different crude oils

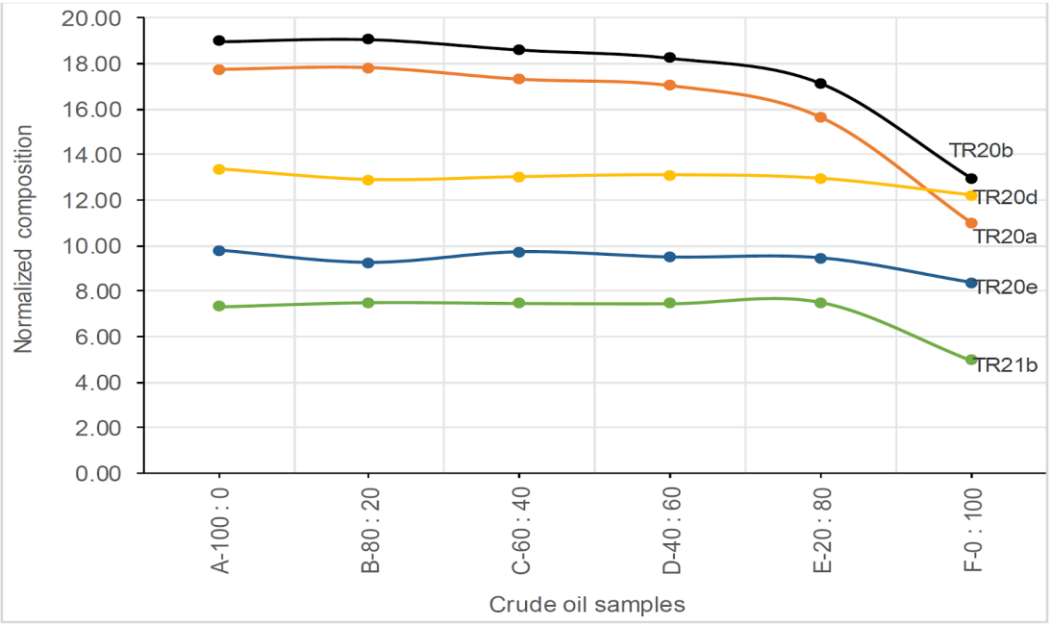
3.3. Geochemical plots

Plots of the normalized compositions of cluster-1 and cluster-2 C_{20} and C_{21} tricyclic terpanes in the oil samples are shown in figures 4 and 5 respectively.



Peak	Code	Equation of graph	Peak	Code	Equation of graph
3	TR20c	y = 0.3402x + 0.1941	10	TR21e	y = 0.2636x + 4.669
6	TR21a	y = 0.165x + 2.7853	11	TR21f	y = 0.4114x + 2.5432
8	TR21c	y = 0.2483x + 4.0322	12	TR21g	y = 1.0307x + 1.3893
9	TR21d	y = 0.4138x + 11.42			

Figure 4: Plots of the normalized compositions of TR20c, TR21a, TR21c, TR21d, TR21e, TR21f and TR21g (cluster-1) against the crude oil samples.



Peak	Code	Equation of plot	Peak	Code	Equation of graph
1	TR20a	y = -1.1562x + 20.14	5	TR20e	y = -0.1897x + 10.015
2	TR20b	y = -1.0367x + 21.138	7	TR21b	y = -0.3345x + 8.2073
4	TR20d	y = -0.156x + 13.466			

Figure 5: Plots of the normalized compositions of TR20a, TR20b, TR20d, TR20e and TR21b (cluster-2) against the crude oil samples.

Figs. 4 and 5 show the variation patterns in the normalized compositions of cluster-1 and cluster-2 C_{20} and C_{21} tricyclic terpanes in the crude oil samples. From the linear equation of each plot (y=mx+c), the slope (m) was

determined and used to evaluate the variation patterns in the normalized compositions of the C_{20} and C_{21} tricyclic terpanes in the oil samples. The slopes ranged from 0.165 to 1.0307 for cluster-1 (Fig. 4) and -0.156 to -1.1562 for cluster-2 (Fig. 5). The positive correlations (slopes) of cluster-1 indicate the compositions of TR20c, TR21a, TR21c, TR21d, TR21e, TR21f and TR21g increased with increase in the proportion of oil sample F-0:100 and the negative correlations (slopes) of cluster-2 indicate the compositions of TR20a, TR20b, TR20d, TR20e and TR21b decreased with increase in the proportion of oil sample F-0:100 vis-à-vis increased with increase in the proportion of oil sample A-100:0.

In the development of parameters for distinguishing geochemical variations in oils, Halpern (1995) used ratios of hydrocarbons most variant and least variant. C_{20} and C_{21} tricyclic terpane isomers with compositions most variant and least variant in the crude oil samples are TR21g (1.0307) and TR21a (0.165) for cluster 1 (fig. 4) and TR20a (-1.1562) and TR20d (-0.156) for cluster 2, respectively (fig. 5) [31]. Ratios of these tricyclic terpanes were plotted against the oil samples (fig. 6).

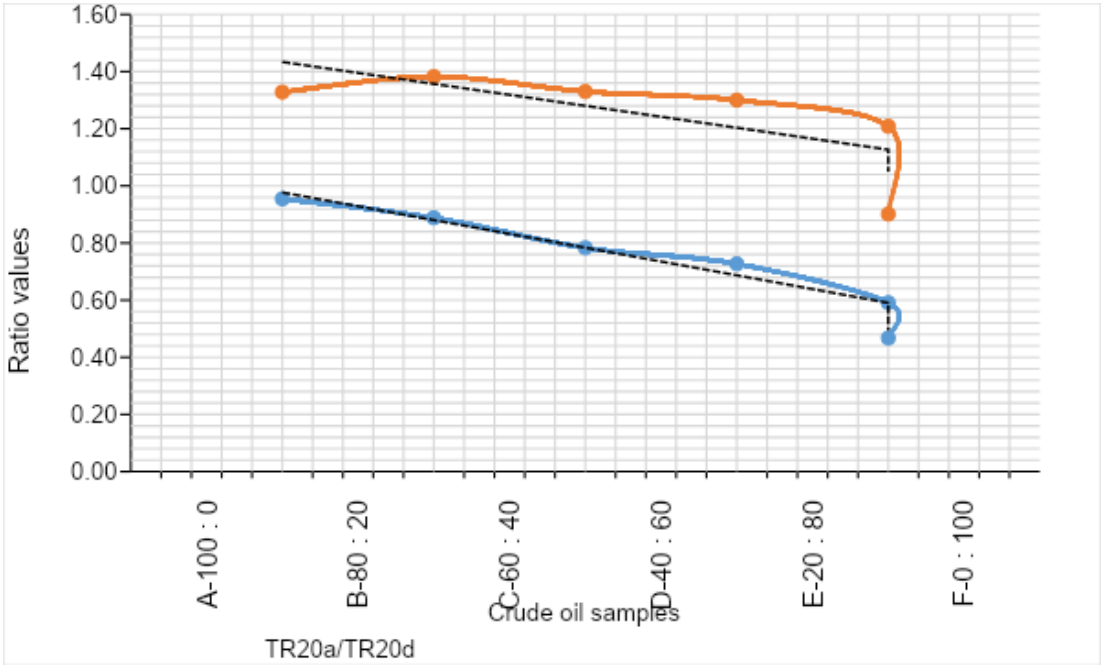


Figure 6: Plots of TR21a /TR21g (cluster 1) and TR20a/ TR20d (cluster 2) ratios against the two end-member oils and the four binary mixtures.

Plots of TR20a/TR20d and TR21a/TR21g ratios against the oil samples show the coefficient of determination (R^2) values of 0.6629 and 0.9828, respectively (fig. 6). Coefficient of determination (R^2) is a statistical measure (between 0 and 1) of how well a variable can be predicted from a set of other variables using the goodness of fit of a model. It is used mainly for the testing of models or prediction of data. The R^2 values determined from the goodness of fit show moderate and very strong correlations between TR20a/TR20d and TR21a/TR21g ratios and the oil samples, respectively. This indicate the geochemical variation associated with the proportion of each end-member crude oil in the samples moderately corresponds with TR20a/TR20d ratio and significantly corresponds with TR21a/TR21g ratio. Also, the R^2 values of TR20a/TR20d and TR21a/TR21g ratios showed moderate and very strong predictability and account for 66.29% and 98.28% of the proportion of the two end-member crude oils in the oil samples, respectively. This indicate TR21a/TR21g ratio will permit meaningful geochemical differentiation of the oil samples and better allocate the proportion of the two end-member Niger Delta crude oils to their binary mixtures.

IV. CONCLUSION

12 peaks, from the partial m/z 191 mass chromatograms of the oil samples, were labelled C_{20} (TR20a - TR20e) and C_{21} (TR21a - TR21g) tricyclic terpanes, respectively. Distributions and correlations of the abundances of C_{20} and C_{21} tricyclic terpanes indicate that all the oil samples were geochemically similar. Hierarchical cluster analysis (HCA) grouped the compositions of the C_{20} and C_{21} tricyclic terpane isomers in the oil samples into two (2). Cluster-1 consist of TR20c, TR21a, TR21c, TR21d, TR21e, TR21f and TR21g, which increased with increase

in the proportion of oil sample F-0:100 and cluster-2 consist of TR20a, TR20b, TR20d, TR20e and TR21b, which increased with increase in the proportion of oil sample A-100:0. Plots of the most and least variant isomers in each cluster, TR20a/TR20d and TR21a/TR21g, gave R^2 values which indicate that the ratios could account for (66.29% and 98.28%) and show moderate and very strong predictability of the proportion of the two end-member Niger Delta crude oils in their binary mixtures, respectively

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