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**Original Research Article**

# Uncommon Distribution of $C_{20}$ and $C_{21}$ Tricyclic Terpanes in Niger Delta Crude Oils

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## Abstract

$C_{20}$ and $C_{21}$ tricyclic terpanes were investigated in crude oils from Niger Delta, Nigeria. From comparison of the mass chromatograms (m/z 191) of two crude oil samples (CEN-21 and WST-69) with related literatures on tricyclic terpanes which eluted from the gas chromatography (GC) within certain retention time, 12 peaks were selected. Peaks 1 - 5 were selected as $C_{20}$ tricyclic terpane isomers (TR20a-e) and peaks 6 - 12 selected as $C_{21}$ tricyclic terpanes (TR21a-g). This distribution is usually as crude oils show a single peak each and indicate the distribution of $C_{20}$ and $C_{21}$ tricyclic terpanes in the Niger Delta crude oils is uncommon. Total abundances showed the $C_{20}$ and the $C_{21}$ tricyclic terpanes were more in CEN-21 than WST-69 with ratios of 3.07 and 1.84, respectively, with TR20a, TR20b, TR20d and TR21d being the most abundant isomers in both oil samples. These abundances indicate CEN-21 was thermally more mature than WST-69 and that the $C_{20}$ tricyclic terpanes were generated more than the $C_{21}$ tricyclic terpanes with increasing thermal maturity of the crude oils. Significant similarities observed in the normalized composition profiles and 66 derived ratios suggest the Niger Delta crude oil samples were genetically related and were predominantly derived from terrigenous Tertiary deltaic petroleum systems. Some differences observed in the composition profile and derived ratios indicate minor input from a different source, depositional environment and/or maturity level and are suggestive as indicators for evaluation, correlation and/or discrimination of the Niger Delta crude oils.

**Keywords:** Tricyclic terpanes, distribution, Niger Delta, GC-MS, abundance, profile, correlation, ratio.



## INTRODUCTION

Hydrocarbon compounds in crude oils with three fused 6-carbon ring and an alkyl side chain are referred to as tricyclic terpanes. They are derived from the chemical and geological transformation of organic matter buried during sedimentary processes (Tissot and Welte, 1984). The most common tricyclic terpanes are the Cheilanthanes (13-methyl, 14-alkylpodocarpanes) which are derived from cheilanthatriol, a natural product of the plant Cheilanthes farinosa (Khan *et al.*, 1971). Bacteria, tasmanite algae, and thermal breakdown of triterpanes in kerogen from which they are cogenerated with related monoaromatic and triaromatic tricyclic hydrocarbons, are also other possible sources of tricyclic terpanes (Aquino Neto *et al.*, 1983; Farrimond *et al.*, 1999; Greenwood *et al.*, 2000; Revill *et al.*, 1994).

Tricyclic terpanes are found in the saturate fraction of crude oils and source-rock extracts. They are usually analysed by gas chromatography-mass spectrometry (GC-MS) and detected using the mass to charge (m/z) 191 fragmentation. $C_{19}$ to $C_{29}$ tricyclic terpanes are usually observed on the m/z 191 mass chromatogram with the higher members of the homologous series, at least up to $C_{54}$, generally obscured by the abundance of hopanes (de Grande *et al.*, 1993; Moldowan *et al.*, 1983). The tricyclic terpanes are thermally more stable than many other terpanes and have been successfully employed for correlation of crude oils and source-rock extracts, predict source-rock characteristics, and evaluate thermal maturity (Peters and Moldowan, 1993; Seifert and Moldowan, 1981; Seifert *et al.*, 1980; Zumberge, 1987).

Crude oils from the Niger Delta region of southern Nigeria have been characterized and correlated using bulk properties, light hydrocarbons, aliphatic hydrocarbons, triterpanes, alkylated polycyclic aromatic hydrocarbons (Alkyl- PAHs) and aromatic steranes (Ekweozor *et al.*, 1979; Eneogwe, 2004; Okoroh *et al.*, 2020; Onyema and Osuji, 2015; Onyema *et al.*, 2018; Sonibare *et al.*, 2008). This research investigates the distribution and characterization of $C_{20}$ and $C_{21}$ tricyclic terpanes in crude oils from Niger Delta, Nigeria.

## EXPERIMENTAL

### *Sample Collection*

Two crude oil samples were obtained from onshore oil producing fields in the Niger Delta region of southern Nigeria, between longitudes 5° and 8° E and latitudes 3° and 6° N. The two crude oils were obtained with the assistance of field technicians from Rivers and Delta States and labelled as CEN-21 and WST-69, respectively.

### *Crude Oil Fractionation*

50 mg of each crude oil sample was weighed into a labelled centrifuge tube and excess pentane added to precipitate the asphaltenes. The pentane soluble fraction was decanted, concentrated with nitrogen gas at 40 $^{o}$C, and placed 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 $^{o}$C.

### *Gas Chromatography-Mass Spectrometry (GC-MS) Analysis*

With the aid of a G4513A automatic liquid sampler, 1 µL of the saturate fraction was injected into a HP-5 silica capillary column (50 m x 320 µm i.d and 0.25µm film thickness) of an Agilent 7890A gas chromatograph (GC) equipped with an Agilent 5975 mass selective detector (MSD) using a splitless mode. The analyses of the saturate fractions were monitored at the mass to charge (m/z) 191 fragmentation ion. Peaks were identified by comparing their mass spectra to related literature and quantification of each peak acquired by area integration which was processed by Chemstation OPEN LAB CDS software.

## RESULTS AND DISCUSSION

### *Identification and Distribution of $C_{20}$ and $C_{21}$ Tricyclic Terpanes*

GC-MS analyses of the crude oil samples at m/z 191 showed peaks (inset figs 1 and 2), which indicate the presence of terpanes in Niger Delta crude oils. From comparison of the GC mass chromatograms of both oil samples with that of related literatures, twelve (12) well-resolved peaks were unambiguously selected (Peters, 2000; Wang *et al.*, 2006; Younes, 2002). The 12 selected peaks are shown in (figs 1 and 2).

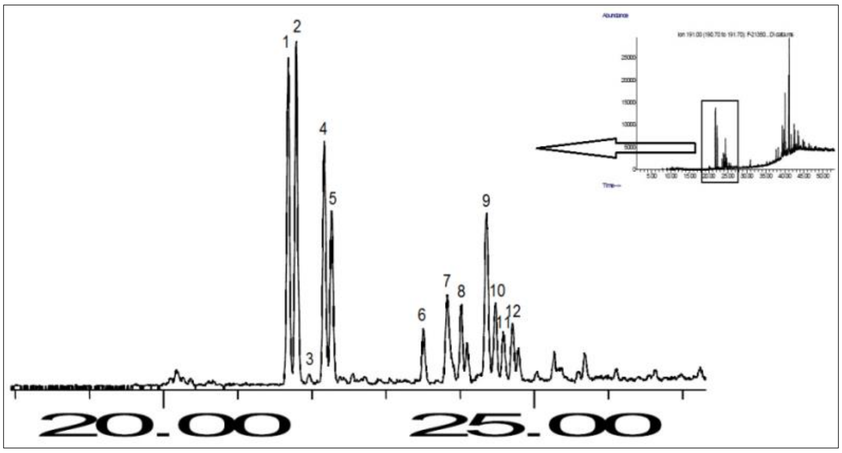


**Figure 1: Mass chromatogram (m/z 191) of oil sample CEN-21 showing the 12 selected peaks**

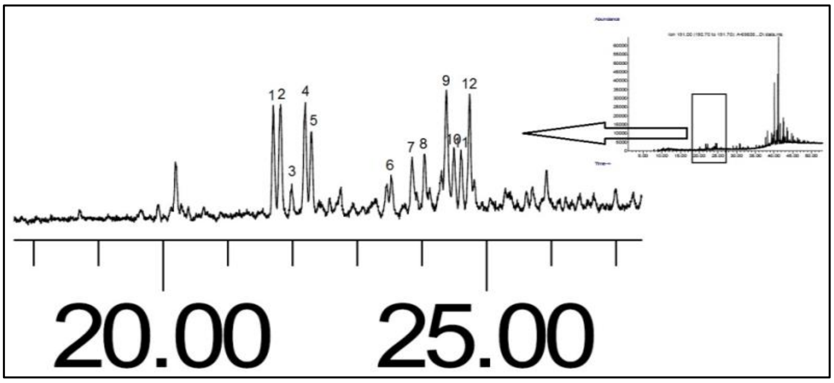


**Figure 2: Mass chromatogram (m/z 191) of oil sample WST-69 showing the 12 selected peaks**

From the mass chromatograms, the 12 selected peaks eluted from the GC between 21 and 25 minutes. Peaks 1 - 5 were closely clustered and separate from peaks 6 - 12, which were loosely clustered (figs. 1 and 2). The mass chromatogram of one ion (m/z) at a given GC retention time is often diagnostic of a class of compounds with similar structures, but different carbon numbers and isomerism (Wang *et al.*, 2006). This suggests peaks 1 - 5 as $C_{20}$ tricyclic terpane isomers and peaks 6 - 12 are $C_{21}$ tricyclic terpane isomers. Mass chromatograms at m/z 191 usually show a single peak each for $C_{19}$ to $C_{24}$ tricyclic terpanes (Peters, 2000; Wang *et al.*, 2006; Younes, 2002) indicating the distribution of $C_{20}$ and $C_{21}$ tricyclic terpanes in the Niger Delta crude oils is uncommon.

$C_{20}$ tricyclic terpane peaks 1, 2, 4 and 5 (TR20a, TR20b, TR20d and TR20e, respectively; see peak labels in table 1) were observed to be prominent in CEN-21 and reduced in WST-69 (figs. 1 and 2). In both mass chromatograms, TR20a and TR20b as well as TR20d and TR20e were almost equal in heights. Also, TR21b and TR21c as well as TR21e and TR21f (see peak labels in table 1) were almost equal in heights. $C_{20}$ and $C_{21}$ tricyclic terpanes discovered in crude oil and source rock samples include 13α(H),14α(H) and 13β(H),14α(H) isomers, which are most common, and ββ and αβ isomers (Chicarelli *et al*, 1988). These isomers often occur in approximately equal abundance (Ekweozor and Strausz, 1983). This suggest the pairs of TR20a/TR20b and TR20d/TR20e as well as TR21b/TR21c and TR21e/TR21f are $C_{20}$ and $C_{21}$ tricyclic terpane isomers with similar structures, but different isomerism and may be derived from a similar source/depositional environment.

**Table 1: $C_{20}$ and $C_{21}$ tricyclic terpane peak labels**

| Peak No. | Tricyclic Terpanes (TR) | Code |
|---|---|---|
| 1 | $C_{20}$ tricyclic terpane (a) | TR20a |
| 2 | $C_{20}$ tricyclic terpane (b) | TR20b |
| 3 | $C_{20}$ tricyclic terpane (c) | TR20c |
| 4 | $C_{20}$ tricyclic terpane (d) | TR20d |
| 5 | $C_{20}$ tricyclic terpane (e) | TR20e |
| 6 | $C_{21}$ tricyclic terpane (a) | TR21a |
| 7 | $C_{21}$ tricyclic terpane (b) | TR21b |
| 8 | $C_{21}$ tricyclic terpane (c) | TR21c |
| 9 | $C_{21}$ tricyclic terpane (d) | TR21d |
| 10 | $C_{21}$ tricyclic terpane (e) | TR21e |
| 11 | $C_{21}$ tricyclic terpane (f) | TR21f |
| 12 | $C_{21}$ tricyclic terpane (g) | TR21g |

Figures 1 and 2 showed TR20c was diminished in height compared to TR20a, TR20b, TR20d and TR20e (see peak labels in table 1) with which it is clustered. This suggests TR20c is a $C_{20}$ tricyclic terpane isomer with different structure and isomerism and may be derived from a different source/depositional environment. TR21d and TR21g have different heights in CEN-21, but almost equal heights in WST-69. This suggests TR21d and TR21g are $C_{21}$ tricyclic terpane isomers possibly suggesting different maturity levels.

### *Profiles of $C_{20}$ and $C_{21}$ Tricyclic Terpanes*

Abundances of the $C_{20}$ and $C_{21}$ tricyclic terpanes were calculated by area integration of each selected peak. Figure 3 shows the abundance profile of $C_{20}$ and $C_{21}$ tricyclic terpanes in the Niger Delta crude oil samples.

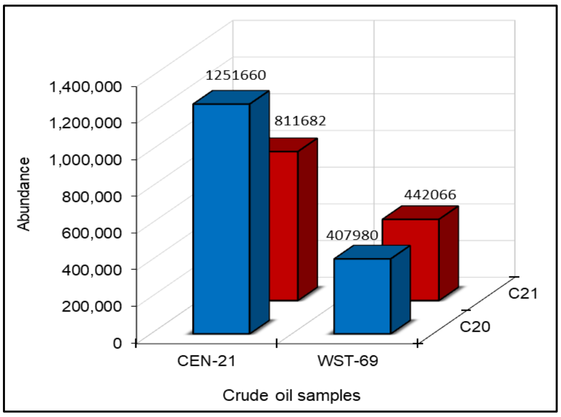


**Figure 3: Profile of total abundances of the $C_{20}$ and $C_{21}$ tricyclic terpanes in Niger Delta crude oil samples**

 

Total abundance of the $C_{20}$ and $C_{21}$ tricyclic terpanes in the crude oil samples were very high with the abundance in CEN-21 significantly higher (2.43 times) than in WST-69 (fig. 3). During organic matter transformation to crude oil, high molecular weight hydrocarbons such as sesterterpanes and triterpanes in kerogen, are thermally degraded to low molecular weight hydrocarbons like the tricyclic terpanes, which gradually become abundant (Aquino Neto *et al.*, 1983; Farrimond *et al.,* 1999; Tissot and Welte, 1984). Consequently, tricyclic terpanes are always abundant in high maturity crude oils regardless of the organic matter source. The total abundances of the $C_{20}$ and $C_{21}$ tricyclic terpanes in the Niger Delta crude oil samples are significantly high and also indicate CEN-21 is thermally more mature than WST- 69. From figure 3, the total abundance of $C_{20}$ tricyclic terpanes was 1.54 times more than $C_{21}$ tricyclic terpanes in CEN- 21, but slightly lower (0.92 times) in WST-69. Also, the total abundances of $C_{20}$ and $C_{21}$ tricyclic terpanes were more in CEN-21 than WST-69 with ratios of 3.07 and 1.84, respectively. This indicates that with increasing maturity of crude oils (CEN-21 being more mature than WST-69), the $C_{20}$ tricyclic terpanes are generated more than the $C_{21}$ tricyclic terpanes.

Figure 4 shows the normalized composition profiles of individual $C_{20}$ and $C_{21}$ tricyclic terpanes in the Niger Delta crude oil samples. The most abundant $C_{20}$ and $C_{21}$ tricyclic terpanes in both oil samples were TR20a, TR20b, TR20d and TR21d (see peak labels in table 1).

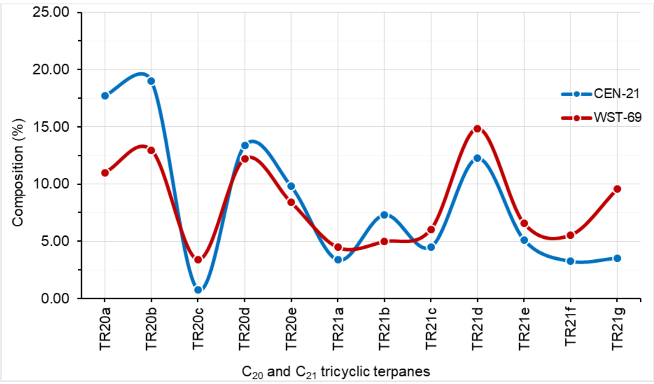


**Figure 4: Profiles of the normalized composition of individual $C_{20}$ and $C_{21}$ tricyclic terpanes in the Niger Delta crude oil samples (CEN-21 and WST-69)**

In CEN-21, TR20b, TR20a, TR20d and TR21d were most abundant and accounted for 18.99%, 17.74%, 13.36% and 12.24%, respectively, while in WST-69, TR21d, TR20b, TR20d and TR20a were most abundant and accounted for 14.85%, 12.97%, 12.22% and 11.01%, respectively (fig. 4). TR20c was observed to be the least abundant in CEN-21 and WST-69 oil samples accounting for 0.78% and 3.40% respectively (fig. 4). Profiles of the normalized composition of $C_{20}$ and $C_{21}$ tricyclic terpanes for CEN-21 and WST-69 were observed to follow similar patterns. Terpanes derived from different sources have distinct compositions and their characteristic profiles are used as fingerprints for correlation and/or differentiation of crude oils (Khalili *et al.*, 1995). The level of similarities observed in the flow pattern of the composition profiles of $C_{20}$ and $C_{21}$ tricyclic terpanes suggest CEN-21 and WST-69 oil samples are not distinct, but significantly related (genetically).

***$C_{20}$ and $C_{21}$ tricyclic terpane characterization of the Niger Delta crude oils***

From the abundances of individual $C_{20}$ and $C_{21}$ tricyclic terpanes in the crude oil samples, 66 ratios were derived and calculated. Their values are shown graphical in figure 5.

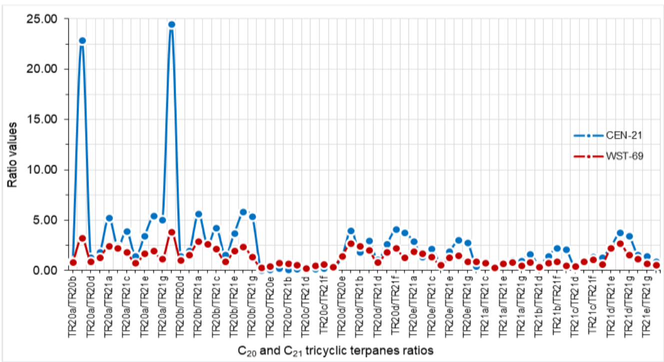


**Figure 5: Graphical representation of the values of 66 derived ratios of $C_{20}$ and $C_{21}$ tricyclic terpanes for the Niger Delta crude oil samples**

From fig. 5, most of the derived ratios showed little difference in values for both oil samples. Crude oils which show little variation in tricyclic terpane distributions and derivable ratios are mostly from terrigenous Tertiary deltaic petroleum systems (Samuel *et al.*, 2010). This indicates the Niger Delta crude oil samples are genetically related and predominantly derived from terrigenous Tertiary deltaic petroleum systems.

Some of the derived ratios of $C_{20}$ and $C_{21}$ tricyclic terpanes showed differences in values which discriminated the crude oil samples (fig. 5). Differences observed on a multivariate plot of crude oil ratios reflect differences in organic matter source, depositional environment, transformation process and/or lithology (Volk *et al.*, 2005). The differences observed in some of the derived ratios indicate minor input from a different source, depositional environment and/or maturity level. Ratios of TR20a/TR20c and TR20b/TR20c had considerably high values of 22.85 and 24.46 for CEN-21 and low values of 3.23 and 3.81 for WST-69, respectively. Also, ratios of TR20c/TR20d, TR20c/TR20e and TR20c/TR21d had relatively low values of 0.06, 0.08 and 0.06 for CEN-21 compared to values of 0.28, 0.41, and 0.23 for WST-69, respectively. These ratios are suggestive as indicators for evaluation of source/depositional environment or maturity of the Niger Delta crude oils.

## CONCLUSION

From the mass chromatograms (m/z 191) of two Niger Delta crude oil samples, CEN-21 and WST-69, 12 peaks, which eluted from the GC between 21 and 25 minutes, were selected as $C_{20}$ (5 peaks) and $C_{21}$ (7 peaks) tricyclic terpanes. This distribution of $C_{20}$ and $C_{21}$ tricyclic terpanes in CEN-21 and WST-69 are uncommon in crude oils. The most abundant $C_{20}$ and $C_{21}$ tricyclic terpanes in both oil samples were TR20a, TR20b, TR20d and TR21d. Total and individual abundances of $C_{20}$ and $C_{21}$ tricyclic terpanes in the oil samples suggest CEN-21 was more mature than WST-69 and that with increasing maturity of the crude oils, the $C_{20}$ tricyclic terpanes were generated more than the $C_{21}$ tricyclic terpanes. Significant similarities in the normalized composition profile and derived ratios of the $C_{20}$ and $C_{21}$ tricyclic terpanes suggest the two Niger Delta crude oil samples genetically related and predominantly derived from terrigenous Tertiary deltaic petroleum systems. Some differences observed in the profile and derived ratios indicate minor input from a different source, depositional environment and/or maturity level and are suggestive as indicators for evaluation of the Niger Delta crude oils.

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