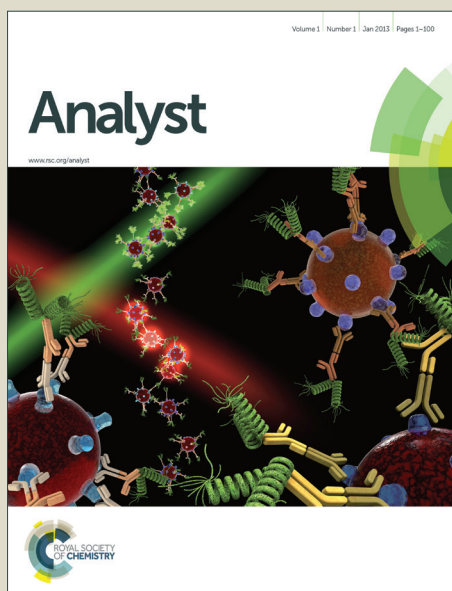


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Discovery and Identification of a series of alkyl decalin isomers in petroleum geological samples

WANG HuiTong^{1, 2}, ZHANG ShuiChang^{1, 2}, WENG Na¹, ZHANG Bin^{1, 2}, ZHU Guangyou^{1,2}, LIU Lingyan^{3*}

¹ PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China;

² State Key Laboratory of Enhanced Oil Recovery, RIPED, PetroChina, Beijing 100083, China

³ School of Chemical Biology and Pharmaceutics, Capital Medical University, Beijing 100069, China

* lingyan@ccmu.edu.cn

Abstract

The comprehensive two-dimensional gas chromatography/time-of-flight mass spectrometry (GC×GC/TOFMS) has been used to characterize a crude oil and a source rock extract sample. During the process, a series of pairwise components between monocyclic alkanes and mono-aromatics have been discovered. After tentative assignments of decahydronaphthalene isomers, a series of alkyl decalins isomers have been synthesized and used for identification and validation of these petroleum compounds. From both the MS and chromatography information, these pairwise compounds were 2-alkyl-decahydronaphthalenes and 1-alkyl-decahydronaphthalenes. The polarity of 1-alkyl-decahydronaphthalenes was stronger. Their long chain alkyl substituent groups may be due to bacteria transformation or different oil cracking events. This systematic profiling of alkyl-decahydronaphthalene isomers provides further understanding and recognition of these potential petroleum biomarkers.

1. Introduction

In geologists' research on fossils, geochemists utilize special biomarkers to trace the ancient environment and discuss the organic composition of stratigraphic origins [1]. By tracing the isomerization of some biomarkers, the extent of specific thermal evolution could be determined. According to the characteristic structures of these biomarkers, geologists and geochemists can determine the correlation between different oil-source rocks [2-5], and explore the hydrocarbon migration with geochromatographic action theory [6, 7]. For example, steranes and hopanes are essential in calculating the ratio of various sources of mixed oil [8, 9], tracing the secondary migration of oil and gas [10], and determining the extent of biodegradation of crude oil [11, 12].

However, the analysis of petroleum samples usually involves extensive efforts due to the sample complexity. It is believed that even a part of unresolved complex mixture consists of thousands of components, presenting as a big "hump" in gas chromatograph (GC) spectrum [13], which remains as a challenging problem in traditional one-dimensional GC (1D) [14]. With higher separation and identification

capabilities, the comprehensive two dimensional gas chromatography coupled time-of-flight mass spectrometry (GC×GC/TOFMS) has been applied to different types of oil samples [15-18]. The comprehensive two dimensional GC utilizes two capillary columns filled with different stationary phase such as non-polar and polar column combination that provides close to orthogonal separation capability. After eluting from the first column, the analytes are collected and refocused by a cryogenic modulator system periodically. The effluent was then sent to the second column for further separation, creating narrow modulated peaks with better sensitivity. Both flame ionization detector (FID) and TOF were used for identification and quantification. Recent years, comprehensive GC×GC/TOFMS has been widely used in analysis of condensate [19-21], crude oil [22, 23], and source rock extracts [24], etc.

In our GC×GC/TOFMS analysis of source rocks and crude oil, we discovered a series of components located between monocyclic alkanes and mono-aromatics. The tentative assignments of these compounds were decalins with different alkyl substituent groups. The compounds found in heavy gas oil with similar mass spectra once aroused attention of Ávila, B. et. al., but these compounds were not studied in further details [25]. Decalins and its short and branched alkyl substituents were also observed by Tran. T. C. et. al. in biodegraded oil samples [26], while no further qualitative proofs have been provided. The present study provides the first systematic profiling of alkyl-decahydronaphthalene isomers for further understanding and recognition. To further validate these isomers, we synthesized series of trans-2-alkyl-decahydronaphthalene isomers for validation. These series of alkyl-decahydronaphthalenes can be potential petroleum biomarkers.

2. Experiments

2.1 Samples and Chemicals

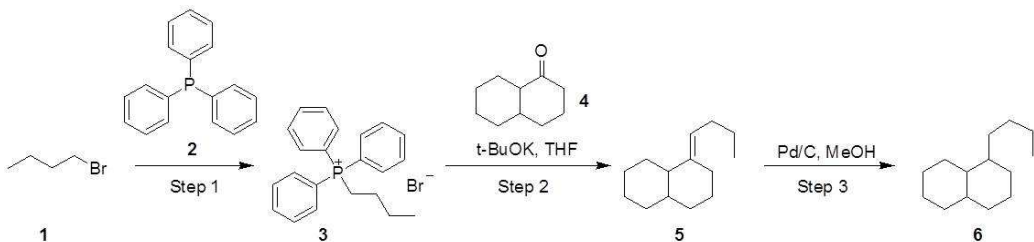
Two petroleum samples were studied. The first sample was the condensate from Well ND1 in Baxian Sag of the Jizhong Depression, located in the west of the Bohai Bay Basin, China. The other was a source rock sample from the Xiahuayuan Town of Hebei Province, China. For GC×GC/TOF-MS analysis, the whole crude oil sample was injected into the instrument without any pretreatment or dilution. The well-developed protocol of hydrocarbon extraction has been applied on the rock source sample, including (a) 200 g rock samples were extracted with 250 mL chloroform and dried; (b) dissolving 20 mg extracts in appropriate amount of n-hexane (re-distilled); (c) packing the extract solution in a glass column with 2 g activated silica gel (100 mesh-200 mesh, activated at 200 °C for 4 h); (d) washing the silica gel 3 time with 15 mL dichloromethane; (e) collecting the hydrocarbon fraction to 1.5 mL by using nitrogen evaporator; (f) transferring the hydrocarbon fraction into a GC sample bottle before analysis. [27]

1-Bromobutane, triphenylphosphane, methylbenzene and all other chemicals used for synthesis were purchased from J&K Scientific Ltd., China

(<http://www.jk-scientific.com/>).

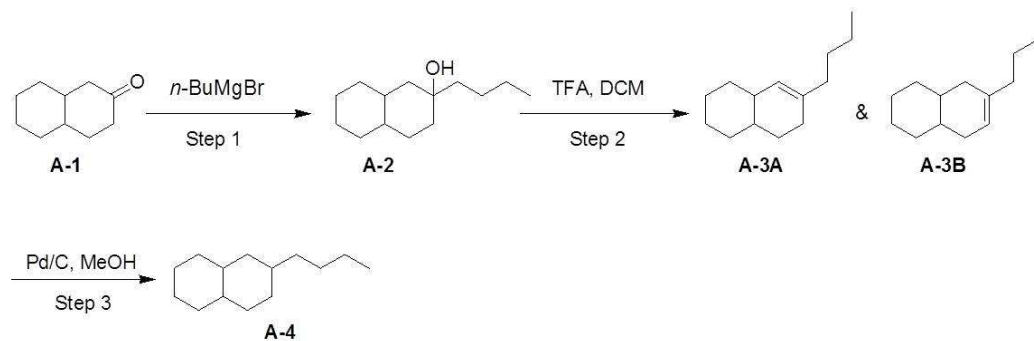
2.2 Synthesis of 1-alkyl decalins and 2-alkyl decalins

The 1-butyldecahydronaphthalene, 1-pentyldecahydronaphthalene, 1-hexyldecahydronaphthalene, and 1-heptyldecahydronaphthalene were synthesized following the steps shown in Eq.1.



Eq. 1. Synthesis route of 1-alkyl decalins.

The 2-butyldecahydronaphthalene, 2-pentyldecahydronaphthalene, and 2-hexyldecahydronaphthalene were produced according to steps shown in Eq.2.



Eq. 2. Synthesis route of 2-alkyl decalins

The details of all synthesis were included in Supplementary Materials. The structures of synthesized compounds were supported by ¹³C-NMR DEPT 135 analysis.

2.3 Analysis of GCxGC/TOF-MS

The crude oil and source rock extracts sample were analyzed on GCxGC/TOF-MS. Synthesized Standard 1 (STN1), which has three synthesized 1-alkyl decalins, 1-butyldecahydronaphthalene, 1-pentyldecahydronaphthalene, and 1-hexyldecahydronaphthalene, were mixed and analyzed using the same parameters as the petroleum sample. 1-heptyl-decahydronaphthalene (C₁₇H₃₂) was excluded due to the mixed impurity. Similarly, the Synthesized Standard 2 (STN2) comprising of four synthesized 2-alkyl decalins was analyzed in the same batch as STN2.

The GCxGC/TOF-MS analysis of both petroleum and standards were performed on Pegasus 4D system (GCxGC/TOF-MS, LECO Corporation, St. Joseph, MI). The

instrument was equipped with an Agilent 7890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) and a liquid nitrogen-cooled pulse jet modulator. The detailed instrument settings were describing below. A 50 m HP-Petro capillary column (100% dimethylpolysiloxane, 0.2 mm I.D. and 0.5 μ m film thickness) was used as the first-dimension (1-D) column and a 3 m DB17-HT capillary column (50%-phenyl-methylpolysiloxane, 0.1 mm I.D. and 0.1 μ m film thickness) was used as the second-dimension (2-D) column. Both columns were purchased from Agilent Technologies, China. The initial temperature was 35 $^{\circ}$ C and hold for 0.2 min. Then it was rose to 210 $^{\circ}$ C at the rate of 1.5 $^{\circ}$ C /min. After holding for 0.2 min, the second round of temperature increase was performed at the rate of 2.5 $^{\circ}$ C/min until 300 $^{\circ}$ C and kept constant for 20 min. The second oven and the modulator oven were operated with the same temperature gradient but with a temperature offset of 5 $^{\circ}$ C and 45 $^{\circ}$ C. Inlet temperature was set at 300 $^{\circ}$ C, with split ratio of 700:1, and the sample injection volume was 0.5 μ L. He was used as the carrier gas, with a flow rate of 1.5 ml/min. The modulation time was 10 s, of which 2.5 s was hot pulse time. The temperatures of transfer line and ion source were set at 300 $^{\circ}$ C and 240 $^{\circ}$ C, respectively. The detector voltage was 1600 V, and mass range was 40–520 amu with an acquisition rate of 100 spectra per second (Hz). The delay time of condensate oil was 0 min, and the delay time of source rock was 11 min. The ChromaTOF software version 4.0 was used to process the raw data from the instrument. The compounds assignments were performed by searching the mass spectra in the US National Institutes of Standards and Technology (NIST) MS database (NIST MS Search 2.0, NIST/EPA/NIH Mass Spectral Library; NIST 2002), and further confirmed with synthesized standard compounds.

3. Results and Discussion

3.1 Alkyl decalins in petroleum samples

Comprehensive two-dimensional GC spectra with non-polar/polar column system used in this study have the features as follows: 1) compounds elution on the first column is according to the boiling point of each compound, which means compounds of lower boiling points will elute earlier than the ones with higher boiling points; 2) on the second column, compounds elution is according to the polarity, which means the compounds of lower polarity will be eluted first. 4955 compounds were found by GCxGC/TOF-MS in the condensate sample. Series of *n*-alkanes (C₁₁-C₃₈, red), *n*-alkyl cyclopentane (green), *n*-alkyl cyclohexane (pink), and *n*-alkyl benzene (blue), etc. were identified and selectively presented in Fig. 1A using extracted ion chromatograms (EICs) of *m/z* 68, 82, 92, and 137, respectively.[28, 29] Among them, a group of pairwise peaks were discovered. These peaks eluted between *n*-C₁₁ to *n*-C₃₈ on 1-D. On the 2-D chromatograph, they appeared from 2.4 to 4.8 s, in the range of polycyclic alkanes. They were further highlighted with EIC of *m/z* 137 in an expanded area (Fig. 1B). Similarly, a total of 5594 compounds were found in the rock extract sample, and the corresponding EICs and expanded *m/z* 137 areas showing the pairwise peaks of interest were present in Fig. S2 (Supplementary). In the following contents, the crude oil was mainly discussed.

The pairwise peaks were labeled from peak 1 (PK1) to peak 11 (PK11) in the crude oil sample. Details of PK1 to PK11 (GC temperature program changed after PK7) were listed in Table. 1. Each pair of peaks could be distinguished by 'a' and 'b' according to their sequence of 2-D eluting times (ex. PK1a eluted earlier than PK1b on 2nd column), which were also labeled in Fig. 1B. Mass spectra of the first six pairs were presented in Fig. 2, and the rest were provided in Fig. S2. The mass range of molecular ions was chosen from 152 to 292. The ChromaTOF software deconvoluted spectra were compared with those in NIST library. The searching results indicated the first four eluted peaks were 2-methyldecahydronaphthalene (PK1a), 1-methyldecahydronaphthalene (PK1b), 2-ethyldecahydronaphthalene (PK2a), and 1-ethyldecahydronaphthalene (PK2b) with similarities all greater than 900. Difference of the molecular weights of each adjacent pair were always 14, suggesting a methylene unit (-CH₂-) inserted.

The whole series had the same characteristic ions of *m/z* 137, indicating a decalin cation. Besides, there were no other ions with significant abundance between molecular ions and the ion with *m/z* 137. This suggested that the single substituent on the decalin ring has high probability, as the loss of whole alkyl groups was the main product. Besides, the substituents were more likely long-chain alkyl groups rather than branched chain groups; otherwise there should be a strong fragment ion in between. The number of C in long alkyl chain could be 1 ~ 26. Other fragmental ions of *m/z* 41, 55, 67, 81, 95, and 109 were commonly observed in the whole series. A representative mass spectrum of PK6 shown in Fig. 3 provided proposed MS fragmentation details.

There are two types of alkyl decalin, *cis*-decalin and *trans*-decalin. Generally, the *trans*-decalins are more stable. In addition, they each have two isomers. Meanwhile, the alkyl group can be substituted on C-1, C-2 or C-9. However, 9-alkyl decaline is hard to be formed because of the steric effect. Comparing 1- and 2- decalines with the same substituted alkyl group, 1-alkyl decaline has larger polarity, while 2-alkyl decaline has higher stability. Since the compounds are relatively stable in geological samples, these pairwise compounds could be *trans*-1-, and *trans*-2-alkyl decalins. From the boiling point variation, the alkyl groups increase from C1 to C_n. Furthermore, chromatography information and synthesized standards were used to discover and validate their structure details.

3.2 1-alkyl decalins and 2-alkyl decalins in synthesized samples

The expanded GC×GC/TOFMS spectrum of STN1 and STN2 were shown in Fig. 4B and Fig. 4C, respectively. The two spectra were obtained in adjacent runs; hence the retention index difference from column aging could be ignored. The GC×GC retention index of each compounds were summarized in Table 2, together with their fragment ions. The NIST search result suggested the peak at 87.07 min, 2.48s (RT1, RT2) from Fig. 3B and the peak at 87.33 min, 2.46s (RT1, RT2) were

butyl-decahydronaphthalene, which conversely verify the synthesized products.

The isomers of each alkyl decalin were sharing the same MS information (Fig. S4). For example, 1-butyl-decahydronaphthalene had the same MS information as 2-butyl-decahydronaphthalene, including both the molecular ion (m/z 194) and fragment ions (m/z 137, 41, 55, 67, 81, 95 and 109). 1-pentyl-decahydronaphthalene and 2-pentyl-decahydronaphthalene had identical mass spectra. 1-hexyl-decahydronaphthalene was almost the same with 2-hexyl-decahydronaphthalene in their mass details.

Although MS was not able to distinguish isomers based on m/z ratios, chromatograms provided different retention index for each isomer. Compared to the corresponding 2-alkyl decalins, C-1 substituted ones had shorter eluting time on RT1 (Fig. 4B), but longer eluting time on RT2 (Table 2). For example, 1-butyldecahydronaphthalene came out earlier at 87.07 min (RT1) but stayed longer on the 2nd dimension (RT2=2.48s), compared to 2-butyldecahydronaphthalene located at 87.33 min, 2.46s (RT1, RT2, Table.2). Based on the non-polar/polar GC system combination, it can be inferred that 1-butyl-decahydronaphthalene had lower boiling points but higher polarity than 2-butyldecahydronaphthalene.

3.3 Comparison of synthesized samples and the petroleum sample

MS spectra of synthesized compounds were compared with PK1~PK11 in the petroleum sample. The MS signatures of both synthesized butyl-decahydronaphthalene isomers were almost the same with those of PK4a and PK4b from the oil sample. They had the same molecular ion (m/z 194), and characteristic fragment ion (m/z 137, 55, 67, 81, and 95) as shown in Table 1 & Table 2.

Similarly, the MS spectra of two pentyl-decahydronaphthalene isomers were analogous to those of PK5a and PK5b (Fig. S3). Hexyl-decahydronaphthalene isomers and 2-heptyl-decahydronaphthalene were almost identical to PK6 (a & b) and PK7 (a & b) in terms of their mass spectra. Hence, we can conclude that PK4 (a & b), PK5 (a & b), PK6 (a & b), PK7 (a & b) were the isomers of butyl-decahydronaphthalene, pentyl-decahydronaphthalene, hexyl-decahydronaphthalene, and heptyl-decahydronaphthalene respectively.

The information of retention index was further investigated. As the STN1 and STN2 were analyzed in the same batch, their retention indexes were comparable. Their chromatogram areas were aligned as shown in Fig. 4B & 4C. Then the expanded chromatogram area of PK4~7 from the oil sample (Fig. 4A) was compared with those of two synthesized standards. Each isomer of PK4 ~ 7 was neatly arranged with the synthesized 1- or 2-alkyl decalines. For example, PK4a and PK4b were closely aligned with 2-butyl-decahydronaphthalene and 1-butyl- respectively. PK5a and PK5b were strictly aligned with 2-pentyl-decahydronaphthalene and

1-pentyl-decahydronaphthalene respectively. Same trend can be found in PK6a and PK6b. The PK7a aligned tightly with 2-heptyl-decahydronaphthalene in STN2.

From both the MS and chromatography information, we can conclude that the series of pairwise compounds were isomers of 1- and 2-alkyl decalines. The peak “a” of each pair was C-2 substituted, while the peaks “b” was C-1 substituted.

3.4 Impact of alkyl substituents

It is well known that with the growth of the alkyl substituents, boiling points of alkanes increase. It was observed that, the boiling point difference (ΔRT_1) between the isomers within a pair changed as the substituent chain grew (Table 1). For example, ΔRT_1 was 1.60 min when comparing 2-methyldecahydronaphthalene (PK1a) to 1-methyldecahydronaphthalene (PK1b). While the number decreased to 0.93 when comparing 2-ethyldecahydronaphthalene (PK2a) with 1-ethyldecahydronaphthalene (PK2b). The trend even started to reverse from 4 carbon hydrocarbyl substituted decalins (PK4), the boiling point of 2-alkyl decalins was higher than that of 1-alkyl decalins ($\Delta RT_1 < 0$). This trend was observed from both petroleum sample and synthesized standards (Table 2). This "inversion" phenomenon in the two-dimensional chromatogram was because of the electronic effect of substituents. From PK1 to PK7, the increasing rate of RT_1 of 2-alkyl decalins was larger than that of 1-alkyl decalins. When the carbon number in hydrocarbyl substituents increased further than 7, the impact on retention time changes arising from substituents position could be negligible, which supported by the consistent ΔRT_1 of -0.80 min. On the other hand, 1-alkyl decalins always had longer eluting time on column 2 ($\Delta RT_2 > 0$), due to their stronger polarities than 2-alkyl decalins. It was also observed that ΔRT_2 kept decreased, which means the substituent position effects decrease on the polarity as the substituents grow.

These alkyl decalins have been discovered in both source rock and crude oil samples. In degradable oil, decalins with short alkyl groups have also been found. Though they always remained in unresolved complex mixture (UCM) part, they started to raise people's interest. The presence of a large number of long-chain substituent groups may suggest that transformation of bacteria plays a significant role on these compounds' formation processes. The different length of side chains may correlate to various degrees of oil cracking [30].

4. Conclusion

In this study, GCxGC/TOF-MS was used to analyze petroleum samples. A series of pairwise peaks in both condensate and source rock extract samples were observed, which have not been resolved in the common GC/MS. The tentative analysis demonstrated that they were alkyl decalins with different substituted positions. As the MS spectra could not clearly differentiate isomers, a series of alkyl decalins isomers were synthesized. The GCxGC/TOF-MS results of synthesized standards were analyzed together with both petroleum samples. With the analogous MS spectra and

close retention index, we can conclude that the pairwise compounds were 1-alkyl-decahydronaphthalenes and 2-alkyl-decahydronaphthalenes, and the former has higher polarity. Their long chain substituent groups may come from bacteria transformation or different oil cracking results. These alkyl decalin isomers could be used as potential petroleum biomarkers representing the source and age related geographical information. More studies are needed to explore their specific geochemical significance.

Acknowledgements

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Table 1. GCxGC/TOF-MS details of PK1 to PK8 from the crude oil sample.

Peak no.	1st Retention Time (RT1, minutes)	2nd Retention Time (RT2,s)	Δ RT1, mins (PKb-PKa)	Δ RT2,s (PKb-Pka)	Molecular ion (m/z)	Fragment ions (m/z)
PK1a	57.27	2.40	1.60	0.05	152	41,55,67,81,95,109,123,137,152
PK1b	58.87	2.45			152	41,55,67,81,95,109,123,137,152
PK2a	68.73	2.42	0.93	0.06	166	41,55,67,81,95,109,123,137,166
PK2b	69.67	2.48			166	41,55,67,81,95,109,123,137,166
PK3a	78.07	2.42	0.13	0.03	180	41,55,67,81,95,109,123,137,180
PK3b	78.20	2.45			180	41,55,67,81,95,109,123,137,180
PK4a	87.27	2.43	-0.27	0.04	194	41,55,67,81,95,109,123,137,194
PK4b	87.00	2.47			194	41,55,67,81,95,109,123,137,194
PK5a	96.07	2.43	-0.53	0.04	208	41,55,67,81,95,109,123,137,208
PK5b	95.53	2.47			208	41,55,67,81,95,109,123,137,208
PK6a	104.33	2.47	-0.67	0.01	222	41,55,67,81,95,109,123,137,222
PK6b	103.67	2.48			222	41,55,67,81,95,109,123,137,222
PK7a	112.20	2.49	-0.80	0.03	236	41,55,67,81,95,109,123,137,236
PK7b	111.40	2.52			236	41,55,67,81,95,109,123,137,236
PK8a	119.53	2.45	-0.80	0.04	250	41,55,67,81,95,109,123,137,250
PK8b	118.73	2.49			250	41,55,67,81,95,109,123,137,250
PK9a	125.67	2.34	-0.67	0.04	264	41,55,67,81,95,109,123,137,264
PK9b	125.00	2.38			264	41,55,67,81,95,109,123,137,264
PK10a	131.00	2.29	-0.67	0.03	278	41,55,67,81,95,109,123,137,278
PK10b	130.33	2.32			278	41,55,67,81,95,109,123,137,278
PK11a	135.53	2.27	-0.53	0.03	292	41,55,67,81,95,109,123,137,292
PK11b	135.00	2.30			292	41,55,67,81,95,109,123,137,292

Table 2. GCxGC/TOF-MS details of peaks from STN1 and STN2.

Sample info.	Name	1st Retention Time (RT1, minutes)	2nd Retention Time (RT2,s)	$\Delta RT1$, mins (PKb-PKa)	Molecular ion (m/z)	Fragment ions (m/z)
STN 2	2-Butyldecahydronaphthalene	87.3333	2.46	-0.2666	194	41,55,67,81,95,109,137,194
STN 1	1-Butyldecahydronaphthalene	87.0667	2.48		194	41,55,67,81,95,109,137,194
STN 2	2-Amyldecahydronaphthalene	96.1333	2.46	-0.5333	208	41,55,67,81,95,109,137,208
STN 1	1-Amyldecahydronaphthalene	95.6	2.48		208	41,55,67,81,95,109,137,208
STN 2	2-Hexyldecahydronaphthalene	104.4	2.47	-0.667	222	41,55,67,81,95,109,137,222
STN 1	1-Hexyldecahydronaphthalene	103.733	2.5		222	41,55,67,81,95,109,137,222
STN 2	2-Heptyldecahydronaphthalene	112.133	2.49		236	41,55,67,81,95,109,137,236

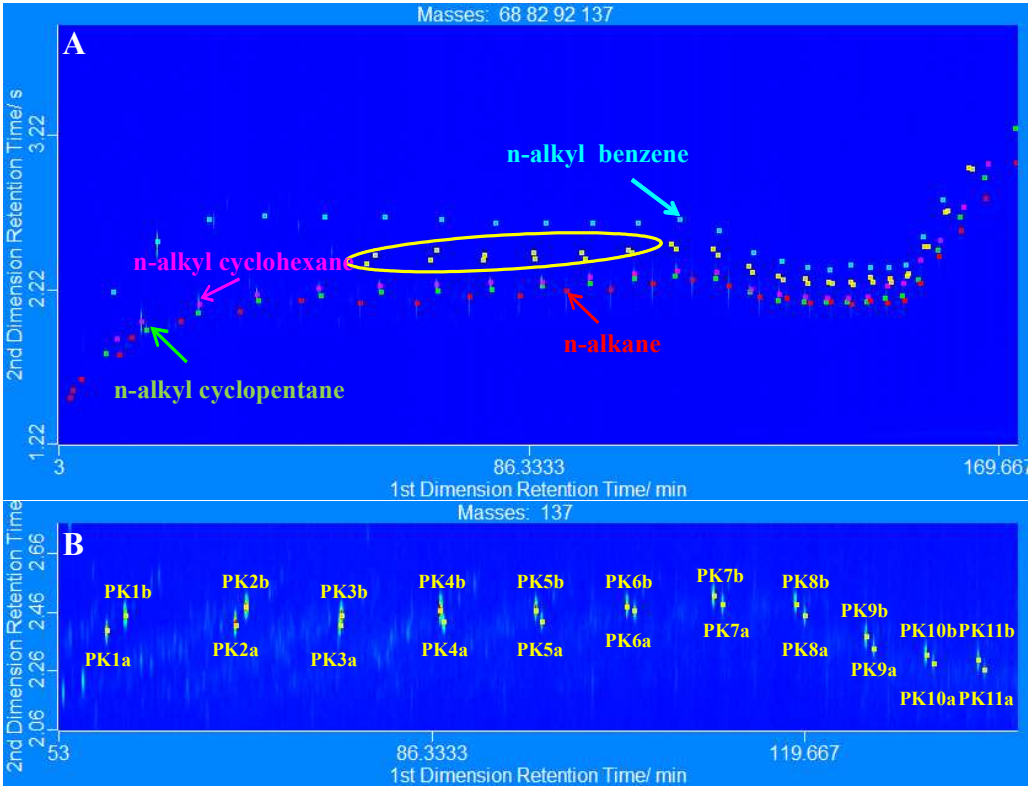


Fig. 1. A) GCxGC-TOFMS EIC (m/z 68+82+92+137) showing petrochemical compounds in an oil sample. B) Representative GCxGC-TOFMS EIC (m/z 137) showing the group of pairwise compounds.

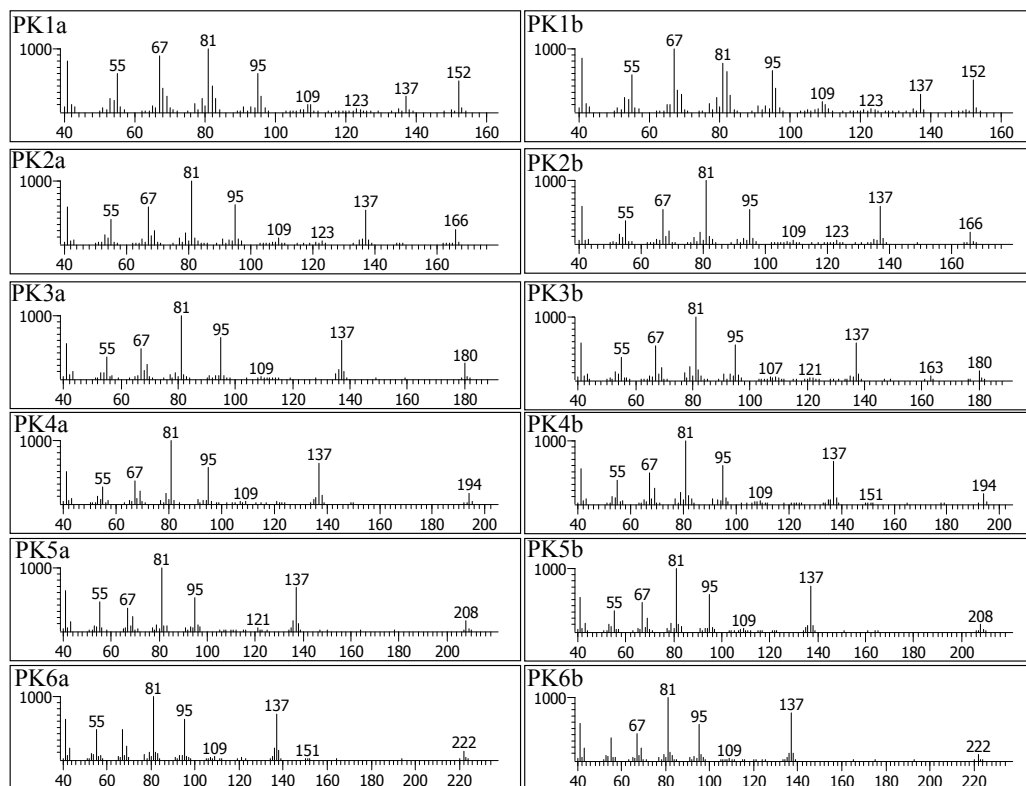


Fig. 2. Mass spectra of PK1a, 1b to PK6a and 6b from the crude oil sample.

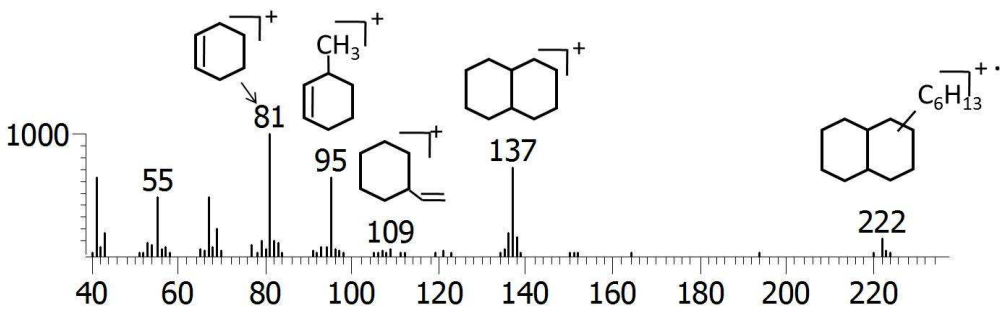


Fig. 3. Proposed MS fragmentation details of PK 6.

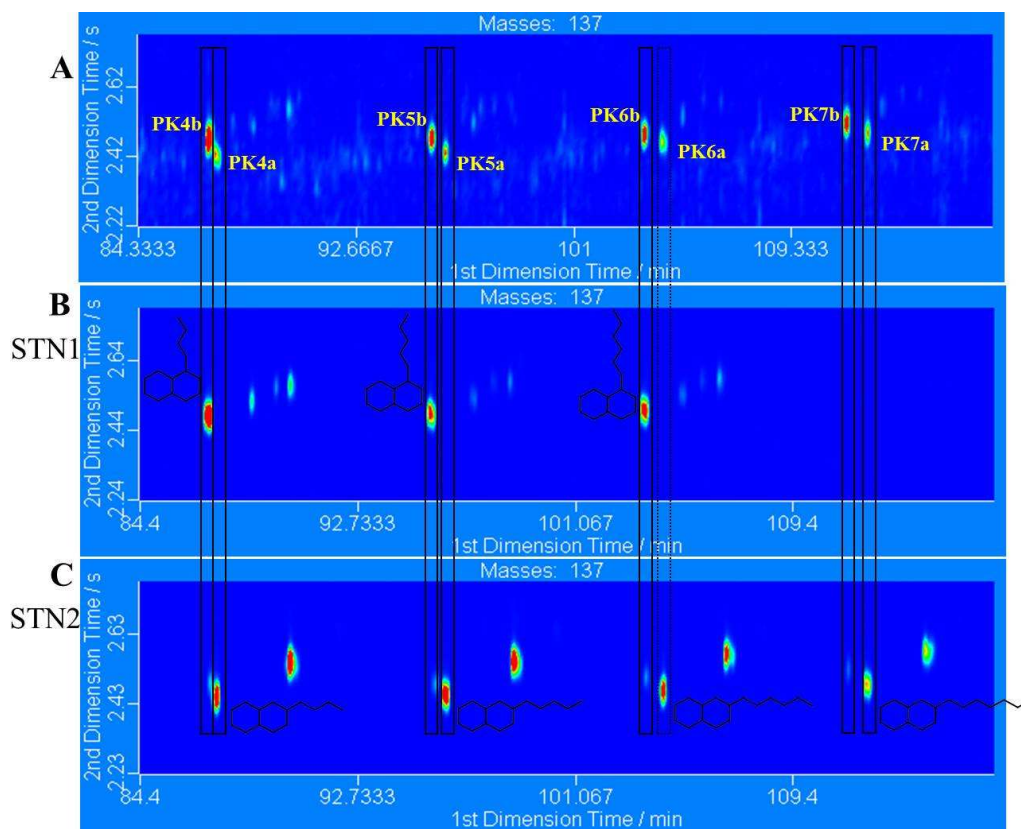


Fig. 4. A) Expanded GCxGC/TOF-MS area of PK4 ~ PK7 area of crude oil sample; B) Expanded GCxGC/TOF-MS area of STN1; C) Expanded GCxGC/TOF-MS area of STN2.