CHEMISTRY

POLYCYCLOALCANE HYDROCARBONS IN TARIBANI OIL

[1]***Natela Khetsuriani,*** *doctor*
[2]***Elza Topuria,*** *PhD*
[3]***Madlena Chkhaidze,*** *MS*
[4]***Vladimer Tsitsishvili,*** *Academy Members, Professor*

Georgia, Tbilisi, TSU, Petre Melikishvili Institute of Physical and Organic Chemistry,
Laboratory of Petroleum Chemistry,
[1]Head of the Petroleum Chemistry laboratory, Chief Research Workers;
[2]Chief research workers;
[3]Scientific workers;
[4]Chief Research Workers

DOI: https://doi.org/ 10.31435/rsglobal_ws/30092018/6132

ARTICLE INFO

Received: 20 July 2018
Accepted: 19 September 2018
Published: 30 September 2018

KEYWORDS

oil,
polycyclic hydrocarbons,
thermal diffusion separation,
thiourea adduction.

ABSTRACT

For the purpose of extraction and identification of cyclic alkane hydrocarbons in oil from the Taribani field, Georgia, concentrates isolated from 200-350ºC fractions have been studied. The concentrate preparation included the following steps: (a) distillation of a crude oil, (b) dearomatization of distillates by silica gel, (c) three-stage thermal diffusion separation of isoalkanes and cycloalkanes, and (d) thiourea adduction. Ten thermal diffusion fractions were obtained. A mixture of the IX and X fractions and separately the VIII fraction were studied. The extracts from these fractions with thiourea were studied as well. Composition of concentrates has been determined by the gas chromatography – mass spectrometry (GC-MS) method.

The main components of the VIII thermodiffusion fraction were C11-C22 isoprenoid alkanes. Among them the predominant were pristane C19 and the phytane C20, the well-known biomarkers of oil. In the VIII thermodiffusion faction including dimethyl-, trimethyl-, tetramethyl-, ethyl-, methyl-ethyl-, diethyl-, propyl, methyl-propyl adamantanes, were identified.

Citation: Natela Khetsuriani, Elza Topuria, Madlena Chkhaidze, Vladimer Tsitsishvili. (2018) Polycycloalcane Hydrocarbons in Taribani Oil. *World Science.* 9(37). doi: 10.31435/rsglobal_ws/30092018/6132

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Introduction. Naphthenic hydrocarbons make up the main part of petroleum hydrocarbons (40-60%). They are the most interesting components, the presence of which determines the valuable chemical and technical properties of petroleum products. Consequently, their study is an integral part of the problems of petrochemistry and oil refining. Lower naphthenes C_5-C_9, boiling up to 200 °C, have been studied quite well. In the middle fractions, the complexity of the composition and structure of bi-, tri-, tetra- and pentacyclic naphthenes represented in them with different type of bonding of five- and six-membered rings (joined, condensed, bridged type, etc.) significantly increases. These hydrocarbons, due to the variety of structural and spatial isomers, are the least studied hydrocarbons, with the exception of adamantane compounds. On the GLC chromatograms of naphthenic concentrates a continuous undivided background in the form of a "hump" is obtained, indicating the exceptional complexity of these fractions. Interest towards the study of polycyclic naphthenes present in the middle fractions of petroleum was caused by the scarcity of information about these fractions and about the tri-, tetra- and pentacyclic alkanes present in them in the form of compact structure of C_{11}-C_{16} composition. Studies of these hydrocarbons in Georgian oils were carried out for the first time at the molecular level, with the aim of determining individual chemical compounds in oils with definite deciphering of their structure and spatial structure.

On the territory of Georgia oil deposits are known from the ancient times, and there are more than 1500 manifestations of oil and gas. The Taribani field is a large under-developed oil field covering an area of approximately 80 km^2 located in the southeast of Georgia, on the Shiraki Valley (Kakheti, the 12th licensed block). Productive zones are situated in the Miocene and Pliocene aged sandstone reservoirs that have been deposited in fluvio- To study the individual hydrocarbon composition of the polycyclic naphthenes of the middle fractions of the investigated oil, modern methods of separation and research were selected to achieve greater differentiation by the type of the structure of molecules of complex hydrocarbon mixtures, since the higher the degree of differentiation of the investigated objects, the higher and more reliable is the effectiveness of methods for their analysis. The crude oil sample was taken from the well # 23 of Taribani oils at a depth between -2345 and -2374m. The Taribani oil is paraffinic (7%), although like all other Georgian oils, at the same time it contains a considerable amount of isoprenoid structures; the content of light fractions (55-350°C) makes up to 60%, sulfur – 0.2%, tar– 8.5%, asphaltenes– 6.2% [1-3].

The main goal of thepresent study was to develop the feasible sequential procedure of oil distillation, dearomatization, separation of isoalkanes from cycloalkanes, and extraction of cycloalkanes for the subsequent analysis by the gas chromatography-mass spectrometry (GC-MS) method.

Purpose of the study. Qualitative determination of polycyclic saturated hydrocarbons in the high-boiling fraction (200-350°C) of the Taribani oil

Materials and methods. All used chemicals were analytical grade. The certified analytical standards of adamantane, methyladamantanes, n-prolyladamantane, 2-n-buthyladamantane, and diamantane were supplied by Sigma-Aldrich (Germany). The HPLC/GC grade methanol, n-pentane, benzene, and petroleum ester were purchased from Sigma-Aldrich and Merck (Germany).Activated fine silica gel(0.07–0.15 and 0.2–0.3 mm)was supplies by Labstatus (Ukraine) and ChemReactiveSnab (Almaty, Kazakhstan), coarse silica gel (0.4–2.5 mm) by Salavat catalyst plant (Russia), the thin layer chromatography silica gel plates were from Sanpont (Czech Republic) and from Merck (Germany); sodium sulfate purchased from Salavat catalyst plant (Russia), thiourea – from Biochem (France). Carrier gas - Hydrogen (CB Index: 87; Product Catalog: 9628, Customer Evaluation: 6, CAS: 1333-74-0; Remarks: Brand: Sigma-Aldrich | Product Number: 295396 | Purity: ≥99.99%/,

Preparation of cycloalkane concentrates

The concentrate preparation included the following steps:

- Distillation collecting two consecutive fractions 200-250°C and 250-350°C;
- Dearomatization of distillates by silica gel adsorption chromatography;
- Three-stage thermal diffusion separation [4-6] of isoalkanes and cycloalkanes on the Mel polder’s fractionating column [7] obtaining ten thermodiffusion fractions; fractions IX and X had almost identical content of polycyclic saturated hydrocarbons and have been united, the fraction VIII was studied separately;
- Extraction of cycloalkanes by thiourea adduction [8].

One of the most difficult problems to solve in oil studies is separation of isoparaffins from cycloparaffins and the latter in terms of their cyclicity. Thermal diffusion is almost the only method that allows solving this problem successfully. The most widely distributed were Mel polder’s vertical columns of "pipe in a pipe" type with a hollow gap and a coil on the outer surface of the inner tube. The coil in the working space significantly increases an efficiency of separation and much shortens the analysis time. By selecting the optimal conditions (temperature gradient, separation time) and column efficiency, it becomes possible to successfully extract the concentrates of different hydrocarbons from the petroleum fractions.

In this study large and micro - TDF columns were used. The height of the large columns was 1500 cm, the volume of the annular space – 50 ml, the clearance – 0.3 mm with a coil in the working space. Stainless steel microcolomns of the original design had a volume of 3, 4 and 4.5 ml. These columns are of the Melpolder's columns type, their efficiency factor in dividing the model mixture of cis-trans decalines (1: 1) is maximal S = 99% in 8-10 hours. Their height is 110 mm. These columns were designed and manufactured at the Petre Melikishvili Institute of Physical and Organic Chemistry, Laboratory of Petroleum Chemistry. The columns have 10 drain cocks that provide separation of mixtures into ten equal-volume fractions.

For extraction of naphthenic concentrates, saturated fractions of 200-250 °C and 250-350 °C were subjected to three-fold thermal diffusion. At each stage mixtures of the two lower fractions (IX + X) were placed into a TDF column for the next separation step, at the end of the process, a mixture of fractions (IX + X) - naphthenic concentrates was taken. The degree of TDF separation was high, estimation was made by change in the refractive index: fraction 200-250 °C – n_D^{20} was changed from 1.4486 to 1.4768 and fraction 250-350 °C – n_D^{20} was changed from 1.4495 to 1.4972.

Gas chromatography-mass spectrometry analysis

The chromatographic separation of mixture in the thiourea extract of IX+X thermal diffusion fractions have been carried out on capillary columns 60m × 0.25mm (200-250°C distillation fraction) and 40m × 0.25mm (250-350°C distillation fraction), linear programming of temperature – from 100°C with a speed of 2°C/min (200-250°C fraction) and from 130°C with a speed of 3°C/min (250-350°C fraction). Compounds in the VIII thermo diffusion fraction and corresponding extract have been separated on the dimethylpolysiloxane GC capillary column 200 m × 0.25 mm, temperature rose from 40°C to 280°C at a speed of 2°C/min during 70 min. Mass spectra have been measured on GC-MS systems with quadruple and magnetic sector analyzers at the department of spectrometric investigations of the National Institute of Standards and Technology (NIST, Gaithersburg, USA), the automated mass deconvolution and identification system (AMDIS) was used for data analysis.

Research results. Chromatograms of the thiourea extracts obtained from the naphthenic concentrate (mixture of the 3rdstage of thermal diffusion fractions IX + X) of the saturated distillation fractions of Taribani oil are shown in Figures 1 and 2.

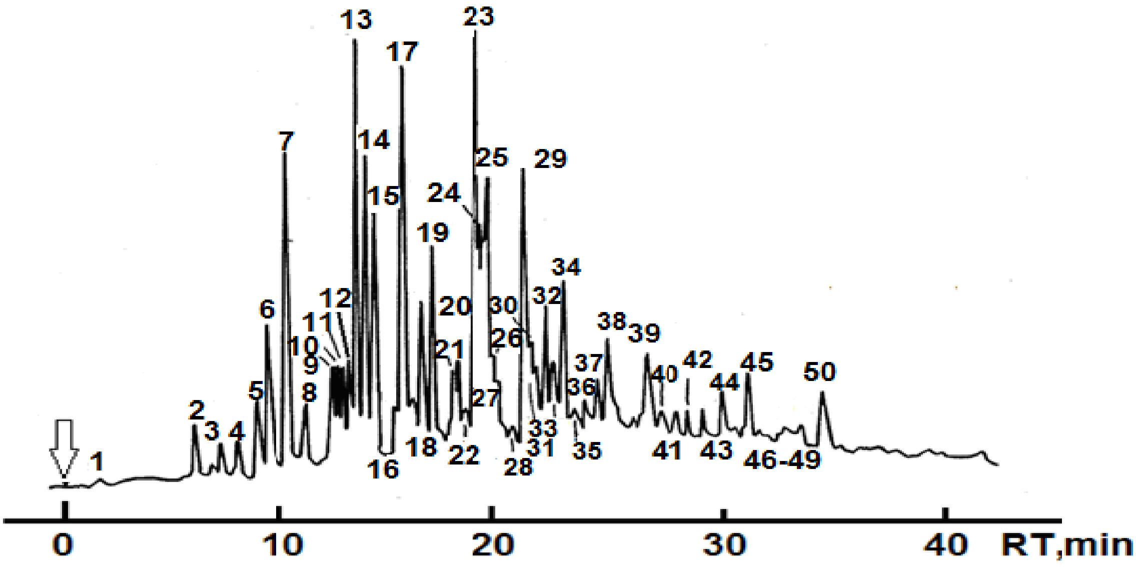

Fig. 1. Chromatogram of the thiourea extract obtained from the naphthenic concentrate

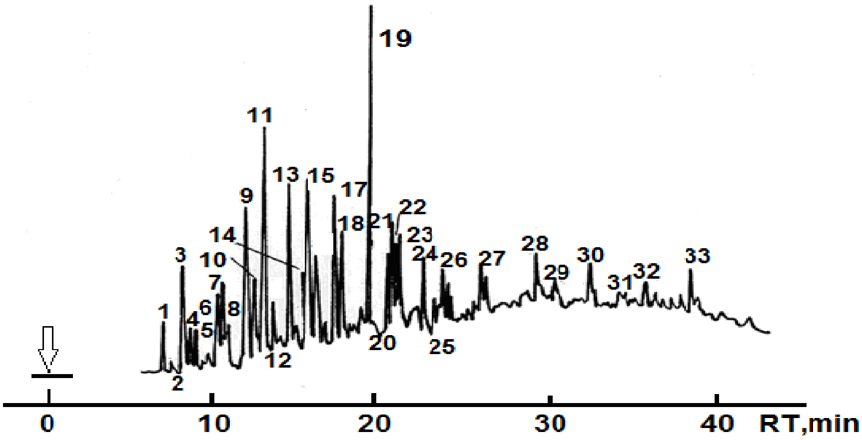

Fig. 2. Chromatogram of the thiourea extract obtained from the naphthenic concentrate of the saturated 250-350°C fraction

According to this experimental data, the concentrate of the 200-250°C fraction contains about 92% of bi-, tri- and tetracycloalkanes, and the concentrate of 250-350°C fraction contains more than 96% of the tri-, tetra- and pentacycloalkanes. More than 50 individual polycyclic alkanes were identified: adamantane and its nine homologues of C_{10}–C_{13} composition; twelve tricyclic C_{11}–C_{13} hydrocarbons (tricycloundecanes and tricyclododecanes – bridge tricycloalkanes, the predecessors of adamantanes in oil [9,10]; ten tetracyclic C_{12}–C_{16} hydrocarbons containing adamantane structure in polycyclic system; four pentacyclotetradecanes – diamantane ($C_{14}H_{20}$) and its three derivatives of $C_{15}H_{22}$ composition; six bicyclic hydrocarbons with sesquiterpene type structure, polymethyl-substituted decalines of C_{14}–C_{16} composition, structure of which have relict character[11].

It should be noted that when studying Taribani oil [1] ten compounds have been detected in oil for the first time: tricyclo[5.2.2.$0^{3,7}$]undecan ($C_{11}H_{18}$, peak 10), 1-n-propyladamantane ($C_{13}H_{22}$, peak 33), 1-ethyl-2-methyl-adamantane ($C_{13}H_{22}$, peak 21, Figure 1), metyltetracyclo [6,3,1,$1^{6.10}0^{2.6}$]tridecan (C14H22, peak 18); 1-methyl- and 3-methyl-diamantanes ($C_{15}H_{22}$, peaks 26 and 29, respectively), tetracyclo[7.3.1.$0^{2,7}$,$1^{7,11}$]tetradecan ($C_{14}H_{22}$, peak 19) and its derivatives up to hexamethyl-substituted analogs ($C_{15}H_{24}$ – $C_{20}H_{34}$, peaks 24,27,28,30,32 and 33 Figure 2).

Chromatogram of the thermodiffusion fraction VIII is shown in Figure3.Complex study of MS data and GC retention indices made it possible to divide isomers, which in itself is a great difficulty in the process of compounds identification.

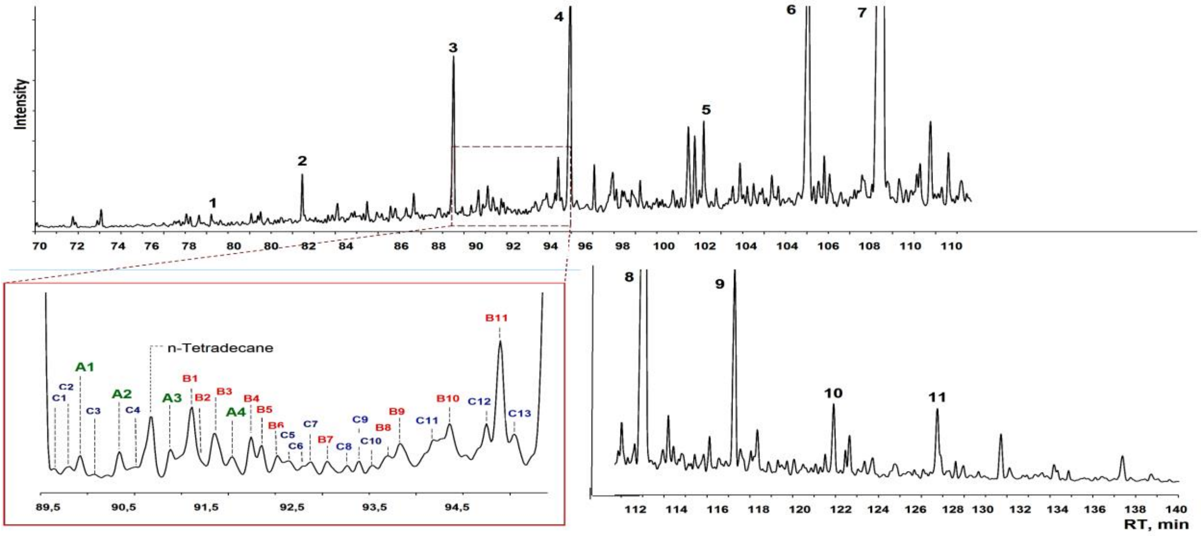

Fig. 3. GC of concentrate VIII obtained after thermal diffusion: Isoprenoides: 1-Undecane 2,6-dimethyl-(C13); 2 -Dodecane 2,6-dimethyl-(C14); 3-Dodecane, 2,6,10-trimethyl-(C15); 4-Tridecane 2,6,9trimethyl-(C16); 5–Tetredecane 2,6,10-trimethyl-(C17); 6 – Pentadecane 2,6,10-trimethyl-(C18); 7 – Pristan-(C19); 8 - Pristan-(C20); 9 -Heptadecane 2,6,10,15-tetramethyl-(C21); 10 – Octadecane 2,6,10,15-tetramethyl-(C22); 11 – Nonadecane 2,6,10,15-tetramethyl-(C23).

The main components of the VIII thermodiffusion fraction, as it was expected, are C_{11}–C_{22}isoprenoid alkanes. Among them the predominant are 2,6,10,14-tetramethylpentadecane (pristane, $C_{19}H_{40}$) and2,6,10,14-tetramethylhexadecane (phytane, $C_{20}H_{42}$), the well-known biomarkers of oil. Cyclopentanes, cyclohexanes and decalineshaving retention times from 89 to 95 minutes (Figure 4) were characterized by low intensity. The list of compounds detected in the extract is presented in Table 1.

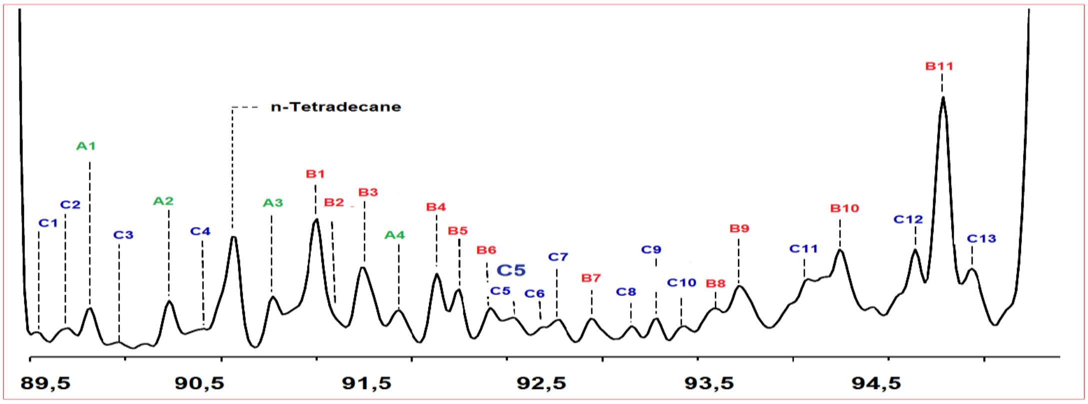

Fig. 4. A part of chromatogram (RT=89-95min) of the VIII fraction:

Table 1. List of hydrocarbons identified in this segment (89 – 95 min)

A1	3-methylhexyl-methylcyclopentane	B1, B3, B5, B8, B10	cyclohexanes with C_9 substituents
A2	1,5-dimethylhexyl-methylcyclopentane	B2, B4, B5, B7, B9	cyclohexanes with C_8 substituents
A3	3-methylhexyl-dimethylcyclopentane	C1-C9	Decalines with 4 C-atoms
A4	3-methylheptyl-methylcyclopentane	C10 – C11, C13	decalines with C_4 substituents
B11	n-octylcyclohexane	C12	1-n-butyldecaline.

Separation of isoalkanes and cycloalkanes present in the thermal diffusion fraction was successfully carried out by formation of inclusion complex (adduct) of thiourea with cycloalkanes and their extraction. Chromatogram of extract obtained after the thiourea adduct formation in the thermal diffusion fraction VIII is shown in Figure 4; extract contains C_{13} – C_{21}bicyclic and C_{19}tricyclic alkanes separated on long capillary column, mass spectra of relict-type bicyclic compounds (decaline and perhydroindane derivatives) are shown in the Figure 5.

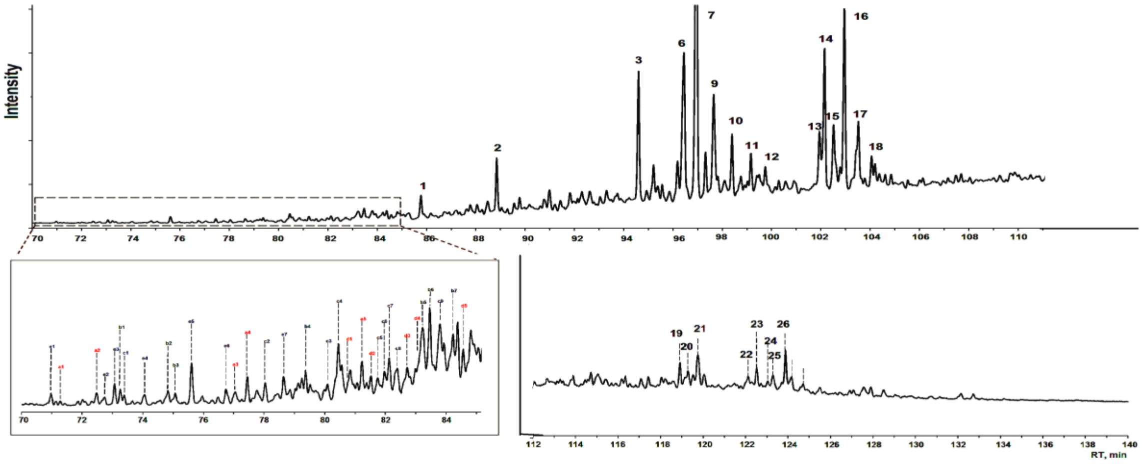

Fig. 5. Chromatogram of extract obtained alter thiorena adduct formation in the VIII fraction 1-Bicycloalkane(C13); 2- Bicycloalkane(C14); 3,4,6,11,13,15- Bicycloalkane(C15); 5,12,14,16,17 - Bicycloalkane(C16); 18 - Bicycloalkane(C17); 19-20 – Bicycloalkane (C20); 23,24,28 – Tricycloalkane (C19); 25-27 - Bicycloalkane(C21).

The initial part of a chromatogram (retention time from 70 to 85 minutes, noted by a dotted rectangle on the Figure 5) is shown on the Figure 7 in the increased scale, and a list of hydrocarbons identified in this segment is presented in Table 2.

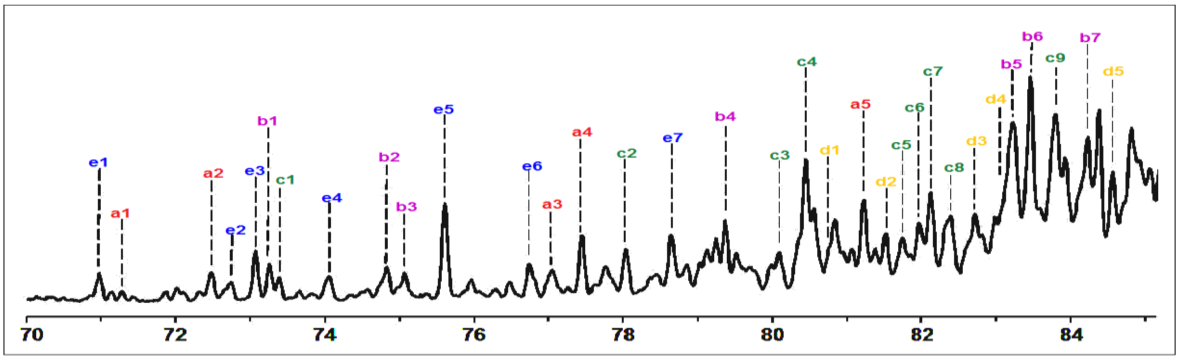

Fig. 6. A segment of chromatogram (RT=70 – 85min) of thiourea extract

Table 2. List of hydrocarbons identified in this segment (70 – 85 min)

a1	3-Methyladamantane	b5	Tricyclo[7.3.0.0^{2,6}]dodecane,
a2	1,4-Dimethyladamantane	b6	Tricyclo[7.2.1.0^{1,6}]dodecane
a3	1,2-Dimethyladamantane	b7	Tricyclo[6.3.1.0^{4,12}]dodecane
a4	1,3-Dimethyladamantane	e1–e5	Methyldecalines
a5	2-Ethyladamantane	e6–e7	Ethyldecalines
d1	1,3,5,6-Tetramethyladamantane	c1	1,3,4-Trimethyladamantane
d2	1-Methyl-3-propyladamantane	c2	1,3,5-Trimethyladamantane
d3	1,3-Diethyladamantane	c3	1,3,4-Triethyladamantane
d4	2-n-Butyladamantane	c4	1-Ethyl-2-methyladamantane
d5	1-n-Butyladamantane	c5	Tricyclo[7.3.1.0^{5,13}]tridecane
b1	Tricyclo[4.3.1.1^{3,8}]undecane	c6	1-n-Propyladamantane
b2	Tricyclo[6.3.0.0^{1,5}]undecane	c7	1-Methyl-3-ethyladamantane
b3	Tricyclo[6.2.1.0^{2,6}]undecane	c8	2-Methyl-1-ethyladamantane
b4	Tricyclo[5.2.2.0^{2,6}]undecane	c9	2-n-Propyladamantane

Among bicycloalkanes the content of the relict-type structures – the long-chain derivative of perhydroindan – 1-(2-methyl, hexyl)-perhydroindan and polymethyl derivatives of decalin – were determined. Typical structures and corresponding mass-spectra are presented on Figure 7.

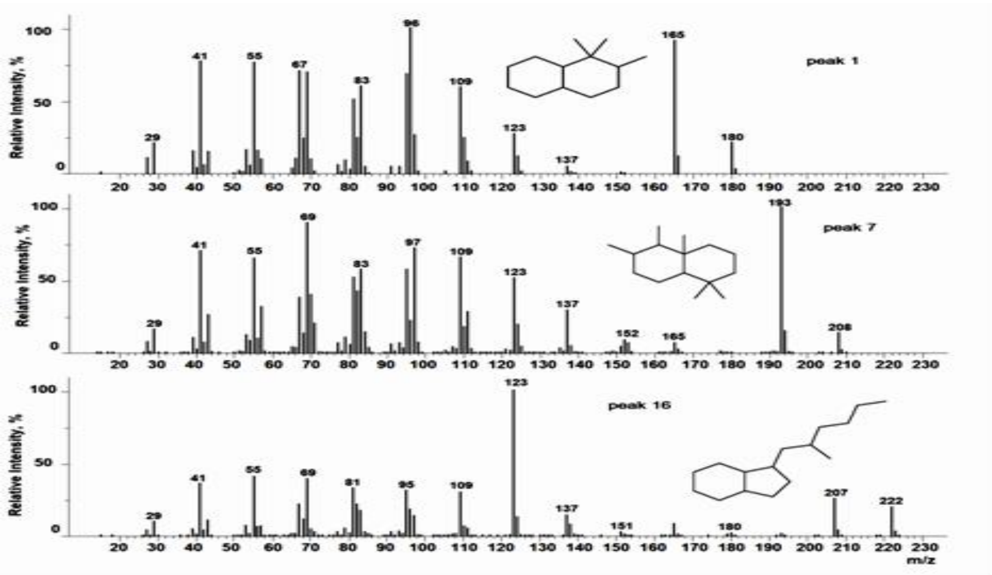

Fig. 7. Mass spectra of (c) 1,1,2-Trimethyldecaline (peak 1), 1,2,3,7,7-Pentamethyldecaline (peak 7) and 1-(2-Methylhexyl)perhydroindane (peak 16).

In the same concentrate were determined protoadamantanes (the adamantanes predecessor compounds in petroleum) – tricycloundecanes (C_{11}), homoadamantane – tricyclo [4,3,1,$1^{3,8}$) undecane having a seven-member cycle in its structure, tricyclododecanes (C_{12}) and perhydrophenalene – tricyclo [7,3,1,$0^{5,13}$]tridecane (C_{13}). The structures of tricycloalkanes with compact structures – polyedranes found in the extract are of particular interest. An efficient separation of these compounds became possible on the above mentioned 200 m capillary column. Typical structures and corresponding mass-spectra are presented on Figure 8.

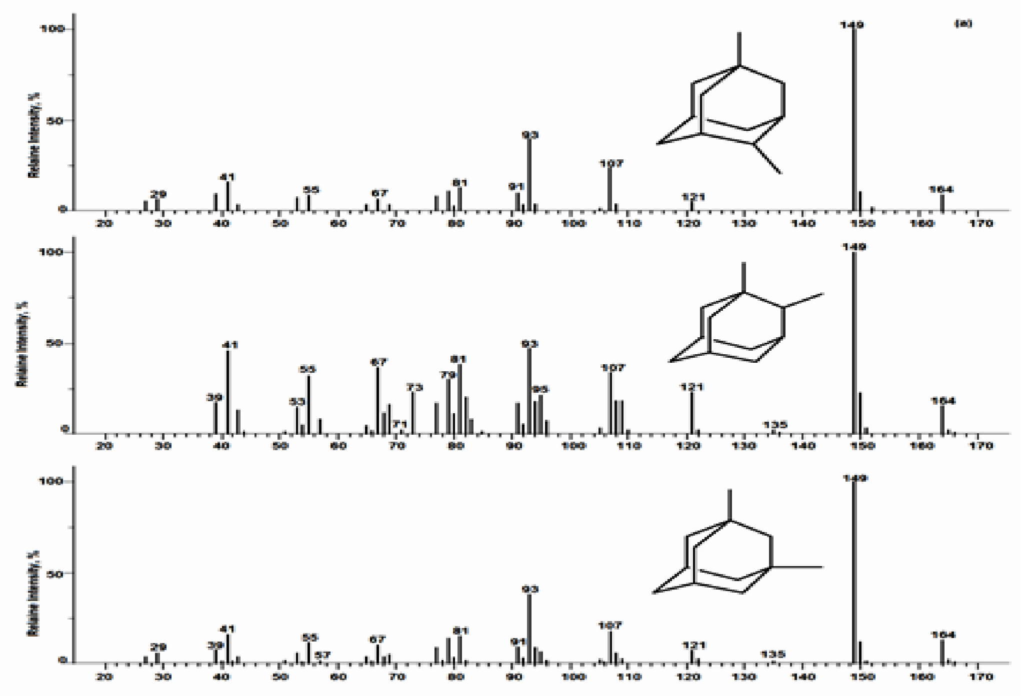

Fig. 8. Mass spectra of (a) 1,4- (peak a2), 1,2- (peak a3) and 1,3-Dimethyladamantanes (peak a4)

18 derivatives of adamantane have been identified, among them not only methyl- and ethyl-substituted, but also propyl- and butyl-adamantane were found. Formation of alkyladamantanes in oil is explained by process of isomerization of condensed tricyclic hydrocarbons at contact with aluminosilicate rocks [9]. Formation of adamantane derivatives with long chains (>C_2) hasn't been

confirmed with model experiments and their existence in oil raised doubts. Nevertheless, in Taribani oil 1-n- and 2-n-propyladamantanes (peaks c6 and c9, Figure 9), 1-methyl-3-propyl-adamantane (peak d2), 1-n- and 2-n-butyladamantanes (peaks d5 and d4, respectively) were detected that is confirmed with the corresponding mass-spectra for all derivatives the adamantly cation $C_{10}H_{15}^+$ (m/z 135) is observed, as well as molecular ions $C_{12}H_{20}^+$ (m/z 164) for ethyl-, $C_{13}H_{22}^+$ (m/z 178) for propyl-, and $C_{14}H_{24}^+$ (m/z 192) for butyl-derivatives are visible in spectra compared with the NIST database.

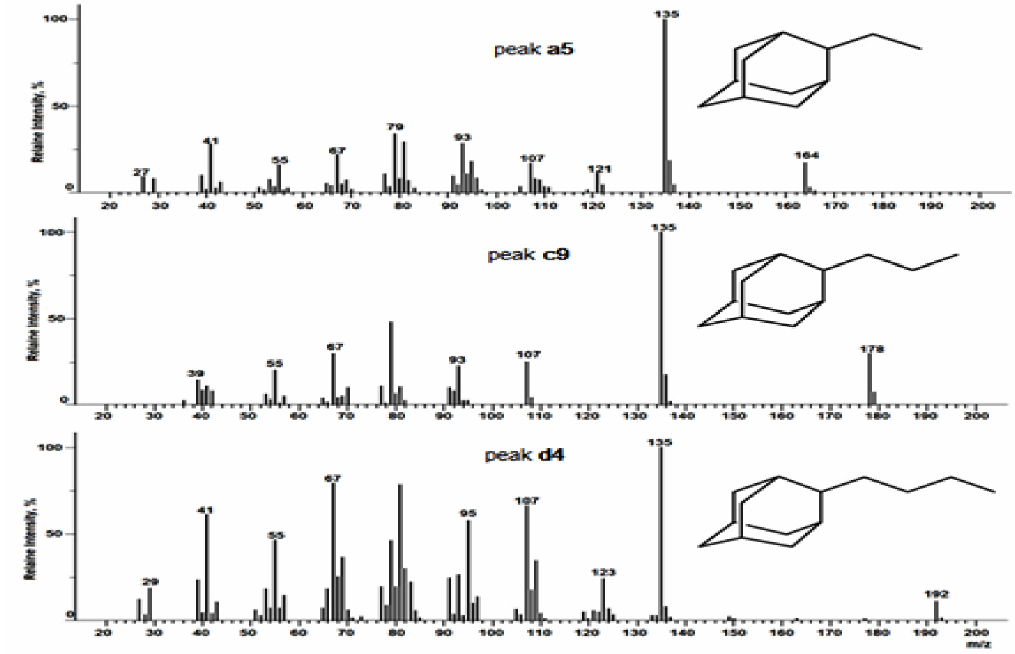

Fig. 9. Mass spectra of (b) 2-Ethyl-(peak a5), 2-Propyl- (peak c9) and 2-Butyladamantanes (peak d4)

Alkyladamantanes with substitute larger than ethyl radical were not found in petroleum prior to our investigation. This could be explained by their formation from tricyclic condenced hydrocarbons by isomerization when entering into contact with aluminosilicate rocks. It was considered that as in such conditions the higher derivatives of adamantane were not formed they could not be present in oils. But 1-n-, 2-n-propyl-, 1-methyl-3-propyl- and 2-n-buthyladamantanes were detected in Taribani oil. The presence of these hydrocarbons is difficult to explain, because their probable predecessors were not detected in petroleum, or it can be proposed that they are products of destruction of higher molecular weight petroleum compounds containing adamantane nucleus.

Conclusions.

On the basis of the applied methodology for investigation of individual composition of C_{11}-C_{16} polycycloalkanes from middle 200-250°C and 250-350° fractions of Taribani oil naphthenic concentrates with high degree of homogeneity were obtained. Subsequent extraction of the concentrates with thiourea made it possible to obtain mixtures of tri-, tetra- and pentacyclic hydrocarbons with compact bridge structure – carcass compounds of C_{11}-C_{16} composition. In the thiourea extracts more than 50 individual polycyclic alkanes were identified by methods of GC, MS and GC-MS: adamantane and its nine homologues of C_{10}–C_{13} composition; twelve tricyclic C_{11}–C_{13} hydrocarbons (tricycloundecanes and tricyclododecanes – bridge tricycloalkanes, the predecessors of adamantanes in oil); ten tetracyclic C_{12}–C_{16} hydrocarbons containing adamantane structure in polycyclic system; four pentacyclotetradecanes – diamantane ($C_{14}H_{20}$) and its three derivatives of $C_{15}H_{22}$ composition; six bicyclic hydrocarbons with sesquiterpene type structure, polymethyl-substituted decalines of C_{14}–C_{16} composition, structure of which have relict character.

It should be noted that at a research of the Taribani oil ten compounds have been detected in oil for the first time: tricyclo [5.2.2.$0^{3,7}$]undecan ($C_{11}H_{18}$,); 1-n-propyladamantane ($C_{13}H_{22}$), 1-ethyl-2-methyl-adamantane ($C_{13}H_{22}$), metyltetracyclo[6,3,1,$1^{6.10}0^{2.6}$]tridecan (C14H22); 1-methyl- and 3-methyl-diamantanes ($C_{15}H_{22}$), tetracyclo[7.3.1.$0^{2,7}$,$1^{7,11}$]tetradecan ($C_{14}H_{22}$) and its homological range of tetracyclo[7.3.1.$0^{2,7}$,$1^{7,11}$]tetradecan up to hexamethyl-substituted ($C_{15}H_{24}$ – $C_{20}H_{34}$).

The main components of the VIII thermodiffusion faction, as it was expected, were C_{11}-C_{22} isoprenoid alkanes. Among them the predominant were pristane C_{19} and the phytane C_{20}, the well-known biomarkers of oil. In the thyourea extract of the VIII thermodiffusion fraction 18 hydrocarbons containing adamantan skeleton, including dimethyl-, trimethyl-, tetramethyl-, ethyl-, methyl-ethyl-, diethyl-, propyl, methyl-propyl adamantanes were identified.

In Taribani oil the presence of following compounds was established for the first time: **2-n-propyladamantane**; 1-methyl,3-propyladamantane and **2-n-buthyladamantane**.

Acknowledgement. The authors express thanks to Carlos Gonzalez, Anzor Mikaia, and the **NIST** (USA) team for carrying out MS measurements.

REFERENCES

1. Topuria E, Lekveishvili E, Khetsuriani N, Edilashvili I (2007) Investigation of hydrocarbon-type content of middle and high-boiling fractions of Georgian oils by mass- and chromato-mass-spectrometry methods. Mass-spectrometry 4(3): 197-226.
2. Topuria E.N, Khetsuriani N.T. (2011) Chromato-mass-spectrometric investigation of polycycloalkanes of middle fractions of Georgian oils. IX International mass-spectrometric conference in petrochemistry, ecology and food chemistry “Petromass”, Moscow (Russia): 143-151.
3. Topuria E.N, Khetsuriani N.T,Tretyakov KV, Gonzalez CA, Mikaia A.I. (2013) GC-MS study of the composition of saturated hydrocarbons in high-boiling fractions of Georgian oils. Eastern Analytical Symposium, Gaithersburg (USA): 97.
4. Jones A.L, Milberger EC (1953) Separation of Organic Liquid Mixtures by Thermal Diffusion. Industrial & Engineering Chemistry 45(12): 2689-2696.doi: 10.1021/ie50528a039
5. Ryzhkov I. I. (2013) Thermal Diffusion in Mixtures: Equations, Symmetries, Solutions and Their Stability (Publishing House of SB RAS, Novosibirsk) (in Russian). 200p.
6. Schimpf M. E. (2000) “Thermal field-flow fractionation,” in Field-Flow Fractionation Handbook, edited by M. E. Schimpf, K. Caldwell, and J. C. Giddings (Wiley, New York), p. 239.
7. Müller G, Vasaru G (2008) TheClusius-Dickel Thermal Diffusion Column – 50 Years after its Invention.Isotopenpraxis Isotopes in Environmental and Health Studies24(11-12):455-464. doi:10.1080/10256018808624027.
8. Schiessler RW, Flitter D (1952) Urea and thiourea adduction of C5-C42-hydrocarbons. Journal of American Chemical Society 74 (7): 1720–1723. doi: 10.1021/ja01127a033
9. Petrov AA (1984) Oil hydrocarbons [in Russian]. Nauka: Moscow, p 264.
10. James G.Speight (2011) Handbook of Industrial Hydrocarbon Processes. English, eBook ISBN: 9780080942711 Imprint: Gulf Professional Publishing; Hardcover ISBN**:** 9780750686327, 636p.
11. Kashirtsev VA, Nesterov II, Melenevskii VN, Fursenko EA, Kazakov MO, Lavrenov AV (2013) Biomarkers and adamantanes in crude oils from Cenomanian deposits of northern West Siberia. Russian Geology & Geophysics 54(8): 958-965. doi: org/10.1016/j.rgg.2013.07.012