

CHEMISTRY

CHEMICAL TYPIFICATION AND GENETIC CRITERIA FOR THE COMPOSITION OF GEORGIAN PETROLEUM

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ABSTRACT

The results of investigation of molecular composition of biological markers of Eastern Georgia crude oils by methods of GLC, MS, GC/MS, genetic and geochemical aspects of their chemical composition, the main geochemical criteria for making various genetic correlations are presented. It was established that though these crude oils belong to different chemical types they all belong to a single genetic type. High concentrations of isoprenoid alkanes, ratio $iC_{19}/iC_{20} > 1$, were revealed. In fractions higher than 420°C amongst the main biomarkers — steranes and triterpanes ($C_{27}-C_{33}$) – prevail hopanes of the 17 α H-hopan series ($C_{30}H_{52}$); steranes ($C_{27}-C_{29}$) are represented by α -steranes and iso-steranes. Based on the main geochemical criteria the degree of catagenesis of oils and the probability of biodegradation of some of them was determined. In some crude oils polymethylsubstituted decalines, the relict type hydrocarbons ($C_{14}-C_{16}$) have been identified.

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Introduction. Organic geochemistry is a scientific direction in chemistry of natural biological compounds, the main task of which is study of composition and chemical evolution of organic molecules in sedimentary rocks [1]. These fossil molecules, chemofossils (relict hydrocarbons) of plant and animal origin, after being deposited in rocks, remained almost unchanged. They are unique as they preserved identity or underwent insignificant change in composition and structure of the carbon skeleton of the

original biological molecules that took part in the processes of oil formation [2]. These relicts are considered as the most important biomarkers or geochemical labels that are used in understanding of biological conditions and many problems of oil genesis. Any regularity in their distribution in samples is geochemical criterion and allows to understand the nature and origin of the source of raw material, its age, degree of decomposition and catagenetic maturity. This information is used to carry out various geochemical correlations, genetic and chemical typifications of oils and to solve various problems of petroleum geochemistry [3]. The composition and molecular-mass distribution of chemofossils in oils determine the genetic type of oils. In contrast to the genetic type, the chemical type (composition) is changed with time under the impact of thermobaric, catalytic factors, water-oil contact and post-genetically changes of oils (biodegradation and migration) [4]. The role of hemofossils in perception of oils in general is invaluable. The most important biomarkers are normal and isoprenoid alkanes, cyclic hydrocarbons with one to five cycles per molecule, C₁₉-C₃₅ sterane and terpane hydrocarbons, sesqui-, di- and triterpane series, terpenes, steroids, porphyrins and relatively little-studied aromatic hydrocarbons with relict type structure [5]. Currently, more than 1000 different biomarkers have been identified in oils and organic matter of rocks. Among them, new representatives of the hemofossils, characteristic of the most ancient organisms belonging to the natural habitat of Bacteria, Archaea, Eucarya, have been discovered [6]. Biomarkers along with isotopic composition of carbon are the main source of information about the bios during the ancient periods of the Earth [7].

In this article are presented the results of the study of molecular composition of relict hydrocarbons of some Georgian crude oils, are considered genetic and geochemical aspects of their chemical composition, the main geochemical criteria that give a possibility to make various genetic correlations.

Purpose of the study: chemical and genetic type of Georgian Petroleum.

Materials and methods. All used chemicals were of analytical grade. The HPLC/GC grade methanol, n-pentane, benzene, and petroleum ether were purchased from Sigma-Aldrich and Merck (Germany) companies. Activated fine silica gel (0.07–0.15 and 0.2–0.3 mm) was supplied by Labstatus (Ukraine) and ChemReactiveSnab (Almaty, Kazakhstan) companies. The coarse silica gel (0.4–2.5 mm) was supplied by Salavat catalyst plant (Russia). Carbamide- CaS Number 57-13-6; Beilstein Number 635724; Sigma-Aldrich (Germany) and 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%). Apiezon L Ultra High Vacuum Grease, Silicone & Halogen Free, CAS #8009-03-8 were supplied by Sigma-Aldrich (Germany).

The following methods were used for the study: distillation, liquid adsorption chromatography, gas-liquid chromatography; deparaffinization by carbamide; three stage thermal diffusion; extraction by thiocarbamide, mass spectrometry and chromatography-mass spectrometry.

The gas-liquid chromatographic separation of the studied fractions was carried out on capillary columns in the following conditions: the fraction 50-200°C (column 100m × 0.25mm, linear programming of temperature from 50 to 200°C with a speed of 2°C/min); the fraction 200-350°C, the VIII fraction of thermodiffusion separation (column 200 m x 0.25 mm with dimethylpolysiloxane, liner programming of temperature from 40°C to 280°C with a speed of 2°C/min, hold 70 min) and filtrates of the thiourea adducts with the mixture of IX+X thermal diffusion fractions (column 50m × 0.25mm, linear programming of temperature – from 100°C to 280°C with a speed of 2°C/min); fractions 200-420°C (column 100m × 0.25mm, 50 thousands of theoretical plates, linear programming of temperature – from 100°C to 320°C with a speed of 2°C/min); the fraction >420°C – the same column, temperature of thermostat 290°C; liquid phase – Apiezon L.

Chromatography-mass spectrometry analysis was performed on the LKB-2091 instrument. The ion source temperature was 50°C and the ionization potential was 70 eV. Stainless steel column 40 x 0.4mm; 50 thousands of theoretical plates; programmed temperature according to samples.

Experimental part.

For the study of molecular composition of relict hydrocarbons, samples of crude oils from the main oil and gas regions of Eastern Georgia – Samgori, Teleti, Shromis-Ubani, Norio, Ninotsminda, Mirzaani, Taribani, Satskhenisi [8] were studied. These oils belong to a single sedimentation basin, are of different chemical type, have close geological age of the host rocks and a different depth of bedding.

The objects of the investigation were saturated hydrocarbons of fractions 50-200°C, 200-350°C, 200-420°C and >420°C, that were dearomatized on activated fine and coarse silica gel; fractions 200-350°C and >420°C were as well deparaffinized by conventional method; the components of composition was studied by GLC.

In the light fractions (50–200°C) of the studied oils, over 100 individual hydrocarbons of C₅–C₁₁ composition were identified. Interesting regularities were found in the composition of cyclopentanes and cyclohexanes; in addition, when studying distribution of isomeric nonanes and decanes the highest levels of 2,3- and 2,6-dimethylalkanes, as well as of 2-methyl-3-ethylheptane, the main relicts of light fractions of oils, were found.

Chromatogram of the thermodiffusion fraction VIII (the 200–350°C fraction of Taribani oil) is shown in Figure 1. 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. The main components of the VIII thermodiffusion fraction, as it was expected, are C₁₁–C₂₂ isoprenoid alkanes. Among them the predominant are 2,6,10,14-tetramethylpentadecane (pristan, C₁₉H₄₀) and 2,6,10,14-tetramethylhexadecane (phytane, C₂₀H₄₂), the well-known biomarkers of oil. Cyclopentanes, cyclohexanes and decalines having retention times from 89 to 95 minutes (Figure 1) were characterized by low intensity.

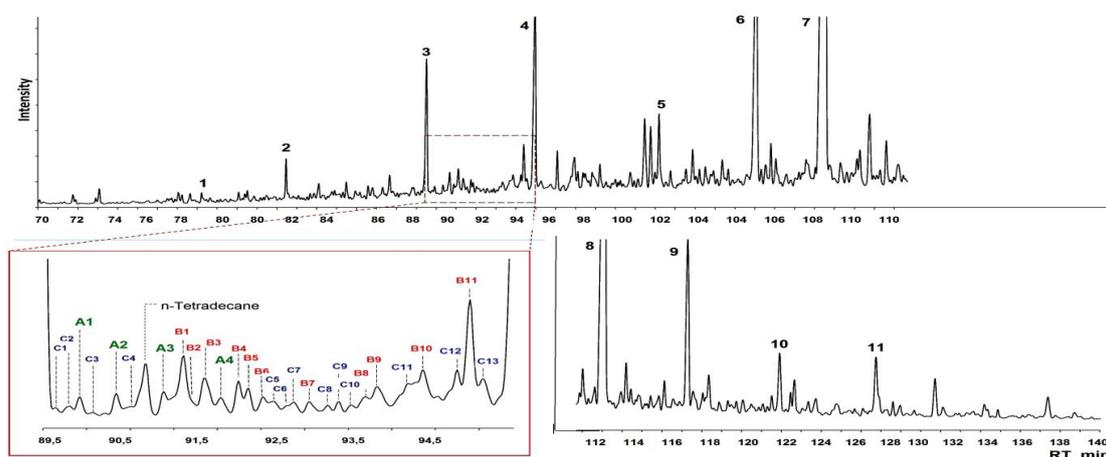


Fig. 1. GC of concentrate VIII obtained after thermal diffusion: Isoprenoids: 1-Undecane 2,6-dimethyl-(C₁₃); 2-Dodecane 2,6-dimethyl-(C₁₄); 3-Dodecane, 2,6,10-trimethyl-(C₁₅); 4-Tridecane 2,6,9-trimethyl-(C₁₆); 5-Tetradecane 2,6,10-trimethyl-(C₁₇); 6-Pentadecane 2,6,10-trimethyl-(C₁₈); 7-Pristan-(C₁₉); 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).

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 2. [9].

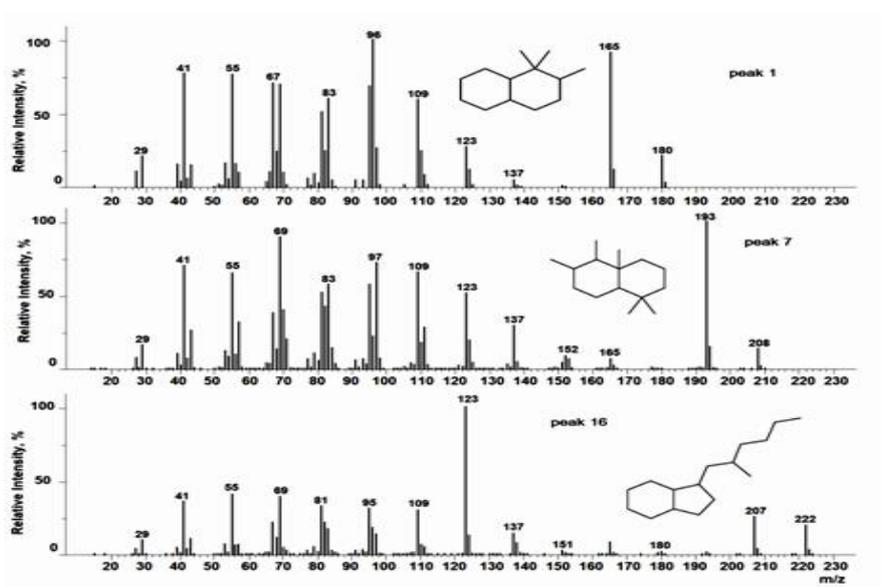


Fig. 2. Mass spectra of (c) 1,1,2-Trimethyldecaline (peak 1), 1,2,3,7,7-Pentamethyldecaline (peak 7) and 1-(2-Methylhexyl)perhydroindane (peak 16).

Based on the study of relative distribution of the main relict hydrocarbons — normal C₁₂-C₃₂ and isoprenoid C₁₄-C₂₂ alkanes in middle fractions boiling away at a temperature of 200–420° C, “the chemical typification” of oils was carried out on highly efficient capillary columns according to the method of prof. Al.A. Petrov [10]. From the chromatograms for all the above listed oils the mentioned above ratios were calculated and the corresponding diagrams were plotted. Relative distribution of normal and isoprenoid alkanes in oils of the type opposite to Taribani A¹ and Satskhenisi B² oils is shown on Figures 1 and 2[11]. Based on the diagrams, the geochemical isoprenoid coefficients $K_i = \frac{\sum iC_{19}-iC_{20}}{\sum nC_{17}-nC_{18}}$ and catagenetic coefficients $K = \frac{\sum nC_{13}-nC_{15}}{\sum nC_{25}-nC_{27}}$, the values of which are related to the biodegradation and catagenetic transformation of oils, as well as geochemical criteria – the ratio of pristane to phytane iC_{19}/iC_{20} , which are used to carry out various geochemical correlations are determined. On the basis of these characteristics the studied oils are confined to various chemical types: Samgori- A¹, Ninotsminda-A¹, Shromis-Ubani-A², Mirzaani-B², Norio-B¹, Teleti-B¹, Taribani-A¹, Satskhenisi-B². Oils of A¹ type by group composition correspond to paraffin oils; B² oil – to naphthenic oils. The oils of A² and B¹ types have intermediate characteristics of chemical composition. The study of the individual composition of oils showed that normal alkanes were present in large quantities in oils of A type. But a characteristic feature of all types of Georgian oils is high concentration of isoprenoid structures, especially of regular isoprenoids (iC_{19} and iC_{20}), moreover, with a large predominance of pristane. Relative distribution of normal and isoprenoid alkanes in 200–420°C fraction of Taribani and Satskhenisi oils are shown in Figures 3 and 4. Therefore, for almost all oils, the ratio iC_{19}/iC_{20} is higher than 1. This indicator ($iC_{19}/iC_{20} > 1$) is an important geochemical characteristic associated both with the origin and with transformation of oil during the processes of biodegradation and catagenesis [12]. Norio oil is an exception: iC_{19} and iC_{20} are completely absent in it, and iC_{14} and iC_{16} are present in high concentrations. Characteristics of the studied oils are given in table 1.

Table 1. Characteristics of Georgian Petroleum

Name of the Crude oil, well No.	Depth of Bedding, m	Age of the enclosed rocks	Density (kg/ m ³)	Tars and asphaltenes, %	S, %	Chemical type	Genetic mark iC_{19}/iC_{20}
Samgori, 7	2800	Middle Eocene	886.0	18.2	0.25	A ¹	2.2
Ninotsminda, 27	2800	Middle Eocene	892.0	18.5	0.23	A ¹	2.2
Shromis-Ubani, 1	3000	Late Miocene	927.0	32.9	0.37	A ²	1.6
Norio, 35	1400	Middle Sarmat	924.0	21.5	0.15	B ¹	1.9
Teleti, 18	500	Middle Eocene	876.0	18.4	0.18	B ¹	1.7
Mirzaani, 109	1100	Lower Pliocene	875.5	14,72	0.22	B ²	0.3
Taribani, 23	2374	Late Sarmat	838.6	14.84	0.25	A ¹	1.7
Satskhenisi, 4	1400	Late Oligocene	836.1	32.68	0.26	B ²	2.2

By the method of mass spectrometry for the hydrocarbons in the paraffin-cycloparaffin part of all studied oils, the structural group composition of the middle (200-420°C) fractions – the relative distribution of alkanes and mono-, bi-, tri-, tetra- and pentacyclic naphthenic hydrocarbons, inherited by oils from the original organic matter, was determined. From the geochemical point of view, this characteristic is one of the genetic characteristics, which indicates both the distribution of naphthenic hydrocarbons and the single genetic type of Georgian oils (the so-called "naphthenic passport"). This characteristic shows that the cyclic compounds in various Georgian oils are represented in high concentrations.

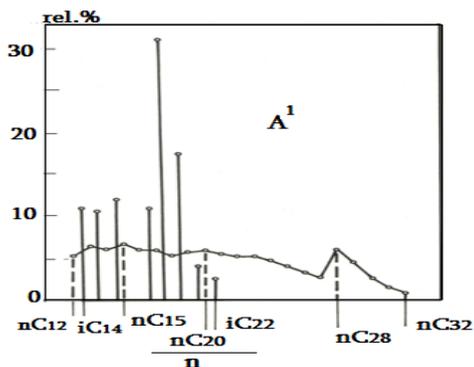


Fig. 3. Relative distribution of normal (C_{12} – C_{32}) and isoprenoid (C_{14} – C_{22}) alkanes in the fraction 200–420°C of Taribani oil.
n – number of carbon atoms in alkanes

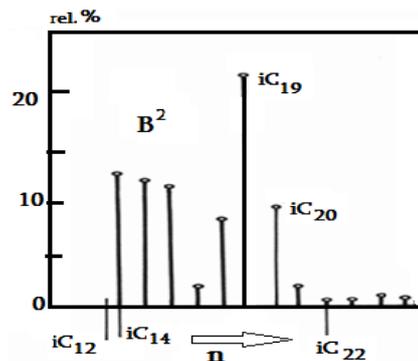


Fig. 4. Relative distribution of isoprenoid (C_{14} – C_{22}) alkanes in the fraction 200–420°C of Satskhenisi oil
n – number of carbon atoms in alkanes

Fractions 200-350°C and > 420°C that contained mainly polycycloalkanes were subjected to thermal diffusion with the aim of separation of concentrates from them. By using of thermal diffusion method with selection of optimal conditions (temperature gradient, separation time) and column efficiency it becomes possible to extract successfully concentrates of different hydrocarbons from oil 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 microcolumns 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- and trans-decalines (1 : 1) is maximum $S = 99\%$ 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 [13]. The columns have 10 drain cocks that provide separation of mixtures into ten equal-volume fractions. For extraction of naphthenic concentrates, saturated fractions of 200-350°C and >420°C were subjected to two-fold thermal diffusion (temperature gradient 130°C–150°C, separation time – 100 hours). At the end of the process a mixture of fractions (IX+X) – naphthenic concentrates was taken [14].

According to data of MS analysis in concentrates of fraction 200–350°C mainly (~90%) tri-, tetra- and pentacycloalkanes of compact structure and bicycloalkanes of C_{14} – C_{16} composition were present. Concentrates, obtained from the 200-350°C fraction in order to hydrocarbons that form adducts were treated with thiocarbamide (conditions: thiocarbamide: fraction = 1 : 1; activator-methanol; diluent-benzene; time 25h; temperature 6°C) [15]. In the residual filtrates of concentrates from Taribani, Satskhenisi, Norio and Teleti oils the relict bicycloalkanes – the polymethylsubstituted decalines of C_{14} – C_{16} composition were identified. Hydrocarbons (1–6) were determined in Taribani, (2, 3, 6) in Satskhenisi and (2, 4) in Norio and Teleti oils [16]. On chromatograms of the filtrates (Fig.5) peaks corresponding to the said hydrocarbons are marked with numbers 1'–6' (for Taribani oil) and 1–3 (for Satskhenisi oil). Composition and structure of the said hydrocarbons is determined by chromatography-mass spectrometry analysis. The characteristic peaks of mass-spectrometric destruction, the assumed structures and gross formulas of the identified polymethylsubstituted decalines are presented in Table 2.

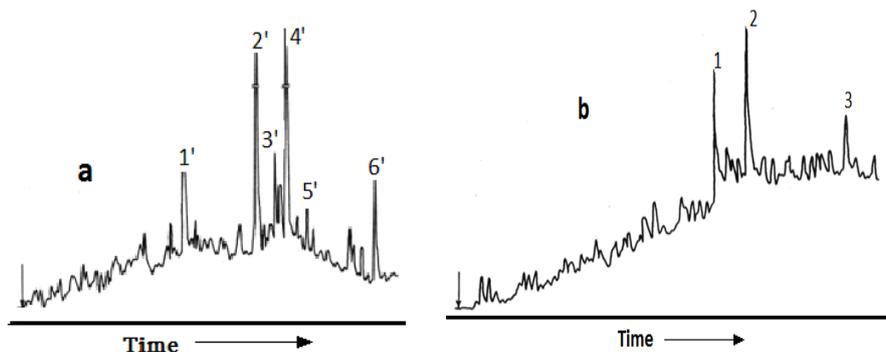
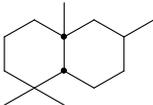
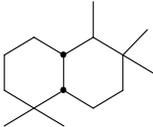
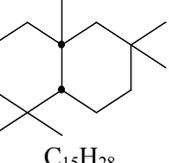
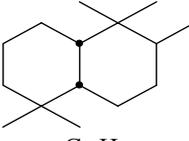
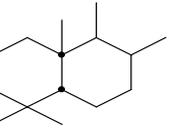
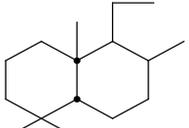


Fig. 5. Chromatogram of bicycloalkanes from the 200–350 °C fractions (a) of Taribani and (b) Satskhenisi Crude Oils

Table 2. Polymethylsubstituted decalines, identified in Georgian Petroleum

# of hydrocarbon In samples ^a				Name of Hydrocarbon	Structural and brutto-formula	Characteristic peaks in mass-spectra (intensity in % of the maximum peak) m/z (I, rel %)
I	II	III	IV			
1	-	-	-	cis-1,3,7,7-tetramethyl-trans-bicyclo-/4,4,0/decane	 C ₁₄ H ₂₆	194(M ⁺ ;21), 180(8), 179(72),138(7), 137(16), 122(18), 121(68), 110(45), 109(69), 97(37), 96(23), 95(75), 83(43), 82(32), 81(100), 69(72),55(40)
2	2	2	2	trans-2,3,3,7,7-pentamethyl-trans-bicyclo-/4,4,0/decane	 C ₁₅ H ₂₈	208(M ⁺ ;16), 194(15), (100), 179(6), 163(9), 149(10), 138(6), 137(35), 124(11), 123((48), 111(21), 110(12), 109(48), 97(27), 96(15), 95(52), 83(52), 82(23), 81(26), 69(55), 57(27), 55(26)
3	3	-	-	1,3,3,7,7-pentamethyl-trans-bicyclo/4,4,0/-decane	 C ₁₅ H ₂₈	208(M ⁺ ;34), 194(9), 193(75), 179(14), 178(10), 177(24),165(24),164(10),163(27), 151(20), 150(9), 149(22), 138(12), 137(33), 124(35), 123(67),111(25),110(25), 109(100), 97(65), 96(43), 95(85), 83(69), 82(41), 81(73), 70(42),69(83), 57(43),55(55)
4	-	4	4	cis-2,2,3,7,7-pentamethyl-trans-bicyclo-/4,4,0/decane	 C ₁₅ H ₂₈	208(M ⁺ ;20), 194(7), 193(100), 179(6), 177(7), 165(11), 163(6), 151(9), 150(9), 149(25), 137(32), 135(12), 124(25), 123(49), 149(51), 97(31), 96(25), 95(85), 83(31), 82(29), 81(61), 70(71), 69(65), 68(13), 67(26), 58(26), 57(29), 55(36)
5	-	-	-	trans-cis-1,2,3,7,7-pentamethyl-trans-bicyclo /4,4,0/decane	 C ₁₅ H ₂₈	208(M ⁺ ;27), 194(6), 193(41), 165(4), 139(2), 138(13), 137((32), 124(17), 123(100), 109(26), 97(7), 96(4), 95(35), 83(9), 82(11), 81(27), 79(2), 69(25), 68(4), 67(16), 57(8), 55(22)
6	6	-	-	1,3,7,7-tetramethyl-2-ethyl-trans-bicyclo /4,4,0/decane	 C ₁₆ H ₃₀	222(M ⁺ ;37), 207(15), 194(5), 193(56), 177(10), 138(20), 137(37), 124(21), 123(100), 111(8), 110(14), 109(63), 97(18), 96(13), 95(58), 83(25),82(6), 81(58), 69(51), 70(12), 67(26), 57(25),55(40)

^a Oils from I - Taribani, II - Satskhenisi, III - Norio, IV - Teleti deposits.

From the geochemical point of view large molecules of relict type saturated hydrocarbons – tetra- and pentacyclic naphthenes, namely steranes and triterpanes, the predecessors of which are considered to be natural steroids and triterpenoids found in various geological objects are of particular interest [17]. Steranes and triterpanes of the saturated hydrocarbon fractions of Georgian oils Norio, Teleti, Mirzaani, Sartichala, Ninotsmindai, Shromis-Ubani, boiling away above 420°C have been studied [18]. Saturated hydrocarbons were separated from oil fractions residues by chromatography on

ASK silica gel. In case of paraffinic oils the normal alkanes were removed by treatment with thiourea. Concentration of tetra- and pentacycloalkanes was carried out by the method of thermomodification. Analysis of concentrates and qualitative identification of the main gas-chromatographic peaks was carried out by gas-liquid chromatography and chromatography-mass-spectrometry methods. The results of the studies are presented in Tables 3 and 4.

Table 3. Relative concentration of 17 α H-hopane series hydrocarbons of Georgian oils in fraction with boiling point > 420°C

Grude Oil deposit	Number of carbon atoms						Σ hopanes, in mass % (per oil)
	27	29	30	31	32	33	
Norio	2,5	11,0	31,2	25,8	16,7	12,8	0,60
Teleti	6,6	10,3	35,9	21,7	14,5	11,0	0,20
Mirzaani	8,2	12,7	30,6	22,7	18,4	7,4	0,20
Samgori	7,7	12,3	33,3	23,3	13,6	9,8	0,40
Ninotsminda	7,9	9,7	26,7	22,1	17,2	16,4	0,35
Shromis-Ubani	1,8	14,7	32,1	26,2	14,2	11,0	0,10

Table 4. Relative concentration of sterane hydrocarbons in fraction with boiling point > 420°C

Crude oil Deposit	Cholestanes C ₂₇			Ergostanes C ₂₆			Sitostanes C ₂₉				$\frac{\Sigma \text{Hopanes}}{\Sigma \text{Steranes}}$	$\Sigma \text{Steranes}$ mass%
	iso	α	$\Sigma \text{iso} + \alpha$	iso	α	$\Sigma \text{iso} + \alpha$	iso	α	$\Sigma \text{iso} + \alpha$	α/iso		
Norio	21,2	6,6	27,8	26,9	14,5	41,4	24,9	5,9	30,8	0,24	2,3	0,30
Teleti	27,6	6,9	34,5	23,6	10,6	34,2	23,7	7,6	31,3	0,32	1,1	0,20
Mirzaani	28,2	7,2	35,4	36,5	6,4	42,9	17,6	4,1	21,7	0,23	0,8	0,25
Samgori	35,1	5,7	40,8	26,9	6,2	33,1	20,4	5,7	26,1	0,28	1,1	0,40
Ninotsminda	28,7	7,3	36,0	25,9	10,8	36,7	17,7	9,6	27,3	0,54	1,2	0,30
Shromis-Ubani	21,1	9,8	30,9	25,5	11,1	36,6	20,3	12,2	32,5	0,60	2,8	0,03

The research results. The structure of polymethylsubstituted decalines from fractions 200-350°C is determined by chromatography-mass spectrometric degradation method according to their characteristic peaks. When determining the location of the alkyl substituent it was taken into account that the presence of two geminal CH₃ groups led to a sharp increase of /M-15/⁺ ion peak intensity in the mass spectra in contrast to the simultaneous presence of geminal and angular groups. In spectra corresponding to hydrocarbons 2, 3 and 4 (Table 2), there are low-intensity peaks of molecular ions M⁺(m/z 208) and maximum intensity peaks of ions (M-CH₃)⁺ with m/z 193 (tearing of methyl from molecular ion). At the same time, there are no fragments with a mass corresponding to tearing of the ethyl- (M⁺-29) and propyl- or isopropyl group (M⁺-43). The hydrocarbons under study are bicycloalkanes with many methyl groups. In hydrocarbons (1, 5, 6) with one geminal group, the peaks of M⁺ ions are insignificant. Hydrocarbons (2, 3, 4) were attributed the structure of the sesquiterpane type, the composition of C₁₅H₂₈ [19], and hydrocarbons (1, 5, 6) – of polymethyl-substituted trans-decalines. The peculiarity of the structure of these hydrocarbons indicates the generality of their genesis [20]. They have a clearly relict character and most probably are genetically associated with important relicts – the hopanes [21].

The results of the study of relative distribution of the main biomarkers of oils – steranes and hopanes, make it possible to establish that the studied crude oils belong mainly to the 17 α H-hopane series [22]; the yield of the sum of hopanes per oil is from 0.1 to 0.6%, and the sum of steranes - from 0.03 to 0.4%. At the same time, 17 α H-hopane itself (C₃₀H₅₂) is present in maximum concentration.

Triterpanes (C_{27} - C_{33}) are represented mainly by hopane homologues. Steranes (C_{27} - C_{29}) in crude oils are represented by α -steranes and isosteranes. They are characterized by cis-coupling of C/D cycles and constitute the main mass of steranes. Mirzaani oil is an exception. There is predominance of sterane structures. The distribution of steranes and hopanes make it possible to determine important geochemical parameters that carry genetic information about the degree of catagenetic conversion of oils, the chemical composition of the oil-producing biomass, etc. [23]. Based on the studied relicts, various genetic correlations were carried out [24]. It was established that despite the difference in chemical composition of oils they belong to a single genetic type in terms of geochemical parameters - the ratio of the main relict hydrocarbons: pristan/phytan (iso- C_{19} /iso- C_{20}), Σ hopanes/ Σ steranes (Tables 1, 3, 4), as well as distribution of n-, iso- and cycloparaffin hydrocarbons in fractions 200-420°C ("naphthenic passport"). To reveal catagenetic maturity of oils, other indicators were calculated, for example: concentrations of secondary steranes of C_{27} composition, ratio α -steranes/iso-steranes, etc. The highest degree of catagenesis was determined for Samgori oil, and the lowest one – for oil from the Shromis-Ubani deposit. The possibility of probable biological degradation of some of these oils in pools is assumed. Although, their different chemical composition may be stipulated to different conditions of bedding and biological oxidation. Formation of B¹ and B² type oils – Teleti, Norio, Mirzaani, Satskhenisi and Shromis-Ubani (A²) – is based on biological oxidation. High concentrations of n-alkanes, isoprenoid alkanes and monocyclic naphthenes in oils of the primary generation A¹ – Samgori, Ninotsminda, Taribani – indicate that they almost did not undergo biodegradation. Biological oxidation probably affects only normal alkanes, leaving isoprenanes unchanged. The data of biological conditions in the oil pools explain the characteristic feature of all types of Georgian oils – the presence of high concentrations of isoprenoid alkanes in them.

Conclusions.

1. Appliance of Georgian oils to different chemical types was determined: Norio, Teleti – B¹; Mirzaani, Satskhenisi – B²; Samgori, Ninotsminda, Taribani – A¹, Shromis-Ubani – A². It was established that despite the differences in chemical composition the studied oils were genetically similar by ratios iC_{19}/iC_{20} , Σ hopanes/ Σ steranes, as well as by "naphthenic passport". The characteristic feature of Georgian oils is revealed – high concentrations of isoprenoid alkanes, pristane (iC_{19}) and phytane (iC_{20}) with high predominance of pristane so the ratio $iC_{19}/iC_{20} > 1$.

2. Polymethylsubstituted decalines, a relict type hydrocarbons the so-called sesquiterpane hydrocarbons of C_{14} - C_{16} composition have been identified in the middle fractions of Taribani, Satskhenisi, Norio and Teleti oils.

3. In high-boiling fractions $> 420^\circ\text{C}$, big tetra- and pentacycloalkane molecules (C_{27} - C_{33}) — steranes and triterpanes with the predominance of hopanes belonging to the 17 α H-hopane ($C_{30}H_{52}$) series have been identified. Hopane itself as 17 α H-hopane is present in maximum concentration. It has been shown that oil steranes (C_{27} - C_{29}) were represented by α -steranes and thermodynamically more stable isosteranes, which constitute the main mass of the steranes studied. The degree of catagenetic conversion of oils was determined according to the ratios $\Sigma nC_{13}-nC_{15}/\Sigma nC_{25}-nC_{27}$, $\Sigma isoC_{19}-isoC_{20}/\Sigma nC_{17}-nC_{18}$, α -isosteranes, etc.

Studies of relict hydrocarbons of Georgian oils have revealed the presence of known biomarkers – saturated relict structures, peculiarity in composition, quantitative and relative distribution of individual biomarkers and their various geochemical ratios that give reason for a more thorough study of the genetic code of Georgian oils.

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