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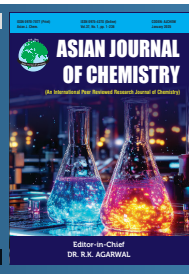

Chemical Composition of Naftalan Oil using Different Analytical Methods

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In this study, the chemical composition of Naftalan oil was analyzed with various techniques like gas-liquid, adsorption chromatography, liquid selective catalytic dehydrogenation and selective isomerization. The isolated components were characterized with IR spectroscopy. The information regarding the structural-group composition of the analyzed fractions, along with IR spectroscopy results, demonstrates a strong correlation and confirms the reliability of this indirect approach for quantifying naphthenic structures.

Keywords: Naftalan oil, Naphthenic hydrocarbons, Silica gel, Adsorbent, Mass spectroscopy.

INTRODUCTION

Naftalan oil, produced in the Naftalan region of Azerbaijan, is one of the few oils with effective therapeutic effects [1]. It has been recognized as an official medicine since early 18th century and has become an effective natural source used in both balneology and pharmaceutical chemistry [2]. Literature showed that Naftalan oil have been successfully carried out in the treatment of a number of diseases such as skin diseases, musculoskeletal system diseases, central and peripheral nervous system diseases, some gynecological diseases and allergic diseases [2].

The therapeutic effects of Naftalan oil on skin conditions are primarily associated with the inflammatory diseases such as psoriasis [3]. In a study conducted at the Special Hospital for Medical Rehabilitation in Naftalan, the impact of naftalan oil therapy on psoriatic skin lesions was evaluated in a group of Danish patients treated between 2006 and 2011 [4]. After three weeks of treatment, the mean PASI (Psoriasis Area and Severity Index) score significantly decreased from 13.8 to 3.8. These findings confirmed the excellent antipsoriatic efficacy of Naftalan oil therapy (Fig. 1).

Mamedaliev [5,6] analyzed the chemical composition of Naftalan oil first time and hypothesized that one of its main active components was polycyclic naphthenic hydrocarbons. This research aimed to understand the therapeutic effects of the hydrocarbons and biologically active compounds present in the oil and is considered one of the first scientific studies supporting the use of Naftalan for medical and cosmetic purposes . These research, especially emphasizing its anti-inflammatory and therapeutic properties, established a foundation for the extensive application of Naftalan oil. However, it is not yet clear which of its components has the greatest biological activity.

Naftalan oil, being unique in its therapeutic effect, differs from the overwhelming number of other oils with its physical and chemical properties [7,8]. It is characterized by a high specific gravity, the lack of light fractions and solid paraffinic hydrocarbons, a substantial resin content and a pronounced propensity to create a highly stable emulsion with water. The intricacy of the hydrocarbon makeup and the specificity of some features of this oil provide significant challenges in analyzing its composition and discerning the biological impact of its individual components on living organisms [9].

Based on a qualitative analysis of the IR absorption spectra of naphthenic hydrocarbon fractions, it can be concluded that the molecules of the latter contain both condensed and isolated

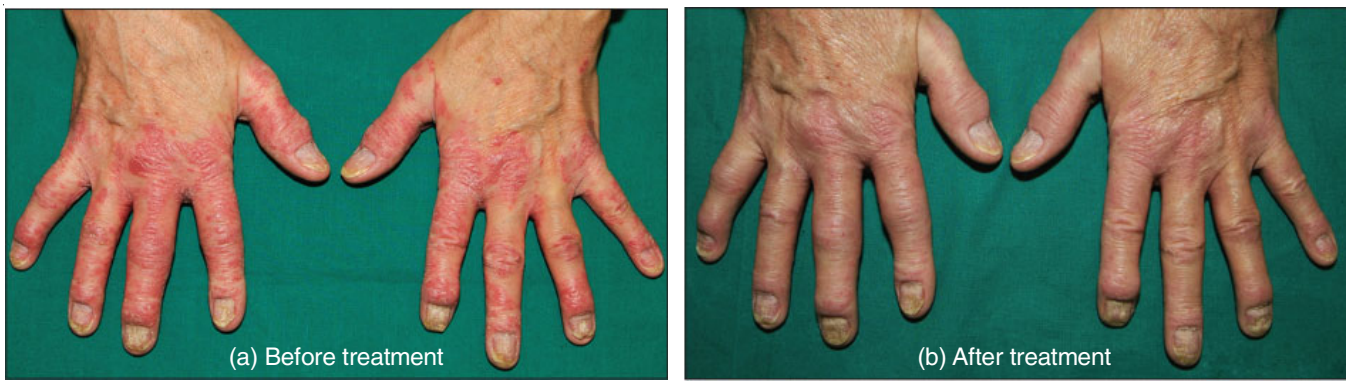

Fig. 1. The impact of naftalan oil therapy on psoriatic skin lesions

rings [10]. The structural units that represent the paraffin chains have methylene group contents ranging from 1 to 6. The number of long chains and short chains, including branched ones, decreases as the boiling point of the fractions increases, which also hold true for the branching of the chains.

A sharp disparity has been identified between the naphthenic hydrocarbons of Naftalan oil and those of other naphthenic base oils [11,12], characterized by their elevated cyclic nature, the predominance of carbon in the cyclic segments of the mole-cules, the presence of short substituents, the potential absence of methylene groups, and the existence of highly cyclic halo-nuclear structures.

EXPERIMENTAL

The chemical compositions of Naftalan oil, procured from the local market of Naftalan region of Azerbaijan, was analyzed with different analytical methods like adsorption chromatography on silica gel, ASK-active silica gel on large-porous aluminum oxide, fractionation under vacuum, thermal diffusion separation, liquid selective catalytic dehydrogenation and selective isomerization. The structural and group composition of naphthenic hydrocarbons was determined using the n-d-M method [13], whereas the aromatic hydrocarbons were analyzed using the Hazelwood method [14]. The chromatographic separation of Naftalan oil after its demulsification was carried out using the accelerated adsorption method used in studying the hydrocarbon composition of lubricating oils [12,13].

Methodology: The separation of naphthenic hydrocarbons from Naftalan oil was carried out in two stages. The first phase involves the extraction of resins from the oil (detarring), followed by the subsequent phase of eliminating aromatic hydrocarbons (dearomatization). The removal of aromatic compounds from oil, which has been de-resined through various methods to obtain naphthenic hydrocarbons, is achieved through adsorption by treating it in a gasoline solution utilizing the contact method. Two methods for isolating naphthenic hydrocarbons from Naftalan oil are recommended. These approaches are more cost-effective than the acid-acid contact cleaning procedure, as they mitigate the loss of precious polycyclic naphthenic hydrocarbons.

Option I: The degumming and dearomatization of oil is carried out by treating with aluminosilicate adsorbent in a gasoline solution.

Option II: Deresinization of Naftalan oil was performed using liquid propane, whereas dearomatization of the deresined oil was achieved through contact treatment with an adsorbent. Deresinization in a liquid propane was conducted in a pilot continuous deasphalting facility, whereas dearomatization was performed in an expanded laboratory setup utilizing contact cleaning methods.

FTIR analysis: A wide fraction of naphthenic hydrocarbons analyzed for the absence of aromatic hydrocarbons was subjected to low-temperature dewaxing (selective solvents and treatment with urea). Dewaxing in selective solvents was carried out at -60 ºC in a mixture of acetone:benzene:toluene (35:35:30) with preliminary heat treatment of a solution of naphthenic hydrocarbons at 60 ºC.

Table-1 presents the physico-chemical parameters of Naftalan oil while Table-2 illustrates its hydrocarbon content and the characteristics of the selected hydrocarbon groups.

RESULTS AND DISCUSSION

Extensive research on the biological effects of naphthenic hydrocarbons and their effective application in treating various diseases has led to address the issue of supplying medical institutions with adequate quantities of these hydrocarbons. In this regard, we have conducted a research to develop a best technology for separating naphthenic hydrocarbons from Naftalan oil.

Table-3 shows the physico-chemical properties of hydrocarbon groups isolated from Naftalan oil. Table-4 shows their elemental and structural group composition. The significant fraction of naphthenic hydrocarbons extracted from Naftalan

TABLE-1
PHYSICO-CHEMICAL PROPERTIES OF NAFTALAN OIL

Specific weight d_4^{20}	Toughness at 50 ºC conditional	Temperature (ºC)		Acidity (%)	Content (%)				Fractional composition	
		Flash	Solidification		Resin silica gel	Asphaltenes	Sulfur	Nitrogen	ºC	Boil-off before 350 ºC, %
0.9395	51.48	125	-20	1.29	2.4	0.49	0.31	0.24	238	25

TABLE-2
COMPOSITION OF HYDROCARBON ISOLATED FROM NAFTALAN OIL AND ITS CHARACTERISTICS

Group hydrocarbons	Exit, % weight	n_D^{20}	d_4^{20}	Mol. weight	Structural and group composition				
					Number of rings in molecule			Content carbon (%)	
					Ko	Ka	Kn	Ck	Cp
Naphthenic	55.0	1.4830	0.8876	285	2.5	–	2.5	59.0	41.0
Aromatic:									
Light	9.0	1.5152	0.9373	330	2.8	0.9	1.9	55.7	44.3
Average	11.7	1.5549	0.9944	290	3.5	1.5	2.0	75.8	24.2
Heavy	10.1	1.6125	1.0492	345	4.7	3.1	1.6	80.0	20.0
Resins	14.2	–	–	–	–	–	–	–	–

Ko = is the total number of rings in the molecule; Ka = aromatic rings in the molecule; Kn = naphthenic rings in the molecule; Ck = carbon content in hydrocarbon cycles; Cp = carbon content in paraffin chains.

oil is distinguished by an average of 2.5 rings per molecule and a predominance of carbon atoms within the rings (C_k) compared to those in the side chains (C_n). The aromatic hydrocarbons with a total number of rings increasing from 2.6 to 4.7 are hybrid structures in which the cyclic increases due to aromatic rings (from 0.9 to 3.1) with an almost constant number of naphthenic rings. A significant rise in the condensation level of aromatic hydrocarbons can be examined by a significant rise in the absence of hydrogen atoms (from 8.4 to 18.5). The ratio of aromatic rings to naphthenic rings in aromatic hydrocarbon molecules with increasing cyclic structures increases significantly when moving from light to heavy fractions.

The constituents of Naftalan oil (naphthenic hydrocarbons and their fractions with varying boiling points) were extracted with adsorption chromatography. Naphthenic hydrocarbons, which contain biologically active components, serve as the primary active principle of Naftalan oil in therapeutic applications and positively influence several physiological functions of the body. They possess non-toxic, non-carcinogenic and non-teratogenic qualities. Simultaneously, resins and aromatic hydrocarbons, particularly polycyclic (heavy) components, exhibit high toxicity and adversely impact numerous organ functions and bodily systems.

Resins isolated from Naftalan oil by chromatographic separation were characterized by high molecular weight and density indicating the presence of sulfur, nitrogen and oxygen. As can be seen from Table-2, the characteristics of individual groups of hydrocarbons in Naftalan oil provide only general, average information about its composition and do not reflect the full complexity and diversity of hydrocarbons contained in this oil. Thus, vacuum distillation and thermal diffusion separation were employed to extract narrow fractions for the investigation of naphthenic and aromatic hydrocarbons.

A wide fraction of naphthenic hydrocarbons isolated from Naftalan oil by adsorption chromatography on silica gel was studied in two aspects like (i) to establish the characteristics of the composition of naphthenic hydrocarbons depending on molecular weight; and (ii) to establish patterns in the structure of the cyclic and aliphatic parts of molecules at equal molecular weight. In first case, vacuum distillation fractions were studied, in second case, fractions obtained by thermal diffusion separation were studied. Pre-treatment with urea and dewaxing in a solution of selective solvents revealed the absence of normal and iso-paraffinic hydrocarbons in this fraction.

The findings indicate that an increase in molecular weight of naphthenic hydrocarbons is attributed to both an increase

TABLE-3
PHYSICO-CHEMICAL PROPERTIES OF HYDROCARBONS ISOLATED FROM NAFTALAN OIL

Hydrocarbons	n_D^{20}	S_4^{20}	S/2	Mol. weight	Kinematic viscosity, Cst at T, ºC		Index viscosity	Ratio of viscosity values at 50 and 100 ºC	Temperature solidification (ºC)
					50	100			
Naphthenic	1.4830	0.8872	1.0392	285	14.4	4.15	110	3.42	-61
Aromatic:									
Light	1.5152	0.9373	1.0466	330	47.74	7.29	38.2	6.0	-56
Average	1.5549	0.9944	1.0577	290	52.46	7.78	58.4	7.2	-21
Heavy	1.6125	1.0492	1.0879	345	–	–	–	–	–

TABLE-4
ELEMENTAL AND STRUCTURAL-GROUP COMPOSITION OF HYDROCARBONS OF NAFTALAN OIL

Group hydrocarbons	Structural and group composition							Elemental composition			S/N (average empirical formula)	General formula
	Number of rings in a molecule			Carbon content (%)								
	Ko	Ka	Kn	Ck	Cn	Ck	Cn	C	H	N		
Naphthenic	2.5	–	2.5	59.0	–	59.0	41.0	86.29	13.71	–	6.30 ($C_{20.4}H_{38.7}$)	C_nH_{2n}-2,1
Aromatic:												
Lungs	2.8	0.9	1.9	55.7	23.4	32.1	44.0	87.90	12.10	–	6.63 ($C_{24.1}H_{30.5}$)	C_nH_{2n}-8.3
Average	3.5	1.5	2.0	75.8	37.9	37.1	24.2	89.48	10.52	–	8.51 ($C_{23.6}H_{30.5}$)	C_nH_{2n}-12.7
Heavy	4.7	3.1	1.6	80.0	55.6	24.4	20.0	90.31	9.69	0.95	9.32 ($C_{25.9}H_{33.3}$)	C_nH_{2n}-18.5

in the number of cycles and an increase in the number of carbon atoms in the side chains. The contribution to molecular weight from the latter exceeds that from the carbon atoms in the cycles, leading to an increased degree of molecular condensation. A sharp difference in the fractions of naphthenic hydrocarbons of Naftalan oil from the corresponding fractions of other oils in terms of physico-chemical properties and structural group composition was found. They are characterized by a significant predominance of the proportion of carbon in the cyclic part of the molecules, high cyclic and a high degree of condensation of the molecules.

FTIR studies: A qualitative analysis of naphthenic hydrocarbon fraction IR absorption spectra shows that its molecules comprise condensed and isolated rings. The structural units of paraffin chains have methylene groups ranging from 1 to 6, and when the boiling point of the fractions rises, long chains increase and short chains, including branched ones, decrease. Based on FTIR spectra (Fig. 2), long paraffin chains containing more than six methylene groups ($(CH_2)_n$–CH_3, n > 6) were detected in the band 725-723 cm^{-1}, starting from the fraction with an intense band of 1302-1309 cm^{-1}. In the fractions 240-300 and 300-350 ºC, *n*-butyl units were also detected in the band 732-736 cm^{-1}. Isopropyl units are detected in the initial three fractions at 1169-1167 cm^{-1}; the second band (919-916 cm^{-1}), indicative of these units, is found alone in the first two fractions. The presence of a tertiary carbon atom is evidenced by the appearance at 1340 and 1210 cm^{-1}, characteristic of the CH- methine at 525-500 and >525 ºC fractions and for the >525 ºC fraction, the first of the bands is presented in the form of a very weak shoulder on the band 1374 cm^{-1} and the second band is present at low-intensity. The bands at 972-961 cm^{-1} indicate the presence of condensed polymethylene rings.

The fractions and residue obtained from thermal diffusion separation were also investigated by IR spectroscopy to quantify the primary structural units of naphthenic hydrocarbons and compare them to n-d-M structural group analysis. Methylene groups in side chains were determined by band intensity in the 800-700 cm^{-1} range and the methyl groups (isolated and geminal) by intensity. The total number of methyl groups, which includes both isolated and geminal groups present in the 1400-1300 cm^{-1} region, decreases with increasing boiling point of the fractions and the methylene groups increase, while the ratio of the number of isolated and geminal groups increases (from 2.6 to 5.1) (Table-5). The number of long chains with six or more methylene groups increases from 15.4 to 35.1% and with four to five from 19.6 to 35.1% when fraction boiling points increase. The hydrocarbons with two or three methylene groups decrease from 49.6% to 33.0% and those with one methylene group decrease too from 15.4% to 4.2%. Furthermore, the 240-300 ºC fraction favoured side chains with two or three methylene groups, whereas the fractions boiling at 350 ºC favoured chains with four or more methylene groups. Similarly, at higher temperatures, 350-420 ºC and 420-500 ºC, the regularities of changes in the structural group composition and also the nature of structure of the side chains of naphthenic hydrocarbons were also established using IR spectroscopy. The naphthenic hydrocarbons of Naftalan oil differ from those of other naphthenic base oils due to their high cyclic, carbon predominant cyclic part, short substituents, absence of methylene groups and highly cyclic halonuclear structures (Fig. 3) [14].

After the catalytic dehydrogenation, naphthenic hydrocarbons were classified by ring type and the quantitative ratio of six- and five-membered rings was determined. Generally, dehydrogenating hydrocarbons have heterogeneous structures

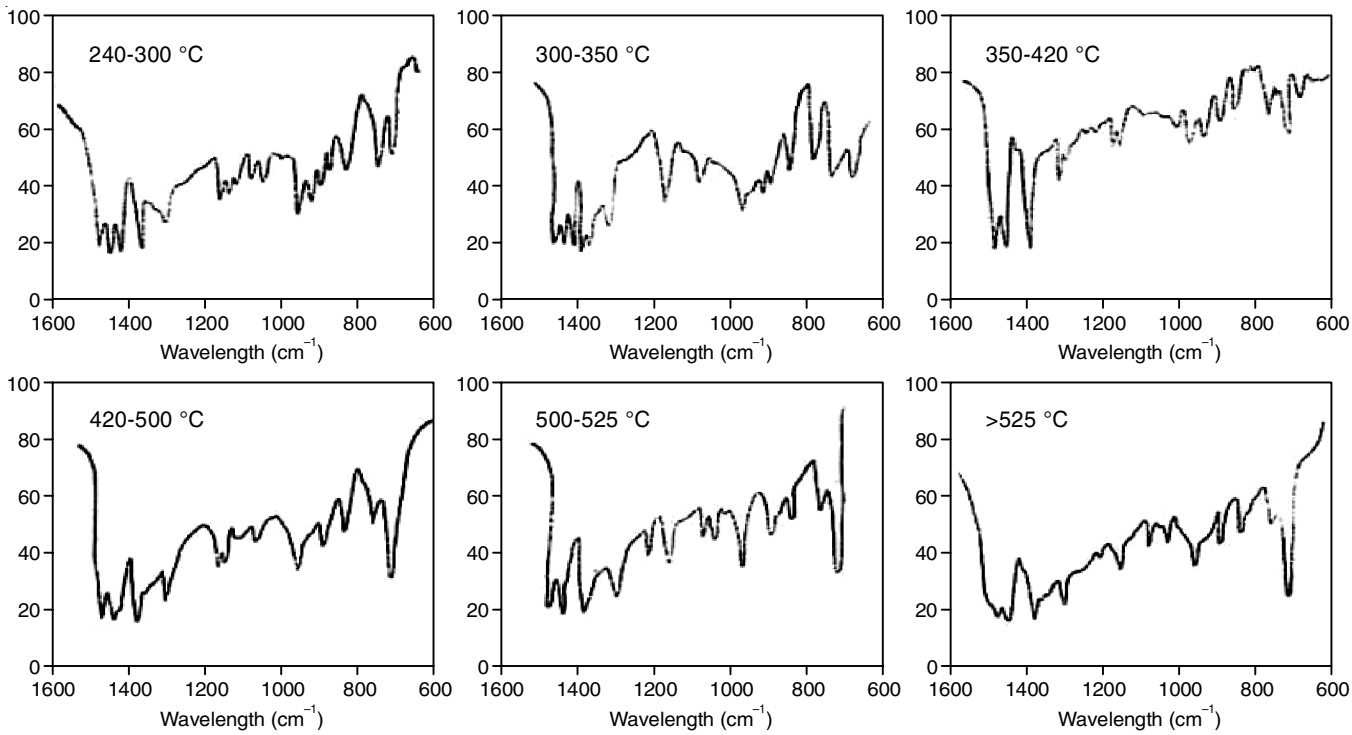

Fig. 2. IR spectra of naphthenic hydrocarbon fraction

TABLE-5
QUANTITATIVE CHARACTERISTICS BY IR SPECTRA OF STRUCTURAL UNITS INCLUDED IN NAPHTHENIC HYDROCARBONS OF VACUUM DISTILLATION FRACTIONS

Fractions (ºC)	Number of groups (%)								
	CH_3 – groups			–(CH_2) – groups					
				Chain link length					Total
	Isolated	Geminal	Total	6	4-5	3	2	1	
240-300	18.5	7.2	25.7	1.8	2.3	2.6	3.2	1.8	11.7
300-350	18.4	4.9	23.3	6.1	2.1	4.8	4.7	1.7	19.4
350-420	17.5	4.7	22.2	7.9	5.2	4.8	3.2	1.3	22.4
420-500	17.3	3.3	20.6	9.2	7.9	6.7	3.8	1.0	27.6
>500	15.7	3.1	18.8	9.8	7.4	6.4	3.0	1.2	28.5

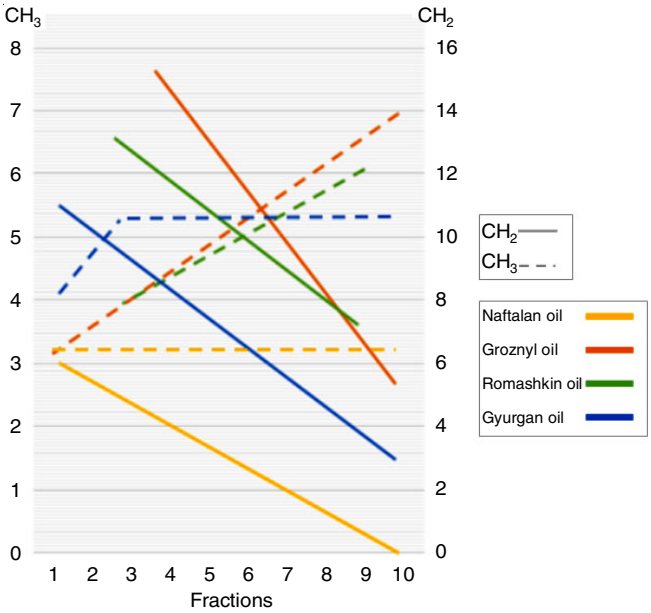

Fig. 3. Changes in the content of structural groups per average molecule for naphthenic hydrocarbons of thermal diffusion fractions. 350-420 ºC fractions of various oils

with less five-membered rings as the molecules cycle. Using selective isomerization followed by dehydrogenation, the non-dehydrogenating part of fractions 320-350, 350-420 ºC, and the residue revealed bridge-shaped hydrocarbons and patterns of quantity changes with increasing cyclic. Studies of naphthenic hydrocarbon fractions by chemical methods determined the content of six-membered, dehydrogenation-capable hydrocarbons, five-membered, selective isomerization-capable hydrocarbons, and hydrocarbons incapable of the above transformations (Table-6).

The latter group includes naphthenic hydrocarbons with geminal, angular substituents and bridging ring hydrocarbons but cannot be precisely interpreted by FTIR analysis. The fifth- and bridge-structured naphthenic hydrocarbons predominate in low-boiling fractions of Naftalan oil, while six-membered hydrocarbons predominate in high-boiling fractions. It has been established that in the 350-420 ºC fraction of Naftalan oil differs significantly from similar fractions of several oils in its higher content of six-membered naphthenic hydrocarbons and lower content of five-membered isomerizing structures. After studying naphthenic hydrocarbons and considering literature on oil structures, we assumed the presence of cyclic structures in thermal diffusion fractions (240-300, 300-350, 350-420 and 420-500 ºC) (Table-7). The initial fractions comprise monocyclic, bicyclic and tricyclic naphthenic hydrocarbons featuring both condensed and articulated structures. Among the hydrocarbons with a bridge-type connection, the existence of derivatives of bicyclo[3,2,1]octane and bicyclo[2,2,2]-octane is probable. In subsequent fractions, a progressive complication in the composition of the cyclic part of naphthenic hydrocarbon is observed, along with a variation in the relative quantitative distribution of structures. Tricyclic structures,

TABLE-6
COMPOSITION OF NAPHTHENIC HYDROCARBONS BY TYPE OF STRUCTURE

Fractions (ºC)	Six-membered, capable of dehydrogenation (%)	Five-membered, capable of dehydrogenation after preliminary isomerization (%)	Five-membered and six-membered, incapable of isomerization and dehydrogenation (%)	Hydrocarbon ratio
320-350	27.5	23.9	48.6	1:0.9:1.8
350-420	49.6	15.1	35.3	1:0.3:0.7
>500	65.0	8.1	27.0	1:0.1:0.4

TABLE-7
RESULTS OF MASS SPECTROSCOPIC ANALYSIS OF NAPHTHENIC HYDROCARBON FRACTIONS

Naphthenic hydrocarbons (%)	Fractions (ºC)				
	240-300	300-350	350-420	420-500	>500
Monocyclic	17.0	14.9	6.0	2.3	1.8
Bicyclic	42.3	39.6	36.5	–	17.3
Tricyclic	33.2	35.1	32.0	29.0	27.4
Tetracyclic	7.5	8.3	22.0	37.2	44.2
Penta- and hexacyclic	–	2.1	3.5	7.0	9.3

including perhydroanthracene and perhydrophenanthrene, along with tetra- and pentacyclic structures, are also present. Alkyl homologs of adamantium (bridge-type ring structures) on tricyclodecane, tricycloundecane, tetracyclododecane and pentacyclotetradecane (diamantane or congressane) are likely present in the oil.

Thus, the isolation of bridged hydrocarbons in the low-boiling fractions of naphthenic hydrocarbons from Naftalan oil, in addition to polycyclic compounds, primarily of the cyclopentanoperhydrophenanthrene type, the therapeutic properties of Naftalan oil are influenced by compounds with bridged ring structures. The former are responsible for the biological activity of high-boiling fractions, while the latter pertain to low-boiling fractions. The findings from various biological investigations into distinct fractions of naphthenic hydrocarbons, which vary in boiling point, support this hypothesis.

Conclusion

A systematic investigation of medicinal Naftalan oil employing chromatographic separation of hydrocarbon groups was conducted for the first time. A technique has been devised for the extraction of naphthenic hydrocarbons from Naftalan oil, comprising two phases *viz*. resin removal (detarring) and aromatic hydrocarbon removal (dearomatization). The identified patterns in the composition of each hydrocarbon group as a whole was characterized and ensured chemical composition with native oil by eliminating thermal effects. The presence of naphthenic hydrocarbons in Naftalan oil is confirmed by a significant predominance of carbon in the cyclic part of the molecules, high cyclicity and condensation and the predominance of five-membered and bridged hydrocarbons in low-boiling fractions and six-membered in high-boiling fractions. The distribution of cyclic structures of naphthenic hydrocarbons among fractions has been revealed.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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