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UDC 550.4.41

NEW DATA ON DIAMOND-LIKE HYDROCARBONS

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Comparative studies were conducted for Absheron OBR oils and essential oils of plants representing Absheron archipelago flora to identify series of adamantoid hydrocarbons. Absheron OBR oils – such fields as Gyarbi Absheron, Absheron, Darvin kyupasi, Pirallahi, Palchyg Pilpelesi, Neft Dashlary, Guneshli and also essential oils of Absheron archipelago plants, such as thuja, bottlebrush, juniper, silver mint, lavender cotton, cypress, lavender were analyzed by chromato-mass-spectrometry method. Among all studied samples adamantoid series hydrocarbons with m/z 135,136,149,163 were determine hydrocarbons formulae are given.

Keywords: adamantoids, chromato-mass-spectrometry, essential oils of plants, Absheron archipelago oil

Introduction

Presence of adamantoid series hydrocarbons in oil and in gas-condensate [1-4] is known in nature. Carboniferous skeleton of adamantan is similar to structural unit of diamond and according to it adamantoid hydrocarbons is also called “hydrocarbons of diamond-like structure”.

The only natural source known of adamantan is still regarded as oil. For the first time adamantan had been recovered from Gondonian field oil before than it was synthesized in lab.

Content of adamantans in oil is 0.0001 – 0.03 % due to base of petroleum. At present about thirty hydrocarbons of adamantan series are found, their general content exceeds content of adamantan by 10 times.

Since recovery of adamantan question dealing with its origin in oil and in condensates has agitated many researches in as much due to lack of adamantans in starter bioorganic compounds. Landa and his colleagues [5] made an assumption that the source of adamantan in oils is cyclic HC and in this case aluminosilicates can play the role of catalysts of their transformation of adamantans. Probably, possible precursors of alkyladamantans

in oil are condensed tricyclic HC [1]. First form: 2 - methyl; 1,2 - dimethyl; 1 - ethyladamantans, etc., then their isomerizations occurs by formation of thermodynamically - stable adamantans such as: 1 - methyl; 1,3 - dimethyl; 1,3,5 - trimethyladamantans.

On the base of this data (Bagrey et al. 1969) one could conclude as mentioned conditions are compared to natural conditions of oils occurrence (Fort, 1976) so this reaction can be studied as a model of alkyladamantans formation under environmental conditions.

Alkylsubstituted adamantanoids then can be transformed to higher adamantanoids representatives (R. Lin and Z.A. Wilk. Fuel, 1995. v. 74, p. 1512-1521).

In works (Z. Wei et al., Org. Geochem. – 2006, v.37, p. 891-911; 2007, v.38, p.227-249) shown hydrocarbons of diamond - like structure are irrelevant to biosynthesis and they form in diagenesis after initial burial of sediments.

The possible precursors of adamantans in oil are condensed tricyclic hydrocarbons-fragments occurring during destruction of relict combinations of oil - steranes, triterpanes, etc. (Bagrey 1989, Petrov 1984, Wei et al

2005,2006), though this idea (Giruts M.V.) is not approved as a whole.

There are probable alternative mechanisms of adamantans formation as well, for example in work [6] is shown adamantan and its homologous present in oils generating by carboniferous beds which don't possess catalytical properties.

If there are not adamantanoids in primary biomass so their formation process in HC fluids reflects to a certain degree one of the ways bio-organic matter transformation to interior. However, the latest research in field of identification of HC adamantanoid series in natural objects made to reconsider above mentioned mechanisms of protoadamantanoid HC formation in oil and gas - condensates.

Chemical matters don't evolve and four billions years before advent of life on the Earth water and carbon dioxide had absolutely the same properties as at present day. However, living organisms constantly "learn" to produce new combinations. This is surely had little to do with so-called primary metabolites-glucose, proteinogenic amino acids and nitrogenous bases of DNA and RNA.

Chemical matters don't evolve. But metabolic ways are in process of evolution and they are under control of genome. This allows to get new combinations from known precursors. And they turned out connected with existing before by genealogical relationship. The main conclusion is in the following: conception of natural matters early or late will be reconsidered due to facts.

We conducted comparative study dealing with essential oils samples of plants representing flora of Absheron archipelago and oils of Absheron OGBR to identify adamantanoid hydrocarbons series by chromat-mass spectrometry method.

Experimental part

Essential oils of plants obtained as a result of steam-water distillation of Absheron archipelago plants, such as thuja, bottlebrush, juniper, silver mint, lavender cotton, cypress, lavender, also oils of Absheron OGBR, such

fields as: Gyarbi Absheron, Absheron, Darvin Kupesi, Pirallahi, Palchyg Pilpelesi, Neft Dashlary, Guneshli.

Chromato-mass-spectrometric study of oils and essential oils of plants carried on Perkin-Elmer chromato-mass-spectrometre Clarus 680 possessing interface with high-efficient mass-selective detector Clarus SQ8T [7-8].

Solvent-carbon sulphide CS₂ was used for native oil analysis on chromato-mass-spectrometer. Chromatograph is with quartz capillary column of 60 m length, 0.25 mm diameter impregnated by Rtx -1 MS phase, carrier-gas-helium.

Discussion of the results

Up to the present adamantan derivatives were found only in plants of *Hypericum sinai-cum* genus growing in deserts of Egypt and Palestine, and also in their close allies from tropics related to *Clusia* genus [9-10].

So, living organisms are able to synthesize diamond-like structures in their cells (may be absolutely they give pharmaceutic features to some plants).

Also, *Mycobacterium* sp. AGS10 [11] possess uncanny ability to grow in medium where the only source of carbon is framework hydrocarbons: 1-methyladamantan; 1,3- dimethyladamantan and 1,3,5 - trimethyladamantan.

That's is why identification of hydrocarbons of adamantanoids series with m/z 135, 136, 149 in essential oils of plants growing on Absheron is of a great importance. Formulas of hydrocarbons for adamantanoids series are given according to NIST – 11 (Fig.1).

In chromatogram of essential oils of plants there are adamantanoids identified in them by amount from 1.0 to 3.3 % with relative m/z.

Further, Absheron archipelago oils were studied by method of chromatomass spectrometry to identify the hydrocarbons of the adamantoid series.

In table 1 as an example of Neft Dashlary field oil there are formulas of identified adamantoids with relevants m/z.

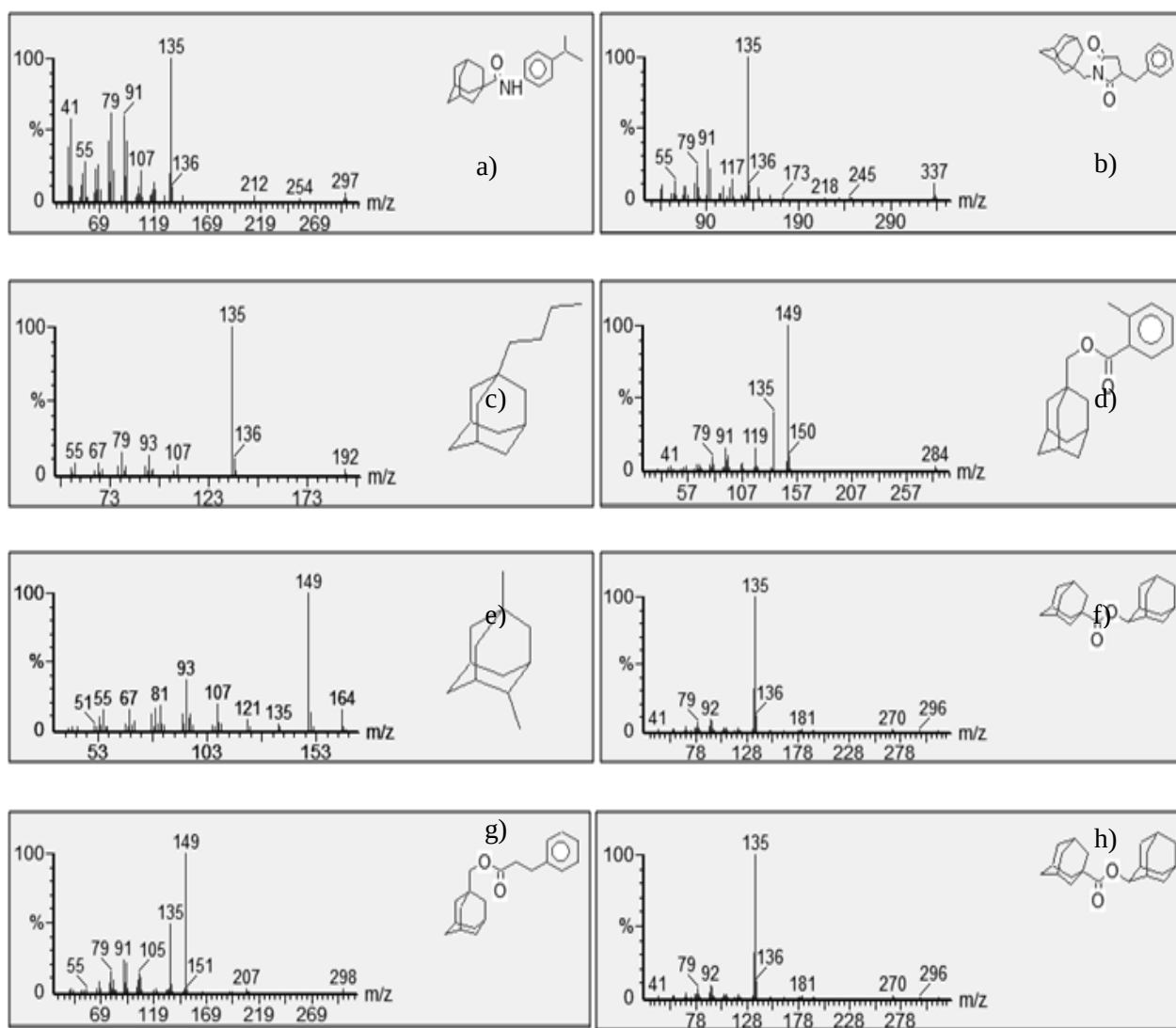


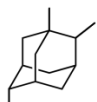
Fig.1. Mass spectrum of essential oil: a- Santolina with m/z 135, b- Cupressus sempervirens with m/z 135, c- Mint silver with m/z 135, d- Mint silver with m/z 149, e- Lavandula with m/z 135, f- Callistemon citrimus with m/z 149, g- Thuja with m/z 135, h- Jumperus with m/z 149

As it is seen from the research (Giruts M.V.) on lab modeling of hydrocarbons formation with framework structure no many oil polycyclic hydrocarbons can be transformed to adamantanoids in the presence of alumosilicate catalysts. Availability of adamantans in oils generated by carboniferous mass and it is not possessing catalytic properties contradict this scheme and also weakly transformed oils don't fit

the mentioned scheme. Probably there are other ways formation of for hydrocarbons of diamond-like structure in oils. At present the origin of adamantanoids is known by the only fact -lack of adamantanoids in initial biosynthesized matter. However, our research has shown the converse, so it is expedient to continue research in this direction.

Table 1

Adamantans in Neft Dashlary oil

1 – Adamantan  m/z 136	9 – 1,2- dimethyladamantan  m/z 149
2 – 1- methyladamantan  m/z 135	10 – 3-methyl-1- ethyladamantan  m/z 149
3 – 2- methyladamantan  m/z 135	11 – 2,4- dimethyladamantan  m/z 149
4 – 1- ethyladamantan  m/z 135	12 – 1,3,5 - trimethyladamantan  m/z 163
5 – 2-ethyladamantan  m/z 135	13 – 1,3,6 – trimethyladamantan  m/z 163
6 – 1,3- dimethyladamantan  m/z 149	14 – 1,3,4- trimethyladamantan cis  m/z 163
7 – 1,4- dimethyladamantan cis  m/z 149	15 – 1,3,4- trimethyladamantan  m/z 163
8 – 1,4- dimethyladamantan trans  m/z 149	16 – 3,5-dimethyl-1- ethyladamantan  m/z 163
17 – 1,2,6 - trimethyladamantan  m/z 163	

Conclusion

Thus, according to chromato-mass-spectrometry one can confirm the availability of diamond - like hydrocarbons not only in oil but in many plants growing on Absheron, Azerbaijan. This conclusion suggests to reconsider the existing ways of hydrocarbons formation of adamantan series in oil.

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ALMAZA BƏNZƏR KARBOHİDROGENLƏR HAQQINDA YENİ MƏLUMATLAR

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Adamantoid karbohidrogenlər ailəsini müəyyən etmək üçün Abşeron arxipelaqının neftlərinin və Abşeron yarımadasının florasını təmsil edən bir sıra bitkilərin efir yağları nümunələrinin müqayisəli tədqiqatları aparılmışdır. Qərbi Abşeron, Abşeron, Darvin küpəsi, Pirallahı, Palçıq Pilpələsi, Neft Daşları, Günəşli neft yataqlarından olan neftlər; o cümlədən tuya, kalistemon, ardıc, gümüşü nanə, santolina, sərv, lavanda bitkilərinin efir yağları xromato-kütlə-spektrometriya üsulu ilə tədqiq edilmişdir. Tədqiq olunan bütün nümunələrdə adamantoid ailəsinin m/z qiyməti 135, 136, 149, 163 olan karbohidrogenlər müəyyən edilmiş, karbohidrogenlərin formulları verilmişdir.

Açar sözlər: adamantoidlər, xromato-kütlə spektrometriyası, bitkilərin efir yağları, Abşeron arxipelaqının nefti

НОВЫЕ ДАННЫЕ ОБ АЛМАЗОПОДОБНЫХ УГЛЕВОДОРОДАХ В ПРИРОДНЫХ ОБЪЕКТАХ АБШЕРОНА

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Проведены сопоставительные исследования нефтей Абшеронского архипелага и эфирных масел ряда растений, представляющих флору Абшеронского полуострова с целью идентификации семейства адамантоидных углеводородов. Методом хромато-масс спектрометрии исследовали эфирные масла растений: туя, калистемон, можжевельник, мята серебристая, сантолина, кипарис, лаванда, а также нефти месторождений: Гярби Абшерон, Абшерон, Дарвин кюпеси, Пираллахи, Палчыг Пилпилеси, Нефт Дашлары, Гюнешли. Во всех исследуемых пробах были идентифицированы углеводороды семейства адамантоидов с m/z 135, 136, 149, 163, приводятся формулы углеводородов.

Ключевые слова: адамантоиды, хромато-масс спектрометрия, эфирные масла растений, нефть Абшеронского архипелага