C_{21} N-ALKYLBENZENE AND 1-N-ALKYLNAPHTHALENE IN OILS: ISOTOPE EFFECTS AT CYCLIZATION / AROMATIZATION?

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The analysis of the composition of aromatic hydrocarbons of oils from Timan-Pechora basin (TPB) revealed a group of oils characterized by a distinct prevalence of C_{21} homologue among n-alkylbenzenes and 1-n-alkylnaphthalenes (Bushnev, Valyaeva 2015). $2*C_{21}/(C_{20}+C_{22})$ coefficient of n-alkylbenzenes is 3.7-29.8. A possible source of *n*-pentadecylbenzene (III) and *n*-undecylnaphtalene (IV) is polyunsaturated aliphatic acid with $C_{22:6n-3}$ composition or its decarboxylation product, i.e. *n*-heneicosahexaene-3,6,9,12,15,18 (I) (Ivanova, Kashirtsev 2010; Bushnev, Valyaeva 2015), which is a part of many marine planktonic algae, in particular some of diatoms (e.g., *Ditylum brightwellii, Rhizosolenia setigera, Skeletonema costatum*) and dinoflagellates (*Gymnodinium splendens*). It is known that the carbon isotopic composition of C_{21} n-alkane and corresponding $C_{22:6}$ aliphatic acid isolated from marine microalgae *Rhizosolenia setigera*, is -23.8 and -22.5 ‰ respectively (Sinninghe Damsté et al, 2000).

Fractions with *n*-alkylbenzenes and long chain *n*- alkylnaphthalenes were isolated from 5 oil samples by liquid column chromatography. These oils are from Upper Devonian deposits of the following fields: Syurkharatinskoe, Verkhne-Kolvinskoe, Yanemdeyskoe, Medynskoye, Myadseyskoye. The $\delta^{13}C$ values of C_{21} alkylbenzene in Timan-Pechora oils range from -35.1 to -30.20 ‰, the corresponding alkylnaphthalene is characterized by the values -32.0 to -26.90 ‰.

Identified in TPB Upper Devonian oils homologous series of *n*-alkylbenzenes and *n*-alkylnaphthalenes with a sharp predominance of C_{21} homologue testifies to a common source of *n*-pentadecylbenzene and 1-*n*-undecylnaphtalene. The isotopic composition of carbon of *n*-pentadecylbenzene and 1-*n*-undecylnaphtalene is characterized by certain variations in the oils from various fields, at that carbon of *n*-alkylnaphthalene is about 2 ‰ heavier, than carbon of *n*-alkylbenzene. This difference exceeds the measurement error and appears significant. This difference may reflect the presence of isotopically isolated precursors with the same number of carbon atoms, or it is an attribute of the influence of the cyclization / aromatization of the initial structure on the isotope fractionation of carbon of the studied components. We consider that unlikely there are two separate sources of *n*-alkylbenzene and *n*-alkylnaphthalene of the same composition with *n*-alkyl fragment in the base (at opening of the cycle). In favor of the cyclization version partially hydrogenated derivatives of C_{21} n-alkylnaphthalene were found in the oils from Syurkharatinskoe field (V-VII, fig.).
Hence, the resulting isotopic difference is a consequence of fractionation during cyclization and aromatization of polyene chain. The isotope effect at aromatization is being challenged. For example the isotopic difference for aromatic hopanes with different numbers of aromatic rings (also about 2-3 ‰) is explained by different sources of these hydrocarbons (Liao et al., 2015). According to (Freeman et al., 1994) the isotopic effect of aromatization can be either positive or negative, and generally unreliable.

The carbon isotopic composition of 5-n-undecyl-1,2,3,4-tetrahydronaphthalene (V) could be measured only for oil of Syurkharatinskoe field and its $\delta^{13}C$ value is -28.1 ‰ (4

measurements, st. dev. is 0.65). $\delta^{13}C$ value of 1-n-undecylnaphtalene is here -26.9 (6 measurements, st. dev. is 0.69), and $\delta^{13}C$ value of *n*-pentadecylbenzene in this oil is -30.2 ‰ (4 measurements, st. dev. is 0.39). That is, for the partially hydrogenated analogue of C_{21} alkylnaphtalene we determined an intermediate value of the carbon isotopic composition between alkylbenzene and alkylnaphthalene, which can indicate a genetic relationship of all three compounds, and an impact of their formation process on the isotopic composition of carbon.

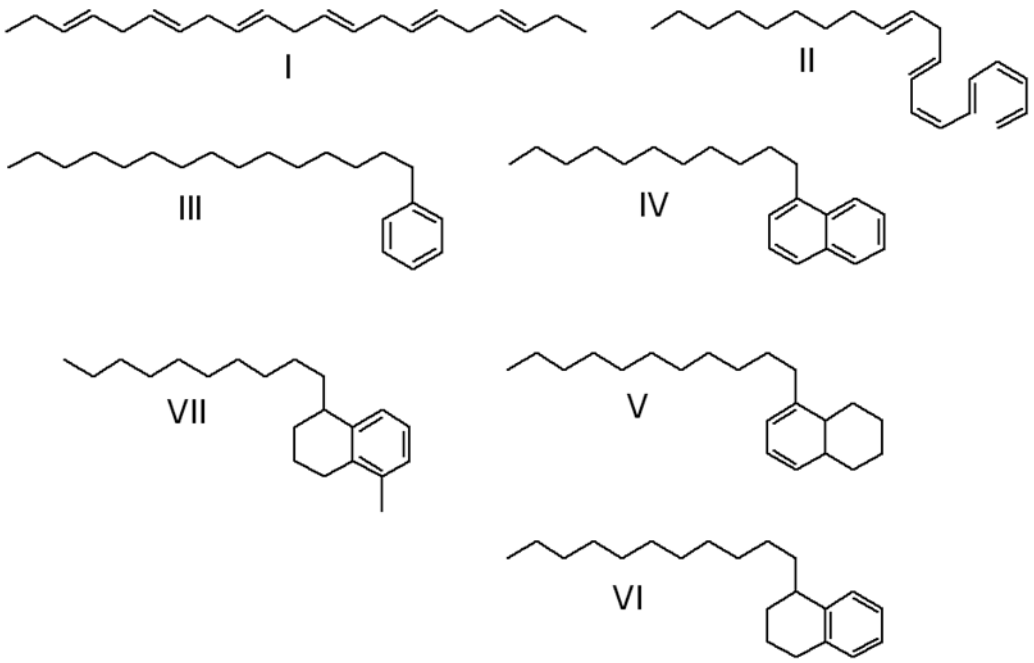

Figure. Structures were discussed.

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