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by V.E. Kovjazin, and Ṡ. Hala

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On the Presence of C_{15}-C_{20} Isoprenoid-like Alkanes in Ozocerite

V.E. Kovjazin[+] and S. Hála

Laboratory for Synthetic Fuels and Petroleum,
Technische Hochschule für Chemie, 166 28 Prag 6
(Technical College of Chemistry, 166 28 Prague 6)

Dedicated to Prof. Dr. S. Landa on his
75th birthday

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Ozocerite from South-Fergana (USSR) contains C_{13}-C_{40} n-alkanes whose distribution curve shows two maxima at C_{16} and C_{33} respectively. The isoprenoid-like alkanes 2,6,10-trimethyldodecane (farnesane), 2,6,10-trimethyltridecane, 2,6,10-trimethyltetradecane, 2,6,10-trimethylpentadecane, 2,6,10,14-tetramethylpentadecane (pristane) and 2,6,10,14-tetramethylhexadecane (phytane) are present in relatively high concentrations in the oil fraction of ozocerite. In the urea extract, the homologous series of C_{15}-C_{22} isoalkanes and anteiso alkanes were identified besides the n-alkanes. The presence of methyl-alkanes with the methyl

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[+] Present address: Severo-zapadnyj Politechničeskij Institut, Leningrad, UdSSR.

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groups closer to the middle of the chain was also determined mass-spectrometrically.

Ozocerite which in nature, like petroleum, occurs in cavities in the earth's strata or in porous rocks, consists mainly of solid hydrocarbons. A close genetic connection between ozocerite and petroleum is assumed since the chemical and physical properties of the hydrocarbon groups present in ozocerite are very similar to those of solid hydrocarbons from petroleum 1). Considering the frequent finds of ozocerite when test drilling for petroleum, the question of the chemical composition of ozocerite and of its relation to petroleum takes on practical significance,too. Although ozocerites from various discovery sites contain different quantities of the various classes of hydrocarbons, as a rule, alkane hydrocarbons 2,3) predominate. Besides the normal alkanes, these hydrocarbons contain an appreciable quantity of branched alkanes about whose structure very little information can be found in the literature. They were recently characterized in more detail by Boiko and co-workers 4) who concluded, based on the IR spectrum of hydrocarbon fractions, that the branched alkanes in ozocerite show a high degree of branching with 4-6 methyl groups in the molecules.

In the present paper, we have concerned ourselves with a thorough investigation of the structure of branched-chain alkanes in the hydrocarbon component of ozocerite from Fergana. We analyzed the oil fraction which can be obtained from ozocerite by vacuum distillation. The lesser complexity of this fraction, which only contains substances /p.2939 up to C_{22}, made the identification of individual hydrocarbons easier and thus the direct estimation of their structural similarity to petroleum hydrocarbons.

Experimental Section

The melting points were determined with a Kofler-Block. For the gas chromomatographic analyses, the Chrom 3 Gas chromatograph (Laboratorni přistroje, Prague) with flame ionization detector was used. It was equipped with a 50 m long stainless steel capillary column with an inside diameter of 0.2 mm which was wetted with OV-225 (cyanopropylmethylphenylsilicone, Applied Science Laboratories Inc.). Nitrogen was used as carrier gas. The analyses were made under programmed temperature with a Pye apparatus of Series 104, Model 64, in a system of two glass columns (150 cm x 0.4 cm) which were filled with 2% SE-30(gas chromatographic quality) on Gas Chrom Q. The mass spectra were obtained at 70 e/V with an LKB 9000 Mass Spectrometer(LKB Produkter AB, Stockholm) coupled with a gas chromatograph which was equipped with a 50 m stainless steel column with an inside diameter of 0.2 mm wetted with OV-225. The spectra were recorded oscillographically. Helium was used as carrier gas.

Ozocerite was obtained from an open-pit mine near Šör-su in South Fergana (USSR) at 15-20 m depth, where it was embedded in crevices in the limestone layer of the Alai mountains. Ozocerite was separated from the accompanying rock in the dark brown, waxy, solid mass by extracting with cyclopentane in a Soxhlet apparatus. The mineral residue consists of limestone containing several percent Al_2O_3 and SiO_2 ; according to semi-quantitative emission spectroanalysis (Qu-24 Spectrograph), it showed an admixture of Fe-, Na- and Mg-compounds in the order of magnitude of tenths of one percent. After distilling the solvent off, the cyclopentane solution yielded 38.7% ozocerite free from mineral matter as a dark coloured, wax-like substance; melting point 59-64.5°C, ultimate analysis 83.56% C, 12.87% H, 1.03% S.

<u>Distribution of the n-Alkanes</u>. The range of molecular weight of the main components contained in ozocerite was determined by gas chromatographic analysis of the hydrocarbon portion. 10.0 g of ozocerite were dissolved in 100 ml of cyclopentane and the solution was/ kept for 5 days in a narrow, closed tube. After settling of the asphaltenes (0.5 g), 25 ml of the solution were pipetted out from the surface and fed /p.2940
into a column packed with silica gel activated for 12 hours at 180°C. After soaking in of the sample, the column was eluted with 200 ml of pure cyclopentane. By evaporating the solvent, 1.67 g (70.2%) of colourless hydrocarbons with a melting point of 58-61.5°C were obtained from the eluate. The analysis of the hydrocarbon portion made with the Pye

Gas chromatograph of Series 104 with a column of SE-30 at a programmed temperature of 100° to 300°C (2°C/min) showed that the main components are n-alkanes, starting with n-tridecane and going / up to n-tetracontane. The relative occurrence of the individual n-alkanes was calculated from the height of the chromatographic peaks without the use of correction factors. The curve in Fig. 1 illustrates the relation of their distribution with the number of C-atoms in the molecule. The total content of n-alkanes in the hydrocarbon portion of ozocerite was determined by extractive distillation with urea, following a method worked out for sheet paraffin and ceresine[5]. The adduct was precipitated out of the tetrachloromethane solution containing 1 g of the hydrocarbon portion, by the addition of methanolic urea solution. After decomposition, the adduct yielded 0.57 g of n-alkanes with a melting point of 63-67.5°C. A gas chromatographic check showed that the distribution of the individual hydrocarbons in the isolated n-alkane group corresponded to the original distribution of the n-alkanes in the hydrocarbon portion.

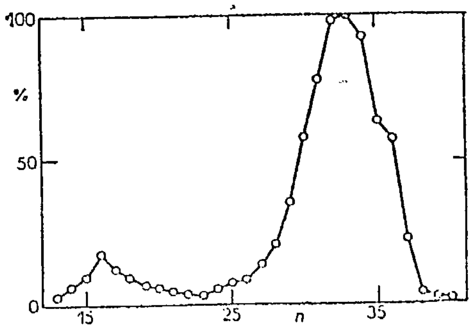


Fig.1. Distribution of n-alkanes in ozocerite as a function of the number of C-atoms in the molecule (n, (C_{33} content= 100%)

Oil Fraction (Diagram 1). 63.8 g of ozocerite were distilled at 0.5 Torr. in a Claisen distillation apparatus. In the temperature interval between 70 and 160°C/0.5 Torr., 7.6 g (11.9%) of a yellowish oil distilled off; its ultimate analysis was 85.78% C, 13.06% H, and 1.44% S. The oil fraction (5.0 g) was dissolved in 25 ml of cyclopentane, added to an activated silica gel column, and eluted with 100 ml of pure cyclopentane. After evaporation of the cyclopentane, the eluate yielded 4.43 g (88.6%) of a clear, colourless oil free from non-hydrocarbons. The gas chromatographic analysis showed that the oil represents a complicated mixture of compounds in which the C_{13}-C_{22} n-alkanes are strongly represented. The content of individual compound categories in the oil was determined by means of a mass spectrometric method which was worked out by Fitzgerald and co-workers$^{6)}$ for the middle distillates of petroleum and which was checked with good results when using the LKB spectrometer$^{7)}$. The composition of the oil was as follows: alkanes 42.3%, monocycloalkanes 12.0%, dicycloalkanes 11.4%, tricycloalkanes 6.1%, alkylbenzenes 8.0%, dicycloaromates 20.1%. The oil consisting of hydrocarbons was separated into the extract (n-alkanes) and the raffinate by extractive crystallization with urea. 3.56 g of oil, 20 g of recrystallized urea and 1,500 ml of cold, saturated methanolic urea solution were heated for 40 minutes under reflux condensation and allowed to crystallize overnight. The separated crystals were filtered off, washed with 50 ml of cyclopentane and decomposed with hot water. The n-alkane layer which is released was isolated by ether extraction with a yield of 1.00 g(28.1%). The remaining methanolic filtrate was evaporated to dryness, the residue digested with water and extracted with ether. From the ether extract, 2.50 g (70.2%) of n-alkane-free oil (raffinate) were isolated.

Analysis of the Extract. The extract was analyzed gaschromatographically at 180°C with the use of a capillary column wetted with OV-225. With the help of internal standards and the logarithmic dependence of the retention times on the number of C-atoms, C_{13}-C_{22} n-alkanes were identified in the extract. On the chromatogram of the extract, a group of four incompletely separated small peaks always appeared between every two consecutively eluted n-alkanes. These smaller peaks were designated with the letters a, b, c and d, following the sequence of the elution. In each group, the concentration of the c-component was more than twice as high as that of the three remaining components. In order to identify these hydrocarbons entrained in the adduct, their retention indices were measured on the capillary column wetted with OV-225 and their mass spectra were measured with the mass spectrometer in conjunction with the gas chromatograph. For comparison, the mass spectra of various synthe- /p.2941
tically prepared C_{16}-C_{19} methylalkanes with the methyl group at the end of the chain (in positions 2 and 3) and closer to

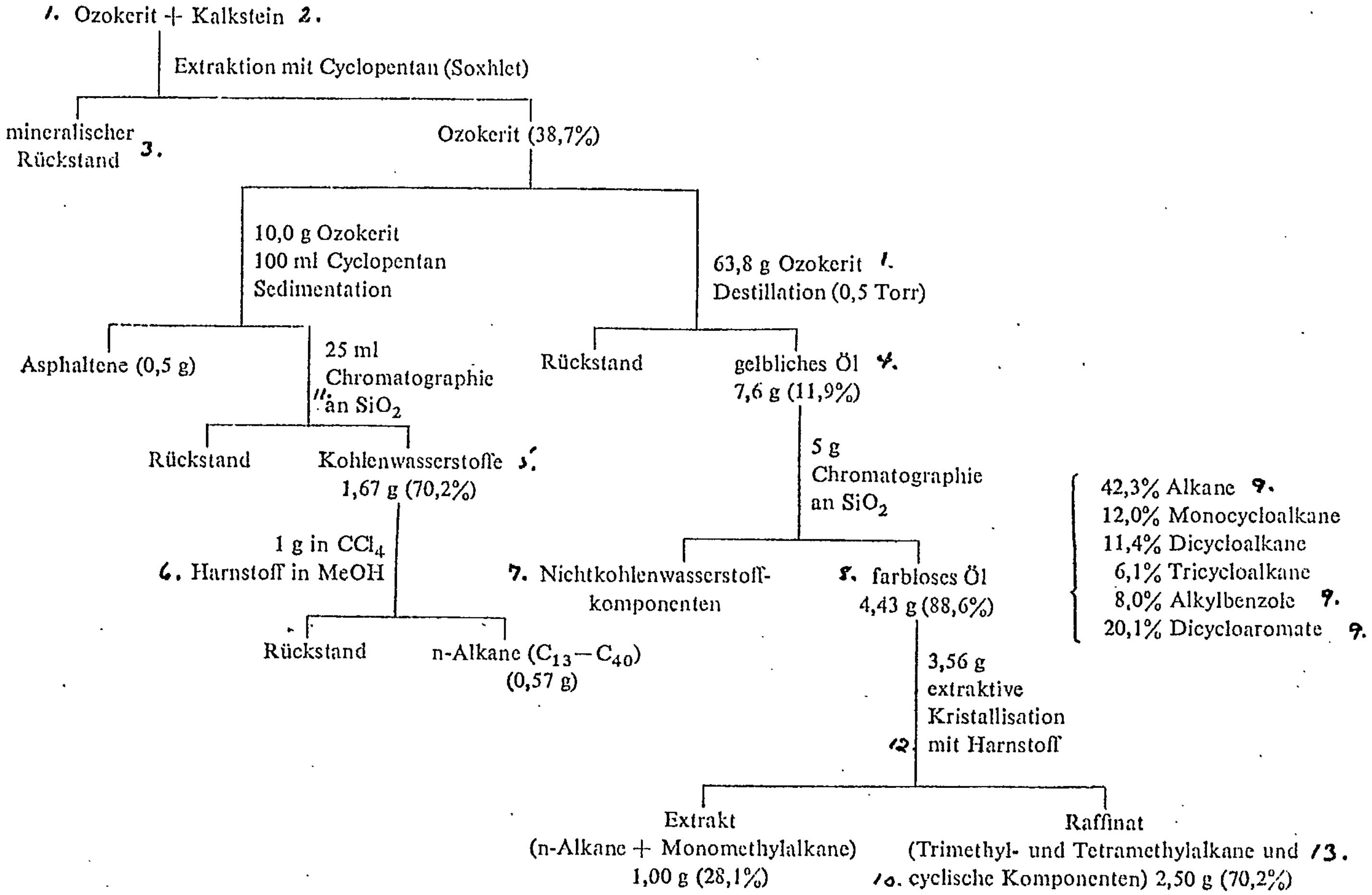
the middle of the chain (in positions 4,5 and 8) were measured. The retention times of the synthetic methylalkanes were compared with the retention times of components a-d by co-injecting them in the chromatographic column.

Analysis of the Raffinate. The gas chromomatographic analysis revealed that the raffinate is a complicated mixture of hydrocarbons in which, in the absence of n-alkanes, six components predominated. Their retention indices, measured at 180°C over OV-225 with an accuracy of ± 1.5 units, showed the values 1786, 1676, 1627, 1556, 1447 and 1361 (at 160°C). Practically the same values for the indices were found at 200°C. Based on the retention times and on the mass spectra measured with the mass spectrometer coupled with the gas chromatograph, the prevailing components were identified as isoprenoid trimethyl- and tetramethylalkanes. In the case of farnesane, pristane and phytane, the identification was confirmed by co-injection of an authentic preparation into the chromatographic column at 160, 180 and 200°C.

Results

n-Alkanes. The predominant part of the hydrocarbons in ozocerite from Fergana consists of the homologous n-alkane series C_{13} - C_{40}. Their distribution curve (Fig.1) with uniform occurrence of even and odd members shows two maxima at C_{16} and C_{33} respectively. The lower C_{13}-C_{23} n-alkanes occur in far smaller quantities than the higher

Diagram 1



1- Ozokerit = ozocerite
2- Kalkstein = limestone
3- mineralischer Rückstand = mineral residue
4- gelbliches Öl = yellowish oil
5- Kohlenwasserstoffe = hydrocarbons
6- Harnstoff = urea
7- Nichtkohlenwasserstoff-komponenten = non-hydrocarbon components
8- farbloses Öl = colourless oil
9- Alkane = alkanes benzole = benzenes aromate = aromatics
10- cyclische Komponenten = cyclic components
11- an = on
12- mit = with
13- und = and

homologs. The n-alkanes with 31-34 carbon atoms are present in the greatest concentration. These four members account for 48% of all the n-alkanes present in the hydrocarbon portion of ozocerite. The content of n-alkanes in the hydrocarbon portion of ozocerite as calculated from the distribution curve and the yield of urea adduct is presented in Table 1. The oil fraction recovered from ozocerite by vacuum distillation contains C_{13}-C_{22} kanes. In contrast to the total hydrocarbon portion of ozocerite, the n-alkane content in the oil fraction is smaller (20%) and the n-alkanes were accompanied by approximately the same number of branched alkanes. The distribution of the individual n-alkanes, both in the oil fraction and in the extract which was separated from the oil by urea adduction, corresponds to the original distribution in ozocerite.

Hydrocarbons	Range of C-atoms	% in hydrocarbon portion	
		in ozocerite	in oil fraction
n-Alkanes	$C_{13}-C_{40}$	57	—
n-Alkanes	$C_{31}-C_{34}$	(27,5)	—
n-Alkanes	$C_{13}-C_{22}$	(3,0)	20,2
Isoalkanes	$C_{15}-C_{22}$	0,57	3,8
Anteisoalkanes	$C_{15}-C_{22}$	0,21	1,4
Übrige Methylalkane*	$C_{15}-C_{22}$	0,41	2,7
Farnesan	C_{15}	0,03	0,2
2,6,10-Trimethyltridecane	C_{16}	0,20	1,3
2,6,10-Trimethyltetradecane	C_{17}	0,15	1,0
2,6,10-Trimethylpentadecane	C_{18}	0,45	3,0
Pristan	C_{19}	0,72	4,8
Phytan	C_{20}	0,42	2,8

Table I. Content of alkane hydrocarbons in ozocerite

* Ubrige Methylalkane = remaining methylalkanes

Methylalkanes. During the urea extraction of the oil fraction obtained from ozocerite, several branched hydrocarbons (peaks a-d) went into the adduct together with the C_{15}-C_{22} n-alkanes. They were identified directly in mixture with the n-alkanes, since the main components of the extract do not interfere with them and no complicated background appears in the chromatogram which could interfere with their identification. The retention indices of components a-d showed regularities which suggest that these components form further homologous series. The retention indices of all a-components on OV-225 at 180°C were approximately 25-26 units higher than those of the adjacent n-alkanes with shorter retention times. A similar regular increase in the /p.2942 retention indices was found for components b-(by approx. 35-36 units), c (approx. 53-55 units) and d (by approx. 69-71 units). Components c, which predominate in the groups of entrained hydrocarbons, were identified mass spectrometrically as homologous series of iso-alkanes. The mass spectra of all c-components exhibited the fragmentation which is typical of 2-methylalkanes, with ions $(M-15)^+$ and $(M-43)^+$ having the greater intensity. For example, during the structural determination of components c which were eluted between n-heptadecane and n-octadecane ($I_{180^\circ}^{OV225} = 1755$) we proceeded from molecular ion m/e 154 which corresponds to the formula $C_{18}H_{38}$. Among the fragmentation ions with more than 10 carbon atoms, the ion at m/e 239, which corresponds to the splitting off of a lateral methyl group, occurs in significant numbers, and the most frequent kind of ion in this range is the ion at m/e 211, which corresponds to the splitting off of a chain-end isopropyl group. From these data the component was identified as 2-methylheptadecane. The structure was verified by the co-injection of the synthetic standard compound. Altogether, eight c-components in the extract were identified as the series of C_{15}-C_{22} 2-methylalkanes.

In a similar way, the d-components were identified as homologous anteisomeric alkane series. In their mass spectra, the ion $(M-29)^+$ occurred most often among the heavier ions corresponding to a methyl group substitution at carbon atom 3 of the alkane chain. The determination of the structure could again be verified gas chromatographically, as the 3-methyalkanes could be easily separated in a capillary column wetted by OV-225 from the iso- /2944
meric 2-methylalkanes which show shorter retention times. The contents of isoalkanes and anteisomeric alkanes presented in Table I were calculated from the chromatogram of the extract by comparing the heights of their peaks to those of the nearest n-alkane peaks.

Components a and b, which almost coincide as a wide doublet on the chromatogram, are a mixture of methylalkanes, based on their mass spectra. According to the molecular ions in the mass spectra, we are dealing / with hydrocarbons which are isomeric with the 2- and 3-methylalkanes and which were eluted close to them. Several $C_nH_{2n+1}^+$ fragmentation ions appear clearly in the middle portion of the spectra and they were accompanied by almost equally intense or even more intense $C_nH_{2n}^+$ ions. From the greater frequency of ions $(M-57)^+$, $(M-71)^+$, $(M-85)^+$ and $(M-113)^+$ etc. and from the relationship of their intensity to that of ions having one hydrogen atom less, it / can be concluded that the methyl groups in the middle portion of the chain / have been substituted at various positions (compare[8,9]). The retention times of these compounds are in agreement with the interpretation of the mass spectra. Thus, for example, synthetic 8-methylpentadecane on OV-225 is eluted right after n-pentadecane, simultaneously with component b. The fact that various methylalkanes with the methyl group near the middle of the chain were eluted in a mixed peak before the peaks of the isomeric 3-methyl- and 2-methylalaknes has also been described for other stationary phases[10].

<u>Isoprenoid</u> <u>Alkanes</u>. The molecular weights of the main components in the raffinate, as determined mass spectrometrically, correspond to the $C_{15}H_{32}$, $C_{16}H_{34}$, $C_{17}H_{36}$, $C_{18}H_{38}$, $C_{19}H_{40}$ and $C_{20}H_{42}$ hydrocarbons. The retention indices of the first four hydrocarbons are lower by 139 to 170 units then the retention indices of n-alkanes with the equivalent number of C-atoms. For the two-last mentioned

hydrocarbons (C_{19} and C_{20}), this decrease is still greater and amounts to 224 and 213 units respectively. The retention time data thus reflect explicitly the difference in the degree of branching of the C_{15}-C_{18} hydrocarbons with 3 lateral methyl groups and of the C_{19}-C_{20} hydrocarbons with 4 methyl substitutions.

In the mass spectra of all hydrocarbons mentioned, the more intense ions $(C_8H_{17})^+$ and $(C_{13}H_{27})^+$, and in the C_{19} and C_{20} hydrocarbons also the ions $(C_{18}H_{37})^+$, occur in the range of m/e values above 99, and they characterize the skeletal arrangement with substitutions in the 2,6,10- and 2,6,10,14- positions respectively. The regular positioning of the methyl groups on every fourth carbon atom is also characterized by the more intense ions at one of the m/e values 127, 141, 155, 169 and 197. Based on the retention data and the agreement with the published spectra of isoprenoid-like alkanes[11,12], the C_{15}-C_{18} hydrocarbons were identified as 2,6,10-trimethyldodecane (farnesane), 2,6,10-trimethyltridecane, 2,6,10-trimethyl- /p.2945 tetradecane and 2,6,10-trimethylpentadecane. The C_{19} and C_{20} hydrocarbons were identified as 2,6,10,14-tetramethylpentadecane (pristane) and 2,6,10,14-tetramethylhexadecane (phytane).

After the n-alkanes, the isoprenoid-like alkanes are the second largest structure group of saturated hydrocarbons in the oil fraction of ozocerite. Their content is as much as two-thirds of the n-alkane content. There are, however, considerable differences in the occurrence of the individual isoprenoids. The largest amount is that of pristane which, in the oil fraction, occurs in the same amount as n-heptadecane. If the small amount of farnesane which is found at the beginning of the boiling range of the oil fraction is not taken into account, 2,6,10-trimethyltetradecane is present in the relatively smallest concentration. Its content is smaller by approximately one quarter than the content of the next lower homolog C_{16} and three times as small as the content of the next higher homolog C_{18}. The contents of all isoprenoid-like alkanes in Table I were calculated from the chromatogram of the oil fraction according to the relative proportion of their peak areas to those of the adjacent n-alkanes.

Discussion

In the oil fraction of ozocerite from Fergana, the same isoprenoid-like alkanes with 3 and 4 lateral methyl groups predominate among the branched alkanes which also occur in considerable quantities in petroleum(11-14) and whose specific biogenic structure serves as biological tagging medium. The relative occurrence of the various isoprenoid-like alkanes in ozocerite- with a preponderance of pristane and a low content of the C_{17} isoprenoid has the same character as in paraffinic petroleum(13-15). The greater portion of monomethylated alkanes in the oil fraction of ozocerite belongs, just as most methylalkanes of petroleum, to the homologous series if iso- and anteiso alkanes. The class of hydrocarbons which is most often found in ozocerite is that of the n-alkanes. Their distribution exhibits no preponderance of the odd-numbered links which is typical of the n-alkanes of recent sediments and recent petroleums, but shows a balanced proportion of even-numbered and odd-numbered links as in the alkanes from petroleum in an advanced stage of development15,16).

The structural identity of alkane hydrocarbons in ozocerite and petroleum mentioned here supports the opinion that ozocerite is the product of the post-genetic separation of solid hydrocarbons from petroleum as a result of changed physical conditions during its migration (see also17)). From this point of view, the first maximum in the distribution curve of n-alkanes from ozocerite (Fig.1) can be explained as a record of the predominating alkanes from the petroleum which was retained as mother liquor in the separated mass when the solid hydrocarbons crystallized.

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Bibliography

1. Wollrab V., Streibl M. im Buch: *Organic Geochemistry* (G. Eglinton, M. T. J. Murphy, Eds.), S. 579. Springer, Berlin, Heidelberg 1969.
2. Schlenk W.: Analyst *77*, 867 (1952).
3. Sergienko S. R., Kozyuro V. I.: Izv. Akad. Nauk Turkm. SSR, Ser. Fiz.-Tech. Chim. i Geol. Nauk *5*, 25 (1965); Chem. Abstr. *64*, 3224 (1966).
4. Boiko G. E., Klimovskaja L. K., Ryltsev E. V., Turkevič V. V., Jatsenko E. F.: Trudy Ukr. Naučn.-Issled. Geol.-Razved. Inst. *5*, 378 (1963); Chem. Abstr. *61*, 9334 (1964).
5. Hessler W., Meinhardt G.: Fette u. Seifen *55*, 441 (1953).
6. Fitzgerald M. E., Cirillo V. A., Galbraith F. J.: Anal. Chem. *34*, 1276 (1962).
7. Kuraš M., Hála S.: Ropa a uhlie *11*, 657 (1969).
8. Herlan A.: Brennstoff-Chem. *50*, 204 (1969).
9. Stránský K., Streibl M., Kubelka V.: diese Zeitschrift *35*, 882 (1970).
10. Jarolímek P., Wollrab V., Streibl M.: diese Zeitschrift *29*, 2528 (1964).
11. Bendoraitis J. G., Brown B. L., Hepner L. S.: Anal. Chem. *34*, 49 (1962).
12. Unger F. G., Ušakova I. B., Rozenberg L. M., Poljakova A. A., Sanin P. I.: Neftechimija *10*, 444 (1970).
13. Rozenberg L. M., Ušakova I. B., Genech I. S., Unger F. G., Smirnov B. A., Zabotnova T. A., Sosylina L. A., Poljakova A. A., Sanin P. I.: Neftechimija *9*, 331 (1969).
14. Krasavčenko M. I., Mnichovskaja A. A., Nikitova N. V., Cedilina A. P., Petrov A. A.: Neftechimija *9*, 651 (1969).
15. Welte D.: Erdöl u. Kohle *20*, 65 (1967).
16. Cooper J. E., Bray E. E.: Geochim. Cosmochim. Acta *27*, 1113 (1963).
17. Kwiecinska B., Ratajczak T.: Bull. Acad. Pol. Sci. Ser., Sci. Geol. Geogr. *17*, 155 (1969); Chem. Abstr. *73*, 132 948 (1970).

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