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INVESTIGATION OF HYDROCARBON COMPONENTS OF A YUGOSLAV SHALE "BITUMEN"

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SUMMARY

Hydrocarbons in the soluble, geolipid portion of Aleksinac (Yugoslavia) shale were investigated in order to find a clue to the origin of the organic material of this sediment.

The *n*-paraffin and branched-cyclic fractions were obtained by using various isolation and separation techniques. Preliminary identifications were made using internal standards in the gas-liquid chromatographic analyses of the fractions.

The major findings were as follows. The *n*-paraffin fraction was found to consist of a C₁₃-C₃₇ homologous series with a predominance of odd-carbon-numbered members in the C₂₅-C₃₇ range. In the branched-cyclic fraction, in addition to phytane and pristane, which were found in considerable amounts, the presence of a series of *iso*-alkanes and of cholestane and coprostane is postulated. Peaks of a great number of other components also existed in the chromatograms of branched-cyclic fractions. However, most of these compounds have yet to be identified.

INTRODUCTION

Hydrocarbons found in soluble shale fractions, often referred to as "bitumen", are of great interest in organic geochemical studies. Many of the hydrocarbons could be considered as "biological markers", compounds that might be related to the plant or animal precursor material, thus giving evidence of the biological origin of the organic matter of sediments.

In order to find a clue to the origin of the organic material, we undertook an investigation of hydrocarbon components in the bitumen of the shale from one of the richest, best known and most investigated deposits in Yugoslavia, located near Aleksinac, Serbia. This shale is of the Miocene age.

The *n*-paraffin and branched-cyclic fractions were obtained by using various isolation and separation techniques. Identifications have been made so far using internal standards in the gas chromatographic (GC) analyses of the fractions.

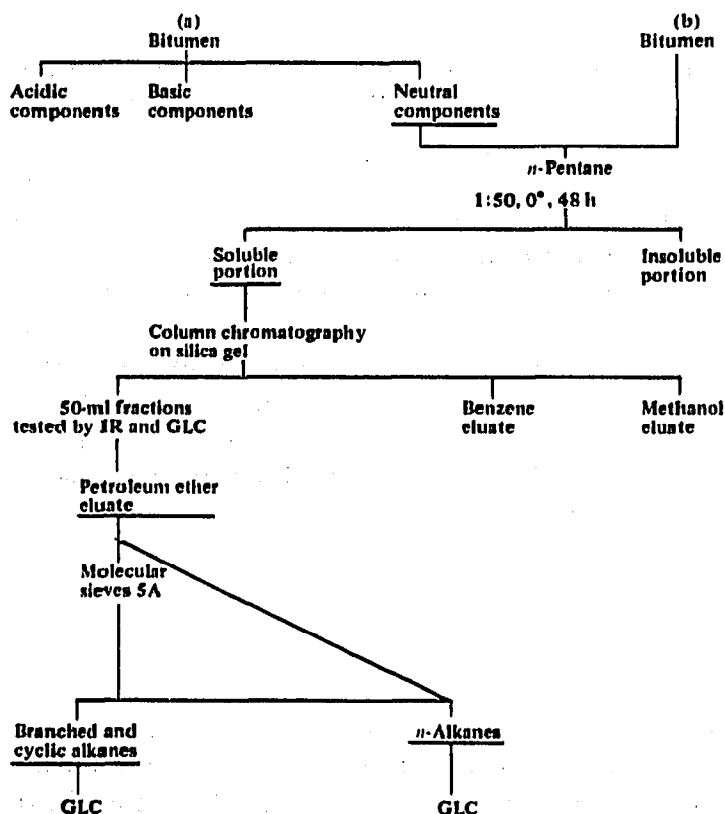
EXPERIMENTAL

There is a difference of opinion in the literature concerning solvents for bitumen isolation. For the sake of comparison, we used the two solvents which are recommended most often, benzene and a benzene-methanol (1:1) mixture.

The bitumens were obtained by 100-h Soxhlet extraction of the powdered shale. By using benzene and benzene-methanol extraction, 1.33% and 4.32% of bitumen, respectively, were obtained, calculated relative to the total organic matter content of the shale.

The hydrocarbon components were separated according to Scheme I.

Two different methods for raw hydrocarbon isolation were used: (a) the bitumen was first separated into neutral, acidic and basic components and then only the neutrals were further processed, and (b) the bitumen was treated directly with *n*-pentane, thus avoiding preliminary separation of acidic and basic components.



Scheme I. Separation procedure.

Petroleum ether eluates were collected in 50-ml portions and tested by IR spectroscopy and GC. Only those fractions whose chromatograms showed a mixture of several homologous series were treated by molecular sieves.

The molecular sieves 5Å were activated at 350° and 1 mm Hg pressure. The usual procedures were used for thiourea adduction.

GC analyses of *n*-paraffin fractions were made on a Varian Aerograph Series 1200 instrument equipped with a flame-ionization detector and a Varian Model 20 recorder. A 0.2 × 200 cm column with 3% of SE-30 on Aeropak was used. The temperature was programmed over the range 50–320° at 10°/min.

TABLE I

YIELD OF PRODUCTS (%)

Components	Method (a)		Method (b)	
	Benzene bitumen	Benzene-methanol bitumen	Benzene bitumen	Benzene-methanol bitumen
Neutral components, relative to bitumen	60.66	43.13	—	—
<i>n</i> -Pentane extract, relative to bitumen				
Soluble portion	54.88	21.01	77.55	28.10
Column chromatography on silica gel (relative to <i>n</i> -pentane solubles)				
Petroleum ether eluate	28.87	18.46	19.83	13.45
Benzene eluate	19.18	9.92	6.49	3.67
Methanol eluate	59.36	68.74	75.39	66.46
Molecular sieve 5A separation (relative to bitumen and to petroleum ether eluate)				
<i>n</i> -Alkanes	4.40 (27.79)	1.27 (32.86)	2.33 (15.14)	0.67 (17.75)
Branched and cyclic alkanes	11.43 (72.21)	2.60 (67.15)	12.82 (83.35)	2.94 (77.82)
Yield of products (relative to shale organic matter)				
<i>n</i> -Alkanes	0.06	0.06	0.03	0.03
Branched and cyclic alkanes	0.15	0.11	0.16	0.13

Branched-cyclic fractions were analyzed on a Perkin-Elmer 800' instrument equipped with a flame-ionization detector and a Varian Model G-14 recorder. A 0.3×300 cm column with 1.5% of SE-30 on 80-100 mesh Gas-Chrom G was used. The temperature was programmed over the range 80-320° at 10°/min.

Hydrogen and argon were used as carrier gases.

RESULTS AND DISCUSSION

Yields of isolated products are given in Table I.

No significant difference was observed between the products obtained by the two different separation procedures.

The relatively low *n*-paraffin content in the bitumen of the Aleksinac shale is consistent with the fact that plant material and more recent sediments contain less *n*-alkanes as compared to ancient sediments¹.

Gas chromatograms of all *n*-alkane fractions were similar. As an example, a gas chromatogram of one of the fractions is shown in Fig. 1a.

Identifications were made by co-injection of two internal standards (Figs. 1b and 1c), viz., pure C₂₈ and C₁₀ *n*-alkanes (supplied by Fluka AG).

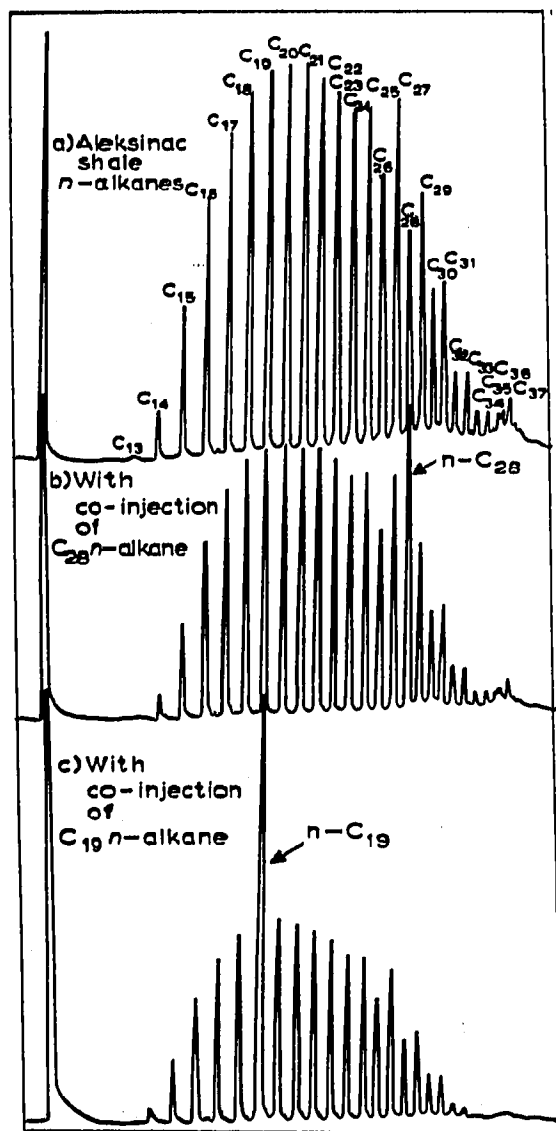


Fig. 1. Chromatogram of the *n*-alkane fraction of Aleksinac shale bitumen (a), and of the same fraction with co-injection of C_{28} (b) and C_{19} (c) *n*-alkanes.

The *n*-alkane fraction was found to consist of a C_{13} to C_{37} homologous series. The number of higher *n*-paraffins identified was very high.

As far as the organic geochemical significance is concerned, it should be pointed out that in the *n*-alkane mixtures isolated from higher plants and from the most recent sediments and some ancient sediments, an excess of odd over even carbon-number compounds has been observed, especially in the C_{26} – C_{34} range^{2,3}.

Therefore, it was of interest to compare the abundances of *n*-alkanes isolated from the Aleksinac shale bitumen. On the basis of peak areas in the chromatograms, approximate weight per cent contents of individual members were calculated. The composition of the C_{24} – C_{37} fraction is presented in Fig. 2. In this range, an excess of odd over even carbon-number compounds was evident.

Gas chromatograms of branched-cyclic fractions represented very complex mixtures. In the region of lower retention times, four prominent peaks were recorded

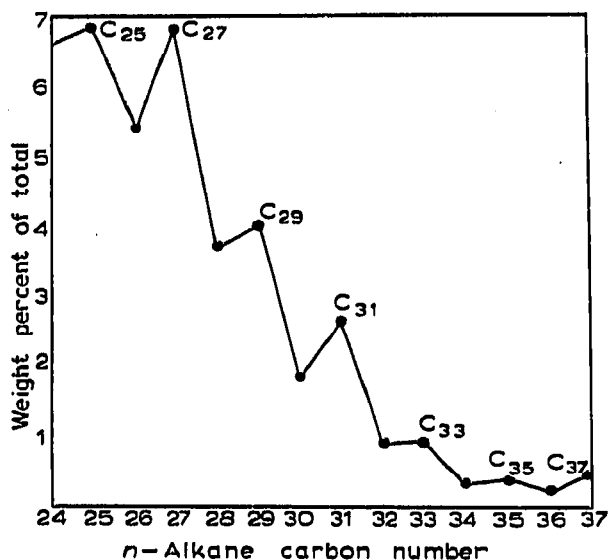


Fig. 2. Composition of the *n*-alkane fraction in the C_{24} - C_{37} range.

(Fig. 3a). By co-injection of two internal standards, *viz.*, of pristane and phytane (Analar), it was shown (Fig. 3b) that the two main peaks corresponded to these isoprenoid hydrocarbons. Phytane was much more abundant than pristane.

In the region of higher retention times of the branched-cyclic fractions poorly separated but very prominent peaks corresponding to other branched alkanes and cycloalkanes were recorded. By co-injection of a mixture of cholestane and coprostane, the presence of these steranes was established (Fig. 4).

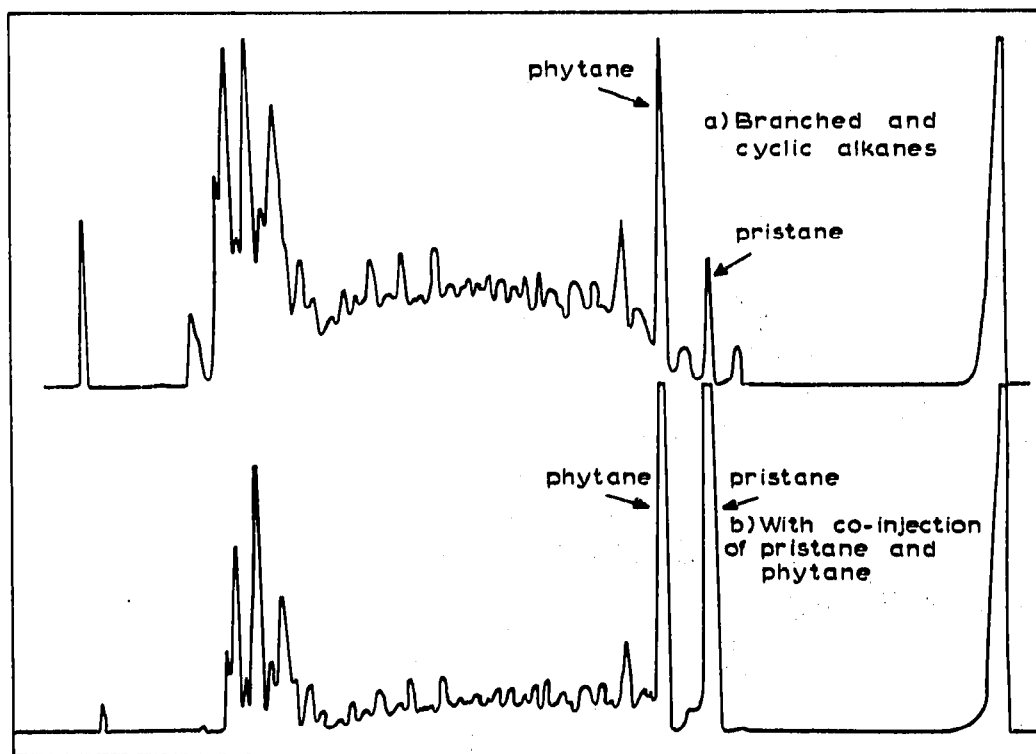


Fig. 3. Chromatogram of the branched-cyclic fraction (a) and of the same fraction with co-injection of pristane and phytane (b).

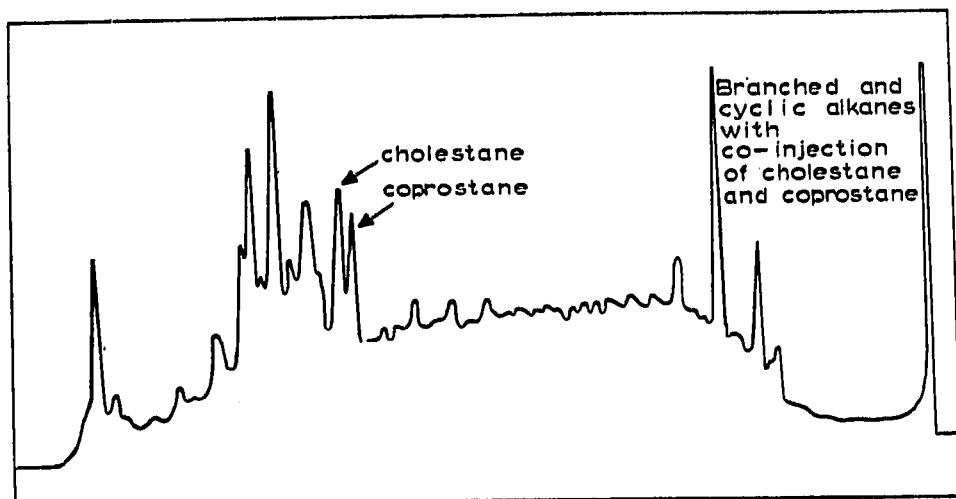


Fig. 4. Chromatogram of the branched-cyclic fraction with co-injection of cholestane and coprostane.

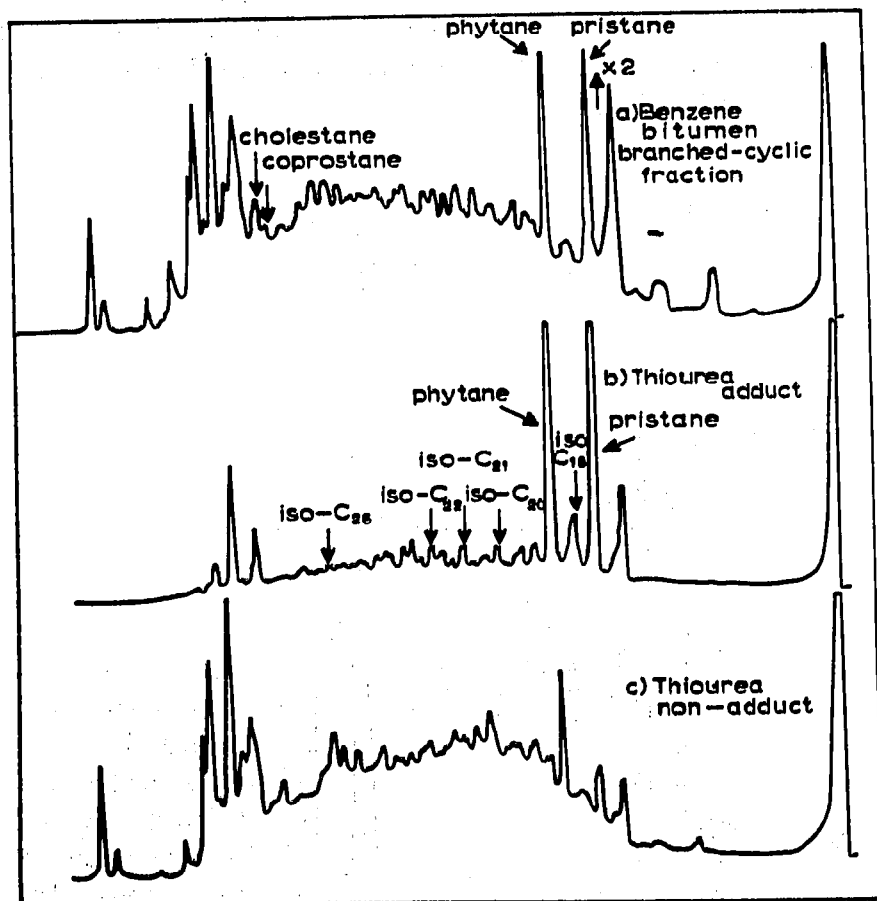


Fig. 5. Chromatograms of (a) benzene bitumen branched-cyclic fraction, (b) thiourea adduct and (c) thiourea non-adduct.

Both acyclic isoprenoid alkanes and non-isoprenoid *iso*- and *anteiso*-alkanes are well known biological markers, being found in significant amounts in many plants and animals as well as in sediments, their abundances varying depending on the origin of the material being investigated^{4,5}. Steranes, cyclic tetra-, tri- and diterpanes are also considered as useful biological markers, in spite of the fact that living organisms so far do not appear to contain saturated isoprenoid cycloalkanes, because their probable precursors are steroids and terpenoids⁶.

Therefore it was of interest to look for the presence of some other classes of biological markers in the branched-cyclic fractions, for example *iso*-alkanes. In order to facilitate the identification, a simplification of the branched-cyclic fraction has been attempted by thiourea adduction.

The ratio of adduct to non-adduct hydrocarbons in the branched-cyclic fraction was 1:6.

The chromatogram of the benzene bitumen branched-cyclic fraction is given in Fig. 5a, together with chromatograms of the thiourea adduct (Fig. 5b) and the thiourea non-adduct (Fig. 5c) of this fraction.

By co-injection of five *iso*-alkanes with the thiourea adduct, the presence of a homologous series of *iso*-alkanes might be established. Two of the *iso*-alkane standards, 2-methylheptadecane and 2-methylnonadecane, were synthesized in our laboratory. Fig. 6 shows a chromatogram of the thiourea adduct with co-injection of 2-methyleicosane, 2-methylheneicosane and 2-methylpentacosane.

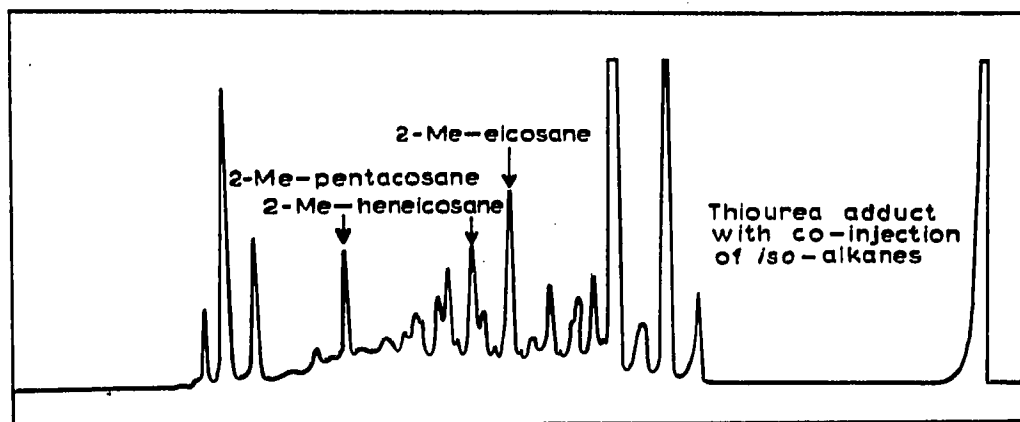


Fig. 6. Chromatogram of thiourea adduct with co-injection of 2-methyleicosane, 2-methylheneicosane and 2-methylpentacosane.

On the basis of the chromatograms, the presence of other branched alkanes, of other steranes and of triterpanes might be assumed. However, for a more complete identification, the complex branched-cyclic fraction should be further investigated. At present we are studying these mixtures by using a gas chromatograph-mass spectrometer system.

CONCLUSIONS

The major findings obtained by investigation of the hydrocarbon components of the Aleksinac shale bitumen were as follows. The *n*-paraffin fraction was found to

consist of a C_{13} – C_{37} homologous series with a predominance of odd-carbon-numbered members in the C_{25} – C_{37} range. In the branched-cyclic fraction, in addition to phytane and pristane, which were found in considerable amounts, the presence of a series of *iso*-alkanes and of cholestane and coprostane is postulated.

The dominance of odd-carbon-numbered *n*-alkanes, as well as of phytane over pristane, indicates a mainly plant origin for the organic matter of this sediment.

ACKNOWLEDGMENTS

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