Classification of Kerogen from Aleksinac (Yugoslavia) Oil Shale Based on its Oxidation Products*

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A twenty-three step alkaline permanganate degradation of kerogen from Aleksinac (Yugoslavia) shale was carried out. A very high total yield of oxidation products was obtained (92.84%) based on original kerogen). Detailed GC-MS analyses of ether-soluble acids, soluble products of further controlled permanganate degradation of precipitated acids and acids from aqueous solutions, served as basis for quantitative estimation of the participation of various types of products and for comparison with other kerogens based on similar criteria. The prevailing saturated long-chain aliphatic structure of oxidation products suggested a predominantly open-chain cross-linked aliphatic structure of Aleksinac shale kerogen, classified as type I kerogen. Nevertheless, noticeable proportion of alkane-polycarboxylic and aromatic acids in the oxidation products indicated a larger share of alicyclic, heterocyclic, and aromatic structures in this kerogen. Oxidative degradation products were shown to enable more precise structural interpretation than the classification based on elemental analysis.

INTRODUCTION

Kerogens, comprising the solvent insoluble organic matter from sedimentary rocks, are the most abundant organic material in the crust of the Earth. They have most often ben classified on the basis of their atomic H/C and O/C ratios (kerogens of type I, II and III)[1,2]. Recently a new method for classification of kerogens was proposed based on the products of their multistep oxidative degradation[3-6]. Contrary to elemental analysis, oxidative degradation was expected to reflect minor structural differences between kerogens, which, being heterogeneous, may represent infinite combinations of mixtures of two

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* Dedicated to Professor Mihailo Lj. Mihailović on the occasion of his 60th birthday.

or more end-types. However, this proposal was based on examination of only three selected representative kerogen samples, i. e. type I from Green River shale, type II from Toarcian shale, Paris Basin, and type III from Mannville shale, Canada.[3-6] Therefore, further degradation studies of kerogens of various provenance were expected to show how general were the conclusions obtained in the initial study of a limited number of kerogen samples.

The currently most detailed structural study of the kerogen from Aleksinac (Yugoslavia) oil shale, presented in this paper, will at the same time represent the first case of verification of the novel kerogen classification method. The kerogen from Aleksinac shale, being most often of type I (infrequently of type II), will primarily be compared with the kerogen from the Green River shale, Colorado, USA, as representative of type I kerogens[3,6].

A careful, 23-step alkaline permanganate degradation of the kerogen concentrate was carried out. The examination of the products consisted of: (a) capillary gas chromatographic (GC) and gas chromatographic-mass spectrometric (GC-MS) analysis of the methyl esters of ether-soluble acids, and (b) further controlled, stepwise alkaline permanganate oxidation of precipitated, ether-insoluble acids, followed by GC-MS analysis of the ether-soluble acids thus obtained. Furthermore, having in mind that some of the oxidation products, being very soluble in water, may have avoided the routine isolation procedure, a further step was introduced. In this step all aqueous solutions remaining after the usual ethereal extraction of oxidation products, were separately worked up in order to isolate the water soluble oxidation products. These products were also analyzed by GC and GC-MS.

EXPERIMENTAL

Sample Preparation and Oxidative Degradation

A sample of oil shale (no. 5 from core S-1, 119.20 to 121.40 m, Fischer assay: 13.00%), was obtained from the Aleksinac coal mine (Serbia, Yugoslavia). The oil shale from Aleksinac is a lacustrine, Tertiary (Miocene) immature sediment. It was difficult to estimate the maturity because of the absence of indigenous vitrinite. An equilavent vitrinite reflectance value was estimated as about 0.3%.

The kerogen concentrate was prepared by treatment of the powdered shale with hydrochloric acid (1 : 4) at 70 °C and then with hydrofluoric acid (1 : 1), followed by a 60 h Soxhlet extraction of the washed and dried residue with an azeotropic mixture of benzene and methanol. The kerogen concentrate contained 31.15% ash and 65.57% kerogen, consisting of 71.87% carbon, 8.73% hydrogen and 3.21% nitrogen, O + S (by difference) being 16.19%. The atomic H/C and O/C ratios were 1.46 and 0.17, respectively, corresponding to type I kerogen.

The kerogen concentrate (3.5697 g, containing 2.3407 g kerogen) was oxidized in 23 steps with 0.5 g $KMnO_4$ per step in 100 cm^3 of 1% KOH, according to the standard degradation scheme as described by Amblès et al.[7]. Experimental conditions were chosen to be identical to those used in the preceding structural studies[3-6]. Permanganate portions (0.5 g) were added in aqueous solution (10 cm^3) to kerogen concentrate suspension heated to a reaction temperature of 75 °C. At the end of each oxidation stage, established by disappearance of the violet and green colours, the remaining solids were separated by centrifugation and washed thoroughly with 0.5—1% KOH to remove all oxidation products. Following each five steps, the accumulated MnO_2 was removed by treatment with an excess of a solution of oxalic acid and thorough rinsing with distilled water. The final oxidation mixture was treated in a similar way. The solid residue was dried at 80 °C and analyzed for organic matter.
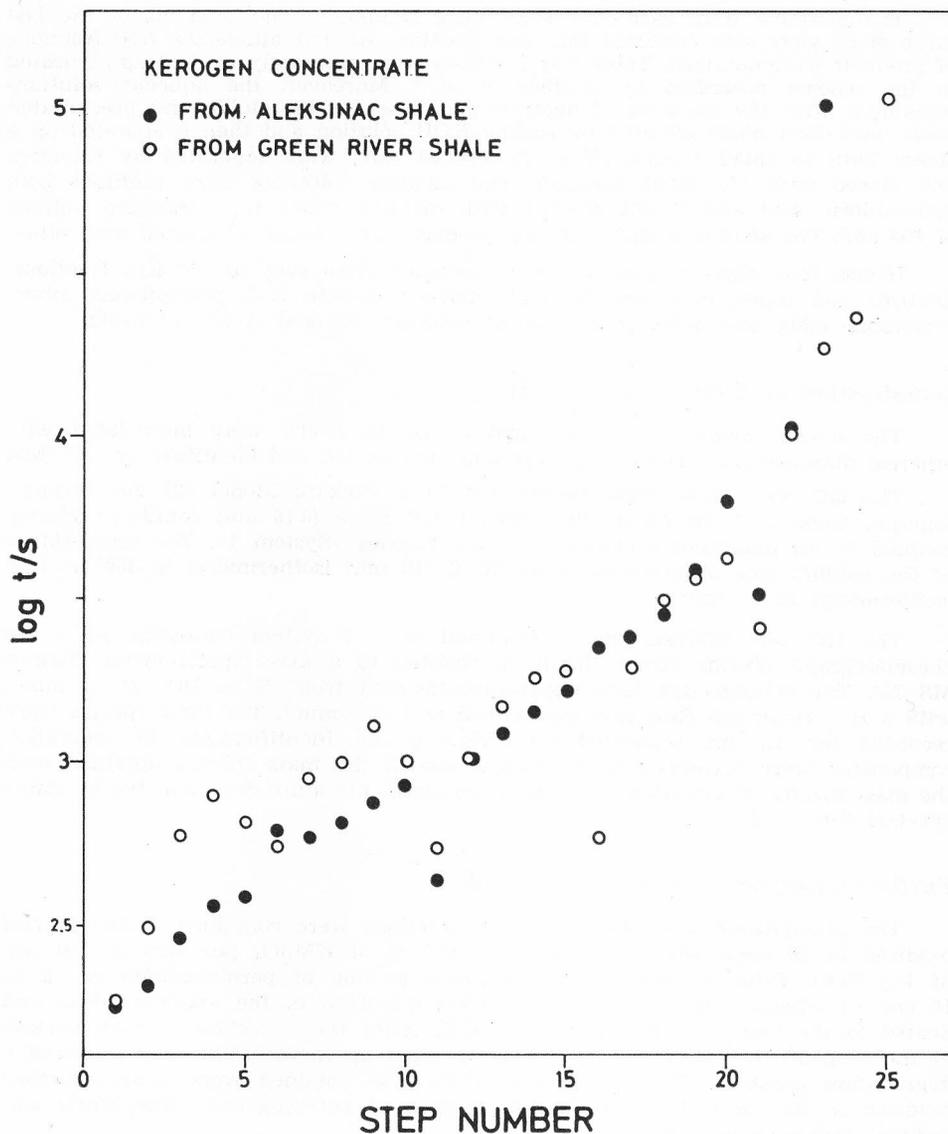
Figure 1. Duration of single degradation steps (log t/s = log time in seconds).

The reduction periods gradually increased during the oxidation procedure as shown in Figure 1. Occasional shorter reduction periods (11th and 21st steps) followed the removal of MnO_2. They were probably partly a result of increased reactivity of purified kerogen concentrates. In Figure 1, as well as in some other figures in this paper, corresponding parallel data obtained in the degradation of the Green River shale type I kerogen[3] are also shown, for the sake of comparison.

The last, 23rd portion of permanganate was reduced in 29 h. This was taken as final degradation step[6].

The products from each five steps were combined. The products of the last three steps were also collected into one fraction, so that altogether five fractions of products were obtained. These five fractions were separately worked up according to the scheme described by Amblès et al.[7,8]. Moreover, the aqueous solutions remaining after the isolation of neutrals and bases, ether-soluble and precipitated acids were first made alkaline by adding KOH solution and then evaporated on a steam bath to small volume. The crystallized salts were separated by filtration and rinsed with 1% KOH solution. The alkaline solutions were acidified with hydrochloric acid and finally diluted with distilled water to a standard volume of 100 cm³. The soluble acidic oxidation products were finally extracted with ether.

Hence, four types of products were obtained from each of the five fractions: neutrals and bases, ether-soluble acids marked A-1 to A-5, precipitated, ether-insoluble acids, and acids from aqueous solutions marked A-1(2) to A-5(2).

Investigation of Ether-Soluble Acids

The soluble acids A-1 to A-5 and A-1(2) to A-5(2) were methylated with ethereal diazomethane. The esters were analyzed by GC and identified by GC—MS.

The GC separations were carried out in a Packard Model 427 gas chromatograph, using a 25 m fused silica WCOT CP Sil 5 (0.16 μm) capillary column, coupled to an integrator-calculator Spectra Physics »System 1«. The temperature of the column was programmed from 70 °C (10 min isothermally) to 300° (5 min isothermally) at 2° min⁻¹.

The GC—MS analyses were performed with a system consisting of a gas chromatograph (Perkin-Elmer Sigma 3) coupled to a mass spectrometer (Kratos MS 25). The column was temperature-programmed from 70 to 300° at 2° min⁻¹, with a He carrier gas flow rate maintained at 1 cm³ min⁻¹. The mass spectra were recorded for all the separated significant peaks. Identifications of individual components were accomplished by comparison of the mass spectra obtained with the mass spectra of available authentic compounds, literature data, and the available spectral data bank.

Further Oxidation of Precipitated Acids

The precipitated acids from the five fractions were combined (1.0667 g) and oxidized in 26 steps with small amounts (0.5 g) of KMnO₄ per step in 100 cm³ of 1% KOH. Prior to addition of each new portion of permanganate (0.5 g in 10 cm³ of aqueous solution), the acids were dissolved in the alkali solution and heated to the reaction temperature of 75 °C. After the reduction of each portion of the reagent, the reaction mixture was worked up in the same way as kerogen degradation products. The precipitated acids thus obtained were always further oxidized in the next step with a new portion of permanganate. The MnO₂ was reduced following each 5 steps.

The reduction periods gradually increased towards the later steps (Figure 2). However, this trend involved several shorter reduction periods (6th, 11th, 16th and 21st steps) which regularly followed the removal of MnO₂.

The small quantity of precipitated acids obtained in the last step was washed and dried at 80 °C. The ether-soluble acids from each five successive steps were combined into five fractions: AP-1 to AP-5. The aqueous solutions from the five stages were worked up in the same way as in the degradation of the kerogen concentrate. Hence, five fractions of acids were isolated. They were marked AP-1(2) to AP-5(2). All the acids were methylated with ethereal diazomethane and analyzed by GC and GC—MS in the same way as the products obtained in the degradation of the kerogen concentrate.
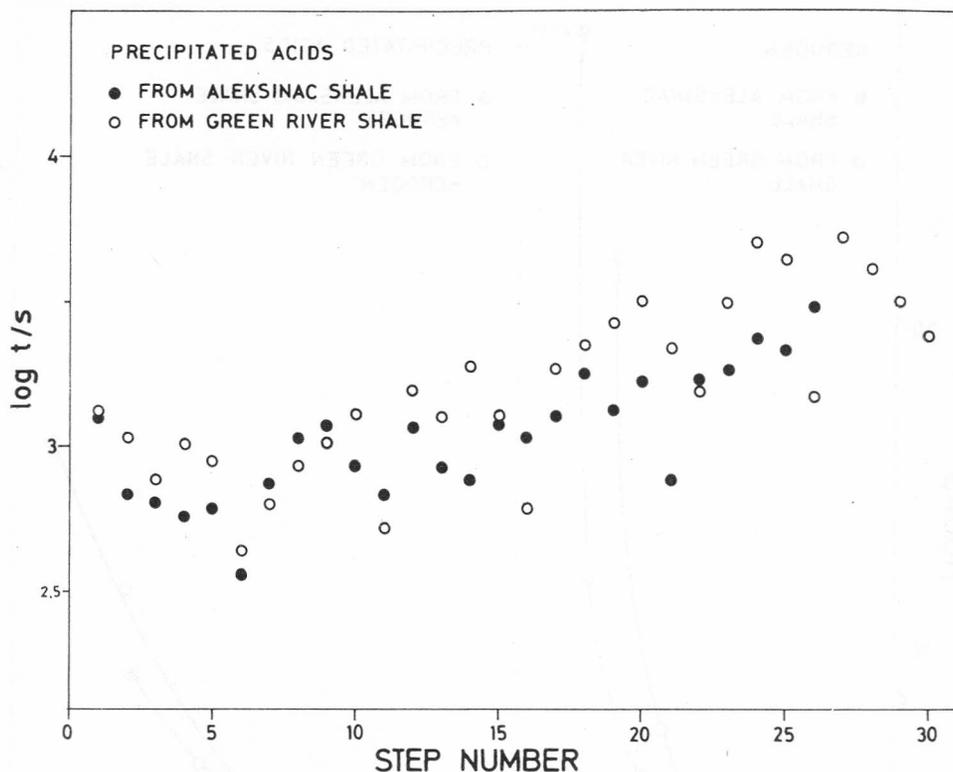
Figure 2. Duration of single degradation steps (log t/s = log time in seconds).

RESULTS

Degradation of the Kerogen Concentrate

The rate of permanganate oxidation, based on one gram of kerogen is presented in Figure 3a. Data obtained in the degradation of the Green River shale type I kerogen[3] are given for comparison purposes.

Twenty three steps were necessary for the degradation of the kerogen and a total amount of 11.5 g of $KMnO_4$ was consumed (4.91 g per gram of kerogen). Approximately 41 h were needed for the twenty three steps, the last, 23rd step being 29 h.

The yields of products in the five oxidation stages are shown in Figure 4a. The yields of neutrals and bases, ether-soluble acids, and precipitated acids were 1.00%, 27.97%, and 45.57%, respectively, relative to the original kerogen, the total yield being 74.54%. The ratio of insoluble vs ether-soluble acids was 1.63. The total yield of acids isolated from aqueous solutions was 18.30% relative to the original kerogen, raising the total yield of oxidation products to 92.84%.

The solid residue which remained after the final oxidation step (0.5464 g) contained 0.2276 g organic matter (9.72% relative to the original kerogen).
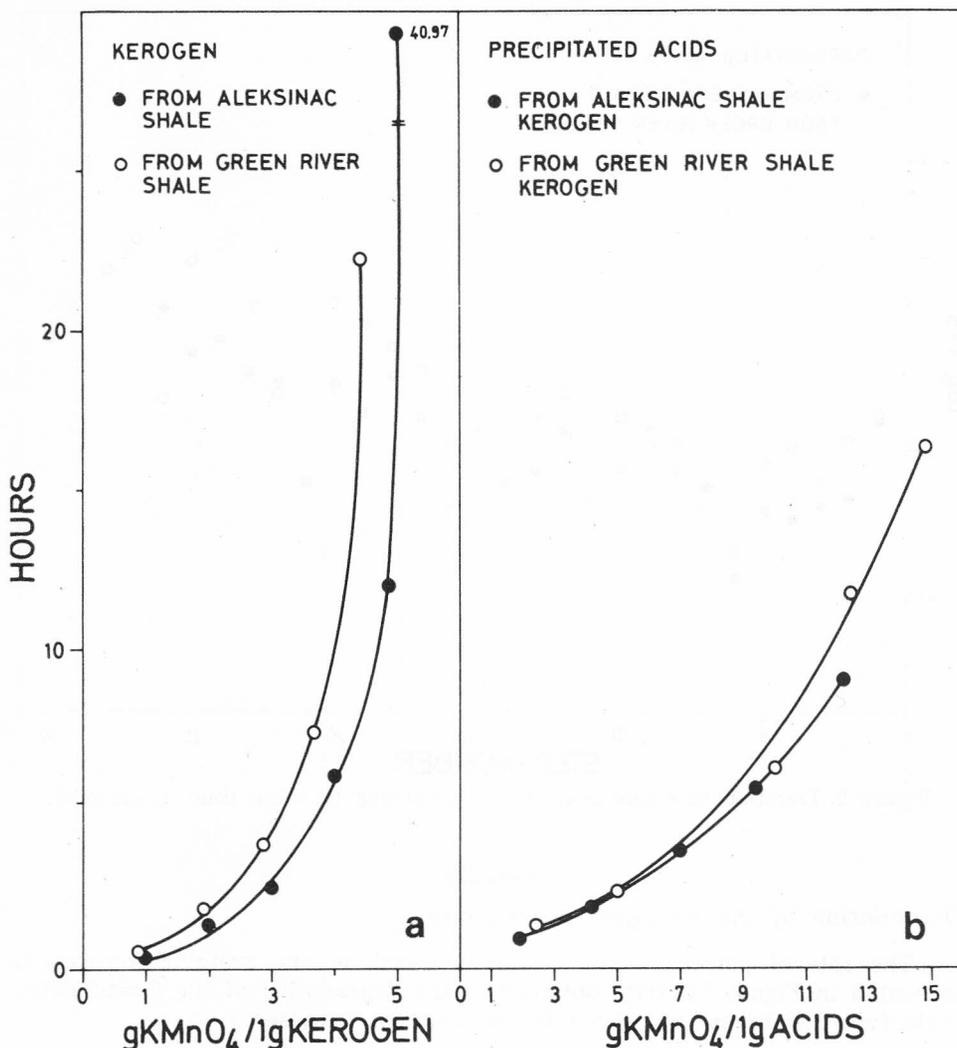
Figure 3. Rates of permanganate oxidation, based on 1 g of kerogen (a) or precipitated acids (b).

The GC-MS analyses of the various fractions of ether-soluble acids revealed the presence of saturated normal mono-and dicarboxylic acids, alkane tri- and tetracarboxylic, isoprenoid and different aromatic mono-, di- and tricarboxylic acids. The identified ether-soluble acids are listed in Table I. There was no marked difference in the compositions of the ether-soluble acids from the five oxidation stages.

The gas chromatogram of combined ether-soluble acids A-1 to A-5 is shown in Figure 5.

TABLE I

Ether-soluble Acids Obtained by Oxidation of Kerogen from Aleksinac Shale

ACIDS	From kerogen	From corresponding aqueous solution	From precipitated acids	From corresponding aqueous solutions
ALIPHATIC				
n-monocarboxylic	C_{10}—C_{30}	C_{14}, C_{16}—C_{18}	C_{12}—C_{32}	C_{12}—C_{14}, C_{16}—C_{18}
α,ω-dicarboxylic	C_7—C_{31}	C_5—C_{11}	C_7—C_{33}	C_6—C_{11}, (C_8 br)
isoprenoid	C_{14}^{α}—C_{17}^{δ}, C_{19}^{α}, C_{20}^{β}, C_{21}^{γ}	—	C_{15}^{β}	—
ALKANE-				
tricarboxylic	C_8—C_{15}	C_6—C_9	C_8—C_{11}	C_6, C_7, C_6 br—C_9 br(?)
tetracarboxylic	C_9—C_{18}	(C_7), C_8—C_{10}	C_9—C_{13}	C_8, C_9, C_9 br, C_{10} br
AROMATIC				
monocarboxylic	$C_{11}H_9$	$C_{11}H_9$, ($C_{15}H_{23}$)	—	$C_{11}H_9$
dicarboxylic	C_6H_4, C_9H_{10}	$C_6H_4(2)^*$, C_7H_6 $C_{11}H_8$, C_7H_6O	C_6H_4, C_7H_6 $C_{13}H_{12}$	$C_6H_4(2)$, C_7H_6, $C_{11}H_8$
tricarboxylic	C_6H_3	$C_6H_3(3)$, C_7H_5	C_6H_3	$C_6H_3(2)$, C_7H_5

* Numbers in parentheses indicate the number of isomers found.

Identifications of the acids A-1(2) to A-5(2), isolated from the corresponding aqueous solutions, are also reviewed in Table I. One gas chromatogram of these acids in the form of methyl esters is given as an example in Figure 6.

The GC-MS analyses revealed the presence of saturated normal mono- and dicarboxylic acids, alkane tri- and tetracarboxylic acids and various aromatic mono-, di- and tri-carboxylic acids. The compositions of the five fractions of acids from aqueous solutions were almost identical.

Degradation of Precipitated Acids

The rate of permanganate oxidation of precipitated acids, based on one gram of the acids, is shown in Figure 3b, involving parallel data for the degradation of the Green River shale type I kerogen. Twenty-six steps were not sufficient for complete degradation of 1.0667 g of precipitated acids. In 26 steps, a total amount of 13 g of $KMnO_4$ was consumed (12.19 g per gram of acids). The total duration of the twenty-six steps was almost 9 h.

The yields of the products obtained in the degradation of the precipitated acids are shown in Figure 4b. The total yields of neutrals and bases and ether-soluble acids were 3.25% and 72.86%, respectively, relative to original precipitated acids. The yield of precipitated acids in the 26th step was 0.1424 g (13.35%). Finally, the total yield of acids isolated from aqueous solutions was 14.01% relative to original acids, making the total yield of products 103.47%.

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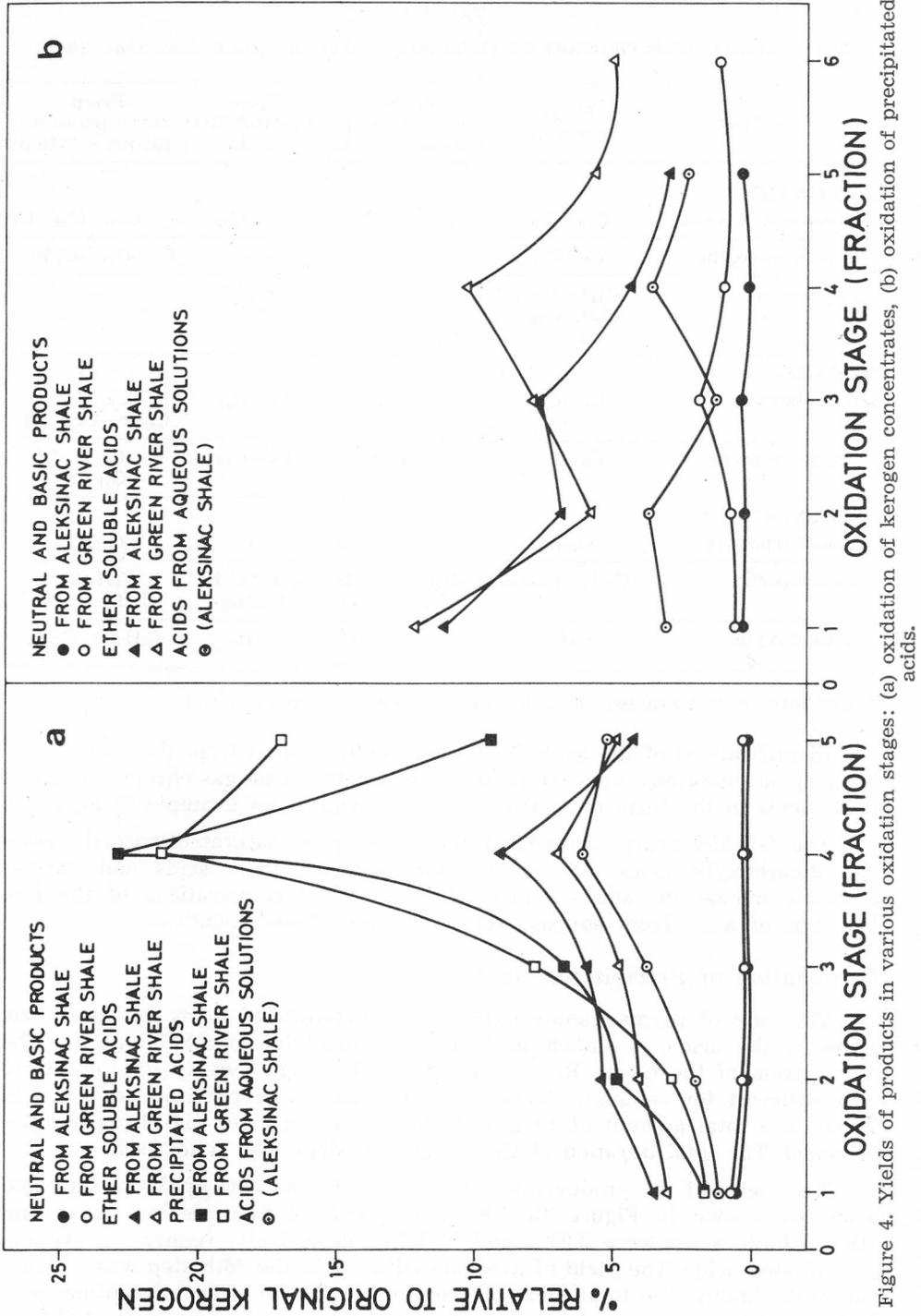Figure 4. Yields of products in various oxidation stages: (a) oxidation of kerogen concentrates, (b) oxidation of precipitated acids.
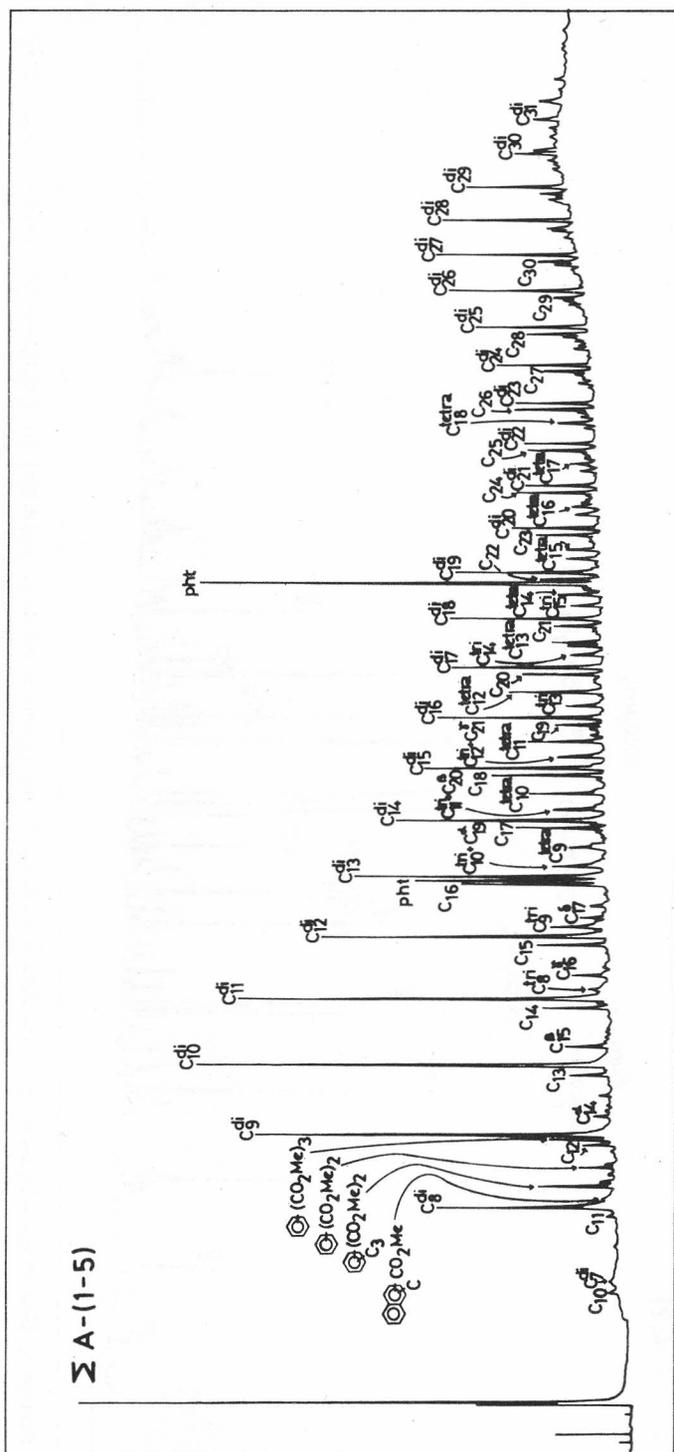
Figure 5. Gas chromatogram of ether-soluble acids A-1 to A-5, in the form of methyl esters. C_x^{di} denotes saturated normal α,ω-dicarboxylic acids, $C_x^{\alpha-\delta}$ isoprenoid acids, C_x^{tri} alkane-tricarboxylic, and C_x^{tetra} alkane-tetracarboxylic acids.

Figure 6. Gas chromatogram of acids A-4(2) isolated from aqueous solution, obtained by oxidation of kerogen concentrate (stage 4),in the form of methyl esters. Denotations are the same as in Figure 5.

A gas chromatogram of one of the fractions of oxidation products of precipitated acids is shown as an example in Figure 7. The GC-MS analyses of the five fractions AP-1 to AP-5 revealed the presence of all types of acids that were found in the oxidation products of the kerogen concentrate. The identified acids are listed in Table I. Slight differences were observed in the distributions of acids obtained in the five oxidation stages.

Identifications of acids AP-1(2) to AP-5(2), isolated from the corresponding aqueous solutions, are also reviewed in Table I. One of the gas chromatograms is given as an example (Figure 8). Identifications included aliphatic normal mono- and dicarboxylic, alkane-tri- and tetracarboxylic, aromatic mono-, di- and tricarboxylic, and several branched dicarboxylic and alkane-tri- and tetracarboxylic acids. No marked difference was observed between the compositions of the five fractions.

DISCUSSION AND CONCLUSIONS

There were two main aims of this paper. On one hand, it was of interest to perform a most detailed structural study of the kerogen from the best known Yugoslav oil shale. On the other hand, a recently proposed classification of kerogens based on their oxidation products[3-6] was expected to be validated by examination of kerogens of different geographic origin.

Therefore, the type I kerogen from Aleksinac shale was chosen for detailed stepwise alkaline permanganate degradation, to be carried out under the same conditions as used in all preceding kerogen structural studies[3-6] which led to the proposal of the new basis for kerogen classification. The choice of experimental conditions was aimed at obtaining as high as possible yields of oxidation products with retained kerogen structural characteristics.

A twenty-three-step alkaline permanganate degradation of Aleksinac shale kerogen, described in this paper, resulted in very high yield of oxidation products, such as neutrals and bases, ether-soluble, and precipitated, ether-insoluble acids (74.54% relative to initial kerogen). However, in this work, for the first time in Aleksinac shale kerogen structural studies, the oxidation products from aqueous solutions were also examined, resulting in additional 18.30% of acidic oxidation products. Hence, the total yield of degradation products reached a very high figure of 92.84% relative to original kerogen.

The major constituents in the fraction of ether-soluble acids (27.97% yield) were found to be the saturated unbranched C_7—C_{31} α,ω-dicarboxylic acids (62.67%). Among them, the most abundant were the acids in the range C_7—C_{19}, although a bimodal distribution of α,ω-dicarboxylic acids was observed (Figure 9). The most abundant component was the C_{10} dicarboxylic acid.

The range of identified saturated normal monocarboxylic acids (C_{10}—C_{30}; 17.53% of ether-soluble acids) is also illustrated in Figure 9. The maximum was found to be at C_{16}. An even/odd predominance was observed in the C_{16}—C_{30} range of normal monocarboxylic acids.

The yield of alkane-tricarboxylic (C_8—C_{15}) and alkane-tetracarboxylic (C_9—C_{18}) acids was noticeable (15.62% of ether-soluble acids). Isoprenoid (1.60%) and aromatic (2.58%) acids were less important but still significant components.

The evidence obtained from ether-soluble acids only, i. e., the dominance of saturated unbranched α,ω-dicarboxylic acids of relatively high molecular mass ($> C_7$), monocarboxylic acids ($> C_{10}$) and isoprenoid acids, making alto-
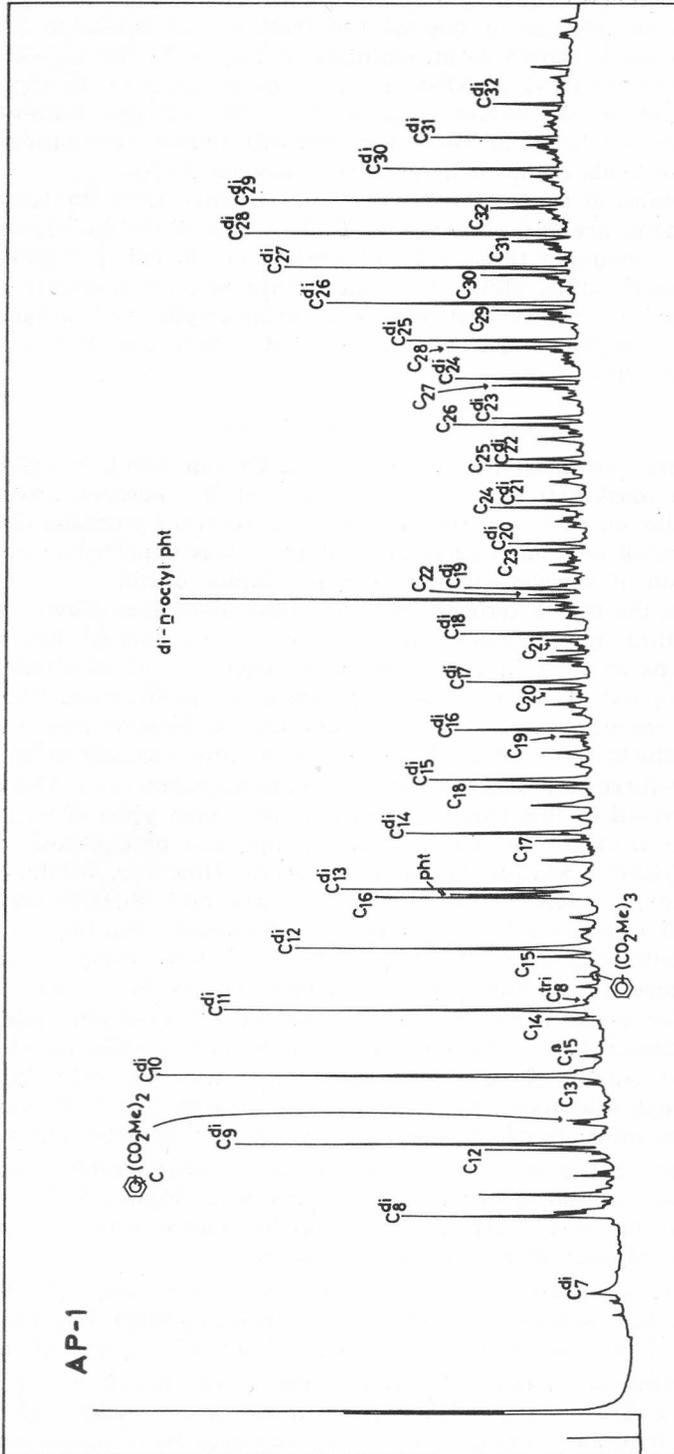
Figure 7. Gas chromatogram of ether-soluble acids AP-1, obtained by oxidation of precipitated acids (stage 1), in the form of methyl esters. Denotations are the same as in Figure 5.
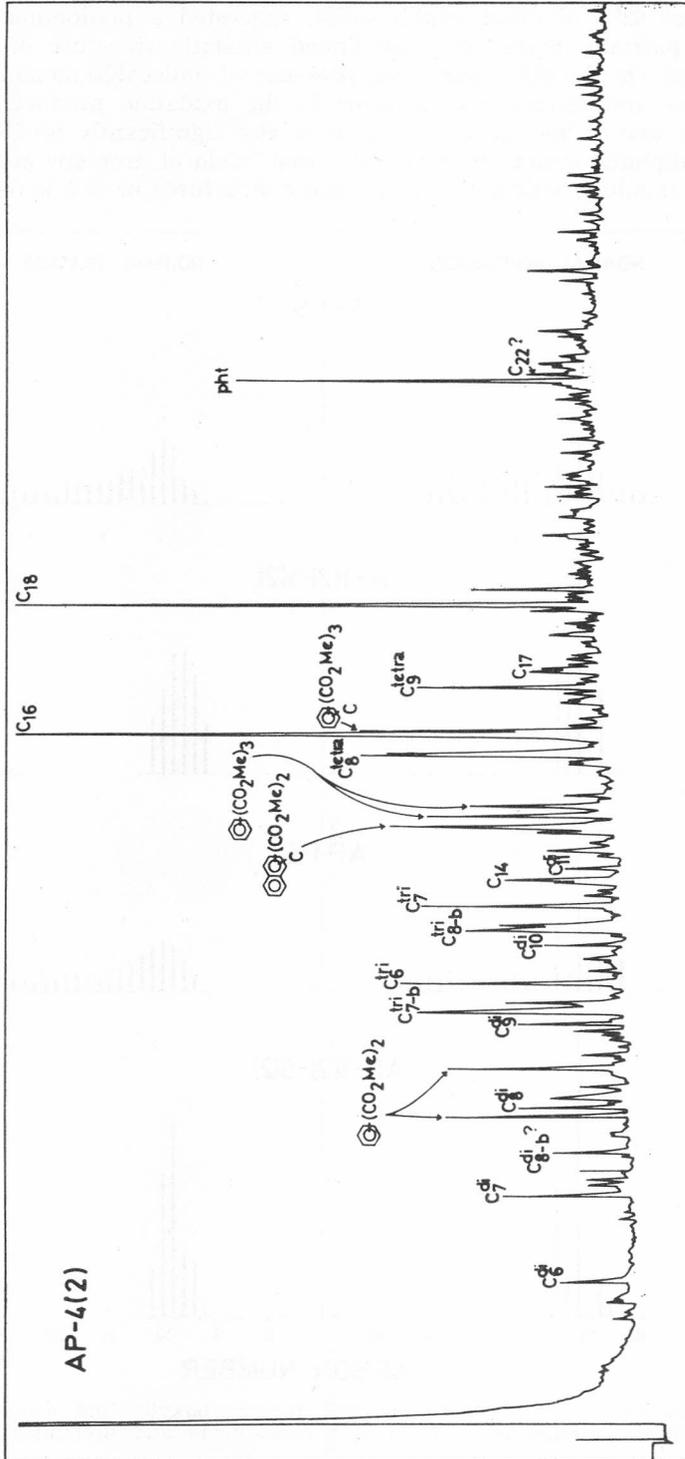
Figure 8. Gas chromatogram of acids AP-4(2) isolated from aqueous solution, obtained by oxidation of precipitated acids (stage 4), in the form of methyl esters. Denotations are the same as in Figure 5.

gether almost 82% of ether-soluble acids, suggested a predominantly open-
-chain and partially branched, cross-linked aliphatic structure of Aleksinac
shale kerogen. On the other hand, the presence of noticeable amount (15.62%)
of alkane-tri- and tetracarboxylic acids in the oxidation products indicated
that alicyclic and/or heterocyclic rings were also significantly involved in the
long-chain aliphatic structure. Relatively small yield of aromatic acids (2.58%)
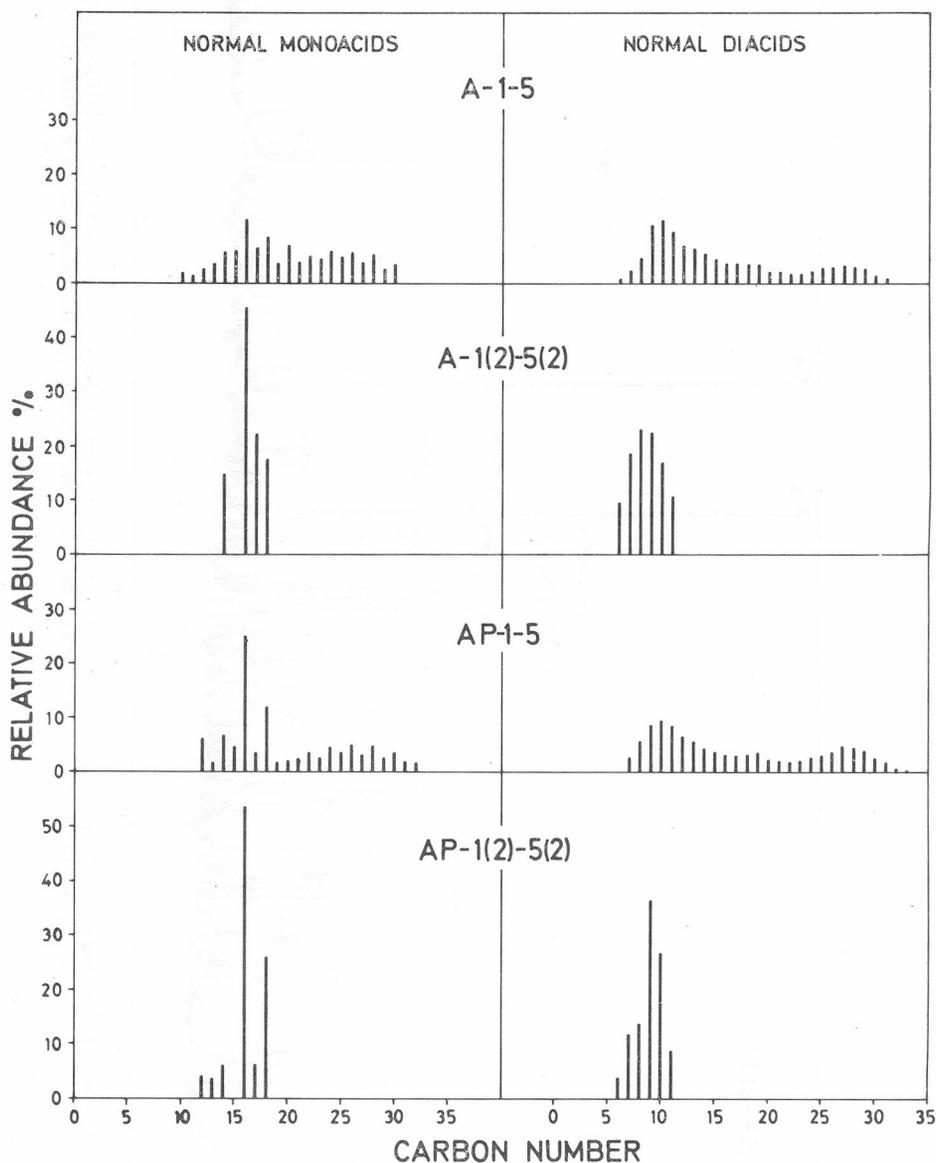suggested a smaller participation of aromatic structures in this kerogen.

Figure 9. Distribution of saturated normal monocarboxylic and α,ω-dicarboxylic
acids obtained in oxidations of kerogen concentrate and precipitated acids.

However, since ether-soluble acids represented less than 30% of all oxidation products, confirmation of such structural interpretation required further examination of other oxidation products, primarily the main product, the precipitated, ether-insoluble acids (45.57% yield), as well as the acids from aqueous solutions (18.30% yield).

Degradation products of controlled oxidation of precipitated acids were obtained in high yield in the form of ether-soluble acids (72.86%, relative to original precipitated acids). Again, saturated unbranched α,ω-dicarboxylic (C_7—C_{33}) acids with a bimodal distribution and a maximum at C_{10} (Figure 9), were found to be the major oxidation product (69.11%). Normal monocarboxylic acids (C_{12}—C_{32}) with a maximum at C_{16} and an even/odd predominance (Figure 9) were also obtained in high yield (23.79%). Alkane-polycarboxylic and aromatic acids were minor oxidation products (5.45% and 1.65%, respectively).

Hence, the structure of precipitated acids, as suggested by oxidative degradation studies, corroborated the structural interpretation based on ether--soluble acids.

Finally, acids from aqueous solutions from both the degradation of kerogen concentrate and the precipitated acids remained to be tested before a final structural interpretation can be attempted. The compositions of acidic mixtures isolated from aqueous solution were different compared to ether--soluble acids from both the degradations of kerogen concentrate and precipitated acids. With the exception of aromatic acids, the distributions of acids were more simple and were displaced towards lower molecular weights.

The major constituents of the acidic mixtures isolated from aqueous solutions in the degradation of the kerogen concentrate were alkane-polycarboxylic acids, 41.03% (tricarboxylic C_6—C_9 acids 9.65%, and tetracarboxylic C_7—C_{10} acids 31.38%), and aromatic acids (27.71%). Among aliphatic acids, the normal α,ω-dicarboxylic acids dominated (C_5—C_{11}; 23.43% relative to total acids). As shown in Figure 9, their maximum was at C_8. The proportion of normal monocarboxylic acids (C_{16}—C_{18}) was found to be the smallest (7.83%), but the maximum was again at C_{16}.

The participation of various types of acids isolated from aqueous solutions in the degradation of precipitated acids was more uniform: alkane-tri-(C_6—C_9) and tetra-(C_8—C_{10}) carboxylic acids 27.70% (13.38% and 14.32%, respectively), aromatic acids 26.75%, normal monocarboxylic C_{12}—C_{18} acids 26.65% and α,ω-dicarboxylic C_6—C_{11} acids 18.90%. With monocarboxylic acids the maximum was found to be at C_{16} and with α,ω-dicarboxylic acids at C_9.

A higher proportion of alkane-polycarboxylic and aromatic acids as well as lower molecular weight normal α,ω-dicarboxylic acids in the products isolated from aqueous solutions, may have been expected because of higher water solubility of these products.

The total balance of all oxidation products is presented in Table II. It shows that isolation of acids from aqueous solutions has changed noticeably the composition of total oxidation products. The proportion of alkane-polycarboxylic and aromatic acids increased. A similar trend has already been observed in the examination of type I (Green River shale) and type II (Toarcian shale Paris Basin) kerogens[9,10].

TABLE II

Composition of Oxidation Products Obtained from Aleksinac Shale Kerogen

ACIDS	% relative to total oxidation product	
	Not counting acids from aqueous solutions	Including acids from aqueous solutions
ALIPHATIC		
monocarboxylic	20.56	18.80
α,ω–dicarboxylic	65.76	55.77
isoprenoid	0.88	0.68
ALKANE-		
tricarboxylic	4.67	6.05
tetracarboxylic	6.01	10.77
AROMATIC	2.12	7.93

Taking into account the high yields of oxidation products and their prevailing saturated long-chain aliphatic structure, a predominantly open-chain and partly branched, cross-linked aliphatic structure is suggested for the kerogen from Aleksinac shale. However, in spite of the fact that according to atomic H/C—O/C ratios this kerogen may be classified as type I kerogen, noticeable participation of alkane-tri- and tetracarboxylic and aromatic acids in the oxidation products (Table II) indicates a larger share of alicyclic and/or heterocyclic and aromatic structural elements in the Aleksinac shale kerogen. The proportions of individual types of oxidation products may serve as basis for semiquantitative estimation of the share of various types of structures in the kerogen matrix.

Obviously, several facts such as application of better degradation method which led to very high yields of oxidation products and powerful separation and identification techniques, as well as examination of previously neglected degradation products from aqueous solutions, enabled improvement of former structural interpretations of Aleksinac shale kerogen[11,12].

Now, how can the type I kerogen from Aleksinac shale be compared with the three mentioned selected representative kerogen samples (type I, II and III)[3-6], particularly with the kerogen from the Green River shale, the representative of type I kerogens[3,6]?

A review of parallel experimental data on the degradations of the two examined type I kerogens is given in Table III.

Further basis for comparison of the two kerogens has already been provided by parallel presentation of experimental data in Figures 1, 2 and 3.

Although the two type I kerogens behaved quite similarly, certain differences should be emphasized. The Aleksinac shale kerogen seems to have been more easily degraded: it had shorter reduction periods, larger amount of $KMnO_4$ consumed per gram of kerogen, shorter total time necessary for degradation, smaller yields of total oxidation products and higher yield of primary ether-soluble acids. These facts may suggest a higher degree of cross--linking in the structure of kerogen from Aleksinac shale, but may also be due to a larger content of oxygen functional groups (atomic O/C ratio being

TABLE III

Oxidative Degradation of Two Type I Kerogens

	Colorado shale[3,6]	Aleksinac shale
Amount of initial kerogen concentrate, g	5.3090	3.5697
Amount of initial kerogen, g	2.6338	2.3407
Kerogen atomic H/C ratio	1.59	1.46
atomic O/C ratio	0.09	0.17
type	I	I
Number of steps necessary for degradation	25	23
Total amount of $KMnO_4$ consumed, g	12.5	11.5
Amount of $KMnO_4$ consumed per gram of kerogen, g	4.75	4.91
Total time necessary for degradation, h	23	12 (22 steps)
not counting the last 30 h step		29 (23rd step)
Total yields, % relative to kerogen		
neutrals and bases	0.86	1.00
ether-soluble acids	24.32	27.97
precipitated, ether-insoluble acids	51.20	**45.57**
total oxidation products	76.38	74.54
organic residue	—	9.72
Ratio of precipitated over ether-soluble acids	2.10	1.63
Acids from aqueous solutions, %	8.12[11,12]	18.30
Amount of initial precipitated acids		
for further degradation, g	1.0010	1.0667
Number of steps	30	26
Amount of $KMnO_4$ consumed per gram of		
precipitated acids, g	14.98	12.19
Total time necessary, h	17	9
Total yields, % relative to precipitated acids		
neutrals and bases	11.22	3.25
ether-soluble acids	96.56	72. 86
residual precipitated acids	5.26	13.35
Acids from aqueous solutions, %	10.13	14.01

0.17 vs 0.09 for the Green River shale kerogen). Paradoxically, in the case of Aleksinac shale kerogen, the organic residues after both the kerogen concentrate and the precipitated acids degradations were larger, indicating higher chemical resistance towards the oxidation reagent of one small portion of the kerogen.

On the other hand, the compared ranges of identified ether-soluble acids and acids from aqueous solutions[3,6,9,10], would suggest a great similarity between the two kerogens. The distributions of identified normal mono- and α,ω-dicarboxylic acids, generally speaking, were quite similar. For example, a maximum at C_{16} with unbranched monocarboxylic acids and at C_{10} with α,ω-dicarboxylic acids was typical for the oxidation products of both kerogens. The major difference was a bimodal distribution of normal mono- and dicarboxylic acids with the degradation products from Aleksinac shale (Figure 9), which has not been observed with the Green River shale kerogen oxidation products.

In spite of the observed similarity in the ranges of identified acids, there was a noticeable difference in the proportions of individual types of acids obtained as oxidation products, indicating definite structural differences between these two kerogens.
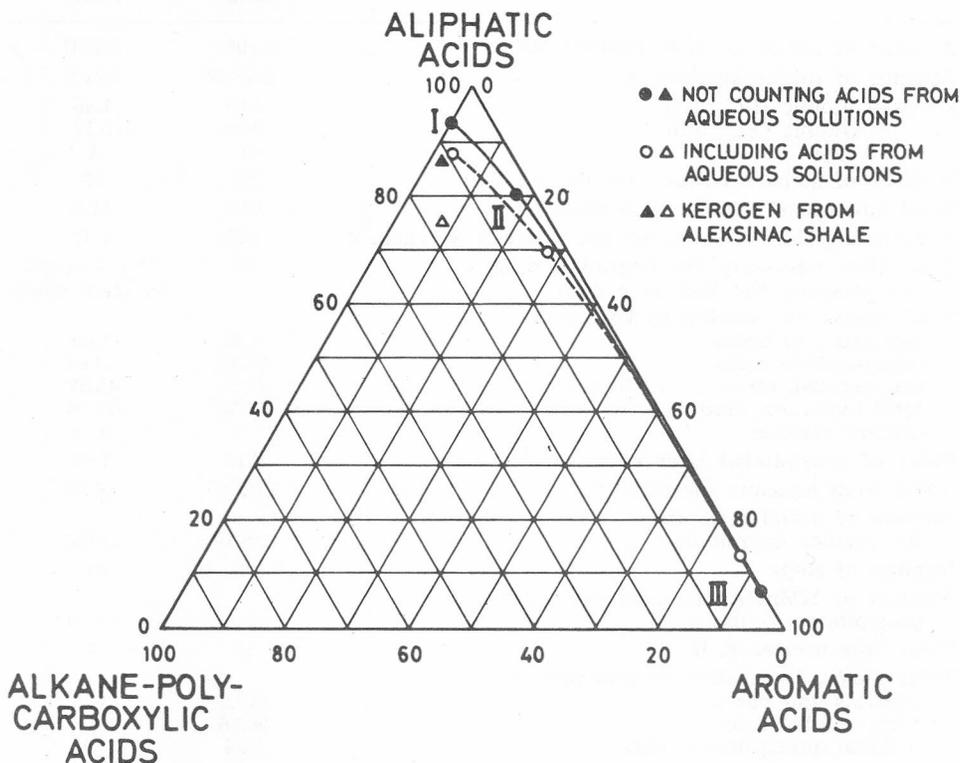

Figure 10. Compositions of oxidation products obtained from Aleksinac shale kerogen and other kerogens of various structural types.

Considering unbranched and isoprenoid acids as oxidation products of aliphatic type structures, alkane-tri- and tetra-carboxylic acids as one of the possible oxidation products of alicyclic or heterocyclic type structures, and aromatic acids of aromatic type material, these three types of acids have already been proposed as basis for classification of kerogens[6]. Therefore, in the same way as with the three representative kerogen types[6], the proportions of various kinds of ether-soluble acids obtained from Aleksinac shale kerogen concentrate and precipitated acids were also estimated (Table II) on the basis of GC chromatograms of individual fractions. The estimated quantitative data from Table II were introduced in a triangular diagram, shown in Figure 10, parallel with data obtained for the representative type I, II and III kerogens.

In order to demonstrate the importance of isolation and examination of acids from aqueous solutions, the proportions of various types of acids in oxidation products in all cases were calculated in two ways, i. e. not counting the acids from aqueous solutions, and also including these acids. Obviously,

by ignoring acids from aqueous solutions one neglects, partially or totally, some parts of the kerogen structure, particularly those whose oxidation products are very soluble in water.

Figure 10 shows that type I kerogen from Aleksinac shale, while generally speaking located in the type I kerogen zone, changed position in the diagram in the direction of higher proportions of alkane-polycarboxylic and aromatic acids, indicating a larger share of alicyclic and/or heterocyclic, and aromatic structures in this kerogen.

The structural interpretation of type I kerogen from Aleksinac shale corroborates the conclusion which resulted from the study of the representative type I kerogen from the Green River shale, i. e. that saturated high molecular mass open-chain acids are the main oxidation product of type I kerogens. Nevertheless, it also shows that higher proportions of alkane-polycarboxylic and aromatic acids in the oxidation products may be expected, indicating larger shares of alicyclic, heterocyclic or aromatic structures in type I kerogens.

In conclusion, classification of kerogens on the basis of their oxidative degradation products, presuming that experimental conditions were chosen as to provide as high as possible yields, enables a more precise structural interpretation as compared to the classification based on atomic H/C—O/C ratios only.

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SAŽETAK

Klasifikacija kerogena aleksinačkog bituminoznog škriljca zasnovana na njegovim oksidacionim proizvodima

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Pri pažljivoj višestepenoj degradaciji kerogena aleksinačkog bituminoznog škriljca alkalnim rastvorom permanganata dobiven je vrlo visok prinos oksidacionih proizvoda (92,84⁰/₀ u odnosu na prvobitni kerogen). Detaljna gasnohromatografsko-masenospektrometrijska analiza kiselina rastvornih u etru, rastvornih proizvoda dalje kontrolisane oksidacije nerastvornih kiselina i kiselina iz vodenih rastvora poslužila je kao osnova za kvantitativnu procenu zastupljenosti pojedinih vrsta proizvoda i za poređenje sa drugim kerogenima, klasifikovanim na bazi njihovih oksidacionih proizvoda. Oksidacioni proizvodi kerogena aleksinačkog škriljca sastojali su se pretežno od alifatičnih kiselina dugih nizova. To je ukazivalo na umreženu, pretežno alifatičnu strukturu ovog kerogena, koji je klasifikovan kao kerogen tipa I. Ipak, zapažena količina alkan-polikarbonskih i aromatičnih kiselina u oksidacionim proizvodima ukazivala je na veće učešće alicikličnih, heterocikličnih i aromatičnih struktura u ovom kerogenu. Pokazalo se da proizvodi oksidativne degradacije omogućavaju precizniju strukturnu interpretaciju kerogena nego klasifikacija zasnovana na elementarnoj analizi.