An organic geochemical correlation study of some Drmno depression crude oils (southern part of the Pannonian Basin, Yugoslavia)

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The results of an investigation of crude oils originating from the Sirakovo and Bradarac-Maljurevac localities (southern part of the Pannonian Basin, Yugoslavia) are reported in this paper. The aim was to estimate the organic geochemical similarity of the crude oils from the Drmno (Kostolac) depression oil fields. The nine selected samples originated from reservoir rocks of various depths. Reliable source and organic geochemical maturation parameters served as the basis for the correlation studies. The similar origin of the investigated Drmno depression crude oils was corroborated, characterized by a significant participation of terrestrial precursor biomass. They were shown to be of relatively low maturity and to have been formed during the earlier stages of the diagenetic-catagenetic sequence of processes leading to the formation of crude oils, most probably in source rocks of Tertiary age, corresponding to vitrinite reflectances between \(R_0 = 0.70\) % and \(R_0 = 0.80\) %. The crude oils from Bradarac-Maljurevac seemed to be somewhat less homogeneous with respect to organic geochemical parameters compared to Sirakovo crude oils.

Keywords: crude oils, Drmno (Kostolac) depression, correlation parameters, source, maturation, age.

INTRODUCTION

The most recent organic geochemical investigations of Drmno (Kostolac) depression crude oils (the southern part of the Pannonian Basin, Yugoslavia) were aimed at correlating them with the crude oils from the Banat and North Bačka depressions. Thus, for example, based on a number of bulk and specific correlation parameters, the Drmno depression crude oils were shown to have a different origin compared to crude oils from three oil fields of the Banat depression and one field from the North Bačka depression.1 The differences between the Drmno depression crude oils and the crude oils

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from the most important Banat depression oil fields Kikinda and Mokrin were corrobo-
rated on the basis of detailed gas chromatographic-mass spectrometric analysis of the
 corresponding sterane and terpane fractions.\textsuperscript{2} Dissimilarities in the type of precursor
 organic material of the mentioned crude oils were also confirmed by carbon isotope
 analysis.\textsuperscript{3} The Drmno depression crude oils are characterized by more negative
 $^{13}$C\textsubscript{PDB} values compared to Banat depression crude oils, \textit{i.e.}, they contain a smaller
 amount of the heavier $^{13}$C isotope. Lastly, a higher participation of terrestrial material
 in the precursor organic biomass of the crude oils from the Drmno depression was sug-
gested compared to the Banat and North Bačka depression crude oils.\textsuperscript{4}

Hence, the different origin of the Drmno depression crude oils compared to most
other Yugoslav crude oils has been repeatedly emphasized. Nevertheless, sporadically,
certain genetic resemblances were indicated between the Drmno depression crude oils
and some crude oils from South Banat oil fields.\textsuperscript{4}

On the other hand, concerning the Drmno depression oil fields and the corre-
sponding crude oils themselves, one question, certainly of great interest for further ex-
ploration of this geological formation, has never been explicitly raised. This is the ques-
tion of the organic geochemical similarity of the Drmno depression crude oils. Namely,
it has never been clearly suggested that their origins and geological histories are quite
the same. On the contrary, a certain heterogeneity in these crude oils was suspected.\textsuperscript{1}

In order to contribute to the solution of this important problem, nine samples of
Drmno depression crude oils, originating from Sirakovo and Bradarac-Maljurevac lo-
calities, were investigated. The samples were selected to represent reservoir rocks of di-
verse depths. To investigate the organic geochemical relationship of these crude oils, re-
liable source and maturation correlation parameters were used.

\textbf{EXPERIMENTAL}

\textit{Geological setting and samples}

Drmno depression crude oils from Sirakovo (5 samples) and Bradarac-Maljurevac (4 sam-
ple) localities were investigated. A list of analyzed crude oils, including the basic geological data, is
 presented in Table I.

The geological column of the Drmno depression is characterized by the following litho-
stratigraphic units:\textsuperscript{5,6}

1. Prebadenian units, which belong to highly heterogeneous clastic sediments. Within Prebade-
nian, “red formations”, characterized by mixed subaquatic to continental development and varying litho-
facies (predominantly marls, shales-sandstones, and sandstones) were found at depths of 2200–1900 m.

2. Ottnangian-Carpathian sediments (Upper Prebadenian), which in fact do represent the main
 object in the investigation of hydrocarbon deposits. These sediments belong to marine and brackish
 lake sediments with very complex lithological heterogeneity (predominantly sandstones and siltsto-
 nes). They are situated at depths of 1700 to 1900 m (oil fields area) and 3250 to 3800 m (depocentre).

3. Badenian sediments, which belong to marine sediments formed during the Mediterranean
development. The maximum depth of the Badenian in the depocentre (Drmno) may be 3250 m, and
the maximum thickness is 1250 m. These sediments (sandstones, clayey sandstones, sandy claystones
and clayey limestones) are characterized by frequent grain size changes, both laterally and vertically.
The Drmno depression was formed either by the collapse of the basement along meridional faults at dif-
ferent periods and of different intensity, or by step-like sinking of the terrain along the faults. Faulting
took place during and after the formation of Neogene deposits.
TABLE I. Geological data on the reservoirs of the sampled and analyzed oils

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample (Well)</th>
<th>Depth interval (m)</th>
<th>Age</th>
<th>Lithology</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sir-1</td>
<td>1782–1778</td>
<td>Ottangian-Carpathian</td>
<td>Sandstone, aleurolite, breccia conglomerate</td>
</tr>
<tr>
<td>2</td>
<td>Sir-2</td>
<td>1704–1701</td>
<td>Ottangian-Carpathian</td>
<td>Sandstone, aleurolite, breccia conglomerate</td>
</tr>
<tr>
<td>3</td>
<td>Sir-18</td>
<td>1548–1544</td>
<td>Ottangian-Carpathian</td>
<td>Sandstone, marlstone, aleurolite, limestone</td>
</tr>
<tr>
<td>4</td>
<td>Sir-19</td>
<td>1436–1429</td>
<td>Ottangian-Carpathian</td>
<td>Sandstone, marlstone, aleurolite, limestone</td>
</tr>
<tr>
<td>5</td>
<td>Sir-20</td>
<td>1444–1440</td>
<td>Ottangian-Carpathian</td>
<td>Sandstone, marlstone, aleurolite, limestone</td>
</tr>
<tr>
<td>6</td>
<td>Bra-Malj-2</td>
<td>2307–2302</td>
<td>Ottangian-Carpathian (partly “Red formation”)</td>
<td>Crystalline rock</td>
</tr>
<tr>
<td>7</td>
<td>Bra-Malj-4</td>
<td>2170–2156</td>
<td>Prebadenian (“Red formation”)</td>
<td>Marlstone, sandstone, breccia conglomerate</td>
</tr>
<tr>
<td>8</td>
<td>Bra-Malj-5</td>
<td>1989–1985</td>
<td>Badenian</td>
<td>Marlstone, sandstone, breccia conglomerate</td>
</tr>
<tr>
<td>9</td>
<td>Bra-Malj-10</td>
<td>1808–1804</td>
<td>Badenian</td>
<td>Marlstone, sandstone, breccia conglomerate</td>
</tr>
</tbody>
</table>

Crude oil samples from boreholes Bra-Malj-2 and 4 (Table I) originated from “red formations” (Miocene) of the Prebadenian units. A large fault was discovered between these two boreholes during seismic investigation.

The boreholes Sirakovo-1, 2 and 18 were located in one zone, i.e., in the deeper, faulty zone, whereas the boreholes Sirakovo-19 and 20 were situated in another, shallower zone of the Ottangian-Carpathian sediments (Upper Prebadenian).

Badenian oil deposits Bradarac-Maljurevac were found at depths of 1808-1804 m (Bra-Malj-10) and 1989-1985 m (Bra-Malj-5).

Analytical methods

Bulk correlation parameters, such as API density, contents of sulphur and asphaltenes, and group composition (proportion of alkanes, aromatics and NSO-compounds), were determined by standard organic geochemical methods, described elsewhere.1,7

The carbon isotope composition, $\delta^{13}C_{\text{PDB}}$, of the aromatic fractions was determined using a mass spectrometer Delta Plus, Thermo Quest, Finnigan MAT, coupled with an Elemental Analyzer, Carlo Erba, NC 2500. Helium was used as a carrier gas (flow rate 120 cm$^3$/min).

$n$-Alkanes and the isoprenoid aliphatic alkanes pristane and phytane, as constituents of the saturated hydrocarbon fractions, were analyzed by gas chromatography (GC) using a Varian 3300 gas chromatograph (FID) fitted with a capillary column coated with BP-1. Hydrogen was used as the carrier gas at 1 cm$^3$/min flow rate.

Polycyclic alkanes of sterane and triterpane types were analyzed by gas chromatography with mass selective detector (GC-MSD), using the single ion monitoring (SIM) method. Steranes were identified from $m/z$ 217 and triterpanes from $m/z$ 191 fragmentograms. A Hewlett Packard 5890, Series II gas chromatograph was used fitted with a capillary column coated with HP-5MS and helium as a carrier gas (flow rate 1 cm$^3$/min), coupled to a Hewlett-Packard 5972 MSD operated at 70 eV.

RESULTS AND DISCUSSION

Bulk correlation parameters

The rationale for using crude oil bulk parameters in correlation studies was described elsewhere.4 The observed bulk correlation parameters are shown in Table II.
TABLE II. Bulk parameters of the analyzed oil samples

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>API º</th>
<th>Sulphur %</th>
<th>Asphaltenes %</th>
<th>Alkanes %</th>
<th>Aromatics %</th>
<th>NSO-compounds %</th>
<th>$^{13}$C&lt;sub&gt;PDB&lt;/sub&gt; of aromatics ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sir-1</td>
<td>46.71</td>
<td>0.21</td>
<td>0.04</td>
<td>59.5</td>
<td>3.4</td>
<td>37.1</td>
<td>–28.0</td>
</tr>
<tr>
<td>2</td>
<td>Sir-2</td>
<td>52.13</td>
<td>0.18</td>
<td>0.4</td>
<td>56.2</td>
<td>4.2</td>
<td>39.1</td>
<td>–28.0</td>
</tr>
<tr>
<td>3</td>
<td>Sir-18</td>
<td>46.86</td>
<td>0.19</td>
<td>0.4</td>
<td>70.3</td>
<td>7.7</td>
<td>21.5</td>
<td>–27.9</td>
</tr>
<tr>
<td>4</td>
<td>Sir-19</td>
<td>46.64</td>
<td>0.34</td>
<td>1.6</td>
<td>50.5</td>
<td>13.8</td>
<td>33.7</td>
<td>–28.0</td>
</tr>
<tr>
<td>5</td>
<td>Sir-20</td>
<td>46.13</td>
<td>0.32</td>
<td>0.1</td>
<td>56.5</td>
<td>4.4</td>
<td>38.9</td>
<td>–27.8</td>
</tr>
<tr>
<td>6</td>
<td>Bra-Malj-2</td>
<td>45.93</td>
<td>0.34</td>
<td>1.0</td>
<td>66.7</td>
<td>3.1</td>
<td>29.2</td>
<td>–28.0</td>
</tr>
<tr>
<td>7</td>
<td>Bra-Malj-4</td>
<td>37.92</td>
<td>0.35</td>
<td>0.2</td>
<td>59.9</td>
<td>10.9</td>
<td>29.0</td>
<td>–28.2</td>
</tr>
<tr>
<td>8</td>
<td>Bra-Malj-5</td>
<td>37.92</td>
<td>0.42</td>
<td>0.1</td>
<td>65.8</td>
<td>5.3</td>
<td>28.7</td>
<td>–27.9</td>
</tr>
<tr>
<td>9</td>
<td>Bra-Malj-10</td>
<td>41.52</td>
<td>0.19</td>
<td>0.3</td>
<td>61.1</td>
<td>11.1</td>
<td>27.3</td>
<td>–26.4</td>
</tr>
</tbody>
</table>

API densities of the nine investigated crude oils were apparently distributed in a relatively wide range (37.92–52.13º, Table II). Crude oils from Bradarac-Maljurevac seem to be somewhat heavier than Sirakovo oils. However, all these values were within the limits typical of light, paraffinic crude oils. This characteristic is generally considered as one of the first indications of substantial participation of terrestrial precursor material in the generation of an oil.8,9

The content of sulphur, a source parameter, was found to be relatively uniform (0.18–0.42 %, Table II). Since crude oils containing higher amounts of sulphur originated from higher saline marine environments, based on the observed values presented in Table II, such a characteristic could not be attributed to either of the nine crude oil samples investigated.

The observed contents of asphaltenes were not uniform (0.04–1.6 %, Table II). This relatively wide range might indicate a possible organic geochemical non-uniformity of the investigated crude oils, the amount of asphaltenes in crude oils generally depending on the length of migration and the degree of maturation.8,9

The group composition of all the examined oils was characterized by a dominance of the alkane fraction (over 50 %), and a noticeably low proportion of aromatics (3.1–13.8 %, Table II). The observed group compositions conformed with the API densities, i.e., they corresponded to the indicated light crude oils type.

Eight out of the nine analyzed aromatic fractions had almost identical carbon isotope composition, $^{13}$C<sub>PDB</sub> (–27.8 to –28.2 ‰, Table II). The observed differences between these eight oils may be considered negligible, the experimental error of the used method being 0.2 ‰. Only the sample Bra-Malj-10 showed a less negative value of this parameter (– 26.4 ‰, Table II). The carbon isotope composition of any crude oil or its components depends mainly on its origin. Crude oils originating from precursor biomass with a higher participation of terrestrial material contain a higher proportion of the lighter isotope $^{12}$C, resulting in more negative $^{13}$C<sub>PDB</sub> values.10 Bitumens from mature ancient sediments and crude oils of dominantly terrestrial origin have 2–4 ‰ more negative values compared to bitumens and crude oils of marine origin.8 Moreover, this
parameter is only slightly affected by the maturation processes, since the lighter carbon isotope, $^{12}$C, forms weaker bonds compared with the heavier $^{13}$C isotope.\textsuperscript{9} Biodegradation, which presumably has affected the sample Bra-Malj-10 and which could have influenced the whole oil isotope ratio $^{13}$C\textsubscript{PDB},\textsuperscript{11,12} should be excluded from consideration in this case, since aromatic fractions, known as relatively resistant towards microbiological decomposition,\textsuperscript{13} were the investigated substrates.

**Specific correlation parameters**

Specific correlation parameters were based on GC analyses of the saturated hydrocarbons ($n$-alkanes and the isoprenoid aliphatic alkanes pristane and phytane), and GC-MSD analyses of the polycyclic alkanes (steranes, $m/z$ 217; triterpanes, $m/z$ 191).

The parameters calculated from gas chromatograms are shown in Table III.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Most abundant $n$-alkane</th>
<th>CPI</th>
<th>Pr/Phyt</th>
<th>Pr/$n$-C\textsubscript{17}</th>
<th>Phyt/$n$-C\textsubscript{18}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sir-1</td>
<td>C\textsubscript{19}</td>
<td>1.03</td>
<td>1.18</td>
<td>0.43</td>
<td>0.32</td>
</tr>
<tr>
<td>2</td>
<td>Sir-2</td>
<td>C\textsubscript{19}</td>
<td>1.03</td>
<td>1.85</td>
<td>0.39</td>
<td>0.17</td>
</tr>
<tr>
<td>3</td>
<td>Sir-18</td>
<td>C\textsubscript{19}</td>
<td>1.03</td>
<td>1.85</td>
<td>0.48</td>
<td>0.21</td>
</tr>
<tr>
<td>4</td>
<td>Sir-19</td>
<td>C\textsubscript{21}</td>
<td>1.03</td>
<td>1.40</td>
<td>0.43</td>
<td>0.26</td>
</tr>
<tr>
<td>5</td>
<td>Sir-20</td>
<td>C\textsubscript{21}</td>
<td>1.04</td>
<td>1.25</td>
<td>0.47</td>
<td>0.32</td>
</tr>
<tr>
<td>6</td>
<td>Bra-Malj-2</td>
<td>C\textsubscript{21}</td>
<td>1.03</td>
<td>2.20</td>
<td>0.52</td>
<td>0.21</td>
</tr>
<tr>
<td>7</td>
<td>Bra-Malj-4</td>
<td>C\textsubscript{25}</td>
<td>1.06</td>
<td>1.17</td>
<td>1.00</td>
<td>0.66</td>
</tr>
<tr>
<td>8</td>
<td>Bra-Malj-5</td>
<td>C\textsubscript{21}</td>
<td>1.02</td>
<td>1.33</td>
<td>0.40</td>
<td>0.23</td>
</tr>
<tr>
<td>9</td>
<td>Bra-Malj-10</td>
<td>C\textsubscript{23}</td>
<td>1.07</td>
<td>1.00</td>
<td>2.37</td>
<td>2.37</td>
</tr>
</tbody>
</table>

According to data shown in Table III, the investigated crude oils seem to be generally similar. Namely, all the chromatograms were characterized by the most abundant $n$-alkane located within the odd C\textsubscript{19}–C\textsubscript{25} carbon number range, by CPI values somewhat higher than 1 (CPI = 1.02–1.07), and by pristane dominating over phytane (with the single exception of the sample Bra-Malj-10, which contained equal amounts of pristane and phytane, Pr/Phyt = 1.00, Table III). These three parameters corroborated the above-mentioned statement that terrestrial type precursor biomass participated considerably in the generation of the crude oils from the Sirakovo and Bradarac-Maljurevac localities, a characteristic of Drmno depression crude oils revealed in earlier studies as well.\textsuperscript{1–4}

Based on the Pr/$n$-C\textsubscript{17} and Phyt/$n$-C\textsubscript{18} parameters, most of the examined crude oils were not exposed to biodegradation (values below one, Table III). According to these parameters, again, the sample Bra-Malj-10 was the exception, the isoprenoid alkanes pristane and phytane being more abundant in this sample, compared to the corresponding $n$-alkanes C\textsubscript{17} and C\textsubscript{18}, respectively (Pr/$n$-C\textsubscript{17} = 2.37; Phyt/$n$-C\textsubscript{18} = 2.37, Table III), data suggesting minor biodegradation.\textsuperscript{9} The Bra-Malj-4 sample also demonstrated somewhat higher values of these parameters compared to the other investigated crude oils (Pr/$n$-C\textsubscript{17} = 1.00; Phyt/$n$-C\textsubscript{18} = 0.66, Table III).
As the observed bulk correlation parameters (Table II) and alkane correlation parameters (Table III) were relatively uniform (with the single clear exception of the sample Bra-Malj-10), similar fragmentograms of the polycyclic alkanes, i.e., triterpanes and steranes, were also anticipated. However, surprisingly, the evidence obtained from the GC-MSD analyses was ambiguous. Fragmentograms typical of the analyzed oils are shown in Fig. 1. The calculated GC-MSD molecular source and maturation parameters are shown in Tables IV and V.

Fig. 1. Fragmentograms of triterpanes (m/z 191) and steranes (m/z 217) in Sir-18 (a), Bra-Malj-2 (b) and Bra-Malj-4 (c) alkane fractions, typical of all the investigated crude oils. a – C_{27-18} (H)-22,29,30-trisnorneohopane (Ts); b – C_{27-17} (H)-22,29,30-trisnorhopane (Tm); c – C_{30-17} (H),21 (H) hopane; d – C_{30-17} (H),21 (H) moretane; e – C_{31-17} (H),21 (H) homohopanes (22S and 22R); O – oleanane; G – gammacerane; 1 – C_{27-13} (H),17 (H) diasterane (20S); 2 – C_{27-14} (H),17 (H) sterane (20R); 3 – C_{29-14} (H),17 (H) sterane (20R); 4 – C_{29-14} (H),17 (H) sterane (20S); 5 – C_{29-14} (H),17 (H) sterane (20R); 6 – C_{29-14} (H),17 (H) sterane (20R). (Detailed identification of the corresponding peaks was discussed in our previous papers).2,3
Firstly, in all \( m/z \) 217 mass chromatograms, the distribution of peaks originating from regular \( R \) steranes was almost identical (C\(_{29}\)-C\(_{27}\)-C\(_{28}\), Fig. 1; Table IV). This observation does not refer to the sample Bra-Malj-10, its corresponding distribution being somewhat different: the proportion of C\(_{29}\) being by far the highest and the abundance of C\(_{28}\) being higher than that of C\(_{27}\). Hence, this reliable source correlation parameter gave one more proof of the similar or identical type of precursor biomass of all the investigated Drmno depression crude oils, except for the oil Bra-Malj-10.

### TABLE IV. GC-MSD molecular source parameters of the analyzed oil samples

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>( R ) steranes%</th>
<th>( O/C_{30} ) hopane</th>
<th>( G/C_{30} ) hopane</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sir-1</td>
<td>C(<em>{27}): 35.1, C(</em>{28}): 19.1, C(_{29}): 45.8</td>
<td>7.4</td>
<td>6.7</td>
</tr>
<tr>
<td>2</td>
<td>Sir-2</td>
<td>C(<em>{27}): 33.0, C(</em>{28}): 20.4, C(_{29}): 46.6</td>
<td>7.6</td>
<td>5.9</td>
</tr>
<tr>
<td>3</td>
<td>Sir-18</td>
<td>C(<em>{27}): 32.7, C(</em>{28}): 18.4, C(_{29}): 48.9</td>
<td>5.7</td>
<td>15.4</td>
</tr>
<tr>
<td>4</td>
<td>Sir-19</td>
<td>C(<em>{27}): 36.1, C(</em>{28}): 19.6, C(_{29}): 44.3</td>
<td>6.8</td>
<td>16.2</td>
</tr>
<tr>
<td>5</td>
<td>Sir-20</td>
<td>C(<em>{27}): 34.5, C(</em>{28}): 19.5, C(_{29}): 46.0</td>
<td>6.0</td>
<td>16.5</td>
</tr>
<tr>
<td>6</td>
<td>Bra-Malj-2</td>
<td>C(<em>{27}): 32.8, C(</em>{28}): 26.6, C(_{29}): 40.6</td>
<td>12.8</td>
<td>10.3</td>
</tr>
<tr>
<td>7</td>
<td>Bra-Malj-4</td>
<td>C(<em>{27}): 37.0, C(</em>{28}): 16.5, C(_{29}): 46.5</td>
<td>1.9</td>
<td>18.8</td>
</tr>
<tr>
<td>8</td>
<td>Bra-Malj-5</td>
<td>C(<em>{27}): 33.0, C(</em>{28}): 18.2, C(_{29}): 48.9</td>
<td>5.7</td>
<td>21.1</td>
</tr>
<tr>
<td>9</td>
<td>Bra-Malj-10</td>
<td>C(<em>{27}): 20.0, C(</em>{28}): 28.2, C(_{29}): 51.8</td>
<td>3.0</td>
<td>9.8</td>
</tr>
</tbody>
</table>

O–oleanane; G–gammacerane.

However, the fragmentograms \( m/z \) 191, shown as examples in Fig. 1, as well as the calculated parameters \( O/C_{30} \) hopane 100 and \( G/C_{30} \) hopane 100 from Table IV, indicated different concentrations of oleanane and gammacerane in the crude oils. These pentacyclic triterpanes are considered to be reliable indicators either of the continental origin (oleanane), or proof of marine evaporite and/or higher salinity media origin (gammacerane).\(^8\)\(^9\)\(^14\) The observed differences were particularly noticeable with the Bradarac-Maljurevac locality crude oils. Nevertheless, generally, the latter evidence does not contradict the conclusion on the predominantly continental origin of the investigated crude oils, all samples containing oleanane at least in small concentrations.

The values of some of the maturation parameters shown in Table V might also explain the non-uniformity in the distribution and abundance of triterpanes and steranes in the nine crude oils (Fig. 1). This refers in the first place to the parameters Ts/Ts+Tm and C\(_{27}\) dia/dia+ster (parameters 1 and 6, Table V). According to these parameters, the sample Bra-Malj-10 was once more unique, being characterized by much lower values. The observed differences might suggest differences in the thermal maturities of the oils. However, in contrast, the uniform values of the parameters 2–5 (Table V) indicate almost the same phase in the isomerization of triterpanes (moretane hopane, and 22\( R \) 22\( S \)) and steranes (\( 22S \), and 20\( R \) 20\( S \)), typical of maturation processes. Hence, it could be suggested that the differences in parameters 1 and 6 do not result from maturation processes, but rather from some other effects. For example, it is well known that isomerization processes Tm Ts (17 \( H \)-22,29,30-trisnorhopane 18 \( H \)-22,29,30-trisnorneohopane), as well as the isomerization of regular steranes...
into diasteranes, are chiefly influenced by mineral catalysts of silicate type (acidic sites on clays), being constituents of source rocks.\textsuperscript{15,16}

**TABLE V. GC-MSD molecular maturation parameters of the analyzed oil samples**

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Ts/Ts+Tm</th>
<th>225/225 +22R C\textsubscript{31} hopanes</th>
<th>Moretane/Hopane C\textsubscript{30}</th>
<th>/ +  C\textsubscript{29} steranes</th>
<th>205/205 + 20R C\textsubscript{29} steranes</th>
<th>C\textsubscript{27} dia/dia + sterane</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sir-1</td>
<td>0.47</td>
<td>0.59</td>
<td>0.12</td>
<td>0.57</td>
<td>0.48</td>
<td>0.21</td>
</tr>
<tr>
<td>2</td>
<td>Sir-2</td>
<td>0.49</td>
<td>0.61</td>
<td>0.13</td>
<td>0.56</td>
<td>0.54</td>
<td>0.62</td>
</tr>
<tr>
<td>3</td>
<td>Sir-18</td>
<td>0.46</td>
<td>0.61</td>
<td>0.11</td>
<td>0.56</td>
<td>0.46</td>
<td>0.19</td>
</tr>
<tr>
<td>4</td>
<td>Sir-19</td>
<td>0.40</td>
<td>0.60</td>
<td>0.13</td>
<td>0.60</td>
<td>0.50</td>
<td>0.22</td>
</tr>
<tr>
<td>5</td>
<td>Sir-20</td>
<td>0.41</td>
<td>0.61</td>
<td>0.11</td>
<td>0.58</td>
<td>0.47</td>
<td>0.19</td>
</tr>
<tr>
<td>6</td>
<td>Bra-Malj-2</td>
<td>0.54</td>
<td>0.62</td>
<td>0.11</td>
<td>0.63</td>
<td>0.55</td>
<td>0.59</td>
</tr>
<tr>
<td>7</td>
<td>Bra-Malj-4</td>
<td>0.24</td>
<td>0.61</td>
<td>0.13</td>
<td>0.39</td>
<td>0.44</td>
<td>0.04</td>
</tr>
<tr>
<td>8</td>
<td>Bra-Malj-5</td>
<td>0.43</td>
<td>0.60</td>
<td>0.11</td>
<td>0.59</td>
<td>0.48</td>
<td>0.20</td>
</tr>
<tr>
<td>9</td>
<td>Bra-Malj-10</td>
<td>0.10</td>
<td>0.60</td>
<td>0.11</td>
<td>0.57</td>
<td>0.45</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Equilibrium values / 0.57–0.62 0.05–0.10–0.15 0.67–0.71 0.52–0.55 /

Parameters:

- Parameter 1
- Parameter 2
- Parameter 3
- Parameter 4
- Parameter 5
- Parameter 6

Comparison of the parameters 2–5 from Table V with the known values characteristic of source rock bitumens and crude oils of high maturity, \textit{i.e.}, equilibrium values corresponding to the related isomerization reactions (their ranges are also shown in Table V),\textsuperscript{17} may serve as a basis for the estimation of the maturity degrees of the investigated samples, \textit{i.e.}, their position in the diagenetic-catagenetic sequence of the processes leading to petroleum formation.

The values of parameter 22S/22S+22R (C\textsubscript{31} hopanes) fitted into the equilibrium range of 0.57–0.62, suggesting that the equilibrium 22R = 22S (parameter 2, Table V) has already been attained in the investigated oils. However, it is known that this equilibrium in the isomerization reactions of polycyclic alkanes is established relatively quickly, already in the early oil-generative stages, and that subsequent maturation processes have no further influence on the 22S/22S+22R ratio. In most cases this stage is characterized by vitrinite reflectances \( R_0 = <0.60 \% \).\textsuperscript{17,18} Therefore, based on this parameter, it is not possible to precisely define the position of the oil samples in the diagenetic-catagenetic sequence of the processes leading to petroleum formation.

It is known that structural changes of moretane into hopane (17\( \text{H} \), 21\( \text{H} \)) lead to changes in the moretane/hopane (C\textsubscript{30}) ratio from the “initial” 0.80 to even 0.05.\textsuperscript{19} However, in addition to heat and geological time the isomerization reactions moretane \[ \text{hopane} \] are influenced by source input and depositional environment as well.\textsuperscript{17,20} Hence, in many source rock bitumens and crude oils of high maturity considerably higher values of this ratio were observed (0.10–0.15, and also up to 0.30). This means that the values of this parameter observed for the crude oils investigated do not exclude that the equilibrium \( \text{moretane} = \text{hopane} \) has been established, \textit{i.e.}, they might be the result of “later” stages in the sequence of reactions leading to crude
oil formation. However, they do not serve as an explicit proof for such a statement, since similar to the isomerization reactions \(22R \leftrightarrow 22S\), i.e., to the establishment of the \(22R \leftrightarrow 22S\) equilibrium, the equilibrium \(20R \leftrightarrow 20S\) is also established in the earlier stage (vitrinite reflectance \(R_\theta = 0.70\%\)).

Sterane maturation parameters (parameters 4 and 5, Table V) may contribute to answering the question of the stage in which the Drmno depression crude oils were formed. Almost all the values of these parameters were found to be lower than those quoted in the literature as typical for the corresponding equilibria. Equilibria \(20R \leftrightarrow 20S\) (steranes) are established in the stage known as the “oil generation peak” (\(R_\theta = 0.80\%\) to \(0.90\%\)). The values observed in this paper indicate that the examined crude oils had not reached this phase. Hence, based on the maturation parameters 2–5 (Table V), the Drmno depression crude oils seem to have been formed in earlier phases of the diagenetic-catagenetic sequence of the petroleum formation processes, i.e., those corresponding to vitrinite reflectances between \(R_\theta = 0.70\%\) (terpanes’ equilibria) and \(R_\theta = 0.80\%\) (initial stages of sterane equilibria).

Maturation parameters 3 and 5 from Table V might also contribute to an indication of the age of the source rocks of the investigated oils. Namely, it was shown earlier that the isomerization reactions moretane/hopane (parameter 3, Table V) and \(20S \leftrightarrow 20R\) (parameter 5, Table V) in addition to heat, necessarily depended on geological time as well. Investigations of a great number of crude oil samples have shown that samples originating from source rocks of the pre-Tertiary age had moretane/hopane parameter values lower than 0.10, and those of parameter \(20S \leftrightarrow 20R \leftrightarrow C_{20}\) steranes higher than 0.50. Parameters 3 and 5 from Table V, compared to boundary values, classified the examined Drmno depression crude oils into the group of oils originating from source rocks of Tertiary age.

Based on all observed group and specific correlation parameters (Tables II–V), the investigated crude oils from the Drmno depression seem to be relatively similar according to their origin and maturation degrees. Naturally, the similarity was not absolute with every examined parameter, but the most important ones indicated the same or similar precursor biomass for all the investigated samples (API, sulphur, alkanes and \(^{13}\)C\text{PDB}, Table II; CPI and Pr/Phyt, Table III; regular steranes distribution and the presence of oleanane, Table IV), as well as similar maturity degrees, i.e., originating from the same phase of the diagenetic-catagenetic sequence of processes leading to crude oil formation (parameters 2–5, Table V). Moreover, the examined crude oils from the Drmno depression may be supposed to have originated from Tertiary source rocks (parameters 3 and 5, Table V). According to certain parameters (\(^{13}\)C\text{PDB}, Table II; partially Pr/Phyt, Pr/\text{n-C}_{17}, \text{Phyt}/\text{n-C}_{18}, Table III; regular steranes distribution, Table IV; parameters 1 and 6, Table V), the sample Bra-Malji-10, originating from the Bradarac-Maljurevac locality, differed from the other examined samples. Generally, the crude oils from this locality are characterized by a somewhat lower level of organic geochemical uniformity compared with crude oils from the Sirakovo locality.

Conclusions concerning the organic geochemical similarity of Drmno depression crude oils may be illustrated by comparing the values of the most important source and maturation correlation parameters from Tables IV and V with the corresponding parameters observed for crude oils from the major oil fields of the Banat and North
Bačka depressions, as well as crude oils from the West Drava, East Drava, Sava, and Slavonija-Srem depressions. According to source correlation parameters (Fig. 2), the investigated crude oils from the Drmno depression obviously differ from other crude oils from the southern parts of the Pannonian Basin. The triangular diagram also demonstrates the remarkable difference of the Bra-Malj-10 sample from the whole group of Drmno depression crude oils, and, to a certain degree, the diversity of the sample Bra-Malj-2 as well, corroborating the general statement concerning the crude oils from the Bradarac-Maljurevac locality and their geological setting. On the other hand, the maturation parameters calculated for the Drmno depression crude oils were similar to those of the Banat and North Bačka depression crude oils, but their maturation degrees were shown to be considerably higher compared to those of the West Drava, East Drava, Sava and Slavonija-Srem depression crude oils.

CONCLUSIONS

Based on source correlation parameters (primarily CPI, Pr/Phyt, distribution of regular steranes), the investigated crude oils from the Drmno depression were once more shown to be of similar origin, characterized by significant participation of terrestrial precursor biomass.

Based on terpane and sterane maturation correlation parameters, the investigated samples were shown to be of relatively low maturity and to have been formed during the earlier stages of the diagenetic-catagenetic sequence of processes leading to petroleum formation, corresponding to vitrinite reflectances of the source rocks between $R_o = 0.70 \%$ (terpanes’ equilibria) and $R_o = 0.80 \%$ (initial phases of sterane equilibria).
Terpane and sterane correlation parameters, substantially influenced by geological time in addition to the influence of heat, suggested that the crude oils from the Drmno depression should be classified into the group of oils originating from source rocks of Tertiary age.

In spite of several common characteristics which were clearly observed with all the investigated crude oil samples, ideal organic geochemical uniformity of this group of oils cannot be suggested. Namely, according to some important correlation parameters (carbon isotope composition of the aromatic fraction, abundance of \( n \)-alkanes, distribution of regular steranes, ratio of some hopane isomers and ratio of diasteranes vs. steranes), the sample Bra-Malj-10 was found to be remarkably different from the other investigated crude oil samples. Generally, the crude oils from the Bradarc-Maljurevac locality were characterized by a somewhat lower level of organic geochemical uniformity than the crude oils from the Sirakovo locality.

Finally, based on the distribution of regular steranes, the origin of the Drmno depression crude oils seems to be different from the origin of the Banat and North Bačka depression crude oils, and also from the West Drava, East Drava, Sava and Slavonija-Srem depression crude oils. Consequently, the Drmno depression crude oils may be distinguished as a distinct crude oil genetic type among the crude oils from the southern part of the Pannonian Basin. On the other hand, their maturation parameters were similar to those of the Banat and North Bačka depression crude oils. In contrast, their maturity degrees were shown to be considerably higher compared to those of the West Drava, East Drava, Sava and Slavonija-Srem depression crude oils.

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IZVOD

ORGANSKO-GEOHEMIJSKA KORELACIJA NEKIH NAFTI DEPRESIJE DRMNO (JUŽNI DEO PANONSKOG BASAENA, JUGOSLAVIJA)

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У овом раду испитивани су узорци сирових нафти депресије Дрмно (Костолац) са локалитета Страково и Брадарац-Малјуревац. Циљ рада био је да се процени органско-геохемијска уједињеност нафти нафтиних поља депресије Дрмно. Изабране су узорци који потичу из резервоарских стена са различитих дубина и у њима су одређени групни и специфични изворни и матурациони органско-геохемијски параметри. Поверђено је да испитивани узорци депресије Дрмно имају слично порекло које карактерише већи удео теретријалне прекурсорске биомасе. Испитиване нафте су нешто нижег
степена матурисаности и настале су у ранијим фазама дијагенетско-катагенетске се-
квенције формирања нафте којима одговарају вредности рефлексије витринита између
$R_o = 0.70 \%$ и $R_o = 0.80 \%$. Највероватније су настале у изворним стенама терцијарне
стариости. Нафте са локалитета Брадарац-Маљуревц карактерише нешто нижи ниво
органско-геохемијске хомогености него нафте са локалитета Сираково.

(Примљено 8. јануара 2001)

REFERENCES