

MOLECULAR INDICATORS FOR COAL-FORMING PALAEOPLANT COMMUNITY. “KATRISHTE” COAL DEPOSIT

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Abstract. Coal deposit “Katrishte” located in south-western Bulgaria, $R_o = 0.34\%$, was subjected to geochemical study. By chromatographic and spectral methods, a variety of coal biomarkers in bitumen extract has been revealed. n-Alkane distribution pattern indicated at least two possible sources, lacustrine and terrestrial ones. The aliphatic fraction was strongly dominated by $16\alpha(H)$ -kaurane and $16\alpha(H)$ -phyllocladane, a proof for the presence of Pinales in coal-forming palaeoplant community. The kaurane prevalence over phyllocladane could indicate the herbaceous flowering plant contribution. The combination of sesquiterpenoids/diterpenoids pointed to Pinaceae and Araucariceae.

As a biomarker assemblage peculiarity, the lack of isoprenoids, tricyclic diterpenoids, and pentacyclic triterpenoids could be indicated.

Our data gave us ground to assume existence of bush moor with the presence of herbaceous flowering plants, and subordinate contributions of conifers and sedge-reeds to coal forming plant taxa of “Katrishte” coal.

Key words: coal, organic geochemistry, biomarker assemblage.

INTRODUCTION

The coal deposit “Katrishte” is located in south-western Bulgaria, 20 km east of town Kyustendil and about 25 km from “Bobov dol” electrical power station, in the valley of Strimon river (Fig. 1). The deposit characteristics are insufficient and quite scarce (Vatsev, Bonev, 1994; Kortenski, Sotirov, 1998; Markova *et al.*, 2000).

Coal deposit is situated below the river bay terrace, mainly on the left side of the riverbed. The general thickness of coal layer is in the range of 2.5–15.2 m, at depth of 5 m to 100 m. Compact formation is characteristic for the deposit but at certain places dark-grey to black layers of silt were distinguished. In the western part, the deposit is covered by Quaternary alluvial materials, and according to Vatsev and Bonev (1994), they are sandy alleviate and bituminous limbic aigrettes, bituminous marls, and fine-grained clay sandstones. According to the same authors and confirmed in later study by Gaudent and Vatsev

(1997), the lake sediments overlying the coal seam are of Badenian–Sarmatian age.

It was determined that the peat-forming conditions in the south-eastern part of the deposit were quite favourable for the auto-oxidation, and on the contrary, in the south-western part,



Fig.1. Location of the coal basins in south-western Bulgaria

1 — Katrishte, 2 — Sofia, 3 — Pernik, 4 — Bobov dol, 5 — Kjustendil, 6 — Oranovo

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they were not favourable (Nenchev, 1979). For "Katrishte" deposit, the authors have determined an oxidation level corresponding to the magnitudes typical for brown coals: 3.6 after Gruner and -0.1193 after Vesselovski. The high inertinite maceral contents could be responsible for the higher auto-oxidation stability. Nevertheless, it was supposed that at the depth of 3–5 m slight auto-oxidation processes proceeded. Markova *et al.* (2000) have assumed that the inertinite maceral micrinite was formed in the peat swamp as result of high temperature.

Kortenski and Sotirov (1998) have studied "Katrishte" coal deposit by petrographic and geochemical methods. They would

like to connect the deposit with Kyustendil, Sofia, Pernik or Bobov dol basins. Significant resemblance, on one hand, and differences, on the other, with Strimon-Mesta and Sofia provinces were registered but authors have had problems in connecting "Katrishte" with any of them.

The aim of the study was to characterise "Katrishte" coal deposit using organic geochemistry, with the idea to find some molecular indications for the coal-forming palaeoplant community, inasmuch biomarker assemblage reflects variations in the nature of source materials and deposition conditions.

EXPERIMENTAL METHODS

The experiments were carried out on "average" sample prepared from the five layers of different samples taken from the cross-section downwards the 5 m thick coal seam. Characteristics can be found in Markova *et al.* (2000). Briefly, huminite makes 82–89% with dominance of ulminite; liptinite — 1–8%, with dominance of sporinite; and inertinite — 9–14%, with dominance of micrinite.

The ultimate reflectance is in the range of 0.30–0.35% R_o and corresponds to brown coal of O_2 rank.

Proximate analysis, wt. %: W^a — 4.65; A^d — 32.4.

Ultimate analysis, wt. % daf: C — 68.6; H — 5.9.

Bitumen extraction. Finely grounded coal sample (~20 g) was subjected to exhausted Soxhlet extraction by benzene-ethanol (1:1). The bitumen was separated by column absorption chromatography. Aliphatic fraction was isolated in accordance

with procedure described in previous paper, Stefanova and Magnier (1997).

Fractions were gas chromatographically analysed by means of DI 700 Delsi® GC instrument, equipped with CP sil 8 CB column (0.22 mm x 30 m; 0.25 μ m film thickness), FID at 300°C and split/splitless capillary injector maintained at 300°C and used in splitless mode. After 1 min at 50°C, the oven temperature increased to 120°C at 30°C/min and then to 120–300°C at 5°/min, and hold this final temperature for 1 hour. Helium was the carrier gas.

Gas chromatography-mass spectrometry (GC-MS) analyses were performed with a Varian 300 GC coupled to an ion Trap ITD 800 (Finnigan Mat) by 2 m capillary interface heated to 300°C. Other GC conditions were identical to those described above. Operating ITD conditions: temperature — 220°C; ionisation energy — 80 eV; 1 scan/2 s, from 50 to 500 amu.

RESULTS AND DISCUSSION

The yield of bitumen mounted to 2.3% of the initial coal. The aliphatic fraction represented about one half of the bitumen extract, 45.8%, or ~1% of the initial coal.

GC separation of aliphatic portion is illustrated on Figure 2. The peaks' surfaces were quantitatively interpreted. Mass spectral identification revealed the distribution in the following compound classes, in rel. %:

n-alkanes	7.10
sesquiterpenoids	6.94
diterpenoids	68.31
i.e. <i>ent</i> -16 α (H)-kaurane	28.36
16 α (H)-phyllocladane	22.11
C-ring monoaromatic steranes	1.52
total	83.87

n-Alkane distribution is illustrated as histogram on Figure 3. Sesquiterpenoids are depicted on Figure 4. The MS of one sesquiterpenoid with molecular mass 206 amu is illustrated on

Figure 5. The C-ring monoaromatic steranes distribution, SIM m/z 253, is monitored on Figure 6.

Structures identified by mass spectrometry are presented in Table 1 and Appendix demonstrates their formula.

Compound classes distribution, presented in rel. % for sample subjected to GC study, confirmed its aliphatic composition. Our idea was to isolate and concentrate aliphatics in "narrow" fraction. Inasmuch, the sum of aliphatics represented about 75% of studied compounds. It could be concluded that the fraction was of predominantly aliphatic character. GC chromatogram was rather simple, strongly dominated by two diterpenoids: *ent*-16 α (H)-kaurane (28.36%), and 16 α (H)-phyllocladane (22.11%). This distribution facilitated MS identification and we succeeded to propose structure for 84% of the sample subjected to GC separation. Respectively, our data could be considered representative for the aliphatic portion. The extremely high preponderance of two compounds was an indication for the presence of definitive palaeoplant contribution in coal forming taxa (see later).

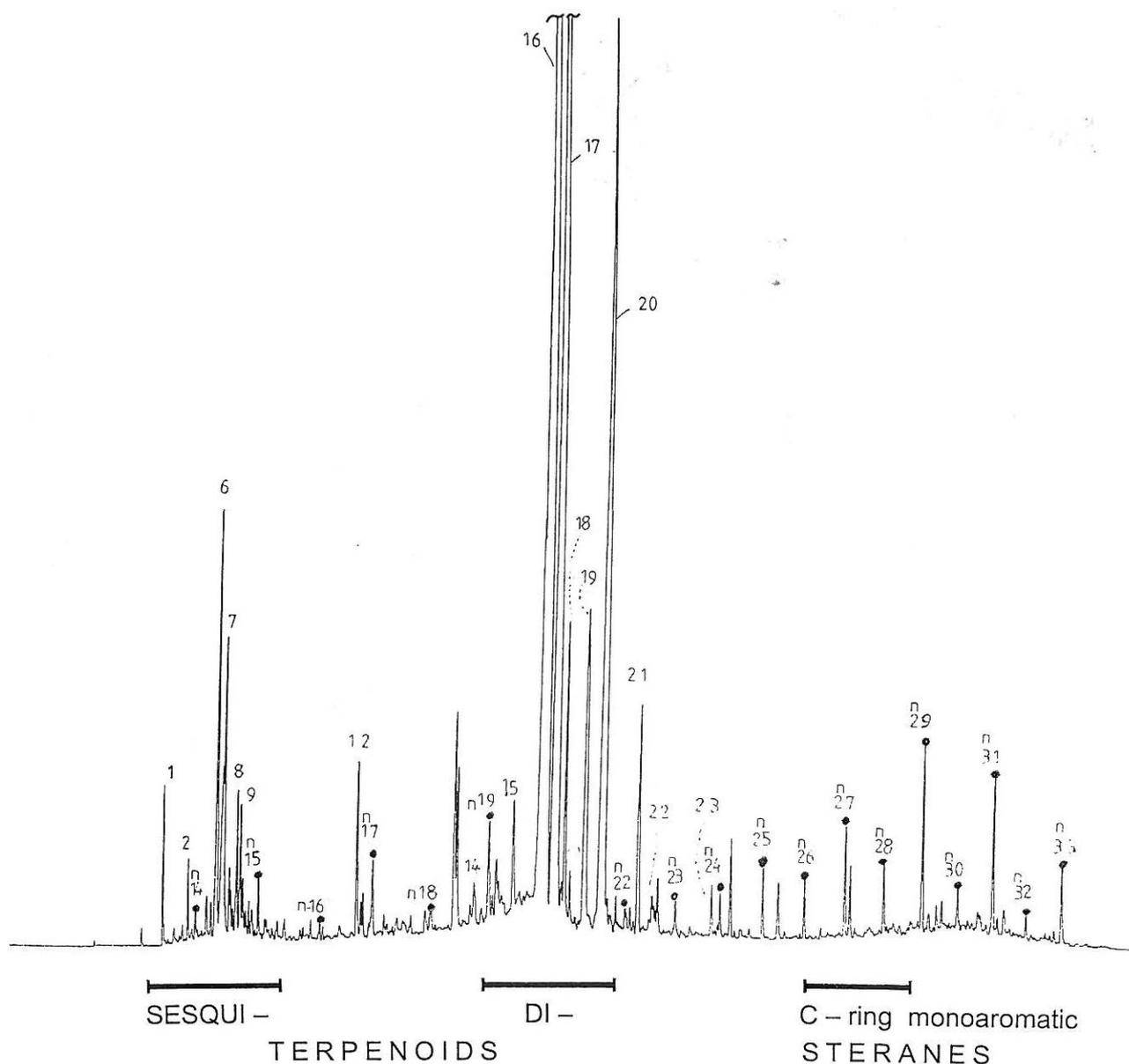


Fig. 2. GC separation of "Katrishte" coal biomarkers

• — n-alkanes, peaks identification in Table 1

Aromatic species were GC-MS registered as well. Their contents were lower comparing to diterpenoids, as could be observed on Figure 2, peaks 15, 22, 23. However, there were aromatic compounds in certain quantities as well: peak 12 — cadalene; peak 18 — dehydroabietane; peak 20 — simonellite; peak 21 — retene. These data were not astonishing as in a lot of studied aliphatic compounds, devoted to coal biomarkers, were firmly accompanied by abietane aromatized or degraded structures.

n-Alkanes

The $C_{14} - C_{33}$ n-alkanes exhibit bimodal carbon-number distribution profile (Figs. 2 and 3). Two ranges were distin-

guished, $n-C_{14} - n-C_{22}$, representing 2.71% of bitumen extract; and $n-C_{22} - n-C_{33}$ — 4.35%, respectively. The CPI ratio, calculated according to Allan and Douglas (1977), was 2.53 and the simple ration odd/even alkanes = 2.64. n-Alkanes maximised at two regions, $n-C_{17}$, $n-C_{19}$ and $n-C_{27}$, $n-C_{29}$, $n-C_{31}$. There were not registered even traces of regular isoprenoids, i.e. phytane and pristane.

Low rank coals are characterised by high values for CPI with magnitudes progressively diminishing with coal maturity increase (Bartle *et al.*, 1978). CPI value calculated in our study is in a good agreement with observations of Nelson *et al.* (1998) where CPI values and Vitrinite reflectance ($\%R_o$) were correlated.

The alkane bimodal distribution is a trait for at least two possible sources. The higher homologues are associated with

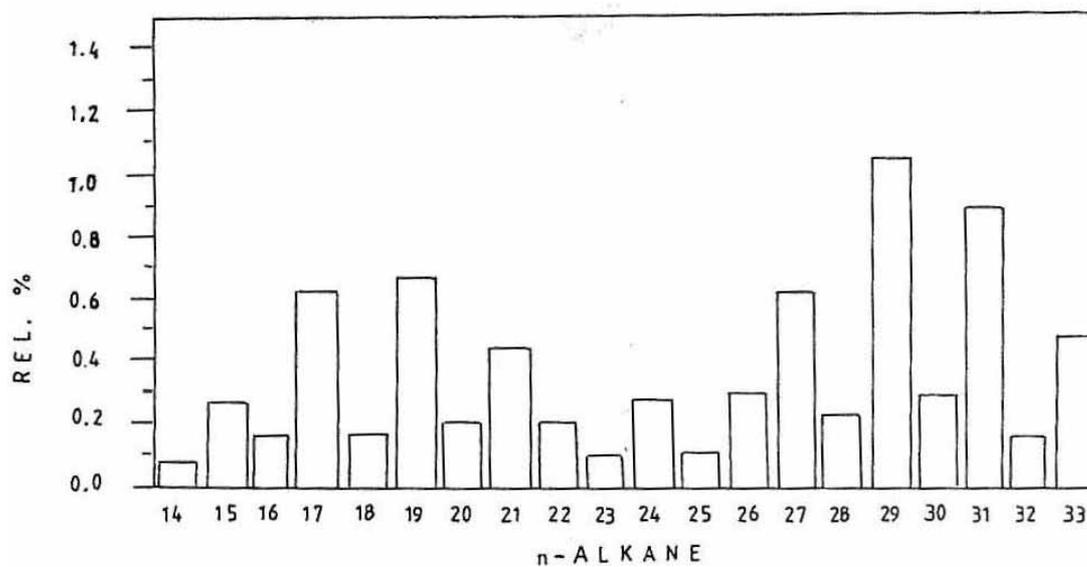


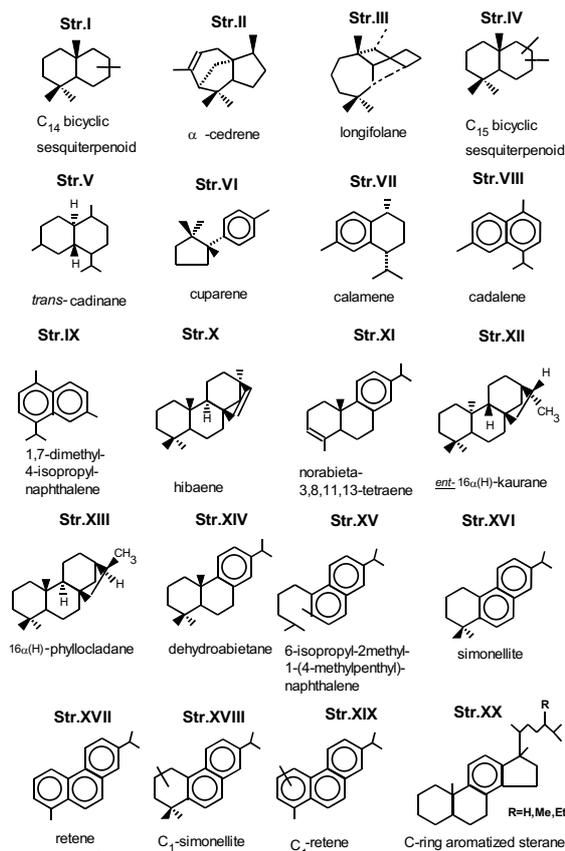
Fig. 3. n-Alkane distribution pattern

Table 1

Compounds identified by mass spectrometry

Peak No.	Formula	MM	m/z [100%]	Structure	Appendix
1	C ₁₄ H ₂₆	194	109	C ₁₄ -bicyclic sesquiterpenoid	I
2-4	C ₁₅ H ₂₆	206		unknown	
5	C ₁₅ H ₂₆	206	93	dihydrovalencene (?)	
6	C ₁₅ H ₂₄	204	119	α-cedrene	II
7	C ₁₅ H ₂₆	206	95	longifolane	III
8	C ₁₅ H ₂₈	208	95	C ₁₅ -bicyclic sesquiterpenoid	IV
9	C ₁₅ H ₂₈	208	109	trans-cadinane	V
10	C ₁₅ H ₂₂	202	132	cuparene	VI
11	C ₁₅ H ₂₂	202	159	calamene	VII
12	C ₁₅ H ₁₈	198	183	cadalene	VIII
13	C ₁₅ H ₁₈	198	183	1,7-dimethyl-4-isopropyl-naphthalene	IX
14	C ₂₀ H ₃₂	272	134	hibaene (Beyer-15-ene)	X
15	C ₁₉ H ₂₆	254	239	norabieta-3,8,11,13-tetraene	XI
16	C ₂₀ H ₃₄	274	123	ent-16α(H)-kaurane	XII
17	C ₂₀ H ₃₄	274	123	16α(H)-phylocladane	XIII
18	C ₂₀ H ₃₀	270	255	dehydroabietane	XIV
19	C ₂₀ H ₂₈	268	197	6-isopropyl-2-methyl-1-(4-methylphenyl)-naphthalene	XV
20	C ₁₉ H ₂₄	252	237	simonellite	XVI
21	C ₁₈ H ₁₈	234	219	retene	XVII
22	C ₂₀ H ₂₆	266	251	C ₁ -simonellite	XVIII
23	C ₁₉ H ₂₀	248	233	C ₁ -retene	XIX

APPENDIX



waxy materials and are maturity influenced (Bartle *et al.*, 1978; Chaffe *et al.*, 1986). The presence of second maximum is an indication for a possible lacustrine contribution. The high quantities of C₁₅, C₁₇, C₁₉ homologues could be attributed to defunctionalised even-number fatty acids, C₁₆, C₁₈ and C₂₀, an

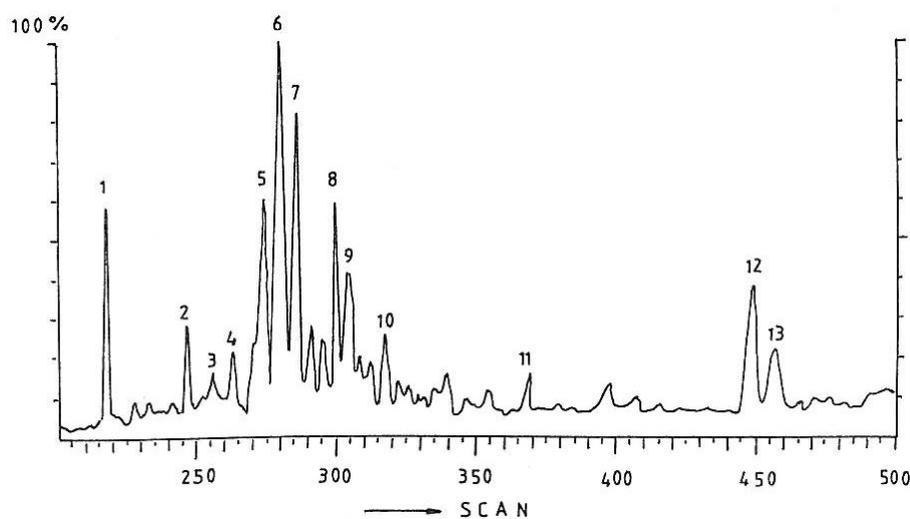


Fig. 4. TIC of sesquiterpenoid region; peaks identification in Table 1

important contribution of plankton derived short chain lipids. Hence, n-alkane composition indicates at least dual contribution, higher plant terrigenous and swamp/lacustrine one.

Sesquiterpenoids

Sesquiterpenoids are typical coals biomarkers. They are present in resins and essential oils from higher plants (Simoneit, 1986). Sesquiterpenoid markers in combination with diterpenoids serve for tagging plant resins in the geological record, and connecting with certain class of resin input (Anderson *et al.*, 1992). The precursors of most of compound are common components of essential oils, resins and ambers (Simoneit *et al.*, 1986; Wang, Simoneit, 1990).

Sesquiterpenoids are present as saturates, unsaturates, aromatized and functionalized derivatives. The main sources for these natural products are Cupressaceae, Compositae, Dipterocarpaceae. The first one is from Gymnospermae plant family and the others from Angiospermae (Dicotyledonae) (Sukh Dev, 1989). Papers for the algal source of sesquiterpenoids have appeared (Elias *et al.*, 1997).

In the sample under study, cadinane, cadinene, calamene, and cadalene were unequivocally identified. Hydrocarbons based on cadinane skeleton are common constituents of petroleum with terrigenous input. Sesquiterpene-related compounds with cadinane structure were identified by Staccioli *et al.* (1993) in terpane hydrocarbons from Pliocene fossil wood. Cadalenes were related to conifer resins because polymers of cadalanes are characteristic for Angiosperm dammar resins (Anderson *et al.*, 1992).

Sesquiterpenoids in sample under study were dominated by α -cedrene, peak 6, and longifolane, peak 7 (Fig. 4). These compounds have been identified in fossil resins from Tertiary lignites and, according to Grantham and Douglas (1980), were characteristic constituents of the essential oils of Cupressaceae (order Coniferales) and some genera of the family Taxodiaceae.

Sesquiterpenoids identified by mass spectrometry belong to the following skeletal types, Sukh Dev (1989):

- cadalene — peaks 9, 11, 12;
- cedrene — peak 6;
- dicyclofarnesane — peaks 1, 8;
- cuparene — peak 10;
- caryophyllane — peak 6;
- peak 5 could be attributed to Eremophilane skeleton.

Sesquiterpenoids were relatively highly abundant in aliphatic fraction from "Katrishte" bitumen. The content of 6.9% was comparable with alkane quantity. Species identified by mass spectrometry gave us hint for the presence of resinous plants in palaeoplant community. The co-existence of cedrene and cuparene could be attributed to the supply of Cupressaceae (order Coniferales) and some genera of the family Taxodiaceae.

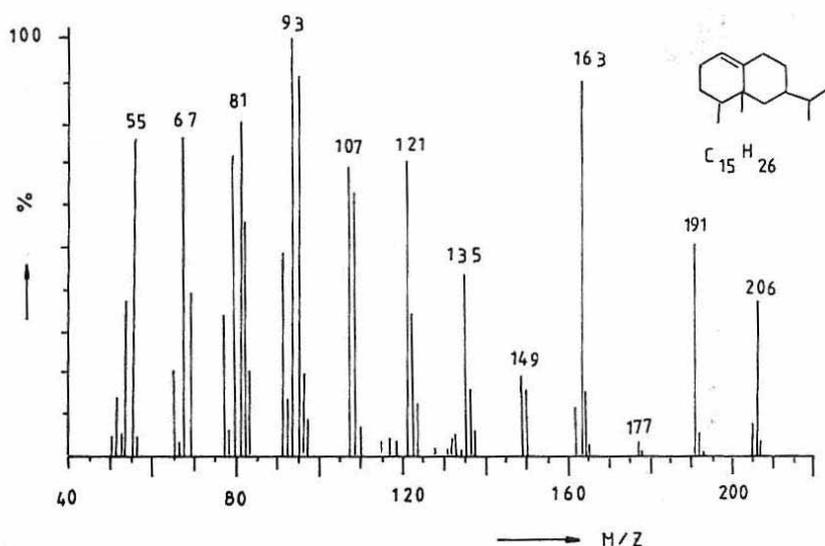
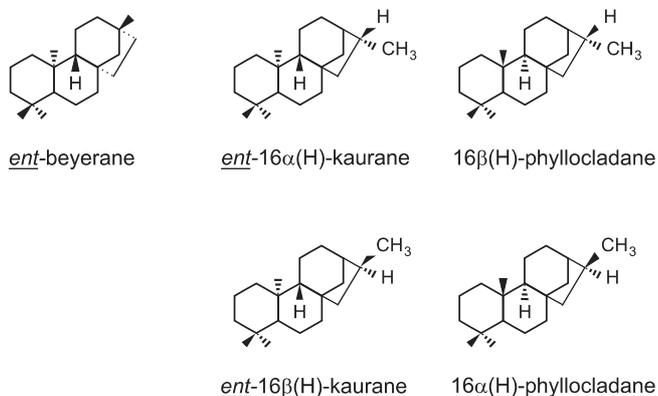


Fig. 5. Mass spectrum of one sesquiterpenoid with MM 206

Diterpenoids

Diterpenoids were represented only by tetracyclic species. The sample was strongly dominated by peaks 16, *ent*-16 α (H)-kaurane, and peak 17, 16 α (H)-phyllocladane, and the sum of compounds mounted to 2/3 of the analysed sample. The other tetracyclic diterpenoid — hibaene (Beyer-15-ene) was in trace, peak 14 (Fig. 2). We have already come across similar distribution pattern. For example, the predominance of diterpenoids was characteristic for the low maturity coal of Thracian province. In our previous studies on Maritza-East and Elhovo basins, we have determined strong 16 α (H)-phyllocladane dominance (Stefanova *et al.*, 1995; Stefanova, Magnier, 1997; Stefanova *et al.*, 1999). A peculiarity in the composition of "Katrishte" aliphatic fraction is the slight but prominent prevalence of kaurane structure over phyllocladane.

Tetracyclic diterpenoids are abundant in oils, sediments, coals, etc. The main tetracyclic skeletons, those of geological importance, are *ent*-beyerane, phyllocladane, and *ent*-kaurane (Noble *et al.*, 1986):



During maturation, 16 α (H)-epimers are converted in 16 β (H)-ones, thermodynamically more stable structures, hence α/β ratio is maturity dependent.

Aromatic tricyclic diterpanes were present in subordinate quantities, peaks 15, 18–23. They could be considered as products of tetracyclic diterpenoids' diagenetic transformation accompanied by bond splitting and aromatisation.

Among the diterpenoids commonly found in oils, phyllocladane is the only tetracyclic compound strictly associated with Gymnosperms, others having been found in Angiosperms (flowering plants), Pteridophytes (ferns), and Bryophytes (mosses and liverworts) (Philp, 1994). There were published studies on phyllocladane possible origin not mainly from conifers but also from primitive plants (the Voltziales) (ten Haven *et al.*, 1992; Disnar, Harouna, 1994).

An attempt was made to use tetracyclic diterpenoids as specific biomarkers for different conifer family. Inasmuch, in recent plants diterpenoids are mainly present in Gymnosperms, and only a few Angiosperms produce them; conifers are preferred as possible precursors (Collinson *et al.*, 1994). The progenitors of tetracyclic diterpanes are particularly abundant in leaf resins of conifers. Kauranes occur in high amounts in waxes of Araucariaceae family (Coniferales). Phyllocladanes are proposed as markers for the Podocarpaceae family, and simonellite/retene (aromatized tricyclic structures) for Pinaceae. According to Otto *et al.* (1997), phyllocladane in the geosphere may originate from species of four different conifer families and should not be used as biomarkers for individual families, but as characteristic molecules for Pinales other than Pinaceae.

The combination of high sesqui-/diterpenoid contents is an evidence for the input of higher plants' residues (conifers), especially when is accompanied by diterpenoid dominance. Resins containing sesqui- and diterpenoids are produced in species of all recent conifer families, but in large amounts in Pinaceae and Araucariaceae. However, Otto *et al.* (1997) advised phyllocladane to be related generally to the whole Coniferales group, but not to individual plant families.

Concerning tricyclic diterpanes, Alexander *et al.* (1987) have proposed relevant hypotheses for their plausible origin. Authors assumed that aromatisation processes have proceeded and phyllocladane/kaurane produced retene, simonellite, dehydroabietane, etc. We are inclined to support this idea, inasmuch, no saturate counterparts of the cited structures were recognised. Probably, aromatisation has preceded the diagenetic transformation to 16 β (H)-epimers as such structures were not identified in the aliphatic portion.

One peculiarity of "Katrishte" coal deposit should be noticed — saturates tricyclic diterpanes with abietane/pimarane skeleton were not registered there.

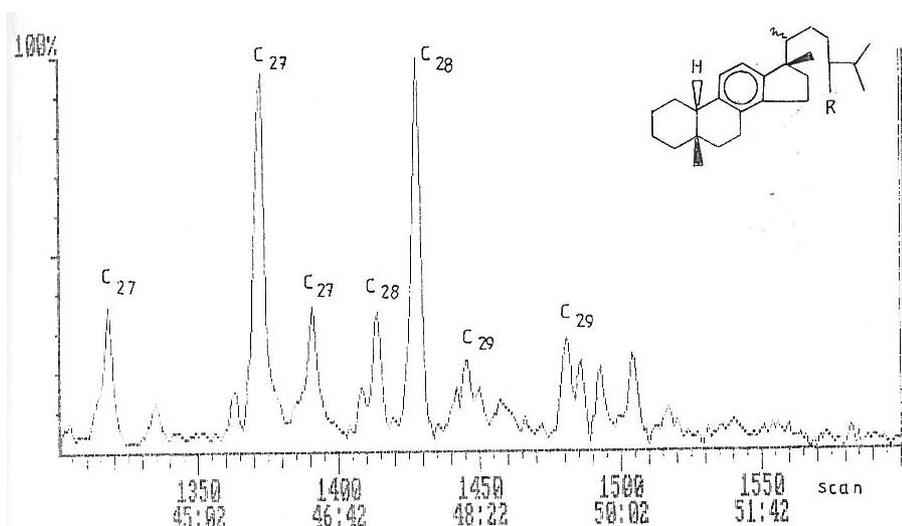


Fig. 6. Distribution of C-ring monoaromatic steranes by SIM m/z 253

C-ring monoaromatic steranes

C-ring monoaromatic steranes represented small portion of the fraction, ~1.5%. Nevertheless, skeletons traceable to steroidal precursors could be valuable in suggesting an algal input.

Aromatic steranes in geochemical samples could be A-, C-ring monoaromatic and triaromatic steranes. By SIM m/z 253, C-ring aromatised steranes were monitored (Fig. 6). These compounds indicate eukaryotic species input (Peters, Moldowan, 1993).

The C-ring monoaromatic steranes distribution is applied for correlation purposes and for maturity indication in petro-

leum/source rocks studies (Philp, 1985). Plot location of C-ring monoaromatic steranes in C_{27} , C_{28} , C_{29} ternary diagrams have been related to various types of source input, i.e. marine, lacustrine or terrestrial.

A great variety of C-ring monoaromatic steranes was determined in petroleum: regular, rearranged (dia-steranes), α/β stereo isomers, S/R couples (Peters, Moldowan, 1993). Stereo isomers are maturity dependent, and are transferred in β epimers. C-ring monoaromatic steranes are not so important structures in shales and coals but at certain level of maturation their quantity prevails over sterane's content (Arefev *et al.*, 1992).

In our study, C-ring monoaromatic steranes are tentatively identified on the base of SIM m/z 253. Molecular masses were MS determined, and C_{27} , C_{28} prevalence over C_{29} homologue was registered (Fig. 6). This is a hint for the probable lacustrine input, inasmuch, C_{29} dominance is a proof for terrigenous contribution. Lack of standards prevents us from further speculation on stereoisomers.

In the process of biomarkers interpretation, we were astonished by the absence of pentacyclic triterpanes, the common biomarkers in coals. We tried in vain to create reconstructed ion chromatogram RIC m/z 191. There was no indication for bacterial contribution to the extractable organic matter as indicated by the absence of hopanoids. There were no products of hopane reworking Des-A/Des-C-hopanes, demethylated hopanes, nor demethylated diterpanes.

CONCLUSIONS

The previous petrological study of "Katrishte" coal revealed the high ulminite content related to the presence of bushes and forest population in coal-forming palaeoplant community (Markova *et al.*, 2000). Smaller content of attrinite and densinite were related to subordinate contributions of herbaceous remnants of sedge-grass and water-grass populations. The petrological observations were partially confirmed by the data on bitumen biomarker composition. The predominance of kauranes over phyllocladane was a proof for Angiosperm higher plants input but such affirmation should be completed with ferns, pteridophytes, mosses etc. as possible progenitors (Philp, 1994). More information on the palaeoplant composition could be obtained by palynological analyses and palaeobotanical study.

It is known that in Tertiary a diverse array of flowering plant trees was associated with the conifers in the peat-swamps. The high quantity of phyllocladane, in combination with sesquiterpenoids, was an unequivocal evidence for the pres-

ence of conifers in the peat-forming community. We assume that in the case of "Katrishte" coal deposit the resinous components occurred in finely dispersed form throughout the coal, firmly attached to minerals. It is a possibility that the discrepancy between maceral composition on the base of MS analyses, indicating low resinite content (~1%) and conifers, could be explained by enrichment in the fraction under study.

Our data made to assume that deposition environment of "Katrishte" coal deposit was that of forested swamp where mire flora was dominated by herbaceous flowering plants Angiosperms, as indicated by maceral analyses, although locally Gymnosperms might also have contributed. Moss-dominated peat, commonly presented in Tertiary peat-forming floras, could not be excluded (high quantity of kaurane).

The low rank of "Katrishte" deposit was confirmed by the high quantities of a epimers for tetracyclic diterpanes (kaurane/phyllocladane) and the lack of their β -counterparts. There were registered some indication for algal phase contribu-

tion. The remarkable maximum for C₂₀-alkanes with odd dominance and C-ring monoaromatic steranes distribution implied an algal input.

The future study of "Katrishte" coal deposit will be focused on determination of other fractions biomarker and comparison with coals of south-western Bulgaria, with the idea to recon-

struct palaeoplant coal-forming community and classify the deposit.

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