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## IDENTIFICATION OF ALKYLPHENANTHRENES IN SHALE OIL AND COAL BY LIQUID AND CAPILLARY GAS CHROMATOGRAPHY AND HIGH-RESOLUTION SPECTROFLUORIMETRY (SHPOL'SKII EFFECT)

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### SUMMARY

The combination of three high-performance liquid chromatographic steps performed on shale and coal extracts allows the collection of subfractions containing one to three C<sub>2</sub>-phenanthrene isomers. The identification was made by comparison with retention indices, gas chromatographic-mass spectrometric data and Shpol'skii emission spectra of the 30 reference C<sub>2</sub>-phenanthrenes that have been synthesized.

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### INTRODUCTION

Dimethylphenanthrenes (DMPs) (Fig. 1) are one of the predominant series of compounds in triaromatic extracts of sedimentary rocks and coals. The relative distribution of these compounds provides information about the maturity levels of the samples<sup>1,2</sup>. The predominance of certain C<sub>2</sub>-phenanthrenes could also indicate the origin of the organic matter, *e.g.*, 1,7-DMP is derived from resin components found in conifers<sup>3,4</sup>. However, the true identification of the 30 C<sub>2</sub>-phenanthrenes has been only partially reported<sup>5</sup>. In a previous study<sup>5</sup>, we identified some C<sub>2</sub>-phenanthrene isomers by gas chromatographic retention indices, gas chromatographic-mass spectrometric (GC-MS) data and high-resolution spectroscopy (HRS) in *n*-alkane crystals at low temperature (Shpol'skii effect).

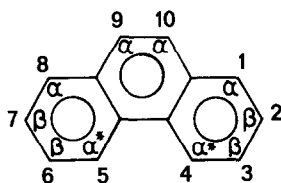


Fig. 1. Numbering of the phenanthrene molecule. Asterisks indicate sterically crowded positions.

This study is a continuation of our previous work to complete the identification of the 30  $C_2$ -phenanthrenes that have been synthesized as reference compounds. GC retention indices on different stationary phases, mass spectra and Shpol'skii fluorescence and phosphorescence spectra have been recorded for each dimethyl- and ethylphenanthrene, to lead to a precise identification of  $C_2$ -phenanthrene isomers in triaromatic subfractions of shale and coal extracts.

## EXPERIMENTAL

### *Synthesis of reference compounds*

The  $C_2$ -phenanthrenes listed in Table I were synthesized at the Institute of Petroleum and Organic Geochemistry, Jülich, F.R.G. (M. Radke and H. Willsch). The DMPs were prepared from dimethylstilbenes by photocyclization<sup>6</sup> and dehydrogenation<sup>7</sup>. The dimethylstilbenes were obtained from methyl- or dimethylbenzyl bromide and (methyl)benzaldehyde or (methyl)acetophenone via the Michaelis-Arbuzov and Pommer reactions<sup>8</sup>. Some DMPs, obtained as mixtures, were separated by high-performance liquid chromatography (HPLC). Identification of  $C_2$ -phenanthrene isomers was based on <sup>1</sup>H NMR data. The purity of standards determined by GC was generally better than 97%.

### *Samples*

The oil shale used was an unweathered sample of Jurassic (Lias epsilon) Posidonia shale, which was taken from a quarry near Dotternhausen, F.R.G. It was the same as that used in previous studies<sup>5,9</sup>.

TABLE I

$C_2$ -PHENANTHRENE ISOMERS STUDIED

Dimethylphenanthrenes			Ethylphenanthrenes	
$\alpha,\alpha$ -Type	$\alpha,\beta$ -Type	$\beta,\beta$ -Type	$\alpha$ -Type	$\beta$ -Type
1,4- 4,5-	1,2- 2,9-	2,3-	1-	2-
1,5- 4,9-	1,3- 2,10-	2,6-	4-	3-
1,8- 4,10-	1,6- 3,4-	2,7-	9-	
1,9- 9,10-	1,7- 3,5-	3,6-		
1,10-	2,4- 3,9-			
	2,5- 3,10-			
9 isomers	12 isomers	4 isomers	3 isomers	2 isomers

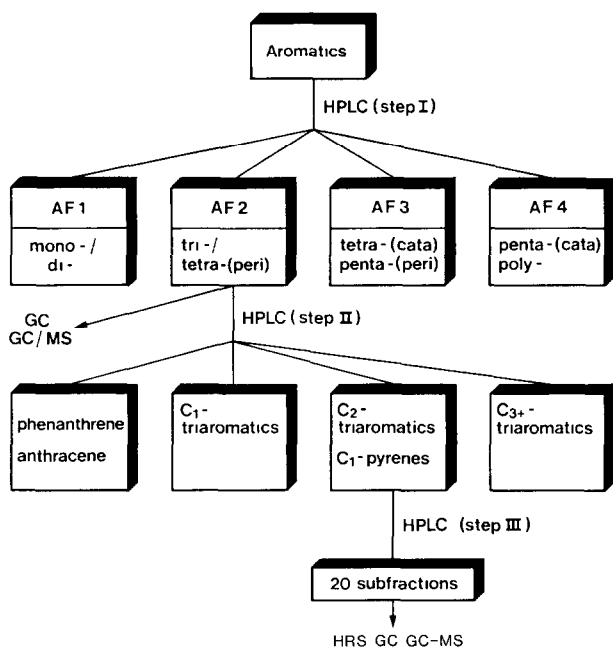


Fig. 2. Analytical scheme for the identification of  $C_2$ -phenanthrenes in aromatic fractions from rock and coal extracts.

The coal used was a core sample, which was taken from a Fourth coal seam in the Falher D, Spirit River formation, Elmworth, Western Canada, at a depth of 2177 m. According to ASTM rank classification, this sample was a high-volatile bituminous A coal. The data obtained from proximate analysis were 0.9% water (ash-free), 17.1% ash, 32.1% volatile matter (dry, ash-free); and from ultimate analysis (dry, ash-free basis), 82.51% C, 5.35% H, 1.09% N, 1.03% S. The mean vitrinite reflectance ( $R_m$ ) value of this sample was 1.10%.

#### Fractionation of aromatics

The analytical procedure for the isolation of  $C_2$ -phenanthrenes from organic extracts is presented in Fig. 2 and involved three HPLC steps as described previously<sup>5</sup>. Briefly, step I (semi-preparative HPLC on alumina) separates aromatic compounds into ring classes and allows the collection of aromatic fraction AF2, which contains triaromatic and pericondensed tetraaromatic compounds. In step II (analytical HPLC on a reversed-phase column), triaromatic compounds were separated with moderate resolution according to the degree of alkylation (Fig. 3), and the  $C_2$ -phenanthrene fraction was collected. In step III, this fraction was further fractionated on a reversed-phase column (Supelcosil, LC-PAH); the collected fractions contained only one to three  $C_2$ -phenanthrenes, which were then analysed by HRS and GC-MS. In order to eliminate interferences from sulphur-containing aromatics, these compounds were removed from the AF2 fraction of the Posidonia shale sample by oxidation with *m*-chloroperbenzoic acid<sup>10</sup>.

### GC and GC-MS analyses

The aromatic subfractions AF2 were analysed by GC on a Varian (Palo Alto, CA, U.S.A.) 3700 gas chromatograph equipped with an inlet splitter (Gerstel, Mülheim/Ruhr, F.R.G.). All capillary columns, of 50 m length, were purchased from Chrompack (Middelburg, The Netherlands). The fused-silica capillary column (50 m  $\times$  0.10 mm I.D.) was coated with CP-Sil 8CB (0.11  $\mu\text{m}$  film thickness) and used with hydrogen as the carrier gas (7.2 bar inlet pressure). After sample injection, the oven temperature was held at 120°C for 2 min, then programmed at 3°C min<sup>-1</sup> to 300°C. The following conditions were used in the determination of retention indices: (a) fused-silica column (50 m  $\times$  0.32 mm I.D.) coated with Silar 10C (0.22  $\mu\text{m}$  film thickness), helium carrier gas (4.6 bar inlet pressure), programmed from 80°C (held for 2 min) to 220°C at 2°C min<sup>-1</sup>; (b) fused-silica column (50 m  $\times$  0.22 mm I.D.) coated with CP-Sil 8 CB (0.13  $\mu\text{m}$  film thickness), helium carrier gas (3.7 bar inlet pressure), programmed from 120°C (held for 2 min) to 270°C at 3°C min<sup>-1</sup>.

GC-MS analyses were performed on a Carlo Erba (Milan, Italy) Fractovap 4160 gas chromatograph. A fused-silica capillary column (25 m  $\times$  0.32 mm I.D.; Hewlett-Packard, Palo Alto, CA, U.S.A.) coated with Ultra 2 (0.17  $\mu\text{m}$  thickness) was connected to a Model 7070E mass spectrometer (VG Instruments, Wiesbaden, F.R.G.) via an open-split coupling. Helium was used as the carrier gas (0.65 bar inlet pressure) and as the interface sweep gas. After splitless injection at 80°C, the temperature was raised to 120°C and then programmed at 3°C min<sup>-1</sup> to 220°C. The mass spectrometer was operated at 70 eV and data were collected in the multiple peak monitoring mode with a DS 50S on-line data system (Kratos, Ramsey, NJ, U.S.A.).

### High-resolution spectrofluorimetry (*Shpol'skii effect*)

Shpol'skii fluorescence and phosphorescence spectra were measured with a laboratory-made spectrofluorimeter, as described previously<sup>11</sup>. Solutions were adjusted to about 10<sup>-6</sup> M solute in *n*-hexane, for both reference compounds and natural extracts. At this low concentration level the formation of aggregates or microcrystals of aromatics at low temperature is minimized<sup>11,12</sup>. Rapid freezing of the solutions in liquid nitrogen (77 K) was also performed before the temperature was lowered to 15 K, to avoid aggregate formation during the cooling procedure.

## RESULTS AND DISCUSSION

### GC and GC-MS analyses

Retention indices of C<sub>2</sub>-phenanthrene reference compounds are reported in the Table II, as defined by Lee *et al.*<sup>13</sup>. The order of elution of the DMP isomers is the same on both phases (slightly polar CP-Sil 8CB and polar Silar 10C); most of the  $\beta,\beta$ -type DMP isomers are eluted first, followed by  $\alpha,\beta$ - and  $\alpha,\alpha$ -DMPs. However, the elution order is occasionally reversed in each DMP group type. A major exception is 4,5-DMP, eluted first, which is a non-planar molecule strained by the strong interaction between the two methyl groups. Ethylphenanthrenes generally are eluted with or before the  $\beta,\beta$ -DMPs.

Co-injection of standard compounds allowed a tentative identification of major representative C<sub>2</sub>-phenanthrenes by GC with flame ionization detection. However, several DMPs with the same retention time were unresolved and thus did not permit an unambiguous identification (Table II).

TABLE II

RETENTION INDICES OF C<sub>2</sub>-PHENANTHRENES ON CP-Sil 8CB AND SILAR 10C PHASES AND RELATIVE INTENSITIES OF MASS FRAGMENTS *m/z* 191 AND 206

Substituent positions	Compound type	Retention index		Relative intensity	
		CP-Sil 8CB	Silar 10C	<i>m/z</i> 191	<i>m/z</i> 206
1-EP	$\alpha$	336.05	318.77	100	90
2-EP	$\beta$	335.44	318.22	100	87
3-EP	$\beta$	332.60	317.02	100	81
4-EP	$\alpha$	331.59	313.23	100	83
9-EP	$\alpha$	335.40	318.65	100	76
1,2-DMP	$\alpha,\beta$	347.90	332.65	39	100
1,3-DMP	$\alpha,\beta$	340.00	323.93	38	100
1,4-DMP	$\alpha,\alpha$	344.00	324.82	83	100
1,5-DMP	$\alpha,\alpha$	344.30	325.56	29	100
1,6-DMP	$\alpha,\beta$	340.80	324.42	22	100
1,7-DMP	$\alpha,\beta$	341.80	324.53	19	100
1,8-DMP	$\alpha,\alpha$	345.20	328.30	23	100
1,9-DMP	$\alpha,\alpha$	343.40	327.21	33	100
1,10-DMP	$\alpha,\alpha$	349.97	335.86	40	100
2,3-DMP	$\beta,\beta$	342.90	327.01	40	100
2,4-DMP	$\alpha,\beta$	340.13	322.64	50	100
2,5-DMP	$\alpha,\beta$	340.84	322.84	44	100
2,6-DMP	$\beta,\beta$	337.04	320.80	23	100
2,7-DMP	$\beta,\beta$	337.70	320.89	20	100
2,9-DMP	$\alpha,\beta$	340.60	323.02	40	100
2,10-DMP	$\alpha,\beta$	339.80	323.53	25	100
3,4-DMP	$\alpha,\beta$	344.40	329.36	48	100
3,5-DMP	$\alpha,\beta$	336.45	318.80	41	100
3,6-DMP	$\beta,\beta$	335.40	321.04	25	100
3,9-DMP	$\alpha,\beta$	340.20	323.32	32	100
3,10-DMP	$\alpha,\beta$	339.90	323.30	22	100
4,5-DMP	$\alpha,\alpha$	327.16	332.36	100	74
4,9-DMP	$\alpha,\alpha$	343.20	324.79	43	100
4,10-DMP	$\alpha,\alpha$	343.40	324.86	50	100
9,10-DMP	$\alpha,\alpha$	348.52	326.21	85	100

Thirteen and eleven peaks (3-EP,1,2-DMP,1,10-DMP, and peaks from DMP1 to DMP10, observed previously<sup>1,4</sup>) were assigned to C<sub>2</sub>-phenanthrenes in the gas chromatogram of the triaromatic AF2 fractions (Fig. 4) from Posidonia shale and the bituminous coal, respectively, on the basis of *m/z* 206 mass chromatograms (Table II).

GC and GC-MS analyses were also performed on subfractions of the AF2 fraction (obtained after HPLC step III, Fig. 5), which contained one to three C<sub>2</sub>-phenanthrene isomers (Fig. 6). Identifications were made as presented in Fig. 7 for the subfraction 4 of the bituminous coal triaromatic fraction. Retention indices on CP-Sil 8CB and Silar 10C of the DMPs contained in this subfraction and the observation of the ratio of *m/z* 206 and 191 (*R*) (Figs. 7 and 8) led to an unambiguous identification of each C<sub>2</sub>-phenanthrene (Table III).

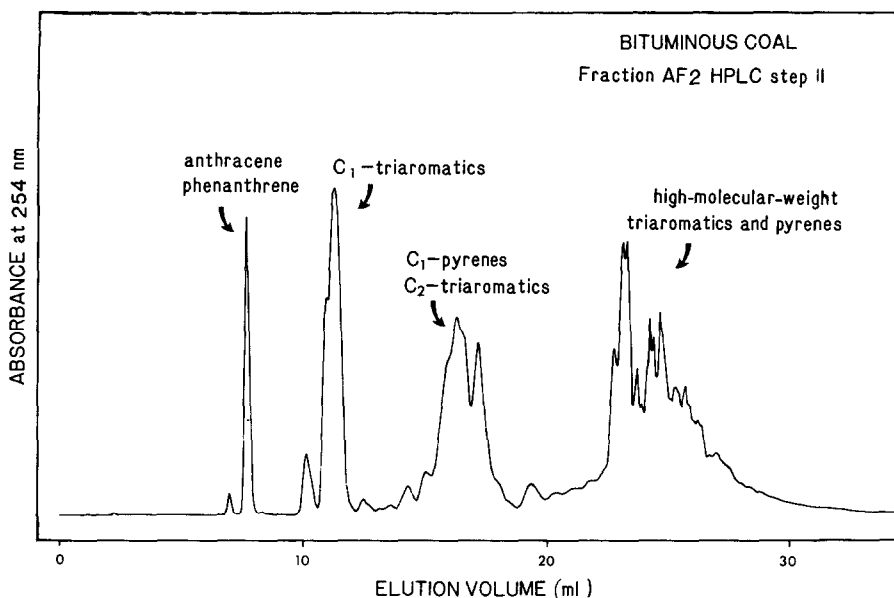


Fig. 3. HPLC (step II) chromatogram of triaromatic subfraction AF2 from bituminous coal. Column, 20 cm  $\times$  4.6 mm I.D., 5  $\mu$ m Spherisorb type S5 ODS; flow-rate, 1 ml min<sup>-1</sup>; eluent, methanol-water (75:25).

#### High-resolution spectrofluorimetry

Fluorescence and phosphorescence emission spectra of C<sub>2</sub>-phenanthrenes in Shpol'skii matrices at 15 K are specific for each isomer<sup>5</sup>, as has been shown for other aromatic series<sup>14</sup>. Fourteen and fifteen C<sub>2</sub>-phenanthrenes were identified by HRS in subfractions (HPLC step III) of Posidonia shale and bituminous coal, as shown in Fig. 9 for subfraction 5 of the coal (identification of 1,3-, 3,10- and 2,3-DMPs). Both the coincidence of the emission peak wavelengths and the relative intensities of the quasilines with those of standard reference spectra permitted unambiguous identifications (Table III) and confirmed the identifications made by GC-MS.

Some C<sub>2</sub>-phenanthrenes do not exhibit quasi-linear spectra. For instance, 2-EP and 3,6-DMP present broad-band spectra and cannot be detected in natural extracts. Also, 1-EP has a low fluorescence quantum yield and cannot be positively identified in natural matrices by the HRS technique. In these instances identification was made only by GC-MS analysis (Table III).

#### Geochemical implications

The two samples studied are representative of two different types of organic matter. The Posidonia shale sample consists mainly of marine organic matter, whereas the bituminous coal was formed by maturation of organic matter derived from terrestrial higher plants. These samples also differ in their maturity level, as the mean vitrinite reflectance ( $R_m$ ) is 0.54% for the oil shale compared with 1.10% for the bituminous coal. These two effects (original material sources and maturity) could influence the C<sub>2</sub>-phenanthrene distribution.  $\beta,\beta$ -DMP isomers are presumably more stable than the  $\alpha,\beta$ -type isomers, as demonstrated in other series such as the di-

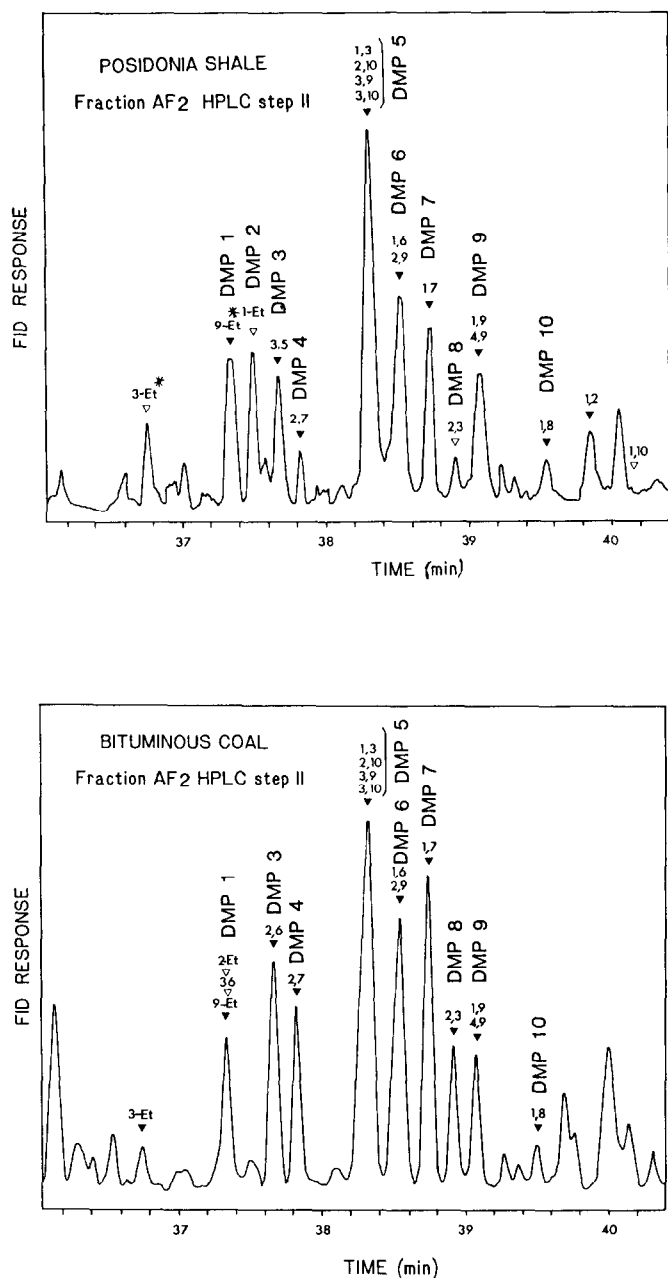


Fig. 4. Partial gas chromatograms of aromatic subfractions AF2 from (top) Posidonia shale (after removal of sulphur-containing aromatic compounds); (bottom) bituminous coal. 50 m × 0.10 mm I.D. fused-silica column coated with CP-Sil 8CB, programmed from 120°C (held for 2 min) to 300°C at 3°C min<sup>-1</sup>. Et = ethylphenanthrene. Compounds identified by HRS and by GC-MS are indicated by solid triangles; compounds identified by GC-MS only are indicated by open triangles. Asterisks indicate coelution of unknown compound with molecular ion at *m/z* 224.

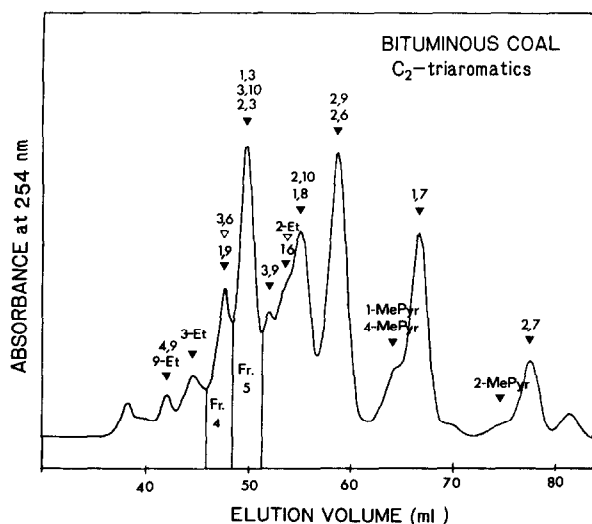


Fig. 5. HPLC (step III) chromatogram of  $C_2$ -triaromatics from bituminous coal. 25 cm  $\times$  4.6 mm I.D. 5- $\mu$ m Supelcosil column, type LC PAH; flow-rate, 2 ml  $\text{min}^{-1}$ ; eluent acetonitrile-water (50:50). Solid triangles indicate components identified by Shpol'skii spectroscopy and GC-MS. Open triangles indicate  $C_2$ -phenanthrenes identified only by GC-MS. Numbers indicate the position of the methyl groups. Et = ethylphenanthrene; MePyr = methylpyrene.

methylnaphthalenes<sup>4,15</sup>, and will appear in relative larger amounts in bituminous coal (high maturity level) than in Posidonia shale (low maturity level). This is actually the case for 2,3-, 2,6-, 2,7- and 3,6-DMPs, which are relatively more abundant in the coal sample than in the shale sample from which some DMPs (3,6- and 2,6-DMP)

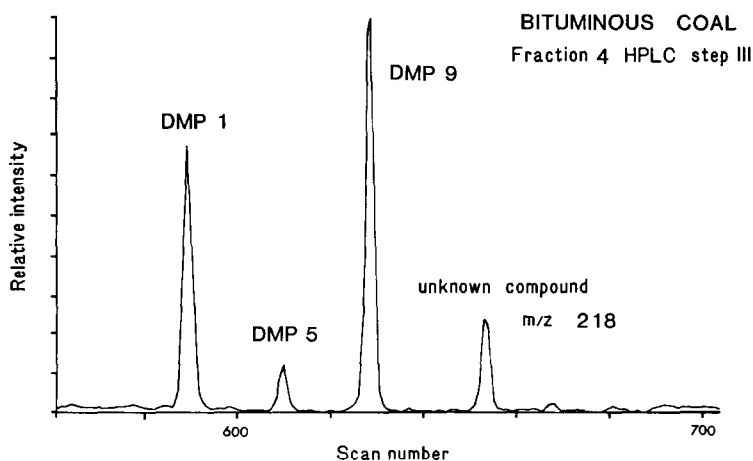


Fig. 6. Partial total ion current gas chromatogram of aromatic subfraction 4 (HPLC step III) from bituminous coal. 25 m  $\times$  0.32 mm I.D. fused-silica column coated with Ultra 2 phase, programmed from 120 to 220°C at 3°C  $\text{min}^{-1}$ . DMP 1, DMP 5 and DMP 9 correspond to chromatographic peaks of  $C_2$ -triaromatics eluted from CP-Sil 8CB (see gas chromatogram in Fig. 4).



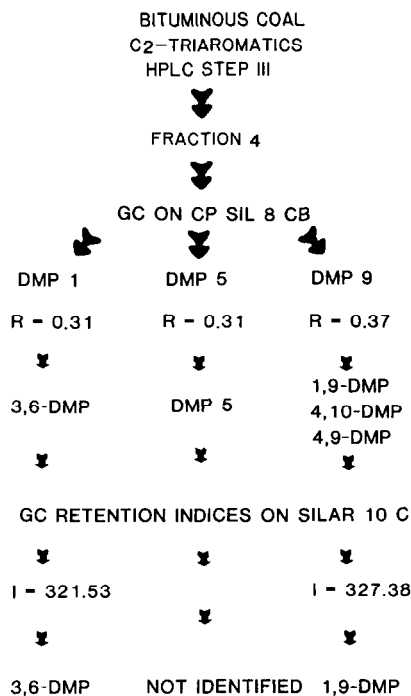


Fig. 7. Example of tentative identification by GC and GC-MS of DMPs in subfractions (HPLC step III) from bituminous coal.  $R$  = ratio of mass fragments  $m/z$  191 and  $m/z$  206.  $I$  = retention indices on Silar 10C. DMP 1, DMP 5 and DMP 9 indicate chromatographic peaks corresponding to C<sub>2</sub>-triaromatics eluted from CP-Sil 8CB (see gas chromatogram in Fig. 4).

are absent. The detection of 3,5-DMP ( $\alpha,\beta$ -type), which is a possible precursor by rearrangement of 3,6-DMP ( $\beta,\beta$ -type) in Posidonia shale, and its absence in the more mature coal sample could confirm the hypothesis of methyl shift reactions<sup>1</sup>. Concerning the ethylphenanthrenes,  $\beta$ -type isomers are expected to be more stable than  $\alpha$ -type isomers, as in the methylphenanthrene series<sup>1</sup>. We observed the presence of 1-EP ( $\alpha$ -substituted isomer) in Posidonia shale and the lack of 2-EP ( $\beta$ -substituted isomer) in Posidonia shale, whereas the reverse was true in the more mature coal sample.

We also observed a high relative abundance of 1,7-DMP (pimanthrene) in the coal. This could indicate that resin components are the major source of organic matter in this sample<sup>3,4</sup>.

## CONCLUSIONS

The combination of several chromatographic techniques (three HPLC steps, two different GC stationary phases) with MS and HRS detection has led to the positive identification of 17 C<sub>2</sub>-phenanthrenes among the 30 possible isomers. The predominance of certain DMP and EP isomers could help to improve our under-

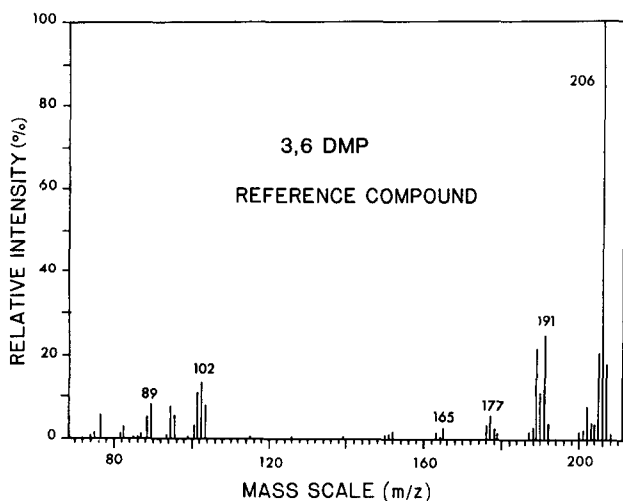
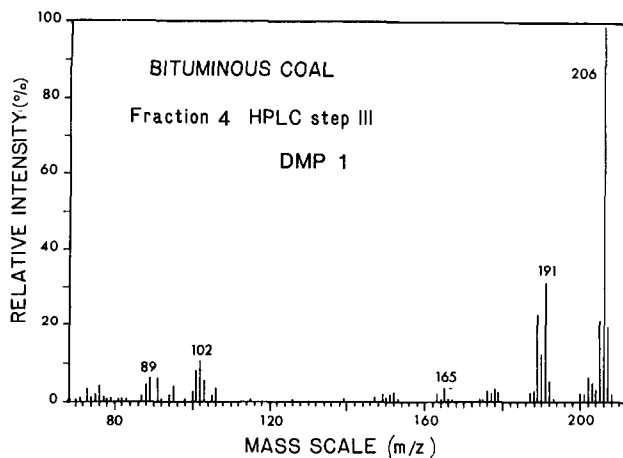


Fig. 8. Mass spectra of (top) peak DMP 1 (see gas chromatogram in Fig. 4) of coal subfraction 4 (HPLC step III); (bottom) 3,6-DMP standard obtained at 70 eV.

standing of the geochemical behaviour of these compounds, which could serve as maturity indices of the organic matter in the sedimentary environment.

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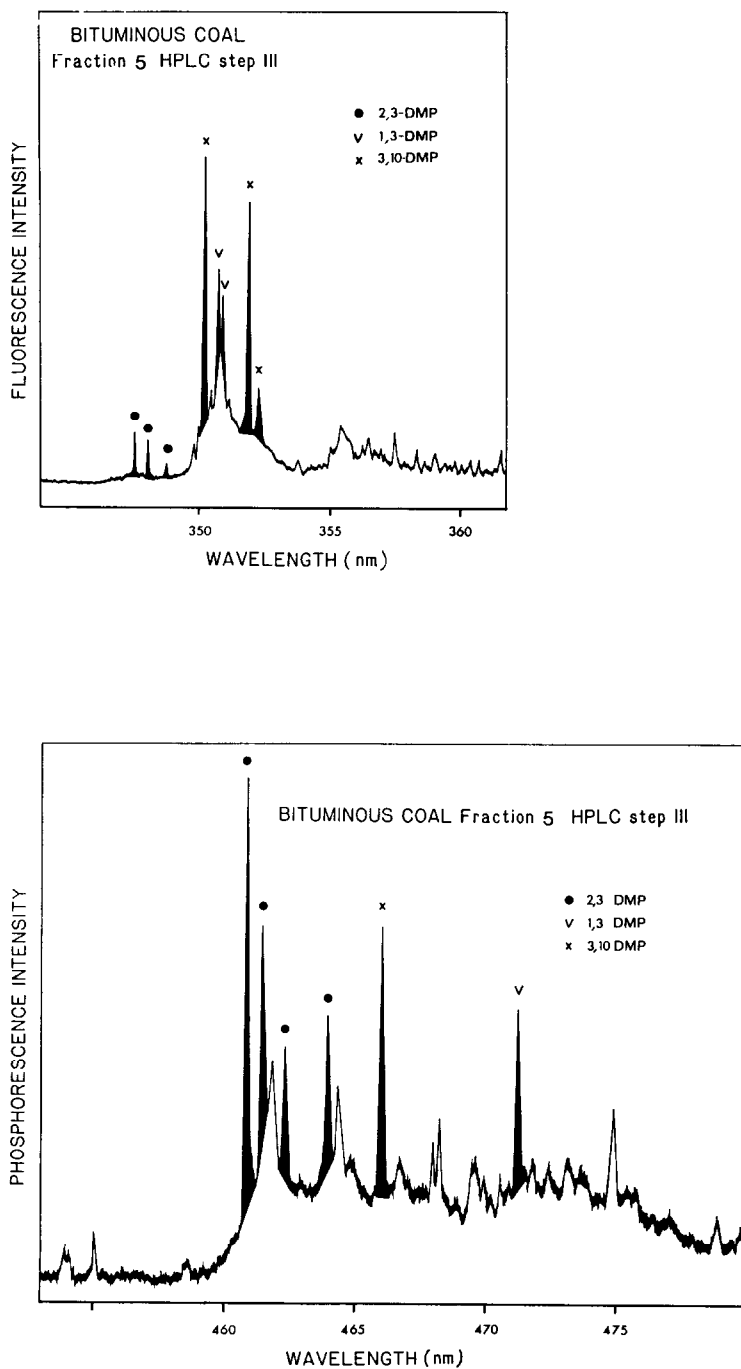


Fig. 9. Fluorescence (top) and phosphorescence (bottom) spectra of 1,3-, 3,10- and 2,3-DMP in bituminous coal subfraction 5 (HPLC step III) in *n*-hexane at 15 K. Excitation wavelength, 258 nm.

TABLE III

C<sub>2</sub>-PHENANTHRENES IDENTIFIED IN ORGANIC EXTRACTS BY HRS AND GC-MS

+ (MS) = Present (detected only by MS); - = absent or undetectable; Et = ethyl; Me = methyl.

Position Me or Et groups	Sample		Position of Me groups	Sample	
	Posidonia shale	Bituminous coal		Posidonia shale	Bituminous coal
1-Et	+(MS)	-(MS)	2,4-Me <sub>2</sub>	-	-
2-Et	-	+(MS)	2,5-Me <sub>2</sub>	-	-
3-Et	+(MS)	+	2,6-Me <sub>2</sub>	+	+
4-Et	-	-	2,7-Me <sub>2</sub>	-	+
9-Et	+	+	2,9-Me <sub>2</sub>	+	+
1,2-Me <sub>2</sub>	+	-	2,10-Me <sub>2</sub>	+	+
1,3-Me <sub>2</sub>	+	+	3,4-Me <sub>2</sub>	-	-
1,4-Me <sub>2</sub>	-	-	3,5-Me <sub>2</sub>	+	-
1,5-Me <sub>2</sub>	-	-	3,6-Me <sub>2</sub>	-	+(MS)
1,6-Me <sub>2</sub>	+	+	3,9-Me <sub>2</sub>	+	+
1,7-Me <sub>2</sub>	+	+	3,10-Me <sub>2</sub>	+	+
1,8-Me <sub>2</sub>	+	+	4,5-Me <sub>2</sub>	-	-
1,9-Me <sub>2</sub>	+	+	4,9-Me <sub>2</sub>	+	+
1,10-Me <sub>2</sub>	+(MS)	-	4,10-Me <sub>2</sub>	-	-
2,3-Me <sub>2</sub>	-	+	9,10-Me <sub>2</sub>	-	-

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