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INVESTIGATION OF HYDROCARBON CONSTITUENTS OF A YOUNG SUB-BITUMINOUS COAL BY GAS CHROMATOGRAPHY–MASS SPECTROMETRY

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SUMMARY

Hydrocarbon fractions were obtained from a coal extract by open-column chromatographic methods. Compounds amenable to gas chromatography were investigated by computerized gas chromatography–mass spectrometry. Several aliphatic and hydroaromatic biomarkers were observed. Monoaromatic compounds not previously reported in the literature were also detected. They are believed to be intermediates of diagenetic aromatization reactions. The retention indices for several pentacyclic hydroaromatic hydrocarbons are reported.

INTRODUCTION

A classical technique used in the investigation of the composition of coal is solvent extraction. The extractable portion of brown coals consists mainly of large molecules (waxes and resins) but also small species trapped in the coal matrix. Among the latter compounds, the hydrocarbons are of special interest, because they are chemically inert and are considered to be the last remnants of the living organisms from which coal was formed. By analysing these hydrocarbons a great number of "biological markers" (compounds derived from living organisms) can be identified. The occurrence of biological markers and their comparison with molecules synthesized by living organisms has been reviewed several times, *e.g.*, ref. 1.

By means of computerized capillary gas chromatography–mass spectrometry (GC–MS), very complex mixtures of organic compounds can be separated and identified; therefore this technique is widely used in the analysis of organic constituents in samples of geological origin. In recent years, several GC–MS investigations of hydrocarbons in coal extracts have been published[2–11]. A preseparation step(s) usually precedes GC–MS analysis, separating the organic material into several fractions. In this way, specific compound classes are concentrated in certain fractions, better reso-

lution can be achieved and higher sensitivity of spectral signals is obtained for the concentrated compounds.

This report describes an investigation of hydrocarbon fractions separated from a brown coal extract, using high-resolution capillary gas chromatography–computerized mass spectrometry. Several aliphatic and hydroaromatic biomarkers were observed, and two unreported hydroaromatic intermediates of the triterpenoid aromatization series were tentatively identified.

EXPERIMENTAL

The coal sample was from the East Elbian coal basin (G.D.R.) and had 5.0% H, 67.3% C, 1.1% N, 24.6% O and 2.1% (m/m) S.

A 25-g amount of the dried coal was Soxhlet extracted with 160 ml benzene–ethanol (3:1) for 48 h. After extraction, the solvent was evaporated at room temperature under vacuum. The aliphatic (fraction A) and aromatic (fraction B) hydrocarbons were obtained by fractionation on a silica gel column (Kieselgel 60; E. Merck, Darmstadt, F.R.G.). A 100-mg sample, dried on 0.5 g Chromosorb W AW (Johns-Manville, Denver, CO, U.S.A.), was loaded on a 20 cm × 1 cm I.D. column. Fraction A was eluted with 50 ml hexane, fraction B with 50 ml hexane–benzene (85:15) with a flow-rate of about 1 ml/min.

The aromatic compounds (fraction B) were further separated on a column (80 cm × 1 cm I.D.) of Amberlyst A-26 ion-exchange resin (Serva, Heidelberg, F.R.G.). The resin was first exhaustively purified. It was treated with 1 mol/dm³ sodium hydroxide, washed with deionized water to neutrality, treated with 1 mol/dm³ hydrochloric acid and washed again to neutrality. This procedure was repeated three times. The water was removed by exhaustive washing with acetone, and the resin was air dried. The resin was Soxhlet extracted with benzene for 48 h, washed with acetone and air dried. The resin (preswollen in hexane) was then packed into the column. The sample loading was analogous to that described for the silica gel column.

About 100 mg of fraction B (obtained from several fractionations on a silica gel column) were loaded onto the Amberlyst A-26 column, and eluted with 100 ml hexane, 50 ml hexane–benzene (95:5) and 50 ml hexane–benzene (90:10) at a flow-rate of about 1 ml/min. Fractions of 25 ml were collected. The composition of the aromatic subfractions is given later.

Gas chromatographic analyses were conducted using an Hewlett-Packard Type 5830 gas chromatograph equipped with split injection system and a flame ionization detector. GC–MS measurements were performed on a computerized Hewlett-Packard 5985A system. The spectra were taken in the electron-impact mode with an electron energy of 70 eV.

The analytical procedure is summarized in Fig. 1.

RESULTS AND DISCUSSION

Fraction A (aliphatic fraction)

Fraction A is a mixture of aliphatic hydrocarbons. In Fig. 2 the reconstructed total ion chromatogram of this fraction is given. It contains n-alkanes (indicated according to their carbon numbers), C_{19}–C_{21} tri- and tetracyclic hydrocarbons and C_{29}–C_{31} pentacyclic hydrocarbons.
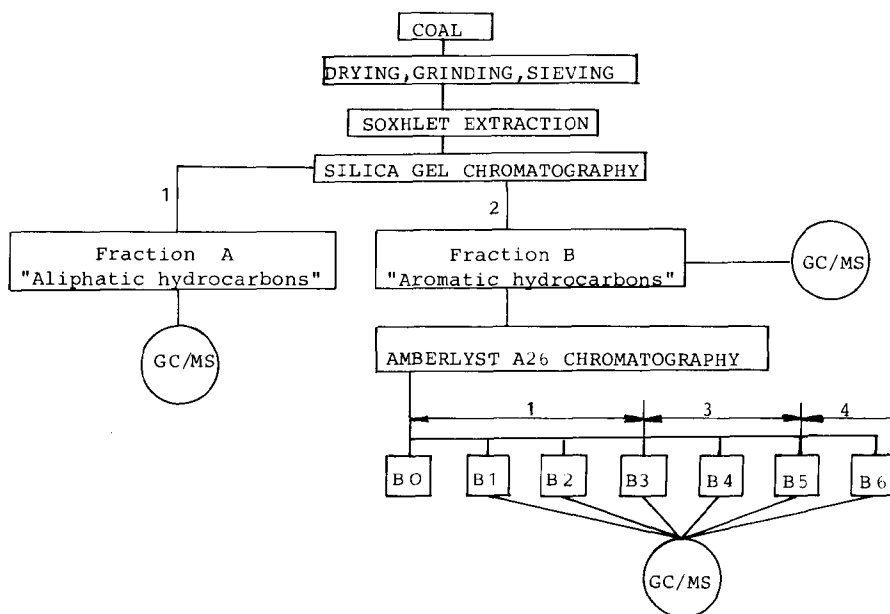
Fig. 1. Analytical scheme. Eluents: 1 = *n*-hexane; 2 = *n*-hexane–benzene (85:15); 3 = *n*-hexane–benzene (95:5); 4 = *n*-hexane–benzene (90:10).
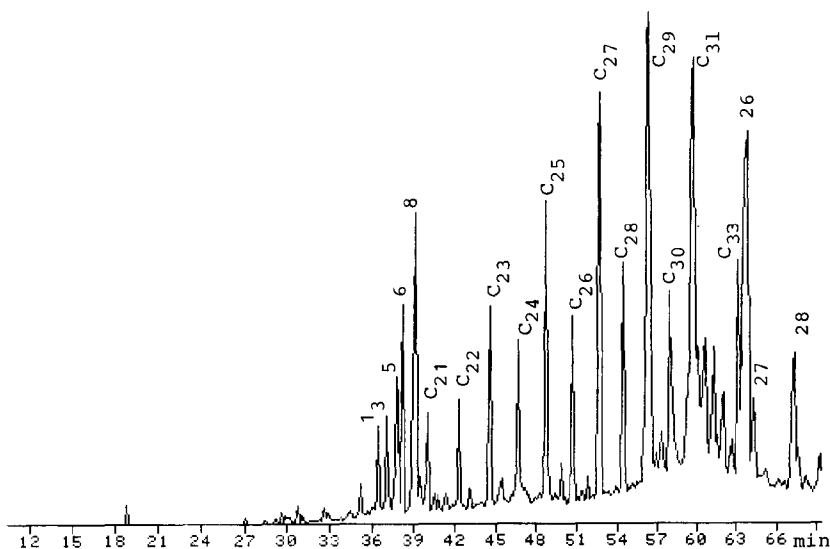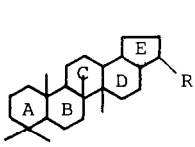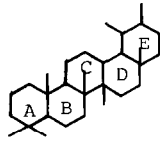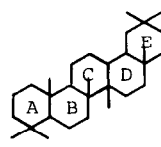

Fig. 2. Reconstructed total ion chromatogram of fraction A. Column: Ultra 2 fused-silica capillary column. Splitting ratio: 1:10. Injection temperature: 270°C. Oven temperature: 80°C, 3 min, isothermal; then increased to 310°C at 4°/min. *n*-Alkanes are indicated according to their carbon numbers; the peak numbers correspond to the numbers in Table I.
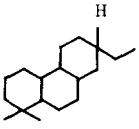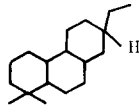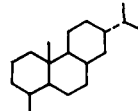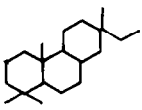
I

hopane

II

ursane

III

oleane

IV

V

VI

VII
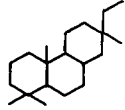
VIII
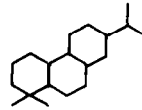
IX
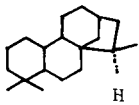
X
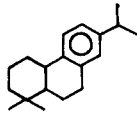
XI
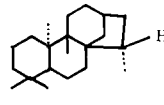
XII

n-Alkanes. It is seen (Fig. 2) that the odd carbon numbered *n*-alkanes are more prominent than the even numbered ones. The ratio between the amounts of the odd and even numbered *n*-alkanes is a characteristic of sediment, oil and coal samples[1]; and is usually expressed by the carbon preference index (CPI) introduced by Bray and Evans[12]:

$$CPI = 0.5 \left(\frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{24} + C_{26} + C_{28} + C_{30} + C_{32}} + \right.$$

$$\left. \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{26} + C_{28} + C_{30} + C_{32} + C_{34}} \right)$$

The CPI is related to the coal ranking and its value decreases with increasing maturity. For young coals, the predominance of odd-carbon numbered species is characteristic, therefore the CPI value is high. The CPI value decreases to 1 in highly ranked coals corresponding to complete elimination of the odd/even dominance. The value varied between 15 and 1 for a set of Australian coals[13] and between 4 and 1 for a set of Hungarian coals[14]. (In ref. 14 the CPI value was calculated between C_{17} and C_{34}.)

The CPI value of the present coal sample is 3.6, indicating its low maturity.

Cyclic alkanes. The cyclic compounds detected in fraction A are listed in Table I. The identification was performed by use of the published mass spectra and retention characteristics[8,15-19].

In mass spectra of many tri- and tetracyclic aliphatic compounds present in samples of geological origin, an ion at m/z 123 was observed in high abundance[15-18].
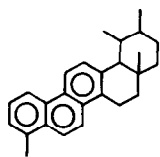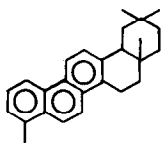
XIII   XIV   XV

XVI   XVII   XVIII
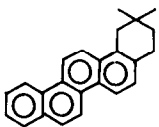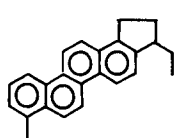
XIX   XX   XXI
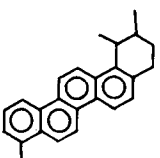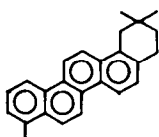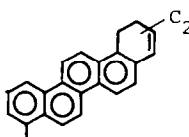
XXII   XXIII   XXIV

TABLE I

CYCLIC COMPOUNDS DETECTED IN FRACTION A

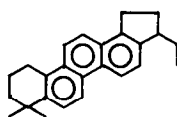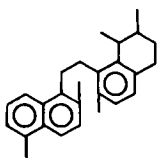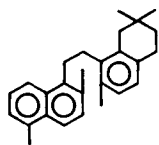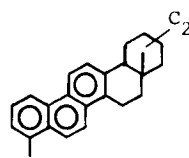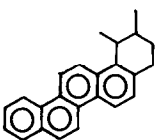| No.	MW	Most significant ions*	Structure	Reference
1	262	55 (100), 163 (40), 191 (40), 233 (45), 247 (10), 262 (35)	IV or V	17
2	276	55 (100), 109 (45), 123 (45), 276 (20)		
3	262 + 274	Unresolved peak		
4	276	55 (100), 123 (40), 163 (40), 191 (20), 261 (15), 276 (20)		
5	262	109 (100), 163 (40), 191 (45), 219 (20), 262 (40), 259 (35	VI	16, 17
6	276	55 (100), 123 (90), 163 (90), 191 (50), 247 (80), 261 (20), 276 (30)	VII or VIII	17
7	276	123 (80), 163 (100), 191 (60), 233 (20), 261 (30), 276 (40)	IX	17
8	274	123 (100), 136 (30), 150 (20), 189 (15), 231 (20), 259 (35), 274 (40)	X	17, 18
9	270	131 (40), 146 (70), 160 (45), 185 (30), 255 (70), 270 (100)		
10	270	159 (100), 173 (90), 185 (60), 255 (100), 270 (40)	XI	19
11	274	123 (100), 189 (20), 231 (20), 259 (40), 274 (40)	XII	18
12	396		C_{29} hopene	
13	368		C_{27} hopene	
14	408		C_{30} hopene	
15	370	149 (100), 191 (60), 355 (10), 370 (10)	C_{27} hopane	
16	398		C_{29} hopane	
17	408		C_{30} hopene	
18	398	177 (100), 191 (80), 383 (5), 398 (5)	C_{29} hopane	
19	410		C_{30} hopene	
20	408		C_{30} hopene	
21	410		C_{30} hopene	
22	410		C_{30} hopene	
23	360		Unknown	
24	410		C_{30} hopene	
25	410	'	C_{30} hopene	
26	426	see Fig. 5a	See text	
27	426	see Fig. 5b	See text	
28	426	see Fig. 5c	See text	

* The values in parentheses are the relative abundances.

In Fig. 3, sections (between retention times of 36 and 41 min) of the total ion chromatogram and the m/z 123 ion profile are given. Several C_{19} (MW = 262) and C_{20} (MW = 276) tricyclic compounds were detected. Two compounds (peaks 8 and 11) with molecular masses of 274 are tetracyclic diterpanes. Two minor compounds (peaks 9 and 10) having monoaromatic tricyclic structures were also eluted in this region; the presence of these species in fraction A indicates a slight overlap in the aliphatic/aromatic separation. Peak 10 is dehydroabietane, a known intermediate in the diagenetic aromatization process of diterpanes[19].

Fig. 3. Comparison of the m/z 123 ion profile and the reconstructed total ion profile for the section between 35 and 41 min. Peak numbers correspond to the numbers in Table I. *n*-Alkanes are indicated according to their carbon numbers. For chromatographic conditions see Fig. 2.
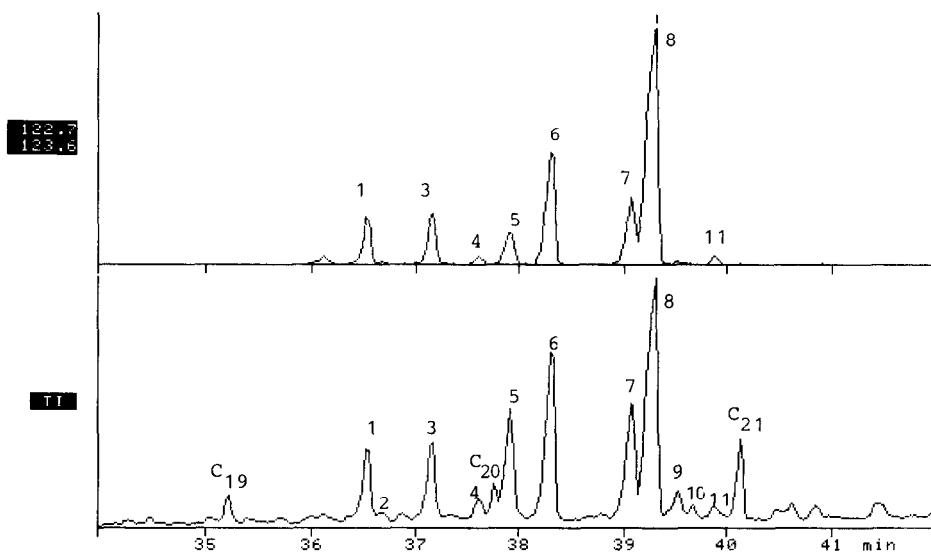
The tricyclic compounds appear to belong to the pimarane (see for example, structure VI) and abietane (*e.g.*, structure VII) classes of compounds. The appearance of compounds having these structures in coals has often been observed[2–4]. Carboxylic acids with abietane and pimarane skeletons are known constituents of conifer resins. Decarboxylation of these acids would lead to the C_{19} hydrocarbons, whereas the C_{20} compounds are products of reduction reactions[17].

The most abundant compound in this region is peak 8, and it was identified as 16αH-phyllocladane (structure X), a tetracyclic diterpane. This compound is thought to be formed from phyllocladene, a constituent of conifer resins. Phyllocladanes have been detected in young coals[3,4,18].

Pentacyclic aliphatic compounds elute in the C_{29}–C_{31} region and often exhibit an intense ion at m/z 191[20]. In Fig. 4, sections (between retention times of 55 and 68 min) of the m/z 191 ion profile and the reconstructed total ion chromatogram are seen. Among pentacyclic compounds, peak 26 is the most abundant. This compound together with peaks 27 and 28 correspond to hydrocarbons with a molecular mass of 426. In Fig. 5 the mass spectra of these species are given. The spectra of peaks 26 and 27 differ very slightly and resemble the published spectra of C_{31} hopanes[8]. The only noticeable difference is the intensity of the ion at m/z 205, being 29 and 66%, respectively. Based on the spectra and the elution order of these two peaks, one might assume that they correspond to 17αH, 21βH,22S (peak 26) and 17αH, 21βH,22R (peak 27) homohopanes. It is known, however, that the ratio of the 22S/22R epimers at equilibrium is about 1.2–1.4[21]. The ratio for peaks 26 and 27 is 11.8 (based on m/z 191 intensities). This deviation may be caused by preferential biodegradative removal of the 22R epimer of 17αH-homohopane compared with the 22S epimer.
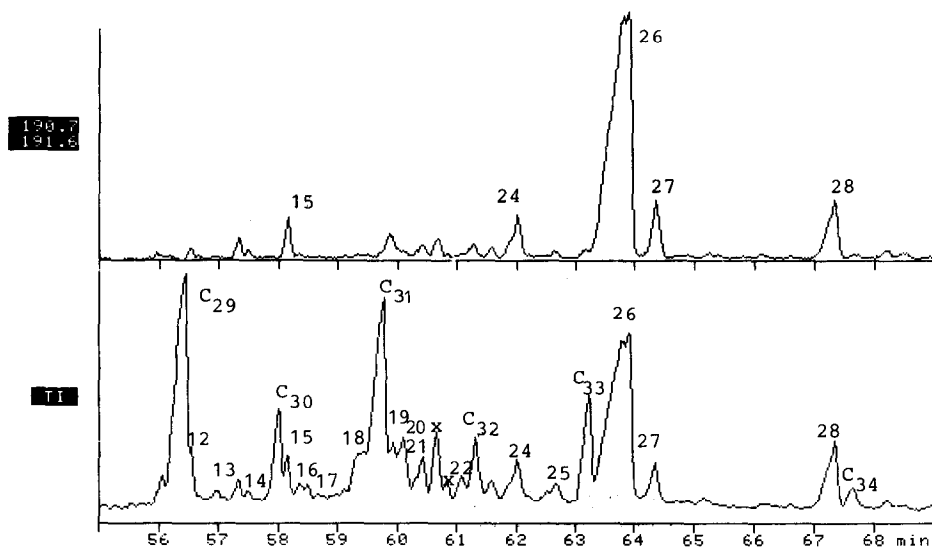
Fig. 4. Comparison of the m/z 191 single ion profile and the reconstructed total ion profile in the section between 56 and 68 min. Peak numbers correspond to the numbers in Table I. *n*-Alkanes are indicated according to their carbon numbers. Peak x is a monoaromatic compound (peak 36, Table II). For chromatographic conditions see Fig. 2.

The lack of other hopane homologues (at least in significant amounts), however, suggests that these C_{31} species are other than 17α-homohopanes. $C_{31}H_{54}$ compounds, having similar retentions and virtually the same spectrum as 17αH, 21βH-homohopanes, were also found in oil samples[22,23]. The spectrum of peak 28 resembles that of 17βH, 21αH-homomoretane[8].

The other peaks eluted in this region belong most likely to hopane type compounds. Most of them are unsaturated species (see Table I).

Fraction B (aromatic fraction)

In Fig. 6 the reconstructed total ion chromatogram of fraction B is shown. It is seen that there are unresolved compounds among the major peaks.

Subfractionation of the aromatic compounds. To obtain better GC results, a simple procedure was needed to separate fraction B into subfractions.

Aromatic hydrocarbons may be separated on dual silica–alumina columns into mono-, di- and polyaromatic subfractions[24]. Unfortunately, no separation is achieved within the polyaromatic compounds, *i.e.*, molecules containing three, four and five aromatic rings are not resolved. A polystyrene-based sorbent, Amberlyte XAD-2, has also been used to obtain subfractions with increasing aromaticity; the fully aromatized hydrocarbons being eluted according to their molecular masses[25]. Using this procedure the aromatic hydrocarbons in a mineral oil sample were separated from the aliphatic matrix, and were divided into fractions containing compounds of lower and higher molecular masses[25].

The macroreticular anion exchanger Amberlyst A-26, which is supposed to be
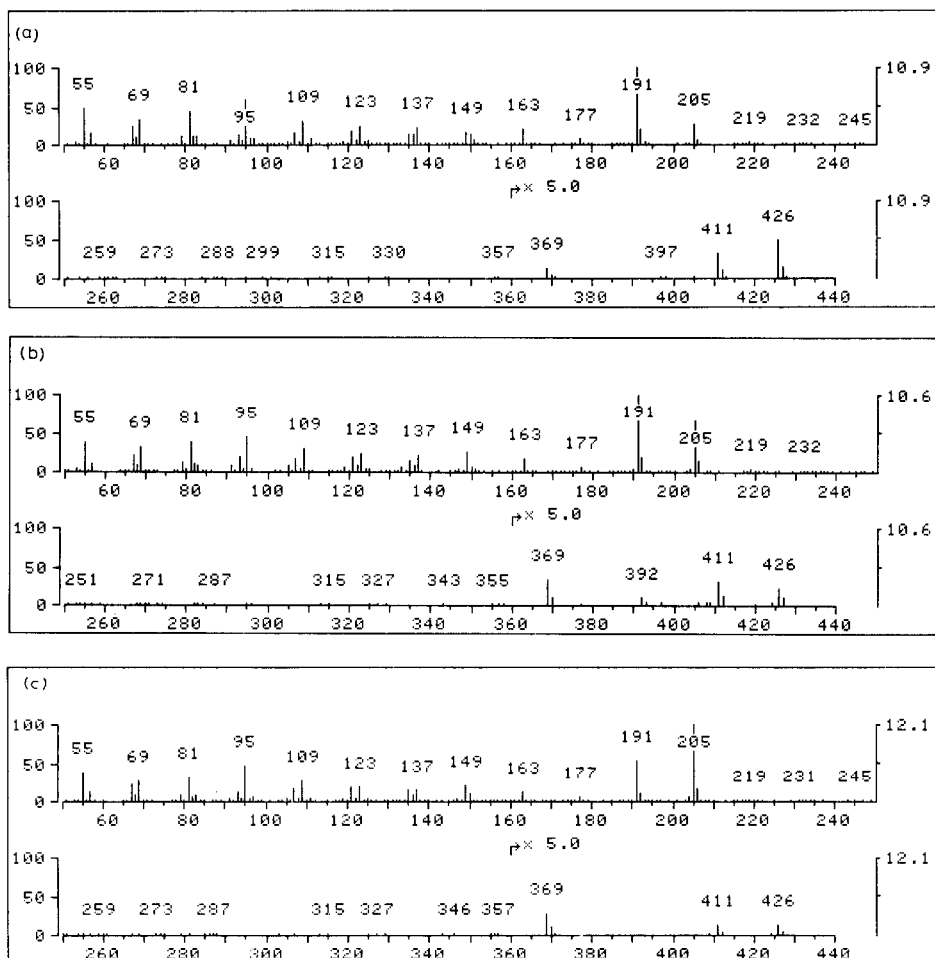
Fig. 5. Mass spectra of $C_{31}H_{54}$ compounds: (a) peak 26; (b) peak 27; (c) peak 28.

used in organic solvents, combines the features of basic alumina and polystyrene packings, namely it has a polystyrene skeleton and a basic surface due to the quaternary amine functional groups.

In preliminary experiments a mixture of hexadecane, naphthalene, anthracene and chrysene was separated by performing the elution with hexane and hexane–benzene mixtures (see Fig. 7). The same separation could not be achieved using Amberlyst A-15 cation exchanger, having the same polymer skeleton but sulphonic acid functional groups. This suggests that the presence of functional groups influences the separation process.

In Fig. 8 sections (between 26 and 30 min) of the total ion chromatograms of subfractions B1, B2, B3, B5, B6 are compared. No complete separation according to aromaticity was achieved, but subfractions enriched in certain compounds were prepared. The compounds detected in fraction B are given in Table II.
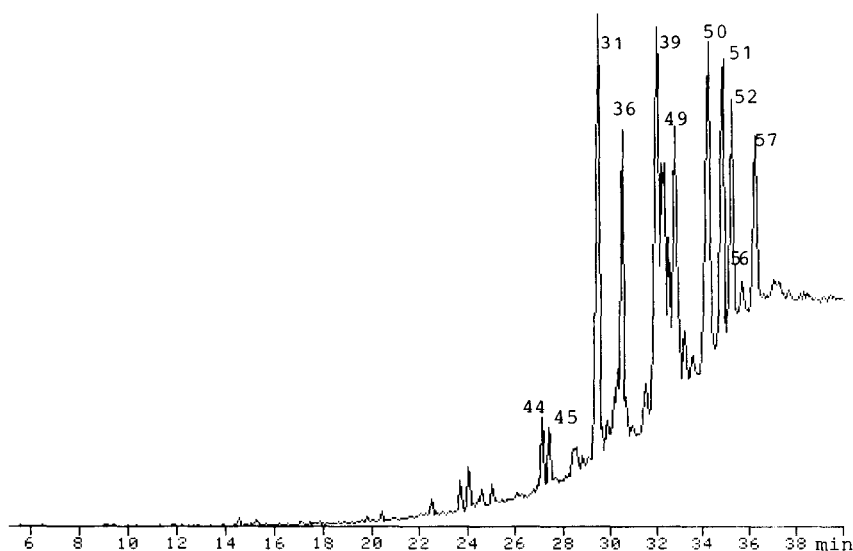
Fig. 6. Reconstructed total ion chromatogram of fraction B. Oven temperature: 200°C, 3 min, isothermal, then increased to 330°C at 4°/min; finally isothermal. Other chromatographic conditions as in Fig. 2.

Subfraction B1 (26–50 ml eluate). In subfraction B1 the two largest compounds of the aromatic fraction were eluted; their mass spectra are shown in Figs. 9 and 10. According to their molecular masses and retentions, these compounds are pentacyclic hydrocarbons containing one aromatic ring (MW 378, Fig. 9) or one aromatic ring and one double bond (MW 376, Fig. 10). The fact that these compounds have weak retention on the Amberlyst A-26 column also supports the assumption that they contain one aromatic ring.

Fig. 7. Separation of a synthetic mixture (hexadecane, naphthalene, anthracene and chrysene) on Amberlyst A-26 (80 cm × 1 cm I.D.). Flow-rate about 1 ml/min.

Fig. 8. Comparison of subfractions B1, B2, B3, B3, B5, B6 between 27 and 42 min. Chromatographic conditions as in Fig. 6.

TABLE II

PEAKS DETECTED IN FRACTION B

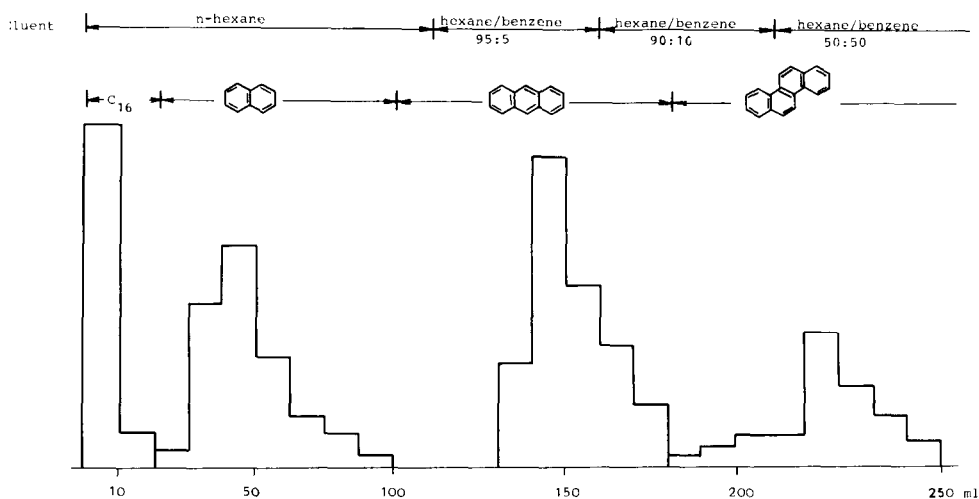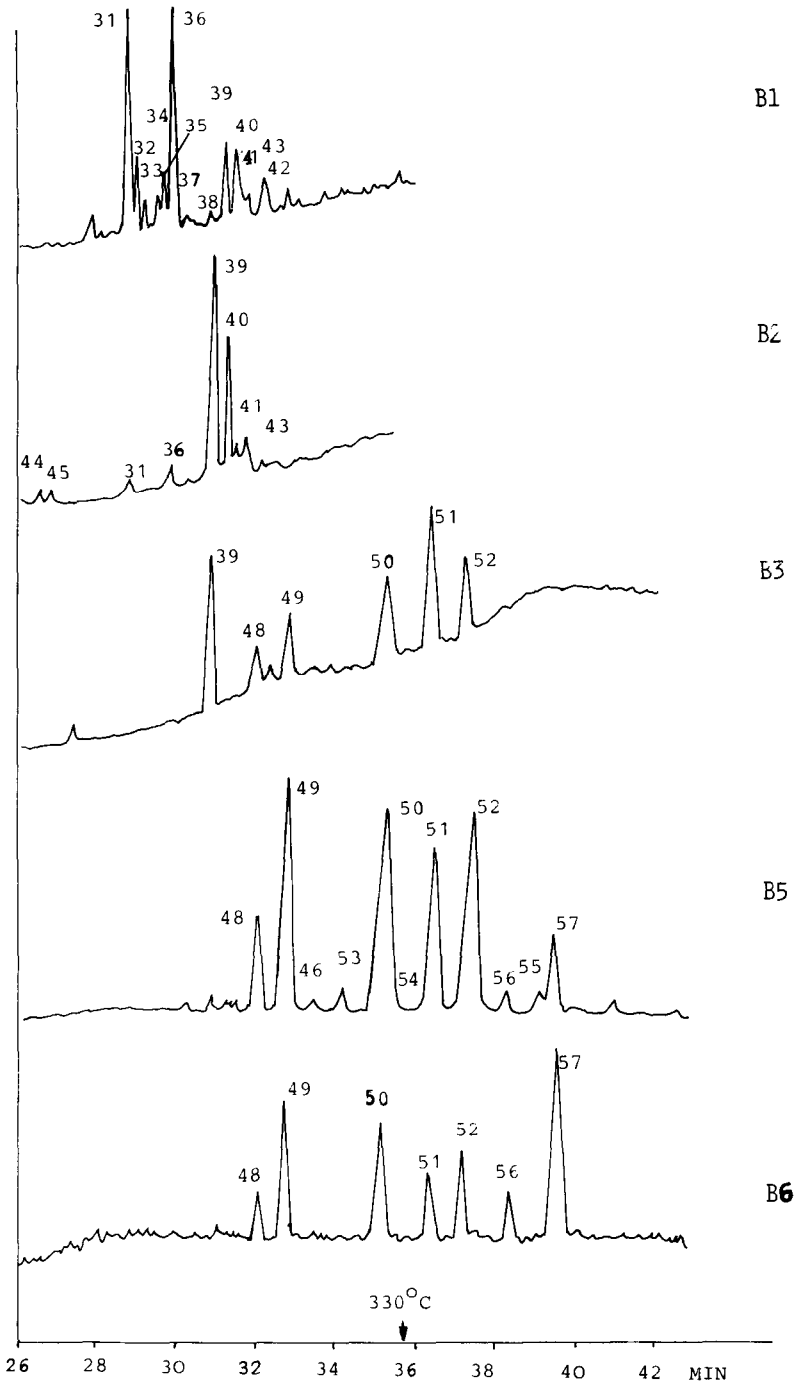| No.	MW	Most significant ions*	Structure	Reference
29	374	109 (40), 155 (50), 156 (60), 169 (70), 170 (100), 374 (20)		
30	374	109 (40), 155 (50), 156 (60), 169 (70), 170 (100), 374 (20)		
31	376	See Fig. 10		
32	374	155 (60), 156 (50), 169 (40), 170 (100), 221 (45), 374 (25)		
33	376 + 374	Unresolved peak		
34	376	145 (100), 158 (40), 172 (20), 361 (40), 376 (30)		
35	376	145 (100), 158 (90), 172 (10), 361 (10), 376 (20)		
36	378	See Fig. 9		
37	376 + 374	Unresolved peak		
38	376	145 (100), 157 (15), 376 (10)		
39	342	218 (30), 231 (25), 342 (100)	XIII	9
40	342	243 (20), 257 (100), 299 (10), 342 (75)	XIV	28
41	328	229 (45), 299 (100), 313 (70), 328 (80)		
42	374	195 (100), 221 (30), 374 (20)		
43	378	145 (100), 157 (25), 172 (20), 378 (1)		
44	356	169 (100), 187 (20), 356 (15)	XVI	10
45	356	145 (20), 169 (100), 187 (20), 356 (15)	XVII	10
46	310	133 (25), 265 (45), 266 (55), 281 (100), 310 (40)	Isomer of peak 50	28
47	342	228 (20), 243 (35), 257 (80), 299 (20), 342 (100)	XVIII	28
48	310	254 (100), 265 (20), 310 (90),	XIX	28
49	310	239 (15), 254 (100), 265 (15), 295 (10), 310 (90)	XX	28
50	310	133 (25), 265 (55), 266 (50), 281 (100), 310 (40)	XXI	28
51	324	239 (10), 252 (20), 265 (30), 279 (35), 294 (20), 309 (95), 324 (100)	XXII	28
52	324	252 (25), 268 (100), 324 (95)	XXIII	28
53	322	292 (60), 307 (100), 322 (80)	XXIV	9
54	322	292 (60), 307 (100), 322 (75)	XXIV	9
55	324	239 (20), 252 (20), 266 (25), 279 (40), 309 (80), 324 (100)	XV	28
56	320	289 (40), 290 (25), 305 (60), 320 (100)	Trimethylpicene	
57	322	276 (10), 292 (30), 307 (55), 322 (100)	XXIV	

* The values in parentheses are the relative abundances.

The source of the abundant ion at m/z 145 in the mass spectra of these compounds is not clear; however, it should be characteristic for a certain type of monoaromatic hydrocarbon, since this ion was also highly abundant in mass spectra of two monoaromatic pentacyclic hydrocarbons isolated from mineral oil[26]. Not only this ion, but also those at m/z 145 (100), 157 (10–20), 171 or 172 (5–10) (abundances in parentheses) should be characteristic for certain monoaromatic cyclic compounds.
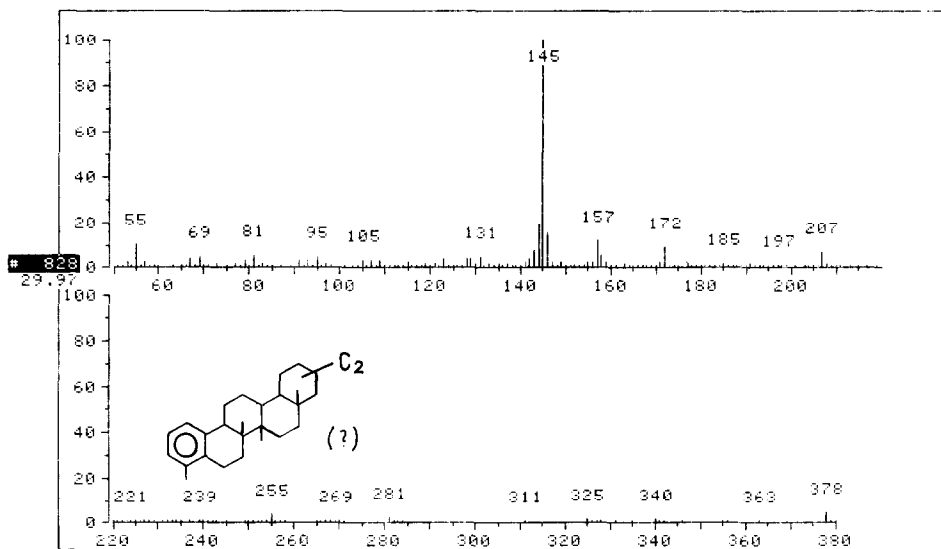
Fig. 9. Mass spectrum of peak 36.

The occurrence of this triplet in a mass spectrum should correspond to a certain molecular configuration. It is present in the mass spectrum of peak 37 (see Fig. 9) and also in that of a tetramethyl-octahydrophenanthrene compound, 13-methyl-podocapra-8,11,13-triene[19]. Greiner *et al.*[27], while investigating a sediment extract, found the same triplet in the mass spectrum of a monoaromatic hopane, but it was missing from the spectrum of the authentic, synthesized compound. We believe that
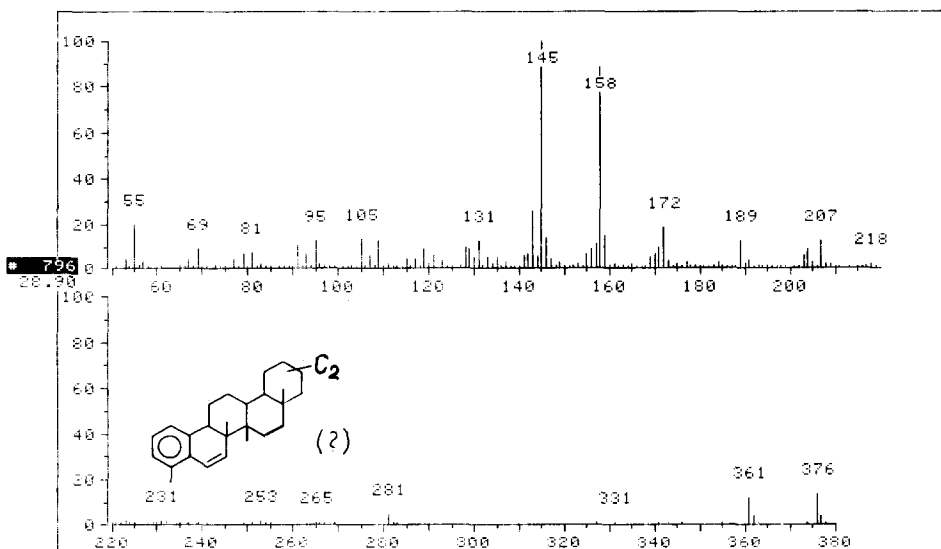
Fig. 10. Mass spectrum of peak 31.

the ions at m/z 145, 157, 172 originate from the mass spectrum of a coeluting mono-aromatic compound with structure similar to that of peak 36.

A possible structure of compound 36 is given in Fig. 9. This is based on the belief that this monoaromatic pentacyclic hydrocarbon has a six membered E ring, since the mass spectrum of the synthesized monoaromatic hopane (pentacyclic tri-terpane with five membered E ring) has a significantly different mass spectrum[27]. Among the major constituents of the aromatic fraction (in subfractions B3–B6), we found aromatized species supposed to be intermediates during the diagenetic aro-matization of oleane (III) and ursane (II) type triterpenoids, compound 36 is also considered to have a six membered E ring.

Compound 31 having a molecular mass of 376 (Fig. 10) is supposed to have one aromatic ring and one double bond, (an unsaturated analogue of compound 36), the double bond position being unknown. Several isomers of this compound were also detected in subfraction B1 (see Fig. 8 and Table II) and had similar mass spectra. Further, in this subfraction we found several peaks having a molecular mass of 374. These compounds are thought to be diaromatic pentacyclic hydrocarbons.

Subfraction B2 (51–75 ml eluate). This contains three unresolved main com-pounds, with molecular masses of 342 and one compound with molecular mass of 328. These pentacyclic hydrocarbons contain three aromatic rings. Compounds 39 and 40 have been found in sediments and brown coals and are considered to be intermediates during aromatization reactions of triterpenoids[2,9,28].

Subfractions B3–B6 (76–175 ml eluate). These contain compounds with three to five aromatic rings. Subfraction B4 (100–125 ml eluate, not indicated in Fig. 8) had the same composition as B5 except that no trimethyldihydropicene (peak 57) was eluted.

Peaks 53 and 54 are trimethyldihydropicene isomers. Their mass spectra are similar to that of the compound described by Chaffee and Johns[9]. A more abundant peak (57), however, shows a slightly different spectrum in spite of having the same molecular mass. Trimethylpicene (peak 56) is the only fully aromatized pentacyclic compound with a six membered E ring detected in this sample.

Retention indices of major peaks. Combining the data obtained from both GC retention and MS strongly increases the accuracy of identification. In the literature, however, no retention data are available for pentacyclic hydroaromatic compounds. Therefore Kováts retention indices were determined for the major compounds in the aromatic fraction (Table III). The unusually high temperature dependence of the Kováts indices is caused by the polycyclic structure; similar dependences were ob-served for tri- and tetracyclic diterpenes ($\delta I/\delta T$ = 1–1.5)[29].

The origin of hydroaromatic compounds in the sample. The pentacyclic hydroar-omatic compounds identified are intermediates in the diagenetic aromatization of triterpenoids[4,9,27,28,30]. The aromatization of triterpenoids with a five membered E ring begins with ring D and continues through ring A[27,28,30]. Compounds 41 and 50 are intermediates in this process.

The aromatization pathway for triterpenoids having a six membered E ring has also been described[27,28]. It is supposed that the dehydrogenation starts on ring A and is accompanied by loss of a methyl group. An oxigenous functionality (in position 3 on ring A) is claimed to be necessary to start the aromatization. The findings of Chaffee and Johns[9] for an Australian brown coal sample support the

TABLE III

KOVÁTS RETENTION INDICES FOR SELECTED HYDROAROMATIC COMPOUNDS

The isothermal retention indices were determined at several different temperatures between 220 and 310°C; the data in the table were obtained from the computed linear regression curve.

	Peak number	Name	Structure	$I_{OV\text{-}1}^{250}$	$\dfrac{\delta I}{\delta T}$
1	31	Hexamethyl-tetradecahydropicene	See Fig. 10	2995	2.2
2	36	Hexamethyl-hexadecahydropicene	See Fig. 9	3031	2.2
3	48	1,2-Dimethyl-tetrahydropicene	XIX	3113	2.3
4	39	Tetramethyl-octahydropicene	XVIII	3117	2.3
5	49	1,1-Dimethyl-tetrahydropicene	XX	3142	2.0
6	50	1,2-Cyclopenta-1'-ethyl-7-methylchrysene	XXI	3211	2.5
7	51	1,2,9-Trimethyl-tetrahydropicene	XXII	3255	2.5
8	52	1,1,9-Trimethyl-tetrahydropicene	XXIII	3277	2.3

aromatization pathway postulated for triterpenoids having a six membered E ring, since they found several aromatic compounds with additional unsaturation fitting into the set of aromatization reactions.

The hydropicene compounds detected in fossils and sediments possess three, four or five aromatic rings[2,4,9,27,28,30]. Monoaromatic pentacyclic compounds (peaks 36, 43, 31 and its isomers) seem to represent the products of the very first steps in the aromatization pathway of triterpenoids with a six membered E ring. Although the existence of these compounds fits the postulated aromatization pathway, there is no indication in the literature that they have been detected in the geosphere. On the other hand, we have also found these compounds in several other coals[31].

Two isomers of ring A non-methylated tetraaromatic pentacyclic hydrocarbons (peaks 48 and 49) were found in amounts similar to those of the ring A methylated analogues. These compounds could be formed either by a mechanism in which both the original ring A methyl groups are eliminated in the first step of aromatization, or by methyl loss of an aromatized intermediate. The fact that we did not find ring A non-methylated triaromatic intermediates suggests that the latter mechanism took place. Fig. 11 shows an hypothetical diagenetic aromatization scheme according to which major aromatic compounds could be formed in this coal sample.

In another mechanism, tetracyclic compounds are produced during aromatization of triterpenoids as a consequence of the cleavage of ring A[32]. Intermediates in this set of reactions (substituted hydrochrysene compounds) were found only as trace amounts.

Recently Chaffee et al.[10] reported several new tetracyclic aromatic compounds detected in a brown coal sample, which are thought to be formed from triterpenoids by a process involving C-ring cleavage. These compounds have a very abundant ion at m/z 169 as the base peak, corresponding to a trimethylnaphthalene fragment. Compounds 44 and 45 are triaromatic compounds belonging to this series of tetracyclic compounds.

peak 36 (or 43)   peak 31   peak 39
                                   or an isomer

peak 57 (or 51 or 52)   peak 51   detected as trace

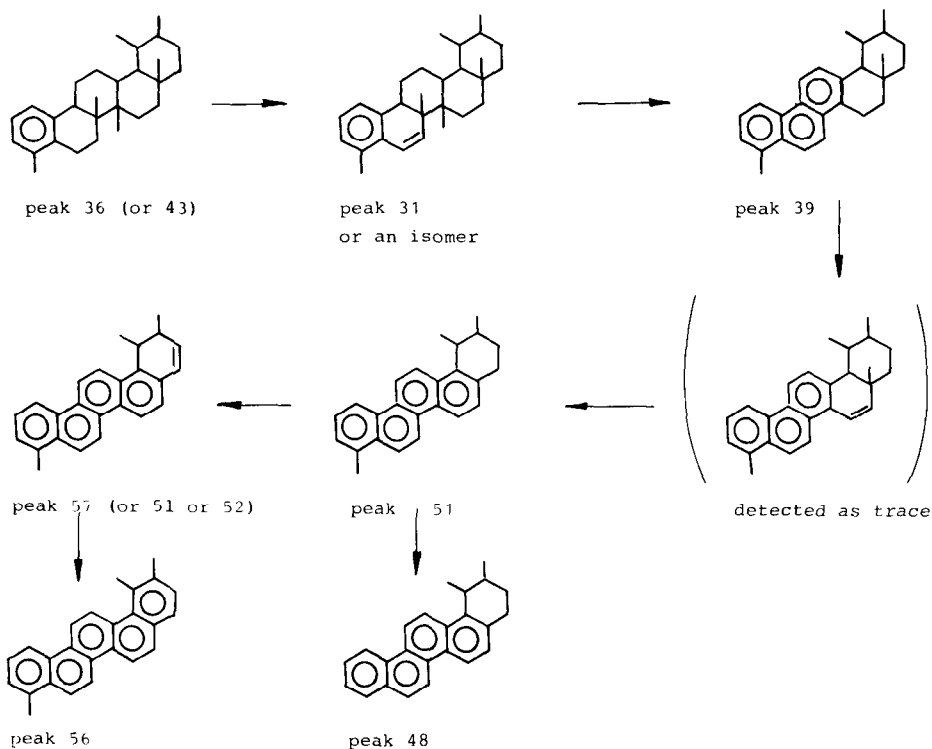peak 56   peak 48

Fig. 11. Hypothetical pathway for formation of the picene derivatives in the sample.

CONCLUSIONS

(1) Major hydrocarbon constituents of a sub-bituminous coal extract were (at least tentatively) identified by computerized GC–MS.

(2) Fractions enriched in components with one and two, three and four aromatic rings were prepared by a simple (open-column chromatographic) procedure.

(3) Retention indices of several important pentacyclic hydroaromatic compounds were measured.

(4) Two monoaromatic pentacyclic hydrocarbons were detected in high amounts. These compounds are presumably intermediates in the diagenetic aromatization pathway of triterpenoids having a six membered E ring. Several isomers of these compounds are also present in the sample.

(5) A hypothetical diagenetic aromatization pathway was suggested to correlate the hydroaromatic triterpane-derived compounds having a six membered E ring. Quantitative data not presented here will certainly yield a more elaborate scheme. These results will be published elsewhere.

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