Journal of Chromatography, 446 (1988) 87–102
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 1336

GAS CHROMATOGRAPHIC–MASS SPECTROMETRIC STUDY OF α-PHYLLOCLADANE DEHYDROGENATION

G. ALEXANDER* and I. HAZAI
Research Laboratory for Inorganic Chemistry, Hungarian Academy of Sciences, Budaorsi ut 45, H-1112 Budapest (Hungary)
and
J. GRIMALT and J. ALBAIGES
Department of Environmental Chemistry, CID-CSIC, Jorge Girona Salgado, 18-26, 08034-Barcelona (Spain)

SUMMARY

Dehydrogenation of α-phyllocladane with several reagents, namely selenium, sulphur and copper sulphide is reported, and provides some insight into this reaction of geochemical importance. The resulting hydrocarbon mixtures were analysed by gas chromatography–mass spectrometry and most of the reaction products were identified, some for the first time. The use of a "reverse search strategy" made possible the identification of minor and/or coeluting components. The semiquantitative interpretation of the reaction mixtures provides an adequate account of the reaction pathway.

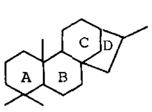
INTRODUCTION

α-Phyllocladane (structure I), is a tetracyclic diterpane commonly found in resin and supportive tissues of a number of species belonging to the Podocarpaceae family of conifers[1]. Phyllocladanes have been found in high concentrations among hydrocarbons of Italian[2], Czechoslovakian[3], German[4,5] and Hungarian[6] coals; they are also present in Australian coals[7]. In addition, they have been reported in some sediments[8] and crude oils[7].

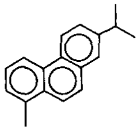
Despite these occurrences, very little is known about their transformation in the geosphere. The isomerization of chiral centres has been recognized[7], similar to that which occurs in triterpanes, *e.g.*, ref. 9. Very recently, however, during an investigation of a set of Hungarian brown coal samples, we concluded that under certain conditions α-phyllocladane is converted into the aromatic hydrocarbon retene (structure II)[6]. The proposed hypothetical reaction scheme contained also dehydroabietane (structure III) and simonellite (structure IV) as partially aromatized intermediate products.

Evidence in support of α-phyllocladane as a precursor for retene (in addition to the well established abietane compounds) is provided by Soltys[10] who as early as

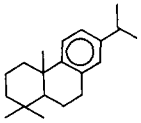
0021-9673/88/$03.50



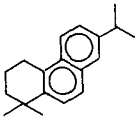
I



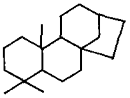
II



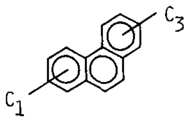
III



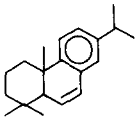
IV



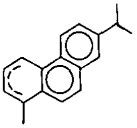
V



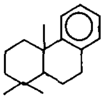
VI



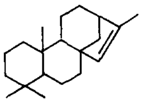
VII



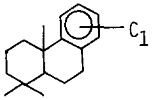
VIII



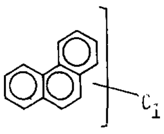
IX



X



XI



XII

1929 found that under laboratory conditions dehydrogenation of phyllocladane (as it was then called, "iosene") yields retene. However, the details of the reactions were not investigated and there is some doubt about the significance of this particular experiment for interpreting the processes occurring under natural conditions.

In a previous paper[6] we reported some preliminary results of laboratory experiments on the aromatization of α-phyllocladane. In this study the reaction with various dehydrogenating agents was investigated. The identification of major and minor reaction products was attempted relying upon various chromatographic and mass spectrometric techniques. A search for molecules considered as intermediates in the hypothetical aromatization pathway of α-phyllocladane was also successful. Our aim was to compare these reaction products with similar compounds found in various coal extracts, and to construct an acceptable geochemical reaction pathway for the aromatization of phyllocladane.

EXPERIMENTAL

Dehydrogenation reactions

Materials. α-Phyllocladane in pure, crystalline form was prepared from a Slovakian lignite using the method described in ref. 3. It contained the β-isomer as well as a series of C_{25}–C_{35} *n*-alkanes as impurities all in a concentration of about 30–70 μg/g; however, it was used without any further purification.

Chemicals. Selenium (Alfa-Ventron, Rotterdam, The Netherlands), sulphur (Reanal, Budapest, Hungary) and ferric chloride (Reanal) were used as received. Calcium carbonate (Reanal) was dried at 110°C before use. Copper sulphide was prepared by precipitation from a 5% aqueous copper sulphate solution with hydrogen sulphide gas, followed by filtration, washing and drying.

Procedure. The reactions were carried out in sealed tubes (15 mm × 2.0 mm I.D.). α-Phyllocladane (*ca.* 0.5 mg) and the reagent (*ca.* 2 mg) were placed into a vial (one end sealed) which was then hermetically sealed using a small oxygen flame while the solids were kept cool (under 35°C).

Thermal treatments were carried out in a small oven. The accuracy of temperature control was ±3°C.

After the reaction the vials were carefully opened (considerable pressure could be developed, *e.g.*, by the hydrogen sulphide gas formed), the contents dissolved in 50 μl of benzene (dissolution was completed in an ultrasonic bath) and then transferred to a well capped sample vial.

A volume of 2 μl was injected for gas chromatography (GC), and 5–10 μl for GC–mass spectrometric (MS) analysis.

Thin-layer chromatography (TLC)

In these experiments, DC-Alufolien Kieselgel 60 (E. Merck, Darmstadt, F.R.G.) chromatosheets were used. Before use the chromatosheets were developed with benzene and dried at 105°C. For separation of the reaction mixture, benzene was used as an eluent. After development and drying, the coloured spots were scraped off and then extracted with 100 μl of benzene. The solutions obtained were further investigated by GC–MS.

Gas chromatography–mass spectrometry

GC–MS analyses were conducted using a computerized system (Hewlett-Packard 5985A). Spectra were obtained in the electron-impact mode with an electron energy of 70 eV. The compounds were identified by using the Wiley Spectral Library and by comparison with published spectra, *e.g.*, ref. 11.

For identification of minor peaks the "reverse search" strategy was applied. It was performed by a computer program, presented elsewhere[12]. Briefly, the program compares the normalized intensities of selected fragment ions to user-defined values (using the absolute difference criteria) for a set of subsequent spectra in a chromatogram. If the match for a given scan is lower than an user-defined threshold, the result of the search is considered positive, the abundances in the chromatogram for the preselected fragment ions are summarized and stored as "summarized abundances" of the scan, otherwise the abundances are rejected. When the procedure has been completed the "plot of summarized abundances" and the total ion abundances are displayed on the screen, forming two chromatograms. Peaks on the "plot of summarized abundances" will then correspond to the compound(s) exhibiting the defined normalized intensities of the preselected mass fragments.

RESULTS AND DISCUSSION

As mentioned above, isomerization and aromatization are likely to be the main transformation reactions of α-phyllocladane in the geosphere. Isomerization at position 16, *i.e.*, conversion of 16α(H)- to 16β(H)-phyllocladane, is now well substantiated by field and laboratory data[6,7]. In this set of experiments we found that an equilibrium was reached with a (β) to (α + β) ratio of 0.70 at 370°C, a figure similar to that found earlier[6,7].

On the contrary, aromatization is less well documented. Therefore, our aim was a detailed investigation of this reaction and a search for geochemically significant dehydrogenating agents.

Selection of reagents and reaction conditions

As expected[10], selenium produced, upon reaction at 370°C for 4 h, an almost colourless oil rich in retene and intermediate products, which were identified by GC–MS (see below). The reaction conditions were selected after optimization.

An alternative candidate in this reaction was sulphur which is often applied as an agent in dehydrogenation reactions[13] and it has also been used in laboratory simulation studies of steroid aromatization, *e.g.*, ref. 14. In spite of the fact that sulphur may cause side reactions during aromatization[13], this reagent was the first choice because it frequently occurs in geological materials.

The results, however, were disappointing. At low temperatures (up to 180°C, and a reaction time of 16 h) no reaction took place, while at considerably higher temperatures ($\geqslant$250°C) an insoluble black residue resulted. At the "optimum" temperature of 230°C however a few reaction products (among them retene) were found (see below).

Similar black residues were found in the reaction mixture with a series of agents (among them ferric chloride) with or without calcium carbonate added, which were tried because of their possible natural occurrence.

If one looks at the normal redox potentials of these dehydrogenating reagents (see Table I[15]) even where the data correspond to room temperature, it is clear that sulphur as well as other systems are too oxidative, yielding black soot in the reaction.

A compound, similar in dehydrogenation strength to selenium, but of higher geochemical relevance is copper sulphide. The reaction with α-phyllocladane at 370°C for 4 h produced an oily mixture containing retene and different intermediates, which were also identified in the GC–MS analysis (see below).

TABLE I

REDOX REACTIONS WITH STANDARD ELECTRODE POTENTIALS[15]

Reaction	E^0_{25} *(mV)*
$Fe^{3+} + e \rightarrow Fe^{2+}$	+771
chinon + $2H^+$ + 2e → hydrochinon	+699
$S + 2H^+ + 2e \rightarrow H_2S$	+141
$CuS + 2H^+ + 2e \rightarrow Cu + H_2S$	−259
$Se + 2H^+\ 2e \rightarrow H_2Se$	−360

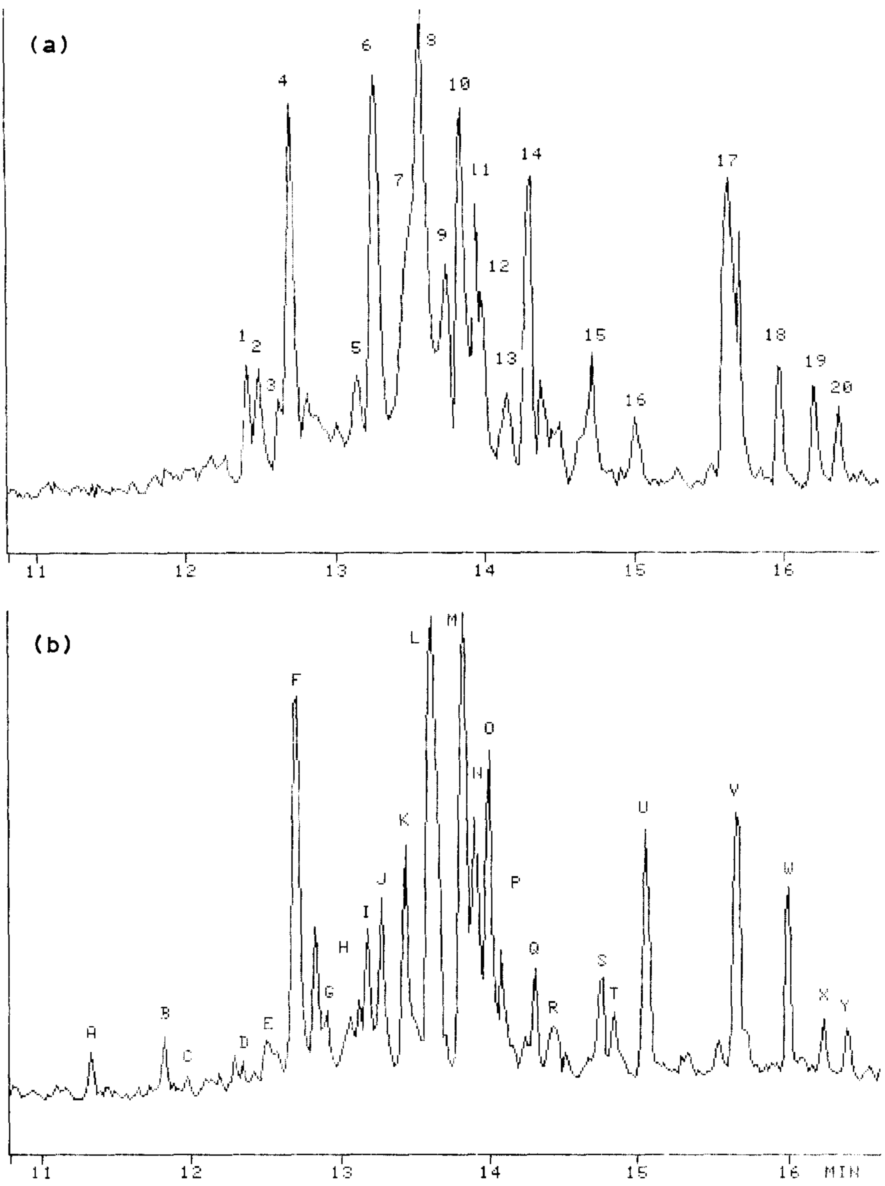


Fig. 1. Sections of computer-reconstructed total ion chromatograms of reaction mixtures obtained with (a) selenium and (b) copper sulphide. Column: 20 m × 0.25 mm, SE-54 coated fused-silica capillary. Injector temperature: 270°C. Oven temperature: 140°C, 3 min isothermal, then programmed to 280°C at a rate of 10°C/min. Peak identifications: see Table II.

Peak identification in reaction mixtures

Selenium. A section of the total ion chromatogram of this mixture is shown in Fig. 1a. The components identified are summarized in Table II. Several peaks could be identified through their retention times and close similarity with published mass

TABLE II

COMPOUNDS IDENTIFIED IN REACTION MIXTURES "Se" AND "CuS"

Peak notation		*Mol. mass*	*Composition*	*Name*	*Structure**	*Identification***
Fig. 1a ("Se")	*Fig. 1b ("CuS")*					
	A	228	$C_{17}H_{24}$		IX	i
	B	210	$C_{16}H_{18}$	C_2 Tetrahydrophenanthrene		i
	D	242	$C_{18}H_{26}$	13-Methylpodocarpatriene	XI	i
1		260	$C_{19}H_{32}$			i
2		276	$C_{20}H_{36}$			i
	E	242	$C_{18}H_{26}$	13-Methylpodocarpatriene (isomer of D)	XI	i
3		272	$C_{20}H_{32}$			i
4	F	192	$C_{15}H_{12}$	Methylphanthrene	XII	p
	G	272	$C_{20}H_{32}$			i
	H	272	$C_{20}H_{32}$	iso-Phyllocladene	X	p (ref. 11, No. 147)
5	I	260	$C_{19}H_{32}$		V	p
6	J	274	$C_{20}H_{34}$			i
		254	$C_{19}H_{26}$			
7	K	256	$C_{19}H_{28}$			i
8	L	274	$C_{20}H_{34}$	β-Phyllocladane	I	Standard
9		274	$C_{20}H_{34}$			i
10	M	274	$C_{20}H_{34}$	α-Phyllocladane	I	Standard
11		274	$C_{20}H_{34}$			i
12	N	206	$C_{16}H_{14}$	C_2 Phenanthrene		p
	O	206	$C_{16}H_{14}$	C_2 Phenanthrene		p
	(O)	270	$C_{20}H_{30}$	Dehydroabietane	III	r
13		220	$C_{17}H_{16}$	C_3 Phenanthrene		p
		236	$C_{18}H_{20}$		VIII	r
		268	$C_{20}H_{28}$		VII	r
	P	206	$C_{16}H_{14}$	C_2 Phenanthrene		p
14	Q	274	$C_{20}H_{34}$			i
	R	206	$C_{16}H_{14}$	C_2 Phenanthrene		p
15	S	252	$C_{19}H_{24}$	Simonellite	IV	p (ref. 11, No. 129)
	T	220	$C_{17}H_{16}$	C_3 Phenanthrene		p
16	U	220	$C_{17}H_{16}$	C_3 Phenanthrene		p
17	V	234	$C_{18}H_{18}$	Retene	II	p (ref. 11, No. 130)
18	W	234	$C_{18}H_{18}$	Methyl-*n*-propylphenanthrene	VI	i
19	X	234	$C_{18}H_{18}$			i
20	Y	234	$C_{18}H_{18}$			i

* For structures see formulae in Introduction.

** Peak identification is based on: p = published spectrum; r = reversed search; i = interpretation of mass spectrum; see text.

spectra (peaks 4, 8, 10, 12, 15–17, 19, 20). However, in several cases further structural assignments were also possible based on the interpretation of mass spectra:

Peak 1 represents a compound with a molecular mass of 260 ($C_{19}H_{32}$). Taking into consideration its retention time and the molecular mass, it seems to be a tricyclic hydrocarbon with one unsaturation. In its mass spectrum (Fig. 2a) there is an intense ion at *m/z* 191 which is characteristic of many tricyclic terpanes[16–18]. Therefore the compound under scrutiny seems to be an unsaturated tricyclic diterpane, since ions at *m/z*) 121, 135 (instead of 123 and 137, characteristic for tricyclic diterpanes[11]) are present in the mass spectrum.

Peak 2 is a compound with a composition of $C_{20}H_{36}$ exhibiting fragments characteristic of tricyclic diterpanes in the mass spectrum (see Fig. 2b). The ions at *m/z* 233, 261 and 276 suggest the presence of an isopropyl side chain. The compound, however, is not identical to the reported $C_{20}H_{36}$ diterpanes[8] either with abietane or

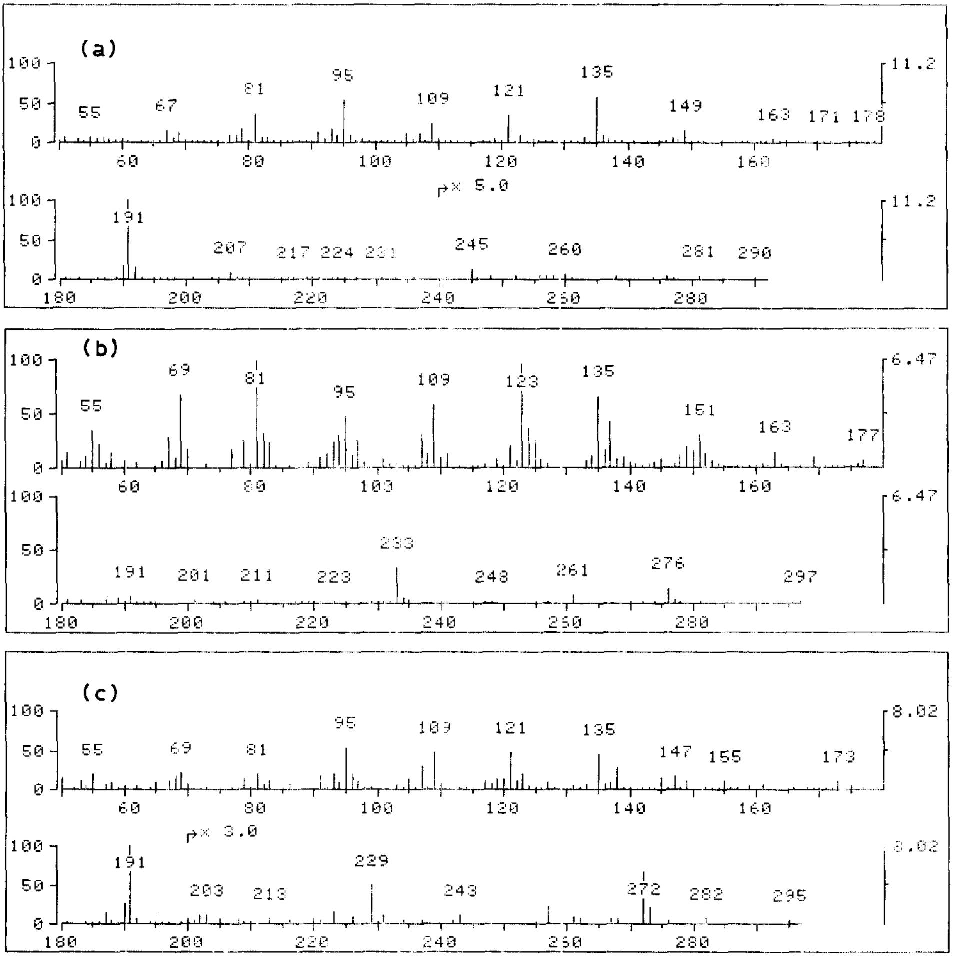


Fig. 2. Mass spectra (a) of peak 1, (b) of peak 2 and (c) of peak 3. For peak numbers see Fig. 1a.

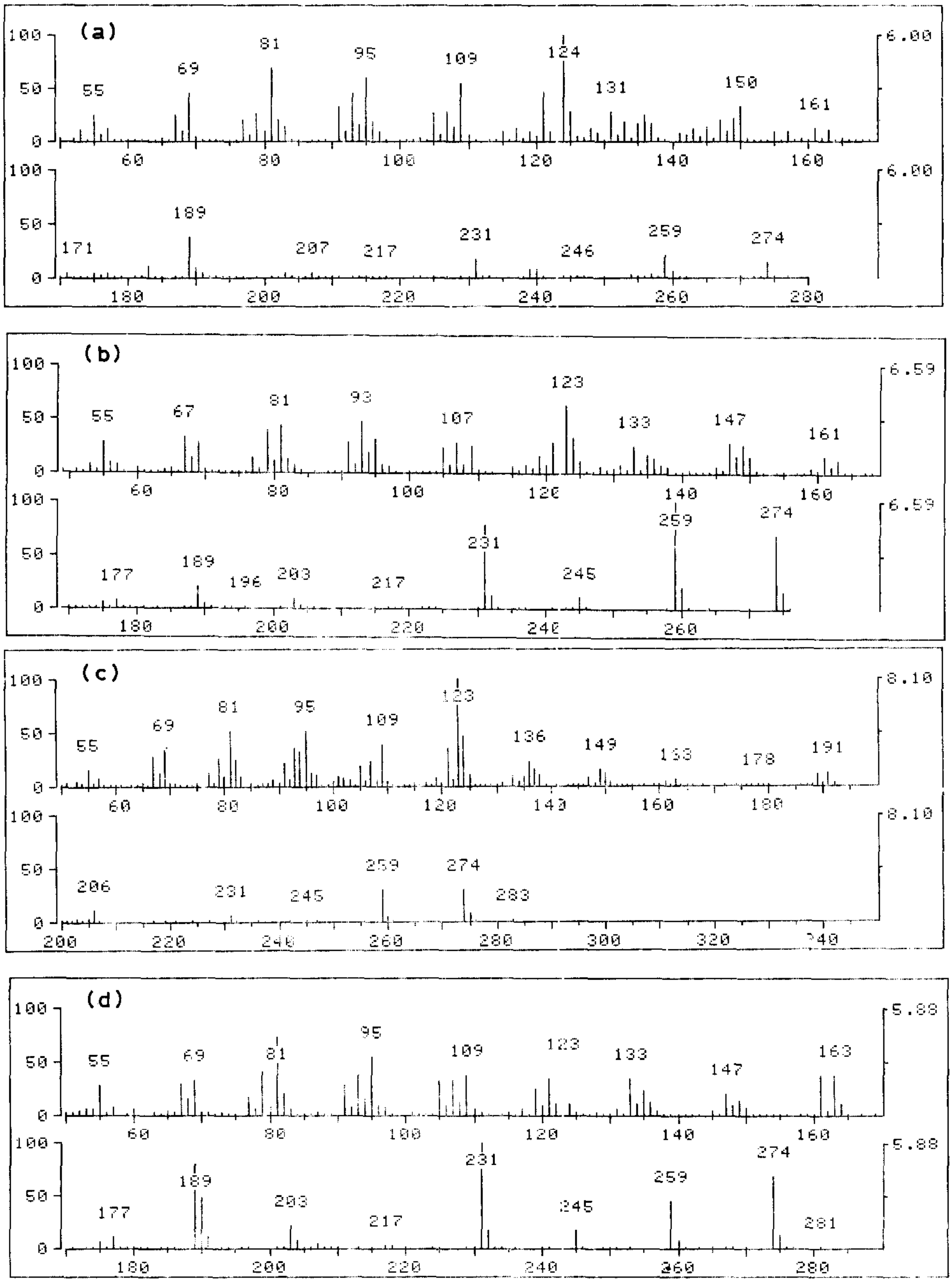


Fig. 3. Mass spectra of $C_{20}H_{34}$ compounds (other than phyllocladanes). (a) Peak 6, (b) peak 9, (c) peak 11 and (d) peak 14. For peak numbers see Fig. 1a.

pimarane structure because of the absence of intense ions at *m*/*z* 163 and 191.

Peak 3 is a $C_{20}H_{32}$ component. In the mass spectrum (see Fig. 2c) an ion at *m*/*z* 191 is exhibited. The presence of ions at *m*/*z* 229, 243, 257 and 272 leads us to suppose that this constituent is a tricyclic diterpane with two unsaturations in the rings and none in the side chain.

In peak 5 at least two compounds are eluted. One of them possesses a mass spectrum strongly resembling that of a compound found in petroleum by Noble *et al.*[19] and tentatively identified as a 17-nor-tetracyclic diterpane ($C_{19}H_{32}$) structure V); *i.e.*, in our case it is a phyllocladane demethylated in ring D.

Peaks 6, 9, 11 and 14 correspond to $C_{20}H_{34}$ compounds (formally isomers of phyllocladane). Their mass spectra are given in Fig. 3. They contain significant ions characteristic for tetracyclic diterpanes (*m*/*z* 123, 149, 189, 231, 259, 274)[7]; the abundances, however, differ significantly from the published ones. It should be noted that in the mass spectrum of peak 6 the base peak is at *m*/*z* 124 (instead of *m*/*z* 123). This is a clear indication that it does not correspond to any of the known tetracyclic diterpanes, therefore it is supposed to be a monounsaturated tricyclic hydrocarbon. Peaks 9, 11 and 14 are probably also tricyclic hydrocarbons with one unsaturation, because monounsaturated C_6 tricyclic diterpanes (with the unsaturation in the ring system) are expected to exhibit the same fragments as the saturated tetracyclic ones[20]. However, the formation of isomers other than β-phyllocladane cannot be ruled out.

In Fig. 4 the mass spectrum of peak 7 is given. According to molecular mass it has the composition $C_{19}H_{28}$, *i.e.*, it seems to be a C_5 tricyclic compound with one aromatic ring. Compounds corresponding to this composition (19-norabietatriene and dehydroabietin) have been observed[21], however the published mass spectra are significantly different.

Peaks 17 (retene), 18–20 are C_4 phenanthrenes. Their mass spectra are given in Fig. 5. Peaks 19 and 20 have virtually the same spectrum as that of retene (peak 17), whereas peak 18 exhibits an ethyl scission indicating an *n*-propyl side chain

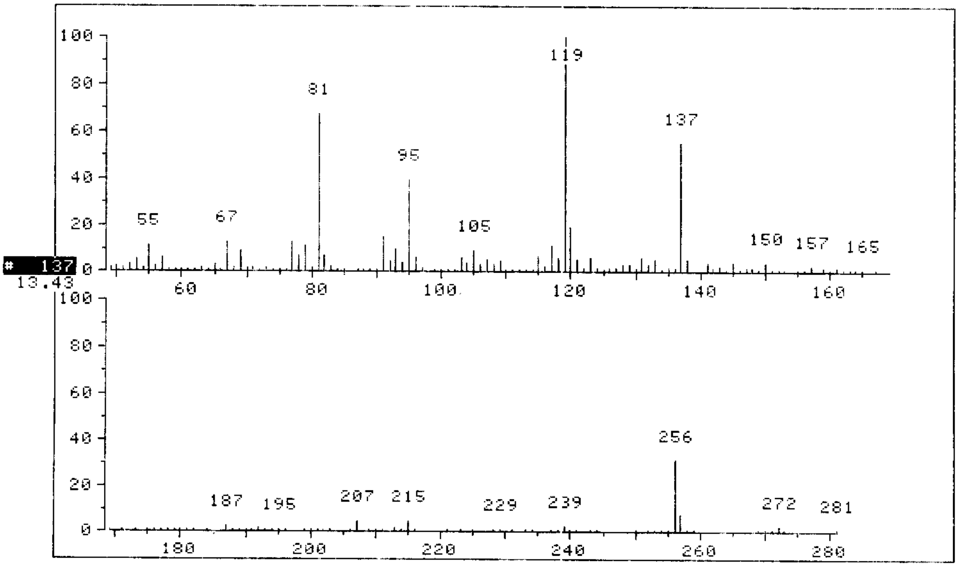


Fig. 4. Mass spectrum of peak 7. For peak number see Fig. 1a.

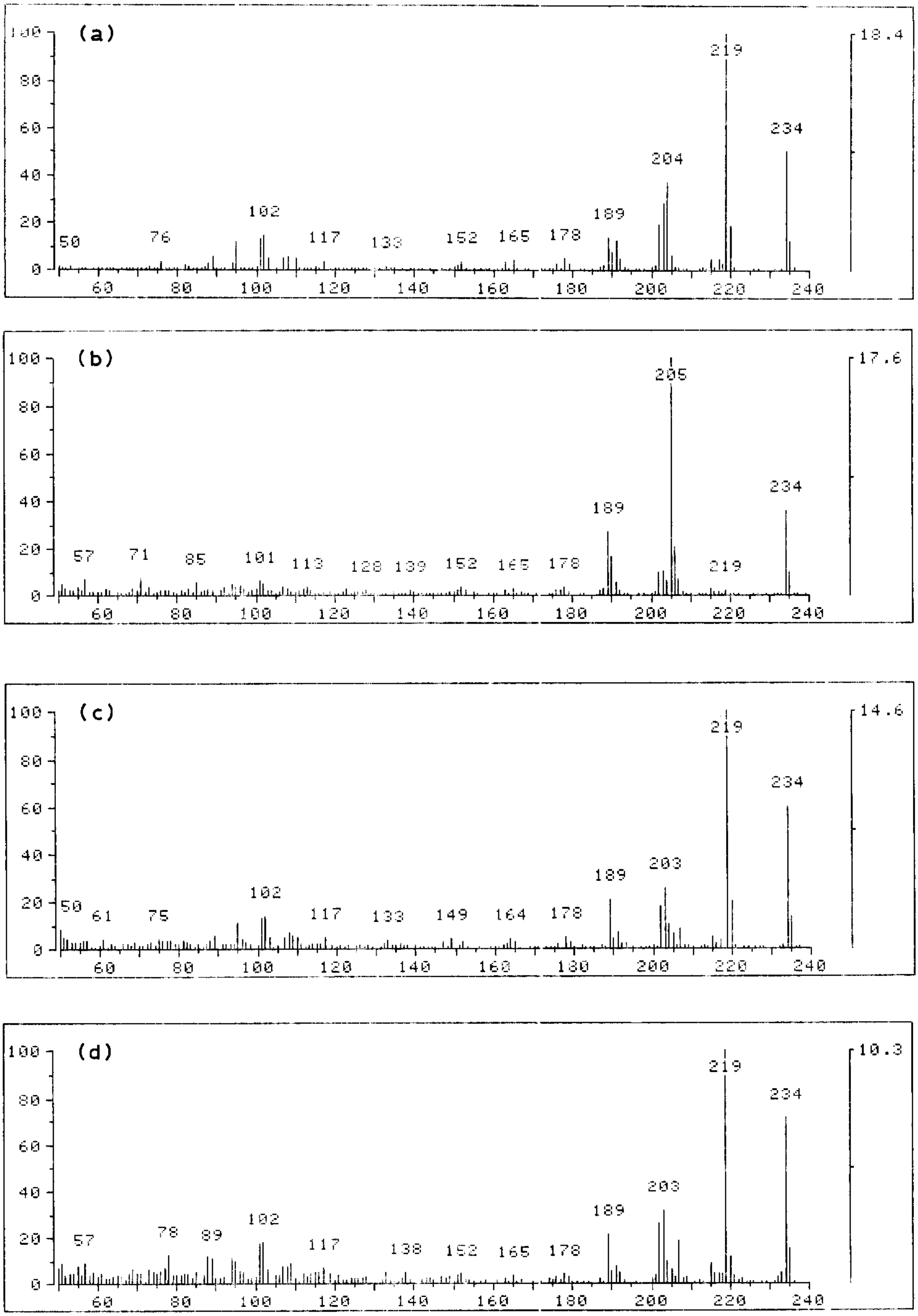


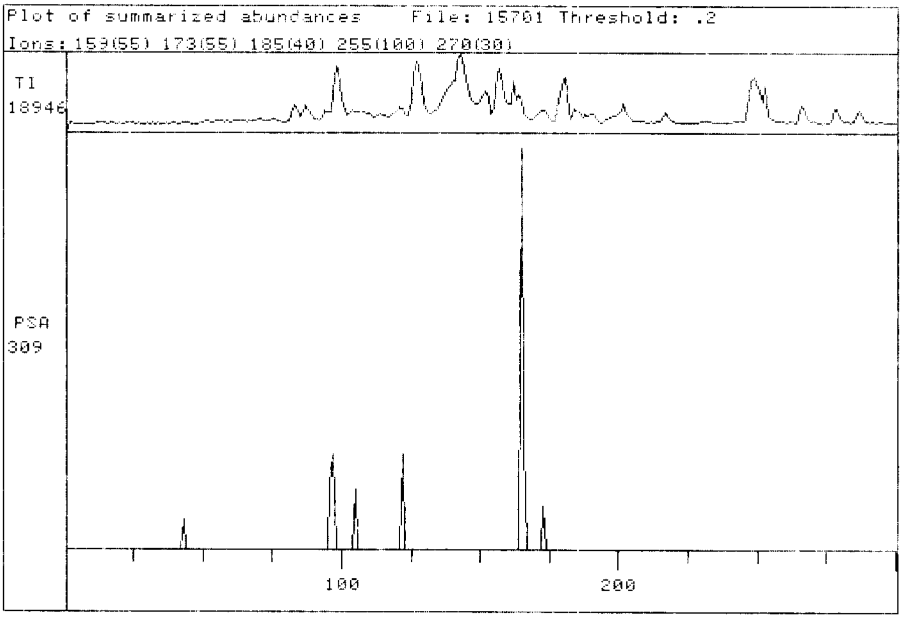
Fig. 5. Mass spectra of $C_{18}H_{18}$ compounds. (a) Peak 17 (retene) (b) peak 18, (c) peak 19 and (d) peak 20. For peak numbers see Fig. 1a.

(structure VI). The presence of the C_4 phenanthrenes other than retene is a clear indication of the migration of alkyl groups.

Major peaks in the chromatogram could be identified or interpreted by considering their mass spectra directly. However, application of the "reverse search strategy" enables the chromatographer to find and identify chromatographic peaks too small to interpret without this technique.

In the hypothetical aromatization pathway of phyllocladane[6] the major intermediates like simonellite and retene could be detected among the major components in the reaction mixture. In the literature, however, several other compounds have been published, together with mass spectra, which can be considered as intermediate in the reaction pathway mentioned above. Through "reverse search" a few of these could really be found among the minor peaks, which otherwise would have been masked by more abundant coeluting compounds, column bleeding or instrument background.

In Fig. 6 the result of a search for dehydroabietane ($C_{20}H_{30}$) (structure III) is given. The relatively abundant peak in the chromatogram of the "plot of summarized abundances" clearly shows that dehydroabietane could be positively found in spite of coelution with much more abundant species (C_2 phenanthrenes and a $C_{20}H_{34}$ compound).



```
Plot of summarized abundances    File: 15701 Threshold: .2
Ions: 159(55) 173(55) 185(40) 255(100) 270(30)
```

Fig. 6. Computer output of a search for dehydroabietane. In the heading of the output the user-defined significant fragment ions (with their intensities in parentheses taken from ref. 21) are displayed. The threshold chosen was 0.2. The threshold may be varied between 0 (perfect match) and 1 (perfect mismatch). The upper chromatogram (TI) is the reconstructed total ion chromatogram; the lower one (PSA) is the "plot of summarized abundances" obtained. For these chromatograms the highest abundances are also presented, *e.g.*, 309 for PSA. The chromatographic peak on the PSA trace between scans 164 and 166 indicates the elution of a compound producing the predetermined intensity ratios for the fragment ions investigated.

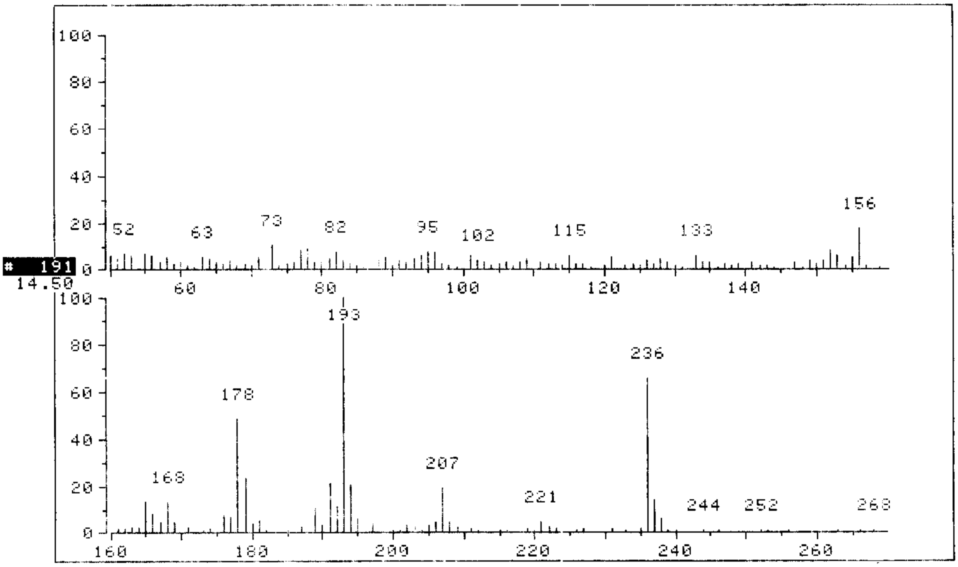


Fig. 7. Mass spectrum of a compound with composition $C_{18}H_{20}$ (structure VIII, see text).

In the same way, species possessing additional unsaturation besides aromatic rings could also be found. Recently a mass spectrum of a compound with molecular mass of 268 (corresponding to a composition of $C_{20}H_{28}$, structure VII) was published[22]. It contains abundant ions at *m/z* 156(20); 197(100), 253(30) and 268(90). Reverse search for similar compounds gave positive results (four peaks). These constituents are supposed to be monounsaturated analogues of dehydroabietane, *i.e.*, they contain four unsaturations. Compounds with identical mass spectra had been found in the aliphatic fraction of a Polish brown coal[23].

Compounds with composition $C_{18}H_{20}$ (molecular mass 236) also fit into the postulated reaction pathway (an intermediate between simonellite and retene). A reverse search for compounds with molecular ions of *m/z* 236 resulted in three compounds. The mass spectrum of the most abundant one is given in Fig. 7 (structure VIII; the position of the double bond in ring A is uncertain). It is interesting that virtually the same spectrum was obtained earlier by us for the aromatic fraction of a brown coal containing large amounts of retene[23].

Copper sulphide. In Fig. 1b a section of the reconstructed total ion chromatogram of this reaction mixture is given. It is qualitatively similar to the previous one, but several different compounds are also present in significant amounts (see Table II).

The compound eluted in peak A has a molecular mass of 228 corresponding to a composition of $C_{17}H_{24}$. The prominent peaks in the mass spectrum at *m/z* 117, 131, 143, 157 and 213 (see Fig. 8) suggest that it is a demethylated analogue of 13-methylpodocarpatriene (structure XI) and the methyl loss has occurred in the aromatized ring (see structure IX).

Peak B corresponds to a compound with a molecular mass of 210. The base

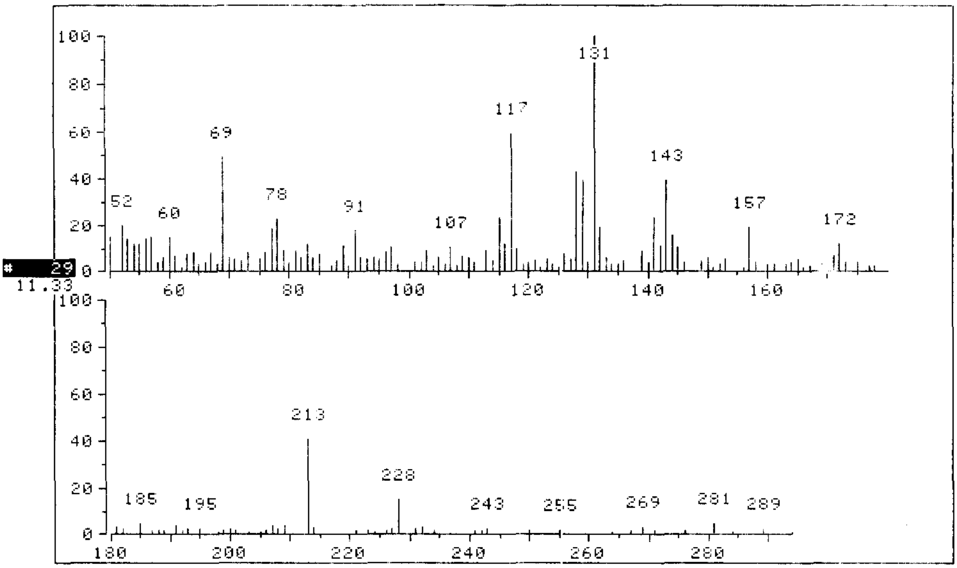


Fig. 8. Mass spectrum of peak A (demethylated analogue of 13-methylpodocarpatriene; structure IX).

peak in the mass spectrum is at *m/z* 195 indicating a loss of a methyl group. A possible structure is a C_2 tetrahydrophenanthrene.

Peaks D and E possess mass spectra strongly resembling that of 13-methylpodocarpatriene, seemingly corresponding to two isomers.

Peak H was identified as iso-phyllocladene (with unsaturation in ring D), based on a comparison with published mass spectral data[11].

In peak J two compounds are present: a $C_{20}H_{34}$ compound with the base peak at *m/z* 124 (identical to peak 6) and a $C_{19}H_{26}$ compound.

As mentioned above, retene (peaks 17 and V) and simonellite (peaks 15 and S) were observed in the mixtures. The monoaromatic constituent (dehydroabietane, structure III) was also found by a reverse search.

Sulphur. α-Phyllocladane, when heated with sulphur at 230°C for several hours, gave a mixture very much different from the previous two. Instead of the numerous and abundant reaction products, only a few could be found, namely: (1) β-phyllocladane, isomer of the original α-compound; (2) a compound with molecular mass of 272 ($C_{20}H_{32}$), similar in retention and mass spectrum to isophyllocladene (structure X) found also in the reaction mixture with selenium and copper sulphide; (3) both simonellite (IV) and retene (II) detected only with the sensitive method of "reverse search".

However, the main product was a compound eluted from the gas chromatograph in the high temperature region, and having a molecular mass of 364. Being of higher molecular mass than the starting material, it was suspected to contain sulphur.

In order to obtain more information about this reaction mixture, it was subjected to TLC. Two coloured spots were observed: a yellow one (R_F 0.80) and a pink one R_F 0.11). The yellow spot, after GC analysis, was found to be identical to the compound with molecular mass 364.

The yellow compound isolated was further investigated by high-resolution MS. The exact mass was found to be 364.1317, corresponding to a composition of $C_{23}H_{24}S_2$. Therefore it was concluded that under the given conditions sulphur was not merely acting as a dehydrogenating reagent, but also yielded sulphur-containing derivatives.

Interpretation of compositional data

Two dehydrogenating agents (out of the series tested) proved to be effective in phyllocladane aromatization, yielding very complex reaction mixtures. The total ion chromatograms (see Fig. 1) cannot be correctly quantified; it was not even our aim at this stage of the work. Nevertheless, the peak sizes and/or ion abundances indicate relative concentrations enabling some conclusions to be drawn.

Major components in the mixtures are as follows.

(1) α-Phyllocladane isomers. In this group, formation of β-phyllocladane is well understood and was expected[6,7]. However, there are a surprisingly high number of other $C_{20}H_{34}$ compounds, some of them probably the result of a simultaneous dehydrogenation, bearing therefore one double bond. This reflects again the fact that α-phyllocladane, however stable, is not the thermodynamically preferred isomer.

(2) Phenanthrene homologues and their isomers. Retene was the expected end product of aromatization. It was found, however, that the dealkylation process does not stop at retene but proceeds further, producing C_1–C_3 phenanthrenes, compounds found in coals more mature than lignite.

Small amounts of many intermediates in various stages of dealkylation and dehydrogenation were also found.

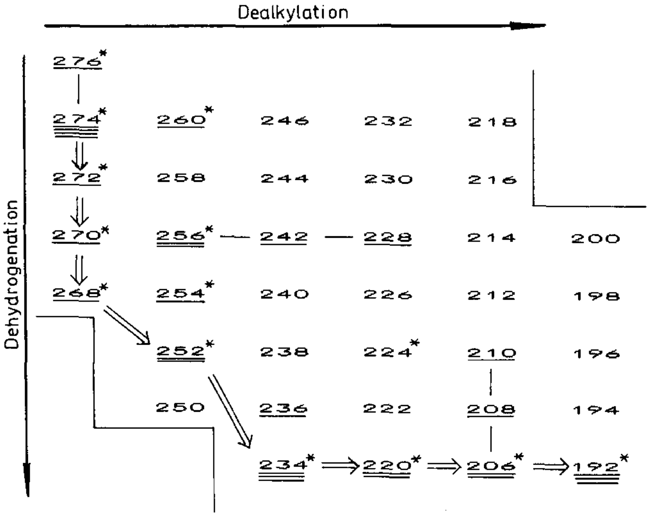


Fig. 9. Reaction pathway of phyllocladane to phenanthrene degradation, under natural and laboratory conditions. (Isomerism, *i.e.*, structural, configurational, stereo, is not shown.) Numbers in grid: molecular masses of all the theoretically possible dehydrogenation and dealkylation products. Mass differences: horizontally, 14; vertically, 2 (274, phyllocladane; 252, simonellite; 234, retene; 192, methylphenanthrene). Amounts in reaction mixtures: (—) small; (=) medium; (≡) large; (≣) very large. Asterisk indicates compound already described in the literature as occurring naturally.

All these compounds are plotted in Fig. 9 according to their molecular masses, irrespective of isomerism, on a grid of every theoretically possible intermediate from phyllocladane down to the fully aromatized and also dealkylated phenanthrene. On this plot are indicated the occurrence of each species in (i) natural samples, coals, sediments, oils, etc., and (ii) in our reaction mixtures, together with their relative amounts.

It should be noted that the widely accepted reaction route from diterpanes with an abietic skeleton, *e.g.*, abietic acid to retene[24,25] can also be followed on this plot. It differs from the phyllocladane to retene route only in the first step which means that the minor intermediate compounds, *e.g.*, the ones with unsaturation in their ring systems, found in our experiments are probably intermediates also in the former reaction pathway.

The relative concentrations given in Fig. 9 suggest that of the two main competitive reactions, *i.e.*, dealkylation and dehydrogenation, the latter seems to be faster. Besides, reactions of hydrogenation (note the presence of a $C_{20}H_{36}$ hydrocarbon) and transalkylation (witnessed by the presence of several C_4 phenanthrenes) also take place.

CONCLUSIONS

Most of the intermediate compounds in the dehydrogenation of α-phyllocladane have been identified, some of them for the first time. The compounds in the reaction mixtures studied are similar to those found in natural samples, *e.g.*, coals in various stages of maturity, thus validating the approach used in studying a geochemical reaction. Nevertheless, the reagent should be selected carefully. In this respect, copper sulphide has proved to be an adequate reagent for simulating the aromatization of tetracyclic diterpanes under laboratory conditions, so that strong evidence for the geochemical reaction under consideration has now been achieved. The semiquantitative interpretation of compositional data suggests that aromatization precedes the dealkylation process. The investigation of reaction kinetics will definitely provide a better understanding of this reaction and is the topic of our further work.

ACKNOWLEDGEMENTS

This work has been done within the framework of the Exchange Program between Consejo Superior de Investigaciones Cientificas (Spain) and Magyar Tudomanyos Akademia (Hungary). We are grateful to Dr. J. Krupčik (Bratislava, Czechoslovakia) for providing the pure α-phyllocladane sample, to Dr. K. Ujszaszy (Budapest, Hungary) for performing the high-resolution MS determination and to Dr. A. Korosy (Budapest) for his assistance with the GC–MS measurements.

REFERENCES

1 J. R. Hanson, *The Tetracyclic Diterpenes*, Pergamon, Oxford, 1968, p. 8–40.
2 E. F. Serantoni, A. Krajewski, R. Mongiorgi, L. Riva di Sanseverino and G. M. Sheldrick, *Acta Crystallogr.*, Sect. B, 34 (1978) 1131.
3 M. Streibl, M. Kristin, J. Krupcik and K. Stransky, *An. Quim.*, 68 (1972) 879.
4 A. Hollerbach, *Erdoel, Kohle, Erdgas, Petrochem.*, 33 (1980) 117.

5 I. Hazai, G. Alexander, T. Székely, B. Essiger and D. Radek, *J. Chromatogr.*, 367 (1986) 117.
6 G. Alexander, I. Hazai, J. Grimalt and J. Albaiges, *Geochim. Cosmochim. Acta*, 51 (1987) 2065.
7 R. A. Noble, R. Alexander, R. I. Kagi and J. Knox, *Geochim. Cosmochim. Acta*, 49 (1985) 2141.
8 A. Livsey, A. G. Douglas and J. Connan, *Org. Geochem.*, 6 (1984) 73.
9 W. K. Seifert and J. M. Moldowan, in R. B. Johns (Editor), *Biological Markers in Sedimentary Records*, Elsevier, Amsterdam, 1986, pp. 261–290.
10 A. Soltys, *Monatsh. Chem.*, 54–54 (1929) 175.
11 R. P. Philp, *Fossil Fuel Biomarkers*, Elsevier, Amsterdam, 1985.
12 I. Hazai, *Abstracts of Presentation of the Budapest Chromatography Conference, July 6–8, 1987.*
13 H. Becker, W. Berger, G. Domschke, E. Fanghänel, J. Faust, M. Fisher, F. Gentz, K. Gewald, R. Gluch, R. Mayer, K. Müller, D. Pavel, H. Schmidt, K. Schwetlick, E. Seiler and G. Zeppenfeld, *Organikum*, VEB Deutsches Verlag d.W., Berlin, Hungarian translation, Muszaki Konyvkiado, Budapest, 1967, p. 334.
14 G. D. Abott, C. A. Lewis and J. R. Maxwell, *Org. Geochem.*, 6 (1985) 31.
15 D. Dobos, *Electrochemical Tables* (in Hungarian), Muszaki Konyvkiado, Budapest, 1965, p. 223.
16 R. C. Barrick and J. I. Hedges, *Geochim. Cosmochim. Acta*, 45 (1981) 381.
17 J. M. Moldowan, W. K. Seifert and E. Gallegos, *Geochim. Cosmochim. Acta*, 47 (1983) 1531.
18 C. M. Ekweozor and O. P. Strausz, in M. Bjoroy (Editor), *Advances in Organic Geochemistry 1981, Proceedings of 10th International Meeting on Organic Geochemistry,* Wiley, Chichester, 1983, p. 746.
19 R. A. Noble, R. Alexander, R. I. Kaigi and J. Knox, *Org. Geochem.*, 10 (1986) 825.
20 M. I. Venkatesan, E. Ruth and I. R. Kaplan, *Geochim. Cosmochim. Acta,* 50 (1986) 1133.
21 B. R. T. Simoneit and M. A. Mazurek, *Atmos. Environ.*, 16 (1982) 2139.
22 T. Katoh and K. Ouchi, *Fuel*, 68 (1987) 58.
23 G. Alexander and I. Hazai, unpublished results.
24 B. R. T. Simoneit, J. O. Grimalt, T. G. Wang, R. E. Cox, *Org. Geochem.*, 10 (1986) 877.
25 M. A. Barnes and W. C. Barnes, in M. Bjoroy (Editor), *Advances in Organic Geochemistry 1981, Proceedings of 10th International Meeting on Organic Geochemistry*, Wiley, Chichester, 1983, p. 289.