

BIOLOGICAL MARKER AND RELATED COMPOUNDS IN NATURAL AND SYNTHETIC LIQUID FUELS

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INTRODUCTION

Molecular level characterization of synthetic crudes using GC and GC/MS techniques has typically involved identifying the major components present, irrespective of chemical class (1-4). This approach differs considerably from the application of these methods for characterizing natural crude oils. These samples are only analyzed for particular compound types whose distributions and use in selected ratios can provide useful geochemical information. The compounds studied are what are generally termed "biological markers", aliphatic components directly related to a biological precursor. These compounds include; n-alkanes, acyclic isoprenoids, diterpanes, triterpanes and steranes (5,6). More recently, however, alkyl aromatics such as dimethylnaphthalenes (7), trimethylnaphthalenes (8,9) and methylphenanthrenes (10) have also been employed in a similar manner.

The literature contains a paucity of reports of analyses of synthetic liquids specifically for biological marker compounds (11-14). These studies, which encompass both coal- and oil shale-derived liquids, suggest that the geochemical data obtained can provide useful information about the source material and different liquefaction processes. Interestingly, the coal derived liquids examined for biological marker compounds were almost exclusively produced from bituminous coals. This is surprising in view of the much reported liquefaction reactivity of the lower ranked, lignites and brown coals. Furthermore, as the use of alkyl aromatics as geochemical indicators is only a recent innovation, the extension of this application to synthetic liquids is as yet unreported.

Two Australian fossil fuel reserves whose liquefaction potential have been extensively investigated are the massive Latrobe Valley (Victoria, Australia) brown coal deposits, and the Rundle oil shale (Queensland, Australia) seams. In fact, a 50 ton-per-day pilot plant based on the SRC I & II processes, and using these brown coals as feedstock is currently nearing completion in the Latrobe Valley. This paper reports on a study of synthetic liquids, produced from these two sources, that have been characterized by GC and GC/MS in an analogous fashion to natural crudes. For comparative purposes, the data obtained from a terrestrial crude oil and a marine crude oil are also included. In addition, the effect of liquefaction process on the respective data is illustrated by the different coal derived liquids.

EXPERIMENTAL

Samples. The coal derived liquids were all produced from a medium-light lithotype Victoria brown coal from the Loy Yang Field (bore 1277, depth 67-68m). The liquefaction processes employed were: solvent extraction (CH_2Cl_2); slow pyrolysis (50-1000°C at 3°C min⁻¹); hydrogenation (tetrafin/ H_2 (10.3 mPa), 375°C, 2hrs) and $\text{CO}/\text{H}_2\text{O}$ (bed moist coal/ CO (6.8 MPa), 350°C, 2hrs). More detailed information on the liquefaction conditions and the product yields and analyses are given elsewhere (15,16).

The oil shale derived liquids were produced from the Rundle oil shale by solvent extraction (CH_2Cl_2) and by the Lurgi-Ruhrgas retorting process (17). In all cases, the synthetic liquids are operationally defined as the methylene dichloride soluble portion of the liquefaction product.

The two natural crude oils represent oils sourced from terrestrial organic matter and marine organic matter, respectively. The former is from the off-shore Gippsland Basin, Australia (the Latrobe Valley coals are part of the on-shore Gippsland Basin) and the latter, the North Sea, Denmark.

Separation Procedure. The sample (30mg) in methylene dichloride (2cm³) was preadsorbed onto silicic acid using the method of Middleton (18). Upon removal of the solvent by rotary evaporation, the preadsorbed sample was placed on top of a column of silicic acid (3g). Successive elution with n-pentane; n-pentane/diethyl ether (95:5) and methylene dichloride/methanol (90:10) gave three fractions: (1) aliphatic hydrocarbons, (2) aromatic hydrocarbons and (3) heteronuclear compounds.

An aliquot of the aliphatic hydrocarbons fraction, in benzene, was subsequently treated with activated 5A molecular sieves to separate the n-alkanes from the branched and cyclic alkanes (19). Similarly, the aromatic hydrocarbons fraction was subjected to thin layer chromatography on alumina, with n-hexane as eluant, to yield a di- and trinuclear aromatic fraction (9). These fractions after appropriate reported workup procedures (19,9), and solvent removal were amenable for analysis by GC and GC/MS.

GC and GC/MS analysis. Gas chromatography was performed using a Hewlett-Packard (HP) 5880A chromatograph, fitted with a 50m x 0.2mm i.d. WCOT fused-silica column coated with 5% crosslinked phenylmethyl silicone (bp-5, SGE Australia). For all analyses, hydrogen was used as carrier gas at a linear velocity of 30 cm sec⁻¹, and detector (FID) and injector temperatures were 300°C and 280°C, respectively. In a typical analysis of a total aliphatic hydrocarbon fraction, the oven of the chromatograph was temperature programmed from 65°C to 280°C at 4°C min⁻¹, then held isothermal for 10 minutes. The oven temperature programme for analysis of the di- and trinuclear aromatic fractions was; 70°C for 1 minute; then 70°C to 190°C at 1°C min⁻¹; followed by 190°C to 300°C at 10°C min⁻¹ and finally, held isothermal for 10 minutes. All GC analysis were integrated using the associated HP data terminal. Component identification was, in both cases, by comparison of the retention times with those of authentic isomers (8,10,19,20).

Only the branched/cyclic alkane fractions were analyzed by GC/MS. The analyses were performed using a HP 5895B capillary GC-quadrupole MS-computer data system, fitted with a 50m x 0.22mm i.d. WCOT fused-silica cross-linked methylsilicone column (Hewlett Packard). Samples for analyses were diluted to a 1% w/w solution in n-hexane and injected on-column at 50°C. The oven was then temperature programmed to 300°C at 4°C min⁻¹, and held isothermal for 20 minutes. Hydrogen was used as carrier gas at a linear velocity of 28 cm sec⁻¹. The samples were analyzed in the selected ion monitor (SIM) mode, using dwell times of 10 msec for each ion monitored. Typical MS operating conditions were: EM voltage 2200V; ionization energy 70eV; source temperature 250°C.

The ions monitored were typical of those used for crude oil biological marker studies. For example, m/z 217, 218, 259 (steranes and diasteranes); m/z 177,191,205 (triterpanes) and m/z 123, 193 (bicyclics and tetracyclics). Specific compounds were identified by comparison of their retention times with literature data. (21-23).

RESULTS AND DISCUSSION

Figure 1 shows gas chromatograms of the total aliphatic hydrocarbon fractions of the synthetic liquids and natural crude oils. The compound distributions evident in these chromatograms for the coal derived liquids differ markedly for the various liquefaction processes. The solvent extract is overwhelmingly dominated by triterpenoids (consistent with the higher plant input of the source material), while the hydrogenation product and pyrolysate have the n-alkanes in the highest relative abundance. It is interesting to note that this observation conflicts with that of Youtcheff and coworkers (12) who found no difference in the distributions of saturate hydrocarbons from several bituminous coal solvent extracts and their corresponding hydrogenation products. In addition, the pyrolysate also contains a homologous series of n-alkanes. The CO/H₂O product is quite distinctive in that it has a bimodal n-alkane distribution and appears to

contain a major group of components which have retention times between $n\text{-C}_{22}$ and $n\text{-C}_{23}$. The oil shale derived liquids can also be differentiated from each other. The solvent extract is predominantly n -alkanes, having the C_{27} member as the most abundant component; while the retort oil is much more complex. Although it has the n -alkanes as the most abundant homologous series, it also contains a series of n -alkenes. However, it differs from the coal pyrolysate in having its n -alkane and n -alkene distributions maximising at lower carbon numbers. In fact, the general shapes of the n -alkanes distributions for the coal pyrolysate and oil shale retort are very similar to those for the terrestrial and marine crudes, respectively. This may suggest that the geochemical processes generating natural crudes are pyrolytic in nature.

Two geochemical indicators determined from chromatograms of the total aliphatic hydrocarbons are the Carbon Preference Index (CPI) and Pristane/Phytane ratio (Pr/Ph). The former is based on the n -alkanes, and the latter, the C_{18} and C_{19} acyclic isoprenoids. The CPI values for the oil shale derived liquids are much higher than those for both the coal derived liquids and natural crudes. Except for the solvent extract, the CPI values for the coal derived liquids are all less than unity, with that for the $\text{CO}/\text{H}_2\text{O}$ product being appreciably so. Interestingly, the CPI values for the two natural crudes are almost identical. However, it is the Pr/Ph ratio values that clearly distinguish the coal derived from the oil shale derived liquids, and the terrestrial from the marine crude. Both the coal derived liquids and the terrestrial crude have considerably higher values of this ratio than their corresponding counterparts. The similarities of values for the coal derived liquids and the terrestrial crude, and the shale derived liquids and the marine crude is not surprising, considering their respective source organic matter. The combined use of CPI and Pr/Ph does, hence, suggest that coal- and oil shale-derived liquids can be differentiated from each other and their respective natural counterparts.

Further confirmation of this possibility is afforded by GC/MS analyses of the respective branched/cyclic fractions. Table 1 presents the data for selected geochemical indicators based on several biological marker compounds. Typical mass fragmentograms of steranes (m/z 217) and triterpanes (m/z 191) are illustrated in Figure 2, for the coal pyrolysate and terrestrial crude oil. Component identification is given in Table 2. The mass fragmentograms show that the samples generally contain the same components, with differences being mainly in individual relative abundances. However, the m/z 191 mass fragmentograms do provide a ready means of distinguishing synthetic from natural crudes. The differences are most apparent in the high relative abundances of: 1) C_{29} to C_{30} α/β -hopanes (peaks F and D, respectively, in Fig. 2a) and 2) the C_{27} β -hopane (peak C in Fig. 2a) for the synthetic liquids compared with the natural crudes.

Kaurane is an unequivocal biological marker for higher plant material in fossilized organic matter (24). The epimer ratio (Table 1) is, therefore, useful for distinguishing the oil shale derived liquids and the marine crude from the coal derived liquids and the terrestrial crude. In fact, the respective values for the coal derived liquids and the terrestrial crude suggest, they too can be differentiated from each other.

The values for the drimane epimer ratios are similar for all the synthetic liquids, but are significantly lower than those for the natural crudes, whose respective values are almost identical. Conversely, the β/α hopane ratios and the moretane/hopane ratios are considerably higher for the synthetic liquids than for their natural counterparts. Again, it is difficult to distinguish, unambiguously, between the oil shale and coal derived liquids. However, these drimane and hopane (moretane) based parameters do permit unequivocal distinction between the natural and synthetic crudes. Similarly, the sterane epimer ratios are significantly different between the synthetic liquids and the natural crudes; the values

for the ratio being much higher in the latter. However, in natural crudes the above parameters have been shown to be maturity dependent; therefore, synthetic liquids produced under more severe thermal conditions may show values approaching those observed for their natural counterparts. This is in fact observed with the coal hydrogenation product and the marine crude. This suggests that this parameter should not be used in isolation, although generally most natural crude oils are generated from mature source rocks and have epimeric ratios of 1.1.

In contrast, the C_{29}/C_{27} sterane ratio can be used to differentiate the coal derived liquids and the terrestrial crude, from the oil shale derived liquids and the marine crude. The values are much higher for the former, than for the latter samples. Actually, this ratio could not be determined for the shale retort oil as the C_{27} sterane was immeasurable. Again the hydrogenation product appears anomalous, with the value for this parameter being much lower than for the other coal derived liquids.

Indeed, the values for the $\beta\beta/\alpha\beta$ hopane ratio and the sterane-based parameters, for the hydrogenation product are of geochemical interest. The low relative abundance of the C_{30} $\beta\beta$ -hopane, and its similarity to those in natural crudes suggests that certain maturation processes can be replicated under laboratory conditions. This is further shown by the value of sterane epimer ratio, which unlike those for other synthetic liquids, indicates a significant degree of configuration isomerization. In addition, the low value for the C_{29}/C_{27} sterane value is consistent with dealkylation of the C_{29} sterane as a result of increased thermal stress. These observations thus suggest that hydrogen transfer processes may be important in the geosphere for crude oil formation.

Inspection of the alkyl aromatic-based parameters, which are presented in Table 3, shows that they too can be employed to distinguish synthetic from natural crudes, and coal derived from shale derived liquids. Figure 3 shows a typical gas chromatogram of a dinuclear and trinuclear aromatics fraction for the coal pyrolysate and terrestrial crude. The numbered peaks, which refer to those used in defining the parameters, are defined in Table 4. The parameters DNR-2, TNR-1 and MPI-1 allow differentiation of the synthetic from the natural crudes. The values for DNR-2 in the synthetic liquids are normally much lower than those observed in natural crudes. The value for the marine crudes, presented here (i.e. 72.6) is anomalously low for oils sourced from this type of organic matter, and is a direct result of the immaturity of this particular sample. For TNR-1 and MPI-1, the synthetic liquids generally have higher values than the natural crudes. However, both the coal pyrolysate and the oil shale retort have similar values to those observed for the terrestrial and marine crudes. This may be further evidence that pyrolytic processes play a role in oil generation.

The coal derived liquids and terrestrial crude have considerably higher values of DNR-6 and TDE-1 than the oil shale liquids and marine crude. Thus, these groups of samples may be distinguished from each other using these parameters. Hence, appropriate combinations of parameters permit the origin and source type of a liquid fuel to be ascertained. For example, high DNR-2 and TDE-1 values infer the oil is a natural terrestrial crude, whereas low values for these two parameters suggest it is an oil shale derived liquid.

In conclusion, the approach outlined here shows that: 1) natural and synthetic crudes can be fingerprinted using known geochemical parameters; 2) the choice of liquefaction process can considerably alter the distribution of total aliphatic hydrocarbons for a given source material; 3) natural and synthetic crudes can be distinguished from each other, as can be their source types, using appropriate combinations of biological marker and/or alkyl aromatic-based parameters; 4) geochemical processes such as the epimerization of steranes and the depletion of $\beta\beta$ -hopanes can be replicated in the laboratory and 5) pyrolytic-, together with hydrogen

transfer processes may be important in the formation of natural crude oils.

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Table 1. Geochemical Parameters based on Biological Marker Compounds.

SAMPLE	Kaurane ^a	Drimane ^b	C ₃₀ ^c	C ₃₀ ^d	C ₂₉ ^e	C ₂₉ /C ₂₇ ^f
	$\frac{16\beta(H)}{16\alpha(H) + 16\beta(H)}$	$\frac{8\beta(H)}{8\alpha(H) + 8\beta(H)}$	Hopanes BR/αR	Moretanes Hopanes (Bα/αB)	Steranes 20S/20R	Steranes
Coal						
Solvent Extract	0.07	0.56	2.00	1.50	N.D.	N.D.
Pyrolysate	0.24	0.50	0.55	1.53	0.20	10.8
Hydrogenation	0.65	0.55	<0.05	1.38	0.58	0.8
CO/H ₂ O	0.20	0.59	0.71	1.48	0.13	17.6
Oil Shale						
Solvent Extract	N.D.	0.78	4.70	0.77	0.10	0.89
Retort	N.D.	0.50	1.01	1.82	0.11	N.D.
Crude Oils						
Terrestrial	0.99	0.99	<0.05	0.10	0.84	5.11
Marine	N.D.	1.00	<0.05	0.13	0.57	0.64

a - $16\beta(H)$ -kaurane/ $16\alpha(H)$ -kaurane + $16\beta(H)$ -kaurane

b - $8\beta(H)$ -drimane/ $8\alpha(H)$ -drimane + $8\beta(H)$ -drimane

c - $17\beta(H)$, $21\beta(H)$ -hopane/ $17\alpha(H)$, $21\beta(H)$ -hopane

d - $17\beta(H)$, $21\alpha(H)$ -moretane/ $17\alpha(H)$, $21\beta(H)$ -hopane

e - (20S)- $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ -ethylcholestane/(20R)- $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ -ethylcholestane

f - (20R)- $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ -ethylcholestane/(20R)- $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ -cholestane

N.D. Not determinable

Table 2. Identification of the Triterpanes (m/z 191) and Steranes (m/z 217) present in the Mass Fragmentograms shown in Figs. 2a and 2b.

Triterpanes (Fig. 2a)		Steranes (Fig. 2b)	
Peak	Compound	Peak	Compound
A	$17\alpha(H)$, 22, 29, 30-trisnorhopane	A	20S-13 β , 17 α -diacholestane
B	$18\alpha(H)$, 22, 29, 30-trisnorheohopane	B	20R-13 β , 17 α -diacholestane
C	$17\beta(H)$, 22, 29, 30-trisnorhopane	C	20S-24 ethyl-13 β , 17 α -diacholestane
D	$17\alpha(H)$, $21\beta(H)$ -30-norhopane	D	20R-5 α , 14 α , 17 α -cholestane
E	$17\beta(H)$, $21\alpha(H)$ -30-normoretane	E	20R-24-ethyl-13 β , 17 α -diacholestane
F	$17\alpha(H)$, $21\beta(H)$ -hopane	F	20S-24-ethyl-5 α , 14 α , 17 α -cholestane
G	$17\beta(H)$, $21\beta(H)$ -30-horhopane	G	20R-24-ethyl-5 α , 14 β , 17 β -cholestane
H	$17\beta(H)$, $21\alpha(H)$ -moretane	H	20S-24-ethyl-5 α , 14 β , 17 β -cholestane
I	22S-17 $\alpha(H)$, $21\beta(H)$ -homohopane	I	20R-24-ethyl-5 α , 14 α , 17 α -cholestane
J	22R-17 $\alpha(H)$, $21\beta(H)$ -homohopane		
K	$17\beta(H)$, $21\beta(H)$ -hopane		
L	22S and R-17 $\beta(H)$, $21\alpha(H)$ -homomoretane		
M	22S-17 $\alpha(H)$, $21\beta(H)$ -bishomohopane		
N	22R-17 $\alpha(H)$, $21\beta(H)$ -bishomohopane		
O	Unknown		
P	$17\beta(H)$, $21\beta(H)$ -homohopane		
Q	22S-17 $\alpha(H)$, $21\beta(H)$ -trishomohopane		
R	22R-17 $\alpha(H)$, $21\beta(H)$ -trishomohopane		

Table 3. Geochemical Parameters based on Dimethylnaphthalenes, Trimethylnaphthalenes and Methylphenanthrenes.

SAMPLE	DNR-2 ^a	DNR-6 ^b	TNR-1 ^c	TDE-1 ^d	MPI-1 ^e
<u>Coal</u>					
Solvent Extract	48.3	4.8	1.3	0.9	2.30
Pyrolysate	23.3	2.3	0.5	6.3	0.73
Hydrogenation	44.3	4.1	1.1	4.8	1.12
CO/H ₂ O	9.3	9.3	0.7	2.7	N.D.
<u>Oil Shale</u>					
Solvent Extract	23.1	1.9	1.3	1.6	1.08
Retort	26.1	1.2	0.8	0.3	0.80
<u>Crude Oils</u>					
Terrestrial	279.0	2.7	0.7	4.9	0.78
Marine	72.6	2.0	0.5	0.3	0.74

- a - 2,7-dimethylnaphthalene/1,8-dimethylnaphthalene
b - 2,6- + 2,7-dimethylnaphthalenes/1,4- + 2,3-dimethylnaphthalenes
c - 2,3,6-trimethylnaphthalene/1,4,6- + 1,3,5-trimethylnaphthalenes
d - 1,2,5-trimethylnaphthalene/1,2,4-trimethylnaphthalene
e - 1.5 x (2- + 3-methylphenanthrenes)/(phenanthrene) + 1-methylphenanthrene + 9-methylphenanthrene
N.D. Not determinable

Table 4. Identification of the Aromatic Compounds used in the Parameters defined in Table 2 and shown in the Gas Chromatogram in Fig. 3.

Peak	Compound	Peak	Compound
1	2,6-dimethylnaphthalene	9	1,2,4-trimethylnaphthalene
2	2,7-dimethylnaphthalene	10	1,2,5-trimethylnaphthalene
3	1,4- and 2,3-dimethylnaphthalenes	11	phenanthrene
4	1,8-dimethylnaphthalene	12	3-methylphenanthrene
5	1,4,6- and 1,3,5-trimethylnaphthalenes	13	2-methylphenanthrene
6	2,3,6-trimethylnaphthalene	14	9-methylphenanthrene
7	1,2,7-trimethylnaphthalene	15	1-methylphenanthrene
8	1,2,6-trimethylnaphthalene		

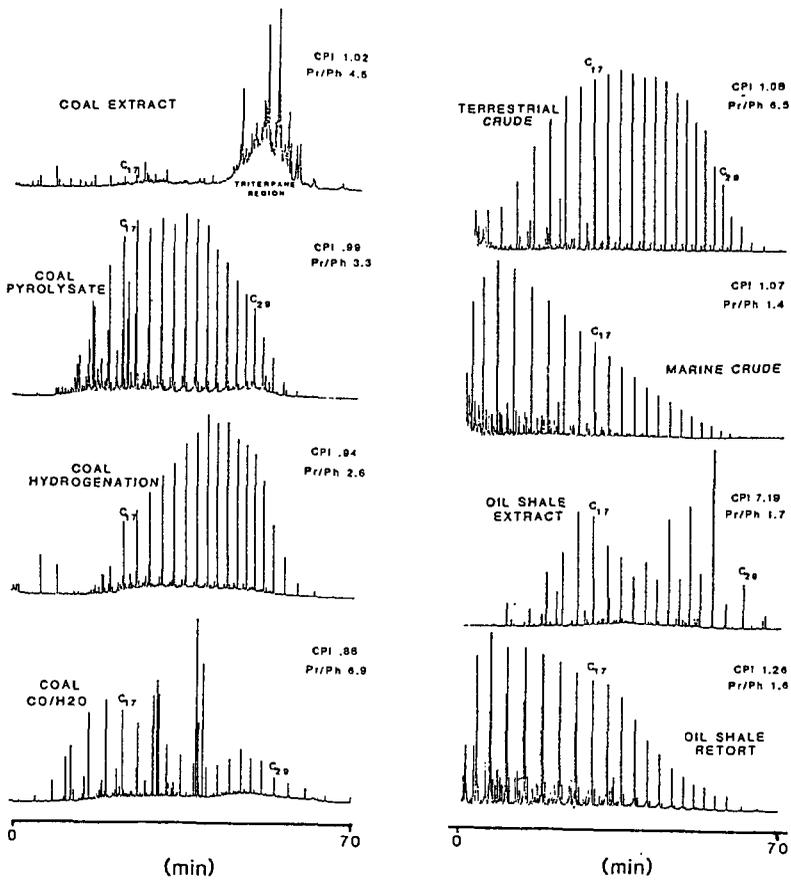


Figure 1. Gas chromatograms of the total aliphatic hydrocarbon fractions of the synthetic and natural crudes.

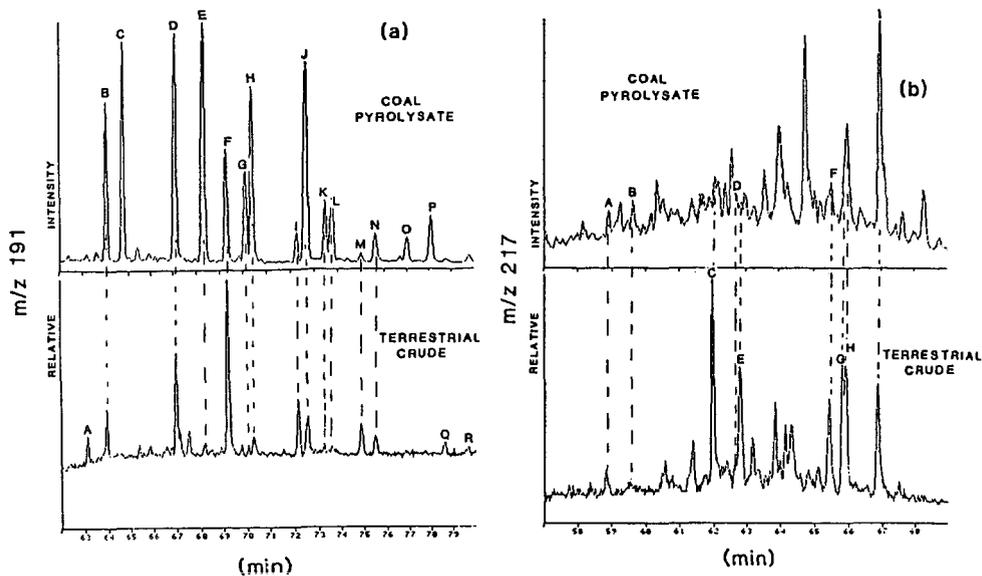


Figure 2. Mass fragmentograms for (a) triterpanes and (b) steranes from the coal pyrolysate and terrestrial crude.

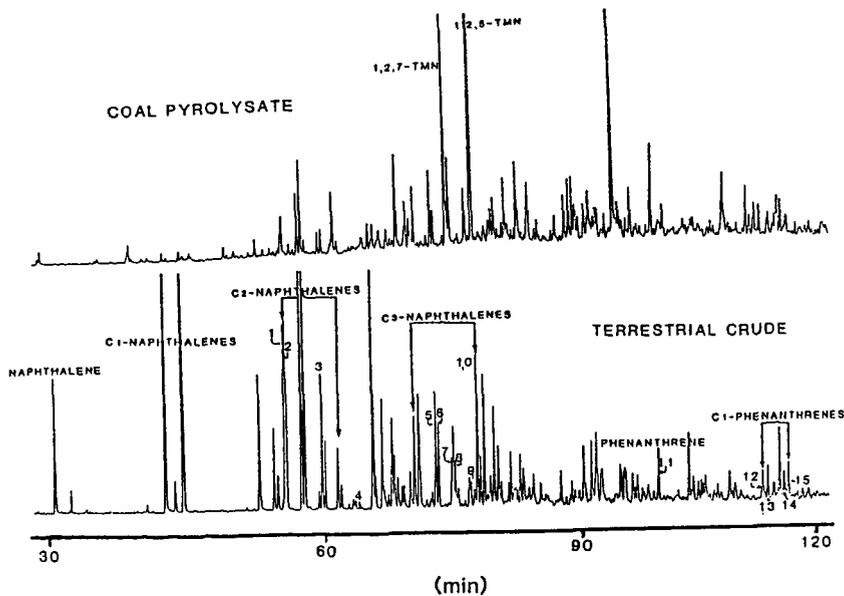


Figure 3. Gas chromatograms of the dinuclear and trinuclear aromatic fractions from the coal pyrolysate and terrestrial crude.