GRØNLANDS GEOLOGISKE UNDERSØGELSE

PRECAMBRIAN ORGANIC COMPOUNDS
FROM THE KETILIDIAN
OF SOUTH-WEST GREENLAND

PART III

BY

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AND

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WITH 46 FIGURES IN THE TEXT

CONTENTS

Abstract

Ketilidian sedimentary rocks nearly 2000 m.y. old and only slightly metamorphosed have been shown to contain fossils and organic compounds.

Results of work on organic material from a 1–3 m thick coal-graphite layer from the Foselv Formation in the Sortis Group in Grænseland are presented.

Aliphatic (straight chain, branched and cyclic) hydrocarbons are dominant in the extract from two coal-graphite samples weighing about 4 kg and 10 kg respectively. Further investigations of these compounds have revealed many saturated straight-chain hydrocarbons, with the n-C_{15} alkane, the most abundant among the normal alkanes, ranging from C_{12} to about C_{21}, and various isoalkanes and anteisoalkanes. Saturated cyclic hydrocarbons like alkyl cyclohexanes, and homologous series of alkyl benzenes and alkyl naphthalenes are also present.

A series of monoterpenoid compounds is present. Six of them are fairly well characterized by their mass spectra.

Fatty acids and methyl esters of fatty acids are present, notably a homologous series of straight-chain fatty acids. Branched acids are also present in minor amounts.

The organic compounds further indicate that this Precambrian coal-graphite layer is the result of biological activity.

INTRODUCTION

The examinations have been carried out by the writers at the Geological Institute (K. RAUNSGAARD PEDERSEN) and the Chemical Institute (J. LAM) of the University of Aarhus.

The organic material described here was obtained from Precambrian low-metamorphic rocks from a part of the Ketilidian fold belt of South-West Greenland. The age of this fold belt has been estimated to be 1700–2000 m. y. (BRIDGWATER 1965).

In two previous publications we have treated organic material extracted from rocks from this area (RAUNSGAARD PEDERSEN and LAM 1968; LAM and RAUNSGAARD PEDERSEN 1968). The material examined was a coal-graphite, and a dark dolomite with small macrofossils (*Vallenia erlingi* Raunsgaard Pedersen) and microfossils. Both types of rocks gave many different organic compounds but in rather small amounts. In order to obtain a better determination of the compounds that were present in smaller amounts it has been necessary to obtain larger samples of the material. One of the authors (RAUNSGAARD PEDERSEN) therefore in the summers of 1966 and 1967 collected material for the further investigations (RAUNSGAARD PEDERSEN 1966 and 1968).

In the earlier publication on the organic compounds from a coal-graphite sample (RAUNSGAARD PEDERSEN and LAM 1968) we mentioned the presence of aliphatic hydrocarbons (n-alkanes, branched and cyclic hydrocarbons). We also mentioned that pristane and phytane were not present in large amounts. Our new examination has not revealed the presence of these two hydrocarbons in any great amount. We have used better separation methods than before — a longer silica gel column and urea inclusion. We have avoided paper filtration since we found great contamination by phthalates from filter paper (LAM 1967). Phthalates are commonly found as contamination in laboratories (LEE, BRITTON, JEFFCOAT and MITCHELL 1966; HUNNEMANN 1968).

The chemical examination of the new material revealed many compounds resembling those occurring in living plants and animals.

Normal alkanes, iso- and anteisoalkanes, besides isoprenoid hydrocarbons, monoterpenoids (such as alcohols and ketones), fatty acids and esters of fatty acids, are the main compounds repeatedly found in our samples. Aromatics are also present, especially as hydrocarbons. Recently aromatic as well as hydroaromatic hydrocarbons and aromatic acids have been reported to be present in the Green River Shale, an Eocene formation in Colorado (Haug, Schnoes and Burlingame 1968). (See also Raunsgaard Pedersen and Lam 1968; Lam and Raunsgaard Pedersen 1968.)
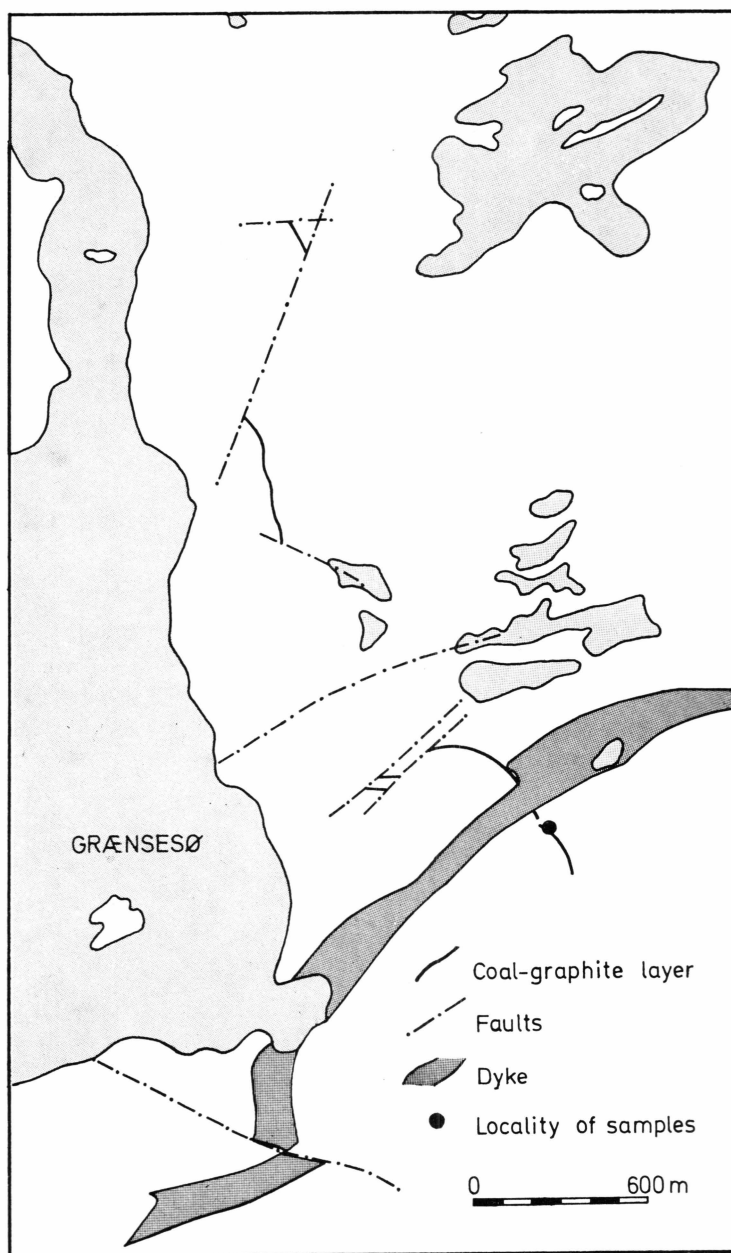
Acknowledgments

Fig. 1. Map showing the position of the coal-graphite layer in northern Grænseland
South-West Greenland.

THE MATERIAL AND THE GEOLOGICAL SETTING

The organic material treated in this paper was extracted from two large samples of coal-graphite from a 1–3 m thick layer of coal-graphite of Precambrian age. The coal-graphite occurs in the Fønland area in northern Grænseland (see fig. 1) where the Ketilidian supracrustals are only a little metamorphosed and still show distinct sedimentary structures. More details about the geology of the Grænseland area have been published previously (BONDESEN, RAUNSGAARD PEDERSEN and JØRGENSEN 1967; RAUNSGAARD PEDERSEN and LAM 1968; LAM and RAUNSGAARD PEDERSEN 1968). The coal-graphite layer from which the samples were collected is situated in the Sortis Group in the upper part of the Ketilidian succession. The lower part of this group consists of well preserved pillow lavas forming the Foselv Formation which is about 1000 m thick (see fig. 2). In this monotonous pillow series the carbonaceous layer is found. The layer varies from a carbonaceous pelite in southern Grænseland to a coal-graphite in the north of Grænseland. The thickness of the carbonaceous layer varies from 1 m to about 3 m; in some parts of the area it is lacking. But it seems likely that the carbonaceous layer is in about the same stratigraphical position everywhere it is found.

In the northern part of the Grænseland area, south-east of the lake Grænsesø, the thickness of the carbonaceous layer is in some localities 3 m and the layer has the characteristics of coal-graphite. The layer is displaced by faults but it has been possible to follow it for about four kilometres (RAUNSGAARD PEDERSEN 1966). In the area where the coal-graphite layer has its maximum thickness it is cut by a great dyke against which the layer is locally more graphitized (see fig. 3).

The coal-graphite layer is both underlain and overlain by pillow lavas (see fig. 4). No differences have been found between the coal-graphite against the pillows and that in the centre nor between pillows against the coal-graphite and those elsewhere; nevertheless the coal-graphite seems to be in the original position where it was deposited. It has not been possible to find indisputable indications of the conditions under which the original material was deposited. The varying thickness of the layer might indicate deposition in small basins in the uneven pillow lava surface.

Fig. 2. The pillow lava series of the Foselv Formation south-east of Grænsesø with the coal-graphite layer in the groove in the central part of the picture. A dyke crosses the layer in the foreground. In the background the Inland Ice.

No macroscopic fossils have been found in or together with the coal-graphite although they do occur in some sediments in other parts of the Ketilidian series of Grænseland (RAUNSGAARD PEDERSEN 1966 and 1967; BONDESEN, RAUNSGAARD PEDERSEN and JØRGENSEN 1967; RAUNSGAARD PEDERSEN 1968). But micropaleontological investigations of the coal-graphite have shown the presence of many types of microscopic fossil structures. The material has been treated in hydrofluoric acid (40 %) and has been slightly oxidized in a mixture of concentrated HNO_3 and $KClO_3$. One of the types of microscopic globules from the layer has been

Fig. 3. Exposure of the coal-graphite layer dipping steeply in the same direction as the shaft of the ice-axe. In the background the underlying pillow lava.

Fig. 4. The pillow lava series above the coal-graphite layer. Note the well preserved forms of the pillows.
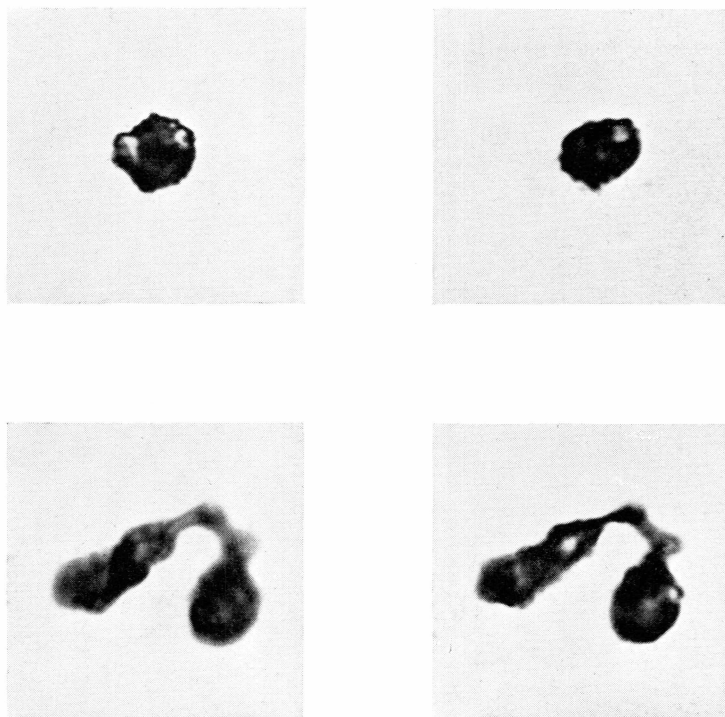
Fig. 5. Microphotos of fossil structures. 1500×(the upper left) and 2000×.

described (Raunsgaard Pedersen in Bondesen, Raunsgaard Peder-
sen and Jørgensen 1967) and other types are shown in fig. 5.

The carbon isotope composition C^{13}/C^{12} of many samples of coal-
graphite has been determined and shows δC^{13} values from -32.6 per mill.
to -32.1 per mill. indicating a biological origin for the layer (Jørgensen
in Bondesen, Raunsgaard Pedersen and Jørgensen 1967).

An earlier investigation of the organic compounds from a small
sample of the coal-graphite showed the presence of compounds which
must be a result of biological activity (Raunsgaard Pedersen and Lam
1968), and the thickness of coal-graphite indicates a considerable accu-
mulation of organic material.

Our extractions of organic material from several types of sediments
from the low-metamorphic part of the Ketilidian have shown that the
coal-graphite gives a greater amount of organic material than the other
sediments, and also many compounds not found in the other sediments.
A further investigation of this promising material was therefore needed
and so new collecting from, and investigation of, the coal-graphite layer
was carried out. As the new material was collected specially for an

organo-chemical investigation, precautions were taken against contamination.

The situation of the area from which the samples have been taken makes "natural" contamination of the material very unlikely because a distance of at least several hundred km separates it from the nearest sediments younger than Precambrian, apart from the sparse moraine material from the last glaciation during which a strong erosion occurred. The recent vegetation is very restricted (see fig. 2 and fig. 3) as the area is situated at about 1000 m above sea level and near the margin of the Inland Ice.

The investigation dealt with in this paper was carried out on nearly 14 kg of coal-graphite, divided in two samples, GGU no. 70634-3 and 70634-5. The samples are from the locality where the coal-graphite layer has the maximum thickness. The locality is indicated on the map fig. 1 and is shown in fig. 2.

The weight of sample no. 70634-3 was 4299 g; this sample in the following is named sample I. The weight of sample no. 70634-5 was 9352 g; this sample is named sample II.

EXTRACTION AND ANALYTICAL METHODS

The extractions were carried out on the two large samples of coal-graphite just described, which had been handled with precautions against contamination.

The samples were cleaned; the outer part was cut off and the samples finally were rinsed in extraction liquid (see below). The samples were only in contact with glass and steel equipment rinsed with extraction liquid.

The rinsed samples were pulverized in an automatic mortar and the pulverized material was extracted in portions of about 700 g. Every single part of the material was extracted three times with a 900 ml mixture of benzene and methanol (3:1 v/v) and with an extraction time of three days per extraction. The first extract was stored; the second extract was used for the first extraction of a new 700 g portion of sample and then stored. The third extract was used for the second extraction of the second 700 g portion and the first extraction of the third 700 g portion of sample. Continuing this procedure the amount of extraction mixture was brought to a minimum in order to limit the possibility of contamination from the solvents ("Merck" benzene and methanol). These are analytical grade chemicals but still the benzene contains small amounts of benzene derivatives and naphthalene and its derivatives which may be detected when the residue after evaporation is subjected to gas chromotography combined with mass spectrometry. The analytical pure benzene has repeatedly been tested for its content of impurities and only aromatics of the above-mentioned types have been detected. No aliphatic hydrocarbons could be detected. The methanol did not give any organic residue after evaporation of one litre.

The extract from sample I was used to determine the aliphatic hydrocarbons. For this purpose the solvents mentioned above can be used without special treatment because for this determination there should be no contamination from the solvents.

Sample II was used for determination of aromatics as well as for checking the determination of the aliphatic hydrocarbons. For this purpose the benzene used was first purified by distillation. 25 l of benzene was distilled in the following way: 1000 ml portions were distilled in an

all-glass equipment; the first 100 ml distilled off and the residues of 100 ml from each portion were discarded, so that from 25 litres was obtained 20 litres of benzene of which a litre, when evaporated to dryness, gave about one mg of non-volatile material while undistilled benzene after evaporation gave about 6 mg of non-volatile products. The residue of one mg from the distilled benzene, when injected to the gas chromatograph, did not show any peaks that might be due to aromatic compounds.

Sample extract I. The extraction from the 4299 g of material (sample I) was evaporated and 205 mg of a yellow oil containing small amounts of black carbonaceous particles was obtained. The oily matter was again dissolved in a few millilitres of distilled light petroleum (b.p. below 50° C) and poured into a silica gel column, which previously had been washed out with light petroleum. The first eluted fractions contained aliphatic hydrocarbons in a very complex mixture of n-alkanes, and branched and saturated cyclic hydrocarbons. No attention was paid to the aromatic fractions following just after, as aromatic compounds may originate from the benzene used for extraction, but the last fractions eluted with increasing amounts of ether were compared to the corresponding fractions of sample extract II.

Sample extract II. The extraction from the 9352 g of material (sample II), extracted with the purified benzene-methanol mixture, gave 485 mg of a crude product of which 385 mg were chromatographed on a silica gel column with c. 150 ml of light petroleum. 183 mg of an aliphatic hydrocarbon mixture — a colourless oil — appeared from the first four fractions of 25 ml each when combined and evaporated. The later fractions contained aliphatic hydrocarbons, alkyl benzenes and alkyl benzenes mixed with naphthalene and derivatives thereof.

In order to get more polar material eluted from the column, ether was added in increasing amounts to the light petroleum. In total 400 ml of light petroleum and 100 ml of ether were used.

Finally the most polar substances were eluted with methanol. This fraction gave about 75 mg of fatty acids and other substances such as monoterpenols and compounds not yet identified.

The fractions between the hydrocarbon fractions and the most polar fraction contained esters, monoterpenoid alcohols and ketones besides many unidentified compounds.

The aliphatic hydrocarbon fractions of sample extracts I and II were separately subjected to urea inclusion separation in order to separate the straight-chain hydrocarbons from most of the branched and cyclic hydrocarbons.

Urea inclusion method: A modified separation by urea inclusion (EVANS, KENNY, MEINSCHEIN and BRAY 1957) was carried out on an

experimental basis in the following way: An artificial mixture (30 mg) of pristane, phytane, n-decane, n-dodecane, n-tetradecane, n-hexadecane, n-octadecane, and n-eicosane was dissolved in 0.5 ml benzene and 1 ml methanol, and 1 g of finely pulverized urea was added. The suspension was stirred repeatedly during the first hour. After 24 hours in a test-tube closed with a glass stopper the solution containing the branched and very little of the straight-chain hydrocarbons was washed twice with 1 ml of a mixture of benzene and methanol (2:1 v/v) saturated with urea. After filtration, 25 ml of light petroleum was added and shaken four times with 25 ml of water in a separating funnel. Then the light petroleum solution was dried with sodium sulphate and filtered (fraction I). The remaining urea crystals were dissolved in 75 ml of water, and 10 ml of dilute hydrochloric acid was added. After one hour the aqueous solution was shaken four times with 20 ml portions of light petroleum. The light petroleum solution was dried with sodium sulphate and filtered (fraction II). Both fractions were gas chromatographed and the chromatograms showed that a very good fractionation had occurred.

When this method was applied to the hydrocarbon fractions from the two sample extracts the separation was not quite perfect since apparently a fairly large amount of branched alkanes is also included in the crystals of urea. As seen from the gas chromatogram (fig. 6), rather high peaks are to be found in between the n-alkane peaks. These peaks correspond to iso- and anteisoalkanes, which are revealed from the mass spectra.

Gas chromatograms and mass spectra were determined after separation in a S.E. 30 column and in a Perkin-Elmer mass spectrometer under the same conditions as described in an earlier publication (RAUNSGAARD PEDERSEN and LAM 1968).

RESULTS

Aliphatic and aromatic hydrocarbons

Figs. 6 and 7 show gas chromatograms of the urea-separated fractions from sample extract I, which are almost consistent with those of sample extract II (see fig. 21).

Gas chromatogram fig. 6

From the gas chromatogram it is seen that the amounts of branched alkanes (iso-and anteisoalkanes) increase smoothly from peak no. 8 to a maximum at peak no. 19 of the gas chromatogram (the latter corre-
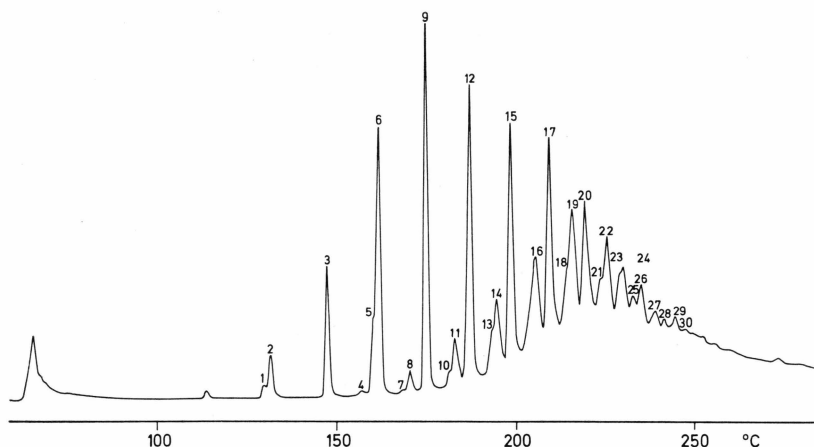

Fig. 6. Gas chromatogram of fraction obtained by urea inclusion separation from sample I. Straight-chain, iso- and anteisoalkanes—1.5 μl. Column, 10 per cent S.E. 30, 2 m. 5° C/min. 60–250° C. Helium flow 30 ml/min.

sponding to a branched C_{21}-alkane) and then decrease. The maximum amount of straight-chain alkane is at peak no. 9 of the gas chromatogram (corresponding to the n-C_{15}-alkane).

Fig. 8 shows the mass spectrum of a mixture of n-C_{14}-hydrocarbon and a compound with a molecular weight of two less than n-C_{14}, most

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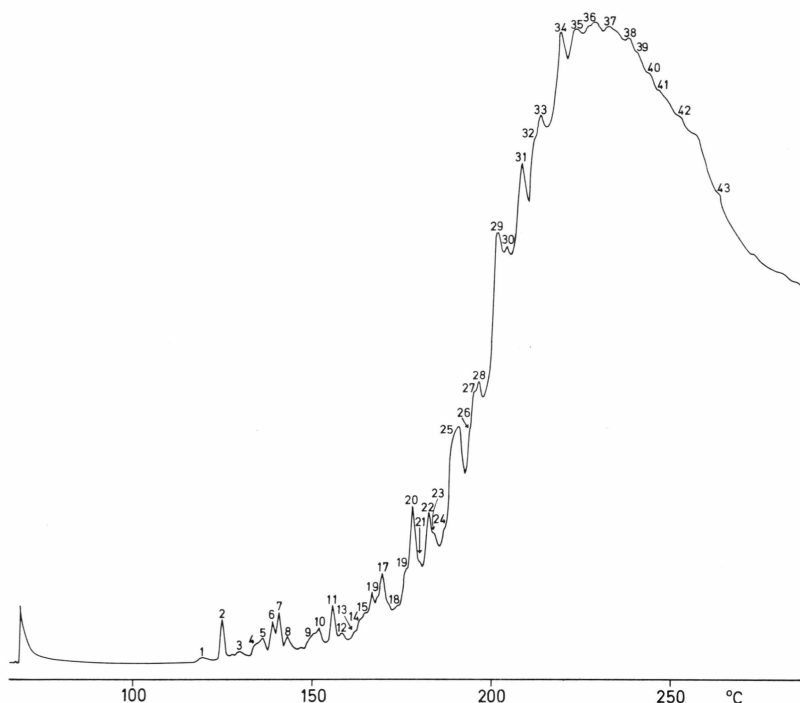
Fig. 7. Gas chromatogram of branched and cyclic alkanes separated from the straight-chain alkanes by urea inclusion from sample I. This fraction still contains small amounts of n-alkanes—1.5 μl. Column, 10 per cent S.E. 30, 2 m. 5° C/min.

likely an alkyl cyclohexane (relatively high intensity mass peaks at 83, 97, and 111 m/e (peak no. 5 of the gas chromatogram)).

Peak no. 6 of the gas chromatogram shows pure n-C_{14}-alkane with almost no peaks at 196, 83, and 97 m/e, while the dominant peaks of the corresponding groups are at 198, 85, and 99 m/e, characteristic of a normal alkane.

From the mass spectra of peaks 8 and 9 of the gas chromatogram (both with a molecular weight of 212) a marked difference is noted. Fig. 10 shows a typical normal alkane spectrum with a base peak at 57 m/e and with smoothly decreasing relative intensities of the fragments, except for the molecular peak which is a fairly high peak. Fig. 9 shows a fragment pattern according to the spectra of branched aliphatic hydrocarbons, with a low intensity of the parent peak and with relatively high fragmentation patterns at 169 and 183 m/e due to fragmentation of the side chains.

Peak 11 of the gas chromatogram appears immediately before the n-C_{16}-alkane peak, where an isoprenoid C_{17}-alkane should be expected.
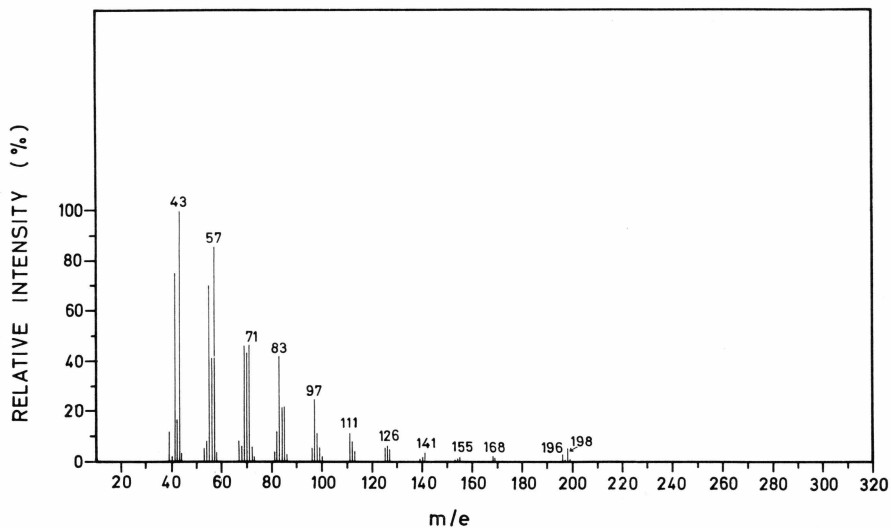
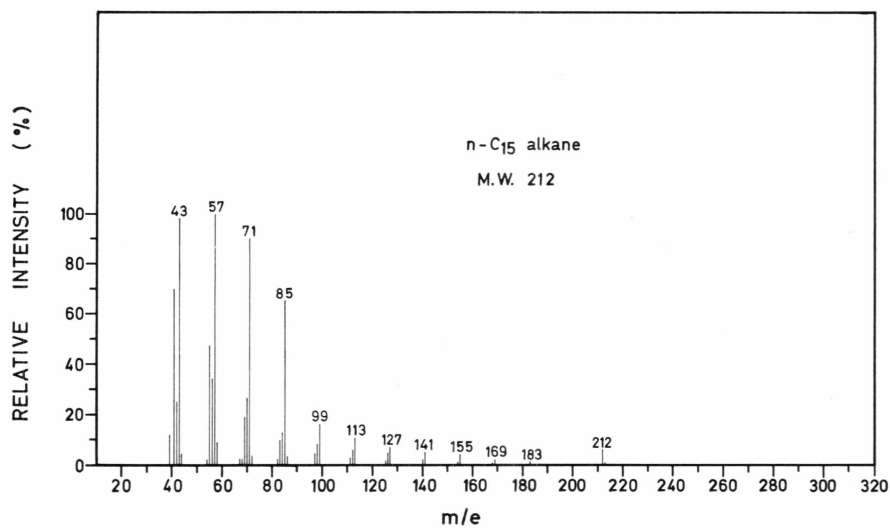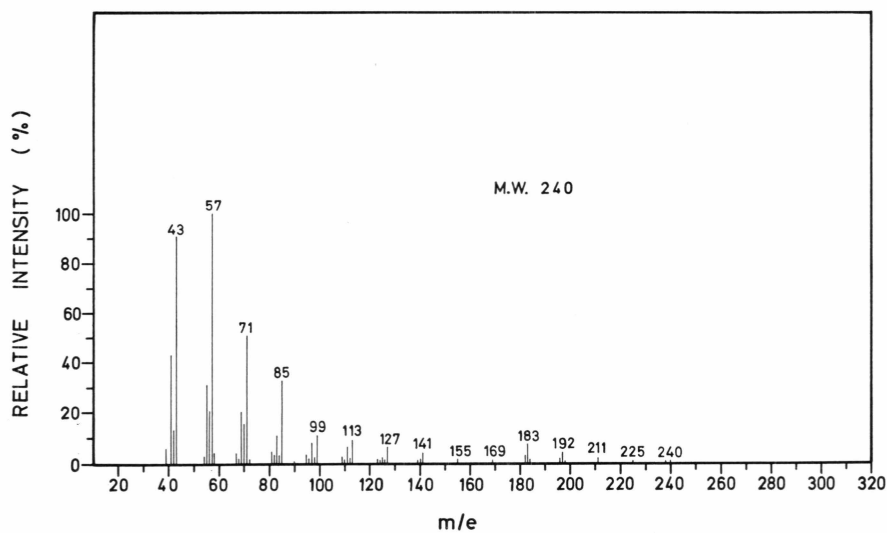Fig. 8. Mass spectrum of n-C_{14}-alkane and a compound with M.W. 196 (an alkyl cyclohexane?) from sample I.
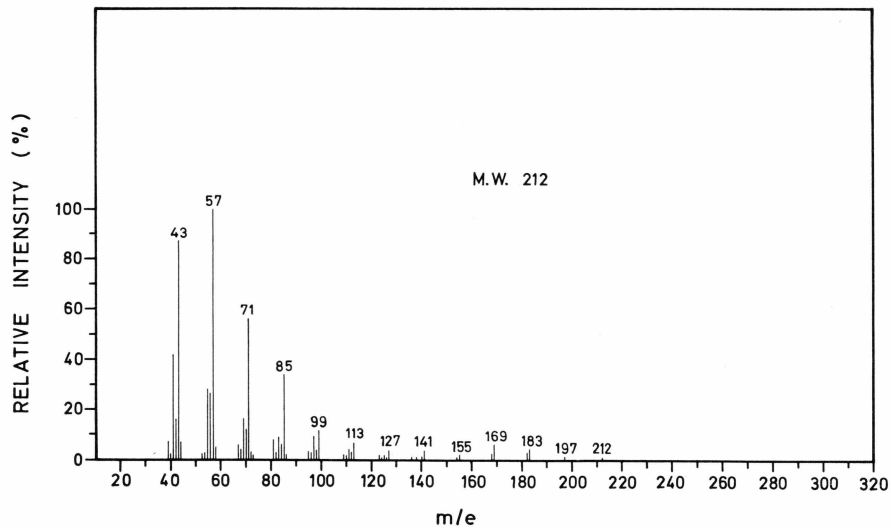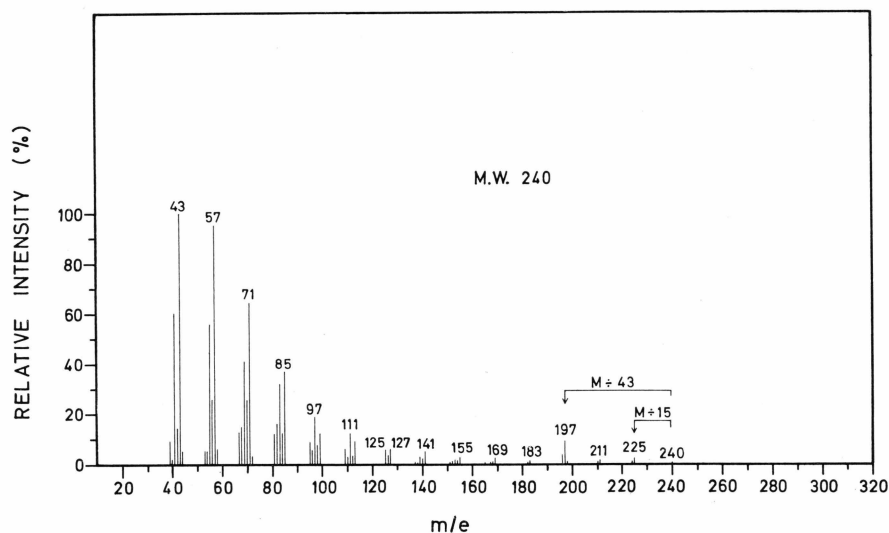

Fig. 9. Mass spectrum of a branched C_{15}-alkane from sample I.

Fig. 10. Mass spectrum of n-C₁₅-alkane from sample I.

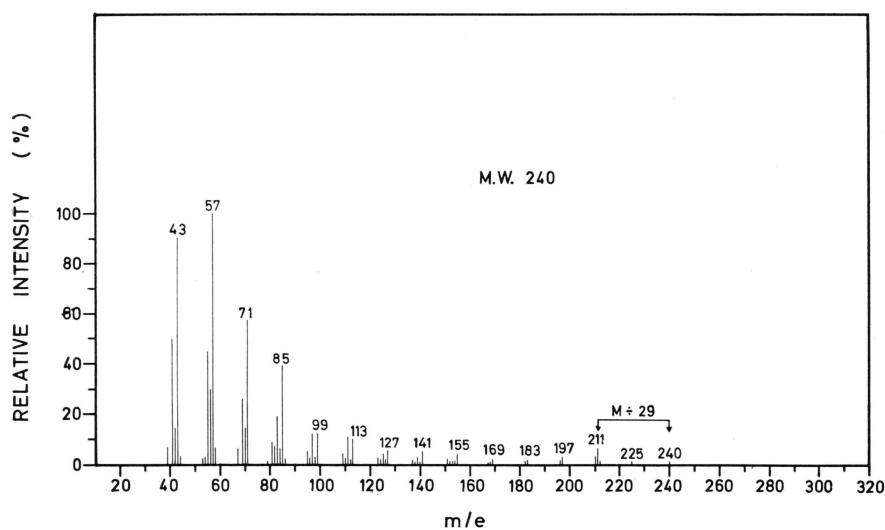Fig. 11. Mass spectrum of a branched C₁₇-alkane from sample I.

Fig. 12. Mass spectrum of a C_{17}-isoalkane from sample I.

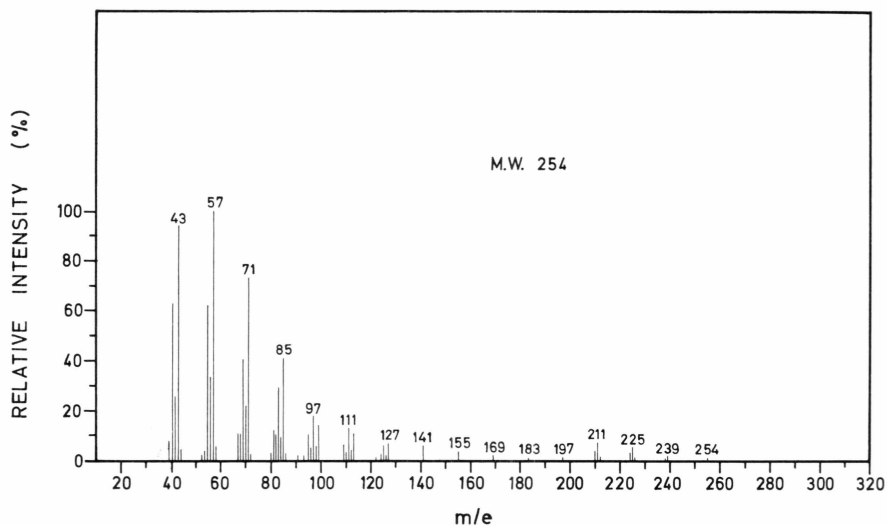Fig. 13. Mass spectrum of a C_{17}-anteisoalkane from sample I.

Fig. 14. Mass spectrum of a mixture of C_{18}-iso- and C_{18}-anteisoalkanes from sample I.
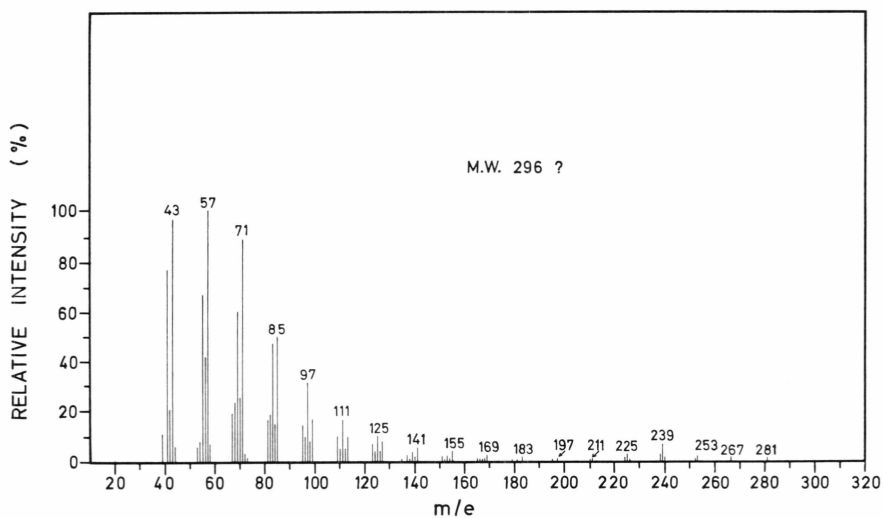
Fig. 15. Mass spectrum of a branched C_{21}-alkane? From sample I.

No prominent parent peak is to be found in the mass spectrum in which fairly high intensities appear at m/e 183, 197, and 211. This points to a branched C_{17}-hydrocarbon from the region before C_{17}-iso- and anteiso-alkanes in the gas chromatogram, indicating a higher branched C_{17}- alkane (fig. 11). The loss of methyl and isopropyl radicals on fragmentation is characteristic of isoalkanes, hence the mass spectrum of peak no. 13 from the gas chromatogram indicates the presence of a C_{17}-isoalkane (fig. 12). The spectrum is very much like that of the C_{17}-isoalkane from the Nonesuch Shale (JOHNS, BELSKY, MCCARTHY, BURLINGAME, HAUG, SCHNOES, RICHTER, and CALVIN 1966, p. 1202).

From the mass spectrum of peak no. 14 (fig. 13) it is seen that a relatively high M-29 fragment occurs, in fact in accordance with that of the spectrum of an anteisoalkane. In the present case it should be the C_{17}-anteisoalkane. The spectrum is fairly consistent with that on p. 1203 in JOHNS et. al. (1966). The fraction no. 16 of the gas chromatogram gives a broad peak with a tendency to form a shoulder and therefore it contains at least two compounds. As the intensities of the m/e 211, 225, and 239 peaks are relatively high it is believed that C_{18}-isoalkane as well as C_{18}-anteisoalkane is present in a mixture (fig. 14).

The intensities (fig. 15) of the m/e 225, 239, and 253 peaks are higher than those of 183, 197, 211, 267, and 281, and the parent peak is lost. The corresponding compound (no. 19 of the gas chromatogram) seems to be a branched alkane with a molecular weight of 296 and is therefore a C_{21}-alkane. The retention value (relative to the normal alkanes) in-dicates the presence of a highly branched hydrocarbon as it appears just before the n-C_{19}-alkane peak of the gas chromatogram. It may be an isoprenoid alkane, although separation by urea inclusion has been carried out.

Gas chromatogram fig. 7

Peak no. 6 of this gas chromatogram exhibits a mass spectrum with M.W. = 168, corresponding to a mono-unsaturated or an alkyl-substituted cyclic (saturated) compound. The relatively high intensities at 41, 55, 69, 83, 97 + $(CH_2)_n$ ... m/e indicate the presence of a dodecane or a hexyl cyclohexane; the mass spectrum is clearly different from that of a saturated non-cyclic compound (fig. 16).

Peak no. 20 is not easily identified on the basis of the mass spec-trum, although it seems to be due to a mixture of a branched C_{16}-alkane (indicated by prominent mass peaks at 43, 57, + $(CH_2)_n$ ....) and an alkyl cyclohexane (a C_{16}-cyclohexyl derivative), in agreement with other prominent intensities at 97, 111, and 125 m/e, and a mass peak of 224 m/e (fig. 17).
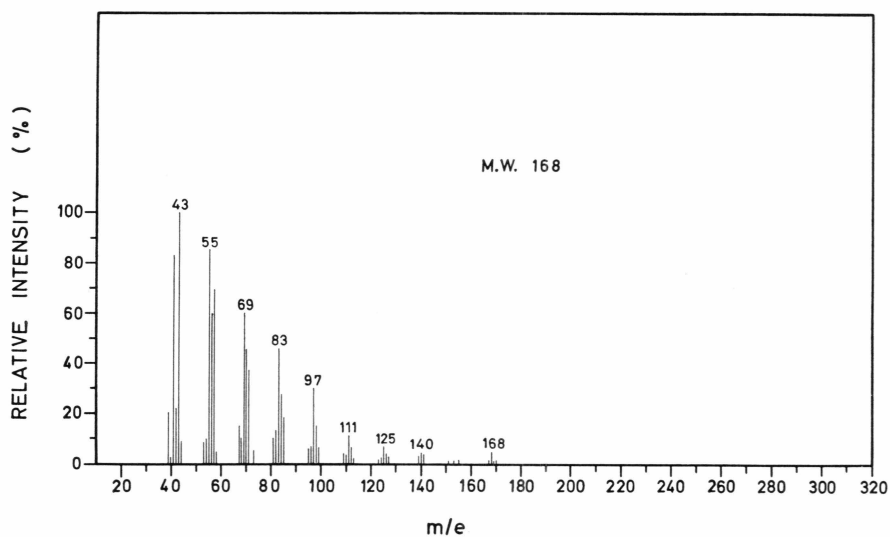
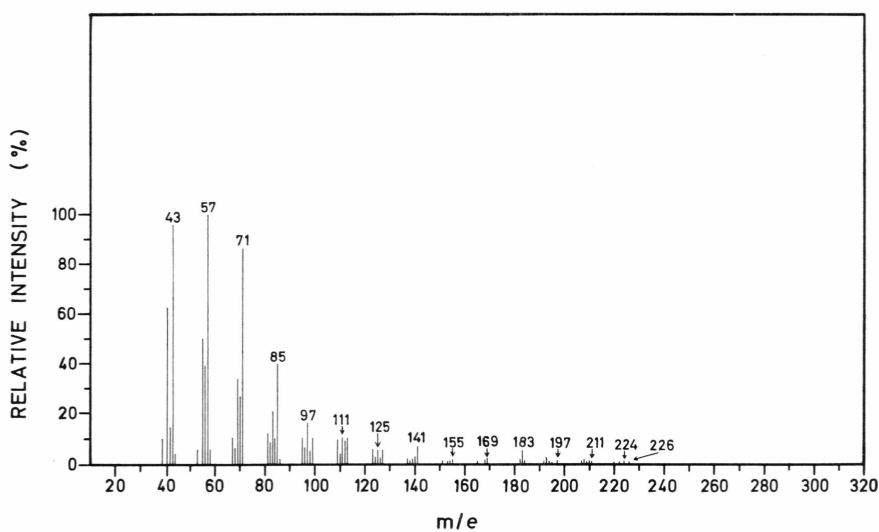Fig. 16. Mass spectrum of an unsaturated or a saturated cyclic compound (M.W. 168). From sample I.

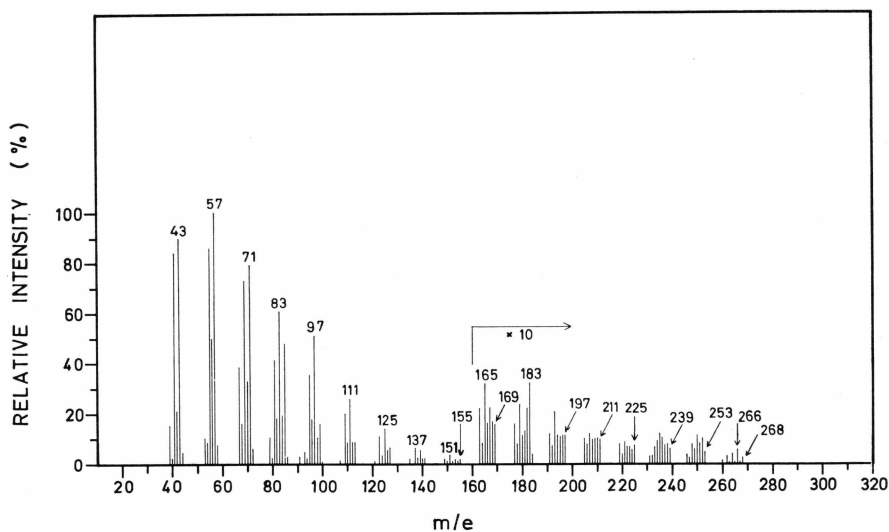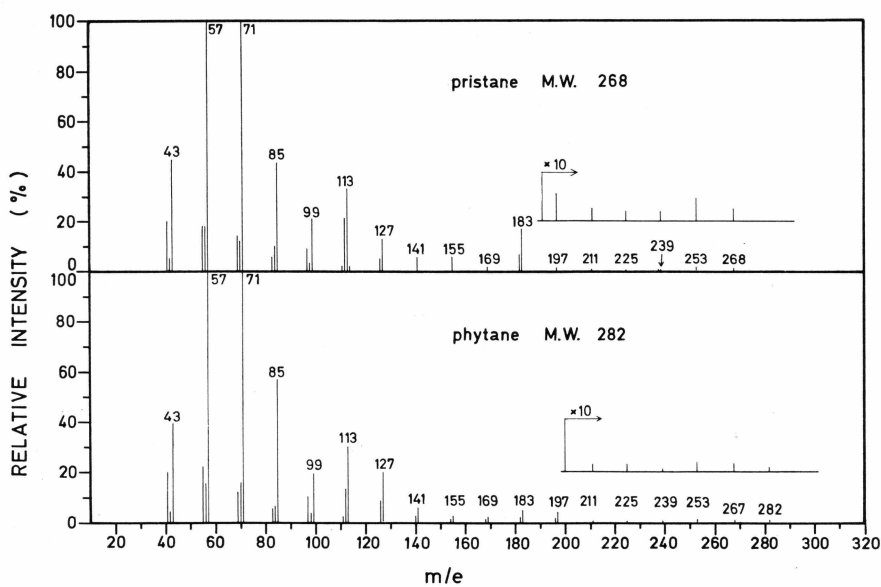Fig. 17. Mass spectrum of a mixture of C_{16}-alkanes M.W. 226 and 224 from sample I.

Fig. 18. Mass spectrum of a mixture of C_{19}-alkanes from sample I. See text.

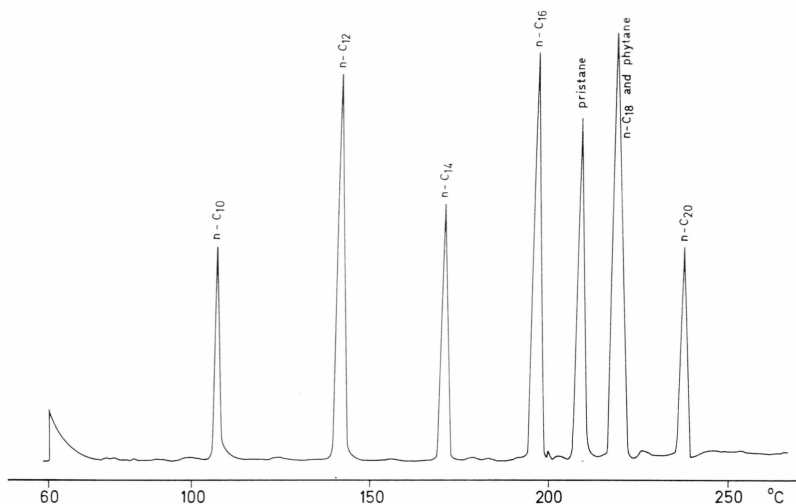Fig. 19. Mass spectra of authentic pristane and phytane.

Fig. 20. Gas chromatogram of an artificial mixture of pristane phytane with C_{10}-, C_{12}-, C_{14}-, C_{16}-, and C_{20} n-alkanes.

When the hydrocarbons increase in number of C-atoms the fragmentation pattern becomes more and more diffuse, but still it is possible to distinguish fairly easily that a branched alkane and a cyclo-alkane are present in no. 31 and fig. 18, as prominent peaks for both types of hydrocarbons appear with varied intensity. From the mass spectrum it is possible to deduce the presence of a branched C_{19}-alkane and an alkyl cyclohexane with 19 C-atoms. This fraction has a retention time in agreement with that of pristane (and n-C_{17}-alkane). However, the fraction is composed of at least two compounds, of which one may be pristane. The intensity of m/e 183 in the mass spectrum is higher than those of m/e 169 and 197, in agreement with the authentic mass spectrum of pristane (fig. 19).

Pristane and phytane are not present to any great extent in the extract. Phytane is to be expected in the no. 34 peak of the gas chromatogram according to the relative retention time in the gas chromatogram (an artificial mixture of pristane and phytane with C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, and C_{20} straight-chain hydrocarbons was run in the gas chromatograph (fig. 20)). From the mass spectrum it is possible to deduce that a hydrocarbon is present showing a M.W. of 282 and peaks corresponding closely in relative intensities to the mass spectrum of authentic phytane.

From the *sample extract II* a hydrocarbon fraction is obtained using the urea inclusion method, which besides straight-chain hydrocarbons, contains the isoalkanes with 14, 15, 16, 17, 18, and 19 C-atoms respectively. Fig. 21 shows the gas chromatogram of this fraction.
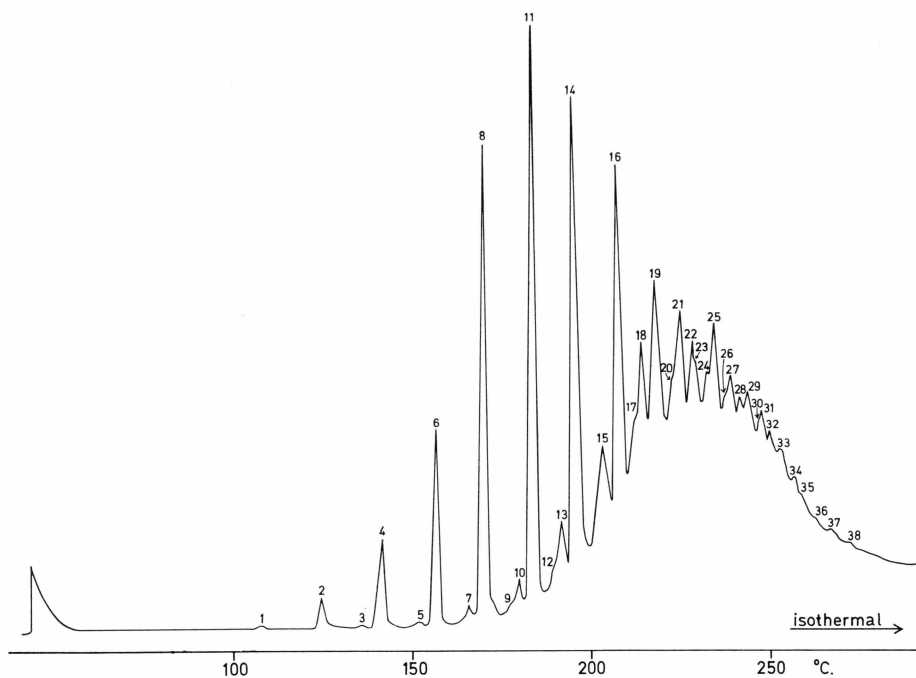
Fig. 21. Gas chromatogram of fraction obtained by urea inclusion from sample II. Straight chain and anteisoalkanes,—1.5 μl. Column, 10 per cent S.E. 30, 2 m, 5° C/min. 60→250° C. Helium flow 30 ml/min.

The mass spectra of these compounds are shown in the figs. 22–27. Fig. 28 is not clearly elucidated but a mixture of C_{20}-isoalkane and C_{20}-anteisoalkane seems to be present.

The greater part (about 75 per cent) of the saturated hydrocarbon fractions from both extractions consists of a mixture of branched and cyclic hydrocarbons according to data obtained from the separation by urea inclusion, the gas chromatograms, the infrared and the n.m.r. spectra, while the straight-chain hydrocarbons plus the iso- and anteisohydrocarbon fraction is about 25 per cent.

From the sample extract II was obtained a fraction of alkyl benzenes of 28 mg (about 7 per cent), and a 30 mg fraction (about 8 per cent) consisting mainly of alkyl naphthalenes.

The mass spectra of the alkyl benzenes show the usual fragments (77, 91, 105, 119 + $(CH_2)_n$ . . . m/e) with varied intensities depending on the substitution patterns of the hydrocarbons of about 60 alkyl benzenes ranging from C_6H_5-C_3 hydrocarbons (with a molecular weight of 120) to C_6H_5-C_{15} hydrocarbons (with a molecular weight of 288).

The substituents in the benzene may be one, two, three or more alkyl radicals and the side chain may be straight or branched.
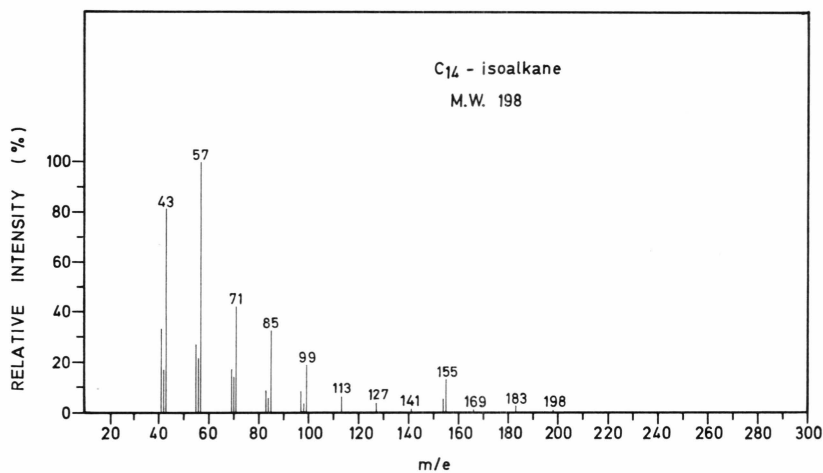
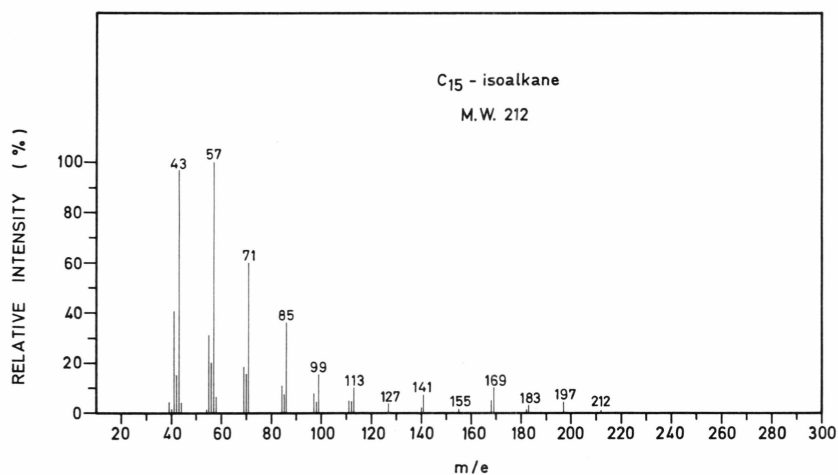Fig. 22. Mass spectrum from sample II.

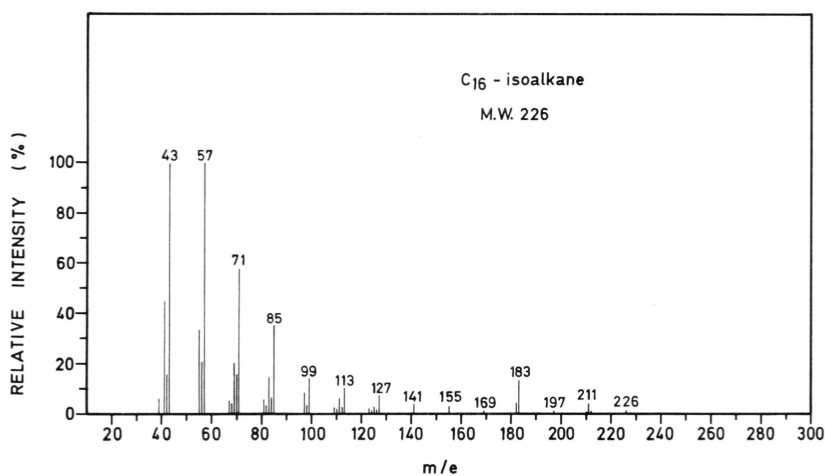Fig. 23. Mass spectrum from sample II.
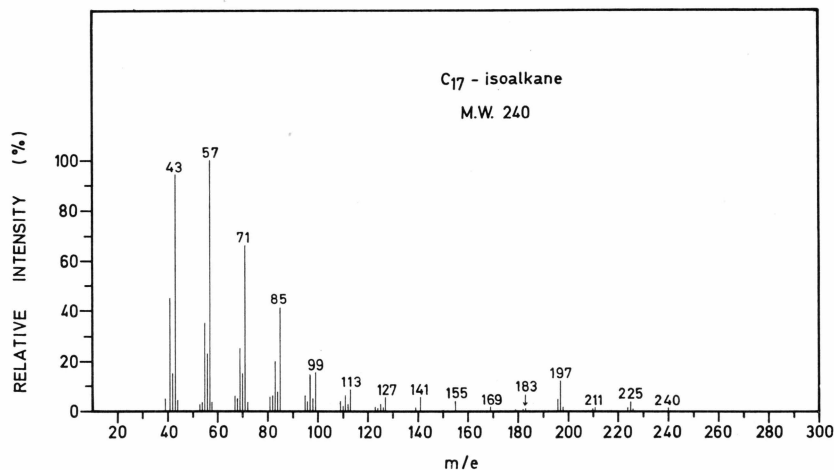

Fig. 24. Mass spectrum from sample II.

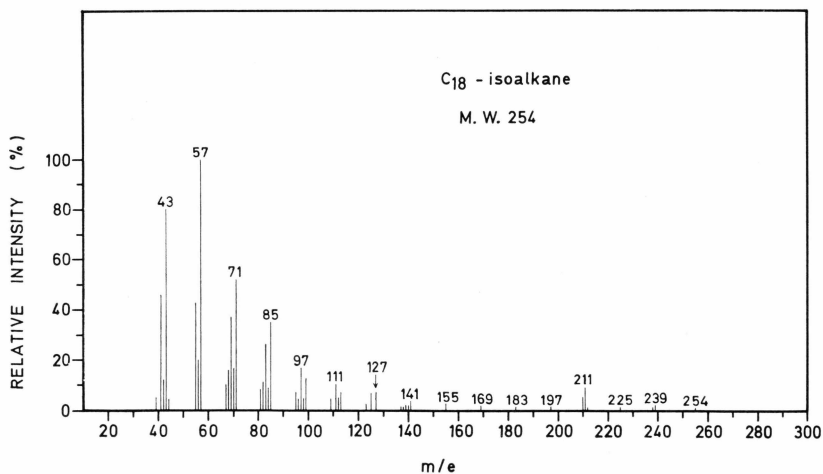Fig. 25. Mass spectrum from sample II.

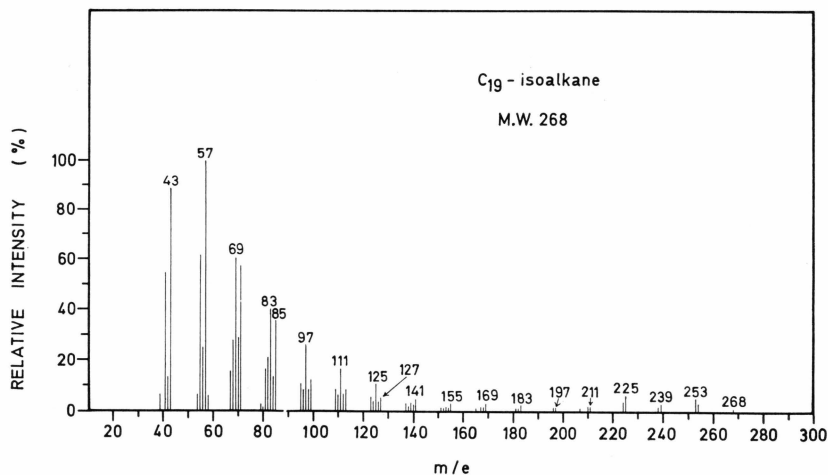Fig. 26. Mass spectrum from sample II.
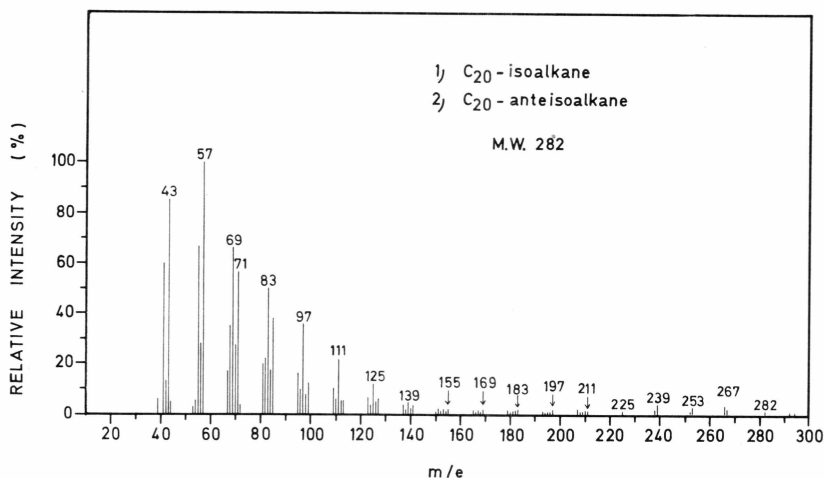

Fig. 27. Mass spectrum from sample II.

Fig. 28. Mass spectrum from sample II.

The naphthalene fractions contain alkyl naphthalenes, identified by the mass spectra and by comparing with the retention times of the corresponding authentic compounds (naphthalene, α- and β-methyl naphthalenes). In the mass spectra of the alkyl naphthalenes peaks 18 m/e higher than the molecular weight of the alkyl naphthalenes are often seen. This is likely to be due to substances containing a CH_2-group and four H-atoms more than the alkyl naphthalenes in question. It is in good accordance with the fact that tetrahydro-naphthalene has a smaller retention time than naphthalene when a 10 % S.E. 30 column is used, which is also the case for other more or less hydrogenated compounds compared to their corresponding aromatics, for instance dihydrophenanthrene and phenanthrene (Raunsgaard Pedersen and Lam 1968). Alkyl naphthalenes and alkyltetrahydro-naphthalenes with one more methylene group may therefore by chance be occurring together in the same peak of the gas chromatogram, and hence give a mixed mass spectrum. Furthermore diphenyl and possibly alkyl diphenyls are present, according to the mass spectra. Compounds with molecular weights of 154 for diphenyl, and 182, 196, and 210 for dimethyldiphenyl, trimethyldiphenyl and tetramethyldiphenyl respectively indicate the presence of such compounds. 3,3'-dimethyldiphenyl, when injected into the gas chromatograph, gives a peak with a retention value in agreement with a peak in the gas chromatogram of the alkylnaphthalene fraction containing a compound with the same molecular weight as the standard.

A high intensity mass peak at 178 m/e is likely due to phenanthrene which is further evidenced by the agreement with the authentic material with regard to the retention values in the gas chromatograms.

Monoterpenoids and fatty acids

The more polar fractions from the developments of the sample extracts I and II in the silica gel columns reveal monoterpenoid substances of the same types from both extracts (ketones and alcohols like for instance camphor and borneol). The molecular weights of the monoterpenoid compounds detected in our investigations are of 152 or 154, or in a single case 150 which is likely due to an aromatic compound of monoterpenoid structure. These molecular data and the mass spectral fragment patterns strongly indicate the presence of a series of about 15 mono-
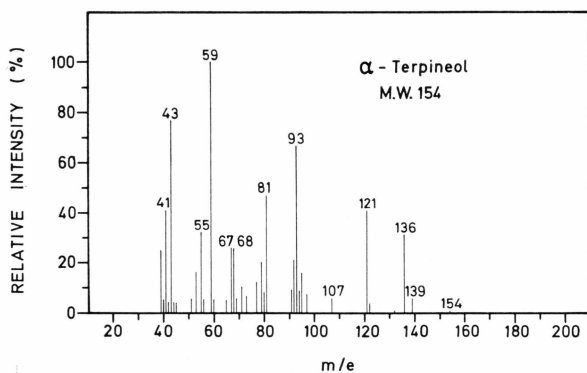

Fig. 29. Mass spectrum from sample II.

terpenoid compounds of which at least six are fairly well established according to their mass spectral resemblance to those described by von Sydow (1963 and 1964). The monoterpenols are characterized by the hydroxyl groups splitting off as H_2O molecules. The retention values in the gas chromatogram of camphor and borneol are consistent with those of the authentic compounds; as the monoterpenoids are more or less well separated by gas chromatography, the identification of the mass spectra is often difficult or impossible. Fig. 29 shows the mass spectrum of a compound suggested to be α-terpineol and in good agreement with that of fig. 10 published by von Sydow (1963), the relative intensities of 68, 81, 93, 107, 121, 136 (M-18) and 139 m/e being fairly consistent with the values in this mass spectrum and with the base peak at 59 m/e in both spectra. The intensity of the molecular peak is of the order of 1 per cent of the base peak while it is missing in the authentic spectrum. Fig. 30 is a mass spectrum very much like that of fig. 12 published by von Sydow (1963) with the base peak at 71 m/e and with the relative intensities of the prominent peaks m/e = 86, 93, 111, 121, 136 (M-18) and 154 (parent peak) in good accordance to the mass spectrum of terpinen-4-ol (von Sydow 1963, fig. 12).
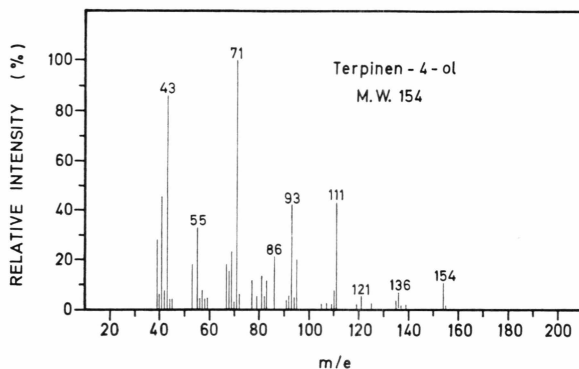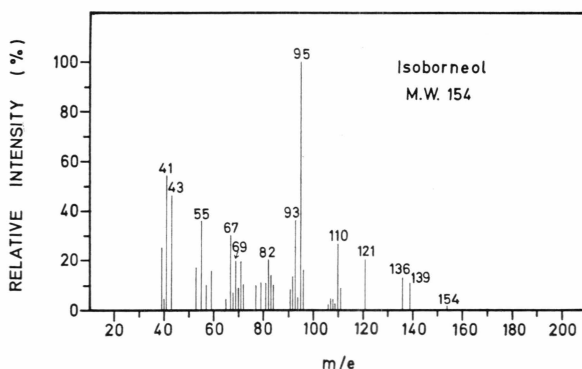
Fig. 30. Mass spectrum from sample II.

Fig. 31. Mass spectrum from sample II.

In fig. 31 is shown the mass spectral fragment pattern of a compound very much like that of fig. 18 (von Sydow 1963). The relative intensities of m/e = 82, 93, 110, 111, 121, 136 (M-18), 139, and 154 (parent peak) and the base peak at 95 m/e agree well with those of von Sydow's fig. 18, which is a mass spectrum of isoborneol. The mass spectrum of borneol is very much like that of isoborneol except that the relative intensities of the prominent fragments m/e = 82, 93, 121, and 136 are lower in the case of borneol; this is seen when fig. 17 is compared to fig. 18 of von Sydow (1963). A mass spectrum (fig. 32) of a fraction in the gas chromatogram exhibits a pattern fitting well with the mass spectrum of borneol.

Fig. 33 shows a mass spectrum with some similarity to that of fenchyl alcohol (fig. 19 in von Sydow 1963). The relative intensities of the m/e = 72, 80, 82, 84, 93, 107, 111, 121, 136, and 154 peaks, which are the prominent peaks of this range, fit well with those in von Sydow's fig. 19, while two rather prominent peaks at m/e = 95 and 139 in the mass spec-
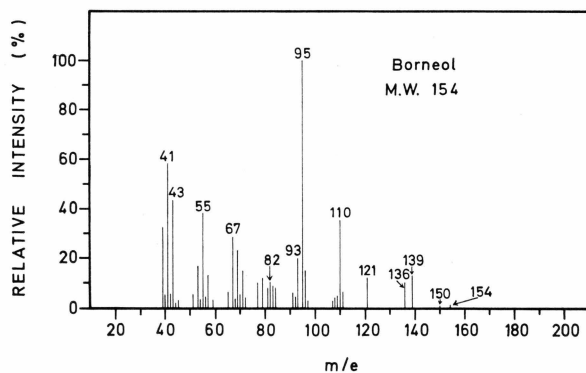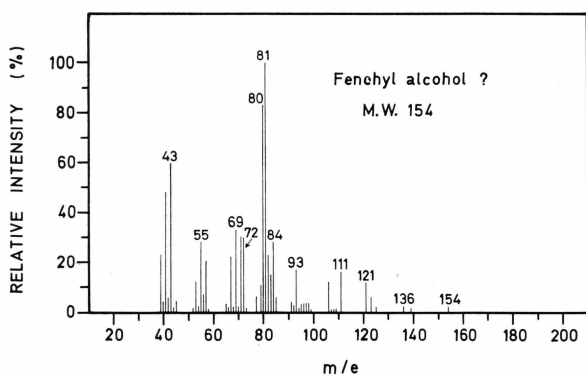
Fig. 32. Mass spectrum from sample II.
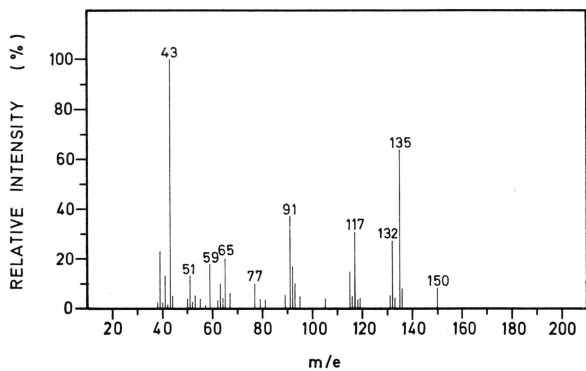

Fig. 33. Mass spectrum from sample II.

Fig. 34. Mass spectrum from sample II.

trum of the authentic material are of very low intensities in fig. 33. The base peak is the m/e = 81 in both spectra.

Fig. 34 is the mass spectrum of a compound with molecular weight 150 indicating an aromatic substance of the monoterpenol type, the
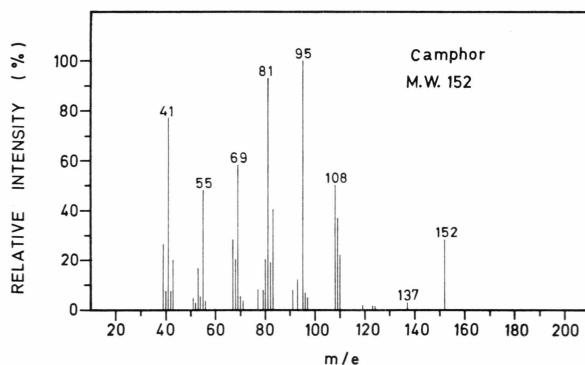
Fig. 35. Mass spectrum from sample II.

aromatic character being further emphasized by the prominent peaks at 135, 132, and 117 m/e which are due to M-15, M-18, and M-18-15 respectively, showing that methyl and hydroxyl groups are split off; the base peak of 43 m/e may be due to the presence of an isopropyl group. The spectrum resembles those of figs. 6, 7, and 8 published by von Sydow (1963) representing thymol, carvacrol, and cuminyl alcohol, although not quite consistent with any of these spectra.

Fig. 35 is a mass spectrum showing a relatively high intensity of the parent peak at 152 m/e (about 30 per cent) and with a fragment pattern very much like that of camphor (von Sydow 1964).

The m/e = 41 and 43 intensities of camphor and the monoterpenols recorded in the present mass spectra are higher than the corresponding 41 and 43 m/e intensities of the recordings of von Sydow; this may be due to differences in instruments.

In the sample extracts I and II there are fatty acids of the homologous series of n-acids from n-C_7H_{15}COOH to n-$C_{17}H_{35}$COOH odd and even, in varied amounts, besides at least two branched $C_{14}H_{29}$COOH compounds, two branched $C_{15}C_{31}$COOH, one branched $C_{16}H_{33}$COOH, and two branched $C_{17}H_{35}$COOH acids. Two unsaturated acids $C_{15}H_{29}$COOH and $C_{17}H_{33}$COOH are present. All these compounds were isolated in mixtures from the silica gel column at the end of the chromatography by final eluting with methanol. From the methanol solution of the fatty acids the methyl esters of the acids were prepared by addition of a catalytical amount of concentrated sulphuric acid. The methyl esters were separated on a S.E. 30 column and the mass spectra recorded. From the data obtained the methyl esters of the above mentioned acids were identified. Some of the most abundant acids have previously been identified as methyl esters in other samples (Raunsgaard Pedersen and Lam 1968; Lam and Raunsgaard Pedersen 1968) and in the present samples from the less
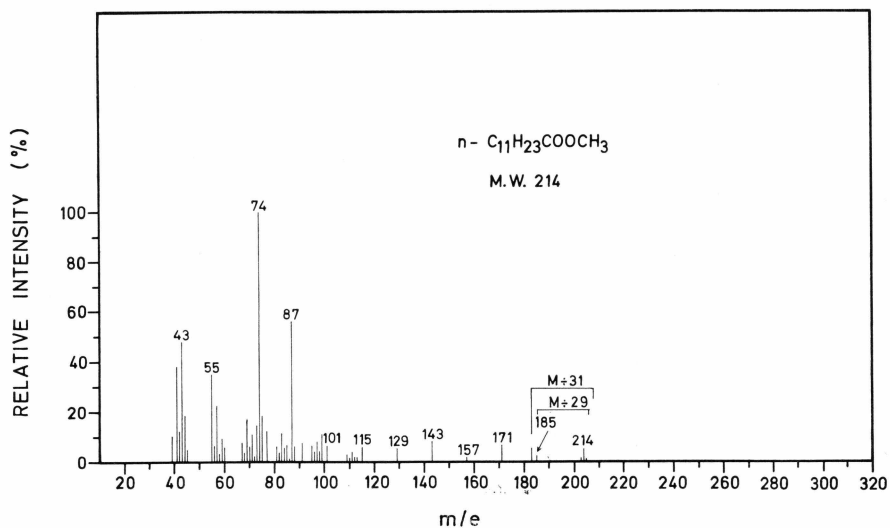
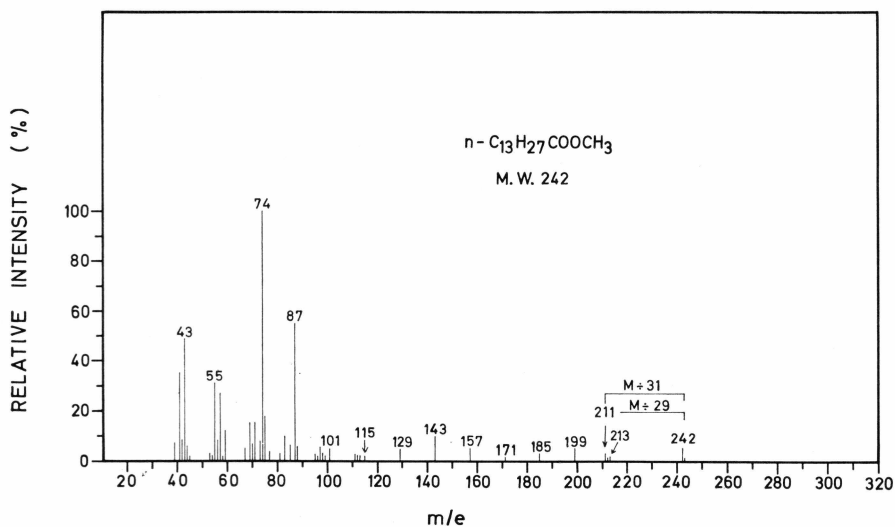Fig. 36. Mass spectrum from sample II (methyl ester of lauric acid).

Fig. 37. Mass spectrum from sample II (methyl ester of myristic acid).
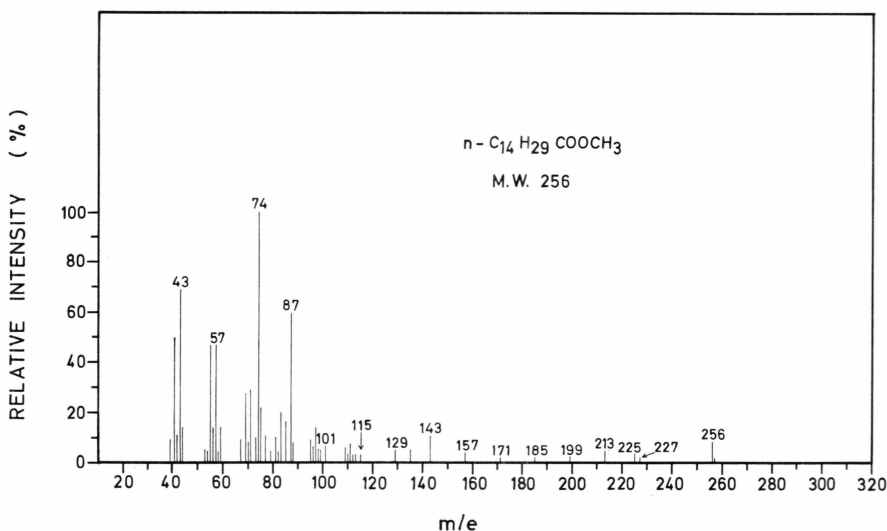
Fig. 38. Mass spectrum from sample II.

polar fractions. This is the case for the esters of lauric, myristic, palmitic and stearic acids.

Figs. 36 and 37 are the mass spectra of lauric and myristic acid methyl esters which are present in almost equal amounts and have the $m/e = M-29$, $M-31$, and $M-43$ fragments characteristic of saturated methyl esters of normal fatty acids.

The relatively large amount of $C_{14}H_{29}COOH$ (fig. 38) is remarkable as uneven acids are not abundant in recent biological material. The $C_{16}H_{33}COOH$ compound is also present in a relatively large amount although not to the same extent as are the $C_{15}H_{31}COOH$ and $C_{17}H_{35}COOH$ acids (palmitic and stearic acids), respectively figs. 39 and 40.

Methyl esters of a C_{16}-mono-unsaturated acid ($C_{15}H_{29}COOH$) and a C_{18}-mono-unsaturated acid ($C_{17}H_{33}COOH$) (figs. 41 and 42) from sample extract I and II have been compared to a methyl ester mixture of a commercial oil containing a high amount of oleic acid (fig. 44) and some palmitoleic acid (fig. 43) and to the data published by HALLGREN, RYHAGE and STENHAGEN (1959). The retention times of authentic methyl esters of fatty acids and of the corresponding compounds from the samples agree well.

Figs. 45 and 46 are gas chromatograms of fractions containing the methyl esters of fatty acids from sample extracts I and II respectively. Peaks no. 6, 11, 14, 18, and 25 of fig. 45 record mass spectra consistent with methyl esters of normal C_{12}-, C_{14}-, C_{15}-, C_{16}-, and C_{18}-acids; peaks no. 17 and 24 record mono-unsaturated acids of chain length C_{16} and C_{18} respectively. Peaks no. 7, 12, and 13 accord with branched acids
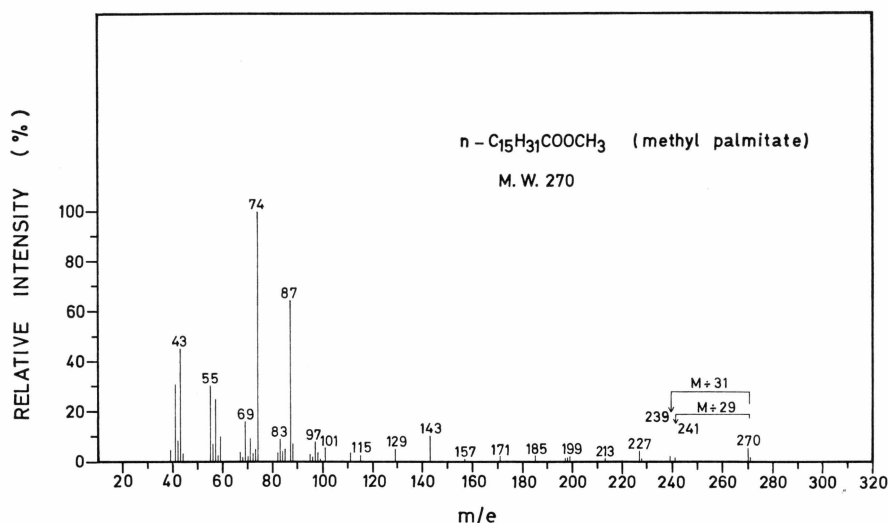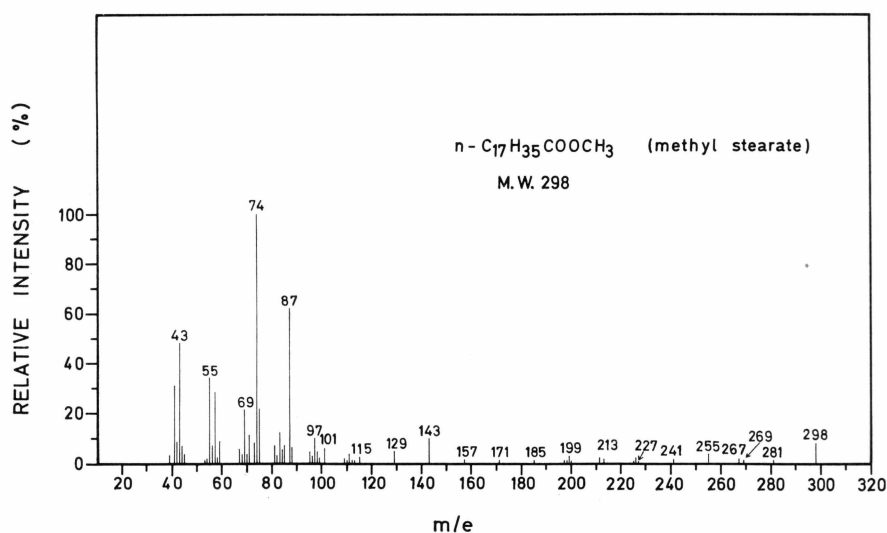
Fig. 39. Mass spectrum from sample II.

Fig. 40. Mass spectrum from sample II.

(mass spectral data). Peak no. 27 of the gas chromatogram shows a fragmentation of a branched methyl ester (C_{20}), not, however, consistent with phytanic acid methylester.

Fig. 46 (from sample II) shows a variety of compounds of which are identified methyl esters of the normal saturated C_8-(5), C_9-(9), C_{10}-(16), C_{11}-(24), C_{12}-(29), C_{13}-(35), C_{14}-(39), C_{15}-(43), C_{16}-(67), C_{17}-(51), and C_{18}-(54) acids, with numbers in parenthesis referring to the numbers in
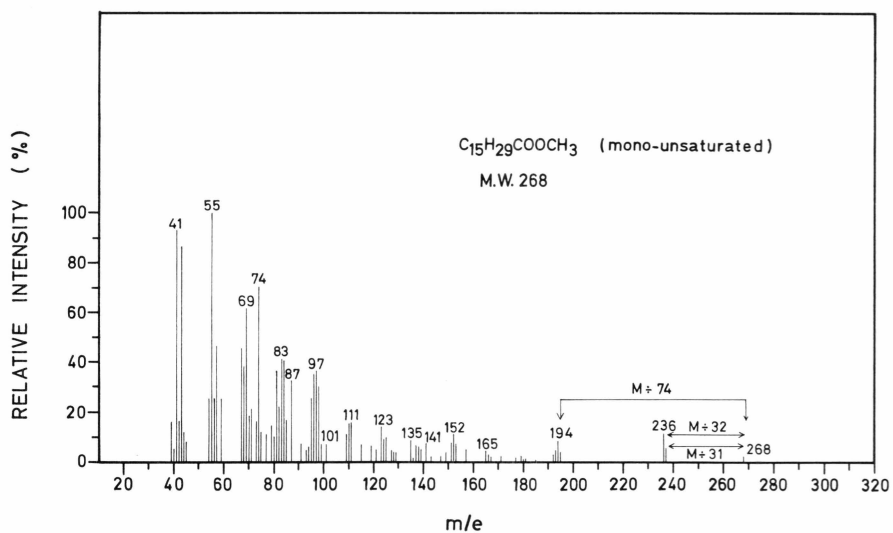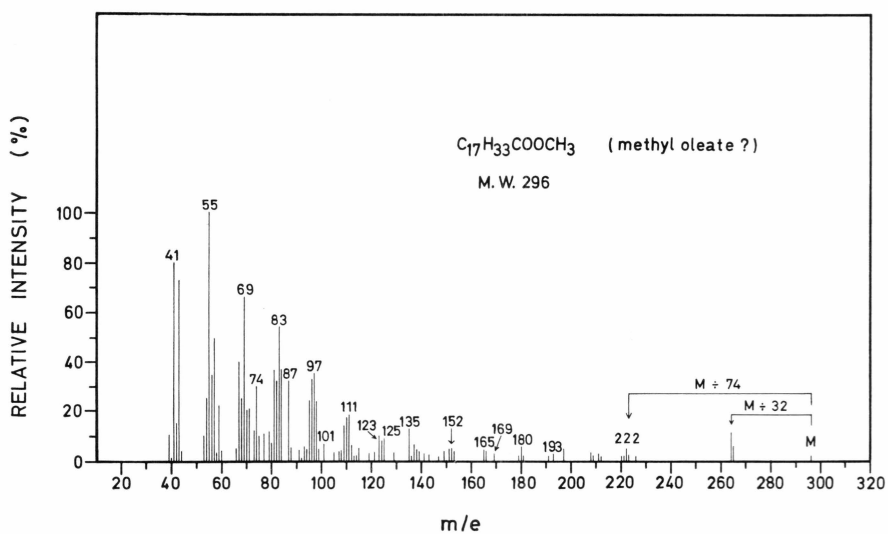
Fig. 41. Mass spectrum from sample II.
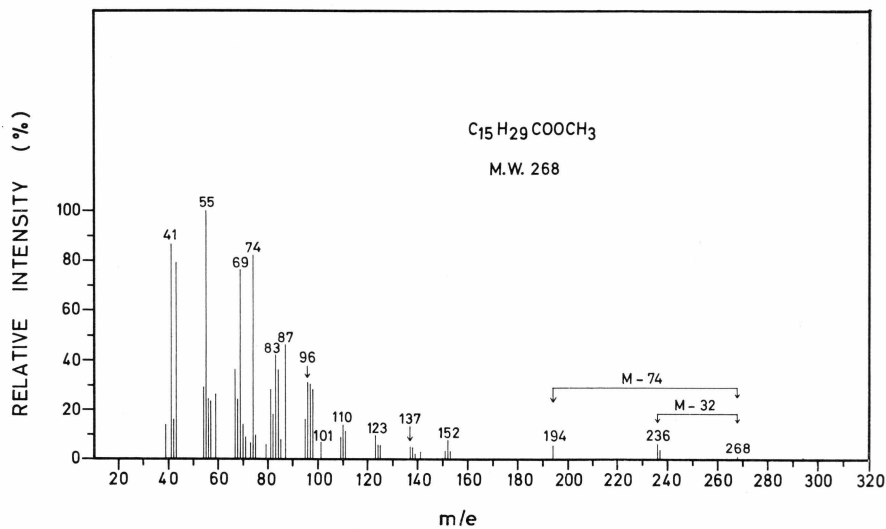

Fig. 42. Mass spectrum from sample II.

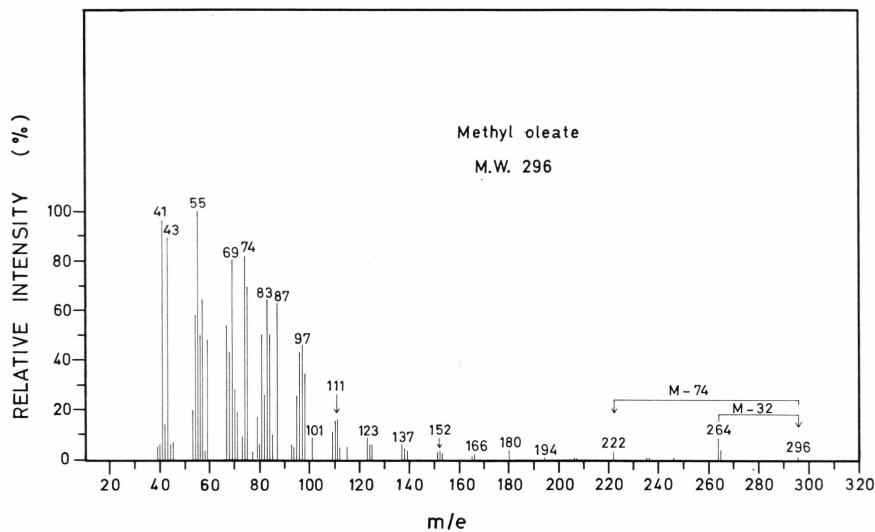Fig. 43. Mass spectrum of mono unsaturated methyl ester of C_{16}-acid.

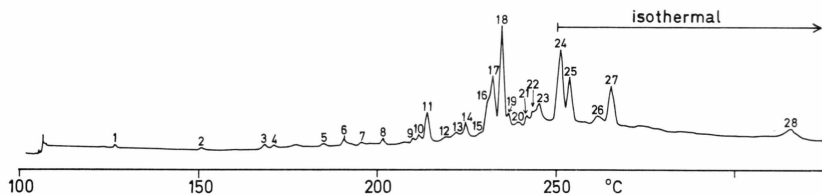Fig. 44. Mass spectrum of methyl oleate (authentic).

Fig. 45. Gas chromatogram of methanol fraction from sample I (the fatty acids as methyl esters). Column, 10 per cent S.E. 30, 2 m. 5° C/min. 100→250° C. Helium flow 30 ml/min.

the gas chromatogram. No. 46 and no. 53 are due to mono-unsaturated C_{16}- and C_{18}-acids respectively. Very minor amounts of branched C_{15}-, C_{16}-, C_{17}- and C_{18}-acids are present in no. 40, 41 (C_{15}-), no. 44, 45 (C_{16}-), no. 49 (C_{17}-) and no. 55 (C_{18}-acids). A very large amount of a terpenoid substance is present (no. 8 of the gas chromatogram). This compound and several others from the polar fractions have not been identified, whereas the methyl esters are easily identified by means of their characteristic mass spectra (high intensities of m/e = 74, 87, 101, 129, 143, 143 + $(CH_2)_n$, and M-31 and M-29).
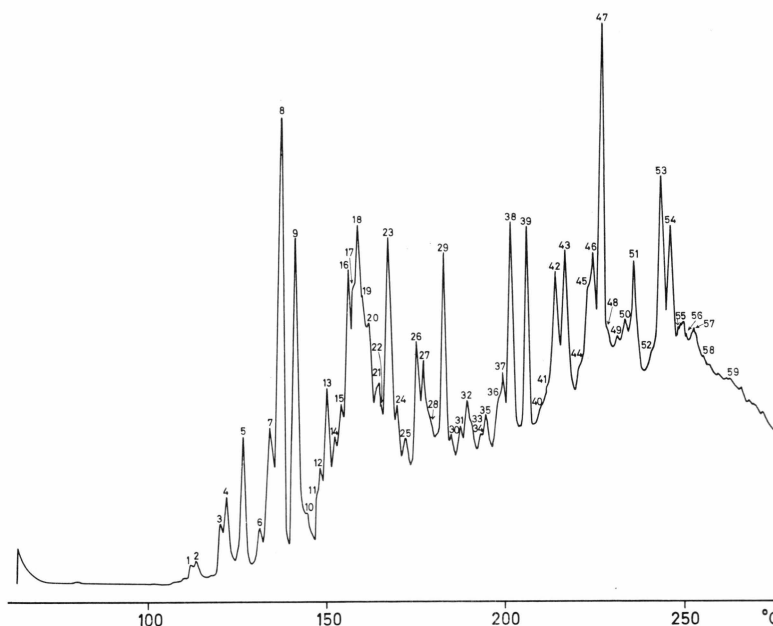

Fig. 46. Gas chromatogram of methanol eluate from sample extract II (the fatty acids as methyl esters). Column, 10 per cent S.E. 30, 2 m. 5° C/min. 60→250° C.

CONCLUSION

Examinations of organic compounds extracted from large samples of a coal-graphite from the low-metamorphic part of the Ketilidian series of Grænseland have been carried out.

Although a perfect separation of the single compounds was not achieved, the physical methods available give valuable information. The primary separation by column chromatography followed by urea inclusion separation of straight-chain hydrocarbons and iso- and anteisohydrocarbons from higher branched and cyclic hydrocarbons, gives fractions suitable for combined gas chromatography and mass spectrometric measurements. The types of compounds are fairly satisfactorily identified when the suggested hydrocarbons agree with co-injected standards in retention times, and when the mass spectra also agree with those of the standards. By these methods the single compounds of the normal alkanes were clearly identified. The presence of alkyl benzenes was also determined by their mass spectra; the identification of naphthalene and single alkyl naphthalenes is quite clear from the gas chromatographic and mass spectral data. Similarly single monoterpenoids and esters of fatty acids have been identified by the agreement in retention values and mass spectral data between standards and sample fractions.

The organic compounds identified, together with the fossils, indicate that there was biological activity in this area nearly 2000 m.y. ago, and the thickness of the coal-graphite shows that this activity has been considerable.

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