

Characterization of Tertiary Catalan lacustrine oil shales: Discovery of extremely organic sulphur-rich Type I kerogens

JAAP S. SINNINGHE DAMSTÉ,* F. XAVIER C. DE LAS HERAS,† PIM F. VAN BERGEN,* and JAN W. DE LEEUW*
Organic Geochemistry Unit, Delft University of Technology, de Vries van Heystplantsoen 2, 2628 RZ Delft, The Netherlands

(Received February 4, 1992; accepted in revised form July 5, 1992)

Abstract—The kerogens of three Tertiary Catalan lacustrine oil shales were analyzed by light microscopy, flash pyrolysis-gas chromatography-mass spectrometry, and bulk composition methods (elemental analysis, Rock Eval pyrolysis). Two of the three kerogens (Ribesalbes and Campins) are extremely rich in organic sulphur (atomic S_{org}/C ratio > 0.04) and hydrogen (atomic ratio H/C ratio > 1.5) and are, consequently, classified as Type I-S kerogens. Very characteristic distribution patterns of flash pyrolysis products (e.g., alkan-9- and -10-ones, alkadienes) of the Ribesalbes kerogen revealed that it is predominantly composed of fossilized organic matter of the freshwater alga *Botryococcus braunii*. These two findings demonstrate that sulphurization of organic matter may also occur in lacustrine sediments provided that sulphate is supplied by external sources. Data on the third kerogen sample (Cerdanya) suggest that the freshwater alga *Pediastrum* may contain a (partly) aromatic biomacromolecule that is selectively preserved upon diagenesis. These findings testify to the large variability in palaeodepositional conditions in lacustrine environments. A comparison of the biomarker composition of the extract of the Ribesalbes oil shale with the kerogen composition indicate that biomarkers often cannot be used to assess the major sources of organic matter in such settings. A similar conclusion can be drawn from a comparison of literature data concerning the Messel Oil Shale.

INTRODUCTION

IN RECENT YEARS THERE is a growing interest in lacustrine source rocks and crude oils generated from them (e.g., FLEET et al., 1988; KATZ, 1990). In certain geographical areas, lacustrine source rocks account for a significant part of the oil reserves. For example, lacustrine source facies are responsible for 95% of the hydrocarbon production of China (HALBOUTY, 1980). The classical example of a lacustrine oil shale is the Green River Formation. This particular oil shale contains hydrogen-rich (atomic H/C ratio is ca. 1.5), low sulphur kerogen representing the Type I kerogen (ESPITALIE et al., 1977; TISSOT and WELTE, 1984). A number of other well-known lacustrine oil shales (e.g., Messel shale, Germany; Autun boghead, France; Tasmanites, Coorongites, and Torbanites from various geographical locations) also contain Type I kerogen (TISSOT and WELTE, 1984). This has brought about a widespread belief that Type I kerogens are typical of lacustrine source rocks in general (TALBOT, 1988). However, Rock Eval data of source rocks from various Chinese and African lakes (YANG et al., 1981; TALBOT, 1988; KATZ, 1988) indicate that Type II and III kerogens are often present in lacustrine sediments as well. Large differences in the composition of organic matter in lacustrine sediments are to be expected, considering the large variations in depositional conditions in lakes (KELTS, 1988). The kerogen type can also vary within a basin: YANG et al. (1985) report that in

the case of the Songliao Basin there is a gradation from Type III organic matter at the edge of the lake sequence to Type I in the central deep-lake facies.

Most undegraded oils generated from lacustrine source rocks are extremely paraffinic and waxy (POWELL, 1986). This observation was perplexing because the most aliphatic kerogens from which these waxy oils were generated formed in the lake centres, remote from the sources of terrestrial higher plant organic matter which was considered to be the precursor for waxy oils (POWELL, 1986; KELTS, 1988). Recent findings have indicated that this apparent paradox could be explained by the fact that many common lacustrine algal species (e.g., *Botryococcus braunii*, *Tetraedron minimum*) contain cell walls comprised of highly aliphatic biomacromolecules, called algaenans, which could be selectively preserved in the fossil record (for a review see DE LEEUW and LARGEAU, 1993). Kerogens which are comprised substantially of these algaenans are highly aliphatic and yield waxy oils upon thermal stress. Extremes in this respect are Coorongites and Torbanites, which are almost exclusively composed of remains of the outer cell walls of *B. braunii* (LARGEAU et al., 1986; DUBREIL et al., 1989), and a very common facies in the Messel oil shale, which consists almost exclusively of cell wall remains of the green microalga *T. minimum* (GOTH et al., 1989).

The finding that the organic matter of the Messel Oil Shale is mainly derived from the alga *T. minimum* seems to contradict other conclusions on the origin of this oil shale. ROBINSON et al. (1989) concluded from a study of the extractable lipids that the major sources of organic matter in the Messel oil shale were dinoflagellates and bacteria, especially cyanobacteria. FREEMAN et al. (1990) studied the carbon isotopic composition of individual branched and cyclic aliphatic hydrocarbons and demonstrated the presence of aerobic meth-

* Present address: Netherlands Institute of Sea Research (N102), PO Box 59, 1790 AB Den Berg, Texel, The Netherlands.

† Present address: Escola Universitària Politècnica de Manresa, UPC, Av. Bases de Manresa 61-73, 08240 Manresa, Catalonia, Spain.

‡ alk-1-en- ω -ones means alkan-9-ones possessing a terminal double bond.

anotrophs and other bacteria in Lake Messel, which in their view was at variance with the results obtained by GOTH et al. (1989). It should be recognized, however, that the extractable organic matter of the Messel oil shale represents at best a few percent of the total organic matter, whilst the kerogen represents often 95% or more. Furthermore, the biomarker fractions of the solvent extract studied by ROBINSON et al. (1989) and FREEMAN et al. (1990) represent only a small part of the total extract. Hence, their conclusions with respect to the bulk of the organic matter (e.g., sources of organic matter) probably suffer from a severe bias. This demonstrates that interpretation of biomarker data with respect to major sources of organic matter should be performed with great caution.

To validate and evaluate the large differences in palaeo-depositional conditions in lakes it is necessary to study the molecular composition and origin of kerogen of a wide variety of lacustrine source rocks. In this paper, we report on the morphology and chemical structure of kerogens from three lacustrine basins belonging to the most southern part of the European rift system (Catalonia, Eastern Iberian). In this rift system, fault-bounded basins developed in which many lacustrine oil shale deposits have been deposited from late Eocene to late Miocene times (ANADÓN et al., 1989). Two of these lacustrine basins contain kerogen with an unprecedented high amount of organic sulphur and lend further support to the large variability in palaeodepositional conditions in lacustrine environments.

SAMPLES: SOURCE AND DESCRIPTION

Ribesalbes oil shale was deposited during the Middle Miocene (Serravallian). The sample investigated is a laminated dolostone obtained from an outcrop of Unit B (ANADÓN et al., 1989) basically composed of Mg-poor dolostones. Very well preserved delicate fossils (e.g., insects, amphibian, higher plant leaves), the absence of benthonic fauna, and the lamination of the dolostones suggest an anoxic depositional environment and stratification of waters during their formation. The high sulphate content of the water was due to the weathering of a surrounding Triassic (Keuper) evaporitic gypsum (ANADÓN et al., 1989).

Campins oil shale was deposited during the Late Oligocene (Stam-pian). It is a laminated mudstone with minor dolostones (less than 50%). It was sampled from an outcrop of the lacustrine unit. It has similar characteristics to the Ribesalbes basin such as well preserved fossils and good lamination, suggesting a similar depositional environment. Sulphate-rich waters originated from weathering of pyrite of granitoids from the surrounding area (ANADÓN, 1986).

Cerdanya oil shale was deposited during the Late Miocene (Tortonian). It is a mudstone which is considered an anapaite vein because of its high amount of phosphorous (15.0% P_2O_5) that appears in the diatomaceous lacustrine unit. Rare bioturbation and fine laminations, as well as good fossil preservation, are also the main characteristics of this sedimentary unit, which is similar to the Eocene Messel Oil Shale (DE LAS HERAS et al., 1989).

EXPERIMENTAL

Preparation of Samples

Lumps of rock were washed with dichloromethane (DCM), freeze dried, powdered in a disc mill, and extracted for 36 h in a Soxhlet apparatus with DCM methanol (2:1 v/v). The extracted and dried powder was decarbonated using 5 N hydrochloric acid to remove carbonates, washed 4 times with bi-distilled water and re-extracted ($\times 3$) with DCM and methanol using ultrasonication. The decarbonated samples were dried in a vacuum stove at 30°C and used for pyrolysis. For elemental analysis, the rocks were demineralized with HCl/HF under standard conditions (DURAND, 1980). For palynol-

ogical investigation, the minerals present in the powdered rock samples were removed by HCl (30%) and HF (38%). The washed and dried residues were subjected to ultrasonical sieving over a 10 μm sieve (VAN BERGEN et al., 1990). Slides for microscopy were prepared in DEPEX (BDH Limited) to prevent fluorescence of the mounting medium. The samples were examined with normal transmitted light and under incident blue light. The assessment of the different types of organic matter was performed according to VAN BERGEN et al. (1990).

Curie Point Pyrolysis-Gas Chromatography-Mass Spectrometry

Kerogens were thermally degraded using a Curie point pyrolyser (FOM 3-LX) and ferromagnetic wires with a Curie temperature of 610°C. The pyrolyser was directly connected to a gas chromatograph (Hewlett-Packard 5890) in tandem with a magnetic sector mass spectrometer (VG-70S) by direct insertion of the capillary column into the ion source. The gas chromatograph was fitted with a fused silica capillary column (25 m \times 0.32 mm i.d.) coated with CP Sil-5 CB (film thickness 0.40 μm) in an oven that was temperature programmed from 0°C to 300°C at 3°C min⁻¹. The oven was first held at 0°C for 5 min and finally at 300°C for 15 min. Helium was used as carrier gas. The mass spectrometer was set at an ionizing voltage of 70 eV, and operated at a cycle time of 1.8 sec over the mass range m/z 40–800 at a resolution of 1000. Data acquisition was started 1 min after pyrolysis.

Desulphurization of Macromolecular Aggregates

The Ribesalbes oil shale was extracted ultrasonically, using mixtures of methanol and dichloromethane. The extract was fractionated into apolar and polar fractions; the latter fraction was desulphurized with Raney Ni and the hydrocarbons obtained were isolated (KOHENEN et al., 1991b).

RESULTS

Bulk Geochemical Data

Elemental analysis of the isolated kerogens from the samples studied revealed that the Ribesalbes and Campins kerogens are highly aliphatic (high to very high atomic H/C ratios) and can be classified as Type I kerogens (Table 1). The Cerdanya kerogen has a lower atomic H/C ratio and a much higher atomic O/C ratio and would plot as an immature Type II/III kerogen in a van Krevelen diagram. It is difficult to precisely determine the amount of organic sulphur in kerogen because of the intimate association of pyrite with the organic matter (DURAND and MONIN, 1980). By measuring the amount of iron present in the kerogen concentrate and assuming that all the iron is pyritic, an estimation of the content of inorganic sulphur is obtained and, thus, by simple subtraction, so is an estimation of the organic sulphur content. This exercise revealed that both the Ribesalbes and Campins kerogens are extremely rich in organic sulphur. In the case of the Ribesalbes kerogen, the value obtained for the atomic S_{org}/C ratio must be considered accurate because the amount of iron present is low, which is in agreement with the low ash content (<1 wt%). In the case of the Campins kerogen, the procedure for determining the organic sulphur content described above seems to be problematic since the estimated amount of pyrite present (19.0 wt%) is higher than the measured ash content (13.3 wt%). As a consequence, the reported atomic S_{org}/C ratio is a minimum value. Nevertheless, this minimum value, just as the value for the Ribesalbes kerogen, is very high for Type I kerogens, since values larger than 0.02 (ORR and SINNINGHE DAMSTÉ, 1990; TISSOT and WELTE, 1984) have not been reported, to the best of our

Table 1. Elemental composition of the isolated kerogens and TOC and Rock Eval data for the extracted whole rocks

	C (wt %)	H (wt %)	N (wt %)	O (wt %)	S _{tot} (wt %)	Fe (wt %)	ash (wt %)	H/C	O/C	S _{org} /C	TOC (wt %)	HI	OI	T _{max}
Ribesalbes	69.1	10.35	0.70	8.9	10.5	0.21	<1.0	1.80	0.096	0.056 ^a	10.3	1001	35	434
Campins	55.2	7.06	1.49	9.1	17.6	8.85	13.3	1.53	0.123	0.051 ^b (0.089) ^c	6.0	823	26	434
Cerdanya	55.1	6.03	1.68	17.0	8.0	7.05	12.1	1.31	0.231	0.000 ^b (0.020) ^c	1.3	108	162	440

^a assuming that all the iron is present as pyrite.

^b as ^a, however the assumed amount of pyrite (wt %) is in that case higher than the ash content.

^c assuming that S_{inorg} (wt %) = Fe (wt %) - ash (wt %).

knowledge. In the Cerdanya kerogen the organic sulphur content is low since most of the sulphur is present as inorganic sulphur. The determination of the organic sulphur content suffers from the same problems as experienced with the Campins kerogen (Table 1).

Rock Eval data (Table 1) are in agreement with the elemental composition data. Both the Ribesalbes and Campins kerogens have high hydrogen indices (HI), testifying to their highly aliphatic nature. Their oxygen indices (OI) are low. The hydrogen index of the Cerdanya kerogen is much lower and the oxygen index much higher than those of the other two kerogens. The T_{max} values are in the range of immature kerogens.

Palynology

Three different organic matter types were observed in the visible organic particles, from which the relative amounts of each type were estimated (Table 2).

Ribesalbes

The dominant acid-resistant organic matter type recognized with normal transmitted light in the Ribesalbes sample is yellow-brown structureless organic material (SOM). Transparent SOM is a major constituent. In addition, few *Botryococcus* spp. and bisaccate pollen grains were recognized. Under incident blue light, the organic material displays a very bright white/yellow to yellowish brown fluorescence. The fluorescence is remarkably similar to the fluorescence of the recognizable *Botryococcus* spp. present in the sample. Furthermore, it is noteworthy that separate particles recognized with normal transmitted light are composed of clusters of organic material when examined under incident blue light.

Cerdanya

The dominant organic matter type is the multicellular freshwater alga *Pediastrum* sp., which is difficult to detect

Table 2. Summary of palynological results

	Ribesalbes	Campins	Cerdanya
Palynomorphs			
<i>Botryococcus</i> spp.	r ^a	-	r
<i>Pediastrum</i> spp.	-	-	60%
Pollen grains	r	-	5%
Structureless palynodebris			
Transparent SOM	20%	-	10%
Yellow-brown SOM	80%	20%	25%
Dark brown SOM	-	80%	-
Average fluorescence			
Intensity	very bright	moderate	weak
Colour	white/yellow to yellowish brown	yellow to dark brown	yellow/green to brown

^a r = rare

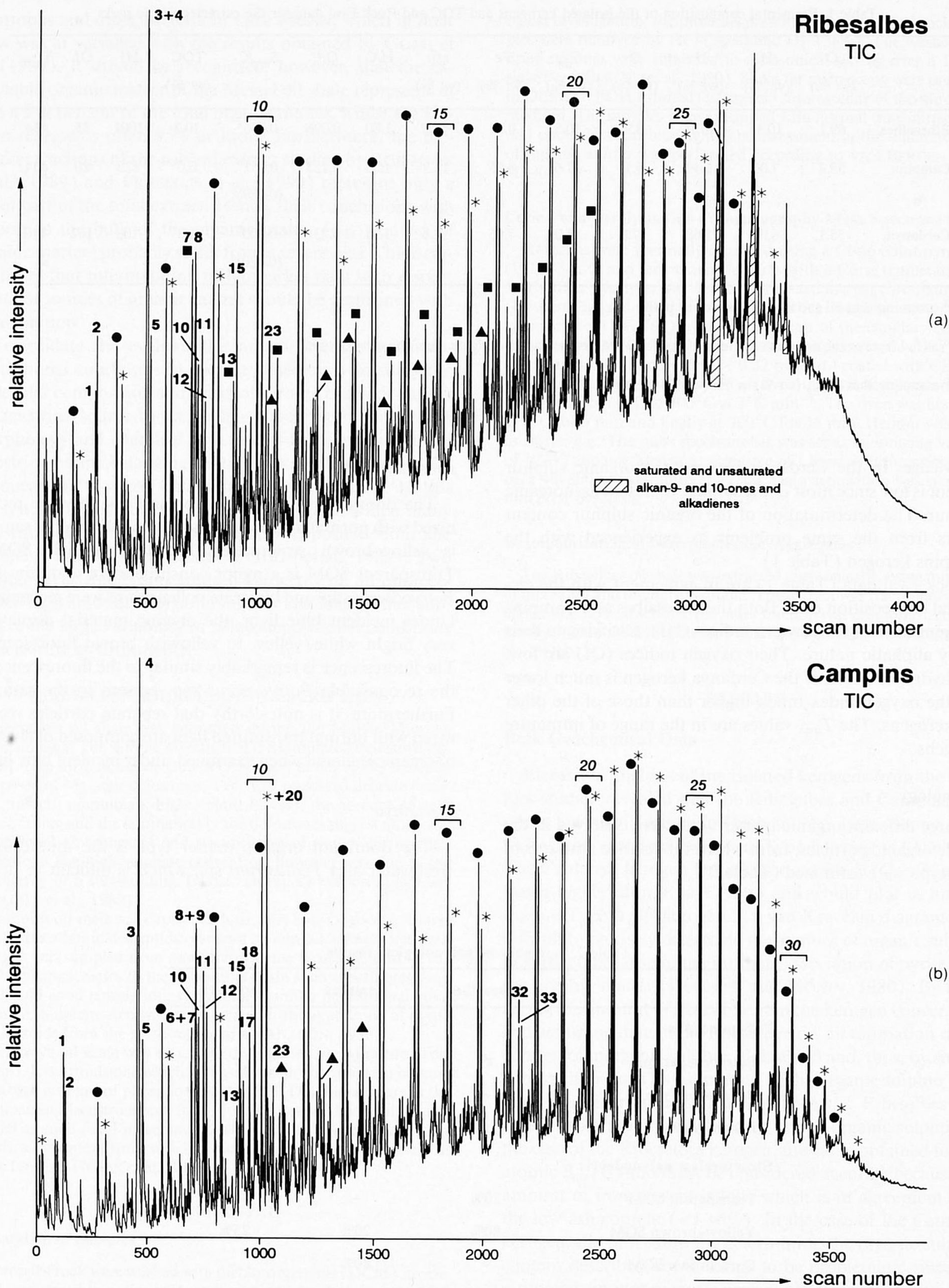


FIG. 1. (a) Total Ion Current (TIC) trace of the flash pyrolysate (Curie temperature 610°C) of the kerogen of the Ribesalbes oil shale. Filled circles and stars indicate the homologous series of *n*-alk-1-enes and *n*-alkanes, respectively. Their number of carbon atoms is indicated with italic numbers. Filled squares and triangles indicate homologous series of 2-alkylthiophenes and alkylbenzenes, respectively. Bold numbers indicate compounds listed in Table 3. (b) TIC trace of the flash pyrolysate (Curie temperature 610°C) of the kerogen of the Campins oil shale. Peak assignments are as in Fig. 1a. (c) TIC trace of the flash pyrolysate (Curie temperature 610°C) of the kerogen of the Cerdanya oil shale. Peak assignments are as in Fig. 1a.

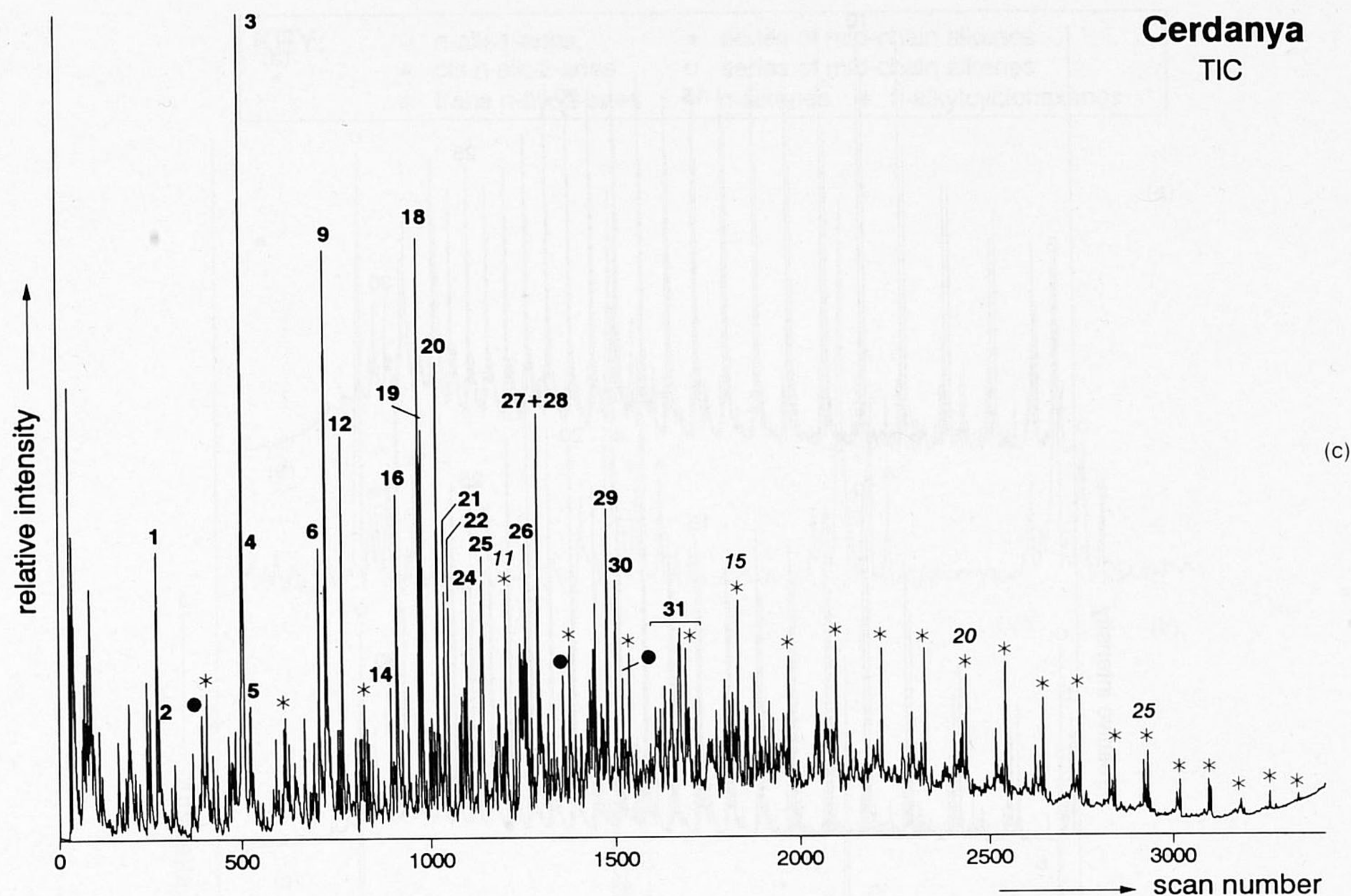


FIG. 1 (Continued)

with normal transmitted light. Under incident blue light, however, its presence is obvious. Other common organic matter types recognized with normal transmitted light are yellow-brown and transparent SOM. *Botryococcus* spp. and pollen grains are rare elements. The colour of the yellow-brown SOM is darker than in the Ribesalbes sample. The fluorescence of the organic particles is weak yellow/green to brown.

Campins

In contrast to the previous samples, the Campins sample does not contain recognizable palynomorphs. The organic matter assemblage is dominated by SOM which is dark brown and contains abundant pyrite inclusions. The fluorescence of the organic material is moderate yellow to dark brown. In addition, similar to Ribesalbes, separate particles recognized in normal transmitted light are composed of clusters of organic particles when examined under incident blue light.

Flash Pyrolysis

The three decarbonated and extracted oil shales were subjected to flash pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) using wires with a Curie temperature of 610°C. The total ion current (TIC) traces of the flash pyrolysates (Fig. 1) reveal significant differences in general composition (Table 6).

Aliphatic Hydrocarbons

Homologous series of *n*-alkanes and *n*-alk-1-enes dominate the pyrolysates of Ribesalbes and Campins kerogens, whereas they are much less abundant in the Cerdanya kerogen pyrolysate (Fig. 1). The summed mass chromatograms of *m/z* 55 + 57 for the three pyrolysates reveal that both homologous series extend up to C₃₄ in the Ribesalbes and Campins pyrolysates (Fig. 2). The abundance of C₂₀₊ *n*-alkanes and *n*-alk-1-enes is typical for pyrolysates of lacustrine kerogens; in pyrolysates of marine kerogens these homologous series generally drop off after C₂₀ (e.g., BEHAR and PELET, 1985; SOLLI and LEPLAT, 1986; GOTH et al., 1989; HORSFIELD, 1989; GRAY et al., 1991).

Apart from *n*-alk-1-enes, other linear alkenes with double bonds in other positions also occur in the flash pyrolysates. In the Cerdanya pyrolysate these unusual alkenes are very abundant (Fig. 3c). For example, in the C₁₀ cluster of alkenes dec-1-ene is only a minor compound relative to the sum of *cis* and *trans* dec-2-ene. The double bond position of the other decenes in this cluster remains as yet unknown, but it is likely on the basis of retention indices (DUBOIS et al., 1980) that dec-3-ene, dec-4-ene, and dec-5-ene also are present. To the best of our knowledge, this is the first time that these homologous series of non-terminal alkenes are reported in pyrolysates of kerogens. As clearly revealed in Fig. 3c, some of these series of non-terminal alkenes start to coelute with the series of *n*-alk-1-enes with increasing number of carbon atoms. This indicates that compounds in kerogen pyrolysates

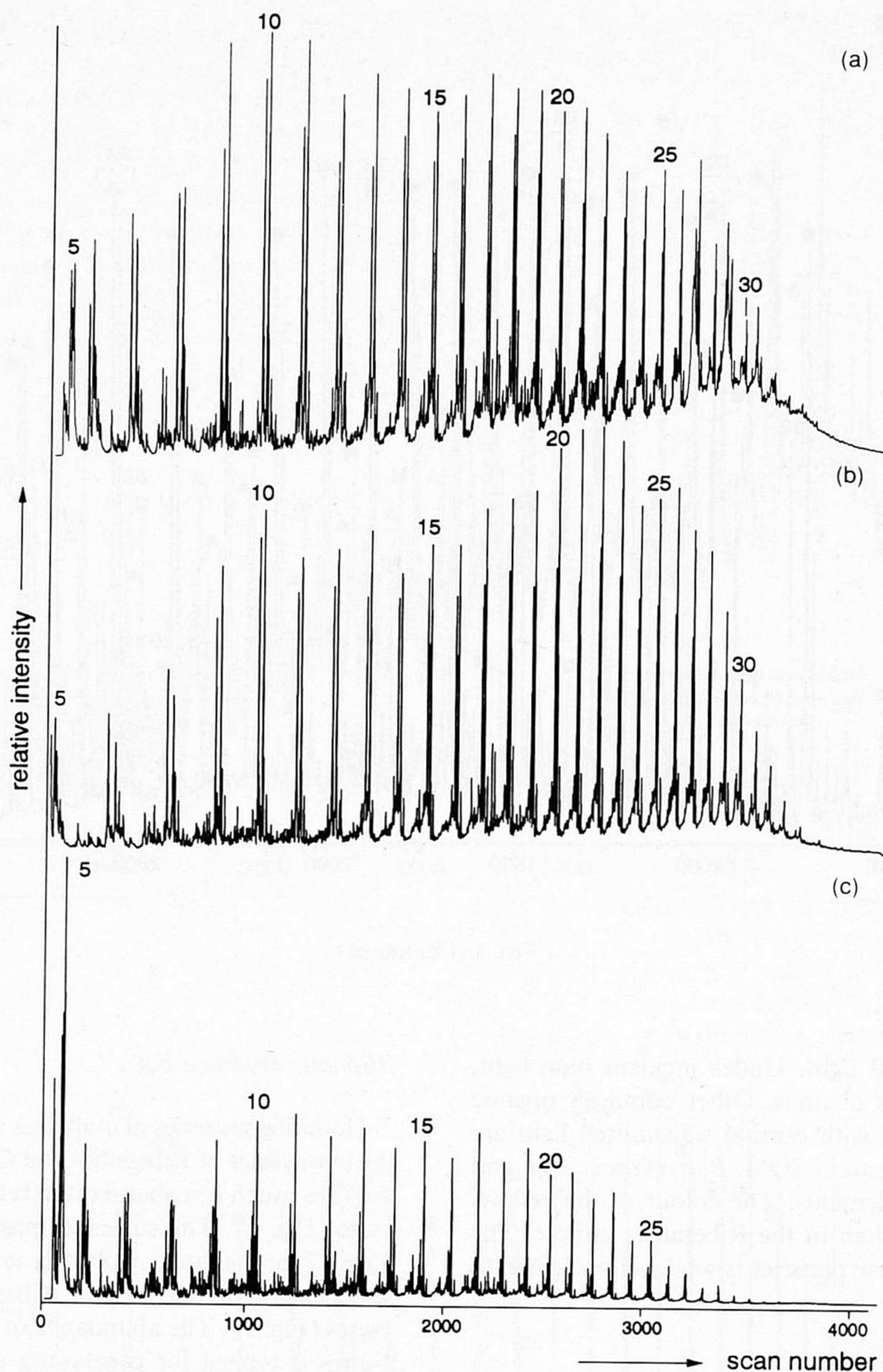


FIG. 2. Summed mass chromatograms of m/z 55 + 57 revealing the distribution patterns of the homologous series of n -alkanes and n -alk-1-enes in the flash pyrolysates of the kerogens of (a) Ribesalbes, (b) Campins, and (c) Cerdanya. Numbers indicate total number of carbon atoms of these homologous series, which occur as doublets in the mass chromatograms (n -alk-1-enes are the first eluting components).

attributed to n -alk-1-enes may actually be mixtures of n -alk-1-enes and certain non-terminal alkenes.

In the Ribesalbes pyrolysate, three relatively abundant alkenes were identified: 1,18-heptacosadiene, 1,20-nonacosadiene, and 1,22-triacontane (Fig. 1). They were identified on basis of relative retention time and mass spectral data described elsewhere (GATELLIER et al., 1993).

Aromatic Hydrocarbons

C_1 - C_4 alkylated benzenes are abundant compounds in all three pyrolysates, but in the Cerdanya pyrolysate they are

the dominant pyrolysis products (Fig. 1; Table 3). These alkylbenzenes were identified on the basis of published mass spectral and relative retention time data (HARTGERS et al., 1992). The summed mass chromatograms of m/z 91 + 92 + 105 + 106 + 119 + 120 + 133 + 134 are used to illustrate the relative abundance of the various alkylbenzene isomers since the ions summed are the major ions in the mass spectra of these compounds. Although these chromatograms look at first glance rather similar, significant differences can be noted, especially when the Ribesalbes and Cerdanya kerogen pyrolysate are compared. In the Ribesalbes kerogen pyrolysate, the "linear alkylbenzenes" (i.e., alkylbenzenes that can be thought of as the result of a cyclization and aromatization

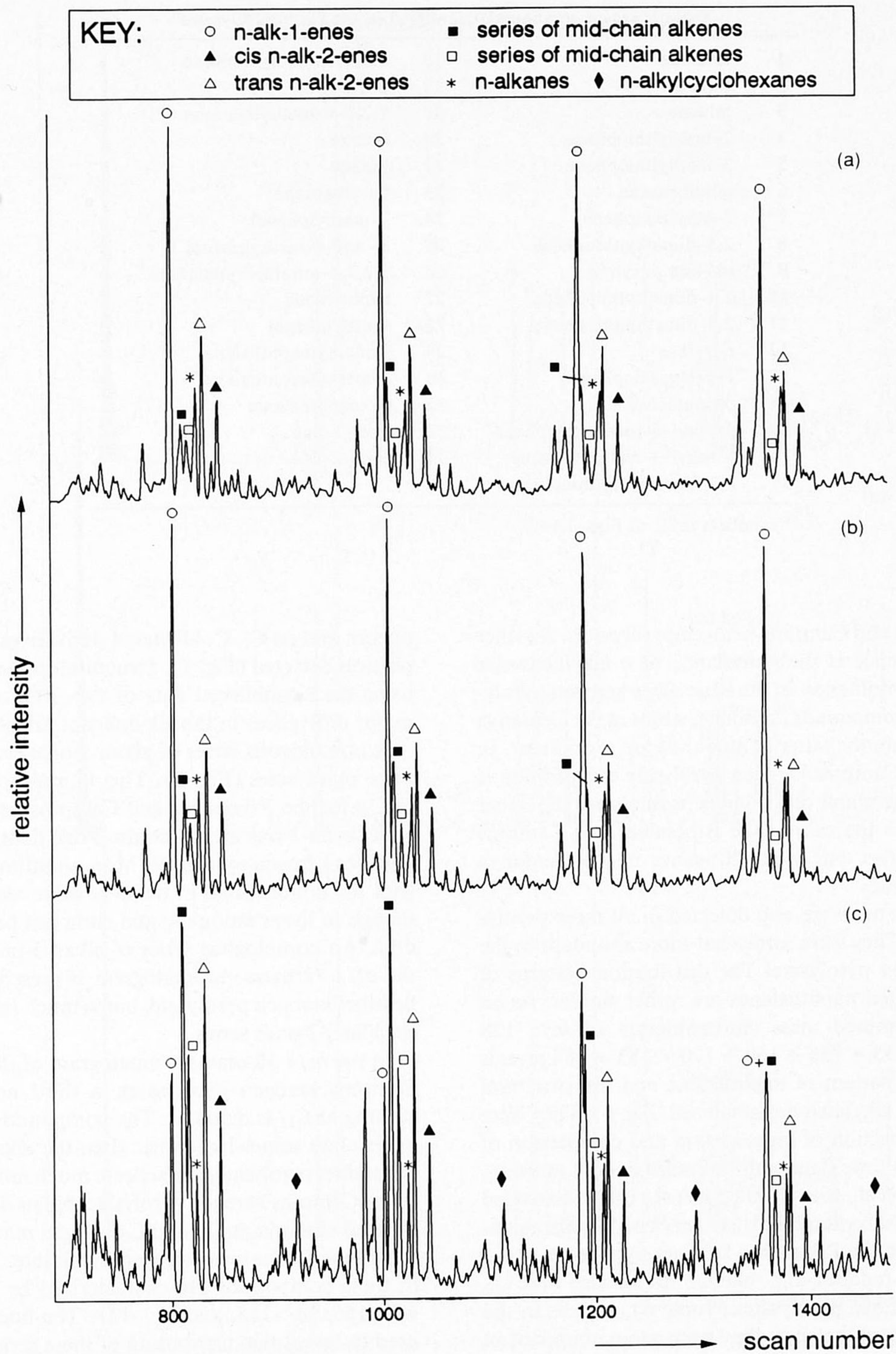


FIG. 3. Partial mass chromatograms of m/z 55 revealing the distributions of the C_9 - C_{12} alkenes in the flash pyrolysates of the kerogens of (a) Ribesalbes, (b) Campins, and (c) Cerdanya.

of a linear precursor) represented by the black peaks (Fig. 4) are relatively more abundant than the other alkylbenzenes. The alkylbenzene distribution of the Campins kerogen pyrolysate is intermediate in this respect.

Series of long-chain alkylbenzenes were also detected in the flash pyrolysates by mass chromatography of m/z 91

+ 92 (*n*-alkylbenzenes) and 105 + 106 (*o*-, *m*-, and *p*-*n*-alkyltoluenes). Bar plots showing the distribution patterns of these homologous series are shown in Fig. 5. In the Ribesalbes and Campins kerogen pyrolysates these series range to C_{34} , whereas in the Cerdanya kerogen pyrolysate, they stop at C_{30} , and C_{15+} members are much less abundant than

Table 3. Major compounds identified in the flash pyrolysates^a

1	benzene	18	1,2,4-trimethylbenzene
2	thiophene	19	phenol
3	toluene	20	1,2,3-trimethylbenzene
4	2-methylthiophene	21	indane
5	3-methylthiophene	22	indene
6	ethylbenzene	23	butylbenzene
7	2-ethylthiophene	24	2-methylphenol
8	2,5-dimethylthiophene	25	3- and 4-methylphenol
9	<i>m</i> - and <i>p</i> -xylene	26	1,2,3,4-tetramethylbenzene
10	2,4-dimethylthiophene	27	naphthalene
11	2,3-dimethylthiophene	28	4-ethylphenol
12	<i>o</i> -xylene	29	1-methylnaphthalene
13	2-propylthiophene	30	2-methylnaphthalene
14	propylbenzene	31	C ₂ -naphthalenes
15	2-ethyl-5-methylthiophene	32	prist-1-ene
16	1-ethyl-3-methylbenzene	33	prist-2-ene
17	2,3,5-trimethylthiophene		

^a numbers refer to Figs. 1A-C

in the Ribesalbes and Campins kerogen pyrolysates. Another important difference is the abundance of *n*-alkylbenzenes relative to *n*-alkyltoluenes. In the Ribesalbes kerogen pyrolysate, the former compounds dominate, whilst in the Cerdanya kerogen pyrolysate the latter compounds are prominent. In this respect, the Campins kerogen pyrolysate composition is intermediate. The major alkyltoluene isomers are the linear *o*-alkyltoluenes in the case of the Ribesalbes and Campins kerogen pyrolysates, but *m*-alkyltoluenes in the Cerdanya kerogen pyrolysate.

Alkylnaphthalenes were also detected in all three pyrolysates (Table 1). They were somewhat more abundant in the Cerdanya kerogen pyrolysate. The distribution patterns of the C₁-C₄ alkylated naphthalenes are rather similar. As an example, the summed mass chromatogram of *m/z* 128 + 141 + 142 + 155 + 156 + 169 + 170 + 183 + 184 reveals the complicated pattern of naphthalene and the structural isomers of C₁-C₄ alkylated naphthalenes (Fig. 6). They were identified by inspection of mass spectra and comparison of relative retention time data with literature data (LEE et al., 1979; ROWLAND et al., 1984; FORSTER et al., 1989). Extended series of 1- and 2-alkylnaphthalenes (*m/z* 141) were tentatively identified in the Ribesalbes kerogen pyrolysate.

Alkylindenes, -indanes, and -phenanthrenes also were encountered in all three pyrolysates (Table 6), and, as in the case of the alkylnaphthalenes, they were more abundant in the Cerdanya kerogen pyrolysate.

Oxygen-containing Compounds

Two classes of compounds were detected as major compounds in the flash pyrolysates; alkylated phenols and alkanones. Their abundance in the pyrolysates was highly variable.

Alkylphenols were very abundant in the Cerdanya kerogen pyrolysate, but represented trace compounds in the Ribesalbes kerogen pyrolysate (Table 6). A partial, summed mass chromatogram of *m/z* 94 + 107 + 108 + 121 + 122 + 135 + 136 for the three pyrolysates reveals the distribution of

phenol and its C₁-C₃ alkylated derivatives, the major alkylphenols detected (Fig. 7). Structural isomers were identified using the unpublished data of VAN BERGEN. There are no major differences in the alkylphenol distributions (Fig. 7).

A homologous series of alkan-2-ones was detected in the three pyrolysates (Fig. 8). This homologous series extends to C₃₂ for the Ribesalbes and Campins kerogen pyrolysate, with decan-2-one and undecan-2-one dominating in the Ribesalbes kerogen pyrolysate. Monounsaturated alkan-2-ones with the double bond in the ω -position also are present, although in lower amounts, and elute just before the alkan-2-ones. An homologous series of alkan-3-ones as revealed by the *m/z* 72 mass chromatogram is present only in the Ribesalbes kerogen pyrolysate, but is much less dominant than the alkan-2-ones series.

In the *m/z* 58 mass chromatogram of the Ribesalbes and Campins kerogen pyrolysates, a third homologous series starting at C₁₂ is detected. The compounds comprising this series elute somewhat earlier than the alkan-2-ones. In the Ribesalbes pyrolysate, this series is much more abundant than in the Campins kerogen pyrolysate and its distribution shows marked maxima at C₂₇ and C₂₉. These maxima also are observed in the Campins kerogen pyrolysate. The mass spectra of these compounds are characterized by ions at *m/z* 58, 141, 155, M⁺-113, and M⁺-127. The first three ions were used to reveal the distribution of these series of compounds (Fig. 9). Although the latter two mass chromatograms seem to match perfectly, the maxima of the peaks consistently differ one scan. A similar phenomenon has been described for the flash pyrolysate of Balkashite and algaenan isolated from cultured *Botryococcus braunii* race A (GATELLIER et al., 1993). These authors have identified these homologous series as comprising almost coeluting alkan-9-ones (giving rise to the ions at *m/z* 58, 141, and M⁺-113) and alkan-10-ones (giving rise to the ions at *m/z* 58, 155, and M⁺-127) using authentic standards. Both series are accompanied by their monounsaturated counterparts, with the double bond in the ω -position

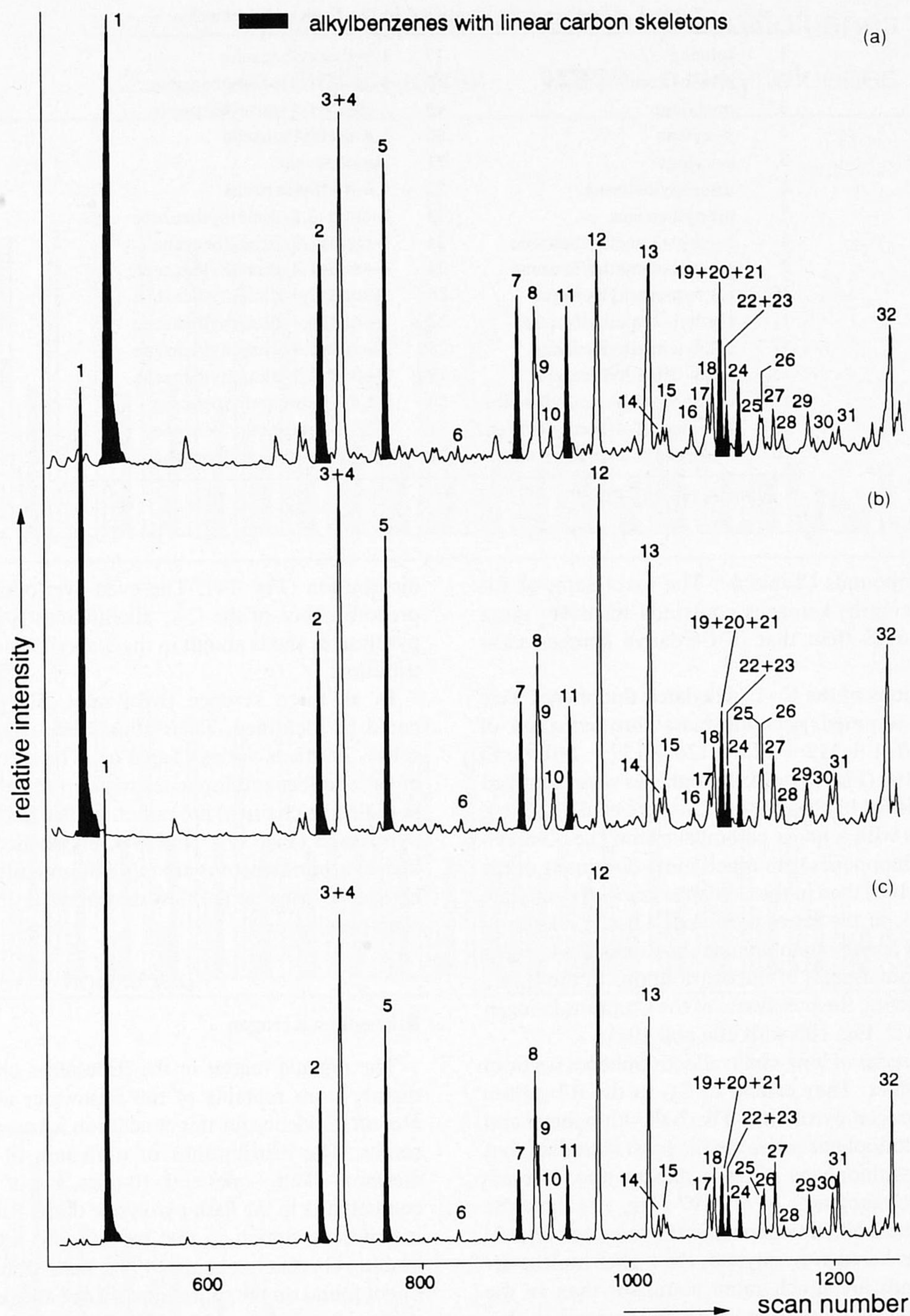


FIG. 4. Partial summed mass chromatograms of m/z 91 + 92 + 105 + 106 + 119 + 120 + 133 + 140 revealing the distributions of the C_1 - C_4 alkylated benzenes in the flash pyrolysates of the kerogens of (a) Ribesalbes, (b) Campins, and (c) Cerdanya. Numbers refer to compounds listed in Table 4. Alkybenzenes with linear carbon skeletons are indicated in black.

(alk-1-en- ω^9 -ones[†] and alk-1-en- ω^{10} -ones), as is clearly revealed in Fig. 9c,d. It should be stressed that the C_{27} and C_{29} members of these series of saturated and mono-unsaturated "mid-chain" ketones are major pyrolysis prod-

ucts in the Ribesalbes kerogen pyrolysate (cf. Fig. 9a,b; Fig. 1a).

Sulphur-containing Compounds

The pyrolysates of all three oil shales contain organic sulphur compounds. Alkylthiophenes are more dominant than alkylbenzothiophenes, and alkylthiolanes and -thianes are

[†] alk-1-en- ω^9 -ones means alkan-9-ones possessing a terminal double bond.

Table 4. Alkylbenzenes identified in the flash pyrolysates^a

1	toluene	17	1,3-diethylbenzene
2	ethylbenzene	18	1-methyl-3-propylbenzene
3	<i>m</i> -xylene	19	1-methyl-4-propylbenzene
4	<i>p</i> -xylene	20	1,4-diethylbenzene
5	<i>o</i> -xylene	21	butylbenzene
6	isopropylbenzene	22	1,2-diethylbenzene
7	propylbenzene	23	1-ethyl-3,5-dimethylbenzene
8	1-ethyl-3-methylbenzene	24	1-methyl-2-propylbenzene
9	1-ethyl-4-methylbenzene	25	2-ethyl-1,4-dimethylbenzene
10	1,3,5-trimethylbenzene	26	1-ethyl-2,4-dimethylbenzene
11	1-ethyl-2-methylbenzene	27	1-ethyl-3,4-dimethylbenzene
12	1,2,4-trimethylbenzene	28	2-ethyl-1,3-dimethylbenzene
13	1,2,3-trimethylbenzene	29	1-ethyl-2,3-dimethylbenzene
14	1-isopropyl-3-methylbenzene	30	1,2,4,5-tetramethylbenzene
15	1-isopropyl-4-methylbenzene	31	1,2,3,5-tetramethylbenzene
16	1-isopropyl-2-methylbenzene	32	1,2,3,4-tetramethylbenzene

^a numbers refer to Fig. 4

only minor compounds (Table 6). The pyrolysates of Ribesalbes and Campins kerogens contained relatively more sulphur compounds than that of Cerdanya kerogen (Table 6).

The distributions of the C₁–C₆ alkylated thiophenes were determined by summed, accurate mass chromatogram of *m/z* 97 + 98 + 111 + 112 + 125 + 126 + 139 + 140 + 153 + 154 + 167 + 168 (Fig. 10). Alkylthiophenes were identified using data published by SINNINGHE DAMSTÉ et al. (1988a). Alkylthiophenes with a linear carbon skeleton (i.e., 2-alkyl- and 2,5-dialkylthiophenes) are much more dominant in the Ribesalbes (Fig. 10a) than in the Cerdanya kerogen pyrolysate (Fig. 10c). Also, in the latter pyrolysate C₄–C₆, alkylthiophenes are much less abundant than in the Ribesalbes kerogen pyrolysate. In both aspects of the distributions of the C₁–C₆ alkylated thiophenes, the pyrolysate of the Campins kerogen is intermediate (cf. Fig. 10b with 10a and 10c).

Homologous series of long-chain alkylthiophenes occur in all three pyrolysates. They extend to C₃₂ in the Ribesalbes and Campins kerogen pyrolysate. The 2-alkylthiophene and 2-alkyl-5-methylthiophene series are the most abundant, but the 2-alkyl-5-ethylthiophene series is present also. The accurate mass chromatograms of *m/z* 97 (Fig. 11) show the distributions of the 2-alkylthiophenes in the three pyrolysates. In the Ribesalbes kerogen pyrolysate, the higher molecular-weight compounds are much more abundant than in the Cerdanya kerogen pyrolysate, in which they extend to C₁₃. The Campins kerogen pyrolysate is, once again, intermediate in this respect. The same holds for the 2-alkyl-5-methylthiophenes (Fig. 12).

Alkylthiolane and -thianes were present only in significant amounts in the Ribesalbes and Campins kerogen pyrolysate. The mass chromatograms of *m/z* 87 reveal the distribution of the 2-alkylthiolanes, which extends to C₃₂ (Fig. 13). The higher molecular-weight 2-alkylthiolanes are much more abundant in the Ribesalbes kerogen pyrolysate. The higher molecular-weight 2-alkyl-5-methylthiolanes and 2-alkylthianes also are more abundant in the Ribesalbes kerogen pyrolysate, although not as pronounced as in the 2-alkylthiolane

distribution (Fig. 14). The even-over-odd carbon number predominance of the C₂₂₊ alkylthianes is observed in both pyrolysates and is absent in the 2-alkyl-5-methylthiolane distribution.

In all three kerogen pyrolysates, alkylbenzothiophenes could be identified. Their abundance relative to other pyrolysis products varies (Table 6). The distribution patterns of the alkylbenzothiophenes with up to three carbon atoms in their side chain(s) are rather similar for the three kerogen pyrolysates (Fig. 15). However, alkylbenzothiophenes with linear carbon skeletons are more dominant in the Ribesalbes kerogen pyrolysate and less dominant in the Cerdanya kerogen pyrolysate.

DISCUSSION

Ribesalbes Kerogen

The organic matter in the Ribesalbes oil shale is derived mainly from remains of the freshwater alga *Botryococcus braunii*. Evidence for this conclusion is based on the pyrolysis results. The distributions of *n*-alkanes, *n*-alkenes, *n*-alkadienes, *n*-alkan-9-ones and -10-ones, and of their unsaturated counterparts in the flash pyrolysate of the Ribesalbes kerogen, is strikingly similar to that reported for a Coorongite (Balkashite; GATELLIER et al., 1993). Balkashite is a Recent sediment found on the shorelines of Lake Balkash (Kazakhstan) and is composed mainly of remains of *B. braunii* race A. Flash pyrolysis of this latter sediment after extraction also generated a pyrolysate consisting of many homologous series of *n*-alk-1-enes, *n*-alkadienes, and *n*-alkanes and abundant C₂₇ and C₂₉ *n*-alkadienes, *n*-alkan-9-ones, *n*-alk-1-en- ω^9 -ones, *n*-alkan-10-ones, and *n*-alk-1-en- ω^{10} -ones (GATELLIER et al., 1993; cf. Figs. 1a and 16). The series of *n*-alk-1-enes, *n*-alkadienes, and *n*-alkanes are the major pyrolysis products of the aliphatic biomacromolecule algaenan of the outer cell walls of *B. braunii*, as demonstrated by Py-GC-MS analysis of the algaenan isolated from a strain of *B. braunii* race A (GATELLIER et al., 1993). The abundant C₂₇ and C₂₉ *n*-alkadienes, *n*-alkan-9-ones, *n*-alk-1-en- ω^9 -ones, *n*-alkan-10-

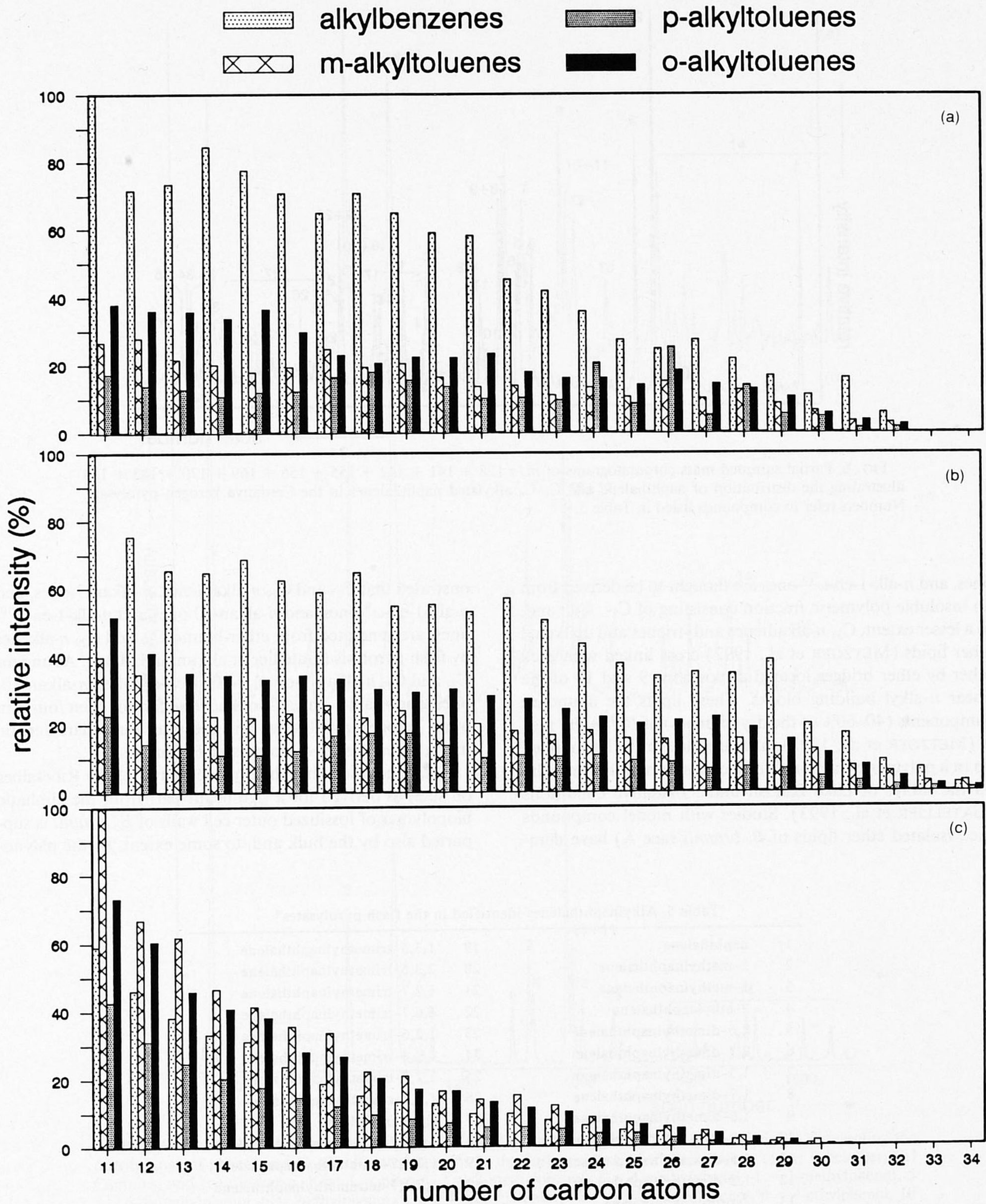


FIG. 5. Bar plots showing the distributions [measured from peak heights in the m/z 91 + 92 (alkylbenzenes) and 105 + 106 (alkyltoluenes) mass chromatograms] of the indicated alkylbenzenes in the pyrolysates of (a) Ribesalbes, (b) Campins, and (c) Cerdanya.

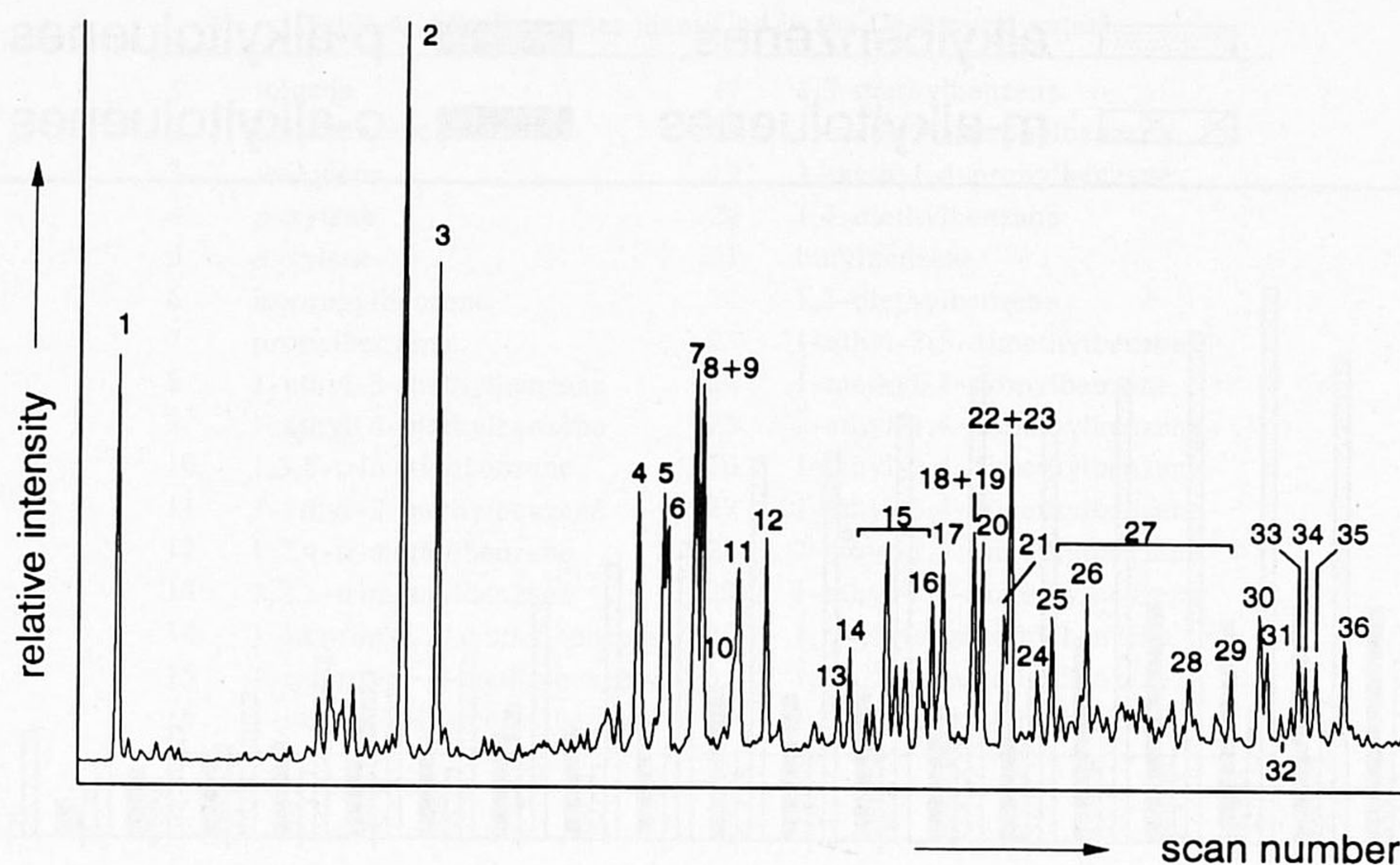


FIG. 6. Partial summed mass chromatograms of m/z 128 + 141 + 142 + 155 + 156 + 169 + 170 + 183 + 184 illustrating the distribution of naphthalene and C_1 - C_4 alkylated naphthalenes in the Cerdanya kerogen pyrolysate. Numbers refer to compounds listed in Table 5.

ones, and n -alk-1-en- ω^{10} -ones are thought to be derived from an insoluble polymeric fraction consisting of C_{27} , C_{29} , and, to a lesser extent, C_{31} n -alkadienes and -trienes and dialkenyl ether lipids (METZGER et al., 1992) cross linked with each other by ether bridges located at positions 9 and 10 of the linear n -alkyl building blocks. These lipids are abundant components (40–60% of the dry biomass) of *B. braunii* race A (METZGER et al., 1992), and are thought to be mopped up in a polymeric fraction during deposition of this material on the shores of Lake Balkish under oxidative conditions (GATELLIER et al., 1993). Studies with model compounds (i.e., isolated ether lipids of *B. braunii* race A) have dem-

onstrated that C_{27} and C_{29} n -alkadienes, n -alkan-9-ones, and n -alk-1-en- ω^9 -ones, and n -alkan-10-ones and n -alk-1-en- ω^{10} -ones, are generated from ether-bound C_{27} and C_{29} n -alkenes by flash pyrolysis (Gatellier et al., unpubl. data). Abundant C_{27} and C_{29} n -alkan-9-ones, n -alk-1-en- ω^9 -ones, n -alkan-10-ones, and n -alk-1-en- ω^{10} -ones have so far not been found in other kerogen pyrolysates and are thus very characteristic markers for fossilized remains of *B. braunii*.

The conclusion that the organic matter of the Ribesalbes oil shale is derived for a significant part from the aliphatic biopolymer of fossilized outer cell walls of *B. braunii* is supported also by the bulk and, to some extent, by the palyno-

Table 5. Alkyl naphthalenes identified in the flash pyrolysates^a

1	naphthalene	19	1,3,5-trimethylnaphthalene
2	2-methylnaphthalene	20	2,3,6-trimethylnaphthalene
3	1-methylnaphthalene	21	1,2,7-trimethylnaphthalene
4	2-ethylnaphthalene	22	1,6,7-trimethylnaphthalene
5	2,6-dimethylnaphthalene	23	1,2,6-trimethylnaphthalene
6	2,7-dimethylnaphthalene	24	1,2,4-trimethylnaphthalene
7	1,3-dimethylnaphthalene	25	1,2,5-trimethylnaphthalene
8	1,7-dimethylnaphthalene	26	1,2,3-trimethylnaphthalene
9	1,6-dimethylnaphthalene	27	C_4 -naphthalenes
10	2,3- and 1,4-dimethylnaphthalene	28	1,3,5,7-tetramethylnaphthalene
11	1,5-dimethylnaphthalene	29	1,3,6,7-tetramethylnaphthalene
12	1,2-dimethylnaphthalene	30	1,2,4,7-tetramethylnaphthalene
13	2-propylnaphthalene	31	1,2,5,7-tetramethylnaphthalene
14	1-propylnaphthalene	32	2,3,6,7-tetramethylnaphthalene
15	ethylmethylnaphthalenes	33	1,2,6,7-tetramethylnaphthalene
16	1,3,7-trimethylnaphthalene	34	1,2,3,7-tetramethylnaphthalene
17	1,3,6-trimethylnaphthalene	35	1,2,3,6-tetramethylnaphthalene
18	1,4,6-trimethylnaphthalene	36	1,2,5,6-tetramethylnaphthalene

^a numbers refer to Fig. 6

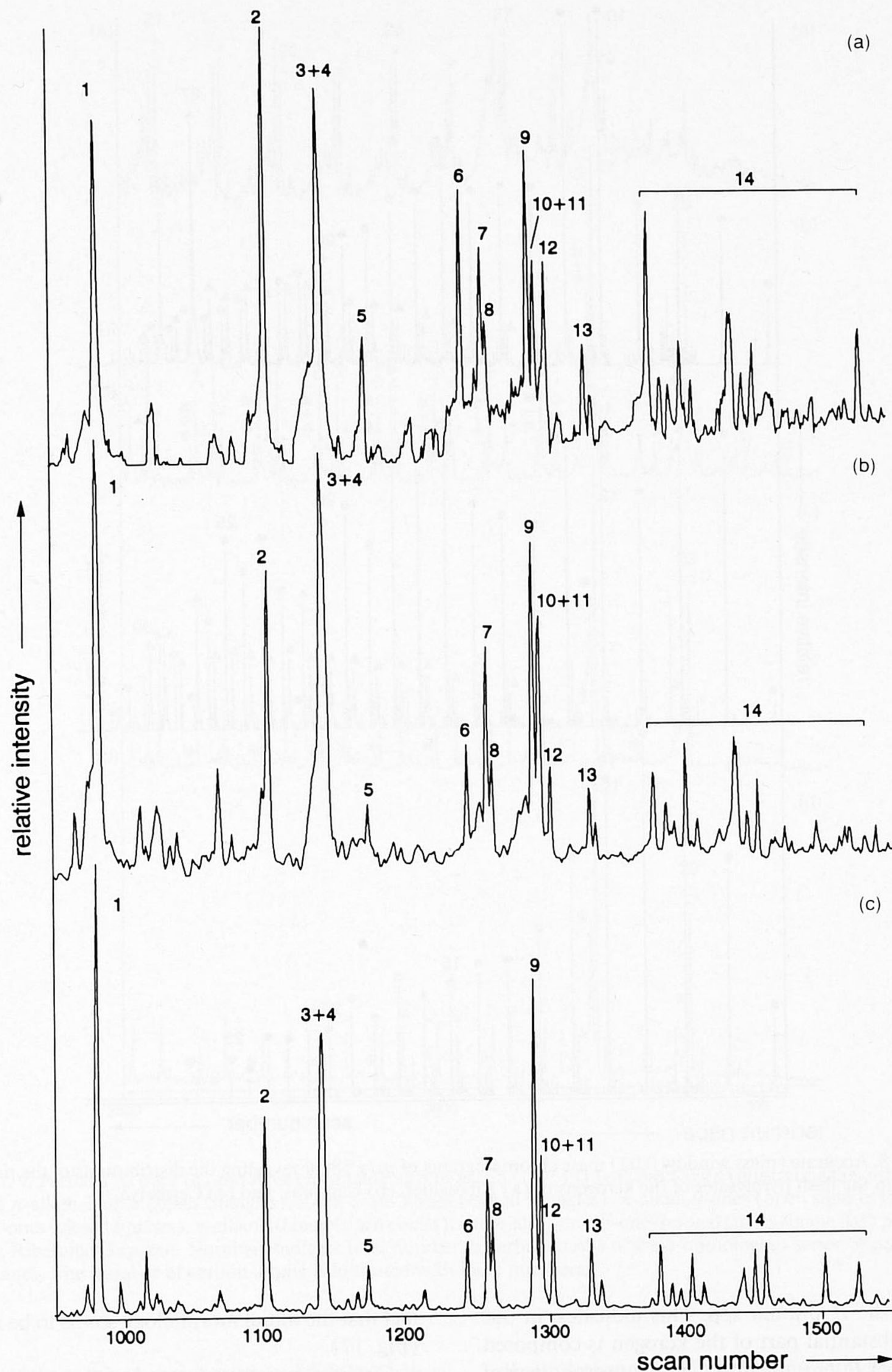


FIG. 7. Partial summed mass chromatograms of m/z 94 + 107 + 108 + 121 + 122 + 135 + 136 revealing the distributions of phenol and C_1 - C_3 alkylated phenols in the flash pyrolysates of the kerogens of (a) Ribesalbes, (b) Campins, and (c) Cerdanya. Key: 1 = phenol, 2 = 2-methylphenol, 3 = 4-methylphenol, 4 = 3-methylphenol, 5 = 2,6-dimethylphenol, 6 = 2-ethylphenol, 7 = 2,4-dimethylphenol, 8 = 2,5-dimethylphenol, 9 = 4-ethylphenol, 10 = 3-ethylphenol, 11 = 3,5-dimethylphenol, 12 = 2,3-dimethylphenol, 13 = 3,4-dimethylphenol, and 14 = C_3 -phenols.

logical data. The very high atomic H/C ratio is consistent with that reported for algaenan isolated from extant *B. braunii* (1.78; LARGEAU et al., 1986) and that of Balkashite (1.82;

GATELLIER et al., 1993). Furthermore, microscopic examination of the Ribesalbes kerogen revealed the presence of few *B. braunii* spp., whilst the fluorescence of the SOM is very

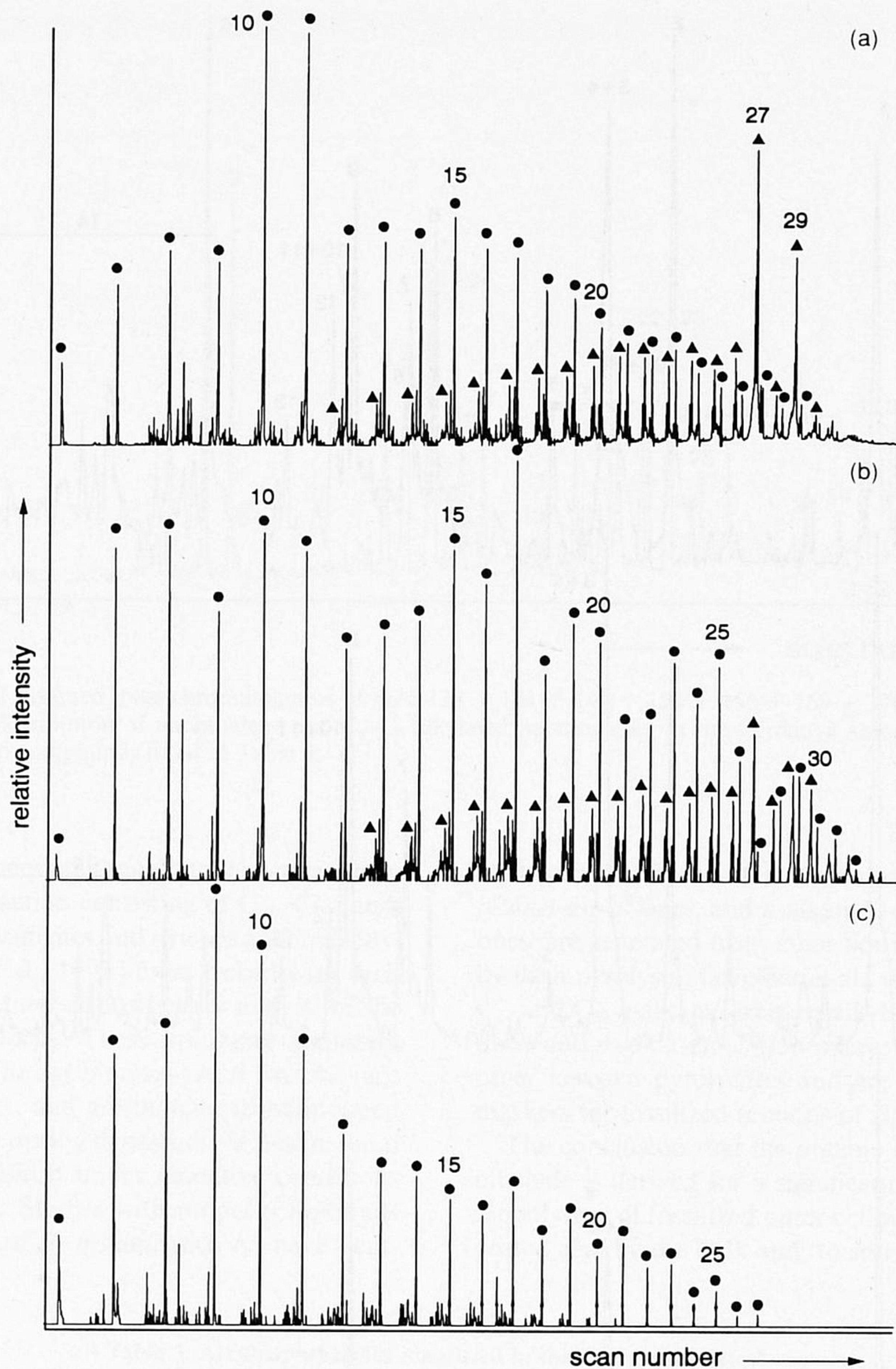


FIG. 8. Accurate (mass window 0.02) mass chromatograms of m/z 58.06 revealing the distributions of the n -alkan-2-ones in the flash pyrolysates of the kerogens of (a) Ribesalbes, (b) Campins, and (c) Cerdanya.

similar to that of the *B. braunii* spp. This indicates, in our opinion, that a substantial part of the kerogen is composed of outer cell walls of *B. braunii*, although the morphology of most of the outer cell walls cannot be recognized anymore by light microscopy, most likely due to diagenetic alteration. This is further supported by micrographs obtained by scanning electron microscopy (Fig. 17) of the Ribesalbes kerogen and the Pliocene Pula alginite from Hungary (S. Derenne and C. Largeau, unpubl. data). This latter sample is composed almost exclusively of well-preserved *B. braunii* colonies in which the morphology is very close to that of extant *B. braunii* colonies (DERENNE et al., 1992). The *B. braunii* colonies can still be recognized in the Ribesalbes kerogen despite the

fact that the initial morphology seems to be markedly affected (Fig. 17).

Circumstantial evidence for diagenetic alteration of the fossilized lipids and algaenan of *B. braunii* is provided by the abundance of alkylbenzenes and sulphur compounds in the flash pyrolysate of the Ribesalbes kerogen (Fig. 1; Table 6). It is known that these compounds are only minor compounds in pyrolysates of algaenans isolated from cultured *B. braunii* (LARGEAU et al., 1986; GATELLIER et al., 1992), indicating that the moieties from which these compounds are derived must have been formed during sediment diagenesis. Inorganic sulphur species (e.g., HS^- , HS_x) can react with functionalized lipids during early diagenesis and lead to the formation of

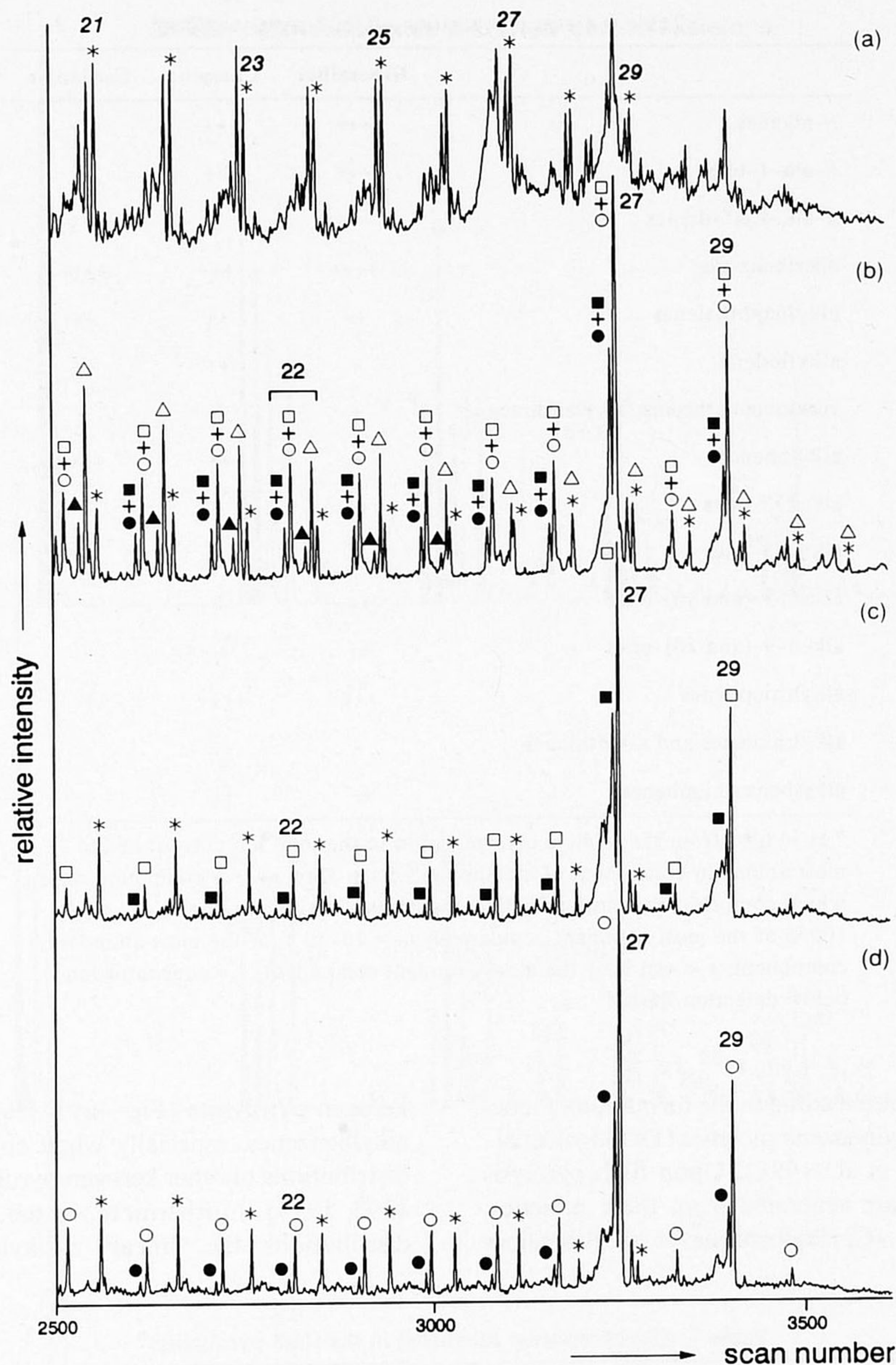


FIG. 9. Partial TIC trace (a) and mass chromatograms of m/z 58 (b); 141 (c); and 155 (d) illustrating the distributions of the n -alkan-2-ones (open triangles), n -alk- ω -en-2-ones (closed triangles), n -alkan-9-ones (open squares), n -alk-1-en- ω -9-ones (closed squares), n -alkan-10-ones (open circles), and n -alk-1-en- ω -10-ones (closed circles) in the flash pyrolysate of the Ribesalbes kerogen. Numbers indicate total number of carbon atoms of these homologous series. Stars indicate n -alkanes. The number of carbon atoms is indicated with italic numbers.

low molecular-weight sulphur compounds and sulphur-containing moieties in high molecular-weight substances, depending on the precursor substrates (for a review see SINNINGHE DAMSTÉ and DE LEEUW, 1990). Incorporation of sulphur in aliphatic biopolymers has been documented (DERENNE et al., 1990b; DOUGLAS et al., 1991, 1992), and leads to the formation of macromolecularly bound thiophene, thiolane, thiane, and benzothiophene moieties with linear carbon skeletons. The distribution of C_1 - C_6 alkylthiophenes in the Ribesalbes kerogen pyrolysate (Fig. 10a) is dominated also by alkylthiophenes with linear carbon skeletons (i.e., 2-

alkylthiophenes and 2-alkyl-5-methylthiophenes) derived from precursor moieties with linear carbon skeletons via β -cleavage of the alkyl side-chain (SINNINGHE DAMSTÉ et al., 1989a; EGLINTON et al., 1992). Since it is well known that the lipids and the algaenan biosynthesized by *B. braunii* contain double bonds (BERKALOFF et al., 1983; KADOURI et al., 1988; GATELLIER et al., 1992) which may act as sites for sulphur addition, diagenetic modification of the structure of the sedimentary algaenan and cross-linked lipids by sulphur incorporation is not unlikely. Another possibility, instead of the addition of sulphur to the double bonds present, is cy-

Table 6. Gross composition of flash pyrolysates^a

	Ribesalbes	Campins	Cerdanya
<i>n</i> -alkanes	+++	++	++
<i>n</i> -alk-1-enes	+++	++	+
<i>n</i> -alk-1,ω ⁹ -dienes	+++	+	-
alkylbenzenes	++++	+++	++++
alkylnaphthalenes	++	++	++
alkylindenes	+	++	++
alkylphenanthrenes/alkylanthracenes	+	+	+
alkylphenols	+	++	+++
alkan-2-ones	++	+	+
alkan-3-ones	+	-	-
alkan-9-(and 10)-ones	++	+	-
alken-9-(and 10)-ones	++	+	-
alkylthiophenes	+++	++++	+
alkylthiolanes and alkylthianes	+	++	-
alkylbenzothiophenes	++	++	+

^a as judged from the relative concentration in the total ion current of the most abundant component of a compound class. Key: ++++ = compound class which comprises the most abundant component in the pyrolysate; +++ = 50-100 % of the most abundant component; ++ = 10-50 % of the most abundant component; + = <10 % of the most abundant component; - = concentration below detection limit.

clization and aromatization leading to the formation of macromolecularly bound alkylbenzene moieties (DERENNE et al., 1989, 1990b; DOUGLAS et al., 1991). Upon flash pyrolysis "linear" alkylbenzenes are generated from these moieties. The distribution of the C₁-C₆ alkylbenzenes in the Ribesalbes

kerogen pyrolysate (Fig. 4a) reveals a dominance of linear alkylbenzenes, especially when compared to alkylbenzene distributions of other kerogen pyrolysates (HARTGERS et al., 1992, 1993). Furthermore, in the long-chain alkylbenzene distributions, the "linear" *o*-alkyltoluenes dominate over

Table 7. Alkylthiophenes identified in the flash pyrolysates^a

1	2-methylthiophene	19	ethyldimethylthiophene
2	3-methylthiophene	20	5-ethyl-2,3-dimethylthiophene
3	2-ethylthiophene	21	ethyldimethylthiophene
4	2,5-dimethylthiophene	22	ethyldimethylthiophene
5	2,4-dimethylthiophene	23	ethyldimethylthiophene
6	2,3-dimethylthiophene	24	2,3,4,5-tetramethylthiophene
7	3,4-dimethylthiophene	25	2-ethyl-5-propylthiophene
8	2-propylthiophene	26	3,5-dimethyl-2-propylthiophene
9	2-ethyl-5-methylthiophene	27	C ₅ -thiophene
10	2-ethyl-4-methylthiophene	28	2-butyl-5-methylthiophene
11	ethylmethylthiophene	29	2-pentylthiophene
12	2,3,5-trimethylthiophene	30	2,3-dimethyl-5-propylthiophene
13	2,3,4-trimethylthiophene	31	ethyltrimethylthiophene
14	3-isopropyl-2-methylthiophene	32	ethyltrimethylthiophene
15	2-methyl-5-propylthiophene	33	2-butyl-5-ethylthiophene
16	2,5-diethylthiophene	34	2-butyl-3,5-dimethylthiophene
17	2-butylthiophene	35	2-methyl-5-pentylthiophene
18	2-ethyl-3,5-dimethylthiophene	36	2-hexylthiophene

^a numbers refer to Figs. 10 and 11

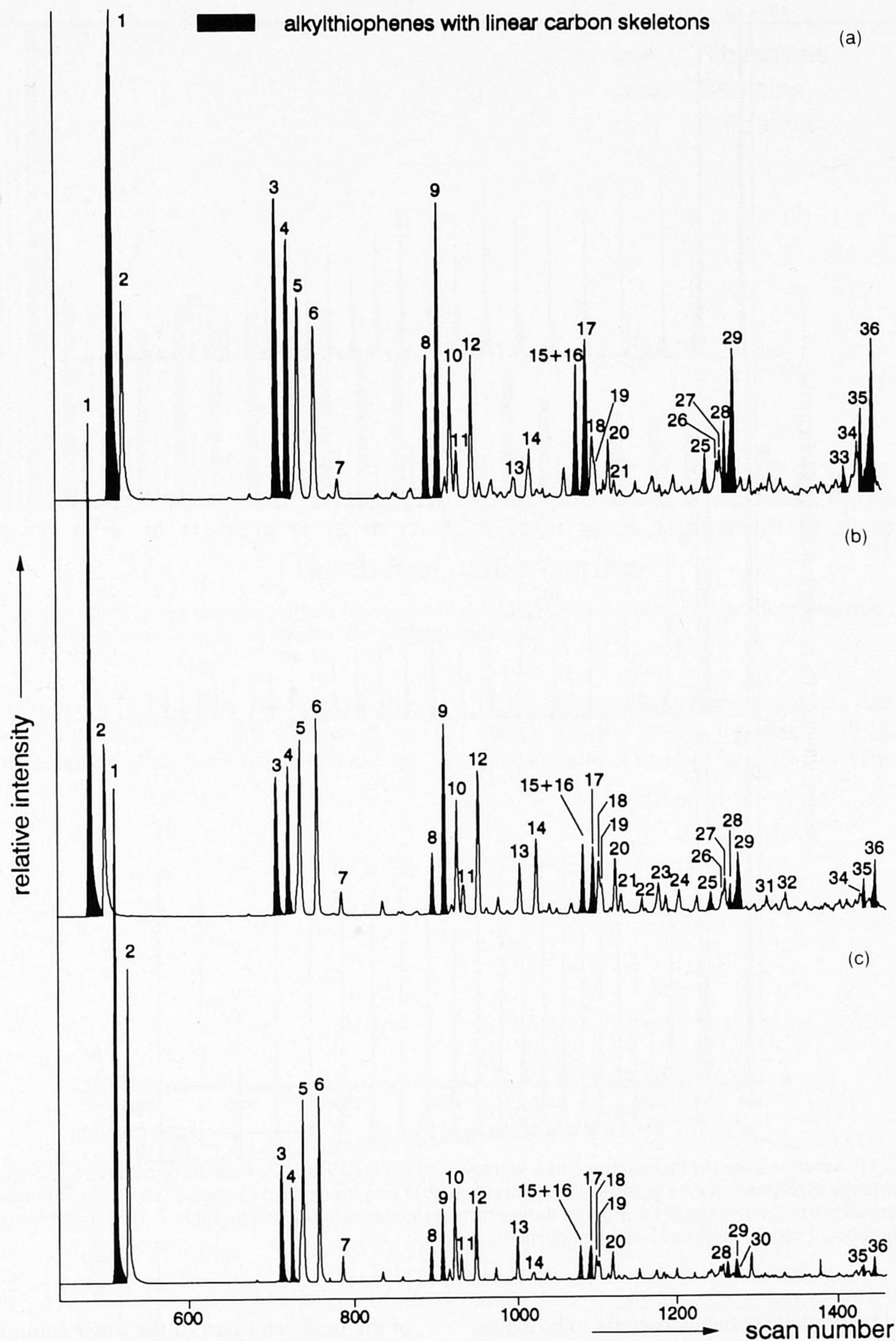


FIG. 10. Partial, accurate (mass window 0.03) summed mass chromatogram of m/z 97.01 + 98.01 + 111.03 + 112.03 + 125.03 + 126.03 + 139.03 + 140.03 + 153.03 + 154.03 + 167.03 + 168.03 illustrating the distribution of the C_1 - C_6 alkylated thiophenes in the flash pyrolysates of the kerogens of (a) Ribesalbes, (b) Campins, and (c) Cerdanya. Numbers refer to compounds listed in Table 7. Peaks corresponding to alkythiophenes with linear carbon skeletons are indicated in black.

other structural isomers (Fig. 5), lending further support to the idea that cyclization and aromatization in the sedimentary algaenan and cross-linked lipids has occurred. These two processes (i.e., sulphurization and cyclization/aromatization)

have altered the structure of the biosynthesized algaenan and also may have led to modification of the morphology.

Sulphur incorporation into organic matter during early diagenesis requires the amount of reduced inorganic sulphur

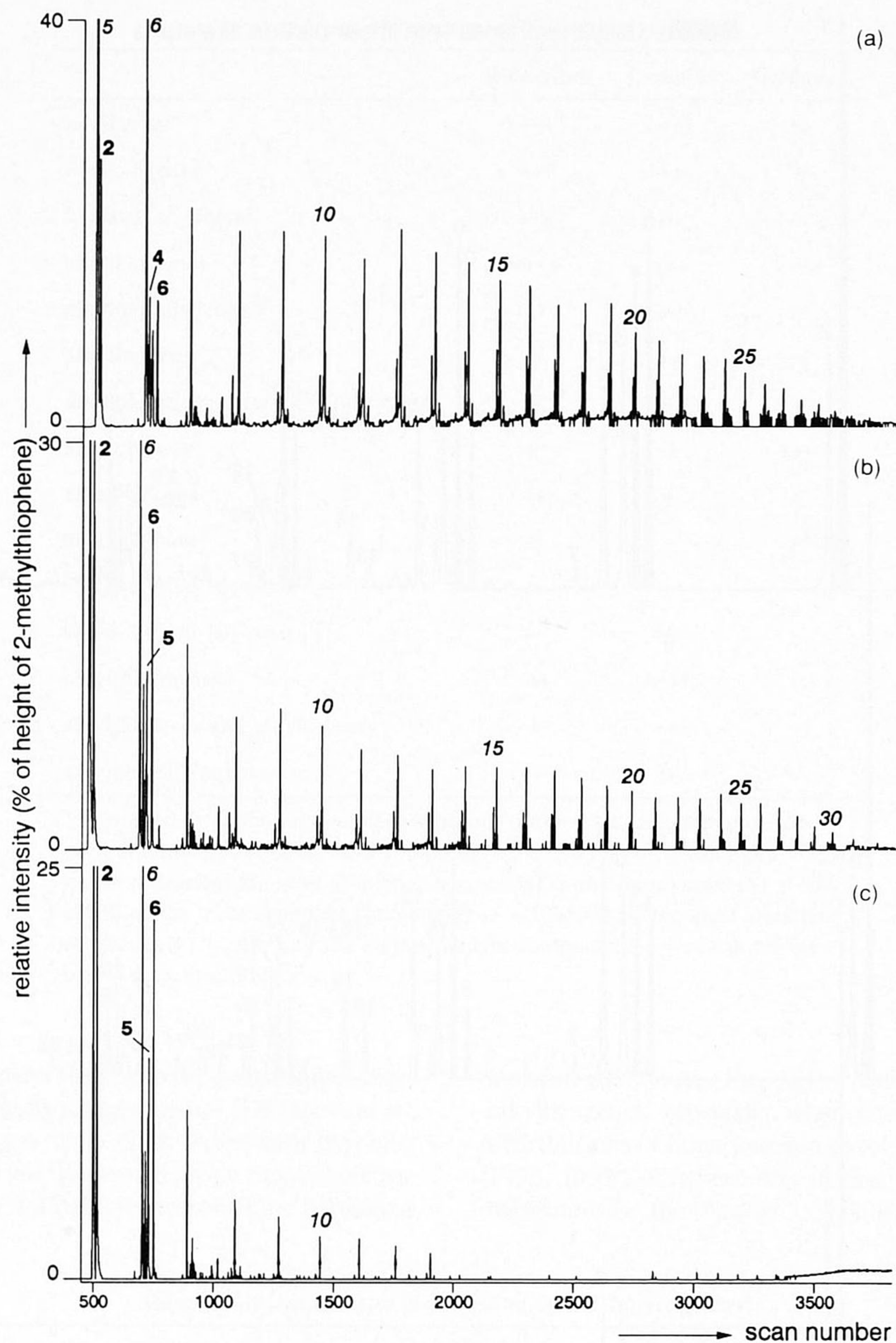


FIG. 11. Accurate mass chromatograms (mass window 0.03) of m/z 97.01 showing the distributions of 2-alkylthiophenes in the pyrolysates of the kerogens of (a) Ribesalbes, (b) Campins, and (c) Cerdanya. The mass chromatograms are normalized to 2-ethylthiophene. Roman numerals refer to compounds listed in Table 7. Italic numbers indicate total number of carbon atoms of 2-alkylthiophenes.

species generated by sulphate-reducing bacteria to be higher than necessary for the conversion of active iron species into iron sulphides. In lacustrine depositional environments, these conditions are quite rare, since sulphate reduction is often limited by the low amounts of sulphate (GRANSCH and POSTHUMA, 1974). In the depositional palaeoenvironment of the Ribesalbes oil shale this was obviously not the case, most likely due to an input of sulphate by weathering of surrounding gypsum rocks (ANADÓN et al., 1989). These rather unusual circumstances led to euxinic conditions in the meromictic lacustrine basin which, in turn, favoured the sulphurization of organic matter produced in the photic zone

of the freshwater part of the water column. Input of active iron species was low since the amount of pyrite in the sediment is low. These conditions led to a very high organic sulphur content and, consequently, to a high atomic S_{org}/C ratio (0.056) of the sedimentary organic matter. In this context, it should be noted that ORR (1986) has defined organic sulphur-rich Type II kerogens as Type II-S kerogens when atomic S_{org}/C ratios were greater than 0.04. Following the same definition, we propose here to classify the Ribesalbes kerogen as a Type I-S kerogen characterized by both high atomic H/C and S_{org}/C ratios.

The fact that the kerogen is comprised mainly of fossilized

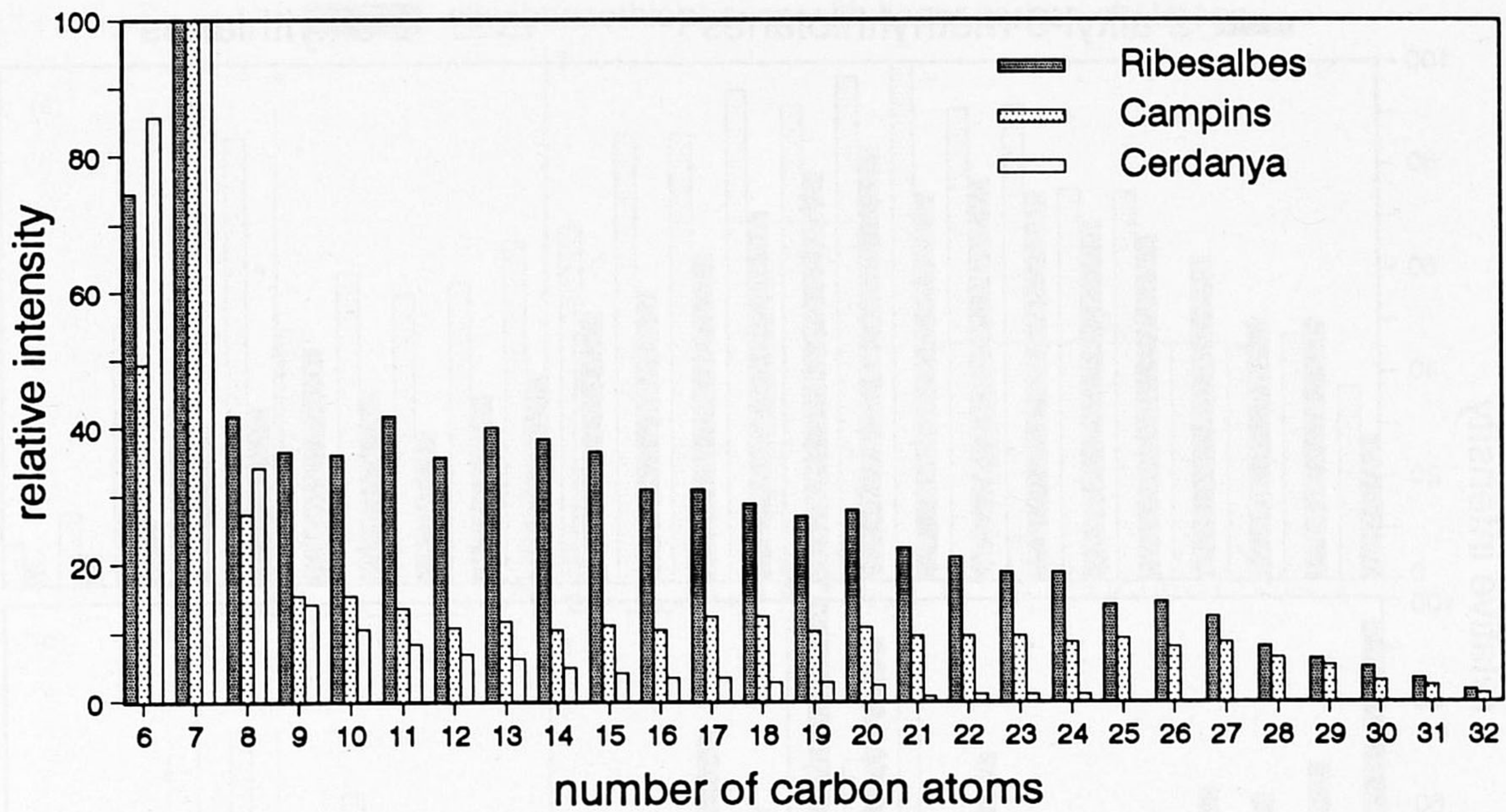


FIG. 12. Bar plot showing the distributions (measured from peak heights in m/z 111 mass chromatograms) of 2-alkyl-5-methylthiophenes in the pyrolysates of the kerogens indicated.

organic matter of *B. braunii* reveals that this alga was the major contributor of organic matter to this sediment. It is, therefore, quite remarkable that such a conclusion is not ap-

parent from the biomarker composition data (DE LAS HERAS, 1989). It is well known that *B. braunii* algae biosynthesize large amount of hydrocarbons (for a review see METZGER et

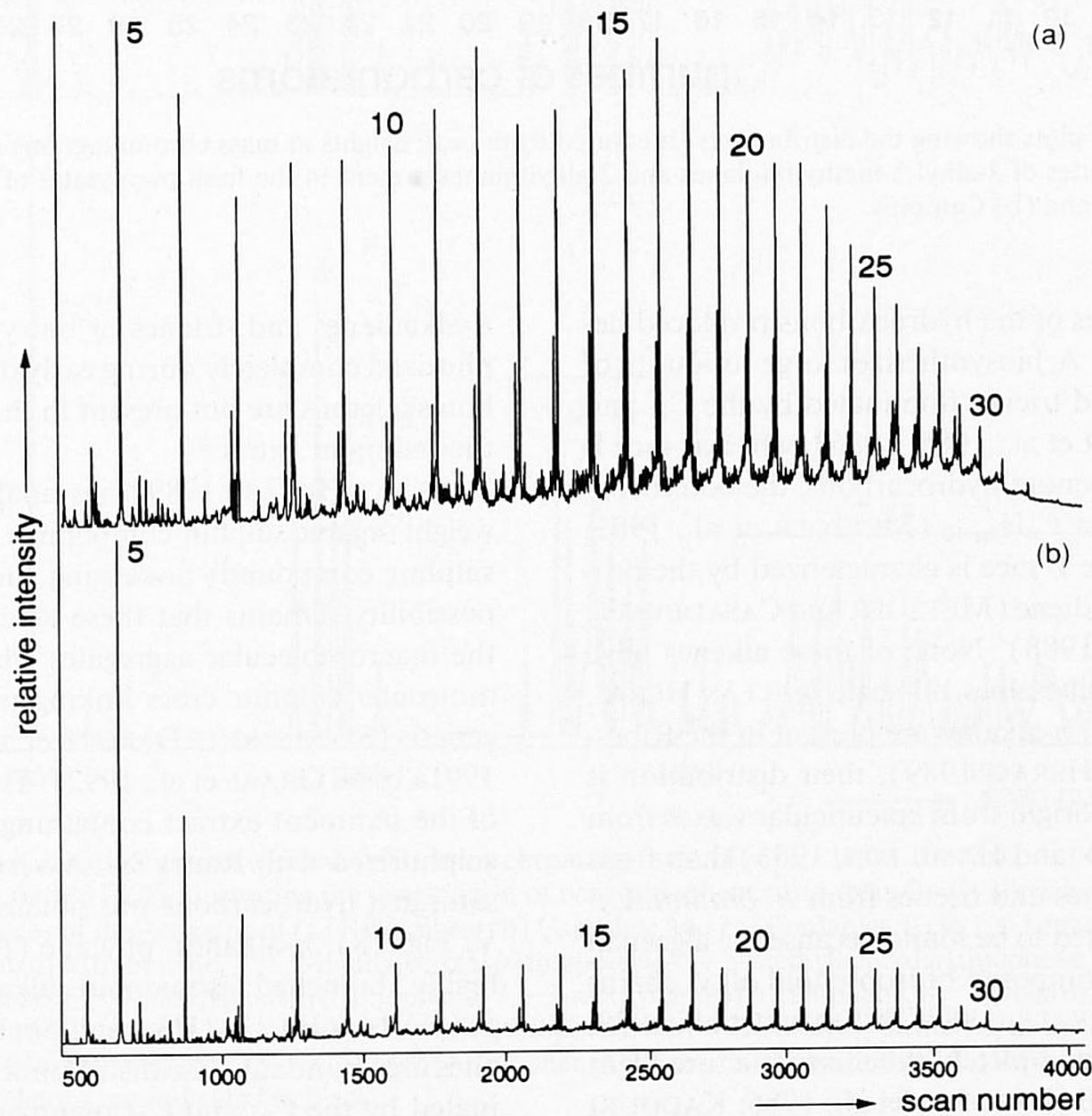


FIG. 13. Mass chromatograms of m/z 87 (major homologous series) showing the distributions of 2-alkylthiolanes and 2-alk- ω -enylthiolanes (eluting just before the 2-alkylthiolanes) in the pyrolysates of the kerogens of (a) Ribesalbes and (b) Campins. Numbers indicate total number of carbon atoms.

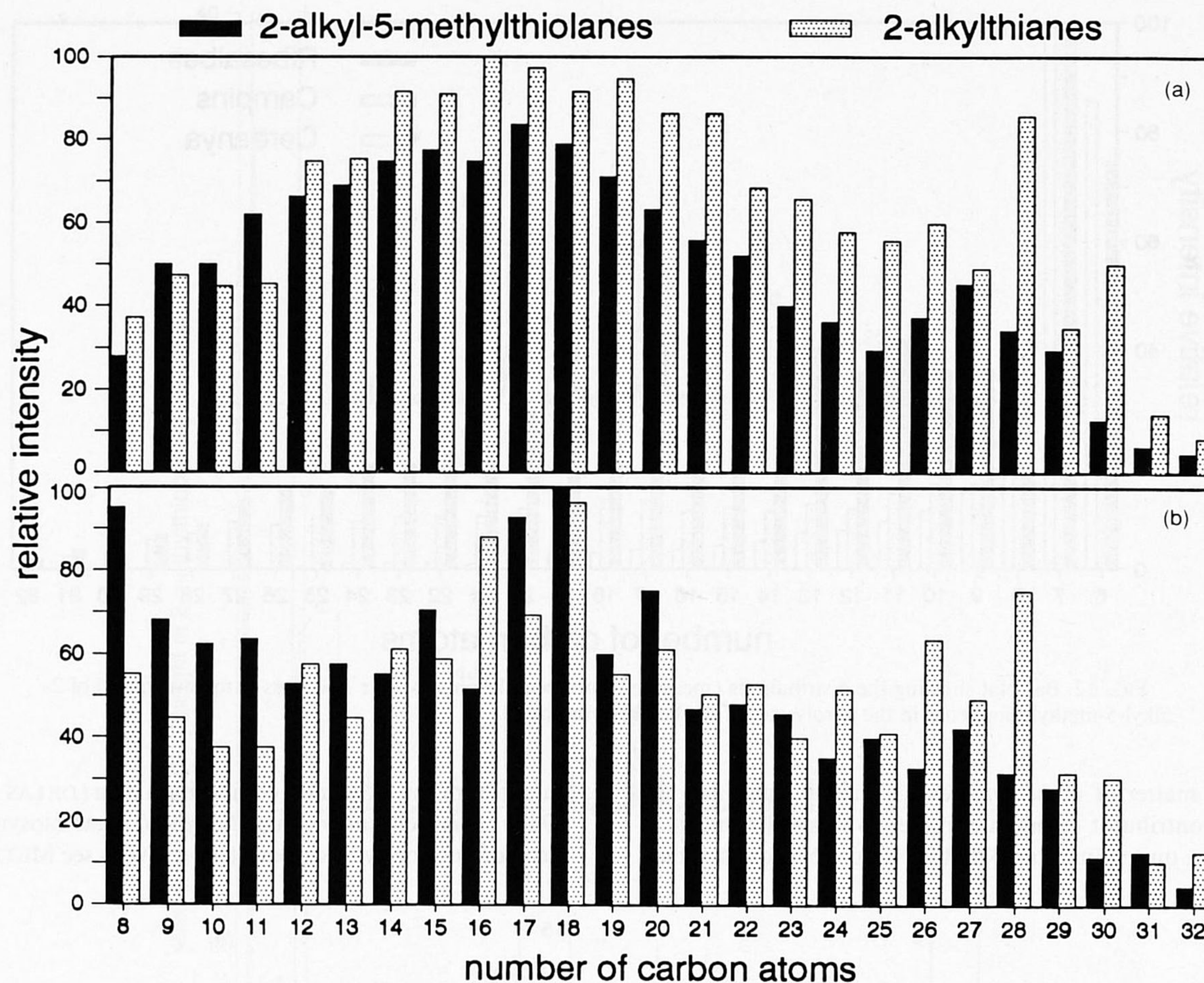


FIG. 14. Bar plots showing the distributions (measured from peak heights in mass chromatograms m/z 101) of the homologous series of 2-alkyl-5-methylthiolanes and 2-alkylthianes present in the flash pyrolysates of the kerogens of (a) Ribesalbes and (b) Campins.

al., 1992). The structures of the hydrocarbons produced depend on the race. Race A biosynthesizes large amounts of C_{23} – C_{31} n -alkadienes and trienes dominated by the C_{27} and C_{29} members (METZGER et al., 1985, 1986), whereas race B produces C_{30} – C_{37} triterpenoid hydrocarbons, the botryococenes of general formula C_nH_{2n-10} (METZGER et al., 1985; DAVID et al., 1988). The L race is characterized by the production of lycopa-14,18-diene (METZGER and CASADEVALL, 1987; METZGER et al., 1988). None of these alkenes have been identified in the Ribesalbes oil shale (DE LAS HERAS, 1989). Although C_{23} – C_{31} n -alkanes are present in the Ribesalbes oil shale (DE LAS HERAS, 1989), their distribution is more consistent with an origin from epicuticular waxes from higher plants (EGLINTON and HAMILTON, 1963) than from hydrogenated n -alkadienes and trienes from *B. braunii*. Lycopadiene was not expected to be found because the algaenan of *B. braunii* race L is composed of isoprenoid alkyl chains (METZGER and CASADEVALL, 1987; DERENNE et al., 1989, 1990a) and, thus, has a completely different structure from those from races A and B (LARGEAU et al., 1986; KADOURI et al., 1988) and the kerogen of Ribesalbes oil shale. However, biomarkers of race A or B should be highly abundant. An explanation for this observed discrepancy could be that the

n -alkadienes and -trienes or botryococenes have been sulphurized completely during early diagenesis so that their carbon skeletons are not present in the hydrocarbon fraction of the sediment extract.

DE LAS HERAS (1989) has analyzed the low molecular-weight organic sulphur compounds but could not find organic sulphur compounds possessing such carbon skeletons. The possibility remains that these alkenes have become part of the macromolecular aggregates which are formed by intermolecular sulphur cross linking of lipids during early diagenesis (SINNINGHE DAMSTÉ et al., 1988b; KOHNEN et al., 1991a,b; DE GRAAF et al., 1992). Therefore, the polar fraction of the sediment extract containing these aggregates was desulphurized with Raney Ni. A very high yield (ca. 60%) of saturated hydrocarbons was obtained. C_{35} hopanes (IV and V, Fig. 18), n -alkanes, phytane (II), C_{20} (I), and C_{25} (III) highly branched isoprenoid alkanes, and C_{27} and C_{29} $5\alpha(H),14\alpha(H),17\alpha(H)$ -, and $5\beta(H),14\alpha(H),17\alpha(H)$ -steranes are abundant. The distribution of the n -alkanes is dominated by the C_{27} and C_{29} members, clearly indicating that the long-chain n -alkadienes and -trienes biosynthesized by *B. braunii* race A have become sulphurized during the early stages of diagenesis. It is worthy of note that the organic matter

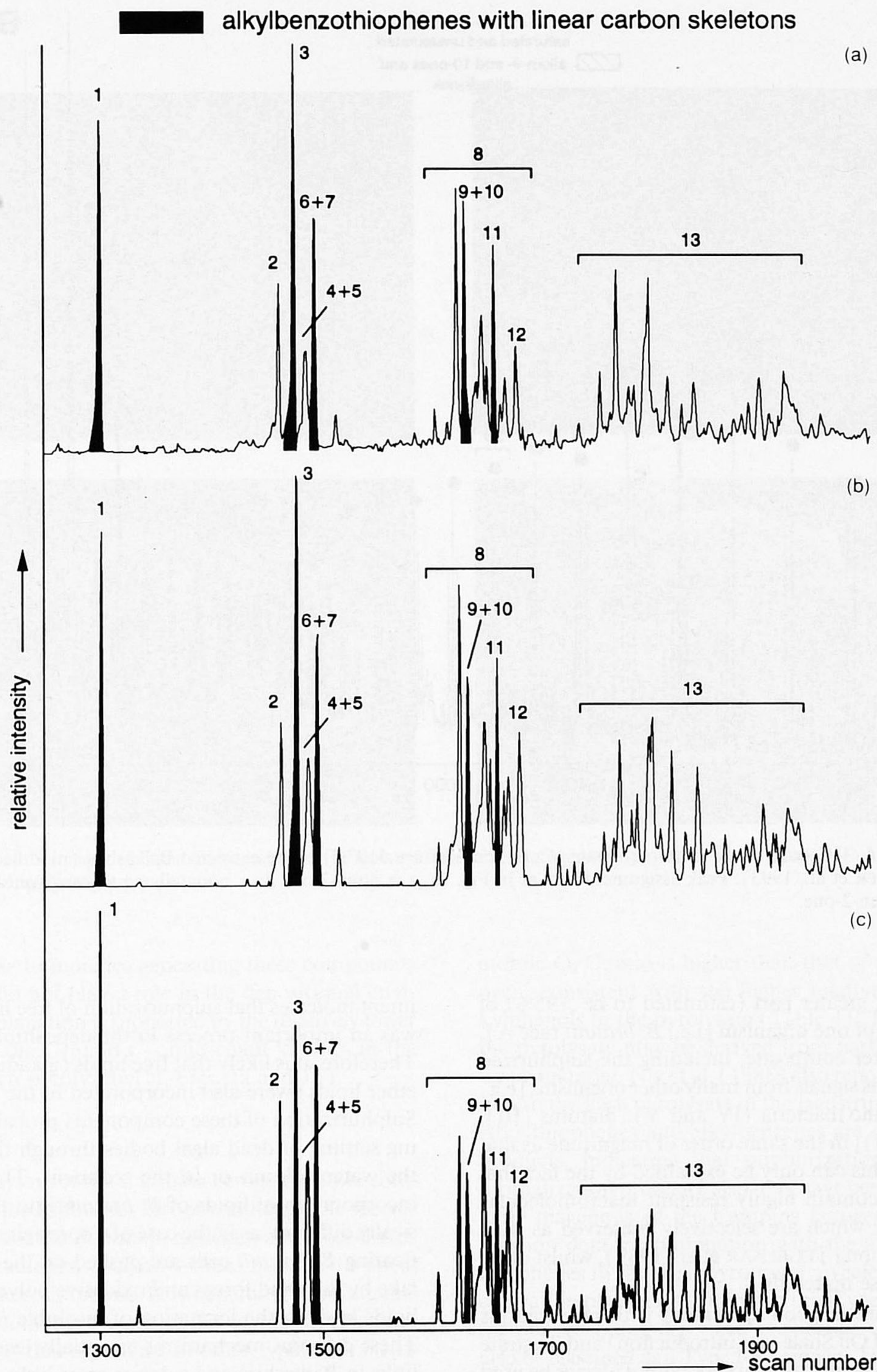


FIG. 15. Partial, accurate (mass window 0.03) mass chromatograms of m/z 134.02 + 147.02 + 148.02 + 161.02 + 162.02 + 175.03 + 176.03 illustrating the distribution of benzothiophenes and their C_1 - C_3 alkylated derivatives in the flash pyrolysates of the kerogens of (a) Ribesalbes, (b) Campins, and (c) Cerdanya. Key: 1 = benzo[*b*]thiophene, 2 = 7-methylbenzo[*b*]thiophene, 3 = 2-methylbenzo[*b*]thiophene, 4 = 5-methylbenzo[*b*]thiophene, 5 = 6-methylbenzo[*b*]thiophene, 6 = 4-methylbenzo[*b*]thiophene, 7 = 3-methylbenzo[*b*]thiophene, 8 = C_2 -benzo[*b*]thiophenes, 9 = 2-ethylbenzo[*b*]thiophene, 10 = 4-ethylbenzo[*b*]thiophene, 11 = 2,4-dimethylbenzo[*b*]thiophene, 12 = 2,3-dimethylbenzo[*b*]thiophene, and 13 = C_3 -benzo[*b*]thiophenes. Peaks corresponding to alkylbenzothiophenes with linear carbon skeletons are indicated in black.

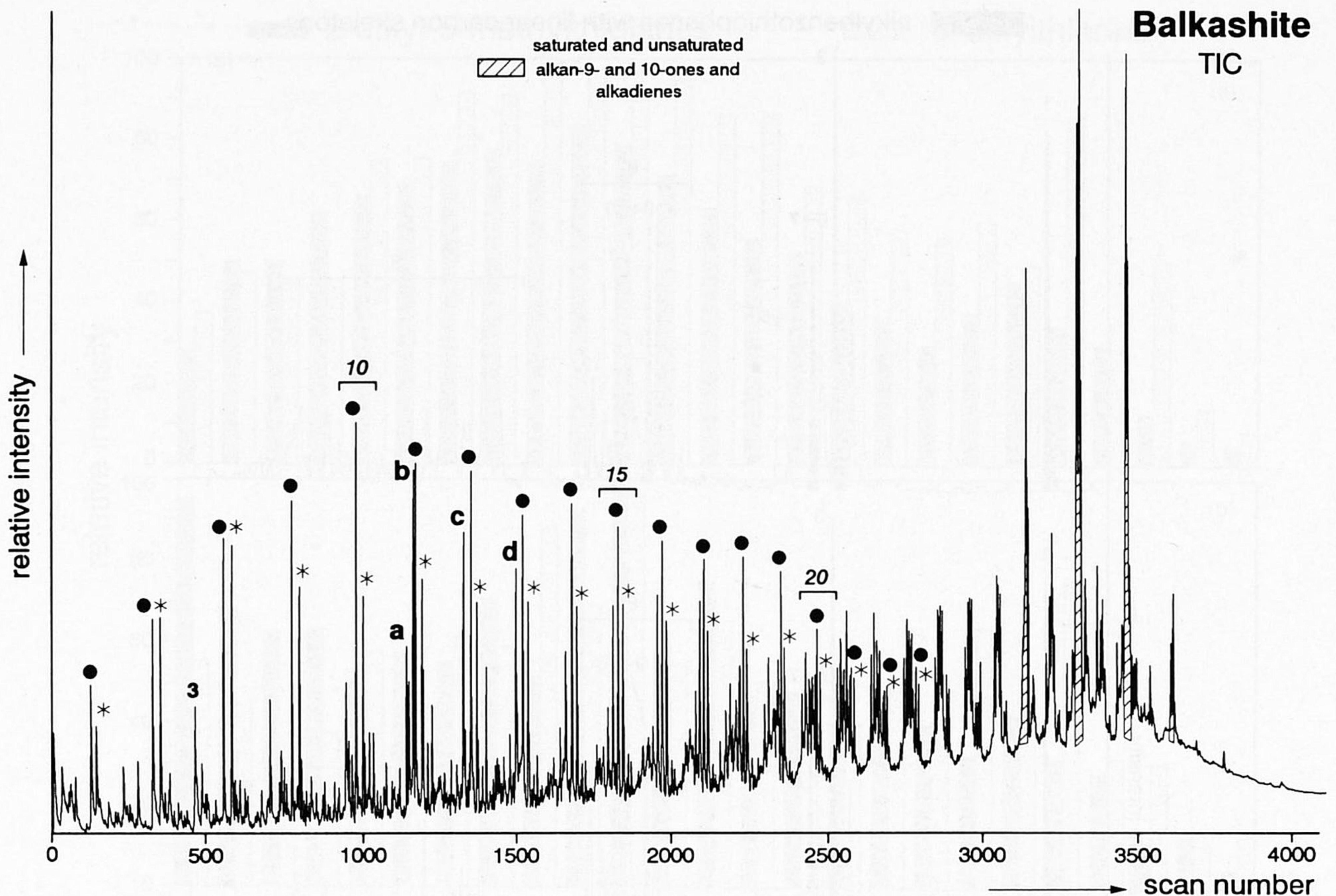


FIG. 16. TIC trace of the flash pyrolysate (Curie temperature 610°C) of the extracted Balkashite (modified from GATELLIER et al., 1993). Peak assignments are as in Fig. 1a. a = nona-2-one, b = nonanal, c = decan-2-one, and d = undecan-2-one.

consists for the far greater part (estimated to be >95%) of preserved material of one organism (i.e., *B. braunii* race A), whilst the biomarker composite, including the sulphurized biomarkers, contains signals from many other organisms [e.g., higher plants, (cyano)bacteria (IV and V), diatoms (III), other green algae (I)] in the same order of magnitude as that from *B. braunii*. This can only be explained by the fact that certain organisms contain highly resistant macromolecular material and lipids which are selectively preserved as such or after sulphurization (TEGELAAR et al., 1989), whilst other organisms lack these materials.

These findings are in good agreement with observations made for the Messel Oil Shale (see introduction) and illustrate that low molecular-weight biomarkers cannot always be used to assess the major contributors of organic matter to sediments. It should be noted that the Messel Oil Shale is not rich in organic sulphur, indicating that natural sulphurization was not an important mechanism for "hiding" biomarkers from the alga *T. minimum*. Therefore, biomarkers can also give a biased view of the major sources of organic matter in depositional environments where sulphurization of organic matter is not an important process.

The abundance of the C₂₇ and C₂₉ *n*-alkanes in the desulphurized polar fraction of the extract of the Ribesalbes sed-

iment indicates that sulphurization of free lipids of *B. braunii* was an important process in the depositional environment. Therefore, it is likely that free lipids (alkadienes and -trienes, ether lipids) were also incorporated in the kerogen fraction. Sulphurization of these components probably occurred during settling of dead algal bodies through the anoxic part of the water column or in the sediment. This mechanism of incorporation of lipids of *B. braunii* into the kerogen is basically different, as in the case of Coorongite formation where floating *B. braunii* cells are pushed on the shorelines of the lake by the wind forces and oxidative polymerization of free lipids leads to the formation of insoluble resistant material. These different mechanisms essentially lead to oxygen cross links in Balkashite and sulphur cross links in the Ribesalbes kerogen. This hypothesis is also consistent with the higher atomic O/C ratio of Balkashite (0.14; GATELLIER et al., 1993) compared to that of the Ribesalbes kerogen (0.09; Table 1). Because thermal degradation in both cases proceeds mainly via reactions associated with the bond between the hetero atom and a carbon atom, the pyrolysis products are similar. In case of the pyrolysate of the Ribesalbes kerogen, the C₂₇ and C₂₉ *n*-alkan-9-ones, *n*-alk-1-en- ω^9 -ones, *n*-alkan-10-ones, and *n*-alk-1-en- ω^{10} -ones must be related to sulphur-bound ether lipids since oxidative polymerization of free lip-

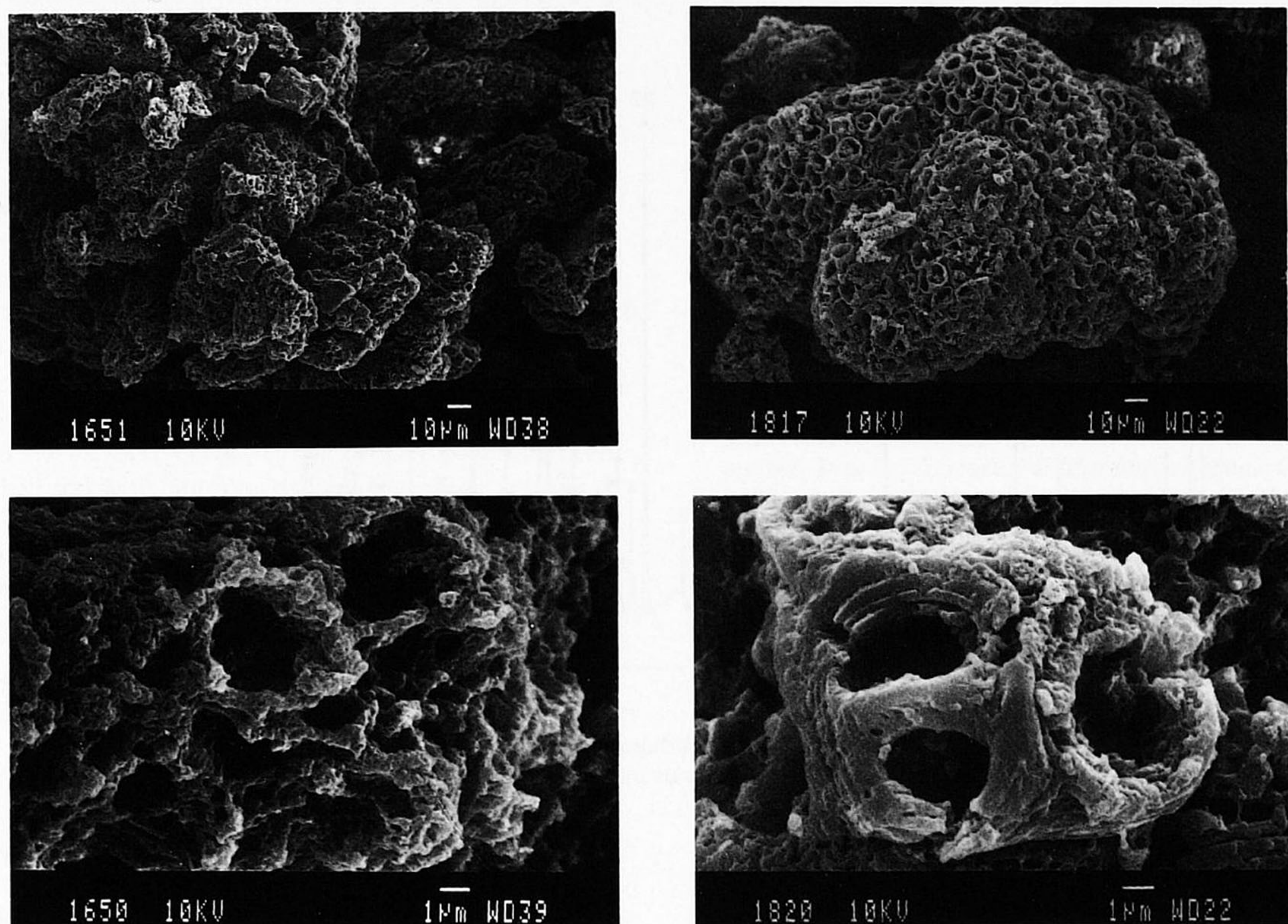


FIG. 17. Scanning electron micrographs of the isolated Ribesalbes kerogen (left panels) and the Pliocene Pula alginite from Hungary (right panels).

ids, also giving rise to moieties generating these compounds upon pyrolysis, did not play a role in the depositional environment. This explanation is supported by the relatively lower concentration of the C_{27} and C_{29} mid-chain ketones in the Ribesalbes kerogen pyrolysate (cf. Figs. 1a and 16).

Campins Kerogen

The flash pyrolysate of the Campins kerogen is quite comparable to that of the Ribesalbes kerogen, although the specific pyrolysis products of the *B. braunii* algaenan and cross-linked lipids (e.g., *n*-alkadienes, *n*-alkan-9-ones, *n*-alkan-10-ones) are significantly less abundant. It is concluded that organic matter of *B. braunii* have contributed to the sedimentary organic matter but that algaenans of other type(s) of lacustrine alga(e) were also important, producing a kerogen with a high atomic H/C ratio (1.53). The microscopic data did not provide a clue to what these other algae may be. In this context it should be noted that algaenans do occur in other types of lacustrine microalgae which cannot be recognized in sediments with light or UV fluorescence microscopy (LARGEAU et al., 1990; DERENNE et al., 1991). The alkylthiophene, alkylbenzene, and alkylbenzothiophene distributions also indicate the mixed origin for the kerogen since the compounds with linear carbon skeletons are less dominant, as in case of the Ribesalbes kerogen pyrolysate. The

atomic O/C ratio is higher than that of the Ribesalbes kerogen, consistent with the higher relative abundance of alkylphenols in the pyrolysate (Table 4). The alkylphenols in the pyrolysate may be derived from partly degraded woody tissue material. NIP et al. (1988) also reported abundant phenols in the flash pyrolysate of the lacustrine Messel Oil Shale. Alkylthiophenes and alkylbenzenes are dominant pyrolysis products, indicating that sulphurization and cyclization/aromatization processes also may have been important during early diagenesis of the Campins kerogen. Elemental composition data in combination with the abundance of alkylthiophenes in the flash pyrolysate revealed the unusual concentration of organic sulphur in this Type I kerogen. Following our reasoning described previously, this kerogen should also be classified as a Type I-S kerogen. The amount of pyrite present in the sediment is quite substantial, as indicated by the elemental composition (Table 1) and the microscopic data. This demonstrates that even with the abundant presence of reactive iron species, sulphurization of organic matter in lacustrine basins can be an important process if sulphate is supplied from external sources.

Cerdanya Kerogen

The kerogen pyrolysate of the Cerdanya sample is strikingly different from those of Ribesalbes and Campins kerogens

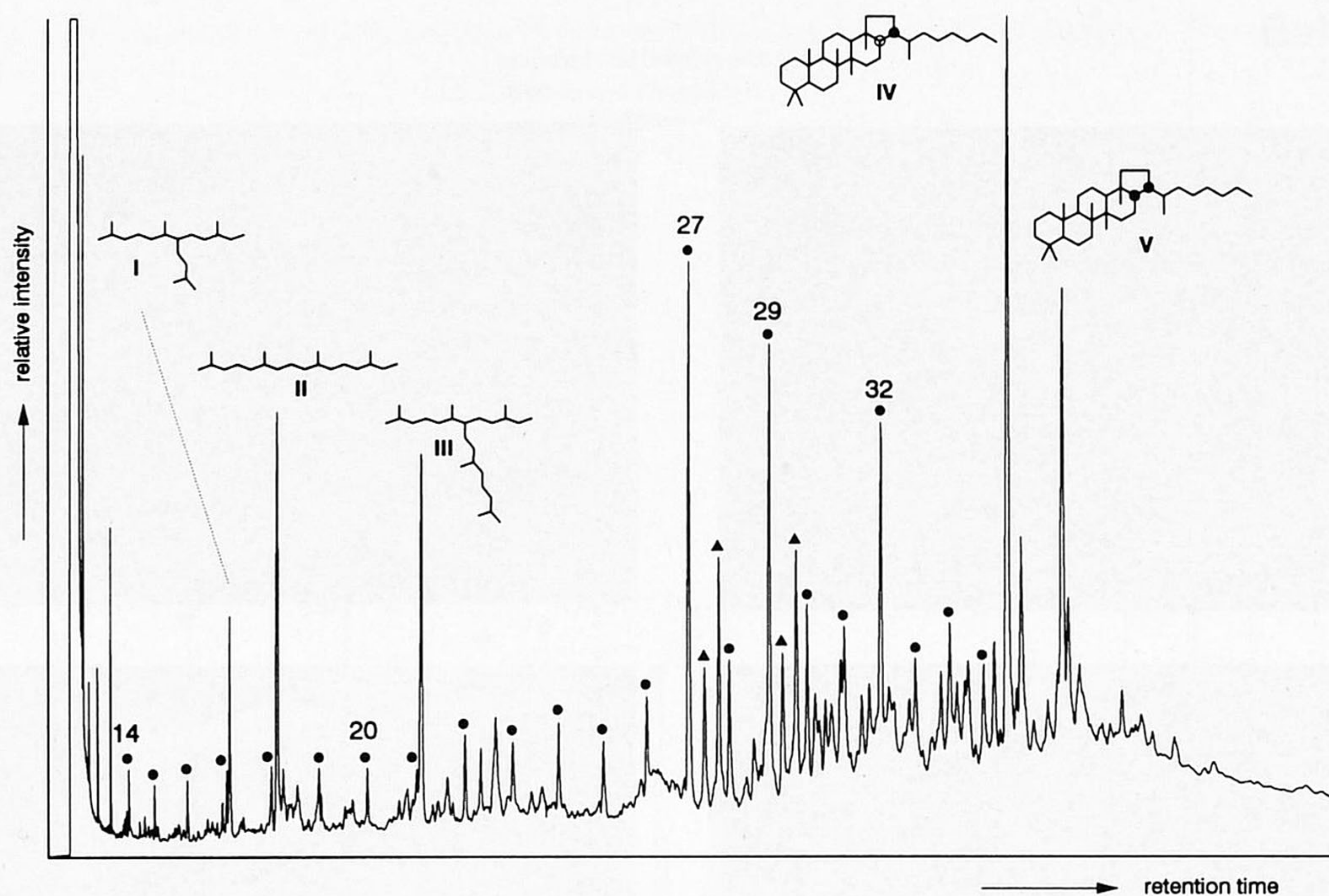


FIG. 18. Gas chromatogram of the saturated hydrocarbons obtained by Raney Ni desulphurization of the polar fraction of the extract of the Ribesalbes oil shale. Numerals indicate number of carbon atoms of *n*-alkanes (indicated with black dots). Filled triangles indicate steranes.

(Fig. 1; Table 6): *n*-alkanes and *n*-alk-1-enes are only minor compounds in the pyrolysate, which is dominated by aromatic compounds (C_1 - C_3 alkylbenzenes and, to a lesser extent, alkylphenols and alkylnaphthalenes). This is consistent with the lower atomic H/C ratio of the Cerdanya kerogen (Table 1). The alkylphenols are relatively more abundant than in the pyrolysates of the Ribesalbes and Campins kerogens, which is in good agreement with the much higher atomic O/C ratio of this kerogen. This is probably due to a higher contribution of terrestrial higher plant material to the kerogen, which is suggested also by the higher amount of pollen grains in this sample (Table 2). The most intriguing observation is that this kerogen contains a significant contribution from remains of the freshwater alga *Pediastrum* (Table 2). Although biomacromolecules so far identified in algal cell walls are always very aliphatic in nature (DE LEEUW and LARGEAU, 1992), we can speculate that the unusual abundance of alkylbenzenes in the Cerdanya kerogen pyrolysate results from the presence of an aromatic or partly aromatic biomacromolecule in *Pediastrum*. In this context, it should be noted that the overall composition of the Cerdanya kerogen pyrolysate is quite similar to that of the Cambrian Alum shale (HORSFIELD et al., 1992), which was shown to be derived mainly from algal remains as well. The unusual structure of kerogen of the uranium-rich Alum shale might have been brought about by uranium-related alteration effects, or, alternatively, its structure might have been inherited directly from biopolymeric or carotenoid-derived precursors in algae and bacteria (HORSFIELD et al., 1992). The first hypothesis was recently deemed unlikely by HARTGERS et al. (1993), but the second suggestion is consistent with our hypothesis. The un-

usual series of non-terminal *n*-alkenes in the pyrolysate of the Cerdanya kerogen also may be related to the presence of an unknown biopolymer in *Pediastrum* spp. These hypotheses are currently under investigation in our laboratory by analyses of cultured *Pediastrum* spp.

CONCLUSIONS

- 1) A new type of kerogen, rich in both hydrogen and sulphur, has been discovered in two lacustrine deposits. It is defined as the Type I-S kerogen with an atomic H/C ratio > 1.5 and an atomic S_{org}/C ratio > 0.04 in analogy with the Type II-S kerogen defined by ORR (1986). The Type I-S kerogen is formed in depositional environments where natural sulphurization (i.e., enrichment of organic matter with organic sulphur by reaction with inorganic sulphides) of hydrogen-rich algal remains is an important process. In lacustrine depositional environments, which are most prone to formation of hydrogen-rich kerogens, formation of Type I-S kerogens will require an external source of sulphate to enable a large production of inorganic sulphides. Sulphur-rich crude oils formed from lacustrine source rocks (e.g., Rozel Point Oil, Utah, USA, 7.5% S; SINNINGHE DAMSTÉ et al., 1987; oils from the Jiangnan Basin, China, 10.4–12.9% S; BRASSELL et al., 1988, SINNINGHE DAMSTÉ et al., 1989b) are possibly generated by thermal degradation of Type I-S kerogens.
- 2) In the Ribesalbes oil shale, ca. 95% of the kerogen originates from organic matter of the alga *B. braunii* race A by selective preservation of algaenan (a biomacromolecule present in the outer cell walls) and sulphurization of free

lipids. This latter process gives rise to high concentrations of highly characteristic C₂₇ and C₂₉ alkadienes and mid-chain ketones in the pyrolyzate due to the presence of sulphurized dialkenyl ether lipids in the kerogen. These characteristic pyrolysis products have also been observed in the pyrolyzate of a Recent Coorongite, although the ether lipids in this kerogen were probably incorporated via oxidative cross linking and not via sulphurization.

- 3) Although the organic matter in the Ribesalbes Oil Shale is mainly derived from *B. braunii*, the biomarkers (including sulphurized biomarkers; KOHNEN et al., 1991a) of this sediment are not at all dominated by chemical fossils derived from *B. braunii*. A similar bias of the biomarker composition is apparent from literature data on the Messel Oil Shale (ROBINSON et al., 1989; FREEMAN et al., 1990 vs. GOTH et al., 1989). Therefore, biomarkers must be used with caution to assess the major sources of organic matter in sediments.
- 4) Results on the Cerdanya sample suggest that the freshwater alga *Pediastrum* contains an aromatic or partly aromatic biomacromolecule.

Acknowledgments—We thank Dr. Anadón for provision of samples and geological data, Dr. H. L. ten Haven for elemental composition data of the kerogens, Dr. G. van Graas for Rock Eval data, and Drs. S. Derenne and C. Largeau for scanning electron microscopy and making unpublished results available. Drs. S. Derenne, C. Largeau, C. C. Walters, S. W. Imbus, and S. A. Macko provided useful comments on an earlier version of this paper. Mrs. A. Knoll-Kalkman and W. I. C. Rijpstra are acknowledged for analytical assistance. F. X. C. d. I. H. thanks the Ministerio de Educacion y Ciencia for a fellowship. This is Delft Organic Geochemistry Unit Contribution 245.

Editorial handling: S. A. Macko

REFERENCES

- ANADÓN P. (1986) Las facies lacustres del oligoceno de Campins (Vallés Oriental, provincia de Barcelona). *Cuadernos de Geología Ibérica* **10**, 271–294.
- ANADÓN P., CABRERA L., JULIA R., ROCA E., and ROSELL L. (1989) Lacustrine oil shale basins in Tertiary grabens from NE Spain (western European rift system). *Palaeogeogr. Palaeoclimatol. Palaeoec.* **70**, 7–28.
- BEHAR F. and PELET R. (1985) Pyrolysis-gas chromatography applied to organic geochemistry. Structural similarities between kerogens and asphaltenes from related rock extracts and oils. *J. Anal. Appl. Pyrol.* **8**, 173–187.
- BERKALOFF C., CASADEVALL E., LARGEAU C., METZGER P., PERACCA S., and VIRLET J. (1983) The resistant polymer of the walls of the hydrocarbon-rich alga *Botryococcus braunii*. *Phytochem.* **22**, 389–397.
- BRASSSELL S. C., SHENG G., FU J., and EGLINTON G. (1988) Biological markers in lacustrine Chinese oil shales. In *Lacustrine Petroleum Source Rocks* (ed. A. J. FLEET et al.); *Geol. Soc. Publ.* **40**, pp. 299–308. Blackwell.
- DAVID M., METZGER P., and CASADEVALL E. (1988) Two cyclobotryococenes from the B race of the green alga *Botryococcus braunii*. *Phytochem.* **27**, 2863–2867.
- DE GRAAF W., SINNINGHE DAMSTÉ J. S., and DE LEEUW J. W. (1992) Laboratory simulation of natural sulphurization. I. Formation of monomeric and oligomeric isoprenoid polysulphides by low-temperature reactions of inorganic polysulphides with phytol and phytadienes. *Geochim. Cosmochim. Acta* **56**, 4321–4328.
- DE LAS HERAS X. (1989) Geoquímica orgànica de conques lacustres fòssils. Ph.D. thesis, University of Barcelona.
- DE LAS HERAS X., GRIMALT J. O., ALBAIGÉS J., JULIA R., and ANADÓN P. (1989) Origin and diagenesis of the organic matter in Miocene freshwater lacustrine phosphates (Cerdanya Basin, Eastern Pyrenees). *Org. Geochem.* **14**, 667–677.
- DE LEEUW J. W. and LARGEAU C. (1993) A review of macromolecular organic compounds that comprise living organisms and their role in kerogen, coal and petroleum formation. In *Organic Geochemistry* (ed. M. H. ENGEL and S. MACKO) (in press).
- DERENNE S., LARGEAU C., CASADEVALL E., and BERKALOFF C. (1989) Occurrence of a resistant biopolymer in the L race of *Botryococcus braunii*. *Phytochem.* **28**, 1137–1142.
- DERENNE S., LARGEAU C., CASADEVALL E., and SELLIER N. (1990a) Direct relationship between the resistant biopolymer and the tetraterpene hydrocarbon in the lycopadiene race of *Botryococcus braunii*. *Phytochem.* **29**, 2187–2192.
- DERENNE S., LARGEAU C., CASADEVALL E., SINNINGHE DAMSTÉ J. S., TEGELAAR E. W., and DE LEEUW J. W. (1990b) Characterisation of Estonian Kukersite by spectroscopy and pyrolysis: Evidence for abundant alkyl phenolic moieties in an Ordovician, marine, Type II/I kerogen. In *Advances in Organic Geochemistry 1989* (ed. B. DURAND and F. BEHAR); *Org. Geochem.* **16**, 873–888.
- DERENNE S., LARGEAU C., CASADEVALL E., BERKALOFF C., and ROUSSEAU B. (1991) Chemical evidence of kerogen formation in source rocks and oil shales via selective preservation of thin resistant outer walls of microalgae: Origin of ultralaminae. *Geochim. Cosmochim. Acta* **55**, 1041–1050.
- DERENNE S., METZGER P., LARGEAU C., VAN BERGEN P. F., GATELLIER J. P., SINNINGHE DAMSTÉ J. S., DE LEEUW J. W., and BERKALOFF C. (1992) Similar morphological and chemical variations of *Gloeocapsomorpha prisca* in Ordovician sediments and cultured *Botryococcus braunii* as a response to changes in salinity. In *Advances in Organic Geochemistry 1991* (ed. C. ECKHARDT and J. R. MAXWELL); *Org. Geochem.* (in press).
- DOUGLAS A. G., SINNINGHE DAMSTÉ J. S., FOWLER M. G., EGLINTON T. I., and DE LEEUW J. W. (1991) Flash pyrolysis of Ordovician kerogens: Unique distributions of hydrocarbons and sulphur compounds released from the fossilized alga *Gloeocapsomorpha prisca*. *Geochim. Cosmochim. Acta* **55**, 275–291.
- DOUGLAS A. G., SINNINGHE DAMSTÉ J. S., EGLINTON T. I., DE LEEUW J. W., and FOWLER M. G. (1992) Distribution and structure of hydrocarbons and heterocyclic sulphur compounds released from four kerogens of Ordovician age by means of flash pyrolysis. In *Early Organic Evolution: Implications for Mineral and Energy Resources* (ed. M. SCHIDLowski et al.), pp. 267–278. Springer.
- DUBOIS J.-E., CHRETIEN J. R., SOJAK L., and RIJKS J. A. (1980) Topological analysis of linear alkenes. *J. Chromatogr.* **194**, 121–134.
- DUBREIL C., DERENNE S., LARGEAU C., BERKALOFF C., and ROUSSEAU B. (1989) Mechanism of formation and chemical structure of Coorongite. I. Role of resistant biopolymer and of the hydrocarbons of *Botryococcus braunii*. Ultrastructure of Coorongite and its relationship with Torbanite. *Org. Geochem.* **14**, 543–553.
- DURAND B. (1980) *Kerogen-Insoluble Matter from Sedimentary Rocks* (ed. B. DURAND), pp. 13–34. Editions Technip.
- DURAND B. and MONIN J. C. (1980) Elemental analysis of kerogen. In *Kerogen-Insoluble Matter from Sedimentary Rocks* (ed. B. DURAND), pp. 113–142. Editions Technip.
- EGLINTON G. and HAMILTON R. J. (1963) The distribution of *n*-alkanes. In *Chemical Plant Taxonomy* (ed. T. SWAIN), pp. 187–208. Academic.
- EGLINTON T. I., SINNINGHE DAMSTÉ J. S., POOL W., DE LEEUW J. W., EIJKEL G., and BOON J. J. (1992) Organic sulphur in macromolecularly sedimentary organic matter: II. Analysis of distributions of sulphur-containing pyrolysis products using multivariate techniques. *Geochim. Cosmochim. Acta* **56**, 1545–1560.
- ESPITALIÉ J., LAPORTE J. L., MADEC M., MARQUIS F., LEPLAT P., PAULET J., and BOUTEFU A. (1977) Méthode rapide de caractérisation des roches mere de leur potentiel pétrolier et de leur degré d'évolution. *Rev. Inst. Fr. Pétr.* **28**, 37–66.
- FLEET A. J., KELTS K., and TALBOT M. R., ed. (1988) *Lacustrine Petroleum Source Rocks; Geol. Soc. Publ.* **40**. Blackwell.

- FORSTER P. G., ALEXANDER R., and KAGI R. I. (1989) Identification and analysis of tetramethylnaphthalenes in petroleum. *J. Chromatogr.* **483**, 384–389.
- FREEMAN K. H., HAYES J. M., TRENDEL J.-M., and ALBRECHT P. A. (1990) Evidence from carbon isotope measurements for diverse origins of sedimentary hydrocarbons. *Nature* **343**, 254–256.
- GATELLIER J. P., DE LEEUW J. W., SINNINGHE DAMSTÉ J. S., DERENNE S., LARGEAU C., and METZGER P. (1993) A comparative study of macromolecular substances of a Coorongite and cell walls of the extant alga *Botryococcus braunii*. *Geochim. Cosmochim. Acta* (submitted).
- GOTH K., DE LEEUW J. W., PUTTMANN W., and TEGELAAR E. W. (1989) Origin of Messel oil shale. *Nature* **336**, 759–761.
- GRANSCH J. A. and POSTHUMA J. (1974) On the origin of sulphur in crudes. In *Advances in Organic Geochemistry 1973* (ed. B. TISSOT and F. BIENNER), pp. 727–739. Editions Technip.
- GRAY N. R., LANCASTER C. J., and GETHNER J. (1991) Chemometric analysis of pyrolysate compositions: A model for predicting the organic matter type of source rocks using pyrolysis-gas chromatography. *J. Anal. Appl. Pyrol.* **20**, 87–106.
- HALBOUTY M. T. (1980) Methods used, and experience gained, in exploration for new oil and gas fields in highly explored (mature) areas. *Bull. AAPG* **64**, 1210–1222.
- HARTGERS W. A., SINNINGHE DAMSTÉ J. S., and DE LEEUW J. W. (1992a) Identification of C₂–C₄ alkylated benzenes in flash pyrolysates of kerogens, coals and asphaltenes. *J. Chromatogr.* **607**, 367–376.
- HARTGERS W. A., SINNINGHE DAMSTÉ J. S., and DE LEEUW J. W. (1993) Geochemical significance of alkylbenzene distributions in flash pyrolysates of kerogens, coals and asphaltenes. *Geochim. Cosmochim. Acta* (submitted).
- HORSFIELD B. (1989) Practical criteria for classifying kerogens: Some observations from pyrolysis-gas chromatography. *Geochim. Cosmochim. Acta* **53**, 891–901.
- HORSFIELD B., BHARATI S., LARTER S. R., LEISTNER F., LITCKE R., SCHENK H. J., and DYPVIK H. (1992) On the typical petroleum-generating characteristics of alginite in the Cambrian Alum shale. In *Early Organic Evolution: Implications for Mineral and Energy Resources* (ed. M. SCHIDLowski et al.), pp. 257–266. Springer.
- KADOURI A., DERENNE S., LARGEAU C., CASADEVALL E., and BERKALOFF C. (1988) Resistant biopolymer in the outer walls of *Botryococcus braunii*, B race. *Phytochem.* **27**, 551–557.
- KATZ B. J. (1988) Clastic and carbonate lacustrine systems: an organic geochemical comparison (Green River Formations and East African lake sediments). In *Lacustrine Petroleum Source Rocks; Geol. Soc. Publ. 40* (ed. A. J. FLEET et al.), pp. 81–90. Blackwell.
- KATZ B. J., ed. (1990) *Lacustrine Basin Exploration; AAPG Mem.* **50**.
- KELTS K. (1988) Environments of deposition of lacustrine petroleum source rocks: An introduction. In *Lacustrine Petroleum Source Rocks; Geol. Soc. Publ. 40* (ed. A. J. FLEET et al.), pp. 3–26. Blackwell.
- KOHNEN M. E. L., SINNINGHE DAMSTÉ J. S., and DE LEEUW J. W. (1991a) Biases from natural sulphurization in palaeoenvironmental reconstruction based on hydrocarbon biomarker distributions. *Nature* **349**, 775–778.
- KOHNEN M. E. L., SINNINGHE DAMSTÉ J. S., KOCK-VAN DALEN A. C., and DE LEEUW J. W. (1991b) Di- or polysulphide-bound biomarkers in sulphur-rich geomacromolecules as revealed by selective chemolysis. *Geochim. Cosmochim. Acta* **55**, 1375–1394.
- LARGEAU C., DERENNE S., CASADEVALL E., KADOURI A., and SELLIER N. (1986) Pyrolysis of immature torbanite and of the resistant biopolymer (PRB A) isolated from extant alga *Botryococcus braunii*. Mechanism for the formation and structure of torbanite. In *Advances in Organic Geochemistry 1985* (ed. D. LEYTHAEUSER and J. RULLKÖTTER); *Org. Geochem.* **10**, 1023–1032.
- LARGEAU C., DERENNE S., CASADEVALL E., BERKALOFF C., COROLLEUR M., LUGARDON B., RAYNAUD J. F., and CONNAN J. (1990) Occurrence and origin of “ultralaminar” structures in “amorphous” kerogens of various source rocks and oil shales. In *Advances in Organic Geochemistry 1989* (ed. B. DURAND and F. BEHAR); *Org. Geochem.* **16**, 889–895.
- LEE M. L., VASSILLAROS D. L., WHITE C. M., and NOVOTNY M. (1979) Retention indices for programmed-temperature capillary-column gas chromatography of polycyclic aromatic hydrocarbons. *Anal. Chem.* **51**, 768–773.
- METZGER P. and CASADEVALL E. (1987) Lycopadiene, a tetraterpenoid hydrocarbon from new strains of the green alga *Botryococcus braunii*. *Tetrahedron Lett.* **28**, 3931.
- METZGER P., BERKALOFF C., CASADEVALL E., and COUTE A. (1985) Alkadiene- and botryococcene-producing races of wild strains of *Botryococcus braunii*. *Phytochem.* **24**, 2305–2312.
- METZGER P., TEMPLIER J., LARGEAU C., and CASADEVALL E. (1986) A *n*-alkatriene and some *n*-alkadienes from the A race of the green alga *Botryococcus braunii*. *Phytochem.* **25**, 1869.
- METZGER P., CASADEVALL E., and COUTE A. (1988) Botryococcenes distribution in strains of the green alga *Botryococcus braunii*. *Phytochem.* **27**, 1383–1388.
- METZGER P., LARGEAU C., and CASADEVALL E. (1992) Lipids and macromolecular lipids of the hydrocarbon-rich microalga *Botryococcus braunii*. Chemical structure and biosynthesis. Geochemical and biotechnological importance. In *Progress in the Chemistry of Organic Natural Products*. (ed. W. HERZ et al.), Vol. 57, pp. 1–70. Springer.
- NIP M., DE LEEUW J. W., and SCHENCK P. A. (1988) Characteristics of the insoluble organic matter of Messel oil shale as indicators of diagenesis and palaeoenvironment. *Cour. Forsch.-Inst. Senckenberg* **107**, 13–28.
- ORR W. L. (1986) Kerogen/asphaltene/sulphur relationships in sulphur-rich Monterey oils. In *Advances in Organic Geochemistry 1985* (ed. D. LEYTHAEUSER and J. RULLKÖTTER); *Org. Geochem.* **10**, 499–516.
- ORR W. L. and SINNINGHE DAMSTÉ J. S. (1990) Introduction and overview: Geochemistry of sulfur in petroleum systems. In *Geochemistry of Sulfur in Fossil Fuels* (ed. W. L. ORR and C. M. WHITE), pp. 2–29. *ACS Symp. Ser. 429*. Amer. Chem. Soc.
- POWELL T. G. (1986) Petroleum geochemistry and depositional setting of lacustrine source rocks. *Mar. Petr. Geol.* **3**, 200–219.
- ROBINSON N., EGLINTON G., CRANWELL P. A., and ZENG Y. B. (1989) Messel oil shale (western Germany): Assessment of depositional palaeoenvironment from the content of biological marker compounds. *Chem. Geol.* **76**, 153–173.
- ROWLAND S. J., ALEXANDER R., and KAGI R. I. (1984) Analysis of trimethylnaphthalenes in petroleum by capillary gas chromatography. *J. Chromatogr.* **294**, 407–412.
- SINNINGHE DAMSTÉ J. S. and DE LEEUW J. W. (1990) Analysis, structure and geochemical significance of organically-bound sulphur in the geosphere: State of the art and future research. In *Advances in Organic Geochemistry 1989* (ed. B. DURAND and F. BEHAR); *Org. Geochem.* **16**, 1077–1101.
- SINNINGHE DAMSTÉ J. S., DE LEEUW J. W., KOCK-VAN DALEN A. C., DE ZEEUW M. A., DE LANGE F., RIJSTRA W. I. C., and SCHENCK P. A. (1987) The occurrence and identification of series of organic sulphur compounds in oils and sediment extracts. I. A study of Rozel Point Oil (USA). *Geochim. Cosmochim. Acta* **51**, 2369–2391.
- SINNINGHE DAMSTÉ J. S., KOCK-VAN DALEN A. C., DE LEEUW J. W., and SCHENCK P. A. (1988a) Identification of homologous series of alkylated thiophenes, thiolanes, thianes and benzothiophenes present in pyrolysates of sulphur-rich kerogens. *J. Chromatogr.* **435**, 435–452.
- SINNINGHE DAMSTÉ J. S., RIJSTRA W. I. C., DE LEEUW J. W., and SCHENCK P. A. (1988b) Origin of organic sulphur compounds and sulphur-containing high-molecular-weight substances in sediments and crude oils. In *Advances in Organic Geochemistry 1987* (ed. L. MATAVELLI and L. NOVELLI); *Org. Geochem.* **13**, 593–606.
- SINNINGHE DAMSTÉ J. S., EGLINTON T. I., DE LEEUW J. W., and SCHENCK P. A. (1989a) Organic sulphur in macromolecular sedimentary organic matter. I. Structure and origin of sulphur-containing moieties in kerogen, asphaltenes and coal as revealed by flash pyrolysis. *Geochim. Cosmochim. Acta* **53**, 873–889.
- SINNINGHE DAMSTÉ J. S., RIJSTRA W. I. C., DE LEEUW J. W., and SCHENCK P. A. (1989b) The occurrence and identification of series

- of organic sulphur compounds in oils and sediment extracts. II. Their presence in samples from hypersaline and non-hypersaline depositional environments and possible application as source, maturity and palaeoenvironmental indicators. *Geochim. Cosmochim. Acta* **53**, 1323–1341.
- SOLLI H. and LEPLAT P. (1986) Pyrolysis-gas chromatography of asphaltenes and kerogens from source rocks and coals—A comparative structural study. In *Advances in Organic Geochemistry 1985* (ed. D. LEYTHAEUSER and J. RULLKÖTTER); *Org. Geochem.* **10**, 313–329.
- TALBOT M. R. (1988) The origins of lacustrine oil source rocks: Evidence from the lakes of tropical Africa. In *Lacustrine Petroleum Source Rocks; Geol. Soc. Publ. 40* (ed. A. J. FLEET et al.), pp. 3–26. Blackwell.
- TEGELAAR E. W., DE LEEUW J. W., DERENNE S., and LARGEAU C. (1989) A reappraisal of kerogen formation. *Geochim. Cosmochim. Acta* **53**, 3103–3106.
- TISSOT B. P. and WELTE D. H. (1984) *Petroleum Formation and Occurrence.*, 2d edn. Springer.
- VAN BERGEN P. F., JANSSEN N. M. M., ALFERINK M., and KERP J. H. F. (1990) Recognition of organic matter types in standard palynological slides. In *Proc. Intl. Symp. Org. Petrol.* (ed. W. J. J. FERMONT and J. W. WEEGINK); *Meded. Rijks Geol. Dienst* **45**, 9–21.
- YANG W.-L., LI Y.-K., and GAO R.-Q. (1981) Formation and evolution of non-marine petroleum in the Songliao Basin, China. Scientific research and design institute of Daging Oil Field, China. Report.
- YANG W.-L., LI Y.-K., and GAO R.-Q. (1985) Formation and evolution of non-marine petroleum in Songliao Basin, China. *AAPG Bull.* **69**, 1112–1122.