

Unique distributions of hydrocarbons and sulphur compounds released by flash pyrolysis from the fossilised alga *Gloeocapsomorpha prisca*, a major constituent in one of four Ordovician kerogens

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Abstract—Kerogens isolated from four rocks of Ordovician age from North America have been analysed by combined pyrolysis-gas chromatography-mass spectrometry to compare and contrast the type and distribution of sulphur-containing compounds, and aromatic and aliphatic hydrocarbons present in the pyrolysates.

When pyrolysed, all of the kerogens released several series of heterocyclic sulphur compounds including alkylthiophenes, alkylthiolanes, alkylthianes, and alkylbenzothiophenes together with *n*-alkanes, *n*-alk-1-enes, and alkylcyclohexanes as well as alkyl-substituted benzenes and naphthalenes. One of the kerogens, isolated from the Guttenberg oil rock, consisted predominantly of the alga *Gloeocapsomorpha prisca*, which produced sulphur compounds and hydrocarbons with fingerprint pyrograms that were different from those of the other three kerogens. The data provide *prima facie* evidence that these distributions may act as pseudo "biological markers" for this species of alga, namely that unsaturated kerogen moieties available for the uptake of sulphur, or which can cyclise to form hydrocarbons, distinguish *Gloeocapsomorpha prisca* from the contributing organisms of the other kerogens analysed.

INTRODUCTION

PREVIOUS STUDIES HAVE indicated that many Ordovician oils display a unique chemistry compared to oils of other ages. These include distinctive distributions of *n*-alkanes, *n*-alkyl, and methyl-*n*-alkylcyclohexanes, and relatively low concentrations of acyclic isoprenoids and polycyclic alkanes (REED et al., 1986; HOFFMANN et al., 1987; LONGMAN and PALMER, 1987; FOWLER, 1991). These unusual oils are sourced from rocks that are rich in the alga *Gloeocapsomorpha prisca* (ZALESSKY, 1917). Organic-rich sediments in which most of the organic matter consists of the remains of *G. prisca* have been termed "kukersites" (HUTTON, 1987). Based on its morphology, ZALESSKY (1917) originally thought that *G. prisca* was a planktonic cyanobacterium. Recently, there have been some attempts to infer the biochemistry of *G. prisca* on the basis of the unique chemistry of Ordovician kukersites and their derived oils. REED et al. (1986) considered it to be a non-photosynthetic prokaryotic benthonic chemoautotroph whilst HOFFMANN et al. (1987) suggested that it was a phototrophic, planktonic, possibly eukaryotic alga. In a recent review, FOWLER (1991) discussed the evidence as to whether *G. prisca* was prokaryotic or eukaryotic, and deduced that no firm decision could be made on current evidence. FOSTER et al. (1989) confirm that further work is necessary to determine the exact nature of *G. prisca* but are of the opinion that the affinity between it and modern *Cyanophyta* is proven.

Finally, STASIUK and OSADETZ (1991) in a study of the Yeoman Formation kukersites of Southern Saskatchewan, which are rich in *G. prisca*, reached conclusions which fell between the two current hypotheses due to REED et al. (1986) and HOFFMAN et al. (1987); that is, *G. prisca* had a life cycle that included both planktonic and benthic life stages.

Flash pyrolysis, in tandem with gas chromatography, or gas chromatography-mass spectrometry has been an important tool in previous investigations aimed at elucidating structural moieties of macromolecular substances of geochemical interest, for example, coal macerals (LARTER and DOUGLAS, 1978; VAN GRAAS et al., 1980; NIP et al., 1989), asphaltenes (BEHAR and PELET, 1985), and kerogens (LARTER et al., 1978; VAN GRAAS et al., 1980; VAN DE MEENT et al., 1980; SOLLI et al., 1984; LARTER, 1984). Recently, this technique has been applied to characterise the organically bound sulphur in kerogens and related materials (SINNINGHE DAMSTÉ et al., 1988a, 1989) leading to the recognition of a number of distinctive groups of sulphur-containing moieties. Previous workers have discussed the hydrocarbon products from the pyrolysis of Ordovician kerogens, especially kukersites (e.g., KLESMENT and NAPPA, 1980; REED et al., 1986; FOWLER et al., 1986; HOFFMANN et al., 1987; JACOBSON et al., 1988). The thrust of the present work was to examine four Ordovician kerogens with a particular interest in characterising the sulphur-containing and aromatic compounds released on pyrolysis.

SAMPLES: ORIGIN AND DESCRIPTION

The kerogens examined in this study were isolated from four Ordovician organic-rich rocks whose extracted saturate fractions have been characterised in some detail (FOWLER and DOUGLAS, 1984; FOWLER et al., 1986). The samples were chosen from a suite of Pa-

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laeozoic rocks whose organic geochemistry was investigated as part of the International Geological Correlation Programme, 157. Here we examine the structure of the kerogens using Curie point pyrolysis-gas chromatography-mass spectrometry. A short preliminary account of some pyrolysis experiments of these samples is available elsewhere (DOUGLAS et al., 1991).

One of the four kerogens, that of the Guttenberg Oil Rock, is from a kukersite-type deposit. When examined in ultra-violet light using a petrographic microscope it was seen to contain almost exclusively the remains of *Gloeocapsomorpha prisca*. The extracted saturate fraction of this sample shows a high abundance of *n*-alkanes with a strong odd-over-even predominance principally at *n*-C₁₇ and *n*-C₁₉, a rapid "fall-off" in the *n*-alkanes above *n*-C₁₉, very low abundance of acyclic isoprenoids, and a high abundance of *n*-alkylcyclohexanes and methylcyclohexanes in the same carbon number range as the *n*-alkanes and with the same odd-over-even distributions. Both geochemical and microscopical evidence indicates that this sample is immature. The other three samples—Vinini, Womble, and Big Fork—contain mostly amorphous organic matter with a few discrete algal bodies of the order Tasmanales discernible in the Vinini and Womble samples. Their extracts show characteristics less specific to the Ordovician, and, for example, the Vinini and Womble samples contain relatively high abundances of acyclic isoprenoids, steranes, and hopanes based on gc and gc-ms data. The Vinini and Womble samples are early mature whilst the Big Fork sample has a maturity that places it in the middle of the oil window. Further geochemical data on these four samples can be found in FOWLER and DOUGLAS (1984).

Guttenberg Oil Rock

The sample was collected from underground lead-zinc workings in the Schullsberg area of southwest Wisconsin. The "oil rock" was formed from the alteration of the limestone of the Guttenberg member of the Middle Ordovician Decorah Formation by mineralising solutions (HEYL et al., 1959). The sample consists of almost equal proportions of laminated light brown limestone and darker brown calcareous shale with several large galena crystals. Microscopical examination in ultraviolet (UV) light showed that the organic matter, which possessed a strong yellow fluorescence, consisted almost entirely of algal bodies with poor morphology squashed parallel to the bedding plane. The algal bodies appear to be of a single type, *Gloeocapsomorpha prisca* (ZALESSKY, 1917), a known major constituent of the Ordovician kukersite oil shale of Estonia; it also occurs in varying proportions in Ordovician source rocks in the Amadeus and Canning Basins of Australia (FOSTER et al., 1986; HOFFMAN et al., 1987) and in the organic matter in the source rocks of US Ordovician "Mid-Continent oils" (REED et al., 1986; LONGMAN and PALMER, 1987). FOWLER and DOUGLAS (1984) reported that the organic matter of this sample is immature type I.

Vinini Shale

This shale sample was collected from an outcrop of the upper part of the Vinini Formation in western Nevada. It is a crumbly laminated black shale which contains a mixture of amorphous organic matter and discrete algal bodies of Tasmanale affinities, which fluoresce yellow in UV light. The rock is saturated with bitumen. The organic matter is thought to be early mature type II/I.

Womble and Big Fork Shales

Both samples of blackish cherty shales were obtained from outcrops in the Ouachita mountain area of southeast Oklahoma. The Womble sample is slightly bitumen stained; the organic matter was mostly amorphous with some distinguishable algal fragments that had a dull orange fluorescence in UV light. This sample is slightly more mature than the Vinini sample. The sample from the overlying Big Fork Formation is heavily bitumen stained. Its organic matter appears in UV light to be amorphous and weakly fluorescent and is probably at peak level of oil generation (approx. equivalent to 0.8% Ro).

EXPERIMENTAL

Isolation of Kerogens

Lumps of rock were washed with methanol and crushed to a fine powder in a disc mill (TEMA) and extracted for 3 days in a Soxhlet apparatus with an azeotropic mixture of dichloromethane/methanol (93:7 v/v). The extracted, dried powder was demineralised by treatment with excess hot (50°C) concentrated hydrochloric acid followed by hot (50°C) hydrofluoric acid (40%). The washed and dried residue was re-extracted with the above azeotropic mixture to give bitumen-free kerogen.

Curie Point Pyrolysis-Gas Chromatography-Mass Spectrometry

Kerogens were thermally degraded using a Curie point pyrolyser, and wires with a Curie temperature of 610°C, directly connected to a gas chromatograph (Hewlett-Packard 5840) in tandem with a magnetic sector mass spectrometer (VG-70S) by direct insertion of the capillary into the ion source. The chromatograph was fitted with a fused silica capillary column (25 m × 0.32 mm i.d.) coated with CP Sil-5 (film thickness 0.45 μm) in an oven that was temperature programmed from 0 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 ionising 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.

Identification of Pyrolysis Products

The pyrolysates were analysed by using mass chromatography of specific *m/z* values: *m/z* 57 for *n*-alkanes, *m/z* 55 for *n*-alk-1-enes, *m/z* 83 for *n*-alkylcyclohexanes, *m/z* 91, 105, 119, and 133 in combination with *m/z* 92 + 14.n for alkylbenzenes, *m/z* 128, 141, 142, 155, 156, 169, and 170 for (alkyl)naphthalenes, *m/z* 97, 111, 125, and 139 in combination with *m/z* 98 + 14.n for alkylthiophenes, *m/z* 87 and 101 for alkylthiolanes and -thianes and *m/z* 134, 147, 148, 161, 162, 175, and 176 for (alkyl)benzo[*b*]thiophenes. Aliphatic and aromatic compounds were all identified by comparison of their mass spectra with those of standard compounds, by comparison of relative retention times (LEE et al., 1979; SCHRODER, 1980), and by linear Kovats plots for homologous series. Sulphur compounds were identified as reported previously (SINNINGHE DAMSTÉ et al., 1988a, 1989). Further, accurate mass chromatograms (mass window 0.05 dalton) were recorded to simplify mass chromatograms of nominal *m/z* values; e.g., mass chromatograms of *m/z* 97 revealed the presence of both alk-1-enes and 2-alkylthiophenes.

RESULTS

General features of the pyrolysates from the four kerogen concentrates are listed in Table 1. All four samples gave pyrolysates dominated to a greater or lesser extent by series of *n*-alkanes and *n*-alk-1-enes. The Guttenberg pyrolysate was most strongly dominated by *n*-alkanes and *n*-alk-1-enes. In addition to *n*-alkanes and *n*-alk-1-enes, alkylbenzenes and alkylthiophenes were also present in significant but variable relative amounts (Table 1). 1,2,3,4-Tetramethylbenzene was the single most abundant pyrolysis product (other than gaseous compounds) in the pyrolysate of the Womble kerogen and was a major constituent in the Big Fork pyrolysate. Alkylcyclohexanes, alkyl-naphthalenes, alkylthiolanes and -thianes, and alkylbenzo[*b*]thiophenes were found to be minor constituents of the pyrolysates. The Big Fork pyrolysate contains only minor amounts of sulphur-containing pyrolysis products, which is consistent with its supposedly more mature character: sulphur compounds are generated from kerogen at a lower level of thermal evolution than hydrocarbons

TABLE 1 GENERAL COMPOSITION OF THE PYROLYSATES^a

COMPOUND CLASS	KEROGEN			
	Guttenberg	Vinini	Big Fork	Womble
n-alkanes	++++	++++	++++	+++
n-alk-1-enes	+++	+++	+++	+++
alkylcyclohexanes	+	+	+	+
alkylbenzenes	++	+++	+++	++++
alkylnaphthalenes	+	+	++	++
alkylthiophenes	++	+++	+	++
alkylthiolanes and -thianes	+	+	+	+
alkylbenzothiophenes	+	+	+	+

^a as judged from the relative concentration in the total ion current of the most abundant component of a compound class

++++ = compound class which comprises the most abundant component in the pyrolysate

+++ = 50-100% of most abundant compound

++ = 10-50% of most abundant compound

+ = less than 10% of most abundant compound

(GRANSCH and POSTHUMA, 1974; ORR, 1986; LEWAN, 1985; EGLINTON et al., 1988, 1990a,b).

Mass chromatography of specific m/z values (see Experimental) revealed the presence of homologous series for several compound classes (Table 2). The carbon number distributions of these series were sometimes virtually superposable for the three non-kukersite type deposits but usually quite different from those of the Guttenberg pyrolysate. Therefore, comparisons are frequently made in the ensuing discussion using only one of the three kerogens with similar fingerprints.

Aliphatic Hydrocarbons

In addition to the higher relative abundance of normal hydrocarbons in the Guttenberg pyrolysate, the distribution of the n -alkanes and n -alk-1-enes was also significantly dif-

TABLE 2 CARBON NUMBER RANGES OF HOMOLOGOUS SERIES PRESENT IN THE PYROLYSATES^a

COMPOUND CLASS	M/z	KEROGEN			
		Guttenberg	Vinini	Big Fork	Womble
n-alkanes	57	6-28 (13)	6-36 (10)	6-36 (10)	6-36 (11)
n-alk-1-enes	55	6-27 (13)	6-36 (10)	6-36 (10)	6-35 (10)
alkylcyclohexanes	83	8-19 (17)	8-26 (8)	8-26 (8)	8-26 (8)
alkylbenzenes	91	7-23 (7)	7-32 (7)	7-28 (7)	7-26 (7)
2-methyl-n-alkylbenzenes	105	8-23 (15)	8-33 (9)	8-30 (9)	8-30 (9)
2-alkylthiophenes	97	5-17 (5)	5-28 (5)	5-10 (5)	5-16 (5)
2-alkyl-5-methylthiophenes	111	6-19 (6)	6-31 (7)	6-16 (6)	6-23 (6)
2-alkyl-5-ethylthiophenes	125	7-19 (15)	7-31 (8)	7-23 (9)	7-27 (9)
2-alkylthiolanes	87	4-19 (6)	4-31 (5)	4-27 (4)	4-30 (5)
2-alkyl-5-methylthiolanes	101	6-19 (15)	6-27 (7)	n.d. ^b	6-18 (7)
2-alkylthianes	101	6-17 (15)	6-26 (7)	n.d.	6-18 (7)

^a maxima of carbon number distributions are given in parentheses: note that the carbon number includes the carbon atoms in the aliphatic, aromatic or heterocyclic ring systems

^b n.d. = not detected

ferent from those of the other three pyrolysates. Figure 1 shows an odd-over-even carbon number predominance and a much reduced abundance of n -alkanes with more than 17 carbon atoms, whilst the other three pyrolysates show a smooth n -alkane carbon number distribution extending up to about C₃₆ (shown only to C₃₀ in Fig. 1). The carbon number distributions of the n -alk-1-enes were generally similar to those of the n -alkanes but showed, at times, a slight predominance of even carbon numbers.

All pyrolysates contained small amounts of alkylcyclohexanes: methylalkylcyclohexanes could not be detected but if present do not occur as significant peaks in the m/z 97 mass chromatograms. This finding is somewhat surprising since these compounds were detected in "hydrous" pyrolysates (sealed-vessel pyrolysis at 330°C/72 h in the presence of excess water) of the Guttenberg kerogen (FOWLER et al., 1986).

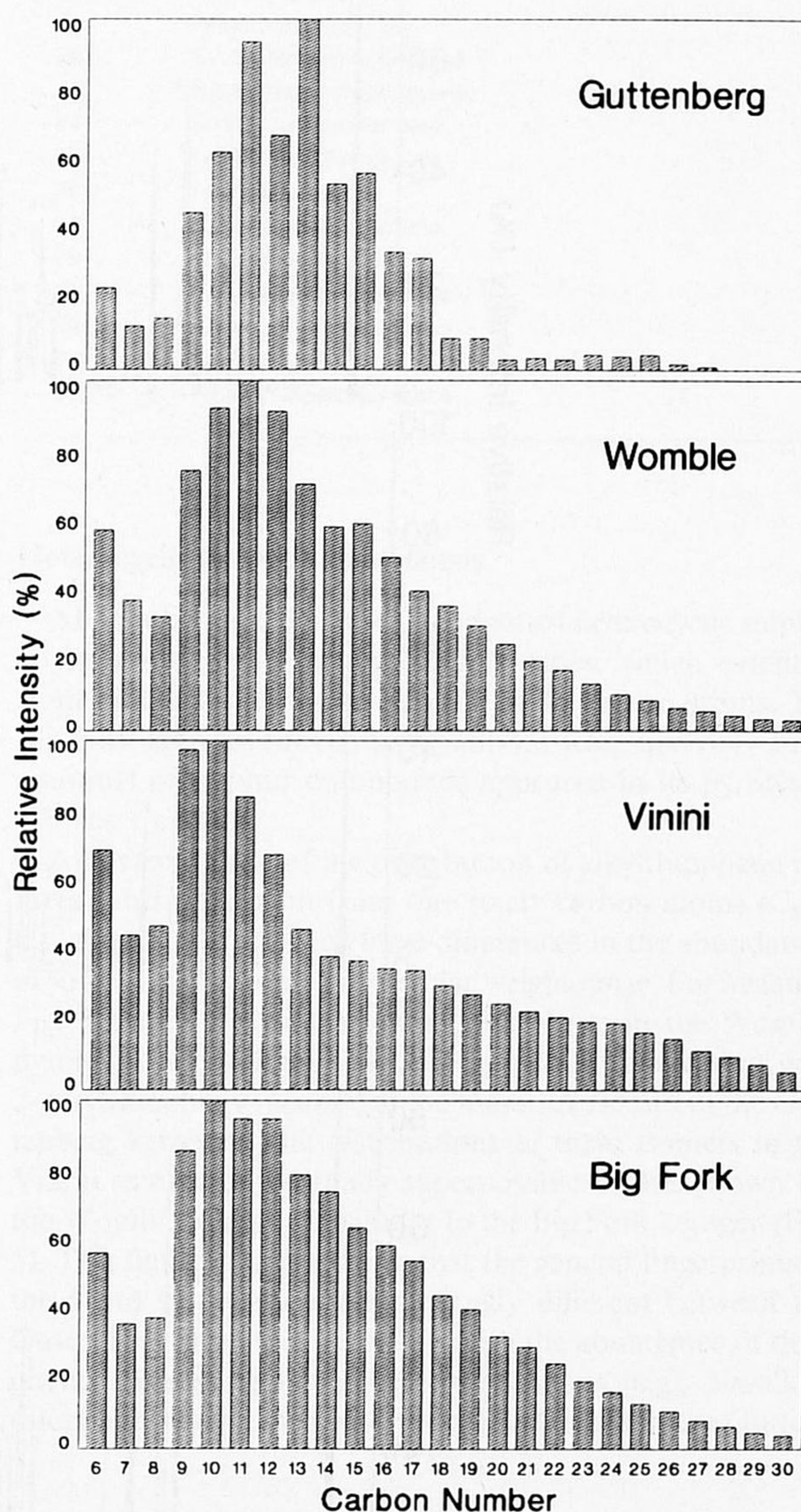
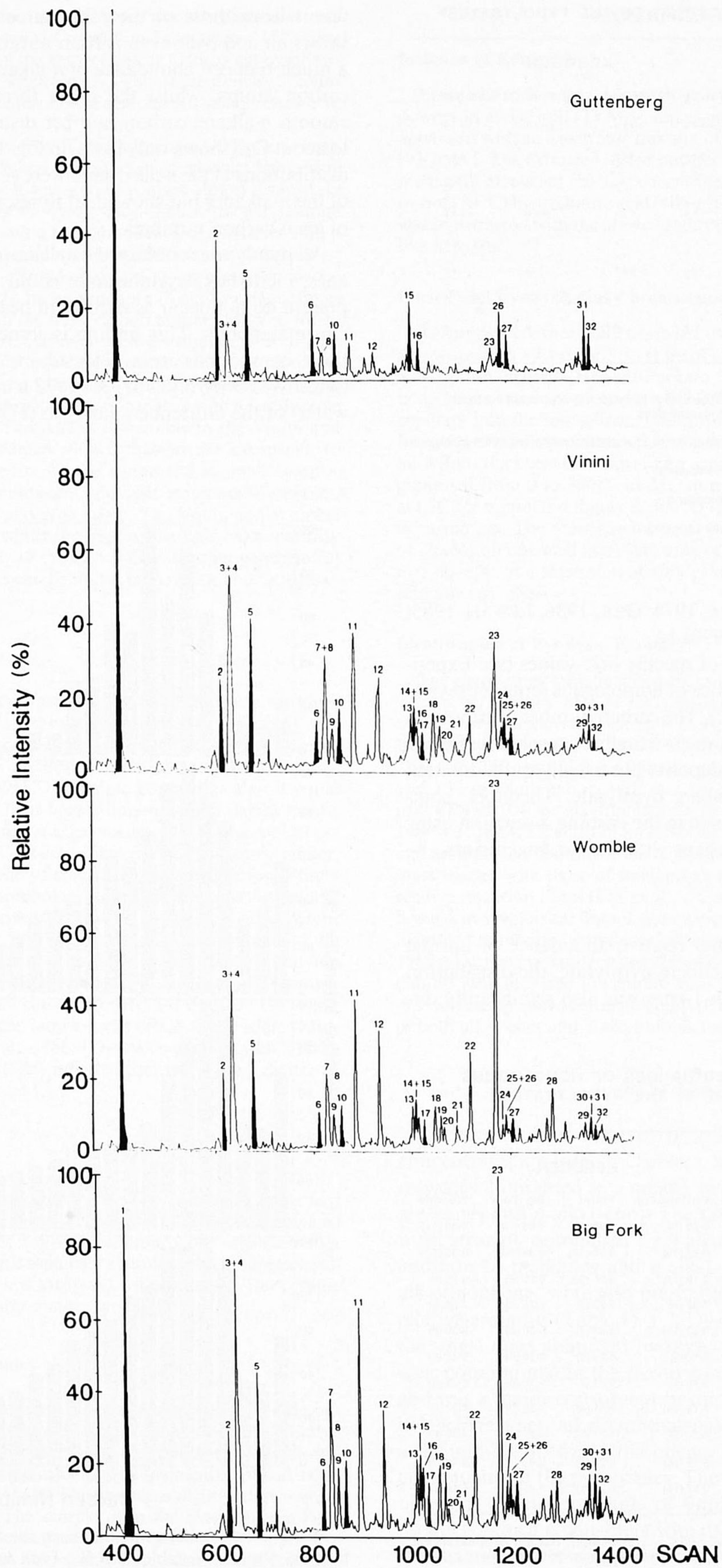


FIG. 1. Distribution of n -alkanes in the flash pyrolysates of Guttenberg, Vinini, Womble, and Big Fork kerogens, measured from mass chromatograms (m/z 57).



Aromatic Hydrocarbons

All four kerogen pyrolysates contained varying amounts of aromatic hydrocarbons, but only the substituted benzenes and naphthalenes are discussed in this paper.

Alkylbenzenes

A large number of alkylbenzenes have been identified in all four kerogen pyrolysates (Table 2). The summed mass chromatograms of the isomeric alkylbenzenes are shown in Fig. 2 for all four kerogens: the solid peaks indicate alkylbenzenes that have a linear carbon skeleton. (Peak numbers 1,2,6,15, 26 and 31 as shown in Table 3.

The fingerprints for the Womble, Vinini, and Big Fork kerogens are remarkably similar, and in all of them the alkylbenzenes with linear carbon skeletons are minor peaks; however, in the Guttenberg kerogen those with linear carbon skeletons clearly distinguish this sample.

The major peak in the Womble and Big Fork mass chromatograms (Fig. 2) is 1,2,3,4-tetramethylbenzene; it occurs in the Vinini mass chromatogram as a moderate peak but is a trace component in the Guttenberg pyrolysate. It is more easily recognised in the m/z 119 mass chromatograms (not shown).

Homologous series on *n*-alkylbenzenes (m/z 91) ranging upwards from toluene were present and are illustrated for the Guttenberg and Big Fork kerogen pyrolysates in Fig. 3. (Note that in this and other figures, the carbon numbers refer to the total number of carbon atoms in the molecule; for instance, in Fig. 3 carbon number 7 refers to toluene.) These distributions, and also those for the Vinini and Womble kerogens (not shown), are similar, which contrasts with most of the other homologies describe in this work. For instance, the mass chromatograms (m/z 105) for alkyltoluenes show striking differences between the Guttenberg and the other three kerogens. Figure 4 illustrates this difference for the four kerogens constructed from the mass chromatograms in which the former contains very large peaks (solid bars) due to homologous *ortho*-substituted *n*-alkyltoluenes (which have linear carbon skeletons), whereas in the latter the *ortho*, *meta*, and *para* substituted homologues are present in more equal abundance.

Alkyl-naphthalenes

Naphthalene and isomeric C_1 to C_3 naphthalenes (m/z 128, 142, 156, 170) were present in all four kerogen pyrolysates. Relative abundances of known methyl and dimethylnaphthalenes (and unidentified C_3 compounds) showed greater similarity between each group of isomers for the Womble, Vinini, and Big Fork kerogens, than when compared with the Guttenberg kerogen (not shown); the latter also contains a somewhat higher relative abundance in the Guttenberg pyrolysate of naphthalenes with linear carbon skeletons (1-methyl-, 1-ethyl-, and 1,5-dimethylnaphthalene).

TABLE 3 ALKYL BENZENES IDENTIFIED IN THE PYROLYSATES

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

Heterocyclic Sulphur Compounds

All four kerogen pyrolysates contained heterocyclic sulphur compounds, some as homologous series, which extended from molecules with 4 to more than 30 carbon atoms. The Big Fork kerogen proved to be sulphur-lean, and only small amounts of sulphur compounds appeared in its pyrolysate (Tables 1 and 2).

An examination of the distribution of alkylthiophene isomers substituted with from one to six carbon atoms (C_5 to C_{10} compounds) showed large differences in the abundances of some isomers in each molecular weight range. For instance, Fig. 5 shows that the major C_6 thiophene in the Womble pyrolysate is 2,5-dimethylthiophene (peak 4), contrasting with 2-ethylthiophene (peak 3) as the major C_6 isomer in the Guttenberg kerogen. The distributions of these isomers in the Vinini sample are virtually superposable to that shown for the Womble and not dissimilar to the Big Fork kerogen (Fig. 5). This figure also illustrates that the general fingerprints of the C_5 to C_{10} isomers are strikingly different between the Guttenberg and other kerogens, with the abundance of thiophenes possessing linear carbon skeletons (e.g., 2-*n*-alkylthiophenes) being the most noticeable feature in the Gutten-

FIG. 2. Summed accurate mass chromatograms (m/z 91.08 ± 92.08 + 105.09 + 106.09 + 119.11 + 120.11 + 133.13 + 134.13 + 147.21 + 148.21 + 161.23 + 162.23) illustrating the distribution of alkylbenzenes in Guttenberg, Vinini, Womble, and Big Fork kerogen pyrolysates. Peak identities are listed in Table 3.

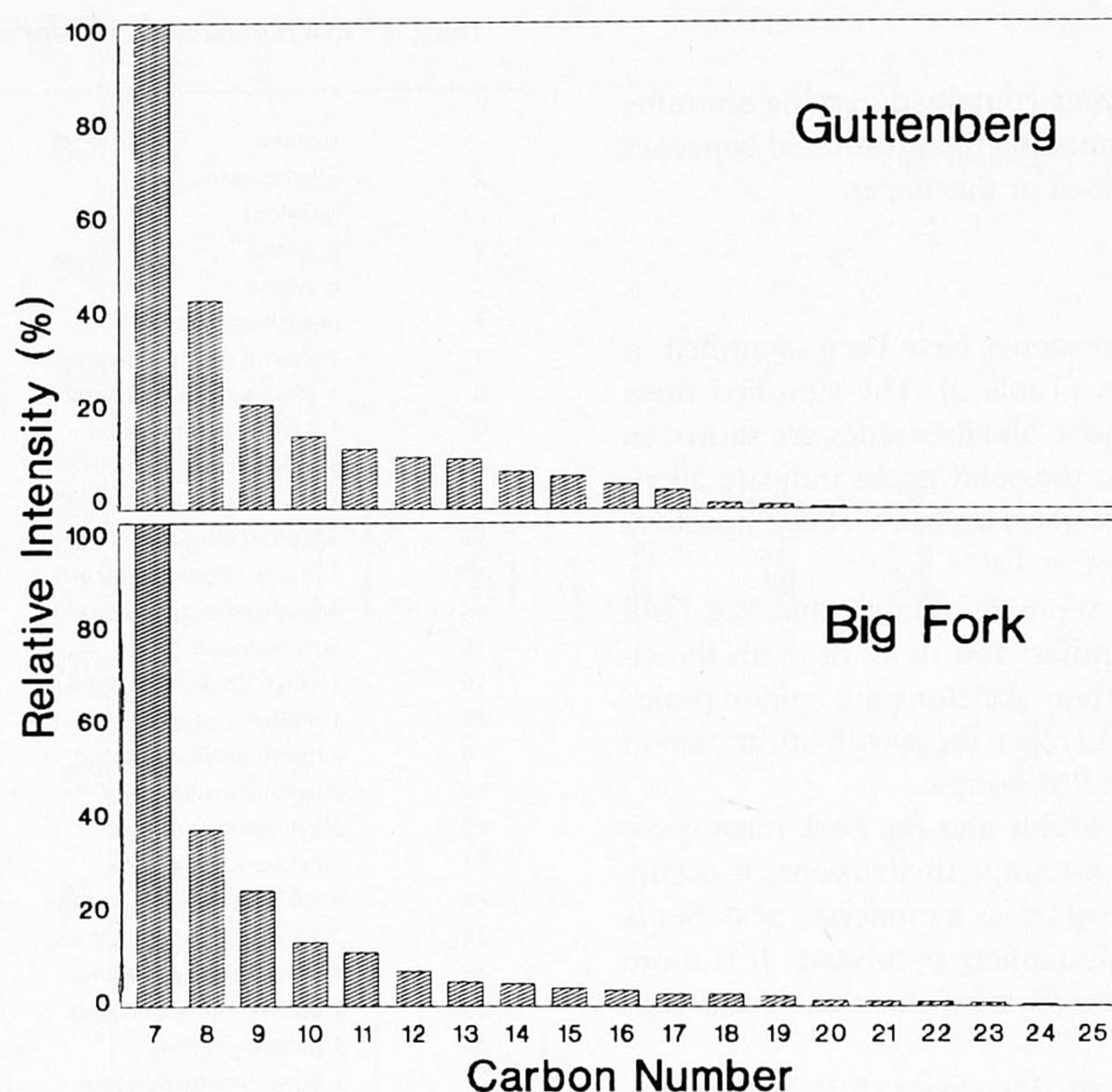


FIG. 3. Distribution of *n*-alkylbenzenes, measured from mass chromatograms (m/z 91), in the pyrolysates of Guttenberg and Big Fork kerogens.

berg distribution, whereas, for the other samples, di- and tri-substituted isomers (with non-linear carbon skeletons) are more abundant and even dominant at some molecular weights.

2-*n*-Alkyl- and 2,5-di-*n*-alkylthiophenes

All four kerogen pyrolysates contained homologous series of 2-*n*-alkylthiophenes, 2-*n*-alkyl-5-methylthiophenes, 2-*n*-alkyl-5-ethylthiophenes and much less abundant 2-*n*-alkyl-5-propylthiophenes. The carbon number ranges of these homologues are indicated in Table 2, but since the full extent of some are difficult to measure exactly (for instance, where peaks begin to overlap) the tabulated ranges may be conservative. The distributions of the 2-*n*-alkylthiophenes (m/z 97) which are shown in Fig. 6 appear rather similar. In all of the kerogens the major compound in the series is 2-methylthiophene, but in the Guttenberg the relative abundance of the higher molecular weight members of this homologous series distinguishes it from the Womble and Vinini kerogens. In the Big Fork kerogen, members of the homologous series of alkylthiophenes with more than ten carbon atoms were not detected.

In contrast to the similar distributions of the 2-*n*-alkylthiophenes in all four kerogens, the fingerprints of the 2-*n*-alkyl-5-methyl and 2-*n*-alkyl-5-ethylthiophenes showed distinct differences between the Guttenberg and the other three kerogens, the latter being similar to distributions shown for a variety of other kerogens (SINNINGHE DAMSTÉ et al., 1988a, 1989). Histograms of the distributions for both series of alkylthiophenes are shown in Fig. 7 (from m/z 111) and Fig.

8 (from m/z 125), respectively. These figures nicely illustrate the relatively large proportion of the higher molecular weight homologues in the Guttenberg kerogen but, however convenient for illustrating relative distributions, do not give any indication of abundances, relative to other compounds, which appear in the mass chromatograms. Figure 9 is included to exemplify the occurrence of the doublet at C_{16} which occurs in some of the Guttenberg homologues (see below).

Alkylthiolanes and Alkylthianes

Alkylated thiolanes (tetrahydrothiophenes) were also present in these kerogen pyrolysates but in much lower abundance than the alkylthiophenes (Table 1). Distributions for the 2-*n*-alkylthiolanes, plotted from m/z 87 mass chromatograms for both the Guttenberg and Womble kerogens, illustrate again the significant differences in their distributions (Fig. 10). The m/z 87 fingerprint for the Guttenberg kerogen, with its high relative abundance of higher molecular weight homologues (up to C_{15}) is similar to that of its 5-methyl-2-*n*-alkylthiophenes (Fig. 7) and *ortho*-substituted *n*-alkyltoluenes (Fig. 4).

Monitoring the fragment ion m/z 101 provides fingerprints of the distribution of 2-methyl-5-alkylthiolanes and also the structurally isomeric 2-alkylthianes (six-membered cyclic sulphides). However, the latter are more strongly retained on the non-polar gc phase used in this work (CP Sil-5) and elute approximately midway between homologous thiolanes (SINNINGHE DAMSTÉ et al., 1988a). In the pyrogram of the Guttenberg kerogen, 2-methyl-5-decylthiolane is the most abundant isomer in a series which extends from 2-methyl-5-butyl

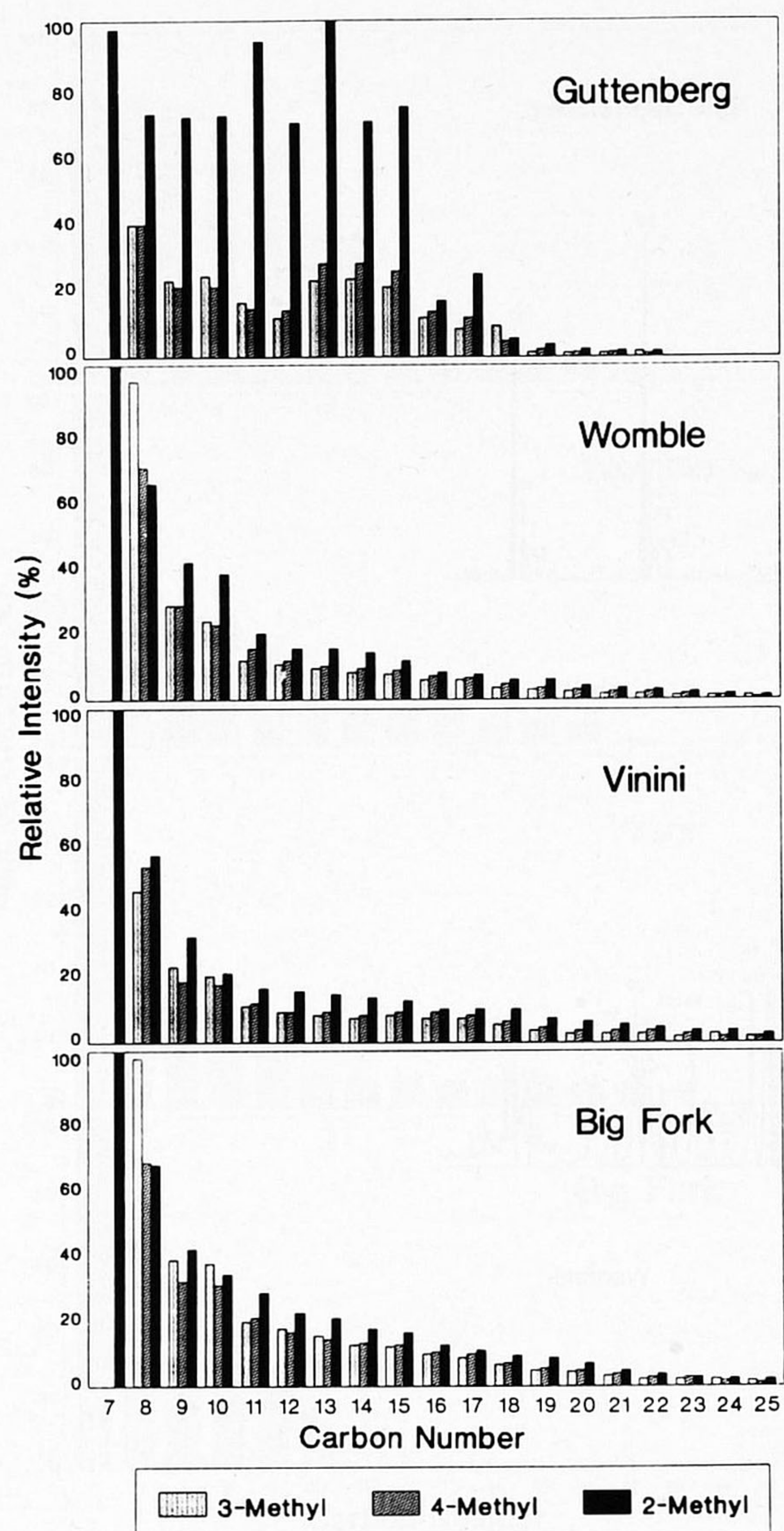


FIG. 4. Distribution of 2-methyl-, 3-methyl-, and 4-methyl-*n*-alkylbenzenes in the pyrolysates of Guttenberg, Vinini, Womble, and Big Fork kerogens measured from mass chromatograms m/z 105.

to -5-tetradecylthiolane. Interestingly, the major thiane in the same range is an isomer of the major thiolane, namely 2-undecylthiane. The close correspondence of the two distributions in this kerogen pyrolysate is shown in Fig. 11. In the Womble and Vinini pyrolysates both series have been identified, extending from C_6 to C_{18} in the Womble and C_6 to C_{26} (thianes) and C_{27} (thiolanes) in the Vinini (Table 2). In the Big Fork pyrolysate they were not detected.

Benzo[*b*]thiophenes

The summed mass chromatograms for benzo[*b*]thiophene and its C_1 , C_2 , and C_3 alkyl isomers for the Guttenberg and Womble kerogen pyrolysates are shown in Fig. 12. The six theoretically possible C_1 (monomethyl) isomers (peaks 2–7) appear to be present in both pyrolysates, although the lack of complete chromatographic resolution indicates that this

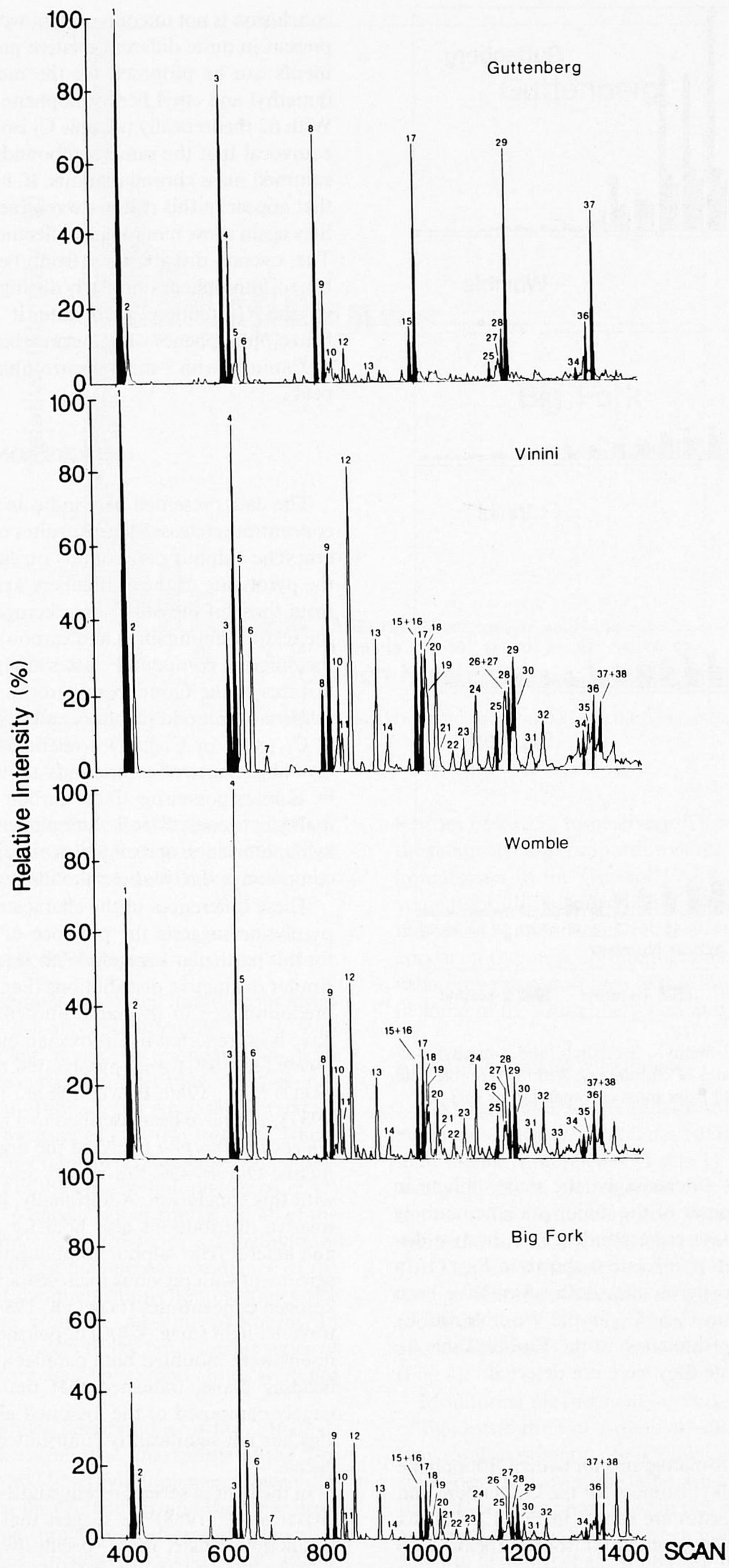
conclusion is not unequivocal; however, the peaks shown are present in quite different relative proportions. Similar arguments can be proposed for the more complex mixture of dimethyl and ethyl benzo[*b*]thiophene centred around peak 9. With 62 theoretically possible C_3 isomers, one cannot be unequivocal that the same compounds are appearing in these summed mass chromatograms. If, however, the seven peaks that appear in this region do represent the same C_3 isomers, they again show remarkable differences in these distributions. The overall distributions from benzo[*b*]thiophene to C_3 benzo[*b*]thiophenes similarly distinguish these two kerogens. In the Guttenberg pyrolysate it should be noted that benzo[*b*]thiophenes with linear carbon skeletons again appear to dominate with 2-methylbenzo[*b*]thiophene being the major peak.

DISCUSSION

The data presented here indicate the Ordovician kerogen concentrates released similar suites of hydrocarbons and heterocyclic sulphur compounds on flash pyrolysis. However, the pyrolysate of the Guttenberg kerogen was quite distinct from those of the other three kerogens with respect to both the relative abundances and carbon number distributions of the different compound classes analysed. The distinguishing features of the Guttenberg kerogen may be summarised as follows: (1) an odd carbon number predominance (maxima at C_{11} , C_{13} , or C_{15}); (2) a restricted carbon number range (low abundance of compounds above C_{19}); (3) a dominance by isomers possessing linear carbon skeletons (also includes *n*-alkylbenzenes, 2-*n*-alkylthiophenes, 2-*n*-alkylthiolanes, alkyl-naphthalenes, and alkylbenzothiophenes). Several of these comparative distributions are illustrated in Fig. 13.

These differences in the characteristics of the Guttenberg pyrolysate suggests the presence of a different precursor(s) for this particular kerogen. With regard to the hydrocarbons, similar distinctive distributions (i.e., an odd carbon number predominance in the same limited carbon number range) have been reported in Ordovician oils and sediment extracts (FOWLER, 1991) and pyrolysates of Ordovician kerogens (REED et al., 1986; FOWLER et al., 1986; HOFFMANN et al., 1987), and have been ascribed to a major contribution from *Gloeocapsomorpha prisca* to the organic matter of the sediments. Our Py-GC-MS results are in complete agreement with this conclusion. Additionally, it appears that these distinctive distributions also hold for aromatic hydrocarbons and heterocyclic sulphur compounds. The results are also in agreement with previous microscopical examinations of these kerogen concentrates (FOWLER, 1984). Thus, analyses in ultraviolet light (mag. $\times 400$) of polished blocks in which specimens were mounted both parallel and perpendicular to the bedding plane, indicated that the Guttenberg kerogen is largely composed of the fossilised alga *G. prisca* whilst this alga has not significantly contributed to the other three kerogens.

In the light of several recent studies (DERENNE et al., 1988; GOTH et al., 1988) we suggest that the reported chemical distinctions relate, more specifically, to the selectively preserved cell-wall material of *G. prisca* which is probably composed mainly of an insoluble, highly aliphatic biopolymer



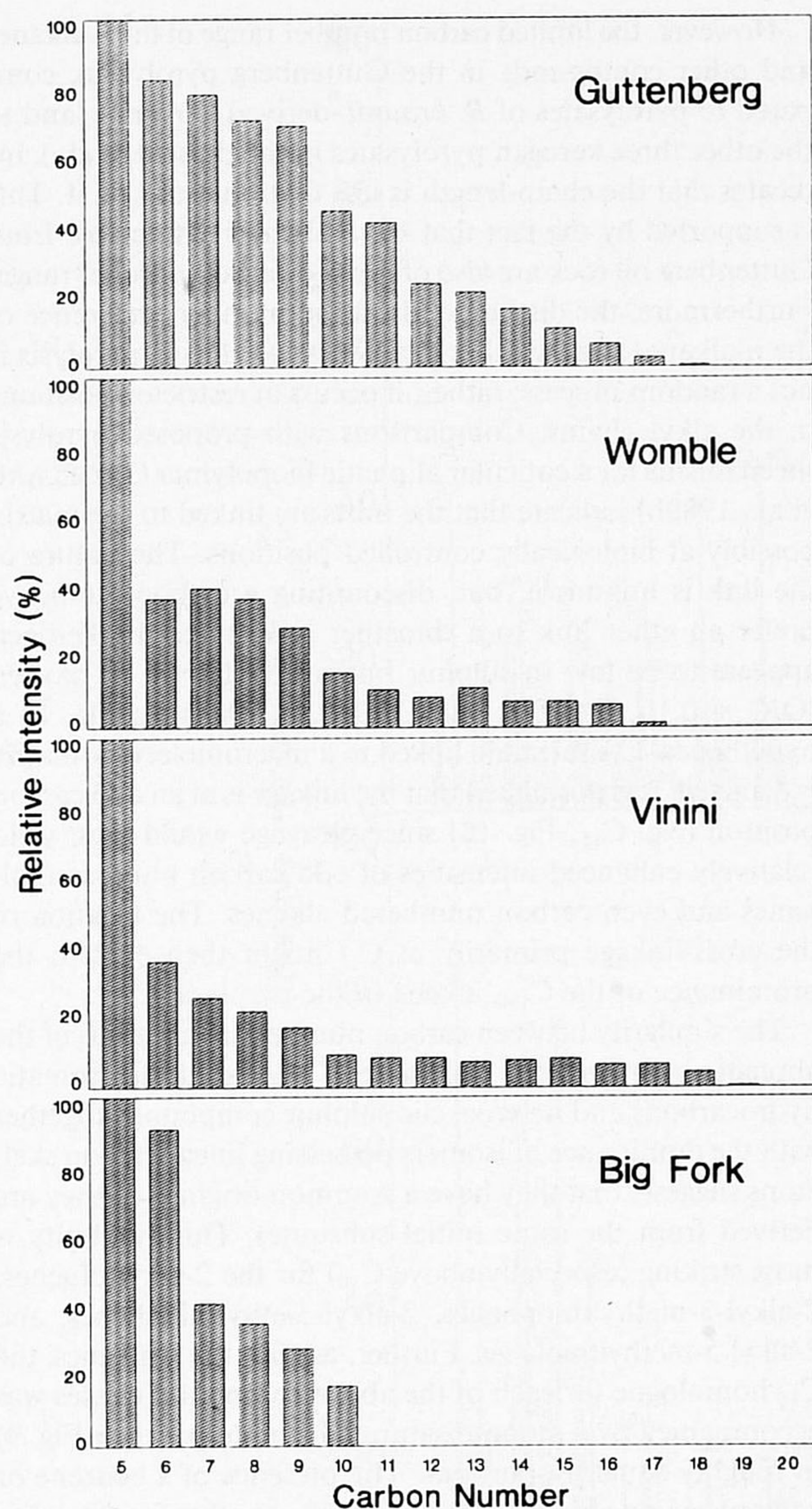


FIG. 6. Distribution of *n*-alkylthiophenes in the flash pyrolysates of the Guttenberg, Vinini, Womble, and Big Fork kerogens as measured from peak heights in mass chromatograms (m/z 97). Numbers refer to the total number of carbon atoms in the molecule; for instance, 2-*n*-propylthiophene is number 7.

("algaenan," TEGELAAR et al., 1989a). Such highly aliphatic biopolymers have been found in all three races of the extant algae *Botryococcus braunii* (LARGEAU et al., 1986; DERENNE et al., 1988), and *Tetraedron minimum* (GOTH et al., 1988), and in their fossil counterparts, torbanites (LARGEAU et al., 1986; DERENNE et al., 1988), and the kerogen of the Messel Oil Shale (GOTH et al., 1988), respectively. The abundance of these cell-wall remains in the sedimentary organic matter gives rise to high atomic H/C ratios and high Rock-Eval hydrogen indices for the kerogen and a dominance of *n*-alkanes

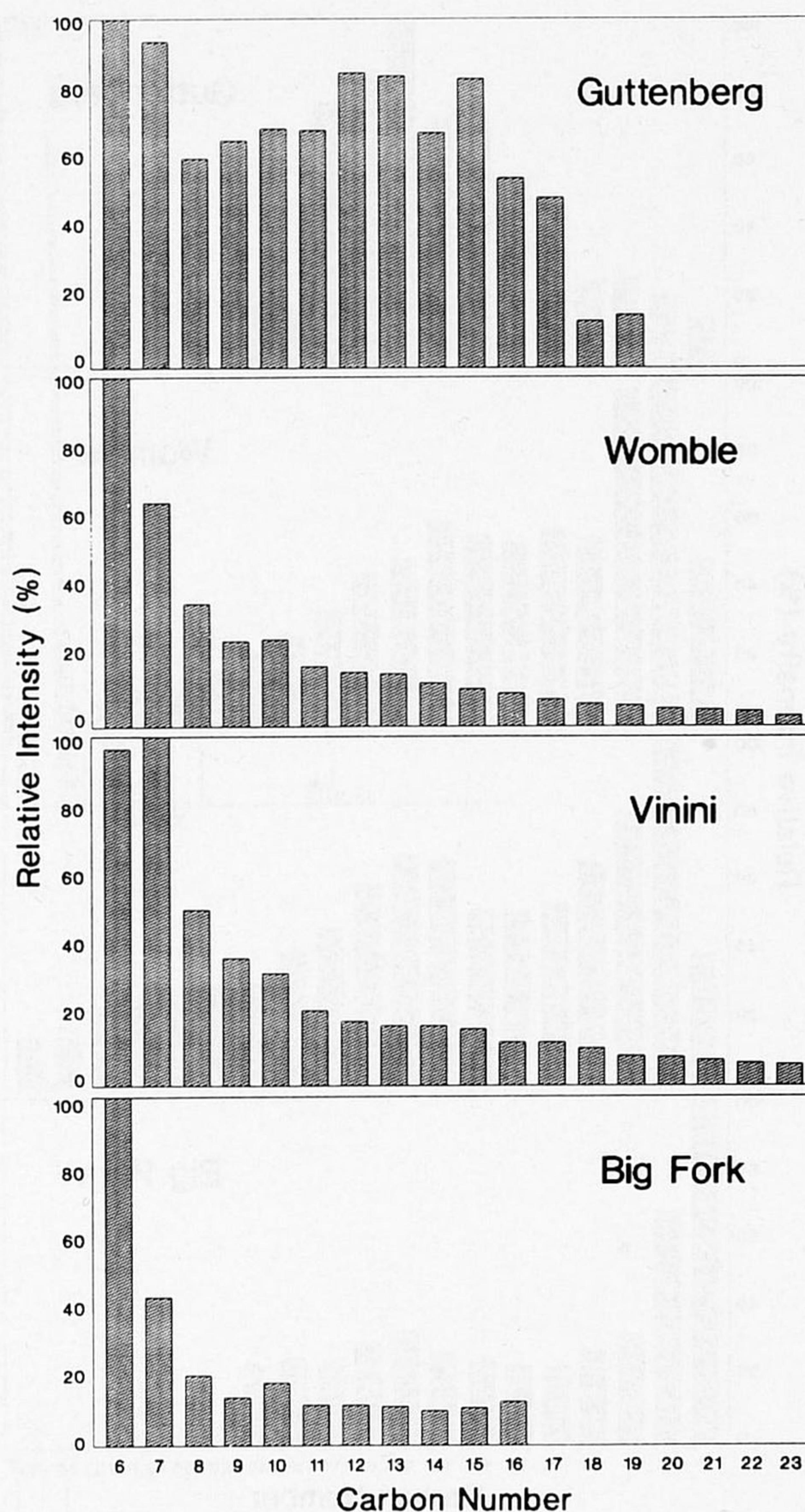


FIG. 7. Histograms of the distribution of 2-methyl-5-*n*-alkylthiophenes in the pyrolysates of Guttenberg, Womble, Vinini, and Big Fork kerogens (measured from peak heights in mass chromatograms m/z 111).

and *n*-alk-1-enes in their flash pyrolysates. These features also hold for the Guttenberg kerogen (H/C = 1.48; HI = 919). Unfortunately, it is not possible to rigorously test this hypothesis by analysing extant *G. prisca* as was possible for *B. braunii* and *T. minimum*, because of the apparent extinction of *G. prisca* at the end of the Ordovician.

On the basis of the distinguishing features of the Guttenberg kerogen pyrolysate, we have attempted to reconstruct a hypothetical precursor for the fossil biopolymer of *G. prisca*. If one assumes that the biopolymers of *G. prisca* derive from

FIG. 5. Summed accurate mass chromatograms (m/z 97.06 + 98.06 + 111.08 + 112.08 + 125.10 + 126.10 + 139.12 + 140.12 + 153.14 + 154.14 + 167.12 + 168.12) illustrating the distributions of alkylthiophenes in the Guttenberg, Vinini, Womble, and Big Fork kerogen pyrolysates; solid peaks indicate compounds with linear carbon skeletons.

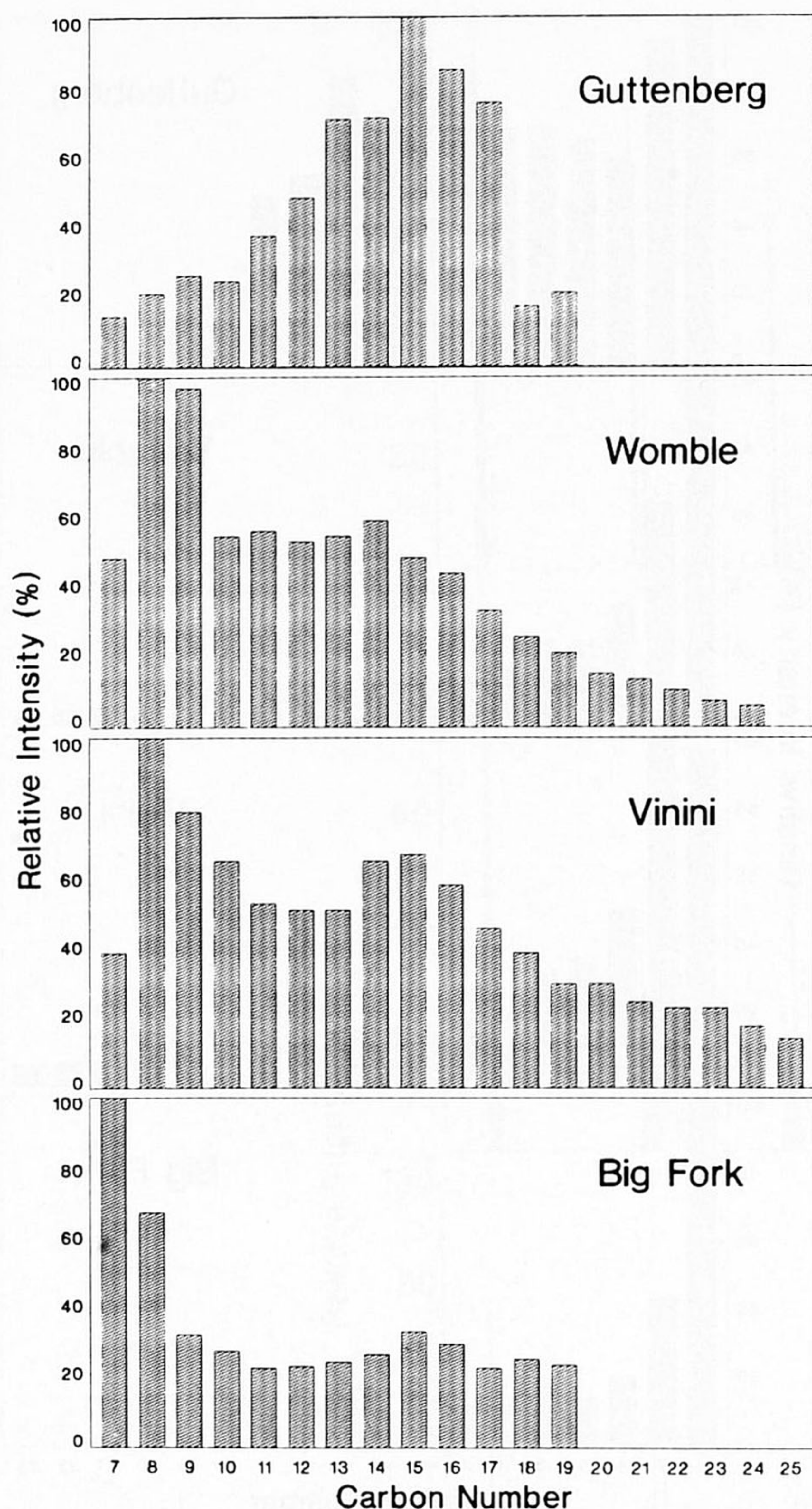
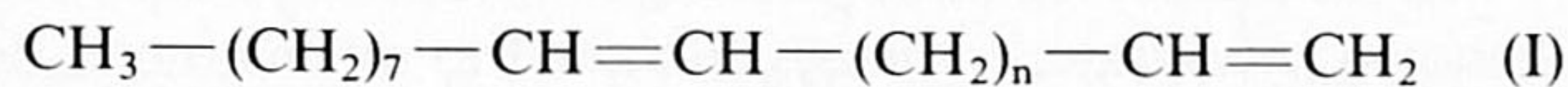
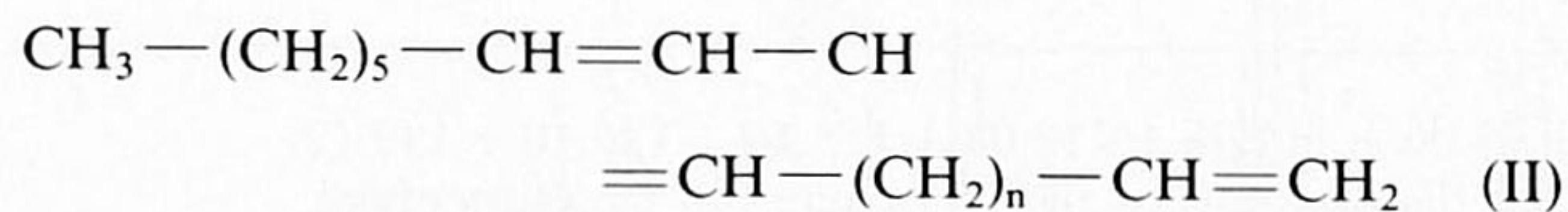


FIG. 8. Histograms of the distribution of 2-ethyl-5-*n*-alkylthiophenes in the pyrolysates of Guttenberg, Womble, Vinini, and Big Fork kerogens (measured from mass chromatograms m/z 125).

the polymerisation of olefins, as is suggested for the biosynthesis of the biopolymer in race A of *Botryococcus*, it seems reasonable to initially suppose that the building blocks consist of similar odd carbon numbered, unsaturated, linear hydrocarbon monomer units (e.g., I and II; BROWN et al., 1969; KNIGHTS et al., 1970; MURRAY and THOMSON, 1977; METZGER et al., 1986):



where $n = 13, 15, 17$ or 19



where $n = 13, 15, 17$ or 19 .

However, the limited carbon number range of the *n*-alkanes and other compounds in the Guttenberg pyrolysate, compared to pyrolysates of *B. braunii*-derived kerogens (and to the other three kerogen pyrolysates in the present study), indicates that the chain-length is less than that of I or II. This is supported by the fact that the *n*-alkanes extractable from Guttenberg oil rock are also of limited carbon number range. Furthermore, the distinct odd carbon number preference of the *n*-alkanes suggests that chain-scission during pyrolysis is not a random process; rather, it occurs at restricted positions in the alkyl chains. Comparisons with proposed pyrolysis mechanisms for a cuticular aliphatic biopolymer (TEGELAAR et al., 1989b) indicate that the units are linked to the matrix possibly at biologically controlled positions. The nature of the link is unknown, but, discounting a carbon atom, we prefer an ether link to a thioether link, since the kerogen appears to be low in sulphur but relatively rich in oxygen ($\text{O/C} = 0.10$, FOWLER and DOUGLAS, 1984). In Fig. 14 a hypothetical C_{19} substrate linked to a macromolecular matrix is depicted. It is postulated that the linkage is at an odd carbon position (e.g. C_{15} , Fig. 14) since cleavage would then yield relatively enhanced intensities of odd carbon numbered alkanes and even carbon numbered alkenes. The location of the cross-linkage primarily at C_{15} might then explain the prominence of the $\text{C}_{16:1}$ alkene in the pyrolysate.

The similarity between carbon number distributions of the aliphatic hydrocarbons and those of several of the aromatic hydrocarbons and heterocyclic sulphur compounds together with the dominance of isomers possessing linear carbon skeletons suggests that they have a common origin (i.e., they are derived from the same initial substrate). This similarity is most striking (especially above C_{10}) for the 2-alkyltoluenes, 2-alkyl-5-methylthiophenes, 2-alkyl-5-ethylthiophenes, and 2-alkyl-5-methylthiolanes. Further, as with the *n*-alkanes, the C_{16} homologue for each of the above compound classes was accompanied by a monounsaturated counterpart (see Fig. 9) in roughly equal proportions. The presence of a benzene or a thiophene ring indicates that originally another functionality was present towards the end of the alkyl chain. For the sulphur compounds in the flash pyrolysates, the presence of isomers possessing linear carbon skeletons has been ascribed to thermal degradation of sulphur-containing moieties with linear carbon skeletons (SINNINGHE DAMSTÉ et al., 1989). The aromatic compounds with linear carbon skeletons are probably generated from the corresponding aromatic moieties in a similar way. In each case this suggests that the putative building blocks with functionalities at the end of the linear alkyl chains of the aliphatic biopolymer of the cell walls of *G. prisca* may also have undergone cyclisation and aromatisation reactions as well as sulphur incorporation. To the best of our knowledge, this is the first evidence which has been presented to demonstrate that inorganic sulphur species may be incorporated into what we have assumed to be existing polymer structures rather than being the agent of polymerisation (SINNINGHE DAMSTÉ et al., 1988b; 1989). With respect to the alkylbenzenes, it is suggested that alkylcyclohexyl moieties may represent intermediates in their formation. The similar odd carbon number dominance of *n*-alkylcyclohexanes and methyl-*n*-alkylcyclohexanes in the bitumen extract of the

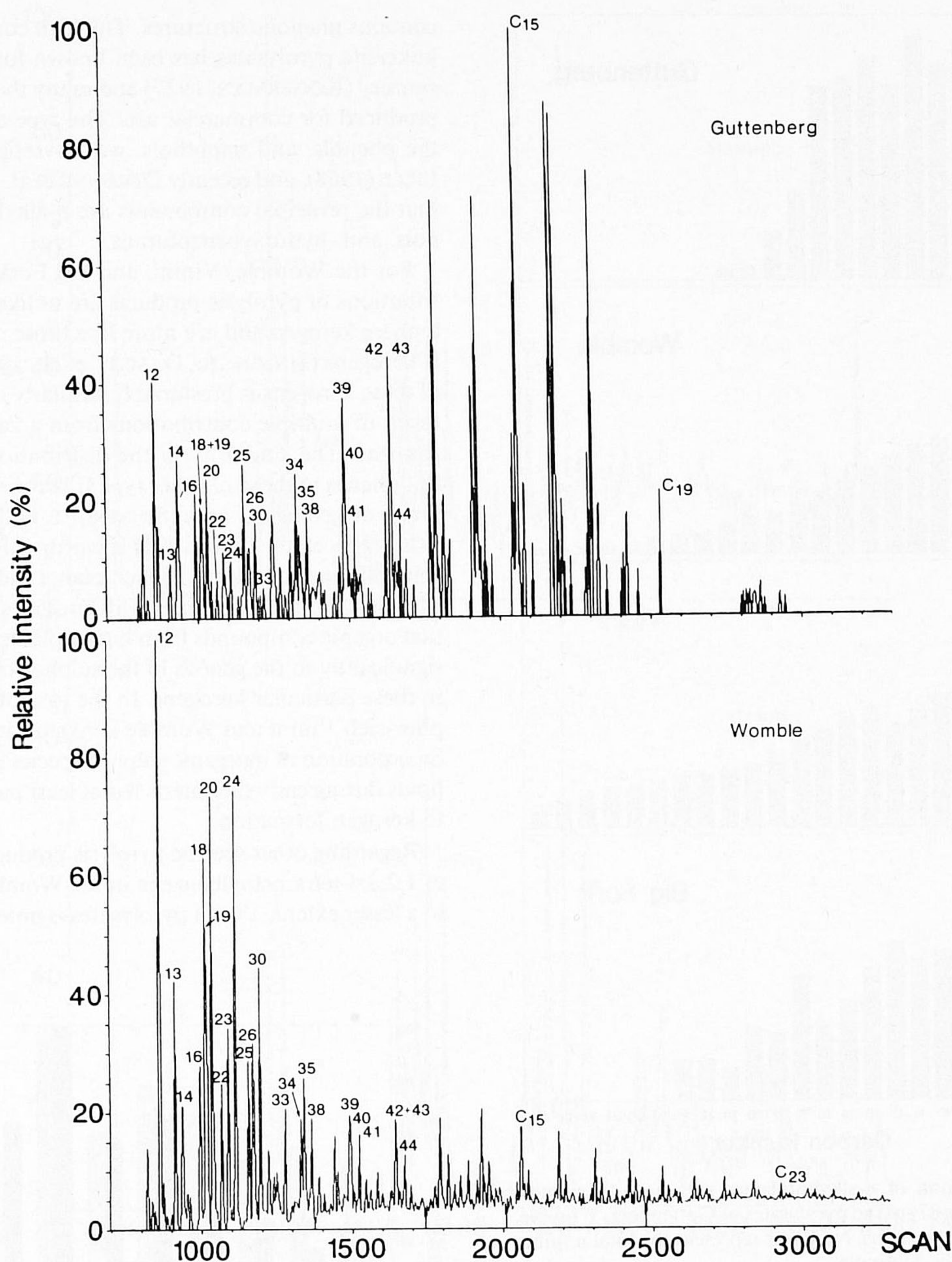


FIG. 9. Distribution of 2-ethyl-5-*n*-alkylthiophenes (from m/z 125.06 and 125.12, respectively) in the pyrolysates of Guttenberg and Womble kerogens. C₁₅ represents the compound with 15 carbon atoms, namely 2-ethyl-5-nonylthiophene.

Guttenberg sample (FOWLER et al., 1986) would appear to support this argument. The higher relative abundance of aromatic and sulphur components $< C_{10}$ relative to the alkanes may be due to alternative cleavages of the *beta* bond of the alkyl side-chain of the benzene or thiophene ring (i.e., *beta*-cleavage).

It is notable that the distribution patterns of the alkylbenzenes, 2-*n*-alkylthiophenes, and, to some extent, the 2-*n*-alkylthiolanes do not appear to fall into the general category described above in that the odd carbon number preference is less pronounced and is also shifted to lower carbon numbers. However, in both cases their relative abundance is high, again reflecting the dominance of pyrolysis products pos-

sessing linear carbon skeletons in the Guttenberg pyrolysate. Whilst the reasons for these differences are not fully understood, it is suggested that the most likely explanations are either (a) a separate original substrate (i.e., another monomer) or (b) different mechanisms for thermal degradation of monosubstituted relative to disubstituted units. Chemical degradation experiments are in progress in an attempt to establish the structure of the constituent units as well as the types of cross-linkages.

Thus, it appears that the following can be concluded about the structural units comprising the *G. prisca* kerogen, possibly consisting of cell-wall aliphatic biopolymer, (1) it is composed of linear alkyl chains of limited chain-length and of odd car-

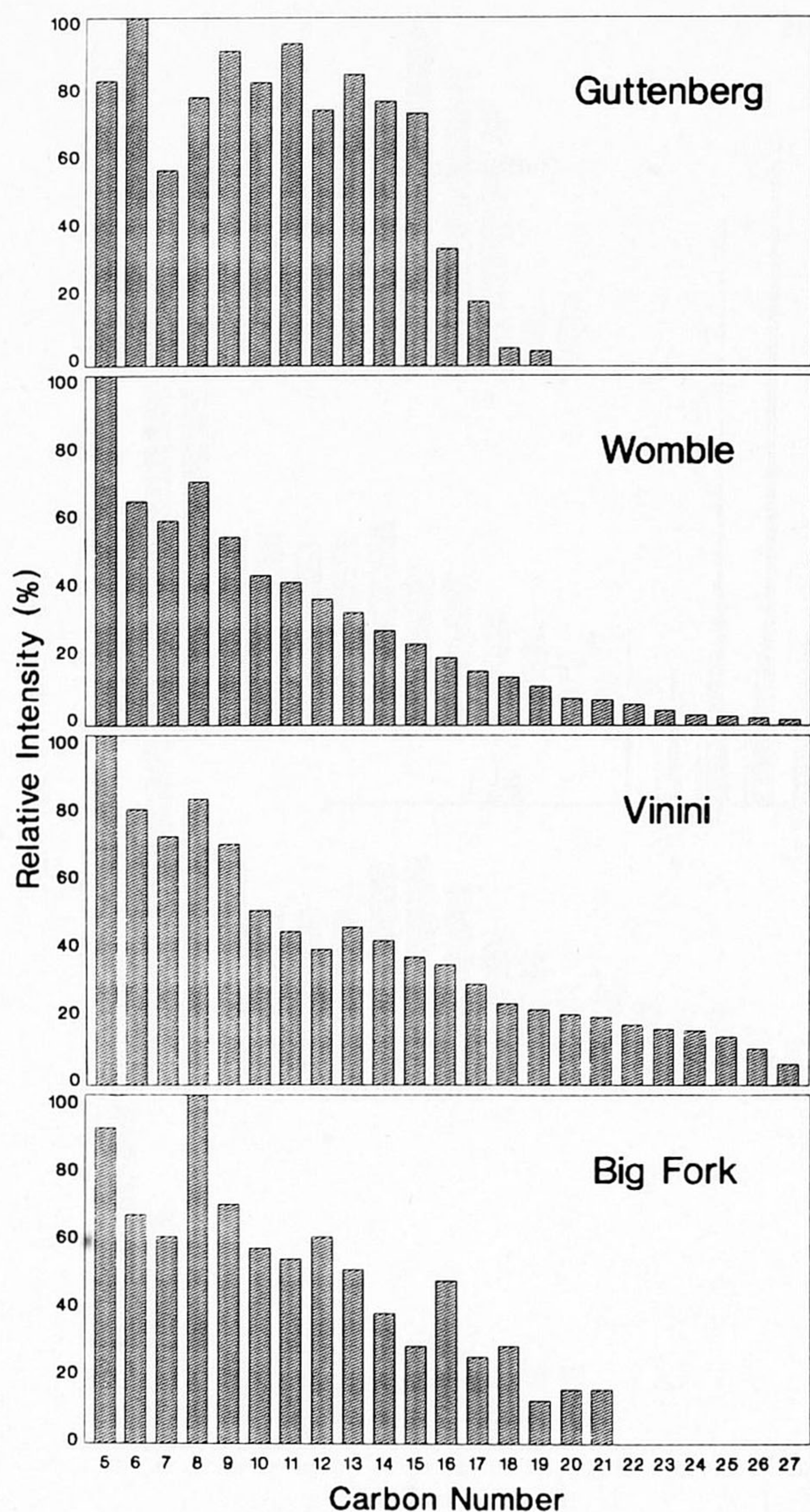


FIG. 10. Distribution of *n*-alkylthiolanes, measured from mass chromatograms (m/z 87) of the pyrolysates of Guttenberg, Womble, Vinini, and Big Fork kerogens. Numbers represent the total number of carbon atoms in the molecule.

bon number; (2) the alkyl chains are linked to the kerogen macromolecule at biochemically determined positions; and (3) the biopolymer possesses functional groups at terminal positions capable of sulphur incorporation and/or cyclisation and aromatisation. This hypothetical scheme is summarised in Fig. 15. Somewhat comparable results have been obtained from flash pyrolysis of *G. prisca*-rich kukersite kerogen from Estonia (KLESMENT and NAPPA, 1980; DERENNE et al., 1991) which therefore provides some independent evidence that this alga imparts a rather unique fingerprint to the organic matter of sediments.

However, the relationship between Guttenberg Oil Rock and kukersite type deposits has not been fully resolved. Both are rich in the alga *G. prisca*, yet the latter, and not the former,

contains phenolic structures. The high content of phenols in kukersite pyrolysates has been known for more than half a century (KOGERMAN, 1927) and many thousands of tons are produced for commercial use. The type and distribution of the phenols, and naphthols, was investigated by *inter alia* LILLE (1968), and recently DERENNE et al. (1991) have shown that the principal components are *n*-alkyl-phenols, -resorcinols, and -hydroxybenzofurans.

For the Womble, Vinini, and Big Fork kerogens the distributions of pyrolysis products are unlike those of the Guttenberg kerogen and are more like those of some other type II kerogens (SINNINGHE DAMSTÉ et al., 1989). The structure of these kerogens is presumably similarly complex, being the result of multiple contributions from a variety of source organisms. The similarity in the distributions of C_1 - C_6 alkylthiophenes to those of other type II kerogens covering a wide range of geological ages (SINNINGHE DAMSTÉ et al., 1989; EGLINTON et al., 1990, 1991) is worthy of comment. As it is generally accepted that higher plants did not evolve until Middle/Late Silurian times, this provides indirect evidence that organic compounds from higher plants did not contribute significantly to the genesis of the sulphur-containing moieties in these particular kerogens. In the case of the relatively sulphur-rich Vinini and Womble kerogens, it is postulated that incorporation of inorganic sulphur species into functionalised lipids during early diagenesis has at least partially contributed to kerogen formation.

Regarding other specific pyrolysis products, the abundance of 1,2,3,4-tetramethylbenzene in the Womble, Big Fork, and, to a lesser extent, Vinini pyrolysates is noteworthy. This sub-

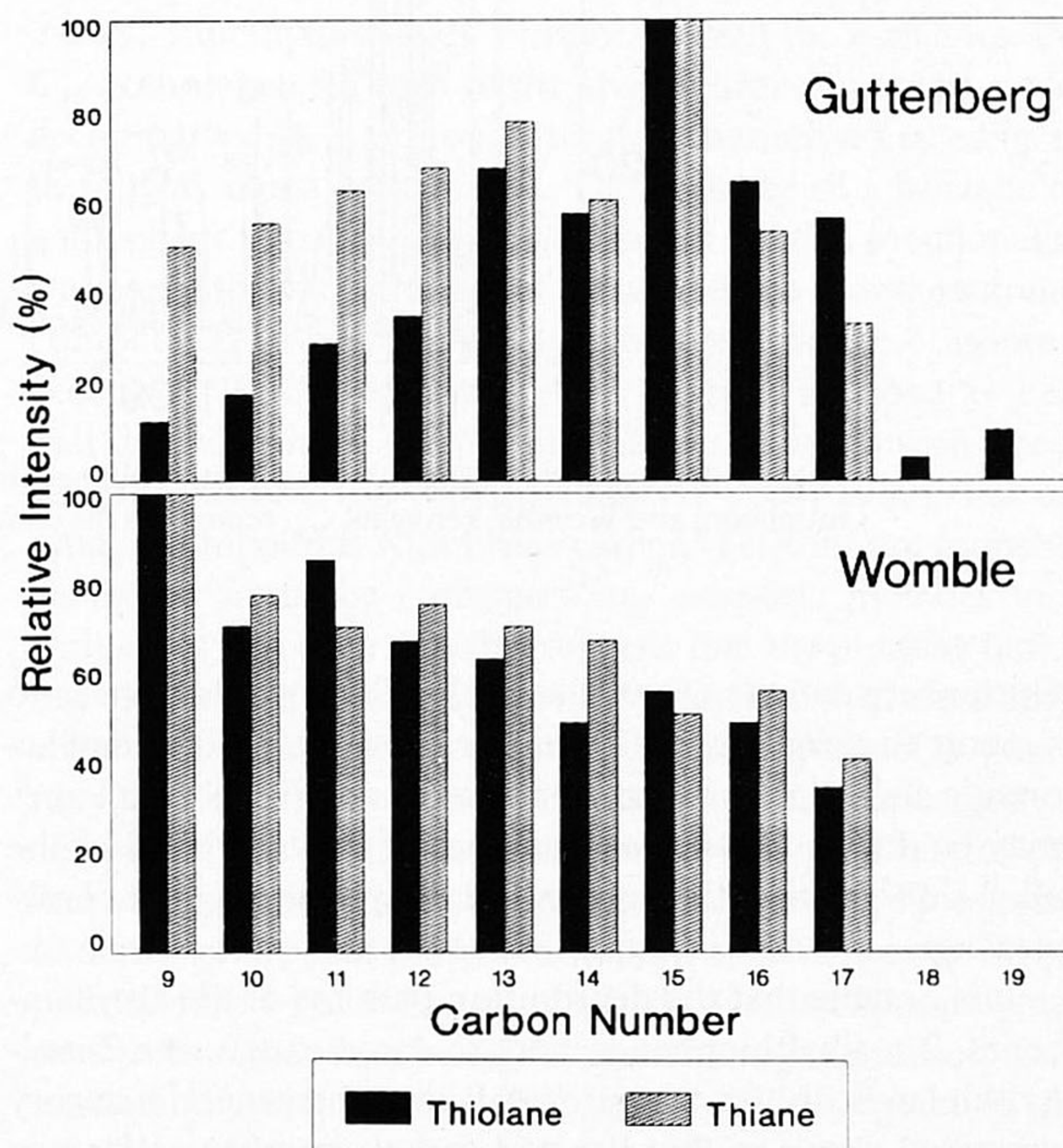


FIG. 11. Histograms prepared from mass chromatograms (m/z 101) representing the distribution of alkylthianes and 2-methylalkylthiolanes in the pyrolysates of Guttenberg and Womble kerogens.

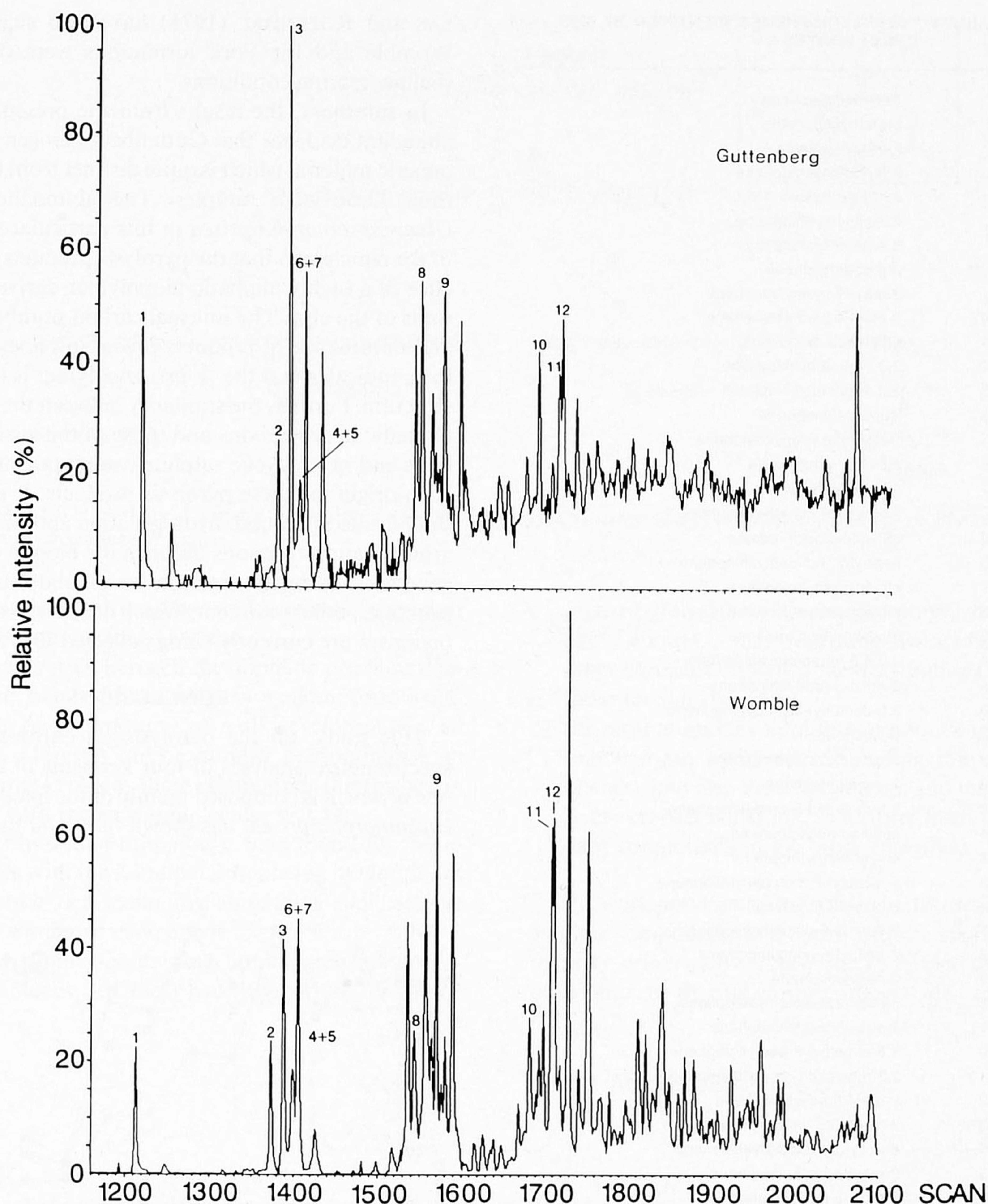


FIG. 12. Distribution of alkylbenzo[*b*]thiophenes (from the summed accurate mass chromatograms 134.06 + 147.08 + 148.08 + 161.10 + 162.10 + 175.11 + 176.11) in the pyrolysates of Guttenberg and Womble kerogens. Peak numbers 1–12 identify these compounds as (1), benzothiophene; (2–7), 7-methyl, 2-methyl, 5-methyl, 6-methyl, 3-methyl, 4-methyl; and (8–12), 2-ethyl, 2,4-dimethyl, 2-propyl, 4-ethyl-2-methyl and 2-ethyl-4-methylbenzo[*b*]thiophene. Identifications of peaks 8–12 inclusive are tentative.

stituted benzene is probably formed by thermal degradation of macromolecularly bound (possibly by sulphide linkages) aromatic carotenoids (SINNINGHE DAMSTÉ and DE LEEUW, in prep.). Such units have recently been shown to occur in the "resin" fraction of bitumen extracts from certain immature sediments (SINNINGHE DAMSTÉ et al., 1990). Natural aromatic carotenoids include the diaromatic compounds, renierapurpurin, renieratene, and isorenieratene which occur in photosynthetic bacteria and marine sponges (LIAAEN-JENSEN, 1978a,b) or their symbiotic bacteria (IMHOFF and TRUPER, 1976, 1980) and the monoaromatic carotenoids, oke-

none, and chlorobactene which occur in two classes of the purple and green photosynthetic bacteria *Chromaticeae* and *Chlorobiaceae*, respectively (LIAAEN-JENSEN, 1978a,b; LIAAEN-JENSEN et al., 1964). All of these aromatic carotenoids are characterised by either a 1-alkyl-2,3,4-trimethyl or a 2-alkyl-1,3,4-trimethyl substitution pattern (or both) in their aromatic ring(s) and when bound to kerogen are likely to generate 1,2,3,4-tetramethylbenzene. Therefore, whilst the abundance of this particular compound in pyrolysates may provide a key to the past, it is not yet possible to discriminate between a contribution of purple or green sulphur bacteria

TABLE 4 ALKYLTHIOPHENES IDENTIFIED IN THE PYROLYSATES

1	2-methylthiophene
2	3-methylthiophene
3	2-ethylthiophene
4	2,5-dimethylthiophene
5	2,4-dimethylthiophene
6	2,3-dimethylthiophene
7	3,4-dimethylthiophene
8	2-propylthiophene
9	2-ethyl-5-methylthiophene
10	2-ethyl-4-methylthiophene
11	ethylmethylthiophene
12	2,3,5-trimethylthiophene
13	2,3,4-trimethylthiophene
14	isopropylthiophene
15	2-methyl-5-propylthiophene
16	2,5-diethylthiophene
17	2-butylthiophene
18	2-ethyl-3,5-dimethylthiophene
19	ethylmethylthiophene
20	5-ethyl-2,3-dimethylthiophene
21	ethylmethylthiophene
22	ethylmethylthiophene
23	ethylmethylthiophene
24	2,3,4,5-tetramethylthiophene
25	2-ethyl-5-propylthiophene
26	3,5-dimethyl-2-propylthiophene
27	C5-thiophene
28	2-butyl-5-methylthiophene
29	2-pentylthiophene
30	2,3-dimethyl-5-propylthiophene
31	ethyltrimethylthiophene
32	ethyltrimethylthiophene
33	5-isobutyl-2,3-dimethylthiophene
34	2-butyl-5-ethylthiophene
35	2-butyl-3,5-dimethylthiophene
36	2-methyl-5-pentylthiophene
37	2-hexylthiophene
38	5-butyl-2,3-dimethylthiophene
39	2-ethyl-5-pentylthiophene
40	3,5-dimethyl-2-pentylthiophene
41	2,3-dimethyl-5-pentylthiophene
42	2-ethyl-5-hexylthiophene
43	2-hexyl-3,5-dimethylthiophene
44	5-hexyl-2,3-dimethylthiophene
45	2-ethyl-5-heptylthiophene
46	2-ethyl-5-octylthiophene
47	2-ethyl-5-nonylthiophene
48	2-ethyl-5-decylthiophene
49	2-ethyl-5-undecylthiophene
50	2-ethyl-5-dodecylthiophene
51	2-ethyl-5-tridecylthiophene

to the organic matter. However, it is noteworthy in this respect that related aryl isoprenoids (2-alkyl-1,3,4-trimethylbenzenes), which were recently identified in source rocks and crude oils, were ascribed to the exclusive presence of photosynthetic green sulphur bacteria in their palaeoenvironments (SUMMONS and POWELL, 1987). Since all photosynthetic sulphur bacteria require both light and hydrogen sulphide it may be concluded, however, that these organic-rich shales were probably deposited from either shallow stratified water columns or from microbial mat-type sediments. NICO-

LAS and ROZENDAL (1975) have also suggested that the Womble and Big Fork formations were deposited under shallow marine conditions.

In summary, the results from the present study provide abundant evidence that Guttenberg kerogen is derived from organic material which is quite distinct from that of the other three Ordovician samples. The abundance of fossilised *Gloeocapsomorpha prisca* in this particular sample leads us to the conclusion that the pyrolysis products reflect the presence of a highly aliphatic biopolymer derived from the cell walls of the alga. The unusual carbon number distributions, and dominance of products possessing linear carbon skeletons, indicates that the *G. prisca* polymer is rather unique in structure. Further, the similarity between the distributions of aliphatic hydrocarbons and those of the aromatic hydrocarbons and heterocyclic sulphur compounds indicates a common origin for these pyrolysis products. It is proposed that sulphur incorporation, hydrogenation and/or cyclisation, and aromatisation reactions occur in the biopolymer during diagenesis. In order to obtain a better understanding of these processes, other sediments which are rich in the debris of this organism are currently being collected for further analysis.

CONCLUSIONS

This study, on the pyrolysis-gas chromatographic-mass spectrometric analyses of four kerogens of Ordovician age, one of which is composed mainly of the fossilised alga *Gloeocapsomorpha prisca*, has shown *inter alia* that

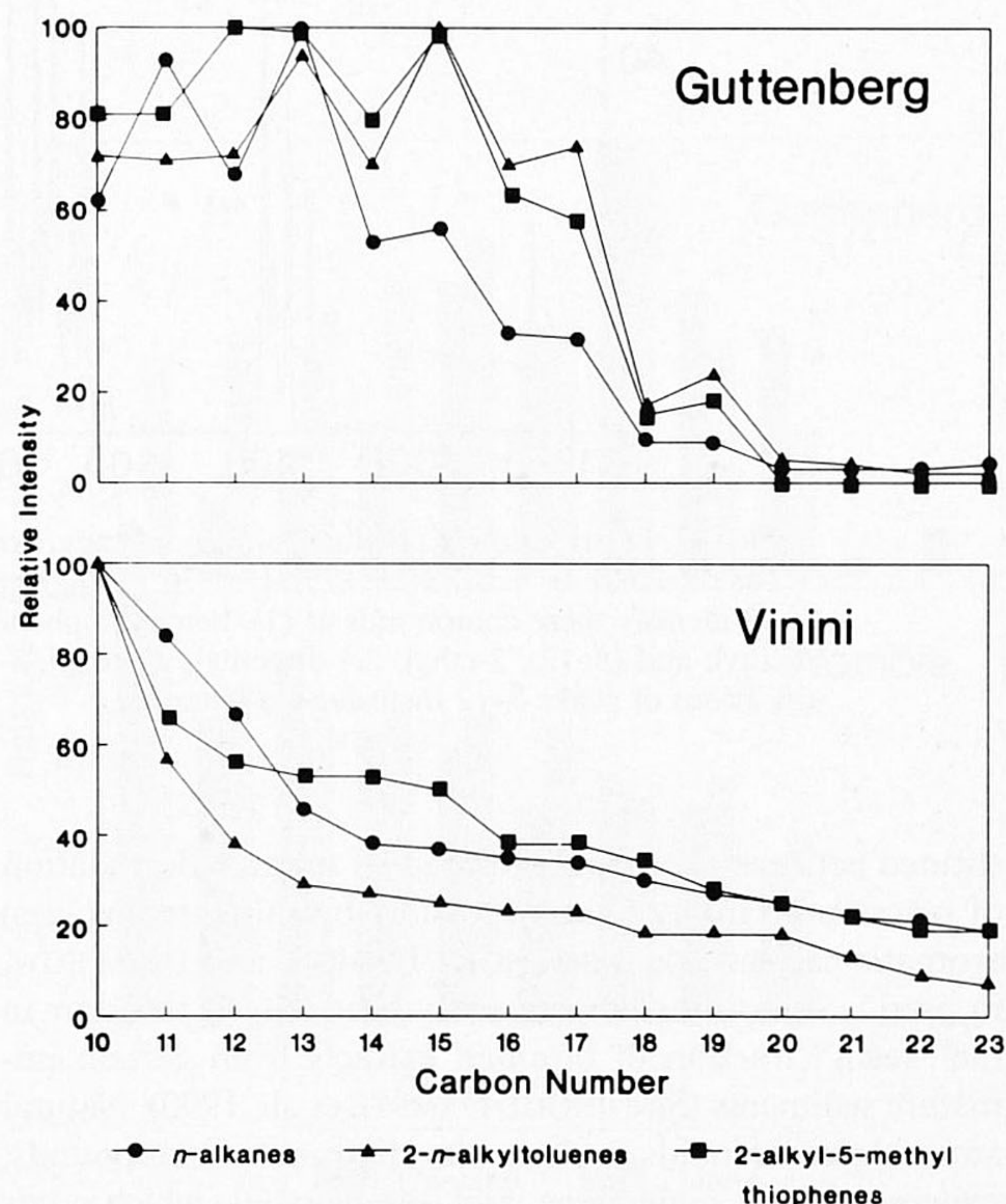


FIG. 13. Comparison of the distributions of *n*-alkanes, 2-*n*-alkyltoluenes and 2-alkyl-5-methylthiophenes in pyrolysates of Guttenberg and Vinini kerogens.

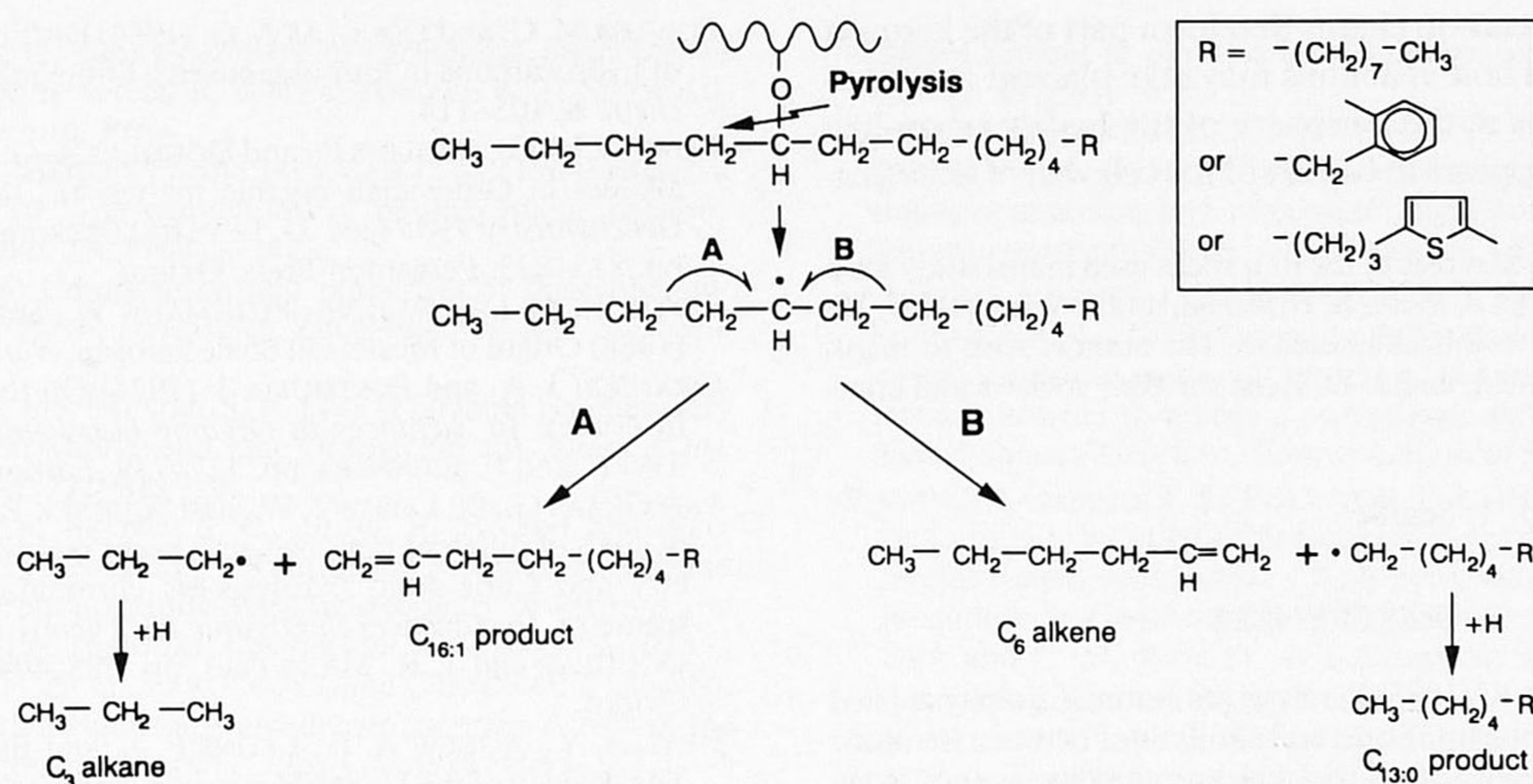


FIG. 14. Hypothetical scheme illustrating the results of pyrolytic cleavage of a C₁₉ substrate linked via an ether bond to a macromolecular matrix.

- 1) pyrolysis released hydrocarbons and heterocyclic sulphur compounds from all four kerogens;
- 2) in the *G. prisca*-rich kerogen the aliphatic products consisted mainly of a restricted range of *n*-alkanes and *n*-alk-1-enes with small amounts of *n*-alkylcyclohexanes, all showing an odd/even carbon number predominance; in the other three kerogens these compounds diminished in abundance with increasing molecular weight;
- 3) similar distributions to the above were found for the *n*-alkyltoluenes with the 2-methyl series being predominant in the *G. prisca*-rich sediments; all of the *n*-alkylbenzene traces were similar to each other;
- 4) most of the sulphur-containing homologues (alkyl-thiophenes, -thiolanes, -thianes) had fingerprints for the *G.*

prisca pyrolysates with sharply diminished abundances above about C₁₇ that were quite distinct from those of the other kerogens, in which the distributions were similar to those for the alkanes;

- 5) the most abundant sulphur compounds in the *G. prisca*-rich kerogen pyrolysate (including the alkylbenzothiophenes), and also the alkyltoluenes and naphthalenes, had linear carbon skeletons, as distinct from the most abundant compounds in the other kerogens.

The work provides added weight to the thesis that the cyclic sulphur compounds, and hydrocarbons, such as those found in the *G. prisca*-rich kerogen, can be formed by incorporation of sulphur, or by ring closure, respectively, of moieties with

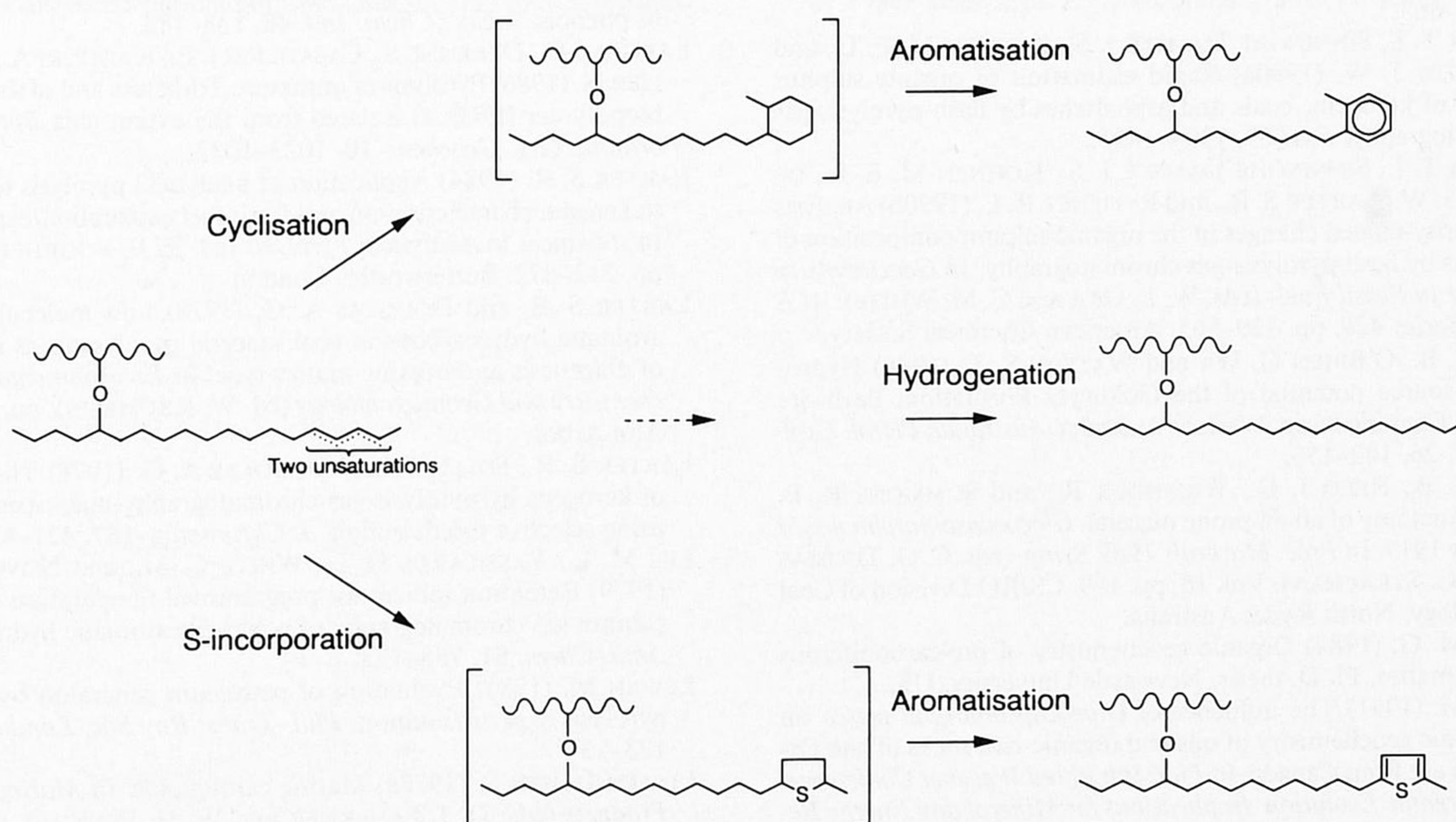


FIG. 15. Hypothetical scheme depicting moieties of an aliphatic biopolymer containing terminal functional groups reacting to form aliphatic, aromatic, and heterocyclic sulphur moieties.

long unbranched carbon chains that form part of the kerogen macromolecule. Those reactions may take place at functionalised attachments at the periphery of the hydrocarbon-like biopolymer that appears to be part of the cell wall of *G. prisca*.

Acknowledgments—Samples of the four rocks used in this study were kindly donated by Drs A. Gize, B. Horsfield, and J. Winters. Mr. W. Pool is thanked for technical assistance. The authors wish to thank J. J. Boon, B. Horsfield, and J. D. Reed for their reviews and comments.

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