

LETTER

The identification and geochemical significance of a second series of alkylthiophenes comprising a linearly extended phytane skeleton in sediments and oils

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Abstract—A series of 5-*n*-alkyl-2-(3,7,11-trimethyldodecyl)-3-methylthiophenes (C₂₁–C₂₆), which possess a linearly extended phytane skeleton, have been identified in a number of bitumens and oils. The carbon skeletons of the C₂₄–C₂₆ members of this series are unusual since they comprise an isoprenoid and a linear part. This series of compounds, and a related series of 2-*n*-alkyl-5-(3,7,11,15-tetramethylhexadecyl)thiophenes, is probably formed by abiogenic sulphur incorporation into functionalised precursor lipids with similar carbon skeletons, possibly biosynthesised by halophilic archaeobacteria.

INTRODUCTION

PREVIOUS OBSERVATIONS HAVE indicated the presence of series of isoprenoid thiophenes (C₂₀–C₂₉) in the "aromatic hydrocarbon" fraction from the solvent extractable material of a bituminous marl of Miocene age from the northern Apennines, Italy (SINNINGHE DAMSTÉ et al., 1986, 1988). As part of our studies aimed at understanding the origin and geochemical significance of these sulphur-containing compounds, we have recently reported (I; see Appendix for structure; PEAKMAN et al., 1989) that one of these series comprises C₂₅–C₂₈ 2-alkyl-5-(3,7,11,15-tetramethylhexadecyl)thiophenes. These components were identified by comparison of the mass spectra and relative GC retention times with those of synthesised standards and by similar comparisons with the desulphurised "aromatic hydrocarbon" fraction and the desulphurised thiophene standards (IIf–i). The carbon skeletons of these alkylthiophenes correspond to linearly extended phytanes (cf. IIf–i). Such compounds and their biosynthesis are presently unknown in living organisms.

Here we report the identification of a second major series of alkylthiophenes also occurring in the northern Apennines marl and in bitumens from Jordan and California (U.S.A.) and in immature oils from Sicily (Italy), Utah (U.S.A.), and China, which also comprise this unusual linearly extended phytane skeleton.

EXPERIMENTAL

For a geological description of the samples used in this study the reader is referred to SINNINGHE DAMSTÉ et al. (1989b). Bitumens and crude oils were fractionated to give either so-called low-molecular-weight aromatic fractions by column chromatography (SINNINGHE DAMSTÉ et al., 1989a) or discrete alkylthiophene fractions by argentatious thin-layer chromatography (SINNINGHE DAMSTÉ et al.,

1989b). These fractions were then analysed by GC and GC-MS as described previously (SINNINGHE DAMSTÉ et al., 1989a,b). Raney Ni desulphurisation was carried out in refluxing ethanol with W-2 Raney nickel under nitrogen for three hours and subsequent hydrogenation (PtO₂, HOAc), when necessary, to remove alkenes.

The C₂₁ thiophene (IIIb) was prepared by coupling of 3,7,11-trimethyldodecanoic acid with 2,4-dimethylthiophene [(i) (COCl)₂, CH₂Cl₂, DMF (ii) SnCl₄] and reduction of the resulting ketone [LiAlH₄/AlCl₃, Et₂O]. The C₂₂–C₂₅ thiophenes (IIIc–f) were prepared by similar couplings of the appropriate carboxylic acid (C₂–C₅) with the C₂₀ thiophene (IIIa), followed by similar reductions of the resulting ketones. The C₂₀ thiophene (IIIa) was prepared by an improved method to that described previously (BRASSELL et al., 1986) whereby 3,7,11-trimethyldodecan-1-al was coupled with 3-methyl-2-thienyllithium, oxidation of the resulting alcohol (PDC, DMF) to a ketone, followed by a modified Wolff-Kishner reduction [(i) H₂N·NH₂, diethylene glycol, Δ (ii) KOH, Δ]. This compound was obtained without any 2,4-isomer impurity. The corresponding alkanes were obtained by desulphurising the alkylthiophenes under the conditions described above. Full experimental synthetic details and detailed ¹H nmr characterisations of these alkylthiophenes will be reported separately, although mass spectral details of the synthesized standards are given in Table 1.

RESULTS AND DISCUSSION

Identification

GC and GC-MS analysis of the desulphurised alkylthiophene fraction from the solvent extract of the northern Apennines marl (Fig. 1) indicates the presence of a series of isoprenoidal components ranging from C₂₁ to C₂₈ (IIf–i). The C₂₅–C₂₈ members (IIf–i) have been identified by us as having a linearly extended phytane skeleton (PEAKMAN et al., 1989). Initial evidence that the C₂₁–C₂₄ components (IIf–e) were indeed lower homologues (cf. SINNINGHE DAMSTÉ et al., 1988) came from reference to the results of SPYCKERELLE et al. (1972) who identified the C₂₁–C₂₃ alkanes (IIf–d) in a Cretaceous shale from Gabon by comparison of the mass spectra of and co-injection studies with authentic compounds. Such compounds have also been observed in other environments (e.g., C₂₁ in Precambrian sediments, MCCAR-

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Table 1. Mass spectral and retention time data of synthetic 5-*n*-alkyl-3-methyl-2-(3,7,11-trimethyldodecyl)thiophenes and the hydrocarbons obtained by desulphurisation of these thiophenes.

Alkylthiophene			Alkane	
Structure number	mass spectrum	retention* index	structure number	retention* index
IIIa	308(10), 111(100)	2096	IIa	1813
IIIb	322(10), 125(100)	2169	IIb	1904
IIIc	336(5), 139(100)	2246	IIc	1982
IIId	350(13), 153(100)	2327	IIId	2074
IIIe	364(14), 167(100)	2421	IIe	2173
IIIf	378(15), 181(100)	2515	IIf	2272

* 25 m CP Sil 5, H₂ carrier, 130°C to 300°C at 4°C min⁻¹

THY et al., 1967; C₂₁ and C₂₃ in waste water effluents, EGANHOUSE and KAPLAN, 1982; C₂₁-C₂₄ in the saline water and water-soluble part of the peloid extract from Lake Karachi, RYZHOVA et al., 1982; and C₂₁-C₂₃ in the products obtained from hydrogenation of coal, YULIN et al., 1987).

A previous analysis of the alkylthiophenes from the solvent extract of the northern Apennines marl (SINNINGHE DAMSTÉ et al., 1986) has suggested the presence of major C₂₁ and C₂₂ alkylthiophenes possessing such a linearly extended phytane skeleton (IIIb, c). A re-inspection of the alkylthiophene fraction using mass chromatography indicated that this series extends up to C₂₆ (Fig. 2). These assignments were confirmed by comparison of the mass spectra and relative GC retention time data (on CP Sil 5 and DB 1701) with those of synthesised C₂₁-C₂₅ alkylthiophene standards (IIIb-f) and the corresponding alkanes obtained by desulphurisation and subsequent hydrogenation (IIb-f). The mass spectral and relative GC retention time data for the alkylthiophenes and the relative GC retention time data for the corresponding alkanes

obtained by desulphurisation and subsequent hydrogenation are given in Table 1. The mass spectra of these alkylthiophenes are characterised by molecular ions (ca. 10%) and cleavage of the isoprenoid chain β to the thiophene ring giving a base peak at m/z 111 + 14*n* where *n* = 0 for the C₂₀ alkylthiophene (IIIa). Two typical mass spectra are shown in Fig. 3.

Occurrence

Examination of the low-molecular-weight aromatic fractions from other bitumens and oils indicates the more widespread occurrence of this series of alkylthiophenes possessing a linearly extended phytane skeleton (IIIb-g). The relative abundances of these components in selected samples, as determined by mass chromatography of m/z 125, 139, 153, 167, 181, and 195, are presented in histogram format in Fig. 4. These distributions show that the C₂₁ member (IIIb) is often, but not always, the dominant member of this series. Furthermore, in a number of samples the complete C₂₁-C₂₆ range is not observed; for example, only the C₂₁ member is detected in samples from the Jurf ed Darawish oil shale (Fig. 4; one example shown). Intermediate situations were observed in two of the three Monterey samples studied (Fig. 4); the third sample (T6) does not contain C₂₁-C₂₆ thiophenes (IIIb-g). The abundance of this series of C₂₁-C₂₆ thiophenes relative to the structurally related C₂₀ thiophene (IIIa) is highly variable (Fig. 5).

Possible origin

Organic sulphur compounds with structures related to biosynthetic precursors are thought to be formed by incorporation of inorganic sulphur species (H₂S, polysulphides)

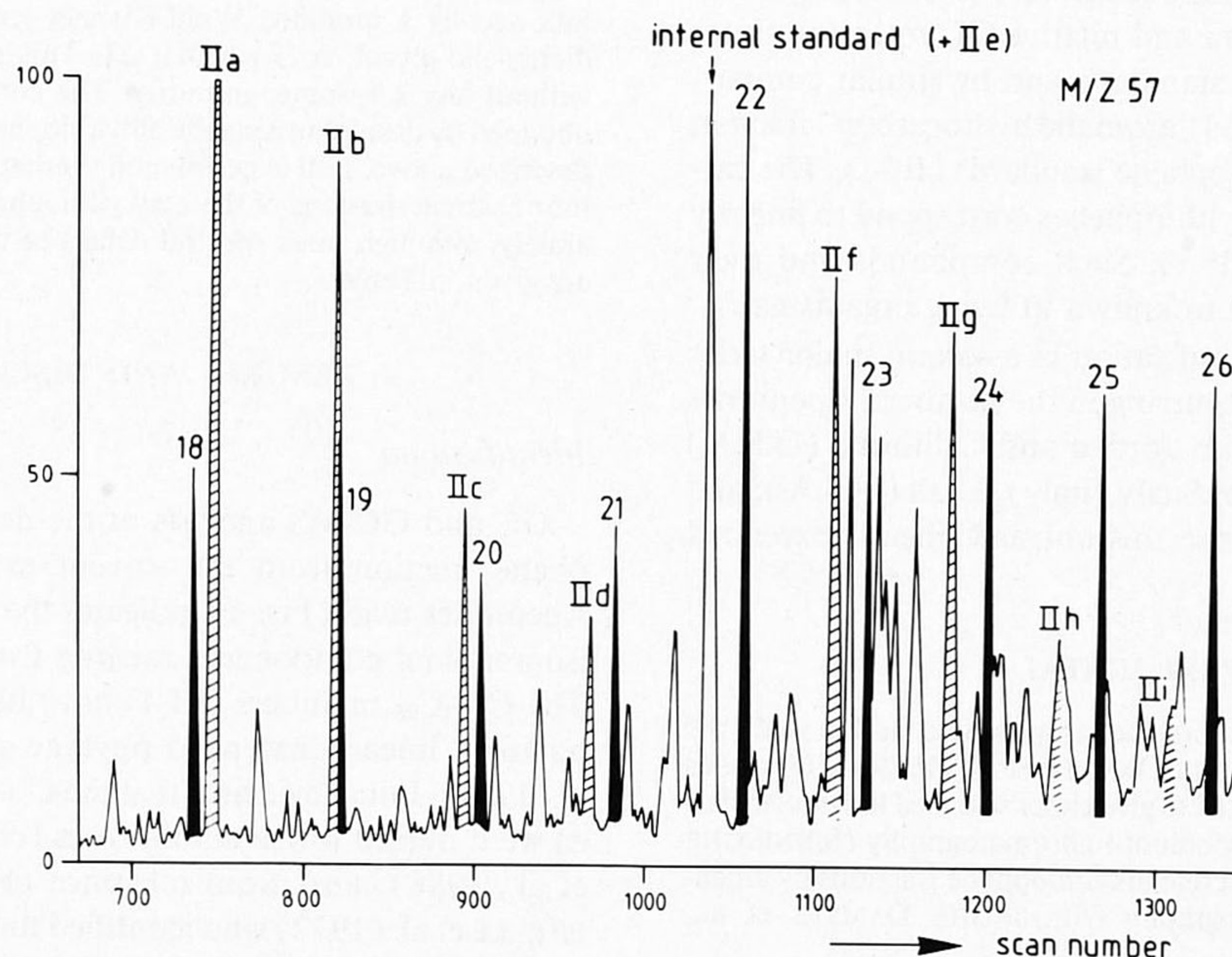


FIG. 1. Partial mass chromatogram of m/z 57 for the desulphurised alkylthiophene fraction of the northern Apennines marl bitumen. Black peaks represent *n*-alkanes; total number of carbon numbers are indicated by arabic numbers. Shaded peaks represent (pseudo) isoprenoid alkanes. The C₂₄ isoprenoid alkane coelutes with the much more dominant internal standard 6-d₂-3-methylheneicosane.

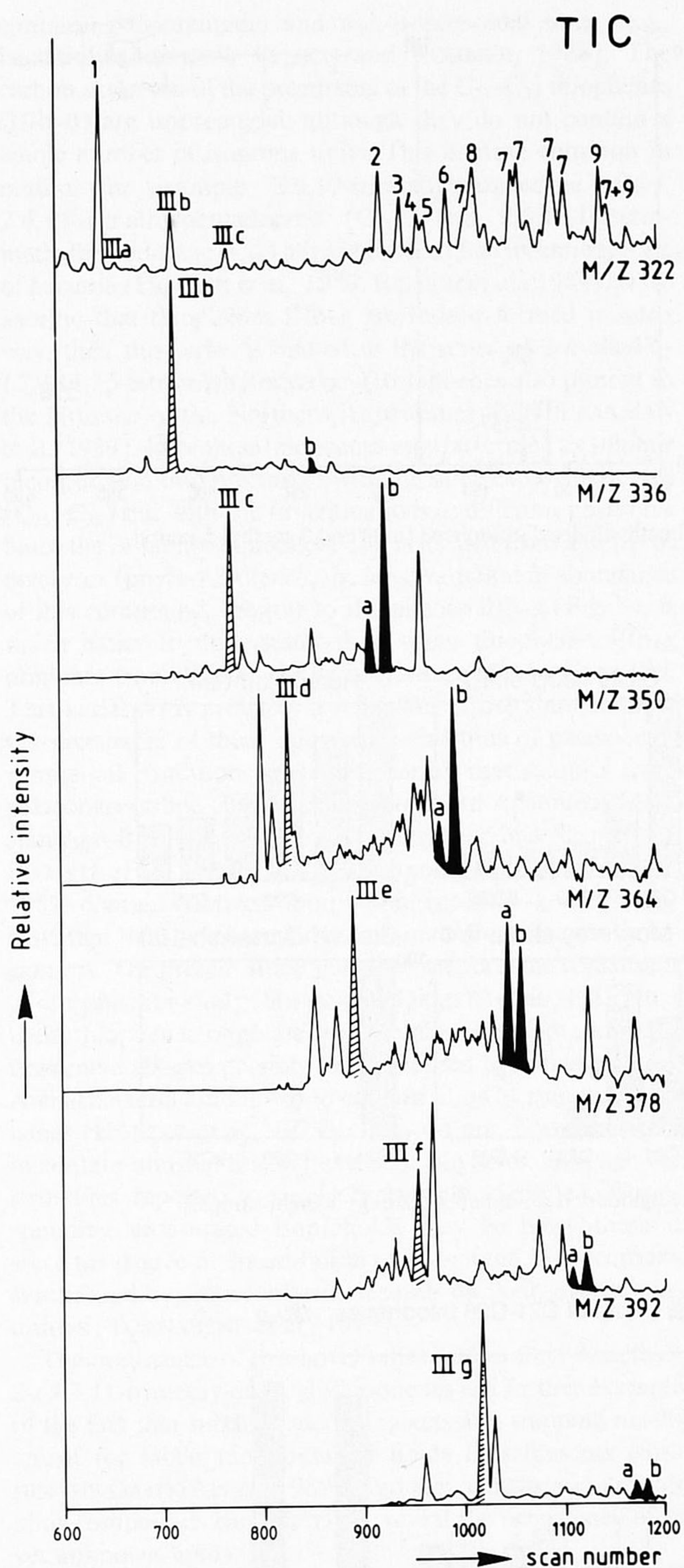


FIG. 2. Partial total ion chromatogram (TIC) and mass chromatograms of m/z 322, 336, 350, 364, 378, and 392 of the alkylthiophene fraction isolated from the northern Apennines marl bitumen. Shaded peaks indicate 5- n -alkyl-3-methyl-2-(3,7,11-trimethylundecyl)thiophenes. Black peaks indicate 2,5-dialkylthiophenes; a = 2-alkyl-5-ethyl-thiophenes, b = 2-alkyl-5-methylthiophenes. Key for TIC: 1 = 2,3-dimethyl-5-(2,6,10-trimethylundecyl)thiophene, 2 = 2,3-dimethyl-5-(1- d_2 -hexadecyl)thiophene (internal standard), 3 = (20S)-diacholestene, 4 = C-ring monoaromatic steroid + isoprenoid C_{26} thiophene, 5 = 2-methyl-5-(3,7,11,15-tetramethylhexadecyl)thiophene (Ia) + minor unknown isoprenoid C_{25} thiophene, 6 = (20R)-diacholestene, 7 = C-ring monoaromatic steroid, 8 = 2-ethyl-5-(3,7,11,15-tetramethylhexadecyl)thiophene (Ib) + 3,5-dimethyl-2-(3,7,11,15-tetramethylhexadecyl)thiophene +

into labile functionalised lipids (VALISOLALAO et al., 1984; BRASSELL et al., 1986; SINNINGHE DAMSTÉ et al., 1986, 1987a,b, 1988, 1989a,b; SINNINGHE DAMSTÉ and DE LEEUW, 1987; KOHNEN et al., 1989). For example, the C_{20} isoprenoid thiophene (IIIa) is most likely formed by incorporation of inorganic sulphur species into phyta-1,3-diene (BRASSELL et al., 1986; DE LEEUW and SINNINGHE DAMSTÉ, 1989). The origin of the C_{21} – C_{26} alkylthiophenes (IIIb–g) is more difficult to assess. We have previously suggested that these compounds, with at that time partially unknown structures, originated from sulphur incorporation into isoprenoid alkenes possibly biosynthesised by archaeobacteria (SINNINGHE DAMSTÉ et al., 1986).

Results from the present study indicate that these alkylthiophenes comprise a series of thiophenes of type III, which are all composed of partial structure IIIa with additional n -alkylation at C-5. In other words, the thiophene ring is located at the same relative position within the series. This structural feature could suggest a possible origin by an abiological formation in sediments from a Friedel-Crafts alkylation reaction of either the C_{20} thiophene (IIIa) with suitable low molecular n -alkyl species such as alcohols or by reaction of farnesol with 2- n -alkyl-4-methylthiophenes (followed by subsequent reduction of the unsaturations in the alkyl side chain). Such types of reactions, which would normally require acid-catalysis (e.g., clay minerals), have recently been suggested to account for the presence of steroid units bonded by a carbon-carbon bond, from C-3 and another position to aromatic units in asphaltenes and coals (TRIFILIEFF et al., 1989). WILLIAMS et al. (1988) also proposed alkylation reactions of benzenes and methylated benzenes to explain the anomalous concentration of pentadecyl-substituted derivatives of benzene, toluene, and xylenes in crude oils from Midland and Michigan Basin reservoirs. However, a number of observations are at variance with such an origin from Friedel-Crafts alkylation reactions. Firstly, Friedel-Crafts alkylation products of other organic sulphur compounds with a monosubstituted thiophene ring occurring widespreadly in sediments (e.g., the C_{35} thiophene ring-containing hopanoid (IV); VALISOLALAO et al., 1984) are unknown. Secondly, the Friedel-Crafts alkylation of 2-alkyl-4-methylthiophenes by farnesol can be rejected since products of such a reaction with ubiquitously occurring phytol are not observed in the sediments and oils studied.

Alternatively, the C_{21} – C_{26} alkylthiophenes (IIIb–g) may originate from sulphur incorporation into specific functionalised precursors. The fixed position of the thiophene ring, within this series of components, suggests the original presence of a series of precursor biological lipids with the same carbon skeleton and having functionalities at the same relative position, which can then react with inorganic sulphur species, eventually leading to the formation of a thiophene ring. The carbon skeletons of these hypothetical precursors are characterised by a phytane unit coupled to a n -alkyl unit (C_1 – C_6), which is rather unusual for the C_{24} – C_{26} members since there are only a few examples of naturally occurring lipids

minor unknown isoprenoid C_{26} thiophene, 9 = C-ring monoaromatic 4-methylsteroid.

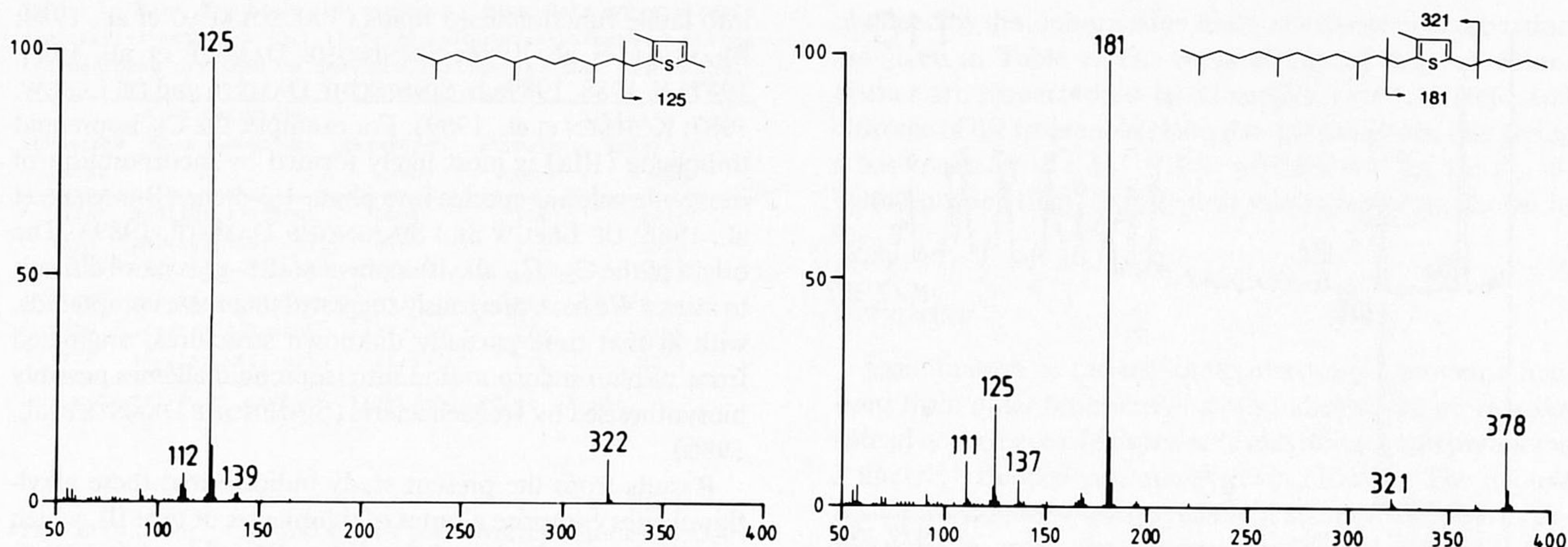


FIG. 3. Mass spectra of synthetic 3,5-dimethyl-2-(3,7,11-trimethyldodecyl)thiophene (left) and 3-methyl-5-pentyl-2-(3,7,11-trimethyldodecyl)thiophene (right).

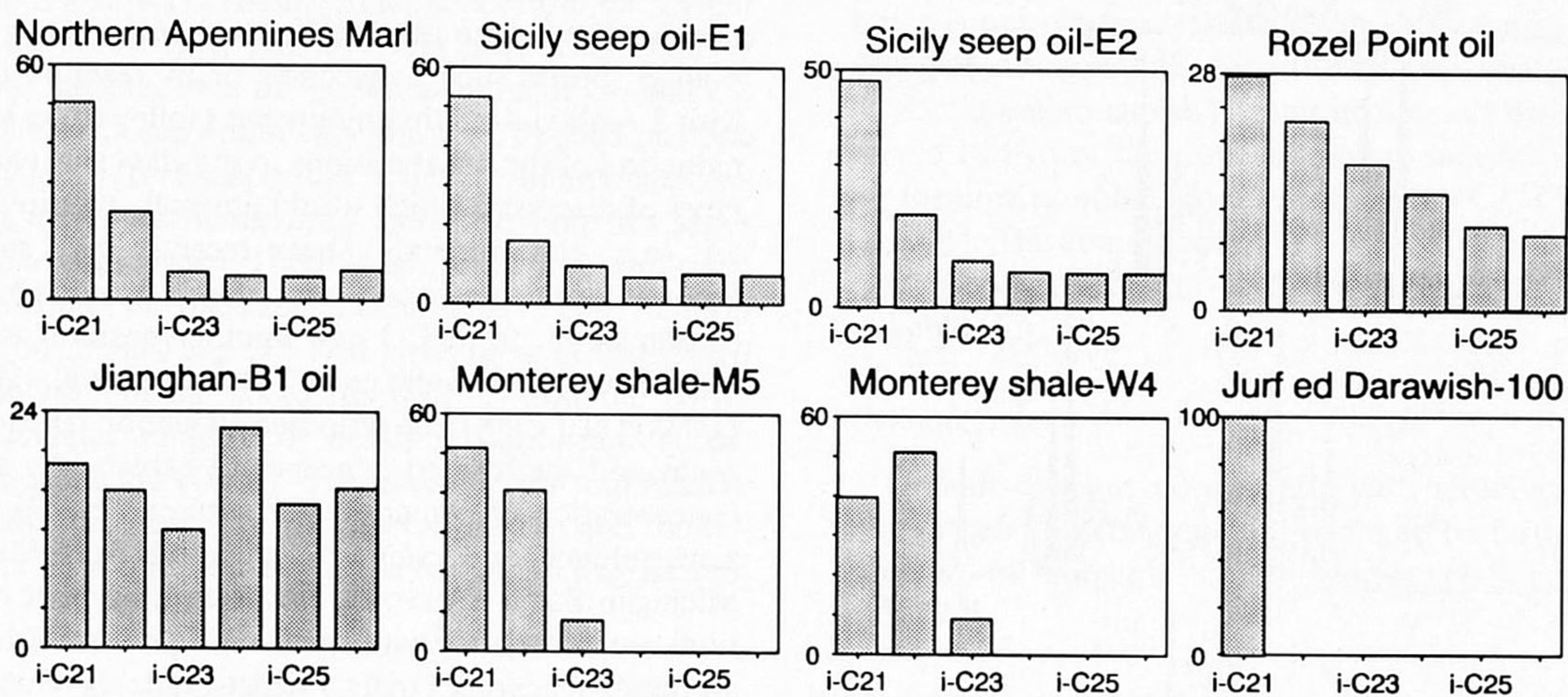


FIG. 4. Distributions of 5-*n*-alkyl-3-methyl-2-(3,7,11-trimethyldodecyl)thiophenes (IIIb-g) in eight samples.

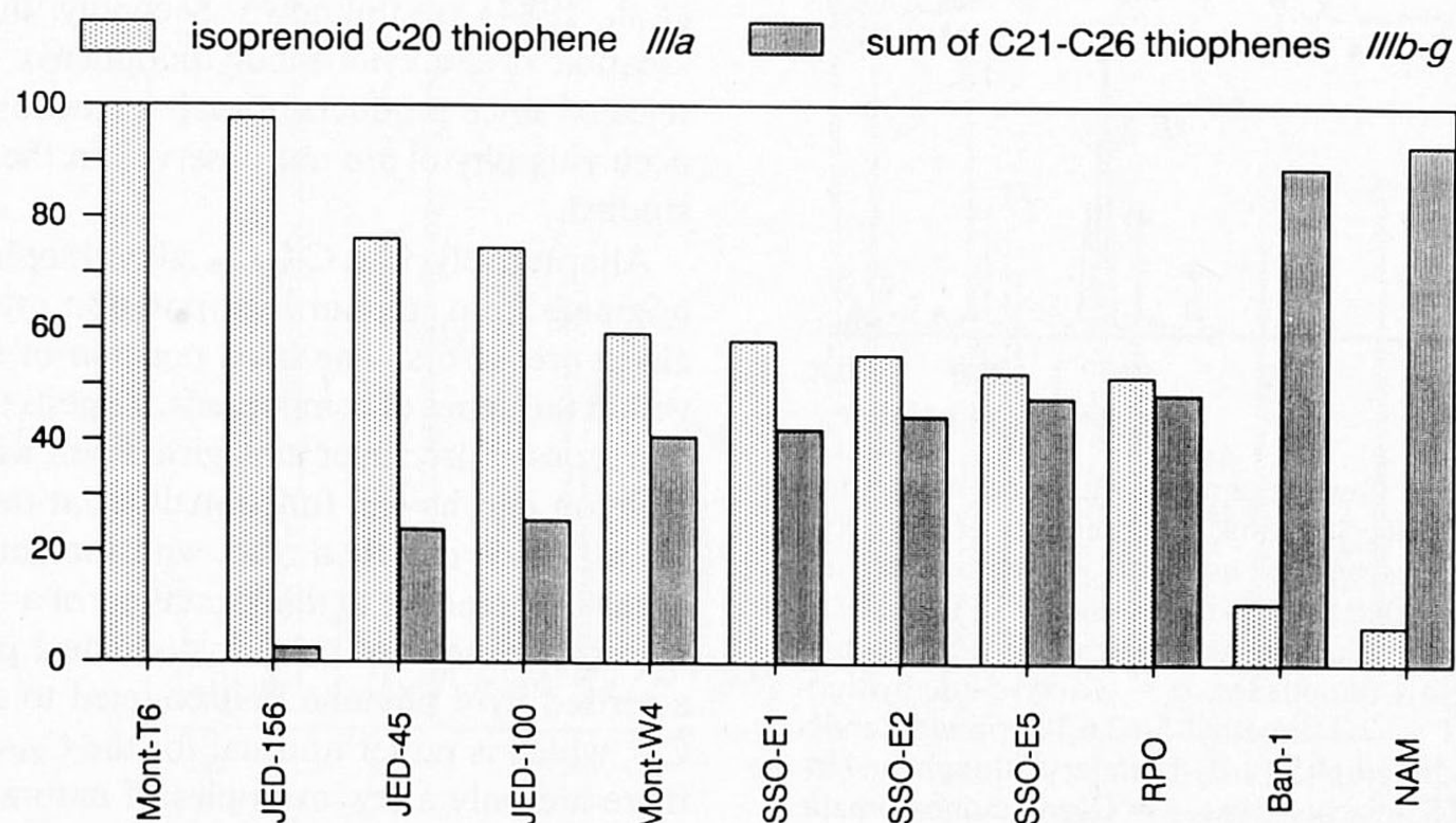


FIG. 5. Abundances of the sum of the C₂₁-C₂₆ 5-*n*-alkyl-3-methyl-2-(3,7,11-trimethyldodecyl)thiophenes (IIIb-g) relative to 3-methyl-2-(3,7,11-trimethyldodecyl)thiophene (IIIa) for the samples studied. Key: Mont = Monterey, JED = Jurf ed Darawish oil shale, SSO = Sicily seep oil, RPO = Rozel Point oil, Ban-1 = Jiangnan-B1 oil, NAM = northern Apennines marl.

containing isoprenoidal and non-isoprenoidal units (e.g., bacteriohopanetetrol; FLESCH and ROHMER, 1988). The carbon skeletons of the precursors of the C₂₁–C₂₃ thiophenes (IIIb–d) are isoprenoidal, although they do not contain a whole number of isoprene units. This is more common in nature; for example, 2,6,10-trimethyltetradecane (C₁₇), 2,6,10-trimethylpentadecane (C₁₈), and 2,6,10,14-tetramethylheptadecane (C₂₁) have been identified in some species of bacteria (HOLZER et al., 1979; RISATTI et al., 1984). If we assume that thiophenes IIIb–g are indeed formed in such way, then this series is related to the series of 2-*n*-alkyl-5-(3,7,11,15-tetramethylhexadecyl)thiophenes also present in the bitumen of the Northern Apennines Marl (PEAKMAN et al., 1989), since these thiophenes may be formed by sulphur incorporation into precursors with the same carbon skeletons (C₂₅, C₂₆) but with the functionalities at different positions. Since the isoprenoid thiophene IIIa is formed from a different precursor (phyta-1,3-diene), the large variation in abundance of this compound, relative to thiophenes IIIb–g (Fig. 5), is much easier to understand than when thiophenes IIIb–g originate from Friedel-Crafts alkylation of thiophene IIIa. This variation is probably a reflection of the abundance of the precursors of these thiophenes and thus of palaeoenvironmental conditions. It is noteworthy that samples from palaeohypersaline environments (Northern Apennines Marl, Jianghan-B1 oil, Rozel Point oil, Sicily Seep oils; SINNINGHE DAMSTÉ et al., 1989b; DE LEEUW and SINNINGHE DAMSTÉ, 1989) contain relatively more thiophenes IIIb–g, which suggests that their precursors may originate from halophilic organisms. The present study therefore supports the conclusion of our previous study (SINNINGHE DAMSTÉ et al., 1986) that these thiophenes originate from sulphur incorporation into isoprenoid alkenes possibly biosynthesised by archaeobacteria. Archaeobacteria are known to contain C₂₁–C₂₈ isoprenoid alkanes (HOLZER et al., 1979). They do not, however, seem to contain unusual linearly extended phytanes, although the structures reported are only tentatively identified. Corresponding unsaturated isoprenoids may be biosynthesised since the degree of unsaturation of isoprenoid hydrocarbons synthesised by archaeobacteria depends on their growth conditions (TORNABENE et al., 1979).

The occurrence of this novel series of 5-*n*-alkyl-3-methyl-2-(3,7,11-trimethyldodecyl)thiophenes is a further example of the fact that sulphur quenching acts as a trapping mechanism for labile functionalised lipids in sediments (SINNINGHE DAMSTÉ et al., 1989a) and that identification of sulphur compounds can, therefore, reveal the occurrence of as yet unknown lipids.

CONCLUSIONS

1. A series of 5-*n*-alkyl-3-methyl-2-(3,7,11-trimethyldodecyl)thiophenes (C₂₁–C₂₆) comprising a linearly extended phytane skeleton has been identified in a number of bitumens and crude oils.
2. This series of alkylthiophenes probably originates from sulphur incorporation into a yet unknown series of functionalised lipids comprising the linearly extended phytane skeleton possibly biosynthesised by halophilic archaeobacteria.

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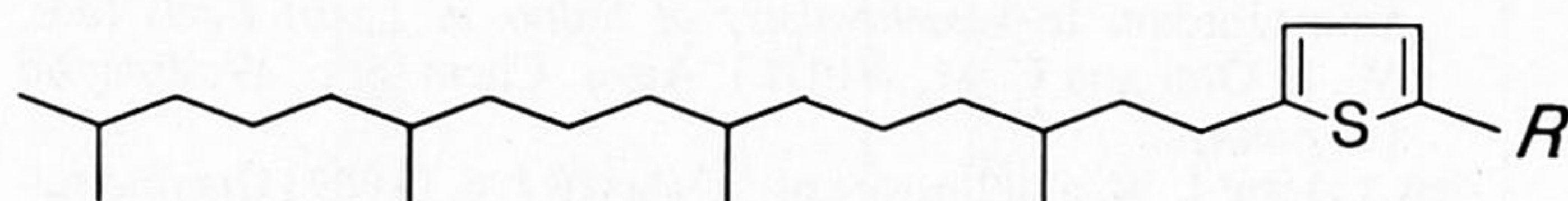
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Appendix

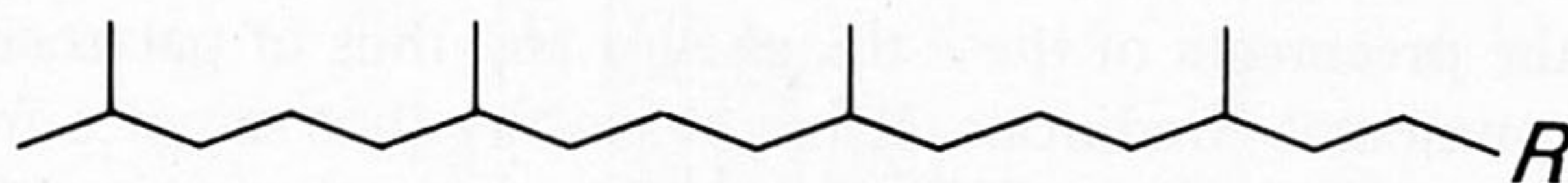


Ia R = CH₃

Ib R = C₂H₅

Ic R = n-C₃H₇

Id R = n-C₄H₉



IIa R = H

IIb R = CH₃

IIc R = C₂H₅

IId R = n-C₃H₇

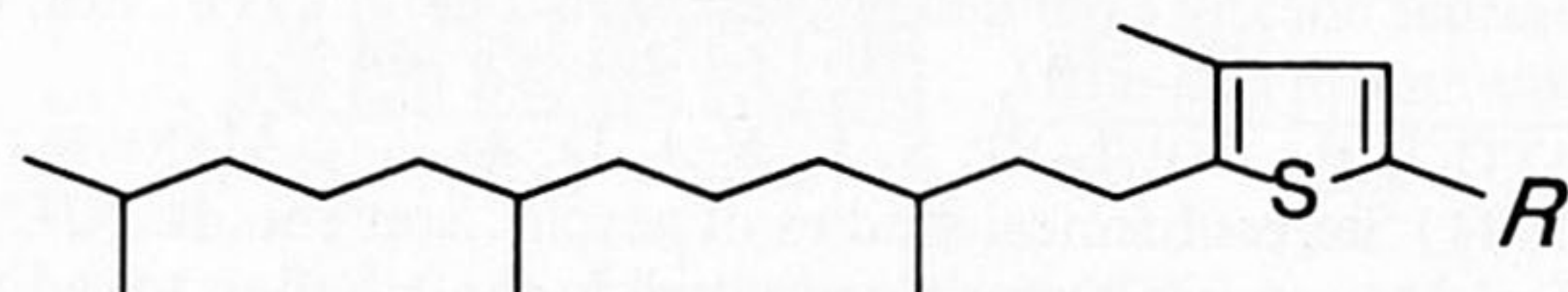
IIe R = n-C₄H₉

IIf R = n-C₅H₁₁

IIg R = n-C₆H₁₃

IIh R = n-C₇H₁₅

IIIi R = n-C₈H₁₇



IIIa R = H

IIIb R = CH₃

IIIc R = C₂H₅

IIId R = n-C₃H₇

IIIe R = n-C₄H₉

IIIf R = n-C₅H₁₁

IIIg R = n-C₆H₁₃

