

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 palaeoenvironments and possible application as source, palaeoenvironmental and maturity indicators*

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Abstract—The organic sulphur compounds (OSC) present in sixteen immature samples (both crude oils and bitumens) from different geographical locations and of different ages representing different palaeoenvironments have been analysed by GC-MS. In all samples OSC (thiolanes, thianes, thiophenes and benzo[*b*]thiophenes) with structures related to well-known geologically occurring hydrocarbons (*n*-alkanes, isoprenoid alkanes, steranes, triterpanes) occur, although the relative amounts and distribution patterns of the various OSC classes vary considerably. This variation is interpreted as a result of different sources of organic matter and different degrees of thermal maturation. The palaeoenvironments of the samples were anoxic and H₂S, produced by sulphate-reducing bacteria, probably has exceeded the input of reactive iron minerals. These conditions resulted in a surplus of free H₂S, which reacted with organic matter, leading to the formation of OSC. The distributions of OSC may be useful as molecular indicators for the assessment of sources of organic matter, palaeoenvironment and thermal maturity and for oil-oil and oil-source rock correlation studies. The distributions of the C₂₀ isoprenoid thiophenes in combination with those of the methylated 2-methyl-2-(4,8,12-trimethyltridecyl)chromans can be used to discriminate non-hypersaline from hypersaline palaeoenvironments.

INTRODUCTION

IN THE PREVIOUS PAPER of this series (SINNINGHE DAMSTÉ *et al.*, 1987c) it has been demonstrated that Rozel Point Oil, an immature, sulphur-rich oil from Utah (U.S.A.) contains a number of novel series of organic sulphur compounds (OSC), together accounting for almost 1000 individual compounds. Series of 2,6-di-*n*-alkylthianes, 2,5-di-*n*-alkylthiolanes, 2,4-di-*n*-alkylbenzo[*b*]thiophenes, isoprenoid thiophenes, thiolanes, benzo[*b*]thiophenes and bithiophenes, and thiolane and thiophene steroids were identified. They represent the major compounds present in the "aromatic" fraction of the oil. These OSC differ essentially from most of the OSC previously identified in oils (*e.g.*, THOMPSON, 1981; AKSENOV and KAMYANOV, 1981; HUGHES, 1984; ARPINO *et al.*, 1987) because their structures are related to bio- and geochemical precursors.

Some of the series of OSC identified in the Rozel Point Oil and some other series of OSC related to bio- and geo-

chemical precursors have also been reported in other samples. PAYZANT *et al.* (1983, 1985, 1986, 1988a) identified a number of terpenoid sulphides and related sulphoxides in a variety of petroleum from the Western Hemisphere. VALISOLALAO *et al.* (1984) reported the presence of a thiophene-ring containing hopanoid in black shales. BRASSELL *et al.* (1986) and RULLKÖTTER *et al.* (1988) identified a number of isoprenoid thiophenes in DSDP samples. SINNINGHE DAMSTÉ *et al.* (1986) reported the presence of 2,5-di-*n*-alkylthiolanes, 2,5-di-*n*-alkylthiophenes, isoprenoid thiolanes and thiophenes in a marl layer from the Northern Apennines (Italy). PERAKIS (1986) identified a series of 2,4-di-*n*-alkylbenzo[*b*]thiophenes in an immature shale from Morocco and in the Rozel Point Seep Oil (Utah, U.S.A.). SCHMID (1986) and SCHMID *et al.* (1987) noted the occurrence of series of 2,5-di-*n*-alkylthiolanes and 2,6-di-*n*-alkylthianes in the Maruejols crude oil (Alès Basin, France) and the Rozel Point Seep Oil. SCHMID (1986) also identified isoprenoid thiophenes, bithiophenes and a tri-thiophene, various types of thiophene and thiolane steroids, hopanoid sulphides and steroid bisulphides in the Rozel Point Seep Oil. CYR *et al.* (1986) reported the presence of a series of hopanoid sulphides ranging from C₃₀ to C₃₅ in heavy oils of Northern Alberta (Canada). SINNINGHE DAMSTÉ and DE LEEUW (1987) reported a number of C₂₀ and C₁₅ isoprenoid OSC occurring in sediment extracts and oils from various locations and ages. An isoprenoid C₂₀ thiophene was identified as one of the most abundant OSC occurring in several oils by SINNINGHE DAMSTÉ *et al.* (1987a). SHENG *et al.* (1987) reported the presence of series of alkylthiolanes and -thiophenes and isoprenoid thiolanes, thiophenes and benzo[*b*]thiophenes in oils from the Jiangnan Basin (China).¹ Series of 2-*n*-alkyl- and 2,5-di-*n*-alkylthiophenes, 2-*n*-alkylthiolanes and -thianes, 2,5-di-*n*-alkylthiolanes, 2,6-di-*n*-alkylthianes, 2-

* For Part I see: SINNINGHE DAMSTÉ *et al.* (1987c).

¹ It should be noted that the assignment of compounds in SHENG *et al.* (1987) is unclear and misleading. Not all assignments are equally justified and some are wrong:

(i) The mass spectrum in Fig. 4C represents a mixture of 5-(2,6-dimethylheptyl)-2-(3-methylpentyl)-3-methylthiophene and lesser amounts of another C₂₀ mid-chain isoprenoid thiophene and not the structure indicated in this figure.

(ii) The black peaks marked "*i* C_{xy}" in Fig. 5A do not represent isoprenoid thiophenes but mid-chain 2,5-di-*n*-alkylthiophenes.

(iii) The black peaks marked "*i* C_{xy}" in Fig. 5B do not represent isoprenoid thiolanes but a series of 2-alkyl-5-methylthianes.

Because of these and some other incorrect assignments the quantitative approach attempted by SHENG *et al.* (1987) is of no value.

and 4-*n*-alkylbenzo[*b*]thiophenes and 2,4-di-*n*-alkylbenzo[*b*]thiophenes have also been identified in flash pyrolysates of kerogens and asphaltenes (SINNINGHE DAMSTÉ *et al.* (1988b, 1989a) and in the pyrolysis oil of the Athabasca asphaltene (PAYZANT *et al.*, 1988b).

In this paper the OSC present in a more extensive set of samples from different geographical locations and of different ages are described, indicating their widespread occurrence. The potential application of OSC as molecular indicators is also discussed.

DESCRIPTION OF THE SAMPLES

The Northern Apennines Marl is from Miocene strata in the Pericara Basin (Italy) which consists of gypsum deposits interbedded with bituminous marl layers. A 10 cm thick marl layer was sampled which is thought to have been deposited in a hypersaline² environment. A detailed geochemical description of the composition of the saturated hydrocarbon and "aromatic" fraction of the bitumen of this sample is given in TEN HAVEN *et al.* (1985) and SINNINGHE DAMSTÉ *et al.* (1986). The organic matter of this sample consists for ca. 60% of bitumen and is therefore thought to be an oil-stained sediment.

Four samples of the Miocene Monterey Formation (California, U.S.A.) were taken from immature outcrop sections at different locations along the coast (Shell Beach (SB), Gaviota Beach (W4), El Capitan Beach (M5), Naples (T6)). The Monterey Formation is a siliceous-phosphorite-carbonate sequence which received a considerable input of phytoplankton (*e.g.*, diatoms) due to the high productivity caused by climatic cooling and intensified upwelling in the late Miocene (ISAACS *et al.*, 1983).

The three samples from the Cretaceous Jurf ed Darawish Oil Shale are taken from a core and are composite samples from 45–46, 100–101 and 156–157 m, respectively. Some organic and inorganic geochemical data of this oil shale have been described by WEHNER and HUFNAGEL (1987). Its depositional environment is thought to be similar to that of the Senonian (Upper Cretaceous) bituminous rocks in Israel. TANNENBAUM and AIZENSHTAT (1985) reported that this sedimentary sequence was deposited in an environment of high organic productivity under reducing conditions in small basins. The source of the organic matter is thought to be mainly marine (algae) with some terrestrial contribution, reworked by bacteria.

Phosphoria Retort Shale is a phosphatic mudstone and dolomitic marlstone sequence of Permian age from the Northwestern part of Montana (U.S.A.) which was deposited in a large embayment with water depths of probably less than 40 meters (MCKELVEY *et al.*, 1959).

The Rozel Point Oil is from the Northwestern part of Utah (U.S.A.). Its source rock is thought to have been deposited in a playa lake environment (MEISSNER *et al.*, 1984). Bulk properties of the oil and a detailed description of both the saturated hydrocarbon and "aromatic" fraction of the oil have been described elsewhere (SINNINGHE DAMSTÉ *et al.*, 1987c; TEN HAVEN *et al.*, 1988).

The three related Sicily Seep Oils-E1, -E2 and -E5 seep out of marl layers of Upper Miocene evaporites deposited in an environment largely comparable with that described for the Northern Apennines Marl (TEN HAVEN *et al.*, 1985, 1988). Information on the geological setting and a description of the saturated hydrocarbon fractions are given by PALMER and ZUMBERGE (1981) and TEN HAVEN *et al.* (1988).

The two Chinese oils (B1 and W1349) from shallow depths (*ca.* 600 and 1200 m, respectively) in the Jiangnan Basin are immature

and are thought to originate from hypersaline lacustrine source rocks. For the location of the well sites and a description of the saturated hydrocarbon fractions of these oils see BRASSELL *et al.* (1988). Some data on the OSC present in these samples can be found in SHENG *et al.* (1987).

The Amposta oil is from the Taragona Basin (Spanish Mediterranean off-shore). The source rock of this oil was probably deposited during mesosaline (carbonate-evaporite) episodes (ALBAIGÉS *et al.*, 1986). Biological markers present in this oil have been described by ALBAIGÉS and TORRADAS (1974) and ALBAIGÉS *et al.* (1986).

EXPERIMENTAL

Extraction. Sediment samples were powdered in a rotary disc mill and extracted in a Soxhlet apparatus with toluene/methanol (1:3, v/v) for approximately 50 h. The extracts were concentrated with a rotary evaporator at 30°C and weighed.

Fractionation. *Ca.* 200 mg of the oil or sediment extract were fractionated (without prior removing of asphaltenes) into saturated hydrocarbon, "aromatic" and heterocompound fractions by a column (50 cm × 10 mm) packed with equal volumes of alumina and overlying silica (both activated for 1 h at 150°C) by elution with pentane (65 ml), toluene (75 ml) and toluene/methanol (1/1, v/v; 75 ml) as eluents. The "aromatic" fractions were further separated on a column of activated (1 h at 150°C) alumina into low-molecular-weight aromatic (LMWA) and high-molecular-weight aromatic fractions using 50 ml hexane/toluene (9/1, v/v) and 50 ml toluene, respectively. The LMWA fraction contained most of the GC-amenable compounds including the OSC described previously (SINNINGHE DAMSTÉ *et al.*, 1987c), chromans (SINNINGHE DAMSTÉ *et al.*, 1987b), *n*-alkylbenzenes and isoprenoid alkylbenzenes (SINNINGHE DAMSTÉ *et al.*, 1988a) and A-, B- and C-ring monoaromatic steroids.

Gas chromatography. Gas chromatography of the saturated hydrocarbon fractions was performed on a Carlo Erba 5300 instrument, equipped with an on-column injector. A fused silica capillary column (25 m × 0.32 mm) coated with CP-Sil 5 (film thickness = 0.12 μm) was used with helium as carrier gas. Detection was accomplished by both a flame ionization detector and a sulphur-selective flame photometric detector (FPD), using a stream splitter at the end of the capillary column. The FPD was used to check the absence of OSC in the saturated hydrocarbon fraction. Samples were injected at 75°C. The oven was programmed from 75 to 130°C at 20°C/min and then at 4°C/min to 320°C.

Gas chromatography-mass spectrometry. Gas chromatography-mass spectrometry (GC-MS) was carried out on a Hewlett-Packard 5840 gas chromatograph connected to a VG-70S mass spectrometer operated at 70 eV with a mass range *m/z* 40–800 and a cycle time of 1.8 s. The gas chromatograph was equipped with a fused silica capillary column (25 m × 0.32 mm) coated with CP-Sil 5 (film thickness = 0.12 μm) and was operated with helium as carrier gas. LMWA fractions (1.0 μl) in ethylacetate (*ca.* 6 mg/ml) were injected on-column at 50°C and the temperature was programmed at 10°C/min to 100°C and then at 4°C/min to 315°C at which it was held for 20 min.

Assignment of compounds. Because the LMWA fractions sometimes contain about 1000 individual OSC, as shown previously for the Rozel Point Oil (SINNINGHE DAMSTÉ *et al.*, 1987c), the compounds present in these fractions were identified by mass chromatography of a number of characteristic ions (Table 1) rather than by inspection of individual mass spectra. These mass chromatograms were compared with those of samples previously studied in detail by separation of OSC in various sub-fractions and subsequent characterisation by gas chromatography-mass spectrometry, Raney-Ni desulphurisation and in some cases NMR spectroscopy (SINNINGHE DAMSTÉ *et al.*, 1986, 1987c, 1989c). In a number of cases these identifications were confirmed by comparison of mass spectral and relative retention time data of geologically occurring OSC and other compounds with those of authentic standards (BRASSELL *et al.*, 1986; SINNINGHE DAMSTÉ *et al.*, 1986, 1987a,b,c, 1988a, 1989b,c). Furthermore, the LMWA fractions of a number of samples were desulphurised using Raney-Ni in order to obtain information about the carbon skeletons of the OSC present (SINNINGHE DAMSTÉ *et al.*, 1988c). In this way all major components were identified.

² The terms "hypersaline" and "hypersalinity" are used in this paper in a general way to describe environments with waters whose salinity is greater than that of seawater (>4.0%), following the definition by KIRKLAND and EVANS (1981). In this paper those terms do not describe a specific salinity range. The mesosaline environment is defined as an environment with water salinities from 4 to 12% (KIRKLAND and EVANS, 1981).

Table 1. Characteristic ions used to identify the various compound classes present in the LMWA fractions.

compound class	characteristic ions ^a	ref. ^b
2,5-di- <i>n</i> -alkylthiolanes	<i>m/z</i> 87+14. <i>n</i>	1,2
2,6-di- <i>n</i> -alkylthianes	<i>m/z</i> 101+14. <i>n</i>	3
2,5-di- <i>n</i> -alkylthiophenes	<i>m/z</i> 97+14. <i>n</i>	1
2,4-di- <i>n</i> -alkylbenzo[<i>b</i>]thiophenes	<i>m/z</i> 147+14. <i>n</i>	3,4
isoprenoid thiolanes	<i>m/z</i> 101+14. <i>n</i>	1,3,5
isoprenoid thiophenes	<i>m/z</i> 97+14. <i>n</i>	1,3,5,6
isoprenoid benzo[<i>b</i>]thiophenes	<i>m/z</i> 175+14. <i>n</i>	5
isoprenoid bithiophenes	<i>m/z</i> 220,221	5
highly branched isoprenoid thiophenes	<i>m/z</i> 125,195,265	7
branched thiophenes	<i>m/z</i> 97+14. <i>n</i>	8
thiolane steroids	<i>m/z</i> 331,129,143	9
thiophene steroids	<i>m/z</i> 341,153,167,154, 168,182,287,301	3,9
thiolane hopanoids	<i>m/z</i> 191,369,168+14. <i>n</i>	9,10
thiophene hopanoids	<i>m/z</i> 191,97,111,287	11
branched octadecyl substituted benzo[<i>b</i>]thiophenes	<i>m/z</i> 175,189,203	12
1,2-di- <i>n</i> -alkylbenzenes	<i>m/z</i> 91+14. <i>n</i>	
isoprenoid benzenes	<i>m/z</i> 92,106,120,134	13
A- and B-ring monoaromatic steroids	<i>m/z</i> 211	14
C-ring monoaromatic steroids	<i>m/z</i> 253,267	15
methylated MTTC	<i>m/z</i> 121,135,149,161,175, 189	16

^a in combination with molecular ions^b (1) Sinninghe Damsté *et al.* (1986), (2) Schmid *et al.* (1987), (3) Sinninghe Damsté *et al.* (1987c), (4) Perakis (1986), (5) Sinninghe Damsté and de Leeuw (1987), (6) Brassell *et al.* (1986c), (7) Sinninghe Damsté *et al.* (1989b), (8) Sinninghe Damsté *et al.* (1989c), (9) Schmid (1986), (10) Cyr *et al.* (1986), (11) Valisolalao *et al.* (1984), (12) Sinninghe Damsté (unpublished results), (13) Sinninghe Damsté *et al.* (1988a), (14) Hussler *et al.* (1981), Hussler and Albrecht (1983), (15) Riolo and Albrecht (1985), Riolo *et al.* (1985), Moldovan and Fago (1986), (16) Sinninghe Damsté *et al.* (1987b)

RESULTS

Sixteen samples (both oils and bitumens) from different geographical locations and of different ages representing different palaeoenvironments have been analysed for OSC and other constituents. Some general and molecular data of these samples are given in Table 2. The composition of the hydro-

carbon fractions of a number of these samples has been described elsewhere as indicated above. The main objective was to study the occurrence and distributions of the OSC present in these samples. The analytical approach previously used to identify the OSC in the Rozel Point Oil (SINNINGHE DAMSTÉ *et al.*, 1987c) was applied. The "aromatic" fraction obtained by standard column chromatography was separated into two fractions; the so-called Low-Molecular-Weight Aromatic (LMWA) fraction, which contains all the OSC previously identified, was analysed by GC-MS.

An overview of the occurrence, the carbon number distributions and, to some extent, the relative abundance of the various classes of compounds is given in Table 3. The data in Table 3 show that OSC are often the major compounds present in the LMWA fractions. For the major classes of OSC a number of examples, in the form of characteristic mass chromatograms, are given, with the aim of showing: (i) the widespread occurrence of the OSC previously described (SINNINGHE DAMSTÉ *et al.*, 1987c), (ii) differences in distributions of OSC for different samples. In the discussion these results are related to differences in the palaeoenvironments of these samples.

2,5-Di-n-alkylthiolanes (I) and 2,6-di-n-alkylthianes (II). 2,5-Di-*n*-alkylthiolanes and 2,6-di-*n*-alkylthianes occur in most of the samples studied (Table 3); the distribution patterns of the various series differ, however, to a great extent.

Figure 1 shows mass chromatograms of *m/z* 101 which is a characteristic ion of 2-alkyl-5-methylthiolanes, 2-alkylthianes and "mid-chain" 2,6-dialkylthianes. The term "mid-chain" will be used for OSC possessing two alkyl side chains, both containing more than three carbon atoms. For the Jianghan-B1 oil the *m/z* 101 mass chromatogram is dominated by a homologous series of 2-alkyl-5-methylthiolanes, which shows an even-over-odd carbon number predominance with maxima at C₁₈ and C₂₆. Sicily Seep Oil-E2 also shows the

Table 2. Geochemical data of the samples studied.

Sample	Age ^a	Lithology	%R ₀ ^b	TOC ^c %	EOM ^d %	S ^e %	Sat. ^f %	Arom. ^g %	NSO ^h %	asph. ⁱ %	LMWA ^j %	CPI ^k	R ₂₂ ^l	Pr/Ph ^m	Ph/C ₁₈ ⁿ	XXXId ^o %
<i>Sediments</i>																
Northern Apennines Marl	Mioc.	bituminous marl	n.d.	1	0.7	10.2	3	14	76	30	6	1.38	1.89	0.06	70.3	0.04
Monterey-SB (Shell Beach)	Mioc.	cristobalitic claystone	n.d.	21	2.3	n.d.	1	13	27	n.d.	7	n.d.	-1	0.60	2.0	-
Monterey-W4 (Gaviota Beach)	Mioc.	muddy opal-CT stone	n.d.	6	1.2	n.d.	24 ^p	16 ^p	60 ^p	77 ^q	n.d.	>1.5	1.18	0.41	22.4	0.83
Monterey-M5 (El Capitan Beach)	Mioc.	mudstone	0.40	24	2.3	7.9	3 ^p	15 ^p	82 ^p	83 ^q	n.d.	>1.5	1.19	0.49	21.1	0.88
Monterey-T6 (Naples)	Mioc.	phosphatic muddy limest.	0.46	13	1.0	4.4	3 ^p	9 ^p	88 ^p	82 ^q	n.d.	>1.5	1.17	0.41	5.1	0.92
Jurf ed Darawish Oil Shale-45	Cret.	bituminous limestone	n.d.	5	0.6	9.9	2	7	26	59	3	1.15	1.38	0.62	0.9	0.66
Jurf ed Darawish Oil Shale-100	Cret.	bituminous limestone	n.d.	8	0.5	12.9	2	8	36	51	4	1.04	1.09	0.62	0.8	0.65
Jurf ed Darawish Oil Shale-156	Cret.	bituminous calc. marl	0.30	17	1.6	13.3	1	24	40	23	10	1.28	0.93	0.37	1.7	0.63
Phosphoria Retort Shale	Perm.	phosphatic mudstone	0.28	16	2.0	10.0	2	35	48	n.d.	17	1.32	0.98	0.64	4.0	0.53
<i>Oils</i>																
Rozel Point Oil	Mioc.	n.a. ^r	n.a.	n.a.	n.a.	7.5	2	43	28	n.d.	12	0.53	1.91	0.03	4.3	0.36
Sicily Seep Oil-E1	Mioc.	n.a.	n.a.	n.a.	n.a.	20.0	1	26	31	n.d.	3	0.65	3.15	0.06	18.0	0.22
Sicily Seep Oil-E2	Mioc.	n.a.	n.a.	n.a.	n.a.	20.4	3	37	n.d.	n.d.	8	0.72	2.97	0.05	17.5	0.25
Sicily Seep Oil-E5	Mioc.	n.a.	n.a.	n.a.	n.a.	19.7	2	33	29	n.d.	9	0.66	3.24	0.05	19.7	0.20
Jianghan-B1	Plio.	n.a.	n.a.	n.a.	n.a.	12.9	3	46	31	n.d.	18	0.52	1.65	0.05	4.6	0.21
Jianghan-W1349	Plio.	n.a.	n.a.	n.a.	n.a.	10.4	4	45	38	n.d.	22	0.71	1.61	0.10	7.4	0.30
Amposta	Mioc.	n.a.	n.a.	n.a.	n.a.	6.7	16	43	16	n.d.	13	0.90	1.00	0.37	0.6	0.25

^a Mioc. = Miocene, Cret. = Cretaceous, Perm. = Permian, Plioc. = Pliocene^b %R₀ = vitrinite reflectance^c TOC = Total Organic Carbon^d EOM = Extractable Organic Matter^e S = total sulphur content of bitumen or oil, this includes elemental S^f Sat. = weight percentage of saturated hydrocarbon fraction of bitumen or oil^g Arom. = weight percentage of "aromatic" fraction of bitumen or oil^h NSO = weight percentage of hetero compound fraction of bitumen or oilⁱ asph. = asphaltene (*n*-heptane precipitation) content of bitumen or oil^j LMWA = weight percent of LMWA fraction of bitumen or oil^k CPI = Carbon Preference Index (measured from C₁₅ to C₃₀)^l R₂₂ = 2 * *n*-C₂₂ / (*n*-C₂₁ + *n*-C₂₃)^m Pr/Ph = pristane/phytane ratioⁿ Ph/*n*-C₁₈ = phytane/octadecane ratio^o XXXId = percentage of trimethyl 2-methyl-2-(4,8,12-trimethyltridecyl)chroman (MMTC; XXXId) to the total amount of methylated MTTC^p on the basis of total recovered material^q Palmer (unpublished results)^r n.a. = not applicable

Table 3. Distribution of compound classes in the LMWA fractions.

Compound class	Sample (sediments) ^b								
	NAM	M-SB	M-W4	M-M5	M-T6	JED-45	JED-100	JED-156	PRS
2,5-di- <i>n</i> -alkylthiolanes	15-26(22)	-	15-22(18)	15-24(18)	-	12-30(18)	12-30(18)	12-38(28)	15-28(18)
2,6-di- <i>n</i> -alkylthianes	16-22(22)	-	-	-	-	14-30(20)	12-30(24)	12-33(28)	15-28(18)
2,5-di- <i>n</i> -alkylthiophenes	15-30(22)	-	18	16-26(18)	-	11-38(18)	11-38(22)	11-38(18)	-
2,4-di- <i>n</i> -alkylbenzo[<i>b</i>]thiophenes	✓	-	✓	✓	-	10-20(12)	10-22(22)	10-26(12)	11-25(18)
isoprenoid thiolanes	20-23(20)	-	20	20	-	20-21(20)	20-22(20)	20-23(20)	20
isoprenoid thiophenes	15-28(20)	20	15-22(15)	15-26(20)	20	20-45(20)	20-45(20)	15-45(20)	15-20(20)
isoprenoid bithiophenes	-	-	-	-	-	-	-	-	-
isoprenoid benzo[<i>b</i>]thiophenes	20-26(20)	-	-	-	-	-	-	20	20
highly branched isoprenoid thiophenes	25	-	25	25	25	25	25	25	-
branched thiophenes	19	-	-	-	-	19	19	17,19(19)	-
thiolane steroids	28-29(29)	-	28-29(28)	28-29(28)	-	28-29(28)	28-29(28)	28-29(28)	-
thiophene steroids	28-29(29)	-	27-29(28)	-	-	-	-	28-29(28)	27-29(28)
thiolane hopanoids	n.d.	-	-	-	35	35	35	35	n.d.
thiophene hopanoids	n.d.	-	35	35	35	35	35,36(35)	35,36(35)	n.d.
branched octadecyl benzo[<i>b</i>]thiophenes	-	-	27-29(28)	27-29(28)	-	28-29(29)	28-29(29)	27-29(29)	27-29(28)
1,2-di- <i>n</i> -alkylbenzenes	-	-	21-30(28)	21-30(28)	-	13-31(26)	13-31(26)	14-31(26)	-
isoprenoid benzenes	26-29(26)	-	22-24(23)	22-24(23)	22-24(23)	27-29(28)	27-29(28)	27-29(28)	26-29(28)
A- and B-ring monoaromatic steroids	-	-	27-29(28)	27-29(28)	27-29(28)	27-29(27)	27-29(27)	27-29(28)	-
C-ring monoaromatic steroids	27-29	-	27-29	27-29	27-29	27-29	27-29	27-29	27-29
methylated MTTC	27-29(28)	-	27-29(29)	28-29(29)	28-29(29)	27-29(29)	27-29(29)	27-29(29)	27-29(29)

Compound class	Samples (oils) ^b						
	RPO	SSO-E1	SSO-E2	SSO-E5	J-B1	J-W1349	AMP
2,5-di- <i>n</i> -alkylthiolanes	12-28(18)	12-30(18)	12-30(18)	12-30(18)	11-32(26)	11-32(26)	12-34(30)
2,6-di- <i>n</i> -alkylthianes	12-28(18)	12-30(18)	12-30(18)	12-30(18)	11-32(26)	11-32(26)	12-32(19)
2,5-di- <i>n</i> -alkylthiophenes	-	13-28(18)	12-30(18)	13-30(18)	11-32(26)	11-32(26)	-
2,4-di- <i>n</i> -alkylbenzo[<i>b</i>]thiophenes	11-24(12)	✓	✓	✓	10-30(11)	10-30(11)	11-33(21)
isoprenoid thiolanes	20	18-23(20)	18-23(20)	18-23(20)	20	20	20
isoprenoid thiophenes	15-40(20)	15-28(20)	15-40(20)	15-27(20)	15-26(20)	15-26(20)	15-20(15)
isoprenoid bithiophenes	15-22(20)	20	20	20	20	20	-
isoprenoid benzo[<i>b</i>]thiophenes	20	20-26(20)	20-26(20)	20-26(20)	20	20	15-20(15)
highly branched isoprenoid thiophenes	20-25(20)	25	25	25	25	25	-
branched thiophenes	19	19	19	19	18-28(28)	18-28(28)	-
thiolane steroids	27-30(29)	27-29(29)	27-29(29)	27-29(29)	27-29(29)	27-29(29)	-
thiophene steroids	27-30(29)	27-29(29)	27-29(29)	27-29(29)	27-29(29)	27-29(29)	27-29(29)
thiolane hopanoids	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
thiophene hopanoids	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
branched octadecyl benzo[<i>b</i>]thiophenes	27-29(28)	27-29(28)	27-29(28)	27-29(28)	-	-	27-29(28)
1,2-di- <i>n</i> -alkylbenzenes	-	-	-	-	-	-	13-40(21)
isoprenoid benzenes	26-29(28)	27-29(28)	27-29(28)	27-29(28)	27-29(28)	27-29(28)	26-29(27)
A- and B-ring monoaromatic steroids	-	-	-	-	-	-	-
C-ring monoaromatic steroids	27-29	27-29	27-29	27-29	27-29	27-29	27-29
methylated MTTC	27-29(28)	27-29(28)	27-29(28)	27-29(28)	27-29(27)	27-29(27)	27-29(27)

^a numbers indicate range of occurrence by carbon number; numbers in parentheses indicate maxima in carbon number distributions; numbers in italics indicate that a member of this compound class is one of the three most abundant components of the LMWA fraction

^b low molecular weight (C₁₀-C₁₆) 2,4-di-*n*-alkylbenzo[*b*]thiophenes are probably present

^b NAM = Northern Apennines Marl bitumen; M = Monterey Shale bitumen; JED = Jurf ed Darawish Oil Shale bitumen; PRS = Phosphoria Retort Shale bitumen; RPO = Rozel Point Oil; SSO = Sicily Seep Oil; J = Jiangnan oil; AMP = Amposta oil

n.d. = not determined

presence of this series although another series, *i.e.* 2-alkylthianes, is also observed. The series of 2-alkylthianes, so-called terminal thianes, was not reported previously in the Rozel Point Oil (SINNINGHE DAMSTÉ *et al.*, 1987c) but is present in this oil as well as a minor series. It is noteworthy that the Sicily Seep Oils also contain relatively high amounts of terminal thiolanes, *i.e.* 2-alkylthiolanes, which are absent in Rozel Point Oil. In the *m/z* 101 mass chromatogram (Fig. 1C) of the Jurf ed Darawish Oil Shale-156 bitumen a third series of OSC occurs, the *trans* mid-chain 2,6-dialkylthianes. The three homologous series show different carbon number distributions, although all three series exhibit (sub)maxima at C₂₆ and show a strong even carbon number predominance in the C₂₂-C₃₀ range. Remarkably, the *cis* mid-chain 2,6-dialkylthianes (not shown in Fig. 1C) are much lower in abundance. In the Amposta oil (Fig. 1D) the homologous series of 2-alkyl-5-methylthiolanes dominates and the even-over-odd carbon number predominance (C₂₄-C₃₀) is much less pronounced.

Figure 2A-C shows mass chromatograms of *m/z* 115, a characteristic ion of *inter alia* 2-alkyl-5-ethylthiolanes and 2-alkyl-6-methylthianes, for the Jiangnan-B1 oil, the Sicily Seep Oil-E2 and the Jurf ed Darawish Oil Shale-100 bitumen. In the Jiangnan-B1 oil and the Sicily Seep Oil-E2 these two series exhibit a strong even-over-odd carbon number predominance

with maxima at C₁₈ and C₂₆ and C₁₈ and C₂₂, respectively, whilst in the Jurf ed Darawish Oil Shale-100 bitumen there is an even carbon number predominance only in the C₂₂-C₃₀ range.

*2,5-Di-*n*-alkylthiophenes (III)*. Homologous series of 2-alkyl-5-methylthiophenes, 2-alkyl-5-ethylthiophenes and 2-alkyl-5-butylthiophenes have been previously reported to occur in the Northern Apennines Marl bitumen (SINNINGHE DAMSTÉ *et al.*, 1986). Some of these series are also present in a number of other samples (Table 3). In addition, homologous series of 2-alkyl-5-propylthiophenes, 2-alkyl-5-pentylthiophenes, 2-alkyl-5-hexylthiophenes, 2-alkyl-5-heptylthiophenes and 2-alkyl-5-octylthiophenes were identified in the Jiangnan-B1 and -W1349 oils and in the Jurf ed Darawish Oil Shale-156 bitumen. A series of 2-alkylthiophenes was present in the Jurf ed Darawish Oil Shale bitumens.

M/z 111 is a characteristic ion of 2-alkyl-5-methylthiophenes and mid-chain 2,5-dialkylthiophenes (*e.g.*, SINNINGHE DAMSTÉ *et al.*, 1989c). Both series are present in the Jiangnan-B1 oil and the Jurf ed Darawish Oil Shale-156 bitumen (Figs. 3A-B). The peaks representing the mid-chain 2,5-dialkylthiophenes are somewhat broader than those of the 2-alkyl-5-methylthiophenes, because the former comprise several structural isomers which have slightly different retention times. Both the 2-alkyl-5-methylthiophenes and the mid-

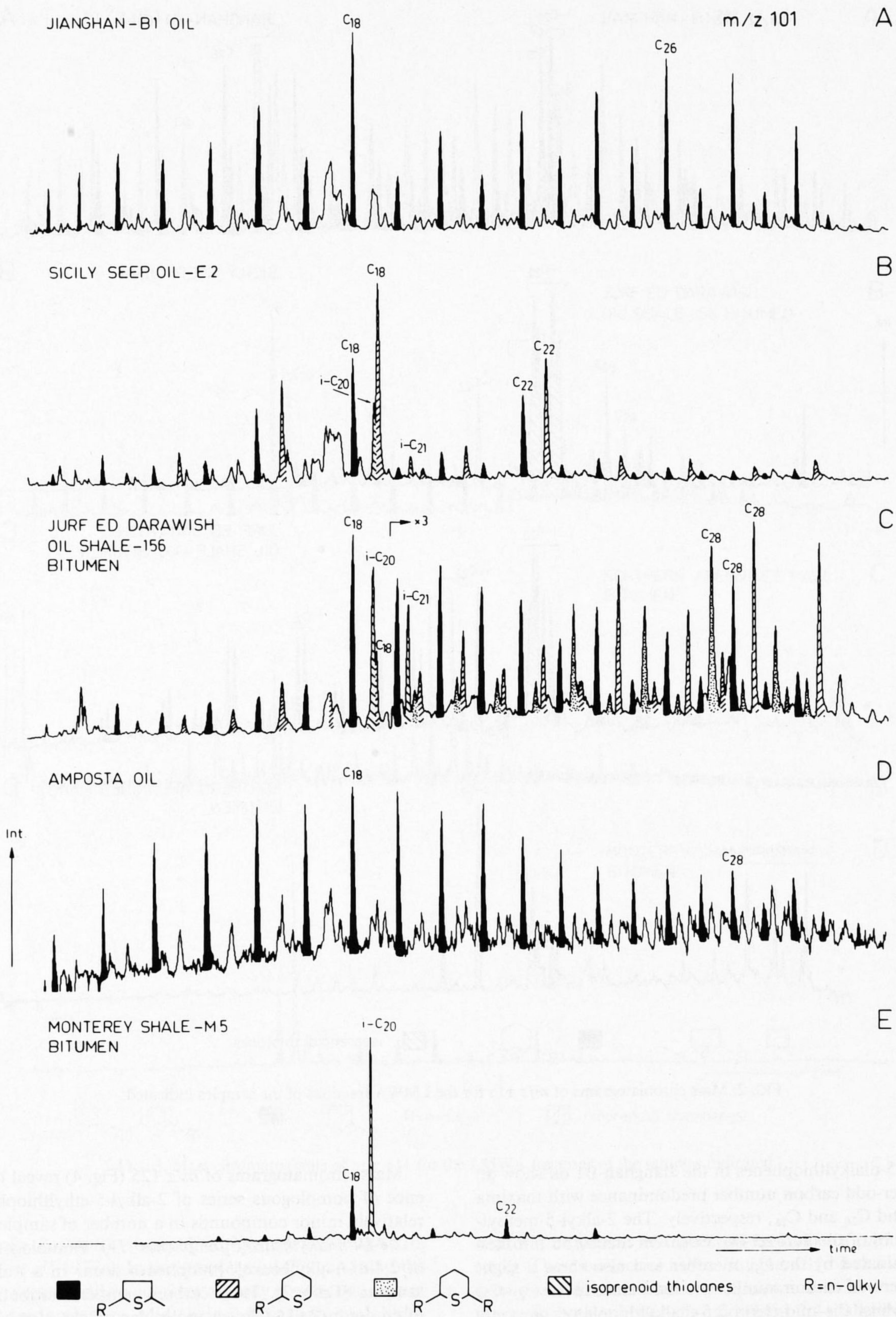


FIG. 1. Mass chromatograms of m/z 101 for the LMWA fractions of the samples indicated. The indicated mid-chain 2,6-di- n -alkylthianes represent the *trans* isomers.

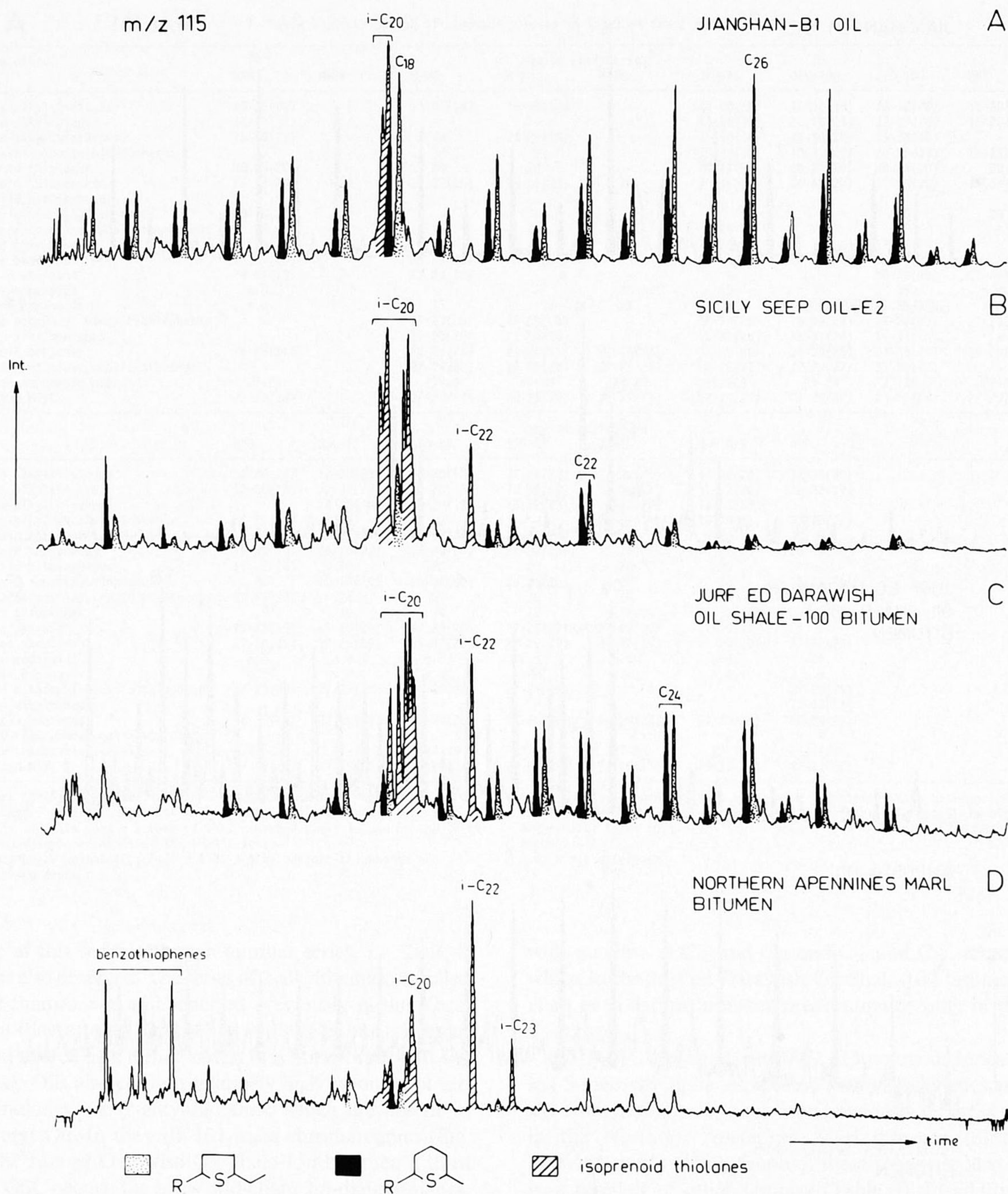


FIG. 2. Mass chromatograms of m/z 115 for the LMWA fractions of the samples indicated.

chain 2,5-dialkylthiophenes in the Jiaghan-B1 oil show an even-over-odd carbon number predominance with maxima at C_{18} and C_{26} and C_{26} , respectively. The 2-alkyl-5-methylthiophenes of the Jurf ed Darawish Oil Shale-156 bitumen are dominated by the C_{18} member and also show a slight even-over-odd carbon number predominance in the C_{22} - C_{32} range, whilst the mid-chain 2,5-dialkylthiophenes are only relatively abundant in the C_{26} - C_{37} range with a maximum at C_{28} . The other two m/z 111 mass chromatograms (Figs. 3C-D; Northern Apennines Marl and Monterey Shale-M5) only reveal the presence of 2-alkyl-5-methylthiophenes.

Mass chromatograms of m/z 125 (Fig. 4) reveal the presence of homologous series of 2-alkyl-5-ethylthiophenes as relatively minor compounds in a number of samples.

2,4-Di-n-alkylbenzo[b]thiophenes (IV). Homologous series of 2,4-di-*n*-alkylbenzo[b]thiophenes occur in a number of samples (Table 3). Their carbon number distributions are often dominated by lower molecular weight members (*e.g.*, C_{11} , C_{12}).

Figure 5 shows the mass chromatograms of m/z 161 for four samples. This ion is characteristic of 4-alkyl-2-methylbenzo[b]thiophenes, 2-alkyl-4-methylbenzo[b]thiophenes and

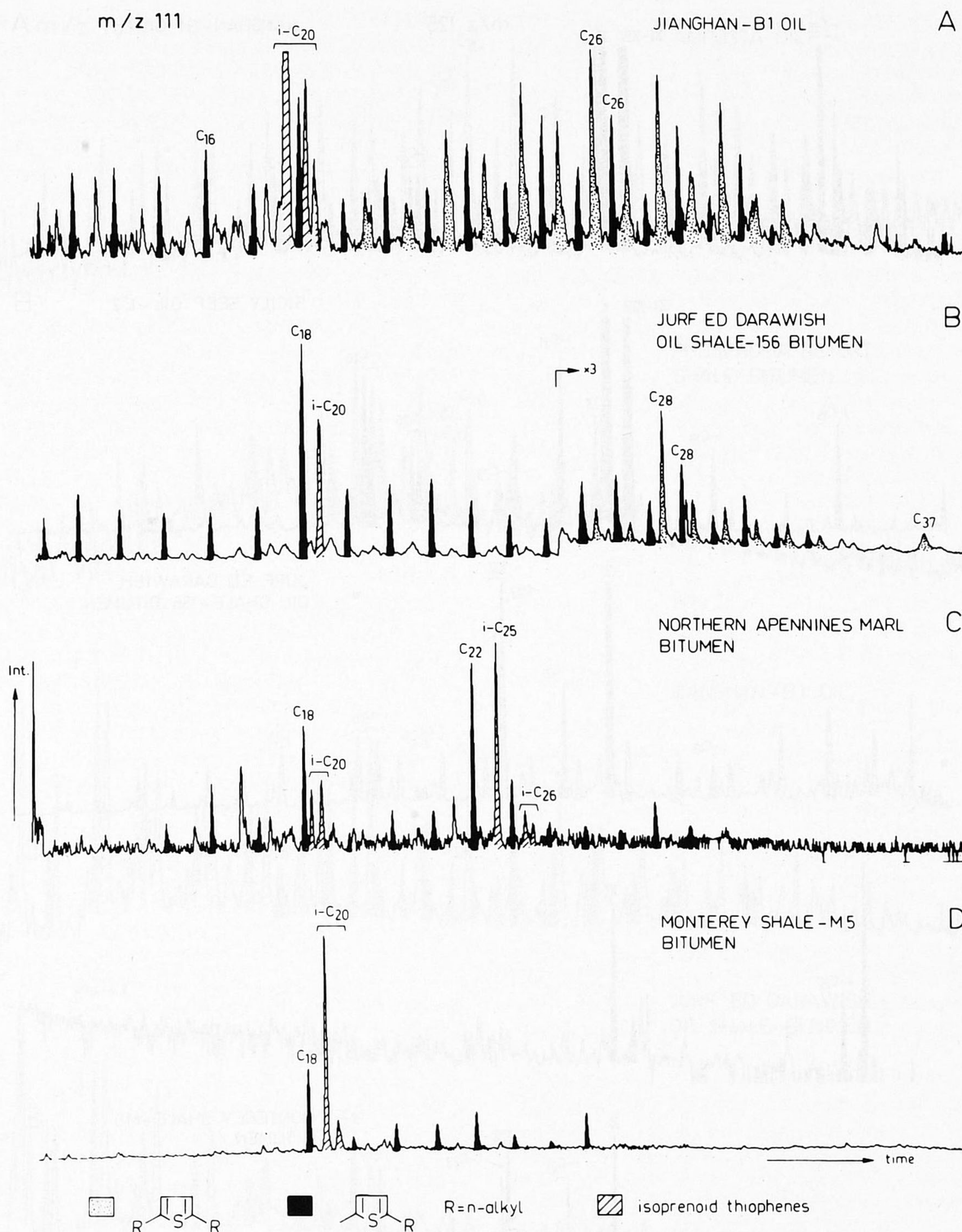


FIG. 3. Mass chromatograms of m/z 111 for the LMWA fractions of the samples indicated.

mid-chain 2,4-dialkylbenzo[*b*]thiophenes (SINNINGHE DAMSTÉ *et al.*, 1987c). In the Amposta oil (Fig. 5A) all three series are present and do not show a strong even or odd carbon number predominance. Mid-chain 2,4-dialkylbenzo[*b*]thiophenes are more dominant in the Phosphoria Retort Shale (Fig. 5B). The m/z 161 mass chromatograms of the Jianghan-B1 oil and the Jurf ed Darawish Oil Shale-156 bitumen are both dominated by the C_{11} members of the 4-alkyl-2-methyl-

benzo[*b*]thiophenes and 2-alkyl-4-methylbenzo[*b*]thiophene series. These two series in the Jianghan-B1 oil show a slight even-over-odd carbon number predominance in the C_{16} - C_{30} range. In both samples the mid-chain 2,4-dialkylbenzo[*b*]thiophenes occur in relatively low amounts.

Isoprenoid thiolanes. Isoprenoid thiolanes are abundant compounds in a number of samples (Table 3) and, if present, they are always dominated by the C_{20} members which consist

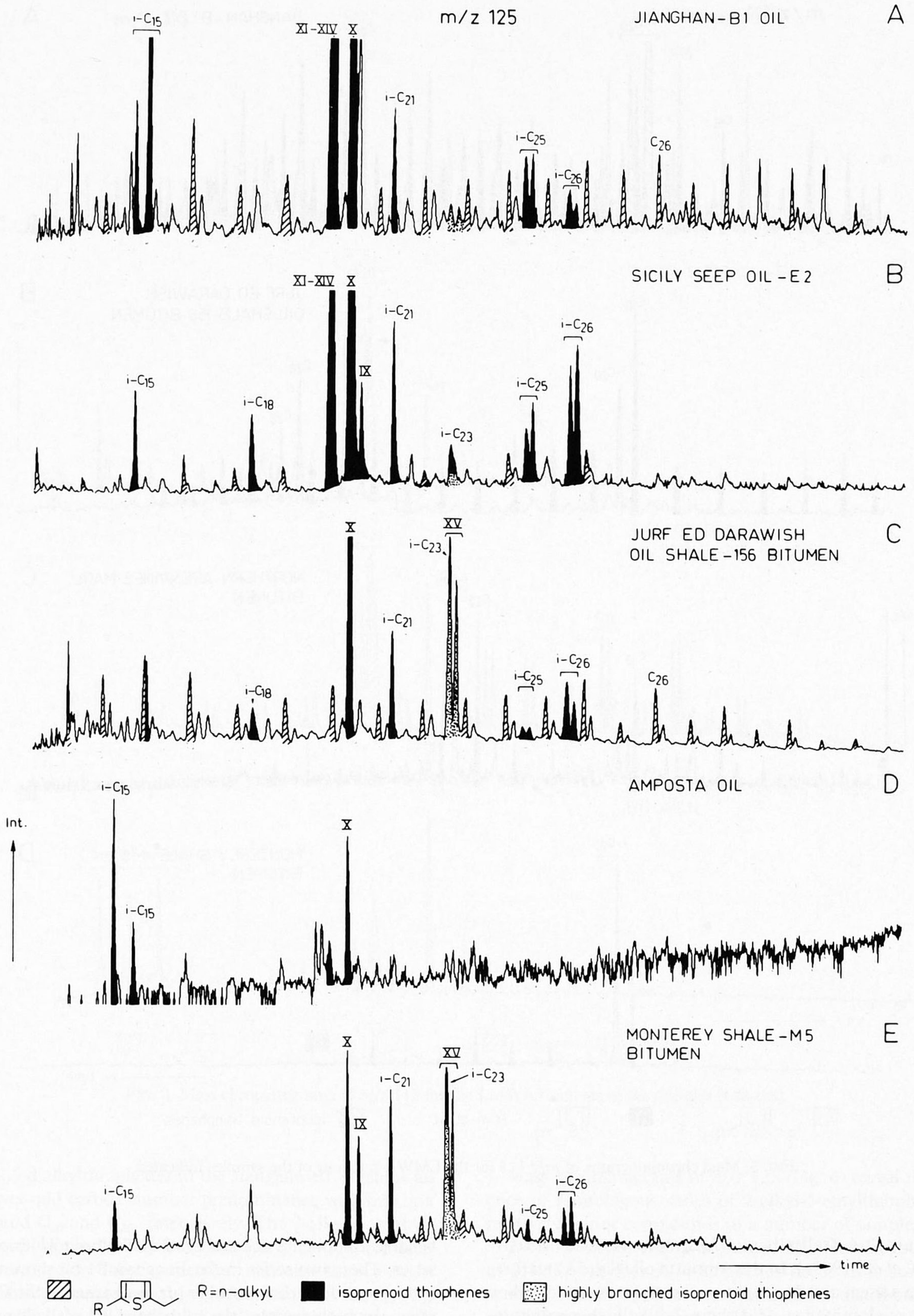


FIG. 4. Mass chromatograms of m/z 125 for the LMWA fractions of the samples indicated.

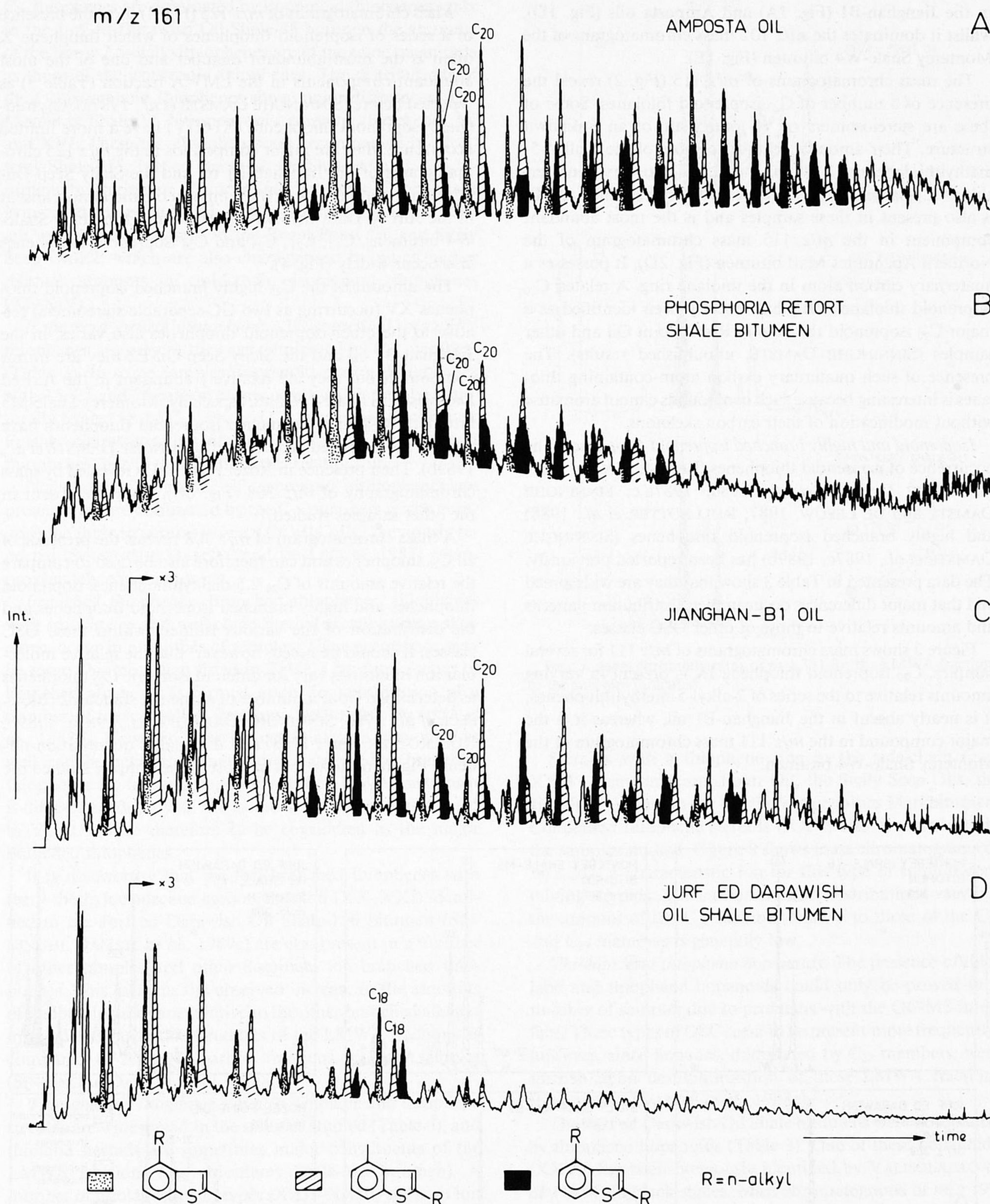


FIG. 5. Mass chromatograms of m/z 161 for the LMWA fractions of the samples indicated.

of a complicated mixture of structural and stereoisomers yet to be fully characterised. Figures 1 and 2 give some examples of the presence of several isoprenoid thiolanes in the samples studied.

Isoprenoid thiolane V shows up in the mass chromatograms of m/z 101; it nearly coelutes with 2-tridecylthiane. Its amount relative to those of the 2-alkyl-5-methylthiolane and 2-alkylthiane series varies to a great extent; it is absent

in the Jianghan-B1 (Fig. 1A) and Amposta oils (Fig. 1D), whilst it dominates the m/z 101 mass chromatogram of the Monterey Shale-W4 bitumen (Fig. 1E).

The mass chromatograms of m/z 115 (Fig. 2) reveal the presence of a number of C_{20} isoprenoid thiolanes. Some of these are stereoisomers of VI, others are of an unknown structure. Their amounts relative to those of the 2-alkyl-5-methylthiolane and 2-alkylthiane series also vary considerably. A C_{22} isoprenoid thiolane, tentatively identified as VII, is also present in these samples and is the most abundant component in the m/z 115 mass chromatogram of the Northern Apennines Marl bitumen (Fig. 2D). It possesses a quaternary carbon atom in the thiolane ring. A related C_{20} isoprenoid thiolane (VIII) has recently been identified as a major C_{20} isoprenoid thiolane in Rozel Point Oil and other samples (SINNINGHE DAMSTÉ, unpublished results). The presence of such quaternary carbon atom-containing thiolanes is interesting because such compounds cannot aromatise without modification of their carbon skeletons.

Isoprenoid and highly branched isoprenoid thiophenes. The occurrence of isoprenoid thiophenes (BRASSELL *et al.*, 1986; SINNINGHE DAMSTÉ *et al.*, 1986, 1987a,c; SINNINGHE DAMSTÉ and DE LEEUW, 1987; RULLKÖTTER *et al.*, 1988) and highly branched isoprenoid thiophenes (SINNINGHE DAMSTÉ *et al.*, 1987c, 1989b) has been reported previously. The data presented in Table 3 show that they are widespread and that major differences occur in their distribution patterns and amounts relative to those of other OSC classes.

Figure 3 shows mass chromatograms of m/z 111 for several samples. C_{20} isoprenoid thiophene IX is present in varying amounts relative to the series of 2-alkyl-5-methylthiophenes; it is nearly absent in the Jianghan-B1 oil, whereas it is the major compound in the m/z 111 mass chromatogram of the Monterey Shale-W4 bitumen.

Mass chromatograms of m/z 125 (Fig. 4) show the presence of a series of isoprenoid thiophenes of which thiophene X often is the most abundant member and one of the most abundant components in the LMWA fraction (Table 3) as reported before (SINNINGHE DAMSTÉ *et al.*, 1987a). C_{20} mid-chain isoprenoid thiophenes (XI-XIV) have a more limited occurrence; they are major compounds in the m/z 125 chromatograms of the Jianghan-B1 oil and the Sicily Seep Oil-E2, minor compounds in the Amposta oil and almost absent in the Jurf ed Darawish Oil Shale-156 and Monterey Shale-W4 bitumens. C_{15} , C_{21} , C_{25} and C_{26} isoprenoid thiophenes also occur widely (Fig. 4).

The amount of the C_{25} highly branched isoprenoid thiophenes XV (occurring as two GC-separable stereoisomers) relative to the other isoprenoid thiophenes also varies; in the Jianghan-B1 oil and the Sicily Seep Oil-E2 they are minor compounds but they are relatively abundant in the Jurf ed Darawish Oil Shale-156 and, especially, Monterey Shale-M5 bitumens. C_{20} highly branched isoprenoid thiophenes have a much more limited occurrence (SINNINGHE DAMSTÉ *et al.*, 1989b). Their presence in Rozel Point Oil is revealed by mass chromatography of m/z 308 (Fig. 6F). They are absent in the other samples studied.

A mass chromatogram of m/z 308 reveals the presence of all C_{20} thiophenes and can therefore also be used to compare the relative amounts of C_{20} 2,5-dialkylthiophenes, isoprenoid thiophenes and highly branched isoprenoid thiophenes and the distribution of the various isomers within these OSC classes. It should be noted, however, that the relative molecular ion intensities vary for different isomeric C_{20} thiophenes as determined from a number of authentic standards (BRASSELL *et al.*, 1986; SINNINGHE DAMSTÉ *et al.*, 1987a, 1989b; RULLKÖTTER *et al.*, 1988) and this makes quantitation difficult. Figure 6 shows that in most of the samples studied the

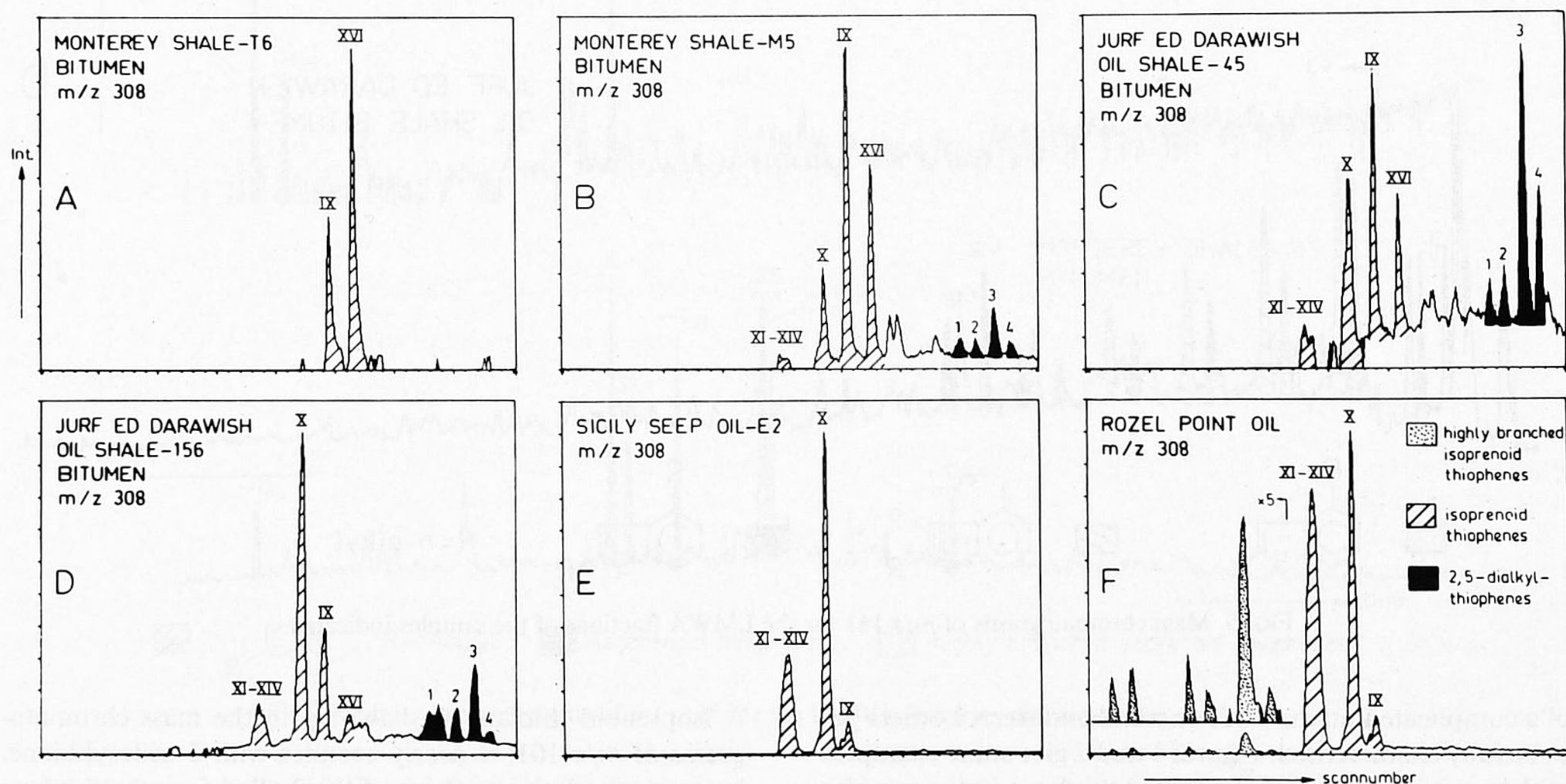


FIG. 6. Mass chromatograms of m/z 308 for the LMWA fractions of the samples indicated.

C_{20} thiophenes are dominated by isoprenoid thiophenes; only in the Jurf ed Darawish Oil Shale-45 bitumen the amounts of the linear 2,5-dialkylthiophenes are of the same magnitude as those of the isoprenoid thiophenes. The distributions of the C_{20} isoprenoid thiophenes show major differences. The Monterey Shale-T6 bitumen only contains thiophenes IX and XVI. These two thiophenes are accompanied in Monterey Shale-M5, Jurf ed Darawish Oil Shale-45 and -156 bitumens by thiophene X and minor amounts of mid-chain isoprenoid thiophenes (XI–XIV). Thiophenes IX and XVI are very minor or absent in the Rozel Point Oil and Sicily Seep Oil-E2, which are also characterised by much higher relative amounts of mid-chain isoprenoid thiophenes (XI–XIV).

Isoprenoid benzo[b]thiophenes. If isoprenoid benzo[b]thiophenes are present they are dominated by C_{20} members (Table 3). In some samples isoprenoid benzo[b]thiophenes with 15, 25 and 26 carbon atoms occur which may be structurally related to the C_{15} , C_{25} and C_{26} isoprenoid thiophenes. Further characterisation of these benzo[b]thiophenes (and thiophenes) has to demonstrate this relationship.

Isoprenoid bithiophenes. If isoprenoid bithiophenes are present they are dominated by the C_{20} members which comprise the three structural isomers (XVII–XIX) previously reported (SINNINGHE DAMSTÉ and DE LEEUW, 1987) in approximately equal amounts.

Branched thiophenes. Branched thiophenes, thiophenes with *iso*, *anteiso* and mid-chain methyl alkane carbon skeletons, occur in a number of samples. Their occurrence may be more common than listed in Table 3 because a series of branched alkanes was formed upon desulphurisation of a number of these LMWA fractions (SINNINGHE DAMSTÉ *et al.*, 1988c). However, these branched alkanes may arise as well from branched thiolanes and/or thianes. Since branched thiophenes are minor compounds of the LMWA fractions it is difficult to identify all the isomers. The compounds listed in Table 3 have therefore to be considered as the major branched thiophenes.

It is noteworthy that the two branched thiophenes with the 9-methyloctadecane carbon skeleton (XX–XXI) identified in the Jurf ed Darawish Oil Shale-156 bitumen (SINNINGHE DAMSTÉ *et al.*, 1989c) are also present in a number of other samples and often dominate the branched thiophenes. This explains the observed increase in the amounts of 9-methyloctadecane relative to the other branched alkanes in the desulphurisation products of the LMWA fractions as compared to the hydrocarbon fractions of these samples (SINNINGHE DAMSTÉ *et al.*, 1988c).

Thiolane and thiophene steroids. Thiolane and thiophene steroids are widespread in the samples studied (Table 3), and thiolane steroids are sometimes major constituents of the LMWA fractions (*e.g.*, Monterey Shale-M5 bitumen). A number of thiolane steroid types (XXII–XXIII) show an ion at m/z 331 in their mass spectra (SCHMID, 1986). This ion can therefore be used to reveal the distribution patterns of these OSC (Fig. 7). This trace is quite complex for the Rozel Point Oil (Fig. 7A), whilst it is relatively simple for the Monterey Shale-M5 and the Jurf ed Darawish Oil Shale-100 bitumens (Figs. 7B–C), where thiolane steroids with the sulphur atom attached to the steroidal side-chain (XXIII) dominate.

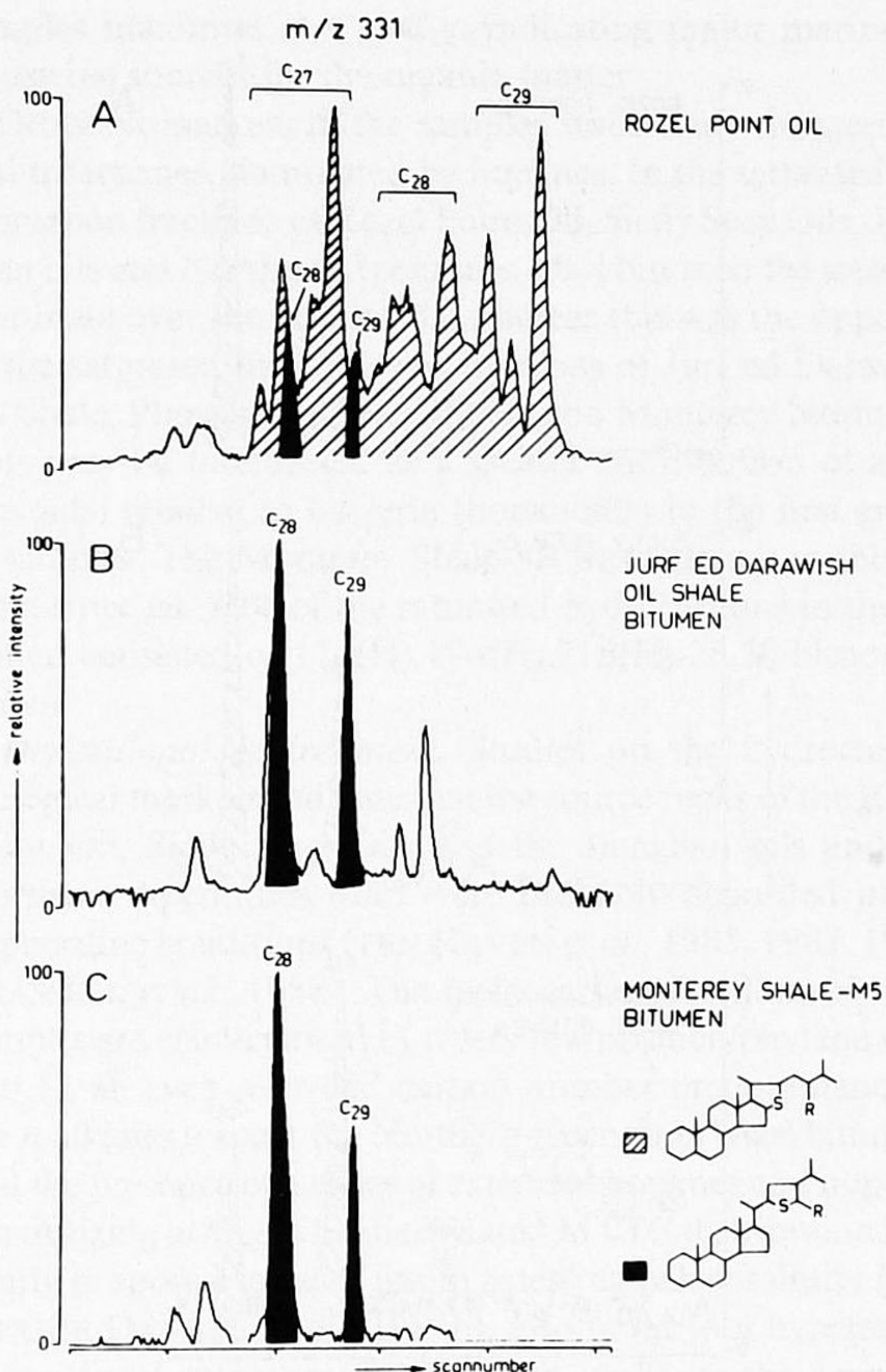


FIG. 7. Mass chromatograms of m/z 331 for the LMWA fractions of the samples indicated.

Steroids with a thiophene ring in the side-chain (*e.g.*, XXIV) occur in Rozel Point Oil, the Sicily Seep Oils, the Jiangnan oils and in the Northern Apennines Marl bitumen. Condensed thiophene steroids (XXV) also occur widely in the samples studied. Figure 8 shows mass chromatograms of m/z 341, a characteristic ion for this type of sulphur-containing steroids. The carbon number distributions vary but the amount of the C_{27} member relative to those of the C_{28} and C_{29} members is generally low.

Thiolane and thiophene hopanoids. The presence of thiolane and thiophene hopanoids could only be proved in a number of samples due to problems with the GC-MS interface. These types of OSC seem to be present more frequently, however, since hopanes, dominated by C_{35} members, were formed upon desulphurisation of these LMWA fractions (SINNINGHE DAMSTÉ *et al.*, 1988c).

The Jurf ed Darawish Oil Shale bitumens were dominated by thiophene hopanoids (Table 3). One of these hopanoids (XXVI) has been previously identified by VALISOLALAO *et al.* (1984) in black shales. Mass chromatograms of m/z 191 (Fig. 9) reveal the presence of a number of structural and stereoisomers of C_{35} thiophene hopanoids and, less abundant, C_{35} hopane sulphides in the three Jurf ed Darawish Oil Shale bitumens studied. The tentatively identified thiophene hopanoid XXVII has not been reported previously. Its mass spectrum shows characteristic ions at m/z 111, 191, 387 and 508. The m/z 191 mass chromatograms are dominated by

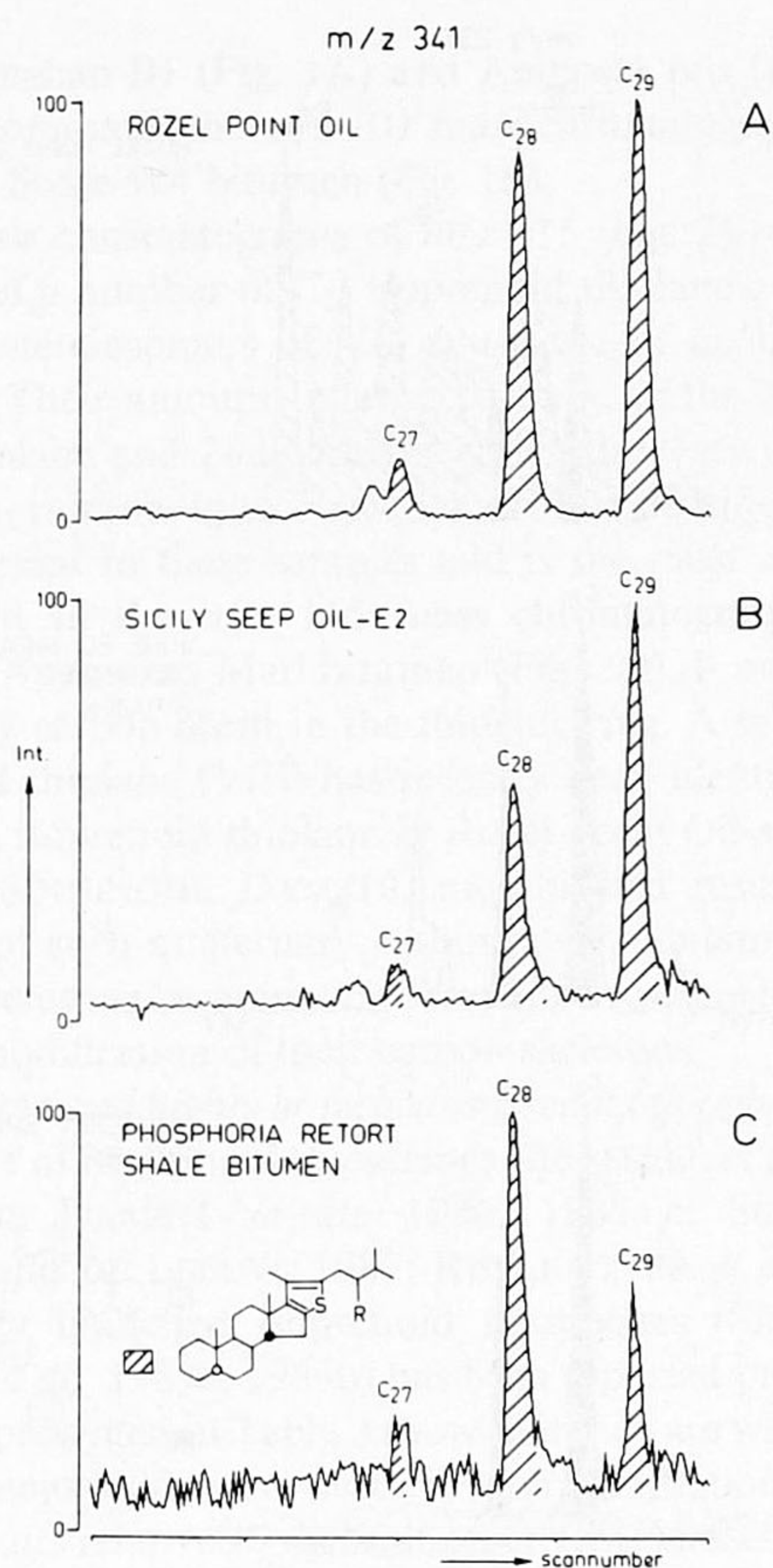


FIG. 8. Mass chromatograms of m/z 341 for the LMWA fractions of the samples indicated.

different stereoisomers of thiophene hopanoids XXVI and XXVII, relatively high amounts of the $17\beta(H),21\beta(H)$ stereoisomer in the bitumen of Jurf ed Darawish Oil Shale-45, relatively high amounts of the $17\alpha(H),21\beta(H)$ stereoisomer in that of the Jurf ed Darawish Oil Shale-156 and approximately equal amounts of both stereoisomers in the Jurf ed Darawish Oil Shale-100 bitumen. The assignment of the different stereoisomers is based on the ratio of the intensity of the ions at m/z 191 and m/z 387 in their mass spectra as described for hopanes (ENSMINGER *et al.*, 1974). Apart from the C_{35} sulphur-containing hopanoids different stereoisomers of a C_{36} thiophene hopanoid, tentatively identified as XXVIII (characteristic ions at m/z 97, 205, 287 and 522), were identified in the Jurf ed Darawish Oil Shale-100 and -156 bitumens. No other sulphur-containing hopanoids were identified in the Jurf ed Darawish Oil Shale bitumens. This raises the question as to where the other hopanes, formed upon desulphurisation of the LMWA fraction of the Jurf ed Darawish Oil Shale-156 bitumen (SINNINGHE DAMSTÉ *et al.*, 1988c), are derived from. A possible explanation is that the LMWA fraction also contains some non GC-amenable material which upon desulphurisation also yields hopanes. They also could have been formed by Raney Ni reduction of a series of hopanoid ketones (XXIX) also present in the Jurf ed Darawish Oil Shale-156 bitumen (J. S. SINNINGHE DAMSTÉ, unpublished results). Carbonyl groups may be reduced with very

active Raney Nickel preparations (HAUPTMANN and WALTER, 1961).

The $17\beta(H),21\beta(H)$ -stereoisomer of XXVI is the major thiophene hopanoid in several Monterey bitumens.

Branched octadecyl substituted benzo[b]thiophenes. A series of novel benzo[b]thiophenes was present in a number of samples (Table 3). The structures of these compounds are tentatively identified as XXXa-d, compounds which have the same carbon skeletons as methylated 2-methyl-2-(4,8,12-trimethyltridecyl)chromans (MTTC, XXXIa-d; SINNINGHE DAMSTÉ *et al.*, 1987b) and as specific isoprenoid alkylbenzenes (XXXIIa-d; SINNINGHE DAMSTÉ *et al.*, 1988a). Their identification awaits further confirmation by comparison of retention time and mass spectral data with those of synthetic standards, a study presently being carried out in this laboratory. They were identified in the LMWA fractions by mass chromatography of m/z 175, 189 and 203. The carbon number distributions of this series are often dominated by the C_{28} member(s) and are not always similar to those of the structurally related MTTC and isoprenoid benzenes (Table 3).

Non-OSC. 1,2-Di-*n*-alkylbenzenes (XXXIII) were abundantly present in the Amposta oil and represent minor compounds in the Jurf ed Darawish Oil Shale and Monterey bitumens. In the latter samples only series of mono alkylben-

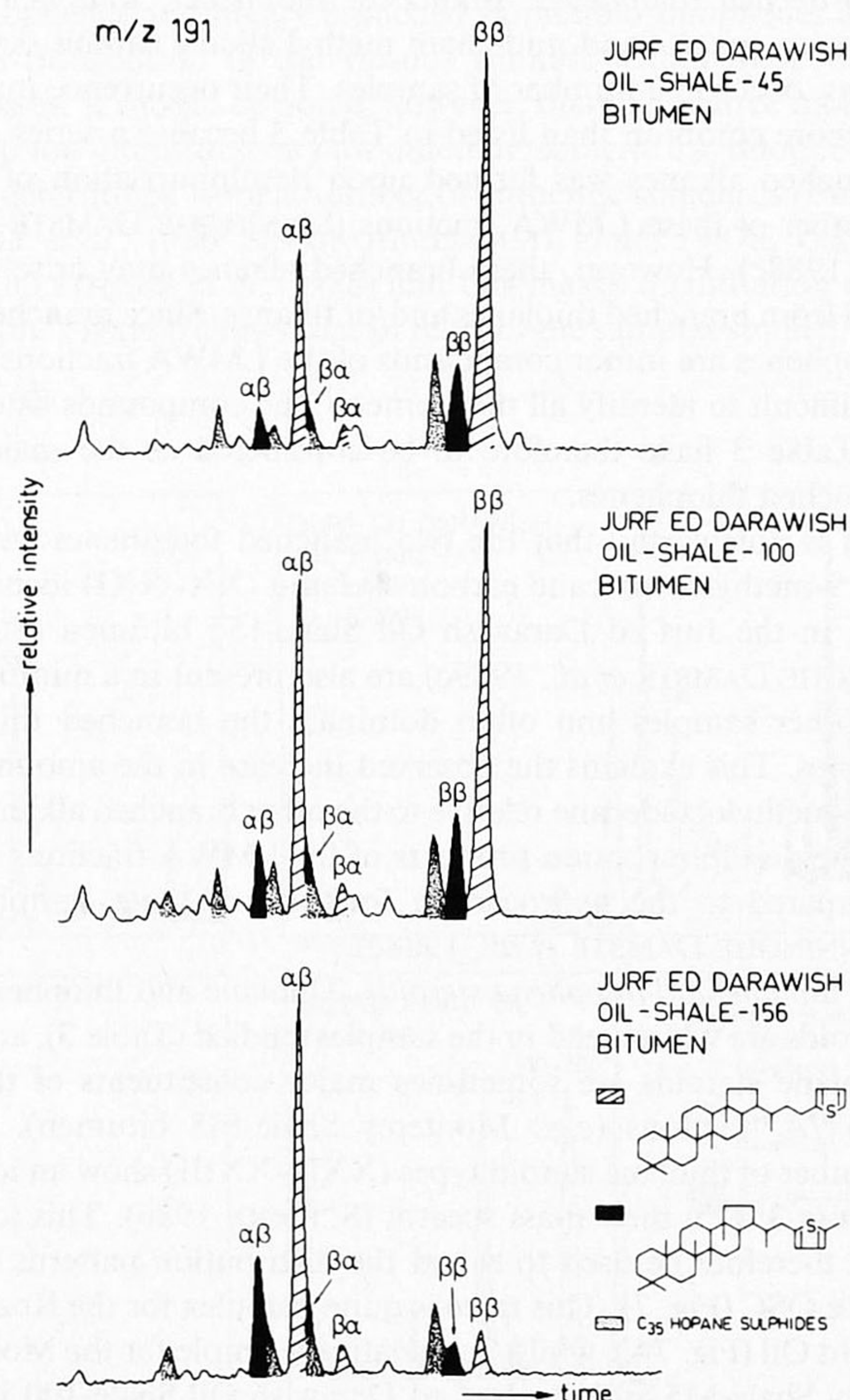


FIG. 9. Mass chromatograms of m/z 191 for the LMWA fractions of the samples indicated.

zenes were identified, whilst in the Amposta oil this series was accompanied by series of 1-alkyl-2-methylbenzenes, as reported previously by ALBAIGÉS *et al.* (1986), 1-alkyl-2-ethylbenzenes, 1-alkyl-2-propylbenzenes, 1-alkyl-2-butylbenzenes and 1-alkyl-2-pentylbenzenes. Isoprenoid alkylbenzenes (XXXII) occur in a number of samples as reported previously. It is noteworthy that C₂₆–C₂₉ isoprenoid alkylbenzenes are absent in the Monterey bitumens but that C₂₂–C₂₄ isoprenoid alkylbenzenes (XXXIVa–c) do occur. These alkylbenzenes are structurally related to the C₂₆–C₂₉ isoprenoid alkylbenzenes but instead of an isoprenoid C₂₀ side-chain they possess an isoprenoid C₁₅ side-chain.

C-ring monoaromatic steroids occur ubiquitously in the samples studied (Table 3), whilst A- and B-ring monoaromatic steroids were present in a more restricted sample suite. The carbon number distributions of the C-ring monoaromatic steroids is not given in Table 3 because members of this series with different carbon numbers coelute and the molecular ions in their mass spectra are very weak.

Methylated MTTC (XXXI) are ubiquitous compounds in the samples studied, but their relative amounts vary; they are major compounds in most of the bitumens, but minor compounds in the oils (Table 3). Their carbon number distributions vary; they are dominated by the C₂₉ member (XXId) in the bitumens (except the Northern Apennines Marl bitumen), whilst those of the oils and the Northern Apennines Marl bitumen show maxima at either C₂₇ (XXXIa) or C₂₈ (XXXIc).

DISCUSSION

Geochemical characteristics of the samples

Maturity. Most of the samples are characterised by very low amounts of saturated hydrocarbons and a high asphaltene content. Further distinct signs of immaturity are strong even-over-odd or odd-over-even carbon number predominances of the *n*-alkanes, high phytane/octadecane ratios, presence of relatively high amounts of sterenes and hopenes and relatively low amounts of 5 α (H),14 β (H),17 β (H) steranes. Only the Amposta oil and the Phosphoria Retort Shale bitumen show about equal amounts of 20R and 20S 5 α (H),14 α (H),17 α (H) steranes. The Amposta oil also contains higher amounts of saturated hydrocarbons, a Carbon Preference Index near unity and a relatively low phytane/octadecane ratio and, therefore, has to be considered more mature than the other oils. The same holds to a lesser extent for the Phosphoria Retort Shale bitumen.

Sources of organic matter. The saturated hydrocarbon fractions of all the samples studied (Table 2) lack abundant biomarkers derived from higher land plants such as *n*-alkanes with a marked odd-over-even carbon number predominance in the C₂₅–C₃₅ range, diterpenoids and oleananes. This testifies to the low amount of terrestrial organic matter relative to autochthonous phytoplankton and bacteria. The Northern Apennines Marl, the Monterey Shale, the Jurf ed Darawish Oil Shale and the source rock of the Sicily Seep Oil-E1 received some higher plant material as can be concluded from the slight to moderate odd-over-even carbon number predominance of the *n*-alkanes in the C₂₅–C₃₅ range. However, the *n*-alkane distribution patterns of most of these immature

samples maximise at C₁₆–C₂₂, indicating major marine or lacustrine sources for the organic matter.

Other biomarkers in the samples studied are the steranes and triterpanes, dominated by hopanes. In the saturated hydrocarbon fractions of Rozel Point Oil, Sicily Seep Oils, Jianghan oils and Northern Apennines Marl bitumen the steranes dominate over the hopanoids, whereas this was the opposite in the saturated hydrocarbon fractions of Jurf ed Darawish Oil Shale, Phosphoria Retort Shale and Monterey bitumens. This may be interpreted as a greater contribution of algae (steroids) relative to bacteria (hopanoids) in the first group of samples. The Monterey Shale-SB was extreme in this respect since *ca.* 80% of the saturated hydrocarbons in the bitumen consisted of 17 α (H),18 α (H),21 β (H)-28,30-bisnorhopane.

Depositional environment. Studies on the hydrocarbon biological markers indicate that the source rocks of the Rozel Point Oil, Sicily Seep Oils and the Jianghan oils and the Northern Apennines Marl were probably deposited under hypersaline conditions (TEN HAVEN *et al.*, 1985, 1987, 1988; BRASSELL *et al.*, 1988). The hydrocarbon fractions of these samples are characterised by a very low pristane/phytane ratio (<0.1), an even-over-odd carbon number predominance of the *n*-alkanes (except the Northern Apennines Marl bitumen) and the presence of a series of extended hopanes and hopenes maximizing at C₃₅. The methylated MTTC distributions, recently proposed to be of use in assessing palaeosalinity (SINNINGHE DAMSTÉ *et al.*, 1987b), also point to a hypersaline depositional environment. This also applies to the Amposta oil. A series of extended hopanes maximizing at C₃₅ is also present in this oil (ALBAIGÉS *et al.*, 1986; SINNINGHE DAMSTÉ *et al.*, 1988c) but the pristane/phytane ratio is somewhat higher (although still low compared to most oils and bitumens) and the carbon preference index much higher than for the other oil samples (Table 2). However, the *n*-alkanes in the C₂₁–C₃₃ range show a slight even carbon number predominance (ALBAIGÉS and TORRADAS, 1974). These differences in biomarker characteristics should not be explained by a different depositional environment but by differences in maturity (see above). The hydrocarbon imprint of the depositional environment is, in the case of the Amposta oil, probably diluted by hydrocarbons from thermal degradation of kerogen and asphaltenes. This also explains the higher amount of saturated hydrocarbons in the oil. The pristane/phytane may have been affected by thermal generation of pristane by breakdown of macromolecularly bound tocopherols (GOOSSENS *et al.*, 1984).

The source rocks of the Sicily Seep Oils, the Northern Apennines Marl and possibly the source rock of the Amposta oil were deposited during the Late Miocene in the Mediterranean Basin. At that time the Mediterranean was a deep, desiccated basin that contained a series of isolated saline lakes in which evaporitic carbonates and evaporites were deposited under shallow but fluctuating water depths (WARREN, 1986). This indicates that the conditions under which deposition of organic matter took place may have varied due to changes in salinity.

The hydrocarbon biological markers from the Jurf ed Darawish Oil Shale bitumens do not show all the characteristics of a hypersaline depositional environment. Although series

of extended hopenes maximising at C₃₅ are present, the pristane/phytane ratios are higher than those of the samples described above (Table 2), and no even-over-odd carbon number predominance of *n*-alkanes is observed. The methylated MTTC distributions maximise at the C₂₉ member indicating a non-hypersaline environment of deposition (SINNINGHE DAMSTÉ *et al.*, 1987b), although it was not reported at which salinity level the changes in the MTTC distributions occur. The samples consist of 40–80% CaCO₃ (WEHNER and HUFNAGEL, 1987) probably deposited by oversaturation of the water column which therefore has to be considered as of slightly enhanced (relative to seawater) salinity (mesosaline). The lower pristane/phytane ratio of the deepest sample of the Jurf ed Darawish Oil Shale suggests that it was deposited from a water column with a more enhanced salinity than those of the other two samples (TEN HAVEN *et al.*, 1987). This is consistent with data presented for the related Ghareb Formation (Jordan Valley) of the same age. SPIRO and AIZENSHTAT (1977) presented evidence that the lowermost beds of this formation were deposited under hypersaline conditions. This indicates that the change in the distribution of the methylated MTTC (SINNINGHE DAMSTÉ *et al.*, 1987b) occurs at a salinity level higher than in normal sea-water.

The Monterey Formation and the Phosphoria Retort Shale represent a non-hypersaline environment of deposition. Although they sometimes show series of extended hopanes and/or hopenes maximising at C₃₅, the pristane/phytane ratios are higher than 0.1, no even-over-odd carbon number predominance of the *n*-alkanes is observed (although there is some even carbon number predominance in the C₁₆–C₂₃ in the Monterey bitumens) and the methylated MTTC distributions maximise at the C₂₉ member.

These changes in biological marker compositions with increasing salinity are visualised in Fig. 10A, which shows a plot of the pristane/phytane ratio *versus* the trimethyl MTTC (C₂₉, XXXId)/total methylated MTTC ratio. Two clusters of samples are observed. One cluster represents samples from "normal marine" (non-hypersaline) to mesosaline depositional environments characterised by a high trimethyl MTTC/total methylated MTTC ratio (>0.5) in combination with a relatively high pristane/phytane ratio (>0.3). The other cluster represents samples from hypersaline depositional environments which are characterised by a low trimethyl MTTC/total methylated MTTC ratio (<0.4) in combination with a very low pristane/phytane ratio (<0.1). The Amposta oil does not fit into this cluster because its pristane/phytane ratio is too high probably because of its more mature nature.

Occurrence of OSC

OSC of the types previously identified in the Rozel Point Oil (SINNINGHE DAMSTÉ *et al.*, 1987c) occur in all the samples studied (Table 3). These OSC are proposed to be formed by sulphur incorporation reactions during early diagenesis (VALISOLALAO *et al.*, 1984; BRASSELL *et al.*, 1986; SINNINGHE DAMSTÉ *et al.*, 1986, 1987a,c, 1988c, 1989b; SINNINGHE DAMSTÉ and DE LEEUW, 1987). Recently it has been demonstrated that hydrogen sulphide is probably the inorganic sulphur species involved in these reactions, although polysulphides cannot be fully excluded (SINNINGHE DAMSTÉ *et*

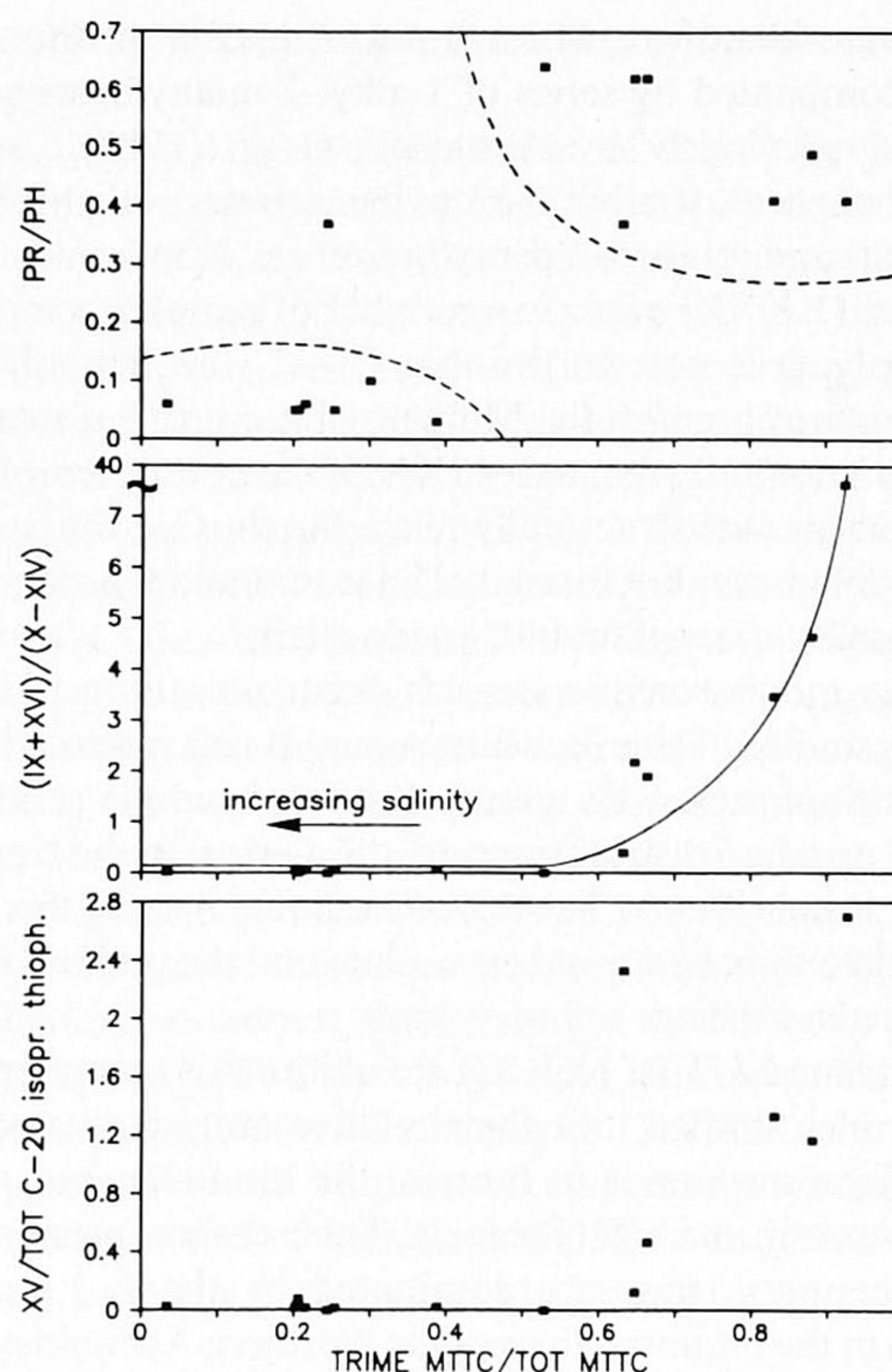


FIG. 10. Plots of the pristane/phytane ratio, the sum of isoprenoid thiophenes IX and XVI/the sum of isoprenoid thiophenes X–XIV ratio and the C₂₅ highly branched isoprenoid thiophenes/total C₂₀ isoprenoid thiophenes ratio *versus* the trimethyl MTTC/total MTTC ratio. The pristane/phytane and trimethyl MTTC/total MTTC ratios are on a weight basis. The other two ratios are not on a weight basis, since they were determined by integration of mass chromatograms of characteristic ions and it is not exactly known how much these ions contribute to the total ion yield of all the compounds involved.

al., 1989c). The widespread occurrence of these types of OSC in immature bitumens and immature oils indicate that sulphur incorporation into lipid material during early diagenesis is a significant and widely occurring mechanism for the sulphur-enrichment of organic matter.

A significant finding is that sulphur incorporation into organic matter does not only take place under hypersaline conditions of deposition but also takes place in marine, highly anoxic sediments such as those of the Monterey Formation. Of course, hypersaline conditions of deposition are in favour of such reactions because hypersalinity often induces a density stratification of the water column and thereby establishes anoxic conditions in the lower part of the water-column and at the sediment-water interface. Iron is generally less abundant in these types of environment, whilst the productivity of organic matter is high. Thus, high levels of H₂S produced by sulphate-reducing bacteria may react with the lipids biosynthesised by phytoplankton, phytobenthos and bacteria, the major producers of organic matter in hypersaline environments (WARREN, 1986). However, in sediments deposited under anoxic conditions due to reasons other than hypersalinity (*e.g.* anoxia caused by upwelling; DEMAISON and MOORE, 1980) these sulphur incorporation reactions may also take place as shown by the presence of OSC in samples from the Monterey Formation. In the palaeoenvironments

of, *e.g.*, the Phosphoria Retort Shale and the lower member of the Jurf ed Darawish Oil Shale, which are characterised by a substantial contribution of terrigenous clays, the amounts of H₂S produced by sulphate-reducing bacteria probably exceed the amount of available iron, since it is thought that H₂S quantitatively reacts with available iron leading to the formation of FeS and FeS₂ (BERNER, 1984, 1985). This only can take place in high productivity environments, since the amount of fresh organic matter is the rate determining factor for sulphate reduction in normal marine sediments (BERNER, 1984).

An implication of the fact that these OSC are probably formed by sulphur incorporation into functionalised lipids is that these OSC represent compounds which have not been formed by thermal degradation of kerogen. The observed strong even-over-odd carbon number predominance of the various homologous series of OSC in most of the samples described supports this. Pyrolysis of kerogens and asphaltenes also generates these series of OSC but with smooth carbon number distributions (SINNINGHE DAMSTÉ *et al.*, 1988b, 1989a; PAYZANT *et al.*, 1988b). The LMWA fractions of the oils, which contain these OSC, represent 3–22% (by weight; Table 1) of the oils studied. Moreover, the high-molecular-weight substances present in the other fractions of these immature bitumens and immature oils (high-molecular-weight aromatic fraction, hetero fraction and asphaltene fraction) probably have a similar origin; a major part of these substances was probably formed through interaction of hydrogen sulphide with unsaturated and functionalised lipids (SINNINGHE DAMSTÉ *et al.*, 1988c, 1989a,c; J. S. SINNINGHE DAMSTÉ, unpublished results) leading to the formation of sulphur-rich high molecular weight substances. This means that the major part of these immature oils (except the Amposta oil which is more mature) has by-passed the stage of being part of insoluble kerogen, in contrast to more mature oils which mainly originate from thermal degradation of kerogen (TISSOT and WELTE, 1984). In fact, these immature oils have to be considered accumulated immature bitumens, and therefore their hydrocarbon and OSC compositions are highly comparable to those of the bitumens studied. It is noteworthy that, despite their unusual origin, the oils from the Jiangnan Basin are commercially produced. The unusual immaturity of the oils studied is thus readily explicable as is the unusually high amount of extractable organic matter relative to the total amount of organic matter in the sediments studied (*e.g.*, in the case of the Northern Apennines Marl 60% of the organic matter could be extracted).

A possible explanation for the accumulation of these immature bitumens has been provided by WARREN (1986), who suggested that the seeps from the Sicilian evaporites (Sicily Seep Oils) were formed by conversion of gypsum to anhydrite within the first several hundred meters of burial. This process implies that the organic material will be flushed as "immature hydrocarbons" from gypsiferous sediments well before catagenesis.

Possible applications of OSC as molecular indicators

The results of this study indicate that the OSC with structures related to well-known geologically occurring hydrocar-

bons and previously identified in the Rozel Point Oil (SINNINGHE DAMSTÉ *et al.*, 1987c), occur as well in a number of other immature bitumens and immature oils. The relative amounts and distributions of the various OSC classes in the samples studied varies considerably, probably as a result of different sources of organic matter and different degrees of thermal maturation. A discussion of their possible application as molecular indicators is therefore worthwhile.

Assessment of sources of organic matter. Although the exact mechanisms of the formation of OSC are as yet unknown it is very likely that these compounds originate from a "quenching" type of reaction of functionalised lipids (*e.g.*, unsaturated fatty acids, alcohols, alkenes) with H₂S during early diagenesis (SINNINGHE DAMSTÉ *et al.*, 1989c). Because the resulting OSC are more stable than the original, functionalised lipids against microbial attack and upon burial of sediments, the structures of the OSC occurring in bitumens and immature oils may provide information on the presence of specific lipid moieties in the depositional environment and thereby represent a new family of biomarkers with complementary information, since the characteristic labile precursors do not survive as such.

A striking example is the C₂₅ highly branched isoprenoid thiophenes XV, which may have been formed by sulphur incorporation into a highly branched isoprenoid alkadiene biosynthesised by certain diatom species (NICHOLS *et al.*, 1988; SINNINGHE DAMSTÉ *et al.*, 1989b). Relatively high amounts of this thiophene were present in the samples from the Monterey Formation, consistent with the fact that it was deposited in an upwelling region. It may represent a useful diatom marker.

Another example are the C₂₀ isoprenoid mid-chain thiophenes (XI–XIV), which were probably formed by incorporation of sulphur into polyunsaturated phytenols, compounds reported to occur exclusively in archaeobacteria and green and purple sulphur bacteria (SINNINGHE DAMSTÉ and DE LEEUW, 1987). The C₂₀ isoprenoid mid-chain thiophenes are, therefore, found only in samples from hypersaline depositional environments (*i.e.*, Rozel Point Oil, Sicily Seep Oils, Jiangnan oils, Amposta oil), although they were absent in the Northern Apennines Marl which also was deposited under hypersaline conditions. The presence of bithiophenes co-occurring with C₂₀ isoprenoid mid-chain thiophenes therefore supports the proposed diagenetic pathways for C₂₀ isoprenoid OSC (SINNINGHE DAMSTÉ and DE LEEUW, 1987).

The C₃₅ sulphur-containing hopanes (XXVI–XXVII) and C₃₆ sulphur-containing methylhopane (XXVIII) are probably formed by sulphur incorporation into bacteriohopanetetrol and 3-methylbacteriohopanetetrol, respectively, and therefore may be used as a bacterial marker.

C₃₇ and C₃₈ mid-chain 2,5-dialkylthiophenes and -thiolanes are probably formed by early diagenetic sulphur incorporation into C₃₇ and C₃₈ di- and triunsaturated methyl and ethyl ketones or their corresponding alkadienes and alkatrienes (SINNINGHE DAMSTÉ *et al.*, 1989c). These long-chain ketones and hydrocarbons are lipids produced by coccolithophorids and these OSC may therefore be of use as biomarkers for these organisms.

These few examples of assessment of sources of organic matter by use of OSC show their potential as molecular in-

dicators. The identification of OSC, alternatively, may lead to the recognition of previously unknown functionalised lipids. For example, the C₂₆ isoprenoid thiophenes (Fig. 4) and thiophenes with a linearly extended phytane carbon skeleton (PEAKMAN *et al.*, 1989) have an as yet unknown precursor.

Assessment of depositional environment. In general the presence of the OSC described in this paper are an indication of an anoxic environment of deposition where the production of H₂S exceeded the amounts of reactive iron minerals as discussed above. However, more detailed information seems to be available from distribution patterns regarding the assessment of palaeoenvironment.

An example are the distribution patterns of the C₂₀ isoprenoid thiophenes which seem to be dependent on the salinity of the depositional environment (Fig. 6). The C₂₀ isoprenoid thiophenes in normal marine (not hypersaline) samples are dominated by thiophenes IX and XVI. For instance, the C₂₀ isoprenoid thiophene distribution of the Monterey-T6 bitumen is dominated by these two thiophenes. They have also been reported to be the major thiophenes in oceanic sediments (BRASSELL *et al.*, 1986; RULLKÖTTER *et al.*, 1988). C₂₀ isoprenoid thiophene X becomes gradually more abundant in the Monterey Shale-M5 and the Jurf ed Darawish Oil Shale-45 and -156 bitumens (Fig. 6B-D). In the Rozel Point Oil and Sicily Seep Oil-E2 (but also in the other Sicily Seep Oils, the Jianghan oils and the Amposta oil; not shown in Fig. 6) thiophene XVI is completely absent, whilst thiophene X dominates over thiophene IX (Figs. 6E-F). The C₂₀ isoprenoid thiophene distributions of the Rozel Point Oil and Sicily Seep Oil-E2 also show relatively high amounts of isoprenoid mid-chain thiophenes (XI-XIV; Figs. 6E-F), which are minor compounds or absent in the other four examples (Figs. 6A-D). These changes in the C₂₀ isoprenoid thiophene distributions seem to co-occur with changes in the salinity of the depositional environment of the samples as derived from geological and other biomarker data (see above). A plot of the (IX + XVI)/(X + XI + XII + XIII + XIV) ratio *versus* the trimethyl MTTC/total MTTC ratio (Fig. 10B) shows this phenomenon. The samples from the Jurf ed Darawish Oil Shale (which originate from a mesosaline palaeoenvironment) lie indeed between those from non-hypersaline and from hypersaline depositional environments. A plot of the C₂₅ highly branched isoprenoid thiophenes/total C₂₀ isoprenoid thiophenes ratio *versus* the trimethyl MTTC/total MTTC ratio (Fig. 10C) shows a similar trend but there seems to be more variation in the C₂₅ highly branched isoprenoid thiophenes/total C₂₀ isoprenoid thiophenes ratio in samples from non-hypersaline to mesosaline depositional environments. This is probably due to differences in organic matter sources (relative contribution of diatoms to total organic matter). Although these changes in distribution of C₂₀ isoprenoid thiophenes are not yet completely understood and may also depend on maturity, they may be useful, in combination with methylated MTTC distributions, in assessing palaeosalinity, especially, since C₂₀ isoprenoid thiophenes are among the most widespread occurring OSC (Table 6).

Assessment of maturity. The types of OSC described here have so far only been found in sediments and immature oils. "Normal" mature oils, however, contain sulphur compounds with thiophene rings as part of more complex ring systems (primarily benzo[*b*]thiophenes, dibenzothiophenes and ben-

zonaphthothiophenes with much shorter alkyl side-chains; *e.g.*, HUGHES, 1984; ARPINO *et al.*, 1987). These differences in OSC distributions were explained by (1) dilution by newly generated sulphur compounds from kerogen maturation and (2) cyclisation and aromatisation of long-chain OSC (SINNINGHE DAMSTÉ *et al.*, 1989a).

Supporting evidence for both explanations is obtained from this study. The distribution pattern of the 2-alkyl-5-methylthiolanes in the Sicily Seep Oil-E2 and Jianghan-B1 oil (Figs. 1A and B) are characterised by a strong even-over-odd carbon number predominance, whilst this distribution in the more mature Amposta oil (Fig. 1D) shows no strong predominance. The depositional environment of the source rocks of these oils is probably similar. Therefore, it is not unlikely that the 2-alkyl-5-methylthiolanes formed during early diagenesis and exhibiting a strong even-over-odd carbon number predominance (as can be seen in the C₂₅-C₃₁ range; Fig. 1D), were diluted by thermally generated 2-alkyl-5-methylthiolanes with no carbon number predominance. Series of 2-alkyl-5-methylthiolanes were generated by flash-pyrolysis of sulphur-rich kerogens (SINNINGHE DAMSTÉ *et al.*, 1988b). Hydrous-pyrolysis, a technique to simulate oil formation, also produced this series (EGLINTON, 1988) indicating that such a generation can take place.

The possible formation of 2,4-di-*n*-alkylbenzo[*b*]thiophenes (IV) from 2,5-di-*n*-alkylthiophenes (III) (PERAKIS, 1986; SINNINGHE DAMSTÉ *et al.*, 1987c) and isoprenoid benzo[*b*]thiophenes from isoprenoid thiophenes (SINNINGHE DAMSTÉ and DE LEEUW, 1987) by cyclisation and subsequent aromatisation reactions have been described previously. The fact that the two somewhat more mature samples (Amposta oil and Phosphoria Retort Shale) contain relatively more 2,4-dialkylbenzo[*b*]thiophenes and virtually no 2,5-dialkylthiophenes (Table 3) strongly support this theory. The transition of 2,5-dialkylthiolanes (I) and possibly 2,6-dialkylthianes (II) into 2,5-dialkylthiophenes (III) by aromatisation is in some cases quite clear because of similar distribution patterns but in other cases less obvious since some samples contain 2,5-dialkylthiolanes and 2,4-dialkylbenzo[*b*]thiophenes but no 2,5-dialkylthiophenes (Table 3).

It seems that when these processes will be better understood the compounds involved may act as maturity indicators (*e.g.*, benzo[*b*]thiophene/thiophene ratios) spanning a large range.

Another possible maturity indicator may be the isomerisation of sulphur-containing steroids and hopanoids. The distributions of the thiophene hopanoids in the Jurf ed Darawish Oil Shale core (Fig. 9) suggest such an application; the probably less stable 17β(H),21β(H) stereoisomers of XXVI and XXVII (assumed to be formed by sulphur incorporation into a precursor with natural 17β(H),21β(H) configuration) are the major stereoisomers in the shallowest Jurf ed Darawish Oil Shale sample, whilst the probably more stable 17α(H),21β(H) stereoisomers dominate in the deepest sample. This suggests that these changes in distribution are due to small differences in maturity as proposed by VALISOLALAO *et al.* (1984). This observed trend co-occurs with a similar trend in the stereochemistry of the C₂₉-C₃₁ hopanes; in the shallowest sample 17β(H),21β(H)-hopanes dominate, whilst they are relatively minor in the deepest sample. WEHNER and HUFNAGEL (1987) ascribed this trend, however, to a change in the depositional environment rather than to the

influence of maturation. Extended hopanes with the 22R 17 α (H),21 β (H)-configuration have, indeed, been found in a sample of predominantly *Sphagnum* peat (TAYLOR *et al.*, 1980). The difference in depth of the shallowest (Jurf ed Darawish Oil Shale-45) and deepest sample (Jurf ed Darawish Oil Shale-156) is only 111 m, which means that the differences in temperature history are small and probably cannot account for the almost complete isomerisation, although isomerisation of 17 β (H),21 β (H)-hopanes to 17 α (H),21 β (H)-hopanes occurs at relatively low levels of maturity (ENSMINGER *et al.*, 1974; OURISSON *et al.*, 1979; MACKENZIE *et al.*, 1988). At present it is thus unknown whether the observed differences in both hopane and thiophene hopanoid distributions are related to differences in input or maturation. More research, in which the other hopanoids (*e.g.*, extended hop-17(21)-enes and hopanoid ketones (XXIX)) have to be taken into account as well, may resolve this question.

Oil-oil and oil-source rock correlation studies. As outlined above differences in sources of organic matter and maturity have a serious impact on the OSC distributions. Therefore, these distributions may be used in fingerprinting oils and bitumens. For example, the distributions of the various classes of OSC in the related Sicily Seep oils (E1, E2 and E5) were indeed very similar (Table 3). A similar observation was made for the two related Jiangnan oils (B1, W1349).

CONCLUSIONS

(1) Organic sulphur compounds (OSC) with carbon skeletons identical to well-known geologically occurring hydrocarbons (*n*-alkanes, isoprenoid alkanes, steranes, triterpanes) occur widely in immature bitumens and immature crude oils.

(2) The palaeoenvironments of the sediments and source rocks of the oils in which these OSC occur were anoxic and H₂S, produced by sulphate-reducing bacteria, has probably exceeded the amount of available iron. These conditions caused a surplus of free H₂S, which reacted with organic matter to form OSC.

(3) The relative amounts and distributions of the OSC vary considerably as a result of different sources of organic matter and different degrees of maturation.

(4) Therefore, OSC may be useful as molecular indicators for the assessment of organic input, depositional environment and maturity and in oil-oil and oil-source rock correlation studies.

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APPENDIX

