

Origin and diagenetic transformations of C₂₅ and C₃₀ highly branched isoprenoid sulphur compounds: Further evidence for the formation of organically bound sulphur during early diagenesis

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Abstract—A number of C₂₅ and C₃₀ highly branched isoprenoid (HBI) sulphur compounds (e.g., thiolanes, 1-oxo-thiolanes, thiophenes, and benzo[b]thiophenes) with 2,6,10,14-tetramethyl-7-(3-methylpentyl)pentadecane and 2,6,10,14,18-pentamethyl-7-(3-methylpentyl)nonadecane carbon skeletons were identified in sediments, ranging from Holocene to Upper Cretaceous. These identifications are based on mass spectral characterisation, desulphurisation, and, in some cases, by comparison of mass spectral and relative retention time data with those of authentic standards. The presence of unsaturated C₂₅ and C₃₀ HBI thiolanes in a Recent sediment from the Black Sea (age 3–6 × 10³ a) strongly supports their formation during early diagenesis. The co-occurrence of HBI polyenes (C₂₅ and C₃₀) and unsaturated HBI thiolanes (C₂₅ and C₃₀) possessing two double bonds less than the corresponding HBI polyenes, in this Recent sediment, testifies to the formation of unsaturated HBI thiolanes by a reaction of inorganic sulphur species with double bonds of the HBI polyenes. Furthermore, a diagenetic scheme for HBI sulphur compounds is proposed based on the identification of HBI sulphur compounds in sediment samples with different maturity levels.

INTRODUCTION

THE PRESENCE OF C₂₀, C₂₅, and C₃₀ hydrocarbons with highly branched isoprenoid (HBI) carbon skeletons (I–III) and varying degrees of unsaturation (0–6 double bonds) in sediments and oils originating from lacustrine, marine, and hypersaline depositional environments has been reported frequently over the last decade (for a review see ROWLAND and ROBSON, 1990). These compounds are often the most abundant hydrocarbons in unpolluted coastal and estuarine Recent sediments (ROWLAND and ROBSON, 1990). The saturated compounds (I–III) were unambiguously identified by synthesis of authentic standards (YON et al., 1982; ROBSON and ROWLAND, 1986, 1988a). The carbon skeletons of the HBI alkenes were identified on the basis of their hydrogenation products. DUNLOP and JEFFERIES (1985) tentatively determined the position of the double bond in a sedimentary C₂₀ (IV) and a C₂₅ (V) HBI monoene by ozonolysis. ROBSON and ROWLAND (1986) presented further indirect evidence that these sedimentary monoenes may contain a methylenic double bond. However, in most cases the exact positions of the double bonds remain unknown.

Information on the biological source of these compounds is scant. ROWLAND et al. (1985) identified the C₂₀ HBI alkane (I), a related monoene, and a pseudohomologous C₂₅ diene in field samples dominated by the green alga *Enteromorpha prolifera*. NICHOLS et al. (1988) reported a C₂₅ HBI diene as a major hydrocarbon in natural populations of sea-ice diatom communities. These authors also suggested that the occur-

rence of this diene in field samples of *Enteromorpha prolifera* may be due to the presence of epiphytic microalgae or bacteria.

Recently, a number of thiophenes with carbon skeletons I and II have been identified in consolidated sediments and immature oils (VI–XVI; SINNINGHE DAMSTÉ et al., 1987, 1989a; XVII, KOHNEN unpubl. results). The C₂₀ HBI thiophenes have, to date, only been observed in two oils (SINNINGHE DAMSTÉ et al., 1989a,c), whereas the C₂₅ HBI thiophenes are widespread in sediments and oils (SINNINGHE DAMSTÉ et al., 1989a,c; TEN HAVEN et al., 1990). Corresponding C₂₅ HBI thiolanes (XVIII) were tentatively identified in immature deep-sea sediments (TEN HAVEN et al., 1990). It has been postulated that the formation of these HBI sulphur compounds is initiated by incorporation of hydrogen sulphide and/or polysulphides into di- and/or poly-unsaturated HBI alkenes during early diagenesis (SINNINGHE DAMSTÉ et al., 1989a).

In this paper we report the occurrence of HBI alkenes, thiophenes, benzo[b]thiophenes, saturated and unsaturated thiolanes and their corresponding sulphoxides in a suite of samples ranging from Holocene to Upper Cretaceous. The results from their detailed analysis provide a better understanding of the origin and the diagenetic pathways of these compounds and, hence, of organic sulphur compounds (OSCs) in general.

EXPERIMENTAL

Samples

Geological background information (see Table 1) of the DSDP samples from the Gulf of California and offshore California is given

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by RULLKÖTTER et al. (1981, 1982), of the Jurfed Darawish oil shale by HUFNAGEL (1984), and of the Black Sea sediment (Unit 2) by BOON et al. (1979).

Extraction and Fractionation

The work-up procedures for the DSDP samples originating from the Gulf of California and offshore California and the Jurfed Darawish oil shale sample are described elsewhere (RULLKÖTTER et al., 1981, 1982; KOHNEN et al., 1990).

The freeze-dried Black Sea sediment (Unit 2) was ultrasonically extracted with methanol ($\times 1$), methanol/ CH_2Cl_2 (1:1, v/v; $\times 1$), and CH_2Cl_2 ($\times 5$), respectively. The bitumen was obtained by removing the solvent with a rotary evaporator at 30°C (1.36 g; 2.3 wt%). The extract was separated, using a separating funnel, into a CH_2Cl_2 layer and a methanol/ H_2O (1:1, v/v) layer, which was re-extracted twice with CH_2Cl_2 . The combined CH_2Cl_2 layers were dried with anhydrous Na_2SO_4 (yield 1.02 g). An aliquot (ca. 200 mg) of this extract was fractionated on a column (25 cm \times 2 cm; column volume 35 mL) packed with alumina (activated for 2.5 h at 150°C) by elution with 150 mL hexane/ CH_2Cl_2 (9:1, v/v; the apolar fraction) and 100 mL methanol/ CH_2Cl_2 (1:1, v/v; the polar fraction). The apolar fraction (ca. 10 mg) was further separated by argentation thin layer chromatography (Ag^+ -TLC) (KOHNEN et al., 1990). Four bands with $R_f = 1.0$ –0.8 (fraction A1), $R_f = 0.8$ –0.6 (fraction A2), $R_f = 0.6$ –0.1 (fraction A3), and $R_f = 0.1$ –0.0 (fraction A4) were scraped off the TLC plate, ultrasonically extracted with ethyl acetate ($\times 3$), and analysed by GC and GC-MS. Subsequently, fraction A4 (ca. 1 mg) was fractionated with a column (6 cm \times 0.6 cm) packed with alumina (not activated) by elution with hexane (1.5 mL; the "polyunsaturated hydrocarbon fraction") and hexane/ CH_2Cl_2 (9:1, v/v; 3 mL; "OSC fraction"). A so-called "low-molecular weight aromatic fraction" (LMWA) was isolated from an aliquot (ca. 200 mg) of the CH_2Cl_2 extract using column chromatography as described elsewhere (SINNINGHE DAMSTÉ et al., 1987).

Gas Chromatography

Gas chromatography (GC) was performed with a Carlo Erba 5300 instrument, equipped with an on-column injector. A fused silica capillary column (25 m \times 0.32 mm) coated with CP Sil-5 (film thickness 0.12 μm) was used with helium as carrier gas. A more polar column (DB17; 30 m \times 0.25 mm; film thickness 0.15 μm) was also used for the coinjections. Detection was accomplished by both a flame ionization detector (FID) and a sulphur-selective flame photometric detector (FPD), using a stream-splitter at the end of the column (split ratio FID:FPD = 1:2). The samples (dissolved in ethyl acetate) were injected at 70°C, and subsequently the oven was programmed to 130°C at 10°C/min and then at 4°C/min to 320°C, at which temperature it was held for 20 min.

Gas Chromatography-Mass Spectrometry

Gas chromatography-mass spectrometry (GC-MS) was carried out on a Hewlett-Packard 5840 gas chromatograph connected with 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 (resolution 1000). The gas chromatograph was equipped with a fused silica capillary column (25 m \times 0.32 mm) coated with CP Sil-5 (film thickness = 0.1 μm). Helium was used as carrier gas. The samples were injected at 50°C, and subsequently the oven was programmed to 130°C at 20°C/min and then at 4°C/min to 300°C, at which temperature it was held for 10 min. In the case of the DSDP samples, GC-MS data stored on magnetic tapes were re-examined. The operating conditions of the GC-MS system are described elsewhere (RULLKÖTTER et al., 1981, 1982).

Catalytic Hydrogenation

Fractions dissolved in acetic acid were hydrogenated for 2 h by bubbling hydrogen through the solution in the presence of PtO_2 . After centrifugation the supernatant was worked up by addition of water and extraction with hexane.

Raney Ni Desulphurisation/Hydrogenation

Low-molecular-weight apolar fractions were submitted to Raney Ni desulphurisation and a subsequent catalytic hydrogenation as described elsewhere (SINNINGHE DAMSTÉ et al., 1988). The resultant hydrocarbons were analysed by GC and GC-MS. Prior to desulphurisation, the polar (resin) fraction of the Black Sea sediment extract was reduced with excess LiAlH_4 in refluxing dioxane for 2 h (PAYZANT et al., 1986). After this reduction step the polar fraction was fractionated with a column packed with alumina into an apolar and a polar fraction as described in the "extraction and fractionation" section. The apolar fraction thus obtained was analysed with GC and GC-MS. The polar fraction was desulphurised, and the resultant hydrocarbons were isolated by column chromatography and analysed by GC and GC-MS.

Synthesis of Authentic Standards

2,3-Dimethyl-5-(7-(2,6,10,14-tetramethyl-pentadecyl)thiolane (XVIII) was synthesised from the corresponding thiophene (four diastereomers of XV) synthesised previously (SINNINGHE DAMSTÉ et al., 1989a) by ionic hydrogenation using triethylsilane (KURSANOV et al., 1975; PARNES et al., 1977) under the conditions described by SINNINGHE DAMSTÉ et al. (1987). Since the target product (XVIII) possesses six chiral centres, achiral synthesis yields a mixture of 64 stereoisomers. This mixture was separated by GC (CP Sil-5) into six partially coeluting peaks. Mass spectra, obtained by GC-MS, of these stereoisomers are almost identical.

1-Oxo-2,3-dimethyl-5-(7-(2,6,10,14-tetramethylpentadecyl)thiolane (XIX) was prepared by oxidation of the synthetic isomeric mixture of XVIII using *N*-chlorosuccinimide in a 1:1 molar ratio. The reaction conditions employed are similar to those described by HARVILLE and REED (1968). This sulphoxide has an additional chiral centre (because of the presence of a lone pair of electrons at the S atom) compared to the corresponding thiolane and hence more stereoisomers. This mixture was separated by GC (CP Sil-5) into eight partially coeluting peaks. Mass spectra of the GC separable diastereomers are similar.

RESULTS

Identification of Saturated C_{25} HBI Thiolanes

In the "aromatic hydrocarbon" fraction of the sediment extract of a DSDP sample from offshore California (467-54-2, 100–115 cm), two diastereomeric C_{25} HBI thiophenes (XV) are major constituents (Fig. 1a). A suite of compounds eluting shortly after these thiophenes (indicated in black in Fig. 1a) shows mass spectra similar to one another. An example of such a mass spectrum is given in Fig. 2a. The molecular ion (m/z 382) is 4 daltons higher than that of C_{25} HBI thiophenes (see SINNINGHE DAMSTÉ et al., 1989a), and the base peak is at m/z 115; both features suggest that these compounds are the corresponding thiolanes (XVIII). The fragment ions at m/z 269 and m/z 311 are consistent with this tentative assignment according to proposed fragmentation pathways of alkylthiolanes (SCHMID et al., 1987; SINNINGHE DAMSTÉ et al., 1987). Cleavage through the thiolane ring accompanied by transfer of a hydrogen atom results in the fragment ion m/z 311. Displacement reactions, probably via a five-membered-ring transition state, result in the formation of the fragment ion at m/z 269 and also lead to formation of the fragment ion at m/z 311. As no other structural isomer of the family of C_{25} HBI thiolanes would show a similar mass spectrum, it is assumed that all these compounds exemplified by the m/z 115 mass chromatogram (Fig. 1b) are C_{25} HBI thiolane stereoisomers (XVIII).

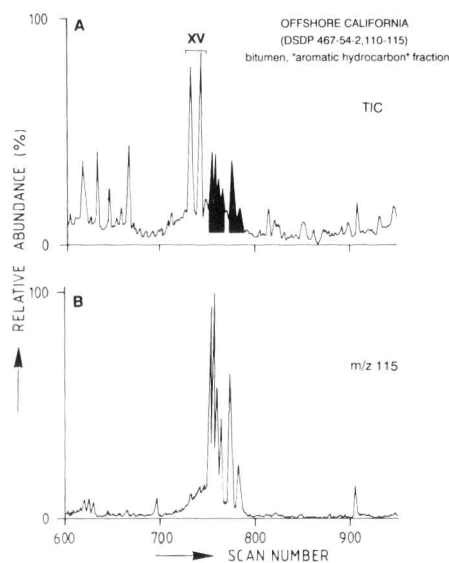


FIG. 1. (a) Partial total ion current chromatogram of the "aromatic hydrocarbon" fraction of the bitumen from an offshore California sediment sample (DSDP 467-54-2, 100-115). Diastereomeric C_{25} HBI thiophenes (XV) are indicated. Stereoisomeric C_{25} HBI thiolanes (XVIII) are shown in black. (b) Partial mass chromatogram of m/z 115 of the same sample, emphasising the distribution of the stereoisomeric C_{25} HBI thiolanes (XVIII).

In order to prove the geological occurrence of these C_{25} HBI thiolanes, these compounds were synthesised by ionic hydrogenation of a C_{25} HBI thiophene standard (XV) previously synthesised (SINNINGHE DAMSTÉ *et al.*, 1989a). A mixture of stereoisomers was obtained. The mass spectra of these compounds are identical to those of the thiolanes present in the sample from offshore California (*cf.* Fig. 2a and b). The presence of several of these C_{25} HBI thiolane stereoisomers in both the synthetic mixture and the DSDP sample is in agreement with the presence of six chiral centres in their structure (Fig. 2b). No attempt was made to assign the diastereomers separated by GC. Coelution of the synthetic C_{25} HBI thiolane mixture with the compounds present in the "aromatic hydrocarbon" fraction confirmed unambiguously the presence of these compounds in the sediment from offshore California.

Identification of Unsaturated C_{25} - and C_{30} HBI Thiolanes

GC-FPD analyses of the four fractions isolated by Ag^+ -TLC from the apolar fraction of the bitumen from a Recent Black Sea sediment (Unit 2) revealed that only the fraction with R_f -values of 0.0-0.1 contains organic sulphur compounds (OSCs). Polyunsaturated hydrocarbons are the major compounds present in this fraction. They are mainly comprised of compounds tentatively identified as C_{30} HBI polyenes with five or six double bonds and squalene (Fig. 3a). (A C_{30} HBI polyene with four double bonds and C_{25} HBI polyenes with three and four double bonds are present in the fraction with R_f -values of 0.1-0.6.) Since all the OSCs present in the TLC fraction with R_f -values of 0.0-0.1 show mass spectra with a major fragment ion at m/z 115, the distribution of these OSCs is delineated by a mass chromatogram of

m/z 115 (Fig. 3b). Four clusters of OSCs (numbered 1-4) are evident in this mass chromatogram.

Raney Ni desulphurisation and subsequent hydrogenation of the OSCs isolated from the TLC fraction yielded C_{25} and C_{30} HBI alkanes (II, III) as determined by co-chromatography with the C_{25} synthetic standard and by comparison of the

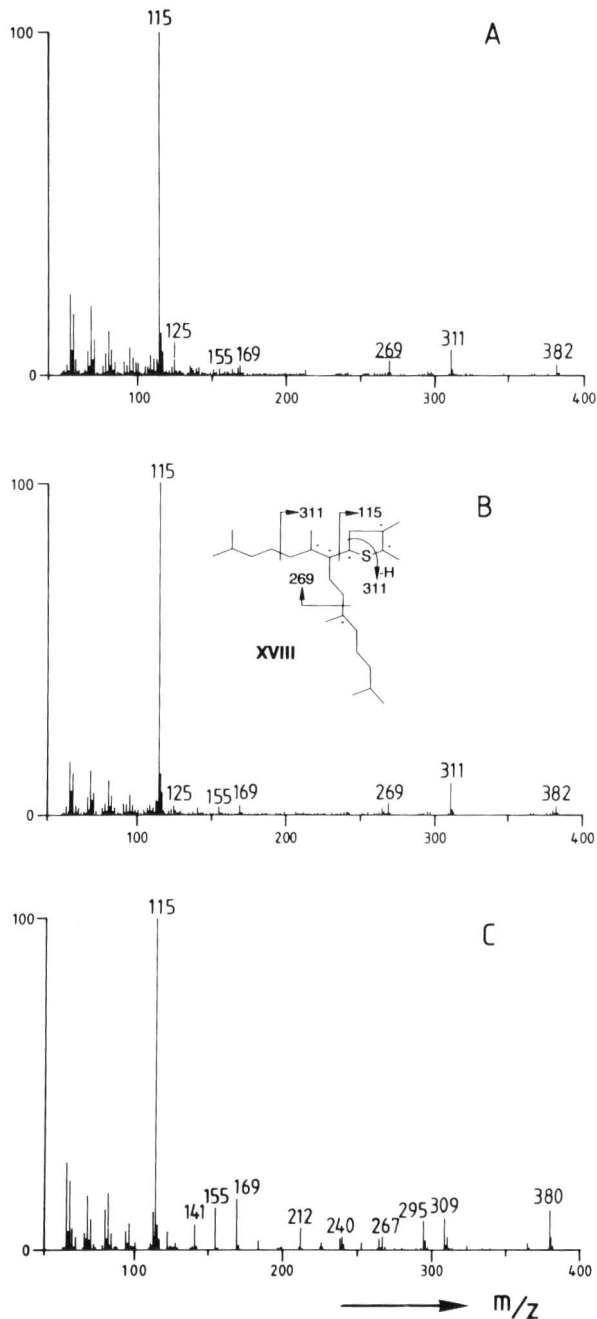


FIG. 2. Mass spectra (subtracted for background) of (a) a C_{25} HBI thiolane (XVIII) present in the extract of the offshore California sediment (DSDP 467-54-2, 100-115), (b) a synthetic C_{25} HBI thiolane (XVIII), and (c) an unsaturated C_{25} HBI thiolane possessing one double bond in the long alkyl side chain (XX) present in the extract of the Black Sea sediment (Unit 2). In (b) the fragmentation pathways of XVIII are exemplified, and the chiral centers are indicated with asterisks.

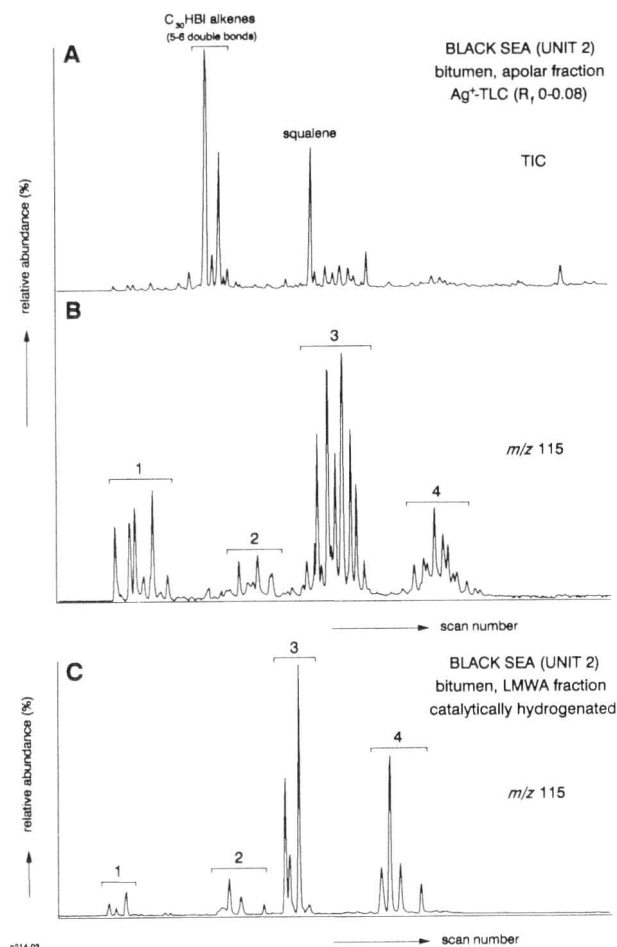


FIG. 3. (a) Partial total ion current trace of the Ag^+ -TLC fraction with $R_f = 0.0-0.08$ from the apolar fraction of the Black Sea sediment (Unit 2) extract. (b) Partial mass chromatogram of m/z 115 of the same sample as in (a) showing the distribution of the various HBI OSC classes. Key: 1 = unsaturated (1-2 double bonds) C_{25} HBI thiolenes (XX); 2 = unsaturated (1-2 double bonds) C_{25} HBI 1-oxothiolenes (XXIV); 3 = unsaturated (2-4 double bonds) C_{30} HBI thiolenes (XXI); 4 = unsaturated (2-4 double bonds) C_{30} HBI 1-oxothiolenes (XXVI). (c) Partial mass chromatogram of m/z 115 of the catalytically hydrogenated LMWA fraction of the Black Sea sediment (Unit 2) extract showing four clusters of HBI OSCs. Key: 1 = C_{25} HBI thiolenes (XVIII); 2 = C_{25} HBI 1-oxothiolenes (XIX); 3 = C_{30} HBI thiolenes (XXII); 4 = C_{30} HBI 1-oxothiolenes (XXV).

mass spectrum and relative retention time of the C_{30} HBI alkane with those reported by ROBSON and ROWLAND (1988a). Minor amounts of a compound tentatively identified as a C_{30} HBI monoene are also present in the desulphurised OSC fraction. Since HBI hydrocarbons are the exclusive products obtained after desulphurisation, the original OSCs must possess a HBI carbon skeleton.

The compounds eluting in cluster 1 (Fig. 3b) show mass spectra with a molecular ion at either m/z 378 or m/z 380 (e.g., Fig. 2c) which, in combination with the data obtained after Raney Ni desulphurisation, indicate that these compounds are C_{25} HBI thiolenes possessing two or one double bonds, respectively. The presence of a major fragment ion at m/z 115 indicates that the double bonds are positioned in the long alkyl side-chain (XX).

The OSCs eluting in cluster 3 (Fig. 3b) exhibit molecular ions at m/z 444, 446, or 448 (e.g., Fig. 4a). Based on these mass spectral data and on the data obtained from the desulphurisation experiment, these compounds are tentatively identified as C_{30} homologues of the above-mentioned unsaturated C_{25} thiolenes having two to four double bonds in the alkyl side chains (XXI).

In order to further substantiate the structural assignments of these polyunsaturated thiolenes, catalytic hydrogenation was performed. The m/z 115 mass chromatogram of the catalytically hydrogenated LMWA fraction (*N.B.* this fraction contains all the OSC present in the Ag^+ -TLC fraction with R_f -values of 0.0-0.1) again shows four clusters but with a less complex nature (cf. Fig. 3b and c). The hydrogenated OSCs of cluster 1 (Fig. 3c) show mass spectra identical to those of the synthetic C_{25} HBI thiolenes (XVIII). Coinjection of the synthetic C_{25} HBI thiolenes with the hydrogenated LMWA fraction confirmed this assignment.

The mass spectra of the hydrogenated OSCs of cluster 3 (Fig. 3c) are also similar to one another (Fig. 4b) and exhibit many fragments identical to those present in the mass spectra of C_{25} HBI thiolenes (XVIII). In addition, fragments which are offset by 70 daltons (m/z 381, 452 versus m/z 311, 382:

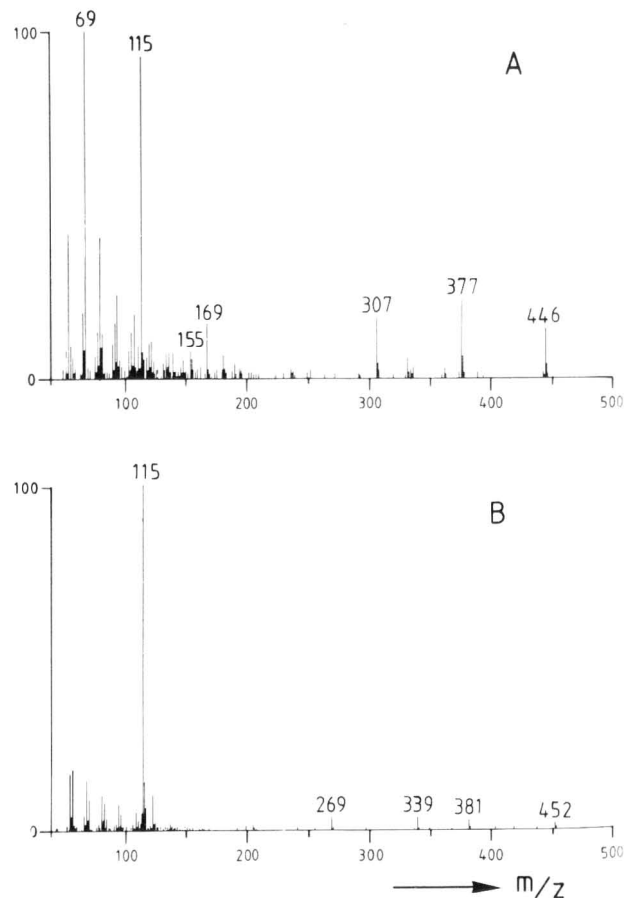


FIG. 4. Mass spectra (subtracted for background) of (a) a polyunsaturated (3 double bonds) C_{30} HBI thiolane (XXI) in the extract of the Black Sea sediment and (b) saturated C_{30} HBI thiolane (XXII) obtained after catalytic hydrogenation of the LMWA fraction of the Black Sea sediment extract.

cf. Figs. 2b and 4c) are also present. These similarities and the desulphurisation data indicate that these hydrogenated OSCs (Fig. 3c) are the C_{30} pseudohomologues (XXII) of the C_{25} HBI thiolanes (XVIII).

The data obtained after hydrogenation are consistent with the tentative assignment of the novel OSCs eluting in clusters 1 and 3 (Fig. 3b) as unsaturated C_{25} HBI thiolanes (XX) possessing one to two double bonds in the long alkyl side-chain and structurally related C_{30} pseudohomologues (XXI) possessing two to four double bonds, respectively. The exact positions and stereochemistry of the double bonds in the side chains remain unknown. OSCs possessing a C_{30} HBI carbon skeleton have not been reported before.

Identification of Unsaturated C_{25} - and C_{30} HBI Sulphoxides

The mass spectra of the OSCs eluting in cluster 2 (Fig. 3b) show a major ion at m/z 115 and important fragment ions at 377 or 379 daltons (e.g., Fig. 5a). After catalytic hydrogenation, all the compounds in cluster 2 (Fig. 3c) show similar mass spectra to one another (Fig. 5b). The highest m/z values are shifted to m/z 381, and fragment ions at m/z 115, 269, and 311 became more prominent (cf. Fig. 5a and b). The

latter fragment ions were also observed in the mass spectra of the C_{25} HBI thiolanes (cf. Figs. 5b and 2b). This similarity and the desulphurisation data indicate that the hydrogenated OSC of cluster 2 (Fig. 3c) are structurally related to the saturated C_{25} HBI thiolanes (XVIII). The virtual absence of a molecular ion in the mass spectra of these OSCs is also a feature of the mass spectra of synthetic sulphoxides of the 1-oxo-2,5-dialkylthiolane type (XXIII). These sulphoxides show an important $M^+ - 17$ fragment ion ($-OH$) and a very weak molecular ion (SINNINGHE DAMSTÉ, unpubl. results). This feature and the retention behaviour of these compounds compared to that of the C_{25} HBI thiolanes suggest that these compounds are the corresponding sulphoxides (XIX). In order to prove this tentative identification, the diastereomeric C_{25} HBI sulphoxides (XIX) were synthesised by oxidation of the aforementioned synthetic mixture of C_{25} HBI thiolanes. Coinjection of the synthetic mixture of C_{25} HBI sulphoxides (XIX) with the hydrogenated LMWA fraction confirmed this identification. Hence, the original compounds (cluster 2; Fig. 3b) are identified as unsaturated C_{25} HBI sulphoxides (XXIV) possessing one to two double bonds in their alkyl side chains.

Catalytic hydrogenation of the OSCs eluting in cluster 4 (Fig. 3b) afforded several compounds (Fig. 3c) showing similar mass spectra (e.g., Fig. 5d). These mass spectra show several

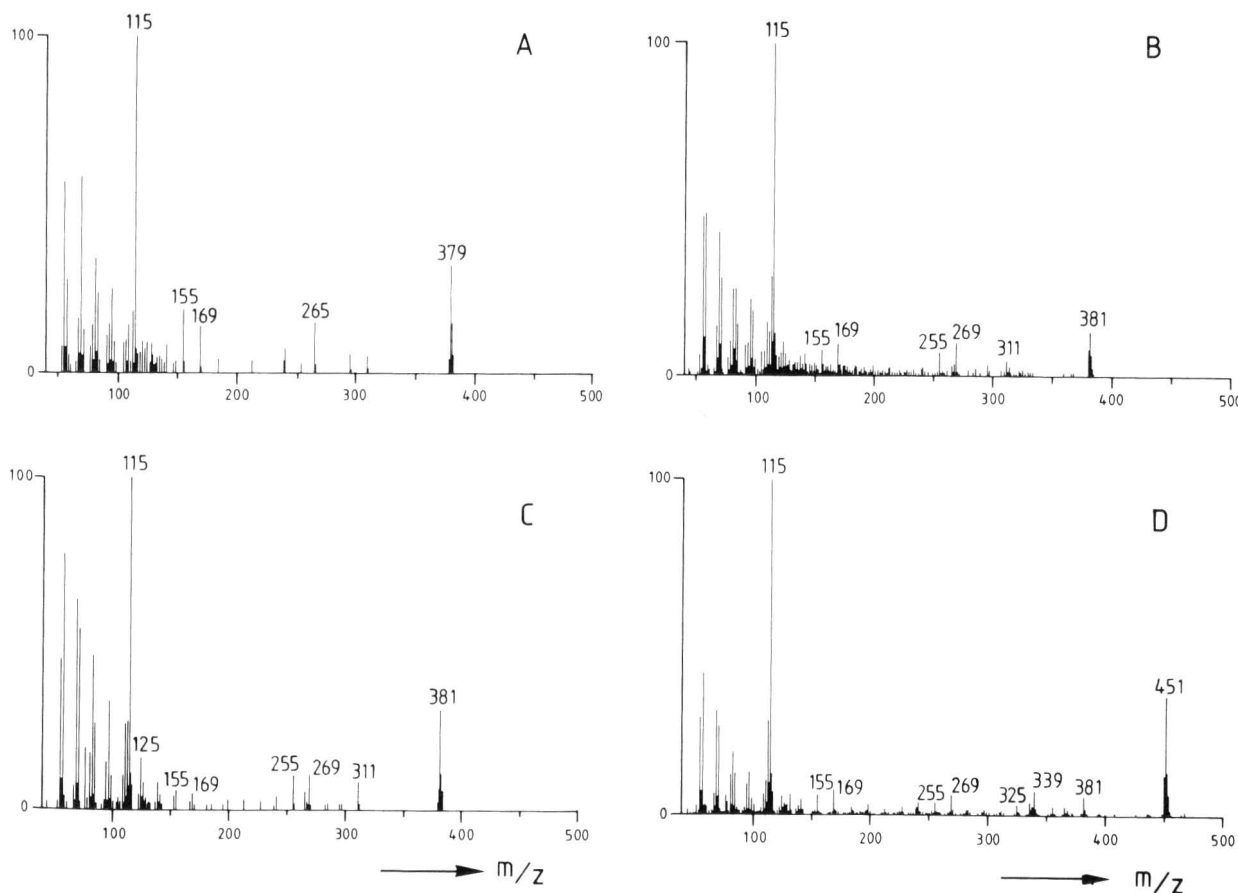


FIG. 5. Mass spectra (subtracted for background) of (a) a mono-unsaturated C_{25} HBI 1-oxothiolane (XXIV) in the extract of the Black Sea sediment, (b) a C_{25} HBI 1-oxothiolane (XIX) obtained after catalytic hydrogenation of the LMWA fraction of the Black Sea sediment extract, (c) a synthetic C_{25} HBI 1-oxothiolane (XIX), and (d) C_{30} HBI 1-oxothiolane (XXV) obtained after catalytic hydrogenation of the LMWA fraction of the Black Sea sediment extract.

fragments (m/z 115, 155, and 169) also present in the mass spectra of the synthetic C_{25} HBI sulphoxides (XIX), in addition to fragments which are shifted 70 daltons (m/z 325, 339, 381, 451 vs. m/z 255, 269, 311, 381; cf. Fig. 5c and d). These similarities and the desulphurisation data indicate that the hydrogenation products of the OSCs eluting in cluster 4 (Fig. 3c) are the C_{30} pseudohomologues (XXV) of the C_{25} HBI sulphoxides (XIX). The highest m/z values present in the mass spectra, of the non-hydrogenated OSCs lead to their tentative identification as unsaturated C_{30} HBI sulphoxides (XXVI) possessing two to four double bonds in the alkyl side chain. The exact position of the double bonds in the alkyl side chain was not determined.

Identification of C_{25} HBI Benzo[*b*]thiophenes

A benzo[*b*]thiophene (XXVII) possessing a C_{25} HBI carbon skeleton is present in relatively small amounts in the Jurfed Darawish oil shale. This identification is based on comparison of the mass spectral data with known fragmentation patterns of alkylbenzo[*b*]thiophenes (PERAKIS, 1986; SINNINGHE DAMSTÉ et al., 1987). The mass spectrum of XXVII shows a molecular ion at m/z 372 (70%), fragment ions at m/z 329 (100%) and m/z 245 (20%) due to β -cleavage, and a secondary fragment ion at m/z 203 (60%). The abundance of the fragment ion at m/z 329 relative to that at m/z 245 is attributable to the formation of a secondary, rather than a primary, alkyl radical. This tentative assignment awaits further confirmation by comparison of relative retention time and mass spectral data with those of an authentic standard.

Desulphurisation of the Polar Fraction of the Black Sea Sediment Extract

SCHMID (1986) and SINNINGHE DAMSTÉ et al. (1988, 1990) have shown that resin fractions may contain sulphur-linked, macromolecularly bound biomarkers which can be released by desulphurisation of these fractions. In order to assess

whether compounds with HBI carbon skeletons also occur in this mode in Recent sediments, the polar fraction (containing resins) of the extract of the Black Sea sediment was desulphurised using Raney Ni. The hydrocarbons obtained after desulphurisation are dominated by phytane, but also contain considerable amounts of C_{25} and C_{30} HBI alkanes (Fig. 6; II and III, respectively). These results indicate that C_{25} and C_{30} HBI carbon skeletons are also part of sulphur-rich resins. A desulphurisation experiment accidentally performed with less reactive Raney Ni (the reactivity of this catalyst decreases upon storage) yielded, in addition to II and III, minor amounts of mono- and polyunsaturated C_{25} and C_{30} HBI thiolanes. This may indicate that these compounds are bonded to the macromolecular network via one or more sulphur bridges.

In order to ensure that the compounds with a HBI carbon skeleton released from the polar fraction upon desulphurisation are bound to a macromolecule via a sulphur linkage, the polar fraction was reduced with $LiAlH_4$ (PAYZANT et al., 1986) prior to desulphurisation. This reduction step was performed to convert any C_{25} and C_{30} HBI sulphoxides and/or sulphones into their corresponding thiolanes. This reduction yielded minor amounts of polyunsaturated C_{25} and C_{30} HBI thiolanes (<0.3 wt% of the polar fraction), indicating the presence of polyunsaturated C_{25} and C_{30} HBI sulphoxides and/or sulphones in the polar fraction. After removal of these thiolanes by column chromatography, the polar fraction was desulphurised with Raney Ni. The hydrocarbons obtained after desulphurisation are the same as those mentioned above. These results indicate that HBI carbon skeletons are bound via a sulphur linkage to a macromolecule.

DISCUSSION

Origin of HBI OSCs

Several recent studies (SINNINGHE DAMSTÉ et al., 1987, 1989a,c; TEN HAVEN et al., 1990) describe the occurrence of

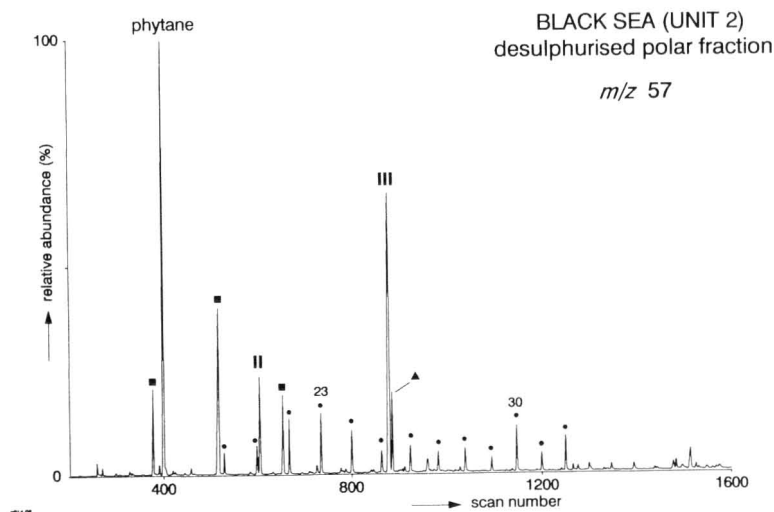


FIG. 6. Partial mass chromatogram of m/z 57 showing the distribution of saturated hydrocarbons obtained after desulphurisation of the polar fraction of the Black Sea sediment extract. Key: squares = C_{14} - C_{18} fatty acid ethylesters (artefacts of the desulphurisation experiment); circles = n -alkanes (the arabic numbers indicate the number of carbon atoms of n -alkanes); triangle = C_{30} HBI monoene.

C₂₀ and C₂₅ HBI thiophenes in consolidated sediments and immature oils. Corresponding thiolanes (C₂₅) have been tentatively assigned in sediments of the Gulf of California (TEN HAVEN *et al.*, 1990). SINNINGHE DAMSTÉ *et al.* (1989a,b) have proposed that abiogenic addition of H₂S to the double bonds of the widely occurring di- and/or polyunsaturated HBI alkenes (ROWLAND and ROBSON, 1990, and references cited therein) initiates the formation of these OSCs during early diagenesis. H₂S addition to a double bond followed by an intramolecular addition of the resulting thiol to another nearby double bond will form cyclic OSCs. Recently, KOHNEN *et al.* (1989) demonstrated the possibility for incorporation of inorganic polysulphides into functionalised lipids during early diagenesis. However, the actual mechanism(s) of sulphur incorporation is (are) still unclear as addition of H₂S or polysulphides to a non-activated double bond will be difficult under the mild conditions (low temperature) prevailing during deposition of marine sediments if some sort of catalysis is not involved. Nevertheless, the presence of a limited number of all possible structural isomers of HBI OSCs (SINNINGHE DAMSTÉ *et al.*, 1987, 1989a,b; TEN HAVEN *et al.*, 1990; and results described in this paper) indicates that the incorporation of inorganic sulphur species occurs at specific sites of the precursor.

The presence of unsaturated C₂₅ and C₃₀ HBI thiolanes in a Recent sediment of the Black Sea (age 3–6 × 10³ a) strongly supports their formation during early diagenesis. The co-occurrence of C₂₅ and C₃₀ unsaturated HBI thiolanes and HBI polyenes with the same carbon skeleton is consistent with a precursor-product relationship between these compound classes. Since it is thought that the presence of at least two double bonds (or other functionalities) in the precursor is a prerequisite for the formation of thiolanes (SINNINGHE DAMSTÉ *et al.*, 1988, 1989b), the fact that the polyunsaturated HBI thiolanes (C₂₅, 1–2 double bonds; C₃₀, 2–4 double bonds) possess two double bonds less than the corresponding HBI polyenes (C₂₅, 3–4 double bonds; C₃₀, 4–6 double bonds) further supports this precursor-product relationship. This relationship testifies to their formation by a reaction of inorganic sulphur species with double bonds of the HBI alkenes and further indicates that these OSC can be considered as biomarkers like their precursor alkenes. The origin of these polyunsaturated HBI alkenes is not known, though an algal source has been suggested (J. K. VOLKMAN, pers. comm., 1989).

The C₂₅ HBI thiolanes (XVIII) found in the samples from the Gulf of California and offshore California are either diagenetic products of unsaturated thiolanes or are formed directly by sulphur incorporation into C₂₅ HBI dienes with double bond positions in the C-1'–C-6' part (see II). A C₂₅ HBI diene with double bonds in that part of the molecule inferred from its mass spectrum was recently identified in field samples of sea-ice diatoms (NICHOLS *et al.*, 1988). Thus, in this case, these OSCs may be considered as possible biomarkers for diatoms.

It is noteworthy that only one structural isomer of both unsaturated C₂₅ and C₃₀ HBI thiolanes is present since additional double bonds (up to four double bonds in the C₃₀ homologue) still exist in these compounds. The reactivity of the additional double bonds towards inorganic sulphur species

is indicated by the fact that HBI sulphur compounds are linked via (a) sulphur bridge(s) to a macromolecule (see desulphurisation results of polar fraction from the Black Sea sediment extract). Hence, the other double bonds are not in a favourable position for incorporation of sulphur in an intramolecular fashion leading to thiolanes and/or thianes. For the formation of such cyclic sulphides the two double bonds have to be separated by 0 to 3 sp³-hybridised carbon atoms (SINNINGHE DAMSTÉ *et al.*, 1989b). DE LEEUW *et al.* (1989) have recently proposed that double bond isomerisations in immature sediments occur only via tertiary carbocations and not via secondary carbocations. TEN HAVEN *et al.* (1989) demonstrated that the isomerisation of Δ⁵-sterenes to the Δ⁴-sterenes starts already in the upper few meters of sediments, which indicates that isomerisation of double bonds via tertiary carbocations is already occurring during the early stages of diagenesis. Considering this and the fact that C₂₅ and C₃₀ polyunsaturated HBI alkenes (up to six double bonds) which possess five to six tertiary substituted carbon atoms exclusively incorporate sulphur in an intramolecular fashion at positions C1' and C4' (see II and III), it has to be concluded that sulphur incorporation occurred before the double bonds may have isomerised.

Diagenetic Pathways of HBI OSCs

Several authors have suggested that a sequence of reactions from thiolanes/thianes via thiophenes to benzo[*b*]thiophenes and finally dibenzothiophenes is related to increasing diagenesis (PERAKIS, 1986; SINNINGHE DAMSTÉ and DE LEEUW, 1987, 1990; SINNINGHE DAMSTÉ *et al.*, 1987, 1989b,c). Supporting evidence for this diagenetic pathway is obtained from this study.

The identical and highly characteristic carbon skeleton of the various HBI OSCs with different sulphur-containing functional groups detected in the samples permits suggestions of product-precursor relationships between these various compound classes. In Table 1 an overview of the samples and the detected C₂₅ HBI alkenes and sulphur compounds is given. The maturity level of the samples investigated is difficult to assess. Vitrinite reflectance data indicate that they all are immature. Undoubtedly, the Recent Black Sea sediment is the least mature sample. On the other hand, since the Jurfed Darawish oil shale sample is the only consolidated sediment investigated it is assumed that this sample represents the relatively most mature sample studied. A diagenetic scheme can be postulated for the C₂₅ HBI alkenes and sulphur compounds as they are encountered in all the samples. The co-occurrence of HBI alkenes and unsaturated HBI thiolanes in the Black Sea sediment, the co-occurrence of saturated HBI thiolanes and HBI thiophenes in the DSDP samples of the Gulf of California, and the co-occurrence of HBI thiophenes and HBI benzo[*b*]thiophenes in the Jurfed Darawish oil shale (Table 1) provide strong evidence for their sequential diagenetic transformations.

It is assumed that the unsaturated C₂₅ HBI thiolanes (XX) present in the most immature sample, the Recent Black Sea sediment, are formed by an addition of sulphur to a double bond of polyunsaturated C₂₅ HBI alkenes, followed by the intramolecular addition of the intermediate thiol to another

Table 1. Background information for samples investigated and HBI hydrocarbons and OSC encountered.

Sample	Hole, core, section interval (cm)	Age	Lithology	C _{org} ^a	%R _o	1	2	3	4	5	6
Black Sea (Unit 2)	site 117, 27-71	Holocene	sapropel	16.1	n.d.	II ^b , III ^c	XX, XXI	n.d.	n.d.	n.d.	XXIV, XV
Gulf of California	DSDP481A-10-2, 110-125	l. Pleist. ^d	diatom. ^e mud	5.76	0.3	n.d.	n.d.	XVIII	XV	n.d.	XIX ^f
offshore California	DSDP471-34-2, 103-107	l. Mioc. ^g	silty claystone	0.81	0.3 ^h	n.d.	n.d.	XVIII	XV	n.d.	XIX ^f
offshore California	DSDP467-54-2, 100-115	l. Mioc. ^g	silty claystone	4.37	0.4 ⁱ	n.d.	XX	XVIII	XV	n.d.	XIX ^f
offshore California	DSDP471-44-1, 100-118	m. Mioc. ^g	silty claystone	1.12	0.4 ^h	n.d.	n.d.	XVIII	XV	n.d.	XIX ^f
offshore California	DSDP467-97-2, 105-109	m. Mioc. ^g	calc. ^j claystone	1.63	0.4 ⁱ	n.d.	n.d.	XVIII	XV	n.d.	XIX ^f
Jurf ed Darawish	165-166m	Senonian	phosphorite	8.29	0.4	n.d.	n.d.	n.d.	XV, XVI	XXVII	n.d.

Key: n.d. = not detected 1 = HBI hydrocarbons 2 = unsaturated HBI thiolanes 3 = HBI thiolanes 4 = HBI thiophenes 5 = HBI benzo[b]thiophenes 6 = HBI sulphoxides
^a in wt.% ^b possessing 3-4 double bonds ^c possessing 4-6 double bonds ^d Pleistocene ^e diatomaceous ^f formed upon sample storage ^g Miocene ^h estimated from vitrinite reflectance versus depth plot for DSDP hole 471 (RULLKÖTTER *et al.*, 1981) ⁱ estimated from vitrinite reflectance versus depth plot for DSDP hole 467 (RULLKÖTTER *et al.*, 1981) ^j calcareous

double bond. The intermediate thiol has not yet been encountered. It is assumed that the unsaturated thiolanes are intermediates in formation of the saturated thiolanes, although, as already mentioned above, the saturated C₂₅ HBI thiolanes could also be formed directly by sulphur incorporation into C₂₅ HBI alkadienes. Subsequent aromatisation of the thiolane ring will yield thiophenes (XV). The benzo[b]thiophene XXVII is detected in the relatively most mature sediment studied (Jurf ed Darawish oil shale). Therefore, the HBI benzo[b]thiophene probably represents the subsequent diagenetic transformation of HBI sulphur compounds and is formed by cyclisation and aromatisation reactions of HBI thiophenes. It is expected that the presence of a double bond in the alkyl side chain of the precursor HBI thiophene would facilitate this cyclisation reaction. However, such a hypothetical precursor has, as yet, not been detected. It is notable that these benzo[b]thiophenes are already formed at low maturity levels as the organic matter of these Jordan Oil Shale samples can be classified as thermally immature according to their vitrinite reflectance (Table 1). Figure 7 summarises the diagenetic reactions proposed for HBI sulphur compounds.

The previous discussion deals with HBI sulphur compounds containing exclusively intramolecularly incorporated sulphur. However, the desulphurisation experiment of the polar fraction of the Black Sea sample indicated the presence of C₂₅ HBI OSCs bound via an acyclic sulphur linkage to a macromolecule. These compounds may be formed either by intermolecular sulphur incorporation into (poly)unsaturated C₂₅ HBI OSCs or by intramolecular incorporation of sulphur into macromolecularly bound C₂₅ HBI alkenes (Fig. 7). Upon increasing diagenesis the weak acyclic or cyclic sulphur bonds may break, leading to the formation of free (poly)unsaturated C₂₅ HBI thiolanes or macromolecularly bound C₂₅ HBI alkenes, respectively (Fig. 7). However, it is expected that upon increasing diagenesis the macromolecularly bound C₂₅ HBI thiolanes will aromatise to thiophenes. Further thermal stress may cause a disproportionation of the relatively weak sulphur bridges, and the HBI thiophenes will be released from the macromolecule (Fig. 7). From the desulphurisation experiments it is not possible to assess if all the macromolecularly bound HBI carbon skeletons contain additional intramolecular sulphur bridges (e.g., thiolanes). The possible macromolecularly bound HBI hydrocarbons, via a sulphur linkage, may also be released during increasing diagenesis (Fig. 7).

With respect to the formation of the HBI-sulphoxides detected in various samples it should be mentioned that re-analyses of the "aromatic hydrocarbon" fractions from the Gulf of California and offshore California samples, which had been stored frozen for almost five years (without solvent), revealed that a large portion of the C₂₅ HBI thiolanes (XVIII) had become oxidized to the corresponding sulphoxides (XIX). The sulphoxides identified in the Black Sea sample may also have been formed during its storage, although the whole sediment was stored frozen and the analyses were carried out without delay in order to minimize exposure to air. Moreover, other sulphur-rich "aromatic hydrocarbon" fractions studied in our laboratory that also were stored at low temperatures for a considerable time span (2-5 years), albeit with solvent, did not contain major amounts of sulphoxides.

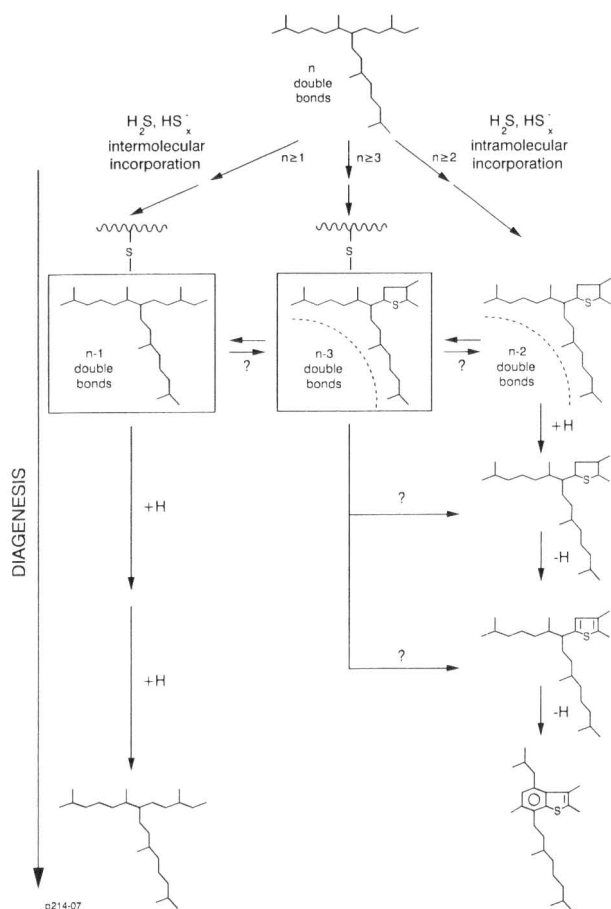


FIG. 7. Diagenetic scheme showing the possible origins and presumed pathways of C₂₅ HBI alkenes and C₂₅ HBI OSCs and macromolecularly bound C₂₅ HBI skeletons encountered in several oils and sediment extracts.

PAYZANT *et al.* (1983) identified terpenoid sulphoxides in virgin oils from the Alberta oil sand reservoirs and concluded that these sulphoxides were formed in the reservoir as a result of mildly oxidative post-depositional conditions. However, such conditions are unlikely for Black Sea sediments belonging to Unit 2 (age 3–6 × 10³ a) as the Black Sea is presently a water body with anoxic conditions below a water depth of about 120 m which have developed since about 9000 years ago (DEUSER, 1974).

Geochemical Implications

OSCs possessing carbon skeletons different from those of HBI OSCs are not expected to show a different diagenetic behaviour or to have a different origin. It is therefore tempting to propose that the early diagenetic formation of HBI sulphur compounds via sulphur incorporation into alkenes and their subsequent diagenetic pathways as described in this study (Fig. 7) are also valid for OSCs in general.

Many studies report depth profiles of the concentrations of HBI alkenes (C₂₀, C₂₅, and C₃₀) in surface sediments from diverse parts of the world (e.g., FARRINGTON *et al.*, 1977; WADE and QUINN, 1979; PRAHL *et al.*, 1980; BARRICK *et al.*, 1980; BARRICK and HEDGES, 1981; VOLKMAN *et al.*,

1983; REQUEJO and QUINN, 1983; REQUEJO *et al.*, 1984; VENKATESAN and KAPLAN, 1987; VENKATESAN, 1988). All these studies, except those made by REQUEJO *et al.* (1984) and VENKATESAN and KAPLAN (1987), showed that the concentrations of the HBI alkenes are highest near the sediment-water interface and decrease markedly with depth to such an extent that at a few centimetres depth their concentration has decreased by an order of magnitude. Most workers demonstrated that these trends are not related to major changes in the abundance of the organisms contributing to the organic matter in the sediments. REQUEJO and QUINN (1983) ruled out hydrogenation as a possible transformation mechanism active in the Narragansett Bay sediments as no HBI alkenes were detected in any sample. VOLKMAN *et al.* (1983) suggested incorporation of the alkenes into humic substances during early diagenesis as an explanation for their rapid decrease in the Peruvian sediments. Biodegradation was also proposed as a mechanism responsible for the observed trends (VOLKMAN *et al.*, 1983). However, laboratory biodegradation experiments showed that HBI hydrocarbons are more resistant to biodegradation than straight-chain hydrocarbons (ROBSON and ROWLAND, 1988b). Therefore, biodegradation cannot be considered as a major mechanism causing the observed trends since, for instance, VOLKMAN *et al.* (1983) observed a slight increase in concentration of *n*-alkanes with depth, which is in sharp contrast with the profile of the HBI alkenes.

The widespread occurrence of HBI OSCs, their early diagenetic formation, and the fact that bacterial sulphate reduction leading to formation of hydrogen sulphide is a common phenomenon in Recent marine organic-carbon-rich sediments suggest that either intra- or intermolecular incorporation of sulphur into HBI alkenes may explain their rapid decrease in surface sediments. TEN HAVEN *et al.* (1990) provided supporting evidence for this hypothesis. They demonstrated that a sediment sample of the Peruvian upwelling area, originating from a sediment depth in which no HBI alkenes were present, contains a considerable amount of C₂₅ HBI carbon moieties bound via a sulphur bridge to a macromolecule. However, in order to confirm this proposed pathway of HBI alkenes, quantitative data are required to demonstrate that HBI OSCs are the transformation products of a significant proportion of the HBI alkenes.

In the literature the structural elucidation of C₂₅ and C₃₀ HBI alkenes has been based mainly on the analysis of their hydrogenation products. However, some confusion was generated since some of these alkenes could not be fully hydrogenated, and it has been concluded by some workers that the hydrogenation products are probably cyclic (although it was also acknowledged that the hydrogenation product could be a partially hydrogenated HBI alkene; VENKATESAN and KAPLAN, 1987). This confusion was clarified by ROWLAND *et al.* (1990) in the case of the C₂₅ HBI alkenes. With respect to the C₃₀ HBI polyenes present in the Black Sea sample, this study provides circumstantial evidence that these compounds are acyclic. Catalytic hydrogenation of the corresponding unsaturated C₃₀ HBI thiolanes yielded exclusively compounds showing a molecular ion at *m/z* 452, which is consistent with a C₃₀ thiolane with an acyclic carbon skeleton. Raney Ni desulphurisation and subsequent hydrogenation of these OSCs yielded (besides the C₃₀ HBI alkane) a minor amount

of a related monoene. Catalytic hydrogenation of the C₃₀ polyenes yielded the fully hydrogenated III and a related monoene. The latter shows a mass spectrum similar to that of the monoene obtained upon desulphurisation of the C₃₀ HBI OSCs. Therefore, it is concluded that the C₃₀ HBI polyenes present in the Black Sea sample are indeed acyclic.

CONCLUSIONS

- The co-occurrence of polyunsaturated HBI alkenes and polyunsaturated HBI thiolanes possessing two double bonds less than these polyunsaturated HBI alkenes in Recent Black Sea sediments is an eloquent testimony to the formation of these OSCs by reactions of inorganic sulphur species with specific double bonds of the HBI polyenes during early diagenesis.
- Unsaturated and saturated HBI thiolanes (C₂₅) are intermediates in the formation of the widely occurring HBI thiophenes. Subsequent ring-closure of the alkyl side chain followed by aromatisation results in a benzo[*b*]thiophene.
- C₂₅ and C₃₀ HBI sulphur compounds and hydrocarbons are bound via a sulphur bridge to a macromolecule. These macromolecularly bound compounds may be released by cleavage of the sulphur bridges, at a later stage of diagenesis.
- OSCs possessing carbon skeletons different from those of HBI OSCs are not expected to show a different diagenetic behaviour or to have a different origin. It is therefore postulated that the early diagenetic formation of HBI sulphur compounds via sulphur incorporation into alkenes and their subsequent diagenetic pathways (Fig. 7) are also valid for OSCs in general.
- Intra- and intermolecular incorporation of inorganic sulphur species into HBI alkenes may explain the frequently observed rapid decrease in concentration of these alkenes with depth in Recent marine sediments.
- HBI thiolanes can be oxidized to the corresponding sulphoxides during sample storage, but sulphoxides may also be formed in sediments (*in situ*).

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APPENDIX

