

Novel polycyclic polyprenoid sulfides in sediments

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A series of polycyclic sulfides (C_{15} , C_{20} , C_{25} , C_{30}) deriving from regular isoprenoids has been characterized in sediments by mass spectrometry, synthesis of C_{20} members, and NMR structural elucidation of two C_{30} isomers isolated from a geological sample.

The structure of numerous organo-sulfur compounds identified in sediments clearly indicates that incorporation of sulfur into biomolecules of decaying organisms takes place at the earliest stages of diagenesis.¹ Sulfurization most likely occurs by reaction of inorganic sulfur species (elemental S, H_2S , polysulfides) generated by bacterial processes with either organic components directly inherited from organisms or their functionalised derivatives. However, the precise mechanisms of these low-temperature sulfurization reactions still remain unclear and are at present the subject of many studies.² Structural determination of organo-sulfur components can give very useful information on their origin and their mode of formation. We report here the identification of a series (C_{15} , C_{20} , C_{25} , C_{30}) of novel polycyclic polyprenoid sulfides in immature sediments, the structures of which imply sulfur incorporation into partially cyclised regular isoprenoids.

Several organic extracts from sulfur-rich sediments were studied³ and the aliphatic sulfide fraction was analysed by GC with a sulfur-specific FPD detector and by GC-MS. In all the samples selected, the m/z 169 mass fragmentogram shows the presence of two major isomeric compounds, the mass spectra of which exhibit a molecular ion at m/z 444 corresponding to an elemental composition of $C_{30}H_{52}S$ (verified by high resolution mass spectrometry) and a fragment triplet at m/z 156, 169 (base peak) and 185, all containing the sulfur atom as demonstrated by tandem mass spectrometry. In the peculiar case of an Italian Triassic marl, however, the m/z 169 mass fragmentogram highlighted four repetitive patterns of eight isomeric structures comprising two major, two minor and four extremely minor compounds more or less well resolved depending on the pattern considered. The molecular ions of each group,‡ respectively at m/z 240 ($C_{15}H_{28}S$), 308 ($C_{20}H_{36}S$), 376 ($C_{25}H_{44}S$) and 444 ($C_{30}H_{52}S$)—the two major C_{30} skeletons being identical to that of the other samples—obviously point towards regular polyprenic structures differing by one isoprenic unit ($\Delta m/z = 68$, respectively). Moreover, each compound displays the same fragment triplet as for the previous C_{30} sulfides, thus suggesting the presence of a common sulfurized moiety. Small quantities of an almost pure major C_{30} compound were obtained after argentation TLC fractionation of a particularly simple sulfide fraction where the two C_{30} species were by far the major components. Desulfurization of the isolated product was achieved under drastic conditions with lithium-ethylamine and afforded a tetracyclic alkane, the mass spectrum of which shows a similar fragmentation pattern to that of scalarane, a tetracyclic sesterterpenoid which results from the cyclisation of a regular C_{25} isoprenoid skeleton. Additional valuable information was obtained from the sulfone formed by treatment of the C_{30} sulfide with OXONE®.⁴ The lack of H-D exchange (BuLi, CD_3SOCD_3)⁵ observed by MS showed the absence of any acidic proton α to the sulfur. These preliminary data indicated that all these closely related unknown compounds could result

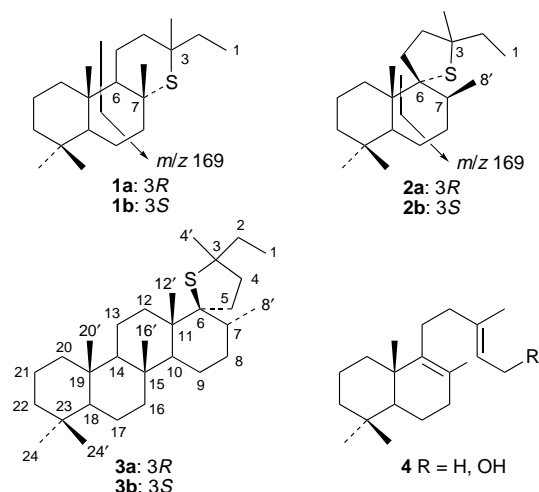
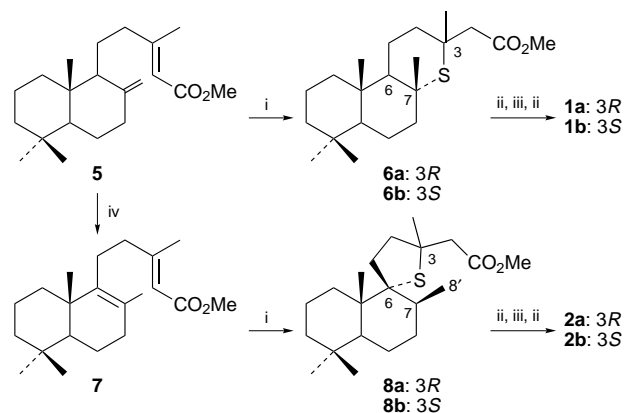


Fig. 1 Postulated (1–3) and identified (2 and 3) structures of the geological sulfides and probable precursors 4 for 2

from sulfur incorporation into partially cyclised regular isoprenoids, leading to structure types 1–3 shown in Fig. 1.‡

Focusing first on the C_{20} sulfide group of the Italian marl which comprises eight well-resolved isomers in the m/z 169 mass fragmentogram, we undertook the synthesis of reference compounds (Scheme 1), starting from methyl copalate here represented as its *ent*-isomer 5 for uniformity with other structures. Hence, sulfurization of 5, achieved in DMF by means of S_8 -NaSH in a 1:4 molar ratio (HSSS⁻ major species),¶ gave exclusively a mixture of the two thiane epimers at position 3, 6a and 6b, which were fully characterised by 2D NMR after TLC separation. Complete reduction of the methoxycarbonyl function of 6a and 6b led to the corresponding thianes 1a and 1b whose mass spectra were markedly different from that of the sedimentary compounds, therefore allowing us to exclude this kind of structure for the naturally occurring components. Other suitable candidates were spiro-



Scheme 1 Synthesis of the C_{20} reference sulfides 1 and 2: i, S_8 -NaSH (1:4, mol/mol) in DMF under argon, 50 °C, 24 h (6, 90%) or 40 h (8, 10%); ii, $LiAlH_4$, THF; iii, $MeSO_2Cl-Et_3N$, CH_2Cl_2 ; iv, HCO_2H , CH_2Cl_2

Table 1 ^1H (500.1 MHz) and ^{13}C (125.8 MHz) NMR data for the sulfide **3a** (Bruker ARX 500; in C_6D_6 ; δ in ppm relative to SiMe_4)

C-atom	δ_{C}	δ_{H}		C-atom	δ_{C}	δ_{H}		C-atom	δ_{C}	δ_{H}	
1	11.05	1.12 t		9	21.10	1.54 (eq)	1.34 (ax)	17	18.82	1.58 (eq)	1.41 (ax)
2	37.36	1.67	1.86	10	54.34	1.15		18	56.69	0.86	
3	56.13			11	39.45			19	37.76		
4	46.90	1.85	1.97	12	36.70	2.33 (eq)	1.55 (ax)	20	40.19	0.82 (ax)	1.75 (eq)
4'	27.82	1.46 s		12'	19.70	1.24 s		20'	16.68	0.92 s	
5	28.96	1.85	2.02	13	17.85	1.66 (eq)	1.44 (ax)	21	19.06	1.49 (eq)	1.72 (ax)
6	76.27			14	61.72	0.77		22	42.54	1.26 (ax)	1.50 (eq)
7	37.82	2.09		15	38.35			23	33.45		
8	32.81	1.17 (ax)	1.71 (eq)	16	42.54	0.91 (ax)	1.79 (eq)	24	33.55	1.02 s	
8'	20.23	1.34 d		16'	17.43	0.90 s		24'	21.56	0.96 s	

thiolanes **2**, which could account for the presence of eight isomers with regard to the possible configurations at C-3, C-6 and C-7. Two of them, **2a** and **2b**, were successfully obtained with the same reaction sequence as above, starting from the methyl copalate isomer **7**, the sulfuration of which specifically afforded, although in moderate yield, compounds **8a** and **8b** epimeric at C-3. Again, their structures were unambiguously determined by 2D NMR studies on the corresponding alcohols which were easily separated by HPLC. Based on comparison of mass spectra and GC retention times, thiolanes **2a** and **2b** were conclusively identified with two of the very minor sedimentary structures.

We finally isolated the two major ubiquitous C_{30} sulfides **3a** and **3b** from the organic extract of a sedimentary rock (Toarcian, Paris basin, France) using a combination of liquid chromatographies. Their structures were established by NMR studies which led to the complete assignment of proton and carbon signals listed for **3a** in Table 1. For each compound, the basic carbon framework was deduced, with the help of the DEPT spectrum, from the HMBC spectrum correlation ($^{2,3}J_{\text{CH}}$ 7 Hz) network clearly showing that these structures indeed result from the cyclisation of a regular C_{30} isoprenoid. Stereochemical information was obtained from the NOESY spectra which showed that **3a** and **3b** are epimeric at C-3 and bear the same *trans-transoid-trans* arrangement of the fused rings with axial ring-junction methyl groups on the same side of the mean plane of the molecule, a $6S'$ configuration—*i.e.* the inverse of that of the synthetic references **2**—and a Me-8' in the thermodynamically stable equatorial position.

In the light of these results, it was inferred that the eight structures belonging to a same molecular pattern are spirothiolanes isomeric at C-3, C-6 and C-7, the four extremely minor compounds being those which bear the 8'-methyl group at C-7 in the thermodynamically unfavourable axial position. Their formation most likely involves sulfur incorporation into partially cyclised regular isoprenoids, such as **4**, still possessing two double bonds in their skeleton. This implies that this process must operate at the earliest stages of diagenesis. Remarkably, apart from the case of the Italian marl, their distribution in all the geological samples investigated is almost exclusively restricted to the two C_{30} members **3a** and **3b**, the other components, if any, being hardly detectable. This could reflect either a stereoselectivity in sulfur incorporation due to the mechanism itself—either linked or not to the existence of particular precursors—or that the $6R$ isomers formed initially are thermodynamically less stable and/or more susceptible to further geochemical transformations than their $6S'$ epimers. Moreover, in most cases, the C_{30} thiolanes overwhelmingly dominate the whole sulfide fraction, a fact which could indicate a major input of their biological precursors in sediments—although these C_{30} tetracyclic terpenoids derived from regular isoprenoids are not known today in living organisms—*or*, more speculatively, that these sedimentary sulfides are directly inherited from producing organisms.

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Footnotes and References

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‡ MS data (Finnigan MAT TSQ 700 EI (70 eV), *m/z* (rel. int.) for the first-eluting major sulfide of each group. $\text{C}_{15}\text{H}_{28}\text{S}$: 240 (M^+ , 58%), 183 (3), 169 (100), 156 (22); $\text{C}_{20}\text{H}_{36}\text{S}$: 308 (M^+ , 38%), 185 (3), 169 (100), 156 (22); $\text{C}_{25}\text{H}_{44}\text{S}$: 376 (M^+ , 41%), 185 (18), 169 (100), 156 (38); $\text{C}_{30}\text{H}_{52}\text{S}$: 444 (M^+ , 56%), 429 (8), 415 (3), 259 (12), 185 (38), 169 (100), 156 (40).

§ Since absolute configurations of the geological compounds are unknown, structures are arbitrarily drawn in the most usual way for terpenoid geochemical markers. All configurations subsequently discussed are relative to that represented on the drawings. Carbon numbering derives from that of the corresponding uncyclised regular isoprenols.

¶ Detailed mechanistic considerations concerning this sulfuration process will be included in an article on sulfur incorporation into unsaturated compounds (P. Schneckenburger, J. Poinsot, P. Adam and P. Albrecht, in preparation).

|| Other polycyclic terpenoids derived from higher regular isoprenoids and of controversial or unknown origin have been identified in sediments: they are ubiquitous tricyclic hydrocarbons (D. Heissler, R. Ocampo, P. Albrecht, J.-J. Riehl and G. Ourisson, *J. Chem. Soc., Chem. Commun.*, 1984, 496) and optically-active highly cyclised hydrocarbons of more restricted distribution (P. Schaeffer, J. Poinsot, V. Hauke, P. Adam, P. Wehrung, J.-M. Trendel, P. Albrecht, D. Dessort and J. Connan, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1166; M. Li, C. L. Riediger, M. G. Fowler, L. R. Snowdon and T. A. Abrajano Jr., *Org. Geochem.*, 1996, **25**, 199).

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