**Table 3.** Bond lengths (Å) and angles (°) around the phosphorus atom in compound (**C**). For experimental data see ref. 7. δ has been evaluated as in ref. 1.

| | Exp.[7] | This work |
|---|---|---|
| P–O(5) | 1.700 | 1.724 |
| P–O(8) | 1.763 | 1.764 |
| P–N(2) | 1.703 | 1.679 |
| P–C(9) | 1.811 | 1.802 |
| P–C(10) | 1.818 | 1.803 |
| O(5)–P–O(8) | 171.6 | 179.8 |
| O(5)–P–C(9) | 94.7 | 89.9 |
| O(5)–P–C(10) | 89.7 | 90.1 |
| O(8)–P–C(9) | 93.3 | 90.1 |
| O(8)–P–C(10) | 89.7 | 89.7 |
| C(9)–P–C(10) | 112.8 | 123.5 |
| N(2)–P–O(5) | 86.6 | 88.8 |
| N(2)–P–O(8) | 87.6 | 91.3 |
| N(2)–P–C(9) | 116.5 | 117.0 |
| N(2)–P–C(10) | 130.6 | 119.4 |
| | | δ = 0.07 (for $D$ = 0.085) |

correct relative steric energies. An n.m.r. study of molecule (**D**) (Figure 2) by Denney *et al.*[8] has shown that, at low temperature, the most stable conformation is trigonal bipyramidal, the nitrogen atom being axial (BPT1). At ambient temperature, equivalence of the protons of the methyl groups suggests the existence of a pseudorotation process (1) leading from TBP1 to TBP1* (same geometry but with exchange of the Me positions) through a higher energy trigonal bipyramid BPT2 and two identical square pyramids (SP and SP*). The estimated barrier in solution, is reported to be 46.0 kJ mol$^{-1}$.

$$\text{TBP1} \rightleftarrows \text{SP} \rightleftarrows \text{TBP2} \rightleftarrows \text{SP*} \rightleftarrows \text{TBP1*} \quad (1)$$

Our results agree well with the n.m.r. conclusions as the steric energies found for the optimized geometries of TBP1, SP and TBP2 are, respectively, 99.1, 106.7, and 109.8 kJ mol$^{-1}$.

Estimation of conformational barriers is not an easy task and depends on the way the reaction co-ordinate (Berry co-ordinate here) is described. Within the very simple scheme of simultaneous closing of the $N_{ax}$–P–$O_{ax}$ angle and opening of the $O_{eq}$–P–$O_{eq}$ angle the barrier on the way from TBP1 to SP has been evaluated as 18 kJ mol$^{-1}$ (nitrogen remaining pyramidal). The highest barrier occurs between SP and BPT2 and is more difficult to estimate because of the change in hybridisation of the nitrogen atom.

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# Organic Geochemical Evidence for a Series of $C_{25}$–$C_{28}$ Sulphur-containing Lipids comprising Regular and Irregular Isoprenoid and Unusual Linearly Extended Phytane Skeletons


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A series of alkylthiophenes ($C_{25}$–$C_{28}$), consisting of regular and irregular isoprenoid and unusual linearly extended phytane carbon skeletons, some of which are presently unknown in living organisms, have been identified in a bituminous marl.


The 'aromatic hydrocarbon' fraction of the extractable organic matter from a bituminous marl layer from the northern Apeninnes (Italy; Miocene, 6 × 10$^6$ years) which was deposited under hypersaline conditions,[1] contains series of alkylthiophenes and thiolanes.[2] The origin of these sulphur-containing compounds is now believed to involve reaction of functionalised lipids with inorganic sulphur species such as hydrogen sulphide and polysulphides during early diagenesis.[3–5]

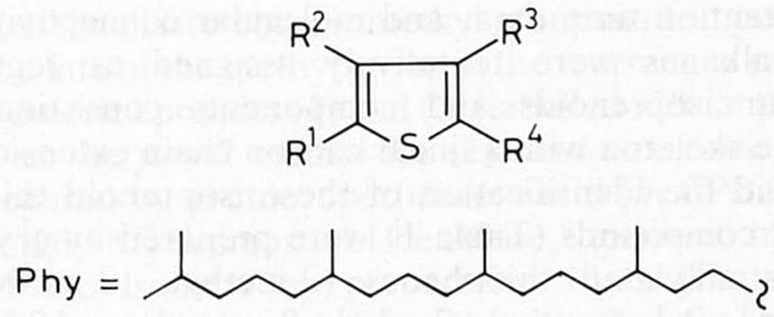


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**Table 1.** Alkyl thiophene standards prepared, the nature of their carbon skeletons, and their abundance in the bitumen (μg/g). Compounds (**1**) and (**2**) were obtained as a mixture (*ca.* 63 : 37).

| | | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Nature of carbon skeleton | Abundance (μg/g) |
|---|---|---|---|---|---|---|---|
| (**1**) | $C_{25}$ | Phy | Me | H | H | Regular isoprenoid | n.d.[a] |
| (**2**) | $C_{25}$ | Phy | H | Me | H | Irregular isoprenoid | n.d.[a] |
| (**3**) | $C_{25}$ | Phy | H | H | Me | Linearly extended phytane | 78[b] |
| (**4**) | $C_{26}$ | Phy | H | Me | Me | Irregular isoprenoid | 59 |
| (**5**) | $C_{26}$ | Phy | Me | H | Me | Regular isoprenoid | 139[c] |
| (**6**) | $C_{26}$ | Phy | H | H | Et | Linearly extended phytane | |
| (**7**) | $C_{27}$ | Phy | H | H | Pr | Linearly extended phytane | 27 |
| (**8**) | $C_{28}$ | Phy | H | H | Bu | Linearly extended phytane | Trace[d] |

[a] n.d. not detected. [b] Includes an additional minor, as yet uncharacterised, $C_{25}$ isoprenoid thiophene. [c] Includes an additional minor, as yet uncharacterised, $C_{26}$ isoprenoid thiophene. [d] Abundance difficult to determine owing to co-elution with another, as yet uncharacterised, $C_{28}$ isoprenoid thiophene.

**Table 2.** Mass spectral characteristics and retention indices of the thiophene standards and retention indices of the corresponding alkanes formed by desulphurisation.[a]

| | Mass spectrum, *m/z* | *I* (thiophenes) | *I* (alkanes) |
|---|---|---|---|
| (**1**) | 378(19), 111(100), 112(50)[b] | 2544 | 2239 |
| (**2**) | | 2544 | 2233 |
| (**3**) | 378(11), 111(100), 112(88) | 2536 | 2270 |
| (**4**) | 392(18), 125(100), 126(68) | 2631 | 2339 |
| (**5**) | 392(16), 125(100), 126(14) | 2610 | 2321 |
| (**6**) | 392(14), 125(100), 126(81) | 2613 | 2367 |
| (**7**) | 406(21), 139(100), 140(81) | 2698 | 2466 |
| (**8**) | 420(25), 153(100), 154(81) | 2793 | 2562 |

[a] The mass spectra were obtained by g.c.–m.s. at 70 eV. Retention indices were measured against co-injected n-alkanes on a CP Sil 5 fused silica capillary column (25 m × 0.32 mm, film thickness 0.12 μm, hydrogen carrier 40 kPa, 130—300 °C at 4 °C $min^{-1}$). [b] Mass spectrum for a mixture of thiophenes (**1**) and (**2**) (*ca.* 63 : 37).

The structure of the major thiophene, 2,3-dimethyl-5-(2,6,10-trimethylundecyl)thiophene, whose carbon skeleton is identical to that of phytane, has recently been established by comparison of the mass spectrum and relative g.c. retention time data with those of a synthesised standard.[3] Other major isoprenoid thiophenes present in the 'aromatic hydrocarbon' fraction from the marl extract occur in the $C_{25}$—$C_{28}$ range.[2] Some structural information on these compounds was obtained from their mass spectra after g.c.–m.s. analysis. The major fragment ions (corresponding to cleavage β to the thiophene ring) indicated thiophene units coupled to a long alkyl chain and smaller alkyl fragments (methyl, dimethyl, ethyl, propyl, and butyl). These cleavages were sometimes accompanied by a significant McLafferty rearrangement ion at 1 *m/z* unit higher. The relative g.c. retention times of these thiophenes indicated that the long alkyl chain was isoprenoidal.

Desulphurisation of the 'aromatic hydrocarbon' fraction with Raney nickel afforded several $C_{25}$–$C_{28}$ isoprenoid alkanes.[5] On the basis of the mass spectra (g.c.–m.s.), relative g.c. retention time data, and molecular connectivity rules,[6] these alkanes were tentatively assigned as regular and irregular isoprenoids and components consisting of the phytane skeleton with a linear carbon chain extension.

To aid the identification of these isoprenoid thiophenes, several compounds (Table 1) were prepared by acylation of various alkylated thiophenes (2-methyl-, 3-methyl-, 2,3-dimethyl-, 2,4-dimethyl-, 2-ethyl-, 2-propyl-, and 2-butylthiophene) with 3,7,11,15-tetramethylhexadecanoic acid [i, $(COCl)_2$, $CH_2Cl_2$, dimethylformamide (DMF); ii, $SnCl_4$], followed by reduction of the resulting ketone ($AlCl_3/LiAlH_4$, $Et_2O$). In the case of the acylation of 3-methylthiophene, a mixture of the 2,3- and 2,4-disubstituted isomers was obtained. The thiophenes and intermediate ketones were fully characterised by mass spectrometry, and high field $^1H$ n.m.r. and i.r. spectroscopy. Desulphurisation of the synthesised thiophenes (W-2 Raney Ni, EtOH, heat) followed by hydrogenation to remove trace amounts of alkenes ($PtO_2$, HOAc, $H_2$) afforded the corresponding alkanes, which were characterised by g.c. and g.c.–m.s. Mass spectral and g.c. retention index data for the alkylthiophenes and g.c. retention index data for the alkanes are given in Table 2.

The alkylthiophenes present in the northern Apennines marl were identified as having structures (**3**)—(**8**), by comparison of their mass spectra and by coelution with the synthesised standards on three stationary phases (CP Sil 5, CP Sil 88, and DB 1701). Similar comparisons were also made with the respective desulphurisation products.

The carbon skeleton of thiophene (**5**) is comparable with that of known lipids[7] which have been identified in bacteria. Thiophene (**4**) has a carbon skeleton which is related to these bacterial lipids, although such a $C_{26}$ compound has yet to be identified. To our knowledge there are no known natural product counterparts with a carbon skeleton similar to those of thiophenes (**3**), (**6**), (**7**), and (**8**) which consist of a linearly extended phytane structure. It is unlikely that these compounds arise from regular or irregular isoprenoids since this would require the breaking of two carbon–carbon bonds during early diagenesis. The origin of such compounds is therefore unknown at present but may reflect an input of functionalised lipids having the same carbon skeleton at the time of sediment deposition. Since the thiophene ring is located at the same relative position, this would suggest that the natural products contain functionalities at the same position, which can then react with inorganic sulphur species during early diagenesis. The biosynthetic origin of such compounds would appear to be unusual since they contain isoprenoidal and n-alkyl units. Examples of known compounds consisting of isoprenoidal and n-alkyl portions are the extended hopanes[8] although in this case the n-alkyl portion derives from defunctionalisation of the polyhydroxy side chain during diagenesis.

An alternative, but less likely, explanation for the formation of (**3**), (**6**), (**7**), and (**8**) may be a reaction in sediments between phytol and 2-n-alkylthiophenes (*cf.* Freidel–Crafts alkylation). Such a process has recently been suggested to account for the presence of steroids bonded by a carbon–carbon bond to aromatic units in asphaltenes and coals.[9]

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# Mechanism of the Boron Trifluoride Etherate-catalysed Rearrangement of an Acyclic Trisubstituted Epoxide to a Carbonyl Compound

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The mechanism of the $BF_3$-catalysed rearrangement of an acyclic trisubstituted epoxide to a carbonyl compound has been studied using (24*S*,25*S*)-[26-$^{13}$C] and (24*R*,25*R*)-[26-$^{13}$C]-desmosterol benzoate 24,25-epoxides (**2**) and (**3**), demonstrating that C-24 hydrogen migration leading to the 24-oxo compound (**4**) occurs with retention of configuration at the migration terminus (C-25), whereas C-23 alkyl group migration leading to aldehyde (**5**) proceeds with inversion of configuration at C-25.

Lewis acid-catalysed rearrangement of epoxides to carbonyl compounds involves the 1,2-shift of a hydride, alkyl, or aryl substituent to an adjacent carbon atom. *A priori* the electron-deficient carbon centre generated by the co-ordination of a Lewis acid to the oxygen atom of an epoxide may either become a discrete carbonium ion or rearrange by a more-or-less concerted mechanism (this implies stereochemical inversion at the migration terminus) into a more stable structure, depending on the particular environment of the epoxide ring. It has been suggested on the basis of the stereochemistry of the products that a discrete carbonium ion plays an intermediary role in the $BF_3$ etherate-catalysed rearrangement, which involves a tertiary cationic centre.[1] Examples of rearrangements involving migration of a substituent *cis* to the departing epoxide oxygen atom have been noted earlier.[2,3] Further, the possible intermediary role of fluorohydrin as well as the isolation of fluorohydrin products has been reported in a few cases.[4] However, these results have been obtained with epoxides on carbocyclic ring systems such as steroidal epoxides and must be interpreted taking into account factors inherent in cyclic systems, *i.e.*, axial–equatorial preference and ring strain. In contrast, few studies have been done on the mechanism of rearrangement of acyclic epoxides,[5] probably because of difficulty in preparing chiral epoxides and in determining the chirality of the resulting carbonyl products. We describe here our results on the mechanism of and, in particular, the stereochemical course at the migration terminus of the $BF_3$-catalysed rearrangement of acyclic trisubstituted epoxides.

Two steroidal epoxides, (24*S*,25*S*)-[26-$^{13}$C] and (24*R*,25*R*)-[26-$^{13}$C]-desmosterol benzoate 24,25-epoxides, (**2**) and (**3**), were used in our study. We selected these epoxides for the following reasons. (i) $BF_3$-Catalysed rearrangement of similar epoxides has been reported.[6] (ii) The epoxides could be prepared easily from desmosterol benzoate and their C-24 stereochemistry has been well established.[7] (iii) The stereochemistry at C-25 of the product ketone (**4**) and at C-24 of the aldehyde (**5**) could be determined by the preparation of appropriate compounds having a defined stereochemistry at these prochiral centres. (iv) The diastereotopic methyl groups at C-25 of (**4**) and at C-24 of (**5**) were expected to be differentiated by the chirality of the steroidal skeleton, yet this might not dictate the stereochemical course of the reactions at the remote terminal of the steroidal side chain. (v) Labelling with $^{13}$C at the diastereotopic methyl group made it possible to follow the fate of the methyl group in the rearranged products.

The isomeric epoxides (**2**) and (**3**) [labelled 92% at the *pro-S* and 8% at the *pro-R* methyl for (**2**), and *vice versa* for (**3**)] were prepared by *m*-chloroperbenzoic acid (*m* CPBA) treatment of [26-$^{13}$C] desmosterol benzoate,[8] followed by separation of the isomers by preparative t.l.c. Treatment of (24*S*,25*S*)-epoxide (**2**) with $BF_3$ etherate (2 equiv. benzene,