Tetrahedron Letters,Vol.28,No.9,pp 957-960,1987
Printed in Great Britain

0040-4039/87 $3.00 + .00
Pergamon Journals Ltd.

THE IDENTIFICATION OF 2,3-DIMETHYL-5-(2,6,10-TRIMETHYLUNDECYL)THIOPHENE, A NOVEL SULPHUR CONTAINING BIOLOGICAL MARKER

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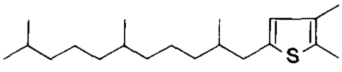
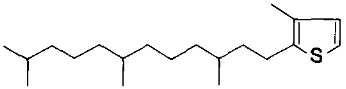
Abstract: The identification of 2,3-dimethyl-5-(2,6,10-trimethylundecyl)thiophene as a major constituent of certain petroleums and sediment extracts was confirmed by synthesis of the standard.

In several previous communications[1-6] we reported the occurrence of an isoprenoid C_{20} thiophene in several sediment extracts and oils. This compound, tentatively identified as 2,3-dimethyl-5-(2,6,10-trimethylundecyl)thiophene (I), is often the most abundant compound of the aromatic hydrocarbon fraction of the oils and sediment extracts investigated.[3-6] Since the aromatic hydrocarbon fraction of these samples represented ca. 50% (by weight) of the total oil or sediment extract, this compound has to be considered as one of their major constituents.

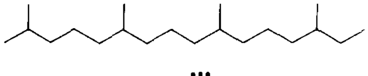
The tentative identification of I was based on mass spectral and relative retention time data[3] in comparison with those of a previously synthesized[2] isoprenoid thiophene (an alkylthiophene with an isoprenoidal carbon skeleton), 3-methyl-2-(3,7,11-trimethyl-dodecyl)thiophene (II). This identification was further supported by desulphurization of a particular subfraction, obtained by several column chromatographic (Al_2O_3) separation steps, of the aromatic hydrocarbon fraction of the Rozel Point oil (a seep oil from the North Western part of Utah, USA). This fraction contained I for ca. 35% together with several so called "midchain" isoprenoid C_{20} thiophenes (40%). Desulphurization of this fraction using Raney nickel afforded a mixture of hydrocarbons in which phytane (III) was the major compound (65%). This experiment proved that the carbon skeleton of I is indeed isoprenoidal. GC-HRMS[6] of I showed that the elemental formula is $C_{20}H_{36}S$.



I



II



III

Confirmation of this tentative assignment came from comparison of I with a synthetic standard. The synthesis scheme is shown in Fig. 1. Farnesol (3,7,11-trimethyl-2,6,10-dodecatrienol, Aldrich) was catalytically hydrogenated after protection of the hydroxyl group by acetylation. Hydrolysis afforded hexahydrofarnesol (IV), which was coupled with stearyl chloride. The resulting ester was pyrolyzed at 400 °C[7] yielding 3,7,11-trimethyltetradec-1-ene (V). V was subsequently oxidized[8] to the isoprenoid C_{14} acid, 2,6,10-trimethylundecanoic acid (VI). VI was coupled with 2,3-dimethylthiophene (VII), obtained via a modified Wolf-Kishner reduction[9] of 3-methyl-2-thiophenecarboxaldehyde (Aldrich). The resulting ketone, 2-(6,10-dimethyl)undecyl-5'-(2',3'-dimethylthienyl)ketone (VIII) was also reduced by a modified Wolf-Kishner reaction to I. The spectral characteristics of I and several intermediate products (Appendix) are in accordance with their structures. The mass spectrum of the synthesized product was indistinguishable from that reported for the geological thiophene.[3] The standard compound coeluted with the geological thiophene on two different capillary columns (CP Sil-5, l=25 m, i.d.=0.32 mm, film thickness =0.12 µm; CP Sil-88, l=25m, i.d.=0.32 mm, film thickness =0.20 µm).

The structure of this isoprenoid C_{20} thiophene has thus unambiguously been established. The carbon skeleton of I, as was already shown by desulphurization, is the same as that of phytane (III). Phytane appears widely in the geosphere. A number of precursors has been suggested for phytane including the phytyl side chain of chlorophylls and archaebacterial membrane lipids.[10] The structural relationship between I and phytane supports the hypothesis[2-4] that the isoprenoid thiophenes have been formed via incorporation of inorganic sulphur into the precursors of the isoprenoid alkanes found in sediments and oils. E.g. incorporation of sulphur into phytol, phytenes and/or phytadienes may lead to the formation of I. The presence of phytane as most abundant compound of the aliphatic fraction of the samples studied strongly supports this theory, since I is the most abundant compound of the aromatic hydrocarbon fraction.

The reaction of inorganic sulphur in the form of e.g. H_2S, HS^- and/or polysulfides requires an euxinic environment of deposition . Therefore I has to be considered as a marker for such an environment.

Acknowledgement. We thank Mr. A. Sinnema and Mrs A.H. Knol - Kalkman for performing the ^{13}C and 200 MHz ^1H NMR and GC-MS analysis respectively.

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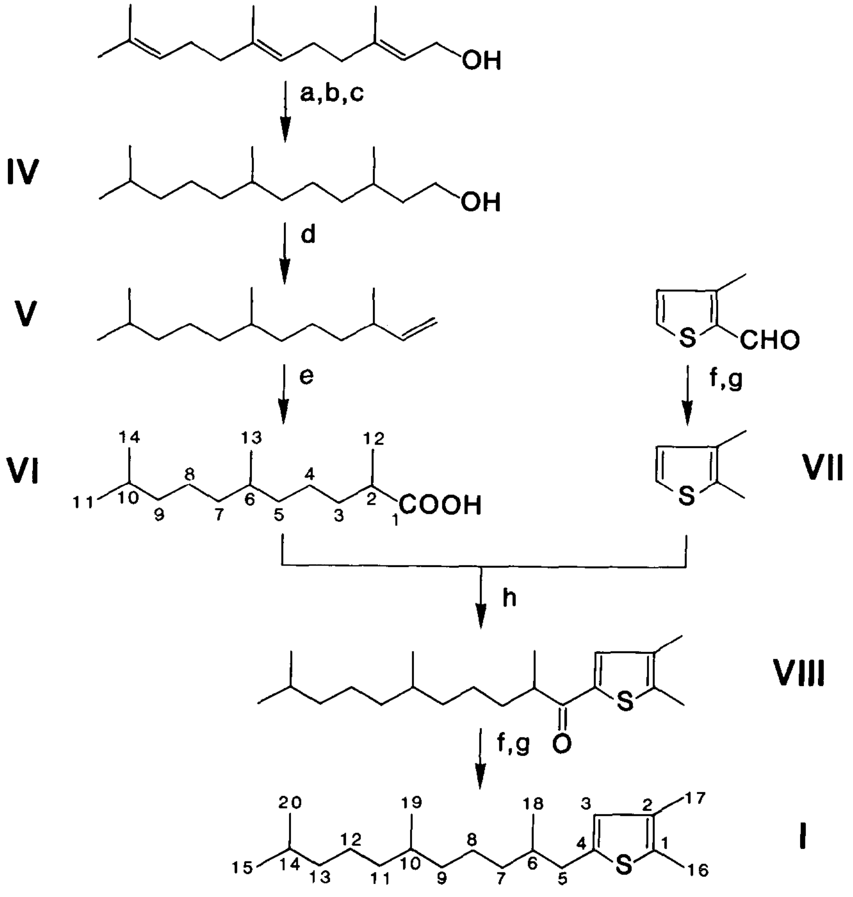

Fig. 1 : The synthesis scheme for I.

a) Ac_2O, N,N-dimethyl-4-aminopyridine b) H_2, PtO_2 c) OH^-, ΔT d) n-$C_{17}H_{35}COCl$, ΔT(400°C) e) $KMnO_4$, HOAc, Adogen 464 f) $H_2N\text{-}NH_2$, ΔT g) OH^-, ΔT h) P_2O_5, ΔT

The numbering of the structures VI and I has been used in the assignments of the ^{13}C NMR spectra of these compounds (Appendix).

APPENDIX

3,7,11-trimethyldodec-1-ene (V)

yellow liquid; IR ν 915, 1000, 1420, 3030 cm^{-1}; ^{1}H NMR (60 MHz, CDCl$_3$) δ(ppm): 4.7-5.15 (m, 2H), 5.4-6.0 (m,1H); GC-MS (70 eV) m/z: 210(<1%), 140(5%), 126(10%), 125(13%), 112(6%), 111(16%), 98(8%), 97(16%), 85(12%), 84 (21%), 83(40%), 71(59%), 70(100%), 69(79%), 68(9%), 67(10%), 57(93%), 56(83%), 55(77%), 54(5%), 53(6%).

2,6,10-trimethylundecanoic acid (VI)

colourless oil; IR ν 3360(broad), 1710(sharp) cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ(ppm): 0.844 (d,3H, J=6.2 Hz), 0.866 (d, 6H, J=7.0 Hz), 1.167 (d, 3H, J=6.2 Hz), 1.1-1.8 (m, ≈14H), 2.25-2.55(m, 1H), 10.047 (s, 1H); ^{13}C NMR (50 MHz, CDCl$_3$) δ(ppm)$^{\#}$: 16.17*, 16.70* (C-12), 19.39 (C-13), 22.40, 22.51 (C-11 and C-14), 24.43 (C-8), 24.57 (C-4), 27.77 (C-10), 32.41 (C-6), 33.66 (C-3), 36.70 (C-5), 37.06 (C-7), 39.12 (C-9), 39.34 (C-2) , 183.09 (C-1);GC-MS (70 eV) m/z(as methyl ester): 242(0.4%), 227(0.1%), 211(0.3%), 199(0.4%), 157(6%), 152(5%), 129(3%), 101(35%), 97(13%), 89(5%), 88(100%), 87(13%), 83(5%), 73(5%), 71(10%), 69(19%), 59(10%), 57(26%), 56(9%), 55(27%).

2,3-dimethylthiophene(VII)

yellow liquid;^{1}H NMR (60 MHz, CDCl$_3$) δ(ppm): 2.04 (s,3H), 2.30 (s, 3H), 6.75 (d, 1H, J=5.4 Hz), 6.85 (d, 1H, J=5.4 Hz); GC-MS (70 eV) m/z: 114(4%), 113(9%), 112(77%), 111(71%), 99(5%), 98(6%), 97(100%), 85(6%), 78(11%), 77(24%), 67(15%).

2-(6,10-dimethyl)undecyl-5'-(2',3'-dimethylthienyl)ketone (VIII)

orange oil; IR ν 1665 cm^{-1}; GC-MS (70 eV) m/z: 322(1%), 280(3%), 279(2%), 181(9%), 180(4%), 170(5%), 169(11%), 168(97%), 167(47%), 141(12%), 140(12%), 139(100%), 138(11%), 112(6%), 111(5%), 69(7%), 67(21%), 57(5%), 55(13%).

2,3-dimethyl-5-(2,6,10-trimethylundecyl)thiophene(I)

colourless liquid;^{1}H NMR (200 MHz, CDCl$_3$) δ(ppm): 0.839, 0.843 (two d, 3H, J=6.4 Hz), 0.865 (d, 6H,J=7.0 Hz), 0.894 (d, 3H, J=6.4 Hz), 0.9-1.7 (m, ≈15H), 2.063 (s, 3H), 2.276 (s, 3H), 2.437 (dd, 1H, J=7.2 and 14.0 Hz), 2.650 (dd, 1H, J=7.2 and 14.0 Hz), 6.414 (s, 1H);^{13}C NMR (50 MHz, CDCl$_3$) δ(ppm)$^{\#}$: 12.77 (C-17), 13.36 (C-16), 19.27*, 19.32*, 19.49*, 19.58* (C-18, C-19), 22.45, 22.54 (C-15, C-18), 24.29 (C-8), 24.62 (C-12), 27.80 (C-14), 32.59 (C-10), 35.07 (C-6), 36.57*, 36.62*, 37.04*, 37.08*, 37.17, 37.29*, 37.37* (C-5, C-7, C-9, C-11), 39.17 (C-13), 127.71 (C-3), 129.75 (C-1), 132.01 (C-2), 139.12 (C-4); GC-MS (70 eV) m/z: 310(0.4%), 309(0.4%), 308(3%), 153(3%), 127(5%), 126(17%), 125(100%), 124(6%), 111(4%), 91(6%), 55(5%).

assignments are tentative and substantiated from comparison of ^{13}C NMR spectra of several isoprenoid hydrocarbons[11] and by using the additivity rules[12].

* there are two pairs of enantiomers because of the presence of two chiral centres in the molecule. These pairs of enantioisomers are recognized by ^{13}C NMR: they give rise to two peaks in the spectrum for certain carbon atoms. The ratio of these two peaks is for these carbon atoms ca. 1:1, which shows that the pairs of enantioisomers are present in a ratio of 1:1, as expected from the applied synthesis scheme.

(Received in UK 15 January 1987)