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SYNTHESIS OF A HIGHLY BRANCHED C_{30} SEDIMENTARY HYDROCARBON

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ABSTRACT The identification of a sedimentary C_{30} isoprenoid alkane as 2,6,10,14,18-pentamethyl-7-(3-methylpentyl)nonadecane is confirmed by synthesis

Synthetic studies conducted by Yon *et al* [1] and more recently by ourselves[2] have shown that the widely distributed and abundant acyclic C_{20} and C_{25} alkenes present in recent sediments are 7-isopranylfarnesenes (I,II), although the exact positions of the double bonds in the various isomers remains unknown The biological sources of these compounds are probably algae[3,4] Co-occurring with the C_{20} and C_{25} hydrocarbons in certain sediments are a number of acyclic C_{30} alkenes[5,6] some of which are readily hydrogenated to an alkane proposed to be pseudohomologous with I and II [*viz* possessing a hexahydrofarnesyl side chain at C-7, III, 2,6,10,14,18-pentamethyl-7-(3-methylpentyl)nonadecane] on the basis of the GC retention index and GCMS[2,5] data

We have now confirmed this tentative structural assignment by synthesis of III (and a mixture of monoenes) according to the preparative scheme shown in Figure 1 Briefly, 2,6-dimethylheptanal (IV,10mmol) was synthesised from commercially available 6-methylhept-5-en-2-one as described previously[2], and condensed in a Grignard reaction (THF, Ar) with 3,7,11-trimethyldodecyl bromide (V,13mmol) The latter was synthesised by standard procedures from farnesol. The secondary alcohol (IV,4mmol) produced by the Grignard reaction was oxidised by the Swern method[7] to 2,6,10,14,18-pentamethylnonadecan-7-one (VII) A second Grignard reaction which involved coupling of VII with 3-methylpentyl bromide gave the tertiary alcohol (VIII) in only 2% yield However, the use of $CeCl_3$ $7H_2O$ as detailed in a recently published adaptation[8] improved this to 76% Finally, dehydration of a small amount (0 2mmol) of VIII in the presence of $POCl_3$/py produced a mixture of monoenes which was characterised by GCMS and then rapidly hydrogenated at ambient temperature and pressure to III The spectral characteristics of III and of important intermediates were in accordance with the structure (see appendix)

The alkane had an identical mass spectrum and GC retention index (RI_{OV1}2524) and coeluted on three phases (OV1, 50m 97% efficiency for n-C_{17}, BP10, 25m, CARBOWAX, 25m) with the hydrogenation product of unidentified C_{30} alkenes from Gluss Voe (Shetland Isles, UK)[9] No separation of diastereomers was noted However, the identification of III in the Eocene Maoming oil shale (China)[10] is incorrect as the compound proposed to be III does not coelute with authentic III

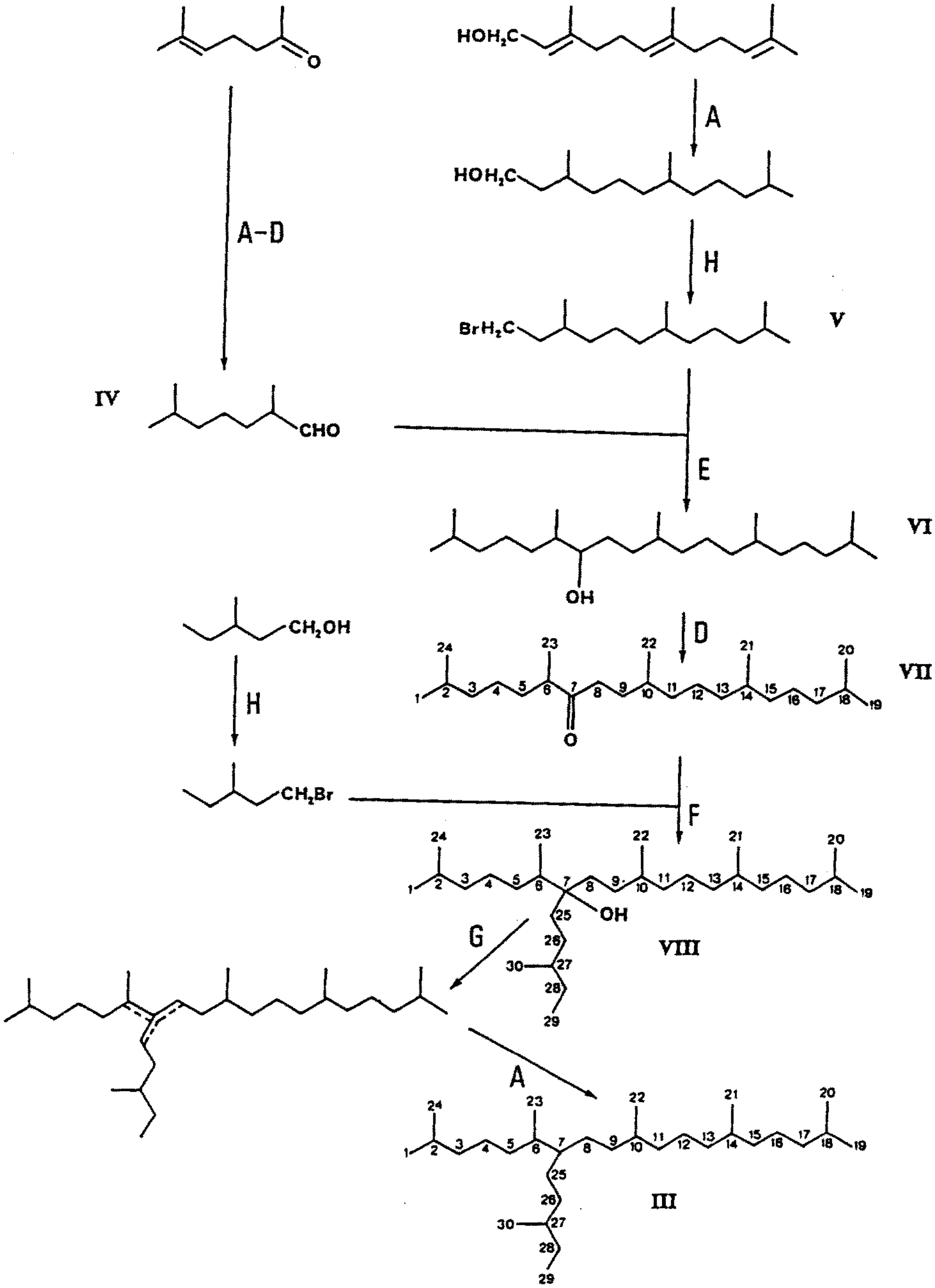

Figure 1: Synthesis of 2,6,10,14,18-pentamethyl-7(3-methylpentyl)nonadecane III
a, H_2,PtO_2,hexane; b, $BrCH_2Br$,Mg,$TiCl_4$; c, B_2H_6,THF,H_2O_2,OH; d, $(COCl)_2$,DMSO; e, Mg,Et_2O; f, Mg,THF,$CeCl_3.7H_2O$; g, $POCl_3$,py; h, HBr,H_2SO_4.

APPENDIX

2,6-dimethylheptanal (IV) oil. GC purity 91%. IR (film; cm^{-1}) ν(C-H) ald 2710, ν(C=O) 1730, δ(C-H) ald. 1389 GCMS (40eV) m/z 142 (M$^+$,1%), 127 (2%), 123 (4%), 71 (22%), 58 (100%) ^{1}H NMR (60 MHz) δppm 0.85 (*d*,6H,C$\underline{\mathrm{H}}_3$-C-C$\underline{\mathrm{H}}_3$), 1 12 (*d*;3H,C$\underline{\mathrm{H}}_3$-CH-CHO), 1.51 (*m*,7H,C$\underline{\mathrm{H}}$ and C$\underline{\mathrm{H}}_2$), 2.36 (*m*,1H,C-C$\underline{\mathrm{H}}$-CHO), 9 63 (*d*,1H,C$\underline{\mathrm{H}}$O)

2,6,10,14,18-pentamethylnonadecan-7-one (VII) oil. GC purity 91% IR (film, cm^{-1}) ν(C=O) 1720, δ_s(CH$_2$-CO) 1405, δ gem dimethyl 1390, 1375, ν(C-CO-C) 1165. GCMS (40eV) m/z 352 (M$^+$,2%), 337 (2%), 268 (1%), 239 (7%), 196 (16%), 156 (12%), 85 (32%), 43 (100%) ^{13}C NMR (400 MHz, CDCl$_3$) δppm[*] 16 3275 (C-21), 19 3390, 19 3961 [Φ](C-22), 19 6284, 19 5630 [Φ](C-23), 22.4946, 22.5973 [ϕ](C-1,C-19,C-20,C-24), 24 3021 (C-16), 24 6943 (C-12), 24 9889 (C-4), 27.7306, 27 8758 (C-2,C-18), 30 6802 (C-9), 32 4177, 32 6808 (C-14,C-10), 33 9868 (C-5), 37 0448 (C-11); 37 1870, 37 6448 (C-15,C-13), 38 7770 (C-17), 38 9012 (C-3), 39 2775 (C-8), 46 2799 (C-6), 215 1225 (C-7)

2,6,10,14,18-pentamethyl-7-(3-methlpentyl)nonadecan-7-ol (VIII) oil GC purity 89% IR (film, cm^{-1}) ν(O-H) 3620 free, ν(O-H) 3480 intermolecularly bonded, ν(C-O) 1155 saturated tertiary GCMS (40eV, TMS ether) m/z 509 (M$^+$ -1,1%), 495 (M$^+$ -CH$_3$,2%), 425 (29%), 397 (41%), 299 (61%), 73 (100%) HRMS (40eV) m/z 227 2370 (C$_{15}$H$_{31}$O requires 227 2373), 325 3466 (C$_{22}$H$_{45}$O requires 325 3468), 353 3778 (C$_{24}$H$_{49}$O requires 353 3781) ^{13}C NMR (400 MHz, CDCl$_3$) δppm 11 2866 (C-29), 13 5218, 13 5811 [Φ](C-23), 19 2144 (C-30), 19 5897, 19 6511 (C-21,C-22), 22 4300-22 5188, 22.6100-22.6566 [ϕ](C-1,C-19,C-20,C-24), 24 3978 (C-16), 24 7096 (C-12), 25 0694 (C-4); 27 8599, 27 8849 (C-2,C-18), 29 3268-29 4244 [Φ](C-28),29 6384-29 7181 [Φ](C-9), 29 8932-30 8708 (2 unassigned carbons), 32 7133 (C-14), 33.4328-33 6532 (3 unassigned carbons), 35 1699 (C-27), 37 2146-37 3617 (C-11,C-13,C-15), 39 2907 (C-3,C-17), 39 9336 (C-6), 76 2349-76 2607 (C-7).

2,6,10,14,18-pentamethyl-7-(3-methlpentyl)nonadecane (III) oil GC purity 91% GCMS (40eV) m/z 337 (0 1%), 336 (0 1%), 309 (2%), 308 (4%), 155 (7%), 85 (36%), 57 (100%) HRMS (40eV) m/z 308 3435 (C$_{22}$H$_{44}$ requires 308 3441), 336 3758 (C$_{24}$H$_{48}$ requires 336 3754) ^{13}C NMR (400 MHz, CDCl$_3$) δppm 11 3108 (C-29), 15 4833-15 7711 [Φ](C-23), 19 1837 (C-30), 19 6647 (C-21,C-22), 22 5327, 22 6110 [ϕ](C-1,C-19,C-20,C-24), 24 3826 (C-16), 24 7161 (C-12), 25 4497 (C-4), 27 1445-27 8836 (C-2,C-18), 28 4948 (C-8), 29 3082 (C-28); 29 5129 (C-25), 32 7147 (C-14), 33.0650-33 1686 [Φ](C-10), 34 2011-34 4046 (C-5,C-26), 34 7590 (C-6), 35 0741-35 4435 [Φ](C-9), 37 2288-37 3929 (C-11,C-13,C-15,C-27), 39 3078 (C-3,C-17), 42 6923-42 8870 [Φ](C-7)

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[*] Tentative assignments made by comparison with ^{13}C NMR spectra of similar acyclic isoprenoids[1,9] and with calculated values from additivity rules[11]

[Φ] The presence of several peaks for certain carbon atoms in the spectra of VII, VIII and III indicates that several diastereomers of each compound are present as would be expected from the non-stereospecific synthetic scheme employed

[ϕ] Magnetic non-equivalence due to conformational differences between the methyl carbons of each isopropyl termini

Studies are currently underway to assess the potential of the 7-isopranyl-farnesenes as environmental indicators.

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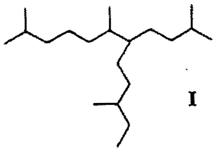
STRUCTURES



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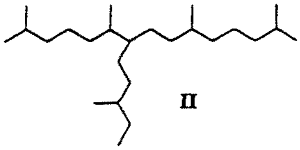

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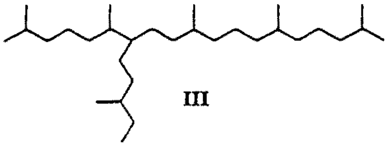

III

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