

2,6,10-TRIMETHYL-7-(3-METHYLBUTYL)-DODECANE, A NOVEL SEDIMENTARY BIOLOGICAL MARKER COMPOUND.

D.A. Yon and J.R. Maxwell*

Organic Geochemistry Unit, School of Chemistry, University of Bristol, Bristol BS8 1TS, U.K.
and

G. Ryback

Shell Research Ltd., Biosciences Laboratory, Sittingbourne Research Centre, Sittingbourne,
Kent ME9 8AG.

Abstract: A C₂₀ isoprenoid alkane (1) reported to occur in several recent sediments, has been isolated from Rozel Point crude oil and its structure confirmed by synthesis.

There are several recent reports of the occurrence, in a variety of marine surface sediments of a C₂₀ highly branched alkane and related compounds¹⁻³. The electron impact spectrum (EI) of the alkane is unusual in that it is characterised by the presence of pairs of ions at m/z 168/169 (ca. 10%, 5% respectively), m/z 196/197 (0.8 : 1; m/z 197 < 1%) and m/z 210/211 (0.7 : 1; m/z 211 < 1%)^{2,3}.

The compound is the second most abundant component of the alkane fraction of Rozel Point crude oil (Utah, U.S.A.; age unknown). A fraction containing it (ca. 80%), 2,6,10,14-tetramethylpentadecane (pristane, 2; ca. 10%) and n-heptadecane (ca. 10%) was isolated by extraction with hexane, column chromatography, distillation and preparative scale gas chromatography (GC). Removal of the n-alkane and pristane by molecular sieving (5A) and thiourea adduction respectively, afforded the C₂₀ alkane (ca. 98% purity by GC on 100m DEGS/PEGS, 3 : 1).

Interpretation of the ¹³C NMR spectra of pristane (2), 2,6,10,14-tetramethylhexadecane (phytane, 3) and the alkane in the light of NMR additivity rules for branched hydrocarbons^{4,5}, integration under conditions giving no nuclear Overhauser enhancement, off resonance proton decoupling, and consideration of the ¹H NMR spectrum, suggested structures (1) or (4) for the latter, using the criterion that the skeleton should contain a recognisable biogenetic isoprene sequence. The EI mass spectrum favoured, however, structure (1), the above pairs of ions being explicable in terms of fragmentation around the C-7 tertiary carbon. Further evidence for (1) was obtained by interpretation of the EI mass spectra (GC-MS) of the carboxylic acids (as methyl esters) and ketones from oxidation with CrO₃/HOAc⁶, the latter products containing the C₁₂ ketone (5) in the Figure. The carbon skeleton of (1) does not correspond to any known natural product although a compound (6) with an analogous skeleton has been isolated previously from tobacco flowers⁷. A tentative biosynthetic scheme, based on the studies of Banthorpe *et al.*⁸ can be envisaged for the skeleton of (1).

Confirmation of the assignment came from comparison of the geological alkane with that synthesised by the scheme in the Figure. 2,8-Dimethyldecan-5-one (5) was reacted with 6-bromo-2-methylhept-2-ene (7) in a Grignard reaction. Dehydration of the resulting C₂₀ unsaturated alcohol (8) afforded a mixture of isomeric dienes (GC-MS), hydrogenation of which afforded the required C₂₀ alkane (1). The latter was indistinguishable (EI mass spectrum, ¹H and ¹³C NMR spectra) from the geological alkane and co-eluted with it on three different GC phases (20m

OV-1, 20m Apiezon-L and 100m DEGS/PEGs, 3 : 1). In addition, GC analysis of the synthetic compound on DEGS/PEGs (100m) under conditions which separate diastereoisomeric acyclic isoprenoid alkanes^{9,10} afforded a 1 : 1 doublet for the four diastereoisomers; an identical doublet was obtained for the geological alkane, showing that it contains at least two of the diastereoisomers, as would be expected from earlier studies^{9,10}. That all four diastereoisomers were present in both the synthetic and geological alkane was confirmed by the complexity of the ¹³C NMR spectrum in each case, which had, for example, four peaks attributable to C-14.

The compound found previously in surface sediments from Grasmere (Cumbria, U.K.), and reported to be a C₁₈ branched alkane in the absence of a molecular ion from GC-MS analysis¹¹, has now been identified as the C₂₀ alkane. The latter has also been observed in other samples of sedimentary organic matter representing different depositional environments and ages up to Oligocene. It does not appear to occur in geological samples as widely as other isoprenoid alkanes such as pristane (2) and phytane (3), suggesting that it may be a useful input marker. GC analysis on several non-polar phases (SE-30, OV-17, OV-1) shows that it has a similar retention time to pristane (2) and co-elutes with it on typical glass capillary columns (20m) if it is present in much higher or lower abundance than pristane. This fact indicates that care must be taken in using pristane/phytane ratios¹² in petroleum geochemistry and exploration.

Studies of the related C₂₅ hydrocarbons in sediments¹⁻³ are in progress.

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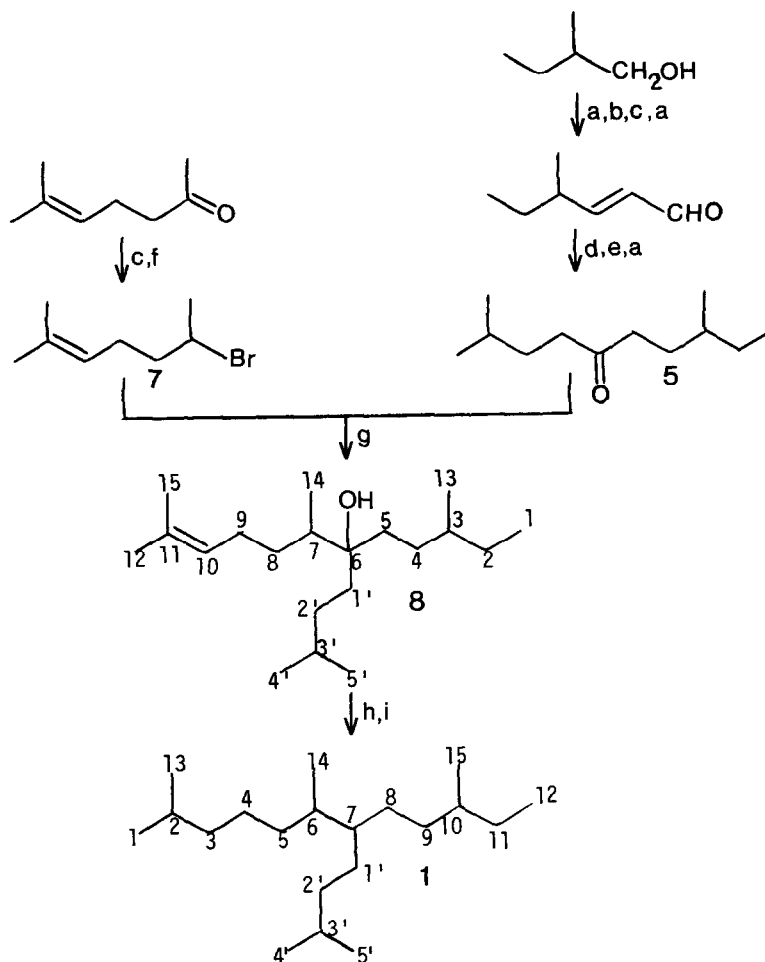
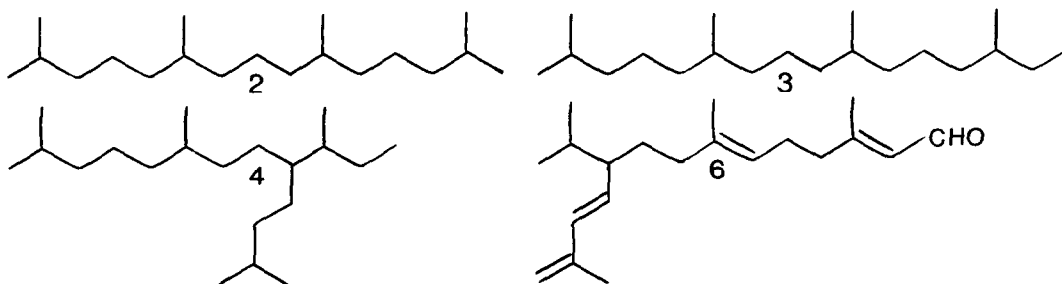


Figure. Outline of synthetic scheme for (1).

a. DMSO, $(\text{COCl})_2$; b. NaH, triphenylphosphonoacetate; c. LiAlH_4 ; d. Grignard ($\text{Mg}, \text{Et}_2\text{O}$) with $(\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{Br}$; e. $\text{H}_2, \text{Pt}/\text{C}, \text{EtOH}$; f. $\text{Ph}_3\text{P}, \text{Br}_2$; g. Mg, THF; h. POCl_3 , pyridine; i. H_2, PtO_2 , HOAc.



2,8-Dimethyldecan-5-one (5).

Oil. $\nu(\text{CS}_2)$ 1710 cm^{-1} (sharp); δ ppm ^1H (200 MHz, CDCl_3) 2.4 (t, 4H, $J \approx 7$ Hz, $\text{CH}_2\alpha$ to C = O); MS (40 eV, GC-MS) m/z 184 (M^+ , 2%), 128 (2%), 114 (5%), 113 (15%), 99 (18%), 95 (33%), 81 (31%), 71 (59%), 58 (base); HRMS (70 eV) m/z 99.0808 ($\text{C}_6\text{H}_{11}\text{O}$ req. 99.0810), 113.0965 ($\text{C}_7\text{H}_{13}\text{O}$ req. 113.0966).

3,7,11-Trimethyl-6-(3-methylbutyl)-dodec-10-en-6-ol (8).

Oil. $\nu(\text{CS}_2)$ 3610 cm^{-1} (sharp); δ ppm ^1H (100 MHz, CDCl_3) 0.88, 0.94 (15H, Me), 1.64 (s, 3H $\text{H}_3\text{C-C=C}$), 1.72 (s, 3H, $\text{H}_3\text{C-C=C}$), 5.12 (t, 1H, $J \approx 6$ Hz, C=C-H); ^{13}C NMR (90 MHz, CDCl_3 , n.a. = not assigned) 11.44 (C-1), 13.57 (C-14), 17.68 (C-15), 19.33 (C-13), 22.71 (C-4', C-5'), 25.74 (C-12), 26.74 (C-9), 28.82 (C-3'), 29.56 (C-2), 29.73 (C-4), 31.12 (n.a.), 32.20 (C-2'), 33.76 (n.a.), 34.07 (C-3), 35.19 (n.a.), 39.48 (C-7), 76.28 (C-6), 124.87 (C-10), 131.45 (C-11); MS (40 eV, GC-MS) 295 (M^+ - H, < 1%), 278 (1%), 225 (5%), 211 (6%), 207 (8%), 196 (13%), 193 (10%), 185 (98%), 111 (35%), 97 (50%), 83 (68%), 69 (base); HRMS (70 eV) m/z 185.1904 ($\text{C}_{12}\text{H}_{25}\text{O}$ req. 185.1905).

2,6,10-Trimethyl-7-(3-methylbutyl)-dodecane (1).

Oil. δ ppm ^1H (200 MHz, CDCl_3) 0.76, 0.77 (d, 3H, $J = 6.8$ Hz, diastereoisomeric $\text{CH}_3\text{CH-}$) 0.85, 0.88 (18H, Me); δ ppm ^{13}C (200 MHz, CDCl_3) 11.41, 11.42, 11.45, 11.48 (C-12)*, 15.43, 15.48, 15.68, 15.72 (C-14)*, 19.29, 19.40 (C-15)*, 22.66, 22.73, 22.85, 22.87, 22.88 (C-1, C-13, C-4', C-5')*, 25.56 (C-4)*, 27.19, 27.30, 27.57, 27.65 (C-2), 27.98 (C-3'), 28.44, 28.49, 28.56, 28.89, 28.91 (C-1', C-11), 29.38, 29.40, 29.63, 29.64 (C-8), 34.13, 34.16, 34.20, 34.30, 34.38 (C-9, C-5), 34.75, 34.85, 34.87, 34.94, 35.03, 35.11 (C-2', C-6), 37.24, 37.32, 37.50, 37.58 (C-10), 39.40 (C-3), 42.82, 43.02 (C-7)*; MS (40 eV, GC-MS) 282 (M^+ , abs.; probe < 1%), 211 (< 1%), 210 (< 1%), 197 (< 1%), 196 (< 1%), 169 (5%), 168 (9%), 139 (7%), 127 (4%), 113 (9%), 99 (14%), 85 (33%), 71 (62%), 57 (base).

* Assignment substantiated by off resonance proton decoupling; all other ^{13}C assignments tentative from comparison with standards and using additivity rules (see text).

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