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THE ISOLATION AND IDENTIFICATION OF THE C_{17} SATURATED ISOPRENOID HYDROCARBON 2,6,10-TRIMETHYLTETRADECANE FROM A DEVONIAN SHALE

THE ROLE OF SQUALANE AS A POSSIBLE PRECURSOR*

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Abstract—A C_{17} saturated isoprenoid hydrocarbon, 2,6,10-trimethyltetradecane, has been isolated from the Antrim Shale and has been characterized on the basis of capillary gas chromatography and mass spectrometry. This represents the first report of this isoprenoid alkane in crude oils and sediments. A standard C_{17} isoprenoid has been synthesized from farnesol. The possibility that a C_{30} isoprenoid, such as squalane, may be a precursor of the isoprenoid alkanes has been investigated. The relatively small proportion of the C_{17} isoprenoid in the Antrim Shale suggests that phytol is the probable precursor. Two C_{19} isomeric alkanes have been synthesized and their mass spectra compared with that of another C_{19} isomeric alkane, pristane. The close similarity of these spectra emphasizes the care necessary is assigning structures to organic compounds isolated from crude oils and sediments, particularly hydrocarbons, without additional confirmation from other physical measurements.

To gain an insight into the chemical transformations that take place during the formation of sediments we have sought to characterize the structure of the organic compounds in them and to establish their precursors. Owing to the complex chemical nature of the organic extract it has been extremely difficult to isolate individual organic compounds in pure form. The synthesis of hydrocarbon standards that are not readily available has therefore become an integral part of our identification procedure by capillary gas chromatography and mass spectrometry. In particular, our interest has centered on the saturated isoprenoid hydrocarbons.

A previous paper[1] describes the isolation and identification of a series of isoprenoid hydrocarbons from the Antrim Shale, Midland County, Michigan, reported as Late Devonian in Age, about 265×10^6 years.† In that paper the procedure for the extraction of the total hydrocarbon content was outlined and we commented upon the consistent absence of the C_{17} isoprenoid from among the isoprenoid alkanes identified in a series of oils and shales. Other authors[2–5] have also failed to report this isoprenoid.

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† We appreciate the generosity of Mr. R. D. Matthews for his sample of the Antrim shale. "The Michigan Geological Survey has published a new 'stratigraphic succession in Michigan' which places the Antrim in the Late Devonian (Chautaquan). A chronology published by Hough which is based on work by Ladd and Ahrens places the end of the Devonian at about 265 million years." Private communication from Mr. R. D. Matthews of October 20, 1964.

[1] R. B. Johns, T. Belsky, E. D. McCarthy, A. L. Burlingame, Pat Haug, H. K. Schnoes, W. Richter and M. Calvin, *Geochimica et Cosmochimica Acta* **30**, 1191 (1966).

[2] G. Eglinton, P. M. Scott, T. Belsky, A. L. Burlingame, W. Richter and M. Calvin, *Advances in Organic Geochemistry* Vol. 2. Pergamon Press (1966).

[3] W. E. Robinson, J. J. Cummins and G. U. Dinneen, *Geochimica et Cosmochimica Acta* **29**, 249 (1965).

[4] J. G. Bendoraitis, B. L. Brown, R. S. Hepner, *Analyt. Chem.* **34**, 49 (1963).

[5] J. G. Bendoraitis, B. L. Brown, R. S. Hepner, *World Petroleum* Congress, Frankfurt/Main, Germany, June 19–26 (1963).

We now report the isolation and identification of this C_{17} saturated isoprenoid hydrocarbon, 2,6,10-trimethyltetradecane in the Antrim Shale. By coinjection techniques on a gas liquid chromatograph capillary column and by comparing the mass spectrum of the standard with that of the compound isolated convincing evidence has been provided for its presence in the shale. The C_{17} isoprenoid standard was synthesized from farnesol by the synthetic scheme outlined in Fig. 1.

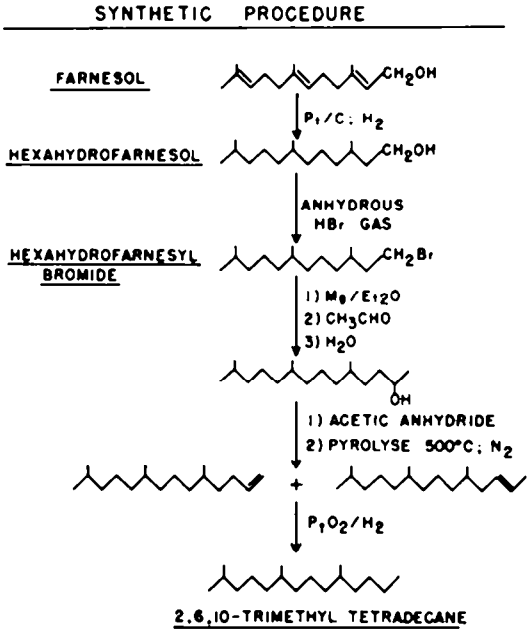


Fig. 1. The synthesis of the C_{17} saturated isoprenoid hydrocarbon, 2,6,10-trimethyltetradecane from farnesol.

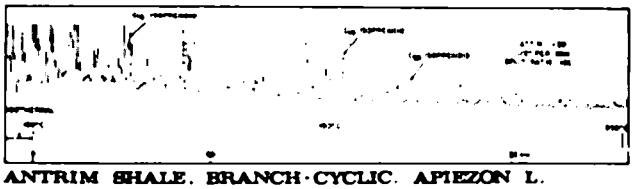


Fig. 2. Capillary gas chromatograph of the branch-cyclic fraction from the Antrim Shale.

The gas chromatogram of the branch-cyclic hydrocarbon fraction of the Antrim Shale is shown in Fig. 2. The inset marked in Fig. 2 is shown in detail in Fig. 3 where it is compared with the gas chromatogram of the branch-cyclic hydrocarbon fraction containing the coinjected C_{17} saturated isoprenoid hydrocarbon. The gas chromatograms, programmed under identical conditions, are highly reproducible so that coinjection with known standards provides a very sensitive method of characterization. The coinjection procedure has been repeated on two other phases, S.E. 30 silicone gum rubber and castorwax,* and the corresponding coincidence again obtained. It should be emphasised that the small increase in relative peak height intensity of the C_{17}

* Standard Perkin–Elmer liquid phases: Designation Z and C-W respectively.

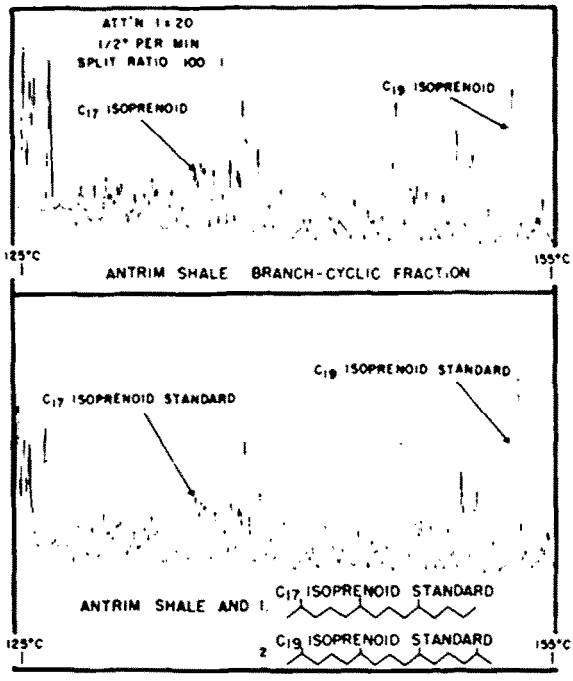


FIG. 3. The upper chromatogram shows the inset from Figure 2; the lower chromatogram shows the same region with the coinjected standards, the C_{17} isoprenoid, 2,6,10-trimethyltetradecane, and the C_{19} isoprenoid, pristane.

saturated isoprenoid hydrocarbon shown in Fig. 3 is reproducible in every instance under the stipulated conditions. Further, an estimation has been made of the relative proportion of the C_{17} isoprenoid hydrocarbon found in the Antrim Shale and this is shown in the following table compared with the relative proportion of the other isoprenoid alkanes identified in the shale.

ISOPRENOID CONTENT OF BRANCHED CYCLIC ALKANE FRACTION OF ANTRIM SHALE

	% (by wgt)
C_{16}	0·45 ± 0·02
C_{17}	0·05 ± 0·04
C_{18}	0·46 ± 0·02
C_{19}	0·27 ± 0·02
C_{20}	0·23 ± 0·02
C_{21}	0·19 ± 0·02

(Identified isoprenoids constitute approx. 1·6% of the branch-cyclic alkanes of the Antrim Shale.)

Although an accurate estimation of the proportion of the C_{17} isoprenoid cannot be made it is present in considerably smaller quantities than any of the other isoprenoids. This is in accord with a diagenetic scheme where phytol is considered the biological precursor of these isoprenoid hydrocarbons.

The upper part of Fig. 4 shows a collection of the C_{17} isoprenoid region from a 10′ × ¼″ preparative column, S.E. 30% phase, before subsequent purification on two other phases. The peak labelled "C_{17} isoprenoid" was enhanced by coinjection of the standard. Further purification of the C_{17} isoprenoid was effected by reinjection on and collection from tetracyanoethylated pentaerythritol and seven-ring-meta polyphenyl

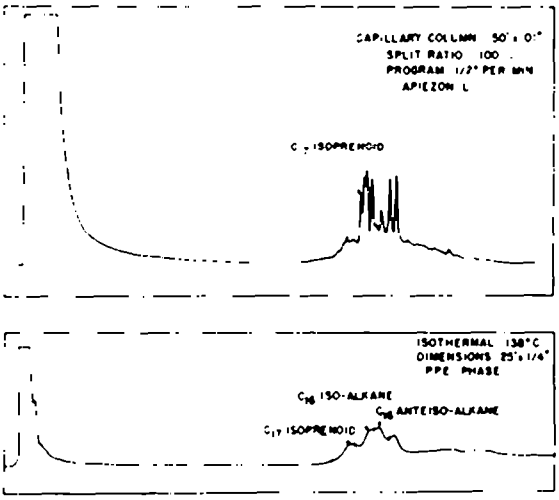


FIG. 4. *Upper:* Capillary gas chromatogram of the C_{17} isoprenoid region collected from a preparative S.E. 30 column, and before subsequent purification on other phases. *Lower:* C_{17} isoprenoid region from the Antrim Shale. The cut corresponding to C_{17} isoprenoid was collected and analysed by mass spectrometry.

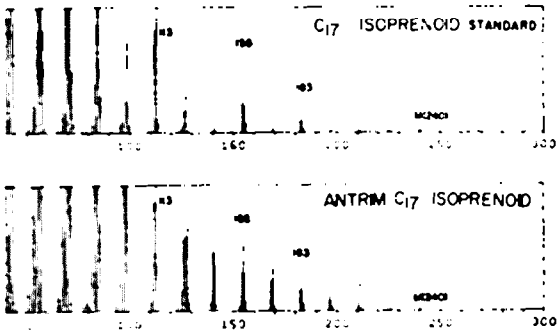


FIG. 5. Mass spectrum of the C_{17} isoprenoid, 2,6,10-trimethyltetradecane, compared with that of the C_{17} isoprenoid isolated from the shale.

ether phases respectively. The lower part of Fig. 4 shows the relative retention times of the C_{17} isoprenoid and the C_{18} *iso-* and *anteiso*-alkanes, using 25′ × ¼″ column with seven ring met-poly-phenyl ether as the phase. The cut corresponding to the C_{17} isoprenoid was collected and analysed by mass spectrometry.

The mass spectrum of the standard C_{17} saturated isoprenoid hydrocarbon, and that of the sample collected from the Antrim Shale, are shown in Fig. 5. The two mass spectra show considerable similarities to each other although certain discrepancies in the relative intensities of the peaks should be noted. This is due to the fact that a

completely pure cut is difficult to obtain. The mass spectra were obtained from chromatographs in which the resolution was far inferior to that obtained on the capillary instrument.

The mass spectra of the C_{16} *iso* and *anteiso*-alkanes isolated from the shale are shown in Fig. 6. Consideration of these spectra should be made when comparing the mass spectrum of the C_{17} isoprenoid standard with that of the compound isolated from the shale. In the shale sample there would seem to be contributions from parent molecular ions at *m/e* 226 and at *m/e* 238. The parent molecular ion at *m/e* 226 might, in part, be reasonably attributed to the presence of the C_{16} *iso*- and *anteiso*-alkanes, which have retention times that are very similar to that of the C_{17} saturated isoprenoid hydrocarbon. The mass spectral peaks at *m/e* 211 and *m/e* 197, more intense than

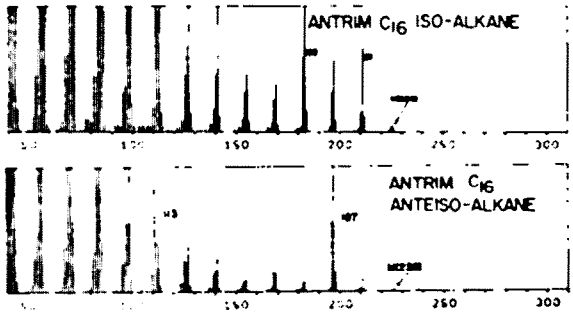


FIG. 6. Mass spectra of the C_{16} *iso*-alkane and the C_{16} *anteiso*-alkane both of which were isolated and identified in the Antrim Shale.

expected, could also arise from small amounts of the C_{16} *iso*- and *anteiso*-alkanes. Further, the C_{16} *iso*-alkane would contribute to the *m/e* 183 mass ion which might account for a more intense *m/e* 183, relative to *m/e* 155, in the shale sample than is actually observed for the C_{17} isoprenoid standard. There is also mass spectrometric evidence for unsaturated components, including a mono-olefin of mol wt 238. The remaining discrepancies might be better understood with a complete knowledge of the structures of the compounds in the cut taken from the C_{17} isoprenoid region of the gas chromatograph shown in Fig. 4. In conclusion, we consider that the available evidence argues very strongly for the presence of 2,6,10-trimethyltetradecane as the major constituent of this region.

It has been previously suggested[5] that phytol might be the precursor to the saturated isoprenoid hydrocarbons. The C_{20} isoprenoid skeleton is shown in Fig. 7 (i). It can be seen that the formation of the C_{16}, C_{18}, C_{19} isoprenoids would require only one cleavage in contrast to the C_{17} isoprenoid which would require two cleavage points; the latter process is considered to be inherently less probable. The relative concentrations of these isoprenoids in the Antrim Shale would seem to vindicate such a scheme.

The possibility that a C_{30} isoprenoid such as squalane might give rise to the C_{17} saturated isoprenoid hydrocarbon has also been considered. If squalane is a major precursor one might expect to find other isoprenoid hydrocarbon types, in particular the C_{19} isoprenoid, 2,6,10-trimethylhexadecane. This would be present in addition to

the C_{19} isoprenoid, 2,6,10,14-tetramethylpentadecane, pristane, which has been isolated from marine sources.[6–8] Such a scheme is shown in Fig. 7 (ii).

The C_{19} isoprenoid 2,6,10-trimethylhexadecane has been synthesized from farnesol by a similar scheme to that used in the synthesis of the C_{17} isoprenoid hydrocarbon, where butyraldehyde rather than acetaldehyde is now allowed to react with the Grignard reagent prepared from hexahydrofarnesyl bromide. The coinjection of this

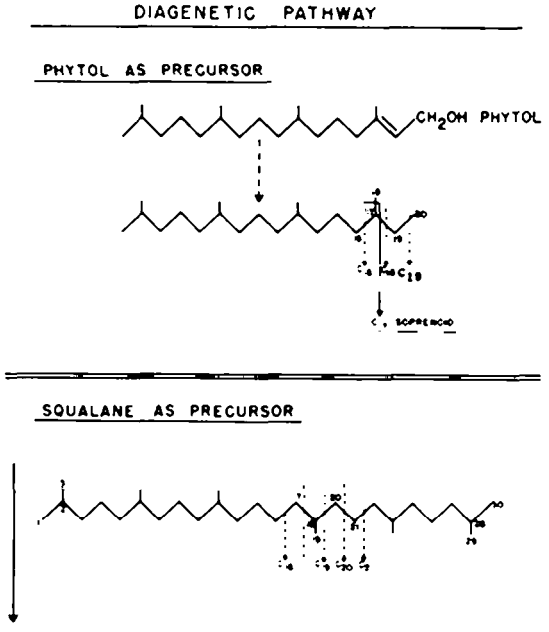
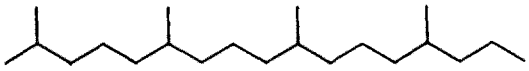


Fig. 7. Diagenetic pathway to the isoprenoid alkanes with (i) phytol as precursor (ii) squalane as precursor.

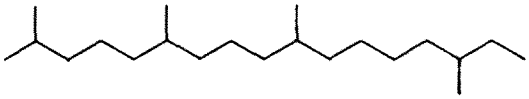
C_{19} isoprenoid standard into the branch-cyclic hydrocarbon fraction of the Antrim Shale does *not* provide convincing evidence for its presence. Certainly, if this isoprenoid is present it is there in small quantities. On the basis of this evidence squalane would not appear to be a significant precursor of the saturated isoprenoid alkanes.

The C_{21} isoprenoid provides a more critical test of this hypothesis. The regular C_{21} isoprenoid, 2,6,10,14-tetramethylheptadecane, already reported by Bendoraitis[5] and tentatively identified by this group,[1] could be derived from a C_{40} isoprenoid precursor, by analogy with our previous diagenetic schemes (Fig. 7). The C_{21} isoprenoid 2,6,10,15-tetramethylheptadecane, could only reasonably arise if a C_{30} isoprenoid such as squalane were a precursor. The mass spectra of these two isomers should exhibit only very minor differences. An unequivocal identification of the C_{21} isoprenoid present in the Antrim Shale might provide evidence for the nature of the precursor.

[6] N. A. Sorenson and J. Mehlum, *Acta Chem. Scand.* **2**, 140 (1948).
[7] M. Blumer, M. M. Mullin and D. W. Thomas, *Science*, **140**, 975 (1963).
[8] J. D. Mold, R. K. Stevens, R. E. Means and H. M. Ruth, *Nature, Lond.* **199**, 283 (1963).



2,6,10,14-Tetramethylheptadecane



2,6,10,15-Tetramethylheptadecane

The coinjection of the regular C_{21} isoprenoid† into the branch-cyclic fraction of the Antrim Shale indicates that this isoprenoid is *not* present in any significant quantity, but was found to have a retention time very similar to that of a major peak in the capillary gas chromatogram of the branch-cyclic fraction from the Antrim Shale. This somewhat surprising result suggests that the alternative C_{21} isoprenoid isomer derived from squalane may represent the structure of the C_{21} isoprenoid isolated from the shale. These two isomers would be closely separated on a capillary gas chromatograph. We are at present synthesizing this alternative C_{21} isoprenoid, 2,6,10,15-tetramethylheptadecane to confirm this prediction. The identification of the C_{21} isoprenoid isolated from the Antrim Shale as 2,6,10,15-tetramethylheptadecane would again bring into question the role of squalane as precursor to these saturated isoprenoid alkanes.

Another isomeric C_{19} alkane, 2,6,10,13-tetramethylpentadecane has also been synthesised by a similar scheme to those previously mentioned. In this case methyl ethyl ketone is allowed to react with the Grignard reagent prepared from hexadydrofarnesyl bromide and the tertiary alcohol so formed is dehydrated with iodine. One would expect that the three C_{19} isomers, pristane, 2,6,10-trimethylhexadecane and 2,6,10,13-tetramethylpentadecane, might have very similar mass spectra and that for a slightly impure sample of a C_{19} isoprenoid isomer isolated from a shale, (which is the case for the Antrim C_{19} isoprenoid), assigning a specific structure to the isomer might be difficult on the basis of mass spectra alone. Moreover this assignment is somewhat critical since the C_{19} alkane, 2,6,10,13-tetramethylpentadecane, would not be expected to derive from the biological precursors generally considered to give rise to isoprenoid hydrocarbons. A comparison of the mass spectra of the C_{19} hydrocarbon isomers together with that of the C_{19} isoprenoid isolated from the shale emphasises this difficulty explicitly (Fig. 8).

The order of elution of the C_{19} isomers is shown in Fig. 9.

Coinjecting standards in this case, enabled a specific structure to be assigned. For the C_{19} isoprenoid isolated from the Antrim Shale there is little doubt that it has the pristane structure. The mass spectrum of the Antrim C_{19} isoprenoid, if anything, shows more resemblance to 2,6,10,13-tetramethylpentadecane than to pristane, but coinjection of the respective standards indicates that the former possibility is not feasible.

The three C_{19} isoprenoid isomers were also distinguished by a close analysis of the 7·25 μ (1380 cm^{-1}) region, (the Me symmetrical bending region) of their IR spectra, obtained from a Beckman IR-7 instrument. Area analysis of the 7·25 μ (1380 cm^{-1})

† We thank Mr. W. H. Van Hoeven for supplying us with a sample of the regular C_{21} isoprenoid.

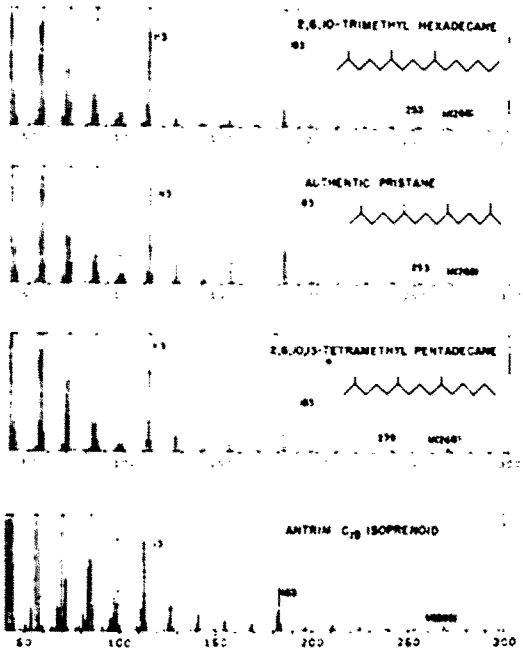


Fig. 8. A comparison of the mass spectra of three C_{19} isomeric alkanes with the mass spectrum of the C_{19} isoprenoid from the Antrim Shale.

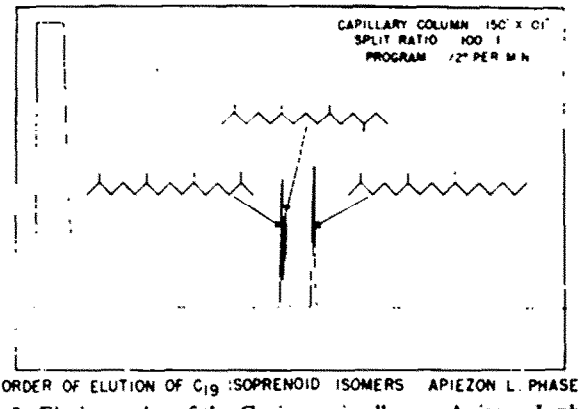


Fig. 9. Elution order of the C_{19} isomeric alkanes, Apiezon L phase.

region can be used in Me group estimation.[9] When two Me groups are on the same carbon atom the 7·25 μ (1380 cm^{-1}) peak splits into two components, one at ~7·22 μ (1385 cm^{-1}) and the other ~7·30 μ (1370 cm^{-1}). These C_{19} isoprenoid isomers therefore, in which the number of *gem*-dimethyl groups and single Me groups is different for each isomer, can be identified on the basis of their IR spectra. NMR might also provide some information. However, the quantity of a pure compound isolated from a sediment is generally so small that this physical measurement is rarely possible.

[9] J. C. D. Brand and G. Eglinton, Chapter IV, *Applications of Spectrometry to Organic Chemistry*. Oldbourne Press, London (1965).

For most sedimentary organic extracts biological precursors are to be anticipated. The unequivocal identification of pristane or the C_{20} isoprenoid, phytane, in organic hydrocarbon extracts of known non-biogenic origin (for example, the Fischer-Tropsch Reaction Product) would seriously undermine the value of these hydrocarbons as criteria for biological precursors. The purpose of this discussion seeks to emphasise the extreme care necessary in assigning structures to constituents of complex hydrocarbon mixtures on the basis of gas chromatographic analysis or mass spectrometric analysis alone.

Many valuable contributions have been made to the problem of hydrocarbon genesis in sediments.[10,11] Apart from oxidation, reduction and decarboxylation which certainly occur during oil generation, there must also occur destruction of simple carbon-carbon bonds. Welte[11] has considered the hypothesis that oil genesis is primarily the result of a "thermal disintegration of finely disseminated organic material in the source rock." Thermal cracking processes, which are non-catalytic, would give rise to lower molecular weight hydrocarbons. Abelson[12] has estimated that such hydrocarbons could have been formed during 100 million years under an average temperature of 160°. Cracking processes of this nature might be reasonably postulated to account for the formation of the saturated isoprenoid hydrocarbons from the biological precursor, phytol.

EXPERIMENTAL

Physical measurements. IR spectra were recorded on a Perkin-Elmer infracord using a thin film for the liquids. For high-resolution IR spectra of micro samples the Beckman IR-7 was used with a Beckman Beam Condenser. NMR spectra were recorded on a Varian A-60 spectrometer, at 60 mc, with CCl_4 as solvent and TMS as internal standard; values on the tau scale (ppm) are reported with reference to TMS at a value of 10. Mass spectra were determined on a modified C.E.C. mass spectrometer, Model 21-103C, with ionising voltage of 70 eV, and an inlet heated to about 200°.

All preparative GLC were run with the following conditions, except where specifically stated in the manuscript: 10 ft × ¼ in; 3% S.E. 30 on 80–100 mesh Chromosorb W (DMCS); 60 ml/min He; dector 245°; injector 280° (Aerograph Model, A-90-P2). Capillary gas chromatograph conditions were as follows: Capillary column 150 ft × 0·01 in; apiezon L; 50 ml/min, He; detector 185°; injector 305°; programmed at 0·5°/min; Perkin-Elmer Model 226.

Hexahydrofarnesol. An 8·9 g sample of hexahydrofarnesol (40 mM) in 25 ml of abs alcohol was hydrogenated in a Brown[9] Hydrogenator[13] (Delmar Scientific Laboratories) using a Pt–C catalyst. The reaction was carried out at room temp and followed quantitatively. The reaction was 95–98% complete after 4 hr. (The use of PtO_2 catalyst instead of Pt–C gives a 95% yield of the hydrogenolysis product, farnesane.) Yield = 8·7 g (90%) [94% hexahydrofarnesol; 5% farnesane; 1% unhydrogenated material (determined by GLC)]. *Physical constants:* (Reaction Product) n_D^{25} 1·4392; [lit.[14], n_D^{25} 1·4487, hexahydrofarnesol; n_D^{25} 1·4303, farnesane.] IR 3·02 μ; 7·25 μ, 7·30 μ. Mass spectrum *m/e* 228 (M), *m/e* 210 (M-18). (Found: C, 78·31; H, 13·79. Calc. for $C_{15}H_{32}O$: C, 78·86; H, 14·13%.)

Hexahydrofarnesyl bromide. An 8 g sample of the reaction product (containing 95% of hexahydrofarnesol) in 35 ml of n-heptane was brominated by bubbling anhyd HBr through the soln, heated at 60° for 10 hr. The crude product was fractionally distilled through the 35 cm Podbielniak column at 1 mm press. The fraction boiling at 122·5°–123·5° was collected, yield = 5·02 g (48%). *Physical constants:* n_D^{25} 1·4605 (lit.[14,15], n_D^{19} 1·4605). Mass spectrum *m/e* 290 (M), *m/e* 292 (M). (Found: Br, 27·45; Calc. for $C_{15}H_{31}Br$: Br, 27·30%.)

[10] J. M. Hunt, *International Scientific Oil Conf. Proc.* preprint, Budapest (1962).
[11] Dietrich H. Welte, *Bull. Am. Ass'n of Petroleum Geologists* **49**, 2246 (1965).
[12] P. H. Abelson, *6th World Petroleum Cong. Proc.* Sec 1; pp. 397–407. Frankfurt/Main (1963).
[13] H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.* **84**, 1493 (1962).
[14] F. G. Fischer, *Liebigs Ann.* **464**, 89 (1928).
[15] I. M. Heilbron and A. Thompson, *J. Chem. Soc.* **1**, 890 (1929).

5,9,13-*Trimethyltetradecane-2-ol.* Following the general procedure for Grignard Reaction: [see e.g. Cason/Rapoport, Lab. Text in Org. Chem., Chapt. 16.] 2·5 g (~8 mM) hexahydrofarnesyl bromide in 5 ml of dry ether and 0·25 g of Mg in 5 ml of dry ether, was allowed to react with 0·35 g of acetaldehyde; Yield = 0·65 g (31%); *Physical constants:* IR 2·98 μ; 7·25 μ, 7·30 μ.

2-*Acetoxy*-5,9,13-*trimethyltetradecane.* A sample of 0·65 g of 5,9,13-trimethyltetradecane-2-ol, 1·1 ml of Ac_2O, and 4 ml of dry benzene were refluxed for 4 hr according to the procedure of Cason and Graham.[16] The reaction mixture was cooled, poured onto 5 g of ice and stirred. The residual Ac_2O was removed by washing with 10% $NaHCO_3$, and the product was extracted with ether, yield = 0·59 g (78%): *Physical constants.* IR 5·70 μ; 8·02 μ; 7·25 μ, 7·30 μ. Mass spectrum NO Mol. ion, *m/e* 238 (M-60).

5,9,13-*Trimethyltetradecenes.* 2-acetoxy-5,9,13-trimethyltetradecane, was pyrolysed at 515°, essentially according to Bailey and Golden,[17] in a 1·0 cm × 20 cm Pyrex tube to a depth of 16 cm with 3 mm Pyrex helices. Dry N_2 was swept through the apparatus continuously and the acetate was allowed to drop onto the heated helices, drop by drop, over 3 min. The pyrolysate was rinsed from the trap with 25 ml of normal heptane. The heptane soln was washed with 10% $NaHCO_3$aq, then with distilled water and dried. To remove the residual acetate the crude product was chromatographed on an alumina column (Merck reagent grade) and eluted with n-heptane. The heptane eluate was then dried and evaporated, yield = 0·23 g (48%): *Physical constants:* IR 6·07 μ: 7·25 μ, 7·30 μ; 10·08 μ, 10·97 μ, 10·35 μ. NMR 4·6 τ, 5·25 τ, (complex multiplets). GLC 3 distinct peaks (capillary column). Mass spectrum *m/e* 238 (M).

2,6,10-*Trimethyltetradecane.* The mixture of alkenes, 0·14 g, in 10 ml of abs alcohol were hydrogenated in a Brown[3] Hydrogenator[18] (Delmar Scientific Laboratories) using 15 mg of PtO_2 as a catalyst. The hydrogenation was complete in 5 min, yield = 0·13 g (94%); *Physical constants:* n_D^{25} 1·4291; IR 7·25 μ, 7·30 μ; mass spectrum *m/e* 240 (M) (Fig. 5). GLC one distinct peak (capillary column).

7,11,15-*Trimethylhexadecane-4-ol.* Following the procedure according to Cason and Rapoport, Lab. Text in Org. Chem., Chapt. 16. 1·0 g (~3 mM) Hexahydrofarnesyl bromide in 5 ml dry ether and 0·15 g of Mg turnings in a 5 ml of dry ether were allowed to react with 0·25 g dry butyraldehyde, yield = 0·47 g (48%); *Physical constants:* IR 2·96 μ; 7·25 μ, 7·30 μ; mass spectrum *m/e* 284 (M); *m/e* 266 (M-18).

4-*Acetoxy* 7,11,15-*Trimethyltetradecane.* Procedure as for 2-acetoxy-5,9,13-trimethyltetradecane; a sample of 0·38 g of 7,11,15-trimethylhexadecane-4-ol, was used as starting material, yield = 0·325 g (75%); *Physical constants:* IR 5·71 μ; 8·01 μ; 7·25 μ, 7·30 μ; mass spectrum No Mol. ion, *m/e* 266 (M-60).

7,11,15-*Trimethylhexadecenes.* The acetate cracking was carried out essentially according to Bailey and Golden,[17] and as described previously for synthesis of 5,9,13-*trimethyltetradecenes.* Starting material: 0·3 g of 4-acetoxy-7,11,15-trimethylhexadecane, yield = 0·14 g (57%). *Physical constants:* IR weak, broad 5·98–6·20 μ; 7·25 μ, 7·30 μ; 10·32 μ. NMR 4·6 τ (complex multiplet). GLC 2 distinct peaks (capillary column). Mass spectrum *m/e* 266 (M).

2,6,10-*Trimethylhexadecane.* The mixture of alkenes, 90 mg in 10 ml of abs alcohol, were hydrogenated in a Brown[3] Hydrogenator[18] (Delmar Scientific Laboratories) using 12 mg of PtO_2 as a catalyst. The reaction was complete after 5 min, yield = 85 mg (94%). *Physical constants:* IR 7·25 μ, 7·30 μ. Mass spectrum *m/e* 268 (M) (Fig. 8). GLC 1 distinct peak (capillary column).

3,6,10,14-*Tetramethylpentadecane-3-ol.* Following the general procedure described in Cason, Rapoport, Lab. Text in Org. Chem., Chapt. 16. 0·38 g (1·5 mM) Hexahydrofarnesyl bromide in 3 ml of dry ether and 0·06 g Mg turnings in 5 ml of dry ether were allowed to react with 0·1 g of methyl ethyl ketone, yield = 0·20 g (54%). *Physical constants:* IR 2·95 μ; 7·25 μ, 7·30 μ. Mass spectrum No Mol. ion, *m/e* 266 (M-18).

3,6,10,14-*Tetramethylpentadecenes.* A sample of 95 mg of 3,6,10,14-tetramethylpentadecane-3-ol, and a few crystals of I_2 were refluxed in 4 ml of boiling toluene for 10 hr. The reaction mixture was cooled and washed with 5 ml of 5% $NaHSO_3$aq and then with 5 ml distilled water. The toluene extract was evaporated and dried. The crude product was purified from any residual alcohol on an alumina column (Merck reagent grade) and eluted with heptane. The heptane eluate was dried over $MgSO_4$.

[16] J. Cason and D. W. Graham, *Tetrahedron* **21**, 471 (1965).
[17] W. J. Bailey and H. R. Golden, *J. Am. Chem. Soc.* **75**, 4780 (1952).

yield ≈ 45 mg (54%). *Physical constants:* IR 7·25 μ, 7·30 μ; weak band 11·2 μ. GLC 5 distinct peaks (capillary column), mass spectrum *m/e* 266 (M).

Synthesis of 2,6,10,13-*tetramethylpentadecane*. The mixture of alkenes, 33 mg, in 5 ml of solvent (3:1 abs alcohol:heptane) were hydrogenated in a Brown[8] Hydrogenator (Delmar Scientific Laboratories) using 4 mg of PtO_2 catalyst and 3 drops of 10% conc HCl. The reaction was followed to completion within an hr, yield ≈ 30 mg. *Physical constants:* IR 7·25 μ, 7·30 μ; mass spectrum *m/e* 268 (M) (Fig. 8). GLC 1 distinct peak (capillary column).

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