

THE SYNTHESIS OF STANDARDS IN THE CHARACTERIZATION OF A C_{21}

ISOPRENOID ALKANE ISOLATED FROM PRECAMBRIAN SEDIMENTS

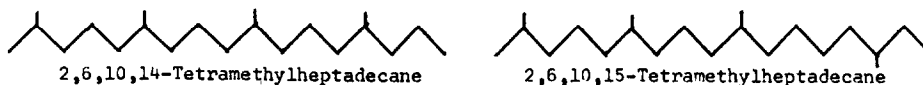
E. D. McCarthy, W. Van Hoeven and Melvin Calvin

Laboratory of Chemical Biodynamics and Space Sciences Laboratory
University of California, Berkeley, California

(Received in USA 26 June 1967)

The saturated isoprenoid alkanes, pristane (C_{19}) and phytane (C_{20}), have been isolated and identified in sediments dating from Precambrian times.^(1,2,3) Other isoprenoid alkanes, in particular the C_{15} (farnesane), C_{16} (homofarnesane), and the C_{18} (norpristane) compounds, have also been isolated and identified in oils and sediments of differing ages.^(3,4,5) Bendoraitis⁽⁶⁾ has characterized a C_{21} isoprenoid alkane in an East Texas gas oil to which he assigned the structure 2,6,10,14-tetramethylheptadecane, but this represents the only report of t isoprenoid alkane in oils or sediments. This structure has been tentatively assigned to C_{21} compounds isolated from the Soudan Shale (2.7×10^9 years) and from the Nonesuch Seep Oil (1.0×10^9 years).⁽³⁾ However, impurities in the mass spectra of these compounds prevent one from assigning an unequivocal structure. In view of the scarcity of reports of the C_{21} isoprenoid alkane we have determined to characterize its structure unambiguously.

The hypothesis that oil genesis is primarily the result of thermal cracking processes has been considered by Welte,⁽⁷⁾ and such processes might be reasonably postulated to account for the occurrence of isoprenoid alkanes. Biogenetic considerations lead one to suppose that a C_{21} isoprenoid alkane would be derived from a C_{30} or a C_{40} isoprenoid precursor, of the squalene or lycopene type, or from a C_{30} or higher polyisoprenoid (head to tail) such as solanesol (C_{45}).⁽⁸⁾ The two C_{21} isoprenoids which would result from lycopene and solanesol in the one case, and squalane in the other, are shown below:



The diagenetic* pathway leading to these C_{21} isoprenoids is shown in FIG. 1. The two compounds differ from each other only in the position of one methyl branch. The mass spectra of these two compounds would be very similar. Owing to the complex nature of the organic extract from oils and sediments it has been difficult to isolate individual components in pure form. The

* Diagenesis: post-depositional transformations

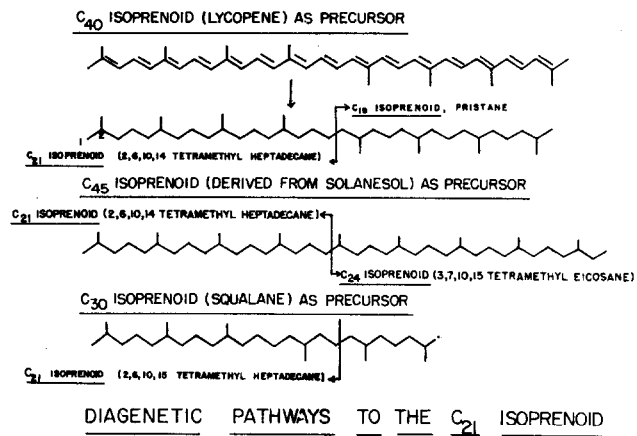


FIG. 1

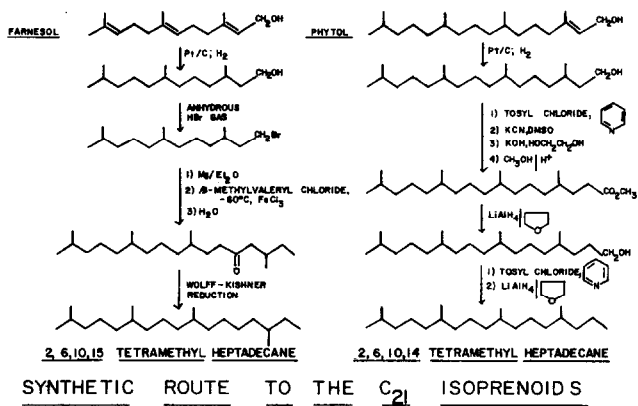


FIG. 2

structural interpretation of the mass spectra of these even slightly contaminated compounds is therefore open to ambiguities.

The value of having available synthetic standards has already been emphasized.^(9,10,11) In an attempt to resolve such ambiguities we have synthesized the two C₂₁ isoprenoid alkanes under consideration starting from the naturally available starting materials, farnesol and phytol. Our synthetic scheme is shown in FIG. 2. These two compounds were then used in our identification procedure by capillary gas chromatography and mass spectrometry. They are readily separated by capillary gas chromatography (FIG. 3). The similarity of these mass spectra is shown in FIG. 4 and comparison of these spectra with the mass spectrum of the C₂₁ compound isolated from the Soudan Shale emphasizes the difficulty of interpreting the structure of such a compound on the basis of mass spectrometry alone.

The coinjection of the standard C₂₁ isoprenoid alkane, 2,6,10,14-tetramethylheptadecane, into the branch-cyclic fraction of the Soudan Shale, indicates the C₂₁ compound isolated from the Soudan Shale has the structure of this standard. This coinjection technique has been repeated on three different phases and an identical result was obtained in each case. Furthermore, coinjection of the alternative C₂₁ isoprenoid, 2,6,11,15-tetramethylheptadecane, indicates that if this alternative compound is present at all it is present in very small quantities. The structural identification of this C₂₁ isoprenoid by gas chromatography is shown in FIG. 5. Using this procedure we have assigned the same structure to the C₂₁ compound isolated from the Nonesuch Seep Oil and the Antrim Shale (300 x 10⁶ years).

The characterization of the structure of the C₂₁ isoprenoid alkane found in oils and sediments as 2,6,10,14-tetramethylheptadecane, along with the apparent absence of the C₂₁ compound, 2,6,10,15-tetramethylheptadecane, suggests that squalene plays a relatively minor role as precursor to the isoprenoid alkanes. Furthermore, the absence of C₁₉ compound, 2,6,10-trimethylhexadecane, which would be expected to occur if squalene were a significant precursor, supports this hypothesis. If an oligoisoprenoid hydrocarbon such as that derived from solanesol (C₄₅), were a source of the C₂₁ isoprenoid (2,6,10,14-tetramethyl^{hepta}decane) the other fragment would be a C₂₄ compound having an unbranched C₅ terminus (see FIG. 1) which, if present at all, is there in only tiny amounts.

The regular head to tail polymerization of isoprene is not limited to biogenic processes.⁽¹²⁾ Furthermore, isoprene itself is produced in significant quantities in the thermal cracking of ethane.⁽¹³⁾ The non-branched carbon sequence, characteristic of the tail to tail

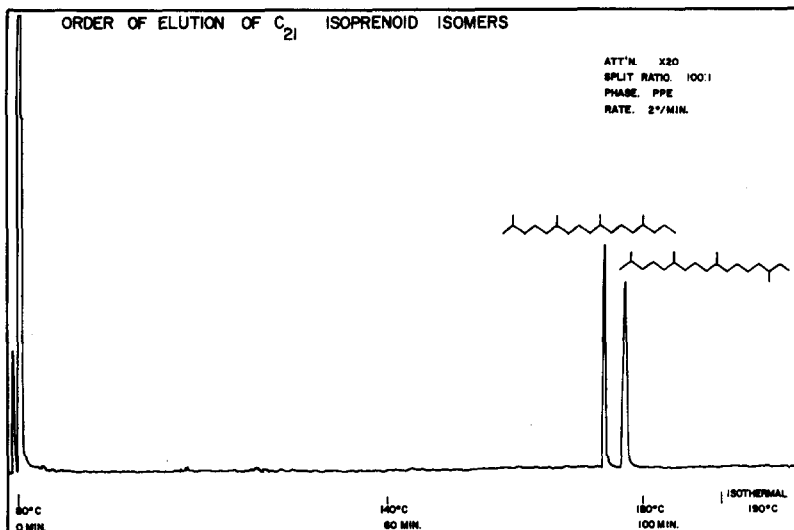


FIG. 3

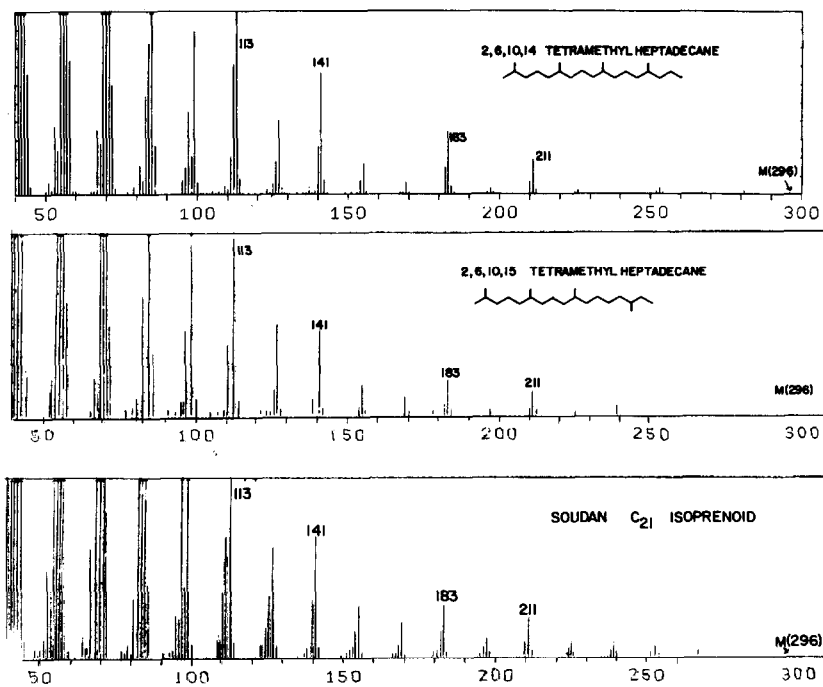
RELATIVE ELUTION TIMES OF THE C_{21} ISOPRENOIDS

FIG. 4

COMPARISON OF THE MASS SPECTRA OF THE C_{21} ISOPRENOIDS

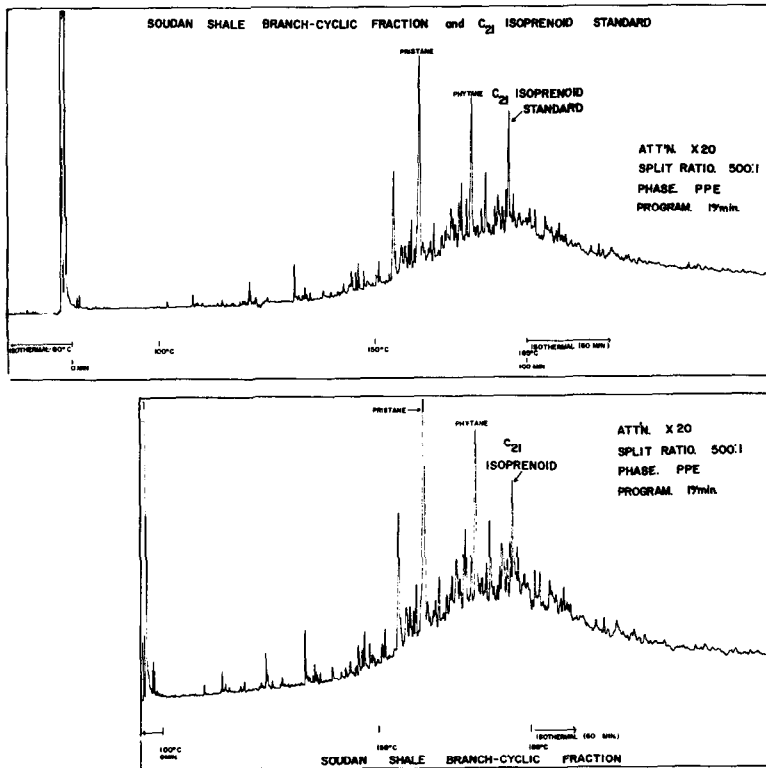


FIG. 5

COINJECTION OF THE C₂₁ ISOPRENOID STANDARD IN THE STRUCTURAL CHARACTERIZATION OF THE 2,6,10,14-TETRAMETHYLHEPTADECANE IN THE SOUDAN SHALE

linkage in squalene (C₃₀) and lycopene (C₄₀), may very well be the unique structural feature we are seeking for the identification of biogenic materials in ancient sediments. Efforts are being made to characterize compounds in oils and sediments which contain this structural feature or derivatives characteristic of it.

Acknowledgement--This work was supported by the National Aeronautics and Space Administration under grant NsC 101-61.

REFERENCES

1. J. Oró and D. W. Nooner, Nature, 213, 1082 (1967).
2. W. G. Meinschein, E. S. Barghoorn and J. W. Schopf, Science, 145, 262 (1964).
3. R. B. Johns, T. Belsky, E. D. McCarthy, A. L. Burlingame, Pat Haug, H. K. Schnoes, W. Richter and M. Calvin, Geochim. et Cosmochim. Acta, 30, 1191 (1966).
4. G. Eglinton, P. M. Scott, T. Belsky, A. L. Burlingame, W. Richter and M. Calvin, in "Advances in Organic Geochemistry, 1964", ed. by G. D. Hobson and M. C. Louis, Pergamon Press, London (1966), 41-74.
5. W. Van Hoveen, Pat Haug, A. L. Burlingame and M. Calvin, Nature, 211, 1361 (1966).
6. J. G. Bendoraitis, B. L. Brown and R. S. Hepner, World Petroleum Congress, Frankfurt/Main, Germany, June 19-26, 1963.
7. Dietrich H. Welte, Bull. Am. Ass'n. of Petroleum Geologists, 49, 2246 (1965).
8. B. O. Lindgren, Acta. Chem. Scand., 19, 1317 (1965).
9. E. D. McCarthy and M. Calvin, Tetrahedron, 23, 2609 (1967).
10. J. Cason and D. W. Graham, Tetrahedron, 21, 471 (1965).
11. J. Cason, and Ahmed I. A. Khodair, J. Org. Chem., 32, 575 (1967).
12. G. Natta, L. Porri and L. Fiore, Gazzetta Chimica Italiana, 89, 761 (1959).
13. Private communication from Dow Chemical Company, Freeport, Texas, which produces isoprene as a side-product in the thermal cracking of ethane in substantial quantities.