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University of California
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ORGANIC GEOCHEMICAL STUDIES. I. MOLECULAR
CRITERIA FOR HYDROCARBON GENESIS

Eugene D. McCarthy and Melvin Calvin

September 22, 1967

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ORGANIC GEOCHEMICAL STUDIES. I. MOLECULAR CRITERIA
FOR HYDROCARBON GENESIS*

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Laboratory of Chemical Biodynamics and Space Sciences Laboratory

University of California, Berkeley, California

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Introduction

In recent years the search for life-forms at the earliest periods of geological time has been continued not only at the morphological level but also at the molecular level. This has been possible as a result of the increase in our biochemical knowledge and with the advent of analytical techniques that are capable of describing the intimate molecular architecture of individual molecules in acute detail. The fundamental premises upon which this organic geochemical approach rest are the following: that certain molecules, possessing a characteristic structural skeleton, show a reasonable stability to degradation over long periods of geological time; that their structural specificity can be understood in terms of known biosynthetic sequences; and that their formation by any non-biological means is of negligible probability. In this manuscript it is proposed to critically re-examine these premises and to establish criteria whereby one can differentiate molecules

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derived from biological systems from those that have their origin in non-biological processes. The importance of establishing such criteria lies in the significance these criteria have in determining whether life exists, or has existed, on other planets. Within the very near future it may be possible to provide an initial answer to this question when the first lunar samples are returned to the earth for analysis.

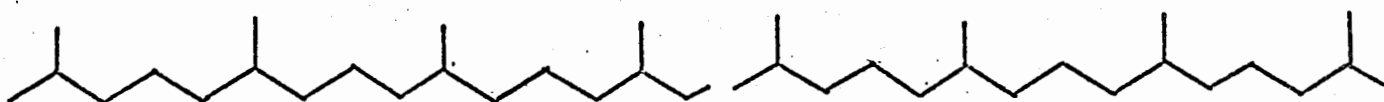
Almost all classes of organic compounds which have been recognised as the constituents of living organisms have been looked for in sedimentary deposits of the geological environment. Such classes of compounds are the nucleic acids, the proteins, the amino acids, the organic pigments, the carbohydrates and the lipids. All these fulfill the structural specificity requirement stated above, but only the lipids and, to a lesser extent, the class of organic pigments known as porphyrins, survive from the earliest periods of geological time to be related to their original form today. All organic compounds in the geological environment are unstable with respect to temperature. The rates of thermal degradation processes will be dependent, therefore, on the nature of the organic compound and upon the geothermal temperatures to which it has been subjected. Since some geothermal temperatures are often quite low and may not have exceeded 30°C,¹ organic compounds may survive long period of time in the geological environment. In some cases thermal degradation will take place very slowly. Conway and Libby² measured the rates of very slow reactions

under various conditions. The specific reaction which they chose to study was the decarboxylation of the amino acid, alanine. The rates were measured using radioactive labelling and low-level counting techniques at room temperature. The half-life for decarboxylation was found to be about 10^9 years; at higher temperatures (420-430°K) the half-life was only 100 years. This experiment suggested that amino acids derived from the hydrolysis of proteins could be stable over millions of years under lower temperature conditions. In keeping with this prediction Abelson³ had identified a series of amino acids, including alanine, in a Trilobite fossil, whose age is believed to be 450 million years.

Other classes of organic compounds might be expected to survive these relatively mild thermal conditions of geological environment. The stable tetrapyrrole portion of the porphyrin molecule has been identified in sediments of Precambrian age.⁴ On the other hand, the carotenoid group of organic pigments are easily destroyed at temperatures about 200°C,¹ in keeping with the almost total absence of these compounds in sediments greater than 20,000 years old.

Of all the classes of organic compounds the lipids have been most generally looked for in the geological environment. Among the lipids the presence of a series of hydrocarbons, whose structures are based on the C_5H_8 isoprene unit, has been invoked as evidence for life-forms in Precambrian times. In particular, two specific hydrocarbons, phytane, thought to be derived from the phytol side chain of the chloro-

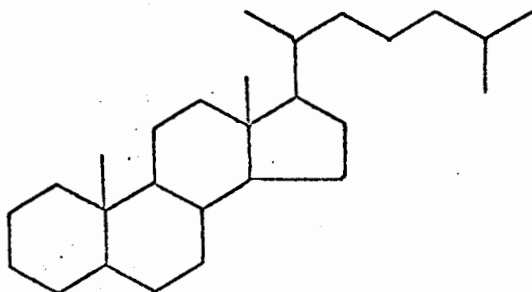
phyll molecules, the green pigment of plants, and pristane, derived from phytol and also present in marine organisms, have been sought in Precambrian sediments.



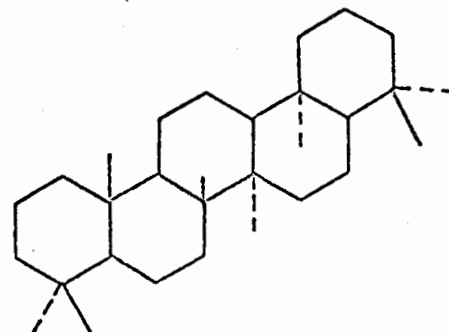
PHYTANE

PRISTANE

Their architectural skeleton, which shows a methyl branch every four carbons, is stable over long periods of time. Hydrocarbons which can be related to the steroid and triterpenoid class of organic compounds have also been found in ancient sediments. Examples from this class are cholestane⁵ and gammacerane⁶ whose structures are shown:



CHOLESTANE



GAMMACERANE

The saturated hydrocarbons are more stable than the porphyrins¹ and would be expected to survive in the geological environment through periods of time greater than the presently-accepted age of the earth (4.5×10^9 years, approximately). The proliferation of isoprenoid hydrocarbons in Precambrian sediments, which have been consistently reported by different research groups,⁷⁻¹¹ is therefore not surprising. Simple calculations for the degradation of hydrocarbons by thermal cracking mechanisms (assuming $E \sim 60$ kcal/mole,¹² a reaction velocity constant (sec^{-1}) ~ 1.0 at about 700°C ¹² and the absence of a catalyst) indicate that hydrocarbons should be stable for more than 10^{22} years, at room temperature, and for 10^{12} years at 100°C . The presence of catalysts in the geological environment will presumably accelerate the rates of these processes.

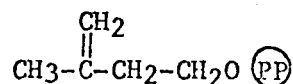
The characteristic architecture of the isoprenoid hydrocarbon molecule until recently has been generally accepted as an unequivocal marker of biological origin. It was thought that no abiogenic synthesis could produce the unique structural features of the isoprenoid molecule. As a result, the idea arose that the isoprenoid hydrocarbons might be used to designate the period in geological history when the transition from chemical evolutionary development to biological evolutionary development was brought about. The absence of isoprenoid hydrocarbons in the organic extract from a Precambrian sediment might serve as a criterion by which the period of chemical evolutionary development might be recognized. That such a transition should exist and that evolution should be continuous, not only in the domain of living

organisms, was a concept that Darwin had clearly recognised himself. Inadequate chemical knowledge at that time about the nature of molecules and their interactions prevented further development of these ideas.

The expectations that such a transition might be recognised at the molecular level of evolutionary development has not been realised for several practical reasons. Most important among these is the paucity of Precambrian sediments known that might form a chronological sequence from the earliest periods of the earth's history to the advent of the Cambrian (600 million years). Moreover, only a few of these sediments have been studied from the organic geochemical standpoint. A more fundamental reason why this transition may not have been recognised, however, now arises with the development of a non-biogenic stereospecific polymerisation of the isoprene molecule to produce polymers that are identical with the isoprenoid polymers synthesised in the living system. The characteristic structure of the isoprenoid molecule may not be as specific as once was thought. In attempting to recognise this transition in evolutionary history, therefore, it is necessary to establish criteria which will distinguish between those organic compounds--and particularly the hydrocarbons--that are derived from abiogenic sources and those that are derived from living systems. Only when this has been achieved can an empirical approach toward the recognition of this transition point be carried out with any reliability.

Biosynthesis of the Isoprenoid Structure

The biosynthetic pathway of the isoprenoid hydrocarbons has been fully elucidated (for a general review, see R. B. Clayton^{13,14}). It has been established that in the biological system isopentenyl pyrophosphate plays an important role. This five-carbon fragment whose structure is shown is the precursor to all the intermediates involved

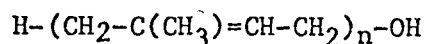


in the isoprenoid pathway. Polymerisation of this five-carbon unit takes place by nucleophilic attack at the 5-position of isopentenyl pyrophosphate and subsequent displacement of the pyrophosphate group to give a 10-carbon fragment, or monoterpene compound. This displacement involves a head to tail linkage and has been shown to take place in a stereospecific manner.¹⁵ This biological mechanism is repeated in further polymerisation reactions. However, the head to tail mechanism is replaced by a tail to tail one at two places:

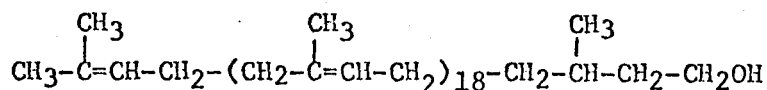
- 1) The C₁₅ compound farnesyl pyrophosphate, reacts with another molecule of farnesyl pyrophosphate to give the hydrocarbon squalene:
- 2) In the biosynthetic pathway to the carotenoids, C₄₀ terpene compounds, an analogous tail to tail linkage is formed between two C₂₀ compounds.

These general features characterise the isoprenoid pathway in biological systems.

Certain other aspects of the stereospecific character of the biosynthetic pathway should be mentioned here. The work of Lindgren¹⁶ has shown that homologous aliphatic C₃₀-C₄₅ terpenols are found in the wood extractives of birch (betula verrucosa Erh.). The alcohols have the general formula

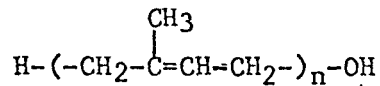


where n is 6,7,8,9. About 60% of their double bonds have the cis configuration. This finding shows that C₃₀ terpenoid and C₄₀ terpenoid structures have been isolated from living organisms containing both the tail to tail linkage and the head to tail linkage. Higher terpenoid compounds have been isolated from pig liver, which is a rich source of dolichol. The alcohol has fifteen or sixteen of its eighteen internal isoprene units in the cis configuration.¹⁷



DOLICHOL

Isoprenyl alcohols, whose structures have been characterised as undeca-isoprenol-1 and dodecaisoprenyl-2, have been isolated from silk/worm feces. The presence of solanesol in the same source was also confirmed, which has the following structure:



SOLANESOL

(n = 9)

This compound had been characterised earlier by other workers¹⁹ who had

isolated this compound from flue-cured tobacco. Its structure was confirmed by Erickson et al.²⁰ and by Kofler et al.²¹ as a C₄₅-isoprenoid compound. Mevalonic acid, which is known to be a precursor of isopentenyl pyrophosphate in the biosynthesis of cholesterol, is also an intermediate in the biosynthesis of ubiquinone, Vitamin K and the tocopherols, all of which contain ^{the} isoprenoid side chain.²²

The biosynthetic pathway to rubber and gutta, which is also a polyisoprenoid and is produced by a small number of tropical species, has been discussed by Bonner.²³ Both rubber and gutta are polymeric substances derived from isoprene in which the isoprene units are linked together through 1,4 linkages. Rubber contains from 500 to 5000 isoprene units, while gutta contains about 100 units. It is of interest to note that the double bonds of the individual isoprene molecules are in the cis configuration for rubber and in the trans configuration for gutta. No high polymers have been found which contain both the cis and trans geometry.

Non-Biogenic Synthesis of the Polyisoprenoid Structure

The biological polymerisation mechanism involves a stereospecific 1,4 linkage of the individual isoprene molecules and it is this feature that has been hitherto assumed a unique aspect of the biosynthetic pathway. Recent studies on the non-biological polymerisation of small molecules, such as propylene and butadiene, have indicated that these reactions proceed with considerable stereospecificity.

Natta was the first to show that the polymerisation of conjugated diolefins can proceed in a stereospecific manner. He demonstrated that butadiene, isoprene and 1,3 pentadiene were converted to polymers containing 99% of linear 1,4 trans structures by means of a highly stereospecific catalyst $\text{Al}(\text{Et})_3\text{-VCl}_3$ (molar ratio 2:1) in heptane.²⁴ The presence of even small amounts of impurities impairs the stereospecificity of the reaction. The infrared spectrum of the polymer resembles that of natural rubber. X-ray diffraction studies show the linearity of the polymers and a periodicity of 4.82 Å along the main axis. The use of TiCl_3 produces a stereospecific 1,4 cis linked polymer. The exact mimicking of the stereospecific features of the biosynthetic pathway in the terpenoid series would seem to dispel the notion that the head to tail linkage is unique to biological systems. Natta's work has shown that not only the 1,4 trans configuration of the biopolymer, gutta, but also the 1,4 cis configuration of the natural rubber can be reproduced by non-biological methods. These findings call into serious question the validity of the isoprenoid compounds as 'biological markers'. Certainly the structure of the

isoprenoid hydrocarbons taken in isolation can no longer be considered to be unambiguously derived from a biological precursor. The presence of the isoprenoid hydrocarbons in crude oils and sediments must be viewed against the background of the other components present.

Non-Biogenic Polymerisation Processes and Chemical

Evolution

One empirical approach which has endeavoured to reconstruct the evolutionary development of the first living organisms attempts to simulate in the laboratory the types of chemical reactions that could have taken place in the primitive atmosphere and given rise to the simple organic molecules that constitute living organisms today. This approach has met with considerable success. By analogy with the atmospheres of other planets, the atmosphere of the primitive earth is considered to be essentially reducing, consisting of hydrogen, methane, ammonia and water. Most of the fundamental building units of living systems including the amino acids, the sugars, the purines and the pyrimidines, have all been synthesised in varying amounts by the 'primordial atmosphere' experiments where energy, such as ionizing radiation in the form of particulate or gamma radiation, acts on this mixture of gases.

Conspicuously absent among the simple molecules synthesised by these reactions is the isoprene molecule. Any chemical evolutionary theory which would seek to account for the synthesis of the polyisoprenoid compounds in the primitive atmosphere by invoking polymerisation reactions of the Natta type, utilising reduced metal catalysts, must,

at the outset, provide a feasible experimental route to the isoprene molecule. No such pathway has been proposed which has been justified on an experimental basis.

Our interest was first directed toward a possible synthetic route to isoprene in the primordial atmosphere by consideration of a well-established commercial process which has been used in industry for many years. Isoprene is produced in significant quantities as a side-product in the thermal cracking of a mixture of propane and ethane.²⁵ These two hydrocarbons are fed into a pyrolysis furnace in various amounts and undergo thermal cracking at temperatures approaching 1100°K. In the primitive atmosphere the starting materials for this pyrolysis reaction, ethane and propane, could be generated from methane in the presence of an external energy source. At 1000°K these reactions proceed endogonically with a change in free energy amounting to ~17 and ~32 kcals/mole, respectively. In addition to isoprene, sizeable quantities of ethylene, propylene and butadiene are produced in this thermal cracking process. In a typical feed, the relative amounts of these molecules produced are shown in the following table:

Starting Materials: 50% ethane, 50% propane

	<u>Rel. Amount (%)</u>
Ethylene	30
Propylene	6 - 8
Butadiene	2
Isoprene	0.2

There is no reason to suppose that subsequent polymerisation processes in the primitive atmosphere should be confined exclusively to isoprene. Indeed, one would expect that polymerisation processes involving isoprene should proceed more slowly than polymerisation processes involving the other three molecules. Unlike the molecule of ethylene, the propylene molecule is structurally asymmetric. The resulting polymer of propylene can be produced in various steric configurations. Under carefully specified conditions, stereospecific polymers may result, the so-called "isotactic" and "syndiotactic" polymers. Stereospecific polymerisations of butadiene may also give rise to ordered configurations: threo-di-isotactic, erythro-di-isotactic and di-syndiotactic.²⁶ Natta has also shown that a cis 1,4 polybutadiene can be synthesised whose steric purity exceeds the steric purity of ^{the} 97 to 98% cis units found in natural rubber.

One may reasonably question the relevance of such polymerisation reactions to the kinds of reactions that took place in the primitive atmosphere. All these polymerisations require specific catalysts to produce polymers of a given steric configuration. The likelihood of these particular catalysts being available on the primitive earth is somewhat remote. On the other hand, the overall simplicity of the polymerisation reaction, taking place in the presence of metals in their reduced oxidation states and using only isoprene as a starting material, gives credence to the hypothesis that stereospecific polymerisation reactions similar to those developed by Natta might have taken place in the

primitive atmosphere, and that the characteristic 1,4 trans, head to tail linkage of the polyisoprenoid compounds may not be confined solely to the biosynthetic mechanisms.

Accepting for the present this hypothesis, one has still to explain why only the polymerisation mechanisms giving rise to polyisoprenoid compounds survived to become an integral part of the biological system. There is no obvious reason why the polyisoprenoid compounds should be retained in evolutionary development in preference to the analogous polymers based on propylene or butadiene. Many of the polyisoprenoid compounds belong to the general class of biological components known as the lipids; the lipids themselves form an important part of the membranes of living cells. The role of lipids in the transition from chemical evolution to biological evolution may have been especially significant. Oparin²⁷ has suggested that an essential step in the transition between these two evolutionary stages might be the formation of membranes around droplets of organic substances produced in the primitive atmosphere. It may be that there is some important structural feature, as yet unrecognised and confined only to the polyisoprenoid compounds, that makes these polymers the best structural constituents of cell membranes. As a result, only the polyisoprenoid compounds would have survived the transition into biological evolution. This is a speculative hypothesis for which there is no experimental foundation at present.

The Fischer-Tropsch reaction has been considered by protagonists of the abiogenic theory for hydrocarbon formation to be a significant

process in the formation of petroleum. (The Fischer-Tropsch reaction is a catalytic reaction involving carbon monoxide and hydrogen at temperatures between 200°C and 300°C and at atmospheric or higher pressures.) Friedel and Sharkey²⁸ were the first to demonstrate that a similarity exists between low molecular weight alkane isomers (up to C₈) in crude oil and those characterised in the Fischer-Tropsch reaction product. This hypothesis has recently been extended by Hayatsu and Anders to account for the formation of hydrocarbons in the early solar system.²⁹ These authors suggested that such a similarity may have some bearing on the origin of the volatile hydrocarbons of petroleum. Hayatsu and Anders, using a mixture of carbon monoxide and deuterium to eliminate the contamination danger, provided mass spectrometric evidence for the presence of a series of deuterated isoprenoid hydrocarbons, ranging in carbon number from C₉ to C₁₄. One member of this series, C₁₁D₂₄, had a structure identical to the C₁₁H₂₄ hydrocarbon, 2,6 dimethylnonane, which these workers had identified in the Murray meteorite. Ambiguities can arise in the structural characterisation of isoprenoid hydrocarbons where the evidence is based on mass spectrometry alone.³⁰ However, if the identification of a homologous series of isoprenoid hydrocarbons is confirmed in the Fischer-Tropsch reaction product this series would be identical with that reported by Gohring, Schenck and Engelhardt in an Italian Cretaceous shale.³¹ In effect this would provide an abiogenic route to the lower molecular weight isoprenoid hydrocarbons that can be vindicated on an experimental basis.

One of the weaknesses of the Fischer-Tropsch theory as a possible inorganic origin of petroleum is that it has not been able to account for the higher molecular weight isoprenoid hydrocarbons (C₁₅-C₂₁), includ-

ing pristane and phytane, which are found ubiquitously in crude oils and shale extracts as the major components of the 'branch-cyclic' hydrocarbon fractions. Furthermore, the presence of steranes, triterpanes and hydrocarbons derived from carotenoid precursors has not been demonstrated in the Fischer-Tropsch product, whereas these classes of organic compounds have been identified in both Precambrian and more recent sediments,^{4,5} and also in crude oils.⁶ The Fischer-Tropsch reaction product therefore exhibits only a partial resemblance to the hydrocarbon constituents of crude oils; it does, however, show a closer resemblance to hydrocarbon extracts from meteorites. As a possible route to the polyisoprenoid hydrocarbons in chemical evolutionary development this process would seem to be subject to the same limitations in accounting for the isoprenoid distribution in crude oils.

Criteria for Biogenic Origin

The experimental evidence points overwhelmingly to a biogenic origin for almost all the organic extracts of crude oil and shales. It is when we come to analyse such extracts from meteorites,³²⁻³⁴ from Thucholite samples,³⁵ and from hydrothermal deposits³⁶ that the origin of the organic extract is much less clear cut. In view of the recent polymerisation studies of Natta which have brought into question the validity of isoprenoid hydrocarbons as 'biological markers' it is important to search for criteria which will provide an unambiguous answer to these uncertainties and which will reconfirm the fundamental premise upon which the organic geochemical approach rests. This is more than

just an academic exercise for it is these same uncertainties about the origin of the organic extracts that may very well arise when the lunar samples are returned to earth for analysis. It is therefore imperative that these uncertainties be resolved.

Among the many approaches that have been adopted in endeavouring to find criteria which will determine whether organic material has an abiogenic or biogenic origin, one particular approach, which has not been utilised to any significant extent, appears to be most promising. This approach involves the determination of the precise stereochemistry, and particularly the absolute configuration of the optical centres, of the individual constituents of these organic extracts.

Optical activity measurements in the past have, in general, been confined to a complex mixture of extracted organic material. Nagy *et al.*³⁷ observed optical activity in the organic extract from the Orgueil meteorite, and on the basis of this and other evidence invoked a biological origin for the organic material. Subsequent work on carbonaceous chondrites by Urey³⁸ and Nagy³⁹ provided additional evidence for the presence of optically active material in such sources. Hayatsu⁴⁰ has consistently criticised the experimental foundation upon which this evidence rests. Even if the experimental foundation were verified, however, it is doubtful what the significance of optical activity in a complex mixture would be unless it was possible to relate the origin of the optical activity to a specific component within the mixture, and to correlate this optical rotation, in magnitude and direction, with a known biological compound. Furthermore, the spontaneous formation of optically active sub-

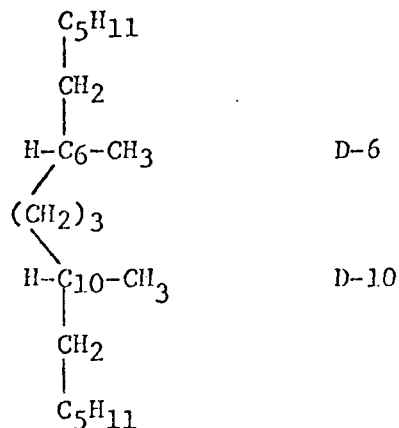
stances from an inactive material, without interference from a directing, asymmetric agency, has been demonstrated on an experimental basis. Havinga⁴¹ showed that methyl-ethyl-allyl-anilinium iodide may crystallise spontaneously into either enantiomer under certain experimental conditions. In general, if a nucleus of one type of enantiomeric crystals should begin to form by spontaneous, statistical fluctuations, an autocatalytic crystallisation process may set in, since such a nucleus tends to grow by the addition of enantiomeric molecules of similar configuration. This observation suggests a mechanism for the formation of the first optically active substance and indicates that optical activity may not be a unique property of the biological system.

In any experimental approach it is necessary to carry out as many measurements as possible on an individual compound to designate an unambiguous structure. No attempt has been made in this laboratory, however, to determine the stereochemistry of the isoprenoid hydrocarbons isolated from the crude oils and shales, nor, in general, have such determinations been made by other research workers in organic geochemistry. There are very good reasons for this. Until just recently it has been felt generally that the very specific structural architecture of the 'biological markers' was in itself adequate evidence for a biological origin. With the isoprenoid hydrocarbons, for instance, the characteristic methyl branch at every fourth carbon atom is so specific that it has generally been accepted to be indicative of a biogenic origin. Further, it has been very difficult to isolate the individual components

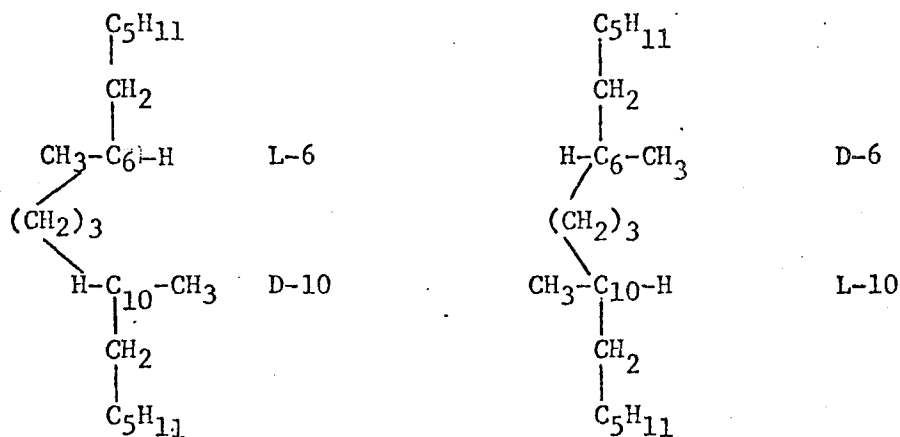
in sufficient quantity and purity from the very complex organic mixtures to obtain a reliable optical measurement. Finally, with the isoprenoid hydrocarbons in particular, the optical rotations are so small that much larger quantities of the compound than normal (20 - 50 mg), as opposed to the optical measurements carried out by Hills and Whitehead⁴² on milligram amounts, are required. Such quantities of individual compounds are impossible to obtain from most organic chemical samples. For these reasons, reports of optical measurements having been carried out in organic geochemistry are scarce.^{42,43}

Despite this experimental difficulty it is important to correlate the stereochemistry of the geological samples with that of the biological precursor from which they are thought to be derived. It might be possible to separate diastereoisomeric forms of a particular isoprenoid hydrocarbon using capillary gas chromatography; preliminary attempts to bring about this separation have so far not been successful in this laboratory. Pristane can exist in two forms, as shown below, and pristane isolated from marine sources is thought to have the meso-configuration.

1) Meso-form



2) Mixture of d,l isomers

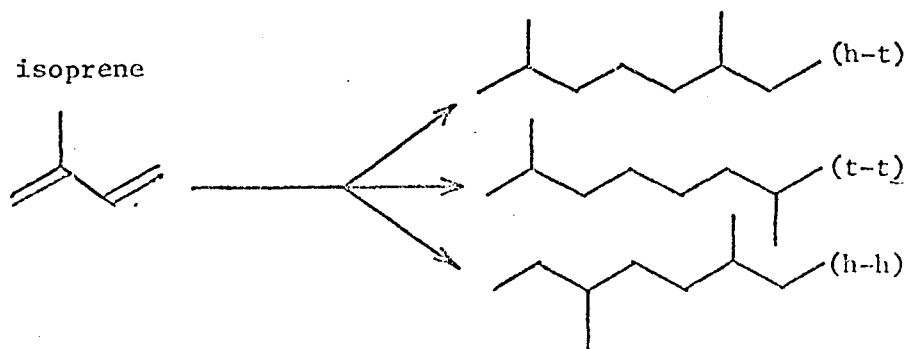


The separation of the diastereoisomers of pristane in very small amounts by capillary gas-liquid chromatography would provide a major breakthrough in experimental techniques in organic geochemistry. More significantly, it would enable one to establish a criterion whereby one could recognise organic compounds derived from abiological sources from those derived from biological sources, since, a priori, one would not expect a C₁₉ saturated isoprenoid hydrocarbon, having exclusively the meso-configuration, to be produced in an abiogenic synthesis.

Another criterion for biogenic origin stems from a consideration of the biosynthetic pathway to the polyisoprenoid compounds in the living system. This pathway is dominated by the occurrence of the head to tail linkage in the polymerisation of isopentenyl pyrophosphate. The characteristic tail to tail linkage seems to take place exclusively at C₁₅ to give C₃₀ compounds such as squalene, the precursor of the steranes and triterpanes, and at C₂₀ to give C₄₀ compounds such as lycopene. It may be that the non-branched four-carbon unit in this tail to tail linkage is the criterion for which we are looking in assigning a biolo-

gical origin to compounds isolated from crude oils and sediments. In this connection we have made several attempts to identify such a 4-carbon unit in our organic geochemical studies. The occurrence of a C₂₁ saturated isoprenoid hydrocarbon 2,6,10,14-tetramethylheptadecane, in a series of sediments suggests that a C₄₀ isoprenoid hydrocarbon such as lycopene, containing a tail to tail linkage, might be a precursor.⁴⁴ It does not demand such a precursor, however, and higher head to tail polyisoprenoids, such as solanesol and dolichol, might be also postulated as precursors. The experimental evidence also seems to indicate that the C₃₀ isoprenoid hydrocarbon, squalene, does not play a significant role as precursor to the isoprenoid hydrocarbons. At present we have been unable to identify this 4-carbon structural unit in the organic extracts from sediments.³⁰

When isoprene is polymerised abiogenically, one might predict, a priori, that the reaction should not proceed stereospecifically, and that three compounds should be formed -- the head to tail linkage (h-t), the tail to tail linkage (t-t) and the head to head linkage (h-h). This is illustrated below:



When we consider the addition of another molecule of isoprene to produce a C_{15} compound, and a further molecule to give a C_{20} compound, then several products should result whose structural skeletons are shown in Figure I. These compounds might be expected to be present in hydrocarbon mixtures if they were derived by an abiogenic process which did not proceed stereospecifically. Thus, the presence of such structures in organic extracts might be used as a criterion for abiogenic origin.

The copolymerisation of the simple olefines and diolefines -- ethylene, propylene, butadiene and isoprene -- which are produced in the thermal cracking of ethane and propane -- can lead to polymeric products which have methyl groups located at irregular intervals along the linear polymer chain. If the non-biogenic polymerisation of isoprene with reduced metal catalysts is invoked to explain the occurrence of polyisoprenoid compounds it is to be expected that copolymerisation reactions would have occurred simultaneously. The polymeric products of these copolymerisation reactions might serve as a criterion, therefore, of abiogenic origin. The structure of the products that are to be expected from such reactions might be predicted from what is already known about copolymerisation reactions. Ethylene is by far the most reactive of the simple olefines and will be the major constituent of the resulting product. The nature of the transition metal compound has been shown to have major control over the monomer composition of ethylene-propylene copolymers prepared with Ziegler-Natta catalysts.⁴⁵ Two examples are given below:

Ethylene (r_1)-Propylene(r_2)with $Al(Et)_3$

<u>Transition Metal</u>	<u>r_1/r_2</u>
$TiCl_4$	38.7
VCl_3	1040

(r = reactivity ratio)

Such polymerisation products would be virtually straight chain in character with the occasional methyl branch. There is a tendency to terminate with propylene, thus producing iso-hydrocarbon homologues.⁴⁶

Pyrophoric metal catalysts can also bring about copolymerisation reaction.⁴⁷ One such catalyst, pyrophoric iron, might have been present in the reducing environment on the primitive earth. These catalysts also have the effect of reducing the reactivity of ethylene relative to propylene by an order of magnitude; on reduced cobalt catalysts they appear to react at the same rates.⁴⁷

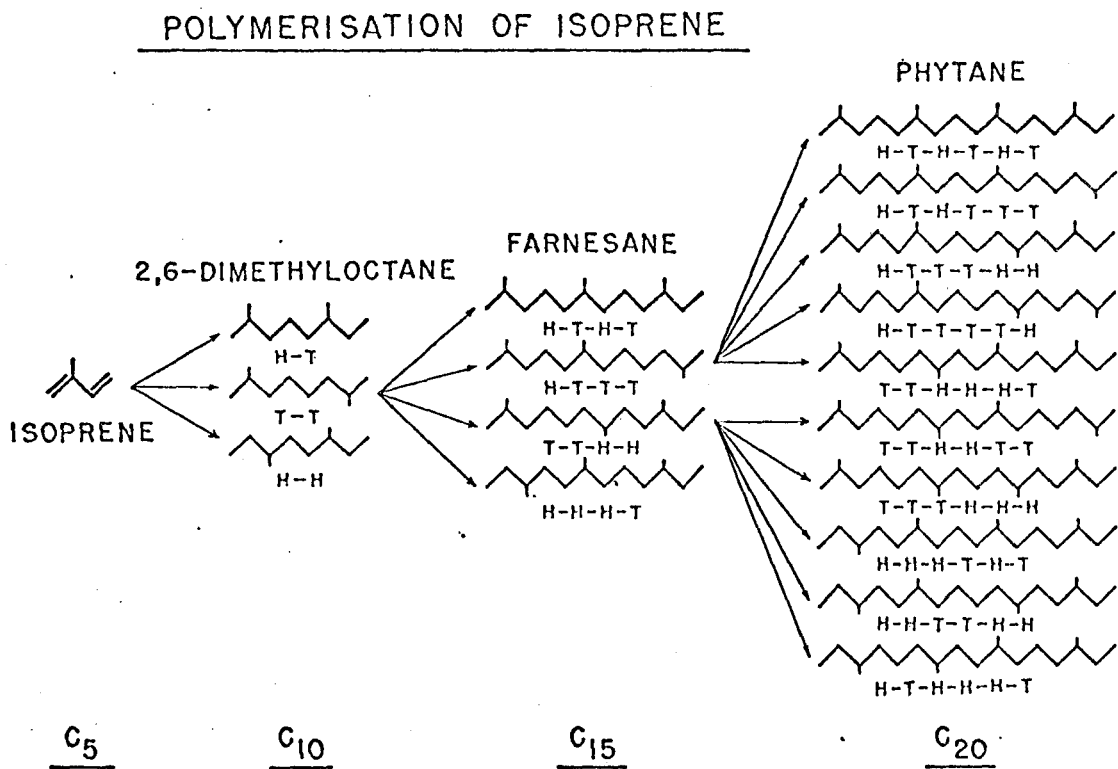
Other criteria for biogenic origin such as the odd to even distribution of normal alkanes are only reliable for most recent sediments. The identification of other 'biological markers', other than saturated isoprenoid hydrocarbons, within a given organic extract is a reliable criterion in complementing the evidence for biological origin. Except for the porphyrins, however, and the steranes and triterpanes, other classes of 'biological markers' do not survive into the most critical region of interest, the Precambrian, which imposes a severe limitation on this approach. The finding of homologous series in crude oils and

sediments, while not in themselves necessarily indicative of biological origin, does augment the evidence for the isoprenoid hydrocarbons, when identified in the same extracts. However, these are nowhere nearly as ubiquitous in organic geochemical samples as the isoprenoid hydrocarbons. A further point, which is often not sufficiently emphasised in establishing criteria for biogenic origin, is the relative amounts in which these isoprenoid hydrocarbons are found. In almost all cases they constitute the major components of the 'branch-cyclic' hydrocarbon fraction, an observation which argues strongly for a biogenic origin.

Another criterion for biogenic origin is the carbon isotope ratios of the organic extract. This approach is based on the fact that photosynthetic organisms discriminate against carbon-13 in preference for carbon-12.^{50,51} Although not definitive in some cases such measurements on organic extracts have already cast some doubt on certain proposals for an abiogenic origin of the hydrocarbons from hydrothermal deposits. Further insights into this problem might also be obtained from a development of the carbon isotope approach. Nobody has studied the carbon isotope ratios of an individual molecule. There are some experimental problems involved in this approach which can be overcome, however. This represents a new field of study which could provide valuable information in ascertaining the origin of hydrocarbons.

Conclusion

The problem of the origin of the isoprenoid hydrocarbons remains inconclusive. The evidence still indicates that isoprenoid hydrocarbons are, in most cases, derived from biological sources, even in the Precambrian samples. It is in this geological time period, however, that we are looking with renewed interest for the transition between chemical evolution and the advent of biological systems. Natta has already demonstrated an experimental, non-biogenic route to the isoprenoid compounds. The possibility of non-biogenic isoprenoid hydrocarbons is a very real one, and criteria must be established which will distinguish between those derived from an abiogenic origin and those derived from biological systems.



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Figure I

References

1. Abelson, P.H., Fortschritte, 17, 379 (1959).
2. Conway, D. and Libby, W.F., J. Amer. Chem. Soc. 80, 1077 (1958).
3. Abelson, P.H., Annual Report of the Director of the Geophysical Laboratory, 1953-1954. Carnegie Inst. Wash. Year Book, 53, 97 (1954).
4. Barghoorn, E.S., Meinschein, W. G. and Shopf, J. W., Science, 148, 46 (1965).
5. Burlingame, A., Haug, P., Belsky, T. and Calvin, M., Proc. Nat. Acad. Sci. U.S. 54, 1406 (1965).
6. Hills, I.R., Whitehead, E.V., Anders, D. E., Cumming, J. J. and Robinson, W. E., Chem. Comm. No. 22, p. 752, 1966.
7. Meinschein, W. G., Barghoorn, E. S. and Schopf, J. W., Science, 145, 262 (1964).
8. Meinschein, W. G., Science, 150, 3696 (1965).
9. Oro, J., Nooner, D. W., Zlatkis, A., Wikström, S. A. and Barghoorn E. S., Science, 148, 77 (1965).
10. Johns, R. B., Belsky, T., McCarthy, E.D., Burlingame, A. L., Haug, P., Schnoes, H. K., Richter, W., and Calvin, M., Geochim. et Cosmochim. Acta, 30, 1191 (1966).
11. Oro, J. and Nooner, D. W., Nature, 213, 1082 (1967).
12. Myers, P.S. and Watson, K. M. National Petroleum News, 38, R-388 (1946).
13. Clayton, R. B., Quart. Rev.(London). Part I: XIX, No. 2, 168 (1965).
14. Clayton, R. B., Quart. Rev. (London), Part II: XIX, No. 3, 201 (1965).
15. Cornforth, J. W. and Popják, G., Proc. Royal Soc., Series B, 163, 435 (1966).

16. Lindgren, B.O., Acta Chem. Scand. 19, 1317 (1965).
17. Butterworth, P.H.W., Draper, H.H., Hemming, F.W. and Morton, R. A. Arch. Biochem. Biophys. 113, 646 (1966).
18. Fukawa, H., Toyoda, M., Shimizu, T. and Murohashi, M., Tetrahedron Letters, 49, 6209 (1966).
19. Rowland, R. L., Latimer, P.H. and Giles, J. A., J. Amer. Chem. Soc. 78, 4686 (1956).
20. Erickson, R. E., Shunk, C. H., Trenner, N. R., Arison, B. H. and Folkers, K., J. Amer. Chem. Soc. 81, 4999 (1959).
21. Kofler, M., Langemann, A., R^uegg, R., Gloor, U., Schweiter, U., W^urch, J., Wiss, O. and Isler, O., Helv. Chim. Acta, 42, 2252 (1959).
22. Thorne, K.J.I. and Kodicek, E., Biochim. Biophys. Acta, 59, 280 (1962).
23. Bonner, J., Chap. 16, Biogenesis of Natural Compounds, ed. P. Bernfelt, Pergamon Press, 1963.
24. Natta, G., Porri, L., Corradini, P. and Morero, D., Chim. e Ind. (Milan), 40, 362 (1958).
25. Private Communication, from Dow Chemical Company, Freeport, Texas.
26. Natta, G., Scientific American, 205, 33 (1961).
27. Oparin, A. I., The Origin of Life, Dover, New York, 1938.
28. Friedel, R. A. and Sharkey, Jr., A. G., Science, 139, 1203 (1963).
29. Hayatsu, R., and Anders, E., preprint (submitted to Science, July 1967).
30. McCarthy, E. D., and Calvin, M., Tetrahedron, 23, 2609 (1967).
31. Gohring, K.E.H., Schenck, P.A. and Engelhardt, E. D., Nature, 215, 503 (1967).
32. Meinschein, W. G., Nagy, B. and Hennesy, D. J., Ann. N.Y. Acad. Sci. 108, 553 (1963).

33. Studier, M.H., Hayatsu, R., and Anders, E., Science, 149, 1455 (1965).
34. Burlingame, A. L., and Schnoes, H. K., Science, 152, 104 (1966); Urey, H. C. and Lewis, Jr. J.S., Science, 152, 102 (1966).
35. Hoefs, J. and Schidlowski, M., Science, 155, 1096 (1967).
36. Ponnamparuma, C. and Pering, K., Nature, 209, 979 (1966); Ponnamparuma, C. and Pering K., Geochim. et Cosmochim. Acta, 31, 1350 (1967).
37. Nagy, B., et al., Nature, 202, 228 (1964).
38. Urey, H. C., Science, 151, 157 (1966).
39. Nagy, B., Science, 150, 1846 (1965).
40. Hayatsu, R., Science, 149, 443 (1965); Hayatsu, R., Science, 153, 859 (1966).
41. Havinga, E., Biochim. Biophys. Acta, 13, 371 (1954).
42. Hills, I.R., and Whitehead, E.V., presented at 3rd Int. meeting on Geochemistry, London, 1966.
43. Louis, M., Revue de L'Institut Francais du Petrole, XIX, Feb. 1964, pp. 277-280.
44. McCarthy, E.D., Van Hoeven, W., and Calvin, M., Tetrahedron Letters (in press.)
45. Lenz, R. W., Chapt. 15 in Organic Chemistry of Synthetic High Polymers, Interscience Publishers, 1967.
46. ibid., Chapt. 15.
47. Aries, R.S., U.S. Patent Office, No. 3,114,719.
48. Bresler, L.S., Dolgoplosk, B.A., Kolechkova, M.F. and Kropacheva, Ye. N., Polymer Science USSR, 4, 1012 (1963).
50. Park, R., and Epstein, S., Geochim. Cosmochim. Acta, 21, 110 (1960).
51. Park, R. and Epstein, S., Plant Physiol. 36, 133 (1961).

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