Geochemistry of Lipids[1]

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Abstract

Lipids, particularly the glycerides, terpenes, sterols, and hydrocarbons, have properties conducive to their preservation either in original or transformed state and are significant constituents of the geochemical biomass. The occurrence of phytane, pristane, and fatty acids in Precambrian sedimentary rocks 2.7 billion years old has been interpreted to indicate the existence of life processes similar to those that are operative today.

The stability of lipids is highly variable. Sterols, terpenes, fatty acids, esters, and hydrocarbons have been isolated from ancient sedimentary rocks; there is evidence, however, that esters may hydrolyze. Under certain conditions, highly unsaturated fatty acids may undergo combined biochemical and chemical transformations that lead to the formation of petroleum hydrocarbons.

Lipids found in geological environments are derived from contributing organisms, which represent specific ecologies. Study of the ultimate products derived from these lipids permits an understanding of the geochemical environments in which they were produced, and of the transformations that occurred.

Introduction

Evaluation of potential contributions of biological products to the mass of organic material that accumulates under geological conditions has led to the conclusion that lipids are of particular importance. Carbohydrates and proteins both undergo hydrolysis to yield water-soluble products of low molecular weight that are ultimately destroyed in biochemical or chemical processes (1). In contrast, many lipids, while subject to some changes following elimination from biological systems, are either preserved intact or converted into transformation products that are stable and tend to be preserved. Only lignin, among the major biological products, behaves more or less as do the lipids with respect to preservation (1).

Lipids have been defined as biochemical compounds soluble in organic solvents such as benzene, chloroform, carbon tetrachloride, ether, hydrocarbons, carbon disulfide, and similar compounds, but insoluble in water. The term "lipids," therefore, embraces, among others, compounds such as glycerides, terpenes, sterols, and hydrocarbons. Hydrocarbons, when defined as lipids, may actually represent original biological products or products derived from the transformation of other lipids such as fats. In some instances, these compounds occur in trace quantities and may serve as indicators of particular biological processes that have been operative in various geological eras, in other cases certain lipids may have been the precursors of geological accumulations of major economic proportions, such as crude oil.

Source of Lipids

Sterols

Although they do not occur in large quantities, sterols are universal products of biological processes

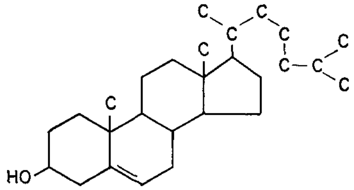

Fig. 1. Cholesterol.

and are known to be present in many substances of geological interest. Cholesterol (Fig. 1) is the principal sterol of vertebrates, but invertebrates are characterized by a wide diversity of sterols that occur in significant quantities. The structures of these compounds have not always been fully elucidated.

Numerous sterols have been isolated from freshly killed, air-dried, or formalin-preserved specimens of marine animals (2), among which are the polyps, corals, gorgonias, jellyfish (3), and sea anemones (4). Cholesterol (Fig. 1) ($C_{27}H_{46}O$) and dehydrocholesterol (Fig. 2) ($C_{27}H_{44}O$), as well as other sterols, have been isolated from various species and are listed in Table I. Sterols, including cholesterol, have also been isolated from starfish, sea urchins, sea cucumbers, horseshoe crabs, and tunicates.

Various sponges have been found to contain sterols in very significant quantities. Thus, the air-dried loggerhead sponge contains 1.5% of total sterols (7) comprising clionasterol ($C_{29}H_{50}O$) and poriferasterol ($C_{29}H_{48}O$), as well as others (8–11).

The various sterols noted occur in invertebrates in the range of from 15 ppm to as much as 1.5%. The list of Table I does not pretend to be all-inclusive, but rather to illustrate the variety and distribution of such compounds in marine and fresh-water invertebrates.

Sterols are also known to occur in soils. Schreiner and Shorey (12) identified a phytosterol in soil, and more recently β-sitosterol and stigmastenol were isolated from peat (13). It has been estimated by Turfitt (14) that soils contain up to 12.7 ppm of sterols. He found, however, that cholesterol is approximately 60% destroyed in one year when mixed with aerated garden soil. Preservation is best under wet, acidic conditions and in the absence of oxygen.

Cosmovici and Anastasiu (15,16) identified sterols in Romanian black shales containing fossil remains of algae, fish, and crustaceans. Sterols have also been tentatively identified in petroleum, guano, asphalt,

TABLE I

Sterols Isolated from Invertebrates

Sterol	Formula	Source
Cholesterol (Fig. 1)	$C_{27}H_{46}O$	Jellyfish Staghorn coral Gorgonia Sponges
Actiniasterol (dehydrocholesterol ?) (Fig. 2)	$C_{27}H_{44}O$	Sea anemone
Clionasterol	$C_{29}H_{50}O$	Gorgonia Sponges
Gorgosterol	$C_{30}H_{52}O$ or $C_{31}H_{54}O$	Gorgonia
Cholestanol (5) (Fig. 3)	$C_{27}H_{48}O$	Sponge
Poriferasterol	$C_{29}H_{48}O$	Sponge
Ergosterol (6) (Fig. 4)		Algae
Chondrillasterol (Fig. 5)		Sponge Algae

[1] Publication authorized by the Director, U.S. Geological Survey.

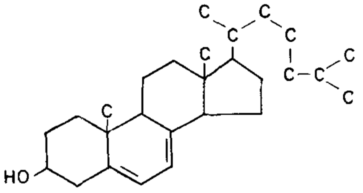

FIG. 2. 7-Dehydrocholesterol.

medicinal muds, lignite, and fossil calcium carbonate shells.

Esters

Concentration of acetone extracts from *Meandra areolata* and other species of corals led Lester and Bergmann to the identification of cetyl palmitate (Fig. 6), which is present in quantities of 0.25–0.50% based on the weight of the dry coral, which contain 2–7% of organic material (17–19). Later, Kind and Bergmann found the same ester in gorgonias (20). It has also been pointed out by Bergmann (21) that this ester is the principal constituent of spermaceti from the head of a sperm whale.

It is hardly necessary to discuss here the nearly universal occurrence of triglycerides. Those triglycerides in which the acids are saturated may be hydrolyzed into water-soluble glycerol, which disappears, and fatty acids that are utilized in other biological processes or which are eventually dissolved in sea water and incorporated into sediments. The same may be said for triglycerides derived from marine fish among which are the menhaden, herring, and sardine. The acids derived from these oils have normal chain lengths of 14 to 24 carbon atoms, but are unique in that these chains tend to be highly unsaturated, having from 4 to 6 double bonds (22). Such unsaturation makes these acids highly reactive and subject to interaction among themselves or with other biological products.

Alcohols

Several alcohols have been isolated from marine invertebrates. Thus, octadecyl alcohol (Fig. 7) and batyl alcohol (Fig. 8) were both found in a gorgonia (*Plexaura flexuosa*) (20), and batyl alcohol was subsequently identified in a starfish, *Asterias rubens* (23). Other unusual compounds, such as selachyl alcohol (Fig. 9) (21) and 11-docosenol (Fig. 10) (24) have also been found in marine organisms. Relatively simple alcohols occur in peat wax; montan wax, isolated from lignite, is known to consist of nearly 25% of alcohols of high molecular weight (C_{24} to C_{30}) (25).

Acids

Numerous fatty and naphthenic acids have been isolated from petroleum and identified. These range from formic (HCOOH) to arachidic acid (C_{20}) for the fatty acids; the naphthenic acids (Fig. 11) include both cyclopentane and cyclohexane derivatives.

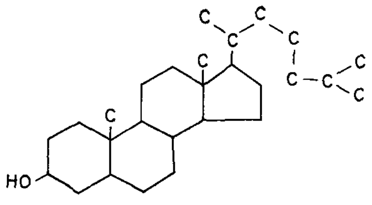

FIG. 3. Cholestanol.

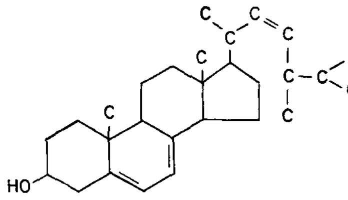

FIG. 4. Ergosterol.

Other acids, such as dihydroxystearic acid, were identified in soils by Schreiner and Shorey over 50 years ago (26).

Some indication as to the stability of these acids under geological conditions can be obtained from studies of sediments. Fatty acids in the C_{26}–C_{30} range were reported by Trask and Wu to occur in concentrations of 20–60 ppm in recent marine sediments (27), whereas oleic and other acids have been found in Black Sea sediments (28) and in lake waters. Fatty acids of low molecular weight have been found in recent muds, as well as in ancient carbonate sediments and boghead coals (29).

Terpenes

Terpenes of all varieties ranging from squalene (Fig. 12), which occurs in shark-liver oil, to "monkey-hair," fossil rubber found in some lignites, are of geochemical interest. Sesquiterpenes and triterpenes also are found and have been given such names as fichtelite, branchite, etc. Bergmann, in one of his last publications, summarized the known occurrences of terpenes (21) of geological interest.

Hydrocarbons

Apart from those hydrocarbons associated with crude oil, numerous examples ranging from $C_{25}H_{52}$ to $C_{31}H_{64}$ have been found in soil and peat. Heptadecane has been found in sardine oil, and n-heptane makes up 98% of Jeffrey pine oil. Nonane, undecane, and pentadecane have all been isolated from natural products (21).

Smith (30) in 1954, anlyzing cores of recent sediments from the Gulf Coast, California, and the Orinoco Delta, uncovered the presence of small quantities of paraffinic, naphthenic, and aromatic hydrocarbons. Carbon-14 analyses showed these compounds to be young, indicating them most likely to be products of bacterial activity. Confirmatory evidence for the occurrence of hydrocarbons in such sediments has since been obtained by numerous other workers. Stevens (31) in 1956 noted an interesting but significant difference between the hydrocarbons of both recent and ancient sediments and those of crude oil. Thus, normal paraffins from soils and marine muds were found to have an "odd-carbon" preference, with C_{29} being the most abundant member of the series; crude oils exhibited no such preference. There has been much investigation to throw light on the significance of the "odd-carbon" preference, but to date many questions regarding the problem still remain unsolved.

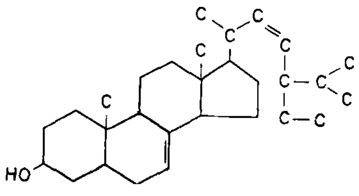

FIG. 5. Chondrillasterol.

$$CH_3(CH_2)_{14}\overset{O}{\overset{\|}{C}}\!-\!O\!-\!CH_2(CH_2)_{14}CH_3$$

FIG. 6. Cetyl palmitate.

This abbreviated survey of occurrences of various lipids is not intended to be all-inclusive. Rather, it is intended that attention be called to the various types of compounds, and their relative importance in geochemical processes.

Occurrences of Lipids

Chondrites

The attempt to trace life processes back in time has led to very extensive studies of carbonaceous chondrites in the past five years. During examination of the Orgueil meteorite, which fell in France in 1864, saponifiable organic material, classifiable as lipid, was isolated and found to exhibit optical activity (32). In a more detailed examination of the same meteorite, Nagy and Bitz (33) were able to isolate and identify long-chain fatty acids ranging from C_{14} to C_{30}. Although the authors concluded that the exact origin of these acids in the meteorite was not clearly established, it is possible that further work in this field and an attendant body of complementary evidence may eventually lead to the conclusion that life existed on the extraterrestrial body from which this meteorite was derived. Besides fatty acids, a number of hydrocarbons have also been isolated from the Orgueil meteorite and identified by mass spectroscopic and gas chromatographic techniques. Larger quantities of odd than even carbon-numbered n-paraffins were found in the C_{23} to C_{30} range (34). Perhaps the outstanding recent discovery in the study of carbonaceous chondrites has been the identification of pristane (Fig. 13) and phytane (Fig. 14) in extracts from the Orgueil and Murray meteorites. Although pristane may be derived from a secondary source, phytane is very likely derived from phytol which, in turn, is part of the chlorophyll molecule (34). Unquestioned proof of the existence of chlorophyll and of a photosynthetic process in extraterrestrial bodies represented by the carbonaceous chondrites would be one of the most sensational and dramatic developments of our generation.

Ancient Sediments

The isolation of organic compounds from ancient sediments has frequently been taken as evidence that a biota at one time existed in the environment. In recent years, particular efforts have been made to identify those substances that occur in Precambrian sediments and which might serve as clues to life processes during the earliest stages of biological history on earth. Moreover, preservation of any such compounds in form sufficient for identification provides an index of stability for the compound.

Recently Barghoorn and co-workers (35) demonstrated the unquestioned existence of primitive life forms in Precambrian sediments. These organisms, which are similar to algae, represent some of the earliest forms of life on earth; it is, therefore, interesting to examine the available evidence for biological processes that may have been operative during early life history.

In a study of the extract from the alum shale of

$$CH_3(CH_2)_{16}CH_2OH$$

FIG. 7. Octadecyl alcohol.

$$CH_3(CH_2)_{16}CH_2\!-\!O\!-\!CH_2CHOHCH_2OH$$

FIG. 8. Batyl alcohol.

Sweden, which has been dated at 500 million years, Abelson and co-workers (36) reported the isolation of 20 to 200 ppm of fatty acids based on the amount of organic matter present. This isolate consisted for the most part of palmitic and stearic acids.

Optically active hydrocarbons, besides phytane, have also been found in the Nonesuch Shale of northern Michigan. These constituents, as well as the presence of porphyrins, provide excellent evidence for abundant photochemical activity as far back as 1.1 billion years ago (35,37). In confirmation of this conclusion, it was also reported (35,37) that an oil thought to be indigenous to the shale contains various terpenes and hydrocarbons ranging up to C_{35}. These hydrocarbons demonstrate an odd-carbon preference characteristic of plant products, with unusually high abundances of C_{27}, C_{29}, and C_{31}.

Organic extract from a somewhat older sediment, the Barreiro Formation of Minas Gerais, Brazil, (about 1.8 billion years) has also been studied (38). The material soluble in chloroform and alcohol-benzene (1/1) amounted to 70 ppm based on the total sample, and could be separated into acid and neutral fractions, the latter containing free alcohols. Along with this work, a similar study of soluble organic matter from the Sharon Springs Member of the Pierre Shale was also conducted. The isolate from this Cretaceous shale was fractionated into acid and neutral constituents, and the latter were found to contain an ester or esters. These esters were saponified and the resulting acids were separated by gas-liquid chromatography and characterized by micro infrared analysis; the same techniques were used in study of the extracts from the Brazilian samples.

On the basis of preliminary work, it was found that the acids isolated from the Precambrian sample were very similar to those obtained by saponification of the ester(s) from the Cretaceous rock. Infrared spectra of the two isolates were identical. It is not known whether the acids and alcohols present in the Precambrian rock existed initially as esters which, with time, were hydrolyzed. Similarly, the ester(s) from the Cretaceous sample may not have had sufficient time to hydrolyze. On the basis of the work already carried out, it is clear that at least those marine biochemical processes that led to the formation of fatty acids and their derivatives did not change appreciably between the Precambrian period studied and Cretaceous time. It is also interesting to note the stability of fatty acids and alcohols for a period of over one billion years.

Among the oldest rocks studied to date are samples of sediments from the Soudan Iron Formation that have been dated at 2.5 billion years (39). The hydrocarbons isolated contain n-paraffins up to C_{27}; pristane and phytane have also been tentatively identified in the extract. Although the thermodynamic stability of linear hydrocarbons is well known, the existence of pristane (Fig. 13) and phytane (Fig. 14) for such a long period of time is particularly noteworthy, assuming these compounds to be indigenous to the rock. If the presence of phytane can be confirmed, its association with such ancient sediments will provide significant evidence for the development of photochemical

$$CH_3(CH_2)_7CH\!=\!CH(CH_2)_7CH_2\!-\!O\!-\!CH_2CHOHCH_2OH$$

FIG. 9. Selachyl alcohol.

$$CH_3(CH_2)_9CH{=}CH(CH_2)_9CH_2OH$$

FIG. 10. 11-Docosenol.

processes during a very early stage of the geological history of the earth.

With reference to the stability of esters under natural conditions, it is interesting that in spite of the known occurrence of many fatty and naphthenic acids and phenolic compounds in petroleum, only one ester, a dioctylphthalate, has as yet been identified (40,41). Although the same compound has been found in Italian crude oil (42), and phthalic acid has been found in French petroleums (43), the origin of the dioctylphthalate still remains unexplained. Hydrolysis of the compound might lead to phthalic acid and octyl alcohol, either or both of which could be removed by solution in water. If this has occurred to any appreciable extent in other oils, then any significant quantities of this ester or related esters may have been lost. It is somewhat futile to speculate in any detail as to the origin of a compound such as phthalic acid other than to note that it may represent an oxidation product derived from a complex aromatic system. The widespread industrial use of dioctylphthalate as a plasticizer led to concern that the compound might have been a contaminant in the oil. Reexamination of the Italian oil with extreme care to prevent contaminaton has, however, proved that the ester is a true constituent of the oil (42).

The identification of terpenes in Precambrian deposits has already been noted. It is of particular interest, however, that such compounds are also being found in other younger sediments of various ages. Bendoraitis, Brown, and Hepner reported in 1962 (44) that crude oils from east Texas and the Mid-continent area contain 0.5 and 0.2%, respectively, of pristane (Fig. 13). These high concentrations of the compound must be related to an appropriate source or sources capable of supplying the terpene to an environment where oil is being formed, and may eventually provide a clue regarding the origin of petroleum or at least the character of the environment. A large step in this direction has already been taken by Blumer, Mullin, and Thomas (45) who found three copepods (planktonic crustaceans) to contain unusually high concentrations of pristane. As they noted, it is possible to account for the high pristane content of the liver oils of sharks and whales from the fact that these animals feed on the pristane-bearing plankton. Thus, the geochemist might well examine the aquatic conditions under which such plankton live to analyze the nature of the environment in which oil may have been derived from such organisms.

The identification of isoprenoids in ancient sedi-

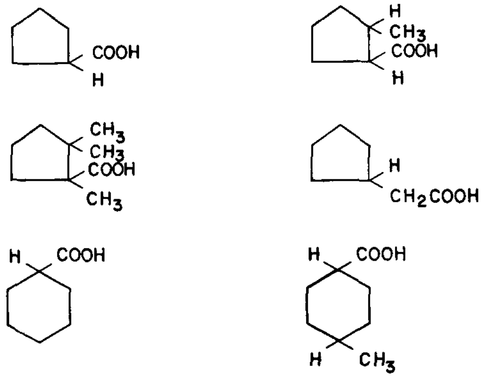

FIG. 11. Naphthenic acids.

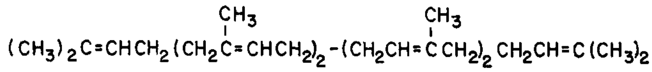

FIG. 12. Squalene.

ments has multiplied as new techniques for their isolation have developed. Cummins and Robinson (46) studied the extracts from the shale of the Mahogany Ledge of the Green River Formation near Rifle, Colorado. This shale, of Eocene age and derived from an old lacustrine environment, yielded on analysis a whole series of n-paraffins ranging from C_{13} to C_{33} in which there was an odd-carbon preference. Of particular interest, however, was the reported detection of pristane (Fig. 13) and phytane (Fig. 14), 2,6,10-trimethylpentadecane (Fig. 15), 2,6,10-trimethyltridecane (Fig. 16), and 2,6,10-trimethyldodecane (Fig. 17). The five isoprenoids compose an appreciable percentage (3.4%) of the bitumen extract from the shale. Additional identifications of isoprenoids may very well provide additional evidence for the origin of petroleum or for the environment in which a shale was deposited. On the other hand, these compounds should be considered tracers rather than thought of as progenitors for petroleum as has recently been suggested. Examination for terpenes in older shale extracts and petroleums, particularly those that may be proved to be indigenous to Precambrian deposits (47), may lead to extremely rewarding results in terms of understanding early life processes.

The relationship of fats and fatty acids to petroleum hydrocarbons has been examined in detail since the work of Engler and Höfer at the end of the nineteenth century (48). The suggestion that fish and animal oils were especially important as progenitors for petroleum was based upon a careful consideration of possible chemical reactions relating crude oil to various biologically produced substances. Although Engler and Höfer noted the thermal degradation of fatty acids to hydrocarbons, they proposed that such transformations could occur at low temperatures maintained over long periods of time. The validity of their suggestion regarding a low-temperature origin for petroleum has been confirmed by geochemical observations made since Engler and Höfer made their proposal.

The suggestion that certain petroleum hydrocarbons may have been derived from fatty acids has persisted for several reasons. Thus, fatty acids ranging from C_1 to C_{20} occur in association with petroleum along with a whole series of cyclopentane and cyclohexane carboxylic acids (naphthenic acids) (Fig. 11). Decarboxylation of these acids, if it occurred, would provide a simple mechanism for the formation of both linear and cyclic hydrocarbons. Unfortunately, no simple bacteriological mechanisms are known that will directly decarboxylate a fatty acid, and it seems rather unlikely that hydrocarbons can be formed by such a simple process. On the contrary, decarboxylation of a fatty or naphthenic acid would probably require a complex series of biological reactions among which may be a two-carbon chain scission.

Little is known about the actual source materials from which petroleum hydrocarbons form other than that they very likely originate from organic debris derived from aquatic life. Such organic matter tends

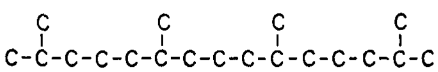

FIG. 13. Pristane.

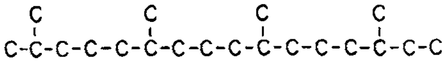

FIG. 14. Phytane.

to have high hydrogen/carbon ratios, with hydrogen contents ranging up to about 10 to 11%. Although actual evidence is lacking, it has been speculated that long-chain, unsaturated acids, derived from aquatic organisms, may serve as the progenitors for petroleum hydrocarbons. Extracts from sea water have been found to contain, besides C_{12} to C_{18} saturated fatty acids, myristoleic, palmitoleic, oleic, linoleic, and linolenic acids (49). Marine oils are also known to contain fatty acids ranging from C_{14} to C_{24} that have high percentages of compounds with 4, 5, and 6 double bonds (22).

Consideration of the chemical reactivity of highly unsaturated fatty acids immediately calls to mind the Diels-Alder reaction through which such compounds may interact. This is a purely chemical process that may take place at room temperature. Sowa (50) has even shown that α,β-unsaturated acids undergo the Diels-Alder reaction readily with conjugated dienes in aqueous media having pH values below 7. It seems likely, therefore, that under a wide variety of conditions a broad spectrum of partially unsaturated cyclic compounds might be produced in this way. An example of such a possible reaction is shown (Fig. 18). The availability of hydrogen produced in recent sediments by biological processes could lead to the ultimate formation of a saturated compound; other compounds might be unstable and lose hydrogen to form aromatic rings.

Elimination of the carboxyl group from such a compound still presents a problem inasmuch as direct biological decarboxylation is not known to occur. On the other hand, bacterial mechanisms are known in which fatty acids are converted to the following type compounds:

$RCH=CHCOOH$	α,β-unsaturated acid
$RCHOHCH_2COOH$	β-hydroxy acid
$RCOCH_2COOH$	β-keto acid

All these compounds are more reactive than the original fatty acids, and are subject to secondary reactions that could lead to decarboxylation. Thus, oxidation of an α,β-unsaturated or β-hydroxy acid will lead to the formation of a β-keto acid from which carbon dioxide is readily eliminated with formation of a ketone; ketones are readily reduced to hydrocarbons by bacterial processes. By this route, therefore, it might be possible to convert a fatty acid residue or a fatty acid itself into a hydrocarbon containing one carbon less than was present in the original chain.

The hypothetical process just outlined for the conversion of fatty acids to petroleum hydrocarbons depends upon a combination of chemical and bacteriological reactions. If it can be demonstrated to occur, then it may explain the formation of normal paraffins from saturated acids, and of naphthenic and aromatic hydrocarbons with and without side chains. The origin of aromatic hydrocarbons associated with petroleum has thus far suffered from lack of an acceptable explanation.

Bacterial processes that lead to two-carbon chain scission can also account for the conversion of fatty acids to hydrocarbons. These processes could lead to the formation of even-numbered hydrocarbons from even-numbered acids. Consideration of the various possible bacterial routes for the decarboxylation of fatty acids might lead to a reasonable explanation for the odd-carbon preference noted among the hydrocarbons in recent sediments and in certain crude oils. An additional explanation for the formation of odd-carbon hydrocarbons is to be found in the work of Jurg and Eisma (51). These workers noted that fatty acids could be converted into hydrocarbons of various chain lengths when the acids were heated in the presence of clays.

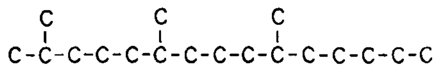

FIG. 15. 2,6,10,-Trimethylpentadecane.

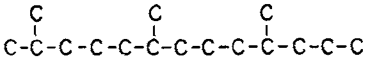

FIG. 16. 2,6,10-Trimethyltridecane.

The formation of highly paraffinic oils could result from an ecology in which most of the fats and associated acids were saturated, whereas naphthenic and aromatic crude oils could arise from those fatty acids that were unsaturated. Moreover, asphaltenes, those complicated aromatic-aliphatic structures of high molecular weight that occur in petroleum, can be thought to be derived from multiple Diels-Alder reactions occurring in long-chain highly unsaturated acids. There is great need for a symbiotic type of relationship between organic chemists, geochemists, microbiologists, and oceanographers through which this thesis for the conversion of fatty acids into petroleum hydrocarbons might be attacked.

Some of the most geochemically interesting occurrences of lipids, or substances derived from lipids, are rather rare. Additional study of such substances may, however, provide a clue as to possible interconversions between lipids and other biogenetically derived products in sedimentary environments. For this reason they deserve somewhat more consideration than may at first appear warranted. Among such substances is that called adipocire, which is a fatty deposit found associated with animal bodies that have been buried for some time in wet places. Reports on the occurrence of this material go back to 1658, when Sir Thomas Browne (See Bergmann, 21, p. 517) described adipocire found with a human body that had been buried for ten years. Later De Fourcroy described similar occurrences based upon his observations during work in the Cemetery of the Innocents in Paris in 1786 (21, p. 517). De Fourcroy, however, was of the opinion that the amount of adipocire associated with the bodies exceeded that to be expected if the fatty material were derived solely from the bodies, especially as the bodies were those of the poor, emaciated, and lean. For this reason, he suggested the conversion of other body constituents to fats, and recent considerations have pointed to protein as the most likely progenitor if such an interconversion occurs.

Similar occurrences of adipocire have been found with buried birds and animals, but in most instances the fatty deposits have been thought to be merely those residues resulting on normal decomposition of other tissues. Reliable chemical studies of adipocire are lacking, but there is some indication that it consists of free fatty acids and, possibly, soaps of calcium and other alkaline earth elements. Although the pros-

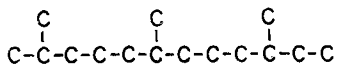

FIG. 17. 2,6,10-Trimethyldodecane.

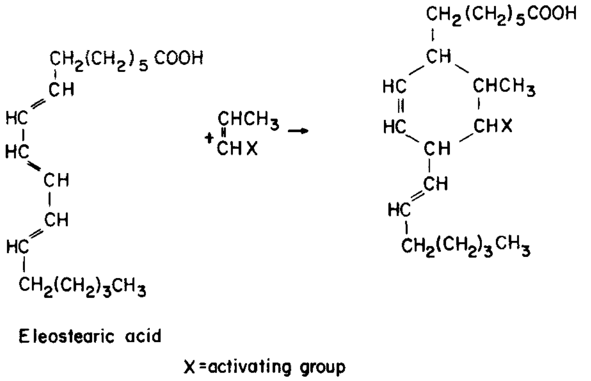

FIG. 18. Example of Diels-Alder reaction.

pect of working with long-dead, partially decayed bodies is, to say the least, macabre and uninviting, it seems clear that when a situation for such study presents itself, careful observations and analyses may go far in clarifying the suggestion of De Fourcroy and others since his time that protein or other biochemical products may be transformed into lipids under natural conditions.

The high lipid content of algae and diatoms has long been recognized. Moreover, Clarke and Mazur (52) found the ether-extractable lipids from diatoms to contain 60–80% of free fatty acids. Under favorable conditions, such lipids are able to interact to produce unusual products, some of which (such as coorongite) may be only curiosities, whereas others (such as boghead coals) may be economically significant. These two substances are mentioned only as examples, and it should be understood that numerous similar products have been described.

Coorongite (53,54) is an algal product found on the shores of salt water lagoons near Coorong, Australia. It is derived from *Elaeophyton coorongiana,* and occurs, when dry, as a brownish, rubbery mass. Analysis has shown the material to contain high percentages of fatty acids and it is thought that it is formed by the polymerization of long-chain unsaturated fatty acids. Stadnikov and Kashtanov (55) suggested that coorongite and similar substances may represent intermediate products in the formation of boghead coals from algae. An excellent summary of such work was published by Stadnikov in 1930 (56). The polymerization process is thought to be preceded by saponification of the fats.

Occurrences of lipids of geochemical significance are so extensive that it is hardly possible to do more than touch upon compounds of particular importance. In reviewing the fate of many of these compounds, it becomes clear that fatty acids, certain terpenes (phytane and pristane in particular), and a few alcohols are able to survive diagenetic vicissitudes that occur during geological time. Esters are "sometime" compounds in the sense that they occasionally survive diagenetic effects, while at other times there is some evidence that they may hydrolyze to glycerine, which is water-soluble and thus lost, and to acids that remain behind. Some alcohols are found in ancient sediments, perhaps because they are insoluble, and occurrences of sterols are only now being properly investigated.

The significance of lipids cannot be overestimated as indicators of geochemical processes or of biochemical processes during geological time. Study of these compounds, based on analytical techniques still being refined, has already permitted preliminary conclusions that certain life processes have not changed appreciably since the early days of the earth's geological history.

Of major interest, however, are those processes, such as the formation of crude oil and boghead coals, where lipids appear to be the progenitors of the products. There is a startling lack of information as to the interplay of biochemical and chemical processes that appear to be involved, and this paper should be interpreted as an appeal to the chemical community interested in lipids to give some thought to the attack on and solution of these problems.

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