Geochemistry of Lipids


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 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 polypl, corals, gorgonias, jellyfish (3), and sea anemones (4). Cholesterol (Fig. 1) (C_{27}H_{46}O) and dehydrocholesterol (Fig. 2) (C_{27}H_{35}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_{48}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. Schriner 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 Turffit (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>
<thead>
<tr>
<th>Sterol</th>
<th>Formula</th>
<th>Source</th>
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<tbody>
<tr>
<td>Cholesterol (Fig. 1)</td>
<td>C_{27}H_{46}O</td>
<td>Jellyfish</td>
</tr>
<tr>
<td>Clionasterol</td>
<td>C_{29}H_{48}O</td>
<td>Sea anemone</td>
</tr>
<tr>
<td>Gorgosterol</td>
<td>C_{29}H_{48}O</td>
<td>Gorgonia</td>
</tr>
<tr>
<td>Cholestanol (5) (Fig. 3)</td>
<td>C_{27}H_{44}O</td>
<td>Sponge</td>
</tr>
<tr>
<td>Poriferasterol</td>
<td>C_{29}H_{48}O</td>
<td>Sponge</td>
</tr>
<tr>
<td>Ergosterol (6) (Fig. 4)</td>
<td>C_{29}H_{48}O</td>
<td>Algae</td>
</tr>
<tr>
<td>Chondrillasterol (Fig. 5)</td>
<td>C_{29}H_{48}O</td>
<td>Algae</td>
</tr>
</tbody>
</table>
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 butyl alcohol (Fig. 8) were both found in a gorgonia (*Plexaura flexuosa*) (20), and butyl 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 (C24 to C36) (25).

**Acids**

Numerous fatty and naphthenic acids have been isolated from petroleum and identified. These range from formic (HCOOH) to arachidic acid (C26) for the fatty acids; the naphthenic acids (Fig. 11) include both cyclopentane and cyclohexane derivatives. 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 C26–C30 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 C25H52 to C34H54 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, analyzing 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 C29 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.