Normal Fatty Acids in Sediments

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Abstract

Normal fatty acids have been found by several investigators in a number of sediments ranging in age from Precambrian to Recent. This paper summarizes these occurrences. A variety of molecular distributions have been observed. In most sediments, even-carbon-numbered normal fatty acids are much more abundant than those with odd carbon numbers; in some sediments, however, concentrations of even- and odd-carbon-numbered normal fatty acids are about equal.

Normal fatty acids have been postulated as possible precursors for normal paraffin hydrocarbons in petroleum because of 1) structural similarities between the two kinds of molecules, 2) ubiquity of fatty acids in biological materials, 3) fatty acid-normal paraffin relationships in sediments, and 4) distribution of normal paraffins in some crude oils. Evidence suggests that normal fatty acids may be precursors for many normal paraffins of intermediate and high molecular weights found in petroleum. Detailed mechanisms of chemical reactions by which normal paraffins can be derived from fatty acids in sediments under geologically reasonable conditions have yet to be defined.

Normal Fatty Acids in Sediments

Introduction

Geochemical interest in fatty acids has increased greatly during the last five years. This increased interest has been due mainly to the development and availability of new analytical techniques, especially gas chromatography. These new techniques have facilitated separation and identification of fatty acids in complex mixtures from geological sources. The fact that fatty acids are major components of all living organisms has stimulated geochemists to investigate the fate of these compounds as they leave the biosphere and become part of the lithosphere. The ultimate fate of fatty acids is of special interest to petroleum geochemists because fatty acids may have served as parent material for some of the hydrocarbons in petroleum.

This paper summarizes occurrences in geological materials of saturated, straight-chain, monocarboxylic acids, hereafter called normal fatty acids. These acids form a homologous series of the general formula C_nH_{2n+1} COOH where $n \geqq 1$. Normal fatty acids will be designated in this paper by the number of carbon atoms in the molecule. For example, palmitic acid, $C_{15}H_{31}$ COOH, will be called C_{16}. Particular attention will be given to occurrences of normal fatty acids in modern and ancient sediments; normal fatty acids in geological materials such as coal, water, petroleum, and meteorites will be discussed briefly. Little will be said about occurrences of unsaturated and branched chain fatty acids in geological substances. Unsaturated, straight-chain fatty acids have been found in modern sediments (1) and in ocean waters (2,3). In both modern sediments and ocean waters concentrations of unsaturated fatty acids decrease rapidly with depth; unsaturated fatty acids have not yet been found in any ancient sediments. Therefore, the geological history of unsaturated fatty acids must be very short. The fate of these acids is most important; their study merits intense consideration. Branched-chain fatty acids have been found in petroleum (4–6) in modern sediments (54), and in Green River oil shale (54,55). Recent discoveries of branched-chain fatty acids in petroleum by Cason and Graham (6) and in marine lipids as summarized by Ackman and Sipos (7) should stimulate active interest in searching for the presence of these compounds in other modern and ancient sediments.

Normal fatty acids are common and essential constituents of living organisms (8) and will be referred to in this paper as natural or naturally occurring fatty acids or as the fatty acids in nature. They are found in oils, fats, and waxes of flora and fauna of marine and terrestrial habitations. Most naturally occurring fatty acids have even numbers of carbon atoms in their chains. Normal fatty acid C_{16} (palmitic acid) is the most abundant and widespread saturated fatty acid (8). All even-carbon-numbered normal fatty acids from C_2 to C_{38} have been found in nature free or most commonly as esters (9). Normal fatty acid components of natural fats contain predominantly even-carbon-numbered molecules C_4 to C_{26} (10); even-carbon-numbered normal fatty acids C_{26} to C_{38} are found principally in waxes of insect and plant origin (9). Normal fatty acids with odd numbers of carbon atoms are found in nature, but their concentrations are small compared with those of even-carbon-numbered normal fatty acids. Hilditch and Williams (10) cited work done largely by Shortland and Hanson, who have found normal fatty acids C_{11}, C_{13}, C_{15}, C_{17}, C_{19}, C_{21} and C_{23} in animal depot and milk fats. In describing organic constituents of higher plants, Robinson (11) wrote that fatty acids found in nature almost always have even numbers of carbon atoms; however, all straight-chain, odd-carbon-numbered acids from C_7 to C_{15} have been found free or as esters in higher plants. Ackman and Sipos (7) in reporting their findings and in summarizing the work of others show that marine lipids from phyto- and zooplankton, squids, fish, seals, and whales contain normal fatty acids with both even and odd numbers of carbon atoms in the range C_{12}–C_{20}; however, concentrations of even-carbon-numbered normal fatty acids always greatly exceed concentrations of odd-carbon-numbered normal fatty acids.

Some naturally occurring fatty acids and related compounds must survive chemical and biochemical degradation and become incorporated in sediments because normal fatty acids have been found in sediments ranging in geologic age from Recent to Precambrian. In recent sediments the distribution of normal fatty acids is most nearly like that of natural normal fatty acids; even-carbon-numbered normal fatty acids are most common, but odd-carbon-numbered acids can be present in low concentrations. In ancient sediments normal fatty acids with even numbers of carbon atoms still dominate, but in many samples proportions of odd-carbon-numbered acids relative to even-carbon-numbered acids are higher compared to proportions found in recent sediments and in nature. In fact, in some ancient sediments odd-carbon-numbered normal fatty acids are almost as abundant as even-carbon-numbered acids. These observations show that not

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only do some normal fatty acids survive in sediments but also that processes likely have altered distributions of normal fatty acids during geologic time.

Summary of Published Results

Published results concerning normal fatty acids in sediments are summarized in Chart I. Information is arranged by geologic age beginning with analyses of Recent sediments and ending with an analysis of a Precambrian rock. Graphs representing approximate distributions of normal fatty acids were constructed from published evidence such as distribution plots, gas chromatograms, and data reported quantitatively. For an individual analysis, fatty acid distributions are shown relative to the fatty acid of highest concentration. The graphs do not have precise quantitative significance.

Recent Sediments and Soils. In their quest to find if petroleum forms in sediments at the time of deposition, Trask and Wu (12) examined four recent sediments. Although they found no liquid hydrocarbons in these organic-rich sediments, they did find constituents which they identified as fatty acids C_6, C_{26}, C_{28} and C_{30}. The reported fatty acids quite likely were mixtures of several fatty acids. Question marks on the graphs (Chart I) indicate that relative amounts of fatty acids found could not be determined from the literature.

Abelson and his associate (13,14) found normal fatty acids C_{14}, C_{16} and C_{18} in three different recent sediments: mud from the Gulf Coast, a core of sediment 5000 years old from Pedernales, Venezuela, and a mud from San Nicolas Basin, offshore California. Of the three acids reported, C_{16} was most abundant. Parker and Leo (1) have examined lagoon and mud flat deposits along the Texas coast and have found normal fatty acids C_{14} C_{16} and C_{18}.

Cooper (15) studied two recent sediments from offshore Southern California, one from San Nicolas Basin and the other from Santa Barbara Basin. He found a complete series of normal fatty acids, both even and odd-carbon-numbered molecules, from C_{10} to C_{36}. Even-carbon-numbered normal fatty acids were much more abundant than odd-carbon-numbered acids, and C_{16} was present in highest concentration. Kvenvolden (16,17) also analyzed a sample from San Nicolas Basin and obtained almost the same distribution of normal fatty acids, but he recovered about four times more total normal fatty acids than Cooper reported. Graphs of Chart I do not reflect the difference in recovery because both distributions are normalized to C_{16} fatty acid. Differences in procedures may account for the dissimilarity in amount of fatty acids recovered. Kvenvolden used a modification of the procedure of Cooper (22). The modifications were designed to permit the quantitative recovery of normal fatty acids as methyl esters ranging from about C_{16} to about C_{34}. In both procedures the sample was saponified with a solution of potassium hydroxide in methanol. The alkaline hydrolysis mixture was recovered from the sediment. Water was added and the mixture was concentrated. Cooper extracted the basic concentrate with carbon tetrachloride in order to remove nonacidic material including hydrocarbons. This extract was discarded. Kvenvolden, on the other hand, acidified the concentrate and extracted with carbon tetrachloride for two reasons. The first was to retain any normal paraffin hydrocarbons present. Normal paraffin hydrocarbons and normal fatty acids, esterified as methyl esters, were carried through the procedure together. Urea adduction was used to separate straight-chain compounds from other lipid material. Because normal paraffin hydrocarbons and normal fatty acids were present together, more straight-chain compounds were available for adduction, and adduction was more efficient. Normal paraffins were separated from normal fatty acids by silica-gel chromatography. Normal fatty acid fractions can be purified further by alumina chromatography. The second reason for extracting the acidified concentrate was to prevent loss of the salts of very long-chain fatty acids. Salts of long-chain fatty acids tend to dissolve in nonpolar solvents. Solubility increases with increasing chain length. Extraction of the basic saponification mixture with carbon tetrachloride removed hydrocarbons and many of the salts of normal fatty acids of high molecular weights especially larger than C_{22}. To avoid this loss the concentrate was acidified and then extracted.

Results of Cooper (15) and Kvenvolden (16,17) on the San Nicolas Basin sediment contrast with the findings of Abelson and Parker (13), who show the presence of normal fatty acids C_{14}, C_{16}, and C_{18} exclusively. Different methods of extracting fatty acids from sediments very likely account for the contrasting results. At first alkaline hydrolysis was believed to be necessary if one wished to recover most of the fatty acid constituents in a sediment. Many investigators (15–19), who have found normal fatty acids of both even- and odd-carbon number over broad molecular weight ranges in various sediments, included alkaline hydrolysis as part of their procedures. Abelson and Parker (13), on the other hand, did not saponify their sediment or sediment extract. Recently, Hoering and Abelson (20) reexamined the sediment sample from San Nicolas Basin (13). Using a new procedure, which also does not involve alkaline hydrolysis, they obtained "free" normal fatty acids with both even and odd numbers of carbon atoms in the range from C_{14} to C_{30}. Their distribution of free normal fatty acids is very similar to the distribution of normal fatty acids reported by Kvenvolden (17), who saponified his San Nicolas Basin sample. With saponification, free fatty acids as well as fatty acids combined as salts and esters likely are recovered. Of interest is the fact that the distributions of free fatty acids and of mixtures of free and hydrolyzed fatty acids are so nearly parallel.

Normal fatty acids present in modern soils are dominantly of even-carbon-number. Meinschein and Kenny (21) found fatty acids in six soil samples and concluded that "a major portion of the wax acids have even carbon numbers and range in size from 14 to 30 carbon atoms." In their study of the Orgueil meteorite Nagy and Bitz (18) also examined the fatty acids in a recent soil and found almost exclusively even-carbon-numbered normal fatty acids from C_{16} to C_{34}.

Tertiary Sediments. Three studies have been made of samples from the Mahogany Zone of Eocene Green River Formation oil shale from near Rifle, Colorado. Abelson and Parker (13) found three normal fatty acids C_{14}, C_{16} and C_{18}. In contrast to these findings Lawlor and Robinson (19) discovered normal fatty acids ranging from C_{10} to C_{34}. They show that from C_{16} to C_{34} even-carbon-numbered normal fatty acids are dominant; however, below C_{16} the C_{11}, C_{13} and C_{15} normal fatty acids appeared to be most abundant. Hoering and Abelson (20) have recovered both even- and odd-carb [illegible] through C_{30} from Green River shale. Even-carbon-numbered fatty acids are most abundant.

Mesozoic Sediments. A number of samples of Cretaceous age have been examined for normal fatty acids. A sample of Eagle Ford Shale from Wood County, Texas, was examined by Cooper (15), who found normal fatty acids C_{11} through C_{34}. Both even- and odd-carbon-numbered acids were present. Later Cooper and Bray (22) reported normal fatty acids in samples of Skull Creek, Mowry, and Thermopolis shales from Wyoming. In all of these shales normal fatty acids of both even- and odd-carbon numbers were present over broad molecular weight ranges. Even-carbon-numbered acids always were more common than odd-carbon-numbered acids. Kvenvolden (16,17) studied in detail Mowry and Thermopolis shales of the Powder River Basin in Wyoming. He found a variety of molecular distributions of normal fatty acids. Some Mowry and Thermopolis shales contain normal fatty acids with even-carbon-numbered acids more abundant than odd-carbon-numbered acids. More important, however, is the observation that other Mowry and Thermopolis shales contain normal fatty acids in which concentrations of odd-carbon-numbered acids almost equal concentrations of even-carbon-numbered acids.

One other analysis of a Cretaceous sample has appeared in the literature. Nagy and Bitz (18) in their meteorite study report the distribution of normal fatty acids in a sample from the Navesink Formation of New Jersey. Prominent normal fatty acids were C_{16} and C_{18}. These were considered to be due to recent contaminations from waters percolating through the outcrop. Even- and odd-carbon-numbered normal fatty acids C_{14} to C_{30} were suggested from gas-chromatographic evidence.

Paleozoic Sediments. Normal fatty acids from two Paleozoic samples have been described in the literature. Cooper (15) found normal fatty acids C_8 to C_{28} in a sample of Chattanooga shale of Mississippian age from Oklahoma. Both even- and odd-carbon-numbered acids are present with the evens most abundant. Abelson and Parker (13) reported normal fatty acids C_{14}, C_{16} and C_{18} in a sample of Alun shale of Cambrian age from Sweden.

Precambrian Sediments. Precambrian Nonesuch Shale of Michigan has been reported to contain normal fatty acids by Hoering and Abelson (23). They identified C_{14}, C_{16}, C_{18}, C_{20} and C_{22} normal fatty acids; they could find no odd-carbon-numbered normal fatty acids.

Normal fatty acids have also been found in lignites and brown coals, in petroleum, and in waters. These occurrences will be considered briefly.

Montan wax which is derived from lignite and brown coal is known to contain normal fatty acids of both even- and odd-carbon numbers in the range C_{22} to C_{34} (24,25). Even-carbon-number normal fatty acids are most abundant.

Normal fatty acids C_1 through C_{18} have been found in petroleum. Hancock and Lochte (4) identified C_1 through C_5, and Quebedeaux and others (5) found C_6 through C_9 in petroleum from California. A West Texas petroleum was reported to have C_7, C_8 and C_9 normal fatty acids (26). Tanaka and Kuwata (27) reported the presence of C_{14}, C_{16}, C_{18} and C_{20} normal fatty acids in petroleum from Japan, California and Borneo. Recently Graham (28) identified C_8 through C_{18} normal fatty acids in a petroleum from the San Joaquin Valley, California. He measured relative concentrations of these acids and found that odd-carbon-numbered acids were almost as abundant as even-carbon-numbered acids. This type of distribution of normal fatty acids is similar to that found in some ancient sediments (17) but quite different from distributions in living organisms.

Oceans waters also contain normal fatty acids. Williams (2) found C_{12}, C_{14}, C_{16}, C_{18}, C_{20} and C_{22} normal fatty acids in samples from the Pacific Ocean. He also reported compounds whose gas chromatographic retention times were the same as C_{15}, C_{17} and C_{19} normal fatty acids (methyl esters). He did not, however, identify these compounds as the odd-carbon-numbered normal fatty acids. Many samples from the Gulf of Mexico were examined for fatty acids by Slowey and others (3). They found normal fatty acids C_{10}, C_{12}, C_{14}, C_{16} and C_{18}.

Formation or subsurface waters have been examined by Cooper (15) and Cooper and Bray (22). They showed that, in five of six petroleum reservoir waters studied, normal fatty acids with almost equal abundances of even- and odd-carbon-numbered molecules were present. The remaining petroleum reservoir water contained traces of only even-carbon-numbered normal fatty acids. The author believes that analytical data for the five waters were incorrectly interpreted because he has been unable to duplicate the results. He has found in petroleum reservoir waters only normal fatty acids C_{14}, C_{16} and C_{18} in very low concentrations. He believes that the extracts from the five waters in question contained dominantly normal paraffin hydrocarbons from the coproduced petroleum due to an incomplete separation step in the procedure. Normal paraffins in petroleum generally have equal abundances of even- and odd-carbon-numbered molecules. In the five extracts the presence of normal fatty acids was determined by gas chromatography without confirming evidence from infrared and mass spectrometry. For the gas chromatographic column used, retention times were the same for the methyl ester of a given normal fatty acid and a normal paraffin with three more atoms than the acid. Additional work needs to be done to confirm or deny the original findings.

To complete this survey of normal fatty acids in geological materials, two additional analyses should be mentioned.

Normal fatty acids were found by Nagy and Bitz (18) in the Orgueil meteorite. These fatty acids ranged from C_{14} to C_{28} and contained even- and odd-carbon-numbered molecules with a slight predominance of even-carbon-numbered molecules.

The last report concerns normal fatty acids obtained from clays that had been exposed to the air for a prolonged period. Bear and Kranz (29) report normal fatty acids C_4 through C_{20}, both even- and odd-carbon-numbered molecules, with even-carbon-numbered acids most abundant, especially C_{16} and C_{18}. They claim that the acids are in an oily extract that appears after the clay has been exposed in a dry atmosphere. The significance of this information is not clear at the present time. The work does suggest that caution should be used when samples are collected from outcrops to avoid weathered material which might contain fatty acids not indigenous to the sediment.

Discussion

Normal Fatty Acids and Normal Paraffin Hydrocarbons

Many people have considered fatty acids as likely precursors for some of the hydrocarbons of petroleum.

At the end of the last century Engler and Hoefer (30), cited in (27), advanced ideas that petroleum originated from fatty substances of animals and plants. Trask (31) and Brooks (32) discussed likely starting materials for petroleum and included fatty acids among them. More recently Hanson (33) mentioned fatty acids as possible petroleum precursors, and Breger (34) discussed possible chemical conversions of fatty acids to hydrocarbons of petroleum. Fatty acids likely have received so much support as petroleum precursors for the following reasons: 1) Fatty acids are ubiquitous in nature being widely distributed in both plants and animals. 2) Fatty acids are structurally similar to some paraffin hydrocarbons which are common in petroleum.

New evidence is being obtained each year relating to fatty acids and their possible role in petroleum generation. One bit of evidence concerns changes in molecular distributions of normal fatty acids and normal paraffin hydrocarbons with time. In biological systems normal paraffin hydrocarbons are present; odd-carbon-numbered normal paraffins are more abundant than normal paraffins with even-carbon numbers (35). In recent sediments concentrations of normal paraffins with odd numbers of carbon atoms greatly exceed concentrations of even-carbon-numbered normal paraffins. With time, however, abundances of even-carbon-numbered normal paraffins increase so that in most crude oils and in some ancient sediments odd- and even-carbon-numbered normal paraffins are about equally abundant (36). An almost parallel process seems to take place with normal fatty acids. In nature even-carbon-numbered normal fatty acids are far more plentiful than odd-carbon-numbered normal fatty acids as has been discussed earlier. Normal fatty acids of even-carbon-numbers are still most abundant in recent sediments, but in ancient sediments and in crude oil ratios of odd- to even-carbon-numbered normal fatty acids increase (15,17,28).

The processes involving the increase with time of even-carbon-numbered normal paraffin hydrocarbons and odd-carbon-numbered normal fatty acids likely are related in some manner. Cooper and Bray (22) thought that the processes are related and postulated a role for fatty acids in petroleum generation. Their scheme involves step-by-step decarboxylation of normal fatty acids. Each acid can lose CO_2 to form intermediates which react to give normal paraffins and normal fatty acids, both having one less carbon atom than the parent acids. Newly generated fatty acids react in the same way as original acids. Operation of this scheme on initially deposited normal fatty acids under conditions favoring formation of more fatty acids than paraffins, produces mixtures in which there is little preference for either even- or odd-carbon-numbered acids or paraffins. Absolute concentrations of fatty acids should decrease while normal paraffins formed from fatty acids should accumulate with initially deposited normal paraffins. In mixtures of 1.0. The scheme of Cooper and Bray (22) cannot account for these distributions. Some other mechanism must also be operative. A possible explanation follows: Step-by-step decarboxylation is the dominant mechanism. At the same time reduction of a small number of carboxyl groups to methyl groups takes place. This reduction step involves no loss of carbon atoms. With decarboxylation and reduction operating concurrently, mixtures of normal paraffins with even-carbon-numbered molecules slightly predominant can be obtained. Reduction of carboxyl to methyl groups as a geochemical process has been mentioned before by Abelson (38) and Bergmann (39), who cite the work of Shabarova. Geochemical evidence for reduction was obtained by Blumer (40) in his study of fossil porphyrins.

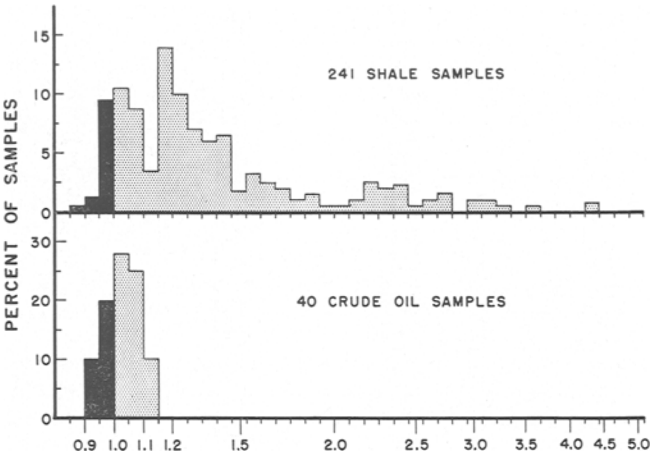

FIG. 1. Ratio of abundances of odd- to even-carbon-numbered paraffins. Samples of shales and oils with ratio of odd- to even-carbon-numbered normal paraffin hydrocarbons less than one. Data from Bray & Evans (37).

More evidence concerning normal fatty acids as precursors of normal paraffin hydrocarbons is presented by Martin et al. (41). In their study of normal paraffins in certain crude oils, they found a predominance of odd- relative to even-carbon-numbered normal paraffins in specific molecular weight ranges. These investigators suggested that precursors for these normal paraffins were normal fatty acids which by some sort of decarboxylation would form normal paraffins of proper chain lengths. In some Paleozoic crude oils, such as Kawkawlin (Fig. 2), normal paraffins with 11, 13, 15, 17 and 19 carbon atoms were slightly more abundant than their even-carbon-numbered neighbors. Fatty acids in fats most commonly are C_{12}, C_{14}, C_{16}, C_{18} and C_{20}; these fatty acids were suggested as source for normal paraffins with 11, 13, 15, 17 and 19 carbon atoms. Uinta Basin oil of Tertiary age contained normal paraffins with odd-carbon-numbered predominances in the range of normal paraffins with 23 to 33 carbon atoms per molecule (Fig. 2). Fatty acids of waxes have longer chain normal paraffins with 23, 25, 27, 29, 31 and 33 carbon atoms per molecule in the Uinta Basin crude oil. Mair (42) has considered the evidence presented by Martin and his associates and concluded that normal paraffins of petroleum are derived for the most part from straight-chain fatty acids and alcohols.

Some additional information relates to fatty acids and paraffins in ancient sediments. Lawlor and Robinson (19) compared the distribution of normal fatty acids and normal paraffin hydrocarbons in the same sample of Green River Formation oil shale. The distributions are almost identical when each normal fatty acid concentration is compared with the concentration of a normal paraffin having one less carbon atom than the acid (Fig. 3). Kvenvolden (16,17) showed a similar parallelism in distributions of normal fatty acids and normal paraffin hydrocarbons in some Mowry and Thermopolis shales (Fig. 4, 4A). These authors interpreted their findings to indicate that normal fatty acids and normal paraffin hydrocarbons in these sediments were related and invoked the scheme of Cooper and Bray (22) as a possible explanation for their findings.

Parallelism in distributions of normal paraffin hydrocarbons and normal fatty acids can also be explained by a scheme involving hydrogenolysis of the fatty acids. Although the scheme is possible, it is unlikely. In a reaction described by Meinschein and Kenny (21) fatty acid esters in the presence of Raney nickel at 200C and 3000 psi hydrogen pressure were converted into hydrocarbons, methane, and water. The hydrocarbon from the fatty acid part of any ester contained one less carbon atom than the original fatty acid. For a mixture of methyl esters of normal fatty acids the normal paraffins resulting from hydrogenolysis, except for methane, would have one less carbon atom than the original fatty acids. The distribution of normal fatty acids would parallel the distribution of normal paraffins with one less carbon atom than the acids. Cooper and Bray (22) treated the methyl esters of normal fatty acids from a Thermopolis shale sample according to the hydrogenolysis procedure (21) in order to verify the fatty acids from the sediment. The results (Fig. 5) show the predicted parallelism between normal fatty acids and normal paraffin hydrocarbons. This hydrogenolysis scheme is considered an unlikely geochemical process for three reasons. First, the conditions of hydrogenolysis as performed in the laboratory are severe compared to geological conditions, and it is difficult to visualize such a reaction taking place in sediments. Secondly, esters of sediments are more complicated than methyl esters. Any long-chain primary alcohol portion of natural esters also would form hydrocarbons under hydrogenolysis. These hydrocarbons would have one less carbon atom than the original alcohols (21). Distributions of normal paraffins produced from both acid and alcohol portions of esters are not likely to parallel distributions of the normal fatty acid portion of esters unless the carbon number distribution of acids and alcohols are similar. Thirdly, this hydrogenolysis scheme does not account for differences in distributions of normal paraffins and fatty acids in recent and some ancient sediments. In recent sediments odd-carbon-numbered paraffins and even-carbon-numbered fatty acids are predominant; in some ancient sediments paraffins and acids have almost equal abundances of both even- and odd-carbon-numbered molecules.

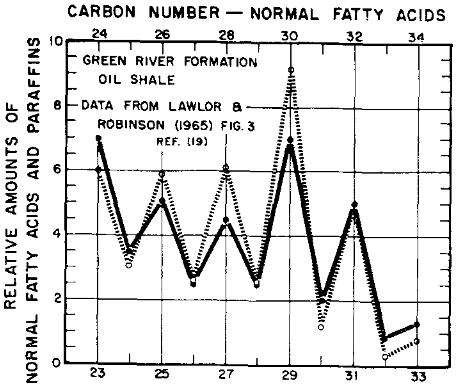

FIG. 3. Distribution of normal fatty acids and normal paraffin hydrocarbons in Green River Formation oil shale.

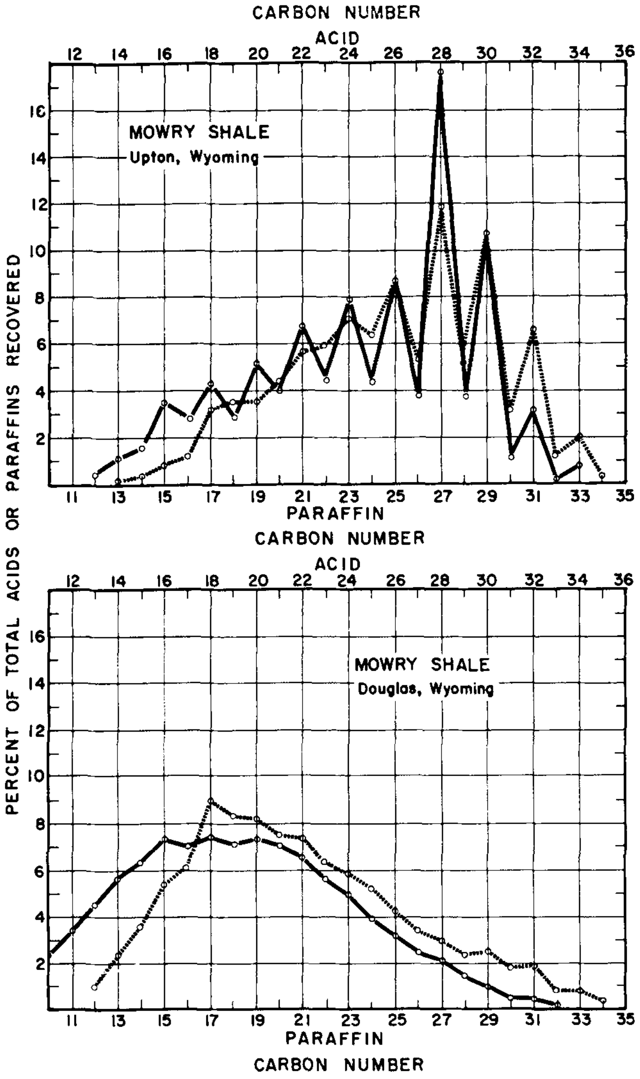

FIG. 4. Relative distributions of saturated fatty acids and normal paraffin hydrocarbons. Solid line, acids; dotted line, paraffins.

Parallel distributions of normal fatty acids and normal paraffin hydrocarbons with one less carbon atom than the acids cannot be explained by chemical oxidations of normal paraffins. Chemical oxidation of paraffins to fatty acids with concurrent loss of a carbon atom from the paraffin chain is not considered likely because oxidation probably would not be specific; all secondary carbon atoms would be equally likely to be attacked. Furthermore, rate of oxidation

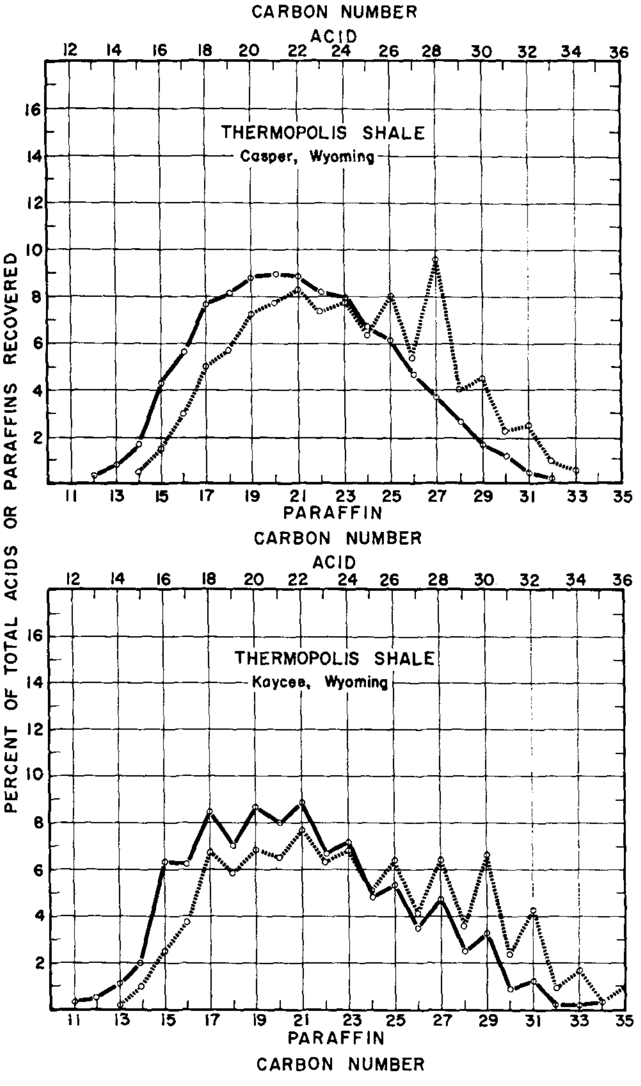

FIG. 4A. Same as Fig. 4.

of any oxidation product probably would exceed the rate of oxidation of the paraffin.

Microbial oxidation of normal paraffins to form fatty acids possibly can explain some parallel distributions of normal fatty acids and paraffins. According to Van der Linden and Thijsse (43) normal paraffins of medium chain-length are degraded via the terminal carbon atom almost exclusively to yield primary alcohols, the aldehydes, and the corresponding fatty acids which are further oxidized by β-oxidation only. Normal paraffins of odd-carbon numbers generally are more frequent in sediments than are even-carbon-numbered paraffins. Microbial oxidation of these paraffins would produce normal fatty acids with a preference for odd-carbon-numbered molecules. β-Oxidation of odd-carbon-numbered fatty acids would produce lower odd-carbon-numbered fatty acids. At the same time originally present normal fatty acids which have a preference for even-carbon-numbered molecules would also undergo β-oxidation to give lower even-carbon-numbered fatty acids. Mixtures of normal fatty acids from bacterial oxidation could have a variety of distributions depending on the proportions and distributions of paraffins and fatty acids undergoing oxidation. Although parallel distributions of normal fatty acids and normal paraffins with one less carbon atom than the acids are possible by this scheme, such parallelism probably would be coincidental.

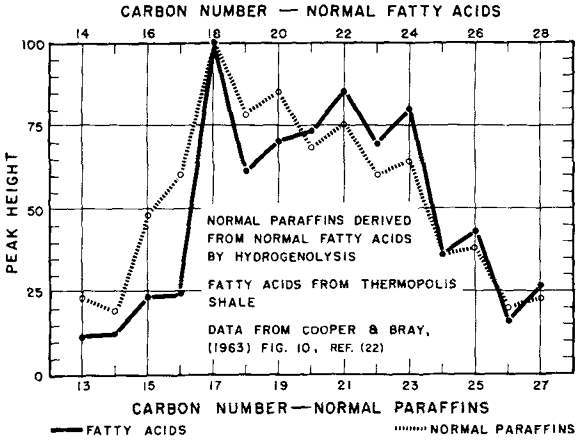

FIG. 5. Distribution of normal fatty acids compared with the distribution of normal paraffin hydrocarbons derived from the fatty acids by hydrogenolysis.

The distributions of normal fatty acids and normal paraffin hydrocarbons in a recent sediment (Fig. 6) have been reported by Kvenvolden (16,17). He showed that the parallelism in distributions of fatty acids and normal paraffins observed in some ancient sediments is not present in the recent sediment. He concluded that normal fatty acids and normal paraffins in the recent sediment do not have a precursor-product relationship as apparently do acids and paraffins in some ancient sediments.

Not all investigators, however, believe that normal fatty acids are the direct precursors of normal paraffin hydrocarbons in petroleum. Abelson (44), after finding fatty acids in recent and ancient sediments and after considering the work of Cooper and Bray (22) concluded that "the level of free fatty acids in even recent sediments is far too low to be capable of accounting for hydrocarbons in petroleum." He suggested that fatty acids which escape biologic attack are converted to kerogen and other nonbiologic materials. Because the total concentration of fatty acids in the organic material of sediments is less than 0.1%, he argued that a much more reasonable source for hydrocarbons is the kerogen and other "non-biologic" material of sediments. In experiments with low-temperature heating of kerogen Hoering and Abelson (45,46) have produced normal paraffins containing one to twelve carbon atoms per molecule. This work showed that thermal degradation of kerogen may account for some of the low molecular weight normal paraffins of petroleum but did not account for high molecular weight paraffins. Abelson (44) pointed out that decarboxylation in sediments likely occurs; however, he indicated that a more important process is breakage of carbon-carbon bonds at points other than carbonyl carbon. If, however, carbon-carbon bond cleavage is a dominant geochemical process, compounds with tertiary carbon atoms should degrade at faster rates than compounds with secondary and primary carbon atoms. Compounds with tertiary carbon atoms such as isoprenoid hydrocarbons likely would disappear. Yet, isoprenoid hydrocarbons occur in crude oils (47,48) and in ancient sediments (49). Sediments as old as Precambrian (50–52) contain pristane and phytane, two long-chain isoprenoid hydrocarbons each with four tertiary carbon atoms. The presence of these isoprenoids suggests that carbon-carbon bond cleavage

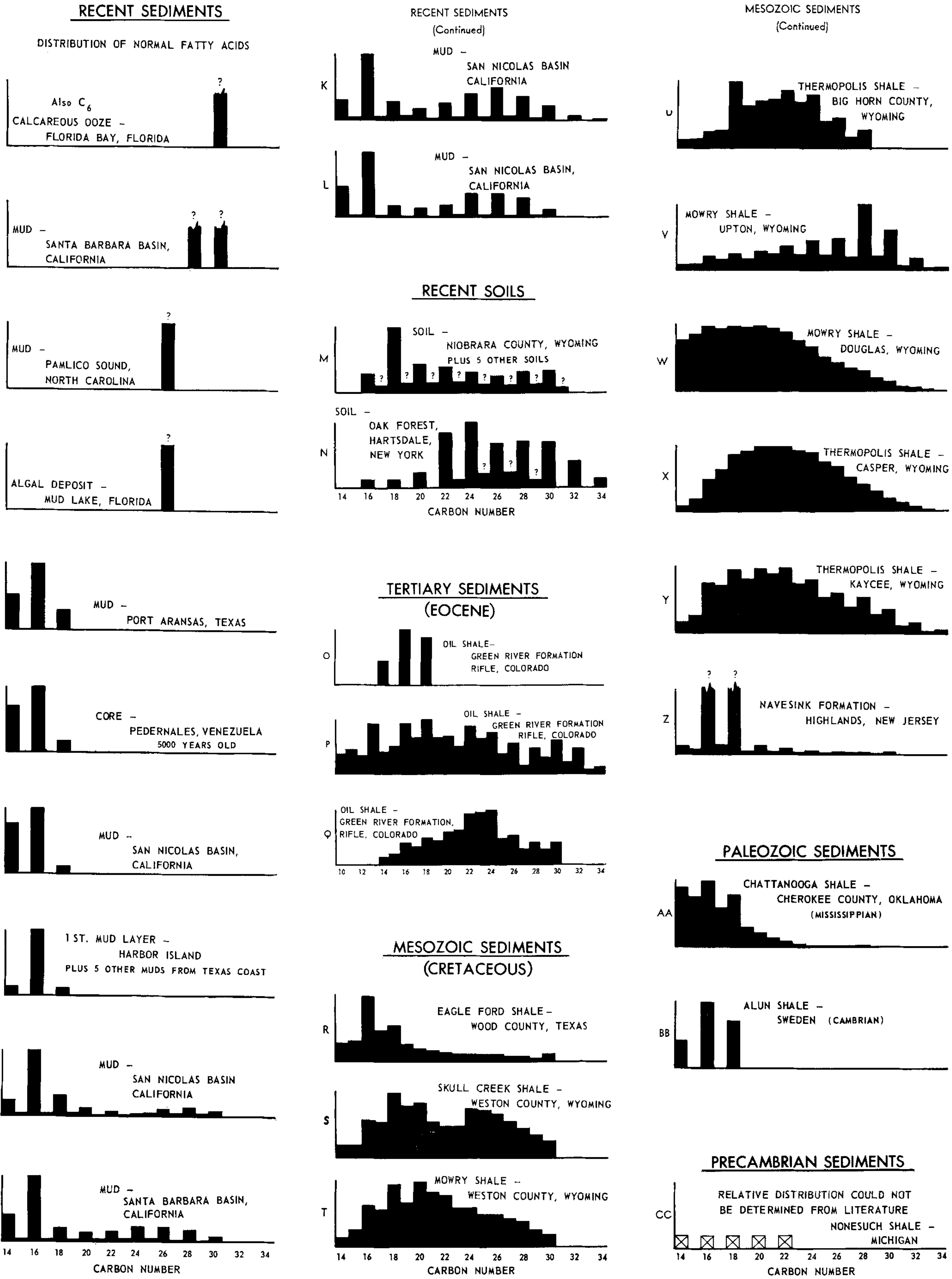

CHART 1. Distribution of normal fatty acids in recent sediments. *A-D*, Trask and Wu (12), Table 1 and 2; *E-G*, Abelson and Parker (13), Fig. 66 and 67; *H*, Parker and Leo (1), Fig. 1, Curve 2; *I-J*, Cooper (15), Table 1, Col. 2 and 3; *K*, Kvenvolden (17), Fig. 7; *L*, Hoering and Abelson (20), Table 31; *M*, Meinschein and Kenny (21), Table 8, Col. 4; *N*, Nagy and Bitz (18), Fig. 3, Curve B; *O*, Abelson and Parker (13), Fig. 65 (top); *P*, Lawlor and Robinson (19), Fig. 2; *Q*, Hoering and Abelson (20), Fig. 78; *R*, Cooper (15), Table 1, Col. 5; *S-U*, Cooper and Bray (22), Table 3, Col. 6, 7 and Fig. 10; *V-Y*, Kvenvolden (17), Fig. 2; *Z*, Nagy and Bitz (18), Fig. 3, Curve C; *AA*, Cooper (15), Table 1, Col. 4; *BB*, Abelson and Parker (13), Fig. 69; *CC*, Hoering and Abelson (23), p. 263.

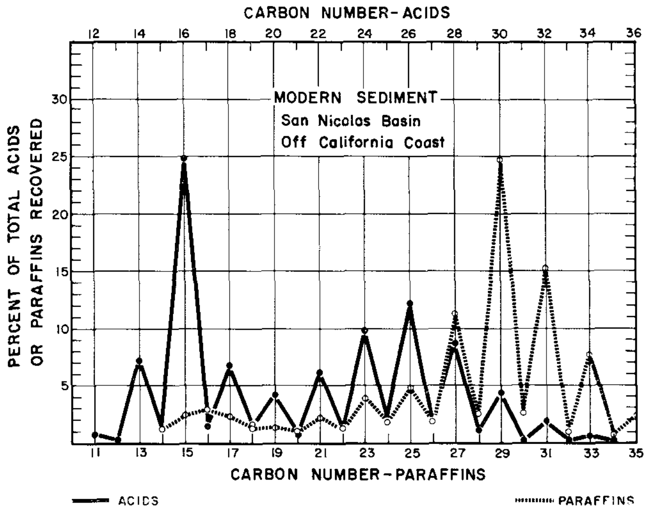

FIG. 6. Relative distributions of saturated fatty acids and normal paraffin hydrocarbons.

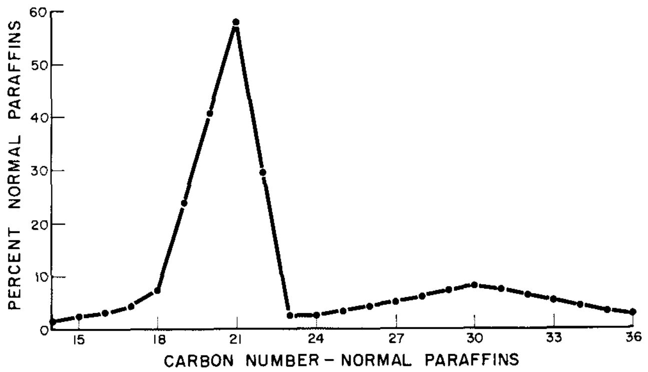

FIG. 7. Distribution of normal paraffin hydrocarbons derived from C_{22} normal fatty acid. Data from Jurg and Eisma (53).

may not be a major geochemical process unless the isoprenoids have been protected during geologic time in some unknown manner.

Some additional information concerning fatty acids has been reported recently by Hoering and Abelson (20). They oxidized kerogen from sediments by chromic acid or potassium permanganate and obtained mixtures of normal fatty acids. Fatty acids from kerogen oxidation were compared with "free" fatty acids recovered by solvent extraction of the total sediment. The distribution of normal fatty acids extracted from Green River shale is comparable to that produced by oxidation of kerogen from the same sediment. However, the ratio of even- to odd-carbon-numbered fatty acids from oxidation is greater than the same ratio calculated for "free" fatty acids. Fatty acids also were recovered from a recent sediment from San Nicolas Basin by sediment extraction and kerogen oxidation. In contrast to the results obtained from Green River shale, the ratio of even- to odd-carbon-numbered fatty acid from oxidation is less than the same ratio determined for fatty acids extracted directly from the sediment. The significance of these contrasting results was not explained. Finally, fatty acids from chromic acid oxidation of McMinn Shale (Precambrian) from Australia have almost equal abundances of both even- and odd-carbon-numbered molecules.

Detailed mechanisms of chemical reactions are not known that can account for various distributions of normal fatty acids and normal paraffin hydrocarbons in sediments and crude oils. The origin of perhaps the simplest compounds in petroleum, i.e., normal paraffin hydrocarbons, is very difficult to understand. A possible scheme to account for many of the normal paraffins in petroleum may involve (1) step-by-step decarboxylation and reduction of normal fatty acids (such as free fatty acids, those combined in salts and esters, and those derived from kerogen) to account for intermediate and high molecular weight normal paraffins and (2) mild thermal degradation of kerogen to account for low molecular weight normal paraffins. When the results of Jurg and Eisma (53) are considered, the whole picture becomes more complicated. They heated normal fatty acid C_{22} in a sealed tube with bentonite and water at 200C. At the completion of the experiment they found an interesting mixture of normal paraffins. Present in the low-molecular weight fraction were normal paraffins with 3, 4, 5 and 6 carbon atoms per molecule. In the high-molecule-weight fraction the normal paraffin with 21 carbon atoms was most abundant. Normal paraffins with 14 to 20 carbon atoms also were present. Most remarkable, however, was that normal paraffins with 22 to 34 carbon atoms also were found (Fig. 7). Recently they found C_{15} to C_{24} fatty acids as products of their reaction (56). Their discovery suggests that normal paraffins in petroleum need not necessarily be derived from normal fatty acids of longer chain lengths; decarboxylation as well as other reactions produce normal paraffins from normal fatty acids.

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