

The Hydrocarbon Constituents of Petroleum and Some Possible Lipid Precursors

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Abstract

This report presents a complete qualitative picture of our knowledge of the hydrocarbon composition of petroleum as of April 1965. The material is presented in detail on an imaginative map called the Hydrocarbon Hemisphere which depicts the hydrocarbons identified in petroleum. All compounds are placed on the map according to boiling point.

The accompanying text illustrates by structural formulas the several types of hydrocarbons identified, presents some quantitative data, and points out the possible geochemical significance of a number of the compounds with particular reference to lipids as possible source material.

Introduction

PETROLEUM, IN ONE OF ITS THREE FORMS, natural gas, crude oil, or asphalt, has been used by man for centuries as a source of light, energy, and plastics. However, until comparatively recent times he lacked the necessary tools to separate and identify petroleum's many components. Recorded study of crude oil seems to start with the work of Silliman (80), an American chemist, followed closely by the report of the separation of several aromatic hydrocarbons by De La Rue and Muller (30) in 1857. Schorlemmer (1863), (77) and Engler (1879) (35) were well-known early researchers in this field. Since then many chemists have studied the composition of petroleum, particularly the crude oil portion, but progress has been slow, although the recent advent of new techniques for separation and identification of organic compounds has added impetus to these studies.

The most widely accepted theory as to the origin of oil is that it is the result of bacterial, chemical, and geological action on organic debris, both plant and animal. Many of today's organic geochemists believe that the part of the organic debris that contributes to petroleum consists predominantly of the lipid portion of fauna and flora. Biochemists have only recently begun to unravel the mysteries of the composition of living material. If crude oil is formed from such substances, it would be expected to inherit at least part of the basic structures and probably some of the more complex materials. Thus, crude oil, like its progenitors, would pose difficult analytical problems. In this connection the application to crude oil of biochemical techniques, such as chromatography, micromanipulations, and countercurrent extractions, has greatly enhanced research on its composition. However, even today our knowledge of the mass of individual compounds boiling above 200°C to 250°C is still meager except for a few specific instances, such as the normal paraffins. In all boiling ranges, except possibly for compounds in the C₁ to C₇ range, our quantitative information lags considerably behind the qualitative data.

The purpose of this report is to present authoritative qualitative data from many sources in such a

manner as to form an authentic and understandable picture of crude oil hydrocarbons as we know them today and to present the latest theories on the sources of these hydrocarbons. The qualitative facts are augmented by some semiquantitative data to provide a somewhat broader perspective.

The Petroleum World

In 1948 the author published a brief article called "The Petroleum World" (82), the main feature of which was an imaginative map showing the components of petroleum as known at that time. The new version of "The Petroleum World" retains the same basic concept with regard to format, location of compounds, and "topographic" terms. However, the very considerable increase in our knowledge of the sulfur, nitrogen, and oxygen compounds in crude oil has made it necessary to show the map as two hemispheres that could imaginatively be considered as joined by the Petroleum Ocean. Thus all the hydrocarbons are shown on one hemisphere (Fig. 1). (References 1, 2, 12, 14, 16-18, 20, 27, 32, 36, 45-49, 51, 53, 54, 59, 63-66, 73, 78, 85-89 in addition to references in the text were used in preparing Fig. 1.) A second hemisphere, not shown in this paper, is devoted exclusively to compounds of sulfur, nitrogen, and oxygen that have been found in crude oil and is called the Heterogeneous Hemisphere (81).

The concept of the map is simple—it represents a hemisphere at the center of which is the carbon atom (called Carbon Peak) surrounded by a stratosphere of hydrogen. From combinations of these two elements stem all the hydrocarbons. Concentric rings, representing isotherms in degrees C, extend from the hydrogen stratosphere at the temperature of liquid hydrogen (-253°C) to over 600°C. Compounds are located according to their boiling points along rivers and streams representing specific types of compounds. The imaginative geographical features such as rivers, creeks and brooks, are symbolic of the importance of the class of compounds portrayed. The map is further divided into quadrants in each of which a general class of compounds is presented, namely alkanes, cycloalkanes, aromatics and cycloalkanoaromatics. Compounds that have been identified are shown by solid circles or solid squares for the normal compounds. A few of the other compounds that may be present but have not been positively identified are shown by open circles. When the boiling point is not known, appropriate locations are indicated by solid triangles. Mountain ranges have been shown whose names are indicative of possible sources for several of the compounds found (the mountains of themselves have no significance), some of which will be referenced farther on.

The Hydrocarbon Hemisphere (Fig. 1) is divided into four quadrants. Each quadrant will be discussed separately in the order, alkanes (Fig. 2), cycloalkanes (Fig. 7), aromatics (Fig. 10), cycloalkanoaromatics (Fig. 12).

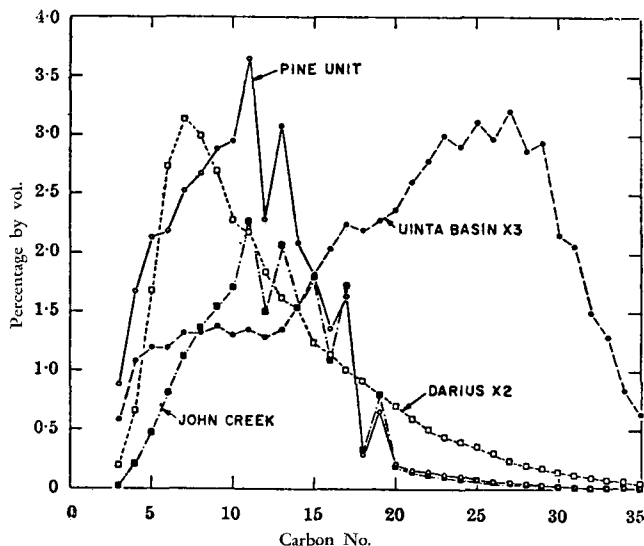


Fig. 4. Distributions of *n*-paraffins in four crude oils (Martin and co-workers [67] Fig. 1).

predominances of odd-numbered carbon atoms, and the *n*-alkane content may decrease sharply at C₁₈. The Pine Unit and John Creek curves illustrate this situation.

3) An unusual distribution is shown by the Uinta Basin crude oil with a maximum at C₂₇ and a slight odd-number predominance from C₂₃ to C₃₂.

4) Other crude oils may show other variations, such as having the maximum *n*-alkane content at C₁₇ or having odd-numbered predominance at different carbon number positions.

n-Alkane Sources

Hydrocarbons. Naturally occurring hydrocarbons seem an obvious source (83). Gerarde and Gerarde (40), in an excellent summary of hydrocarbons in nature, show that hydrocarbons from C₇ to C₃₇ are found in the leaves and fruits of plants and in some insects. However, most of the *n*-alkanes in natural products are in the C₂₀ to C₃₀ range and show a decided predominance for odd-numbered *n*-alkanes. This is contrary to the data for most crude oils which indicate little predominance for either odd or even. This does not preclude that naturally occurring hydrocarbons may be contributors as mentioned by Mair (59). On the positive side, Koons and co-workers (50) have recently shown that in marine organisms as typified by sponges and coral there are hydrocarbons present in the range C₂₄–C₃₄ and they show no odd or even preference similar to most crude oils.

Saturated Fatty Acids. Martin and co-workers (67) suggest saturated fatty acids as precursors for the C₁₁–C₁₉ *n*-alkane range. This view is substantiated by the work of Cooper (23) and by Lawlor and Robinson (52) and concurred in by Mair (59) among others. Saturated fatty acids from C₁₂ through C₁₈ are major constituents of many natural vegetable and animal fats. Cooper has shown that fatty acids survive in sediments (23) and has proposed a mechanism for the decarboxylation reaction (24). Jurg and Eisma (44) have shown that thermal cracking of higher molecular weight fatty acids in the presence of bentonite must not be overlooked both as a decarboxylation reaction and as a means of forming *n*-paraffins with smaller carbon numbers.

Unsaturated Fatty Acids. Martin and co-workers (67) suggest unsaturated fatty acids as precursors

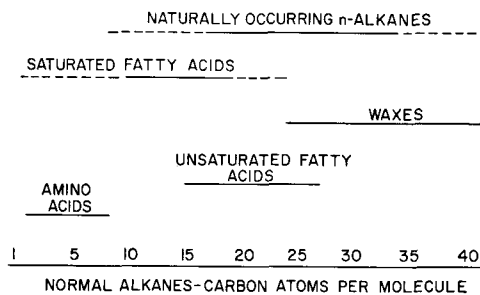


Fig. 5. Sources of normal alkanes.

particularly in the C₁₈–C₂₀ range. Most unsaturated fatty acids are C₁₈ compounds with different degrees on unsaturation and accordingly different reactivities.

Waxes. Waxes are esters of fatty acids and complex alcohols and thus could be precursors of *n*-alkanes in the C₂₃ and higher range as suggested by Martin and co-workers (67) and Lawlor and Robinson (52).

Amino Acids. Erdman (37) has suggested that simple amino acids, hydrolysis products of proteins, may be the precursors for both normal and isoalkanes in the C₂–C₈ range.

Summary

Fig. 5 shows the major sources for *n*-alkanes that have been suggested in relation to the size of the *n*-alkane molecule. All sources except the amino acids are lipids. On these figures the solid lines indicate the carbon-atom range normally found. The dash lines indicate extensions that might result from cracking or molecules larger than usual.

Isoalkanes

The tributaries on the Alkane River are composed entirely of the branched paraffins or isoalkanes, but even as of now few compounds above 10 carbon atoms have been identified. This molecular size represents the upper limit of the gasoline boiling range, and until very recently there was little interest in the composition of the portion having more than 10 carbon atoms. This factor together with increasing molecular complexity has resulted in very few identifications above the decanes, as shown in Table II. Presumably the increased demand for information concerning jet and diesel fuels will correct this situation.

Several important discoveries have been made recently of isoprenoid-type compounds 2, 6, 10-trimethylundecane and 2, 6, 10-trimethyldodecane by Mair and co-workers (60) and of 2, 6, 10, 14-tetramethylpentadecane (pristane) (5,29) and 2, 6, 10, 14-tetramethylhexadecane (phytane) (5,29), and more recently (4) 2, 6, 10-trimethyltridecane, 2, 6, 10-trimethylpentadecane, 2, 6, 10, 14-tetramethylheptadecane. The related structures and content of these isoprenoids as determined by Bendoraitis and co-workers (4) for East Texas crude oil are given in Table III. These values are high for the quantity of an individual hydrocarbon in crude oil.

In general the isoparaffins with the fewest and simplest branches are most prevalent, and dimethylalkanes, trimethylalkanes, and tetramethylalkanes

TABLE II
Alkane Isomers Possible and Identified

Isomers	Carbon atoms in molecule												
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃
Possible	1	1	1	2	3	5	9	18	35	75	159	335	802
Identified	1	1	1	2	3	5	9	18	30	12	1	1	1

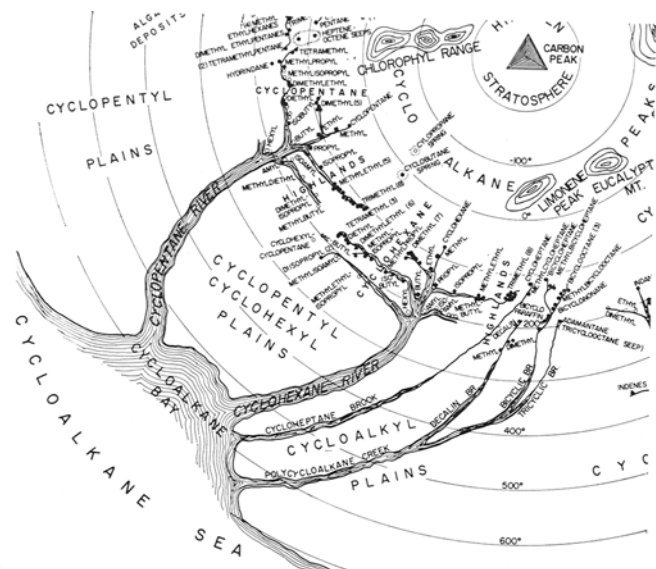


Fig. 7. Cycloalkane quadrant.

saturated hydrocarbons or olefins, *n*-hexene, *n*-heptene and *n*-octene were identified by Putscher (75) in Pennsylvania crude oil, ordinarily considered to be more saturated in terms of hydrogen than most crude oils. However, it also has less evidence of having had contact with reactive material such as sulfur, so this may be the reason these olefins have survived. It does seem probable that olefins were present at some stage of petroleum evolution. For example possibly incomplete hydrogenation in the decarboxylation and deamination of amino acids could result in olefins. They could not come from unsaturated acids as these start at C₁₀.

Cycloalkane Quadrant

The cycloalkane quadrant is shown in Fig. 7. Cycloalkanes, often called naphthenes and sometimes cycloparaffins, are ring compounds. They can be imagined as most often being formed from a five- or six-membered normal paraffin joining ends to form a ring and losing two hydrogens in the process. All cycloalkanes are completely saturated with hydrogen and all except the parent members of the series have alkyl side-chains. Cycloalkanes are often monocyclic, and of this class there are two major subdivisions, cyclopentanes with five carbon atoms and cyclohexanes with six carbon atoms. Cyclobutane and cycloheptanes are also known, as well as bi- and polycyclic naphthenes. Representative types are shown on Table IV. Cyclopropane, shown on the map, has never been found in petroleum.

The cycloalkane quadrant contains two principal rivers—the Cyclopentane and the Cyclohexane. In addition there are Cycloheptane Brook, Bicycloalkyl Creek, and Cyclobutane Spring that evaporates as fast as it forms for no stream emanates from the spring. The rivers originate in the Cyclopentane and

TABLE IV
Representative Types of Cycloalkanes

Name	Found in
Cyclopentane.....	Gasoline
Cyclohexane.....	Gasoline
Hexylcyclohexane.....	Not reported (possible in diesel fuel)
3,3,0-Bicyclooctane.....	Gasoline
Tricyclo [3,3,1,1 ^{3,7}]-decane (adamantane).....	Gasoline
Decahydronaphthalene (decalin).....	Gasoline

TABLE V
Cyclopentane Isomers Possible and Identified

Isomers	Carbon atoms in molecule					
	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀
Possible	1	1	6	15	55	150 ^a
Identified	1	1	6	15	8	0

^a Estimated from logarithmic plot of available data.

Cyclohexane Highlands where there are several tributaries formed by alkylated cycloalkanes. The rivers then wind through the Cyclopentyl and Cyclohexyl Plains where no tributaries have been discovered and empty into Cycloalkane Bay, Cycloalkane Sea and the Petroleum Ocean. Cycloheptane Brook is small, and not much increase in size is expected. Bicycloalkane Creek originates in the Cyclohexane Highlands and there are several contributors along the way, notably the decalins. This creek is not well known—when better explored possibly it will deserve the stature of a river. At the edge of the Highland is a seep containing a tricycloalkane, adamantane.

Monocyclopentanes

The monocyclopentanes have been identified to a lesser extent than the isoalkanes, generally only to about 150C. All of the possible monocyclopentanes through C₈ have been identified, but the recognition above that is small, as seen from Table V.

The quantitative data on the cyclopentanes is not easily simplified (66) but in general methylcyclopentane is present to a greater extent than cyclopentane by an order of magnitude, and the dimethyl derivatives are intermediate between the mono- and trimethyl compounds in decreasing order. Mair (58) indicates a substantial content of a tetramethylcyclopentane. More data on more crude oils, especially through the C₉ compounds, are needed.

Monocyclohexanes

Forty-two monocyclohexanes have been identified, 11 more than monocyclopentanes. The methyl derivative is found in roughly twice the quantity of cyclohexane itself, but again there are not enough data in the literature to form firm conclusions as to other types most prevalent. A number of C₁₀ cyclohexanes have been identified, but none of higher carbon number. Table VI shows the data.

Other Monocycloalkanes

Three other monocycloalkanes have been reported: cyclobutane in Western Venezuela crude oil (25), cycloheptane in Ponca City crude oil (58), and methylcycloheptane in a California naphtha (55).

Bicycloalkanes

Enough bicycloalkanes have now been identified, although generally in small quantities, to justify Bicycloalkyl Creek. Bicycloheptanes, -octanes, -nonanes and -decanes are found near the headwaters, and recent work (55) has shown the presence of their

TABLE VI
Cyclohexane Isomers Possible and Identified

Isomers	Carbon atoms in molecule					
	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁
Possible	1	1	8	40 ^a	225 ^a	900 ^a
Identified	1	1	8	14	18	0

^a Estimated from logarithmic plot of available data.

methyl derivatives. The bicyclodecanes, or decalins, are present in good quantities, and indications are that several other bicyclo compounds will be found in appreciable amounts as more data become available. For example, bicyclo [3,2,1] octane is found in considerable quantity in a California naphtha (55).

Tricycloalkanes

One tricycloalkane, present to 0.0008%, has been identified in Ponca City crude oil (62). This, a tricyclodecane, is known as adamantane and may be of interest genetically.

Cycloalkane Sources

Naphthenes are possibly the most important general type of hydrocarbon component in crude oil, but there is little in the literature except unproved theories as to their origination. There is general agreement that their original source material is lipid including primarily terpenes; terpene oxygenated derivatives such as alcohols, ketones and aldehydes, and unsaturated fatty acids and waxes.

Brooks (13) in 1952 suggested catalytic cyclizations of dienes in the presence of an acid catalyst through a carbonium ion mechanism. The major source of most dienes would be the unsaturated fatty acids. These are prevalent in both terrestrial and marine organisms. Both Brooks (13) and Breger (11) believe that the Diels-Alder reaction between an acyclic diene and a second component having an ethylenic linkage flanked by one or more activating groups such as carbonyl or carboxyl is possible and probable. This reaction again requires unsaturated compounds most easily found in the unsaturated fatty acids.

A third source that offers promise is the terpenoids, including the hydrocarbon terpenes and their simple oxygenated derivatives such as alcohols and ketones. This theory is put forth by Mair (59). A glance at the terpenoid section of Robinson's book (76) on the organic constituents of higher plants presents many structures that could reasonably be transformed into petroleum naphthenes. Fig. 8, which shows terpenoid pathways, is taken from Robinson and while the mechanisms are not known, for the most part the end products are. The possibilities for conversion to mono- and polycycloparaffins can be seen. It is obvious that much research is needed in this area.

Summary

Fig. 9 shows the major sources of cycloalkanes that have been suggested. All are lipids.

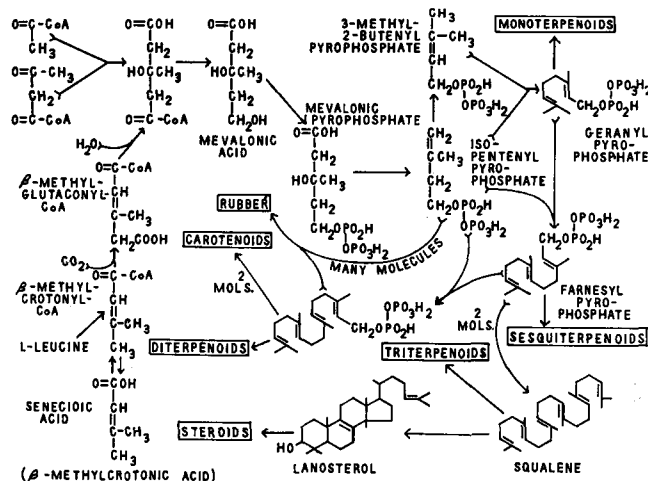


Fig. 8. Terpenoid and steroid pathways (Robinson's [76] Fig. 8-1).

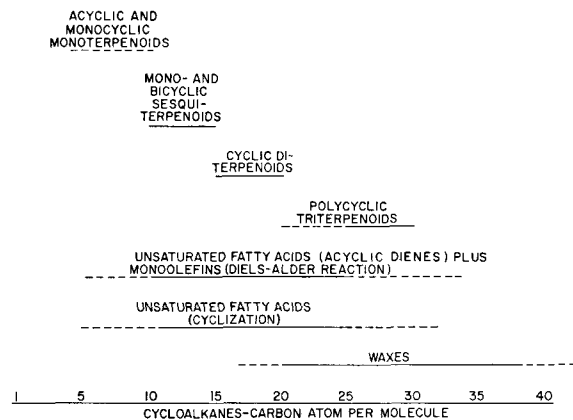


Fig. 9. Sources of cycloalkanes.

Aromatic Quadrant

The aromatic quadrant is shown in Fig. 10. Whereas the alkane quadrant had only one river, and the cycloalkane only two large rivers, the aromatic quadrant has a number of important streams, in general representing increases in molecular size by increments of one benzene ring from one through four. This also means considerably higher boiling points. The stream situation in the alkane and cycloalkane quadrant was simple, but there is a multiplicity of streams in the aromatic quadrant. So far exploration has disclosed two major rivers, the Benzene and the Naphthalene. The Benzene River rises in the Monocyclic Aromatic Highlands and a few tributaries have been found, but none above the 200C isotherm. In contrast the Naphthalene River originates where the Condensed Multicyclic Aromatic Plain joins the Highlands. It too has several tributaries, all between the 200C and 300C isotherms.

Still further in this part of the Condensed Aromatic Plain is found Phenanthrene Creek. Only the headwaters of this stream are known, but it is believed that it will be of river size when fully explored. It lies in the 340C to 600C area. Finally, wandering through the high temperature part of the Condensed Multicyclic Aromatic Plain are two creeks, Anthracene and Tetracyclic; the tetracyclic creek has three branches, Pyrene, Benzanthracene, and Chrysene.

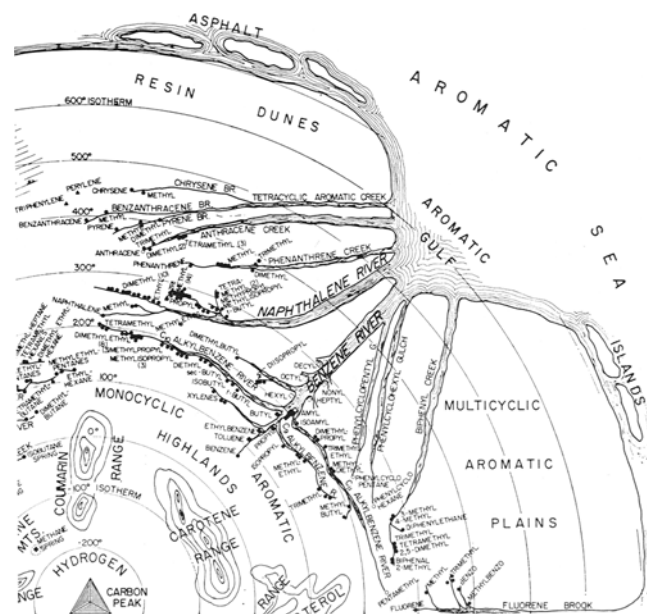


Fig. 10. Aromatic quadrant.

On the other side of the Benzene River on the Noncondensed Multicyclic Aromatic Plain, there are two dry gulches, Phenylcyclopentane and Phenylcyclohexane. No flow has ever been found, although it has been expected. Finally there is Biphenyl Creek, with headwaters at about the 250C isotherm just at the Aromatic Highland foothills. All of the streams flow into the Aromatic Gulf, in some cases near Resin Dunes and around Asphalt Islands. They ultimately meet the Aromatic Sea and Petroleum Ocean.

Monocyclic Aromatics

The only aromatics present in crude oil up to a boiling point of 218C are benzene and its alkylated homologues exemplified in Table VII. They are less prevalent than either the alkanes or cycloalkanes, but some crude oils contain enough so that certain aromatics can be separated commercially, as was toluene during the last two world wars. The tendency is for the mono- and dimethyl substituted forms to be predominant, although certain tri- and tetraalkylbenzenes, such as 1,2,4-trimethylbenzene, are often present in appreciable quantity (58,88). Virtually no benzenes boiling above 200C have been identified; however, single benzene rings condensed with cyclopentane or cyclohexane rings are prevalent, but in this presentation are considered under cycloalkanoaromatics.

Table VIII shows the possible alkylbenzene isomers for C₈ through C₁₁, and the compounds identified. All have been found through C₁₀, but only 11 of the 51 C₁₁ isomers are reported—again the 200C point seems to be the end of most research.

It appears to be a good possibility that accumulated data will provide some interesting and useful quantitative relationships. A cursory survey of a few Russian reports showed with regard to aromatic contents: 1) Toluene is almost always greater than benzene, generally by a factor of 3 to 6; 2) ethylbenzene is almost always less than toluene; 3) 1,3-dimethylbenzene is almost always greater than the 1,2- or the 1,4-isomer; 4) when the 1,3-isomer is less than the 1,2- and 1,4-isomers, then ethylbenzene is greater than toluene; 5) *n*-propylbenzene is usually greater than isopropylbenzene; 6) 1-methyl-3-ethylbenzene is usually greater than 1-methyl-2 and 1-methyl-4-benzene; 7) 1,2,4-trimethylbenzene is usually greater than 1,2,3- and 1,3,5-trimethylbenzene; 8) *n*-butylbenzene is greater than other butylbenzenes; 9) 1,2,3,5-tetramethylbenzene is greater than 1,2,3,4- and 1,2,4,5-tetramethylbenzenes. Such data, if confirmed by more extensive investigations, could furnish significant identifying factors for use in tracing the possible evolution and migration of crude oil.

Condensed Multicyclic Aromatics

Condensed ring aromatics are formed by the fusion

TABLE VII
Representative Types of Aromatics

Name	Found in
Benzene.....	Gasoline
1,2,3-Trimethyl-4-ethylbenzene.....	Kerosine
2,3,6,7-Tetramethylnaphthalene.....	Diesel fuel
1,8-Dimethylphenanthrene.....	Gas oil
2,6-Dimethylanthracene.....	Gas oil
Pyrene.....	Gas oil, lubricating oil
1-Methylchrysene.....	Gas oil, lubricating oil
Diphenylmethane.....	Not reported (possible in diesel fuel)
2-Methylbiphenyl.....	Diesel fuel

TABLE VIII
Alkylbenzene Isomers Possible and Identified

	Isomers	
	Possible	Identified
C ₈ Alkylbenzenes (4)		
Ethyl	1	1
Dimethyl	3	3
C ₉ Alkylbenzenes (8)		
Propyl (<i>n</i> - and <i>iso</i> -)	2	2
Methylethyl	3	3
Trimethyl	3	3
C ₁₀ Alkylbenzenes (22)		
Butyl (<i>n</i> -, <i>sec</i> -, <i>iso</i> -, <i>tert</i> -)	4	4
Methylpropyl	3	3
Methylisopropyl	3	3
Diethyl	3	3
Dimethylethyl	6	6
Tetramethyl	3	3
C ₁₁ Alkylbenzenes (51)		
<i>n</i> -Pentyl	3	3
Isopentyl	4	1
Neopentyl	1	0
Methyl- <i>n</i> -butyl	2	1
Methyl- <i>sec</i> -butyl	3	0
Methylisobutyl	3	0
Methyl- <i>tert</i> -butyl	3	1
Ethyl- <i>n</i> -propyl	3	0
Ethylisopropyl	3	0
Dimethyl- <i>n</i> -propyl	6	2
Dimethylisopropyl	6	0
Methyldiethyl	6	2
Trimethylethyl	6	1
Pentamethyl	1	0

of two or more benzene rings at different positions. Up to now aromatics with two, three, four and five fused rings have been found in petroleum.

Bicyclic Aromatics. Naphthalene is the only fused bicyclic aromatic, and its alkylated derivatives are commonly found in petroleum. Alkyl-naphthalenes with five or less carbon atoms in the alkyl chain have been found, but virtually no naphthalenes boiling above 300C have been identified. All of the C₁₂ naphthalenes, including 2 ethyl and 10 dimethyl naphthalenes, have been found as well as all C₁₃ trimethyl-naphthalenes.

Tricyclic Aromatics. There are two basic forms of tricyclic aromatics, the anthracene and phenanthrene types, and both have been found in petroleum, but the phenanthrene type predominates. Many believe this predominance has a direct relationship to possible organic progenitors such as steroids (59). The compounds that have been identified all boil between 340C and 400C and represent the simple alkylated forms. Of the parent compounds of the two series, phenanthrene has been identified, but anthracene has not.

Tetracyclic Aromatics. There can be several arrangements of fused tetracyclic aromatics, and three types have been found in petroleum; pyrene (58), benzanthracene (19), and chrysene (71). The approximate boiling points of the initial compounds of these series of similar molecular weight are as follows: pyrene 360C, benzanthracene 390C, chrysene 450C. Alkylated derivatives boiling to 460C have been found. Except for a few normal paraffins and probably a picene mentioned in the section on cycloalkanoaromatics, these are the highest boiling compounds that have been identified in crude oil.

Noncondensed Bicyclic Aromatics

These consist of a series of compounds starting with biphenyl, which structurally is two benzene rings joined by a single carbon to carbon bond. Several of the alkylated compounds as well as the parent compound have been identified (58). However, they are

represents a new addition to the explored petroleum world, and its contribution to the total hydrocarbon hemisphere is small. Investigations have been limited by high-boiling points and associated analytical difficulties. Because the available evidence indicates that above the 300C isotherm most of the hydrocarbons are mixed types (alkylated cyclopentano or cyclohexano aromatics in which either the cycloalkane rings or aromatic rings or both may be monocyclic or polycyclic), it seems possible that this may become the most explored area in the future. This is especially true as the need to upgrade heavy distillates and residuals increases. Recent advances in the application of mass spectra to elucidate structures of compounds found in petroleum fractions of this boiling range point in this direction (43).

At the moment five types of cycloalkanoaromatic hydrocarbons have been found, as exemplified in Table IX. The cycloalkanoaromatic quadrant has four streams—the Indane and Tetralin Rivers and Fluorene and Cycloalkanophenanthrene Creeks. The rivers rise in the Cycloalkane Aromatic Hills at about the 200C isotherm, but only a few of the tributaries are known, although it seems probable they exist. The two creeks originate in the foothills at the edge of the Cycloalkane Aromatic Plains in the 300C to 400C isotherm range. Several small tributaries of Fluorene Creek have been found, but little is known of Cycloalkanophenanthrene Creek. All the rivers and creeks flow into the Cycloalkanoaromatic Sea and then into the Petroleum Ocean. Resin Dunes are found along the beaches. These rivers and creeks are relatively unexplored—it is expected they will eventually be found to be streams of great extent with numerous tributaries.

Indanes

Only four indanes have been identified—indane itself and a few methyl derivatives. All of these are at the 200C isotherm. They are present in small amounts. Recently Lumpkin (56) reported indenenes.

Tetralins

The tetrahydronaphthalenes or tetralins are fairly prevalent in crude oil. In fact this particular bicyclic configuration, whether it be in the tetrahydro state, completely hydrogenated to decalin, or completely dehydrogenated to naphthalene, seems to be one of the dominant structures in crude oil. Even though only a few of each type have been found thus far, those that have been found are usually present in considerable quantity (58).

Fluorene

Several alkylated derivatives of fluorene have been found (58) in the 200C to 300C isotherm, but the extent of their occurrence is not known.

Cyclopentanophenanthrene

Two compounds of this type have been found (61) boiling at about 290C, but again the quantities present are not known. The structure suggests that steroids such as stigmasterol were the original source material for those compounds arriving at the hydrocarbons by dehydrogenation—if such can be postulated as occurring under geological conditions.

Tetrahydropicene

Carruthers and Watkins (21) recently reported identification of 1,2,3,4-tetrahydro-2,2,9-trimethyl-

picene from a high-boiling American petroleum distillate.

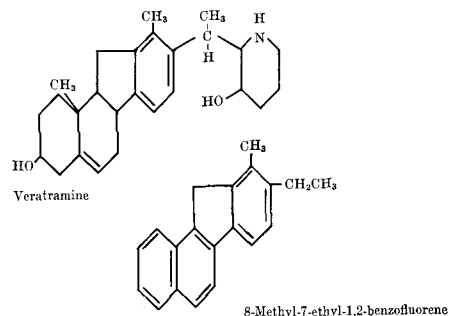
Cycloalkanoaromatic Sources

With knowledge of source material for cycloalkanes and aromatics so little advanced, it is not surprising that there is not much known regarding the cycloalkanoaromatics. Probably the best source on the basis of present knowledge is again the steroids. Mair

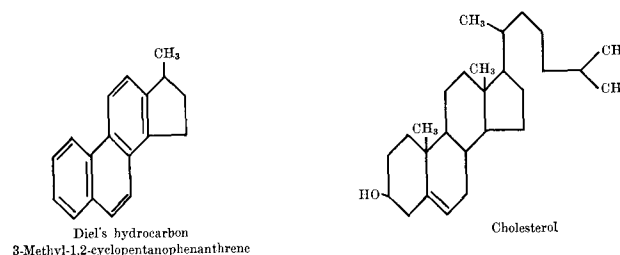
TABLE IX
Representative Types of Cycloalkanoaromatics

Name	Found in
1-Methylindane.....	Kerosine
2-Methyltetrahydronaphthalene.....	Kerosine
2-Methylfluorene.....	Gas oil
3-Methyldihydro-1H-cyclopenta [1] phenanthrene.....	Gas oil, lubricating oil
1,2,3,4-Tetrahydro-2,2,9-trimethylpicene.....	Lubricating oil

(59) gives veratramine as an example of an alkaloid source which could yield a methyl-ethyl-benzofluorene. Similar compounds have been isolated from petroleum (20).



Another example would be Diel's hydrocarbon recently isolated from petroleum (61) which is very similar in structure to cholesterol.



Needs for Future Research

One cannot prepare a review like this without having several research needs come forcibly to attention.

1) Qualitative knowledge of the composition of that part of crude oil boiling above 200C is badly needed for most classes of hydrocarbons with the exception of the *n*-alkanes.

2) Quantitative knowledge of the composition of petroleum is needed over the entire boiling range, although there are good data for a number of petroleum up through the C₇ compounds.

3) Lipids appear to offer the most important probable source of hydrocarbons, but here again more knowledge is needed of their kinds and distribution in the flora and fauna that can be considered as the basic sources.

4) There are many speculative ideas about the reactions that convert lipids into the hydrocarbons of

petroleum. With today's excellent analytical tools and the ability to study reactions in the micro quantity range, it is time for studies of many of the suggested reactions in two ways: (a) to definitely establish that the desired reactions will occur when conducted under favorable conditions. The work of Jurg and Eisma (44) on the thermal cracking of behenic acid and of Douglas and Mair (33) on the action of sulfur on cholesterol and farnesol are good examples. (b) to determine whether the reactions will occur under less favorable circumstances study model systems that approach more nearly geological conditions. For example, the same experiments as mentioned above at lower temperatures, at high pressures, in the presence of moisture, and with various matrices. Our analytical techniques today are capable of detecting very small quantities of reaction products.

Some of these activities are underway at various laboratories around the world. If in some way a good clearing house for recording these researches could be established it would hasten the day when a reasonably complete understanding of the origin of petroleum could be seen on the horizon.

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