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Isoprenoid petroleum hydrocarbons

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ABSTRACT. The outcome of studies on the chemistry of petroleum carried out during the last 10–15 years is examined. It is shown that petroleum is a very complex mixture of natural products, the most important place among which is occupied by $C_{10}-C_{40}$ isoprenoid hydrocarbons represented by aliphatic, alicyclic, and aromatic compounds.

The relations between the isoprenoid petroleum hydrocarbons and their possible bioorganic precursors are discussed. The possibility of using isoprenoid hydrocarbons (as biomarkers) in discovering the pathways leading to the genesis and chemical evolution of petroleums and also prospecting for petroleum deposits is demonstrated.

The bibliography includes 104 references.

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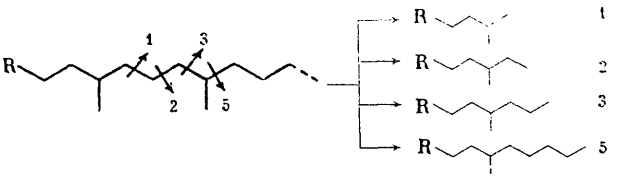
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I. Introduction

The identification of a large number of relict hydrocarbons (biomarkers)—compounds retaining the main features of the structure of the initial bioorganic molecules—in petroleums, coals, shales, and other fossil fuels is undoubtedly one of the most important advance in the organic chemistry of the second half of the XXth century. A new independent scientific discipline—organic geochemistry—arose in the middle of the 1960s. Its aim is the study (at the molecular level) of the characteristic features of the composition and structure of the organic molecules in the Earth's core, seas, and oceans. It involves the study of both "modern" compounds as well as compounds formed hundreds of millions of years ago. Much attention has also been devoted to questions concerning the chemical changes in organic molecules under geological conditions. In the course of its development, organic geochemistry has been based on the present scientific level of its precursor—the chemistry of natural products, utilising fully both the methodology and the analytical procedures of the latter. The advances in the study of organic molecules in the Earth's core and, in particular, hydrocarbons, achieved during the last 20–25 years, are very considerable. Thus more than 300 $C_{10}-C_{40}$ hydrocarbons, having a clear biological origin, have been identified in petroleums and other fossil fuels. Not only their structure but also the characteristic features of their stereochemistry, frequently changing during the transformation of bioorganic molecules under geological conditions, have been determined. The practical importance of such studies, especially in the prospecting for petroleum deposits and in problems concerning ecology and the protection of the environment has led to the biannual holding of International Congresses on Organic Geochemistry. The publishing house Pergamon Press has been publishing a special periodic journal. In a number of developed capitalist countries, there are institutes (or large departments) concerned with various problems of organic geochemistry.

The framework of the present review restricts us to the isoprenoid petroleum hydrocarbons. However, this group of compounds is the most important and the most representative. Advances in this field have been achieved by the efforts of a large group of investigators in England, France, the Federal Republic of Germany, the Soviet Union, the USA, and many other countries.

All the isoprenoid petroleum hydrocarbons can be divided into three large groups: aliphatic isoprenoids, alicyclic isoprenoids, and isoprenoids containing aromatic rings. A common property of the majority of petroleum isoprenoids is their homologous nature. This property is associated with the characteristic features of their genesis. The homologous nature of isoprenoids has one important feature. Since petroleum hydrocarbons are frequently formed via a stage involving the degradation of biopolymers, after three homologues, the next (fourth) homologue is usually (for a regular chain structure) "omitted" as a result of the branched structure of the isoprenoid chain.



The homologous nature of these hydrocarbons makes it necessary to give preference to the term isoprenoid hydrocarbons and to avoid using the term, which is in many cases more usual, terpenoid compounds.

In studies on the most complex mixtures of petroleum hydrocarbons, modern achievements in the analytical chemistry of organic compounds have played a very important role, especially methods such as gas chromatography using high performance capillary columns, combined gas chromatography–mass spectrometry (with computer treatment of data), mass fragmentography and mass chromatography, and also ^1H and ^{13}C nuclear magnetic resonance. Numerous syntheses of model hydrocarbons have undoubtedly played a special role. The majority of compounds examined below were first obtained in laboratories. An extensive scientific literature has been devoted to isoprenoid petroleum hydrocarbons. Here we shall quote references mainly to studies during the last 10–15 years especially since there are already reviews and monographs devoted to

these aspects.[1-3] The data on the mass spectra of certain isoprenoid hydrocarbons examined below may be found in the review of Golovkina et al.[4]

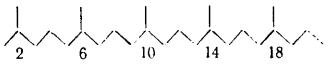
II. Aliphatic isoprenoids

Isoprenoid alkanes (isoprenanes) are compounds whose discovery in natural fossil products has promoted the establishment of modern organic geochemistry. Hydrocarbons important for petroleum such as pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane) have been described.[5]

Aliphatic petroleum isoprenoids have both regular and irregular carbon chains, the number of their carbon atoms ranging from 9 to 45. There is no doubt that the leading role is assumed by irregular isoprenoids having a structure of the main carbon chain with "head to tail" fragments, which is characteristic of polyisoprene.

1. Regular isoprenoids

It is possible to distinguish the following homologous series of these hydrocarbons: 2,6-dimethylalkanes (C_9-C_{13}); 2,6,10-trimethylalkanes ($C_{14}-C_{18}$); 2,6,10,14-tetramethylalkanes ($C_{19}-C_{23}$); 2,6,10,14,18-pentamethylalkanes ($C_{24}-C_{28}$), etc. For understandable reasons, hydrocarbons having the C_{12}, C_{17}, C_{22}, C_{27}, etc. compositions are absent from the homologous series.



The degradation of any C—C bond in the main chain can result in the formation of only regular isoprenoids. Fig. 1 presents chromatogram of the saturated hydrocarbons of the petroleum from the Severo-Tol'kinskoe deposit (Western Siberia). The predominance of regular $C_{14}-C_{20}$ isoprenoids, which is usual for petroleums, and the much lower concentration of similar structures having the $C_{21}-C_{25}$ composition can be clearly seen. Data on the proportions of regular isoprenoids in other petroleums in the Soviet Union can

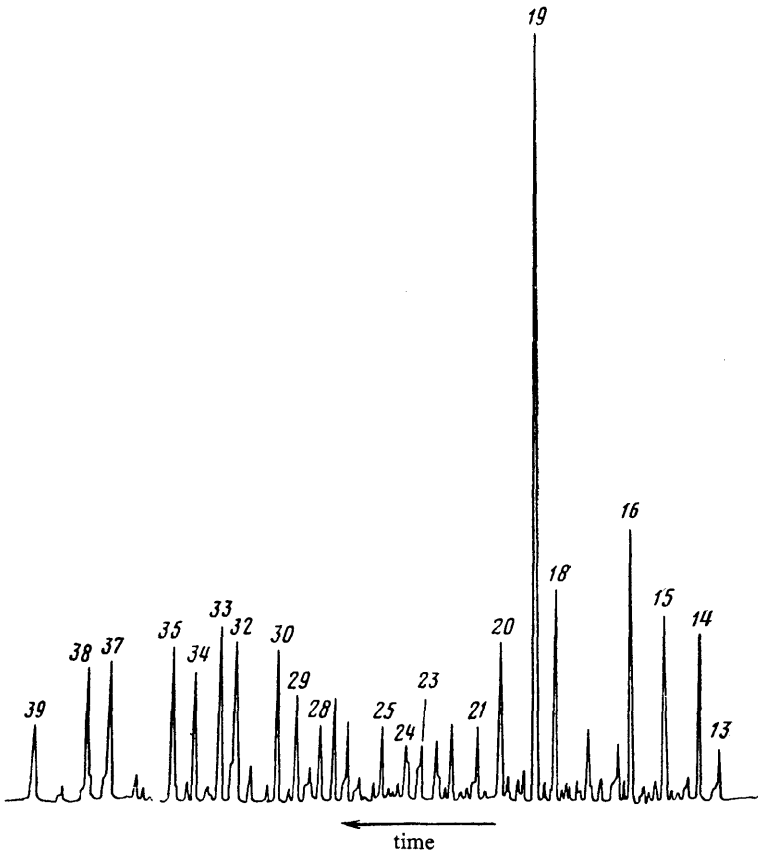
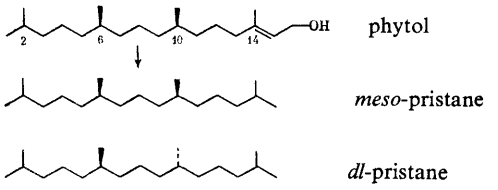


Figure 1. Chromatogram of a mixture of saturated hydrocarbons from petroleum of the Severo-Tol'kinskoe deposits; capillary column (80 m) with Apiezon; linear temperature programming (4 K min^{-1}). Analysis started at 100 °C and ended at 320 °C; the number of carbon atoms in the molecule is indicated; $C_{13}-C_{25}$, isoprenoid alkanes with a regular structure (2,6,10-trimethylalkanes, 2,6,10,14-tetramethylalkanes, etc.); $C_{28}C_{39}$, irregular isoprenoids ("head to head" fragment); 2,6,10,14,17,21,25,29-octamethylhentriacontane (C_{39}); 2,6,10,14,17,21,25,29-octamethyltriacontane (C_{38}); 2,6,10,14,17,21,25-heptamethyltriacontane (C_{37}); nonacosane (C_{35}), etc.[13]

be found in monographs.[1,6] The main source of regular isoprenoids in petroleums is phytol (C_{20}) and solanosol (C_{45}).[7,8] The stereochemistry of isoprenoid alkanes is of interest.[9–11] The relation between the stereochemistry of phytol and the pristane formed from it is considered in Scheme I, whereas *meso*-pristane [having the configuration of the C(6) and C(10) chiral centres characteristic of phytol] clearly predominates in recent fossil deposits (young, "unripe" deposits and also in brown coals), a 1 : 1 mixture of the *meso*- and *dl*-epimers is usually found in petroleums.

Scheme I

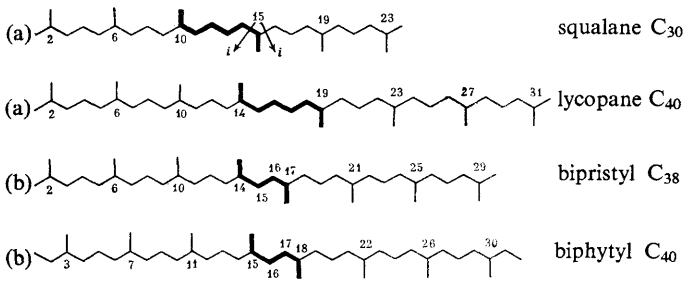


Another (minor) series of regular isoprenoid alkanes belonging to the series of 3,7-dimethyl-, 3,7,11-trimethyl-, and 3,7,11,15-tetramethylalkanes has been described.[1–8] In the original communication,[8] such structures have been called "quasi-regular".

2 Irregular isoprenoids

Two types of isoprenoid alkanes with an irregular structure of the main carbon chain have been found in petroleums: (a) those having an irregular unit of the "tail to tail" type and (b) those having an irregular unit of the "head to head" type (Scheme I).

Scheme II

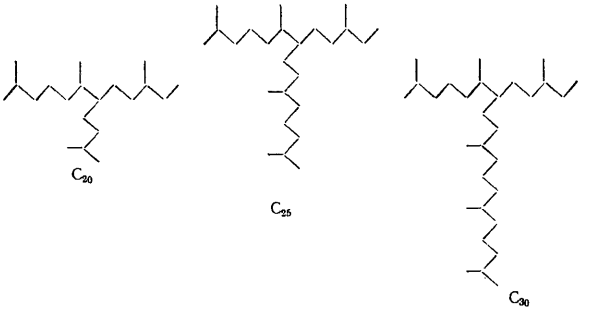


The degradation of the aliphatic chain of irregular isoprenoids can lead to the appearance of two series of homologues: (1) irregular homologues if an irregular unit is retained on degradation, for example, 2,6,10,15-tetramethylalkanes from squalane and 2,6,10,14,17-pentamethylalkanes from bipristyl; (2) the so called pseudoregular homologues[12] in those cases where the rupture of the bond involves an irregular unit. In particular, the degradation of squalane via the pathways (*i*) yields "forbidden" regular 2,6,10-trimethyltetradecane (C_{17}) and 2,6,10-trimethylhexadecane (C_{19}).

The homologous series of irregular isoprenoid $C_{28}-C_{39}$ alkanes (having a "head to head" unit) has been found in the petroleum the Severo-Tol'kinskoe deposit already mentioned[13] (Fig. 1). These hydrocarbons have been identified also in other petroleums.[14,15] The formation of these structures can be accounted for by the microbiological abstraction of hydrogen from the C(1) atom of regular isoprenoids (pristane, phytane, etc.) with subsequent coupling of the radicals (15–16 and 16–17 bonds are formed in bipristyl and biphytyl respectively).

A new series of isoprenoid alkanes, having a T-shaped structure, have been discovered in petroleums in recent years[16,18] (Scheme III).

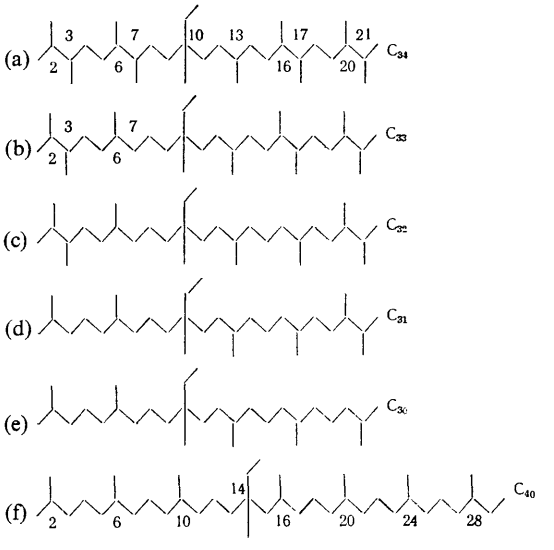
Scheme III



It is of interest that these hydrocarbons are represented only by compounds having the C_{20}, C_{25}, and C_{30} compositions, i.e. they are diterpenoids, sesterterpenoids, and triterpenoids.

There is an unusual group of petroleum isoprenoids containing a geminal methylethyl group.[19–22] Botryococcane (C_{34}) and its lower-molecular-weight homologues ($C_{33}-C_{30}$) and also isolycopane (C_{40}) merit attention here (Scheme IV).

Scheme IV



III. Cyclic isoprenoids

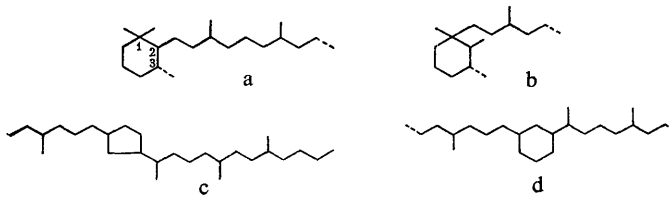
Saturated cyclic petroleum isoprenoids are characterised by different numbers of rings in the molecule (from one to six). These compounds constitute the basis of relict petroleum hydrocarbons (biomarkers).

1. Monocyclic isoprenoids

The simplest monocyclic isoprenoids are 1,2- and 1,4-methylisopropylcyclohexanes.[23] The interesting $C_{10}-C_{30}$ homologous series of isoprenoids, formed by the degradation of the aliphatic chain of β-carotane, has been described.[24,25] The first representative of these hydrocarbons, namely 1,1,3-trimethylcyclohexane, is present in appreciable amounts in almost all petroleums.[1]

Apart from the main homologues (Va), the products of their 1,2-rearrangement (Vb) have also been found.

Scheme V

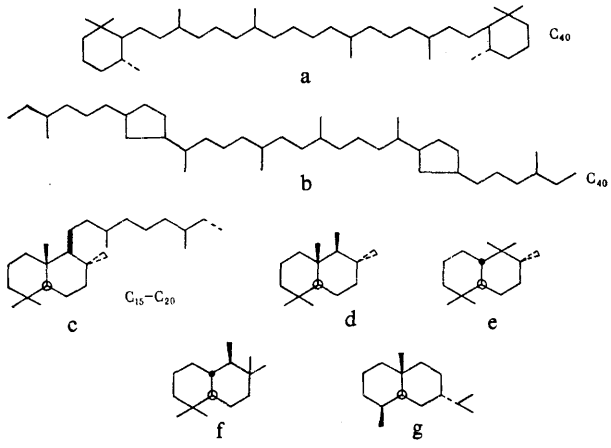


It has been stated that monocyclic isoprenoids with long isoprenoid chains of both irregular (Vc) and regular (Vd) types are present in petroleums.[9] The hydrocarbon (Vd) must be regarded as a saturated compound corresponding to the product of the dimerisation of phytadiene via the Diels–Alder reaction. The presence of lower-molecular-weight homologues of these hydrocarbons in petroleums is also probable.

2. Bicyclic isoprenoids

Among bicyclanes with isolated rings, except perhydro-β-carotane (VIa), bicyclic five-membered cyclanes with isolated rings and isoprenoid chains (VIb) have also been identified in petroleums. There is a larger group of bicyclanes with condensed rings (Scheme VI).

Scheme VI



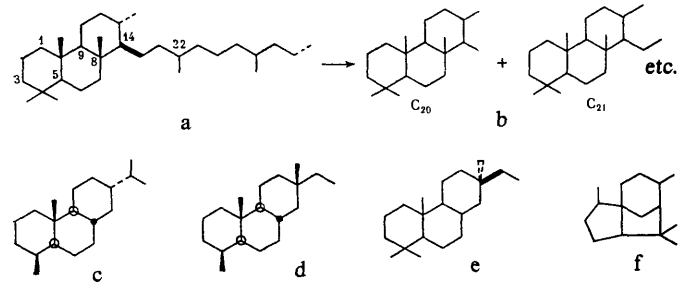
In this group of compounds, both hydrocarbons with the 8βH-drimane† (VId) skeleton and the products of their 1,2-rearrangement—the structures (VIe) and (VIf)—have been determined in hydrocarbons.[26–28] The parent of this group of compounds is probably the C_{20} hydrocarbon—labdane (VIc); the degradation of its chain results in the formation of the homologous series of tetramethylalkyldecalins. Eudesmane (cadinane) (VIg), present only in the form of the "pure" sesquiterpane, has a different structure.

3. Tricyclic isoprenoids

The most interesting representatives of the tricyclic petroleum isoprenoids are undoubtedly hydrocarbons belonging to the homologous series of pentamethylalkylperhydrophenanthrenes, which have been called hydrocarbons of the cheilanthane series. A number of these compounds having the $C_{18}-C_{40}$ composition have been discovered. The compounds have a regular isoprenoid chain which is the reason for the absence of the C_{22}, C_{27}, etc. homologues.[29–32]

The formulae of the hydrocarbons considered are listed in Scheme VII. The C_{25} and higher hydrocarbons are eluted on the chromatograms in the form of two diastereoisomers (22*S* and 22*R*) because the C_{22} atom becomes chiral.

Scheme VII



The hydrocarbons (VIIa, b) can be conveniently identified by mass fragmentography on the basis of the fragment ion with m/z = 191. Apart from cheilanthanes, tricyclic diterpenoids such as fichtelite (VIIc), norpimarane, and pimarane (VIId, e) have also been found in petroleums.[34] Nor can one rule out the possibility of the presence of the sesquiterpane cedrane (VIIf).

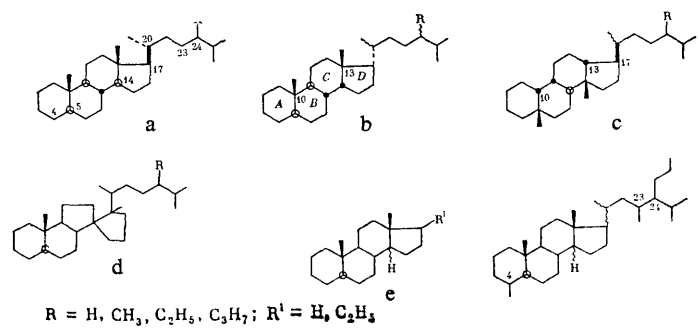
4. Tetracyclic isoprenoids

Tetracyclic isoprenoids constitute the largest and most interesting group of isoprenoid petroleum hydrocarbons. Sterane hydrocarbons (Scheme VIII) play an especially major role, because these compounds contain a very large amount of information for the solution of a series of geochemical problems (more will be said about this below).

Furthermore, the steranes, formed from the chemically fairly labile steroids, undergo a series of interesting structural and stereochemical transformations in the Earth's core leading to the formation of a series of hydrocarbons which have no analogues in living nature and which are present only in petroleums. Such are, for example, isosteranes (the 14β,17β-epimers), rearranged steranes, etc.

Thus, as was already mentioned previously, petroleum is a source of completely new types of organic molecules; an example is the discovery of hydrocarbons of the adamantane series in petroleums. Scheme VIII presents the formulae of the principal sterane hydrocarbons discovered in petroleums[1,2,35–41] [a mixture of the (24*S*)- and (24*R*)-epimers for R = C_1-C_3]:

Scheme VIII



R = H, CH_3, C_2H_5, C_3H_7; R¹ = H, C_2H_5

† Here and henceforth the suffixes β and α denote the orientation of the hydrogen atom.

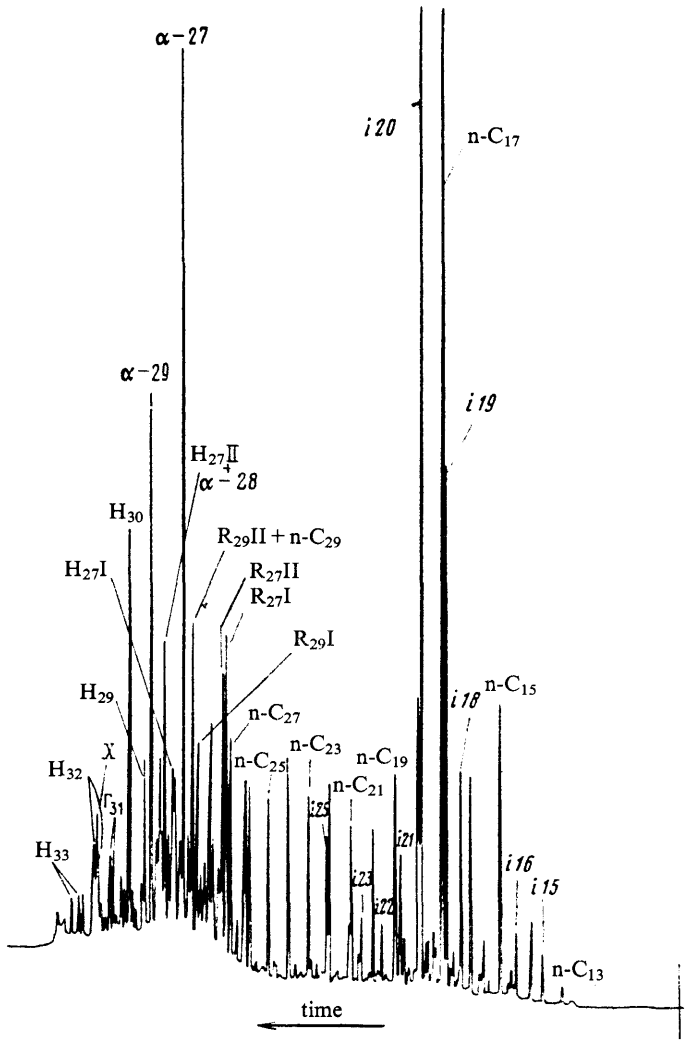


Figure 2. Chromatogram of a mixture of saturated hydrocarbons in the petroleum of the Vostochno-Vystupovichskoe deposit; the analytical conditions were the same as in Fig. 1; n, normal alkanes; *i*, isoprenoid alkanes; α-27, α-28, α-29, regular steranes (5α, 14α, 17α, 20*R*); R_{27}, R_{28}, R_{29}, rearranged steranes (13β, 17α, 20*S* and 20*R*); H, hopanes; in the $C_{31}-C_{35}$ doublet peaks, (22*S*)-epimers are eluted first; X, gammacerane; the numerals indicate throughout the number of carbon atoms in the molecule for R [I (20*S*) and II (20*R*)] and for H_{27} [I (18α-H) and II (17α-H)].

In terms of the steric structure, the hydrocarbons (VIIIa) belong to the series of biological steranes in which the most important chiral centres having the (5α, 14α, 17α, 20*R*)-configuration.[35] Fig. 2 presents a chromatogram of the saturated hydrocarbons of the petroleum from the Vostochno-Vystupovichskoe Deposit (Belorussia).‡ The peaks due to the C_{27}, C_{28}, and C_{29} (5α, 14α, 17α, 20*R*)-steranes (VIIIc) having the same composition are clearly seen.

The concentration of the stereochemically modified (5α, 14β, 17β, 20*S*)- and the corresponding (20*R*)-epimers of compound (VIIIb) in this petroleum is low. The isosteranes/α-steranes ratio is ~0.1. However, in other petroleums this ratio can reach 5 and more up to thermodynamic equilibrium value which is 7 (at 400 K).[1,35] The epimerisation of (5α, 14α, 17α, 20*R*)-steranes with formation of (5α, 14β, 17β, 20*S*)- and the corresponding (20*R*)-epimers is thermodynamically extremely favourable, since the change from the *trans*-junction of the *C/D* rings to the *cis*-junction removes all the strain characteristic of angularly substituted methyl-*trans*-hydrindans. As a result of the simultaneous epimerisation of the C(17) chiral centre, the hydrogen atoms at C(17)–C(20) and the angular methyl group [at C(13)] cease being eclipsed. At the same time, the quaternary C(10) and C(13) carbon atoms remain unaltered, which in fact preserves the high optical activity of the petroleum isosteranes formed. Apart from the epimerisation of the C(14) and C(17) centres, the epimerisation of C(20) also takes place and leads to the appearance on the chromatograms of doublet peaks of the

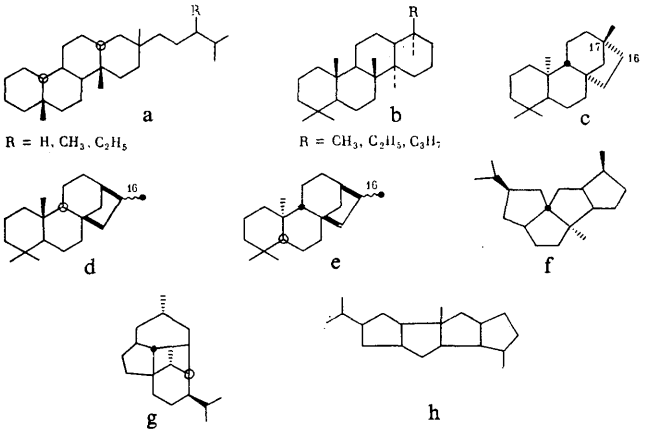
‡ Al A Petrov, Geologiya Nefti i Gaza, 1988, No. 10, p. 50.

hydrocarbons with the (α, β, β, 20*S*)- and (α, β, β, 20*R*)-configurations formed, whose thermodynamic stabilities are similar. The rearranged steranes (VIIIc) have the characteristic (10α, 13β, 17α)-configuration and also exist in the form of pairs of (20*S*)- and (20*R*)-epimers (these hydrocarbons are sometimes called diasteranes). The proportions of steranes with different molecular weights, the ratio of the α, α, α-steranes and isosteranes, as well as the relative concentrations of the rearranged steranes are some of the most important geochemical characteristics of the petroleums investigated.§ Apart from the steranes already examined, the spirosteranes (VIIId) as well as steranes with shorter substituents at C(17)—androstane and pregnane (VIIIe)—have also been determined in petroleums.[42] In addition, a series of C_{30} steranes (VIIIf), having either a propyl substituent at C(24) or methyl substituents at C(4), C(23), and C(24), have also been found in petroleum.[43] All these steranes can also exist in petroleum in the form of the biological α, α, α-epimers and in the form of their reaction products—(α, β, β, 20*S*)- and the corresponding (20*R*)-steranes with a rearranged skeleton.

Spirosteranes are formed via the acid rearrangement of steranes followed by saturation as a result of a redistribution of hydrogen. Steranes in petroleums are usually determined with the aid of gas chromatography-mass spectrometry on the basis of the principal fragment ions: m/z = 217 for the regular structures and m/z = 259 for the rearranged structures (m/z = 231 and 273 respectively for the 4-methylsteranes).

Hydrocarbons with the perhydrochrysene structure (IXa, b), in particular 17*D*-homosteranes (IXa) and 17, 21, secohopanes (IXb), also belong to tetracyclic isoprenoids.[1,29,44] (The dots designate quaternary and tertiary carbon atoms exhibiting a strong downfield shift in the ^{13}C NMR spectra.)

Scheme IX



17-*D*-Homosteranes, identified from the fragment ion with m/z = 287, are also products of the skeletal rearrangement of sterenes, proceeding via a carbonium ion mechanism, and can be regarded as compounds formed from diasteranes as a result of the expansion of the *D* ring.

§ Among the regular steranes, the most important hydrocarbons any structure are the (5α, 14α, 17α, 20*R*)-epimers (biosteranes), (5α, 14α, 17α, 20*S*)-epimers, (5α, 14β, 17β, 20*S*)-epimers, and the corresponding (20*R*)-epimers (geosteranes). Among the rearranged steranes, the (10α, 13β, 17α, 20*S*)- and the corresponding (20*R*)-epimers are most important. Data concerning the equilibrium of the epimers considered have been published in a monograph.[35]

The hydrocarbons with the structure (IXb)—the products of the degradation of the *E* ring of hopanes (see below)—are 17, 21-secohopanes having the $C_{24}-C_{27}$ composition.

The group of petroleum diterpanes comprising beyerane (IXc), phyllocladane (IXd), and kaurane (IXe) is very interesting.[45] The hydrocarbons (IXd, e) exist in the form of epimeric pairs (16α- and 15β-).

A remarkable group of tetracyclic C_{19} hydrocarbons (IXf–h), containing mainly five-membered rings, has been examined recently.[46] The compact packing of the carbon atoms make it possible to create a tetracyclic system consisting of only 14 carbon atoms. The key factor in the determination of the structure of the hydrocarbons (IXf–g) is the strong downfield shift in the ^{13}C NMR spectra (65–66 p. p. m. relative to TMS). The hydrocarbons (IXf–h) are most probably formed via the microbiological C_5 cyclisation of the unsaturated monocyclic isoprenoids, such as, for example, cembrene,[47] although, in principle, other pathways and sources are also possible. The relatively very high concentration of the hydrocarbons (IXf–h) in certain petroleums, reaching 1–2%, is noteworthy.

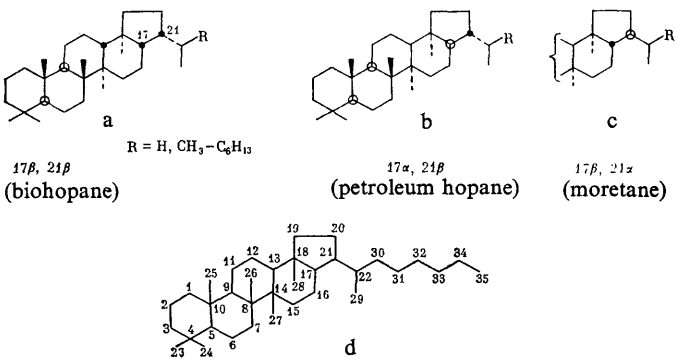
5. Pentacyclic isoprenoids

Together with tetracyclic hydrocarbons, pentacyclic hydrocarbons occupy one of the most important places in the chemistry of petroleum hydrocarbons. Compounds of this type belong to the class of triterpenoid hydrocarbons (triterpanes), although homologous properties are observed here also. It is possible to differentiate two main types of structures:

(a) hydrocarbons with the perhydropicene skeleton (all the rings are six-membered);

(b) hydrocarbons with the cyclopentanoperhydrochrysene skeleton. Hydrocarbons of the second type are much more common in petroleums.

Scheme X



We shall begin the examination of pentacyclic hydrocarbons with the important homologous series of hopane hydrocarbons (Scheme X). Studies by Ourisson's school (France) have played an outstanding role in the determination of the structure and stereochemistry of petroleum hopanes. Ourisson has justly referred to these hydrocarbons as "ubiquitous",[48] because they are present in almost all caustobioliths: in petroleums, coals, shale, peat, etc.[1] The hopane series hydrocarbons are formed in the microbiological processing of natural organic compounds in the early stages of their fossilisation. The pentacyclic tetrahydric alcohol bacteriotetrol (see below), which forms part of the composition of the lipid component of membranes of ancient bacteria, is the source of the hopanes

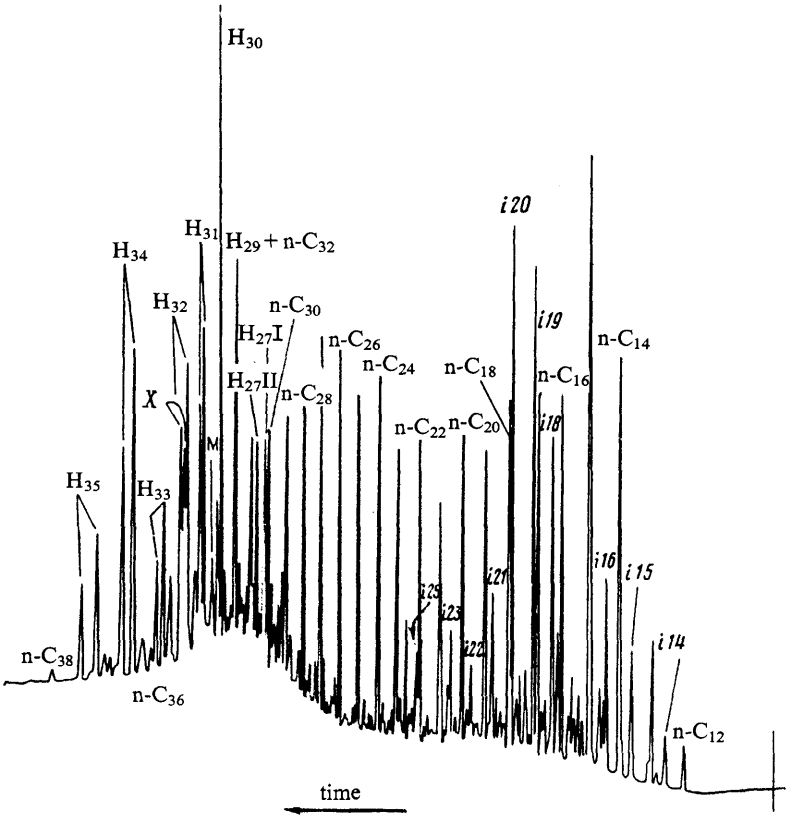


Figure 3. Chromatogram of a mixture of saturated hydrocarbons from the Zapadno-Slavan'skoe deposit; the chromatographic conditions were the same as in Fig. 1; the legend is the same as in Fig. 2. M = moretane.

themselves. We may also note that the studies by the school of the famous English organic geochemist Eglinton have played a no less important role in the determination of the structures of other isoprenoid biomarkers (chemofossils) and in establishing organic geochemistry as an independent scientific discipline.[49,50]

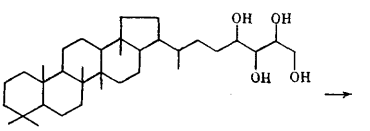
A large number of studies have been published on petroleum hopanes.[1,2,51–55]

Scheme X presents the formulae of hopanes having different stereochemistry: (a) biohopane; (b) petroleum hopane; (c) moretane, which is also encountered in petroleums. The numbering of carbon atoms is indicated in the formula (Xd).

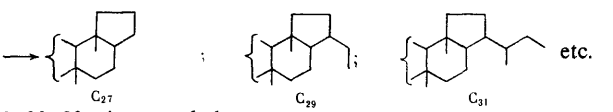
The principal factor determining the energy gain in the isomerisation of the 17β,21β-epimers to the 17α,21β-epimers is again the greater stability of the *cis*-fused angular methylhydrindan. In addition, the change in the configuration of the C(17) chiral centre removes the strain present in biohopane (17β), which arises because the 17–16 and 21–22 bonds (*cis*-orientation) are eclipsed. Calculations have shown that only 3% of biohopane, 12% of moretane, and 85% of petroleum hopane may be present under equilibrium conditions at 400 K.[1] The composition of hopanes in petroleums is very closely represented by the above figures.

As already stated, the tetrahydric C_{35} alcohol bacteriotetrol is believed to be the source of hopanes (Scheme XI).

Scheme XI



C_{35}
bacteriotetral



C_{27} C_{29} C_{31} etc.

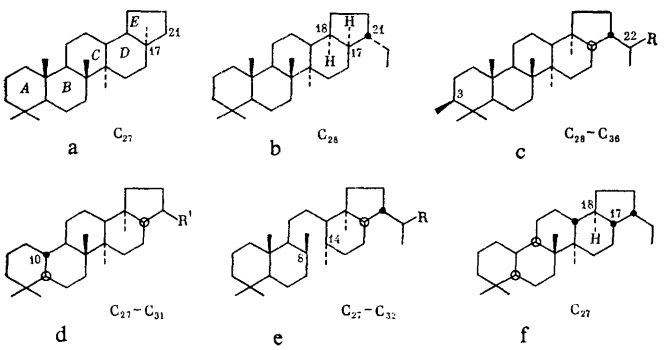
22, 29, 30-trisnormethyl-hopane adiantane homohopane

The degradation of the main chain of this compound gives rise to the homologous series of $C_{27}-C_{35}$ hopanes (naturally with the exception of the C_{28} hopane).

The minor series of $C_{36}-C_{40}$ hopanes with higher molecular weights has been described.[56] Their aliphatic chains have no additional branches. Dimeric forms of hopanes and saturated

codimers of hopenes and sterenes have also been found.[57,58] The C(22) atom in C_{31} and higher hydrocarbons is chiral and readily undergoes epimerisation. For this reason, the $C_{31}-C_{35}$ petroleum, hopanes emerge on the chromatograms in the form of doublets consisting of the (22*S*)- and (22*R*)-epimers; the (22*R*)-configuration is characteristic of biohopane [the (22*S*)-epimers are naturally absent from biohopanes]. Fig. 3 presents a chromatogram for the petroleum from the Zapadno-Slavan'skoe deposit.¶ This petroleum is exceptionally rich in hopanes. The $C_{27}-C_{35}$ hopane peaks are clearly seen, including the doublet peak due to the $C_{31}-C_{35}$ 17α,21β-hopanes. The hopanes in petroleums are determined usually by mass fragmentography on the basis of the most important fragment ion with $m/z = 191$. Apart from the main ("classical") hopanes examined above, numerous representatives of hopanes with a modified skeleton have been found in petroleums.[1,53,59-63] Some of these compounds are presented in Scheme XII. (We draw attention to the fact that in the names of hydrocarbons the lost methyl group has a number assigned to it as the usual nomenclature for gopanes—see Scheme XI.)

Scheme XII



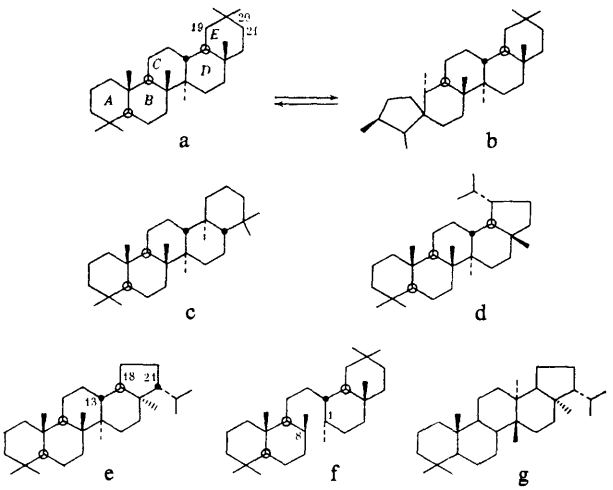
Thus the structure (XIIa), i.e. 17-methyl-22,29,30-trisnormethylhopane, is formed via the rearrangement of the usual C_{27} hopane. The rearrangement proceeds only in the C_{27} hopane, i.e. the hopane having no substituent at C(21). The structure (XIIb), i.e. 28,30-bisnormethylhopane, was first discovered in Sivinskaya petroleum [Perm Priural'e (Sub-Ural Region)].[1] In constrast to the remaining hopanes, here there is no methyl substituent at C(18). Since the angular methyl group (in the *D*/*E* rings) is absent, the system with a *D*/*E trans*-junction between the rings is more stable. In petroleums, this hydrocarbon is present as two epimers having the following steric structures: 17α,18α,21β and 17β,18α,21α; the structures (XIIc), i.e. 3-methylhopanes, present as a homologous series, have an additional methyl substituent in the *A* ring. The principal fragment ion in this series of hydrocarbons has $m/z = 205$. The chirality of the C(22) atom is manifested in this case starting from C_{32} hydrocarbons. On the other hand, a characteristic feature of the hydrocarbons in the homologous series (XIId) is the loss of the methyl group at C(10). The C(22) atom acquires chiral properties in this case starting with C_{30} hydrocarbons and the principal fragment ion in the mass spectra has $m/z = 177$. These hydrocarbons are mainly present in highly biodegradated petroleums.

The homologous series (XIIe) is represented by the so called 8,14-secohopanes, which are formed via the degradation of the most labile 8—14 bond. Their stereochemistry is the same as that of hopanes. The hydrocarbon (XIIf) is 25,28,30-trisnormethylmoretane.

Whereas the origin of hopanes is attributed mainly to the activity of micro-organisms, petroleums contain also other triterpanes (with the C_{30} composition), whose origin has a direct bearing on the plant materials involved in Continental genesis.[49,64-70]

The structures of some of these compounds are presented in Scheme XIII. All the hydrocarbons illustrated in Scheme (XIII) are triterpanes and contain 30 carbon atoms. Demethylated structures are encountered more rarely.

Scheme XIII

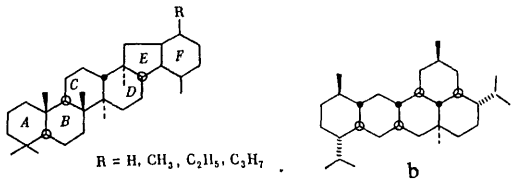


The hydrocarbons (XIIIa) and (XIIIb) (oleanane and spirotriterpane), belonging to the first group, are closely related via the carbonium ion 1,2-rearrangement. Lupane (XIIId), formed as a result of the contraction of the *E* ring with formation of the 19—21 bond and dissociation of the 20—21 bond, is closely related to them. The hydrocarbon (XIIIc) (gammacerane) has been found in large amounts in the petroleum produced by Continential genesis (China, Indonesia, Australia). The hydrocarbon neohopane (isohopane) (XIIIe) is usually present in brown coal, although it is found in small amounts also in petroleums. The hydrocarbon 8,14-secooleanane (XIIIF) is formed as a result of the degradation of the strained 8—14 bond of oleanane similarly to the 8—14-secogopanes examined previously. Fernane (XIIIg) is present in lichens, mosses, and peat.

All the hydrocarbons examined in Scheme (XIII) (including hopane) can be formed as a result of the cyclisation of squalane present in different conformations.[71] Like steranes, all the petroleum triterpanes exhibit a high optical activity, because they each contain four chiral centres formed by non-epimerising quaternary carbon atoms.

In conclusion of this Section, one should consider the homologous series of hexacyclic $C_{32}-C_{35}$ terpenoids discovered recently in petroleums[72] and also dicadinane—a C_{30} pentacyclic triterpenoid[73] (Scheme XIV).

Scheme XIV



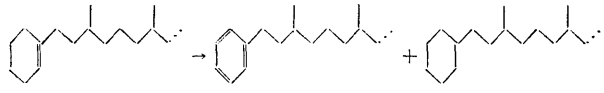
¶ Al A Petrov, *Geologiya Nefti i Gaza*, 1988, No. 10, p. 50.

The hydrocarbons of the first series (XIVa) are formed from bacteriotetrol simultaneously with benzohopanes having a similar structure (with the aromatic *F* ring). This reaction will be examined in greater detail in the next Section.

Bicadinane (XIVb) can be regarded as the product of the dimerisation of cadinene (eudesmane). The presence of two isopropyl groups leaves no doubt about its isoprenoid nature. Bicadinane has certain structural features characteristic of the tetracyclic C_{19} diterpenoids considered above.

IV. Aromatic isoprenoids

Aromatic isoprenoid compounds are usually absent from natural bioorganic objects. Therefore this Section will deal with the secondary products formed as a result of the redistribution of hydrogen (on clays) in hydrocarbons whose six-membered rings contain multiple bonds. Thus the aromaticity of these hydrocarbons is a secondary feature.

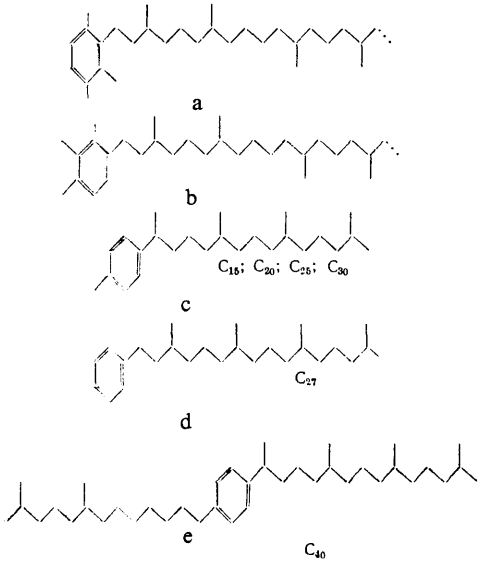


However, the character of the hydrocarbons examined below leaves no doubt about the isoprenoid nature of the compounds from which they have been formed. As will be shown below, overall the aromatic isoprenoid hydrocarbons are very similar in their structure (naturally with certain exceptions) to their alicyclic analogues.

1. Monocyclic hydrocarbons

Scheme (XV) presents the formulae of hydrocarbons [represented mainly by the $C_{10}-C_{30}$ homologous series (XVa, b)] containing a benzene ring and an aliphatic isoprenoid chain.

Scheme XV

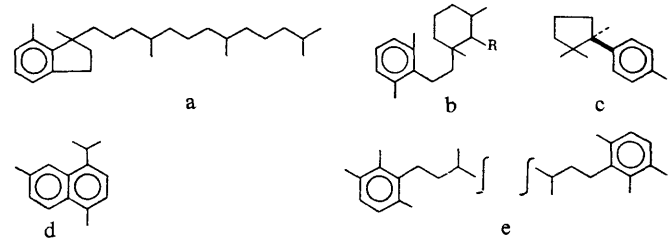


The structure of the hydrocarbons (XVa) and also the absence of the C_{12}, C_{17}, C_{23}, and C_{28} homologues from this series leaves no doubt that we are dealing here with aromatic derivatives of carotane. Hydrocarbons of the series (XVb) having a similar structure are present at lower concentrations. Apart from aromatic derivatives of carotane, $C_{15}-C_{30}$ methylalkylbenzenes (XVc), having a regular isoprenoid chain, have been found in petroleum. In contrast to aromatic carotenoids, C_{15}, C_{20}, C_{25}, and C_{30} hydrocarbons clearly predominate here, i.e. these hydrocarbons are sesquiterpanes, diterpanes, sesterterpanes, and triterpanes. A C_{27} hydrocarbon (XVd), having a regular isoprenoid chain, is present in certain petroleums at very high concentrations. An interesting aromatic phytadiene "dimer" (XVe) has been described.[75]

2. Bicyclic hydrocarbons

The C_{27} indan homologue (XVIa), with a regular isoprenoid chain, has been reliably identified in a number of petroleums[74] (Scheme XVI).

Scheme XVI

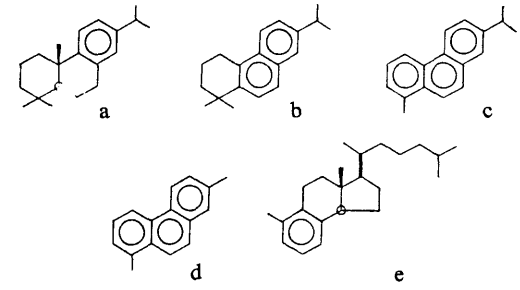


A group of phenylethylcyclohexanes (XVIb), formed via the degradation of the middle ring of the tricyclic isoprenoids (VIIa), has also been described.[57] The interesting hydrocarbon cuparene (XVIc) is a representative of the rarely encountered group of aromatic sesquiterpenoids.[2] Among naphthalene derivatives, cadalane (XVId) is undoubtedly isoprenoid in character.[76] A biaromatic analogue (XVIe) of β-carotane has been described. The hydrocarbon has been called isorenieratene.

3. Tricyclic hydrocarbons

Tricyclic aromatic isoprenoids are relatively less abundant in petroleums. Scheme (XVII) presents the formulae of four hydrocarbons formed on aromatisation of diterpenoids: dehydroabietane (XVIIa), simonellite (XVIIb), retene (XVIIc), and pimanthrene (XVIId).[78] The structure (XVIIe) is formed on degradation on the *A* ring in regular steranes (sterols).[79]

Scheme XVII



4. Tetracyclic hydrocarbons

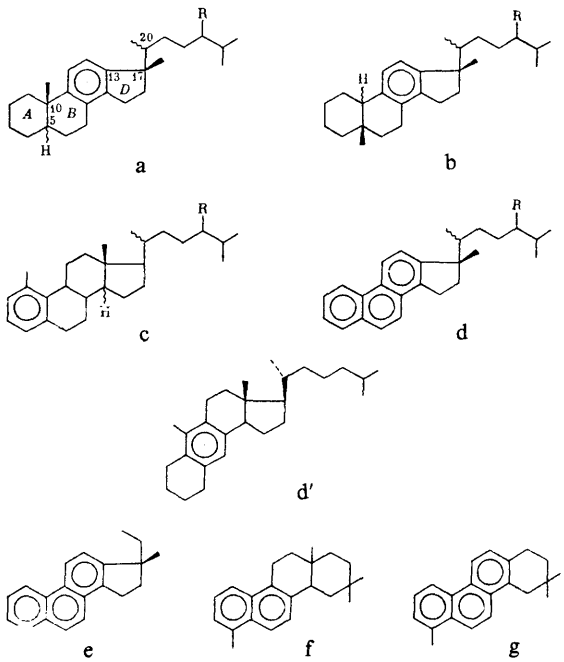
This group of compounds is extremely abundant in petroleums because the interaction of sterols with clays results in the formation, apart from saturated steranes, also of their aromatic analogues having from one to three aromatic rings in the molecule.[80,81]

A fairly large amount of attention has been devoted in the scientific literature to aromatic petroleum steranes.[1,2,82-90]

It has been found that the *C* ring is preferentially aromatised in steranes (steranes with the aromatic *A* ring are less common). Subsequently the *B* and *A* rings are aromatised simultaneously in *C*-aromatic steranes, which leads to triaromatic steranes containing the phenanthrene system. On aromatisation of the *A* ring, the angular methyl group at C(13) migrates to the C(17) atom. On exhaustive aromatisation, the methyl group at C(10) is usually eliminated. Monoaromatic steranes (*C* ring) have been identified in the mass spectra from the fragment with $m/z = 253$ (abstraction of an aliphatic group). In the mass spectra of steranes with an aromatic *A* ring, the principal fragment ion has $m/z = 211$. Triaromatic steranes are characterised by a fragment ion with $m/z = 231$ (also with abstraction of an aliphatic group).

Scheme (XVIII) presents the formulae of the most important aromatic steranes identified in petroleums as well as the formulae of certain other tetracyclic compounds.[91]

Scheme XVIII



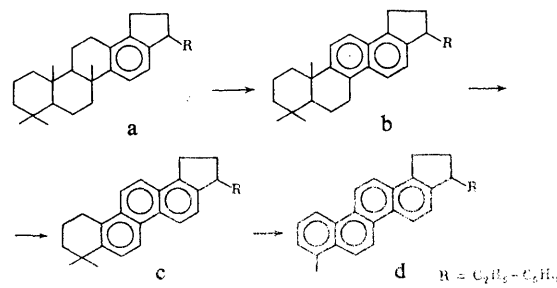
Monoaromatic steranes (XVIIIa) are present in the form of four epimers: 5α,20*R*; 5α,20*S*; 5β,20*R*; 5β,20*S*. In contrast to saturated steranes, in this case the 5β-isomers are more stable (because of the distortion of the *B* ring).[84] The structures (XVIIIa, d) are the most common in petroleums. Their ratio is widely used as an important correlation factor determining the degree of catagenic maturity of the petroleum. Since the exhaustive aromatisation process is accompanied by the degradation of the side chain in steranes, the petroleums contain, apart from the $C_{26}-C_{28}$ steranes [structures of the type (XVIIId)], a series of triaromatic steranes with shorter aliphatic chains, for example, compound (XVIIIe).[89]† Partly aromatised molecules of the pentacyclic triterpanes (XVIIIf, g), which have undergone degradation (*E* rings), have been found in petroleums.[91]

† The sterane (XVIIId′) with an aromatic *B* ring belongs to the class of the rarely encountered anthrasteroids.[89]

5. Pentacyclic hydrocarbons

The formation of pentacyclic aromatic petroleum isoprenoids is wholly associated with the aromatisation of triterpenoids, especially hopane and its homologues. Aromatic derivatives of adiantane, hopane, and homohopanes have been described.[92,93] The aromatisation of the rings takes place gradually in the sequence $D \rightarrow C \rightarrow B \rightarrow A$ with the simultaneous loss of methyl substituents (Scheme XIX).

Scheme XIX

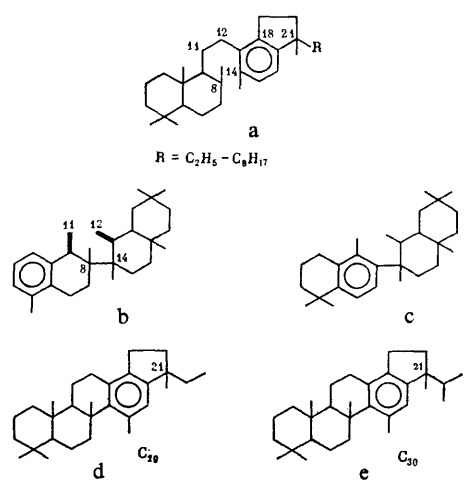


Another group of aromatic hydrocarbons formed from hopanes has also been discovered.[94-96] It has been shown that the aromatisation (of the *D* ring) takes place with the simultaneous dissociation of the most labile 8–14 bond. This results in the formation of tetracyclic monoaromatic 8,14-secohopanes of type (XXa) [we may note the interesting 1,3-migration of the methyl group from C(18) to C(21)[96] (Scheme XX)].

An example of other secotriterpanes (XXb, c), formed from oleanane (β-amyrin) with dissociation of the 11–12 bond, has been quoted.[76]

Interesting pentacyclic hopanes (XXd, e) with an aromatic *D* ring have been discovered in Soviet petroleums.[94] As in the case of secohopanes, their formation probable involved the migration of the methyl group from the C(18) atom to the C(21) atom. An intense fragment ion with $m/z = 363$ is characteristic of the mass spectra of these hydrocarbons. It is formed as a consequence of the elimination of the aliphatic substituent at C(21), similar to the elimination of the substituent in monoaromatic steranes ($m/z = 253$) or in secohopanes ($m/z = 365$).

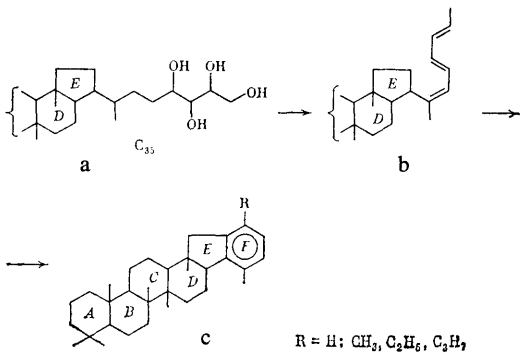
Scheme XX



6. Hexacyclic hydrocarbons

A series of hexacyclic hydrocarbons with one aromatic ring can be obtained from bacteriohopane with the simultaneous formation of hydrocarbons of the hopane series[96–98] (Scheme XXI). These hydrocarbons have been called benzohopanes.

Scheme XXI



The dehydration of the tetrol (XXIa) on clays leads to a series of polyenes (XXIb), capable of intramolecular cyclisation with formation of an aromatic *F* ring. This entails the partial degradation of fragments of the aliphatic chain. In addition to compounds (XXIc), their saturated heterocyclic analogues, described previously, are also formed simultaneously. It is striking that only $C_{32}-C_{35}$ hexacyclic compounds have been found in petroleums in both cases.

V. Conclusion

We shall now describe certain conclusions which arise from the data examined. The large number of studies carried out in recent years on the chemistry and geochemistry of petroleum have demonstrated an appreciable content of aliphatic, alicyclic, and aromatic isoprenoids in the test objects. The structures of all the compounds identified are directly related to those of their biological precursors.

The number of isoprenoid hydrocarbons in petroleums reaches 300 items and their overall concentration is in many instances 20–25% relative to the petroleum hydrocarbons. We may note that the sulphur- and oxygen-containing components of petroleum are also made up mainly of the same structural fragments with a clear predominance of isoprenoid structures.[99,100] All these findings undoubtedly confirm the bioorganic nature of the petroleum, which is a product of the transformation of the lipid component of ancient living matter: algae, bacteria, and higher plants. Petroleum hydrocarbons, which preserve information about the composition and structure of their bioorganic precursors because of their relative chemical stability, have therefore been called biological labels or chemofossils. They are sometimes also referred to as relict compounds.

However, the role of biological labels is not limited to the conclusion that petroleum is bioorganic in origin. They are much more important in modern geochemical methods used in prospecting for petroleum deposits.[1,2,101–104] Thus the characteristics of the qualitative and quantitative distribution of isoprenoid hydrocarbons in petroleums are used to determine the type of organic matter: marine (seaweed, plankton), continental, and highly modified by microbiological action. Typical parameters of the marine matter are, for example, high concentrations of steranes (especially with the C_{27} composition) and phytane. On the other hand, in the petroleums generated from continental (plant) organic matter pristane predominates, there are no steranes, and at the same time triterpanes, such as, for example, oleanane, and diterpanes, such as phyllocladane and kaurane, are present. The intense microbiological processing of organic matter is also indicated by the high concentrations of gopanes and the presence of irregular aliphatic isoprenoids with "head to head" fragments, etc. Isoprenoid petroleum hydrocarbons can be used also to determine the paleo-conditions for the accumulation of deposits and the transformation of organic matter into petroleum. Thus T-shaped isoprenanes and gammacerane arise in highly saline media. Rearranged steranes are usually absent from carbonate deposits (rocks), which are in fact most often formed in terrigenic (argillaceous) deposits. In addition, the proportions of aliphatic isoprenoids, steranes, and hopanes excellent "fingerprints" of particular petroleums,[1,2] which make it possible to determine the source from which they have been formed and the ways in which petroleums have migrated in the Earth's core.

Finally, the change in the stereochemistry of hopanes and especially steranes is widely used to determine the degree of "maturation" (catagenic modification) of organic matter in the regions and deposits up to the petroleum level which have been investigated. This is based on the fact that the initial (immature) organic matter always has the natural (biological) configuration of the labile chiral centres, for example C(17), C(21), and C(22) in hopanes and C(14), C(17), and C(20) in steranes. Petroleums usually consist of a catagenically fairly mature product (corresponding to the E–D stage on the coal metamorphism scale) which has been stereochemically modified. The formation of appreciable petroleum deposits is therefore possible, in principle, only in those places where the organic matter is characterised by the presence of 17α,22β-hopanes and (14β,17β,20*S*)- and the corresponding (20*R*)-steranes.

The distribution of isoprenoid hydrocarbons is also used for the chemical (geochemical) classification of petroleums and also for the estimation of the degree of microbiological transformation of petroleum.[1,2] Thus the practical importance of isoprenoid petroleum hydrocarbons (as well as other biomarkers) is very great. There is no doubt that these compounds have great potential possibilities and that there are good prospects for their wide scale practical use.

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