

The Formation Features of C₁₀–C₂₀ Regular Petroleum Isoprenanes

G. N. Gordadze*, M. V. Giruts, A. R. Poshibaeva, and V. N. Koshelev

Gubkin Russian State University of Oil and Gas (National Research University), Moscow, Russia

*e-mail: gordadze@rambler.ru

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Abstract—To model the formation processes of C₁₀–C₂₀ petroleum isoprenanes, thermolysis of regular and irregular C₂₀–C₄₀ isoprenanes (phytane, crocetane, squalane, and lycopane) and the suggested precursors of regular petroleum isoprenanes (phytol and isophytol) has been conducted. It has been shown that the thermolysis of these compounds results in the formation of regular, irregular, and pseudoregular isoprenanes; the trends in their distribution have been revealed; and the retention indices have been determined. It has been assumed that the pristane/phytane ratio, which is used in petroleum geochemistry, should be treated with caution.

Keywords: regular, irregular, and pseudoregular petroleum isoprenanes, thermolysis

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Aliphatic petroleum isoprenanes have regular, irregular, and pseudoregular carbon chains with the number of carbon atoms of 9 to 45 [1–5]. Isoprenanes are known to consist of isoprene (2-methylbutadiene-1,3) units, which can be connected in the “head-to-tail” mode called regular or in the “tail-to-head” and “tail-to-tail” modes in one molecule to make it named irregular. Pseudoregular isoprenanes are formed from irregular ones in the case if the C–C bond breaking site is in the region of the irregular unit. As a rule, regular isoprenanes prevail in crude oils, condensates, coals, and dispersed organic matter (OM) of rocks. Note that all caustobioliths contain the homologous series of regular isoprenanes to C₂₀ and do not contain C₁₂ and C₁₇ isoprenanes. It is believed that regular isoprenanes in crude oils were derived from phytol (unsaturated C₂₀ alcohol with the regular isoprenane structure as a side chain of chlorophyll) [4–7] and the absence of C₁₂ and C₁₇ isoprenanes is due to a low probability of the simultaneous rupture of two C–C bonds at the tertiary carbon atom. It is also believed that phytane or 2,6,10,14-tetramethylhexadecane is formed if phytol gets into mainly reducing environment (the number of carbon atoms in the isoprenane chain is preserved) and, getting into oxidizing environment, phytol is oxidized to phytolic acid, which is subsequently decarboxylated to give the regular isoprenane pristane (2,6,10,14-tetramethylpentadecane) having one carbon atom less. Furthermore, some scientists associate high concentrations of pristane with the presence of this hydrocarbon in appreciable amounts in biomass of various kinds, in particular, zooplankton lipids [8, 9]. A certain amount of isoprenoid structures can be produced from iso-

prenoid acids, such as farnezanic and phytanic acids, which are found in a large amount in a variety of paraffinic oils [10]. The process of formation of isoprenoid alkanes from isoprenoid acids is apparently the same as the process of conversion of fatty acids into *n*-alkanes. Isoprenanes are also formed by the thermolysis of kerogen, petroleum asphaltenes and resins, and rock organic matter [11, 12]. Recently, we have found that bacterial metabolites contain regular C₁₇ isoprenane along with other regular isoprenanes and suggested that it could be formed from squalene, which has also been found in the soluble part of the bacterial biomass [13, 14].

We are aware that the identification of the formation routes of petroleum hydrocarbons (HCs), in particular, isoprenanes is a very complicated process. The difficulty is due both to the composition and structure of the original OM and to various geochemical environments of OM transformation to hydrocarbons. However, it is obvious that regular C₁₀–C₂₀ petroleum isoprenanes (including pristane and phytane, the ratio of which is considered a genetic indicator) can be generated not only from the fatty (lipid) material (acids, esters of saturated and unsaturated fatty acids) occurring in marine and/or continental sediments, but also from the high-molecular-mass hydrocarbons regular and irregular isoprenanes as a result of their thermal transformations.

EXPERIMENTAL

As the initial objects of research we selected the regular isoprenane C₂₀ phytane (2,6,10,14-tetramethylhexadecane); the irregular isoprenanes C₂₀ croce-

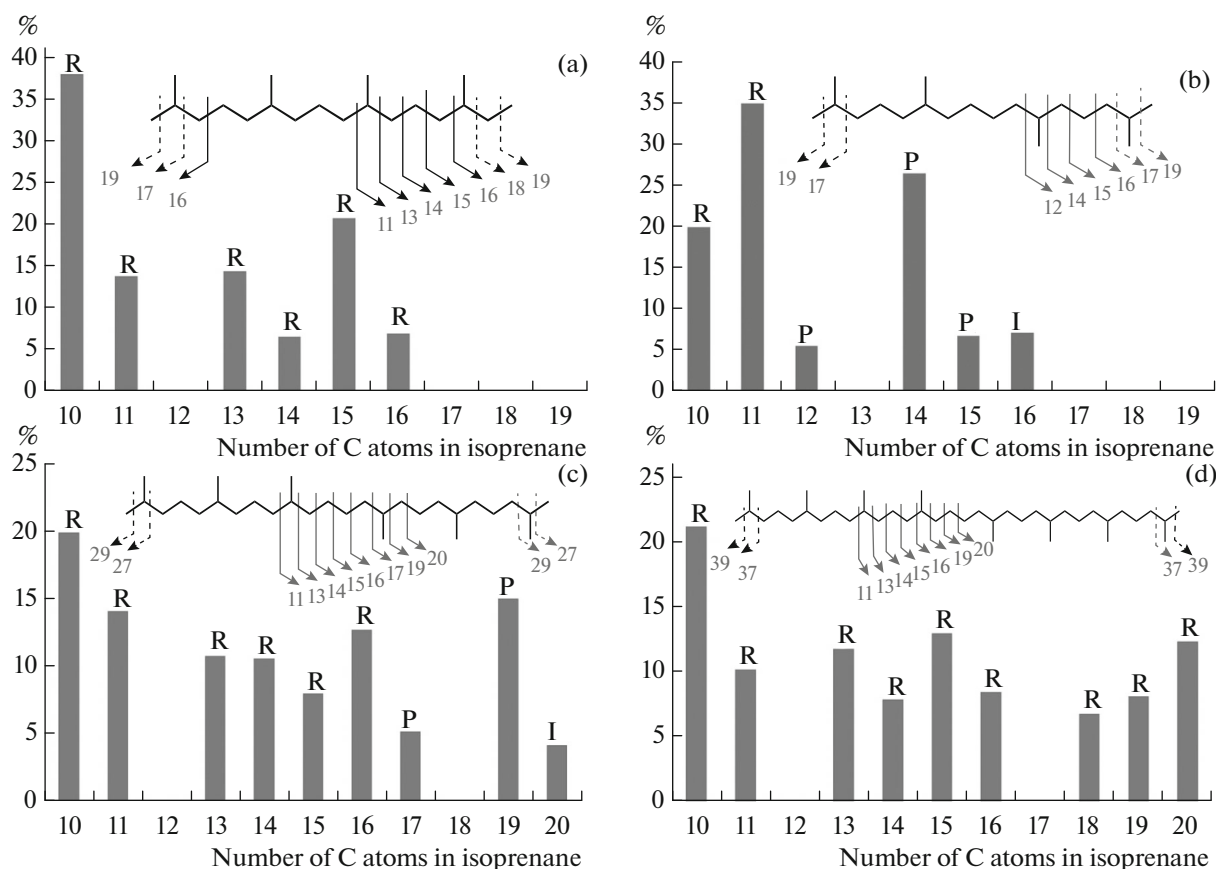


Fig. 1. Distribution of C₁₀–C₂₀ isoprenanes in thermolysis products of (a) phytane (b) crocetane, (c) squalane, and (d) lycopane. R, I, and P stand for regular, irregular, and pseudoregular isoprenanes, respectively. The numbers under the arrows indicate the number of carbon atoms in isoprenane.

tane (2,6,11,15-tetramethylhexadecane), C₃₀ squalane (2,6,10, 15,19,23-hexamethyltetracosane), and C₄₀ lycopane (2,6,10,14,19,23,27,31-octamethyldotriacontane); and the regular C₂₀ isoprenoid alcohols 3,7,11,15-tetramethylhexadecen-2-ol-1 (phytol) and 3,7,11,15-tetramethylhexadecen-3-ol-1 (isophytol).

Thermolysis was carried out in sealed ampoules for 6 h at a temperature of 330°C. We experimentally found that in the temperature range of 330–400°C, there was no fundamental difference in the relative distribution of C₁₀–C₂₀ isoprenanes produced by the thermolysis, whereas the thermolysis hardly occurs at lower temperatures and almost all the HCs undergo cracking to light hydrocarbons at higher temperatures. It is in the same temperature range that we previously performed the thermolysis of resins, asphaltenes, kerogen, the insoluble part of the prokaryote biomass, and some heteroatomic compounds as precursors of petroleum hydrocarbons and, subsequently, studied the patterns of their distribution [11, 12, 15].

Products of thermal transformations were analyzed by gas chromatography–mass spectrometry on an Agilent 6890N/5975S instrument. The column oven temperature was programmed to be elevated from 70

to 290°C at a rate of 4°C/min. The carrier gas was helium. All the spectra were taken using an ionization energy of 70 eV and an accelerating voltage of 3500 V. The temperature of the ionization chamber was 250°C. Hydrocarbons were separated on an HP-1 capillary column (25 m × 0.25 mm × 0.5 μm). Compounds were identified by adding suggested reference compounds to test samples, as well as by matching their mass spectra with those available in the NIST library.

RESULTS AND DISCUSSION

Table 1 and Fig. 1 show the distribution of regular (R), irregular (I), and pseudoregular (P) C₁₀–C₂₀ isoprenanes formed by thermal decomposition of the regular and irregular isoprenanes phytane, crocetane, squalane, and lycopane and the regular isoprenoids phytol and isophytol. It is noteworthy that the thermolysis did not result in unsaturated hydrocarbons.

Consider the basic patterns in the distribution of isoprenanes in the thermolysis products of the above compounds. To begin with, the formation of regular

Table 1. Relative distribution (%) of C₁₀–C₂₀ isoprenanes in the thermolysis products of C₂₀–C₄₀ isoprenanes, phytol, and isophytol

Number of C atoms in isoprenane	Hydrocarbon	Isoprenane type	Products of thermolysis of					
			phytane	crocetane	squalane	lycopane	phytol	iso-phytol
10	2,6-dMC8	R	38.0	18.9	26.4	21.2	10.1	7.7
11	2,6-dMC9	R	13.7	17.9	10.0	10.2	10.5	6.7
12	2,6-dMC10	P	–	4.8	–	–	–	–
13	2,6-dMC11	R	14.4	–	12.2	11.8	14.6	15.8
14	2,6,10-tMC11	R	6.4	–	7.4	7.9	14.8	14.5
	2,6-dMC12	P	–	13.1	–	–	–	–
15	2,6,10-tMC12	R	20.7	–	5.4	13.0	17.5	24.0
	2,6,11-tMC12	H	–	10.3	–	–	–	–
16	2,6,10-tMC13	P	6.8	–	13.1	8.5	14.2	16.4
	2,6,11-tMC13	I	–	10.2	–	–	–	–
17	2,6,10-tMC14	P	–	–	3.7	–	–	–
	2,6,11-tMC14	I	–	–	–	–	–	–
18	2,6,10-tMC15	R	–	–	–	6.8	9.1	11.3
19	2,6,10,14-teMC15 (pristane)	R	–	–	–	8.1	6.6	1.8
	2,6,10-tMC16	P	–	–	19.0	–	–	–
	2,6,11-tMC16	I	–	–	–	–	–	–
	2,6,10,14-teMC16 (phytane)	R	–	–	–	12.4	2.3	1.9
20	2,6,10,15-teMC16	I	–	–	2.7	–	–	–
	2,6,11,15-teMC16 (crocetane)	I	–	–	–	–	–	–
	Pristane/phytane		–	–	7.0 ^{*)}	–	2.9	0.9

R is regular, I is irregular, and P is pseudoregular isoprenane; ^{*)} irregular isoprenanes; d, t, and te stand for di-, tri-, and tetra-, respectively; M is methyl; and “C” is the number of carbon atoms in the isoprenane main chain.

isoprenanes C₁₈ and C₁₉ (pristane) as a result of thermolysis of the regular isoprenane *i*-C₂₀ phytane should be expected. However, this was not the case (Table 1, Fig. 1a). At the same time, as in the case of crude oils, there are no regular C₁₂ and C₁₇ isoprenanes in the phytane thermolysis products for the reason specified above.

As a result of thermolysis of the irregular isoprenane *i*-C₄₀ lycopane, the same regular C₁₀–C₂₀ isoprenanes as those present in crude oils are formed. In other words, there are also no C₁₂ and C₁₇ isoprenanes produced in this case. It is interesting to note that the value of the pristane to phytane ratio in the lycopane thermolysis products (0.7) resembles that in marine oils (Table 1, Fig. 1d). It should be noted that C₃₇–C₃₉ isoprenanes are not produced from lycopane; i.e., there is no detachment of terminal methyl and isopropyl groups, as would be expected.

By the thermolysis of the irregular isoprenane *i*-C₂₀ crocetane, C₁₀ and C₁₁ regular isoprenanes are formed

as in the case of phytane (Table 1, Fig. 1b), but, unlike the latter, C₁₂ and C₁₄ pseudoregular isoprenanes and C₁₅ and C₁₆ irregular isoprenanes are produced. At the same time, crocetane thermolysis products do not contain C₁₃ and C₁₈ isoprenanes because of a low probability of simultaneous breaking of two C–C bonds at the tertiary carbon atoms. As in the case of lycopane, there is no detachment of terminal methyl and isopropyl groups, i.e., C₁₇ and C₁₉ isoprenanes are not formed.

The thermolysis of the irregular isoprenane *i*-C₃₀ squalane likewise does not result in C₁₂ and C₁₈ isoprenanes for the aforementioned reason (Table 1, Fig. 1c). However, the formation of C₁₀, C₁₁, C₁₃–C₁₆ regular; C₁₇ and C₁₉ pseudoregular; and C₂₀ irregular isoprenanes is observed. As in the cases of crocetane and lycopane, the thermal degradation of squalane does not lead to the abstraction of the terminal methyl and isopropyl groups and, hence, C₂₇ and C₂₉ isoprenanes are not produced. Note that C₁₉ pseudoreg-

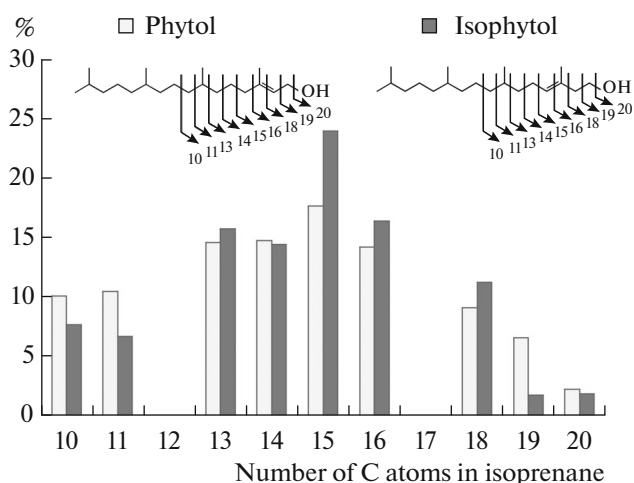


Fig. 2. Distribution of regular C₁₀–C₂₀ isoprenanes in the phytol and isophytol thermolysis products. The numbers under the arrows indicate the number of carbon atoms in isoprenane.

ular isoprenane significantly prevails over C₂₀ irregular isoprenane in the squalane thermolysis products: the ratio of C₁₉/C₂₀ irregular isoprenanes is 7.0.

Unlike the thermolysis of regular and irregular isoprenanes, the thermolysis of isophytol and phytol results in the formation of regular C₁₈ and C₁₉ iso-

prenanes together with the regular *i*-C₂₀ isoprenane phytane. Similarly, regular C₁₂ and C₁₇ isoprenanes are not formed for the same reason (Table 1, Fig. 2). It should be noted that the pristane/phytane ratio resulting from phytol thermolysis is 2.9, whereas that is the case of isophytol is considerably less, 0.9.

As noted above, in accordance with the today's concept of the formation of pristane and phytane in oils, their ratio is a genetic indicator. Moreover, high values of this ratio (greater than 3) suggest the continental genesis of oil and low values (1 or less) are indicative of the marine origin. Meanwhile, from Table 2, which shows the retention indices of regular, irregular, and pseudoregular C₂–C₁₀ isoprenanes on the HP-1 polymethylsilicone stationary phase, it is seen that the retention indices of regular 2,6,10,14-tetramethylhexadecane (phytane) and irregular 2,6,11,15-tetramethylhexadecane (crocetane) and 2,6,10,15-tetramethylhexadecane having the same number of carbon atoms in the molecule are almost identical. Therefore, the value of the pristane/phytane ratio as a genetic indicator should be treated with caution, since phytane can be eluted together with its isomers, which may originate not only from phytol (or isophytol), but also from higher regular and irregular isoprenanes present in oils. Thus, the pristane/phytane ratio will be overestimated.

Table 2. Retention indices of regular, irregular, and pseudoregular C₁₀–C₂₀ isoprenanes on HP-1

Number of C atoms in isoprenane	Hydrocarbon	Isoprenane type	I _{HP-1}
10	2,6-dMC8	R	931
11	2,6-dMC9	R	1022
12	2,6-dMC10	P	1118
13	2,6-dMC11	R	1215
14	2,6,10-tMC11	R	1275
	2,6-dMC12	P	1314
15	2,6,10-tMC12	R	1379
	2,6,11-tMC12	I	1375
16	2,6,10-tMC13	R	1464
	2,6,11-tMC13	I	1481
17	2,6,10-tMC14	P	1560
18	2,6,10-tMC15	R	1652
19	2,6,10,14-teMC15 (pristane)	R	1710
	2,6,10-tMC16	P	1718
20	2,6,10,14-teMC16 (phytane)	R	1813
	2,6,10,15-teMC16	I	1813
	2,6,11,15-teMC16 (crocetane)	I	1816

R is regular, I is irregular, and P is pseudoregular; d, t, and te stand for di-, tri-, and tetra-, respectively; M is methyl.

CONCLUSIONS

As a result of thermolysis of regular and irregular isoprenanes found in crude oils (phytane, crocetane, squalane, and lycopane) and natural precursors of regular petroleum isoprenanes (phytol and isophytol), regular, irregular, and pseudoregular C₁₀–C₂₀ isoprenanes have been obtained.

It has been found that the thermolysis of phytane, crocetane, squalane, and lycopane does not result in the detachment of terminal methyl, ethyl, or isopropyl groups, nor the simultaneous breaking of C–C bonds occurs at the tertiary carbon atoms in isoprenane molecules. The thermolysis of phytol, isophytol, and lycopane gives the same regular C₁₀–C₂₀ isoprenanes that are present in crude oils. It should be noted that the pristane/phytane ratio resulting from phytol thermolysis is 2.9, whereas its value is considerably lower, 0.9, in the case of isophytol. In addition, it is necessary to bear in mind that phytane can be eluted together with its isomers, which may form not only from phytol (or isophytol), but also from higher regular and irregular isoprenanes occurring in oils. Thus, the value of the genetic index pristane/phytane ratio, which is used for correlation in oil–oil and oil–dispersed rock organic matter systems should be treated with caution.

It has been found that there is no formation of unsaturated compounds during the thermolysis of the above compounds.

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