Pyrolytic Formation of C_{19} Isoprenoid Hydrocarbons from Dihydrophytol: in Relation to the Genesis of Pristane in Petroleum

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This study was concluded to elucidate a pathway for formation of C_{19} isoprenoid hydrocarbons (isops) in petroleum from chlorophylls. C_{19} isops are predominantly produced when dihydrophytol is heated at 320˚C for a period ranging from 1 to 5 h under vacuum while C_{20} isops are predominantly produced when chlorophyll *a* or phytol is heated. A radical chain reaction of decomposition of dihydrophytol is proposed as plausible pathway for producing C_{19} isops.

The ratio of pristane (2,6,10,14-tetramethylpentadecane: saturated C_{19} isoprenoid hydrocarbon) to phytane (3,7,11,15-tetramethylhexadecane: saturated C_{20} isoprenoid hydrocarbon) in petroleum and geolipids (organic solvent extracts of sedimentary rocks) is often used as an indicator to assess oxic/anoxic conditions of sedimentary environment.[1] Phytyl side chain (a in Figure 1) of chlorophyll *a* (chla, Figure 1) has been hypothesized[1] as a possible source of both pristane and phytane. A number of heating experiments of chla[2-7] and phytol (3,7,11,15-tetramethyl-2-hexadecenol)[8-10] have been carried out so far for proving this hypothesis.

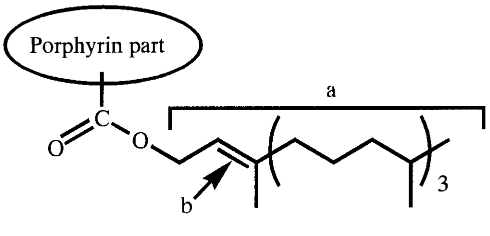


Figure 1. Phytyl chain (a) of chlorophyll pigment.

Since C_{20} isoprenoid hydrocarbons (phytenes and phytadienes) are major products in these experiments, chla is commonly recognized as a major precursor of phytane. However, a yield of C_{19} isoprenoid hydrocarbons (pristenes) is considerably smaller than that of C_{20} isoprenoid hydrocarbons (isops) in all experiments, which cannot explain wide ranges of ratios of pristane to phytane observed for petroleum/geolipids (0.1-12).[1,9,11,12] Therefore, precursor of pristane is a controversial issue. Goossens et al. proposed tocopherol as an alternative precursor of C_{19} isops because a large amount of 1-pristene was obtained on its flash pyrolysis.[13]

Recent development of isotopic ratio mass spectrometry (IRMS) of organic compounds revealed that carbon isotopic ratios of phytane and pristane from the same geological samples are similar in many cases, implying that these compounds are of the same origin, chlorophylls.[14] Our study of heating of chla[5] and phytol[8] showed that relationship in carbon isotopic ratios between C_{19} isops and C_{20} isops produced on heating is similar to that observed in common petroleum.[15,16]

As to the mechanism of C_{19} isops and C_{20} isops from chlorophyll pigments, it is reasonable to consider that: the presence of C-C double bond (b in Figure 1) in phytyl side chain is favorable for the formation of C_{20} isops on decomposition because C_{20} isops are formed *via* β scission of the double bond.[3] Actually, the ratios of C_{19} isops over C_{20} isops are less than 1 in the heating experiments of chla or phytol.[2-4,7] Formation of C_{19} isops is hindered by the double bond; that is scission of C-C bonds at α position of double bond, which results in the formation of C_{19} isops, is unfavorable. Therefore we predict that dihydrophytol (DHP) would yield larger amount of C_{19} isops on heating. To verify our prediction, we heated DHP at 320 ˚C for 1, 2.5 or 5 h in a sealed Pyrex glass ample under vacuumed pressure in this study.

DHP was prepared by the following procedure. (1) Phytol was hydrogenated by bubbling H_2 gas with PtO_2 in hexane for 10 min. (2) Since the hexane solution obtained was too emulsified for the catalyst to be removed by filtration, hexane was evaporated and the residue was dissolved in benzene/ methanol (3:1). (3) After the catalyst was removed, benzene/methanol was evaporated from the filtrate and the residue was dissolved in hexane, which was passed through silica-gel column with hexane and methanol successively. (4) DHP was obtained as a methanol fraction, which was confirmed by GC-MS analysis.

About 10 mg DHP thus prepared was heated in a Pyrex glass ample (ca. 4 mm i.d. x ca. 100 mm) under conditions shown above. The pyrolyzates were analyzed by GC-MS. Major products were pristane, 1-pristene, phytane and phytenes and some unidentified compounds as exemplified in Figure 2. Smaller molecular weight compounds were not analyzed since we focused only on the yield ratio of C_{19}/C_{20} isops. As Table 1 shows, the total yield of C_{19} isops is larger than that of C_{20} isops, and the ratio of former to the latter increases with heating time.

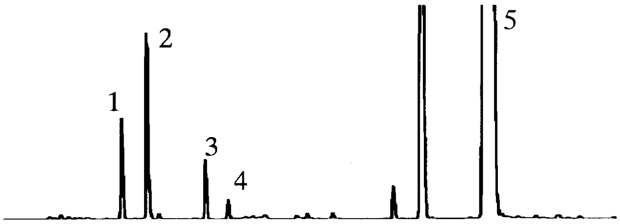


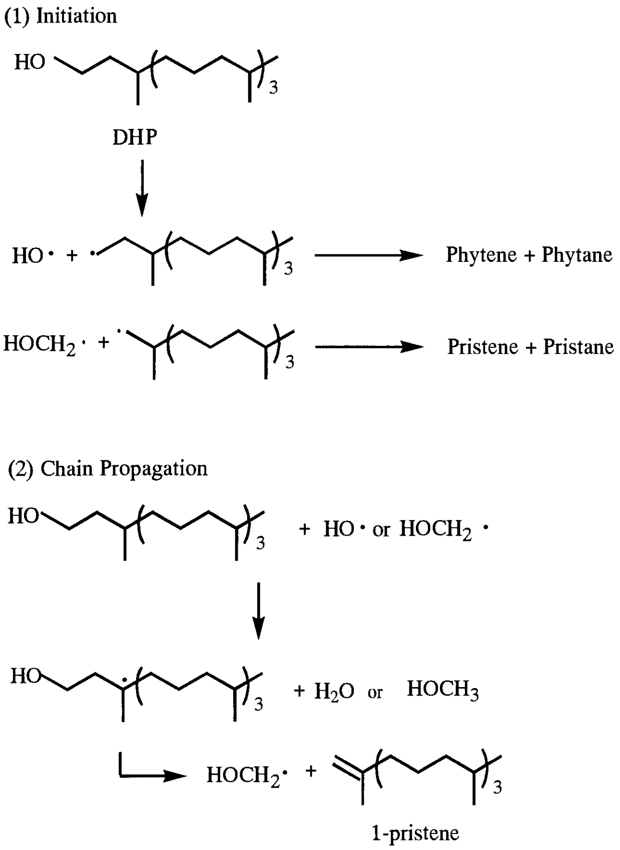
Figure 2. A gaschromatogram of dihydrophytol pyrolyzate. 1; pristane, 2; pristene, 3; phytene, 4; phytane, 5; dihydrophytol, others; unidentified.

Table 1. The yields (% mole mole^{-1}) of C_{19} and C_{20} isoprenoid hydrocarbons produced on heating of dihydrophytol at 320 °C for various heating times

Heating time /h		1	2.5	5
C_{19}	Pristane	0.4	1.0	8.8
	Pristene	1.3	1.9	18.5
C_{20}	Phytane	0.3	0.2	0.3
	Phytene	0.3	0.6	1.0
C_{19} / C_{20} ratio		2.8	3.6	21.0
Dihydrophytol remained		91.2	55.4	18.1

The yield of C_{19} isops predominates that of C_{20} isops in all cases, and the ratio of the former to the latter increases with increase of heating time as we predicted. This result can explain the ratios of pristane to phytane in petroleum/geolipids. Moreover, carbon isotope compositions of pristane and phytane which were obtained by reduction of C_{19} and C_{20} isops, give similar values (difference within 0.5‰). The scheme shown below is a plausible reaction for thermal decomposition of DHP. The radical chain reaction sufficiently explains the formation of C_{19} isops as well as C_{20} isops. Similar reactions are assumable for the formation of C_{19} isops in sediment because thermal processes including radical and catalytic reactions may account for the formation of most hydrocarbons in petroleum.[17]

Scheme 1.



In conclusion, the results of the present study implies, therefore, that DHP can be an important precursor of pristane in petroleum/geolipids. DHP is a reduction product of phytol, which is produced by cleavage of the phytyl side chain of chlorophylls. For the production of DHP, the following processes are known to play an important role under oxic condition: a grazing of planktonic detritus by benthos,[18] reduction through the guts of copepods,[19] or microbiological reduction of phytol in early diagenesis.[20]

We hypothesize consequently that large ratios of pristane over phytane frequently observed in petroleum/geolipids is brought about by the following steps: (1) Formation of DHP from phytol (hydrolysis product of chla) by microbial reaction under oxic conditions, (2) formation of both C_{19} and C_{20} isops by geothermal heating of DHP or DHP-incorporated kerogen,[21] and (3) subsequent reduction of C_{19} and C_{20} isops.

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