Compositional and Carbon Isotopic Behavior of C_{19} and C_{20} Isoprenoid Hydrocarbons Produced by Laboratory Heating of Phytol: A Study of Formation of Pristane and Phytane from Chlorophylls on Diagenesis

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Carbon isotopic ratios ($\delta^{13}C$) of isoprenoid hydrocarbons (isops) produced by heating (300-350 ℃) of phytol were measured for understanding diagenetic reaction of chlorophylls. C_{19} isop was isotopically lighter than the phytol at the early stage of the heating and lighter than C_{20} isop regardless of heating temperature and time. Difference in $\delta^{13}C$ between C19 and C_{20} isops observed in this study was similar to that observed for some petroleum.

Pristane (2,6,10,14-tetramethylpentadecane) and phytane (3,7,11,15-tetramethylhexadecane) are generally present in petroleum and bitumen (organic solvent extracts of sedimentary rocks) as characteristic isoprenoid hydrocarbons. The ratio of pristane/phytane of these geolipids is often used as an indicator of redox potential of the source sediments.[1]

It is highly likely that the phytyl ($C_{20}H_{40}$ isoprenoid) chain of chlorophyll-a (chl*a*) is the precursor of phytane because chl*a* is ubiquitous in nature and it produces C_{20} isops (phytadienes: $C_{20}H_{38}$ and phytenes: $C_{20}H_{40}$) by heating in a wide temperature range.[2-5] On the other hand, the precursor and formation process of pristane are still controversial because the yields of C_{19} isops (pristenes: $C_{19}H_{38}$) are much lower than those of C_{20} isops when chl*a* is heated under laboratory conditions,[2-5] in contrast to the ratio of pristane/phytane of geolipids which varies widely (about 0.1 - 12).[1,6,7]

Hayes et al.[8] reported $^{13}C/^{12}C$ isotopic ratios ($\delta^{13}C$ related to PDB standard) of pristane, phytane and geoporphyrins isolated from geolipids, showing that (1) $\delta^{13}C$ of these two isops resemble each other, (2) the difference in $\delta^{13}C$ between these isops and the geoporphyrins is almost the same as that between phytol and porphyrin compound, which are obtained by hydrolysis of chl*a*. These observations suggest that the precursor of the pristane present in the geolipids is chl*a*.[8]

Trindade and Brassel[9] found petroleum having pristane which is lighter by about 1.5‰ than phytane. Bjorϕy et al.[10] reported that pristane in Paris Basin oils and oils generated by hydrous pyrolysis of Paris Basin shale (kerogen type II) are lighter by about 1‰ than phytane. The authors of these papers[9,10] claimed that the precursor of the pristane is different from that of the phytane.

In a previous paper,[4] we studied behavior in $\delta^{13}C$ of C_{19} and C_{20} isops by heating of chl*a* at 250 - 350 ℃ and found that C_{19} isop was isotopically lighter by 1.1‰ than C_{20} isop. Since the difference in $\delta^{13}C$ between C_{19} and C_{20} isops was similar to those reported by Trindade and Brassel[9] and by Bjorϕy et al.,[10] we considered that our experiment succeeded in simulating one of the reactions producing pristane and phytane in nature.

In the present study, in order to understand the mechanism producing the isotopic difference between C_{19} and C_{20} isops in more detail, we heated phytol (3,7,11,15-tetramethyl-2-hexadecen-1-ol) alone and examined changes in molecular and isotopic composition of isops produced by heating. Heating of phytol has been carried out so far with a clay mineral both in the presence and absence of oxygen,[11] with sandstone[12] or with water in the presence of insoluble fraction of Yalloum pollen coal.[7] However, in these cases, no $\delta^{13}C$ of the products was reported.

Phytol (10 mg - 15 mg) was taken in a small Pyrex glass vessel (inner vessel: 1 mm i.d. x 15 mm). The inner vessel was placed in a larger Pyrex glass vessel (outer vessel, 6-7 mm i.d. x 200 mm). The outer vessel was closed by heating at about 150 mm from the bottom under vacuum, then placed in an oven kept at 300, 320 or 350 °C for a period ranging from 1 to 5 hours. Then the liquid product was dissolved in hexane and analyzed by using a Shimadzu 9A gas chromatograph equipped with a flame ionization detector and a DB-5 coated fused silica capillary column. The products were identified from their mass spectral interpretation by using a Varian 3400-Finigan INCOS 50 GC-MS system with a DB-5 fused silica capillary column.

The unsaturated isops produced were hydrogenated into the corresponding saturated isops by bubbling H_2 with PtO_2 in hexane for 15 min. When necessary, silica gel chromatography of the hexane solution of the hydrogenated sample was carried out to remove the hump of unresolved complex mixtures. Then the $\delta^{13}C$ of the saturated isops were determined by gas chromatography-combustion-isotopic ratio mass spectrometry (GC/C/IRMS) consisting of an HP Model 5890 gas chromatograph equipped with a DB-5 coated fused silica capillary column connected to a Finnigan MAT delta-S mass spectrometer via combustion interface. The error in $\delta^{13}C$ measurement is within ± 0.5‰.

As shown in Figure 1, several isops smaller than C_{20} are produced by heating of phytol. At the early stage of the heating (e.g. 320 °C, 1 h), C_{19} isop (prist-1-ene) and C_{20} isops (phytenes and phytadienes) are produced and the yield of C_{19} isop is markedly lower than the total yield of C_{20} isops. As the heating proceeds, however, the ratio of C_{19} isops (pristenes) over C_{20} isops increases (max. 0.6, see Figure 3) and yields of isops smaller in size than C_{18} increase. The kind of isops produced and the change of their molecular distribution with longer heating are similar to those observed by heating of Chl*a*.

The $\delta^{13}C$ results for C_{19} and C_{20} isops produced on the heating are shown in Figure 2: (1) C_{19} isop obtained under the all temperature/time conditions examined are isotopically lighter than the corresponding C_{20} isop, (2) C_{19} isop obtained at the early stage of heating is lighter by 0.6 - 1.3‰ than the starting material (phytol), (3) $\delta^{13}C$ of C_{20} isop obtained is similar to that of phytol at the early stage of heating, while it becomes heavier as the severity of the reaction conditions increases, (4) $\delta^{13}C$ of

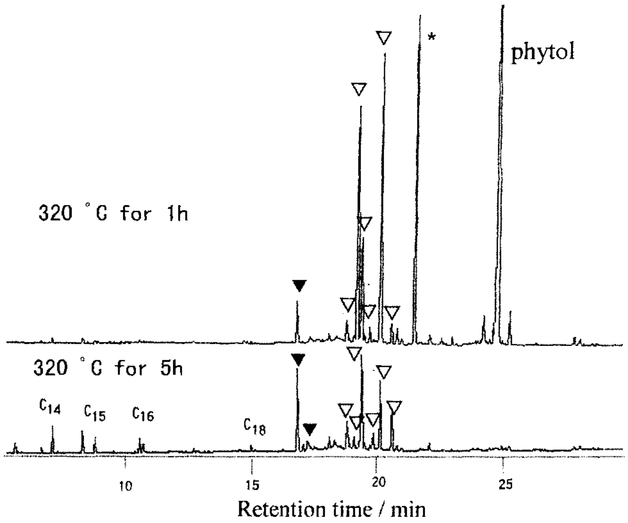

Figure 1. Isoprenoid hydrocarbons produced by heating of phytol.
▼ : C_{19} isop, ▽ : C_{20} isop, * : unidentified product.

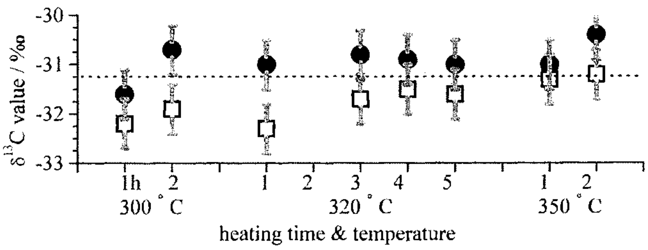

Figure 2. $\delta^{13}C$ values of C_{19} and C_{20} isops produced by heating of phytol under various conditions. □ : C_{19} isop, ● : C_{20} isop, ········ $\delta^{13}C$ value of starting material (phytol).

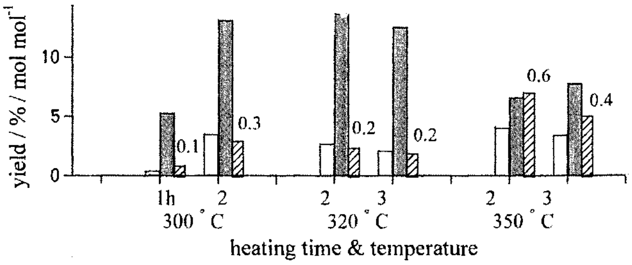

Figure 3. Yields and yield ratio of C_{19} and C_{20} isops produced by heating of phytol under various heating conditions.

□ C_{19} yield, ▦ C_{20} yield, ▨ C_{19} yield vs. C_{20} yield.

C_{19} isop becomes closer to that of phytol as the heating proceeds.

In the previous study by heating chla,[4] C_{19} isop was isotopically lighter than C_{20} isop regardless of heating temperature. We explained this result as follows: ^{12}C-^{12}C bond next to the C-C double bond decomposes appreciably faster than ^{12}C-^{13}C bond because α cleavage of double bond is highly unfavorable, and the bond involved in the formation of C_{19} isop is located at next to the C-C double bond of phytol. The present study revealed that difference in $\delta^{13}C$ between C_{19} and C_{20} isops obtained from phytol is similar to that obtained from chla.

This means that ^{13}C-depletion for C_{19} isop should be explained by kinetic isotope effect (differences in rate constants for ^{12}C and ^{13}C) on the formation of C_{19} isop from phytyl chain,[13] although detailed mechanism has not been clarified. Similar kinetic effect was reported by O'Leary and Marlier[14] who observed that the ratios of reaction rates of ^{12}C vs. ^{13}C of the carbonyl carbon on the alkaline hydrolysis and hydrazinolysis of methyl benzoate are 1.04.

Figure 3 illustrates decrease in the yield of C_{20} isop by heating at 350 °C, which indicates that C_{20} isop decomposes as the reaction proceeds. The increase in $\delta^{13}C$ of C_{20} isop with decreasing the yield indicates that isotopic fractionation also occurs on the decomposition of C_{20} isop.

C_{19} isop becomes isotopically as heavy as the substrate (phytol) when reaction proceeds (Figure 2). This observation can be explained by decrease in ^{12}C in the substrate with proceeding of the reaction. In addition, C_{19} isop chain would decompose at advanced stage of the heating. The ratio of decomposition/ formation rates of C_{19} isop chain may be smaller than that of C_{20} isop chain under the present experimental conditions because the yield ratio of C_{19} isop vs. C_{20} isop increases with increasing temperature or time (Figure 3).

Most of the $C_{14\text{-}18}$ isops are isotopically lighter than phytol (e.g. both of the $\delta^{13}C$ of C_{14} and C_{15} isops produced by heating at 320 °C for 3h are -33.0‰). These observations can be explained also by kinetic isotope effect which was described above for the ^{13}C-depletion for C_{19} isop.

Consequently, we conclude that the ^{13}C-depletion by ca. 1‰ for pristane relative to phytane observed in nature[9,10] can be explained by a single source (phytyl chain) model. Moreover, the results of the present study seem to fairly coincide with our recent observation where $\delta^{13}C$ of pristane are slightly smaller than those of phytane for some crude oils in Japan (Yabase oil field) and $\delta^{13}C$ of these compounds increase with increasing maturation.[15]

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