CHEMISTRY LETTERS, pp. 875-878, 1990.

The Effect of Preheating Treatment on the Pyrolysis of Chlorophyll-*a*. Simulation of Diagenetic Processes in Kerogen Formation

Mariko ISHIWATARI,* Ryoshi ISHIWATARI,† Haru SAKASHITA,†† Takashi TATSUMI,*†† and Hiro-o TOMINAGA††
Engineering Research Institute, Faculty of Engineering, The University of Tokyo, Yayoi, Tokyo 113
†Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo 158
††Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Tokyo 113

Pyrolysis of chlorophyll-*a* preheated at 250 °C has been carried out to investigate the precursor of 1-pristene often observed in pyrolysis products of kerogens. The 1-pristene/(phytadienes + phytene) ratio increased with increasing preheating time, suggesting the significance of the moiety derived from chlorophyll as the precursor of 1-pristene.

Kerogen has been defined as the fraction of sedimentary organic matter which is insoluble in common organic solvents. When decomposed either thermally or chemically, kerogens produce compounds whose structures are related to their precursor materials (biochemicals). Detailed studies of generation mechanisms of these pyrolysis products should provide useful information about the structure, origin and formation process of kerogens.1) 1-Pristene (2, 6, 10, 14-tetramethyl-1-pentadecene) is frequently found in the products of flash pyrolysis of kerogens. The phytyl (3, 7, 11, 15-tetramethyl-2-hexadecenyl) side chain of chlorophyll-*a* is the expected precursor of 1-pristene. However, flash pyrolysis of chlorophyll-*a* alone gives predominantly phytadienes ($C_{20}H_{38}$ isoprenoids); 1-pristene is produced only in a trace amount.2)

Goossens et al.3) claimed that tocopheryl moieties are the most likely precursor of 1-pristene on the basis of pyrolysis studies of tocopherols. In view of wide distribution of chlorophylls in nature through the long geological periods, however, it is rather difficult to rule out chlorophylls as precursors of 1-pristene. Our hypothesis is that chlorophylls are incorporated into sediments, and following their long-term diagenesis, they are gradually converted into the structure which produces 1-pristene upon flash pyrolysis. The aim of this study is to test this hypothesis. Chlorophyll-*a* was subjected to simulated maturation (heating under mild conditions) and subsequently analyzed by pyrolysis-gas chromatography (Py-GC).

Chlorophylls used in this study were chlorophyll-*a* from spinach (Sigma Chemical Company) or chlorophyll-*a* from spirullina (Wako Pure Chemical Industries Ltd.). The samples were preheated at 250 °C for a period ranging from 3 min to 24 h. A kerogen sample isolated from Colorado oil shale (USA) was also subjected to the flash pyrolysis. Details of the kerogen-isolation procedure are described elsewhere.4) A chlorophyll sample (0.2 mg - 0.5 mg) was placed in a small quartz tube (2 mmϕ x 20 mm), preheated, and then pyrolyzed by using a coil heater in a pyrolysis chamber connected to a Shimadzu GC-9A with a flame ionization detector (FID). The coil heater and the pyrolysis chamber are the parts of a Chemical Data Systems Pyroprobe 120. The structure of the pyrolysis chamber has been shown elsewhere,5) and the outline of Pyroprobe pyrolyzer was described by Iglauer et al.6) The coil heater was set at 650 °C for 20 s. The actual pyrolysis temperature was measured beforehand using a thermocouple inserted into the quartz tube. It was observed that the inside temperature went up to 470°C in 5 s and that this temperature was maintained while the coil heater worked. When the coil heater went off, the inside temperature went down immediately. When the heating time was set at 1 s, the inside temperature reached a maximum of 400 °C. The pyrolyzate was introduced into the gas chromatograph through a split injector (1:50) with a helium gas flow and analyzed on an OV-1 coated fused-silica capillary column (50 m x 0.25 mm i.d.). A kerogen sample (5 mg) was pyrolyzed at 430 °C for 15 s (the coil heater was set at 600 °C for 20 s). For the Py-GC-MS analysis, a Finnigan INCOS 50 GC/MS system was used with a Hewlett Packard UP-2 fused-silica capillary column (24 m x 0.2 mm i.d.).

When unpreheated chlorophyll-*a* was pyrolyzed for 1 s (maximum temperature: 400 °C) pyrolysis products consisted predominantly of two phytadiene isomers. The pyrogram was similar to that reported by van de Meent et al.2): a small amount of phytene ($C_{20}H_{40}$ isoprenoids) was also obtained, whereas 1-pristene was produced only in a trace amount. Yields of 1-pristene, phytadienes, and phytene were estimated to be 0.3%, 20.0%, and 1.8% (mol/mol), respectively, giving a 1-pristene/(phytadienes + phytene) ratio of 0.013. The precise structures of the phytadienes and phytene have not been determined. When chlorophyll-*a* preheated for 3 min was pyrolyzed under the same pyrolysis conditions (400 °C, 1 s), the yield of 1-pristene increased to 0.9%, whereas the yields of phytadienes and phytene were almost unchanged. The 1-pristene /(phytadiene + phytene) ratio, consequently, increased to 0.038.

When chlorophyll-*a* preheated for 3 min was pyrolyzed at 470 °C for 15 s (coil heater was set at 650 °C for 20 s), the yields of 1-pristene, phytadienes, and phytene increased to 1.7%, 29.3%, and 5.2% (mol/mol), respectively, resulting in the increase in the 1-pristene/(phytadienes + phytene) ratio to 0.048. Unheated chlorophyll-*a* gave 1-pristene in 1.0 mol% yield under these pyrolysis conditions. Pyrolysis at 470 °C of chlorophyll-*a* preheated for a longer time revealed that the yield of phytadienes decreased gradually with increasing preheating time, whereas the yield of 1-pristene was not changed significantly. Thus the 1-pristene/(phytadienes + phytene) ratio increased gradually with preheating time, as shown in Fig. 1.

Pyrolysis of chlorophyll-*a* preheated for 24 h gave several unidentified products in addition to the products mentioned above. The yield of 2-pristene became comparable to that of 1-pristene, and phytene became the major product, resulting in a pristenes/(phytadienes + phytene) ratio of 0.194. Isoprenoids from C_9 to C_{18} (except for C_{12} and C_{17}), and some pyrrole derivatives were produced from both unpreheated and preheated chlorophyll-*a* samples on pyrolysis.

The pyrogram of Colorado kerogen showed peaks between paraffin/olefin doublets in the C_{12}-C_{18} region; they were attributed to isoprenoid hydrocarbons ranging from C_{13} to C_{19}. The distribution of isoprenoid hydrocarbons was similar to that from preheated chlorophyll-*a* except for the absence of phytadienes and phytene.

Phytadienes, the main products from chlorophyll-*a*, are expected to be formed from the phytyl side chain of the chlorophyll molecule because cleavage at the β-position of C-C double bonds is relatively easy. A radical pathway starting with homolytic cleavage of the C-O bond may be operative. The allylic

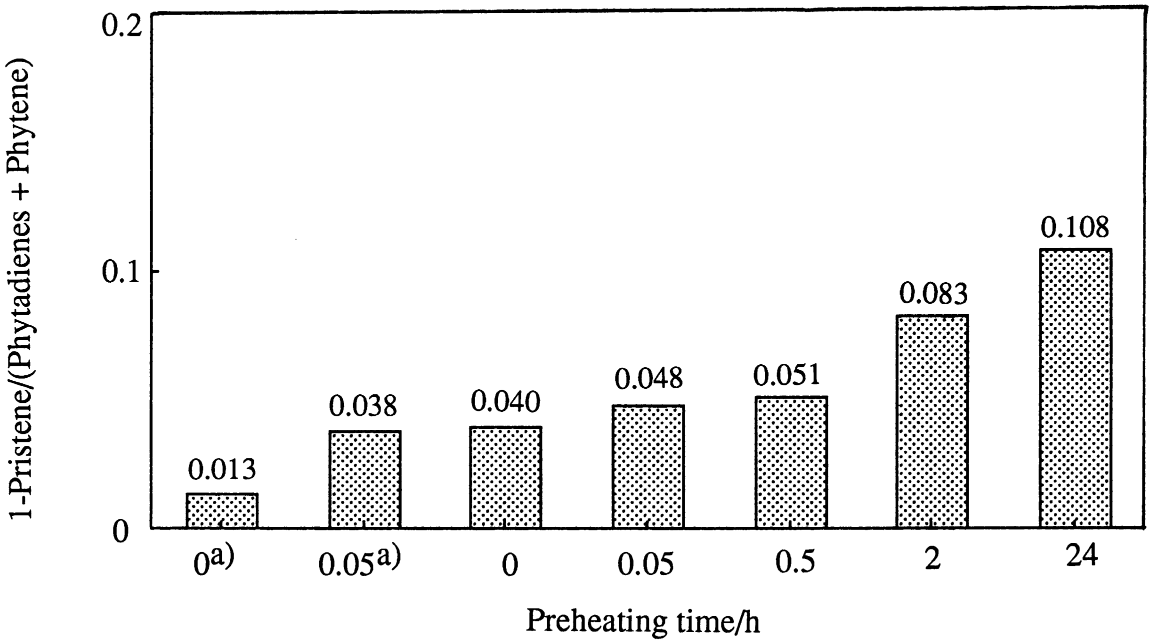
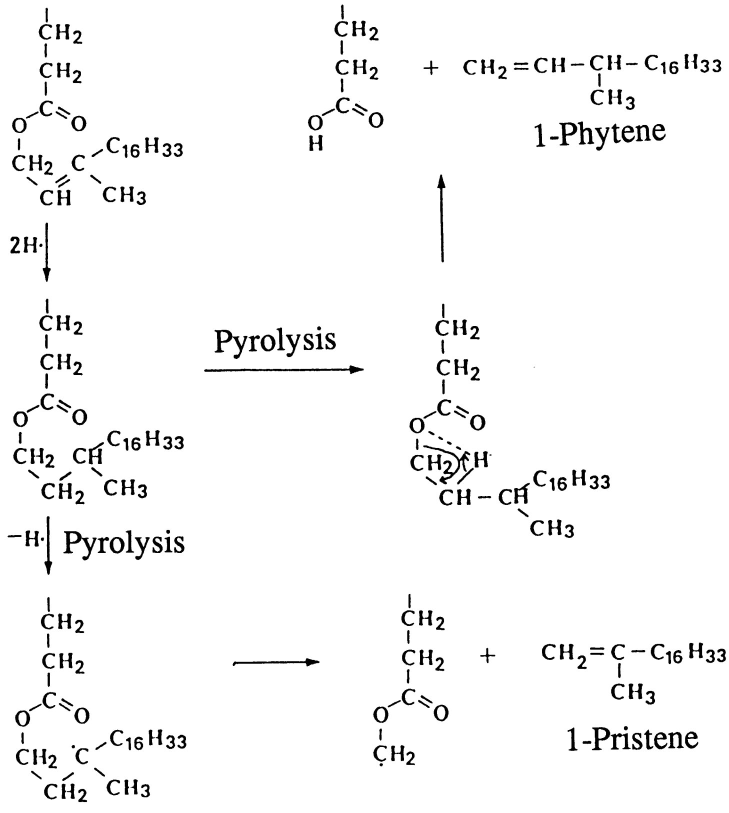


Fig. 1. 1-Pristene/(phytadienes + phytene) ratio under various preheating and pyrolysis conditions. Preheated at 250 °C and pyrolyzed at 470 °C for 15 s.
a)Pyrolyzed at 400 °C for 1 s.



Scheme 1.

Table 1. The effect of addition of 9,10-dihydroanthracene[a)]

9,10-Dihydro-anthracene	Product yield/mol%	
	Absent	Present[b)]
1-Pristene	1.7	2.4
Phytadienes	22.6	13.7
Phytene	6.0	11.4

a) Preheated at 250 °C for 30 min and pyrolyzed at 470 °C for 15 s.
b) Chlorophyll-*a*/9,10-dihydroanthracene = 5 (weight).

radical formed may be stabilized by abstracting a hydrogen atom from some hydrogen-donating substances or by releasing a hydrogen atom. The former process produces phytene and the latter phytadienes, respectively. The direct formation of pristene by degradation of the phytyl side chain cannot be expected to occur since α-cleavage next to the C-C double bond is highly unfavorable. Thus the structure of the phytyl side chain seems to have gradually changed during preheating. One possible pathway is the reduction of the double bond. As shown in Scheme 1, abstraction of the tertiary hydrogen followed by β-cleavage of the radical on pyrolysis should give 1-pristene. Otherwise the C-O bond cleavage may produce phytene. Simultaneous increases in the yields of pristenes and phytene for the preheated samples may support this scheme. Hydrogen atoms should be supplied from tertiary and/or allylic hydrogens of the chlorophyll-*a* molecule because they are easily abstractable. Such reactions may take place under natural sedimentary conditions, because the reduction of double bonds in organic molecules has often been observed during diagenesis.[7)]

Pyrolysis of chlorophyll-*a* preheated with 9,10-dihydroanthracene, an effective hydrogen donor, gave 1-pristene in higher yield than pyrolysis of the sample preheated alone, as shown in Table 1. This finding may support the above scheme involving hydrogen addition prior to pyrolysis. The presence of 9,10-dihydroanthracene also resulted in an increase in the yield of phytene at the expense of phytadienes.

Chlorophylls are much more abundant in most natural photosynthetic organisms than tocopherols. The similarity of kerogen to preheated chlorophyll-*a* in the isoprenoid (including 1-pristene) composition of the pyrolysis products except for phytene and phytadienes may imply that chlorophylls are likely precursors of these isoprenoids. Indeed, discrepancies exist between chlorophyll-*a* and kerogen in the pyrolysis products: the former produces phytadienes and phytene whereas kerogen does not. However, this discrepancy does not seem to be seriously unfavorable to the above hypothesis. The yield of phytadienes from chlorophyll-*a* clearly tends to decrease with increasing preheating time and thus will eventually disappear, as shown in Fig. 1. Preheating is considered to correspond to early thermal alteration under natural conditions. We can thus expect that the chemical structure of chlorophyll-*a* will change with increasing degree of thermal alteration, into a structure producing neither phytadienes nor phytene. We propose that the preheating treatment of chlorophyll-*a* can essentially simulate the natural diagenetic process.

This study was supported in part by a Grant-in-Aid for Scientific research No. 62101008 from the Ministry of Education, Science and Culture.

References

1) S.R. Larter, H. Solli, A.G. Douglas, F. de Lange, and J.W. de Leeuw, *Nature*, **279**, 405 (1979).
2) D. van de Meent, J.W. de Leeuw, and P.A. Schenck, "Advances in Organic Geochemistry 1979," ed by J.R. Maxwell and A.G. Douglas, Pergamon, Oxford (1980), p. 469.
3) H. Goossens, J.W. de Leeuw, P.A. Schenck, and S.C. Brassell, *Nature*, **312**, 440 (1984).
4) R. Ishiwatari, M. Ishiwatari, B,G. Rohrback, and I.R. Kaplan, *Geochim. Cosmochim. Acta*, **41**, 815 (1977).
5) M. Ishiwatari, H. Sakashita, T. Tatsumi, and H. Tominaga, *J. Anal. Appl. Pyrolysis*, in press.
6) N. Iglauer and F.F. Bentley, *J. Gaschromatographic Sci.*, **12**, 23 (1974).
7) M. Blumer, *Science*, **149**, 722 (1965); A.S. Mackenzie, S.C. Brassell, G. Eglinton, and J.R. Maxwell, *Science*, **217**, 491 (1982).

(Received February 23, 1990)