P198-TU

CHEMOTAXONOMIC STUDY ON REFRACTORY MACROMOLECULES IN FOSSILS OF PLANT ACHENES AND CONES FROM THE NEOGENE TOKAI GROUP OF CENTRAL JAPAN

Ken SAWADA[1, *], Takaaki ARAI[1] and Minoru TSUKAGOSHI[2]

1. Department of Natural History Sciences, Faculty of Science, Hokkaido University, N10W8, Sapporo 060-0810, Japan (sawadak@ep.sci.hokudai.ac.jp).
2. Osaka Museum of Natural History, Nagai Park 1-23, Osaka 546-0034, Japan.

Recently, higher plant-derived biomarkers such as terpenoids have suggested being applicable as molecular palaeontological indicators such as chemotaxonomic and biogeochemical markers (*e. g.* van Aarssen et al., 2000). Alternatively, (bio)macromolecule constituting plant 'organic body' is refractory and well preserved even in ancient fossil, and therefore, can be also powerful tool for reconstructing plant chemotaxonomy and paleo-vegetation. However, there few studies for chemotaxonomy in fossil plant macromolecule. We have analyzed higher plant biomarkers such as triterpenoids and diterpenoids bound in macromolecule of plant macrofossils collected from sediments of Neogene Tokai Group (Tokiguchi Porcelain Clay Formation and Toki Sand and Gravel Formation), which were deposited in fluvial system and contained excellent-preserved plant macrofossils, in Tounou area of central Japan (Arai et al., 2003). In this study, we focus on alkyl compounds obtained as hydrolytic products from refractory (geo)macromolecules in the Neogene plant macrofossils from Tokai Group in order to examine their potentials as chemotaxonomic markers.

A pinecone fossil of *Pinus fujiii* from Miocene Tokiguchi Porcelain Clay Formation (ca. 11Ma), a pinecone fossil of *Pinus trifolia* from Toki Sand and Gravel Formation KS-2 (ca. 10-9Ma), and an achene fossil of *Liquidambar formosana* and an endocarp fossil of *Nyssa* sp. from Toki Sand and Gravel Formation NN06 (ca. 4Ma) were used. Also, extant plant achenes of *L. formosana* and *Liquidambar styraciflua*, and pinecones of *Pinus ridida* were used. Plant samples were treated by hydrolysis (saponification) with KOH/MeOH. The hydrolytic products were fractionated by silicagel column chromatography, and analyzed by gas chromatography (GC) and gas chromatography / mass spectrometer (GC/MS).

Lignin phenol, n-alkanol, α, ω-diol, fatty acid, α, ω-dicarboxylic acid, and ω-hydroxylic acid were mainly detected as hydrolytic (saponified) products from the plant macrofossils. Fatty acids characterized by higher even carbon number predominance (CPI>4.3), showing low maturity level. Detection of lignin phenol by saponification indicated that structure of lignin polymers, which were commonly polymerized with ether bond, altered to that constructing with ester bond in these macrofossils. Syringic compounds, angiospermous lignin phenol, were detected in *L. formosana* and *Nyssa* sp. hydrolyzate. Vanilic compounds generally detected in hydrolyzates of both angiosperm and gymnosperm were identified in all the samples. In addition, oleanoidal triterpenoids (angiospermous biomarker) and pimarane- and abietane-type diterpenoids (coniferous biomarker) have been identified in *L. formosana*, as well as *P. trifolia* and *P. fujiii*, respectively (Arai et al., 2003). Hence, it was confirmed that the lignin phenols and the terpenoid biomarkers in fossil plant can be useful as chemotaxonomic markers at the broad level of taxa.

Compared fossil with extant plant samples, carbon number distributions of alkyl compounds such as carboxylic and hydroxyl acids as well as diol in hydrolyzates were quite different between these samples. This fact indicates that the structure of alkyl chains within macromolecules significantly altered by cleavage accompanied with oxidation and/or defunctionalization during diagenesis. Nevertheless, it was found that carbon number distributions of only n-alkanols in hydrolyzates were almost similar between fossil and extant plant samples. The n-alkanol is known to be one of the monomer composed of suberin polymer in periderm tissue. Thus, the n-alkanol moiety bound in suberin polymer with ester bond is presumably well preserved in plant fossil. Furthermore, distribution patterns of n-alkanols in hydrolyzates (maximal peak of C_{24} homologue) of fossil and extant *L. formosana* as well as extant *L. styraciflua* were similar to that of Fagaceae in (sub)class Hamamelidae, which includes liquidamber (Holloway, 1983). Also, maximal peak of n-C_{20} alkanol in hydrolyzates was observed in fossil *Nyssa* sp., which agreed with the results of Aceraceae, (sub)class Rosidae (including Nyssa) (Holloway, 1983). From these results, it is suggested that the carbon number distribution of n-alkanols constituting suberin polymer within plant fossil can be applicable and reliable as chemotaxonomic marker at the level of (sub)class, although examination is necessary.

REFERENCES

Arai, T., Sawada, K., Suzuki, N. & Tsukagoshi, M. (2003) Search for chemotaxonomic markers in Neogene plant fossils from Tokai Group, Japan. *Geochimica et Cosmochimica Acta* 67/18S, A21.

Holloway, P. J. (1983) Some variations in the composition of suberin from the cork layers of higher plants. *Phytochemistry* 22, 495-502.

van Aarssen, B. G. K., Alexander, R., Kagi, R. I. (2000) Higher plant biomarkers reflect palaeovegetation changes during Jurassic times. *Geochimica et Cosmochimica Acta* 64, 1417-1424.