

## Molecular paleontological aspects of resistant macromolecules constituting angiosperm leaf fossils

Hideto Nakamura<sup>1\*</sup>, Ken Sawada<sup>1</sup>

<sup>1</sup>Grad. Sch. of Science, Hokkaido Univ.

Extractable compounds (so called biomarkers) are the only small portion of carbonaceous plant fossils. Organic matter residue after the extraction is typically resistant geomacromolecule, which is originated from selectively preserved resistant biomacromolecules (e.g. lignin, cutin, suberin). The resistant bio-macromolecules are chemically stable, and are much more resistant against microbial degradation compared to the other biomacromolecules like nucleic acids, proteins, and carbohydrates. The cutin and suberin consist of lipophilic polyester structures, and their compositions of ester-bound moieties vary depending on plant taxa, and different organs in the same plant. Therefore, alkaline ester cleavage experiments on organic residue may provide information for chemotaxonomy, organ specificity, and the other physiological states recorded in such polyester biomacromolecules.

In this study, fossil leaves of *Sabalites nipponica* (Palmae, Angiosperms), *Platanus* sp. (Platanaceae, Angiosperms), *Zamites* sp. (Bennettitales, Gymnosperms) were analyzed. The Cretaceous fossil conifer wood and coal, and a leaf of extant *Trachycarpus wagnerianus* were also analyzed to provide more reliable comparison in taxonomy and diagenesis. Analytical procedure followed by [1]. Briefly, free lipids were ultrasonically extracted from powdered samples with methanol and dichloromethane. The lipid extract was separated by silica gel column to four fractions. The residue after extraction was saponified with 1M KOH in methanol to obtain bound lipids. MeOH extraction at the same temperature/pressure condition were added between solvent extraction and saponification for the *Trachycarpus wagnerianus*. These fractions were analyzed by GC/MS. From maturity index  $C_{31}$ hopanes 22S(22S + 22R), these fossils reach late diagenetic stage in all fossils. The components released from resistant macromolecules by saponification consist mainly of n-alcohols, n-fatty acids, and dicarboxylic acids. Their carbon preferential indices show consistently higher values in bound compounds than free compounds, which suggests good preservation of biological information. The carbon number distributions of the n-fatty acids are almost similar to the samples showing typical cutin constituents (mainly composed of  $C_{16}$ ,  $C_{18}$ ) [2], or possibly due to *in situ* polymerization of fatty acids proposed in the literature [3]. However, the carbon number distributions of n-alcohol significantly vary. Short-chain ( $<C_{16}$ ) n-alkanols were commonly detected in this study, while in doubt as original content of cutin or suberin polymer, in terms of such shorter chain lengths are rare in biological macromolecules. Thus, the carbon number distribution of long-chain n-alkanols is the most favorable data to be compared over samples in search of chemotaxonomic characteristics. The result of extant palm (*Trachycarpus wagnerianus*) shows possible contribution of very long-chain n-alkanols ( $C_{28}$ - $C_{34}$ ) originate from noncovalently bounded wax moieties, meanwhile distinct contribution of long-chain n-alkanols ( $C_{20}$ - $C_{24}$ ).

### References

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