

## Chemotaxonomy of Cretaceous plant fossils from compositions of molecular units in resistant macromolecule

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Resistant macromolecules such as cutin and suberin polymers constituting living plants are known to be stable and much resistant to microbial degradation and diagenesis. Furthermore, the composition of molecular unit (monomer) constituting resistant macromolecules are various according to taxonomy. If variability of these compositions preserved in plant fossils that had undergone diagenetic alteration, these compositions can be useful as chemotaxonomic indicator. In the present study, we analyzed plant carbonized fossils collected from three Cretaceous coal layers to investigate variability of composition of molecular units in their resistant macromolecules, and to examine applicability of these compositions for chemotaxonomic study.

We analyzed plant fossils of angiosperms and gymnosperms collected from three locations; 1) Hirono, Fukushima Prefecture (Ashizawa Formation, Futaba Group), 2) Mukawa, Hokkaido (Hakobuchi Formation, Yezo Group), and 3) Mikasa, Hokkaido (Mikasa Formation, Yezo Group), Japan. For example, we used fruit fossils of *Hironoia fusiformis* and *Archaeofagacea futabensis*, flower fossils of *Esgueiria futabensis*, leaf fossils of *Juniperus* and *Platanus*, a stem fossil of *Ephedra*, as well as some fossils of fruits, seeds and woods that were taxonomic uncertain. Powder samples of above fossils were extracted with methanol and dichloromethane, and were subsequently refluxed under high temperature to remove free compounds completely. Finally, the residues were saponified by KOH/methanol to obtain ester-bound compounds. GC-MS analysis was performed for identification and quantification of compounds.

As ester-bound molecular units in resistant macromolecule of all fossil samples, C<sub>10</sub>-C<sub>28</sub> n-alkanoic acids and C<sub>10</sub>-C<sub>28</sub> n-alkanols were mainly detected. It was found that distributions of carbon number of n-alkanoic acids were clearly different between woody and non-woody fossils in the Futaba samples. In the non-woody fossils (e. g. flowers, fruits and leaves), which were organs that have cuticles, C<sub>18</sub> /C<sub>16</sub> ratios of n-alkanoic acids were lower. In the Hakobuchi plant fossils, we could obtain such difference for the C<sub>18</sub> /C<sub>16</sub> alkanolic acid ratios between woody and non-woody fossils. On the other hands, the C<sub>18</sub> /C<sub>16</sub> ratios of n-alkanoic acids are higher in wood fossils. In addition, C<sub>14</sub> /C<sub>16</sub> ratios of n-alkanoic acids in non-woody fossils tended to be higher than those in woody fossils. These results imply that the characteristics of the compositions in the n-alkanoic acid units might be attributed to monomer compositions of cutin and suberin. From scatter diagram for relationships between C<sub>18</sub> /C<sub>16</sub> and C<sub>14</sub> /C<sub>16</sub> ratios as independent variables, a linear function which can distinguish non-woody fossils from wood fossils was obtained. From scatter diagram for the relationship between C<sub>20</sub> /C<sub>18</sub> and C<sub>20</sub> /C<sub>16</sub> ratios of n-alkanols as independent variables, wood fossils could be roughly separated from flower, fruit and leaf fossils. The higher ratios of C<sub>20</sub> n-alkanol in woody fossils suggested high contribution to suberin-derived monomer in the fossils. From these results, we propose that the alkanolic acid and alkanol units from polyesters of resistant macromolecule can be powerful chemotaxonomic indicators for ancient plant fossil, although further examination is necessary.

Keywords: Cretaceous plant fossil, resistant macromolecule, chemotaxonomy, suberin, cutin, fossil polyester