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白亜系双葉層群産の花化石の有機分子分析による化学分類指標の探索

Search for chemotaxonomic indicator by analyses of organic molecules in flower fossils from the Cretaceous Futaba Group

池田 慧[1*], 沢田 健[1], 中村 英人[1], 高橋正道[2]

Kei Ikeda[1*], Ken Sawada[1], Hideto Nakamura[1], Masamichi Takahashi[2]

[1]北海道大学大学院理学研究院, [2]新潟大学大学院自然科学研究科

[1]Faculty of Science, Hokkaido University, [2]Faculty of Science, Niigata University

Terrestrial higher plant-derived biomarkers such as terpenoids have been used as chemotaxomonic indicators and paleoclimatic proxies. Compounds released from resistant plant biomacromolecules (e. g. lignin phenols, alkyl compound from cutin and suberin) in sediments have been used for evaluating paleo-vegetation, for example, gymnosperm vs. angiosperm contributions, but there have been few studies, especially in ancient geological samples such as the Paleozoic and Mesozoic. In this study, we analyzed terpenoid biomarkers and compounds released from resistant macromolecule in well-preserved fossils of angiosperm flower and fruit from the Cretaceous immature coal layer of the Ashizawa Formation, Futaba Group, Kamikitaba, northeastern Japan, in order to obtain fundamental data for chemotaxonomic aspect and diagenetic alteration of organic compounds in fossil. In addition, the fossil gymnosperm woods and leaves that had been collected from the same layer in the Ashizawa Formation.
Angiosperm-derived triterpenoids and gymnosperm-derived diterpenoids were identified as free biomarkers in all fossils, and their class distributions are almost similar. This indicates that free compounds possibly moved within the coal layer and attached into fossil grains. Therefore, the free biomarkers in fossils from immature coal layer may not be indigenous compounds.
The class distributions of long-chain ($C_{20}$to C_{28}) n-alkanols released from macromolecules in angiosperm flower and fruit fossils are different from those of gymnosperm wood and leaf fossils. The ratios of long-chain n-alkanols in all n-alkanols released from gymnosperm fossils are significantly higher than those in angiosperm fossils. In general, the long-chain n-alkanols are thought to be alkyl moieties with hydroxyl group in suberin polymer. Thus, the suberin polymer may be constituent in resistant macromolecule in gymnosperm wood and leaf fossils. Interestingly, we could identify the diterpenoid acids such as dehydroabietic acid released from angiosperm fruits and all gymnosperm fossils by saponification, although the relative abundances of dehydroabietic acid are much lower in angiosperm fruits. Furthermore, we identified isopimaranoic acid released from only gymnosperm wood fossils by saponification. These diterpenoids might be the compounds bound in resistant macromolecules in fossil with ester bonds, and are more abundantly contained in resistant macromolecule in gymnosperm fossils. Thus, these compounds bound in fossil resistant macromolecules are possibly useful as chemotaxonomic indicators even in the Cretaceous fossil.

キーワード:白亜紀花化石,被子植物進化,テルペノイドバイオマーカー,抵抗性高分子,クチン,化学分類

Keywords: Cretaceous flower fossil, evolution of angiosperm, terpenoid biomarker, resistant macromolecule, cutin, chemotaxonomy