Isotopic analysis of individual compounds: a tool to investigate fossil plants isotopic signal

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Discrimination against ^{13}C in favour of ^{12}C during photosynthesis in modern terrestrial plants leads to characteristic differences between atmospheric CO_2 and the carbon isotopic composition of the terrestrial plant tissues (Nier & Gulbransen 1939). Carbon isotopic abundances are expressed as $\delta^{13}C$ values:

$$\delta^{13}C = [(^{13}R_{sample}/^{13}R_{standard}) - 1] \times 1000 ‰$$

where ^{13}R stands for the ratio $^{13}C/^{12}C$, standard being PDB (marine carbonate: belemnite from the Pee Dee Formation). Isotopic fractionation of carbon associated with photosynthesis in living terrestrial plants depends upon three main factors (e.g. O'Leary, 1981): (1) the photosynthetic pathway of the plant, C_3, C_4 or CAM, (2) the inorganic-carbon source and (3) environmental parameters. Such factors can be recorded by fossil plant *via* $\delta^{13}C$ values. Carbon isotope ratios were often used to investigate the emergence of C_4 photosynthetic pathway in fossil plants. Stable carbon isotopic abundances were also studied to research an isotopic record of palaeoatmospheric condition in terrestrial fossil plants, to reconstruct local palaeoenvironments or as chemostratigraphic tool.

However, stable carbon isotope abundances in fossil plants can be diagenetically altered if the carbon lost by degradation has $\delta^{13}C$ values significantly different of the carbon which is preserved. Hedges *et al.* (1985) showed that lignin is selectively preserved to the detriment of cellulose in buried wood. Since lignin is ^{13}C-depleted when compared to the whole tissue, that may lead to significant changes in $\delta^{13}C$ values as demonstrated by Benner *et al.* in a modern salt marsh (1987). However, several experimental studies on modern plants (e.g. Balesdent and Mariotti 1996) and investigations on fossil ones suggested that fossil plants typically have retained their original isotopic composition. That could be explained by the presence of remnant of carbohydrates in fossil plants.

Nevertheless, significance of $\delta^{13}C$ values in fossil plants is strongly dependent on the level of diagenesis. The aim of the present study was thus to get a tool allowing for investigation of the isotopic signal in fossil plant whatever the level of preservation of bulk $\delta^{13}C$ values. Isotopic analysis of an individual molecular biomarker, present in substantial amounts in fossil plants and stable through geological time, could constitute an adequate methodology. The identification of such a biomarker was first undertaken in leaf lipids since most lipid constituents are stable through geological times, and, were shown not to move into the surrounding sediment during burial (Logan *et al.*, 1995). To validate the use of a given biomarker it was necessary to measure its $\delta^{13}C$ value in fossil plants in which the bulk isotopic signal is well preserved, and, to compare these values with those obtained in modern counterparts.

The Cenomanian lagoonal Member of the 'Argiles du Baugeois' (Anjou, France) yielded a rich and exceptionally well preserved fossil flora. Preliminary studies have shown that the bulk $\delta^{13}C$ values were not significantly altered in these fossil plants. $^{13}C/^{12}C$ ratios thus allowed the reconstruction of the ecological distribution of each species studied, along a decreasing salinity gradient from the lagoonal zones to the flood plain. Leaf lipids from the most abundant species of the deposit, the Ginkgoale *Eretmophyllum andegavense*, were thus analysed, and compared to the ones of its extant counterpart *Ginkgo biloba*.

GC-MS analyses of leaf lipids from both Ginkgoales reveal the presence of 3 common compounds in *E. andegavense* and its modern counterpart: long chain *n*-alkanes, predominantly even *n*-acids and alkyl, dimethoxycoumarins. They all constitute potential biomarkers of the isotopic signal. Isotopic analyses were first undertaken on n-

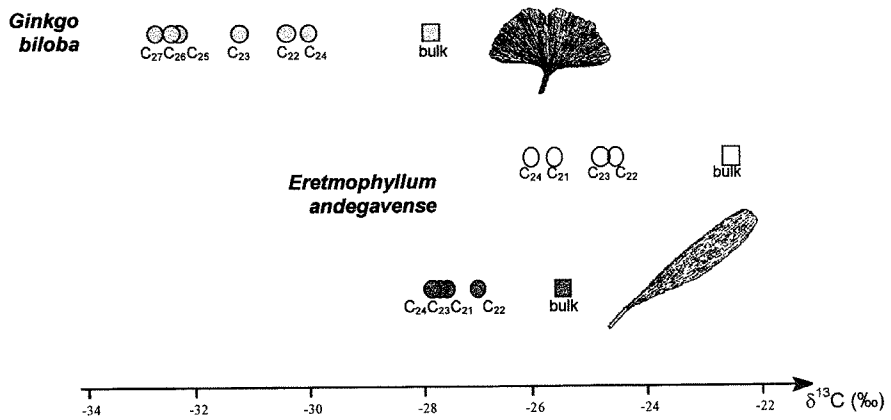

FIG. 1. Results of the isotopic analysis on fossil and extant Ginkgoales.

alkanes because they were previously shown to be the most stable compounds of *G. biloba* leaf lipids.

Results of isotopic analysis on individual *n*-alkanes and on the corresponding leaves are summarised in Fig. 1. *n*-Alkanes of *G. biloba* leaf lipids appear ^{13}C-depleted by about 3.5‰ when compared to the bulk leaves. This depletion varies from 2.3 to 5.1‰ according to the chain length, in agreement with literature data. When two distinct batches of *E. andegavense* leaves, with bulk $\delta^{13}C$ values separated by 3‰ are examined, similar depletion patterns are observed. Such results first confirm that the bulk isotopic signal is not significantly altered in *E. andegavense* fossil leaves. Secondly, they validate the use of free *n*-alkanes as biomarker of the isotopic signal of fossil Ginkgoales. Similar studies are under progress in order to validate the use of these biomarkers in other plant families. That should allow the investigation of the isotopic signal of carbon, on a wide range of fossil flora, even when bulk ratios are diagenetically altered.

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