Comparison of leaf lipids from a fossil Ginkgoale and its modern counterpart at two degradation stages

T. T. Nguyen Tu — Laboratoire de Biogéochimie isotopique, UMR 7618, Université Paris VI - CNRS - INRA, Case courrier 120, 4 Place Jussieu, 75 252 Paris Cedex 05, France

S. Derenne
C. Largeau — Laboratoire de Chimie Bioorganique, UMR 7573, ENSCP - CNRS, 11 Rue Pierre et Marie Curie, 75 231 Paris Cedex 05, France

A. Mariotti
H. Bocherens — Laboratoire de Biogéochimie isotopique, UMR 7618, Université Paris VI - CNRS - INRA, Case courrier 120, 4 Place Jussieu, 75 252 Paris Cedex 05, France

The investigation of fossil flora by organic geochemical methods has been widely used for the last decade and numerous studies established the precise chemical composition of lipids from fossil plants (*e.g.* Logan and Eglinton, 1994). Such studies provided a better understanding of the origin of organic matter in various sediments (*e.g.* Rieley *et al.*, 1991). While several studies investigated early and late diagenesis of sedimentary lipids (*e.g.* Cranwell 1981), little is known about diagenesis of lipids in fossil leaves themselves. In the present study, we examined the effects of diagenesis on leaf lipids, by investigating the chemical composition of total leaf waxes from a fossil plant, and from its modern equivalent at two different degradation stages.

The fossil plant studied is the Ginkgoale *Eretmophyllum andegavense,* was collected in an exceptionally well preserved fossil flora occurring in the 'Argiles du Baugeois', a Cenomanian lagoonal Member located near Angers, France (Pons *et al.*, 1981). Waxes from fresh leaves and leaves from a litter of the only extant Ginkgoale, *Ginkgo biloba,* were analysed along with leaf waxes from *E. andegavense* in order to: (i) establish a stability scale for the leaf lipids of *G. biloba*, (ii) test this stability scale on *E. andegavense*, and (iii) reveal possible common compounds of taxonomic value between both extant and fossil Ginkgoale.

Waxes of fresh leaves of *G. biloba*

Total waxes of *G. biloba* fresh leaves appear primarily constituted by phenolic compounds (Fig. 1): alkylphenols and alkyl, hydroxybenzoic acids with C_{13}, C_{15}, $C_{15:1}$, C_{17} and $C_{17:1}$ chains; and, to a lesser extent, dimethoxy, alkylcoumarins with C_{12}, $C_{14:1}$ and $C_{16:1}$ chains. These compounds are followed, in order of decreasing abundance, by nonacosan-10-ol, α-tocopherol and, to a lesser extent, nonacosan-10-one. More usual components of higher plant lipids are also detected in substantial amounts: C_{21}-C_{36} *n*-alkanes, C_8-C_{30} predominantly even fatty acids, C_{10}-C_{29} predominantly even primary alcohols and wax esters. Finally, a number of chlorophyll-derived compounds are identified in waxes from *G. biloba* fresh leaves: phytol, phytadiene and the regular C_{18} isoprenic ketone.

Evolution of *G. biloba* leaf waxes through litter formation

The content of total waxes (as weight % of the whole leaves) markedly decreases from the fresh samples of *G. biloba* to the litter (11.9 % instead of 29.0 %) showing that total waxes, as a whole, are more degraded than the non-waxy leaf constituents. The chemical composition of *G. biloba* leaf lipids does not undergo important qualitative upheavals through the early stages of degradation, however some trends are taking shape. On the one hand, a relative enrichment is noted for the acyclic isoprenoid constituents (phytol, phytadiene and C_{18} isoprenic ketone) and for the nonacosan-10-one. This shall reflect such compounds are not primary products and originate from the degradation of the phytyl chain of chlorophyll and of nonacosan-10-ol, respectively. On the other hand, a relative depletion is observed for all the primary waxy constituents of *G. biloba* leaves. The apparent level of degradation of the primary waxy compounds, calculated from variations in relative abundances between the fresh leaves and

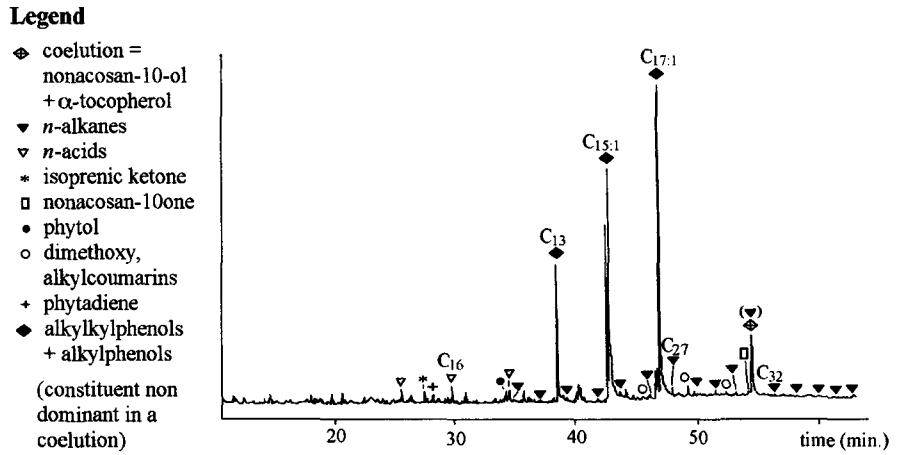

FIG. 1. Chromatogram of the crude extract of fressh leaves of *G. biloba*.

the litter, was used for establishing the following relative stability scale in *G. biloba* leaf waxes: *n*-alkanes > alkyl, hydroxybenzoic acids ⩾ alkylphenols > secondary alcohol > α-tocopherol > *n*-acids and dimethoxy, alkylcoumarins > primary fatty alcohols. This stability scale is in agreement with the one determined by Cranwell (1981) from studies on lake sediments.

Waxes of fossil leaves of *E. andegavense*

Waxes from the fossil Ginkgoale *E. andegavense*, appear less complex than the one of its extant counterpart. Except elemental sulphur and C_7-C_{12} α,ω diacids originating from the surrounding sediment and microbial degradation respectively, only C_{23}-C_{35} *n*-alkanes and C_{10}-C_{32} predominantly even acids are present in substantial amounts. Trace amounts of wax esters and $C_{14:1}$ and $C_{16:1}$ dimethoxy, alkylcoumarins are also detected. The occurrence, in *E. andegavense* extracts, of these typical compounds which are also present in *G. biloba* leaf waxes, confirms, on chemical bases, the phylogenetic link between both ginkgoales. According to the well known poor stability of unsaturated compounds through geological time, the presence of these coumarins shows that the excellent morphological preservation of *E. andegavense* leaves is associated with an unexpectedly high preservation of some wax lipids.

References

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