

## THE IMPORTANCE OF MOLECULAR PALAEOBOTANY

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**ABSTRACT.** Molecular palaeobotany involves the use of geochemical techniques to study morphologically well-characterised, discrete plants fossils. Selected examples are summarised of applications in 1) chemosystematic assessment of extinct plants, 2) interpretation of the taphonomic history and potential taphonomic bias of plant fossil assemblages, 3) understanding chemical transformations during diagenesis and potentially 4) to discover the original chemical composition of tissues in ancient plants and trace their chemical evolution.

**KEY WORDS:** chemosystematics, preservation, taphonomy, diagenesis, molecule, resistance, plant, geochemistry

### INTRODUCTION

The plant fossil record largely results from preservation of plant tissues and organs which are often decay resistant, having a strengthening or protective role during life. These plant parts contain a range of resistant macromolecules which exhibit various degrees of resistance to biodegradation (van Bergen *et al.* 1995a). These include the cyclic resins and aliphatic compounds (Fig. 1) algaenan (algal cell walls); cutin & cutan (cuticles); suberin & suberan (periderm); mixed sporopollenin (spore and pollen walls) or aromatic (Fig. 3) lignin (propagule walls, wood); tannins (secretions), resistant macromolecules. Results from geochemical analyses of fossils of these plant parts are valuable for many aspects of palaeobotany. Here we summarise selected examples of applications in systematics, taphonomy and the understanding of diagenesis.

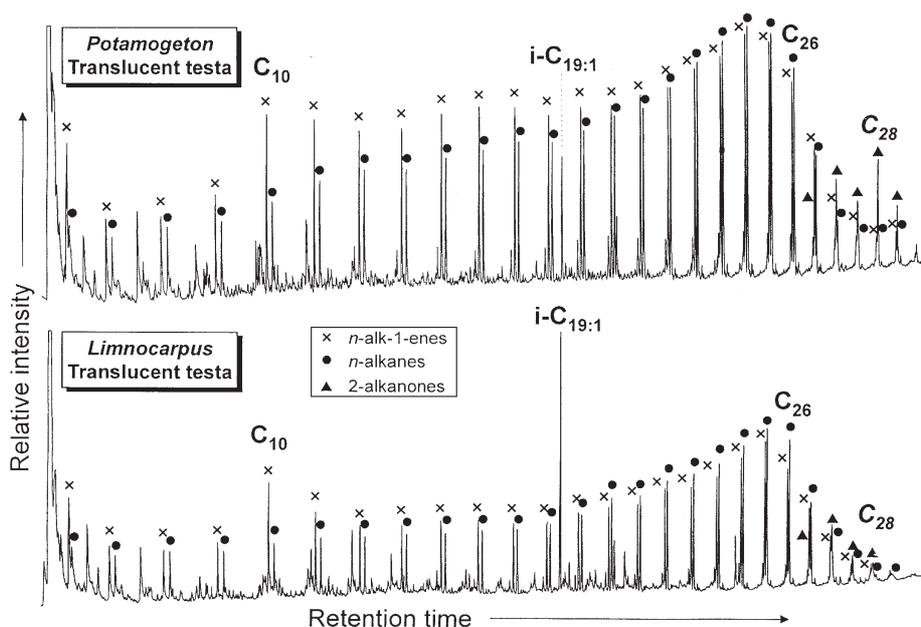
### METHODS

The morphology and, where appropriate, ultrastructure of the fossils is monitored by scanning and transmission electron microscopy in order to precisely characterise what is being analysed chemically. Chemical analytical approaches fall into three categories – pyrolysis, chemolysis and spectroscopy. Only the latter is non-destructive. A simple overview of the information obtained by each method is given in van Bergen *et al.* (1995a: 321–322). Pyrolysis is a well-established technique for studies of small samples of resistant organic material (van Bergen *et al.* 1995a). Statistical methods in combination with pyrolysis have proved to be a valuable tool (Stankiewicz *et al.* 1997). Detailed methods are given in the papers cited.

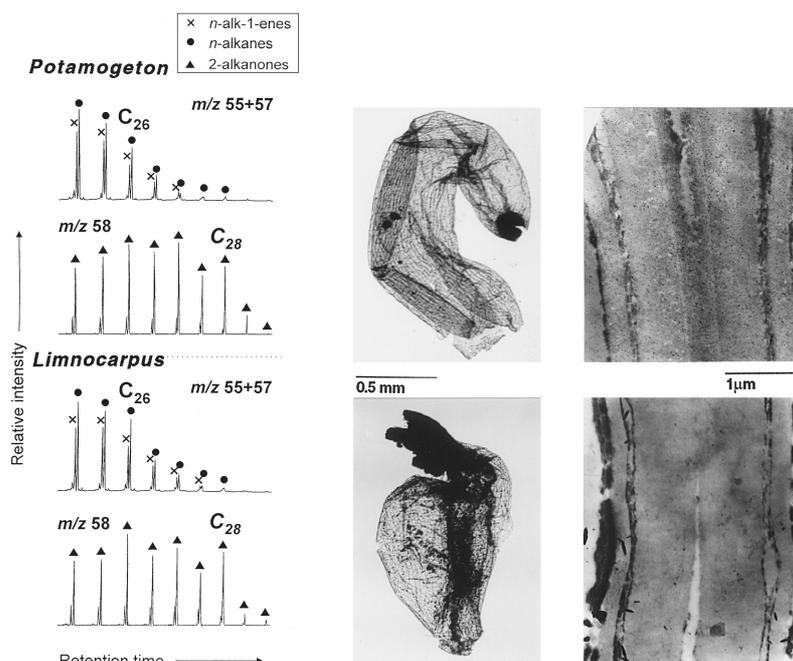
### CHEMOSYSTEMATICS AND CHEMICAL COMPOSITION

Diagenetic alterations make original chemical composition hard to deduce in older (e.g. Palaeozoic) plant fossils (Collinson & Jones 1996). Results may be equivocal as in Carboniferous medullosan ‘resin rodlets’ (van Bergen *et al.* 1995b) the chemistry of which may represent merely a strongly altered, hence unidentifiable, tannin or a secretion unique to medullosans. Permineralised periderm of a Carboniferous arborescent lycophyte showed an aliphatic suberan-like composition (Collinson *et al.* 1994). This needs further confirmation, but if universal has implications for biomechanical interpretations.

Distinctive chemical signatures have been shown to survive in Carboniferous lycopsid and seed megaspores; Carboniferous lycopsid, cordaite and pteridosperm cuticles; and Mesozoic conifer and *Ginkgo* cuticles (Collinson *et al.* 1994, 1998, Hemsley *et al.* 1995, Möslle *et al.* 1998, Stankiewicz *et al.* 1998). However, these are not yet sufficiently well-characterised to be used for chemosystematic purposes. In contrast, clear chemosystematic signatures have been recorded in various Cainozoic seeds and fruits both in the aliphatic and aromatic macromolecules. The distribution patterns (Figs 1, 2) of *n*-alkenes and *n*-alkanes and 2-alkanones in total ion chromatograms (Fig. 1) and individual mass chromatograms (Fig. 2) from the translucent testa cuticle of extinct *Limnocarpaceae* from Eocene/Oligocene transitional strata of England show clear chemosystematic relationship with *Potamogeton*. This is fully supported by morphological comparisons (Fig. 2; Collinson 1982). These signatures



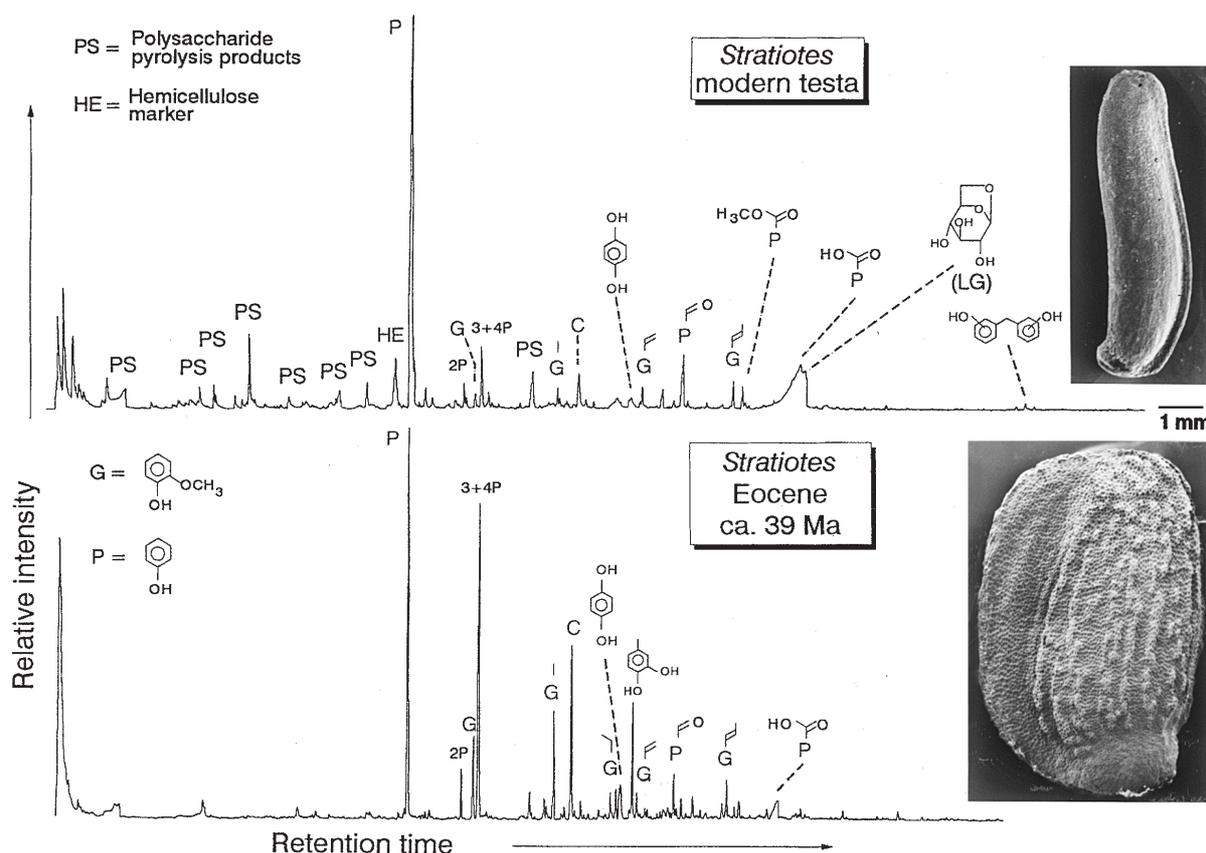
**Fig. 1.** Total ion chromatograms of aliphatic macromolecules dominated by alkene-alkane doublets and showing the chemosystematic affinity between extinct *Limnocarpus* and *Potamogeton*. Both samples from the Eocene/Oligocene transitional strata of the Isle of Wight, England. Further detail shown in Fig 2



**Fig. 2.** Portions of mass chromatograms from material in Fig. 1 confirming the strength of the chemosystematic affinity between *Limnocarpus* and *Potamogeton*. Material analysed is illustrated by LM (center) and TEM (right), the latter showing clearly the cuticular nature of these structures as well as identical organisation in the two genera

are quite distinct from those of other translucent testa and tegmen cuticles from the same strata such as those of *Sparganium* and *Typha* which themselves share a common chemosystematic signature supporting their close systematic affinity (van Bergen *et al.* 1995a, van Bergen *et al.* unpublished). Specific chemical markers from the

sclerotesta of modern *Stratiotes* seeds have been recorded in the modified lignin of Eocene *Stratiotes* testae (Fig. 3) (van Bergen *et al.* 1995a). Van Bergen *et al.* (in preparation) have documented the chemosystematic affinity of extinct *Spirematospermum* with Musaceae through recognition of characteristic chemical signatures



**Fig. 3.** Total ion chromatograms of sclerotic testae showing a typical modern aromatic macromolecule, the lignin-cellulose-hemicellulose complex, and its modified condition in Eocene material with loss of PS and HE but with the retention of most lignin markers i.e. G (Guaiacyl) and P (para-hydroxyphenyl) units. In spite of the chemical alteration specific markers of chemosystematic significance in *Stratiotes* (1,4-benzenediol, 4-formyl-phenol and 4-carboxy-phenol) still survive. Material analysed is illustrated by SEM

in the sclerotesta. Stankiewicz *et al.* (1997) showed chemosystematic relationship between seeds and cones of modern and Polish Miocene *Sequoia* and *Pinus* sp. using principal component analysis based on pyrolysis results.

Van Aarsen *et al.* (1994) reported the occurrence of resins with a polycadinene structure *in situ* in fossil mastixioid Cornaceae fruits. This work thus proved that this resin type was not unique to dipterocarps and provided a potential source for biomarkers present in oils from outside Southeast Asia.

#### TAPHONOMIC HISTORY AND CHEMICAL TRANSFORMATIONS

Assessment of chemical alterations is relevant to all taphonomic studies but is rarely applied (Collinson & Jones 1996). Hooker *et al.* (1995) showed the distinction between morphologically well-preserved and poorly preserved *Stratiotes* seeds, the former with modified lignin chemistry (Fig. 3, Eocene) and the latter with chemistry drastically altered to a simple polyphenol-type macromolecule. The latter seeds were thought to have undergone chemical degradation in oxidative conditions at the

sediment or water surface prior to deposition. It is very clear from this and other studies on seeds and fruits (van Bergen *et al.* 1996 and summary in van Bergen *et al.* 1995a) and studies of cuticles (Collinson *et al.* this volume, 1998, Möslle *et al.* 1998, Stankiewicz *et al.* 1998) that major chemical changes to both aromatic and aliphatic macromolecules can take place with minimal (or no recordable) alteration to morphology and ultrastructure. Given this fact 'chemotaphonomy' has considerable potential to reveal otherwise cryptic taphonomic and diagenetic history. Explanations for chemical transformations in lignin-cellulose complexes must allow for the retention of morphology even after drastic chemical alteration (Van Bergen *et al.* 1994a).

Van Bergen *et al.* (1995a) reported an exceptionally high preservational quality of the lignin-cellulose-hemicellulose complex in the testa of middle Miocene *Stratiotes* from Belchatow, Poland, which was taken to indicate minimal diagenetic effects/thermal maturation on that seed-containing sequence. The preservation contrasted with even Pleistocene examples of other sclerotestae where the more labile constituents are already altered (Van Bergen *et al.* 1994a, 1995a, 1996). Retention of intact gross morphology in seeds or endocarps may

contribute to a dramatic reduction in decomposition of the more labile biomacromolecules. This may partly explain the retention of cellulose in Polish Miocene *Stratiotes* (above) and Polish Miocene *Symplocos* as well as the abundance of syringyl moieties in Miocene & Oligocene *Nyssa* (Boon *et al.* 1989, Stankiewicz *et al.* unpublished). Van Bergen *et al.* (1994b) reported that enclosing lithology can affect the preservation of the sclerotesta lignin-cellulose complex with, counter-intuitively, the coarser-grained lithologies favouring better preservation. In contrast, preservation of the aliphatic macromolecules of the tegmen cuticles was not affected by lithology (Van Bergen *et al.* 1994b) and it is judged that these macromolecules survive with minimal alteration (Van Bergen *et al.* 1995a). Chemical compositions of aliphatic macromolecules in fossil leaf cuticles have also been shown to be unaffected by differences in enclosing lithology or age or thermal maturity (Mösle *et al.* 1998).

Combined studies of aromatic and aliphatic macromolecules from a single sample thus have considerable potential to reveal taphonomic and diagenetic history. Seeds, fruits and cones which often combine both types of macromolecules, represent an ideal tool for this work. Major advances in this field require increased understanding of the factors which control or facilitate specific chemical changes.

#### TAPHONOMIC BIAS

Tegelaar *et al.* (1991) suggested that selective preservation of the highly resistant macromolecule cutan was involved in preservation of fossil leaves and argued that the fossil record would be biased against those leaves which did not contain cutan. In contrast, Collinson *et al.* (1998, this volume) have shown that modern cuticles of conifers and *Ginkgo* yield no recoverable resistant residue. Therefore, they either contain no cutan or only a minute amount of cutan and hence selective preservation of cutan cannot explain the preservation of leaves of *Ginkgo* or conifers as fossils. Furthermore, a highly resistant original chemical composition of cuticles is not a prerequisite for the preservation of leaf cuticles as fossils. Preservation will be influenced by the existence of conditions (as yet not understood) which facilitate the chemical changes to cuticles which render them resistant i.e. formation of a macromolecular matrix by within-cuticle stabilisation of normally labile constituents (probably including cutins and entrained and surface waxes) (Collinson *et al.* 1998, Stankiewicz *et al.* 1998).

Van Bergen *et al.* (1996, 1997) have shown that the sclerotic tissue of the propagule of *Nelumbo* (Nelumbaceae) has a quite different chemistry (a tannin-

polysaccharide complex) from the lignin-cellulose complex of the testa of other water lilies s.l. of the Nymphaeaceae or Cabombaceae. This difference may well account for the absence of a fossil record of *Nelumbo* propagules. The fossil record is likely to be strongly biased against fruits and seeds which lack a sclerotic layer containing a lignin-cellulose complex and which also lack cuticular layers (for which resistance may be due to original presence of cutan-like macromolecules (van Bergen *et al.* 1995a) or possibly due to early diagenetic modification).

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