Research article

The nature and fate of natural resins in the geosphere XIII: a probable pinaceous resin from the early Cretaceous (Barremian), Isle of Wight

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Abstract

Terpenoid resin is produced by all families and most genera of the order Coniferales (the conifers), and the distribution of terpenes present in most conifer resins is characteristic of the originating family. Analyses of early Cretaceous (Barremian) amber (fossil resin) from the English Wealden, Isle of Wight, southern England, by pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), indicate a terpene distribution dominated by abietane- and labdane-type terpenes. Similar distributions are observed in some species of the extant family Pinaceae. The Pinaceae are well represented within the Wealden deposits of southern England, by only one (known) species, Pityites solmsii (Seward) Seward, whereas the macro-fossil record of these deposits is dominated by the extinct conifer family Cheirolepidiaceae, for which no resin chemistry has been reported. By analogy with modern materials, it is probable that the ambers found in these deposits are derived from an extinct member of the Pinaceae, but given the absence of evidence concerning the chemotaxonomy of the Cheirolepidiaceae, this family cannot be excluded a priori as a possible paleobotanical source. These ambers may therefore be assigned to either the Pinaceae or to the Cheirolepidiaceae. These samples are the oldest ambers to date to yield useful chemotaxonomic data.

Background

The Isle of Wight, off the south coast of England, is well known for rich lower Cretaceous (Barremian) fossil beds. In addition to numerous fossil fauna, (the Isle of Wight is widely recognized as one of the most important dinosaur fossil sites in the world), extensive floral remains have also been reported. The paleoenvironment of these deposits has been characterized by Insole and Hutt [1] as semi-arid, with distinct wet and dry seasons. Based upon macrofossil evidence, Oldham [2] concluded that the paleoflora contributing to these strata was dominated by genera of the extinct conifer family Cheirolepidiaceae. Alvin et al. [3] further refined this assignment and have reported that the dominant conifer in this environment was Pseudofrenolopsis parceramosa, creating stands wherein Brachyphyllum obesum grew beneath the canopy. Infrequent examples of other taxa, including species assigned to the Pinaceae, Araucariceae, and Taxodiaceae (now considered part of the Cupressaceae), have also been reported in the Wealden [2,4,5], although the assignment of these early Cretaceous specimens to modern families has been challenged [5].

Almost all modern conifers produce resinous exudates. In extant species, these resins are dominated by di- tri- and/or tetracyclic diterpenes. Mono and sesquiterpenoids are

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also common constituents, and triterpenoids are present in some cases [6], but these are less important overall than diterpenoids in most conifer resins. Resins are also highly durable materials that are resistant to many of the biogeochemical processes that degrade other plant tissues and are, therefore, of considerable chemotaxonomic value as geochemical markers of fossil taxa. Nicholas et al. [7] have reported small amounts of well preserved fossil resin (amber) in association with the fossil flora within lignitic marls of the Grange Chine, Wessex Formation: Wealden Group (Barremian: Early Cretaceous) on the south west coast of the Isle of Wight. The lignitic marls are associated with fossiliferous green-gray mudstones that are characterized by abundant plant debris [8]. The locality is described in detail by Nicholas et al. [7]. Nicholas et al. [7], and later Seldon [9], have reported infrared spectra of amber from the Isle of Wight and on the basis of the results obtained have suggested familial affiliation with the extant families Cupressaceae, Araucariaceae, or Taxodiaceae. However, spectroscopic analyses of complex mixtures such as resins provide only a broad "fingerprint" and are, therefore, significantly less reliable than detailed molecular level characterization for chemotaxonomic purposes. The objective of this work was to attempt to determine possible paleobotanical sources of these ambers by using Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) analyses.

Experimental
Samples of amber from the Isle of Wight were obtained by request from the Dinosaur Isle Museum, Isle of Wight. Py-GC-MS analyses of the amber were performed as previously described [10]. Pyrolytic techniques for resin analysis require minimal sample (typically <500 μg/analysis), provide detailed molecular level data for individual products and, by variation of pyrolysis conditions, can provide information concerning both occluded low molecular weight components and macromolecular constituents of the sample [11]. For the studies described herein, samples were fractured, and small pieces (~200–400 μg) were pyrolyzed with tetramethylammonium hydroxide (TMAH) and the resulting products analyzed by gas chromatography mass spectrometry. Samples were pyrolyzed at temperatures of Tpy = 300 or 480°C to differentiate pyrolyzed with tetramethylammonium hydroxide behavior with those of known standards.

Results
The results of Py-GC-MS analysis (Tpy= 480°C) of Isle of Wight amber are illustrated in Figure 1. Supporting data are also given in Additional File 1. Except as noted below in discussion of experiments carried out at different pyrolysis temperatures, all of the data generated in these analyses are identical to the results illustrated in Figure 1, indicating that all of the individual amber fragments analyzed are derived from a common botanical source. The structures of the products identified are illustrated in Figure 2.

The products observed in all analyses are dominated by abietane-type diterpenoids, especially dehydroabiatic acid (23), 18-nor dehydroabietane (9) and lesser amounts of analogous and isomeric products. Small amounts of bicyclic products (5 and 6) and related decarboxylation products (2), characteristic of regular polylabdanoids [13-15], are also observed. Trace amounts of a single pimarane-type diterpenoid (15) are also observed. Diterpenoids of other structural families are apparently absent.

The distribution of intact diterpenoids observed in experiments carried out at Tpy = 300°C is indistinguishable from that observed in Figure 1. Under these conditions, macromolecular materials are not broken down into lower molecular weight volatile fragments and hence, are not represented in the observed analytes (i.e. compounds 2, 5, and 6 are absent in these data). The identity of the distributions of abietane-type terpenoids in the 480°C and 300°C data indicates that these compounds are present as occluded materials that are not bound into a macromolecular network.

Discussion
Previous reports of analyses of Cretaceous ambers contain familiar, multi-class terpene distributions [10,16,17] and there is no reasonable geochemical route for conversion of other diterpenoids into the abietane-type structures observed in this distribution. There is also no geochemical evidence suggesting significant thermal alteration or excessive oxidation of these samples, and the depositional setting from which they were recovered suggests a very mild geologic history. Therefore, these data represent a unique chemotaxonomic signature of the original source resin.

Labdanoid- and abietane-type diterpenoids are common constituents of the resins of many extant conifer families but typically occur in conjunction with a variety of other types of diterpenoids. In modern resins, the exclusive presence of labdanoid- and abietane-type diterpenoids is an indicator of the Pinaceae [6,18-20]. Pinaceae resins are usually predominated by abietanoic acids and lack phenolic diterpenes such as ferruginol or sugiol [6]. These
observations are consistent with the results presented here, wherein the Isle of Wight analyses are dominated by dehydroabietic acid and phenolic abietanes are absent. Pinaceae resins are also marked by an absence of tetracyclic terpenoids, e.g. kaurane or phyllocladane [6], also consistent with the data presented here.

By analogy with extant resins the observed distribution of diterpenes in these samples suggests a paleobotanical affinity with the Pinaceae. This assignment is supported by the minor presence of an early pinaceous species (Pityites solmsii (Seward) Seward) within the Wealdon deposits [4].

However, macrofossil evidence indicates that species belonging to the Cheirolepidiaceae were by far the dominant conifers contributing to these deposits. Phylogenetic relationships between the Cheirolepidiaceae and extant conifer families are uncertain [21]. To date, only one instance of possibly cheirolepidiaceous amber has been reported [22] and no rigorous geochemical analysis of amber unambiguously associated with the Cheirolepidiaceae has been described [16]. Data describing the extract of fossil leaves of Frenelopsis alata has been reported [23], showing that the extract contained many terpenoids associated with conifer resins, including some abietane type diterpenes. However, the relationship between the terpene composition of leaf extracts and resins is tenuous. Furthermore, the leaf extracts reported are from the cheirolepidiaceous genus Frenelopsis. The genera of Cheirolepidiaceae present in the Isle of Wight deposits are reported to be Pseudofrenelopsis and Brachyphyllum. Despite the similarity of the names assigned to these genera (Frenelopsis and Pseudofrenelopsis), these are distinct taxa and therefore, these data do not preclude the possibility that the resin chemistry of the Cheirolepidiaceae genera present in the Isle of Wight deposits may have been similar to the resin chemistry of the extant Pinaceae. Hence, the lack of geochemical data, as well as the dominance of the Cheirolepidiaceae within
these deposits, precludes a priori exclusion of this family as a potential source of these samples. Therefore, in the absence of additional data, the Cheirolepidiaceae must be included as a possible source for the samples characterized in the present study.

Conclusion
Py-GC-MS analyses of early Cretaceous resin from the Isle of Wight, southern England, indicate that these resins are dominated nearly exclusively by abietane-type and labdanoid-type diterpenes. While this distribution provides a compelling argument for the assignment of these samples to the Pinaceae, the lack of geochemical data for the dominant conifers in the deposits, the Cheirolepidiaceae, precludes the exclusion of this family as a possible source of these samples. It is also not unreasonable to suggest that the Pinaceae may be under represented in the fossil record or that Pityites solmsii (Seward) Seward, the only well represented pinaceous species from the Isle of Wight, may have been a copious resin producer in the environment. Therefore, until clear data concerning the resin chemistry of the Cheirolepidiaceae is presented, the distribution presented here is equivocally assignable to either family. This work has demonstrated the use of resin chemistry in the Early Cretaceous, and these resins are the oldest resins to date to yield useful chemosystematic data.

Figure 2
Structure Key. Numbering of individual structures corresponds with numbering of chromatographic peaks illustrated in Figure 1.
Additional material

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References

1. Insole AN, Hunt S: The palaeoecology of the dinosaurs of the Wessex Formation (Wealden Group, Early Cretaceous), Isle of Wight, Southern England. Zool J Linn Soc 1994, 112:197-215.
2. Oldham TCB: Flora of the Wealden Plant Debris Beds of England. Paleontology 1976, 19:437-502.
3. Alvin KL, Fraser CJ, Spicer RA: Anatomy and palaeoecology of Pseudofrenelopsis and associated conifers in the English Wealden. Paleontology 1981, 24:759-778.
4. Watson J, Alvin KL: An English Wealden floral list, with comments on possible environmental indicators. Cretaceous Res 1996, 17:5-26.
5. Hughes NF: Plant succession in the English Wealden strata. Proc Geol Assoc 1975, 86:439-455.
6. Otto A, Wilde V: Sesqui- and triterpenoids as chemosystematic markers in extant conifers – a review. Bot Rev 2001, 67:141-238.
7. Nicholas CJ, Henwood AA, Simpson M: A new discovery of early Cretaceous (Wealden) amber from the Isle of Wight. Geol Mag 1993, 130:847-850.
8. Wright VP, Taylor KG, Beck VH: The paleohydrology of Lower Cretaceous seasonal wetlands, Isle of Wight. J Sediment Res 2000, 70:619-632.
9. Seldon PA: First British Mesozoic spider, from Cretaceous amber of Isle of Wight, Southern England. Palaeontology 2002, 45:973-983.
10. Anderson KB: The nature and fate of natural resins in the geosphere. XII. Investigation of C-9 aromatic diterpenoids in Raritan amber by pyrolysis-GC-matrix isolated FTIR-MS. Geochem Trans 2006, 7:2.
11. Anderson KB, Winsans RE: The nature and fate of natural resins in the geosphere. I. Evaluation of pyrolysis-gas chromatography/mass spectrometry for the analysis of natural resins and resinites. Anal Chem 1991, 63:2901-2908.
12. Zinkel DF, Zink LC, Wieloslowski MF: Diterpene resin acids. A compilation of infrared, mass nuclear magnetic resonance ultraviolet spectra and gas chromatographic retention data (of methyl esters) U.S. Department of Agriculture; 1971:191.
13. Anderson KB: New evidence concerning the structure, composition, and maturation of Class I (Polylabanoid) resinites. In ACS Symposium Series Volume 617. Edited by: Anderson KB, Crelling JC. Washington: ACS; 1995:105-129.
14. Anderson Ken B, Winsans RE, Botto RE: The nature and fate of natural resins in the geosphere-II. Identification, classification, and nomenclature of resinites. Org Geochem 1992, 18(6):829-41.
15. Anderson KB: The Nature and Fate of Natural Resins in the Geosphere. IV. Middle and Upper Cretaceous Amber from the Taimyr Peninsula, Siberia – Evidence for a New Form of Polylabanoid Resinite and Revision of the Classification of Class I Resinites. Org Geochem 1994, 21(2):209-212.
16. Alonso J, Arillo A, Barron E, Corral JC, Grimalt J, Lopez JF, Lopez R, Martinez-Delcos X, Ortuño V, Penalver E, Trincas PR: A new fossil resin with biological inclusions in lower Cretaceous deposits from Alava (Northern Spain, Basque-Cantabrian Basin). J Paleontol 2000, 74:158-178.
17. Chaler R, Grimalt JO: Fingerprinting of Cretaceous higher plant resins by infrared spectroscopy and gas chromatography coupled to mass spectrometry. Phytochem Anal 2005, 16(4):446-450.
18. Hautevelle Y, Michels R, Malartre F, Troullier A: Vascular plant biomarkers as proxies for palaeoclimatic changes at the Dogger/Malm transition of the Paris Basin (France). Org Geochem 2006, 37:610-625.
19. Otto A, Simonite BRT: Biomarkers of Holocene buried conifer logs from Bella Coola and north Vancouver, British Columbia, Canada. Org Geochem 2002, 32:1241-1251.
20. Otto A, Simonite BRT, Wilde V, Kunzmann L, Puttmann W: Triterpenoid composition of three fossil resins from Cretaceous and Tertiary conifers. Rev Palaeobot Palynol 2002, 120:203-215.
21. Watson J: The Cheirolepidiaceae. Origin and Evolution of Gymnosperms 1998:382-447.
22. Schmidt AR, Ragazzi E, Crippiotti O, Roghi G: A microwORLD in Triassic amber. Nature 2006, 444:835.
23. Nguyen Tu TT, Derenne S, Largeau C, Mariotti A, Bocherens H, Pons D: Effects of fungal infection on lipid extract composition of higher plant remains: comparison of shoots of a Cenomanian conifer, uninfected and infected by extinct fungi. Organic Geochemistry 2000, 31:1743-1754.

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