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Natural Product Terpenoids in Eocene and Miocene Conifer Fossils

Angelika Otto,[1]*† James D. White,[2] Bernd R. T. Simoneit[1]

Numerous saturated and aromatic hydrocarbons, but not polar compounds, originating from plants and microorganisms (biomarkers) have been reported in sediments, coals, and petroleum. Here we describe natural product terpenoids found in two fossil conifers, *Taxodium balticum* (Eocene) and *Glyptostrobus oregonensis* (Miocene). A similar terpenoid pattern is also observed in extant *Taxodium distichum*. The preservation of characteristic terpenoids (unaltered natural products) in the fossil conifers supports their systematic assignment to the Cypress family (Cupressaceae sensu lato). The results also show that fossil conifers can contain polar terpenoids, which are valuable markers for (paleo)chemosystematics and phylogeny.

Most sediments contain solvent-extractable organic compounds that are derived from natural product precursors biosynthesized by living organisms. These biomolecules are degraded before and after burial in sediments to their diagenetic products (geomolecules). Despite various chemical transformations, the geomolecules retain their characteristic basic structural skeletons and can thus be used as biomarkers for their biological origin. Such biomarkers can provide information on the source of organic matter in sediments, paleoclimate, and gas and coal geochemistry, and they can be used as tracers in environmental studies (*1–4*). Most of the previous studies have focused on the saturated and aromatic biomarker hydrocarbons. Because the degradation of numerous polar precursor molecules may result in the generation of the same hydrocarbon product (*5, 6*), the hydrocarbons are characteristic only for wider groups of organisms, such as conifers, angiosperms, or bacteria. In contrast, only slightly degraded or unaltered polar compounds are more specific biomarkers, because the natural product precursors have a distinct distribution in living organisms. For this reason, the composition of polar compounds in geological samples is of particular significance. The preservation potential of polar compounds in sediments is believed to be very low (*7*) because they generally undergo rapid diagenetic processes, such as degradation, reactions with other compounds, or bonding to the insoluble kerogen (*8*). Here we show that polar terpenoids can be preserved as unaltered natural products in fossil conifers and discuss their implications for chemosystematics and phylogeny.

[1]Environmental and Petroleum Geochemistry Group, College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, USA. [2]Department of Chemistry, Oregon State University, Corvallis, OR 97331, USA.

*Present address: Johann Wolfgang Goethe-Universität Frankfurt/Main, Institut für Mineralogie–Umweltanalytik, Georg-Voigt-Strasse 14, D-60054 Frankfurt/Main, Germany.

†To whom correspondence should be addressed. E-mail: a.otto@kristall.uni-frankfurt.de

We analyzed the extractable organic matter of seed cones of *Taxodium balticum* from clays of the Eocene Zeitz formation, Germany, to search for preserved resin compounds that might be useful as chemosystematic markers (*9–11*). The phenolic abietane diterpenoids ferruginol (compound 1), 6,7-dehydroferruginol (compound 2) and sugiol (compound 3) were major components in the aromatic fraction of the extract from the Eocene *Taxodium balticum* cone (Fig. 1A) (table S1). Two compounds (4 and 5) with a molecular mass of 448 daltons and similar mass spectra are also detectable as major components in the aromatic fraction. We also identified 6,7-dehydroferruginol, ferruginol, sugiol, and the two unknown compounds (4 and 5) in the total extract of a *Glyptostrobus oregonensis* cone from the Miocene Clarkia formation, USA (*12–13*) (Fig. 1B). Ferruginol has also been reported previously from lignites (*14*) and an Oligocene sediment rich in *Taxodium balticum* (*15*).

When we analyzed the seed cone of extant *Taxodium distichum* (swamp cypress) (Fig. 1C) for comparison of the terpenoid contents, we also detected 6,7-dehydroferruginol, ferruginol, sugiol, and the two unknown compounds (4 and 5) together with some diterpenoids (f, g, and k), which were previously reported from the species (*16*). The mass spectra of the newly observed compounds matched the mass spectrometric fragmentation patterns of the triterpenoids isochamaecydin (4) and chamaecydin (5), which have been published (*17*). Both the mass spectra and the gas chromatography retention indices of the two triterpenoids (as both free

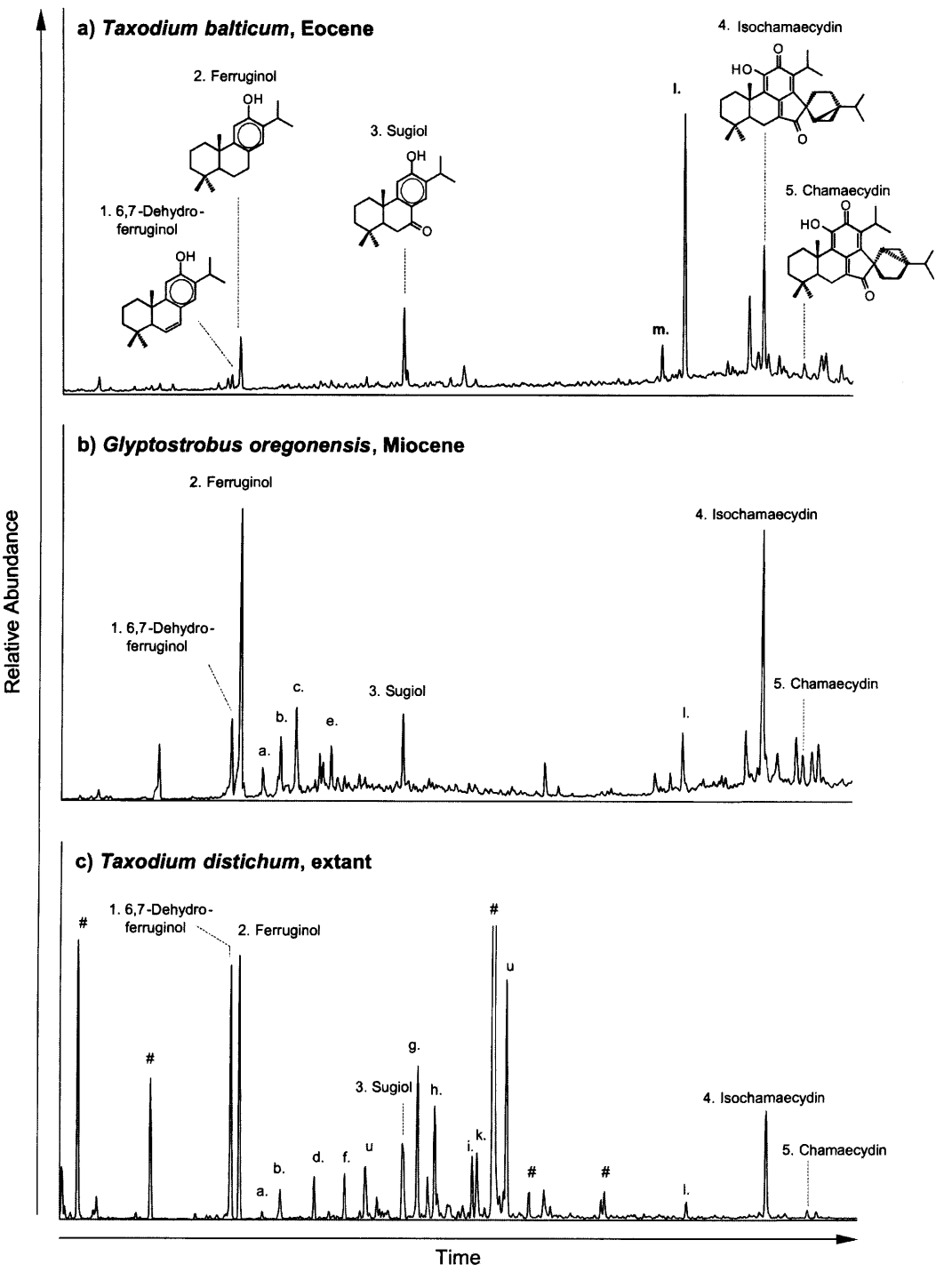

Fig. 1. Gas chromatography–mass spectrometry traces of total ion current (TIC) of (**A**) the aromatic compound fraction from the extract of the seed cone of Eocene *Taxodium balticum*, (**B**) the total extract of the seed cone of Miocene *Glyptostrobus oregonensis*, and (**C**) the total extract of the seed cone of extant *Taxodium distichum*. Compounds are analyzed after trimethylsilyl (TMS) derivatization: 1. 6,7-dehydroferruginol; 2. ferruginol; 3. sugiol; 4. isochamaecydin; 5. chamaecydin; a. taxodione acetate; b. pimaric acid; c. 18- or 19-hydroxyferruginol; d. 7-acetoxy-6,7-dehydroroyleanone; e. communic acid; f. royleanone; g. taxoquinone; h. 6-hydroxytaxoquinone; i. isomer of g; k. taxodone; l. inuroyleanone; 11,14-dioxolambertic acid, 11,14-dioxopisiferic acid, or similar compound; m. isomer of l; u. unknown; # = sugars.

and derivatized compounds) are identical for the extant and fossil samples (table S2). The extract of a seed cone of extant *Glyptostrobus pensilis* (Chinese water pine) contained 6,7-dehydroferruginol, ferruginol, sugiol, pimaric acid (b), and 18- or 19-hydroxyferruginol (c), as observed in the Miocene *Glyptostrobus oregonensis* cone, but isochamaecydin and chamaecydin could not be detected (*13*) (fig. S1).

Terpenoids are abundant constituents of extant conifers and are used as chemosystematic characteristics (*18–21*). Ferruginol, 6,7-dehydroferruginol, and sugiol are common in extant conifers, especially in the families Cupressaceae, Taxodiaceae, and Podocarpaceae (*18, 20–22*). The unusual triterpenoids isochamaecydin and chamaecydin have hitherto been identified in only two conifer species, Hinoki cypress (*Chamaecyparis obtusa*) and Sugi cedar (*Cryptomeria japonica*) (*17, 23, 24*). We were able to confirm these findings and identified isochamaecydin and chamaecydin in the extracts of seed cones of both species. *Taxodium, Glyptostrobus*, and *Cryptomeria* were formerly treated as members of the Taxodiaceae, and *Chamaecyparis* was assigned to the Cupressaceae, but Taxodiaceae and Cupressaceae were recently merged into one family, Cupressaceae sensu lato (s. l.) on the basis of morphological and molecular genetic data (*25, 26*). The terpenoid compositions detected here in fossil and extant species of former Taxodiaceae support this merger. The similarity of the terpenoids in *Taxodium* and *Glyptostrobus* is not surprising, as these genera are closely related (*25*). The terpenoid characteristics of fossil *Taxodium balticum* and *Glyptostrobus oregonensis* identified here are thus in accordance with their systematic assignment to the Cupressaceae s. l. based on their morphological characteristics.

The results show that polar natural product precursors can be preserved unaltered in fossil conifers and can be used as chemosystematic markers. The applied methods offer a new approach for studying the (paleo)chemosystematics and phylogeny of conifers. The low degree of degradation observed in the analyzed material may be due to the preservation of terpenoids in resinous plant material where the compounds are probably trapped in the resin and protected from degradation or bonding into kerogen. Furthermore, the clayey sediments should prevent the oxidation of the fossil plant material by oxygen-rich waters.

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Supporting Online Material

www.sciencemag.org/cgi/content/full/297/5586/1543/DC1
Materials and Methods
Fig. S1
Tables S1 and S2

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Global Biodiversity, Biochemical Kinetics, and the Energetic-Equivalence Rule

Andrew P. Allen,* James H. Brown, James F. Gillooly

The latitudinal gradient of increasing biodiversity from poles to equator is one of the most prominent but least understood features of life on Earth. Here we show that species diversity can be predicted from the biochemical kinetics of metabolism. We first demonstrate that the average energy flux of populations is temperature invariant. We then derive a model that quantitatively predicts how species diversity increases with environmental temperature. Predictions are supported by data for terrestrial, freshwater, and marine taxa along latitudinal and elevational gradients. These results establish a thermodynamic basis for the regulation of species diversity and the organization of ecological communities.

Global gradients in biodiversity exist for all major groups of terrestrial (*1*), freshwater (*2*), and marine taxa (*3*), but the general principles underlying their origin and maintenance remain unclear (*4, 5*). Here we present a theoretical framework that explains gradients of species diversity in terms of energetics. Our model is derived by extending the well-established "energetic-equivalence rule" (*6*) to include temperature. In its original form, the energetic-equivalence rule states that the total energy flux of a population per unit area, B_T, is invariant with respect to body size. Species of different size have similar values of B_T because individual metabolic rates, B_i, increase with body size, M_i, as $B_i \propto M_i^{3/4}$, whereas population densities per unit area, N_i, decrease with body size as $N_i \propto M_i^{-3/4}$ ($B_T = N_i B_i \propto M_i^{-3/4} M_i^{3/4} = M^0$). This inverse relation between abundance and body size is observed for plants and for endothermic and ectothermic animals; it reflects mechanistic connections between individual metabolic rates, rates of energy flux by populations, and the partitioning of available energy among species in a community (*6, 7*).

We can extend the energetic-equivalence rule to include temperature by incorporating the biochemical kinetics of metabolism. Recent work has shown that whole-organism metabolic rate varies with body size and temperature as $B = b_o M^{3/4} e^{-E/kT}$ (*8*), where b_o is a normalization constant independent of size

Department of Biology, University of New Mexico, Albuquerque, NM 87131, USA.

*To whom correspondence should be addressed. E-mail: drewa@unm.edu