

CHARACTERIZING MODERN AND FOSSIL GYMNOSPERM EXUDATES USING MICRO-FOURIER TRANSFORM INFRARED SPECTROSCOPY

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Infrared absorption spectra of exudates from 65 species of gymnosperms were measured using micro-Fourier transform infrared (FTIR) spectroscopy. On the basis of the infrared spectra, three compositionally distinct groups of exudates can be distinguished: resins, volatile-rich resins, and gums. Resins and volatile-rich resins are mainly composed of terpenoids, whereas gums are polysaccharides. Resins and volatile-rich resins are restricted to conifers (Pinophyta). Gums, on the other hand, are produced by some conifer families including Araucariaceae and Podocarpaceae; nonconifer gymnosperms including *Ginkgo* (Ginkgophyta), cycads (Cycadophyta), and *Welwitschia* (Gnetophyta); and angiosperms. Using spectral band ratios, conifer resins can be subdivided quantitatively into two distinct resin types that reflect compositional differences in their terpenoid constituents and broadly parallel different conifer families. The first type of resin (pinaceous resin) is produced by members of Pinaceae and consists mainly of diterpenes that are based on abietane/pimarane skeletal structures. The second type (cupressaceous resin) is associated with members of the Cupressaceae, Sciadopityaceae, Araucariaceae, and Podocarpaceae and consists mainly of diterpenes that are based on the labdanoid structures. Variability within the resin spectra correlates with the number of free hydroxyl groups, and it can be used to assess the degree of resin polymerization. Volatile-rich resins are found exclusively within Pinaceae, reflecting a generally higher abundance of volatile mono- and sesquiterpenoids in resins of this family. The results of the FTIR spectroscopy have direct implications for the assessment of the fossil potential and the chemotaxonomic interpretation of modern and fossil gymnosperm exudates.

Keywords: chemotaxonomy, plant resin, gum, conifers, paleobotany.

Introduction

Exudates, as secondary metabolites of plants, are the products of genetically controlled metabolic pathways and can contain valuable information concerning phylogenetic relationships (Bohlmann et al. 1998; Croteau et al. 2000). Plants produce a range of exudates, with resins being the best known and most widely distributed (Langenheim 2003). Among the gymnosperms, conifers are the most important resin producers, and the production of copious amounts of resin in modern conifers is typically associated with species belonging to Pinaceae and Araucariaceae. However, some species within the Cupressaceae, which includes the formerly separate Taxodiaceae (Brunsfield et al. 1994; Kusumi et al. 2000), are also known to produce considerable amounts of resins (Langenheim 2003). For other conifer families, including Podocarpaceae, Sciadopityaceae, and taxads (Taxaceae and Cephalotaxaceae), information concerning exudates is incomplete or lacking.

Some plant exudates, primarily resins, have considerable fossilization potential and can persist as amber or resinite in the geological record. The compositional characterization of plant exudates, therefore, not only allows correlations between modern plant taxa but is also useful in determining

the relationships between modern and fossil taxa (Lambert et al. 2008). However, to use plant exudates as paleobotanical or chemotaxonomic indicators, it is necessary to implement a compositional classification scheme and determine their distributional patterns across a broad range of taxa.

For the compositional characterization of modern and fossil plant exudates, various analytical techniques have been used, including infrared spectroscopy (Langenheim and Beck 1965; Langenheim 1969; Beck 1986), Raman spectroscopy (Winkler et al. 2001; Jehlicka et al. 2004), nuclear magnetic resonance (NMR) spectroscopy (Lambert and Frye 1982; Cunningham et al. 1983; Lambert et al. 2005), gas chromatography–mass spectrometry (GC-MS; Grantham and Douglas 1980; Mills et al. 1984; Poinar and Haverkamp 1985; Anderson et al. 1992), and other mass spectrometry techniques (Tonidandel et al. 2008).

Infrared spectroscopy is still widely used in the study of fossil resins (e.g., Trevisani et al. 2005; Roghi et al. 2006) because of its low analytical costs, the common availability of infrared spectrometers, and the nondestructive nature of spectroscopic analysis. Early applications of infrared spectroscopy focused on determining the botanical sources of fossil resins, with the research generally conducted on amber from major amber deposits (Langenheim and Beck 1965; Broughton 1974). The analysis of amber and other fossil resins with traditional infrared spectroscopy has been limited because of the relatively large sample size requirements and the lack of comprehensive spectral libraries from modern

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plant exudates for comparison. To better constrain the range and chemotaxonomic characteristics of gymnosperm exudates, we present the results of state-of-the-art infrared analyses from a range of exudates of modern gymnosperms, including from species that have not been previously examined. The results are intended to contribute to a broadly applicable classification scheme for gymnosperm exudates that may provide further insights concerning phylogenetic relationships as well as the interpretation of fossil resins.

Material and Methods

Exudates from 94 specimens of 60 conifer species were sampled from wild trees, cultivars, and herbarium specimens (table 1). In addition, exudates from five species of nonconifer gymnosperms, including *Ginkgo* (Ginkophyta), cycads (Cycadophyta), and *Welwitschia* (Gnetophyta), were analyzed. Samples were preferentially collected from the trunks, but exudates from branches as well as from cones were also used if exudates were not present on the trunk. Although hardened exudates were preferentially sampled, soft and viscous materials were also collected and analyzed.

The absorption spectra were collected in the range 4000–650 cm^{-1} (wavenumbers) using a Thermo Nicolet Nexus 470 Fourier transform infrared (FTIR) spectrometer equipped with a Nicolet Continuum IR microscope. The spectral resolution was set to 4 cm^{-1} . A total of 200 individual interferograms were collected and averaged for each spectrum. Spectra were collected from the hardened material from inclusion-free, freshly broken chips that were placed on an infrared-transparent NaCl disc. To avoid the effects of oversaturation in the spectra, the sample thickness was kept to $\leq 5 \mu\text{m}$. Soft samples were spread thinly onto the NaCl disc. Depending on the quality of the sample, the beam size was set to a value between 50 and 100 μm . No additional spectral manipulations, such as continuum removal or smoothing, were applied to the spectra. Compared with conventional infrared spectroscopy, the micro-FTIR technology does not require pelletization of samples with KBr. This shortens preparation time and preserves additional spectral features relating to the presence of free hydroxyl (OH^-) groups in the sample. In conventional FTIR spectroscopy, these spectral features can be distorted due to the interference of atmospheric water adsorbed to the KBr, which is hygroscopic (Beck 1966). Another advantage of the micro-FTIR technique is the small sample size requirement. Compared with the hundreds of milligrams that are needed in traditional infrared spectroscopy, only tens of micrograms of sample material are needed for a micro-FTIR analysis. All raw spectra reported in this study are available from the authors upon request.

Results

On the basis of major differences in the position and amplitude of absorption features in the infrared spectra, three main types of exudates were identified: resins, volatile-rich resins, and gums (table 2). The spectroscopic characteristics and distribution among taxa are described below.

Resin

Resin is the most widespread type of gymnosperm exudate, but among the gymnosperms examined, it is restricted to members of the conifer families (table 1). In addition to the major features that characterize resin spectra, minor spectral differences were used to identify two distinct types of resin. The first type of resin is predominantly produced by members of the Pinaceae and will, therefore, be referred to as pinaceous resin. However, *Torreya californica*, a member of the taxads (Taxaceae-Cephalotaxaceae) was also found to produce this type of resin. Cupressaceae and Araucariaceae are the main producers of the second type of resin, which will be referred to as cupressaceous resin. Cupressaceous resin is also produced by species of Podocarpaceae and Sciadopityaceae.

For both resin types, the spectral range between 3700 and 3100 cm^{-1} is dominated by a broad peak at $\sim 3400 \text{ cm}^{-1}$ of variable amplitude (fig. 1), which is attributed to the symmetrical stretching of O-H bonds. The only other absorption feature in this region is a small peak located at 3076 cm^{-1} , which likely relates to C-H stretching of monoalkyl groups.

The spectral range 3050–2400 cm^{-1} is dominated by a strong peak at 2935 cm^{-1} (fig. 1). This peak commonly masks another absorption feature at $\sim 2960 \text{ cm}^{-1}$, which is present as either a weak peak or a shoulder. An additional peak of medium intensity is present at 2870 cm^{-1} , and a distinctive peak or a weak shoulder is observed at 2848 cm^{-1} . The absorption features between 3050 and 2400 cm^{-1} are related to the vibrational frequencies of aliphatic single C-H bonds. The absorption features at 2935 and 2848 cm^{-1} are interpreted as a doublet produced by methylene groups, whereas the doublet at 2960 and 2870 cm^{-1} is associated with methyl groups. In this spectral range, pinaceous and cupressaceous resins can generally be distinguished by differences in the absorption feature located at 2848 cm^{-1} . This absorption feature is always present as a distinct peak in cupressaceous resins but is either poorly expressed or absent in pinaceous resins.

The most prominent peak in the spectral range 1800–1600 cm^{-1} is located at 1693 cm^{-1} . This peak commonly overlaps with a weaker absorption feature at 1722 cm^{-1} , which is a shoulder on the flank of the dominant 1693 cm^{-1} peak. These absorption features are related to C-O double bonds in carboxyl groups of resin acids. An additional absorption feature at 1640 cm^{-1} , which is a peak of medium intensity or a shoulder, is probably an O-H bending band.

The spectral range 1550–650 cm^{-1} contains the largest number of absorption features (fig. 2), but not all absorption features in this range can be assigned to a specific molecular functional group. Pinaceous and cupressaceous resins can be distinguished in this range by the presence of absorption features at 1460 and 1448 cm^{-1} . At 1460 cm^{-1} , pinaceous resin spectra have a peak whereas cupressaceous resin spectra have a trough. In turn, cupressaceous resins produce a distinct peak at 1448 cm^{-1} , whereas this position in pinaceous resins is occupied by either a peak that is weaker than the 1460 cm^{-1} peak or a shoulder. The absorption features in the range 1550–1350 cm^{-1} can be assigned to the C-H bending motions of methyl and methylene functional groups; the spectral range 1300–1100 cm^{-1} contains absorption features that are generally assigned to C-O single bonds.

Table 1

Gymnosperm Specimens Sampled

Division, family, species	Locality	Origin	Physical characteristics	Exudate type
Pinophyta:				
Pinaceae:				
<i>Abies balsamea</i> (L.) Mill.	Edmonton, Alberta	Cultivar	Hard, yellow	Resin
<i>Abies concolor</i> (Gord. & Glend.) Lindl. ex Hildebr.	Seattle, WA	Cultivar	Soft, pale yellow	Resin
<i>Abies grandis</i> (Dougl.) Lindl.	Falkland, British Columbia	Wild	Soft, pale yellow	Volatile-rich resin
<i>Abies lasiocarpa</i> (Hook.) Nutt.	Fortress Mountain, Alberta	Wild	Soft, yellow	Resin, volatile-rich resin
<i>Cedrus deodara</i> (Roxb.) Loud.	Washington, DC	Cultivar	Soft, colorless	Volatile-rich resin
<i>Cedrus deodara</i> (Roxb.) Loud.	Victoria, British Columbia	Cultivar	Hard, pale yellow	Resin
<i>Cedrus libani</i> (A. Rich.)	Washington, DC	Cultivar	Soft, yellow	Volatile-rich resin
<i>Cedrus atlantica</i> (Endl.) Manetti ex. Carr.	Seattle, WA	Cultivar	Soft, colorless	Resin
<i>Larix lyallii</i> (Parl.)	Mount Assiniboine, British Columbia	Wild	Hard, yellow	Resin
<i>Larix occidentalis</i> (Nutt.)	Edmonton, Alberta	Cultivar	Soft, yellow	Resin
<i>Picea engelmannii</i> (Carr. ex Engelm.)	Mount Assiniboine, British Columbia	Wild	Hard, yellow	Resin, volatile-rich resin
<i>Picea engelmannii</i> (Carr. ex Engelm.)	Kananaskis, Alberta	Wild	Hard, yellow and reddish	Resin, volatile-rich resin
<i>Picea engelmannii</i> (Carr. ex Engelm.)	Lake Louise, Alberta	Wild	Hard, pale yellow	Resin, volatile-rich resin
<i>Picea glauca</i> (Moench) Voss	Edmonton, Alberta	Cultivar	Hard, pale yellow	Resin
<i>Picea glauca</i> (Moench) Voss	Woking, AB, Canada	Cultivar	hard, pale yellow	Resin
<i>Picea mariana</i> (Mill.) Britton, Sterns & Poggenb.	Mount Robson, Alberta	Wild	Hard, pale yellow	Resin
<i>Picea orientalis</i> (L.) Link	Washington, DC	Cultivar	Hard, pale yellow	Resin
<i>Picea orientalis</i> (L.) Link	Seattle, WA	Cultivar	Soft, colorless	Resin
<i>Picea polita</i> (Siebold & Zucc.) Carr.	Washington, DC	Wild	Hard, pale yellow	Resin
<i>Picea pungens</i> (Engelm.)	Edmonton, Alberta	Cultivar	Hard, pale yellow	Resin
<i>Picea sitchensis</i> (Bong.) Carr.	Pacific Rim National Park, British Columbia	Wild	Soft, colorless	Resin
<i>Pinus aristata</i> (Engelm.)	Seattle, WA	Cultivar	Soft, pale yellow	Resin
<i>Pinus banksiana</i> (Lamb.)	Woking, Alberta	Cultivar	Hard, yellow	Resin
<i>Pinus contorta</i> (Dougl.)	Mount Galatea, Alberta	Wild	Hard, yellow and white	Resin
<i>Pinus contorta</i> (Dougl.)	Sooke, British Columbia	Wild	Hard, yellow	Resin
<i>Pinus contorta</i> (Dougl.)	Lake Louise, Alberta	Wild	Hard, yellow	Resin
<i>Pinus flexilis</i> (James)	Mount Galatea, Alberta	Wild	Hard and soft, yellow	Resin
<i>Pinus flexilis</i> (James)	Washington, DC	Cultivar	Soft, pale yellow	Resin
<i>Pinus mugo</i> (Turra)	Seattle, WA	Cultivar	Soft, yellow	Volatile-rich resin
<i>Pinus nigra</i> (J.F. Arnold)	Washington, DC	Cultivar	Hard, yellow	Resin
<i>Pinus ponderosa</i> (Dougl. ex C. Lawson)	Armstrong, British Columbia	Wild	Hard, yellow	Resin
<i>Pinus radiata</i> (D. Don)	Edmonton, Alberta	Cultivar	Hard, yellow	Resin
<i>Pinus schuerinii</i> (Wiethorst)	Washington, DC	Cultivar	Soft, colorless	Resin
<i>Pinus strobus</i> (L.)	Washington, DC	Cultivar	Soft, pale yellow	Resin
<i>Pinus strobus</i> (L.)	Washington, DC	Cultivar	Soft, pale yellow	Resin
<i>Pseudolarix amabilis</i> (Nelson) Rehder	Seattle, WA	Cultivar	Soft, pale yellow	Resin
<i>Pseudotsuga menziesii</i> (Mirb.) Franco	Roberts Creek, British Columbia	Wild	Hard, yellow	Resin
<i>Pseudotsuga menziesii</i> (Mirb.) Franco	Kananaskis, Alberta	Wild	Hard, yellow and reddish	Resin
<i>Pseudotsuga menziesii</i> (Mirb.) Franco	Sooke, British Columbia	Wild	Soft, milky reddish	Volatile-rich resin
<i>Pseudotsuga menziesii</i> (Mirb.) Franco	Falkland, British Columbia	Wild	Hard, yellow	Resin
<i>Tsuga heterophylla</i> (Raf.) Sarg.	Pacific Rim National Park, British Columbia	Wild	Soft, colorless	Resin
<i>Tsuga heterophylla</i> (Raf.) Sarg.	Cathedral Grove, British Columbia	Wild	Soft, colorless	Resin

Cupressaceae:

<i>Chamaecyparis lawsoniana</i> (A. Murray) Parl.	Gold Beach, OR	Herbarium	Hard, yellow	Resin
<i>Chamaecyparis obtusa</i> (Siebold & Zucc.) Endl.	Washington, DC	Cultivar	Hard, yellow	Resin
<i>Chamaecyparis pisifera</i> (Siebold & Zucc.) Endl.	Seattle, WA	Cultivar	Soft, pale yellow	Resin
<i>Cunninghamia lanceolata</i> (Lamb.) Hook.	Edmonton, Alberta	Cultivar	Hard, pale yellow	Resin
<i>Cupressus macrocarpa</i> (Hartw. ex Gordon)	Victoria, British Columbia	Cultivar	Hard, yellow	Resin
<i>Cupressus nootkatensis</i> (D. Don) Florin	Victoria, British Columbia	Cultivar	Hard, yellow	Resin
<i>Cupressus sempervirens</i> (L.)	Edmonton, Alberta	Cultivar	Soft, pale yellow	Resin
<i>Cupressus sempervirens</i> (L.)	Seattle, WA	Cultivar	Soft, pale yellow	Resin
<i>Juniperus chinensis</i> (L.)	Washington, DC	Cultivar	Hard, yellow	Resin
<i>Juniperus scopulorum</i> (Sarg.)	Victoria, British Columbia	Cultivar	Hard, pale yellow	Resin
<i>Juniperus scopulorum</i> (Sarg.)	Falkland, British Columbia	Wild	Hard, pale yellow	Resin
<i>Metasequoia glyptostroboides</i> (Hu & W.C. Cheng)	Edmonton, Alberta	Cultivar	Soft, colorless	Resin
<i>Metasequoia glyptostroboides</i> (Hu & W.C. Cheng)	Washington, DC	Cultivar	Hard, pale yellow	Resin
<i>Neocallitropsis pancheri</i> (Carr.) de Laub.	New Caledonia	Herbarium	Hard, yellow	Resin
<i>Sequoia sempervirens</i> (D. Don) Endl.	Victoria, British Columbia	Cultivar	Soft, pale yellow	Resin
<i>Sequoiadendron giganteum</i> (Lindl.) J. Buchh.	Edmonton, Alberta	Cultivar	Soft, pale yellow	Resin
<i>Sequoiadendron giganteum</i> (Lindl.) J. Buchh.	Washington, DC	Cultivar	Hard, pale yellow	Resin
<i>Tetraclinis articulata</i> (Vahl) Masters	Edmonton, Alberta	Cultivar	Soft, pale yellow	Resin
<i>Thuja occidentalis</i> (L.)	Edmonton, Alberta	Cultivar	Hard, yellow	Resin
<i>Thuja plicata</i> (Donn ex D. Don)	Roberts Creek, British Columbia	Wild	Hard, yellow	Resin
<i>Thuja plicata</i> (Donn ex D. Don)	Edmonton, Alberta	Cultivar	Soft and hard, yellow	Resin
<i>Thuja plicata</i> (Donn ex D. Don)	Sooke, British Columbia	Wild	Hard, yellow	Resin
<i>Thuja plicata</i> (Donn ex D. Don)	Vavenby, British Columbia	Wild	Hard, yellow	Resin
<i>Widdingtonia dracomontana</i> (Stapf.)	Edmonton, Alberta	Cultivar	Hard, pale yellow	Resin

Sciadopiaceae:

<i>Sciadopitys verticillata</i> (Thunb.) Siebold & Zucc.	Unknown	Herbarium	Hard, pale yellow	Resin
<i>Sciadopitys verticillata</i> (Thunb.) Siebold & Zucc.	Seattle, WA	Cultivar	Soft, pale yellow	Resin

Araucariaceae:

<i>Agathis australis</i> (D. Don) Loud.	New Zealand	Herbarium	hard, yellow	Resin
<i>Agathis robusta</i> (C. Moore ex F. Muell.) F.M. Bailey	Los Angeles, CA	Cultivar	Soft, pale yellow	Resin
<i>Agathis robusta</i> (C. Moore ex F. Muell.) F.M. Bailey	Adelaide, South Australia	Cultivar	Hard, yellow	Resin
<i>Agathis robusta</i> (C. Moore ex F. Muell.) F.M. Bailey	Melbourne, Victoria	Cultivar	Hard, yellow	Resin
<i>Araucaria araucana</i> (Molina) K. Koch	Edmonton, Alberta	Cultivar	Soft, colorless	Resin
<i>Araucaria araucana</i> (Molina) K. Koch	Seattle, WA	Cultivar	Soft, yellow	Resin
<i>Araucaria araucana</i> (Molina) K. Koch	Victoria, British Columbia	Cultivar	Soft, colorless	Resin
<i>Araucaria araucana</i> (Molina) K. Koch	Los Angeles, CA	Cultivar	Soft, brownish	Gum
<i>Araucaria biovillii</i> (Molina) K. Koch	Adelaide, South Australia	Cultivar	Hard, yellow	Gum
<i>Araucaria columnaris</i> (J.R. Forst.) Hook.	Adelaide, South Australia	Cultivar	Hard, yellow	Resin
<i>Araucaria cunninghamii</i> (Aiton ex D. Don)	Edmonton, Alberta	Cultivar	Hard, pale yellow	Resin
<i>Araucaria cunninghamii</i> (Aiton ex D. Don)	Seattle, WA	Cultivar	Hard, pale yellow	Resin
<i>Araucaria cunninghamii</i> (Aiton ex D. Don)	Adelaide, South Australia	Cultivar	Hard, pale yellow	Resin
<i>Araucaria heterophylla</i> (Salisb.) Franco	Edmonton, Alberta	Cultivar	Hard, pale yellow	Resin
<i>Araucaria heterophylla</i> (Salisb.) Franco	Adelaide, South Australia	Cultivar	Hard, milky white	Gum
<i>Araucaria laubenfelsii</i> (Corbasson)	Adelaide, South Australia	Cultivar	Hard, yellow	Resin
<i>Araucaria rulei</i> (F. Muell)	Edmonton, Alberta	Cultivar	Hard, yellow	Resin
<i>Wollemia nobilis</i> (W.G. Jones, K.D. Hill & J.M. Allen)	Adelaide, South Australia	Cultivar	Hard, pale yellow	Resin
			Hard, white	Resin

Table 1
(Continued)

Division, family, species	Locality	Origin	Physical characteristics	Exudate type
Podocarpaceae: <i>Phyllocladus alpinus</i> (Hook. f.)	Mount Cook, New Zealand	Herbarium	Hard, yellow	Resin
<i>Podocarpus totara</i> (G. Benn. ex D. Don)	Los Angeles, CA	Cultivar	Soft, yellow	Gum
Cephalotaxaceae/Taxaceae: <i>Torreya californica</i> (Torr.)	Edmonton, Alberta	Cultivar	Soft, pale yellow	Resin
Ginkgophyta: Ginkgoaceae: <i>Ginkgo biloba</i> (L.)	Toronto, Ontario	Cultivar	Soft, pale yellow	Gum
Cycadophyta: Zamiaceae: <i>Dioon purpusii</i> (Rose)	Edmonton, Alberta	Cultivar	Hard, colorless	Gum
<i>Dioon spinulosum</i> (Dyer)	Edmonton, Alberta	Cultivar	Hard, colorless	Gum
Cycadaceae: <i>Cycas circinalis</i> (L.)	Edmonton, Alberta	Cultivar	Hard, colorless	Gum
Gnetophyta: Welwitschiaceae: <i>Welwitschia mirabilis</i> (Hook. f.)	Arcata, CA	Cultivar	Soft, brownish	Gum

A large number of absorption features located $<1100\text{ cm}^{-1}$ can be used to distinguish pinaceous and cupressaceous resins. Pinaceous resins are characterized by the presence of peaks at 823 and 710 cm^{-1} , whereas cupressaceous resins have peaks at 1091 , 1030 , 887 , and 791 cm^{-1} (fig. 2). Absorption features in this range generally have low amplitudes and are caused by vibrations within macromolecular structures. An exception to this is the strong peak at 887 cm^{-1} in spectra from cupressaceous resins, which is attributed to the out-of-plane C-H bending motions in terminal methylene groups.

Band Ratios and Resin Chemotaxonomy

In order to quantitatively differentiate between pinaceous and cupressaceous resins, we used selected band ratios. To minimize errors caused by background distortion, only absorption features that were in close proximity to each other were used. The most useful band ratios for the distinction of resins of pinaceous and cupressaceous resins are as follows:

$$r_1 = \frac{\text{abs.}823\text{ cm}^{-1}}{\text{abs.}791\text{ cm}^{-1}}, \quad (1)$$

$$r_2 = \frac{\text{abs.}1460\text{ cm}^{-1}}{\text{abs.}1448\text{ cm}^{-1}}, \quad (2)$$

$$r_3 = \frac{\text{abs.}1448\text{ cm}^{-1}}{\text{abs.}1385\text{ cm}^{-1}}, \quad (3)$$

$$r_4 = \frac{\text{abs.}2858\text{ cm}^{-1}}{\text{abs.}2848\text{ cm}^{-1}}. \quad (4)$$

These band ratios enable pinaceous and cupressaceous resins to be differentiated with a high degree of fidelity (fig. 3). The band ratio plots in figure 3, however, also illustrate that the use of only single band ratios may produce ambiguous results. Therefore, it is necessary to apply multiple band ratios in order to determine the resin type accurately. In this data set, only a single sample of *Pinus radiata* consistently plots outside the expected field for pinaceous resin (fig. 3B). The spectrum from this sample, however, is unusual, as it is characterized by a small absorption peak at 1516 cm^{-1} that is not present in any other resin spectrum. One sample of *Sequoia sempervirens* resin also falls consistently outside of the predicted field for cupressaceous resins (fig. 3). This sample is also characterized by an additional absorption peak, located at 1600 cm^{-1} . Sample impurities are a possible cause for these anomalous samples. Resins from *Phyllocladus alpinus* (Podocarpaceae) and *Sciadopitys verticillata* (Sciadopityaceae) clearly plot in the field of cupressaceous resins, whereas resin from *Torreya californica*, the only taxad considered in our analyses, plots in the field of pinaceous resins (fig. 3).

Variability within Resin Spectra

In addition to the conservative absorption features that are used to identify and classify resin spectra, conifer resins also

contain absorption features that are variable in their amplitude. The most obvious is the peak centered at 3400 cm^{-1} , which reflects the number of free hydroxyl groups that are present in the resin. This peak is distinct and broad in some resin spectra but virtually absent in others (fig. 1). In order to measure the height of this peak, the following band ratio was used:

$$r_{\text{OH}} = \frac{\text{abs. } 3400\text{ cm}^{-1}}{\text{abs. } 3076\text{ cm}^{-1}}. \quad (5)$$

The resulting ratio values for pinaceous and cupressaceous resins range from ~ 0.3 to ~ 1.6 .

Additional absorption features that show a high degree of variability are located between 1200 and 1300 cm^{-1} (fig. 2). For pinaceous resins, a doublet is located at 1248 and 1277 cm^{-1} . The following band ratio was used to document the variability of this doublet:

$$r_5 = \frac{\text{abs. } 1277\text{ cm}^{-1}}{\text{abs. } 1248\text{ cm}^{-1}}. \quad (6)$$

In the spectra from cupressaceous resins, a similar doublet is located at slightly lower wavenumbers (1234 and 1265 cm^{-1}). The variability of this doublet is documented using the following band ratio:

$$r_6 = \frac{\text{abs. } 1265\text{ cm}^{-1}}{\text{abs. } 1234\text{ cm}^{-1}}. \quad (7)$$

The absorption features of these doublets cannot be ascribed to a particular functional group, but their band ratios (eqq. [6] and [7]) correlate with the amplitude of the hydroxyl peak at 3400 cm^{-1} as illustrated by the band ratio plots in figure 4. It is notable that the relative amplitude of the peaks in each doublet decreases exponentially as the amplitude of the hydroxyl peak increases.

Additional Absorption Features in Resin Spectra

Resins from three conifer species (*Cedrus atlantica*, *Pseudolarix amabilis*, and *Sciadopitys verticillata*) produced spectra that are overall similar to typical resins, but they have additional absorption features in the 1100 – 1300-cm^{-1} range (fig. 5). Each of these resins is characterized by a strong peak at 1160 cm^{-1} and a broad shoulder between 1200 and 1300 cm^{-1} . These absorption features resemble those observed in spectra from Baltic amber, where they are assigned to the presence of succinic acid esters (succinate).

Volatile-Rich Resins

Exudates that are spectrally and physically distinct from the resins described above were collected from species belonging exclusively to Pinaceae (fig. 6; table 1). These exudates are usually soft and strongly odoriferous, and they commonly occur along with hardened resins on the same tree. The differences in the spectra from these exudates compared with those from the typical resins are sufficient to classify these exudates as a separate type: the volatile-rich resins.

Volatile-rich resins are characterized by the presence of a strong hydroxyl absorption peak at 3400 cm^{-1} . Compared

Table 2

Frequency and Relative Intensity of Infrared Absorption Peaks of Gymnosperm Exudates

Frequency (cm ⁻¹)	Frequency (μm)	Pinaceous resin	Cupressaceous resin	Volatile-rich resin	Gum
3400	2.94	Variable, broad	Variable, broad	Very strong, broad	Very strong, broad
3076	3.25	Weak	Weak	Weak	Absent
2960	3.38	Shoulder	Shoulder	Shoulder	Absent
2935	3.41	Very strong	Very strong	Medium	Medium
2870	3.48	Weak	Weak	Weak	Absent
2848	3.51	Weak	Shoulder or absent	Weak	Absent
1705	5.87	Absent	Absent	Strong	Absent
1722	5.81	Shoulder or absent	Shoulder or absent	Absent	Absent
1693	5.91	Very strong	Very strong	Absent	Absent
1640	6.10	Medium shoulder	Medium shoulder	Absent	Absent
1605	6.23	Absent	Absent	Strong	Strong
1516	6.60	Absent	Absent	Strong	Absent
1460	6.85	Medium	Absent	Absent	Absent
1448	6.91	Weak or shoulder	Medium	Strong (triple peak)	Absent
1417	7.06	Absent	Absent	Absent	Strong
1385	7.22	Strong	Strong	Medium	Medium-weak
1277	7.83	Variable	Absent	Very strong	Medium
1265	7.91	Absent	Variable	Absent	Absent
1248	8.01	Variable	Absent	Absent	Absent
1234	8.10	Absent	Variable	Very strong	Absent
1207	8.29	Absent	Absent	Medium-strong	Absent
1178	8.49	Medium-strong	Medium-strong	Absent	Absent
1155	8.66	Absent	Absent	Medium-strong	Absent
1160	8.62	Strong or absent	Strong or absent	Absent	Absent
1124	8.90	Absent	Absent	Medium	Absent
1091	9.17	Absent	Weak	Absent	Absent
1077	9.29	Absent	Absent	Absent	Very strong
1030	9.71	Absent	Medium	Very strong	Strong
887	11.27	Absent	Strong	Absent	Weak
833	12.00	Absent	Absent	Strong	Absent
823	12.15	Medium	Weak	Weak	Absent
791	12.64	Absent	Medium	Absent	Absent
710	14.08	Weak-medium	Absent	Absent	Weak

with spectra from typical (volatile-poor) resins, the amplitude of this hydroxyl peak is generally higher than the amplitudes of the methyl and methylene peaks in the 3100–2800-cm⁻¹ region (fig. 6). Absorption features located in the range 1800–650 cm⁻¹ occur at different positions and have different amplitudes compared with those observed in the spectra from typical resins (table 2). The most notable differences are the peaks at 1605 and 1516 cm⁻¹ in the spectra of volatile-rich resins (fig. 6). Additional differences are marked by the presence of strong peaks at 1030 and 833 cm⁻¹. The absorption peak at 1277 cm⁻¹ is also more prominent in volatile-rich resins.

In order to evaluate the relationship between the volatile-rich resins and typical resins originating from the same tree, a volatile-rich resin from *Abies lasiocarpa* (Pinaceae) was placed in a vacuum (25 mTorr) for 72 h. The resulting spectrum was indistinguishable from the spectrum of a typical resin from the same tree (fig. 7). Additional heating of the volatile-rich resin to 50°C during evacuation did not further affect the spectrum. These results demonstrate that the spectral characteristics of the volatile-rich resins are caused solely by the presence of volatile compounds and that the absorption features produced by these compounds overprint the

absorption features that characterize typical resin spectra. Among the terpenoids, mono- and sesquiterpenoids are, by far, the most ubiquitous volatile components in Pinaceae, and their presence may be responsible for the absorption features that define the volatile-rich resins.

Gums

A distinctive type of exudate occurs together with resins in several taxa belonging to the families Araucariaceae and Podocarpaceae. Although these exudates are often not physically distinguishable from resins, their distinct spectra are characterized by a very large hydroxyl peak (~3400 cm⁻¹) when compared with the spectra of resins and volatile-rich resins (fig. 6). The spectra of these exudates are very similar to each other, and they resemble the spectra of gum exudates that are also produced by other plant groups, including angiosperms (e.g., *Acacia senegal* [Leguminosae]; fig. 6). These exudates are, therefore, classified as gum. The nonconifer gymnosperms (*Ginkgo*, cycads, and *Welwitschia*) were found to exclusively produce gums that were spectroscopically very similar to the gums from the araucarian and podocarp conifers (fig. 8).

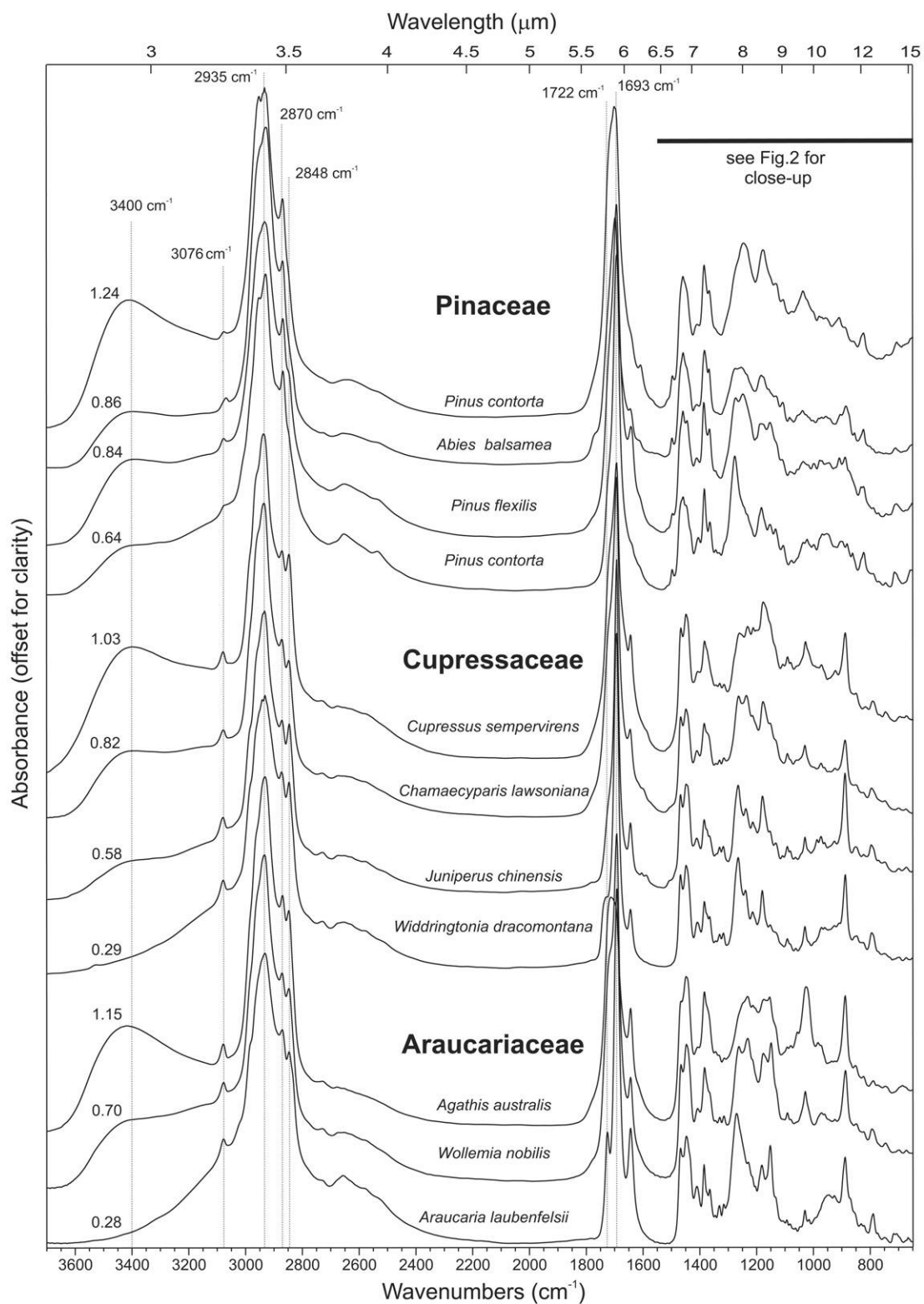


Fig. 1 Examples of Fourier transform infrared (FTIR) spectra of resins from members of the most dominant resin-producing conifer families: Pinaceae, Cupressaceae, and Araucariaceae. Numbers represent the height of the absorption peak at 3400 cm^{-1} , expressed as band ratio $\text{abs. } 3400\text{ cm}^{-1}/\text{abs. } 3076\text{ cm}^{-1}$. The spectra within each family are arranged by decreasing $\text{abs. } 3400\text{ cm}^{-1}/\text{abs. } 3076\text{ cm}^{-1}$ band ratios.

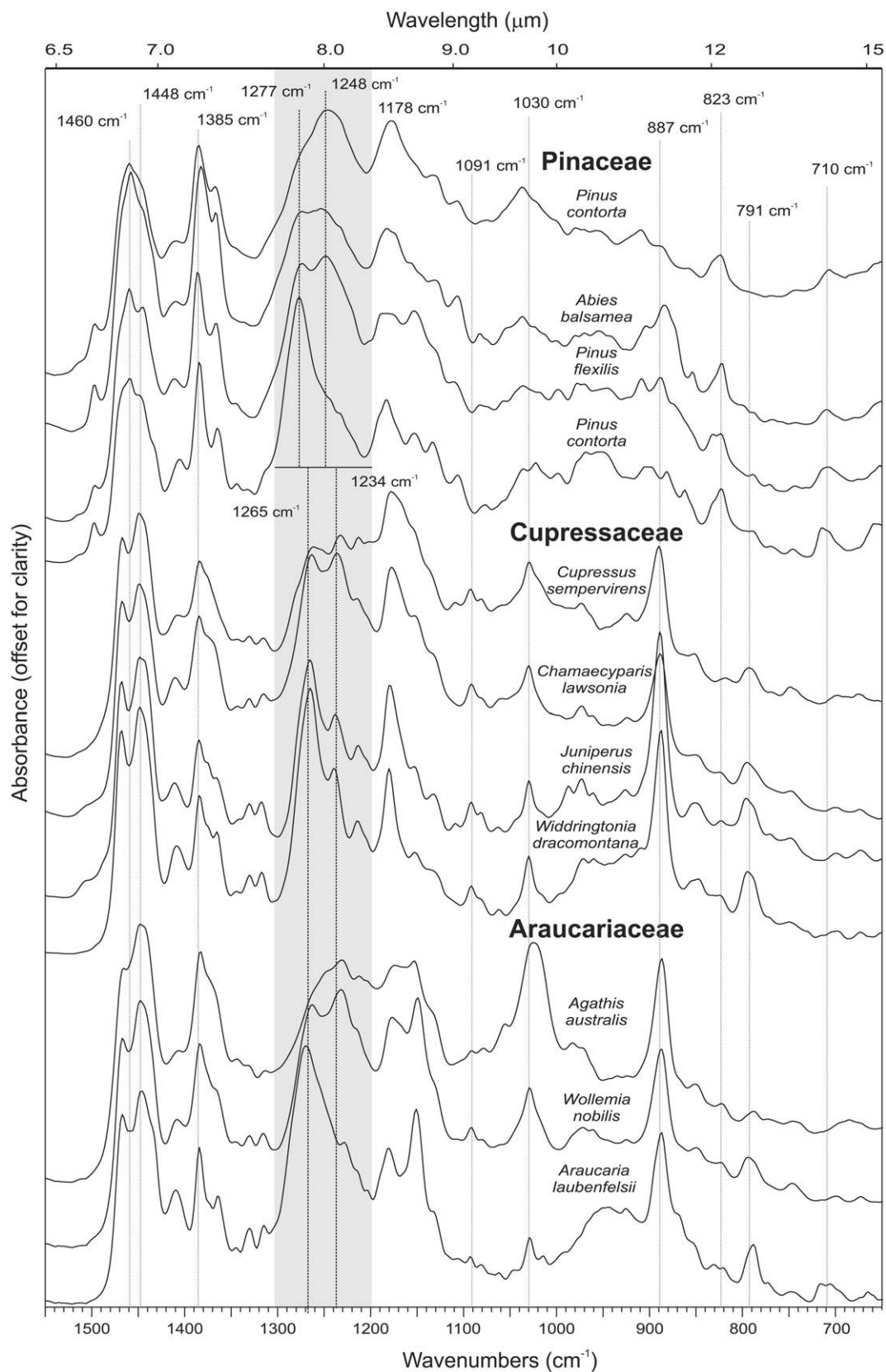


Fig. 2 Close-up of the spectral region $1550\text{--}650\text{ cm}^{-1}$ of the Fourier transform infrared (FTIR) spectra from conifer resins shown in fig. 1. The gray box marks regions with highest variability in the spectra.

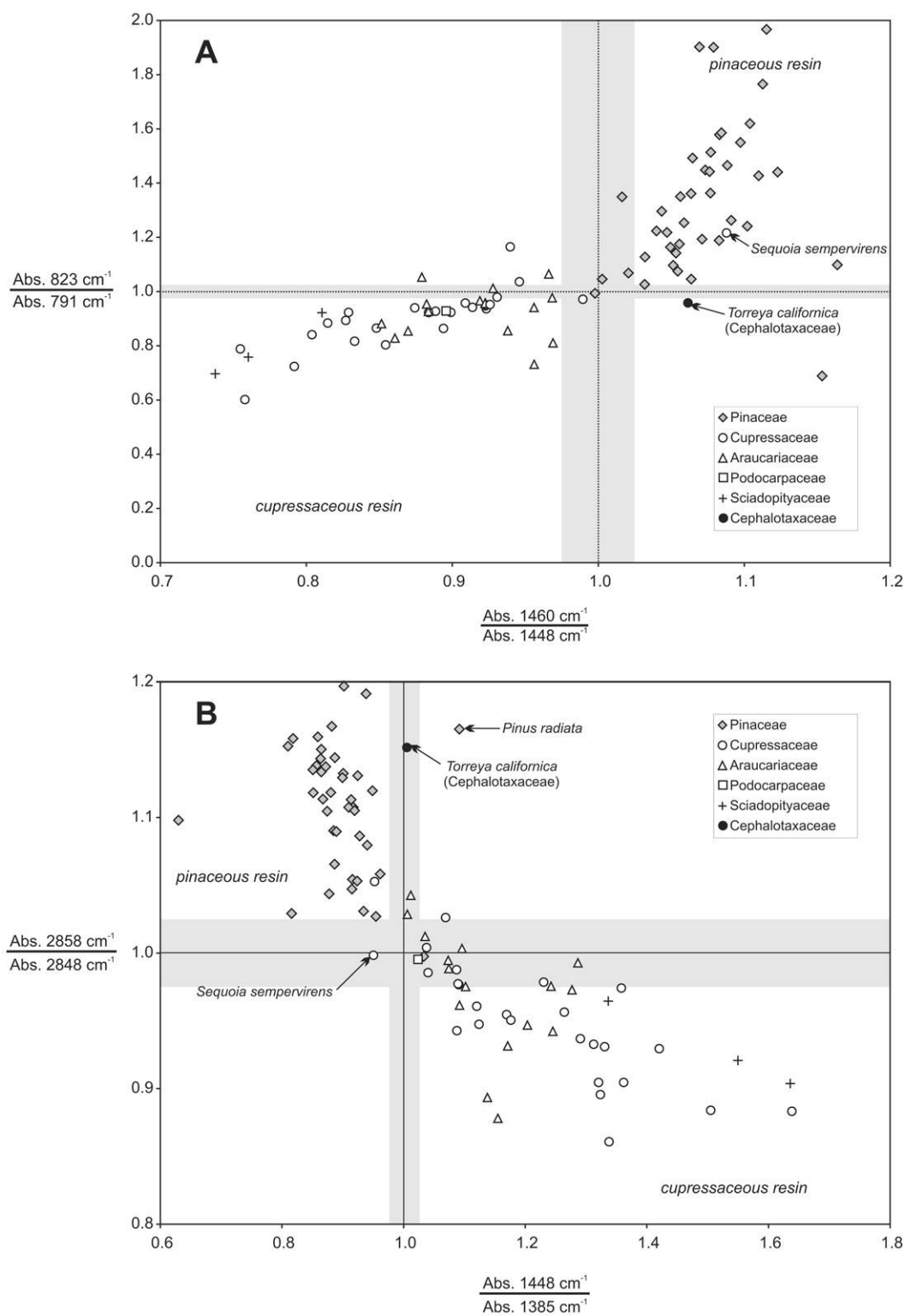


Fig. 3 Absorption band ratio plots for conifer resins from various families. Dotted lines represent the expected boundaries for different conifer resin types. The shaded area marks the 2.5% error margin range.

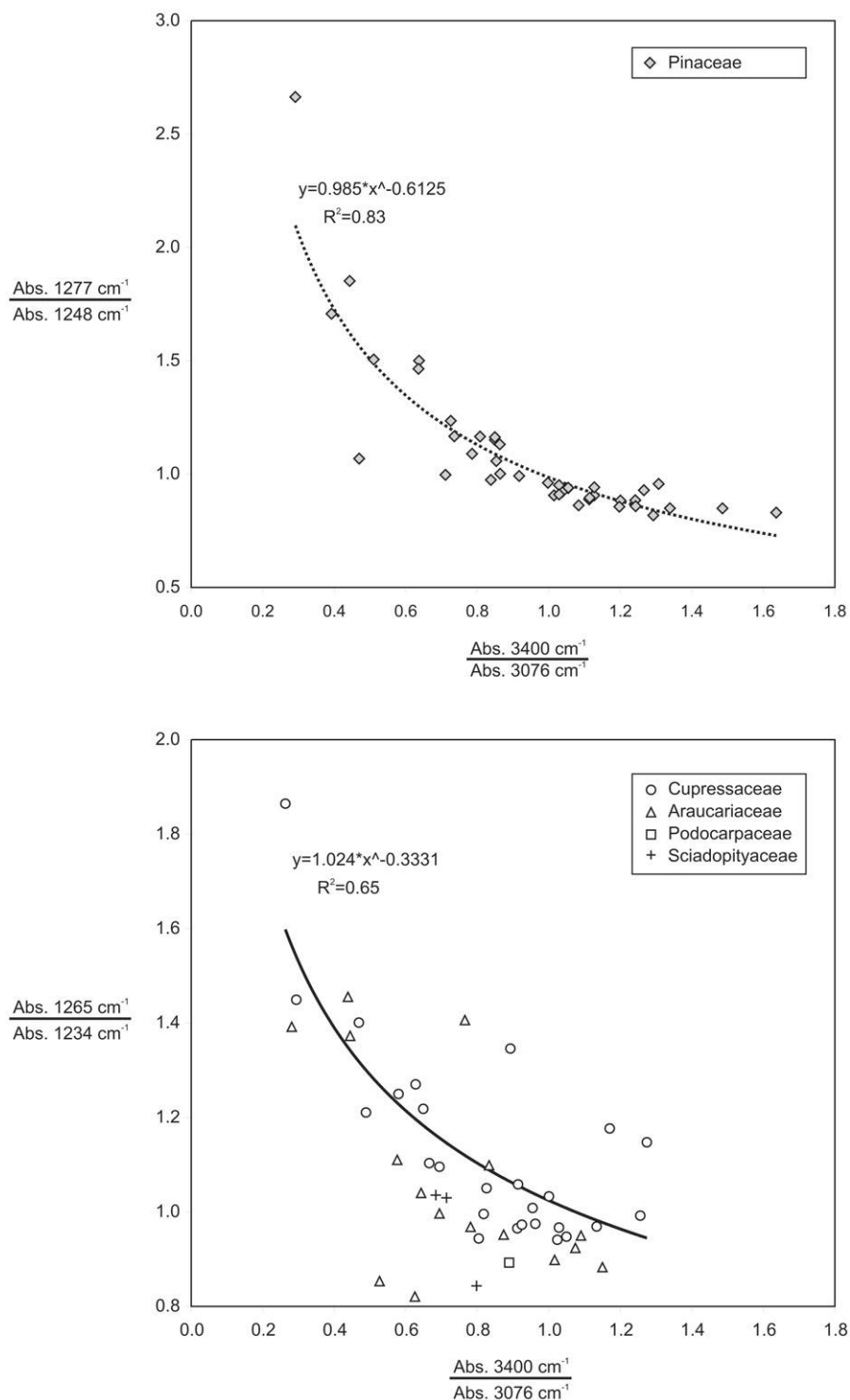


Fig. 4 Plots of $\text{abs. } 3400 \text{ cm}^{-1} / \text{abs. } 3076 \text{ cm}^{-1}$ against other variable absorption features, expressed as $\text{abs. } 1277 \text{ cm}^{-1} / \text{abs. } 1248 \text{ cm}^{-1}$ for Pinaceae and $\text{abs. } 1265 \text{ cm}^{-1} / \text{abs. } 1234 \text{ cm}^{-1}$ for Cupressaceae.

In addition to the very large hydroxyl peak, gums have diagnostic absorption features in the range $1800\text{--}650 \text{ cm}^{-1}$. A peak at 1516 cm^{-1} , which is observed in the spectra of volatile-rich resins, is absent in the spectra from gums. The

spectra of gums also have a very strong peak at 1077 cm^{-1} that is not observed in the spectra of resins or volatile-rich resins. Compositionally, gums are primarily polysaccharide derivatives with considerably lower amounts of terpenoids

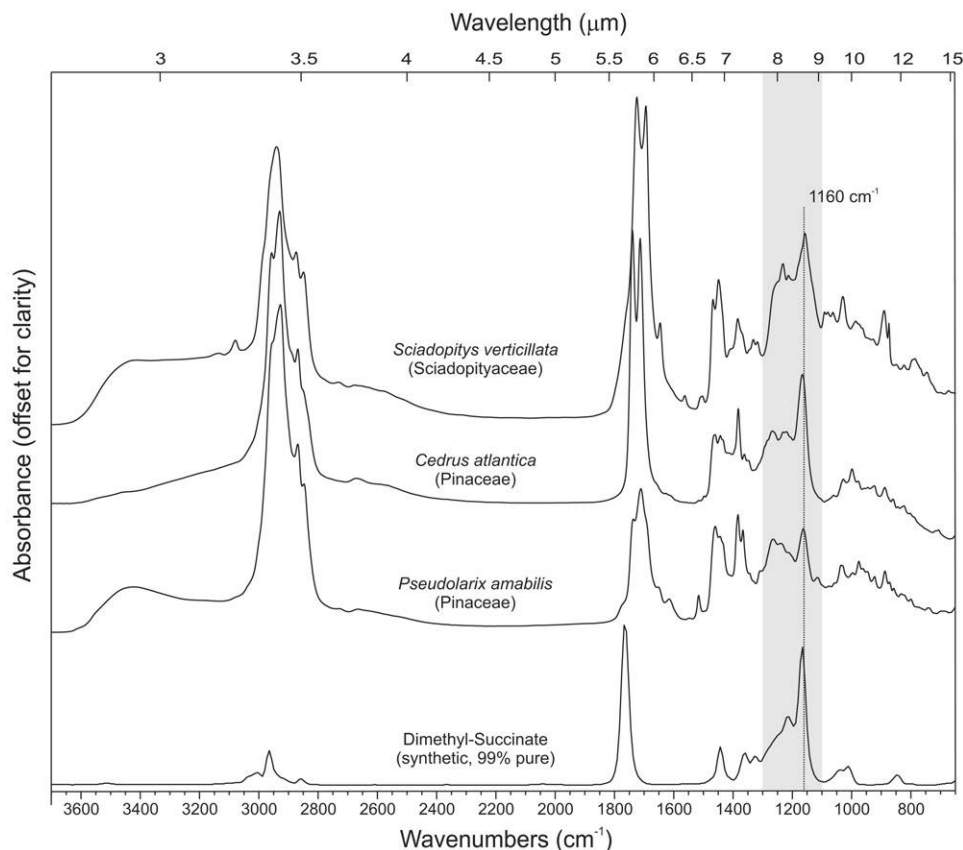


Fig. 5 Fourier transform infrared (FTIR) spectra of conifer resins that exhibit distinctive absorption features in the region $1300\text{--}1100\text{ cm}^{-1}$ (gray box), which includes a strong absorption peak at 1160 cm^{-1} and a broad shoulder between 1200 and 1300 cm^{-1} that is equivalent to the “Baltic shoulder” in northern European amber. An absorption spectrum of a pure succinic acid ester is shown for comparison.

compared with resins. Gums are not only widely distributed among gymnosperms, but they can also be found with angiosperms and ferns, as illustrated in figures 6 and 8.

Discussion

Chemotaxonomic Interpretation of FTIR Spectra

The spectroscopic differences observed between the three groups of gymnosperm exudates discerned here (i.e., resins, volatile-rich resins, and gums) reflect fundamental differences in their chemical composition and, therefore, differences in the metabolic pathways adopted by the various gymnosperm taxa (table 3). Resins and volatile-rich resins are mainly composed of terpenoids (Gough and Mills 1972; Langenheim 2003), whereas gums are dominantly polysaccharide derivatives (Whistler 1993).

The ability to differentiate between pinaceous and cupressaceous resins with the use of band ratios is due to the presence of distinct terpenoid assemblages in each resin type. Similar differences in the terpenoid assemblages can also be used to differentiate between gymnosperm and angiosperm resins as a whole, but a systematic differentiation scheme based on infrared data has not been established yet.

The main components of pinaceous resins are diterpenoids that are based on abietane and pimarane structures, such as

abietic and pimaric acids. On the other hand, the main components of cupressaceous resins, which are produced by members of the Cupressaceae, Araucariaceae, and Podocarpaceae, consist primarily of diterpenoids that are based on the labdane structure, such as communic and agathic acids (Gough and Mills 1972). As a result, infrared spectra of araucarian and podocarp resins are generally indistinguishable from resins produced by members of the Cupressaceae. This suggests that the phylogenetic relationship between these families is closer than their phylogenetic relationship to Pinaceae. This conclusion is supported by both molecular (Stefanović et al. 1998; Schmidt and Schneider-Poetsch 2002) and fossil (Hart 1987; Miller 1999) evidence.

The band ratio plots in figure 3 also reveal that *Sciadopitys verticillata* produces cupressaceous-type resin, suggesting that this resin also primarily consists of diterpenoids with labdane structure. However, *S. verticillata* resin is spectroscopically distinct from other cupressaceous resins in that it expresses a strong peak at 1160 cm^{-1} and a broad shoulder in the range $1200\text{--}1300\text{ cm}^{-1}$. These absorption features have also been identified in some modern Pinaceae resins, such as those from *Pseudolarix amabilis* and *Cedrus atlantica* (fig. 5). Similar absorption features are considered to be diagnostic in the identification of Baltic amber, which is one of the most abundant fossil conifer resins (Beck et al. 1964; Langenheim 1969). Traditionally, these absorption features have been at-

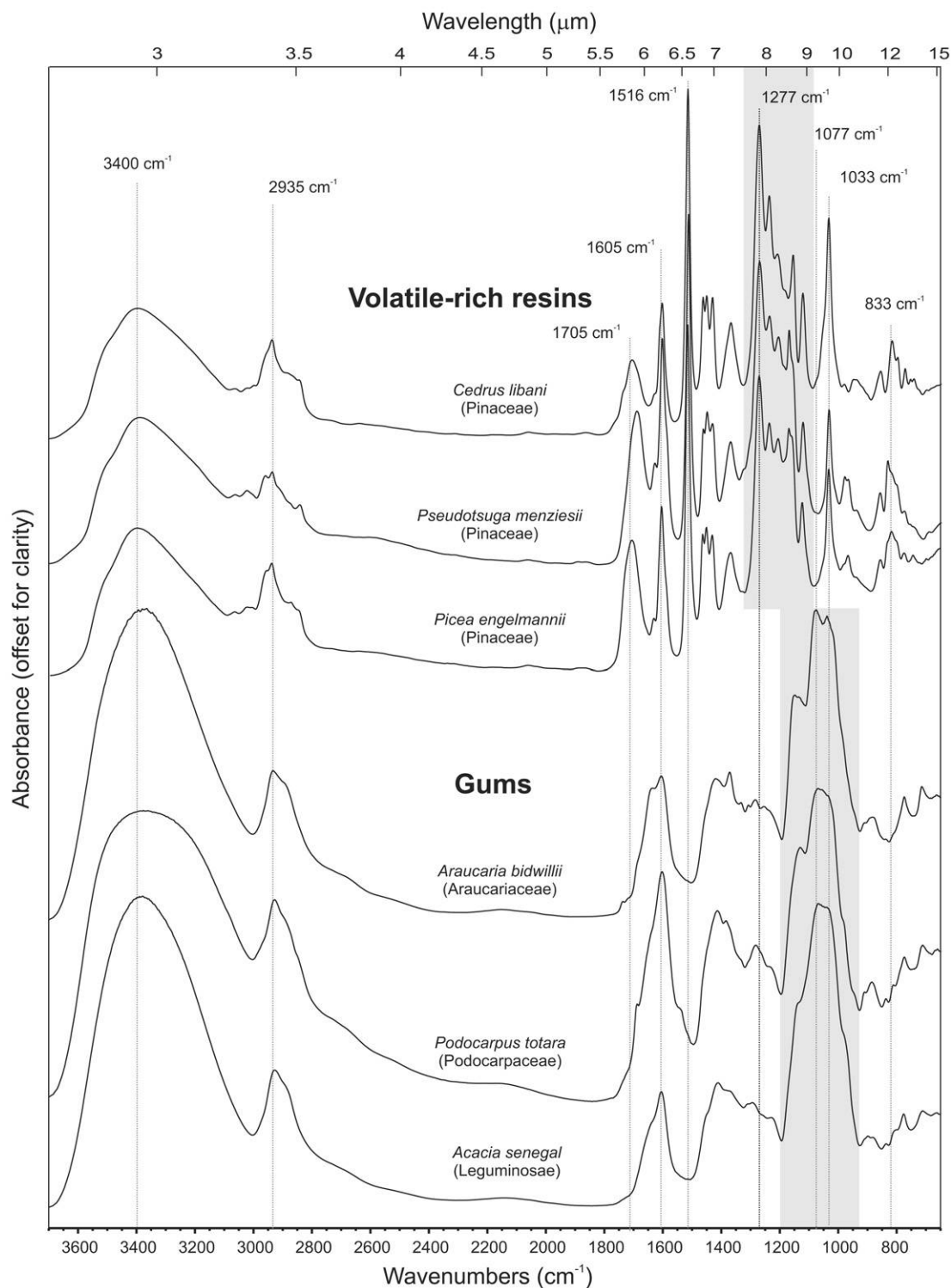


Fig. 6 Examples of Fourier transform infrared (FTIR) spectra of volatile-rich resins and conifer gums.

tributed to the presence of succinic acid esters in resins (Beck et al. 1964). However, the analysis of *S. verticillata* resin using methanolytic gas chromatography–mass spectrometry (GC-MS) was not successful in identifying the presence of succinic acid esters in this resin (Wolfe et al. 2009). The ab-

sorption features traditionally assigned to succinates, therefore, may relate to different and as of yet unidentified compounds that produce similar absorption features. Despite this uncertainty, the absorption spectrum of *S. verticillata* resin is distinct and indicates that *S. verticillata* has a unique

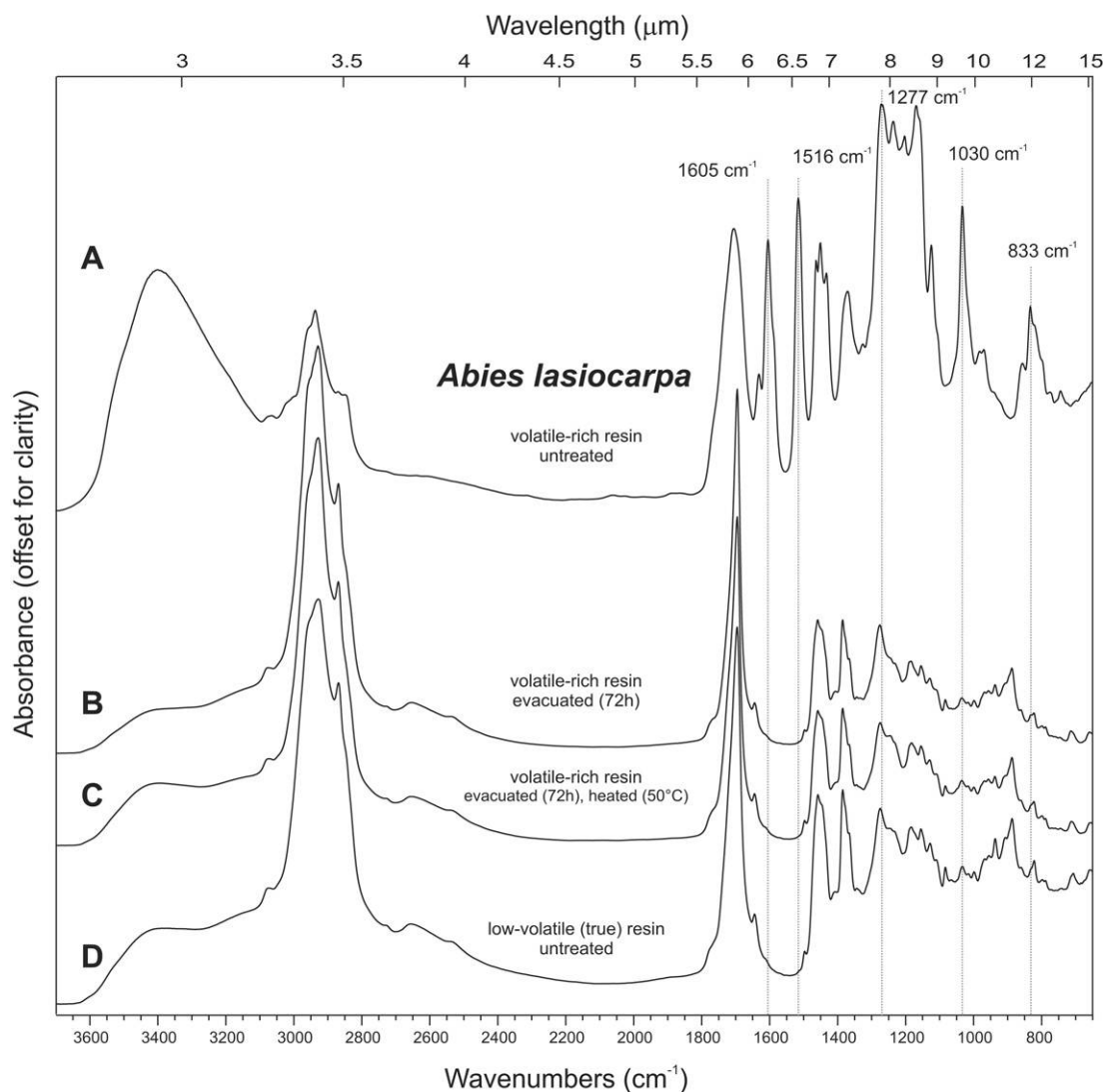


Fig. 7 Results of evacuation and heating experiments with exudates (resin and volatile-rich resin) from *Abies lasiocarpa* that were collected from the same tree specimen. A, Fourier transform infrared (FTIR) spectrum of untreated, volatile-rich resin. B, FTIR spectrum of the volatile-rich resin after evacuating for 72 h. C, FTIR spectrum of the volatile-rich resin after evacuating and simultaneous heating to 50°C for 72 h. D, FTIR spectrum of untreated (low-volatile) resin for comparison.

phylogenetic position within the Pinophyta. Our spectroscopic results, coupled with molecular evidence (Stefanović et al. 1998; Quinn et al. 2001), therefore support the original propositions of Hayata (1931) that *Sciadopitys* should be considered the sole extant genus within the family Sciadopityaceae and that the Sciadopityaceae occupy a basal position with respect to Cupressaceae.

The spectral differences between the abietane/pimarane-based resins of Pinaceae and the labdane-based resins of Cupressaceae, Sciadopityaceae, Araucariaceae, and Podocarpaceae reveal major differences in the metabolic pathways for resin production. Different resin synthases are likely to have implications regarding the evolutionary histories, and indeed the phylogenies, of these conifers. For example, molecular data (Stefanović et al. 1998; Rai et al. 2008) in conjunction with paleobotanical evidence (Miller 1999) support

the early divergence of Pinaceae, which is consistent with the observation that this family produces distinctive resins based on abietane/pimarane diterpene skeletal structures. *Torreya californica* is the only other conifer species that was found to produce resin that falls into the pinaceous spectroscopic field (figs. 3, 9), and it is also the only taxad in the present data set. Morphologically, the taxads have been considered to be derived from an ancestral group of conifers (Sahni 1920; Miller 1999). However, the taxads and Pinaceae do not form a monophyletic group in recent molecular phylogenies (Stefanović et al. 1998; Quinn et al. 2001), and so it seems more probable that either taxads and pinaceous conifers evolved similar biochemical pathways independently or that taxads alone retain the primitive biochemical pathways that characterize extant pinaceous conifers. These possibilities mandate further spectroscopic analyses of taxad exudates, but we note

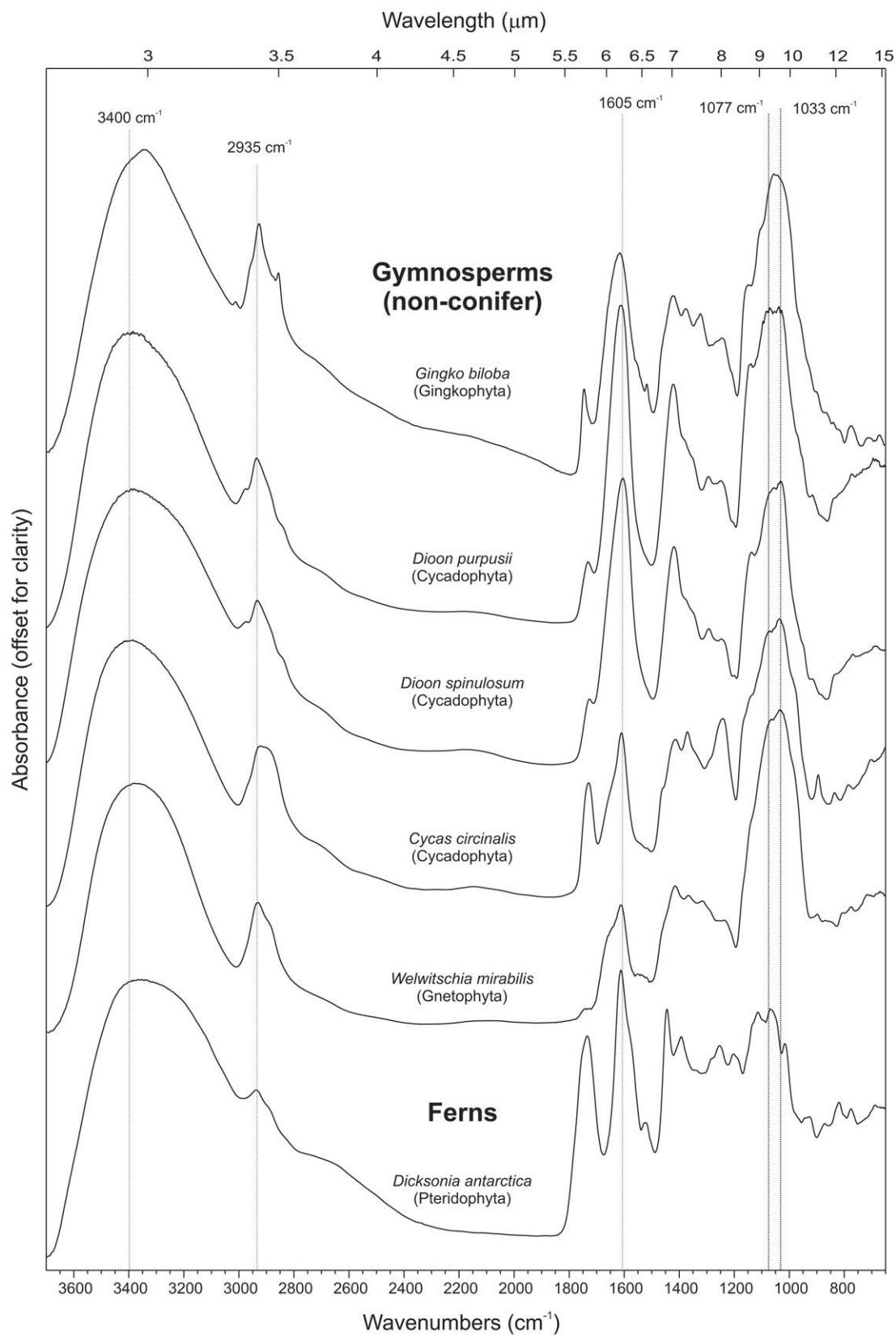


Fig. 8 Examples of Fourier transform infrared (FTIR) spectra of gum exudates from nonconifer gymnosperms and a fern (Pteridophyta).

Table 3

Exudates with Distinct Infrared Characteristics, Including Their Distribution between Plant Taxa and Their Main Chemical Compounds		
Spectral group, resin type	Plant taxa	Characteristic chemical compounds
Resin:		
Pinaceous ^a	Pinaceae, taxads	Diterpenoids, abietane/pimarane based
Cupressaceous ^a	Cupressaceae, Sciadopityaceae, Araucariaceae, Podocarpaceae	Diterpenoids, labdane based
Volatile-rich resin	Pinaceae	Mono-/sesquiterpenoids (volatile), diterpenoids, abietane/pimarane based
Gum	Araucariaceae, Podocarpaceae, Ginkgophyta, Cycadophyta, Gnetophyta	Polysaccharides

^a Additional spectral features at 1100–1300 cm^{-1} , related to succinate or similar compound, can be present.

that, despite repeated sampling attempts, the majority of taxads do not produce sufficient resins for analysis and are thus unlikely to prove relevant in the investigation of fossil resins from the geological record.

Spectroscopic Assessment of Resin Polymerization

Micro-FTIR spectroscopy facilitates the in situ analysis and quantification of absorption features, including those produced by hydroxyl groups in the 3400 cm^{-1} region. In conventional infrared absorption spectroscopy, these features are obscured by the use of hygroscopic KBr in embedding samples before analysis. The band ratio used to describe this region (r_{OH}) efficiently captures the relative amounts of free hydroxyl groups in resins from both pinaceous and cupressaceous resin types (fig. 1). Correlations between r_{OH} and secondary absorption features expressed by r_5 and r_6 (fig. 5) imply that only resins with similar hydroxyl content will produce overall similar FTIR absorption spectra. Together, these

features express the degree of polymerization of any given resin sample. Polymerization reduces the number of free hydroxyl groups, such as conjugated dienes, and at the same time it modifies the involved carbon-oxygen bonds. The complex nature of these transformations explains why polymerization modulates resin FTIR spectra in both the 3400- and 1200–1300- cm^{-1} regions. Nonetheless, the r_{OH} ratio provides a useful first approximation of these processes, being inversely proportional to the degree of polymerization of both modern and fossil resins.

Applications to Fossil Resins

The application of infrared spectroscopy in the chemotaxonomic interpretation of fossil plant exudates is restricted to those types of exudates that polymerize into stable resin polymers and, therefore, persist in the geological record. Gums, as water-soluble complex sugars, for example, have an extremely limited fossilization potential and are not likely

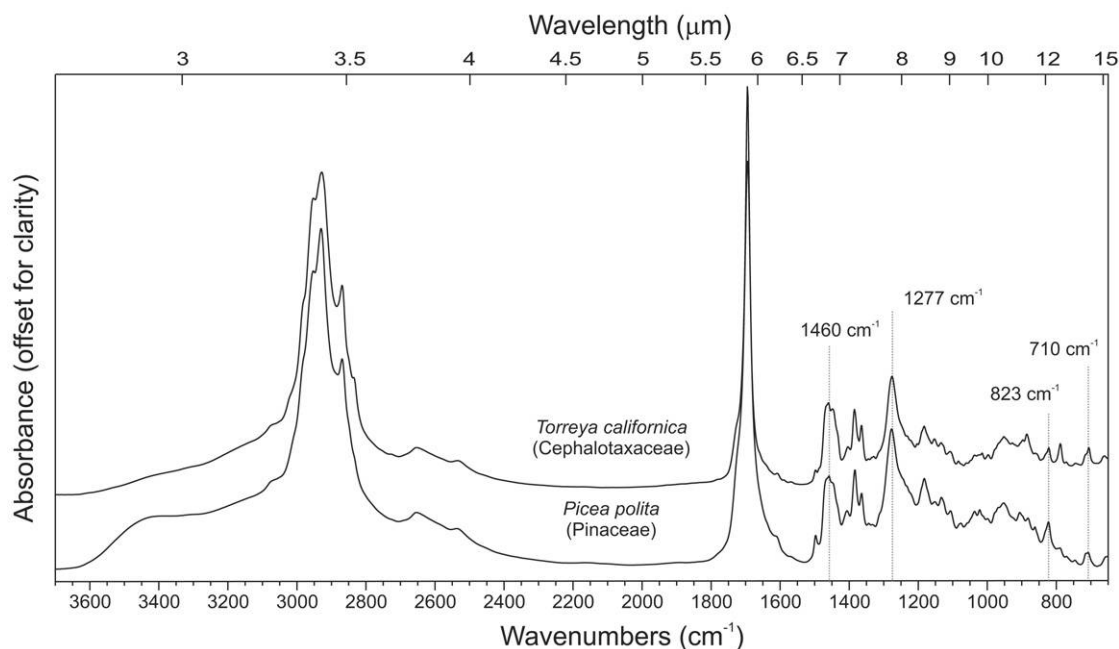


Fig. 9 Comparison of Fourier transform infrared (FTIR) spectra of resin from the taxad *Torreyia californica*, with resin from *Picea polita* (Pinaceae) to illustrate the visual similarities between the resins.

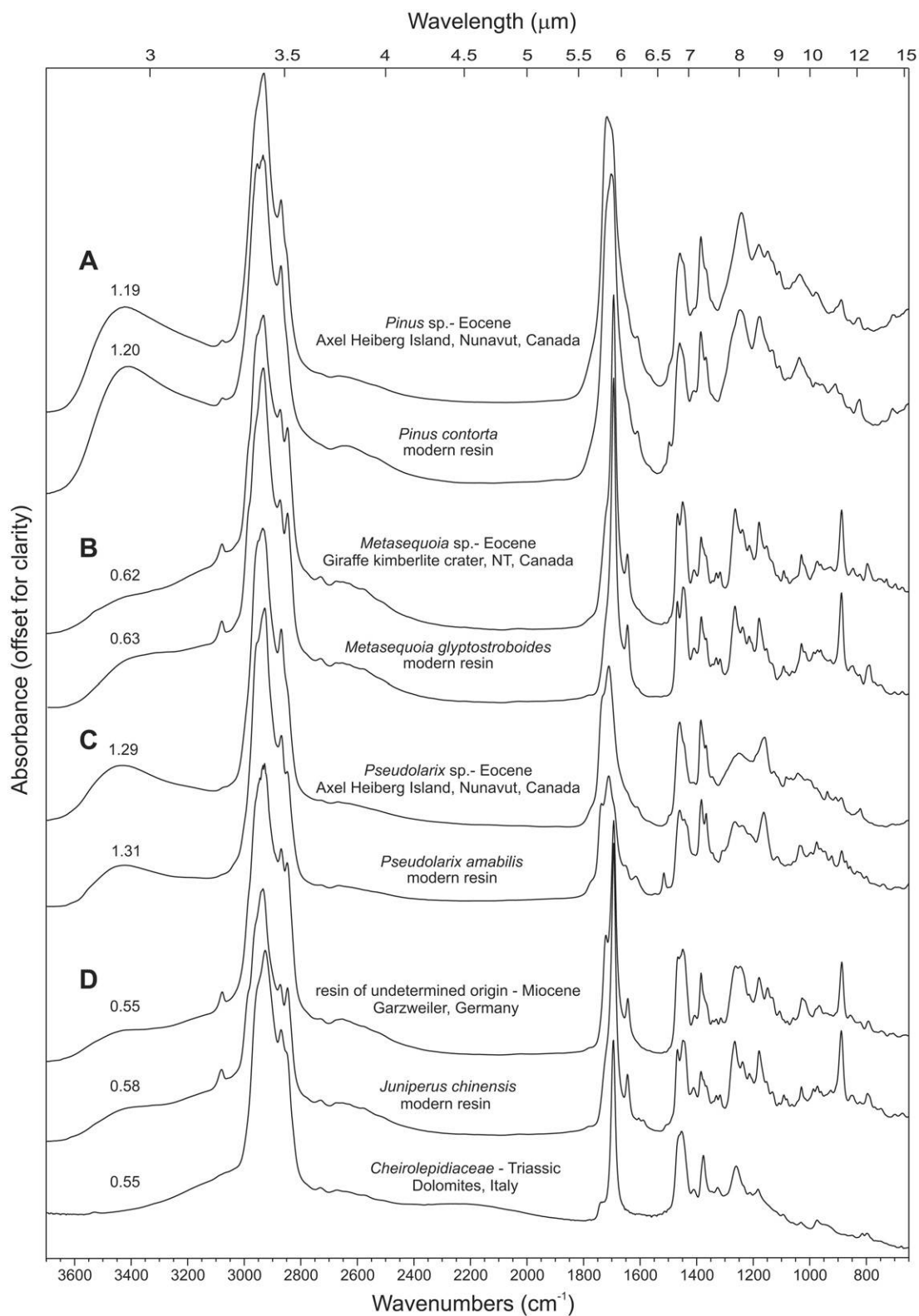


Fig. 10 Comparison of Fourier transform infrared (FTIR) spectra of fossil resins with spectra of resins from modern conifers. Numbers denote $\text{abs. } 3400 \text{ cm}^{-1} / \text{abs. } 3076 \text{ cm}^{-1}$ values for each resin as a relative measure of the abundance of free hydroxyl groups. The spectral comparison is shown for modern-fossil resin pairs (A–D) with similar $\text{abs. } 3400 \text{ cm}^{-1} / \text{abs. } 3076 \text{ cm}^{-1}$ values.

to be preserved over geological time. Similarly, volatile-rich resins will lose their volatile components shortly after formation and convert to typical resins. As a result, resins are the only types of gymnosperm exudate that have the potential to be preserved in the fossil record in the form of amber or resinite.

Infrared spectroscopy has been used extensively to characterize fossil resins and amber since pioneering work was performed in the 1960s (Beck et al. 1964, 1965; Langenheim and Beck 1965). Assigning conclusive botanical affinities to fossil resins on the basis of infrared absorption spectroscopy, however, has proven to be complicated by progressive chemical alterations that can occur over time. Early investigations, in addition, were fraught by large sample size requirements (>100 mg) and the overprinting influences of embedding media on critical portions of the spectrum. The technical advances inherent to micro-FTIR spectroscopy circumvent many of the problems of conventional infrared spectroscopy. In addition, the expanded library of modern FTIR spectra (table 1) provides a new reference for comparisons between modern resins and their fossil counterparts.

The chemotaxonomic classification schemes that we have developed appear to be sufficient to differentiate abietane/pimarane- from labdane-based fossil resins. In addition, it is possible to elucidate the degree of polymerization or degradation of a fossil resin using the absorption features produced by hydroxyl groups. To reinforce these points, we provide examples of FTIR spectra from three Eocene fossil resins of pinaceous and cupressaceous origin, a Miocene resin of unknown botanical affinity, and a Triassic resin sample, which represents one of the oldest known fossil resins. The spectra of these fossil resins are compared with the spectra of resins from modern congeners (fig. 10). Eocene resins of *Pinus* and *Pseudolarix* species were obtained from mummified cones in forest litter beds of the Buchanan Lake Formation on Axel Heiberg Island (Nunavut, Canada; Basinger 1991). Droplets of *Metasequoia* resinite were obtained from peat in a drill core from the Giraffe kimberlite crater (Northwest Territories, Canada), which contained abundant and well-preserved *Metasequoia* leaf fossils. The micro-FTIR spectra of the Eocene fossil resins are visually and quantitatively indistinct from those of modern *Pinus contorta*, *Pseudolarix amabilis*, and *Metasequoia glyptostroboides*, respectively (fig. 10). The fact that the spectra of the fossil resins and their modern counterparts are nearly indistinguishable reflects the exceptional states of preservation of the fossil resins despite ages in excess of 40 million yr.

The Miocene resin sample was recovered from coal of the Garzweiler coal seam, which was exposed in a large open-cut mine near Cologne, Germany. No identifiable plant remains were directly associated with the resin sample, which had a diameter of <0.5 mm (fig. 10D). Irrespective of the lack of paleobotanical information, the resin is readily identifiable as a cupressaceous resin on the basis of its distinct absorption spectrum.

The Triassic resin sample was collected from sediments of the Heiligkreuz-Santa Croce Formation, near Cortina d'Ampezzo, Dolomites, Italy. On the basis of close associations with wood and foliage, it has been suggested that the resins from this locality were produced by unspecified members of the extinct family Cheirolepidiaceae (Roghi et al. 2006). Despite an

age of the resin samples of >200 million yr, their spectra show that the resins were only marginally affected by alteration and reveal several characteristics of cupressaceous-type resins (fig. 10D). Although the relationship between Cheirolepidiaceae and modern conifer families is controversial (Taylor et al. 2008), the resin spectra indicate that the Cheirolepidiaceae synthesized resins using similar biochemical pathways as modern conifers within the Cupressaceae-Araucariaceae-Podocarpaceae. These results provide considerable encouragement with regard to renewed efforts in the application of current FTIR techniques toward the identification of source trees responsible for the production of fossil resins and amber.

Conclusions

Three distinct types of gymnosperm exudates, including resins, volatile-rich resins, and gums, can be distinguished on the basis of differences in their infrared absorption spectra, which were acquired using micro-FTIR spectroscopy. The most prominent type of gymnosperm exudate is resin. However, among the gymnosperms, the production of resins is restricted to conifers. On the basis of the positions of diagnostic absorption features and in combination with discrete absorption band ratios, two types of conifer resins can be quantitatively differentiated: pinaceous and cupressaceous resins. The most useful FTIR band ratios for their distinction were found to be $\text{abs. } 823 \text{ cm}^{-1} / \text{abs. } 791 \text{ cm}^{-1}$, $\text{abs. } 1460 \text{ cm}^{-1} / \text{abs. } 1448 \text{ cm}^{-1}$, $\text{abs. } 1448 \text{ cm}^{-1} / \text{abs. } 1385 \text{ cm}^{-1}$, and $\text{abs. } 2858 \text{ cm}^{-1} / \text{abs. } 2848 \text{ cm}^{-1}$. The spectroscopic differences between the two types of conifer resins reflect differences in the underlying skeletal structures of their terpenoid compounds. Pinaceous resins are mainly based on terpenoids with abietane or pimarane structures, whereas cupressaceous resins are based on terpenoids with labdane structures. These two distinct resin types outline fundamental differences in genetically mediated terpenoid synthases and are therefore of phylogenetic relevance. As a result, pinaceous resin is produced by all investigated representatives of the Pinaceae and the only member of the taxads, while cupressaceous resin is produced by members of the Cupressaceae, Araucariaceae, Podocarpaceae, and Sciadopityaceae. In addition to the conservative absorption features, which can be used to differentiate resin types, some features in resin spectra are highly variable and are linked to the presence of free hydroxyl groups. These variable absorption features can be used as a measure of the degree of polymerization of the resin.

Volatile-rich resins were found exclusively from representatives of the Pinaceae, which reflects the fact that conifers of this family generally produce resins that contain a greater amount of volatile mono- and sesquiterpenoids. Removal of the volatiles by evacuation in the laboratory or by polymerization in nature yields resins that can be directly compared with typical (low-volatile) resins.

Gums are exudates that are composed of polysaccharides. Within the conifers, gums are produced only by some species in the families Araucariaceae and Podocarpaceae. However, gums are the only type of exudate produced by nonconifer gymnosperms including *Ginkgo*, cycads, and *Welwitschia*, which implies that the production of terpenoid-based resins is a defining metabolic trait of the conifers. Results from the micro-FTIR spectroscopy not only have implications for the chemotax-

onomic interpretation of modern gymnosperm exudates, but they can also be applied in the assessment of the fossil potential of exudates and, more importantly, the paleobotanical identification of fossil resins from the geological record.

Acknowledgments

We thank Thomas Stachel for unrestricted access to the micro-FTIR spectrometer housed in his laboratory, Ruth

Stockey and Steve Williams for access to cultivars, and James Basinger and Guido Roghi for sharing fossil material from Axel Heiberg Island and the Dolomites, respectively. Additional modern resin samples were provided by Atis and Lucija Muehlenbachs. Amber Garrett performed some of the FTIR analyses. We would also like to thank the anonymous reviewers for their thoughtful and constructive comments. Funding was primarily obtained from the Natural Sciences and Engineering Research Council of Canada.

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