



Direct chemical characterization of natural wood resins by temperature-resolved and space-resolved Fourier transform infrared spectroscopy



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ABSTRACT

Wood resins are valuable natural products with wide utilizations. Either in the form of resin exudates or in the form of resin-containing woods, natural wood resins are usually complex mixtures consisting of various compounds. Therefore, effective chemical characterization methods are necessary for the research and quality control of natural wood resins. No need for separation or labeling, wood resin samples can be measured directly by Fourier transform infrared (FT-IR) spectroscopy, which reduces the testing costs and avoids the possible distortions caused by the pretreatments. However, the absorption bands of various compositions in the resin sample are assembled in a single spectrum by the separation-free measurement, which makes it difficult to identify the compounds of interest and decreases the limits of detection. In this research, the temperature-resolved and space-resolved FT-IR techniques are proposed to resolve the overlapped signals for the direct, selective, and sensitive characterization of natural wood resins. For resin exudates, the temperature-resolved FT-IR spectroscopy and two-dimensional correlation analysis can resolve the absorption bands of different compounds according to their responses to the thermal perturbations. For resin-containing woods, the FT-IR microspectroscopic imaging and principal component analysis can resolve the absorption bands of different compounds according to their positions. The study of six kinds of wood resins proves the feasibility of temperature-resolved and space-resolved FT-IR techniques for the direct, selective, and sensitive chemical characterization of natural wood resins.

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1. Introduction

Wood resins are valuable natural products with a variety of utilizations. There has been a long history of using wood resins as natural perfumes and medicines in some regions. Nowadays, many kinds of compounds can be obtained from wood resins. Natural wood resins are usually complex mixtures composed of various compounds, which may be changed significantly by genetic and environmental factors. Therefore, analytical techniques for the chemical characterization play a very important role in the research and utilization of natural wood resins.

Fourier transform infrared (FT-IR) spectroscopy is a direct and universal analytical technique which can be used to characterize

the compositions of natural botanic materials without any separation or derivation. So there is no doubt about the possible changes of the compositions during the sample preprocessing. The testing costs of time, money, and chemical reagents are also reduced significantly. FT-IR spectra can provide the original information about the molecular structures and contents of most organic and inorganic compounds in mixture materials at the same time. Therefore, FT-IR spectroscopy has been successfully applied in the research and quality control of many kinds of botanical materials [1–3], and the potential of FT-IR spectroscopy in the chemical characterization of natural wood resins can be expected.

However, the absorption bands of many kinds of compounds in the resin sample are measured in a single spectrum without isolation of each component for obtaining its spectrum. Overlapping of absorption bands usually makes it difficult to identify the characteristic spectral bands of the compounds of interesting, and in consequence the limits of detection are decreased significantly.

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Therefore, some signal-resolving approaches are necessary to resolve the FT-IR spectra of natural wood resins for the selective and sensitive detection of compounds of interesting.

Many compounds in wood resin exudates are vulnerable to thermal stimulations. But different compounds usually respond in different ways to the same thermal stimulation. Therefore, the FT-IR absorption bands of different compounds may be discriminated according to their responses to the given thermal stimulation. For example, the spectral bands from the same compound will decrease synchronously if this compound evaporates when the sample is heated, meanwhile the spectral bands of other stable compounds remain [4]. The responses of the absorption bands of wood resin exudates to a given thermal stimulation can be recorded by the temperature-resolved FT-IR technique. Two-dimensional correlation infrared (2D-IR) spectroscopy [5–7] is a convenient tool to interpret the relationships of the spectral changes induced by an external perturbation and resolve the absorption bands of compounds which respond in different ways to the perturbation [4].

For resin-containing woods, the FT-IR absorption bands of resins are usually overlapped with the absorption bands of the wood matrix such as cellulose and lignin in the cell walls. Since the resins usually exist in the canals and cavities, the microscopic FT-IR technique may collect the spectra of resins and cell walls separately. Therefore, the resin-containing woods can be measured by FT-IR microspectroscopic imaging to obtain the spectra of a large number of pixels. An imaging pixel is the sampling area for a single spectrum. Exploratory multivariate analysis such as principal component analysis (PCA) can cluster the pixels according to their spectral features, which makes it easy to identify the pixels corresponding to resins, cell walls, or other tissue structures. In other words, the FT-IR absorption bands of resins and other compounds can be resolved by their x, y coordinates [8–10].

To examine the feasibility of the above approaches for the direct, selective, and sensitive chemical characterization of natural wood resins, some wood resin exudates (Olibanum, Gamboge, and Benzoinum) are characterized by the temperature-resolved FT-IR spectroscopy and two-dimensional correlation analysis in this research, meanwhile some resin-containing woods (*Dalbergia Odoriferae Lignum*, *Aquilariae Lignum Resinatum*, and *Sappan Lignum*) are characterized by the FT-IR microspectroscopic imaging and principal component analysis.

2. Materials and methods

2.1. Materials

Six kinds of certificated medicinal wood resins were purchased from Chinese National Institutes for Food and Drug Control. In the form of wood resin exudates are Olibanum (from *Boswellia carterii* Birdw.), Gamboge (from *Garcinia hanburyi* Hook.f.), and Benzoinum (from *Styrax tonkinensis* (Pierre) Craib ex Hart.). In the form of resin-containing woods are *Dalbergia Odoriferae Lignum* (the heartwood of *Dalbergia odorifera* T. Chen), *Aquilariae Lignum Resinatum* (the resin-containing wood of *Aquilaria sinensis* (Lour.) Gilg.), and *Sappan Lignum* (the heartwood of *Caesalpinia sappan* L.). Poplar cellulose and lignin are gifts from Dr. An-min Huang (Research Institute of Wood Industry, Chinese Academy of Forestry).

2.2. Conventional FT-IR spectroscopy

Macroscopic FT-IR spectra of all samples at room temperature were recorded using the KBr pellet method. Each sample was finely powdered by a ceramic mortar and screened with a 100-mesh stainless steel sieve. 1–2 mg of the fine powder was

homogeneously mixed with 100 mg of KBr powder, then the mixture was pressed into a thin pellet using a manual hydraulic press. A Frontier FT-IR/NIR spectrometer (PerkinElmer, Waltham, MA, USA) with a DTGS detector was used to collect the transmission spectra of the pellets. The OPD velocity was 0.2 cm/s. The apodization function was Norton-Beer strong. No further smoothing was applied to the collected spectra. Each spectrum was the average of 32 scans in the range of 4000–400 cm^{-1} with a spectral resolution of 4 cm^{-1} . The influence of H_2O and CO_2 was subtracted automatically by the instrument. In this case, the peak-to-peak noise was 0.0041% in the range of 2100–2000 cm^{-1} and 0.017% in the range of 900–800 cm^{-1} .

To be compared with the FT-IR microspectroscopic imaging spectra, the resin-containing woods (*Dalbergia Odoriferae Lignum*, *Aquilariae Lignum Resinatum*, and *Sappan Lignum*) were extracted by sonicating about 0.1 g of the wood powder in 1 mL of alcohol for 10 min, centrifuging, and volatilizing the solvent of the supernatant. The extracts were measured by the above spectrometer with a universal ATR accessory (PerkinElmer, Waltham, MA, USA). The internal reflection element of the accessory was a combination of diamond and ZnSe and the angle of incidence was 45°. ATR spectra of the samples were recorded in the range of 4000–750 cm^{-1} with a resolution of 8 cm^{-1} , and each spectrum was the average of 8 scans. The OPD velocity was 0.2 cm/s. The apodization function was Norton-Beer strong. No further smoothing was applied to the collected spectra.

All sample spectra were optimized by the software Spectrum v6.0 (PerkinElmer, Waltham, MA, USA). First, the spectral ordinate was transformed into absorbance. Then, the spectral baseline was corrected automatically. Finally, the spectrum was normalized to make the maximum and minimum absorbance values be one and zero, respectively. For the ATR spectra, the ATR correction with a zero contact factor was applied before the automatic baseline correction. The default peak threshold (2%T) is used to identify the absorption bands.

2.3. Temperature-resolved FT-IR spectroscopy

The temperature-resolved infrared spectra of the resin exudates (Olibanum, Gamboge, and Benzoinum) were collected using a variable temperature transmission holder controlled by the temperature controller CKW-1110 (Chaoyang Automation Instrument Co., Beijing, China). The KBr pellet was fixed into the holder and placed in the sample compartment of the Frontier FT-IR/NIR spectrometer. The pellet was heated from the ambient temperature to 120 °C at a rate of 2 °C/min. FT-IR spectra were recorded from 50 °C to 120 °C with an interval of 10 °C. Each spectrum was the average of 32 scans in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} . The OPD velocity was 0.2 cm/s. The apodization function was Norton-Beer strong. No further smoothing was applied to the collected spectra.

All recorded sample spectra were optimized by the Spectrum software. First, the ordinate of each spectrum was transformed into absorbance. Then, the baseline was corrected by the software automatically. After that, the offset baseline was further corrected by subtracting a constant to make the minimum absorbance value in the range of 2400–2200 cm^{-1} zero. 2D-IR spectra were calculated by the software MATLAB v7.0 (The MathWorks, Natick, MA, USA) with homemade scripts using the algorithm proposed by I. Noda [5,6].

2.4. FT-IR microspectroscopic imaging

FT-IR microspectroscopic imaging of the resin-containing woods (*Dalbergia Odoriferae Lignum*, *Aquilariae Lignum*

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