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Rapid identification and quantification three chicken-wing woods of *Millettia leucantha, Millettia laurentii and Cassia siamea* by FT-IR and 2DCOS-IR

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ABSTRACT

The chicken-wing wood belongs to "hongmu", which comes from the heartwood of three kinds of trees, *M. leucantha*, *M. laurentii* and *C. siamea*. In this study, tri-step infrared spectroscopy macro-fingerprinting technique was employed to discriminate the three chicken-wing wood. Though three chicken-wing woods are extremely similar, some differences in chemical components emerged through Fourier Transition Infrared (FT-IR) spectra. Among them, *M. leucantha* and *M. laurentii* are cellulose-rich, while *C. siamea* is lignin-rich. Besides, *M. leucantha* and *C. siamea* have two peaks at 1328 and 782 cm^{-1} belonging to calcium oxalate. An effective modeling approach to predict the content of cellulose was proposed. The result shows that cellulose content of *M. leucantha*, *M. laurentii* and *C. siamea* were 45.84%, 40.92% and 38.85% respectively. According to Two-dimensional correlation infrared spectra (2DCOS-IR), number, position and intensity of auto-peaks in the range of 1250–1800 cm^{-1} could be selected as the indicator to identify the three chicken-wing woods.

1. Introduction

The chicken-wing wood (*Millettia* spp. *Cassia* sp.) is a kind of "hongmu" with V-shaped pattern like chicken wings on the tangential section of heartwood. The chicken-wing wood has been widely used as construction and furniture materials. Hongmu furniture is one of the Chinese national treasure with aesthetics and value-added potential [1]. In China, national standard of Hongmu (GB/T18107-2000) stipulated that the chicken-wing wood included three species woods of *Millettia leucantha*, *Millettia laurentii* and *Cassia siamea* [2]. The three chicken-wing woods have been listed as "critically endangered" in the Red List of the International Union for the Conservation of Nature (IUCN) and Appendix II of Convention on International Trade in Endangered Species of Wild Fauna and Flora (Appendix II, CITES) for overexploited [3]. *Millettia leucantha* Kurz. (*M. leucantha*), is a lofty tree, with pinnate leaves and white flowers, growing throughout Myanmar and Thailand [4]. *Millettia laurentii* De Wild. (*M. laurentii*) is belonging to the Leguminosae–Millettia, which is found in the rain forest of Congo, Cameroon, North Gabon, and Zaire [5]. The plant of *Cassia siamea* Lam. (*C. siamea.*) belongs to the Cassia genus. It is widespread in Asia and Africa [6]. In China, *C. siamea.* has been widely used as traditional Chinese medicine for treatment of diarrhea, gastritis, ringworm, and fungal skin infections [7,8].

All the furniture made of the chicken-wing wood show chicken wing pattern. The common used verification technology of chicken-wing wood is to identify the variety of heartwood according to the color, smell and cell structure. There are some differences in the micro-section of the three species wood. These wood anatomy features must be observed and analyzed by professionals. Through aspect of esthetics principle and the pattern creation, Liu et al. designed the pattern style of furniture based on the macroscopic and microscopic structure characteristics of the three chicken-wing woods [9]. Zhao et al. measured and analyzed geometric parameters of three kinds of cells morphology of *M. leucantha*, *M. laurentii* and *C. siamea*. The result shows that the size of drum-like vessels in *M. laurentii* is the biggest, and *M. leucantha* and *Cassia siamea* include more gum [10]. In order to identify the species and classifications of the chicken-wing wood, the furniture must be destroyed or cut into slice. Therefore, it is very important to establish an efficient, effective and non-

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destructive method for the three chicken-wing woods.

A method of tri-step IR macro-fingerprinting techniques containing Fourier transform infrared (FT-IR) spectroscopy, second derivative infrared (SD-IR) spectroscopy and two-dimensional correlation infrared (2DCOS-IR) spectroscopy with statistical pattern recognition was therefore employed to discriminate the complex mixtures. The quick, easy, and non-destructive FT-IR spectroscopy has been widely applied to the identification and quality control of samples due to the versatile available sampling techniques and the considerable number of bands [11–15]. Furthermore, 2DCOS-IR spectroscopy, which was established by Isao Noda thirty decades ago, can be used to unfold FT-IR spectra on a second dimension to acquire a remarkably improved spectral resolution and to obtain more chemical structural information such as proteins, peptides, polymers, crystals, pharmaceuticals, wood etc. [16–23].

Cellulose is the skeleton material of the wood cell wall. The chemical properties of cellulose are relatively stable. The content of cellulose not only affects the properties of the wood, but also a very important quantitative indicator for functional of wood. When the content of cellulosed is higher, the tensile strength of wood became stronger. Rodrigues developed a method of a linear regression FT-IR spectroscopy to estimate the lignin content of *Eucalyptus globulus* wood samples which have only small differences in chemical composition due to natural variability [24]. Therefore, this effective modeling approach was proposed to predict the content of cellulose in three chicken-wing woods.

2. Experimental

2.1. Materials and sample preparation

The heartwoods of *M. leucantha*, *M. laurentii* and *C. siamea* (Fig. 1) were provided by Research Institute of Wood Industry, Chinese Academy of Forestry, China. The air-dried wood was pulverized before the measurement. Each sample (about 1–2 mg) was blended with KBr (100 mg), grounded into powder (200 mesh), and then the mixture was further grounded and pressed under 10 tons of pressure to produce a thin disk with 13 mm in diameter. Cellulose, NaSCN and lignin were purchased from Macklin Chemistry Co. Ltd.

2.2. FT-IR spectroscopy

Spectrum GX FT-IR spectrometer (PerkinElmer, USA) equipped with a deuterated triglycine sulfate (DTGS) detector was used. Each IR spectrum was recorded from an accumulation of 16 scans in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. The interferences of H_2O and CO_2 were subtracted when scanning.

a b c

Fig. 1. The heartwood of *M. leucantha*, *M. laurentii* and *C. siamea*.

The FT-IR spectra of all samples were collected at room temperature. The software Spectrum v6.3 (PerkinElmer, MA, USA) was used to auto-correct the spectral baseline and calculate the derivative spectra.

2.3. 2DCOS-IR spectroscopy

IR spectrometer is the same as section 2.2. A CKW-II programmable temperature controller (Beijing Chaoyang Automatic Instrument Co. China) was used to perform the thermal perturbation. The temperature range is 50–120 °C with a heating rate of 2 °C/min 2DCOS-IR spectra were calculated by the 2DCOS-IR software developed by Tsinghua University (Beijing, China).

3. Results and discussion

3.1. FT-IR spectra of M. leucantha, M. laurentii and C. siamea

M. leucantha, *M. laurentii* and *C. siamea* are three kinds of wood species with precious value. The main components of wood cell walls are cellulose and lignin, which take up more than 70% of wood mass. Though three chicken-wing woods of *M. leucantha*, *M. laurentii* and *C. siamea* are extremely similar, they have some difference in chemical components as shown in FT-IR spectra in the range of 4000–2600 cm^{-1} and 1800–750 cm^{-1} (Fig. 2). Some significant peaks are assigned in Table 1.

From Fig. 2 and Table 1, we can see clearly that *M. leucantha*, *M. laurentii* and *C. siamea* are rather similar. The peak at ~2929, ~1463 and ~1424 cm^{-1}is assigned as $-CH_2-$ groups belonging to the lignin. The C=O stretching vibration at ~1733 cm^{-1} groups indicates that *M. laurentii* and *C. siamea* contain more unconjugated ketone, carbonyl and aliphatic groups. The peak at ~1623 cm^{-1} in *M. leucantha* is assigned as C–O stretching belonging to calcium oxalate. The strong peak at ~1603, ~1409, ~1269 and~1043 cm^{-1} which refers to the aromatic skeletal stretching, means that *C. siamea* is rich in the lignin. In addition, the strong peak at ~1372, ~1158, ~1059 and~1033 cm^{-1} which refers to the aromatic skeletal stretching, means that *M. leucantha* and *M. laurentii* are rich in the cellulose.

Calcium oxalate crystals, in many plant species, is a kind of secondary metabolite in the process of plant growth and development. The existence, size, and morphology of this substance are

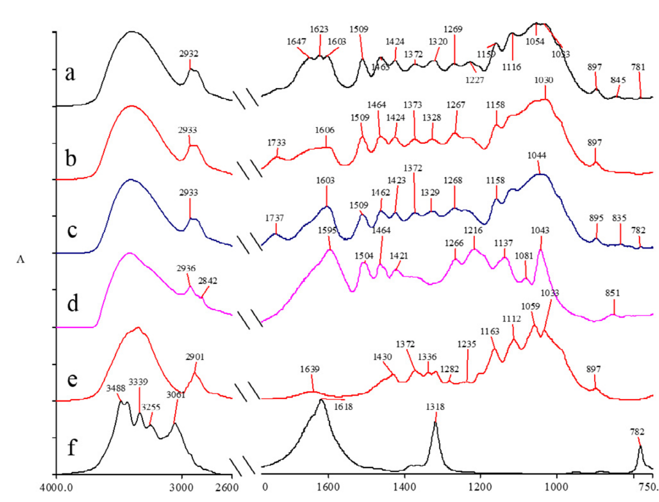

Fig. 2. FT-IR spectra of (a) *M. leucantha*, (b) *M. laurentii*, (c) *C. siamea*, (d) lignin, (e) cellulose and (f) calcium oxalate.