DIFFERENT SOLVENT EXTRACT OF *TOONA SINENSIS* WOOD BY FT-IR AND GC-MS

by

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Original scientific paper
https://doi.org/10.2298/TSCI190506034Y

Forest biomass energy material is the natural material for human survival. Wood is the main material for human development. In order to save energy, the active chemical components in wood are extracted by modern equipment and applied to biomedicine, high-grade cosmetics, precious spices and other products to promote the high attachment of wood processing industry and Value-added development. The FT-IR was used to analyze and compare the extracts of Toona sinensis with ethanol, methanol and benzyl/ethanol in different solvents. Because of benzene ring of lignan suffered the most destruction from benzene/ethanol extractives, the FT-IR results showed that the absorbance of each peak was maximal at the benzene/ethanol extractives and minimal at the methanol extractives. In the gas chromatography-mass spectrometer (GC-MS) test, the ethanol extractives of Toona sinensis wood had a main retention time between 10-20 minute, which accounts for 38.44% of the total relative content; methanol extractives had a main retention time between 5-15 minute, which accounts for 41.22% of the total relative content; the benzene/ethanol extractives between 10-20 minute accounted for 44.46% of the total relative content. The chemical composition and retention time of the three solvent extracts are different. The measurement and analysis of the experimental data opened up a new way for the development and utilization of woody plant energy.

Key words: *Toona sinensis, chemical composition, FT-IR, GC-MS, difference*

Instructions

It is a new method of wood energy development that extends from traditional wood biology, physics and mechanics research to multi-scale molecular depth, and from primary wood product utilization to secondary and tertiary wood product utilization. *Toona sinensis* (TS) is widely distributed in China, commonly known as Chinese mahogany [1]. It is an endemic species of the *Toona* genus (*Meliaceae* family) native to the Asia and naturally distributed from southern North Korea through most parts of China to Thailand, Myanmar, India, Malaysia, and Indonesia [2, 3]. The TS is not only used as building materials, but also has more important medicinal value after extraction. All parts of TS, including its root, bark, petiole, leaf, fruit and seed, have been used for medicinal purposes. The extraction of chemicals in TS has becomes a hot topic. Moreover, itsextracts have been shown to exhibit anti-cancer effects in human ovarian cancer cell lines, human promyelocytic leukemia cells, and human lung adenocarcinoma [4]. Crude water and/or ethanol extracts of leaves contains many polyphenols and

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avonoids, exerting pleiotropic biological activities, such as antioxidant [5], anti-diabetes [6], anti-in amatory [7], and hypolipidemic [8].

Most of the studies focused on the leaves, but the quality of the leaves was poor field. In recent years, the health function of wood has been studied. The health function of wood is actually the function of organic volatiles in wood. Organic volatiles do not have much use in actual wood utilization [9, 10]. These beneficial extracts can be recycled and reused to improve and expand the utilization of wood. The extracts of different solvents in wood are different [11, 12]. In order to find a better source of raw materials, different solvent extracts are used to make full use of their greater medicinal value [13-21]. Various modern instruments make more in-depth the chemical research of TS taking it as the main research object, andthe extraction from three different organic solvents was detected and identified by FT-IR and GC-MS [22-24]. The results showed that extract contained a large number of bioactive components, and most components are healthy and abundant [25]. The main active ingredients are alpha-bismyrrh alcohol, squalene, propionic acid, 2-methyl-3-hydroxy-2,2,4-trimethyl amyl ester, p-cresol, (-) -vertol and heptanone. It has potential application prospects in bioenergy, biomedicine, cosmetics, skin care products, spices and other fields. The study of the chemical composition provides a scientific basis for the development and utilization of the TS.

Material and method

Experimental material

Three years old TS trunk above the first branch was collected in Hunan province. The fresh wood was cutted up, powdered and hold in vacuum. Ethanol, methanol and benzene/ethanol (1:1) were chromatographic grade, and were used for the test. Cotton thread and cotton bag were both extracted by ethanol, methanol, benzene/ethanol (1:1) solution for 12 hours [26].

Experiment method

Weigh 60 grams of powder and divide it into three parts (0.1 mg accuracy), and parceled into the cotton bag, tied by the cotton thread. The solvents were 350 ml for ethanol, methanol and benzene/ethanol (1:1), respectively, and were extracted by FOSS method for 7 hours. After extraction, three extracts were obtained by evaporation at 60-70 °C [27].

The FT-IR analysis

The extractives samples were recorded on a Thermo Nicolet FT-IR spectrometer (Thermo Fisher Nicolet, 670 FT-IR). Thirty-two scans were collected per sample at a spectral resolution of 4 cm^{-1}, and the collected spectra were normalized against air. The spectral range was from 4000 to 500 cm^{-1} [28].

The GC-MS analysis

The GC-MS analysis was conducted on a GC-MS-QP2010 (Shimadzu Corp., Japan), which was linked to a mass selective detector. The GC-MS condition: Each 1.0 mg of TS extractives was analyzed via online linked GC-MS, respectively. The elastic fused silica capillary column DB-5 (30 m × 0.25 mm) was used. The carrier gas was helium and the injection port temperature was 250 °C. For ethanol and methanol extractives, the split injection ratio was 5:1 and the GC column temperature was programmed as follows: 8 °C/min from 50 to 200 °C, and 5 °C/min from 200 to 300 °C. For benzene-methanol extractives, the split injection ratio was 3:1, the GC column temperature was programmed as follows: 20 °C/min from 50 to 90 °C, 2 °C/min from 90 to 200 °C, 12 °C/min from 200 to 300 °C. The program of MS was scanned over the 35-335 (m/z), respectively, with an ionizing voltage of 70 eV and an ionization current of 150 μA of electron ionization (EI). The flow velocity of helium was 1.0 ml/min [29].

Results and discussion

Analysis of FT-IR

The FT-IR spectrums of wood extractives from three TS extractions is shown in fig. 1. The most important O-H stretching in hydroxyl group was assigned to the 3354-3404 cm^{-1} region. The broad peak is an intermolecular association absorption peak near 3400 cm^{-1}.

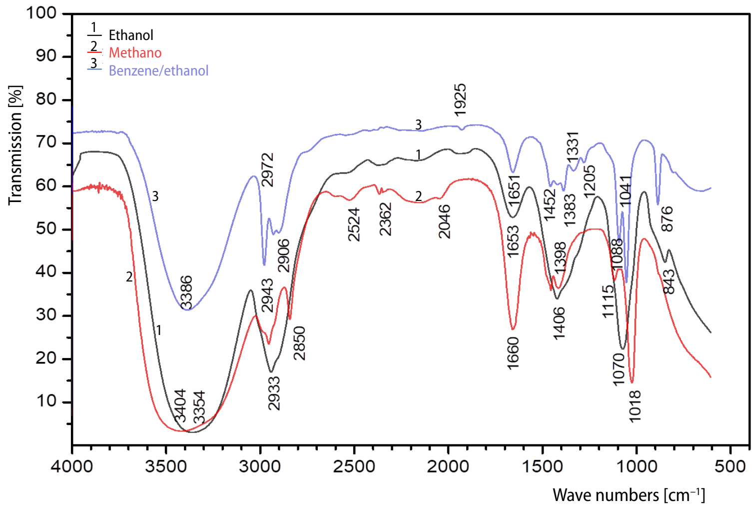

Figure 1. The FT-IR spectra of samples ethanol, methanol, and benzene/ethanol (1:1) extraction

Ethanol (blank): At 3354 cm^{-1}, 2933 cm^{-1}, 1653 cm^{-1}, 1406 cm^{-1}, 1070 cm^{-1}, 843 cm^{-1} were O-H stretching in hydroxyl group, Carboxylic acids O-H stretching, Alkenes C=C stretching Alkanes C-H scissoring and bending, Alcohols, Ethers, Carboxylic acids and Esters C-O stretching, respectively.

Methanol (red): At 3404 cm^{-1}, 2943 cm^{-1} or 2850 cm^{-1}, 1660 cm^{-1}, 1406 cm^{-1}, 1398 cm^{-1}, 1115 cm^{-1} or 1018 cm^{-1} were O-H stretching in hydroxyl group, Carboxylic acids O-H stretching, and Alkenes C-H stretching, Carboxylic acids O-H stretching and Alkenes C-H stretching, Alkenes C=C stretching, Alkanes C-H scissoring and bending, Alcohols, Ethers, Carboxylic acids and Esters C-O stretching, respectively.

Benzene/ethanol (blue): At 3386 cm^{-1}, 2972 cm^{-1}, 2906 cm^{-1}, 1951 cm^{-1}, 1452 cm^{-1}, 1331 cm^{-1}, 876 cm^{-1} were O-H stretching in hydroxyl group, Carboxylic acids O-H stretching, Phenyl Ring Substitution Overtones C-H fingerprint region, Carboxylic acids O-H stretching and Alkenes C-H stretching, Carboxylic acids O-H stretching and Alkenes C-H stretching, Alkanes C-H scissoring and bending Phenyl Ring Substitution Overtones C-H fingerprint region, Amines C-N stretching, Alkenes C=C stretching, and Alkanes C-H bending, respectively. Their assignments were obtained according to relevant papers.

The absorbance of peaks at 3354-3404 cm^{-1} increased from 0.274 to 0.347. The absorbance of peaks at 1651-1660 cm^{-1} decreased from 0.632 to 0.268, and the absorbance of peaks at 1383-1406 cm^{-1} decreased from 0.588 to 0.343. Suggesting that the benzene ring of lignan reached the most destructive at benzene/ethanol extractives. The results show that the absorbance of each peak was maximal at the benzene/ethanol extractives and minimal at the methanol extractives.

In a word, the absorption peaks of the TS extract are mainly concentrated in the wave segments of 3354-3404 cm^{-1}, 3000-2800 cm^{-1} and 1660-750 cm^{-1}. The main chemical components are phenols, alcohols, ethers, fatty acids, hydrocarbons and aromatic compounds [30].

Analysis of GC-MS

The GC-MS analysis results show the molecular distribution of TS wood extractives. According to the results of GC-MS analysis, 34 chemical constituents were identified in 39 peaks of ethanol extraction; 44 chemical constituents were identified in 44 peaks of methanol extraction; 49 chemical constituents were identified in 50 peaks of benzene/ethanol (1:1) extraction, respectively. The extraction spectrum is shown in figs. 2-4.

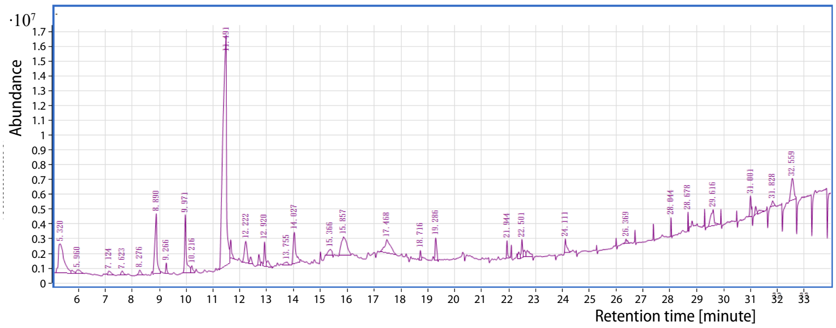

Figure 2. Total ion chromatograms of ethanol extraction

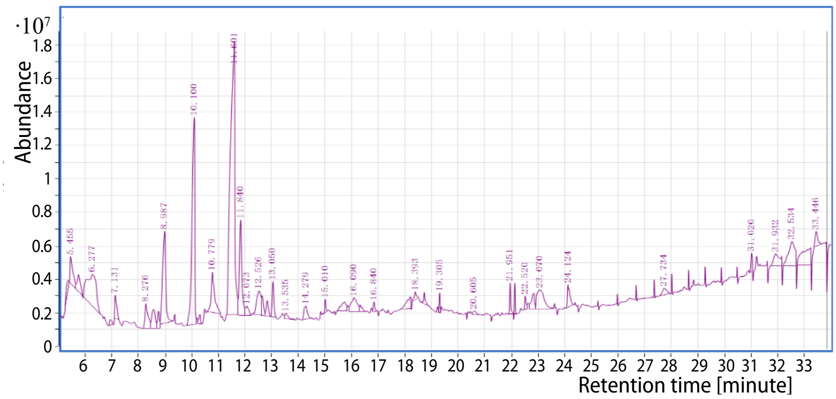

Figure 3. Total ion chromatograms of methanol extraction

In the first sample, the result showed that the main components were 5-Hydroxymethylfurfural(41.5%), Furfural(7.55%), D-Alanine, N-propargyloxycarbonyl-,Isohexylester(5.93%), D-Allose(4.92%), 4H-Pyran-4-one,2,3-dihydro-3,5-dihydroxy-6-methyl-(4.74%), 1,4-Dioxane,2-ethyl-5-methyl-(3.72%), Lactose(4.12%),Cyclotrisiloxane, hexamethyl-(2.96%), Acetoxyacetic acid, nonyl ester(2.75%), alpha.-Tocopherylacetate(2.54%), Ethypropionylacetate(1.6%), and 4-Hydroxy-2-methoxycinnamaldehyde(1.59%).

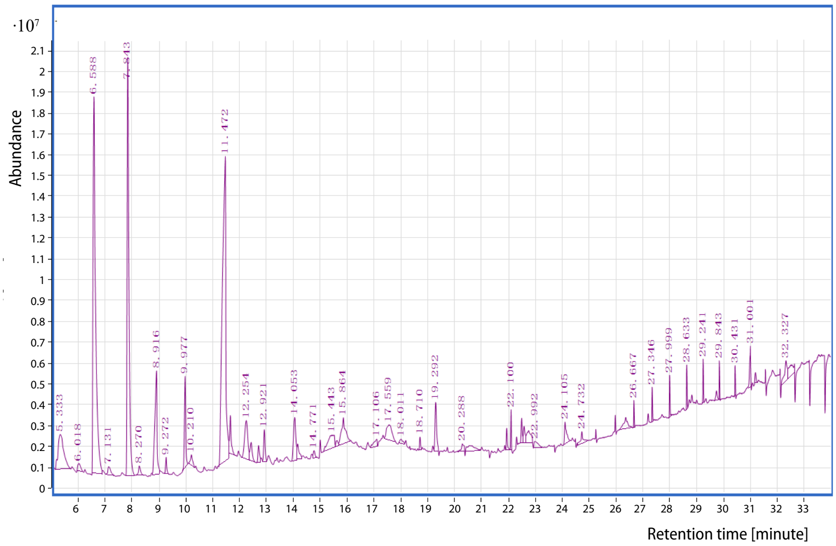

Figure 4. Total ion chromatograms of benzene/ethanol (1:1) extraction

In sencond sample, the result showed that the main components were 5-Hydroxymethylfurfural(26.67%), 4H-Pyran-4-one,2,3-dihydro-3,5-dihydroxy-6-methyl--(12.41%), Melezitose(9.74%), Dihydroxyacetone(6.45%), Maltol(6.42%), Hexadecanoic acid, 3-hydroxy-, methyl ester(5.14%), Cyclotetrasiloxane,octamethyl-(6.71%), gamma.-Sitosterol(3.09%),IsosorbideDinitrate(3.04%), Lactose (1.81%), Levoglucosenone (1.66%) and DL-Arabinose (1.66%).

In third sample, the result showed that the main component were Ethanol (23.7%), 3,5-Dimethylpyrazole(21.23%), Formamide,N,N-diethyl-(2.47%), 5-Hydroxymethylfurfural (2.1%), D-Alanine, N-propargyloxycarbonyl-(2.02%), isohexylester(2.02%), Isosorbide Dinitrate(1.75%), Cyclotetrasiloxane, octamethyl-(1.75%), Melezitose(1.66%), 1,4-Dioxane, 2-ethyl-5-methyl-(1.63%), and DL-Arabinose(1.2%).

The distribution characteristic of three samples studied via GC-MS are shown in fig. 5.

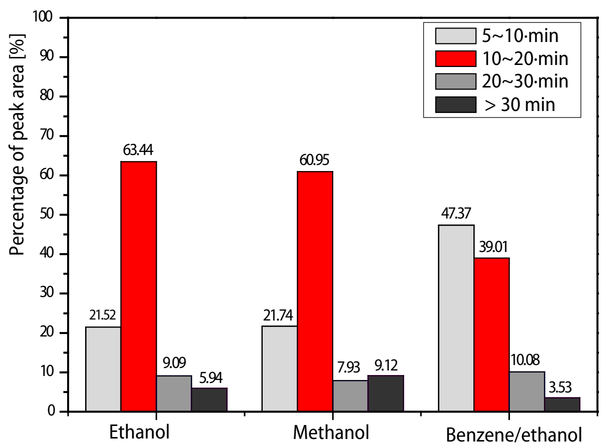

Figure 5. Distribution characteristic of ethanol, methanoland benzene/ethanol (1:1)

The retention times of the different components from TS wood extractives show a particular trend. For the first sample, 21.52%, 63.44%, 9.09%, and 5.94% of the sample had retention times of 5-10, 10-20, 20-30 and longer than 30 minute, respectively. For the second sample, 21.74%, 60.95%, 7.93%, and 9.12% of the sample had retention times of 5-10, 10-20, 20-30, and longer than 30 minute, respectively. For the third sample, 47.37%, 39.01%, 10.08%

and 3.53% of the sample had retention times of 5-10, 10-20, 20-30 and longer than 30 minute, respectively.

The results suggest that the molecular content of first, second and third samples increased gradually for the sample retention time of 5-15 minutes. The molecular content of samples third, second and first increased gradually at the sample retention time of 10-20 minute. The molecular content of samples 2, 1, and 3 increased gradually at a sample retention time of 20-30 minute. The molecular content of samples 3, 1 and 2 increased gradually at a sample retention time above 30 minute. The results of GC-MS better confirm that the group structures of the extractive and further determine the content ratio of each chemical component.

Conclusion and discussion

The TS powder after extraction by ethanol, methanol and benzene/ethanol and log powder was the main research object. In the FT-IR test, and the results showed that the absorbance of each peak was maximal at the benzene/ethanol extractives and minimal at the methanol extractives, indicating that the extractive of TS contained acids, ethers, esters and other alcohols. According to GC-MS test, the ethanol extractives of TS wood had a main retention time between 10-20 minute, which accounts for 38.44% of the total relative content. The methanol extractives had a main retention time between 5-15 minute, which accounts for 41.22% of the total relative content. The benzene/ethanol extractives had a main retention time between 10-20 minute which accounts for 44.46% of the total relative content. The GC-MS further determined the content ratio of each chemical component. In addition to the discovery of differences in wood extracts between different solvents, and this experiment also found many active ingredients in wood. Because of the time relationship, there is no in-depth excavation. If each active ingredient is thoroughly analyzed in the later experiment. It will certainly be able to dig out the *golden* substances in forest energy, and make high value-added use of forest resources to provide a solid data base.

Acknowledgment

This research was supported by the Planned Science and Technology Project of Hunan Province, China (No.2016SK2089; No.2016RS2011), Major scientific and technological achievements transformation projects of strategic emerging industries in Hunan Province (2016GK4045), and the Academician reserve personnel training plan of lift engineering technical personnel of Hunan Science and Technology Association (2017TJ-Y10). Samples of Toonasinensis wood was provided by Henan Forestry Research Institute for basic operations funds (201611817).

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Paper submitted: May 6, 2019
Paper revised: May 9, 2019
Paper accepted: September 17, 2019