CHEMICAL COMPOSITIONS AND FUNCTIONS OF CHINESE FIR VOLATILES

by

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Chinese fir is an important economic tree species in China. In addition to the application of alive trees and wood, the abundant chemical compositions of Chinese fir as a non-wood resource also have very important position. This study used Chinese fir wood powder as material, analyzing the chemical composition of Chinese fir volatiles by Fourier transform infrared spectroscopy (FT-IR), thermogravimetry (TG), pyrolisis-gas chromatography-mass spectrometry (Py-GC-MS), thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS). Through the analysis of the detected we can know that volatiles main were phenolic (cedrol, alpha-bisabolol and beta-eudesmol), ester (dimethyl phthalate, diisobutyl phthalate and dibutyl phthalate), ketone (hydroxyacetone and benzofuran) and aldehyde (hexanal and nonanal) and so on. This compounds and their derivatives can use at wide medical, biology, cosmetics and textile industry.

Key words: *Chinese fir, volatiles, FT-IR, TG, Py-GC-MS, TD-GC-MS*

Introduction

Chinese fir (*Cunninghamia Lanceolata*) is subtropical species and belongs to taxodiaceae, cunninghamia. It is species which is the most extensive planted, growth fast and has high economic value in Yangtze river basin and south of the Qinling mountains. Chinese fir has fragrance, straight texture, homogeneous structure and processing easily, using in fields of shipbuilding, furniture industry and construction *etc*. [1-5]. Thousands of years ago, people already realized that Chinese fir's flower, leaf, fruit could be used at cosmetics and medical field. Chinese fir's essential oils have natural resistance to fungus and termite [6, 7]. This results in that Chinese fir has fostered several million Chinese [8]. However, the most products made from Chinese fir wood are low value-added [5]. The resource utilization of non-wood material of wood is also part of applied ecology. Study the chemical compositions of wood also can solve the problem which has caused people's attention in environment and resource administration [9].

Material and methods

Study area

The material of this experiment was taken from Chinese fir wood in Central South University of Forestry and Technology in Changsha of Hunan province, China. Changsha is a

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subtropical monsoon climate. It is located between longitude 111°53’ and 114°15’ E and latitude 27°51’ and 28°41’ N. The annual average temperature is 17.2 ºC and rainfall is 1361.6 mm. Summer and winter is lengthy, spring and autumn is short. The temperature fluctuates wildly in spring; the rainfall is heavy in early summer; there is long-term high temperature in late summer and early autumn; the diurnal temperature variation is huge in late autumn; there is few cold weathers in winter [10].

Then put the material into micro plant grinding machine to obtain wood power.

The FT-IR analysis

First, we should put the material into micro plant grinding machine to obtain wood power, and put the powder into drying oven. Set the temperature to 100 °C and dry for 6 hours to evaporate the free water from the sample. Then making the dried Chinese fir powder filtered through 200 meshes sieve. This experiment used pure KBr as a solid dispersion medium. The finely ground Chinese fir powder was dispersed in KBr at 1:100. The range of the spectrum was set to 400-4000 cm^{-1} [11].

The TG analysis

First the Chinese fir powder was put into drying oven, setting the temperature to 100 °C and drying for 6 hours to evaporate the free water from the sample. Then making the dried Chinese fir powder filtered through 200 meshes sieve. The temperature range was 30-250 °C, gas atmosphere was nitrogen, gas flow was 60 mL/min; heating rate was 5 °C/min [12].

The Py-GC-MS analysis

The material of the experiment was untreated Chinese fir powder which was filtered through a 200 meshes sieve. Pyrogenation temperature was 500 °C, heating rate was 20 °C/min, pyrolysis time was 15 seconds; carrier gas was high purity He; chromatographic column was TR-5MS; capillary column was (30 m × 0.25 mm × 0.25 μm); the temperature of transfer line of pyrolysis product and the injection valve was set at 300 °C; shunting mode, split ratio was 1:60, shunting rate was 50 mL/min. The temperature of GC program started at 40 °C and kept for 2 minute, rose to 120 °C at a rate of 5 °C/min, then rose to 200 °C at a rate of 10 °C/min and kept for 15 minute. The temperature of ion source was 280 °C, scanning range was 28 amu-500 amu [13].

The TD-GC-MS analysis

The material of the experiment was untreated Chinese fir powder which was filtered through 200 meshes sieve. First Chinese fir powder was put into drying oven, setting the temperature to 100 °C and drying for 6 hours to evaporate the free water from the sample.

Setting the temperature of TDS program started at 30 °C and kept for 1 minute, rising to 100 °C at a rate of 10 °C/min and keeping for 5 minute. Then rose to 200 °C at a rate of 10 °C/min, transmission line temperature was 230 °C. Cold injection system started at –50 °C and rose to 230 °C at a rate of 10 °C/min and kept for 1 minute [3].

The GC-MS: The temperature of GC program started at 50 °C and kept for 2 minute and rose to 250 °C at a rate of 8 °C/min, then rose to 300 °C at a rate of 5 °C/min and kept for 3 minute. The MS program scanning quality range was 30-600 amu. Ionization mode was EI, ionization voltage was 70 eV, and ionization current was 150 μA. Ion source temperature was 230 °C, quadrupole temperature was 150 °C [4, 14].

Results and discussion

Analysis of FT-IR

Figure 1 is FT-IR spectrogram at 500-4000 cm^{-1} of Chinese fir. The spectrogram show that characteristic peaks are stretching vibration absorbance peak (3458 cm^{-1}) of –OH (phenolic hydroxyl), stretching vibration absorbance peak (2900 cm^{-1}) of C-H (cellulose), stretching vibration absorbance peak (1740 cm^{-1}) of C=O (hemicellulose, esters, ketones), stretching vibration absorbance peak (1651 cm^{-1}) of C=C (olefins), two framework ring stretching vibration absorbance peaks (1512 cm^{-1} and 1462 cm^{-1}) of benzene ring (lignin, aromatic), scissoring vibration absorbance peak (1425 cm^{-1}) of C-H (lignin, cellulose), flexural vibration absorbance peaks (1371 cm^{-1}) of C-H (cellulose, hemicellulose), stretching vibration absorbance peak (1336 cm^{-1}) of C-N (amine), stretching vibration absorbance peak (1244 cm^{-1}) of C-O or C-C (lignin) and stretching vibration absorbance peak (1055 cm^{-1}) of C-O (esters) [15-18].

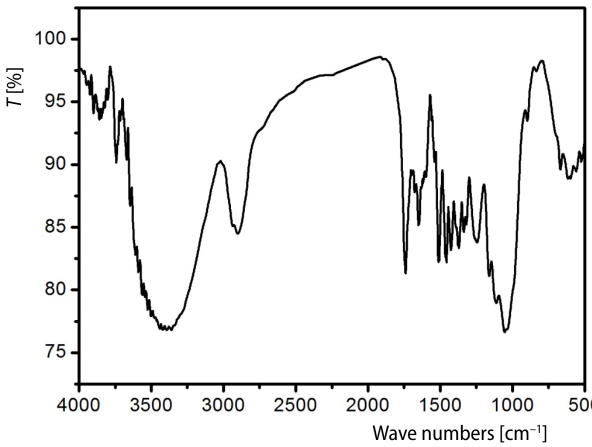

Figure 1. The FT-IR spectrogram of Chinese fir wood powder

Because the mainly chemical component of wood are lignin, cellulose and hemicelluloses, the results of FT-IR analysis were interfered.

Analysis of TG

The TGA is a technology that measure the relationship between mass and temperature of sample under the program controlling temperature. The main function is to observe the change of sample weight with test temperature increasing. Then we can observe the percentage of weightlessness, initial decomposition temperature, finally temperature and reaction rate of sample and so on [15, 16].

As shown in fig. 2, first we divided the temperature into three stages. We used T_1 to denominate the first stage (35-100 °C), used T_2 to denominate the second stage (100-160 °C), and used T_3 to denominate the third stage (160-245 °C). The DTG curve is first differential of TGA, reflecting speed of sample weight change. At T_1, temperature was increased 65 °C and sample mass was reduced 7.42%. And sample mass was reduced because of sample's bound water was evaporated. At

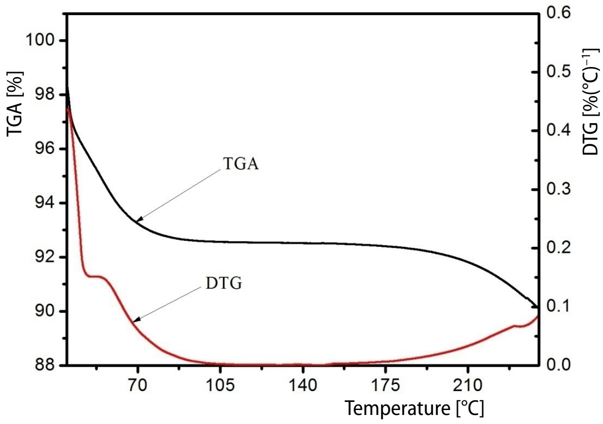

Figure 2. The TGA and DTG thermal curves of Chinese fir wood powder

this stage, except water evaporation, trace of hemicellulose was decomposed, but the properties of wood will not change significantly. At T_2, temperature was increased 60 °C, but sample mass was only reduced 0.10%. This stage is continued endothermic process of wood powder. At T_3, temperature was increased 85 °C and sample mass was reduced 6.13%. At this stage, the rate of decline in sample mass was increased obviously. This phenomenon was because thermal motion of solid molecules will increase with temperature increased. And thermal conductivity coefficient will increase as heat conduction of wood pore air and radiation energy between hole walls increased.

Analysis of Py-GC-MS

The Py-GC-MS quality report shown that 46 peaks were obtained from Chinese fir wood powder volatile and 9 component swhich occupy 25.23% of total peaks areas were identified (as shown in fig. 3). The main chemical components were ammonium carbamate (8.39%), methyleugenol (3.67%), guaiacol (3.06%) and so on.

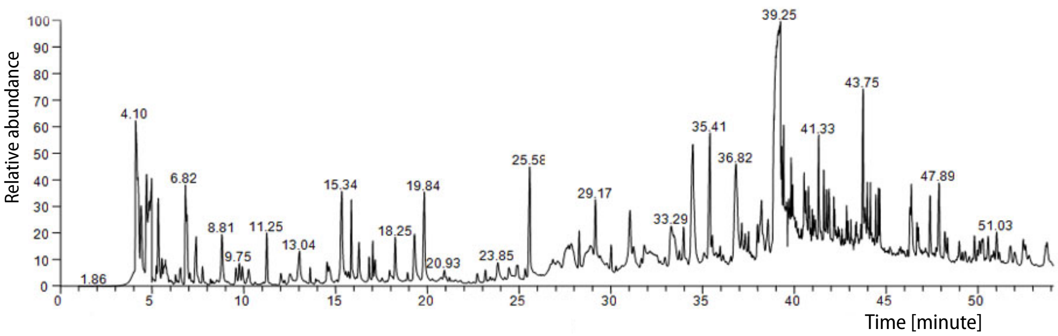

Figure 3. Total ion chromatograms by Py-GC-MS

Methyleugenol (3.67%) has many functions especially related to the chemical defence of plants, such as anti-fungal, anti-bacterial, anti-nematode, toxic effects on pathogens and cause insect herbivores antifeedant and anti-pollination [18]. Methyleugenol also is as naturally occurring components of a traditional diet and as added flavouring substances. It does not pose a significant cancer risk, but the dose needs further studies to define by risk [17]. Guaiacol (3.06%) can use in medical, synthesis of spices and dye. Exogenous compounds guaiacol can be absorbed changing the global volatile composition of fruits and produce a negative or positive effect in their aroma by contacting with the plants [19-21]. Benzofuran (1.76%) derivatives have antitumor, antiviral [22], antiarrhythmic [23] and others effects in medical field.

Analysis of TD-GC-MS

In this analysis, 48 peaks were obtained from the Chinese fir wood powder and 18 components were identified (as shown in tab. 1). The main chemical components were diisobutyl phthalate (39.75%), 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene- (10.4%), dibutyl phthalate (2.21%), 2-(2-butoxyethoxy) ethyl acetate (2.05%) and so on.

Diisobutyl phthalate (39.75%) has similarities to Dibutly phthalate, and is increasingly being used as a substitute. Diisobutyl phthalate has similar effects on fetal testicular testosterone production and histopathology as the known toxic phthalates. It is recognized as an additional inhibitor of fetal steroidogenesis. Diisobutyl phthalate can reduced plasma insulin levels. It can reduced plasma leptin levels in a similar manner as the insulin-sensitizing drug

Table 1. The analytical results of Chinese fir wood powder by TD-GC-MS

No.	Retention time [min]	Peak area [%]	Component
1	3.14	1.29	Hexanal
2	4.92	0.44	2-Ethyl-1-butanol
3	7.74	0.21	Nonanal
4	8.52	0.34	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-
5	9.28	0.33	Ethanol,1-(2-butoxyethoxy)-
6	11.25	0.55	N,N-Dibutylformamide
7	12.22	2.05	2-(2-Butoxyethoxy)ethyl acetate
8	12.43	0.75	3-hydroxy-2,2,4-trimethylpentyl isobutyrate
9	13.71	0.68	Dimethyl phthalate
10	14.54	0.51	2,4-Di-tert-butylphenol
11	15.21	1.35	Benzene, 1,2,3-trimethoxy-5-(2-propenyl)-
12	16.06	0.83	Cedrol
13	16.72	1.59	beta-Eudesmol
14	17.13	0.56	alpha-Bisabolol
15	19.57	39.75	Diisobutyl phthalate
16	20.10	1.41	Phthalic acid, butyl hex-3-yl ester
17	20.22	10.40	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-
18	20.68	2.21	Dibutyl phthalate

rosiglitazone [24]. Dibutly phthalate (2.21%) is used as a plasticizer in elastomers, textile lubricating agent, resin solvent, and in safety glass, printing inks, paper coatings, and adhesives. Osol valves, as a skin emollient, as a suspension agent for solids in aerosols, as an antifoamer. Dibutly phthalate is known to be a developmental and reproductive toxicant. It exerts adverse effects on uterine of rodents, and these effects are responsible, at least in part, for the early embryonic loss [25]. Beta-eudesmol (1.59%) is a small molecule, and it can inhibited proliferation of porcine brain microvascular endothelial cells and human umbilical vein endothelial cells. It also inhibited the human umbilical vein endothelial cells migration stimulated by basic fibroblast growth factor and the tube formation by human umbilical vein endothelial cells in Matrigel. Some scholars considered that beta-eudesmol may aid the development of drugs to treat angiogenic diseases [26]. Beta-eudesmol can induces neurite outgrowth in some cells, which is accompanied by mitogen-activated protein kinase activation. It may be a promising lead compound for potentiating neuronal function [27]. A pre-harvest application of enhanced freshness formulation combined with post-harvest treatment of hexanal may enhance the quality and shelf life of sweet cherry [28]. Hexenal (1.29%) has a significant inhibitory effect against pathogenic microorganisms frequently isolated from raw materials [29]. Cedrol (0.83%) has sedative effect. The changes of respiratory and cardiovascular which is caused by exposure to cedrol might ameliorate autonomic disturbances in chronic heart failure [30]. The mechanism of cedrol's sedative effects is via a pathway other than the olfactory system regardless of the animal species or the functional state of the autonomic nerves [31, 32]. Dimethyl phthalate (0.68%) is a plasticizer that is highly soluble in a wide range of resins. It can dissolved with many kinds of cellulosic resin, rubber and vinylester resin. And it has good film-forming property, adhesiveness, and waterproofing quality. Dimethyl phthalate can be used as the solvent of mosquito repellent oil, polyvinyl chloride coating, methyl ethyl ketone peroxide and DDT. Alpha-bisabolol (0.56%) may attenuate nociceptive sensorimotor responses and central sensitization evoked by noxious or ofacial stimuli. And that this natural product may be useful clinically for the treatment of or ofacial pain. Alpha-bisabolol has anti-inflammatory, antibiotic function [33].

Conclusions

In analysis of FT-IR, there were 11 major peaks obvious. The corresponding functional groups were -OH, C-H, C=O, C=C, C-O and C-N. The possible chemical components were cellulose, hemicelluloses, lignin, phenolic hydroxyl, esters, ketones, olefins, aromatic and amine.

We obtained several kinds of chemicals by Py-GC-MS analysis and TD-GC-MS analysis. Phenolic compounds main were guaiacol, methyleugenol, 4-ethyl-2-methoxyphenol, 4-allyl-2,6-dimethoxyphenol and 2,4-di-tert-butylphenol. Alcohol compounds main were cedrol, alpha-bisabolol, beta-eudesmol and 2-ethyl-1-butanol. Ester compounds main were dimethyl phthalate, diisobutyl phthalate, dibutyl phthalate, 3-hydroxy-2,2,4-trimethylpentyl isobutyrate and 2-(2-Butoxyethoxy)ethyl acetate. Ketone compounds main were hydroxyacetone and benzofuran. Aldehyde compounds main were hexanal and nonanal. Except this compounds, and it also detected ammonium carbamate, N, N-dibutylformamide, acetic acid and styrene and so on. This compounds and their derivatives can use at wide medical, biology, cosmetics and textile industry and so on. The rational application of non-wood resources in forests is also an important part of the world's sustainable development.

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