MOLECULAR CHARACTERISTICS OF *SALIX CHEILOPHILA* CHEMICAL COMPONENTS

by

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Salix cheilophila plays a role in sand control. However, due to the lack of systematic and in-depth analysis on the chemical composition of Salix chei lophila, it is difficult to develop higher-value products, resulting in low efficiency or even outright abandonment. In this paper, the components of Salix cheilophila and its change rule before/after extraction were introduced, and the thermal loss rules and pyrolysis properties of Salix cheilophila were also explained. The analytic result of FT-IR further confirmed that: the Salix cheilophila contains components including esters, aldehydes, alcohols and ethers, etc., and the organic solvent extraction does not made compound groups of Salix cheilophila significantly changed. There are four obvious stages in thermal loss treatment of Salix cheilophila. During thermal loss treatment, three critical turning points of temperature (44 °C, 78 °C, and 219 °C) were observed, accompanied by significantly chemical changes such as macromolecule pyrolyzed into small volatile molecules. The pyrolysis products of Salix cheilophila extractive including esters, acid, alcohols, aldehyde, ethers, alkene, ammonium, anhydride, phenols, ketone, furans and heterocyclic compounds. There were quite differences among properties and functions of the components. Thus, the application prospects were also significantly different.

Key words: *Salix cheilophila, pyrolyzates, organic solvent extractive, component characteristics*

Introduction

Salix cheilophila belongs to an erect shrub or small tree of Salix, it is shaped like a torch, the main vegetation type in the desert and the preferred species of artificial vegetation in sand, and a rare species that can grow in saline-alkali land. Because of its strong resistance, drought resistance, poor resistance, wind and sand, cold weather and hot summer, it is more likely to be buried in the sand, and it will be more and more alive [1]. In recent years, it has been widely cultivated, and is also one of the first-choice trees of *sanbei shelterbelt* [2].

Its natural distribution area is mainly in Mu Us Sandy Land, Kubuk Desert, Bayanur City, Erdos City, Inner Mongolia and the Yulin Area in Shaanxi Province, and the Hedong Area of Ningxia, which is as high as 3.2 × 104 m^2 [3].

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With the development of the forest products industry, the *Salix cheilophila* has been raised from the original general shrubs to the status of industrial raw materials. First of all, *Salix cheilophila* is the important raw material for fiber board, particle board, textile, papermaking, and biomass power raw materials. the chemical composition of the extract, after analysis of utilization, also can be used as a raw material used in the industrial production. Secondly, it can be used as fodder for cattle, sheep, camel and other animals or as mixed feed with grasses, crop stalks, *etc.* It also has some medicinal value. Give full play to all aspects of the value of *Salix cheilophila* timber resources, and we should try to be the comprehensive sustainable utilization of resources. At the same time, the resource advantage into economic advantage, effectively ways innovation, and actively develop the green industry, by way of thinking to guide the ecological construction of industrialization, develop the forest products processing and conversion, extend the industry chain, truly achieve forest products zero pollution zero waste of resources [1]. In this experiment, *Salix cheilophila* solid was analyzed by thermogravimetry (TG) and pyrolysis gas chromatography and mass spectrometry (Py-GC-MS), and the volatile organic compound (VOC) components of *Salix cheilophila* extractive from benzene/ethanol were detected by GC-MS, and its residues were carried on the analysis by FT-IR.

Materials and methods

Materials and reagents

Salix cheilophila was provided by Jiangsu Province Nantong forging equipment Co., Ltd. After being dried under the nature condition (about 40 °C), the *Salix cheilophila* was smashed into power by using FZ102 Disintegrator suitable for plant (Tanjing Taisite Ins. Corp., China) in succession, 200 mesh powders were sieved out using AS200 Sieving Instrument (USA).

Methods

Salix cheilophila extraction by benzene/ethanol

Salix cheilophila sample were mixed with benzene/ethanol (2:1), with the solid-liquid ratio of 1:20. After immersing at room temperature for 12 hours, the mixed solution were fully extracted by automatic FOSS Soxhlet Extracted apparatus (Agilent, USA) at 70 °C for 5 hours, and then filtrated fast with filter paper immersed in ethanol for 24 hours. The filtrated extraction was evaporated at 45 °C under a vacuum of 0.01 MPa and concentrated to 20 mL for the following determination.

Extracted VOC analysis by GC-MS

The GC conditions: capillary column (30 m × 250 μm × 0.25 μm). The initial temperature was 50 °C, kept 1 minute, increased to 150 °C at 5 °C/min, kept 10 minute, then to 250 °C at 8 °C/min, stayed 2 minute; the carrier gas was high purity He (99.99%); injection volume of 1 μL; no a split mode; vaporization chamber temperature was 280 °C. The MS detection conditions: the program of MS was scanned over the 35-600 AMU (m/z) respectively, with an ionizing voltage of 70 eV and an ionization current of 150 μA of electron ionization (EI) [4].

Salix cheilophila and its extracted residue analysis by FT-IR

The spectra of *Salix cheilophila* samples were obtained by FT-IR spectrophotometer (IR100) using KBr wafers containing 1.00% finely ground samples.

Salix cheilophila thermostability by TG

Salix cheilophila samples was conducted using a TG analyzer (TGA Q50 V20.8 Build 34, USA), empty crucible clamp as a reference. An accurate mass of *Salix cheilophila* sample (6.60600 mg) was placed in a TG crucible. High purity nitrogen was used as carrier gas, and the TG temperature program started at 30 °C, increased to 600 °C at the rate of 10 °C/min, and the flow rate was 40 mL/min.

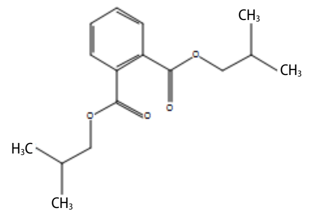
Extractives analysis by Py-GC-MS

Salix cheilophila sample were pyrolyzed in helium atmosphere using pyrolysis apparatus PY-2020iS (Frontier Co., Ltd, Japan), and then the pyrolyzed products were analyzed by online linked GC-MS (Agilent5975C/6890N USA), which is linked to a mass selective detector. The elastic quartz capillary column db-5 ms (30 m × 0.25 mm × 0.25 μm) was used, the carrier gas was helium, and the inlet temperature was 250 °C. The temperature program for gas chromatography starts at 50 °C and rises to 450 °C at 10 °C/min. In split mode, the split ratio is 30:1. The ms program was scanned at 35-550 amu (m/z) with an ionization voltage of 70 ev and an ionization current of 150 μa [5, 6].

Results and analysis

The VOC components analysis of extractive from Salix cheilophila

The GC-MS chromatograms of the extractive' VOC of *Salix cheilophila* in the range of 50 °C to 250 °C were shown in fig. 1. It can be seen that the extractive had four obvious peaks at 19.56 minute, 23.57 minute, 24.44 minute, and 25.36 minute. It can be found that the substance present at 19.56 minute was 1,2-Bezenedicarboxylic acid, bis(2-methylpropyl) ester, the chemical formula was $C_{16}H_{22}O_4$, and molecular structure.



Molecular structure

The relative contents were 34.17%. It is colorless transparent oily liquid, not volatile, slightly aromatic smell, flammable and toxic. Mainly as plasticizer, it can make the products have good softness, but the volatile and water extraction is bigger, so the durability is poor. The substance present at 23.57, 24.44, and 25.36 minute have not been detected, and the relative contents were 18.14%, 13.42% and 100%, respectively. From the GC-MC data, it can be specu-

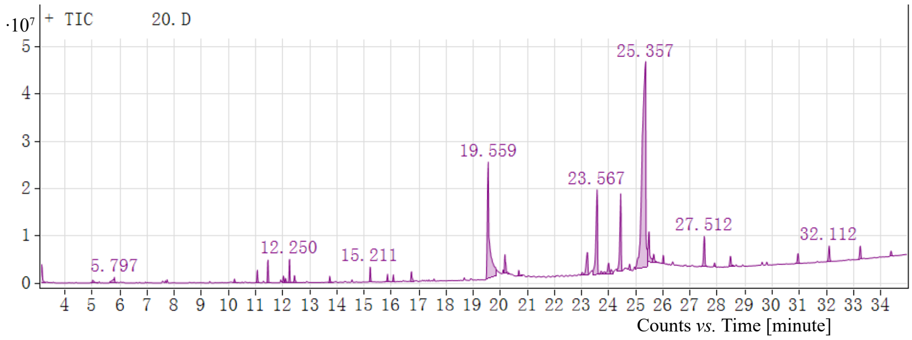


Figure 1. The 20.D are the ion chromatograms of VOC of benzene/ethanol extractive from *Salix cheilophila* by GC-MS

lated that the compound should be the main components of VOC of *Salix cheilophila* extractive.

From the results of GC-MS, it was found that 11 organic compounds were detected from benzene/ethanol extractive by GC-MS. Most of these volatile organic compounds are aldehydes and esters, such as Hexanal (relative content 2.66%), the chemical formulas is $C_6H_{12}O$. It is easily soluble in ethanol, ether and slightly soluble in water. The odor of aldehydes, automatic oxidation and polymerization, is more pronounced when a small amount of acid exists. And it's mainly used as plasticizer and organic synthesis for rubber, resin and insecticides. At RT 11.07 minute and 11.46 minute, 2,4-Decadienal, (E,E)-, the chemical formulas is $C_{10}H_{16}O$, was present in VOC of extractive, respectively, with the relative content 1.39%, and 2.26%. It is a kind of spice, mainly used in the preparation of chicken essence and potato chips, citrus, Fried and spicy food. Ethanol, 2-(2-butoxyethoxy)-,acetate, Propanoic acid, 2-methyl-, 3-hydroxy-2,2,4-trimethylpentyl ester, Dimethyl phthalate and 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate, these compounds are all esters, the relative content is 2.49%, 0.94%, 0.7%, 0.38% and 34.17%, respectively. Mainly used as plasticizer, And the Dimethyl phthalate is also used as an anti-mosquito oil. Cedrol (relative content 0.64%), the chemical formulas is $C_{15}H_{26}O$, a kind of sesquiterpene alcohol, widely used in wood incense, xin xiang and Oriental essence. It is also used as an agent for disinfectant and sanitary products. Benzene, 1,2,3-trimethoxy-5-(2-propenyl)- (relative content 1.64%) at the retention time of 15.21min was detected in the extractiveas a source of the anesthetic. 1-Butanol, 2-ethyl- is a kind of saturated alcohol, And cis-Trismethoxyresveratrol, their purpose are unclear at present.

Chemical group change characteristics of Salix cheilophila and residues

The FT-IR is a rapid detection technology, with a high sensitivity, which is applied in the identification of chemical bond and functional groups of various compounds [7-9]. In this experiment, the changes of the *Salix cheilophila* and extracted residues' chemical groups were shown in fig. 2, in the range from 4000-400 cm^{-1}.

As shown in infrared spectroscopy of fig. 2, it showed a total of 20 absorption peaks examined in *Salix cheilophila* sample. First, there was a strong absorption peak near 3445 cm^{-1}, indicating that there was the O-H stretching vibration present, which was consistent with the result of GC-MS, having alcohols compound: 1-Butanol, 2-ethyl-. In 1751 cm^{-1}, there was a strong absorption peak, 2924 cm^{-1} and 2896 cm^{-1} also has two absorption peaks, the first one strong absorption peaks are caused by C-O stretching, the last two are aldehyde group C-H stretching vibration, prove the existence of aldehydes compounds, consistent with the results of GC-MS [10, 11]. In 1300-1000 cm^{-1}, there are two peaks, respectively, C-O-C symmetric stretching vibration (weak peak near 1140-1030 cm^{-1}) and asymmetric stretching vibration (strong peak near 1300-1150 cm^{-1}), in the vicinity of 3450 cm^{-1} also can often observe the weaker C=O stretching vibration frequency doubling of absorption. It can be determined that there are esters. And at 1118 cm^{-1}, it's absorbed, it's probably ethers. There are several absorption peaks of 900-650 cm^{-1}, which can determine the cis trans configuration of the compound. 1732-1729 cm^{-1}, and 732-1503 cm^{-1} carbonyl C=O double bond stretching vibration and C-H in-plane bending vibration; 1370 cm^{-1} C-O and C-C frame vibration, 674-664 cm^{-1} C-C scale, 1510-1510 cm^{-1} near the benzene ring of vibration, *etc.*, corresponding to a variety of oxygen-containing organic compounds, such as phenols, aldehydes, acids, ketones and other substances [12]. In summary, *Salix cheilophila* mainly contains fat hydrocarbon and aromatic structure and various kinds of oxygen-containing functional groups [13]. The

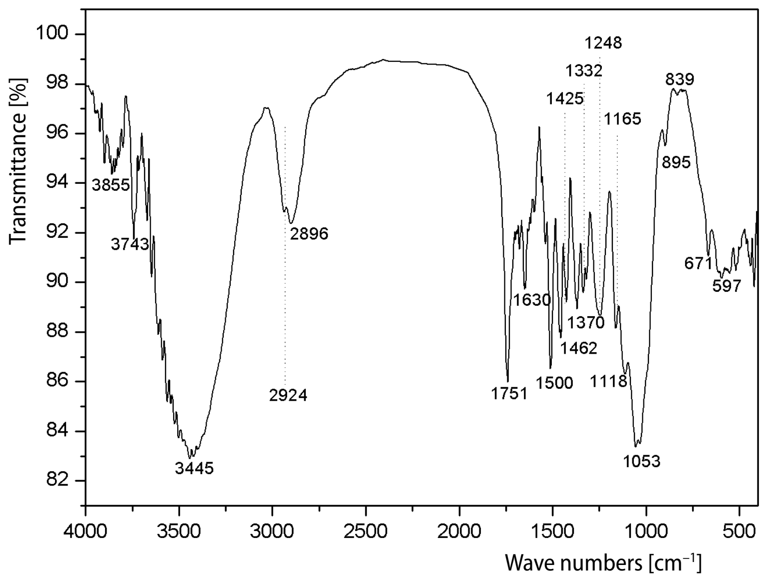


Figure 2. Infrared spectra of VOC of benzene/ethanol extractives from *Salix cheilophila*

groups in the chemical structure of VOC detected by GC-MS is consistent with the result of FT-IR [14], further indicating that the *Salix cheilophila* samples containing aldehydes, esters and alcohols, *etc.* In addition, it can be concluded that organic solvent extraction does not made compound groups of *Salix cheilophila* significantly changed [15-18].

Volatility characteristic of Salix cheilophila by thermostability analysis

The change of *Salix cheilophila* mass from 30-250 °C was shown in fig. 3. There are four obvious stages of thermal loss for *Salix cheilophila*: the first stage was from the initial temperature of 30-44 °C, with the quality of 4.70207 mg at 44 °C, and this part of the mass loss should be the evaporation of water and a small amount of volatile matter freed [19]. The second stage is the fastest mass loss, from 44-78 °C, the mass is reduced to 4.40724 mg, the loss is 50.45%. During this process, the obvious peak value was observed in the corresponding DTG curve and reached its maximum value at 50 °C, indicating that the mass loss rate of Salix cheilophila was the fastest in this temperature range [20]. The third stage starts at 78 °C until the mass decreases to 4.30335 mg at 219 °C, with a slight loss of mass (17.78%). This should be caused by further shrinkage between molecules. The fourth stage begins with a mild mass loss process at 219 °C until the pyrolysis of Salix cheilophila is basically completed at 246 °C, with a mass loss of 17.90% to 4.19872 mg. There are three critical temperature turning points in the whole thermogravimetric analysis process. At these temperatures, the *Salix cheilophila* mass changed significantly, which may be caused by significant chemical changes, such as macromolecule pyrolyzed into small molecules more volatile [21, 22]. Therefore, these temperature points can provide a theoretical basis for *Salix cheilophila* heating treatment, *etc.*

Component characteristics of pyrolyzates from extractive

There were 50 peaks detected in the pyrolyzate of the *Salix cheilophila* extractive by gas chromatography. The results were analyzed by MS, and combined with literature [23, 24].

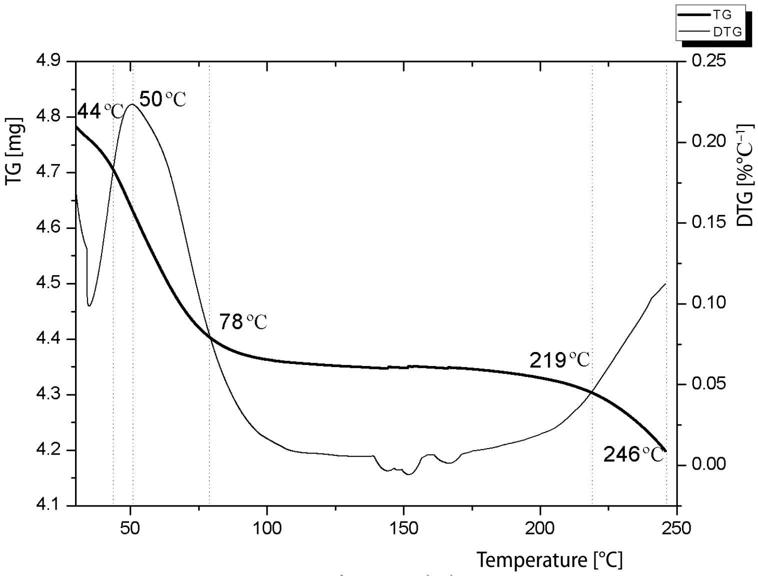


Figure 3. The TG curve of Salix cheilophila

There were 136 compounds (99.03% of the total peak area) identified. For example, the total ion flow diagram of the products of the extractive pyrolysis was shown in fig. 4.

From the results of fig. 4, the pyrolysis products of *Salix cheilophila* extractive includes esters, acid, alcohols, aldehyde, ethers, alkene, ammonium, anhydride, phenols, ketone, furans and heterocyclic compounds. The most compounds are acid, esters, ketone and phenols, and it's high in content. The nature and function of the detected components are quite different, and their application prospects in different industry fields are also quite different [25, 26].

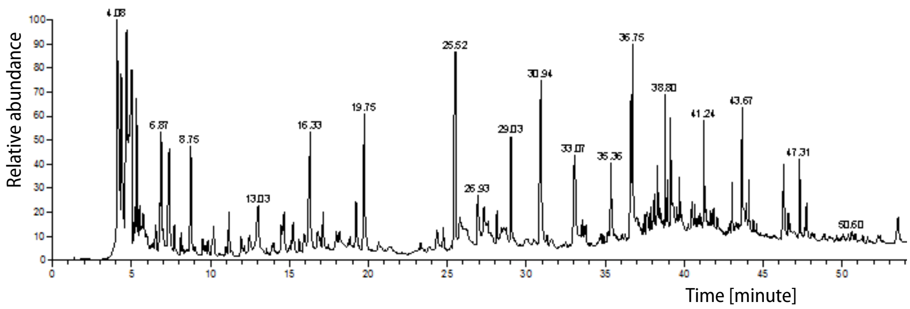


Figure 4. The total ion flow diagram of the pyrolyzate of *Salix cheilophila* extractive

Conclusion and discussion

Most of the VOC are of esters in the benzene/ethanol extractive of *Salix cheilophila*. Mainly used as plasticizer. In addition, various beneficial VOC such as Benzene, 1,2,3-trimethoxy-5-(2-propenyl)-, 2,4-Decadienal, (E,E)-, Hexanal, Cedrol, Dimethyl phthalate, Their function is different, in the actual processing and utilization, can according to the function different, produce all sorts of useful product, thus make the resource get full and effective use.

The results of FT-IR further confirms that the group structures of *Salix cheilophila* samples and the extracted residues are consistent with that in the chemical structure detected by

GC-MS, indicating that the samples of *Salix cheilophila* contained esters, aldehydes, alcohols and ethers, *etc.*, and showing that organic solvent extraction does not made compound groups of *Salix cheilophila* significantly changed.

There are four obvious stages of thermal loss for *Salix cheilophila*: the first stage 30-44 °C, the second stage 44-78 °C, the third stage 78-219 °C, and the fourth stage 219-246 °C. The order of the mass loss is the second stage, the first stage, the fourth stage and the third stage. During the whole thermogravimetric process, the DTG curve reached a maximum at 50°C and formed a sharp peak, with three critical turning points of temperature (44 °C, 78 °C and 219 °C). At these temperatures, the *Salix cheilophila* mass changed significantly, which may be caused by significant chemical changes, such as macromolecule pyrolyzed into small molecules more volatile. The pyrolysis products of *Salix cheilophila* extractiveincludes esters, acid, alcohols, aldehyde, ethers, alkene, ammonium, anhydride, phenols, ketone, furans and heterocyclic compounds.

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