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LETTER TO THE EDITOR

Pyrolysis Molecules of *Pinus armandii* Leaves for Potential Reuse

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Thermogravimetric and pyrolytic analyses were carried out to detect the various active ingredients and chemical substances in the leaves of Chinese white pine (*Pinus armandii Franch*), which were then analyzed and studied to understand their functions and the functions of their chemical components. The chemical substances contained therein mainly represent acrylamide, glycidol, pyruvic aldehyde, formic acid, cyclopentadiene, acetic acid, isovaleraldehyde, benzoic acid, and stearic acid. These chemical ingredients can be applied to new bioenergy, medicinal fields, and food ingredients such as spices. These chemical components also provide a new scientific basis and developmental direction for the utilization of *Pinus armandii*.
Keywords: Pinus armandii Franch leaves; TG; Py-GC-MS

I Introduction

Chinese white pine (*Pinus armandii* Franch) is a tall tree of the Pinus genus. Its body is tall and straight, its bark is grayish green, its needles appear in bundles of five, and it is a good green landscaping tree. To beautify the landscape, this tree can be planted in courtyards, parks, and campus settings, but it also can be planted near the water (Ballin 2016, Gao et al. 2017). *Pinus armandii* is not only a scenic tree and useful for firewood, but it also conserves water, maintains water and soil, prevents wind and sand erosion, and is also a good building timber and industrial raw material. The pine wood is light and soft, the texture is fine, easy to process, it is resistant to water and corrosion, and has a reputation of “water immersion for thousands of years” (Ben Mariem and Chaieb 2017, Guerrini et al. 2018). It is a veritable pillar with leaves that are needle-shaped, and the needles can be used to distill and refine aromatic oils, and also to produce wine, sound insulation board, paper, artificial cotton wool, and rope (Dong et al. 2016, Gong et al. 2018). The pine needles of *Pinus armandii* can also be made into pine needle powder and used as livestock feed. After detailed molecular analysis, many more uses may be found for *Pinus armandii* and its components (Nasrollahzadeh and Sajadi 2015, Werle et al. 2017).

II Material and Methods

Experimental Materials

Samples were collected from the Xixia Forest District in Henan Province. The samples were processed into powders.

Experimental Methods

Thermogravimetric Analysis (TGA): The samples of *Pinus armandii* leaves underwent TGA (TA Instruments Q50 V20.8 Build 34). The nitrogen release rate was 60 ml/min; the TG temperature program began at 30°C and increased to 300°C at a rate of 5 °C/min (Jia 2018, Lam et al. 2019).

Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS) Analysis: Catalyzed and pretreated samples were analyzed by pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS, JSB CDS 5000, Agilent 7890B-5977A ISQ). The carrier gas was high purity helium, with a pyrolysis temperature of 500°C, heating rate of 20 °C/ms, and pyrolysis time of 15 s. The pyrolysis product transfer line and injection valve temperature was set at 300°C; an HP-5MS capillary column (60 m × 250 μm × 0.25 μm) was used in parallel mode, with a split ratio of 1:60 and shunt speed of 50 mL/min. The temperature of the GC program was increased from 40°C for 2 minutes, increased to 120°C at a rate of 5 °C/minute, and then increased to 200°C at a rate of 1 °C/minute for 15 minutes. An ion source (EI) temperature of 230°C was used with a scanning range of 28 amu-500 amu (Zhang et al. 2015).

III Results and Discussion

Thermogravimetry-derivative thermogravimetry (TG-DTG) Analysis

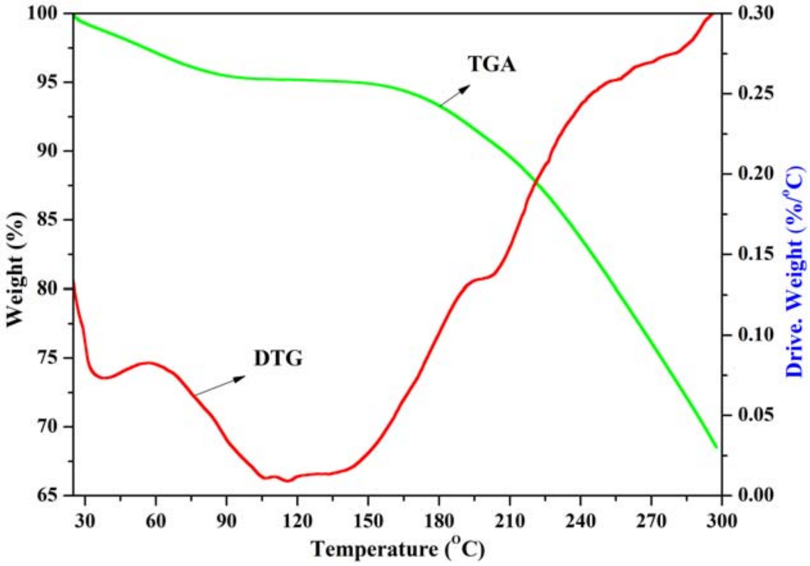

Figure 1. TGA and DTG thermal curves of *Pinus armandii* leaves.

A TGA test was performed on the original powder of Pinus armandii leaves (Wan et al. 2016). As can be seen from Figure 1, the weight loss process of pyrolysis can be broadly divided into three phases (Peng et al. 2015). The first stage is between 25-77°C, wherein the weight loss rate is 3.86%. The weight loss is mainly caused by the evaporation of water and the loss of biomass. The weight loss of the sample is small at this stage; the second stage is at 77- Between 155°C, the weight loss rate is 1.27%, which is the transformation of the preheated solution. The differential curve at this stage is relatively flat, indicating that the pyrolysis rate is relatively stable, and the weight loss is mainly due to the depolymerization and recombination of a small amount of polymer in the sample. The third stage is between 155-300°C, the weight loss rate is 27.72%, which is the combustion stage of the remaining components. With the increase of temperature, the cellulose and hemicellulose in Huashan pine are rapidly cracked, resulting in a large amount of volatilization. Sexual gases cause severe weight loss. These three stages exhibited different properties with different kinetic parameters and reaction mechanisms, and the final residual mass of the sample was 68.5%. Throughout the process, the blade has a thermal gravity loss of only about 20%, a small mass change, and a low rate. The TGA experimental data shows that Pinus armandi has high resource utilization potential and high application value, which can provide certain convenience for our life (Ge et al. 2018).

Py-GC-MS analysis

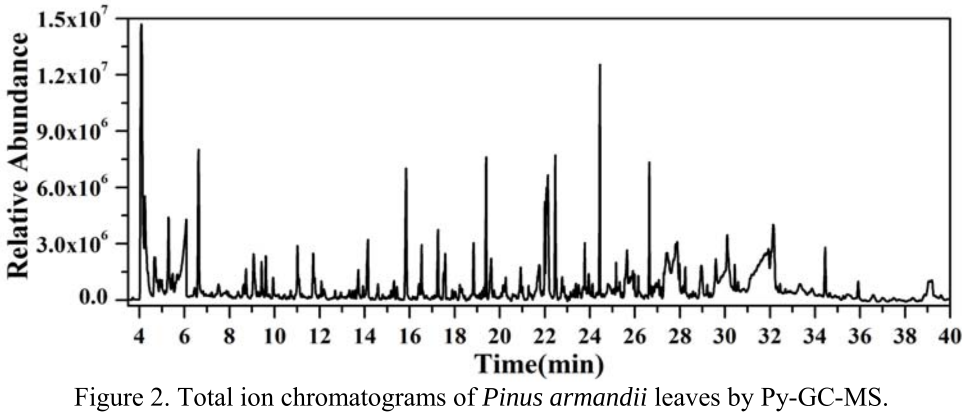

Figure 2. Total ion chromatograms of *Pinus armandii* leaves by Py-GC-MS.

According to the results of the Py-GC-MS analysis (Figure 2), a total of 269 peaks and 214 compounds were detected in the original powder of *Pinus armandii*, of which the highest levels were: ethyne, fluoro- (6.19%), benzoic acid, 3-hydroxy- (4.85%), catechol (3.52%), acetic acid (3.24%), .β.-D-glucopyranose, 1,6-anhydro- (2.94%), benzenepropanol, 4-hydroxy-3-methoxy- (2.57%), 4,6-di-O-methyl-.α.-d-galactose (2.37%), 2-methoxy-4-vinylphenol (2.12%), 1,3,5,7-tetramethyl-adamantane (2.05%), 2-propanone, 1-hydroxy- (1.91%), ethanol, 2,2'-[1,2-ethanediylbis(oxy)]bis-, diacetate (1.79%), silane, dimethyl(4-methoxyphenoxy)butoxy- (1.59%), bicyclo[3.1.1]heptane, 2,6,6-trimethyl- (1.54%), benzoic acid (1.37%), benzofuran, 2,3-dihydro- (1.33%), acetaldehyde, hydroxy- (1.30%), phenol, 2-methoxy- (1.27%), 4-O-methylmannose (1.19%), butane (1.00%).

Analysis of Function

2-Propenamide is used as a monomer in the production of polyacrylamide, and its polymer or copolymer is used as an additive for chemical grouting materials, soil conditioners, flocculants, adhesives, and coatings to increase oil recovery. It can be used as a flocculant for wastewater treatment or as a paper enhancer (Arabi et al. 2016). Glycidol is an important fine chemical raw material used as a stabilizer for natural oils and vinyl polymers, demulsifiers, dyeing delaminators, and as an intermediate for the synthesis of glycerol, and glycidyl ethers (amines, etc.) (Merkle 2018). It can also be used for gels for surface coatings, chemical synthesis, pharmaceuticals, pharmaceutical chemicals, fungicides, and solid fuels, but it is mainly used as an epoxy resin thinner, and is incorporated in plastics, fiber modifiers, stabilizers for halogenated hydrocarbons, food preservation agents, fungicides, refrigeration system desiccants, and aromatic extractants (Weiss 2014). Derivatives of glycidol are industrial raw materials for resins, plastics, pharmaceuticals, pesticides, and auxiliaries.

In addition to being used directly as a fuel, Butane is also used as a solvent, a refrigerant, and an organic synthetic raw material. It is mainly used as the standard gas for analytical instruments in petrochemical enterprises. Methyl glyoxal can be used as a raw material used for the production of cimetidine, lactic acid, pyruvic acid, analgesics, anticancer and antihypertensive drugs, desensitizing agents, and cosmetics. Formic acid is a basic organic chemical raw material, widely used in pesticides, leather, textiles, printing and dyeing, medicine, and rubber industries. It can also be used to prepare various solvents, plasticizers, rubber coagulants, animal feed additives, and new processes for synthesizing insulin (Zhang 2014). 1,3-Cyclopentadiene is used in pesticides to synthesize the intermediates of the insecticides chlordane and endosulfan, as well as tetrachlorocyclopentane, and can also be used as an intermediate for the production of the insecticide imidacloprid (Wu 2018). In addition, it is mainly used in the resin industry and as a synthetic rubber. 2,3-Butanedione is mainly used in the preparation of cream, fermented cheese flavor, and coffee flavors. It is the main raw material for the production of pyrazine flavors, and can also be used in small amounts for cosmetics and fresh fruit flavors or new flavors. It can be used as a gelatin hardener and photographic adhesive (Hall and Hausenloy 2016).

2-Methylfuran is used to prepare vitamin B1, chloroquine phosphate, and primaquine phosphate, and for synthesis of pyrethroid pesticides and flavors. It is not only a raw material for the pyrethroid methrin, and an intermediate allyl alcohol ketone, but it is also a good solvent. In addition, it also has an anesthetic effect (Green 2016). Isovaleraldehyde is naturally present in essential oils such as citrus and lemon. It has an apple-like aroma when it is highly diluted, but has a peach aroma when the concentration is less than 10 ppm, and thus, it is mainly used to prepare a variety of fruit flavors (Palau 2015). This product is an intermediate of anti-inflammatory drugs, and is also used as a rubber accelerator and food flavor (Whiteson et al. 2014, Assadi 2014).

Propionic acid is used as an organic reagent, an esterifying agent, and a plasticizer, and is also used as a preservative for the preparation of food flavors, an antifungal agent, and a fragrance (Nielsen 2018). It is a viscous substance that is used as an inhibitor for beer or as a feed antifungal agent. Benzoic acid can be used as a chemical reagent and preservative. It is an important acid-type food preservative. Under acidic conditions, it can inhibit mold, yeast, and bacteria, but it has weak effects on acid-producing bacteria. It can be used during the production of medicines, dye carriers, plasticizers, perfumes, and food preservatives (Li et al. 2016, Mohammed et al. 2017). It is also used in the performance improvement of alkyd resin coatings, and as a plant growth hormone. It is the most commonly used acid spice and can be used to prepare artificial civet. It is the main component of honey flavor, but it can also be used in water-based fragrances and soap scents, as well as in food and tobacco flavors. It is used to prepare plasticizers and perfumes, and is also used as a rust inhibitor for steel equipment.

Phenylacetic acid is used as an intermediate for fungicides such as benzathine, insecticides for rice flour, rodenticides, and chloroprene. It is an important raw material for synthetic medicines, pesticides, and spices (Yang et al. 2015). Stearic acid is widely used in cosmetics, plastic plasticizers, mold release agents, stabilizers, surfactants, rubber vulcanization accelerators, water repellents, polishing agents, metal soaps, metal mineral flotation agents, softeners, pharmaceuticals, and other organic chemicals. Stearic acid can also be used as a solvent for oil-soluble pigments, a crayon smoothing agent, a stencil polishing agent, and an emulsifier for stearic acid glycerides (Foraita et al. 2015, Sari et al. 2015). Palmitic acid is a raw material for the production of candles, soaps, greases, softeners, and synthetic detergents. It can also be used in perfumery as a precipitant, and as a chemical and water repellent (Mancini et al. 2015).

IV Conclusions

Our TGA-DTG study shows that the weight loss process in the pyrolysis process of Pinus armandi can be divided into three stages. The decrease in the curve that occurs in the first stage is caused by the evaporation of water molecules contained in the leaves and small molecules with relatively low boiling points. The second stage is the transition phase of the preheated solution, the weight loss of which is mainly due to the depolymerization and recombination of a small amount of polymer in the sample. The third stage of weightlessness is caused by the rapid cracking of cellulose and hemicellulose in Huashan pine and the production of a large amount of volatile gases. The final residual mass of the sample was 68.5%. From the experimental data analysis, Huashan pine has a high potential for resource utilization.
In the Py-GC-MS assay. The identified compounds can be classified into acids, hydrocarbons, lipids, glycerol, aldehydes, and phenols. In the Py-GC-MS assay. The identified compounds can be classified into acids, hydrocarbons, lipids, glycerol, aldehydes and phenols. The various chemical components detected have different properties, some of which can be used to extract essential oils or to prepare daily fragrances and food flavors. Daily fragrances can increase the comfort of life, and food flavors can make foods more delicious. Some substances can be used as chemical reagents, used in chemical experiments, to promote the development of the chemical industry, and some can be used to produce medicines, which have a significant role in medicine.
Through the analysis and research on the chemical constituents of the polymerous leaves of *Pinus armandii* under high temperature cracking, the organic substances and chemical components contained in the leaves can be clearly understood, which provides a reference for the pharmaceutical and spice industries, and also for the practical significance of *Pinus armandii* and its value.

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