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LETTER TO THE EDITOR

Pyrolysis Molecule of Pinus armandii Bark for Potential Biomedicine

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Thermogravimetric analysis (TGA) was used to study the thermal weight loss behavior of Pinus armandii Franch bark. The results showed that the pyrolysis reaction of P. armandii Franch bark was mainly carried out after 220°C, and the thermal stability was better before 220°C. The pyrolysis behavior and products of P. armandii Franch bark were studied by pyrolysis-gas phase-mass spectrometry (Py-GC/MS). The identified compounds can be classified into esters, alcohols, carbohydrates, acid anhydrides, aldehydes, ketones, alkenes, and organic acids.

Key words: Pinus armandii Franch bark; TG; PY-GC-MS

I Introduction

The bark of trees has many practical uses, one of which is artistic bark painting, commonly birch bark and silver brocade painting. Birch bark painting is based on the birch epidermis and deep skin of trees in the Changbai Mountain (Masendra et al. 2018). The bark characteristically exposes many layers, has good toughness, soft and smooth texture, and is easy to engrave and color. As early as the Qing Dynasty, Jilin used the birch bark to make a tribute for the palace (Treinyte et al. 2018).

The bark not only absorbs many toxic substances in the environment, but also is an excellent indicator of the atmosphere. It can monitor the pollution of the atmospheric environment from the amount of toxic substances adsorbed by the bark over the years (Geetha and Chakravarthula 2018).

Pinus armandi Franch adapts to cool and humid climate, is not resistant to cold and damp heat, slightly resistant to dryness and thinness (Ogundajo et al. 2018). It is used for materials in construction, furniture, and wood fiber industry. The trunk can cut the resin; the bark can extract the tannin; the needle can extract the aromatic oil; the seed can be eaten or pressed. Its pollen, known in medicine as “song yellow”, soaked in warm clothes, has the effect of healing traumatic bleeding, scalp and swelling, and can also be used as a talcum powder to prevent sweat rash (Fu et al. 2018). Using a sharp knife to cut the cortex of the pine trunk, the rosin is discharged, and the turpentine is fractionated to separate the volatile turpentine, leaving a hard, transparent amber rosin (Marius et al. 2018).

In this study, thermogravimetry (TG) and pyrolysis gas chromatography/mass spectrometry (PY-GC-MS0 techniques were used to analyze the composition of Pinus armandii Franch bark, which provided a theoretical basis for the rational use of Pinus armandii in the pharmaceutical and food industries (Li et al. 2018, Okoye et al. 2017, Rebeca Cardenas-Moreno et al. 2016).

II Material and Methods

Experimental Materials

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

TG Analysis

The samples of Pinus armandii Franch bark were analyzed by thermogravimetric analyzer (TGA Q50 V20.8 Build 34) (Rojek and Wesolowski 2018). The nitrogen release rate was 60 ml/min. The temperature program of TG started at 30ºC and rose to 300ºC at a rate of 5 ºC/min (Bobrowski et al. 2018, Lam et al. 2019).

Py-GC-MS Analysis

Catalyzed and pretreated samples were analyzed by pyrolysis-gas chromatography-mass spectrometry (CDS5000-Agilent 7890B-5977A ISQ) (Dong et al. 2013, Orozco et al. 2008). Carrier gas for high purity helium, pyrolysis temperature of 500°C, heating rate of 20 °C/ms, pyrolysis time of 15 s. The pyrolysis product transfer line and injection valve temperature was set at 300°C; HP-5MS column; capillary column (60 m × 250 μm × 0.25 μm); parallel mode, the split ratio 1:60, shunt speed 50 mL /min (Yuan et al. 2015). The temperature of the GC program was raised from 40°C for 2 min, raised to 120°C at a rate of 5 °C/min and then raised to 200°C at a rate of 10 °C/min for 15 mins. Ion source (EI) temperature of 230°C, the scanning range of 28 amu-500 amu (Xie et al. 2007).

III Analysis of TGA and DTG

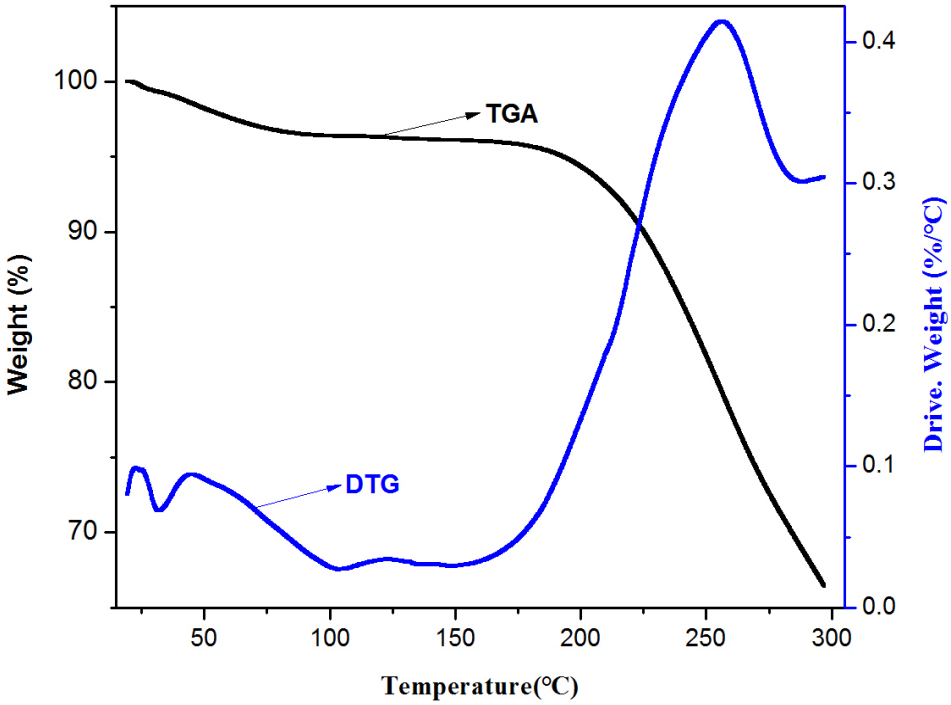

Figure 1. TGA and DTG thermal curves of the bark of Pinus armandii Franch

Figure 1 shows the TGA and DTG curves of Pinus armandii Franch bark. As can be seen from the figure, the weight loss process of pyrolysis can be divided into three stages. The first stage is between 18°C and 100°C, which is the evaporation phase of water. At this stage, the weight loss of the sample is small, and the weight loss is mainly caused by the loss of biomass. The mass ratio at this stage is reduced from 100% to 97%, and only 2% of the mass loss. The second stage is between 100°C-200°C, when the mass ratio decreased from 97% to 95%, the mass loss was 2%, and the weight loss was less, indicating that the material has good thermal stability (Chen et al. 2015, El-Sayed and Mostafa 2015). The third stage is between 256°C and 300°C. During the combustion phase of the remaining components, as the temperature increases, the cellulose and hemicellulose in the pine bark of Pinus armandii Franch rapidly cleave and generate a large amount of volatile gas, resulting in weightlessness (Ahmed et al. 2018). These three stages exhibit different properties, with different kinetic parameters and reaction mechanisms, and the final residual mass is 66.46%. In the whole process, the thermal gravity of the bark is only about 30%, the weight loss is small, the mass change is small, and the rate is low. TG test shows that Pinus armandii Franch bark has high resource utilization potential.

IV Analysis of Py-GC-MS

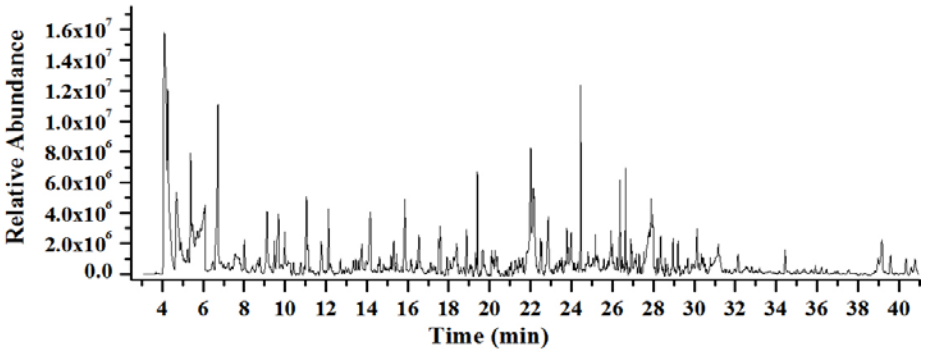

Figure 2: Total ion chromatograms of Pinus armandii Franch bark via PY-GC-MS.

According to the results of PY-GC-MS analysis in Figure 2, 266 peaks were detected, and 241 chemical constituents were identified. The content of more substances are as follows:.β.-D-Glucopyranose, 1,6-anhydro-(2.10%),2-Propanone, 1-hydroxy-(3.06%), Acetic acid (4.20%), Catechol (2.44%), Creosol (2.24%), Ethyne, fluoro- (6.54%), Glycido l(4.33%) ,Methyl glyoxal (2.49%), Propanoic acid, 2-oxo-, methyl ester (1.65%), Propanoic acid, 2-methyl-(1.20%), Methyl-.β.-D-thiogalactoside (1.45%), 2-Methoxy-4-vinylphenol (1.61%), Acetaldehyde, hydroxy- (1.50%), 5-Hydroxymethylfurfural (1.25%), 2,3-Butanedione (1.16%), 2-Cyclopenten-1-one, 2-hydroxy- (1.13%), 3R-acetamido-4cis, 6cis-bis (acetoxy)-5trans-dimethylamino (1.54%), Furfural (1.17%), and Formic acid(1.10%).

Analysis of Function

The identified compounds can be classified into esters, alcohols, carbohydrates, acid anhydrides, aldehydes, ketones, alkenes, and organic acids. Among them, pyruvic aldehyde is used as medicine, pesticide intermediate, and as a biochemical reagent for cimetidine, lactic acid, pyruvic acid, analgesic, anticancer, antihypertensive, desensitizing, cosmetic and other raw materials (Albuquerque et al. 2015, Feliczak-Guzik et al. 2018, Molenda et al. 2015). Glycidol is an important chemical intermediate used in the synthesis of glycerol, glycidyl ether (amine, etc.), as well as in surface coatings, chemical synthesis, pharmaceuticals, pharmaceuticals, fungicides and solid fuel gels. (Aasa et al. 2017, Lockhart et al. 2018). 2,3-Butanedione has a creamy aroma, high vapor pressure, and rapid evaporation at room temperature, formulated with a variety of milk flavor flavors, flavoring agents for creams, margarines, dry and sweets, as gelatin hardeners and photographic binders (Chung et al. 2015, Marri et al. 2017, Morgan et al. 2012). Sterols are good solvents for resins, varnishes, pigments, and rocket fuels. They can also be used as raw material and anti-corrosion coating for synthesizing various furan-type resins in synthetic fiber, rubber, pesticide and foundry industries (Currie et al. 2014, Gylling et al. 2014, Ras et al. 2014). Phenol is an important organic chemical raw material, which can be used to prepare phenolic resin (Hui et al. 2016,). It has industrial applications such as synthetic fibers, plastics, synthetic rubber, pharmaceuticals, pesticides, perfumes, dyes, coatings, disinfectants, and oil refining. Cassia has a sweet orange flavor and a balsamic gas. Hydrocarbon synthetic perfumes are mainly used in cologne and deodorant, and synthesis of terpene perfumes. Octyl ketone It used in the fields of fibers, medicines, pesticides, perfume chemicals, as synthetic fiber oil agents, antifoaming agents and surfactants, and flotation agents for coal mines. (Wu et al. 2016).

The potential value of Pinus armandii Franch bark in many areas is very high.

V Conclusion

The pyrolysis weight loss process of Pinus armandii Franch bark was divided into three stages. Through the analysis of the three-stage pyrolysis weight loss, it is found that the weight loss of the bark is small and the rate of change is low throughout the process. The material has good thermal stability between 100°C and 200°C. TG analysis shows that the Pinus armandii Franch bark has high potential for resource utilization in various industries.

PY-GC-MS analysis revealed 266 peaks, and 241 chemical constituents were identified and classified as esters, alcohols, carbohydrates, acid anhydrides, aldehydes, ketones, alkenes, and organic acids. We have demonstrated that Pinus armandii Franch bark has an exceedingly wide range of potential industrial and medicinal uses, which will be further revealed by future research and development.

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