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LETTER TO THE EDITOR

Resourcing Potential of Diverse Functional Components from *Chaenomeles Sinensis* Immature Fruits

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Chaenomeles sinensis is an excellent ornamental tree suitable for Beautiful China Project. However, the current researches on *C. sinensis* mainly focused on cultivation and landscape, and lacked of high valued-added utilization of components from *C. sinensis* immature fruits. Therefore, the components were extracted from *C. sinensis* immature fruit with benzene, acetone and ethanol, then functional components were identified by FT-IR, GC/MS and QTOF-UPLC/MS. The main volatile organic compounds (VOCs) of *C. sinensis* immature fruit are esters, acids, alcohols, aldehydes, ketones, heterocycles, alkanes. Non-VOCs are esters, acids, alcohols, aldehydes. VOCs of all three extracts contain rich bioactive components including .beta.-Sitosterol, Hexadecanoic acid, 9,12-Octadecadienoic acid Benzaldehyde, while Non-VOCs contain rich biomedicine components including Pinoresinol dimethyl ether, 11-Oxo-kansenonol, Liquidambaric lactone, 28-Deacetylbelamcandal, umbelliferone, Methyl Caffeate, trichosanic acid, fritilleinide A, Soyacerebroside II. Interestingly, some new components including baicalin, methyl arteisinate and mangiferonic acid were firstly reported here.

I Introduction

Chaenomeles sinensis is a famous ornamental plant and widely distributed in the world (Qin et al. 2018). It has strong adaptability and low requirement for soil. People can see *C. sinensis* was planting in warm and humid semi dry climate (Zhao et al. 2017, Gao et al. 2017). In China, it is not only regarded as an ornamental plant (Oh et al. 2018), its fruit is also considered as pulp food, and popular with high nutritional value (Kim et al. 2017, Reyna Carranza et al. 2017, Sinaga et al. 2019). In addition, the wood of *C. sinensis* can also be used as raw material for charcoal (Xie et al. 2018). In recent years, the planting area of ornamental *C. sinensis* has been further expanded (Melucci et al. 2013), a large number of *C. sinensis* immature fruits have been directly abandoned, and enormous biomass resources have been wasted, these even cause air pollution problems. In order to study the potential bioactive components of ornamental *C. sinensis* immature fruit, the *C. sinensis* immature fruit was extracted and determined by FT-IR, GC/MS and QTOF-LC/MS.

II Materials and Methods

(1) Materials

The *C. sinensis* immature fruits were collected from the *C. sinensis* plantation of Henan Agricultural University. After fully dried at 40°C by air blowing thermostatic oven, the *C. sinensis* immature fruits were separated from the nutmeat. The samples were smashed into powder by using FZ102 Disintegrator suitable for plant (Tanjing Taisite Ins. Corp., China), in succession, 200 mesh powders were sieved out.

(2) Extraction by three solvents

The *C. sinensis* immature fruits were extracted by ethanol, acetone and benzene, respectively, with the solid-liquid ratio of 1:30. After immersing for 12 h at room temperature, the mixed samples were fully extracted by automatic FOSS Soxhlet Extracted apparatus (Agilent, USA) at 78°C, 55°C, 80°C for 4 h, and then filtrated fast with filter paper immersed in ethanol, acetone and benzene, respectively for 24 h. The filtrated extraction was evaporated at 40-45°C under 0.01 MPa vacuum, and concentrated to 20 mL, then transferred to a sealed reagent bottle (Ouyang et al. 2017).Concentrated extracts were kept in 4°C refrigerator for the subsequent determination (Zhang 2018).

(3) Analysis of group changes during extraction by FT-IR

The powders of *C. sinensis* immature fruit, and their extracted residues were dried at 100°C for 4 h, in succession, put in the dry container with desiccant to prevent moisture absorption, so as not to affect the detection. A certain amount of potassium bromide were ground and sieved out using AS200 Sieving Instrument (USA), put in the dry pot, then keep in the muffle furnace (with SX-2.5-10 box-type control resistance furnace control box) at 150°C for 5 h, after that, removed under a heating lamp cover. Take 200 mg of potassium bromide to an agate mortar with a smooth surface, and 0.5-2 mg of the sample was mixed fast and completely with potassium bromide in the mortar, and then placed in the tablet press for tableting. As a liquid solution, the extracts were directly placed in the tablet press for tableting. The pressed samples were tested in a Fourier transform infrared spectroscopy (SHIMADZU, IR Affinity-1) from 4000 cm^{-1} – 400 cm^{-1} (Cheng et al. 2018, Lam et al. 2019).

(4) Component analysis by GC/MS

The characteristic and relative content of components from extracts were analyzed by GC/MS.

GC condition: quartz capillary column was 30 mm×0.25 mm × 0.25 um, started at 50°C (Zhang et al. 2015), then followed by a rate of 8 °C/min up to 250°C, finally reached 300°C at a rate of 5 °C/min. The temperature of the inlet was 250°C, column flow was 1.0 ml/min, split ratio was 20:1, and the carrier gas was high-pure helium. MS condition: ionization mode was EI, the electron energy was 70 Ev, the temperature of ion source was 230 °C, the temperature of quadrupole was 150°C, and the starting scanning point was 30-600 (Liu et al. 2018).

(5) High-performance liquid chromatography–QTOF–Mass spectrometry

High-performance liquid chromatography/Mass spectrometry: Agilent 1290 Infinity chromatograph. Chromatographic column: Thermo Scientific Acclaim RSLC C18 100 × 2.1 mm (2.2 μm, 120 A). Mobile phase: A phase (0.1% FA, 99.9% H_2O); B phase (0.1% FA, 99.9% ACN) (Jiang et al. 2017). Mass spectrometry: Mass Spectrometry Type: Compact High-resolution Mass Spectrometer. Ion source: ESI source. Scan mode: positive ion mode scan. Scanning range: m/z 100–1000 (Xu et al. 2018).

III Results

(1) Chemical Group change characteristics of raw powders and extracts

Fourier transform infrared spectroscopy (FT-IR) is an effective method to identify and analyze the structure of substances. The C-O stretching vibration has an absorption peak mainly at 1058 $cm^{-1}$and 1260 cm^{-1}, (Fig. 1. A_0) the main absorption peak of the carbonyl group is 1747 cm^{-1}. At 2925 cm^{-1}, there is methylene C-H antisymmetric stretching vibration. There (Fig. 1. A_1) is an absorption peak at 1164 cm^{-1}, which is due to the antisymmetric stretching of C-O-C. The absorption peak at 1280 cm^{-1} is C-O stretching vibration, there is a peak near 1375 cm^{-1} indicating CH_3 symmetry angle. There (Fig. 1. A_2) are two absorption peaks at 1076cm^{-1} and 1240cm^{-1} show that C-O stretching, and it may exit alcohols. Absorption peak near 1454 cm^{-1} is scissor deformation of CH_3, which is a characteristic peak of alkanes. An absorption peak near 1714cm^{-1}, indicating that C=O exists and there may be ketones and acids. First, there (Fig. 1. A_3) is an absorption peak near 1080 cm^{-1}, which is C-O stretching, which means that there are alcohols. The absorption peak near 1441 cm^{-1} is C=C stretching vibration, indicating the presence of olefins. There is an absorption peak near 1722 cm^{-1} due to C=O stretching vibration, and may exist aldehydes and esters. There is a distinct absorption peak near 2855 cm^{-1} due to the methylene symmetry stretching, indicating alkanes.

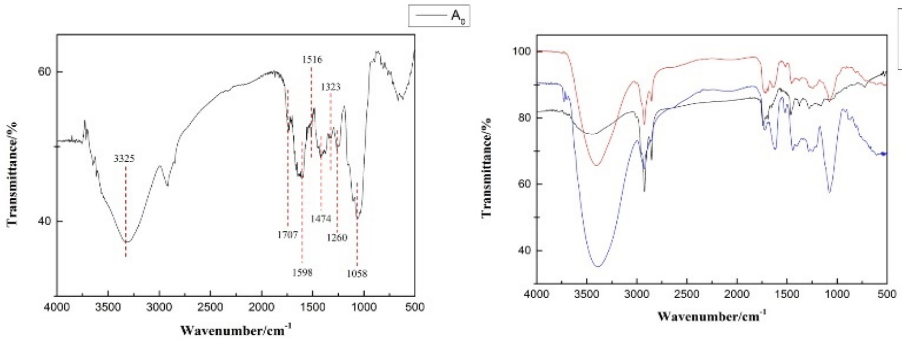

Fig. 1. Infrared spectra of raw powders and its extracts of C. sinensis immature fruit

A_0: raw powders; A_1: benzene, A_2: acetone, A_3: ethanol extracted

(2) *C. sinensis* immature fruit extracts contain a variety of volatility liquid bioactive components.

Volatile omponents are abundant, a total of 9 different types of substances are contained, and the extract contents of different solvents are significantly different. *C. sinensis* immature fruit benzene extractive is mainly Alcohols (accounting for 25.788% of the total), followed by Esters (accounting for 18.984% of the total), and other content is less. The main volatile active ingredients of *C. sinensis* immature fruit acetone extractive contain acids and alcohols, which account for 32.712% and 32.846% of the total respectively, and aldehydes and ketones substances appear, their relative content is less, just 3.86% and 5.263% respectively. However, *C. sinensis* immature fruit ethanol extractive contains the same average species, namely aldehydes (16.996%), alkanes (16.671%), alcohols (15.75%), acids (12.7%). Among them, the content of aldehydes and ketones in *C. sinensis* immature fruit, Ethanol extractive is higher than other solvents, while the relative contents of Esters and Heterocycles are relatively less, 6.06% and 2.009% respectively.

(3) *C. sinensis* immature fruit contain rich Non-volatile liquid biomedicine components.

The thanol extract is the most abundant, but the relative content is not particularly prominent. In ethanol extract, the non-volatile active ingredients are esters (19.791%), acids (11.791%), alcohols (6.345%), ketones (3.262%), aldehydes (2.349%), and ethers (1.235%). Among the non-volatile active ingredients of Acetone extract, Alcohols have the best extraction efficiency, the relative content is 21.757%, and the other substances are acids (14.349%), esters (11.509%), and aldehydes (4.481%). Among the non-volatile active ingredients of benzene extract, the contents of esters and alcohols are relatively high at 29.541% and 22.472% respectively, followed by acids (12.951%), ethers (1.991%), and ketones (0.658%). On the whole, different types of organic solvents can be selected according to the requirements to extract the corresponding non-volatile active ingredients, which can effectively improve the efficiency.

IV Conclusion

According to the results of FT-IR, GC/MS and LC/MS, it is known that the main volatile active ingredients of *C. sinensis* immature fruit can be identified as esters, acids, alcohols, aldehydes, ketones, heterocycles, alkanes. Non-volatile components can be identified as esters, acids, alcohols, aldehydes. The results of the infrared spectroscopy further confirm that the active components of the original sample and extract of *C. sinensis* immature fruit are identical. In terms of chemical structure, the results of GC/MS and LC/MS show that the organic solvent extraction do not significantly change the complex group of *C. sinensis* immature fruit. Perhaps complex physiological and biochemical changes occur during fruit ripening, in which these substances react to other substances. But this is only a conjecture, which needs to be verified by subsequent experiments.

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