Analysis and Comparison for Main Volatile Compounds of *Pericarpium Arecae* in Different Drying Methods

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Abstract. The main volatile compounds of *Pericarpium Arecae* (PA) dried by different methods were analysed via SPME-GC-MS combined with retention index (RI) method and standard. There were multiple volatile components of the PA dried by the five methods respectively identified; meanwhile, each one was quantified by area normalization method. The results indicated that the content of arecoline, the index constituent, was low in sample F (5.11%) and sample BD (6.97%), but high in sample D (38.88%), sample MFMD (26.45%) and sample HFMD (35.64%). It can be seen that drying has less damage to the known active ingredients such as arecoline. The microwave drying method of middle fire (MFMD) had better effect to get comprehensive ingredients, due to less damage to volatile components. In conclusion, different drying methods have great influence on the volatile components of PA. And the drying method (D) has a great advantage on the active components such as arecoline. However, the method (MFMD) has less time consuming and can preserve more complete volatile components.

1. Introduction
*Pericarpium Arecae* (PA), the dry pericarp of *Areca catechu* L., belongs to the *Palmae* family. PA originally from Southeast Asia and East Africa has now widely been cultivated in Hainan, Yunnan, Guangxi, Guangdong, Fujian and Taiwan provinces in China (Yu et al., 2016). PA was first recorded in “*Kai Bao Materia Medica*”, and has been used in clinical drug and other areas for more than 1000 years in China. It has been used for abdominal distension, constipation, and edema treatment in Traditional Chinese Medicine (Wang et al., 2004; Indriana, A. et al., 2016). Modern pharmacological studies have shown that PA has various effects including antiparasitic, antioxidant, antibacterial, antifungal, anti-allergic, anti-inflammatory and analgesic; as well as effects on digestive, nervous and cardiovascular systems; and regulatory effects on blood glucose and lipids, etc. based on its wide spectrum of biological and pharmacological activities (Kuo et al., 2015).

As a qi regulating Chinese medicine, volatile compounds are one of the important one of the indicators of evaluating quality which is directly affected the sensorial quality of fresh and processed products (Peng et al., 2015). Therefore, the studies for main volatile compounds of PA with different drying method were to be developed in the present paper. The current results will provide useful information for the quality control of PA’s processed products.
2. Materials and methods

2.1. Plant materials and processed products
The medicinal materials collected from Hainan province were identified as PA by Associate Professor Lin in the agricultural products processing institute of the Chinese Academy of Tropical Agricultural Sciences (Zhanjiang, China).

The fresh materials (50 g) processed to less than 10% water by boiling and drying (BD) to a yellowish color like the traditional method. Besides, other medicinal materials (each 50 g) were processed by drying (D), microwave drying method of middle fire (MFMD), and microwave drying method of high fire (HFMD) respectively. The specific methods were shown in Table 1.

| Methods                        | Temperature (℃) | Time   |
|--------------------------------|-----------------|--------|
| Boiling and drying (BD)        | Boiling 100     | Boiling 10s |
|                                | Drying 80       | Drying 4h |
| Drying (D)                     | 50              | 6h     |
| Middle fire microwave drying   | 60              | 45min  |
| HFMD                            | 100             | 20min  |

2.2. Reagents and apparatus
The reagents used in this study included: n-alkanes std. (C7~C30) was acquired from Supelco (Sigma-Aldrich Chemical Co., USA). Water was Milli-Q (Millipore, USA).

The apparatus used in this study included: GCMS-QP2010Plus instrument equipped with a quadrupole mass analyzer (Shimadzu, Japan). AOC-5000 instrument equipped with headspace, solid-phase microextraction (SPME) and liquid three in one automatic injector (Shimadzu, Japan).

The fiber, coated with divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS, 50/30μm, Supelco, USA) was used for extraction.

A fused silica capillary Rtx-5ms (Restek, USA) column (30 m × 0.25 mm i.d., 0.25 μm film thickness, 5% diphenyl-95% dimethylsiloxane phase) was used for the separation.

Otherwise, CPA225D electronic balance (Sartorius, Germany), DHG-9145A air-circulating oven and WGZ-2000 microwave drying apparatus (Shenzhen liangyi laboratory instrument Co., Ltd., China), were used in the study.

2.3. Preparation of sample solution
PA samples were divided into five parts. One was a fresh sample for not handling (F); One was dried at 50℃ after boiling in 100℃ 5 min (BD); One was only dried at 50℃ (D); One was processed with microwave drying (middle fire, MFMD), the rest was dealt with microwave drying (high fire, HFMD). Then, these materials were crushed respectively.

2.4. Sample extraction
The HS-SPME procedures were performed using AOC-5000 autosampler (Shimadzu, Japan). The instrument was equipped with a SPME fiber/syringe holder, a temperature-controlled agitator tray, and a temperature-controlled, needle heater port. The SPME device was purchased from Supelco (Bellefonte, PA, USA). The fiber, coated with divinylbenzene-carboxen-polydimethylsiloxane (DVB/CAR/PDMS, 50/30μm) was used for extraction. Prior to sampling, the fiber was preconditioned at 250℃ in the GC injection for 0.5 h.

PA sample above (about 2 g) were respectively put in a 20 mL sealed vial and used as the sample solution. For balance, the vial was put in the temperature-controlled agitator tray at 90℃ for 3 min with magnetic stirring (250rpm). Subsequently, the SPME device was automatically inserted into the sealed vial through the septum and the fiber was exposed to the sample headspace mode for 15 min.
under the same state. After extraction, the SPME device was introduced in GC and maintained at 250°C for 3 min. After each sampling procedure, the fiber was automatically reconditioned for 5 min in the Needle Heater port at 250°C. This reconditioning procedure was enough to guarantee no peaks in blank runs.

2.5. Gas chromatography-mass spectrometry (GC-MS) analysis

The isolation, identification, and semi-quantification of the volatile compounds were performed on a GCMS-QP2010Plus instrument equipped with a quadrupole mass analyzer (Shimadzu, Japan). A fused silica capillary Rtx-5ms (Restek, USA) column (30 m × 0.25 mm i.d., 0.25 μm film thickness, 5% diphenyl-95% dimethylsiloxane phase) was used for the separation. The GC injection and MS interface temperatures were respectively maintained at 250°C and 280°C. Electron ionization (EI) was used as the ion source; and the electron impact energy was 70 eV as well as the ion source temperature was 230°C. The following temperature program was used with a 1 min solvent delay. Initially, the temperature began at 70°C (held for 2 min) and then increased to 130°C (held for 2 min) at a rate of 10°C/min, and then gradually increased to 280°C (held for 2 min) at a rate of 15°C/min using splitless mode. The constant flow rate of the carrier gas (Helium) was 1 mL/min. The EI mass spectra were set to full scan from 35 to 550 atomic mass units (amu).

2.6. Compounds identification

The volatile compounds were identified by National Institute of Standards and Technology mass spectral library (NIST14) and Wiley Registry of Mass Spectral Data, 9th Edition (Wiley9) on the basis of standard substance, retention index (RI), or EI mass spectra from the literature. Among them, RI was calculated using n-alkanes (C7~C30) as a reference.

3. Results and discussion

The volatile components were identified by comparing their relative retention times, mass spectra similarity, retention index and comparison with standards. The results of analyses were listed in Table 1, in which the compounds were shown in the order of their elution time on the column.

Chemical compositions of PA processed in different drying methods were led to the identification of 23 constituents, respectively accounting for 87.46%, 91.72%, 81.26%, 88.41% and 88.96%.

Table 2. The volatile components of PA processed by different methods

| No. | Compounds¹ | Retention time² | Retention index | Ident³ | CAS             | Relative content (%) |
|-----|------------|----------------|-----------------|--------|-----------------|----------------------|
| 1   | Benzaldehyde | 5.189          | 964             | a,b    | 100-52-7        | 1.98                 |
| 2   | Benzeneacetaldehyde | 6.544          | 1047            | a,b    | 122-78-1        | 2.39                 |
| 3   | Guaiacol     | 7.301          | 1093            | a,b    | 90-05-1         | 2.38                 |
| 4   | Benzeneethanol | 7.752          | 1119            | a,b    | 60-12-8         | 3.32                 |
| 5   | Methyl 1-methyl-1,2,3,6-tetrahydropyridine-3-carboxylate | 8.609          | 1168            | a,b    | 86447-15-6      | 3.11                 |
| 6   | Arecoline    | 9.863          | 1234            | a,b,c  | 63-75-2         | 5.11                 |
| 7   | Homoarecoline | 11.278         | 1304            | a,b    | 28125-84-0      | 1.74                 |
| 8   | Hydrocinnamic acid | 12.007         | 1349            | a,b    | 501-52-0        | 1.78                 |
| 9   | trans-Ethyl cinnamate | 13.813         | 1474            | a,b    | 4192-77-2       | 6.46                 |
| 10  | trans-β-Ionone | 14.107         | 1496            | a,b,c  | 79-77-6         | 1.81                 |
| 11  | Dodecanoic acid | 14.866         | 1564            | a,b,c  | 143-07-7        | 2.87                 |
| 12  | Ethyl dodecylate | 15.196         | 1594            | a,b    | 106-33-2        | 4.17                 |
| 13  | Tetradecanoic acid | 16.755         | 1760            | a,b,c  | 544-63-8        | 1.69                 |
| 14  | Ethyl tetradecanoate | 17.042         | 1793            | a,b    | 124-06-1        | 3.77                 |
| 15  | Ethyl cis-9-pentadecenoate | 17.64          | 1867            | a,b    | 56219-09-1      | 1.83                 |
As shown in Table 2, the relative content of arecoline which is considered as the main active substance in PA (Xiang, et al., 2013), was low in sample F (5.1%) and sample BD (6.97%). Due to arecoline is easy to soluble in water. The moisture content of the sample F was high, and the water in sample BD was taken away with arecoline. However, the relative content of arecoline was high in sample D (38.88%), sample MFMD (26.45%) and sample HFMD (35.64%).

Methyl 1-methyl-1,2,3,6-tetrahydropyridine-3-carboxylate generated by arecoline is also easy to dissolve in water like arecoline. Therefore, it can’t be found in the sample BD.

It can be seen from Table 1 and 2, it could be preserved more volatile components by method MFMD, because of its lower heating temperature and shorter time. If the heating time is too long or the heating temperature is too high, like method D and method HFMD, some ethyl fatty acids would be lost, but the active substances like arecoline and homoarecoline would be gained more.

4. Conclusion
The fresh arecas are not resistant to storage and easy to mold. Accordingly, the main processing method of them is dry products. The results showed that different drying methods had a great influence on the volatile components of PA via SPME-GC-MS. It could be seen that both the method D and the method HFMD had a great advantage on the active components such as arecoline. However, the method MFMD has less time consuming and can preserve more complete volatile components. If arecoline and other similar substances could not be wanted, the method BD is a suitable drying method. Suitable method should be chosen according to the actual needs of development and utilization of specific.

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