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Influences of Drying on the Volatile Compounds in Chinese Jujube

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The effects of different drying methods on the volatile compounds of Chinese jujube (*Ziziphus jujuba* Mill.), an important fruit and traditional herbal medicine in China, were first studied. The mature fruits were dried using different drying methods: oven-drying at 50, 60, 70 ºC and air-drying at ambient temperature. The volatile compounds from fresh and dried fruits were isolated by simultaneous distillation extraction and analyzed by gas chromatography-mass spectrometry. The major components in fresh Chinese jujube were (Z)-11-hexadecenoic acid (26.5 %), (Z)-7-tetradecenoic acid (24.25 %), ethyl 9-hexadecenoate (16.98 %) and dodecanoic acid (12.51 %). In the three oven-dried samples at 50, 60, 70 ºC, the major components were the same: (Z)-11-hexadecenoic acid (34.2, 40.59, 43.22 %), (Z)-7-tetradecenoic acid (28.82, 29.6, 28.16 %) and dodecanoic acid (13.56, 14.3, 10.67 %). In air-dried sample, the main constituents were: (Z)-11-hexadecenoic acid (51.16 %), myristoleic acid (26.07 %) and dodecanoic acid (12.52 %). The aroma compounds naphthalene,1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, (1S-*cis*)- and 2-naphthalenemethanol, decahydro-α,α,4a-trimethyl-8-methylene-, [2R-(2.α.,4a.α.,8a.β) were first discovered in Chinese jujube. The volatile compounds of fresh and differently dried samples showed distinct qualitative and quantitative differences. The results showed that oven-drying at 60 ºC is the more suitable method for drying of Chinese jujube in terms of volatile compounds.

Key Words: *Ziziphus jujuba* Mill., Drying method, Volatile compounds.

INTRODUCTION

Fruit quality is a multivariate attribute, which depends on visual appearance, textural properties, taste and volatile nature. Volatile components are important constituents of natural products and play an important role in the fruit quality. A considerable amount of literatures have reported the volatile components of fruits such as apple[1-4], pear[5-7], orange[8-10] and strawberry[11-13]. The volatile compounds are grouped into chemical categories such as esters, aldehydes, ketones, acids, alcohols and their derivatives, furan and pyran derivatives. The importance of aromatic plants is considerable owing to their application in folk medicine and their potential for commercial value in various fields as spices, beverages, perfumery, cosmetics, pharmaceutics and aromatherapy[14,15].

Chinese jujube (*Ziziphus jujuba* Mill.), a native plant of China, belongs to the family of Rhamnaceae and has been cultivated for over 7000 years[16]. It is distributed throughout China and more than 40 other countries with a total planting area of 1,600,000 hectares and yearly production of over 4 million tons. Its fruits are not only nutritional food but also famous traditional Chinese medicine. The chemical compounds isolated from Chinese jujube include cyclic AMP[17], polysaccharides[18], flavonoids[19], saponins[20], phenolic compounds[21] and vitamins[22]. The fruits can be used in stomach diseases and for metabolic regulation in Tibetan medicine. They are even used for the treatment of cardiovascular and neurological diseases, chronic infection and tuberculosis of various organs in China. Moreover, it is used as a sedative and lactogenic remedy in Korean and Arabian medicine, respectively[23].

As to the volatile of Chinese jujube, present research showed that it is related to maturity stages, varieties and producing areas. Zhao Feng[24] analyzed the volatile compounds of *Ziziphus jujuba* Mill. 'Jinsi4' at white-mature stage, half-red stage and full-red stage and there were 13, 38 and 27 kinds of aroma components at the three stages, respectively. Zhu Feng-mei[25] extracted the essential oil from Jinsixiaozao and Muzao with 19 and 21 volatile compounds identified, respectively.

In the present work, we investigated for the first time the influences of different drying methods on the volatile compounds of Chinese jujube. The main aim of this study was to make sure about the proper drying method for Chinese jujube in terms of volatile compounds.

EXPERIMENTAL

The mature fruits of *Ziziphus jujuba* Mill. 'Zanhuangdazao' were collected from Cangzhou, Hebei province (P.R. China) in 2011. The sample was divided into five batches. One batch was stored at -70 ºC, the remaining four batches were immediately dried using one of the drying methods as described below.

Drying methods: The fruits for drying were cut into small pieces. Three batches were oven-dried using a laboratory oven at the temperature of 50, 60 and 70 ºC, respectively. The last one sample was air-dried at ambient temperature in a dark, well-ventilated room. The moisture content of dried fruits was around 5 %.

Isolation of the volatiles: Simultaneous distillation extraction (SDE) was used for extraction of volatiles from Chinese jujube. Samples (100 g) after crushing was blended with water (500 mL) and then extracted for 6 h in a Likens-Nickerson apparatus with dichloromethane (50 mL) as the extraction solvent. After the end of extraction, the dichloromethane was dried over anhydrous Na_2SO_4 and concentrated to *ca.* 5 mL in volume by rotary evaporation at the temperature of 38 ºC. The extraction was stored in a sealed vial at 4 ºC for GC-MS analysis.

GC-MS analysis: Quantitative and qualitative analysis of the volatile compounds was performed using a GC-MS system (Trace, Finnigan, USA) equipped with a DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm). Helium gas was used as a carrier gas and the flow rate was 1 mL/min. The split ratio was 1:20. The temperature was increased from 60-120 ºC at a rate of 10 ºC/min and then increased to 260 ºC at a rate of 5 ºC/min and held for 15 min at 260 ºC. The injection volume was 1 μL. The MS was operated in EI mode at 70 eV, source temperature was kept at 200 ºC and the mass acquisition range was 40-610 amu. Qualitative analysis was achieved using the NIST Mass Spectral Search Program.

RESULTS AND DISCUSSION

The volatile constituents of Chinese jujube were obtained by simultaneous distillation extraction and analyzed by GC-MS method, which are presented in Table-1. Identification of these compounds was performed by matching the reference mass spectra of the GC-MS data system. The quantitative analysis was obtained from electronic integration peak areas.

Volatile compounds of fresh Chinese jujube: Among the forty-three different compounds of Chinese jujube, eleven were identified from fresh fruit, including 6 acids, 2 esters and 3 aldehydes, which constituting 90.77 % of the total volatile compounds. The major components in fresh Chinese jujube were (Z)-11-hexadecenoic acid (26.5 %), (Z)-7-tetradecenoic acid (24.25 %), ethyl 9-hexadecenoate (16.98 %) and dodecanoic acid (12.51 %).

Volatile compounds of oven-dried Chinese jujube: The effect of oven-dried methods on Chinese jujube at three different temperatures (50, 60, 70 ºC) were investigated. From jujube dried at 50, 60 and 70 ºC, 14, 28 and 17 volatile compounds were identified, which represented 97.48, 98.21 and 93.82 % of total peak area, respectively. The volatile compounds of oven-dried Chinese jujube at 50 ºC included 7 acids, 6 hydrocarbons and 1 aldehyde. The volatile components of oven-dried Chinese jujube at 60 ºC were 8 acids, 3 aldehydes, 4 ketones, 2 alcohols, 5 esters and 6 hydrocarbons. The volatile compounds of oven-dried Chinese jujube at 70 ºC included 6 acids, 3 aldehydes, 3 hydrocarbons, 3 esters, 1 alcohol and 1 ketone. The major components in the three samples were the same: (Z)-11-hexadecenoic acid (34.2, 40.59, 43.22 %), (Z)-7-tetradecenoic acid (28.82, 29.6, 28.16 %) and dodecanoic acid (13.56, 14.3, 10.67 %).

Compared with the fresh sample, 27 new compounds were indentified in oven-dried samples, *i.e.*, toluene, dihydro-2-methyl-3(2*H*)-furanone, 2-furanmethanol, ethylbenzene, *p*-xylene, 2-cyclopentene-1,4-dione, *o*-xylene, 1,2-dimethylbenzene, 1-(2-furanyl)-ethanone, (1-methylethyl)benzene, benzeneacetaldehyde, 5-methyl-2-furancarboxaldehyde, 5-hydroxymethyldihydrofuran-2-one, 2-ethyl-1,4-dimethylbenzene, 1,2,4,5-tetramethylbenzene, *n*-hexadecanoic acid 1,2,3,4-tetramethylbenzene, dimethyl phthalate, dodecanoic acid, methyl ester, naphthalene, 1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, (1S-*cis*)-, 2-naphthalenemethanol, decahydro-α,α,4a-trimethyl-8-methylene-,[2R-(2.α.,4a.α.,8a.β.), methyl(Z)-11-tetradecenoate, pentadecanoic acid, (Z)-7-hexadecenoic acid, methyl ester, oleic acid, (Z)-9-hexadecenoic acid, methyl ester and pentadecanoic acid, 14-methyl-,methyl ester.

Volatile compounds of air-dried Chinese jujube: From air-dried Chinese jujube, eighteen volatile compounds were obtained, which representing 99.12 % of the total volatile compounds. They were composed by 7 acids, 5 aldehydes, 3 esters, 1 alcohol, 1 hydrocarbon and 1 oxide. The main constituents were: (Z)-11-hexadecenoic acid (51.16 %), myristoleic acid (26.07 %) and dodecanoic acid (12.52 %).

The new compounds indentified in air-dried sample compared with the fresh sample were heptanal, benzaldehyde, ledene oxide-(II), (E)-9-tetradecenoic acid and myristoleic acid.

The aroma of dried Chinese jujube, especially the oven-dried sample, is stronger than that of fresh one on the sensory. By comparing their GC-MS analysis results, the proportion of acids became larger after dried, which was in accordance with the previous studies[26]. Acids are related to the aroma of heavy cream and musk in Chinese jujube. In this study some special compounds in dried samples, *e.g.*, toluene and *o*-xylene have special aroma[27]. 1-(2-Furanyl)-ethanone with strong balsam and sweet flavor is probably the degradation product of ascorbic acid. There have been reported that acid treatment and even distillation induce the oxidation of ascorbic acid[28]. As an aroma compound, furaneol is also a bioactive compound, which exhibits a suppression effect on lipid peroxidation in human plasma and inhibits cataract formation[29]. The odor description of heptanal is fatty, sweet, woody, nutty and fruity[30]. Dimethyl phthalate can be used as fixative agent in spices[31]. The aroma compounds naphthalene,1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, (1S-*cis*)- and 2-naphthalenemethanol,decahydro-.α.,α.,4a-trimethyl-8-methylene-,[2R-(2.α.,4a.α.,8a.β.) were first discovered in Chinese jujube. The former exists in fennel[32], *Cinnamomum zeylanicum*[33], sawara falsecypress[34], *Magnolia liliflora*[35] and dry bupleurum[36]. The latter has been identified in sawara falsecypress, *Magnolia liliflora*, dry bupleurum and is also the main volatile compound in *Bidens* L. species[37].

TABLE-1
VOLATILE COMPOUNDS OF FRESH AND DRIED CHINESE JUJUBE

Peak No.	Components	Fresh (%)	Oven-dried at 50 ºC (%)	Oven-dried at 60 ºC (%)	Oven-dried at 70 ºC (%)	Air-dried at amsient temp. (%)
1	Toluene	–	1.31	–	–	–
2	Hexanal	1.59	–	–	0.66	0.37
3	Dihydro-2-methyl-3(2*H*)-furanone	–	–	0.61	–	–
4	Furfural	0.94	2.04	3.02	1.63	1.35
5	(E)-2-Hexenal	2.16	–	–	0.1	0.19
6	2-Furanmethanol	–	–	0.62	–	–
7	Ethylbenzene	–	1.75	–	–	–
8	*p*-Xylene	–	4.84	0.15	0.17	–
9	2-Cyclopentene-1,4-dione	–	–	0.12	–	–
10	*o*-Xylene	–	–	0.08	0.09	–
11	1,2-Dimethylbenzene	–	1.92	–	–	–
12	Heptanal	–	–	–	–	0.14
13	1-(2-Furanyl)-ethanone	–	–	0.27	0.12	–
14	(1-Methylethyl)benzene	–	0.24	–	–	–
15	5-Methyl-2-Furancarboxaldehyde	–	–	0.38	–	–
16	Benzaldehyde	–	–	–	–	0.07
17	Hexanoic acid	0.81	0.99	0.93	–	–
18	Benzeneacetaldehyde	–	–	0.08	–	–
19	5-Hydroxymethyldihydrofuran-2-one	–	–	0.08	–	–
20	2-Ethyl-1,4-dimethylbenzene	–	–	0.03	–	–
21	1,2,4,5-Tetramethylbenzene	–	–	0.02	–	–
22	1,2,3,4-Tetramethylbenzene	–	–	0.01	–	–
23	*n*-Decanoic acid	1.91	1.68	1.92	0.76	1.36
24	Dimethyl phthalate	–	–	0.05	–	0.03
25	Naphthalene,1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-,(1S-*cis*)-	–	0.17	0.05	0.63	0.05
26	Dodecanoic acid,methyl ester	–	–	0.04	–	0.03
27	Dodecanoic acid	12.51	13.56	14.3	10.67	12.52
28	Dodecanoic acid,ethyl ester	0.21	–	–	–	–
29	Ledene oxide-(II)	–	–	–	–	0.04
30	2-Naphthalenemethanol,decahydro-.α.,α.,4a-trimethyl-8-methylene-,[2R-(2.α.,4a.α.,8a.β.)	–	–	0.02	0.16	0.06
31	Methyl (Z)-11-tetradecenoate	–	–	0.1	0.17	–
32	(E)-9-Tetradecenoic acid	–	–	–	–	0.07
33	(Z)-7-Tetradecenoic acid	24.25	28.82	29.6	28.16	
34	Myristoleic acid	–	–	–	–	26.07
35	Tetradecanoic acid	2.91	4.68	3.79	5.1	4.34
36	Pentadecanoic acid	–	–	0.09	–	–
37	(Z)-7-Hexadecenoic acid,methyl ester	–	–	–	0.24	–
38	(Z)-9-Hexadecenoic acid,methyl ester	–	–	0.24	0.29	0.2
39	Pentadecanoic acid,14-methyl-,methyl ester	–	–	0.02	–	–
40	(Z)-11-Hexadecenoic acid	26.5	34.2	40.95	43.22	51.16
41	Ethyl 9-hexadecenoate	16.98	–	–	–	–
42	Oleic acid	–	1.28	–	–	–
43	*n*-Hexadecanoic acid	–	–	0.88	1.65	1.07

Conclusion

Table-1 showed that drying conditions had a great influence on the volatile compounds of Chinese jujube, not only the volatile compositions, but also their concentrations. The aroma compounds naphthalene,1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-,(1S-*cis*)- and 2-naphthalene-methanol,decahydro-.α.,α.,4a-trimethyl-8-methylene-,[2R-(2.α.,4a.α.,8a.β.) were first discovered in Chinese jujube. Compared with other drying methods, there were more volatile compounds identified in oven-dried at 60 ºC samples. And it was fast, simple and easy to control, so it is the more suitable method for drying of Chinese jujube in terms of volatile compounds.

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