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Effect of Drying of Jujubes (*Ziziphus jujuba* Mill.) on the Contents of Sugars, Organic Acids, α-Tocopherol, β-Carotene, and Phenolic Compounds

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ABSTRACT: This study investigated the changes in sugars, organic acids, α-tocopherol, β-carotene, phenolic profiles, total phenolic content (TPC), and antioxidant capacity of jujube fruits after four drying treatments (sun-, oven-, microwave- and freeze-drying). Sugar, organic acid, phenolic compounds, α-tocopherol, and β-carotene were qualitatived and quantitatived by high-performance liquid chromatography. The TPC and antioxidant activity of jujube samples were evaluated using the Folin−Ciocalteau method and 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) radical scavenging activity, respectively. Freeze-drying resulted in jujubes with higher antioxidant activity and was also a good choice for the preparation of β-carotene from jujubes for the food industry. Microwave-dried jujubes had a higher content of protocatechuic acid, catechin, and epicatechin and maintained the same antioxidant capacity with the freeze-dried jujubes. The combination of microwave- and freeze-drying may be an efficient alternative with shorter processing time and, consequently, less impact on the nutritional value of the jujube.

KEYWORDS: *α-Tocopherol, β-carotene, drying methods, fresh jujube, sugars, organic acids, phenolics*

INTRODUCTION

Jujube (*Zizyphus jujuba* Mill.) belonging to the Rhamnaceae family, is a key member of Chinese herbs. Jujube is widely distributed in the temperate and subtropical areas of the northern hemisphere, especially the inland region of north China.[1] Jujube fruit can be consumed fresh, dried, preserved, canned, and candied. Fresh and dried jujubes are especially rich in fiber, trace minerals, proteins, sugars, organic acids, and volatile compounds that provide a pleasant characteristic aroma.[2] Also, jujube fruits are considered as a good source of phytochemicals, such as phenolics, carotenoids, and vitamins, which significantly contribute to their taste, color, and nutritional and functional values. Currently, there is a considerable interest in these biologically active components because of their antioxidant properties and ability to alleviate chronic diseases.[3,4]

Jujubes are perishable in their fresh state and may deteriorate within a few days after harvest. One way to preserve jujube fruits is to dry them to conserve their desirable qualities, reduce storage volume, and extend their shelf life. However, the growers have little fresh jujube fruit preservation experience, and sometimes the weather conditions are less favorable for drying; most of the jujubes are consumed fresh. Therefore, proper methods for fruit drying have to be established. Different ways of drying have been developed for foods, and each method has its own characteristics. With the traditional drying method, sun-drying can ensure proper preservation of jujubes. However, the produce is exposed to direct solar irradiation, and because the drying parameters cannot be controlled, the quality of the product is not excellent. Sun-drying is, therefore, not homogeneous, and the final product is caramelized and crusted. Direct exposure to the sun also destroys the color, vitamins, and flavor of the jujubes.[5] In terms of oven-drying, water is usually removed by evaporation. In comparison, oven-drying has gained importance because it has many advantages over sun-drying, such as reduced microbial contamination, controllable drying parameters, which give a more uniform product with less quality degradation, shorter drying time, and lower labor costs. Microwave-drying may be an efficient alternative, with even shorter processing time and, consequently, less impact on the nutritional value of the fruits.[6] In the case of freeze-drying, food is first frozen and then water is removed by sublimation. Because of the absence of liquid water and the low temperature required for the process, most of the deterioration and microbiological reactions are prevented, which gives the final product an excellent quality.[7,8] Michalczyk et al.[9] reported that freeze-drying is much more effective in preserving valuable food compounds than those traditional methods. Wojdylo et al.[10] compared four methods to dehydrate strawberry fruits: freeze-, convection-, vacuum-, and vacuum microwave-drying. Their results revealed that freeze-drying improved the content of some phenolics, such as kaempferol 3-*O*-glycoside and catechin in "Elsanta" variety and cyanidin 3-*O*-glucoside in "Kent" variety, around 1.3 times compared to non-dried strawberry.

Although jujube is an important fruit variety consumed either fresh or dried in many countries, information regarding its contents of sugars, organic acids, phenolic compounds, α-tocopherol, and β-carotene as well as antioxidant properties

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affected by various drying methods were not available. Because fresh jujubes are not available all year round, many consumers usually choose dried fruit instead. Therefore, the contents of the same bioactive compounds and antioxidant activity of fresh and properly sun-, oven-, microwave-, and freeze-dried jujubes were determined and compared.

MATERIALS AND METHODS

Chemicals. The following standards: sucrose, glucose, fructose, citric acid, succinic acid, malic acid, vanillic acid, gallic acid, protocatechuic acid, *p*-hydroxybenzoic acid, catechin, epicatechin, rutin, cinnamic acid, *p*-coumaric acid, ferulic acid, α-tocopherol, and β-carotene were obtained from Sigma (St. Louis, MO). Water for the mobile phase was twice distilled and purified with the Milli-Q system (Millipore, Bedford, MA).

Plant Material and Experimental Design. A local cultivar of *Z. jujube* Mill., called 'Muzao' is planted in Yulin (110° 17′ E, 37° 36′ N; average elevation, 1049 m), a Loess Plateau region of China. All trees were managed according to integrated cultivation protocols.[11] Fresh jujubes were picked by hand in autumn (October), 2011. The jujube fruits were picked physiologically mature as defined by experienced horticulturists based on color, flavor, and structure of the fruits. A total weight of 5 kg of jujube fruits from 20 jujube trees were collected and used for experiments. A total of 1 kg of jujube fruits was subjected to each drying method, and 1 kg of jujube fruits remained fresh.

Jujube fruits obtained were carefully washed, halved, and stoned. The retaining edible portions (flesh and skin) were thinly sliced (3 mm thickness) and separated into two batches, one fresh with the moisture content of 64% and another to be subjected to one of the following drying methods: (a) being immediately exposed to the sun at a height of 1 m from the ground surface in the daytime and placed indoors at night for 3 weeks to reach a moisture content of 22%, (b) being dried in an oven (Gallenkamp, U.K.) at 70 °C for 8 h to reach a moisture content of 1.8%, (c) being freeze-dried in a freeze-drier, model G5200H at a temperature of −50 °C for 48 h to reach a moisture content of 0.2%, and (d) being dried in a microwave oven [Galanz G70F20N2L-DG (S0); 700 W] for 4 min to reach a moisture content of 25%. Each drying experiment was carried out in triplicate.

High-Performance Liquid Chromatography (HPLC) Analysis of Sugars and Organic Acids. The samples were analyzed for their content levels of sugars (sucrose, glucose, and fructose) and organic acids (malic, citric, and succinic acids). A total of 5 g of fresh jujube fruits or 2 g of dried jujube fruits were immersed in 50 or 20 mL of purified water and homogenized with a T-25 Ultra-Turrax (Ika-Labortechnik, Stauden, Germany). The samples were left for extraction by ultrasonification for 0.5 h at room temperature. The supernatant was separated, and the residue was re-extracted by repeating the above steps under the same conditions. The two filtrates were combined and filtered in vacuum and rinsed with 100% purified water, and then the solvent was evaporated using a rotary evaporator at 65 °C until the weight of the evaporated filtrate was less than 10% of the weight of the original filtrate. All extracts were stored at −20 °C in the dark until use. The supernatants were filtered through 0.45 μm cellulose filters (Shearwater Polymers, Inc.) and transferred to vials.

Samples were analyzed on a Waters HPLC system. For each analysis, 5 μL of sample was used. Analysis of sugars was carried out on an Inertsil NH_2 column (4.6 × 250 mm, 5 μm) (GL Sciences, Japan) with a flow of 1.4 mL/min, and the column temperature was maintained at 35 °C. The elution solvent used was 80% acetonitril and 20% deionized water, and a refractive index detector was used for identification. Organic acids were analyzed on an Atlantis T_3 column (4.6 × 150 mm, 3 μm) (Waters Corp., Milford, MA), maintaining the column temperature at room temperature. The eluent was monitored by ultraviolet (UV) detection at 210 nm. For the mobile phase, 0.5% $NH_4H_2PO_4$ (pH 2.6) was used with a flow rate of 0.8 mL/min. The concentrations of sugars and organic acids were calculated with the help of corresponding standards. The concentrations were expressed in milligrams per 100 g of dry weight (DW) and used for comparing the results that came from different sample treatments.

HPLC Analysis of α-Tocopherol and β-Carotene. α-Tocopherol and β-carotene were analyzed by the modified procedure from San and Yildirim.[12] A total of 5 or 10 mL of hexane was added to 2 g of fresh jujube fruits or 2 g of dried jujube fruits in a tube and vortexed. This process was repeated 4 times, and the supernatants were combined. The upper phase was centrifuged at 2000 rpm for 3 min, and the hexane within the supernatant was evaporated at 40 °C under vacuum. Remnants were dissolved in 1 mL of mobile phase. The solution was passed through 0.45 μm membrane filters, and 20 μL of the solution was injected into HPLC (Waters) equipped with an UV−vis detector (2487) and a Dikma Diamonsil C18 column (250 × 4.6 mm, 5 μm) (Dikma Technologies, Inc., Lake Forest, CA) operated at 40 °C. This process was repeated 3 times for each jujube sample. α-Tocopherol and β-carotene contents were analyzed at 296 and 450 nm, respectively. The mobile phase was methanol/acetonitrile/tetrahydrofuran (73:20:7, v/v/v) with a flow rate of 1.0 mL/min. Peak identification was performed according to the retention time and the UV spectrum of the standards. The quantities of α-tocopherol and β-carotene were assessed from peak areas. Concentrations were expressed as milligrams per kilogram of dry weight (DW) and used for comparing the results that came from different treatments.

HPLC Analysis of Phenolic Compounds. A total of 20 g of fresh jujube fruits or 5 g of dried jujube fruits were extracted with 200 or 50 mL of methanol in a cooled ultrasonic bath for 20 min. The supernatant was separated, and the residue was re-extracted by repeating the above steps under the same conditions. The two filtrates were combined and filtered in vacuum and rinsed with 100% methanol, and then the solvent was evaporated using a rotary evaporator at 45 °C until the weight of the evaporated filtrate was less than 10% of the weight of the original filtrate and then transferred to a vial prior to being injected into a HPLC system. Samples were analyzed using a Waters HPLC system with a UV−vis detector (2487) at 280 nm. An Atlantis T_3 column (4.6 × 150 mm, 3 μm) (Waters Corp., Milford, MA) operated at 30 °C was used. The injection volume was 20 μL, and the flow rate was maintained at 0.8 mL/min. The solvents used were as follows: A, methanol; B, ultrapure water (pH 2.6). The gradient profile was as follows: 15% A at 0 min, 25% A at 15−25 min, 75% A at 65 min, and 15% A at 70 min. Identification of compounds was achieved by comparing retention times and spectra of the chromatographic peaks to those of authentic standards analyzed under the same conditions. Concentrations of phenolic compounds were calculated from the peak areas of the sample and the corresponding standards. The concentrations were expressed in milligrams per kilogram of DW and used for comparing the results that came from different treatments.

Determination of the Total Phenolic Content (TPC). The extraction of fruit samples for the determination of the TPC was made according to the same protocol as for individual phenolics. The TPC of the extracts was assessed using the Folin−Ciocalteu phenol reagent method.[13] A total of 500 μL of deionized water and 125 μL of Folin−Ciocalteu reagent were added to 125 μL of the sample extracts, and after 6 min at room temperature, 1.25 mL of sodium carbonate (7%, w/v) and 1 mL of twice distilled water were added. The extracts were mixed and allowed to be kept for 1.5 h before the absorbance at 760 nm was measured on a spectrophotometer. A mixture of water and reagents was used as a blank. The TPC was expressed as gallic acid equivalents (GAE) in milligrams per 100 g of DW. Absorptions were measured in three replicates.

Determination of Antioxidant Activity. For the 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) assay, the procedure followed a laboratory procedure, with some modifications.[14] $ABTS^{\cdot+}$ solution was diluted with phosphate buffer solution (pH 7.4) to an absorbance of 0.70 (±0.02) at 734 nm. Jujube extracts (200 μL) were reacted with 3 mL of diluted $ABTS^{\cdot+}$ solution in the dark for 1 min, then the absorbance value was taken using the spectrophotometer. Blank solution and solutions of known 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) concentrations were prepared in exactly the same solvent as the samples. The antioxidant activity was expressed as millimoles of Trolox equivalent per 100 g of DW.

Statistical Analysis. The data were analyzed using SPSS software (PASW Statistics 18.0). All results are expressed as the mean ± standard deviation (SD) of three replicates. One-way analysis of variance (ANOVA) was used to evaluate differences between treatments. All of the statistical differences were carried out at a significance level of $\alpha = 0.05$.

RESULTS AND DISCUSSION

Sugar and Organic Acid Contents. Glucose, fructose, and sucrose of fresh jujubes and jujubes dried by four different techniques are presented in Table 1. Fructose and glucose were found to be the dominant sugars in all accessions analyzed, while sucrose levels were very low, which is in accordance with the results by Slatnar et al.[5] The same results have been reported by Barboni et al.[16] in the kiwi fruit that the major soluble sugar was fructose, followed by glucose and sucrose. There is no statistically significant difference in the fructose content when fruits of the four drying methods were compared; the content of glucose was statistically higher in sun-dried jujubes compared to fruits dried by other drying methods. Fructose has a higher relative sweetness than glucose.[15] Therefore, the perception of sweetness in jujube accessions is likely due to the prevalence of fructose.

Table 1. Content of Sugars (mg/100 g of DW) in Fresh Fruit and Dried Fruit of Four Drying Methods[a]

	fructose	glucose	sucrose
fresh	1648 ± 36.9 a	274.5 ± 9.0 ab	37.1 ± 10.8 c
freeze-drying	1437.3 ± 246.3 a	247.5 ± 25.7 bc	58.1 ± 7.3 b
microwave-drying	1387.5 ± 137.8 a	250.7 ± 5.9 bbc	112.3 ± 3.9 a
oven-drying	1386.7 ± 153.7 a	229.5 ± 36.1 c	nd[b]
sun-drying	1598.8 ± 70.5 a	306.7 ± 1.3 a	nd

[a]Mean ± SD; $n = 3$. Different letters in the columns indicate statistically significant differences in the contents of individual compounds between the treatments for jujube fruits at $p < 0.05$. [b]nd = not detected.

In jujube fruits, malic, citric, and succinic acids were determined among organic acids (Table 2). Malic and citric acids were determined to be the two predominant organic acids in jujube samples (Figure 1). The identification of the quantitative analysis of the major organic acids present in fruits is considered to be of great importance for both food technology and quality evaluation. These acids influence not only fruit flavor but also their stability, nutrition, acceptability, and keeping quality. They have been proposed as an index of maturity, ripeness, or spoilage in fruits.[6] Drying treatments slightly decreased malic acid and citric acid contents, with no significant differences found. A statistically higher content of succinic acid was determined in freeze-drying samples compared to other treatments.

Table 2. Content of Organic Acids (mg/100 g of DW) in Fresh Fruit and Dried Fruit of Four Drying Methods[a]

	malic acid	citric acid	succinic acid
fresh	206.7 ± 11.1 ab	198.9 ± 6.4 a	14.8 ± 1.7 bc
freeze-drying	175.5 ± 4.5 ab	173.2 ± 27.4 ab	23.4 ± 2.5 a
microwave-drying	187.9 ± 15.5 ab	140.4 ± 7.6 b	12.2 ± 1.7 c
oven-drying	220.8 ± 71.9 a	198.1 ± 50.3 a	16.3 ± 0.2 b
sun-drying	146.6 ± 6.9 b	152.1 ± 15.1 ab	13.1 ± 1.6 bc

[a]Mean ± SD; $n = 3$. Different letters in the columns indicate statistically significant differences in the contents of individual compounds between the treatments for jujube fruits at $p < 0.05$.

α-Tocopherol and β-Carotene. There was no published study in the literature that compared α-tocopherol and β-carotene in the jujube fruits treated with different drying methods until the present study. The levels of α-tocopherol and β-carotene in fresh and dried jujubes were given in Table 3. A small amount of α-tocopherol was detected in the fresh fruits, as well as oven- and freeze-dried jujube samples. β-Carotene was significantly higher in the freeze-dried samples (156.4 mg/kg of DW) than the other selections. Oven-dried jujube fruits also resulted in a 1.9-fold increase of the β-carotene content compared to the fresh fruits. A similar study in vegetables also showed an increase in the β-carotene content.[17] Microwave-drying treatment reduced 61% of the β-carotene content compared to the fresh jujube fruits. Bernhardt et al.[18] reported that the β-carotene content in red bell pepper was reduced 35−40% by several cooking methods. β-Carotene was only not detected in sun-dried jujubes. β-Carotene is the most important provitamin A, mainly because of its prevalence in plant foods consumed by human, and it is provitamin A that has the greatest activity.[19] However, when taken as a separate supplement, it can have harmful effects.[20] Hence, freeze-dried jujube fruit is an excellent source of β-carotene.

Phenolic Compounds. A number of studies have shown that the presence of phenolics in food and especially in fruit can be particularly important for consumers, because of their antioxidant properties. Besides the antioxidant effects, phenolic compounds possess a wide spectrum of biochemical properties and can also have a beneficial effect in preventing the development of diseases, such as neurodegenerative diseases.[21] In our study, 10 phenolic compounds in fresh and dried jujubes were identified (Figure 2). The predominant phenolic compound was catechin. The highest contents of individual phenolic compounds were recorded at the microwave-drying sample for most phenolics (Table 3). Two phenolic acids from the hydroxycinnamate subclass (chlorogenic and caffeic acids) and three flavonoids (catechin, epicatechin, and rutin) were detected in extracts of dried Chinese jujube fruit by Hudina et al.[22] These results showed that the selection of the right drying method is of high importance because it ensures a high content of substances in dried jujubes that are vital for human health.

The following compounds from the group of benzoic acid were determined: vanilic acid, gallic acid, protocatechuic acid, and *p*-hydroxybenzoic acid (Table 3). *p*-Hydroxybenzoic acid was not detected in freeze- and microwave-dried jujubes, and its content was low in jujubes. A statistically higher amount of protocatechuic acid (21.3 mg/kg of DW) was measured in jujubes dried in the microwave oven. The protocatechuic acid content decreased with freeze-, oven-, and sun-drying treatments, but with microwave treatments, it increased by up to 37%. The amount of vanillic acid significantly decreased ($p < 0.05$) in freeze- and oven-drying treatments compared to the fresh jujube fruits. Interestingly, there was no gallic acid present in fresh fruits and microwave- and sun-drying samples.

Both catechin and epicatechin from the group of flavan-3-ols were determined in fresh and dried jujubes (Table 3). The microwave-drying treatment significantly increased ($p < 0.05$) the contents of epicatechin and catechin, which is consistent with the literature consulted.[6] Catechin was the predominant analyzed phenolic compound in our study, ranging from 2.5 mg/kg of DW in oven-dried jujubes to 45.1 mg/kg of DW in

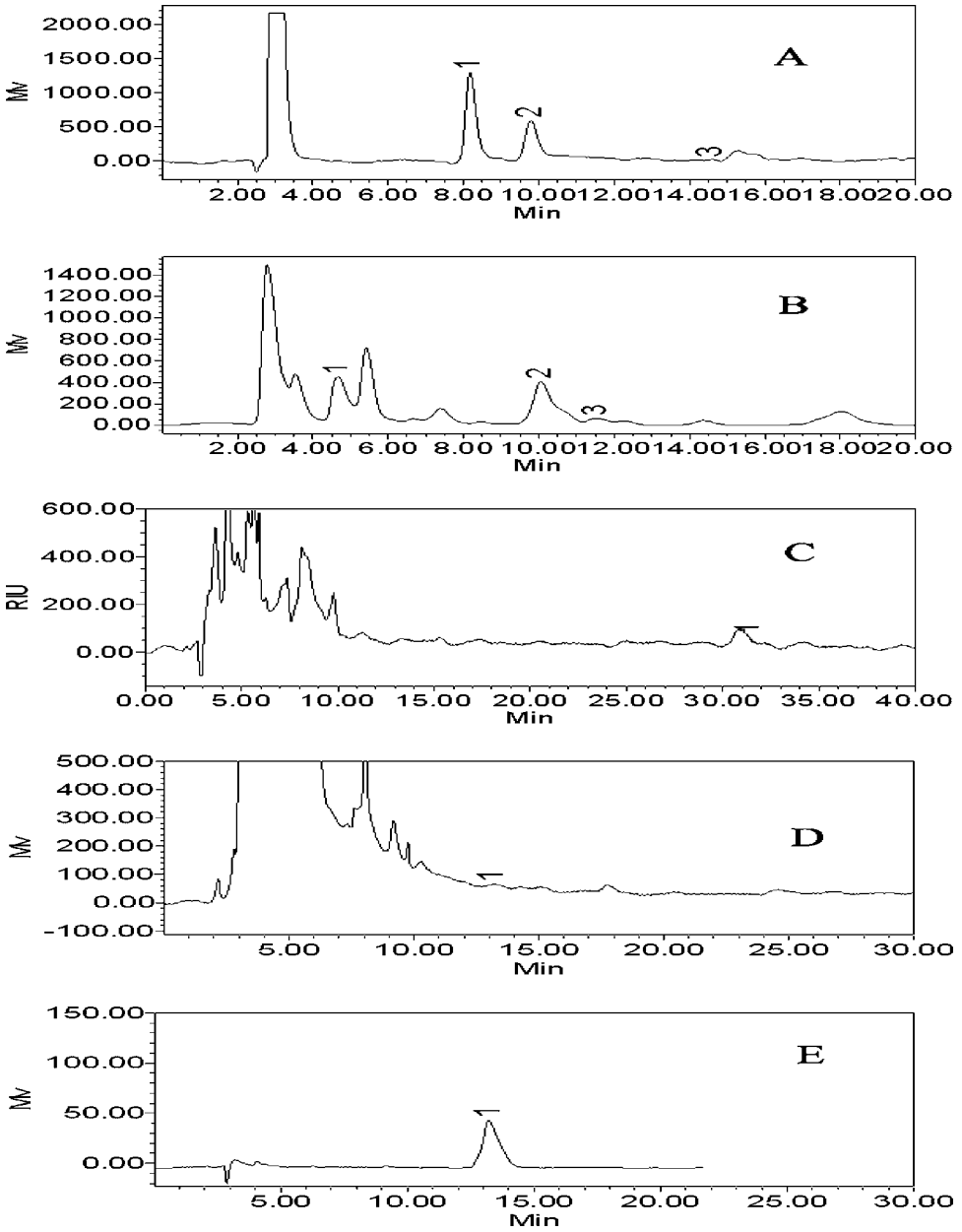

Figure 1. HPLC profiles of (A) sugars, (B) organic acids, (C) β-carotene, and (D) α-tocopherol in the fresh jujube fruits and (E) α-tocopherol standard. The peaks in profiles A represent (1) fructose, (2) glucose, and (3) sucrose. The peaks in profiles B represent (1) malic acid, (2) citric acid, and (3) succinic acid.

microwave-dried jujubes. Catechin seems to be more stable with the microwave treatment, and its content in microwave-dried jujubes was 2-fold that in the fresh fruits. Freeze- and oven-dried samples have reduced the content of catechin up to 65 and 88%, respectively. Catechin was not detected in sun-dried jujube samples. In all samples, the content of epicatechin was lower than that of catechin. A statistically higer content of epicatechin was measured in jujubes dried in the microwave oven. There was a similar trend in the content of epicatechin affected by different drying methods.

Among the group of flavonols, only rutin was determined. All of the dried samples showed a significant decrease ($p < 0.05$) in the rutin content. Our results indicate that the drying process has a negative influence on the content of rutin.

In the group of derivatives, cinnamic acid, *p*-coumaric acid, and ferulic acid were determined. Both freeze- and oven-drying methods decreased cinnamic acid by up to 69% when compared to the fresh fruits, but it was stable with microwave- and sun-drying methods. *p*-Coumaric acid reduced with oven-drying method. Sun-drying seems to increase the *p*-coumaric acid from 1.8 to 4.3 mg/kg of DW. *p*-Coumaric acid was absent in freeze- and microwave-drying treatments. The ferulic acid content only increased with the sun-drying treatment by up to 48% compared to the fresh jujube fruits.

According to Yao et al.,[23] thermal treatment seems to have an influence on the phenolics. Phenolic compounds are mainly present in the bound form, linked to the cell-wall structural components. Thermal processing, pasteurization, and freeze-drying contribute to the release of these bound phenolic compounds.[24]

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Table 3. Content of Phenolic Compounds, α-Tocopherol, and β-Carotene (mg/kg of DW) in Fresh Fruit and Dried Fruit of Four Drying Methods[a]

	fresh	freeze-drying	microwave-drying	oven-drying	sun-drying
gallic acid	nd[b]	12.7 ± 1.6 a	nd	3.2 ± 0.4 b	nd
protocatechuic acid	15.5 ± 1.0 b	0.9 ± 0.2 c	21.3 ± 1.2 a	0.3 ± 0.2 c	1.7 ± 0.2 c
catechin	20.8 ± 1.2 b	7.2 ± 0.3 c	45.1 ± 5.6 a	2.5 ± 1.2 c	nd
p-hydroxybenzoic acid	0.8 ± 0.5 b	nd	nd	0.1 ± 0.0 c	2.9 ± 0.1 a
vanillic acid	2.4 ± 1.4 b	0.3 ± 0.1 c	1.3 ± 0.2 bc	0.2 ± 0.0 c	6.0 ± 0.4 a
ferulic acid	2.7 ± 0.3 b	0.1 ± 0.0 d	1.0 ± 0.1 c	0.3 ± 0.0 d	4.0 ± 0.7 a
rutin	27.0 ± 1.8 a	2.8 ± 0.9 d	24.1 ± 1.5 b	2.1 ± 1.1 d	12.6 ± 1.4 c
cinnamic acid	1.3 ± 0.8 a	0.4 ± 0.1 b	1.4 ± 0.0 a	0.4 ± 0.1 b	1.1 ± 0.0 a
epicatechin	14.0 ± 1.1 b	3.7 ± 0.3 c	36.1 ± 0.8 a	0.5 ± 0.1 d	nd
p-coumaric acid	1.8 ± 0.2 b	nd	nd	0.1 ± 0.0 c	4.3 ± 0.3 a
α-tocopherol	1.7 ± 0.1 b	3.1 ± 0.3 a	nd	3.2 ± 0.2 a	nd
β-carotene	45.6 ± 0.9 c	156.4 ± 3.6 a	17.9 ± 0.9 d	86.4 ± 0.8 b	nd

[a]Mean ± SD; $n = 3$. Different letters in the columns indicate statistically signifcant differences in the contents of individual compounds between the treatments for jujube fruits at $p < 0.05$. [b]nd = not detected.

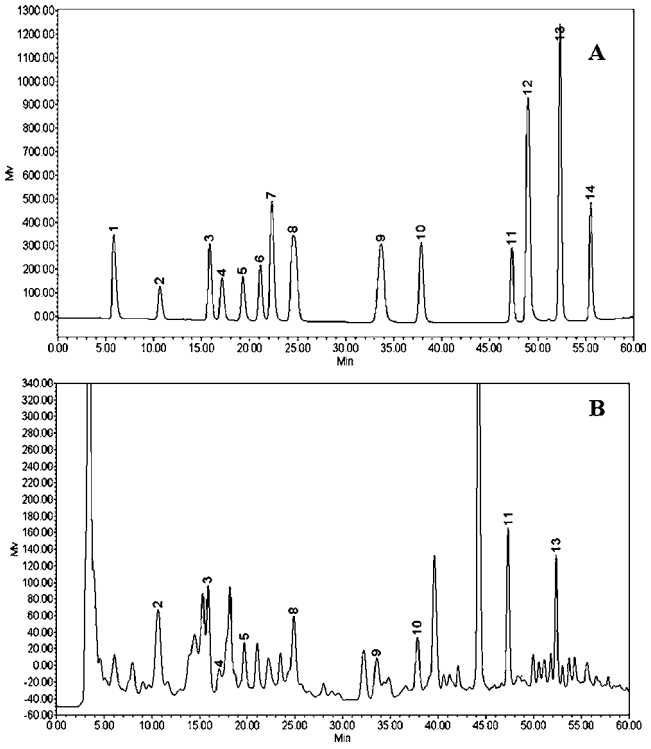

Figure 2. HPLC profiles of (A) phenolic standards and (B) phenolic compounds in the fresh jujube fruits. The peaks in profiles A and B represent (1) gallic acid, (2) protocatechuic acid, (3) catechin, (4) *p*-hydroxybenzoic acid, (5) vanillic acid, (6) caffeic acid, (7) syringic acid, (8) epicatechin, (9) *p*-coumaric acid, (10) ferulic acid, (11) rutin, (12) ellagic acid, (13) cinnamic acid, and (14) quercetin.

According to Morales-de la Peña et al.,[25] high-intensity pulsed electric fields or thermal treatment has great influence on the phenolic acid composition.

TPC and Antioxidant Activity. Table 4 presents the results of the TPC and ABTS radical scavenging activity of fresh and dried jujube fruits using different drying methods. The variation in the TPC and antioxidant activity was observed among various batches of jujubes. In this study, freeze-dried jujube fruits did not reveal any decline in the TPC value and, instead, resulted in significantly higher TPC. Sun-drying caused the highest TPC loss of 77% compared to fresh samples, which consequently resulted in a significant decrease in the antioxidant activity exhibited by the reduction in ABTS free radical scavenging activity (2.5 mmol of Trolox equiv/100 g of DW). The loss of the TPC after sun-drying may be caused by the enzymatic processes that occurred during the process. Sun-drying did not immediately deactivate degradative enzymes, such as polyphenol oxidases; therefore, they are able to degrade phenolic compounds before the jujube fruits are completely dry. Sun-drying is also affected by climatic factors, which leads to an uneven loss of the TPC. Oven-drying also resulted in a lower content of the TPC of 1526.7 mg of GAE/100 g of DW, as compared to 2195.9 mg of GAE/100 g of DW in the fresh samples. The drop in the TPC leads to a corresponding decrease in ABTS of 3.2 mmol of Trolox equiv/100 g of DW for oven-dried jujubes. Oven heating at 70 °C was shown to rapidly inactivate polyphenol oxidases present in jujube fruits; however, some of their initial activities may have occurred earlier and caused some phenolics to be degraded. The microwave-drying method only caused a slight but not significant drop of the TPC in jujubes by 5%. Similarly, there

Table 4. TPC (mg of GAE/100 g of DW) and Antioxidant Activity (mmol of Trolox equiv/100 g of DW) of Fresh Fruit and Dried Fruit of Four Drying Methods[a]

	TPC[b] (mg of GAE/100 g of DW)	ABTS (mmol of Trolox equiv/100 g of DW)
fresh	2195.9 ± 127.9 b	7.2 ± 2.2 a
freeze-drying	2986.9 ± 38.4 a	5.9 ± 0.9 a
microwave-drying	2094.7 ± 18.1 b	6.0 ± 0.9 a
oven-drying	1526.7 ± 77.0 c	3.2 ± 0.3 b
sun-drying	513.1 ± 14.7 d	2.5 ± 0.2 b

[a]Mean ± SD; $n = 3$. Different letters in the columns indicate statistically significant differences in the contents of individual compounds between the treatments for each sample at $p < 0.05$. [b]TPC = total phenolic content.

was no significant difference in the antioxidant activities using the microwave-drying method. Microwave heating could inactivate degradative enzymes much faster than oven heating, yet the loss of the TPC was observed. Data obtained from this study indicate that drying of jujube fruits tend to change the TPC to a varying extent, depending upon which method is employed. A reduction in TPC values because of various drying treatments was accompanied by the respective decrease in ABTS free radical scavenging activity. The TPC seems to be a good indicator of the antioxidant potential in fruit.

Processing methods are known to have variable effects on the TPC and antioxidant activity of fruit samples. Effects include little or no changes, significant losses, or enhancement in antioxidant properties.[26] Food processing can improve the properties of naturally occurring antioxidants or induce the formation of new compounds with antioxidant properties, so that the overall antioxidant activity increases or remains unchanged.[27]

Many studies have reported losses in the TPC and antioxidant activity of plant samples following drying treatments. Losses were mainly reported in vegetables.[28,29] Losses in antioxidant properties of heat-treated samples have been attributed to thermal degradation of phenolic compounds.[30] Declines in the antioxidant activity have been attributed to degradative enzymes, thermal degradation of phytochemicals, and the loss of antioxidant enzyme activities.[31]

There is no thermal degradation in freeze-drying, and the process does not allow for degradative enzymes to function. Furthermore, freeze-drying is known to have high extraction efficiency because the ice crystals formed within the plant matrix can rupture the cell structure, which allows for the exit of cellular components and their access to solvent and, consequently, better extraction.[26] Freeze-dried marionberry, strawberry, and corn yielded higher TPC than air-dried samples.[8]

In summary, to our knowledge, this is the first study comparing the contents of selected primary and secondary metabolites in jujubes subjected to different drying methods to those of fresh jujube fruits. Results showed that freeze-drying is superior to other drying methods in preserving the TPC of jujube fruits. Thermal drying (microwave-, oven-, and sun-drying) resulted in significant declines in the TPC and antioxidant activity. Non-thermal drying, freeze-dried jujube fruits had significant gains in the TPC but had a minimal effect on the antioxidant activity. HPLC analysis showed the presence of greater amounts of minor compounds in microwave-dried samples than fresh jujube fruits. Because of its high operation cost, freeze-drying can be applied to produce high-value jujube products. Microwave-dried samples had the highest content of individual phenolic compounds, with particularly high amounts of epicatechin, catechin, rutin, protocatechuic acid, and cinnamic acid. Taking all of these considerations into account, the industrial processing of dried jujubes may be improved using microwave energy, because the drying time is considerably reduced and the obtained fruit had a higher phenolic content while maintaining the antioxidant capacity. The combination of microwave- and freeze-drying may be an efficient alternative with even shorter processing times and, at the same time, less impact on the nutritional value of the jujube.

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