

TOTAL ANTIOXIDANT CAPACITY, PHENOLIC COMPOUNDS AND SUGAR CONTENT OF TURKEY *Ziziphus jujubes*

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Abstract. The phenolic compounds, sugar, mineral contents and antioxidant capacity of the *Ziziphus jujube* (Hunnap) fruits collected from five different locations in Turkey were determined. Total phenolic contents ranged from 652.4 to 1348.4 mg GAE 100 g⁻¹ g fruit dry weight. Fourteen phenolic compounds; gallic acid, catechin, epicatechin, chlorogenic acid, caffeic acid, coumaric acid, para-coumaric acid, hesperidin, naringin, rutin, ellagic acid, quercetin, naringenin and vanillin were identified and quantified. Among the jujubes, considerable differences in phenolic materials were found. Catechin levels ranged from 5.95 to 100.96 mg 100 g⁻¹, and ellagic acid levels ranged from 5.87 to 26.32 mg 100 g⁻¹ for jujube fruits in dry weight basis. Potassium, phosphorus, calcium and magnesium were the major mineral constituents in jujube fruits. The antioxidative capacity of the jujube extracts, evaluated with the % inhibition, the 2,2-diphenyl-1-picrylhydrazyl (DPPH•), and the 2,2-azinobis (3-ethylbenzothiazoline-6-sulfonicacid) (ABTS•+) scavenging methods. A positive correlation was found between total phenolic contents and antioxidant activity of jujubes.

Key words: jujube, bioactive compounds, phenolics, polisaccharide, mineral

INTRODUCTION

A member of the Rhamnaceae family, *Zizyphus jujuba*, commonly called jujube, is fruit of a tree which has 40 species and grows mainly in the warm and subtropical areas of Southeast Asia, China and the Mediterranean [Singh and Arya 2011], including Marmara, western and southern Anatolia in Turkey.

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This edible fruit is consumed fresh, dried or processed (jams, loaf, cakes, etc.) as food, and as food additive and for flavoring [Pareek 2002]. Jujube hosts a rich source of medicinal compounds. Medicinal properties such as antifertility, antimicrobial and antioxidant [Gao et al. 2011], anti-inflammatory [Choi et al. 2012], immune stimulating [Yu et al. 2012], analgesic, and antidiabetes [Erenmemisoglu et al. 1995, Borgi et al. 2008], hypoglycemic [Glombitza et al. 1994], sedative and hypnotic [Han et al. 1990] makes it considerable to be used in the production of multifunctional bioactive compounds [Kou et al. 2015]. In addition to the use of jujube in traditional medicine for the treatment of insomnia and anxiety [Choi et al. 2012, Yeung et al. 2012], extracts of *Z. jujuba* showed, in modern medicine, protection against hydroquinone induced cytogenesis, digestive disorders, diarrhea, skin infections, liver complaints, tumors and cardiovascular diseases [Pawlowska et al. 2009, Zhang et al. 2010]. There are additional studies which proved pharmaceutical benefits of jujube such as anxiolytic effect [Peng et al. 2000], anti-steroidogenic activity [Gupta et al. 2004], anti-cancer activity [Huang et al. 2007, Plastina et al. 2012], anti-cytotoxic activity [Huang et al. 2008], anti-allergic and anti-anaphylactic activity [Naik et al. 2013], antiglycation activity [Siriamornpum et al. 2015].

Jujube is a fruit with high amounts of sugar, phosphorus and calcium [Pareek 2002]. In addition, Hudina et al. [2008] separated some phenolics from jujube fruit including chlorogenic acid, caffeic acid, catechin, epicatechin and rutin.

Resistance to various stress factors and high quality of a fruit depend on its content of phenolics which have a major physiological role in fruit. In addition, phenolic compounds have significant levels of antioxidant activity and are free radical scavengers [Sheng et al. 2009]. Due to their low toxicity and little side effects, polysaccharides recently attract increasing attention for their benefits to health and therapeutical uses [Simas-Tosin et al. 2012, Krifa et al. 2013]. According to some studies, for example, polysaccharides act as antioxidants [Cui et al. 2013, Elaloui et al. 2015], and they function as immunomodulatory reagents [Zhang et al. 2010]. Moreover, the study of Cui et al. [2013] shows the contribution of polysaccharides to the medicinal and nutritional values of fruits.

Mineral content has significance in terms of human and plant nutrition. Li et al. [2007] made a comparative study on five cultivars of jujubes in China regarding their differences in nutritional compositions (minerals, vitamins). Pareek [2013] also reported the nutritional composition of jujube fruit.

The study showed that the major mineral constituents in jujube fruit are potassium, phosphorus, calcium and magnesium, and that other minerals found in considerable amounts are iron, sodium, zinc, manganese and copper. This mineral content of jujube contributes to enhancing the cardiovascular health and the metabolism.

The antioxidant activity of jujube is considered to be due to its high level content of phenolic compounds, including chlorogenic acid, gallic acid, protocatechuic acid and caffeic acid [Zhang et al. 2010]. San and Yıldırım [2010] are also among the scientists who report jujube as a good source of phenolic compounds. However, there is no study on nutritional properties and nutritional composition of fresh jujube samples taken from different locations in Turkey.

To analyze and determine soluble sugar, mineral and total phenolic content and the phenolic composition of jujube fruits from five different cities in Turkey; to make a comparison among fruit extracts regarding their antioxidant properties; to determine whether there was any correlation between the bioactive components (phenolic compounds) and antioxidant activity of the fruit; and to make an assessment of jujube fruit in terms of its nutritional values were the objectives of this study. Depending on the results of statistical analysis was conveyed chemical composition, mineral content, and polysaccharide composition of jujube fruit samples taken from different cities; and to determine if there are any regional differences in the fruit composition.

MATERIALS AND METHODS

Jujube samples. Jujube fruits were hand picked at the full red phase of maturity in October, 2015 from five different cities in west and south of Turkey. These cities included with latitude and longitude, respectively, Afyon (35°50'E, 38°46'N), Kayseri (35°30'E, 38°, 43'N), Manisa (27°25'E, 38°36'N), Mersin (34°38'E, 36°48'N) and Sakarya (30°58'E, 40°46'N). Then, immediately transported to the laboratory. Selected jujube fruits judged according to uniform shape were free from visible blemishes or disease. The plants were grown with the different ecological conditions.

Fruits were washed with tap water and then rinsed with distilled water. 500 g of sun dried fruit was crushed and mixed in a homogenizer. Crushed fruit samples were placed in plastic bags and stored at 0°C until they were used for analysis.

Physico-chemical analyses. pH determination. 10 gram samples were diluted with 50 ml distilled water. The pH values were determined by using digital pH meter (Eutech Cyberscan 2700 model) [Anupama 2002].

Water activity. Water activity (a_w) was measured with Novasina Labmaster water activity meter, Switzerland, following [AOAC 1990] method.

Measurement of total phenolics content and antioxidant activity. Preparation extracts. Mixture of methanol-water (50:50 by volume) was added into 5 g sample. Ultrasonic water bath for 10 min, the samples treated with the help of a mechanical stir for 15 min. After refrigerated centrifugation at 4°C, at 8500 rpm min⁻¹ for 20 min, the supernatant was collected and stored at -24°C in amber glass bottles until analyzed. These samples were used for antioxidant activity and phenolic determination. All experiments were carried out in triplicate.

Measurement of total phenolics content. The total amount of phenolic compounds in the extract was determined using the Folin-Ciocalteu reagent by the method Singleton et al. [1999] with modification. Gallic acid was used as a standard phenolic compound. 1000 µL extracts were put in 100 ml flasks. The total volume was completed to 46 ml with pure water. 1 ml of Folin-Ciocalteu reagent was added and after 3 minutes 3 ml of 3% Na₂CO₃ solution was added. Thus, the total volume was made up to 50 ml. Mixture was shaken at room temperature for 2 hours and then the absorbance of samples was read at 720 nm against distilled water. The control was distilled water. Gallic acid content corresponding with the absorbance value of the samples were determined using standard graph equation and the results were expressed as gallic acid equivalents.

Results were expressed as milligrams of gallic acid equivalents per 100 g dried weight (mg GAE 100 g⁻¹ DW). The absorbance of the resulting solution was measured at 517 nm with a spectrophotometer.

Total antioxidant activity determination. Antioxidant capacity of the samples were determined using the method of Soares et al. [1997]. DPPH color is changed when antioxidant is present. Absorbance spectrometer length can be monitored at 517 nm. 1 ml extract was mixed with 1.0 ml of DPPH (Sigma Company, St. Louis, USA). The absorbance of the mixture was kept at room temperature in the dark for 30 min, then, it was measured at 517 nm in UV- 1800 (Shimadzu, Kyoto, Japan) spectrometer. Deionized water is used as a control. Results are given as % inhibition.

DPPH radical scavenging activity. The effect of methanolic extracts on DPPH radical was estimated according to the method reported previously [Hatano et al. 1988]. One milliliter of various extracts in methanol was added to 1ml of the DPPH radical solution in methanol (final concentration of DPPH was 131.87 mol L⁻¹). Then the mixture was shaken vigorously and allowed to stand for 30 min; the absorbance of the resulting solution was measured at 517 nm with a spectrophotometer and % inhibition was calculated with DPPH formula:

$$\% \text{ Inhibition} = [(A_{\text{DPPH}} - A_{\text{extract}}) / A_{\text{DPPH}}] \times 100$$

ABTS• + scavenging capacity. 2.45 mM K₂S₂O₈ and 7 mM ABTS (2,2'-azino-bis(3-ethylbenzothiazol-6-sulfonic acid)) was 1:1 by stirring at room temperature and left for 16 hours incubate in the dark. The absorbance of ABTS radical solution was measured at 734 nm and then diluted with ethyl alcohol until reached at the absorbance of 1.850 ± 0.05. This absorbance was used as control (blank) absorbance. Then, 4 ml were taken in test tubes from this radical solution. By addition of 100 ml of the sample onto the tube and allowed to incubation in the dark at room temperature for two hours. After two hours, the absorbance of samples was recorded at 734 nm in PBS (Phosphate Buffer, pH = 7.4) [Wu et al. 2009]. Absorbance reduction value gives the amount of ABTS radicals scavenge [Keser et al. 2013]. How many extracts would reduce ABTS radicals in the environment has been calculated using the following formula:

$$\% \text{ ABTS Activity} = [(A_0 - A_1) / A_0] \times 100$$

A₀ is the absorbance of control, A₁ is absorbance of sample.

HPLC analysis of phenolic compounds. Aqueous extract prepared from samples passed through 0.45 µm filters and then were injected directly into the HPLC system [Karaaslan et al. 2014]. Analysis was performed at 25°C, at 1 ml min⁻¹ flow rate. HPLC conditions were as follows:

Column: C18 (250 × 4 mm ID)

Mobile phase A: water: acetic acid (98:2, v:v) Mobile phase B: Methanol

HPLC mobile phase condition was shown in Table 1.

Table 1. HPLC mobile phase condition

Time (min)	0	3	18	25	30	35	40	55	65	70	75
%A	0	5	20	20	25	30	40	50	60	0	0
%B	100	95	80	80	75	70	60	50	40	100	100

Mineral analysis. Potassium, calcium, magnesium, manganese, iron, sodium, zinc and copper were determined using atomic absorption spectrophotometer (Agilent, Spectra-AA240, Varian Co., USA) after digestion in mixed acids (nitric acid: perchloric acid = 4:1). Phosphorus content was determined by the molybdenum-blue method in the wavelength of 660 nm according to the method described by Huang [1989].

Sugar extraction and analysis. Sugar analysis were performed with some modifications according to the method of the international honey committee for the jujube samples [IHC 2009]. 5 g sample was dissolved in 40 ml of distilled water and completed with ultra distilled water up to 100 ml in flask. Then, it passed through 0.45 μ l membrane filter and put in the vials. Mobile phase was acetonitril (Sigma): water (80:20, v/v). Stainless column had 4.6 mm diameter and 250 mm length and contained the amine-modified filler having a particle size of 5–7 μ m (Inertsil HPLC column, GL Sciences, Japan). Mobile phase flow rate was 1.3 ml min⁻¹, column temperature 30°C and injection volume 20 μ l. HPLC (Schimadzu LC 20A, Japan) instrument that had autosampler and Refractive Index Detector (RID) were used for sugar analysis.

The retention times of the sugar samples were compared for their identifications.

Statistical analysis. The average results of five different varieties of jujubes subject to the dependent variable were compared by the use of variance analysis (one-way MANOVA). Duncan multiple comparison test was used to determine whether observed differences occurred between the groups. The relationship between the dependent variable of the samples was shown by the Correlation Test [Norusis 1993]. Statistical analysis was utilized the SPSS 20.0 software package. The results shown are presented as means of three determination \pm SD (standard deviation). p values of < 0.05 were considered to be statistically significant.

RESULTS AND DISCUSSION

The results for pH, water activity, antioxidant capacity and total phenolic compounds of five jujubes were given in Table 2.

pH. The results for the pH of the jujubes in this research demonstrated that five jujubes are different in pH of fruit. Significant differences ($p < 0.05$) were revealed among the jujubes for pH. Manisa jujube had the highest value of pH, 4.82. The pH values obtained in the current study are lower than those (pH = 6.1) reported for jujube cultivars grown in China [Gao et al. 2011].

Water activity. The water activity (a_w) of five jujubes ranged from 0.81 (Mersin jujube) to 0.60 (Sakarya). a_w of different jujubes exhibited significant differences ($p < 0.05$) except for Sakarya. The water activity values observed were lower than those of jujube reported by [Pareek 2013].

Total phenolic contents. The results indicated that the differences in total phenolic content among Turkish jujube fruits were statistically significant ($p < 0.05$) (tab. 2). Total phenolic contents ranged from 652.4 to 1348.4 mg GAE 100 g⁻¹ dried weight (tab. 2).

A wide variation had been reported for total phenolic content in Chinese jujube fruits ranging from 25 to 42 mg GAE/g dry weight basis [Kamiloglu et al. 2009]. These differences in phenolic composition may be characterized by the influence of many external factors such as soil composition, growing regions, climates, the varieties and light intensities [Poyrazoglu et al. 2002]. Phenolic compounds also play a role in plant defensive mechanisms by counteracting reactive oxygen species (ROS), thus minimizing molecular damage due to microorganisms, insects, and herbivores [Vaya and Aviram 1997].

Phenolic compounds present in the jujube fruits sampled in Turkey are given in Table 3. Fourteen phenolic compounds; gallic acid, catechin, epicatechin, chlorogenic acid, caffeic acid, coumaric acid, para-coumaric acid, hesperidin, naringin, rutin, ellagic acid, quercetin, naringenin and vanillin were identified and quantified. Predominant phenolics were catechin, p-coumaric acid, ellagic acid and epicatechin. Among the jujube selections, considerable differences in phenolic materials were found. Catechin levels ranged from 5.95 to 100.96 mg 100 g⁻¹, and ellagic acid levels ranged from 5.87 to 26.32 mg 100 g⁻¹ for jujube fruits. Gallic acid, catechin, epicatechin, para-coumaric acid, rutin, ellagic acid were present in all the fruit samples. Quercetin was present in Sakarya and Afyon jujubes, while naringin was only in Afyon. Chlorogenic acid was detected in all samples except in Sakarya jujube. Vanillin, naringin and caffeic acid were not identified in any fruit jujubes. Hesperidin was detected in four jujubes except in Kayseri jujube. Manisa jujube had significantly higher catechin and chlorogenic acid content than the other jujubes (tab. 3). Significant differences were observed for the contents of gallic acid, catechin, epicatechin, hesperidin, rutin, chlorogenic acid, coumaric acid and ellagic acid among jujubes. Hudina et al. [2008] detected chlorogenic acid, caffeic acid, catechin, epicatechin, and rutin in jujube fruits. San and Yildirim [2010] showed that the jujube fruits contain p-hydroxybenzoic acid and ferulic acid.

Epicatechin content was high in Mersin jujube (53.32 mg 100 g⁻¹) followed by Kayseri (47.54 mg 100 g⁻¹) and Afyon jujubes (41.19 mg 100 g⁻¹).

Significant differences were observed for the content of ellagic acid among jujubes (tab. 3). Ellagic acid is the bioactive agent that offers protection. Ellagic acid is a phenolic compound that has become known as a potent anti-carcinogenic/anti-mutagenic compound. It possesses antioxidant, antihepatotoxic, antisteatotic, anticholestatic, anti-fibrogenic, antihepatocarcinogenic and antiviral properties that improves the hepatic architectural and functions against toxic and pathological conditions [Cuartero et al. 2011, García-Nino and Zazueta 2015].

Antioxidant activity. The antioxidative capacity of the jujube extracts evaluated with the % inhibition the 2,2-diphenyl-1-picrylhydrazyl (DPPH•) and the 2,2-azinobis (3-ethylbenzothiazoline-6-sulfonicacid) (ABTS•+) scavenging methods, showed that the antioxidant activity of the extracts of Mersin jujube was excellent for free radical scavenging and a potent natural antioxidant of commercial value.

The capacity of scavenging free radicals was assessed by most easily from the reaction of the test material with a stable free radical such as DPPH and ABTS. The antioxidant capacity results for different extracts of jujube fruit determined by DPPH and ABTS are reported in Table 2.

The ABTS values varied from 51.21 (Sakarya) to 98.37 (Manisa) as a % inhibition value. Choi et al. [2012] and Wu et al. [2012] demonstrated that the antioxidant capacity decreased with the maturity of fruits [Choi et al. 2012, Wu et al. 2012]. The ABTS scavenging capacities found in the Kou et al. [2015] study were 2–3 times higher than the levels of other common fruits, such as apples, bananas, blackberries, cherries, grapes, kiwi, fruits, lemons, mangoes, peaches, pears, plums and watermelons.

There is correlation between total phenolic contents and antioxidant capacities of jujubes was found in this study. Krishna and Parashar [2013] paper is in agreement with our data.

Table 2. pH, water activity, antioxidant capacity and total phenolic compounds (TPC) of five jujubes (% of dry weight basis)

Results \ Sample	Afyon	Kayseri	Manisa	Mersin	Sakarya
pH	4.45 ±0.06 ^e	4.77 ±0.06 ^b	4.82 ±0.05 ^a	4.67 ±0.04 ^c	4.64 ±0.05 ^d
a _w	0.708 ±0.04 ^c	0.737 ±0.04 ^b	0.61 ±0.03 ^d	0.81 ±0.05 ^a	0.607 ±0.08 ^d
DPPH (% inhibition)	92.14 ±0.25 ^d	97.01 ±0.5 ^b	94.33 ±0.5 ^c	98.46 ±0.3 ^a	92.06 ±0.3 ^d
ABTS (% inhibition)	94.93 ±0.5 ^b	97.94 ±0.6 ^a	98.37 ±0.6 ^a	97.74 ±0.7 ^a	51.21 ±0.2 ^c
TPC	652.4 ±15.5 ^e	1196.4 ±18 ^b	924.4 ±14 ^c	1348.4 ±19 ^a	776.4 ±15 ^d

Different letters within same row are significantly different ($p < 0.05$)

Table 3. Polyphenolic compounds of five jujubes (% of dry weight basis)

Results \ Sample	Afyon	Kayseri	Manisa	Mersin	Sakarya
Gallic Acid	0.63 ±0.01 ^e	0.85 ±0.02 ^c	1.16 ±0.01 ^b	0.78 ±0.01 ^d	4.94 ±0.03 ^a
Catechin	10.94 ±1.2 ^d	68.10 ±0.6 ^b	100.46 ±0.6 ^a	34.55 ±1.1 ^c	5.95 ±0.04 ^e
Epicatechin	20.59 ±0.9 ^c	23.77 ±0.5 ^b	13.91 ±0.4 ^d	26.66 ±0.6 ^a	3.88 ±0.01 ^e
Chlorogenic acid	1.93 ±0.01 ^c	1.72 ±0.01 ^d	2.62 ±0.02 ^a	2.015 ±0.04 ^b	ND
Cumaric acid	ND	0.17 ±0.02 ^b	0.15 ±0.04 ^c	0.25 ±0.02 ^a	0.15 ±0.01 ^d
p-cumaric acid	38.81 ±0.9 ^b	38.67 ±0.5 ^d	38.67 ±0.8 ^d	37.77 ±0.7 ^c	38.91 ±0.8 ^a
Hesperidin	3.56 ±0.8 ^c	ND	4.67 ±0.4 ^b	27.26 ±1.5 ^a	1.46 ±0.05 ^d
Naringin	0.96 ±0.02 ^a	ND	ND	ND	ND
Rutin	0.77 ±0.04 ^d	3.44 ±1.1 ^b	0.84 ±0.05 ^c	4.07 ±0.9 ^a	0.73 ±0.07 ^e
Ellagic acid	20.47 ±0.2 ^c	12.45 ±0.4 ^d	5.86 ±0.3 ^e	26.31 ±0.9 ^a	25.72 ±0.2 ^b
Quercetin	1.47 ±0.01 ^a	ND	ND	ND	1.46 ±0.04 ^b

ND – not detected; Different letters within same row are significantly different ($p < 0.05$)

The measured antioxidant capacity of a sample is dependent on the methodology and the generated free radical or oxidant used in the measurement [Apak et al. 2007]. As a result, no single method can fully evaluate the total antioxidant capacity of foods.

According to the results obtained, Mersin jujuba had the strongest DPPH free radical scavenging activity. This activity was followed by Kayseri. Afyon and Sakarya were two varieties, which exhibited the lowest DPPH free radical scavenging activity (tab. 2). Therefore, phenolic compounds may contribute to the antioxidant capacity because of their ability to scavenge free radicals, superoxide and hydroxyl radicals.

Our results are in agreement with some studies that have demonstrated a correlation between phenolic content and antioxidant capacity [Yang et al. 2002]. However, Li et al. [2007] reported no correlation between total phenolic contents and antioxidant activities in jujube fruits.

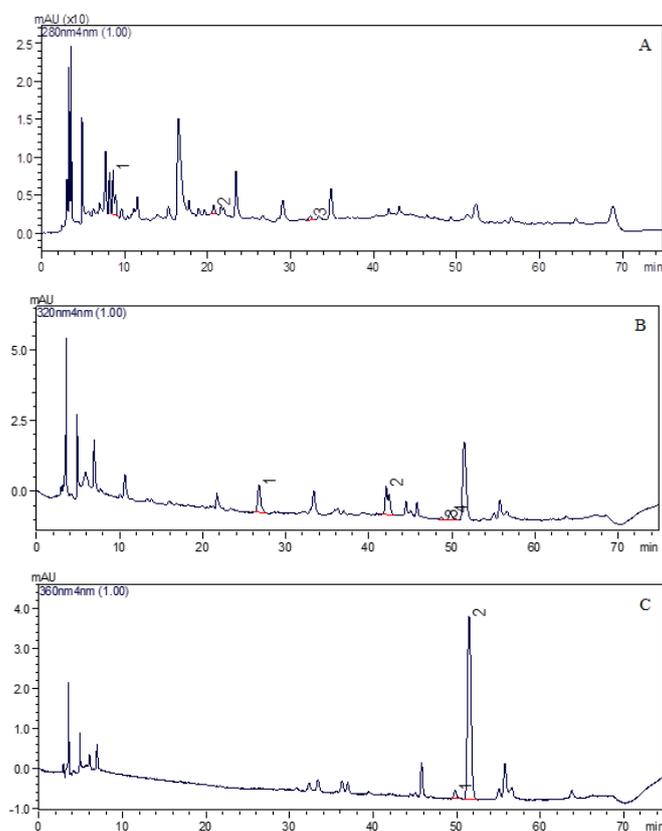


Fig. 1. HPLC chromatogram of some phenolic compounds of jujube fruits: A – detection at 280 nm (1 – gallic acid, 2 – catechin, 3 – epicatechin); B – detection at 320 nm (1 – chlorogenic acid, 2 – p-cumaric acid, 3 – Hesperidin, 4 – Naringin); C – detection at 360 nm (1 – rutin, 2 – ellagic acid)

Mineral analysis. Among the minerals K, P, Ca and Mg contributed major portion, while Fe, Na, Zn, Mn and Cu were also found in good amounts.

Jujube samples are summarized in Table 4. The data indicated that potassium, phosphorus, calcium and magnesium were the major mineral constituents in the five Turkish jujubes tested % of dry weight basis. Iron, sodium, zinc, manganese and copper were also detected in appreciable amounts. Potassium was the predominant mineral in the five jujubes. The potassium contents ranged from 269.24 to 833.36 mg 100 g⁻¹. The richest source of potassium in this study was from Sakarya city. From the statistical analysis, the potassium contents of five jujubes were significantly different ($p < 0.05$). Regarding phosphorus contents the highest value was found in Manisa (120 mg 100 g⁻¹) followed by Afyon (104.33 mg 100 g⁻¹), Mersin (98 mg 100 g⁻¹) Sakarya (96.6 mg 100 g⁻¹) and Kayseri (82 mg 100 g⁻¹).

The calcium contents ranged from 20.90 to 116.62 mg 100 g⁻¹. Calcium was the major mineral found in jujubes. It is known that calcium may play a role in maintaining bone health and dental health as well as lowering blood pressure [Osborne et al. 1996, Zemel 1997].

The richest source of magnesium was Manisa (47.092 mg 100 g⁻¹). The Turkish jujube with the lowest magnesium content was Kayseri (27.12 mg 100 g⁻¹). Magnesium is required by many enzymes, especially the sugar and protein kinase families of enzymes that catalyse ATP-dependent phosphorylation reactions.

Table 4. Mineral contents of five jujubes (mg 100 g⁻¹ dry weight)

Sample	Afyon	Kayseri	Manisa	Mersin	Sakarya
Na	8.22 ± 0.74 ^a	6.94 ± 0.62 ^c	7.88 ± 0.71 ^b	4.52 ± 0.41 ^d	8.32 ± 0.74 ^a
Zn	0.91 ± 0.05 ^a	0.66 ± 0.04 ^c	0.69 ± 0.04 ^c	0.83 ± 0.05 ^b	0.50 ± 0.03 ^d
Cu	0.29 ± 0.03 ^c	0.25 ± 0.02 ^d	0.52 ± 0.04 ^a	0.25 ± 0.02 ^d	0.32 ± 0.03 ^b
Mn	0.31 ± 0.04 ^c	0.38 ± 0.05 ^b	0.37 ± 0.05 ^b	0.48 ± 0.06 ^a	0.24 ± 0.03 ^d
K	269.24 ± 2.4 ^e	429.09 ± 3.8 ^c	707.90 ± 6.3 ^b	361.3 ± 3.2 ^d	833.36 ± 7.4 ^a
Ca	111.04 ± 7.7 ^b	66.74 ± 4.5 ^d	20.90 ± 1.4 ^e	116.6 ± 8.0 ^a	72.82 ± 5.0 ^c
Mg	31.23 ± 2.1 ^d	27.12 ± 1.9 ^e	47.09 ± 3.3 ^a	41.48 ± 2.8 ^b	37.53 ± 2.6 ^c
Fe	1.56 ± 0.12 ^b	1.27 ± 0.1 ^d	2.23 ± 0.17 ^a	1.62 ± 0.13 ^b	1.51 ± 0.12 ^c
P	104.33 ± 13.5 ^{ab}	82.00 ± 10.6 ^c	120.0 ± 15.6 ^a	98.00 ± 12.7 ^{bc}	96.66 ± 12.5 ^{bc}

Different letters within same row are significantly different ($p < 0.05$)

The iron contents ranged from 1.27 to 2.23 mg 100 g⁻¹. Manisa was the highest in iron. These iron contents presented here were lower than those reported in jujube in Li et al. [2007].

The sodium contents ranged from 8.32 to 4.52 mg 100 g⁻¹. Sakarya and Afyon were higher in sodium. The lowest 4.52 mg 100 g⁻¹ (Mersin). The sodium contents of

different jujubes exhibited significant differences ($p < 0.05$) except for Sakarya and Afyon.

Afyon jujubas contained relatively high amounts of zinc ($0.918 \text{ mg } 100 \text{ g}^{-1}$).

In total, the mineral contents could be affected by climate, soil nutrient content, altitude and time of harvest. It is noteworthy that minerals are important not only to help to support cardiovascular health but to enhance metabolism. Nutritional changes with advancement of growth, maturation should be studied in jujube fruits for future research.

Sugar composition. Sugar present in jujubes % of dry weight basis are shown in Table 5.

Jujube polysaccharides have been demonstrated to have anticancer, immunological effects [Wang et al. 2012]. Fructose and glucose were identified as major soluble sugars found in all five *Ziziphus jujuba* samples, while sucrose contributed lesser amounts. Our result was in agreement with the findings of Li et al. [2007] except the rhamnose amount. Rhamnose was not detected. The levels of fructose varied from $29.49 \text{ g } 100 \text{ g}^{-1}$ (Sakarya) to $19.49 \text{ g } 100 \text{ g}^{-1}$ (Manisa). Levels of glucose ranged from $28.78 \text{ g } 100 \text{ g}^{-1}$ (Sakarya) to $18.99 \text{ g } 100 \text{ g}^{-1}$ (Manisa). Pareek [2013] found that *Z. Jujuba* pulps had 18.6% of fructose and 19.2% of glucose.

Sucrose contents ranged from $2.66 \text{ g } 100 \text{ g}^{-1}$ (Mersin) to $1.78 \text{ g } 100 \text{ g}^{-1}$ (Manisa). The results can be beneficial in the selection of jujubes for special food, for instance, the relatively high content of fructose makes Sakarya jujuba useful for diabetics.

The amount of fructose and glucose was not significantly different in all samples except Afyon jujube. Gao et al. [2012] reported similar data regarding fructose and glucose content.

The dried *Z. jujuba* sugar content was $40.26\text{--}60.44 \text{ g } 100 \text{ g}^{-1}$. The sugar values were higher than the values ($9.8\text{--}14.7 \text{ g } 100 \text{ g}^{-1}$) of Chinese jujube cultivars Gao et al. [2011] found.

Table 5. Sugar content of five jujubes ($\text{g } 100 \text{ g}^{-1}$ dry weight)

Sample	Fructose	Glucose	Sucrose
Afyon	24.68 ± 1.4^c	25.21 ± 1.3^b	1.96 ± 0.04^c
Kayseri	26.96 ± 0.8^b	24.99 ± 1.2^b	1.97 ± 0.08^c
Manisa	19.49 ± 0.1^d	19.00 ± 0.6^d	1.78 ± 0.04^d
Mersin	24.69 ± 1.1^c	23.11 ± 1.5^c	2.66 ± 0.4^a
Sakarya	29.49 ± 1.8^a	28.78 ± 2.3^a	2.17 ± 0.5^b

Different letters within same column are significantly different ($p < 0.05$)

Table 6. Correlation coefficients of antioxidant capacity, phenolic compounds and sugar content of five jujubes

	DPPH	ABTS	GA	CN	EN	CA	Co A	Rutin	EA	Q	TP	F	G	S
DPPH	1	.567*	-.519*	.399	.744**	.422	.772**	.951**	-.038	-.854**	.978**	-.134	-.364	.533*
ABTS		1	-.987**	.577*	.848**	.947**	.025	.448	-.503	-.659**	.433	-.681**	-.741**	-.100
GA			1	-.443	-.886**	-.907**	.073	-.439	.401	.549*	-.375	.606*	.644**	.063
CN				1	.191	.677**	.330	.148	-.900**	-.811**	.370	-.711**	-.826**	-.456
EN					1	.659**	.172	.764**	-.040	-.552*	.634*	-.244	-.351	.328
CA						1	.001	.229	-.609*	-.638*	.296	-.879**	-.900**	-.209
Co A							1	.695**	.092	-.708**	.856**	.023	-.208	.594*
Rutin								1	.179	-.678**	.943**	.134	-.092	.639*
EA									1	.508	.015	.666**	.693**	.791**
Q										1	-.835**	.496	.708**	-.113
TP											1	-.044	-.290	.576*
F												1	.963**	.341
G													1	.236
S														1

* (p < 0.05)

** (p < 0.01)

GA – Gallic acid; CN – catechin; EN – epicatechin; CA – chlorojenic acid; CoA – coumaric acid; EA – ellagic acid; Q – quercetin; TP – total phenolics; F – fructose; G – glucose; S – sucrose

Correlation analysis. Table 6 shows the correlation involving functional attributes of jujubes. Rutin and coumaric acid were positively correlated with total phenolics (TP) ($r = 0.943$ and 0.856 , respectively; $p < 0.05$). Zhang et al. [2010] suggested that there is a positive correlation between antioxidant activities and TP. A striking correlation between TP and antioxidant capacity of the extracts was also noted in our results (DPPH, $r = 0.978$, $p < 0.05$; ABTS $r = 0.433$, $p < 0.05$), which was consistent with previous report [Kou et al. 2015]. A poor correlation was noted between ABTS activity and TP contents of jujube ($r = 0.433$). Sun et al. [2002] reported similar results that the contribution of phenolic content to the total antioxidant activities was low in the fruits such as peach (0.76%), apple (0.40%), and red grape (0.35%). Moreover, the present data showed that rutin content was highly correlated with DPPH ($r = 0.951$); while chlorogenic acid and epicatechin were significantly correlated with ABTS ($r = 0.947$ and $r = 0.848$, respectively). p-coumaric acid, gallic acid and ellagic acid content were highly correlated ($r = 0.658/0.776$, $r = 0.606/0.644$, $r = 0.666/0.693$ respectively, $p < 0.05$) with fructose and glucose. All these results suggest an association between phenolic compounds and antioxidant activity, coumaric acid and rutin could be 2 of the main components responsible reducing ability of jujubes, and TPs could be main components responsible for free radicals scavenging ability of jujubes. Gao et al. [2012] paper reported the similiar data regarding phenolic and antioxidant capacity association.

CONCLUSION

This study of antioxidant activity, sugar, mineral and phenolic profiles of jujubes obtained from the five different locations in Turkey were examined. The present data indicated that the composition of bioactive compounds (phenolic compounds) in jujubes varied with locations. Three sugars, nine minerals and eleven phenolic compounds were detected in jujubes. Especially, rutin, coumaric acid, epicatechin, hesperidin (for DPPH activity) and chlorogenic acid (ABTS activity) contribute significantly to the antioxidant activity of jujubes. The correlation analysis indicates that TP highly correlates with rutin and coumaric acid content. Sakarya jujuba is excellent for direct consumption containing high levels of fructose, and glucose, which may be useful for diabetics. Mersin jujuba is a good source of natural antioxidant because of its high levels of total phenolics and antioxidant activity, which should be a better choice for manufacturing companies. Therefore, Turkish jujube from the different locations has a great potential to be exploited for fresh consumption and health benefits. In addition, it is necessary to encourage the pharmacological and cosmetic industries to manufacture products based on jujubes.

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REFERENCES

- Anupama, D., Bhat, K., Sapna, V. (2002). Sensory and physicochemical properties of commercial samples of honey. *Food Res. Int.*, 36, 183–191.
- AOAC (1990). Official methods of analysis (15th Ed.), Arlington, VA: Association of Official Analytical Chemists, Inc.
- Apak, R., Guclu, K., Demirata, B., Ozyurek, M., Celik, S.E., Bektasoglu, B., Berker K. I., Ozyurt, D. (2007). Comparative evaluation of various total antioxidant capacity assays applied to phenolic compounds with the CUPRAC assay. *Molecules*, 12, 496–547.
- Borgi, W., Recio, Mc., Ri'Os, J.L., Chouchane, N. (2008). Antiinflammatory and analgesic activities of flavonoid and saponin fractions from *Zizyphus lotus* (L.) Lam. *S. Afr. J. Bot.*, 74, 320–324.
- Choi, S.H., Ahn, J.B., Kim, H.J., Im, N.K., Kozukue, N., Levin, C.E. (2012). Changes in free amino acid, protein, and flavonoid content in jujube (*Zizyphus jujube*) fruit during eight stages of growth and antioxidative and cancer cell inhibitory effects by extracts. *J. Ag. Food Chem.*, 60(41), 10245–10255.
- Cuartero, M., Ortuño, J.A., Truchado, P., García, M.S., Tomás-Barberán, F.A., Albero, M.I. (2011). Voltammetric behaviour and square-wave voltammetric determination of the potent antioxidant and anticarcinogenic agent ellagic acid in food stuffs. *Food Chem.*, 128, 549–554.
- Cui, G., Zhang, W., Zhang, A., Mu, H., Bai, H., Duan, J. (2013). Variation in antioxidant activities of polysaccharides from fructus jujube in South Xinjiang area. *Int. J. Biol. Macromol.*, 57, 278–284.
- Elaloui, M., Laamouri, A., Fabre, J., Mathieu, C., Vilaren, G., Hasnaoui, B. (2015). Distribution of free amino acids, polyphenols and sugars of *Zizyphus jujuba* pulps harvested from plants grown in Tunisia. *Nat. Prod. Res.*, 29(1), 94–97.
- Erenmemisoglu, A., Keletimur, F., Koker, A.H., Utsuol, H., Tekol, Y., Ustidal, M. (1995). Hypoglycemic activity of *Zizyphus jujuba*. *J. Pharm. Pharmacol.*, 47, 72–74.
- Gao, Q.H., Wu, P.T., Liu, J.R., Wu, C.S., Parry, J.W., Wang, M. (2011). Physico-chemical properties and antioxidant capacity of different jujube (*Zizyphus jujuba* Mill.) cultivars grown in loess plateau of China. *Sci. Horticult.*, 130, 67–72.
- Gao, Q.H., Wu, C.S., Yu, J.G., Wang, M., Ma, Y.J., Li, C.L. (2012). Textural characteristic, antioxidant activity, sugar, organic acid, and phenolic profiles of 10 promising jujube (*Zizyphus jujuba* Mill.) selections. *J. Food Sci.*, 77(11), 1218–1225.
- García-Nino, W.R., Zazueta, C. (2015). Ellagic acid: Pharmacological activities and molecular mechanisms involved in liver protection. *Pharmacol. Res.*, 97, 84–103.
- Glombitza, K.W., Mahran, G.H., Mirhom, Y.W., Michel, K.G., Motawi, T.K. (1994). Hypoglycemic and antihyperglycemic effects of *Zizyphus spina-christi* in rats. *Planta Med.*, 60, 244–247.
- Gupta, M., Mazumder, U.K., Vamsi, M.L.M., Sivakumar, T., Kandari, C.C. (2004). Anti-steroidogenic activity of the two Indian medicinal plants in mice. *J. Ethnopharm.*, 90, 21–25.
- Han, B.H., Park, M.H., Han, Y.N. (1990). Cyclic peptide and peptide alkaloids from seeds of *Zizyphus vulgaris*. *Phytochem.*, 29, 3315–3319.
- Hatano, T., Kigawa, H., Yasuhara, T., Okuda, T. (1988). Two new flavonoids and other constituents in licorice root—their relative astringency and radical scavenging effects. *Chem. Pharm. Bull.*, 36, 2090–2097.
- Huang, W.K. (1989). Food testing and analysis. China. Light Industry Press.

- Huang, X., Kojima-Yuasa, A., Norikura, T., Kennedy, D.O., Hasuma, T., Matsui-Yuasa, I. (2007). Mechanism of the anti-cancer activity of *Zizyphus jujuba* in HepG2 Cells. *Am. J. Chin. Med.*, 35(3), 517–532.
- Huang, X., Kojima-Yuasa, A., Xu, S., Norikura, T., Kennedy, D.O., Hasuma, T., Matsui-Yuasa, I. (2008). Green tea extract enhances the selective cytotoxic activity of *Zizyphus jujuba* extracts in HepG2 Cells. *Am. J. Chin. Med.*, 36(4), 729–744.
- Huang, Y.L., Yen, G.C., Sheu, F., Chau, C.F. (2008). Effects of water-soluble carbohydrate concentrate from Chinese jujube on different intestinal and fecal indices. *J. Agric. Food Chem.*, 56, 1734–1739.
- Hudina, M., Liu, M., Veberic, R., Stampar, F., Colaric, M. (2008). Phenolic compounds in the fruit of different varieties of Chinese jujube (*Zizyphus jujube* Mill.). *J. Hort. Sci. Biotech.*, 83, 305–308.
- IHC (2009). Harmonised Methods of the International Honey Commission, 1–63.
- Kamiloglu, O., Ercisli, S., Sengul, M., Toplu, C., Serce, S. (2009). Total phenolics and antioxidant activity of jujube (*Zizyphus jujube* Mill.) genotypes selected from Turkey. *Afr. J. Biotechnol.*, 8, 303–307.
- Karaaslan, N.M., Ince Kaplan, O., Ince, M. (2014). Fenolik Bileşiklerin HPLC-DAD ile Tayini İçin Metod Geliştirilmesi ve Validasyonu. VII. Ulusal Analitik Kimya Kongresi, 1–5 Eylül, Kahramanmaraş (in Turkish).
- Keser, S., Celik, S., Turkoglu, S. (2013). Total phenolic contents and free-radical scavenging activities of grape (*Vitis vinifera* L.) and grape products. *Int. J. Food Sci. Nutr.*, 64(2), 210–216.
- Krifa, M., Bouhleb, I., Ghedira-Chekir, L., Ghedira, K. (2013). Immunomodulatory and cellular anti-oxidant activities of an aqueous extract of *Limoniastrum guyonianum* gall. *J. Ethnopharmacol.*, 146(1), 243–249.
- Krishna, H., Parashar, A. (2013). Phytochemical constituents and antioxidant activities of some Indian jujube (*Zizyphus Mauritiana*) cultivars. *J. Food Chem.*, 37, 571–577.
- Kou, X., Chen, Q., Li, X., Li, M., Kan, C., Chen, B., Zhang, Y., Xue, Z. (2015). Quantitative assessment of bioactive compounds and the antioxidant activity of 15 jujube cultivars. *Food Chem.*, 173, 1037–1044.
- Li, J.W., Fan, L.P., Ding S.D., Ding, X.L. (2007). Nutritional composition of five cultivars of chinese jujube. *Food Chem.*, 100(2), 454–460.
- Naik, S.R., Bhagat, S., Shaha, P.D., Tarea, A.A., Ingawalea, D., Wadekar, R.R. (2013). Evaluation of anti-allergic and anti-anaphylactic activity of ethanolic extract of *Zizyphus jujuba* fruits in rodents. *Rev. Bras. Farmacogn.*, 23, 811–818.
- Norusis, M.J. (1993). SPSS for Windows: Base System User's Guide, SPSS, Chicago.
- Osborne, C.G., Mctyre, R.B., Dudek, J., Roche, K.E., Scheuplein, R., Silverstein, B. (1996). Evidence for the relationship of calcium to blood pressure. *Nutr. Rev.*, 54, 365–381.
- Pareek, S., Fageria, M.S., Dhaka, R.S. (2002). Performance of ber genotypes under arid condition. *Curr. Agric.*, 26, 63–65.
- Pareek, S. (2013). Nutritional composition of jujube fruit. *Emir. J. Food Agric.*, 25(6), 463–470.
- Pawlowska, A.M., Camangi, F., Bader, A., Braca, A. (2009). Flavonoids of *Zizyphus jujuba* L. and *Zizyphus spina-christi* (L.) Willd (*Rhamnaceae*) fruits. *Food Chem.*, 112, 858–862.
- Plastina, P., Bonofiglio, D., Vizza, D., Fazio, A., Rovito, D., Giordano, C., Barone, I., Catalano, S., Gabriele, B. (2012). Identification of bioactive constituents of *Zizyphus jujube* fruit extracts exerting antiproliferative and apoptotic effects in human breast cancer cells. *J. Ethnopharmacol.*, 140(2), 325–332.

- Peng, W.H., Hsieh, M.T., Lee, Y.S., Lin, Y.C., Liao, J. (2000). Anxiolytic effect of seed of *Ziziphus jujuba* in mouse models of anxiety. *J. Ethnopharmacol.*, 72(3), 435–441.
- Poyrazoglu, E., Gokmen, V., Artik, N. (2002). Organic acids and phenolic compounds in pomegranates (*Punica grgranatum* L.) grown in Turkey. *J. Food Comp. Anal.*, 14, 567–75.
- San, B., Yıldırım, A.N. (2010). Phenolic, alpha-tocopherol, beta-carotene and fatty acid composition of four promising jujube (*Ziziphus jujuba* Miller) selections. *J. Food Comp. Anal.*, 23, 706–710.
- Simas-Tosin, F.F., Abud, A.P.R., De Oliveira, C., Gorin, P.A.J., Sasaki, G.L., Bucchi, D.F. (2012). Polysaccharides from peach pulp: Structure and effects on mouse peritoneal macrophages. *Food Chem.*, 134(4), 2257–2260.
- Singh, S., Arya, R. (2011). *Zizyphus*: An Extroversion Gift of Nature. *J. Sci.*, 1, 15–20.
- Sun, J., Chu, Y.F., Wu, X.Z., Liu, R.H. (2002). Antioxidant and antiproliferative activities of common fruits. *J. Agric. Food Chem.*, 50, 7449–7454.
- Sheng, G., Yu Ping, T., Jin, A.O.D., Shu Lan, S., Wei An, D. (2009). Two new terpenoids from fruits of *Ziziphus jujube*. *Chin. Chem. Lett.*, 20, 197–200.
- Singleton, V.L., Orthofer, R., Lamuela-Raventós, R.M. (1999). Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin-Ciocalteu reagent. *Meth. Enzymol.*, 299, 152–178.
- Siriamornpun, S., Weerapreeyakul, N., Barusrux, S. (2015). Bioactive compounds and health implications are better for green jujube fruit than for ripe fruit. *J. Funct. Foods.*, 12, 246–255.
- Soares, J.R., Dins, T.C.P., Cunha, A.P., Almeida, L.M. (1997). Antioxidant activity of some extracts of *Thymus zygis*. *Free Rad. Res.*, 26, 469–478.
- Vaya, J.B., Aviram, P. (1997). Antioxidant constituents from licorice roots: isolation, structure, elucidation and antioxidative capacity toward LDL oxidation. *Free Rad. Biol. Med.*, 23, 302–313.
- tive effects of the polysaccharides from *Zizyphus jujube* cv. *Shaanbeitanzao*. *Carbohydr. Polym.*, 88(4), 1453–1459.
- Wu, L., Chang, L., Chen, S., Fan, N., Ho, J.A. (2009). Antioxidant activity and melanogenesis inhibitory effect of the acetonetic extract of *Osmanthus fragrans*: A potential natural and functional food flavor additive. *LWT – Food Sci. Technol.*, 42, 1513–1519.
- Wu, C.S., Gao, Q.H., Guo, X.D., Yu, J.G., Wang, M. (2012). Effect of ripening stage on physico-chemical properties and antioxidant profiles of a promising table fruit pear-jujube (*Zizyphus jujuba* Mill.). *Sci. Horticult.*, 148, 177–184.
- Yang, J.H., Lin, H.C., Mau, J.L. (2002). Antioxidant properties of several commercial mushrooms. *Food Chem.*, 77, 229–235.
- Yeung, W.F., Chung, F., Poon, M.M., Ho, F.Y., Zhang, S.P., Zhang, Z.J., Ziea, E.T., Wong, V.T. (2012). Chinese herbal medicine for insomnia: A systematic review of randomized controlled trials. *Sleep Med. Rev.*, 16, 497–507.
- Yu, L., Jiang, B.P., Luo, D., Shen, X.C., Guo, S., Duan, J.A., Tang, Y.P. (2012). Bioactive components in the fruits of *Ziziphus jujuba* Mill. against the inflammatory irritant action of Euphorbia plants. *Phytomedicine*, 19, 239–244.
- Zhang, H., Jiang, L., Ye, S., Ye, Y., Ren, F. (2010). Systematic evaluation of antioxidant capacities of the ethanolic extract of different tissues of jujube (*Ziziphus jujuba* Mill.) from China. *Food Chem. Toxic.*, 48, 1461–1465.
- Zemel, M.B. (1997). Dietary pattern and hypertension: the DASH study. *Nutr. Rev.*, 55, 303–305.

CAŁKOWITA ZDOLNOŚĆ ANTYOKSYDACYJNA, ZWIĄZKI FENOLOWE ORAZ ZAWARTOŚĆ CUKRU W JUJUBIE POSPOLITEJ

Streszczenie. Określono zawartość związków fenolowych, cukru i minerałów w owocach *Ziziphus jujube* (jujuba) zebranych w różnych miejscowościach w Turcji. Całkowita zawartość związków fenolowych wynosiła od 652,4 do 1348,4 mg GAE 100 g⁻¹ suchej masy owoców. Zidentyfikowano i określono ilościowo czternaście związków fenolowych: kwas galusowy, katechinę, epikatechinę, kwas chlorogenowy, kwas kofeinowy, kwas kumarowy, kwas para-kumarowy, hesperydynę, naringinę, rytynę, kwas elagowy, kwercetynę, naringeninę oraz wanilinę. W jujubie stwierdzono znaczne różnice jeśli chodzi o materiał fenolowy. Poziom katechiny w owocach jujuby wahał się od 5,95 do 100,96 mg 100 g⁻¹, a kwasu elagowego od 87 do 26,32 mg 100 g⁻¹ suchej masy. Potas, fosfor, wapń i magnez były głównymi składnikami mineralnymi w owocach jujuby. Stwierdzono pozytywną korelację między całkowitą zawartością fenoli a antyoksydacyjnym działaniem jujuby.

Słowa kluczowe: jujuba pospolita, składniki bioaktywne, fenole, polisacharydy, związki mineralne

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