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Original article

Assessment of the Physicochemical and Antioxidant Profile of Dried Goji Berries

(Lycium barbarum)

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Summary. This study aimed to determine the physicochemical properties and antioxidant capacity of the dry goji berry fruit. Sun-dried goji berry fruits (*Lycium barbarum*) harvested in Manisa-Turkey and sold in the local market were collected. Total phenolic content (TPC) was determined by the Folin-Ciocalteu method, and the ferric reducing ability of plasma (FRAP) assay was utilized for antioxidant activity. 2,6 dichlorophenolindophenol spectrophotometric method was used in the ascorbic acid analysis. Mineral contents and the percentage contribution to the recommended daily allowance (RDA) of dry fruits were determined. TPC values of samples were 207.2±1.51 mg GAE/100 g and their antioxidant activities were found to be 32.6±1.82 μmol TE/g. The fruit samples of 100 gram included 31.0±1.62 mg of ascorbic acid. Mineral contents and the percentage contribution to the RDA of 100 grams of dry goji berry fruits were as follows: calcium:49.0 mg (5.0%), phosphorus:370.0 mg (67.2%), sodium:1.32 mg (94.2%), potassium: 193.0 mg (>4000%), magnesium:120.0 mg (36.9%), iron:0.04 mg (0.3%), copper: 0.01 mg (0.7%) and manganese:0.008 mg (0.26%), The results of the present study suggest that goji berry cultivated in not only Asia but also Turkey certainly deserve further investigation because it contains a significant amount of vitamin C and some essential minerals, and with its phenolic content/antioxidant capacity even if it is traditionally sun-dried.

Key words: Goji berry, Dried Fruit, Antioxidant, Polyphenols

Introduction

Goji berry, which is the fruit of *Lycium barbarum* and *Lycium chinense*, which are of Solanaceae family, has been used for a long time in traditional medicine in Asia (1). In recent years, due to its nutritional value, some pharmacological activities, and functional properties, it has become popular in many communities, foremost being Europe and North America (2).

Goji berry, is a perennial plant in the form of a bush that can grow in almost any type of soil, is fusiform shaped, 6-20 mm long, 3-8 mm in diameter, and the color of which can change from orange to dark red. Goji berry, which has a sweet-sharp aroma, can be harvested from late summer to autumn (3). In Turkey, the goji berry is rather known as wolfberry, but in the world, it is known by different names such as Lycium Fruit, Fructus lycii, lycii berries, lycii fructus, lycii fruit, wolfberry, barbary wolfberry, Chinese boxthorn (gouqizi or gou qi zi), Tibetan goji berry (4). Nowadays, goji berry is consumed in different ways. For example, the fruit may be eaten as raw and dried, or it can be used as a juice or tea or mixed with tea, and may be used as an additive in the soft and alcoholic beverage or added to cereals, granola, bars. In Asian societies, dried goji berry can be cooked and added to soups (1, 5). Besides, due to its biologically active secondary metabolites, it is also offered to consumers as a nutritional supplement, essential oil, nutritional supplement, and/or functional food (6).

The use/consumption of the fruit has recently become very popular due to its potential health effects as well as its traditional/cultural use (2). The idea of goji berry fruit's reducing oxidative stress due to its high antioxidant potential and preventing deoxyribonucleic acid (DNA), lipid, and protein damage caused by free radicals and having a health protective effect come forward in its widespread use (7). Besides, in some studies, it has been reported that goji berry fruit may show anti-inflammatory and antitumor activity and may have protective effects in terms of diabetes and cardiovascular diseases (5, 8). These protective effects are attributed to the natural antioxidant compounds and / or the nutritional properties it involves (9). However, information about the physicochemical properties, compositions and antioxidant contents of goji berry fruits grown, harvested, or marketed by using different processing methods in different geographical regions are almost nonexistent.

In this study, it is aimed to determine the physicochemical properties and antioxidant capacities of the dry goji berry fruit *(Lycium barbarum)* harvested in Turkey.

Materials and Methods

Sample Selection

In this cross-sectional study, goji berry fruits *(Lycium barbarum)* harvested from different geographical regions of the Manisa province (Turkey) seasonably (summer term) and offered for sale in the domestic retailers (n=5) of this province with a sun-dried declaration were used. Dried fruits that were sold in the domestic retailers without packaging were supplied at least 1 kg±10 g amounts from every retailer for use in this study. Regarding the supply of fruits, attention was paid to ensure that they are new crops, that their color is not tarnished and all quality criteria specific to dried fruits according to Turkish Standards Institution (TSE).

Analysis of Samples

The supplied samples were brought to the laboratory for analysis without waiting. Sampling was made randomly to represent each retailers and sample preparation specific to each analysis was made. All analyzes were carried out in duplicate.

Physicochemical Analysis of Samples

Moisture Content: 100 g of dried fruits as a test sample was taken and homogenized with Waring commercial blender (Blender 8011ES, USA). Then, 5 g of homogenized sample were transferred to the each of weighing molds. Moisture content for dried fruits measured under the operating conditions specified in AOAC Official Method 972.20 (1990). The moisture content is expressed as a percentage by mass (grams per 100 grams).

Water Soluble Dry Matter (WSDM):10 g of dried fruit samples were blended with Waring commercial blender (Blender 8011ES, USA) with 100 mL ultrapure water (1/10 ratio) and then filtered. WSDM quantities were determined using a refractometer (Atago PAL-1, Japan) and results were expressed in percentage (%) (10).

Amount of Titratable Acid (TA): After diluting 2 mL sample from goji berry solution used in the measurement of WSDM with 15 ml of distilled water, it was titrated with 0.1 N sodium hydroxide (NaOH) until the pH reached 8.1 and the amount of titratable acid (meq/100 mL) was calculated based on the amount of NaOH spent in titration (10).

Color Analysis: Fruit color was measured in CIE L*a*b* plane with Minolta colorimeter (CR-400, Minolta Co., Tokyo, Japan). Color measurements were determined by making 3 measurements from the equatorial part of each fruit. The instrument was calibrated with standard white calibration plate (L*= 97.26, a*=+0.13, b*=+1.71) before measurements. In the plane used L* is expressed as brightness, a* value is expressed as redness-greenness and, b* value is expressed as yellowness-blueness. Croma (C*) value indicates the saturation of the color. While chroma value decreases in dull colors, it increases in vivid colors. Hue angle (h) is a color circle and red-purple colors take the color value between 0°-360° yellow takes the color value 90° and bluish green colors take the color value between 180°-270^0 (11).

$$C^* = \sqrt{}(a^{*2}+b^{*2})^{1/2} \qquad h^o = \tan^{-1}(b^*/a^*)$$

Ascorbic Acid Analysis of Samples

Homogenization was performed with the Waring commercial blender (Blender 8011ES, USA) by adding 1 L of oxalic acid (0.4%) to 100 g sample (Blender 8011ES Two Speed Blender ™) taken randomly from goji berry fruit samples to represent repetition.

The spectrophotometric method, which was based on the reduction of the 2,6-dichlorophenolindophenol indicator by ascorbic acid, was used for the the ascorbic acid analysis of the samples (12). Ascorbic acid analyzes of duplicate samples were performed at 518 nm using Varian Cary 100 Bio UV-Visible Spectrophotometer™.

Total Phenolic Content and FRAP Analysis of Samples

25 grams of dried goji berry samples taken randomly were mixed with 200 mL methanol and homogenized with a homogenizer. Extraction processes from goji berry fruits were performed to determine the total amount of phenol (TPC) and antioxidant activity by adapting the method of Thaipong et al. (13). The amount of TPCs in the goji berry fruits was determined by Folin-Ciocalteu colorimetric method (14). TPCs were expressed as mg/L gallic acid equivalents (GAE) extract.

The ferric reducing ability of plasma (FRAP) assay was carried out according to Benzie and Strain (1999) with slight modifications (15). The FRAP reagent was prepared from acetate buffer (pH=3.6), 10 mmoL TPTZ (2, 4, 6-tripyridyl-striazine) solution in 40 mmoL HCl and 20 mmoL $FeCl_3 6H_2O$ (ferric chloride solution) in proportions of 10:1:1 (v/v), respectively. 100 µl of the sample was added to 3 mL of FRAP reagent. The reaction mixture was incubated for 4 min at room temperature. The absorbance of the reaction mixture was measured at 593 nm (16). The results were expressed as mmol Trolox equivalent/g.

Mineral Analysis of Samples

1 gram of each food sample was taken with 20 mL of acid mixture (HNO_3 + $HClO_4$; 4: 1 ratio) in a conical flask and kept for digestion overnight for the first stage. Wet decomposition was performed and potassium (K), calcium (Ca), and sodium (Na) of dried fruits were analyzed with a flame photometer. As for magnesium (Mg), iron (Fe), zinc (Zn), manganese (Mn), and copper (Cu), they were measured by atomic absorption spectrophotometer. Phosphorus (P) was determined spectrophotometrically by vanadomolybdo phosphoric yellow color method (17).

As for the mineral contents determined in dried fruit samples, they were compared with the Recommended Dietary Allowances (RDA) for adults according to Turkey Nutrition Guideline (TÜBER)-2015 and the percentage contribution to the RDA of both 100 grams and 1 portion (30 g) dry fruits were determined (18).

Statistical Analysis

The data were analyzed with SPSS 22.0 statistical package software. Minimum (min)-maximum (max), median, arithmetic mean±standard deviation ($\overline{x}$±SD) values were given as the descriptive statistics for the variables.

Results

Some physicochemical properties of dry goji berry fruit samples are shown in Table 1. Accordingly, the moisture content of dried fruit samples (%) is 20.4±0.15 and WSDM (%) is 57.6±21.90. As for TA values of fruit samples, they are 21.8±2.85 meq/100 mL. The color values of the samples are L^*= 22.8±1.95, a^* = 23.5±2.85, b^* = 1.19±1.87, C= 30.3±3.28 and $h°$=39.1±0.99 (Table 1).

The average ascorbic acid (mg/100 g), TPC (mg GAE/100 g) contents and antioxidant activities (µmol TE/g) of 100 grams of dry goji berry fruit samples are shown in Table 2. It was determined that 100 grams of fruit samples included 31.0 ± 1.62 mg (RDA:~30%) of ascorbic acid. While the TPC values of samples were 207.2 ± 1.51 mg GAE/100 g, their antioxidant activities were found to be 32.6 ± 1.82 µmol TE/g (Table 2).

Mineral contents of 100 grams of dry goji berry fruit samples and and the percentage contribution to the RDA of 100 grams and 1 portion (%) are given

Table 1. Physico-chemical properties of dried goji berry fruitsɣ

Physico-chemical properties	Min-Max	x̅±SD
Moisture (%)	20.4-20.5	20.4±0.15
WSDM (%)	56.0-59.0	57.6±21.90
TA (meq/100 mL)	20.0-25.0	21.8±2.85
Color values		
L*	20.6-24.3	22.8±1.95
a*	20.4-25.5	23.5±2.85
b*	17.2-20.5	1.19±1.87
C*	26.7-32.7	30.3±3.28
h°	38.3-40.2	39.1±0.99

WSDM: Water soluble dry matter; TA: Titration acidity; L*: brightness, a*: redness-greenness, b*: yellowness-blueness, Croma (C*): color saturation; Hue angle (h°); red-purple colors: 0°-360°, yellow: 90°, bluish green: 180°-270°
ɣDried fruit samples were supplied from the 5 domestic market/retailers. All analyzes were carried out in duplicate.

in Table 3. According to this, the mineral amounts (RDA%) contained in 100 grams of dry goji berry fruits are as follows: calcium: 49.0 mg (5.0%), phosphorus: 370.0 mg, (67.2%), sodium: 1.32 mg (94.2%), potassium: 193.0 mg (> 4000%), magnesium: 120.0 mg (36.9%), iron: 0.04 mg (0.3%), zinc: 0.02 mg (0.04%), copper: 0.01 mg (0.7%) and manganese: 0.008 mg (0.26%). The ratio of minerals contained in 1 portion (30 g) of the fruit samples to contribute the RDA are respectively: potassium:> 1000%, sodium: 28.2%, phosphorus: 20.1%, magnesium: 11.0%, calcium: 1.5%, copper: 0.2%, iron: 0.09%, manganese: 0.07% and zinc: 0.04%. (Table 3).

Table 2. The mean ascorbic acid (mg/100 g), TPC (mg GAE/100 g) contents and antioxidant activities (μmol TE/g) of 100 grams of dry goji berry fruits *

Physico-chemical properties	Min-Max	x̅±SD
Ascorbic acid (mg /100 g)	29.3-32.2	31.0±1.62
TPC (mg GAE/100 g)	207.0-208.6	207.2±1.51
Antioxidant activity (μmol TE /g)	30.7-33.4	32.6±1.82

TPC: Total phenolic content
* The results were calculated on dry matter.

Discussion

Goji berry fruit has been called "super food" in recent years with its nutrient composition and bioactive compounds and its popularity has been increasing with each passing day in societies other than Asian, foremost being Turkey (19). The literature on the nutritional composition and biological activity of the goji berry fruit, which is frequently consumed in dried form, have been carried out frequently on fresh fruit and using fruits harvested from Asia (20). In this

Table 3. The mineral content of 100 grams of dry goji berry fruits and the percentage contribution to the RDA of 100 grams and 1 portion (%) *

Minerals	Median	RDA (mg/day)	RDA (%) per 100 gram	RDA (%) per portion (30 g)
Calcium (mg)	49.0	950-1000	5.0%	1.5%
Phosphorus (mg)	370.0	550	67.2%	20.1%
Sodium (mg)	1.32	1.3-1.5	94.2%	28.2%
Potassium (mg)	193.0	4.7	> 4000%	>1000%
Magnesium (mg)	120.0	300-350	36.9%	11.0%
Iron (mg)	0.04	11-16	0.3%	0.09%
Zinc (mg)	0.02	7.5-16.3	0.1%	0.04%
Copper (mg)	0.01	1.3-1.6	0.7 %	0.2%
Manganese (mg)	0.008	3	0.2%	0.07%

RDA: Recommended Dietary Allowance refers to the recommended intake ranges for men and women aged 19-70 years. The midpoint of the ranges was used to determine the percentage of RDA.
* The results were calculated on dry matter.

context, in this research, the physicochemical properties and antioxidant capacities of dried goji berry fruits (*Lycium barbarum*) harvested in Turkey were evaluated.

In this research, sun dried goji berry fruits were used as samples and moisture content of dried fruit samples (%) was found as 20.4 ± 0.15 and WSDM (%) was found as 57.6 ± 21. 90(Table 1). Drying processes in foods is an application that aims to remove water from foods to prevent microbial spoilage and physicochemical changes. By drying the food, space and weight are saved and the shelf life of the food can be extended (21). Drying is divided into two groups as sun drying under natural conditions or artificial drying with the help of heat obtained from other sources. Drying is carried out in the sun under natural conditions in crops and regions where the harvest period is hot and dry, and in these conditions, the rate of water in dried fruits can be reduced to 15-20% (22). The moisture content of the fruits can be reduced even more by using other drying methods, In a study, drying performed using the method of air-dried in a convective dryer could reduce the moisture rate to 9.3±0.02 (23). In this research, the moisture content of sun dried fruit samples was found to be parallel to the expected moisture/dry matter ratio with the sun drying method. Although sun drying is an inexpensive and easy method, it can negatively affect the quality of fruits due to dusting, insect infestation and bird and similar animal damage (21). Therefore, it is thought that it will be beneficial to choose alternative drying methods. In this study, dried fruit samples were not evaluated microbiologically, but it is thought that it will be important to evaluate sun-dried fruit samples in this aspect in future studies.

Goji berry fruit is a fruit that is similar to red grapes, which has a reddish-orange color (24). In this study, the color values of the samples were L^*=22.8±1.95, a*= 23.5±2.85, b*= 1.19±1.87, C=30.3±3.28 and h°=39.1±0.99 and were also found to be parallel to the expected color spectrum in this study (Table 1). The reddish-orange color of the fruits is caused by a group of carotenoids found in the fruit at a rate of 0.03-0.5% (25). While zeaxanthin is the most dominant carotenoid type in goji berry fruit, it is mostly found as dipalmitate esters and is associated with many health benefits (23).

Goji berry fruit and its products are claimed to be rich in micronutrients, natural antioxidants and many trace elements (20). According to various studies, there is a total of 9.12 g carbohydrates, 4.49 g protein, 2.33 g total lipid (fat), 0.23 mg thiamine, 0.33 mg riboflavin, 1.7 mg niacin in 100 grams of fresh fruit, (11, 13). In fresh goji berry fruits harvested from the Italy region, 15.3 g carbohydrates, 2.5 g protein, 1.1 g fat, 2.9 g fiber and 0.84 g ash were found (24). As a result of drying these fruits, the nutrient content was determined as 61.3 g carbohydrates, 10.2 g protein, 4.4 g fat, 11.4 g fiber, and 3.4 g ash. According to USDA databases, 100 g of dried goji berry fruit contains 349 kcal energy, 77.06 g carbohydrate, 14.26 g protein, 0.39 g total lipid (fat), 13 g dietary fiber and 0.78 g ash (26). Another component that stands out due to its nutritional properties and health effects in dried fruit is polysaccharides (*Lycium barbarum* polysaccharides, LBP), which constitutes 5-8% of dried fruit (5). Polysaccharides isolated from goji berry fruit have been reported to have many biological activities and potential health roles such as antioxidant, immunomodulation, antitumor, neuroprotection, radioprotection, anti-diabetes, hepatoprotection, anti-osteoporosis and antifatigue (27).

In the present study, ascorbic acid and some trace element contents of dried goji berries were investigated (Table 2, Table 3). It was determined that there was a significant amount (31.0±1.62 mg and RDA:~30%) of vitamin C (ascorbic acid) in 100 grams of dry goji berry fruit samples. In the literature, the vitamin C amounts of sun-dried goji berry fruits are reported as 42-48 mg/100 g (26, 28). In this study, mineral contents of dried goji berry fruits and their contribution to nutrition were also investigated (Table 3). According to this, the mineral amounts (RDA%) contained in 100 grams of dry goji berry fruits are as follows: calcium: 49.0 mg (5.0%), phosphorus: 370.0 mg, (67.2%), sodium: 1.32 mg (94.2%), potassium: 193.0 mg (>4000%), magnesium: 120.0 mg (36.9%), iron: 0.04 mg (0.3%), zinc: 0.02 mg (0.04%), copper: 0.01 mg (0.7%) and manganese: 0.008 mg (0.26%). The ratio of minerals contained in 1 portion (30 g) of the fruit samples to contribute the RDA are respectively: potassium:>1000%, sodium: 28.2%, phosphorus: 20.1%, magnesium: 11.0%, calcium: 1.5%, copper: 0.2%, iron: 0.09%, manganese: 0.07% and zinc: 0.04%. (Table 3).

It is thought that goji berry fruits constitute an important resource in terms of copper, iron, selenium, and zinc (29). In another study, it was reported that fresh goji berries (100 g) are an important source of copper (RDA%:25), and dry goji berries are an important source of K, P, Cu, Fe Mn, Zn. Besides, it was stated that daily consumption of 30 g of dry goji berry could contribute 25% to Cu, 13% to K, and less than 10% to other elements (23). In the present study, mineral levels especially potassium content differed from other studies. It is thought that this high level especially detected in potassium content in dry goji berry fruits may be due to the uncontrolled use of potassium fertilizer in the cultivation of fruits. Short-term potassium intake of ~2500 mg/d (64 mmol/d) of a usual diet seems to be safe for healthy people. However, there is accumulated evidence that very high doses of potassium intake acutely or chronically can cause some dangerous adverse reactions especially in some people with kidney disease, diabetes, heart failure, adrenal insufficiency, etc (30). In the present study, the potential reason of detected high potassium amount of fruits is that the use of fertilizer with nitrogen, phosphorous, and potassium is widespread in Turkey and it is obvious that the amount of use of this type fertilizers should be paid attention by cultivators (31). Besides, the reason for the detection of different amounts of vitamin C and minerals in this study is that different drying techniques are used in fruits and there may be differences in cultivated geographical regions and the cultivation/harvesting techniques.

TPC values in 100 grams of dry goji berry fruits were found to be 207.2±1.51 mg GAE/100 g and antioxidant activities were found to be 32.6±1.82 μmol TE/g (Table 2) in the present study. Goji berry fruit, extract and infusions is a fruit rich in bioactive compounds such as carotenoids, flavonoids and antioxidant vitamins (vitamin E, vitamin C) with antioxidant activity (32-34). In a study, phenolic substance content and FRAP) assay as antioxidant activity of dried goji berry (*Lycium barbarum*) was compared with kaki and kiwi and TPC content was found to be 210.9 mg GAE/100g dry weight for kiwi, 872.6 mg GAE / 100g dry weight for kaki and 502.3±71.22 mg GAE/100g dry weight for goji berry. In the same study, it was also found that monoterpenes were the predominant physiochemical in goji berry, and anthocyanins were not detected in dried fruits because anthocyanins turned into phenolic acids due to the drying process. While the antioxidant capacity of goji berry was found to be 23.09 mmol Fe^{2+}/kg dry weight, the highest antioxidant activity was found in dry kaki fruit (137.5 mmol Fe^{2+}/kg dry weight) (35). In another study in which dry goji berrry *(Lycium barbarum),* cranberry and raisin were compared, it was reported that the antioxidant capacity of goji berry fruit was the most profitable for the consumers (36). Another study investigating in terms of phytochemical analysis and with 2,2-diphenyl-1-picrylhydrazyl (DPPH) antioxidant activity goji berry harvested from Greece (*Lycium barbarum*), TPC 14.1±0.40 (water fraction) and 109.7±4.09 (ethyl acetate fraction) mg gallic acid equivalent/g dry extract were found. Moreover, ethyl acetate extract showed the highest antioxidant effect (4.7±0.20 mg/mL) (9). In the same research, 17 phenolic compounds, foremost being cinnamoylquinic acids and derivatives, hydrocinnamic acids and flavonoid derivatives were identified; besides, quercetin 3-*O*-hexose coumaric ester and quercetin 3-*O*-hexose-*O*-hexose-*O*-rhamnose were identified for the first time in goji berry fruit (9). In this study, although a detailed phenolic substance characterization was not performed the phenolic substance and antioxidant capacities of dried goji berry fruits were found to be remarkably high, similar to the literature. Among at least 70 species of Lycium, it is stated that the one with the most biological activity is *Lycium barbarum* used in this study (33). In a study that supports this, it was reported that the carbohydrates and phenolic substances in *Lycium barbarum* fruit are more compared to other species of Lycium and in parallel to this, show higher antioxidant activity (32). Moreover, it has been shown that the drying method types used can affect the content of Lycium species' bioactive substances and antioxidant capacity. Although it causes negative effects on taste and vision a higher amount of phenolic substance and anti-oxidant activity were detected in *Lycium ruthenicum* fruits in air drying method compared to freeze drying and low temperature oven drying methods (37). The present study shed light on the phenolic substance amount and antioxidant capacity of *Lycium barbarum* fruit dried by the traditional drying method in the sun.

Conclusion

As far as is known in this study, the physico-chemical and nutritional properties of goji berry fruits (*Lycium barbarum)* harvested in Turkey and dried in the sun were investigated and their antioxidant capacities were revealed the first time. So, goji berry is thought to certainly deserve further investigation because it contains a significant amount of vitamin C and some minerals, and with its phenolic content/antioxidant capacity. However, most importantly further detailed clinical researchs especially randomized controlled trials (RCTs) is required in this regard.

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