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Comparatives of physico-chemical composition, mineral and heavy metal properties of the grape juices, grape pekmez and dried grape products in difference plant

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K E Y W O R D S: Grape juice, grape pekmez, dried grape, mineral and heavy metal content

ABSTRACT: Traditional Turkish product grape juices, grape pekmez, and dried grape; products make that grapes, is commonly made differences region of Turkey. Comparatives of some physical and chemical composition, mineral and heavy metal properties of grapes samples were analyzed products that grape juices, grape pekmez and dried grape. The samples were analyzed L, a and b colour, dry mater, ash, total phenolic, DPPH reducing antioxidant power and some mineral and heavy metal, as Ca, Mg, Na, Mn, Fe, Cu, Zn, Cr, Co Pb, Ni, Sn, Cd and Mo contents. The grape juices, grape pekmez, and dried grape products that grapes were showed differences statistically on colour values, dry mater, ash, total phenolic, DPPH antioxidant power and some mineral and heavy metal.

Introduction

Grape juice consists of 79% water and 20% carbohydrates, 1% organic acids and trace amounts of organic acids, phenolic, vitamins, minerals and nitrogenous compounds. Grape pekmez is a natural sugar source that is obtained by concentration of fruit juice up to 70–80% soluble dry matter concentration. A dried grape, dehydration has been extensively utilized for decades as one of the principal food preservation techniques. Grapes, and in particular grape products, are rich in phenolic compounds. In grapes, they are present in the pulp, skin, and seeds. They are considered one of the most important quality parameters of grapes and their products since they contribute to their colour and organoleptic characteristics such as flavour, bitterness, and astringency. Phenolic compounds are also effective antioxidants. The effect of consuming food and beverages rich in polyphenols in terms of preventing diseases such as cancer and coronary diseases is quite significant. Polyphenols can also reduce damage to DNA and production of free radicals in the body. Many of the flavonoids found in grape juice, such as catechin, epicatechin, quercetin, and anthocyanin's are known to have antioxidant, anti-inflammatory, and platelet inhibitory effects, as well as for being able to reduce LDL oxidation and oxidative damage to DNA, both in vitro and in animal studies (Sinlgletary et al., 2003). Grape juice consists of 79% water and 20% carbohydrates, 1% organic acids and trace amounts of organic acids, phenolics, vitamins, minerals and nitrogenous compounds. The sugars, organic acids and phenolics give the juice its flavour, while the vitamins, minerals and nitrogenous compounds are, in many cases, essential to yeast growth and fermentation (Burin et al., 2010).

Pekmez is a food product made from grapes, figs or mulberry by boiling the fruit paste. It is mainly produced and consumed in Turkey. Grape pekmez is produced from grapes or raisins in an open kettle or vacuumed tank. About 657,000 tons of grapes are processed into pekmez annually in Turkey. Pekmez is traditionally made in rural areas. However, commercial pekmez production in small to mid-sized plants has been on the rise in recent years. Grape pekmez is a thick, concentrated product and is produced from grape or raisin paste by decreasing its acidity. Vacuum application may be applied to concentrate the product. Although grape is mostly used in pekmez production, fruits such as carob, mulberry, fig, plum, apple, apricot, pomegranate or watermelon may also be used. About 37% of harvested grapes are used in pekmez production in Turkey (Tosun et al. 2014).

Dehydration has been extensively utilized for decades as one of the principal food preservation techniques. The intent of this process is to produce shelf stable foods with specific applications and sensory characteristics. Currently, conventional thermal methods such as sun drying and hot-air drying are used in the food industry to preserve fruits and vegetables. However, the quality of conventionally dried fruits is affected, and there is little resemblance to the fresh fruit (Ratti 2001). The objective of this study was to evaluate the total phenolic content, colour, and antioxidant activity of commercial, organic, and homemade dried grape, grape pekmez and grape juices produced in the eastern and southern Anatolia.

Materials and Method

Materials

Grapes, and in particular grape products, are rich in phenolic compounds. In grapes, they are present in the pulp, skin, and seeds. Pekmez is a food product made from grapes, figs or mulberry by boiling the fruit paste. It is mainly produced and consumed in Turkey. Dehydration has been extensively utilized for decades as one of the principal food preservation techniques. The intent of this process is to produce shelf stable foods with specific applications and sensory characteristics. The dried grape, grape pekmez and grape juices samples were obtained from different regions produced in the eastern and southern Anatolia. Researches samples were purchased from dried grape, grape pekmez and grape juices produced in the from 10 different regions produced in eastern and southern Anatolia

Methods

Physico-chemical Analyses

Dry matter content was determined by oven-drying 5 g samples at 105°C until a constant weight was obtained. Determination of the ash content of the samples was performed by the method described (AOAC, 2000). 5g of sample was weighed into a clean dry pre weighed silica dish. Then the sample was ignited slowly over a Bunsen flame in a fume cupboard until no more fumes are evolved. Then the dish was transferred to muffle furnace and incinerated until it was free of black carbon particles and turn into white in colour (about three hours). Dish was removed carefully and cooled in desiccators. Weight was taken after cooling. Process of ashing, cooling and weighing was repeated till no further loss in weight was indicated. The acidity and pH values were determined according to Cemeroglu (2013) and pH was measured with a pH meter (model Starter 3100; OHAUS, NJ, USA).

Colour Characteristics Analysis

For colour analysis, the instrument was calibrated with a white reference tile before measurements. The colour of pekmez samples was measured using the CIELAB system with a colorimeter (Minolta CR 400, Minolta Camera Co. Ltd, Osako, Japan) calibrated with a white tile (Minolta calibration plate, No. 21733001, Y = 92.6. x = 0.3136. y =0.3196) at 2° observation angle with a C illuminant source. L* (lightness; 100 = white, 0 = black), a*(redness; +, red; -, green) and b* (yellowness; +, yellow; -, blue) values were recorded. The pekmez samples were put into an optically flat glass dish for measurements.

Total Phenolic Analysis

Extraction of samples: dried grape juices, grape pekmez and dried grape samples acidified methanol (methanol containing 100 µl conc. HCl) 12 hours grape juices, grape pekmez and dried grape samples kept in shaker at room temperature, and then the extract was filtered over Whatman No.1 paper under vacuum, solid parts were removed. Total phenolic content was done according to the method of Thaipong et al. (2006) with some modification. The 20 µL of extract, 1580 µL of pure water, and 100 µL of 0.25 N Folin-Ciocalteu reagents were combined in a plastic vial and then mixed well using a Vortex. The mixture was allowed to react for 3 min then 300 µL of 1.0 N Na_2CO_3 solution was added and mixed well. The solution was incubated at room temperature in the dark for 2 hours. The absorbance was measured at 760 nm using a spectrophotometer. Results were expressed as milligrams of gallic acid equivalents per 100 gram.

Antioxidant activity Analysis

Antioxidant activity was determined by DPPH (1,1-dipheynl-2-picrylhydrazyl) assay. For the determination of free radical scavenging activity, the samples were extracted with methanol (methanol containing 100 µl HCl) by using a shaker at room temperature for 12 hours. Then, and then the extracts were filtered over Whatman No.1 paper under vacuum. Free radical scavenging activity was measured according to the principle of Nakajima et al., (2004) with some modifications reported by Chiou et al. (2007). Fifty microliters of the diluted extracts were added to 1.0 mL of 6×10^{-5} mol L^{-1} DPPH (free radical, 95%, Sigma–Aldrich Chemie GmbH, Steinheim, Germany) in methanol. The mixture was shaken and left at room temperature for 30 min; the absorbance was measured with spectrophotometer at 515 nm. Methanol was used as the experimental control. The percent of reduction of DPPH was calculated according to the following equation: % DPPH reduction= (Ac –As/Ac) ×100. Where A_c is the absorbance of control and A_s is the absorbance of added sample (Tarakci et al. 2013).

Mineral elements analysis

In order to determine the mineral and heavy metal contents of the samples, 2 g of each treatment samples were ashed in a porcelain crucible, solubilized with 10 ml of 6 N HCl, quantitatively transferred into 50 ml volumetric flasks, and diluted to volume with double-deionized water and filtered after 5-6 hours with blue-band filter paper and again regulated to 50 ml (AOAC 2000). Concentrations of calcium (Ca), sodium (Na), magnesium (Mg), zinc (Zn), iron (Fe), copper (Cu), manganese (Mn), molybdenum (Mo), cadmium (Cd), cobalt (Co), Stannum (Sn), Chromium (Cr), nickel (Ni) and lead (Pb) were measured by Inductively Coupled Plasma Optical Emission Spectrometer (ICP–OES, Varian Vista-Pro, Australia). All the analyses were performed in duplicate and the results reported as mean values.

Statistical analysis

The study was designed according to randomized design using 10 grape juices, 10 grape pekmez and 10 dried grape samples. Square root transformation was applied to the grape juice samples, grape pekmez samples and dried grape samples on each chemical, physical mineral and heavy metal contents of the samples were estimated using the SSPS® (2000) statistical software.

Results and Discussion

Chemical and physical characteristics

The chemical and physical characteristics of grape juices, grape pekmez and dried grape samples are given in Table 1. The dry matter, ash and acidity contents of grape product samples were changed between drying types significantly (P<0.05). For grape pekmez, these results are higher than those observed by Bilgicli and Akbulut (2009) for grape pekmez (70.20%), these values similar with the findings of Akbulut et al. (2011) for anther pekmez samples and with the findings of Tüfekci and Fenercioglu (2010) for commercial fruit juices samples. Our pH results are similar observed by Şengül et al. (2007) for carob pekmez samples, Cakmakci and Tosun (2009) for mulberry pekmez with cornelian cherry and with the findings of Haight and Gump (1995) for ret and white concentrate juice samples. For dried grape samples, these results are lower than those observed by Cvetković et al. (2009) for dried fruit samples. These values similar with the findings of Clary et al. (2007) for improving grape quality using microwave vacuum drying associated with temperature control.

L* value is an estimation of food whiteness. The appearance of foodstuffs is the only permitted way to evaluate food products. In that respect, colour is a clue for many qualities of food such as flavor, naturalness or maturity, and drives consumers' choices. An attractive aspect is therefore a key for food marketing, and this has led the food industry to devote much effort in offering pleasant and suggestively colored products (Tarakci et al., 2013). The colour characteristics of grape juices, grape pekmez and dried grape samples dried with differences types methods are shown in Table 1. As shown in Table 2, L* (lightness) values of grapes product samples were important differences significantly (P<0.05). When compared with other samples, lowest L* values were determined in the grape pekmez samples. This is probably because of dark tone of pekmez samples colour. These results are in good agreement with the findings of Bilgiçli and Akbulut et al. (2009) for colour characteristics of the grape pekmez samples. As shown at Table 1, a* (redness; +, red; -, green) and b* (yellowness; +, yellow; -, blue) values of grapes samples were showed important between product types statistically (P<0.05). The pekmez samples that concentrated with thermal showed the lowest values in a* colour. The values of a* and b* color are in good agreement with the findings of Bilgiçli and Akbulut et al. (2009) for colour characteristics of the grape pekmez samples. This situation was also acceptable in the industrial production of grape juices, grape pekmez and dried grape samples for which colour intensity of the product needs to meet the consumers' demands.

Table 1. Grape juice, grape pekmez and dried grape some chemical, phenolic and color values

	Grapes juice	Grape pekmez	Dried grapes
Dry matter (%)	17.22±2.86b	78.73±2.71a	92.08±2.08a
pH	4.05±0.51b	5.32±0.19a	4.57±0.62a
Ash (%)	1.61±0.08c	2.77±0.48b	3.09±0.38a
L values	52.37±2.37a	18.28±0.98c	35.72±2.49b
a values	5.28±0.73a	1.93±0.39b	6.15±1.43a
b values	24.49±2.74a	0.54±0.28c	17.73±2.19b
Total Phenolic (mgGAE/100g)	176.11±4.07c	329.40±8.37b	471.64±6.91a
DPPH reducing power (%)	31.72±3.90b	64.13±1.95a	39.28±0.37b

DPPH reducing power (%); 2,2 diphenyl-1- picrylhydrazyl

Fruits and vegetables account for a small part of our daily caloric intake; however their benefits to health surpass their caloric contribution (Loliger, 1991). As shown in Table 2, total phenolic contents of grape juices, grape pekmez and dried grape samples were changed between product types significantly (P<0.05), the highest level of phenolic content of samples was found in sulfuring dried grapes samples; 471.64±6.91 mgGAE/100g, while the lowest content was found in grape juices, grape pekmez and dried grape samples in grapes juices samples; 176.11±4.07mgGAE/100g, samples of the pekmez samples, as found 329.27±8.37 mgGAE/100g. However, these results are higher than those observed by Sultana et al. (2012) for dried grape juices, grape pekmez and dried grape samples with difference drying methods and than those values 0.72-0.59 mgGAE/100g observed by Sultana et al. (2012) for dried apricot pestil samples, but lower than those values (4900-7310 mgGAE/100g) found by Ali et al., (2011) apricot varieties in growing Pakistan and found Akin et al. (2008) values (4233-8180 mgGAE/100g) for Malatya apricot varieties. As seen, total phenolic in apricot were decreasing by drying. It is well-known that phenolic compounds contribute to fruit quality and nutritional value by modifying color, taste, aroma, and flavor, and also by providing beneficial health effects. These 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 (Kamiloglu et al., 2009). During the juice processing stages and, particularly, during their storage, the anthocyanin content decreased progressive and irreversibly forming more stable polymeric pigments. These pigments are responsible for changing the grape juice aroma, colour, and flavour (Burin et al., 2010).

Mineral and heavy metal properties of grape product samples

The mineral contents of grape juices, grape pekmez and dried grape samples are shown in Table 2. Differences among the grape product species were observed based on the mineral compositions. The Ca contents of grape juices, grape pekmez and dried grape samples were determined 11.08mg/100g, 14.90mg/100g and 21.11 mg/100g, respectively. Mg content amount of grape juices, grape pekmez and dried grape samples were 7.67, 20.15 and 27.79mg/100g, the Na contents of samples was found to be similar Ca and Mg containing were not changed, 7.11, 14.73 and 12.09 mg/100g. Mn content was found high value amount dried pekmez and grapes samples as 1583 mg/100g, 1796 mg/100g and, while Mn content (285mg/100g) of grapes juices samples were found lowest level, Mn contents were significantly greater ($P<0.05$). (Ustun and Tosun, 2003) studied on pekmez samples similar Ca and Mg content than in the present study, but lower Na and Mn content. (Çakmakcı and Tosun ,2010) studied pekmez samples added cornelian cherry and they found lower Ca and Na content Mg contents with the present study, but lower level Mn (Şimşek and Artık, 2002) reported that Ca and Mg contents in pekmez of grapes growing in Turkey were higher than that of our findings, but lower Na, Mn contents. It can be explained that all the products had different mineral content, because they have different areas. Generally, minerals from plant sources are less bioavailable than those from animal sources. The more important minerals involved in the building of rigid structures to support the body, i.e. Ca, P and Mg, were well furnished by the vegetable species studied. These three elements in appreciable amounts are essential for the proper formation of bones and teeth. For example, in Ca, 99% of the total amount (i.e. 1000-1200 g in adult) occurs in bones and teeth while about 600-700 g of P is also present in bones and teeth. The two elements, together with a much smaller quantity of Mg (20-80 g), form a crystal lattice, which is largely responsible for the rigidity and strength of bones and teeth (Aletor et al. 2002).

Table 2 shows Fe, Cu, Zn, Cr and Co mineral contents of the grape juices, grape pekmez and dried grape samples. The Fe contents of grape juices, grape pekmez and dried grape samples were found between 74.79mg/kg, 126.57 mg/kg and 175.92 mg/kg, respectively. Cu and Zn containing of grape juices, grape pekmez and dried grape samples were between 21.47, 78.51 and 96.97mg/kg, the Cr and Co contents of samples were changed 1.51, 6.20 and 4.54 mg/kg and 1.44, 2.31 and 2.81mg/kg, respectively. Cvetković et al. (2009) studied on dried fruit samples and they found similar Ca and Na, but lower Fe content than in the present study. Clary et al. (2007) found lower Ca contents in dried fruit samples with the present study, but higher Fe content. Katherine and Gump (1995) reported similar that Ca, Na, Fe content, but higher Mg of red and white grape juice concentrate samples lower than that of our findings. Fe and Cu contents of fruit and vegetable play an important role in the final quality of the products as well as their nutritional and biological role, when certain alternative reactions intervene. The presence of high Fe and Cu concentrations from adventitious contamination are damaging to product quality since in an ionized form, they catalyze oxidation reactions of the lipids with development of unusual flavours (Sancak et al. 2008). Bilgicli and Akbulut (2009) studied minerals and trace elements in dried grapes varieties. They found Ca and Na content higher than in the present study, but lower Mg, Co, Cr, Fe, Cu and Zn content. Akbulut and Özcan (2009) studied minerals and trace elements in mulberry fruit and their pekmez. They found similar Ca, Na and Mg contents. Koca et al. (2008) studied minerals and trace elements in mulberry furit pulp and they found higher Ca content than in the present study, lower Cu, Fe, Zn, Mg, and Mn contents.

Table 2. Grape juice, grape pekmez and dried grape mineral and heavy metal content (mg/kg)

	Grapes juice	Grape pekmez	Dried grapes
Mn	285.29±37.36	1583.15±42.19	1796.09±76.47
Ca	11.08±2.15	14.90±4.01	21.11±6.15
Mg	7.67±3.08	20.15±7.12	27.79±5.17
Na	7.11±3.34	14.73±4.75	13.09±5.28
Fe	74.79±8.09	126.57±18.12	175.92±42.15
Cu	21.47±5.13	78.51±13.25	96.97±23.18
Zn	26.39±6.72	38.36±8.43	77.46±11.2
Cd	3.83±0.81	6.20±1.45	6.57±1.19
Mo	0.01±0.00	0.02±0.01	0.06±0.03
Sn	0.33±0.13	0.78±0.25	0.29±0.09
Pb	0.14±0.12	0.24±0.21	0.47±0.17
Cr	1.51±1.48	6.20±0.82	4.54±1.25
Co	1.44±0.15	2.31±0.73	2.81±0.56
Ni	0.33±0.11	3.68±0.28	1.53±0.49

Table 2 shows Pb, Ni, Sn, Cd and Mo heavy metal contents of the grape juices, grape pekmez and dried grape samples in difference drying methods. The sources of high levels of Pb and Cd are likely to be the transferred from the tin can and salt used in the brine. The FAO/WHO has set a limit for heavy metal intakes based on body weight. For an average adult (60 kg body weight), the provisional tolerable daily intakes for lead, iron, copper and zinc are 214 µg, 48 mg, 3 mg and 60 mg, respectively (FAO/WHO, 1999). Turkdogan et al. (2003) studied heavy metals of vegetables and fruits grown in East Anatolian region. Their Cd results were higher than in the present study. Differences might have been due to various sources of raw materials used in the manufacture. There is overwhelming evidence that several media including road dust and plants sampled in the vicinity of roads carrying heavy traffic are contaminated by some elements. Our phenolic and flavonoid results of grape juices, grape pekmez and dried grape samples support this idea. It is clear that phenolic acids levels in red and black grapes variety explain their sour, astringent taste. The variation of phenolic compounds in the fruits depends on many factors, such as degree of maturity at harvest, genetic differences, and environmental conditions during fruit development (Erçişli and Orhan, 2007).

Overall, our region was an agricultural region, substantial amounts of artificial fertilizers are used and it was also very dusty. B, Cd, Co, Pb, and Zn elements may be passed to herbs by means of wind-blown dust, soil and water. Other inorganic elements which may contribute to biological processes, but which have not been established as essential, are barium, bromine, cadmium, lead and lithium (Macrae et al. 1993). As a result, it is considered to be important because of their nutritive, physiological and technological significant. Also this study, attempts to contribute to knowledge of the nutritional properties of these cultivated apricot fruits. In addition, knowledge of the mineral contents, as fruits is of great interest (Haciseferogullari et al., 2007). Due to the limited number of samples determined in this work, this conclusion should be for sweet apricot dried samples.

As a conclusion of this study, it can be said that mulberry fruits are a valuable horticultural product, based on their rich and beneficial nutrient composition. Certain growing conditions and cultural management techniques, affecting the nutritional value of mulberry grape juices, grape pekmez and dried grape samples, grapes species, will be the subject of further research projects.

Conclusion

The mineral composition of grape product variety depended, not only on the species or varieties, but also on the growing conditions, such as soil and geographical conditions. In this study, while the existence of ten elements was determined in all grape juice, grape pekmez and dried grape species, Mn was predominant, followed by Fe, Cu, Zn, Mg, Na, Ca and Mo. As a conclusion of this study, it can be said that mulberry fruits are a valuable horticultural product, based on their rich and beneficial nutrient composition. Certain growing conditions and cultural management techniques, affecting the nutritional value of mulberry species, will be the subject of further research projects. Consumption of these products may become widespread as an antioxidants, phenolic, mineral and heavy metal source. The study on these products is detailed in order to achieve more standardization of the results.

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