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Investigation of pesticide residues in fresh Sultani grapes and antioxidant properties of fresh/sun-dried/oven-dried grapes

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Abstract: Grape is one of the most common crop plants in the world, and Turkey is seventh in fresh grape production. The seedless Sultani grape (*Vitis vinifera* L.) produced in Manisa is famous worldwide. The determination of antioxidant properties and phenolic substance levels, as well as investigation of the effects of different drying processes on these levels in grapes, is important in terms of revealing their contribution to health. Additionally, determining the levels of pesticide residues in fruit is another important issue for health. Therefore, the aim of this study was to determine the levels of pesticide residues and antioxidant substances in fresh grapes and to evaluate the benefits and harm to health and the effect of drying methods on total antioxidant capacity (TAC), total phenolic content (TPC), and total flavonoid content (TFC). The TAC, TPC, and TFC values of fresh grapes were found to be 12.56 ± 2.33 mg AE/g dry weight (DW), 2.85 ± 1.10 mg GAE/g DW, and 2.51 ± 1.27 mg QE/g DW, respectively. At least one pesticide residue was detected in all samples; iprodione and lambda-cyhalothrin were detected in 82.35% of samples. However, pesticide residues were found to be below the maximum residue levels specified in the Turkish Food Codex. Losses in TAC, TPC, and TFC of the Sultani grapes were found to be 47.45%, 55.02%, and 81.05% and 80.00%, 72.91%, and 72.11% for oven-dried and sun-dried grapes, respectively, in our study. The sun-drying method leads to less loss in TPC and TFC values; in terms of TAC value, the best drying method is the oven-drying method. The antioxidant properties of fresh grapes investigated in our study were slightly higher compared to other white grapes in the literature, and there was no significant health risk with respect to pesticides determined in our study.

Key words: Antioxidant, drying, flavonoid, pesticide, phenolic, Sultani grape

1. Introduction

Phytochemicals are naturally occurring chemicals primarily found in vegetables and fruits and are assumed to be predominantly responsible for protective health benefits. Vitamins, minerals, and phenolic compounds are important phytochemicals in vegetables and fruits (Canan et al., 2016; Rodriguez-Casado, 2016; Aubert and Chalot, 2018). Previous studies have shown the positive effects of phytochemicals on human health. Phenolic compounds have strong antibacterial and antioxidant activities. In addition, in vitro, in vivo, epidemiological, and clinical trial data suggest that a diet that includes vegetables and fruits can reduce the risk of some human cancer types (Meyskens and Szabo, 2005; Ercişli et al., 2007). Grapes (*Vitis vinifera* L.) contain significant varieties of vitamins and polyphenolic compounds (Rodriguez-Casado, 2016; Aubert and Chalot, 2018); consumption of grapes as fruits, raisins, wine, or juice is preferred by most people. The positive effects of phenolic compounds in grapes on various diseases have been reported in recent studies, such as antiinflammatory effects (Terra et al., 2007) and antihyperglycemic effects (Pinent et al., 2004). Grape is one of the most common crop plants in the world. Today, approximately 7.6 million hectares of land produce grapes around the world. Turkey is seventh in the world in terms of fresh grape production[1]. An average of 4,200,000 tons of grapes produced in the world are dried and evaluated. Our country has shared the first two places in the world with the US for production of seedless raisins for many years. Raisins obtained from seedless Sultani grapes in Turkey are famous worldwide. Manisa in the Aegean region is the most important place in terms of Sultani grape production, and is responsible for 31% of total grape production and 80% of the production of seedless grapes in Turkey. Approximately 95% of the grapes produced in Manisa Province are Sultani grapes. One of the leading export areas is Turgutlu district in Manisa, where Sultani grapes are produced in about 77,500 square meters of land[2]. To determine the antioxidant properties of such a significant fruit produced in our country and to determine

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how drying methods affect these properties is a very important issue, because of their various health benefits.

Pesticides are frequently used in the preharvest period and postharvest storage of crops because of various diseases and types of pests that cause harm to the grapes (Gazioğlu Şensoy et al., 2017; Yakar, 2018). Several studies have shown the presence of pesticides in grapes, with levels exceeding maximum residue levels (MRLs). For example, a total of 999 samples including 180 fresh grape samples were studied between 1996 and 2000 in the project carried out by Ankara and İzmir Provincial Control Laboratory Directorates and Bursa Food Control and Central Research Institute. As a result of the study, values of tolerance were found to be 6.6% in fresh grape samples (KKGM, 2002). In another study, it was determined that 72 of 87 grape samples taken from the Aegean region contained pesticide residues and the residual amounts of 18 samples were higher than MRLs listed in the Turkish Food Codex (Bakırcı et al., 2014). In a study conducted in 2008, of 173 samples collected from vineyard areas in İzmir, Denizli, and Manisa and analyzed, 17 of 99 fresh grape samples and 7 of 74 raisin samples were found to surpass the MRL (Örnek, 2008). The fresh grapes harvested from 6 different vineyards from Alaşehir in Manisa in 2015 were investigated by Dinçay et al. (2017); at least one pesticide over the MRL was found in harvests from 2 vineyards. In another study, a total of 280 samples of table grapes were collected from supermarkets, bazaars, and greengrocer shops located in 4 provinces of Turkey from August to October 2016; one or more pesticide residues were detected in 59.6% of the table grapes (Gölge and Kabak 2018). Residues above the EU maximum residue levels were in 20.4% of the samples in this study. Moreover, Turkey leads with 83 notifications in the category of fruit and vegetable products in terms of pesticide residue hazard according to the Rapid Alert System for Food and Feed (RASFF) annual report 2017 published by the European Union (EU) (RASFF, 2018). For this reason, it is very important to examine the pesticide residues in any health evaluation of the grapes grown in our country. Increased and uninformed consumption of pesticides results in adverse effects in terms of human health and environmental pollution (Ersoy et al., 2011). Recent studies have reported that pesticides may be related to many diseases such as cancers, leukemia, hormone disorders, asthma, allergic reactions, and hypersensitivity reactions (Van Maele-Fabry et al., 2010; Kim et al., 2017). Moreover, they cause health problems such as decreased birth weight, birth defects, and fetal death (Bell, 2001; Kalliora et al., 2018). Therefore, compliance with the legislation on pesticide residues needs to be strictly controlled to protect human and environmental health. In order to evaluate grapes in all aspects of health, it is necessary to examine both antioxidant properties and pesticide residue levels. Therefore, our first aim was to determine the antioxidant properties and pesticide residue levels of fresh Sultani grapes and to evaluate the results from this study in respect to health. In addition, Sultani grapes produced in our country are mostly consumed and exported as raisins. Thus, the second aim of this study was to determine the impacts of sun- and oven-drying methods on total antioxidant capacity and phenolic and flavonoid contents of Sultani grapes. We did not find any studies evaluating Sultani grapes with these 2 purposes together in a literature survey.

2. Materials and methods

Samples of Sultani grapes were collected from the villages of Turgutlu in Manisa. The samples were collected at the proper harvest time. Approximately 5-kg samples of Sultani grapes from 17 different vineyards grown in the Turgutlu district were collected homogeneously from the vineyards to represent the entire area according to the guidelines of the Turkish Food Codex Communiqué on Sampling Methods for Official Control of Pesticide Residues in Foods (GTHB, 2011). The samples were immediately transported to the laboratory located in Kastamonu in cooling containers and stored in a cold room at 4 °C until drying and antioxidant activity analyses (storage time was 1 day) and pesticide residues analysis processes (storage time was 2 days). One kg of the collected samples was reserved for fresh grape analysis; the remaining 4 kg was divided into 2 equal parts for the sun and oven drying. Two replicates were performed in all of the analyses. All of the chemicals and reagents used in this study were of analytical purity. Folin and Ciocalteu's phenol reagent and gallic acid, ascorbic acid, and quercetin standards were obtained from Sigma Chemical Co. (St Louis, MO, USA). The pesticide standards were purchased from Supelco/Sigma-Aldrich (St Louis, MO, USA) and Dr. Ehrenstorfer GmbH (Augsburg, Germany). Q-sep QuEChERS Q150 extraction kit and Q350 Q-sep dSPE clean-up kit (AOAC 2007.01) used for pesticide residues from grapes were purchased from Restek (Bellefonte, PA, USA). Hach Lange DR6000 UV-visible spectrophotometer (Hach Company, Loveland, CO, USA), Elma-S 100H ultrasonic bath (Elma Schmidbauer GmbH, Singen, Germany), Hettich 320 Universal centrifuge (Andreas Hettich GmbH, Tuttlingen, Germany) were used in the antioxidant activity analyses. QP 2010 Ultra GC-MS (Shimadzu, Kyoto, Japan) equipped with Rtx-5MS-Low-Bleed GC-MS Column [30 m length, 0.25 mm inner diameter (ID), 0.25 μm film thickness (df); Restek, Bellefonte, PA, USA] and 8030 Plus HPLC-MS-MS (Shimadzu, Kyoto, Japan) devices, and an Inertsil ODS-4 HP HPLC column [100 Angstrom (Å), 3μm, 4.6 × 50 mm; GL Sciences Inc., Tokyo, Japan] were used in the pesticide

analyses. A Protech PLF brand oven (PROTEK, Ankara, Turkey) was used in the oven-drying process.

2.1. Drying methods

2.1.1 Oven drying

Fresh grapes were placed into the drying oven in a tray at 60 °C. Some undesirable reactions (especially related to sugars in fruit; these reactions may also lead to weight losses other than loss of moisture of fruit, resulting in incorrect moisture analysis) occurrs at temperatures above 60 °C in fruits. Furthermore, 60 °C is the common commercial drying standard temperature. The drying process time of the grapes in the oven was 24 h (Cemeroğlu, 2013). A standard oven (Protech PLF) was used for the drying process. The final moisture content of the oven dried grapes was 19.12 ± 3.84% on average.

2.1.2. Sun drying

Fresh grapes were spread on trays and placed in sunlight. The relative humidity and air temperature during sun drying were between in the range of 52%–90% and 24.6–30.9 °C, respectively. The duration of drying in the sun lasted 14 days; the grapes were turned over every day by hand. Thus, homogenous drying was ensured for all parts of the grapes. The final moisture content of the sun-dried grapes was 11.17% ± 3.13%, averagely.

2.2. Sample preparation for antioxidant analyzes

Each grape sample was homogenized and extracted with 30 mL of acidified methanol for 30 min with the aid of an ultrasonic bath. This extraction process was repeated 3 times. The combined extracts were centrifuged at 8000 × g for 15 min. The supernatants were stored at –20 °C until used in the analyses (Meng et al., 2011; İçli, 2017).

2.3. Determination of total phenolic content (TPC)

Gallic acid was used as standard; stock standard solution of gallic acid at a concentration of 100 mg/L was prepared in methanol, and 5 different concentrations of gallic acid were obtained by dilution from this concentration. Then, 200 µL of each grape extract was placed into the test tubes and 1 mL of Folin–Ciocalteu reagent was added to each tube. Later, 2 mL of 7.5% Na_2CO_3 solution was added to each sample tube and the total volume was brought to 7 mL with distilled water. The mixture was kept in the dark for 2 h under room conditions and the absorbance at 765 nm was measured. All of these processes were completed for standard solutions of gallic acid. The TPC of grape extracts is given as mg gallic acid equivalent per g dry weight of grape samples (mg GAE/g DW) (Slinkard and Singleton, 1977).

2.4. Determination of total flavonoid content (TFC)

Quercetin stock standard solution was prepared at a concentration of 200 mg/L in methanol; dilution from this concentration yielded 5 different concentrations of quercetin calibration standard solutions. Grape extracts were incubated with the same volume of 2% $AlCl_3$ for 10 min under room conditions. The absorbances of the samples were recorded at 415 nm. The same procedure was performed for quercetin as standard and the TFC of the samples was calculated as mg quercetin equivalent per g dry weight of samples (mg QE/g DW) (Arvouet-Grand et al., 1994).

2.5. Determination of total antioxidant capacity (TAC)

There are several methods in the literature for determining total antioxidant capacity. The phosphomolybdenum method is based on the reduction of Mo (VI) to Mo (V) and the formation of a green phosphate/Mo (V) complex in an acidic environment, and a quantitative method to investigate the reduction reaction rate among antioxidants. This method is advantageous in that it is simple and uses inexpensive reagents, as well as directly measuring the reducing capacity of the antioxidant and, unlike CUPRAC and FRAP, forms a green phosphonolybdenum complex without induction of the solution of free metal ions (Prieto et al., 1999; Phatak and Hendre, 2014). Ascorbic acid was prepared as a stock standard solution at 500 mg/L concentration and diluted to 5 different concentrations for calibration. Then, 0.6 M H_2SO_4 solution, 28 mM $Na_2HPO_4.12H_2O$ solution, and 4 mM ammonium molybdate solution were prepared, and 25 mL of each were used as reagent solution. A 0.3-mL sample of grape extract was placed in separate tubes and 3 mL of the reagent solution was added to these tubes. The tubes were vigorously stirred and incubated at 95 °C for 90 min. The absorbance of the solutions was recorded at 695 nm at the end of the incubation time. The same procedure was performed for ascorbic acid, which was used as a standard antioxidant. TAC was calculated as mg ascorbic acid equivalent per g dry weight of samples (mg AE/g DW) (Prieto et al., 1999).

2.6. Pesticide residue analysis

The pesticides with MRLs identified or banned in "The Regulation of Maximum Residue Limits of Pesticides" of the Turkish Food Codex for grape and vine leaf were selected for this study. The pesticides used for cherries and olives, which are widely produced in Manisa Province, and their MRLs in this regulation were also considered due to the possibility of contamination. In addition, the pesticides that were examined in previous studies (Tatlı, 2006; Örnek, 2008; Turgut et al., 2011; Bakırcı et al., 2014; Yakar, 2018) on grape in Manisa Province were considered. Consequently, those present in the Kastamonu University Central Research Laboratory were selected for the study. Aldicarb, aldicarb sulfoxide, aldoxycarb, carbaryl, carbofuran, 3-hydroxycarbofuran, methiocalb, methomyl, oxomyl, and propoxur were analyzed by HPLC-MS-MS (Shimadzu) device in this laboratory. Aldrin, dieldrin, azinphos-ethyl, azinphos-methyl, bifenthrin, beta-

cyfluthrin, bromopropylate, captan, chinomethionate, chlorothalonil, chlorpropham, chlorpyrifos-methyl, alpha-BHC, beta-BHC, gamma-BHC, demeton-S, diazinon, dicofol, dinobutone, disulfotone, alpha-endosulfan, beta-endosulfan, endosulfan sulfate, ethion, esfenvalerate, fenvalerate-2, fenitrothion, folpet, hexachlorobenzen, heptachlor, iprodione, formothion, malathion, parathion, parathion-methyl, procymidone, permethrin-1, permethrin-2, alpha-cypermethrin, cypermethrin, kresoxim-methyl, lambda-cyhalothrin, methamidophos, oxyfluorfen, tau-fluvalinate, tetradifon, trifluralin, and vinclozolin were investigated by GC-MS. The pesticide extraction method was followed by the QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method (Lehotay et al., 2005). The QuEChERS (AOAC 2007.01) method has found a very common application area for pesticide analysis for several foods, due to its simplicity and effectiveness. Ten g of the homogenized sample and Q-sep QuEChERS Q150 extraction kit (QuECHERS Extraction Salt 6 MgSO4, 1.5 g NaOAc) were transferred to a 50-mL centrifuge tube, and 10 mL of acetonitrile solution containing 1% acetic acid was added to the same tube. The tube was capped tightly and shaken vigorously for 1 min and then centrifuged at 5000 rpm for 1 min. The supernatant and a Q350 Q-sep dSPE clean-up kit (1200 mg MgSO4 + 400 mg PSA) were transferred to a 15-mL tube. The tube was capped tightly and shaken vigorously for 30 s, and then tube contents were centrifuged at 5000 rpm for 1 min. Finally, 0.5 mL of the filtered supernatant was placed into a glass vial and the vial was placed in the autosampler of HPLC-MS-MS or GC-MS devices for pesticide analysis. QP 2010 Ultra GC-MS with equipped Rtx-5MS-Low-Bleed GC-MS Column were used in the pesticide analyses; total analysis time, injection volume, injection temperature, injection mode, sampling time, carrier gas, column flow, ion source temperature, interface temperature, solvent cut time, and detector voltage were 24 min, 2 µL, 270 °C, splitless, 1 min, He, 1.69 mL/min, 230 °C, 270 °C, 3 min, and 0.6 kV, respectively. An 8030 Plus HPLC-MS-MS (Shimadzu, Kyoto, Japan) device and an Inertsil ODS-4 HP HPLC column were used in the pesticide analyses; total analysis time, injection volume, flow rate, interface, nebulizing gas flow, DL temperature, heat block temperature, drying gas flow, and column oven temperature were 10 min, 10 µL, 0.40 mL/min, ESI, 3 L/min, 250 °C, 400 °C, 15 L/min, and 40 °C, respectively. Gradient elution mode was used in the HPLC-MS-MS analysis and the 5 mM ammonium format in water and acetonitrile were used as mobile phases A and B, respectively. The gradient elution program of HPLC-MS-MS analysis and oven temperature program of GC-MS analysis are given in Table 1.

Selected ions of each pesticide and a chromatogram of standard mixture and a real sample are provided in a supplemental table for this article. The amounts of pesticide residue for fresh grape samples were lower than MRL levels; thus, pesticides were not investigated in the dried samples. Pesticides are exposed to both heat and light when dried in the sun, and they are exposed to heat greater than that of sun drying when dried in an oven (Cabras et al., 1998). The reason why we did not perform pesticide analysis after drying is that there have been several studies (Cabras et al., 1998; Özbey 2003; Özbey and Uygun, 2006) showing that pesticide residues decreased to a great extent (64.2%–92.73%) at the end of the drying period for both sun drying and oven drying.

2.6.1. Method performance parameters

Stock pesticide standard mixture solution (2000 ppb) was prepared by spiking into grapes free of residues. The calibration standard solutions were prepared by diluting with chromatographic acetonitrile from this stock solution. The linear calibration curve was constructed using standard solutions of pesticides in the range of 5–200 ppb (6 point). The correlation coefficients (R^2) of this calibration curve were in the range of 0.9983–0.9999 and 0.9800–0.9996 (except for permethrin and trifluralin; R^2: 0.9657 and 0.9700, respectively) for the HPLC-MS-MS and GC-MS multiresidue pesticide analysis methods, respectively. However, it is acceptable to have more than 0.98 in multiple residue analysis studies (AOAC, 2002; Thompson et al., 2002). The limit of detection (LOD) (3 × signal/noise)

Table 1. The gradient elution program of HPLC-MS-MS analysis and oven temperature program of GC-MS analysis.

Gradient program of HPLC-MS-MS			**Oven temperature program of GC-MS**			
Time (min)	Mobile phase A %	Mobile phase B %	Level	Rate (°C/min)	Final temperature (°C)	Hold time (min)
0	5	95	0	-	90	2
5.50	5	95	1	30	150	0
5.51	95	5	2	10	300	10
10	95	5				

values were found to be between 0.09–1.13 and 1.20–3.54 ppb in HPLC-MS-MS and GC-MS analyses, respectively. The limit of quantification (LOQ) of the methods were expressed as the lowest spike level of the validation meeting these method performance acceptability criteria according to the SANTE guidance document (2017) and in the range of 0.31–5.15 and 2.73–7.05 ppb for HPLC-MS-MS and GC-MS, respectively. To check the accuracy, spiking with standards to the blind matrix was performed at 2 different concentrations (10 and 100 ppb) and each concentration was subjected to 6 replicate analyses. The average recovery values were determined as 89%–105% and 51%–127% for the HPLC-MS-MS and GC-MS methods, respectively. The RSD of repeatability (RSDr) values were between 5.0% and 12% of HPLC-MS-MS and between 5.4% and 16.9% of GC-MS methods, respectively. The RSD of reproducibility (RSDR) values were between 13.0% and 19.2% of HPLC-MS-MS and between 18.4% and 24.7% of GC-MS methods, respectively. All details of these method performance parameters are provided in a supplemental table for this article. Acceptable mean recoveries obtained in a validation process are those within the range 70%–120% and RSD of repeatability (RSDr) ≤20%, for all pesticides within the scope of a method according to SANTE's guidance document (2017). The recovery rates of some pesticides (for 4 pesticides) in our study were determined to be outside this range. However, the recovery rates outside the range of 70%–120% may be acceptable if they are consistent (RSDr ≤ 20%), and the mean recovery should not be lower than 30% or above 140%, according to the SANTE guidance document (2017). Since the recovery rates of very few pesticides were outside the acceptable range in our study, and the results obtained were in accordance with the abovementioned criteria, the method performance of our study was considered to be acceptable.

2.7. Soluble solids and dry matter analysis

Soluble solids and dry matter analyses were performed according to AOAC Official Method 932.12 and AOAC Official Method 934.06, respectively.

2.8. Statistical analyses

Statistical data evaluation was completed using the analysis of variance (ANOVA) and the differences among the means were compared with Duncan's multiple range tests using the SPSS 17 statistical software program.

3. Results and Discussion

The best drying efficiency of the Sultani seedless grape variety was 20–22 °Bx. Thus, the amount of sugar present in the grapes at the beginning of drying was around 20% (Akdeniz, 2011). Therefore, the samples were collected with the appropriate brix value at the proper harvest time. The average soluble solids in the grape samples in our study were found to be 20.29 ± 1.94 °Bx. This result shows that we collected samples at the right time for the drying processes. The average dry matter amounts of fresh, sun-dried, and oven-dried grapes are given in Table 2.

TAC, TPC, and TFC analyses were then applied to fresh, sun-dried, and oven-dried samples. The amounts of TAC, TPC, and TFC of fresh, sun-dried, and oven-dried Sultani grape samples are given in Table 3.

The TAC, TPC, and TFC values of the fresh seedless Sultani grape variety, which is a white grape, were found to be 12.56 ± 2.33 mg AE/g DW, 2.85 ± 1.10 mg GAE/g DW, and 2.51 ± 1.27 mg QE/g DW, respectively (Table 4). These results are slightly higher than but consistent with the results reported in the literature for white grapes. For example, the TPC level of Sultanina grapes was determined to be 1.54 ± 28 mg GAE/g DW in the study by Fabani et al. (2017). Similarly, TPC values of various white grapes were found to be 2.18 mg GAE/g (Furmint grape), 1.49 mg GAE/g (Palomino grape), 1.42 mg GAE/g (Semillon grape), and 1.13 mg GAE/g (Sauvignon Vert grape) in a study conducted in Mexico (Franco-Bañuelos et al., 2017). On the other hand, dark grapes have been shown to have higher TPC content in the literature. For example, the highest TPC was found in Rubired grapes, followed by Merlot, Petite Syrah, and Cabernet Sauvignon in a study investigating red grapes by Franco-Bañuelos et al. (2017). In the study about Ekşikara black grapes, a very high TPC value was determined at 20.21 mg GAE/g DW in fresh grapes due to the high content of anthocyanin (Çoklar and Akbulut, 2017). However, the antioxidant capacity and phenolic and flavonoid contents of the white Sultani grape are considerable amounts and should not be underestimated. In addition, these grapes are greatly appreciated by consumers in terms of taste and appearance.

At least one pesticide residue was detected in each fresh sample in our study. The results of pesticide analysis of fresh Sultani grapes are given in Table 5. Iprodione and lambda-cyhalothrin were detected in 14 of the 17 samples (82.35%) in this study. Iprodione is a fungicide used for *Botrytis Cinerea* mould and lambda-cyhalothrin is an insecticide used against *Agrotis ypsilon* and *Lobesia*

Table 2. The average dry matter amount of fresh, sun-dried, and oven-dried grapes.

Sample type			
Dry matter (%w/w)	Fresh	Sun-dried	Oven-dried
Lowest	32.07	86.31	93.7
Highest	19.68	74.10	83.42
Average ± SD	24.11 ± 3.38	80.88 ± 3.84	88.83 ± 3.13

SD: Standard deviation.

Table 3. TAC, TPC, and TFC levels of grape samples.

Samples no	Drying process	TAC (mg AE/g DW)	TPC (mg GAE/g DW)	TFC (mg QE/g DW)
1	A	15.97 ± 0.03	1.69 ± 0.01	1.77 ± 0.01
	B	5.70 ± 0.00	0.39 ± 0.00	0.47 ± 0.00
	C	8.35 ± 0.07	0.34 ± 0.01	0.43 ± 0.02
2	A	12.53 ± 0.03	2.80 ± 0.01	2.57 ± 0.00
	B	5.67 ± 0.01	0.52 ± 0.01	0.69 ± 0.03
	C	6.58 ± 0.03	0.59 ± 0.02	0.63 ± 0.01
3	A	8.75 ± 0.00	1.72 ± 0.02	1.37 ± 0.01
	B	5.59 ± 0.01	0.80 ± 0.00	0.91 ± 0.01
	C	7.60 ± 0.00	0.65 ± 0.00	0.69 ± 0.00
4	A	13.69 ± 0.00	2.99 ± 0.01	3.43 ± 0.02
	B	5.19 ± 0.00	0.55 ± 0.00	0.72 ± 0.00
	C	6.04 ± 0.00	0.59 ± 0.00	0.68 ± 0.02
5	A	9.84 ± 0.01	3.94 ± 0.00	1.99 ± 0.00
	B	6.00 ± 0.00	0.61 ± 0.01	0.74 ± 0.00
	C	5.71 ± 0.01	0.59 ± 0.01	0.81 ± 0.01
6	A	12.59 ± 0.02	2.90 ± 0.00	2.45 ± 0.05
	B	5.63 ± 0.07	0.62 ± 0.02	0.71 ± 0.01
	C	6.62 ± 0.02	0.49 ± 0.06	0.73 ± 0.03
7	A	9.54 ± 0.00	3.63 ± 0.01	1.98 ± 0.02
	B	5.30 ± 0.00	0.75 ± 0.00	0.69 ± 0.01
	C	7.91 ± 0.01	0.48 ± 0.02	0.64 ± 0.00
8	A	12.83 ± 0.00	2.13 ± 0.01	2.92 ± 0.02
	B	5.29 ± 0.01	0.54 ± 0.00	0.98 ± 0.00
	C	6.79 ± 0.01	0.49 ± 0.01	0.44 ± 0.00
9	A	14.54 ± 0.01	4.95 ± 0.00	6.30 ± 0.01
	B	5.99 ± 0.00	0.66 ± 0.00	1.20 ± 0.00
	C	7.48 ± 0.02	0.78 ± 0.02	1.35 ± 0.00
10	A	14.31 ± 0.02	3.39 ± 0.00	2.91 ± 0.02
	B	5.89 ± 0.00	0.55 ± 0.00	0.80 ± 0.00
	C	6.69 ± 0.00	0.60 ± 0.01	0.70 ± 0.00
11	A	14.77 ± 0.03	2.39 ± 0.00	1.81 ± 0.01
	B	4.95 ± 0.00	0.59 ± 0.00	0.56 ± 0.01
	C	5.98 ± 0.02	0.58 ± 0.02	0.72 ± 0.00
12	A	9.28 ± 0.02	1.72 ± 0.00	1.19 ± 0.00
	B	5.50 ± 0.00	0.44 ± 0.01	0.45 ± 0.00
	C	5.95 ± 0.07	0.50 ± 0.00	0.74 ± 0.01
13	A	14.09 ± 0.01	2.29 ± 0.02	3.14 ± 0.02
	B	5.94 ± 0.00	0.69 ± 0.01	0.79 ± 0.01
	C	5.74 ± 0.01	0.44 ± 0.01	0.51 ± 0.01

Table 3. (Continued).

14	A	11.38 ± 0.02	2.19 ± 0.00	1.81 ± 0.03
	B	5.65 ± 0.00	0.50 ± 0.00	0.54 ± 0.01
	C	6.59 ± 0.01	0.49 ± 0.01	0.89 ± 0.01
15	A	12.57 ± 0.00	2.84 ± 0.01	2.49 ± 0.02
	B	5.63 ± 0.01	0.58 ± 0.02	0.71 ± 0.02
	C	6.59 ± 0.02	0.54 ± 0.00	0.67 ± 0.01
16	A	12.64 ± 0.01	4.84 ± 0.01	2.88 ± 0.02
	B	6.39 ± 0.01	0.59 ± 0.00	0.59 ± 0.01
	C	5.95 ± 0.00	0.64 ± 0.01	0.49 ± 0.00
17	A	14.30 ± 0.02	2.12 ± 0.00	1.64 ± 0.01
	B	5.71 ± 0.00	0.40 ± 0.00	0.44 ± 0.00
	C	5.64 ± 0.01	0.49 ± 0.01	0.50 ± 0.00

A: Values of fresh grapes; B: Values of sun-dried grapes; C: Values of oven-dried grapes. DW: Dry weight.

Table 4. The effect of drying process on TAC, TPC, and TFC values of grape samples.

Process		TAC (mg AE/g DW) Mean ± SD	TPC (mg GAE/g DW) Mean ± SD	TFC (mg QE/g DW) Mean ± SD
A		12.56 ± 2.33^{c}	2.85 ± 1.10^{c}	2.51 ± 1.27^{c}
B		5.65 ± 0.37^{a}	0.57 ± 0.12^{b}	0.70 ± 0.21^{b}
C		6.60 ± 0.88^{b}	0.54 ± 0.10^{a}	0.68 ± 0.23^{a}
Source	DF			
Grape sample (X)	16	**	**	**
Process (Y)	2	**	**	**
X × Y	32	**	**	**
Error	51			
Total	102			

A: Values of fresh grapes; B: Values of sun-dried grapes; C: Values of oven-dried grapes. DW: Dry weight. Means followed by the same superscript letter within each column are not significantly different at $P < 0.01$ probability levels; ** significant at 0.01 probability levels, respectively.

botrana in the vineyards. Chlorpropham was found in only 1 sample. The amounts of chlorpropham, iprodione, and lambda–cyhalothrin were found to be below the maximum residue levels (MRL) specified in the Turkish Food Codex, Regulation on Maximum Residue Limits of Pesticides (GTHB, 2016). Similarly, while 73.33% of fresh grape samples taken from Manisa contained pesticide residues, 26.66% of the grapes were found to be free of residues (Tatlı, 2006). There are important data in the literature for iprodione. Iprodione was detected at an average amount of 0.504 ppm (MRL 0.02 ppm) in 5 of 191 table grapes of Italian origin, and an average of 0.457 ppm in 77 of 203 South African samples (Poulsen et al., 2007). In a study carried out by Örnek in 2008, the pesticides identified in fresh Sultani grapes from Manisa and Turgutlu production areas are below MRLs, in accordance with our study. Iprodione and lambda-cyhalothrin were among the pesticides found in that study. Turgut et al. (2011) determined lambda-cyrothrin and iprodione in 15 of 45 and 3 of 45 samples taken from Manisa, respectively, in a study of samples from vineyards in Manisa, İzmir, and Denizli. In another study, it was determined that 72 of 87 grape samples taken from the Aegean region contained pesticide residues; the residual amounts of 18 samples were higher than MRLs listed in the Turkish Food Codex (Bakırcı et al., 2014). Eleven different pesticide residues

Table 5. The amounts of some pesticide residues that can be detected in fresh Sultani grapes and MRLs of pesticides.

Pesticide Concentrations* (mg/kg or ppm) (X ± U)			
Sample no	Chlorpropham	Iprodione	Lambda-cyhalothrin
1	<LOQ	0.115 ± 0.058	0.107 ± 0.54
2	<LOQ	0.032 ± 0.016	<LOQ
3	<LOQ	0.165 ± 0.083	0.001 ± 0.001
4	<LOQ	0.200 ± 0.10	0.002 ± 0.001
5	<LOQ	0.035 ± 0.018	0.054 ± 0.027
6	<LOQ	<LOQ	0.003 ± 0.002
7	0.041 ± 0.21	0.028 ± 0.014	<LOQ
8	<LOQ	0.185 ± 0.093	0.049 ± 0.025
9	<LOQ	<LOQ	0.051 ± 0.026
10	<LOQ	0.205 ± 0.10	0.026 ± 0.013
11	<LOQ	0.102 ± 0.051	0.002 ± 0.001
12	<LOQ	0.205 ± 0.10	0.002 ± 0.001
13	<LOQ	0.162 ± 0.081	<LOQ
14	<LOQ	<LOQ	0.004 ± 0.002
15	<LOQ	0.038 ± 0.019	0.029 ± 0.015
16	<LOQ	0.062 ± 0.031	0.07 ± 0.035
17	<LOQ	0.22 ± 0.11	0.027 ± 0.014
MRL (mg/kg or ppm)	0.05	20	0.2
Number of samples > MRL	0	0	0

X: Mean result.
U: Expanded uncertainty.
* Since the other pesticides examined in our study could not be detected in any sample (<LOQ), these pesticides are not shown in this table.

were detected in 30 of 60 seedless grape samples obtained from local markets in Hatay (Yakar, 2018). Carbendazim, azoxystrobin, cypermethrin, cyprodinil, metalaxyl, chlorpyrifos, myclobutanil, fludioxonil, dimethomorph, and imazalil residues were detected in this study; the carbendazim and imazalil amounts of 9 samples exceeded the MRL.

ADI levels were 0.05 mg/kg body weight (bw) for chlorpropham, 0.02 mg/kg bw for iprodione, and 0.0025 mg/kg bw for lambda-cyhalothrin according to the EU Pesticides Database[3]. Thus, a person weighing 70 kg can tolerate a maximum of 3.5 mg chlorpropham, 1.4 mg iprodione, and 0.175 mg lambda-cyhalothrin intake in a day if we consider these ADI values. We may make an inference if we do not consider the possibility of pesticide exposure from other sources and do a calculation considering the lowest and highest pesticide residue levels in Table 5. If this person eats 85.4 kg of sample number 7, which contains chlorpropham residue, its tolerable value will be exceeded. The amount of iprodione taken daily cannot be tolerated if a person eats samples polluted by iprodione residue in the range of 6.36–50 kg. Similarly, the amount of lambda-cyhalothrin taken daily cannot be tolerated if a person eats between 1.65 and 175 kg of samples polluted by lambda-cyhalothrin residue. Thus, it is obviously seen that there is no significant health risk in respect to these pesticides as determined in our study, once again.

Phytochemicals with antioxidant properties are known to be adversely affected by heat and sunlight. The antioxidant properties in all samples, fresh and dried by the two methods, were statistically significantly different from each other (Table 4). The highest decrease in TPC and TFC values compared to the values of fresh grapes was observed with the oven-drying method in our study. Losses in TPC and TFC of the Sultani grapes were found to be 81.05% and 80.00% and 72.91% and 72.11% for oven-dried and sun-dried grapes in our

study, respectively. Although the percentages of TPC and TFC loss of the drying methods are close to each other, there is a statistically significant difference between TPC and TFC values of the two drying methods ($P < 0.01$) (Table 4). Unlike the results of our study, the sun-drying method was the more detrimental method in grape-drying methods with respect to TPC losses in the study by Çoklar and Akbulut (2017). Losses in TPC of Ekşikara grapes were found to be 20.26% and 46.79% for oven- and sun-dried grapes, respectively, in their study. The reason for this may be that the grapes which are the subject of our study are white grapes, unlike theirs, and therefore do not contain anthocyanins. The stability of anthocyanins is greatly affected by different parameters such as temperature, oxygen, pH, ascorbic acid, and light (Castañeda-Ovando et al., 2009; Contreras-Lopez et al., 2013). In addition, the temperatures were not too high and sun rays were often inclined during the sun-drying period in Kastamonu Province and these might be other reasons. The highest decrease in TAC was observed with the sun-drying method compared to fresh grapes, unlike TPC and TFC, in this study. Losses in TAC of Sultani grapes were found to be 47.45% and 55.02% for oven-drying and sun-drying methods, respectively. Other antioxidants such as vitamins contribute to TAC in white grapes, apart from phenolic and flavonoid substances, and the cause of this may be that vitamins are sensitive to sunlight and decompose under the sun. In conclusion, it was found that higher levels of TAC, TPC, and TFC, which have positive effects on health in our study, were found in fresh grapes and that consumption of fresh grapes during the season could be more beneficial. However, it is obvious that the consumption of raisins is also beneficial for health, in the absence of fresh grapes.

It would be a more accurate approach to evaluate benefits and risks together rather than merely addressing positive properties when talking about the health effects of foods. According to the results obtained from this study, fresh Sultani grapes showed better results in terms of TAC, TPC, and TFC than their counterparts in the literature, and it is obvious that their adequate consumption would be beneficial for the protection of human health. Thus, it is possible to benefit from the antibacterial, antioxidant, antiinflammatory, antihyperglycemic, and anticarcinogenic properties of phytochemicals in grapes. Grapes are among the fruits that may contain residues of pesticides to which they are exposed during production along with the phytochemicals that provide benefits. According to the results of our study, the pesticide residue levels did not exceed the MRL levels determined for grapes. In addition, it has been calculated that the ADI levels determined for these pesticides can only be exceeded by consuming amounts that a person cannot normally consume in a day. Thus, it was observed that there would be no negative health effects in terms of the pesticides that we examined in our study.

Consequently, in our study, the sun-drying method leads to less loss in TPC and TFC values; in terms of TAC value, the better drying method is oven drying. In addition, antioxidant properties in fresh grapes were slightly higher compared to other white grapes in the literature; it was also observed that there was no significant health risk in terms of pesticide residues investigated in this study. However, it is still very important to carry out continuous monitoring, because Turkey is in the lead with 83 notifications in the category of fruit and vegetable products in terms of pesticide residue hazard, according to the 2017 RASFF annual report (RASFF, 2018). Therefore, it is recommended that the authorities take the necessary measures and carry out residue monitoring activities in cooperation with universities at regular intervals throughout the country.

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Footnotes

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Supplemental Table. Method performance parameters for HPLC-MS-MS and GC-MS and selected ions of pesticides.

Pesticide names	Selected ions m/z and ref. ions	r^2	LOQ (ppb)	Mean recovery (%)	RSDr (%)	RSDR (%)	Retention time	Equipment
Aldicarb	208-89-116	0.9996	0.97	97.30	7.40	13.70	3.154	HPLC-MS-MS
Aldicarb sulfoxide	207-89-132	0.9991	1.85	95.40	6.70	13.00	1.916	HPLC-MS-MS
Aldoxycarb	240-223-148	0.9983	5.15	92.70	6.90	14.30	2.052	HPLC-MS-MS
Carbaryl	237-72-90	0.9987	0.33	91.90	11.00	19.20	2.157	HPLC-MS-MS
Carbofuran	222-123-165	0.9988	0.31	102.44	5.40	13.00	3.413	HPLC-MS-MS
3-Hydroxycarbofuran	255-163-181	0.9998	3.33	89.30	5.00	15.10	2.797	HPLC-MS-MS
Methiocarb	226-121-169	0.9995	1.50	105.00	7.80	17.40	3.926	HPLC-MS-MS
Methomyl	163-106-88	0.9984	2.52	93.70	12.00	18.90	2.345	HPLC-MS-MS
Oxomyl	237-72-90	0.9993	5.02	101.40	7.50	13.90	2.157	HPLC-MS-MS
Propoxur	210-111-168	0.9996	0.59	89.00	6.00	13.80	3.385	HPLC-MS-MS
Aldrin	66-263-91	0.9992	5.02	92.00	9.70	19.40	12.110	GC-MS
Dieldrin	139-141-250	0.9953	3.50	94.20	9.80	20.00	14.145	GC-MS
Azinphos-ethyl	346-132-160	0.9980	4.20	94.00	8.00	19.10	17.905	GC-MS
Azinphos-methyl	340-132-160	0.9965	5.10	110.00	11.40	20.10	17.280	GC-MS
Bifenthrin	181-166-165	0.9960	3.70	98.00	11.00	18.70	16.445	GC-MS
Beta-Cyfluthrin	163-206-227	0.9936	4.50	94.50	13.50	19.20	16.510	GC-MS
Bromopropylate	55-341-69	0.9952	5.30	97.80	7.20	18.50	16.505	GC-MS
Captan	149-79-81	0.9957	5.00	88.30	10.40	19.60	14.140	GC-MS
Chinomethionate	206-234-116	0.9955	6.00	91.00	10.20	20.00	13.375	GC-MS
Chlorothalonil	266-264-124	0.9920	5.20	80.60	9.40	19.30	10.555	GC-MS
Chlorpropham	43-127-41	0.9980	5.50	96.80	7.40	18.60	8.695	GC-MS
Chlorpyrifos-methyl	288-125-109	0.9950	5.00	99.20	12.00	20.00	11.200	GC-MS
Alpha-BHC	181-183-219	0.9985	5.00	103.40	9.00	19.00	9.340	GC-MS
Beta-BHC	109-181-183	0.9960	5.00	99.80	11.50	20.10	9.900	GC-MS
Gamma-BHC	181-183-219	0.9965	5.30	96.30	11.70	19.90	9.990	GC-MS
Demeton-S	263-169-329	0.9958	4.10	91.20	10.00	18.90	10.330	GC-MS
Diazinon	137-179-152	0.9990	5.30	96.90	9.80	18.90	10.175	GC-MS
Dicofol	139-111-141	0.9960	5.00	96.80	14.30	20.20	12.250	GC-MS
Dinobutone	43-127-213	0.9980	3.90	81.50	15.10	19.30	8.690	GC-MS
Disulfotone	88-108-60	0.9991	3.00	117.10	7.90	19.70	8.295	GC-MS
Alpha-endosulfan	241-195-239	0.9970	4.80	90.40	9.60	20.00	13.625	GC-MS
Beta-endosulfan	237-241-195	0.9963	5.10	90.90	10.50	19.20	13.625	GC-MS
Endosulfan sulfate	272-88-274	0.9968	5.00	99.10	9.40	18.60	15.575	GC-MS
Ethion	231-97-125	0.9969	3.80	116.80	10.20	18.80	14.870	GC-MS
Esfenvalerate	225-167-250	0.9968	4.90	99.10	11.00	19.30	19.330	GC-MS
Fenvalerate-2	197-55-69	0.9963	5.10	97.00	10.70	19.30	20.555	GC-MS
Fenitrothion	125-261-109	0.9920	5.00	101.20	5.40	18.40	11.585	GC-MS
Folpet	261-130-95	0.9947	5.00	94.70	15.10	19.90	16.510	GC-MS
Hexachlorobenzen	284-286-282	0.9969	5.20	90.00	7.30	18.40	9.500	GC-MS
Heptachlor	100-272-274	0.9969	3.90	97.30	9.80	19.90	11.400	GC-MS
Iprodione	70 -314- 187	0.9968	5.10	95.00	10.90	19.60	13.595	GC-MS

Supplemental Table. (Continued).

Formothion	127-125-93	0.9963	4.30	101.60	8.90	18.70	11.890	GC-MS
Malathion	127-173-93	0.9960	5.00	100.80	12.00	19.00	11.890	GC-MS
Parathion	139-97-291	0.9969	5.00	111.80	7.80	20.00	12.170	GC-MS
Parathion-methyl	125-109-277	0.9940	5.10	102.50	9.60	18.40	11.740	GC-MS
Procymidone	96-67-283	0.9968	3.90	100.60	6.70	18.70	13.175	GC-MS
Permethrin-1	183-163-55	**0.9657**	5.80	75.70	9.40	18.90	18.280	GC-MS
Permethrin-2	183-163-165	0.9967	5.00	85.20	10.40	20.10	18.405	GC-MS
Alpha-Cypermethrin	181-163-91	0.9920	2.90	95.00	9.00	19.40	22.650	GC-MS
Cypermethrin	181-163-93	0.9900	4.70	94.40	11.00	19.70	16.515	GC-MS
Kresoxim-methyl	116. 131. 206	0.9941	5.10	98.90	6.40	19.90	14.220	GC-MS
Lambda-cyhalothrin	181-197-208	0.9950	5.00	95.50	8.50	18.70	17.470	GC-MS
Methamidophos	94-141-95	0.9969	3.90	97.30	8.40	18.40	4.920	GC-MS
Oxyfluorfen	252-55-69	0.9968	4.60	98.20	9.80	18.70	14.110	GC-MS
Tau-fluvalinate	55-129-69	0.9800	6.70	**51.00**	12.80	18.50	19.520	GC-MS
Tetradifon	111-55-159	0.9960	5.30	93.00	7.90	20.00	17.075	GC-MS
Trifluralin	264-306-43	**0.9700**	7.05	**127.00**	16.90	**24.70**	8.875	GC-MS
Vinclozolin	212-187-198	0.9968	5.00	103.30	7.20	18.80	11.185	GC-MS

Bold values are those outside the basic acceptance limits of the SANTE guideline.