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Characterization of volatile compounds of Gök Üzüm raisins produced from grapes pre-treated with different dipping solutions

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Abstract

Background Raisins contain a wide range of secondary metabolites, including volatile compounds that may contribute to the health benefits and preference of consumers. To our knowledge, this is one of the first studies concerning the analysis of volatile compounds in raisin. The goal of this study was to compare volatile composition of Gök Üzüm (*Vitis vinifera* L.) raisins produced from grapes dried before the application of two pre-treatments solutions: wood ash (WA) and potassium carbonate (K_2CO_3).

Results Gök Üzüm raisins produced from grapes dipped into the WA solution presented higher contents of most of the studied volatile compounds (including the total contents of C6 compounds, alcohols, benzenoids, esters, aldehydes, terpenes and C_{13} norisoprenoids) and lower contents of (Z)-2-hexenol and 2-hexenoic acid than the raisins produced from grapes dipped into K_2CO solutions. Gök Üzüm raisins were characterized by fruity, floral and grass aromas according to their odor activity values. Drying Gök Üzüm grapes after the treatment of WA solutions promotes a higher aromatic composition compared to K_2CO solutions.

Conclusion These findings can greatly assist raisin producers in deciding which dipping solution to use before using a dipping solution to dry the grapes.

Keywords Dried grapes, Autochthonous variety, Gök Üzüm, Wood ash, Potassium carbonate

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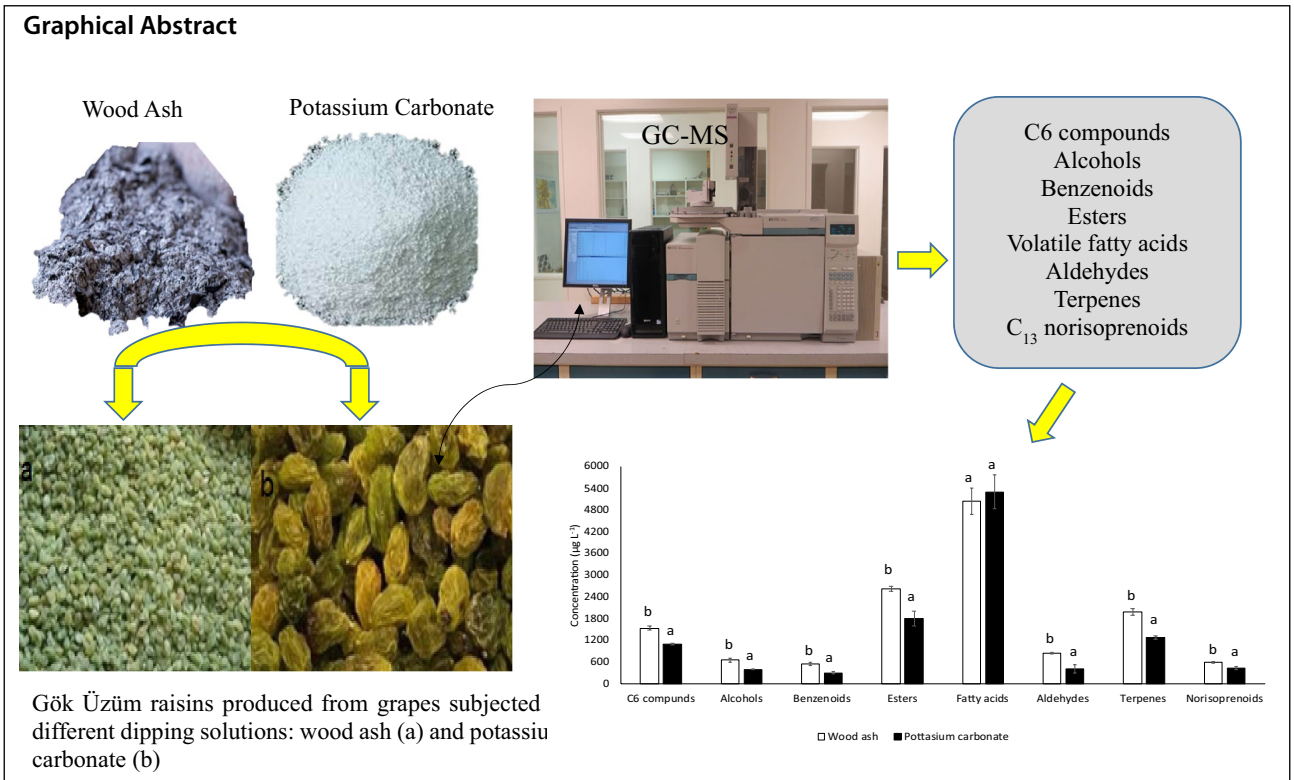

Introduction

Grapes are grown in many regions of the world for different purposes, including table grapes, raisins, grape juice, wine, distillates, and local consumption products, such as kofter, vinegar and grape molasses [1]. Turkey is the fifth major vine growing country [2], and close of 1.6 million tons (37% of total) of the produced grapes are dried for raisin production. Gök Üzüm, Ekşikara, Sergi Karası, Dımışkı, Dimrit, Besni, Sultani Çekirdeksiz, Horoz Karası, Zeynebi, among other varieties, are the most important for raisin production. Despite that these varieties are grown in many regions of the country, some of them are famous for their unique taste, and aroma characteristics. Gök Üzüm (*Vitis vinifera* L.) is a local grape cultivar grown only in Hadim (Konya Province, Mediterranean Region, Turkey), and is one of the high-quality raisin varieties that preserves its distinctive green color when dried [3]. Gök Üzüm grapes are dried on the rooftops of the houses at shady conditions for 3–4 weeks, which allows to preserve their taste and green color on the produced raisins.

Raisins are rich in nutritional composition, and they are not only consumed as snacks, but also could be incorporated to other foods to improve their flavor and nutritional value [4]. Terpenes, C_{13}-norisoprenoids, fatty acids, C6 compounds, alcohols, esters, and aldehydes are important volatile organic compounds (VOCs) that play a vital role as quality characteristic in table grapes owing to their contribution to grape berry flavor [5, 6]. These VOCs can influence consumer acceptance and preference and provide important information related to the nutritional character of foods [5–7]. A recent study has determined differences on VOCs in Bronx Seedless and Italia table grapes established in the Aegean Region in Turkey [5]. Based on the scientific literature, the content of volatile compounds in grapes is affected by many factors, including variety, rootstock, pedoclimatic conditions, geographic location, season, degree of berry maturity and viticultural techniques [8–10]. Some studies have shown that sugar concentration in grapes is increased due to the drying process [11]. As a result of this, there is a significant improvement of the fiber content, nutrient composition, antioxidant activity and total phenolic compounds in raisins compared to fresh fruit [12]. Traditionally, raisin producers dry the harvested grapes by shade, sun, or mechanical drying process. Before drying, the grapes are subjected to different pre-treatment process to ensure water removal rate during the drying process [13]. Dipping solutions have been applied for a long time to accelerate grape drying in the Mediterranean region by using solutions containing a mixture between wood ash and olive oil in hot water and formulations containing

potassium carbonate (K_2CO_3) and olive oil. Despite that most of the commercial dipping solutions are used in combination with ethyl esters of fatty acids and K_2CO_3 as active ingredients in unheated water, wood ash is still preferred by raisins producers because it is an organic residue, which is also cheap and easy to obtain.

A drying typical method is widely used by local raisins producers in Hadim, in which grapes are dipped in solutions prepared with both potassium carbonate plus olive oil mixture and wood ash. In this method, the clusters are dipped in these solutions with a temperature of 70–90 °C for 5–10 s under shade conditions, which provides to raisins a distinctive emerald-green color. Based onto the empirical experience, shade drying in raisins can be expected to result in better quality products than the raisins produced from other drying process in terms of their biochemical component, including volatile compounds. However, to our knowledge, there is not published paper that scientifically analyze the volatile composition of Gök Üzüm raisin after shade drying. Therefore, the aim of this trial was to study the VOCs of Gök Üzüm raisins produced from grapes subjected to different pre-treatments before drying.

Materials and methods

Study site and plant material

Grapes were harvested from a Gök Üzüm commercial vineyard in Hadim, Konya, Turkey. Hadim is located in the Mediterranean region, but it does not fully display the characteristics of the Mediterranean climate. As exposed by Keskin et al. [14], it shows a transition feature between the continental climate and the Mediterranean climate. The district receives more precipitation than the regions where the continental climate is dominant. The vines were 15–20 years old and were planted at a distance of 3.0 × 3.0 m, grafted onto 5-BB rootstocks, and trained with the goblet system. The vineyard was carried out under similar irrigation, fertilization, disease, and pruning management.

Study site and plant material

Harvest and treatments were performed according to the exposed by Keskin et al. [14]. Briefly, all the clusters per plant were harvested and subsequently dipped into two pre-treatments solutions. Then, the clusters were dried in the shade to obtain the raisins. Pre-treatments were performed separating the grapes into two groups as is commercially performed: (1) the clusters were pre-treated with a dipping solution that was composed by potassium carbonate (K_2CO_3), at a temperature of 70–90 °C for 5–10 s; (2) the clusters were pre-treated by dipping using a wood ash solution at a temperature of 70–90 °C for 5–10 s. K_2CO_3 solution contained 5–6% of K_2CO_3 plus 0.5–1.0% of olive oil and water, whereas the wood ash solution contained wood ash and water (50:50, v/v). In this study, there is not a comparison respect to a "control" since raisins are not produced from the natural dehydration of grapes due the long time that this process takes to produce raisins, which is economically unfeasible (Fig. 1).

Subsequently, the clusters were placed in an airing attic (the length of the drying room was 4–5 m, the height was 2.5–4.0 m, and the width was close to 4 m with neat square vents) to dry the clusters in the shade. Drying duration was performed over 3–4 weeks and once the clusters reached 15% moisture loss, they were removed from the attic. The study was set up in a randomized complete block design, accounting four replicates per treatment. Each replicate was composed by 1 kg of grapes. Thus, a total of 4 kg of grapes were dried after dipping in wood ash and 4 kg of grapes dried by dipping in K_2CO_3 solution. After drying ends, the samples were placed in polyethylene bags and stored at 20 °C until the time of analysis.

Chemical and reagents

Glucose, sodium chloride (NaCl), tartaric acid, citric acid, sodium dihydrogen phosphate and sodium hydroxide (NaOH) were from Sigma-Aldrich (Millipore,

Fig. 1 Gök Üzüm raisins produced from grapes subjected to different dipping solutions: wood ash (**a**) and potassium carbonate (**b**) as is commercially performed

Bedford, MA, USA). Pure water was obtained from the Milli-Q purification system. Dichloromethane, methanol, and ethanol were purchased from Sigma-Aldrich (Millipore, Bedford, MA, USA). The following chemical standards for analysis purchased from Sigma-Aldrich (St. Louis, MO) were used for quantification and identification: 1-octanol (99.0%), 3-methyl-1-butanol (99.0%), octanoic acid (99.0%), 2-ethyl-1-hexanol (99.0%), 1-octen-3-ol (98.0%), benzyl alcohol (98.0%), heptanoic acid (99.0%), 2-methylpropanoic acid (99.5%), 1-nonanol (99.0%), hexanal (98.0%), benzaldehyde (99.0%), nonanal (95.0%), (E)-2-hexenal (98.0%), octanal (99.0%), benzeneacetaldehyde (90.0%), ethyl acetate (99.8%), hexanoic acid (99.5%), methyl salicylate (99.0%), ethyl phenylacetate (99.0%), diethyl succinate (99.0%), 6-methyl-5-hepten-2-one (99.0%), *p*-cymene (98.0%), acetoin (96.0%), limonene (97.0%), neral (95.0%), ethyl nonanoate (98.0%), geraniol (99.5%), α-terpineol (90.0%), linalool (97.0%), geranylacetone (containing 35% nerylacetone), hotrienol (97.0%), terpinolene (97.0%), β-citronellol (95.0%), β-damascenone (> 90.0%), geranic acid (85.0%), 2-ethyl-6-methylpyrazine (99.5%), naphthalene (99.0%), 3-ethyl-2,5-dimethyl pyrazine (98.0%), furfural (99.5%), 5-methyl-2-furfural (99.0%) phenol (99.9%), 2,3-diethylpyrazine (98.0%), and 4-methyl-2-pentanol (98.0%, internal standard). Also, glycosidase AR2000 (Rapidase) was purchased from DSM Food Specialties (France). Cleanert PEP-SPE (200 mg 6 mL^{-1}) was obtained from Sigma-Aldrich (Millipore, Bedford, MA, USA).

Sample pre-treatment

In the study, each application was prepared in triplicate and 100 raisins of similar weight were kept in distilled water at 4 °C overnight. The following day it was homogenized in a blender and softened for 240 min. The pulp was then centrifuged three times for 10 min at 8000 rpm at 4 °C until all the supernatant was obtained.

Preparation of bound- and free-form volatiles

Volatile organic compounds of Gök Üzüm raisins were extracted by headspace solid phase micro-extraction (HS-SPME) and determined by gas chromatography–mass spectrometry (GC–MS). The extraction of volatile compounds was performed using the previously optimized method performed by Wen et al. [15] and Wang et al. [16]. The samples were tested in triplicate. The Cleanert PED-SEP column was activated by 10 mL methanol and 10 mL water separately, before 1 mL supernatant was added. Then, acid and sugar were removed by 5 mL water, and most of the free-form volatiles for samples were washed out with 5 mL dichloromethane. Finally, 20 mL of methanol was utilized to elute the glycosidically bound volatiles, which were collected in a 50-mL flask. The solvent was then removed by decreased pressure distillation in 30 °C water bath to finally obtain the bound-form volatile compounds. Then, 5 mL of phosphate/citrate (2 M) buffer solution at pH 5 was added into the flask, the bound-form volatile compounds were enzymatically hydrolyzed with the action of 100 lL AR2000 (100 mg L^{-1} in 2 M citrate/phosphate buffer at pH 5.0) for 16 h at 40 °C in an incubator [15–17].

SPME conditions

The extraction of the free and bound-form volatiles in raisin was conducted with the following conditions: 10 lL 4-methyl-2-pentanol (1.0018 mg L^{-1}) and 5 mL of sample were blended in a 15 mL vial containing a magnetic stirrer. Then, 1.3 g NaCl were added, and the vial was capped with a PTFE-silicon stopper. After, the sample vial was equilibrated at 60 °C for 40 min on agitation and a heating platform. Afterwards, the extraction coating fiber of CAR/PDMS/DVB was placed in the headspace to extract the volatiles for 40 min with continuous agitation and heating. Then extraction, the fiber was directly desorbed into the GC injection port for 8 min.

GC/MS analysis

The analysis identification and separation was carried out with a 60 m × 0.25 mm id. HP-INNOWAX capillary column with a 0.25 mm film thickness in an Agilent 7890 GC equipped with an Agilent 5975 MS (J&W Scientific, Folsom, CA). In this research, the GC–MS temperature conditions were appropriately altered from the method published by Wu et al. [18] in a previous report. In the unpartitioned GC inlet mode, helium was used as the carrier gas at a flow rate of 1 mL min^{-1}. Initially, the oven temperature was set up at 50 °C (for 1 min), then it was raised to 220 °C at 3 °C min^{-1} and held at 220 °C for 5 min, and after, it was raised from 220 to 250 °C at 5 °C min^{-1} and subsequently, it was held at 250 °C for 5 min. Mass spectra were detected in the electron impact (EI) mode (source temperature (230 °C and ionization energy, 70 eV). The acquisition was in selective ion mode and also in full-scan mode (mass range m/z 20–450) under autotune conditions. Under the same chromatographic conditions, the retention indices (RI) were calculated by the retention time (RT) of a C7–C24 n-alkane series (Supelco, Bellefonte, PA). The mass spectra were compared with the NIST08 library and identification was conducted based on the RI of available standards. Tentative identifications were carried out by comparison of mass spectra with those in RI reported in the literature and the NIST08 library when reference standards were not available.

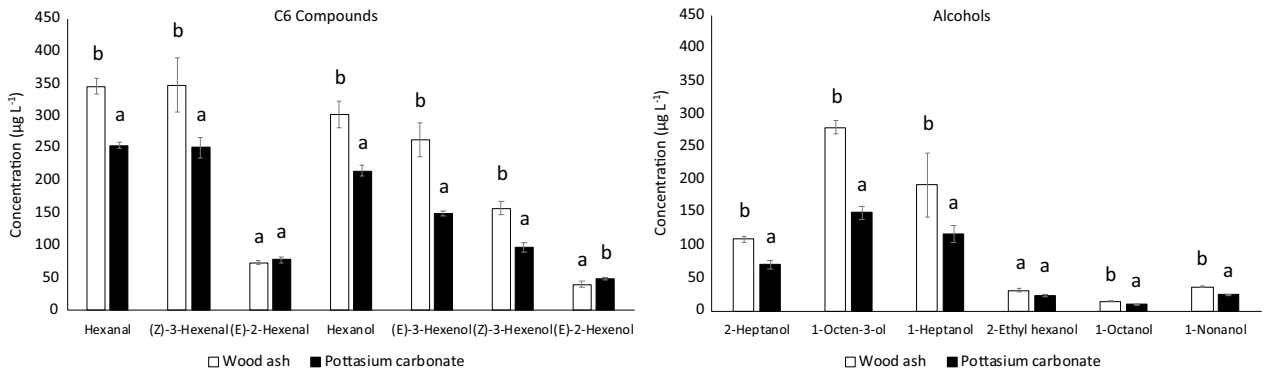

Fig. 2 Alcohols and C6 compounds content (µg L^{-1}) of Gök Üzüm raisins produced from grapes subjected to different dipping solutions: wood ash and potassium carbonate. Data are expressed as mean of the data with their corresponding deviation. Different letters in bars of each volatile compound represent significant differences (Duncan test, $p < 0.05$)

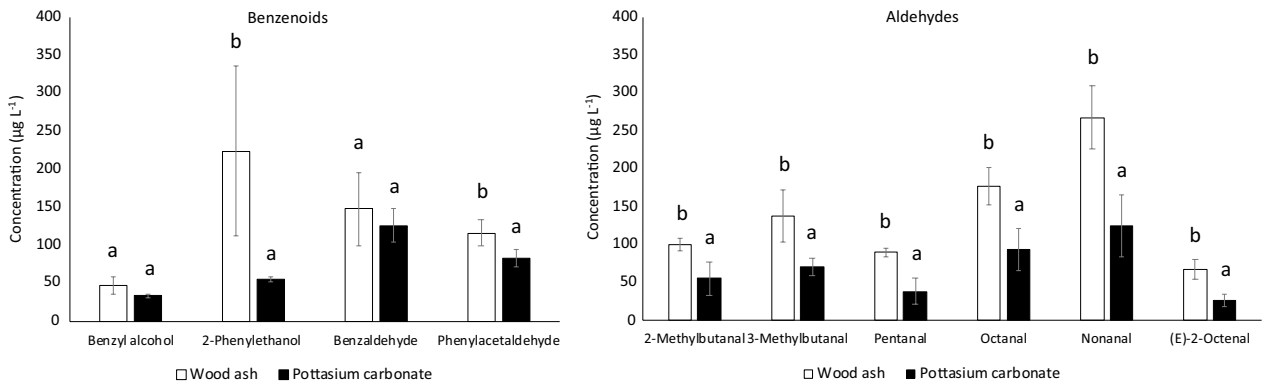

Fig. 3 Benzenoids and aldehydes contents (µg L^{-1}) of Gök Üzüm raisins produced from grapes subjected to different dipping solutions: wood ash and potassium carbonate. Data are expressed as mean of the data with their corresponding deviation. Different letters in bars of each volatile compound represent significant differences (Duncan test, $p < 0.05$)

Quantification and OAVs calculation

Based on the average concentration of sugar and acid in the raisin supernatant, the preparation of the simulated raisin solution was carried out. The solution for samples was prepared with distilled water, including 5 g L^{-1} tartaric acid and 400 g L^{-1} glucose, and the pH of solution was adjusted to 4.2 with a 1 M NaOH solution. The known concentrations of standard volatile components individually dissolved in HPLC grade ethanol were then added to the solution, and the mixed flavor standard solution was diluted to 15 times using a simulated raisin solution. The aroma standard solutions were extracted and analyzed in the same way as the sample supernatant. Estimates for the concentrations of the volatile compounds in raisin that did not have standards were conducted with those standards that had similar numbers of C atoms and same functional group as the volatile compounds [18]. The volatile compounds were quantified from the characteristic ion peak areas with regard to the internal standard of 4-methyl-2-pentanol (1.0018 mg L^{-1}).

Odor activity values (OAVs) of each volatile compound were calculated by dividing the concentration of the compound by its odor threshold obtained in table grapes from the literature [5, 19, 20].

Statistical analysis

The variables were subjected to a one-way ANOVA test that was performed using the Statgraphics Centurion XVI.I (The Plains, VA, USA) statistical package. The significance of the differences was determined by Duncan's test ($p \leq 0.05$).

Results

Alcohols and C6 compounds in Gök Üzüm raisins

Alcohols and C6 compounds contents of Gök Üzüm raisins produced from grapes dipped into wood ash and potassium carbonate solutions before drying are shown

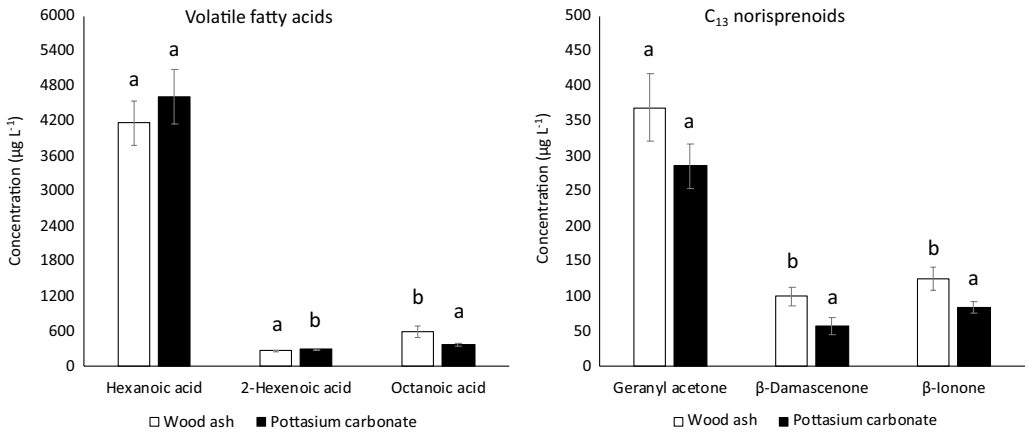

Fig. 4 Volatile fatty acids and C_{13} norisoprenoids contents (µg L^{-1}) of Gök Üzüm raisins produced from grapes subjected to different dipping solutions: wood ash and potassium carbonate. Data are expressed as mean of the data with their corresponding deviation. Different letters in bars of each volatile compound represent significant differences (Duncan test, $p < 0.05$)

Table 1 Terpenes contents (µg L^{-1}) of Gök Üzüm raisins produced from grapes subjected to different dipping solutions: wood ash and potassium carbonate

	Wood ash	Potassium carbonate
Terpenes		
α-Pinene	41.95 ± 3.20 b	18.46 ± 1.38 a
β-Pinene	26.49 ± 8.34 a	21.14 ± 10.60 a
Phellandrene	142.80 ± 12.57 b	87.52 ± 9.64 a
β-Myrcene	38.83 ± 1.39 b	30.09 ± 1.67 a
D-Limonene	45.82 ± 2.93 b	24.73 ± 2.27 a
γ-Terpinene	154.69 ± 6.70 b	110.09 ± 2.90 a
o-Cymene	28.43 ± 2.29 b	23.97 ± 0.74 a
Terpinolene	8.19 ± 0.70 b	5.58 ± 0.23 a
(Z)-Rose oxide	93.43 ± 18.27 b	42.64 ± 13.43 a
(E)-Rose oxide	36.26 ± 2.18 b	29.61 ± 0.92 a
Nerol oxide	1.08 ± 0.07 a	1.11 ± 0.07 a
Linalool	10.03 ± 0.52 b	6.69 ± 0.32 a
4-Terpineol	4.16 ± 0.35 b	3.39 ± 0.17a
Hotrienol	40.05 ± 4.63 a	32.54 ± 1.95 a
Neral	4.57 ± 0.15 a	4.50 ± 0.29 a
α-Terpineol	5.56 ± 0.28 a	5.08 ± 0.27 a
Geranial	6.90 ± 0.82 b	4.84 ± 0.41 a
Citronellol	81.97 ± 11.93 b	51.70 ± 4.08 a
Myrtenol	249.43 ± 52.38 a	196.03 ± 28.21 a
Nerol	405.48 ± 77.64 b	220.21 ± 24.05 a
Geraniol	72.66 ± 18.84 a	45.02 ± 8.71 a
E-Nerolidol	382.41 ± 68.58 b	244.86 ± 46.69 a
Cedrol	97.25 ± 6.21 b	52.49 ± 4.81 a
Geranic acid	56.78 ± 4.66 a	50.82 ± 5.19 a

Data are expressed as mean of the data with their corresponding deviation. Different letters within a row represent significant differences (Duncan test, $p < 0.05$)

Table 2 Esters contents (µg L^{-1}) of Gök Üzüm raisins produced from grapes subjected to different dipping solutions: wood ash and potassium carbonate

	Oak ash	Potassium carbonate
Esters		
Ethyl acetate	51.57 ± 4.35 a	49.60 ± 4.42 a
Ethyl propionate	95.34 ± 17.36 a	207.76 ± 10.29 b
Ethyl isobutyrate	93.78 ± 17.23 a	77.89 ± 13.07 a
Propyl acetate	100.40 ± 5.33 b	43.68 ± 1.91 a
Ethyl butyrate	179.66 ± 40.72 a	117.25 ± 13.61 a
Ethyl 3-methylbutanoate	69.79 ± 8.78 b	31.54 ± 2.18 a
Butyl acetate	33.52 ± 6.10 a	73.05 ± 3.62 b
Ethyl pentanoate	128.88 ± 16.22 a	85.20 ± 25.14 a
Ethyl hexanoate	26.81 ± 4.88 a	22.91 ± 6.18 a
Hexyl acetate	118.62 ± 36.70 a	80.59 ± 20.46 a
(Z)-3-Hexenyl acetate	192.20 ± 10.24 b	128.13 ± 13.37 a
Ethyl heptanoate	411.99 ± 33.73 b	196.43 ± 37.83 a
Ethyl octanoate	1003.05 ± 92.00 b	637.27 ± 41.92 a
Ethyl 3-hydroxybutyrate	118.88 ± 5.27 a	129.73 ± 7.02 a

Data are expressed as mean of the data with their corresponding deviation. Different letters within a row represent significant differences (Duncan test, $p < 0.05$)

in Fig. 2. Gök Üzüm raisins contents of (E)-2-hexenal and 2-ethyl hexanol were not affected by the dipping solutions. Gök Üzüm raisins produced from grapes dipped into the wood ash solution presented higher contents of hexanal, (E)-3-hexenol, (Z)-3-hexenal, hexanol, (Z)-3-hexenol, 1-octen-3-ol, 2-heptanol, 1-octanol, 1-nonanol, and 1-heptanol, and lower content of (E)-2-hexenol than the raisins produced from grapes dipped into potassium carbonate solution.

Benzenoids and aldehydes in Gök Üzüm raisins

Benzenoids and aldehydes contents of Gök Üzüm raisins produced from grapes dipped into wood ash and potassium carbonate solutions before drying are shown in Fig. 3. Gök Üzüm raisins contents of benzyl alcohol and benzaldehyde were not affected by the dipping solutions. Gök Üzüm raisins produced from grapes dipped into the wood ash solution presented higher contents of 2-phenylethanol, phenylacetaldehyde, 3-methyl-butanal, 2-methyl-butanal, pentanal, nonanal, octanal, and (E)-2-octenal than the raisins produced from grapes dipped into potassium carbonate solution.

Volatile fatty acids and C_{13} norisoprenoids in Gök Üzüm raisins

C_{13} norisoprenoids contents and volatile fatty acids of Gök Üzüm raisins produced from grapes dipped into wood ash and potassium carbonate solutions before drying are shown in Fig. 4. Gök Üzüm raisins contents of hexanoic acid and geranyl acetone were not affected by the dipping solutions. Gök Üzüm raisins produced from grapes dipped into the wood ash solution presented higher contents of octanoic acid, β-damascenone and β-ionone, and lower content of 2-hexenoic acid than the raisins produced from grapes dipped into potassium carbonate solution.

Terpenes in Gök Üzüm raisins

Terpenes contents of Gök Üzüm raisins produced from grapes dipped into wood ash and potassium carbonate solutions before drying are shown in Table 1. Gök Üzüm raisins contents of β-pinene, nerol oxide, neral, hotrienol, myrtenol, α-terpineol, geraniol and geranic acid were not affected by the dipping solutions. Gök Üzüm raisins produced from grapes dipped into the wood ash solution presented higher contents of α-pinene, D-limonene, phellandrene, β-myrcene, o-cymene, γ-terpinene, terpinolene, (E)-rose oxide, (Z)-rose oxide, linalool, 4-terpineol, geranial, E-nerolidol, nerol, citronellol, and cedrol than the raisins produced from grapes dipped into potassium carbonate solution.

Esters in Gök Üzüm raisins

Esters contents of Gök Üzüm raisins produced from grapes dipped into wood ash and potassium carbonate solutions before drying are shown in Table 2. Gök Üzüm raisins contents of ethyl isobutyrate, ethyl acetate, ethyl pentanoate, ethyl butyrate, ethyl hexanoate, hexyl acetate and ethyl-3-hydroxybutyrate were not affected by the dipping solutions. Gök Üzüm raisins produced from grapes dipped into the wood ash solution presented higher contents of (Z)-3-hexenyl acetate, ethyl-3-methylbutanoate, propyl acetate, ethyl heptanoate and ethyl octanoate, and lower contents of ethyl propionate and butyl acetate than the raisins produced from grapes dipped into potassium carbonate solution.

Total content of volatile compounds

Total content of C6 compounds, alcohols, benzenoids, esters, volatile fatty acids, aldehydes, terpenes and C_{13} norisoprenoids of Gök Üzüm raisins produced from grapes dipped into wood ash and potassium carbonate solutions before drying is shown in Fig. 5. Gök Üzüm raisins total content of volatile fatty acids was not affected by the dipping solutions. Gök Üzüm raisins produced

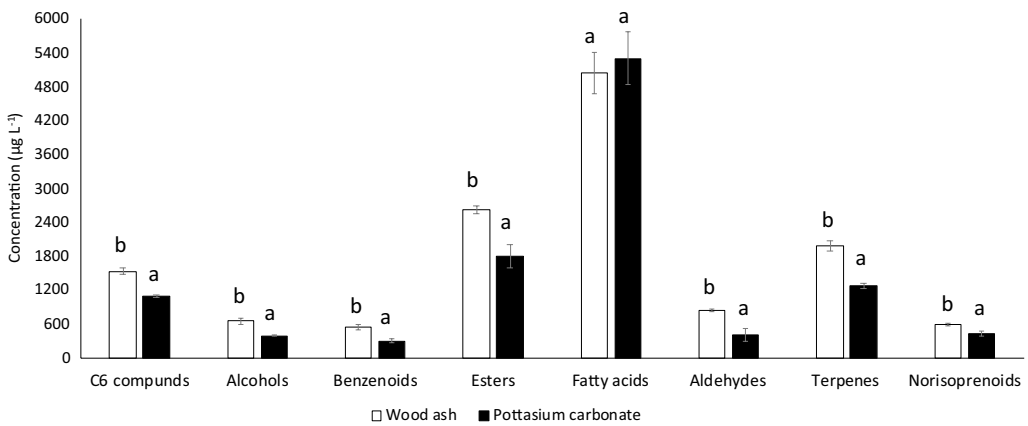

Fig. 5 C6 compounds, alcohols, benzenoids, esters, volatile fatty acids, aldehydes, terpenes and C_{13} norisoprenoids total volatile contents (μg L^{-1}) of Gök Üzüm raisins produced from grapes subjected to different dipping solutions: wood ash and potassium carbonate. Data are expressed as mean of the data with their corresponding deviation. Different letters in bars of each volatile compound represent significant differences (Duncan test, $p < 0.05$)

Table 3 Odor activity values (OAVs) and aroma descriptor found in the literature for each volatile compounds determined in Gök Üzüm raisins produced from grapes subjected to different dipping solutions: wood ash and potassium carbonate

	Wood ash	Potassium carbonate	Aroma descriptor
C6 compounds			
Hexanal	76.79	56.57	Green
(Z)-3-Hexenal	1,390.29	1,005.49	Grass
(E)-2-Hexenal	4.36	4.63	Grass, herbaceous
Hexanol	0.60	0.43	Flower, green, cut grass, grass, herbaceous, wood
(E)-3-Hexenol	0.26	0.15	Green, bitter, fatty, herbaceous, fresh
(Z)-3-Hexenol	2.26	1.39	Grass, herbaceous, green, fatty, bitter
(E)-2-Hexenol	0.40	0.49	Herbaceous, green
Alcohols			
2-Heptanol	1.55	1.00	Fruity, herbaceous
1-Octen-3-ol	279.2	149.8	Mushroom
1-Heptanol	0.45	0.28	Oily
2-Ethyl hexanol	0.12	0.08	Floral
1-Octanol	0.13	0.09	Jasmine, lemon
1-Nonanol	0.73	0.49	Rose-orange
Benzenoids			
Benzyl alcohol	0.00	0.00	Roasted, toasted, sweet, fruity
2-Phenylethanol	0.20	0.05	Floral, rose, honey
Benzaldehyde	0.42	0.36	Sweet, fruity, roasted, almond, fragrant, burnt sugar
Phenylacetaldehyde	28.92	20.57	Flowery, rose
Esters			
Ethyl acetate	0.01	0.01	Pineapple, fruity, solvent, anise, balsamic
Ethyl propionate	9.53	20.78	Banana, apple
Ethyl isobutyrate	937.78	778.91	Fruity
Propyl acetate	0.02	0.01	Celery
Ethyl butyrate	179.66	117.25	Fruity
Ethyl 3-methylbutanoate	697.91	315.41	Fruity
Butyl acetate	0.51	1.11	Fruity
Ethyl pentanoate	85.92	56.8	Grass
Ethyl hexanoate	26.81	22.91	Fruity, green apple, banana, wine-like, brandy
Hexyl acetate	0.18	0.12	Apple, floral, fruity, banana, pear, brandy
(Z)-3-Hexenyl acetate	0.26	0.17	*Fruity, green leaves
Ethyl heptanoate	206.00	98.22	Wine-like, brandy, fruity
Ethyl octanoate	5.17	3.28	Sweet, floral, fruity, banana, pear, brandy
Ethyl 3-hydroxybutyrate	0.01	0.01	Grape, fruity, caramel, toasted
Volatile fatty acids			
Hexanoic acid	1.39	1.54	Rancid, cheese, fatty, sweat
2-Hexenoic acid	0.27	0.30	Fatty, rancid
Octanoic acid	0.20	0.13	*Rancid, cheese, fatty, sweat
Aldehydes			
2-Methylbutanal	77.27	42.71	*Green, malty
3-Methylbutanal	687.52	354.50	*Fresh grass, cocoa
Pentanal	7.52	3.22	Fat, green
Octanal	252.20	133.42	Honey, green, fatty, fruity, citrus, lemon, fat, soap
Nonanal	267.34	124.85	Fat, citrus, green, fruity
(E)-2-Octenal	22.33	13.10	*Green, nut, fat
Terpenes			
α-Pinene	6.99	3.08	Pine, resinous

Table 3 (continued)

	Wood ash	Potassium carbonate	Aroma descriptor
β-Pinene	0.19	0.15	Woody, resinous
Phellandrene	3.57	2.19	Terpene, fruity, minty, herbal
β-Myrcene	1.08	0.84	Green burning, green
D-Limonene	4.58	2.47	Fruity, lemon
γ-Terpinene	0.15	0.11	Fruity, lemon-like
o-Cymene	2.49	2.10	Citrus, green
Terpinolene	0.04	0.03	Piney
(Z)-Rose oxide	186.86	126.64	Floral, lychee-like, rose
(E)-Rose oxide	72.52	59.22	Rose
Nerol oxide	0.00	0.00	Oil, flower
Linalool	1.67	1.12	Citrus, floral, sweet, grape-like
4-Terpineol	0.03	0.03	Flowers, nutmeg, moldy
Hotrienol	0.36	0.30	Fresh, floral, fruity
Neral	0.00	0.00	Fruity
α-Terpineol	0.02	0.02	Lilac, floral, sweet
Geranial	0.22	0.15	Citrus, citric fruit
Citronellol	2.05	1.29	Rose
Myrtenol	35.63	28.00	Flowery, mint
Nerol	0.14	0.07	Flower, grass, floral, green
Geraniol	1.82	1.13	Citric, floral, orange flower, roses, geranium
E-Nerolidol	1.53	0.98	Rose, apple, green, citrus, waxy, woody
Cedrol	194.50	104.99	*Cool, camphor
Geranic acid	1.42	1.27	Green
C_{13} norisoprenoids			
Geranyl acetone	6.15	4.76	Fresh, floral
β-Damascenone	49,885.62	28,938.67	*Sweet, fruity, floral, honey, black apple
β-Ionone	17,781.61	12,078.41	Balsamic, rose, violet

*Information obtained from the report published by Wu et al. [20]. The rest of the presented information about odor threshold and aroma descriptor of each volatile compound was obtained from the data published by Wu et al. [20].

from grapes dipped into the wood ash solution presented higher total contents of C6 compounds, alcohols, benzenoids, esters, aldehydes, terpenes and C_{13} norisoprenoids than the raisins produced from grapes dipped into potassium carbonate solution.

Odor activity values (OAVs) of volatile compounds of Gök Üzüm raisins

Table 3 shows the odor activity values (OAVs) of each volatile compounds, including their odor threshold and aroma descriptor of Gök Üzüm raisins produced from grapes subjected to wood ash and potassium carbonate solutions. Based on the OAVs, β-damascenone, which contributes to the sweet, fruity, floral, honey and black apple aromatic profile, presented the highest OAV, followed by β-ionone (balsamic, rose and violet), (Z)-3-hexenal (grass), ethyl 3-methylbutanoate (fruity), ethyl isobutyrate (fruity), and 3-methyl-butanal (fresh grass and cocoa). Gök Üzüm raisins produced from grapes subjected to wood ash dipping solutions presented higher OAVs of β-damascenone, β-ionone, (Z)-3-hexenal, ethyl 3-methylbutanoate, ethyl isobutyrate, and 3-methylbutanal than the raisins produced from grapes dipped into potassium carbonate solution.

Odor activity values (OAVs) of each volatile compound were calculated by dividing the concentration of the compound by its odor threshold obtained in table grapes from the literature [5, 19, 20].

Discussion

As far as our knowledge, there is no published paper that evaluates the concentration of volatile compounds in Gök Üzüm raisins obtained from grapes subjected to different pre-treatments to dry. Based on this study, the most abundant volatile compounds in Gök Üzüm raisins were hexanoic acid, ethyl octanoate, octanoic acid, ethyl heptanoate and nerol. Some studies showed that dried grapes are characterized by different volatile compounds such as

(Z)-1,5-octadien-3-one (geranium), (−)-massoia lactone (coconut and dried figs) [21, 22], which were not detected in this study. On the other hand, Wang et al. [23] reported that (E,E)-2,4-nonadienal, 1-heptanol, (E)-2-heptenal, 1-hexanol, nonanal, decanal, 2-ethyl-1-hexanol, were higher in fresh Thompson Seedless raisins. Javed et al. [24] reported that floral aroma and the main fruity contributors of Zixiang Seedless, Centennial Seedless and Thompson Seedless raisins were geraniol, limonene, rose oxide, ethyl hexanoate and β-damascenone. In another paper, Javed et al. [25] reported that in Thompson Seedless raisins, floral aroma and the main fruity contributors were ethyl hexanoate, β-damascenone, β-ionone, decanal, and 1-octen-3-ol. Some volatile compounds, such as (Z)-3-hexenal, β-ionone, β-damascenone, ethyl isobutyrate, ethyl 3-methylbutanoate and 3-methylbutanal contributed mostly to fruity, floral, and green aroma of Gök Üzüm raisins (Table 3). Based on the exposed data, Gök Üzüm raisins were characterized by fruity, floral and grass aroma. Thus, it is possible to suggest that volatile composition of raisins is widely affected by the variety factor.

Based in this study, most of the C6 compounds, alcohols, benzenoids, esters, aldehydes, terpenes and C_{13} norisoprenoids, including their total volatile composition showed higher concentration in grapes dried on wood ash than on potassium carbonate solutions (K_2CO_3). Dipping solutions used in this study are emulsions that allow to accelerate grape drying. Drying emulsions containing K_2CO_3 allows to neutralize free fatty acids and fixed charges on the berry surface which also enhances water loss. In addition, drying grapes in alkali solutions prevent raisin color from darkening by controlling oxidase polyphenol and decreasing drying time [26]. Pre-treatments before drying with chemicals can affect berry skins by inducing microscopic cracks as well as solubilizing waxy layer, which affects moisture diffusivity [26, 27]. Based on this, an acceleration in the drying rate induced by grape shrinkage in alkali conditions (K_2CO_3) before drying can affect volatile compounds content of the resulted raisins. Shriveled berries are characterized by high γ-nonalactone (coconut) and β-damascenone (fruit and honey-like) concentrations and produced wines with low ethyl esters of fatty acids and higher alcohol acetates [21, 22, 28]. Terpenes are usually inversely correlated to high temperature probably because terpenes are lost by volatilization [29, 30]. Based on this, it is possible that most of the volatile compounds were degraded in a high rate during grape dehydration because of alkali pre-treatment solution on waxy layer structure at grape surface. Besides, volatile compounds are distributed in both the flesh and mostly in the skin [31], and drying induced crystallization of sugars and the remotion and the subsequent evaporation of water from inside the cell and probably, some of the volatile compounds found in berry flesh.

Wood ash is used as pre-treatment in raisin production from ancient times in the Mediterranean region since it is easy to find and is cheaper than K_2CO_3 solutions. Locally, producers coincided that this solution helps the grape to retain their texture when it is dry. A study on Gelin, Osmanca and Razaka (*Vitis vinifera* L.) varieties reported that wood ash applied as pre-treatment in drying processes induced lower values of 'L', 'a', 'b', hue and chroma color properties, as well as lower total phenolics and total flavonoids, including higher 'a/b' values than K_2CO_3 solutions [32]. In addition, in all varieties, K_2CO_3 pre-treatment caused a faster drying time than wood ash with a difference of at least two days [32]. On the other hand, (Z)-2-hexenol and 2-hexenoic acid were the only volatile compounds that reached lower content in wood ash pre-treated raisins than the ones dried before the application of K_2CO_3. Some volatile organic compounds, including (Z)-2-hexenol characterizes phloem tissues in different ash species [33]. Based on the above mentioned, it is possible that wood ash induced a slower drying process that favors a slow volatilization or degradation of volatile compounds compared to K_2CO_3 solutions.

Conclusions

Based on our results, there were significant differences between the two dipping solutions applied before drying grapes, regarding volatile compounds in Gök Üzüm raisins. The most abundant volatile compounds in Gök Üzüm raisins were hexanoic acid, ethyl octanoate, octanoic acid, ethyl heptanoate and nerol. In addition, most of the C6 compounds, alcohols, benzenoids, esters, aldehydes, terpenes and C_{13} norisoprenoids, including their total volatile composition showed higher concentration in grapes dried on wood ash than on K_2CO_3 solutions. Based on the above mentioned, it is possible that wood ash induced a slower drying process that favors a slow volatilization or degradation of volatile compounds compared to K_2CO_3 solutions.

Author contributions

OK and FA designed the study. FA, SK, MAA and HSH were responsible for the performance of the research and collection. OK, HSH and GGG interpreted the results, data analysis. OK wrote the manuscript. MT determined biochemical analysis. All authors have read and agreed to the published version of the manuscript.

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Competing interests
The authors declare that they have no known competing financial interests.

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