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Use of Principal Component Analysis and Cluster Analysis for Differentiation of Traditionally-Manufactured Vinegars Based on Phenolic and Volatile Profiles, and Antioxidant Activity

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This study aimed to characterize twelve vinegar samples produced by the traditional method with the use of whole fruits and without any preservatives in terms of their physicochemical properties, total phenolic content (TPC), total flavonoid content (TFC), phenolic compound profiles, antioxidant activity (DPPH• scavenging activity, FRAP, CUPRAC), and volatile compositions, as well as their abilities to delay oxidation in mayonnaise. Types of raw material significantly affected all of the above parameters ($p<0.05$). Gallic acid, protocatechuic acid, and caffeic acid were detected as the major phenolic acids in all vinegar samples. Among, flavonoids, rutin, and kaempferol were also identified. The major volatiles belonged to acetic acid esters and alcohol groups, and isoamyl acetate was determined in all vinegar samples at changing ratios. The high positive correlation coefficient ($r>0.70$) was determined between DPPH• scavenging activity of vinegars and induction period of accelerating oxidation based on the OXITEST of mayonnaises produced with these vinegars. Vinegar types significantly affected the oxidative stability of mayonnaise ($p<0.05$). Furthermore, it was demonstrated that vinegar samples could be clearly discriminated by principal component and cluster analyses. This study suggests that fruit type should be considered as a crucial factor in the production of vinegars affecting not only sensory properties but also their physicochemical and bioactive properties.

INTRODUCTION

Vinegar is produced from fruits and vegetables containing sugar or starch through a two-stage fermentation process, namely alcohol and subsequently acetic acid fermentation. In the first stage, fermentable sugars are converted to ethanol and CO_2 under anaerobic conditions by yeast, and in the second stage where alcohol formed in the first stage, is converted to acetic acid by acetic acid bacteria [Ho *et al.*, 2017]. Vinegar is mainly used for pickling of fruits and vegetables and in the preparation of mayonnaise, salad dressings, mustard, and other food condiments due to its taste and aroma. Besides, it is one of the most famous folk medicines used to curb infections [Chen *et al.*, 2016]. The presence of various types of polyphenols and other bioactive compounds contribute to its therapeutic effects, among them antimicrobial, antidiabetic, antihypertensive, antiobesity, and lipid-lowering ones [Chou *et al.*, 2015; Samad *et al.*, 2016].

The chemical composition and physicochemical parameters of vinegar are affected by the manufacturing techniques and raw materials used. Traditional vinegar typically results from a long fermentation (up to a month) and uses natural vinegar as the starter culture, whereas industrial vinegar typically can be manufactured in approximately one day [Budak *et al.*, 2014]. Research on producing new types of vinegar has been ongoing to obtain not only different organoleptic and sensorial properties but also provide a varying phenolic composition, antioxidant activities, and volatile compounds. For example, in the study of De Leonardis *et al.* [2018], compared to apple, white wine, and balsamic vinegars, olive vinegars provided the highest amount of total phenolics (3600 mg GAE/L, almost three times higher than those of balsamic vinegar, 1227 mg GAE/L) and displayed a high presence of hydroxytyrosol (1019 mg/L) which is a potent antioxidant and its daily intake of 5 mg can prevent low-density lipoprotein (LDL) oxidation [Lopez-Huertas & Fonolla, 2017]. In other respect, the use of second-quality strawberry to produce vinegar rich in anthocyanins also resulted in the formation of furaneol, mesifurane, and γ-decalactone which are considered to be the major contributors of fruit flavor due to their low odor threshold and their high quantities [Ubeda *et al.*, 2013]. Among other different raw materials used for vinegar production, onion juice [Horiuchi et al., 1999], oat, buckwheat [Yu *et al.*, 2018], coconut, pineapple juice [Mohamad *et al.*, 2018], hawthorn, artichoke [Ozturk *et al.*, 2015], and tomato [Lee *et al.*, 2013] can also be listed. In Turkey, apple, lemon, and grape are the most widely used raw materials for vinegar production, however, vinegar production with new sources and traditional methods has attracted growing interest lately due to the increase in consumer demand and the market value of vinegars.

Thus, the aim of the present study was to perform a comparative analysis of vinegar samples manufactured according

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to the traditional method using different raw materials, *i.e.* rosehip, fig, lemon, jujube fruit, artichoke, blackberry, guelder-rose, walnut, pomegranate, red grape, apple, and hawthorn, concerning their physicochemical properties (acidity, pH, color, and °Brix), bioactive properties (phenolic compound profiles and antioxidant activities), and volatile composition. Also, mayonnaise samples were produced with the use of vinegars and subjected to accelerated lipid oxidation tests, and the correlation between the antioxidant activity values of vinegars and oxidative status of mayonnaise samples was evaluated.

MATERIALS AND METHODS

Materials

Twelve vinegar samples, namely rosehip, fig, lemon, jujube fruit, artichoke, blackberry, guelder-rose, walnut, pomegranate, red grape, apple, and hawthorn vinegar, at least three samplings for each vinegar, were supplied from the same manufacturer (Nahita, Icmeli Dogal Urunler Co) that produces according to traditional methods by using whole fruits and without adding any preservatives. The vinegar samples were stored in the laboratory at a constant temperature of 25±1°C before analysis. All chemicals and reagents used for the analyses were of analytical or high-performance liquid chromatography (HPLC) grade and obtained from Merck (Darmstadt, Germany) unless otherwise specified. 6-Hydroxy-2,5,7,8-tetramethylchroman-2 carboxylic acid (Trolox, 97%), 2,2-diphenyl-1-picrylhydrazyl (DPPH, 95%), 2,4,6-tripyridyl-s-triazine (TPTZ), neocuproine and phenolic standards used for HPLC analysis were obtained from Sigma-Aldrich Ltd. (Steinheim, Germany).

Physicochemical properties

The pH values of the samples were measured by using a pH meter (InoLab 720, WTW GmbH, Weilheim, Germany). The titration acidity of the samples was calculated as acetic acid equivalents. After titration of 5 mL of vinegar with 0.1 N NaOH, spent volume of NaOH was noted, and titration acidity as a percent was calculated:

$$\text{Titration acidity (\%)} = \frac{V \times E \times 100}{M} \quad (1)$$

where: V was the spent volume of NaOH, E was taken as 0.006005 g acetic acid (major acid for vinegar) equivalent to 1 mL of 0.1 N NaOH spent, and M was the sample weight [Bakir *et al.*, 2017].

°Brix values of the vinegars were measured using an Abbe refractometer (Reichert, Benchtop Refractometers AR 700, New York, NY, USA) calibrated with distilled water. The values were expressed as °Brix.

Color values of the vinegar were measured using a chromameter (Lovibond RT Series Reflectance Tintometer, Amesbury, UK). Color was expressed as L* (whiteness/darkness), a* (redness/greenness), and b* (yellowness/blueness).

Total phenolic and total flavonoid content

Vinegar samples were filtered using a 0.45 μm polytetrafluoroethylene (PTFE) syringe filter and appropriately diluted with methanol for further analysis. Total phenolic content (TPC) of the vinegar was determined with the Folin-Ciocalteu (FC) reagent according to the method described by Singleton & Rossi [1965]. Gallic acid was chosen as a reference standard. An aliquot of 0.5 mL of the sample was added to 2.5 mL of FC reagent (0.2N) and 2 mL of Na_2CO_3 (2%). The final mixture was incubated for 30 min at room temperature in the dark, the absorbance was measured at 760 nm using a Shimadzu 150 UV-1800 spectrophotometer (Kyoto, Japan). The results were presented as mg gallic acid equivalent (GAE) per 100 mL of vinegar. The linear range of the standard curve was from 0.01 to 0.6 mg/mL (r^2=0.999).

Total flavonoid content (TFC) of the vinegar was determined according to the method described by Zhishen *et al.* [1999]. The sample (1 mL) was mixed with 4 mL of distilled water, 0.3 mL of $NaNO_2$ (5%), and 0.3 mL of $AlCl_3$ (10%) solution, and allowed to stand for 6 min. Then, 2 mL of NaOH (1 M) was added and the volume was completed to 10 mL with distilled water. Absorbance was measured at 510 nm using a Shimadzu 150 UV-1800 spectrophotometer. The results were presented as mg catechin equivalents (CE) per 100 mL of vinegar. The linear range of the standard curve was from 0.01 to 0.5 mg/mL (r^2=0.998)

Antioxidant activity assays

The DPPH assay was performed as described by Brand-Williams *et al.* [1995]. Volumes of 0.1 mL of each vinegar diluted with the same ratio (1:12, *v/v*) were added to 4.9 mL of DPPH$^\bullet$ solution (6×10^{-5} M in methanol). The mixture was incubated at room temperature for 20 min in the dark. The absorbance was measured at 517 nm by Shimadzu UV-1800 spectrophotometer, and the results were given as inhibition percentage (*I*%) according to the following equation.

$$\text{I (\%)} = \frac{Abs_C - Abs_S}{Abs_C} \times 100 \quad (2)$$

where: Abs_S and Abs_C were the absorbances of the sample and control (DPPH$^\bullet$ solution), respectively.

The CUPRAC assay (the cupric-reducing antioxidant capacity) was carried out according to the method of Apak *et al.* [2004] with slight modifications. The 1-mL portions of $CuCI_2$ solution (0.01 M), neocuproine (7.5 mM), and 1 M ammonium acetate buffer (pH 7.0) solutions were added to a test tube. After the addition of 0.1 mL of vinegar sample, the total volume was adjusted to 4.1 mL with distilled water. All samples were incubated at room temperature for 1 h in the dark. The absorbance was measured at 450 nm using a Shimadzu UV-1800 spectrophotometer. The results were expressed as mg Trolox equivalent (TE) per 100 mL of vinegar. The standard curve ranged from 25 to 400 μM (r^2=0.994).

The FRAP assay (ferric reducing antioxidant power) was performed according to Benzie & Strain [1996]. The FRAP reagent was produced by mixing 300 mM acetate buffer (pH 3.6), 10 mM TPTZ solution and 20 mM $FeCl_3\times6H_2O$ in a 10:1:1 (*v/v/v*) ratio just before use. The TPTZ solution was prepared in 40 mM HCl. A 100 μL sample was mixed with 900 μL of H_2O and 2 mL of FRAP reagent and incubated at room temperature for 30 min in the dark. The absorbance

was measured at 593 nm using a spectrophotometer. The results were expressed as mg Trolox equivalent (TE) per 100 mL of vinegar. The curve for the Trolox was linear in the concentration range of 10-100 μM (r^2=0.999).

HPLC analysis of phenolic compounds

Phenolic profiles of vinegar were evaluated using the HPLC system (LC-20AD pump, SIL-20A HT autosampler, CTO-10ASVP column oven, DGU-20A5R degasser, and CMB-20A communications bus module) coupled to a diode array detector – SPDM20A DAD (Shimadzu Corp., Kyoto, Japan). Standard calibration curves were prepared by using gallic acid, protocatechuic acid, *p*-hydroxybenzoic acid, caffeic acid, syringic acid, *p*-coumaric acid, rutin, and kaempferol. The samples were filtered through a 0.45-μm membrane filter and 1 mL of the filtered samples was placed into vials and analyzed. Separations were conducted at 40°C on an Inertrsil® ODS C-18 reversed-phase column (250 ×4.6 mm, 5 μm particle size, GLSciences, Tokyo, Japan). The mobile phase included solvent A (distilled water with 0.1% (*v/v*) acetic acid) and solvent B (acetonitrile with 0.1% (*v/v*) acetic acid). A gradient elution as follows: 10% B (0 to 2 min), 10% to 30% B (2 to 27 min), 30% to 90% B (27 to 50 min) and 90% to 100% B (51 to 60 min), and at 63 min returns to initial conditions. The flow rate was 1 mL/min. Chromatograms were recorded at 278, 320, and 360 nm. Identification and quantitative analyses were done based on the retention times and external standard curves. HPLC--DAD results were presented as mg of individual phenolic per L of vinegar for all samples.

Volatile compound analysis

Volatile compounds of vinegars were identified using the GCMS-QP2010 system (Shimadzu, Milan, Italy) combined with a CTC-Combi-PAL-Autosampler (Bender and Holbein, Zurich, Switzerland).

The column used for chromatographic separation was Restec (Bellefonte, USA) Rtx-5MS fused silica capillary column (30 m×0.25 mm, 0.25 μm). Firstly, vinegar samples were transferred to 20 mL of headspace vials. The samples were heated to 70°C and agitated at 500 rpm for 15 min. The headspace parameters used were: incubation temperature, 70°C; incubation time, 15 min; syringe temperature, 70°C; agitation speed, 500 rpm; injection volume, 500 μL; fill speed 200 μL/s; pull up delay 500 ms; injection speed, 350 μL/s; pre-injection delay, 500 ms; and post-injection delay, 1500 ms. Volume of 0.5 mL of the headspace sample was injected into the column of GC-MS system. GC conditions were: injection temperature, 150°C; oven temperature, 40°C for 3 min, then programmed at 8.0°C/min to 176°C, finally 176°C for 20 min; interface temperature, 280°C; and ion source temperature, 230°C. The carrier gas was helium with a flow rate of 1.71 mL/min. The mass spectrometer was operated in the selected ion-monitoring mode with an electron impact ionization voltage of 70 eV, and data were collected over a range of *m/z* 35–550. Analyses were performed in duplicate for each sample. The identification of volatiles was performed by comparison of the mass spectra of detected volatile compounds with the commercial mass spectra libraries (NIST27 and WILEY7). Quantification was performed based on the relative peak areas that were used directly to give the percentage volatile composition of the vinegar by dividing the area of each peak by the total area under all of the peaks.

Analysis of lipid oxidation in mayonnaise samples

Preparation of mayonnaise samples

The recipe contained the following ingredients in a weight ratio (*w/w*): sunflower oil (70%), egg yolk (10%), vinegar (18%), sugar (0.82%), salt (0.82%), and xanthan gum (0.36%). A coarse emulsion was initially formed by dissolving egg yolk, sugar, salt, xanthan gum, and vinegar. Mayonnaise was prepared by adding the oil to the aqueous mixture at a steady rate and mixing the ingredients using an IKA T-25 Ultra-Turrax high-speed homogenizer (IKA®-Werke GmbH & Co. KG, Staufen, Germany) at 7000 rpm for 5 min until a homogenous emulsion was obtained.

Oxidation tests

Oxidation of mayonnaise samples was monitored using an OXITEST–Oxidation stability Reactor (Velp Scientifica, Usmate, Milan, Italy), equipped with two separate oxidation chambers. After placing the sample in a chamber, it was hermetically sealed and heated to 90°C. Then, pressurized oxygen (99.9999% purity) was injected into the chamber. The analysis was initiated after the oxygen pressure reached 6 bar. The OXITEST reactor monitors the absolute pressure change inside the chambers calculating the oxygen uptake of the oxidizable compounds of the samples and automatically generates the induction period (IP) of oxidation. The higher the IP value, the higher the resistance of the sample to the oxidation.

The data obtained from the OXITEST reactor were set to first-order oxidation kinetics to estimate the oxidation rate constant (*k*). The change in the pressure by time was fitted to the first-order kinetic equation, kinetic parameters were calculated by using nonlinear regression analysis using Statistica software (StatSoft, Tulsa, USA). First-order kinetic equation followed:

$$C = C_0 \times \exp(-k \times t) \quad (3)$$

where: C_0 represents the initial pressure value (bar) in the sample vessel of the OXITEST device, *k* introduces the rate constant for oxidation kinetics, C represents the pressure that varies with time, and time is defined as *t* in hours.

Statistical analysis

All data were presented as a mean of at least three measurements, *i.e.* ± standard deviation for each vinegar. The differences among the vinegar samples were evaluated by one--way analysis of variance (ANOVA) combined with the Tukey comparison test at $p<0.05$ significance level. Principal component analysis (PCA) was performed to analyze all data. Multivariate data analysis was performed to discriminate vinegar samples by applying PCA and hierarchical clustering analysis (HCA). PCA data matrix consisted of TPC, TFC, color parameters, antioxidant activity, induction period, and phenolic content as variables. HCA data matrix consisted

TABLE 1. Physicochemical properties of vinegars.

Vinegar type	Color values			Total acidity (%)	pH	°Brix
	L*	a*	b*			
Rosehip	60.4±0.426^{de}	7.62±0.278^{c}	39.4±0.241^{a}	3.74±0.040^{d}	2.59±0.006^{e}	4.01±0.006^{c}
Fig	79.0±0.620^{bc}	-0.227±0.029^{g}	13.7±1.54^{f}	4.01±0.028^{b}	2.66±0.006^{d}	4.87±0.058^{a}
Lemon	82.1±0.780^{a}	-1.54±0.078^{h}	5.70±0.530^{h}	3.04±0.046^{g}	2.71±0.010^{b}	4.17±0.058^{c}
Jujube Fruit	77.3±0.200^{c}	-1.36±0.086^{h}	14.2±0.355^{f}	2.55±0.023^{h}	2.64±0.000^{d}	4.53±0.058^{b}
Artichoke	80.5±1.06^{ab}	-1.41±0.040^{h}	8.84±1.47^{g}	2.19±0.006^{j}	2.78±0.006^{a}	3.67±0.148^{d}
Blackberry	60.2±0.772^{de}	6.41±0.355^{d}	32.4±0.311^{c}	3.80±0.009^{d}	2.56±0.006^{f}	4.13±0.058^{c}
Guelder-rose	55.1±1.07^{gh}	11.5±0.354^{b}	36.7±0.905^{ab}	5.04±0.030^{a}	2.55±0.010^{f}	4.03±0.028^{c}
Walnut	57.2±1.32^{fg}	2.70±0.562^{f}	20.4±1.79^{e}	3.78±0.009^{d}	2.68±0.006^{c}	4.43±0.058^{b}
Pomegranate	41.5±0.556^{i}	12.5±0.146^{a}	22.4±0.475^{e}	3.29±0.015^{f}	2.50±0.006^{g}	3.23±0.058^{ef}
Red grape	58.0±0.68^{ef}	11.8±0.180^{ab}	28.1±0.118^{d}	3.89±0.009^{c}	2.35±0.006^{h}	3.33±0.058^{e}
Apple	53.7±1.07^{h}	8.19±0.375^{c}	34.5±0.220^{bc}	3.50±0.016^{e}	2.72±0.006^{b}	4.17±0.106^{c}
Hawthorn	61.3±0.62^{d}	4.47±0.343^{e}	33.1±1.72^{c}	2.29±0.017^{i}	2.76±0.006^{a}	3.17±0.058^{f}

Data represent the means ± standard deviations of three measurements. The comparison is between values in rows, means with the same letter are not significantly different ($p>0.05$).

of major volatiles observed in vinegar samples. Data analyses were conducted with Minitab® 17.3.1 (Minitab Inc., State College, USA) software. The Pearson correlation test was employed to determine the correlation coefficients between antioxidant assays and total phenolic and flavonoid contents.

RESULTS AND DISCUSSIONS

Physicochemical properties

The physicochemical properties of vinegar samples are given in Table 1. The pH levels of the vinegar samples were between 2.35 and 2.77, and the total acidity ranged between 2.19 and 5.04%, the guelder-rose vinegar had the highest, whereas artichoke and hawthorn vinegars had the lowest acidity. °Brix value represents the sugar equivalents in vinegar, and it is related to the fermentation since the level of soluble sugars decreases as a result of microorganism activity. The raw material, type of starter cultures, and the methods of production affect °Brix values [Nakamura *et al.*, 2010]. In our study, fig vinegar had the highest °Brix value. The color properties of vinegar are important regarding consumer perception. L*, a*, and b* parameters indicate the lightness-darkness, redness--greenness, and yellowness-blueness of the samples, respectively. L* values of the samples ranged from 41.5 (pomegranate vinegar) to 82.1 (lemon vinegar), a* values ranged from -0.227 (fig vinegar) to 12.5 (pomegranate vinegar), b* values were between 5.70 (lemon vinegar) and 39.4 (rosehip vinegar), and the color of the vinegar samples was mainly related to the raw material.

Total phenolic, total flavonoid content and antioxidant activities

Bioactive properties, namely total phenolic content (TPC), total flavonoid content (TFC), DPPH radical scavenging activity, cupric-reducing antioxidant capacity (CUPRAC), and ferric reducing antioxidant power (FRAP) of vinegar are given in Table 2. TPC of vinegar ranged from 25.0 to 88.1 mg GAE/100 mL, and TFC varied from 9.74 to 34.9 mg CE/100 mL of vinegar. ANOVA revealed significant differences between the vinegar samples ($p<0.05$) according to the type of raw material. The highest contents of both TPC and TFC were determined in blackberry, rosehip, and guelder-rose vinegars, whereas the lowest ones in lemon and artichoke vinegars. Except for artichoke vinegar, TPC and TFC of vinegars in our study were higher (between 17 and 90 mg GAE/100 mL for TPC, and 2.4 and 34 mg CE/100 mL for TFC) than those found for the similar vinegars studied by Bakir *et al.* [2017] who investigated the antioxidant activities of different types of vinegar in Turkey. The DPPH radical scavenging activity of vinegar in our study ranged from 7.97 to 55.9%; walnut vinegar had the highest DPPH radical scavenging activity, followed by pomegranate, hawthorn, blackberry, and guelder-rose vinegars. Similarly to DPPH radical scavenging activity, the highest CUPRAC was determined in walnut vinegar, and it was significantly higher than in the other vinegars ($p<0.05$) that had high CUPRAC values, namely blackberry, rosehip, guelder-rose, and pomegranate vinegars. In terms of FRAP, the highest value was determined in blackberry vinegar, followed by hawthorn, walnut, and guelder-rose vinegars, though the difference between blackberry and hawthorn vinegars was not significant.

The bioactive properties of vinegars can vary depending on the type of raw material used. In our study, lemon, artichoke, jujube fruit, and fig vinegars showed the lowest values regarding all antioxidant activity tests. Different than our results, it was found that traditional home-made artichoke vinegar had higher DPPH radical scavenging activity than hawthorn and pomegranate vinegars [Ozturk *et al.*, 2015]. However, similar to our results, Bakir *et al.* [2017] deter-

TABLE 2. Total phenolic content (TPC), total flavonoid content (TFC), and antioxidant activities of vinegars.

Vinegar type	TPC (mg GAE/100 mL)	TFC (mg CE/100 mL)	DPPH• scavenging activity (%)	CUPRAC (mg TE/100 mL)	FRAP (mg TE/100 mL)
Rosehip	81.4±0.356^{b}	33.6±0.315^{a}	47.4±0.510^{b}	247±4.64^{bc}	36.6±0.404^{c}
Fig	46.9±0.577^{i}	12.8±0.010^{e}	19.2±0.572^{d}	132±0.814^{g}	10.7±1.01^{f}
Lemon	26.8±0.153^{j}	9.74±0.185^{f}	9.09±0.242^{f}	91.1±6.75^{h}	15.5±0.817^{f}
Jujube fruit	57.9±0.456^{f}	9.84±0.185^{f}	7.97±0.716^{f}	135±5.61^{fg}	16.1±1.18^{ef}
Artichoke	25.0±0.214^{k}	11.2±0.010^{ef}	11.7±0.557^{e}	62±3.49^{i}	14.8±1.26^{f}
Blackberry	88.1±0.761^{a}	33.9±0.543^{a}	54.4±1.36^{a}	263±0.814^{b}	58.1±0.524^{a}
Guelder-rose	81.9±0.384^{b}	34.9±1.67^{a}	54.4±1.04^{a}	233±4.25^{c}	49.3±2.96^{b}
Walnut	67.2±0.410^{c}	16.2±0.364^{d}	55.9±0.840^{a}	315±8.20^{a}	49.9±2.14^{b}
Pomegranate	62.7±0.064^{e}	21.4±0.364^{c}	55.3±0.916^{a}	214±6.37^{d}	41.9±1.95^{c}
Red grape	48.1±0.100^{h}	20.2±0.656^{c}	46.8±0.159^{b}	163±8.34^{e}	25.3±1.32^{d}
Apple	50.7±0.213^{g}	15.3±0.010^{d}	39.4±0.485^{c}	147±5.21^{efg}	21.5±1.01^{de}
Hawthorn	64.7±0.115^{d}	26.1±1.45^{b}	54.9±0.399^{a}	151±11.4^{ef}	54.4±3.96^{ab}

GAE, gallic acid equivalent; CE, catechin equivalent; TE, Trolox equivalent; CUPRAC, cupric- reducing antioxidant capacity; FRAP, ferric reducing antioxidant power. Data are means ± standard deviations of triplicate determinations (n=3). Comparison is between values in rows, means with the same letter are not significantly different ($p>0.05$).

mined that blackberry, rosehip, and guelder-rose vinegars had higher antioxidant potential determined as CUPRAC, FRAP and DPPH• scavenging activity than artichoke vinegar. Some studies have demonstrated that antioxidant activity of vinegars is correlated with their phenolic content since the aromatic phenolic ring in their structure can stabilize unpaired electrons [Verzelloni *et al*., 2007; Xie *et al.*, 2017]. In our study, the Pearson correlation coefficients (r) for correlations of the results of antioxidant activity tests and TPC were 0.752, 0.844, and 0.802 when antioxidant potential was analyzed as DPPH• scavenging activity, CUPRAC, and FRAP, respectively. The r values for correlations between the antioxidant activity and TFC were 0.767 (DPPH• scavenging activity), 0.652 (CUPRAC), and 0.780 (FRAP).

Phenolic profiles

Gallic acid, protocatechuic acid, and caffeic acid were the main phenolics identified in vinegars (Table 3). In the study of Yun *et al*. [2016], eleven vinegars made out of fruits, cereals, and nuts were screened for their phenolic content, and gallic acid, protocatechuic acid, and caffeic acid were most abundant phenolics detected in their samples. In our study, regarding these three phenolic acids, their total content was significantly higher in blackberry and guelder-rose vinegar, followed by pomegranate, red grape, and walnut vinegar. Gallic acid content ranged from 7.41 to 22.3 mg/L, and the highest concentration was determined in blackberry vinegar, followed by red grape, guelder-rose, and pomegranate vinegars. The level of caffeic acid ranged from 10.8 to 14.1 mg/L, and the difference among the samples was not significant. The protocatechuic acid content of the samples varied between 5.63 and 9.08 mg/L, although the guelder-rose had the highest levels, its difference from pomegranate, hawthorn, and rosehip vinegars was only significant (Table 3).

Considering the content and number of individual phenolics identified in our samples, the content was the highest in walnut, blackberry, and guelder-rose vinegars. Kaempferol was only identified in blackberry vinegar, and syringic acid was determined in hawthorn vinegar (Table 3). Rutin was detected in hawthorn at the highest concentration and followed by apple and walnut vinegars. The presence of rutin in apple vinegars was also reported by Kelebek *et al*. [2017]. The content of *p*-coumaric acid in guelder-rose vinegar was significantly ($p<0.05$) higher than those of blackberry, walnut, and apple vinegars. Bakir *et al.* [2017] determined significantly higher *p*-hydroxybenzoic acid content in guelder-rose, pomegranate, and artichoke vinegars among their vinegar samples. In our study, although the content of *p*-hydroxybenzoic acid was also the highest in guelder-rose, the difference among other samples was not found as significant ($p>0.05$). It has already been reported that the different production methods (conventional or submerged), biotechnological process (alcoholic fermentation or acetous fermentation), or the raw materials involved in vinegar processing may have substantial effects on the bioactive components of the final product [Ho *et al.*, 2017]. For example, Kelebek *et al.* [2017] screened eight apple and grape vinegars with different brands and produced in different geographical regions for their bioactive components and revealed that the content of individual compounds varied in different grape and apple vinegar samples. In another study, unpolished rice vinegars contained more phenolic compounds compared to rice vinegar, because rice bran in the unpolished rice provided a higher amount of phenolic acids such as dihydroferulic acid, dihydrosinapic acid, sinapic acid, vanillic acid, and *p*-hydroxycinnamic acid [Shimoji *et al*., 2002].

The PCA was conducted to reduce the number of dimensions and to obtain a small number of factors that show the maximum variability between the samples. Three princi-

TABLE 3. Contents (mg/mL) of individual phenolics in vinegars.

Vinegar type	Gallic acid	Protocatechuic acid	Caffeic acid	*p*-Hydroxybenzoic acid	Syringic acid	*p*-Coumaric acid	Rutin	Kaempferol
Rosehip	8.48±2.15^{de}	5.63±0.858^{c}	12.46±3.19^{a}	–	–	–	–	–
Fig	9.99±1.94^{de}	8.11±1.61^{ab}	13.65±1.72^{a}	1.55±0.679^{a}	–	–	–	–
Lemon	7.41±0.344^{e}	6.90±0.728^{abc}	10.8±0.532^{a}	3.04±1.00^{a}	–	–	–	–
Jujube fruit	10.9±0.869^{cde}	6.83±0.878^{abc}	10.9±0.744^{a}	–	–	–	7.72±0.244^{c}	–
Artichoke	7.87±0.348^{e}	7.96±0.393^{abc}	10.8±0.258^{a}	2.12±1.09^{a}	–	–	8.14±0.219^{c}	–
Blackberry	22.3±4.98^{a}	7.46±1.36^{abc}	14.1±0.879^{a}	–	–	1.21±0.344^{b}	–	2.84±0.548
Guelder-rose	14.9±2.55^{bc}	9.08±0.714^{a}	14.1±0.900^{a}	3.09±0.758^{a}	–	2.77±0.754^{a}	–	–
Walnut	11.3±0.380^{cde}	8.35±0.487^{ab}	14.1±0.125^{a}	2.59±1.04^{a}	–	1.30±0.170^{b}	8.59±1.46^{bc}	–
Pomegranate	13.2±2.49^{bcd}	6.18±0.878^{bc}	12.7±1.55^{a}	1.59±0.481^{a}	–	–	–	–
Red grape	16.9±1.06^{b}	6.99±0.876^{abc}	12.0±0.620^{a}	–	–	–	–	–
Apple	8.54±0.441^{de}	7.44±0.797^{abc}	13.2±1.61^{a}	2.00±0.756^{a}	–	1.14±0.437^{b}	10.19±0.785^{b}	–
Hawthorn	8.55±0.561^{de}	6.25±0.694^{bc}	12.28±1.04^{a}	–	1.71±0.163	–	14.7±1.48^{a}	–

Data represent the mean ± standard deviations of three measurements. "-" not detected. The comparison is between values in rows, means with the same letter are not significantly different ($p>0.05$).

pal components (PCs) with eigenvalues >1 accounted for 80.1% of the total variance. PC1 and PC2 explained 54.2% and 17.5% of the total variance, respectively. According to biplot in Figure 1, artichoke, lemon, and jujube fruit vinegars were located on the left side of the plot, whereas blackberry, walnut, and guelder-rose vinegars were located on the right side, which showed that they have roughly opposite responses. PC1 revealed the highest variation, the differences among the samples along the PC1 axis explained more, compared to the similar distances along the PC2 axis. The variables affecting PC1 were related to blackberry, guelder-rose, walnut, rosehip, and pomegranate vinegars. The last two most likely differed from the others based on the effects of the variables on PC2. The variables, including TPC, TFC, and antioxidant activity values were correlated with each other and contributed similar information on PC1. The color parameters a* and b* were also in the same group and were negatively correlated with L* values. Comparing the angles between variables, it could be evaluated that CUPRAC, IP, and p1 (gallic acid content) were more correlated with each other, and that TPC, TFC, DPPH• scavenging activity, FRAP, a* and b* values were closely correlated. The content of p2 (protocatechuic acid), p4 (p-hydroxybenzoic acid), and p6 (rutin) did not show any correlation with the antioxidant activity values.

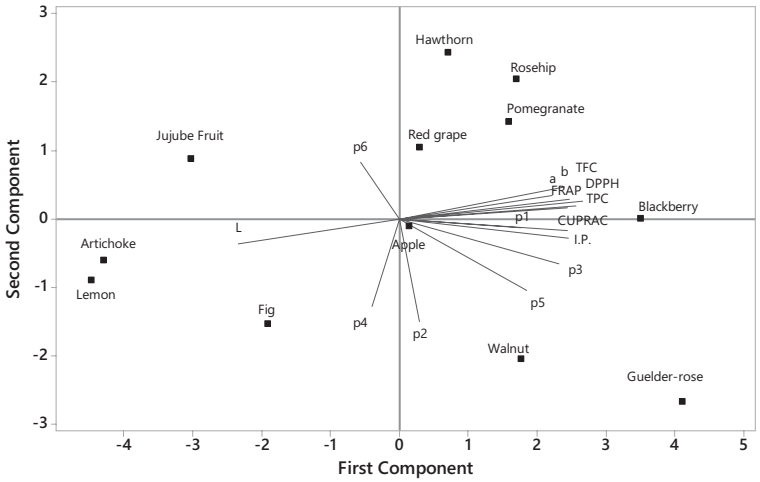

FIGURE 1. Principal component analysis (PCA) biplot for vinegars.

Variables are total phenolic content (TPC), total flavonoid content (TFC), DPPH• scavenging activity (DPPH), cupric- reducing antioxidant capacity (CUPRAC), ferric reducing antioxidant power (FRAP), induction period of mayonnaise oxidation by OXITEST (IP), color parameters: L* (lightness), a* (redness) and b* (yellowness), and content of gallic acid (p1), protocatechuic acid (p2), caffeic acid (p3), *p*-hydroxybenzoic acid (p4), *p*-coumaric acid (p5), and rutin (p6).

Volatile compounds

A total of 114 individual volatile compounds were identified in the vinegar samples and listed in Table 4. The volatile composition of vinegar is widely variable; it usually includes higher content of alcohols, esters, and some aldehydes and ketones. The compounds belonging to acetic acid esters and alcohol groups were the major volatiles. Among acetic acid esters, isoamyl acetate was determined in all vinegars at changing ratios. Except for blackberry, pomegranate, and lemon vinegar, acetic acid esters were more abundant, whereas the ratio of alcohols was more prominent in these samples. Isoamyl acetate and ethyl acetate are among the compounds with the highest odor activity value in vinegar [Baena-Ruano *et al.*, 2010]. It is related to the fruity aroma, and the production of isoamyl alcohol and acetic acid during fermentation. Similar to that, isoamyl alcohol was the most abundant volatile constituent belonging to the alcohol group, it was determined in all vinegars except for fig vinegar. It was also reported that isoamyl alcohol (3-methyl-1-butanol) was the most abundant volatile in vinegar samples [Callejón *et al.*, 2008]. α-Terpineol was only detected in lemon and jujube fruit vinegar. α-Terpineol has been proposed as an indicator for predicting the storage time of citrus fruits, and it was produced from its putative precursors in citrus juice (D-limonene and linalool). Its content was found higher in lemon juice than in orange or grapefruit juices stored for a month. Leonés *et al.* [2019] showed the decrease of α-terpineol content during the transformation of lemon juice to lemon vinegar. 3-Methyl-2-pentanone was only found in blackberry and pomegranate vinegars at high portions of total volatile compounds.

To study the possible similarities among the volatile compositions of the samples, the data (main peaks belonging to each group) was subjected to a hierarchical clustering analysis by taking the squared Euclidean as a distance measure and the Ward linkage method. The dendrogram showed two clusters (Figure 2). In one cluster, rosehip and artichoke vinegars showed the highest similarity, followed by blackberry and hawthorn vinegara. This similarity could be due to a higher isoamyl alcohol proportion in rosehip, artichoke, and blackberry vinegars compared to other samples. Additionally, rosehip and artichoke vinegars had a higher proportion of 1-methyl-propyl acetate, whereas blackberry had a lower one.

1-Methylpropyl acetate proportion of hawthorn vinegar was also approx. 75% of acetic acid esters and with this content hawthorn vinegar significantly differed from the other samples. The similarity of jujube fruit vinegar to other samples in their cluster was low, its differences are based on the proportion of 1-hexyl acetate (in acetic acid ester group), propyl propionate, and ethyl butyrate (ester group). In the study of Yang *et al*. [2019], it was determined that in the later storage period of fresh jujube fruits, hexyl acetate was one of the most important volatile components.

Oxidative stability of mayonnaise samples

The capacity of vinegars to delay the oxidation of mayonnaise was measured by the OXITEST method, and induction periods (IP) of mayonnaise samples prepared with different vinegars are given in Table 5. Compared to lemon vinegar, widely used in mayonnaise production, IP of the mayonnaise samples prepared with guelder-rose, pomegranate, fig, hawthorn, and a few other vinegars was significantly higher. IP of mayonnaise samples prepared with jujube fruit, artichoke, and red grape vinegar was not significantly different ($p>0.05$) compared to the sample prepared with lemon vinegar. The coefficients of Pearson correlations between IP and antioxidant activity of vinegars were found as 0.760 ($DPPH^{\bullet}$ scavenging activity), 0.627 (CUPRAC), and 0.598 (FRAP), whereas these determined between IP and TPC and TFC were at 0.694 and 0.623, respectively.

Oxidative stability of emulsions is one of the crucial factors determining the shelf life of products. Several factors such as types of oil, formulation, and pH, oxygen concentration,

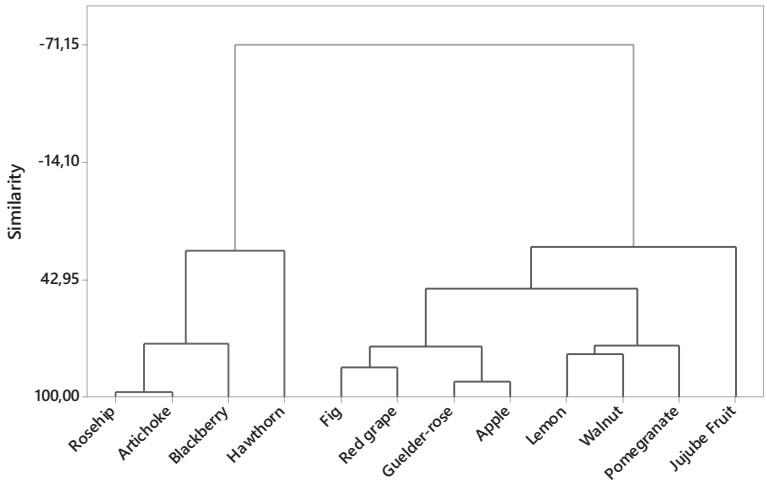

FIGURE 2. Hierarchical cluster analysis of volatiles of vinegars. The dendrogram was obtained using the squared Euclidean distance measure and Ward method as linkage.

The variables included are individual proportions of 1-methylpropyl acetate, isoamyl acetate, isobutyl acetate, 2-methylbutyl acetate, *n*-butyl acetate, 1-hexyl acetate, 3-methyl-2-pentanone, 2-methyl-1-butanol, isoamyl alcohol, α-terpineol, propyl propionate, ethyl isovalerate, ethyl butyrate, ethyl lactate, methyl propyl ether, and 1-chloromethane. The proportion of the variables was more than 90% of the total volatile area for each vinegar sample.

TABLE 4. Compositions and relative content (% area) of volatiles in vinegars.

Volatiles	Rosehip	Fig	Lemon	Jujube fruit	Artichoke	Blackberry	Guelder–rose	Walnut	Pomegranate	Red grape	Apple	Hawthorn
Acetic acid esters												
1-Methylpropyl acetate	30.6	–	–	–	22.2	5.44	27.9	20.3	4.65	–	14.7	54.9
Isoamyl acetate	20.9	25.6	28.3	18.2	23.4	19.7	16.9	38.9	19.5	23.4	17.1	6.77
2-Methylpropyl acetate	2.85	–	4.95	4.24	6.35	8.57	8.14	7.25	9.97	11.6	1.25	–
2-Methylbutyl acetate	–	25.7	–	–	–	–	18.3	–	–	23.7	22.8	8.64
n-Butyl acetate	–	10.6	7.03	–	–	–	–	0.74	–	–	7.49	2.57
2,3-Butanediol diacetate	–	2.21	–	0.27	–	–	–	–	–	–	–	–
Phenethyl acetate	–	0.16	–	–	–	0.18	–	–	–	–	–	–
1-Hexyl acetate	–	–	0.22	27.3	1.79	–	–	–	–	–	–	–
n-Propyl acetate	–	–	–	–	–	–	–	–	–	–	–	–
1,2-Dimethylpropyl acetate	–	–	–	–	–	–	–	–	–	–	0.69	–
Menthyl acetate	–	–	–	–	–	0.27	–	–	–	–	–	–
Acids												
2-Oxovaleric acid	0.13		–	–	–	–	–	–	–	–	–	–
2,3-Dibromobut-2-enedioic acid		0.41	–	–	–	–	–	–	–	–	–	–
Aldehydes												
3-Methylglucose	0.14	–	–	–	–	–	–	–	–	–	–	–
Tetradecanal	0.30	–	–	–	–	–	–	–	–	–	–	–
Octadecanal	0.29	–	–	–	–	–	–	–	–	–	–	–
n-Hexanal	0.14	–	–	–	–	–	–	–	–	–	–	–
1,6-Anhydro-β-D-glucopyranose	–	0.88	–	–	–	–	–	–	–	–	–	–
Benzeneacetaldehyde	–	0.15	–	–	–	–	–	–	–	–	–	–
Phenylacetaldehyde	–	–	–	1.08	–	–	–	–	–	–	–	–
Ketones												
2-Pentadecanone	0.13	–	–	–	–	–	–	–	–	–	–	–
Isomenthone	–	0.22	–	–	0.09	–	–	–	–	–	–	–
3,7,7-Trimethylbicyclo[4.1.0] heptan-4-one	–	0.21	–	–	–	–	–	–	–	–	–	–
Acetoin	–	–	–	–	–	–	0.72	0.76	1.07	0.20	–	–
3-Hydroxycyclohexanone	–	–	–	–	–	–	–	–	–	–	0.39	0.49

TABLE 4. Continued

Volatiles	Rosehip	Fig	Lemon	Jujube fruit	Artichoke	Blackberry	Guelder–rose	Walnut	Pomegranate	Red grape	Apple	Hawthorn
Ketones												
Tetrahydrothiopyran-4-one	–	0.24	–	–	–	–	–	–	–	–	–	–
p-Menthan-3-one	–	–	–	0.13	–	–	–	–	–	–	–	–
3-Methyl-2-pentanone	–	–	–	–	–	19.5	–	–	17.6	–	–	–
Alcohols												
2-Methyl-1-butanol	–	12.4	19.6	–	–	–	18.8	20.1	33.6	28.5	25.2	–
Isoamyl alcohol	33.1	–	12.4	6.44	34	39.9	6.62	7.33	10.4	9.08	8.22	13.3
trans-1,2-Cyclopentanediol	0.11	–	–	–	–	–	–	–	–	–	–	–
4-Ethyl-1-octyn-3-ol	0.14	–	–	–	–	–	–	–	–	–	–	–
Eucalyptol	–	–	1.44	–	–	0.24	–	–	–	–	–	–
Cyclopentanol	–	–	–	–	–	–	–	–	–	–	–	0.30
Phenethyl alcohol	0.15	0.17	–	–	0.19	0.32	–	0.13	–	–	–	–
l-Menthol	0.28	–	–	0.32	–	–	–	–	–	–	–	–
2-Ethyl-1-decanol	–	–	–	0.24	–	–	–	–	–	–	–	–
Fenchyl alcohol	–	–	0.78	0.28	–	–	–	–	–	–	–	–
6-Tridecanol	–	–	–	–	–	–	–	1.58	–	–	–	–
α-Terpineol	–	–	18.5	3.19	–	–	–	–	–	–	–	–
Terpinen-4-ol	–	–	1.23	0.26	–	–	–	–	–	–	–	–
2-Heptanol	–	–	–	–	–	–	–	–	0.33	–	–	–
2-Ethoxyethanol	0.21	–	–	–	–	–	–	–	0.17	–	–	–
Linalool	–	–	–	–	–	–	–	–	–	–	–	0.12
2-Propoxyethanol	–	–	–	–	–	–	0.42	–	–	–	–	–
3-Octanol	–	–	–	–	–	–	–	–	–	–	–	0.28
Neomenthoglycol	0.05	–	–	–	–	–	–	–	–	–	–	–
Carvomenthol	–	–	–	–	–	0.12	–	–	–	–	–	–
2-Methyl-2-methylamino-1-propanol	–	–	–	–	–	–	–	–	–	–	–	0.83
2,4-Dimethyl-3-hexanol	0.14	–	–	0.67	–	–	–	–	–	–	–	–
n-Hexanol	–	–	–	–	1.85	0.14	–	–	–	0.16	–	–
Borneol	–	–	0.29	–	–	–	–	–	–	–	–	–

TABLE 4. Continued

Volatiles	Rosehip	Fig	Lemon	Jujube fruit	Artichoke	Blackberry	Guelder–rose	Walnut	Pomegranate	Red grape	Apple	Hawthorn
Alcohols												
1-(4-Methoxyphenyl)ethanol	–	0.27	–	–	–	–	–	–	–	–	–	–
2-Isopropoxyethanol	–	0.17	–	–	–	–	–	–	–	–	–	–
2,3-Butanediol	–	–	–	1.83	–	–	–	–	–	–	–	–
Heptane-1,7-diol	–	0.18	–	–	–	–	–	–	–	–	–	–
1,3-Butylene glycol	–	0.49	–	–	–	–	–	–	–	–	–	–
2-Ethyl hexanol	–	0.22	–	–	–	–	–	–	–	–	–	0.18
Nonan-2-ol	–	0.33	–	–	–	–	–	–	–	–	–	–
Isomenthol	–	0.51	–	–	–	–	–	–	–	–	–	–
2-(4-Methylphenyl)-2-propanol	–	–	–	–	–	–	–	–	–	–	–	–
Esters												
Ethyl butanoate	0.20	–	–	–	–	0.31	–	–	0.37	0.10	–	0.73
Ethyl 2-methylbutyrate	–	–	–	0.79	0.49	–	–	–	–	–	–	–
Propyl butyrate	–	–	–	0.24	–	–	–	–	–	–	–	–
Methyl 5-hydroxypentanoate	–	0.22	–	–	–	–	–	–	–	–	–	–
Hexyl formate	–	–	–	0.50	–	–	–	–	–	–	–	–
2-Methylpropyl 2-hydroxypropanoate	0.40	–	–	–	–	–	–	–	–	–	–	–
Butyl propionate	0.23	–	–	–	–	–	–	0.16	–	–	–	–
Pentyl propionate	–	–	–	0.35	–	–	0.30	–	–	–	–	–
Ethyl octanoate	–	–	–	–	0.59	0.67	–	0.23	–	–	–	–
Ocimenyl acetate	–	–	–	0.22	–	–	–	–	–	–	–	–
Amylpropionate	–	–	–	–	–	–	–	–	–	–	0.18	0.19
Propyl propionate	–	–	–	8.06	0.59	–	–	–	–	–	0.13	2.40
sec-Butyl propionate	–	–	–	–	–	–	–	–	–	–	–	–
Diethyl carbonate	–	–	–	–	0.150	–	–	–	–	–	–	0.87
Ethyl isovalerate	0.29	0.71	0.31	2.86	0.67	0.85	0.25	0.16	0.58	0.66	–	0.51
sec-Butyl acetate	0.49	–	–	–	–	–	–	–	–	–	–	–
Methyl 3-hydroxyhexanoat	0.13	–	–	–	–	–	–	–	–	–	–	–
Ethyl hexanoate	0.22	–	0.91	1.31	1.36	0.78	–	0.41		0.19	0.39	0.73

TABLE 4. Continued

Volatiles	Rosehip	Fig	Lemon	Jujube fruit	Artichoke	Blackberry	Guelder–rose	Walnut	Pomegranate	Red grape	Apple	Hawthorn
Esters												
Ethyl butyrate	–	0.15		4.99	1.73	–	–	0.63		0.57	–	–
3-Hydroxypropyl prop-2-enoate	0.28	–	–	–	–	–	–	–	–	–	–	–
Isopropyl butanoate	–	–	–	–	–	–	–	–	–	–	–	0.17
Propyl valerate	–	–	–	0.20	–	–	–	–	–	–	–	–
Isobutyl lactate	–	–	–	0.46	–	–	–	–	–	–	–	–
Ethyl lactate	–	1.47	2.19		3.17	0.97	–	–	0.55	0.22	–	4.18
Ethyl heptanoate	–	0.27	–	0.11	0.15	–	–	–	–	–	–	–
Methyl 2-methoxy-3-methyl-2-butenoate	–	0.18	–	–	–	–	–	–	–	–	–	–
Bornylester	–	0.51	–	0.21	0.10	–	–	–	–	0.22	–	–
Isopropyl laurate	–	0.24	–	–	–	–	–	–	–	–	–	–
8-Bromo-3-oxo-octanoic acid methyl ester	–	0.18	–	–	–	–	–	–	–	–	–	–
Others												
2,4,5-Trimethyl-1,3-dioxolane	0.16	3.73	–	0.34	–	0.28	0.50	0.16	–	–	–	–
Cyclohexasiloxane	2.54	–	–	0.27	0.15	–	–	–	–	–	–	–
Vitispirane	0.77	–	0.16	–	0.25	0.33	0.33	–	–	0.50	–	0.88
Methyl propyl ether	–	–	–	14.6	–	–	–	–	–	–	–	–
1,1,2-Trimethylcyclohexane	0.30	–	–	–	–	–	–	–	–	–	–	–
1-Nonadecene	0.25	–	–	–	–	–	–	–	–	–	–	–
1,4-Cineole	–	–	0.77	–	–	–	–	–	–	–	–	–
2-Carene	–	–	0.24	–	–	–	–	–	–	–	–	–
2-Hydroxyheptane	–	–	–	–	–	–	–	–	0.33	–	–	–
5-Eicosene	0.23	–	–	–	–	–	–	–	–	–	–	–
6-(Methylthio)purine	–	0.27	–	–	–	–	–	–	–	–	–	–
Phenyl-2-nitropropene	0.31	–	–	–	–	–	–	–	–	–	–	–
Limonene	–	–	0.17	–	–	–	–	–	–	–	–	–
Linaloyl oxide	–	–	0.46	–	–	–	–	–	–	–	–	–
Nonylbenzene	0.35	–	–	–	–	–	–	–	–	–	–	–
2,2-Dimethyldecane	–	–	–	–	–	–	–	–	–	–	–	0.14

TABLE 4. Continued

Volatiles	Rosehip	Fig	Lemon	Jujube fruit	Artichoke	Blackberry	Guelder–rose	Walnut	Pomegranate	Red grape	Apple	Hawthorn
Others												
Methyl pentyl disulfide	–	0.21	–	–	–	–	–	–	–	–	–	–
1-Heptadecene	0.94	–	–	–	–	–	–	–	–	–	–	–
1-Chloropentane	–	6.98	–	–	–	–	–	–	–	–	–	–
[3-(2-Cyclohexylethyl)-6-cyclopentylhexyl]benzene	0.48	–	–	–	–	–	–	–	–	–	–	–
6-Phenylhexylamine	–	0.23	–	–	–	–	–	–	–	–	–	–
1-Nonadecene	0.27	–	–	–	–	–	–	–	–	–	–	–
2,2,4,6,6-Pentamethylheptane	–	0.27	–	–	–	–	–	–	–	–	–	–
2-Methyl-1,3-dioxolane	1.49	3.32	–	–	0.22	0.55	0.32	0.33	–	–	–	–

TABLE 5. Induction period (IP) and rate constant (k) of oxidation of the mayonnaises prepared with different kinds of vinegar.

	IP (min)	C_0 (bar)	k	R^2
Rosehip	356 ± 5.5^{abc}	6.40	1.89^{c}	>0.99
Fig	359 ± 2.0^{ab}	6.55	1.80^{d}	>0.99
Lemon	318 ± 2.5^{e}	6.81	2.11^{a}	>0.99
Jujube fruit	331 ± 4.0^{cde}	6.45	2.08^{a}	>0.99
Artichoke	325 ± 3.0^{de}	6.54	2.07^{a}	>0.99
Blackberry	355 ± 4.5^{bc}	6.34	1.90^{c}	>0.97
Guelder-rose	382 ± 7.0^{a}	6.69	1.91^{c}	>0.99
Walnut	358 ± 7.0^{abc}	6.68	1.80^{d}	>0.99
Pomegranate	363 ± 6.5^{ab}	6.70	1.76^{d}	>0.99
Red grape	340 ± 17.0^{bcde}	6.66	2.12^{a}	>0.99
Apple	351 ± 7.5^{bcd}	6.65	2.01^{b}	>0.98
Hawthorn	357 ± 21.5^{abc}	6.33	1.78^{d}	>0.99

Data are means ± standard deviations of triplicate determinations (n=3). R^2 is the coefficient of determination and C_0 is the inital presure in the sample vessel. The comparison is between values in rows, means with the same letter are not significantly different ($p>0.05$).

antioxidants presence, interfacial characteristics, and droplet characteristics affect the oxidative stability of the mayonnaise-type emulsions [Paraskevopoulou *et al.*, 2007]. In our study, the induction period (IP) and oxidation rate constant (k) were used in evaluating the oxidative stability of emulsions. IP value ranged from 318 to 382 min and differed significantly among vinegar types ($p<0.05$). The samples formulated with guelder-rose and lemon vinegars showed the highest and the lowest IP value, respectively. The high positive correlation (0.760) was observed between $DPPH^{\bullet}$ scavenging abilities of vinegar and IP value, meaning that the samples prepared with vinegar with high radical scavenging ability showed more resistance to the oxidation. Oxidation data, namely time *versus* pressure, were set to the first-order kinetic model to determine the oxidation rate of mayonnaise samples at 90°C and the effect of vinegar type on oxidation rate. The k values were used to compare the oxidation rate of the samples. They differed significantly among vinegar types and ranged from 1.78 to 2.12 (Table 5). The samples with high IP values showed lower k values. The higher k values were determined for the samples prepared with lemon, jujube fruit, red grape, and artichoke vinegars. Therefore, both oxidation rate and shelf life were closely related to vinegar types, and the oxidative stability of the mayonnaise type emulsions could be improved by the selection of vinegar showing high radical scavenging abilities.

CONCLUSION

In this study, different types of vinegars manufactured with the traditional method were characterized regarding their physicochemical properties, total phenolic and total flavonoid contents, antioxidant activity, individual phenolic

content, and volatile composition. The capabilities of vinegars to delay lipid oxidation in mayonnaise samples, and its correlation with antioxidant activity values were also evaluated. In terms of the analyzed properties, blackberry, guelderrose, and walnut vinegars can be recommended over the other vinegars. Due to their antioxidant properties, vinegar types should be accounted for an important factor in the production of mayonnaise to improve its oxidative stability. PCA and HCA presented similarities and differences among the vinegars based on the variables studied. The vinegars produced from different raw materials could be easily differentiated according to antioxidant activities, individual phenolics, and volatile compounds. This study suggests that fruit type should be considered as a crucial factor in the production of vinegars affecting not only sensory properties but also their physicochemical and bioactive properties.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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REFERENCES

1. Apak, R., Güçlü, K., Özyürek, M., Karademir, S.E. (2004). Novel total antioxidant capacity index for dietary polyphenols and vitamins C and E, using their cupric ion reducing capability in the presence of neocuproine: CUPRAC Method. *Journal of Agricultural and Food Chemistry*, *52*(26), 7970–7981. https://doi.org/10.1021/jf048741x
2. Baena-Ruano, S., Santos-Dueñas, I.M., Mauricio, J.C., García--García, I. (2010). Relationship between changes in the total concentration of acetic acid bacteria and major volatile compounds during the acetic acid fermentation of white wine. *Journal of the Science of Food and Agriculture*, *90*(15), 2675–2681. https://doi.org/10.1002/jsfa.4139
3. Bakir, S., Devecioglu, D., Kayacan, S., Toydemir, G., Karbancioglu-Guler, F., Capanoglu, E. (2017). Investigating the antioxidant and antimicrobial activities of different vinegars. *European Food Research and Technology*, *243*(12), 2083–2094. https://doi.org/10.1007/s00217-017-2908-0
4. Benzie, I.F.F., Strain, J.J. (1996). The ferric reducing ability of plasma (FRAP) as a measure of "Antioxidant Power": The FRAP Assay. *Analytical Biochemistry*, *239*(1), 70–76. https://doi.org/10.1006/abio.1996.0292
5. Brand-Williams, W., Cuvelier, M.E., Berset, C. (1995). Use of a free radical method to evaluate antioxidant activity. *LWT – Food Science and Technology*, *28*(1), 25–30. https://doi.org/10.1016/S0023-6438(95)80008-5
6. Budak, N.H., Aykin, E., Seydim, A.C., Greene, A.K., Guzel--Seydim, Z.B. (2014). Functional properties of vinegar. *Journal of Food Science*, *79*(5), R757–R764. https://doi.org/10.1111/1750-3841.12434
7. Callejón, R.M., González, A.G., Troncoso, A.M., Morales, M.L. (2008). Optimization and validation of headspace sorptive extraction for the analysis of volatile compounds in wine vinegars. *Journal of Chromatography A*, *1204*(1), 93–103. https://doi.org/10.1016/j.chroma.2008.07.064
8. Chen, H., Chen, T., Giudici, P., Chen, F. (2016). Vinegar functions on health: Constituents, sources, and formation mechanisms. *Comprehensive Reviews in Food Science and Food Safety*, *15*(6), 1124–1138. https://doi.org/10.1111/1541-4337.12228
9. Chou, C.-H., Liu, C.-W., Yang, D.-J., Wu, Y.-H. S., Chen, Y.-C. (2015). Amino acid, mineral, and polyphenolic profiles of black vinegar, and its lipid lowering and antioxidant effects *in vivo*. *Food Chemistry*, *168*, 63–69. https://doi.org/10.1016/j.foodchem.2014.07.035
10. De Leonardis, A., Macciola, V., Iorizzo, M., Lombardi, S.J., Lopez, F., Marconi, E. (2018). Effective assay for olive vinegar production from olive oil mill wastewaters. *Food Chemistry*, *240*, 437–440. https://doi.org/10.1016/j.foodchem.2017.07.159
11. Ho, C.W., Lazim, A.M., Fazry, S., Zaki, U.K.H.H., Lim, S.J. (2017). Varieties, production, composition and health benefits of vinegars: A review. *Food Chemistry*, *221*, 1621–1630. https://doi.org/10.1016/j.foodchem.2016.10.128
12. Horiuchi, J.-I., Kanno, T., Kobayashi, M. (1999). New vinegar production from onions. *Journal of Bioscience and Bioengineering*, *88*(1), 107–109. https://doi.org/10.1016/S1389-1723(99)80186-8
13. Kelebek, H., Kadiroğlu, P., Demircan, N.B., Selli, S. (2017). Screening of bioactive components in grape and apple vinegars: Antioxidant and antimicrobial potential. *Journal of the Institute of Brewing*, *123*(3), 407–416. https://doi.org/10.1002/jib.432
14. Lee, J.-H., Cho, H.-D., Jeong, J.-H., Lee, M.-K., Jeong, Y.-K., Shim, K.-H., Seo, K.-I. (2013). New vinegar produced by tomato suppresses adipocyte differentiation and fat accumulation in 3T3-L1 cells and obese rat model. *Food Chemistry*, *141*(3), 3241–3249. https://doi.org/10.1016/j.foodchem.2013.05.126
15. Leonés, A., Durán-Guerrero, E., Carbú, M., Cantoral, J. M., Barroso, C.G., Castro, R. (2019). Development of vinegar obtained from lemon juice: Optimization and chemical characterization of the process. *LWT – Food Science and Technology*, *100*(June 2018), 314–321. https://doi.org/10.1016/j.lwt.2018.10.096
16. Lopez-Huertas, E., Fonolla, J. (2017). Hydroxytyrosol supplementation increases vitamin C levels *in vivo*. A human volunteer trial. *Redox Biology*, *11*, 384–389. https://doi.org/10.1016/j.redox.2016.12.014
17. Mohamad, N.E., Keong Yeap, S., Beh, B.K., Romli, M.F., Yusof, H.M., Kristeen-Teo, Y. W., Sharifuddin, S.A., Long, K., Alitheen, N.B. (2018). Comparison of *in vivo* toxicity, antioxidant and immunomodulatory activities of coconut, nipah and pineapple juice vinegars. *Journal of the Science of Food and Agriculture*, *98*(2), 534–540. https://doi.org/10.1002/jsfa.8491
18. Nakamura, K., Ogasawara, Y., Endou, K., Fujimori, S., Koyama, M., Akano, H. (2010). Phenolic compounds responsible for the superoxide dismutase-like activity in high-brix apple vinegar. *Journal of Agricultural and Food Chemistry*, *58*(18), 10124–10132. https://doi.org/10.1021/jf100054n

19. Ozturk, I., Caliskan, O., Tornuk, F., Ozcan, N., Yalcin, H., Baslar, M., Sagdic, O. (2015). Antioxidant, antimicrobial, mineral, volatile, physicochemical and microbiological characteristics of traditional home-made Turkish vinegars. *LWT – Food Science and Technology*, *63*(1), 144–151. https://doi.org/10.1016/j.lwt.2015.03.003
20. Paraskevopoulou, D., Boskou, D., Paraskevopoulou, A. (2007). Oxidative stability of olive oil–lemon juice salad dressings stabilized with polysaccharides. *Food Chemistry*, *101*(3), 1197–1204. https://doi.org/10.1016/j.foodchem.2006.03.022
21. Samad, A., Azlan, A., Ismail, A. (2016). Therapeutic effects of vinegar: a review. *Current Opinion in Food Science*, *8*, 56–61. https://doi.org/10.1016/j.cofs.2016.03.001
22. Shimoji, Y., Tamura, Y., Nakamura, Y., Nanda, K., Nishidai, S., Nishikawa, Y., Ishihara, N., Uenakai, K., Ohigashi, H. (2002). Isolation and identification of DPPH radical scavenging compounds in Kurosu (Japanese unpolished rice vinegar). *Journal of Agricultural and Food Chemistry*, *50*(22), 6501–6503. https://doi.org/10.1021/jf020458f
23. Singleton, V.L., Rossi, J.A. (1965). Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. *American Journal of Enology and Viticulture*, *16*(3), 144 LP–158. http://www.ajevonline.org/content/16/3/144.abstract
24. Ubeda, C., Callejón, R.M., Hidalgo, C., Torija, M.J., Troncoso, A.M., Morales, M.L. (2013). Employment of different processes for the production of strawberry vinegars: Effects on antioxidant activity, total phenols and monomeric anthocyanins. *LWT – Food Science and Technology*, *52*(2), 139–145. https://doi.org/10.1016/j.lwt.2012.04.021
25. Verzelloni, E., Tagliazucchi, D., Conte, A. (2007). Relationship between the antioxidant properties and the phenolic and flavonoid content in traditional balsamic vinegar. *Food Chemistry*, *105*, 564–571. https://doi.org/10.1016/j.foodchem.2007.04.014
26. Xie, X., Zheng, Y., Liu, X., Cheng, C., Zhang, X., Xia, T., Yu, S., Wang, M. (2017). Antioxidant activity of chinese shanxi aged vinegar and its correlation with polyphenols and flavonoids during the brewing process. *Journal of Food Science*, *82*(10), 2479–2486. https://doi.org/10.1111/1750-3841.13914
27. Yang, L., Liu, J., Wang, X., Wang, R., Ren, F., Zhang, Q., Shan, Y., Ding, S. (2019). Characterization of volatile component changes in jujube fruits during cold storage by using Headspace-Gas Chromatography-Ion Mobility spectrometry. *Molecules* (*Basel, Switzerland*), *24*(21), 3904. https://doi.org/10.3390/molecules24213904
28. Yu, X., Yang, M., Dong, J., Shen, R. (2018). Comparative analysis of the antioxidant vapacities and phenolic compounds of oat and buckwheat vinegars during production processes. *Journal of Food Science*, *83*(3), 844–853. https://doi.org/10.1111/1750-3841.14074
29. Yun, J.-H., Kim, Y.-J., Koh, K.-H. (2016). Investigation into factors influencing antioxidant capacity of vinegars. *Applied Biological Chemistry*, *59*(4), 495–509. https://doi.org/10.1007/s13765-016-0185-4
30. Zhishen, J., Mengcheng, T., Jianming, W. (1999). The determination of flavonoid contents in mulberry and their scavenging effects on superoxide radicals. *Food Chemistry*, *64*(4), 555–559. https://doi.org/10.1016/S0308-8146(98)00102-2

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