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Differentiation of olive oils based on rheological and sensory characteristics obtained from six olive cultivars

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RESEARCH ARTICLE

Abstract

This study was conducted to differentiate between olive oils obtained from different cultivars, namely, Arbequina, Memecik, Uslu, Domat, Hojiblanca and Gemlik, based on their pigment concentration, phenolic and volatile profiles and rheological properties. The phenolic and volatile profiles and rheological and sensorial properties of olive oils obtained from these olive cultivars were compared in this study. Tyrosol and hydroxytyrosol were found to be the most abundant phenolic compounds and determined to be 0.80-14.81 mg/kg and 0.24-13.82 mg/kg, respectively. Of the six cultivars, Gemlik had the highest concentrations of both tyrosol and hyrdoxytyrosol. Additionally, 44 different volatile compounds were identified and their distributions significantly differed across the six cultivars. A steady shear test was conducted to determine flow behaviour properties of olive oil samples, and results revealed that their viscosity values did not significantly differ and ranged from 0.0574 to 0.0610 Pa·s (P<0.05).

Keywords: olive oils, phenolics, rheology, sensorial, volatile compounds

1. Introduction

Virgin olive oil (VOO) is an important part of the Mediterranean diet, and its consumption is linked with health aspects, such as reduction of the risk of coronary disease, prevention of several cancers and developing of the immune and inflammatory responses. Health benefits of VOO can be attributed to some its chemical compounds, such as oleic acid, phenolic antioxidants, phytosterols, carotenoids and tocopherols. Therefore, VOO is considered as a functional food due to the presence of these compounds, which have some therapeutic effects (Segura-Carretero *et al.*, 2010). In addition to these positive health effects, VOO has considerable economic importance because of the its high production and demand.

Phenolic compounds are one of the most important chemical groups contributing to the nutritional and sensory qualities, and increasing the stability of olive oil. These compounds also have positive effects on human health because of their antioxidant, antimicrobial and anti-carcinogenic activities (Rigane *et al.*, 2013). Several types of phenolic compounds have been reported in VOO, such as phenolic alcohols, secoiridoid derivatives, phenolic acids, lignans and flavonoids (Artajo *et al.*, 2007).

In addition to the phenolics, volatiles compounds affect sensory and nutritional quality of the olive oils. Furthermore, volatile compounds are responsible for the characteristic aroma of the olive oils. The cultivar is one of the main factors affecting the volatile and phenolic composition of the olive oils (Gomez-Rico *et al.*, 2006).

Rheological characterisation of the edible oil is very important for different applications, such as crystallisation studies of palm oil; oil absorption in the frying process; and for the development, optimisation and new formulation for the pharmaceutical field (Sánchez-Gutiérrez *et al.*, 2015). VOO is obtained from the olive fruits by mechanical or physical processes, such as washing, crushing, pressing,

centrifugation, decantation and filtration under thermal conditions. The rheological properties of olive oils are very important parameters in the design of the pump and in the decantation and filtration processes. In addition, rheological properties affect the sensory characteristics of the final product (Bonnet *et al.*, 2011). Although some studies have investigated the rheological properties of some vegetable and olive oils (Rubalya Valantina *et al.*, 2013; Santos *et al.*, 2005), studies on the effect of the olive cultivar on the rheological and sensory properties of the olive oil are limited (Bonnet *et al.*, 2011).

As can be seen, the sensory and technological qualities of VOO are highly related to its chemical composition, which is affected by the geographic area and cultivars. The characterisation of VOOs in terms of their chemical composition is an important issue for the selection of new cultivars with good characteristics. This study aimed to differentiate between olive oils obtained from different cultivars by evaluating their phenolic and volatile compounds and rheological and sensory properties.

2. Materials and methods

Arbequina, Domat, Gemlik, Hojiblanca, Memecik and Uslu cultivars grown in the same orchard were used in this study. Olive samples were harvested in December in 2012 and 2013.

Olive ripening index

Olive samples were handpicked at the stage of the ripening index (RI) based on the degree of skin and pulp pigmentation (Kayahan and Tekin, 2006). Only healthy fruits without any kind of infection or physical damage were processed. The RI was determined on 100 randomly selected fruits (in triplicates) to obtain a numerical value for the olive sample appearance. The analysis was performed in triplicate.

Extraction of olive oil

To perform the experiment, the fruits were mechanically processed at laboratory conditions by using two-phase batch equipment (Hakki Usta Machinery, Aydin, Turkey). The steps of the extraction process were as follows: (1) removing the leaves from olive fruits, (2) milling of drupes by a disc miller and (3) kneading of the resultant paste for 45 min at 27 °C (Hakki Usta Machinery). Both time and temperature were standardised during the extraction, centrifugation and separation processes. The oil samples were stored in a freezer at -20 °C until their analysis.

Determination of total chlorophyll and carotenoid content, and colour value

The extraction of chlorophyll and carotenoid pigments from olive oil was carried out according to the method described previously (Minguezmosquera *et al.*, 1991). The chlorophyll and carotenoid fractions in the absorption spectrum were determined at 670 and 470 nm, respectively, using a spectrophotometer (T70+UV/VIS spectrophotometer, PG Instruments, Lutterworth, UK).

The chlorophyll and carotenoid contents were calculated using Equations 1 and 2, respectively:

$$\text{Chlorophyll (mg/kg)} = \frac{(A_{670} \times 10^6)}{(613 \times 100 \times L)} \quad (1)$$

$$\text{Carotenoid (mg/kg)} = \frac{(A_{470} \times 10^6)}{(2{,}000 \times 100 \times L)} \quad (2)$$

The chlorophyll and carotenoid pigments were expressed as mg pheophytin *'α'* per kg oil using Equation 3, where Aλ is the absorbance and L is the spectrophotometer cell thickness (10 mm) (Pokorny *et al.*, 1995).

For pheophytin *'α'* (mg/kg oil as Pheo α) =

$$345.3 \left(A_{670} - \frac{(A_{630} + A_{710})}{2}\right) / L \quad (3)$$

The colour value of the olive oil samples was assessed by a colorimeter (Konica Minolta Chroma meter CR-300, Tokyo, Japan). The samples were measured by immersing the probe into the samples. Ten measurements of the L*, a* and b* values were recorded, and their average value and standard deviation were calculated.

Determination of phenolic composition

The phenolic composition of the olive oil samples was determined by the method described by Caponio *et al.* (1999) with some modifications. The phenolic compounds of the olive oil samples were extracted by a liquid/liquid extraction method using a solution of methanol/water (40:60, v/v). The solvent was evaporated in a rotary evaporator at 35 °C under vacuum. The residue was dissolved in methanol, and filtered through a 0.45-mm-pore size membrane filter (Vivascience AG, Hannover, Germany). Detection and quantification were carried out with a SCL-10A VP system controller, a SIL-10AD VP auto sampler, an LC-10AD-VP pump, a DGU-14a degasser, a CTO-10 A VP column heater and a diode array detector at 278 nm (Shimadzu Corporation, Kyoto, Japan). The 250 × 4.6 mm (i.d.), 5-mm column filled with Luna Prodigy was used (Phenomenex Inc., Torrance, CA, USA). The

Table 1. Solvent gradient conditions with linear gradient.[1]

Final time (min)	3	20	28	35	45	60	62	70	75	80
A %	95	75	72	70	65	63	55	50	20	0
B %	5	25	28	30	35	37	45	50	80	100

[1] A (solvent) = acetic acid:water (2:98, v/v); B (solvent) = methanol.

flow rate was 1 ml/min, the injection volume was 10 ml and the column temperature was set at 30 °C. Gradient elution was carried out with two solvents: solvent A consisted of acetic acid:water (2:98, v/v) and solvent B was methanol. The gradient program is given in Table 1. The data were integrated and analysed using the Shimadzu Class-VP Chromatography Laboratory Automated Software system (Shimadzu Corporation). The amount of phenolic compounds in the extract was calculated as mg/kg oil using external calibration curves. All determinations were carried out in triplicate and the average results were given.

Total phenolic content

Total phenolic content of the samples was determined spectrophotometrically at 760 nm according to modified method described by Singleton and Rossi (1965). The method for extraction of the phenolic compounds was explained previously. A 1 ml olive oil extract was mixed with 2.5 ml of Folin-Ciocalteu reagent and 2 ml of 7.5% sodium carbonate solution. The mixture was thoroughly shaken on a vortex mixer and incubated for 20 min. After incubation, absorbance was measured at 760 nm. The results were expressed as milligrams of gallic acid equivalents per kilogram (mg GAE/kg).

Extraction and determination of volatile compounds

Headspace solid-phase micro extraction method was used for aroma extraction from olive oil. Approximately 2 g of the oil samples were inserted into a 10-ml headspace screw-top vial and allowed to equilibrate for 10 min at 40 °C. The headspace of the samples was extracted for 15 min at 45 °C using a CTC Combi PAL auto sampler equipped with 75 µm carboxen/polydimethylsiloxane solid-phase micro extraction fibre (CTC Analytics AG, Zwingen, Switzerland). The volatile compounds were desorbed by directly inserting the fibre for 45 min into the injection port of the gas chromatograph coupled to a mass spectrometer (GC-MS) maintained at 250 °C.

Analyses of volatile compounds were performed using a GC-MS (Shimadzu Corporation) with a quadrupole detector (QP2010 SE; Shimadzu Corporation) system fitted with an Rx-5 SilMS capillary column (30 m × 0.25 mm (i.d.), film thickness 0.25 mm; Restek Corporation, Bellefonte, PA, USA). Detector and injector temperature were set at 250 °C. The temperature program was 40 °C (2 min) to 250 °C at a rate of 4 °C/min followed by holding at 250 °C for 5 min. Helium was used as a carrier gas at a flow rate of 14 psi (split 1:10 ml/min) and the injection volume of each sample was 1 ml. The ionisation energy was set at 70 eV. Qualitative analysis was based on the comparison of retention times with those of the authentic reference compounds, by determining their linear retention index relative to the series of n-hydrocarbons (C7-C30), and the computer mass spectra libraries using Wiley, Nist and FFNSC. The percentage composition was computed based on the GC peak areas.

Rheological analysis

Steady shear properties

Steady shear properties of the olive oils were evaluated to determine flow behaviour of the samples by using a stress- and strain-controlled rheometer (MCR 302; Anton Paar, Graz, Austria) equipped with a Peltier heating system. Shear rate measurements were performed in the shear rate range of 1-100 s^{-1} at 25 °C using a plate-plate configuration (50 mm diameter, 0.5 mm gap). Each measurement was performed with three replicates. The apparent viscosity of the sample was determined as a function of shear rate.

Temperature sweep test

Temperature sweep test was performed at 50 s^{-1} shear rate and within the temperature range of 5-80 °C. The obtained η versus temperature data was fitted to the Arrhenius equation:

$$\eta = A_0 \exp\left(\frac{E_a}{RT}\right) \quad (4)$$

where A_0 is the constant parameter of the model, η is the apparent viscosity at shear rate 50 s^{-1}, E_a is the activation energy (kj/kg), R is the ideal gas constant and T is the temperature (in Kelvin).

Sensory measurements

Sensory analysis of the olive oil samples was performed by eight selected panellists according to the method described by Ogutcu *et al.* (2008). All the selected panellists were trained to evaluate the aroma, flavour and mouthfeel attributes of the olive oil samples. These sensory attributes of each olive oil sample was assessed. For the sensory analysis, special glass trays were used and filled to three-fourth level with olive oil samples.

Statistical analysis

Nonlinear regression was conducted using Statistica 8.0 (StatSoft Inc., Tulsa, OK, USA) software package and the Levenberg-Marquardt algorithm. The results of this study were reported as mean values of the three replicates and standard deviation. Statistical analysis was performed using Statistica 8.0 (StatSoft Inc.) statistical package program. Significant differences among the means of the samples were evaluated by analysis of variance using Duncan's multiple range tests at 95% confidence (P<0.05).

3. Results and discussion

Ripening index, pigments and colour values of the olive oil samples

Olive oil quality and oil extraction yield are significantly affected from the time of harvest of olive fruits. The lipid content of the olive fruit generally increases during ripening and decreases at the end of the harvest season due to oil degradation (Cevik *et al.*, 2014). Therefore, RI is a useful tool in obtaining olive oil with high quality and extraction yield (Baccouri *et al.*, 2007). RI values of the olive oil samples are shown in Table 2. The RI values of the olive oil samples were determined and found to be in the range of 3.97-5.97. The lowest RI value was obtained for Arbequina samples while the highest RI value was found for Gemlik samples. Baccouri et al. reported that olive oil of high quality and yield were obtained when the RI values were between 3 and 4.5 (Baccouri *et al.*, 2007). Similar results were reported by Salvador *et al.* (2001).

Chlorophylls and carotenoids are the main factors affecting colour of the VOO, which varies from yellow-green to greenish gold. In addition, they have an important role in the oxidative stability of olive oils because of their antioxidant properties in the dark and prooxidant activity in the light (Criado *et al.*, 2008). Chlorophylls, carotenoids and pheophytin-α contents of the olive oil samples are presented in Table 2. As shown in Table 2, these compounds varied from sample to sample. The chlorophyll, carotenoid and pheophytin-α levels were calculated as mg/kg and ranged from 0.09-0.18, 0.14-0.28 and 0.22-0.79 mg/kg, respectively. The pheophytin-α contents were higher than those of the other pigments for all olive oil samples. Pheophytin-α was also found to be the major pigment (0.49-19.42 mg/kg) in the study of Giuffrida *et al.* (2011). Chlorophyll and carotenoid contents were reported to be 7.33-8.83 and 7-14 mg/kg in the report by Arslan *et al.* (2013). In another study, the chlorophyll and carotenoid concentrations were reported to be 2.53-5.02 and 0.42-0.73 mg/kg, respectively, in Chemlali Sfax and Arbequina oils (Chtourou *et al.* 2013).

Table 2 also presents the L*, a* and b* colour values of the olive oil samples. The L* value ranged from 26.98 to 28.43. The highest L* value was obtained for the Gemlik sample while the lowest L* value was determined for the Memecik sample. The a* and b* values ranged from 0.29-1.48 and 1.10-3.70, respectively. It can be inferred from Table 2 that there was a negative trend between the b* value and pheophytin-α concentration.

Phenolic compounds of olive oil samples

The total phenolic content of the olive oil samples varied from 53.50 to 120.14 mg/kg. The highest and lowest values were obtained from the olive samples extracted from the Arebequina and Gemlik cultivars, respectively. The results were in agreement with those of a previously published study (Gouvinhas *et al.*, 2014). The individual phenolic

Table 2. Ripening index (RI), pigments and colour (L*, a*, b*) of olive oil samples.[1]

Cultivars	RI	Chlorophyll (mg/kg)	Carotenoid (mg/kg)	Pheophytin α (mg/kg)	L*	a*	b*
Arbequina	3.97±0.40^{c}	0.12±0.00^{c}	0.18±0.00^{c}	0.38±0.00^{c}	27.60±0.03^{d}	1.12±0.01^{c}	1.67±0.043^{e}
Domat	4.03±0.29^{c}	0.15±0.01^{b}	0.15±0.00^{d}	0.30±0.00^{d}	28.13±0.01^{b}	0.76±0.07^{d}	2.47±0.04^{c}
Gemlik	5.97±0.06^{a}	0.09±0.00^{d}	0.15±0.00^{d}	0.23±0.01^{e}	28.43±0.03^{a}	1.19±0.01^{b}	3.70±0.03^{a}
Hojiblanca	5.37±0.06^{b}	0.17±0.01^{a}	0.28±0.00^{a}	0.62±0.00^{b}	27.82±0.04^{c}	1.19±0.02^{b}	2.06±0.02^{d}
Memecik	4.13±0.47^{c}	0.18±0.00^{a}	0.25±0.00^{b}	0.79±0.01^{a}	26.98±0.01^{a}	0.29±0.04^{a}	1.10±0.01^{f}
Uslu	5.40±0.20^{b}	0.11±0.00^{c}	0.14±0.00^{e}	0.22±0.00^{e}	28.11±0.04^{b}	1.48±0.28^{d}	3.27±0.02^{b}

[1] Means within a column indicated by the same letters are not statistically significant (P>0.05).

compounds and their concentrations in terms of mg/kg of the six different olive oil samples are presented in Table 3. As shown in the table, distribution of the phenolic compounds and their concentrations significantly changed depending on the olive cultivars ($P<0.05$). Table 3 also reveals that hydroxytyrosol and tyrosol were the major phenolic fractions in all olive oils with the exception of the Arbequina samples. These results were in agreement with previously reported data, which revealed that hydroxytyrosol and tyrosol were the most abundant phenolic compounds in different olive oil and olive fruit samples (Arslan *et al.*, 2013; Dağdelen *et al.*, 2013; Ouni *et al.*, 2011; Reboredo-Rodríguez *et al.*, 2014; Yildiz and Uylaser, 2015). The tyrosol and hydroxytyrosol concentrations were found to be 0.80-14.81 and 0.24-13.82 mg/kg, respectively, and the tyrosol content was generally higher than the hydroxytyrosol contents of the samples. Of the six samples, oil from the Gemlik cultivar had the highest concentrations of both tyrosol and hydroxytyrosol while the Arbequina samples had the lowest concentrations of these compounds. The tyrosol and hydroxytyrosol levels of the current study were in agreement with those reported in a previous study (Kesen *et al.*, 2013).

The vanillic acid and vanillin contents were found to be 0.44-2.03 and 0.11-2.15 mg/kg, respectively. The highest vanillic acid and vanillin contents were determined in Hojiblanca samples while the lowest content was obtained from the Memecik cultivar. The samples containing higher vanillic acid contents also showed the highest luteolin concentration.

Phenolic acids are other phenolic compounds identified in this study. These compounds are linked to fruit ripening, colour and sensory qualities and antioxidant properties of fruits (Segura-Carretero *et al.*, 2010). The vanillic acid concentration of the samples were higher than the concentrations of the other phenolic acids, namely, coumaric, ferulic and cinnamic acids. With the exception of vanillic acid, the phenolic acid concentrations were found to be lower than 1 mg/kg. Similar results were reported by Ouni *et al.* (2011) and Rigane *et al.* (2013). Coumaric acid was not detected in Arbequina and Memecik samples, while it was found to be the highest in the Hojiblanca samples. The ferulic acid contents ranged from 0.08 to 0.22 mg/kg and the highest ferulic acid concentration was obtained from Uslu samples. Cinnamic acid was determined from only two samples (Arbequina and Gemlik) at low levels. Generally, with the exception of vanillic acid, our samples had lower phenolic acid contents when compared to those reported previously (Kesen *et al.*, 2013; Saitta *et al.*, 2009).

Quercetin was found to be a major phenolic in Arbequina samples, and Memecik samples were found to have the highest level of quercetin. The quercetin level was determined to be 0.59-1.54 mg/kg. Luteolin is one of the main flavonoid compounds found in VOO. In this study, luteolin was found in all samples and its level ranged from 0.29 to 1.83 mg/kg. Hojiblanca samples showed the highest luteolin concentration while Memecik samples had the lowest luteolin concentration. The luteolin concentrations of our samples in this study were lower than those reported by Kesen *et al.* (2014) in their study. The luteolin concentration was reported to be 1.51-7.57 mg/kg in their study and determined to be 3.43-5.73 mg/kg in the study of Jiménez *et al.* (2013).

Determination of volatile compounds

Volatile compounds are an important parameter and key information for the quality and traceability control of VOOs because of the their contribution toward odour perception (Tena *et al.*, 2007).

The volatility profiles of the olive oil samples are shown in Tables 4 and 5 as a percentage value of each sample. A total of 44 different volatile compounds, including aldehydes, acids, esters, ketones, alcohols, terpenoids, hydrocarbons and furans have been identified. It can be clearly understood from Table 4 that the volatile compounds of the olive oil samples differed according to cultivars.

Table 3. Phenolic compounds of olive oil samples (mg/kg oil).[1]

Cultivars	Hydroxytyrosol	Tyrosol	Vanillic acid	Vanilin	*p*-Coumaric acid	Ferulic acid	Cinnamic acid	Quercetin	Luteolin
Arbequina	0.24±0.03^{e}	0.80±0.10^{f}	0.77±0.07^{ab}	0.12±0.02^{d}	0.00±0.00^{f}	0.08±0.00^{c}	0.04±0.00^{a}	1.46±0.16^{a}	1.34±0.06^{bc}
Domat	5.79±0.20^{b}	11.68±0.30^{c}	1.97±0.45^{a}	0.34±0.04^{b}	0.12±0.01^{b}	0.16±0.03^{b}	0.00±0.00^{a}	1.53±0.10^{a}	0.79±0.09^{d}
Gemlik	13.82±0.20^{a}	14.81±0.10^{a}	2.03±0.03^{a}	0.38±0.03^{b}	0.10±0.00^{c}	0.15±0.01^{b}	0.10±0.00^{a}	0.88±0.08^{b}	1.15±0.10^{c}
Hojiblanca	2.97±0.20^{c}	13.27±0.07^{b}	2.03±0.03^{a}	2.15±0.04^{a}	0.29±0.02^{a}	0.15±0.02^{b}	0.00±0.00^{a}	0.59±0.01^{c}	1.83±0.03^{a}
Memecik	1.14±0.04^{d}	10.77±1.00^{d}	0.44±0.02^{b}	0.11±0.00^{d}	0.00±0.00^{e}	0.09±0.00^{c}	0.00±0.00^{a}	1.54±0.14^{a}	0.29±0.04^{e}
Uslu	1.37±0.07^{d}	3.95±0.30^{e}	0.94±0.10^{b}	0.23±0.02^{c}	0.08±0.00^{d}	0.22±0.01^{a}	0.00±0.00^{a}	0.67±0.02^{c}	1.48±0.28^{b}

[1] Means within a column indicated by the same letters are not statistically significant ($P>0.05$).

Table 4. Chemical classes and volatile compounds detected in the olive oil samples of the cultivars (results expressed in % of total area).

Volatile groups	Compounds	LRI[1]	Cultivars					
			Arbequina	Domat	Gemlik	Hojiblanca	Memecik	Uslu
Aldehydes								
	isobutanal	<700	0.08	0.07	0.00	0.29	0.00	0.05
	3-methylbutanal	<700	0.07	0.04	0.20	0.18	0.06	0.06
	2-methylbutanal	<700	0.60	0.54	3.42	1.61	0.57	0.99
	pentanal	<700	0.21	0.24	0.00	0.00	0.94	0.00
	trans-2-pentenal	751	0.12	0.22	0.36	0.55	0.07	0.11
	cis-3-hexenal	796	0.00	0.00	0.00	10.07	0.00	0.00
	hexanal	801	25.70	39.23	51.74	43.85	17.18	39.48
	trans-2-hexenal	850	68.54	54.23	27.95	16.23	56.94	23.29
	2.4-hexadienal	914	0.31	1.02	0.88	2.71	0.00	0.36
	trans-2-heptenal	956	0.00	0.03	0.00	0.00	0.00	0.00
	nonanal	1,107	0.00	0.00	0.00	0.00	0.00	0.05
Acids								
	acetic acid	<700	0.11	0.31	1.19	0.64	0.00	0.12
	propionic acid	752	0.00	0.00	0.19	0.00	0.00	0.05
Esters								
	isopropyl acetate	<700	0.09	0.00	0.99	0.34	0.00	0.13
	butyl acetate	813	0.00	0.01	0.10	0.00	0.00	0.00
	ethyl 2-methylbutyrate	842	0.00	0.00	0.42	0.00	0.00	0.00
	2-methylbutyl acetate	873	0.00	0.00	0.19	0.00	0.00	0.00
	hexyl acetate	1,012	0.14	0.04	0.60	0.76	0.00	0.06
	2-methylpropyl butanoate	1,035	0.00	0.08	0.00	0.23	0.00	0.00
	cis-3-hexenyl acetate	1,008	0.40	0.28	4.41	6.36	0.00	0.20

[1] LRI = linear retention indices.

Aldehydes were found to be predominantly volatile compounds in all the analysed samples. We identified 11 different aldehyde compounds, and their distribution varied from sample to sample. Among the aldehydes, *n*-hexenal and trans-2-hexenal were found to be most abundant volatile compounds. These compounds accounted for more than 60% of the volatile compounds for all the samples and reached about 95% of the all volatile compounds in the Arbequina and Domat samples, indicating that aldehydes are most important fraction of volatile compounds of the analysed olive oils from a quantitative point of view. *n*-Hexenal was predominantly volatile in the Gemlik, Hojiblanca and Uslu samples while trans-2-hexenal was the most abundant compound in the Arbequina, Domat and Memecik cultivars. Trans-2-hexenal has also been reported to be the most abundant volatile compound in VOO (Kiralan *et al.*, 2012; Luna *et al.*, 2006; Zarrouk *et al.*, 2008). Trans-2-hexenal, which contributes to the positive attributes of the fruity, pungent and bitter aroma of olive oil, is produced by enzymatic process of lipooxygenase pathway (Kiritsakis, 1998). Considering the other aldehyde compounds, *cis*-3-hexenal was only found in the Hojiblanca samples and its value was nearly 10%. 3-Methylbutanal and 2,4-hexadienal were the other aldehyde compounds detected with a percentage value greater than 1%.

Among the acids, acetic acid and propionic acid were the other aromatic compounds determined in olive oil samples at a low level. These compounds are linked to sensory defects in olive oils (Kalua *et al.*, 2007). In this study, the alcohol compounds were the other major aromatic group detected in the VOO samples. Trans-3-hexen-1-ol was the predominant alcoholic volatile compound. Trans-3-hexen-1-ol was determined in the Hojiblanca, Memecik and Uslu samples at 6.79, 13.41 and 6.97%, respectively. The other alcoholic volatile compounds were present at lower than 1%.

Three different ketone compounds including 1-penten-3-one, 3-pentanone and heptan-2-one were identified in olive oil samples. 1-Pentene-3-one was determined in all samples and its value was in the range of 0.62-3.28% (Table 5). Most of the short-chain ketones, which have five to seven carbon

Table 5. Some volatile compounds of olive oil samples.

Volatile groups	Compounds	LRI[1]	Cultivars					
			Arbequina	Domat	Gemlik	Hojiblanca	Memecik	Uslu
Ketones								
	1-penten-3-one	<700	0.62	1.19	1.80	3.23	0.91	3.28
	3-pentanone	<700	0.00	0.00	0.00	0.80	0.00	1.20
	heptan-2-one	898	0.11	0.10	0.30	0.22	0.41	0.15
Alcohols								
	3-methyl-1-butanol	730	0.00	0.00	0.00	0.00	0.00	0.04
	2-methyl-1-butanol	733	0.00	0.00	0.00	0.00	0.00	0.05
	cis-pent-2-enol	767	0.09	0.16	0.00	0.37	0.39	0.45
	trans-3-hexen-1-ol	850	0.00	0.00	0.00	6.79	13.41	6.97
	cis-2-hexen-1-ol	861	0.17	0.05	0.00	0.37	0.68	8.88
	n-hexanol	867	0.21	0.12	0.38	0.70	1.25	12.10
Terpenes								
	anisole	918	0.00	0.16	0.00	0.00	0.00	0.00
	α-pinene	933	0.05	0.03	0.09	0.00	0.00	0.04
	l-limonene	1,030	1.79	0.13	0.58	0.18	0.93	0.27
	β-ocimene	1,046	0.00	0.00	0.00	0.00	0.00	0.15
	α-copaene	1,375	0.00	0.00	0.14	0.13	0.00	0.00
	farnesene	1,504	0.00	0.00	0.16	0.00	0.00	0.07
Hydrocarbons								
	1.2-dimethyl benzene	863	0.02	0.05	0.36	0.25	0.50	0.00
	3-ethyl-1.5-octadiene	891	0.00	0.11	0.00	0.21	0.00	0.00
	3-ethyl-1.5-octadiene	951	0.29	0.44	0.20	0.83	0.39	0.41
	3-ethyl-1.5-octadiene	994	0.28	0.50	0.19	0.88	0.48	0.44
	cis-5-octadecene	1,205	0.00	0.28	2.62	0.23	0.95	0.36
	n-tetradecane	1,400	0.00	0.00	0.09	0.00	0.00	0.06
	heptane	700	0.00	0.00	0.00	0.00	3.96	0.00
Furans								
	5-ethyl-2(5h)-furanone	957	0.00	0.32	0.44	0.99	0.00	0.14

[1] LRI = linear retention indices.

atoms, are associated with positive sensory properties, while the long-chain ketones, which have higher than eight carbon atoms, are indicative of sensory defects (Kalua *et al.*, 2007). In this study, long-chain ketones were not identified in any of the samples.

Esters are produced from alcohol as a result of the catalytic activity of alcohol acetyl transferases (Kalua *et al.*, 2007). Seven ester compounds were found in samples at a very low value compared to other volatile compounds (Table 5). The percentage values of isopropyl acetate and hexyl acetate were higher than those of the other ester compounds.

Terpenoid compounds were the other identified aromatic compounds in this study. Six different terpenoid compounds were determined, and their distribution varied from cultivar to cultivar. Among the terpenoid compounds, limonene showed the highest percentage value ranging from 0.13-1.72%. Hydrocarbon and furan compounds had very low levels with the exception of heptane, which was found only in the Memecik samples at a percentage of 3.96% (Table 5).

It can be summarised that the volatile compound profiles of the olive oil samples varied among samples. Some similarities and differences were observed when compared to previous literature. Different results might have resulted from several factors such as agronomic, climatic and technological aspects; cultivar; geographic region; ripening; harvest and processing methods and extraction methods of volatile compounds (Luna *et al.*, 2006).

Rheological properties of olive oil samples

Flow behaviour properties

Figure 1 depicts measurements of shear stress as function of shear rate. The linear dependence of shear stress on shear rate was observed, meaning that viscosity of the olive oil samples was not affected by shear stress and defined as Newtonian fluid behaviour. These results were in accordance with those in other studies, which revealed that edible oils are Newtonian fluids (Ashrafi, 2012; Kalogianni *et al.*, 2011). Navarra *et al.* (2011) reported that olive oil viscosity showed shear thinning non-Newtonian behaviour below the 5 shear rate value and beyond this value, the oil exhibited Newtonian behaviour. The viscosity of olive oils ranged from 0.0574 to 0.0610. The Gemlik sample had the highest viscosity value while the Uslu sample had the lowest viscosity. Statistical analysis showed that there were no significant differences between olive oil viscosity, indicating that different olive cultivars did not significantly affect olive oil viscosity. The slight differences observed between viscosity values of the olive oils might have resulted from differences in chemical composition such as composition of phenolic compounds, sterol and other molecules. Several authors have reported that fatty acid composition is a very important parameter affecting the rheological properties of edible oils (Santos *et al.*, 2005; Yalcin *et al.*, 2012). Santos *et al.* (2005) stated that concentration of polyunsaturated chains should be affect viscosity to a greater extent than the monounsaturated fatty acid content. They also suggested that antioxidant content did not affect the viscosity of edible oils.

Temperature dependency properties of olive oil viscosity

The temperature sweep test was conducted to determine the effects of temperature on the viscosity of the olive oil samples. Figure 2 represents changes in the viscosity values as a function of temperature. As shown in Figure 2, the viscosity of olive oil decreased with increasing temperature. This can be explained by the decrease in the intermolecular interaction by great thermal movement that improves the flow and reduces viscosity. This result was in agreement with the results of other studies (Bonnet *et al.*, 2011; Santos *et al.*, 2005). Temperature dependency parameters of the samples were determined by modelling the obtained data to the Arrhenius equation. R^2 values showed that the Arrhenius equation can be applied satisfactorily to describe the temperature dependency characteristics of olive oils (R^2>0.98). The E_a values of olive oil samples ranged from 21.43 to 22.94 and no significant differences were observed, meaning that sensitivity of the olive oil viscosity to temperature was not significant (Table 6). These results were in accordance with those of previously published studies (Bonnet *et al.*, 2011). The highest activation energy value was observed in Hojiblanca samples while the lowest value was obtained from Arbequina samples. The E_a values of olive oil samples ranged from 31.951-32.854 kJ/mol in the study by Bonnet *et al.* (2011) and from 22.12 to 23.63 kJ/mol in Rubalya according to Valantina *et al.* (2013).

Sensory measurement

The results of the sensory evaluation, namely, aroma, flavour and mouthfeel attributes, are shown in Tables 7, 8 and 9, respectively. Among the aroma descriptors, 'olive' is considered a positive attribute, while 'rancid' and 'musty/muddy' are negative attributes. 'Olive' is related to the fresh olive fruit and its highest and lowest results were obtained from the Hojiblanca and Uslu samples, respectively. As an indicator of the oxidative deteriorations, 'rancid' was found to be 0.02-0.32 and the mean value of the samples was not significantly different (P>0.05). Significant differences between 'grassy' and 'musty/muddy' scores were found. 'Musty/muddy' is another negative aroma descriptor, which is resulted from using olives spoiled by fungi (Boskou, 1996). The lowest and highest results of the

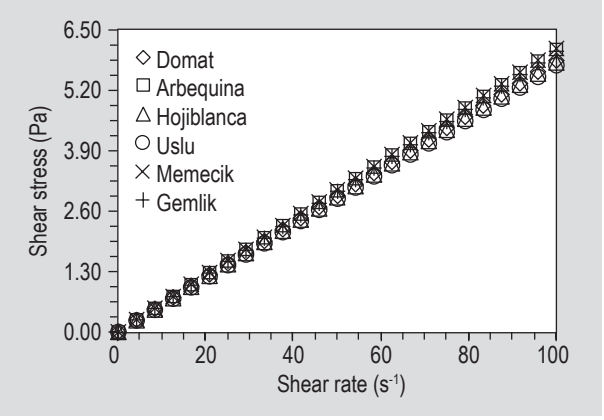

Figure 1. Flow behaviour properties of the olive oil samples obtained from different olive cultivars.

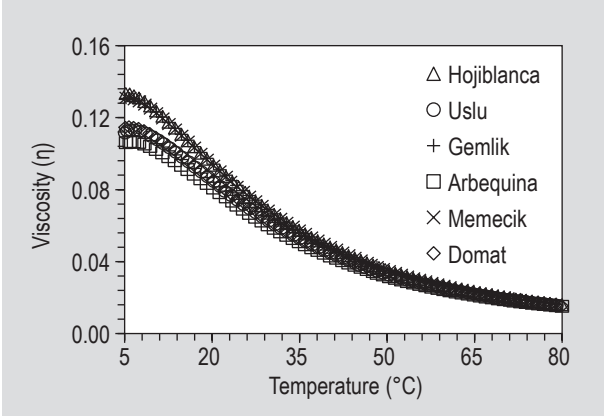

Figure 2. Effect of temperature on the viscosity of the olive oil samples.

Table 6. Apparent viscosity (η) and temperature dependency parameters of the olive oil samples.[1]

Cultivars	η (Pa.s)	Temperature dependency variables		
		A	E_a (Kj/mol)	R^2
Gemlik	0.0606±0.002[a]	7.39×10^{-6}	22.57±0.61[a]	0.9933
Domat	0.0585±0.003[a]	9.66×10^{-6}	21.67±0.76[a]	0.9922
Arbequina	0.0602±0.001[a]	1.17×10^{-5}	21.07±1.25[a]	0.9908
Hogiblanca	0.0582±0.002[a]	6.34×10^{-6}	22.94±1.05[a]	0.9947
Uslu	0.0574±0.003[a]	1.03×10^{-6}	21.48±0.65[a]	0.9919
Memecik	0.0605±0.002[a]	7.08×10^{-6}	22.66±0.84[a]	0.9939

[1] Means within a column indicated by the same letters are not statistically significant (P>0.05).

Table 7. Sensory scores of the aroma of olive oil samples.[1]

Cultivars	Olive	Grassy	Rancid	Musty/ muddy
Arbequina	6.01±1.44[a]	8.85±2.34[ab]	0.25±0.09[a]	0.10±0.16[b]
Domat	6.93±1.32[a]	10.17±1.89[a]	0.12±0.05[a]	0.06±0.10[b]
Gemlik	7.77±2.21[a]	7.87±1.97[ab]	0.32±0.11[a]	0.38±0.13[a]
Hojiblanca	7.81±1.64[a]	8.55±2.16[ab]	0.23±0.03[a]	0.05±0.10[b]
Memecik	6.23±1.60[a]	7.51±2.52[b]	0.03±0.07[a]	0.23±0.17[ab]
Uslu	5.78±2.05[a]	8.73±2.65[ab]	0.02±0.07[a]	0.06±0.17[b]

[1] Means within a column indicated by the same letters are not statistically significant (P>0.05).

Table 8. Sensory scores of the flavour of olive oil samples.[1]

Cultivars	Acid	Astringent	Bitter	Soap	Metallic
Arbequina	0.62±0.49[a]	1.31±0.65[a]	0.45±0.23[ab]	0.98±0,61[a]	0.42±0.28[a]
Domat	0.71±0.22[a]	1.73±0.35[a]	0.63±0.25[ab]	0.95±0.55[a]	0.43±0.35[a]
Gemlik	0.46±0.20[a]	1.13±0.65[a]	0.27±0.11[b]	0.51±0.25[a]	0.46 ±0.15[a]
Hojiblanca	0.46±0.23[a]	1.66±0.44[a]	0.75±0.27[a]	0.72±0.35[a]	0.25±0.11[a]
Memecik	0.65±0.25[a]	1.12±0.45[a]	0.51±0.21[ab]	0.73±0.42[a]	0.38±0.20[a]
Uslu	0.70±0.26[a]	0.76±0.63[a]	0.76±0.22[a]	0.72±0.45[a]	0.72±0.43[a]

[1] Means within a column indicated by the same letters are not statistically significant (P>0.05).

'musty/muddy' scores were obtained from the Hojiblanca and Gemlik samples.

Among the flavour descriptors, 'bitter' was considered to be a positive attribute, while 'metallic' and 'soap' were considered negative attributes. Significant differences were found between 'bitter' results (P<0.05). Uslu shows the highest 'bitter' scores while Gemlik had the lowest 'bitter' scores. The differences between 'metallic', 'soap' and 'astringent' and 'acid' values were not significant (Table 6). The results of the flavour descriptors were in agreement with those in a previously published study (Ogutcu *et al.*, 2008).

The mouthfeel attributes of 'throat catching' and 'thickness' were also analysed and their scores were found to be 3.81-7.75 and 4.67-5.65, respectively. The results of the samples obtained from 'throat catching' attribute differed significantly across the samples (P<0.05). However, the results of the 'thickness' across the different samples were relatively close (P>0.05).

Table 9. Sensory scores of the mouthfeel/after taste of olive oil samples.[1]

Cultivars	Throat catching	Thickness
Arbequina	3.81±1.83[c]	4.67±1.78[a]
Domat	6.81±1.61[ab]	5.51±1.85[a]
Gemlik	5.03±1.99[bc]	5.31±1.71[a]
Hojiblanca	7.37±1.43[a]	5.65±1.64[a]
Memecik	7.75±1.79[a]	5.51±1.24[a]
Uslu	6.43±2.58[ab]	5.43±2.09[a]

[1] Means within a column indicated by the same letters are not statistically significant (P>0.05).

4. Conclusions

Olive oil samples obtained from six different cultivars were characterised based on the chemical compounds and rheological properties. The results of this study showed that the cultivar has a significant effect on the phenolic and volatile profiles and sensorial properties of olive oil samples. These results suggest that olive oil from different cultivars could be differentiated based on the individual phenolic compounds and their concentrations. As expected, all samples showed Newtonian flow behaviour. This study also suggested that steady flow behaviour and temperature dependency parameters of the samples could not be used to differentiate between olive oils. Significant differences between aroma, flavour and mouthfeel attributes were found. The highest 'throat catching' attribute was found in Memecik cultivar, while Arbequina scored the lowest for this attribute. Olive oil obtained from Gemlik showed the highest phenolic content and viscosity.

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