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ORIGINAL PAPER

Effect of cultivar and harvest time on C_6 and C_5 volatile compounds of Turkish olive oils

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Abstract Aroma is an important quality criterion for extra virgin olive oil. The goal of this study was to determine C_6 and C_5 volatile compounds in different Turkish olive oils. Two factors namely (1) olive cultivar including Ayvalik, Memecik, and Topakasi, and (2) harvest time (ripening degree) were studied. Both factors significantly affected the volatile profiles of the studied oils. Headspace solid phase micro-extraction with GC/MS was used to detect volatiles in different olive oils. The detected volatile compounds included up to 11 compounds (4 from C_5, and 7 from C_6). Hexanal and (*E*)-2-hexanal were predominated as the major volatiles in Ayvalik, and Memecik oils, while pentanal, and hexanal were predominated in Topakasi oil. Topakasi oil was also characterized by its low content of (*E*)-2-hexenal. The only clear trend observed during ripening of olives was the increase in the total content of esters. Therefore, the information obtained in this study is useful in selecting the proper harvest time for each cultivar according to the desired volatile compounds found in the oil.

Keywords Extra virgin olive oil, HS-SPME–GC/MS · Aroma · Aldehydes · Lipoxygenase pathway · Olive variety · Ripening

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Introduction

Extra virgin olive oil has a unique aroma among vegetable oils. Olive oil flavour consists of volatile and non-volatile compounds. Volatile compounds responsible for desirable odour of olive oils are generated through the lipoxygenase (LOX) pathway by enzymatic oxidation of linolenic and linoleic acids [1, 2]. The distinctive aroma of olive oil is attributed to C_6 and C_5 volatiles including aldehydes, esters, alcohols, hydrocarbons, furans, and ketones [3–5].

Olive oil quality is directly associated with its aroma compounds. Olive oil quality and consequently volatile aroma compounds depend on the geographical production area (soil composition, altitude, and latitude), the cultivar, the harvest period, extraction procedure, cultural practices, and the ripening stage [6–9]. Changes in the physicochemical traits of olive oils as affected by the ripening stage and/or the olive cultivar were studied [10–13]. These studies evaluated some analytical parameters, including peroxide value (PV), free fatty acids, UV absorptions at 232 and 270 nm, pigments, fatty acid profile, sterol composition [10], sensory characteristics, oxidative stability [14], and phenolic compounds [15, 16]. The scientific literature presents information about the volatile compounds of olive oils from different cultivars [17–19].

Baccouri et al. [5]; Zarrouk et al. [20]; Kandylis et al. [21] and Ben Mansour et al. [22] studied the effect of ripening degree on the volatiles profile from Tunisian olive cultivars. The levels of volatiles showed significant differences throughout the maturity process. The main volatile compounds were C_6 derivatives, and the aroma also contained reasonable amounts of C_5 derivatives. Garcia et al. [23] investigated the influence of cultivar and ripeness stage on the composition of olive oils. 1-Penten-3-one had the highest contribution for the aroma. Recently, Romero et al. [24] studied the influence of ripeness stages on volatile compounds of Chilean olive oils.

Turkey is the fifth olive oil producer in the world and has different olive cultivars with their own unique aroma. Ayvalik and Memecik are domestic economically important olive cultivars that mainly used for the production and exportation of olive oil. Topakasi is a local olive cultivar, where its cultivation is restricted to the Mediterranean region of Turkey. Topakasi olive is generally used for table olives production and only marginally used for the manufacturing of oil. Some chemical parameters such as fatty acids, tocopherols [25], free fatty acids, PV, UV absorptions [26], and sterols [27] have been evaluated in Turkish olive oils. Studies on volatile composition of some Turkish olive oils were reported in recent years, and the effects of olive cultivar have been evaluated [28–30]. Recently, Toker et al. [31] studied the influence of maturity on the volatiles profile of Ayvalik olive oil produced in Turkey. *E*-2-hexenal followed by hexanal, and *E*-1-pentene-3-one were the main volatile compounds.

The main goal of this study was to investigate the influence of the stage of fruit ripening, and olive cultivar on the volatile compositions of olive oils from Ayvalik, Memecik, and Topakasi cultivars grown in Turkey.

Materials and methods

Plant material and orchard

The experiment was carried out during the 2012–2013 olive harvest season on Ayvalik, Memecik, and Topakasi cultivars grown in the orchards in Sutculer/Isparta, in south-western Turkey. Climatic conditions including annual mean temperature (°C), relative humidity (%), and total rainfall (mm) of the area were provided from www.worldclim.org. The latitude, longitude, and altitude of the area were calculated with the global positioning system (GPS) apparatus. Latitude, longitude, and altitude (m) were 37°24′49″N–30°53′30″E (298 m), 37°24′56″N–30°53′28″E (296 m), and 37°25′24″N–30°53′25″E (286 m) for Ayvalik, Memecik, and Topakasi, respectively. A typical Mediterranean climate which is characterized by dry-hot summers and rainy winters is dominated in the district as described by Ozkan and Gulsoy [32]. Annual average rainfall and the mean annual temperature are approximately 720 mm-year^{-1} and 15.9 °C, respectively. The reddish-brown mediterranean soil type is dominated in the study area. Twelve trees between 15 and 20 years-old of the cultivars were selected from each orchard. The samples of fruits were collected from each tree at three stages of ripeness based on the pigmentation degree of skin and pulp.

Ripening index (RI)

The olive ripening index (RI) was determined according to the method developed by the Agronomic Station of Jaén [33] that based on the evaluation of the skin, and pulp colours of 100 olives. Olives are classified in eight categories: (0) intense green epidermis; (1) yellowish green epidermis; (2) green epidermis with red spots; (3) red or purple colour in more than half of the fruit; (4) black epidermis with white pulp; (5) black epidermis with half purple pulp; (6) black epidermis with purple pulp; and (7) black epidermis with completely purple pulp. The RI was calculated according to the following equation, where N_i indicates the number of fruits from each *i* categories, from 0 to 7.

$$\mathrm{RI} = \left(\sum N_i \times i\right)/100$$

All ripening indexes were determined in triplicate for each sample, and the results were expressed as the mean value ± standard deviation.

Extraction of olive oil

Only healthy fruits of Ayvalik, Memecik, and Topakasi cultivars, without any kind of infection or physical damage, were processed. At each sampling date, 3 kg of olives were processed using a small scale experimental olive mill (Hakki Usta Ogulları, Aydin, Turkey) equipped with a hammer crusher, a vertical malaxator, and a basket centrifuge. Malaxation (mixing) temperature was set at 27 °C, and the duration of malaxation was 45 min. The obtained olive oil was filtered using cotton and anhydrous sodium sulphate. The filtered oils were stored in amber glass bottles at 4 °C without headspace until the time of analysis. All extractions were done in triplicate for each sample (three ripening stages and three olive cultivars).

Yields and quality parameters of olive oil

Yields of oil (%) from olive fruits were extracted using Soxhlet extractor. Free acidity of oil sample was determined by the official method Ca 5a-40 [34] as an equivalent of oleic acid (%). The official method Cd 8–53 [34] was used for PV (meq O_2 kg^{-1} oil) determination of oil sample. UV extinction coefficient K232 was determined by Codex Alimentarius [35]. All measurements were taken in triplicate.

Determination of volatile compounds by HS-SPME–GC/MS

Volatile compounds of olive oils were analysed by HS-SPME–GC/MS according to the method reported by Vichi et al. [36] and Risticevic et al. [37], with slight modifications. Two grams of the sample was weighed into a 15-mL vial closed with a silicone septum. The sample was placed on a heating block at 45 °C under magnetic stirring. After equilibration for 15 min, a Carboxen/polydimethylsiloxane manual SPME fibre (75 µm Fused Silica, Supelco Ltd., Bellefonte, PA, USA) was inserted into the vial and maintained in the headspace for 30 min at 45 °C to extract volatile compounds from olive oil. The fibre was inserted into the injection port of gas chromatograph for 5 min at 250 °C for desorption of the volatile compounds. GC/MS analyses were performed on a Shimadzu GC-2010 gas chromatograph equipped with a mass spectrometer MS-QP2010 plus (Shimadzu Corporation, Kyoto, Japan). Helium was the carrier gas at a flow 1.6 mL/min, measured at 40 °C. An Rxi-5Sil MS (30 m × 0.25 mm × 0.25 µm; Restek, Bellefonte, PA, USA) capillary column was used to separate volatile compounds. Column temperatures were held at 40 °C for 2 min then increased to 250 °C at a rate of 4 °C/min, and maintained for 5 min. The temperature of the ion source and the transfer line was 200 and 250 °C, respectively. Electron impact mass spectra were recorded at ionization energy of 70 eV. GC/MS analyses were performed in SCAN mode in the 40–300 amu mass range. Volatile compounds were tentatively identified by Wiley FFNSC mass spectra library search and Kovats retention indices (KI), wherein the results were given as % area.

Statistical analysis

Results were tested for statistical significance by MANOVA. Differences were considered statistically significant at the $p \leq 0.05$ level.

Results and discussion

C_6 and C_5 compounds represent the most important volatiles in olive oils. C_6 and C_5 compounds are enzymatically produced through LOX pathway. Therefore, C_6 and C_5 levels are depend on the activity of enzymes involved in LOX pathway and on the oil fatty acid profile [23]. Reboredo-Rodríguez et al. [38] reported that, independently of the cultivar, C_6 and C_5 volatiles have their biogenesis mainly in pulp (80–90%) and seed (20–10%). In addition, cultivar and ripening stage of olive affect the levels of volatiles. Consequently, this knowledge might be used to produce olive oils with particular sensory notes at certain ripening stages from chosen cultivars [39, 40]. *E*-2-hexenal (green leaf), (*Z*)-3-hexenol (green leaf, green banana), and hexanal (green leaf, apple) are major aroma-giving compounds in olive oils [3, 31].

Olive oil quality is based on analytical parameters describing alteration status and assuring genuineness, but levels and profile of those quality markers related to health and sensory aspects such as monounsaturated fatty acids (MUFA), as well as C_5 and C_6 volatiles are not mentioned [11]. The levels of volatiles in olive oil are influenced by agronomic conditions and technological factors during oil extraction [1, 2]. This paper focuses on the effects of olive cultivar and the stage of fruit ripening on the volatile profile of selected Turkish olive oils.

In the current study, oils are extracted from olive fruits (Ayvalik, Memecik, and Topakasi cultivars), harvested at three early stages, solely by mechanical or other physical methods, which include washing, crushing, kneading of resulting pastes and separation of oily phase according to the Codex Alimentarius, IOOC, and EC regulations. After oil extraction, yield and some quality parameters such as free acidity, PV, and K232 of olive oils were determined. The oil yields (%) were 51.1 ± 2.70, 57.9 ± 0.52 and 64.9 ± 1.27 for Ayvalik fruits at 2.26, 3.93, and 4.34 of RI, 46.5 ± 1.53, 53.8 ± 0.59, 62.2 ± 1.70 for Memecik fruits at 2.09, 3.46, and 4.56 of RI, and 51.0 ± 1.85, 53.6 ± 0.94, 56.8 ± 2.90 for Topakasi fruits at 2.09, 3.66, and 4.11 of RI, respectively. As known, olive oils are classified with respect to free acidity, and some physicochemical traits including PV, and K_{232} according to EU-regulations. Free acidities (% oleic acid), PV (meq O_2 kg^{-1} oil), and K232 values of oils extracted from the cultivars at approximately 2.0, 3.0, and 4.0 ripening stages were exhibited in Table 1. All oil samples obtained from these cultivars at three early stages were found to be in the highest quality category “extra virgin olive oil” (free acidity ≤ 0.8%, PV ≤ 20 meq O_2 kg^{-1} oil, and K232 ≤ 2.50).

Our results revealed that RI of the early stages of olives were I, II, III, and IV, while the late stages were V, VI, and VII. RI values of the tree cultivars under study are shown in Table 2. RI of the second, third, and fourth stages of olives was 2.26, 3.93, and 4.34 for Ayvalik; 2.09, 3.46, and 4.56 for Memecik, and 2.09, 3.66, and 4.11 for Topakasi, respectively. All samples used for the extraction of olive oils were at three early stages of ripeness (2, epidermis of yellow/green colour with reddish spots; 3, red or light

Table 1 Physicochemical properties of olive oils from cultivars with different RIs

	Ayvalik			Memecik			Topakasi		
	First sampling	Second sampling	Third sampling	First sampling	Second sampling	Third sampling	First sampling	Second sampling	Third sampling
Free fatty acid (% oleic acid)	0.50 ± 0.00	0.56 ± 0.00	0.34 ± 0.00	0.22 ± 0.00	0.22 ± 0.00	0.22 ± 0.00	0.41 ± 0.03	0.43 ± 0.03	0.52 ± 0.03
Peroxide value (meq O_2/kg)	10.48 ± 0.01	9.94 ± 0.01	7.41 ± 0.15	6.25 ± 0.01	6.92 ± 0.08	7.43 ± 0.06	4.01 ± 0.05	3.82 ± 0.09	3.58 ± 0.08
K_{232}	1.58 ± 0.00	1.59 ± 0.01	1.56 ± 0.00	1.40 ± 0.00	1.41 ± 0.01	1.35 ± 0.01	1.51 ± 0.01	1.58 ± 0.01	1.50 ± 0.01

Table 2 Ripening indexes (RI) of olive cultivars under study

Cultivars	Harvesting period		
	First sampling	Second sampling	Third sampling
Ayvalik	2.26 ± 0.51 c[a]	3.93 ± 0.68 b	4.34 ± 0.48 a
Memecik	2.09 ± 0.55 c	3.46 ± 0.55 b	4.56 ± 0.50 a
Topakasi	2.09 ± 0.51 c	3.66 ± 0.55 b	4.11 ± 0.31 a

[a] Values followed by the same letter, with the same column, were not significantly different at $p < 0.05$

violet epidermis; and 4, black epidermis and totally white pulp) based on the pigmentation degrees of skin and pulp [33].

Unsaturated and saturated forms of the C_6 compounds represent the most important part of the volatile aroma compounds found in high-quality olive oils [41]. C_6 compounds are mainly responsible for the green and fresh attributes of virgin olive oil [42]. The main volatile aroma compounds which gives these attributes to olive oil are reported in Tables 3, 4, 5 [43]. In general, the predominant volatile compounds were hexanal (sensory descriptors: fatty and green) and (*E*)-2-hexenal (almond, apple, green, plum, and vegetable), which belong to the C_6 aldehyde fraction. Their contents were significantly affected by the harvesting period, but their trends were different for each olive cultivar.

The Ayvalik olive oil had the simplest volatile profile of the three studied olive oils. Only seven compounds (1 from C_5 and 6 from C_6) were detected in Ayvalik oil (Table 3). The predominant volatile compound in the last two samplings was (*E*)-2-hexenal, while its level increased continually through the ripening of olives from 33.1 (first sampling) to 64.7% (third sampling). Simultaneously, a continuous decrease was observed in the hexanal (the predominant compound in the first sampling) content along the olive ripening. The content decreased from 39.8 to 16.6%. The reduction in hexanal levels could be a result of the reduction of hydroperoxide lyase activity [31]. 2-Pentenal, (*Z*)-3-hexenal, 1-hexanol and (*Z*)-3-hexenyl acetate, and hexyl acetate were the other C_5 and C_6 identified compounds in olive oils. 2-Pentenal is a pentene dimer found in olive oil, which content seems to be slightly increase along the ripening of olives. (*Z*)-3-Hexenal can be converted to (*E*)-2-hexenal with the aid of *cis*-3-:*trans*-2-enal isomerase [44]. In this way, the content of (*Z*)-3-hexanal in the Ayvalik oil decreased from 4.51 to 2.59%, while (*E*)-2-hexenal increased along with the ripening of Ayvalik olive. 1-Hexanol only appeared at the last two stages of ripening. In Ayvalik oil, the formation of esters was limited to the last two samplings, with (*Z*)-3-hexenyl acetate being only found in the last sampling, and hexyl acetate being present in the

Table 3 Content (% of total area) of C_6 and C_5 volatile compounds in Ayvalik olive oil

Compound	KI	Harvesting period		
		First sampling	Second sampling	Third sampling
2-Pentenal	751	0.53 ± 0.02 b[a]	0.52 ± 0.01 b	0.74 ± 0.04 a
(*Z*)-3-Hexenal	796	4.51 ± 0.71 a	3.33 ± 0.47 b	2.09 ± 0.07 c
Hexanal	801	39.77 ± 0.48 a	31.17 ± 2.00 b	16.64 ± 1.42 c
(*E*)-2-Hexenal	850	33.12 ± 0.85 c	48.01 ± 0.54 b	64.70 ± 1.08 a
1-Hexanol	867	nd b	0.46 ± 0.21 a	0.40 ± 0.02 a
(*Z*)-3-Hexenyl acetate	1008	nd b	nd b	2.60 ± 0.08 a
Hexyl acetate	1012	nd c	0.33 ± 0.02 b	0.60 ± 0.01 a
Total		77.93	83.82	87.77

[a] Values followed by the same letter, with the same column, were not significantly different at $p < 0.05$

Table 4 Content (% of total area) of C_6 and C_5 volatile compounds in Memecik olive oil

Compound	KI	Harvesting period		
		First sampling	Second sampling	Third sampling
1-Penten-3-one	677	2.16 ± 0.10 c[a]	4.74 ± 0.03 b	5.61 ± 0.01 a
Pentanal	696	nd b	2.41 ± 0.52 a	nd b
2-Pentenal	751	0.47 ± 0.04 b	0.51 ± 0.03 b	0.58 ± 0.01 a
1-Penten-3-ol	767	nd c	1.48 ± 0.01 a	1.25 ± 0.10 b
(*Z*)-3-Hexenal	796	9.33 ± 0.97 a	4.71 ± 0.61 b	9.26 ± 0.28 a
Hexanal	801	12.89 ± 0.12 c	17.85 ± 0.35 b	21.51 ± 0.26 a
(*E*)-2-Hexenal	850	47.90 ± 0.78 a	43.82 ± 0.11 b	13.75 ± 0.05 c
(*Z*)-3-Hexen-1-ol	853	nd b	nd b	9.59 ± 0.09 a
1-Hexanol	867	0.45 ± 0.19 c	1.56 ± 0.01 b	3.28 ± 0.02 a
(*Z*)-3-Hexenyl acetate	1008	3.37 ± 0.01 c	6.86 ± 0.09 b	20.42 ± 0.12 a
Hexyl acetate	1012	1.03 ± 0.04 c	2.38 ± 0.08 b	3.42 ± 0.07 a
Total		77.60	86.32	88.67

[a] Values followed by the same letter, with the same column, were not significantly different at $p < 0.05$

Table 5 Content (% of total area) of C_6 and C_5 volatile compounds in Topakasi olive oil

Compound	KI	Harvesting period		
		First sampling	Second sampling	Third sampling
1-Penten-3-one	677	4.67 ± 0.39 c[a]	5.55 ± 0.23 b	12.79 ± 0.06 a
Pentanal	696	11.50 ± 0.33 a	9.40 ± 0.43 b	5.71 ± 0.40 c
2-Pentenal	751	0.59 ± 0.01 b	0.66 ± 0.05 b	0.97 ± 0.04 a
1-Penten-3-ol	767	0.80 ± 0.05 c	4.24 ± 0.14 a	2.63 ± 0.15 b
(*Z*)-3-Hexenal	796	7.14 ± 0.15 b	5.56 ± 0.21 b	12.23 ± 1.65 a
Hexanal	801	47.66 ± 0.01 a	41.89 ± 1.14 b	30.57 ± 0.17 c
(*E*)-2-Hexenal	850	9.02 ± 0.20 a	8.43 ± 0.73 ab	7.98 ± 0.08 b
1-Hexanol	867	0.40 ± 0.02 b	2.26 ± 1.33 a	1.83 ± 0.49 ab
(*Z*)-3-Hexenyl acetate	1008	nd c	0.45 ± 0.01 b	0.79 ± 0.06 a
Hexyl acetate	1012	0.65 ± 0.01 b	nd c	0.90 ± 0.10 a
Total		82.43	78.44	76.40

[a] Values followed by the same letter, with the same column, were not significantly different at $p < 0.05$

last two samplings. Recently, Toker et al. [31] reported that C_6 aldehydes (*E*-2-hexenal, hexanal), C_6 alcohols (1-hexanol, *E*-2-hexenol, *E*-3-hexenol, *Z*-2-hexenol, *Z*-3-hexenol), C_5 aldehyde (*E*-2-pentenal), C_5 alcohols (1-pentanol, 1-penten-3-ol, *Z*-2-pentenol), C_5 ketone (1-penten-3-one), and esters (hexyl acetate, *Z*-3-hexenyl acetate) were among the analysed major volatiles in Ayvalik oil.

The Memecik olive oil showed the most complex volatile aroma profile (Table 4), which consisted of 11 compounds (4 from C_5, and 7 from C_6). The predominant compounds from the first sampling were (*E*)-2-hexenal, and hexanal (representing 60.8% of the total volatiles). Ben Temime et al. [45] and Haddada et al. [46] reported that Tunisian olive oils were particularly rich in C_6 aldehydes (hexanal, (*E*)-2-hexenal, and (*Z*)-3-hexenal). Baccouri et al. [5] reported that *E*-2-hexenal was the major C_6 aldehyde in Tunisian and Sicilian olive oils in almost the ripening stages. The volatiles profile in Memecik olive oil was completely changed in the last sampling, wherein (*Z*)-3-Hexenyl acetate was detected in high levels. The predominant compounds were hexanal (21.5%), (*Z*)-3-hexenyl acetate (20.4%), and (*E*)-2-hexenal (13.8%). The trends of the two main aldehydes [hexanal, and (*E*)-2-hexenal] were different from that previously found in Ayvalik oil. In Memecik oil, hexanal increased while (*E*)-2-hexenal decreased. Other compounds that increased along the ripening of Memecik olives were 1-penten-3-one, 2-pentenal, (*Z*)-3-hexen-1-ol, 1-hexanol, hexyl acetate, and especially (*Z*)-3-hexenyl acetate. The increment behaviour of those compounds with RI increase was found in Cretan olive oils at different locations [21]. 2-pentenal, (*Z*)-3-hexen-1-ol, 1-hexanol, hexyl acetate, and (*Z*)-3-hexenyl acetate formed by alcohol dehydrogenase, and alcohol acyl transferase in the lipoxygenase pathway. These increases in aroma compounds of olive oils could be related to those enzymes in olive [4, 47].

Even though Topakasi olives are mainly cultivated for the preparation of table olives, the Topakasi olive oil showed a complex volatile aroma profile, which consisted of 10 compounds (4 from C_5, and 6 from C_6) as reported in Table 5. Considerable amounts of C_5 volatiles compounds were found in Topakasi olive oil. In the first sampling of Topakasi oil, hexanal (47.7%), and pentanal (11.5%) was the most abundant volatile compounds. The contents of these two aldehydes, hexanal and pentanal decreased during ripening. Pentanal was the main C_5 aldehyde quantified in Tunisian and Sicilian olive oils [5, 31]. Kalua et al. [4] reported that C_5 aldehydes and alcohols contribute to the positive attributes of oil correlated with bitterness. Another compound that decreased during ripening was (*E*)-2-hexenal. The most important finding regarding Topakasi oil is its low content of (*E*)-2-hexenal compared to the other studied olive oils. The mean levels of (*E*)-2-hexenal were 48.6, 35.2, and 8.5% in Ayvalik, Memecik, and Topakasi olive oils, respectively. On the other hand, 1-penten-3-one and (*Z*)-3-hexenal showed the highest content in the last sampling accounting for 12.8 and 12.2%, respectively. It is worthy to mention that in the three types of olive oils under study, the content of esters [(*Z*)-3-hexenyl acetate and hexyl acetate], formed through LOX pathway, was increased during ripening. Toker et al. [31] mentioned that the levels of both esters varied according to the harvest periods and that is are linked to alcohol acetyl transferase activity.

Conclusions

C_6 and C_5 compounds are enzymatically produced through LOX pathway, and these compounds were significantly affected by olive cultivar and olive ripening. The analysis of the three Turkish virgin olive oils has shown that there were differences between the volatile profiles. The simplest volatile profile was found in Ayvalik olive oil, with two compounds (hexanal, and (*E*)-2-hexenal) clearly predominating. In Memecik olive oil, (*Z*)-3-hexenyl acetate played a key role, especially at the last sampling. Finally, the volatile profile of Topakasi olive oil was dominated by up to five compounds including hexanal, pentanal, 1-penten-3-one, (*Z*)-3-hexenal, and (*E*)-2-hexenal. The content of esters always increased along the ripening of olives. The observed differences among volatiles could be sourced from the different activities of the enzymes in different olive cultivars and ripening stages. The results suggest that they could be utilized to judge the authenticity for early or late harvested Turkish olive oil.

Compliance with ethical standards

Conflict of interest None.

Compliance with ethics requirements This article does not contain any studies with human or animal subjects.

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