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A COMPARATIVE STUDY ON POMOLOGICAL TRAITS, FATTY ACID COMPOSITION AND VOLATILE AROMA COMPOUNDS OF IRRIGATED AND RAIN-FED ALMOND

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ABSTRACT

Rain-fed agriculture is a common growing system relies on rainfall for water requirements of crops. This fact brings some drawbacks in cultivation that causes significant differences in yield and quality. However, fruits from rain-fed trees are generally accepted as better tasting thanks to their richer flavor and aroma compounds. This study compares pomological parameters, some selected chemical properties, fatty acid composition and volatile aroma compounds of irrigated and rain-fed grown 'Ferragnes' and 'Ferraduel' almond cultivars. Results indicated significant differences between cultivars and growing systems. Total oil was significantly lower in rain-fed samples (24.8% for 'Ferragnes' and 24.9% for 'Ferraduel') when compared with irrigated samples (44.1% for 'Ferragnes' and 40.2% for 'Ferraduel'). Palmitic and oleic acid was higher in irrigated samples, whereas linoleic acid was higher in rain-fed samples. Most of the aroma compounds detected in this present study are new record for almond aroma-active compounds. In an overall view, rain-fed samples resulted with higher contents of aroma compounds.

Key words: almond, aroma compounds, irrigated, quality, rain-fed

INTRODUCTION

Almond (*Prunus amygdalus* Batsch syn., *Prunus dulcis* Mill. [D.A. Webb]) belongs to *Prunus* genus of Rosaceae family [Bate-Smith 1961]. The almond tree is the most important tree-nut crop of Mediterranean area and the almond fruit is the second most produced nut fruit in the world [FAO 2019]. Almond is a popular nut fruit and its unique taste and texture allow the nut having a wide range of applications in the food industry. Additionally, many reports have been published regarding the health benefits of almond in recent years [Kamil and Chen 2012].

Almond yield is mainly evaluated with the fruit load and weight [Kester et al. 1996, Esparza et al. 2001], whereas quality is assessed with fruit size and composition (fat, protein, and carbohydrates), and yield and quality determinants of all together generate the commercial value of nuts [Nanos et al. 2002, Kodad and Socias 2006]. Cultivation practices are known to influence yield and quality of crops, but among those practices, irrigation is accepted as one of the most significant factors [Hutmacher et al. 1994], notwithstanding with the tolerance capacity of the almond tree against water stress [Fereres and Goldhamer 1990, Hutmacher et al. 1994]. Many previous studies have proven the yield increasing effect of irrigation in almonds, together with the influences on fruit quality aspects [Schirra and Agabbio 1989, Nanos et al. 2002]. Indeed, deficit irrigation (irrigating with a reduced amount of water than full requirements) has been reported with its increasing effect on fruit quality

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in several fruit species, also in almonds [Mpelasoka et al. 2000, Egea et al. 2009].

Rain-fed agriculture is a common farming practice that only relies on rainfall for water requirement of the cultivated crop. Especially in developing countries, most of the consumed foods are provided this way. Indeed, more than 90% in Latin America, 75% in North Africa and 60% in East and South Asia [IMWI 2010]. Almond is also commonly grown under rain-fed conditions in most of the countries including leading almond growing countries such as Iran, Spain, Turkey [Rahemi and Yadollahi 2005, Miarnau et al. 2010]. Rain-fed agriculture and irrigated agriculture are not only different in water supplementation, but also different in fertilization because of limited opportunities of rain-fed agriculture which is deprived of fertigation and dependent on rainfall for fertilization in order to dissolve the fertilizer in water. According to these facts, great differences in fruit quality are expected between rain-fed and irrigated orchards. Supportively, farmers growing their almond in Turkey under rain-fed conditions imply that their almonds are richer in flavor and aroma, preferred by traders and even can be sold at higher prices when compared with fruits obtained from irrigated trees. Nevertheless, previous studies lack in comparing those growing systems in terms of fruit quality aspects, especially aroma-active compounds. Sánchez-Bel et al. [2008] investigated the influence of irrigation on some physical and chemical properties of almond kernel samples. However, their samples were collected from orchards located in different locations. Similarly, Kazantzis et al. [2003] and also Nanos et al. [2002] compared kernel quality and composition in two orchards, irrigated and non-irrigated, located in two different locations which would cause additional differences generated by climatic variations. On the other hand, genotype is another significant factor affecting chemical composition of the almonds [Zamany et al. 2017].

For all of those reasons, in order to determine the impacts of rain-fed agriculture on various quality aspects of almond including aroma-active volatile compounds, fatty acid composition, pomological and chemical properties, this study was conducted to compare the final quality of almonds from trees of almond two cultivars grown in two nearby orchards under irrigated and rain-fed conditions.

MATERIALS AND METHODS

The study was conducted in Kahta county of Adıyaman Province in Turkey in 2018 which was a normal year in terms of climatic conditions for the area. Plant materials of the study consisted of 8 years old irrigated and rain-fed grown trees of 'Ferragnes' and 'Ferraduel' cultivars grafted on wild almond (*Prunus amygdalus* var. *amara*). Irrigated and rain-fed trees were grown in two nearby orchards that eliminate climatic influences.

The study was conducted according to randomized block design including the plantation and fruit sampling, and from each genotype representative fruit samples were collected as required at harvest maturity stage [Güneyli and Onursal 2014]. Fruit samples were subjected to hull separation and obtained nuts were sun dried for 4 days until 7% moisture level. After two months of preservation of dried nuts at room temperature, pomological properties, chemical composition, fatty acid composition, and volatile aroma compounds of collected fruit samples were examined.

Pomological evaluations. With this regard, nut weight (NWE), nut length (NLE), nut width (NWI), nut thickness (NTH), kernel weight (KWE), kernel length (KLE), kernel width (KWI), kernel thickness (KTH), kernel/nut ratio (K/N), and number of kernels in one ounce (K/oz) were measured. Nut and kernel width (mm), height (mm), and thickness (mm) were measured using digital calipers. Nut and kernel weights (g) were measured by precision scales (0.1 g), and kernel/nut ratio was calculated by division of these values.

Chemical composition. Total oil, total protein, total ash, and moisture were detected in terms of chemical composition. Total oil content was analyzed by extraction of oil with n-hexane (60°C) for 6 h using Soxhlet extractor [Sherlock MIS 2000]. Total protein content was calculated by multiplication of total N content which was detected according to the Kjeldahl method with 6.25 [James 1995]. Total ash was determined by burning almond kernels for 24 h at 200°C and 6 h at 600°C, respectively [Baymış 2008]. Kernel moisture content was measured according to the weight difference after heating the samples in an oven at 105°C for 24 h [USDA 1970].

Fatty acid composition. Fatty acid composition was evaluated by determination of palmitic acid, palmitoleic acid, stearic acid, oleic acid, linoleic acid contents. The fatty acid methyl esters were detected in a gas chromatograph (Shimadzu, QP2010 ULTRA) with a flame ionization detector and Rtx-5 MS capillary column according to MAPA [1993]. Obtained results were expressed as percentages of each fatty acid with regard to total oil content.

Volatile aroma compounds. Volatile aroma compounds were detected semi-quantitatively. Semi-quantitation (peak measurement) was done using another gas chromatograph (Agilent GC7890A) with a flame ionization detector and DB-5 ms capillary column (60 m × 0.320 mm i.d. and 1 µm, film thickness), and 2-methyl-3-heptanone (internal standard) was used as internal standard. Peaks were identified by comparing retention times and mass spectra of eluted compounds with those of the Wiley library (Wiley7, Nist 05, J. Wiley & Sons Ltd., West Sussex, England).

Statistical calculations. Pomological parameters were measured in four replicates and obtained results were analyzed according to Duncan's test ($P \leq 0.05$) using SPSS 23.0 for Windows software. Data of compositional analyzes represents the average of multiple parallel measurements. Semi-quantitation was performed by comparing relative peak areas observed using FID detection, divided by the concentration in solution and compared again to that of 2-methyl-3-heptanone using headspace analysis.

RESULTS AND DISCUSSION

Fruit samples which were collected from irrigated and rain-fed almond trees were evaluated in terms of pomological traits, chemical and fatty acid composition and volatile aroma-active compound contents. Results of pomological evaluations, chemical, fatty acid, and aroma compounds compositions were presented in Tables 1–4, respectively.

Pomological evaluations. Significant differences were found in all evaluated pomological parameters, except NWE which was not significantly differed between the cultivars and the growing systems. In terms of nut and kernel sizes, various results were obtained. Highest NLE was found in irrigated 'Ferragnes' samples (35.8 mm), whereas the highest NWI and NTH values were measured in rain-fed 'Ferraduel' samples (15.9 and 24.4 mm, respectively). KLE was higher in 'Ferragnes' but not changed between growing systems in both of the cultivars. KWI and KTH results were generally similar between the cultivars and growing systems. Even though kernel weight was not significantly varied both between cultivars and growing systems, kernel weight was significantly higher in 'Ferragnes' samples. Similarly, K/N and K/oz significantly varied between cultivars but not between growing systems. K/N values were 35.5 and 34.7% in 'Ferragnes' samples, while 26.4 and 25.8% in 'Ferraduel'. Results indicated heavier kernels for 'Ferragnes' cultivar comparing to 'Ferraduel' but no significant difference between growing systems in both cultivars. Results of the pomological evaluations are presented in Table 1.

In the previous studies, almond cultivars included in this study were investigated in terms of pomological parameters under irrigated and rain-fed growing conditions. Parlakçı [2007] evaluated most of the pomological parameters also included in this present study as part of his cultivar adaptation study performed in Şanlıurfa city of Turkey and included 'Ferragnes' and 'Ferraduel' cultivars. Nanos et al. [2002] compared the effects of harvest time on almond kernel weight under irrigated and rain-fed conditions, and indicated no influence of irrigation on kernel weight. Results reported by Nanos et al. [2002] were similar with this present study, whereas results presented by Parlakçı [2007] were slightly lower when compared with samples from irrigated trees. The differences were probably caused by climatic differences caused by the year and environment.

Chemical composition. In terms of chemical composition, significant differences found between samples from irrigated and rain-fed trees in total oil contents. Total oil contents of 'Ferragnes' and 'Ferraduel' samples were 44.1 and 40.2% in irrigated samples, and 24.8 and 24.9% in rain-fed samples, respectively. There were no correlations found between total protein, ash and moisture contents and irrigation. Highest total protein content was found in rain-fed 'Ferraduel' samples (22.2%), whereas rain-fed 'Ferragnes' samples presented the lowest value (19.4%). Total ash and moisture were higher in 'Ferraduel' samples (3.2% in both samples). Proximate chemical compositions results are presented in Table 2.

Yildirim et al. [2016] investigated some almond cultivars under irrigated conditions and reported

Table 1. Pomological properties of almonds from irrigated and rain-fed orchards

Properties	Unit	'Ferragnes'		'Ferraduel'	
		irrigated	rain-fed	irrigated	rain-fed
NWE	g	3.8 ±0.1 ns	3.8 ±0.1 ns	4.1 ±0.3 ns	4.2 ±0.3 ns
NLE	mm	35.8 ±1.1 a	34.2 ±1.2 b	33.6 ±0.9 b	33.4 ±0.8 b
NWI	mm	21.5 ±0.2 c	21.5 ±0.2 c	22.8 ±0.6 b	24.4 ±0.4 a
NTH	mm	15.5 ±0.2 ab	15.1 ±0.3 b	15.3 ±0.4 b	15.9 ±0.2 a
KWE	g	1.3 ±0.1 a	1.3 ±0.0 a	1.1 ±0.1 b	1.1 ±0.0 b
KLE	mm	27.2 ±1.3 a	26.4 ±0.4 a	24.7 ±0.8 b	24.3 ±0.8 b
KWI	mm	14.0 ±0.6 ab	13.8 ±0.4 b	14.0 ±0.7 ab	14.7 ±0.4 a
KTH	mm	7.9 ±0.2 a	7.9 ±0.2 a	7.6 ±0.1 a	7.1 ±0.3 b
K/N	%	35.5 ±2.3 a	34.7 ±1.9 a	26.4 ±1.9 b	25.8 ±1.6 b
K/oz	Nr	21.3 ±1.1 b	21.6 ±0.5 b	26.4 ±1.5 a	26.6 ±0.4 a

Differences between values signed with different letters within the rows are significant at $P \leq 0.05$
NWE – nut weight, NLE – nut length, NWI – nut width, NTH – nut thickness, KWE – kernel weight, KLE – kernel length, KWI – kernel width, KTH – kernel thickness, K/N – kernel/ nut ratio, K/oz – kernels in 1 ounce

Table 2. Chemical composition (%) of almonds from irrigated and rain-fed orchards

%	'Ferragnes'		'Ferraduel'	
	irrigated	rain-fed	irrigated	rain-fed
Total oil	44.1	24.8	40.2	24.9
Total protein	20.1	19.4	21.6	22.2
Total ash	3.1	3.0	3.2	3.2
Moisture	4.3	4.0	4.5	4.6

Table 3. Fatty acid compositions (%) of almonds from irrigated and rain-fed orchards

%	'Ferragnes'		'Ferraduel'	
	irrigated	rain-fed	irrigated	rain-fed
Palmitic acid (C16:0)	6.9	6.2	6.5	6.4
Palmitoleic acid (C16:1)	0.7	0.7	0.7	0.8
Stearic acid (C18:0)	2.2	1.9	2.2	2.3
Oleic acid (C18:1)	79.5	78.3	75.0	74.0
Linoleic acid (C18:2)	10.7	12.9	15.6	16.5

Table 4. Volatile aroma compounds of almonds at irrigated and rain-fed orchards

t_r (min)	Volatile aroma compounds (µg/kg)	'Ferragnes'		'Ferraduel'	
		irrigated	rain-fed	irrigated	rain-fed
1.12	acetone	–	127.9	79.5	194.9
1.53	hexane	10.1	–	14.8	–
1.81	butanal	2.2	8.8	4.6	13.1
1.84	2,4-dimethylpentane	0.3	–	0.4	–
2.42	butanol	14.5	–	13.1	10.9
2.51	2-methyl-4,5-dihydrofuran	–	–	–	1.9
5.55	butyl acetate	106.6	126.1	191.9	134.8
5.81	hexamethylcyclotrisiloxane	–	–	2.0	–
6.35	2-phenyl-2-propanol	6.6	14.1	14.5	15.7
6.74	ethyl benzene	25.6	22.2	42.9	25.7
7.78	heptan-3-one	7.6	6.7	9.3	12.5
8.63	butyl isobutyrate	–	–	3.3	–
8.67	butyrolactone (gamma)	–	–	1.2	–
8.77	isoamyl acetate	–	–	3.9	–
8.95	valeric acid	–	37.7	30.0	169.3
9.93	o-chlorotoluene	197.8	197.8	374.3	241.3
10.08	p-chlorotoluene	144.6	160.5	290.6	196.2
10.32	2-methyl-3-heptanone	12.7	–	–	–
10.34	2-methyl-3-heptanol	–	6.2	–	11.1
10.62	4-octanone	359.2	343.5	205.5	359.2
10.94	2-methyloct-2-en-4-one	–	4.0	–	–
10.93	artemisia ketone	–	–	3.5	–
10.95	2-methyl-2-hepten-4-one	2.0	–	–	–
11.13	3-octanone	1.7	–	1.5	1.2
11.32	5-acetyloxolan-2-one	–	–	–	3.8
11.34	1-isopropyl-2,2-dimethyl-4-oxacyclobutane	–	–	0.5	–
11.46	butyl butyrate	–	–	0.6	1.5
11.71	2-methylpentanal	320.8	53.0	464.1	333.0
11.95	pinacol	88.0	191.3	155.2	249.0
12.40	butyroin	–	6.6	5.9	10.6
12.49	2,5-dimethyl-3-hexanone	38.5	–	30.7	29.3
12.52	2,2-dimethyl-3-heptanone	–	29.6	–	–
12.85	isobutyroin	6.8	6.8	5.4	7.7
13.02	isobutyric acid 3-oxo-but-1-enyl ester	47.5	39.3	41.5	40.7
13.61	diethylbenzol	10.5	8.4	12.4	10.9
14.63	2-nonanone	13.2	11.0	16.4	28.2
14.69	butyl valerate	0.8	1.0	0.4	–
16.86	pentadecane, 2-methyl-2-phenyl-	13.4	9.7	17.0	20.8
18.21	2-(1,5-dimethyl-hexyl)-[1,3]dithiane	9.9	6.9	9.9	–
18.28	3-chloropentane-2,4-dione	2.1	1.8	1.9	–
18.28	1-chloro-2,2,4-trimethylpentan-3-one	–	–	–	2.1
18.37	diacetone alcohol	–	–	–	4.7
20.60	4,6-dimethyl-4-hydroxyheptanoic acid	12.5	48.9	35.2	77.7
28.86	ethyl phthalate	–	–	8.5	11.2
29.89	3-hydroxypropionic acid n-butyl boronate	–	–	7.8	9.6
31.38	gamma-undecalactone	6.0	–	5.0	7.8
31.39	gamma-decalactone	–	8.7	–	–
	Total	1461.5	1478.5	2105.2	2236.4

t_r – retention time

higher total oil contents for 'Ferragnes' and 'Ferraduel' cultivars than the results of this present study. Nanos et al. [2002] compared total oil of 'Ferragnes' under irrigated and rain-fed conditions and reported no significant influence of irrigation on total oil. Sánchez-Bel et al. [2008] investigated the effects of irrigation on total oil contents of 'Guara' cultivar. The authors indicated no influence of irrigation on total oil. These authors also investigated total protein and moisture. They found higher protein content in rain-fed samples, but no influence of irrigation on moisture. Besides the influence of irrigation, results of the previous studies are in accordance with total protein and moisture content results of this current study but in the opposite way for total oil content. While irrigation significantly affected total oil in this current study, the related previous studies indicated no influence. Sánchez-Bel et al. [2008] reported an opposite influence of irrigation also for protein content. Relevant differences could be caused by multiple factors including environmental differences, cultivar, post-harvest processing, storage conditions, etc. [Valdés et al. 2015].

Fatty acid composition. Fatty acids investigated as part of fatty acid composition were presented significant differences between the samples, except palmitoleic acid and stearic contents. Palmitic and oleic acid contents were higher in irrigated samples, whereas linoleic acid was higher in rain-fed samples in both of the cultivars. The highest oleic acid was found in irrigated 'Ferragnes' samples (79.5%), whereas the highest linoleic acid content was detected in rain-fed 'Ferraduel' samples (16.5%). Palmitic acid was highest in irrigated 'Ferragnes' samples (6.9%), and lowest in rain-fed 'Ferragnes' samples (6.2%). Besides, stearic acid was highest in rain-fed 'Ferraduel' samples (2.3%), and lowest in rain-fed 'Ferragnes' samples (1.9%). Fatty acid compositions of the samples included in the study are presented in Table 3.

The strong influence of cultivar and irrigation on fatty acid composition was also reported by previous studies. Zamany et al. [2017] compared fatty acid composition of fruit samples collected from twenty almond cultivars, and reported a high variation between the cultivars. Yildirim et al. [2016] investigated fatty acid compositions of 'Ferragnes' and 'Ferraduel' cultivars grown under irrigated conditions and indicated results showed similar percentages with the results of irrigated samples included in this present study. Nanos et al. [2002] compared 'Ferragnes' and 'Texas' cultivars and found significant differences in terms of fatty acid compositions. The authors also investigated the effects of irrigation and found no effect on stearic acid content, higher palmitic, palmitoleic, and linoleic acid contents, but lower oleic acid contents in rain-fed samples. Sánchez-Bel et al. [2008] indicated significant differences among irrigated and rain-fed systems in terms of oleic, linoleic and palmitic acid contents, but no effects on palmitoleic and stearic acid contents. The authors found higher oleic acid contents in irrigated samples, and higher linoleic and palmitic acid contents in rain-fed samples. Results of these previous studies were basically found convenient with the results of this present study and the variant results between irrigated and rain-fed would probably caused by the differences in climatic conditions, soil properties, cultivation differences etc.

Volatile aroma compounds. A total of 47 aroma--active volatile compounds were identified in almond kernel samples included in the study. The volatile aroma compounds consisted of ketones (19), terpenes (3), alcohols (6), esters (10), alkanes (7), and aldehydes (2). When all of the volatile compounds were classified according to the absence in irrigated or rain-fed samples, irrigated samples presented a higher number of compounds. Irrigated 'Ferragnes' samples presented 27 compounds and while 26 compounds found in rain-fed 'Ferragnes' kernels. These values were 37 in irrigated 'Ferraduel' and 31 in rain-fed 'Ferraduel' samples. On the other hand, overall volatile compound contents were higher in rain-fed samples in both of the cultivars. These values were calculated as 1461.5 and 1478.5 μg/kg for 'Ferragnes', 2105.2 and 2236.4 μg/kg for 'Ferraduel' irrigated and rain-fed samples, respectively (Tab. 4).

Among the detected aroma-active compounds; acetone, butanal, valeric acid, 2-phenyl-2-propanol, pinacol, butyroin, and 2-methyl-3-heptanol contents were higher in rain-fed samples in both of the cultivars. Besides, 2-methyl-3-heptanol was only detected in rain-fed samples but not in irrigated samples of both cultivars. On the other hand, some of the volatile compounds were detected in rain-fed samples of one of the cultivar, while not found in the other cultivar. For example, 2-methyloct-2-en-4-one, 2,2-dimethyl-3-heptanone, and gamma-decalactone were only found in rain-fed 'Ferragnes' samples, whereas 5-acetyloxolan-2-one, 1-chloro-2,2,4-trimethylpentan-3-one, and diacetone alcohol were only detected in rain-fed 'Ferraduel' samples.

Some of the volatile aroma compounds such as butanol, ethyl benzene, 2-methylpentanal, isobutyric acid 3-oxo-but-1-enyl ester, diethylbenzol, 2-(1,5-dimethyl-hexyl)-[1,3]dithiane, 3-chloropentane-2,4-dione were higher in irrigated samples in both of the cultivars. On the other hand, hexane and 2,4-dimethylpentane were only detected in irrigated samples in both of the cultivars. Additionally, some of the volatile compounds were detected in irrigated samples of one of the cultivar, while not found in the other cultivar. For example, 2-methyl-3-heptanone and 2-methyl-2-hepten-4-one were only found in irrigated 'Ferragnes' samples, whereas hexamethylcyclotrisiloxane, butyl isobutyrate, butyrolactone (gamma), isoamyl acetate, and 1-isopropyl-2,2-dimethyl-4-oxacyclobutane were only detected in irrigated 'Ferraduel' samples.

On the other hand, some of the aroma-active compounds were detected in both irrigated and rain-fed samples of a cultivar but not detected in both samples of the other cultivar. For example, ethyl phthalate and 3-hydroxypropionic acid n-butyl boronate were detected only in 'Ferraduel' samples. Results of the aroma compound analyzes are presented in Table 4.

Thanks to its nutritional value and sensorial characteristics, almonds constitute a regular part of the human diet [Sathe et al. 2008, Gonçalves et al. 2018]. Nut quality determines consumer preferences which is not only influenced by attractiveness such as color, size, and shape [Kader 2008], but also aroma play key role in market acceptability [Aceña et al. 2010, Shakerardekani et al. 2013]. For this reason, evaluation of aroma compounds is important for the determination of the final quality of the products. Xiao et al. [2014] analyzed aroma compounds in raw almond samples and detected totally 41 volatile compounds from the groups of alcohols, aldehydes, ketones, and pyrazines. Erten and Cadwallader [2017] investigated aroma-active compounds in raw, dry roasted and oil roasted almonds and detected totally 59 aroma compounds including aldehydes, ketones, nitrogen-containing compounds, sulfur-containing compounds, acids, furanones, and other unknown compounds. Previously reported studies on volatile compounds in almonds showed that there are a large variety of compounds active in aroma specification of almonds that varies in absence and concentration in depending on various factors [Valdés et al. 2015, Erten 2016]. Erten and Cadwallader [2017] also suggested further studies for the identification of potentially important unknown aroma compounds in almonds. In furtherance of this suggestion of the authors, as far as our knowledge most of the aroma-active compounds detected in this present study (all compounds except acetone, hexane, butanal, butanol, butyrolactone (gamma), ethyl benzene, heptan-3-one, 2-phenyl-2-propanol) were not reported by previous studies in almonds [Erten 2016, Kesen et al. 2018].

CONCLUSIONS

This study was conducted to compare almond samples collected from irrigated and rain-fed almond trees of two different cultivars. Results indicated no significant effect of growing systems on almost all of the pomological measures in both of the cultivars included in the study. Variable results were found between fatty acid compositions of irrigated and rain-fed samples among the cultivars. Volatile aroma compound analyzes indicated a series of volatile aroma compounds in the studies fruit samples, and together with the various compounds detected, rain-fed samples were found richer in the total amount of aroma compounds.

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