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Influence of Irrigation and Organic/Inorganic Fertilization on Chemical Quality of Almond (*Prunus amygdalus* cv. Guara)

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The chemical quality of almonds variety Guara cultivated in nonirrigated farming (NI) and drip-irrigated farming (DI) conditions with different fertilizing treatments, two organic treatments (T1 and T2) and a mineral treatment (C), all of them with a N−P−K proportion of 1−2−1, is studied. Almonds obtained in irrigated farming showed higher content in sugars and organic acids and a better quality of oil. Among the fertilizing treatments employed, the organic ones have shown the best results related to chemical quality, regardless of the quantity of fertilizer employed (9.5 kg per T1 tree vs 4.5 kg per T2 tree). The organic treatments produced almonds with a higher content of sugar, organic acids and fiber and a similar fat content. These results are interesting from a commercial point of view since the consumers, even under the same conditions of chemical quality, prefer those products cultivated under organic conditions due to their benefits for health and because these practices are environment-friendly.

KEYWORDS: Almond; fertilization; irrigation; fatty acids; MUFAs; PUFAs; carbohydrates; fiber; peroxide index; UV index; organic acids

INTRODUCTION

In the Mediterranean regions, the almond is the most widespread crop of nuts. The production of almond has gradually increased during the past 20 years. The United States, Spain, Iran and Morocco are the countries with the highest increases of the surface cultivated with almond trees in the past years (*1*). As a consequence of a higher demand of almonds worldwide, the trend of almond consumption has increased in the production areas and in other countries mainly due to the fact that it is considered a healthful and natural food contributing essential fatty acids to the diet. In recent years, numerous scientific studies have demonstrated the beneficial effects of the consumption of nuts for human health, these being an important component of a balanced diet due to their high nutritional value. In spite of their high fat content, they possess elevated levels of mono- and polyunsaturated fatty acids and large quantities of vitamin E and fiber. Also, they represent a source of vegetable proteins interesting because of their amino acid composition and of iron, calcium, and oxalic acid.

The quality of almonds is usually measured in terms of chemical composition: moisture content, fiber content, composition of fatty acids, indexes of oxidation of the lipid fraction (UV index, peroxide index), composition of sugars, protein content, etc. This quality mainly depends on genetic (*2*) and edaphoclimatic factors and on cultivation practices. Therefore, although it can be stated in general terms that the chemical composition of the almond is fat (50−60%), proteins (20−25%) and carbohydrates (20%), these percentages depend on the variety of the almond and the cultivation conditions.

At present, the trends of the agricultural production are based on the technical knowledge acquired through an intense research activity. The quick extension of the studies about genetic resource management, natural fertilization, biological control and ecological agricultural are deeply affecting the food production capacity. Among the cultivation techniques, irrigation and fertilization are the factors with the highest influence on the nutritional quality of the almonds. Therefore, many authors have observed an increase in the yield of the almond when they are farmed in irrigation and an influence of the irrigation on the final composition of the fruit (*3, 4*).

Consumers consider that those foods cultivated with organic fertilizers are better than those traditionally cultivated (*5*). However, for farmers, this kind of crop has some disadvantages due to the lower production yields. One of the main difficulties is to achieve that the nutrient availability in the organic crops is enough and balanced since the organic fertilizers release the nutrients more slowly than the inorganic fertilizers. (*6*)

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Table 1. Characteristics of the Soils of the Plots

	Jumilla	Vélez-Rubio	Pinoso	La Murada
pH (H_2O)	8.0	7.9	7.9	8.2
pH (KCl)	7.0	7.1	7.5	7.6
cation exchange capacity ($cmol_{(+)} \cdot kg^{-1}$)	12	13.3	7.4	9.9
conductivity (ext sat.) ($dS \cdot m^{-1}$)	0.4	0.7	0.4	0.5
oxidable organic matter ($g \cdot kg^{1-}$)	6.2	6.7	9.4	8.7
total N ($g \cdot kg^{1-}$)	0.4	2.2	0.5	0.6
ratio C/N	9.0	0.7	10.1	8.7
total carbonates (% $CaCO_3$)	38.0	37.4	34.7	49.9
active carbonates (% $CaCO_3$)	10.0	12.3	9.8	14.0
Mg ($g \cdot kg^{-1}$)	1.5	0.45	0.75	0.58
Na ($g \cdot kg^{-1}$)	0.6	0.17	0.6	0.9
K ($g \cdot kg^{-1}$)	0.9	0.23	0.02	0.5
Fe (ppm)	0.7	3.9	0.6	0.4
Mn (ppm)	3.0	15.6	1.2	0.4
Cu (ppm)	0.9	0.4	0.4	0.2
Zn (ppm)	0.3	1.0	0.2	0.2
B (ppm)	0.5	0.5	0.5	0.9
texture	loamy sand	sandy	loamy sand	loamy

Therefore, the aim of this work is the study of the impact of the irrigation and dry farming and different treatments with organic and inorganic fertilizers on the final chemical quality of almonds.

MATERIALS AND METHODS

Plant Material and Experimental Design. The field experiment was carried out in plots of four almond tree orchards (*Prunus amygdalus* D.A. Webb, cv. Guara) located in SE Spain, at La Murada (drip-irrigation system, DI), Pinoso (DI), Jumilla (nonirrigated, NI) and Vélez-Rubio (NI). In all plots, a complete soil analysis was carried out (anthropic horizon) in order to know the fertility degree. **Table 1** shows the physical, physicochemical and chemical composition of the soil surface horizon for the four tested plots. Two plots were used for each kind of irrigated crops during two consecutive years. In each of the 4 plots, 60 trees were studied (20 trees per fertilizing treatment, C, T1 and T2).

In each plot, 3 biological repetitions per treatment and plot were carried out (corresponding to 6 trees per repetition). These biological repetitions were separated into subsamples of a minimum of 1 kg of almonds each, and these subsamples were employed as technical repetitions. The number of technical repetitions was different regarding the quantity of the sample in each biological repetition; but, in all cases, at least 3 technical repetitions were carried out.

For each field, this study was carried out during four consecutive years; the two first were previous assays where a monthly control of the nutritional state of the almond trees was carried out, and the two last years derived in this study. Three fertilizer treatments were applied in both plots: one simple inorganic fertilizer (superphosphate 45%, $(NH_4)_2SO_4$ and KNO_3) with an N−P−K ratio of 1−2−1 used as control (C) and two organic treatments (T1 and T2) with fertilizer units and costs per tree similar to the inorganic treatment. Organic matter (OM), composed of sheep manure and peat (1:3 ratio), was applied at doses of 9.5 (T1) and 4.5 (T2) kg per tree (26.5% water in the OM) after mixing with the soil. **Table 2** shows the chemical composition of the organic fertilizer. In dry farming plots, the fertilizing treatments were carried out by cover fertilization in December. In irrigated plots, the inorganic fertilizer was applied with fertirrigation and in both organic treatments the irrigation water was applied by drip-irrigation. The OM was placed in 25 cm deep holes at two points below the tree canopy, 30 cm from the tree trunks on either side and below the drip irrigation line. The application of irrigation was carried out according to the recommendations of the Program of Advise for Irrigation from the Regional Ministry of Agriculture, Water and Environment of the Region of Murcia (Spain) for the cultivation of almond trees considering the crop coefficient (K_c) for each month. 16.8 m^3 of water was applied per month and tree. **Table 3** shows the irrigation regime of the two plots and the annual distribution of macronutrients N, P and K. **Table 4** presents the analyses of the irrigation water employed in each plot. For the comparison of results, OM was incorporated in the nonirrigated plot in the same way. Almond (cv. Guara) was used for all the experiments in this study. Fruit samples were collected at random with three replications per treatment and plot. The optimum moment for

Table 2. Physicochemical Analysis and Chemical Composition of the Organic Fertilizer

physicochemical analysis	conductivity (1:10) dS/m	9.6
	pH (H_2O) (1:10)	5.7
chemical analysis	total organic matter	524.0
carbon forms (g/kg DW)	oxidable C	234.7
	extractable carbon	77.3
	C of fulvic acids	54.3
	C of humic acids	23.0
	ratio C_{ext}/C_{ox}	0.3
	ratio HA/FA	0.4
macronutrient analysis (g/kg DW)	total N	46.2
	organic N	33.7
	ammonium nitrogen	8.5
	nitric nitrogen	4.0
	ratio C_{ox}/N_{org}	6.9
	total P	12.4
	S	24.0
	K	14.6
micronutrient analysis (g/Kg DW)	B	69.2
	Fe	5086.0
	Mn	663.0
	Cu	65.9
	Zn	3503.0

Table 3. Irrigation Regime Applied in Cultivation Plots and Annual Distribution of Macronutrients N, P and K

month	crop coefficient (K_c)	m^3/tree/month	% N	% P	% K
January	0.07	0.1		10	
February	0.22	0.1	5	10	5
March	0.33	0.5	10	10	10
April	0.42	1.2	15	10	15
May	0.43	2.0	15	10	15
June	0.56	3.2	15		15
July	0.61	3.5	15		15
August	0.61	3.5	15	10	15
September	0.61	2.2	10	10	10
October	0.54	0.2		10	
November	0.38	0.2		10	
December	0.23	0.1		10	

Table 4. Analysis of Irrigation Water of the Experimental Irrigation Farming Plots

	Pinoso	La Murada (March−July)	La Murada (Aug−Sept)
pH	7.60	7.31	7.43
conductivity 25 °C (dS/m)	0.62	0.71	0.90
total salt (mg/L)	384.41	448.23	576.12
Na^+ (mg/L)	12.61	20.67	29.61
K^+ (mg/L)	1.32	1.94	2.92
Mg^{2+} (mg/L)	36.80	46.82	36.82
Ca^{2+} (mg/L)	95.20	85.21	65.2
Fe (mg/L)	0.15	0.12	0.13
Cu (mg/L)	0.02	0.02	0.04
Mn (mg/L)	0.12	0.14	0.11
Zn (mg/L)	0.09	0.07	0.09
Cl^- (mg/L)	32.52	52.52	45.25
HCO_3^- (mg/L)	496.81	362.81	325.7
SO_4^{2-} (mg/L)	16.97	26.9	48.3
$B(OH)^-$ (mg/L)	0.21	0.65	0.7

harvesting was established according to the standards of Gall (*7*). This moment was the point where approximately 80% of the almonds showed a mesocarp with a pronounced opening. Each subsample included approximately 1 kg of almonds. All the analytic determinations were carried out in peeled seeds without tegument.

Lipid Extraction. The fat was extracted in a 6-unit extractor (Det-Gras J.P. Selecta S.A., Barcelona, Spain), using petroleum ether (40−60 °C) as extractant; in order to avoid fat oxidation during the extraction, the ether evaporation was carried out in a vacuum. The fat content was analyzed in duplicate in each subsample, and the results were expressed as grams of lipids per 100 g of fresh weight (g/100 g FW).

Fatty Acid Methyl Ester (FAME). The fatty acid methyl esters were obtained according to the *Official Methods of Analysis* (*8*), with some modifications. The preparation of the fatty acid methyl esters was carried out by direct interesterification of the fat in two stages: formation of free fatty acids by saponification with methanolic NaOH and a later free fatty acids esterification with methanolic HCl.

The methyl esters were analyzed in a gas chromatograph (CG14A; Shimadzu Corporation, Kyoto, Japan) with a FID detector and a TR-Wax capillary column 0.25 mm × 25 m (Technokroma, S. Coop. C. Ltda., Barcelona, Spain); the carrier gas was nitrogen with a flow of 0.8 mL/min, the temperature of the column was isothermal at 200 °C, the temperature in the detector and in the injector was 275 °C, and the identification of the fatty acids was carried out using the retention times relative to commercial standards of Supelco fatty acids (Sigma-Aldrich Quimica, S.A., Madrid, Spain). The results were expressed as a percentage of each fatty acid with regard to the total fat.

Peroxide Value. The peroxide value was determined on the extracted fat, being estimated from the iodine released as a product of the oxidation of potassium iodide by the peroxides, or other similar products of fat oxidation. The value obtained was expressed as milliequivalents of O_2 per kg of almond; the procedure was carried out according to the methods described in the AOAC (*9*).

Oil Ultraviolet Absorption Coefficients (UV Index). Oil quality was evaluated as the absorbance of a solution containing 0.05 g of oil in 10 mL of cyclohexane under UV light (K_{230}, K_{270}), using a spectrophotometer (model UVIKON 930; Kontron Instruments Ltd.). The value of the UV index was expressed as $R = (K_{232}/K_{270})$ according to the methods described in the AOAC (*10*).

Moisture Content. This was determined by accurately weighing ground almond samples after heating them in an oven at 105 °C for 24 h (*11*). Two measurements were carried out per subsample and the results expressed as percentage of moisture per 100 g of fresh weight (g/100 g of FW).

Color. The color was measured by reflectance in the chopped almond using a Minolta CR-300 colorimeter calibrated with a white standard. Duplicate measurements were made for each subsample and the results expressed as the color coordinate *L*, this being the one which best shows the variations in the white tonality.

Protein Content. The content of globular proteins, which constitutes 90% of the total proteins present in almond, was measured. For this, a defatted sample (0.5 g) was homogenized with 50 mL of water in a Polytron PT10-35 (Kinemática AG, Switzerland) coupled with a PTA-10 generator for 1 min at top speed (13.5 m/s) and then centrifuged for 20 min at 10000*g* (at 20 °C). For the resulting supernatant, protein quantification was performed by the method of Lowry et al. (*12*), modified according to the protocol accompanying the Biorad DC Protein Assay kit (Biorad Laboratories, Spain); absorbance was measured at 750 nm in a UVIKON 930 spectrophotometer (Kontron Instruments, Ltd.). The protein contents of the samples were calculated using a calibration curve obtained for bovine serum albumin standards (0−1.5 mg) treated in the same way. Two extractions were carried out per subsample, and each extraction was analyzed in duplicate, the results being expressed as grams of protein per 100 g of fresh weight (g/100 g of FW).

Fiber. The determination of the fiber content was performed for the defatted samples, according to the methods described in the AOAC (*13*). The neutral detergent fiber (NDF) was measured in duplicate for each subsample, following the method of Robertson and Van Soest (*14*). The results are expressed as grams of NDF per 100 g of fresh weight (g/100 g of FW).

Sugar and Organic Acids Content. Sugars and organic acids were extracted according to the procedure of Sánchez-Bel et al. (*15*). The extract was filtered through a Durapore 0.45 μm HV (Milipore Corporation) membrane disk and then passed through a C18 Plus Sep-Pak cartridge (Waters Corporation, Massachusetts).

Quantification was carried out by HPLC, using a Shimadzu HPLC machine (Kyoto, Japan) having an ion exchange column (ION 300, Teknochroma) and two detectors: a Shimadzu Refractive Index Detector (Kyoto, Japan), at 30 °C, for detection of sugars, and a Shimadzu UV−vis detector for organic acids (Kyoto, Japan) in tandem with the refractive index detector. The mobile phase was $c(H_2SO_4) = 5$ mmol/L at a flow rate of 0.4 mL/min. The detection wavelength was 210 nm for oxalic acid and 230 nm for citric, malic, and succinic acids. The sugar and organic acid concentrations in the tissue were obtained using calibration curves for each compound. Two extractions were performed for each bag or subsample, and each extract was analyzed in duplicate. For sugars, the results are expressed in grams per 100 g of fresh weight (g/100 g of FW) and for the organic acids in milligrams of acid per 100 g of fresh weight (mg/100 g of FW).

Statistics. Data were analyzed using the General Linear Model of the SPSS (version 14.0) statistical package. First, an exploratory study of data was carried out in order to observe their distribution, the relation between variables and the multivariate profiles of data. After this study, a comparison of means for the different dependent variables was carried out between the two groups organized according to the harvesting year by applying the statistical Student's *t* test, and it could be observed that the harvesting year did not show statistically significant differences.

Then, a MANOVA multivariate analysis was carried out using fertilizer and irrigation as fixed factors, when differences were significant ($p < 0.05$), multiple comparisons were made using Tukey's test. In this analysis, both the effect of each factor on the studied parameters and the possible interaction between the factors were analyzed. This interaction was not significant in any case. Therefore, regardless the fertilizing treatment employed, the response toward the irrigation/dry farming was the same and vice versa. Therefore, the data regarding each separate factor where the means for each variable include all the levels of the other factor under study are shown.

RESULTS

In general, almonds have low moisture content. This low moisture content is important for keeping quality and shelf life of seeds as it decreases the probability of microbial growth, unwarranted fermentation, premature seed germination, and many undesirable biochemical changes normally associated with these processes. The proximate composition of the samples is summarized in **Table 5**. Moisture content presents slightly differences among drip-irrigated (DI) (2.66%) and nonirrigated (NI) (3.13%) systems, but these differences were not statistically significant. There were also differences ($p < 0.05$) in moisture content between the different fertilizer treatments. The inorganic treatment (C) had higher moisture content (3.18%) than the organic treatments (2.73% and 2.56% for T1 and T2, respectively); out of these three treatments, T1 and T2 were ranged in the same homogeneous subset when the Tukey test was applied.

The mean values of luminosity and protein content in both water regimes (NI and DI) statistically ($p < 0.05$) differed. Luminosity ranged from 93 to 97.3 for drip-irrigated and nonirrigated systems, respectively; protein content was higher under the NI system (22.44%) than the DI one (20.88%). However, there were no differences in luminosity values and protein content when the three fertilization treatments (C, T1 and T2) were compared (**Table 5**).

Oil content and percentage of tegument did not statistically differed under both water regimes (52.91−52.82% and 5.62−5.29% for DI and NI, respectively); the oil content and the tegument did not significantly varied when different fertilizer treatments (C, T1 and T2) were applied.

Table 5. Proximate Chemical Composition of Almonds (Means ± SD) at Different Irrigation Systems (DI, NI) and Fertilization Treatments (C, T1, T2)[a]

	irrigation system		treatment			irrigation system		treatment		IS × T	
(g/100 g of FW)	DI	NI	C	T1	T2	F	*p*-value	F	*p*-value	F	*p*-value
moisture	2.66 ± 0.44	3.13 ± 0.58	3.18 ± 0.65 a	2.73 ± 0.40 b	2.56 ± 0.24 b	3.03	0.09	10.94	0.00	2.24	0.06
luminosity	93.00 ± 5.15	97.34 ± 1.29	95.9 ± 3.09	95.42 ± 5.31	96.44 ± 3.06	11.81	0.00	1.22	0.31	1.76	0.12
protein	20.88 ± 2.73	22.44 ± 3.15	21.98 ± 2.93	22.53 ± 1.92	22.20 ± 3.39	6.10	0.02	1.97	0.09	1.69	0.14
oil	54.52 ± 2.51	52.61 ± 3.70	53.21 ± 2.42	52.43 ± 2.07	52.50 ± 3.02	1.23	0.07	1.56	0.05	1.73	0.15
tegument	5.56 ± 0.38	5.25 ± 0.35	5.27 ± 0.29	5.45 ± 0.50	5.55 ± 0.54	1.47	0.09	1.61	0.16	0.50	0.81
fiber	5.09 ± 1.09	4.73 ± 1.47	4.74 ± 1.29 a	5.77 ± 1.09 b	6.01 ± 1.46 b	1.42	0.10	6.36	0.00	1.39	0.23

[a] Statistical differences were analyzed by ANOVA ($p < 0.05$). *p*-value < 0.05 means that there are significant differences. Letters a, b are the homogeneous subset obtained from the multiple comparisons test.

Table 6. Fatty Acid Composition (Percent) of Oil Content at Different Irrigation Systems (DI, NI) and Fertilization Treatments (C, T1, T2) and Organic Treatments (Palmitic Acid ($C_{16:0}$), Palmitoleic Acid ($C_{16:1}$), Stearic Acid ($C_{18:0}$), Oleic Acid ($C_{18:1}$) and Linoleic Acid ($C_{18:2}$)) (Mean ± SD)[a]

		$C_{16:0}$	$C_{16:1}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$
irrigation system	DI	6.52 ± 0.27	0.40 ± 0.04	2.97 ± 0.24	71.55 ± 1.76	17.74 ± 1.35
	NI	6.81 ± 0.61	0.42 ± 0.08	2.98 ± 0.27	69.45 ± 2.54	19.20 ± 2.24
treatment	C	6.83 ± 0.90	0.41 ± 0.07	2.94 ± 0.23	70.01 ± 3.01	18.56 ± 2.59
	T1	6.60 ± 0.35	0.43 ± 0.08	2.99 ± 0.25	71.74 ± 1.94	17.31 ± 1.30
	T2	6.69 ± 0.50	0.47 ± 0.15	2.97 ± 0.30	70.72 ± 2.21	17.99 ± 1.63

	F	*p*-value	F	*p*-value	F	*p*-value	F	*p*-value	F	*p*-value
irrigation system	2.59	0.01	1.18	0.24	0.25	0.80	4.23	0.00	3.40	0.00
treatment	0.45	0.64	1.33	0.28	0.15	0.86	0.13	0.86	1.81	0.17
IS × T	0.69	0.66	1.22	0.30	0.77	0.60	0.98	0.45	1.87	0.10

[a] Statistical differences were analyzed by ANOVA ($p < 0.05$). *p*-Value < 0.05 means that there are significant differences.

The application of one or another fertilizer treatment significantly affected the fiber content. Therefore, when organic fertilizers (T1 and T2) were applied, higher fiber content was observed in the fruit than when an inorganic fertilizer (C) was employed. When applying the Tukey's test for these three treatments, the control treatment (C) and the organic treatments (T1 and T2) formed two different homogeneous subsets. There were no significant differences in the fiber content between treatments T1 and T2 despite the different quantities of fertilizer applied, maybe due to the fact that with the fertilizer dose applied in treatment T2 a maximum value of fiber content is achieved and, when applying higher quantities of this fertilizer (T1), there are no significant differences.

Effect of Irrigation and Fertilization on Fatty Acid Composition. The fatty acid composition (**Table 6**) predominantly contains monounsaturated fatty acids (MUFAs) plus polyunsaturated fatty acids (PUFAs). $C_{18:1}$ (oleic acid) and $C_{18:2}$ (linoleic acid) were the predominant contributors to the makeup of the MUFAs and PUFAs respectively, as well as the total lipids in the almond with 71.55−69.45% and 17.74−19.20% for DI and NI respectively. Other major fatty acids in almond were $C_{16:0}$ (palmitic acid), $C_{18:0}$ (stearic acid) and $C_{16:1}$ (palmitoleic acid) with 6.52−6.81%, 2.97−2.99% and 0.40−0.42% for DI and NI respectively. Traces of $C_{18:3}$ (linolenic acid) and $C_{20:0}$ (araquidic acid) were also found in quantities lower than 0.1% (data not shown). There were significant differences ($p < 0.05$) among NI and DI systems only in oleic, linoleic and palmitic acid contents (**Table 6**). Higher contents in oleic acid ($C_{18:1}$) were obtained in DI system ($p < 0.01$) whereas the opposite was true for linoleic ($C_{18:2}$) ($p < 0.01$) and palmitic ($C_{16:0}$) acids ($p < 0.05$). **Table 6** also shows the variation in fatty acid composition for the fertilization treatments (control, T1 and T2). $C_{18:1}$ (oleic acid), $C_{18:2}$ (linoleic acid), $C_{16:0}$ (palmitic acid), $C_{18:0}$ (stearic acid) and $C_{16:1}$ (palmitoleic acid) contents in control, T1 and T2 were found to be 70.01−71.74−70.72%, 18.56−17.31−17.99%, 6.83−6.60−6.69%, 2.94−2.99−2.97%, 0.41−0.43−0.47% respectively. There were no differences between fertilization treatments in any case.

Percentage of unsaturated fatty acids was higher ($p < 0.01$) in DI plots than NI ones, and the opposite was true for the saturated fatty acid percentage ($p < 0.05$). Unsaturated to saturated fatty acid ratio calculations showed that irrigated plots had higher ratio ($p < 0.01$) than nonirrigated ones (**Table 7**). Similar differences ($p < 0.01$) were found between DI and NI system with the calculated oleic/linoleic acid ratio. There were no differences among C, T1 and T2 fertilization treatments for percentage of unsaturated and saturated fatty acids, unsaturated to saturated fatty acid ratio and oleic to linoleic acid ratio.

Effect of Irrigation and Fertilization on UV Index and Peroxide Values. Polyunsaturated fatty acids, such as linolenic and linoleic acid, have their double bonds placed according to the system called "malonic". One of the reactions occurring during the lipid oxidation implies the transformation of the malonic systems into conjugated systems, which are less stable against later oxidations. These conjugated systems can be detected by UV spectrophotometry, and they tend to break down and result in carbonylic compounds, aldehydes, and ketones, which, together with other compounds, give the food the "rancid smell" that is disliked by the consumer (*16*). The index R (K_{232}/K_{270}), which compares the absorbances at 232 and 270 nm, is employed for evaluation of the fat oxidation (the higher the oxidation, the lower the value of the index) and, together with the peroxide value, it is a good indicator of the oil quality (*17, 18*).

In this study, oil UV absorption coefficients ratio (K_{232}/K_{270}) under both water regimes (NI and DI) was 28.80% and 26.69%, respectively. K_{232}/K_{270} was 29.17, 28.65 and 29.93 for C, T1 and T2 respectively there were no significant differences in any case (**Table 8**). The value of peroxide index was found higher ($p < 0.05$) in T1 (1.12 mequiv of O_2/kg of il) and T2 (1.57

Table 7. Variation of Total Fatty Acids Saturated, Unsaturated, Unsaturated/Saturated, and the Ratio $C_{18:1}/C_{18:2}$ at Different Irrigation Systems (DI, NI) and Fertilization Treatments (C, T1, T2) (Mean ± SD)[a]

		saturated	unsaturated	unsaturated/saturated	$C_{18:1}$ /$C_{18:2}$
irrigation system	DI	9.41 ± 0.37	89.92 ± 0.57	9.56 ± 0.42	4.06 ± 0.40
	NI	9.79 ± 0.67	88.98 ± 1.18	9.12 ± 0.61	3.68 ± 0.54
treatment	C	9.77 ± 0.13	88.98 ± 0.21	9.17 ± 0.11	3.86 ± 0.65
	T1	9.55 ± 0.14	89.74 ± 0.22	9.40 ± 0.12	4.17 ± 0.40
	T2	9.66 ± 0.19	89.18 ± 0.31	9.24 ± 0.17	3.97 ± 0.47

	F	*p*-value	F	*p*-value	F	*p*-value	F	*p*-value
irrigation system	2.09	0.04	3.34	0.00	2.87	0.01	2.69	0.01
treatment	0.59	0.56	3.00	0.6	0.98	0.38	1.38	0.26
irrigation × treatment	0.71	0.64	0.56	0.76	0.87	0.52	1.54	0.17

[a] Statistical differences were analyzed by ANOVA ($p < 0.05$). *p*-Value < 0.05 means that there are significant differences.

Table 8. UV Index Variation and Peroxide Value at Different Irrigation Systems (DI, NI) and Fertilization Treatments (C, T1, T2) (Mean ± SD)[a]

		K_{232}	K_{270}	R ($K_2$32/$K_2$70)	peroxides (mequiv of O_2/kg)
irrigation system	DI	1.61 ± 0.82	0.06 ± 0.04	26.69 ± 5.75	1.03 ± 0.52
	NI	1.82 ± 0.71	0.07 ± 0.03	28.80 ± 5.88	0.93 ± 0.34
treatment	C	1.57 ± 0.69	0.05 ± 0.04	29.17 ± 6.29	0.69 ± 0.29 a
	T1	1.32 ± 0.08	0.05 ± 0.01	28.65 ± 2.09	1.12 ± 0.33 b
	T2	1.32 ± 0.10	0.05 ± 0.01	29.93 ± 2.69	1.57 ± 0.36 c

	F	*p*-value	F	*p*-value	F	*p*-value	F	*p*-value
irrigation system	1.79	0.18	0.14	0.71	1.82	0.71	1.02	0.31
treatment	1.20	0.21	0.20	0.81	0.25	0.70	28.16	0.00
IS × T	2.25	0.12	0.97	0.39	0.40	0.67	2.38	0.10

[a] Statistical differences were analyzed by ANOVA ($p < 0.05$). *p*-Value < 0.05 means that there are significant differences. Letters a, b and c are the homogeneous subset obtained from the multiple comparisons test.

Table 9. Sugar Composition (g/100 g of FW) at Different Irrigation Systems (DI, NI) and Fertilization Treatments (C, T1, T2) (Mean ± SD)[a]

		sucrose	fructose	glucose
irrigation system	DI	5.53 ± 2.91	0.14 ± 0.10	0.31 ± 0.15
	NI	3.67 ± 01.41	0.15 ± 0.13	0.23 ± 0.13
treatment	C	4.94 ± 2.51 a	0.11 ± 0.07	0.24 ± 0.14 a
	T1	7.09 ± 1.90 b	0.11 ± 0.03	0.36 ± 0.11 b
	T2	6.88 ± 2.45 b	0.11 ± 0.01	0.39 ± 0.10 b

	F	*p*-value	F	*p*-value	F	*p*-value
irrigation system	6.35	0.00	1.27	0.25	8.60	0.00
treatment	4.55	0.01	0.37	0.96	7.61	0.01
irrigation × treatment	0.12	0.88	0.01	0.98	1.60	0.21

[a] Statistical differences were analyzed by ANOVA ($p < 0.05$). *p*-Value < 0.05 means that there are significant differences. Letters a, b are the homogeneous subset obtained from the multiple comparisons test.

mequiv of O_2/kg of oil) than control (0.69 mequiv of O_2/kg of oil). The content of unsaturated fatty acids was higher in treatments T1 and T2 than in control.

Effect of Irrigation and Fertilization on Sugar and Organic Acid Composition. Sucrose was the main soluble sugar found in almonds whereas fructose and glucose were the main reducing sugars (**Table 9**). From the data in the literature about the different analyzed varieties, it can be stated that the distribution of the carbohydrates found in the almond is 85−91% sucrose, and the remaining 10−15% is made up of different monosaccharides like glucose, fructose, sorbitol, rafinose and inositol (*19*). The fact that sucrose is the main sugar is due to its preferential production and its accumulation in the almond during ripening and to the fact that many of the minority sugars are a substrate for sucrose synthesis.

The organic fertilizer treatments showed a higher content in sucrose and glucose than the inorganic control treatment ($p < 0.05$). Irrigation resulted in almonds kernels with higher amounts ($p < 0.05$) in sucrose and glucose. Oxalic, citric and malic acids contents were higher in DI systems ($p < 0.05$) whereas succinic acid content was higher in NI system ($p < 0.05$). Citric and malic acids contents in T2 treatments were higher than control and T1 treatments (**Table 10**). Organic fertilizers release nutrients not as fast as mineral fertilizers and, therefore, plants supplied with organic fertilizers grow more slowly compared to plants fertilized with readily available mineral nutrients. This might reduce their water content leading to a higher concentration of plant compounds e.g. sugars and acid (*20*).

DISCUSSION

In all kinds of cultivation system, the availability of nutrients for the plant is influenced by the fertilizer applied (organic and inorganic), the moment of application, quantity of applications and even the solubility in water of the fertilizer employed (*21*). On the other hand, the irrigation or not of crops also significantly affects the yield of the plant and the final composition and physical properties of the fruit (*22*). In our experience, the yields of the plants were affected only by irrigation (data not shown): almond trees cultivated in irrigation regime shown higher yields than those cultivated in NI system. The almonds cultivated in irrigation were darker (lower values of *L*) and with a lower protein content ($p > 0.05$), while the treatment with organic fertilizers produced almonds with a higher fiber content ($p < 0.05$). It has been reported in many studies that protein and crude

Table 10. Organic Acid Composition (g/100 g of FW) at Different Irrigation Systems (DI, NI) and Fertilization Treatments (C, T1, T2) (Mean ± SD)[a]

		oxalic acid	citric acid	succinic acid	malic acid
irrigation system	DI	0.25 ± 0.18	0.61 ± 0.36	0.26 ± 0.17	0.15 ± 0.10
	NI	0.14 ± 0.04	0.21 ± 0.08	0.60 ± 0.15	0.07 ± 0.02
treatment	C	0.17 ± 0.11	0.32 ± 0.27 a	0.50 ± 0.26	0.08 ± 0.05 a
	T1	0.18 ± 0.12	0.34 ± 0.28 a	0.44 ± 0.20	0.10 ± 0.07 a
	T2	0.26 ± 0.28	0.74 ± 0.5 b	0.40 ± 0.29	0.23 ± 0.14 b

	F	*p*-value	F	*p*-value	F	*p*-value	F	*p*-value
irrigation system	2.62	0.01	4.08	0.00	6.13	0.00	3.70	0.00
treatment	0.61	0.55	3.72	0.03	0.32	0.73	6.16	0.00
irrigation × treatment	0.00	0.93	1.14	0.34	1.40	0.25	0.66	0.42

[a] Statistical differences were analyzed by ANOVA ($p < 0.05$). *p*-Value < 0.05 means that there are significant differences. Letters a, b are the homogeneous subset obtained from the multiple comparisons test.

fiber were affected by climate, variety, geographical origin, harvest year and the methods of cultivation (*23*). These almonds are also clearer (higher values of *L*) and they are, therefore, more attractive for the consumer.

The lipid fraction of immature almonds represents around 3.5% and, during the development of the almond, this proportion increases up to 50−60% in the mature almond. Therefore, it is not only the most significant fraction but it is also the one with the higher variations during the process of development and ripening (*24, 25*). The available data in the literature suggest that genetic factors as well as environmental factors strongly influence fatty acid composition. The investigators found that in tree nuts, besides the cultivar (genetic factors), environmental factors such as the year of production and growing location also strongly influenced the fatty acid composition (*26*). The fatty acid composition of tree nuts is important from several perspectives including oil stability to oxidative deterioration, melting point and other physical and chemical important properties. Based on oil composition data, irrigation resulted in almonds with higher oleic acid content, unsaturated/saturated fatty acid ratio and lower palmitic acid content than almonds from nonirrigated plots.

Oil UV absorption coefficients (K_{232} and K_{270}) which revealed the oxidative deterioration and purity of the oils (*27*), were not affected by irrigation system and fertilization treatment, but peroxide values, which measure hydroperoxide secondary oxidation products of the oils (*28*), were high for T1 and T2 fertilization treatments; this means that conjugated hydroperoxides and their diene secondary products remains equal among C, T1 and T2 fertilization treatments whereas peroxide values increased in organic fertilization treatments.

Regarding the glucidic composition and the composition of organic acids, the irrigation produced almonds with a higher content in sucrose and glucose and in oxalic, citric and malic acids. The content in sucrose and glucose was also higher in plants treated with organic fertilizer than in those treated with inorganic fertilizer, as it happened in the case of citric and malic acids. Heeb et al. (*29*) observed in tomatoes an increase in the concentration of citric and malic acids after treatments with organic fertilizers, and Souza et al. (*30*) observed in grapes an increase of these same organic acids in grapes under irrigation. However, there are few studies about the composition of organic acids in almond (*15*).

Some authors have stated that irrigation can cause a delay in ripening and, therefore, although almonds have the same appearance at a macroscopic level, they are not in the same ripening state (*3*). Something similar could be observed when almond trees are cultivated using organic fertilizers since the immediate availability of nutrients in organic fertilizers is lower than that in inorganic fertilizers and, therefore, when using these last ones, plants are better fed and both the plant and the fruit are more quickly developed.

During fruit ripening, there is a sucrose transportation from leaves to cotyledons and, once there, it is degraded into fructose and glucose which will be employed in different biosynthetic paths. In the case of almond, fructose and glucose are quite abundant during the first stages of almond development, and their content drastically decreases around 60 and 64 days after fruit set, a moment coincident with the increase of the lipid fraction in the almond, until day 100, the moment when the final content has been achieved and it remains stable (*25*). This decrease is faster in the case of glucose, because its initial content is also higher. On the other hand, during almond ripening, the moisture content showed a constant decrease from day 100 after fruit set until the harvesting moment (data not shown). The sugar content is, therefore, stable in the early stages of ripening while the water content decreases during the whole ripening process.

Therefore, the results seem to indicate that the almonds cultivated under different fertilizing and irrigation conditions show different ripening degrees after the same number of days after fruit set with a solute concentration due to the higher content of moisture. Since almonds reach the definitive composition 100 days after fruit set, from that moment until the end of ripening, all changes are related to water loss.

The almonds obtained in irrigated farming showed interesting characteristics like a higher content in sugars and organic acids, higher oleic acid content, unsaturated/saturated fatty acid ratio and lower palmitic acid content. In general, the organic treatments produced almonds with higher content of sugars, organic acids and fiber, although they showed a slight trend toward lipid oxidation (higher peroxide index). These differences were the same in both organic fertilizer treatments. Therefore, among the fertilizer treatments under study, the organic treatments showed the better results, regardless of the quantity of fertilizer employed (9.5 kg per tree T1 vs 4.5 kg per tree T2). This point is quite interesting from both the farmer point of view (the costs of treatment T2 are lower due to the lower quantity of fertilizer employed) and the commercial point of view since the consumers, under the same conditions of chemical quality, prefer products cultivated under organic conditions due to their benefits for health and because the cultivation practices are environment-friendly.

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