



Article Effects of the Irrigation of Chelva Grapevines on the Aroma Composition of Wine

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Abstract: Climate change scenarios are predicting an increase in temperature as well as more scarce and torrential rainfall episodes. Due to this, an imbalance between grape technological and phenolic maturity is being observed, which detrimentally affects the grapes' composition. In semi-arid areas, irrigation management is a main field practice used to influence grape ripening. The goal of the present study was to investigate the influence of vine irrigation on the aroma composition and sensory characteristics of La Mancha Chelva wines. Volatile compounds were studied by gas chromatography–mass spectrometry (GC/MS). A total of 75 aroma compounds were identified and quantified in Chelva wines elaborated with grapes of irrigated and non-irrigated vines. The results show that the application of irrigation during vine cultivation produced small changes in the concentration of wine volatile compounds. Nevertheless, it increased, in general, the intensity of the attributes of the main aroma sensory profile of the wines. According to the results, the vine irrigation of Chelva cultivated in the La Mancha region can be used as a method to increase the aroma of wines.

Keywords: irrigation method; volatile composition; odor activity values; Chelva grape variety; white wines

1. Introduction

The aroma of wine is an important characteristic of wine quality that can be influenced by grape variety, cultural practices, soil, and climate. In addition, the ripening of grapes is conditioned by other factors, such as irrigation, leaf removal, and vine load [1].

Climate change is modifying the temporal distribution of rainfall, producing a situation of low rainfall, mainly concentrated in autumn and winter, and higher overall temperatures and summers with reduced precipitations, which leads to an advance of maturation and an imbalance between grape sugars and phenolic maturity [2], which affects the grape composition and decreases the wine quality [3]. This has produced a great concern in the winemaking sector [4,5]. Castilla-La Mancha does not produce enough rainfall to cover the water needs of the wine sector throughout much of the vine-growing season, which can be negative because it can cause production losses as well as a decrease in the quality of the must [6].

According to this, irrigation is becoming an increasingly useful tool in the vineyards, especially in those regions where rainfall is scarce, in order to homogenize yields and minimize interannual variability [7]. Although the use of irrigation of vines for wine production is a common cultural practice in New World countries, it was prohibited in Spain up until 1996 [8]. Since then, several studies have been specifically aimed at



Citation: Delgado, J.A.; Osorio Alises, M.; Alonso-Villegas, R.; Sánchez-Palomo, E.; González-Viñas, M.A. Effects of the Irrigation of Chelva Grapevines on the Aroma Composition of Wine. *Beverages* **2022**, *8*, 38. https://doi.org/10.3390/ beverages8030038

Academic Editors: Antonietta Baiano, Pasquale Massimiliano Falcone and Matteo Marangon

Received: 11 March 2022 Accepted: 22 June 2022 Published: 27 June 2022

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). determining the effects of various types of irrigation protocols on the yield of the vine and the composition of red grapes under water scarcity conditions [9–11]. In this sense, the most convenient strategy could be to apply a moderate water deficit before veraison and then apply unrestricted irrigation [8].

The water status of a vine produces changes in the volatile composition of grapes and can affect the aroma composition of the wines [12]. In general, in non-irrigated vines, slight water stress seems to improve wine quality. The irrigation of vines reported a higher concentration of total C13-norisoprenoids in wines [13]. On the other hand, the monoterpene concentration increased in Gewürztraminer vines with irrigation deficits [14].

Some studies have shown that irrigation modifies the sensory characteristics of wines, providing herbaceous notes that change with the amount of water applied [15]. In fact, the concentration of aroma compounds in grapes change during ripening depending on the temperature and water availability [16], which shows that irrigation management is a fundamental tool to control growth and the composition of grape berries [17].

Vitis vinifera Chelva grape is grown in a small area of the La Mancha region (Spain). Although it is traditionally used for eating, the few published studies on must and wine volatile composition suggest that wines made from this neutral variety contain interesting flavor notes [18], but no bibliographic references have been found about the influence of vine irrigation on the aroma of La Mancha Chelva wines.

In the present study we research the influence of surface drip irrigation of vines on the aroma composition and sensory properties of La Mancha Chelva wines.

2. Materials and Methods

2.1. Grapes

The experiment was carried out in 2018 in a Chelva vineyard planted in 1980 on gobletpruned 110-Richter grapes. The planting frame was set to 3.00 m between rows and 2.00 m between plants. The vineyard was located in Manzanares (Ciudad-Real, SW Spain) in the La Mancha region ($38^{\circ}59'10.5''$ N, $3^{\circ}55.744'$ W with an altitude of 911 m above sea level). The experimental design consisted of two treatments: rainfed, which only received rainfall water, and surface drip irrigation, with two replications in both vineyards using complete rows per replication. The irrigation was carried out with drip irrigation from flowering to veraison (from 15 May to the end of August). The weekly water supply amounted to $9 L/m^2/week$ (16 L/strain), which amounted to 72 L/m² of soil or 128 L/strain over a period of nine weeks.

2.2. Winemaking Process

Grapes from the different treatments (two rainfed and two surface drip irrigation) were manually harvested, transported to the winery, and separately processed. The wines were elaborated using approximately 10 kg of grapes and following the traditional white winemaking method with slight contact of the must with the solid parts of grapes. After stemming and crushing the grapes, the must obtained by pressing was added to 100 mg/L SO₂ as K₂S₂O₇. In order to conduct the clarification process by natural settling, the must was kept in repose for 24 h at 10 ± 2 °C. Then, the must was transferred to 3 L fermentation vessels. The inoculum used was the Saccharomyces cerevisiae cerevisiae strain (CECT n° 10835). The alcoholic fermentation (AF) was conducted at 18 °C and controlled by measures of the density. At the end of fermentation, the wines were racked, passed through 0.45 µm filters (Millipore, Bedford, MA, USA), bottled, and stored in controlled conditions at 8–10 °C. All fermentations were carried out in duplicate (a total of eight wines, four wines elaborated from rainfed grapes and four from grapes with surface drip irrigation).

2.3. Enological Parameters of Musts and Wines

The methods proposed by OIV [19] were used to determine the °Brix, pH, and titratable acidity in musts and the pH, titratable and total acidity, alcohol strength ($(\sqrt[6]{v}/v)$), and free

and total SO₂ in Chelva wines. The conventional analysis of wines was carried out one month after bottling.

2.4. Analysis of Minor Volatile Compounds in Wine Aroma

The isolation of the free volatile compounds of wines was carried out by solid-phase extraction (SPE) according to the method proposed by Sánchez-Palomo et al. [20]. A sample of 100 mL of wine, with 40 μ L of 4-nonanol added as the internal standard (1 g/L), was passed through previously conditioned cartridges of polypropylene-divinylbenzene phase (LiChrolut EN Merck, 0.5 g phase). After this, the cartridges were rinsed with 50 mL of milli-Q water, and subsequently, free volatile compounds were eluted using 10 mL of dichloromethane. The organic extracts were concentrated to a final volume of 200 μ L under nitrogen stream and then stored at -20 °C until analyzed by gas chromatography coupled to mass spectrometry (GC-MS).

An Agilent model 6890 N gas chromatograph coupled to a model 5973 inert mass selective detector equipped with a BP-21 capillary column (60 m × 0.25 mm i.d.; 0.25 µm film thickness) was used. The injection volume was 1 µL in the splitless mode (0.5 min). Helium was the carrier gas at a flow rate of 1 mL/min. The oven temperature program was 5 min at 70 °C, 1 °C/min up to 95 °C (10 min), 2 °C/min to 200 °C, and this temperature was held for 40 min. The injector temperature was 250 °C. The MS operated in the electron impact mode with an electron energy of 70 eV. The global run time was recorded in full scan mode (40–450 *m*/*z* mass range) with an ion source temperature of 280 °C.

The retention time, NBS75K mass-spectral library, and pure volatile compounds were used for the identification, confirmation, and preparation of standard solutions of volatile compounds. The quantification of volatile compounds was conducted using calibration curves for each standard at eight different concentration levels in cases where standards were available. In cases where authentic standards were not available, a response factor equal to one using semi-quantitative analysis was assumed.

2.5. Analysis of Major Volatile Compounds in Wine Aroma

Major volatile compounds were analyzed according to the method proposed by Sánchez-Palomo et al. [20]. A sample of 1.5 mL of wine with 90 μ L of 2-pentanol (1 g/L) added was injected in the split mode (1:15 split ratio) into a Hewlett Packard 5890 Series II gas chromatograph coupled to a flame ionization detector. A capillary column, CP-Wax 57 CB Chrompack (50 m × 0.25 m i.d.; 0.25 μ m film thickness), was used. The GC conditions were the following: inlet temperature, 250 °C and detector temperature, 280 °C. The column temperature was 40 °C (5 min) ramped at 4 °C/min to 120 °C. Helium (1 mL/min) was used as the carrier gas. Identification was carried out by comparing the analyte retention times with those of commercial standards, and the quantification was based on calibration curves produced using pure standards.

2.6. Determination of Impact Aroma Compounds

To evaluate the contribution of a chemical compound to the aroma of a wine, the odor activity value (OAV) was determined. The equation used to calculate the OAV is: OAV = c/t, where "*c*" represents the concentration of each quantified compound in the aroma of the wines and "*t*" represents the threshold of olfactory perception of said compound as described in the literature. When the OAV is higher than one, a possible contribution to the wine aroma is considered.

Moreover, in order to relate the chemical composition to the sensory characteristics of the wine, the aroma compounds with similar sensory descriptors were grouped into aromatic series, and the intensity of each of the aromatic series was calculated as the sum of the OAVs of the molecules assigned to each series. This allowed the sensory profile of the wine to be approximately established [21–23].

2.7. Sensory Evaluation

After two months of storage under controlled temperature and light conditions (8–10 °C and darkness), the wines were analyzed by a sensory panel of trained expert tasters using the quantitative descriptive analysis (QDA) technique. The panel was formed by five tasters from the staff of the Faculty of Chemical Sciences, aged between 34 and 60 years, with great experience in the quantitative descriptive sensory analysis of wines. For the sensory sessions, a standard sensory-analysis chamber equipped with 14 separate booths was used [24]. Samples were presented at a temperature of 10 °C, and standard wine-testing glasses were used according to the standard UNE 87022:1992 [25].

The sensory evaluation of wines was carried out in four sessions. In each session, the tasters evaluated two wines identified by three-digit codes. The attributes had been selected by previous work [18]. The tasters were asked to score the intensity of each descriptor by using a 10 cm unstructured scale from 0 (not perceptible) to 10 (strongly perceptible).

2.8. Statistical Analysis

To establish significant differences in the results of conventional analysis, for the concentration of volatile compounds and the mean intensity of the sensory attributes of La Mancha Chelva wines, an analysis of variance (ANOVA) was carried out. The treatments were performed using the statistical package SPSS version 23.0 (SPSS Inc., Chicago, IL, USA).

3. Results and Discussion

3.1. Influence of Irrigation on the Enological Parameters of Musts and Wines

The enological parameters of musts and wines made with Chelva grapes from irrigated and non-irrigated vines are shown in Table 1. According to these results, musts obtained from rainfed grapes presented higher values of °Brix than the musts from grapes with surface drip irrigation. This difference is due to the fact that rainfed grapes were generally smaller in size, and the sugars in them were therefore more concentrated [1].

Table 1. Enological parameters of Chelva musts and wines made with grapes from non-irrigated and irrigated vines. Mean concentrations and relative standard deviations (n = 4).

	Non-Irrigated	Irrigated
Must composition		
°Brix	19.51 (0.58)	19.03 (0.76)
Total acidity (g/L) *	7.50 ^b (0.50)	6.75 ^a (0.01)
pH	3.27 (0.02)	3.20 (0.02)
Wine composition		
pĤ	3.16 (0.02)	3.12 (0.01)
Ethanol $(\% v / v)$	13.21 ^b (0.59)	12.01 ^a (0.54)
Total acidity (g/L) *	5.89 (0.84)	5.89 (2.76)
Residual sugars (g/L) ***	0.53 (0.27)	0.49 (0.21)
Volatile acidity (g/L) **	0.33 (8.24)	0.31 (8.16)
Free SO ₂ (mg/L)	9.00 ^b (0.32)	12.00 ^a (2.15)
Total SO ₂ (mg/L)	68.00 ^b (1.03)	61.00 ^a (1.17)

* As tartaric acid. ** As acetic acid. *** As glucose + fructose, ^{a,b} Different superscripts in the same row indicate statistical differences at the 0.05 level according to the ANOVA.

The surface drip irrigation of vine had a slight effect on the pH and total acidity of musts. Musts obtained from grapes without irrigation presented higher pH values and higher total acidity values than those obtained from grapes with irrigation, although these differences were only statistically significant in the total acidity values. When we researched the influence of vine irrigation on the enological parameters of wine, only the content of ethanol was modified significantly. Wines from non-irrigated vines showed significant major values of ethanol, probably due to the different composition of the musts. In general, the results show that the general compositions of all studied Chelva wines were in concordance with a correct elaboration and within the usual values shown by white wines of the La Mancha region [18,20,23]. The total SO2 concentration was in the limits established by the legislation.

Volatile acidity accounts for approximately 10–15% of the total acidity, with acetic acid being responsible for 90% of the volatile acids, but no significant differences were found with vineyard irrigation [1].

3.2. Influence of Irrigation on the Volatile Composition of Wines

The volatile composition of La Mancha Chelva wines is shown in Tables 2 and 3. The data are expressed as the mean concentrations (μ g/L) of the GC-MS analyses of duplicate extractions, and they correspond to the averages of the analyzed wines (four parts in duplicate).

Table 2. Mean concentrations of varietal volatile compounds (μ g/L) and relative standard deviations (n = 4) of Chelva wines made with grapes from non-irrigated and irrigated vines.

RI ^A	Source	Compound	Non-Irrigated	Irrigated
1282	Fluka	1-Hexanol	346 ^b (0.44)	435 ^a (0.31)
1286	Sigma-Aldrich	(E)-3-Hexen-1-ol	5.42 ^b (0.85)	12.7 ^a (3.38)
1296	Sigma-Aldrich	(Z)-3-Hexen-1-ol	323 ^b (0.69)	369 ^a (0.70)
1300	Sigma-Aldrich	(E)-2-Hexen-1-ol	1.33 ^b (0.90)	2.50 ^a (0.68)
1394	Sigma-Aldrich	2-ethyl-1-hexanol	2.41 ^b (1.23)	3.18 ^a (0.45)
	-	Total C_6 compounds	678.16	822.38
1529	Fluka	Linalool	0.86 ^b (0.15)	0.47 ^a (0.43)
1650	Tentatively identified	Ho-trienol	2.31 ^b (0.23)	1.23 ^a (0.34)
1755	Fluka	β-citronellol	Tr	n.d.
1777	Fluka	Nerol	Tr	n.d.
1801	Firmenich	β –damascenone	1.87 ^b (0.10)	0.82 ^a (0.27)
1831	Fluka	Geraniol	1.04 (0.46)	1.06 (0.34)
1902	Tentatively identified	2,6-dimethyl-3,7-octadiene-2,6-diol	8.43 (0.230	8.56 (0.23)
2200	Tentatively identified	(E)-8 hydroxy-linalool	12.0 (0.23)	11.6 (0.34)
2582	Tentatively identified	3-oxo-α-ionol	n.d.	0.89 ^a (0.26)
2722	Tentatively identified	3-Hydroxy-7,8-dihydro-β-ionol	0.20 (0.03)	0.20 (0.10)
3170	Tentatively identified	Vomifoliol	53.4 (10.78)	55.1 (11.23)
		Total terpene and	80.11	79.93
		C ₁₃ -norisoprenoids compounds	00.11	
1503	Sigma-Aldrich	Benzaldehyde	4.80 (1.03)	4.87 (1.96)
1505	Tentatively identified	3(2H)-2-methyldihydro-thiophenone	5.49 ^b (0.19)	5.52 ^a (1.02)
1882	Sigma-Aldrich	Guaiacol	0.26 (0.15)	0.27 (0.12)
1895	Sigma-Aldrich	Benzyl alcohol	19.0 ^b (0.61)	10.3 ^a (0.46)
1899	Tentatively identified	1,2-Benzothiazole	0.61 (1.33)	0.61 (5.83)
1971	Sigma-Aldrich	Phenol	0.79 ^b (0.01)	0.80 ^a (0.14)
2193	Sigma-Aldrich	Eugenol	0.20 (0.13)	0.21 (0.12)
2193	Sigma-Aldrich	Acetophenone	76.0 (3.24)	75.4 (2.54)
2219	Sigma-Aldrich	4-vinylguaiacol	15.0 (0.38)	13.0 (2.68)
2302	Lancaster	Isoeugenol	0.37 ^b (0.55)	0.39 ^a (2.59)
2345	Tentatively identified	2,3-dihydro benzofuran	36.4 ^b (1.53)	32.8 ^a (1.15)
2378	Sigma-Aldrich	Benzoic acid	4.39 ^b (0.34)	2.46 ^a (0.10)
2511	Panreac	Vanillin	0.20 (0.73)	0.20 (0.60)
2936	Sigma-Aldrich	Zingerone	n.d.	0.70 ^a (4.37)
		Total Bencenic compounds	163.51	147.53

^A Linear retention index on a BP21 capillary column; n.d., not detected; Tr, Traces [<0.05 μ g/L]. ^{a,b} Different superscripts in the same row indicate statistical differences at the 0.05 level according to the ANOVA.

Table 3. Mean concentrations (μ g/L) and relative standard deviations (n = 4) of volatile compounds formed principally during alcoholic fermentation of Chelva wines made with grapes from irrigated and non-irrigated vines.

RI ^A	Source	Compound	Non-Irrigated	Irrigated
		Aldehydes		
800	Sigma-Aldrich	Acetaldehyde *	72.3 (1.01)	74.9 (3.02)
	-	Esters		
834	Sigma-Aldrich	Ethyl acetate *	30.3 (2.98)	33.4 (4.96)
1080	Fluka	Ethyl butyrate	16.6 ^b (7.40)	22.7 ^a (4.51)
1145	Sigma-Aldrich	Isoamyl acetate	208 ^a (1.02)	239 ^{a,b} (3.55)
1294	Sigma-Aldrich	Hexyl acetate	9.80 (4.98)	9.92 (3.49)
1326	Sigma-Aldrich	Ethyl lactate	260 (7.61)	327 (7.78)
1185	Fluka	Ethyl hexanoate	134 (11.6)	145 (10.7)
1436	Sigma-Aldrich	Ethyl octanoate	366 (7.91)	382 (2.40)
1655	Fluka	Ethyl decanoate	179 (3.00)	198 (7.86)
1499	Tentatively identified	3-hydroxy, ethyl butyrate	31.7 ^b (2.90)	44.2 ^a (2.24)
1522	Tentatively identified	Ethyl-dl-2-hydroxycaproate	1.02 ^b (0.70)	1.09 ^a (0.65)
1605	Sigma-Aldrich	Diethyl malonate	0.27 ^b (0.52)	0.28 ^a (0.25)
1702	Fluka	Diethyl succinate	47.8 ^b (2.78)	60.2 ^a (1.27)
1787	Fluka	Methyl salicylate	Tr	1.03 ^a (0.69)
1827	Tentatively identified	4-hydroxy, ethyl butyrate	350 ^{a,b} (14.7)	467 ^a (2.57)
1936	Fluka	2-phenylethyl acetate	46.2 ^{a,b} (5.05)	55.1 ^a (3.97)
2070	Sigma-Aldrich	Diethyl malate	38.8 (2.00)	40.5 (10.3)
2286	Fluka	Ethyl cinnamate	Tr	Tr
2331	Tentatively identified	Monoethyl succinate	277 ^b (5.27)	325 ^a (0.48)
	,	Acids		
1426	Sigma-Aldrich	Acetic acid	4.82 ^b (1.62)	3.67 ^a (3.47)
1546	Sigma-Aldrich	Propanoic acid	2.37 ^b (2.09)	1.44 ^a (2.46)
1583	Fluka	Isobutyric acid	294 (14.4)	258 (1.10)
1600	Fluka	Butyric acid	16.9 ^b (7.53)	10.2 a (7.33)
1642	Sigma-Aldrich	Isovaleric acid	170 (4.16)	154 (11.2)
1703	Fluka	Valeric acid	2.24 ^b (4.42)	1.07 ^a (0.46)
1816	Fluka	Hexanoic acid	441 (2.08)	360 (1.96)
1929	Sigma-Aldrich	(E)-2-hexenoic acid	0.95 ^b (0.45)	0.80 ^a (0.89)
2024	Fluka	Octanoic acid	474 ^b (2.69)	381 ^a (2.23)
2289	Sigma-Aldrich	Decanoic acid	350 ^b (6.25)	253 ^a (14.2)
2439	Sigma-Aldrich	Dodecanoic acid	22.0 (9.97)	21.3 (2.49)
_ 10 /		Alcohols		_ (_)
879	Sigma-Aldrich	Metanol *	21.1 ^{a,b} (5.97)	23.4 ^a (0.72)
1060	Sigma-Aldrich	1-propanol *	25.1 ^b (4.51)	35.7 ^a (2.56)
1214	Merck	Isobutanol *	24.1 ^b (5.08)	35.3 ^a (0.26)
1214	Sigma-Aldrich	2-methyl-1-butanol *	41.5 ^b (4.26)	48.0 ^a (7.21)
1221	Sigma-Aldrich	3-methyl-1-butanol *	124 ^b (1.14)	138 ^a (14.29)
1155	Sigma-Aldrich	1-butanol	1.67 ^b (0.85)	$2.72^{a} (0.52)$
1155 1260	Sigma-Aldrich	1-pentanol	1.46 ^b (0.89)	1.93 ^a (0.67)
1328	Fluka	4-methyl-1-pentanol	3.01 ^b (1.41)	$3.84^{a} (0.55)$
1328 1341	Fluka	3-methyl-1-pentanol	8.72 (0.73)	8.94 (0.33)
	Fluka		0.34 ^b (0.21)	$0.66^{a} (0.53)$
1472 1545		1-heptanol	40.0 ^b (1.65)	
1545 1585	Fluka	2,3-butanedial (levo)		42.3 ^a (0.32)
1585 1725	Fluka	2,3-butanediol (meso)	5.49 ^b (4.25)	6.19 ^a (0.68)
1725	Sigma-Aldrich	3-(methylthio)-1-propanol	165 ^b (8.41)	178 ^a (10.7)
1892	Fluka	2-phenylethanol *	18.1 ^b (5.23)	15.4 ^a (0.87)
1(50		Lactones	1 F A b (0 A1)	
1650	Sigma-Aldrich	γ-butyrolactone	1.74 ^b (0.41)	1.90 ^a (0.37)

^A Linear retention index on a BP21 capillary column; n.d., not detected; Tr, Traces [<0.05 μ g/L]. * Concentration [mg/L]. ^{a,b} Different superscripts in the same row indicate statistical differences at the 0.05 level according to the ANOVA.

Varietal aroma volatile compounds of La Mancha Chelva wines from grapes with and without irrigation are shown in Table 2. A total of 30 varietal compounds were identified, including C_6 , terpenic, benzene, and C_{13} -norisoprenoid compounds, in concentrations similar to those previously found in this wines cultivated in the same conditions [18].

The C_6 compounds are related to "vegetable" and "herbaceous" notes of wine aroma and generally have undesirable consequences on the quality of the wine when their concentrations are above their threshold values of odor. In both cases, 1-hexanol and (*Z*)-3-hexen-1-ol were the main compounds in all studied wines, in agreement with the results obtained by Sánchez-Palomo et al. [18] for grapes of the same variety.

The application of irrigation to the vine produced a general increase in the total concentration of C_6 compounds, which was significant for all identified compounds. These results are in agreement with those obtained for Tempranillo y Chardonnay grapes grown in dry soil [26,27] and contradict those observed for white grapes of the Godello variety [28]. These differences could be due to the different cultural practices and to the climatic differences that provided a lower level of water stress in the Godello vineyards. Therefore, the metabolism of the vine was not restricted.

Terpene compounds, which are characteristic of aromatic varieties such as Muscat, have a low olfactory threshold and are generally associated with floral and citric aromas [29]. In this study, the concentrations of terpene and C_{13} -norisoprenoid compounds of La Mancha Chelva wines were in agreement with previous studies [18], and their contribution to the aroma of wines seemed negligible when their odor thresholds were considered [29]. β -damascenone is normally considered a positive contributor to wine aroma, and its odor threshold (0.05 µg/L) [29] was exceeded in all the studied wines.

The application of irrigation to vines produced a slight decrease in the total concentration of terpenes and C_{13} -norisoprenoids, although the individual differences were not always statistically significant. These results were similar to those obtained by Bouzas-Cid et al. [30] in Treixadura grapes grown in dry soil and with an irrigated regime.

Benzene compounds are a group that is important to varietal aroma, which are abundant in La Mancha Chelva wines, including aromatic alcohols, aldehydes, volatile phenols, and shykimic acid derivates [18]. These compounds may have a positive or negative influence on the sensory characteristics of wines, which mainly depends on their concentrations in the wine aroma. In our study, all Chelva wines, regardless of whether irrigation had been applied to the vine or not, had concentrations of these compounds below the values considered necessary to produce unpleasant aromas [29,31], so the benzene compounds can be considered a positive influence on the aroma of Chelva wines. The application of irrigation in the vineyard produced a slight decrease in the total concentration of benzene compounds.

Different studies have shown that the aroma of wine is related not only to the varietal aroma compounds, which are transferred from the must to wine without being modified, but also to the compounds produced mainly during the alcoholic fermentation process. This group of compounds is highly influenced by the yeast metabolism and is key for defining the sensory characteristics of the wines, especially the fruity notes [32,33]. The concentration of these compounds can be influenced by the must composition and fermentation conditions. In this case, the irrigation of vines produced differences in the composition of the must (see Table 1). Therefore, a detailed study of the aroma of wines is necessary.

Table 3 shows the mean concentrations (μ g/L) of the volatile compounds formed principally during alcoholic fermentation in La Mancha Chelva wines. Independent of vine irrigation, a total of 45 volatile compounds were identified and quantified, among which were aldehydes, esters, alcohols, acids, and lactones in concentrations similar to those obtained by other authors for wines of the same variety [18].

Acetaldehyde, related to dried fruits and nutty odors, is the principal aldehyde identified in La Mancha Chelva wines. The main factors determining the amount of acetaldehyde present in the medium are the enzymatic abilities of the yeast strain [33,34] and the fermentation conditions, mainly the added dose of SO_2 [35]. In the current study, the winemaking conditions were same for all wines. Consequently, the variations in the concentration of this compound could be due to the changes in the composition of the initial musts (Table 1).

Aromatic esters are typically described as cherry, floral, dry plum, and stone fruit, improving the quality of young wines [31]. Among the most abundant esters identified in the volatile fraction of La Mancha Chelva wines were ethyl lactate, ethyl 4-hydroxybutyrate, ethyl octanoate, ethyl decanoate, ethyl hexanoate, ethyl acetate, hexyl acetate, 2-phenylethyl acetate, and isoamyl acetate. The total concentration of esters was affected by the irrigation of the vine. Although a slight increase in the total concentration of the esters was detected in wines made from grapes of irrigated vines, when considering the different compounds, only the concentrations of ethyl butyrate, ethyl 3-hydroxybutyrate, and monoethyl succinate were statistically significative.

Fatty acids are formed mainly during alcoholic fermentation by the metabolism of yeasts, and their formation is influenced by the initial composition of the must and by the fermentation conditions [36,37]. Fatty acids are related to aromas resembling fruit, cheese, fat, and rancid odors [29,31]. Isobutyric, isovaleric, octanoic, hexanoic, and decanoic acids were found with the highest concentrations in all studied wines. The concentrations of these compounds were similar to those reported by Sánchez-Palomo et al. [18] for wines of this grape variety. A slight decrease was observed in the concentration of some acids, such as acetic, valeric, isovaleric, hexanoic, and octanoic acids, when the vines were irrigated.

Alcohols are quantitatively the largest group of volatile compounds in La Mancha Chelva wines synthesized by yeast during the alcoholic fermentation process [1]. The contribution of higher alcohols to the wine aroma can be positive or negative. Below the level of 300 mg/L, they influence the aroma of the wine in a positive way, which enhances the aromatic complexity of the wine [31]. In all studied wines, the concentrations of these compounds were lower than this value, so they contributed in a positive way to the aroma of the wine, which enhanced their aromatic complexity. It is also important to note that 2-phenylethanol is present in concentrations above its threshold of olfactory perception (10,000 μ g/L), which has been associated with the floral notes of wines [31]. The irrigation of vines generated a slight increase in the total concentration of alcohols in wines.

3.3. Influence of the Irrigation on the Sensory Profiles of La Mancha Chelva Wines

The odor activity value (OAV) was calculated in order to evaluate the impact of each volatile compound. It was calculated as the ratio between the concentration of the aroma compound in the wine and the odor threshold of this compound in the same matrix obtained from the bibliographic references [29,31,38]. Table 4 shows that 21 out of the 75 quantified volatile compounds (Tables 2 and 3) in La Mancha Chelva wines with OAVs > 0.1, only acetaldehyde, ethyl octanoate, β -damascenone, ethyl hexanoate, isovaleric acid, isoamyl acetate, 3-methyl-1-butanol, 2-phenylethanol, ethyl acetate, and hexanoic acid were found at higher concentrations than their corresponding odor thresholds. Therefore, they are potential contributors to the global bouquet of the wine.

Nevertheless, the contribution to the aroma compounds with OAV < 1 cannot be neglected because they can enhance some existing notes through synergies with other compounds [38].

With over 70 aroma components of wide-ranging intensities and no single character impact compounds, it is difficult to predict the overall aroma impact of these wines from the sheer size of the data. To estimate the overall wine aroma, the odor descriptors were grouped in different aromatic series, every compound was assigned to one or several aromatic series based on the similar odor descriptors used (Table 4), and the total intensity of each aromatic series was calculated as the Σ OAV of the volatile compounds assigned to each series.

The total intensities of every aromatic series were calculated as the sum of the OAVs of each of the compounds assigned to this series, and the results are graphed in Figure 1.

The intensity patterns in the categories suggest that the major aroma characteristics of these wines would consist of fruity, fatty, sweet and floral, regardless of the irrigation on the vine.

Table 4. Odor descriptors, odor threshold (μ g/L), aromatic series, and odor activity values of some volatile compounds of Chelva wines made with grapes from irrigated and non-irrigated vines.

Commence	Odor Descriptor	Odor Threshold (µg/L)	Aromatic Series *	\sum OAVs	
Compounds				Non-Irrigated	Irrigated
Acetaldehyde	Pungent, ripe, apple	500	1,6	151	150
Ethyl octanoate	Caramel, fruity	5	1,4	73.3	76.5
beta-damascenone	Sweet, fruity	0.05	1,4	16.4	37.4
Ethyl hexanoate	Green apple	14	1	9.57	10.4
Isovaleric acid	Acid, rancid	33	4,6	5.15	4.67
Isoamyl acetate	Banana	30	1	6.95	7.97
3-methyl-1-butanol	Burnt, alcohol	30,000	4,6	4.13	4.60
Ethyl acetate	Fruity, solvent	7500	1,6	4.05	4.45
2-phenylethanol	Floral, rose	10,000	2	1.82	1.54
Hexanoic acid	Sweat	420	6	1.05	0.86
Octanoic acid	Sweat, cheese	500	6	0.95	0.76
(Z)-3-Hexen-1-ol	Green, cut grass	400	3	0.92	0.81
Ethyl decanoate	Caramel, fruity	200	1,4	0.90	0.99
Ethyl butyrate	Fruity	20	1	0.83	1.14
Isobutanol	Bitter, green	40,000	3,6	0.60	0.88
Decanoic acid	Rancid fat	1000	6	0.35	0.25
4-Vinylguaiacol	Spicy, curry	40	5	0.33	0.38
2-phenylethyl acetate	Floral	250	2	0.22	0.19
3-methylthio-1-propanol	Cooked vegetable	1000	6	0.18	0.18
Isobutytiric acid	Rancid, butter, cheese	2300	6	0.11	0.13
Butyric acid	Rancid, cheese, sweat	173	6	0.10	0.06

* 1 = fruity; 2 = floral; 3 = green, fresh; 4 = sweet; 5 = spicy; 6 = fatty; 7 = others.

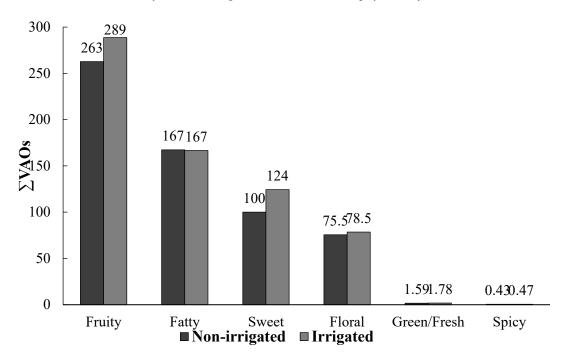


Figure 1. Aromatic series in La Mancha Chelva wines made with grapes from irrigated and non-irrigated vines (Σ VAOs).

The fruity series, comprising seven esters, two aldehydes, four alcohols, and a C_{13} -norisoprenoid, presented the highest intensity, followed by those corresponding to the

fatty, sweet, and floral aromatic series. As shown in Figure 1, vine irrigation produced increases in the intensities of the fruity, sweet, and floral series.

Although the aromatic series fatty is one of the principal aromatic series in the aroma of Chelva wines from Castilla-La Mancha, these aroma notes were not detected on the sensory aroma profile of the wines (Figure 2). On the other hand, the aromatic series green/fresh was the minor aroma series, and this attribute was used by the tasters to define the sensory profile of La Mancha Chelva wines. These results can be attributed to the fact that the total intensity of the aromatic series was calculated as the sum of the individual OAVs of each volatile compound without considering the rest of the compounds present in the wine matrix. The irrigation of the vine produced increases in the total intensities of the fruity, floral, and sweet aromatic series, which can enhance the aroma of the wine.

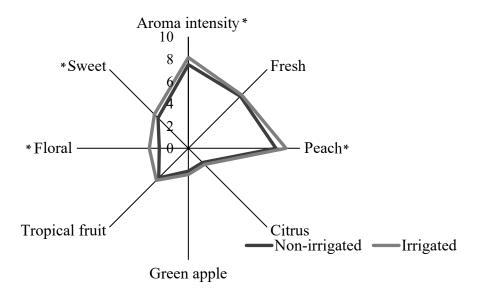


Figure 2. Mean scores of aroma sensory profile of Chelva wines made with grapes from irrigated and non-irrigated vines. * Statistical differences at the 0.05 level according to the ANOVA.

Figure 2 shows the mean aroma-intensity attributes of La Mancha Chelva wines from grapes grown under dry-land and the selected irrigation conditions. As can be seen, wines elaborated with rainfed grapes presented a sensory profile characterized by fresh, peach, floral, tropical fruit, and sweet aromas with green apple and citrus notes [18]. The application of surface drip irrigation to the vines produced an increase in the total aroma intensity of La Mancha Chelva wines and in the intensity of the principal attributes of aroma sensory profile. This increase was statistically significant in the peach, sweet, and floral aroma attributes and in the total aroma intensity. This could be due to the increase in the concentration of esters, terpenes, and benzyl alcohol in wines from grapes grown with surface drip irrigation, which had already been revealed by the analyses of the aromatic series of the wines. These results are in agreement with those obtained in wines from the Treixadura grape variety grown under non-irrigated and irrigated regimes and in Chardonnay wines from irrigated grapes, which showed greater aromatic complexity [27,31]. Moreover, the increase in fresh aromas could be due to the increase in C_6 compounds in wines made from irrigated grapes.

4. Conclusions

The current study assessed the effects that irrigation may have on the volatile composition of La Mancha Chelva wines. The irrigation slightly increased the concentrations of higher alcohols, ethyl esters, acetates, and C_6 compounds in the wines, with no changes in the concentrations of terpenes and C_{13} -norisoprenoides. The aroma sensory characteristics affected by irrigation increased the aroma intensity of the principal attributes of La Mancha Chelva wines. In conclusion, in spite of the fact that irrigation slightly affected the wine aroma composition, it did modify its sensory characteristics. Therefore, it is necessary to adapt the irrigation management to maintain the quality of the obtained wine according to climatic conditions.

Author Contributions: Conceptualization, E.S.-P. and M.A.G.-V.; methodology, M.O.A. and J.A.D.; formal analysis, M.O.A. and J.A.D.; investigation M.A.G.-V.; resources, R.A.-V.; data curation, R.A.-V.; writing—original draft preparation, M.O.A. and J.A.D.; writing—review and editing, E.S.-P.; visualization, E.S.-P.; supervision, M.A.G.-V. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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