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Assessment of fatty acids profile, oil yield and tocopherol content of four Almond cultivars grown in Eastern Morocco

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Abstract

The most cultivated varieties of almond in eastern Morocco (Beldi (B), a local ecotype, Marcona (M) from Spain, Ferragnes-Ferraduel (F-F) and Fournat de Breznaud (FNB) from France), were studied during three consecutive crop years in order to evaluate variations in kernel oil yield, Fatty acid (FA) profile and physicochemical properties. For this purpose, extraction of almond oils was carried out by mechanical press. The yield of varieties B, M, (F-F) and FNB ranged between 50.68%- 54.33%, 41.46%- 52.59%, 47.70%-52.39% and 51.66%-56.10%, respectively. Oleic, linoleic and palmitic acids are the major fatty acids (FA) ranging between 57.54%- 72.90%, 17.80%- 29.81% and 6.50%-8.48%, respectively. Results showed a noticeable effect ($P<0.001$) of variety on total phenolic content (TPC), oxidative stability and α-, β-, γ-, δ-tocopherol isomers; however, acidity and peroxide indexes, were affected with a lower manner by "variety" factor. In addition, all analyzed parameters were highly ($P<0.001$) affected by climatic conditions of the crop year. Additionally, the highest variations for the analyzed almond oils were recorded for their contents on α-tocopherol, γ-tocopherol, oleic and linoleic acids. According to the observed results, the couple Ferragnes-Ferraduel seems to produce stable and high quality almond oil compared to the other varieties.

Keywords: *Almond oil; Fatty acid; Oil yield; Oxidative stability; Tocopherol.*

1. Introduction

Almond (*Prunus amygdalus dulcis*), which belongs to the Rosacea family, is the main tree nut grown in the Mediterranean area. Morocco is the third producer worldwide, with an average production of 116.900 Tones in 2017 [1]. As a dry fruit, almond is often eaten raw or toasted. Almonds are also used in various processed foods as essential ingredient, especially in pastry and confectionery products [2]. In Morocco, almonds and almond oil are widely used in both sweet and savory dishes (Pastry, Paslilla, Tagine, etc. ...), although, almond oil is mostly intended for cosmetic use. In eastern Morocco, almond production is based on locally adapted ecotypes (Beldi), with minimum to no inputs, and traditional management. Many orchards consist of seedlings; when grown in mixed cultures with other crops under minimal care, yields are low. Recently, as part of the Green Morocco program, eastern region of Morocco was supported by the Belgian development agency for planting more than 6000 ha of almond trees. Ferragnes-Ferraduel (F-F), two French varieties known for their late flowering in March, were chosen for planting these new almond orchards instead of Marcona (M) and Fournat de Breznaud (FNB), which were introduced previously in this region, unfortunately they are vulnerable to spring frosts because of their early flowering in February. In eastern Morocco, almonds are harvested between mid-Julys to end of August. They are spread in an open area for drying under the sun, and the nuts are then gathered and delivered for processing. Almonds, broken or defective, are sold in bulk or sorted into whole kernels. Defective batches of almonds are unsaleable because of their size, shape, appearance (loss of kernel skin) and presence of fragments of kernels as a result of mechanical processing. Traditionally, defective and broken almonds are intended for the production of almond paste or the extraction of almond oil. Despite the increasing demand for almond oils as cosmetic product, few researches has been conducted on quality and oxidative stability of almond oils produced in Morocco [3; 4; 5]. Thus this study, conducted over three crop years, aimed to evaluate the possible influences of the almond variety and climatic conditions on the yield and quality of sweet almond oils produced in eastern Morocco. Furthermore, in this study, quality parameters of almond oils of new varieties, (F-F), M and FNB were compared to those of almond oil of the local ecotype Beldi.

2. Materials and methods

2.1. Plant material and climatic conditions

Table 1. Minimum and Maximum monthly temperatures (∘C) and rainfall (mm) measured at the closest meteorological station located at Oujda city in eastern Morocco

	Average temperature (°C)									**Accumulated rainfall (mm)**		
	Min			**Max**			**Mean**					
Month	CY1	CY2	CY3	CY1	CY2	CY3	CY1	CY2	CY3	CY1	CY2	CY3
January	5.4	7.1	4.0	16.5	17.1	16.6	10.96	12.09	10.3	56.8	37.4	44.3
February	4.4	7.4	5.6	15.8	17.6	14.8	10.12	12.49	10.2	31.6	17.3	28.2
March	8.8	8.2	6.3	20.2	20.6	20.8	14.48	14.37	13.5	38.1	19.1	11.8
April	10.1	11.2	10.8	22.6	27.3	24.4	16.32	19.22	17.6	14	12.8	14.6
May	11.2	12.2	13.8	24.9	26.9	29.7	18.06	19.55	21.7	28.4	18.5	42.7
June	14.2	16.1	16.0	29.2	30.2	31.1	21.68	23.17	23.6	0.1	9.8	0.4
Jull	19.0	18.5	21.0	33.0	34.2	37.9	25.95	26.30	29.4	2.2	0	0
August	19.9	19.6	21.4	35.0	34.9	35.5	27.48	27.24	28.5	11.2	0.7	6.9
September	17.24	18.4	16.8	30.82	31.9	30.8	24.03	25.16	23.8	15.7	26.9	14.9
October	14.43	14.4	14.4	29.44	29.0	27.2	21.94	21.65	20.8	0	7	23.7
November	7.35	11.4	8.2	20.02	21.1	21.9	13.69	16.25	15.1	29.5	41	17.9
December	5.55	5.6	5.5	16.80	16.6	21.2	11.18	11.14	13.3	62	41	0
T° mean / cumulative rainfall	11.5	12.5	12	24.5	25.6	26.0	18.0	19.1	19.0	289.6	231.5	205.4

CY: Crop year

Almonds for this experiment were harvested from trees grown in an orchard located at Sidi Bouhria, eastern Morocco (34°44′13.6′′ N, 002°20′15.0′′ W). Almond trees are grown under rainfall, but additional irrigations are provided during periods of acute drought, particularly for newly introduced European varieties in this region. The selected almond varieties for this study were the autochthon ecotype Beldi (B), and European varieties: Marcona (M) native of Spain, Ferragnes-Ferraduel couple (F-F) and Fournat de Breznaud (FNB), which are native of France. Total area of studied orchards is between 10 and 15 ha. Three orchards were selected, which are undergoing the same agricultural practices. Seven almond trees aged as six years old were chosen in each orchard and 7 kg of almond (with shell) were collected from each variety. Sweet almonds were obtained by sampling fruits at an optimal ripening stage during three consecutive harvesting seasons. The climatic conditions at the evaluated growing site are presented in table 1.

2.2. Extraction of almond oils

For each varieties of almond, mechanical extraction of almond oils was done separately and the yield is determined. Mechanical oil extraction was performed by pressing 3kg of crushed almond kernels by means of a press system, (Komet Oil Press, IBG Monforts Oekotec GmbH & Co.KG, Germany). The screw speed was 60 round per minutes (RPM), and the fine particles were removed from the almond oil by filtration followed by a centrifugation at 3000 RPM for 15min. Yields of almond oils from mechanical extraction (YME) was expressed as a percentage of dry weight (% DW). Extracted oil samples were stored at 4°C in dark glass bottles to avoid oxidation until analysis.

The efficiency of mechanical extraction was evaluated by comparison with chemical extraction using hexane as solvent [6]. The yield of chemical extraction (YCE) and gaps was calculated and compared to the yield of mechanical extraction (YME).

2.3. Chemical quality of almond oils

Determination of chemical quality parameters of almond oils, mainly acidity index (AI: g of oleic acid/100 g of oil), and peroxide index (PI: meq O_2/kg), was carried out following the analytical methods (EEC/2568/91) described in the European Commission regulations [7].

2.4. Fatty acid analysis

Fatty acid methyl esters (FAME) were prepared according to the method described by Mansouri et al [8]. Fatty acid profile of almond oils was performed by gas-chromatograph analysis using an HP 6890 series gas chromatography system equipped with FID detector and a capillary column (Supelco Omega wax: 30 m × 0.25 mm × 0.25 µm). The injection volume was 1 µl in split-less mode. The carrier gas was nitrogen, supplied at a flow rate of 1.7 ml min-1. The initial temperature of the injector was 50°C, it was gradually increased to 150°C at a rate of 30°C min-1 and then at a rate of 4°C min-1 up to 250 °C. A standard (FAME) composed from 37 methyl esters of fatty acids was used to identify individual peaks.

2.5. Tocopherols analysis

Tocopherols analysis according to the AOCS method [9], was performed by HPLC (Agilent technology series 1200 system), equipped with a fluorescence detector (excitation wavelength set at 290 nm and emission wavelength at 330nm) and a column of silica Ubisphère 120 Å NH_2 (150 mm x 3 mm x 3 µm particle size, Interchim France). Elution was done with a mobile phase composed of n-hexane / iso-propanol (99/1: v/v) in isocratic conditions at a flow rate of 1 ml min-1. The identification was performed using commercial tocopherol standards (α, β, γ and δ-tocopherol, Sigma-Aldrich, USA).

2.6. Colorimetric determination of phenols content of almond oil

Almond oil phenols content was analyzed according to the method described by Ollivier et al. [10], adopted in our laboratory for the determination of total phenols in seed oils [8; 11]. Almond oil phenols contents were determined by the Folin-Ciocalteu colorimetric method. A mixture of 1-ml of a methanol/water solution (80/20 v/v) was added to 1 g of almond oil in a centrifuge tube. After 10 min of vigorous mixing, and centrifugation (3500 g/15 min), the methanolic phase was recovered and this operation was repeated twice. After that, to 2 ml of extracted solution, 5 ml distilled water, 1 ml Folin-Ciocalteu reagent and 5 ml Na2CO3 (10%) were added and finally phenolic contents were determined by absorbance at λ 750 nm. Total phenols concentration was then calculated from the external calibration curve (r^2 >0.98), using caffeic acid as a standard.

2.7. Oxidative stability of almond oils

Oxidative stability of almond oils was evaluated by an accelerated automated test using the Rancimat apparatus, model 743 (Metrohm Co., Switzerland). Rancimat vessels containing 3 g of oil were covered with the heads connected to the apparatus. When temperature reached 100°C, the vessels head outlets were connected to the conductivity cells, the air flow rate was increased to 15 L/h. After that, measurement starts until a sharp increase of conductivity is detected. The total time taken is the induction time (IT) and is expressed in hours [12].

2.8. Statistical analysis

Statistical analyses of the data obtained were performed using the SPSS software for Windows (SPSS 21, SPSS Inc., Chicago, IL, USA). Data are expressed as the means of results of the analyses carried out in triplicate with the corresponding standard deviation (SD). Significant differences between the varieties ($P < 0.05$) were determined by ANOVA one-way test. The ANOVA two way was used to determine the significant differences between the results of the three crop seasons.

3. Results and Discussions

3.1. Extraction efficiency and quality parameters of mechanically extracted almond oils

Besides the almond oil yield, which depends on the extraction method, research on almond oils focuses on oil chemical quality, fatty acid profile and content of bioactive compounds such as tocopherols, phytosterols, phenols and terpenoïds. In this study, during three consecutive crop years, kernel's oil richness of a local Beldi almond and four European varieties recently introduced in eastern Morocco have been examined. The yields of almond oils for the two methods of extraction, chemical (YCE) and mechanical (YME), of almond oils are shown in Table 2. For the three consecutive crop years of this study, the highest oil contents were recorded for Ferragnes-Ferraduel (F-F), respectively 66.85%, 61.09% and 58.16% for YCE and 56.10%, 58.42% and 51.66% for YME. In contrast, the lowest yields were observed for Marcona (M), which is a more demanding variety in rainfall with respectively 55 %, 50.5%, 50.23% for YCE and 52.59%, 41.46%, 41.74 for YME. Thus, a high variability in almond oil content was observed over the three crop years of this study. For instance, percentage of variation of YME ranges from 41% for (M) to 58% for (F-F). This variability seems to depend mainly on the almond variety (cultivar) but also on climatic conditions of the agricultural year as it has been demonstrated by other studies [13; 14; 15]. For all varieties, mechanical oil extraction was less efficient than the chemical method. The difference between YME and YCE is due to the fact that the mechanical extraction of the oil appears to be disturbed by the moisture content of the sample. This result is in concordance with other research, which demonstrates that yield, and oil quality, depend both on almond kernels' moisture and on the press temperature [16; 17]. In the same way, the yield of mechanical extraction of almond oil is in agreement with many authors around the world, who have reported that oil content of almond kernels is ranging from 40% to 65 % DM [3; 13; 14; 15]. In similar studies, it has also been shown that variety, eco-physiological factors, growing practices and timing of harvest affect almond oil content [18; 19; 20; 21].

Table 2. Efficiency of mechanical extraction and quality parameters of almond oil in three consecutive crop years

	Cultivar	YCE (%)	YME (%)	Gap (%)	AI (%)	PI (meq O_2/kg)
Crop year 1	B	59.92 ± 0.97^{bc}	54.33 ± 1.85^{bcd}	5.59	0.54 ± 0.02^{b}	16.40 ± 3.00^{d}
	M	55.00 ± 1.10^{ab}	52.59 ± 1.12^{bcd}	2.41	0.57 ± 0.06^{bc}	14.30 ± 0.30^{cd}
	FNB	57.62 ± 1.05^{bc}	52.39 ±2.93^{bcd}	5.23	0.62 ± 0.08^{bc}	6.40 ± 2.70^{ab}
	F-F	66.85 ± 0.05^{d}	56.10 ±1.75^{cd}	10.75	0.62 ± 0.16^{bc}	8.10 ± 2.80^{ab}
Crop year 2	B	54.86 ± 0.18^{ab}	52.76 ±3.21^{bcd}	2.1	0.86 ± 0.01^{d}	17.15 ± 2.65^{d}
	M	50.50 ± 0.20^{a}	41.46 ±3.05^{a}	2.41	0.74 ± 0.03^{cd}	14.32 ± 0.29^{bc}
	FNB	51.25 ± 0.54^{a}	50.86 ± 3.30^{bc}	0.74	0.56 ± 0.07^{bc}	7.19 ± 2.40^{ab}
	F-F	61.09 ± 5.74^{c}	58.42 ± 3.13^{d}	2.67	0.86 ± 0.03^{d}	7.21 ± 2.32^{ab}
Crop year 3	B	51.37 ± 0.46^{a}	50.68 ± 3.49^{bc}	0.68	0.27 ± 0.01^{a}	10.39 ± 0.31^{bc}
	M	50.23 ± 0.20^{a}	41.74 ± 3.67^{a}	8.49	0.49 ± 0.07^{b}	15.79 ± 1.39^{cd}
	FNB	50.32 ± 0.18^{a}	47.70 ± 2.24^{ab}	2.62	0.28 ± 0.01^{a}	4.89 ± 0.46^{ab}
	F-F	58.16 ± 1.13^{bc}	51.66 ± 0.57^{bcd}	6.5	0.27 0.00^{a}	3.85 ± 1.17^{a}

Almond oil yield of chemical extraction (YCE) or mechanical extraction (YME) are expressed as percentage of dry matter; Gap is deference between chemical and mechanical oil extraction; Acidity index (AI) expressed as percentage of oleic acid; Peroxide index (PI). Significant difference are shown by different letters (a-d) at P<0.05.

Quality of mechanical extracted almond oils was examined. The parameters (Acidity (AI) and peroxide (PI) index) of analyzed samples are given in table 2. For acidity and peroxide index, the best chemical quality of the analyzed almond oils was recorded for the crop year 3. Indeed, ANOVA analysis shows that AI and PI present significant differences between the crop years respectively at $P< 0.001$ and $P< 0.01$ (Table 5). In addition, conducted studies over these three crop years indicate that almond oils of varieties native of France (Ferragnes-Ferraduel (F-F) and Fournat de Breznaud (FNB)) have the lowest PI values. This appears to be a variety effect. Indeed, almond oil extracted from (F-F) kernels shows a higher level of natural antioxidants (α-tocopherol and total phenols) than those of other varieties (Table 4). Over the tree crop years, AI and PI values recorded are close to those reported in the literature [3; 14; 15] and are in accordance to limits established by codex Alimentarus [22]. Concerning the yield of mechanical extraction (YME), the efficiency of chemical extraction (YCE) is slightly better. Low gaps of 0.68 to 5.59% for B and FNB have been recorded but high gaps ranging between 2.41% and 10.75% were registered for M and (F-F) varieties. Variance analysis (Table 5) shows significant differences between the three crop years. The most significant differences for kernel oil yield and chemical quality of almond oils (AI, PI) also appear to be variety related and affected by climatic conditions of the crop year.

3.2. Fatty acids profile of almond oils

Table 3 provides fatty acid composition of mechanical extracted almond oils over three consecutive crop years of this study. In terms of quantity, oleic acid (C18:1), linoleic acid (C18:2) and palmitic acid (C16:0) are the three predominant fatty acids. Their contents range from 57.54% to 72.90% for C18:1, from 17.80% to 29.81% for C18: 2, and from 6. 50% to 8.48% for C16:0. This result are in agreement with previous studies [4; 19; 23; 24; 25]. For instance, Sathe et al. [19] determined that oleic acid contents vary from 57.54% to 73.94% of total oil in eight almond varieties from California. Kodad et al. [24] reported that oleic acid represents 61.8% to 80.2% of total oil in kernels of selected almond varieties from different regions of central and northern Morocco. For the Spanish almond genebank collection, oleic acid contents range from 64.97% to 79.59% of oleic acid. Alike, Yildirim et al. [25] determined that oleic acid contents range from 55.14% to 83.35 % for oils of some almond varieties grown in Turkey. With regard to the most abundant fatty acids (FA), unsaturated fatty acids (UFA) account for approximately 87% to 90% of the total fatty acids, while saturated fatty acids (SFA) represent only 8.5% to 11.63% of analyzed almond oils. Concerning the UFA fraction, oleic acid represents a much larger proportion than linoleic acid. For the same variety, there are differences in the fatty acid profile of almond oils between growing seasons. Significant differences are particularly noted for unsaturated fatty acid contents. Table 1 shows the minimum, maximum and mean temperature values for the three consecutive crop years. The first crop year has the lowest temperatures, while second and third crop years has warm temperatures during spring that corresponds to the critical fruiting period when kernels of almonds ripen and grow to full size. In literature, it is commonly known that cold climates cause an increase of unsaturated fatty acid contents [26]. Furthermore, warmer temperature has a positive effect on the synthesis of oleic acid but has a negative effect on the syntheses of linoleic and linolenic acids in plants [18; 25], which it correspond to our results.

Table 3. Fatty acid (FA) composition of mechanical extracted almond oils over three consecutive crop years

	Cultivar	Palmitic acid (C16:0) (%)	Stearic acid (C18:0) (%)	Oleic acid (C18:1) (%)	Linoleic acid (C18:2) (%)	ΣSFA (%)	ΣUFA (%)	O/L
Crop year 1	B	6.80 ± 0.10^{ab}	2.00 ± 0.10^{ab}	71.60 ± 0.50^{e}	18.70 ± 0.30^{ab}	8.80 ± 0.10^{ab}	90.36± 0,12^{ab}	3.80 ± 0.10^{ef}
	M	7.20 ± 0.14^{ab}	2.20 ± 0.10^{bc}	66.90 ± 0.70^{c}	22.80 ± 0.60^{cd}	9.40 ± 0.20^{abc}	89.71± 0,16^{ab}	2.90 ± 0.10^{c}
	FNB	7.90± 0.05^{bcd}	2.20 ± 0.04^{bc}	63.50 ± 0.30^{b}	25.50 ± 0.30^{e}	10.10 ±0.02^{bcd}	88.99± 0,03^{ab}	2.50 ± 0.04^{b}
	F-F	6.50 ± 0.10^{a}	2.00 ± 0.04^{ab}	72.90 ± 0.40^{e}	17.80 ±0.40^{a}	8.50 ± 0.10^{a}	90.71± 0,08^{b}	4.10 ± 0.10^{f}
Crop year 2	B	8.00 ± 0.62^{bcd}	1.81 ± 0.16^{a}	68.43 ± 0.63^{cd}	20.75 ±1.18^{bc}	9.81 ±0.77^{abcd}	89.17± 0.58^{ab}	3.31 ±0.22^{d}
	M	8.48 ± 0.14^{d}	2.80 ± 0.08^{d}	57.87 ± 0.22^{a}	29.69 ± 0.35^{f}	11.28 ±0.21^{de}	87.56± 0.18^{a}	2.00 ±0.03^{a}
	FNB	7.27 ± 0.00^{abcd}	2.19 ± 0.04^{bc}	67.16 ± 0.44^{c}	22.29 ± 0.25^{c}	9.47 ±0.04^{abc}	90.38± 1.21^{ab}	3.02 ±0.05^{cd}
	F-F	7.55 ± 0.18^{abcd}	2.00 ± 0.14^{ab}	64.08 ± 1.53^{b}	24.84 ± 0.81^{de}	9.56 ±0.04^{abc}	88.92± 0.71^{ab}	2.58 ±0.14^{b}
Crop year 3	B	8.24 ± 0.77^{cd}	2.44 ± 0.14^{c}	62.09 ± 0.93^{b}	26.75 ± 1.28^{e}	10.68 ±0.91^{cde}	88.85± 2.13^{ab}	2.32 ±0.08^{b}
	M	8.40 ± 0.99^{cd}	3.23 ± 0.23^{e}	57.54 ± 0.13^{a}	29.81 ± 1.31^{f}	11.63 ± 1.23^{e}	87.35± 1.20^{a}	1.93 ± 0.09^{a}
	FNB	8.09 ± 0.02^{cd}	3.20 ± 0.00^{e}	58.48 ± 0.04^{a}	29.10 ± 0.01^{f}	11.28 ± 0.03^{de}	87.58± 0.03^{a}	2.01 ± 0.00^{a}
	F-F	7.23 ± 0.50^{abcd}	2.35 ± 0.09^{c}	70.33 ± 2.15^{de}	19.45 ± 0.08^{ab}	9.58 ± 0.42^{abc}	89.78± 2.10^{ab}	3.62 ± 0.12^{e}

FA contents are expressed as a percentage (%) of total lipids, palmitic and stearic acids correspond to the saturated fatty acids fraction (SFA), oleic and linoleic respectively represent monounsaturated (MUFA) and polyunsaturated (PUFA) of the unsaturated fatty acids fraction (UFA), O / L corresponds to the oleic / linoleic FA ratio. Values are means of tree replicates ± Standard Deviations, Means within a raw followed by different letters (a-f) indicate significantly different at P<0.05.

The influence of temperature is more important during lipid accumulation in almond kernel. Oleic and linoleic acids showed opposing accumulation pattern and variation of fertilization, temperature, rootstock or light penetration may be the key for manipulating the fatty acid between 95 and 136 days post-anthesis [27]. In agreement with the literature and as shown in Table 6, our results show a highly significant (p<0.01) negative correlation between oleic acid and linoleic acid

In the other hand, O/L ratio range from 1.93 to 4.1 and the highest ratio was registered for Ferragnes-Ferraduel couple (F-F). These differences could be attributed to different climatic conditions of varieties between crop years. Variance analysis (Table 5), showed that variety and climatic conditions of the crop year (temperature and cumulated rainfall) had important effects on the yield and fatty acids profile of almond oils. Ferragnes Ferraduel (F-F), which are the late blooming couple of almond varieties newly introduced in eastern morocco, present a high content of unsaturated FA and have the highest O/L ratio due certainly to the high temperature in June and July that correspond to phase of synthesis and accumulation of fatty acids in kernels. Kester [28] considered that O/L ratio is an important parameter to evaluate almond oil quality, because oleic acid reduces the oxidation of almond oil [29]. That would explain why (F-F) couple present the highest induction time value (Table 4).

3.3. Total phenols content of almond oils

Total phenols content of mechanical extracted almond oils is expressed as their equivalent caffeic acid (TPC: mg caffeic acid /kg oil) and the results are given in table 4. In first crop year, TPC ranged from 151.67 to 239.46 mg·kg−1 for M and (F-F) couple respectively. In the second year, for all the assessed varieties TPC are lower and vary from a minimum of 70.98 mg·kg-1 for B to a maximum of 137.58 mg·kg-1 for (F-F) couple. The crop year 3, show the highest TPC values for three varieties, which are 225.5, 230.4 and 299.6 mg·kg-1 respectively for B, (F-F) and M, in opposition FNB recorded the lowest TPC for the three consecutive years of this study. These observations confirm the complexity of the combined effects of variety and environment on biosynthesis and the accumulation of phenols in almond kernels. Variance analysis of TPC shows significant ($P< 0.001$) variation between variety effect, the crop year, and “variety x crop year” interaction (Table 5). Total phenols contents (TPC) recorded for almond oils of main varieties from eastern Morocco are higher than the data reported by Rabadan et al. [30] for Spanish varieties, which appears to be too low and range from 6.53 to 21.57 mg·kg-1. However, they are at least 50% lower than TPC reported for almond varieties from northern Morocco, which varies from 560 to 760 mg·kg-1 [5]. Variability in TPC is known to be very high in almond oils and it depend on variety. The difference in phenols content could be also due to different type of extraction and the standard used gallic or caffeic acids [31].

3.4. Tocopherol isomers of almond oils

The α-Tocopherol is the main vitamin E isomer in oils of almond while other homologues (β-, γ- and δ-tocopherol) are minor components. In this study, compared with α-tocopherol, the levels of γ- β- and δ-tocopherol are very low in oils of all almond varieties assessed across the three crop years. Total and individual contents of tocopherols vary and depend on the varieties and the crop year (Table 4). They are lower to those reported in other studies [23; 32], but similar to recent results published by Zhu et al. [27]. Indeed, the content of tocopherols in almond oils varies between 200 and 500 mg·kg−1 of oil according to the varieties and pedoclimatic conditions. In this study, the content of α-tocopherol in almond oils of the varieties assessed ranges between 166 and 290 mg·kg−1, and the contents of β-, γ-tocopherol are low and respectively range between 1.3 – 3.68 mg·kg−1 and 0.7 – 7.22 mg·kg−1, whereas δ-tocopherol is nearly absent or in traces. During the three consecutive crop years of this study, the highest values of α-tocopherol were recorded for FNB and F-F; they are successively 177.66, 200.90 and 232.37 mg·kg−1 for FNB and 180.58, 194.22 and 290.82 mg·kg−1 for F-F. According to the variety and the crop year, significant differences are observed for total and individual tocopherol contents in almond oils of the varieties assessed.Variance analysis showed significant ($P < 0.001$) difference between crop year factor, variety factor, and “crop year x variety” interaction, with the exception of β-tocopherol, which no significant difference was detected (Table 5). Our data are less than other results [23; 24; 32] but more than Zhu [33] data, which ranged between 82 and 215 mg/kg. Zamany et al. [34] also have found that α-tocopherol ranged between 139.1–355.0 mg/kg of oil. Oil mechanical extraction process used in this study would influence the tocopherol content, because temperature of extraction could destroy a part of tocopherols. Thus, α-tocopherol is stable at high temperature if no oxygen is present. However, in normal atmosphere conditions, oxidation and degradation of α-tocopherol is accelerated [35]. The highest content of α-tocopherol was observed for the third crop year compared to the other crop years. The first year presents the lowest temperature, whereas second and the third third account for the highest one (Table 1). Thus, we observe that, α-tocopherol content in almond oil increases when the mean year temperature increases. Indeed, the environmental temperature affects the concentration of tocopherol in almond oil [3], showing that this component depends on the temperature and the incidence of drought during fruit ripening. This observation was reinforced by other authors, which found positive correlation between environmental temperature and tocopherol contents [36]. Those results is in agreement with our data. However, the impact of temperature on tocopherol content remains controversial. Izquierdo et al. [37] have demonstrated that the sunflower oil tocopherol content is reduced when night temperature is increased in the early seed filling.

3.5. Oxidative stability of almond oils

The oxidative stability index (OSI) of almond oils represented as induction time (IT) in hours was determined by Rancimat test (Table 4). Registered OSI values are in the range of 27 to 30 hours and the highest ones were observed for almond oil of (F-F) varieties and which are 27.60, 27.20, and 29.27 hours over the three consecutive crop years of this study. Significant (P<0.01) differences were detected in the case of varying both the crop year and the cross interaction "crop year x variety" as presented in table 5 for the effect of crop year and for effect of the cross interaction "crop year x variety". Highly (P<0.001) significant differences were also observed for all studied varieties.

Table 4. Total phenol contents (TPC), Tocopherol isomers and oxidative stability (IT hours) of mechanical extracted almond oils over three consecutive crop years.

	Cultivar	α–tocopherol (mg/Kg)	β–tocopherol (mg/Kg)	γ–tocopherol (mg/Kg)	δ–tocopherol (mg/Kg)	TPC (mg/Kg)	IT (h)
Crop year 1	B	169.83 ±1.65^{bc}	2.85 ±0.10^{cd}	5.51 ±0.18^{h}	0.00 ±0.00	175.32 ±2.03 ^{bcde}	23.48 ± 0.60^{bc}
	M	166.27 ±2.84^{b}	2.84 ±0.14^{cd}	3.73 ±0.14^{f}	0.00 ±0.00	151.67 ±20.70^{bc}	20.30 ± 0.50^{ab}
	FNB	177.66±4.79^{cd}	3.68 ±0.02^{d}	7.22 ±0.01^{j}	0.00 ±0.00	159.65 ±32.90^{bcd}	21.20 ± 3.30^{ab}
	F-F	180.58 ±1.49^{d}	2.79 ±0.10^{bcd}	4.20 ±0.13^{g}	0.00 ±0.00	239.46 ±20.80^{ef}	27.60 ± 0.70^{de}
Crop year 2	B	181.85 ±2.78^{d}	1.64 ±0.31^{abc}	2.01 ±0.02^{cd}	0.09 ±0.01^{a}	71.00 ±3.54^{a}	25.04 ± 0.14^{cd}
	M	147.97 ±1.00^{a}	1.40 ±0.05^{a}	6.66 ±0.22^{i}	0.58 ±0.01^{c}	137.28 ±30.40^{ab}	21.21 ± 0.208^{ab}
	FNB	200.90 ±2.27^{ef}	1.47 ±0.10^{a}	1.63 ±0.09^{b}	0.10 ±0.01^{a}	131.37 ±6.44^{ab}	25.32 ± 0.30^{cd}
	F-F	194.22 ±3.15^{e}	1.30 ±0.21^{a}	1.68 ±0.20^{bc}	0.12 ±0.02^{b}	137.58 ±30.22^{ab}	27.20 ± 0.20^{de}
Crop year 3	B	202.41 ±3.74^{ef}	2.30 ±0.02^{abc}	0.80 ±0.02^{a}	0.00 ±0.00	225.50 ±7.74^{cdef}	20.10 ± 0.10^{a}
	M	204.13 ±2.90^{f}	1.90 ±0.20^{abc}	2.70 ±0.05^{e}	0.00 ±0.00	299.60 ±26.10^{f}	21.00 ± 0.10^{ab}
	FNB	232.37 ±4.70^{g}	1.52 ±1.43^{ab}	1.11 ±0.03^{a}	0.00 ±0.00	99.60 ±13.00^{ab}	20.54 ± 1.84^{ab}
	F-F	290.82 ±0.81^{h}	1.52 ±0.10^{ab}	2.15 ±0.03^{d}	0.00 ±0.00	230.41 ±4.80^{def}	29.27 ± 0.40^{e}

TPC (mg caffeic acid/Kg); oxidative stability expressed as induction time (IT) in hours.

Values are means of tree replicates ± standard error, Means within a raw followed by different letters (a-j) indicate significantly different at P<0.05.

In this study, registered values for OSI expressed as IT, are higher than those reported for almond oils by Madawala et al. and Moayedi et al. [38; 39]. Several factors, such as the percentage of unsaturated fatty acids, light, oxygen, metallic ions, temperature, enzymes and storage conditions affect the oil oxidation [21; 40; 41]. The degree of unsaturation of fatty acids is the main factor affecting the stability of oils. Thus, more the fatty acids have double bonds more the attack by the free radicals occur, and therefore linolenic acid oxidizes rapidly, followed by linoleic and oleic acids. As the analyzed almond oils are rich in oleic acid, they are more stable to oxidation and show high OSI values [12; 42]. In addition, other minor almond oils components, such as tocopherols, phenols, which are natural antioxidants, contribute to stability of almond oils. Table 6 shows Pearson's correlation matrix were data is presented as a number between -1 and +1 that indicates the extent to which two variables are linearly related. Considering our data, significant ($P < 0.01$) positive correlations, were observed between OSI (IT (h)), oleic acid (C18:1), and O/L ratio but a negative correlation for linoleic acid (C18: 2). Warner et al. [43] reported that at high temperatures, γ-tocopherol is much more effective as an inhibitor of polymerization and protection against oxidation than α-tocopherol, whereas our results show the opposite, which established a positive correlation of + 0.586 between α-tocopherol content of almond oils and its OSI (IT (h)) and, no correlation between the OSI and γ-tocopherol content -0,198. Otherwise, theses correlations were not significant. Results showed also that there is no relationships among the TPC contents and IT found in this study. This means that almond oil stability depends mainly on oleic and linoleic acids, which are the most abundant fatty acid in almond oil respectively. However, we have noted that regardless of the climate conditions, (F-F) couple is distinguished by its high oxidative stability correlated with the highest content of oleic acid and α-Tocopherol.

Table 5. Three crop years analysis of variance for: Yield of mechanical extraction (YME); Main fatty acids; Quality parameters; Total phenols content (TPC); Tocopherol isomers; Oxidative stability expressed as induction time (IT)

Source of variance	Crop year (df: 2)	Cultivars (df : 3)	Year * Cultivars (df:6)
Yield of mechanical extraction (%)	***	***	**
Oleic acid (C18:1) (%)	***	***	***
Linoleic acid (C18:2) (%)	***	***	***
Stearic acid (C18:0) (%)	***	***	***
Palmitic acid (C16:0) (%)	***	**	*
Acidity (AI) (%)	***	*	***
Peroxide index (PI: meq O_2/kg)	**	***	NS
α-Tocopherols (mg/kg)	***	***	***
β-Tocopherols (mg/kg)	***	NS	NS
γ –Tocopherols (mg/kg)	***	***	***
δ-Tocopherols (mg/kg)	***	***	***
Total phenols content (TPC) (mg/kg)	***	***	***
Induction time (IT) (h)	**	***	**

NS: non-significance, *, ** and *** indicate, significance at P= 0.05, 0.01 or 0.001 levels respectively

Table 6. Pearson Correlation for main physicochemical parameters of almond oil over the three crop years of this study

	C18:1	C18:2	α – T	β- T	γ – T	IT	O/L	TPC	AI
C18:2	**-0.998****								
α – T	0.079	-0.101							
β- T	0.309	-0.271	-0.379						
γ – T	0.048	-0.034	**-0.578***	**0.591***					
IT	**0.677****	**-0.698****	**0.586***	-0.3	-0.198				
O/L	**0.987****	**-0.991****	0.096	0.276	0.072	**0.695****			
TPC	0.014	-0.001	0.26	0.231	0.019	0.048	0.068		
AI	0.114	-0.123	**-0.656***	-0.048	0.341	0.223	0.094	-0.436	
PI	-0.047	0.037	**-0.629***	0.1	0.248	-0.365	-0.019	-0.011	0.4

Oleic (C18:1) and Linoleic (C18:2) acids, α, β and γ-tocopherols (α-T, β-T, γ–T), Induction time (IT), Oleic/Linoleic ratio (O/L) Total phenols content (TPC), Acidity index (AI)

* Significant correlation at P< 0.05; ** Significant correlation at P< 0.01

Conclusion

The quality of almond oil in terms of fatty acids, tocopherols and total phenols is the major factor considered by users. The aim of this work was to evaluate the variability of composition in almond oil in local variety and introduced cultivars in eastern Morocco during three crop years. Data obtained show that this variability is influenced by cultivar and climatic condition mainly temperature. Although there are differences in chemical composition, (B) presents an oxidative stability, which is closer to that of FNB and M. However, we have noted that regardless of the climate conditions, (F-F) couple is distinguished by its high oxidative stability correlated with the highest content of oleic acid and α-Tocopherol. Those results allow us to conclude that (F-F) couple could be recommended as varieties for oil extraction by cooperatives in eastern Morocco.

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