

Study of the Chemical Composition of Argan Oil According to its Mode of Extraction, Its Origin of Production and Altitude

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Abstract

In this work, we studied the chemical composition of argan oil (*Argania spinosa* (L.) Skeels, Sapotaceae) according to its mode of extraction, its origin of production and its altitude of the argan tree. To carry out this work, we compared the physico-chemical characteristics and the chemical composition of five samples differing by their mode of extraction or coming from different regions of Morocco. The study of the physicochemical characteristics of the five samples shows that the roasting of the almonds of the argan fruit appears as a parameter can increase the value of the peroxide index, decrease the percentage of α -tocopherol, and decrease the unsaponifiable rate in percentage. We also found that geographic origin can influence fatty acid values (behinic C22:0). The results of the specific extinction and the refractive index do not give any precise information on the origin, the altitude and the method of extraction of argan oil. The study of the triglyceride fraction shows that the geographical origin of north-eastern Morocco can increase the value of triglyceride SOP (S: Stearic acid, O: oleic acid and P: Palmitic acid). Our study has demonstrated the high quality of argan oil extracted by mechanical pressing and the results of this work have helped support the commercialization of argan oil worldwide.

Keywords: Argan; Sapotaceae; Chemical Composition; Extraction Origin; Altitude; Marketing

Introduction

Morocco is one of the rare countries in North Africa to have a set of endemic ecosystems of remarkable biodiversity [1]. *Argan Argania spinosa* (L.) Skeels, is a specifically Moroccan endemic [2], it is a rustic, xero-thermophilic species, which belongs to the tropical family of Sapotaceae, of which it is the only northern representative in the Mediterranean region (Algeria and Morocco) hence its marked endemism in this region [3]. It is a multi-use forest tree (forest-fruit-fodder) of great importance for the country both biologically, phylogenetic and ecological biodiversity as well as economically and socially. It has great medicinal and therapeutic benefits [4], thanks to the oil extracted from its fruits. In addition, it is highly sought after in cosmetics as a skin and hair conditioning agent. This ecosystem is based on a balance between resources and human exploitation, and also plays an important role in the fight against desertification and erosion [5]. Argan oil is the main product of the argan tree. It is extracted by women in an ancestral way and sometimes under very precarious conditions. The artisanal extraction of a liter of oil requires 20 hours of strenuous and intense work [6].

Traditionally extracted argan oil goes rancid after a few months. This is caused by several factors: the early dehulling of the fruit of the argan nut, the use of nuts rejected by goats, the precarious hygienic conditions during the extraction of artisanal oil, the packaging in bottles recycled and improperly cleaned and the use of water in the preparation of the oil. Argan oil is rich in oleic acid, which makes this oil particularly interesting in the regulation of cholesterol. In addition, argan oil is also rich in phytosterols which have an important activity and whose incorporation in a diet is supposed to offer cancer prevention [7]. Studies also show that polyphenols and phytosterols as well as a certain number of their derivatives have anti-tumor properties. Great efforts have been made to develop argan oil by improving its extraction technology and allowing forest users to benefit from this added value by creating cooperatives in the region that produces and sells argan oil [8].

This work had repercussions in the production region, both socio-economic and environmental. We are currently witnessing an international craze for this oil whose beneficial virtues have been demonstrated. However, good marketing of argan oil first requires

the establishment of quality standards. Argan oil has a fatty acid composition close to the fraction of peanut or sesame oil, and their unsaponifiable fraction is of the same order of magnitude as that commonly observed in vegetable oils. Our work tried to make a study of the exhaustive physico-chemical composition of argan oil according to its mode of extraction and its origin of production, proving to be essential. The aim of this work is to study the influence of the region or the altitude near or far from the sea and the extraction method on the physicochemical characteristics and the chemical composition of argan oil, in order to know the parameters that can degrade the quality of argan oil.

Materials and Methods

Preparation of Different Samples of Argan Oil

Biological Material

This present work, we have selected 5 samples of the argan fruit having different regions and its different mode of extraction (southwest, northeast and northwest of Maorc). Table 1 gives information on the origin, the extraction method and the altitude of the argan tree of each sample.

Argan Oil Extraction

After the selection of five different samples by the mode of extraction or from different regions of Morocco. Argan oil is prepared by two different methods [7]:

- HPT: Argan oil is extracted by mechanical pressing from roasted almonds (HPT).
- HPNT: Argan oil is extracted by mechanical pressing from unroasted almonds (HPNT).

These oils are then analyzed in the Official Laboratory of Analysis and Chemical Research (LOARC) of Casablanca in Morocco, the physico-chemical characteristics and the chemical composition of all the samples are determined (fatty acid, sterols, triglycerides, tocopherols). The oils are analyzed according to the analysis methods already described in the literature [9].

Table 1 provides information on the origin and method of extraction of each sample of argan oil.

N° Samples	of extraction mode	The region	Province	Altitude	The distance between the region and the sea
1	Roasted almond extracted by mechanical press (HPT)	Tidzi	Essaouira North-West	150 meters	25 Km
2	Unroasted almond extracted by mechanical press (HPNT)	Tidzi	Essaouira North-owest morocco	150 meters	25 Km
3	Unroasted almond extracted by mechanical pressing (HPNT)	Beniznassen	Oujda North-eastern morocco	1532 meters	100 km
4	Unroasted almond extracted by mechanical pressing (HPNT)	Ait mzal	Chtouka ait baha Southwest Morocco	933 meters	75 Km
5	Unroasted almond extracted by mechanical pressing (HPNT)	Ighrem	Taroudant Southwest of Morocco	1277 meters	170 Km

Table 1: Origin and method of extraction of the 5 samples

Physicochemical Analyzes of Oils

All analyzes were done in the Official Laboratory of Chemical Analysis and Research (LOARC) in Casablanca, Morocco. Determination of acidity [9], the peroxide value [10], the refractive index [11] of the absorbance in the ultraviolet [12], the saponification number [13], the unsaponifiable content [14] were measured according to the standardized methods of reference.

Determination of Composition and Nature in Total Sterols

Reference ISO 6799 [15]

Operating Mode

Weigh 2.5 g of argan oil and put into a 20 ml flask. 25 ml of a solution of potassium hydroxide (1N of ethanol) is added. The flask is heated under reflux for 30 minutes until the solution becomes clear. Then, 25 ml of distilled water is added to stop the reaction. The extraction of the unsaponifiable is carried out using 75 ml of hexane or petroleum ether. The organic phase is subjected to a series of washing with 15 ml of mixture (water/ethanol 95°) (90/10) in a separatory funnel. The hexane phase is transferred from the top of the ampoule into a 100 ml flask. After evaporation of the solvent using a rotary evaporator, the unsaponifiable material is recovered. The unsaponifiable agent, diluted with 300 µl of hexane or petroleum ether, is filtered on a silica column (25 cm × 4 mm). The HPLC device is equipped with a 205 nm-254 nm UV detector. The eluent is an isooctane/isopropanol (99/1) mixture whose flow rate is 1.2 ml/min. The duration of the analysis is 15 min, the sterol fraction recovered according to standard NF 12228 May 1999, is evaporated to dryness.

The sterols are converted to silylated derivatives (TMS) using a mixture of pyridine, hexamethyldisilazane (HMDS) and trimethylchlorosilane (TMCS), (9/1/1), (v/v/v). The pyridine is evaporated to dryness and the silylated derivative is diluted with 60 µl of heptane or hexane. The TMS sterols are analyzed by gas chromatography (GC) on an apolar column (Chroma pack) (30m × 0.32mm, DI: 0.25µm, phase: CPSIL8CB). The HP Hewlett Packard 6890 GC Series Chromatograph is equipped with FID detector (T°: 300 °C). The carrier gas is nitrogen and its flow rate is 1 ml/min (P.E: 8.6 bar). The analysis is performed in temperature programming (200 °C up to 270 °C with a speed of 10 °C/min and an isotherm at 270 °C for 35 min).

Analysis of Cis Fatty Acids

Reference: NF ISO 5509 COFRAC code: CC30 (Normalization 2015)

Operating Mode

The test sample of argan oil 1g is supplemented with 0.5 ml of methanolic KOH for HPLC (minimum 98%) and 10 ml of methanol in a 100 ml flask. The mixture is refluxed for 15 minutes until the solution is clear. Then 1 ml of heptane is added to the reaction mixture after cooling. The heptanic phase containing the methyl esters is transferred to a test tube and then a solution of sodium carbonate Na₂CO₃ is added. This neutralizes all free acids by giving sodium salts with a release of carbon dioxide. The methyl esters, which are in the organic phase, are removed using a 2 ml cone pipette and placed in a test tube. The methyl esters undergo a series of washing 20ml are taken from the esters, which are placed in a tube of nominal capacity of 2 ml and then filled with heptane.

The fatty acid methyl esters are analyzed by GC gas chromatography. The HP Hewlett Packard 6890 GC Series GC chromatograph is equipped with a divider (T: 240 °C) and a FID (T: 260 °C) injector. The carrier gas is nitrogen (PE: 12.4 bar). The analysis is carried out in temperature programming (140 °C to 200 °C with a speed of 10 °C / min and an isotherm at 200°C for 40 min) on a capillary column (polyethylene glycol) (30 m × 0,32 mm, DI: 0.25 µm).

Tocophérols Analysis (Lara-Ortega, et al. 2017)

Operating Mode

In a 25 ml volumetric flask, 2 g of argan oil was diluted with 2,2,4-trimethyl pentane. The test sample is added to 2, 2, 4-trimethyl pentane up to the mark, then mixed thoroughly.

The tocopherols are analyzed by HPLC, on a silica column (25 cm × 4 mm), according to the AOCS method, official method CE8-89 revised 1990 updated 1992. The SHIMADZU brand device is equipped with a fluorimetric detector (excitation wavelength 290 nm - emission wavelength 330 nm). The elution is carried out with a mixture (isooctane/isopropanol) (99/1) with a flow rate of 1.2 ml/min during the analysis time (20 min).

Triglyceride Analysis

Reference: IUPAC No. 2.0 324 [16]

To 0.15 g of the argan oil are added 0.5 ml of hexane and 15 ml of a mixture of hexane/diethyl ether (87/13). This solution is poured into a supelco brand cartridge with 0.5 g of silica gel previously activated with hexane. The triglyceride fraction is thus separated from the diglycerides and monoglycerides. It is recovered in a 100 ml flask. It is subjected to analysis after evaporation of the solvent and dilution with 1.5 ml of acetone. The triglycerides are analyzed by HPLC on a reverse phase C18 column (250 mm × 4.6 mm, Φ silica 5 µm), according to IUPAC Method No. 2.0324. The HPLC apparatus is equipped with an HP refractometric detector 10 47A. Elution is carried out with a mixture (acetonitrile/acetone) (v/v) with a flow rate of 0.5 ml/min during the analysis time (90 min).

Results

Analysis of Physico-Chemical Characteristics

Table 2 and Figure 1 shows the results of the acidity value, the unsaponifiable rate, the saponification index and the specific extinction values at 270 nm (k₂₇₀). All the acidity values observed are less than 1%. This result shows that argan oil is characterized by low acidity compared to other vegetable oils (acidity of olive oil ≤ 2%) [17]. The acidity of samples 1 and 2 (0.33%, 0.50% respectively) (belonging to the same batch of Tidzi) is higher compared to other samples such as 4.5, (0.28%, 0.14% respectively) (belonging to different lot). These results suggest that the origin may influence the acidity values of argan oil. Roasting also appears as a parameter influencing the acidity value of argan oil (sample 1 and 2). The acidity value of sample 3 is higher compared to that of other samples. This result can be linked to the geographic origin of the sample because this sample comes from the higher elevation lot (1532m). The unsaponifiable rate of argan oil is less than 0.8% (for virgin olive oil, it is less than or equal to 1.50%) [18]. Argan oil extraction technology can influence the level of unsaponifiable matter in argan oil. Indeed, the unsaponifiable rate of sample 1 obtained by extraction by mechanical pressing from roasted almonds is lower (0.55%) than that which is prepared by mechanical press from non-roasted almonds (0.71 %).

N° Samples	1	2	3	4	5
Acidity in%	0.33	0.5	0.67	0.28	0.14
Unsaponifiable rate in%	0.55	0.71	0.63	0.56	0.54
Saponification index	197.9	180	189.6	183.3	183.5
Peroxide index in meq of O ₂ / kg	1.23	0.24	2.4	1.46	1.68
Specific extinction at 270 nm (k ₂₇₀).	0.228	0.282	0.291	0.392	0.277
The refractive index 20°C	14,705	14,705	14,691	14,667	14,682

Table 2: The main physico-chemical constants of the 5 samples of argan oil studied

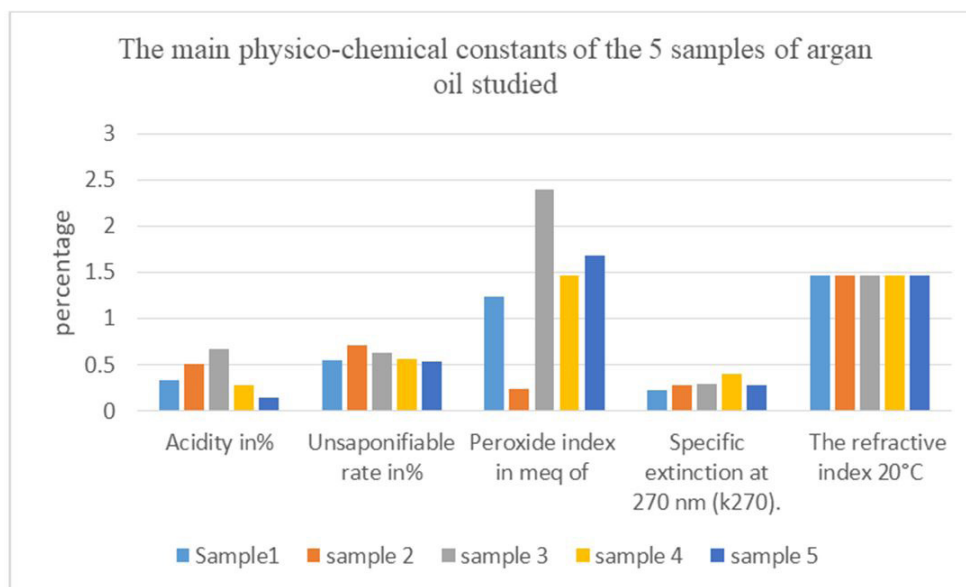


Figure 1: The main physico-chemical constants of the 5 samples of argan oil studied

The argan oil saponification index (Table 2) was found between 180.0 and 199.0. For virgin olive oil, it is between 180 and 198) [17]. The study of this work shows a great variation between the values of the saponification index of argan oil extracted from roasted and non-roasted almonds of the same batch (Tidzi). Indeed, samples 2 have a low saponification value (180). The specific extinction of argan oil was determined at 270 nm. In general, the values found are higher than that of olive oil, they vary between 0.228 and 0.426 for argan oil. The peroxide index results for the 5 samples of argan oil. For all samples, a peroxide index lower than that required for virgin olive oil was observed. The peroxide index in sample 1 is higher. Indeed, this sample is taken from a lot nearest the Atlantic Ocean and at the same time is extracted from roasted almonds. This result clearly indicates that some components of argan oil are extremely sensitive to oxidation.

The high peroxide content is observed for sample 1. This is probably related to the extraction method, the hygienic and extraction conditions and the use of water in the preparation of the oil and also related to the geographic location. The determination of the peroxide index seems to be a critical measure for the evaluation of the quality of argan oil. The determination of the refractive index, in general, is used for a quick and reliable verification of the purity of a substance. Both the refractive index and the density depend on the chemical composition of the oil and its temperature. It grows with the establishment and presence on fatty chains of secondary functions. The refractive index was determined at 20 °C. The results show that this index varies between 1.4667 and 1.4705.

Analysis of Fatty Acids

The fatty acid composition of the different oils was determined after methylation of the oil and analysis of the methyl esters by gas chromatography on a capillary column. Table 3 and Figure 2 groups together the results obtained for the 5 samples.

Samples	C _{14:0}	C _{15:0}	C _{16:0}	C _{16:1}	C _{17:0}	C _{18:0}	C _{18:1}	C _{18:2}	C _{18:3}	C _{20:0}	C _{20:1}	C _{22:0}
1	0.12	0.04	12.45	0.04	0.08	5.44	47.11	33.53	0.09	0.36	0.44	0.11
2	0.11	0.04	12.06	0.01	0.08	5.77	47.76	32.69	0.08	0.4	0.47	0.14
3	0.15	0.04	12.06	0.09	0.07	6.35	48.32	31.73	-	0.35	0.41	0.38
4	0.11	0.04	12.56	0.07	0.08	6.94	45.05	33.74	0.1	0.47	0.43	0.17
5	0.11	0.05	12.75	0.08	0.08	6.12	47.64	31.73	0.08	0.44	0.49	0.17

Table 3: Fatty acid composition of samples 1 to 5 (in %)

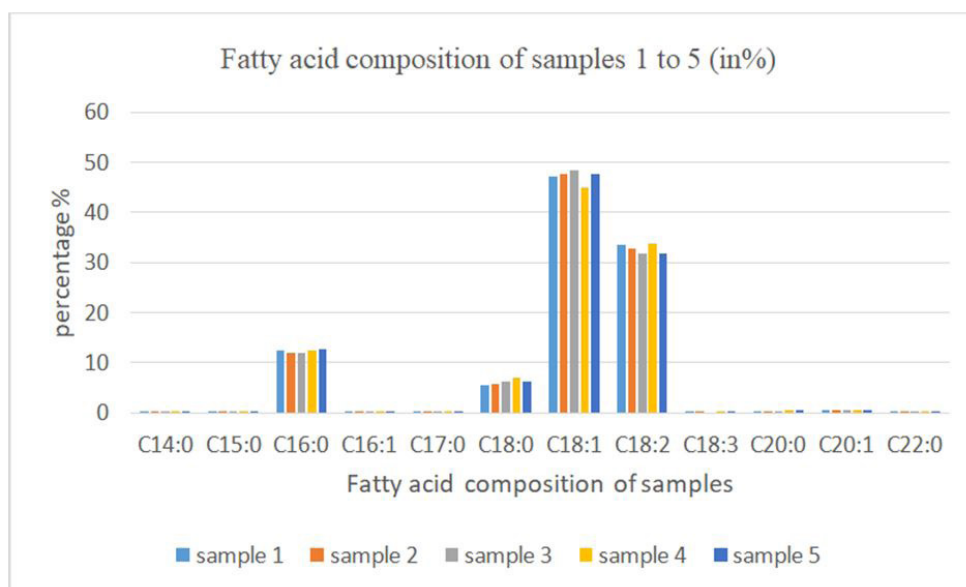


Figure 2: Fatty acid composition of samples 1 to 5 (in %)

The fatty acid composition corroborates with data from the literature [19]. Argan oil contains 80% unsaturated fatty acids. It is of the oleic – linoleic type and contains between 29 to 35% of essential fatty acids: linoleic acid (29 to 34%) (Vitamin F). This acid is said to be essential because it cannot be synthesized by the body and must be provided by food. Unsaturated fatty acids play an essential role in the prevention of cardiovascular disease and the omega 6 family (such as linoleic acid) is essential for the growth of the child [20]. Its oleic acid content makes argan oil particularly interesting in regulating cholesterol. The other fatty acids present are: myristic acid C14: 0 (0.10 to 0.15%), palmitic C16: 0 (11 to 13%) and stearic C 18: 0 (5 to 7%). The percentage of linolenic acid (C18: 3) in argan oil does not exceed 0.1%. Note the presence in argan oil of long chain fatty acids such as C20:0 (0.4%), C20:1 (0.5%), and C22:0 (0.1 %).

No significant variation was observed between the different samples. Sample 3 contains a higher percentage of behenic acid (C22:0) (0.38%). On the other hand, this percentage does not exceed 0.1% for all the other samples, this sample is prepared from argan almonds gathered in the Benaiznassen plantation. These variations can be considered useful markers to ascertain the geographical origin of argan oils. No major significant variation was observed between samples. This demonstrated that the origin and the geographical process cannot influence the dietary qualities of argan oil. These results agree with those reported by [21,22] which showed that climatic conditions have no marked influence on the fatty acid composition of the oils of argan fruit from different localities.

Trans Fatty Acid Analysis

The trans fatty acid composition of the different oil samples was determined after methylation of the oil and analysis of the methyl esters by gas chromatography. Table 4 groups together the results obtained for the 5 samples. It appears from this result that the percentage of trans oleic and linoleic acid (C18: 1 and C18: 2), (elaidic acid) in argan oil is low and varies between 0.01% and 0.02%. The results are similar to those found for olive oil [17]. The presence of trans fatty acids in “virgin” argan oils, suitable for consumption, is an indication of the fraudulent presence of refined oil. For this reason, the trans fatty acid content has been limited by the standard to 0.05% for both elaidic acid and the sum of the trans isomers of linoleic and linolenic acids.

N° samples	1	2	3	4	5
%C18 :1 trans	0.02	0.01	0.01	0.01	Trace
%C 18:2trans	0.02	0.02	0.02	0.02	0.01

Table 4: Composition of trans fatty acids in samples 1 to 5

Triglyceride Analysis

The triglycerides of the different argan oil samples analyzed by high performance liquid chromatography are grouped in Table 5. Analysis of the triglyceride fraction of argan oil by HPLC allowed the separation of the individual triglycerides. We note the predominance of triglycerides LLO (12 to 14%), LOO (13 to 16%), LOP (14%), OOO (11 to 14%) and POO (15 to 16%). It is also noted that the oleic and linoleic acids occupy most of the Sn-2 position. Our results are in agreement with the data in the literature [17] which indicate that the triglycerides LLL, LLO, LOO, LOP, OOO and POO are predominant in argan oil. Samples 3 has a high percentage of triglycerides SOP (4%) this result clearly shows that the geographical location or the origin of the argan fruit can influence the chemical compositions.

Samples	LLL	LLO	LLP	LOO	LOP	PPL	OOO	POO	OPP	LPS	SOO	SOP
1	6.89	13.22	5.85	15.96	14.18	1.94	13.77	16.05	4.06	0.31	4.58	2.25
2	7.43	13.8	6.17	16.27	13.96	2.05	13.74	15.74	3.76	0.32	4.69	1.91
3	6.84	12.2	6	14.31	13.22	2.08	13.98	15.48	4.39	0.66	6.04	4
4	7.69	13.41	6.55	13.93	14.57	2.14	11.32	15.17	4.37	0.11	4.61	2.11
5	7.54	12.91	5.77	14.8	13.64	1.86	14.03	16.32	4.16	0.21	4.1	1.77

Table 5: Triglyceride composition of samples 1 to 5 (in %)

Sterol Analysis

The sterol composition of the various argan oil samples was determined by gas chromatography after silylation of the sterol fraction. The latter is obtained by fractionation of the unsaponifiable matter of argan oil by HPLC on a normal phase. This analysis was carried out in the presence of an internal witness: 0.2% α -cholestanol in chloroform. The various sterols encountered were identified by gas chromatography coupled to mass spectrometry and by comparison with data from the literature [23]. Their individual and total assay was possible by GPC using an internal standard: α -cholestanol 0.2% in chloroform. Table 6 and Figure 3 summarizes the results obtained for the 5 samples selected. The total sterol content of all samples of argan oil ranges from 130 to 206mg / 100g of fat. This is not negligible compared to other seed and olive oils. The sterolic composition is in accordance with data from the literature [17]. They are essentially Δ -7-stigmasterols. The main products are schottenol (or Δ -7-stigmasterol) and spinasterol. Their proportion varies respectively between 42 and 48%, and 34 and 42%.

Samples	Campest.	Stigma 8,22	Spinast.	Schott.	Stigma 7,24	Total
1	0.2	4.31	37.07	46.66	4.81	142
2	0.17	4.57	38.5	43.39	5.94	158.2
3	0.11	4.85	35.44	48.47	2.57	206.3
4	0.24	4.77	39.17	44.99	4.71	147.4
5	0.31	5.4	39.29	46.12	3.55	130

Table 6: Composition in sterols of samples 1 to 5 (mg / 100g)

Campest: Δ 5-campesterol; 8.22 Stigma: Stigmasta-8, 22-diene-3 β -ol; Spinast: spinasterol; Schott: schottenol; Stigma 7.24: stigmasta-7.24-diene-3 β -ol

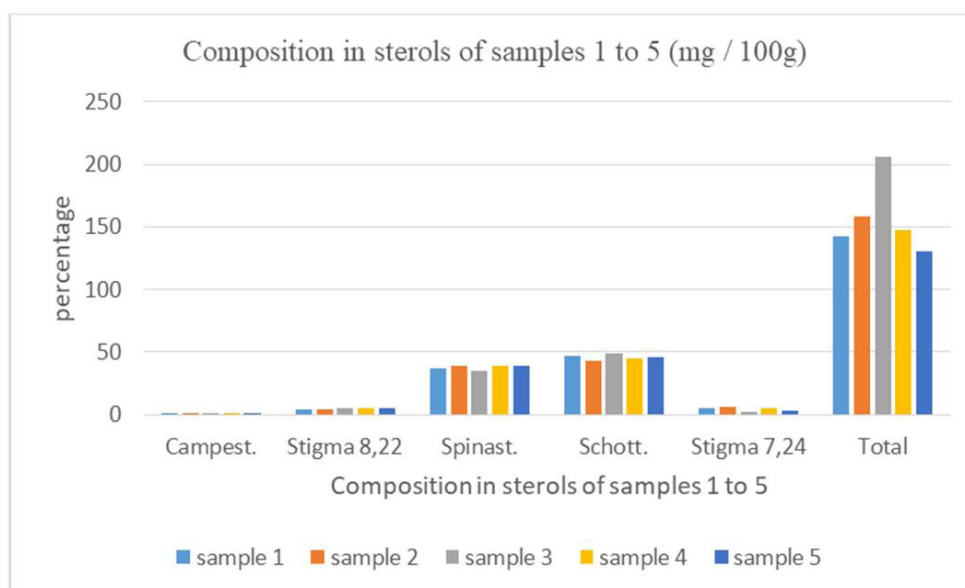


Figure 3: Composition in sterols of samples 1 to 5 (mg/100g)

Schottenol and spinasterol are rarely found in vegetable oils and are characteristic of this oil. Two minority sterols were identified on the basis of their mass spectrum obtained by GC / MS and by comparison with data from the literature [24]. These are stigmast-8,22-diene and stigmasta-7,24-28-diene (or Δ -7-avenasterol). Their proportion varies between 2.6% and 6.9% of the mixture of total sterols. We find that the content of campesterol in argan oil is very low (0.3%) compared to other seed oils and olive oil. This parameter can be taken as a marker to detect adulteration of argan oil. We found that the percentage of total sterols is higher for the sample extracted from unroasted almonds (2 to 1). The variation in the sterol composition of the different samples is not significant.

Tocopherol Analysis

The tocopherols were analyzed by HPLC on a column in the normal phase, directly from vegetable oil without saponification. They were identified by comparison of their chromatogram with controls injected under the same conditions. Their dosage was possible by the use of α -tocopherol. The results obtained are grouped in Table 7 and Figure 4. Argan oil is richer in tocopherol (633 to 775 mg / kg) than olive oil (50 to 150 mg / kg) and than hazelnut oil (300 to 550 mg / kg).

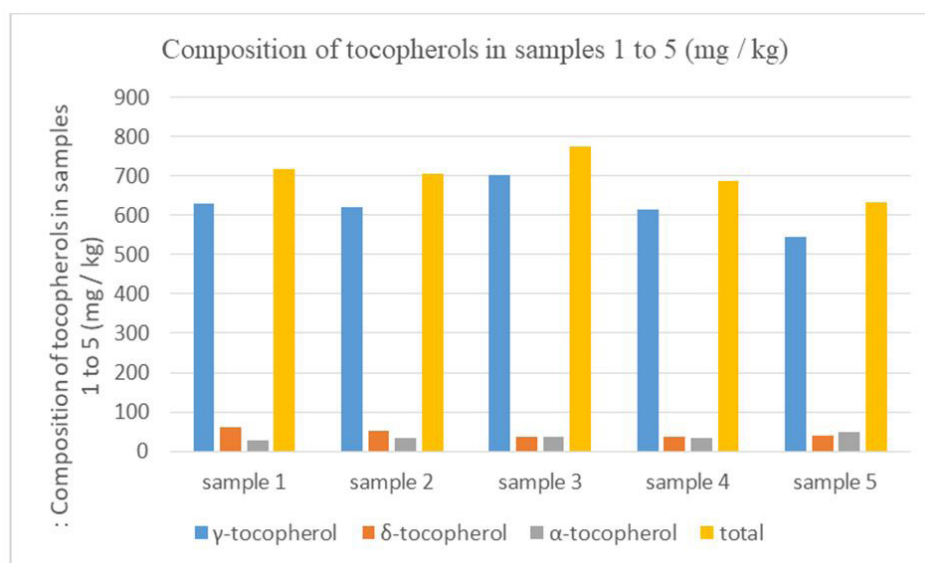


Figure 4: Composition of tocopherols in samples 1 to 5 (mg/kg)

Samples	γ -tocopherol	δ -tocopherol	α -tocopherol	β -tocopherol	Total
1	631.3	59.5	26.6	-	717.4
2	621.1	50.9	32.7	-	704.7
3	701.1	37.2	37.2	-	775.5
4	615.6	38	33.2	-	686.8
5	545.9	38.7	49.3	-	633.9

Table 7: Composition of tocopherols in samples 1 to 5 (mg/kg)

Tocopherols have vitamin E activity. This vitamin is a powerful antioxidant that captures free radicals and neutralizes destructive oxidation [25]. Our study shows that our samples are rich in γ -tocopherol (80 to 90%), Tocopherols are natural antioxidants, gamma tocopherol has the highest antioxidant power. Rich in gamma tocopherol, argan oil is a valuable nutraceutical. Tocopherols (vitamin E) and polyphenols are natural antioxidants. These play an essential role in the prevention of several diseases [26], because they are anti-free radicals. We found that samples 5, have a low content of total tocopherols (633 mg / kg). The roasting of almonds has an influence on total tocopherols. Indeed, the oils extracted from unroasted almonds have a higher total α -tocopherol content compared to the samples extracted from roasted almonds (sample 1 versus 2).

Discussion

As part of the development of argan oil, we conducted a comparative study of the different physico-chemical parameters of argan oil according to its mode of extraction and its origin of production. To carry out this work, we selected 5 samples of argan fruit located in different geographical localities of Morocco and extracted in different ways (by mechanical pressing from roasted and non-roasted almonds). The study of the physico-chemical characteristics shows that all the acidity values of argan oils are less than 1.40%. This result shows that argan oil is characterized by low acidity compared to other vegetable oils (acidity of the olive oil $\leq 2\%$). Our study shows that roasting appears as a parameter influencing the acidity value of argan oil. This is because the acidity value is higher in argan oil samples prepared from unroasted almonds. We also found that the argan oil sample from Tamanar batch had a higher acidity value compared to the samples. This finding suggests that geographic origin may influence acidity values.

The results concerning the unsaponifiable rate shows that argan oil is characterized by a low unsaponifiable rate (the unsaponifiable of the argan oil $\leq 0.81\%$) (unsaponifiable of the Olive oil $\leq 1.50\%$) [27]. Argan oil extraction technology can influence the unsaponifiable level of argan oil. In fact, the level of unsaponifiable matter in the sample prepared from roasted almonds is lower (0.56%) than that prepared from non-roasted almonds. Our study also shows that the roasting and the origin of the argan fruit have an influence on the reduction of this parameter (sample 1 and 2). Analysis of the peroxide index shows that the sample of argan oil extracted from roasted almonds has a higher peroxide content compared to sample 2 (same batch). The determination of the peroxide index seems to be a critical measure for the evaluation of the quality of argan oil. The specific extinction and the refractive index give no precise information on the origin and the method of extraction of argan oil.

Analysis of fatty acids shows that argan oil contains 80% unsaturated fatty acids. It is of the oleic – linoleic type and contains between 29 to 35% of essential fatty acids: linoleic acid (29 to 34%) (Vitamin F). Its oleic acid content makes this oil particularly interesting in regulating cholesterol. Our results show that the percentage of behenic acid (C22:0) is higher in the sample which was prepared from the argan almonds gathered in the Benaïznassen plantation. These variations can be considered useful markers to ascertain the geographical origin of argan oils. Sterol analysis shows that the total sterol levels of argan oil vary between 130 to 206mg / 100g of fat. The sterolic composition consists essentially of Δ -7-stigmasterols. The main products are schottenol (or Δ -7-stigmasterol) and spinasterol. It is noted that schottenol and spinasterol, which are very rare in vegetable oils, can be a parameter for the detection of adulteration of this oil. Two minority sterols were identified on the basis of their mass spectrum obtained by GC / MS. These are stigmast-8,22-diene and stigmasta-7,24-28-diene (or Δ -7-avenasterol).

The sterol composition does not show any significant variation. These results agree with those reported in the literature [28]. The sterol composition does not show any significant variation. These results agree with those reported in the literature. Argan oil is richer in tocopherols (633 to 775 mg / kg) than olive oil (50 to 150 mg / kg) and hazelnut oil (300 to 550 mg / kg). The results for tocopherols show that the extraction method and roasting can influence the composition of tocopherols. In contrast, the sample obtained from roasted almonds has a lower content of total α -tocopherols. Roasting decreases the total α -tocopherol content [17]. Analysis of the triglyceride fraction of argan oil allowed the separation of individual triglycerides. We note the predominance of triglycerides LLO (12% -14%), LOO (13% -15%), LOP (14%), OOO (12% -14%), and POO (14% -17%) in l'Argan Oil. These triglycerides represent approximately 73% of each fraction of triglycerides in argan oil. The triglyceride results do not give any specific information on the geographical origin and the extraction process of the argan fruit [29,30].

Conclusion

In this work we have studied the chemical composition of argan oil (*Argania spinosa* (L.) Skeels, Sapotaceae) according to its mode of extraction and its origin of production. To carry out this work, we compared the physico-chemical characteristics and the chemical composition of 5 samples differing by their mode of extraction or coming from different regions of Morocco. The results of this work show that the extraction method and the origin of the fruit of the argan tree can influence the peroxide index, the rate of unsaponifiable matter, fatty acids (including behenic: C22:0), the content of α -tocopherol and triglycerides (SOP). Our study has demonstrated the high quality of argan oil extracted by mechanical pressing and the results of this work have helped support the commercialization of argan oil worldwide.

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Reference

1. Faouzi K, Rharrabti Y, Boukroute A, Mahyou H, Berrichi A (2015) Distribution map of the argan tree (*Argania spinosa* L. Skeels) in the eastern region of Morocco by GPS combined with GIS. *Nat Technol* 12: 16-24. (Cartographie de l'aire de répartition de l'arganier (*Argania spinosa* L. Skeels) dans la région orientale du Maroc par le GPS combiné au SIG).
2. El Youbi AEH, Boustia D, Ouahidi I, Aarab L (2010) Primary pharmacological screening of an endemic plant native to southern Morocco (*Tetraena gaetula* [Emb. And Maire] Beier and Thulin). *Biology Reports* 333: 736-43. (Criblage pharmacologique primaire d'une plante endémique originaire du Sud Marocain (*Tetraena gaetula* [Emb. and Maire] Beier and Thulin). *Comptes Rendus Biologies*).
3. Vêla E, Benhouhou S (2007) Assessment of a new plant biodiversity hotspot in the Mediterranean Basin (North Africa). *Biol Rep* 330: 589-605. (Évaluation d'un nouveau point chaud de biodiversité végétale dans le Bassin méditerranéen (Afrique du Nord). *Comptes rendus biologies*).
4. Moukal A (2004) The argan tree, *Argania spinosa* L. (Skeels), therapeutic, cosmetic and food use. *Phytotherapy* 2: 135-141. (L'arganier, *Argania spinosa* L.(Skeels), usage thérapeutique, cosmétique et alimentaire. *Phytothérapie*).
5. Bellefontaine R, Ferradous A, Alifriqui M, Monteuiis O (2010) Vegetative propagation of the argan tree, *Argania spinosa*, in Morocco: the John Goelet project. *Trop Woods For* 304: 47-59 (Multiplication végétative de l'arganier, *Argania spinosa*, au Maroc: le projet John Goelet. *Bois and forêts des tropiques*).
6. Charrouf Z, Guillaume D (2007) Argan oil produced when grown. *Lab Technol* 2(6) (Huile d'argan une production devenue adulte. *Les technologies de laboratoire*).
7. Cherki A (2016) *Anachronistic memory*. Aube editions (Mémoire anachronique. Éditions de l'Aube).
8. Faouzi H (2012) Impact of women's cooperatives on the preservation and enhancement of the argan grove: the case of the Tafyoucht cooperative (confederation of Ait Baâmrane, Anti-Atlas, Morocco). *Borders. Revue franco-Brésilienne de géographie / Revista franco-brasilera de geografia* pp. 14. (Impact des coopératives féminines sur la préservation et la valorisation de l'arganeraie: cas de la coopérative Tafyoucht (confédération des Ait Baâmrane, Anti-Atlas, Maroc). *Confins. Revue franco-brésilienne de géographie/Revista franco-brasilera de geografia*, 14).
9. Européenne Norme (1999) Animal and vegetable fats-Determination of acid number and acidity. French standard NF EN ISO 660: 60-204. (Corps gras d'origines animale et végétale-Détermination de l'indice d'acide et de l'acidité. Norme Française NF EN ISO).
10. Lagardere L, Lechat H, Lacoste F (2004) Determination of the acidity and the peroxide index in virgin olive oils and in refined oils by near infrared Fourier transform spectrometry. *Oilseeds, Fats, Fat*, 11: 70-5. (Détermination de l'acidité et de l'indice de peroxyde dans les huiles d'olive vierges et dans les huiles raffinées par spectrométrie proche infrarouge à transformée de Fourier. *Oléagineux, Corps gras, Lipides*).
11. ISO, NFEN 6320: 2000 (2017) Animal and vegetable fats and oils - Determination of the refractive index.
12. De Normalisation (2002) O. I. Corps gras d'origines animale et vegetale. Determination de l'alcalinite.
13. Denormalisation, Organisation Internationale (2002) Corps gras d'origines animale et vegetale. Determination de l'alcalinite.

14. Sylvester ND, Ainsworth AN, Hughes EB (1945) The determination of fat in mixtures containing fatty acids, and the determination of unsaponifiable matter in oils and fats. *Analyst* 833: 295-8.
15. Aïssi VM, Soumanou MM, Tchobo FP, Kiki D (2009) Comparative study of the quality of refined edible vegetable oils in use in Benin. *West African Society of Chemistry Information Bulletin* pp. 25-37. (Etude comparative de la qualité des huiles végétales alimentaires raffinées en usage au Bénin. *Bulletin d'Informations de la Société Ouest Africaine de Chimie*).
16. Brand WA, Coplen TB, Vogl J, Rosner M, Prohaska T (2014) Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report). *Pure and Appl Chem* 86: 425-67.
17. Hilali M, Charrouf Z, Aziz Soulhi AE, Hachimi L, D Guillaume (2005) Influence of origin and extraction method on argan oil physico-chemical characteristics and composition. *J Agric Food Chem* 53: 2081-7.
18. Barjol JL (2014) The global economy of olive oil. *OCL*, 21: D502 (L'économie mondiale de l'huile d'olive).
19. Rahmani M (2005) Chemical composition of "virgin" argan oil. *Agricul Notebooks* 14: 461-5. (Composition chimique de l'huile d'argane «vierge». *Cahiers Agricultures*).
20. Lapillonne A (2007) Omega-3 and omega-6 fatty acids during pregnancy and early childhood. *Nutrition and Diet Books*. (Acides gras oméga-3 et oméga-6 au cours de la grossesse et de la petite enfance. *Cahiers de Nutrition et de Diététique*) 4: 38-42.
21. Louni S (2009) Extraction and physicochemical characterization of Moringa oleifera seed oil. (Extraction et caractérisation physico-chimique de l'huile de graines de Moringa oleifera) (Doctoral dissertation).
22. Kechairi R (2009) Contribution to the ecological study of the Argan *Argania spinosa* (L.) Skeels. In the Tindouf region (Algeria). Doctoral thesis. University of Mascara (Contribution à l'étude écologique de l'Arganier *Argania spinosa* (L.) Skeels. Dans la région de Tindouf (Algérie). Thèse de doctorat. Université de Mascara).
23. Gharby S, Harhar H, Kartah BE, Monfalouti HE, Denhez C, et al. (2013) Can fruit-form be a marker for argan oil production?. *Nat prod commun* 8: 1934578X1300800106.
24. Hamia C, Yousfi M (2007) Contribution to the composition and the chemical study of the oil of the Argan fruit "*Argania spinosa*" (Doctoral dissertation). (Contribution à la composition et à l'étude chimique de l'huile du fruit de l'Arganier "*Argania spinosa*").
25. Nkhili EZ (2009) Food Polyphenols: Extraction, Interactions with Iron and Copper Ions, Oxidation and Antioxidant Power. Cadi Ayyad-Marrakech University. (Polyphénols de l'Alimentation: Extraction, Interactions avec les ions du Fer et du Cuivre, Oxydation et Pouvoir antioxydant. Université Cadi Ayyad-Marrakech).
26. Jager FC (1968) Determination of Vitamin E Requirement in Rats by Means of Spontaneous Haemolysis *in vitro*. (Bestimmung des Vitamin-E-Bedarfes der Ratte durch Spontanhaemolyse *in vitro*/Détermination du besoin en vitamine E chez le rat au moyen de l'hémolyse spontanée *in vitro*). *Nutritio et dieta* pp. 215-223.
27. Charrouf Z, Guillaume D (2008) Argan oil: Occurrence, composition and impact on human health. *European J Lipid Sci Technol* 110: 632-6.
28. Monfalouti HE, Guillaume D, Denhez C, Charrouf Z (2010) Therapeutic potential of argan oil: a review. *J Pharm Pharmacol* 62: 1669-75.
29. De normalisation, Organisation Internationale (2015) Fats of animal and vegetable origins. Determination of chloropropanediol esters (MCPD) and fatty acids and glycidol esters of fatty acids by CPG / SM. Pt. 1: Method by rapid alkaline transesterification and measurement for 3-MCPD and by differential measurement for glycidol. (Corps gras d'origines animale et végétale. Détermination des esters de chloropropanediols (MCPD) et d'acides gras et des esters de glycidol et d'acides gras par CPG/SM. Pt. 1: Méthode par transestérification alcaline rapide et mesure pour le 3-MCPD et par mesure différentielle pour le glycidol).
30. Lara Ortega FJ, Gilbert López B, García-Reyes JF, Molina Díaz A (2017) Fast automated determination of total tocopherol content in virgin olive oil using a single multicommuted luminescent flow method. *Food Analyt Meth* 10: 2125-2131.