



## The Effect of Storage Conditions and Roasting Kernels on Extra Virgin Argan Oil Quality

S. Gharby<sup>1,2\*</sup>, H. Harhar<sup>1</sup>, Z. Bouzoubaâ<sup>3</sup>, N. Elmadani<sup>1</sup>, Z. Charrouf<sup>1</sup>

<sup>1</sup>Laboratoire de Chimie des Plantes et de Synthèse Organique et Bioorganique, Faculté des Sciences, Université Mohammed V-Agdal, BP 1014- Rabat, Morocco

<sup>2</sup>Etablissement Autonome de Contrôle et de coordination des exportations, Agadir, (Maroc) ;

<sup>3</sup>INRA-CRRA Agadir- Unité de Recherche Ressources Naturelles et Produits de Terroir ;Laboratoire d'Agrophysiologie, B.P. 124, Inezgane, (Maroc)

Received 07 March 2014; Revised 1 June 2014; Accepted 1 June 2014.

\*Corresponding Author. E-mail: [s.gharby@yahoo.fr](mailto:s.gharby@yahoo.fr); Tel: (+212 670266965)

### Abstract

The aim of this study was to determine the evolution of the quality index of both extra-virgin argan oils (edible and beauty), stored and packaged in different conditions during two years. The selected quality parameters were: acidity index, peroxide value (PV), K232 and K270 coefficients, iodine index, induction time, fatty acid (FA) and sterols profile. Both of oils were packaged in dark and transparent glass bottles. The results showed that the acidity and K270 parameters increased slightly in all cases, while PV changes were significant in both oils stored in transparent glass bottles and at 40°C. Fatty acid and sterol profiles did not significantly vary over two years. The variations of these parameters were followed over a period of 2 years at 5°C, 25°C (protected or exposed to sunlight), or 40°C. After two years, mechanically pressed argan oil still presents an excellent physicochemical profile. Beauty oil presents after the same delay much less satisfactory properties.

*Keywords: Edible argan oil, beauty argan oil, roasting, kernels, Storage, oil quality, oxidative stability*

### Introduction

Argan oil is extracted from the kernels of the fruit of argan-tree (*Argania spinosa* (L.) Skeels; Sapotaceae), an exclusively endemic tree of Morocco. Argan oil exists as beauty and edible oil. Beauty oil that is prepared from unroasted kernels, it's endowed with numerous dermocosmetological properties [1]. Edible argan oil is prepared from roasted kernels. It's the basic ingredient of the amazigh diet [2] and its regular consumption is beneficial for human health [3]. Virgin edible argan oil extraction requires at least six steps: fruit collection, sun-drying, dehulling, nut breaking, kernel roasting, and cold-pressing. Skipping the roasting step leads to the production of beauty-grade oil. Each processing step can dramatically influences the quantity and the quality of the resulting oil. Edible argan oils are known to be more resistant to oxidation than other edible oils because of their natural antioxidant content, particularly tocopherols, phospholipids and their relatively low content of polyunsaturated fatty acids [4-5]. It is known that the storage conditions are a major factor in the shelf life of argan oil, as well as its composition. Therefore the producer must make predictions based on the oils chemical composition and how the oil will be stored in order to determine what will be the oil's shelf life and gives the product a "use-by" or "best before" date. Predicting the shelf life of the argan oil is a complex process because of the influence of several factors on it such; as temperature, light and oxygen availability. Extending the shelf life of argan oil is important for the benefit of the consumer but also for the long-term viability of the product. Sensory characteristics of argan oil are expected to be of high quality during storage and up to the time of consumption. The assessment of stability is important for the prediction of shelf life and used-by-dates. Measurement of all components such as fatty acid, peroxide value and K270 coefficient can assist in predicting the stability of oil. The oxidative stability of the three marketed types of edible argan oil has already been studied [6]. The latter study, conducted over two years showed that the best conservation is obtained away from light and at 25 °C [6]. We also determine the effects of the production conditions on the

sensory quality and storage stability of edible argan oil. Storage was at 20 °C and at 60 °C [4]. The high content of tocopherols and low linolenic acid are responsible for its resistance to oxidation. Phospholipids argan oil have recently shown their contribution to the preservation of the oil [5,6], but for the first time a comparative study between the effect of storage conditions on the beauty argan oil quality and the edible argan oil have been investigated. In our study, oil samples were kept at 5°C, 25°C, and 40°C. Because oil samples refrigerated at 5°C or heated at 40°C were necessarily sunlight protected (fridge or oven), and since light is well-known to possibly influence edible oil oxidation, we also decided to evaluate the influence of light on our oil samples kept at 25°C by using the clear-glass or dark-glass bottles.

## 2. Materials and methods

### 2.1. Sample preparation

Argan oils were prepared by the women of the cooperative of Tiout (Taroudant city, Morocco) using their current and traditional technology. To prepare edible argan oil, kernels were roasted at 110°C for 20 min using a SMIR roaster (Technotour, Agadir, Morocco). Roasting temperature was controlled using a Testo 945 sensor/thermometer (Testo, Casablanca, Morocco). Kernel cold-pressing was carried out using a Komet DD 85 G press (IBG Monforts Oekotek GmbH & Co. KG, Mönchengladbach, Germany). Beauty oil was similarly prepared from unroasted kernels.

### 2.2. Sample distribution

Oil samples were immediately distributed in 60 mL glass bottles. Samples stored at 5°C were analyzed after 5, 11, 17, and 23 months of storage. Samples stored at 25°C or 40°C were analyzed after 1 month of storage then every two months over two years.

### 2.3. Chemicals reagents

All the reagents were of analytical or HPLC grade. 2,2,4-trimethylpentane heptane and isopropanol used in chromatography and cyclohexane used for extinction coefficient determination were purchased from Professional Labo (Casablanca, Morocco). Clear and brown-glass bottles were purchased from Cfimu (Casablanca, Morocco).

### 2.4. Analytical determination

#### 2.4.1. Acidity:

Acidity was determined using the International Standard Organization method [7]. Oil (10 g) was dissolved in 80 mL neutralised taste ethanol (96°). Two drops of phenolphthalein (1% in ethanol) were added to the solution. The solution was then titrated with 0.1N sodium hydroxide (NaOH), previously standardised against hydrochloric acid (HCl). The volume of titrant was recorded and the results calculated as a percentage of the oil (expressed as oleic acid).

#### 2.4.2. Peroxide value:

Peroxide value was determined using the International Standard Organization method, [8]. Oil (5 g) was dissolved in acetic acid / 2, 2, 4-trimethylpentane mixture (3:2). To this solution, 1 mL of saturated potassium iodide (KI), (70 g KI/40 mL water), was added and shaken for 1 minute. Water (70 mL) was added, followed by approx 0.5 mL of 1 % starch solution (1 g starch/100mL water). The solution was titrated with previously standardised 0.01N sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ). The volume of titrant was recorded and the peroxide value calculated and reported as mEq of active oxygen/kg oil.

#### 2.4.3. Iodine index

Iodine index was determined using the International Standard Organization method [9]. It was experimentally determined by treatment with Wijs reagent followed by titration of the iodine excess with  $\text{Na}_2\text{S}_2\text{O}_3$ .

#### 2.4.4. Ultraviolet absorption

Ultraviolet absorption was determined using the International Standard Organization method [10]. Oil (0.25g) was weighed into a 25 mL volumetric flask and made to volume with cyclohexane. The absorbance of the oil sample was measured on a double beam spectrophotometer, using cyclohexane in 1 cm cellpath length, at 232 and 270 nm.

#### 2.4.5. FA Composition

Fatty acid composition was determined using the International Standard Organisation (Organization) method [11]. Fatty acids were converted to fatty acid methyl esters before analysis by shaking a solution of 60 mg oil and 3 mL of hexane with 0.3 mL of 2 N methanolic potassium hydroxide. They were analyzed by gas chromatograph (Varian CP-3800, Varian Inc.) equipped with a FID. The column used was a CP- Wax 52CB column (30 m×0.25 mm i.d.; Varian Inc., Middelburg, The Netherlands). The carrier gas was helium, and the total gas flow rate was 1 mL/min. The initial column temperature was 170 °C, the final temperature 230 °C, and the temperature was increased by steps of 4 °C/min. The

injector and detector temperature was 230 °C. Data were processed using Varian Star Workstation v 6.30 (Varian Inc., Walnut Creek, CA, USA). The results were expressed as the relative percentage of each individual fatty acid (FA) presents in the sample.

#### 2.4.6. Sterols composition

Sterol composition was determined using the International Standard Organization method [12]. Sterol composition was determined after trimethylsilylation of the crude sterol fraction using a Varian 3800 instrument equipped with a VF-1 ms column (30 m & 0.25 mm i.d.) and using helium (flow rate 1.6 mL/min) as carrier gas. Column temperature was isothermal at 270 °C, injector and detector temperature was 300 °C. Injected quantity was 1 µL for each analysis. Data were processed using Varian Star Workstation v 6.30 (Varian Inc., Walnut Creek, CA, USA).

#### 2.4.7. Tocopherols composition

Tocopherols composition was determined using the International Standard Organization method [13]. High performance liquid chromatography (HPLC) was used for the determination of tocopherols, using a solution of 250 mg of oil in 25 mL of n-heptane. Tocopherols were analyzed by HPLC using Shimadzu CR8A instruments (Champ sur Marne, France) equipped with a C18-Varian column (25 cm×4 mm; Varian Inc., Middelburg, The Netherlands). Detection was performed using a fluorescence detector (excitation wavelength 290 nm, detection wavelength 330 nm). Eluent used was a 99:1 isooctane/isopropanol (V/V) mixture, flow rate of 1.2 mL/min.

#### 2.4.8. Oxidative Stability of Argan Oils

Induction time was determined using the International Standard Organization method [14]. The oxidative stability was evaluated by the Rancimat method. Stability was expressed as the oxidative induction period (IP, hours) measured at 110 °C on a Rancimat 743 (Metrohm Co, Basel) apparatus using 3 g of oil sample with an air flow of 20 L/h. Volatile oxidation products were stripped from the oil and dissolved in cold water, whose conductivity increased progressively. The time taken to reach a level of conductivity was measured.

#### 2.5. Statistical Analysis.

Values reported in tables and figures are the means ± SD (Standard Deviation) of three replications. Separation of means was performed by Tukey's test at the 0.05 significance level.

### 3. Results and discussion

#### 3.1. Determination of the initial physicochemical parameters of the oil samples.

The initial composition of each extra virgin argan oil (EVAO) at the start of the analytical period is shown in Table-1. All samples fulfil the requirements Morocco Regulations for EVAO: acidity, PV and K270. The amount of free FAs is an indicator of the oil quality and is traditionally used as an indicator for the classification of the different commercial types of EVAO. It can be seen that at the beginning of this study, all EVAO varieties showed an acidity index 0.3%, which is much lower than the regulated 0.8% as maximum for any EVAO [15]. Concerning Peroxide value (PV), this index is considered to be an indicator of primary oxidation [16-17]. The two argan oil considered here showed low PV values, with the beauty argan oil yielded the highest value with 0.93 meq O<sub>2</sub>/kg. In any case, none of the analyzed oils surpassed 15 meq O<sub>2</sub>/ kg oil, which is the limit that is established for EVAO [15]. Another quality index specified in Moroccan Regulations is K270 [15]. An increase indicates that oil oxidation has begun, which could be due to some factors affecting storage conditions or to an inadequate EVAO processing. In this study, K270 coefficients less than 0.2, compared to a maximum established by Moroccan Regulations for EVAO that is 0.35 [15].

Other studied parameters (fatty acid, tocopherols and sterols) were remarkably constant; any of them had changed significantly. Induction time is a test designed to measure the relative stability of an oil sample. The most stable oils resist oxidation and result in longer induction time [17]. Rancimat induction periods at 110°C were observed within both oils. Edible argan oil displayed much longer Rancimat induction periods than beauty argan oil. The difference between the mean Rancimat induction period of edible argan oil and beauty argan oil was 18±2 hrs. Since only kernel roasting differentiates between the preparative processes of these oils, such Rancimat induction time decrease high lights the dramatic influence of roasting on argan oil preservation. Although induction time can be used to compare oils relative stability it cannot be used to precisely represent shelf life, as the conditions in which the oil is stored will have a major influence on shelf life. Induction time can be used to indicate the relative stability of oil when stored under the same conditions [17,18].

**Table 1.** Physicochemical parameters of freshly prepared virgin beauty and edible argan oils

Studied parameters	Types of oil	
	Edible oil	Beauty oil
Acidity (%)	0.2 ± 0.05	0.3± 0.05
PV (MégO2/Kg)	0.5 ± 0.3	0.9± 0.2
E232	1.06 ± 0.01	1.22 ± 0.01
E270	0.18 ± 0.01	0.20± 0.01
Rancimat (H)	31 ± 2.5	13 ± 1.5
Fatty acids (%)		
Palmitic acid C16:0	13.1 ± 0.3	13.1 ± 0.5
Stearic acid C18:0	5.4 ± 0.1	5.3 ± 0.3
Oleic acid C18:1	48.1 ± 0.4	47.9 ± 0.6
Linoleic acid C18:2	32.5 ± 0.4	32.9 ± 0.9
Linolenic acid C18:3	0.3 ± 0.1	0.1 ± 0.1
Sterols (%)		
Schotenol	46 ± 2	47 ± 2
Spinasterols	40 ± 2	39 ± 2
Delta-7-Avenasterol	5,5 ± 2	4 ± 2
Stigma-22-dien-3B	5 ± 2	4 ± 2
Tocopherols (mg/kg)	674 ± 10	682± 10

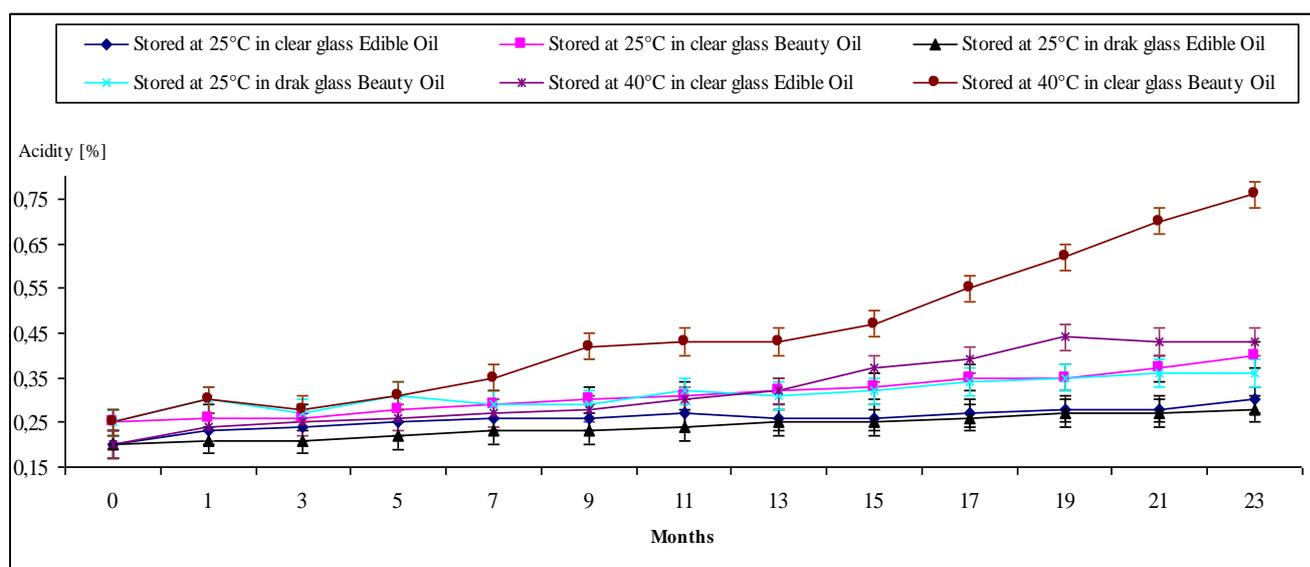
### 3.2. Physico-chemical properties of stored oils.

The quality parameters of the stored oils behaved differently during storage.

#### 3.2.1. Changes in free fatty acids

Acid value of edible and beauty argan oils stored at 5°C did not significantly changed over two years. Initial acid value was 0.2 for edible argan oil and 0.3 for the beauty argan oil. After two years at 5°C, acid value was 0.23 and 0.4 for edible and beauty argan oils respectively (data not shown).

Acid value of edible argan oil also remained remarkably stable over two years independently on the storage temperature and bottles color (Figure-1). After two years at 25°C, acid value of edible argan oil was 0.3±0.1 and 0.4 after two years of storage at 40°C. The beauty argan oil showed the highest increase for this index at the end of the storage period with 0.77.



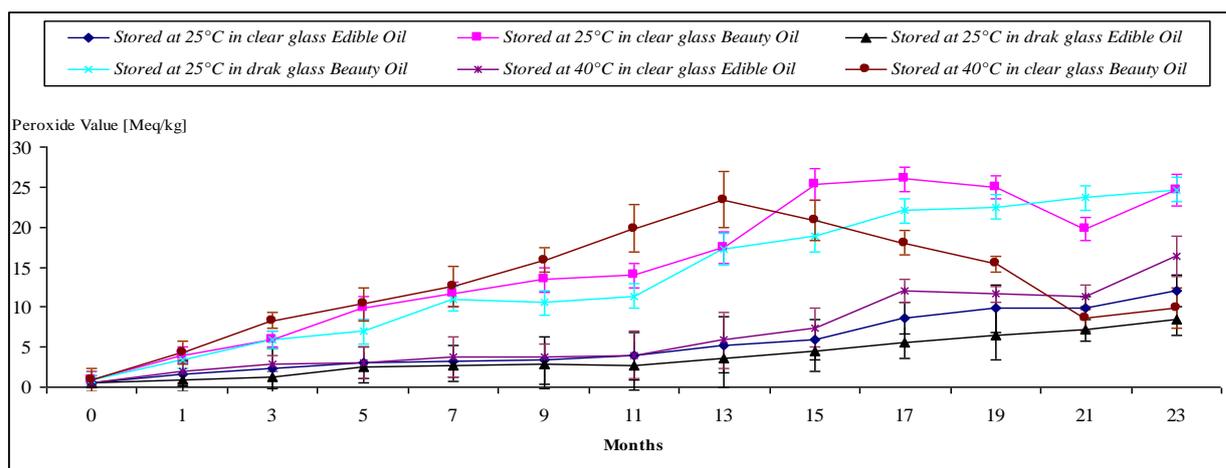
**Figure 1.** Acid value of the two types of argan (edible and beauty) oil stored in dark glass bottles at 25°C, in clear glass bottles at 25°C and at 40°C in clear glass bottles.

### 3.2.2. Changes in Peroxide value

Oxidation and the formation of peroxides occur at oil extraction and processing and can continue after bottling and during storage. Peroxides are intermediate oxidation products of oil which lead to the formation of a complex mixture of volatile compounds such as aldehydes, ketones, hydrocarbons, alcohols and esters responsible for the deterioration of organoleptic proprieties [17]. Therefore, their formation dramatically impacts oil shelf life and consumer acceptance. High temperature and light are two well-known factors generally promoting peroxide formation [16-19]. Initial peroxide value of edible, and beauty oils was found to be below 1 meq of O<sub>2</sub>/kg oil, below the maximum peroxide value of 15 meq O<sub>2</sub>/kg oil necessary for the extra virgin argan oil label [15]. For both oils, storage at 5°C for two years led only to a very slight increase of the peroxide value; the highest peroxide value of 3 meq O<sub>2</sub>/kg oil being observed for beauty oil (data not shown). Peroxide value of edible and cosmetic oils stored at 25°C or 40°C behaved differently. Edible argan Oil has evolved throughout the storage period, and it increased from 0.5 to 16.3 Meq (O<sub>2</sub>)/kg (Figure-2).

The beauty oil is passed two phases, the first where we observe a strong increase during the first 13 months to reach the maximum value of 23.4 Meq (O<sub>2</sub>)/kg where it lost its label extra virgin oil after 8 months of storage. The second phase, where we found a decrease in PV from the 13th month of storage to reach 9.8 Meq (O<sub>2</sub>)/kg. Although the final value of PV in the 2nd phase is below the standard, 15 Meq (O<sub>2</sub>)/kg, this does not reflect the quality of the oil, because in general the oxidation of oil passes through two stages, the first where there is a formation of hydroperoxides and a second stage where there is a proliferation of hydroperoxides which are transformed into secondary products of oxidation, aldehydes and ketones [19 - 22]

At 25 °C in transparent bottles, PV of the edible oil changed slightly, and this change remains lower than that observed at 40 °C, it increased from 0.5 to 12.06 keeping quality of oil extra virgin (Figure-1). Beauty oil, though, has been changed, but less intensive than at 40 °C going from 0.9 to 26.01 Meq (O<sub>2</sub>)/kg to undergo the 17th month then a slight decrease to reach 20 meq (O<sub>2</sub>)/kg. This oil has lost its quality of extra virgin after 12 months of storage. In brown bottles both oils underwent a less intense evolution than the storage at the same temperature in the light (Figure-1). These results are also similar to those reported for soybean oil [23] and olive oil [24-27]. This is probably due to the protection induced by a combination of natural antioxidants in argan oil [28-30]. Indeed, at 25 °C and in brown bottles, edible and beauty oils, increased by 0.5, 0.9 to 8.5; 24.6 respectively. Finally, we can conclude that the condition of 5°C is the best to keep the organoleptic and nutritional properties of argan oil, followed by the storage at 25 °C in brown bottles and storage at 25 °C in transparent bottle and finally the storage at 40°C which favors the formation of hydroperoxides under the effect of heat [20, 21]. These results are consistent with those reported for other vegetable oils such as olive oil [25, 31] sunflower oil [32], soybean oil [23] and palm oil [33].



**Figure 2.** Peroxide value of the two types of argan (edible and Beauty) oil stored , in dark glass bottles at 25°C, in clear glass bottles at 25°C and at 40°C in clear glass bottles.

### 3.2.3. Changes in K232 parameter

The UV spectrum provides information on the oxidation state of the oils. Indeed, the oxidation products of the oils having a characteristic spectrum in the UV as well the hydro peroxides linolenic and the oxidized fatty

acids that are dienes resulting from the decomposition of peroxides present an absorption band in the vicinity of E232 nm [21, 34-35]. During two years of storage at 5°C, K232 of edible and beauty oils remained practically constant (initial value 1.06, and 1.2 vs final value 1.2 and 1.4 for edible oils and beauty oils respectively) as expected from the results of the peroxide value study (data not shown).

When edible oil was stored at higher temperature, K232 was observed between 1.6 and 2 after 2 years. Edible oil has undergone a linear evolution phase during the whole period of storage. The extinction E232, of this oil increased from 1.06 to 1.9, Beauty oil recorded the highest values of absorbance in the vicinity of E232, it went three phases (Figure-3), the first corresponded to the initial oxidation that began, the second month until the eleventh month of storage, during this time, we noticed that the E232 became more intense to reach the maximum 2.5, then a decrease which lasted 8 months to get 2.3. This was due to the degradation of peroxides and the formation of secondary oxidation products. Finally, a new evolution began at the 19th month of storage and reached 2.6, after two years of storage which would probably due to the formation of new primary oxidation product.

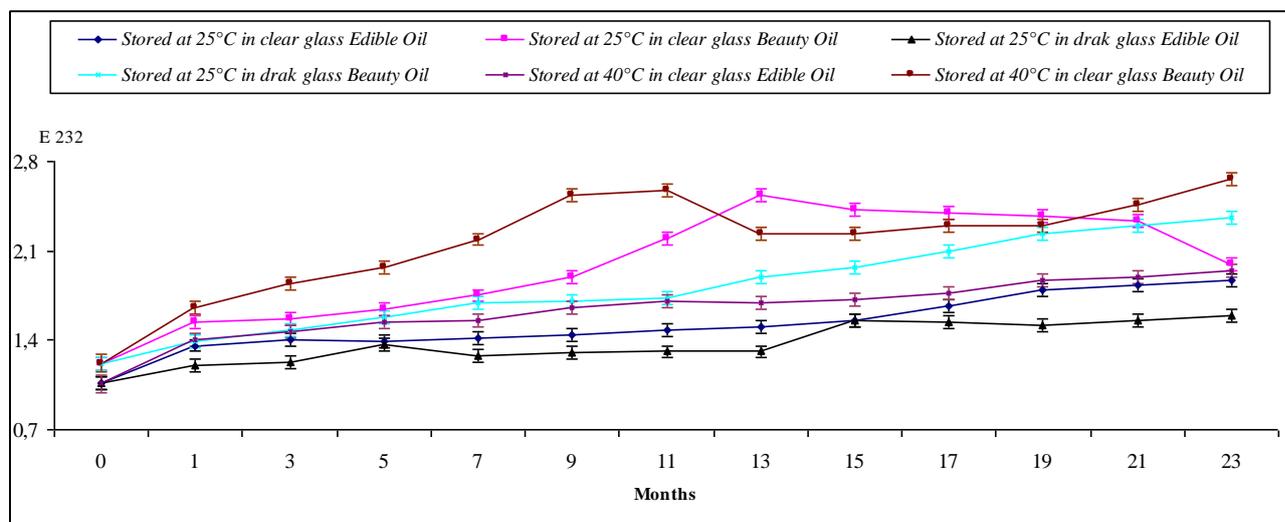
### 3.2.3.1. Packaging in clear bottles

In clear bottles at 25°C, the edible oil changed slightly, but remained below the trend observed at 40°C, it increased from 1.06 to 1.8 after two years of storage (Figure-3). At this temperature we observed that the absorbance at E232 and peroxide evolved similarly [31, 35], thus suggesting the low incidence of light on the formation of secondary oxidation products in edible oil. This can be explained that the oil is still in the initial phase of oxidation as we have noticed in the analysis of the peroxide. In addition, we observed that the oil absorption E232 for beauty oil has evolved from a linear manner to achieve the maximum value 2.5 after 13 months of storage and then decreased to reach 2 after 2 years of storage. Both K232 and peroxide value should depict the formation of primary oxidation product. The apparent sample-dependent correlation observed between K232 and peroxide value supported the idea of different ratio of hydroperoxides depending on the type of argan oil.

### 3.2.3.2. Packaging in brown bottles

In all studied oils, similar findings were also noted in brown bottles stored at 25 °C, but less intense compared to those stored in transparent bottles at 25 °C and 40 °C. Those results were in harmony with previous studies for soybean oil [23] and olive oil [23, 26-27]. Edible and beauty Oils underwent a linear trend less intense than the storage at the same temperature in the light (Figure-3). Indeed, at 25 °C in brown bottles, edible and beauty oils have increased respectively from 1.02 and 1.2 to 1.6 and 2.3.

In this study we found a good correlation between K232 and the peroxide value, several authors have shown similar findings [20-21]. Others authors have suggested that the absorbance at E232 can replace the peroxide value in the control of the oil quality [31, 36].



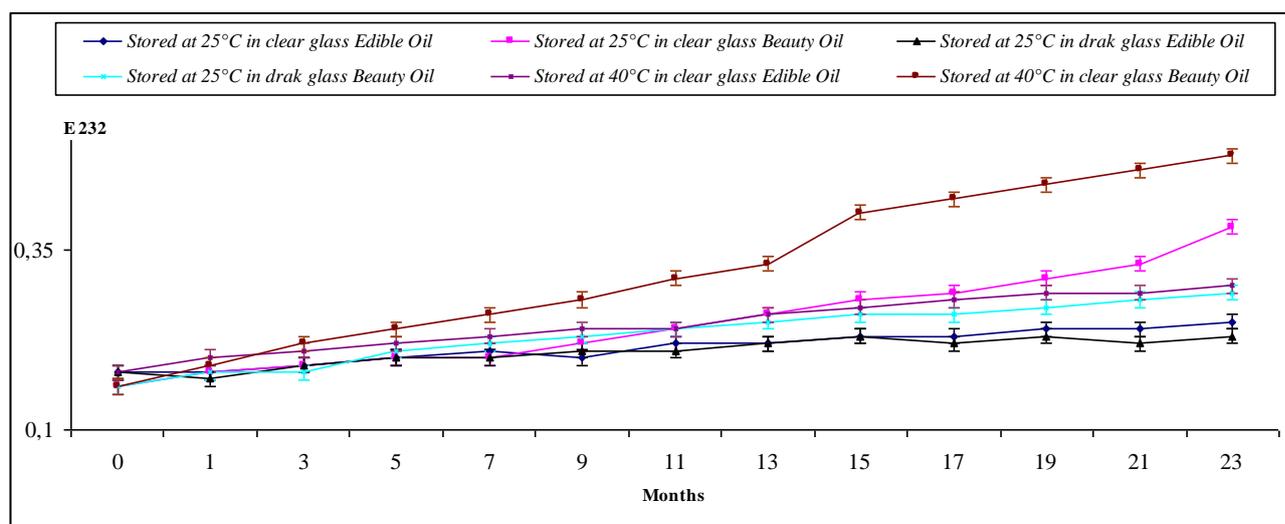
**Figure 3.** E232 of the two types of argan (edible and beauty) oil stored, in dark glass bottles at 25°C, in clear glass bottles at 25°C and at 40°C in clear glass bottles .

### 3.2.4. Changes in K270 parameter

Carbonyl compounds (aldehydes and ketones) are the most abundant secondary oxidation products formed in edible oils [37, 38]. Their formation is known to be accelerated by elevated temperature and metal traces [19]. UV absorption at E270 nm (K270) is one of the markers used to follow secondary oxidation formation. Moroccan regulation has set the maximum value for K270 at 0.35 [15]. Overall, K270 values did not significantly changed over the 2 years. Initial values are given in Table-1. Argan oil samples stored at 5°C over 2 years displayed stable K270 was not surprising (data not shown). That this trend also occurred for oil samples stored at higher temperature was unexpected. Final K270 values for edible argan oil were  $0.24 \pm 0.05$  and  $0.31 \pm 0.05$  when samples were stored at 25°C, and 40°C, respectively. For beauty oil, the rate of formation of secondary oxidation products is tripled in a period of two years from 0.16 to 0.48, following two phases:

The first phase had a small linear increase in absorbance E270 starting from 0.16 to 0.33 during 13 months of storage with an average of 0.02 units per month. As for the second, it has increase from the 13th month of storage starting from 0.33 to 0.48. Indeed, this strong evolution in the second phase is explained by the formation of strong secondary oxidation products, which coincides with the degradation of hydro peroxides that we have already shown by the analysis of the peroxide value and absorbance at E232. It is noteworthy that this oil has lost its label extra virgin oil to move to a virgin after 14 months of storage.

At 25 °C, transparent bottles of beauty oil, the rate of secondary oxidation products has undergone a greater change, but intense compared to that observed at 40 °C. Indeed, the rate of oxidation by-products increased from 0.16 to 0.38. For samples stored in drake bottles (Figure-4), it's recorded the same changes at the rate of secondary products of oxidation than those recorded for transparent bottles, but in lower proportions. Thus, the edible oil increase from 0.18 to 0.23 and beauty oil increased from 0.16 to 0.29.



**Figure 4.** E270 of the two types of argan (edible and beauty) oil stored in dark glass bottles at 25°C, in clear glass bottles at 25°C and at 40°C in clear glass bottles.

### 3.2.5. Changes in Fatty acid composition

Fatty acid composition is an essential indicator of the nutritional value of oil [39]. Argan oil is particularly rich in unsaturated fatty acids. Its oleic and linoleic acid levels are between 42 and 47%, and between 31 and 35%, respectively. In addition, argan oil also contains two saturated fatty acids: palmitic acid (12–14%) and stearic acid (5–7%) [15]. Our studied on beauty argan oil consisted of 12.9% palmitic, 4.9% stearic, 46.8% oleic, and 33.8% linoleic acids. Edible Argan oil consisted of 12.5% palmitic, 5.1% stearic, 46.7% oleic, and 34.4% linoleic acids. No significant effect of storage temperature or packaging condition on the fatty acid profile of the oils in this study was found (Table-2). After two years of storage at 5°C, 25°C and 40°C, the saturated, monounsaturated and polyunsaturated fatty acid composition of most of the oils were either exactly the same as the initial analysis or very similar. These results are similar to the findings of other authors [40]. There was no significant difference between the fatty acid composition of the samples stored in the dark and those stored exposed to light. While there were definitely changes in the overall structure of the oil, including

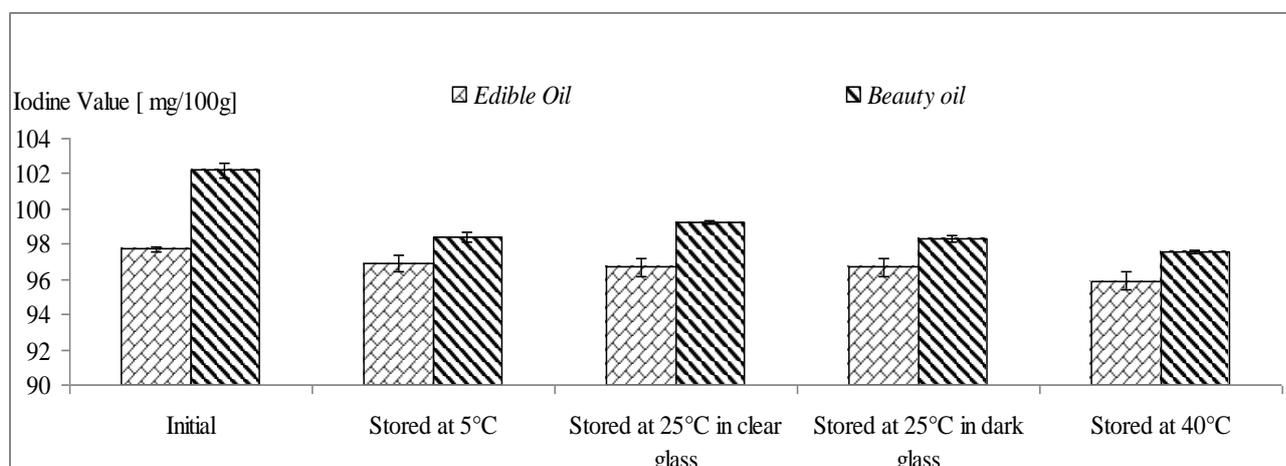
the triacylglycerol structure (evidenced by the change in FFA, PV and UV absorbance) as well as some of the minor components due to the storage temperature, there was no significant change observed in the overall fatty acid profile of the oil. As the method used for this determination is only qualitative, the actual changes in the amount of each fatty acid present are not observed.

**Table 2.** Fatty acid composition (initial and final) of edible and beauty argan oil samples stored for 2 years at 5°C, 25°C in clear or dark glass, and at 40°C.

Types of oil and parameters	Storage conditions				
	Initial	Stored at 5°C	Stored at 25°C in dark glass	Stored at 25°C in clear glass	Stored at 40°C in clear glass
<b>Edible oil</b>					
Palmitic acid	13.1 ± 0.3	13,6 ± 0,3	13,6 ± 0,3	14,4 ± 0,5	13,9 ± 0,1
Stearic acid	5.4 ± 0.1	5,3 ± 0,1	5,3 ± 0,1	5,5 ± 0,1	5,1 ± 0,1
Oleic acid	48.1 ± 0.4	48,2 ± 0,3	48,2 ± 0,3	47,9 ± 0,3	48,4 ± 0,1
Linoleic acid	32.5 ± 0.4	31,6 ± 0,1	31,6 ± 0,12	31,6 ± 0,1	31,1 ± 0,1
<b>Beauty oil</b>					
Palmitic acid	13.1 ± 0.5	13,9 ± 0,2	13,4 ± 0,1	13,7 ± 0,2	13,5 ± 0,1
Stearic acid	5.3 ± 0.3	5,7 ± 0,04	5,5 ± 0,07	5,4 ± 0,2	5,5 ± 0,1
Oleic acid	47.9 ± 0.6	48,7 ± 0,1	48,4 ± 0,9	47,9 ± 0,2	48,1 ± 0,1
Linoleic acid	32.9 ± 0.9	30,9 ± 0,1	32,0 ± 0,4	32,3 ± 0,2	30,8 ± 0,1

### 3.2.6. Changes in Iodine index

High concentration of unsaturated fatty acid in argan oil is essential for its preservation and pharmacological activity [41]. We also decided to analyze some of the physicochemical parameters of our oil samples after two years in order to possibly detect variations affecting unsaturated fatty acid essential components. Iodine value is a parameter that provides information on the unsaturation number, the initial values was in the order of 97.7 g I<sub>2</sub>/100g of oil for edible oil and 102.2 g of I<sub>2</sub> / 100g of oil for beauty oil, these values are higher than olive oil which has a value of 80 g I<sub>2</sub>/100g of oil, which explains that argan oil is more unsaturated than olive oil [42]. However, it is less unsaturated than soybean oil and sunflower oil which have respective values of 120 and 140 g I<sub>2</sub>/100g of oil [43]. Over two years of storage, the iodine value has decreased significantly under different storage conditions for both oils. However, this decrease is consistent with the standard [15]. At 40 °C hence the decrease was more intense, edible oil decreased from 97.7 to 95.9 g I<sub>2</sub>/100g of oil, and beauty oil from 102.2 to 97.6 g I<sub>2</sub>/100g of oil (Figure-5). We noted that throughout the storage period, the degradation of the iodine value is more intense in storage at 40 °C followed by storage at 25 °C in transparent bottles. Storage at 25 °C in brown bottles and 5 °C showed the best condition of conservation of iodine (number of unsaturation) during the two years of storage.



**Figure 5.** Iodine value, (initial and final) of edible and beauty argan oil samples stored for 2 years at 5°C, 25°C in clear or dark glass, and at 40°C in clear glass.

### 3.2.7. Changes in Sterols composition

Argan oil sterol fraction contains five compounds [44], mainly stigmasta-8, 22-dien-3-ol(3.2–5.7%), spinasterol(34–44%), schottenol (44–49%), and delta-7-avenasterol (4,0 - 7,0 %). Campesterol is also found but at a low concentration close to 0.3%. Concerning the sterols distribution in each oil samples, no significant changes were observed over two years of storage whatever the storage condition and the type of oil studied. Results are represented in Table-3.

**Table 3.** Sterol composition (initial and final) of edible and beauty argan oil samples stored for 2 years at 5°C, 25°C in clear or dark glass, and at 40°C.

Sterol composition	Storage conditions				
	Initial	Stored at 5°C	Stored at 25°C in dark glass	Stored at 25°C in clear glass	Stored at 40°C in clear glass
<b>Edible oil</b>					
Schottenol	46 ± 2	46,5 ± 2	46,5 ± 2	46,5 ± 2	45 ± 2
Spinasterol	40 ± 2	40 ± 2	39 ± 2	40 ± 2	37 ± 2
Delta-7-avenasterol	5,5 ± 2	4,5 ± 2	4 ± 2	4 ± 2	4 ± 2
Stigmasta-8,22-dien	5 ± 2	5 ± 2	3,5 ± 2	3,5 ± 2	3 ± 2
<b>Beauty oil</b>					
Schottenol	47 ± 2	46 ± 2	46 ± 2	45 ± 2	44 ± 2
Spinasterol	39 ± 2	40 ± 2	40 ± 2	40 ± 2	36 ± 2
Delta -7-avenasterol	4 ± 2	5 ± 2	4 ± 2	4 ± 2	4 ± 2
Stigmasta-8,22-dien	4 ± 2	4 ± 2	4 ± 2	4 ± 2	4 ± 2

## Conclusion

This study showed that the different storage conditions had a significant effect on the quality and shelf life of argan oil. Storage of argan under poor conditions will result the loss of quality, and therefore the value of the product. This can occur throughout the life of the argan oil.

This study provides the best indication to evaluate shelf life for argan oils. It indicates that the storage conditions have an influence on the oxidative stability of the oil. It also shows that some analyses are valuable in illustrating the oxidation of the argan oil, such as ; Peroxide value, K232, K270, free fatty acids and iodine index. This is an important information for those involved in the production, storage and sale of argan oil. These results will assist the industry to make important, informed decisions about the storage of argan oil. A combination of these results provided detailed information about the oil. After this period of time, mechanically pressed argan oil still presented an excellent physicochemical profile. Beauty oil presented after the same delay much less satisfactory properties. The better stability of argan oils prepared from roasted seeds could be explained by a better extractability of antioxidant compounds from the kernels or the formation of such compounds such as Maillard reaction products (MRP) during the roasting step.

**Acknowledgements-**This work was performed in the frame of “Projet Arganier” and financially supported by “Agence du Développement Social” and EEC (#AR05A061P704). Association Ibn Al-Baytar, Lesieur-Cristal, and Women’s cooperative of Tiout are thanked for their support, interest, and assistance.

## References

- Guillaume D, Charrouf Z. *Alternative Medicine Reviews*, 16 (2011) 275-279.
- Charrouf Z, Guillaume D. *Critical Reviews in Food Science and Nutrition*, 50 (2008) 473-477.
- El Monfalouti H, Guillaume D, Denhez C, Charrouf Z. *Journal of Pharmacy and Pharmacology*, 62 (2010) 1669-1675.
- Matthäus B, Guillaume D, Gharby S, Haddad A, Harhar H and Charrouf Z. *Food Chem.* 120 (2010) 426-432.
- Gharby S, Harhar H, Guillaume D, Haddad A and Charrouf Z. *Nat. Prod.Com* 7 (2012), 1-3.
- Gharby S, Harhar H, Guillaume D, Haddad A, Matthäus B, Charrouf Z. *LWT- Food Science and Technology*, 44 (2011) 1-8.
- ISO-660 (2009). Animal and vegetable fats and oils - Determination of acid value and acidity.
- ISO-3960. (2007). Animal and vegetable fats and oils - Determination of peroxide value – Iodometric (visual) endpoint determination
- ISO 3961. (2009). Animal fats and vegetable - Determination of iodine index.

10. ISO 3656. (2002) animal fats and vegetable "Determination of ultraviolet absorbance expressed as specific extinction in ultraviolet light
11. ISO 5508. (1990). Animal and vegetable fats and oils - Analysis by gas chromatography of methyl esters of fatty acids
12. ISO 6799. (1991). Determination of the sterol fraction by gas chromatography
13. ISO 9936. (2006). Animal fats and vegetable "Determination of tocopherols and tocotrienols by liquid chromatography high performance."
14. ISO 6886. (2006). Animal and vegetable fats and oils-Determination of oxidative stability (accelerated oxidation test).
15. SNIMA ; Service de Normalisation Industrielle Marocaine (2003). Huiles d'argane. Specifications. Norme marocaine NM 08.5.090 Rabat
16. Marmesat S, Morales A, Velasco J, Ruiz-Méndez M. V and Dobarganes M. C. *Grasas y Aceites*, (60) 2 (2009) 155-160.
17. Gharby S, Harhar H, Kartah B, Chafchaoui I, Sibawayh Z and Charrouf Z. (2013). *J. Mater. Environ. Sci* (4) 6 (2013) 935-942.
18. Mailer R.J, Conlan D and Ayton, J. (2005). RIRDC publication no. 05/013. A report prepared for the Rural Industries Research and Development Corporation, Canberra.
19. Judde A.. *Oléagineux, Corps Gras, Lipides* (11) 6 (2004) 414-418.
20. Giovacchino. L. Di, Mucciarella. M.R, Costantini. N, Ferrante M.L and Surricchio. G. *J. Am. Oil Chem. Soc.*(79) 4 (2002). 339-344.
21. Tchiégang C, Ngo O. M, Dandjouma A, and Lapse C. *J. Food Eng.* (62) (2004) 69-77.
22. Ruir M.G, Plivillo M.M, Velasco J and Dobarganes C. *Eur. J. Lipid. Sci. Technol.* (110) (2008) 465-471.
23. Anwar F, Chatha S. A. S and Hussain A. I. *Grasas Y Aceites*, (58) 4 (2007) 390-395.
24. Vekiari S. A, Papadopoulou P, Koutsafakis A. *Grasas y Aceites* (53) (2002) 324-329.
25. Vekiari S. A, Papadopoulou P, Kiritsakis A. *Grasas y Aceites* (58) (2007) 237-242.
26. Guil-Guerrero J. L. and Urda-Romacho J. *Grasas y Aceites* (60) 2, (2009). 125-133.
27. Dabbou S, Gharbi I, Dabbou S, Brahmi F, Nakbi A and Hammami M. *African Journal of Biotechnology* (10)74 (2011) 16937-16947.
28. Chimi H, Cillard J and Cillard P. *Sci. Aliments* (14) (1994) 117-24.
29. Chimi H. *Cahiers Agric.* (14) (2005) 467-471.
30. Charrouf Z, Harhar H, Gharby S, Guillaume D. *Oleagineux Crops Gras Lipides*.(15) (2008) 269-271.
31. Campos M. V, Fregapane G, Desamparados and Salvador M. *Eur. J. Lipid. Sci. Technol.* (110) (2008) 969-976.
32. Guillermo H, Crapiste M. I.V. B and Amalia A. C. *J. Am. Oil Chem. Soc.*(76) 12, (1999) 1437-1443.
33. Shiel P.M, Sreerama Y. N and Gopala Krishna A. G.. *J. Am. Oil Chem. Soc.* (81) 12, (2004) 1125-1129.
34. Wolff J. P. (1991). analyse des constituants alimentaire. Lavoisier, Paris (France): Tec et Doc.
35. Grigoriadou K, Vasilakakis M, and Eleftheriou E. P. *Plant Cell, Tissue and Organ Culture.* (71) (2002). 47-54.
36. Grigoriadou D, M. Tsimidou. *Eur. J. Lipid Sci. Techn.* 108 (2006) 61- 69.
37. Charrouf Z, Guillaume D. *Crit Rev Food Sci Nutr.*, 50 (2010) 473-477.
38. Harhar H, Gharby S, Kartah B. E, El Monfalouti H, Charrouf Z and Guillaume D. *Natural Product Communications* (5) 11, (2010) 1799-1802.
39. Gharby S, Harhar H, Bouzoubaa Z, Roudani A, Chafchaoui I, Kartah B and Charrouf Z. *Journal Materials and Environment Science.* 5 (2) (2014) 464-469
40. Mendez A and Falque E. *Food Control* 18(5) (2007). 521-529
41. Khallouki, F. Younos, C. Soulimani, R. Oster, T. Charrouf, Z. Spiegelhalder, B. Bartsch, H. Owen, R. W. *Eur. J. Cancer Prev.* 12 (2003). 67-75
42. Gharby S, Harhar H, El Monfalouti H, Kartah B, Maata N, Guillaume D and Charrouf Z. *Mediterranean Journal of Nutrition and Metabolism*, (44), (2011) 1-8
43. Lecerf, J.-M. *Médecine des maladies Métaboliques* (5) 3 (2011) 257-262.
44. Hilali M, Charrouf Z, El Aziz Souli A, Hachimi L and Guillaume D. *J. Agric. Food Chem.* 53 (2005) 2081-2087.

(2015); <http://www.jmaterenvirosnci.com>