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Stability oxidative from cosmetic and alimentary argan oil Of thermal treatments

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ABSTRACT*: Changes in the physico-chemical parameters of extra virgin argan oils after heating for 120 h at 100 °C with an air flow 10 L/h were investigated. The experimental study was carried out on the two predominant argan oil, edible oil from roasted argan kernel and cosmetic argan oil from unroasted argan kernel. The data obtained showed that oils from roasted argan kernel were more stable than those from unroasted argan kernel. Peroxide values and spectrophotometric data showed higher amounts of oxidation products in oils from unroasted argan kernel than in those from roasted argan kernel. After thermal treatment fatty acid composition was changed more in cosmetic argan oil; particularly the amounts of polyunsaturated fatty acids dropped significantly, while tocopherol of the cosmetic argan oil was completely depleted. The content of tocopherol of the edible argan oil decreased from 674.8mg/kg to 286.5mg/kg.*

Keywords - *Argan oil, Rancimat, roasted argan kernel, oxidative stability, tocopherol, unroasted argan kernel,*

I. INTRODUCTION

The argan tree [*Argania spinosa (L.) Skeels*], of the family Sapotaceae, is endemic in southwestern Morocco where the argan forest was recognised as a biosphere reserve by the UNESCO in 1998. The argan forest is currently covering slightly more than 800,000 ha, but its extension was twice as large at the end of the nineteenth century [1]. The argan fruits are distinguishable in form apiculate, spherical, oval, or fusiform [2]. The argan tree plays a major role in the biodiversity and economy of the argan forest [3]. However, overgrazing, overexploitation, excessive clearance of woodlands, improper tapping, consecutive droughts, and genetic erosion have dramatically endangered the argan tree [4; 5]. Inside a milky pulp covered by a thick peel is a hard shell containing a kernel that affords known edible oil [6]. The oil has high dietetic value, unsaturated fatty acids being the major components. Oleic and linoleic acid make up 80% of the fatty acids, whereas linolenic acid is present only as traces [7; 8].

The unsaponifiable matter contains carotenes (37%), tocopherols (8%), triterpene alcohols (20%), sterols (29%), and xantophyls (5%) [9]. The argan oil is about twice richer in tocopherol than olive oil [7]. (620 mg/kg vs 314 mg/kg) with the following distribution: α-tocopherol (35-46 mg/kg), δ-tocopherol (111- 122 mg/kg), and γ-tocopherol (480-504 mg/kg) [7;10]. The presence of these antioxidant tocopherols and phosphlipides in relatively significant quantities is probably responsible for the good preservation qualities of argan oil [11; 12; 13]. Several additional triterpenoid alcohols have also been isolated from the unsaponifiable matter. These are butyrospermol, tirucallol, β-amyrin, lupeol, 24- methylene cycloartanol, citrostadienol, and cycloeucalenol [14].

Four sterols have been found in argan oil with the following relative distribution: schottenol (48%), spinasterol (44%), stigmasterol (4%), and Δ-7-avenasterol (4%) [11;12;15].

Oxidation is the most important cause of oil and fat deterioration. The primary lipid oxidation products are hydroperoxides, which are very unstable and further react to form secondary products such as hydrocarbons, alcohols, ketones and aldehydes, which can be oxidized to carboxylic acids [15; 16]. The quantitative determination of oxidation is very difficult [17; 18]. Classical methods of studying oxidation reactions refer to only one class of compounds present in the complex mixture formed during the oxidation process. Therefore, they offer only limited information about the oxidation process [19]. The peroxide value is useful in monitoring the initial stage of oxidation, because primary oxidation products are measured [20]. However, the use of peroxide value as a measure of lipid oxidation is limited, because it decreases as oxidation proceeds due to rapid decomposition of hydroperoxides, which are very unstable at elevated temperature [21]. The changes in fats and oils after heating or frying procedures have been the subject of numerous studies and experimental

investigations [22]. All chemical changes of fats and oils at elevated temperatures originate in oxidation, hydrolysis, polymerisation, isomerisation or cyclisation reactions [23; 24]. These reactions affect the sensorial, nutritional and safety properties of oil [25]. All these reactions may be promoted by oxygen, moisture, traces of metal and free radicals [26]. Several factors, such as contact with air, temperature and length of heating, type of vessel, degree of oil unsaturation, and the presence of pro-oxidants or antioxidants, affect the overall performance of oil [21].

The aim of this study was to establish the chemical changes occurring in oil after exposure to high temperature (100°C) and air flow (10L/h) for a period of time equaling or even exceeding the induction period determined with the Rancimat.

II. MATERIALS AND METHODS

2.1 Samples

Argan oils were prepared by the women of the cooperative of Tiout (Taroudant county, Morocco). For each harvest, fruit was dried, peeled, argan kernels were manually collected and processed to deliver argan oil after mechanical pressing. To prepare edible argan oil, kernels were roasted at 110°C for 20 min using a SMIR roaster (Technotour, Agadir, Morocco). Kernel cold-pressing was carried out using a Komet DD 85 G press (IBG Monforts Oekotec GmbH & Co. KG, Mönchengladbach, Germany).

2.2. Thermal treatment

Heat treatment of oil samples was conducted in a Rancimat 730 apparatus (Metrohm, Herisau, Switzerland). The samples were passed through anhydrous sodium sulphate before the experiment. Two vessels were filled with 10 g of oil and the same operating conditions were set as for the determination of stability (100°C, flow of air 10 L/h). After 120 h, when the conduction curve of the most stable sample started to increase rapidly, the experiment was stopped. The samples were transferred to glass vials under a nitrogen atmosphere and kept in the dark at 8 °C prior to analyses. The analyses were performed on oils before heating and after heating.

2.3. Quality parameters

Acidity index, peroxide value (PV), and extinction coefficients (K270) determination were carried out following the analytical methods described in the Regulations EEC/2568/91 of the European Union Commission (1991). Acidity was expressed as the amount of oleic acid as %. PV was expressed as milliequivalents of active oxygen per kilogram of oil (mEq. O2 / kg oil), and extinction coefficient K270 was expressed as the specific extinctions of a 1% (w/v) solution of oil in 2, 2, 4-trimethylpentane in 1 cm cellpath length.

2.4. FA Composition

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 ratewas 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.

Iodine values (IV) were calculated from fatty acid percentages using the formula: IV = (% Palmitoleic ×1.001) + (% Oleic × 0.899) + (% Linoleic ×1.814) + (% Linolenic × 2.737).

2.5. Tocopherol composition

Analysis of tocopherol contents High performance liquid chromatography (HPLC) is 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.

2.6. Oxidative Stability of Argan Oils

The oxidative stability of each sample was determined as the induction period (IP, h) recorded by a 743 Rancimat (Metrohm, Switzerland) apparatus using 3 g of oil sample. Samples placed into Rancimat standard tubes were subjected to the normal operation of the test by heating at 110°C with an air flow of 20 L/h.

2.7. Statistical Analysis.

Values reported in tables and figures are the means ± SE of two to three replications. The significance level was set at P=0.05. Separation of means was performed by Tukey's test at the 0.05 significance level.

III. RESULTS AND DISCUSSION

3.1. Quality Parameters

The values of physical and chemical parameters in oils before and after thermal treatment are given in Tables 1–2. As expected, most of the measured physico-chemical parameters changed during heating. The changes were greater in cosmetic argan oil sample, which had shorter induction periods measured with the Rancimat apparatus than the edible argan oil sample. This is in agreement with other results already reported in the literature [25].

The increase in acidity during heating of fats and oils can be caused by the hydrolysis of triacylglycerols as well as by the formation of secondary oxidation products, namely volatile carboxylic acids, such as formic or acetic acid [26]. In our study, the acidity increase was larger in cosmetic argan oil than in edible argan oil.

The most evident difference between the two oils was the change of peroxide value. After heating, the peroxide values of cosmetic sample was over 62 meq/kg, while in edible argan oil the measured peroxide value after heating was over 14 meq/kg. In a similar study for olive oil, [27] heated oil samples for 100 h at 100 °C in an oven. The peroxide numbers increased to 71.25 méq/kg, which are similar to the results for cosmetic argan oils in our study.

Antioxidants in oil react with radicals, and the peroxide value is expected to increase only when insufficient antioxidants are left to compensate for radical formation. On the other hand, the formation of peroxides is a chain reaction that occurs so rapidly that peroxide formation and radical scavenging start, apparently, simultaneously [28].

K232 and K270 are simple and useful parameters for assessing the state of oxidation of olive oil [29]. K232 is a measure of the primary oxidation products, conjugated dienes, which are formed by a shift in one of the double bonds [20; 29]. K270 is increased by conjugated trienes (the primary oxidation products of linolenic acid) and secondary products of oxidation, such as aldehydes and ketones [20; 26]. Both spectrophotometric parameters increased during heating. The increase of K270 was much greater than the increase of K232, probably because most of the primary oxidation products underwent further oxidation [29].

	Edible argan oil		Cosmetic argan oil	
	Before	After	Before	After
Acidity (%)	0.3±0.1	0.73±0.2	0.21±0.1	1.25±0.2
Peroxide Value (Méq/kg)	1.45±0.2	14.35±2.5	3.2±1	62.75±5.5
E232	1.31±0.01	2.34±0.01	1.28±0.01	2.81±0.01
E270	0.18±0.01	0.34±0.01	0.20±0.01	2.88±0.01
Indice d'iode	104.23	102.14	102.42	87.12

Table 1: Quality parameters and oxidative stability of edible and cosmetic extra virgin argan oils before and after thermal treatment for 120 hours at 100 °C with a flow of air of 10 L/h

3.2. Fatty acid composition

Oil fatty acid (FA) composition is an essential indicator of its nutritional value [30]. The fatty acid composition of argan oils before and after thermal treatment is given in Table 2. There is only a slight difference between the fatty acid compositions of the fresh samples of the two kind of oil. The changes in the fatty acid composition in cosmetic argan oils and edible argan oils are presented in Fig 1 & 2. The percentages of fatty acids below the dashed line decreased during heating, and the percentages of fatty acids above the dashed line increased during heating. The larger the distance of the data point from the dashed line, the greater is the change in content of fatty acid. The changes of fatty acid composition give us an insight into the kinetics of fatty acid oxidation reactions. It is evident from Fig. 2 that the linoleic acid content was reduced the most. After heating, there was a significant increase in the contents of saturated fatty acids, the contents of monounsaturated acids, including the predominating fatty acid oleic acid, remained unaltered for cosmetic oil but we observe significant increase after heating. These observations are in agreement with an ^{1}H nuclear magnetic resonance study, which confirmed the fact that the fatty acid degradation rate increases with the number of double bonds in the molecule [19].

	Edible argan oil		Cosmetic argan oil	
Fatty Acid (%)	**Before**	**After**	**Before**	**After**
Myristic Acid (C14 :0)	**0.1±0.1**	**0.1±0.1**	**0.1±0.1**	**0.2±0.1**
Palmitic Acid (C16 : 0)	**14±0.1**	**14.2±0.1**	**14.2±0.1**	**16.8±0.1**
Palmitoleic Acid (C16: 1)	**0.1±0.1**	**0.1±0.1**	**0.1±0.1**	**0.1±0.1**
Stearic Acid (C18: 0)	**5.1±0.1**	**5.6±0.1**	**5.5±0.1**	**7.2±0.1**
Oleic Acid (C18 : 1)	**44.7±0.1**	**45±0.1**	**44.5±0.1**	**52.4±0.1**
Linoleic Acid (C18 : 2)	**35.1±0.1**	**33.8±0.1**	**34.2±0.1**	**22±0.1**
Linolenic Acid (C18 : 3)	**0.1±0.1**	**0.1±0.1**	**0.1±0.1**	**0.0**
Total saturated fatty acids	**19.6±1.5**	**20.3±1.5**	**20.2±1.5**	**24.7±1.5**
Total unsaturated fatty acids	**80.4±1.5**	**79.4±1.5**	**79.2±1.5**	**74.9±1.5**

Table 2: Fatty acid composition (given as % of total fatty acids) of edible and cosmetic extra virgin argan oils before and after thermal treatment for 120 hours at 100 °C with a flow of air of 10 L/h. Values are given as means of three replicates ± SD.

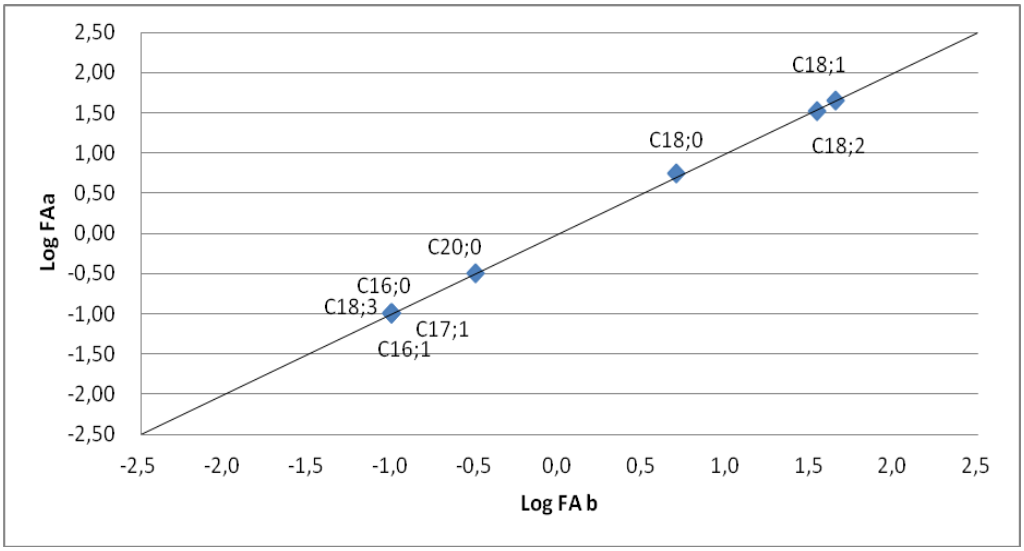

Fig.1. Relationship between the content of individual fatty acids before and after thermal treatment (FAb – % of fatty acid before thermal treatment; FAa – % of fatty acid after 120 h at 100 °C with a flow of air of 10 L/h of edible argan oil.

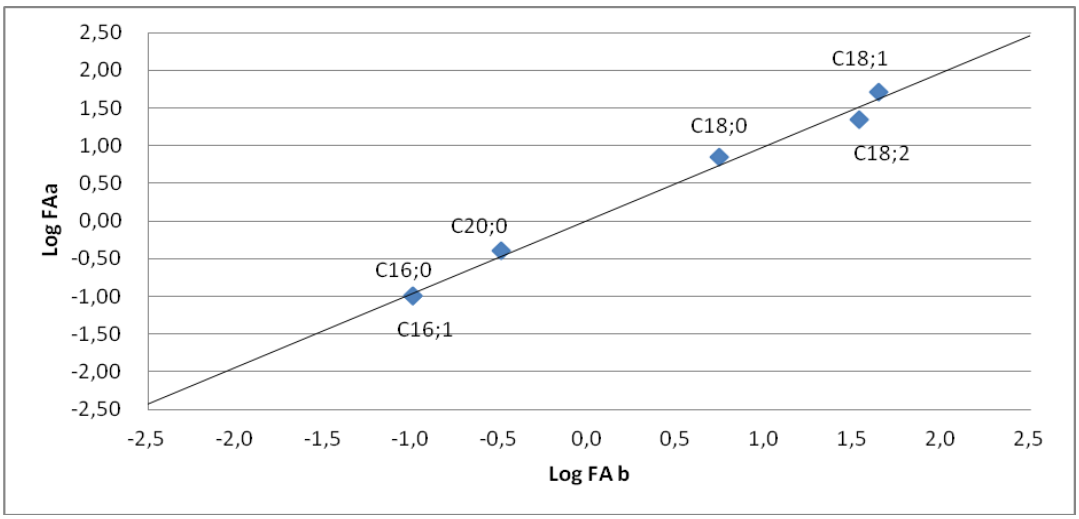

Fig.2. Relationship between the content of individual fatty acids before and after thermal treatment (FAb – % of fatty acid before thermal treatment; FAa – % of fatty acid after 120 h at 100 °C with a flow of air of 10 L/h of cosmetic argan oils.

	Edible argan oil		Cosmetic argan oil	
	Before	**After**	**Before**	**After**
α -Tocopherol (mg /Kg)	**58.6±10**	**27.2±10**	**54.6±10**	**-**
β -Tocopherol (mg /Kg)	**6.07±2**	**-**	**4.1±1.5**	**-**
γ -Tocopherol (mg /Kg)	**529.7±15**	**236.9±10**	**558.5±15**	**-**
δ-Tocopherol (mg /Kg)	**51.3±5**	**13.62±2.5**	**55.9±5**	**-**
Total (mg /Kg)	**674.8±15**	**286.5±10**	**682.8±15**	**-**

Table 2: Tocopherols composition of edible and cosmetic extra virgin argan oils before and after thermal treatment for 120 hours at 100 °C with a flow of air of 10 L/h. Values are given as means of three replicates ± SD.

3.3. Tocopherol

The content of tocopherol was higher in edible argan oils than in cosmetic argan oils, which is in agreement with previous research [30]. After heating tocopherol was depleted in cosmetic argan oils samples [27] also reported that tocopherol was completely depleted during 100 h heating at 100 °C, even when the oxidation was not accelerated by bubbling air through the sample, while the content of tocopherol in edible argan oils decreased from 674.8mg/kg to 286.5mg/kg.

IV. CONCLUSION

The two kind of extra virgin argan oils were evaluated for the first time the influence of heating on physico-chemical parameters. Edible extra virgin argan oil had good oxidative stability than cosmetic oil.

There were more oxidation products and more intense changes in fatty acid composition in cosmetic oil after 120 h of heating to 100 °C. Tocopherol was completely depleted in cosmetic oil samples, while it decreases for the edible oil samples.

The better stability of edible argan oil prepared from roasted seeds could be explained by a better extractability of antioxidative compounds (phospholipids, carotenes, phenolics, and tocopherols) from the kernels and the formation of such compounds such as Maillard reaction products (MRP) during the roasting step.

However, the experimental conditions in the study presented were very severe (a long heating time and air bubbling) and all the parameters were only measured at the beginning and at the end of heating. Hence, further investigations will be necessary in order to draw conclusions about how long oil can be heated before the deterioration increases to such a level that it is no longer acceptable for human consumption.

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