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Evaluation of the Effect of Argan Kernel Roasting on Physicochemical Properties and Oxidative Stability of Cold-Pressed Argan oil

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ABSTRACT: Argan oil extracted from the fruit of *Argania Spinosa L.* has many nutritional and therapeutic properties. This study was conducted to investigate the effect of Argan kernel roasting on physicochemical properties of cold-pressed oil. In this study, Argan kernels were roasted at 110 ° C for 30 minutes, and Argan oil was extracted from unroasted and roasted kernels by cold pressing. The results showed that in the oils extracted from unroasted and roasted Argan kernels, the predominant fatty acid was oleic acid and then linoleic and palmitic acids, respectively. γ-Tocopherol made up more than 80% of the tocopherol compounds in the samples, and spinasterol (78.44% in unroasted and 47.35% in roasted samples) were the predominant sterol compound of Argan oil. The sterol compounds of schottenol (38.69%), chlorophyll (0.43 ppm) and carotenoid contents (15.2 mg/kg) in oil extracted from roasted Argan kernels were higher, and there was no statistically significant difference ($p < 0.05$). According to the results, the oil extracted from roasted Argan kernels could be considered as a product with more desirable organoleptic properties and higher oxidative stability than the oil extracted from unroasted kernels during storage.

Keywords: Argan Oil, Carotenoids, Chlorophyll, Fatty Acid Composition, Tocopherol.

Introduction

Argan oil is extracted from the fruit of *Argania Spinosa L*. This tree grows slowly and belongs to the Sapotaceae family (El Abbassi *et al*., 2014; Harhar *et al*., 2010). It is a thorny and evergreen tree, 10 meters high, 200 years old, and is native only to southwestern Morocco (Morton and Voss, 1987). Pure argan oil has a high content of oleic acid and linoleic acid, high antioxidant capacity, and nutritional and therapeutic properties due to its richness of unsaturated fatty acids (UFA), especially omega-6 fatty acids and bioactive compounds such as polyphenols, tocopherols, and phytosterols (El Abbassi *et al*., 2014; Cabrera-Vique *et al*., 2012).

Argan oil for medicinal and cosmetic applications is extracted from unroasted kernels using a mechanical press (Ökmen and Görmez, 2010). Edible argan oil is extracted from roasted kernels, the color of

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which is browned while stirring constantly over a fire, using a press or by the traditional method of tapping by hand. This step is important in the development of organoleptic properties that are preferred by consumers (Ökmen and Görmez, 2010). Edible argan oil can be stored longer than medicinal organ oil. The quality of edible argan oil is maintained at 25 ° C for up to 2 years, while the shelf life of the medicinal type is 3-4 months (Gharby *et al*., 2011). In industry, oil kernels are heated to increase oil extraction efficiency, reduce kernel moisture, and inactivate lipases and lipoxygenases that can cause fatty acid oxidation (Ökmen and Görmez, 2010). Oxidation can lead to loss of nutritional value and reduced shelf life (Choe and Min, 2006). Besides, roasting oil kernels can increase the stability of vegetable oils by increasing the extraction efficiency of antioxidant compounds (Vaidya and Choe, 2011). The most important antioxidants in vegetable oils are tocopherols, and there is conflicting information about the effect of roasting on their content. Roasting may decrease or increase the tocopherol content depending on the nature and variety of the oily kernels. Since tocopherols are heat sensitive, their final concentration in oil depends on the roasting temperature and time (Jannat *et al*., 2013).

According to Cherki *et al*. (2005), the beneficial effects of argan oil were lowering cholesterol and triglyceride levels and protective effects. In a study by Hilali *et al*. (2005), the effect of the extraction method on the physical and chemical properties and composition of argan oil was investigated and found that cold-pressed oil was of higher quality than that extracted by traditional methods. Gharby *et al*. (2011) reported that mechanically extracted Argan oil that was stored at 25 °C and away from sunlight for two years had the same physicochemical and oxidative stability properties as freshly extracted oil and therefore exposure to light is the main factor in the oxidation of Argan oil.

Argan kernels cultivation has developed in North Africa, especially Morocco, with increasing the public interest in original argan oil and increasing demand for it. Pure argan oil is expensive because its production and extraction are limited to a few specific regions in the world. This means that impure or counterfeit samples may also be on the market. Accordingly, it is important to identify the composition and properties of this oil that has been offered in the domestic market in recent years.

No studies have been conducted on the properties of oil extracted from roasted Argan kernels in Iran. Therefore, this study is conducted to investigate the effect of Argan kernel roasting on physicochemical properties, tocopherol and sterol compounds, and oxidative stability of cold-pressed oil, because it has nutritional and therapeutic values.

Materials and Methods

3 kg of Argan kernels belonging to the southwest of Morocco were first purchased from the local market of Tehran and a visual inspection was performed to separate damaged kernels, contamination and foreign particles. Then 1.5 kg of Argan kernels was then roasted in an oven at 110 °C for 30 minutes. The oil of roasted and unroasted kernels was extracted mechanically and cold-pressed (model BD 45) at room temperature then stored in dark jars in the refrigerator to prevent oxidation. All chemicals and solvents used, including toluene, methanol, glacial acetic acid, hexane, ethanol, petroleum ether, diethyl ether, phenolphthalein, potash, chloroform,

potassium iodide, sodium thiosulfate, starch reagent, isooctane, anisidine reagent, and sodium, were provided by Merck, Germany, and rhodamine 6G was provided by Sigma, USA.

- ***Oil extraction efficiency***

Oil extraction efficiency was calculated using Equation (1):

$$\text{Extraction percentage} = \frac{\text{Oil weight (g)}}{\text{Sample weight (g))}} \times 100 \quad (1)$$

- ***Fatty acid composition***

After sample preparation as fatty acid methyl ester derivatives, a gas chromatography device (GC) was employed to quantify and identify the fatty acids according to Ghavami *et al.*, 2008.

5 drops of the test oil were mixed with 1 ml of toluene and 2 ml of 0.5 N sodium methoxide to methylate the fatty acids, and the contents of the test tube were placed in a 50 ° C water bath for half an hour. 0.1 ml of glacial acetic acid and 5 ml of distilled water were added into the test tube to neutralize the existing alkali, and the contents of the tube were stirred well for a few seconds witha vortex. 5 ml of hexane was then added into the test tube, and the contents of the test tube were stirred again with the vortex for a few seconds. The test tube remained stationary for several minutes. After this period, two phases were formed; the lower phase was the aqueous phase, and the supernatant contained hexane and fatty acid methyl ester. The supernatant was transferred to another test tube using a pipette, and the solution was placed under a hood in a 70 ° C water bath until its volume, which was about 10 ml, was reduced to approximately 1-2 ml. 1 µl of the solution was injected into a gas chromatography device (SHIMADZU company, model 2030 Nexis, made in Japan) equipped with flame ionization detector (FID) and Dikmacap-2330 with a column length of 60 m and a column diameter of 0.25 mm with hydrogen gas at a flow rate of 2 ml/min to determine the type of fatty acids and their content. The initial temperature was set at 60 ° C and remained the same for 2 minutes. It then reached a temperature of 200 ° C with a gradient of 10 ° C/min. In the next step, it reached a temperature of 240 ° C with a gradient of 5 ° C/min and remained the same for 6 minutes until there was enough time for all the fatty acids to leave the column. The output gas chromatography was plotted as a chromatography peak in which each peak represents a fatty acid and the area below each peak represents the percentage of that fatty acid.

- ***Iodine value***

Iodine value is a measure of the degree of unsaturation in oils and fats expressed as the grams of iodine absorbed by 100g of fat. The iodine value was calculated by the percentage of fatty acids obtained by gas chromatography based on Equation (2) (Ghavami *et al*., 2008):

IV = (% C16:1 × 0.950) + (% C18:1 × 0.860) + (% C18:2 × 1.732) + (% C18:3 × 2.616) + (% C20:1 × 0.785) + (C22:1 × 0.723)

C16: 1 palmitoleic acid, C18: 1 oleic acid, C18: 2 linoleic acid, C18: 3 α-linolenic acid, C20: 1 arachidic acid, C22: 1 erusic acid

- ***Oxidative stability***

Oxidative stability was measured using a Rancimat device (Herisau 743 Metrohm, made in Switzerland) according to the AOCS Official Method cd 12b-92 for 2.5 g of oil sample at 110 ° C. The airflow rate was 18-20 liters per hour. Oxidative stability was determined by a rapid change in the slope of the curve and reported hours with a reference to the temperature of the sample characteristics. The end of the stability time was when the specific

conductivity increased rapidly relative to the start time (AOCS, 1992).

- ***Melting point***

The melting point was measured in 3 replications according to the AOCS Official Method Cc 1-25. The melting point was determined using a capillary tube with a length of 75 ml and an inner diameter of about 1 ml. The capillary tube was immersed up to about 10 ml in a sample of homogenized oil. The end of the capillary tube where the sample was placed was closed with a gentle flame, and the area around the tube was cleaned. The capillary tube containing the sample was placed in the refrigerator for 16 hours. It was then glued to the mercury thermometer therefore the lower end of the tube containing the sample was flush with the mercury bubble. Boiled and cooled distilled water was poured into a 600 ml beaker, and the capillary tube and thermometer were placed inside the beaker with a base and clamp so that about 3 cm of the thermometer was immersed in water. A gas burner was placed under the beaker, and a gentle flame was used. The water was stirred frequently using a stirrer. When the fat in the capillary tube became completely transparent, the temperature was recorded and reported as the melting point (AOCS, 1997).

- ***Determination of tocopherol content***

The tocopherol content was determined according to the AOCS standard No. 89-8ce using HPLC (Young Lin Company, Model 9000, South Korea). About 2 g of the sample was weighed into a 25 ml volumetric flask and volumized with hexane. 20 µl of the sample was injected into the HPLC device equipped with Fluorescence type detector model Jasco FP-4025 Excitation wavelength: 290nm, Emission wavelength: 330 nm and RStech Hector-M Silica HPLC Column with dimensions of 0.5 mm × 4.6 mm µm × 150 with hydrogen gas at a flow rate of 0.5 ml/min. The output of gas chromatography was plotted as a chromatography peak in which each peak represents tocopherol and the area below each peak represents the percentage of tocopherol. Equation (3) was used for calculation (AOCS, 1993).

$$\text{α-tocopherol (ppm)} = \frac{C \times a \times D \times 25}{A \times m} \quad (3)$$

Where:

C: The concentration of α-tocopherol in standard solution (g/mLµ)

a: The area below the α-tocopherol curve in the sample

D: The dilution factor

A: The area below the standard α-tocopherol curve

m: The sample weight in grams

- ***Nonsaponifiable matters***

The nonsaponifiable matters were loaded on a TLC plate using a capillary tube, and the plate was placed in a TLC tank containing 4: 1 hexane and diethyl ether solvents. The tank cap was then closed to saturate the interior with solvent vapor. The solvent spread along with the plate and carried upward the nonsaponifiable components. When the solvent level reached about 2-3.5 cm, the TLC plate was removed from the tank and dried in the medium. The stains then appeared. Equation (4) was used for calculation (Ghavami et al., 2008):

$$\text{The percent of nonsaponifiable matters} = \frac{(m_1 - m_0)}{W} \times 100 \quad (4)$$

Where:

m_0 = The weight of the empty tank (g)

m_1 = The weight of the tank and nonsaponifiable compounds in grams

W = The weight of the oil sample (g)

- Determination of sterol content

A gas chromatography device (Shimadzu company, model 2030, made in Japan) was used to determine the sterol content. TLC-separated sterol bands were shaved from the TLC plate and injected into the GC column. After spraying rhodamine 6G solution on the TLC plate and detecting the bands of the nonsaponifiable compounds, the sterol band was shaved off the TLC plate using a laboratory razor and carefully transferred to the test tube. The contents of the test tube were stirred well with a stirrer after adding some anhydrous sodium sulfate for dehydration and diethyl ether and filtered with a funnel and filter paper after 15 minutes. Silica gel and sodium sulfate were then separated from the ether phase. The resulting ether phase contained oil sterol compounds. Sterile bands were injected into the gas chromatograph device (Young Lin, Model 6000, made in South Korea) and column 5 Restek, RS with a column length of 30 m and a column diameter of 0.25 mm with a flow rate of 2 ml/min to determine the sterol type and content. The injector, column, and detector temperatures were set at 260, 280, and 300 ° C, respectively (Ghavami et al., 2008).

- Color evaluation

The color of the oil samples was determined according to the AOCS Official Method Cc 13e-92 and by the Lovibond with 133.4 mm cell using a series of standard red, yellow, and blue glasses with a solid color. These standards vary from white to red, yellow, and dark blue. In this method, the color of light passing through a sample of molten oil or fat with a certain optical path length is compared with the color of light produced from the same source and passing through standard colored glass (AOCS, 1993).

- Chlorophyll content

The absorbance of oil samples was measured by spectrophotometer (Perkin Elmer company, Lambda 25 model, USA) in three wavelengths of 630, 670, and 710 nm according to the AOCS Official Method Cc 13d-55, and chlorophyll content (parts per million or mg/kg of oil) was determined using Equation (5). Quantitative calculations were performed based on the adsorption property of pheophytin a, which is the main chlorophyll pigment of unroasted vegetable oils (AOCS, 2004).

$$\text{Chlorophyll content} = \frac{A_{670} - (A_{630} + A_{710})/2}{0.1086 \times L} \quad (5)$$

Where:

A: Absorption at the mentioned wavelength

L: The spectrophotometer cell thickness (mm)

- Carotenoid content

Carotenoid content (fraction per million or mg/kg of oil) of oil samples was measured by spectrophotometry. 1 g of oil was weighed to the nearest 1 mg and volumized in a 100 ml volumetric tank with cyclohexane. The oil solution was poured into a 1 cm glass cell, and the other glass cell (control) was filled with cyclohexane. The light absorption was then read at 470 nm by spectrophotometer, and the carotenoid content was calculated using Equation (6) (Minguez-Mosquera et al., 1991):

$$\text{Carotenoid (mg/kg)} = \frac{A_{470} \times 10^6}{2000 \times 100 \times d} \quad (6)$$

Where:

A: The absorption rate at 470 nm

2000: Extinction coefficient (E0)

d: The cell thickness (cm)

- ***Oven test***

The oxidative stability of unroasted and roasted oil samples was compared using an oven test. For this purpose, oil samples were placed at 60 ° C for 5 days. The oxidation progression process was performed at intervals of 24 hours by measuring the acid value, peroxide value, and anisidine value according to the AOCS Official Method Ca 5a-40, Cd 53-8, and Cd 18-90, respectively. 3 g of the oil was weighed, and 30 ml of diethyl ether ethanol and 2 ml of phenolphthalein reagent were added to measure the acid value. The compound was titrated with 0.1 N sodium hydroxide until a pale pink color appeared (AOCS, 1996). 1 g of oil was dissolved in 30 ml of a mixture of 96% acetic acid and chloroform to measure peroxide value. 0.5 ml of potassium iodide saturated solution was then added to it and placed in the dark for 1 minute. The released iodine was titrated with 0.01 N sodium thiosulfate, and about 0.5 ml of 0.01 starch solution was added before reaching the endpoint of the titration. The titration continued until the blue color faded (AOCS, 1996). 4 g of the oil sample was weighed 250 ml in a volumetric tank and volumized with isooctane to measure the anisidine value, and the adsorption rate at 350 nm was determined using spectrophotometry and a glass cell (AOCS, 1996).

- ***Statistical analysis***

All tests were performed in three replications, and data were analyzed using SPSS statistical software (version 22) and t-test at a 95% confidence level ($P < 0.05$). Graphs were drawn using Excel software.

Results and Discussion

Oil extraction efficiency was 28% for unroasted Argan kernels and 30% for roasted Argan kernels. The results of the analysis of unroasted and roasted Argan oil extraction efficiencies were in line with the results of the study by Demnati *et al*. (2020) on the optimal conditions for roasting Argan kernels to produce high-quality edible Argan oil.

Protein denaturation, especially at high temperatures, may damage cell membranes and improve oil extraction capacity (Liaotrakoon *et al*., 2016; Perren and Escher, 1997). According to Escher, dehydration during roasting destroys the natural structure of plant cells, increases their porosity, and consequently increases the release of oil and its compounds.

Matthäus *et al*. (2010) conducted a study on the effect of processing on the quality of edible Argan oil. The results showed that the extraction efficiency of Argan oil changed from 16.56% to 32.45%. Changes in the structure of oil-carrying kernels and cells increased with increasing roasting temperature and time.

The results of physical and chemical tests on Argan oil samples are as follows. The fatty acid composition in oils extracted from unroasted and roasted Argan kernels is presented in Table 1.

The oil extracted from unroasted Argan kernels contained 47.38% oleic acid, 31.01% linoleic acid as the predominant unsaturated fatty acid, 13.33% palmitic acid, and 6.29% stearic acid as the predominant saturated fatty acid. There was no statistically significant difference between the samples of Argan oil in terms ofthe content of myristic (C14: 0), palmitoleic (C16: 1), stearic (C18: 0), oleic (C18: 1), linoleic (C18: 2), linolenic (C18: 3), arachidic (C20: 0), eicosanoic (C20: 1) and behenic acids (C22: 0) ($P < 0.05$). The oil extracted from roasted Argan kernels contained 47.22% oleic acid, 30.24% linoleic acid, 13.52% palmitic acid, and 6.32% stearic acid. No significant change in the fatty acid composition occurred by

Table 1. The fatty acid composition in oils extracted from unroasted and roasted Argan kernels

Fatty acids composition (%)	Chemical symbol	Oil extracted from unroasted Argan kernels (%)	Oil extracted from roasted Argan kernels (%)
Myristic acid	C14:0	0.18	0.24
Palmitic acid	C16:0	13.33	13.52
Palmitoleic acid	C16:1	0.11	0.16
Margaric acid	C17:0	0.10	0.10
Heptanoic acid	C17:1	0.03	0.04
Stearic acid	C18:0	6.29	6.32
Oleic acid	C18:1	47.38	47.22
Linoleic acid	C18:2	31.01	30.24
Alpha-linolenic acid	C18:3	0.09	0.15
Arachidic acid	C20:0	0.43	0.52
Eicosanoic acid	C20:1	0.38	0.42
Behenic acid	C22:0	0.17	0.17
Erucic acid	C22:1	0.03	0.08
Lignoceric acid	C24:0	0.08	0.10
Total saturated fatty acids	SFA[a]	20.58	20.97
Total unsaturated fatty acids	MUFA[b]/PUFA[c]	79.03	78.31
Other		0.39	0.72

[a] Saturated Fatty Acids (SFA); [b] Monounsaturated Fatty Acids (MUFA); [c] Polyunsaturated Fatty Acids (PUFA)

roasting. This could be due to the protective effect of Argan kernel tissue, which limits the contact between unsaturated fatty acids and oxygen, which is responsible for initiating oxidative reactions (Chirinos *et al.*, 2016). Moreover, natural antioxidants such as polyphenols and tocopherols can have protective effects against UFA oxidation. The results of the analysis of the fatty acid composition of unroasted and roasted Argan oil were in line with the results of a study by Harhar *et al.* (2011) on the effect of Argan. kernel roasting time on virgin Argan oil composition and its oxidative stability. Vegetable oils are usually evaluated based on their fatty acid composition. The nutritional value of edible oils concerns the content of essential fatty acids (omega-3 and omega-6 family) (Belcadi-Haloui *et al.*, 2018). Oleic acid is the most abundant monounsaturated fatty acid (MUFA) found in nature, which is naturally present in various animal and vegetable fats and oils (Sayers *et al.*, 2019). Evidence from biological studies suggests that higher proportions of MUFAs, especially oleic acid, in the diet are associated with a reduced risk of coronary heart disease and lower blood pressure. An important feature of oleic acid in the body is the reduction of blood LDL levels, and its presence in the oil increases heat resistance (Lopez-Huertas, 2010). The results of the analysis of the fatty acid composition of the oil extracted from unroasted and roasted Argan kernels were in line with the results of previous studies in this field and similar results have been reported concerning the fatty acid composition of the oil extracted from the unroasted and roasted kernels (Harhar *et al.*, 2011; Belcadi-Haloui *et al.*, 2018; Lee *et al.*, 2004; Rueda *et al.*, 2014). Argan oil is most similar first to sesame oil (41.12% oleic acid content) and then to high oleic sunflower oil (53.11% oleic acid content) in terms of fatty acid composition (Rueda *et al.*, 2014).

As can be seen in Figure (1-a), there was no significant statistical difference between the samples in terms of iodine

value (P <0.05). The Codex Standard for Vegetable Oils provides no information on the iodine value of Argan oil (Codex, 2019). The iodine value of Argan oil samples was reported between 91 and 110 by Marocaine (Marocaine, 2003) and 102 by Guillaume and Charrouf (Guillaume and Charrouf, 2011).

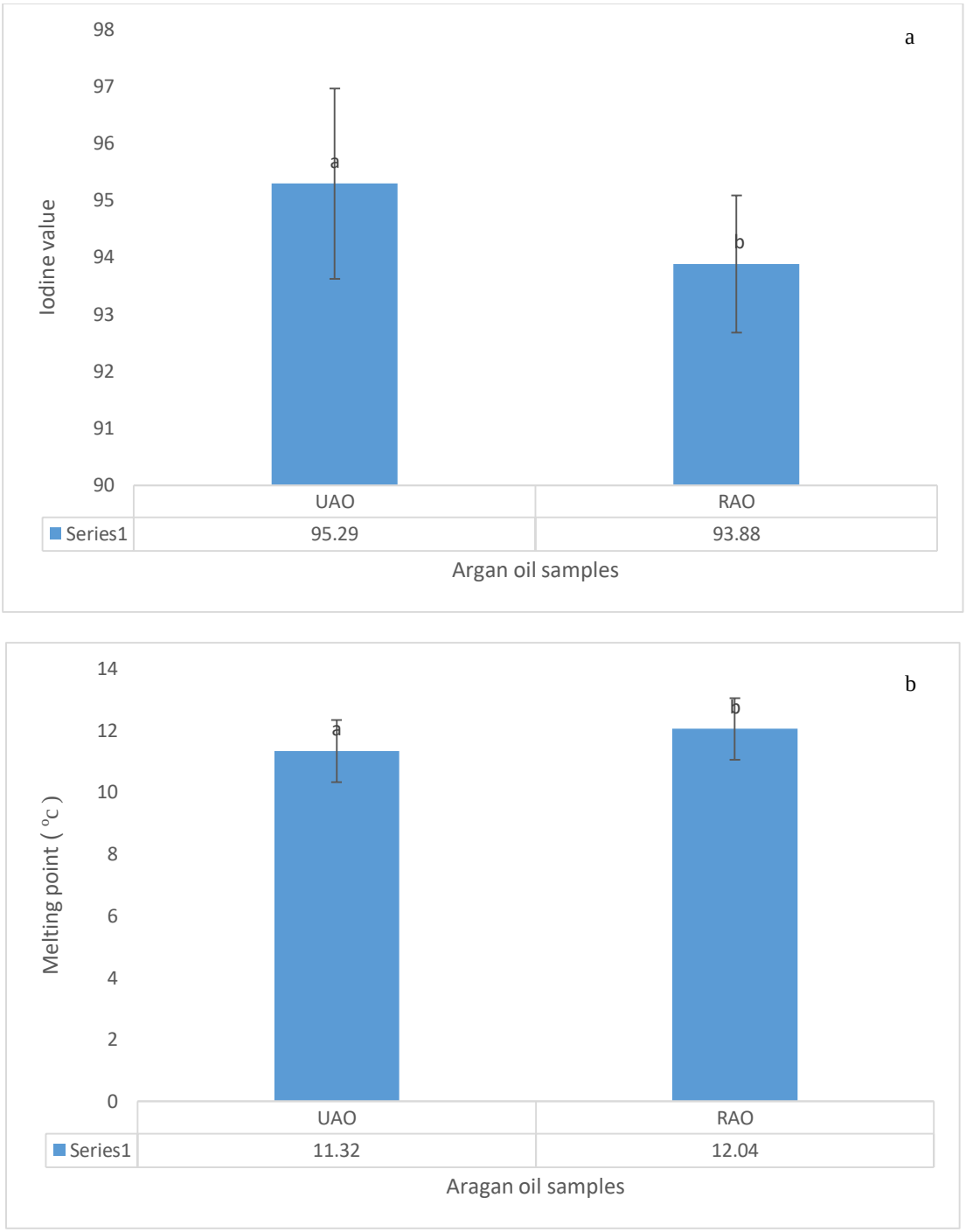

Fig. 1. Comparison of (a) iodine value and (b) melting point of unroasted (UAO) and roasted argan oil (RAO).

The results suggested that the mean stability time for the oil extracted from unroasted and roasted Argan kernels was 22:31 hours and 23:23 hours at 110 ° C, respectively. The degree of unsaturation in the oil extracted from unroasted Argan kernels was higher than the oil extracted from roasted Argan kernels, but the oil extracted from roasted Argan kernels was more resistant to oxidation. The stability of vegetable oils against oxidation depends on the fatty acid composition, especially the degree of unsaturation. In other words, there is an inverse relationship between oxidative stability and unsaturation of the oil. The presence of some natural antioxidants such as tocopherols, carotenoids, and sterols can also increase the oxidation stability of vegetable oils. Among tocopherols, γ-tocopherol is the most effective in increasing oxidative stability. The γ-tocopherol content of RAO was measured less than that of unroasted Argan oil (UAO). It had little effect on the stability of the oils given that the difference was minor. Higher carotenoid concentrations increased the stability of RAO more than UAO. There was no statistically significant difference between the samples in terms of stability time (P <0.05).

Gharby *et al*. (2013) investigated the effect of heat treatments on the oxidative stability of cosmetic and edible Argan oils and found that when the oils were exposed to 10 l/h airflows for 120 hours at 100 ° C, edible Argan oil had higher oxidative stability than cosmetic type. In cosmetic Argan oil, more oxidation products and more severe changes in fatty acid composition were observed after heating to 120 ° C for 120 hours. The higher stability of edible Argan oil prepared from roasted kernels could be attributed to the greater extractability of antioxidant compounds (phospholipids, carotenes, phenolics, and tocopherols) from the kernels and the formation of such compounds as Maillard reaction products during roasting. In oils extracted from roasted kernels, pyrazines are usually produced during the Maillard reaction (Monfalouti *et al*., 2013).

Matthäus *et al*. (2010) studied the effect of processing on the quality of edible Argan oil, arguing that roasting had a positive effect on the stability of the resulting oils.

The melting point of oil samples extracted from unroasted and roasted Argan kernels was measured at 11.32 and 12.04 ° C, respectively, and there was no statistically significant difference between the samples in terms of melting point (P <0.05).

Tocopherols are lipophilic antioxidants. The antioxidant activity of tocopherols in fat systems is as follows: $\gamma > \delta > \alpha > \beta$. Therefore, high concentrations of γ-tocopherol and δ-tocopherol are antioxidant protection factors for the extracted oil (Chirinos *et al*., 2016).

As can be seen in Table 2 and Figure 2, the total tocopherol content of oil extracted from unroasted Argan kernels (650.37 ppm) was higher than oil extracted from roasted Argan kernels (596.99 ppm). The difference was statistically significant (P<0.05). The studied Argan oil samples contained α-tocopherol, γ-tocopherol, and δ-tocopherol. γ-tocopherol accounted for 82.61% of the tocopherols in oil extracted from unroasted Argan kernels and 80.53% of the tocopherols in oil extracted from roasted Argan kernels. Decreased tocopherol content after roasting could be the result of oxidation and polymerization during the process. Thermal decomposition occurred in these compounds due to their sensitivity to heat (Liaotrakoon *et al*., 2016).

The α-tocopherol content in oil extracted from unroasted Argan. kernels was 61.46%. It increased to 66.30% in oil extracted from roasted Argan kernels. The increase in tocopherol content in roasted kernels could be attributed to the thermal decomposition of the cell structure, which led to better extraction conditions and greater availability of tocopherols. In previous studies, similar results have been reported on the tocopherol content of Argan oil (Chirinos *et al.*, 2016).

According to Matthäus *et al.* (2010), the content of α-tocopherol and γ-tocopherol in Argan oil extracted from roasted kernels decreased during 14 days of storage, but the δ-tocopherol content increased. Harhar *et al.* (2011) investigated the effect of Argan kernel roasting time on virgin Argan oil composition and oxidative stability and found that long roasting time created color and increased phosphorus content while the fatty acid composition and tocopherol content changed slightly. Considering the variety of results in previous studies, it can be argued that roasting can affect the structure and content of tocopherol in different ways depending on the type of kernels, cell constituents, and the intensity of the temperature used (Chirinos *et al.*, 2016).

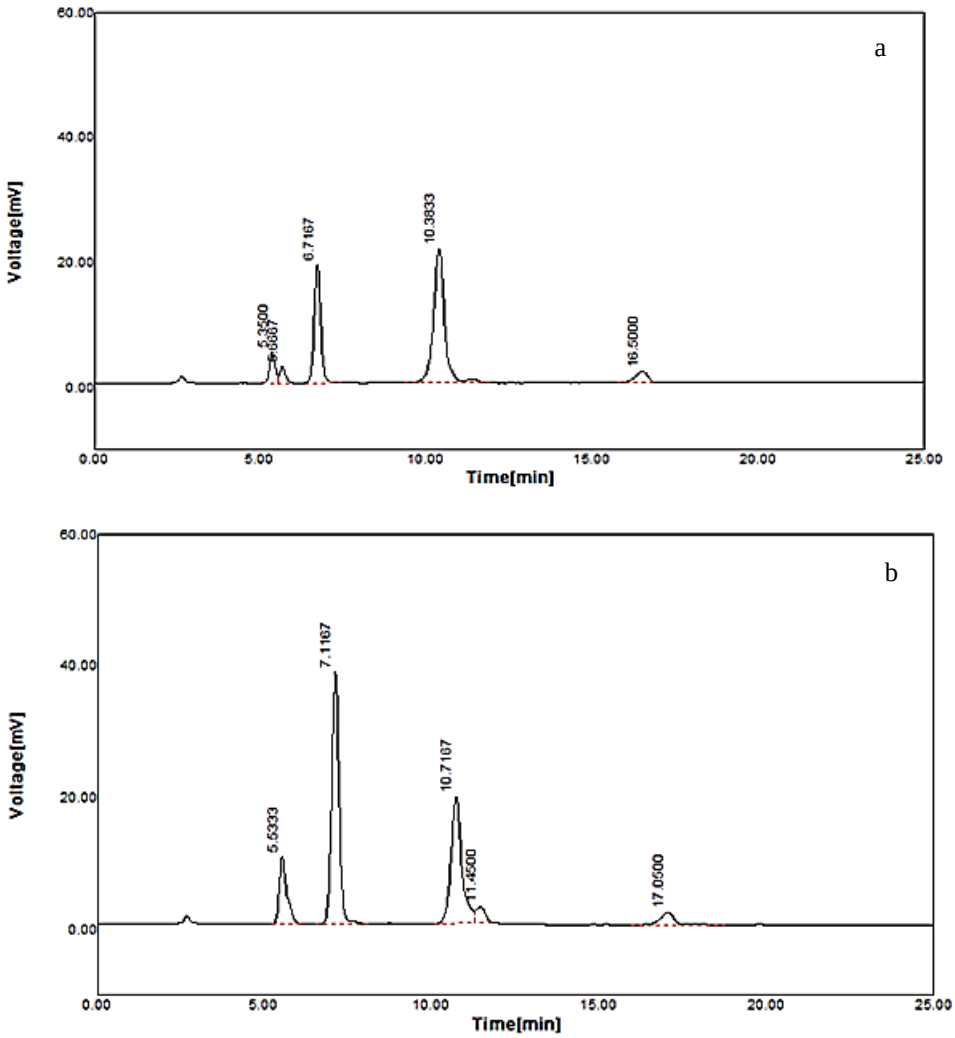

Fig. 2. HPLC chromatogram of tocopherols in oil extracted from unroasted Argan kernels (a) and (b) roasted Argan kernels.

Table 2. The tocopherol compounds of oils extracted from unroasted and roasted Argan kernels

Tocopherol	Oil extracted from unroasted Argan kernels (mg/Kg)	Oil extracted from roasted Argan kernels (mg/Kg)
α-tocopherol	61.46	66.30
γ-tocopherol	537.26	480.77
δ-tocopherol	51.65	49.92
Total tocopherol content	650.37	596.99

In the studied Argan oil samples, the identified sterol compounds included campesterol, stigmasta-22,8-dien-3-ol, spinasterol, shottenol, and stigmasta-24,7-dien-3-ol (Figure 3 and Table 3). The predominant sterol compound was spinasterol, the content of which in unroasted and roasted Argan oil was 78.44 and 47.35%, respectively. Shottenol content in oil extracted from unroasted Argan kernels was 12.73%. This value increased to 38.69% in oil extracted from roasted Argan kernels. There was a statistically significant difference between the content of all sterol compounds in Argan oil samples except campesterol ($P < 0.05$). Changes in humidity during sample roasting have been reported to facilitate the extraction of phytosterols (Chirinos *et al*., 2016).

Hilali *et al*. (2007) conducted a study to detect fraud in Argan oil using the determination of campesterol content by gas chromatography (Hilali *et al*., 2007). Determination of campesterol content in Argan oil can be used as the main method of analysis to evaluate the purity of Argan oil up to 98%. In a study by Charrouf and Guillaume (Charrouf and Guillaume, 1999), the presence of cyclooctanol and citrostadinol in Argan oil was reported. These methyl sterols do not appear to play a specific biological role and maybe mediators of biosynthesis in the evolution of triterpene alcohols and sterols (Charrouf and Guillaume, 1999).

The results showed that the content of nonsaponifiable compounds was 0.19% in the oil extracted from unroasted Argan kernels and 0.27% in the oil extracted from roasted Argan kernels (Figure 4). Oil extracted from roasted Argan kernels has more nonsaponifiable compounds than oil extracted from unroasted Argan kernels due to its higher total carotenoid content. However, there was no statistically significant difference between the samples in terms of the content of nonsaponifiable compounds ($P <0.05$). Therefore, it could be concluded that roasting Argan kernels did not have a significant effect on the content of nonsaponifiable compounds. Roasting alters cell structure and facilitates the extraction of antioxidants. The results of previous studies indicate that roasted kernels contain more polyphenols and tocopherols (Wijesundera *et al*., 2008). In a study by Hilali *et al*. (2007), the effect of origin and extraction method on the physical and chemical properties and composition of argan oil was investigated and it was found that extraction technology affects the content of nonsaponifiable compounds in argan oil. The results showed that samples with less nonsaponifiable compounds (between 0.34 and 0.56%) were prepared by extraction through hexane.

The amount of yellow and red colors in oils extracted from unroasted Argan kernels was 9.97 and 3.06 units of Lovibond, respectively, which increased from 20.82 and 4.43 units of Lovibond in oils extracted from roasted Argan kernels, respectively. There was a statistically significant difference ($P <0.05$) between

argan oil samples in terms of yellow color, while this was not the case in terms of red color ($P < 0.05$). There was a significant difference between the color of argan oil extracted from roasted Argan kernels and oil extracted from unroasted Argan kernels. Roasting made the oil color browner. The results were consistent with the results of previous research. (RAO) was brownish yellow, and (UAO) was golden yellow (Figure 5).

Table 3. The Sterol compounds of oils extracted from unroasted and roasted Argan kernels

Sterol	Oil extracted from unroasted Argan kernels (%)	Oil extracted from roasted Argan kernels (%)
Cholesterol	-	0.57
Campesterol	0.32	0.35
stigmasta-22,8-dien-3-ol	6.7	7.87
spinasterol	78.44	47.35
Shottenol	12.73	38.69
stigmasta-24,7-dien-3-ol	1.81	4.79
Other	-	0.38

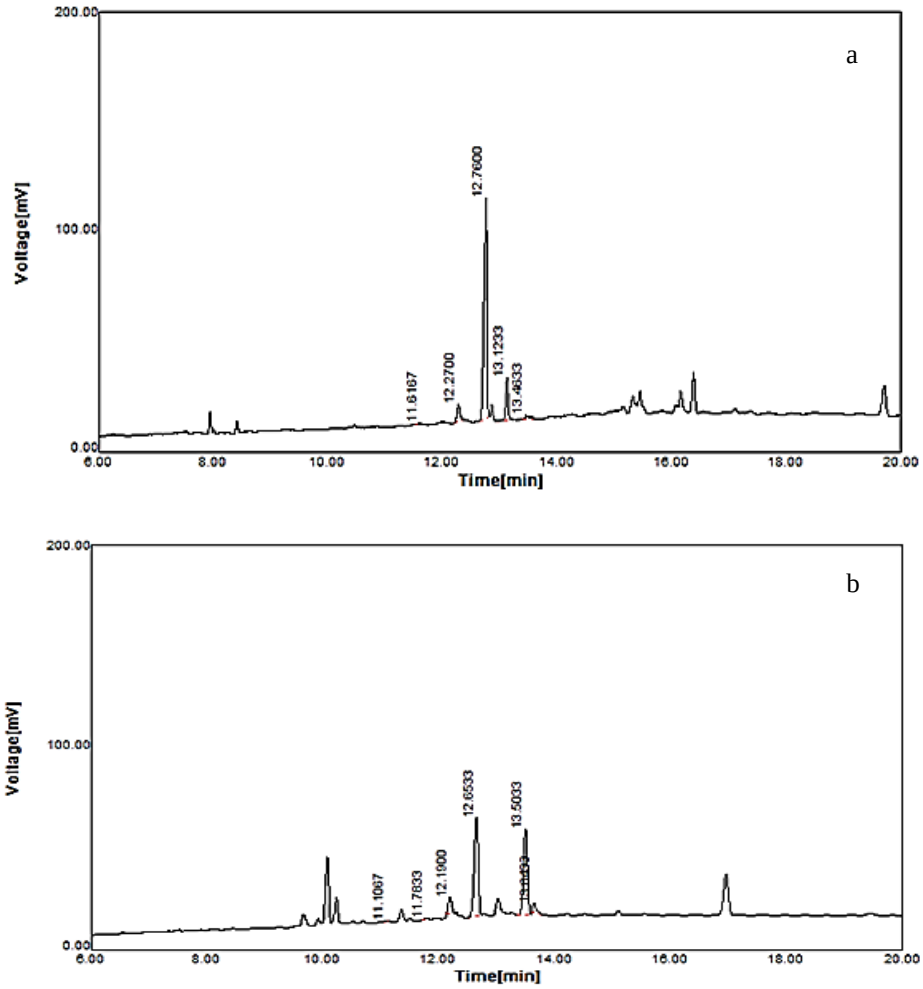

Fig. 3. GC chromatogram of sterol compounds oil extracted from unroasted Argan kernels (a) and (b) roasted Argan kernels.

According to Gharby *et al*. (2011), when Argan kernels were roasted at 110 ° C, there were no significant immediate changes in the extracted oils, indicating that large amounts of secondary oxidation products were not formed.

In a study by Belcadi-Haloui *et al*. (2018), it was found that the browning index increased significantly during the roasting of Argan kernels at temperatures above 100 ° C. Increasing the roasting time or temperature results in the formation of brown compounds in edible oils as a result of non-enzymatic reactions such as Maillard, caramelization, and phospholipid degradation. These brown compounds have protective properties and are partly responsible for the greater stability of edible argan oil compared to the cosmetic type (Matthäus *et al*., 2010).

The chlorophyll content of oil extracted from unroasted and roasted Argan kernels was 0.32, and 0.43 mg/kg, respectively, in terms of pheophytin a (Figure 6). There was a statistically significant difference between the studied oil samples in terms of chlorophyll content ($P < 0.05$).

Addou *et al*. (2016) investigated the use of fluorescence spectroscopy and chemometric instruments to detect adulteration in argan oil with olive oil, suggesting that the presence of impurities in virgin argan oil can be detected by detecting the chlorophyll fluorescence signal that is present in olive oil and not completely present in argan oil (Addou *et al*., 2016).

The total carotenoid content was 12 mg/kg for oil extracted from unroasted Argan kernels and 15.2 mg/kg for oil extracted from roasted Argan kernels (Figure 7). There was a statistically significant difference between the studied oil samples in terms of carotenoid content ($P < 0.05$).

According to Charrouf and Guillaume (1999), the carotenoids in (UAO) are xanthophylls and account for 42% of the nonsaponifiable compounds. Palozza and Krinsky (1992) argued that the content of β-carotene and phosphorus/phospholipids in unroasted argan oil was significantly lower than in (RAO). β-carotene is a highly lipophilic molecule known as a compound that has antioxidant properties in cooperation with α-tocopherol (Palozza and Krinsky, 1992).

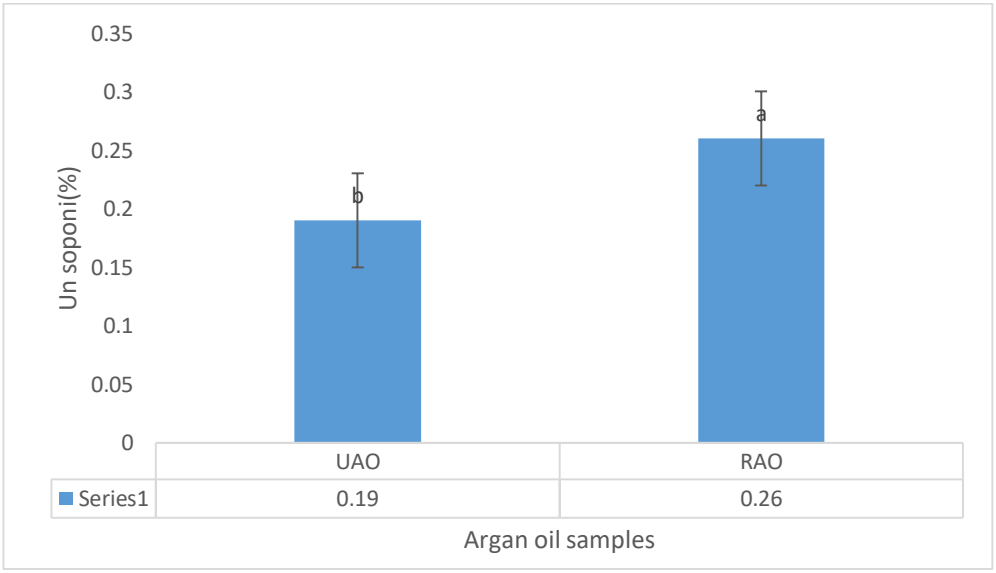

Fig. 4. Comparison of the content unsaponifiable compounds in unroasted and roasted Argan oil.

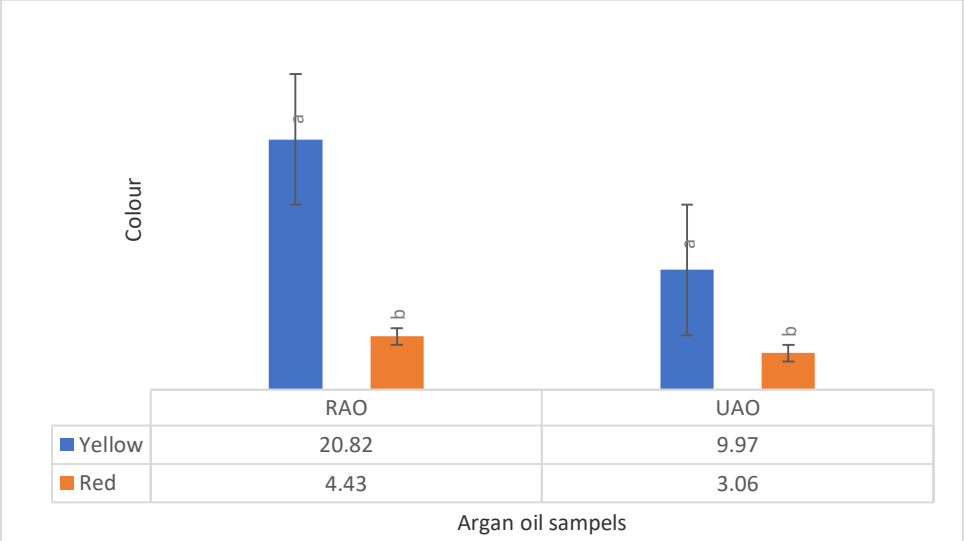

Fig. 5. Comparison of the color in unroasted and roasted Argan oil.

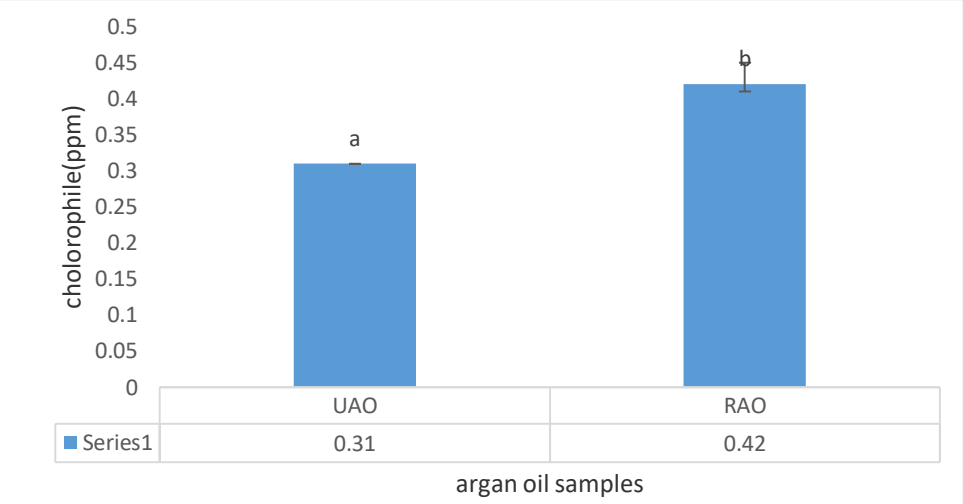

Fig. 6. Comparison of the content of chlorophyll in unroasted and roasted Argan oil.

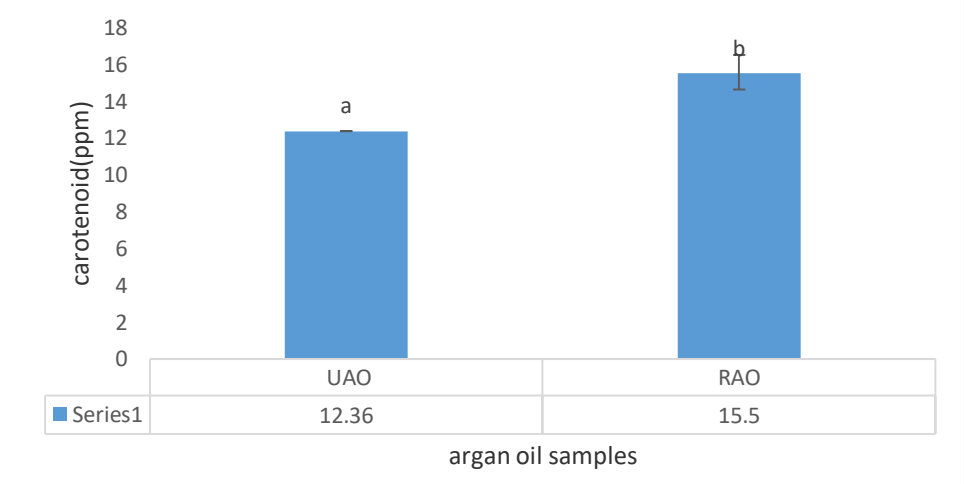

Fig. 7. Comparison of the content of carotenoids in unroasted and roasted Argan oil

Comparison of the acid value of oils extracted from unroasted and roasted Argan kernels during 5 days of ovening at 60 ° C (Figure 8) showed that there was a statistically significant difference (P <0.05) between the oil samples extracted from unroasted and roasted Argan kernels on the first and fourth days, but this was not the case on the second, third, and fifth days (P <0.05). The acid value in oils extracted from unroasted Argan kernels was 0.87 mgKOH/g on the first day and reached 1.26 mgKOH/g on the fifth day. The acid value in oils extracted from roasted Argan kernels was 0.17 mgKOH/g on the first day and reached 1.18 mgKOH/g on the fifth day. In other words, the acid value in both samples increased during 5 days of ovening affected by temperature. However, the trend of changes in the acid value of the two samples showed different patterns over time. This upward trend was slower in samples extracted from roasted kernels. The highest acid value was observed on the fifth day of ovening, and the acid value of the oil extracted from unroasted Argan kernels was higher than the oil extracted from roasted kernels. These results were in line with the results of previous studies (Belcadi-Haloui *et al*., 2018; Gharby *et al*., 2013). The acid value can be increased as a result of the release of fatty acids following the hydrolysis of triglycerides, which are the major constituents of vegetable oils. This can cause oxidative decomposition reactions of the oil due to the peroxidative function of free fatty acids (Scrimgeour, 2005).

Evaluation of the peroxide value of oil samples extracted from unroasted and roasted. Argan kernels during 5 days of ovening at 60 ° C (Figure 9) showed that there was a statistically significant difference between the samples on the second, third, fourth, and fifth days (P <0.05), but this was not the case on the first day (P <0.05). The peroxide value of oil samples increased gradually from the beginning of oven test and reached a maximum on the fifth day. The peroxide value was 0.8 meq/Kg on the first day. It increased significantly over time and reached 1.9 meq/Kg in oils extracted from unroasted kernels and 1.46 meq/kg in oil extracted from roasted kernels on the fifth day. The trend of increasing peroxide value in oil extracted from roasted kernels was slower than oil extracted from unroasted kernels. The peroxide value is a parameter that is commonly used to evaluate the initial oxidation products during processing and storage and indicates the content of hydroperoxides formed by the oxidation of UFAs. Therefore, it is a very important indicator in determining spoilage in fatty products. According to the Codex Standard for Vegetable Oils, the maximum acceptable peroxide value is 10 meq/Kg for refined oils and 15 meq/Kg for cold-pressed oils (Codex, 2019). This value was within the allowable range for 5 days during the review period.

Previous studies on other oil kernels have shown an increase in the oil peroxide value with increasing roasting temperature (Rękas *et al*., 2015). In a study by Belcadi-Haloui *et al*. (2018), it was found that roasting at high temperatures leads to oil oxidation, which can affect the stability of the oil during storage.

Gharby *et al*. (2013) investigated the effect of heat treatments on the oxidative stability of cosmetic and edible argan oils. The results indicated that when the oils were exposed to 10 l/h airflows for 120 hours at 100 ° C, edible argan oil had higher oxidative stability than cosmetic type.

Measurement of anisidine value is a method to determine the content of

secondary oxidation products such as aldehydes and ketones of UFAs in oils and fats during oxidation that can affect the taste. The anisidine value was measured for argan oil samples at 5-day intervals.

As can be seen in Figure 10, the anisidine value of oils extracted from unroasted and roasted kernels on the first day was 0.95 and 0.66, respectively. This value increased gradually from the beginning of oveninig and reached its highest values, 2.23 and 1.68, respectively, on the fifth day due to the increase in secondary oxidation products (Houhoula and Oreopoulou, 2004). Comparison of anisidine value at different times showed that there was a statistically significant difference ($P < 0.05$) between the samples in the first, second, third, fourth, and fifth days. The anisidine value in oils extracted from unroasted Argan kernels was higher than in oils extracted from roasted Argan kernels. The lower anisidine value indicated lower secondary oxidation. The trend of increasing the anisidine value in oils extracted from roasted kernels was slower than those extracted from unroasted kernels, indicating higher oxidative stability of RAO. In other words, in oils extracted from unroasted kernels, the oxidation process was faster and less stable than oils extracted from roasted kernels due to higher unsaturation and the presence of more free fatty acids in oil extracted from unroasted kernels. The results were consistent with the results of the study by Matthäus *et al*. (2010) on the effect of processing on the quality of edible argan oil. According to this study, the anisidine value of oil extracted from unroasted kernels increases significantly faster than oil extracted from roasted kernels.

Conclusion

The studied argan oils were evaluated nutritionally according to the fatty acid composition, degree of unsaturation, oleic acid, γ-tocopherol, and sterol contents. According to the results, roasting increases the extractability of bioactive compounds of roasted Argan kernels during oil extraction by cold pressing. The results also indicated that the oil extracted from roasted Argan kernels could be considered as a product with more desirable organoleptic properties and higher oxidative stability than the oil extracted from unroasted kernels, especially during storage.

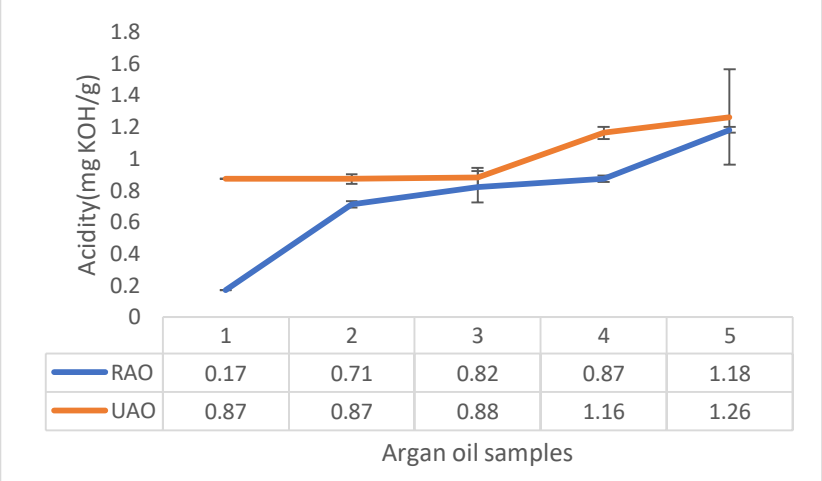

Fig. 8. Comparison of acid value in unroasted and roasted Argan oil.

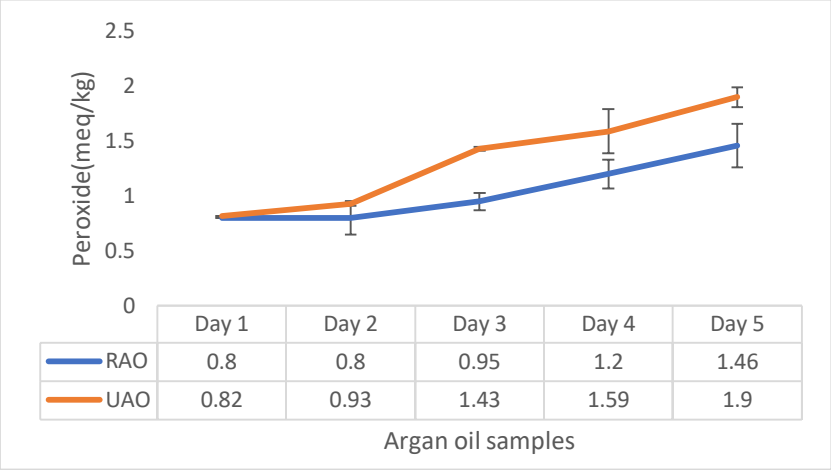

Fig. 9. Comparison of peroxide value in unroasted and roasted Argan oil

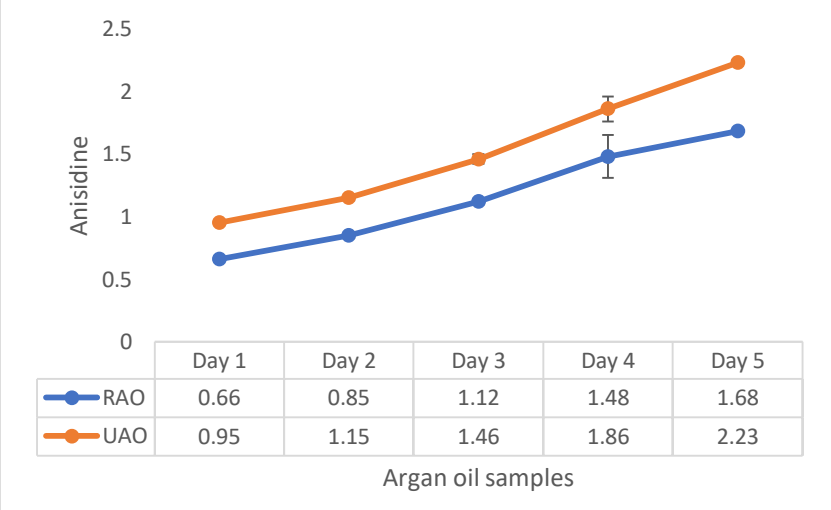

Fig. 10. Comparison of anisidine value in unroasted and roasted Argan oil

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