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Influence of Origin and Extraction Method on Argan Oil Physico-Chemical Characteristics and Composition

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Twenty one samples of argan oil of different geographical origin (Tidzi, Tamanar, Benaiznassen, Ait mzal, Ait Baha, Ighrem, Aoulouz) and/or prepared following a different process (traditional, mechanical, or industrial) were collected and their physico-chemical properties analyzed. Sample acidity was found between 0.14 and 1.40%, unsaponifiable matter between 0.34 and 0.79%, saponification value between 180.0 and 199.6, highest peroxide index was 5.72 meq/kg, refractive index (20 °C) between 1.4644 and 1.4705, and UV absorption at 270 nm between 0.228 and 0.605. This study, carried out on randomly selected samples, clearly demonstrates that press extraction does not alter either the chemical composition of argan oil or its physico-chemical characteristics. It also demonstrates that press extraction respects the critical factors reported for traditionally prepared oils and necessary to obtain a beneficial effect on human health (a specific fatty acid balance and high tocopherol and sterol levels). In addition, this study should be useful for the establishement of a national quality standard.

KEYWORDS: Argan oil; *Argania spinosa*; argan tree; oil chemical analysis; quality; fatty acids; Morocco

INTRODUCTION

During the last 15 years, the status of argan oil has been metamorphosed from a mainly exotic tourist curiosity into a prized oil of high dietetic value. This change is principally consecutive to the ascertainment of the monounsaturated fatty acids (MUFAs) and diunsaturated fatty acids (DUFAs) high level (oleic and linoleic acids) in argan oil (*1*). Indeed, the beneficial effect, on human serum lipids, of MUFAs and DUFAs is now undiscussed and, consequently, oils rich in unsaturated fatty acids are largely recommended as substitutes of saturated fatty acid-containing fats in industrialized countries. In addition, argan oil is also rich in phytosterol whose diet incorporation is supposed to offer cancer protection (*2*, *3*).

Argan oil is prepared following a multistep process from the fruits of the argan tree (*Argania spinosa* (L.) Skeels; syn. *A. sideroxylon* Roem & Schult.; sapotaceae) (*1*). In the parts of Morocco where it grows endemically, this tree participates in the biodiversity preservation (*4*) and has an important local economic impact (*5*). Although multiple industrial uses of argan tree secondary metabolites (*1*, *6*) are currently being actively investigated (*4*, *6*, *7*) argan oil, which is now widely traded on the dietetic, nutraceutic, and lucrative cosmetology markets, is, from an economical standpoint, the predominant output of the argan tree.

Traditionally, dietary argan oil is extracted by women with a millstone. However, traditional extraction is frequently achieved in unsatisfactory sanitary conditions. Consequently, an attempt was recently made to increase argan oil value by improving its extraction technology. For this, several cooperatives aimed at producing and commercializing quality certified argan oil have been initiated in South-West Morocco (*4*). The quality of argan oil produced in these cooperatives has now boosted its national and international demand, making necessary the determination of a national quality standard.

The aim of this present work is to study the influence of the geographical origin and extraction process on the argan oil quality in order to select some parameters that could be possibly used to establish a unarguable national standard. This latter should account for geographic specificities but allow the discarding of oils of improper quality. For this purpose, the most important physico-chemical properties that are used as quality criteria to certify olive oil quality were determined on 21 samples of argan oil randomly selected from argan oil producers (cooperatives, traditional, industrial).

MATERIAL AND METHODS

Sample Collection. Argan oil samples from the cooperatives of Tamanar, Tidzi (Essaouira county, Morocco), and Ait Baha (Chtouka-

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Ait Baha county, Morocco) were prepared by press extraction using similar instruments in each cooperarive.

From the Tidzi area, argan fruits were harvested during the summer of 2001 and argan seeds were prepared in February 2002. Sample 1was prepared by press extraction of roasted argan seeds and sample 2 by press extraction of nonroasted argan seeds.

From the Tamanar area, argan fruits were harvested during the summer of 2001 and argan seeds were prepared in February 2002. Two batches of argan seeds were prepared. Batch 1 was made of argan seeds kept in bags of 20 kg for 4 to 7 weeks prior to the oil extraction as generally performed in the cooperatives. Oil of argan seeds constituting batch 2 was extracted less than 24 h after the nut harvest.

From batch 1, samples 3.1 and 4.1 were prepared from roasted and nonroasted nuts, respectively and sample 5 was prepared using the traditional millstone method; samples 3.2 and 4.2 were prepared from roasted and nonroasted nuts, respectively, coming from batch 2. From batch 1, samples 6 and 7 were prepared by hexanes extraction of roasted and nonroasted argan nuts, respectively. Samples 8 and 9 were prepared using Tamanar technology from nonroasted and roasted, respectively, fresh argan seeds obtained from goat dejections (traditional method) and collected in the Tamanar area. Sample 10 was purchased from local dwellers living in the Tamanar area and collecting goat digested argan nuts. A six months old sample of 4.1 constituted sample 11.

Samples 12 and 13 were purchased on a local market of Casablanca (Morocco) as roasted and nonroasted argan oil, respectively.

Sample 14 was prepared in the ccoperative of Tidzi by press extraction of roasted argan seeds collected in the Benaiznassen area (northern Morocco).

Samples 15−17 were prepared by hexanes extraction of nonroasted argan nuts collected in the Ait mzal, Ighrem, and Aoulouz area, respectively.

Samples 18−19 were prepared from nonroasted argan nuts collected in the Ait Baha area, by press extraction and hexane extraction, respectively.

Sample Preparation. A detailled description of argan oil preparation acccording to the traditional process has already been reported (*6*). Argan seeds used to prepare press-extracted argan oil were obtained following roughly the first steps described for the traditionally prepared oil (argan seeds were mechanically freed of their pulp). Roasted seeds were prepared by heating the fresh nuts at 100 °C for 2 h in a homemade gas roaster. Argan oil was then directly obtained using a vegetable oil expeller (Komet DD85G-IBG Montforts Oekotec GmbH). Argan nuts obtained from goat dejections were obtained by feeding goats with fresh argan fruits. Then, naturally depulped argan nuts were collected and processed within 24 h. Hexanes-extracted argan oil samples were obtained by extracting for 8 h ground argan seeds in a Soxhlet apparatus (1l of hexane for 200 g of seeds).

Analytical Methods. Acidity and peroxide value, UV light absorption (K_{270}), (trans)-fatty acids, sterol, content of oil residue, and determination of the percentage of saturated fatty acid at the triglyceride 2-position were carried out by adapting the analytical methods described in Regulations EEC/2568/91 of the European Union Commission for olive oil (*8*). Refractive index, saponification values, and unsaponifiable matters were carried out according to reported AOCS methods (*9*).

The acidity value was determined by titration of a solution of oil in ethanol/ether 1:1 with ethanolic KOH and is expressed as percent of oleic acid.

The peroxide value was determined by iodine titration with a sodium thiosulfate solution of a solution of oil in dichloromethane/acetic acid 2:1 that had been left in darkness in the presence of potassium iodide.

K_{270} extinction coefficients were measured in cyclohexane using a Perkin-Elmer Lambda 2 UV spectrophotometer.

Triglyceride composition was determined by HPLC analysis using a C18 analytical column (250 × 4.6 mm) packed with silica according to regulation EEC/2568/91. A mobile phase of dry acetonitrile/acetone (50:50) was used at the rate of 0.5 mL/min. Detection was performed using a HP10 47A refrectometer.

For the fatty acid and *trans*-fatty acids composition determination, the methyl esters were analyzed on an HP PEG column (30 m × 0.32 mm i.d.) using nitrogen as a carrior gas (Regulation EEC/2568/91). For the fatty acid determination, initial oven temperature was set at 140 °C; ramp rate 10 °C/mn; final temperature 200 °C; injector temperature 240 °C; detector temperature 260 °C. For the *trans*-fatty acid determination, the initial oven temperature was set at 140 °C; ramp rate 2 °C/mn; final temperature 210 °C; injector temperature 240 °C; detector temperature 260 °C.

Tocopherols (α, *β*, *γ*, and *δ*) analysis was carried out by HPLC following the AOCS, CE 8-89 method (1990 updated 1992). A Shimadzu fluorescence detector was used. The sample was injected into an analytical column (250 × 4 mm) packed with silica. A mobile phase of dry *iso*-octane/2-propanol (99:1) was used at the rate of 1.2 mL/min. Detection was performed at an excitation wavelength of 290 nm and an emission wavelength of 330 nm. Standards of α-, *β*-, *γ* -, and *δ*-tocopherols were used for identifiation and calibration purpose.

Sterol composition was evaluated by GLC−FID/capillary column following the NFT 60-254 method. Briefly, sterols purified from unsaponifiable matters by HPLC were transformed into their trimethylsilyl ethers counterparts using pyridine, hexamethyldisilazane, and trimethylchlorosilane 9:3:1 (vol). The sterol profile was analyzed using a gas-phase chromatograph fitted with a chroma pack CP SIL 8 C B column (30 m × 0.32 mm i.d.) and a flame ionization detector. The temperature of the injector and detector were both 300 °C. The column temperature was 200 °C and programmed to increase at the rate of 10 °C/mn to 270 °C. The carrier gas was dry oxygen-free nitrogen, and the internal pressure was 8.6 bar. Sterol quantification was achieved by use of an internal 0.2% chloroformic solution of α-cholestanol.

Benzo[*a*]pyrene concentration was determined following the AOCS, CD 21-29 method (1992 updated 1993). Quantitative analysis was performed by HPLC using a C18 column (250 × 4.6 mm i.d.) and a fluorometry detector (280−462 nm). Elution was performed using an isochratic 1:1 water/acetonitrile mixture and a constant flow rate of 1.2 mL/mn.

Statistical Analysis. The reported results are the average value of at least five independent measurements. The results are shown as tables or plots of mean values. Standard deviations are indicated as absolute value or as a percentage of the mean value. The differences between the plots in each parameter on different oil samples were analyzed using the analysis of variance, after the homogeneity of variance had been tested.

RESULTS AND DISCUSSION

To fully cover the variation induced by the argan grove diversity and the different methods of extraction, we decided to collect 21 samples of oil. Among those, 13 oil samples prepared from different batches of argan nuts coming from the two major argan groves where the cooperatives of Tamanar and Tidzi are implanted were analyzed. Argan nuts coming from these two argan groves were used as reference nuts to prepare traditional, press extracted (regular cooperative oil), and hexanes−extracted oil. The results of the analyses were compared to those obtained from (1) two argan oil samples purchased on the local market, (2) one argan oil sample collected in a remote argan grove of Benaiznassen (northern Morocco) (3) two argan oil samples collected in the argan grove of Ait Baha, and (4) three argan oil samples prepared for industrial purpose by hexanes−extraction of nonroasted seeds prepared from nuts collected in argan groves other than Tamanar and Tidzi. Results are principally analyzed in comparison to (1) traditionally prepared argan oil, to evaluate the quality improvements brought by the press extraction method used in the cooperatives, and (2) virgin olive oil for which quality factors acceptable on the European community market are well-determined and broad enough to accommodate variations induced by the different geography of the production countries (including Morocco). Such comparison could be highly useful in view of identifying, in the future, inter-oil aldulteration criteria and of possibly applying to argan oil readily available analysis techniques.

Figure 1 shows the results of the acidity value, unsaponifiable matters, saponification value, and specific extinction at 270 mn

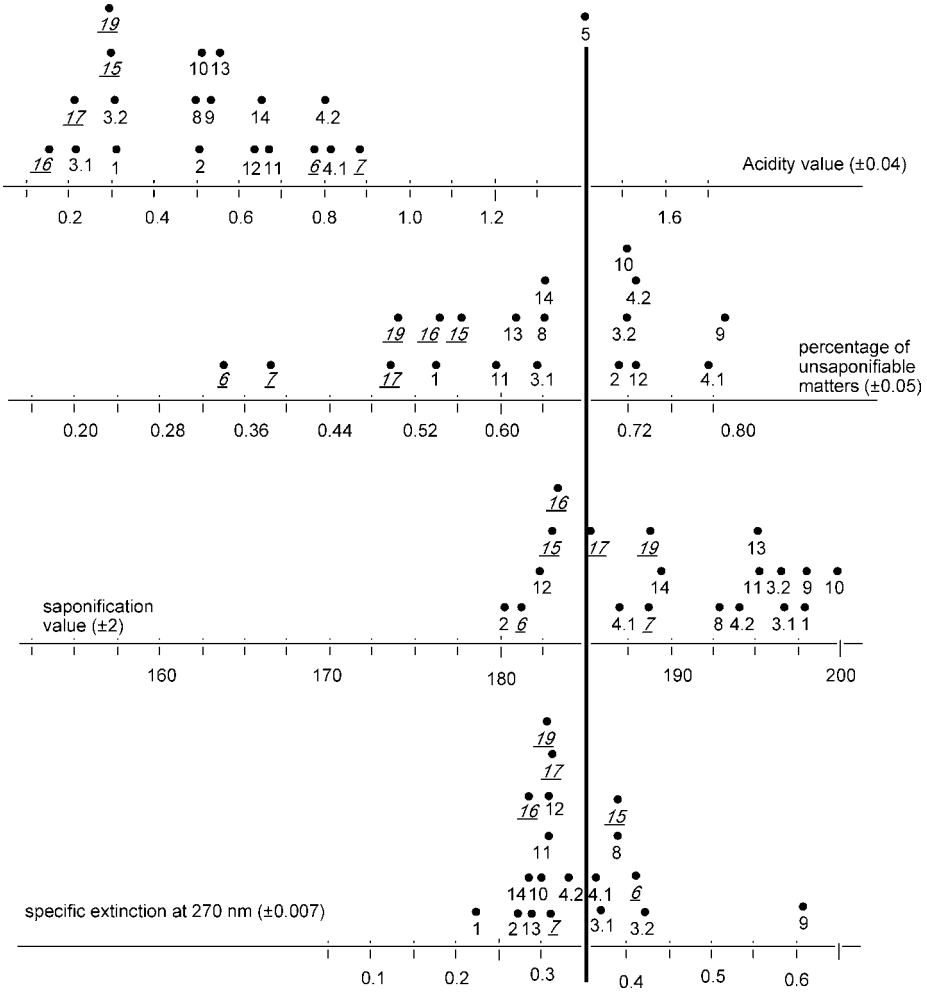

Figure 1. Acidity value, saponifiable matters, saponification value, and specific extinction of argan oil samples. The values found for sample 5 (traditionally prepared using certified argan nuts and sanitary conditions) are indicated by the bold line. Underlined and italic numbering refers to hexanes-extraction preparation mode (sample 18 was not included in this study.

(K_{270}) for all samples but 18. The results are reported comparatively to sample 5 (bold line) that had been specially prepared for this study in the Tamanar cooperative according to the traditional method, using quality certified (harvested and not goat digested) nuts from the Tamanar area and controlled sanitary conditions. All acidity values were found to be lower than 1.40, a value inferior to that requested for mass marketed olive oil (an acidity value lower than 2 is requested for virgin olive oil (*8*)). These results suggest that geographical origin may influence the acidity value of argan oil since five of the oil samples (samples 4.1, 4.2, 6, 7, 11) prepared from argan nuts collected around Tamanar were found to have a high acidity value. Nut roasting also appeared as a parameter possibly influencing the acidity value of oil. Indeed, acidity value of oil samples prepared from roasted nuts was consistently lower than those of oils prepared from nonroasted nuts (see 3.1 vs 4.1; 3.2 vs 4.2; or 1 vs 2, **Figure 1**). However, oil prepared from batches 1 and 2 had a similar acidity value reflecting clearly that storage of the nuts does not modify this parameter. So, variation of the acidity value could reflect geographical specificities and/or differences in technology. Indeed, if the high acidity value of sample 5, compared to 12 or 13 could be rationnalized in terms of geography, this explanation does not fit with samples 5 and 10 that have both been prepared from nuts collected in the Tamanar argan grove. However, with traditionally prepared oils being obtained from seeds "roasted" by mild heating in clay pans for "a certain amount of time", it is likely that the observed discrepancies in acidity value between samples 5 and 10 are the result of a different roasting time (2 h at 100 °C in the case of sample 5, unknown time and temperature in the case of sample 10). Consequently, the difference in acidity value observed between 5 and 10 is probably a technology marker whose generality needs to be demonstrated.

Unsaponifiable matters (**Figure 1**) were found to be lower than 0.81% (unsaponifiable matters of virgin olive oil have to be lower than 1.5 (*8*)). Extraction technology was found to influence the quantity of unsaponifiable matters in argan oil. Indeed, samples with lower unsaponifiable matters (between 0.34 and 0.56%) were found to have been been prepared by hexanes−extraction. Oil samples derived from roasted and nonroasted seeds displayed close unsaponifiable matter values (between 0.6 and 0.81%).

Saponification values of argan oils (Figure 1) were found between 180.0 and 199.0, a larger range of value than required for virgin olive oil (between 184 and 196) (*8*), but similar to that of other commun oils (*10*, *11*). In more details, saponification values of all hexanes−extracted oils were found in the same low range (between 181.6 and 188.5) and most of the press extracted and traditionally prepared oils were found to have saponification values between 192.4 and 199.6. A large variation of saponification value was observed for the local and traditionally prepared oils. Samples 5 and 12 dispalyed low saponification values (185.5 and 180.2, respectively), whereas samples 13, 9, and 10 (traditionally prepared from goat digested nuts)

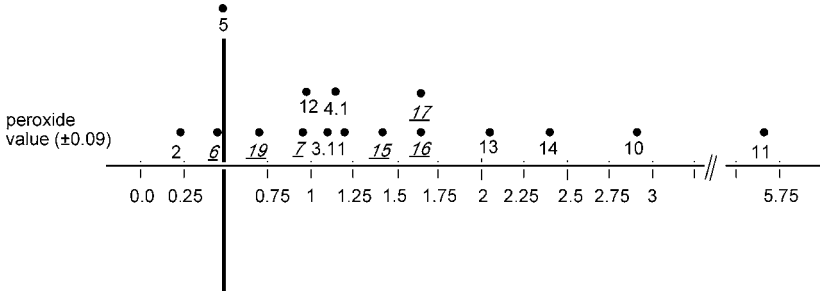

Figure 2. Peroxide value of argan oil samples. The value found for sample 5 (traditionally prepared using certified argan nuts and sanitary conditions) is indicated by the bold line. Underlined and italic numbering refers to hexanes-extraction preparation mode (sample 18 was not included in this study, peroxide values of samples 3.2, 4.2, 8, and 9 were below detection sensitivity).

had saponification values similar to those observed for press-extracted oils. Seed roasting also seemed to influence the saponification values of the oils. Indeed, sample 1, prepared from roasted nuts collected in the Tidzi area, had one of the highest saponification values (197.9), whereas sample 2 prepared from nonroasted nuts coming from the same batch had the lowest value (180.0). However, a smaller variation of the saponification values was observed for Tamanar oils (197.3 vs 187.2 (sample 3.1 and 4.1, respectively); 196.3 vs 193.1 (sample 3.2 and 4.2, respectively); 197.2 vs 192.4 (sample 9 and 8, respectively)). As observed for the acidity index, this reduced variation of Tamanar oils could reflect a geographical specificity, and it also indicated the lack of influence of the storage period on the saponifiation values.

Similar K_{270} values (Figure 1) were obtained for all oil samples (between 0.228 and 0.426) but sample 9. This latter, prepared from roasted nuts collected from goat dejections was found to have a specific extinction at 270 nm of 0.605. However, sample 8, prepared the same batch of nuts, but nonroasted, showed an average K_{270} (0.391). No precise explanation can be given for this observed high value, although contamination of argan seeds by heat-sensitive impurities present on argan shells is generally advanced by local dwellers to justify the darker color of traditionally prepared argan oil compared to press-extracted oil.

Figure 2 shows the results of the peroxide value of all samples but 18. For all samples, a peroxide value much lower than that required for virgin olive oil (*8*) was observed. The relatively high peroxide value of the six months old sample 11, prepared by storage at room temperature (18 to 30 °C) and unprotected from the sun light an aliquot of 4.1, clearly indicates that some argan oil components are highly sensitive to oxidation and, consequently, that preservation of argan oil should be carefuly realized. The high peroxide values observed for traditionally prepared samples 10 and 13 are also likely to result from unsatisfatory conditions used during the oil preparation. Interstingly, samples 8, 9, 3.2, and 4.2 presented peroxide values below the detection level, whereas the peroxide values of 3.1 and 4.1 were found to be 1.19 and 1.22, respectively. It is highly likely that the low values observed for 3.2 and 4.2 are a direct consequence of the reduced delay (less than 24 h) separating the nut harvest from the oil extraction. In the case of samples 8 and 9, since goats were feed with fresh fruits and the oil prepared within 24 h after collection, it seems reasonable that the argan shell protects the argan seeds from digestive attack, consequently maintaining a very low peroxide level. As it is very likely that decomposition of the peroxides during prolonged storage would have dramatic effects on argan oil diet properties, peroxide value determination appears to be a critical measurement for the ascertainment of argan oil quality.

Table 1. Refractive Index of Argan Oil Samples[a]

sample	refractive index at 20 °C	sample	refractive index at 20 °C
1	1.4705	10	1.4701
2	1.4705	11	1.4704
3.1	1.4705	12	1.4705
3.2	1.4698	13	1.4703
4.1	1.4705	14	1.4691
4.2	1.4697	*15*	1.4667
5	1.4703	*16*	1.4682
6	1.4647	*17*	1.4644
7	1.4656	18	1.4700
8	1.4699	*19*	1.4651
9	1.4699		

[a] Italic sample number indicates hexanes-extracted samples.

Refractive indexes determined at 20 °C are listed **Table 1**. All values were found in the 1.4656−1.4708 range attesting to the low level of trienes in the studied oils.

Table 2 shows the fatty acid (FA) composition of the 21 argan oil samples. No dramatic variations were observed between the samples in which UFA (oleic and linoleic acids) consistently composed 80% of the FA fraction. This evidenced that the geographical origin and process had no, or little, influence on the oil dietary qualities. However, it could be observed that samples 10, 12, 13, 15, and 18 which presented the smallest oleic acid ($C_{18:1}\omega$-9) content also contained the highest level of linoleic acid ($C_{18:2}\omega$-6). On the opposite batch, two derived samples (3.2 and 4.2) presented a high level of oleic acid and displayed a low level of linoleic acid. It is also noteworthy that all oil samples prepared from batch 1 (3.1, 4.1, 5, 6, and 7) presented a similar oleic acid linoleic acid ratio. Therefore, this clearly witnesses that the oil processing does not strongly alter the oil FA composition even though some biochemical processes could occur during the weeks following the nut harvest. Also of interet was the high content of behinic acid ($C_{22:0}$) of sample 14 (0.38% vs an average of 0.13%) prepared from argan nuts collected in the remote argan grove of Benaiznassen. If confirmed over the years, these variations could become useful markers to ascertain the geographical origin of argan oils. Finally, nonadecanoic acid ($C_{19:1}$) could be detected in two out of the three oils prepared from goat digested nuts. The eventuality of using nonadecanoic acid as a marker should also be explored.

trans-Fatty acid ($C_{18:1}$ and $C_{18:2}$) content was determined by GLC. Only traces of *trans*-fatty acids (data not shown) were detected (between 0.01 and 0.03%) for all of the the samples but 15 for which the percentage of *trans*-linoleic acid was found to be 0.04%. Similar results have been reported for olive oil (*12*).

Table 2. Percentage of Fatty Acid in Oils (±5%)[a]

	fatty acid in oils												
sample	$C_{14:0}$	$C_{15:0}$	$C_{16:0}$	$C_{16:1}$	$C_{17:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	$C_{19:1}$	$C_{20:0}$	$C_{20:1}$	$C_{22:0}$
1	0.12	0.04	12.45	0.04	0.08	5.44	47.11	33.53	0.09		0.36	0.44	0.11
2	0.11	0.04	12.06	0.01	0.08	5.77	47.76	32.69	0.08		0.40	0.47	0.14
3.1	0.12	0.04	12.26	0.04	0.07	5.19	47.63	33.24	0.08		0.36	0.43	0.13
3.2	0.12	0.04	13.0	0.08	0.08	6.11	50.05	29.12	0.06		0.43	0.48	0.13
4.1	0.10	0.04	12.07	0.01		6.01	48.23	32.10	0.08		0.43	0.50	0.12
4.2	0.12	0.04	12.89	0.08	0.08	5.98	50.03	29.19	0.07		0.40	0.48	0.12
5	0.10	0.04	12.12	0.02	0.07	5.75	48.45	32.04	0.08		0.41	0.48	0.16
6	0.10	0.04	12.08	0.02	0.08	6.00	48.88	31.37	0.07		0.45	0.52	0.17
7	0.10	0.04	12.09	0.02	0.08	5.91	49.01	31.21	0.06		0.42	0.49	0.15
8	0.12	0.04	12.49	0.08	0.08	5.93	48.13	31.33	0.04	0.08	0.42	0.48	0.15
9	0.11	0.04	12.91	0.07	0.07	6.26	48.73	30.10	0.07		0.45	0.48	0.08
10	0.10	0.04	11.82	0.07	0.08	5.80	46.10	34.26	0.03	0.09	0.43	0.49	0.17
11	0.10	0.04	11.87	0.02	0.08	5.81	48.74	31.81	0.07		0.40	0.49	0.15
12	0.11	0.04	12.09	0.07	0.08	6.19	46.64	33.26	0.09		0.44	0.48	0.08
13	0.14	0.04	12.47	0.08	0.08	5.39	46.56	34.06	0.09		0.34	0.44	0.11
14	0.15	0.04	12.06	0.09	0.07	6.35	48.32	31.73			0.35	0.41	0.38
15	0.11	0.04	12.56	0.07	0.08	6.94	45.05	33.74	0.10		0.47	0.43	0.17
16	0.11	0.05	12.75	0.08	0.08	6.12	47.64	31.73	0.08		0.44	0.49	0.17
17	0.10	0.04	12.40	0.10	0.10	6.22	47.80	31.63	0.08		0.48	0.49	0.18
18	0.14	0.05	13.49	0.05	0.08	5.87	45.84	33.07	0.10		0.39	0.42	0.11
19	0.12	0.04	13.08	0.09	0.07	6.82	46.06	32.43	0.09		0.49	0.46	0.19

[a] Italic sample number indicates hexanes-extracted samples.

Table 3. Triglyceride Composition in Percentage (±2%)[a,b]

sample	LLL	LLO	LLP	LOO	LOP	PPL	OOO	POO	OPP	LPS	PPP	SOO	SOP
1	6.89	13.22	5.85	15.96	14.18	1.94	13.77	16.05	4.06	0.31	0.11	4.58	2.25
2	7.43	13.80	6.17	16.27	13.96	2.05	13.74	15.74	3.76	0.32		4.69	1.91
3.1	7.28	13.26	5.77	15.66	13.41	2.05	14.12	16.17	4.38	0.37		5.11	2.24
3.2	5.77	11.59	5.48	14.73	13.46	1.97	14.34	16.95	4.12	0.29		5.18	2.61
4.1	7.35	13.79	6.17	16.12	13.92	1.76	14.22	16.02	3.63	0.24	0.18	4.61	1.34
4.2	5.93	11.52	5.78	14.14	12.61	2.50	13.91	16.39	5.20	0.82		5.20	2.54
5	7.20	13.58	5.78	16.28	13.72	1.93	14.40	15.98	3.81	0.46	0.23	4.68	1.69
6	7.12	13.60	5.82	16.17	13.65	2.02	14.45	16.25	3.87	0.44	0.21	4.55	1.62
7	6.95	13.27	5.83	16.10	13.90	1.84	14.99	16.59	3.80	0.20	0.03	4.70	1.59
8	6.47	12.71	6.10	15.19	13.94	2.17	13.39	16.02	4.40	0.42		4.71	2.33
9	6.00	16.67	4.35	14.01	13.27	1.87	12.71	15.57	3.89	0.21		4.48	2.21
10	7.45	13.72	6.40	15.28	13.97	2.25	12.57	14.94	4.47	0.57		4.66	2.22
11	7.12	14.03	5.86	16.35	13.65	1.75	14.45	16.19	3.91	0.18		4.58	1.80
12	7.77	14.09	6.23	15.81	14.15	1.85	12.75	15.46	3.62	0.24		4.83	2.30
13	8.11	12.87	6.26	15.09	13.33	2.07	13.07	15.45	3.85	0.34	0.43	5.02	2.95
14	6.84	12.20	6.00	14.31	13.22	2.08	13.98	15.48	4.39	0.66		6.04	4.00
15	7.69	13.41	6.55	13.93	14.57	2.14	11.32	15.17	4.37	0.11		4.61	2.11
16	7.54	12.91	5.77	14.80	13.64	1.86	14.03	16.32	4.16	0.21		4.10	1.77
17	7.46	12.88	5.99	14.47	13.27	1.81	13.86	16.08	3.90			4.31	2.05
18	7.24	13.70	6.45	15.63	15.02	0.38	9.00	17.49	5.04			4.80	3.16
19	7.00	12.61	6.27	13.69	14.06	2.15	12.03	15.95	4.76	0.17	0.12	5.17	2.54

[a] Italic sample number indicates hexanes-extracted samples. [b] L, linoleic acid; O, oleic acid; P, palmitic acid; S, stearic acid.

Table 3 shows the triglyceride composition of the 21 samples of oil. Five triglycerides (LLO, LOO, LOP, POO, and OOO) composed roughly 73% of each oil triglyceride fraction. Triglycerides presenting two or three linoleic acid residues were detected in lower quantities in the second batch of press-extracted argan nuts collected from Tamanar (samples 3.2 and 4.2). Conversly, higher levels of palmitic acid-containing triglycerides were detected in these samples. FA composition determination had already indicated a low level of linoleic acid for 3.2 and 4.2. The lower quantities of triglycerides presenting two or three linoleic acid residues could also reflect the supposed biochemical process occurring during the preliminary nut storage.

Figure 3 shows the percentage of saturated FA at the triglyceride 2-position. Samples 3.1 and 5 displayed the highest percentage (0.43 and 0.39 respectively) and all of the other samples presented similar values. Consequently, no specific information, in terms of process or geographical origin, was obtained from this analysis.

Tocopherols are important oil components since they possess both antioxidant and vitamin action (*10*). One of the specificities of argan oil is its high content of tocopherols, γ-tocopherol being the major one (*3*). Indeed, tocopherol levels are at least four times higher in argan oil than in olive oil and two times higher than in hazelnut oil (*13*). **Table 4** shows the content of different tocopherols in the 21 oil samples as determined by HPLC. Samples 5 and 10, which both had been traditionally prepared, were found to have the lowest levels of total tocopherols. However, samples 12 and 13 prepared in uncertain conditions showed average levels of tocopherols. β-Tocopherol was absent or only detected as traces.

Roasting seemed to more particularly affect α-tocopherol levels since every sample prepared from roasted argan seeds displayed an α-tocopherol level inferior to its nonroasted

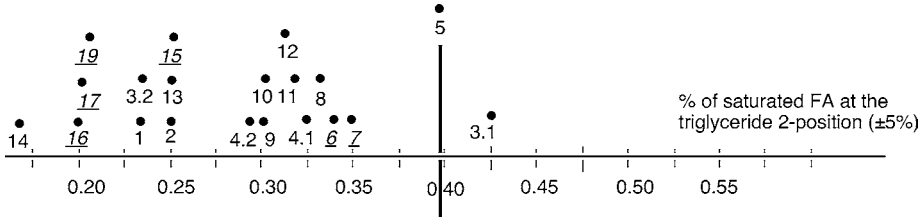

Figure 3. Percentage of saturated fatty acids at the triglyceride 2-position. The value found for sample 5 (traditionally prepared using certified argan nuts and sanitary conditions) is indicated by the bold line. Underlined and italic numbering refers to the hexanes-extraction preparation mode (sample 18 was not included in this study).

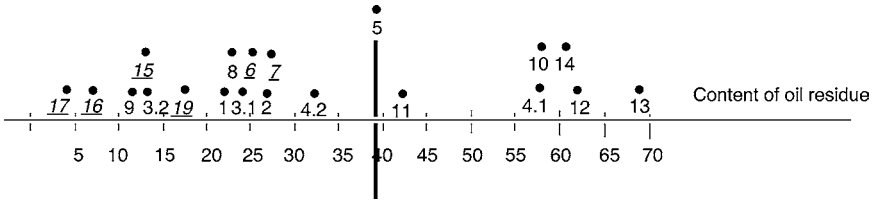

Figure 4. Content of oil residue in mg/kg. The value found for sample 5 (traditionally prepared using certified argan nuts and sanitary conditions) is indicated by the bold line. Underlined and italic numbering refers to hexanes–extraction preparation mode (sample 18 was not included in this study).

Table 4. Tocopherol Content in mg/kg of the Oil Samples (±8%)[a]

sample	γ-tocopherol	δ-tocopherol	α-tocopherol	β-tocopherol	total
1	631.3	59.5	26.6		717.4
2	621.1	50.9	32.7		704.7
3.1	562.6	47.7	29.4		639.7
3.2	606.7	48.6	38.0		693.3
4.1	681.6	53.8	34.4	1.4	771.2
4.2	642.0	69.0	33.0		744.0
5	524.0	43.5	29.7		597.2
6	581.3	56.3	29.6	1.2	668.4
7	640.0	45.4	32.0	1.1	718.5
8	599.3	46.4	33.0		678.7
9	619.1	50.2	29.6		698.9
10	550.3	65.8	28.6		644.7
11	642.2	51.6	37.3	1.2	732.3
12	651.4	50.3	35.2	1.5	738.4
13	639.4	55.2	35.8	1.2	731.6
14	701.1	37.2	37.2		775.5
15	615.6	38.0	33.2		686.8
16	545.9	38.7	49.3		633.9
17	608.5	45.7	63.6		717.8
18	586.7	44.8	39.7		671.2
19	649.6	42.0	57.9	4.3	753.8

[a] Italic sample number indicates hexanes-extracted samples.

Table 5. Sterol Content (mg per 100 g of Oil) of the 21 Oil Samples (±2%)[a,b]

sample	campest.	Stigma 8,22	Spinast.	Schott.	Stigma 7,24	total
1	0.20	4.31	37.07	46.66	4.81	142.0
2	0.17	4.57	38.50	43.39	5.94	158.2
3.1	0.28	3.37	36.96	47.20	5.04	164.5
3.2	0.11	4.76	37.16	46.16	4.41	188.3
4.1	0.18	4.67	36.17	44.65	6.54	167.1
4.2	0.05	4.72	37.29	45.83	4.46	223.5
5	0.22	4.82	37.15	46.60	4.68	130.0
6	0.20	4.99	36.91	45.39	4.48	133.6
7	0.16	4.21	37.05	44.62	6.89	155.9
8	0.14	3.01	38.54	47.43	4.67	216.8
9	0.16	4.08	36.11	46.03	4.48	186.5
10	0.18	4.25	34.46	48.14	5.05	198.5
11	0.24	3.19	37.75	47.15	5.57	163.4
12	0.22	5.57	36.85	45.63	5.27	174.2
13	0.11	5.35	37.85	44.44	5.09	169.0
14	0.11	4.85	35.44	48.47	2.57	206.3
15	0.24	4.77	39.17	44.99	4.71	147.4
16	0.31	5.40	39.29	46.12	3.55	130.0
17	0.19	5.83	40.45	44.07	3.28	152.8
18	0.39	4.82	38.19	44.58	4.22	150.3
19	0.24	5.11	42.11	42.35	4.13	136.0

[a] Italic sample number indicates hexanes-extracted samples. [b] Campest., Δ^5-campesterol; Stigma 8,22, Stigmasta-8,22-diene-3-ol; Spinast., spinasterol; Schott, schottenol; Stigma 7,24, stigmasta-7,24-dien-3-ol.

counterpart. Although δ-tocopherol is generally considered as having the greater antioxidant activity (*10*), surprinsingly, sample 11 did not present the low δ-tocopherol level anticipated at the view of its peroxide value.

Total phytosterol concentration was found in the range of 130−223 mg/100 g. Similar values have been reported for commun oils (*14*, *15*). Content of stigmasat-8,22-dien-3-ol, spinasterol, schottenol ((24*S*-Δ^7-stigmasterol), and stigmasta-7,24−28-dien-3-ol (Δ^7-avenasterol), the main sterols in argan oil (*1*), is listed **Table 5**. The quantitative analysis of Δ^5-campesterol (24*R*-methylcholest-5-en-3β-ol) was also carried out for each sample since this sterol is relatively abundant in olive, sunflower, and hazelnut oils (*11*) and even more abundant in moringa oil (*16*, *17*). Results showed little variation in the sterol content. The high level of sterol observed in sample 4.2 could not be observed in 3.2, prepared from roasted nuts, and since 3.1 and 4.1 displayed similar sterol levels, it cannot be ruled out that some sterol decomposition occurs in the early days following the nut harvest. More interesting was the consistent very low level of Δ^5-campesterol observed independently of the extraction process. This parameter seems essential to detect adulteration of argan oil with other vegetable oils.

Figure 4 shows the content of oil residue. Samples purchased on local markets (samples 10, 12, and 13) were found to be those with the highest content of residue. Although attenuated, the content of oil residue of sample 5 was also found among the highest together with press-extracted samples 4.1 and 14. However, sample 4.2 prepared from the second batch of Tamanar seeds (certified fresh seeds) showed a moderate level of oil residue. In consequence, the origin of the oil residue could be reasonably explained by a unsatisfactory extraction/filtration process that prevents the elimination of a residue that could possibly predominantly be formed in nuts stored in unsatisfactory conditions. This result suggests that argan nuts should not be kept for long period of time after the harvest or should be kept in fresh and ventilated areas. Interestingly, all hexane extracted oils were found to have a low content of residue indicating that

all, or most of, the residue is not produced after the oil conditioning but is washed away during the extraction step.

Because roasting is known to possibly produce benzo[*a*]pyrene (*18*), a carcinogenic chemical (*19*), we also decided to investigate the benzo[*a*]pyrene level in some samples in order to evaluate the influence of the roasting step on the oil composition. For this analysis, we only compared two oils produced from nonroasted argan nuts (2 and 4.1) to their counterpart produced from roasted argan nuts (1 and 3.1). Sample 5 was also analyzed. Similar benzo[*a*]pyrene concentrations were found for samples 1, 2, 3.1, and 5 (0.06 ppb $\pm$ 0.01) suggesting that the roasting does not produce significant quantities of benzo[*a*]pyrene. Sample 4.1 displayed a benzo[*a*]pyrene level of 0.14 ppb. Though inferior to the 0.2 ppb authorized limit for drinking water, this result was surprising since 4.1 was prepared from nonroasted nuts. However, combined with the content of oil residue analysis, it supports the idea that high levels of benzo[*a*]pyrene and of oil residue could be associated.

Our study has evidenced the high quality of the press-extracted oils. This technology preserves the chemical composition the oil, compared to traditionally prepared oil, and particularly the specific fatty acid balance that is beneficial for human health. This study has also evidenced that, if some physico-chemical parameters of argan oil are not affected by a prolonged storage, oils of general higher quality are obtained when fresh argan seeds are used. Finally, though preliminary, this study already suggests that regulations should define the length and conditions of argan nuts storage prior to oil extraction. This study has also permitted the identification of the sterol composition as an analytical tool allowing the detection of argan oil adulteration. Evaluation of the statistical relevance of other parameters is still necessary and is currently being carried out in our laboratory.

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