



Article Nutritional and Health Values of Tunisian Edible Oils from Less-Used Plant Sources

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Abstract: The reclaim of less-used plant sources is a novel approach to the growing demand for healthy and eco-friendly foods, and it constitutes a sustainable alternative to replace conventional food ingredients and sources of bioactives. In this work, a phytochemical profile in terms of mineral elements, total polyphenols, fatty acids, α -tocopherol, sterols, and squalene was realized for several commercial edible oils of bitter almond, pumpkin seed, apricot kernel, nigella, souchet, and wheat germ sourced in the Tunisian market. Wheat germ oil, which showed the most significant nutritional and healthy impact, contained the highest contents of Mg (52.37 mg kg⁻¹); Na (40.75 mg kg⁻¹); Mn (2.39 mg kg⁻¹); total sterols (1713.80 mg/100 g); and PUFAs (61.01%). The high levels of squalene detected on pumpkin seed oils (1160.01 mg kg⁻¹) allows to proposet it as valuable functional food. The highest total polyphenolic content found in nigella oils (109.01 mg GAE kg⁻¹) justifies its stability and antioxidant properties. A daily consumption of 10 g of bitter almond or souchet oil contributes to a 17.53% and 8.6% alpha-tocopherol daily intake, respectively. The usual consumption of these minor oils may represent a sustainable and convenient source of bioactives with beneficial effects on both human health and nutrition.

Keywords: less-used plant sources; recovery; sustainable food; edible oils; phytochemical profile; nutritional value; healthy value

1. Introduction

Satisfying a growing global population (10 billion expected to be reached by 2050) with healthy diets from sustainable food systems is a strong and urgent challenge for international politics and involves the scientific community, especially in view of the United Nations Sustainable Development Goals (UN-SDGs) [1,2]. The current increasing demand for healthy and eco-friendly foods has encouraged the development of new and different approaches, such as the substitution of food components and the development of new production technologies [3]. In particular, the first consist of the circular reclaim of by-products in food as sustainable alternative to conventional ingredients but also as promising sources of highly nutritional bioactives [4–6]. By-products from the agri-food industry (e.g., peels, seeds, shells, pomace, and leaves) are valuable and often underestimated sources of important nutrients, such as phenols, peptides, carotenoids, anthocyanins, fatty acids, fibers, and enzymes. All of them can be exploitable in food, pharmaceutical, and cosmetic industries [7–10]. Many studies have shown that different types of fruit and vegetable



Citation: Vadalà, R.; Nava, V.; Turco, V.L.; Potortì, A.G.; Costa, R.; Rando, R.; Ben Mansour, H.; Ben Amor, N.; Beltifa, A.; Santini, A.; et al. Nutritional and Health Values of Tunisian Edible Oils from Less-Used Plant Sources. *Agriculture* **2023**, *13*, 1096. https://doi.org/10.3390/ agriculture13051096

Academic Editors: Alessio Cappelli and Anders S. Carlsson

Received: 17 February 2023 Revised: 27 April 2023 Accepted: 10 May 2023 Published: 20 May 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). by-products can be well-incorporated in the development of functional foods [11–13]. The global nuts and seeds market is increasingly fragmented, and it is estimated to surpass \$9.2 billion by 2025, wherein it is expected to grow at a rate of 6% during the years from 2020 to 2025 [14]. In this scenario, the seeds, nuts, and fruit kernels are considered to be byproducts of interest. These may represent an alternative source of nutrients to support the global demand for functional foods and as one of the strategies to cope with food growing needs [15]. Large amounts of different nuts, fruit kernels, and seeds (more than 60 Mtons metrics in 2020–2021) are globally obtained by the fruit and vegetable industry and then discarded every year as by-products of food processing. These agro-industrial by-products represent a valid source for the production of edible oils obtained by mechanical cold pressing [16] (INC 2021). Cold pressing procedures are characterized by low temperatures and are considered as sustainable alternatives to traditional practices. In fact, the absence of overheating of raw materials determines a better preservation of the beneficial natural components in cold-pressed oils [4,13,17,18]. Nuts, fruit kernels, and seed oils are an object of health-related and commercial interest, given the great emphasis that has been devoted to their phytochemical characterization [19,20]. The circular reclaim of nuts, fruit kernels, and seed oils can constitute an approach that is convergent with the FAO's Strategic Framework 2022–2031, which, at the same time, also supports the 2030 Agenda through the transformation to more efficient, inclusive, resilient and sustainable agri-food systems for better production, nutrition, and for the environment [21]. The recovery of vegetable oils from these agro-industrial by-product produces both economic and environmental benefits, and it represents a currently unexploited opportunity to generate additional revenue streams for farmers and agribusinesses. Using these by-products to create added value products can potentially increase their profitability and sustainability. This approach can reduce the amount of by-products and the associated environmental impact. By diverting these by-products from landfills or incineration, the environmental burden of their disposal can be reduced. Overall, the recovery of vegetable oils from agro-industrial by-products represents a promising avenue for sustainable economic development and environmental stewardship. In this work, a phytochemical profile, in terms of mineral elements, total polyphenols, fatty acids, α -tocopherol, sterols, and squalene, was traced for several commercial samples of nuts, fruit kernels and seed oils, which were obtained by the mechanical cold pressing of bitter almond, pumpkin seed, apricot kernel, nigella, souchet, and wheat germ. All samples investigated were sourced in the Tunisian market. The aims of the work were: (i) to evaluate the nutritional and healthy added value of the investigated oils in order to define possible routes of inclusion for these less-used plant sources within foods in place of usual ingredients or, alternatively, as fortifying agents and (ii) to collect information that enables the use of new alternative sources of edible oils, obtained from agro-industrial by-product, which may serve as sustainable, convenient, and healthy raw material for food and non-food sectors.

2. Materials and Methods

2.1. Sampling

Commercially available cold pressed oils from fruit kernels, nuts, and seeds were purchased in 2021 from the local market in Mahdia, Tunisia. In particular, the oils were obtained from bitter almond (*Prunus dulcis*, var. amara); pumpkin (*Cucurbita maxima*) seeds; apricot (*Prunus Armeniaca* L.) kernels; nigella (*Nigella sativa*); souchet (*Cyperus esculentus*); wheat germ (*Triticum aestivum*). All the oils were produced in Mahdia, Tunisia. Six different oils were then considered in the present study, and a total of 18 samples (three samples for each oil type) were considered for the analyses. Botanical and Tunisian provenience of the oil's raw materials was guaranteed by the suppliers, as well as the extraction method (cold pressing). Oil samples were transferred by aircraft from Tunisia to Italy under suitable packaging conditions and controlled temperature (2–8 °C). Sample temperature and integrity were continuously monitored during the shipment.

2.2. Materials and Reagents

Argon, air, nitrogen, and hydrogen gases of 99.9990% purity and helium gas of 99.9995% purity were supplied by Rivoira gases (Milan, Italy). Methanol, *n*-hexane, ethyl acetate (HPLC grade), *n*-heptane, ethanol, diethyl ether (reagent grade), Folin–Ciocalteu reagent, gallic acid, and nylon membrane for clarification (diameter = 0.45μ n) were purchased from Merck Life Science (Merck KGaA, Darmstadt, Germany). Nitric acid (HNO₃, 65% v/v) and hydrogen peroxide (H₂O₂, 30% v/v) used were of suprapure grade and purchased from J.T. Baker (Mallinckrodt Baker, Milan, Italy). Ultrapure water was obtained through a Barnstead Smart2Pure 12 system (Thermo Scientific, Monza, Italy). Commercial standard solutions of Li, Be, B, Na, Mg, Al, K, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Sb, Ba, Tl, Pb, Bi, and Cd (prepared by diluting 1000 mg in 1 L of a 2% solution of nitric acid) were obtained from Merck (Darmstadt, Germany); the solution of Re at 1000 mg/L in 2% nitric acid was acquired by Fluka (Milan, Italy). For direct mass analyzer (DMA) measurements. A stock standard solution of Hg (Hg $(NO_3)_2$ in 10% HNO₃, 1000 mg L⁻¹) was purchased from Merck-Millipore (Merck KGaA, Darmstadt Germany). Cartridges of Supelco Discovery DSC-Si Silica were purchased by Supelco Spa Certified; matrix Pine Needles NIST 1575 (National Institute of Standards & Technology, NIST, Gaithersburg, MD, USA). Bis-trimethylsilyl-trifluoroacetamide and trimetylchlorosilane (BSTFA:TMCS 99:1), silica gel type G, standard solutions of squalene, tetradecane and fatty acid methyl esters (FAMEs) reference standards (C4-C24), and α -tocopherol reference standard (98% purity) were purchased from Merck Life Science (Merck KGaA, Darmstadt, Germany).

2.3. Elemental Analysis

2.3.1. ICP-MS

Samples were digested in triplicate using a closed-vessel microwave digestion system— Ethos 1 (Milestone, Bergamo, Italy)—equipped with sensors for temperature and pressure control and provided with PTFE (polytetrafluoroethylene) vessels capable of withstanding pressures of up to 110 bar. An amount of 0.3 g of each sample was accurately weighed into acid-prewashed PTFE vessels, added with 1 mL of internal Re standard at 0.5 mg L⁻¹, and then was digested with 8 mL of HNO₃ (65%, v/v) and 2 mL of H₂O₂ (30%, v/v). Temperature program is reported in the Supporting Information in Table S1. Blank solutions, consisting of HNO₃ and H₂O₂, 8:2 v/v, were processed in the same way and were run with each batch of digested samples. The certified reference materials were digested under the same conditions as the samples. All determinations were carried out in triplicates.

The determination of Li, Be, B, Na, Mg, Al, K, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sb, Ba, Tl, Pb, and Bi was carried out by Thermo Scientific iCAP-Q ICP-MS spectrometer Thermo Scientific, Monza, Italy) powered by a 27 MHz radiofrequency solidstate generator at 1550 W. The ICP torch was a classic Fassel-type torch with wide diameter (2.5 mm) fitted with a shield torch system. ICP-MS was equipped with an autosampler ASX520 (Cetac Technologies Inc., Omaha, NE, USA) and an integrated sample introduction system. This instrument includes a standard cyclonic spray chamber made of PFA with a nebulizer with a 6 mm outside. The instrument has a system that produces acceleration ions via an initial ion lens stack into a RAPID (right angle positive ion deflection) lens that efficiently deflects analyte ions by 90° before entry into the QCell. Ni sampler and skimmer cones of 1.1 mm and 0.5 mm, respectively, were used. A Qcell system of collision/reaction quadrupole with helium gas to minimize polyatomic interferences arising from plasma and matrix (KED mode) was used. The ICP-MS operating conditions are reported in Supporting Information in Table S2. The instrument was operated in KED mode. Monitored isotopes were ⁷Li, ⁹Be, ¹¹B, ²³Na, ²⁴Mg, ²⁷Al, ³⁹K, ⁴⁷Ti, ⁵¹V, ⁵²Cr, ⁵⁵Mn, ⁵⁶Fe, ⁵⁹Co, ⁶⁰Ni, ⁶³Cu, ⁶⁶Zn, ⁷⁵As, ⁷⁸Se, ⁸⁸Sr, ⁹⁸Mo, ¹⁰⁷Ag, ¹¹⁴Cd, ¹²¹Sb, ¹³⁸Ba, ²⁰⁵Tl, ²⁰⁸Pb, and ²⁰⁹Bi. These were chosen to maximize sensitivity and to minimize interferences due to the matrix. Integration times were 0.01 s/point for Mg, Na, and K; 0.5 s/point for As, V, Se, and Fe; and 0.1 s/point for other elements. Three replicate acquisitions were taken. The followings information

are reported in the Supporting Information: (i) the operating conditions for instrumental analysis by ICP-MS (Table S2) and the validation of analytical method and the analytical parameters for method validation (Table S3).

2.3.2. Determination of Hg Content

Each sample was analyzed for the determination of Hg by Direct Mass Analyzer (DMA-80) (Milestone, Metuchen, NJ, USA). This instrument was used according to the US EPA 7473 method. One hundred μ L of each sample was put in a specific cuvette, dried at 200 °C for 3 min, and combusted at 650 °C for 3 min in oxygen-enriched air atmosphere. Detection of mercury was based on absorption spectroscopy, with measurement of mercury absorbance at 253.65 nm. The mercury (Hg) contents were calculated by the instrumental software EASYDOC software version 3.3 for DMA-80 in accord with the calibration curve constructed using Hg 1000 mg L⁻¹ certified standard (CZECH Metrology Institute Analytika). Five concentration levels were chosen as concentration points in the range 0.05–10 mg L⁻¹. Each standard solution was injected six times. The method was validated according to the EURACHEM guidelines [22].

Analytical methods for mineral elements determination were validated with the help of commercial standards in terms of linearity, limit of detection (LOD), and limit of quantification (LOQ), according to Eurachem criteria [22]. Linearity was assessed by means of calibration curves of each analyte, which were constructed according to the linear least-square regression method. Specifically, seven-point calibration curves were obtained using mixed working standard solutions in the following concentrations: 0.5, 1.0, 2.0, 5.0, 10, 20, and 50 μg L⁻¹ for Li, Be, B, Na, Mg, Al, K, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sb, Ba, Tl, Pb, and Bi. Each solution was injected six times (n = 6). LODs and LOQs were experimentally calculated as 3.3 σ /S and 10 σ /S, respectively, where σ is the standard deviation of the analytical blank (N = 6), and S is the slope of the relative calibration curve. A good linearity was obtained for all elements investigated with R2 values ranging from 0.9982 (for Na) to 0.9999 (for V). The limits of detection (LODs) ranged from 0.001 to 0.461 μ g kg⁻¹, and limits of quantification (LOQs) ranged from 0.003 to 1.521 μ g kg⁻¹. The lowest average recovery was observed for potassium with 91.13%, while the highest was obtained for arsenic with 102.56%. Accuracy was assessed by evaluating six determinations on certified reference material (Pine Needles NIST 1575) and was reported as the percent recovery between the value found with the calibration curve and the true value reported in the certified reference materials. When the element was not certified in the reference material, the matrix was spiked with the known amount of analyte and was analyzed following the procedures discussed before. Based on these results, the analytical characteristics (linearity, sensitivity, and accuracy) could be considered satisfactory for the purposes of the analysis.

2.4. Total Polyphenol Analysis

The polyphenols analysis was performed according to the Folin–Ciocalteau method [23,24]. Oil sample (6 g) was added to 6 mL of a solution MeOH/H₂O 80:20 (v/v). An amount of 0.2 mL of extracted sample was mixed with 10 mL of Folin–Ciocalteau reagent and sodium carbonate (Na₂CO₃) solution (7.5%) in a 20 mL flask and added with distilled water up to the mark. The mixture was kept in the dark for 90 min, and the absorbance was detected at a wavelength of 765 nm with an UV-visible spectrophotometer (UV-2401 PC, Shimadzu, Milano, Italy). Sample measurements were conducted in triplicate together with analytical blanks. The total phenol content was calculated as milligrams of gallic acid equivalents (GAEs) in 1 kg of vegetable oil (mg GAEs kg⁻¹).

2.5. Fatty Acids Profiling

The determination of fatty acid methyl esters (FAMEs) in all the oil samples was performed according to the protocol reported in the EU Regulation n. 1833/2015 (European Commision, 2015). Fatty acids were transformed by transesterification into the respective

methyl ester and analyzed by gas chromatography using a Dani Master GC1000 gas chromatograph equipped with a split/splitless injector and a flame ionization detector (FID) (Dani, Instrument, Milan, Italy). A Zebron ZB-WAX capillary column with 30 m \times 0.25 mm ID and 0.25 μ m film thickness (Phenomenex, Torrance, CA, USA) was used. The chromatographic conditions were the following: column oven temperature ranged from 130 °C to 200 °C (20 min hold) at 3 °C/min; injector and detector temperature was, respectively, 220 and 240 °C; linear velocity of helium was 30 cm/s (constant). The injection volume was 1 μ L, with a split ratio of 1:75. All samples were run in triplicate. Individual FAMEs (expressed as percentage) were calculated in relation to total area of chromatogram.

2.6. Determination of Squalene

All oil samples were extracted and analyzed for squalene content according to the validated method reported in Salvo et al., 2017 [5]. Squalene was extracted by means of cartridges of Supelco Discovery DSC-Si Silica, using *n*-hexane, to perform a solid phase extraction (SPE). Squalene was eluted with 10 mL of *n*-hexane after the sample had been analyzed by a gas chromatography system (GC-2010, Shimadzu, Kyoto, Japan) coupled to a single quadrupole mass spectrometer (QP-2010 Plus, Shimadzu, Kyoto, Japan). Chromatographic separations occurred on a SPB-5MS capillary column (30 m \times 0.25 mm i.d. \times 0.25 μ m film thickness, Supelco, Bellefonte, PA, USA). The oven temperature program ranged from 80 °C (1 min hold) to 140 °C at 20 °C min⁻¹, and finally to 290 °C (2 min hold) at 5 °C min⁻¹. The injection port was at 250 °C. Sample injection was conducted in splitless mode, with sampling time of 60 s, then split ratio 1:10. Injection volume was 1 µL. Carrier gas was used at a linear velocity of 30 cm s⁻¹. The MS conditions were EI source temperature of 230 °C; ionization energy and emission current of 70 eV and 250 μ A, respectively; and interface temperature of 290 °C. Acquisition was performed both in full scan (mass range: 40-400 m/z) and selected ion monitoring (SIM) based on the monitoring of four characteristic mass fragments for squalene (121, 137, 161, and 175 m/z). Identification of squalene occurred by comparison of its retention time and mass spectra with that of commercial standard. Quantification of squalene took place in SIM mode, considering its relative base peak ion and it was obtained from its corresponding calibration curve using tetradecane (200 mg L^{-1}) as internal standard.

2.7. Determination of Phytosterols

The determination of the phytosterols was performed according to the protocol reported in EU Regulation n. 1348/2013 [24]. The sample was saponified using an ethanolic KOH solution, while the unsaponifiable fraction was extracted with ethyl ether. The unsaponifiable fraction was fractionated using silica gel G in 25 mL of 2 N NaOH and then activated by heating at 110 °C for 90 min. Diethyl ether solutions of the unsaponifiable fraction were put on the plates using a 100 μ L syringe. Elution was performed with 100 mL of *n*-hexane:diethyl ether (65:35 v/v) in a glass developing chamber (27.0 \times 26.5 \times 7.0 cm) using two plates at a time. Elution time was about 45 min. Plates were then sprayed with a 0.2% (w/v) ethanolic solution of 2,7-dichlorofluorescein to highlight the bands under a UV source (366 nm). The sterols band was separated and extracted from the silica gel with 10 mL of hot ethyl acetate. After removing the ethyl acetate under vacuum, the residue was also analyzed after derivatization by using 0.1 mL of bis(trimethylsilyl)trifluoroacetamide and trimethylchlorosilane (BSTFA-TMCS 99:1) at room temperature for 30 min. Trimethylsilyl ether (TMSE) derivates were analyzed by GC (Dani Master GC1000) equipped with a split/splitless injector and a flame ionization detector (FID) (Dani, Instrument, Milan, Italy). A Supelco SPB-1 capillary column, 15 m \times 0.20 mm ID, 0.20 μ m film thickness (Bellefonte, PA, USA), was used. The oven temperature was programmed as follows: from 240 °C (5 min hold) to 290 °C (5 min hold) at 2 °C min⁻¹. Injector and detector were respectively set at 280 °C and 290 °C. Linear velocity of helium was 30 cm/s (constant). The injection volume was 1µL, with a split ratio of 1:50. The individual peaks were identified based

on the retention times and by comparison with the mixture of sterol TMSE, which was analyzed under the same conditions.

2.8. *α*-Tocopherol Measurement

For the determination of α -tocopherol, all the oil samples were analyzed without any pretreatment according to the method proposed by Dugo, L. et al. 2020 [24]. Each sample was diluted with *n*-hexane (1:10 v/v) before HPLC analysis then analyzed in triplicate. Analyses were performed by an HPLC system (Shimadzu, Milan, Italy) with an RF-20A fluorescence detector. A LiChrosorb[®] Si60 column of 4.6 mm × 250 mm I.D. with a 5 µm particle size (Merck KGaA, Darmstadt, Germany), was used. Analyses were performed at 40 °C, under isocratic conditions, with a mobile phase consisting of *n*-hexane/ethyl acetate (90:10 v/v). The injection volume was 20 µL, and the flow rate was 0.8 mL min⁻¹. The identification of α -tocopherol was obtained by a direct comparison with the retention time of α -tocopherol from the standard solution at excitation and emission wavelength, respectively, of 290 nm and 330 nm, while the quantitative analysis was performed by using an appropriate calibration curve for α -tocopherol. Every sample was analyzed in triplicate along with analytical blanks.

2.9. Statistical Analysis

Dataset is expressed as mean \pm standard deviation (s.d.) of triplicate measurement. Significant differences (p < 0.05) within means were analyzed by one-way ANOVA then by Tukey's honestly significant difference (HSD), using XLStat statistical software Microsoft Excel data analysis add on (Microsoft Corporation, Redmond, WA, USA).

3. Results and Discussion

3.1. Multiement Measurement

Inductively coupled plasma mass spectrometry (ICP-MS) is considered to be a highly performing, accurate, and sensitive technique with low detection limits, and, for these reasons, it is deemed particularly appropriate for multielemental screening in foods matrices [24–27]. The elemental profile of a vegetal oil is always conditioned by different variables such as soil characteristics [28], agronomic techniques [29], and metal contamination during the production and storage processes [30]. The availability of studies on the elemental composition of oils obtained from the cold pressing of nuts, fruit kernels, and seeds is very limited. Major and trace elements exert a tremendous influence on all body functions due to trace elements that mediate vital biochemical reactions by acting as cofactors or catalysts for many enzymes. In particular, the accumulation or deficiency of metals may stimulate alternative pathways, which might produce diseases [31].

The major (Na, Mg, K) and trace elements were determined according to the World Health Organization [32]. The detected trace elements were divided into essential (Fe, Zn, Cr, Cu, Mo, Ni, Se, Mn, Co, Ba); probably essential (Li, V, B, Al, Ti); and potentially toxic (Hg, As, Cd, Pb). The contents (mg Kg⁻¹) of major and trace elements determined by ICP-MS analysis in all oil investigated are reported in Table 1 and expressed as means \pm their standard deviations.

The contributions of major and trace elements to the dietary reference intakes (DRIs) (NIH, 2022) were evaluated. DRIs are reference values that vary by age and sex and are used to assess the nutrient intakes of healthy people [33]. These values include: (i) recommended dietary allowance (RDA)—the average daily level of intake sufficient to meet the nutrient requirements of nearly all (97%-98%) healthy people; (ii) adequate intake (AI)—established when evidence is insufficient to develop an RDA and set at a level assumed to ensure nutritional adequacy; and (iii) tolerable upper intake level (UL)—the maximum daily intake unlikely to cause adverse health effects. Moreover, the contribution of toxic metals to the provisional tolerable daily intake (PTDI) was estimated. All evaluations were assessed by considering a daily assumption of around 10 g of vegetable oils for an adult of 60 kg body weight. This value approximates the central value of the average daily consumption of

several vegetable oils in North Africa (11.56 mg kg⁻¹) and Europe (8.43 mg kg⁻¹) [34]. The levels of Na, Mg, and K were variable among all oil samples analyzed. In particular, the highest Mg and Na contents, 52.37 mg kg⁻¹ and 40.75 mg kg⁻¹, respectively, were found in wheat germ oil; while the maximum amount of K of 71. 92 mg kg⁻¹ was detected in apricot kernel oil. The contribution to the RDA of major elements (Na, Mg, K) resulting from the daily consumption of the oils investigated can be summarized as follows: 10 g of wheat germ oil contribute to 0.16 and 0.12% of Mg intake, respectively, for males and females aged between 31–50 years old. The same amount of apricot kernel oil covers 0.02% of K daily intake in males and females aged 31–50 years old. In particular, wheat germ oils showed the highest levels of Mn, Zn, and Ba at amounts of 2.39 mg kg⁻¹, 1.27 mg Kg⁻¹, and 0.38 mg kg⁻¹, respectively.

Table 1. Contents (mg kg⁻¹ w/w) of major and trace elements in the investigated oils and expressed in terms of the mean \pm standard deviation from three samples (N = 3); each of them was analyzed in triplicate.

Elements	Oil Samples					
Licilicities	Apricot Kernel	Bitter Almond	Nigella	Pumpkin Seed	Souchet	Wheat Germ
Major elements						
Na	$29.50\pm4.54~^{\rm a}$	12.51 ± 2.26 ^b	$21.81\pm3.33~^{\rm a}$	9.76 ± 1.29 ^b	$14.55 \pm 2.52^{\ b}$	$40.75\pm5.53~^{\rm c}$
Mg	$20.55\pm3.32~^{\rm a}$	11.80 ± 2.64 ^b	12.14 ± 1.98 ^b	7.48 ± 1.32 ^b	16.62 ± 1.55 ^b	$52.36\pm8.64~^{\rm c}$
ĸ	71.92 ± 9.83 ^a	3.17 ± 0.18 ^b	$23.74\pm3.36~^{\rm c}$	$2.93\pm7.62^{\text{ b}}$	$3.88 \pm 7.62^{\ b}$	5.64 ± 7.62 ^b
Trace elements						
Fe	$3.680\pm0.12~^{a}$	0.261 ± 0.003 ^b	$0.542 \pm 0.001 \ ^{\mathrm{b}}$	0.164 ± 0.07 ^b	$0.247 \pm 0.003 \ ^{\mathrm{b}}$	$0.805 \pm 0.002^{\ \text{b}}$
Zn	0.358 ± 0.003 $^{\rm a}$	0.38 ± 0.005 ^a	0.178 ± 7.62 ^a	0.210 ± 0.01 a	0.183 ± 0.02 a	1.27 ± 0.090 ^a
Cr	0.031 ± 0.001 a	$0.020\pm0.001~^{\rm a}$	$0.029\pm0.002~^{\rm a}$	$0.005 \pm 0.001 \ ^{\mathrm{b}}$	$0.013\pm0.002~^{\rm a}$	$0.011\pm0.003~^{\mathrm{a}}$
Cu	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
Mo	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
Ni	0.037 ± 0.002 $^{\rm a}$	0.007 ± 0.001 ^b	0.010 ± 0.003 ^ a	<lod< td=""><td>0.002 ± 0.001 ^b</td><td>$0.011\pm0.001~^{\rm a}$</td></lod<>	0.002 ± 0.001 ^b	$0.011\pm0.001~^{\rm a}$
Se	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
Mn	0.326 ± 0.02 ^a	0.021 ± 0.040 ^b	0.067 ± 0.030 ^b	0.010 ± 0.001 ^b	0.012 ± 0.001 ^b	$2.390 \pm 0.0830 \ ^{\rm c}$
Co	0.005 ± 0.000 ^ a	0.003 ± 0.000 ^a	0.002 ± 0.000 ^ a	0.001 ± 0.000 ^ a	0.002 ± 0.000 ^ a	$0.003 \pm 0.000~^{a}$
Ba	$0.116\pm0.001~^{\rm a}$	$0.038 \pm 0.002^{\text{ b}}$	0.093 ± 0.013 ^b	0.032 ± 0.009 ^b	0.049 ± 0.007 ^b	$0.386 \pm 0.110 \ ^{\rm c}$
Li	0.005 ± 0.000 ^ a	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>$0.001 \pm 0.000~^{\rm a}$</td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td>$0.001 \pm 0.000~^{\rm a}$</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>$0.001 \pm 0.000~^{\rm a}$</td></lod<></td></lod<>	<lod< td=""><td>$0.001 \pm 0.000~^{\rm a}$</td></lod<>	$0.001 \pm 0.000~^{\rm a}$
V	0.010 ± 0.001 $^{\rm a}$	0.004 ± 0.001 ^b	0.007 ± 0.002 ^b	0.002 ± 0.001 ^b	0.005 ± 0.001 ^b	$0.004 \pm 7.62^{\text{ b}}$
В	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
Al	3.540 ± 0.172 a	0.256 ± 0.020 ^b	0.608 ± 0.018 ^b	0.183 ± 0.090 ^b	$0.336 \pm 0.012^{\ \mathrm{b}}$	0.417 ± 0.015 ^b
Ti	0.003 ± 0.000 a	0.003 ± 0.000 a	0.003 ± 0.000 a	0.003 ± 0.000 a	0.003 ± 0.000 a	$0.003\pm0.000~^{\rm a}$
Hg	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
As	0.010 ± 0.003 $^{\rm a}$	0.001 ± 0.000 ^b	0.001 ± 0.000 ^b	0.001 ± 0.000 ^b	<lod< td=""><td>0.001 ± 0.000 ^b</td></lod<>	0.001 ± 0.000 ^b
Cd	0.002 ± 0.00 $^{\rm a}$	0.002 ± 0.00 a	$0.001\pm0.00~\mathrm{^b}$	$0.001\pm0.00~\mathrm{^b}$	$0.001\pm0.00~^{\rm b}$	$0.001 \pm 0.00 \ ^{\mathrm{b}}$
Pb	0.036 ± 0.001 a	0.056 ± 7.62 a	0.045 ± 7.62 a	$0.042\pm7.62~^a$	0.067 ± 0.004 a	$0.065\pm7.62~^a$

Different superscript letters indicate significantly different values (p < 0.05 by post hoc Tukey's HSD test); the same superscript letters in the same column indicate not significantly different values (p > 0.05 by post hoc Tukey's HSD test).

A daily assumption of 10 g of this oil contributes to 1% and 0.78% of Mn intake, respectively, for males and females aged between 31–50 and to 0.10 and 0.15% of Zn intake, respectively, for males and females aged between 31–50. Zn levels found in the wheat germ oil samples analyzed were higher than those detected by Nasr et al. on Tunisian and European extra virgin olive oils, which varied respectively between 0.03 mg kg⁻¹ and 0.19 mg kg⁻¹ and from 0.03 mg kg⁻¹ to 0.15 mg kg⁻¹. Zinc is known to be involved in most metabolic pathways in humans. It contributes significantly to the proper functioning of the endocrine and exocrine pancreas, spermatogenesis, and testosterone metabolism. Due to its proven anti-inflammatory and antioxidant effect, the attention towards the Zn levels in food matrices has significantly increased [33]. Regarding the Fe content, the highest

value, namely, 3.69 mg kg⁻¹, was found in the apricot kernel oils, while the lowest value of 0.16 mg kg⁻¹ was detected in the pumpkin seed oil.

Then, a daily consumption of 10 g apricot seed oil contributes to 0.20% and 0.46% of Fe intake, respectively, for females and males aged between 31–50. Iron is a trace element of central importance for human health, as its deficiency causes microcytic anemia and the possible onset of cardiovascular disease [35]. The spread of new eating habits, such as vegetarian diets, requires for a proper balanced intake of essential micronutrients such as Fe that can be provided by vegetable oils. Regarding to the essential elements, Li levels were <LOD for pumpkin seed, bitter almond, and soushet oils, while 0.001 mg kg⁻¹ were found in wheat germ oils and 0.005 mg·kg⁻¹ were found in apricot kernels oils. All oil analyzed showed a content of B < LOD, while the average content of Ti was the same (0.003 mg kg⁻¹) for all type of oils analyzed.

The levels of V resulted in a range between 0.002 mg kg⁻¹ in pumpkin seeds oils and 0.01 mg kg⁻¹ in apricot kernels. The highest level of Al, 3.54 mg kg⁻¹, was found in apricot kernel, while the pumpkin seed oils showed the lowest level of this element at 0.183 mg kg^{-1} . The results confirmed that Li, B, Ti, Li, and V mean levels detected were well below the established TULs for these elements [35]. The potentially toxic elements, Pb, Cd, and Hg, are included in the European regulation setting maximum levels of certain contaminants in foodstuffs (Commission Regulation (EU) No. 1881/2006) [36]. The levels of Hg were < LOD for all types of oil analyzed; the contents of Pb were in a range between 0.036 mg kg^{-1} for apricot kernel and 0.067 mg kg^{-1} for souchet oils; the concentration of Cd was around 0.001 mg kg⁻¹ in wheat germ, pumpkin seed, souchet, and nigella oils, and it was approximately 0.002 mg kg^{-1} in bitter almond and apricot kernel; this last showed the highest value of As at 0.01 mg kg⁻¹. The levels of Pb were well below the maximum levels of 0.10 mg kg⁻¹ as fixed by EU Reg. N. 1881/2006 for this element in oils and fats. Moreover, the contribution of the daily portion (10 g) of each oil to the estimated benchmark dose level/limit (BMDL₀₁) of As (0.0003–0.008 mg kg⁻¹ bw day⁻¹) may be considered negligible, assuming total the As to be equal to the levels of inorganic As set by the European Food Safety Authority [37,38].

Finally, PTDI values of Cd were calculated considering the provision tolerable weekly intake (PTMI) of Cd (0.025 mg kg⁻¹ bw month) set by the Joint FAO/WHO Expert Committee on Food Additives [39,40]. The cadmium intake determined by a daily consumption of 10 g of bitter almond covers a maximum of 2.5% of the PTDI established for this element.

3.2. Total Polyphenol Determination

Quantifying the total contents of polyphenols in vegetable oils is essential to identify their health and nutritional values. These compounds play an important role in the prevention of degenerative diseases such as cancer, cardiovascular disease, and osteoporosis. Moreover, thanks to their antioxidant and anti-inflammatory properties, polyphenols preventoxidative damages [41]. The concentrations of total polyhenols in the different oils analyzed are reported in Table 2. Nigella oil showed the highest total polyphenols content (109.01 mg GAE kg⁻¹). According to several studies, the oil of Nigella sativa is usually considered to be stable to oxidation, due to its reducing phenolics that neutralize the radical reactions responsible for lipid oxidation. For these reasons, Nigella oil is considered a highly exploitable multi-purpose product for industrial, nutritional, cosmetic, and pharmaceutical uses [42]. Looking at the literature, the total polyphenols detected by Cheikh-Rouhou in Tunisian and Iranian samples of Nigella sativa seed oil, obtained by cold solvent extraction, were equal to 245.00 mg GAEs kg⁻¹ and 309.02 mg GAEs kg⁻¹, respectively. These higher values are justified by the fact that solvent extraction is certainly more effective [42].

Oil Samples	Total Polyphenols
Apricot kernel	50.04 ± 2.31 a
Bitter almond	44.11 ± 1.97 a
Nigella	109.01 ± 7.62 ^b
Pumpkin seed	48.03 ± 1.44 a
Souchet	46.06 ± 1.24 a
Wheat germ	47.03 ± 1.58 a

Table 2. Levels (mg GAEs kg⁻¹) of total polyphenols in the investigated oils, expressed as the mean \pm the standard deviation of three samples (N = 3); each of them was analyzed in triplicate.

Different superscript letters indicate significantly different values (p < 0.05 by post hoc Tukey's HSD test); the same superscript letters in the same column indicate not significantly different values (p > 0.05 by post hoc Tukey's HSD test).

3.3. Determination of Fatty Acid Profile

Each group of fatty acids (saturated, monounsaturated, and polyunsaturated) and individual fatty acids (FAs) has a specific role in many biopathways, and imbalance in their dietary intake could result in many serious illnesses, such as cardiovascular and autoimmune disease, as well as diabetes [43]. The FA profile of the oils examined is reported in Table 3. The results are expressed as mean GC-FID peak area percent \pm standard deviation. The major levels of SFAs were detected in souchet, pumpkin seed, and wheat germ oils (22.80%; 17.55%; and 16.82%, respectively). In particular, the highest levels of palmitic and stearic acids were respectively observed in wheat germ (15.39%) and souchet (8.15%) oils. The apricot kernel oil showed the lowest amount of palmitic (5.93%) and stearic (1.46%) acids. Comparable contents of total SFAs were estimated by Cicero et al. 2018 in Brazilian cold-pressed olive (16.73%), avocado (16.93%) and macadamia (14.56%) oils. In this work, the highest levels of monounsaturated fatty acids (MUFAs) were observed in bitter almond (65.28%) and souchet (64.72%), while the wheat germ oils showed the lowest level (20.80%) [44]. The MUFA profiles of all oils investigated in this work were strongly influenced by the content of oleic acid (18:1n9). Indeed, very significant levels of oleic acid were detected in bitter almond (64.55%); souchet (64.23%); and apricot kernels (56.93%). All samples showed low contents of palmitoleic acid (16:1n-7) and eicosenoic (20:1n-9) acid. Comparable values of MUFAs were observed by Orsavova et al. 2015 in coldpressed oils from almond (67.90%) and wheat germ (20.90%). Investigated polyunsaturated fatty acids (PUFAs) were mainly represented by linoleic (18:2 n-6), α -linolenic (18:3n-3), and arachidonic (20:4n-6). The highest PUFA contents were detected in wheat germ (61.01), nigella (57.12%), pumpkin seeds (46.81%), and apricot kernels (32.32%), while souchet oils revealed the lowest content of PUFAs (11,53%), followed by bitter almond (23.98%). Very similar average levels of PUFAs in pumpkin seed oils were detected by Orsavova et al. 2015 (54.30%) [44]. Linoleic acid was the prevalent polyunsaturated fatty acid in all oils analyzed, and its values ranged from 55.65% in wheat germ to 11.53% in souchet oils. The α -linolenic content ranged from 0.06% in bitter almond to 5.24% in wheat germ. This last value in really interesting, since it was higher when compared to the 1.2% value determined on the same type of oil by Orsavova et al. 2015 [44]. Cold-pressed oils usually contain significant levels of α -linolenic acid. The principal biological role of α -linolenic acid (α -LNA; 18:3n-3) appears to be as a precursor for the synthesis of longer chain n-3 polyunsaturated fatty acids (PUFA). Increasing α -LNA intake for a period of weeks to months results in an increase in the proportion of eicosapentaenoic acid (EPA; 20:5n-3) in plasma lipids, in erythrocytes, leukocytes, platelets, and in breast milk, but there is no increase in docosahexaenoic acid (DHA; 22:6n-3), which may even decline in some pools at high α -LNA intakes [45,46]. The detected MUFA profiles of bitter almond, souchet, and apricot kernel were very similar to the levels observed by Kostik et al. 2013 in peanut (58.5%) and canola (59.5%) oils, while the PUFA profiles of wheat germ, nigella, and souchet were comparable with those determined by Kostik et al. 2013 for corn (25.1%), cottonseed (22.4%), linseed (22.10%), and palm kernel (22.50%) oils [47].

Fatty A side	Oil Samples						
Fatty Actus	Apricot Kernel	Bitter Almond	Nigella	Pumpkin Seed	Souchet	Wheat Germ	
C14:0	$0.01\pm0.003~^{\rm a}$	$0.04\pm0.001~^{\text{a}}$	$0.15\pm0.007~^{b}$	$0.13\pm0.27^{\text{ b}}$	$0.12\pm0.27^{\text{ b}}$	0.09 ± 0.27 ^c	
C16:0	5.93 ± 0.21 $^{\rm a}$	$7.03\pm0.74~^{\rm a}$	12.01 ± 1.11 ^b	11.7 ± 1.04 ^b	13.53 ± 0.90 ^b	15.39 ± 1.29 ^b	
C16:1n-7	0.87 ± 0.002 $^{\rm a}$	0.57 ± 0.001 ^b	$0.21\pm0.007~^{\rm c}$	$0.17\pm0.002^{\text{ c}}$	$0.27\pm0.09~^{\rm c}$	$0.27\pm0.001~^{\rm c}$	
C17:1n-7	0.04 ± 0.001 $^{\rm a}$	0.06 ± 0.017 $^{\rm a}$	$0.07\pm0.005~^{\rm a}$	0.12 ± 0.02 ^b	0.07 ± 0.014 $^{\rm a}$	$0.05\pm0.005~^{a}$	
C17:1n-9	0.12 ± 0.027 ^a	0.09 ± 0.007 $^{\rm a}$	0.05 ± 0.003 ^b	$0.06 \pm 0.001 \ ^{ m b}$	$0.03 \pm 0.002 \ ^{\mathrm{b}}$	$0.05 \pm 0.015 \ ^{\rm b}$	
C18:0	1.46 ± 0.27 a	2.81 ± 0.27 ^b	3.44 ± 0.27 ^b	$5.18\pm0.27~^{ m c}$	8.15 ± 0.27 ^d	0.95 ± 0.27 $^{\mathrm{a}}$	
C18:1n-9	56.93 ± 3.23 a	64.55 ± 2.47 ^b	$25.24\pm2.36~^{\rm c}$	$34.28\pm1.21~^{\rm c}$	64.23 ± 2.15 ^b	$19.15 \pm 1.55 \ { m d}$	
C18:2n-6	32.19 ± 2.32 a	23.92 ± 1.97 ^b	54.1 ± 3.17 ^c	46.49 ± 2.22 ^d	$11.36\pm1.36~^{\rm e}$	55.65 ± 2.98 ^c	
C18:3n-3	0.13 ± 0.004 a	$0.06 \pm 0.001 \ ^{ m b}$	$0.54\pm0.002~^{\rm c}$	0.32 ± 0.008 ^d	$0.17\pm0.009~{\rm e}$	5.24 ± 0.15 $^{ m f}$	
C20:0	$0.14\pm0.05~^{\rm a}$	$0.16\pm0.02~^{\rm a}$	0.24 ± 0.003 ^b	$0.36 \pm 0.007 {}^{\mathrm{b}}$	$0.87\pm0.002~^{\rm c}$	$0.15\pm0.001~^{a}$	
C20:1n-9	0.08 ± 0.001 $^{\rm a}$	0.07 ± 0.001 $^{\rm a}$	0.32 ± 0.09 ^b	$0.12\pm0.01~^{\rm c}$	$0.19\pm0.007~^{\rm c}$	1.33 ± 0.07 ^d	
C20:2n-6	0.01 ± 0.001 $^{\rm a}$	0.02 ± 0.001 $^{\rm a}$	2.48 ± 0.07 $^{ m b}$	$0.01\pm0.002~^{\rm a}$	$0.01\pm0.001~^{\rm a}$	$0.12\pm0.008~^{\rm c}$	
C22:0	$0.06\pm0.002~^{\rm a}$	$0.02 \pm 0.001 \ ^{\mathrm{b}}$	0.03 ± 0.001 ^b	0.03 ± 0.001 ^b	0.03 ± 0.002 ^b	$0.08\pm0.002~^{\rm c}$	
C24:0	0.05 ± 0.004 $^{\rm a}$	$0.02 \pm 0.001 \ ^{\mathrm{b}}$	0.02 ± 0.001 ^b	$0.03 \pm 0.002^{\ \mathrm{b}}$	$0.03 \pm 0.001 \ ^{\mathrm{b}}$	$0.09\pm0.003~^{\rm c}$	
SFA	7.69 ± 1.46 $^{\rm a}$	10.14 ± 2.39 ^b	$15.96\pm1.98~^{\rm c}$	$17.55\pm2.44~^{\rm c}$	22.80 ± 3.49 ^d	$16.82\pm1.91~^{\rm c}$	
MUFA	58.00 ± 2.57 $^{\rm a}$	65.28 ± 2.81 ^b	$25.82\pm1.25~^{\rm c}$	34.63 ± 1.88 ^d	$64.72 \pm 1.39 \ ^{b}$	$20.80\pm1.57~^{\rm c}$	
PUFA	$32.32\pm0.27~^{a}$	$23.98\pm0.27~^{b}$	$57.12\pm0.27~^{\rm c}$	$46.81\pm0.27~^{\rm d}$	$11.53\pm0.27~^{\rm e}$	$61.01\pm0.27~^{\rm f}$	

Table 3. Individual fatty acids and total SFA, MUFA, PUFA composition (mean GC-FID peak area percent \pm standard deviation.) of examined oils, expressed as the mean \pm the standard deviation of three samples (N = 3); each of them was analyzed in triplicate.

Different superscript letters in the same row indicate significantly different values (p < 0.05 by post hoc Tukey's HSD test); the same superscript letters in the same column indicate not significantly different values (p > 0.05 by post hoc Tukey's HSD test).

3.4. Measurement of Squalene

Squalene, a polyunsaturated triterpene containing six isoprene units, is a basic intermediate product in sterols biosynthesis [48]. Many physiological functions, such as anticancer action, the reduction of serum cholesterol levels, enhancing immune responses and anti-aging, have made it widely used in medicine, foods, and cosmetic sectors [49]. The squalene levels detected are reported in Table 4. Pumpkin seeds oils showed the highest levels at 1160.01 mg kg⁻¹, followed by bitter almond at 200.10 mg kg⁻¹.

Table 4. Contents (mg kg⁻¹ w/w) of squalene in the investigated oils. Expressed as mean \pm the standard deviation of three samples (N = 3); each of them was analyzed in triplicate.

Oil Samples	Squalene		
Apricot kernel	151.01 \pm 7.77 $^{\mathrm{a}}$		
Bitter almond	200.10 ± 9.48 ^b		
Nigella	49.90 ± 4.64 ^c		
Pumpkin seed	1160.01 ± 22.44 ^d		
Souchet	46.06 ± 1.24 c		
Wheat germ	133.04 ± 9.63 a		

Different superscript letters indicate significantly different values (p < 0.05 by post hoc Tukey's HSD test); same superscript letters in the same column indicate not significantly different values (p > 0.05 by post hoc Tukey's HSD test).

The high content of squalene in pumpkin seed oil and the ability of squalene to potentiate the cytotoxicity and antitumor effects of anticancer agents promotes these oils as valuable functional foods with, among the others, positive effects on small urinary disorders [50]. The contents of squalene in bitter almond, apricot kernels, and wheat germ oils were very comparable with those reported for camellia oil: 160.00 mg kg⁻¹ was reported by Xie Su and Liang 2012, and, for grape seed oil, 130 mg kg⁻¹ was reported by Wen et al. 2016 [51,52].

3.5. Phytosterols Profiling

Phytosterols are regarded as powerful nutraceutical ingredients due to their effects on blood cholesterol reduction and potential contributions to cardiovascular disease prevention [53]. The compositions and contents of single and total sterols were determined, and the results are reported in Table 5. Wheat germ oil showed the highest content of total sterols at 1713.80 mg/100 g of oil, followed by apricot kernels at 285.55 mg/100 g of oil and pumpkin seeds at 218.33 mg/100 g of oil. The most prevalent sterols was β -sitosterol, and its content ranged between 987.57 mg/100 g of oil in wheat germ and 67.35 mg/100 g of oil in nigella.

Table 5. Contents of single (%) and total (mg/100 g of oil) sterols in the investigated oils, expressed as mean \pm the standard deviation of three samples (N = 3). Each of them was analyzed in triplicate.

	Oil Samples					
Sterols	Apricot Kernel	Bitter Almond	Nigella	Pumpkin Seed	Souchet	Wheat Germ
Colesterol	0.24 ± 0.04 a	0.26 ± 0.01 $^{\rm a}$	$1.08\pm0.07^{\text{ b}}$	0.24 ± 0.02 a	0.37 ± 0.05 $^{\rm a}$	0.10 ± 0.04 ^b
Brassicasterol	0.48 ± 0.26 $^{\rm a}$	$0.00\pm0.00~^{\rm b}$	$0.00\pm0.00~\mathrm{^b}$	0.00 ± 0.00 ^b	$0.15\pm0.05~^{\rm c}$	0.00 ± 0.00 b
Campesterol	3.61 ± 1.22 ^a	2.92 ± 0.99 ^b	$11.14\pm2.37~^{ m c}$	$3.28\pm0.92~^{\rm c}$	$15.23\pm3.399~^{\rm c}$	$22.83\pm9.01~^{\rm c}$
Campestanol	0.37 ± 0.02 $^{\rm a}$	$0.29\pm0.01~^{\rm a}$	1.01 ± 0.08 $^{\rm a}$	0.40 ± 0.04 a	0.48 ± 0.04 a	2.21 ± 2.25 ^b
Stigmasterol	10.15 ± 3.17 $^{\rm a}$	$3.95\pm1.17^{\text{ b}}$	$13.91\pm2.13~^{\rm c}$	5.36 ± 1.31 ^b	16.27 ± 2.42 ^a	1.38 ± 2.15 $^{\rm a}$
Δ^7 -campesterol	0.30 ± 0.27 $^{\rm a}$	0.66 ± 0.27 $^{\rm a}$	1.08 ± 0.27 $^{\rm a}$	0.71 ± 0.27 ^a	0.74 ± 0.27 $^{\mathrm{a}}$	1.88 ± 0.27 ^b
Clerosterol	0.72 ± 3.23 ^a	0.97 ± 2.47 $^{\rm a}$	$0.84\pm2.36~^{a}$	1.87 ± 1.21 ^b	0.77 ± 2.15 ^a	$0.59\pm1.55~^{\rm c}$
β-Sitosterolo	70.93 ± 2.32 $^{\rm a}$	$72.93\pm3.97^{\text{ b}}$	$51.43\pm4.27~^{\rm c}$	$49.25\pm4.22^{\text{ b}}$	56.46 ± 3.36 ^b	57.62 ± 7.98 ^d
Δ^5 -avenasterol	$8.85\pm1.94~^{\rm a}$	13.04 ± 1.91 $^{\rm a}$	$14.93\pm1.52~^{\rm a}$	$3.78\pm1.18^{\text{ b}}$	2.71 ± 0.99 ^b	$5.78\pm2.33~^{\rm c}$
$\Delta^{5,24}$ -stigmastanol	1.04 ± 0.09 $^{\rm a}$	1.36 ± 0.03 $^{\rm a}$	1.51 ± 0.04 $^{\rm a}$	14.17 ± 2.27 ^b	0.71 ± 0.07 ^a	1.44 ± 2.51 ^b
Δ^7 -stigmastenol	2.30 ± 1.13 ^a	2.51 ± 0.91 $^{\rm a}$	1.95 ± 0.89 ^b	$9.31\pm1.15~^{\rm c}$	4.54 ± 1.67 ^a	2.22 ± 4.45 ^d
Δ^7 -avenasterolo	$100\pm0.09~^{\rm a}$	$1.12\pm0.08~^{a}$	1.93 ± 0.09 $^{\rm a}$	11.63 ± 2.52 ^b	1.56 ± 0.05 $^{\rm a}$	$3.95\pm2.48~^{\rm c}$
Total Sterols	$285.3\pm12.52~^{a}$	$212.8\pm9.97~^{a}$	$131.0 \pm 5.691 \ ^{\rm b}$	$218.2\pm11.05~^{\rm a}$	$215.3\pm10.42~^{\rm a}$	$1713.8\pm24.62~^{\rm c}$

Different superscript letters in the same row indicate significantly different values (p < 0.05 by post hoc Tukey's HSD test); the same superscript letters in the same column indicate not significantly different values (p > 0.05 by post hoc Tukey's HSD test).

Wheat germ oils showed the highest levels of campesterol (391.19 mg/100 g of oil), campestanol (37.90 mg/100 g of oil), Δ^7 -campesterol (23.66 mg/100 g of oil), Δ^5 -avenasterol (99.13 mg/100 g of oil), Δ^7 -stigmasterol (37.96 mg/100 g of oil), and Δ^7 -avenasterol (67.63 mg/100 g of oil). The highest levels of $\Delta^{5,24}$ -stigmastanol (30.92 mg/100 g of oil) were detected in pumpkin seeds oils, while the lowest content was detected in nigella oil (1.51 ± 0.07 mg/100 g of oil). The levels of β -sitosterol detected in wheat germ oils were significantly higher than the levels presented by Han et al. 2018 in corn oil (266.33 mg/100 g of oil) [54]. β -sitosterol possesses various biological actions such as anxiolytic and sedative effects, analgesic, immunomodulatory, antimicrobial, anticancer, hepatoprotective, antioxidant, and antidiabetic activities [55]. The European Foods Safety Authority (EFSA) suggested that consumption of about 1.5–2.4 g/day of phytosterols reduces cholesterol levels in the blood, thus protecting against heart disease, and it is also approved by the U.S. Food and Drugs Administration (FDA) [56]. Therefore, a daily consumption of 10 g of wheat germ oils, apricot kernel oils, and souchet oils contributes respectively to 11.4%, 1.90% and 1.45% of the minimum recommended daily consumption of phytosterols.

3.6. α -Tocopherol Levels

Vitamin E has a significative impact on the prevention of chronic diseases, and it is considered to be a strong antioxidant agent that protects cell membranes from the lipid peroxidation chain reaction [52]. α -Tocopherol is the most available bioactive form of vitamin E and has shown strong antioxidative and immunoregulatory properties [57]. The α -tocopherol levels were found in all investigated oils, and the results are reported in

Table 6. The highest levels of α -tocopherol were detected in wheat germ oils (263.07 mg kg⁻¹), followed by bitter almond (193.03 mg kg⁻¹) and souchet oils (129.11 mg kg⁻¹). These results were compared with those obtained, using the same analytical approach, by Grilo et al. 2014 from different Brazilian vegetable oils [58]. The average contents of α -tocopherol were comparable with our determination from almond and souchet oils, which resulted in 120.3 mg kg⁻¹ from canola oils and 173.0 mg kg⁻¹ from corn oils.

Table 6. Levels of (mg Kg⁻¹ w/w) of α -tocopherol in the investigated oils expressed as mean \pm standard deviation of three samples (N = 3). Each of them was analyzed in triplicate.

Oil Samples	α-Tocopherol		
Apricot kernel	59.32 ± 3.39 ^a		
Bitter almond	193.03 ± 8.89 ^b		
Nigella	17.13 ± 2.24 c		
Pumpkin seed	37.07 ± 6.64 a		
Souchet	129.11 ± 9.63 ^b		
Wheat germ	263.07 ± 11.11 ^e		

Different superscript letters in the same row indicate significantly different values (p < 0.05 by post hoc Tukey's HSD test); same superscript letters in the same column indicate not significantly different values (p > 0.05 by post hoc Tukey's HSD test).

According to the dietary reference intakes (DRIs), the daily recommendation (RDA) of vitamin E for healthy individuals from 14 years onward is 15 mg of alpha-tocopherol [59]. The contribution to the RDA of vitamin E resulting from the daily consumption of the oils investigated can be summarized as follows: a daily consumption of 10 g of wheat germ, bitter almond, or souchet oil contribute to 17.53%, 12.86%, and 8.6%, respectively, of alpha-tocopherol daily intake.

4. Conclusions

In this work, the phytochemical profiles of a variety of Tunisian edible oils obtained by the cold pressing of nuts, fruit kernels, and seeds were traced. All the oils analyzed were considered to be less used plant sources. The observed results indicated and estimated the nutritional and healthy potential of these oils in order to individuate their possible inclusion in foods replacing conventional ingredients or as fortifying and functional ingredients. Indeed, an effective placement of these edible oils in the food sector could represent a circular and sustainable strategy to meet the consumption of an increasing global population. The obtained phytochemical profiles varied considerably. Concerning the essential elements concentration, wheat germ oil had the highest levels of Mg, Na, Mn, Zn, and Ba, while apricot kernel oil had the highest level of K and Fe. In all the oils investigated, the levels of Li, B, Ti, and V were well below the established tolerable upper intake levels (TULs) for these elements, while the levels of potentially toxic elements, including Pb, Cd, and Hg, were within the maximum levels established by the European Regulation for these contaminants in foodstuffs.

Wheat germ oil showed the most significant nutritional and healthy impact but also good quality and storability characteristics. This can be deduced from the high levels of several major and trace elements as well as from the contents in phytosterols and α -tocopherol. In fact, a daily consumption of 10 g this oil contributes to 17.53% of alphatocopherol daily intake and 11.4% of the minimum recommended daily consumption of phytosterols. The highest levels of squalene detected in pumpkin seeds oils (more than 1100 mg kg⁻¹ w/w) may make it possible to propose it as valuable functional food with health-promoting effects, especially for the urinary tract. The high total polyphenolic content found in nigella oils justifies the stability and antioxidant properties of this oil, thus suggesting its use in the food and non-food sectors. The study provides valuable information on the FA profiles of different oils and their potential health implications. Oleic acid was the predominant MUFA in all the oils, with bitter almond, souchet, and apricot kernels having very significant levels of this fatty acid. Palmitoleic and eicosenoic acids were present in low amounts in all the oils. Wheat germ, nigella, pumpkin seed, and apricot kernel oils had the highest contents of PUFAs, and linoleic acid was the prevalent polyunsaturated fatty acid in all the oils.

The overall fatty acid profile of apricot kernel, bitter almond, and souchet oils is indicative of their ability to counteract serious pathologies such as cardiovascular diseases, inflammatory, autoimmune, and metabolic syndrome. In the future, the usual consumption of these presently considered minor oils may represent an interesting and convenient source of bioactive compounds with beneficial effects for both human health, and nutrition.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/agriculture13051096/s1, Table S1: Operative conditions for the microwave oven digestion; Table S2: ICP-MS experimental parameters; Table S3: Analytical parameters for method validation; Table S4: Contents (mg/100 g of oil) of single and total sterols in the investigated oils expressed as mean \pm standard deviation of three samples (N = 3); each of them was analyzed in triplicate.

Author Contributions: R.V.: Conceptualization; Writing, Reviewing, and Editing; Data curation; V.N.: Methodology, Formal analysis and Data curation; V.L.T.: Conceptualization, Writing, Reviewing, and Editing; A.S.: Reviewing, Supervision, Reviewing, and Editing; Validation; A.G.P.: Data curation; Validation; R.C.: Validation, Writing; Reviewing, and Editing; R.R.: Methodology, Formal analysis and Data curation; H.B.M.: Supervision; N.B.A.: Investigation, Data curation; A.B.: Investigation; G.D.B.: Conceptualization, Validation, Supervision, and Project Administration; Funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data Availability Statements are available in Supplemantary Materials: Tables S1–S4.

Conflicts of Interest: The authors declare no conflict of interest.

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