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Article

Measurement: Food 10 (2023) 100082

Contents lists available at ScienceDirect

Measurement: Food

journal homepage: www.elsevier.com/locate/meafoo

Comparative assessment of different coconut oils: Chromatographic and spectrometric analyses of pesticide residues, toxic heavy metals, and associated contents ☆,☆☆

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ARTICLE INFO

Keywords:
Pesticides
Heavy metals
Coconut oil
Nigerian
Toxicity
Bioaccumulation

ABSTRACT

The nutrients, toxic metals and pesticide levels of imported and local samples of coconut oil were determined using ICP-OES and HPLC following standard procedures. The imported coconut oil contains significantly higher levels of lead, cadmium, arsenic, nickel, aluminium and chromium (0.01-0.03 mg/kg) than the local samples (0.008-0.02 mg/kg). Nineteen pesticide residues were detected in the oil samples with varying levels ranging from 0.03 to 7.10 µg/kg oil. Interestingly, the levels of the toxic metals and pesticide residues were several folds lower compared to the FAO/WHO, EU and China limits (0.05-1.0 mg/kg). The essential amino acids, nutrient elements and vitamin profile levels were comparable to the WHO reference standards for dietary proteins. These findings suggest that coconut oil is nutritionally beneficial to human health. However, monitoring contamination of pesticide residues and toxic metals in imported coconut oil is crucial to avoid toxic health hazards due to bioaccumulation.

Ethical statement: Our sample was oil and non-living organism. Therefore, ethical clearance or statement is not applicable to this study. Thank you.

1. Introduction

Coconut tree (*Cocos nucifera L.)* is an economic tree and food source ubiquitously distributed in several countries in different regions globally. The mature coconut fruit may be consumed raw or used in preparation of rice delicacies and extraction of coconut oil. Coconut oil is traditionally consumed in Sri Lanka, India, Thailand, Philippines, Indonesia and the islands of the South Pacific and parts of West Africa, including Nigeria [1]. Recently, the demand for coconut oil has increased rapidly in the Western countries due to its notable beneficial health effect [2]. However, the chemistry of coconut oil shows that it contains medium-chain saturated fatty acids corresponding to 64% of total fat and are responsible for the oil's cooking flavor, long shelf-life and resistance to oxidation [3–5]. Literature reveals that coconut oil extracted from coconut meat by wet method (virgin coconut oil) possesses pharmacological health benefits than commercial copra oil extracted by dry method and processed via refining, bleaching and deodorizing [6,7]. The virgin coconut oil contains tocopherols and bioactive phytochemicals associated with its numerous biological effects [2,6,8–10].

Many studies have shown that coconut oil lowers blood glucose level and lipid profile [11], prevents toxicities of anticancer drugs and gentamicin on many organs [8,9], helps to reduce arthritis [12], prevent bacteria growth [13], oxidative stress [14], and inflammation [12,15]. Studies have suggested that these beneficial health effects can be caused

☆ Source of Funding: Self-funded work
☆☆ The authors declare no conflict of interest
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https://doi.org/10.1016/j.meafoo.2023.100082
Received 19 October 2022; Received in revised form 15 February 2023; Accepted 17 February 2023
2772-2759/

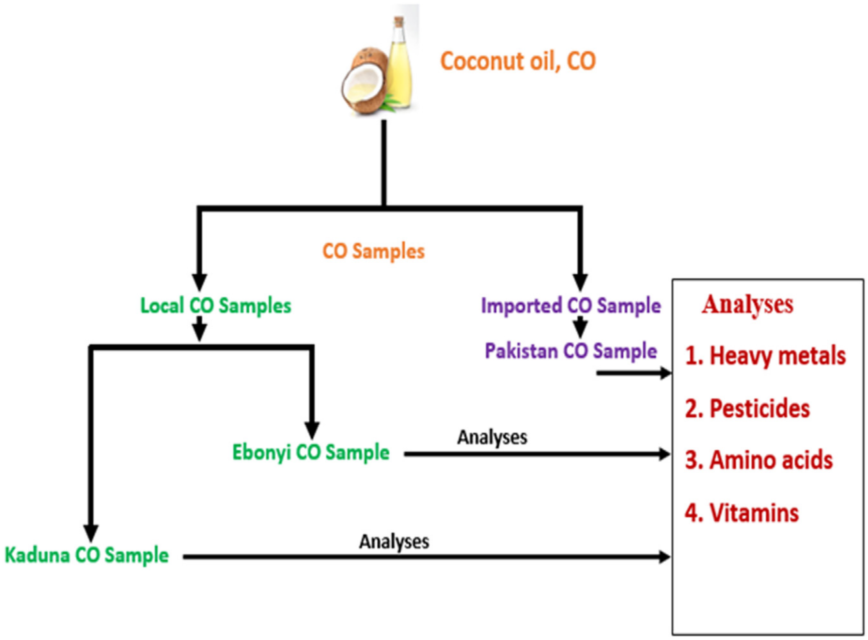

Fig. 1. Schematic overview of the experimental design and analysis.

by the phenolic compounds present in coconut oil [15,16]. In another very recent study, coconut oil enhances the absorption of chlorogenic acid in humans [17]. Saturated fatty acids are the major components of coconut oil regardless of the method of extraction. Some of these saturated fatty acids have been associated with beneficial properties that promote human health [2,5,10]. In addition to the anticancer effect of the major fatty acid, lauric acid [5,10], the study of Zhu et al. [18] found that medium-chain length fatty acids derived from coconut oil are potent repellants of blood-sucking insect vectors, including biting flies, ticks, bed bugs and mosquitoes. Fatty acid-related compounds and inorganic salts used as cosmetic products have also been reported as components of coconut oil [19]. Its popularity is growing and the public awareness of it is increasing. Therefore, the demand for coconut oil for domestic use and consumption is increasing globally. Heavy metals, including toxic lead (Pb), arsenic (As), and cadmium (Cd) have been found in similar natural oils like sesame oil, corn oil, soybean oil, olive oil, sunflower oil and cottonseed oil [20,21]. It is known that Cd, Pb, As and mercury (Hg) are classic toxicants even at low levels; they cause debilitating oxidative effects on health [21]. Extensive use of agrochemicals for crop production is an unavoidable source of pesticides [22]. Therefore, heavy metals and pesticides contaminate plant soil via environmental anthropogenic activities, application of fertilizers and metal-containing agrochemicals [21,22,23]. Food crops take up heavy metals and pesticides via root uptake or by direct deposition from the atmosphere onto plant surfaces. Existing literature reveals that lipid components and phytochemicals of coconut oil have been delineated and published [2,3,6,7,10]. There is a paucity of reports on the contents of heavy metals and pesticide residues in coconut oil worldwide. However, the coconut pulp obtained from coconut samples in Brazil were found to contain different pesticides [24]. Furthermore, coconut water and coconut pulp from three different regions of Brazil were reported to contain pesticides, although below the recommended standards [25]. Pesticides and heavy toxic metals were detected in both fresh and packaged tender coconut water collected from the southern states of India (Andhra Pradesh, Kerala, and Tamil Nadu) [26]. To our knowledge currently, there are no report on the contents of these contaminants in coconut oil used or consumed in Nigeria. To bridge this gap, we have attempted in this study to determine the profile levels of heavy metals, pesticide residues, amino acids and vitamins in coconut oil samples extracted in Nigeria and a sample imported to Nigeria for various uses, including domestic consumption.

2. Materials and methods

2.1. Sample collection

A sealed small bottle of coconut oil imported to Nigeria for sale was purchased in an open commercial market in Kaduna, Kaduna State, Nigeria. The imported oil was produced by Hemani International KEPZ, Karachi, Pakistan. The Nigerian coconut oil samples were obtained from local producers of commercial coconut oil (as labelled virgin coconut oil) from Faith Avenue, Kakau, Kaduna (North-West, Nigeria) and 8 Lagos Street, Old Meat Market, Abakaliki, Ebonyi State (South-East, Nigeria). The oils were purchased between July and August, 2021. The samples were contained in 10 ml sample bottles and stored frozen till analysis. The schematic overview of the experimental design is shown in Fig. 1.

2.2. Heavy metal analysis

At the initial stage, vials and glasswares were washed with soap and rinsed with tap water. Afterward, they were submerged in 14% HNO_3 (v/v) for 24 hours, and then cleaned with deionized water and dried. Deionized water was used for the preparation of solutions; reagents and chemicals were of analytical grade. The heavy metals were analysed by ICP-OES (Model: Perkin Elmer Optima 8000, USA) after the digestion of the oil samples using Kjeldahl digester (VELPE SCIENTIFIC, Japan). According to the method of Hafuka et al. [27]. Two (2) grammes of oil sample was added to 80 mL of 0.1 M HCl and the mixture was stirred at room temperature for 10 min. The mixture was centrifuged (10 min at 8000 g) and the supernatant filtered using a 1.0-μmpore-size cellulose ester membrane to obtain the extract. One (1) mL of concentrated HNO_3 plus 9 mL of extract were added in 10 mL test tubes. The extract in the acid sample was injected into inductively coupled plasma-optical emission spectrometer (ICP-OES) for determination of heavy metal levels in triplicate analysis [28,29].

2.3. Analysis of pesticide residues

The analysis of pesticide residues followed the method described by Emmanouil et al. [30]. Dilution standard solutions were prepared from stock solutions with acetonitrile with their respective dilution solvents. The samples dissolved in 100 μL acetonitrile was vortexed for about

30 seconds and 20 μL were injected in the HPLC-DAD system, Agilent Technologies 1200 series model (Agilent Technologies, Waldbronn, Germany), which consisted of an on-line degasser system, a thermo stated column compartment, a quaternary gradient pump, a Rheodyne injector valve with a 20 μL loop (Cotati, CA, USA) and a DAD.

2.3.1. Chromatographic condition

The chromatographic separation was of the selected compounds was done by Reverse Phase C18, 5 μm (250 × 4.6 mm) column (MZ Analysentechnik, Mainz, Germany). The mobile phase consisted of acetonitrile: water (30:70% v/v) and a gradient program was applied from 30:70% v/v (t=0 min) to 100:0% v/v (t=14 min). The column was thermo stated at 30°C during analysis as detailed in a previous study [29].

2.4. Analysis of water-soluble vitamins

Water soluble vitamins were estimated by HPLC with UV detector (Agilent Technologies Model 1200, Germany) according to the procedures of Otemuyiwa and Adewusi [31]. Two (2) grammes of oil was weighed into 200 mL Erlenmeyer flask to which 30 mL of 0.1 M HCl was added. The mixture and the mixture was subjected to heat at 40°C for 5 minutes. After heating, the mixture was filtered using a filter paper and the filtrate was centrifuged for 10 minutes at 1800 rpm. The supernatant was sonicated and 20 μL was injected into the column and separated. Peaks were identified by comparing the retention time to that of known standards and the value of vitamins was obtained from computer printout (Chemstation software).

2.4.1. Chromatographic conditions

The reverse type-HPLC was a reversed phase type with column and stainless steel (4.6 × 150 mm) Eclipse XDD, and 5 μm C18 columns with an integrated UV detector which was set at 254 nm wavelength to monitor the column effluent. The mobile phase is 90% 0.01M sodium mono-hydrogen phosphate and 10% HPLC grade methanol sonicated for 30 min before use. The elution was isocratic and the flow rate was 0.60 mL/min [31].

2.5. Analysis of fat-soluble vitamins

The vitamins A, D, E and K contents of the oil samples were estimated by Qian and Sheng method [32]. Two (2) grammes of oil was weighed into a 10 mL extraction tube. Afterwards, n-hexane (4 mL) was added and flushed with a steam of nitrogen gas (N_2) before capping. The setup was well shaken and left for 5 minutes. After centrifugation (4000 rpm for 5 minutes), 1 mL of the supernatant in a 1.5 mL vial and evaporated under nitrogen to remove the solvent. N-butanol (0.3 ml) was used to dissolve the residue before injection into the HPLC system for the analysis of their vitamin contents. Standards of vitamins were procured from Sigma and Aldrich Chemical Company, USA, and dissolved in n-butanol.

2.6. Analysis of amino acid profile

The method of Thomas et al. [33] was used for analysis of amino acid profile. Briefly, 2 g of the oil was weighed into 5 mL 6 N HCL and the heating was carried out at 110°C for 24 hr. The hydrolysate was mixed with 400 μL of 50 μmol/mL of L-α-amino-n-butyric acid as internal standard. Then, distilled water was used to make it up to 100 mL. This was followed by filtration with Whatman No. 1 filter paper. Before injection into the HPLC column, amino acid derivation was carried out by 10 μL of sample and 20 μL AccQ reagent (6-aminoquinolyl-N hydroxysuccinimidylcarbamate) following the detailed procedures in David et al. [29].

Table 1
Levels of macro- and micro-minerals in coconut oil (mg/kg).

Metal	COI	COS	CON
Calcium	248.09 ± 8.54^a	157.87 ± 7.12^b	149.11 ± 7.22^b
Magnesium	132.90 ± 6.43^a	84.57 ± 5.87^b	79.88 ± 5.10^b
Potassium	182.42 ± 7.89^a	116.08 ± 7.10^b	108.64 ± 6.66^b
Sodium	580.01 ± 15.34^a	369.09 ± 10.34^b	348.61 ± 9.35^b
Phosphorus	49.62 ± 2.21^a	31.57 ± 1.89^b	29.82 ± 2.01^b
Sulphur	189.92 ± 8.12^a	120.85 ± 7.49^b	114.15 ± 5.99^b
Manganese	98.0 ± 2.12^a	62.3 ± 0.00^b	58.8 ± 1.67^b
Iron	108.5 ± 1.43^a	69.1 ± 1.11^b	65.2 ± 0.74^b
Zinc	47.4 ± 1.00^a	30.15 ± 1.54^b	28.48 ± 0.51^b
Copper	22.3 ± 1.10^a	14.2 ± 0.98^b	13.4 ± 0.12^b
Cobalt	0.06 ± 0.00^a	0.03 ± 0.00^b	0.03 ± 0.00^b
Chromium	0.15 ± 0.01^a	0.09 ± 0.00^b	0.09 ± 0.00^b
Silver	0.06 ± 0.00^a	0.04 ± 0.00^b	0.03 ± 0.00^c
Molybdenum	0.07 ± 0.00^a	0.04 ± 0.00^b	0.04 ± 0.00^b
Selenium	1.26 ± 0.01^a	0.80 ± 0.00^b	0.76±0.00^b
Boron	0.821 ± 0.10^a	0.523 ± 0.12^b	0.494 ± 0.10^b
Beryllium	0.008 ± 0.00^a	0.005 ± 0.00^b	0.005 ± 0.00^b
Gold	0.028 ± 0.003^a	0.018 ± 0.004^b	0.017 ± 0.007^b

a–cMean with different superscripts along the rows are significantly different ($p < 0.05$). Values are presented as mean ± SEM of three determinations. COI: Coconut Oil Imported; COS: Coconut Oil from Southern Nigeria; CON: Coconut Oil from Northern Nigeria.

2.7. Statistical analysis

Statistical analysis of data was carried out using SPSS 17.0. Data were presented as mean ± standard error of mean (SEM). All analyses were carried out in triplicates. Statistical analyses were carried out by ANOVA to compare the sample groups. The significant difference between mean values was considered at $p < 0.05$.

3. Results

3.1. Levels of macro- and micro-elements in coconut oil

Table 1 presents the profile of macro-elements and micro-elements in imported (COI) and local coconut oil samples from the southern (COS) and northern (CON) locations in Nigeria. Macro-elements detected in the oil samples include potassium (K), sodium (Na), magnesium (Mg), phosphorus (P), calcium (Ca). The levels of all macro-elements in COI were significantly higher ($p<0.05$) than that of COS and CON. Furthermore, the levels of macro-elements in COI range from 49.62 (phosphorus) to 580.01 (sodium) mg/kg, whereas levels of macro-elements in the local coconut oil samples (COS and CON) range from 29.82 (phosphorus) to 369.09 (sodium) mg/kg. Our observation regarding the micro-elements reveals consistent trend as that of macro-elements. The micro-element levels in COI were markedly ($p<0.05$) higher than micro-element levels in COS and CON. The levels in COI range from 0.008 (beryllium) to 189.92 (sulphur) mg/kg, while that of COS and CON ranges from 0.005 (beryllium) to 120.85 (sulphur) mg/kg.

3.2. Contents of toxic heavy metals in coconut oil

Toxic metal levels in coconut oil samples are presented in Table 2. Toxic metals, including Cd, As, Pb, Al, and Ni were detected in the three samples of coconut oil; while mercury (Hg) was undetected in the all samples of coconut oil. However, the levels of these toxic heavy metals in COI were significantly higher ($p<0.05$) than the corresponding toxic metal levels in COS and CON. We observed that there were no marked ($p>0.05$) differences in the toxic metal levels between COS and CON. Comparatively, each of the toxic metal level in all samples was several folds lower than the FAO/WHO reference standard for oil.

Table 2
Comparison of toxic heavy metal levels (mg/kg) of coconut oil with FAO/WHO reference standard for oils.

Toxic metal	COI	COS	CON	FAO/WHO reference [34]
Lead	0.01 ± 0.00^{a}	0.008 ± 0.00^{b}	0.008 ± 0.00^{b}	0.10
Cadmium	0.02 ± 0.00^{a}	0.01 ± 0.00^{b}	0.01 ± 0.00^{b}	0.05
Mercury	ND	ND	ND	NA
Arsenic	0.02 ± 0.001^{a}	0.01 ± 0.00^{b}	0.01 ± 0.00^{b}	0.10
Nickel	0.01 ± 0.00^{a}	0.008 ± 0.00^{b}	0.008 ± 0.00^{b}	0.20
Aluminium	0.03 ± 0.001^{a}	0.02 ± 0.00^{b}	0.02 ± 0.00^{b}	1.0

ND: Not detected. ^{a,b}Mean with different superscripts along the rows are significantly different ($p < 0.05$). Values are presented as mean ± SEM of three determinations. COI: coconut oil imported; COS: coconut oil from southern Nigeria; CON: coconut oil from northern Nigeria. NA: not available.

Table 3
Vitamin composition (mg/100 g) in coconut oil.

Vitamin	COI	COS	CON
Vitamin A	16.6 ±0.01^{a}	9.90 ±1.0^{b}	10.5 ±1.20^{b}
Vitamin B_1	0.15 ±0.00^{a}	0.09 ±0.00^{b}	0.09 ±0.00^{b}
Vitamin B_2	0.13 ±0.00^{a}	0.10 ±0.00^{a}	0.20 ±0.00^{b}
Vitamin B_3	0.36 ±0.01^{a}	0.68 ±0.01^{b}	0.79 ±0.00^{b}
Vitamin B_6	0.52± 0.00^{a}	0.24 ±0.00^{b}	0.48 ±0.00^{a}
Vitamin B_{12}	0.15 ±0.00^{a}	0.09 ±0.00^{b}	0.19 ±0.00^{a}
Vitamin C	1.94 ±0.21^{a}	2.15 ±0.38^{b}	1.29± 0.11^{c}
Vitamin D	**ND**	**ND**	**ND**
Vitamin E	0.07± 0.00^{a}	0.14 ±0.00^{b}	0.16 ±0.00^{b}
Vitamin K	0.37 ±0.00^{a}	0.11 ±0.00^{b}	0.27 ±0.00^{c}

a–cMean with different superscripts along the rows are significantly different ($p < 0.05$). Values are presented as mean ± SEM of three determinations. COI: coconut oil imported; COS: coconut oil from southern Nigeria; CON: coconut oil from northern Nigeria. **ND: Not detected**

3.3. Level of vitamins in coconut oil

Table 3 depicts the water/fat-soluble vitamins detected in samples of coconut oil. The fat-soluble vitamins, K, E, and A were found in the oils. Vitamin D was undetected. Levels of vitamin A and K in COI were significantly higher ($p<0.05$) than that of COS and CON. Conversely, the level of vitamin E, an antioxidant vitamin, was significantly ($p<0.05$) lower in COI compared to the level of vitamin E in COS and CON. Water-soluble vitamins, including B_1, B_2, B_3, B_{12} and C were detected in the oil samples. Level of B_1 was markedly ($p<0.05$) higher in COI than in COS and CON; B_2 in COI was prominently lower ($p<0.05$) compared to B_2 in CON; B_3 in COI was significantly lower ($p<0.05$) compared to B_3 in COS and CON. Vitamin B_6 and B_{12} levels in COI were considerably higher ($p<0.05$) in comparison to COS and CON. Vitamin C level in COS was significantly higher compared to COI and CON levels.

3.4. Amino acid composition in coconut oil

Table 4 presents the percentage content or composition of amino acids in coconut oil samples. The total contents of the amino acids in COI sample were found significantly higher ($p<0.05$) than that of local oil samples, COS and CON. However, the amino acid content of CON was significantly higher ($p<0.05$) than that of COS. Strikingly, the percentage composition of an amino acid, Threonine, was particularly high in the three samples of coconut oil.

3.5. Essential amino acids in coconut oil

Table 5 reveals the comparison of amino acid contents of coconut oil samples with the WHO reference standards. The three oils contain the dietary essential amino acids. The threonine content in COI, COS and CON was higher than the WHO standard. Phenylalanine in CON was higher than the WHO standard. Methionine content in COI and CON was higher than the WHO level. However, the content of tryptophan in COS was also higher than the WHO standard.

Table 4
Percentage composition (%) of amino acids in coconut oil

Amino acid	COI	COS	CON
Alanine	0.73 ± 0.01^{a}	0.64 ± 0.10^{b}	0.42 ± 0.01^{c}
Arginine	0.80 ± 0.00^{a}	0.48 ± 0.02^{b}	0.68 ± 0.01^{c}
Asparagine	1.88 ± 0.02^{a}	2.05 ± 0.13^{b}	1.53 ± 0.01^{c}
Aspartic acid	0.49 ± 0.00^{a}	0.18 ± 0.03^{b}	0.63 ± 0.01^{c}
Cysteine	0.03 ± 0.00^{a}	0.13 ± 0.04^{b}	0.09± 0.01^{c}
Glutamic acid	0.98 ± 0.01^{a}	0.59 ± 0.01^{b}	0.79 ± 0.02^{c}
Glutamine	0.14 ± 0.00^{a}	0.33 ± 0.00^{b}	0.24 ± 0.01^{c}
Glycine	0.08 ± 0.00^{a}	0.37 ± 0.01^{b}	0.28 ± 0.01^{b}
Histidine	0.75 ± 0.02^{a}	1.63 ± 0.54^{b}	0.97 ± 0.01^{c}
Isoleucine	0.42 ± 0.01^{a}	0.37 ± 0.00^{b}	0.30 ± 0.01^{b}
Leucine	0.04 ± 0.00^{a}	0.20 ± 0.00^{b}	0.13 ± 0.01^{b}
Lysine	0.53 ± 0.04^{a}	0.27 ± 0.00^{b}	0.31 ± 0.01^{b}
Methionine	0.78 ± 0.02^{a}	0.23 ± 0.00^{b}	0.66 ± 0.02^{a}
Phenylalanine	0.93 ± 0.03^{a}	0.76 ± 0.05^{b}	1.08 ± 0.01^{a}
Proline	1.30 ± 0.13^{a}	0.92 ± 0.01^{b}	1.28 ± 0.01^{a}
Serine	0.93 ± 0.02^{a}	0.89 ± 0.12^{a}	0.92 ± 0.01^{a}
Threonine	6.66 ± 0.98^{a}	3.87 ± 0.09^{b}	4.45 ± 0.02^{c}
Tryptophan	0.59 ± 0.01^{a}	0.77 ± 0.07^{b}	0.59 ± 0.01^{a}
Tyrosine	1.83 ± 0.01^{a}	1.25 ± 0.01^{b}	1.58 ± 0.01^{c}
Valine	0.51 ± 0.01^{a}	0.37 ± 0.01^{b}	0.46 ± 0.00^{a}
Total amino acids	20.4 ± 0.61^{a}	14.3 ± 0.54^{b}	17.39 ± 0.39^{c}

a–cMean with different superscripts along the rows are significantly different ($p< 0.05$). Values are presented as mean ± SEM of three determinations. COI: coconut oil imported; COS: coconut oil from southern Nigeria; CON: coconut oil from northern Nigeria

Table 5
Essential amino acids (% of total amino acids) of coconut oil compared with the WHO reference standard for dietary proteins.

Amino acids	COI	COS	CON	WHO [35]
Phenylalanine	4.56	4.67	6.24	6.0
Histidine	3.67	10.03	5.60	NA
Isoleucine	2.06	2.28	1.73	4.0
Leucine	0.19	1.23	0.75	7.0
Lysine	2.60	1.66	1.79	5.5
Methionine	3.83	1.41	3.81	3.5
Threonine	32.66	23.82	25.69	4.0
Tryptophan	2.89	4.74	3.41	3.6
Valine	2.50	2.28	2.66	5.0

Values are based on three determinations. NA: Not available; COI: coconut oil imported; COS: coconut oil from southern Nigeria; CON: coconut oil from northern Nigeria.

Table 6
Pesticide residues (μg/kg) in coconut oil in comparison with maximum residue level

Pesticide	COI	COS	CON	MRL (μg/kg)
Cyclodienges	0.89 ± 0.01[a]	0.75 ± 0.01[b]	0.46 ± 0.00[c]	NA
Cyclohexane	0.97 ± 0.01[a]	0.75 ± 0.01[b]	0.93 ± 0.00[a]	NA
DDT	0.50 ± 0.01[a]	0.63 ± 0.01[b]	0.75 ± 0.00[c]	50*
DDD	0.63 ± 0.01[a]	0.79 ± 0.01[b]	0.84 ± 0.01[b]	50*
Dicofol	0.33 ± 0.01[a]	0.42 ± 0.01[b]	0.34 ± 0.01[a]	50***
Perthane	0.03 ± 0.01[a]	0.04 ± 0.00[a]	0.07 ± 0.00[b]	10*
Methoxychlor	0.32 ± 0.01[a]	0.46 ± 0.01[b]	0.82 ± 0.01[c]	10**
Aldrin	0.22 ± 0.01[a]	0.32 ± 0.01[b]	0.57 ± 0.01[c]	20**
Dieldrin	0.22 ± 0.01[a]	0.27 ± 0.01[b]	0.20 ± 0.00[a]	50##
Heptachlor	0.06 ± 0.00[a]	0.07 ± 0.00[a]	0.09 ± 0.00[b]	50##
Chlordane	0.12 ± 0.01[a]	0.15 ± 0.01[b]	0.16 ± 0.00[b]	20##
Endosulfan	0.52 ± 0.01[a]	0.63 ± 0.01[b]	0.75 ± 0.01[c]	50*
Hexachlorobenzene	0.14 ± 0.01[a]	0.17 ± 0.01[b]	0.23 ± 0.00[c]	NA
Pentachlorobenzene	0.07 ± 0.01[a]	0.09 ± 0.01[a]	0.07 ± 0.00[a]	NA
Mirex	0.05 ± 0.00[a]	0.06 ± 0.00[a]	0.04 ± 0.00[a]	10*
Toxaphene	0.08 ± 0.01[a]	0.09 ± 0.00[a]	0.07 ± 0.00[a]	100#
alpha-HCH	0.08 ± 0.01[a]	0.15 ± 0.01[b]	0.26 ± 0.00[c]	200**
beta-HCH	0.15 ± 0.01[a]	0.26 ± 0.01[b]	0.45 ± 0.00[c]	200**
gamma-HCH	5.36 ± 0.01[a]	6.09 ± 0.01[b]	7.10 ± 0.01[c]	10*

Values are reported as mean ± SD of three determinations. [a-c]Means with different superscripts along the rows are significantly different ($p < 0.05$). MRL: Maximum residue level

* European Union MRL (2005) [36]

** FAO/WHO MRL (1992) [37]

*** Thailand MRL (2014) [38]

\# Leonards et al. (2011) [39]

\## China MRL (2015) [40], DDT: Dichlorodiphenyltrichloroethane; DDD: Dichlorodiphenyldichloroethane; HCH: hexachlorocyclohexane (HCH); NA: not available at the time of this report.

3.6. Pesticide residues in coconut oil samples

Table 6 shows the levels of various pesticide residues in the coconut oil samples. The residues ranged from 0.03 to 7.10 μg/kg. Pesticide residues varied from 0.03 ± 0.01 to 5.36 ± 0.01 μg/kg in COI, 0.04 ± 0.00 to 6.09 ± 0.01 in COS, and CON was 0.04 ± 0.00 to 7.10 ± 0.01. However, the highest concentration of gamma hexachlorocyclohexane (7.10 μg/kg) was detected in CON, followed by COS (6.09 μg/kg) and then COI (5.36 μg/kg).

4. Discussion

Human exposure to toxicants via dietary sources is a growing global concern [20]. Food contaminants have been suggested to impact health and increase susceptibility to cancer via induction of genetic and epigenetic changes [21]. Emerging literature suggests increasing global consumption of coconut oil for human health and recently for recovery from COVID-19 infection [16], whereas its safety in relation to hazardous chemicals have not been published widely. The primary thrust of the current study was to determine the possible levels of pesticide residues and toxic metals in imported refined oil (COI) and Nigerian samples of virgin coconut oil (COS and CON). The oil samples contain nutritional profiles of amino acids, vitamins, mineral elements and essential metals that mediate cellular homeostasis, signaling and health. Although toxic metals and pesticides were found but at an extremely insignificant amount.

The coconut oil samples contain macro- and micro-elements involved in electrolyte balance, enzyme action, antioxidant mechanism and cellular homeostasis. Macro-elements, sodium, potassium, iron, magnesium, calcium and phosphorus, and micro-element, selenium, zinc, cobalt, sulphur, copper and manganese were significantly found in the imported sample than the Nigerian coconut oil samples (Table 1). The levels of the mineral elements range from 0.005 mg/kg in Nigerian samples to 580.01 mg/kg in imported sample. It is noteworthy to observe that the imported coconut oil (COI) is richer in micro-essential metals such as zinc, selenium, copper, cobalt and manganese. Zinc and copper are cofactors for a number of metabolic and antioxidant enzymes [41]. Zinc exerts a critical role in pancreatic synthesis of insulin and glucose utilization by fat cells and muscles. Selenium is present in glutathione peroxidase as an antioxidant cofactor; glutathione peroxidase is abundant in the cytosol and mitochondria and performs the role of reducing hydroperoxide radicals. Cobalt is present in vitamin B_{12} and in some metalloproteins as a metal constituent; however, its deficiency is associated with pernicious anemia [42]. Sulphur is a component of cellular protein and thiol group (-SH) for modulation of redox balance. Chromium is more abundant in COI. Chromium is a trace element required by humans in trace amounts and its biological role is associated with glucose tolerance [41,43]. However, excess amount emanating from exposures could precipitate hepatorenal toxicity [41]. Our findings herein thus reveal that the imported coconut oil may be a better source of mineral elements than the Nigerian virgin coconut oil. Previous studies suggest that the heavy metals in edible oil could be from the soil that supports plant growth or during industrial processing of oil [23,44]. Our imported sample was a commercial coconut oil known as copra oil due to a high temperature involved in its industrial processing [6]. The Nigerian coconut oil samples were extracted from mature kernel by natural traditional means, and thus known as virgin coconut oil [6,8]. Therefore, the higher levels of mineral elements in imported coconut oil might be contributed by the industrial processing and/or variations in soil contents.

Cadmium (Cd), lead (Pb), arsenic (As), nickel (Ni) and aluminium (Al) were detected in the coconut oil samples, while mercury was undetected (Table 2). In a study conducted in India, cadmium (Cd), chromium (Cr), lead (Pb), and stannum (Sn) were also detected in fresh and packaged coconut water [26]. These metals could penetrate to the oil through plant root or by atmospheric deposition on soil or plant surfaces. They are non-essential environmental toxicants with hazardous impacts in humans and animals. Intriguingly, our results reveal that the toxic metal levels in COI were significantly higher than that of the Nigerian virgin coconut oil, COS and CON. The levels ranged from 0.008 mg/kg for Pb and Ni in COS and CON to 0.03 mg/kg for Al in COI, which is a refined copra oil. This range is comparable to the amount of Pb and Ni reported for soybean, palm and olive oil samples in Ridyah, South Africa [45]. In China, the Pb range was found to be comparable to 0.009–0.018 mg/kg for soybean oil, corn oil, peanut oil, sesame oil, rapeseed oil, cottonseed oil, olive oil, blend oil and sunflower oil sample [21]. In the study of Jonnalagadda et al., 2022 [26], the levels of the toxic metals range from 0.2 mg/kg to 77.8 mg/kg. It was indicated in the study that the levels of Cd, Cr, and Pb in the fresh coconut water exceeded the permissible limits set by the WHO [34] contrary to our findings in this study. Contamination with heavy metals in fresh coconut kernels, coconut cream, and coconut milk powder was also reported in previous studies [26]. However, Pb is a classic environmental toxicant with no known biological benefit and safe level. The adverse health effects of lead include neuronal damage, sterility and decreased cognition and intelligent quotient in children [46]. Lead exposure is associated with hematological, immunological, hepatic, and renal dysfunctions [47]. The range of Pb levels in the oils was obtained as 0.008 to 0.03 mg/kg which is several folds lower compared to the permissible level for Pb (0.1 mg/kg) according to the FAO/WHO [34]. In previous studies [20,48], the levels of Pb in virgin sesame oil and refined sesame oil and sunflower oil were higher than the levels found in this study. Cadmium is a ubiquitous non-essential toxic heavy metal that exerts a number of toxicities on delicate organs of the body. Humans are unavoidably exposed to Cd via foods, water, fertilizers, batteries, plastics, pigments, metal plating, and various industrial alloys [49]. Cadmium is a trigger of oxidative stress which incites oxidative DNA damage and aberrant epigenetic changes for development of various cancers and chronic diseases [50]. We found Cd with 0.02 mg/kg level in imported coconut oil (COI), whereas 0.01 mg/kg was detected in Nigerian oils (COS and CON) compared to 0.05 mg/kg set by the FAO/WHO [34]. In contrast, the levels of Cd in virgin sesame oil and refined sesame oil were lower than the levels found in virgin coconut oil and imported refined oil in this study [20]. However, the levels reported for Cd in sesame oil fractions in Poland were higher than our values in this study. The differences in the contents of soil, method of extraction, anthropogenic activities and genetic make-up of the oil-plants may contribute to these differences [51]. Drinking water is the major source of exposure to As globally [52]. Leaching of mine deposits and emissions from industries are other sources of As [53]. The health hazards of As is related to neurotoxicity, brain damage and neurological disorders due to prenatal exposure and chronic bioaccumulation in adults [53]. However, As level in COI was 0.02 mg/kg, whereas it was 0.01 mg/kg in COS and CON which is significantly lower in several fold compared to 0.1 mg/kg FAO/WHO level, whereas it is comparable to the levels of As reported by Szyczewski et al. [51]. Our reported values for As were lower compared to that of Alrajhi and Idris [45] for vegetable oils in Saudi Arabia. These levels of As in this study are comparable to the levels obtained in sesame oil by Rounizi et al. [20]. However, the As levels reported by Sobhanardakani [54] in canola and soybean oils were higher than our As level in this study. Nickel is a carcinogenic and nephrotoxic metal, and exposure to it is via ingesting contaminated foodstuffs or inhaling cigarette smoke [55]. Non-occupational human exposure to Al is primarily by ingestion of food and water. The intake of Al can be increased greatly through the use of Al-containing pharmaceutical products. Chronic accumulation of Al has been implicated in disorders like osteomalacia, hematopoietic diseases, Alzheimer's disease, and Parkinsonism. The levels of Ni and Al in the oil samples were significantly higher in COI than that of COS and CON. However, these levels are considerably lower when compared to 0.2 and 1.0 mg/kg FAO/WHO, respectively. Moreover, the higher level of these toxic metals in imported coconut oil may be linked to the industrial processing method and the soil content differences [23,48]. Our careful observation from the literature shows that the levels of toxic metals in coconut oil in this study are within the tolerable levels and lower compared to the levels in other natural oils [48,56]. In consistent with the report of Jonnalagadda et al., 2022 [26], none of the samples in this study contained mercury (Hg).

Vitamins were detected in the three coconut samples, and they include vitamin A, B_1, B_2, B_3, B_6, B_{12}, C, E and K in various amounts (Table 3). Vitamin A is the most abundant (10.5 to 16.6 mg/100 g of oil) while vitamin E is the least (0.07 to 0.16 mg/100 g). In previous studies, virgin coconut oil which is our COS and CON, has been reported to contain vitamin E as α-tocopherol, which is present in the human plasma [57,58]. For the first time, in this study, the presence of vitamin E in commercial refined coconut oil is reported. This may confirm the anecdotal report among women that, commercial coconut oil enhances hair growth, and this potential is attributed to vitamin E in the refined oil. Vitamin E has an antioxidant role in humans; it activates microsomal enzymes and apoptosis in tumour cells; it modulates immune system, cell-membrane stability, erythrocyte formation and gene expression [59]. It was observed that levels of vitamin A and K in COI were significantly higher than that of COS and CON. Conversely, the level of vitamin E was significantly lower in COI compared to the level of vitamin E in COS and CON. This may be attributed to the high temperature involved in COI production process [6]. However, given that they are micro-nutrients, coconut oil may supply the needed amount and still engenders beneficial health effect. The water-soluble vitamins, B_1, B_2, B_3, B_6, B_{12} and C were detected in the oil samples. B vitamins act as coenzymes involved in transfer of aldehyde groups, neurotransmission, ATP production, macromolecule synthesis and inhibition of pathogenesis [59]. B_6, pyridoxine, is the most abundant and it ranges from 0.24 to 0.52 mg/100 g, with highest level in COI. Its biochemical derivatives include pyridoxal and pyridoxamine. The active form of B_6 is pyridoxal-5'-phospate which is critically involved in glucose metabolism. Vitamin C level in COS was significantly higher compared to COI and CON levels. Ascorbic acid is a cofactor in several biological reactions, it specifically acts as an efficacious antioxidant in the synthesis of collagen, neuropeptide and carnitine; it increases iron absorption and immune system, while inhibiting histamine release [59]. It is a free radical scavenger and mediator of oxidative damage to DNA and tissue pathologies.

The profiles of amino acids in oil samples are shown in Table 4. The oils are rich in essential amino acids available in diets (Table 5). The total content of amino acids in COI was found to be significantly higher than that of COS and CON. Interestingly, the amino acid content of CON was significantly higher than that of COS. The CON sample was obtained from the northern part of Nigeria, and it was prepared by traditional method as COS. However, the farming practice and type of agricultural manure may contribute to the differences. Strikingly, the percentage composition of an amino acid, threonine, was particularly the highest in each of the three samples of coconut oil (3.87 to 6.66 %) followed by asparagine (1.53 to 2.05), tyrosine (1.58 to 1.83), proline (0.92 to 1.30), etc. Threonine is an essential amino acid harvested from human diet (Table 5). Threonine is decarboxylated by decarboxylase to form a biogenic amine, propanol amine, which is a constituent of vitamin B_{12}. It supports connective tissues and heart and recovery from injury. Optimum levels of amino acids are important for synthesis of functional proteins, hormones, neurotransmitters, muscle growth, and several other biological processes [60]. The percentages of total amino acid for phenylalanine, methionine and threonine in CON were higher than the value set by the WHO as reference standards. In COS, threonine and tryptophan were higher than the WHO standards, whereas in COI, methionine and threonine were higher. It thus appears that the Nigeria virgin coconut oil may exert better nutritional benefits due to its amino acid contents.

The levels of pesticide residues in the coconut oil samples are presented in Table 6. In the Table, there are nineteen pesticide residues in the oil samples with levels ranged from 0.03 to 7.10 µg/kg (parts per billion). In previous studies, pesticide residue levels have been determined in coconut pulp, and coconut water in Brazil and India [Jonnalagadda et al., 2022; Ferreira et al., 2016; Silva et al., 2008] [24–26]. Pesticide contamination of food is a growing global health concern [61]. The extensive use of pesticides in the world's agricultural countries raises concerns about the consequences for the human health. Studies show that there are established regulations on pesticide maximum residue limits (MRLs) in foods; however, these regulations are not adhered to by many countries [61]. Long-term consumption of foods contaminated with pesticides has been associated with cancers, depressive disorder, and male infertility [22,62]. In this study, CON sample from the northern Nigeria has the highest range of pesticide residues, 0.04 to 7.10 μg/kg. Comparatively, our range levels for coconut oil pesticides in this study are obviously lower compared to the range levels of pesticides in coconut water in previous studies found to be 0.5 μg/kg and 51.6 μg/kg [26], although it is below the international MRL [36,37]. According to Ferreira et al. (2016) [25], levels of pesticides in coconut water and coconut pulp were below the recommended standards. Herein, the extensive agricultural activities and frequent pesticide use in the Northern part of Nigeria may be associated with the pesticide residue levels in CON. However, these levels were significantly lower compared to the MRLs (10-200 μg/kg) set by the European Union [36], FAO/WHO [37], Thailand [38], China [40], and Leonards et al. (2011) [39]. Furthermore, olive oil has been reputed a highly nutritional oil. It was interesting to found that the levels of total endosulfan in our study herein (0.52-0.75 μg/kg) were several folds lower that the level found in olive oil (8.4 μg/kg) by Amvrazi and Albanis (2009) [63]. Therefore, the non-significant levels of these pesticide residues found in these oil samples suggest safety in their consumption.

5. Schematic overview of the experimental program

Abundant evidence is available in the literature reporting antioxidant phytochemicals and pharmacological benefits of coconut oil. This study has been designed, not to repeat what is already available in the literature but to analyse heavy metals, pesticides, vitamins and amino acids present in the local and imported samples of coconut oil. This is very important due to the increase in the consumption of coconut oil in various diets. The flow diagram for the design of this study is given in Fig. 1.

6. Conclusion

In conclusion, our study confirms toxic heavy metals, pesticide residues, nutritional elements, amino acids and vitamins in coconut oils extracted by natural means and the refined sample imported to Nigeria. The significance of this study is associated with the growing in popularity of coconut oil as beneficial food oil with increasing public awareness. Interestingly, the levels of toxic metals as well as pesticide residues are several folds lower than the standard limits set by the national and international regulatory bodies. In addition, the profiles of the elements, vitamins and amino acids contain essential amino acids and bioactive nutrients that could enhance consumers' health. Nevertheless, moderate consumption of coconut oil is important to avoid health hazards associated with pesticides and toxic metal bioaccumulation. It is still needful for future studies to embark on the large-scale analysis of coconut oil samples from different countries around the world to promote health impact and global nutritional safety of coconut oil.

Credit authorship contribution statement

ACF, CAE and EKM conceived the design of the study. ACF, CAE, CO, SCK carried out the research works, analyzed the data, and wrote the manuscript. EEB carried out the research work and analyzed the data. ACF, EEB SCK contributed to the data analysis and edited the manuscript. All authors contributed to the final edition and approval of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

None.

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