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Physicochemical Properties, Heavy Metals and Aflatoxins Content of Crude Palm and Groundnut Oils Produced and Marketed in Benue State, Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

The study aims at assessing the physicochemical properties, heavy metals, and aflatoxins content of crude palm and groundnut oils produced and sold in the Adikpo, Wadata, and Otukpa areas of Benue state, Nigeria. Specific gravity, refractive index, acid value, saponification value, peroxide value, moisture content, and smoke point are the physicochemical properties evaluated. The heavy metals analyzed include; Lead, Nickel, Copper, Iron, Arsenic, and Iron. Total aflatoxins were determined by Enzyme-linked immunosorbent assay (ELISA). Findings revealed that most of the physicochemical properties of palm and groundnut oils from these areas deviated from the Food and Agricultural Organization/World Health Organization (FAO/WHO) standard range. A high

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amount of Cadmium (0.89 mg/kg, 1.01 mg/kg, and 0.92 mg/kg) was detected in the local groundnut oil samples but lesser in palm oils from Adikpo, Wadata, and Otukpa respectively, while Copper content was within the FAO/WHO safe limits. The arsenic content of palm oil produced in the region was not as high as those in groundnut oil but was higher than the recommended maximum limit of 0.1 mg/kg. The Nickel content in the oil samples was higher than the 0.50 mg/kg permissible limit, but Lead was within the safe limits. Total Aflatoxin content in crude groundnut oil was within the range of 9.05 ppm to 10.13 ppm, while a range of 2.03 ppm to 2.74 ppm was recorded in crude palm oil. The locally produced oils are of lower quality, suggesting that refining should be adopted and quality seeds should be used for the extraction of oils.

Keywords: Palm oil; groundnut oil; heavy metals; aflatoxins.

1. INTRODUCTION

According to the United States Department of Agriculture, 168.85 million metric tonnes of vegetable oils are estimated to be produced globally. Vegetable oils are widely used in the cooking, cosmetic, pharmaceutical, and chemical industries. They are beneficial and popular due to their low cholesterol effect [1]. Groundnut and palm oils belong to popular vegetable oils used in the food, cosmetic, and pharmaceutical industries**.** They are a good source of essential fatty acids and Lipid Soluble Vitamins [2,3]. The oil palm is an important economic crop in the tropics [4]. An estimation of about 34% accounted of palm oil vegetable oil, and 63% of the global export of vegetable oil globally [4,5]. Groundnut oil is extracted from groundnut kernels. It contains only a small proportion of non-glyceride constituents. Utilization includes cooking, frying, basting, and manufacturing margarine [6].

Due to the abundant benefits of palm oil and groundnut oil, it is therefore very important to investigate the quality of these oils produced and sold in Nigeria's local markets. Findings have indicated poor physicochemical properties (not correct) in the oil samples, signifying some level of adulteration as regard Standard Organisation of Nigeria guidelines (SON) [7,8]. Several quality indices can portray if palm oil is of good quality or not. Examples include physical, chemical, and microbiological parameters. Poor hygiene, processing, and storage condition of palm oil and groundnut oil could be the main cause of the poor physicochemical properties of the oils [9,10].

Groundnut oil may be one of the most cardio-protective foods readily consumed according to several kinds of literature that abound. The monounsaturated fatty acids present in this oil aid to lower the blood cholesterol level [10]. Roughly 80% of the produced palm oil is meant for human consumption. Palm oil serves as the main cooking oil in Nigeria [11]. Some researchers have emphasized the benefits of palm oil, geared towards its nutritional, antioxidant, and therapeutic benefits [2,8,12].

Cadmium (Cd), mercury (Hg), lead (Pb), copper (Cu), and zinc (Zn), are the primary type of heavy metal contaminants that draw worldwide concern because they cause environmental and human health problems [13]. Studies have shown that these metals contaminate soils and trace levels above required limits have been estimated in fruits, oil-extracting seeds, and other food crops [14,15,16]. The concentration of trace metals has been used to relate to the quality of vegetable oils. Trace elements found in edible oils can be a result of environmental contamination, extraction, and refining process of the oil. Regulatory bodies have documented just a few acceptable levels of metals in edible oils; for example, the World Health Organization (WHO) fixes the maximum concentrations of 0.1 ppm for Cu and Cr, and 0.05 ppm for Cd [17].

Aflatoxin contamination in food is a global food safety issue [18]. Aflatoxins are approximately 20 related fungal metabolites produced in cereals, maize grains, peanuts, and animal feeds mainly by the fungi *Aspergillus flavus* and *Aspergillus parasitica* [19]. Aflatoxin B1 is a lethal naturally occurring such metabolite that is a potent liver carcinogen [20]. In an overview, the Food and Agriculture Organization of the United Nations (FAO) states that about 25% of the world's crops are contaminated with mycotoxins (Aflatoxin) during the growth or storage period [21]. Identification of aflatoxin was linked to a groundnut meal contaminated with *A. flavus* leading to the mysterious disease “Turkey X disease” that killed more than 1,00,000 Turkey poultry birds in England in the 1960s [22].

Studies have assessed the physicochemical quality of edible oils produced in various parts of Nigeria. But information on the heavy metal content and the level of aflatoxins in local groundnut oil and palm oil in Makurdi of recent has been poorly reported. Hence the study aims at assessing the physicochemical properties, some heavy metals, and aflatoxin content of crude palm and groundnut oils produced and sold in Adikpo, Wadata, and Otukpa areas of Makurdi.

2. MATERIALS AND METHODS

Crude groundnut oil and palm oil were purchased from Adikpo Market, Wadata Market, and Otukpa markets. Reagents and chemicals include; Hydrochloric acid (HCl), Sodium hydroxide (NaOH), Potassium hydroxide (KOH), Iodobromine (IBr), Sodium thiosulphate ($Na_2S_2O_3$), Potassium iodide (KI), Acetic acid (CH_3COOH) Nitric acid (HNO_3) and, Hydrogen Peroxide (H_2O_2). All reagents were of analytical grade. Whatman N$^{\underline{o}}$ 1 filter paper, ELISA Reader (ABER-02AccuBioTech), Atomic Absorption Spectrophotometer (Phoenix-986, Biotech engineering, UK) thermometer, refractometer, electric Oven, water bath.

2.1 Sample Collection

Locally processed groundnut and palm oils were purchased from local producers at Adikpo Market, Wadata Market, and Otukpa markets which is a representative sample of the three geopolitical zones (Zone A, Zone B, and Zone C) in Benue state,

2.2 Physicochemical Properties

Specific gravity, refractive index, peroxide value, saponification values, and the moisture content of the samples were determined using the method of AOAC [23]. The acid value was measured by titration [24]. The smoke point of the oils was determined as described in the literature [25]. The temperature at which 10 mL of the sample gave off a thin bluish smoke continuously was recorded as the smoke point.

2.3 Determination of Heavy Metals

Heavy metal assay of the samples was carried out using atomic absorption spectrophotometer (AAS) following the Methods described by AOAC [23]. The lamps were allowed to warm up for 15 minutes and the monochromator was positioned to a wavelength corresponding to the metals needed (217.0 nm for lead, 232.0 nm for nickel, 324.7 nm for copper, 213.9 nm for iron, 228.8 nm for arsenic and 328.4 nm for Cadmium).

2.4 Analysis of Total Aflatoxin

Determination of total Aflatoxins was carried out by the ELISA method [26].

2.5 Statistical Analysis

Values were reported as mean ± standard deviation of triplicate determinations. Mean values were compared using One Way Analysis of Variance (ANOVA) at $p<0.05$ using the statistical package for social sciences (SPSS) software version 22. Duncan multiple range tests (DMRT) were used for mean separation.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Properties of the Oils

The specific gravity of vegetable oil depends on the type of oil and temperature. Specific gravities recorded for local groundnut and palm oils are shown in Table 1. Crude groundnut oils samples from Wadata, Adikpo, and Otukpa had specific gravities of 0.950, 0.985, and 0.968 respectively, while palm oils from these areas had a specific gravity of 0.895, 0.901, and 0.894 respectively. Specific gravities of palm and groundnut oils made from these areas show no significant difference ($p>0.05$) but were greater than the FAO/WHO recommended range (0.919-0.925) and (1.454 -1.456) for groundnut oil and palm oil respectively [27]. The presence of fatty acid in unrefined oils may be the reason for the high specific gravity recorded in these oils [28]. The values of the refractive index recorded in this study all agree with those reported by some authors but are slightly higher than those reported by others [29].

Groundnut oils had an average acid value of 2.6 $mgKOHg^{-1}$ while palm oils had an average acid value of 8.1 $mgKOHg^{-1}$. The acid value is used to indicate the level of rancidity and edibility of oils [30]. It is the mg of KOH required to neutralize the free fatty acid in 1 g of oil. Local groundnut oil had higher acid values than FAO/WHO recommended value of 0.6 $mgKOHg^{-1}$ which suggests high moisture content and the presence of free fatty acids [30]. This suggests that groundnut oils are liable to undergo degradation and produce off-flavors within a short period during storage. Palm oil acid values range from 8.12 mg/KOHg^{-1} to 9.18 KOHg^{-1}. All recorded acid values were within the standard (10.00 mgKOHg^{-1}) [27]. This contradiction has also been observed in other studies [31]. Saponification values of groundnut oils and palm oils ranged from 106.07-1888.47 mgKOHg^{-1} and 203.92 – 215.76 mgKOHg^{-1} respectively. Saponification values provide information about the quantity, type of glycerides, and mean weight of the acids in a given oil sample [31,32]. The lower the saponification value, the larger the molecular weight of fatty acids in the glycerides of the number of ester bonds is less [32] Locally made groundnut oil recorded saponification values that were within the acceptable range of 189-195 mgKOHg^{-1} which also indicates that the groundnuts were of good quality. Palm oil recorded saponification values within the safe limits but oil produced in Makurdi recorded a saponification value of 215.76 mgKOHg^{-1} which was higher than the FAO/WHO standard range (190-209 mgKOHg^{-1}) [27].

Table 1. Physicochemical properties of crude groundnut and palm oils consumed in Benue state

Parameters	**groundnut oil**			**palm oil**		
	C_1	**C_2**	**C_3**	**D_1**	**D_2**	**D_3**
Specific gravity	0.950^a±0.01	0.985^a±0.01	0.968^a±0.01	0.895^a±0.01	0.901^a±0.01	0.894a±0.01
Refractive index at (^{o}BX)	1.474^a±0.01	1.475^a±0.01	1.475^a±0.01	1.467a±0.01	1.473^a±0.01	1.467a±0.01
Acid value (mgKOHg^{-1})	2.62^a±0.01	2.60^a±0.01	2.63^a±0.01	8.12^b±0.01	9.18^a±0.03	8.10b±0.01
Saponification value (mgKOHg^{-1})	186.07^a±0.01	186.12^a±0.01	188.47^a±0.01	204.83a±0.01	215.76^a±0.01	203.92a±0.01
Peroxide value (mEq.O_2kg^{-1})	23.64^a±0.01	24.91^a±0.01	23.84^a±0.01	13.29b±0.01	15.30^a±0.01	13.49b±0.01
Iodine value	148.00^a±0.01	148.05^a±0.01	149.12^a±0.01	53.90a±0.01	64.13^a±0.01	54.86a±0.01
Moisture (%)	$2.71.0^c$±0.01	3.02^a±0.01	2.98^b±0.01	4.76b±0.01	4.99^a±0.02	4.18c±0.01
Smoke point (°C)	219.0^a±0.01	219.0^a±0.01	219.0^a±0.01	230b±0.01	211^a±0.01	229b±0.01
Ester value (mgKOH/g)	183.45^a±0.01	183.52^a±0.01	185.84^b±0.01	196.71a±0.01	206.58b±0.01	195.82a±0.01

Values are mean ± SD of triplicate replications. Means with the same superscripts on a role are not significant, means with different superscripts are significantly different at $p<0.05$

C_1 = locally made groundnut oil from Adikpo, C_2 = Locally made groundnut oil from Wadata, Market, C_3 = Locally made groundnut oil from Otukpa

D_1 = locally made palm oil from Adikpo, D_2 = locally made palm oil from Wadata, Makurdi, D_3 = locally made palm oil from Otukpa

Table 2. Heavy metals content (mg/kg) of crude groundnut oil in Benue state

Heavy metals	**Groundnut oil**			**Palm oil**		
	C1	**C2**	**C3**	**D1**	**D2**	**D3**
Cadmium	0.89^b±0.01	1.01^a±0.01	0.92^b±0.01	0.37^a±0.01	0.41^a±0.01	0.39^a±0.01
Arsenic	0.48^a±0.01	0.52^a±0.01	0.48^a±0.01	7.05^b±0.01	7.11^a±0.01	7.07^b±0.01
Copper	5.59^a±0.01	5.61^a±0.01	5.63^a±0.01	0.51^b±0.01	0.54^b±0.01	0.59^a±0.01
Nickel	0.77^a±0.01	0.77^a±0.01	0.76^a±0.01	0.05^a±0.01	0.07^a±0.01	0.07^a±0.01
Lead	0.08^a±0.01	0.08^a±0.01	0.08^a±0.01	8.03^b±0.01	8.74^a±0.01	8.00^a±0.01
Iron	6.92^a±0.01	6.97^a±0.01	6.99^a±0.01	1.39^b±0.01	1.53^a±0.01	1.41^b±0.01

Values are mean ± SD of triplicate replications. Means with the same superscripts on a role are not significant, means with different superscripts are significantly different at $p<0.05$

C_1 = locally made groundnut oil from Adikpo, C_2 = Locally made groundnut oil from Wadata, Makurdi. C_3 = Locally made groundnut oil from Otukpa

D_1 = locally made palm oil from Adikpo, D_2 = Locally made palm oil from Makurdi. D_3 = Locally made palm oil from Otukpa

Table 3. Aflatoxin content of some oils consumed in Benue state

Oils	Sample	Total aflatoxin concentration (ppm)
Groundnut oil		
	C_1	$9.05^c \pm 0.01$
	C_2	$10.13^a \pm 0.01$
	C_3	$9.45^b \pm 0.01$
Palm oil		
	D_1	$2.03^b \pm 0.01$
	D_2	$2.74^a \pm 0.01$
	D_3	$2.00^b \pm 0.01$

Values are mean ± SD of triplicate replications. Means with the same superscripts per oil are not significant, means with different superscripts are significantly different at p<0.05

C_1 = locally made groundnut oil from Adikpo, C_2 = locally made groundnut oil from wadata, Makurdi, C_3 = locally made groundnut oil from Otukpa

D_1 = locally made palm oil from Adikpo, D_2 = locally made palm oil from Makurdi, D_3 = locally made palm oil from Otukpa

Local groundnut oil had a peroxide value of 23.64 – 24.91 mEq.O_2kg^{-1} while palm oils had a peroxide value of 13.29–15.30 mEq.O_2kg^{-1}. Peroxide values predict the quality and stability of oils. High peroxide value could have resulted from a high degree of unsaturation and increases with the storage time, temperature, light, and contact with atmospheric oxygen [31]. The peroxide value of groundnut oils was higher than the standard range stipulated by regulatory bodies. The high peroxide values recorded in the groundnut oils as a result of autoxidation may be caused by poor storage conditions [10]. Palm oil from Otukpa had a peroxide value greater than deviated from that of regulatory bodies.

Iodine values ranged from 148.00 to 149.12 Wijj's for groundnut oils and 53.90 to 64.13 Wijj's for palm oils. The iodine value is the number of iodine grams absorbed by 100 mL of a given oil sample. It indicates the degree of saturation. Iodine values were higher than the standard iodine value of groundnut oils (120–143 Wijj's) [31]. The high iodine values show the presence of impurities and polyunsaturated fatty acids. SON reported that oil iodine values above 145 Wijj's are not of good quality for humans. Thus, the iodine values of 148.00, 148.05, and 149.12 Wijj's recorded, rated the oils low quality. Although the iodine value of palm oil of Adikpo and Otukpa were within the safe range of iodine value for palm oil (48-60 Wijj's) recommended by FAO/WHO [27]. Palm oil from Makurdi however, recorded an iodine value (64.13 Wijj's) that was higher than the recommended range, suggesting the presence of impurities, possible adulteration with another oil source or red dye color adulterant, whose use in oil adulteration has been widely reported [33]. The addition of chemical adulterants such as red dye color has been linked with health complications such as cancer and other cardiovascular diseases [34].

Moisture content was higher in the palm oil samples (4.7%) than in the groundnut oils samples (2.7%). The maximum allowed moisture content in edible oils is 0.2% [31]. Both oils had moisture content that was higher than the recommended value. The higher moisture content observed in the local products could be the poor moisture refining process as the companies are using low technology for oil production. Previous studies have found that oils that were produced using low technology displayed higher moisture content. Therefore, the higher moisture content could be due to this reason. Moisture favors microbial growth [31]. Locally made groundnut oils recorded a smoke point of 219 ^oC which deviated from the standard value. The low smoke point of the groundnut oil samples may be due to the presence of impurities and a high concentration of triglycerides. Studies have shown that oils containing high triglycerides have a low smoke point because when the oil is heated, the glycerides irreversibly disintegrate giving rise to glycerol and free fatty acids which smoke at a temperature lower than the 232 ^oC for refined oils [27].

Except for Makurdi palm oil, the smoke points of other palm oil samples were slightly closer to the values accepted by FAO/WHO (230-232°C) [27]. This demonstrates that oil samples contained impurities and need refining. Ester value is the milligram of potassium hydroxide required to saponify the esters in 1.0g of fat and oil [24]. The crude groundnut oil had an ester value within the threshold allowed by FAO. Makurdi crude palm oil had higher ester values that were not within the acceptable limit.

3.2 Heavy Metals Composition of the Oils

Heavy metals analyzed include; Cadmium, Arsenic, Copper, Nickel, Lead, and Iron as shown in Table 2. A high amount of cadmium (0.89 mg/kg, 1.01 mg/kg, and 0.92 mg/kg) was detected in locally made groundnut oil from Adikpo, Wadata, and Otukpa markets respectively. This suggests that high content of cadmium was in the groundnuts used in producing the oils.

Groundnut oils recorded 0.48 mg/kg, 0.52 mg/kg, and 0.48 mg/kg of Arsenic in samples from Adikpo, Wadata and Otukpa markets respectively. The Arsenic content of palm oil produced in the regions under study was not as high as those in the groundnut oil samples but was higher than the recommended maximum limit of 0.1 mg/kg [35].

The copper content of locally made crude groundnut oil from Adikpo (5.59 mg/kg), Makurdi (5.61 mg/kg), and Otukpa (5.63 mg/kg) was within the FAO/WHO safe limits (10 mg/kg). Other studies have highlighted that the copper content of most vegetable oils was not a course for concern as they were majorly within stipulated safe limits [36]. Palm oil contained 7.05 mg/kg, 7.11 mg/kg, and 7.07 mg/kg of copper. This result agrees with Orji and Mbata [37] who reported 7.05 mg/kg copper in palm oil sold in other towns of Nigeria. Groundnut oils contain Nickel contents higher than the 0.50 mg/kg recommended maximum limits [36]. Palm oil produced in Otukpa recorded the highest Nickel content among the oil samples. High nickel absorption in groundnut could be the source of nickel detected in the oil as reported [38].

Lead contents were as low as 0.08 mg/kg in groundnut oil samples but relatively higher in palm oil samples (average 8.3 mg/kg). Lead content in groundnut oils and palm oils samples was within the safe limits in consumable foods. These results show that groundnut used in producing the oils were not cultivated on soils highly contaminated with lead.

The iron content of the groundnut oils was within 6.9 mg/kg, while that of palm oil varied from 1.3 – 1.5 mg/kg. Iron is an important trace element needed by the body. Values of iron recorded in locally made groundnut and palm oils were also low.

3.3 Total Aflatoxin Content of the Oils

The result of levels of aflatoxin in locally produced groundnut oil is presented in Table 3. Total Aflatoxin in locally made groundnut oil was 9.05 ppm, 10.13 ppm, and 9.45 in samples from Adikpo, Wadata, and Otukpa markets respectively, which are considerably high as 1 ppm has been reported to be injurious to health [39]. The major sources of aflatoxin contamination of crops and their processed products are delays in the harvest of the crops and unhygienic product production practices [21]. Locally made palm oil recorded total aflatoxin content of 2.03 ppm, 2.74 ppm, and 2.00 ppm respectively. These values are lower than those recorded for palm oil locally produced in other places in the country [38]. The soil type and climatic conditions are huge contributors to the crops' aflatoxin content [16]. Drought has been identified as a major climatic condition that accelerates the level of aflatoxins in growing crops [40]. This gives a hint that the groundnut used for the production of the oils may have been grown on soil high in *Aspergillus flavus* and *Aspergillus parasiticus* and/or subject to unfavorable climatic conditions during growth. Research reported that consumption of peanut butter having total aflatoxin content of 1.05 ppm has caused aflatoxicosis [20].

4. CONCLUSION

Groundnut and palm oil locally produced and freely consumed in these areas is of lower quality as stipulated by regulatory bodies. Consumption of these oils may, in the long run, put the health of consumers at risk due to their high levels of aflatoxins and some toxic heavy metals like cadmium, arsenic, and nickel which were all higher than their maximum limits permitted in consumable food products. The research also suggested refining these locally produced oils before consumption as the way forward.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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