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Physicochemical Properties and Mineral Compositions of Pawpaw and Watermelon Seed Oils

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Abstract: The physicochemical properties and mineral contents of ripe and unripe pawpaw and water melon seed oils were evaluated. The physicochemical evaluation showed that the oils have low saponification, low iodine, low peroxide and low acid values. These values indicated that the oils have good commercial values and uses apart from their nutritional values and can also be stored for a long period of time. The assay of mineral contents also showed that the oils contained useful macro and micro nutrients especially high amount of phosphorous which suggests that it can be used to treat hypophosphatemia. The ripe and unripe seed oils have almost the same physicochemical properties which suggest that the oil can be harvested when the pawpaw is ripe or otherwise. The three seed oils have more long chain saturated fatty acid (moderate saponification value) which makes them good oils for soap making. Also their calorific values are high enough to make them a good source of bio-fuels. The oils should be evaluated for toxicological effect before it is recommended for human consumption and its melting point and flash point also be evaluated to know its grade as a biofuel.

Key words: Watermelon seed, Pawpaw seed, seed oil, physicochemical, mineral composition, nutritional values

INTRODUCTION

Watermelon, *Citrullus lanatus* belonging to the family Cucurbitaceae is a vine-like flowering plant usually green with dark green stripes or yellow spots and a juicy, sweet interior flesh, usually deep red to pink, but sometimes orange, yellow, or white, with many seeds. The seeds have a nutty flavor and can be dried and roasted. The seeds also have a much higher food value than the flesh and have a significant amount of vitamin C; minerals, fat, starch and riboflavin. They can be dried, roasted and eaten as such or ground into flour to make bread. The seed contains a high percentage of oil which is similar to pumpkin seed oil and can be used in cooking (Moldenke and Moldenke, 1952). The increasing cost of fossil fuels coupled with the rising desire to cut down on the release of greenhouse gases into the atmosphere has resulted to the growth in the production of biodiesel which is principally fatty acid methyl esters (Hassan *et al*., 2013). The seed oil of watermelon has an anthelmintic action which is better than that of pumpkin seed oil (Jackson, 1990). The seed oil consists of linoleic acid and unsaturated fatty acids. The predominant fatty acid in the oil was linoleic acid, oleic, palmitic and stearic acids, with Linolenic, palmitoleic and myristic acids as minor constituents (Hassan *et al*., 2013). Other physicochemical properties of watermelon seed oil found in the literature are the refractive index, acid value, peroxide value, free fatty acids, saponification value and iodine value which were determined to be 1.4696 (25°C), 2.82 (mgKOH/g oil), 3.40 (mequiv oxygen/kg oil), 1.41 (% as oleic acid), 201 (mg KOH/g oil) and 115 (g iodine/100-g oil, respectively (Hassan *et al*., 2013; El-Adawy and Taha, 2001a, b).

Pawpaw, also known as *Carica papaya* is a perennial, fast-growing, semi-woody tropical herb. The seeds which represent a considerable amount of papaya fruit waste in processing units account for about 16% of the fresh fruit weight. Papaya seeds have the potential to produce 30 to 34% oil with nutritional and functional properties highly similar to olive oil. Besides, there is an excellent source of amino acid (about 24.91%), especially in the sarcotesta and fiber in the seeds (Saran *et al*., 2013). However, the edibility of papaya seed oil has not been confirmed by previous studies. Papaya seed oil is a liquid with yellow color. It is suggested that the oil has potential for edibility and may possess some industrial uses as similar to the use of palmitic acid, oleic acid and linoleic acid. Moreover, papaya seed oil is steady against oxidation with vital antioxidant activity (Li *et al*., 2015; Bouanga-Kalou *et al*., 2011). Each seed is made up of sarcotesta and endosperm (Afolabi *et al*., 2011; Puangsri *et al*., 2005). The seeds are numerous, small, black, round and covered with gelatinous aril and have been confirmed in animals to have contraceptive, abortifacient capability, anthelminthic and anti-amoebic activities (Afolabi *et al*., 2011; Okeniyi *et al*., 2007; Oderinde *et al*., 2002; Lohiya *et al*., 2008). The seed has also been shown to be a

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good source of oil (25.6%) which may be useful for medicinal, biofuel and industrial purposes (Afolabi *et al*., 2011).

This research is further exploring and comparing the nutritional values of seed oils of watermelon and that of ripe and unripe pawpaw by obtaining their physicochemical properties as well as their mineral contents. Full toxicological evaluation needs to be carried out on the oils to affirm their edibility.

MATERIALS AND METHODS

Sample collection and pre-treatment: Mature ripe and unripe *Carica papaya* fruits were harvested from a *Carica papaya* tree within Babcock University premises while mature *Citrullus lanatus* fruits were purchased from Ilishan market in Ogun state, Nigeria. The fruits were washed with distilled water, cut into two longitudinal halves and their individual seeds removed manually. The slimy sac-like substance coating the *Carica papaya* seeds were removed by bursting with the aid of a mortar and pestle, followed by copious washing with distilled water. The resulting clean seeds were thereafter oven dried at 50°C for 48 h and then pulverized with the use of laboratory blender. The pulverized samples were packaged separately in waterproof polyethylene bags and stored at 4°C until required for analysis.

Extraction of carica papaya and citrullus lanatus seed oils: Solvent extraction was carried out on 50 g of each pulverized sample with soxhlet apparatus for a period of eight hours using n-hexane as the extraction solvent. The extraction solvent was removed *in vacuo* using rotary evaporator (Eyela N-1001) at 40°C to recover the seed oil. The oil was placed on a water bath at 50°C for 2 h to ensure complete removal of residual solvent after which it was stored in a glass bottle and the analysis was carried out on the freshly extracted seed oils. The samples were analyzed in triplicates; mean and standard error were calculated.

Determination of physicochemical properties of oil: The oils extracted from the seeds of pawpaw and watermelon were assayed for their physicochemical properties and mineral contents by using various standard methods. The color and state of the oils at room temperature were noted by visual inspection while ester value was obtained by finding the difference between the saponification value and the acid value (Duduyemi *et al*., 2013).

Percentage yield of oil: The percentage oil yield of the seeds was determined and calculated by using the following equation:

$$\text{Percentage yield} = \frac{\text{Weight of extracted oil}}{\text{Weight of seed}} \times 100$$

Specific gravity: The specific gravity of the oil was determined by employing the weight ratio of the oil to the equivalent weight of water according to the following formula:

$$\text{Specific gravity} = \frac{W_1}{W_2}$$

where, W_1 is the weight of the oil, W_2 is the weight of equivalent volume of water.

Acid value: Ethanol was boiled on a water bath for a few minutes to remove dissolved gases. It was then neutralized by adding a few drops of phenolphthalein and about 10 ml 0.1M potassium hydroxide until a pale pink color was obtained. 6.0 g of oil was weighed into a conical flask and 50 ml of hot previously neutralized ethanol was added. The mixture was later boiled on a water bath. The hot mixture was then titrated with 0.1N potassium hydroxide solution until the pink color (stable for few minutes) returned (AOAC method, 1990).

The acid value (A. V.) was calculated from the following equation:

$$\text{A.V.} = \frac{\text{Titre value (ml)} \times N \times 56.1}{\text{Weight of sample}}$$

where, N = normality of KOH = 0.1M and 56.1 = molar mass of KOH.

Percentage free fatty acid: Percentage free fatty acid (% FFA as oleic acid) was determined by multiplying the acid value with the factor 0.503.

Thus Percentage FFA = 0.503 x acid value (Akubugwo *et al*., 2008).

Saponification value: 2.0 g of oil was weighed into a conical flask and 25 ml of 0.5 N alcoholic KOH was added. A blank was also prepared by placing 25 ml of alcoholic KOH in a similar flask. Reflux condensers were fitted to both flasks and the contents were heated in a water bath for one hour, swirling the flask from time to time. The flasks were then allowed to cool a little and the condensers washed down with a little distilled water. The excess KOH was titrated with 0.46 M HCl acid using phenolphthalein indicator (AOAC method, 1990).

The saponification value (S.V) was calculated using the following equation:

$$\text{S.V.} = \frac{(b-a) \times F \times 28.05}{\text{Weight of sample}}$$

where, b: titre value of blank (ml), a: titre value of sample (ml), F: factor of 0.46 M HCl = 1 (in this case) and 28.05 = mg of KOH equivalent to 1 ml of 0.46 M HCl.

Peroxide value: Peroxide value of the oil was assayed as described by the International Standard Organization

(ISO) 3960, 1975 method. 2.0 g of oil sample was weighed into a 500 ml conical flask and 10 ml of chloroform was added to dissolve the sample. This was followed by addition of 15 ml of acetic acid and 1 ml of freshly prepared saturated potassium iodide solution. The flask was then immediately closed, stirred for 1 minute and kept at room temperature for exactly 5 minutes away from light. About 75 ml of distilled water was added to the content of the flask and then shaken vigorously. Few drops of starch solution were added as indicator. The liberated iodine was titrated against 0.01N sodium thiosulphate solution. The same procedure was carried out for blank and the peroxide value (P.V) expressed in milliequivalent of active Oxygen/kg of sample was calculated thus:

$$P.V = \frac{V_1 - V_0 \times T \times 1000}{M}$$

where, V_0 is the volume of the sodium thiosulphate solution used for blank, V_1 is the volume of the sodium thiosulphate solution used for determination of sample, T is the normality of the sodium thiosulphate used and M is the mass of the test sample in gram.

Iodine value: Iodine value of the oil was assayed according to the titrimetric method of Pearson (1970). 2.0 g of oil sample was weighed into a dry 250 ml glass stopper bottle and 10 ml of carbon tetrachloride was added to the oil. About 20 ml of Wij's solution was then added and allowed to stand in the dark for 30 min. 15 ml of Potassium Iodide (10%) and 100 ml of water was added and the resulting mixture was then titrated with 0.1M Sodium thiosulphate solution using starch as indicator just before the end point. A blank determination was carried out alongside the oil samples. Iodine value (I.V) was calculated from the formula:

$$I.V = \frac{(V_2 - V_1) \times 1.269}{\text{Weight of sample (g)}}$$

where: V_2 = titer value for blank,
V_1 = titer value for sample.

Determination of mineral contents of oil: The oil samples were digested separately for mineral analysis by wet digestion method described by Oluremi *et al.* (2013). 0.5 g of the sample was weighed and transferred into 75 mL micro digestion tubes. Concentrated H_2SO_4 (4 ml) and H_2O_2 (2 ml) were added carefully. The tubes were heated in a block digester (pre-heated to 270°C) for 30 min. They were then taken out and allowed to cool. Another portion of H_2O_2 (2 mL) was added and heated further to achieve complete digestion which was indicated by appearance of clear solution. Magnesium, copper, zinc, iron and calcium were determined using an Atomic Absorption Spectrophotometer (Buck scientific Model, 2010), after the equipment had been calibrated using 100 mg/L of the standard solution of each element to be determined. Meanwhile, potassium and sodium were determined with the use of Flame Photometer (Jenway FP 160 model) while phosphorus was determined with the use of a Spectrophotometer (Spectro SC LabMed model).

RESULTS AND DISCUSSION

Physicochemical properties: Table 1 shows the results of the physicochemical properties of the seed oils examined in this work and the literature. The table shows that the specific gravity values of the three oils is about the same (~0.90 g/mL) and also about the same value as reported in the literature (Afolabi and Ofobrukweta, 2011). The acid value of the ripe pawpaw seed oil is much lower compared to the unripe pawpaw and the water melon seed oils and the data reported in the literature for the two seeds oils (Hassan *et al.*, 2013; Afolabi and Ofobrukweta, 2011). This indicates that the ripe pawpaw seed oil is more stable against rancidity than the unripe pawpaw seed oil. The saponification value of the unripe pawpaw seed oil however is lower than that of the ripe pawpaw seed oil and it is about half that of water melon seed oil. The values however, are an indication that the oils have a reasonable number of long chain fatty acids in its structure. The saponification value reported in this work is much lower for the water melon seed oil than the one reported in the literature (Hassan *et al.*, 2013). The iodine values obtained were very low for the three seed oils (almost the same value) and this suggests that the oils are highly saturated and will be a good material for soap making. The values are also much lower than the one reported in the literature (Hassan *et al.*, 2013; Afolabi and Ofobrukweta, 2011). The peroxide values of the three oils obtained are also very low which suggests that they are stable to auto-oxidation and will have a long shelf life.

Mineral composition of water melon and pawpaw seed oils: Minerals are important for the body to stay healthy. The body uses minerals for many different functions that include building bones, making hormones and regulating heartbeat. There are two kinds of minerals: macrominerals and trace minerals. Macrominerals are minerals the body needs in larger amounts and these include calcium, phosphorus, magnesium, sodium, potassium, chloride and sulfur. The body needs just small amounts of the trace minerals which include iron, manganese, copper, iodine, zinc, cobalt, fluoride and selenium (minerals http//nlm.nih.gov). The best way to get the minerals the body needs is by eating a wide variety of foods. The mineral compositions of the ripe, unripe pawpaw and watermelon seed oils are shown in

Table 1: Physicochemical properties of melon and pawpaw seed oil

				Literature	
	WMSO	URCPSO	RCPSO	Water[a] Melon	Pawpaw[b] (Ripe)
Color	Orange	Lemon green	Pale yellow	Golden yellow	
Odour	Fruity	Fruity	Fruity	Fruity	Fruity
State at room temp	Liquid	Liquid	Liquid	Liquid	Liquid
Specific gravity (g/mL)	0.90±0.10	0.89±0.10	0.90±0.05	0.918±0.002	
Percentage oil yield	32.71±0.21	33.81±0.11	36.30±0.10	30-34%[7,8]	
Acid value (mg KOH/g)	3.77±0.10	4.58±0.20	1.62±0.12	2.282	5.556±0.006
% free fatty acids (as oleic acid)	1.89±0.10	2.30±0.20	0.81±0.12	1.14	0.277±0.006
Saponification value (mg/KOH/g)	70.13±1.00	30.86±0.60	49.79±0.75	201	32.900±0.006
Peroxide value (meq. O2/kg)	9.00±0.90	3.00±0.81	0.50±0.01	3.4	
Ester value	66.36±0.20	26.28±0.05	48.17±0.01		
Iodine value (GI2/100g)	5.10±0.10	5.33±0.01	4.95±0.02	115	

Data expressed as mean±standard error of three replicates, RCPSO: Ripe carica papaya seed oil, URCPSO: Unripe carica papaya seed oil, WMSO: Watermelon seed oil, a: Ref. 8, b: Ref. 1

Table 2: Mineral contents of melon and pawpaw seed oil

	mg/100 g P	mg/100 g Ca	mg/100 g Mg	mg/100 g K	mg/100 g Na	mg/100 g Fe	mg/100 g Cu	mg/100 g Zn
RCPSO	23.65	1.47	1.33	1.33	3.24	1.11	0.27	0.25
URCPSO	14.76	2.43	3.02	1.51	3.01	0.42	0.4	0.22
WMSO	32.23	1.76	2.76	1.1	1.92	0.3	0.62	0.7

RCPSO: Ripe carica papaya seed oil, URCPSO: Unripe carica papaya seed oil, WMSO: Watermelon seed oil

Table 3: Nutritional value of pawpaw seed oil (Afolabi, 2001)

Component	Pawpaw oil[c]	Corn oil/100 g[d]	Canola/100 g[e]	Sunflower/100 g[f]
Moisture content (%)	0.223±0.035, 0.013±0.001			
Ash content (%)	0.590±0.017			
Protein (%)	0.823±0.012	0	0	0
Fat (%)	26.660±0.052	100	100	100
Crude fibre value (%)	0.603±0.006			
Carbohydrate by difference (%)	72.690±0.062	0	0	0
Energy value (Kcal/100 g)	524.913±0.591	900	884	884
Thiobabituric acid value (μM/g)	0.451±0.005			

Values are mean of three determinations±standard deviation. c: Ref.1, d: Ref. 6, e: Ref. 5, f: Ref.24

Table 2. The table shows that the three oils are rich in the macro minerals which include phosphorous, calcium, Magnesium, Potassium, Sodium and micro minerals such as iron, copper and zinc. The table also indicates that the ripe pawpaw seed oil has almost twice the value of phosphorous in the unripe seed oil and the water melon has almost one and a half times the value of the amount in the ripe pawpaw seed oil. The unripe pawpaw seed oil has a slightly higher value of macro minerals than the ripe pawpaw seed and water melon seed oil except in iron while the ripe pawpaw seed oil is richer in micro minerals than unripe pawpaw seed and water melon seed except in Zinc. Water melon seed oil is however, richer in copper and zinc than the ripe and unripe seed oil. The main function of phosphorus is in the formation of bones and teeth. The main food sources of phosphorous are the protein food groups of meat and milk (phosphorus, http// www.nlm. nih.gov). Pawpaw and watermelon seed oils will be another good source of phosphorous for the body.

Nutritional evaluation: Table 3 shows the results of the nutritional qualities of pawpaw seed oil, corn oil, canola oil and sunflower oil as reported in the literature (Afolabi and Ofobrukweta, 2011), corn, (http// www.google). com.ng, Canola, (http/ www.nutritiondata.self.com/), sunflower, (http// www.nutritiondata.self.com). Pawpaw seed oil has a little of carbohydrates, protein, fat and minerals which are absent in corn, canola and sunflower oils. Pawpaw seed oil also has macro and micro nutrients as shown in Table 2 which are absent in the other three oils. Corn, Canola and sunflower seed oils are available commercially for human consumption but are composed of mostly fats. Therefore, one can suggest that pawpaw seed oil can be a good source of minerals for human consumption because it has additional nutrients. Pawpaw seed oil also has a slightly higher calorific value than the other three seed oils. This suggests that it can be used as a source of biofuel.

Conclusion: The results obtained in this research work in comparison with literature have shown that the % yield of the three seed oils are high (~30%) enough to be commercialized. If harvested, it will reduce the amount of agricultural waste and serve as a source of additional employment and income on the farm. The three oils have a lot of nutritional values and can be consumed and also used for soap making. From the data obtained, the three oils contain a high level of phosphorus and therefore we suggest that these seed oils could be used to treat people suffering from hypophosphatemia. The peroxide values for the three oils indicate that it is stable to auto-oxidation and can be stored for a long time under normal condition. The oils are saturated oils (low saponification and iodine values) which make them less susceptible to rancidity. The water melon seed oil has almost double the amount of long chain saturated fatty acids in the pawpaw seed oils and the unripe pawpaw seed oil is more acidic than the ripe pawpaw and water melon seed oils.

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