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Mineral Composition, Physicochemical Properties and Fatty Acids Profile of *Citrullus Vulgaris* Seed Oil

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Abstract

*Soxhlet extraction (using n-hexane) of the oil from sun-dried and crushed seed of citrullus vulgaris gave yellow colour oil with a yield of 27 % oil per 100 g of the seeds. The fatty acids profile was obtained using gas chromatography mass spectroscopy (GC-MS), physicochemical properties were determined using standard methods and atomic absorption spectrophotometer (AAS) was used to obtain the concentrations of Fe, Ca, K, Mg and Na. The fatty acid profile revealed four compounds with linoleic acid (76.24 %) and Palmitic acid (14.42 %) as predominant compounds, while stearic acid (9.01 %) and oleic acid (0.33 %) were low. Physicochemical properties of the oil were determined as follows Specific gravity (0.864), colour (light yellow), Iodine value (58.54 g/100g oil), peroxide value (10 meq/g), acid value 9.58 mgKOH/g and texture at 37°C. These are very vital in considering the oil quality. Also, saponification value of 255.26 mgKOH/g was obtained in this study thereby confirmed its industrial applications. **I**n order to understand the chemistry of it's industrial applications, this paper reports some selected mineral compositions, fatty acid content and other important properties of the extracted seed oil.*

Keywords: Gas chromatography mass spectrometry, fatty acid profile, seed oil, *citrullus vulgaris.*

Introduction

The plant *citrullus vulgaris* belongs to the family Cucurbitaceae. It normally exists as shredded green plant with circular or spherical shapes, features common to some plants. The fruits of this plant have many glossy compacted seeds that are thickened at the margins which are black or yellowish white in colour. It is locally known as "Kankana" by Hausas in the Northern Nigeria. The seeds can form emulsion through water rubbing and agitation. The resulting emulsion has been found important in curing fever, urine imperfections and related diseases. Recently, application has been extended to expel tape worm[1].

This watermelon usually consumed as a fruit because of its sweet flavor and high nutritional value. It has been widely used in several regions of the world, especially in Africa and Asia, not only as a source of nutrition but also as a folk remedy for the treatment of strangury[2].

Oil from the seeds is light, piercing and contains significant amount of fatty acids. It is also known as Kalahari oil is another name associated to it. The plant contains approximately six percent by weight sugar with water mainly constituting the rest. Vitamin C is also sourced from it like many other fruits. In Africa, it's seeds have been prized high for the highly nutritive oil that they contain[1].

Several Cucurbitaceae species provide good source of balance nutritive fractions including protein and minerals and can be employed as native medicines. Some of the species studied include the seed kernels from cucurbit fruits and vegetables such as melon, watermelon, cucumber and gourd, traditionally called "Charmagaz" are well-known in the sub-continental region for their therapeutic properties[3,4].

Watermelon is a fruit that contains lots of water[5]. Several researchers have reported on characterization of *citrullus lanatus* seed oil, not much on *Citrullus vulgaris* very common species. The prepared seeds of water melon are important ingredients for domestic purposes like local snacks manufacture in Arab and Asian regions due to their high nutritional values. The seeds are very rich in proteinous materials (up to 37%) and fat and oil (up to 46%). The appearance of watermelon seed oil is light and is valued as a potential source of essential fatty acid (linoleic acid) with health benefits[6,7]. Watermelon seed oils, often characterized by high-linoleic acid content, have been studied in different parts of the world such as West Africa and the Middle East[6]. Properties of selected melon seeds were probed by Mabaleha et al., 2007 to determine their conceivable uses for edibility[4]. Currently, much research is intensified with greater emphasis of investigating other newer and underutilized species of plants as oil sources due to escalating vegetable oil demands, [8,9]. For this reason, several seed oils have been gauged as newer sources for mostly industrial and food uses[10-12]. In the last two to three years more than two million metric tons of vegetable oil were imported to Pakistan, according to Pakistan Oilseeds and Products Annual Report[13]. Still in Pakistan, almost 75 percent of the total domestic consumption of vegetable oil is met through imports[14] while only 25 percent is derived from the local vegetable oil seed resources. Watermelon fruit is widely consumed in Nigeria yielding a considerable amount of seeds, which are often discarded as waste. In line with the present needs, these seeds can be used for oil extraction.

This paper was therefore aimed at evaluating the mineral composition, physicochemical properties, profile of fatty acid and characterization of the *citrullus vulgaris* seed oil.

Material and Methods

The fresh fruits of *citrullus vulgaris* were obtained from Samaru market, Zaria, Kaduna state, Northern Nigeria. They were screened for proper identification by an expert Botanist in Ahmadu Bello University, Zaria.

Extraction: A soxhlet extractor was initially loaded with 100g of sun dried and carefully crushed and grinded seeds. The extraction solvent was n-hexane and the extraction period was 6 h. The extraction set-up was initially validated with known procedures for known compositions.

Fatty acid composition: IUPAC transmethylation procedure was adopted in converting the fatty acids in the oil to corresponding methyl esters. Gas chromatographic method was therefore employed and the GC peak area provides the relative fraction of FAME. The GC program include raising oven temperature to 280°C from ambient temperature using 10 dgrees per minutes ramping rate. The initial and final column temperature was held for 0 and 5 minutes, respectively. The injector temperature was carefully programmed to 250 °C. The identification of the unknown FAMEs was based on the similarity search performed using NIST 2OO5 Library on the basis of peak areas by a Chromatography GCMS solution for SHIMADZU GCMS-QP 2010 data-handling program.

Physico-chemical characteristics: The fundamental oil parameters such as, saponification, acid and iodine values as well as the peroxide factor, in addition to specific gravity were determined by adopting AOCS method[15,16].

Acid value: A mixture of 25cm^3 diethyl ether with 25cm^3 of ethanol and 1cm^3 1% phenolphthalein solution was carefully neutralized with 0.1M KOH, A 0.1 molar KOH solution was used to titrate 2g of the solvent homogenized oil, with constant agitation until the content of the flask which turns pink for 15 seconds was obtained.

$$\text{Acid value} = \frac{(\text{v} - \text{b}) \times \text{N} \times 56.1}{\text{W}} \quad (1)$$

Where, W is the weight of the oil sample employed in the units of grams, N stands for basic normality, the cm^3 titre value of the blank is b and v parameter represents the sample titre value in similar units.

Iodine value: Exactly 10 ml of 15%KOH (w/v) was added to a 250 ml flask containing two grams of oil and thirty milliliters of Hanus reagent mixture that was stationed initially for 30 min in cupboard. The resulting solution was titrated with sodium thiosulphate (0.1200 molar). For appropriate computations and extrapolations, the titration was carried out for the blank employing similar parameters. The titre values obtained were employed to compute the iodine value.

$$\text{Iodine value of oil} = \frac{(\text{B} - \text{R}) \times \text{molarity of Na2S2O3} \ (0.3 \times 12.69)}{\text{W}} \quad (2)$$

Where B and R stand for blank and oil samples in term of titre values, respectively.

Saponification value: Oil (exactly 2g) was introduced to a flask (250 ml size), initially having 25 ml of ethanol-potassium hydroxide solution was added, the flask was configured to a condensing set-up and heated on a water-bath for 1 hour with frequent shaking, 1cm^3 of 1 % phenolphthalein solution introduced followed by warmed excess alkali and titrated against 0.5000 M HCl. Equivalent titration was performed for the blank and generated values were employed for computation according to the following relation.

$$\text{Saponification value (S.V)} = \frac{\text{volume of HCl used} \ (\text{B} - \text{S}) \times 28.05}{\text{W}} \quad (3)$$

Peroxide value: Exactly, 1.0g of the sample was transferred into 250cm^3 flask and 1g of powdered potassium iodide (KI) and a solvent mixture (2:1 of glacial acetic and trichloromethane) were then added. The solution was then placed on a water bath for a few minutes for complete dissolution. 20cm^3 of 50% potassium iodide were introduced and the sample titrated with 0.0020N $Na_2S_2O_3$. The indicator was a regular starch solution. Blank experiment was similarly performed.

$$\text{Peroxide value} = \frac{(\text{RxB}) \times \text{molarity of Na2S2O3}}{\text{W}} \quad (4)$$

Where, R and B take their usual meanings and notations as in the case above.

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

$$\text{Specific gravity} = \frac{\text{W3} - \text{W2}}{\text{W1}} \quad (5)$$

Where W1, W2 and W3 are the respective weights of equivalent water, empty bottle and oil.

Free Fatty Acid (%FFA): The fatty acid content was obtained via titration method. A warmed 2g of the oil was titrated with 0.1400 M of KOH solution. The indicator solution was a phenolphthalein and while constant shaking was ensured until the regular end point was achieved. The fatty acid percent is equivalent to the product of titre value and KOH molar concentration divided by the oil weight extrapolated to 100%.

Mineral composition: The compositions of Fe, Ca, K and Na in the seeds were determined spectroscopically using a SHIMADZU AAS6800 spectrophotometer based on the method previously validated.

Results and Discussion

Table 1 showed the Fatty acid profile of the oil with four main fatty acids namely: oleic (0.33%), linoleic (76.24%), palmitic (14.42%), and stearic acid (9.01%). The linoleic acid shows the highest composition. The promising amount of linoleic acid entails disease curing potentials and also presents cardiovascular linear option for other oils[1]. Similarly, adequate concentration of omega 6 (linoleic acid 76.24%) is also indicating a potentially useful food additive and can be converted to gamma-linoleic acid that can be used as a dietary increment to surge the production of anti-inflammatory 1-series prostaglandins. Series 1 Prostaglandins play a crucial role in controlling blood thickness and blood pressure, it therefore means having an anti-inflammatory effect and is a vital nerve tissue food helping in the maintenance of brain and nerve function[17]. Pregnant women have an increased demand for omega-3 and omega-6 fatty acids which serves essentially for fetal growth, development of brain, learning and behavior. Also since infants receive their basic fatty acids through the breast milk, lactating women should also increase their fatty acids intake.

Table-1
Percentage composition of *citrullus vulgaris* seed oil

Components	Percentage (%)	R_{time} (s)
Oleic acid	0.33	18.174
Linoleic acid	76.24	16.869
Stearic acid	9.01	16.614
Palmitic acid	14.42	14.959

Table-2
Physicochemical properties of *citrullus vulgaris* seed oil

Properties	Result
Colour	Light yellow
Texture at 37 °C	Liquid
Specific gravity	0.86
Iodine value (g/100g)	58.54 ± 0.1
Saponification value (mgKOH/g)	255.26 ± 0.01
Acid value (mgKOH/g)	9.58 ± 0.04
Peroxide value (meq/g)	10.00 ± 0.3
Free fatty acid (mgKOH/g)	4.88 ± 0.03

Important characteristic parameters of the oil were observed as seen from table 2. The oil's saponification value was 255.26 ± 0.01 mgKOH/g which is above the what was reported previously; 188-196 mgKOH/g but their are cases of higher compositions especially with coconut, palm and butter fat 225 oils (values can exceed 250 mgKOH/g). Oils with high saponification values were reported to contain high proportion of short-chain fatty acids[18].

The oil in comparison with *Plukenetia conophora* (11.5 mgKOH/g) and benni seed (47.6 mgKOH/g) has low acid value of 9.58 ± 0.04 mgKOH/g according to a report by Aremu et al., 2006b[19], but this value is higher than what was reported for cashew nut oil (0.82 ± 0.4 mgKOH/g)[20]. Acid value has was reported to be an industrially qualitative parameter for selective seed oils applications[21]. The iodine value of *citrullus vulgaris* (58.54 ± 0.1g/100g) is higher than the value (28.6±0.1 g/100g) of *citrullus lanatus* seed oil, Hausa melon seed (38.50 ± 0.67g/100g and 44.4 ± 0.1g/100g for cashew nut oil[21]. *citrullus vulgaris* seed oil can be categorized as a non-drying oil because drying oils have an iodine value above 100 g/100g[3]. This non-drying attribute means the oil can be used effectively in the paint industry[3]. The iodine value is also used as an index for evaluating the ability of oil to go rancid[22,23]. The iodine value obtained (58.54±0.1 g/100g) in this study indicates that the oil contain substantial level of unsaturated bonds therefore the type of storage to be used for this seed oil should ensure protection of the oil from oxidative deterioration.

The peroxide value is very useful criteria for indicating the deterioration of oils. Values of fresh oils are less than 10 meq/g. Values between 20 and 40meq/g result in rancid taste. The low peroxide value (10.00±0.30meq/g) indicates that the oil is stable. The free fatty acid value of 4.88 ± 0.03 mgKOH/g falls within the maximum limit of 5 mgKOH/g for free fatty acids in high grade palm oil in Nigeria[24]. The oils could therefore be used as edible oil.

Table-3
Selected Mineral Composition of *citrullus vulgaris* seed oil

Mineral Element	Concentration (ppm)
Fe	2.10
Ca	1.40
K	3.80
Na	4.80
Mg	5.75

Table 3 above shows Fe, Ca, K, Na and Mg contents of the oil extracted from *citrullus vulgaris* seed as 2.10 ppm, 1.40 ppm, 3.80 mg/ml, 4.80 mg/ml and 5.75 ppm respectively. From this results, it can be seen that the Ca and K contents of *citrullus lanatus* melon seeds are below the values obtainable with *citrullus vulgaris* seeds, concentration of Fe from *citullus lanatus* seed oil is larger than from the oil of *citrullus vulgaris.* On the other hand, Mg concentration for both oils from *citrullus vugaris* and *citrullus lanatus* seeds are closely similar[25].

Conclusion

In conclusion, the seeds characteristically contained high levels of oil and are rich in linoleic fatty acid. Most of the physicochemical properties of the studied oil were favorably compared with other conventional seed oils like palm kernel oil, peanut oil, and soyabean oil. While the mineral constituents are in good agreement with *citrullus lanatus* (another specie of water melon). The seed oil therefore has potential for use as domestic and industrial oil.

References

1. Sodeke V.A., Extraction of oil from water melon seed and analysis, Quarterly Research service, 25-30 **(2005)**

2. Ziyada A.K. and Elhussien S.A., Physical and chemical characteristics of *Citrullus lanatus Var. Colocynthoide* seed oil. *J. Phy. Sci.,* **19,** 69-75 **(2008)**

3. Dosumu M.I. and Ochu C., Physicochemical properties and fatty acid composition of lipids extracted from some Nigerian fruits and seeds, *Global J. Pure Appl. Sci.,* **1,** 45-47 **(1995)**

4. Mabaleha M.B., Mitei Y.C., Yeboah S.O., A comparative study of the properties of selected melon seed oils as potential candidates for development into commercial edible vegetable oils. *J. Am. Oil Chem. Soc.,* **84,** 31-36 **(2007)**

5. El Adawy T.A and Taha K.M., Characteristics and composition of watermelon, pumpkin, and paprika seed oils and flours, *J. Agric. Food Chem.,* **49,** 1253-1259 **(2001)**

6. Anhwange B.A, Ajibola V.O. and Oniye S.J., Chemical studies of the seeds of m*oringa oleifera* (Lam) and *detarium microcarpum* (Guill and Sperr), *J. Biol. Sci.,* **4(6),** 711-715 **(2004)**

7. Taiwo A.A., Agbotoba M.O., Oyedepo J.A., Shobo O.A., Oluwadare I. and Olawunmi M.O., Effects of drying methods on properties of water melon (*Citrullus lanatus*) seed oil, *Afr. J. Food Agr. Nutr. Dev.,* **8,** 1684- 5374 **(2008)**

8. Anwar T., Banger M.I., Anwar F., Khan M., Shahid R. and Iqbal S., A comparative characterization of different non-conventional oilseeds found in Pakistan, *J. Chem. Soc. Pak.,* **28,** 144-148 **(2006)**

9. Ramadan M.F., Sharanabasappa G., Parmjyothi S., Seshagiri M. and Moersel J.T., Profile and levels of fatty acids and bioactive constituents in mahua butter from fruit-seeds of buttercup tree [Madhuca longifolia (Koenig)], *Eur. Food Res. Technol*., **222,** 710-718 **(2006)**

10. Adhikari P., Hwang K.T., Shin M.K., Lee B.K., Kim S.K., Kim S.Y., Lee K.T. and Kim S.Z., Tocols in craneberry seed oils, *Food Chem.,* **111,** 687-690 **(2008)**

11. Matthaus B., and Ozcan M.M., Fatty acids and tocopherol contents of some prunus spp. kernel oil, *J. Food Lipids,* **16,** 187-199 **(2009)**

12. Nehdi I.A., Characteristics and composition of Washingtonia filifera (Linden ex André) H. Wendl, Seed and seed oil, *Food Chem*., **126,** 197-202 **(2011)**

13. Pakistan Oilseeds and Products Annual (POPA) Report, Written by Shafiq-Ur-Rehman approved by Joseph MC. Report Number: PK11003, **(2011)**

14. Duel, H.J., The lipids: their Chemistry and Biochemistry Vol. 1 New York Inter Science Publishers pp. 53-57 **(1951)**

15. Official methods and recommended practices of the AOCS, official methods of analysis of AOCS, fats, oils and lipid related analytical methods, 6th edition, **(1995)**

16. Garba, Z.N., Gimba, C.E., Emmanuel, P., Production and characterization of biobased transformer oil from jatropha curcas seed, *J Phy. Sci.,* **24(2),** 49-61 **(2013)**

17. Eromosele, C.O. and Pascal, N.H., Characterization and viscosity parameters of seed oils from wild plants, *J. Bioresources Tech.,* **86,** 203-205 **(2003)**

18. Akintayo, E.T. and Bayer, E., Characterization and some possible uses of plukenetia conophora and adenopus breviflorus seeds and seed oils, *Biores. Technol.,* **85,** 95-97 **(2002)**

19. Aremu M.O., Olonisakin A., Bako D.A. and Madu P.C., Compositional studies and physicochemical characteristics of cashew nut (*Anarcadium occidentale*) flour, *Pak. J. Nutr.,* **5(4),** 328-333 **(2006b)**

20. Oladimeji, M.O., Adebayo, A.O. and Adegbesan, A.H., Physico-chemical properties of Hausa melon seed flour, *Ultra Sci.,* **13,** 374-377 **(2001)**

21. Aremu, M.O., Olaofe, O. and Akintayo, T. E., A Comparative study on the chemical and amino acid composition of some Nigerian underutilized legume flours. *Pak. J. Nutr*., **5,** 34-38 **(2006a)**

22. Eka, O.U., Proximate composition of bush mango tree and some properties of dika fat, *Nig. J. Nutr. Sci*., **1,** 33-36 **(1980)**

23. Amoo, I.A., Eleyinmi, A.F., Ilelaboye, N.A.O. and Akoja, S. S., Characteristics of oil extract from gourd (*Cucurbita maxima*) seed. *Food, Agric. and environ.,* **2,** 38-39 **(2004)**

24. Basil, S., Kamel, H., Dawson, V. and Kakuda Y., Characteristics and composition of melon and grape seed oils and cakes, *J. Am. Chem. Soc.,* **62,** 881-883 **(1985)**

25. Mariod, A.M., Yousif M.A., Bertrand M., Galaleldin K., Andeen S., Aied M.G. and Ibrahim A., A comparative study of the properties of six Sudanese cucurbit seeds and seed oils, *J. Am. Oil Chem. Soc.,* **86(12),** 1181 – 1188 **(2003)**