IJAAR PUBLISHING® DOI: 10.46654

Scholarly Journal of Science and Technology Research & Development | ISSN: **2955-0807**
Vol. 1, Issue 5 (October, 2022) | www.ijaar.org/sjstrd

Physico-chemical and GC-MS analysis of Oil extracted from two varieties of Tiger nut (*Cyperus Esculentus*)

[1]Umar, A., [1]Osesua, B. A., [1]Aliyu, A., [2]Yusuf .M. and Abdullateef .Y.T.

[1]Chemisty unit, Department of Science Technology, Waziri Umaru Federal Polytechnic, Birnin Kebbi.

[2]Microbiology unit, Department of Science Technology, Waziri Umaru Federal Polytechnic, Birnin Kebbi.

Correspondence: abukalgo99@gmail.com.07038414041

ABSTRACT

The research was on the physico-chemical analysis of oil extracted from two varieties of dried Cyperus esculetus (Tiger nut). N-hexane (solvent) and Soxhlet extraction method was employed in the oil extraction. The physicochemical property determinations of the two varieties of the Tiger Nut tuber were conducted. The parameters analyzed were; percentage oil yield, moisture content, saponification value, peroxide value, iodine value, free fatty acid value, appearance, colour, odour and Gas Chromatograph-Mass Spectrometer (GC-MS) analysis. The result obtained for the two varieties (yellow and brown tiger nut) shows the followings: Oil yield of 18% and 10% for yellow and brown tiger nut respectively, Moisture content of 4.2% and 3.3%, Saponification value of 208mgKOH/g and 207mgKOH/g, Peroxide value of 2.0mEq/kg and 3.0mEq/kg, Iodine value of 6.6gI_2/100g and 7.66gI_2/100g, and Free fatty acid value of 9.8% for both samples. The GC-MS analysis results indicate that for the yellow Tiger nut variety; 15 fatty acid compounds were registered in varying percentage yields and the dominant Fatty acid was Vaccenic acid (11-octadecanoic acid) with 30.02%. While for the brown Tiger nut variety; 14 fatty acid compounds were registered, and Vaccenic acid (11-octadecanoic acid) with 32.76% was obtained as the dominant fatty acid. These results were in favour of the utilization of Tiger nut (Cyperus Esculetus) tuber Oil in cosmetic and food industries.

Keywords: *Cyperus esculetus*, oil extraction, physico-chemical, GC-MS analysis.

INTRODUCTION

Tiger nut (*Cyperus Esculentus*) is an underutilized crop cultivated worldwide, which is sweet and rich in fat (Aliyu and Sani, 2009). Tiger nut (*Cyperus esculentus*) has always been in use as food, eaten raw, roasted, dried, baked, or made into beverages (Adejuyitan, *et al.*, 2009). Tiger nut are daily ingredients of the diet of many people in North Africa and Spain (Oladele *et al.*, 2009). According to Mason, (2005), tiger nuts have long been recognized for its health benefits with high content of soluble glucose, oleic acid, along with high energy content and also rich in mineral (Matinez, 2003). Tiger nut produces high quality oil about 25.5% of its content the edible and stable oil obtained from the tuber is said to be superior oil that compares favourably with olive oil (Muhammad *et al*., 2011).Tiger nut oil has golden colour and a nutty taste which makes it ideal for different users.

Tiger nut oil is used in preparation of therapy for some cardiac and intestinal pathology, because of its high content of monounsaturated fatty acids (Adejuyitan *et al*., 2009, Shaker *et al*., 2009). Tiger nut oil extracted from tiger nut is used naturally with salads or for frying (Shaker *et al*., 2009). Furthermore, less fat is absorbed into the food as it creates a crust on the surface during cooking, preventing the oil itself being absorbed into the product. The oil compares well with corn; soybean, olive and cotton seed oil and can thus serve as a substitute for these oils especially in times of scarcity. In the textile industry, the oil is used to waterproof textile fibres. The oil is a potential source of biodiesel and much research has been conducted (Shaker *et al*., 2009).

The high rate of production and lack of awareness of the benefits of tiger nut had been underutilized resulting in its wastage. There is no information on the effect of moisture content on the yield of the oil from tiger nut. But due to increasing awareness of the use of tiger nut oil, there is need to determine the appropriate set of processing parameters necessary for the optimum extraction of the oil (Adejumo and Salihu, 2018).

MATERIALS AND METHODS

SAMPLE COLLECTION, IDENTIFICATION AND TREATMENT

The Sample of dried tubers of the two varieties of *Cyperus esculantus* L. i.e. yellow and brown were purchased from Birnin Kebbi Central market. The tubers were sorted, washed in a basin of tap water, rinsed with distilled water, and made free from bad, broken and foreign material. The tubers were then oven dried at 70^{o}C for 24 hours, then ground into powder and sieved with 20-mesh-sieve. The powdered sample was stored and kept in a plastic container for further analysis (Aliyu *et al.*, 2017).

EXTRACTION OF OIL USING SOXHLET EXTRACTOR

50g of each tiger nut powder sample was transferred into a porous thimble of a soxhlet extractor and the oil was extracted using n-hexane at 69^{0}C for 3 h. The oil was separated from the solvent using a rotary evaporator.

GC-MS ANALYSIS

The analysis of the fatty acids in the *Cyperus esculantus* L. tuber oil sample was done at National Institute of Chemical Technology (NARICT), Zaria, Nigeria, a Shimadzu QP2010 plus series gas chromatography coupled with Shimadzu QP 2010 plus mass spectroscopy detector (GCMS) system was used. The temperature programmed was set up from 70°C to

280°C. Helium gas was used as carrier gas. The injection volume was 2 µL with injection temperature of 250°C and a column flow of 1.80 mL/min for the GC. For the mass spectroscopy ACQ mode scanner with scan range of 30-700 amu at the speed of 1478 was used. The mass spectra were compared with the NIST 05 mass spectral library.

DETERMINATION OF *CYPERUS ESCULENTUS* TUBER OIL YIELD

The percentage (%) Oil yield was obtained using the formula:

$$\text{Oil yield (\%)} = \frac{weig\,ht\ of\ oil\ extracted}{weig\,ht\ of\ powdered\ \ seed\ tubers\ \ used} \times 100$$

DETERMINATION OF MOISTURE CONTENT

In determining the moisture content of an acid, a clean flat dish of silica, platinum was dried, the cool dish was weighed (W_0) and 2g of the oil was introduced into the dish and was spread after which it was weighed accurately (W_1). The dish and its content W_1 was transferred into an oven at 105^{o}C to dry for about 3 hours. Then a pair of tongs was used to transfer the dish into desiccators, allowing it to cool down before the oven for half an hour and was allowed to cool in the desiccators after which it was then weighed (W_2). Finally the dish was returned to the oven for half an hour and was allowed to cool in the desiccators after which it was then weighed (Nielsen, 2010).

$$\% \text{ Moisture Content} = \frac{W_1 - W_2}{W1 - W0} \times 100$$

Where:

W_0 = is the weight of the empty dish

W_1 = is the weight of the dish and sample before drying

W_2 = is the weight of dish and sample after drying

DETERMINATION SAPONIFICATION VALUE

METHOD

0.5g of the oil sample was placed into 250ml round bottom flask 25ml of 0.1M alcoholic potassium hydroxide was added into the flask and boiled continuously for about one hour under a reflux condenser. The content of the flask was swirled at frequent interval and titrated while hot with standard 0.5M Hcl using phenolphthalein as the indicator. The saponification value was calculated using this formula.

$$S.V = 56.1 \times \frac{(T_1 - T_2)}{W}$$

Where T_1 and T_2 are the value for sample and blank titration respectively, and W is weight of the oil sample in grams (Nielsen, 2010).

DETERMINATION OF PEROXIDE VALUE

METHOD

5g of the oil sample was placed into 250cm^3 conical flask and 30 cm^3 of acetic acid – chloroform mixture was added. The mixture was swirled to dissolve the oil and 0.5 cm^3 of saturated potassium iodine solution was added and mixture allowed standing with occasional shaking for one minute 30 cm^3 of distilled water was added and titrated slowly with 0.1M sodium thiosulphate using starch indicator (Nielsen, 2010).

$$\text{Peroxide Value} = \frac{(B - S) \times M}{W} \times 1000$$

Where S = sample titre value in cm^3
W = weight of sample in grams
M = Molarity of titrant ($Na_2S_2O_{3)}$
B = Blank titre value in cm^3

3.4.8 DETERMINATION OF FREE FATTY ACID (FFA)

5g of oil sample was placed into a clean 250 cm^3 flask. 50ml of ethanol was measured into another flask and heated to boiling point on hot plate. Then, 0.5 cm^3 of phenolphthalein indicator was added to the ethanol and was neutralized with 0.1M sodium hydroxide solution. The neutralized solution was poured into the flask containing the oil sample. The mixture was heated to boiling on the hot place and titrated while still hot with 0.1M sodium hydroxide solution. The free fatty acid value was calculated using the formula (AOAC, 2009).

$$\text{FFA} = \frac{2.5 \times T}{W}$$

Where T = is the titrated value
W = is the weight of the sample

2.5 is constant

3.4.9 DETERMINATION OF IODINE VALUE

METHOD

Iodine value determination was by Wijs method (AOAC, 2009). Into a 250 ml stopper flask 0.2 g oil extract was added, 10 ml tetrachloride (CCl_4), 25 ml Wijs solution where also added and the flask was swirled. This was allowed to stand (incubation) for 30 minutes at 27 ^{O}C. Thereafter, 20 ml KI solution followed by 100 ml distilled water were added to the flask. The solution obtained was gradually titrated with 0.1 N sodium thiosulphate $Na_2S_2O_2$ solutions which gave yellow coloration until the colour disappears. Then, 1 ml starch solution indicator was further added and this gave a blue colour. Titration continued until sudden disappearance of blue colour. A reaction blank containing all ingredients except the oil sample ran simultaneously (AOAC, 2009).

$$\text{Iodine value IV} = \frac{[(B-S) \times N \times 12.692]}{W}$$

Where B = is the titre of blank in cm^3

S = is the titre of sample in cm^3

M = is the molarity of $Na_2S_2O_3$

W = is the weight of the sample

12.69 is constant

RESULT AND DISCUSSIONS

Results

The yield and analysis of crude oil obtained from tiger nut are given in the table below;

Table 1: PHYSICO-CHEMICAL PROPERTIES OF TIGER NUT OIL

S/N	Analysis parameter	Yellow Variety	Brown Variety
1.	Oil Yield	18%	10%
2.	Moisture Content	4.3%	3.3%
3.	Saponification Value	208mg / KOH	207mg / KOH
4.	Peroxide Value	2.0meq / kg	3.0meq / kg
5.	Iodine Value	$6.6gl_2$ / 100g	$7.6gl_2$ / 100
6.	Free Fatty acid Value	9.8mg	9.8mg
7.	Appearance	Fluid oily liquid	Fluid oily liquid
8	Colour	Golden clear liquid	Golden brown liquid
9	Odour	Nutty odour	Nutty odour

Table 2: FATTY ACIDS FOUND IN THE OIL OF YELLOW TIGERNUT *(CYPERUS ESCULENTUS*) TUBERS.

S/N	FATTY ACID	M.F	PERCENTAG YIELD %
1.	11-octadecanoic (Vaccenic) acid methyl ester	C19H36O2	30.02
2.	Hexadecanoic (Palmitic) acid methyl ester	C17H34O2	17.13
3.	Hexadecanoic acid, 2-hydroxy-1-3propanediyl ester	C35H68O5	12.67
4.	9-Octadecenoic (Oleic) acid(Z)	C18H34O2	11.89
5.	Octadecenoic (Stearic) acid methyl ester	C19H38O2	6.19
6.	Hexacosanoic (Cerotic) acid methyl ester	C27H54O2	4.31
7.	1, 2-15, 16-Diepoxyhexadecane	C16H30O2	3.81
8.	Octadecenoic acid,(2-Phenyl-1-3-dioxolan-4-yl) methyl ester	C28H44O2	3.79
9.	Eicosanoic (Arachidic), methyl ester	C21H42O2	3.72
10.	Triacontanoic (Melissic) methyl ester	C31H62O2	2.04
11.	Tridecanoic acid, methyl ester	C14H28O2	1.83
12.	Decanoic(Capric) acid, methyl ester	C11H22O2	0.87
13.	Hexanoic acid, methyl ester	C9H16O2	0.59
14.	11-Hexadecanoic acid methyl ester	C18H34O2	0.58
15.	7-methoxy-3,7-dimethyloctanal	C11H22O2	0.55

Above table shows the fatty acid found in the yellow tiger nut, the molecular formula (M.F) and the percentage yield of each

Table 3: FATTY ACIDS FOUND IN THE OIL OF BROWN TIGERNUT *(CYPERUS ESCULENTUS)* TUBERS.

S/N	FATTY ACID	M.F	PERCENTAGE YIELD %
1.	11-Octadecenoic (Vaccenic) acid methyl ester	C19H36O2	32.76
2.	Hexadecanoic (Palmitic) acid methyl ester	C17H34O2	19.43
3.	Hexadecanoic acid, 2-3 dihydroxy propyl ester	C17H34O2	19.43
4.	9-Octadecenoic (Oleic) acid methyl ester	C18H34O2	11.07
5.	Octadecanoic (Stearic) acid methyl ester	C19H38O2	6.63
6.	Docosanoic (Behenic) acid methyl ester	C23H46O2	3.69
7.	Eicosanoic (Arachidic) acid methyl ester	C28H56O2	3.64
8.	Glycerol 1,2-dipalmitate	C39H76O5	3.34
9.	Dodecanoic (Lauric) acid methyl ester	C13H26O2	2.65
10.	Triacontanoic acid methyl ester	$C_{31}H_{62}O_2$	2.13
11.	Tetradecanoic (Myristic) acid methyl ester	C15H30O2	1.26
12.	Hexane,2,5 dimethoxy-2-5 dimethyl	C10H22O2	0.85
13.	Hexadecanoic acid, 15 methyl-, methyl ester	C18H36O2	0.32
14.	4 - Dimethylsilyloxytetradecane	C16H36OSi	0.31

Above table shows the fatty acid found in the brown tiger nut, the molecular formula (M.F) and the percentage yield of each.

DISCUSSION

An oil yield of 18% and 10% were obtained for yellow and brown tiger nut varieties, which is lower than 23.7% obtained by Oyedele, *et al.*, (2015) and within the range of 12.14%, obtained by Adejumo and Salihu (2018).

The moisture content of tiger nut oil was found to be 4.2% and 3.0% for yellow and brown, this shows that the oil of tiger nut had a small percentage of moisture and the low moisture content of the oil remain an asset in storage and preservation of the oil.

The saponification value of tiger nut oil was found to be 208mg/KOH and 207 mg/KOH for yellow and brown, which is within the range of 143.06%, 185.13% and 260.87% obtained by Adejumo and Salihu (2018). This value considered to be useful in soap making which is a disadvantage for bio-diesel production (Kamalu and Orghome, 2008).

The peroxide value of the oil was found to be 2.0meq/kg and 3.0meq/kg. Low peroxide value is an index of resistance to free oxidation thus; the oil is likely to have good shelf life when stored without going rancid. This could be probably due to presence of alpha-tocophenol that is known to be present in this oil (Almustafa, *et al.,* 1995).

The iodine value of the oil was 6.6 gl_2/100g and 7.6 gl_2/100g were obtained for Yellow and Brown Tiger nut respectively.

Free fatty acid values refer to the number of milligram of potassium hydroxide necessary to neutralize the free acid in 1g of the oil sample. It measures the extent to which hydrolysis has liberated the fatty acids from their ester linkage to the parent glyceride molecules. It is partially for the reason that acidity is extensively quoted as "free-fatty acid content". The acidity of the oil gives oil refiner an immediate estimate of the amount of oil that will be lost when batch of oil is neutralized to remove those free-fatty acids. The free fatty acid tiger-nut was found to be 9.8mg for both samples.

GC-MS ANALYSIS RESULT OF THE YELLOW AND BROWN TIGERNUT OIL.

The GC-MS results obtained, shows that 11-octadecenoic acid (Vaccenic acid), a mono-unsaturated fatty acid methyl ester was found to be the most dominant fatty acid in both the yellow and brown Tiger nut varieties with percentage yield of 30.02%, 32.76% respectively. Presence of Vaccenic acid in Tiger nut is associated with the following health benefits;

1. Cardiovascular problems

Limited evidence is obtained from human trials and animal models that Vaccenic acid does not have adverse impact on cardiovascular biomarkers which includes C-reactive protein (Emily, 2019). It is also clear that consuming a Vaccenic acid (V A) rich butter reduced cholesterol-induced hyperlipidemia and atherosclerosis in mice. The present studies suggest that the generalization that all Trans–fatty acid (TFA) contribute to cardiovascular disease warrants further investigation (Chantal *et al*., 2010). The discovery of new bioactive properties of VA is supported by clinical studies which have shown that dietary supplementation of VA effectively reduces not only fasting lipids, but also postprandial triacylglycerol and chylomicron concentrations in obese rats(Wang *et al*., 2010.Field *et al.*, 2009)

2. Prevention of cancer

Some conducted studies have shown direct association between reduction in risk of cancer (such as prostate cancer and breast cancer). Most of the studies conducted in animal models and cancer cell lines have shown reduction in growth of cells or tumor metabolism (Emily, 2019).

3. Inflammation and immune function

Animal study on short term shows that Vaccenic acid has positive influence on immune response. Thus benefits could be experienced with the long term intake of Vaccenic acid. A 16-week trial which involved rodent models with diet enriched with Vaccenic acid significantly promoted immune function (Emily, 2019). Vaccenic acid has been shown to have a variety of health benefits including increasing insulin sensitivity as well as anti-inflammatory (Singh *et al.,* 2021).

CONCLUSION

The physico-chemical properties results obtained for the two analysed oil indicates a very close and similar related data, which can be attributed to their cultivation condition. Also it shows that tiger nut oil has the potential to be used as an alternative source of edible oil as

well as industrial oil. The results of fatty acid composition from the two varieties of tiger nut (*Cyperus esculentus* L) tubers through GC-MS analysis indicates the presence of Vaccenic acid as the dominant methyl ester, which has many health benefits, and also the Oils have many similar fatty acid constituents.

REFERENCE

Adejumo, B.A and Salihu, M.E (2018). Effect of moisture content on the yield and quality of oil from tiger nut (*Cyperus esculentus*) *Annals. Food Science and Technology*. Vol 19, issue 2: 236-243.

Adejuyitan, J. A., Otunola, E. T., Akande, E. A., Bolarinwa, I. F. and F. M. Oladokun (2009), Some Physicochemical properties of Flour obtained from fermentation of tiger nut (*Cyperus esculentus*) sourced from a market in Ogbomoso, Nigeria, *African Journal of Food Science*, 3:51-55

Aliyu A.W., Leye J.B., Adedara A.O., Basiru D.I. (2017). Characterization of Oil Extracted from Two Varieties of Tiger Nut (*Cyperus esculentus* L.) Tubers. *American Journal of Heterocyclic Chemistry*. Vol. 3, No. 3, pp. 28-36.

Aliyu, H. N. and U. Sani. (2009). Production of Biscuit from Composite Flour as a Substitute for Wheat. *Journal of Bioscience Research Communication* 3:21-27.

AOA C. (2009).Official Methods and recommended practices of the AOCS, 6th edition. American Oil Chemist Society, Champaign, IL.

Chantal M. C. Bassett, Andrea L. Edel, Amanda F. Patenaude, Richelle S. McCullough, David P . Blackwood, P. Yvan Chouinard , Paul Paquin , Benoît Lamarche , Grant N. Pierce.(2010). Dietary Vaccenic Acid Has Antiatherogenic Effects in LDLr−/− Mice. The Journal of Nutrition, Volume 140,1: 18–24, Retrieved at: https://doi.org/10.3945/jn.109.105163

Emily. (2019). Facts and Food Sources of Vaccenic acid. Retrieved at: https://www.healthbenefitstimes.com/nutrition/vaccenic-acid/

Field, C, J.; Blewett, H. H., Proctor, S., Vine, D. (2009) Human health benefits of Vaccenic acid. Applied Physiology, Nutrition & Metabolism. Vol. 34, 5:979-991

Kamalu, C.I.O and Oghome, P. (2008). Extraction and Characteristics of Tiger Nut Oil. *Journal of Chemistry Society of Nigeria.* Vol. 33, pp. 79-89.

Martinez, V. (2003), scientific analysis of effects of tiger nut on heart disease and related aspects In: Tiger Nut and Health, *Research Journal of Applied Sciences.*1-2

Mason, D. (2005). Tiger Nuts. Retrieved from http://www.nvsuk.org.uk/growing_show_vegetable_1/tiger_nut.php

Muhammed, N.O., Bamishaiye, E. L., Bamishaiye, O. M., Usman, L. A., Salawu, M. O., Nafiu, M. O. and Oloyede, O. B.(2011). Physicochemical properties and fatty acid composition of *Cyperus esculantus* (Tiger nut) Tuber oil, Bioresearch Bulletin 5:51-54.

Nielsen.S.S(2010). Food analysis laboratory manual. Second Edition, Springer Science + Business Media, LLC.PP; 105-110

Oladele K.A., Osundahunsi, F. O. and Adebowale, A. Y (2009). Influence of Processing Techniques on the Nutrients and anti-nutrients of Tiger nut (Cyperus esculentus L.) *World Journal Dairy & Food Science.* 2: 88-93.

Oyedele, O.A., Oladipo, I.O., and Adebayo,A.O. (2015). Investigation into edible and non-edible oil potentials of Tiger nut (*Cyperus esculentus*) grown in Nigeria. *Global Journal of Engineering, Design and Technology*, Vol 4(4): 20-24

Shaker, M. A., Ahmed, M. G., Amany, M. B. and Shereen, L. N. (2009). Chufa Tuber (Cyperus esculentus L.): As a New Source of Food. *World Applied Science Journal* 2:151-156.

Singh.V.P., Fontaine. M.A., Mangat. R., M. Fouhse. J., Diane A., Willing. B.P., Proctor .S.D (2021). High Vaccenic Acid Content in Beef Fat Attenuates High Fat and High Carbohydrate Western Diet Induced Changes in Lipid Metabolism and Gut Microbiota in Pigs. Article. Microorganisms, 9(12), 2517. Retriaved at; https://doi.org/10.3390/microorganisms9122517

Wang,Y.M,. Jacome-Sosa. M., Vine D. F., Proctor. S. D. (2010). Beneficial effects of Vaccenic acid on postprandial lipid metabolism and dyslipidemia: Impact of natural trans-fats to improve CVD risk. Journal of lipid technology.Volume22, 5:103-106. Retrieved at; https://doi.org/10.1002/lite.201000016