The Pharmaceutical and Chemical Journal, 2019, 6(5):103-109

Available online www.tpcj.org

Research Article

ISSN: 2349-7092
CODEN(USA): PCJHBA

Comparative Study of Physicochemical and Fatty Acid Profiles of Oils from under Utilised Nigerian Oil Seeds

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Abstract Many plants have oil bearing seeds or fruits. Utilisation of oils from plants for food and non-food purposes is strongly related to their properties. This study investigates the physicochemical and fatty acid profiles of some fatty oils obtained from Nigerian underutilized oilseeds: beniseed, Moringa oleifera, kenaf (cuba variety), neem seed and their potential applications in food and non-food (cosmetics, industrial lubricants, resins and biofuel production).

The oilseeds were extracted with n-hexane by cold maceration and soxhlet extractor was used to recover residual oil. The physicochemical parameters were determined according to standard methods. The fatty acid composition was determined using gas chromatography mass spectrometry (GC-MS).

From the results obtained, the percentage oil content was found to be 30.01, 35.34, 14.78, 30.7; acid value 2.8mgKOH/g, 1.4mgKOH/g, 3.8mgKOH/g and 1.6 mgKOH/g for beniseed, moringa, kenaf, and neem oils respectively. The predominant acid expressed as fatty acid methyl ester is oleic for moringa (82.9%), kenaf (46.8%) and neem (36. 5%) oil samples while beniseed oil is predominantly linoleic (41.97%). The iodine value which relates to degree of unsaturation is above100 for beniseed, kenaf and neem oils.

This suggests that beniseed, kenaf, and neem oils have potential as substitute for soya bean in alkyd resin production. Moringa oil is rich in monounsaturated fatty acid (MUFA) with iodine value of 76.7g I/100g).

The high saponification values of the samples (188-192) suggest their potential in cosmetics and soap production. The obtained results show that these oilseeds have very great industrial potentials in food and non-food utilization.

Keywords Beniseed, Fatty acid Kenaf, Moringa oleifera, Neem

Introduction

Beni seed (*Sesamum indicum* L.), also known as Gingelly, Sim Sims, Sesame and Till belongs to the family Pedaliaceae. It is amongst the most significant oil bearing seeds; grown particularly in the countries of Africa and Asia. About 36 species have been identified. The origin is Ethiopia in Africa from where it was taken to India [1]. According to world atlas (2017), India is the largest producer of beniseed, followed by China. Nigeria ranked 3rd in world production of beniseed with 580,000 metric tonnes in 2012 [2]. Beniseed is a major world oilseed crop with an excellent source of fatty oil. It has been reported that 65% of beniseed is used for oil extraction and 35% is used as food. The seed contains approximately 50 – 60% oil, 18-25% protein, 13.5% carbohydrate and 5% ash [3]. The oil is liquid at room temperature with a pleasant flavor. It also contains vitamin A, D, E and antioxidants (sesamolin, Sesamolinol, sesaminol and sesamin). The presence of antioxidants account for the excellent stability of beniseed oil

making it suitable for food industry. Also, beniseed oil has high therapeutic values. Some of the health benefits include: antioxidant, anticancer, anti-hypertensive and immunoregulatory actions [4].

Beniseed oil contains oleic (43 %), linoleic (35 %), palmitic (11 %), and stearic acid (7%). Based on the predominant fatty acid beniseed oil belongs to the oleic/linoleic acid group like Soybean, cottonseed, peanut and sunflower oils [5]. It is classified as a semi drying oil due to its ability to "air dry" forming a coherent film on exposure to the atmosphere.

Moringa oleifera Lam. a sole genus of Moringaceae family is a fast growing drought tolerant plant that originates from sub-Himalayan tracts of India, Pakistan, Bangladesh, and Afghanistan [6]. It is widely distributed and naturalized in many African countries [7]. The plant is commonly known as horseradish tree or drumstick (English). In Nigeria, it is known by various tribes as: Ewe ile (Yoruba), Zogali, (Hausa) and Okochiegbu (Igbo) [8, 9]. All parts of *Moringa oleifera* are used for different applications (food, medicine, water purification, animal and aquaculture feeds, wood pulp, biodiesel etc.). The seeds contain between 25.1-41.4% edible oil high in oleic acid [10-11]. *M. oleifera* oil is a pale yellow liquid at room temperature with a flavor like peanut. *M. oleifera* oil is categorized as a high-oleic oil, and it contains a high monounsaturated to saturated fatty acids (MUFA/SFA) known to be associated with reduced risk of cardiovascular mortality/events, and stroke [12]. It is commercially known as Ben oil due to its content of behenic acid. Moringa oil is resistant to oxidative degradation. The oil resembles olive oil in its fatty acid composition. It is an excellent substitute for olive oil with an advantage of a milder odour.

Apart from oil, the oilseed has been reported to contain 28.5-34.0% protein, 16.5-17.8% carbohydrate, 6.5-7.5% fibre, and 6.5-7.5% ash [13].

Kenaf (*Hibiscus cannabinus* L.) is a multipurpose crop from the Malvaceae family grown in about 20 countries particularly in China, India, and Thailand as major producers [14]. It resembles okra and cottonseed [15]. Kenaf is an economic tree mainly cultivated as a source of fibre used in the production of agro-sacks, pulp and paper; the leaves are edible and consumed in human and animal diets. These needs are growing rapidly because of increasing world population [16]. According to FAO (2015), the world production of kenaf stabilized under 250,000 t in 2015, with Africa contributing about 6% of the world production [17]. Currently in Nigeria, there is an increase attention on kenaf plant because of its environmental and economic potential [18]. The plant has potential to absorb CO_2 and NO_2 from the atmosphere 3 to 5 times faster than forests [19, 20]. It contains various phytochemicals: tannins, saponins, polyphenolics, alkaloids, essential oils and steroids, responsible for its use in traditional folk medicine [21, 22].

Despite its importance, little or no attention is given to Kenaf seed which is treated as an agricultural waste. Kenaf seed contains various bioactive constituents such as fatty acids, phenolic compounds, phytosterols and tocopherols [23, 24].

Kenaf seed yields between 16 – 22% edible oil depending on the method of extraction used. The oil is used in different industrial applications: cooking, medicine, cosmetics; lubricants paints and varnishes and for biofuel production [25]. The oil contains high percentage of polyunsaturated fatty acids (PUFA) which are necessary for normal growth and health (reducing cholesterol and heart diseases). Also, kenaf seed extract and kenaf seed oil have potential as sources of natural anti-cancer agents [26]. Kenaf seed has an oil and protein composition similar to cottonseed oil with the advantage of having a milder odour and it does not contain the toxic compound gossypol present in cottonseed oil [27, 28].

Neem (*Azadirachta indica*) is a tree in the mahogany family Maliaceae. Also known as *dogoyaro*. It is a fast growing, evergreen tree native to India from where it was distributed to Africa and America. Neem is reported to be the most researched tree in the world with most of its parts (fruits, seeds, leaves, bark and root) containing a wide variety of biological compounds with antiseptic, antiviral, antipyretic, anti-inflammatory, antiulcer and antifungal uses [29]. In Nigeria, neem tree is used to prevent desert encroachment; while the potential of the seed is not fully exploited. The seed contains about 45% oil and 55% seed cake. Neem oil is non edible, brownish yellow colour liquid with a smell similar to garlic. The major fatty acid composition are oleic, stearic and palmitic [30]. Neem oil is reported to contain at least 100 biologically active compounds. The major constituents are triterpenes known as limonoids (azadirachtin, meliantriol, nimbin, nimbidin, nimbinin, nimbolides, and salanin). The presence of various

bioactive compounds in different parts of neem exert antimicrobial and other medicinal properties and this explain its various uses in Neem tea, soap, cosmetics, insect repellent and herbal dentifrices [31].

Materials and Methods

Beniseed and moringa seed were purchased from local markets in Lagos while neem oilseeds were harvested from neem plants in Nigerian Armed Forces Resettlement Center (NAFRC) Oshodi Lagos Nigeria. The oilseeds were cleaned, dried and dehulled and ground using a blender. Kenaf oilseeds (Cuba) were collected from the Institute of Agricultural Research and Training Ibadan, Oyo State, Nigeria. The whole seeds after washing and drying were ground without separation of the episperm from the kernel. The oils were extracted from ground seeds by cold maceration and soxhlet extractor used to recover residual oil from the cake [32]. The extraction solvent was n-Hexane. Physicochemical properties: specific gravity, colour, odour, refractive index, acid value, free fatty acid, peroxide, iodine, saponification values were determined according to standard methods [33]. The fatty acid composition was determined by trans esterification of known quantity of oils respectively with methanol using potassium hydroxide as catalyst. Catalyst concentration was 1% w/w of the oil. The reaction mixture was stirred using a magnetic stirrer heated to 60^{o}C; and refluxed for 1hr. The temperature was fixed at 60 ^{o}C based on previous work [34]. The mixture was allowed to separate overnight; the upper layer consisting of fatty acid methyl ester (FAME) was separated and sent for analysis to determine the fatty acid composition using gas chromatography-mass spectrometry (GC-MS). The FAME of the oils were analyzed by GC-MS (Shimadzu QP 2010 Ultra) under the following conditions: injector programme was 50 ^{o}C for 2 min then increased to 250 ^{o}C at 7 ^{o}C/ min. The initial and final holds up temperature was 2 min, respectively. The ion source temperature and interface temperature were held at 230 and 250 ^{o}C respectively. Helium was used as the carrier gas. Identification of the fatty acids was done by comparing retention times with standards analyzed under the same conditions. Relative percentages of each fatty acid were determined based on measurement of peak area.

Results and Discussion

The results for the physicochemical analysis of the oils is summarized in Table 1. Values for the analysis are given as mean ± SD of triplicate determinations.

Table 1: Physicochemical Properties of the Oils

S/N	Parameters	Beniseed	Moringa	Kenaf (cuba)	Neem
1	% Yield	Approx. 30.01± 5	35.34 ± 2	14.78 ±1.3	30.7
2	Colour	Light yellow	Light yellow	Golden yellow	Brownish yellow
3	Refractive Index	1.4771± 0.002	1.4609± 0.003	1.4761± 0.003	1.4740± 0.006
4	Density	0.9106 ± 0.01	0.8927 ± 0.005	0.9059 ± 0.01	0.9062 ± 0.01
5	AV (mgKOH/g)	2.80 ± 0.25	1.4 ± 0.3	3.80 ± 0.2	1.68 ± 0.1
6	FFA (% oleic)	1.4 ± 0.13	0.7 ± 0.15	1.9 ± 0.10	0.84 ± 0.05
7	SV (mgKOH/g)	192.2 ± 4.0	186.5 ± 1.4	192.1 ± 1.4	188.80± 2.0
8	IV (g I_2/100g	120 ± 1.0	76.7 ± 1.2	121.0 ± 2.16	118± 2.50
9	PV(meq O_2/kg)	1.47 ± 0.03	1.3 ± 0.2	5.0 ± 0.5	3.6 ± 1.20

AV= acid value, **SV**= saponification value, **IV**= iodine value, **PV**= peroxide value

The oils are liquid at room temperature and light yellow in colour for beniseed and moringa seed; golden yellow for kenaf seed and brownish yellow for neem seed. The chemical properties as shown in table 1 are amongst the most important properties used to determine the quality of oils. The percentage yields as shown in table 1 are lower than values reported previously in literature [7, 23, 35]. This is probably due to differences in agro climatic conditions, extraction method, ripening stage and harvesting time of the seeds. However, the range of oil content (30-35 %) for beniseed, moringa and neem seeds were higher than those reported for soybean (17.0-21.0 %). The acid value which represents free fatty acid in the oil is a valuable measure of quality. It also shows the level of hydrolytic rancidity. Oils become rancid when peroxide value is between 22 and 40 meq O_2/kg [36]. From the results obtained, all the oil samples showed peroxide values less than 10 meq O_2/kg thus indicating good storage stability, high saponification

values obtained suggest that the oils have potential to be used in soap and cosmetics industries. The iodine value indicates the degree of unsaturation. The present investigation shows high iodine value for beniseed, kenaf and neem oils. However, *M. oleifera* oil shows iodine value less than 100 g I_2/100g due to high oleic acid content (table 2). The low iodine value and high percentage oleic acid in *M. oleifera* oil confers good stability and nutritional properties.

Table 2 shows the predominant fatty acids in the oil samples. They include oleic, linoleic, stearic, palmitic, tridecanoic and behenic, (detected only in moringa) acids. Linolenic acid was not detected in any of the oil samples. *M. oleifera* oil was found to contain Cis 15-tetracosenoic acid or Nervonic acid which is an essential MUFA beneficial to brain health.

Table 2: Fatty Acid Composition of Beniseed, Moringa Kenaf and Neem Seed Oils

Fatty Acid	Beniseed	Moringa	Kenaf (cuba)	Neem
Palmitic (C16:0)	nd	1.8	nd	13.91
Stearic (C18:0)	nd	5.4	nd	16.71
Oleic (C18:1, ω 9)	37.67	82.9	33.0; Δ-9 (Z) 13.8-oleic acid	36.45
Linoleic (C18:2, ω 6)	41.97	--	27.2; Δ-9,12 (EE) 1.1; Δ-9,15	nd
Linolenic (C18:3, ω 3)	nd	--	nd	nd
Docosanoic (Behenic) (C22:0)	nd	4.8	--nd	nd
Cis 15-tetracosenoic acid (C24:1, ω -9)or Nervonic		1.17		
Tridecanoic (C13:0)	-6.83-		13.4	nd

The higher percentage of oleic acid in beniseed, moringa, and kenaf oil samples confers the oils with good storage stability and make them more desirable in terms of nutrition especially with the present trend of replacing polyunsaturated vegetable oils with those containing high content of monounsaturated acids. Also, high oleic and absence of linolenic acid give them better oxidative stability in applications like frying. The notations in parenthesis signify the number of carbon atoms and double bonds respectively.

Figure 1 shows the comparison of fatty acid profiles of oil samples with soybean and olive oils.

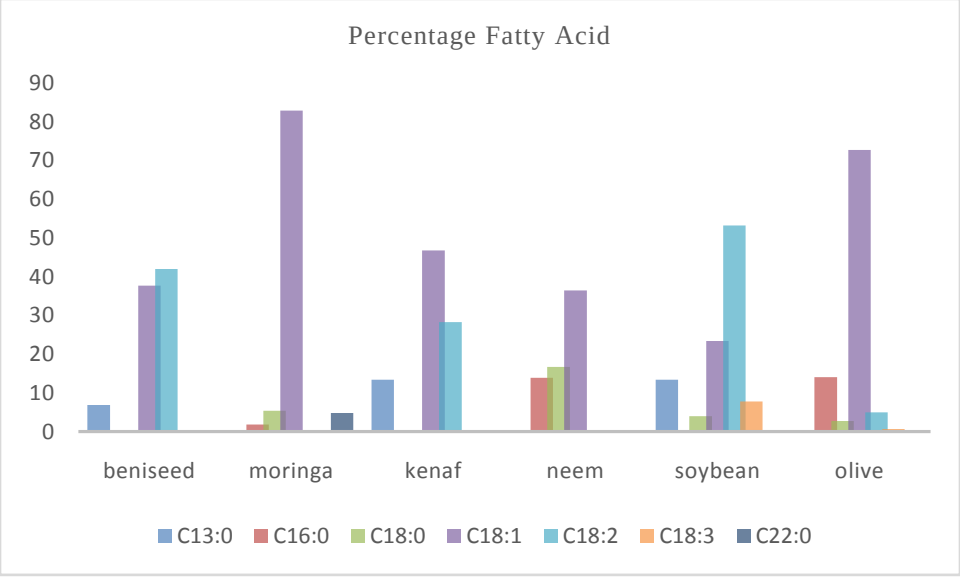

Figure 1: Comparison of fatty acid profile of investigated oil samples with soybean and olive oils

The result shows that the oil samples (beniseed, moringa, kenaf, neem) have similar fatty acid profile in comparison with soybean and olive oils respectively. However, MUFA content of the tested samples are higher than the values reported for soybean oil. Soyabean oil has the highest value of PUFA (53.2%). This can possibly be explained by the difference in agro climatic conditions and type of oilseed.

Conclusion

In this study, oils extracted from four underutilized oilseeds grown in Nigerian were investigated for their physicochemical and fatty acid compositions. The percentage oil content ranged from14.78 to 35.34%; *M. oleifera* had the highest yield (35%). The high oil content makes it a potential source of edible oil for the oil industry. Also, the fatty acid compositions of *Moringa oleifera* and neemoil are predominantly oleic while beniseed and kenaf oils are oleic/linoleic oils. The high oleic acid (82.9%) obtained from *M. oleifera* seed oil makes it an acceptable substitute for expensive olive oil when compared to other conventional oils like soybean. In addition, presence of nervonic acid in *M. oleifera* oil makes the oil a natural source of Nervonic acid one of the major fatty acids used for cognitive impairment. The physicochemical and fatty acid profile of the oil samples compare with values obtained in literature [7, 10, 25]. All the oil samples contain high amount of monounsaturated (MUFA) and polyunsaturated fatty acids (PUFA) which are considered healthy dietary fat than saturated and trans fat. However, neem oil contains high level (36.45%) of trans MUFA which provide no known health benefit to human. In addition, presence of alpha amyrin (21.89 %) a triterpene detected in neem oil makes it a source of potential antioxidant and anti-inflammatory agent for use in cosmetics and ointment preparations. Also, the high degree of unsaturation as evidenced by the iodine values for beniseed, kenaf and neem oils suggest their potential use as substitute for soya bean in alkyd resin production. Therefore, the results of this investigation will aid in the choice of their application for food and non-food purposes.

Acknowledgments

The authors thank the Management of Federal Institute of Industrial Research Oshodi for funding this research.

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