Original Research Article

COMPARATIVE ANALYSIS OF SOME SELECTED CITRUS SEEDS OIL FROM NORTH CENTRAL, BENUE STATE, NIGERIA

Abstract

The physicochemical properties of oils from citrus seeds of different species; tangerine (citrus reticulate), sweet orange (citrus sinesis), lime(citrus aurantifolia) and Grape(citrus paradise) were investigated. *The seeds of each specie were collected from the central zone of plateau state, washed, sun dried for three days and finally crushed with mortar and pestle. One hundred grams (100 g) of each seeds were measured for oil extraction using n-hexane with soxhlet extractor for six hours.* The percentage yield and moisture content of each oil extracted from seeds of each species were determined. *The physicochemical properties for seeds were also carried out using Wijs method for Iodine value and Titration method for Acid value, Saponification value, Peroxide value and Free Fatty Acids. The results reveals that the moisture content ranges from 2.25 – 4.08 %, percentage yield 30 – 42.20 %, iodine value 78.32 – 98.04 gI_2/g, acid value 2.06 – 4.44 %, saponification value 187.38 – 196.06 mgKOH/g , peroxide value 36.52 – 53.57 mEq/kg , free fatty acid 1.41 – 8.74 % and density 0.78 – 0.96 gml^{-1}. The result obtained indicates that oils from these seeds can be used as raw material for the production of cosmetics, soap and domestic cooking.*

Key words: *saponification value, FFA value, peroxide value, citrus,* density, moisture content.

1.0 Introduction

Lipids are fats and oils derived from plants and animals. Physically, oils are liquid at room temperature and fats are solid. Chemically, both fats and oils are composed of triglycerides. Triglycerides are tri-esters consisting of a glycerol bound to three fatty acid molecules. Alcohols have a hydroxyl (HO–) group. Organic acids have a carboxyl (–COOH) group. Alcohols and organic acids join to form esters. The glycerol molecule has three hydroxyl (HO–) groups and each fatty acid has a carboxyl group (–COOH). Triglycerides are the main constituents of body fat in humans and other vertebrates, as well as vegetable fat. [2] They are also present in the blood to enable the bidirectional transference of adipose fat and blood glucose from the liver, and are a major component of human skin oils. Many types of triglycerides exist. One specific classification focuses on saturated and unsaturated types. Saturated fats have no C=C groups; unsaturated fats feature one or more C=C groups. Unsaturated fats tend to have a lower melting point than saturated analogues; as a result, they are often liquid at room temperature. Plants and fish oil generally contain a higher proportion of unsaturated acids, although there are exceptions such as coconut oil and palm kernel oil.

Although many plant parts may yield oil, in commercial practice oil, oil is extracted primarily from seeds [1]. They are insoluble in water and greasy to touch. The major characteristic is that they have caloric content more than twice compared to the other food stuff [2]. Also they act as lubricants during mixing of ingredient and as media for heat transfer carrier for fat soluble vitamins. Also, they are a source of external fatty acid [3]. The plants and animals that produce oils and fats in plentiful quantity and insufficiently available form for it to be an article of commerce are comparatively few. The seeds of annual trees are the major sources of oils [4].

The saturated acid tends to be solids, while the unsaturated are usually liquid. This circumstance also extends to fats and oils. Fats are made up of fatty acid that is mostly saturated, while oils are primarily composed of fatty acid portions that have greater numbers of double bonds. In other words, unsaturation lowers melting point [5,6].

The natural source of fats and oil includes plants (or its seed), animal and marine organisms. Extraction of oils from these sources is done locally (domestic), at industrial level (commercial purpose) and in labs. Seeds have nutritive and calorific value, which makes it necessary in diets. They are also good source of edible oil and fats [7].

Fats and oils, particular vegetable oils are both used at domestic front and in industry for the production of soap, cosmetic products, lubricant, candles, perfumes and are also used in making paints and other wood treatment product. In addition, they are used as source of ole chemicals which are biodegradable and thus can replace some petrochemicals [8,9].

There are quite a few seeds and nuts which are rich in fat contents. Thus soya beans, groundnut, palm kernel and mustered sesame seed are all important source of edible oil [6,10]. The citrus species which belongs to the family of Rutacea are major vegetable crops in the middle belt region of Nigeria. Members of this family includes; sweet oranges, lemon, tangerine and lime [3]. They are mostly grown in the tropical and sub-tropical and are generally evergreen shrubs or small trees, bearing flowers yielding a strong scent. The fruits size (Orange, Lime, Tangerine and Grape) varies with cultivar and crop, but most often measures between 3.8 to 14.5 cm in diameter [11]. The shape of the fruit (Lime, Grape, Orange and Tangerine) is spherical to oblong or elongated, with peel thick and is ether smooth or rough pebbly. Citrus seeds have been recognized as an important source for vegetable oils and proteins [12]. Plant seed oils can be used for food, industrial and medicinal purposes. The medicinal value of the plant oils are considered as a rich resources of ingredients which can be used in drug development either pharmacopoeial, non- pharmacopoeial or synthetic drugs. As per data available over three-quarters of the world population relies mainly on plants and plant extracts for their health care needs. More than 30% of the entire plant species, at one time or other were used for medicinal purposes [17].

Their application in different industries depends on their fatty acid composition, the presence and amount of minor constituents, the sensory properties of the oil, processing yield, and cost. Citrus oils are considered suitable for food applications, soap and detergent production, cosmetic production, pharmaceutical applications. They can also be used as paint and varnish ingredients, lubricants, organic pesticides, dispersants, and surface coatings [12]. The purpose of this study is to make comparative analysis of the physicochemical properties of sweet orange, lime, tangerine and grape within the middle-belt region.

2.0 Aim of Research

The purpose of this work is to compare the physicochemical properties of oils from citrus seeds of different species: Tangerine(citrus reticulate), sweet orange(citrus sinesis), lime(citrus aurantifolia) and Grape(citrus paradise).

2.1 Objectives of Research

1. Determine the percentage yield of oil extracted from seeds of each species.
2. Determine the moisture content of each seed species.
3. Determine the physicochemical parameters of the seed species.

3.0 Materials and Method.

3.1 **Collection and Preparation of Sample.**

The samples of study are lime seeds, sweet orange seeds, Grape seeds and Tangerine seeds which are all citrus. The fruit seeds of Sweet orange and Lime were obtained from local fruits vendors in Pankshin town while the fruit seed of Tangerine and Grape were gotten from fruit vendors in Mangu town both of Plateau state. The seeds were collected separately, washed and sun dried for three days under sun. This seeds were crushed with mortar pestle in Chemistry department, Federal College of Education Pankshin, Pankshin Plateau state. The fine powered samples was stored in a clean and dry sample container for analysis. The following are the photographs of the citric seeds: sweet orange seed, lime seed, grape seed and tangerine seed.

Photograph of sweet orange seed

Photograph of Lime seed

Photograph of Grape seed

Photograph of tangerine seed

3.2 Extraction of oils

Several method of extracting oils from seed plants exist which includes conventional methods (solvent and mechanical extraction) and nonconventional or improved techniques (supercritical fluid extraction, ultrasound, microwave, and enzyme assisted extraction. Soxhlet extractor was used to extract the oils from the various citrus seeds. Soxhlet extractor is originally designed for the extraction of a lipid from a solid material. It has been used widely for extracting valuable bioactive compounds from various natural sources. In this extraction, a small amount of dry sample is placed in a thimble, which is placed in a distillation flask containing the solvent of particular interest. The extractor has three main sections: a percolator (boiler and reflux) which circulates the solvent, a thimble (usually made of thick filter paper) which retains the solid to be extracted, and a siphon mechanism, which periodically empties the thimble.

The extraction of the oils was done on each of the sample with 250 ml absolute n-hexane. 100 g of each samples was weighed, wrapped in a filter paper and placed into the thimble of the soxhlet extractor. The method was used because the samples has a limited solubility in the solvent, and the impurity is insoluble in the solvent used. It allows for unmonitored and unmanaged operation while efficiently recycling a small amount of solvent to dissolve a larger amount of material and it also ensures that all the analytes are extracted from the sample. The extraction process lasted for 6 hours within the temperature range of 25 ^{0}C and 30 ^{0}C. The various oil samples were then collected and measured.

3.3 Chemical Analysis of samples oils

3.3.1 Saponification value

0.5g of the oil was weighed into 250ml conical flask fitted with an air condenser. It was dissolved in 10ml alcohol and 10ml of 2.5KOH solution. The sample flask and the blank was kept on the water bath to boil gently and steadily until it saponified and an appearance of clear solution about an hour later. It was cooled and two drops phenolphthalein was added and was titrated with standard 1M oxalic acid until the pink color disappear [13].

Calculation:

$$SV\ (mgKOH/g) = \frac{(B-S)\times N \times 56.10}{W} \quad \text{- (1)}$$

B = Blank titre

S= Sample titre

N= Normality

W=Weight of sample.

3.3.2 Iodine value (IV)

1g of the oil and 25ml of chloroform was weighed into 500ml conical flask. 30ml of wij's solution was also added. The flask was shaken and was allowed in the dark for 30 minutes. 30ml 15% KI and 10ml of water was added. The liberated iodine was titrated with standard 0.1M sodium thiosulphate solution using starch [13,14].

Calculation:

$$IV\ (g\ I_2/g) = \frac{(B-S)\times N\times 12.692}{W} \quad \text{-------------------------- (2)}$$

B = Blank titre

S= Sample titre

N= Normality of $Na_2S_2O_3$

W=Weight of sample.

3.3.3 Acid value (AV)

A known weight of the oil (5-10 g) is taken in a conical flask and 50 mil of acid free alcohol or methylated spirit is added. The flasks and its content are then heated over a water bath for about half an hour. The content of the flask is then titrated against 0.1 N KOH using phenolphthalein as indicator.

Calculation:

$$AV = \frac{(0.1N)mil(NKOH)\times 5.6}{W} \quad \text{-------------------------- (3)}$$

Where 5.6 is the amount of KOH present in mg in 1 mil of the 0.1 N KOH and W weight of oil taken in gram.

3.3.4 Free fatty acid.

2g of the sample oil was weighed into 250ml conical flask, 25ml 96% alcohol was added and 1ml phenolphthalein was added as indicator and was shaken. The solution was titrated with 0.1M NaOH, with constant shaking until pink color was obtained, but the pink color disappears after a while [13,14].

3.3.5 Peroxide value

1g of the sample oil was weighed in to 250ml conical flask, 25ml of a solvent (n – hexane), 15ml KI solution was added and was allowed in the dark for 5 minutes. 35ml of distilled water and 3ml of starch oil was added. The solution was titrated with 0.1M sodium thiosulphate. The same procedure was taken for the blank using distilled water [13].

Alternatively, weigh 5 g of oil or fat sample in a round bottom flask. Add 30 ml of glacial acetic acid/chloroform solution (3:2). Swirl the content in the flask until is dissolved. Add 0.5 ml of saturated KI solution and allow to stand for 1 minute with occasional shaking. Add 30 ml of distilled water and 0.5 ml of starch indicator. Next titrate with 0.01N $Na_2S_2O_3$ until the color changes from blue to colorless.

Calculation:

$$PV\ (meq/kg) = \frac{(B-S)\times N \times 1000}{W} \quad \text{- (4)}$$

S = titration value of sample

B = titration value of blank

N = normality of $Na_2S_2O_3$

W = weight of sample.

3.3.6 Moisture content

Wash, dry the moisture dish and cool in a desiccator. Tare-weight the moisture dish,W_2 . Add approximate 10 g of the test material to the dish and reweight W_1. Dry the sample at 150 ^{0}C for 3 hours or 120 ^{0}C for 1 hour. Cool the dish and sample in the desiccator. Reweigh the cool, dried sample in the dish W_3..

Calculation:

$$MC = \frac{(w_1 + w_2) - w_3 \times 100}{w_1} \quad \text{- (5)}$$

3.3.7 Color of sample oil

The color of the various oil samples was determined visually. The color of sweet orange was found to be orange-brown in color; tangerine with pale yellow color while lime seed oil and tangerine seed oil had similar color as light green.

3.3.8 Density of the extracts

This is calculated using the formula M/V g/cm^3. Where M represents the mass of the sample in grams (g) and V represents the volume of the sample in $cm^{3.}$ Grape had a density of 0.81$gml^{-1,}$ tangerine 0.86gml^{-1}, sweet orange 0.96gml^{-1} and lime 0.78gml^{-1}

4.0 Results and Discussion

Table 1 shows the result of the physicochemical properties of oil from sweet orange, lime, tangerine and grape

Table 1:

Physicochemical properties of seed oil from Grape, Tangerine, sweet orange and lime

PARAMETER	RESUIT			
	Grape	Tangerine	Sweet orange	Lime
Percentage yield (%)	34.20	32.00	42.20	30.00
Moisture content(%)	3.56	3.00	2.25	4.08
Saponification value mgKOH/g	196.06	194.22	187.38	188.26
Free fatty acid mg(KOH)	1.97	1.41	8.74	4.79
Acid value (mgKOH/g)	2.82	4.44	2.06	2.16
Peroxide value (Meq/Kg)	36.52	53.57	41.47	43.94
Iodine value (gI_2/g)	98.04	78.32	87.84	95.78
Density (gml^{-1})	0.81	0.86	0.96	0.78

Discussion

The physicochemical properties of seed oil from Grape, Tangerine, Sweet orange and Lime are shown in Table 1. The % yield of oil extracted shows that sweet orange has the highest yield of 42.20 % followed by grape (34.20 %), tangerine (32.00 %) and lime (30.00 %). This shows that all can serve as a good raw material that will produce oil in commercial quantity. The % of the oil extracted is close to ground nut oil (60%) which is in line with the report of [13]. Sweet orange have the least moisture content of 2.25 %. Low moisture content is a requirement for long storage (shelf life). The maximum allowable limit for moisture content by APCC is 0.1 – 0.5 % [15]. According odoom *et al*., (2014), the process of drying seeds is a factor to moisture content. In his determination of moisture content for coconut, the drying was under 104 ^{0}C in an oven for 4 hours. However, for this present work, the drying was done under normal temperature for three days. Thus, difference in moisture content. It also affects the physical and chemical aspect of the oil which relates to freshness. The saponification value for the samples is within the codex standard for oil (168 – 265 mg/g). Saponification value indicates the average molecular weight of oil [6,16]. High saponification value indicates shorter fatty acid chain and lower molecular weight, And low saponification value means the oil have longer fatty acid chain with higher molecular weight than the common oil. Oils with high saponification values can be used for candle and soap production and as chemical feed stocks for lubricant [17]. The value for FFA shows that Tangerine seed oil is the best with 1.41 mg (KOH) followed by Grape seed oil with 1.97 mg (KOH). This value falls below the codex standard. Thus acceptable for commercial purpose. When the acid value of oil is high, it implies a higher magnitude of hydrolytic deterioration resulting in generation of objectionable flavor and odors. So the sweet orange has the best value followed by lime, grape and tangerine. The value for sweet orange, grape and lime fall short of the codex standard which is 4 mgKOH/g [15]. Thus, these oils are of quality. Peroxide value measures the level of hydroperoxide (oxidative deterioration of oils). So high PV implies that the oil has been damaged by free radicals and will give rise to aldehydes and ketones which are responsible for smell musty and rancid. The PV for the citrus oils are above the codex standard. However, grape has the least value among the others. Iodine value is the mass of iodine in 100 g of a chemical substance. It also determines the amount of unsaturated fatty acids. High amount of unsaturated fatty acids helps to reduce blood cholesterol levels and thus lower the risk of heart disease. This shows that the oil is semi – drying oil because the iodine value for semi – drying oil ranges from 85 – 130.00mg/g. And drying oil range from 150 – 200mg/g. within this range is very good for the manufacture of cosmetic and adhesives [8,9].

5.0 Conclusion and Recommendation

The oils extracted from citric seeds species of the fruit are found to be of medical values and are also used as materials for the production of cosmetics and domestic cooking. The extraction of citrus oils from their seeds not only saves environment but can be used in various applications including soap making. The results in the study indicated that Sweet orange seed oil appears to be of high quality, followed by Grape, Tangerine and Lime. However, these oils can still be of use for both domestic consumptions and industrial purpose such as the production of toiletry, perfume industry and confectionery. Based on the findings, the researchers recommend the following:

1. Government (mostly third world country) should encourage farmers through finance and policy making to embark on large citrus plantation, particularly sweet orange and grape.
2. Also with increase funding in the areas of research, scientist can come up with improved seed for citrus seeds like tangerine and lime with acceptable physicochemical value. These steps will certainly turn the economic fortune of the country.

3. Further work for these seeds on melting point, unsaponifiable matter, refractive index, GC-MS analysis and viscosity should be carried out.

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