Sudan University of Science and Technology

College of Graduate Studies

Assessment of Quality of Sesame and Groundnut Oils Produced by Traditional and Industrial Methods

تقدير جودة زيوت السمسم والفول السوداني المنتجة بواسطة الطرق التقليدية والصناعية

A Thesis Submitted in Partial Fulfillment of the Requirements for the Master Degree in Chemistry

By

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DEDICATION

To my:

Parents

Brothers and sisters

Acknowledgments

I would like to thank and praise the almighty Allah who always guiding me to the right path of life. Without his grace this project could not become a reality.

At last, but not the least I am thankful to my supervisor Dr. Kamal Mohamed Saeed who is always being helpful and encouraging me though out this work.

The abstract

The present research was designed to assess the quality of sesame and groundnut oils products by industrial and traditional methods, the Oil have been tested for other physical and chemical properties.

For sesame oil: the moisture content (1.23% and 0.23%), refractive index (1.4785 and 1.4767), color: blue (0.9 and 0.0), yellow (37.5 and 32.1) and red (6.8 and 5.5) density (0.9319 and 0.9204 g/cm^3), viscosity (64.7 and 60.2 poise), acid value (1.18 and 0.49 mg KOH/g), saponfication value (194.9 and 188.0), unsaponification value (5.57 and 1.90 mg KOH/g), peroxide value (8.8 and 1.8 mg O_2/g) and iodine value (112.4 and 98.9 mg KOH/g) for traditional and industrial products of the oil respectively.

For groundnut oil: moisture content (0.73 and 0.23%), refractive index (1.4680 and 1.6695), color: blue (0.2 and 0.1), yellow (36.5 and 35.3) and red (6.4 and 5.7), density (0.9217 and 0.91945g/cm^3), viscosity (63.2 and 60.3 poise), acid value (1.03 and 0.55 mg KOH/g), saponification value (191.32 and 188.27 mg KOH/g), unsaponification value (3.76 and 1.60 mg KOH/g), peroxide value (7.74 and 2.62 mg O_2/g) and iodine value (114.8 and 98.5 mg I/g) for traditional and industrial products of the oil respectively.

The oils were also analyzed by GC- MS. For sesame oil 18 different compounds were identified. Traditional method revealed oleic acid (37.0%) as a predominant product followed by linoleic acid (36.9 %), steric acid (14.8%) and Palmitic acid (5.9%) while industrial method revealed linoleic acid (40.9%) is predominant product followed by Oleic acid (25.6%), steric acid (20.6%) and palmitic acid (6.7%).

For groundnut oil 11 different compounds were identified. Traditional method revealed oleic acid (57.0 %) as a predominant product followed by linoleic acid (25.8 %), Palmitic acid (5.5 %) and steric acid (2.9 %) while industrial method revealed oleic acid (32.35%) as a predominant product followed by linoleic acid (14.3 %), behenic acid (13.9 %) and steric acid (11.8 %).

مستخلص البحث

صُمم هذا البحث لتقييم جودة زيوت السمسم والفول السوداني المنتجة بالمصنع والطريقة التقليدية ، واختبار خصائصها الفيزيائية والكيميائية. كانت نتائج زيت السمسم كالآتي: نسبة رطوبة (1.23 و 0.23٪) ، معامل انكسار (1.4767 و 1.4785) ، درجات الألوان: (0.9 و0.0) للأزرق ، (37.5 و32.1) للأصفر و (6.8 و 5.5) للأحمر، الكثافة (0.9319 و0.9204 جرام / سم^3) ، اللزوجة (64.7 و 60.2 poise)، قيمة الحمض (1.18 و0.49 ملجم هيدروكسيد بوتاسيوم/ جرام)، قيمة التصبن (194.9 و 188.0 ملجم هيدروكسيد بوتاسيوم/ جرام) ، قيمة عدم التصبن (5.6 و1.9 ملجم هيدروكسيد بوتاسيوم/ جرام) ، قيمة البيروكسيد (8.8 و1.8) ملجم جزئ أكسجين/ جرام) ، وقيمة اليود (112.4 و 98.9 ملجم يوديد بوتاسيوم / جرام زيت) بالنسبة للمنتج التقليدي بالعصر ولمنتج المصنع بالترتيب.

وكانت نتائج زيت الفول السوداني كالآتي: محتوى الرطوبة (0.73 و0.23٪)، معامل الانكسار(1.4680 و 1.6695) ، بينما كانت درجات الألوان: (0.2 و0.1) للأزرق ، (36.5 و35.3) للأصفر (6.4 و 5.7) للأحمر ، وكانت الكثافة (0.9217 و 0.91945 جرام / سم^3) ، اللزوجة (63.2 و60.3 poise)، قيمة الحمض (1.03 و 0.55 ملجم هيدروكسيد بوتاسيوم/ جرام. زيت) ، قيمة التصبن (191.315 و188.27 ملجم هيدروكسيد بوتاسيوم/ جرام. زيت) ، قيمة عدم التصبن (3.76 و 1.60 ملجم هيدروكسيد بوتاسيوم/ جرام) ، قيمة البيروكسيد (2.615 م ملجم جزئ أكسجين/ جرام. زيت) ، وقيمة اليود (114.8 و 98.525 ملجم يوديد بوتاسيوم / جرام).

تم أيضًا تحليل الزيوت بواسطة جهاز الطيف اللوني لمطياف الكتلة. تم التعرف على 16مكوناً مختلفًا لزيت السمسم، وكان المكون السائد بالنسبة للمنتج التقليدي بالعصر هو حمض الأوليك نسبته (37.0٪) ، يليه حمض اللينوليك نسبته (36.9٪) ، وحمض الستريك نسبته (14.9٪) وحمض البلاماتيك نسبته (5.9٪)، بينما كان المكون السائد بالنسبة للمنتج الصناعي هوحمض اللينوليك نسبته (40.9٪) يليه حمض الأوليك نسبته (25.7٪) ، حمض الستريك نسبته (20.6٪) وحمض بلاماتيك نسبته (6.7٪).

تم التعرف على 11مكوناً مختلفًا الفول السوداني ، وكان المكون السائد بالنسبة للمنتج التقليدي بالعصر هو حمض الأوليك نسبته(57.0٪) يليه حمض اللينوليك نسبته (25.8٪) وحمض البلازماتيك نسبته (5.6٪) وحمض الستريك نسبته (2.9٪)، بينما كان المكون السائد بالنسبة للمنتج الصناعي هوحمض

الأوليك نسبته (32.4٪) يليه حمض اللينوليك نسبته (14.3٪) وحمض البنيهيك نسبته (13.9٪) وحمض الستريك نسبته (11.8%)

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1.Introduction

1.1 Lipids

Lipids are biological molecules that are insoluble in water but soluble in nonpolar solvents.

Lipids have a wider spectrum of compositions and structures because they are defined in terms of their physical properties (water solubility).

Lipids are the waxy, greasy, or oily compounds found in plants and animals.

–wax coating that protects plants

-sed as energy storage

–structural components (cell membranes)

– Insulation against cold(kevein,2014)

1.1.1 Classification of Lipids

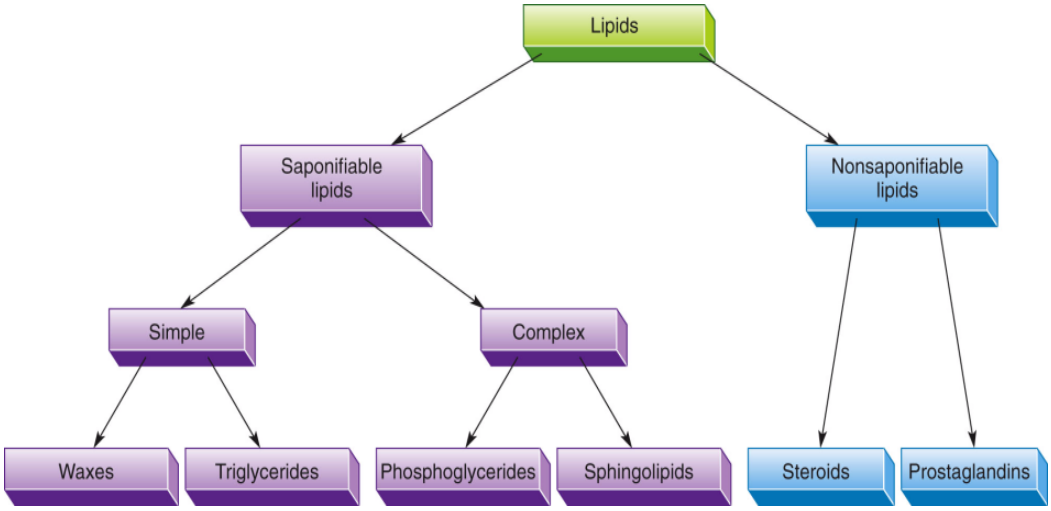
1.1.1.1 Nonsaponifiable lipids do not contain ester groups, and cannot be saponified (steroids, prostaglandins)

1.1.1.2 Saponifiable lipids contain esters, which can undergo saponification (hydrolysis under basic conditions) (waxes, triglycerides, phospho-glycerides, sphingolipids)

1.1.1.2 Saponifiable lipids can also be divided into groups:

-Simple lipids contain two types of components (a fatty acid and an alcohol)

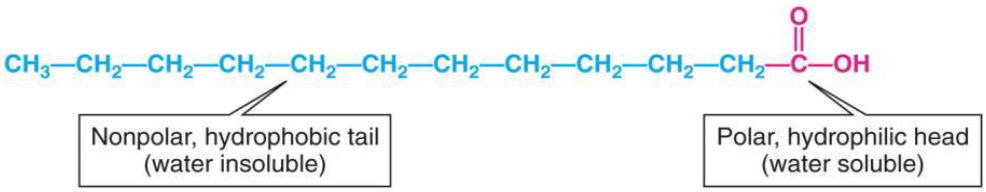
-. Complex lipids contain more than two components (fatty acids, an alcohol, and other components) (kevein,2014)



Scheme.1. classification of lipid

1.2.1. **Fatty Acids**

Fatty acids are long-chain carboxylic acids:



Scheme2. Fatty Acids

1.1.1.2 Properties of Fatty Acids

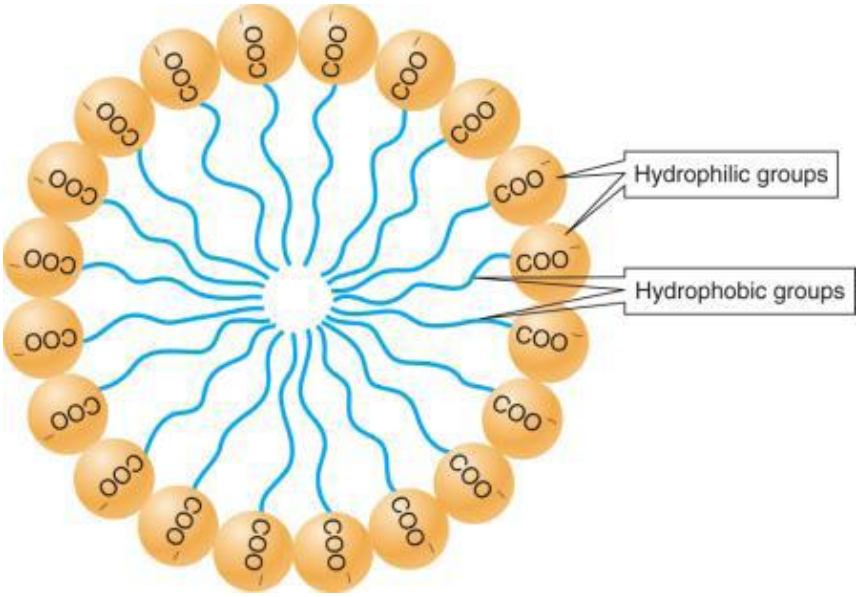
The long, nonpolar hydrocarbon tails of fatty acids are responsible for most of the fatty or oily characteristics of lipids.

The carboxyl (COOH) group is hydrophilic under basic conditions, such as physiological pH (7.4):

1.2.1. **2.Fatty Acid Micelles**

In aqueous solutions, fatty acids associate with each other in spherical clusters called **micelles**, in which the hydrocarbon tails tangle each other up through dispersion forces, leaving a "shell" of polar carboxylate ions facing outwards, in contact with the water.

–Micelles are important in the transport of insoluble lipids in the blood, and in the actions of soaps. (kevein,2014)



Scheme3. Fatty Acid Micelles

1.2.1. **3.Characteristics of Fatty Acids**

They are usually having straight chains (no branches) that are about 10 to 20 carbon atoms in length.

They usually have an even number of carbon atoms (counting the carboxyl carbon).

The carbon chains may be saturated (all single bonds) or unsaturated (containing double bonds). Other than the carboxyl group and the double bonds, there are usually no other functional groups.

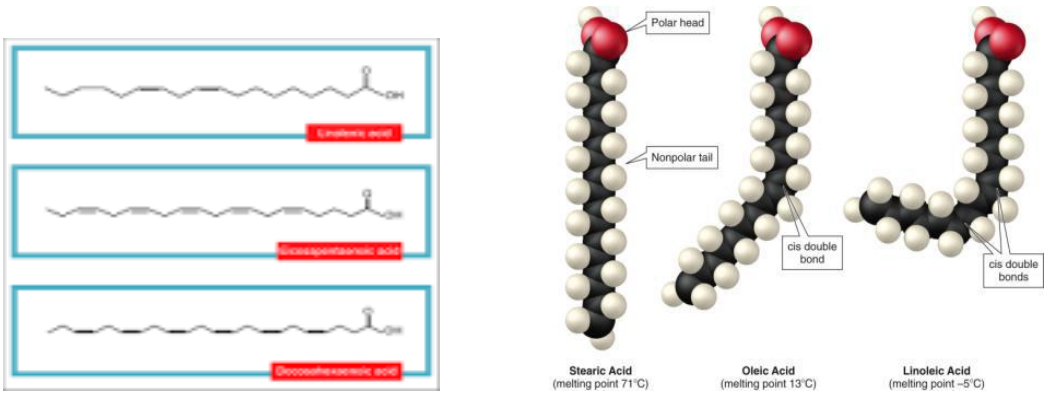
Shorter fatty acids usually have lower melting points than longer ones (stearic acid [18C] = 70°C, palmitic acid [16C] = 63°C).

The double bonds are usually in cis configurations:

1.2.1. 4.Saturated and Unsaturated Fatty Acids

The cis-double bonds in unsaturated fatty acids put an inflexible "kink" in the carbon chain, preventing the molecules from packing together as tightly as saturated fatty acids do.

–For example, stearic acid (saturated), oleic acid (one double-bond), and linoleic acid (two double bonds) all has 18 carbons in the chain, but their melting points are drastically different:

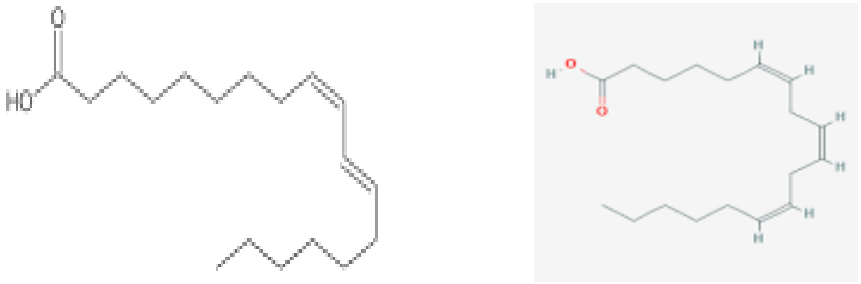


Scheme4. Saturated and Unsaturated Fatty Acids

1.2.1. 5.Essential Fatty Acids

Most of the fatty acids we need can be synthesized in the body. Two fatty acids, linoleic acid and linolenic acid, both polyunsaturated fatty acids with 18-carbon chains, cannot be synthesized in the body and must be obtained from the diet. These are **essential fatty acids**. Both are found in plant and fish oils. In the body, they are used to produce hormonelike substances that regulate blood

pressure, blood clotting, blood lipid levels, the immune response, and inflammatory reactions.



Scheme 5. linoleic acid and linolenic structures

Table.1.1.Some Important Fatty Acids

#C's	Name	Formula	MP	Common Sources
Saturated				
14	Myristic acid	$CH_3(CH_2)_{12}COOH$	54°C	Butterfat, coconut oil, nutmeg oil
16	Palmitic acid	$CH_3(CH_2)_{14}COOH$	63°C	Lard, beef fat, butterfat, cottonseed oil
18	Stearic acid	$CH_3(CH_2)_{16}COOH$	70°C	Lard, beef fat, butterfat, cottonseed oil
20	Arachidic acid	$CH_3(CH_2)_{18}COOH$	76°C	Peanut oil
Monounsaturated				
16	Palmitoleic acid	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	-1°C	Cod liver oil, butterfat
18	Oleic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	13°C	

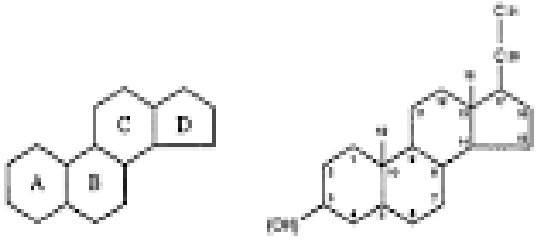
				Lard, beef fat, olive oil, peanut oil
Polyunsaturated				
18	Linoleic acid	$CH_3(CH_2)_4(CH=CHCH_2)_2(CH_2)_6COOH$	-5°C	Cottonseed oil, soybean oil, corn oil, linseed oil
18	Linolenic acid	$CH_3CH_2(CH=CHCH_2)_3(CH_2)_6COOH$	-11°C	Linseed oil, corn
20	Arachidonic acid	$CH_3(CH_2)_4(CH=CHCH_2)_4(CH_2)_2COOH$	-50°C	Corn oil, linseed oil, animal tissues
20	Eicosapentaenoic acid	$CH_3CH_2(CH=CHCH_2)_5(CH_2)_2COOH$		Fish oil, seafoods
22	Docosahexaenoic acid	$CH_3CH_2(CH=CHCH_2)_6CH_2COOH$		Fish oil, seafoods

1.3. Nonsaponifiable lipids

1.3. 1.Steroids

Steroids are classified as lipids because they are soluble in nonpolar solvents, but they are non-saponifiable because the components are not held together by ester linkages.

The basic steroid structure contains four fused rings:



Scheme6. Steroid ring system

Cholesterol is the most abundant steroid in the body. It is an essential component of cell membranes, and is a precursor for other steroids, such as the bile salts, sex hormones, vitamin D, and the adrenocorticoid hormones.

There is apparently a correlation between high levels of cholesterol in the blood and atherosclerosis(kevein,2014)

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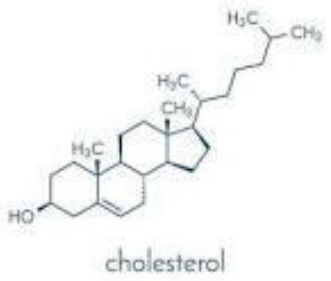
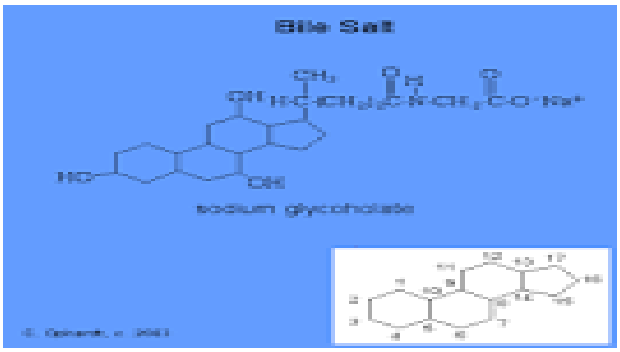


Scheme.7.Cholesterol structure

Bile is a yellowish brown or green fluid produced in the liver and stored in the gall bladder.

Bile salts act like soaps and other emulsifiers: they contain both polar and nonpolar regions, helping to break fats in foods into smaller pieces, allowing them to be hydrolyzed more easily.



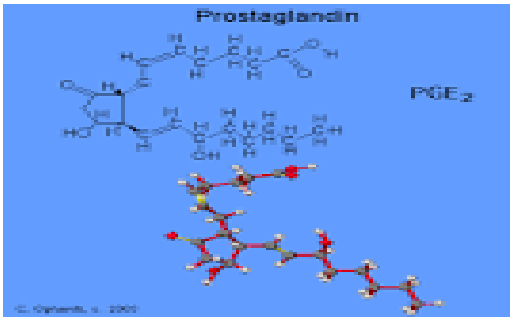
Scheme.8.Bile Salts structure

Bile salts also emulsify cholesterol in the bile, so it can be removed in the small intestine. If cholesterol levels are too high or the levels of bile salts are too low, the cholesterol precipitates and forms gallstones.

–Gallstones can block the duct that allows bile to be secreted into the duodenum. Fats are no longer digested properly, and bile pigments absorbed into the blood causes the skin to become yellow and the stool to become gray.

1.3.2. Prostaglandins

Prostaglandins are cyclic compounds synthesized from arachidonic acid. Like hormones, they are involved in a host of body processes, including reproduction, blood clotting, inflammation, and fever. (Aspirin works by inhibiting prostaglandin production, alleviating inflammation and fever.)

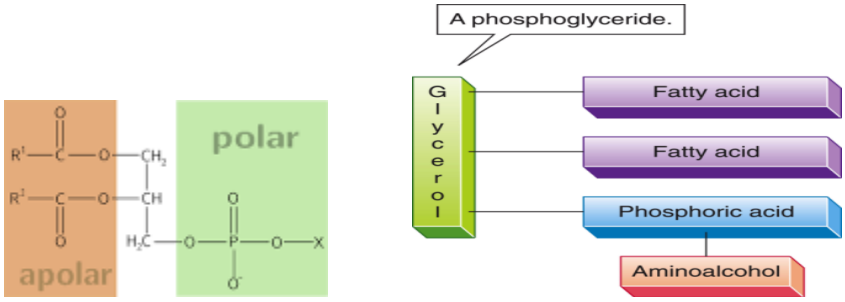


Scheme.9. Prostaglandins

1.4. Saponifiable

1.4.1. Phosphoglycerides

Phosphoglycerides are complex lipids that are major components of cell membranes. Phosphoglycerides and related compounds are also called phospholipids.

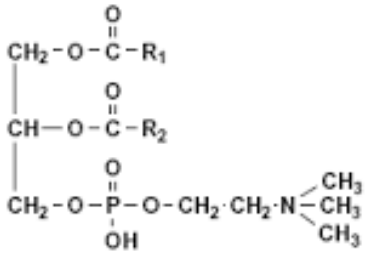


Scheme.10.Aminoalcohols in Phosphoglycerides

The most abundant phosphoglycerides contain the alcohols choline, ethanolamine, or serine attached to the phosphate group:

1.4.1.1. Lecithin

Phosphoglycerides that contains the aminoalcohol choline are called lecithins:



Lecithin (phosphatidyl choline)

Scheme.11. Lecithin

The fatty acids at the first and second positions are variable, so there are a number of different possible lecithins.

Because lecithins contain negatively charged oxygen atoms in the phosphate group and positively charged nitrogen atoms in the quaternary ammonium salt group, that end of the molecule is highly hydrophilic, while the rest of the molecule is hydrophobic.

This allows lecithin to act as an emulsifying agent:

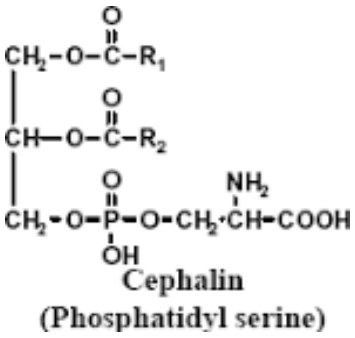
–forms an important structural component of cell membranes.

–forms micelles which play a role in the transport of lipids in the blood stream.

–Commercially, lecithin extracted from soybeans is used as an emulsifying agent in margerine and candies to provide a smooth texture(kevein,2014).

1.4.1.2. Cephalin

Phosphoglycerides that contains the aminoalcohols ethanolamine or serine are called cephalins:

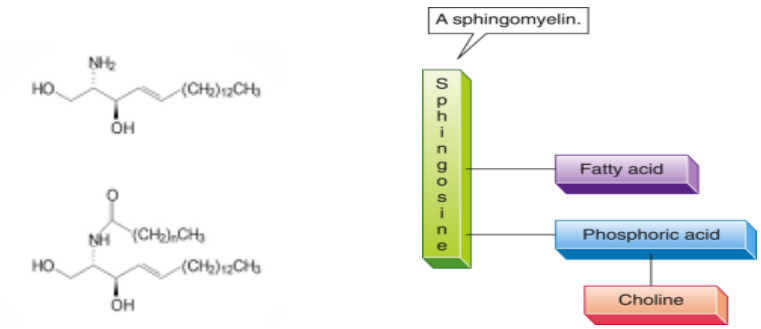


Scheme.12. Cephalin

Cephalins are found in most cell membranes, and are particularly abundant in brain tissue. They are also found in blood platelets, and play a role in blood-clotting.

1.4. 2.Sphingolipids

Sphingolipids are complex lipids that contain sphingosine instead of glycerol.

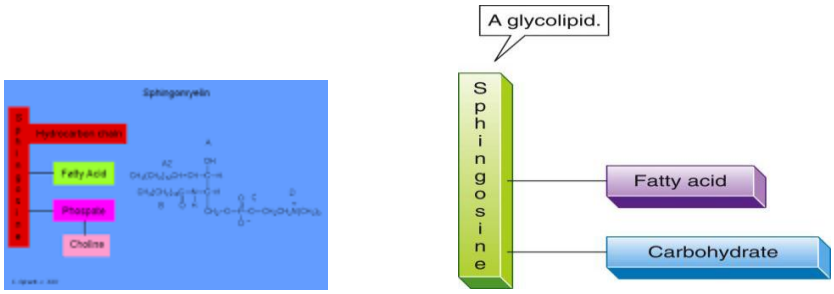


Scheme.13. One important type of sphingolipds is the sphingomyelins:

1.4. 2.1.Sphingomyelin

In the sphingomyelins, a choline is attached to sphingosine through a phosphate group, along with a single fatty acid attached to the sphingosine N via an amide linkage.

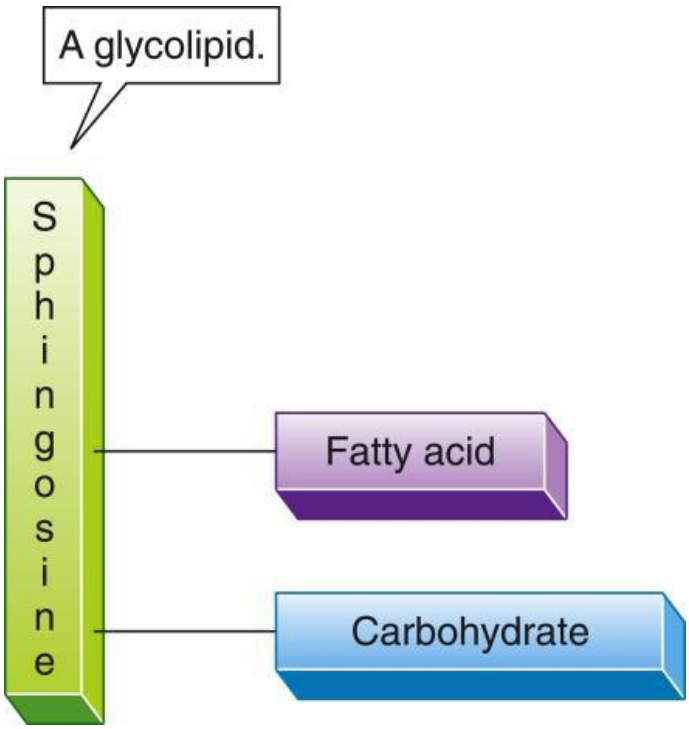
Sphingomyelins are found brain and nerve tissue, and in the myelin sheath that protects nerves.



Scheme.14. Sphingomyelin

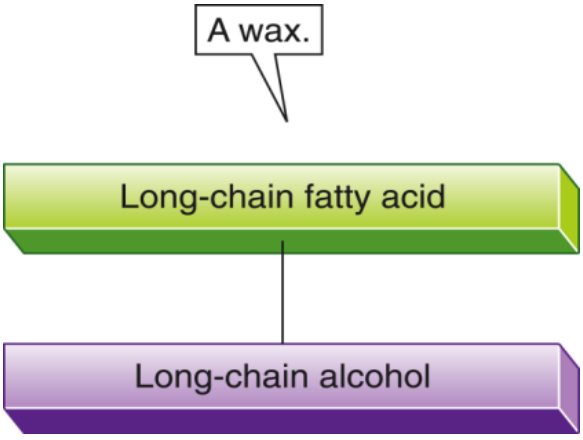
1.4. 2.2.Glycolipids

are sphingolipids that contain carbo-hydrates (usually monosaccharides). They are also referred to as *cerebrosides* because of their abundance in brain tissue.



1.4.3. Waxes

Waxes are simple lipids contain a fatty acid joined to a long-chain (12-32 carbons) alcohol:



Scheme.15. Waxes

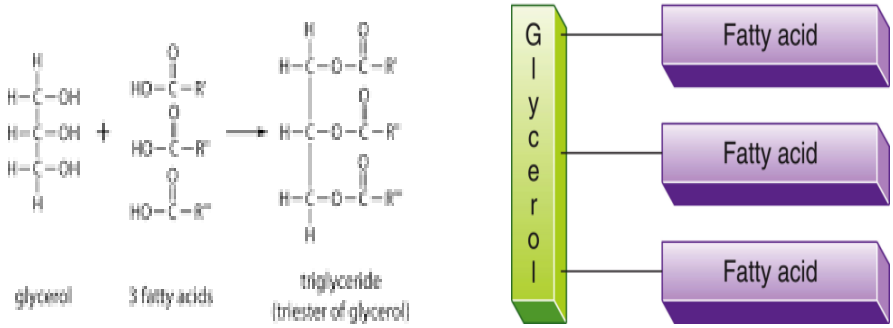
Waxes are insoluble in water and not as easily hydrolyzed as fats and oils. They often occur in nature as protective coatings on feathers, fur, skin, leaves, and fruits.

Sebum, secreted by the sebaceous glands of the skin, contains waxes that help to keep skin soft and prevent dehydration.

Waxes are used commercially to make cosmetics, candles, ointments, and protective polishes

1.4.4. Fats and oils

Animal fats and vegetable oils are esters composed of three molecules of a fatty acid connected to a glycerol molecule, producing a structure called a **triglyceride** or a **triacylglycerol**:



Scheme.15. Triglycerides

The fatty acids in a triglyceride molecule are usually not all the same; natural triglycerides are often mixtures of many different triglyceride molecules

Fats are triglycerides that are solids at room temp.

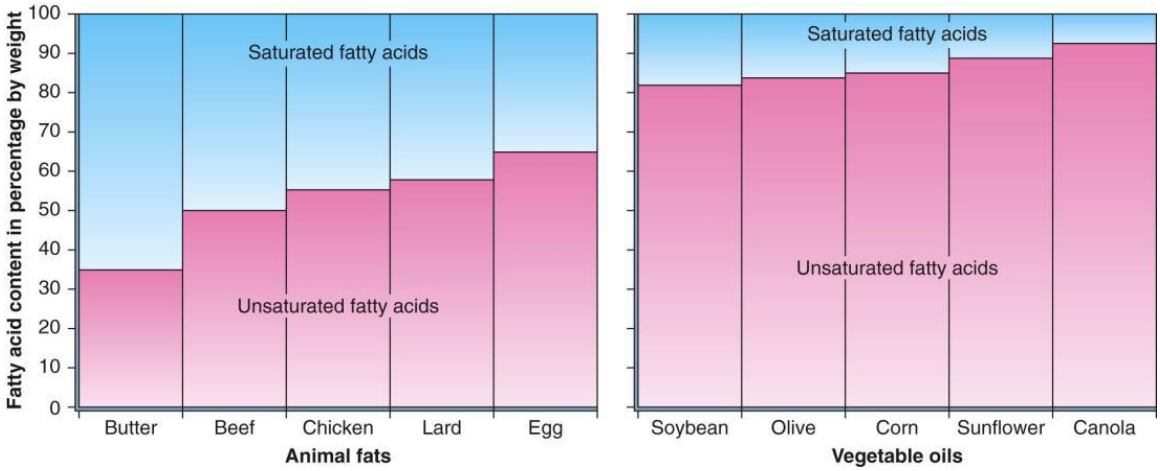
–usually derived from animals

–mostly saturated fatty acids

Oils are triglycerides that are liquids at room temp.

–usually derived from plants or fish

–mostly unsaturated fatty acids

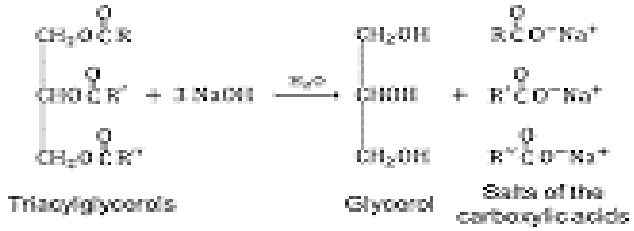


Scheme16 A comparison of saturated and unsaturated fatty acids in some foods

1.4.4.1. Chemical Properties of Fats and Oils

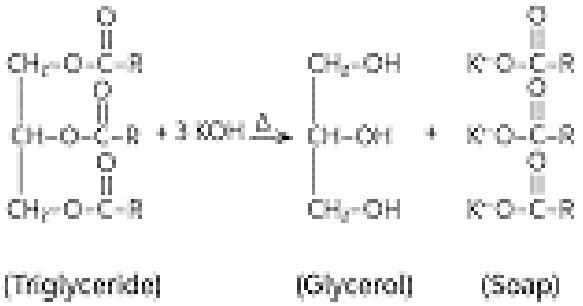
1.4.4.1.1 Hydrolysis of Triglycerides

Triglycerides can be broken apart with water and an acid catalyst (**hydrolysis**), or by digestive enzymes called **lipases**:



1.4.4.1.2 Saponification of Triglycerides

In **saponification** reactions, triglycerides react with strong bases (NaOH or KOH) to form the carboxylate salts of the fatty acids, called **soaps**:



1.4.4.1.3 Soaps:

NaOH produces a "hard" soap, commonly found in bar soaps; KOH produces a "soft" soap, such as those in shaving creams and liquid soaps.

These salts combine two solubility characteristics:

A long, nonpolar, water-insoluble (hydrophobic) hydrocarbon "tail."

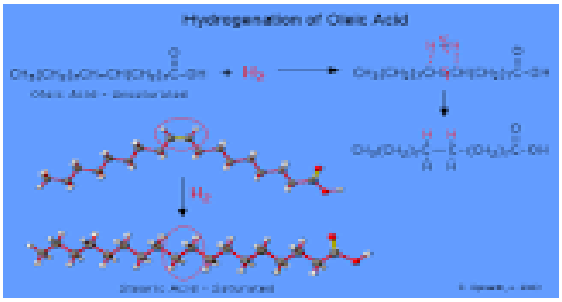
a charged, water-soluble (hydrophilic) "head."

In water, the "tails" become tangled, leaving the charged heads sticking out into the solution, forming a structure called a **micelle**.

1.4.4.1.4 Hydrogenation

In **hydrogenation** reactions, alkenes are converted into alkanes with hydrogen gas (H2) and a catalyst (Pt, Ni, or some other metal). This process is used to convert unsaturated vegetable oils, which are liquids at room temp., to saturated fats, which are solids at room temp. (Shortening, etc.).

In partially hydrogenated vegetable oils, not all of the double bonds are saturated, allowing the texture of the product to be controlled. In the process, this twists some of the naturally-occurring cis double bonds into Trans isomers (Trans fats). (Kevein,2014)



1.5. Groundnut oil:

Peanut (*Arachis hypogaea* L.) is the fourth major oilseeds crop of the world next to soybean, rapeseed and cotton. In 2015, peanut contributed 8.7% of the total oil seeds production (45 million ton) in the world (Anonymous, 2015). Peanut is an important oilseed crop for vegetable oil production (Arioglu, 2014). About two-thirds of total peanut production is crushed for oil and the remaining one-third is used in confectionery products in the world (Dwivedi et al., 1993). Peanut seeds contain 9.5-19.0% carbohydrate on a dry seed basis it is a good source of mineral (P, Ca, Mg and K) and vitamins (E, K and B group). Peanuts are also a cheap source of protein, a good source of essential vitamins and minerals, and a component of many food products (Dwivedi et al., 1996; Yav et al., 2008; Ingale & Shrivastava, 2011; Chamberlin et al., 2014; Chowdhury et al., 2015). Peanut contain 13 different fatty acids (palmitic, palmitolic, heptadecylic, heptadecenoic, stearic, oleic, linoleic, linolenic, arachidic, eicoseonic, behenich, nervonic and lignoceric). Oleic and linoleic acids are two important unsaturated fatty acids and both of them comprised about 80% of fatty acid composition. The rest of fatty acids are saturated fatty acids (20%). Peanut cultivars varied in their fatty acid composition (Ahmed & Young, 1982) The nutritional and storage qualities of peanut are determined by its fatty acids composition. According to Andersen & Gorbet (2002) peanut oil contains both saturated and unsaturated fatty acids. Among these, the amount of saturated and unsaturated fatty acids in peanut oil varies from 10.92 to 17.47% and from 81.13 to 94.81%, respectively. Oleic acid content in peanut genotypes can vary from 21 to 85% and linoleic acid from 2 to 43%.

The fatty acid composition of peanut is becoming increasingly important diet for healthy living. The oleic to linoleic acid ratio and iodine value were used to determine the quality of peanut oil. Moreover, the degree of unsaturated fatty acid and the stability of peanut oil were determined by using the iodine value. High-oleic peanut has longer self-life than low-oleic peanut and it has better

flavor quality or stability than low-oleic peanut (Brown et al., 1975; Yav et al., 2008; Chaiyadee et al., 2013)

Several factors such as variety, seasonal variation, genotype, location, air and soil temperature, planting date, soil nutrient, moisture availability, growing conditions and maturity affect the fatty acid content in peanut oil (Young & Worthington, 1974; Brown et al., 1975; How & Young, 1983; Hashim et al., 1993; Dwivedi et al., 1996; Hassan et al., 2005; Isleib et al., 2008; Hassan & Ahmed, 2012; Chaiyadee et al., 2013).

The actual impact of seed maturity is dependent on genotype, climatic conditions, and genotype/climate interactions. Lower temperature during the seed development normally is associated with more unsaturated oil due to the increased activity of oleatedesaturase, which promotes the synthesis of linoleic acid. The increase in oleic acid concentration with increasing seed maturity is normally accompanied by a decrease in palmitic, linoleic, arachidic, eicosenic, behenic and lignoceric acid. Bovi (1982) and Holaday & Pearson (1974) found that higher temperatures during the last 4 weeks before harvest resulted in higher oil and oleic acid content and correspondingly higher O/L ratios.

Oil content and fatty acid composition of peanut have been studied in different cultivars and under different environmental condition and it has been reported that the oil content of peanut cultivars varied between 37.9-56.3%, oleic acid 37.7-82.2%, linoleic acid 2.9-41.5, palmitic acid 9.6-13.2%, stearic acid 1.6-3.7%, arachidic acid 1.2-1.7%, behenic acid 1.2-3.5% and iodine value varied between 88.6 to 105.4 (Dwivedi et al., 1996; Özcan & Seven, 2003; Yav et al., 2008; Önemli, 2012; Hassan & Ahmed, 2012; Chaiyadee et al., 2013; Mzimbiri et al., 2014; Chowdhury et al., 2015; Escobedo et al., 2015).

1.5.1. Uses of groundnut oil:

Peanut oil is naturally trans fat free, cholesterol free, and low in saturated fats. It consists mostly of oleic acid (*n*-9), a monounsaturated fatty acid (MUFA)

(52%), and linoleic acid (*n*- 6), a polyunsaturated fatty acid (PUFA) (32%) (Beare-Rogers et al., 2001; O¨ zcan, 2010). The oil is also a source of natural occurring compounds such as antioxidants, vitamin E, phytosterols, squalene, and *p*-coumaric acid, which are all beneficial in maintaining health. Peanut oil shows many positive biological effects, which are mostly connected with its high oleic acid content. A number of studies have shown the unique properties of this fatty acid and the importance of maintaining its intake at as high level as possible. Oleic acid has been shown to have a positive influence on cardiovascular risk factors, such as lipid profiles, blood pressure, and glucose metabolism. These beneficial effects were first observed for olive oil, which is also rich in oleic acid, but they are now also being reported for peanut oil, as well as peanut seeds alone, or even products made of peanuts (O¨ zcan, 2010).

***Anti-inflammatory Activity**

Peanut oil contains resveratrol that could effectively inhibit lipopolysaccharide (LPS)-induced nitric oxide (NO) production.

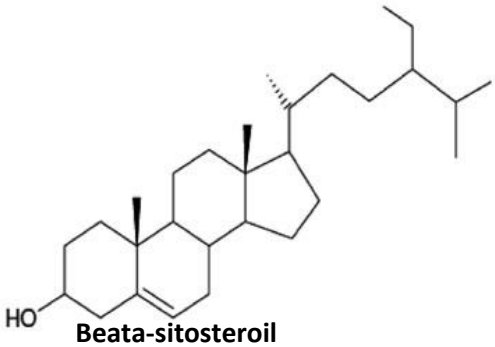
This resveratrol perform effective anti-inflammatory activity.

This compound might be of importance in further development for nutraceutical or chemopreventive applications (Chang et al., 2006; Djoko et al., 2007; Kang et al., 2010). Resveratrol treatment of mice presented protection against colitis through up regulation of SIRT1 in immune cells in the colon (Singh et al., 2010). Recently, it was invested that resveratrol, in an ex vivo model, inhibited tumor necrosis factor-R (TNF-R) and interleukin-6 (IL-6) released from macrophages, hence suppressing macrophage-CM-induced inflammatory response in adipocytes (Djoko et al., 2007). Also, resveratrol exerts anti-inflammatory effects in microglia and astrocytes by inhibiting different proinflammatory cytokines and key signaling molecules (Lu et al., 2010).

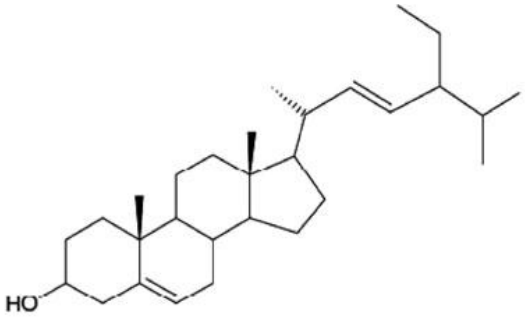
***Antitumor Activity and Anticancerous Activity**

Peanuts and peanut oil contain different phytochemicals such as β-sitosterol, resveratrol, campesterol, and sigmasterol (Fig. 3), this gives a strong evidence of protective role in different cancers like breast, colon, and especially prostate

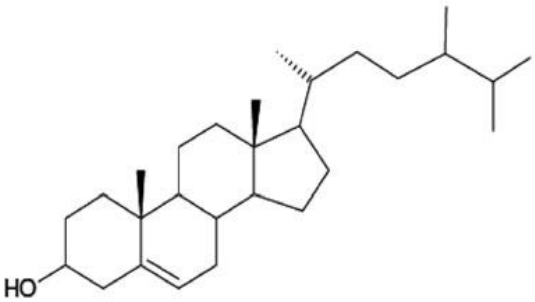
(Awad et al., 2000; Lopes et al., 2011). It was noticed that roasted peanuts contain 61–114 mg PS/100 g depending on the peanutvariety, 78–83% of which is in the form of β-sitosterol. Unrefined peanut oil contains 207 mg PS/100 g, these higher values give confirmation of strong anticancerous property of peanut oil (Awad et al., 2000).



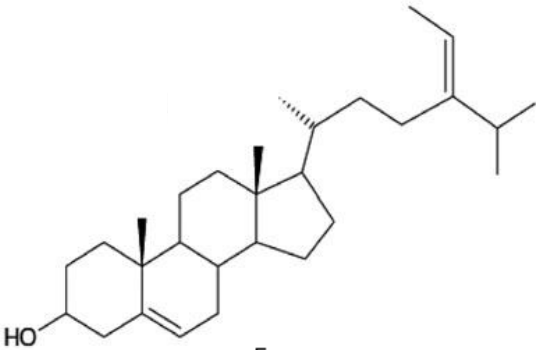
Beata-sitosteroil



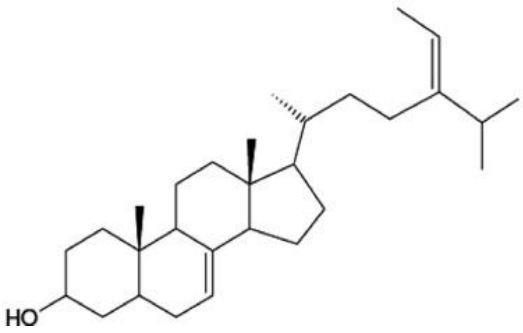
Stigmasteroil



Campesteroil



Δ^5 **–Avenasteroil**



Δ^7 **–Avenasteroil**

Scheme.17.Functional compounds present in peanut oil (Francisco and Resurreccion, 2008).

The beginning of promotion and progression of tumors. Resveratrol inhibits free radical formation, which will inhibit tumor formation; it acts as an antimutagen (Bishayee et al., 2010). Peanut consumption may help to reduce colorectal cancer risk in women. This anticancer effect is suggested to be a result of the action of nutrients found in peanuts, such as folic acid, phytosterols, phytic acid, and resveratrol, which have been reported to have anticancer effects (Yehetal, 2006). These results suggest potential applications for peanuts and their by-products as natural chemotherapeutic or chemopreventive agents.

***Peanut Oil and Cardiovascular Diseases**

Peanut, peanut oil, and fat-free peanut flour reduced the cardiovascular disease factor and the development of atherosclerosis in animals consuming an atherosclerosis inducing diet. This was confirmed in recent human clinical trials (Ghadimi et al., 2010; Stephens et al., 2010).

Peanut oil consumption can also elicit significant blood pressure reduction in normolipidemic adults (Sales et al., 2008). Stephens et al. (2010) evaluated cardiovascular effects on Syrian golden hamsters by giving diet rich in fat-free peanut flour, peanuts, and peanut oil.

***Protection against Alzheimer's disease**

Peanut oil is a rich source of vitamin E and other phytochemicals.

Niacin and vitamin E are two important constituents that provide protection against Alzheimer's disease. In almost 4000 people 65 years or older, niacin from food slowed the rate of cognitive decline (Morris et al., 2004). the consumption of vitamin E from supplements had no effect on the incidence of Alzheimer's disease, vitamin E intake from food was protective (Morris et al., 2002).

***Anti-Diabetic Activities**

Peanuts were also proved to be beneficial in lowering the risk of type 2 diabetes. People with this type of diabetes do not produce adequate amounts of insulin for

the needs of the body and cannot use insulin effectively. A study conducted on INS-1 (a rat pancreatic beta cell line) showed that oleic acid and peanut oil high in oleic acid were able to enhance insulin production. Pretreatment with oleic acid reversed the inhibitory effect of TNF-α on insulin. Peanut oil ultimately reversed the negative effects of inflammatory cytokines observed in obesity and noninsulin dependent diabetes mellitus. Type 2 diabetic mice that were administered a high-oleic acid diet derived from peanut oil had decreased glucose levels compared with animals given a high-fat diet with no oleic acid (Vassiliou et al., 2009).

***Peanut Allergy**

In recent years, concern for peanut allergy has increased. Peanut allergy is associated with a higher incidence of fatal food-induced anaphylaxis than any other food allergy, for unknown reason. Hypersensitivity to foods occurs in 6–8% of children and about 1% of adults. In the United States, in survey it was suggested that 0.7% of children are allergic to peanuts in varying degrees. Avoidance is the only current method to deal with food allergy. Significant research efforts are in process to deal with peanut allergy. Various peanut allergens have been identified and all are proteins (Burks, 2008). Refined peanut oil after all protein removal is not allergenic; however, oils contaminated with peanut protein can produce significant allergic reactions in peanut-sensitive individuals. Cold-pressed oils are more likely to contain peanut proteins as compared with hot pressed oils (Gunstone, 2011).

1.6. Sesame oil:

Sesame (Sesamum indicum L.) from Pedaliaceae, is an important oil seed crop being cultivated in the tropics and the temperate zone of the world. (Biabani, and Pakniyat, 2008). It is one of the oldest oil crops and is widely cultivated in Asia and Africa. (Ali et al., 2007).It was a highly prized oil crop of Babylon and Assyria at least 4000 years ago (Ross, 2005). Sesame oil, otherwise also referred to as gingelly oil, is one of the major sources of edible oil in India and is

culturally associated from the Vedic period. The Sanskrit word for oil, taila is derived from the Sanskrit word for sesame tila. (Shanthasheela et al., 2007). It is called "sesame" internationally, while it is called "benniseed" in West Africa; "simsim" in East Africa and "Till" in

India.Within Nigeria it is called different names in different localities. It is generally called "ridi" in the Northern States. The Igalas, Idomas and Tivs of Benue State call it "Igogo", "Ocha" and "Ishwa" respectively. The Ibos call it "isasa" and Yorubas call it "Ekuku" or "Eeku" in parts of Ogun, Ondo and Oyo states and Ilorin in Kwara State. (Aboje, 2011).

Natural sesame oil derived from good quality seed has a very pleasant flavour and can be consumed without further purification. The natural oil has excellent stability due to the presence of high levels of natural antioxidants (Lyon, 1972). Report has shown the impact of environment on the seed yield.

Seed Production Environment and Potential Seed Longevity of Rain-fed Sesame (Sesamum indicum L.) Genotypes was reported by Adebisi, et al.,(2011). The oil is used widely in the some injectable drug formulations. The lignans such as sesamin, episesamin, sesaminol and sesamolin are major constituents of sesame oil and all have chemically methylenedioxyphenyl group (Gokbulut, 2010). It ranks ninth among the top thirteen oilseed crops which make up 90% of the world production of edible oil.(Adeola et al., 2010).

The oil is also useful in the industrial preparation of perfumery, cosmetics (skin conditioning agents and moisturizers, hair preparations, bath oils, hand products and make-up), pharmaceuticals (vehicle for drug delivery), insecticides and paints and varnishes (Chemonics International Inc., 2002).

Sesame seed has higher oil content (around 50%) than most of the known oil seeds (Hwang, 2005)

The seed has 40-60 per cent of oil with almost equal levels of oleic (range 33-50%, typically 41%) and linoleic acids (range 33-50%, typically 43%) and some palmitic acid (range 7-12%, typically 9%) and stearic acid (range 3-6%, typically 6%) (Gunstone, 2004).

Sesamum indicum L. oil can be classified in the oleiclinoleic acid group. The dominant saturated acids were palmitic (up to 8.58%) and stearic (up to 5.44%) (Nzikou et a.l, 2009).

1.6.1. Uses of sesame oil:

***Nutritional profile of sesame seeds**

The nutrient composition of sesame seeds is have desirable physiological effects including antioxidant activity, blood pressure and serum lipid lowering potential as proven in experimental animals and humans (Sirato-Yasumoto et al., 2001)

The major protein fraction (globulin) in sesame contains about 95% of 13S globulin and seems to be a simple, salt soluble, very susceptible to heat denaturation and similar in subunit structure to soybean 11S globulin with more hydrophobic properties.

The last property limits the use of sesame proteins in certain food formulation, particularly in fluids and beverages, which indicates the need to modify the functionality of sesame proteins before it can be used in processing of imitated dairy products.

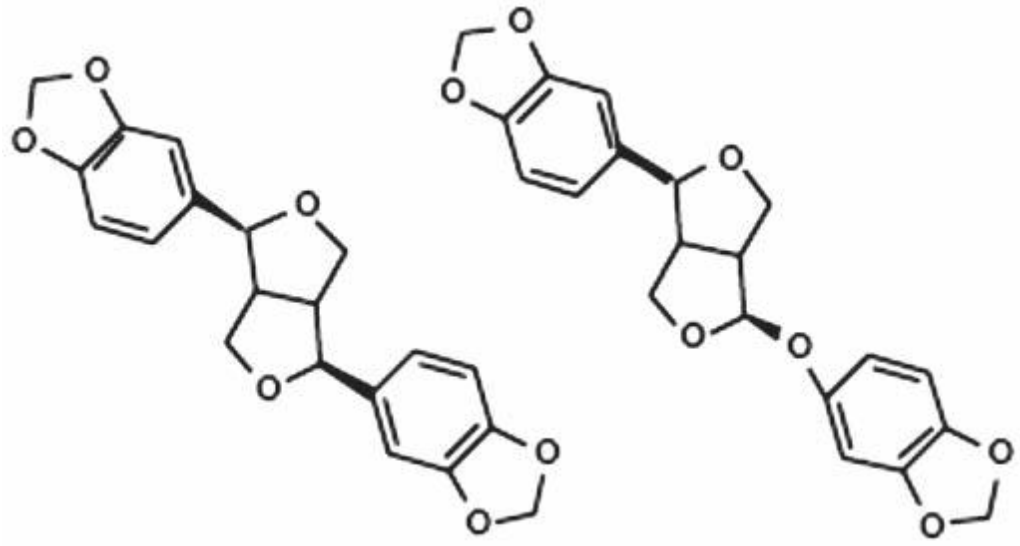


Fig.1.22.Chemical structure of bioactive compounds from sesame

Sesame is rich in sulfur containing amino acids and limited in lysine and contains significant amounts of oxalic (2.5%) and phytic (5%) acids (Kapadia et al., 2002). Sesame seeds contain two unique substances, sesamin and sesamolin (Fig. 2) whence during refinement the two phenolic antioxidants, sesamol and sesaminol, are formed. Both of these substances belong to lignans and have been shown to possess cholesterol-lowering effect in humans (Ogawa et al., 1995; Hirata et al. 1996) and to prevent high blood pressure and increase vitamin E supplies in animals (Yamashita et al., 1992; Kamal-Eldin et al., 1995). Sesame seeds are an excellent source of copper and calcium. It is also rich in phosphorous, iron, magnesium, manganese, zinc and vitamin B1. A chlorinated red naphthoquinone pigment possessing antifungal activity, named chlorosesamone (2-chloro-5, 8-dihydroxy-3-3methyl-2-butenyl)-1, 4-naphthoquinone), has been reported from sesame root (Hasan et al., 2000).

In another research, three anthraquinones, Anthrasesamones

A, B and C, were isolated from the root of sesame (Furumoto et al., 2003).

***Medicinal properties of sesame seeds and health issues**

Sesame oil is mildly laxative, emollient and demulcent. The seeds and fresh leaves are also used as a poultice. The oil has wide medical and pharmaceutical application. Sesamin has been found to protect the liver from oxidative damage. The oil has been used for healing wounds for thousands of years. It is naturally antibacterial for common skin pathogens such as Staphylococcus and Streptococcus as well as common skin fungi such as athlete's foot fungus. It is anti-viral and anti-inflammatory. In recent experiments in Holland by Ayurvedic physicians, the oil has been used in the treatment of several chronic diseases including hepatitis, diabetes and migraines. Analgesic activity of the ethanolic extract of *Sesamum indicum* has been tested by acetic acid-induced writhing model in mice by Nahar and Rokonuzzaman (2009). Sesame oil has been found to inhibit the growth of malignant melanoma in vitro and the proliferation of human colon cancer cells (Smith and Salerno, 1992).

***Food and industrial uses of sesame seeds**

There are many foods with sesame as an ingredient. Europeans use it as a substitute for olive oil. Sesame oil is an excellent salad oil and is used by the Japanese for cooking fi sh. Aqua hulled sesame seeds undergo a special hulling process which produces a clear white seed. These seeds are washed, dried and used on hamburger buns. This special process makes the seeds to stick to the bun while maintaining a white color after baking. Nearly 35% of the imported crop from Mexico is purchased by McDonalds to prepare sesame seed buns. The seeds are also used on bread and then eaten in Sicily. In Greece, seeds are used in cakes, while in Togo and Africa the seeds are a main soup ingredient. Mechanically hulled sesame seed enriches bakery and candles and is also the base for the creamy, sweet wholesome tahini. Sesame flour has high protein content, high levels of methionine and tryptophan and 10-12% sesame oil. Sesame seeds contain three times more calcium than a comparable measure of milk.

Refined sesame oil has antioxidant properties allowing for its greater shelf-life for use in the food industry. Roasted sesame oil resists rancidity due to the antioxidants formed during seed roasting and the particular roasted sesame flavor improves taste of fried products. African countries use the seeds as spice, seed oil, frying vegetables and meat, eaten raw or fried and used in confections such as candy and baking. Other products sold in

US grocery and health stores with sesame seed as an ingredient include sesame crackers, honey puffed kasha, sesame blue chips, unhulled sesame seed and sesame seed candy. Many recipes contain sesame seeds as an ingredient such as sesame seed sprouts, sesame spread, tanferine and sesame, sesame seed cookies, hummus, sesame seed bagels, sesame granola, sesame broccoli rice, sesame mustard sauce, ginger sesame chicken, sesame pastry, sesame seed sauce and sesame green beans. Sesame meal is excellent feed for poultry and livestock.

African people use sesame to prepare perfumes and cologne has been made from sesame flowers. Myristic acid from sesame oil is used as an ingredient in

cosmetics. Sesamin has bactericide and insecticide activities plus it also acts as an antioxidant that can inhibit the absorption of cholesterol and the production of cholesterol in the liver. Sesamolin also has insecticidal properties and is used as a synergist for pyrethrum insecticides (Morris, 2002). Sesame oil is used as a solvent, oleaginous vehicle for drugs, skin softener and used in the manufacture of margarine and soap. Chlorosesamone, obtained from roots of sesame, has antifungal activity (Begum et al., 2000).

Sesame lignans have antioxidant and health promoting activities (Nakai et al., 2003). Feeding sesame lignans to rats have shown to reduce Fe2+ induced oxidative stress. Compared with those fed with groundnut oil, sesame oil fed rats had lower levels of hepatic thiobarbituric acid reactive substances, serum glutamate oxaloacetate transaminase activities and serum glutamate pyruvate transaminase activities. The level of these enzymes indicates protection against Fe2+ induced oxidative stress (Hemalatha et al., 2004; Hu et al., 2004). The antioxidant and free radical scavenging activities of sesamol using a nanosecond pulse radiolysis technique have been reported by several scientists (Unnikrishnan et al., 2005; Juan et al., 2005). A good free radical scavenging potency of antioxidants from sesame cake extract has also been reported (Shyu and Hwang, 2002; Suja et al., 2004). Antifungal activity toward *Cladosporium fulvum* of Chlorosesamone, hydroxysesamone and 2,3-epoxysesamone was established in a study by Hasan et al. (2001). Sesame seed consumption increases plasma γ-tocopherol and enhances vitamin E activity, which is reported to prevent cancer and heart diseases (Cooney et al.,

2001). Sesamin is thermostable and remains at 90% of the original level after roasting (Abe et al., 2001) indicating its viability for food and non-food applications. The total phenolic content (TPC), Trolox equivalent antioxidant capacity assay, free radical scavenging capacity, inhibition of low density lipoprotein (LDL) cholesterol and metal chelating capacity of extracts of whole black and whole white sesame seeds and their hull fractions in 80% aqueous ethanol were investigated. Results demonstrated considerable antioxidant

activity of sesame products tested especially black sesame hulls (Shahidi et al., 2006). Cephalin from sesame seed has hemostatic activity. Historically, fiber is used as an antidiabetic, antitumor, antiulcer, cancer preventive, cardioprotective and laxative. Fiber ranges from 27,100 to 67,000ppm in the seed with up to 166,000 ppm in the leaf. Lecithin of sesame seeds, ranging from 58 to 395 ppm, possesses antioxidant and hepatoprotective activity. It is also likely effective for reducing hepatic steatosis in long term parenteral nutrition patients and a successful treatment for dermatitis and dry skin (Jellin et al., 2000). The antihypertensive and protective effect of sesamin against renal hypertension and cardiovascular hypertrophy is also reported (Kita et al., 1995; Matsumura et al., 1995 and 2000). Flavonoids from *S. indicum* were effective in raising the hemoglobin levels in rats (Anila and Vijayalakshmi, 2000).

The effects of ethanolic extract of sesame coat on oxidation of LDL and production of nitric oxide in macrophages were investigated.

The results showed that extract in the range of 0.01–0.8 mg/ml markedly inhibited copper-induced LDL oxidation and H2O2 induced cell damage that implies that ethanolic extract could exhibit a protective action on biomolecules and generation of inflammatory mediators *in vitro* (Wang et al., 2007).

1.7. Objective:

This research was undertaken to investigates the properties and assess quality of the sesame and groundnut oils product by industrial and traditional methods which include:

1. Determination of some physiochemical properties of oils.
2. Identification of the major components of oils using Gas Chromatography-Mass Spectroscopy.

Chapter Two

Materials and Methods

2. Materials and Methods

2.1. Collection of samples

Sesame and groundnut oils were Purchased from the local market in February 2021

2.2. Methods of analysis

2.2.1. Physicochemical properties of the oil

2.2.1.1. Specific gravity

Determined by AOAC method. The dry pyconometer was filled with prepared sample in such a manner to prevent trap of air bubbles after removing the cap of the side arm. The stop [per was inserted in the pyconometer and immersed immediately in water bath 30.0 $\pm$ 0.2 and held for 30 minutes. Any oil came off the capillary opening of the pyconometer stopper was wiped out carefully. The was removed from the bath, cleaned and dried thoroughly. The cap of the side arm was removed and quickly the bottle was weighed ensuring the temperature do not fall below 30 ^{0}C.

Specific gravity at 30 ^{0}C/ 30 ^{0}C = $\frac{A-B}{C-B}$

Where:

A: weight (g) of bottle and oil.

B: weight of bottle.

C: weight in gm of water.

2.2.1.2. Determination moisture content

Moisture content was determined according to the Association of official's analytical chemists AOAC (1990).

2 grams of each sample was accurately weighed in dry, clean, pre-weighed crucible and left overnight at 105˚C in a hat air oven. Each crucible was then cooled in desiccator and allowed to cool then reweighed. The process of

drying, cooling and weighing was repeated until constant weight was measured.

$$MC\% = \frac{(W2-W1)-(W3-W1)}{W2-W1} \times 100$$

Where: MC: moisture content, W1: weight of empty crucible, W2: weight of crucible with the sample and W3: weight after drying.

2.2.1.3. Refractive index

The refractive index of the oil was determined by AOAC [48].The refract meter was first adjusted at 1.3330 at 20^0 C with pure distilled water as a blank reading. A drop of the oil was placed in the instrument and telescope was adjusted so that the cross hairs were distinct and in focus. The adjustment of the knob was rotated until the lower part of the field was dark and the upper part was light and a clear definite boundary appeared. The coarse adjustment knob was moved first and then the fine adjustment knob until the boundary line coincided with the intersection of the cross hair in the telescope. The instrument was read when temperature is stable.

2.2.1.4. Determination of color

Color was determined according to handbook of food analysis. The sample liquid and filtered through a filter paper to remove any impurities and traces of moisture till is sure that the sample was absolutely clear and free from turbidity. The glass cell of desired size cleaned with carbon tetrachloride and allowed to dry. The cell filled with the oil and placed in position in the tintometer. The color matched with sliding red, yellow and blue colors.

Report the color of the oil in terms of Lovibond units as follows:

Color reading = (a Y + 5 b R) or (a Y + 10 b R).

Where a = sum total of the various yellow slides (Y) used

b = sum total of the various red (R) slides used

Y + 5R is the mode of expressing the color of light colored oils; and

Y + 10 R are for the dark-colored oils.

2.2.1.5. Viscosity

Viscosity was determined according to Lemuel M. Diamante and Tianying Lan. The absolute viscosities of the different vegetable oils were determined using a Lamy viscometer RM100 (Lamy, France), a rotating viscometer with coaxial cylinder. Approximately 25 mL of oil was placed in the Tube DIN 1 outer cylinder, and then the bob MK Din-9 was inserted. The radius of the tube (R_a) is 16.25 mm and the radius of the bob is (R_i) 15.5 mm. The length of the bob is 54 mm. The correct mode was set for the appropriate measuring system (MS 19) and the measurement time was fixed at 60 seconds. The torque of each sample at the different temperatures was recorded at a range of shear rate (Ẏ) from 64.5 to 4835 s^{-1}. All viscometric measurements of the samples were carried out in triplicate. Every replicate was run twice the mean torque value of the two runs was recorded for each replicate at a given shear rate. The shear stress was obtained from.

2.3.2. Chemical properties of the oils

2.3.2.1. Acid value

Acid value was determined according to handbook of food analysis [47]. The oil mixed thoroughly before weighing. About 5 of cooled oil sample accurately weighed in a 250 ml conical flask and 50 ml added to 100 ml of freshly neutralized hot ethyl alcohol and about one ml of phenolphthalein indicator solution. The mixture boiled for about five minutes and titrated while hot against standard sodium hydroxide shaking vigorously during the titration. The weight of the oil taken for the estimation and the strength of the alkali used for titration shall be such that the volume of alkali required for the titration does not exceed 10 ml.

Calculation

$$\text{Acid value} = \frac{56.1VN}{W}$$

Where , V= Volume in ml of standard sodium hydroxide used

N = Normality of the Sodium hydroxide solution

W = Weight in g of the sample

The acidity is frequently expressed as free fatty acid for which calculation shall be.

$$\text{Free fatty acids as oleic acid Per cent by weight} = \frac{28.2\ VN}{W}$$

Acid value = Percent fatty acid (as oleic) x 1.99

***2.3.2.2.* Saponification value**

Saponification value was determined according to handbook of food analysis. About 1.5 to 2.0 g sample were transferred into a 200 ml conical flask. A 30 mL of 0.5 N potassium hydroxide ethanol, and fix a cooling pipe to the flask.The flask gently heated and occasionally shaked while adjusting the heat so that back flow ethanol will not reach the top of cooling pipe. After heated for 1 hour, immediately cooled, and titrated with 0.5 N Hcl before the test liquid is solidified. Blank test performed for 3 times to obtain mean value of titration volume of 0.5 N hydrochloric acid.

The saponification was calculated as followed:

Saponification value (mg / g) = (BLl－EPl) × TF × Cl × K1 / SIZE

Where:

EPl： Titration volume (mL)

BLl : Blank level (25.029mL)

TF : Reagent (HCl) factor (1.006)

Cl : concentration conversion coefficient (28.05 mg/mL)

(Potassium hydroxide in Eq.:56.11×0.5)

Kl : Unit conversion coefficient (1)

SIZE: Sample size (g).

2.3.2.3. Unsaponification value

Unsaponification matters were determined according to Handbook of Food Analysis. Accurately 5 g of well mixed oil / fat sample weighed into a 250ml conical flask. Add 30ml of alcoholic potassium hydroxide solution. The content boiled under reflux air condenser for one hour or until the saponification is complete (complete saponification gives a homogeneous and transparent medium). Take care to avoid loss of ethyl alcohol during the saponification. The condenser washed with about 10 ml of ethyl alcohol. The saponified mixture was transferred while still warm to a separating funnel. The saponification flask washed first with some ethyl alcohol and then with cold water, using a total of 50 ml of water to rinse the flask. Cool to 20 to 25°C. Fifty ml of petroleum ether were added to the flask, shacked vigorously, and allowed the layers to separate. The lower soap layer transferred into another separating funnel and repeats the ether extraction for another 3 times using 50 ml portions of petroleum ether. The combined ether extract was washed three times with 25 ml portions of aqueous alcohol followed by washing with 25 ml portions of distilled water to ensure ether extract is free of alkali (washing are no longer alkaline to phenolpthalen). The solution transferred to 250 ml beaker, rinse separator with ether, added rinsings to main solution. Evaporated to about 5ml and transferred quantitatively using several portions.

2.3.2.4.Peroxide value

Peroxide value was determined according to Handbook of food analysis [47]. Five grams of the sample were delivered into a conical flask with stopper. About 25 mL of solvent (15 ml acetic acid+10 ml choloroform) were added and gently shake to dissolve the sample completely. The air inside flask gently replace with nitrogen to remove remaining oxygen. One ml of saturated potassium iodide was added and immediately seals the flask and gently shakes it for one minute. The flask left at room temperature 15 to 20°C in a dark room. Thirty mL of pure water were added, and the flask sealed and stirred. Titration with 0.01mol/L sodium thiosulphate was performed to measure peroxide value.

The peroxide value was measured as followed:

Peroxide value (meq / kg) = (EP1－BL1) × TF × R / SIZE

Where:

EP1 ：Titration volume (mL)

BL1 ：Blank level (0.00mL)

TF ：Factor of reagent (1.006)

R ：Constant (10)

SIZE ：Sample size (g)

2.3.2.5.Iodine value

Iodine value was determined according to Handbook of Food Analysis [47]. To 300 ml conical flask with ground-in stopper 0.1g sample was added. Twenty ml of carbon tetrachloride were added and the flask was sealed. Twenty five mL Hanus solution also added and the flask also sealed. The flask content shacked for one minute. And kept sealed and left in a dark room (about 20°C) for 30 minutes with continuous shaking every 5 minutes. Ten m of 15% potassium iodide and 100 ml of water were added, and the flask sealed and shaked for 30 seconds. The flask content titrated with 0.1mol/L sodium thiosulfate to obtain iodine value. Likewise, perform blank test to obtain blank level.

The Iodine value was calculated as follow:

Iodine value (c g / g) = (BL1－EP1) × TF × C1 ×K1 / SIZE
Where:
EP1 ：Titration volume (mL)
BL1 ：Blank level (47.074mL)
TF ：Factor of titrant (1.006)
C1 ：Concentration conversion coefficient (1.269)
(Atomic mass of iodine: 126.9/100)
K1 ：Unit conversion coefficient (1)
SIZE ：Sample size (g)

2.3.3. GC-MS

***Sample Preparation**

2ml of the sample was mixed thoroughly with 7ml of alcoholic sodium hydroxide (Noah) that was prepared by dissolving 2 g in 100 ml methanol. 7 ml from alcoholic sulfuric acid (1ml H_2SO_4 to 100 ml methanol) was then added. The mixture was then shaked for 5 minutes .The content of the test tube was left to stand overnight.1 ml of Super saturated sodium chloride (NaCl) was then added and the contents being shaken. 2ml of normal hexane was added and the contents were shaked thoroughly for three minutes. Then the n-hexane layer (the upper layer of the test tube) was taken using disposable syringe. 5 µl from the n-hexane extract was diluted with 5 ml of diethyl ether .Then the mixture was filtered through syringe filter 0.45 µm and dried with 1g of anhydrous sodium sulphate as drying agent and 1µl of the diluted sample was injected in the GC.MS instrument. ***GC/MS Conditions**

The qualitative and quantitative analysis of the sample was carried out by using GM/MS technique model (GC/MS-QP2010-Ultra) from japans 'Simadzu Company, with serial number 020525101565SA and capillary column (Rtx-5ms-30m×0.25 mm×0.25µm).The sample was injected by using split mode, helium as the carrier gas passed with flow rate 1.61 ml/min, the temperature program was started from 60c with rate 10c/min to 300c as final temperature degree with 5 minutes hold time , the injection port temperature was 300c, the ion source

temperature was 200c and the interface temperature was 250c.The sample was analyzed by using scan mode in the range of m/z 40-500 charges to ratio and the total run time was 29 minutes .Identification of components for the sample was achieved by comparing their retention index and mass fragmentation patents with those available in the library, the National Institute of Standards and Technology (NIST). , results were recorded.

Chapter three

Results and discussion

3-Results and discussion

Table.3.1. shows the physical and chemical properties of sesame oil (industrial) ; moisture (0.23±0.04), Refractive index (1.4767±0.0005), density (0.9204±0.001), viscosity (60.195±0.03), iodine value (98.94±0.33), peroxide value (3.605±0.26), saponfication value (188.015±0.21), unsaponfication value (1.895±0.23), acid value (0.49±0.02) and color

(blue 00±00, yellow 32.10±0.4 and red 5.5±0.1).

Jeong and Oshodi (2004) reported the un saponification value of oil ranged from (1.84-3.73)mg KOH/g oil, amin and kothan (1990) reported the iodine value of oil ranged from (97.08-107) mg KOH/g oil, Mohamed and Hamza (2008) reported the saponfication value of oil (186.96-189.6) mg KOH/g oil and acid value (0.5) mg KOH/g oil, Earlier (2008) reported the peroxide value 6.88 mg KOH/g oil

Table.3.1. Physical and chemical properties of sesame oil (factory)

parameter	result
Moisture	0.23±0.04
Refractive index	1.4767±0.0005
Density	0.9204±0.001
Viscosity	60.195±0.03
Iodine value	98.94±0.33
Peroxide value	3.605±0.26
Saponfication value	188.015±0.21
Un Saponfication value	1.895±0.23
Acid value	0.49±0.02
Color	Blue 00±00 Yellow 32.10±0.4 Red 5.5±0.1

Table.3.2. Physical and chemical properties of sesame oil (traditional)

parameter	result
Moisture	1.23±0.05
Refractive index	1.4785±0.0003
Density	0.93195±0.00025
Viscosity	64.695±0.385
Iodine value	112.42±0.2
Peroxide value	8.815±0.145
Saponfication value	194.91±1.6
Un Saponfication value	5.565±0.295
Acid value	1.175±0.005
Color	Blue 0.85±0.05 Yellow 37.5±0.5 Red 6.75±0.05

Table.3.2. shows the physical and chemical properties of sesame oil (traditional) the moisture (1.23±0.05), refractive index (1.4785±0.0003), density (0.93195±0.00025), viscosity (64.695±0.385), iodine value (112.42±0.2), peroxide value (8.815±0.145), saponfication value (194.91±1.6), un saponfication value (5.565±0.295), Acid value(1.175±0.005) and color (blue 0.85±0.05, yellow 37.5±0.5 and Red 6.75±0.05). murwan (2008) reported that the density (0.890 %), refractive index (1.473 %), viscosity (26.40 %), moisture (2.7 %), iodine value (97.7-114.85 %), saponification value (174-198.20%), peroxide (2.22-15.07%) and acid value (3.10-9.30%).

Table.3.3. Physical and chemical properties of groundnut oil (factory)

parameter	result
Moisture	0.23±0.04
Refractive index	1.6695±0.00015
Density	0.91945±0.00025
Viscosity	60.305±0.035
Iodine value	98.525±0.045
Peroxide value	2.615±0.055
Saponfication value	188.275±1.005
Un Saponfication value	1.595±0.255
Acid value	0.55±0.05
Color	Blue 0.1±00 Yellow 35.3±0.1 Red 5.7±0.1

Table.3.3. shows physical and chemical properties of groundnut oil (factory), the moisture (0.23±0.04), refractive index (1.6695±0.00015), density (0.91945±0.00025), viscosity (60.305±0.035), iodine value (98.525±0.045),

peroxide value (2.615±0.055), saponfication value (188.275±1.005), un saponfication value (1.595±0.255), Acid value (0.55±0.05) and color(blue 0.1±00 ,yellow 35.3±0.1 and Red 5.7±0.1).

Michel and Bailey (1951) has reported the moisture content (23%), Jacob (1973) reported the Refractive index ranged from (1.46-1.465) , Goodrum and low (1982) reported that the viscosity (70.7%), CEC (2005) reported the iodine value ranged from (86-107) gI_2/kg oil, CEC (2005) has reported the peroxide value 1.0 mgO_2/g oil, Jacob(1973) has reported that the saponification value ranged from (187-196)mg KOH/g oil, CEC (2005) reported the acid value 0.6 mg KOH /g oil.

Table.3.4. Physical and chemical properties of groundnut oil (traditional)

Parameter	result
Moisture	0.725±0.055
Refractive index	1.4685±0.0007
Density	0.9217±0.0005
Viscosity	63.715±0.635
Iodine value	114.815±2.545
Peroxide value	7.735±0.225
Saponfication value	191.315±0.045
Un Saponfication value	3.76±0.1
Acid value	1.03±0.08
Color	Blue 0.15±0.05 Yellow 36.45±0.25 Red 6.35±0.05

Table.3.4. shows the physical and chemical properties of groundnut oil (traditional) , the moisture (0725±0.055) , refractive index (1.4685±0.0007) , density (0.9217±0.0005), viscosity(63.715±0.635), iodine value (114.815±2.545), peroxide value (114.815±2.545), saponfication value (191.315±0.045), un Saponfication value(3.76±0.1), acid value (1.03±0.08) and color(blue 0.15±0.05, yellow 36.45±0.25 and red 6.35±0.05).

aluyor (2009) reported that the density (0.916 mg KOH/g), refract index (1.462 mg KOH/g), saponification (192 mg KOH/g), acid value (2.890 mg KOH/g), iodine value (mg KOH/g) and un saponification value (mg KOH/g).

Table.3.5. Fatty acid composition of groundnut (Traditional)

Fatty acid	Determination value%
Oleic acid	56.98
Linoleic acid	25.74
Plamitic acid	5.54
cis-11-Eicosenoic acid	2.86
Stearic acid	2.85
Arachidic acid	2.55
Behenic acid	2.50
Tetracosanoic acid	0.87
13-Docosenoic acid	0.05
Heptacosanoic acid	0.04
Tricosanoic acid	0.02

Table.3.5 shows high availability of 9-octadecenoic acid (56.98%), 9, 12-octadecadienoic acid (25.74%), hexadecanoic acid (5.54%), cis-11-

eicosenoic acid (2.86%), methyl stearate (2.85%), ricosanoic acid (2.55%), docosanoic acid (2.50%), tetracosanoic acid (0.87%), 13-docosenoic acid (0.05%), heptacosanoic acid (0.04%) and tricosanoic acid (0.02%).

aluyor (2009) reported that the oleic acid (58.687%), Linoleic acid (21.7656%), plamitic acid (8.228%), stearic acid (2.4581%), arachidic acid (1.8313%) and behenic acid (3.8852%).

Table.3.6. Fatty acid composition of groundnut (factory)

Fatty acid	Determination value%
Oleic acid	32.35
Linoleic acid	14.25
Behnic acid	13.84
Srearic acid	11.73
Arachidic acid	8.28
Plamitic acid	7.58
Tetracosanoic acid	5.79
cis-11-Eicosenoic acid	4.69
Hexacosanoic acid	0.62
13-Docosenoic acid	0.28
Tricosanoic acid	0.16
beta.-Sitosterol	0.15
Squalene	0.12
Heneicosanoic acid	0.08
Stigmast-5-en-3-ol	0.05
Alphatocopherol	0.01
Margaric acid	0.01
9-Hexadecenoic acid	0.01

Table.3.6 shows high availability of 9-octadecenoic acid (32.35%), 9, 12-octadecadienoic acid (14.25%), docosanoic acid(13.84%), methyl stearate(11.73%), eicosanoic acid(8.28%), hexadecanoic acid(7.58%), tetracosanoic acid(5.79%), cis-11-eicosenoic acid(4.69%), hexacosanoic acid(0.62%),13-docosenoic acid(0.28%), tricosanoic acid (0.16%), beta.-sitosterol(0.15%), squalene(0.12%), heneicosanoic acid(0.08%), stigmast-5-en-3-ol(0.05%), vitamin e(0.01%), heptadecanoic acid(0.01%) and 9-hexadecenoic acid(0.01%).

steven (2003) reported that the oleic acid (0.3-48.4%) and plamitic acid (0.31-10.83%), dwivedi (1996) reported that the Linoleic acid (2.9-41.5%).

Table.3.7. Fatty acid composition of sesame oil (factory)

Fatty acid	Determination value%
Linoleic acid	40.93
Oleic acid	25.56
Stearic acid	20.57
Plamitic acid	6.86
Arachidic acid	3.44
cis-11-Eicosenoic acid	1.08
Behenic acid	0.66
Tetracosanoic acid	0.50
Tricosanoic acid	0.10
Pentacosanoic acid	0.09
Hexacosanoic acid	0.09
beta.-Sitosterol	0.04
Stigmast-5-en-3-ol	0.03
Heneicosanoic acid	0.01
Margaric acid	0.01

Table.3.7 shows high availability of 9, 12-octadecadienoic acid (Z, Z)-(40.93%), 9-octadecenoic acid (Z)-(25.56%), Methyl stearate**(**20.57**%),** hexadecanoic acid **(**6.86**%),** eicosanoic acid**(**3.44**%),** cis-11-eicosenoic acid**(**1.08**%),** docosanoic acid**(**0.66%), tetracosanoic acid(0.50%), tricosanoic acid(0.10%), pentacosanoic acid(0.09%), hexacosanoic acid (0.09%), beta.-sitosterol(0.04%), stigmast-5-en-3-ol(0.03%), heneicosanoic acid(0.01%) and heptadecanoic acid (0.01%).

antoni (1997) reported that the oleic acid (28.59%), gunstone (2004) reported that the oleic acid ranged from (33-50) typically 41%, Linoleic acid (33-50) typically 43%, plamitic acid (7-12) typically 9%, Stearic acid (3-6) typically 6%.

nzikon (2009) reported that the dominate saturated acid were plamitic acid up to (8.58%) and stearic acid up to (5.44%).

Table.3.8. Fatty acid composition of sesame oil (traditional)

Fatty acid	Determination value%
Olieic acid	36.99
Linoleic acid	36.92
Stearic acid	14.84
Plamitic acid	5.93
Arachidic acid	3.96
cis-11-Eicosenoic acid	0.89
Behenic acid	0.39
Tetracosanoic acid	0.06
Margaric acid	0.01
9-Hexadecenoic acid	0.01

Table.3.8 shows high availability of 9-octadecenoic acid (Z)(36.99%),9,12-octadecadienoic acid**(**36.92**%),** methyl stearate**(**14.84**%),** hexadecanoic acid

(5.93%), eicosanoic acid(3.96%), cis-11-eicosenoic acid(0.89%), docosanoic acid(0.39%), tetracosanoic acid(0.06%), heptadecanoic acid(0.01%) and 9-hexadecenoic acid(0.01%) .

murwan, khogalielnur and Abu elgasim (2008) arachidic acid (0.35%), Behenic acid (0.02%)

Comparative:

Table.3.4. Physical and chemical properties of groundnut oil (traditional) results showed that the color values in both factory and traditional method are similar.

The moisture values in traditional method greater due to the low temperature during extraction process and the structure of finely milled particle have been high aggregation.

In density, results showed no significant difference in both methods.

Refractive index, values showed similar and high value of refractive index also showed that the oil sample contain long chain fatty acids with a large a number of carbon atoms.

Viscosity values showed that the traditional method has greater value; low viscosity value indicates the high unsaturated molecules (Nangbes, 2013).

Unsaponification value high in traditional this due to several factors such as air, soil temperature and planting date, soil nutrient groundnut condition effect of fatty acid content in groundnut oil extraction (Hassan, 1983).

Saponification value for factory sample (188,275±1.005) and 191,315) for traditional sample. Value through the results showed that the traditional value is greater than factory; the saponification value was in acceptable range of most vegetable edible oils. The saponification value of 200mgg^{-1} indicated a high percentage of fatty acid of low molecular weight and carbon chain length, this indicates that the oil my not have a potential for use in soap making, this

property makes them useful source of essential fatty acid required in the human body(Akanniel, 2005)

Peroxide value in traditional greater than factory, that indicate the extent of peroxidation of oil during storage, rancidity brought by the action of oxygen or micro molecular carbonyl compound increase the peroxide value during storage (Damame, 1988). Any edible vegetable oil should be lower than 10.

Acid value in traditional samples showed higher, but the desirable acid value for vegetable oils should be lower than 2 (Salunkheel, 1992), acid value indicate it's level of free acid which increase during storage.

Iodine value of traditional samples greater, iodine value used to indicate the degree of unsaturated and stability of groundnut oil.

Table 3.5 showed that the Oleic acid has highest value in traditional sample (565.987%) and lowest value (32.35%) factory, linoleic acid recorded high value (25.74%) in traditional sample and lowest value (14.25%) in factory sample. the verity in oleic and linoleic acid due to environment, genetic factors and extraction process (Brown, 1975; Hashim, 1993 and Hassan, 2005).

Oleic and lnioleic acid ratio and iodine value used to determine the quality of oil, moreover the degree of unsaturated and the stability 0of groundnut oil was determine by iodine value, high oleic acid of peanut oil has longer shelf life than lowest and has better flavor quality or stability (Bronel,1973).

From table (3.5) ratio (O/L) (2, 2129) for traditional and (2, 2702) for factory groundnut oil.

Saturated fatty acid in groundnut oil for both traditional and factory samples variation due to several factors effect including seasonal variation, genotype, location air and temperature, soil nutrient, moisture and extraction process (Hassan, 2005).

Table (3.1) showed that the color value in traditional sample (Blue 0.85±0.05, Yellow 37.5±0.5 and Red 6.75±0.05).

Color in factory sample (3.2) (Yellow 32.10±0.4, Red 5.5±0.1) the color in both samples similar but blue color in factory sample absent.

Moisture value 0.23±0.04 in factory and 1.23±0.05 in traditional sesame sample, the result showed that the moisture in traditional sample gre3ater than than factory, due to the lower temperature in extraction process.

Density value in traditional sample (0.93195±0.00025) and (0.9204±0.001) in factory.

Refractive index value (0.23±0.04) in factory and (1.4785±0.0003) in traditional sample, the Obtained value for both traditional and factory sample (Arya, 1969).

Viscosity (60.195±0.03) factory and (64.695±0.385) in traditional, the result of traditional sample showed greater due to that the process of refining and extraction done in low temperature.

Iodine value (98.94±0.33) in factory and (112.42±0.2) in traditional the iodine value indicate the degree of unsaturated of the oil higher, the high un saturation better nutrition quality due to high levels of essential fatty acid (vibhakel, 1981).

Peroxide value 3.605±0.26 in factory and 8.815±0.145 in traditional, the traditional value greater and the peroxide value for any edible vegetable oil should be lower than 10 mg/kg. The peroxide value indicates the extent peroxidiation of oil during storage; ranciditition was brought by the action of oxygen or by micro-organism.

Acid value of traditional sesame oil (1.175±0.005) and (0.49±0.02) for factory. The traditional value is greater than factory; value for any edible vegetable should be lower than (2.0) Salunkhe, 1992).

Saponfication value (188.015±0.21) in factory and (194.91±1.6) in traditional sample, the result showed that the traditional value is greater and the saponification value was measure of mo0lecul or weight of constituent fatty acid present in oil (Salunkhel, 1992).

Un Saponfication value (1.895±0.23) in factory and (5.565±0.295) in traditional sample, the traditional value is greater due to the extraction process.

Table (3.7) and (3.8) that the Oleic acid (36.99%) traditional and (25.56%) for factory.

linoleic acid (40.93%) for factory and 36.92%) for traditional sample oil, from the result the ratio of tradtiti0onal sample O/L (1.0019) and factory (0.6245).

Results showed that the saturated fatty acids for factory sample (6.86 for Plamitic, 20.57 for steric acid, 3.44 for arachidic acid and 0.66 for behinic acid) and for traditional sample (5.93 for plamitic acid, 14.84 for steric acid, 3.96 for arachidic acid and 0.39 for behinic acid).

Steric acid in traditional sample is lower than in factory due to extraction process was not completed, behinic acid and arachidic acid was found almost simi9lar in both factory and traditional sesame oils.

Conclusion:

The physicochemical properties analyzed of the oil showed high saponification value (191.315mgKOH/g), high peroxide (7.735mgO_2/g) and acid value (1.03mgKOH/g) for groundnut traditional oil.

The GC-MS study identified 18 components of which oleic acid (32.35%) is predominant followed by linoleic acid (14.25%), behnic acid (13.84%) and steric acid (11.73%) for factory groundnut oil.

The GC-MS study identified 11 components of which oleic acid (56.98%) is predominant followed by linoleic acid (25.75%), plasmatic acid (5.54%) and steric acid (2.85%) for traditional groundnut oil.

Factory groundnut oil is high quality than traditional because:

-High oleic to linoleic ratio (2.27) for factory oil and (2.2129) for traditional.

-Level of peroxide is lower for factory than traditional.

-Level of acid value is lower too.

The physicochemical properties analyzed of the oil showed high saponification value (194.91mg/KOH g) used to the soaps making , high peroxide value (8.815mg O_2/g) , high acid value (1.175mgKOH/g) for traditional sesame oil.

The GC-MS study identified ten components of which oleic acid (36.99%) is predominant followed by linoleic acid (36.99%), steric acid (14.84%) and plametic acid (5.93%) for the traditional sesame oil.

The GC-MS study identified 18 components of which linoleic acid (40.93%) was predominant followed by oleic acid (25.5%), steric acid (20.57%) and plasmatic acid (6.66%) for factory sesame oil.

Factory sesame oil is high quality than traditional because:

-Level of peroxide and acid value in factory oil is lower

Recommendations:

- Extracting oils by industrial methods is better because it is complete and we get a large amount of the product and most of the ingredients in proportion to the efficiency of the extraction.
- Industrial oils are of higher quality. It is preferable to use them for boiling and cooking foods.
- Under suitable storage conditions, industrial oils can remain for a period of time and at their quality.
- Industrial oils can be controlled by adding quality-improving materials, deleting undesirable materials, or reducing the proportion of materials present in them to increase quality.
- Conventional extraction oils can be used for industrial purposes.

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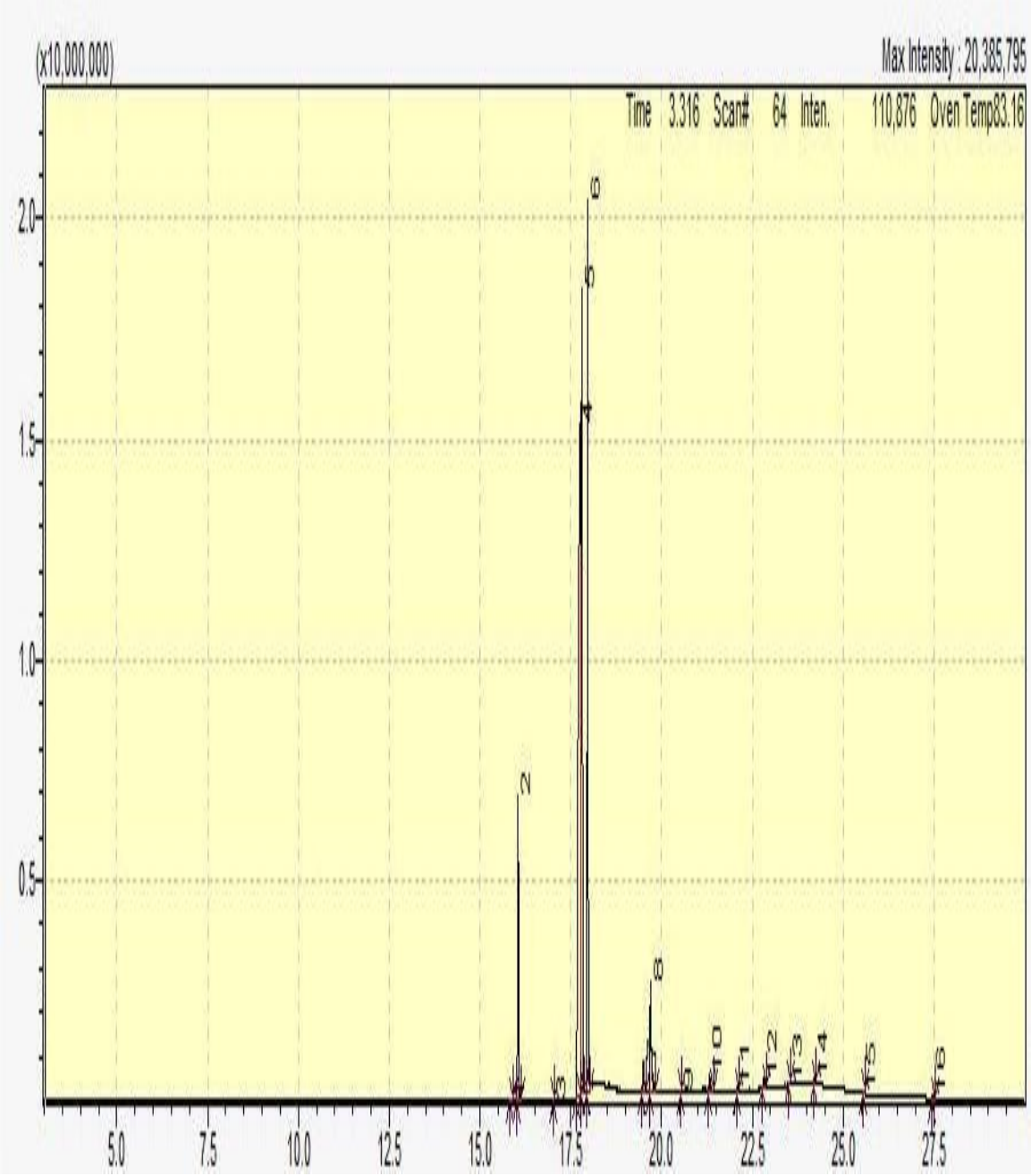
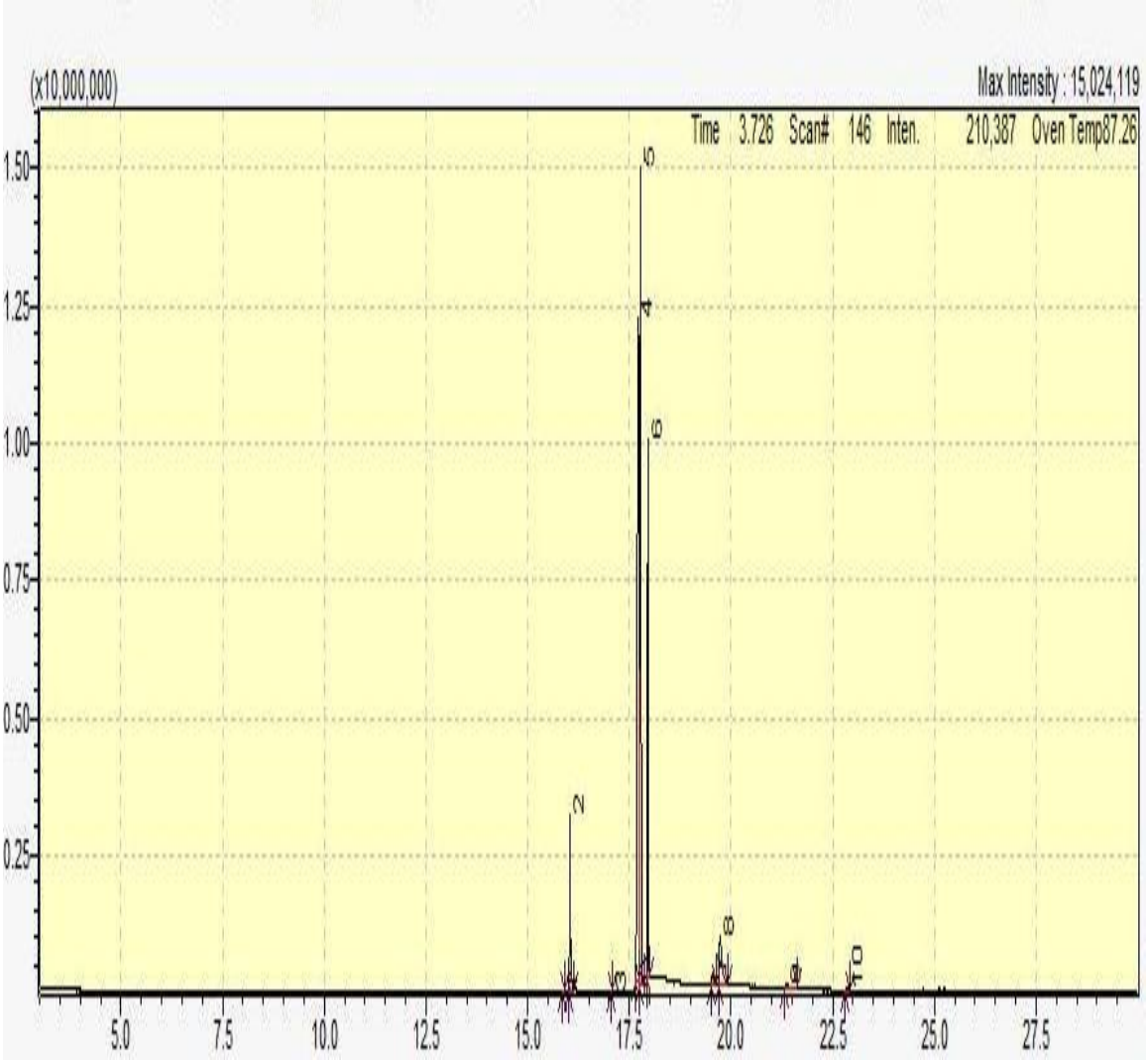
Appendixes:

Appendix (1) GC-MS analysis of sesame oil (Factory)



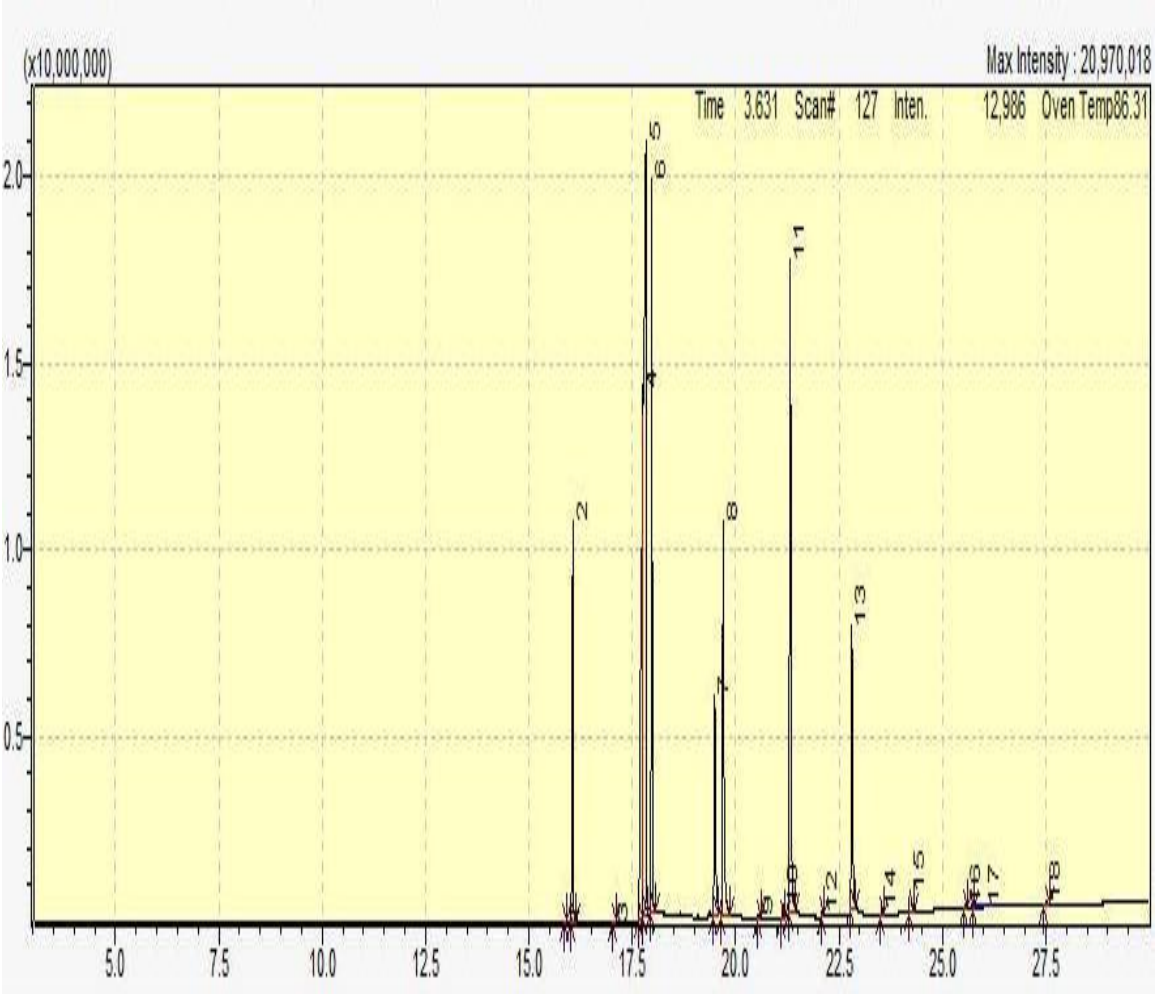
ID#	Name	Ret.Time	Area	Area%
1.	9-Hexadecenoic acid, methyl ester, (Z)-	15.855	46530	0.03
2.	Hexadecanoic acid, methyl ester	16.051	11716911	6.86
3.	Heptadecanoic acid, methyl ester	17.029	19877	0.01
4.	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	17.755	69983686	40.93
5.	9-Octadecenoic acid (Z)-, methyl ester	17.808	43686070	25.56
6.	Methyl stearate	17.965	35161076	20.57
7.	cis-11-Eicosenoic acid, methyl ester	19.497	1838401	1.08
8.	Eicosanoic acid, methyl ester	19.696	5880156	3.44
9.	Heneicosanoic acid, methyl ester	20.532	13858	0.01
10.	Docosanoic acid, methyl ester	21.318	1120035	0.66
11.	Tricosanoic acid, methyl ester	22.083	167718	0.10
12.	Tetracosanoic acid, methyl ester	22.812	857631	0.50
13.	Pentacosanoic acid, methyl ester	23.524	150581	0.09
14.	Hexacosanoic acid, methyl ester	24.205	158606	0.09
15.	Stigmast-5-en-3-ol, oleate	25.558	43298	0.03
16.	.beta.-Sitosterol	27.480	67176	0.04

Appendix (*2*) GC-MS analysis of sesame oil (traditional)



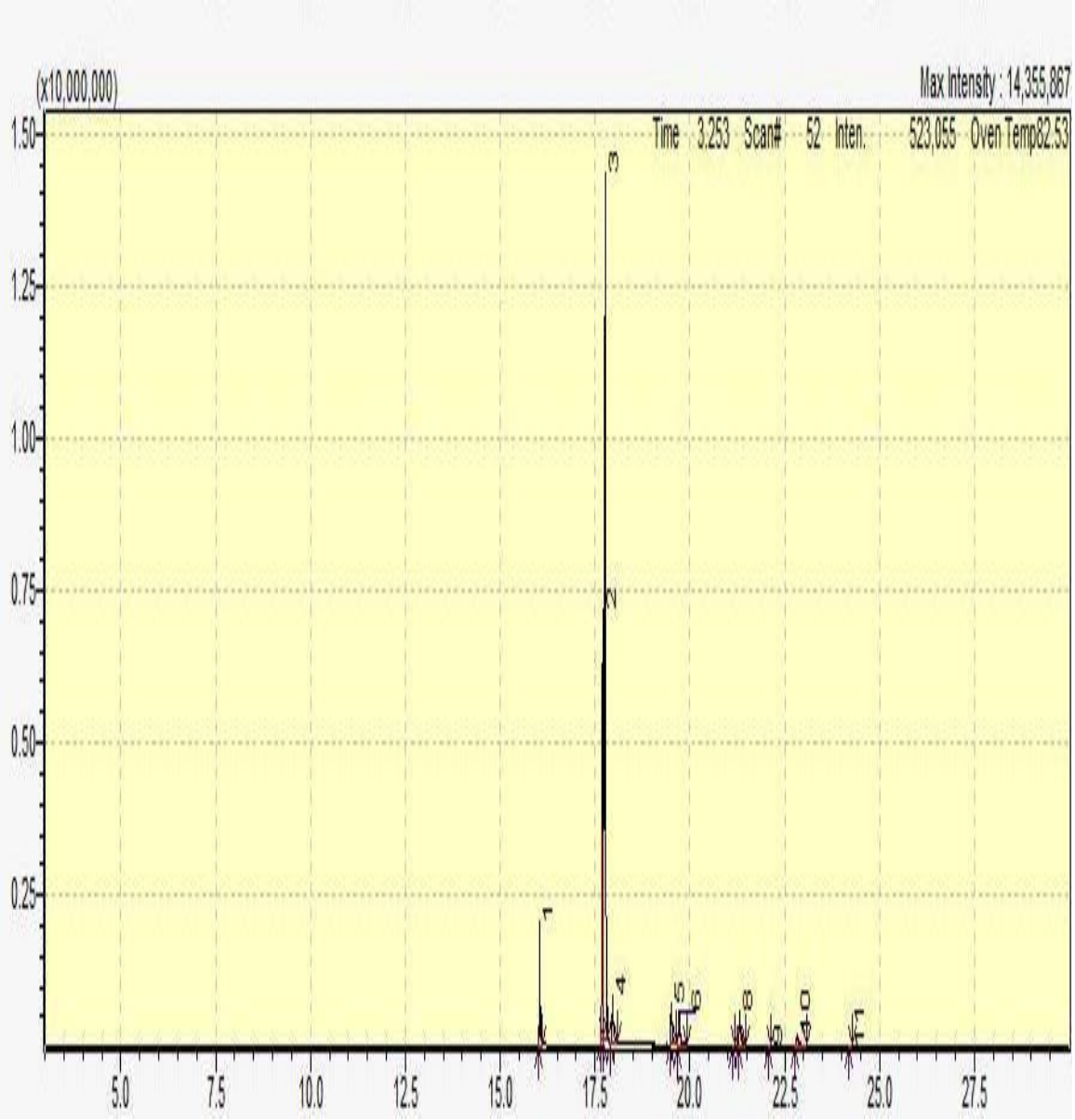
ID#	Name	Ret.Time	Area	Area%
1.	9-Hexadecenoic acid, methyl ester, (Z)-	15.889	11738	0.01
2.	Hexadecanoic acid, methyl ester	16.042	5474037	5.93
3.	Heptadecanoic acid, methyl ester	17.078	10302	0.01
4.	9,12-Octadecadienoic acid, methyl ester	17.719	34105093	36.92
5.	9-Octadecenoic acid (Z)-, methyl ester	17.778	34157082	36.99
6.	Methyl stearate	17.954	13707955	14.84
7.	cis-11-Eicosenoic acid, methyl ester	19.540	823688	0.89
8.	Eicosanoic acid, methyl ester	19.731	3660049	3.96
9.	Docosanoic acid, methyl ester	21.367	363080	0.39
10.	Tetracosanoic acid, methyl ester	22.875	54577	0.06

Appendix (*3*) GC-MS analysis of groundnut oil (factory)



ID#	Name	Ret.Time	Area	Area%
1.	9-Hexadecenoic acid, methyl ester, (Z)-	15.868	35397	0.01
2.	Hexadecanoic acid, methyl ester	16.064	21673536	7.58
3.	Heptadecanoic acid, methyl ester	17.048	37149	0.01
4.	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	17.750	40733632	14.25
5.	9-Octadecenoic acid (Z)-, methyl ester	17.828	92474072	32.35
6.	Methyl stearate	17.970	33540903	11.73
7.	cis-11-Eicosenoic acid, methyl ester	19.494	13410568	4.69
8.	Eicosanoic acid, methyl ester	19.697	23668089	8.28
9.	Heneicosanoic acid, methyl ester	20.545	224078	0.08
10.	13-Docosenoic acid, methyl ester, (Z)-	21.143	797127	0.28
11.	Docosanoic acid, methyl ester	21.319	39557172	13.84
12.	Tricosanoic acid, methyl ester	22.090	451585	0.16
13.	Tetracosanoic acid, methyl ester	22.808	16565395	5.79
14.	Squalene	23.531	337634	0.12
15.	Hexacosanoic acid, methyl ester	24.217	1784714	0.62
16.	Stigmast-5-en-3-ol, oleate	25.570	130391	0.05
17.	Vitamin E	25.751	17004	0.01
18.	.beta.-Sitosterol	27.500	418820	0.15

Appendix (4) GC-MS analysis of groundnut oil (traditional)



ID#	Name	Ret.Time	Area	Area%
1.	Hexadecanoic acid, methyl ester	16.042	3426595	5.54
2.	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	17.706	15927888	25.74
3.	9-Octadecenoic acid (Z)-, methyl ester	17.774	35264879	56.98
4.	Methyl stearate	17.959	1764916	2.85
5.	cis-11-Eicosenoic acid, methyl ester	19.509	1770700	2.86
6.	Eicosanoic acid, methyl ester	19.710	1577486	2.55
7.	13-Docosenoic acid, methyl ester, (Z)-	21.154	31085	0.05
8.	Docosanoic acid, methyl ester	21.314	1550260	2.50
9.	Tricosanoic acid, methyl ester	22.109	11321	0.02
10.	Tetracosanoic acid, methyl ester	22.820	540972	0.87
11.	Heptacosanoic acid, methyl ester	24.243	24913	0.04