# بسم الله الرحيم Sudan University of Science and Technology College of Graduate studies

# Effects of Thermal Processing on Physicochemical Characteristics of Kernels and Extracted Oil from Seeds of *Balanites Aegyptiaca*

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

دراسة تأتير المعالجة الحرارية على الخواص الفيزوكيميائية لأنوية بذور و زيت اللالوب

By:

Sara Mubarak Ahmed Elbadawi (B.Sc., Honors Chemistry)

**Supervisor:** 

Dr. Essa Esmail Mohammad

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# **Dedication**

To my parents, Mubarak Elbadawi and Ahlam Bashir for everything they have done for me.

# Acknowledgement

First of all I would like to thank almighty Allah for giving me strength, patience and blessing to complete this work.

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#### **Abstract**

The objective of this is study was to examine the effects of thermal processing (roasting and boiling) on the proximate compositions of the kernel seeds and the physicochemical properties of the oils which were extracted from raw and processed samples of Balanites aegyptiaca. Boiling was carried out by immersion of the kernel seeds in a boiling tap water at  $100^{\circ}\mathrm{C}$  for one hour whereas roasting was conducted by heating the kernels in an oven at 180°C for 15 minutes. Proximate compositions of raw, boiled and roasted samples were determined. The results have displayed that thermal processing has significant effects on the proximate composition of the kernels. Roasting has decreased moisture considerably from 3.74 to 2.18% and protein from 42.41 to 38.52% whereas the oil content was increased significantly from 39.98 to 46.23%. On the other hand, boiling has decreased ash content from 2.88 to 2.32% whereas total carbohydrate content was increased from 10.99 to 14.25%. Furthermore, the physical and physicochemical characteristics of the oils extracted from raw and thermally processed samples were determined. Both roasting and boiling have increased viscosity from 63.5 to 66.0 poise for roasting and 63.5 to 67.0 for boiling and alter color significantly from 13.2Y + 0.4R to 20.2Y + 1.5R for roasting and 13.2Y + 0.4R to 20.1Y + 1.2R for boiling. The peroxide value, on the other hand, has shown interesting trend for thermally processed samples. Roasting has drastically decreased the peroxide value from 13.34 to 4.56 meg/kg while boiling considerably increased it from 13.34 to 18.06 meg/kg.

# ملخص البحث

هدف هذا البحث إلى دراسة تأثير المعالجة الحرارية (بالغليان و التحميص) لنواة بذرة اللالوب على التركيب التقريبي للنواة وكذلك على الخواص الفيزوكيميائية للزيوت المستخلصة من البذور الخام و المعالجة. أجريت عملية الغليان و ذلك بغمر العينة في ماء مغلى  $^{\circ}$ C) لمدة ساعة أما عملية التحميص فقد تمت بتسخين العينة لمدة 15 دقيقة في فرن درجة حرارته ℃ 180. تم تحديد التركيب التقريبي للعينات الخام و المغلية و المحمصة أوضحت النتائج أن المعالجة الحرارية ذات أثر كبير على التركيب التقريبي للعينات. أدت عملية التحميص إلى إنخفاض مهم في محتوى الرطوبة من 3.74% إلى 2.18% والبروتين من 42.41% إلى 38.52% بينما إرتفعت نسبة الزيت بصورة مقدرة من 39.98% إلى 46.23%. في الجانب الآخر فإن عملية الغليان قد أدت إلى نقصان نسبة الرماد من \$2.88 إلى 2.32% بينما زاد المحتوى الكلي من الكاربو هيدرات من 10.99% إلى 14.25%. بالاضافة الى ذلك تم تحديد الخواص الفيزوكيميائية لزيت اللالوب من العينة الخام والعينات المعالجة حراريا لوحظ زيادة اللزوجة للعينتين حيث كانت الزيادة للعينة المحمصة من 63.5 إلى 66.0 بويز والمغلية من 63.5 إلي 67.0 بويز وتغير اللون بدرجة مقدرة للعينتين المحصمة من 13.2Y+0.4R إلى 20.2Y+1.5R والمغلية من £13.2Y+0.4R إلى £20.1Y+1.2R. بينت نتائج رقم البيروكسيد تغييرا مميزا، حيث أدت عملية التحميص لنقصان كبيرجدا في رقم البيروكسيد من 13.34 إلى 4.56 ملى مكافئ لكل كيلوجرام بينما أدت عملية الغليان لزيادة مقدرة لرقم البيروكسيد من 13.34 إلى 18.06 ملى مكافئ لكل كيلوجرام.

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# List of symbols and abbreviations

∝	Alpha tocopherols and tocotrienos.
β	Beta tocopherols and tocotrienos.
γ	Gamma tocopherols and tocotrienos.
δ	Delta tocopherols and tocotrienos.
FTIR	Fourier transform infrared spectroscopy

#### **Chapter One**

#### Introduction

Balanites aegyptiaca belongs to the family of Balanitaceae and species of the genus Balanites aegyptiaca (L) delile. It is widespread in most arid, semi-arid to sub-humid tropical savannas in Africa, all over the Sahel extending from the Atlantic coastline of Senegal to the red sea and Indian Ocean and the Arabian Peninsula [1]. In Sudan, it is commonly found on dark cracking clays of the central Sudan often associated with Acacia seyal on short grass savanna [2]. Southern kordofan, Blue Nile, and Darfur as well as many other sites which include almost all zones of Sudan were reported as distribution regions of Balanites aegyptiaca [1,3,4].

*Balanites aegyptiaca* has been used as a potential source of medicines, pesticides, edible oil, animal feed, nuts, soap and fuel wood. Besides other uses which include hand tools, praying beads (seibha), saddle, Quran tablets, furniture, and shade [5,6].

The oil of *Balanites aegyptiaca* (*L.*) *Del.* has found special interest from local people where the tree distributes (human foods), few African countries and some researchers. A number of research articles have been published in the physical, physicochemical and potential applications of *Balanites aegyptiaca* oils. The results have revealed interesting characteristics of this oil which makes it applicable in many areas such as food cooking, cleansing agent, shampoo, biodiesel, antimicrobial, and anti-ulcer [3-10]. Al Ashaal *et al.* [9] have studied the chemical composition and the biological activities of the fixed oil of *Balanites aegyptiaca*. Their results have shown that the oil have anticancer, antimutagenic, antiviral and antimicrobial activities. Toxicity study [11] in rats has demonstrated that crude oil of *Balanites aegyptiaca* does not has serious safety concern.

Despite the wide distribution of *Balanites aegyptiaca* tree among almost all the regions of Sudan and the amazing characteristics of its oil, limited attention has been given to this multipurpose tree and its products; especially the oil. To the best of our knowledge, there are

no published articles on the effects of thermal processing (boiling and roasting), which are used frequently by local communities for obtaining the oil, of the kernel seeds on the proximate composition of the kernels and the physical and physicochemical properties of the resulting oils.

# 1.1 Objective

The objective of the present study is to investigate the effects of roasting and boiling processes on the proximate composition of the kernels and the physical and physicochemical characteristics of the oils of Balanites aegyptiaca trees grown in Sudan.

#### **Chapter Two**

#### Literature review

#### 2.1 Definition and classification of lipids

Many definitions have been used for lipids in literature and there is no agreed one. Lipids are defined by Christie as a wide variety of natural products including fatty acids and their derivatives, steroids, terpenes, carotenoids, and bile acids, which have in common a ready solubility in organic solvents such as diethyl ether, hexane, benzene, chloroform, or methanol. The lipid can be classified based on physical properties at room temperature (oils are liquid and fats are solid), their polarity (polar and neutral lipids), their essentiality for humans (essential and non essential fatty acids), or their structure (simple or complex) [12].

# 2.2 The major components of edible oils and their functions

#### 2.2.1 Triglycerides

Triglycerides consist of three fatty acids attached to one glycerol molecule. If all three fatty acids are identical, it is a simple triglyceride. The more common forms however are the mixed triglycerides in which two or three kinds of fatty acids are present in the molecule. The fatty acids in a triglyceride define the properties and characteristics of the molecule [13].

#### 2.2.2 Glycerol

Glycerol (propane-1,2,3-triol) is the one and only alcohol to which fatty acids are esterified into triglycerides, i.e. oils and fat. Glycerol is a symmetrical triple alcohol and is important as the basic components of all triglycerides. However, as the one and only identical alcohol present in all triglycerides, it becomes unimportant for the technology of fats and oil [14].

# 2.2.3 Fatty acid

There is no agreed definition of fatty acids but it has been suggested that fatty acids are compounds synthesized in nature by condensation of malonyl coenzyme A units under the influence of a fatty acid synthase complex [15]. The physical and chemical characteristics of fats are influenced greatly by the kinds and properties of the component fatty acids and the way in which these are positioned on the glycerol molecule. The predominant fatty acids are saturated and unsaturated carbon chains with an even number of carbon atoms and single carboxyl group. Fatty acids occurring in edible fats and oils are classified according to their degree of saturation:

- (i) Saturated fatty acids: Those containing only single carbon to carbon bonds are termed saturated and are the least reactive chemically. The melting point of saturated fatty acids increases with chain length. Decanoic and longer chain fatty acids are solid at room temperature.
- (ii) Unsaturated fatty acids: Fatty acids containing one or more carbon to carbon double bonds are termed unsaturated e.g. Oleic acid. When the fatty acid contains one double bond it is called monounsaturated. If it contains more than one double bond, it is called polyunsaturated. The reactivity of unsaturated fatty acids is more than saturated fatty acids. This reactivity increases as the number of double bond increases.
- (iii) Polyunsaturated fatty acids e.g. linoleic, linolenic, arachidonic, eicosapentaenoic and docosahexaenoic acids [13].

#### 2.3 The minor components of vegetable oils and their functions

#### 2.3.1 Monoacylglycerols

Monoacylglycerols (formerly called monoglycerides) and their derivatives are used extensively as food emulsifiers and are easily made from oils and fats by glycerolysis. monoacylglycerols are formed in the intestine during digestion of fat and are absorbed and transported before being reconverted to triacylglycerols for transport through the blood as lipoproteins [15].

#### 2.3.2 Diacylglycerols

The diacylglycerols (diglycerides) exist in symmetrical and unsymmetrical forms with the symmetrical isomer being the most stable. The diacylglycerols are most important intermediates in the biosynthesis and metabolism of triacylglycerols and phospholipids [15].

#### 2.3.3 Free fatty acid

The free fatty acids are the unattached fatty acids present in a fat. The presence of free fatty acids in oil is an indication of insufficient processing, lipase activity, or other hydrolytic actions. Some unrefined oils may contain as much as several percent free fatty acids. The levels of free fatty acids are reduced in the refining process [12,13].

#### 2.3.4 Phosphatides

Phosphatides or phospholipids are natural surfactants and emulsifiers consisting of an alcohol such as glycerol, one or two molecules of fatty acids and a phosphoric acid compounds. They are found in all plants and animals and include such substance like lecithin, cephalin, and sphingamyelin. Phospholipids contribute to the stability and quality of edible oils.

Phospholipids can be removed from crude oil during refining at the degumming stage. The most important members of this class of lipids found in edible fats are phosphatidylethanolamine, phosphatidylinositol, phosphatedylserine, and phosphatidly choline [15,16].

#### **2.3.5** Sterols

Sterols free are esterified with fatty acids and are found in small concentration in edible fats. Sterols such as cholesterols are alcohols with the cyclopentanophenanthrene ring system. Cholesterol is primary animal fat sterol and is found in vegetables oils in only trace amount. The plant sterols called Phytosterols are rather simple mixture of closely related organic compounds. The analysis of sterols is important for detection oil adulteration [16].

# 2.3.6 Tocopherols and Tocotrienols

Tocopherols and tocotrienols are the most important antioxidants present in edible oil. The common types of tocopherols and tocotrienols are alpha ( $\propto$ ), beta ( $\beta$ ), gamma ( $\gamma$ ) and delta ( $\delta$ ). They vary in antioxidants and vitamin E activity. Tocopherols contents of edible oils are affected by the cultivar, processing and storage of oil. The refining process especially deodorization reduces tocopherol content [13,17].

#### 2.3.7 Chlorophylls

Chlorophylls are common pigments in edible vegetable oil. They are generally removed during oil processing especially the bleaching process. Chlorophylls act as sensitizer in the presence of light and atmospheric (auto-oxidation) and accelerate the oxidation of oil [17].

#### 2.3.8 Carotenoids

Carotenoids are a group of tetraterpenoids consisting of isoprenoids. These are minor components in many vegetable oils and particularly in palm oil. They contain a long chain of conjugated unsaturation and are yellow/orange/red in colour.  $\beta$  – Carotene is the one of the most studied carotenoids. Edible oils especially unrefined oils contain  $\beta$  – carotene [15,17].

# 2.3.9 Wax ester

The wax ester formed by the reaction of alcohols (aliphatic, triterpenic, methylsterols and sterols) and free fatty acids are present in seed and fruit. During the oil extraction process a fraction of these esters is transferred into the oil depending on the oil extraction system. So solvent extracted oils contain higher concentration of wax ester compared with cold pressed and centrifuged ones. The determination of waxes is important to evaluate the quality and genuineness of some vegetable oils [16].

#### 2.3.10 Phenolic compounds

These are transferred from fruits and seeds to raw oils during processing. Phenolic compounds other than tocopherols in edible oils also exert antioxidant activity. The importance of phenolic compound is in the sensory quality and the stability of oils [16,17].

# 2.3.11 Other minor components

Besides the previously mentioned minor components, the presence of minor components such as fat soluble vitamins, hydrocarbons, protein fragment, various resinous and mucilaginous has been reported in the literature [15,16].

#### 2.4 Processing of seeds before oil extraction: Thermal processing

Different thermal treatments can applied on seeds before oils extraction to obtain and modify different characteristics of the produced oils. Thermal treatments include boiling, roasting, steaming and frying [18-20].

#### **2.4.1 Boiling**

In boiling, the seeds are heated or cooked in tape water at varying temperatures (80 to 105°C) depending on type of seeds. The properties of oil extracted from boiled seeds were found to differ based on type of seeds [19,20]. Mariod *et al.* [20] have studied the effect of roasting and boiling on the chemical composition, amino acids and oil stability of safflower seeds. They found that the moisture, total carbohydrates, fiber and minerals were decreased in boiled seeds whereas fat, protein and ash were increased. Furthermore, their results showed that the fatty acid composition of oil did not change as a result of boiling seeds. It was also noticed that the amino acids and peroxide value were both increased and the FTIR spectra of the raw and boiled samples were different.

Arinola and Adesina [21] have studied the effect of thermal processing on the nutritional, antinutritional and antioxidant properties of *tetracarpidium conophorum* (African walnut). They found that the fiber, ash and protein were decreased in the boiled seeds whereas the fat and total carbohydrates were increased. The loss in protein content was attributed to denaturation or solubilization of some nitrogenous compounds during processing whereas the increase of fat content was explained by the effect of heat which facilitates the release and extraction of oil from seeds. Furthermore, the decrease in ash content was attributed to leaching of some mineral nutrient during hydrothermal processing whereas the increase in the total carbohydrate could be due to the relative reduction in protein content and hydrolysis

effect. It has also been noticed that boiling has reduced the phytate and tannin contents of the sample. Leaching or solubilization into cooking medium was probably the main cause of this reduction besides the degradation of these constituents by heat.

#### 2.4.2 Roasting

In roasting, the sample is heated using different heating sources such as electric muffle furnace, oven, electric forced-air oven and microwave at different temperatures which range between 50 and 200°C for varying time. The roasting of seeds was reported to enhance the quality of oils in a number of cases whereas in few cases opposite effect was noticed. This variation was found to depend on type of seeds and roasting temperature and time [20,22-24].

Jeong *et al.* [22] have studied the effect of seeds roasting conditions on the antioxidant activity of defatted sesame meal extracts. The sesame seeds were roasted in a muffle furnace at different temperatures for different times. Their results have shown that the oil extracted from roasted sesame meal is more stable than the one which extracted from unroasted sesame meal. In addition, it was found that the amounts of phenolic antioxidants were increased in the oil extracted from roasted sesame meal. This was attributed to the highest sesamol content in roasted seeds oil.

Wijesundera *et al.* [23] have reported that the seeds roasting improve the oxidative stability of canola (B. napus) and mustard (B. juncea) seed oils. Additionally, the results demonstrated that the content of alpha tocopherols in oils from roasted seeds did not change and the content of gamma tocopherols was increased. Also they found that the rate of production of the aldehydes during stability study were minimum at the oils from roasted seeds. They concluded that the roasting process has increased the oxidative stability of the oils.

Mariod *et al.* [20] have investigated the effect of roasting and boiling on the chemical composition, amino acids and oil stability of safflower seeds. They found that the moisture, total carbohydrates, fiber and minerals were decreased in roasted seeds but the fat, protein and ash were increased. Furthermore, they found that the fatty acid composition did not change in oil extracted from roasted seeds but the amino acids and peroxide value were increased. They have also reported different FTIR spectra for the oils extracted from roasted and unroasted samples.

Mariod *et al.* [24] have examined the effect of different processing techniques on Indonesian Roselle (*hibiscus radiates*) seed constituents. They used an electric forced-air oven and microwave for roasting the seeds. They found that the moisture, total carbohydrate and tocopherols were decreased whereas the fat, ash, fiber and protein were increased in roasted seeds. Also they noticed that the fat and fiber in microwave roasted seeds were higher when compared with oven roasted ones. Furthermore, they found that the fatty acid composition did not change in oils from roasted seeds and the main fatty acids were palmitic and linolenic acids.

#### 2.5 Methods of oils extraction

#### 2.5.1 Cold pressing extraction

Cold pressing extraction can be done by expeller or screw press extraction. Expeller pressing mechanically squeezes the oil from the seeds. In the screw press, the cooked flakes are separated into crude oil and press cake [19]. Cold pressing is favored for the production of niche products where it is desirable that solvent should not be used. The recovery of oil under these conditions is less efficient and will be reflected in the price. However after recovery of cold pressed oil, it is possible to collect further oil by solvent extraction [15].

#### 2.5.2 Solvent extraction

When the seeds are not very rich in oil pre-pressing is not undertaken and the seeds suitably adjusted to size and moisture content is extracted directly with solvent. The organic solvent use is generally (n-hexane) which is a mixture of hexane and methyl pentane. Hexane is more toxic and expensive but of lower boiling point and has well efficiently. Ethanol and isopropanol are other possible solvent but with higher boiling point and higher latent heats there will be higher energy costs.

Supercritical carbon dioxide can be used as an extraction solvent. It has some environmental advantage compared with more traditional solvents. The oil extracted in this way differs from conventional solvent extracted oil in the proportion of more polar and less polar lipids present [15].

#### 2.6 Physical and chemical characteristics of oils

The physical characteristics of fats or oils are directly related to their chemical composition. The physical parameters which can be measured in fats or oils include density, colour, moisture, viscosity, refractive index and melting point [14].

#### 2.6.1 Iodine value

The iodine value is a measure for the average number of double bonds of fat or oil. Iodine value is defined as the grams of iodine absorbed per 100 g of sample. The higher the amount of unsaturation, the more iodine is absorbed and the higher the iodine value [25].

#### 2.6.2 Peroxide value

The peroxide concentration usually expressed as peroxide value is a measure of oxidation or rancidity in its early stages. Peroxide value measure the concentration of substance that oxidized potassium iodide to iodine. Oxidation of lipids is major cause of their deterioration and hydroperoxides formed by the reaction between oxygen and the unsaturated fatty acids are the primary products of this reaction. Hydroperoxides have no flavor or odor but break down rapidly to form aldehydes, which have a strong disagreeable flavor and odor [19].

#### 2.6.3 Saponification value

The saponification value is the amount of alkali (milligram of potassium hydroxide) required to saponify a definite quantity of fat or oil. The saponification value is a measure indirectly for the average molecular weight of the triglycerides of fat and therefore characteristic number [14]. Glycerides containing short chain fatty acids have higher saponification values than those with longer chain fatty acids. The saponification values along with iodine value determination have been useful screening tests both for quality control and characterizing types of fats and oils [19].

#### 2.6.4 Free fatty acids and acid value

Acid value is the amount of potassium hydroxide required for neutralization whereas free fatty acid utilizes sodium hydroxide for neutralization. Measure of fat acidity normally reflects the amount of fatty acids hydrolyzed from triacylglycerols. Free fatty acid is an important fat quality indicator during each stage of fats and oil processing. This method is uses for check up the rancidity of fat and oil [19,25].

#### 2.7 Lipid oxidation

Lipid oxidation causes nutritional losses and produced undesirable flavor, color and toxic compounds which make foods less acceptable or unacceptable to consumers [26].

Oxidation of oil also destroys essential fatty acids and oxidized polymer. Different chemical mechanisms autoxidation and photosensitized oxidation are responsible for the oxidation of edible oils during processing and storage depending upon the type of oxygen reacts with oil. Two type of oxygen reacts with lipid; single oxygen and triplet oxygen. Triplet oxygen reacts

with lipid radical and causes autoxidation but single oxygen reacts directly with double bonds

and causes photosensitization. Oxidation of oil is influenced by an energy input such as light

or heat, composition of fatty acids, type of oxygen and minor compounds such as metals,

pigment, phospholipids, free fatty acids and antioxidants. Oxidative stability is an important

indicator to determine oil quality and shelf life because low molecular weights off flavor

compounds are produced during oxidation [17].

2.7.1 Methods for measurement of lipid oxidation

Determining the oxidative stability using actual shelf life determination at ambient conditions

of storage (usually room temperature) requires month or even years. Accelerated tests have

been developed to evaluate the oxidative stability of bulk oils and fats. Accelerated active

oxygen methods stability can do by Oxygen pump method, Oil stability index, Schaal oven

test [25].

2.8 Advantage of vegetables oils

The importance of oils and fats for human nutrition is source of energy, its role as an animal

feed produced from the processing of must oil plants and the economic importance of oils and

fats. The fats and oils are regenerating raw materials in which the chemical and

pharmaceutical industries have a special interest [14]. They also enhance the foods we eat by

providing texture and mouth feel, imparting flavor and contributing to the feeling of satiety

after eating [13].

2.9 **BALANITES AEGYPTIACA** 

29.1 **Taxonomical profile** [27].

Kingdom: plantae.

Division: Magnoliophyta.

Class: Magnoliopside.

Order: sapindales.

Family: Balanitaceae (Zygohyllaceae).

Genus: Balanites Delile.

Species: Balanites Aegpytiaca (L) Delile.

2.9.2 Description

A small to medium-sized semi-deciduous tree which attains a height of about 8-10 m and a

stem diameter of 30 cm. The crown is spherical or irregular. Bark grey to dark brown with

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deep vertical fissures exposing the new yellow bark; spines straight, stout, rigid, up to 8cm long; petioles up to 1 cm long. The leave consists of two leaflets on a short petiole and varies considerably in size, leaflets 2 to 5 cm long and 1 to 2.5 cm wide, ovate to rhomboid, entire; nerves prominent. Flowers yellow-green, about 1.3 cm across; sepals 5, deciduous; petals 5, about 0.5 cm long; disc fleshly covered with white hairs. Fruit green turning yellow or brown, oblong ellipsoid, 3-4 cm long, smooth or wrinkled with a yellow brown sticky edible flesh and a large hard stone. Flowers Nov – April; fruits Dec- July [1,2].

#### 2.9.3 Distribution

Balanites Aegpytiaca is found in most arid, semi-arid to subhumid tropical savannas in Africa, all over the Sahel and on many sites of the Sudan savanna common on dark cracking clays of the central Sudan, often associated with Acacia Seyal on short grass savanna, extending from the Atlantic coastline of Senegal to the red sea and Indian Ocean and the Arabian Peninsula. Other studies have been found in hot dry areas, along watercourses and in woodlands. It border seasonally inundated black clay plains and grows well in valleys on river banks in depressions, and on the slopes of rocky hills [1,2].

# 2.9.4 Propagation

Reproduction mainly by direct seeding but also by root suckers and cuttings, seeds are easily available. A mature tree may yield about 10,000 pieces of fruit per year. These are consumed by birds and animals and the hard seeds thus widely dispersed [1].

#### 2.9.5 Seed Treatments

Fruit turns from green to yellow when ripe, each containing 1 pit. These can be stored for up to a year if kept air dry and insect free. When ready to plant, soak the fruit overnight in lukewarm water until the pulp can be removed and the pit extracted [28].

# 2.9.6 Seeding Management

Does not withstand transplanting well because of the deep tap root, for best result plant in a container with the seed vertical. Plants should remain in the nursery for 18 to 24 weeks before outplanting at the beginning of the rainy season. Average rooting success from stem cuttings is about 60 to 70% [1,28].

#### 2.9.7 Products and Uses

#### (i) Fruit

The fruit is eaten fresh or dried as "desert date". The fruits can be processed to produce multipurpose intermediate products. The mesocarp of the fruit is a source of fermentation

products (e.g. ethanol) and steroidal sapogenins or can be incorporated into animal feed. The cellulosic shell of the fruit is a source of fuel [1].

#### (ii) Medicine

The fruit have been used in the treatment of liver and spleen diseases. The fruit is also known to kill the snails which carry schistosomiasis and bilharzia flukes. The roots are used for abdominal pains and as a purgative. Gum from the wood is mixed with maize meal porridge to treat chest complaints [28].

#### (iii) Other uses

The crude Balanites oil is used a source of edible vegetable oil or otherwise used in various industries (e.g. soap-making). The kernel cake after extraction of the oil is a source of protein and carbohydrates for livestock. *Balanites Aegpytiaca* as fine-grained dense and heavy heartwood it is easily worked and takes a good polish. Although valued for furniture it may be twisted and difficult to saw. Root cuttings readily form a live fence. Proteins rich leaves and shoots are an excellent source of fodder. The leaves make very good mulch and the tree is nitrogen fixing [1,28].

#### 2.9.8 Chemical composition of *Balanites Aegpytiaca* kernel seeds and oil

Mohamed *et al.* [29] have studied physical, morphological and chemical characteristics, oil recovery and fatty acid composition of *Balanites Aegyptiaca Del.* kernels. They found that the kernel hardness was relatively high (10.4x10<sup>5</sup>N/m<sup>2</sup>) and the morphological structure of lalob kernels showed a protein matrix surrounded by oil droplet. Furthermore, they found that lalob kernels constitute of crude protein (32.4%), crude fat (49.0%), crude fiber content (1.4%), total ash content (3.3%), calcium (246.9mg/100g), magnesium (239.3mg/100g) and zinc (5.8mg/100g). Also the results showed that the Phytic acid content of the kernels was slightly high (1.5%) and the Sapogenine contents of the full fat, defatted and the flours were 1.5, 2.7 and 3.0%, respectively.

Manji *et al.* [7] have studied the potentials of *Balanites Aegyptiaca* seed oil as a raw material for the production of liquid cleansing agent. They found that the saponification value was (168.76mgKOH/g), the iodine value (78.7g I<sub>2</sub>/100g), the % free fatty acid (0.18mgKOH/Kg), and the peroxide value (6mgEq/Kg). They have also reported the presence of saponin. Furthermore, their results have shown that the oil yield was (49.9), the moisture content (0.27%), the specific gravity (0.927), and the refractive index (1.4784).

Nour *et al.* [3] have studied the chemical composition of *Balanites Aegyptiaca L.* (Lalob) fruits (mesocarp and kernels) grown in Sudan at different regions. The findings have revealed that the moisture was 3.2 and 3.1, the protein was 34.3 and 26.1, the fat was 45 and 46.1, and the total carbohydrate was 24.1 and 21.3 at Kordofan and hawata seeds samples respectively. Variations in calcium and iron between the two regions were also observed. In addition, the results have shown significant differences in the physicochemical parameters (except acid value) of the extracted oils from the two regions. Also they found that palmitic, stearic, oleic and linoleic were the major fatty acids in the two samples. Similar results were obtained by Elfeel [4], who studied the effect of location on proximate composition of the kernels and the physicochemical properties of oils for three samples originated from Sudan. The obvious variations in the measured parameters could be attributed to the differences in the altitude, rainfall and soil (clay) between the different regions under consideration.

# **Chapter Three**

# **Experimental**

#### 3.1 Sample collection

Balanites Aegyptiaca sample was purchased from Omdurman market (Souq Omdurman), Khartoum State, Sudan, January 2015.

### 3.2 Pretreatment of the sample

The epicarps of *Balanites Aegyptiaca* fruit were removed manually and the remaining edible flesh (mesocarp) plus the endocarps were soaked in a tap water for overnight. After complete removing of the edible flesh the endocarps were dried in sun light for two days. Finally, the endocarps were removed by hand using a hammer and the kernels were stored at 10°C for the next steps.

#### 3.3 Pretreatment of the kernels

## 3.3.1 Boiling

The kernels were immersed into a boiling tap water at 100°C at ratio of 1:4 kernel/water for one hour in a 500 mL beaker with continuous heating and stirring until the pieces were well cooked. The cooked sample was dried and ground in a grinder.

#### 3.3.2 Roasting

Kernels were arranged in a single layer in an aluminium tray and placed in a roaster oven at  $180^{\circ}$ C for 15 minutes and finally the sample was allowed to cool to ambient temperature, and stored at  $10^{\circ}$ C.

#### 3.4 Chemicals

Sodium hydroxide (minimum assay 96%), was purchased from Nice. Potassium hydroxide (minimum assay 85%), was purchased from CDH laboratory Reagent. Sodium sulphate anhydrous (minimum assay 99%), was purchased from laboratory Reagent. Calcium oxide extra pure (minimum assay 97%), was purchased from LOBA CHEMIE. Potassium iodide pure (minimum assay 99.5 %), was purchased from LABCH. Sodium thiosulphate pentahydrate (minimum assay 99%), was purchased from CDH laboratory Reagent. Iodine monochloride (minimum assay 95%, b.p = 97.4°C, density = 3.24 g/mL at 25 °C), was purchased from Sigmaaldrich. Dichloromethane (minimum assay 98%), was purchased from OXFORD Laboratory Reagent. Nitric acid (minimum assay 69-72%, density = 1.41-

1.42g/mL at 20 °C), was purchased from ALPHA CHEMIKA. Hydrochloric acid (minimum assay 35-38%, density = 1.18g/mL at 20 °C), was purchased from ALPHA CHEMIKA. Ethanol absolute anhydrous (minimum assay 99.9%, b.p = 78.3-78.8 °C), was purchased from CARLO ERBA. n-Hexane (minimum assay 95%, b.p = 65-70 °C), was purchased from SD Fine-Chem Limited (SDFCL). Acetic acid glacial (minimum assay 99.7%), was purchased from DUKSAN. Acetone (minimum assay 99%, density = 789-792 g/mL at 20 °C), was purchased from ALPHA CHEMIKA. Chloroform (minimum assay 99.5%, density = 1.474-1.480 g/mL at 20 °C), was purchased from ALPHA CHEMIKA. Sulfuric acid (minimum assay 90%), was purchased from LOBA CHEMIE. Copper sulfate pentahydrate (minimum assay = 98.5-101%), was purchased from ALPHA CHEMIKA. Sodium sulfate anhydrous (minimum assay 99%), was purchased from LOBA CHEMIE. Boric acid (minimum assay 99.5%), was purchased from LOBA CHEMIE.

# 3.5 Proximate analyses

# 3.5.1 Determination of moisture

2g of sample (kernel of lalobe) was weighed and placed in a clean and dry porcelain crucible. The crucible with its content was weighed and transferred into an air oven at 105 °C and left for 18 hours. After completion of the specified time, it was removed from the oven and left to cool in a desiccator and reweighed again. The previous step was repeated till constant weight was obtained. The experiment was repeated three times and the mean and standard deviation were calculated. The moisture was calculated using the following equation:

Moisture 
$$\% = (W_1 - W_2) \times 100/W_0$$
. (3.1)

Where  $W_1$  = the weight of sample and crucible before drying,  $W_2$  = the weight of sample and crucible after drying,  $W_0$  = Original weight of the sample.

## 3.5.2 Determination of ash

2g of sample was weighed in a clean and dry porcelain crucible. The crucible with its content was placed in a muffle furnace at 550 °C for 3 hours. The crucible was removed from the furnace and left to cool in a desiccator and reweighed again. The previous step was repeated till constant weight was obtained. The experiment was repeated three times and the mean and standard deviation were calculated. The ash was calculated using the following equation:

Ash % = 
$$(W_2 - W_1) \times 100/W_0$$
....(3.2)

Where  $W_1$  = weight of the empty crucible,  $W_2$  = weight of the crucible and ash,  $W_0$  = Original weight of sample.

### 3.5.3 Determination of crude protein

0.2g of sample (cake-defatted kernel) was weighed and placed in digestion flask (Kjeldahl flask). 3.5 mL of concentrated sulfuric acid and 0.4g of a mixture of (copper sulfate + sodium sulfate) were added. The flask was placed in a heating unit (digestion apparatus) and heated gently until frothing ceases. Then it was boiled briskly for 3 hours until the solution was clear. The digested sample was placed in distillation unit and 20 mL of 40% sodium hydroxide was added. 10 mL of boric acid contains 3 drops of mixture of methyl red + methylene blue indicator was placed in conical flask. The flask was connected with the distillation blub on condenser and returned to heat source. The apparatus was continued working until the volume of solution was become 50mL and the colour in the conical flask was changed from red to greenish-blue. The solution (ammonium borate) was titrated against 0.02 N hydrochloric acid to the end point of the indicator (greenish-blue to red). The experiment was repeated three times and the mean and standard deviation were calculated. The crude protein was calculated using the following equation:

$$N \% = V \times 0.02 \times 14 \times 100/Wt \times 1000$$
 (3.3)

Where N % = percentage of nitrogen, V = volume of hydrochloric acid, 0.02 = normality of hydrochloric acid, 14 = Nitrogen atomic weigh, Wt = weight of sample.

Protein 
$$\% = N \% \times 6.25$$
.....(3.4)

#### 3.5.4 Determination of total carbohydrate

Carbohydrate content was estimated by difference of the other components, using the following formula:

Carbohydrate content % = 100% - (% moisture + % protein + % fat + % ash) .................................(3.5)

#### 3.5.5 Extraction of oil

50g of coarsely ground lalob kernels were weighed and transferred to an extraction thimble. The oil was extracted in a Soxhlet extractor using 500 mL of n-hexane as a solvent for 5 hours. n-Hexane was removed from the oil using a rotary evaporator and the oil was stored in a freezer for further analyses.

### 3.6 Physico-chemical properties of the crude oil

#### 3.6.1 Peroxide value

2.50g of oil was weighed into 250ml (glass-stoppered flask) Erlenmeyer flask and 15mL of a mixture of (3acetic acid:2chloroform) was added and swirled till complete dissolution. 0.3mL saturated KI solution was added to the previous content of the flask and shaken well. Finally, 15 mL of distilled water was added slowly and titration against 0.01N sodium thiosulphate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) was carried out with vigorous shaking until the colour of the solution was changed to pale yellow. Then 0.5 mL 1% starch solution was added and the titration was continued until the dark blue was disappeared colour. The experiment was repeated three times and the mean and standard deviation were calculated. Peroxide value was calculated using the following equation:

#### 3.6.2 Acid value

3.53g of oil was weighed and mixed well in 250mL flask. 25 mL of ethanol was added (previously neutralized by adding 2 mL of phenolphthalein solution and enough 0.1N sodium hydroxide (NaOH) to produce faint permanent pink color). The content of the flask was titrated against 0.025N sodium hydroxide (NaOH) with vigorous shaking until permanent faint pink color was appeared and persisted ≥1min. The experiment was repeated three times and the mean and standard deviation were calculated. Acid value was calculated using the following equation:

Acid value (mg KOH/g sample) =  $40 \times V \times N/g$  of sample.....(3.7)

Where 40 = Molecular weight of sodium hydroxide, V = volume of sodium hydroxide solution, N = normality of sodium hydroxide solution, g = weight of the sample.

#### 3.6.3 Iodine value

0.25g of oil was weighed into 250 mL glass stoppered conical flask. 10 mL of dichloromethane was added which followed by 20 mL of Wijs reagent. The flask was closed and placed in a dark cupboard for 30min. 15 mL of 10% potassium iodide and 100 mL of distilled water were added to the content of the flask. The mixture was titrated against (0.1N) sodium thiosulphate solution with vigorous shaking until the colour of the solution was changed to pale yellow. 5 mL of 1% starch solution was added and the titration was continued until the disappearance of the dark blue colour. The experiment was repeated three times and the mean and standard deviation were calculated. Iodine value was calculated using the following equation:

Iodine value 
$$(gI_2/100g) = 1.269 \text{ x } (V_0-V_s)/\text{weight of sample}.$$
 (3.8)

Where  $V_o$  = volume of sodium thiosulphate equivalent to iodine absorbed by blank solution,  $V_s$  = volume of sodium thiosulphate equivalent to iodine absorbed by sample solution.

#### 3.6.4 Saponification number

2g of crude oil was weighed into a 250mL conical flask and 25mL of 10% alcoholic potassium hydroxide was added. A reflux air condenser was attached to the flask and refluxed at a water bath for 30 mints with occasional swirling. 1mL of phenolphthalein indicator was added at the end of reflux time and the solution was titrated against 0.5 M hydrochloric acid. The experiment was repeated three times and the mean and standard deviation were calculated. The saponification number was calculated using the following equation:

Saponification number = number of mg KOH required to saponify 1g oil = 28.05 (B - S)/ g sample.....(3.9)

Where B = mL of 0.5 N hydrochloric acid required by blank.

Where  $S = mL \ 0.5 \ N$  hydrochloric acid required for sample.

# 3.7 The physical properties of crude oil

#### 3.7.1 Determination of relative density

An empty and dry pycnometer was weighed and filled by distilled water at  $25\,^{\circ}$ C and reweighed again. Dry pycnometer was refilled by oil at the same temperature and weighed. The density was calculated using the following equations:

$$W_0 = W_{0+p} - W_p$$
.....(3.10)

$$W_{w=}W_{w+p}-W_{p}......(3.11)$$

Density = 
$$W_0/W_w$$
.....(3.12)

Where  $W_o$  = weight of oil,  $W_{w}$  = weight of water,  $W_p$  = weight of empty pycnometer,  $W_{o+p}$  = weight of empty of pycnometer + weigh of oil,  $W_{w+p}$  = weight of empty pycnometer + weight of water.

### 3.7.2 Determination of viscosity

The viscosity of oil was measured using Thermo Scientific HAAKE viscotester 6 plus. About 40 mL of oil sample was placed in a beaker and the rotor was immersed inside the oil. The velocity of round of the instrument was adjusted at 200 rounds per min. The viscosity was read directly from the screen of the instrument. The experiment was repeated two times and the mean and standard deviation were calculated.

#### 3.7.3 Determination of color

The color of the oil was determined using Lovibond Tintometer type 4D. Oil was placed in a standard sized glass cell and visually compared with red, yellow and natural color standards. Results were expressed in terms of numbers associated with the color of standards.

# 3.7.4 Determination refractive index

The refractive index of oil was measured using Abbe refractometer. 3 drops of oil was placed on a surface of lower prism. Prism and mirror were adjusted until it was given sharpest reading.

#### 3.7.5 Fourier transform infrared spectroscopy (FTIR)

FT-IR spectrum of oil was recorded using a Shimadzu FT-IR 8400s spectrophotometer. The sample was scanned in the range between 4000 and 500 cm<sup>-1</sup>. The number of scans was adjusted to 10 scans with resolution of 4 cm<sup>-1</sup>.

#### **Chapter Four**

#### Results and discussion

#### 4.1 Proximate composition

The effects of boiling and roasting processes on the chemical composition of *balanites aegyptiaca* kernel seeds is shown in table 4.1. As can be seen from the table, the oil and protein contents differ marginally between raw and boiled samples. The marginal difference in oil content could be due to leaching of some oil during boiling process which was observed as an oily layer floating above water (during boiling experiment). On the other hand, the slight decrease in protein content in boiled sample compared to raw one could be attributed to solubilisation of some nitrogen-containing compounds in boiling process or denaturation [21]. The results also showed that the ash and moisture contents were both decreased observably. Leaching of minerals by water during boiling process was reported by some authors [21,30] as the main cause of this decrease in ash content. In the case of moisture content, the observable decrease could be attributed to the effect of boiling process which facilitates oil extraction by decreasing its viscosity, releasing oil from intact cells and removes moisture [31]. Boiling of kernels has significantly increased the carbohydrate content from 10.9% to 14.25%. This is probably due to the decrease in oil, protein, ash and moisture contents of the boiled sample.

Table 4.1 also displays the effects of roasting in proximate composition of kernel seeds of Balanites aegyptiaca. As can be seen from the table, the protein and moisture contents have changed noticeably as a result of roasting. The observable decrease in protein content in roasted sample compared to raw could be due to denaturation of some nitrogen-containing compounds during roasting process [21] In the case of moisture content, the apparent decrease could be explained by the same reasons as in the boiled sample which was discussed above. On the other hand, the ash content and total carbohydrate were slightly changed. In addition, the oil content was significantly increased compared to raw sample (about 16%). This considerable increase is possibly attributed to application of heat (roasting) which facilitates extraction of oil by releasing it from the intact cells [21].

**Table 4.1** Proximate chemical composition of raw and boiled kernel seeds of *balanites* aegyptiaca.

Sample	Moisture%	Ash%	Protein%	Total	Oil%
				carbohydrate %	
Raw	3.74 ±0.69	2.88±0.13	42.41±0.03	10.99	39.98 <u>+</u> 1.24
Boiled	3.35±0.21	2.32±0.11	41.80±0.06	14.25	38.28±2.22
Roasted	2.18±0.20	2.92∓0.01	$38.52 \pm 0.11$	10.15	46.23±1.38

# 4.2 The physical properties of the extracted oils.

The physical properties of the extracted oils from raw, boiled and roasted kernels are displayed in table 4.2. As can be seen from the table, the density did not change appreciably due to thermal processing (boiling and roasting) but the refractive index for the roasted sample has increased observably. The influence of thermal processing (roasting) of seeds on the refractive index of oils has been investigated by many authors [32,33]. In conclusion, the results have revealed that in some cases refractive index has decreased whereas in other cases no effects were noticed. In addition, an increase in refractive index with roasting has been reported in literature. The decrease in refractive index was explained by polymerization of unsaturated fatty acid or decrease in the molecular weight during roasting at higher temperatures. In the cases where refractive index increased, the increase in the double bonds in fatty acids of a lipid molecule was reported to be the main cause. Most probably the last one is the case in our results. In addition, the viscosity of oils extracted from boiled and roasted samples did change noticeably compared to raw one. Generally, viscosity has a direct relationship with some chemical characteristics of the lipids, such as the degree of unsaturation and the chain length of the fatty acids that constitute the triacylglycerols [34].

On the other hand, boiling process has intensified the color (color changes from light yellow to deep yellow) of the oil as shown in table 4.2. This could probably be due to the increase in  $\beta$ -carotene content as a result of thermal processing (boiling) which facilitates the distribution or extraction of  $\beta$ -carotene from kernels to oils. This was clearly observed from the color of the defatted cakes of the raw (yellowish) and the boiled (off white) samples. In the case of roasted sample, the color of the oil was changed from light yellow to light brown. Moreover, the color of the defatted cake was also changed to brown. Formation of brown color during roasting was noticed by some researchers [32,35] and was explained by formation of

browning substance which results from Maillard-type non-enzymatic reactions, caramelization, and phospholipid degradation.

**Table 4.2:** Shows the physical properties of oils.

Sample	Density	Viscosity	RI	Colour	
	(g/cm <sup>3</sup> )	Poise		yellow	red
Raw	0.9137	63.5±0.7	1.470	13.2	0.4
Boiled	0.9132	67 ±1.4	1.468	20.1	1.2
Roasted	0.9125	66 ± 3.5	1.740	20.2	1.5

# 4.3 Fourier transform Infrared spectroscopy (FT-IR)

The FT-IR analyses were carried out to examine the main functional groups of oil from raw seeds and the effect of thermal processing (boiling and roasting) of seeds in the chemical composition of the extracted oil. The FT-IR spectra of oil from raw, boiled and roasted seeds are shown in Figures 4.1 to 4.3.

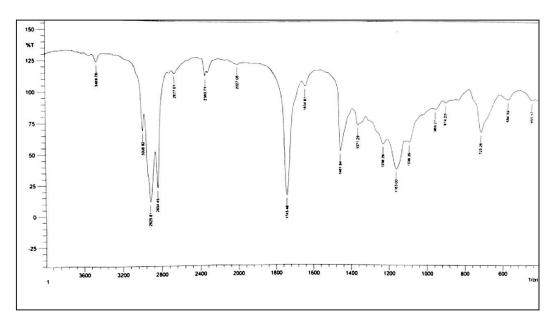


Figure 4.1: FT-IR spectrum of oil from raw sample

As can be seen from Figure 4.1, the characteristic absorption peaks of oil from raw seeds appear at 3007 cm<sup>-1</sup> (C-H stretching vibration of the cis-double bond (=CH)), 2926 cm<sup>-1</sup> and 2854 cm<sup>-1</sup> (Symmetric and asymmetric stretching vibration of the aliphatic CH<sub>2</sub> groups), 1745 cm<sup>-1</sup> (Ester carbonyl functional group of the triglycerides), 1655 cm<sup>-1</sup> (C=C stretching vibration of cis-olefins), 1462 cm<sup>-1</sup> and 1371 cm<sup>-1</sup> (Bending vibration of the CH<sub>2</sub> and CH<sub>3</sub> aliphatic groups), 1236 cm<sup>-1</sup> and 1163 cm<sup>-1</sup> (Stretching vibration of the C-O ester group), 723

cm<sup>-1</sup> (Overlapping of the CH<sub>2</sub> rocking vibration and the out of plane vibration of cis-disubstituted olefins). The FT-IR spectra of boiled and roasted samples (Figures 4.2 and 4.3) display almost identical FT-IR absorption bands to the one of the raw sample and no changes could be observed as a result of thermal processing (boiling and roasting).

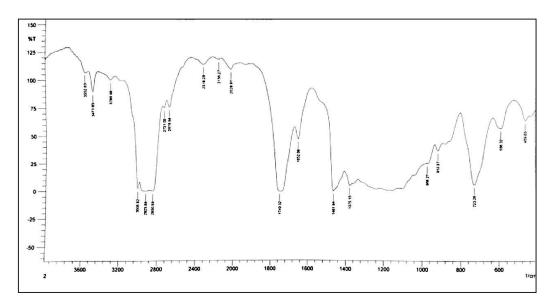


Figure 4.2: FT-IR spectrum of oil from boiled sample

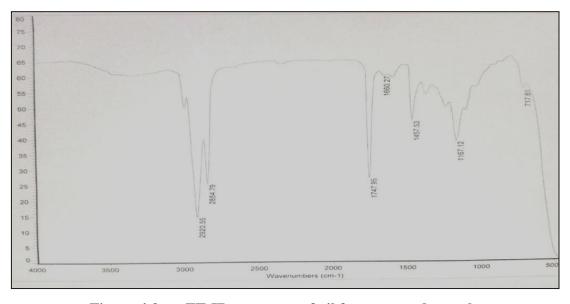


Figure 4.3: FT-IR spectrum of oil from roasted sample

# 4.4 Physico-chemical properties of oils

The physico-chemical properties of oils of Balanites aegyptiaca are presented in table 4.3. As can be seen from the table, the peroxide values of the oils from thermally processed seeds have changed significantly. Compared to the peroxide value of the oil from raw sample, the peroxide value of the oil from roasted sample has decreased drastically whereas considerable increase in peroxide value for the oil from boiled sample has been noticed. The drastic change in peroxide value for boiled sample is due to increase of oxidation of oil caused by heating (boiling) which accelerates the oxidation processes as well as the hydrolysis in aqueous medium which also increases the rate of rancidity. In contrast to boiling, the considerable decrease in peroxide value for the oil of the roasted seeds could be due to formation of some materials which inhibits the oxidation of the oils. Roasting of seeds prior to oil extraction has been reported by some articles [23,36] to enhance the oxidative stability of oils. In contrary, some authors have found that roasting has a negative effect on the oxidative stabilities of oils extracted from roasted seeds [20,32]. Wijesundera et al. [23] have reported that roasting (at 165 °C for 5 min) of canola and mustard seeds increases the oxidative stability of the extracted oils and did not affect the content of tocopherols. Moreover, it was reported that canola seeds are very rich source of polyphenols. The enhancement in oxidative stability of canola oil was attributed to formation of 2,6-dimethoxy-4-vinyl phenol (DMVP) during roasting. Furthermore, thermal processing did not change the saponification value of the oils appreciably. However, slight increase for the roasted sample could be seen. The acid value, on the other hand, remains fairly unchanged for thermally processed samples compared to raw one.

**Table 4.3:** The physico-chemical properties of oils from raw oils from raw and boiled samples

Sample	Peroxide value (meq/kg)	Acid value (mg KOH/g)	Saponification value(mg KOH/1g)
Raw	13.34±0.28	0.30±0.02	200.31±2.45
Boiled	18.06 <u>+</u> 0.46	0.34±0.03	200.47±5.54
Roasted	4.56±0.28	$0.34 \pm 0.00$	203.55±6.31

# **Chapter Five**

#### Conclusion

The effects of thermal processing on the physicochemical properties of kernels and oil seeds of Balanites aegyptiaca were investigated in the present study. The results have shown that the chemical composition of kernels and the physiochemical proprieties of the extracted oil of *Balanites aegyptiaca* were significantly affected by thermal processing. Roasting has increased the oil content and the oxidative stability of the oils appreciably whereas boiling has decreased the oxidative stability of the oil and the ash content of the kernels significantly.

For future work, examination of different roasting times and temperatures of the kernels on the quality of the oil and how this influence the oxidative stability positively will be very informative and needs further investigation. In addition, study of oxidative stability of the oil using differential scanning calorimetry and Rancimat methods should be carried out for better understanding of the characteristics of the oil. Detailed examination of fatty acids composition and their changes during processing should also be studied.

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# Appendix



Figure A.1: Balanites aegyptiaca tree (the photo was taken from Omdurman-Alshati)



Figure A.2: Balanites aegyptiaca tree (the photo was taken from Omdurman-Alshati)



Figure A.3: Balanites aegyptiaca seeds



Figure A.4: Balanites aegyptiaca (mesocarp)



Figure A.5: Balanites aegyptiaca (endocarp)



Figure A.6 Kernels of Balanites aegyptiaca

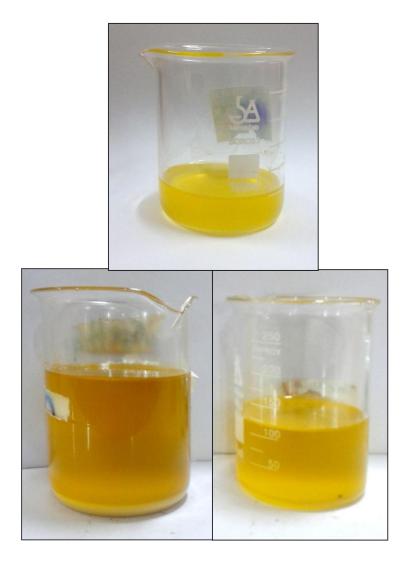


Figure A.6 Oils of raw (above), roasted (left) and boiled (right)