

# الآيه

بسم الله الرحمن الرحيم

(( أقرأ بأسم ربك الذي خلق\* خلق الأنسان من علق\* إقرأ وربك الأكرم\* الذي علم بالقلم\* علم الإنسان ما لم يعلم))

صدق الله العظيم

الآيات من (1-5)

سورة العلق

# *Dedication*

TO MY:

PARENTS ,

BROTHERS,

SISTERS .

# *Acknowledgment*

**We full thanks a lot of in first the supervisor Dr: Elfatih Ahmed Hassan who help & support us to reach here and also we thanks anybody who sharing to complete this work .**

# *Abstract*

The aim of the study was to extract orange oil from peel, The sample was collected from alsoog alarabi , extracted by steam distillation . The percentage of the oil in this peel was founded to be 0.267 %, the extracted oil characterized by refractive index , specific gravity , saponification value , acid value , peroxide value .

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## **Introduction**

### **1-1 Orange oil:**

Orange oil derives from orange rinds of both sweet and sour orange. It contains d-limonene, a compound that seems to help control termites. In addition, orange oil has become popular as an essential oil used in aromatherapy to combat stress and relieve tension and anxiety.

People who use vaporizers often add orange oil. It is expressed from the rind during a process known as cold pressing, which occurs in an industrial setting with special equipment that mechanically presses the orange rinds. Individuals can extract citrus oil on a small scale at home as well.

The simple, vacuum and fractional distillations are applicable to completely soluble (miscible) mixtures only. When liquids are not mutually soluble (immiscible), they can also be distilled, but with a somewhat different result.

### **1-2-2 Steam Distillation**

Steam distillation is a special type of distillation (a separation process) for temperature-sensitive materials like natural aromatic compounds.

Many organic compounds tend to decompose at high sustained temperatures. Separation by normal distillation would then not be an option, so water or steam is introduced to the distillation apparatus. By adding water or steam, the boiling points of the compounds are

depressed, allowing them to evaporate at lower temperature, preferably below the temperature at which deterioration of the material becomes appreciable. If the substances to be distilled are very sensitive to heat, steam distillation can be combined with vacuum distillation. After distillation the vapour is condensed as usual. Usually yielding a two-phase system of water and the organic compound allowing for simple separation.

### **1-2-3. Principle**

When a mixture of two practically immiscible liquids is heated while being agitated to expose the surface of both the liquids to the vapour phase, each constituent independently exerts its own vapour pressure as a function of temperature as if the other constituents were not present. Consequently the vapour pressure of the whole system increases. Boiling begins when the sum of the partial pressures of the two immiscible liquids just exceeds the atmospheric pressure (approximately 101 kPa at sea level). In this way many organic compounds insoluble in water can be purified at temperatures well below the point at which decomposition occurs. For example the boiling point of bromobenzene is 156°C and the boiling point of water is 100°C, but a mixture of the two boils at 95°C. Thus bromobenzene can be easily distilled at temperatures 61°C below its normal boiling point.



#### **1-2-4. Application**

Steam distillation is employed in the manufacture of essential oils, for use in perfumes, for example. In this methods, steam passed through the plant material containing the desired oils, Eucalyptus oil and orange oil are obtained by this method on the industrial scale. Steam distillation is also sometimes used to separate intermediate or final products during the synthesis of complex organic compounds. Steam distillation is also widely used in petroleum refineries and petrochemical plants where it commonly referred to as “steam stripping” off redistilled, cohobation, in order to obtain the water-soluble fraction of the rose oil such as phenyl ethyl alcohol which are vital component of the aroma and which make up the large bulk, 80% of the oil the two oils are combined and make the final rose otto.

Rose otto is usually dark olive-green in color and will form white crystals at normal room temperature which disappear when the oil is gently warmed it will tend to become more viscous at lower temperature due to this crystallation of some of the components.

The essence have a very strong odor, but is pleasant when diluted and used for perfumes. Attar of rose was once made in India, Persia, Syria and the ottoman Empire. The Rose valley in Bulgaria, near the town of Kazanluk, is among the major procedures of Attar of roses in the world.

Due to heat required for distillation, some of the compounds extracted from the rose undergo denaturing or chemical break down. As such rose otto does not smell very similar to “fresh” rose.

The hydrosol portion of distillate is known as rosewater. This inexpensive by – product is used widely as food flavoring as well as in skin care.

### **1-2-5. Steam distillation method**

Two methods for steam distillation are in general use in the lab the direct method and the live steam method. In the first method, steam is generated in situ by heating distillation flasks containing the compound and water. In the second method, steam is generated outside and is passed into the distillation flask using an inlet tube.

#### **A. Direct method**

##### **Standard scale:**

A large scale direct method steam distillation illustrated in figure 11.3. Although a heating mantle may be used, it is probably best to use a flame with this method, because a large volume of water must be heated rapidly. A boiling stone must be used to prevent bumping. The separatory funnel allows more water to be added during the course of the distillation. Distillation is collected as long as it is either cloudy or milky white in appearance. Cloudiness indicates that an immiscible liquid is

separating. When the distillate runs clear in the distillation, it is usually a sign that only water is distilling. However there are some steam distillations where the distillate is never cloudy. Even though material has codistilled. You must observe carefully, and be sure to collect enough distillate that all of the organic material codistills.

Steam from boiling water is passed through the raw material for 60-105 minutes, which drives out most of their volatile fragrant compounds. The condensate from distillation, which contains both water and the aromatics, is settled in flatentince flask. This allows for the easy separation of the float to the top of the distillate. The water collected from the condensate, which retains some of the fragrant compounds and oils from the run material, is called hydrosol and is sometimes sold for consumer and commercial use.

This method is most commonly used for fresh plant materials such as flowers, leaves, and stems. Popular hydrosols are rose water, lavender water, and orange blossom water. Many plants hydrosols are have un pleasant smells and are therefore not sold.

Most oils are distilled in a single process. One exception is ylong. Ylong (*canange odorata*), which takes 22 hours to complete distillation. It is fractionally distilled, producing several grades (Y long – Y long, “extra” I, II, III and “couplet” in which the distillation is run from start to finish with no interruption).

## **Micro scale:**

The method of steam distillation is the only one suitable for micro scale reactions. Steam is produced in the conical vial or distillation flask (insitu) by heating water to its boiling points in the presence of the compound to be distilled. This method works well for small amounts of materials. A micro scale steam distillation apparatus is shown in the other paper. Water and the compound to be distilled are placed in the flask and heated. A stirring bar or a boiling stone should be used to prevent bumping.

The vapors of the water and the desired compound codistill when they are heated. They are condensed and collect in the Hickman head. When the Hickman head fills, the distillate is removed with a Pasteur pipet and placed in another vial for storage. For the typical micro scale experiments, it will not necessary to fill the well and know the distillate or four times. All of these distillate fractions are placed in the same storage container.

The efficiency in collection the distillate can sometimes be improved if inside walls of the Hickman head and rinsed several times into the well. A Pasteur pipet is used to perform the rinsing. Distillate is withdrawn from the well, and then it is used to wash the wall of the Hickman head all the way around the head. After the walls have been washed and when the well is full. The distillate can be withdrawn and

transferred to the storage container. It may be necessary to add more water during the course of the distillation. More water is added through the condenser if used through the center of the Hickman head by using a Pasteur pipet.

**Semi Micro scale:** the apparatus shown next may be also used to perform as steam distillation at the micro scale level or slightly above. This apparatus avoids the need to empty the collected distillate during the course of the distillation as required when a Hickman head is used.

## **B. Live steam method:**

### **Standard scale**

A large scale steam distillation using the live steam method is shown next. If steam lines are available in the laboratory, they may be attached directly to the steam trap (purge them first to drain water). If steam lines are not available, an external steam generator (scale in set) must be prepared. The external generator usually will require a flame to produce steam at a rate fast enough for the distillation.

## **1-3. compounds of orange**

### **1-3-1. Terpenoid compound**

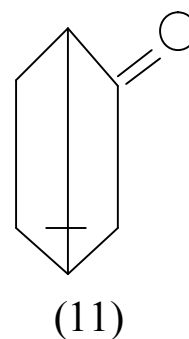
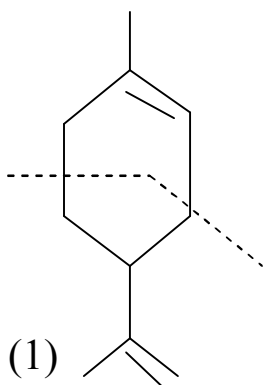
It has been known for a long time that the leaves, fruits, flowers and roots of many plants, contain large varieties of volatile odoriferous constituents known as essential oils. These substances can be extracted

from the different part of the plant by the application of the pressure, or by conventional steam distillation or solvent extraction, or by briefly heating the leaves by direct injection of the plant tissue into a gas chromatograph or by micro dissection of the oil glands.

These extracts consist of complex mixture of compounds, a cyclic, alicyclic, aromatic and heterocyclic in character. The more volatile fractions of these constituents are known as terpenes, or more generally as terpenoid compound, which are of wide natural occurrence in such plant extracts. These terpenoid compounds are invariably hydrocarbons, alcohols, aldehydes, ketenes and oxides.

### 1-3-2. classification of terpenoid compounds

The classification of terpenoid compounds is based mainly on the number of carbon atoms; and the unit from which the terpenes are built is one of five carbon atoms known as the “isoprene unit”. A simple terpene is said to be formed by a head – to tail union of two isoprene units as shown for limonene (1) and camphor (11)



Condensation of these units leads to the formation of monoterpenes (C<sub>10</sub>), sesquiterpenes (C<sub>15</sub>), diterpenes (C<sub>20</sub>), terterpenes (C<sub>30</sub>), teraterpenes (C<sub>40</sub>), and polyterpenes (C<sub>40</sub>).

These terpenoid compounds are acyclic or cyclic hydrocarbons, alcohols, aldehydes, ketenes, oxides and peroxides.

### **Monoterpenes:**

The acyclic monoterpenes are liquids at room temperature and include hydrocarbons (myrcene), aldehydes (citral) and alcohols (geraniol). Cyclization of these acyclic monoterpenes can take place under suitable conditions to give either P. methan derivatives such as the cyclization of citronellal to menthene or a derivative of 1:1:3-trimethyl cyclohexane as illustrated by the cyclization of citral to A and B cyclocitral.

The larger group of monocyclic monoterpenes is that which has a p-cymene skeleton. These are hydrocarbons (limonene 1) terpinolene and peroxides (ascaride)

The bicyclic monoterpenes are conveniently divided into five groups and the representative members of each group are derived from the saturated bicyclic hydrocarbons, thusbornane, camphane, pinane, camphane and fenchane.

## **Sesquiterpenes**

The sesquiterpenes are naturally occurring compounds, and may also be acyclic or cyclic hydrocarbons, alcohols, or ketenes. The acyclic sesquiterpenes are the hydrocarbons,  $\beta$ -farnesene and the primary alcohol farnesol.

The monocyclic sesquiterpenes are also hydrocarbons (bisabolene) and alcohols (camphor) while the bicyclic representatives are cadinene, sclerenchrolene, eudesmol, and the ketones  $\alpha$ -cyperene and eremophilone.

## **Diterpene**

The diterpenes are widely distributed in plants, particularly in the resin. Phytol, the alcohol fragment of chlorophyll molecule, is an acyclic diterpene while vitamin A, and A<sub>2</sub> represent the monocyclic group.

The ditertiary glycol, sclareol is a bicyclic diterpene while the resin acids, abietic represent the tricyclic diterpenes.

## **Triterpenes**

The triterpenoid compounds are widely distributed in plant resin and saps in the free state and as esters or glycosides – squalene is an acyclic triterpenoid hydrocarbon occurring in various plant sources. The optically active tertiary alcohol, ambrein. The secondary alcohol lanosterol and



$\alpha$ -amyrins are representatives of the tricyclic, tetracyclic and pentacyclic triterpenes respectively.

## **Tetraterpenoids:**

These compounds constitute the group of natural pigments and generally known as carotenoids which are conveniently isolated from the green leaves by extraction with a suitable solvent. This group includes the carotenes the hydroxyl- carotenoids and ketones.

### **1-3-3. separation of terpenoid compounds**

The separation of the individual terpenes from the essential oils, is accomplished by a variety of methods both chemical (7-8) and physical, (9-12) ones. Terpenic hydrocarbons, usually liquids, can be separated by fractional distillation, but as many of them are sensitive both to heat and atmospheric oxygen, the fractionation is usually done under reduced pressure and an inert atmosphere with the use of efficient fractionating and condensing system.

Due to the saturation of many terpenic hydrocarbons, their separation can be affected via the formation of additive products with bromine, hydrogen bromide hydrogen chloride and nitrosylchloride. The adducts are usually crystalline and have been used for purification. The monocyclic terpene, dipentene for example, reacts additively with two molecules of hydrogen chloride to give dipentene dihydro chloride (48).

Terpene alcohols can be separated by the treatment with excess of phthalic anhydride to form the acid esters which can be extracted and hydrolyzed. Carbonyl compounds can be separated by the treatment with atypical carbonyl group reagent such as sodium bisulfate, phenylhydrazine or Girard reagents, P. and T

But the most common method of separation are the physical ones, of which chromatography, in its various forms, is the most applicable tool.

Estimation of constituents (13,14) and measurements of physical constants:

### **1-1-1. What is limonene?**

Limonene takes its name from the lemon, as the rind of the lemon, like other citrus fruits, contains considerable amount of this compound, which contributes to their odor. Chemically limonene is a relatively stable terpene and can be distilled without decomposition. Although at elevated temperatures it cracks to form isoprene. It oxidizes easily in moist air to produce carveol, carvone, and limonene oxide. With sulfur, it undergoes dehydrogenation to p-cymene. Infrared spectrum of limonene from the spectrum above for limonene the only absorption at 2850-3100 cm<sup>-1</sup> wave number indicates there are C-H bonds only. Mass spectrum of limonene. <sup>1</sup>H-NMR of limonene for the <sup>1</sup>H-NMR we can tell:

The PPM between 1 and 2 shows all carbon adjacent has C-H bonds. The PPM around 4-8 indicates the adjacent carbon has C=C with no hydrogen since it is a singlet. The proton present in the compound has 7 different environments.

Limonene is colorless, liquid hydrocarbon classified as a cyclic terpene the more common D isomer possesses a strong smell of orange.

- From the IR-spectrum, there are only C-H bonds.
- From the MS the final M/Z value add up to 136 since the molecular formula  $C_{10}H_{16}$
- From the HNMR spectrum, the fact that C=C involved.
- From the CNMR the benzene ring present in limonene,

The limonene has two separated double bonds; these double bonds are ordinary  $sp^2$  by grids, so the overall cyclic structure does not exhibit a very different spectrum. The movement in the banal change from slightly due to the not too much-strain. But if the structure were something like cyclo propane, then we would expect a change from the normal sigma band. This change would be assigned to the abnormal change in the angle for  $sp^3$  CN or mally (109, 5 degrees).

Botanical name: Citrus sinensis

Family name: Rutaceae

Common name: orange

Part used: peel

Specific gravity: 0.910 – 0.965

Optical rotation: 90 to 115 degree

Refractive index: 2-44 – 1-52

Blends well with: cinnamon, gringer cloues, sandalwood, black pepper, frankincense and vetiver.

**Uses:** orange oil is used in aroma therapy, flavors, comdies, and deodorant medicinally, it is used to cure flue and cold. It is used as a pesticide and in secticide.

Extraction process: orange oil is extracted from orange peel. It is the byproduct of orange jucie. It is obtained by employing a procedure called coldpress, which yields around 0-3 to 0-4 percentage of oil.

### **1-1-3. Commonly know benefits:**

#### **Antiseptic:**

It has antiseptic properties and hence can be applied on the small wounds and cuts.

#### **Antidepressant:**

It has a pleasant smell hence it is used in aromatherapy for patients who have stress related ailments. Its aroma increase the blood flow and produces a calming effect on the nervous system, which helps in reducing strain on the mind.

Anti spasmodic: spasm are produced in the body when we it makes sudden moments. Orange oil is fond to reduced spasm when applied on the affected part.

#### **Digestive:**

When taken in small quantity cures stomach related ailments such as stomach pain and indigestion.

**Anti-inflammatory:**

It helps in reducing in inflammations caused due accidents and indigestion.

**Carminative:**

It clears the stomach from gas formation. Gas is formed in the stomach due to indigestion, food poisoning and bad food habits. The oil reacts with stomach secretion and brings down the effect of gas considerably.

**Diuretic:**

It balances the water level in the body, helping patients who suffer from difficulty in passing of urine.

**Pesticide:**

This oil acts as toxic on insects like mosquitoes and ants. When blended with some chemical. It produces maximum effect on insects. Research have found that orange oil wipes off the trail left by insects like ants and cock roaches; hence it used to clear off colonies of these insects. Some of the routine tests carried out on fats and oils are as follows:

1- Acid value / free fatty acid (FFA)

2- Saponification value, SV ( also termed saponification number).

3- Iodine value, IV (also termed iodine number\_

4- Unsaponifiable matter.

5- Refractive index

6- Melting point (F solid and semi solid items)

7- Moisture content.

Theories: Saponification value is a measured of the free acid and saponifiable ester group. It is expressed as the number of milligrams of potassium hydroxide required to neutralize the free acids and saponify the esters contained in one gram of material.

### **Experimentals :**

- Sample origin and preparation
- Collection: the sample is collected from alsoog elarabi .
- Winnowing : the separation of the shell from the orange .
- Weighting .
- Distillation .

# ***Chapter two***



## 2-1 Equipments Apparatus:

Burette – pipette – conical flask – beaker – funnel – sensitive balance – measuring cylinder – dropper.

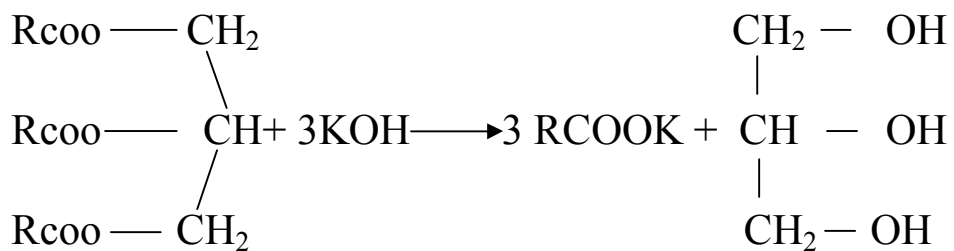
Acid value is the milligrams of potassium hydroxide that needed to neutralize the amount of free acid present in one gram of fat or oil “as the glycerides in fat slowly decompose the acid value increase”.

## 2-2. Chemicals:

Orange oil sample, Ph.ph indicator, diethyl ester, potassium hydroxide solution (0-1M).

Alcoholic potassium hydroxide (0,5M), hydrochloric acid solution (0.5M) orange oil sample, and phenol phthalein indicator. Mixture of acetic acid and chloroform, KI , potassium thiosulfate .

Theories: Saponification value is a measured of the free acid and saponifiable ester group. It is expressed as the number of milligrams of potassium hydroxide required to neutralize the free acids and saponitify the esters contained in one gram of material.



## **Peroxide value (PV)**

Detection of peroxide gives the initial evidence of rancidity in unsaturated fats and oils, other methods are available but peroxide value is the most widely used, it gives a measure of the extent to which an oil sample has undergone primary oxidation, extent of secondary oxidation may be determined from P. anisidine test, the double bonds in fats and oils play a role in autoxidation, oils with a high degree of unsaturation are most susceptible to autoxidation. The best test for intermediates in the autoxidation reaction.

The peroxide value is defined as the number of equivalents of peroxide per 1 kilogram of fat or oil.

### **2-3 Methods:**

#### **2-3-1 determination of saponification value:**

0.5 g of oil was weighed in a conical flask, 25 ml of alcoholic potassium hydroxide was added from a burette. Refluxed on water bath for about 15 minutes. Cooled and titrated against hydrochloric acid solution until the end point using phenolphthalein indicator. The titration was repeated without the sample.

#### **2-3-2 Determination of peroxide value:**

0.5 g of oil are weighed in a conical flask, 3 ml of mixture of acetic acid and chloroform are added by measuring cylinder, shaken well,

then 1ml of k are added , shacked for 1 minute ans tirated against standard potassium thiosulfate solution using stroch as indicator.

### **2-3-3Determination of acid value:**

0.5 g of oil was weighted in aconical flask, 20 ml of ethanol and ether was added by measuring cylinder , shaked well and titrated against standard potassium hydroxide solution .The titration was repeated without the sample .

### **2-3-4. infrared (IR) spectra:**

#### **. instrumentation:**

IRspectra were reorded in K BR or per kim. Elmer spectrum BX series FT-IR spectrometer.

Name of instrument: FT-IR spectromer.

Make: SHIMADZUE model No (FT-IR.8400).

Date issue: June 2009.

**Results :**

**Table 3-1 (physical properties of orange oil)**

Odour	Tangy , sweet smell
Taste	Sweet
Appearance	Yellow to orange
Density	0.873g/cm <sup>3</sup>
Refractive index	1.467
Specific gravity	0.94
Usage	Flavor and perfume

**Table 3-2 (chemical properties of orange oil)**

<b>Saponification value</b>	<b>185.13</b>
<b>Acid value</b>	<b>1.122</b>
<b>Peroxide value</b>	<b>240 meq/kg</b>

## **Discussion:**

The percentage of extracted oil = 0.267% , the oil extracted from Evgptation orange ,this orange stored by different ways, so the quantity of oil was depressed from fresh oil, this decrease the percentage of extracted oil = 0.267% , when compared with sesame oil , the saponification value for other oils as sunflower oil, olive oil and corn oil were found to be 192.5 , 190 , 190 respectively . that means the orange oil result agreement with standard .the acid value of clove oil is 6.95 of oil and two of sesame oil the value is higher in clove oil due to free fatty acids present . from IR spectrum we obtained: OH stretch at 3350, CH aliphatic stretch at 2950, 2860, C=O stretch at 1065 this result are for standard orange oil.

Orange oil which we extracted show that : 3419.56 for OH stretch , 2925.18 , 2727.16 for CH aliphatic stretch , 1037.63 for C=O .

## **Conclusion:**

The percentage oil content of orange peel was found to be 0.267%w/w. the acid value of orange oil was three time equivalent to that of sesame oil , where as its iodine value and saponification value compare very well with sesame , sunflower and corn oil the saponification value of orange oil was found to be comparable to that of sesame oil , sun flower , olive oil and corn oil were found to be 89.33 , 190.5 , 192.5 , 190 and 190 respectively .

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