An-Najah National University

Faculty of Graduate Studies

EFFECT OF HARVESTING DATE ON "NABALI BALADI" OLIVE OIL FATTY ACID PROFILE

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Dedication

Our teacher and our Noble Messenger Muhammad, may God bless him and grant him peace, who enlightened us with life.

We honor all the martyrs, the wounded, and the prisoners who sacrificed for our beloved Palestine.

My parents who continue to support and encourage me until the last day of my life.

My dear wife and icon of dedication and encouragement, my brothers, my sisters, my daughters dear to my heart; who supported and encouraged me to complete this work.

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First and foremost, I would like to express my thanks and gratitude to my dear and generous family

To everyone who contributed and gave me help and support, I thank you from the bottom of my heart.

Declaration

I, the undersigned, declare that I submitted the thesis entitled:

EFFECT OF HARVESTING DATE ON "NABALI BALAD" OLIVE OIL FATTY ACID PROFILE

I declare that the work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

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Date: 23/2/2022

Table of Content

List of Tables

List of Figures

List of Appendices

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ABSTRACT

Background: Olive is the main agricultural crop in the Palestinian territories, mainly cultivated for olive oil production. Nabali Baladi olive variety is the most predominant olive tree in Palestine. Several factors can influence the quality of olive oil, including harvesting date and location, which can influence the chemical and physical qualities and composition of olive oil.

Amis: This research aims to study the relationship of harvesting date and location on the chemical composition and physical characteristics of olive oil.

Materials and methods: Fruit samples were harvested from Jenin, Tubas and Tulkarm, governorates in northern West Bank. Fruit samples were collected monthly from September to January. Each sample was tested for fruit physical properties including; maturity index, fruit retention force, moisture content, average weight, length and width, average weight (flesh, kernel, ratio) and total fat (ether extract). Oil was extracted by mechanical method and tested for acidity, peroxide, oil fatty acids composition, UV Light Coefficient K, pigments and polyphenols.

Results: Throughout the harvesting dates, the maturity index, average weight, length and width, average weight (flesh, kernel, and ratio) and total fat and oil acidity were significantly increased in three locations, and decreased fruit retention force. Peroxide values were increased during harvesting dates, but started to decrease in the last collection date (January) in all locations. K_{232}, K_{272}, ΔK were within the limits of the Standard International Oil Council for extra virgin oil in three locations. Both chlorophyll and carotenoid in Jenin were increased from (15.5, 5.3) mg/kg to (25.6,9.3) mg/kg respectively, but in Tubas were decreased from (17.3, 6.1) mg/kg to (6.5, 2.8) mg/kg respectively, and Tulkarm were decreased from (22.7,7.0) mg/kg to (9.8,3.9)

mg/kg respectively. The highest total polyphenols were observed in Jenin and Tulkarm from November collected samples (524.4 mg/kg, 111.9mg/kg) respectively, however, in Tubas, the highest value was measured during October (304.8 mg/kg).

Conclusion: There is a relationship between the maturity color index, total fat and weight fruits. But negative relationship to fruit retention force and total fat, in three locations studied.

Keywords :(harvesting date, chemical properties, physical properties**,** extra virgin oil**).**

Chapter One

Introduction

The cultivated Olive **(O*lea europaea*L.)** is a long-lived evergreen tree. [1]It is one of the most important commercially produced fruit trees in the countries of the Mediterranean basin.

Olive is the major agricultural crop and a stable food in most of the Mediterranean countries including Palestine. More than 98% of the production of olive oil and table olives is to be found in this region. In addition, the Palestinian oil is characterized by is the highest quality oils, a percentage of the other olive oils in the world.[2]

There are many varieties of olives, each with a specific flavor, texture and shelf life that makes them somewhat suitable for different applications, such as direct human consumption for bread or in salads, indirect consumption in home cooking or catering, or industrial uses such as animal feed or engineering applications. . During the ripening stages the color of the olives changes from green to purple and then black. The taste characteristics of olive oil depend on the stage of ripening of the olive fruits being collected.[2][3]

There are different varieties in Palestine, but Nabali Baladi is the most prevalent variety due to its tolerance of rain-fed agriculture and high oil productivity.[3]

In Palestine, olive occupies the largest cultivated area and has the highest contribution in the Palestinian agricultural income. Approximately 100.000 hectares of olives are grown in the West Bank.

Most of the olive orchards are grown under extensive non-irrigated conditions with relatively low yield. The mean annual oil production in the West Bank is about 20.000 tons. [4]

Oil is considered one of the basic commodities. The average annual per capita oil consumption is 3.6 liters. [5]The majority of olive growing in Palestine is organic and picked by hand, which has a beneficial impact on olive oil quality.

Olive oil has a wide range of health benefits. Antioxidants such as vitamin E, pigments, and polyphenols are found in olive oil and are one of the most important components that influence the oil's quality and combat free radicals. [3]

Olive oil is also considered a natural and safe lubricant, and it can be used to lubricate kitchen machines (grinders, blenders, cooking utensils, etc.). It can also be used for illumination (oil lamps) or as a base for soaps and detergents. Some cosmetics also use olive oil as their base, and it can be used as an alternative to machine oil. Olive oil has also been used as a solvent and a linker in the synthesis of cadmium selenide quantum dots. [3]

Fresh oil, as available in an oil-producing region, tastes significantly different from older oils available elsewhere. Over time, the oils deteriorate and become old. A one-year-old oil may still be bland to the taste, but it is less fragrant than a fresh oil. After the first year, olive oil is more convenient for cooking than serving raw.[5]

Previous studies have shown that olive oil can help prevent cancer and minimize heart disease by lowering harmful cholesterol levels. Olive oil also has a distinctive healthful character due to pigments (chlorophyll and carotenoids) and a significant proportion of unsaturated fatty acids with high nutritional value, as well as vitamin E and phenolic compounds. These materials are one of the most important factors that determine the oil's quality.

The beneficial effects of the Mediterranean diet can be linked in part to the high ratio of unsaturated to saturated fatty acids in olive oil, as well as the antioxidant properties of its phenolic components. [6]

Several factors affect the quantity and quality of the oil, among them the variety, harvest method, cultural practices, handling, processing, storage, harvest time, environmental conditions and soil condition.

It is known that the time of harvest affects the quality of the oil to a high degree.[5] Therefore, this study aims to find out the effect of harvest date on olive oil quality at three different locations.

1.1 Objective

The primary objective of this research is to compare the effect of different harvesting dates of Nabali olive cultivar on oil properties in three different locations. The research will in clued:

- Study the effect of harvesting date on physical properties including; maturity index, fruit detachment force, moisture content, average weight, length and width, average weight (flesh, kernel, ratio) and total fat.
- Study the effect of harvesting date on Peroxide value, acidity.
- Investigate the effect of harvesting date on coefficients (K &ΔK).
- Study the effect of harvesting date on fatty acid composition and total polyphenol of olive oil.
- Study the effect of harvesting date on pigments, (total chlorophyll and total carotenoids) of olive oil.

Chapter Two

Theoretical Background

2.1 Olive tree, fruit and oil for (Nabali Baladi CV)

The olive tree is one of the oldest cultivated fruit trees, [7][8] Cultivated olive (Olea europaea L.) was advanced by domesticating wild olives, Olea europaea L. subsp. oleaster (Hoffmann's. &Link) Nevoid, they share with each other some close genetic traits.[9]

It is no coincidence that local olives tend to retreat into the cold upon return to the wild. The crop was known to all the valuable civilizations that passed through the Mediterranean, and it is expected that it arose in many areas independently.[10]

The currently available olive variety, which we know today, is a variety resulting from selective breeding during the past years, which began about 6000 years ago.[11]

To the Syrian and Palestinian farmers, and perhaps also to those in a wide area stretching from the southern Caucasus to the Iranian plateaus,[7] managed to get one or more types of fruits with a lot of oil, but without the thorns of the wild variety.

The original wild olive may have originated in Asia and was very popular at this time, but because of the hard thorns, the small size of the olives and the very low oil content, it was difficult to use it for culinary or ritual purposes.[7]

The genus Olea includes at least 30-35 species that belong to the family *Oleaceae*, subfamily *Oleoideae* (n=23). The cultivar olive **(O*lea europaea*L.)** is and romonoecious,i.e, an individual terr bears both hermaphroditic and staminate flowers. The flowers are grouped in dichotomous panicles with 12-40 flowers. However, only one fruit sets per inflorescence. [12] The inflorescences arise from the axils of the leaves on the growth of the previous season.[13]

Olive trees Nabali Baladi CV among its characteristics, which was characterized by scattered branches and moderate shape of the canopy, and the flowers bloom in the end of March to the beginning of April, the weight of the fruit at maturity is about 2.49 grams and the weight of the seed is about 0.39 grams. [2][3]

Fruit color become black (dark purple) when fully ripened, the fruit is 2.3 cm long and 1.46 cm in diameter. The color of the fruit begins to change after mid-October; properties of the oil in Palestine are Phenols 37 mg / kg oil, delta K -0.002, the proportion of oleic acid 66.3% and palmitic acid 15.6%. [(2)(3)]

The olive fruit production of rain-fed trees decreased by 34% compared to irrigated trees. [(14] Studying the extent to which the oil content is affected by the rise in the (CV NB) variety. It was found to be an inverse relationship. The farms were low and the percentage of oil was high, but in the case of the high farm, the oil quality was high and the time of harvesting the fruits was delayed.[(15)]

NB fruit weight In maturity, it reaches 2.5.[(16)]A number of samples from different governorates (Salfit, Nablus, Qalqilya, Jenin, and northern governorates) were compared. The samples collected from Nablus had 73% oleic acid value and 468 polyphenol content (mg/kg oil).[(17)]

In 2013, oil samples taken from multiple regions in Palestine were studied, it was noted that 34% of the sample acidity<0.8 and PV <12 meq O2/kg, which was identical to the specifications standard a special class Premium Ultra.[(18)]

2.2 Olive oil standards

The chemical characteristic of olive oil often indicates the quality of the oil. Extinction coefficient shows the absorption spectroscopy at specific wavelengths(232-266-270-274nm), this test indicates the primary and secondary oxidation products and can be used to assess the cases of mixing different oils and adulteration, while peroxide values parameter specifying the content so oxygen as peroxide.

Acidity is a relative measure of rancidity as free fatty acids are normally formed during the breakdown of triglycerides and re-establishment of the physiological (health) state of olive fruits and olive trees.

Health benefits and the stability of Olive oil depend on the concentration of polyphenols the phenolic compounds antioxidant activity is of large interest to the food industry. Moreover, their preventive role in cardiovascular diseases and cancer as well as delay of the ageing period,[19]and pigments the especial colour of olive oil attached to its pigment content.[20]

The color changes from light gold to rich green. Because it is high in chlorophyll pigment, the product of green olives is green oil. Ripe olives produce a yellowish oil due to the carotenoids (yellow, red). Pigments such as chlorophyll and carotenoids, which have an important role in human health and nutrition, and there is some research indicating that these phyto-chemicals have an important and essential role in plant maturation and work to prevent photo-oxidation.[21][3][18]

One of the benefits of organic olive oil is that it has high qualities that maintain good health and get rid of harmful substances form the body.[22]The appropriate degree of maturity of the fruits gives oil of high nutritional value and good specifications.[14]

Quality criteria of olive oil requirements of the Palestinian Institution for Standards had matched with the international Oil Council for the classification depending on the sensory and chemical characteristics to achieve fair competition in trade and ensure the nutritional value of essential part of the population diet.[18][22]

Table 2.1

Olive oil quality standard. The International Olive Council (IOC).[23]

Test	Free Acidity %	Peroxide Value meq. O_2/kg	K_{232}	K_{270}	ΔK	Palmitic acid % C 16:0	Stearic acid % C 18:0	Oleic acid % C 18:1	Linoleic acid % C 18:2
Extra Virgin	≤ 0.8	≤ 12	≤ 2.5	≤ 0.22	≤ 0.01				
Fine Virgin	≤ 2	≤ 20	≤ 2.6	≤ 0.25	≤ 0.01	7.5-20.0	0.5-5.0	55-83	3.5-21.0
Ordinary Virgin	≥ 3.3	≤ 20	N/A	≤ 0.30	≤ 0.01				

2.3 The effect of fruit maturity on the chemical properties of olive oil

2.3.1 Acidity and peroxide

2.3.1.1 Free Fat Acidity

This is a crude indicator of the quality of the oil based on the fruit handling methods before grinding. It is a measure of the hydrolysis of fatty acid chains, which results in the release of fatty acids. Expressed as a percentage (%), of oleic acid-based free fatty acids, due to the predominant fatty acids in olive oil.[18]

It can be easily determined for a potassium hydroxide titration that neutralizes acidity. It is generally called acidity or free acidity.

The free acidity oil differs from the acidity found in other foods. Free fatty acids (acidity) in olive oil cannot be tasted, at least not at the levels normally present.[24]

The acidity in the oil is the product of the breakdown of triglycerides, due to a chemical reaction that breaks down fats. Because of this reaction and decomposition, free fatty acids are produced. (There are in some exceptional circumstances, they may contain significant amounts of acidity in cases of oils made from healthy fresh olives, which may result from some abnormalities During the formation of oil in the fruits).[25]

In poor-quality fruits, the extracted oil tolerates too high a breakdown of triglycerides into fatty acids. These "breakdowns" are called free fatty acids. In some cases, it breaks down to one of the three fatty acids, leaving diacylglycerol. In the case of separated into two, it will remain monoglycerol.

There are several factors that have a significant role in the high acidity in the oil, including delaying the harvesting process, the oil extraction process, infection with fruit flies, and zsome fungal diseases (gloesporium, etc.).

Wrong extraction methods, the oil remains in contact with water for a long time (after the oil has been extracted). And the stage of storing olives in piles or silos leads to the enzymes breakdown of the cell structure, and thus becomes the stage of oil extraction (as is traded in Portugal and other countries) and thus no high quality and low acid oil is produced.[25]

Thus, the free fatty acid is an important measure of the quality of the oil, and it reflects the care taken from the stage of flowering and fruiting to the stage of marketing and consumption of the oil.

Free fatty acid measurement is a very simple procedure that can be measured in a laboratory test. The results are presented in grams of oleic acid per 100 grams of oil. In the case of fresh oil, carefully extracted, and using moderate heat, from fresh and healthy fruits, the acidity is often low, well below 0.49% FFA. Extra virgin oil contains less than 0.79% FFA.[25]

2.3.1.2 Peroxide Value

The peroxide value (PV) is an indicator of the extent to which primary oxidation has occurred in the oil, and the formation of peroxide compounds in the oil. Expressed as a value in miles-equivalents of free oxygen per kilogram of oil (meq O2/kg).[18][23]

The relationship of acidity values is directly related to the progression of ripening dates, while the peroxide decreases. As shown in previous studies, the maturity date is the main influence that plays an important in free acidity and PV.[26][27][28][29]

However, There are studies that show a decrease in the acidity value and a rise in peroxide with the progression of the maturity date,[30][31]

Another study showed no association between low FFA and PV during maturation.[32]Peroxides are the primary oil oxidation process products. It oxidizes when fats and oils come into contact with oxygen. Oxygen may be present in the containers and dissolved in the oil.

Oxidation products always have a bad flavor and unpleasant odor, leading to a loss of nutritional value. This destroys essential fatty acids such as linoleic and linolenic, and some vitamins disappear through their dissolution in fats.[33]

2.3.2 UV Light Extinctions K

Extinction coefficient indicates the index ΔK is the standard used to distinguish between good and bad quality extra virgin olive oil. K and ΔK measurements were prepared at a

suitable wavelength of 232, 266, 270 and 274 nm. In the case of increased K232 and K268 values in olive oil, this indicates the presence of refined oils.

Spontaneous oxidation reactions are also associated with coupling, due to the formation of carbon-carbon bonds or carbon-oxygen bonds, which leads to an increase in the absorption ratio between 225 and 325 nm.[34]

The oxidation of olive oil causes the formation of conjugated binary and triple systems, which absorb ultraviolet radiation with wavelengths from 232 to 272 nm. In the EEC method, olive oil is dissolved in a specified solvent, and the absorbance is measured at wavelengths of 232, 264, 268, and 272 nanometers. Higher absorbance at these wavelengths indicates a greater degree of oxidation and a lower quality. In general, the lower the Delta K value, the purer and fresher the oil will be.[26][35]

The changes in the value of ΔK that appear are due to exposure to light, while K270 is proportional to the concentration of conjugated trienes. However, the 18 conjugated diene oxidation compounds contribute to K232 while the secondary oxidation compounds (aldehydes, ketones, etc.) contribute to K270. Modification of Nabali Baladi EVOO chemical parameters as a function of exposure to sunlight and air.[35]

During maturity, the value of K232 increases relative to the value of K270 decreasing.[26]In other studies, the value decreases of K232, while the K270 value of increases during ripening.[30]

During a study in Algeria for the Chemlal variety, there was no change in the value of K270 during maturity, while the value of K232 increased during maturity.[27]

2.3.3 Fatty acid composition (FAC)

FAC is a carboxylic acid that is derived from triglycerides and quantified by gas chromatography, which contributes to the distinction between olive varieties. Saturated and unsaturated fatty acids are divided into mono-unsaturated fatty acids (MUFAs) and poly-unsaturated fatty acids (PUFAs).[36]

The middle carbon of the triglyceride molecule, natural virgin olive oil, contains approximately unsaturated fatty acids such as oleic or linoleic.[37] In a previous study, the

relationship of ripening progression to the fatty acid components of different olive species showed a decrease in the ratio of linoleic and oleic during the ripening period.[26][28][38]

In other studies, there was no change in the oleic ratio during maturation, but there was an increase in linoleic.[27][29][30]A Chemlali cv oil study in Tunisia showed a low oleic content during ripening.[29]

In another study, Kalamata cv oil showed an increased oleic content in Egypt during maturity.[31]

Several factors play a major role in The fatty acid composition in olive oil, which are the variety, maturity of the fruit, climate, altitude, and other factors. The major fatty acids in olive oil are: Oleic Acid (C18:1), aomega-9 mono-unsaturated fatty acids. ratio range 55-83% of olive oil. Linoleic Acid (C18:2), aomega-6 poly-unsaturated fatty acid that ratio range 3.5-21% of olive oil. Palmitic Acid (C16:0), a saturated fatty acid ratio range 7.5-20% of olive oil. Stearic Acid (C18:0), a saturated fatty acid ratio range 0.5-5% of olive oil.[37]

Compared to other vegetable oils, Olive oil contains more oleic acid and less linoleic and linolenic acids, which indicates that it contains more mono-unsaturated than poly-unsaturated fatty acids.

In general, this makes olive oil more resistant to oxidation, in the event of an increase in the double bonds of fatty acids, the result was that the oil was unstable and easily broken by light, heat, and other factors.[25]

In regions considered cooler (eg Tuscany), the oil produced in which the proportion of oleic acid is higher thanto those in warm regions. In the cold region the oil is mono-saturated higher than in the warm regions.[39]

2.3.4 Pigments (chlorophyll and carotenoid)

Some changes occur during ripening, among which the color of the fruit changes in stages from green to yellow, then purple and then black. This change is accompanied by a low content of chlorophyll and carotenoids, which leads to an increase in the proportion

of anthocyanins. Dyes are proven to provide a measure of oil quality.[37]

The green color of the oil extracted from green olives is an indicator of freshness. When chlorophyll turns into phytovitin, the color of the oil changes from green to yellow.

Measurements of pheophytin and pheophytin a can be used to measure the level of decomposition. Thus, chlorophyll pigments and carotenoids dissolve in fats, which gives the oil its high nutritional value and the desired distinctive color.[37]

Depending on the variety, after the oil extraction process, approximately 20% chlorophyll and 50% carotenoids remain in the oil.[40]During the stage of full maturity, it was found that the percentage of chlorophyll and carotenoids decrease, as shown by many studies.[16][27][30][32]It has been shown in many studies that changing the location does not affect the ratio of chlorophyll and carotenoids.[16][29]

Pigments, which are synthesized exclusively from plants and assimilated by humans only through the diet, can be divided into two main categories: carotenoids and derivatives of chlorophyll. Olive oils contain a relatively rich variety of carotenoids (for example, carotene, lutein, violaxanthin, neoxanthin, and other xanthophylls in minor percentages) and chlorophyll derivatives (such as chlorophyll a and b, phytovitins A and b, and other minor derivatives). Numerous works have demonstrated the potential health benefits of carotenoids and chlorophyll derivatives.[38][40]

In Turkey with the two most prevalent varieties, the percentage of pigments during the ripening period in Memecik CV was higher than that of Edremit CV.[30]

Olive oil has a distinctive color due to the presence of pigments such as chlorophyll and carotenoids. There are several factors that play a role in the presence of these dyes, such as the variety, maturity, climatic conditions, soil type, the method of oil extraction and beyond.

According to Apostolos Kiritsakis, an olive oil researcher, fresh oil has a chlorophyll ratio of parts per million1 to 10. The source of the chlorophyll in the oil is mostly when the olives are milled with some leaves remaining. It is known that some producers deliberately allow the leaves in the mill to increase the "grassiness" of the oil.

When the oil is exposed to light, chlorophyll and phytovitin will accelerate oxidation, but will act as an antioxidant in the absence of light. There are some studies that have proven that chlorophyll does not act as an antioxidant and an oxidizing agent.[39]

2.3.5 Total phenols content

The phenolic compounds in the oil are secondary components of the oil. Polyphenols fall into four groups in VOO: flavonoids, simple phenolic acids, oleuropein, and cinnamic acids. The four most abundant phenols in EVOO are oleocanthal, oleacein, ligstrosidea glycon, and oleuropeina glycon.[41]

These substances enhance the antioxidant capacity of VOO and decrease auto-oxidation which gives it remarkable stability, gives the desired taste and flavor.[42] Polyphenols, concentration differs between olive varieties from (50-1000 mg/kg). The studies show the effect of the extraction method on the polyphenol content ,the hammer crushers are advised.[37]

The amount and type of phenolic compounds in olives clearly depend on the variety, maturity of the fruit, climatic conditions, storage time and processing technology. There are many different procedures for analyzing phenolic substances, but very few of them are used in olive analysis except for anthocyanins or chromatographs. HPLC methods that provide specific information on individual substances are becoming more and more popular as the importance of some phenolic substances is better understood.[28][32]

Some studies (human, animal and laboratory) confirm that there are effects of positive phenolic compounds in olive oil on inflammatory markers, bone health, and antimicrobial activity.[43]

The phenolic compounds in olives are recognized as biologically active products and may have antioxidant and therapeutic properties that produce anticancer, antiviral, anti-inflammatory, hypolipidemic and hypoglycemic effects.[43]

There are also some studies that indicate that the content of phenols increases during ripening until it reaches its highest value and then decreases with increasing maturity.[26][28][32]During the ripening stage, the polyphenol content in the oil was low, as shown by some studies.[27][31]

The polyphenol content of the Chimlali variety in Tunisia is low,[29]The proportion of polyphenols during the fruit ripening stage of Gemlik was higher compared to Adana CV.[28]It has been shown in Gordal Sevillana CV that polyphenols in the ripening stage of fruits continue to be produced.[38]

2.3.6 Maturity index

During the progression in the ripening stages of the fruits, the anthocyanin substance in the fruits accumulates sat the same time that the oil content continues to increase.

In advanced stages of maturity, photosynthetic activity decreases and both chlorophyll and carotenoids begin to decline.[44]When the fruit ripening stage is completed, the color of the fruits due to the accumulation of anthocyanins changes to purple or violet.[45]

The color of the fruit is a common sign of the level of maturity expressed as an indicator of ripeness(MI). In some studies, the rate of MI increase depended on the amount of the crop.

The maturity index (MI) suggested by Uceda and Frias for olives takes into account the color of the peel and pulp of plants and ranges from dark green to black. This indicator has found wide acceptance, although it has been criticized for being subjective, vague and lacking uniformity across cultivars unless combined with parameters directly related to the biochemistry of ripening, such as anthocyanin content and fruit stability.[46]

Improving the harvest time will be beneficial to the income of olive growers. Early harvest results in the production of olive oil that is rich in phenolic compounds and usually has high nutritional value and organoleptic properties, but with low oil content it may imply severe properties, such as intense bitterness and excessive sensitivity, which is undesirable in some cases while delaying the harvest increases production Oil, oil quality decreases.[46]

However, the proposed MI is largely cultivar dependent, while environmental conditions, cultivation practices, crop load and alternate load also influence the ripening process, and thus the optimal MIs for olive harvest during fruit development.

During the seasons fruit load was high (On year), MI increased slowly while in low fruit loads (Off year) the increase in MI progressed faster. Harvest season 7/2006 was exceptional as the footsteps between harvest date and MI began in 'Barnea' only later in the season (November).

This might be due to the lower temperatures throughout the 7/2006 season (Average of 12 0C in 7/2006 and 14-15 0C in other years) It can slow down the fruit ripening process.[45][46]

2.3.7 Fruit parameter

Olive oil from the original olive varieties is highly regarded by consumers and used by producers to manage their olive oil brand.[46] Included; fruit retention force, fruit Weight, endocarp (Stone) morphological characterization, endocarp weight**,** fresh and dry fruit weight.

According to available data, ‘Buža’ (50.7%) dominates in old Istria olive orchards, followed by ‘Istars kabjelica’ (30.2%) and ‘Rošinjola’ (5.7%).[47]When fruit is fully developed, fruit of ‘Buža’ weights about4.38 g, ‘Puntoža’ 4.25 g, ‘Istars kabjelica’ 3.09 g and ‘Rošinjola’2.09 g.[48]

Drupes consist of an inner, stony cortex surrounding the seed as well as a fleshy mesocarp and a thin exocarp. Endocarp and mesocarp growth, the two largest tissues by volume and active cost, are closely related due to their common origin in the ovarian mantle. However, the endocarp and mesocarp also appear to compete as troughs, as has long been proposed in explaining the characteristic double sigmoid curve growth pattern.[50]

The timing and degree of water deficit have been reported to influence yield, fruit size, mesocarp weight, mesocarp to inner shell ratio, phenol concentration and organoleptic properties of the oil.[49][50]

Olive fruits consist of four main parts: exocarp or skin, the mesocarp or chile, it is the edible part of table olives, the part from which the olive oil begins to accumulate, and the rough inner shell that surrounds and protects the semen or seeds. Endocarp development begins 8-10 weeks after the flowering period.[49]

The qualitative parameters of olive oil are influenced by different variables. During the ripening of olives, many metabolic reactions take place, with subsequent differences in the physical properties and concentration of certain chemical compounds.

In particular, advanced ripening implies a decrease in positive organoleptic qualities due to a decrease in aromatic compounds, pigments and phenolic compounds, which directly affects the qualitative characteristics of olives (eg, average weight, flesh / pit ratio, oil yield) and olive oil.[49]

After that, intense monocarp development begins that increases its cross-sectional area approximately twice form 8 to15 weeks after bloom [50]

Chapter Three

Methodology

3.1 Location and Plant Material

Various orchards of commercial olives from NB CV, from three locations each with an approximate area of 2 dunums, were chosen to conduct the study. Olive fruits need to be processed in the shortest possible time after harvest to maintain the quality of the oil. Poor quality fruit results in low quality oil, so evaluation of fruit quality is an important step for manufacturers to ensure that the oil obtained meets the highest grade.

The fruits should be inspected to ensure that the peel is intact, that the fruit is not infested with insects or other plant pathogens, and that no discoloration occurs as a result of frost damage. The samples were taken during the 2017/2018 harvest season.

Olives should be transported from the orchard to the pressing point in open containers that allow the heat to dissipate. Without proper storage conditions, the heat generated during storage will lead to fermentation of the fruit resulting in poor quality of the fruit and oil.

The three locations (Jenin, Tubas and Tulkarm) were selected as typical regions of Palestine's various climatic zones. The coastal climate is represented by Tulkarm region, is 120 m above sea level and 15 km from the Mediterranean Sea. Jenin represents the eastern slope semiotic region of 394 m above sea level. Tubas classified semi-arid zone area with of this465 m above sea level (Table 3.1).

Table 3.1

The location and the coordinates for three orchards study area by GPS device

Locations	Tubas	Jenin	Tulkarm
Longitude	36s0719909	36s0714012	36s0102032
Latitude	3578359	3580744	3528020
Above sea level	465m	394m	120m

The distance between the planted trees is approximately 10 meters between each tree and the other, table 3-1 is shown the location and the coordinates for three orchards study area.

Table 3.2

Average rainfall in the previous three years.[51]

Rainfall/location	Jenin(ml)	Tulkarm(ml)	Tubas(ml)
2015/2016	395	466	261
2016/2017	326.8	434	256
2017/2018	516.9	583.9	346

Three trees from each orchard were randomly selected at each site. Then soil samples were taken from each site for soil analysis.

Five samples were taken between September 15, 2017 and January 15, 2018, at 30-day intervals for each location. Fruits were harvested by hand from different areas of the tree canopy, at different heights, and from all four sides of each tree.

Figure 3.1

Trees and harvest method

During the harvesting process, some sensory and physical examinations are carried out on the fruits before they are picked. After the harvest process, the fruits are stored in dry wooden boxes and then transported to the National Agricultural Research Center in Jenin Governorate.

The oil extraction process begins using the olive press shown in Figure 2-3, with the same common mechanical method that farmers used to extract the oil, and the weight of each sample was taken from the three trees identified from each site 10 kg, and after the oil extraction process, the oil will be clear if filtered or left to set, but may be cloudy when fresh.

The oil will also be turbid if it contains moisture, but this will separate and settle to the bottom after standing for a while. the oil is stored in opaque black containers for the required laboratory chemical analyzes.

Figure 3.2

Olive pressing machine

3.2 Physical analysis

3.2.1 Soil samples tests

Soil samples from each field were collected and tested; pH, electrical conductivity (EC), Moisture content ratio, Organic matter and soil texture.[52]

3.2.2 Fruit, flesh and kernel weight

One hundred fruits were collected every month to weigh them in order to know the one fruit's average weight, then the kernels were separated from the flesh and weighed to calculate the ratios between them at the same time to follow up the fruit growing and ripening.[50]

3.2.3 Average length and width of the olive fruit

100 olive fruits were taken randomly from each sample collected from the three study sites. An average measurement was made for each fruit's length and width, and the measurements were taken using graph paper divided into millimeters.[50]

3.2.4 The fruit retention force (FRF)

Fruit detachment force was measured using a Push-Pull dynamometer on approximately 50 olives/tree. The force of fruit separation was expressed in Gram (g).[46]

Figure 3.3

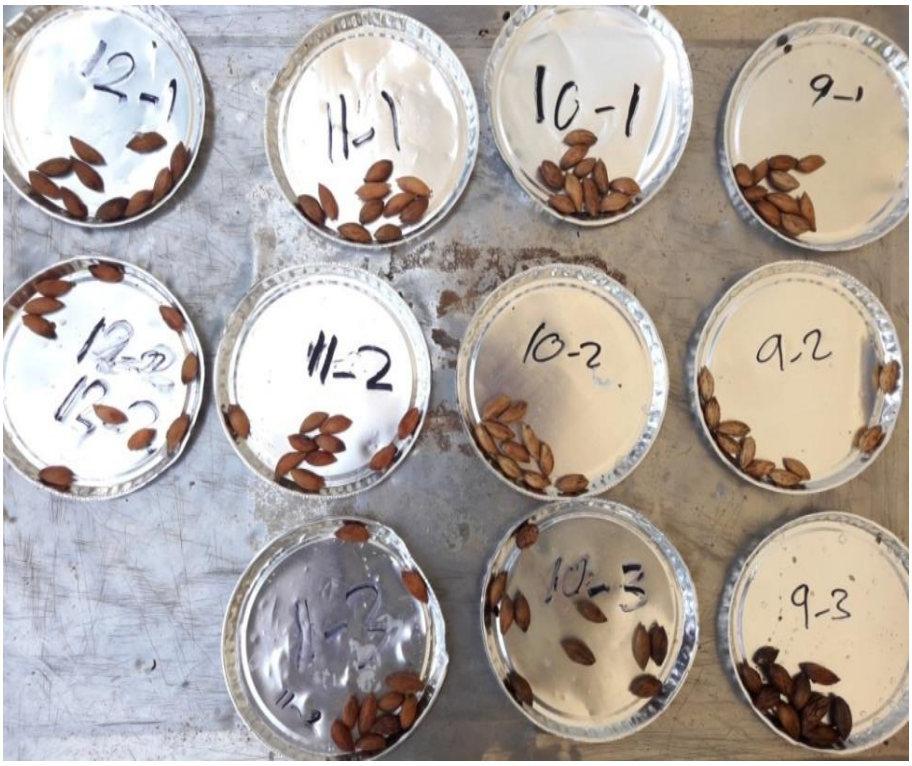
Olive fruit retention force measurement by Push-Pull dynamometer

3.2.5 Endocarp (Stone) morphological characterization

Samples were taken from each tree at each site of 100 endocarps/tree for each fruit variety for morphological characterization, where the characteristics were evaluated and categorized according to the approved criteria and standards for each characteristic.[53]

Figure 3.5

Samples of Endocarp olive fruits for morphological characterization



3.2.6 Fresh and dry fruit weight

Done through the weight of samples of 100 olives/tree one by one after the new weight, then dry in the oven temperature of 105°C for overnight.[46]

3.2.7 Olive maturity index

The method approved by the International Olive Council to measure the degree of maturity of olive fruits, which depends on the degree of change in the color of the olive during the stage of maturity that is observed through the eye.

The ripeness of the fruits determines not only the quality of the olive oil, but also the amount of olive oil obtained. The oil content increases rapidly as the olives ripen but the rate slows down as the fruit begins to change color.

Harvesting olives at a later (ripe) stage increases the risk of fruit spoilage resulting in lower oil quality because the fruit is softer and more susceptible to spoilage. 100 fruits were randomly collected from each sample collected from the three study sites and the degree of maturity of the fruits was checked and visually graded after classification.[54]

Class 0: Skin color deep green-fruit hard.

Class1: Skin color yellow-green-fruit starting to soften.

Class2: Skin with < half the fruit surface turning red or purple.

Class3: Skin color with > half the surface turning red or purple.

Class4: Skin color all purple or black with white or green flesh.

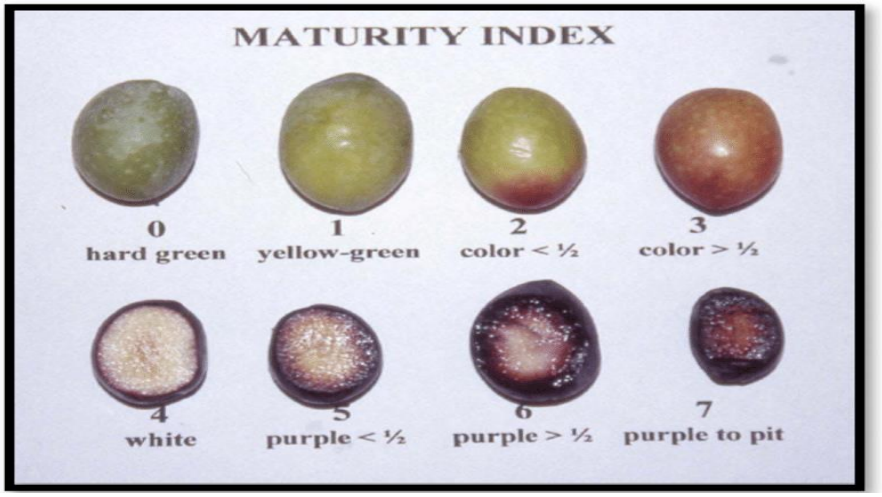
Class5: Skin color all purple or black with < half the flesh turning purple.

Class6: Skin color all purple or black with > half the flesh turning purple.

Class7: Skin color all purple or black with all the flesh purple to the pit.

Figure 3.6

Olive fruit at different stages of maturity.



The maturity index was found using the following equation

M.I = (Fruit Number of Class 0*0+ FNC 1*1+ FNC 2*2+ FNC 3*3+ FNC4*4+ FNC5*5+ FNC6*6 + FNC7*7)/100.

FNC: Fruit Number of Class.[54]

3.3 Chemical analysis procedures

3.3.1 Acidity

Free fatty acid is determined according to the procedure specified in iso660/2009.[55]

Materials

Diethyl ether peroxide-free**,** ethanol 95%**,** 1:1 mixture by volume, sodium hydroxide, Phenolphthalein, distilled water.

Principle

The sample is dissolved in the appropriate solvent mixture and then titrated with an Ethanolic or Methanol Potassium solution or Sodium Hydroxide.[55]

Equation Determine of Acidity = (V.C.M)/ (10.m)

V= Is the Volume, in milliliters, of Potassium Hydroxide.

C= Concentration moles per liter, of Sodium Hydroxide solution used= (0.1mol/l).

M= Molar mass of oleic acid = 282 g/mol.

m= Is the mass of the oil test sample in grams.

3.3.2 Peroxide value iso1960

Material

Sample of 5 g of oil, Water, Starch solution 5 g/l, Acetic acid/isooctane solution 60:40 (by volume), Glacial acetic acid, and Potassium iodide solution and free from free iodine and iodates, Isooctane, Sodium thiosulfate solution.

Procedure: Peroxide value = the amount of material that oxidizes potassium iodide in the sample according to the procedure.[56] PV is a common quality parameter and is often used for fats and oils, and there is more than one method used to determine its value.

The basis of the reaction between a solution of saturated potassium iodide and an oil sample.

This method is based on the ability of hydroperoxides to oxidize iodide ions (I-) to iodine (I2), as described in equation:

R-O-O-R + 2H+ + 2KI ---------- I2 + ROH + H2O + 2K

Iodine gives a quantitative measure of the hydroperoxides available when titrated against sodium thiosulfate with starch as an indicator of the end of a reaction, as described in equation

I2+ 2NaS2O3 ----------Na2S2O6 + 2NaI

Expressed as the peroxide meq/kg.[56]

An oil sample is treated with a solution of acetic acid and isooctane with a potassium iodide solution.

Equation for determining the value of peroxide = PV

$P= 1000(V-V_0).C/m$

V=Sodium thiosulfate volume solution in milliliters

V_0=Sodium thiosulfate volume solution for the blank, in milliliters, V_0= 0.

C= Concentration Sodium thiosulfate solution, moles per liter= 0.01 mol/L

m = Mass of the oil sample in grams.

3.3.3 Moisture content ratio

Five fruits were collected crushed fine weighed and let in oven at 105C overnight then the deference between the weights before drying and after drying was divided on the weight before drying.[57]

When calculating the moisture content, the dried samples were weighed and calculated by the following equation:

Moisture content ratio = (Weight before entering oven -- weight after drying) / weight before entering the oven.

3.3.4 Total fat

Materials

Sample of 10 olive fruits, drying oven, pestle grinder, Petroleum ether as solvent, Oil extraction device (figure 3-5).

Method

The method Rapid Determination of Oil/fat The use of high-temperature solvent extraction.[58] AOCS Official Procedure Am 5-04.

Crude fat was extracted with petroleum ether, the fruit sample was ground by pestle and mortar, weighed and recorded, samples were put into filter bags (XT4), then put in the oven at 102±2 ° C for 3 hours.

Was sealed and was placed in the (ANKOM^{xt15}) device for extraction.

The desired extraction time 60 minutes at 90° C

Figure 3.7

Ankom^{xt15}Device

After the extraction, the samples were dried 15-30 minutes in the oven at 102±2 ° C. The filter bag was reweighed.

Total Fat ratio Calculation

Total Fat ratio in the dry sample =100*(Weighing the sample with the filter bag before extraction - Weighing the sample with the filter bag after extraction) / Sample weight with filter bag before drying.

3.3.5 K and ΔK analysis

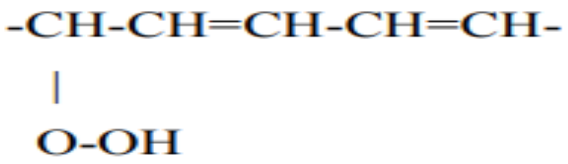
IOOC COEFFECIENT k

Material

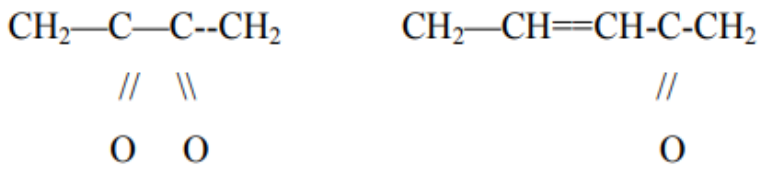
Sample oil 1g, spectrophotometer device, distilled water, quartz cuvettes, With an optical length of 1 cm, pure cyclohexane.[18]

Principle

The moving double bond that we will get induces the formation of conjugated diene systems between carbon atoms:



This conjugate system provides maximum wavelength absorption of 232 nm. Alternatively, in advanced oxidation states, products are created using paired Diene systems such as carbon and oxygen:



In this case, the highest absorption is between 260/280 nm wavelength. The UV absorption curve of the oil it is highly affected by oxidation products, some of which increase the absorbance at 232 nm and others at 270 nm.

This curve is called Delta k, and this is the test we performed to measure the purity and degradation of the oil.

Absorption at wavelengths depends on the presence of paired diene and triene systems.[18]Are expressed these absorptions as specified extinctions ($1\%E_{1cm}$).[59]

Equation of K and ΔK

$$\mathbf{K_{\lambda} = E_{\lambda} / (C.S)}$$

$\mathbf{K_{\lambda}}$ = Extinction specific wavelength ʎ

$\mathbf{E_{\lambda}}$ = Extinction wavelength ʎ. (ʎ=232,266,270,274)

C = Concentration solution g/100 ml

S= Thickness cuvette cm (=1cm)

$$\mathbf{\Delta K = K_{270} - (K_{266} + K_{274})/2}$$

3.3.6 Chlorophyll and Carotenoid Content

As for the carotene content in oils, it is determined by measuring the absorbance of the hexanoic oil solution at a wavelength of 450 nm using a UV–Vis spectrophotometer. Various amounts (ranging from 0 to 2 mg) of B-carotene were used as the standard for the titration curve. The chlorophyll content at a wavelength of 670 nm was measured in cyclohexane as described.[20]

Material

Sample oil 7.5g, Spectrophotometer device, pure cyclohexane, Quartz cuvettes.

Principle

Changes that occur during the change of oil color are directly related to the difference in maturity with the content of the dye, 7.5 g of sample is taken with 25 ml of cyclohexane.[60][61]

Equation Chlorophyll and Carotenoid Content:

Chlorophyll (mg/kg) = (A670*1000000)/(613*100*d)

Carotenoid (mg/kg) = (A470*1000000)/(2000*100*d)

Note: d cell thickness (1 cm).

3.3.7 Total Polyphenol Content

The total polyphenol content was determined using folin-ciocalteus method.[58]

Material

double beam spectrophotometers hematsu, Folin – Ciocalteaus reagent (1:10), bid stilled water, Sodium Carbonate (Na_2CO_3) 20 % (W/V), Gallic acid standard (Faluka),n-hexane 97%, Aqueous Methanol 80% (Aqueous Methanol fresh- prepared Aqueous Methanol).

Extraction procedure

Weight 10 gm of the sample, dissolve in 50 ml Hexane 97%, extract with Aqueous Methanol 80%, three portion 25 ml portions, make up to 100 ml with bidistilled water and let to stand overnight, take 1 ml aliquot of extract, and 5 ml diluted Folin Ciocalteau 1:10 in double distilled water, shake well and let to stand for 5 min, added 1 ml Na_2CO_3 20%, let to stand 1 hour (in d.d water), read the absorbance at 755 nm, prepare blank in the same way.[58]

Figure 3.8

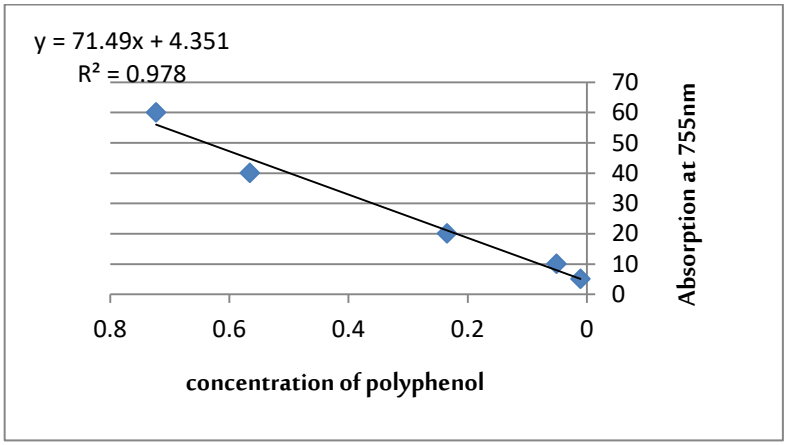
samples preparation for polyphenols extraction to read absorbance in spectrophotometers

Principle

T.P.C used method Spectrophotometric was determined,[62]an aliquot of methanol solution was added of extract to Folin – Ciocalteus solution 1:5 (V/V) ml in double distilled, then adding sodium carbonate 20% and let to stand in dark for 1hour.The absorbance wavelength= 755 nm, (figure 3-7). The concentration was expressed of Gallic acidin terms equivalent (mg of GA/ kg of oil).

Figure 3.9

The curve calibration T.P.C and equation determine



Equation for TP Content determine

The calibration equation curve was **Y**=71.49**X**+4.351

Y = concentration of polyphenol in olives oil sample.

X = reading absorption at 755 nm

3.3.8 Fatty acid composition

Materials and equipment

Thermo Finnegan Trace GC/MS^{plus} split less, sample of 150 g of oil,volume1µL in ejection, He gas, standard reference FAME's the four most important elements were readoleic, palmetic, stearic and linoleic. Potassium methoxide.BF3 (15%) in methanol, isooctane, heat in mantels, sodium chloride saturated.

Figure 3.10

Prepare samples for reading on Thermo Finnigan Trace GC/MS

Extracted samples as mentioned above were analyzed using GCMS. Using FAME reference Standard which contain four main fatty acids, gas chromatography separates the deferent fatty acids in the sample in deferent time comparing it's with standard results we determine which of the peaks related to which fatty acid.

Using mass spectroscopy, we know the molecular weight of the separated fatty acid and its fragment what help us determine the fatty acid, these results shown in the screen as peaks, and the area under the peak helps us calculate the concentration of each one comparing with others.

The percentage ratio of each FA to the total area of all FAs reflects the proportional of each one, so we can compare with the international published data.[63]

The main fatty acids in olive oil are monounsaturated FA (oleic (C 18:1)), saturated FAs (palmetic (C 16:0), stearic (C 18:0)), polyunsaturated FA (linoleic (C 18:2)). (Figure 3-7).

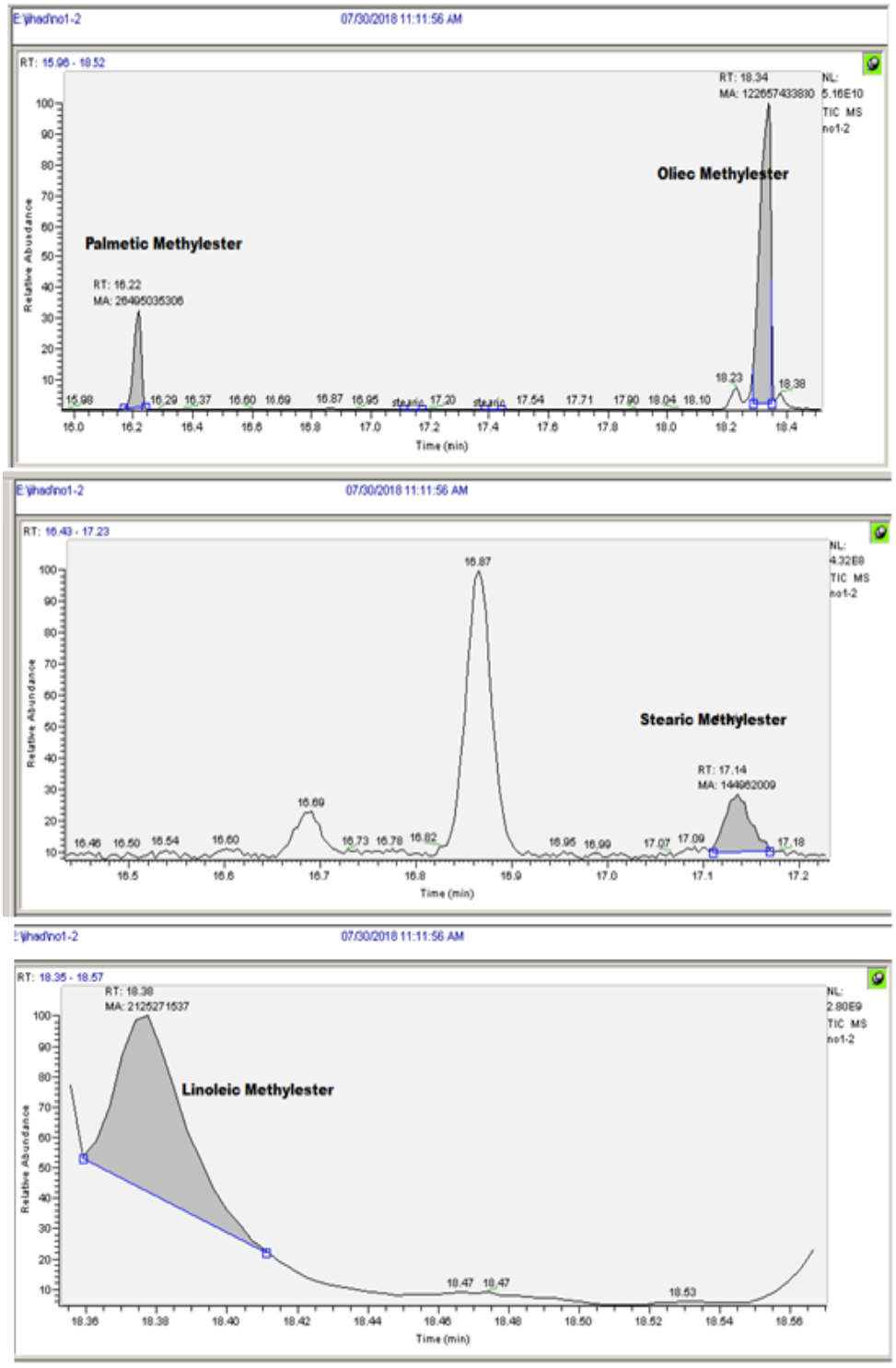
Equation of fatty acid concentration:

Total area under peak= Palmetic ME area + Oleic ME area + Stearic ME area + Linoleic ME area

FAC Percentage= under peak area of FAME*100/ Full area.

Figure 3.11

Chromatography of olive oil FAME and Area under curve for (palmetic ME, oleic ME, stearic ME, linoleic ME)



3.4 Statistical analysis method

Collected replicated data were analyzed as unbalanced factorial treatment design for both location and harvesting date factors, followed by Benforoni mean separation test using SPSS statistical package.

Chapter Four

Results and Discussion

Effect of harvest time on physical fruit characteristics related to oil quality include Soil tests**,** maturity index, fruit retention force, moisture content ratio, weight, length and width.

4.1 The effect of harvest time on fruit physical characteristics related to oil quality

4.1.1 Soil tests

Soil texture test and chemical analysis to organic matter, moisture, PH, and EC in three location studies.

Table 4.1

Soil texture and chemical analysis of soil in the three locations.

Location/Test	%Organic matter	%Moisture	PH	EC(µs)	Soil texture
Tulkarm	9.62	3.58	7.56	739	Sandy clay loam
Tubas	8.68	6.63	7.84	285	Sandy loam
Jenin	7.05	5	7.93	742	Sandy clay

Table 4-1 shows the results for soil texture in Jenin, the soil type was sandy clay, and organic matter, moisture, ph, and EC**,** respectively (7.05, 5, 7.93, 742).

In Tubas was sandy loam, and organic matter, moisture, ph, and EC, respectively (8.86, 6.63, 7.84, 285). In Tulkarm was sand clay loam, organic matter, moisture, ph, and EC, respectively (9.62, 3.58, 7.56, 739).

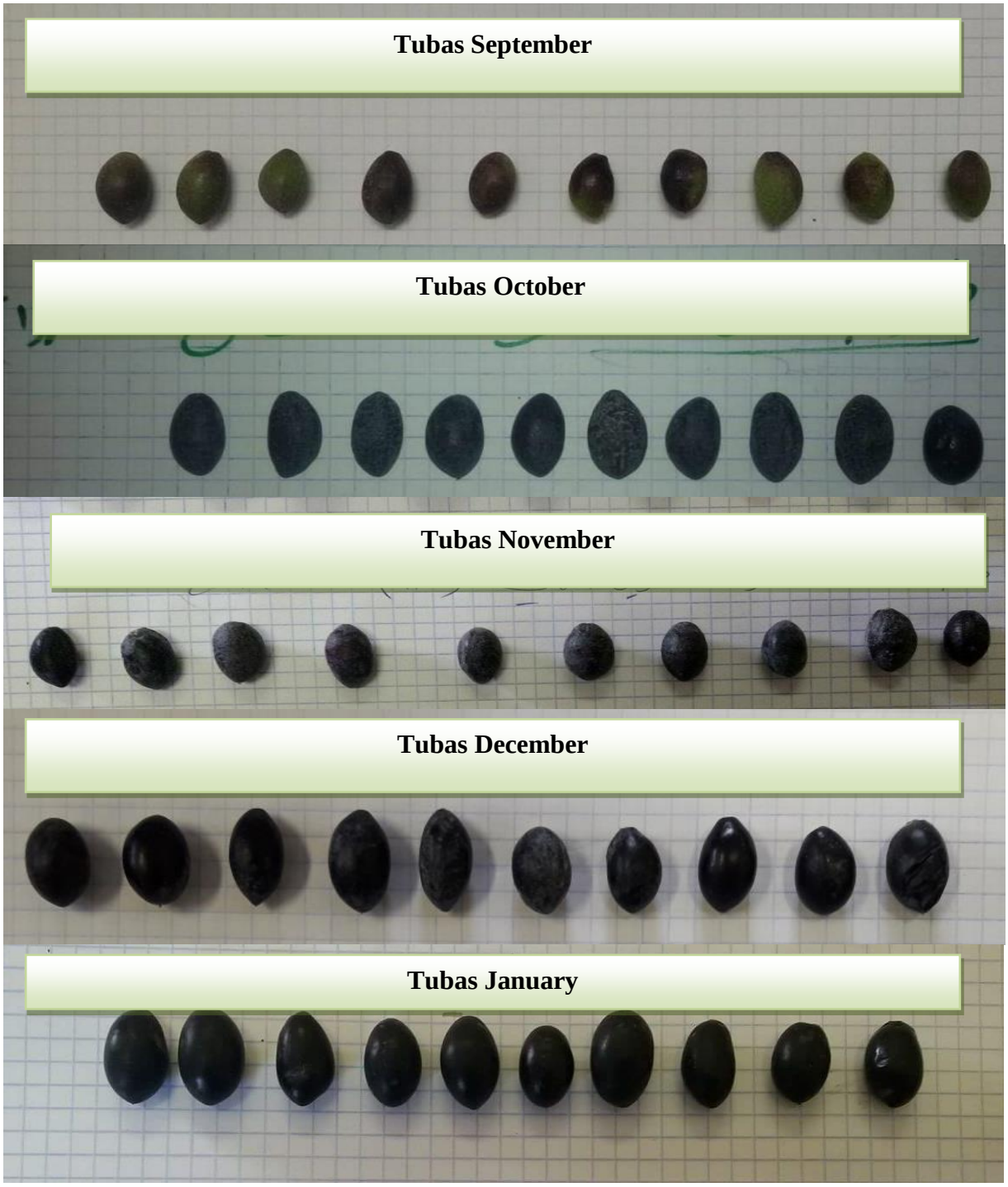
4.1.2 Maturity color Index

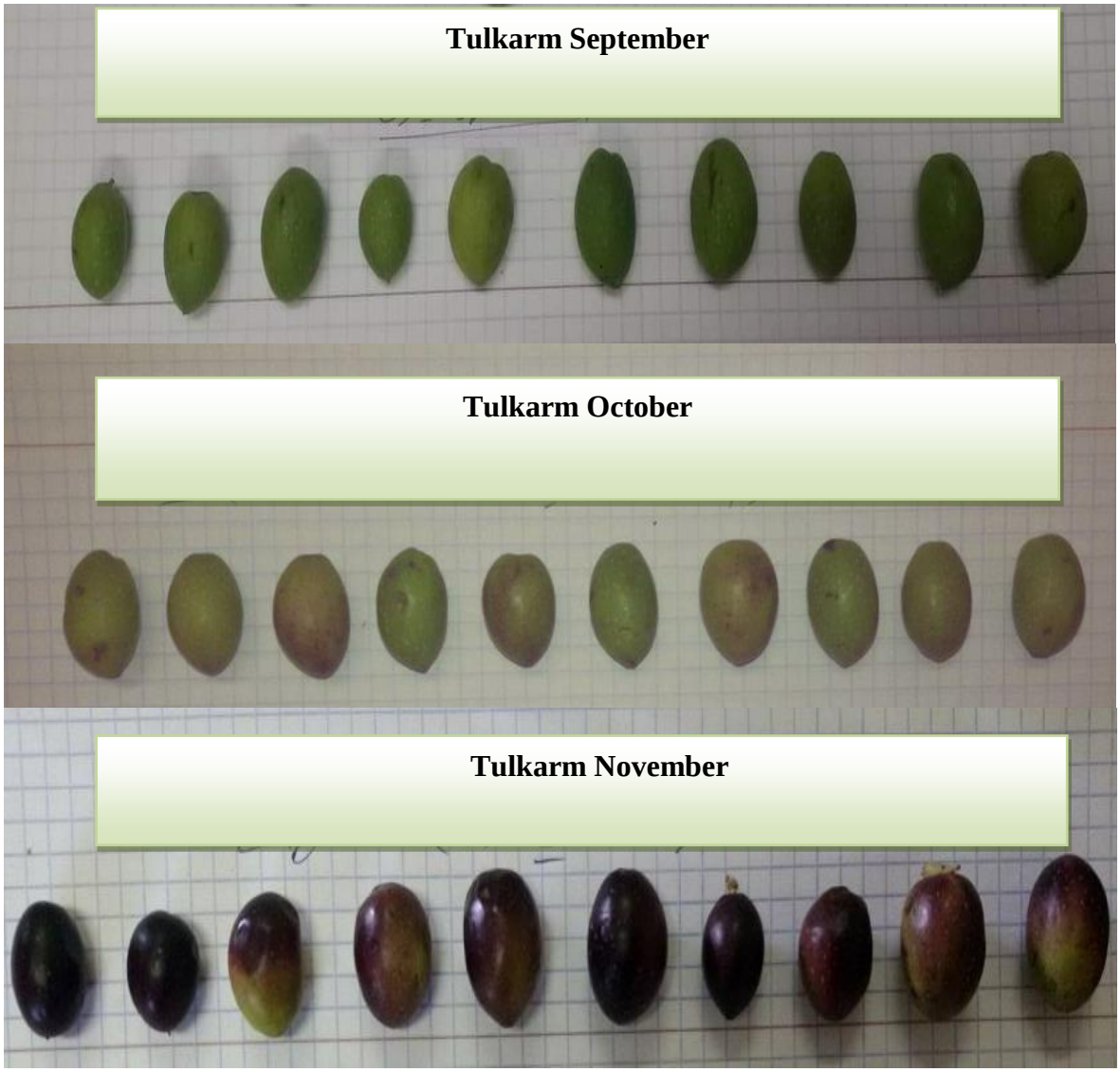
Through the results we obtained during conducting the analysis, it was noted that there was an increase in the index during the different harvest dates in which the samples were taken, as it was 0 on the date of the first harvest and reached a degree of 7 on the day of

the last harvest date. Figure 4-1 shows us the degree of change in the color of the fruits during the five harvest dates, from September/2017 to January/2018.

Figure 4.1

Photos of fruits for NB CV in the three locations during harvesting dates.


Tubas September
Tubas October
Tubas November
Tubas December
Tubas January



In Jenin and Tulkarm fruits color started to change from green to violet or purple in November, increased slowly during of season high fruit-load, due to the lower temperatures, and high of rainfall.

In tubas start color change early to violet or purple at October, MI advanced faster because lower fruit-load, due to the high temperatures, and lower of rainfall.[44]

Table 4-2 showed the effect of the harvesting dates on physical parameters in three location studies of NB CV. Although there was a significant correlation between fruit weight, length, width and total fat, they cannot be considered reliable indicators of the change in chemical properties with harvest dates, but they were mainly affected by agricultural practices and climatic.

Table 4.2

Physical parameters in the three-study location of NB CV during harvesting dates

Date/ test	weight/1friut (g)	stone /1friut (g)	flesh/1friut(g)	ratio f/s%	Length (cm)	Width (cm)	length/width (cm)	Maturity Index	Fruit retention force (g)	Total fat %	Moisture content ratio %
Jenin											
Sep	1.09	0.44	0.65	1.453 [c]	2.5	1.6	1.56	0.13	419.3	32.063 [d]	19.733 [c]
Oct	1.38	0.45	0.93	2.09[bc]	2.33	1.43	1.63	1.83	430	38.51 [b]	19.47 [c]
Nov	1.83	0.5	1.33	2.6 [ab]	2.48	1.77	1.4	3.33	537.8	48.347 [a]	29.85 [b]
Dec	2	0.52	1.48	2.8 [ab]	2.55	1.66	1.54	5.51	375.5	32.88 [c]	32.88 [b]
Jan	2.04	0.47	1.56	3.323 [a]	2.48	1.62	1.53	6.86	303.2	41.663 [a]	41.66 [a]
Tubas											
Sep	0.82	0.36	0.46	1.847 [c]	1.74	1.11	1.57	3.24	397	33.307 [c]	28.46 [b]
Oct	0.87	0.42	0.45	2.91 [ab]	1.98	1.1	1.81	6.09	521	33.387 [c]	41.283 [a]
Nov	1.15	0.48	0.67	1.96 [c]	1.92	1.14	1.69	6.56	578.8	31.647 [c]	18.77 [c]
Dec	1.23	0.44	0.79	2.717 [b]	1.92	1.14	1.68	6.76	451.2	42.533 [b]	21.477 [c]
Jan	1.84	0.48	1.36	5.523 [a]	1.98	1.22	1.62	7	315.2	53.323 [a]	25.36 [b]
Tulkarm											
Sep	1.92	0.64	1.27	1.27 [a]	2.15	1.6	1.35	0.14	533.4	21.57 [b]	24.097 [a]
Oct	1.94	0.52	1.42	1.09 [a]	2.4	1.63	1.47	2.14	479.1	27.833 [a]	16.717 [b]
Nov	2.29	0.51	1.78	1.443 [a]	2.21	1.66	1.34	5.04	251.6	28.077 [a]	16.927 [b]

When the fruit ripening stage is completed, the color of the fruit turns purple or violet at the end of the ripening process, due to the excess of anthocyanins accumulated in the fruit.[45]

Although there is a significant relationship between the weight of the fruit and the oil content in it, farmers and researchers tend to use the color of the fruit as an indicator for them to link the best harvest date to chemical properties, maturity index of 2.5 to 4.5 is commonly used for most olive oils. At maturity 3 to 5 olives have reached the maximum oil content.

Olives may reach this sooner or later in the year depending on the weather or other reasons. olive fruits reached the needed maturity index in Jenin at November to December, in Tubas from September to October, so we need to correlate it with oil content. in jenin and tulkarm the relationship between the maturity index and oil content was approved, but in Tubas it reached the maximum oil content in December when the index was 6.76, and the results was in agreement with previous studies.[45]

The Fruit retention force reached maximum values in both Tubas and Jenin at the med of November then began decreasing, indicating that the maturity stage is beginning. In Tulkarm, the result different the decreasing begins in October, the fruit retention force decrease through of the fruit until respectively at the last date of harvest (303, 315, and 251.6).

One of the NB CV olive tree characteristics is that the fruits do not fall off during the ripening period and the color of the fruit changes in the maturity stage from 0 to 7 during the five harvest dates in three locations.[26]

The effective precipitation during the last two harvest expansions of the clearly affects the increase in the percentage of moisture content and thus, it was noticed in the last dates of harvesting the fruits that there was an increase in the weight of the fruits and the ratio of flesh/stone, in three study location, reaching a weight in Jenin, Tubas and Tulkarm(2.04g, 1.84g, 2.29g) respectively, the seeds length was(2.48cm, 1.98cm, 2.21cm)respectively, and the width was (1.62 g, 1.22 g, 1.66 g) respectively, and ratio flesh/stone was (3.32, 5.52, 1.44)respectively, also it noticed the increasing in the total fat ratio was (41.66%, 53.32%, 28.07%) respectively.[15,16] Previous studies agreed with the

results of the study, as there was an increase in moisture content and an increase in total fat,[26,31,32] in contrast to the results of previous studies conducted on Chemlali olive oil.[27]

The results were represented in the five dates of harvest in the three locations of olive fruits on the following for the average weight, length and width respectively (1.67g, 2.47cm, 1.62 cm), (1.18g, 1.9cm, 1.14cm), (2.05g, 2.25cm, 1.63cm), and this agrees to studied on fruit NB CV in Palestine.[4]

4.2 The effect of harvest dates on the olive oil chemical characteristics related to oil quality

Table 4-3 showed acidity results, at September acidity in both Jenin and Tulkarm respectively (1.09, 1.11) was high then it decreased in October and continued increase until the last harvesting date. However, in Tubas it continued to increase through the harvesting dates, highest value in January (1.11).

The results show that the quality kept the super virgin limits until the med of November then became fine virgin limits. The results that appeared with us are in agreement with previous studies. An increase in acidity was observed during harvest dates.[27][28][29][31] And contrary to with, In Turkish cultivars (Memecik and Edremit), a decrease in acidity was observed during ripening).[30] But increase in acidity value lead to oil include fruit fly infestation, delays between harvesting and extraction fungal diseases in the fruit.[25]

In Jenin during the period October, Tubas in the first three harvesting dates and Tulkarm location in October. However, on the last harvest date, it was noted that the oil was not fit for consumption and marketing.

Table 4.3

Chemical quality parameters for NB CV in the three location studies during the different harvesting dates

Jenin					
Date/test	Acidity Value(%)	peroxide value (meq/kg)	k232	k270	Δk
Sep	0.109[c]	2.903 [a]	1.572 [b]	0.122 [b]	-0.0014[a]
Oct	0.7 [b]	1.983 [a]	1.963[a]	0.213[b]	-0.0021[a]
Nov	0.893 [a]	2.233 [a]	1.905[b]	0.235[a]	0.0057[a]
Dec	0.98 [a]	2.673 [a]	1.884[b]	0.231[ab]	-0.0017[a]
Jan	0.1097 [c]	1.183 [b]	1.8[b]	0.194[c]	-0.0029[a]
Tubas					
Date/ test	Acidity Value (%)	peroxide value (meq/kg)	k232	k270	Δk
Sep	0.553 [c]	1.36[a]	2.195 [b]	0.26[d]	0.0002[a]
Oct	0.543 [c]	1.63 [c]	2.039 [c]	0.21[d]	-0.0018[a]
Nov	0.697 [c]	3.17 [b]	2.235 [a]	0.25[c]	-0.0029[a]
Dec	0.903 [b]	2.673 [b]	2.027 [c]	0.28[a]	-0.0017[a]
Jan	1.11 [a]	1.3 [c]	1.734 [d]	0.16 [e]	-0.0022[a]
Tulkarm					
Date/l test	Acidity Value (%)	peroxide value (meq/kg)	k232	k270	Δk
Sep	1.107 [a]	4.01[b]	1.876 [b]	0.242 [a]	0.0003[a]
Oct	0.697 [c]	4.07[b]	2.039 [d]	0.209[b]	-0.0004[a]
Nov	0.983 [b]	6.413[a]	2.07 [a]	0.234[a]	0.0023[a]

This is due to many factors, including pests. Before the end of November in Jenin, Tubas harvest olive before the end of December. Tulkarm harvest olive before November. The peroxide test is raw indicator of primary oxidation amount, and indicates the peroxide compounds available in the oil.[18][23]

PV in Jordan NB CV increased during the advance in harvest dates.[16] Another study indicated that during ripening PV decreases.[32]Peroxide value in Jenin location increase during the period October(1.98) to December(2.67) and decreases at last harvesting date, but in Tubas location increase during the period September(1.36) to December(2.67) and decreases at last two harvesting dates. And Tulkarm increased from September (4.01) to December (6.41).

It was noted that the results that appeared with us for peroxide values for extra virgin oil were within the specifications of IOC.

There were no significant differences in ΔK as the results were within the IOC extra virgin oil standard.[18] Through maturity, increase the value of K232 and the value of K270 decreases.[26] The results of K_{232} it is part of the IOC specifications for extra virgin oil.[14]

The results in three location less than 2.5. The results of K270 in jenin location the period September and October extra virgin oil and at lasts three harvesting dates virgin oil, tubas location the period October and January extra virgin oil, and tulkarm location the period of October extra virgin oil. The results agree to the results of previous studies.[27]

Table 4-4 show the results of fatty acid composition during the different harvesting dates, in Jenin, the percentage of palmetic acid increases from 13.9 in Sep to 16.4%in December, but it decreases after that, the oleic increase 74-78%, and Stearic increase 1-2.2% to the December, but decrease after that, and the linoleic decrease and increase through period. But the saturated increase 14.9-18.5% to the December, and decrease after that, and the saturated decrease 85-81% to December and increase after that. M/PUFAs the less value in November 4.85%.

Table 4.4

Fatty acid composition of fruits for NB CV in the three location studies during harvesting date

Jenin	palmetic%	oleic%	stearic%	linoleic%	Saturated	un	un/sa	M/PUFAs
Sep	13.91	74.18	1.03	10.88	14.94	85.06	5.69	6.81
Oct	16.69	77.38	0.62	5.31	17.31	82.69	4.78	14.58
Nov	13.34	68.60	3.91	14.15	17.25	82.75	4.80	4.85
Dec	16.37	75.01	2.19	6.43	18.56	81.44	4.39	11.66
Jan	11.01	78.05	1.67	9.28	12.67	87.33	6.89	8.41
Tubas	palmetic %	oleic%	stearic%	linoleic%	Saturated	un	un/sa	M/PUFAs
Sep	15.41	80.46	0.58	3.55	15.99	84.01	5.25	22.67
Oct	7.61	75.53	1.18	15.69	8.78	91.22	10.38	4.81
Nov	9.67	70.16	0.56	19.61	10.23	89.77	8.77	3.58
Dec	9.56	70.18	0.58	19.68	10.14	89.86	8.86	3.57
Jan	7.71	83.75	0.55	7.99	8.25	91.75	11.11	10.48

Tulkarm	palmetic %	oleic%	stearic%	linoleic%	Saturated	Un	un/sa	M/PUFAs
Sep	13.76	77.62	4.24	4.38	18.00	82.00	4.55	17.71
Oct	18.28	76.35	0.70	4.67	18.98	81.02	4.27	16.35
Nov	9.41	77.76	0.55	12.27	9.96	90.04	9.04	6.34

In Tubas show the result through harvested period, the percentage of palmetic decrease 15.4-7.7%, and the oleic decrease 80.4-70.1% to the December, but increase after that, and the Stearic unchanged, and linoleic increases 3.5-19.6% to the December and decrease after that. But the saturated decrease 15.9-8.2% and unsaturated increase 84-91%. M/PUFAs the less value in December 3.57%.

In Tulkarm show the result through harvested period, the percentage of palmetic increase to October and decrease in November, and oleic unchanged, and Stearic decrease 4.2-0.5%, and linoleic increase 4.3-12.2% to the November. But the saturated decreased 18.0-9.9% to November, and unsaturated increase 82-90% to the November. M/PUFAs the less value in November 6.34%. The fatty acid composition of olive oil varies greatly depending on the cultivar, fruit ripening, altitude, climate and other factors.[39]

In Tubas, Olive oil contains a high percentage of oleic acid and a lower percentage of linoleic and linolenic acids compared to vegetable oils, that is, it contains more monounsaturated than polyunsaturated fatty acids. This makes olive oil more resistant to oxidation because in general, the more double bonds in a fatty acid, the more unstable and easily broken down by light, heat and other factors, the oil is warmer climates.[39]

In Jenin and Tulkarm, the decreased of ratio MUFAs/PUFAs,[27][30][32]and the increased ratio of USFs/SFAs.[27][31] Due to the high rainfall and higher fruits yield.

4.3 The effect of harvest date on olive oil antioxidants includes Pigments, Polyphenols.

Table 4-5 showed the date of harvest had a significant effect on the content oil, chlorophyll, and carotenoids. The results of polyphenols in Jenin location increased during the first three harvesting dates. The highest value was 524.4 mg/kg at November, in Tubas location it increased the first two harvestings dates and decreased in the third and fourth harvesting, and the highest value was 304.8 mg/kg in October.

Table 4.5

Pigments of fruits for NB CV in the three locations studies during harvesting dates

Location/Date	Jenin		
	Chlorophyll	Carotinode	Total Polyphenols (mg/kg)
Sep	15.48 [c]	5.25 [c]	147.86 [d]
Oct	18.33 [b]	6.91 [b]	244.04 [c]
Nov	6.67 [d]	2.63 [d]	524.4 [a]
Dec	6.81 [d]	2.93 [d]	246.63 [c]
Jan	25.63 [a]	9.3 [a]	280.88 [b]
Location/Date	Tubas		
	Chlorophyll	Carotinode	Total Polyphenols(mg/kg)
Sep	17.31 [a]	6.5 [b]	165.42 [b]
Oct	18.69 [a]	7.25 [a]	304.85 [a]
Nov	7.82 [c]	3.17 [d]	130.87 [d]
Dec	10.93 [b]	3.95 [c]	102.16 [e]
Jan	6.08 [d]	2.83 [d]	140.95 [c]
Location/Date	Tulkarm		
	Chlorophyll	Carotinode	Total Polyphenols(mg/kg)
Sep	22.78 [a]	9.86 [a]	57.45 [c]
Oct	14.22 [b]	6.71 [b]	79.47 [b]
Nov	7.02 [c]	3.97 [c]	111.87 [a]

These findings are agrees with previous studies.[27][31]In Tulkarm location, the results increased and the highest value was 111.8 mg/kg at November.[26][28]

In the light, chlorophyll and phytovitin promote the formation of the presence of oxygen and accelerate the oxidation process, but in the dark antioxidant chlorophyll acts. There are some physiological studies, Chlorophyll in the body and does not have an antioxidant effect or as an oxidizing agent.[39]

The results of harvest date, the highest value of chlorophyll and carotenoid srespectively in three locations, Jenin in January (25.6, 9.3), Tubas in October (18.7, 7.3), Tulkarm in September (22.8, 9.9), that was in agreement studied TP for NB CV in Nablus.[17] Several studies showed that the content of phenols increases during ripening until it reaches a maximum and then decreases with increasing ripening.[26][28][32] Other studies have shown a decrease in the polyphenol content of olive oil during the ripening process.[27][31]

Chapter Five

Conclusions and Recommendations

5.1 Conclusions

1. The study results found an effect harvest time on fruit physical characteristics related to oil quality for NB CV. There is a significant correlation between the color of the fruit at maturity, total fat and weight fruits. But the correlation between percentage of Fruit detachment force and total fatwa negative, in three locations studied.
2. The effect of harvest time on the chemical properties of olive oil related to oil quality indicated increasing acidity during harvesting dates in three locations studied.
3. Peroxide, ΔK, and K results were indicated for NB CV oil during the harvesting dates, in every location studied, was within the IOC for extra virgin oil.
4. The results of the effect of harvest time on olive oil antioxidants including pigments and polyphenols, the increasing oil content at the first harvesting dates in three locations studied.
5. In every location studied, there was a significant increase in total polyphenols at the first harvest dates.
6. The results showed at the Fatty acid composition (FAC) (palmetic, oleic, stearic, linoleic) percent in every location studied at range.

5.2 Recommendations

1. It is highly recommended not to delay the date of the olive harvest NB CV after November in Jenin and Tulkarm, but tubas delay the harvesting date to December or January.
2. Work to set up fruit fly traps and monitor the health status of trees to reduce oil quality loss.
3. It is necessary to conduct extensive studies and research on the different varieties present in Palestine in different climatic conditions and to determine the best varieties in each region.
4. The study should be repeated for several years and approximate sampling every two weeks.
5. The work should be extended to include rainfall and climate change in all location.

List of Abbreviations

Abbreviation	Meaning
CV	Cultivar
ºC	Centigrade
ΔK	Delta K, The variation of the specific extinction
FFA	Free Fatty acid
FAC	Fatty Acid Composition
FAME	Fatty Acid Methyl Esters
IOC	International Olive Oil Council
K_{232}	Extinction Coefficient for ultraviolet of 232 wavelengths
K_{270}	Extinction Coefficient for ultraviolet of 270 wavelengths
Meq	Milliequivalent, unit for the concentration of electrolytes solution.
MI	Maturity Color Index
MUFAs	Monounsaturated Fatty Acids
Mm	Milli meter
NB	Nabali Baladi
EC	Electrical Conductivity
OO	Olive Oil
PUFAs	Polyunsaturated Fatty Acids
PV	Peroxide Value
SFAs	Saturated Fatty Acids
TP	Total phenols, Total Polyphenol
USFs	Unsaturated Fatty Acids
UV	Ultra violet
VOO	Virgin Olive Oil
EVOO	Extra Virgin Olive Oil

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Appendix A

Main instruments specification

Thermo Finnegan Trace GC/MS^{plus} Gas Chromatographic

Gas Chromatographic Options: Multiple-level temperature program with seven ramps and eight levels settable from 0.1°C to 120°C/min, Capillary split/split less injectors with Digital Pressure and Flow Control (DPFC) including gas saver, Cold on-column injector for true on-column and large volume injections**.**

External Ion Source: Electron energy adjustable between 0 and 130 eV and emission current up to 850 µA, independently-controlled heating from 125°C to 300°C for stable operation and superior chromatographic integrity, GC interface temperature up to 350°C.

Quadruple Ion Trap Mass Analyzer: Unit mass resolution throughout the mass range of 10 – 1000 amu, Computer-controlled variable damping gas option for improved sensitivity.

Vacuum System Options: 250 L/s turbo molecular pump allows greater flexibility in GC flow rate and column selection (recommended for CI).

Xcalibur™ Data System: optimization software for MS/MS experiments in either EI or CI mode.

Figure A-1
Finnigan Trace GC/MS^{plus}

Appendix B

Jen Way Model 7305, Spectrophotometer
Wavelength Range 198 to 1000nm, Accuracy ± 2nm.

Photometric Transmittance (0 to 199.9%), Absorbance (-0.300 to 2.500A) Accuracy ±1%T, ±0.01Abs at 1.000 Absorbance. Light source Xenon lamp, Power 24V.

Figure B-1
Jen Way spectrophotometer 7305

جـامعـــة النجاح الوطنية

كليـــة الدراســـات العليـــا

تأثير موعد الحصاد على الأحماض الدهنية في زيت الزيتون النبالي البلدي

إعداد

جهاد علي حمد رضوان

إشراف

ا. د. حسان أبو قاعود

د. عروه حوشيه

قدمت هذه الأطروحة استكمالا لمتطلبات الحصول على درجه الماجستير في الإنتاج النباتي، من كلية الدراسات العليا، في جامعة النجاح الوطنية، نابلس– فلسطين.

2022

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الملخص

المقدمة: يعتبر الزيتون المحصول الزراعي الرئيسي في الأراضي الفلسطينية، حيث يُزرع في بشكل رئيسي لإنتاج زيت الزيتون. ويعد صنف الزيتون النبالي البلدي هو الصنف الأكثر انتشارًا في فلسطين. يمكن أن تؤثر عدة عوامل على جودة زيت الزيتون. من بين هذه العوامل تاريخ الحصاد والموقع، والتي يمكن أن تؤثر على الصفات الكيميائية والفيزيائية وتكوين زيت الزيتون.

الأهداف: يهدف هذا البحث إلى دراسة العلاقة بين موعد الحصاد والموقع على الخصائص الكيميائية والفيزيائية لزيت الزيتون.

الطريقة والمواد: تم جمع عينات ثمار الزيتون من محافظات جنين وطوباس وطولكرم شمال الضفة الغربية. كانت فترة جمع عينات من شهر سبتمبر حتى يناير. تم إجراء فحوصات على الخصائص الفيزيائية لكل عينة، وشملت الفحوصات: مؤشر النضج، محتوى الرطوبة، قوة الشد لثمار، متوسط وزن الثمرة، الطول والعرض، متوسط وزن (اللحم والنواة والنسبة بينهما) وإجمالي الدهون. كانت الطريقة الميكانيكية هي الطريقة المستخدمة في استخلاص الزيت من الثمار وتم إجراء الفحوصات التي من خلالها يتم تحديد الخصائص الكيمائية في الزيت وتشمل الحموضة والبيروكسيد وقيمة الإخماد الضوئي K ومعامله ΔK ونسبة مكونات الزيت من الأحماض الدهنية

ومحتوى الزيت من الكلوروفيل والكاروتينويد ولفينولات الكلية، وتم تحليل البيانات باستخدام برنامج SPSS الإحصائي واختبار البنفورني غير متوازن المؤثرات.

النتائج: خلال عملية الحصاد كان هناك ازدياد معنوي على مؤشر النضج ومتوسط الوزن والطول والعرض ومتوسط الوزن (اللحم والنواة والنسبة بينهما للثمرة) وإجمالي الدهن وحموضة الزيت في ثلاثة مواقع وكان هناك انخفاض ملحوظ لقوة الشد لثمار. كان هناك زياد في قيم البيروكسيد خلال مواعيد الحصاد، لكنها بدأت في الانخفاض في آخر موعد في شهر (يناير) في جميع المواقع. بينما كانت قيم كل من K_{232}, K_{272}, ΔK ضمن مواصفات مجلس الزيت لزيت زيتون بكر. أما بنسبة الأحماض الدهنية، فقد كان هناك زيادة في نسبة حمض الأوليك في جنين من 74٪ إلى 78٪ طوال مواعيد الحصاد، ومع ذلك فقد زادت النسبة حمض الستيرك من 1٪ إلى 2.2٪ في ديسمبر، وتراوحت نسبة اللينوليك والبالمتيك بين 14.4٪، 16.4٪ على التوالي. في طوباس لوحظ زيادة في نسبة حمض اللينوليك من 3.5٪ إلى 19.6٪، لكن النسبة الستيرك كانت مستقرة 0.6٪. انخفضت نسبة البالمتيك والأوليك إلى 7.7٪ و 70٪ على التوالي. في طولكرم لوحظ زيادة في نسبة حمض اللينوليك من 4.3٪ إلى 12.2٪، وانخفضت نسبة حامض الستيرك من 4.2٪ إلى 0.5٪. كانت نسبة حمض الأوليك والبالمتيك مستقرة في المدى 77٪، 13٪ على التوالي. كان هناك زيادة على كل من الكلوروفيل والكاروتينويد في جنين من (15.5, 5.3) ملغم/كغم إلى (25.6, 9.3) ملغم/ كغم على التوالي، ولكن في طوباس انخفضت من (17.3, 6.1) ملغم/كغم إلى (6.5, 2.8) ملغم/كغم على التوالي, وانخفضت في طولكرم من (22.7, 7.0) ملغم/كغم إلى (9.8, 3.9) ملغم/كغم على التوالي. وكانت أعلى قيمة لبوليفينول في جنين وطولكرم من العينات التي تم جمعها في نوفمبر (524.5 مجم/كجم و111.9 مجم/كجم) على التوالي، في طوباس،

كانت أعلى قيمة خلال شهر كانون الثاني (304,8ملغم / كغم)، ومن ناحية أخرى، لوحظت أدنى قيم لبوليفينول خلال شهر سبتمبر في جنين، وطوباس في شهر ديسمبر، وطولكرم في شهر سبتمبر، مما يجعل نتائج هذه الدراسة مفيدة لدراسات لاحقة لتحديد موعد الحصاد الأمثل لكل موقع.

التوصيات: عدم تأخير موعد حصاد ثمار الزيتون بعد تشرين الثاني في كل من جنين وطولكرم، لكن طوباس تأخير موعد الحصاد إلى نصف كانون الأول أو بداية كانون الثاني. والعمل على متابعة إصابة ذباب الفاكهة ونصب المصائد للحد منها ومراقبة الحالة الصحية للأشجار للحصول على أعلى جودة لزيت الزيتون.

الكلمات المفتاحية: (تاريخ الحصاد، الخواص الكيميائية، الخواص الفيزيائية، الزيت البكر الممتاز).