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PHYSICAL AND CHEMICAL STUDIES ON TABLE OLIVE

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ABSTRACT

Table olives, must be produced using appropriate, environmental acceptable technologies under safe conditions for consumers and workers. Two varieties of table olives (Baldy, and Egizi Shami) were investigated for the changes of physicochemical parameters during processing. Chemical composition (Moisture, Protein, Fat, Ash, Fibers and degree of acidity) in brine solution during fermentation were determined. Free acidity increased with increasing the fermentation period up to 12 months for the two varieties.

The pH values of the fresh fruits of the two cultivars are approximately the same. The pH value decreased during the fermentation period (9 months).

The untreated fresh olives contained the highest total phenols in all cultivars as compared to the treated samples .The total phenols decreased as the NaOH increased from 1.5 to 2% after lye and washing treatments. However in all cases, the total phenols decreased as the fermentation process continued up to 9 months. In the fresh olive fruits, after pickling the polyphenols of all varieties decreased. The separation and determination of Fatty acids composition of olive oil extracted from fresh and pickling olive fruits of varieties (Balady, and Egizi Shami) were carried out by gas liquid chromatography. The results showed that 7fatty acids(F.A%) were the highest in all cultivars and oleic acid decreased gradually as the fermentation period continued to (12months).The oleic acid percentage reduced (72.18, 72.28%) of the fresh olives variety (Baldy, and Egizi shami) respectively. After pickling, oleic acid percentage, was (70.21, and 69.46%) respectively.The total saturation generally, increased with increasing the fermentation time compared to the total saturation of

the fresh olives in the two varieties. The results of most fatty acids of all pickled samples showed slight changes compared to the control. Amino acids composition were also determined in fresh olive varieties showed a great difference of protein content. Sixteen amino acids of protein in each cultivar of which seven were essential amino acids (Valine, Methionine, Isoleucine, Leucine, Phenyl alanine and Lysine and in all varieties the protein contents decreased after pickling with all treatments.

Key words: Table olive – Chemical composition- pickling.

INTRODUCTION

Table olives (*Olea Europaea L.*) are traditional product and of represent the most important components of the Mediterranean diet. Olives (*Olea europaea*) constitute an integral part of the Mediterranean diet and are considered to contribute to the daily intake of nutritional antioxidants, (Boskou and Visioli 2003). Since they contain an array of polyphenolic photochemicals including various hydroxytyrosol derivatives (e. g., Oleuropein) and flavones glycosides (Romero, Brenes, and Garrido, 2002).

The world production of table olives, mainly concentrated in the Mediterranean region, is increasing and amounted to an all time high of (1,730 ,000) tones in the production year 2004-2005.(IOOC, 2006). The olive fruit is an important agricultural product in the Mediterranean countries. Because it is avaluable food staff and olive cultivation is a branch of agriculture that holds noteworthy position in the economy of producing countries (Beltran *et, al* 1999). Production of Spanish – style green olives processing by treatment with NaOH solution (1.8 - 3.0%W/V) which penetrates about 2/3 to 3/4 of the pulp followed by two or three times washing to eliminate excess of NaOH. The olives are then brined in a (10 - 12% W/V) NaCL solution in which they undergo lactic acid fermentation (Fernandez *et al.*, 1984). The Spanish processing method includes treatment with sodium hydroxide solution, for the total removal of the bitter compound Oleuropein, washing, brining and fermentation, sorting and size grading and packaging (Romero *et al.*, 2004).The lye treatment had two effects: it caused degradation and loss of polysaccharides and ,on the other hand, it increased their retention in the cell walls. The brine may be acidified to pH value 4 with lactic and acetic acids and

in anaerobic /aerobic conditions to prevent fermentation. To improve texture, calcium chloride could be added during this period. The Production of Spanish style green olives like other natural vegetable fermentation, is a spontaneous, traditional lactic acid fermentation based on an empirical process which relies upon micro-organisms present in the raw material and processing (Garrido Fernandez *et al.*, 1997).

In general, any processing method aims to remove the natural bitterness of this fruit, caused by the glucoside Oleuropein. Natural Green olives, turning color are preserved in brine fermented or not, darkened by oxidation in an alkaline medium and preserved in hermetically sealed containers subjected to heat sterilization. They would attain be a uniform black color and black olives are placed directly in and Black (Ripe) Olives (darkened by oxidation).The growth and activity of bacteria is enhanced by the presence of some undesirable spoilage microorganisms. At the beginning of pickling, the added salt causes the diffusion of juices from the raw fruits. These juices contain minerals, nitrogen and sugars needed for the activity of normal flora, mainly the lactic acid bacteria which produce organic acids, leading to desirable changes in taste, aroma and texture (Georget., et al 2003).

The aim of this work was to study the physico –chemical profile of table olives and the evaluation of changes of physico-chemical parameters during processing.

MATERIALS AND METHODS

Materials; Green table olive fruits of (Balady, and Egizi Shami) cultivars were obtained from olive trees planted in the reclaimed land at the desert road (Cairo- Alx) Season (2006-2007).

Samples preparation:

Weight of fruits (g)

The Fresh olive fruits (100 fruits) from each cultivation were weighted and the weight of fruit was calculated (g).

Size of fruits/Cm³ Specific weight of each cultivation was determined according to the A.O.C.S. (1989).

By immersing a specific weight of fruits in specific unit volume of water and the specific weight was expressed as weight /unit

volume. (25 fruits) were put in graduated jar filled with water and the average volume per fruit was calculated.

Processing

By the traditional method olives were washed with tap water to remove dust. The freshly prepared olive fruits were placed directly in brine solution (1Kg NaCL/3Lwater), then left for natural fermentation for 12 months.

In the Spanish-style method, green olive brining procedure was followed (Garrido Feranadez *et al.*, 1997). Green olives were treated for 6h with a NaOH solution 2% NaOH, w/v) to reach 2/3 of the flesh, Phenolphthalein was used as indicator to know the end point of lye treatment. Washing the treated fruits several times by tap water to eliminate the residue of lye in flesh.

Filling glass jars with olives and putting the foam plate above olive fruits. Addition of the brine and parathion oil to cover the brine.

Chemical properties evaluation:

Moisture content, lipid content, crude protein, Ash, fiber, pH value, Reducing sugars, Fatty acid component in olive oil.

- 1- Moisture content: was determined according to the A. O. A. C. (1990).
- 2- Lipid content of fresh fruits was extracted using the chloroform /methanol 2:1 according to Folch method (A. O. C. S. 1989).
- 3- Crude protein was determined according to the (A. O. A. C, 1990). Calculated by multiplying the total nitrogen by a factor of 6.25.
- 4- Total titratable acidity, was determined according to the A. O. A. C. (1990).
- 5- Determination of ash process was carried out in a muffle furnace by heating at 550C ° until a constant weight as described by the (A. O. A. C., 1990).
- 6- The fiber content: was determined according to the A O A C., 1990).
- 7- The PH value: of olive fruits was measured with an Orion model 901 pH meter.
- 8- Reducing sugars in the samples were determined according to the Lane- Eynon method as described in the A.O.A.C (1990).

Total phenol contents:

Total phenols (TP) contents of the olive oil were extracted three times with 10 ml of a methanol/water mixture (60: 40; vol/ vol). The pooled extracts were washed with 10 ml of n-hexan and solvents were removed with a rotating evaporator under vacuum. Total phenols (TP) content of the methanolic extract of olive oil were colorimetrically determined using the Folin-ciocalteu method (Gomez-Meza *et al.*, 1999) where an aliquot (1ml) of methanolic extract was mixed with diluted ethanol amine (1ml) at room temperature. After 5 min the absorbance was measured at 750nm using spectrophotometer (JENWAY 6405 UV/Vis. Spectrophotometer, England). using method reported by (A.O.C.S, 1989) .

Determiration of amino acid content of table's olive:

Amino acids content of olive was determined using HPLC-PICO –TAG method according to the method described by Cohen *et al.*, (1989).

Chemical analysis of olive oil**Fatty acids composition of olive oil:**

Gas liquid chromatography (PYE-UNICAN PU 4550) equipped with dual flame ionization detector was used. The fractionation of fatty acid methyl ester was conducted using a coiled glass column (1.5ml *4 mm) packed with diatomite C^o (100-120mesh) and coated with 10% polyethylene glycol a dip ate. The oven temperature was programmed at 8 C^o/min from 70 C^o to 190 C^o then isothermally at 190 C^o for 10 min with nitrogen at 10 ml/min as a carrier gas. The flow rate for hydrogen and air were 30 ml/min and 330/min respectively. Detector and injector temperature were 300 C^o and 250 C^o respectively. The chromatogram of the authentic fatty acid was used and the characters of the unknown fatty acids were obtained according to their retention time. The present composition of each fatty acid was calculated by the normalization with the response factor method using the PU 4810 computing integrator (Philips).

The fatty acid composition was expressed as percentage of total fatty acid, using method reported by (A O C S, 1989).

RESULTS AND DISCUSSION

The two varieties of table olives (Balady and Egizi Shami) were investigated for changes of chemical composition of the two varieties during fermentation.

Flesh/Kernel ratio of table olives

The characteristics of each type of table olives are presented in Table (1). The percentage of flesh in table olives varies between 76% and 82% and of kernel between 18% and 24%. The highest flesh/kernel ratio appeared in Egizi Shami type, 6:1 while the ratio in Baldy types 4:1. Fruit size is an important characteristic in table olive. The size of fruit of Egizi Shami (365.cm³) while the fruit size of Baldy cultivar equals (227.3cm³). The fruit weight in Egizi Shami cultivar being (5.22gm) higher than the Baldy cultivar (4.15gm).

Table (1) Size (Cm³) and Weight of olive varieties

Olive varieties	Size Cm ³	Weight (gm)
Balady	227.3	4.15
Egizi Shami	365	5.22

Flesh / kernel ratio.

Pulp/Kernel Balady =4/1

Pulp /Kernel Egizi Shami = 6/1

Chemical composition of fresh olive fruits:

The total fat percentage in flesh is higher than that in kernel .The highest percentage of oil in flesh determined in Egizi Shami variety (8.08%) and in Baldy (8.71 %). The percentage of humidity in the pulp varies between 60.02 and 62.32% .Egizi Shami cultivar contains the highest moisture in pulp while Baldy is the lowest one. Data also revealed that the tow cultivars had low crude protein contents which varied from 1.2 1% for Baldy cultivar. Verities content 1.81%, Egizi Shami. Data also reveal that Ash content among the two cultivars. The lowest Ash content 2.83% in Egizi Shami cultivar and Baldy cultivar showed highest content of ash (3.23%). Egizi Shami showed the highest content of fiber (2.91%). However Balady cultivar showed the

lowest fiber content (2.27%). In general, reducing sugars are the most important of the olive flesh. Data show that reducing sugars varied among the two cultivar. Egizi Shami showed the highest sugars content (5.99%), and Baldy have (5.66%). The inverse relationship between sugars and oil gave rise to a hypothesis on their biochemical relationship. Sugars decrease in a continuous manner when oil is accumulated in the fruit. (Sanchez Gomez and Fernandez Diez 1998).

Table (2): chemical characteristics of fresh olive fruits

characteristics	Balady	Egizi Shami
Moisture%	60.02	62.23
Lipids (%)	8.71	8.08
Crude protein%	1.21	1.81
Ash%	3.23	2.83
Fiber%	2.27	2.91
Reducing sugars %	5.66	5.99

Chemical composition changes in table olives during fermentation **Changes In pH values during fermentation of olive fruits:**

Changes in the pH value, except for the initial value were very similar as shown in Table (3) and fig (1) shows the effect of lye concentration and time of storage during fermentation process for 180 days on the pH values of the pickled olives. Results reveal that the pH values of the brine were approximately close 7.50 for Baldy cultivar and (8.52) Egizi Shami. Results also reveal that during the normal fermentation process the pH values of the untreated samples progressively decreased during storage for (180) days. This decrease was sharp during the first 3 weeks of storage then steadily declined during the rest of the storage period. The reduction rates in the pH values were almost close and varied from for (3.8) in Balady to (5.0) for Egizi Shami cultivar after storage for (180 days). However, Baldy cultivars had the lowest pH value decline.

Table (3) changes of pH value during fermentation time on olive fruits.

pH value Olive Varieties	Baldy	Egizi shami
Zero time	7.5	8.57
3 days	6.2	5.07
5 days	4.7	5.25
10 days	4.5	5.07
15 days	4.4	5.31
30 days	4.3	5.07
60 days	4.2	5.31
90 days	4.0	5.08
120 days	4.0	5.12
180 days	3.8	5.0
7 months	3.4	4.62
8 months	3.2	3.03
9 months	3.0	3.0

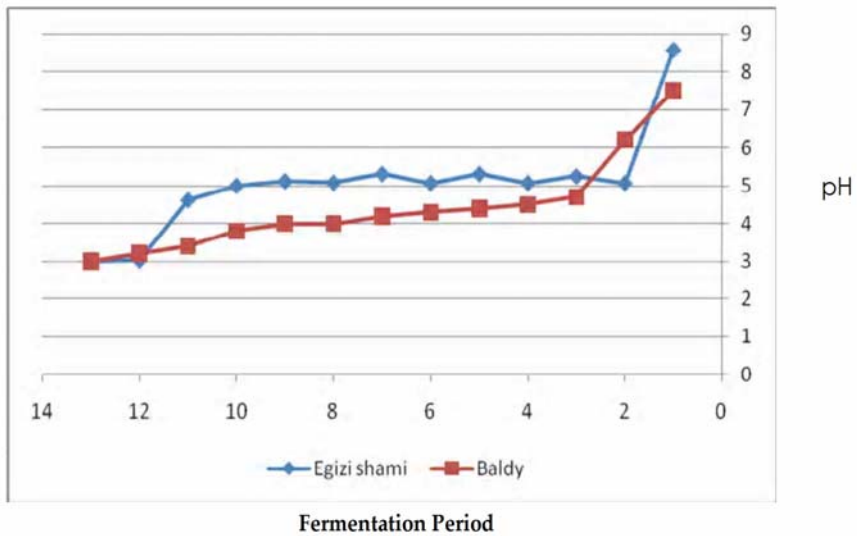


Fig (1) Changes of pH values during fermentation

Changes of free acidity during fermentation of olive Fruits:

Free acidity (% as lactic acid) of the fresh, pickled olive, during fermentation periods are shown in table (4). Total Acidity increased much more slowly at the beginning of the fermentation. In fresh olive fruits, free acidity was almost the same in two varieties. The result was similar to that of acidity fermentation seemed to progress faster by inoculation. However, whether inoculated or not, all fermenters reached the same free acidity by 21 days of fermentation, indicating that differences were detectable only during the first 3 weeks. Nevertheless, it must be stressed again that it is precisely during these first days that the risk of spoilage, due to growth of non-LAB bacteria, is highest. Furthermore, the initial differences of the delay in reaching equilibrium between olive fleshes and surrounding brine are evident. These results are in agreement with that reported by (Sanchez *et al.*, 2001)

Table (4): Change of Free acidity During Fermentation time of olive Fruits

Fermentation time	Olive varieties	
	Balady	Egizi shami
Fresh-zero time	0.05	0.08
3 days	0.22	0.14
5 days	0.24	0.15
10 days	0.35	0.19
15 days	0.32	0.24
30 days	0.34	0.35
60 days	0.40	0.38
90 days	0.42	0.38
120 days	0.44	0.40
150 days	0.45	0.37
180 days	0.48	0.42
11 month	1.1	1.0
12 month	1.2	1.0

Change in reducing sugars during fermentation:-

The sugar content of olive fruits is extremely important, since it represents the fermentable material used by lactic acid bacteria for producing lactic acid which is responsible to great extent for acceptability of the pickled product (soliman, 1981). As shown in table (5). sugars in pickled olive fruits of different varieties were decreased gradually till reaching to zero level after 45 days .The present results are in agreement with those obtained by Wafaa(1980), Who confirmed that reducing sugars were zero% after 84 days of pickling . From the same table the results indicated that the highest decrease for total sugars was recorded in the pickled olive fruits at the end of fermentation periods. The reducing sugar content of fresh fruit were 3.91, and 3.82 in Balady and Egizi Shami varieties respectively. The reducing sugars in pickled olives decreased at the end of fermentation time (10 months) in the two varieties the reducing sugars decreased as the fermentation period continued up to 10 months. These data are in agreement with Yassa *et al* (1995). Who found that sugar level in green olives reached minimum level when they were pickled by using Spanish treatment.

Table (5): Changes of reducing sugars of olives during fermentation.

Fermentation Time	Balady	E.Shami
Zero Time	3.91	3.82
After months	3.22.	3.41
2months	2.42	3.12
3months	2.10	2.01
4months	1.45	1.97
5m0nth	1.02	1.04
6months	0.33	1.00
7 months	0.21	0.70
8 months	0.0	0.26
9months	0.0	0.0

Changes of Phenols Contents for olives during fermentation:

Two varieties of table olives (Baldy, and Egizi shami) were investigated for the total phenol contents. phenolic compounds constitute an important group of naturally occurring compounds in olive. The presence of polyphenols in olive fermentation juice is also characteristic.

In general, phenols in olives are hydrolyzed during lye treatment and are partially during this operation and in subsequent washings. Thus, the concentration and types of phenols in treated and fermented fruits are different from those in the raw materials. The qualitative and quantitative determination of polyphenols was performed in flesh. (Kaliora *et al.*, 2004).

Table (6) and fig (2) show the effect of fermentation period for 10 months on the total phenols of the pickled olives. Results reveal that the untreated fresh olives contained the highest total phenols percentages in two cultivars as compared to lye treated samples. The total phenols decreased as the NaOH concentration increased after lye and washing treatments. However, the total phenols decreased. Fermentation process continued up to 10 months in all cases. Data in the table (6) and fig (2) show that Polyphenols content of two varieties decreased after pickling. This decrease in polyphenols content may be attributed to the difference in the efficiency of the hydrolyzing enzymes located in the different varieties of olive fruits. (Marsilio *et al* 2000).

The antimicrobial activities of these compounds have been shown to effect other microorganisms as well as lactobacilli (Tassou and Nychas, 1995). In the olive fruits, the main phenolic compounds is *oleuropein*, a heterosidic ester (Romero *et al* 2004). Other phenolic compounds were isolated in olive fruits (Amiot *et al.*, 1990). The most important changes in the phenolic fraction are due to the depletion of *oleuropein* during the olive fruits development and the concentration increase of tyrosol and hydroxytyrosol. (Ferreira *et al* 2002). (Kalua *et al.*, 2007) and Gomez - Alonso *et al*, (2007) reported that total phenol content during fermentation decreased in the two cultivars but the rate of decrease was clearly different between one sample to another

Table (6): Changes in Total Phenol contents (mg / Kg) during Fermentation:

Olive cultivars	Total Phenol Contents (mg / Kg)		
	Fresh olive	After pickling for 6 months	After pickling for 12 months
Balady	830	400	167
Egizi Shami	540	210	94

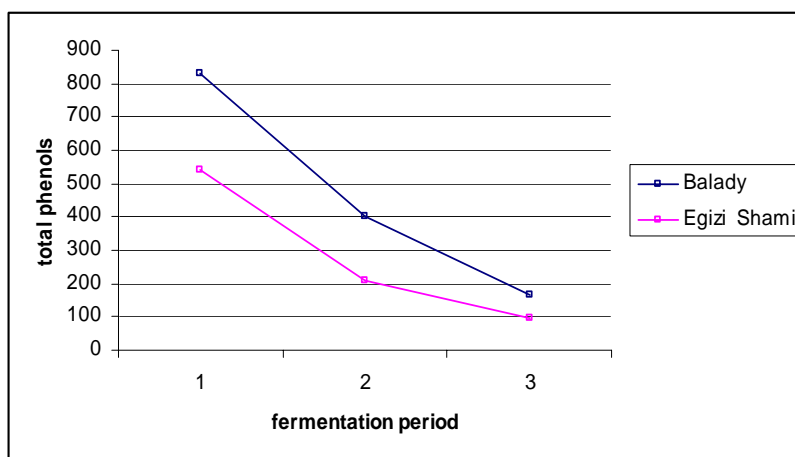


Fig (2): Changes of total phenols contents (mg/kg) on olive fruits during fermentation.

Changes of fatty acid Composition during fermentation:

The extracted oil samples from fresh and pickled olive fruits in different levels of sodium chloride concentrations for 90 days were subjected to analysis using the techniques of gas liquid chromatography (GLC). Data for fatty acids evaluation are graphically presented in Table (7). It can be noticed that oleic acid is the predominant fatty acid in the two oil samples, where it represent 72.18, and 72.28 % in the extracted oil from fresh olive fruits of Baldy and Egizi Shami, respectively . While, in the oil of pickled fruit after 90 days was 70.12, and 69.46%, respectively. The obtained results

approximately agree with those found by international olive oil (I.O.O.C., 1984) whereas, the percentage of oleic acid ranged from 56- 83. From the same table, it can be observed that the percentage of palmitic acid ranged from 15.28 to 16.28 from Balady before and Egizi Shami after pickling. Myristic acid were decreased after pickling of the Balady and Egizi Shami cultivars. The total saturation and unsaturation of oil from fresh fruits also varied according to the cultivars. Baldy cultivar showed the highest total saturation percentage (21.37 %), whereas Egizi Shami cultivar showed the lowest percentage (19.04 %), Egizi Shami cultivar reveals to contain the highest total unsaturated (78.87%) and Balady (78.62%). Egizi Shami And Baldy cultivars contained proximately the same fatty acid composition. (Garrido Fernandez *et al.*, 1997). Regarding the effect of fermentation periods after 12 months on the fatty acid composition of oils, results reveal that Myristic acid

C_{14:0} completely disappeared during fermentation after pickling in the two cultivars.

Table (7) Fatty acids composition of the extracted oil from fresh and pickled olive fruits:

Fatty acids	Fatty acids on fresh olive fruits		Fatty acids on olives after pickling	
	Baldy	Egizi Shami	Baldy	Egizi Shami
Myristic C _(14:0)	0.64	0.44	-----	----
Palmitic (C _{16:0})	15.28	14.08	16.28	16
Palmiioleic C _(16:1)	1.76	2.70	1.83	2.80
Heptad ecanoic C _(17:0)	0.28	0.07	0.44	0.08
Stearic C _(18:0)	4.68	4.00	4.22	5.32
Oleic C _(18:1)	72.18	72.28	70.21	69.46
Linoleic C _(18:2)	4.87	5.19	4.2 2	5.60
Linolenic C _(18:3)	0.84	0.70	0.52	0.41
Arachidic C _(20:0)	0.29	0.45	0.3 2	0.23
Total Saturated Fatty acids	21.37	19.04	22.26	21. 63
Total unsaturated fatty acid	78.62	78.87	77.38	78.33

Olive Protein Content and amino acids Composition:

Olive Fruit quality is correlated amongst other things with protein content and amino acid composition. The proteins were analyzed in olive buds. All of the common amino acids were present in the free amino acid pool. arginine, alanine, aspartic acid, glutamic acid, and glycine constituted approximately 60% of the free amino acids. Olive fruit protein contained all of the common amino acids present in other plant proteins. Arginine constituted approximately 25% of all essential amino acids, followed by leucine and valine. The results showed that no a great difference in protein content among varieties. Amino acid contents of the table olive were shown in table (8).

Table (8) Amino acids content in olive variety

Amino acids	Baldy cultivar	Egizi Shami Cultivar
Aspartic	115.93	121.63
Threonine	66.46	43.51
Serine	72.64	103.44
Glutamic acid	189.76	242.28
Glycine	40.46	51.54
Alanine	92.28	122.06
Valine*	70.30	96.16
Methionine*	11.83	96.32
Isoleucine*	62.91	109.95
Leucine*	134.40	200.44
Tyrosine*	115.89	154.18
Phenylalanine*	125.35	175.28
Histidine	97.44	159.94
Lysine*	3.73	4.58
NH₄⁺	160.28	184.40
Arginine	120.35	170.48

*=Essential amino acids

Protein content was the highest as in Table (8) the (Egizi Shami cultivar (1.81 %) but this content in Balady cultivar was (1.12%). Sixteen amino acids were detected in the protein of the olive fruits studied, seven of which were essential. In all varieties, which are methionine, isoleucine, leucine, tyrosine, phenyl alanine, valine and lysine are Essential amino acids .Asparagin, and glutamin acids accounted for the largest share of the total amino acids. Buds and mature fruits had the highest content of essential amino acids. In the group of essential amino acids, valine had the highest content for the two varieties are shown in Table (8). In the Egizi shami variety Methionine was the least essential amino acid represented while, as in the case of the (Balady variety) valine was the most represented. The content of other amino acids ranged from 0.05% (Histidine,) to 3.03% (asparagines acid) depending up on the plant organ concerned. From the group of protein non essential amino acids, asparagines and glutamic acid were the most represented .The results obtained in this study show that protein content varied among the varieties examined, as well as among the fruit organs. Sixteen amino acids were detected in the proteins, of which, seven were essential. (Manoukas, *et al* 1973)

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دراسات طبيعية و كيميائية على زيتون المائدة

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تعتبر ثمار الزيتون من الثمار المباركة و التى ذكر اسمها فى الكتب السماوية لاهميتها الغذائية والصحية حيث انها تحتوى على نسبة عالية من الزيت ويمتاز هذا الزيت باحتوائه على حامض الاوليك مما يجعله فى مقدمة الزيوت الطبيعية الصحية لما لها من اثر على مقاومة امراض القلب وتصلب الشرايين وايضا مخفضة لكوليستيرول LDL فى الدم .

وتعتبر عملية التخليل فى حد ذاتها صناعة هامة و رئيسية لانتاج زيتون المائدة حيث ان المخلات تعد من الاغذية المحببة جدا فى مصر الا ان عدم اتباع طرق تكنولوجيا وقياسية عالمية تؤدى الى تنوع المنتج المصرى و تقلل من جودته و قيمته الغذائية و الصحية .

والهدف من هذا البحث هو دراسة الخواص الطبيعية و الكيميائية لزيتون المائدة و مقارنة تأثيرها على التركيب الكيماوى لاصناف الزيتون المختلفة . قد تم اختيار صنفين من اصناف الزيتون المستخدمة فى التخليل وهى البلدى و العجيزى الشامى. تم دراسة التركيب الكيماوى لاصناف الزيتون قبل التخليل ويشمل تقدير الرطوبة واللييدات والبروتين والرماد والالياف وشملت التقديرات الكيماوية:

تقدير قيم ال-pH و الحموضة الكلية و الفينولات و الاحماض الدهنية والاحماض الامينية وتقدير السكريات المختزلة وتقدير التغيرات التى طرأت على التركيب الكيماوى للزيتون اثناء التخمر وبعد مرور 12 شهر.

لوحظ زيادة تدريجية فى نسبة الحموضة الكلية خلال فترة التخمر التى استمرت 12 شهر قلت السكريات.

المختزلة اثناء فترة التخليل تدريجيا الى ان اختفت تماما فى نهاية فترة التخمر. لوحظ تناقص تدريجي بطئ فى محتوى الثمار من الزيت حتى نهاية فترة التخليل . قيم values pH قلت اثناء عملية التخمر فى جميع الأصناف. تم دراسة المواد الفينولية حيث وجدت الفينولات بكثرة فى الثمار الطازجة فى صنفى الزيتون مقارنة بالعينات التى عوملت بالصودا حيث قلت الفينولات مع زيادة تركيز الصودا وايضا مع زيادة فترة عملية التخمر (12شهر) لصنفى الزيتون البلدى والعجيزى العاصى.