# EFFECT OF ETHYL FORMATE ON THE CHEMICAL PROPERTIES FOR SOME CULTIVARES DATE PALM

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ABSTRACT
The current study aimed to investigate the effect of using ethyl formate in fumigating three varieties of Iraqi dates (Al-Zahdi hard, Al-Sayer semi-hard, and soft Baraben) on their chemical properties during six months of storage at a temperature of 4 ºC for the cultivar Al-Zuhdi and Al-Sayer and -18º C for the cultivar Barben. The results showed that the treatment with ethyl formate did not affect the percentage of total sugars, protein, fat, ash, tannins, and total phenols, which amounted to (67.37%, 0.34%, 0.2%, 1.27%, 0.001%, 48.00 µg/ml) respectively for the Zuhdi variety,and (67.97%, 0.40%, 0.3%, 1.15%, 0.001%, 71.82 µg/ml) respectively for the treated Al-Sayer variety, and (65.82%, 0.63%, 0.4% 1.10%, 0.01%, 47.50 µg/ml) respectively for the treated Baraben cultivar. No significant differences were observed between the control and treatment samples for the same item. However, the percentage of these components decreased during the storage period for all varieties, with an increase in the moisture percentage for all studied varieties. In particular, the Baraben class as one of the soft varieties. The moisture content reached 28.8% for the control sample after six months of storage, and adding ethyl formate reduced the total acidity in the treatment samples relative to the control samples for each variety, where the highest value of the total acidity of the Sayer control sample was 0.115%. The lowest value was for the Sayer treatment sample, 0.012%. The results showed no effect on the concentrations of mineral elements as a result of treating date varieties with ethyl formate. The concentrations of vitamins for the samples treated with ethyl formate were higher than the concentrations of vitamins for the control samples and all the studied varieties during the storage period.

Key words: Dates storage - zuhdi - sayre - barben
*Part of Ph.D. dissertation of the 1st author.

## INTRODUCTION

The palm tree is considered the tree of life and one of the oldest cultivated plants in Mesopotamia, about 4,000 years ago. Palm trees are plants that can withstand harsh environmental conditions such as high temperatures, moisture, long dry periods, and high levels of salinity in the soil. It also withstands all seasonal fluctuations and, in return, gives high nutritional value and long productive life of up to 100 years and multiple uses in addition to creating a good climate within the ecosystems, useful in maintaining the fragile soil structure and reducing the risks of desertification. The date palm is distributed throughout the Middle East and North Africa, the eastern and southern regions of Africa, the Arabian Peninsula, Iraq, and even in certain parts of Europe and the USA (33). The cultivation of dates has increased significantly over the past twenty years. Production doubled in 1996, with about 5 million tons of dates collected, while in 2016 - about 8.5 million tons (28). Due to increased production and exports,

dates are now available worldwide and can be an integral part of the daily diet (21).

Date fruit is a highly nutritious food rich in carbohydrates, dietary fiber, proteins, minerals, and vitamin B complex such as thiamin (B1), riboflavin (B2), niacin (B3), pantothenic (B5), pyridoxine (B6), and folate (B9). Carbohydrates constitute 70% of date fruits, mainly in the form of monosaccharides, including glucose and fructose. The minerals in date fruits are calcium, iron, magnesium, selenium, copper, phosphorous, potassium, zinc, sulfur, cobalt, fluorine, and manganese. Dates are highly nutritious and may therefore confer many potential health benefits (17). It is one of the few nutritional sources that has been closely related to the survival and well-being of humans living in hot and dry environments. This plant is mainly responsible for human settlement and expansion in hot and arid parts of the world. It is the most sustainable agricultural ecosystem in harsh dry environments. Therefore, date fruits occupy an important economic resource and income and must be taken care of, especially after harvesting (33), as well as paying attention to educational methods and means in the field of palm cultivation, production and processing of dates, and dissemination of the results of scientific research and agricultural technologies (3). The dates found in different parts of the world are consumed in the date stage for the dry and semi-dry varieties. As for the soft varieties, it is difficult to preserve and circulate at room temperature, as low temperatures must be used because dates are exposed to many pests and diseases and many pathogenic fungal causes that cause much damage to the fruit (1), making them unfit for human consumption and unacceptable for marketing.

However, at present, industries have moved away from using chemical vaporizers of methyl bromide for fumigation after harvest due to the presence of restrictions regarding its use by the Montreal International Protocol. Therefore, some materials are used for fumigating dates, including methyl bromide and phosphine. In addition, some pests have developed resistance to phosphine; therefore, an effective, safe, and immutable alternative to these phosphines is highly recommended. One of these materials is the use of ethyl formate, which is a fumigant that has proven effective on a large number of products against associated pests. Ethyl formate is a suitable alternative to other fumigants. It requires a short exposure time and is classified as GRAS (generally recognized as safe). The advantages of ethyl formate include the natural presence in food, the rapid killing of insects (within 2-4 hours), rapid decomposition of residues in natural products, and low toxicity to humans. It is considered a natural insecticide, volatile antimicrobial compound, and a good alternative to other fogging materials. This study aimed to identify the effect of ethyl formate on dates by treating three types of local dates (Zuhdi, Al-Sayer, and Baraben) with ethyl formate fumigation to maintain their quality. A study of the effect of this substance on the chemical properties of the treated varieties of dates.

## MATERIALS AND METHODS

### 1. Date samples collection

Three varieties of Iraqi dates were obtained from different local origins (Al-Zuhdi, Al-Sayer, and Al-Barben) in the dates stage for the 2020 season, Al-Zuhdi (solid) from Baghdad Governorate, Al-Sayer (semi-solid) from Dhi Qar and Al-Barben (soft) from Anbar Governorate. The dates were sorted, prepared, and treated as follows:

### 2.Sorting and cleaning

The dates were sorted manually, and the fruits that were unsuitable for packing were excluded. Then, general cleaning of the dates was carried out to get rid of the dust stuck to the fruits and eliminate impurities.

### 3.Selection of fumigant and fumigation

Liquid ethyl formate was imported from Sigma Aldrich Company, with a purity of 97% and a volume of 500 ml for one package.

Ethyl formate liquid was used to evaporate the dates, the percentage of use was 10 ml/kg, The process of fumigating the dates was carried out by spraying ethyl formate on the dates in a special evaporator, which is a small, airtight room and contains vacuums to draw the air and leave the dates in the evaporator for two hours.)2 (

**5.Packing and storage**

The treated and controlled varieties of dates were packed in plastic containers (polyethylene), closed tightly, and the samples were stored varieties (Al-Sayer and Al-Zuhdi) refrigerated for six months at 4ºC, while the treated Barben was stored in the freezer at -18ºC.

**6.Estimation of total carbohydrates.**

The method proposed by (9) was followed in preparing the sample for the determination of total carbohydrates by weighing 100 mg of date powder (Date samples were dried at 40ºC) and transferring it to a test tube fitted with a lid, then adding to it 5 ml of hydrochloric acid solution at a concentration of 2.5 N and mixing well with an electric mixer and leaving it in a boiling water bath for 2 - 3 hours. Cool the mixture to room temperature, transfer the tube contents into a volumetric flask, and fill the volume to 100 ml using distilled water. Then the solution was centrifuged at a speed of 10000 xg for 10 minutes, sludge filtration was carried out using No.1 Whatman filter paper, and the precipitate was discarded. The total carbohydrates in the clear filtrate were estimated according to the method proposed by (28) by taking 0.1 ml of the filtrate and adding to it 1 ml of the prepared crystalline phenol solution at a concentration of 5% and mixing well with the electrolyzer, then adding to the mixture 5 ml of sulfuric acid solution at a concentration of 96% Mix well with the electric mixer. The tubes were left for 10 minutes, then transferred to a water bath at 30°C for 20 minutes, and the optical absorbance of the solution was measured at a wavelength of 490 nm. Distilled water was used as a control sample, Blank. The standard curve estimated the amount of total carbohydrates in date powder.

**7.Estimation of total reducing sugars**

Total reducing sugars in the date powder extract was estimated according to the method used by (5) and suggested by (37) by taking 0.1 ml of the extracted date powder solution (prepared at a concentration of 0.5%) and transferring it to suitable test tubes and completing the volume to 1 ml With distilled water, 1 ml of (3,5-DNSA) reagent (which was prepared by dissolving 1 g of 3.5-DNSA in 30 ml of distilled water away from light) was added to it, then 30 g of Rochelle salt was gradually added to it until Complete dissolution, then 20 ml of 2 N sodium hydroxide solution was added to it and left on the mixer until complete dissolution, and kept in an opaque glass bottle away from light after completing the volume to 100 ml using distilled water). Moreover, the tubes were mixed well on the electric mixer. The tubes were transferred to a water bath at a temperature of 100 °C for 5 minutes, then cooled in an ice bath to room temperature, then 10 ml of distilled water was added to each tube and mixed well with the electrophoresis, and the optical absorption was measured at a wavelength of 540 nm.

**8.Protein**

Micro Keljdahl's method was used to estimate the percentage of protein in the samples based on the method mentioned in (41).

**9.Fats**

The fat was estimated based on the method described by (22).

**10.Ash**

The percentage of ash was estimated based on (22).

**11. moisture**

The moisture percentage was estimated according to the previous method described by (22)

**12.Determination of the total phenolic content:**

The total phenolic content of date extract was determined according to the method described by (26)

**13.Estimation of tannins:**

I followed the method given in (4).

**14.Total acidity**

Method described in (31) was used to estimate the total acidity.

**15.Estimation of metallic elements**

The sample was analyzed in the laboratories of the Department of Environment and Water / Ministry of Science and Technology in order to estimate the total minerals (Ca Mg, Fe, K, Cr, Zn, Na) according to the method mentioned by (42) using a flame atomic absorption spectrometer (SHIMADZU Sample AA7000(.

**16.Estimation of water-soluble vitamins**

The examination was carried out in the Ministry of Science and Technology - Department of Environment and Water laboratories, using high-performance liquid chromatography technology, sample HPLC SYKAMN (Germany of origin), which was used for analysis by adding the detection of thiamethoxam. The mobile phase was composed of acetonitrile: distilled water: and formic acid in a ratio (50:47:3) with a carrier phase flow rate of 1 ml/min. The column was ( C18-ODS 25 cm * 4.6 mm) and UV-215 reagent, nm

**17.Estimation of fat-soluble vitamins**

The analysis was carried out using liquid chromatography (HPLC) technology (SYKAMN - Germany), the separation column (C18 - ODS was 25 cm * 4.6 mm), and the mobile phase was methanol-water (98:2, v/v). The flow rate was the mobile phase 1.0 ml/min, the injection volume was 50 µL, and the column oven temperature was 35 °C. Detected using a UV-vis detector at 265 nm.

**RESULTS AND DISCUSSION**

**total sugars**

Figure (1) shows the effect of treatment with ethyl formate on the total sugar ratio of the three treated varieties (Al-Zuhdi, Al-Sayer, and Barben). We note no significant differences at the probability level ($P \leq 0.05$) during the storage periods between the control and treatment samples within the same variety. That is, the treatment with ethyl formate did not affect the percentage of total sugars. The results also showed a decrease in the percentage of total sugars in general during the storage period due to the decomposition of sucrose along with the enzymatic activity (13). The results showed significant differences between the three varieties during the storage periods, as we found the highest value of the percentage of the total sugar in the pre-storage period was for the control sample for the Al-Sayer variety. Which amounted to 70.4%, while the lowest value for the percentage of total sugars for the treatment sample for the Barben variety, which amounted to 63.0%, and these results were less than the results reached by (24) for the dates of the Kingdom of Saudi Arabia. The values of total sugars reached 71-81 g / 100 g and less. Also, the results of (27) for Iranian dates were 84.51 to 96.28 g / 100 g for total sugars. As for the three-month storage period, the highest value of the percentage of the total sugar for the control sample for the Al-Sayer variety was also 72.3%, while the lowest value for the treatment sample for the Barben variety was 62.1%, and this is

due to the different varieties and the different areas of cultivation of these varieties. While in the six-month storage period, there are no significant differences between the three varieties. The difference between physical, chemical, and nutritional treatments can be attributed mainly to the difference between varieties (8).

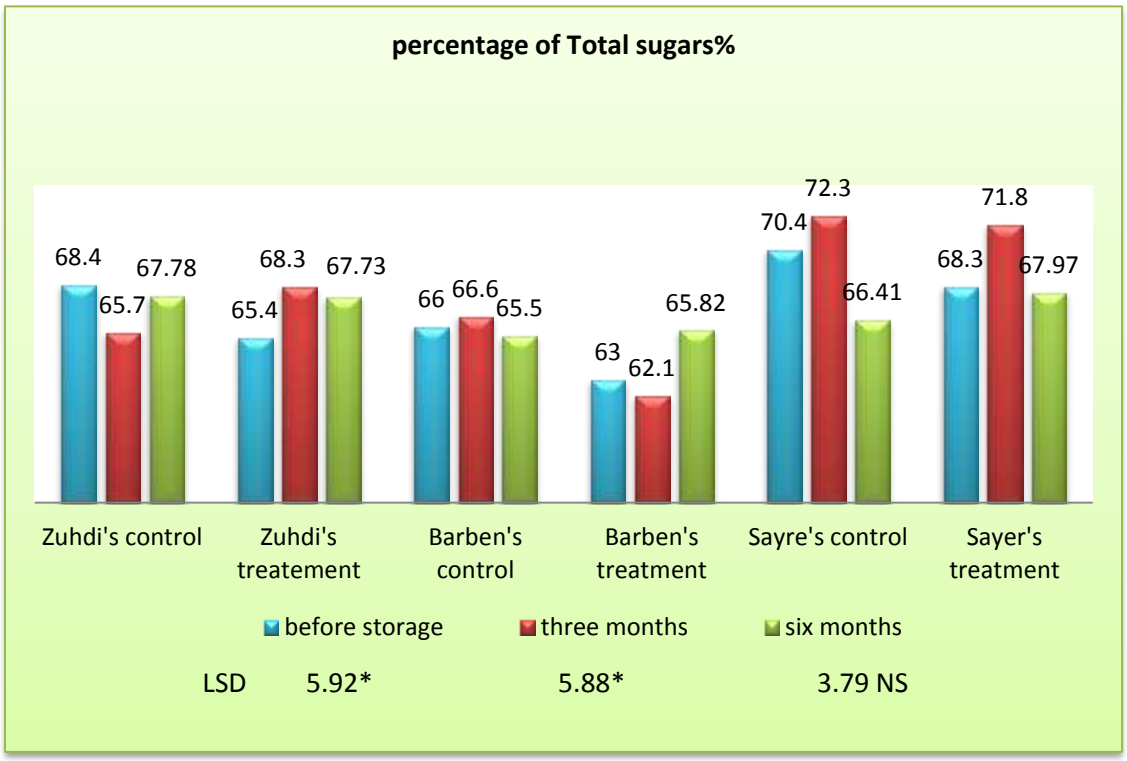


**Figure 1. Effect of ethyl formate and storage period on total sugars perce ntage for some date varieties.**

**Monosaccharides**

Figure (2) shows the effect of ethyl formate treatment and storage period on the percentage of monosaccharides. There were significant differences at the probability level ($P \leq 0.05$) among the three varieties during the storage periods. In the pre-storage period, we found the highest value of monosaccharides was for the Sayer control sample. The value was 65.0%. At the same time, the lowest value for the Barben treatment sample was 44.59%. The results of this study were higher than the values mentioned by Thouri *et al*.,(38) for reducing sugars, ranging from 24.37 to 34.66%. parvin *et al*., (38) analyzed three cultivars of dates grown in Bangladesh, and the percentage of reducing sugars was 42 - 48%. Over three-month storage period, the highest value of monosaccharides for the Sayer treatment sample was 64.28%, while the lowest value was for the Barbin control sample and the Zuhdi treatment sample, where the values were 44.43% and 44.82%, respectively. As for the storage period of six months, there were no significant differences between the Al-Sayer variety and the Barben variety, but there were significant differences between these two varieties and the Al-Zuhdi

variety. Figure (2) shows there were significant differences for the same treatment within the storage and pre-stocking periods, where the Barben control sample showed an increase in the percentage of monosaccharides from 50.84% to reach 65.01% in the period after six months of storage. As well as the Barben treatment sample, it has been noticed an increase in the proportion of monosaccharides from 44.59% in the pre-storage period to 60.13% after six months of storage. As for the Sayer treatment sample, the proportion of monosaccharides, increased from 53.18% in the pre-storage period to 64.28% after three months of storage. The value rises to 65.18% after six months of storage, and the reason for this is due to the decomposition of sucrose up on the enzymatic activity in the date fruit, and this is consistent with studies of Al-Mashhadi *et al*., Alhamdan *et al*., (18, 13). While no significant differences noticed within the samples of Zuhdi control and Zuhdi treatment within the storage periods. The conversion of disaccharides to monosaccharides in dry dates is slow. It is clear from the results that there are no significant differences between the value of the control sample and the treatment sample for the same variety, except for the Barben in the pre-storage period and the three months of storage and the Al-Sayer variety in the pre-storage period only. ethyl formate treatment had no significant effect on the percentage of monosaccharides

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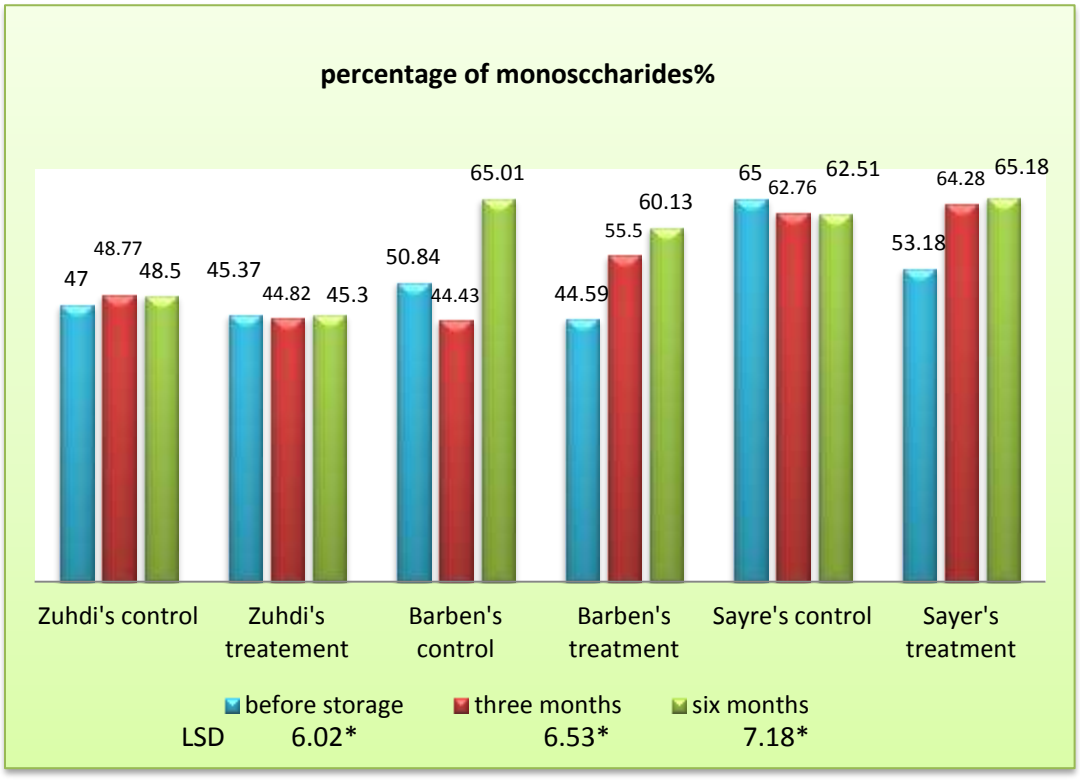


**Figure 2. Effect of treatment with ethyl formate and storage periods on the percentage of monosaccharides for varieties of dates.**

**Protein ratio**

Figure (3) shows the effect of the treatment with ethyl formate and the storage period on the percentage of protein for the three date varieties (Zuhdi, Al-Sayer, and Baraben). Before storage and a period of three months and six months of storage. there were no effect of treating with ethyl formate on the percentage of protein, however there were a decrease in the percentage of protein within the treatment during storage periods. there were significant differences at the level of probability (P≤0.05) among the three-date cultivars during the storage periods. The highest value was in the pre-storage period for the Sayer treatment sample, and the percentage of protein was 3.9%, while the lowest value was for the Barben control sample, which amounted 2.1%. As for the three months of storage, the highest protein percentage for the Sayer treatment sample was 1.5%. The lowest percentage of protein for the Baraben control sample was 0.7%. These results can be attributed to differences in the variety, environmental conditions, analysis methods (27), or different varieties. Attaha *et al*., (15) studied 17 types of Iraqi dates they found a change in the protein content. As for six months of storage, no significant differences were observed among the varieties. As dates do not contain a high percentage of protein, they contain more than other fruits.

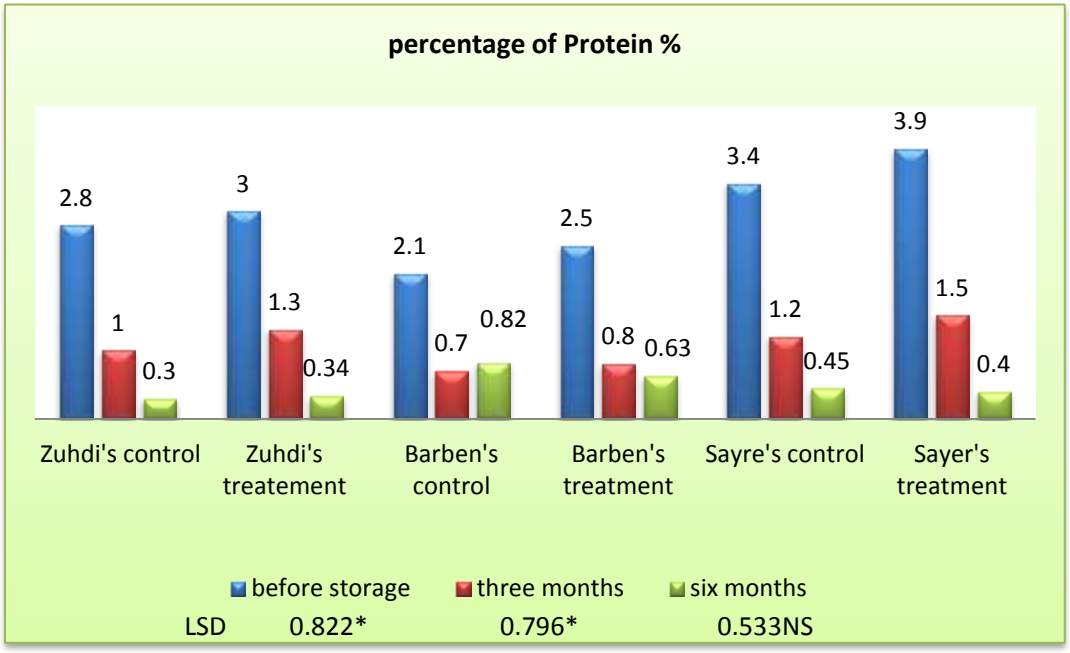


**Figure 3. Effect of treatment ethyl formate during storage periods on the percentage of protein for date cultivars.**

**Fat percentage**

The results in Figure (4) show the effect of ethyl formate treatment on the fat percentage in the three date cultivars (Zuhdi, Al-Sayer, and Barben) during the storage periods. We note significant differences between the cultivars in fat percentage value at the probability level (P≤0.05) during the storage and pre-store periods. We find that in the pre-storage period, the highest value of the percentage of fat was

for the Sayer treatment sample and the Zuhdi treatment sample. The value was 0.9% for both samples. While the lowest value of the fat percentage in this period for the control sample was Zuhdi, and the value was 0.4%. These results were higher than the results obtained (27) for the cultivars that were analyzed. The fat percentage ranged between 0.037 - 0.113% and less than the results of (14) for the Omani date varieties. We find in this period before storage that there are significant differences between the treatment sample and the control sample for the Zuhdi variety only, where the value of the control sample for the Zuhdi variety was 0.4%, and the value of the treatment sample for the Zuhdi variety was 0.9%. As for the three-month storage period, we find the highest value of the Sayer treatment sample, which amounted to 0.7%, and The lowest value of the control sample was Zuhdi, which amounted to 0.2%. At the same time, we do not find any significant differences between the treatment and control samples for the same category.

In the six-month storage period, the highest value of the percentage of fat for the Barben control sample was 0.6%, the lowest value was for the ascetic treatment sample and the ascetic control sample, and the value was 0.2% for both samples. In this storage period, there are no significant differences between the control sample and the sample treated with ethyl formate for the same variety. That is ethyl formate treatment's effect on fat percentage. Through the results, we note a decrease in the percentage of fat during storage periods. In general, dates are a fruit with a low percentage of fat content.

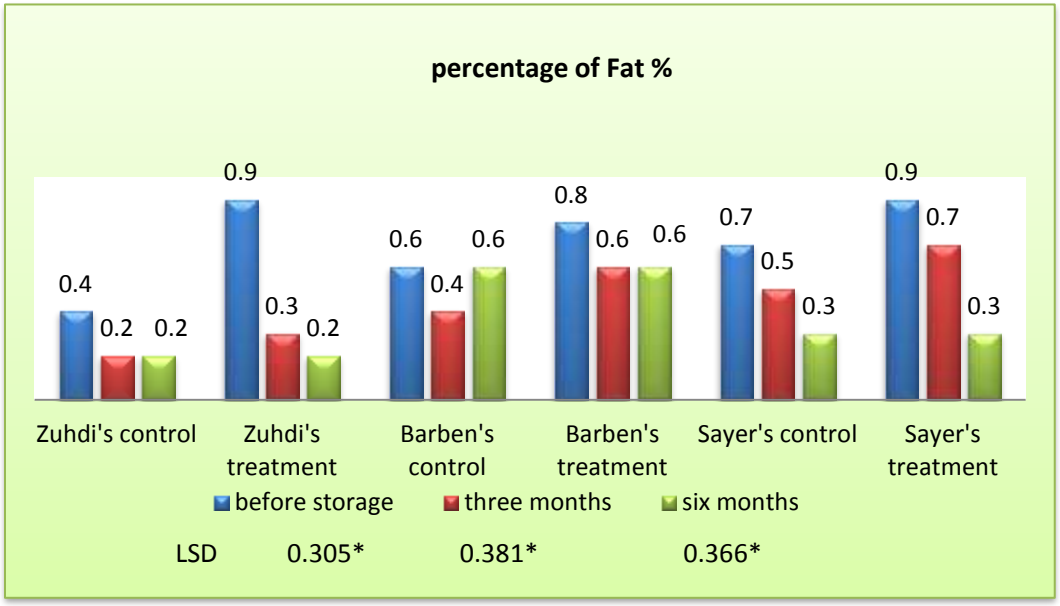


**Figure 4. Effect of treatment with ethyl formate and storage periods on the fat percentage of date cultivars.**

**Ash ratio**

It is clear from the results in Figure (5) the effect of ethyl formate treatment on the percentage of ash for date varieties (Zuhdi, Al-Sayer, and Barben) during the storage and pre-storage periods, where we find significant

differences among the varieties for the ash percentages at the probability level (P≤0.05) in the pre-storage period only. The highest value of the treatment sample was Zuhdi, which amounted to 1.64%, and the lowest value was for the Sayer control sample, which amounted to 0.98%, and these percentages were close To the percentages obtained by djaoudene *et al*., (26), which amounted to 1.25-1.99%. After three and six months of storage, the results showed no significant differences between the date varieties during each period. Also, we did not find any significant differences between the values of the single sample during the storage periods, and the results in Figure (5) did not show any significant differences between the values of the control sample and the values of the treatment sample for each of the items used during the storage periods. That is, ethyl formate treatment has no effect on the percentage of ash for date varieties.

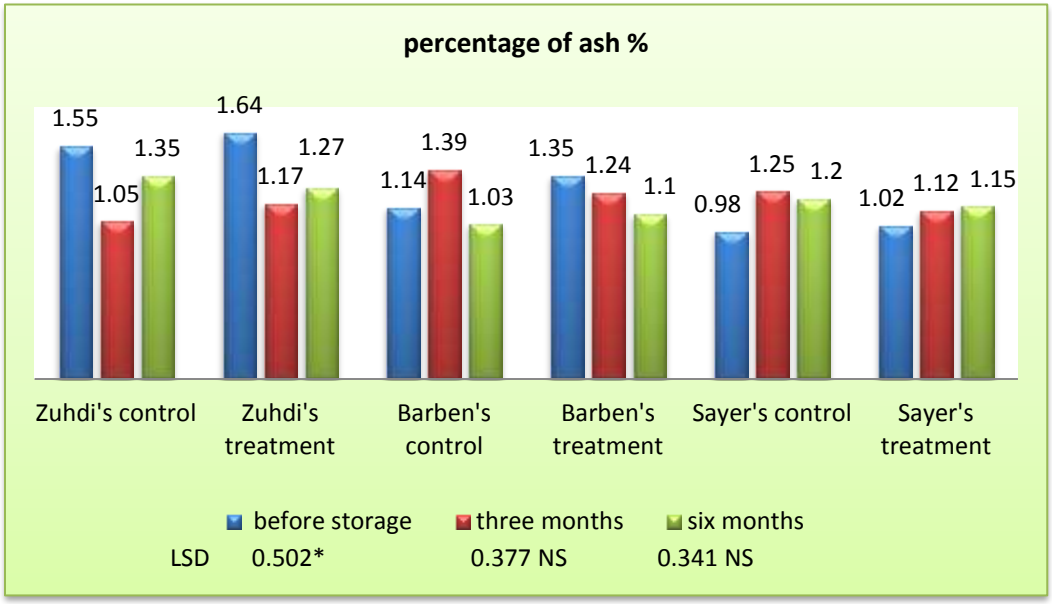


**Figure 5. Effect of adding ethyl formate during storage periods on the percentage of ash for date cultivars.**

**Moisture content**

Figure (6) represent the effect of treatment with ethyl formate on the varieties of dates (Zuhdi, Al-Sayer, and Barben) during the storage periods on the percentage of moisture, where we find a high percentage of moisture in general for all varieties during the storage periods. The Barben variety sample, which is considered one of the soft dates, had the highest value of moisture percentage in the pre-storage period for the control sample and the treatment sample, which amounted to 19.4% and 20.4%, respectively, followed by the Al-Sayer cultivar samples, as it is one of the semi-dry dates, where the moisture percentage of the control sample was 15.9 % and for the treatment sample 16.9%. The samples of the Al-Zuhdi cultivar had the lowest moisture because it is considered one of the dry cultivars, where the moisture ratio of the control sample was 13.1%, while the moisture ratio of the treatment sample was 14.9%. No significant differences were observed among the percentages of moisture

between the control sample and the sample Treatment of the same variety during storage periods, except for the Barben variety. After six months of storage, significant differences appeared at the level of probability (P≤0.05) between the control sample, which amounted to 28.8%, and the treatment sample, which amounted to 22.9%. The increase in the moisture content during storage may be because the moisture levels in the fruit remain more or less stable under low-temperature storage. However, prolonged storage often produces low moisture content (7). However, in the current study, a significant increase in moisture content was observed in all cultivars, and these results are consistent with the results of (10).

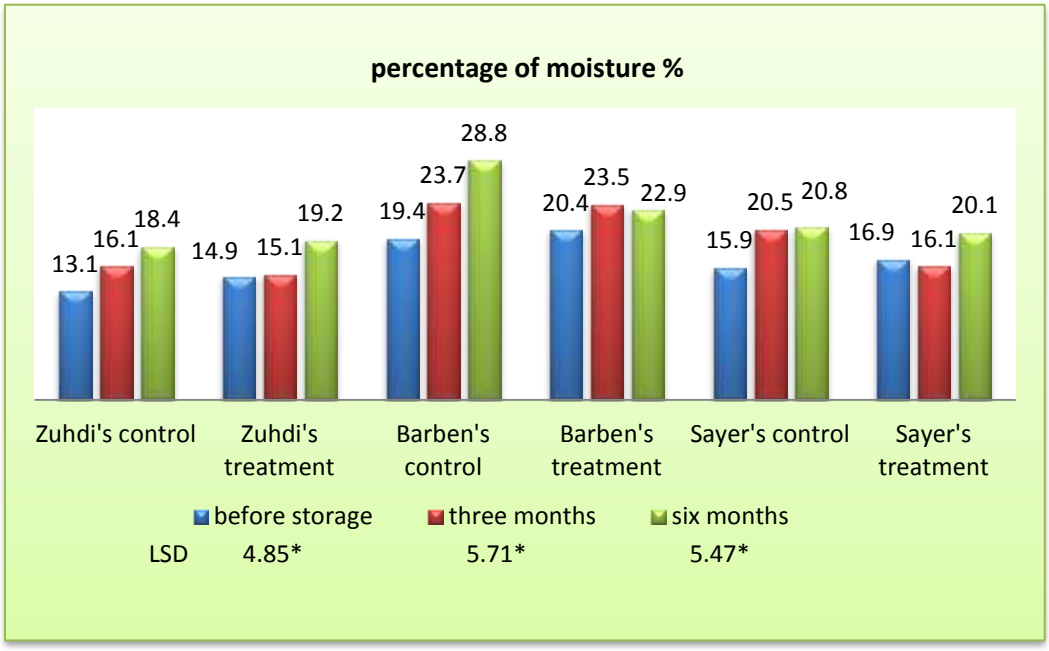


**Figure 6. Effect of treatment with ethyl formate and storage periods on the moisture percentage for date varieties.**

**Total phenol concentration**

The results in Figure (7) show the effect of ethyl formate treatment and storage periods on the concentration of total phenols of date cultivars (Zuhdi, Al-Sayer, and Barben). The results show that there are significant differences at the probability level (P≤0.05) among the three varieties during each storage period, where we find the highest concentration of total phenols in the pre-storage period for the Sayer control sample at 116.02 µg/ml and the lowest concentration of total phenols for the control sample Zuhdi 73.00 µg /Ml. Also, we find significant differences between the control and treatment samples for each variety in the pre-storage period. However, in the three months of storage, we find that the highest value of the Barben control sample is 76.00 µg/ml and the lowest value of the total phenol concentration for the Barben treatment sample is 41.39 µg/ml as well as the presence of significant differences between the control sample and the treatment sample for the two varieties of Barben and Al-Zuhdi. Because Barben is a soft variety, the moisture content increases during storage, while the percentage of soluble solids decreases.. As

for the Al-Sayer variety, there were no significant differences between the control sample and the treatment. After the six months of storage, the highest value of the total phenol concentration for the Sayer treatment sample was 71.82 µg/ml and the lowest value for the control sample. Sayer, which amounted to 41.33 µg/ml, and there were no significant differences between the control sample and the treatment sample for the Zuhdi and Barben variety only, the Sayer variety. In general, we find a decrease in the concentration of total phenols for each sample during storage periods and significant differences between the values of the concentration of total phenols for each sample during storage periods. It may return. These differences in the concentration of total phenols between cultivars are due to different cultivars, genetic factors, climatic conditions, irrigation methods, cultivation conditions, and fruit picking stage, in addition to an increase in the enzymatic activity of polyphenol oxidase enzymes that oxidize phenolic compounds and convert them to other compounds (12,13).

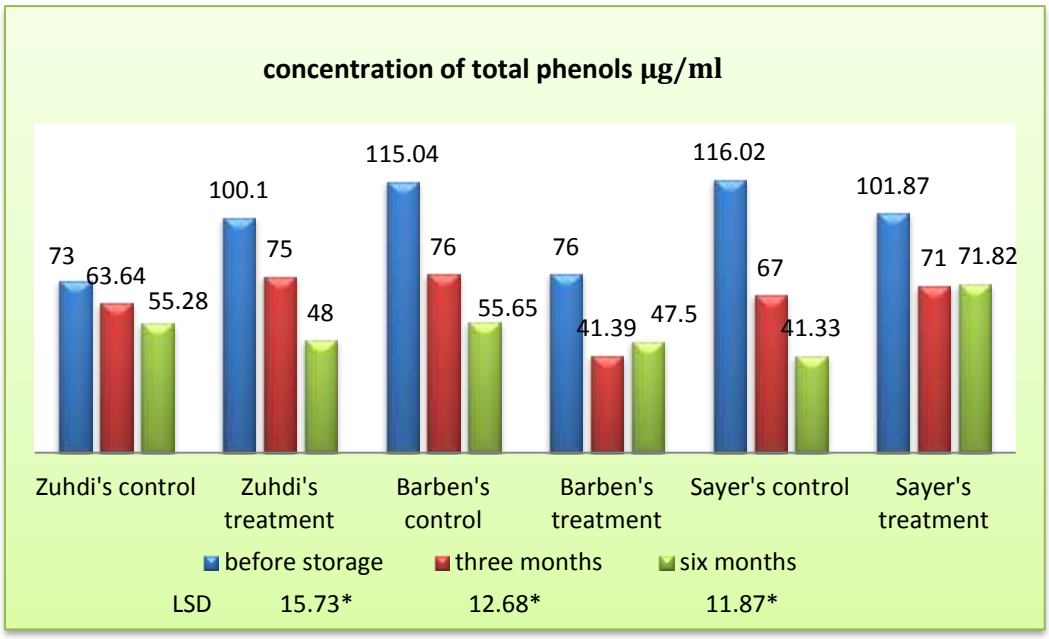


**Figure 7. Effect of treatment with ethyl formate and storage periods on the concentration of total phenols of date cultivars**

**Total tannins**

Figure (8) show the effect of ethyl formate treatment and storage period on the percentage of tannins for date varieties (Zuhdi, Baraben, and Al-Sayer). Has been noticed a decrease in the percentage of total tannins for all types. Tannins are water-soluble polyphenols. The tannin material is deposited in the large cells, which converts it from the soluble state to the insoluble state (4). These results agreed with the results of (10), where it was found that the tannins content in dates decreased during 12 months of cold storage. The reason may be a non-enzymatic activity (19 ,6). It is noted from the Figure that there were no significant differences between the values of the control sample and the values of the treatment sample for each of the varieties. during storage periods,

that is, adding ethyl formate to the tannin percentage is not affected.

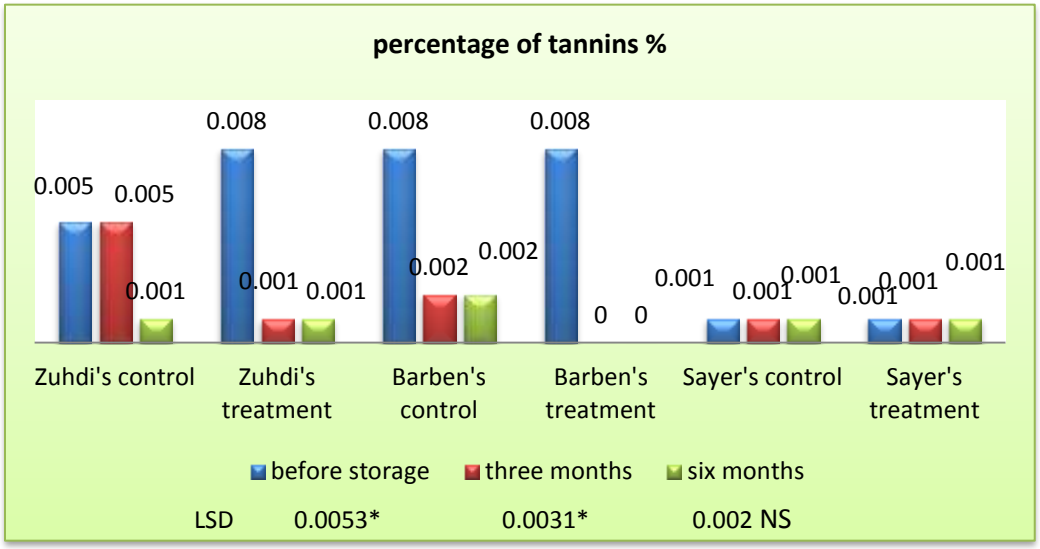


**Figure 8. Effect of ethyl formate treatment and storage periods on the percentage of tannins for date cultivars**

**Total acidity**

Figure (9) shows the effect of ethyl formate treatment and storage period on the percentage of total acidity of the varieties (Zuhdi, Al-Sayer, and Barben). Significant differences were found among the cultivar samples during each storage period at the probability level ($P \leq 0.05$). In the pre-storage period, the highest value of the total acidity percentage of the Sayer control sample was 0.064%. The lowest value was for the Sayer treatment sample, 0.012%. As for the three months of storage, we find the highest value of the percentage of total acidity of the Sayer control sample, which amounted to 0.115%. While the lowest value was for the Barben treatment sample, which amounted to 0.038%, the highest value was in the six-month storage period for the Zuhdi control sample, which amounted to 0.089%, and the lowest value for the percentage of total acidity was for the barben treatment sample, and the value was 0.038%. Djaoudene *et al*., (26) reported the acidity values were 0.16% - 0.33% and close to the results obtained by (34), which amounted to 0.03 to 0.14 g of malic acid / 100 g of dry weight. Through the results in Figure (9), it has been noticed that there were significant differences between the control samples and the treatment samples for each variety during the storage periods, meaning that the treating with ethyl formate reduced the total acidity in the treatment samples relative to the control samples for each variety. However, there were no significant differences among the values of acidity percentages. Total for each sample during storage periods.

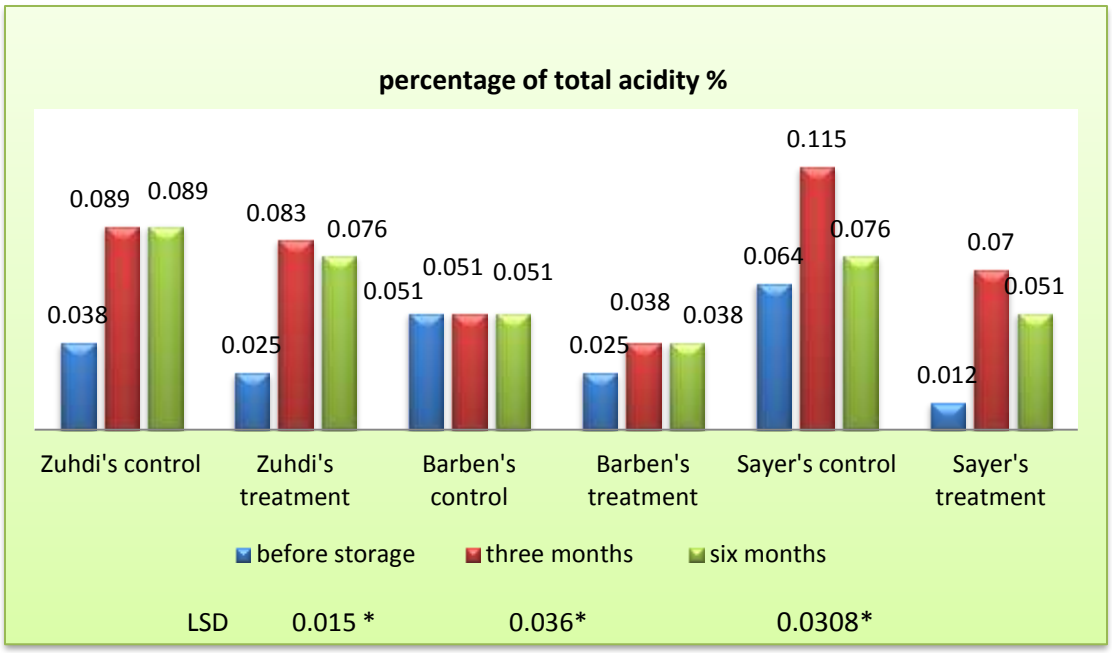


**Figure 9. Effect of treatment with ethyl formate and storage periods on the percentage of total acidity of date cultivars**

**Estimation of metallic elements**

Table (1) shows the concentration of mineral elements in three varieties of date palm (Zuhdi, Barben, and Al-Sayer) using an atomic absorption flame device, where the concentration of seven mineral elements was diagnosed and estimated, namely (K, Cr, Ca, Na, Mg, Zn, Fe The results in Table (1) in the pre-storage period showed that there were significant differences between the values of mineral element concentrations for the three studied varieties at the probability level (P≤0.05). We found the highest concentration of metallic elements (K, Cr, Ca, Na, Mg, Zn, Fe) for the Sayer treatment sample, which amounted to (84.9, 8.6, 7.9, 7.1, 178.9, 1.73, 152.3 ppm, respectively, and it was the lowest value for the concentrations of metallic elements (K, Cr, Ca, Na, Mg, Zn, Fe) for the Zuhdi control sample, which reached (68.9, 4.1, 3.5, 3.6, 136.5, 0.5, 98.6) ppm, respectively. We note from the results that there are no significant differences among the values of mineral element concentrations for the control sample and the treatment sample for the same variety. That is, the treatment with ethyl formate did not affect the concentrations of metallic elements. Moreover, we notice, after three months of storage, that there are significant differences at the probability level (P≤0.05) between the values of the concentrations of mineral elements for the three varieties (Zuhdi, Barben, and Al-Sayer), where we find the highest value of the concentrations of metallic elements (K, Cr, Ca, Na, Mg, Zn, Fe) for the Sayer treatment sample, which amounted to (68.9, 4.2, 4.0, 3.5, 104.5, 0.51, 84.9) PPM, respectively, while it was less A value for the concentrations of mineral elements (K, Cr, Ca, Na, Mg, Zn, Fe) for the Barben control sample and the values were (50.8, 2.3, 2.2, 1.7, 81.4, 0.25, 62.8) PPM, respectively. It was found through the results

that there were no significant differences between the values of the concentrations of mineral elements for the control sample and the treatment sample for the same variety, meaning that the treatment with ethyl formate did not affect the concentrations of mineral elements. The results showed, after six months of storage, that there were significant differences at the probability level ($P \leq 0.05$) between the values of the mineral element concentrations of the three types (Zuhdi, Barben, and Al-Sayer), where we find the highest value for the concentrations of mineral elements (K, Cr, Ca, Na, Mg, Zn, Fe) for the Sayer treatment sample, where the concentrations reached (60.5, 3.4, 3.4, 3.0, 99.5, 0.41, 78.5) ppm, respectively, while the lowest value was for the concentrations of metallic elements (K, Cr, Ca, Na, Mg, Zn), Fe) for the Barben control sample and the concentrations were (51.8, 1.8, 1.7, 1.2, 77.1, 0.20, 57.8) PPM respectively. The results also showed that there were no significant differences between the values of the concentrations of the seven metallic elements mentioned for the control samples and the treatment samples for the same class, i.e., there is no effect on the concentrations of mineral elements as a result of treating date varieties (Zuhdi, Barben, and Al-Sayer) with ethyl formate. The results showed a decrease in the concentrations of mineral elements as the storage period progressed from three months to six months. The results showed that the best concentrations were generally during the mentioned storage periods. It had Ca, K, and Fe elements, followed by Zn, Mn, and Na elements, while it was the lowest b for the element Cr, and these results agree with what he mentioned by (24 ,19), as well as agree with the results of (11, 16 ,34). The concentration of minerals in date fruits as affected by soil fertility, diversity, and maturity stage (36).

**Table 1. Effect of ethyl formate treatment and storage periods on the concentration of mineral elements in the studied varieties. (concentration ppm)**

| Mineral element analysis values before storage | | | | | | | |
|---|---|---|---|---|---|---|---|
| Fe | Zn | Mg | Na | Ca | Cr | K | Sample code |
| 68.9 | 4.1 | 3.5 | 3.6 | 136.5 | 0.58 | 98.6 | Zuhdi's control |
| 69.4 | 5.6 | 4.2 | 4.4 | 144.5 | 0.63 | 113.5 | Zuhdi's treatment |
| 74.6 | 4.6 | 4.7 | 4.5 | 154.8 | 1.58 | 120.8 | Barben's control |
| 76.8 | 7.4 | 5.3 | 6.0 | 164.8 | 1.64 | 129.9 | Barben's treatment |
| 81.5 | 5.0 | 6.2 | 5.6 | 162.3 | 1.66 | 147.9 | Sayer's control |
| 84.9 | 8.6 | 7.9 | 7.1 | 178.9 | 1.73 | 152.3 | Sayer's treatment |
| 7.75 * | 1.90 * | 1.69 * | 1.85 * | 21.94 * | 0.804 * | 18.70 * | LSD value |
| Evaluation of metallic element analysis after three months of storage | | | | | | | |
| Fe | Zn | Mg | Na | Ca | Cr | K | Sample code |
| 54.8 | 3.1 | 2.7 | 2.4 | 92.7 | 0.41 | 79.2 | Zuhdi's control |
| 62.5 | 3.5 | 3.6 | 2.8 | 96.5 | 0.45 | 84.1 | Zuhdi's treatment |
| 58.9 | 3.7 | 3.4 | 2.9 | 97.5 | 0.44 | 81.4 | Sayer's control |
| 68.9 | 4.2 | 4.0 | 3.5 | 104.5 | 0.51 | 84.9 | Sayer's treatment |
| 50.8 | 2.3 | 2.2 | 1.7 | 81.4 | 0.25 | 62.8 | Barben's control |
| 52.4 | 2.5 | 2.8 | 2.4 | 85.4 | 0.28 | 65.4 | Barben's treatment |
| 8.276 * | 0.804 * | 0.791 * | 0.890 * | 8.95 * | 0.161 * | 7.03 * | LSD value |
| Evaluation of mineral analysis after six months of sorting | | | | | | | |
| Fe | Zn | Mg | Na | Ca | Cr | K | Sample code |
| 47.9 | 2.4 | 2.0 | 2.0 | 88.7 | 0.35 | 75.4 | Zuhdi's control |
| 50.1 | 3.0 | 3.0 | 2.2 | 91.4 | 0.30 | 76.8 | Zuhdi's treatment |
| 56.4 | 3.5 | 3.0 | 2.3 | 90.8 | 0.36 | 80.8 | Sayer's control |
| 60.5 | 3.4 | 3.4 | 3.0 | 99.5 | 0.41 | 78.5 | Sayer's treatment |
| 51.8 | 1.8 | 1.7 | 1.2 | 77.1 | 0.20 | 57.8 | Barben's control |
| 54.9 | 2.0 | 2.0 | 2.0 | 80.2 | 0.21 | 60.9 | Barben's treatment |
| 6.924 * | 0.729 * | 0.706 * | 0.855 * | 8.391 * | 0.152 * | 6.833 * | LSD value |

**Vitamin rating**

Table (2) shows the values of vitamins estimation in ppm units in the extracts of three varieties of dates (Zuhdi, Barben, and Al-Sayer) when separation and diagnosis were made using HPLC high-performance liquid chromatography in the presence of standard vitamins and by analyzing the extracts of three varieties of dates (Zuhdi, Baraben, and Al-Sayer). The vitamins B1, B2, B5, C, A, and Folic acid are present in all the varieties under study, and it is noted through the results that the retention time of the standard vitamins is similar to their content in the three classes, and this is consistent with the results (11). Table (2) shows the effect of treatment with ethyl formate on the concentrations of these vitamins in the studied varieties and during the pre-storage periods and the three- and six-month storage period. (23) As well as the presence of significant differences between the values of vitamin concentrations for the treatment samples and the control samples for the same variety at the probability level ($P\leq 0.05$). Sayer, which amounted to 68.29 ppm, while the highest concentration of vitamins A, B1, and B2 was for the Zuhdi treatment sample and amounted to (477.38, 258.70, 133.16) ppm, respectively, and the lowest concentration of these three vitamins was for the Sayer control sample. It amounted to) 91.66, 75.80, 34.30. As for vitamin B5, the highest concentration was for the Barben treatment sample, which amounted to 2.669.18 ppm, and the lowest concentration for the Zuhdi control sample was 314.25 ppm. In comparison, the highest concentration of vitamin Folic acid for the Zuhdi treatment sample was 692.70 ppm, and the lowest concentration for the Sayer control sample was 106.90 ppm. After three months of storing the studied varieties and treatment, we noticed a general decrease in the concentrations of vitamins. However, the concentrations of vitamins for the treatment samples were higher than the concentrations of vitamins for the control samples and for all varieties studied, where the highest concentration of vitamins 1B, B2, B5, vitamin C, vitamin A, and Folic acid was for the Sayer treatment sample, where the concentrations were (7.308, 6.354, 28.903, 9.511, 10.174, 20.983) ppm, respectively, while the lowest concentration of these vitamins was For the Barben control sample, the concentrations were (0.934, 0.258, 1.077, 1.386, 1.677, 0.848) ppm, respectively. The results in Table (2) show that after six months of storage for the studied varieties and treatment, we find that the concentrations of vitamins also decreased, but with a small difference from the three months. Respectively, the lowest concentration of these vitamins was for the Barben control sample, where the concentration was (0.942, 1.829) ppm, respectively. As for vitamins B2, B5, and Folic acid, the highest concentration for the treatment sample was (2.905, 17.697, 11.630) ppm, respectively, and less The concentration of these vitamins was for the Barben control sample, which amounted to (0, 5.411, 1.879) PPM, respectively, where we notice that there is no concentration of vitamin B2 for the Barben control sample after six months of storage. As for the concentration of vitamin B2, the highest concentration of the Sayer treatment sample was 3.821 parts. The lowest concentration was for the Barben control sample, which amounted to 2.039 PPM. The best concentrations of vitamins B1, B2, B5, vitamin A, and Folic acid and the lowest concentration of vitamin C were in dates, which is consistent with what I mentioned US Department of Agriculture USDA (40).

**Table 2. Effect of treatment with ethyl formate and storage periods on the concentration of vitamins in the studied varieties (concentration PPM)**

| The concentration of vitamins before storage | | | | | | |
|---|---|---|---|---|---|---|
| Vit Folic | Vit B5 | Vit $B_2$ | Vit $B_1$ | Vit A | Vit C | Sample code |
| 211.17 | 314.25 | 71.720 | 77.982 | 299.54 | 152.34 | Zuhdi control |
| 692.70 | 1041.95 | 133.16 | 258.70 | 477.38 | 211.45 | Zuhdi'streatement |
| 339.24 | 639.36 | 89.43 | 154.20 | 126.81 | 70.43 | Barben control |
| 666.62 | 2,669.18 | 111.39 | 211.60 | 341.99 | 161.13 | Barben'streatment |
| 106.90 | 12730 | 34.30 | 75.80 | 91.66 | 68.26 | Sayre's control |
| 485.97 | 908.37 | 129.77 | 179.82 | 455.49 | 278.53 | Sayer's treatment |
| 196.37 * | 238.15 * | 39.02 * | 47.95 * | 52.61 * | 16.73 * | LSD value |
| The concentration of vitamins after three months of storing | | | | | | |
| Vit Folic | VitB5 | $VitB_2$ | $VitB_1$ | Vit A | VitC | Sample code |
| 4.198 | 11.235 | 2.102 | 3.164 | 4.179 | 4.609 | Zuhdi's control |
| 11.461 | 27.207 | 4.709 | 5.122 | 7.471 | 8.011 | Zuhdi's treatment |
| 0.848 | 1.077 | 0.258 | 0.934 | 1.677 | 1.386 | Barben's control |
| 3.443 | 4.770 | 2.187 | 1.3526 | 2.444 | 2.080 | Barben treatment |
| 8.340 | 15.968 | 4.304 | 3.587 | 6.502 | 6.825 | Sayer's control |
| 20.983 | 28.903 | 6.354 | 7.308 | 10.174 | 9.511 | Sayer's treatment |
| 5.03 * | 4.72 * | 1.86 * | 2.19 * | 3.07 * | 2.61 * | LSD value |
| The concentration of vitamins after six months of storing | | | | | | |
| Vit Folic | VitB5 | $VitB_2$ | $VitB_1$ | Vit A | Vit C | Sample code |
| 8.978 | 13.629 | 2.151 | 3.697 | 7.162 | 5.675 | Zuhdi's control |
| 11.630 | 17.697 | 2.905 | 3.684 | 7.051 | 5.503 | Zuhdi's treatment |
| 1.879 | 5.411 | 0 | 2.039 | 1.829 | 0.942 | Barben's control |
| 7.586 | 8.706 | 1.132 | 2.370 | 2.939 | 1.867 | Barben'streatment |
| 6.703 | 11.847 | 1.880 | 3.68 | 5.387 | 4.302 | Sayer's control |
| 8.301 | 16.017 | 1.623 | 3.821 | 5.670 | 4.304 | Sayer's treatment |
| 3.63 * | 4.27 * | 0.955 * | 1.27 * | 1.88 * | 2.17 * | LSD value |

## REFERENCES

1-Jabr, Kamel Salman. Hussain al-Jubouri's freedom. Ibrahim Jadu` al-Jubouri. 2005. Detection of the causes of the phenomenon of deterioration of palm trees in the Ain Al-Tamr area - Karbala governorate. Iraqi Journal of Agricultural Sciences -36 (5): 103-110.

2- Al-Bakr, Abdul-Jabbar. (1972). The date palm, its past, its present and the new in its cultivation, industry and trade. Al-Ani Press. Baghdad.

3- Al-Khazraji, Raad Muslim Ismail. 2015. The Mechanism of Planning Specific Exhibitions for Palms and Dates in the Directorate of Diwaniyah Agriculture. Iraqi Journal of Agricultural Sciences.- 46 (3): 456-664.

4- Sahi, Ali Ahmed. 1986. The Practical Book on the Technology of Dates. Directorate of Books for Printing and Publishing, University of Mosul.

5- Al-Abadi, Abbas Mereb Dakhil. 2019. Study of Some Functional Properties of Axial Inulin, Ph.D. thesis. Food science. College of Agriculture - University of Baghdad

6- Abu-Goukh, A.A., A.E. Shattir and M.M.E. Balla, 2003. Effect of harvesting method on quality and storability of dry dates in Sudan. Trop. Sci., 43:53-56.

7- Afoakwa, E.O. and S. Sefa-Dedeh, 2001. Chemical composition and quality changes occurring in Dioscorea dumetorum pax tubers after harvest. Food Chem., 75: 85-91.

8- Agomuo, E. and P. Amadi, 2018. Nutritional Properties of Oils from Various Parts of Three Varieties of Pears Consumed in South East Nigeria. *Acta Universitatis Cibiniensis. Series E: Food Technology*, 22(2), 3-12. DOI.

9- Agrawal, N., D. K. Minj, and K. Rani .2015. Estimation of Total Carbohydrate Present in Dry Fruits. IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT), 1(6): 24-27.

10- Aleid, S.M., A.M. Elansari, T. Zhen-Xing, and . A.A Sallam. 2014. Effect of Cold Storage and Packing Type on Khalas and Sukkary Dates Quality, Advance Journal of Food Science and Technology 6(5): 603-608,

11- Al-Farsi, M. and C.Y. Lee. 2008. Nutritional and Functional Properties of Dates: A Review. Critical Review in Food Science and Nutrition, 48, 887-884.

12- Al-Farsi, M., C.Alasalvar, A. Morris, M. Baron, and F. Shahidi. 2005 Compositional and Sensory Characteristics of Three Native Sundried Date (*Phoenix dactylifera* L.) Varieties Grown in Oman. Journal of Agriculture and Food Chemistry, 53, 7586-7591.

13- Alhamdan, A. B. Hassan, H. Alkahtani , D . Abdelkarim, and M. Younis .2018. Freezing of Fresh Barhi Dates for Quality Preservation During Frozen Storage, Saudi Journal of Biological Sciences 25, 1552–1561.

14- Al-Harrasi, A., N. U. Rehman, J. Hussain, A. L. Khan, A. Al-Rawahi, S. A. Gilani, M. Al-Broumi and L. Ali .2014. Nutritional assessment and antioxidant analysis of 22 date palm (*Phoenix dactylifera*) varieties growing in Sultanate of Oman. Asian Pac J Trop Med, 7, S591-S598. DOI. 10.1016/S1995-7645(14) 60294-7.

15Attaha,A.H.,Mhoder,T.Y.,andAbd,A.K.M(.2 013 )Protein Pattern of Phoenix dactylifera Seeded Strains Grown in Basrah Region Using Cluster and Principal Component Analysis. *Journal of Plant Studies*,2(2),149.

16- Ali-Mohamed, A.Y., A.S. Khamis. 2004. Mineral Ion Content of the Seeds of Six

Cultivars of Bahraini Date Palm (*Phoenix dactylifera*). J Agric Food Chem 52: 6522–6525.

17- Aljaloud,S.; H.L Colleran, S.A. Ibrahim. 2020 . Nutritional Value of Date Fruits and Potential Use in Nutritional Bars for Athletes, Food and Nutrition Sciences, 11, 463-480 .

18- Al-Mashhadi, A.S., A.F. Al-Shalhat, A. Faoual, A.A. Abo-Hamrah. 1993. Storage and preservation of Dates at Rutab Stage. In: Proceedings of the Third Symposium on the Date Palm in Saudi Arabia, King Faisal University, Al-Hassa, Saudi Arabia, January 17–20, pp. 253–266 .

19- Al-Ogaidi, H.K. and H.H. Mutlak, 1986. The Phenolic Compounds of Four Date Cultivars During Maturity Stages. Date Palm J., 4: 191-196.

20- Al-Shahib, W. and R.J Marshall. 2003 The Fruit of the Date Palm: Its Possible Use as the Best Food for the Future? International Journal of Food Sciences and Nutrition, 54, 247-259.

21- Al-Yahyai, R., A. Manickavasagan .2012. An Overview of Date Palm Production. In: Manickavasagan A, Essa MM, Sukumar E (eds) Dates: production, processing, food, and medicinal values. CRC Press, Boca Raton, pp 3–12

22- AOAC (Association of Official Analytical Chemists) 1995. Official Methods of Analysis, 16th Edition. AOAC International, Gaithersburg, MD.

23- Aslam, J., S.H. Khan, S.A. Khan. 2011. Quantification of Water Soluble Vitamins in Six Date Palm (*Phoenix dactylifera* L.) Cultivar's Fruits Growing in Dubai, United Arab Emirates, through high performance liquid chromatography. J Saudi Chem Soc 17: 9–16.

24- Assirey, E. A. R. 2015. Nutritional Composition of Fruit of 10 Date Palm (*Phoenix dactylifera* L.) Cultivars Grown in Saudi Arabia. J Taibah Univ Med Sci, 9(1), 75-79. DOI. 10.1016/j.jtusci.2014.07.002

25- Barreveld, W.H. 1993 Date palm products Food and Agriculture Organization of the United Nations, Agricultural Services Bulletin no. 101, Food and Agriculture Organization of the United Nations Rome, Italy.

26- Budrat, P. and A. Shotipruk.2008. Extraction of phenolic compounds from fruits of Bitter Melon (Momordica charantia) with subcritical water extraction and antioxidant activities of these extracts. Chiang Mai J. Sci. 35(1): 123-130.

27- Djaoudene,O., M,B. bey, H. louaileche,.2019. physicochemical characteristics and nutritional compositions of some date (*phoenix dactylifera* l.) fruit cultivars acta universitatis cibiniensis series e: food technology 129 vol. no. 2

28- Dubois, M., K. A. Gilles, Hamilton, J. K., P. T. Rebers and F. Smith.1956. Colorimetric method for determination of sugars and related substances. Analytical chemistry, 28(3), 350-356.

29- FAOSTAT . 2019. Crops.

30- Fayadh, J. and S Al-Showiman. 1990. Chemical composition of date palm (*Phoenix dactylifera* L.). *J. Chem. Soc. Pak*, 12(1), 84-103.

31- Howrtiz , W. 1995. Official Methods of Analysis.16th edition. Association of Jain SM .2007. Recent advances in date palm tissue culture and mutagenesis. Acta Hortic 736:205–211.

32- Jain, S.M., J.M. Al-Khayri, D.V. Johnson.2011. Date Palm Biotechnology . Springer Science+Business Media B.V. 2011.

33-Jain, S.M., 2007. Recent advances in date palm tissue culture and mutagenesis. Acta Hortic 736:205–211

34- Kuras,M.J., M. Zielin´ska-Pisklak, J. Duszyn´ska, J. Jabłon´ska .2020. Determination of the Elemental Composition and Antioxidant properties of Dates (Phoenix dactyliferia) originated from different regions. J Food Sci Technol.

35- Lemine, F. M. M., A. Samb, O. B. Zein el Abidine, M. V. Ahmed, T.-K. O. Djeh and A. O. M. Boukhary .2014. Assessment of physicochemical diversity in fruit of Mauritanian date palm (*Phoenix dactylifera* L.) cultivars. African J Agric Res, 9(28), 2167-2176. DOI. 10.5897/AJAR2013.8250.

36- Marzouk, H.A., H.A. Kassem .2011. Improving fruit quality, nutritional value and yield of Zaghloul dates by the application of organic and/or fertilizers. Sci Hortic 127:249–254.

37-Miller, G. L. 1972. Use of Dinitrosalicylic Acid Reagent for Determination of Reducing Sugar. Analytical chemistry, 31(3), 426-428. official Analyticl chemists , Washington , D.C. , U.S.A.

38- Parvin, S., D.Easmin, A.Sheikh, M. Biswas, S. C. D. Sharma, M. G. S. Jahan, M. A. Islam, N. Roy and M. S. Shovon .2015. Nutritional analysis of date fruits (*Phoenix dactylifera* L.) in perspective of Bangladesh. *Am J Life Sci*, 3(4), 274-278. DOI. 10.11648/j.ajls.20150304.14

39- Thouri, A., H. Chahdoura, A. El Arem, A. O.Hichri, R. B. Hassin and L. Achour. 2017. Effect of Solvents Extraction on Phytochemical Components and Biological Activities of Tunisian Date Seeds (var. Korkobbi and Arechti). BMC complement alternat med, 17(1), 248. DOI. 10.1186/s12906-017-1751-y

40- USDA . 2020. Food Data Central: Dates, medjool

41- Van Dijk, D. ; V.J.G. Houba .2000. Homogeneity and Stability of Material distributed within the Wageningen Evaluating Programmes for Analytical Laboratories Commun. Soil.Sci.Plant.Anal, 31 (11-14), 1745-1756

42- Wodaje, A. and A. Alemayehu .2017. Determination of Heavy Metal Concentration in Soils used for Cultivation of Allium Sativum L. (garlic) in East Gojjam Zone, Amhara Region, Ethiopia, Addis & Abebaw, Cogent Chemistry ,3: 1419422.