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STUDY OF THE COMPOSITION AND FUNCTIONAL PROPERTIES OF ZAHDI DATES POMACE REMAINS FROM DATE SYRUP INDUSTRY

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ABSTRACT

The current study was carried out to investigate phenolic compounds in zahdi dates pomace that remains from date syrup industry. The experiment was included studying the chemical content of (50:50v/v) alcohol-aqueous extract of zahdi date pomace, quantitative estimation of phenolic compounds and its antioxidant efficacy by assessing its ability to bind iron(ll) ion and scavenging hydrogen peroxide. Results of chemical analysis of zahdi date pomace showed that the moister and ash percentage reached 6% and 3, 45%, while the total content of sugars, fats and protein reached 20.7, 1.808 and 2.989g/100g respectively. Quantitative estimation of total phenols and flavonoids in alcohol extract of zahdi date pomace showed increasing in total phenols content(TPC) amounted 151mg/100g, while total flavonoids content(TFC) reached 16.4mg/g estimated depending on dry weight. Phenolic extract of zahdi date pomace showed an ability to bind iron (ll) ion in comparison with EDTA-2Na compound and citric acid using different concentrations. Results also showed that the best ability of zahdi pomace to bind iron (ll) ion in 2, 4 and 8mg/ml concentration at $P<0.01$. Whereas, the ability of zahdi date pomace to scavenging hydrogen peroxide reached 55% compare to ascorbic acid.

Keywords **:** *Phoenix dactylifera*, zahdi cultivar, iron (ll) ion, dates pomace.

Introduction

Date palm (*Phoenix dactylifera* L.) is an important tree that belongs to Palmaceae (Arecaceae) and it is one of the oldest cultivated plants. It is grown in many regions globally including Asia, Africa and Middle East (Nasir *et al*., 2015). Date fruits contain some important nutrients provides human body with energy as well as it is consider as valuable commercial crop and there are nearly 2000 different varieties including 650 in Iraq (AL-Mudhafer, 2019). The productivity and consuming of dates have been increased as the global yield reached 7.5 million metric ton (FAOSTAT, 2016) and in Iraq, the production of dates reached 662 thousands metric ton in 2015 (FAOSTAT, 2015) which presents about 11% of global yield. Nutritional analysis of date fruit showed that it mainly contains carbohydrates (70-80%) as a sugars that are easy for the body to absorb, in addition, dates and their products are rich source of minerals such as calcium, potassium and iron (Al-Farsi *et al*., 2007). The interest of researchers in the field of health and food has been increased recently particularly the importance of eating functional foods for its role in preventing many chronic diseases such as heart diseases and cancer (Maqsood *et al*., 2020).

Date extracts are characterized by their antioxidant activity, which is mostly attributed to their content of phenolic compounds that considered as natural antioxidant and can curb damage from fat oxidation, nucleic acids and proteins through its ability to break down free radicals and inhibit LDL oxidation. Studies showed that eating food rich of phenols associated with lower deaths caused by the coronary artery disease (Borochov-Neori *et al*., 2015; Nasir *et al*., 2015). Many studies have been done on the phenolic structure of various dates cultivars in last decade (Bammou *et al*., 2014; Al-Harrasi *et al*., 2016), however, only few studies mentioned some information about secondary products and its related phenolic compounds.

Date syrup is a product that made from second-class dates in a big amount in Iraq, most amounts is exported and the rest is used as sweet syrup and in many food industries. Dates pomace is a secondary product remaining from date syrup industry and presents about 50% of produced syrup weight (Mazaheri and Nikkhah, 2002), and it used as animal feed or thrown in an open places which causes environmental and economic problems. Due to the lack of information on the structural and functional properties of date pomace, the current study was conducted to investigate these properties.

Materials and Methods

All chemical substances and solutions used in this study produced by BDH Company (United Kingdom). Samples of seedless zahdi date pomace were collected from Faculty of Agriculture factory, University of Kufa in May 2018, and then dried under the sun light at average of 35^0C for 7 days. Date pomace samples were grinded in laboratory using Heilbron mill (Germany) then kept in closed polyethylene bags at -18^0C until used.

Preparation of extract

Zahdi date pomace was prepared following Biglari *et al*. (2008) procedure by weighting 100g of dry pomace powder then 300ml of water-methanol solvent (50:50 v/v). Extraction was done in room temperature for 5 hours with continuous shaking then filtered by filter paper (Whatman No.1) and centrifuged on 4000 c/m for 10 minutes. Extract was concentrated at 40^0C for 3 hours using rotary evaporator to get raw extract which was kept in dark closed bottle in refrigerator until used.

Chemical analysis

Moisture and ash were estimated according to A.O.A.C. (1990) ant total carbohydrates was estimated following Masuko *et al.* (2005) method, while total fat estimated using Fringsand Dunn, (1970) procedure and total protein was estimated using Bradford method (Kruger, 2009).

Estimation of total phenolic compounds

Total phenolic compounds in the extract of zahdi date pomace was estimated following Ayoola *et al.* (2008) method by adding 2.5ml of Folin-Ciocalteu reagent to 0.5ml of alcohol extract of zahdi pomace (1mg/ml) then the mixture was left in room temperature for 10 minutes after that 2ml of Na_2CO_3 7.5% was added and the mixture was left at 25º for 30 minutes then absorbance was measured at a 760 nm. All determinations were performed in triplicates. Total phenolic contents obtainedwere obtained from the regression equation of the calibration curve of gallic acid (y = 0.0243x = 0.0201, R2 = 0.97), and expressed as gallic acid equivalents (GAE).

Estimation of total flavonoid compounds

The procedure of Ayoola *et al.* (2008) was used to estimate flavonoid compounds in alcohol extract of zahdi pomace when 2ml of $AlCl_3$ at 2% concentration was added to 2ml of (1mg/ml) extract then the mixture was shaken well and left for one hour at room temperature then absorbance was measured at a 420 nm. Determinations were performed in triplicates. Total flavonoid contents were obtained from the regression equation of the calibration curve of rutin (y = 2.9215x + 0.3292, R2 = 0.93), and expressed as rutin equivalents (RE).

The ability of Zahdi pomace to bind ferrous ion

The ability of zahdi pomace extract to bind ferrous ion was estimated following Rashad *et al.* (2015) method. 1ml of different concentrations (2-10 mg/ml) of zahdi pomace extract was mixed with 3.7ml of methanol and 0.1ml of ferrous chloride at 2 mm then 0.2ml of Ferrozine at 5 mm. The mixture was left at room temperature for 10 minutes then absorbance was measured at a 562 nanometer wavelength. The low absorbance indicates the power to bind ferrous ions. The control sample was prepared using the same method with adding phenolic extract as follows:

Chelating effect (%) = [1– absorbance sample / absorbance control] x 100%

The ability to scavenging hydrogen peroxide

The ability of the phenolic extract of zahdi pomace to scavenging hydrogen peroxide was estimated following Ruch *et al.* (1989) by mixing 1 ml of the extract prepared at 1-7 mg/ml concentration with 0.6 ml of hydrogen peroxide at 2 mm concentration (was prepared in phosphate solution at 7.4 pH then after 10 minutes then absorbance was measured at a 230 nanometer wavelength. The control sample was prepared using the same method without adding the sample with using ascorbic acid and rutin compound as a control samples then the ability of the phenolic extract of zahdi pomace to scavenging hydrogen peroxide was as follows:

Scavenging hydrogen peroxide % =

$$\left[\frac{\text{absorbance of sample} - \text{absorbance of control}}{\text{absorbance of control}}\right] \times 100$$

Statistical analysis:

Data were analyzed by using Statistical Analyses System - SAS (2012) program and Chi-square test was used to compare significant differences between phenolic extract of zahdi pomace and Ethylene Di-amine Tetra acetic acid Di-sodium (EDTA-2Na) compound with citric acid to determine the significance on affecting the ability to bind ferrous ion and between phenolic extract of zahdi pomace and ascorbic acid and its effect on scavenging hydrogen peroxide according equation below:

$$X^2 = \sum \frac{(ObservedNo. - ExpectedNo.)^2}{ExpectedNo.}$$

Results and Discussion

Chemical analysis

Results of chemical analysis showed decreasing in moisture percentage % in zahdi pomace powder and recording 6% (Table 1) and it was less than the finding of Al-Farsi *et al.* (2007) who studied the structural and functional properties of some Omani dates cultivars and its residues when the average of moisture reached 9.5%, while Mohammed, (2017) mentioned that moisture content in Iraqi zahdi date was 12.6 in mature stage on the basis of fresh weight. Aljazy, (2019) found that the moisture of zahdi residues amounted 9.36% which is higher than current study results.

Ash percentage in zahdi date pomace amounted 3.45% which consistent with the finding of Al-Farsi *et al.* (2007) and close to Pattara *et al.* (2010) results on olive pomace when recorded about 3-4% of ash. Marchiani *et al.*, (2016) confirmed that the percentage of ash amounted 8.26 in grape pomace and the percentage of ash in residues was differed depending on the type of treatments. The percentage of ash and other chemical contents of plant residues which are remained from food industries of fruits and vegetables was affected by many factors such as plant cultivar, it genetic structure, ecological factors (salinity, irrigation water), fertilizers and pesticides, pollution by dust during harvesting, methods and storage period before processing, treating type and the places of gathering agricultural residues (environmental conditions of these residues, drying methods and extraction methods) (Al-samaraee, 2010; Lima, 2017).

Table 1 : Chemical composition of zahdi date pomace.

Chemical composition	Content
Moisture%	6
Ash%	3.45
Total Carbohydrates g/100g	20.8
Total Fat g /100g	1.808
Total Proteinm g/100g	2.989

Results also showed that the total carbohydrates in zahdi pomace reached 20.8g/100g (Table 1) and can take an advantage of this amount many industrial fields despite of it was less than in mature zahdi date 86.5% (Ali, 2017). In general, the average of carbohydrates in mature dates amounta 77.13g/100g (Naushad and Lichtfouse, 2019), so the amount of zahdi pomace in this study was higher compare to the amount of carbohydrates in some plant residues such as olive pomace 18.4 g/100g (Haddadin *et al.*, 1999) and 48g/100g in apple pomace on the basis of dry weight (Joshi and Attri, 2006) and this mainly occurred due to the treatments type during dates syrup industry.

The amount of total fats in zahdi pomace powder in current study reached 1.808g/100g and this consistent with Al-Farsi *et al.* (2007) who recorded 1.58, 1.40 and 2.2g/100g respectively in Aum sala, Almublsi, and Omani Sahal dates. While, Aljazy, (2019) mentioned an increasing in the amount of fat in zahdi dates pomace when recorded 8.56g/100g. Fat amount in date pomace is affected by date cultivar and process method of syrup. The chemical structure of date syrup was studied by El-Nagga and El-Tawab, (2012) who recoded 2.40g/100g of total fats on the basis of fresh weight. The total protein in zahdi date pomace of this study was increased and amounted 2.989g/100g in comparison with zahdi date pulp in mature stage which amounted 2.12% (Mohammed, 2017), generally, the average of protein is considered higher due to its content of different amino acids (Al-Farsi and Lee, 2008).

Total of phenolic content

The amount of phenolic compounds in zahdi pomace powder was estimated on the basis of Gallic acid 100/g of dry weight. Figure 1 showed that the amount of phenolic compounds reached 151mg/100g and this consistent with Alya, (2011) who mentioned that the highest amount of phenolic compounds in Iraqi zahdi dates was 161.11mg/100g when it was extracted by water and ethanol and the lowest amount was 103.88mg/100g when extracted by hexane. Abdul-Hamid *et al.* (2019) compared between the total phenolic content in pulp and seed of dates in Algerian (Deglet) and Saudi (Ajwa) cultivars and recorded 3.49, 10.37 and 3.25, 9.85mg Gallic acid/g of pulp and seed respectively estimated on the basis of dry weight. The differences in the amount of phenolic compounds depending on date cultivar, cultivation conditions, mature degree, environmental conditions during mature stage, temperature and sun light which increases the content of phenolic compounds and the solvent type used in the extraction processes (Al-Farsi *et al.*, 2005).

Total content of flavonoids

Results of Figure 1 showed decreasing in total content of flavonoids in comparison with total phenols in in zahdi date pomace powder that extracted by water and methanol when recorded 16.4mg rutin acid/100g on the basis of dry weight. This decreasing may occurred mainly due to high temperatures during drying dates and syrup process stages (Paes *et al.*, 2014). However, flavonoids amount in current study is considered higher compare to pulp content of flavonoids in fresh date during mature stage, Hamad *et al.*, (2015) mentioned that the highest content of total flavonoids reached 2.821mg rutin acid/100g dry weight of Saffawy cultivar when they studied the metabolic analysis of different Saudi cultivars.

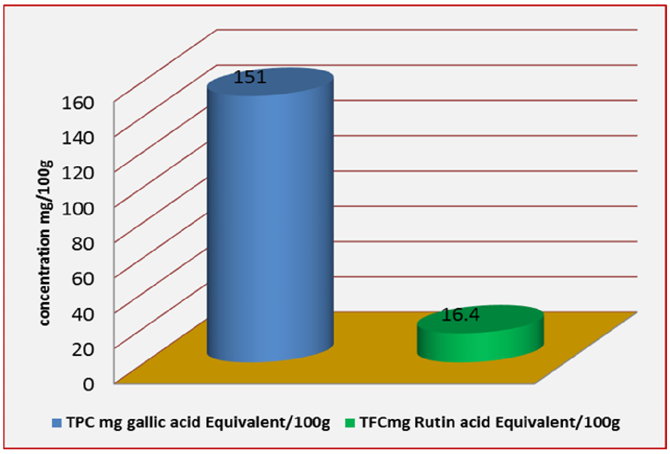

Fig. 1 : The total content of phenolic compounds and flavonoids in zahdi date pomace.

The ability of zahdi pomace to bind ferrous ion

Figure 2 showed the percentage of binding ferrous ion by the phenolic extract of zahdi pomace in comparison with Ethylene di-amine tetra acetic acid- disodium (EDTA-2Na) and citric acid using 2, 4, 6, 8 and 10 concentrations. It can be noticed that EDTA-2Na was significantly exceled citric acid and phenolic extract of zahdi pomace when it showed a high ability to bind ferrous ion reached 93.43% at 10mg/ml while, citric acid recorded 81% followed by phenolic extract of zahdi pomace with 60.80%. Results of statistical analysis showed that there were significant differences in the ability of phenolic extract of zahdi pomace, EDTA and citric acid to bind ferrous ion at 2-4mg/ml, while, there was highly significant difference (P<0.01) at 6mg/m concentration when it recorded 59.00% in EDTA. Whereas, there were no significant differences between phenolic extract of zahdi pomace, EDTA and citric acid at 8mg/ml, but it was significant (P<0.05) at 10mg/ml concentration. The best ability to bind ferrous ion was appeared in the phenolic extract of zahdi pomace at 2, 4 and 8 mg/ml due to the convergence of its effect with the standard compound EDTA and citric acid results which means that there is an economic feasibility of using the alternative substance at the mentioned concentration. It can be clearly noticed from current study results that the ability of phenolic extract of zahdi pomace to bind ferrous ion was differ depending on the concentration (Li *et al.*, 2009). This may occurred due to the ability of phenolic compounds to bind metal ions that stimulate oxidation such as iron and copper (Sarikurkcu *et al.*, 2008).

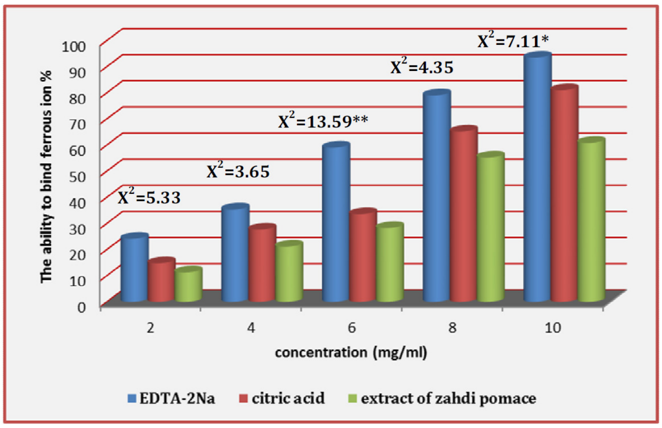

Fig. 2 : The ability of phenolic extract of zahdi pomace to bind ferrous ion.

The ability of capturing hydrogen peroxide

Results of Fig. 3 showed the ability of the phenolic extract of zahdi date pomace to scavenging hydrogen peroxide (H_2O_2) when using 1, 3, 5, and 7 mg/ml concentrations in comparison with ascorbic acid. It can be noticed that the ability of ascorbic acid to scavenging H_2O_2 was higher than zahdi date pomace as it recorded 73% at 7 mg/ml concentration compare to 55% in the phenolic extract of zahdi date pomace at the same concentration. Results statistical analysis showed that there were no significant differences between phenolic extract of zahdi date pomace and ascorbic acid in the ability of capturing H_2O_2 at all other concentrations, so any concentration can be used and give a same result when using ascorbic acid as a standard substance. These results were higher than the finding of Arshad *et al.* (2015) on dates seed extract of Ajwa and zahdi which recorded 26.90 and 26.2% respectively, and similar to what Gupta, (2016) found, as he mentioned that the ability of phenolic extracts of some plants to scavenging H_2O_2 amounted 59.78% in the peel of pomegranate, 39.46% in the peel of watermelon, 61.24% in the peel of sweet lime and 61.90% in apple seed. The capturing of hydrogen peroxide by phenolic compounds occurred due to its ability to donate electrons (Wettasinghe and Shahidi, 2000).

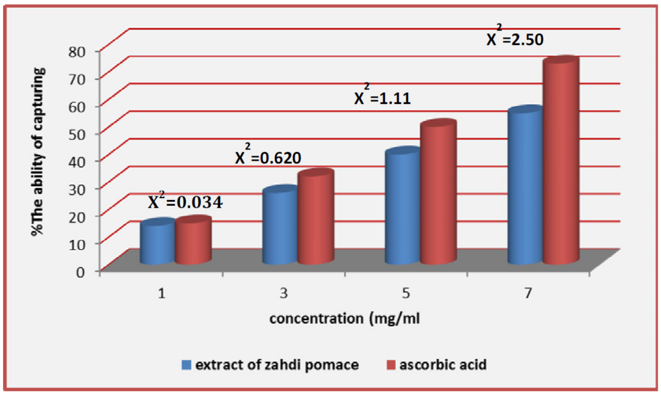

Fig 3. The ability of capturing hydrogen peroxide in zahdi pomace extract.

To conclude, results of current study showed that the potential of taking advantage from zahdi dates pomace due to its good content of natural antioxidants such as phenolic compounds in many industries particularly food industry as a preservatives which reduces the oxidative activity of processed food and thus extends its storage period. Dates pomace also contains good level of carbohydrates and protein which can be used in various industrial fields in future.

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