Some Physicochemical Properties of Date Syrup, Concentrate, and Liquid Sugar in Comparison with Sucrose Solutions

A. Farahnaky¹,², M. Mardani², Gh. Mesbahi¹, M. Majzoobi¹, and M. T. Golmakani¹

ABSTRACT

The date fruit is of high nutritional value and its chemical composition is unique in providing energy, minerals, and vitamins for human. Date syrup, date concentrate and liquid date sugar are among semi-finished liquid products produced from low quality dates at industrial scale. In this research, some physicochemical properties of date syrup, concentrate, and liquid sugar in comparison with sucrose solutions were studied and the possibility of replacing sucrose with date liquid products was investigated. The results showed that the main chemical component of all three date products was simple sugars of fructose and glucose. Ash and protein contents of date liquid sugar were much lower than date syrup. pH values of date liquid products were also significantly different. Concentration of total phenolic and flavonoid compounds in date syrup was much greater than date liquid sugar. Overall, processing of date syrup to date liquid sugar reduced its nutritional quality while improving technological properties. It can be concluded that in choosing date liquid products as raw materials in food formulation, for the products that brown color of date liquid products does not affect the appearance of the final products, usage of date syrup or date concentrate is proposed. However, in other foods where brownish color of date syrup or date concentrate deteriorates sensory attributes of the final products, date liquid sugar is suggested. Date liquid products are also good candidates for high sugar products with sugar crystallization problem.

Keywords: Fructose, Glucose, Nutritional quality, Replacing sucrose.

INTRODUCTION

Large quantities of date fruits in the desert regions of Southwest Asia, North Africa, USA, and worldwide are produced by date palm (Phoenix dactylifera L) as high-value products. There are more than 2,000 different types of dates and, depending on growing condition and date type, dates fruits vary in size, shape, and weight. Total world production has been reported to be about 6.4 million tons in 2007 and date fruit is an important product in economy of date growing countries.

Date flesh is rich in sugars, mainly fructose and glucose, but is found to be low in fat and protein (Al-Farsi and Lee, 2008). Most of date sugar is in the form of simple sugars that the human body can easily absorb (Ahmed and Ahmed, 1995). Date is a good source of many minerals such as potassium, phosphorous, magnesium, sodium, iron, and calcium (Joseph et al., 1999; Dillard and German, 2000; Prior and Cao, 2000; Wargovich, 2000). Date fruit also contains high amounts of antioxidants, which are well known to have fundamental roles in the prevention of cancers (Dragsted et al., 1993), cardiovascular disease (Renaud...
and De Lorgeril, 1992; Fuhrman et al., 1995), neurodegenerative diseases, such as Parkinson and Alzheimer diseases (Okuda et al., 1992).

Due to biological and physical characteristics of different types of date fruits, large quantities of the produced dates do not meet the minimum quality attributes for direct use. Fruit size, physical defects, or damages during harvesting and processing are among the main reasons for quality deteriorations. Therefore, low and medium quality dates that are not directly consumed by human have been used as raw materials in fermentation industry or animal feed for many years, and valued at low price.

In the recent years innovative date by-products processing are being developed aiming at producing value added products of higher quality and value. In this context, production of date by-products as sweeteners (as substitutes of sucrose) with high nutritional quality of date is a prime target. Different unit operations are being used for processing of low price dates into new products and a number of final products have been developed and marketed.

Nowadays, continuous production lines are operating to produce a wide number of date products of commercial value including date syrup, date concentrate, and liquid sugar. Date syrup has the following standard specifications: minimum Brix of 70°, pH value range of 4.2-6, maximum ash content of 2%, and a minimum reducing sugars of 58% (INSO 5075, 2013). These three date products can be used directly by the consumers or the food producing factories as semi-finished products in producing different foods such as cake, biscuit, and canned foods as sweeteners. Physicochemical and nutritional properties of these emerging products are of great importance to the consumers and food processors.

The main aim of this study was to investigate the effects of processing stages on physicochemical properties of some liquid by-products obtained from date fruit processing and compare different characteristics of date syrup, date concentrate, and date liquid sugar with sucrose solutions.

**MATERIALS AND METHODS**

Date syrup, date concentrate, and date liquid sugar were produced at an industrial scale production line (Minoo Date Factory, Shiraz Grand Industrial Estate Zone, Shiraz, Iran). The processing chart and conditions are shown in Figure 1. The low and medium quality date fruit of Kebkaab variety was used for production of date syrup, concentrate, and liquid sugar. Granular sucrose of minimum 99% purity was purchased from the local market and its properties met Iran Standard specifications and used to prepare sucrose solutions. All chemicals used in this research were of analytical grade and purchased from Merck (Darmstadt, Germany).

**Preparation of Solutions**

At three different stages of industrial production process (Figure 1), date syrup, concentrate, and liquid sugar were sampled, packed in polyethylene terephthalate, and sealed. The samples were transferred to a cold room set at 4ºC and stored for further experiments. The samples were then diluted to 12, 35, 65 and 72° Brix, using Pearson's Square. Sucrose solutions of 12, 35, 65 and 72° Brix were also prepared and tested.

**Determination of Chemical Composition**

Chemical compositions of the samples were determined according to the approved methods of Association of Official Analytical Chemists (AOAC, 1997). Measurements included moisture content by vacuum oven drying at 80°C, ash by heating at 550°C, and protein by micro-Kjeldahl method with nitrogen to protein factor of
6.25. Soxhlet method with hexane was used to determine the fat content and total carbohydrate was calculated by subtracting the total percent values of other measurements from 100. Total soluble solids (ºBrix) was determined (AOAC, 1997) with a refractometer (Carl Zeiss, Germany).

**Determination of pH and Density**

The pH value was measured with a pH-meter (pH-meter Basic 20, Iran) supplied with a glass-combined electrode (AOAC, 1997). Density was determined using 50 mL Pycnometers. To verify possible changes in their volume due to thermal expansion, each Pycnometer was calibrated with distilled water at 25°C. Pycnometers were filled with samples and placed in a thermostatic bath (±0.1°C) set at 25°C for equilibrium. The Pycnometers were then quickly weighed using a four digits Sartorius-GE412 balance (Germany) according to Cepeda and Villaran (1999).
Measurement of Total Antioxidants

The antioxidant activity was determined using the DPPH method according to Brand-Williams et al. (1995). Briefly, distinct dilutions of the extract were prepared for the test. One mL of the DPPH solution was added to 2 mL of each sample and vortexed. Solutions were stored in a dark and a dry environment for 60 minutes. The decrease in the absorbance was determined at 517 nm, using an array spectrophotometer in a 10 mm quartz cuvette. Methanol was used to zero the spectrophotometer.

Antioxidant Activity = IC50 of TBHQ/IC50 of sample

Determination of Total Phenolic Content

Total phenolic content of each sample was determined according to the Folin–Ciocalteu method (Lu et al., 2011). In a test tube, 200 µL samples, 750 µL Folin 10% were added and vortexed, after 10 minutes, 750 µL of aqueous sodium carbonate (2%) was added, and the mixture was vortexed and allowed to stand at room temperature with exclusion of light, for 60 minutes. The absorbance was read at 765 nm, using a MSE (Micro-Structured-Electrode) diode array spectrophotometer. The total phenol concentration was calculated using the calibration curve of Gallic acid as a standard, and the results were expressed as mg of Gallic Acid Equivalents (mg GAE 100 g⁻¹ sample).

Determination of Total Flavonoids Content

Aluminum chloride colorimetric method was used for total flavonoids content determination (Chen et al., 2011). Therefore, 500 µL of each sample (100 mg mL⁻¹) in methanol was separately mixed with 100 µL of 10% aluminum chloride, 100 µL of 1M potassium acetate and 2.8 mL of distilled water and kept at room temperature for 30 minutes. The absorbance of the reaction mixture was determined at 415 nm. A calibration curve of quercetin was prepared by using distinct concentration in methanol, and the total flavonoids content was expressed as Quercetin Equivalent (mg QE 100 g⁻¹ sample).

Measurement of Sugars Content

Sugars (glucose and fructose) were determined by AOAC (AOAC, 1990). An aliquot (2.5 g) of each sample was mixed with 100 mL of distilled water and the solution was homogenized. The mixture was then centrifuged at 9,200 rpm for 10 minutes. The supernatant was filtered through a 0.45 mm membrane and 20 mL of filtrate was injected to HPLC, with an Agilent 1200 series, equipped with a Refractive Index Detector (RID), Chemstation software (Agilent Technologies), a quaternary pump, an online vacuum degasser, an autosampler and a thermostated column compartment, on an Agilent Zorbax Carbohydrate, 4.6x250 mm (FT), 5 µm (ID), column, at a flow-rate of 0.8 mL min⁻¹. Isocratic solvent of acetonitril: deionized water (65:35 v/v) was used as mobile phase and the detector temperature and the column temperature both were 30ºC. The injected sample volume was 20 µL and total running time was 10 minutes (Caliskan and Polat, 2011).

Measurement of Hydroxymethyl Furfural (HMF)

Hydroxymethyl furfural was analyzed by HPLC method (Lo Coco et al., 1996). A sample of 1 g was mixed with 5 mL of distilled water. Then, 2 mL of Carrez 1 and 2 solutions were added and diluted to 10 mL with deionized water. The mixture was then centrifuged at 5,000 rpm for 5 minutes to remove any fine debris present in the sample. The supernatant was filtered
through a 0.45 mm membrane and 20 µL of the filtrate was injected to HPLC, with an Agilent 1200 series, equipped with a Diode Array Detector (DAD) and UV detector, Chemstation software (Agilent Technologies), a quaternary pump an online vacuum degasser, an autosampler and a thermostated column compartment, on an Agilent Zorbax Eclipse XDB-C18, 4.6×150 mm (FT), 5 µm (ID), column, at a flow-rate of 1 mL min\(^{-1}\). Isocratic solvent of acetonitril: deionized water (15:85 v/v) was used as mobile phase and total running time was 5 minutes. The chromatograms were plotted at 285 nm.

**Measurement of Mineral Elements**

The method described by AOAC (1997) was used for minerals analysis (Ca, Zn, Cu, Fe, Mn and Mg). The mineral elements were determined by an atomic absorption spectrophotometer (Shimadzu, Model AA670G). Sodium and potassium contents (Na and K) were determined by the flame photometer (Model 405 CORNING, England).

**Statistical Analysis**

The results are given as means±standard deviation of at least three independent determinations. One way Analysis Of Variance (ANOVA) was used to compare the means and then the means were separated by Duncan’s multiple range test. All statistical analysis was performed at \(P<0.05\) using the SPSS 17.0.

### Results and Discussion

The objective of the research was to investigate the potential of using date processing products in different food products. Therefore, the three date products were diluted to different concentrations to cover a wide range of applications from drinks to jams. The comparison was made against sucrose solutions to determine the potentials of date processing products to replace sucrose as the main sweetener in food industry.

#### Chemical Composition of Date Syrup, Concentrate, and Liquid Sugar

Table 1 presents the chemical compositions of date syrup, date concentrate, and date liquid sugar. Moisture, ash, protein, and fat content of date syrup were 24.07, 2.18, 1.43, and 0.005%, respectively. These results were in agreement with those reported by Al-Hooti et al. (2002) and El-Sharnouby et al. (2009) for type and range of the chemical compositions. Moisture, ash, protein, and fat content of date liquid sugar were 27.17, 0.02, 0.61, and 0.004%, respectively. There was a significant difference between the protein content of date syrup and those of date concentrate and liquid sugar. The ash contents of date syrup and concentrate were more than 2% while this value for date liquid sugar was 0.02%, which is due to purification process and removing of minerals and other insoluble compounds and impurities. The pH values of date syrup (the
The pH values of solutions of date syrup, concentrate, liquid sugar, and sucrose solutions with a wide range of Brix values are presented in Table 2. Overall, the pH values of all date liquid products were significantly lower than their corresponding sucrose solutions. The maximum and minimum pH values recorded for all date products were 4.62 and 3.33, respectively, while these values were 7.88 and 7.38 for sucrose solutions. This can have practical implications in using date products instead of sucrose, i.e. high percentages of date syrup, date concentrate or date liquid sugar can reduce the final pH of food formulations in comparison with sucrose solutions. A general trend of increasing pH with decreasing Brix in all three date products and sucrose solution was also observed. For example, the pH of date liquid sugars with Brix values of 12, 35, 65 and 72 were 4.06, 3.53, 3.39 and 3.33, respectively. Higher concentrations of date processing products caused greater pH reduction, which is due to the fact date syrup, concentrate, and liquid sugar all add compounds to water that are able to reduce pH. These could come from organic acids present in date fruit or produced during processing. This trend was also seen for sucrose solutions.

| Table 2. pH of date syrup, concentrate and liquid sugar compared with sucrose solution of 12, 35, 65, and 72° Brix (total soluble solids). |
|-----------------|---------|---------|---------|---------|
|                  | 12      | 35      | 65      | 72      |
| Date syrup       | 4.62 ± 0.01 A,b | 4.46 ± 0.01 B,b | 4.28 ± 0.02 C,b | 4.24 ± 0.01 C,b |
| Date concentrate | 4.26 ± 0.02 A,c | 4.08 ± 0.01 B,c | 3.90 ± 0.02 C,c | 3.80 ± 0.01 D,c |
| Date liquid sugar| 4.06 ± 0.02 A,d | 3.53 ± 0.01 B,d | 3.39 ± 0.04 C,d | 3.33 ± 0.04 C,d |
| Sucrose solution | 7.88 ± 0.04 A,a | 7.84 ± 0.02 A,a | 7.46 ± 0.03 B,a | 7.38 ± 0.03 C,a |

Values are mean±SD of three replicates. Different capital letters show significant difference in each row and different small letters show significant difference in each column between the treatments. All statistical analysis was performed at P<0.05.

| Table 3. Density (g cm⁻³) of date syrup, date concentrate and date liquid sugar compared with sucrose solution of 12, 35, 65 and 72° Brix at 25°C. |
|-----------------|---------|---------|---------|---------|
|                  | 12      | 35      | 65      | 72      |
| Date syrup       | 1.045 ± 0.011 D,a | 1.150 ± 0.074 C,c | 1.317 ± 0.024 B,a | 1.351 ± 0.009 A,a |
| Date concentrate | 1.044 ± 0.021 D,b | 1.150 ± 0.025 C,ab | 1.315 ± 0.105 B,b | 1.342 ± 0.067 A,ab |
| Date liquid sugar| 1.043 ± 0.014 C,c | 1.149 ± 0.003 B,b | 1.309 ± 0.011 A,d | 1.309 ± 0.020 A,c |
| Sucrose solution | 1.042 ± 0.023 C,d | 1.147 ± 0.017 B,c | 1.311 ± 0.033 A,c | 1.324 ± 1.850 H,c |

Values are mean±SD of three replicates. Different capital letters show significant difference in each row and different small letters show significant difference in each column between the treatments. All statistical analysis was performed at P<0.05.
were found between densities of date syrup, date concentrate, date liquid sugar and sucrose solutions with same Brix values. For example, density of syrup, concentrate, and liquid sugar at Brix 45 were 1.150, 1.150, 1.149 and 1.147 g cm$^{-3}$, respectively. The densities of sucrose solutions were closer to date liquid sugar among the three date products. By decreasing soluble solids (Brix) the density of all four samples decreased significantly, for example the density of date concentrate at Brix values of 12, 35, 65 and 72 were 1.044, 1.150, 1.315 and 1.342 g cm$^{-3}$, respectively. This is in line with the report of Zuritz et al. (2005) on clear grape juice at different soluble solid concentrations and temperatures.

**Antioxidant Activity: DPPH Radical Scavenging Activity**

A lower IC$_{50}$ indicates better radical scavenging. According to Table 4, antioxidant activity (IC$_{50}$ of BHT/IC$_{50}$ of sample) of date syrup is greater than date concentrate and date liquid sugar. This indicates the possible removal or destruction of antioxidant compounds during processing, enzyme treatment, and clarification or filtration. This finding is in agreement with those reported by Abbès et al. (2013).

### Table 4. Antioxidant activity, total phenolic and flavonoid content, glucose and fructose and hydroxymethyl furfural of date syrup, date concentrate and date liquid sugar.a

<table>
<thead>
<tr>
<th></th>
<th>HMF (µg kg$^{-1}$)</th>
<th>Antioxidant (IC50 TBHQ/IC50 Sample)</th>
<th>Phenol (mg of GAE 100 g$^{-1}$sample)</th>
<th>Flavonoid (mg QE 100 g$^{-1}$sample)</th>
<th>Glucose (g 100 g$^{-1}$sample)</th>
<th>Fructose (g 100 g$^{-1}$sample)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date Syrup</td>
<td>456.11</td>
<td>0.18 ± 0.03$^A$</td>
<td>453.04 ± 0.50$^A$</td>
<td>11.93 ± 0.52$^A$</td>
<td>27.75</td>
<td>25.16</td>
</tr>
<tr>
<td>Date concentrate</td>
<td>639.24</td>
<td>0.05 ± 0.01$^B$</td>
<td>173.78 ± 0.18$^B$</td>
<td>5.02 ± 0.65$^B$</td>
<td>26.43</td>
<td>23.19</td>
</tr>
<tr>
<td>Date liquid sugar</td>
<td>787.99</td>
<td>0.02 ± 0.00$^B$</td>
<td>48.36 ± 0.20$^C$</td>
<td>3.31 ± 0.17$^C$</td>
<td>33.55</td>
<td>27.09</td>
</tr>
<tr>
<td>Sucrose solution</td>
<td>0.16</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Values are mean±SD of three replicates. Different capital letters show significant difference in each column. All statistical analysis was performed at $P<0.05$.

### Total Phenolic and Flavonoid Contents

Total phenolic compounds level of date syrup was almost 10 times greater than that of date liquid sugar and values of 453.04, 173.78 and 48.36 (mg GAE/100g sample) were recorded for date syrup, date concentrate, and date liquid sugar, respectively (Table 4). The highest and the lowest amounts of total flavonoid were found for date syrup and liquid sugar, respectively. Total flavonoid compounds were 11.93, 5.02 and 3.31 mg (QE/100g sample) for date syrup, concentrate, and liquid sugar, respectively. In a previous study, date syrup was found to be a good source of phenolic compounds ranging from 39.56 to 88.27 (mg catechin 100 g$^{-1}$ of syrup) (Abbès et al., 2013). The difference in the results could be due to date variety and possible variations in determination method (Al-Farsi and Lee, 2008). These findings show that processing unit operations used from date syrup to date liquid sugar reduce or remove the natural functional compounds of date syrup.

### Sugar Content

Chromatograms of sugar analysis of the samples are presented in Figure 2 and sugar contents are given in Table 4. Glucose...
Figure 2. HPLC chromatograms of sugars: (A) Date syrup; (B) Date concentrate, and (C) Date liquid sugar. The peaks at about 7.4 and 7.8 min are for glucose and fructose, respectively.

Hydroxymethyl Furfural Content

HydroxyMethyl Furfural chromatograms (HMF) of date products are shown in Figure 3 and the calculated HMF contents are presented in Table 4. The HMF content of sucrose was close to zero and HMF of all date liquids was much greater than sucrose. This could be due to the presence of reducing sugars, amino acids, and high temperature evaporation step of date liquid products. However, in sucrose production line, due to crystallization of sucrose molecules and a more complete purification and separation of reducing sugars and amino acids, browning reactions are not favored. The ability of sucrose to crystallize is of key importance in this regards (Fallico et al., 2004). On the other hand, date syrup, concentrate, and liquid sugar are produced and stored in the form of liquid concentrates, while sucrose is stored in its solid form. Generally, chemical and physical reaction rates of materials in liquid and rubbery states are much greater than the crystal state (Farahnaky et al., 2009). Although the color of date liquid sugar is lighter than date syrup and concentrate, HMF content of date liquid sugar was greater than the other samples, and this might be due to its lower pH and/or processing stages (Fallico et al., 2004; Khalil et al., 2010). HMF contents of date processing products tested in this study were in the range of 456-788, but the HMF
Mineral Content

The main elements of date products and sucrose are presented in Table 5. Potassium concentration was the highest (this was in line with the report of El-Sharnouby et al., 2009), followed in descending order by magnesium, sodium, calcium, and iron. However, Al-Hooti et al. (2002) reported sodium concentration to be the greatest followed by potassium, calcium, and magnesium as the second.

As observed, the concentration of all minerals, except for magnesium and manganese, decreased during the process of converting date syrup to date concentrate and then date liquid sugar. Processing filtered out these minerals. This may be regarded as a decline in the nutritional quality of date concentrate and date liquid sugar. However, taking into account the extra daily intake of sodium by many consumers, lower sodium levels of date concentrate and, in particular, date liquid sugar were beneficial.
sugar could be positive in formulation of healthy foods.

CONCLUSIONS

Three date liquid products were all produced with Brix of about 75° in a fully automated production line at industrial scale and their physicochemical properties were investigated and compared. The main chemical component of all three date products was carbohydrates, mainly simple sugars of fructose and glucose. Ash and protein contents of date liquid sugar were much lower than date syrup. The pH values of date liquid products were also significantly different. Concentration of total phenolic and flavonoid compounds in date syrup was much greater than date liquid sugar, and this could be regarded as a negative point in processing date syrup to produce date liquid sugar (in order to improve its color), as it may remove useful components with functional properties. Overall, processing of date syrup to date liquid sugar reduces its nutritional quality while improving its technological properties. Taken together, it can be concluded that in choosing date liquid products as sweetener and flavorant, in products that dark color of date liquid products is not affecting the consumer acceptance of final products adversely, the use of date syrup or date concentrate is proposed. However, in other foods where darker color of date syrup or date concentrate deteriorates sensory attributes of the final products, date liquid sugar is suggested. Date liquid products are also good candidates for high sugar products such as marshmallow and other sucrose based products in which sugar crystallization may limit their shelf life and quality.

ACKNOWLEDGEMENTS

Date syrup, date concentrate, and date liquid sugar were produced at an industrial scale production line in Minoo Date Factory, Shiraz Grand Industrial Estate Zone, Shiraz, Iran. Cooperation of the productions staff of Minoo Date Factory (Fars, Iran) is gratefully acknowledged.

REFERENCES

برخی ویژگی‌های فیزیکوشیمیایی شرهر، کستنتره و قند مایع خرما در مقایسه با محلول‌های شکر

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جکیده

میوه خرما دارای ارزش تغذیه‌ای بالایی است و ترکیبات شیمیایی منحصر بفردی را برای تامین انرژی، مواد معدنی و ویتامین‌های مورد نیاز انسان دارد. شیره، کستنتره و قند مایع خرما فراورده‌های مایع نه‌اماده یه هستند که از فراوری خرما های دارای کیفیت پایین در مقیاس صنعتی تولید می‌شوند. در این تحقیق برخی ویژگی‌های فیزیکوشیمیایی شرهر، کستنتره و قند مایع خرما در مقایسه با محلول‌های شکر مطابعه و امکان جایگزینی شکر با فراورده‌های مایع خرما بررسی گردید. نتایج نشان داد که ترکیب اصلی هر سه محصول خرما را قند سه فرکوز و گل‌گر کردن شکل می‌دهند.

خاکستر و پرودین قند شیره خرما بسیار پایین تر از قند شیره خرما بود. مقادیر pH فراورده‌های مایع خرما اختلاف معنی‌داری از دار نشان دادند. غلظت ترکیبات فلزی کل و فلاژونیئد شیره خرما بیشتر از قند شیره خرما بود. با فراوری شیره خرما به قند شیره خرما، کیفیت بهبود یافت. در انتخاب فراورده‌های مایع خرما برای فرمولاسیون مواد غذایی، برای محصولاتی که رنگ قهوه ای فراورده‌های مایع خرما بر کیفیت ظاهری غذا اثر نموده و نمی‌گذارد، شیره خرما و کستنتره خرما پیشنهاد می‌گردد. در حالتی که در سایر مواد غذایی که رنگ قهوه ای شیره خرما و کستنتره خرما اثرات نموده این استفاده از قند شیره خرما مناسب نیست. همچنین فراورده‌های مایع خرما، شیرین کننده مناسبی برای مواد غذایی دارای میزان بالایی قند که با مشکل کریستالیزه شدن قند مواجه هستند می‌باشد.