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REGULAR ARTICLE

Fructose-rich syrup from Ghars cultivar dates (Phoenix dactylifera L.)

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Abstract

This study was conducted to develop a protocol for diffusion syrups high in fructose from dates of cv. Ghars. Date syrups prepared were cooled to 4°C for more than 70 days to induce crystallization of glucose. This treatment improved the nutritional quality of the syrup and reduction of the glucose fraction bringing the sugar composition closer to that of the second and third generation of high fructose corn syrup HFCS (55 and 90%, respectively) as compared to 42% of the first generation. The content of fructose achieved reached 78% as confirmed by thin layer chromatography marking a significant reduction in glucose content and suggesting that this prepared syrup is an excellent potential product as a dietary replacement to regulate blood glucose.

Key words: Algeria, Date palm, Diabetes, HFCS, Obesity, Ouargla, Syrup

Introduction

The date palm (Phoenix dactylifera L.) is an abundant fruit tree species in southeastern Algeria, a semi-arid area with a wide genetic diversity of date palms marked by more than 900 cultivars (Hanachi and Khitri, 1998). To exploit this richness, preserve local production and conserve heritage palm plantations, commercial opportunities for consumption have to be identified. Thus it is necessary to develop effective processes for the preparation and extraction of useful products starting with raw dates (Mimouni, 2009).

Fructose presents various advantages over other simple sugars for intake by the diabetics and dieters. These include having a higher sweetening power than glucose and sucrose and a lower glycemic index (Stevenson et al., 2005; Atkinson et al., 2008; Little et al., 2009). In addition, fructose is low in calories and its metabolism does not require insulin (Forsee et al., 2007; Pal et al., 2008; Radulian et al., 2009). However, numerous studies show that excessive consumption of pure fructose increases the risk of cardiovascular diseases (George, 2004; Hella, 2005; Forsee et al., 2007; Angelopoulos, 2009; Dray et al., 2009). These effects were particularly observed with consumption of high fructose corn syrup (HFCS) (Stanhope and Havel, 2008). The food industry, especially in the USA, makes frequent use of HFCS. These are series of corn syrups which have undergone enzymatic processing in order to increase their fructose content (Bray et al., 2004). Overuse of these syrups is currently of dietary concern (Schaefer et al., 2009). When consumed in fruits, fructose is associated with other nutritional elements such as minerals and fiber which control its absorption and reduces side effects as compared to consumption in pure form (Al-Farsi et al., 2005; Elleuch et al., 2008; Münstedt, 2009; El Hadrami et al., 2011). Thus, there is a need to obtain fructose in a formulation similar to that found in fruit.

Dates are an important source of fructose (Aleid, 2006; Al Jasser, 2009; Baliga et al., 2011; Mimouni and Siboukeur, 2011). Syrup can be

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easily prepared from dates by simple techniques, as compared to those used to produce HFCS. Therefore, the development of processes that enhance fructose content in date syrup can result in a product with a similar sugar composition to HFCS at a competitive cost. In this context, the current research was conducted to develop a technological process for the preparation of date syrup with the potential for marketing locally as well as on an international scale. This syrup product is aimed at individuals seeking dietary supplements high in fructose and with a carbohydrate composition comparable to the second and third generation of HFCS from corn starch.

Materials and Methods

Plant materials
Ghars date palm cultivar was selected for study on the basis of its soft consistency, facilitating the extraction of diffusion syrup. Dates were harvested at the Tamar (mature) stage from groves located in the region of Ouargla.

Chemical analysis
The physicochemical parameters (Moisture, Total solids, Ash content, °Brix and mineral) were analyzed using standard methods (AOAC, 2005). Total and reducing sugars content were determined by the Bertrand method (Pomeranz and Meloan, 1987). Content of sucrose was estimated using the following formula:

\[
\% \text{ Sucrose} = (\% \text{ total sugars} - \% \text{ reducing sugars}) \times 0.95.
\]

For glucose, an enzymatic method was used; glucose was oxidized by dissolved oxygen into gluconic acid. The reaction was catalyzed by glucose oxidase (AOAC, 2005). The determination of fructose was achieved by a method that explores the Seliwanoff reaction as reported by AOAC (2005). The keto hexoses are much less resistant to the action of hydrochloric acid compared to aldo hexoses. They give rise to the hydroxy-methyl-furfural which reacts with resorcinol (1-3 tow-hydroxy-benzene) to form a red-colored complex which is subjected to spectrophotometric analysis at 420 nm. The protein assay was performed using the method of Lowry et al. (1951). Spectrophotometric analysis was made at 750 nm. Soluble fiber (pectin) were dosed in the form of calcium pectate, after extraction with hot water (100°C), and then saponified with NaOH, and CaCl₂ precipitation in acetic acid medium (AOAC, 2005). Pectin content was estimated using the following formula:

\[
Pectin (\%) = \left( \frac{A \times 200 \times 0.9235 \times 100}{50 \times a} \right)
\]

where:

- 0.9235: Transformation coefficient of the calcium pectate in pectin
- A: Weight in grams of the precipitate
- a: Weight of the sample in grams
- 200: Volume of the filtrate

The qualitative analysis of sugars is achieved by monodimensional and bidimensional thin layer chromatography on silica gel (OJEU, 2006). The solvent system used was composed of 59% acetic acid, 6% distilled water and 35% chloroform. The developer used was Nigrum (2% diphenylamine, 2% aniline, 10% orthophosphoric acid and 86% acetone). In bidimensional TLC, the sample is focused 3-4 cm from one corner of the square plate was then carried to the first elution. The plate is then dried and returned to 90°C, a second elution was carried out with the same solvent system. Solvents and other materials (glucose oxidase, resorcinol) were supplied by SEPPIM S.A.S industrial area (France).

Preparation of primary date syrup
The extraction method adopted was derived from the extraction of sugar from beets described by Turner (1986) and Sarafis (1998). One volume of macerated dates was placed in two volumes of distilled water at 80°C and left to dissolve for 24 h. The resulting solution was then filtered through a 1 mm filter to remove any solids. Concentration of the syrup was then achieved by evaporation of water in an oven set at 60°C until the syrup was 72-75° Brix.

Physical treatment of the primary syrup
To reduce its glucose content, the primary syrup was subjected to crystallization. Crystallization of glucose was achieved by storage of prepared syrup at 4°C for more than 70 days (Roe and Labuza, 2006). The crystals which formed were then removed by sieving with a 1mm filter to produce the modified syrup.

Results and Discussion

Chemical composition of date syrup
The composition and principle characteristics of the extracted syrup are presented in Table 1. The extraction procedure (diffusion) of date syrup gave a yield of 25% solids after concentrating at 60°C for cv Ghars. This value seems high compared to those recorded for cvs Deglet-Nour (20.36%), Degla-Beida (15%) and Mech Degla (14.5%) (Mimouni and Siboukeur, 2014). However, this value seems low compared to that recorded by Aleid (2006) which was equal 86.5%, after heating equal amounts of date cv. Khalas fruit and water at 80°C for 30 min. The effect of extraction method on the chemical and physical properties of date
syrups was studied by El-Shaarawy et al. (1989). They found that autoclaving dates at 15 psi for 10 minutes in 2.5 times their weight of water was the best extraction method. However, a dark color as well as an over-cooked flavor resulted.

The date syrup produced had 80.73% total sugars. It was obvious that the amount of total solids was related primarily to the sugar content due to the high sugar concentration in the syrup. The reducing sugars were dominant in date syrup. Aleid (2006) analyzed date syrups and showed that reducing sugars predominated (81%).

Table 1. Chemical composition of primary date syrup (%).

| Component     | Concentration (%) |
|---------------|-------------------|
| Moisture      | 13.7              |
| Total Solids  | 86.3              |
| Ash content   | 0.57              |
| Total sugars  | 80.73             |
| Reducing sugars | 79.96        |
| Sucrose       | 0.77              |
| Protein       | 1.15              |
| Pectin        | 3.86              |

The mineral composition of date syrup showed a high amount of Cl, Na, Fe, and low amounts of Ca, Mg and Zn (Table 2). Our results are similar to those achieved by Al-Shahib and Marshall (2003). Trace elements function as enzyme cofactors reactions such as glucose metabolism. Organic from of trace elements was found to be superior to the inorganic form due to improved absorption (Wiernsperger and Rapin, 2010).

Table 2. Mineral composition of primary date syrup.

| Mineral | Concentration (mg/100g) |
|---------|-------------------------|
| Fe      | 27.41                   |
| Mg      | 0.30                    |
| Ca      | 5.45                    |
| Cl      | 173.86                  |
| K       | 17.55                   |
| Zn      | 0.74                    |
| Na      | 50.0                    |

Primary date syrup

Extracted primary cv. Ghars syrup has an amber color with a clear and acceptable consistency, as shown in Figure 1A. The color and flavor of date syrup is related to the extraction method and the cultivar (El-Shaarawy et al., 1989; Mimouni and Siboukeur, 2011). The texture and color achieved was similar to that of dark honey and in a form ready for consumption. This confirms both the simplicity of manufacturing of the primary syrup. On the other hand, the manufacturing process of HFCS requires a series of enzymatic transformations to arrive at the syrup stage (Bray, 2004).

The primary syrup of cv. Ghars dates has a sugar content $40.86\% \pm 0.01$ glucose, $39.10\% \pm 0.02$ fructose and $0.77\% \pm 0.02$ sucrose. These represent results from three repeated experiments. Our results are close to those recorded by Aleid (2006); namely 39%, 41% and 1% sucrose to glucose and fructose, respectively. These primary levels of glucose are less than those in the first generation of HFCS (58%) (Wallinga et al., 2009). Also, the fructose content was close to that in the first generation of HFCS (42%).

Based on our analysis, the protein content of the syrup in cv. Ghars was 1.15%. This is in accord with results reported by Alkaabi et al. (2011) where the syrup of five date palm cultivars contained 1.16—1.62% protein.

The content of the dietary fiber was 3.86%; a similar value (2-3%) to that obtained by Miller et al. (2003). It is worth noting that the content of the dietary fibers differ among cultivars and changes according to the ripening stage; the Tamar stage has the lowest percentage of dietary fiber (Alkaabi et al., 2011).

These additional components (protein and soluble fibers) enhance the nutritional value of the syrup, especially because the amino acid proteins in dates are qualitatively well balanced (Matallah, 1970; Aleid, 2011).

Figure 1. Physical appearance the date syrups prepared. A. shows the primary syrup; B. the primary syrup after crystallization at 4°C, while C. highlights the separated crystallized fraction; D. is a sample of the modified syrup.
Modified syrup

After storage at 4°C for more than 70 days the formation of crystals in the syrup as observed is shown in Figure 1B. The qualitative assessment of the fractions separated from the date syrup after the physical treatment was performed by thin layer chromatography on silica gel as shown in Figure 2. It revealed the absence of the spot corresponding to sucrose. The appearances of four distinct spots whose report frontal (Rf) and color are similar to sugar cookies, appear on the chromatogram in Figure 2. The crystallized portion (1 and 1’) of syrup has an Rf and coloring similar to sugar reference "glucose" Rf 0.57. The non crystallized part (2 and 2’) has an Rf and a color similar to that of fructose (Rf 0.55). Two-dimensional thin layer chromatography was used to evaluate the purity of the fractions (Figure 3).

| Syrup               | Glucose    | Fructose   | Sucrose    |
|---------------------|------------|------------|------------|
| Primary date syrup %| 40.86 ± 0.01 | 39.10 ± 0.02 | 0.77 ± 0.02 |
| Modified syrup %    | 1.8 ± 0.01  | 78 ± 0.01  | -          |

Table 3. Carbohydrate composition of primary date syrup and after crystallization.

Figure 2. Assessment of the composition of the separated fractions from date syrup. Thin layer chromatography was used with samples - S: Sucrose; G: Glucose; F: Fructose. The samples (1, 1’) represent the crystallized portion; (2, 2’) non-crystallized portion.

Figure 3. Assessment of the purity of the separated primary syrup fractions. Low to high 1, 2 and 3: Sucrose, Glucose and Fructose respectively. The samples (1, 1’) represent the crystallized portion; (2, 2’) non-crystallized portion.
Biochemical analysis of the carbohydrate composition of the non-crystallized fraction (modified syrup) indicates a desired increase in fructose content to 78% compared to 39.10% prior to crystallization, with the glucose content reduced significantly to 1.8% after the treatment. This brought the fructose content in the modified syrup to levels higher than that in the second generation of HFCS (55% fructose) and close to that in the third generation HFCS (90% fructose) (Bray et al., 2004). In our work, the differences in crystallization between glucose and fructose at low temperatures were exploited (Labuza and Labuza 2004). This phenomenon is well reported and studied in relation to the crystallization of honey (Richard and Shastry, 1999). According to Rosalen et al. (1996), in many foods low in water content, monosaccharides are present in the amorphous state. Below certain water content, the amorphous form is unstable and crystallizes releasing water.

Our results achieved with the date syrup after modification suggest that syrup high in fructose could be prepared with a simple technique, minimal reagents and processing. All these properties make the date syrup cheap to prepare and thus support its production both at a small scale and at an industrial level. This product is likely to maintain some nutritional advantages of dates and reduce the cost of such syrups to the consumer as opposed to that of HFCS produced through complex processing (Bray et al., 2004). Moreover, the research in this work exploits a local product, which could increase its use and production as well as support the maintenance of local date palm groves if mass production of the syrup were initiated.

The syrup developed has nutritional value important for its composition fructose, protein, soluble fiber and other elements. According to Chenon et al. (1984) the rapid rise of blood glucose after eating carbohydrates depends mainly on gastric transit time and accessibility to digestive enzymes. In another study, the speed of gastric emptying was reduced by increased fat, protein and dietary fiber (Jenkins et al., 1981). Dietary fiber is part of a group of non-digestible polysaccharides which are carbohydrates. The human intestinal tract is capable of only partially digesting fiber, which slows gastric emptying and movement of food through the initial part of the intestine and reduces the absorption of carbohydrates. We conclude that our prepared syrup can be a significant source to regulate blood sugar levels and as a dietary product for some individuals.

**Conclusion**

The syrup product developed in this study represents a good nutritional source of fructose which differs from HFCS by the presence of nutrients from dates. Date syrup has the advantage of being able to be produced by simple technology which could be advantageous for scale-up to an industrial or semi-industrial level. Furthermore, production requirements are limited making these products potentially are less expensive than HFCS, which are produced by enzymatic methods which involve extensive processing. These results are of particular importance because they offer promise in dealing with the major public health problems of obesity and diabetes, and present a good use of a local natural product which would aid in the preservation of an agricultural heritage of date palm cultivation.

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