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Nutritional and Functional Potential of Carob Syrup *Versus* Date and Maple Syrup

Running title: Chemical and Antioxidant Profiles of Carob Syrup

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SUMMARY

Research background. The carob tree (*Ceratonia siliqua* L.) is grown primarily for its seeds that are utilized in the production of the highly-prized locust bean gum. The material left after the separation of seeds, from the pods, is utilized in the production of a range of traditional products including carob syrup usually in cottage-type industries. The international market penetration of carob syrups is rather limited and, accordingly, scant information exists on their composition and phytochemical properties in comparison with mainstream syrups. The present study aims to determine key chemical parameters, phenolic profiles, and antioxidant properties of carob syrups and benchmark these against those of date and maple syrups.

Experimental approach. Carob syrups were prepared from 19 accessions of the carob, under laboratory conditions, by a similar procedure to those practiced by small-scale producers. The syrups were analyzed along with branded samples of date and maple syrups for pH, browning index, proteins, minerals, hydroxymethylfurfural, sugar composition, total phenols, antioxidant capacity, and phenolic profiles.

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Results and conclusions. The pH and sugar compositions of the carob syrups were intermediate to those of date and maple syrups. In general, the carob syrups contained more proteins, minerals, phenolic acids and flavonoids, and total phenols, and exhibited higher antioxidant capacity than the date and maple syrups. The carob syrups exhibited excessive browning and contained more, or comparable levels of, hydroxymethylfurfural than the date and maple syrups. The data indicate that carob syrups provide more nutrients and possess superior antioxidative potentials to date and maple syrups. The high levels of the carcinogenic hydroxymethylfurfural of the carob syrups warrant milder heating regimens in the concentration step during production.

Novelty and scientific contribution. In contrast to studies based on commercial and/or homemade syrups, this work utilized a relatively large number of laboratory-prepared samples for creating a robust database for carob syrup. The results indicated that carob syrups possess superior health promotion and disease-protection effects than the widely-traded date and maple syrups. In addition to their potential positive contribution to public health, carob syrups have been shown to be promising candidates for bolstering the economic returns of farmers in carob-producing countries.

Keywords: syrup; *Ceratonia siliqua* L.; nutritional content; phenolic profile; antioxidant capacity; hydroxymethylfurfural

INTRODUCTION

Fruit- and tree-sap-based syrups have been used for millennia as sweeteners in local cuisines worldwide. In addition to providing sweetness, fruit- and tree-sap-syrups contain proteins, minerals, vitamins, and a range of phytochemicals possessing antioxidant activity (*1*). Because of their superior health properties, food product developers are increasingly using these syrups as sugar substitutes to satisfy the demands of the health-conscious consumers for “safer” and more “natural” foods (*2*). Tree-sap syrups are made by tapping the trunks of endemic trees, collecting the exuding sap, and concentrating the sap into a thick syrup (*3*). Fruit syrups are usually made by heating fruit juices to different levels of total solids until the target consistencies are attained (*2*). The heating step during the making of syrups increases viscosity, generates the brown color, and develops the unique flavor profiles of the products (*4*). In addition to their functionality as sweeteners, syrups are used in the food industry to add viscosity, impart brown color and desirable flavors, and mask bitterness in a range of food products (*4*). Amongst the tree-sap syrups, maple syrup is the leading syrup with a forecasted

global market value of $1.7 billion in 2023 (*5*). Data on the market value of fruit syrups are difficult to locate. However, inferences about the size/market penetration of fruit syrups can be made from the production statistics of the fruit, established practices of syrup production, and the availability of literature on the properties and uses of the syrup. To this end, the annual production of dates has been reported at 8.4 million tons in 2018 (*6*) with syrup production being routinely practiced in date-growing countries (*7*) and frequently used as a sugar substitute in the formulation of foods (*2,5*).

Maple syrup (MS) exhibits interesting health properties including more favorable metabolic responses as compared to those generated after ingestion of refined sugar (*8*) and antioxidant-, anticancer- and antimicrobial-activities (*9*). Broadly similar health properties have been ascribed to date syrup (DS) with antioxidant- and antimicrobial-activities being reported for the commodity (*10*).

In the Middle East and North Africa, the carob tree (*Ceratonia siliqua* L.) is widely cultivated due to its adaptability to harsh environmental conditions and the ability to grow on marginally productive lands with low to medium rainfall (250-500 mm/year) (*11*). The carob tree bears pod-shaped fruits that are made up of a fleshy pulp that envelops several seeds. The seeds are rich in galactomannans and are commercially utilized in the production of locust bean gum. The carob pulp contains appreciable amounts of sugars (chiefly sucrose, glucose, and fructose), dietary fiber and polyphenols, and also some proteins and a range of minerals and vitamins (*11*). The carob pulp is utilized in the preparation of a range of traditional foods including carob syrup (CS) that is extensively used as a sweetener in many parts of the world (*12*). In addition to its sweetening functionality, CS has been shown to possess antioxidant activity (*13*) and superior anti-inflammatory and anti-mutagenic activities to cane, grape, and sorghum syrups (*14*). Despite its long history of use as a sweetener and its potentially valuable health-promoting properties, scant data is available on the physicochemical and radical-scavenging properties of CS. Recently, the physicochemical properties of homemade CS have been reported (*15*). However, there is a dearth of information on the physicochemical properties of syrups prepared from different carob accessions under laboratory conditions. Still, no studies have attempted comparing, under the same test conditions, the antioxidant potential of CS to leading tree-sap and fruit syrups viz. maple and date syrups. Creating a database on the physicochemical parameters and potential health effects of traditional food products and benchmarking them against known/recognized commodities, within the product category, are pivotal for their valorization, including possible recognition as Protected Designation of Origin

(PDO) (*16*), and positioning in the global food market. Within this framework, carob syrups (CSs) were prepared, under laboratory conditions, from 19 carob accessions indigenous to Lebanon, and their physicochemical parameters, antioxidant capacity, and phenolic profiles were determined and compared to those of commercial maple and date syrups.

MATERIALS AND METHODS

Materials

Potassium hexacyanoferrate trihydrate (Carrez I), zinc acetate dehydrate (Carrez II), ammonium molybdate, ammonium metavanadate, acetonitrile, water, sodium metabisulfite, sodium bisulfite, sodium hydroxide, glucose, fructose, sucrose, Folin-ciocalteu reagent, ferric chloride (hexahydrate), TPTZ (2,4,6-tri(2-pyridyl)-s-triazine), sodium acetate trihydrate, acetic acid, trolox (6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid), ABTS (2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid), DPPH (2,2-diphenyl-1-picrylhydrazyl), potassium persulfate, gallic acid, p-coumaric acid, caffeic acid, t-cinnamic acid, syringic acid, catechin, epigallocatechin-3-gallate, quercetin, and the atomic absorption standards (Ca, Na, Mg, and K) were obtained from Sigma-Aldrich (Gillingham, Dorset, UK). Sodium carbonate, ferrous sulfate, sodium thiosulfate, and mercuric oxide were purchased from Merck KGaA (Darmstadt, Germany), hydrochloric acid (37 %), sulfuric acid (95 %) and methanol were procured from VWR International (Lutterworth, Leicestershire, UK). Light (Amber color grade A, Kirkland, USA) and dark (Dark color grade A, Member's Mark, USA) maple syrups, and date syrup (Alwadi Al Akhdar, Beirut, Lebanon) were procured from the local market.

Nineteen carob accessions, growing in the different regions of Lebanon, were used in the preparation of carob syrups. The accessions grow under diverse climatic conditions ranging in elevation between 16 and 654 m, precipitation between 491 and 1038 mm, and average temperatures between 17 and 22 °C (*17*). The samples were sorted by removing damaged pods and then washed with distilled water to remove adhering impurities. The pods were left to dry at room temperature (~25 °C) and were then placed in cloth bags and stored at room temperature until use.

Morphological parameters of carob pods

The pod length (cm), width (cm), thickness (cm), and mass (g), and the number of seeds/pod were measured on 10 randomly selected pods as described by Naghmoushi *et al*. (*18*) and are presented in Table S1.

Preparation of carob syrups

The syrups were prepared according to commercial practices followed in the production of CS. The carob pods were deseeded and the coarsely-ground kibbles were soaked in distilled water (1:3 *m/V*), at room temperature, for 24 h and the resulting liquor was passed through a cheesecloth to remove suspended materials and then boiled in a steam-jacketed kettle until total solids of ~78-80 °Bx were reached. The hot syrups were placed in glass jars, cooled promptly in running water (Fig. S1), and stored at 4 °C until used.

Chemical and physicochemical analyses

Spectrophotometric analyses were performed with an Evolution 300 UV-VIS Spectrophotometer (Thermo Scientific, Loughborough, UK) using Suprasil quartz cuvettes (Mettler-Toledo Ltd., Leicester, UK). All analyses were performed in triplicate and results were reported on a dry mass (dm) basis.

Determination of total soluble solids (TSS), pH, moisture, protein, 5-hydroxymethylfurfural (HMF), and browning index (BI)

TSS, pH, and HMF were determined according to the International Honey Commission (*19*). The TSS were determined, at room temperature, by placing enough syrup to evenly cover the prism of an Abbe refractometer (Bellingham + Stanley, Kent, UK) and reading the TSS levels in ˚Bx. The pHs of the syrups were determined, at room temperature, on solutions of the samples (3 g in 15 mL of distilled water) with a pH meter (SevenCompact PH/ Ion meter S220, Mettler-Toledo AG, Schwerzenbach, Switzerland). 5-hydroxymethylfurfural was determined colorimetrically as per the procedure of White by treating a solution of the syrup (2.5 g in 15 mL of distilled water) with Carrez I (0.25 mL) and Carrez II (0.25 mL) solutions and making up to 25 mL with distilled water. The solutions were filtered, and aliquots of the filtrate (2 mL) were treated with water (2 mL) or 0.2 % sodium metabisulfite solution (2 mL), and the absorbance was read at 284 and 336 nm. The HMF contents of the syrups were expressed in mg/kg.

Moisture and protein (N × 6.25) were determined according to AOAC methods 925.45 (*20*) and 955.04 (*21*), respectively. Moisture was determined by mixing a diluted sample of the syrup (1.2 – 1.5 g in ~10 mL water) with acid-washed sand, heating on a steam bath for 20-30 min, and then at 100 °C to a constant mass (~ 3-4 h). Proteins were determined by treating the syrup (~ 2 g) with HgO (0.7 g), anhydrous Na_2SO_4 (15 g), and concentrated H_2SO_4 (25 mL) and boiling until a clear green liquid is obtained (~1.5 h). After cooling to room temperature, the contents of the flask were diluted with distilled water (200 mL), treated with

$Na_2S_2O_3$ (25 mL, 0.3 M), and layered with concentrated NaOH (35 mL, 11 M). The NH_3 in the flask was distilled into 0.1 M HCl and the excess HCl was titrated with 0.1 M NaOH.

The BI was determined by measuring the absorbance of appropriate dilutions of the samples at 420 nm and converting it to the absorbance of the original sample (*22*).

Determination of minerals

For the determination of Na, Mg, Ca, and K, the syrup (~ 0.5 g) was treated with concentrated HCl (15 mL) and heated at 200 °C for 30 min in a microwave digestion system (Ethos Up, Milestone, Sorisole/BG, Italy). After cooling to room temperature, the digest was diluted to 50 mL with deionized water, and Na, Mg, Ca, and K were measured by AAS (Solaar S4 with ASX-510 autosampler, Thermo Scientific, Loughborough, UK) by reference to standard curves prepared according to AOAC method 984.27 (*23*). P was measured colorimetrically by dry ashing the syrup (~2 g) at 550 °C for 16 h, dissolving the ash in concentrated HCl (2 mL) and heating to dryness. The resulting residue was dissolved by heating in distilled water (10 mL) and the solution was filtered and made up to 50 mL with distilled water. Aliquots (5 mL) of the solution were treated with concentrated HCl and ammonium molybdate-ammonium metavanadate and the absorbance of the resulting yellow-colored solution was read at 400 nm. The concentration of P was determined by reference to a standard curve prepared with known concentrations of phosphorus (0–50 µg/mL) (*24*).

Determination of sugars

Determination of glucose, fructose, and sucrose in the syrups was carried out according to Fidan *et al.* (*25*) with some modifications. The sample (~ 1 g) was dispersed in deionized water (25 mL), sonicated at 30 °C for 30 min and the extracts were filtered and stored at -18 °C until analyzed. The levels of sucrose, fructose, and glucose in the extracts were measured with HPLC using a Telos NH_2 column (5 µm, 25 cm x 4.6 mm), Telos NH_2 guard column (5 µm, 1 cm x 4.6 mm), refractive index detector, and acetonitrile:water (70:30 v/v) as mobile phase. The quantification of the sugars was made by reference to calibration curves constructed with standard solutions of sucrose, glucose, and fructose.

Determination of total phenolic content (TPC) and antioxidant capacity (AC)

The phenols were extracted by shaking the syrup (4 g) with methanol/water (50 % v/v; 10 mL), in a shaking water bath, for 30 min (*26*). The solution was filtered and the filtrate kept at -80 °C until used.

Determination of TPC. The TPC content was determined according to Singleton *et al*. (*27*). An aliquot of the extract (1 mL) was mixed with 5 mL diluted folin-ciocalteu reagent (1:1, *V:V*; in water) and 20 % Na_2CO_3 (4 mL), vortexed, incubated at room temperature in the dark for 1 h and the absorbance of the solution was read at 765 nm. TPC was expressed in mg gallic acid equivalents (GAE) /100 g syrup by reference to a standard curve prepared with known concentrations of gallic acid (0–200 mg/L).

AC by ferric reducing antioxidant power (FRAP). The FRAP assay was carried out according to Benzie and Strain (*28*) with slight modifications. An aliquot of the extract (100 µL) was mixed with distilled water (900 µL), FRAP reagent (2 mL) and incubated at 37 °C for 30 min. The absorbance was measured at 593 nm against a blank (1 mL water + 2 ml FRAP reagent). FRAP was expressed in µM Fe (II)/100 g syrup by reference to a calibration curve constructed with aqueous solutions of ferrous sulfate (0-100 µM).

AC by Trolox equivalent antioxidant capacity (TEAC). The TEAC assay was performed as described by Fu *et al*. (*29*) with slight modifications. An aliquot of the extract (100 µL) was added to the $ABTS^{\bullet+}$ solution (3.8 mL) and kept in the dark, at room temperature, for 30 min. The absorbance was measured at 734 nm against a blank containing methanol and TEAC was expressed in mmol Trolox equivalents (TE)/100 g syrup by reference to a standard curve prepared with known concentrations of Trolox (25-500 µM).

AC by the DPPH method. The DPPH assay was executed as per Dhaouadi *et al* (*13*). An aliquot of the syrup extract, or a dilution therefrom, or ascorbic acid standard solution (50 µL), at different concentrations (0 – 600 mg/L), were added to 60 µM DPPH in methanol (1950 µL) and incubated, in the dark at room temperature, for 30 min. The absorbance was read at 515 nm against a blank containing the same amount of $DPPH^{\bullet}$ solution and 50 µL of distilled water. The percentage $DPPH^{\bullet}$ inhibition was calculated using the following equation:

$$\%\ DPPH^{\bullet}\ \text{inhibition} = \frac{(A_0 - A_S)}{A_0} \times 100 \qquad /1/$$

where A_0 is the absorbance of the blank sample and A_s is the absorbance of the tested solution (syrup extract or ascorbic acid solution).

The results were expressed as the extract concentration providing 50 % inhibition (IC_{50}) in mg extract/L as determined from the plot of absorbance *vs* extract concentration. The IC_{50} of the syrups were also compared to the IC_{50} of known ascorbic acid solutions determined under the same conditions.

Identification and quantification of phenolic composition by LC-MS/MS analysis

Quantification of individual phenols was performed with LC-MS/MS system composed of Electrospray (ESI) MS/MS ABI 4000 Sciex® (Toronto, Canada) coupled with liquid chromatography station comprised of a quaternary pump (LC-20AD-LPG-20), autosampler (SIL-20A), and column oven (CTO-20AC) and VP-ODS column (150 x 2 mm id, 5 µm) (Shimadzu®, Kyoto, Japan). The mobile phase was composed of A: deionized water with 0.1 % acetic acid, and B: 0.1 % acetic acid in acetonitrile, and the gradient program was 0-4 min 85 % A and 15 % B, 4.01-5.00 min from 15 % B to 50 % B, 5.01-8.00 min 50 % A and 50 % B, and finally 8.01-12.00 min 85 % A and 15 % B. The flow rate of the mobile phase was 0.2 mL/min, the injection volume was 10 µL and the column temperature was set at 30 ˚C. The ESI parameters were 30 psi for the nebulizer gas pressure, 25 psi for the drying gas pressure, and 400 ˚C for the ion source temperature. Standards of caffeic acid, *t*-cinnamic acid, *p*-coumaric acid, gallic acid, syringic acid, catechin, epigallocatechin gallate, and quercetin were used in the quantification of the samples' phenols. Apart from catechin and syringic acid which were analyzed in the negative mode with a needle voltage of -4500 V, data for the phenols were acquired in the positive mode and a needle voltage of +5500 V.

Statistical analysis

Descriptive statistics were performed and presented to summarize the study variables of interest as means and standard deviations. Values of the measured parameters were subjected to one-way analysis of variance (ANOVA) and the means were separated by Duncan's Multiple Range Test when *F* values were significant. All reported p-values were based on two-sided tests and were compared with a significance level of 5 %. The Statistical Package for Social Sciences (SPSS) V.25.0 for Windows (*30*) was used to analyze the data.

RESULTS AND DISCUSSION

Physicochemical parameters, browning index, protein contents, and HMF levels of carob, date, and maple syrups

While 89.7 % of the CSs had higher soluble solids ($p<0.05$) than the date syrup (DS), all CSs had higher TSS ($p<0.05$) than the MSs (Table 1). Further, the TSS of CSs prepared in the present work were higher than those of commercial syrups from Tunisia and Turkey being marketed at 73−75 and 66.6−73.7 °Brix, respectively (*15*) and those of date and maple syrup reported at 75 °Brix (*7*) and 67.1–67.4 °Brix (*9*), respectively. In addition to being set by national standards, the TSS levels are the chief determinants of fruit- and tree sap-syrups' viscosity/thickness which, expectedly, exhibits broad national preferences.

All CSs exhibited higher and lower pH ($p<0.05$) than DS and MS, respectively (Table 1). The pH of fruit and tree-sap syrups are shaped by the levels of organic acids and minerals of the sap/juice as well as microbial contamination during processing and storage (*7*). The pH of DS and MS were close to those reported at 4.2 (*31*) and 6.7−7.1 (*9*), respectively. Further, the pH of CS samples was similar to those of samples marketed in Tunisia and Turkey with ranges of 4.4-5.4 (*15*).

All CSs contained more proteins ($p<0.05$) than MS while 89.7 % of the CSs had higher protein contents ($p<0.05$) than the DS sample (Table 1). These findings indicate that CS provides more proteins, for human nutrition, than DS and MS. The protein content of the DS sample was close to those of commercial samples at 1.14-1.45 g/100 g (*32*) while the MS samples contained less protein than reported at 0.37 g/100g (*33*).

The MS samples exhibited the least browning ($p<0.05$), as measured by the BI, when compared to the other syrups (Table 1). Further, the CSs browned less than DS as reflected by the lower BI ($p<0.05$) exhibited by 89.5 % of the samples and bracketed the BI values reported for 6 homemade CS samples from Tunisia at a mean BI value of 34 (*15*) (Table 1). The BI reflects the levels of melanoidins (*34*) produced through the Maillard reaction between sugars and amino compounds and caramelization of sugars upon heating and subsequent storage. The low degree of browning observed in the MS samples, as compared to the other syrups, could be attributed to their markedly lower protein content ($p<0.05$), higher pH ($p<0.05$), lower levels of reducing sugars ($p<0.05$) (Table 2), and the mild conditions for concentrating the maple sap incorporating the requisite duration of heating needed to develop the typical color and flavor of the finished product (*34,35*). The lower degree of browning exhibited by the CS samples than that of DS might have resulted

from their lower contents of reducing sugars ($p<0.05$) (Table 2) and higher pH ($p<0.05$) which limits the inversion of sucrose during the heat concentration step.

The MS and DS samples exhibited the lowest and highest average levels of HMF, respectively, amongst the investigated syrups. Further, while only one sample did not differ in HMF content ($p>0.05$), the other 18 CSs contained more HMF ($p<0.05$) than the MS samples. Further, only one sample contained more HMF ($p<0.05$) while the other CS samples either did not show differences ($p>0.05$) or contained less HMF than the DS sample (Table 1). Hydroxymethylfurfural is formed through the dehydration reactions that take place during the caramelization of sugars and heating of sugars in the presence of amino compounds in the Maillard reaction (*34*). While the formation of HMF during caramelization of sugars is independent of the confounding effects of amino compounds, the determination of the precise contribution of caramelization and the Maillard reaction to the formation of HMF in heated sugar-amino compounds is a daunting task; however, during heating of model systems comprised of fructose and lysine 10-36 % of the HMF produced is derived from the caramelization reactions (*36*). The formation of HMF during caramelization and heating of sugar-amino compounds is influenced primarily by the types and concentrations of sugars and amino compounds, heating regimen, and pH. To this end, the HMF levels tend to be higher in systems comprised of reducing sugars, basic amino acids and acidic pH (*37*). The low HMF levels of the MS samples can be attributed to their lower contents of glucose and fructose ($p<0.05$), lower levels of proteins ($p<0.05$) and higher pH ($p<0.05$), as compared to those of the CSs (Table 1 and Table 2), and the mild heating regimen applied in their production (*35*). The higher HMF levels in the DS sample, as compared to CS samples, might have been precipitated by its higher contents of glucose and fructose ($p<0.05$) and lower pH ($p<0.05$) in view of the similar heat-concentration procedure, entailing open pan evaporation, practiced in the production of CS and DS. Pearson's correlation analysis registered -6.58 ($p<0.01$), -0.647 ($p<0.01$), and 0.510 ($p<0.05$) between HMF levels and pH, sucrose, and fructose, of the syrups, respectively. These correlations are in accord with previous findings from model systems where the formation of HMF was shown to be favored at acidic pHs from fructose (*38*). Further, the negative correlation between sucrose and HMF levels is indicative of the lower reactivity of the non-reducing disaccharide sucrose in caramelization and the Maillard-type browning as reflected in the lower tendency of the high-sucrose containing syrups, and notably the maple syrups, to undergo browning and accumulate HMF (Table 1 and Table 2).

Notwithstanding its beneficial antioxidant activity, HMF has been shown to be carcinogenic and mutagenic and to induce hepatic- and nephrotoxicity in laboratory animals thereby prompting regulatory agencies to set limits on its levels in foods (*38*). Of the different approaches to mitigate the levels of HMF in foods, reducing the severity of heat treatment during the concentration step in the production of fruit and tree-sap syrups is the most effective. To this end, ~10 and 2.5-fold reduction in HMF levels were achieved upon reducing the temperature during the sap/juice concentration from 100 °C to 70 °C in the production of date (*39*) and palm sugar syrups (*40*), respectively. The HMF levels of the CS samples bracketed the HMF values reported for Tunisian CS at 450 mg/kg (*15*) and the HMF concentrations of 1000-2675 mg/kg reported for commercial DS produced by open pan evaporation (*39*).

Table 1

Sugar composition of carob, date, and maple syrups

All CSs contained more ($p<0.05$) glucose and fructose and less sucrose ($p<0.05$) than MS samples. Further, the CS samples had less glucose and fructose ($p<0.05$) and, apart from 1 sample that showed no differences ($p>0.05$), more sucrose ($p<0.05$) than DS (Table 2). The sugar contents of the CSs appeared to be intermediate to those of MS that contains almost only sucrose and DS where an invert-sugar-like composition predominates (Table 2). The levels of glucose, fructose, and sucrose of the CSs bracketed the levels reported for 10 commercial CSs from Turkey (*41*). The glucose, fructose, and sucrose levels of MS and DS were similar to those reported for commercial DS (*32*) and MS (*3*). The high sugar contents of CS are responsible for their widespread utilization in the making of a range of ethnic products and their potential use as sugar substitutes in the formulation of "healthier" confections in view of their provision of nutrients and phytochemicals in addition to sweetness. Further, because of its high sugar content, CS has been reported to be a promising substrate for the production of a range of fine chemicals by industrial fermentation (*42*).

Table 2

Mineral composition of carob, date, and maple syrups

In general, the majority of CS samples (13−19 samples; 68.4−100 %) contained more K ($p<0.05$), P ($p<0.05$), Mg ($p<0.05$) and Na ($p<0.05$), and less Ca ($p<0.05$) while the others either did not show differences ($p>0.05$) (3−6 samples; 16-32 %) or contained less

($p<0.05$) (1−2 samples; 5.3−10.5 %) of the minerals than the MS samples (Table 3). Further, in general, the majority of CS samples (16−18 samples; 84.2−84.7 %) contained more Mg ($p<0.05$) and Na ($p<0.05$) and 1−4 samples (5.2−21.1 %) contained more ($p<0.05$) Ca, K and P while the others either did not show differences ($p>0.05$) (1−10 samples, 5.3−52.6 %) or contained less ($p<0.05$) (5−10 samples; 26.3−52.6 %) of the minerals than DS (Table 3). The relative levels of the investigated minerals in MS were similar to those reported for the product with K and Na being present at the highest and lowest levels, respectively (*3*). The mineral composition of the DS sample was, in general, within the ranges reported for the commodity (*10*) (Table 3). These findings indicate that CS is a significant source of K and a good source of Ca, Na, Mg and P and will potentially be, therefore, a significant contributor to the mineral nutrition of consumers.

Table 3

Total phenols and antioxidant capacity

Apart from 2−4 samples that did not differ in their TP contents ($p>0.05$), CS samples contained more TP ($p<0.05$) than MS samples (Table 4). Further, apart from 3 samples that contained less TP ($p<0.05$), CS samples contained more ($p<0.05$) (9 samples, 47.4 %) or did not differ in their TP contents ($p>0.05$) (7 samples, 36.8 %) from DS (Table 4). Notwithstanding the different solvents used in the extraction of polyphenols from the syrups, CS bracketed the average TP levels of 8 CS samples from Tunisia (2.1−2.2 g GAE/100 g dm) (*15*) and 10 samples from Turkey (0.72−1.2 g GAE/100 g dm) (*41*). The TP contents of MS samples were higher than reported for amber and dark MS at 45.6 ± 18.7 mg GAE/100 g dm and 72 ± 18.2 mg GAE/100 g dm, respectively (*9*). The high TP content of CS is an added advantage for the use of these syrups as sugar substitutes in the formulation of foods in view of their ability to quench reactive oxygen species and, consequently, to retard/mitigate the development/harmful effects of degenerative diseases (*43*).

Apart from 5 samples that did not differ ($p>0.05$) from MS, all CS exhibited higher AC ($p<0.05$), as determined by the FRAP assay, than MS (Table 4). Further, 14 CS samples (73.7 %) did not differ ($p>0.05$) while 5 samples (26.3 %) showed higher antioxidant capacity ($p<0.05$), by the FRAP assay, than DS (Table 4).

All CSs exhibited higher AC ($p<0.05$), as determined by the TEAC procedure, than the MS samples and, apart from 4 samples (21.1 %) that did not show differences ($p>0.05$), the CS samples had higher AC ($p<0.05$) than the DS sample (Table 4).

All CSs exhibited higher AC ($p<0.05$), as determined by the DPPH procedure, than the MS samples. Further, 3 CS samples had higher AC ($p<0.05$) while the others did not show differences in their AC ($p>0.05$) from that of the DS sample (Table 4). The CSs registered higher mean AC (lower IC_{50}) as compared to that reported for CS at 47.2 mg extract/L (*13*). For comparison, ascorbic acid exhibited an IC_{50} of 74 ± 5.7 mg/L under the same conditions in the present work. The DPPH IC_{50} values of MS (647.1 and 501 mg/L) were higher than the IC_{50} values of ethanol extracts of MS at 97.6−102.4 mg/L (*44*).

Notwithstanding the differences in the assay protocols and the use of extracts or whole syrups in the determinations, CSs have been reported to contain significant quantities of TP and to exhibit high AC, comparable to that of butylated hydroxytoluene, in several *in vitro* AC assays (*13,15,41*). Similar findings have been reported for the TP and AC of MS (*1,9,44*) and DS (*45*). However, when analyzed under the same conditions, the vast majority of CS samples contained more TP than amber and dark MS and comparable or higher levels of TP than DS (Table 4). Similar patterns were observed for the AC with most of the CS samples exhibiting higher AC than amber and dark MS and comparable or higher AC than DS in the ABTS, DPPH and FRAP assays (Table 4).

Table 4

The antioxidative potential of foods is frequently determined by a combination of several tests that are based on different principles and expressed in different units. Accordingly, indices that integrate data from the different antioxidant assays are often utilized to construct measures of the total antioxidant capacity of foods (*46*). To this end, the data from the different antioxidant tests were normalized and the derived z scores were averaged to generate relative antioxidant capacity indices (RACI) (*46*) for the different syrups (Fig. 1). All the CSs exhibited higher RACIs than MS, and, apart from 3 CS that had close RACIs, DS (Fig. 1). The total phenols, as determined by the Folin-Ciocalteu reagent, correlated strongly with the RACIs ($r=0.881$, $p<0.01$) thereby lending further support to the modulation of the AC of foods and biological materials by their endogenous phenolics (*47*).

Fig. 1

Given the pivotal role of phenols and their associated antioxidative potential in combating the development and progression of degenerative disease and mitigating their ill effects (*43*), the present findings indicate the superiority of CS as a functional dietary ingredient as compared to DS and MS. The reported higher anti-inflammatory and anti-mutagenic efficacies of CS as compared to those of cane, grape and sorghum molasses

(*14*) further attest to its advanced health-promoting effects relative to those of cereal, fruit and tree-sap syrups.

The acquired data were subjected to principal component analysis (PCA) to discern the variables that are operative in mediating the relationships amongst the syrups and to identify possible groupings of the investigated samples. Two principal components accounting for 62.5 % of the total variance resolved the syrups into distinct groupings (Fig. 2). The first principal component (PC1), that explained 47.1 % of the total variance, related chiefly to the sugars (glucose, fructose, and sucrose), proteins, pH, TSS, BI, and Ca while the second principal component (PC2) associated mainly with the BI, HMF, TP, RACI, and K. It is noteworthy that the reactants, conditions, and the index of caramelization and the Maillard-type of browning loaded on PC1. To this end, fructose, glucose, proteins, and BI loaded on the positive side of PC1 thereby confirming the direct relationship between browning intensity and these reactants, while the pH and sucrose loaded heavily on the negative side of PC1 in accord with the intensification of browning at acid pHs and the sluggish reactivity of sucrose in browning under the conditions of syrup production. The TP, RACI, HMF, and BI loaded on the positive side of PC2 thereby suggesting that this principal component is mainly associated with AC of the syrups given the high correlation between TP and AC and the reported antioxidative properties of HMF (*38*). While the CSs exhibited a diffuse pattern in sugar composition, the DS and MS loaded heavily on the opposite sides of PC1 in congruence with the invert-sugar-like composition of the former and the almost exclusive presence of sucrose in the latter. All the CSs loaded higher than the MSs on PC2 indicative of their higher TP, HMF, and AC levels; however, the DS loaded amongst the CSs on PC2 in accord with its TP, HMF, and AC levels being within the ranges of these parameters exhibited by the CS samples.

Fig. 2

Phenolic profiles of carob, date, and maple syrups

Most CS samples contained more ($p<0.05$) phenolic acids (caffeic, *t*-cinnamic, *p*-coumaric, gallic, syringic acid) with few showing no differences in their phenolic acid contents from amber and dark MS (Table 5). In the analyzed flavonoids, all CS samples contained less catechin ($p<0.05$) while most did not show differences (7−15 samples, $p>0.05$) or contained more (4−12 samples, $p<0.05$) quercetin than MS (Table 5). Further, all CS samples contained less ($p<0.05$) caffeic acid, more ($p<0.05$) *p*-coumaric, syringic, and *t*-cinnamic acids, and, apart from 8 samples that did not show differences ($p>0.05$),

more gallic acid than DS (Table 5). Moreover, apart from 7 and 8 samples that did not exhibit differences ($p>0.05$), CS samples contained more ($p<0.05$) catechin and quercetin than DS (Table 5). Of the analyzed phenolics, gallic acid correlated with TP ($r=0.864$, $p<0.01$) and RACI ($r=0.972$, $p<0.01$), quercetin with TP ($r=0.586$, $p<0.01$) and RACI ($r=0.621$, $p<0.01$), and catechin with RACI ($r=-0.490$, $p<0.05$) thereby suggesting that these phenolics are the most operative in shaping the TP and AC of the investigated syrups.

The phenolic profiles of fruit and tree-sap syrups are shaped by the liquid-liquid extraction protocol, use of resins or solid-phase extraction to remove interfering compounds, and the chromatographic conditions employed in the identification and quantification of the individual phenolics. Accordingly, only broad comparisons of phenolic profiles of syrups reported by different workers are plausible. Under the conditions of analysis employed in the present work, gallic acid was the major phenolic in CS, DS, and MS samples (Table 5). The preponderance of gallic acid in CS has been attributed to its preferential extraction and release from other gallic acid-containing phenolics in the kibbles during syrup preparation (*48*). Furthermore, notwithstanding the differences in analytical protocols, the phenolic patterns of the CSs obtained in the present work were, in general, comparable to those reported for CS (*13*). The predominance of gallic acid in the DS sample may be related to it being the chief phenol in the different varieties and clones of dates (*49*). In contrast to the present findings, protocatechuic acid, coniferyl alcohol, and vanillin were the major phenolics in methanol extracts of maple syrup prepared by solid-phase extraction (*50*).

Table 5

CONCLUSIONS

Laboratory-made carob syrups contained more proteins than date and maple syrups and more minerals (Ca, Mg, Na, K, and P) than maple syrup and, in general, higher, or at least similar, levels of the indicated minerals than date syrup. The carob syrups exhibited sugar compositions intermediate to those of the invert-sugar-like composition of date syrup and the overwhelmingly sucrose-containing maple syrup. Further, the vast majority of carob syrups contained more total phenols than maple syrup and higher, or at least comparable, levels of total phenols than date syrup. Similar patterns to those of total phenols were registered for the antioxidant capacity of the syrups by *in vitro* antioxidant capacity assays. Gallic acid was the major phenolic acid in the carob, date, and maple syrups, and, in general, the carob syrups contained more phenolic acids and flavonoids than the other syrups. The carob syrups browned more and generated more hydroxymethylfurfural than maple syrup during the heat-

concentration step and, in general, were less brown and contained lower levels of hydroxymethylfurfural than date syrup. These findings indicate that carob syrup exhibits a favorable phenolic profile, provides more proteins and minerals, contains more total phenols, and possesses a higher antioxidative potential than maple and date syrups. These traits render carob syrups, strong candidates to the category of mainstream syrups in international trade with obvious economic returns to the largely less-developed carob-producing countries. However, the age-old practice of heat concentration in open vats leads to excessive browning and the concomitant formation of high levels of the potentially mutagenic and carcinogenic hydroxymethylfurfural and, therefore, milder heating regimens are warranted in the production of carob syrups.

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CONFLICT OF INTEREST

The authors declare no conflict of interest

SUPPLEMENTARY MATERIALS

All supplementary material is available at www.ftb.com.hr

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AUTHORS' CONTRIBUTION

I. Toufeili conceptualized, supervised the chemical analyses, secured funding, and drafted the manuscript. M. Itani and M. Zeidan performed the chemical analyses and processed the collected data. O. Al Yamani developed and carried out the HPLC analyses. S. Kharroubi worked out the statistical design and supervised the statistical analyses. All authors have read and approved the final manuscript. I. Toufeili approved the final version of the manuscript.

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Table 1. Total soluble solids (TSS), proteins, browning index, pH, and hydroxymethylfurfural (HMF) of carob, maple, and date syrups

Carob accession	TSS/°Brix	*w*(protein)/(g/100g dm)	Browning index	pH	HMF/ (mg/kg dm)
Akkar	(75.33±0.76)^{b}	(2.74±0.02)^{h}	(73.07±3.09)^{ef}	(4.91±0.04)^{jkl}	(1712.11±0.34)^{gh}
Selaata	(79.75±0.25)^{hi}	(2.50±0.01)^{g}	(68.30±1.11)^{de}	(4.93±0.02)^{kl}	(1350.85±426.33)^{fg}
Wadi El Hojeir	(77.03±2.57)^{cd}	(1.83±0.02)^{e}	(87.80±0.20)^{g}	(4.72±0.01)^{h}	(1812.61±185.93)^{h}
Batroun	(78.28±0.46)^{efg}	(1.91±0.02)^{e}	(45.80±2.07)^{c}	(4.97±0.01)^{kl}	(881.13±94.57)^{cdef}
Maaroub	(78.70±0.35)^{fgh}	(1.85±0.03)^{e}	(31.33±0.95)^{b}	(4.93±0.08)^{kl}	(610.36±242.30)^{bc}
Bourjin	(78.48±0.28)^{fg}	(1.75±0.01)^{f}	(88.85±1.77)^{g}	(4.83±0.02)^{ij}	(1777.74±264.75)^{gh}
Marjayoun	(76.92±0.14)^{cd}	(1.77±0.00)^{e}	(48.97±1.08)^{c}	(5.17±0.04)^{m}	(779.46±6.09)^{bcd}
AUB1	(77.58±0.14)^{def}	(2.14±0.01)^{f}	(49.07±1.39)^{c}	(4.68±0.01)^{gh}	(1270.91±303.43)^{ef}
AUB2	(78.40±0.30)^{fg}	(4.40±0.06)^{k}	(85.53±10.51)^{fg}	(4.88±0.02)^{jk}	(1045.97±27.29)^{cdef}
AUB3	(80.18±0.08)^{i}	(1.81±0.02)^{e}	(56.70±8.66)^{cd}	(4.90±0.13)^{jkl}	(814.27±117.03)^{bcde}
AUB4	(79.43±0.06)^{ghi}	(3.21±0.31)^{j}	(57.90±1.20)^{g}	(4.45±0.01)^{d}	(519.17±210.24)^{h}
AUB6	(80.32±0.16)^{i}	(2.39±0.06)^{g}	(49.77±2.11)^{c}	(4.75±0.05)^{hi}	(874.15±50.53)^{bcde}
AUB7	(76.28±0.30)^{bc}	(2.94±0.07)^{i}	(52.40±3.97)^{c}	(4.56±0.00)^{ef}	(1103.44±352.25)^{def}
AUB8	(78.83±0.15)^{gh}	(0.98±0.02)^{b}	(32.40±3.27)^{b}	(4.99±0.10)^{l}	(711.41±91.27)^{bcd}
AUB9	(78.47±0.42)^{fg}	(4.82±0.01)^{l}	(86.93±12.07)^{cd}	(4.37±0.01)^{c}	(2168.79±513.89)^{b}
AUB10	(78.92±0.14)^{gh}	(1.35±0.02)^{c}	(88.13±0.59)^{g}	(4.62±0.04)^{fg}	(1783.54±171.88)^{gh}
AUB11	(78.75±0.15)^{gh}	(2.49±0.14)^{g}	(32.13±6.82)^{b}	(4.73±0.02)^{h}	(1120.86±302.09)^{def}
AUB12	(80.25±0.25)^{i}	(2.22±0.01)^{f}	(109.87±16.60)^{h}	(4.25±0.00)^{b}	(4048.94±181.92)^{i}
AUB14	(77.25±0.05)^{cde}	(2.97±0.02)^{i}	(127.27±5.36)^{i}	(4.49±0.01)^{de}	(1810.16±250.28)^{h}
Date Syrup	(75.50±0.00)^{b}	(1.55±0.07)^{d}	(98.00±23.36)^{gh}	(4.01±0.03)^{a}	(1986.62±283.49)^{h}
Maple Syrup (Amber)	(66.60±0.13)^{a}	(0.08±0.01)^{a}	(3.93±0.20)^{a}	(6.00±0.06)^{n}	(66.23±2.95)^{a}
Maple Syrup (Dark)	(66.92±0.14)^{a}	(0.16±0.00)^{a}	(4.14±0.17)^{a}	(6.60±0.06)^{o}	(72.46±2.20)^{a}
Range of carob syrups	75.33-80.32	0.98-4.82	31.33-127.27	4.25-5.17	519.71-4048.94
Mean ± SD of carob syrups	(78.38±1.37)	(2.45±0.940	(67.16±27.15)	(4.74±0.24)	(1378.76±809.04)

dm=dry mass, a, b, c,…=values with different superscripts in the same column are different ($p<0.05$) by Duncan's Multiple Range Test

Table 2. Fructose, glucose and sucrose contents of carob, maple and date syrups

Carob accession	*w*/(g/100 g dm)		
	Fructose	Glucose	Sucrose
Akkar	(12.10±0.96)^{b}	(6.89±0.77)^{bc}	(61.95±1.67)^{hi}
Selaata	(17.68±0.95)^{cd}	(5.89±0.79)^{b}	(59.25±3.02)^{gh}
Wadi El Hojeir	(21.67±1.44)^{fgh}	(10.68±0.94)^{gh}	(59.25±3.02)^{gh}
Batroun	(18.80±2.49)^{de}	(10.04±1.48)^{fgh}	(74.35±9.82)^{k}
Maaroub	(16.81±0.66)^{cd}	(8.30±0.55)^{cdef}	(65.22±3.81)^{hij}
Bourjin	(13.00±1.21)^{b}	(7.14±1.03)^{bcd}	(61.91±6.00)^{hi}
Marjayoun	(15.66±0.67)^{c}	(5.72±0.19)^{b}	(67.27±0.99)^{ijk}
AUB1	(23.61±2.17)^{hi}	(12.73±1.50)^{i}	(53.65±4.85)^{fg}
AUB2	(17.83±1.53)^{cd}	(9.42±1.07)^{efgh}	(49.85±3.99)^{ef}
AUB3	(19.32±2.18)^{def}	(10.80±1.30)^{gh}	(62.23±7.97)^{hij}
AUB4	(19.13±0.49)^{j}	(10.61±1.96)^{k}	(39.70±1.13)^{d}
AUB6	(22.98±0.66)^{gh}	(13.24±0.80)^{i}	(43.42±2.23)^{de}
AUB7	(25.39±1.72)^{i}	(16.89±1.03)^{j}	(58.05±3.96)^{gh}
AUB8	(16.20±1.09)^{c}	(7.95±0.47)^{cde}	(71.32±5.28)^{jk}
AUB9	(39.80±0.85)^{def}	(25.59±0.39)^{gh}	(5.41±0.34)^{a}
AUB10	(20.81±1.64)^{efg}	(11.46±0.66)^{hi}	(42.68±3.16)^{de}
AUB11	(19.19±1.20)^{def}	(8.90±1.15)^{defg}	(71.02±4.50)^{jk}
AUB12	(21.11±2.57)^{efg}	(9.39±0.16)^{efgh}	(31.71±3.85)^{c}
AUB14	(37.55±0.50)^{j}	(24.93±2.75)^{k}	(24.48±4.34)^{b}
Date Syrup	(43.20±0.78)^{k}	(42.89±0.78)^{l}	(3.74±0.83)^{a}
Maple Syrup (Amber)	(0.34±0.00)^{a}	(0.00±0.00)^{a}	(94.95±1.72)^{l}
Maple Syrup (Dark)	(0.35±0.00)^{a}	(0.35±0.00)^{a}	(96.48±4.15)^{l}
Range of Carob samples	12.10-39.80	5.72-25.60	5.41-74.35
Mean ± SD of carob syrups	(20.98±7.09)	(11.40±5.58)	(52.92±17.93)

dm=dry mass, a, b, c,…=values with different superscripts in the same column are different ($p<0.05$) by Duncan's Multiple Range Test

Table 3. Mineral composition of carob, date and maple syrups

Carob accession	*w*/(mg/100 g dm)				
	P	Ca	Mg	K	Na
Akkar	(116.54±2.95)^{a}	(234.28±0.00)^{k}	(83.14±4.00)^{h}	(1238.31±33.89)^{hi}	(7.89 ±0.80)^{ab}
Selaata	(703.81±96.54)^{fgh}	(184.25±1.12)^{hi}	(46.05±0.78))^{cde}	(885.41±36.94)^{de}	(30.51 ±1.90)^{c}
Wadi El Hojeir	(621.90±20.74)^{efg}	(170.77±21.40)^{gh}	(45.84±8.79))^{cde}	(1072.77±20.09)^{fg}	(39.92 ±0.44)^{e}
Batroun	(536.02±5.89)^{cde}	(169.78±3.34)^{gh}	(59.77±2.98)^{g}	(1037.27±60.41)^{fg}	(43.18 ±5.47)^{e}
Maaroub	(551.00±9.93)^{def}	(149.05±15.04)^{fg}	(42.51±6.36)^{cd}	(945.30±43.58)^{de}	(31.85 ±5.81)^{c}
Bourjin	(606.02±44.55)^{efg}	(162.59±53.03)^{gh}	(41.51±3.91)^{cd}	(788.68±53.99)^{cd}	(40.14 ±4.94)^{e}
Marjayoun	(659.45±47.53)^{efgh}	(108.12±2.63)^{bcd}	(51.63±2.29)^{efg}	(1102.00±48.22)^{g}	(37.64 ±2.82)^{de}
AUB1	(737.88±106.52)^{gh}	(120.89±12.37)^{cdef}	(58.94±4.56)^{g}	(975.24±8.23)^{ef}	(50.58 ±3.78)^{f}
AUB2	(787.89±42.19)^{hi}	(97.38±19.88)^{abc}	(52.74±7.06)^{efg}	(846.81±4.74)^{cde}	(29.72 ±1.67)^{c}
AUB3	(790.61±97.56)^{hi}	(111.46±1.84)^{bcde}	(52.16±3.73)^{efg}	(951.80±27.97)^{ef}	(41.59 ±4.60)^{e}
AUB4	(108.40±27.10)^{i}	(128.99±15.41)^{bcd}	(40.29±6.08)^{def}	(779.09±97.51)^{i}	(9.48 ±0.13)^{de}
AUB6	(589.02±31.63)^{efg}	(113.55±11.80)^{bcde}	(48.06±2.73)^{def}	(970.36±135.66)^{ef}	(34.16 ±3.42)^{cd}
AUB7	(258.39±32.46)^{ab}	(77.57±18.51)^{a}	(25.62±4.16)^{a}	(735.31±55.46)^{bc}	(12.41 ±1.41)^{b}
AUB8	(631.29±25.46)^{efg}	(95.30±4.39)^{abc}	(37.82±2.13)^{bc}	(816.31±24.36)^{cd}	(49.81 ±2.34)^{f}
AUB9	(908.13±174.05)^{a}	(110.76±6.91)^{def}	(48.20±1.66)^{bcd}	(1324.44±73.96)^{cd}	(37.81 ±2.57)^{ab}
AUB10	(1714.20±400.07)^{j}	(112.52±0.55)^{bcde}	(33.17±0.04)^{ab}	(1148.51±39.00)^{gh}	(94.65 ±1.89)^{h}
AUB11	(626.35±83.34)^{efg}	(142.39±18.60)^{efg}	(52.45±6.45)^{efg}	(852.40±4.57)^{cde}	(39.19 ±2.93)^{de}
AUB12	(287.01±12.09)^{b}	(142.35±12.34)^{efg}	(55.65±8.43)^{fg}	(1535.57±67.86)^{j}	(29.63 ±2.92)^{c}
AUB14	(408.62±11.58)^{bcd}	(86.78±7.43)^{ab}	(32.36±3.85)^{ab}	(631.33±43.49)^{b}	(79.67 ±3.28)^{g}
Date syrup	(561.28±2.79)^{ef}	(166.35±3.23)^{gh}	(78.35±0.87)^{h}	(1102.60±167.72)^{g}	(11.45 ±0.27)^{b}
Maple syrup (Amber)	(392.44±22.62)^{bc}	(220.54±11.66)^{jk}	(33.42±0.43)^{ab}	(322.15±1.92)^{a}	(5.88 ±1.10)^{a}
Maple syrup (Dark)	(120.46±6.08)^{a}	(203.09±22.85)^{ij}	(32.11±1.97)^{ab}	(349.62±18.71)^{a}	(5.17 ±0.43)^{a}
Range of carob syrups	108.40-1714.20	77.57-234.28	25.62-83.14	631.33-1535.57	7.89-94.65
Mean ± SD of carob syrups	(612.76±347.51)	(132.57±39.02)	(47.79±12.54)	(976.75±222.48)	(38.42±20.95)

dm=dry mass, a, b, c,…=values with different superscripts in the same column are different ($p<0.05$) by Duncan's Multiple Range Test

Table 4. Total phenols and antioxidant capacity of carob, maple and date syrups

Carob accession		Antioxidant capacity		
	w(total phenols as GAE)/(100 g dm)	FRAP/(μmol/100 g dm)	IC_{50}/(g/L)	TE/(mmol/100 g dm)
Akkar	(728.04±84.02)^{f}	(2.04±0.04)^{efg}	(31.97±2.00)^{ab}	(5.64±1.05)^{ghi}
Selaata	(732.02±72.68)^{f}	(1.39±0.26)^{bcde}	(16.54±1.54)^{ab}	(6.28±0.81)^{hi}
Wadi El Hojeir	(1367.93±40.37)^{g}	(1.65±0.03)^{cdef}	(16.96±0.63)^{ab}	(5.62±0.60)^{ghi}
Batroun	(442.87±69.00)^{cd}	(0.67±0.06)^{ab}	(18.59±0.91)^{ab}	(4.24±0.67)^{def}
Maaroub	(370.51±84.48)^{bc}	(1.43±0.50)^{bcde}	(46.17±6.83)^{b}	(2.53±0.36)^{bc}
Bourjin	(780.68±55.73)^{f}	(2.40±0.95)^{fg}	(16.553±1.49)^{ab}	(8.28±0.92)^{j}
Marjayoun	(357.85±12.42)^{b}	(1.14±0.08)^{bcd}	(26.56±0.92)^{ab}	(3.18±0.76)^{bcd}
AUB1	(494.58±15.37)^{de}	(1.13±0.04)^{bcd}	(14.36±1.85)^{ab}	(4.63±0.06)^{efg}
AUB2	(700.89±61.65)^{f}	(2.68±0.04)^{g}	(13.74±0.77)^{ab}	(4.85±0.57)^{efg}
AUB3	(520.89±12.96)^{de}	(0.94±0.08)^{bcd}	(18.70±0.00)^{ab}	(4.36±0.83)^{defg}
AUB4	(441.94±47.53)^{f}	(1.37±0.14)^{bcde}	(34.07±0.91)^{ab}	(3.58±0.66)^{cde}
AUB6	(453.20±8.55)^{de}	(1.49±0.19)^{bcde}	(24.15±1.80)^{ab}	(2.29±1.00)^{bc}
AUB7	(487.35±1.34)^{e}	(1.81±0.31)^{def}	(21.12±2.76)^{ab}	(4.18±0.16)^{def}
AUB8	(344.62±52.45)^{b}	(0.86±0.02)^{abc}	(36.33±0.72)^{ab}	(2.53±0.18)^{bc}
AUB9	(733.69±83.57)^{cd}	(1.38±0.80)^{bcde}	(20.20±0.16)^{ab}	(5.19±0.48)^{fgh}
AUB10	(1566.41±2.29)^{h}	(2.73±0.36)^{g}	(10.09±1.26)^{ab}	(6.59±0.65)^{i}
AUB11	(336.16±38.51)^{ab}	(1.02±0.08)^{bcd}	(36.25±0.90)^{ab}	(2.42±0.23)^{bc}
AUB12	(2214.66±5.62)^{i}	(14.85±1.41)^{h}	(4.92±0.70)^{a}	(20.53±2.24)^{k}
AUB14	(740.69±17.40)^{f}	(2.38±0.76)^{fg}	(19.85±0.00)^{ab}	(5.63±0.52)^{ghi}
Date Syrup	(461.20±12.70)^{de}	(1.06±0.02)^{bcd}	(33.69±0.62)^{ab}	(2.07±0.02)^{b}
Maple Syrup (Amber)	(260.96±2.60)^{a}	(0.10±0.00)^{a}	(647.08±14.53)^{c}	(0.39±0.01)^{a}
Maple Syrup (Dark)	(314.05±2.27)^{ab}	(0.11±0.00)^{a}	(500.97±59.04)^{d}	(0.41±0.00)^{a}
Range of carob syrups	336.16-2214.66	0.67-14.85	4.92-46.17	2.29-20.53
Mean ± SD	(729.12±486.98)	(2.28±3.11)	(22.97±10.78)	(5.40±4.00)

dm=dry mass, GAE=gallic acid equivalents, TE=Trolox equivalents, FRAP=ferric reducing antioxidant power, TEAC=Trolox equivalent antioxidant capacity,

DPPH=2,2-diphenyl-1-picrylhydrazyl, a, b, c,...=values with different superscripts in the same column are different ($p<0.05$) by Duncan's Multiple Range Test

Table 5. Phenolic acids and flavonoids profiles of carob, maple and date syrups

Carob accession	*w*/(μg/g dm)						
	Gallic acid	Syringic acid	Caffeic acid	*t*-cinnamic acid	*p*-coumaric acid	Catechin	Quercetin
Akkar	(425.96±6.59)^{cdef}	(1.24±0.29)^{f}	(0.92±0.18)^{bcdef}	(14.17±1.05)^{de}	(13.28±0.78)^{hi}	(1.04±0.14)^{de}	(1.21±0.01)^{abc}
Selaata	(770.00±46.2)1^{j}	(0.08±0.02)^{a}	(1.01±0.14)^{cdefg}	(17.61±2.69)^{gh}	(12.89±2.16)^{gh}	(1.05±0.03)^{de}	(1.31±0.05)^{cde}
Wadi El Hojeir	(1377.07±91.41)^{gh}	(1.93±0.01)^{hi}	(1.26±0.1)9^{h}	(15.01±0.82)^{ef}	(11.05±0.96)^{efgh}	nd^{a}	(1.56±0.00)^{f}
Batroun	(204.12±18.61)^{ab}	(0.92±0.06)^{def}	(0.72±0.03)^{b}	(15.50±2.80)^{efg}	(9.81±1.08)^{cdef}	(1.28±0.03)^{de}	(1.32±0.19)^{cde}
Maaroub	(564.74±7.14)^{fg}	(1.67±0.05)^{gh}	(0.78±0.06)^{bc}	(13.69±0.52)^{de}	(8.82±0.50)^{cde}	(1.57±0.34)^{f}	(1.69±0.03)^{f}
Bourjin	(2350.97±333.10)^{l}	(0.41±0.08)^{bc}	(1.12±0.01)^{fgh}	(8.14±0.87)^{bc}	(15.34±0.02)^{ij}	(0.19±0.01)^{a}	(1.23±0.02)^{abcd}
Marjayoun	(522.84±14.93)^{efg}	(0.34±0.09)^{abc}	(1.04±0.01)^{defgh}	(8.36±0.17)^{bc}	(8.17±1.45)^{bcd}	(0.63±0.08)^{bc}	(1.23±0.01)^{abcd}
AUB1	(827.92±76.15)^{hi}	(0.90±0.06)^{de}	nd^{a}	(10.45±1.15)^{c}	(13.34±0.77)^{hi}	(1.04±0.14)^{de}	(1.32±0.03)^{cde}
AUB2	(955.05±67.43)^{i}	(1.75±0.30)^{ghi}	nd^{a}	(7.66±0.50)^{b}	(10.62±0.07)^{efg}	(0.31±0.07)^{ab}	(1.29±0.04)^{bcde}
AUB3	(657.01±84.33)^{bcdef}	(0.63±0.02)^{cd}	(1.09±0.11)^{fgh}	(8.13±1.71)^{bc}	(15.94±1.25)^{j}	(0.88±0.08)^{cde}	(1.19±0.06)^{ab}
AUB4	(394.29±24.12)^{hi}	nd^{j}	(0.80±0.14)^{defgh}	(18.31±0.85)^{fgh}	(25.43±0.13)^{def}	(0.07±0.02)^{a}	(1.25±0.02)^{abcd}
AUB6	(488.69±60.84)^{cdefg}	(0.77±0.23)^{de}	(0.89±0.09)^{bcdef}	(23.50±0.45)^{j}	(11.76±1.17)^{fgh}	(1.00±0.10)^{de}	(1.55±0.04)^{f}
AUB7	(658.90±21.37)^{gh}	(1.57±0.52)^{g}	(0.77±0.09)^{bc}	(19.88±0.01)^{i}	(12.89±1.28)^{gh}	(1.08±0.18)^{de}	(1.35±0.06)^{e}
AUB8	(361.44±23.63)^{abcd}	(2.00±0.28)^{ij}	(1.06±0.09)^{efgh}	(28.99±2.13)^{k}	(15.66±0.83)^{j}	(1.02±0.12)^{de}	(1.17±0.05)^{ab}
AUB9	(838.32±27.04)^{bcde}	(2.26±0.23)^{a}	(1.04±0.13)^{bcd}	(16.59±1.53)^{hi}	(9.93±1.38)^{l}	nd^{a}	(1.23±0.02)^{abcde}
AUB10	(1890.78±185.51)^{k}	(1.07±0.20)^{ef}	(0.82±0.11)^{bcde}	(12.65±0.92)^{d}	(7.55±0.75)^{bc}	(1.20±0.24)^{e}	(1.31±0.02)^{cde}
AUB11	(292.96±70.24)^{hi}	(0.16±0.07)^{ab}	(0.77±0.02)^{bc}	(22.58±2.54)^{j}	(17.64±1.82)^{jk}	(0.79±0.16)^{cd}	(1.15±0.07)^{a}
AUB12	(7666.09±370.46)^{m}	(2.02±0.07)^{ij}	(0.89±0.01)^{bcdef}	(8.85±0.65)^{bc}	(5.96±1.10)^{b}	nd^{a}	(1.84±0.08)^{g}
AUB14	(947.56±29.72)^{i}	(1.61±0.21)^{gh}	(1.17±0.17)^{gh}	(14.98±1.29)^{ef}	(18.49±3.74)^{k}	(0.33±0.07)^{ab}	(1.33±0.08)^{de}
Date Syrup	(253.58±16.87)^{abc}	nd^{a}	(7.72±0.42)^{i}	nd^{a}	(2.82±0.25)^{a}	(0.14±0.02)^{a}	(1.15±0.03)^{a}
Maple Syrup (Amber)	(134.87±26.22)^{a}	nd^{a}	nd^{a}	nd^{a}	(0.71±0.08)^{a}	(2.56±0.31)^{g}	(1.23±0.02)^{abcd}
Maple Syrup (Dark)	(221.03±85.71)^{abc}	nd^{a}	nd^{a}	nd^{a}	(0.87±0.13)^{a}	(1.75±0.03)^{f}	(1.25±0.03)^{abcde}

Range of carob syrups	(204.12-7666.09	nd-2.26	nd-1.26	7.66-28.99	5.96-25.43	nd-1.57	1.15-1.84
Mean ± SD	(1165.77±1666.59)	(1.13±0.72)	(0.85±0.34)	(15.00±5.91)	(12.87±4.58)	(0.71±0.50)	(1.34±0.19)

dm= dry mass, nd= not detected

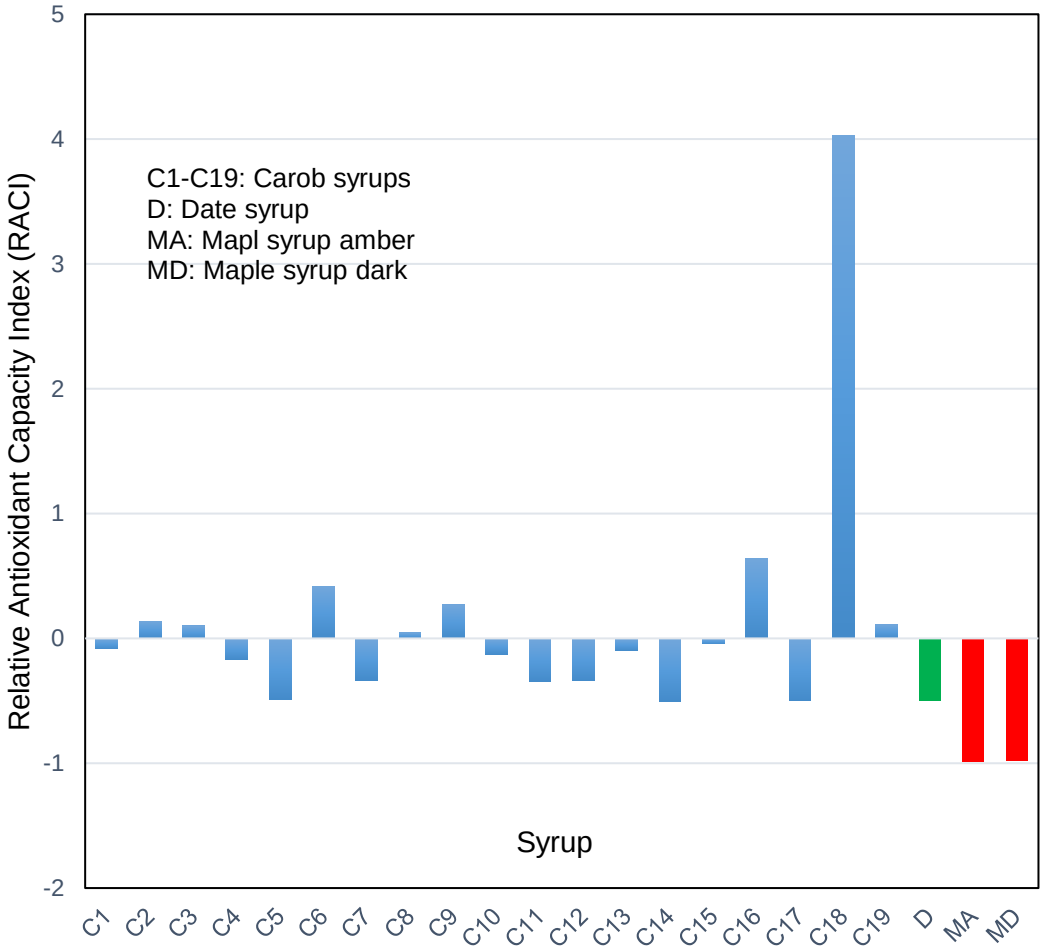

Fig. 1. Relative antioxidant capacity indices (RACI) of the analyzed syrups (C1-C19 refer to the carob syrups prepared from the carob accessions as listed in Tables 1-5)

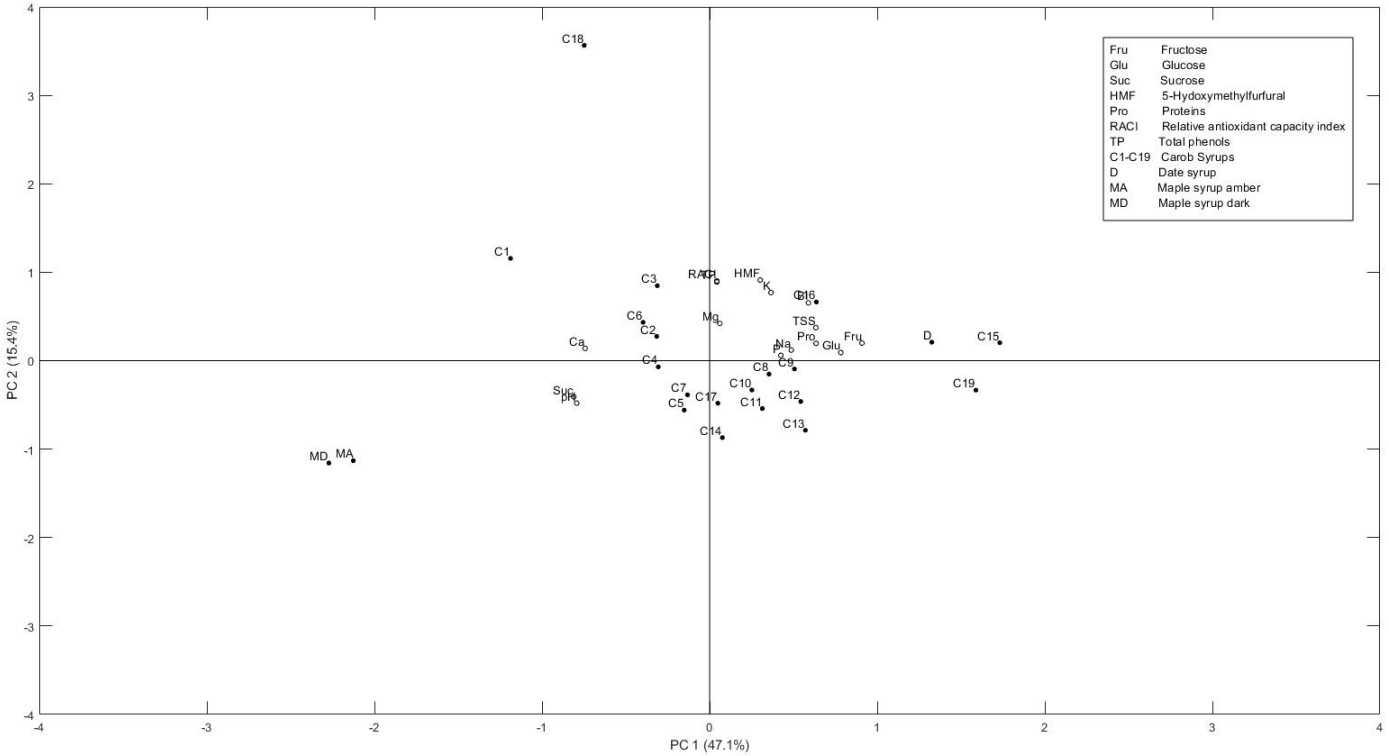

Fig. 2. Principal component analysis biplot showing relationships amongst the chemical and physicochemical parameters and the analyzed syrups (C1-C19 refer to the carob syrups prepared from the carob accessions as listed in Tables 1-5)

Table S1. Morphological characteristics of carob pods from the accessions used in molasses making

Carob accession	*m*/g	*l*/cm	*w*/cm	*t*/cm	*N*(seed)
Akkar	(23.80±5.20)^{g}	(18.52±2.87)^{h}	(3.02±2.07)^{ab}	(0.91±0.19)^{defg}	(11±1.48)^{hij}
Selaata	(19.38±3.68)^{ef}	(13.17±1.70)^{cde}	(2.25±0.17)^{a}	(0.78±0.16)^{bcd}	(9±1.14)^{cdef}
Wadi El Hojeir	(11.73±2.07)^{abc}	(15.30±0.67)^{efg}	(1.65±0.10)^{a}	(0.60±0.10)^{a}	(12±1.90)^{j}
Batroun	(18.10±3.59)^{def}	(10.97±1.28)^{ab}	(2.29±0.15)^{a}	(0.99±0.20)^{efg}	(11±1.63)^{hij}
Maaroub	(15.67±1.77)^{cde}	(10.08±0.49)^{a}	(1.86±0.13)^{a}	(0.80±0.26)^{bcde}	(9±1.43)^{bcd}
Bourjin	(19.18±5.75)^{ef}	(14.18±2.28)^{def}	(2.40±0.19)^{ab}	(0.96±0.16)^{defg}	(11±1.26)^{ghij}
Marjayoun	(15.57±2.41)^{cde}	(9.99±0.60)^{a}	(1.71±0.31)^{a}	(0.89±0.13)^{defg}	(8±1.18)^{ab}
AUB1	(21.08±3.57)^{fg}	(17.08±2.16)^{gh}	(2.22±0.33)^{a}	(0.79±0.13)^{bcd}	(10±0.48)^{fghij}
v/vAUB2	(12.83±4.77)^{abc}	(13.15±2.54)^{cde}	(2.17±0.23)^{a}	(0.71±0.09)^{abc}	(13±0.52)^{k}
AUB3	(25.10±5.58)^{g}	(15.86±3.96)^{fg}	(2.24±0.37)^{a}	(0.93±0.12)^{defg}	(11±0.48)^{hij}
AUB4	(18.07±4.02)^{a}	(10.22±2.86)^{abc}	(2.30±0.38)^{a}	(0.68±0.09)^{ab}	(8±1.07)^{bc}
AUB6	(11.05±2.18)^{ab}	(9.88±1.82)^{a}	(1.98±0.26)^{a}	(0.94±0.16)^{defg}	(9±2.31)^{cdefg}
AUB7	(14.54±4.38)^{bcd}	(14.64±2.13)^{def}	(3.77±5.91)^{b}	(0.85±0.15)^{cdefg}	(11±1.05)^{hij}
AUB8	(18.14±4.12)^{def}	(10.07±1.35)^{a}	(2.23±0.28)^{a}	(1.01±0.10)^{g}	(10±0.88)^{efghi}
AUB9	(25.34±8.06)^{g}	(11.34±2.1)^{de}	(1.70±0.26)^{ab}	(0.65±0.13)^{defg}	(8±0.57)^{cde}
AUB10	(11.81±3.33)^{abc}	(12.71±1.88)^{bcd}	(1.89±0.27)^{a}	(0.98±0.19)^{efg}	(10±1.52)^{defgh}
AUB11	(22.25±4.75)^{fg}	(10.27±1.94)^{a}	(2.31±0.33)^{a}	(0.85±0.17)^{cdefg}	(7±0.88)^{a}
AUB12	(10.46±2.62)^{ab}	(12.54±4.03)^{bcd}	(1.86±0.22)^{a}	(0.88±0.36)^{bcdef}	(11±0.97)^{ij}
AUB14	(19.15±4.70)^{g}	(11.60±0.17)^{a}	(2.14±0.59)^{a}	(0.89±0.03)^{fg}	(15±1.34)^{l}

a, b, c,…=values with different superscripts in the same column are different ($p<0.05$) by Duncan's multiple range test

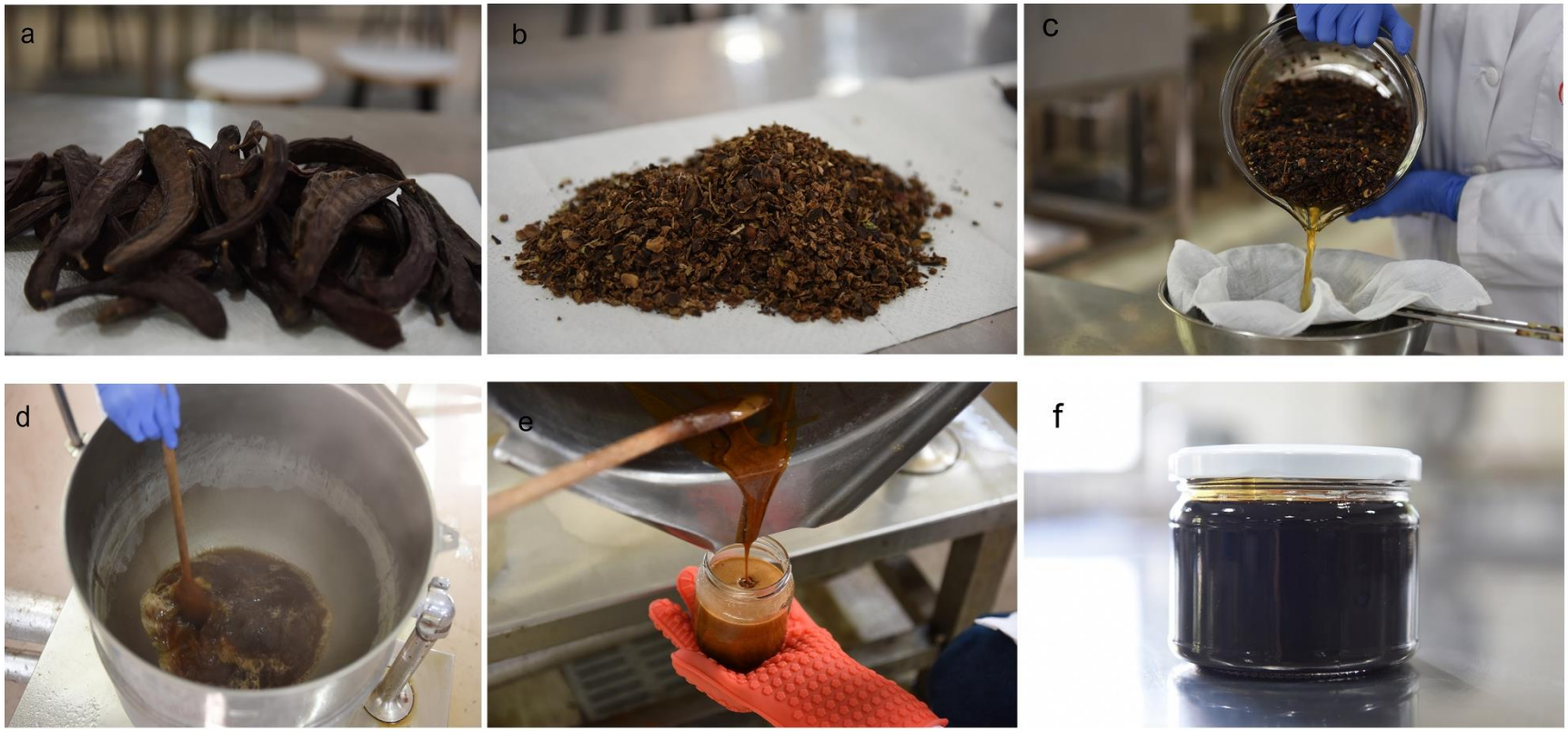

Fig. S1. Preparation of carob syrup: a) carob pods, b) coarse-ground carob kibbles, c) filtering the carob extract, d) heat concentration of the carob extract, e) pouring the hot syrup into glass jars, and f) carob syrup