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Properties of Rose Hip Marmalades

Oktay Yildiz^{1*} and Mehmet Alpaslan²

¹Vocational School of Maçka, Karadeniz Technical University, TR-61000 Trabzon, Turkey ²Department of Food Engineering, Inonu University, TR-44280 Malatya, Turkey

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Summary

Rose hip, also known as wild rose, is a summer fruit. The aim of this research is to present physical, chemical, rheological, sensory and antioxidant properties of rose hip marmalades. Rose hips cultivated in Turkey are processed into pulp and then marmalade is made by using vacuum evaporator or classical method. For the purposes of this investigation, marmalades produced on a factory scale using two methods were compared to commercial marmalades purchased on market. The marmalades exhibited high levels of antioxidant activity as well as total phenolic content. The consistency indices for the marmalades were determined to be between 64.2 and 321 Pa·sⁿ. Colour parameters, namely *L*, *a*, *b*, were measured and correlations between the examined parameters were calculated.

Key words: rose hip, marmalade, sensory properties, chemical properties, rheological properties, antioxidant properties

Introduction

A member of Rosaceae family, rose hip fruit resembles cornelian cherry. It is a dwarf plant of 2 to 3 m high with ovoid pinkish red fruits. Its main native land is West Asia and North Europe and it is grown especially in the Middle and North-East of Anatolia. Gümüşhane, Turkey, and its districts have a rich rose hip population (1–3).

Rose hip, as many plants do, can synthesize aromatic substances, most of which are phenols or their oxygen-substituted derivatives. In many cases, these substances serve in plant defense mechanisms to counteract reactive oxygen species (ROS) in order to survive, and prevent molecular damage or damage by microorganisms, insects and herbivores (4,5). Rose hip is rich in vitamins (A, B, K, and especially C and P), minerals (Mg, K, P), phenolics, antioxidants, pectin, organic acids, essential fatty acids, and tannins (2,6–10,11). The main importance of rose hip is that it is rich in vitamin C. Ascorbic acid, a constituent of vitamin C, is the most well-known antioxidant and an important molecule in plant tissues that protects plants against oxidative damage caused by the

oxidative metabolites of photosynthesis and aerobic processes (12).

Edible parts of the fruit are rarely eaten directly as fresh, they are mostly consumed dried as well as in the form of marmalade, nectar, wine, tea, pulp, or drinks (13,14). Rose hip pulp is produced by mechanical crushing of fruits (15), then pulp, sugar, water, and citric acid are mixed and evaporated to manufacture marmalade. At pH=3.2 to 3.8 marmalades are sterilized at 85–95 °C for 8–40 s

The EU Council Directive (16) and Turkish Food Codex (17), related to jams, jellies, marmalades and sweet chestnut purée intended for human consumption, both specify definitions and labels of jams and related products (18). According to Turkish Food Codex (17), traditional marmalade is a mixture, pulp and/or purée of one or more kinds of fruit and water, brought to a suitable gelled consistency of sugars. The quantity of pulp and/or purée used for the manufacture of 1000 g of finished traditional marmalade products shall not be less than 450 g as a general rule. Traditional marmalades must have a soluble dry matter content of 55 % or more

determined by refractometer. This product is called jam or extra jam in the EU Council Directive. However, jams should include undivided, unstrained fruit according to the Turkish Codex.

There have been studies on the physicochemical properties of rose hip fruits (2,3,13,19) and on the dehydration of rose hip (9,11). However, this is the first report about the procedure of rose hip marmalade production and its chemical, rheological, sensory and antioxidant properties.

Materials and Methods

Fruits

Wild rose hip fruits collected from Gümüşhane (Eastern Black Sea Region, Turkey) at the end of summer, after full ripening, were used in this study. Nearly 7 tonnes of fresh fruits were brought to Gümüşsu Food Co. in Gümüşhane, Turkey. The fruits were frozen in bags at –10 °C until the beginning of the production of marmalades.

Marmalade production

Marmalades were produced on a factory scale. Thawed fruits at room temperature were washed in a washing pool (UWM, Kurtsan Stainless Steel Industry, Bursa, Turkey) and transferred to carving unit (Turbo crusher, Kurtsan Stainless Steel Industry) with water nearly 1 to 1.5 times of fruit mass. Fruit pieces of 6–7 mm were poured into a boiler (Kurtsan Stainless Steel Industry). Extraction process was followed at 90 °C for 120 min. The mixture was moved to a two-stage pulper (Turboextraktör, Kurtsan Stainless Steel Industry) working at 800 rpm. Mesh size in the first stage was 2 mm and those in the second stage, with three nested sieves, were 1.1, 0.7 and 0.4 mm. The mix was separated in a centrifugal separator (SOZA separator, Maschinenfabrik Kyffhäuserhütte, Artern, Germany). Separated product (pulp) was processed to marmalade by the addition of appropriate amount of sugar to reach 55 °Brix in the final products with 450 g of pulp (12 °Brix) for 1000 g of marmalade (17) using two different production methods. In the first method (marmalades produced using vacuum), double jacket vacuum evaporator (Buller, Danışman, Bursa, Turkey) was used at 650 mmHg (60 °C), and in the second method (marmalades produced with classical method), 500-litre classical conventional open-type boiler (diameter 2 m and height 1.8 m) was used at atmospheric pressure (90 °C). Samples of marmalades produced by both procedures were randomly selected for this study, and they were filled in hot, dark coloured 800-mL jars and sterilized at 95 °C for 120 s.

Three different brands of commercial marmalades were purchased from local markets and refrigerated at $4~^\circ\text{C}$ until analysis.

Chemicals

Trolox[®] (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid, 97 %), gallic acid (GA), phenolphthalein, Folin-Ciocalteu reagent, sodium carbonate and other basic chemicals were purchased from Sigma-Aldrich (Steinheim,

Germany). All the chemicals used were of analytical grade. Beet sugar used in the production was supplied from a local company in Gümüşhane, Turkey.

Physical, chemical and antioxidant capacity analyses

Total acidity, pH, dry matter, ash, total sugar and reducing sugar content were analyzed according to AOAC methods (20). Refractometric soluble solid content was determined according to Tanner and Brunner (21) by means of an ATAGO™ Abbe refractometer Type 1 (Atago, Tokyo, Japan). Ascorbic acid content was determined according to the method of Farajzadeh and Nagizadeh (22).

Protein content was determined by a semiautomatic micro-Kjeldahl assay. The protein content, assuming all the nitrogen is of protein origin, was calculated by multiplying total N with coefficient 6.25 (23).

Hydroxymethylfurfural (HMF) was determined with a spectrophotometer (Shimadzu UV-2450, Shimadzu Corporation, Kyoto, Japan) at 550 nm (24-26). Total phenolic compounds were determined by the Folin-Ciocalteu method (27) with simple modification and expressed as gallic acid equivalent (GAE). A mass of 2 g of sample (lyophilized fruit powder and marmalades) was dissolved in 20 mL of distilled water, centrifugated at 6000×g for 10 min and the supernatant was separated. A volume of 0.1 mL of the supernatant was mixed with 5 mL of distilled water and 0.5 mL of commercial Folin-Ciocalteu reagent (0.2 M based on sodium hydroxide titration). The content was mixed well and kept at room temperature for 5 min followed by the addition of 2.0 mL of 10 % aqueous sodium carbonate and incubation at room temperature for 1 h. Absorbance of the developed blue colour was read at 760 nm against a blank reagent. For calibration curve, five standard gallic acid solutions (0-100 mg/L) were prepared in distilled water and their absorbances were read according to the same protocol.

The antioxidant capacity of the marmalades was examined using FRAP (ferric ion reducing antioxidant power) method by comparison with the activity of a known antioxidant, Trolox® (Trolox equivalents: TE) (28). Total anthocyanins were determined spectrophotometrically according to Wrolstad (29) using pH differential method at 510 nm with the molar absorption coefficient of cyanidin-3-glucoside (ε =29 600 M⁻¹cm⁻¹). Determination of carotene content was conducted according to Davies (30) and Pirone et al. (11) with slight modifications. Marmalades were extracted several times with acetone/petroleum ether (1:1) at -18 °C and every sample collected in 100-mL volumetric flasks was covered with dark coloured paper so as not to be affected by light. Absorbances were read at 460 nm. The molar absorption coefficient for red and yellow carotenes was determined to be 2000 M⁻¹cm⁻¹.

Colour measurement of the marmalades was carried out using a colorimeter (CR-10, Minolta, Osaka, Japan) and the measurements were recorded as Hunter L, a and b colour values (31). Colour values for each sample were computed by using three measurements from different positions. The colour values were expressed as L for darkness/lightness (0 black, 100 white), -a greenness, +a redness, -b blueness, and +b yellowness.

Pectin content was determined according to the rapid and quantitative method used by Shelukhina and

Fedichkina (32). This method is based on the precipitation with ethanol acidified after the extraction of pectins. The dry ground material (50 g) was extracted with hot water (0.5 L, twice, 70–75 °C, 1 h). The combined aqueous extracts were concentrated and precipitated with two portions of 70 % aqueous ethanol acidified with HCl to pH=2.9–3.5. The resulting precipitate was suspended in water and lyophilized. The yield of water-soluble pectins was calculated.

Viscosity measurement and rheological behaviour

The viscosity (Pa·s) of marmalades was measured at 30, 40, 50, 60 and 70 °C using a Brookfield rotational viscometer (Model RVDV-I+, Brookfield Engineering Laboratories, Stoughton, MA, USA) equipped with spindle no. 6 at the speed of 0.6, 1.5, 3, 6, 12, 30 and 60 rpm. Enough marmalade in a 600-mL beaker was used to immerse the groove on the spindle with the guard leg. Three readings were taken per sample at 30-second intervals. Temperature was maintained using a thermostatically controlled water bath (33).

Sensory evaluation

Sensory properties of marmalades were evaluated according to Turkish Standards Institution (34) and Aksu et al. (35) with slight modifications. The panel consisted of 5 male and 5 female, aged 18 to 32, nonsmoker panelists who were familiar with rose hip marmalade. All panelists were selected among 24 candidates from a training course on the recognition of basic sensory stimuli.

For evaluation, approx. 30 g of each marmalade sample were given to assessors labelled with random 3-digit codes. The samples were brought to room temperature before testing and served under white lightning in porcelain plates. Each panelist received a rating form, a slice of white bread, and a knife for each blend. At each session, sensory attributes were discussed. The descriptors were selected for use in formal sessions. Panelists were required to stir each sample for 15 s before evaluation. Water was served to the panelists to cleanse the palate between evaluations. After palate cleaning, a pause (15 s) was imposed before the panelists could assess the next sample. Marmalades were rated for the colour and appearance (1-5 scale), consistency (1-5 scale), odour (1-4 scale) and taste (1-6 scale). Lower scores mean less desirable property, while the highest scores represent the most desirable property.

Sensory evaluation is an important quality criterion in foods. Both taste and health properties of traditional foods such as traditional rose hip marmalade need to be improved.

Statistical analysis

All the experimental results were presented as mean values±S.D. of triplicate measurements and the data were evaluated by using the analysis of variance (ANOVA). The mean values statistically different from each other were compared using Duncan's multiple comparison test. SPSS v. 9.0 for Windows software was used for statistical analyses (SPSS Inc., Chicago, IL, USA). Differences were considered significant at p<0.05.

Results and Discussion

Physical, chemical and antioxidant properties of fruits and marmalades

Many factors affect the composition of plants including region, variety, state of ripening, soil type and condition, irrigation and weather (36,37). The composition of the wild rose hip affects the properties of marmalades. The physical and chemical properties of rose hip fruits and marmalades are given in Tables 1 and 2. As shown in Table 1, pH, acidity (%), dry matter (%), phenolic content as GAE (mg/100 g), and ascorbic acid content (mg/100 g) of fresh fruits were 3.86, 3.2, 32.5, 9982 and 895.1, respectively. The studied parameters of rose hip fruits were similar to those found by Ercisli (19) and Pirone *et al.* (11).

The determined properties of marmalades indicated that there were some differences among marmalades produced using vacuum evaporator, marmalades produced by classical method and commercially purchased marmalades. They contain a considerable amount of vitamin C and phenolic compounds. Total dry matter and soluble solid content of marmalades produced using vacuum evaporator and those purchased commercially were higher than of those produced by classical method. Total acidity of marmalades produced using vacuum evaporator, purchased commercially and produced by classical method was 0.6, 0.79, and 0.9 %, respectively. At low acidity, inversion was insufficient; the content of reducing sugar was low. As a matter of fact, correlation (correlation is significant at p=0.01 level) coefficient between reducing sugar and acidity was found to be 0.008 (Table 3). As it can be seen, strong positive relationship was observed

Table 1. Physical, chemical and antioxidant properties of rose hip fruits

Properties	Content
m(1000 fruits)/g	1870.3±205
w(fruit flesh)/%	66.9±12.2
η (total soluble solid content)/°Brix	22.1±2.9
pH	3.86 ± 0.12
acidity as citric acid/%	3.2±0.1
w(total dry matter)/%	32.5±4.2
<i>w</i> (ash)/%	3.2 ± 0.5
w(protein)/%	7.2 ± 0.4
w(pectin)/%	4.1±0.3
w(total phenolic composition as GAE per mass of fresh fruit)/(mg/100 g)	9982±90
w(ascorbic acid per mass of fresh fruit)/(mg/100 g)	895.1±58
FRAP antioxidant capacity as TE per mass of fruit/ (mM/g)	1.840±0.22
w(anthocyanins as cyanidin-3-glucoside)/ (mg/kg)	28.2±3
w (carotenes as β -carotene)/(mg/kg)	44.2±4

All data represent the mean values of three determinations±S.D. (standard deviation)

Table 2. Physical, chemical and antioxidant properties of marmalades

	Marmalade samples				
Parameter	produced using vacuum evaporator	produced by classical method	commercially purchased marmalades		
w(total dry matter)/%	(82.30±2.20) ^b	(70.20±3.1) ^a	(79.30±1.1) ^b		
total acidity as malic acid/%	$(0.60\pm0.12)^a$	$(0.9\pm0.1)^{b}$	$(0.79\pm0.1)^{ab}$		
pH	(3.50±0.15) ^a	$(2.8\pm0.2)^{a}$	$(3.0\pm0.12)^a$		
w(ash)/%	$(0.23\pm0.03)^a$	$(0.20\pm0.02)^{a}$	$(0.25\pm0.03)^a$		
η (total soluble solid content)/°Brix	$(55.50\pm0.50)^{b}$	$(53.0\pm1.0)^a$	$(55.0\pm0.50)^{b}$		
w(ascorbic acid)/(mg/100 g)	$(45.40\pm1.70)^{b}$	(25.05±7.5) ^a	(125.20±9.5) ^c		
w(crude protein)/%	$(3.3\pm0.3)^{b}$	$(2.3\pm0.4)^{a}$	$(2.1\pm0.3)^{a}$		
w(total sugar)/%	(49.77±0.30) ^a	$(48.08\pm2.10)^{a}$	$(54.27\pm1.40)^{b}$		
w(reducing sugar)/%	(9.89±0.30) ^a	$(22.9\pm0.90)^{c}$	(14.5±0.80) ^b		
w(HMF)/(mg/kg)	$(3.86\pm0.45)^a$	(32.64±1.15) ^c	$(5.64\pm0.85)^{b}$		
w(pectin)/%	$(0.33\pm0.04)^a$	$(0.28\pm0.04)^{a}$	$(0.62\pm0.1)^{a}$		
L	(30.20±0.10) ^c	$(23.40\pm0.20)^{a}$	$(27.40\pm0.20)^{b}$		
a	$(16.60\pm0.20)^{b}$	$(10.30\pm0.10)^a$	(19.20±0.10) ^c		
b	(8.90±0.10) ^a	$(15.10\pm0.10)^{c}$	$(12.50\pm0.10)^{b}$		
w(total phenolic content as GAE per mass of marmalade)/(mg/100 g)	$(645.6\pm64.2)^a$	(912.4±82.5) ^b	(761.2±42.4) ^a		
FRAP antioxidant capacity as TE per mass of marmalade/(mM/g)	(26.15±1.25) ^a	$(41.25\pm4.02)^{b}$	(30.05±2.05) ^a		
w(anthocyanin as cyanidin-3-glucoside)/(mg/kg)	(55.22±3.1) ^a	(62.45±2.1) ^b	$(50.83\pm1.10)^a$		
w(carotene as β-carotene)/(mg/kg)	(71.42±2.4) ^a	(88.05±3.5) ^b	(68.52±3.1) ^a		

Mean values followed by the same letter are not statistically different (p<0.05)

Averages values are expressed as mean±S.D. of three replicate determinations. Values of commercially purchased marmalades (average values of three different brands) are also of three replicate determinations

Table 3. Correlations (R and p values) between some parameters

	Reducing sugars	HMF	L	а	b	Total phenolic composition	FRAP antioxidant capacity	Colour and appearance
Total acidity	0.807, 0.008**	0.692, 0.039*	-0.763, 0.017*	-0.448, 0.226	0.834, 0.005**	0.959, 0.00**	0.868, 0.002**	
Reducing sugars	1	0.953, 0.00**	-0.986, 0.0**	-0.793, 0.011*	0.963, 0.00**	0.920, 0.00**	0.964, 0.00**	-0.974, 0.00**
HMF		1	-0.928, 0.0**	-0.939, 0.0**	0.847, 0.004**	0.852, 0.004**	0.943, 0.00**	-0.878, 0.002**
L			1	0.758, 0.018*	-0.978, 0.00**	-0.877, 0.002**	-0.915, 0.001**	0.953, 0.00**
a				1			-0.803, 0.009**	0.681, 0.044*
b					1	0.899, 0.001**	0.892, 0.001**	-0.960, 0.0**
Total phenolic composition						1	0.969, 0.0**	-0.900, 0.001**
FRAP antioxidant capacity							1	-0.933, 0.0**

R=Pearson's correlation coefficient (p<0.05), p=significance, *weak correlation, **strong correlation

between the reducing sugar and acidity values (R=0.807, p=0.008). Total sugar content of commercially purchased marmalades was considerably higher than of other marmalades. This may be attributed to the added sugar for higher profitability. Total sugar values of rose hip marmalades had previously been determined to be between 39 and 56.9 % (15). It can be seen in Table 2 that the highest ascorbic acid content was found in the commercially purchased marmalades. As expected, in the marmalades produced by classical method, ascorbic acid content (25.05 mg/100 g) was the lowest and HMF content (32.64 mg/kg) was the highest. This may be attributed to the negative effect of temperature. Although the content of HMF can be influenced by temperature changes, ascorbic acid can be degraded by factors such as temperature, metal ions, oxygen, moisture content and light (38). HMF limits in marmalades are not specified in the Turkish Food Codex. However, the determined level of HMF in marmalades is distinctly lower than the values of the first class jam and honey (40 mg/kg) in literature (17,39). Correlation coefficient (R) and the level of significance (p) between the reducing sugar and HMF were calculated to be 0.953 and 0.00, respectively (Table 3). According to these results, strong positive relationship was observed between the reducing sugar and HMF values. Hydroxymethylfurfural content is widely used as an indicator of the Maillard reaction, which occurs between reducing sugars and amino acids (40-42). The direction and speed of reaction depend on many factors, such as material composition. In our study, the higher the reducing sugar content was, the higher the HMF content was. Our findings showed similarity with previous reports (26,43). The amount of HMF in plum, apple and apricot marmalades was between 18.3 and 25.7 mg/kg and HMF content of mulberry pekmez was between 18.0 and 152.3 mg/L (26,43). Pekmez is one of the most common and known concentrated fruit juices (especially mulbery, grape, date, apricot, sugar beet) in Turkey. Since pekmez contains high amount of sugar, mineral and organic acids, it is very important food product for human nutrition (26). It is consumed mainly for breakfast instead of jam or marmalade.

The total antioxidant capacity of marmalades as TE per mass of fresh fruit ranged from 26.15 to 41.25 mM/g and total phenolics as GAE per mass of fresh fruit ranged from 645.6 to 912.4 mg/100 g. The antioxidant value and total content of phenolics were higher in marmalades produced by classical method than in other marmalades. Correlation coefficients and significant values (Table 3) show that positive correlation was observed between total phenolic composition and total acidity (R=0.807, p=0.008), total phenolic composition and reducing sugar (R=0.920, p=0.000), total phenolic composition and HMF (R=0.852, p=0.004), total phenolic composition and antioxidant capacity (R=0.969, p=0.000), and between HMF and antioxidant capacity (R=0.943, p=0.000). Similarly, Turkmen et al. (44) found that antioxidant activity correlated with increased browning of honey samples. Another study reported that there was positive correlation between HMF and DPPH radical scavenging activity (45).

Antioxidant capacity as TE per mass of dry sample of cherry laurel fruits (46) and Andean tubers (12) had previously been reported to be between 3.363 and 19.981 mM/g,

and 0.35 and 11.8 μ mol/g, respectively. Total phenolic content calculated by using the same method of marmalades was considerably higher than of black currant (3.61–4.35 mg/g), blueberry (2.70–3.48 mg/g), strawberry (1.61–2.94 mg/g) and raspberry (2.7–3.03 mg/g) (47).

Total anthocyanins (62.45 mg/kg) and carotenes (88.05 mg/kg) of marmalades produced by classical method were higher than of the other two types, probably because of better extraction. It had previously been shown that total anthocyanin and carotene content of rose hip nectars were 31 and 42.6 mg/kg, respectively (11). Our results were higher than those of that study because of higher fruit content in marmalades.

Pectin content in marmalades produced using vacuum, classically and commercially produced was 0.33, 0.28, and 0.62 %, respectively. Commercially purchased marmalades contained additional pectin. The amount of crude protein in marmalades produced using vacuum evaporator was higher than in other marmalades. There was not any statistical difference in the ash content of marmalades.

The colour index is one of the most important factors in the quality of fruit products such as marmalades produced by heat treatment. Manufacturing processes such as dilution, drying and baking can affect final product colour. Significant differences were found in colour values of all three types of marmalades. Table 2 shows that marmalades produced using vacuum evaporator had the highest lightness/brightness values (L=30.20), whereas marmalades produced by classical method had the lowest L values (23.40). The greenness/redness values (a) of the products ranged from 10.30 to 19.20 and blueness/yellowness values (b) ranged from 8.90 to 15.10, while in another study a values were from 17.75 to 31.80 (15). In the marmalades produced using vacuum evaporator and the commercially purchased marmalades, L and a values were higher, but b values were lower. The strong negative correlation was calculated between the L values and total phenolic composition (R=-0.877, p=0.002), L values and reducing sugar (R=-0.986, p=0.00), and L values and HMF (R=-0.928, p=0.00).

Rheological properties of marmalades

The empirical data obtained for samples were converted into shear stress and shear rate (48,49). Average shear stress and shear rate were calculated as:

$$\sigma_a = k_{\alpha\sigma} \cdot (C \cdot \text{the value read from the viscometer})$$
 /1/

$$\gamma_{a} = k_{N\gamma} \cdot N$$
 /2/

where σ_a is the average shear stress (Pa), $k_{\alpha\sigma}$ is the shear stress conversion factor (Pa) and C is the spring constant (C=1.0 for the Brookfield viscometer RV model). The $k_{\alpha\sigma}$ for spindle no. 6 is 2.35, γ_a is the shear rate (s⁻¹) and N is the rotational speed in rpm. $k_{\rm N\gamma}$ (the shear rate conversion factor) was between 1.366 and 0.238 (48,49).

Dividing Eq. 1 by Eq. 2 yields an expression for apparent viscosity:

$$\eta_a = \sigma_a / \gamma_a$$
 /3/

The experimental data obtained for marmalades at different temperatures and speeds were calculated. The flow behaviour of marmalades produced using vacuum evaporator is given in Fig. 1. The rheological behaviour of marmalades is described by the power law model (Eq. 4) (50):

$$\eta_a = k \cdot \gamma^{(n-1)}$$
 /4/

where η_a is the apparent viscosity (Pa·s), k is the consistency index (Pa·sⁿ), γ is the shear rate (s⁻¹) and n is the flow behaviour index (dimensionless). Linear regression analysis was applied on the data to find n, k and correlation coefficient (R²), the results of which at different temperatures are given in Table 4. The power law model appears to be suitable for describing the flow behaviour of marmalades as indicated by high R² values.

The R^2 values ranged from 0.962 to 0.994 for all samples. As shown in Table 4, n and k values ranged from 0.22 to 0.32, and 64.2 to 321, respectively. All marmalades exhibited a pseudoplastic behaviour because the values of flow behaviour index (n), a measure of the departure from Newtonian flow (43), were less than 1 (51). The magnitude of the consistency coefficient (k) decreased with the increase in temperature. Increasing the temperature from 25 to 75 °C considerably decreased the k value. Similar results were also obtained in the pekmez, which is one of the most important viscous products, and peach dietary fibre suspensions (41,51).

The viscosity of marmalades generally decreases as the temperature increases. As shown in Figs. 1 and 2, as the temperature and speed increased, the viscosity of all marmalades decreased. In the literature, similar flow diagrams were found for pekmez samples and some beverages (26,41,49,51). As it can be seen in Fig. 1 and Table 2, viscosity and pectin content of commercially purchased marmalades were higher than those of other samples. The structure of commercially purchased marmalades can be improved by using stabilizing agents (such as pectin).

The consistency index can be used to describe the variation in viscosity with temperature changes using the Arrhenius equation (41,49,52):

$$\ln k = \ln k_0 + E_a / R \cdot T_a \qquad /5/$$

where k_0 is the Arrhenius constant (Pa·sⁿ), E_a is the activation energy (J/mol), R is the universal gas constant (J/mol) and T_a is the absolute temperature (K). The constant k_0 (Pa·sⁿ) and E_a (J/mol) parameters were obtained from

Arrhenius-type equation with the linear regression analysis (Eq. 5). E_a and k_0 for marmalade flow are shown in Table 5. E_a values of marmalades produced using vacuum

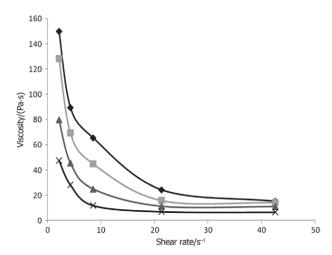


Fig. 1. The flow behaviour of rose hip marmalades produced using vacuum evaporator at different temperatures (→ 25 °C, → 40 °C, → 60 °C, and → 75 °C)

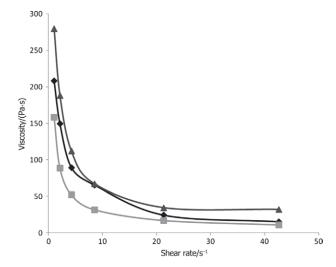


Fig. 2. The flow behaviour of rose hip marmalades (→ produced using vacuum evaporator, → produced by classical method, and → commercially purchased marmalades) at 25 °C

Table 4. The consistency index (k) and flow behaviour index (n) of marmalades at different temperatures

				Mar	malade sam	ples			
Temperature	produced using vacuum evaporator			produced by classical method			commercially purchased marmalades		
°C	$\frac{k}{\text{Pa}\cdot\text{s}^{\text{n}}}$	п	R ²	$\frac{k}{\text{Pa} \cdot \text{s}^{\text{n}}}$	п	R ²	$\frac{k}{\text{Pa}\cdot\text{s}^{\text{n}}}$	п	R ²
25	240.4	0.28	0.989	175.8	0.23	0.993	321.0	0.32	0.981
40	197.1	0.27	0.985	140.2	0.24	0.986	261.5	0.25	0.988
60	129.4	0.28	0.985	93.1	0.22	0.987	156.2	0.28	0.992
75	80.2	0.25	0.977	64.2	0.22	0.962	109.8	0.22	0.994

k and n (dimensionless) indices were obtained by fitting rotational speed and viscosity data to the power law model (Eq. 4)

evaporator, marmalades produced by classical method, and commercially purchased marmalades were calculated as 18 670, 17 335 and 18 930 J/mol, respectively. The values of k_0 were found to be 0.139, 0.165 and 0.170 Pa·sⁿ in the marmalades produced using vacuum evaporator, purchased commercially, or produced by classical method, respectively. E_a values in our study were found to be

Table 5. Arrhenius-type equation parameters for marmalades

Marmalade samples	$k_0/(\text{Pa·s}^n)$	$E_a/(J/mol)$	R ²
produced using vacuum evaporator	0.139	18670	0.957
produced by classical method	0.170	17335	0.981
commercially purchased marmalades	0.165	18930	0.978

 k_0 and E_a parameter were obtained from Arrhenius-type equation (Eq. 5)

lower than those of pekmez/tahini blends (30 329 J/mol at 0 % pekmez content) but k_0 values were found to be higher (53). Higher k_0 values obtained for marmalades indicate an increase in viscosity. Consequently, these values indicate that pekmez/tahini blend is more fluid, and has more homogeneous texture and uniform particle distribution than marmalades.

Sensory properties of marmalades

Sensory evaluation of food products consists of establishing sensory profiles. To recognize the desirable sensory properties of a specific food and to apply previous knowledge of statistics to the analysis of collected sensory data and experimental design are very important for food quality classification. The complexity of the tasks given to the panel required longer training periods together with more complex skills in statistical analyses. Moreover, training does not always improve the ability of panelists to discriminate between products (54,55). Rose hip marmalade can be considered as a typical product in which specific ingredients are included (rose hip, pulp and sugar). Sensory evaluations of marmalades are presented in Table 6. The highest score for colour and appearance (4.87) had the marmalade produced under vacuum. Of the tested samples, consistency of purchased marmalades was the highest. There was no statistically significant difference in odour and taste of different samples of marmalades. Significant differences and correlations between some parameters were calculated and given in Table 3. These values show that strong positive correlation (correlation is significant at p=0.01 level) was observed between colour/appearance and L values (R=0.953, p=0.00). Positive correlation at p=0.05 level was calculated between colour/appearance and a values (R=0.681, p=0.044) and between consistency and total sugar (R=0.790, p=0.011). In the statistical calculations, strong negative correlation was found between colour/appearance and reducing sugar (R=-0.974, p=0.00), HMF (R=-0.878, p=0.002), b values (R=-0.960, p=0.00), total phenolic composition (R=-0.900, p=0.001), and antioxidant capacity (R=-0.933, p=0.00).

Conclusions

The obtained results imply that rose hip marmalades have high dry matter, sugar, ascorbic acid and phenolic content, and low HMF and pseudoplastic viscosity behaviour. In addition, marmalades show marked antioxidant activity and sensory properties, which provide a valuable source of nutrients and require further investigation with regards to their antioxidant components.

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References

- P.H. Davis: Flora of Turkey and the East Aegean Islands, Vol. 4, Edinburgh University Press, Edinburgh, UK (1972) pp. 106–128.
- F. Demir, M. Özcan, Chemical and technological properties of rose (*Rosa canina* L.) fruits grown wild in Turkey, *J. Food* Eng. 47 (2001) 333–336.
- R. Yamankaradeniz, The investigation on the content and evaluation of the wild rose hip in Erzurum, PhD Thesis, Agricultural Faculty of Atatürk University, Erzurum, Turkey (1983) (in Turkish).
- J. Vaya, P.A. Belinky, M. Aviram, Antioxidant constituents from licorice roots: Isolation, structure elucidation and antioxidative capacity toward LDL oxidation, *Free Radic. Biol. Med.* 23 (1997) 302–313.
- S. Kolayli, M. Küçük, C. Duran, F. Candan, B. Dinçer, Chemical and antioxidant properties of *Laurocerasus officinalis* Roem (cherry laurel) fruit grown in the Black Sea region, *J. Agric. Food Chem.* 51 (2003) 7489–7494.
- S. Başgel, S.B. Erdemoğlu, Determination of mineral and trace elements in some medicinal herbs and their infusions consumed in Turkey, Sci. Total Environ. 359 (2006) 82–89.
- S. Erenturk, M.S. Gulaboğlu, S. Gültekin, The thin-layer drying characteristics of rose hip, *Biosyst. Eng.* 89 (2004) 159–166.

Table 6. Sensory properties of marmalades

Marmalade samples	Colour and			Taste
produced using vacuum evaporator	appearance (4.87±0.12) ^c	(4.60±0.10) ^b	(3.70±0.26) ^a	(5.33±0.58) ^a
produced using vacuum evaporator produced by classical method	$(4.10\pm0.12)^a$	$(4.20\pm0.17)^a$	$(3.83\pm0.29)^a$	$(5.50\pm0.50)^{a}$
commercially purchased marmalades	(4.50±0.10) ^b	$(4.87\pm0.12)^{c}$	$(3.63\pm0.32)^{a}$	$(5.17\pm0.29)^{a}$

- Y. Hashidoko, The phytochemistry of Rosa rugosa, Phytochemistry, 43 (1996) 535–549.
- G.Y. Zhao, A.W. Hou, F.T. Gao, Study on the change of vitamin C content of rose fruit during its storage and processing, J. NEFU, 16 (1988) 102–105.
- L. Su, J.J. Yin, D. Charles, K. Zhou, J. Moore, L. Yu, Total phenolic contents, chelatting capacities, and radical-scavenging properties of black peppercorn, nutmeg, rosehip, cinnamon and oregano leaf, Food Chem. 100 (2007) 990–997.
- B.N. Pirone, M.R. Ochoa, A.G. Kesseler, A. De Michelis, Chemical characterization and evolution of ascorbic acid concentration during dehydration of rosehip (*Rosa eglanteria*) fruits, Am. J. Food Technol. 2 (2007) 377–387.
- T.G. Salluca, J.M. Peñarrieta, J.A. Alvarado, B. Bergenståhl, Determination of total phenolic compounds content and the antioxidant capacity of Andean tubers and roots (Isaño, Oca, Ulluco and Arracacha), Rev. Boliv. Quim. 25 (2008) 58–61.
- O. Yildiz, M. Alpaslan, M. Kara, Effects of different process temperatures on chemical and sensory properties of rosehip nectar, *Proceedings of the 5th International Congress on Food Technology*, Thessaloniki, Greece (2007) pp. 659–666.
- X. Gao, L. Björk, V. Trajkovski, M. Uggla, Evaluation of antioxidant activities of rose hip ethanol extracts in different test systems, J. Sci. Food Agric. 80 (2000) 2021–2027.
- 15. F. Özdemir, M.I. Aksu, S. Nas, The quality characteristics of marmalades produced at different sugar/pulp ratios by using rosehips pulp obtained without heating, *J. Eng. Sci.* 3 (1997) 353–358 (in Turkish).
- Council Directive 2001/113/EC, relating to fruit jams, jellies and marmalades and sweetened chestnut purée intended for human consumption, Commission of The European Communities (2004).
- Turkish Food Codex, Communiqué on Food Additives Other Than Colours and Sweeteners 2002/10, Ministry of Agriculture and Rural Affairs, Turkey (2002).
- R. Fügel, R. Carle, A. Schieber, Quality and authenticity control of fruit purées, fruit preparations and jams – A review, Trends Food Sci. Technol. 16 (2005) 433–441.
- S. Ercisli, Chemical composition of fruits in some rose (Rosa spp.) species, Food Chem. 104 (2007) 1379–1384.
- Official Methods of Analysis of AOAC International, Gaithersburg, MD, USA (2000).
- H. Tanner, H.R. Brunner: *Drink Analysis*, Heller Chemie und Verwaltungsgesellschaft, GmbH, Schwäbisch Hall, Germany (1979) (in German).
- M.A. Farajzadeh, S. Nagizadeh, A simple and reliable spectrophotometric method for the determination of ascorbic acid in pharmaceutical preparations, J. Anal. Chem-Engl. Tr. 58 (2003) 927–932.
- C. S. James: Analytical Chemistry of Foods, Blackie Academic and Professional, London, UK (1995) pp. 117–120.
- International Federation of Fruit Juice Producers Methods.
 In: Analysen-Analyses, Vol. 12, Zug, Switzerland (1984) pp. 1962–1974.
- H.S. Burdurlu, F. Karadeniz, Effect of storage on nonenzymatic browning of apple juice concentrates, Food Chem. 80 (2003) 91–97.
- R. Aliyazicioglu, S. Kolayli, M. Kara, O. Yildiz, A.O. Sarikaya, S. Cengiz, F. Er, Determination of chemical, physical and biological characteristics of some pekmez (molasses) from Turkey, Asian J. Chem. 21 (2009) 2215–2223.
- 27. A. Meda, C.E. Lamien, M. Romito, J. Millogo, O.G. Nacoulma, Determination of the total phenolic, flavonoid and proline contents in Burkina Fasan honey, as well as their radical scavenging activity, *Food Chem.* 91 (2005) 571–577.

- I.F. Benzie, J.J. Strain, The ferric reducing ability of plasma (FRAP) as a measure of antioxidant power: The FRAP assay, Anal. Biochem. 239 (1996) 70–76.
- R.E. Wrolstad, Color and pigment analyses in fruit products, Oregon Agric. Exp. Station Bull. No. 624 (1976).
- B.H. Davies: Carotenoids. In: Chemistry and Biochemistry of Plant Pigments, Vol. 2, T.W. Goodwin (Ed.), Academic Press, London, UK (1976) pp. 38–165.
- 31. M. Alpaslan, M. Hayta, The effects of flaxseed, soy and corn flours on the textural and sensory properties of a bakery product, *J. Food Qual.* 29 (2006) 617–627.
- N.P. Shelukhina, L.G. Fedichkina, A rapid method for determination of pectic substances, *Acta Bot. Neerl.* 43 (1994) 205–207
- M. Alpaslan, M. Hayta, Effect of soymilk substitution on the rheological and sensory properties of salep (traditional Turkish milk beverage), *Int. J. Food Prop.* 10 (2007) 413–420.
- Sensory Ratings of Marmalade, Turkish Standard No. 3734,
 Turkish Standards Institution, Ankara, Turkey (2006) (in Turkish).
- I.M. Aksu, F. Özdemir, S. Nas, The quality characteristics of marmalades produced at different sugar/pulp ratios by using rosehip pulp obtained by application of preheating process, J. Eng. Sci. 3 (1997) 243–248 (in Turkish).
- S.H. Häkkinen, A.R. Törrönen, Content of flavonols and selected phenolic acids in strawberries and *Vaccinium* species: Influence of cultivar, cultivation site and technique, *Food Res. Int.* 33 (2003) 517–524.
- S.Y. Wang, W. Zheng, G.J. Galletta, Cultural system affects fruit quality and antioxidant capacity in strawberries, J. Agric. Food Chem. 50 (2002) 6534–6542.
- A.M. Rojas, L.N. Gerschenson, Ascorbic acid destruction in aqueous model systems: An additional discussion, J. Sci. Food Agric. 81 (2001) 1433–1439.
- 39. Codex Alimentarius, Standard for Honey, Codex Alimentarius Commission FAO/WHO (2001).
- M. Zappalà, B. Fallico, E. Arena, A. Verzera, Methods for the determination of HMF in honey: A comparison, Food Control, 16 (2005) 273–277.
- M. Sengül, M.F. Ertugay, M. Sengül, Rheological, physical and chemical characteristics of mulberry pekmez, Food Control, 16 (2005) 73–76.
- 42. O. Yildiz, H. Sahin, M. Kara, R. Aliyazicioglu, Ö. Tarhan, S. Kolayli, Maillard reactions and importance of reaction products in foods, *Akademik Gida*, 8 (2010) 44–51 (in Turkish).
- 43. E. Yurdagül, A research on plum based traditional marmalade within mixed fruit, *MSc. Thesis*, Department of Food Engineering, Institute of Natural and Applied Science, Çukurova University, Adana, Turkey (2007) (in Turkish).
- N. Turkmen, F. Sari, E.S. Poyrazoglu, Y.S. Velioglu, Effects of prolonged heating on antioxidant activity and color of honey, Food Chem. 95 (2006) 653–657.
- M. Küçük, S. Kolayli, S.A. Karaoglu, E. Elusoy, C. Baltaci, F. Candan, Biological activities of three different Turkish honey, Food Chem. 100 (2007) 526–534.
- C.M. Liyana-Pathirana, F. Shahidi, C. Alasalvar, Antioxidant activity of cherry laurel fruit (*Laurocerasus officinalis* Roem.) and its concentrated juice, *Food Chem.* 99 (2006) 121–128.
- J.M. Heinonen, A.S. Meyer, E.N. Frankel, Antioxidant activity of berry phenolics on human low-density lipoprotein and liposome oxidation, *J. Agric. Food Chem.* 46 (1998) 4107–4112.
- 48. L.P. Mitschka, Simple conversion of Brookfield RVT readings into viscosity functions, *Rheol. Acta*, 21 (1982) 207–209.

- 49. J.L. Briggs, J.F. Steffe, Using Brookfield data and the Mitschka method to evaluate power law foods, *J. Text. Stud.* 28 (1997) 517–522.
- M.S. Chhinnan, K.H. McWatters, V.N.M. Rao, Rheological characterization of grain legume pastes and effect of hydration time and water level on apparent viscosity, *J. Food* Sci. 50 (1985) 1167–1171.
- N. Grigelmo-Miguel, A. Ibarz-Ribas, O. Martín-Belleso, Rheology of peach dietary fibre suspensions, *J. Food Eng.* 39 (1999) 91–99.
- D. Costaldo, L. Plamer, A. Lo Voi, P. Costabile: Rheological Characterisation of Purees and Concentrates of Babaco. In:
- *Engineering and Food, Vol. 1,* W.E.L. Spiess, H. Schubert (Eds.), Elsevier Science Publishers, London, UK (1990) pp. 143–150.
- M. Alpaslan, M. Hayta, Rheological and sensory properties of pekmez (grape molasses)/tahin (sesame paste) blends, J. Food Eng. 54 (2002) 89–93.
- 54. N. Cayot, Sensory quality of traditional foods, *Food Chem.* 102 (2007) 445–453.
- 55. S. Chollet, D. Valentin, The degree of expertise has an influence on the odor? Some elements of answer in the field of wine, *Annee Psychol.* 100 (2001) 11–36 (in French).