Yoghurt production from camel (Camelus dromedarius) milk fortified with samphire molasses and different colloids

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Abstract

In this study, yoghurt was produced from camel (Camelus dromedarius) milk with whey protein isolate (3 % w/v) and fortified with 3 % (w/v) traditional samphire molasses (TSM) (YTSM), 3 % (w/v) TSM+0.1% (w/v) κ-carrageenan (YTSMC) or 3 % (w/v) TSM+0.05 % (w/v) xanthan gum (YTSMX). In yoghurt samples, physical-chemical properties, texture, color and sensory analysis were determined on the 1st, 5th, 10th and 14th days of storage, while total phenolics (TF) levels were determined on the 14th, 24th, 32nd, 48th, 72nd, 120th, 240th and 336th hours of storage. In all samples during storage, hardness and viscosity increased along with the acidity increase, although the increases in YTSM and YTSMC were lower than in YTSMX. In YTSMX, in spite of the increase in acidity after the 1st day, serum separation was very low while viscosity and hardness values were higher compared to the other samples. YTSMX was found to be superior to the other samples in terms of physicochemical, textural, microbiological and sensory properties. Total phenolic contents and L* a* b* levels increased in all samples throughout storage, the highest values of which were in YTSMX. After the 5th day of the storage, Lactobacillus delbrueckii subsp. bulgaricus became the dominant microbial flora. After the 5th day of storage, Lactobacillus delbrueckii subsp. bulgaricus and Streptococcus thermophilus levels were highest in YTSMX.

Key words: yoghurt, samphire molasses, camel milk, colloids

Introduction

In the production of yoghurt, in addition to the technological processes applied in order to increase viscosity and reduce syneresis, different colloids can be added to the milk (Lucey, 2002; Tamime and Robinson, 1985). Fortification with WPI (Whey Protein Isolate), which contains a minimum of 90 % protein and is an important source of Ca and minerals (Ha and Zemel, 2003), improves the consistency and micro-structure in set type yoghurts and generates a less sticky structure in yoghurts (Guggisberg et al., 2007). κ-carrageenan, which is an anionic colloid, interacts with the positive charges on casein micelles, which strengthens the casein network and reduces syneresis (Everett and McLeod, 2005). It has been reported that using low concentrations (0.15 %) of κ-carrageenan provides a strong gel in the yoghurt structure (Erve Glicman, 1972). Xanthan gum, which is a neutral colloid, increases the viscosity by a different mechanism (Everett and McLeod, 2005; Hansen, 1993), improves the texture, increases the hardness and prevents syneresis (El-Sayed et al., 2002). Xanthan gum is used in the food industry due to its desirable effects on structure and texture (El Sayed et al., 2002). As a result, xanthan gum and κ-carrageenan are both used for reducing syneresis in yoghurt during storage (Hematyar et al., 2012).
There are studies on production of yoghurt, probiotic yoghurt (Al-Awadi and SriKumar, 2001; Attia et al., 2001), stabilizer-supplemented yoghurt (Muliro et al., 2013), yoghurt supplemented with different spices (Shori et al., 2013) and flavored yoghurt (Hashim et al., 2009) from camel milk. It has been reported that some problems occur during yoghurt production from camel milk during fermentation and that the viscosity of the product does not change during gelation (Jumah et al., 2001). These problems were associated with the high antimicrobial content of camel milk (El-Agamy, 2000), the content of heat-stable serum proteins which make up 20-25 % of the total protein (Desouky et al., 2013), the weak interaction between denatured serum proteins and casein, low or no content of different β-casein derivatives and β-lactoglobulin amongst the serum proteins (Shabo et al., 2005), and low casein ratio (3.47 %) compared to cow’s milk (13 %) (Laleye et al., 2008).

Nevertheless, it was reported that yoghurt with a low viscosity but with a hard structure can be produced by using the main components of milk and yoghurt culture in twice their amounts (Hashim et al., 2009). It was detected that the lack of coagulation and structure in the production of camel milk and the long period of lag and decline phases of starter cultures are significant challenges (Attia et al., 2001). Additionally, lactic acid bacteria have been reported to be more metabolically active in camel milk (Omer et al., 2007). The dominant flora developing in fermented dairy products produced from camel milk was reported to be Lactobacillus ssp. (Ashmaig et al., 2009; Omer et al., 2007).

Molasses, a traditional food product in Turkey, is currently produced from fruits rich in sugars including grapes, mulberries, figs and samphire by using traditional and technological methods. Samphire (Juniperus drupacea L), which is cultivated in Mediterranean Region, belongs to the Cupressaceae family and has blue-black conifers (Baytop, 1994). Samphire molasses (SM) is produced from these conifers by traditional or industrial methods. In the traditional method, conifers, following washing, granulation and breaking processes, are mixed with water (1:3 w/v) and heated to 80-90 °C in the open air in an extraction process. The temperature/duration and the materials used during the heating have an effect on the taste, color, protein, pH, and total phenolic content (Ozdemir et al., 2004). The extract obtained is evaporated up to 70° brix (Topuz et al., 2004).

In this study, the possibility of yoghurt production from camel (Camelus dromedarius) milk, the dry matter of which was increased with whey protein isolate, fortified with κ-carrageenan (C), xanthan gum (X) and traditional samphire molasses (TSM) was investigated.

Materials and methods

Materials

The raw camel (Camelus dromedarius) milk (CaM) used in our study was obtained from a local camel farm located in Sarayköy, Denizli (Turkey). TSM (according to consumer data; pH 5.47; 5-HMF 1.32 mg/kg; total phenolics 3163 mg GAE L⁻¹; total dry matter 70.15 %; protein 0.71 %; total sugar 33.51 %; sucrose, 11.98 %; glucose 7.21 %, fructose 14.32 % and ash 3.21 %) was obtained from a local producer in Mersin (Turkey). WPI produced by the microfiltration method (according to consumer data; minimum 90 % protein; 2.60 % minerals; <1 % lactose; <1 % fat) was obtained from PowerPros (Land-O-Lakes, Perham, MN). Alfasol® fully refined κ-carrageenan (E-407) (according to consumer data (07.11.2014); pH 7.8; viscosity 60 cps; water gel strength 1663 g; potassium gel strength 1606 g; microbiology: concordant) and xanthan gum (E-415) (according to consumer data (7.11.2014); pH 6.77; viscosity 1420 cps; moisture 8.85 %; ash 6.27 %; particle size 100 %; heavy metal ratio and microbiology concordant) were obtained from Kimbiotek Chemical Agents Inc. (Istanbul-Turkey). JOINTEC V8530 freeze-dried yogurt culture was obtained from CSL laboratories (Strade per Merlino, 3,26839, Italy). Yoghurt samples were produced in pilot plants at Ege University, Faculty of Agriculture, Department of Dairy Technology.

Methods

Set type yoghurt production

Raw camel milk was standardized to 14 % dry matter by WPI addition (3 % w/v) and fortified with TSM, xanthan gum (X), or κ-carrageenan (C). Yoghurt was produced with addition of the starter culture (Lb. bulgaricus and Str. thermophilus) (Figure 1). Xanthan gum was added to the milk (5 g L⁻¹ concentration) that was higher than the reference value (3 g L⁻¹) reported by Everett and McLeod (2005) and Hemar et al. (2001). κ-carrageenan concentration was determined through preliminary trials.
In yoghurt production, CaM was divided into three parts, each of which was fortified with 3 % (w/v) WPI. TSM (3 % w/v) was added to all parts before pasteurization in order to prevent the degradation of anthocyanins (Bonerz et al., 2007) and lessen effects on the color properties. The 1st part was fortified with only 3 % (w/v) TSM, the 2nd part was fortified with 3 % (w/v) TSM + 0.5 % (w/v) xanthan gum (X) and the 3rd part was fortified with 3 % (w/v) TSM + 0.1 % (w/v) κ-carrageenan (C), homogenized with an Ultra Turrax Blender (at 1200 rpm for 40 seconds) (IKA, Merc, Germany) and pasteurized at 85 °C for 20 minutes. Then the samples were cooled to 42-43 °C and inoculated with 3 % (w/v) starter cultures, thus preparing YTSM, YTSMC and YTSMX samples. Samples were added to 200 g plastic cups and left to incubate. The incubation was ended at pH 4.60 (14 hours). Samples were stored for 14 days at 4 °C±1 and physicochemical, rheological, color, microbiological and sensory analyses were conducted on the 1st, 5th, 10th and 14th days of the storage. Total phenolic contents were determined at the 14th, 24th, 32nd, 48th, 72nd, 120th, 240th and 336th hours of the storage.

**Analysis of raw camel milk and yoghurt samples**

**Physical-chemical analysis**

Yoghurt dry matter (Binder ED-53, Germany) and ash (Protherm PFL 110/6, Turkey) content measurements was performed according to the gravimetric method, fat was determined according to the Gerber method, titratable acidity was determined as lactic acid %, pH was measured with a SS-3 Zeromatic pH meter (Beckman Instruments Inc., California, USA), protein content was analyzed by the Kjeldahl method (AOAC, 1990), lactose levels were measured with an Atago Polax x 2L (Japan) polarimeter (Horwitz, 1965), serum separation was analyzed according to Farooq and Haque (1992), texture analysis was performed with a Brookfield CT3 4500 Texture Analyzer (USA/ Shape Cylinder; target 10 mm; test speed 1 mm/s), color measurements were performed with a Hunter color and color difference measuring device (Model D25A-9) (Hunter, 1973) (after the zero calibration and adjustments were done according to a white plate (L=95.4, a=-1.3, b=2.1)), and viscosity levels were measured with a Brookfield Digital Viscometer (Model DV-II+PRO, USA) [180 rpm, 10 °C, in CaM and yoghurt samples LV2 spindle (23.47 g), between 13-42 % Torque] as cP (Gassem and Frak, 1991).

**Total phenolics (TP)**

Total phenolic (TP) levels of yoghurt samples were measured by spectrophotometer (Optima SP-300, Japan) at 720 nm according to the Folin-Ciocalteus method and determined as "mg gallic acid equivalent (GAE) L⁻¹" (Singleton and Rossi, 1965). TP analyses were replicated three times for each yoghurt sample. First, gallic acid stock solution at (500 mg L⁻¹ concentration) was prepared. Then, solutions were prepared by adding appropriate amounts of the stock solution (1, 2, 4, 6 or 8 mL). Absorbance values were read at 720 nm, linear regression analysis was applied and a gallic acid standard curve and the equation describing the curve were obtained (Figure 2). Absorbance values of yoghurt samples were read at 720 nm, these values were calculated by placing in the equation describing the standard curve.
Microbiological analysis

Starter culture counts of the yoghurt samples were performed according to International Dairy Federation standard method (IDF, 1997 No: 149A, IDF, 2003 No: 117). *Lb. bulgaricus* enumeration was carried out by incubating the Petri dishes in microaerophyllic conditions (5 % CO₂) at 37 °C for 72 hours on De Mann Rogosa Sharpe (MRS) Agar (pH 5.4) (Merc Darmstadt, Germany). *Stg. thermophilus* enumeration was conducted by incubating the Petri dishes in aerobic conditions at 37 °C for 48 hours on Ml7 Agar (Merc Darmstadt, Germany). At the end of the incubation, colonies formed in Petri dishes were counted as cfu/mL on the 1st, 5th, 10th and the 14th days of storage.

Sensory evaluation

The sensory evaluation of yoghurts was performed by a consumer acceptance test (Villanueva and Da Silva, 2009) based on the appearance, texture, flavor, aroma, and overall impression of the product using a 9-point hedonic scale (1-disliked extremely; 9-liked extremely). The sensory evaluation of the yoghurt samples was performed after 1 and 10 days of refrigerated storage.

Statistical analysis

Samples were examined with 3 parallels and 2 repetitions. SPSS version 15 (IBM SPSS Statistics) statistical analysis package software was used for analyses. Significance according to analysis of variance (ANOVA) was tested according to the Duncan multiple comparison test at p < 0.05 level.

![Figure 2. Gallic acid standard curve and equation](image)

Results and discussion

In raw camel milk, the concentration of dry matter was 9.62 %, fat 2.30 %, protein 2.66 %, lactose 2.84 %, ash 1.610 %, lactic acid 0.132 %, pH 6.53, density 1.0288 g/mL and viscosity was 1.42 cp (20 °C). Dry matter and viscosity of CaM was low, other values were compatible with the literature (Al Haj and Al Kanhal, 2010).

pH values decreased during storage and lactic acid % (LA%) value increased. YTSMX showed the highest acidity increase between the 1st and the 14th days, although the same levels of increase were not detected in YTSM and YTSMC. The relationship between the increase in acidity and the colloid type was found to be significant (p<0.05).

The increase in acidity detected in YTSMX was associated with the heteropolysaccharide block structure of xanthan gum. In 1 molar xanthan gum, D-glucose, D-mannose and D-glucuronic acid are found in 2.8:3.0:2.0 ratios respectively (Rocks, 1971). According to Kumar and Mishra (2004), colloid type and content has an effect on the acidity development. According to Singh and Muthukumarappan (2008), this relationship is not important in alginate and gelatine use. In a previous study, it was found that lactic acid bacteria showed better growth and more acidity production especially in the presence of glucose and some other sugars (saccharose, maltose) (Shirai et al., 2001). The results in our study were consistent with those in the literature. The highest increase in acidity occurred in YTSMX due to the glucose content of the xanthan.

Dry matter decreased between the 1st and the 14th days. The decrease from largest to smallest was YTSMX, YTSMC, and YTSM. No significant relationship was found between the colloid type and dry matter (p>0.05).

Fat did not change in YTSMX during storage but it was at low levels in other samples. The decrease in YTSMC was greater than that in YTSM. This change in the fat values was consistent with that reported by Eissa et al. (2011). The relationship between the colloid type and the fat value was not significant (p>0.05).

Protein and lactose decreased during storage. The highest amount of decrease in protein and lactose were in YTSMX and YTSMC respectively. The relationships between the increase in acidity and colloid type and protein and lactose were significant (p<0.05). Ash % values decreased during storage; the amount of ash decrease from highest to lowest was YTSMX, YTSMC, YTSM respectively (p>0.05).
Table 1. Physicochemical properties of $Y_{\text{TSM}}$, $Y_{\text{TSMC}}$ and $Y_{\text{TSMX}}$ samples (n=3)

<table>
<thead>
<tr>
<th>Time storage</th>
<th>$Y_{\text{GAP}}$</th>
<th>$Y_{\text{GAPC}}$</th>
<th>$Y_{\text{GAPX}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st day</td>
<td>16.26±1.10$^{Aa}$</td>
<td>15.28±0.99$^{Ab}$</td>
<td>16.65±1.15$^{Aa}$</td>
</tr>
<tr>
<td>5th day</td>
<td>15.63±0.95$^{Aa}$</td>
<td>14.29±1.00$^{Ab}$</td>
<td>16.64±1.05$^{Ac}$</td>
</tr>
<tr>
<td>10th day</td>
<td>14.61±0.97$^{Aa}$</td>
<td>12.75±1.10$^{Ab}$</td>
<td>16.64±1.15$^{Ac}$</td>
</tr>
<tr>
<td>14th day</td>
<td>13.85±1.05$^{Aa}$</td>
<td>12.42±1.00$^{Ab}$</td>
<td>16.63±1.07$^{Ac}$</td>
</tr>
<tr>
<td>1st day</td>
<td>970±4.63$^{Aa}$</td>
<td>390±5.30$^{Ab}$</td>
<td>1853±6.30$^{Ac}$</td>
</tr>
<tr>
<td>5th day</td>
<td>1387±5.25$^{Ac}$</td>
<td>1095±6.10$^{Ab}$</td>
<td>2413±6.20$^{Ac}$</td>
</tr>
<tr>
<td>10th day</td>
<td>2557±4.83$^{Ac}$</td>
<td>1885±6.25$^{Ab}$</td>
<td>3523±6.00$^{Ac}$</td>
</tr>
<tr>
<td>14th day</td>
<td>2940±4.75$^{Ac}$</td>
<td>2517±5.10$^{Ab}$</td>
<td>4044±6.23$^{Ac}$</td>
</tr>
<tr>
<td>1st day</td>
<td>5.63±0.25$^{Aa}$</td>
<td>14.78±0.98$^{Ab}$</td>
<td>0.038±0.002$^{Ac}$</td>
</tr>
<tr>
<td>5th day</td>
<td>10.85±1.80$^{Aa}$</td>
<td>20.41±0.95$^{Ab}$</td>
<td>0.04±0.01$^{Ac}$</td>
</tr>
<tr>
<td>10th day</td>
<td>14.12±1.85$^{Aa}$</td>
<td>24.14±1.16$^{Ab}$</td>
<td>0.041±0.01$^{Ac}$</td>
</tr>
<tr>
<td>14th day</td>
<td>14.74±1.93$^{Aa}$</td>
<td>25.81±1.20$^{Ab}$</td>
<td>0.0412±0.01$^{Ac}$</td>
</tr>
<tr>
<td>1st day</td>
<td>0.928±0.15$^{Aa}$</td>
<td>0.959±0.25$^{Ab}$</td>
<td>0.911±0.13$^{Ac}$</td>
</tr>
<tr>
<td>5th day</td>
<td>1.012±0.05$^{Aa}$</td>
<td>1.043±0.05$^{Ab}$</td>
<td>1.083±0.15$^{Ac}$</td>
</tr>
<tr>
<td>10th day</td>
<td>1.086±0.08$^{Aa}$</td>
<td>1.079±0.07$^{Ab}$</td>
<td>1.109±0.09$^{Ac}$</td>
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<tr>
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<tr>
<td>1st day</td>
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<td>3.06±0.99$^{Ab}$</td>
<td>3.46±0.90$^{Ac}$</td>
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<td>5th day</td>
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<td>3.03±0.90$^{Ab}$</td>
<td>3.24±0.95$^{Ac}$</td>
</tr>
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<td>3.01±0.88$^{Ac}$</td>
</tr>
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<td>2.73±0.87$^{Ac}$</td>
</tr>
<tr>
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</tr>
<tr>
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<td>1.94±0.20$^{Ab}$</td>
<td>2.03±0.23$^{Ac}$</td>
</tr>
<tr>
<td>10th day</td>
<td>1.78±0.30$^{Aa}$</td>
<td>1.65±0.23$^{Ab}$</td>
<td>1.54±0.19$^{Ac}$</td>
</tr>
<tr>
<td>14th day</td>
<td>1.53±0.29$^{Aa}$</td>
<td>1.12±0.25$^{Ab}$</td>
<td>0.95±0.15$^{Ac}$</td>
</tr>
<tr>
<td>1st day</td>
<td>2.03±0.32$^{Aa}$</td>
<td>1.77±0.23$^{Ab}$</td>
<td>1.63±0.18$^{Ac}$</td>
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<tr>
<td>5th day</td>
<td>1.23±0.27$^{Aa}$</td>
<td>1.33±0.19$^{Ab}$</td>
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<td>1.26±0.20$^{Ab}$</td>
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</tr>
<tr>
<td>14th day</td>
<td>1.11±0.28$^{Aa}$</td>
<td>1.24±0.15$^{Ab}$</td>
<td>1.14±0.15$^{Ac}$</td>
</tr>
</tbody>
</table>

a, b, c: The differences between the values in the same column are statistically significant (p<0.05)
A, B, C, D: The differences between the values in the same line are statistically significant (p<0.05).
Rheological properties

Coagulum stability is an important yoghurt quality determinant. Many factors affect the consistency such as the rheological property of the coagulum, serum separation and viscosity. Among these factors, pH value, dry matter and protein contents (Torre et al., 2003), denatured serum protein content, and interactions between β-lactoglobulin and κ-casein are especially of importance (Puvanenthiran et al., 2002).

Serum separation was low in YTSMX during storage. Serum separation and the decrease in dry matter in YTSM were lower than in YTSMC. The relationship between the increase in acidity and serum separation was found to be significant (p<0.05).

The relationship between viscosity and colloid type was found to be significant (p<0.05). Viscosity increased in all samples during storage; the decreases from highest to lowest were YTSMX, YTSM, YTSMC, respectively. Patocka et al. (2004) and Patocka et al. (2006) reported that using 2-8 % WPI decreased viscosity while 10 % WPI increased viscosity in yoghurt production. In our study, using 3 % WPI (w/v) increased viscosity in all samples throughout the storage. In yoghurts produced from camel milk, viscosity increased with the increase in acidity and the prolongation of cold storage (Beal et al., 1999). The highest increase in acidity between the 1st and the 14th days was determined in YTSMX; the increase in viscosity was 2191 cp. The acidity in YTSMX on the 1st day of the storage (4.51 pH) was lower and viscosity (1853 cp) was higher than in other samples. This was associated with the colloid type. In the further days of the storage, the increase in acidity was greater compared to the other samples (Table 1). Consequently, increases in the hardness and viscosity levels were observed. Between the 10th and the 14th days, the increase in viscosity in YTSMX was higher than that in YTSM. This was verified by the decrease in dry matter, protein and lactose depending on the increase in acidity and serum separation in YTSMC between the 10th and 14th days.
Consistency values of the samples were significant in terms of colloid type x storage period interaction (p<0.05). Coagulum stability (hardness) increased during storage; the effect of storage was significant (p<0.05). Texture properties of the samples, except YTSMX, showed similar changes (Table 2). It was found that stickiness, gumminess, flexibility, chewiness and hardness increased in YTSM and YTSMC whereas gumminess and, on the 5th day, flexibility decreased; the increases in stickiness, chewiness and hardness parameters were higher than those of other samples. According to Guggisberg et al. (2007), with WPI addition, sticky structure decreases in yoghurts. However, textural properties observed in this study varied depending on the colloid type. It has also been reported elsewhere that colloids have an effect on the textural properties in yoghurts (Abd El-Salam et al., 1996, El-Sayed et al., 2002; Hansen, 1993).

In this study, yoghurt production from camel milk fortified with WPI (3 % w/v) rich in Ca ++ (Ha and Zeme, 2003) and three different colloids in order to avoid the problems associated with the composition of camel milk was explored. Conclusively, it was found that yoghurt with desirable characteristics cannot be obtained from camel milk fortified with TSM (YTSM) or TSM with κ-carrageenan (YTSMC). However, it was found that the rheological properties of YTSMX were superior to those of YTSM and YTSMC. The rheological properties of YTSM were more acceptable than those of YTSMC; however, YTSM and YTSMC were not in yoghurt gel structure but in a dairy drink viscosity. This result was consistent with previous reports on problems in fermented dairy production using camel milk (El-Agamy, 2000; Kappeler et al., 1998; 2003; Laleye et al., 2008; Shabo et al., 2005).

However, these results were not consistent with the results of the studies reporting that κ-carrageenan causes a strong adsorption in yogurths throughout storage and reduces the syneresis (Everett et al., 2005; Hematyar et al., 2012; Nikoofar et al., 2013). According to Pliero and Meugniot (1990), κ-carrageenan, which is not a reliable colloid, should be used with other colloids. In previous studies on κ-carrageenan, it was reported that coagulation took place between the negatively charged sulfate groups found in composition the colloid and casein fractions in the medium (especially κ-casein) (pH 4-4.6) as a result of strong interaction (milk reaction) (Christensen, 1991).

Our results were consistent with the literature. However, this might be associated with the presence of the WPI which was added to milk to increase the dry matter content. In YTSM, parallel to the increase in acidity during storage, serum separation decreased and hardness and viscosity increased. From this point of view, the results seem to be compatible with the literature. However, the lower hardness and viscosity values compared to other samples parallel to the increase in serum separation showed that yoghurt with desired characteristics cannot be obtained from camel milk with addition of WPI, TSM, and κ-carrageenan. However, it was determined that viscosity and hardness values obtained in YTSM during storage were higher than in YTSMC; the gel formed was harder than that of YTSM but not adequate.

In our study, in contrast to studies reporting problems during yoghurt production from camel milk, it was determined that yoghurt can be produced with the addition of WPI (3 % w/v), TSM (3 % w/v) and xanthan gum (0.5 % w/v) (YTSMX). Due to the lack of change in the yoghurt gel stability, YTSMX having the lowest serum separation values among all samples, and the constant increase in viscosity and hardness in spite of the increase in acidity during storage (the sample with the highest acidity increase), our results were found to be compatible with the literature (Christensen, 1991; Erve Glicman, 1972).

**Total phenolics (TF)**

TF levels of YTSM, YTSMC and YTSMX are given in Figure 3. The relationships between TF levels and storage period, serum separation, protein and colloid type were significant (p<0.05). TF level, which was 3163 mg GAE L⁻¹ in TSM, decreased in the samples by the end of the incubation (at the 14th hour). The decrease in YTSM (2463 mg GA L⁻¹) and YTSMC (2462 mg GA L⁻¹) were close to each other, although lower than that of YTSMX (2341 mg GA L⁻¹). This was associated with the complex structure formed as a result of phenolic-protein interaction. This complex forms as a result of the hydrogen binding of OH groups in the phenols with the NH- and CO- groups in protein (Bartolome et al., 2000; Halsam et al., 1999). Hydroxycinnamic acids with low molecular weight (including caffeic, ferulic, conumaric acid) and condensed phenols (catechin, epicatechlin) are abundant in TSM (Özdemir et al., 2004).
Condensed phenols are capable of forming especially strong bonds with proteins (Siebert, 1999). As a result of protein-phenolic interaction, a complex structure forms at a pH close to the isoelectric point (Asguith and Butler, 1986). Consequently, a large part of the protein precipitates and a small part dissolves (Hagerman and Robins, 1987). It was reported that precipitated protein-phenol complexes have more antioxidant activity compared to dissolved complexes (Riedl and Hagerman, 2001). As a result of the interaction between hydrophobic regions of proteins and the aromatic rings of the condensed tannins, nucleophilic groups of proteins (SH, OH, NH₂) and condensed phenolic groups concentrate and TF content increases during storage.

In our study, TF levels increased in YTSMX from the 14th hour until the end of the storage, and in Y GAP and Y GAPC until the 24th hour and increased beginning from the 24th hour. Although the increases in acidity and proteolysis were high in YTSM and Y TSMC, the high rates of serum separation caused a decrease in TF levels.

In YTSMX, which had the highest increase in acidity (4.42 pH), the lowest protein content (3.06 %) and the highest serum separation (14.78 %), TF level was 2349 mg GA L⁻¹ at the 24th hour. This value was lower than that of YTSM (2379 mg GA L⁻¹). The increase in TF content in YTSM after the 24th hour was associated with the high serum separation (0.038 %) in spite of the high increase in acidity (Table 1). TF level increased in YTSM (2452 mg GAL⁻¹) after the 48th hour until the end of the storage, an increase that was higher than that in YTSM (2428 mg GA L⁻¹). This increase continued until the end of the storage process.

Color changes (Hunter Lab values)

Anthocyanins found in flavonoids are bound sugars as glycosides and in different color forms (Turk, 2009). The relationships between L*a*b* values and pasteurization temperature, increase in acidity, proteolysis and storage period (Table 3) were significant (p<0.05). There was a significant relationship between the increase in acidity (decrease in pH) and color loss in anthocyanins (Castañeda-Ovando et al., 2009). Anthocyanin stability and reactivity vary depending on the presence of oxygen and acetaldehyde, pigment and co-pigment concentrations (Revilla and González-Sanjose, 2001), pH (Castañeda-Ovando et al., 2009), temperature (Bonzer et al., 2007), presence of enzymes (Seeram et al., 2001) and light (Ribéreau-Gayon and Glories, 2006). According to Bonzer et al. (2007), anthocyanin significantly decomposes in a pasteurization carried out at 85 °C for 25 minutes. The degradation rate of the anthocyanin increases as the storage temperature increases (at 20 °C compared to 5 °C for example). Seeram et al. (2001), reported that glucosidase (anthocyanin) enzyme hydrolyses the glycosidic bonds found in anthocyanin and causes a spontaneous decomposition and discoloration. According to Castañeda-Ovando et al. (2009), anthocyanins turn to different color forms depending on the pH of the solution, forming blue colors.

Table 3. L*a*b* values of YTSM, YTSMC and YTSMX samples

<table>
<thead>
<tr>
<th>Time storage</th>
<th>Y GAP</th>
<th>Y GAPC</th>
<th>Y GAPX</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st day</td>
<td>12.17±2.30</td>
<td>12.16±2.25</td>
<td>11.76±2.27</td>
</tr>
<tr>
<td>5th day</td>
<td>12.42±2.20</td>
<td>12.55±2.20</td>
<td>15.84±2.29</td>
</tr>
<tr>
<td>10th day</td>
<td>12.71±2.27</td>
<td>12.64±2.30</td>
<td>16.48±2.80</td>
</tr>
<tr>
<td>14th day</td>
<td>12.79±2.25</td>
<td>12.82±2.35</td>
<td>17.52±2.85</td>
</tr>
</tbody>
</table>

Table 3. L*a*b* values of YTSM, YTSMC and YTSMX samples

<table>
<thead>
<tr>
<th>Time storage</th>
<th>Y GAP</th>
<th>Y GAPC</th>
<th>Y GAPX</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st day</td>
<td>1.32±0.25</td>
<td>1.34±0.27</td>
<td>2.28±0.55</td>
</tr>
<tr>
<td>5th day</td>
<td>1.3±0.30</td>
<td>1.30±0.30</td>
<td>1.21±0.25</td>
</tr>
<tr>
<td>10th day</td>
<td>1.27±0.25</td>
<td>1.28±0.27</td>
<td>0.17±0.01</td>
</tr>
<tr>
<td>14th day</td>
<td>1.22±0.33</td>
<td>1.19±0.33</td>
<td>0.12±1.02</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time storage</th>
<th>Y GAP</th>
<th>Y GAPC</th>
<th>Y GAPX</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st day</td>
<td>0.64±0.05</td>
<td>0.59±0.02</td>
<td>0.94±0.33</td>
</tr>
<tr>
<td>5th day</td>
<td>0.64±0.07</td>
<td>0.6±0.05</td>
<td>1.94±0.20</td>
</tr>
<tr>
<td>10th day</td>
<td>0.66±0.05</td>
<td>0.62±0.04</td>
<td>1.95±0.25</td>
</tr>
<tr>
<td>14th day</td>
<td>0.71±1.03</td>
<td>0.64±0.03</td>
<td>2.01±0.40</td>
</tr>
</tbody>
</table>

Figure 3. TF changes in YTSM, YTSMC and YTSMX samples during storage.
in pH 2-4 and colorless forms in pH 5-6 (carbinol pseudobase and chalcone). As a result of the reaction between proanthocyanidin and anthocyanin, proanthocyanidin-anthocyanin pigments form and colorless dimers emerge He et al. (2008). Anthocyanins lose their color if exposed to light for a few days by a reaction that depend on the presence of oxygen and on the type and concentration of alcohol in the medium (such as ethanol and methanol) (Ribéreau-Gayon and Glories, 2006).

$L^*$ values increased during storage; the highest values by the end of the 14th days were determined in $Y_{\text{TSMX}}$, $Y_{\text{TSMC}}$ and $Y_{\text{TSM}}$ in decreasing order of magnitude respectively. The highest increases in acidity and proteolysis levels during storage were determined in $Y_{\text{TSMX}}$. The levels of increase in acidity in $Y_{\text{TSM}}$ and $Y_{\text{TSMC}}$ were similar to one another, although proteolysis level was higher in $Y_{\text{TSMC}}$. The increase in acidity and proteolysis levels in $Y_{\text{TSMC}}$ between the 10th and the 14th days were higher compared to $Y_{\text{TSM}}$. The increase in $L^*$ value in this period was higher compared to the other time periods (Figure 4). In spite of the increase in $L^*$ value during storage, $a^*$ value decreased. In decreasing order of magnitude, the largest decreases in $a^*$ values were found in $Y_{\text{TSMX}}$ (2.16), $Y_{\text{TSMC}}$ (0.15) and $Y_{\text{TSM}}$ (0.1). $b^*$ values increased in all samples during storage, the highest increase of which was measured in $Y_{\text{TSMX}}$. The increase in $L^*$ value in $Y_{\text{TSMC}}$ was higher than in $Y_{\text{TSM}}$. The increase of $L^*$ value was associated with the pasteurization temperature applied in yoghurt production, increase in acidity, proteolysis and storage period. According to Sengul et al. (2005), a molasses with low redness and high brightness is regarded as a quality molasses. High $a^*$ value, which corresponds to redness, indicates that the sugars are excessively caramelized, which is not desirable. $L^*$ value corresponds to brightness, high values of which are important in terms of quality.

Microbiological properties

$Lb.\ bulgaricus$ increased until the 5th day of storage in all samples and then decreased in the further days (Table 4). The highest $Lb.\ bulgaricus$ values on the 1st day of the storage were in $Y_{\text{TSMX}}$, $Y_{\text{TSM}}$ and $Y_{\text{TSMC}}$, respectively. The largest increase was measured in $Y_{\text{TSMX}}$ while the increases in $Y_{\text{TSMC}}$ and $Y_{\text{TSM}}$ were at the same level. $Lb.\ bulgaricus$ levels decreased on the 10th and the 14th days of the storage; the highest decrease was determined in $Y_{\text{TSMC}}$ followed by $Y_{\text{TSM}}$. This result was associated with the high serum separation levels determined in $Y_{\text{TSMC}}$ and $Y_{\text{TSM}}$ during storage.

According to Tamime and Robinson (1985), the symbiotic relationship between the starter culture strains is broken down with increasing serum separation. In $Y_{\text{TSMC}}$, in spite of the high difference in serum separation levels (5.63 %) between the 1st and the 5th days, $Lb.\ bulgaricus$ levels were higher than in $Y_{\text{TSM}}$. This was indicated with the larger increase in acidity and proteolysis in $Y_{\text{TSMC}}$ compared to $Y_{\text{TSM}}$ (Table 1). Also, $Lb.\ bulgaricus$ levels in $Y_{\text{TSM}}$ and $Y_{\text{TSMC}}$ between the 10th and the
14th days were lower than on the 1st day of the storage. In YTSMC, *Lb. bulgaricus* levels were higher on the 10th and the 14th days of the storage compared to the 1st day. This result was associated with the low serum separation in YTSMX in spite of the increase in acidity and proteolysis during storage (especially the 10th and the 14th days).

*Str. thermophilus* levels decreased in yoghurt samples during storage. The sizes of the decreases by the end of the storage from highest to lowest were YTSMX, YTS, YTSMC respectively. Lower levels of *Str. thermophilus* in YTSMC compared to other groups from the 5th day of the storage until the end of storage were associated with the disruption of symbiotic relationship between the microorganisms due to the serum separation.

The relationships between the microorganism levels and storage period, serum separation and increase in acidity were significant (p<0.05). Also, a significant relationship was found between the microorganism growth and colloid type. These results were compatible with the literature (Kumar and Mishra, 2004). *Lb. bulgaricus* and *Str. thermophilus* levels in YTSMX were higher than in other samples during storage except on the 1st day. The level of microorganism in YTSM in the same period were higher than in YTSMC. The increases in *Lb. bulgaricus* and *Str. thermophilus* levels in YTSMX and YTSM after the 1st day of the storage were associated with the sugar content of xanthan gum and samphire molasses; this result was consistent with the literature.

According to Shirai et al. (2001), lactic acid bacteria grow better in the presence of certain sugars (glucose, maltose, sucrose). *Lb. bulgaricus* and *Str. thermophilus* levels were higher in YTSMC compared to other samples only on the 1st day of storage. This was associated with the interaction in YTSMC between κ-carrageenan and milk proteins. In fact, depending on the increase in microorganism levels in YTSMC on the first day of the storage, the increases in acidity, serum separation and proteolysis were higher than in other samples.

Additionally, the decrease in lactose in YTSMC on the 1st day of storage was higher than in other samples. It was determined that *Lb. bulgaricus* was the dominant microbe in yoghurt samples from the 5th day of the storage onward. Our results were compatible with the findings of previous studies (Abdel Moneim et al., 2006; Ashmaig et al., 2009; Omer et al., 2007). Lag phase (14 hours) of the starter cultures was long, which is consistent with Attia et al. (2001). Additionally, it was determined that combined use of microorganisms was important in yoghurt production from camel milk, a finding that is compatible with previous reports (Abu-Tarboush, 1996; Al-Awadi and Sri Kumar, 2001; Gassem and Abu-Tarboush, 2000).

However, in the study, it was found that *Str. thermophilus* levels were higher than *Lb. bulgaricus* levels until the 5th day (except the 5th day). This result was compatible with some studies (Abu-Tarboush, 1996), but not compatible with others (Abdel Rahman et al., 2009).

**Sensory evaluation**

The acrid taste of samphire molasses is associated with phenolic compounds passing to the extract during the extraction of the fruit (Ozdemir et al., 2004). Additionally, samphire molasses is rich in phenolics such as catechin and epicatechin. Acrid taste determined in yoghurt samples was lower than in TSM; the sample acidities from lowest to highest were YTSMX, YTS, YTSMC respectively. Acidity decreased depending on the increase in acidity and proteolysis. Additionally, according to He et al. (2008), proanthocyanidins, flavonoids and anthocyanins cause changes in taste as a result of different chemical reactions, and proanthocyanidin and anthocyanin levels change constantly during storage causing a reduction in acidity and bitterness. It was found that acridity decreased during storage depending on the increase in L*. The most favored samples in terms of taste were evaluated according to their L* value. Accordingly, YTSMX with the highest L* value, was more favored than the other samples. However, although L* was higher in YTSMC compared to YTS, it received lower texture scores than YTS. The sample most favored by the panelists in terms of taste, color and texture was YTSMX. YTS received lower taste and color scores and higher texture scores compared to YTSMX. YTS received higher taste and color scores and lower texture scores compared to YTS.
Conclusion

It was determined that $Y_{TSMC}$ was an unsuitable yoghurt product in terms of physicochemical, rheological, microbiological and sensory properties due to the interaction between WPI and κ-carrageenan. Rheological properties obtained in $Y_{TSM}$ with WPI (3 % w/v) + GAP (3 % w/v) fortification were found to be superior to those of $Y_{TSMC}$ and the yogurt gel was harder than in $Y_{TSMC}$. Additionally, TF and Hunter $L^*$ levels increased in YTSM and YTSMC during storage. It was concluded that both of the samples might be evaluated as fermented dairy drinks with functional properties. In contrast with the studies reporting problems during yoghurt production from camel milk (Jumah et al., 2001), yoghurt was produced from camel milk with the addition of WPI (3 % w/v) + TSM (3 % w/v) and xanthan gum (0.5 % w/v) (YTSMX) with suitable physicochemical, rheological, microbiological and sensory properties. In consequence, functional yoghurt can be produced from camel milk, which has proven beneficial health effects, with traditional samphire molasses and xanthan gum colloid fortification. Further studies on this subject for future commercial production are warranted.

Jogurt od devinog mlijeka i melase borovice

Sažetak

Jogurt od devinog mlijeka (Camelus dramedarius) proizведен je u 3 varijante: (A) uz dodatak proteina sirutke (3 % w/v) i melase borovice (3 % w/v); (B) uz dodatak proteina sirutke (3 % w/v) i melase borovice (3 % w/v ) + 0,1 % (w/v) κ-karagenana; (C) uz dodatak proteina sirutke (3 % w/v ) i melase borovice (3 % w/v ) + 0,05 % (w/v) ksantan gume. Fizikalno-kemijska svojstva, tekstura, boja te senzorska svojstva pruženi su 1., 5., 10. i 14. dana skladištenja. Koncentracija fenola analizirana je nakon 14, 24, 32, 48, 72, 120, 240 i 336 sati skladištenja. U svim uzorcima utvrđeno je povećanje kiselosti, čvrstoće i viskoziteta tijekom skladištenja, ali u jogurtu (C) to povećanje je bilo jači izraženo, te je u tom jogurtu (C) izdvađanje sirutke bilo vrlo slabo izraženo. Također, jogurt (C) je pokazao bolja fizikalno-kemijska, teksturalna, mikrobiološka i senzorska svojstva u odnosu na druga dva jogurta (A, B). Ukupna koncentracija fenola također se povećavala tijekom skladištenja, a najveće vrijednosti utvrđene su u jogurtu C. Najveća koncentracija Lactobacillus delbrueckii subsp. bulgaricus i Streptococcus thermophilus bakterija nakon 5. dana skladištenja utvrđena je u jogurtu C.

Ključne riječi: jogurt, melasa borovice, devino mlijeko, koloidi

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