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Physicochemical Composition and Selected Quality Characteristics of the New Product: Ready to Eat Shrimp

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Research Article

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Abstract

In this study, it was aimed to develop an alternative product for seafood consumption by applying the smoking and marinating process on shrimp. Physicochemical, microbiological, and sensory analyzes were performed on a certain day of each month to determine the quality and shelf life of the obtained smoked product. Firstly, hot smoking process was applied and then the marination process was applied on shrimp used in the study. According to the results of microbiological analysis, while the number of TMAB was detected as 1.54 LogCFU/g in fresh shrimp, the number of microorganisms was determined lower than 1 LogCFU/g in the smoked and marinated product. It was determined that the products which were kept in refrigerator conditions for 10 months started to lose quality in the 8th month of storage and the shelf life of the product was determined as 7 months for the consumer.

Keywords: Pink deep-water shrimp (*Parapenaeus longirostris*), hot smoking, marinate, fatty acids, shelf life.

Yeni bir Ürünün Fizikokimyasal Kompozisyonu ve Bazı Kalite Parametreleri: Tüketime Hazır Karides

Özet

Bu çalışmada, karides etine dumanlama ve marinasyon işlemi uygulanarak su ürünleri tüketimine alternatif bir ürün geliştirilmeye çalışılmıştır. Elde edilen dumanlanmış marine ürünün buzdolabı koşullarındaki kalitesini ve raf ömrünü tespit etmek amacıyla her ayın belirli bir gününde fiziksel, kimyasal, mikrobiyolojik ve duyusal analizler yapılmıştır. Çalışma kapsamında karidesler önce dumanlanmış ardından marine edilmiştir. Mikrobiyolojik analiz sonuçlarına, göre taze karideste tespit edilen TMAB sayısı 1,54 LogKOB/g iken yapılan marinasyon+dumanlama işlemi ile bu değer 1LogKOB/g altına düşmüştür. Dumanlanmış marine karideste depolama süresince mikroorganizma yükü 1LogKOB/g'ın altındadır. Buzdolabı koşullarında 10 ay muhafaza edilen ürünlerin, depolamanın 8. ayında kalitesini kaybetmeye başladığı belirlenmiş, tüketici için belirlenen raf ömrü ise 7 ay olarak tespit edilmiştir.

Anahtar kelimeler: Pembe derin su karidesi (*Parapenaeus longirostris*), sıcak dumanlama, marinat, yağ asitleri, raf ömrü.

INTRODUCTION

Seafood is a valuable human food that is used especially in meeting the needs of protein, minerals, and essential fatty acids and in changing healthy eating habits. Today, with the developing technology, like other foodstuffs, seafood is processed in a wide variety of forms, making it ready for consumption. For people to have adequate and balanced nutrition, they need to increase their food resources or make more use of existing food resources. The demand for seafood, which constitutes an important food group in this field, is increasing day by day.

The purpose of the smoke technology, which is one of the oldest protection methods, which is widely used in the world, economically important and known, is to improve the sensory properties of the product by taking advantage of the aroma and color given by the smoke, to extend the shelf life of the product by benefiting from the effects of heating and water loss and smoke components (antimicrobial, antioxidant) (Gülyavuz and Ünlüsayın, 1999). Another of the oldest known methods of conservation is marination. The purpose of this technology is enzymatic maturation of fish in acid and salt solution without heat treatment. The product obtained by adding sugar, spices, brine, sauce, or vegetables to add different flavors is a preservation method created by placing it in glass bottles or plastic containers (McLay, 1972). The raw material is made edible with the marinating process and

semi-canned products can be created by reducing the losses caused by cooking (Kılınç and Çaklı, 2004a; Björkoth, 2005).

Shrimp, valuable seafood rich in protein, is easy to digest due to the low amount of connective tissue. Pink deep-water shrimp have a great economic value all over the world. It has a good market, frozen or canned. It has a great economic value in our country as it is the most caught shrimp in Turkey. Today, new products are developed by applying different methods to extend the shelf life of the foods. When the shelf life of the food is increased, the producer is provided with a longer time to market the product and the consumer to consume it and the product becomes more economical (Morrais and Kai 1981; Mermelstein, 1998). Cold marinated (Cadun et al., 2005; Kalıştır, 2008; Cadun et al., 2008), baked and marinated (Bilgin et al., 2006; Erdem and Bilgin, 2004) and freeze (Bingöl et al., 2013) of different shrimp species; are found in the literature. Although there is some seafood (Dalgıç, 2000; Ozogul et al., 2010; Balıkçı, 2009, Karslı, 2013; Keskin, 2019) where both smoking and marination are applied together, no such study has been observed in shrimp.

In this study, it was aimed to determine the shelf life as a result of the evaluation of chemical, microbiological and sensory quality criteria, as well as to create a new product for the food sector, by changing the composition of the nutrient composition and the chemical, microbiological and sensory quality criteria during the storage of marinates obtained from smoked shrimp (*Parapenaeus longirostris*, Lucas 1846).

MATERIALS and METHODS

Materials

As research material, a total of 15 kg of pink deep-water shrimp (*Parapenaeus longirostris* Lucas 1846), with an average length of 11.67±0.19 cm and an average weight of 7.37 ± 0.36 g, were caught from the Istanbul-Tuzla fishermen's shelter. The caught shrimp were immersed in boiling water for 1 minute as soon as the ship arrived at the port and cooled in the air stream. The cooled shrimp were placed in a single row in locked bags, with an average of 500 g, and one layer of the product was placed (four layers in total including shrimp and sea ice) in a Styrofoam box and brought to the laboratory under a cold chain.

Smoking process of shrimp

Shrimp meat was salted for 10 minutes in salt brine, shrimp: brine ratio was 1:2, for 15 minutes and filtered. Then it was lightly lubricated with sunflower oil, lined up on the oven wires, and subjected to smoke treatment. Shrimp were pre-drying at 30 °C for 20 min., then kept at 60 °C for 10 min. were smoked. After this process, shrimp were removed from the oven and rested at room temperature before marinating (Figure 1).

Figure 1. Smoking process of shrimp (a: pickling in brine, b: draining, c: smoking, d: resting)

Marination process of smoking shrimp

The rested shrimp meat was placed in marinate brine (1 % alcohol vinegar, 2.2 % salt, and ‰ 0.4 citric acids) (shrimp: brine ratio, 1:9) and matured under refrigerator conditions for 2 days (Figure 2a).

Packaging process of marinated smoked shrimp

Marinated smoked shrimp were leaked in a strainer for 2 hours. At the end of this process, its average weight was 130g smoked marinated shrimp meat was placed in the packages and it was filled with sunflower oil and closed without air bubbles. The products were stored monthly at +4 °C and analyzed monthly (Figure 2 b-f).

Figure 2. Packaging of marinated shrimp (a: marination, b: draining, c: adding sunflower oil, d-f: packaging and storage)

Methods

During the study (10 months), chemical, microbiological and sensory analyzes were performed monthly and 2 repetitions were performed in 2 parallel, and the shelf life of the products was tried to be determined in refrigerator conditions.

Proximate Composition Analyses of Shrimp

Crude protein and crude fat analysis were performed according to the Kjeldahl method (AOAC, 1980) and Soxhlet method (AOAC, 2005). Dry matter and crude ash analyzes were done according to AOAC (1995). After calculating the carbohydrate value of shrimp, the energy value was calculated according to the Atwater method (Falch et al., 2010).

Fatty acids composition was performed according to the IID-19 method by IUPAC (1979) on Thermo Scientific Trace 1310.

Physicochemical Analysis

Total Volatile Basic Nitrogen (TVB-N) amount of fresh samples and products obtained was determined by the Lucke-Geidel method, modified by Antonopoulos (Ludorf and Meyer, 1973). To

detect fatty acid oxidation, Erkan et al. (2011) TBARs analysis modified and applied was used. The amount of total salt and total acid (in terms of acetic acid) of shrimp were calculated according to Varlık et al. (2007). Shrimp meat was diluted with pure water at a ratio of 1:1 and pH measurement was made with the portable pH-meter probe of WTW Multi 340i model (Curran et al., 1980). Water activity measurements were determined according to AOAC (1980) using the Novasina LabSwift water activity measurement device. Konica Minolta /CR-A 33a color measuring device was used for color measurements (Osaka, Japan). Values of L*, a*, and b* were measured according to the International Commission on Illumination (CIE, 1976).

Microbiological Analyses

The microbiological analysis in the study were Total mesophilic aerobe bacteria (TMAB), total psychrophilic aerobe bacteria (TPB), total yeast-mold (TYM), and total coliform bacteria (TC) count. The outer surface of the packages was wiped with 70 % ethyl alcohol and then opened with the help of a sterile knife. 10 grams of fish samples with sterile spatula were taken into sterile stomacher bags and homogenized in the stomacher by adding 90 ml of peptone solution beside the flame (Sivertsvik et al., 2003). Dilutions of 10^{-1}-10^{-6}; prepared using 1ml homogenate and 9 ml 0.85 % NaCl solution. All of the analyzes were performed as 2 repeats and 2 parallel. Plate Count Agar (PCA, Merck no: 105463.0500) was used for TMAB and TPB. Petri dishes were incubated for 2 days at 37 °C for TMAB and 10 days at 7 ^{o}C for TPB. Potatoes Dextrose Agar (PDA, Merck no: 1.10130) was used for TYM analysis. It was left at 3-day incubation at 28 °C. Violet Red Bile Agar (VRBA, Merck no: 1.01406) was used for TC count and incubated at 37 °C for 24 hours (Halkman 2005).

Sensorial Analysis

For sensory analysis, 5 experienced panelists (academics of the Seafood Processing Technology department) were selected and a form was given to the panelists to evaluate the products. Sensory evaluation form Varlık (1993) and modified from the table for marinated products used by Schormüller (1968). The products were rated between 0 and 5 in terms of color, odor, flavor, texture, and general taste (0-1: Inexpensive, 1-2: Bad, 2-3: Not bad, 3-4: Good, 4-5: Very good), products below 2 points are considered as inexhaustible.

Statistical Evaluation

The average values and standard deviations of the results obtained in the research were made using Microsoft Office Excel 2018 package program and statistical evaluations using one-way analysis of variance and Tukey test with the help of Minitab 17 package program (Sümbüloğlu and Sümbüloğlu, 2000).

RESULTS and DISCUSSION

Average Weight, Length, and Meat Yield of Shrimp

The average weight and length of shrimp used in the study were 7.37±7.30.36 and 11.67±0.19, respectively. It was determined that the meat yield of the shrimp was 35 %, and the meat yield of the product was 26.56%. Total weight loss was determined as 73.44 % until the final product was obtained. The reason for the high loss; it is thought that the scalding process used in killing shrimp and the loss of head and shell extraction due to the small shrimp were affected. Diler and Ataş (2003) reported the meat yield of shrimp (*P. semisulcatus*) as about 1.36 %, while Zamorano et al. (2009) stated that shrimp lose 50 % weight after cleaning. Similarly, Çankırılıgil and Berik (2017) determined that the meat yield of deepwater pink shrimp was 48.46 %. The meat yield of the species used in our study was lower compared to the shrimp species in the literature; it may be due to less length and weight, and hence greater shell weight. Also, meat yield of shellfish products; may vary depending on size, species, sex, hunting area, nutritional status, and the structure of the shell and head (Venugopal and Gopakumar, 2017). Our study also shows that differences in processing methods significantly affect meat yield. Indeed, as a result of heat treatment during smoking, the moisture content of shrimp meat decreases, which reduces efficiency. Also, the amount of salt used in brine causes shrimp meat to lose weight.

Proximate Composition Results of Shrimp

In Table 1, the proximate composition analysis results of fresh shrimp, after smoking, marination, the beginning of storage (1st day), and end of storage period (10th month) samples are given.

Table 1. The proximate composition analysis results and energy values of shrimp.

	Moisture (%)	Crude Protein (%)	Crude Fat (%)	Crude Ash (%)	Energy (Kcal/100g)
Fresh shrimp	78.08±0.43[a]	18.82±0.27[b]	0.23±0.02[e]	1.52±0.02[b]	82.78±1.70[d]
Smoked shrimp	59.62±0.21[e]	20.90±0.05[a]	2.67±0.07[c]	4.32±0.28[a]	157.55±0.39[b]
Marinated shrimp	70.84±0.60[b]	19.00±0.10[b]	0.83±0.07[d]	1.04±0.02[b]	116.64±2.83[c]
Packed shrimp (1th day)	66.24±0.13[c]	18.56±0.19[b]	4.17±0.09[b]	1.07±0.06[b]	151.62±0.79[b]
Packed shrimp (10th monhts)	61.56±0.41[d]	17.42±0.10[c]	8.55±0.14[a]	1.44±0.07[b]	190.76±2.33[a]

ab ↓: Difference between groups is important in the same column ($p<0.05$)

In the present study, moisture, crude protein, crude oil, and a crude ash content of fresh shrimp were as follows; 78.08±0.43 %, 18.82±0.27 %, 0.23 ± 0.02 %, and 1.52 %. The moisture, crude protein, crude oil, and crude ash contents of shrimp were investigated by different researchers. These values vary according to the shrimp type; for moisture; 75.40 % in *P. semisulcatus*, 72.90 % in *P. japonicas,* and 70.95 % in P. *monodon* (Diler and Ataş, 1999), for crude protein; 17 % in *P. borealis* and *P. jordani* (Oner and Yıldırım, 2018), 20.13 % in *P. semisulcatus* (King et al., 1990), for crude fat; 0.35 % in *P. longirostris* (Cadun, 2002) and for crude ash; 1.60 % (Yanar, 2003) in *M. monoceros* and *P. semisulcatus*. Hacıoğlu (2010), moisture, crude protein, crude oil, and crude ash amounts of pink deep-water shrimp were 76.72 %, 10.86 %, 2.14 %, and 8.13 %, respectively.

After the smoking process, the moisture content of shrimp meat decreased to 59.62±0.21 % ($p<0.05$) with the effect of heat treatment, and the amount of crude protein increased by 20.90±0.05 % ($p<0.05$). The smoking process also caused an increase in the crude fat and crude ash content of raw shrimp ($p <0.05$). With the marination after the smoking process, the moisture content of the product increased ($p <0.05$), and a decrease in crude protein, crude fat, crude ash content were observed ($p <0.05$). Shrimp that had been smoked and then marinated were packaged with the addition of oil. On the first day of this process, the crude protein content of the final product was statistically similar ($p> 0.05$) to the marinated shrimp. At the end of the ten-month storage period, a decrease in the crude protein content ($p <0.05$) and an increase in the crude fat content ($p> 0.05$) was observed.

Cadun et al. (2005) determined the moisture, crude protein, crude fat and crude ash amount of raw and marinated pink deep-water shrimp as 85.49 %, 11 %, 0.35 %, 2.43 % and 75.48 %, 20.4 %, 0.54 %, 2.78 %, respectively. Similar to the present study, the process of marination caused water loss in the product. In another marinate study made from *M. stebbingi*, it determined the moisture, crude protein, crude fat, and crude ash contents of fresh shrimp as 81.41 %, 16.29 %, 1.1 %, 0.65 %, respectively. These values after marination were 75.24 %, 20.77 %, 1.32 %, 2.98 % respectively (Kalıştır, 2008). In a study in which smoking, and marination processes were applied separately and in combination, the researchers reported that the content of the proximate composition increased with the procedures applied as in the present study (Karslı, 2013).

While the energy content of raw shrimp was 87.78 Kcal/100g, a calorie increase was detected after smoking. Due to the loss of water in the product; especially the increase in crude fat and carbohydrate content was the reason for the increase in calorie value. Also, energy reduction was observed with the removal of crude fat and water-soluble carbohydrates from shrimp tissue by marinating (116.64 Kcal/100g). The oil used as a filling during storage also caused an increase in calories.

Fatty acid composition results

Fatty acid contents of fresh, smoked, marinated, and packaged shrimp are given in Table 2. The total saturated fatty acid (Σ SFA), total monounsaturated fatty acid (Σ MUFA), and total polyunsaturated fatty acids (Σ PUFA) values of fresh shrimp were found as 25.48±0.25, 30.923±0.18, 43.57±0.41, respectively. Emami (2014) reported the rates of SFA, MUFA, and PUFA of *P. vannamei* and *P. semisulcatus* as 37.26 %, 24.9 %, 37.84 % and 49.12 %, 33.76 %, 16.9 %, respectively. Turan et al. (2011) reported the rate of SFA in brown shrimp as 33.04 % and PUFA content as 29 %. Ouraji (2011) stated the SFA values of natural and culture samples in Indian shrimp as 32.88 % and 33.79 %, respectively. The ΣMUFA value of the same kind of shrimp in the present study was 26.09 % (Oksuz et al., 2009), this difference in fatty acid ratios may be due to the caught area, seasonal conditions, and other environmental factors.

The amounts of ΣSFA, ΣMUFA, and ΣPUFA of the smoked shrimp were determined as 19.97±0.14, 35.81±0.45, 44.20±0.57 %, respectively. In this process step, as in raw shrimp, the dominant SFA were palmitic acid and stearic acid. However, an increase in the content of behenic acid was observed with the smoking process ($p<0.05$).

The third processing step applied to the product before storage was marination. Shrimp after marinating; the amounts of ΣSFA, ΣMUFA, and ΣPUFA were 23.07±0.11, 28.89±0.41, and 48.04±0.28 %, respectively. In this step, an increase in stearic acid content was observed compared to smokes ($p <0.05$), but this value was found similar to raw shrimp ($p> 0.05$).

The amounts of ΣSFA, ΣMUFA, and ΣPUFA were determined as 22.83±0.62, 32.47±0.29, 44.70±0.40 %, respectively, on the first day of storage in the packaged product. The ΣSFA amount of the packaged product was not different from the marinated product ($p> 0.05$). However, the contents of ΣMUFA and ΣPUFA were different ($p <0.05$). The oleic acid content of the product increased with the addition of oil ($p <0.05$). The fatty acid content of the sunflower oil used is highly oleic and linoleic acid (38.78 % oleic acid, 49.99 % linoleic acid). Therefore, both the oleic and linoleic acid content of the packaged product increased ($p<0.05$). The addition of sunflower oil proportionally affected the EPA and DHA content of the product, and the EPA+DHA content caused approximately a half decrease compared to the previous process step.

Table 2. The fatty acid composition of shrimp.

	Fresh shrimp	Smoked shrimp	Marinated shrimp	Packed shrimp (1th day)	Packed shrimp (10th months)
C4:0	0.01±0,01^{a}	-	0.01±0.01^{a}	-	0.02±0.01^{a}
C6:0	-	-	0.01±0.01^{a}	-	0.01±0.00^{a}
C8:0	-	0,02±0.00^{c}	0.01±0.00^{d}	0.04±0.00^{b}	0.06±0.00^{a}
C12:0	0.02±0.00^{a}	0.01±0.00^{b}	0.02±0.01^{ab}	0.01±0.00^{b}	0.01±0.00^{b}
C13:0	0.01±0.00^{a}	-	0.01±0.00^{a}	-	-
C14:0	1.29±0.02^{a}	0.58±0.05^{c}	0.90±0.01^{b}	0.48±0.02^{cd}	0.44±0.02^{d}
C15:0	1.27±0.02^{a}	0.46±0.04^{c}	0.96±0.00^{b}	0.39±0.00^{c}	0.24±0.01^{d}
C16:0	11.22±0.04^{a}	10.20±0.23^{b}	9.49±0.10^{bc}	9.01±0.23^{c}	11.35±0.16^{a}
C17:0	1.53±0.03^{a}	0.53±0.02^{c}	1.24±0.02^{b}	0.48±0.02^{c}	0.29±0.03^{d}
C18:0	9.20±0.09^{a}	5.00±0.40^{b}	8.79±0.05^{a}	9.89±0.37^{a}	4.42±0.28^{b}
C20:0	0.23±0.01^{a}	0.18±0.02^{ab}	0.18±0.00^{ab}	0.09±0.03^{c}	0.13±0.00^{bc}
C21:0	0.11±0.02^{a}	0.08±0.02^{ab}	0.08±0.00^{ab}	0.04±0.01^{b}	0.04±0.01^{b}
C22:0	0.38±0.03^{e}	2.63±0.04^{b}	1.25±0.03^{d}	2.23±0.07^{c}	3.34±0.04^{a}
C23:0	0.05±0.00^{a}	0.01±0.00^{c}	0.03±0.00^{b}	0.01±0.00^{c}	-
C24:0	0.14±0.01^{a}	0.28±0.25^{a}	0.12±0.01^{a}	0.15±0.03^{a}	0.04±0.04^{a}
Σ SFA	**25.48±0.25^{a}**	**19.97±0.14^{c}**	**23.07±0.11^{b}**	**22.83±0.62^{b}**	**20.39±0.42^{c}**
C14:1	0.39±0.01^{a}	0.13±0.01^{c}	0.29±0.01^{b}	0.11±0.00^{c}	0.06±0.00^{d}
C15:1 cis10	0.55±0.02^{a}	0.18±0.01^{c}	0.44±0.01^{b}	0.16±0.01^{c}	0.09±0.00^{d}
C16:1	4.82±0.02^{a}	2.14±0.12^{c}	3.51±0.04^{b}	1.76±0.02^{d}	1.50±0.06^{d}
C17:1 cis10	1.98±0.02^{a}	0.75±0.03^{c}	1.56±0.01^{b}	0.64±0.02^{d}	0.42±0.01^{e}
C18:1n9c	13.50±0.10^{e}	27.39±0.24^{b}	16.51±0.03^{d}	25.51±0.06^{c}	36.61±0.78^{a}
C18:1n9t	5.48±0.04^{a}	2.87±0.15^{bc}	3.57±0.42^{b}	2.66±0.33^{bc}	1.56±0.57^{c}
C20:1 cis 11	1.81±0.05^{a}	1.32±0.10^{b}	1.33±0.02^{b}	1.04±0.02^{c}	1.32±0.03^{b}
C22:1n9	1.04±0.05^{a}	0.36±0.06^{c}	0.71±0.01^{b}	0.22±0.02^{cd}	0.11±0.01^{d}
C24:1	1.35±0.01^{a}	0.67±0.02^{c}	0.99±0.01^{b}	0.39±0.03^{d}	0.61±0.13^{cd}
Σ MUFA	**30.923±0.18^{cd}**	**35.81±0.45^{b}**	**28.89±0.41^{d}**	**32.47±0.29^{c}**	**42.27±0.88^{a}**
C18:2n6c	0.34±0.01^{d}	25.62±0.83^{b}	17.54±0.00^{c}	29.05±0.51^{a}	26.97±0.40^{ab}
C18:2n6t	0.55±0.03^{a}	0.31±0.08^{ab}	0.33±0.03^{ab}	0.24±0.08^{b}	0.13±0.00^{b}
C18:3n3	0.41±0.02^{e}	1.27±0.05^{b}	0.74±0.02^{d}	1.10±0.04^{c}	1.73±0.01^{a}
C18:3n6	1.21±0.04^{a}	0.78±0.11^{b}	0.67±0.01^{b}	0.50±0.02^{b}	0.41±0.16^{b}
C20:2 cis11.14	1.57±0.03^{a}	0.64±0.04^{c}	1.27±0.02^{b}	0.57±0.11^{c}	0.54±0.03^{c}
C20:3n3 cis11.14.17	0.86±0.07^{a}	0.26±0.09^{bc}	0.36±0.00^{b}	0.14±0.02^{bc}	0.07±0.00^{c}
C20:3n6 cis8.11.14	2.50±0.04^{a}	0.87±0.08^{c}	1.48±0.01^{b}	0.65±0.02^{d}	0.40±0.02^{e}
C20:4n6	7.44±0.03^{a}	3.13±0.07^{c}	5.25±0.02^{b}	2.45±0.08^{d}	1.39±0.08^{e}
C20:5n3cis5.8.11.14.17	13.94±0.39^{a}	5.60±0.11^{c}	10.45±0.30^{b}	5.26±0.49^{c}	2.80±0.17^{d}
C22:2 cis13.16	0.15±0.02^{d}	0.27±0.01^{ab}	0.19±0.01^{cd}	0.25±0.02^{bc}	0.32±0.01^{a}
C22:6n3 cis4.10.13.16.19	14.61±0.22^{a}	5.45±0.04^{c}	9.78±0.03^{b}	4.49±0.24^{d}	2.55±0.14^{e}
Σ PUFA	**43.57±0.41^{b}**	**44.20±0.57^{b}**	**48.04±0.28^{a}**	**44.70±0.40^{b}**	**37.31±0.47^{c}**
TOTAL	**99.98±0.01**	**99.98±0.00**	**99.10±0.03**	**100.01±0.00**	**99.97±0.00**
ω 3	**29.82±0.51^{a}**	**12.57±0.11^{c}**	**21.33±0.31^{b}**	**10.99±0.70^{c}**	**7.16±0.32^{d}**
ω 6	**12.04±0.06^{d}**	**30.71±0.66^{b}**	**25.26±0.02^{c}**	**32.89±0.45^{a}**	**29.29±0.35^{b}**
ω3/ω6	**2.48±0.06^{a}**	**0.41±0.01^{c}**	**0.84±0.01^{b}**	**0.34±0.03^{cd}**	**0.24±0.01^{d}**
PUFA/SFA	**1.71±0.03^{d}**	**2.21±0.04^{a}**	**2.08±0.00^{ab}**	**1.96±0.07^{bc}**	**1.83±0.02^{cd}**
EPA+DHA	**28.55±0.49^{a}**	**11.04±0.09^{c}**	**20.23±0.33^{b}**	**9.76±0.73^{c}**	**5.35±0.31^{d}**

ab→: Difference between groups is important in the same column ($p<0.05$)

At the end of storage (10th month), ΣSFA, ΣMUFA, and ΣPUFA amounts of the product were determined as 20.39±0.42, 42.27±0.88, 37.31±0.47 %, respectively. At the end of the 10-month storage period, the SFA content of the final product decreased and it was found statistically different from the first day of the packaged product ($p> 0.05$). In a similar study conducted on marinated anchovy, it was determined that the SFA content of the samples increased during storage, and the PUFA content decreased as in our study, and it was stated that this was caused by oxidation in fatty acids during storage (Özden, 2005).

Omega 3 fatty acids, which are very important in terms of health, were detected at high rates in shrimp. The total ω3 content of fresh shrimp decreased with the applied smoking process, increased with marination, but decreased again with the added sunflower oil. In our study, the ω3 content of fresh shrimp was found to be 29.82 %. Similarly, Beydoun et al. (2007) reported ω3 content of raw shrimp as 35 mg/100g. The amount of ω6 in fresh shrimp was found as 12.04±0.06 and the processing

methods applied to the product and the addition of sunflower oil increased this value. The amount of ω6 increased with the effect of processing methods decreased the ratio of ω3/ω6 from 1.71 to 0.24 at the end of the storage period. Both the effect of processing methods and increased storage time led to a decrease in this rate. The desired rate for ω6/ω3 intake is between 1/1 and 4/1 (Simopoulos, 2002). When the findings obtained from the study were evaluated, it was found that the ratio of ω6 / ω3 in raw shrimp was quite low, the smoking and marination process increased this rate, but the differences in the process applied statistically were not significant ($p > 0.05$).

The PUFA / SFA ratio was determined to be 1.71±0.03 in fresh shrimp. This value had reached the level of 2.21±0.04 with the smoking process and it had been determined that the highest amount among the groups was in this group. The PUFA / SFA ratio decreased after this processing step until the end of the storage and reached 1.83±0.02. The optimum PUFA / SFA ratio is specified by HMSO (1994) as 0.45. It was determined that the PUFA/SFA ratio was above the optimum value in all groups. Ozogul et al. (2010) found the PUFA/SFA ratio of the hot smoked anchovy marinate produced by using similar processing methods as 1.32 at the beginning of the trial and stated that there was no significant difference with the beginning and at the end of the storage period. In the present study, a decrease in this rate was found and it is thought that this difference is due to the combination of sunflower oil added to the package.

The fresh shrimp contained 0.23 g/100g of crude oil, so the EPA+DHA content of 200 g fresh deep-water pink shrimp meat was 0.06 g, which was low compared to most fish meat. Lee et al. (2003) reported that blue crab (natural) and shrimp (natural) of shellfish contain <200 mg EPA+DHA, and mussels and oysters contain 500-100 mg EPA+DHA. The present study was similar to this literature.

Physicochemical analyses results

Physicochemical analyses results of fresh, smoked, and marinated shrimp

TVB-N, TBARs, salt, total acid, pH values of fresh shrimp, smoked shrimp, and marinated shrimp are given in Table 3.

Table 3. TVB-N, TBARs, salt, total acid, pH values of fresh, smoked, and marinated shrimp

	TVB-N (mg/100g)	TBARs (mgMDA/kg)	Salt (%)	Total acid (%)	pH	Aw
Fresh shrimp	7.96±0.32^{c}	0.26±0.01^{c}	2.33±0.02^{b}	0.17±0.01^{c}	7.16±0.06^{a}	0.97±0.00^{a}
Smoked shrimp	11.18±0.27^{a}	1.12±0.01^{a}	3.12±0.00^{a}	0.27±0.01^{b}	6.41±0.01^{b}	0.95±0.00^{b}
Marinated shrimp	9.92±0.15^{b}	0.62±0.01^{b}	1.15±0.01^{c}	1.04±0.01^{a}	2.56±0.06^{c}	0.95±0.00^{b}

ab ↓: Difference between groups is important in the same column ($p<0.05$)

In the study, the TVB-N value of fresh shrimp was determined as 7.96 mg/100g. Some researchers reported TVB-N values of different types of shrimp as 1.02 mg/100g in *P. adspersus* (Erdem and Bilgin, 2004), 8.87mg /100g in *C. crangon* (Bilgin and Erdem, 2006), 8.24 mg /100g in *P. semisulcatus* (Oner and Yıldırım, 2018). TVB-N is one of the most used chemical methods in determining the freshness of seafood (Varlık et al. 1993). It is known that this value affects factors such as the variety of seafood, fishing season, degree of maturity, sex, and age. The TVB-N value of the shrimp was increased by the smoking process (11.18±0.27 mg/100g) and it was determined as 9.92±0.15 mg/100g by decreasing in the marination ($p<0.05$). Similarly, with our study, it was reported by Kılınç and Çaklı (2004b) that the marination applied to the sardine caused a decrease in TVB-N value and that this is due to the dissolution of some of the TVB-N components in a salt-water solution.

The primary analysis used in the determination of oxidation of fatty acids in seafood is TBARs. The TBARs content of raw shrimp was determined as 0.26 ± 0.01 mgMDA/kg, increased in smoke and reached 1.12 ± 0.01 mgMDA/kg and decreased to 0.62 ± 0.01 mgMDA/kg by marination ($p<0.05$).

Salt used in the marinating process affected the flavor, ripening, and texture of meat, flavor formation, and shelf life of the product. The recommended brine salt ratio for lean raw materials is 6-8% (Varlık et al., 1993). As a result of the sensory data obtained from the preliminary studies, it was determined that the use of less amount of salt than the stated ratios would be more suitable for deepwater pink shrimp. In this study, the salt ratio of brine was 1.05%. The salt content of fresh

shrimp was at the rate of 2-3 % salt, which was defined as full salt, and the salt content of the end product was below 1.5 %, which is called light saline (Varlık et al., 2004).

While the average amount of total acid before storage was 0.17±0.01 in fresh shrimp, it increased slightly due to water loss after smoking and reached 0.27±0.01, and it was found to be 1.04 ± 0.01 by increasing with the effect of acid used in brine after marinating. A statistically significant difference was found between the groups ($p < 0.05$). Different researchers emphasize that the acid concentration to be used in marination should be 2-7 %, at least 4% for complete ripening and 1-2% in the final product (Kılınç and Çaklı, 2004a; Özden and Varlık, 2004). The acid concentration of the brine used in the present study was 2.4%, the acid concentration of the final product was 1.04%. Similar to the present study, Keskin et al. (2018) reported that approximately 50 % of the amount of total acid in the brine passes into fish meat and a balance occurs between fish and brine.

The pH value before storage was determined as 7.16±0.06 in fresh shrimp and 2.56 ± 0.06 in marinated shrimp and a statistical difference was observed between the groups ($p < 0.05$). Reported that the pH value of fresh shrimp was between 7-7.64. It has been reported by different researchers that the smoking process decreases the pH value (Kaya 2006; Günlü, 2007; Özoğul et al., 2010; Tosun and Özden, 2014).

The water activity (aw) in fresh shrimp was 0.97± 0.00, decreased due to the processes performed before storage and statistically, a significant difference was found between fresh shrimp and marinated shrimp groups ($p < 0.05$). In salted products, the water activity value is low, so these products are more durable (Çaklı and Kışla 2003).

Physicochemical analyses results of packed shrimp

The TVB-N values of the packed shrimp showed a time-dependent change during storage (Table 4). TVB-N values of the packaged product were below the limit values. TVB-N was determined as 10.26±0.25 mg/100g at the end of the storage. TVB-N analysis does not give direct results in marinating products, the results are far below the limit values and the changes are not stable (Varlık et al. 1993). It can be said that the use of TVB-N analysis as a parameter of deterioration is not suitable for smoked shrimp marinades.

Table 4. TVB-N, TBARs, Salt, Total acid, pH, and aw values of packed shrimp during storage.

		TVB-*N* (mg/100g)	TBARs (mg MDA/kg)	Salt (%)	Total acid (%)	pH	aw
	1st Day	9.72±0.05^{de}	0.32±0.01^{e}	1.36±0.01^{e}	0.85±0.01^{e}	2.87±0.01^{f}	0.96±0.00^{a}
Months	***1***	12.37±0.09^{ab}	0.45±0.01^{ab}	1.46±0.05^{e}	1.23±0.00^{a}	2.71±0.01^{g}	0.95±0.00^{ab}
	2	13.50±0.28^{a}	0.39±0.01^{bcd}	1.43±0.01^{e}	0.87±0.00^{de}	3.11±0.01^{e}	0.94±0.00^{bc}
	3	11.50±0.34^{bc}	0.46±0.02^{a}	1.4±0.06^{e}	0.96±0.01^{cd}	3.32±0.02^{d}	0.93±0.00^{cd}
	4	13.25±0.40^{a}	0.42±0.00^{abc}	1.45±0.04^{e}	1.12±0.00^{b}	3.28±0.01^{d}	0.93±0.00^{def}
	5	7.90±0.17^{f}	0.32±0.00^{e}	1.51±0.04^{e}	0.98±0.02^{c}	3.42±0.01^{c}	0.94±0.00^{bc}
	6	9.99±0.41^{de}	0.34±0.03^{de}	1.11±0.01^{f}	0.86±0.04^{e}	3.51±0.01^{b}	0.92±0.00^{ef}
	7	9.23±0.27^{ef}	0.35±0.00^{cde}	2.32±0.04^{d}	0.73±0.02^{f}	3.53±0.01^{b}	0.93±0.00^{cde}
	8	10.97±0.25^{bcd}	0.38±0.03^{cde}	2.51±0.03^{c}	0.58±0.02^{g}	3.65±0.01^{a}	0.94±0.00^{cd}
	9	10.56±0.43^{cde}	0.37±0.01^{cde}	2.74±0.01^{b}	0.56±0.02^{g}	3.62±0.01^{a}	0.93±0.00^{def}
	10	10.26±0.25^{cde}	0.42±0.02^{abc}	3.22±0.05^{a}	0.55±0.04^{g}	3.67±0.01^{a}	0.92±0.00^{f}

ab ↓: Difference between groups is important in the same column ($p<0.05$)

At the beginning of storage, TBARs value was determined as 0.32 mgMDA/kg, fluctuated during storage, and did not exceed 0.46 mgMDA/kg. A TBA value of less than 3 indicates that the product is in a "very good" condition in terms of oxidation (Varlık et al. 1993). Karslı (2013) reported that the amount of TBA between 0.52-1.05 (mg MDA/kg) during storage in a smoked marinated cockle. Kalıştır (2008) detected 0.66 mg/kg in the fresh sample of the marinated shrimp (*M. stebbingi*), while this value increased during the storage in the refrigerator and reported that it was 4.05 mgMDA/ kg at the end of storage. Cadun et al. (2008) obtained marinate from deep pink water shrimp and TBA value of fresh shrimp was 0.26 mg MDA/kg, this value increased to 0.9 mgMDA/kg after marination, and they ended the study because they exceeded the consumable limit value on 75th day after storage.

While the salt content of the packed shrimp smoked during the storage period was not statistically different until the 6th month (p> 0.05), it increased until the end of the trial after the 6th month (p <0.05).

During the storage period, the amount of vinegar fluctuated up to the 4th month and continued to decrease until the end of the trial after the 4th month. There was no statistical difference between the groups at the beginning of the trial (1st day), 2nd, and 6th months (p> 0.05), and no statistical differences were observed after the 8th month.

During the storage period, the amount of total acid fluctuated up to the 4th month and continued to decrease until the end of the storage. There was no statistical difference between the groups at the beginning of the storage (1st day), 2nd, and 6th months (p> 0.05), and no statistical difference was observed after the 8th month.

Average pH values fluctuated between 2.70 and 3.70 during storage. The maximum pH value was measured at 10 months and this value was statistically not different between the 8th and 9th months (p> 0.05). The initial pH value increased over time due to the sunflower oil added to the product.

Water that fumes away by smoking caused aw drop and no change was observed by marination. The aw value fluctuated during storage. Similar results were also identified by Šimat et al. (2011), Karslı (2013), Kocatepe et al. (2019).

Color analysis results

Color analysis results of fresh, smoked, and marinated shrimp

The L * (brightness) value of fresh shrimp was determined as 77.92 and this value decreased with the effect of smoking (Figure 3). The composition of the smoke may have adversely affected the brightness of the product. After marinating, the brightness of the product increased and it was found statistically similar to raw shrimp (p> 0.05). It is known that the marinating effect increases the brightness of the product. Marine products are requested by consumers to be bright. It can be said that marinating reduces the negative effect of hot smoke on brightness and a more attractive product was developed for the consumer. In the fresh product, a (+) redness value of 3.72 was found and this value increased with the effect of smoking, but the effect of the marination process was found insignificant (p> 0.05). After the smoking process, the b (+) yellow value of the raw shrimp increased, but the yellowness of the color decreased after the smoked marination (p <0.05). Yellowness decreased due to the lightening properties of the acid during the marination process.

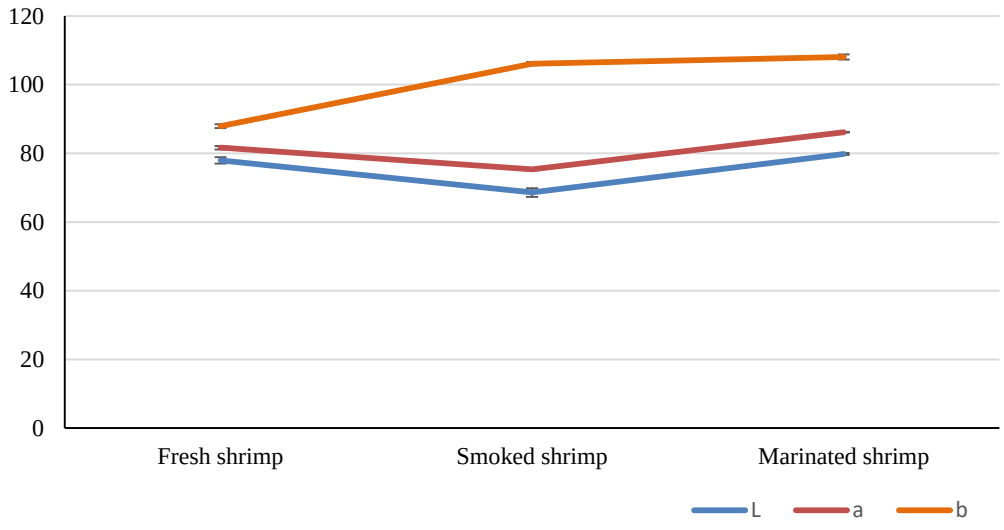

Figure 3. Color analysis results of fresh, smoked, and marinated shrimp

Color analysis results of packed shrimp

The brightness of marinated shrimp fluctuated during storage and all values were detected lower than the first day of marination. The brightness value decreased by 11.6 % in the 6th month of storage compared to the previous month (p <0.05). A (+) red value of the final product fluctuated during

storage. B (+) yellow value increased after the 1st day of marination (Figure 4). Karslı (2013) reported that the brightness value of the smoked clam marinades decreased during storage.

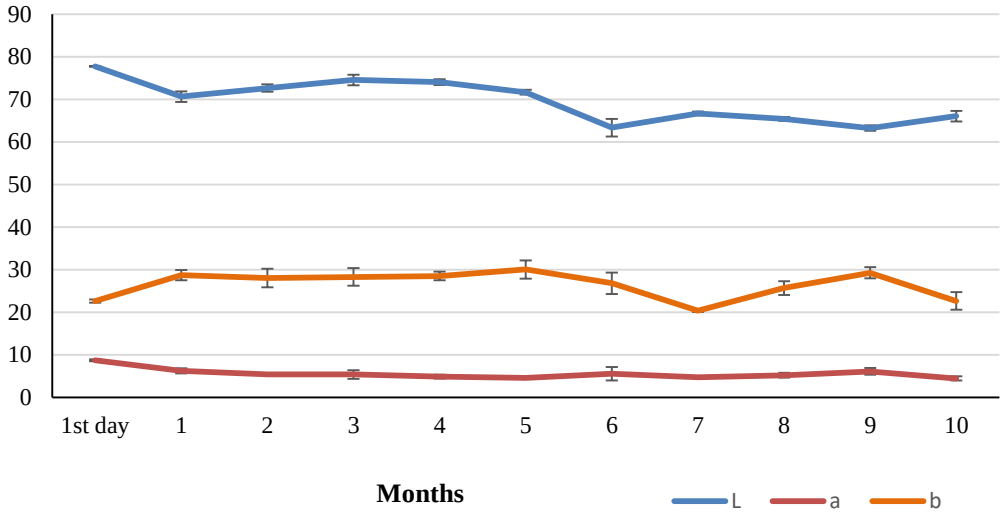

Figure 4. Color analysis results of packed shrimp

Microbiological analysis results

In the study, all groups were examined in terms of Total Mesophilic Aerobe Bacteria (TMAB), Total Aerobe Mesophyll Bacteria (TPB), Total Yeast-Mold (TYM), and Total Coliform Bacteria (TC) count given in Table 5.

Table 5. Microbiological analysis results of shrimp (Log CFU/g)

	TMAB	TPB	TYM	TC
Fresh shrimp	1.54±0.06 ^{a}	1.92±0.02 ^{a}	<1 ^{b}	<1 ^{a}
Smoked shrimp	1.45±0.15 ^{a}	1.59±0.11 ^{a}	1.39±0.09 ^{a}	<1 ^{a}
Marinated shrimp	<1 ^{b}	<1 ^{b}	<1 ^{b}	<1 ^{a}

ab ↓: Difference between groups is important in the same column ($p<0.05$)

The number of bacteria of fresh shrimp TMAB, TPB, TYM, and TC was 1.54, 1.92, <1, and <1 LogCFU/g respectively. Oner and Yıldırım, (2018), TMAB and TC counts of *P. semisulcatus* were 3.84 and <2.0 LogCFU/g. However, Diler and Ataş (2013) reported that the number of TMAB and TC were $5.8x10^4$ and $1.9x10^2$ CFU/g in the same shrimp. Patir et al. (2009) reported the TC count of raw shrimp meat as 2.53 LogCFUg-1 and the TYM content as 1.78 LogCFU/g. After removing the shells of the deepwater pink shrimp used in our study, the meat ready for processing was analyzed microbiologically and the microbiological load was found to be quite low from this literature. These data show that the shrimp used in the present study were exposed to cross-contamination at very low levels until processing. With the effect of heat treatment and antimicrobials in the smoke, TMAB and TPB count decreased, but they were found statistically insignificant ($p> 0.05$). However, it has been observed that the smoking process increases the total number of yeast molds of shrimp. This number fell below 1 LogCFU/g again by marinating.

Inal (1992) reported that the number of TC should not be more than 2 Log CFU/g in fresh shrimp meat. Coliform group bacteria are used as an indicator of fecal contamination. The Japan Food Sanitation Law stated that Coliform should be 0 tolerant in frozen foods including cooked shrimps (Department of Fisheries, 2004).

The counts of microorganisms (TMAB, TPB, TYM, TC) determined in packed shrimp has remained below the detectable limit value (<1 LogCFU/g) during the storage period, with the protective effect of both hot smoking and marination.

Sensory analysis results

After the smoked and marinated shrimp meat was packed, they were analyzed monthly starting from the first day; the product was evaluated by scoring between 0 and 5 in terms of color, odor, flavor, texture, and general taste (0-1: Inexpensive, 1-2: Bad, 2-3: Not bad, 3-4: Good, 4-5: Very good). The product that is under 2 points is considered as non-consumable. Sensory analysis results did not fall below 4 points in terms of smell and there was no statistical difference from day 1 to month 7 ($p > 0.05$). When it was evaluated as flavor, it decreased to 1.2 ± 0.12 at the end of the storage period and reached not consumable value in the 9th month (Figure 5).

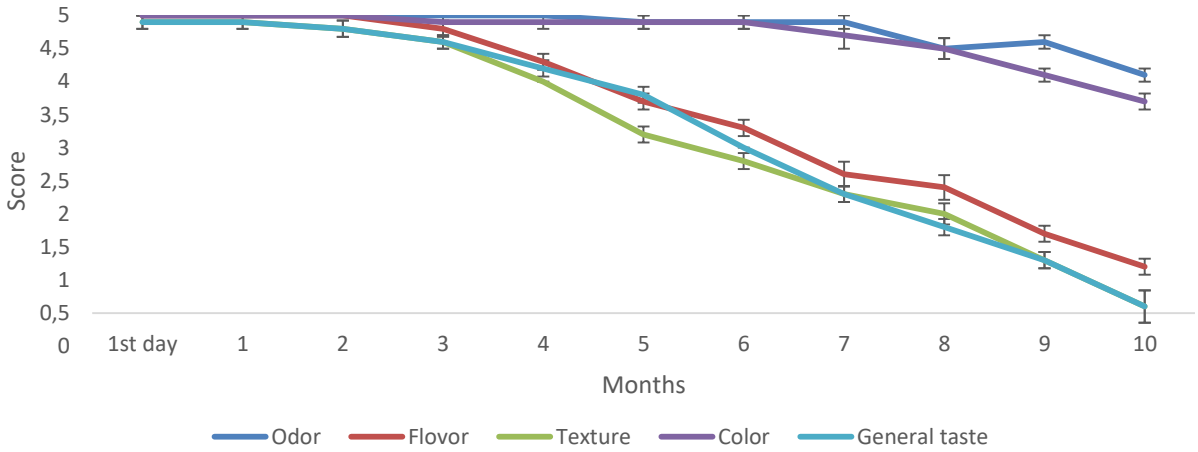

Figure 5. Sensory analysis results of shrimp

CONCLUSION

In this study, a very delicious and aromatic product had been obtained by smoking and marinating process, and it had been concluded that this product had high nutritional value and that smoking, and marination affect the shelf life of the product positively. Sensory analysis results were evaluated very precisely in this study and the shelf life of smoked deepwater pink shrimp marinate was determined as 7 months.

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