Effect of Pickling Solution on Maturing and Storage Time of Marinated Sea Bass Fillets

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Abstract: In this study, it was aimed to detect the convenience of the sea bass (Dicentrarchus labrax) to marination process, its maturation time and specific parameters that affect the maturation of fillets stored in their own pickling solution. Sea bass fillets were taken into the pickling solution that contains 2.5% acetic acid and 11% NaCl at (4±1)°C for 10 weeks. Fillets were analysed for following parameters; pH, moisture, acetic acid and NaCl. In the cold storage, scaled fillets matured after 48 h and scaleless and skinless fillets maturated in 30 h. Important changes were determined after the fish samples had been taken into their own pickling solution. After dippng into marination solution, acetic acid and NaCl contents of fillets increased within 1 h. On the contrary, moisture and pH content decreased. Rapid decrease in pH was observed in following 2 h. Acetic acid content of scale fillets decreased after 48 h of marination process. As for scaleless and skinless fillets acetic acid decreased after 30 h of marination process. The least NaCl content among the sea bass fillets in storage period were obtained in skinless fillets.

Key words: Dicentrarchus labrax, cold storage, seabass marinade, maturation time

INTRODUCTION

The marinating process is one of the oldest preservation methods of fish popular in Europe. Marinated seafood consists of fish or a combination of other seafood (i.e., shrimp, octopus, squid) that are treated with acids (acetic or citric), salt, sugar, spices and oil in order to improve the flavour and textural properties of seafood (Hwang and Tamplin, 2005). Marinades are semipreserves; acid, usually acetic acid and salt are added to the fish to retard the action of bacteria and enzymes, resulting in a product with a characteristic flavor and an extended but limited shelf life (Gokoglu, 2003). In general, the shelf-life and safety of non-thermally treated marinated seafood is because of the kind of organic acid, the NaCl concentration and the final pH value that is used (Gallart-Jornet et al., 2007; Giuffrida et al., 2007).

The preserving principal is the combination of acetic acid and salt. Proper penetration of salt(s), acid(s) and other ingredients in marinades improves texture and other sensory qualities of marinated meat products (Yashoda et al., 2005). Salt and acetic acid intake depends on many factors including species, muscle type, fish size, fillet thickness, weight, composition (lipid content and distribution), physiological state, salting method, brine concentration, duration of salting step and fish-to-salt ratio, ambient temperature, freezing and thawing. The preservative effect of salt has been recognised as being due to a decrease

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in water activity, less availability to microbial attack and enhancement of functional properties, leading to an increase of the shelf-life time (Yanar et al., 2006; Gallart-Jornet et al., 2007). Recently, in Italy, marination technology has also been spreading to some reared fish, like gilthead seabream and sea bass (Giuffrida et al., 2007). Sea bass is one of the main marine fish species aquacultured in Mediterranean countries and Turkey. In Europe, the demand for fresh aqua-cultured sea bass has been constantly increasing over the past 15 years due to its high nutritional quality and excellent sensory properties. Total production in Turkey was 41,900 tons in 2007 (Paleologos et al., 2004; Anonymous, 2007). Sea bass is generally consumed as fresh. The white flesh, mild flavour and low fat content of sea bass are major attributes sought by the consumer. These attributes have made several bass species popular and high valued around the world. In Turkey an increasing in production of this species as an aquaculture product has raised its importance of keeping it in good quality for long periods of time (Kyrana and Lougovois, 2002; Cakli et al., 2006). Generally anchovy are commercially used for marinated fish production, but usage of sea bass is not common in Turkey and other countries. However, little literature regarding the use of sea bass in marinade production is available.

In this study, the usage of sea bass in marinade production was experienced. The aim of this study was to produce sea bass (scaly, scaleless and skinless fillets) marinade and to determine its shelf life at 4°C (±1).

MATERIALS AND METHODS

Raw Material

Aquacultured fresh sea bass, Dicentrarchus labrax (average weight and length: 325±25 g and 240±10 mm) were cultivated in net cages in Turkish fish farm (Kılıç Fisheries Co., Muğla) and harvested during the period of October 2007. A total of 60 kg fish were slaughtered by immersing in flaked ice-cold water (hypothermia), packed with flaked ice (2.1, fish ice) in polystyrene boxes provided with holes for drainage and transported to the laboratory (whole as scaly and scaleless) within 18 h of harvesting.

Marination Process

All the fish were headed, eviscerated, washed thoroughly of blood and filleted. Before starting this study, preliminary experiments with marination solutions in different concentrations were performed in order to determine the acceptable taste (total 6 experiments). After the taste tests, it was decided that the best tastes were obtained with 2.5% acetic acid (v/v) and 11% NaCl (w/v). The marination process was achieved by immersing the fish into solutions containing acetic acid and NaCl for 10 weeks. Fish were separated into three groups as scaly fillet, scaleless fillet and skinless fillet. Fillets were taken into the pickling solution that contains 2.5% acetic acid (v/v) and 11% NaCl (w/v) in 5 L glass jars at 4°C (±1). Fish were classified as 1.5/1: solution ratio/fish (v/w).

Analysis

For ten weeks (0, 1st, 2nd, 3rd, 4th, 5th, 6th, 9th, 12th, 18th, 24th, 30th, 36th, 42nd, 48th, 54th, 60th, 66th, 72nd, 4th, 5th, 6th days, 1st, 2nd, 3rd, 4th, 6th, 8th, 10th weeks), fish meat in each group were analyzed for following parameters; pH, moisture, acetic acid and NaCl. Four sea bass fillets were chosen randomly at each sampling time for analyses. Reagents of analytical grade and deionized water were used throughout the experiments. Mentioned before analysis, four fish fillets from every jar were randomly taken and all the fish were pooled. Then the fish flesh were homogenized using a kitchen blender. In this study, all analysis were done and analysis carried out as 4 parallels.
pH Measurement

Sea bass fillets homogenised using a food processor. Samples were prepared according to Manthey et al. (2007) by blending 5 g of the homogenate with 5 mL distilled water for 1 min at room temperature in an Ultra-Turrax (IKA T 25 Basic, Staufen, Germany). pH was monitored using a WTW-pH-meter (Ina Lab Level 1 model, Weilheim, Germany).

Moisture Content

Moisture content was determined by 5 g of minced fish at 105°C for 3 h to constant weight (AOAC, 1980).

Salt in Fish Flesh

NaCl content in fish muscle was determined by the volumetric method of Volhard (AOAC, 1980). The NaCl content was calculated as percentage of the sample.

Acidity in Fish Flesh

Acidity was determined as acetic acid according to the method given by Karl (1994). The method was based on titration using NaOH and phenolphthalein as an indicator.

Statistical Analysis

The results of analyses were reported as Means±SD. One way ANOVA test followed by the least significant difference test (LSD) in the statistical software program SPSS were used to evaluate any significant difference (at p<0.05). The software used was SPSS version 11.0.

RESULTS

The changes in moisture value during the storage period within pickling solution of sea bass fillets are shown in Fig. 1.

![Fig. 1: Moisture results of scaly, scaleless and skinless seabass fillets](image-url)
Mean moisture content measurements over the period of storage are shown in Fig. 1. In raw scaly, scaleless and skinless sea bass fillets, the moisture content at the beginning of the marination process decreased from 74.27±0.87 to 64.38±0.21, 67.58±0.81, 65.72±0.48, respectively. Moisture content of fillets within marination pickled increased until maturation time and then decreased between 6 and 36 h and again increased at the end of storage with marination. Especially a gradual increase was observed after 42 and 48 h in all fillets. The least moisture content among the sea bass fillets was obtained in scaleless fillets. When we checked the moisture analysis results statistically, there was no statistical difference between the scaly and scales samples (p>0.05) but there was an important difference between the skinless samples and the other scaly and scaleless ones (p<0.05).

The changes in pH value during the storage period within pickling solution of sea bass fillets are shown in Fig. 2. Mean pH measurements over the period of storage are shown in Fig. 2. The pH of scaly, scaleless and skinless fresh sea bass fillets decreased appreciably, from 6.35±0.01 to 5.24±0.01; 4.94±0.03; 5.23±0.01 during the 1st h of marination processing, respectively. The fast decrease in pH before 2 h was followed. The pH content in all sea bass fillets after 5 h of storage with marination solution decreased. During the first 36 h of the storage of marinated sea bass there were significant changes in pH. During the subsequent storage there were no significant changes in pH. The least pH value among the sea bass fillets were obtained in skinless fillets. The difference between the skinless and scaleless samples were statistically insignificant (p>0.05) but there was an important difference between the scaly samples and the other scaleless and skinless ones (p<0.05).

The changes in acetic acid value during the storage period within pickling solution of sea bass fillets are shown in Fig. 3. The average acetic acid contents are shown in Fig. 3. Acetic acid content of scaly sea bass fillets decreased after 48 h of marination process. As for scaleless and skinless fillets
Acetic acid content decreased after 30 h of marination process. The least acetic acid content was found in skinless fillets. The difference between the scaly and scaleless samples were statistically insignificant (p>0.05) but there was an important difference between the skinless samples and the other scaly and scaleless ones (p<0.05).

The changes in NaCl value during the storage period within pickling solution of seabass fillets are shown in Fig. 4.
The average NaCl contents are shown in Fig. 4. The change in NaCl content was similar to the change in acetic acid content. NaCl content of skinless, scaleless and scaly sea bass fillets decreased after 24, 30 and 48 h of marination process, respectively. The least NaCl value among the sea bass fillets were obtained in skinless fillets. There was no difference between the scaly and scaleless samples (p>0.05) but there was an important difference between the skinless samples and the other scaly and scaleless ones (p<0.05).

**DISCUSSION**

During the marination process, the fillets were surrounded by salt in pickling, which initially dissolves in the surface moisture of the fish. Sufficient salt was then available to go into solution and maintain the brine at saturation point as salt penetrates the fish and water is removed. Nketsia-Tubiri and Sefa-Dedeh (2006) concluded that salting time was an important processing variable influencing product moisture content. At higher acid and salt concentrations the moisture uptake after marination was also higher. The more moisture means the meat absorbed more acid during marination (Aktas and Kaya, 2001). In the raw fillets of salting of cod (*Gadus morhua*) 81.8% water and 0.4% salt has been observed. During brining, the salt content of the fillets increased and the water content decreased. The water content was found 57.6-58.4%. During storage the water content decreased further as changes in salt content were smaller. Throughout rehydration, water contents of all groups increased above the average ratio determined in the fresh fillets. During rehydration the rate of salt loss and water intake was at its highest rate in the beginning of the process and occurred at a relatively much higher rate than the changes observed in salt and water content during brining (Thorarinsdottir et al., 2004).

Marinades have low pH value due to acetic acid content. Marination involves increasing the ionic strength and decreasing the pH (Bjorkoth, 2005). In marinated products, pH value should not be more than 4.8 (Rehbein and Oehlenschlager, 1996). Aksu et al. (1997) reported that pH value in anchovy marinated with 4% acetic acid changed from 3.89 to 3.95 during the storage of 8 months. Poligne and Collignan (2000) also reported that the pH levels of anchovies pickled with acetic acid increased from 3.90 to 4.21 (peak value) after 20 d of storage and then remained constant (4.18) until the end of the storage period. During storage, the slight water loss, salt loss and pH increase were due to weak product exudation, which was limited because of the dripping stage (1.5 h) before storage. Just after pickling and immediately thereafter, cross mass transfers occurred simultaneously with salt and acid diffusion from the surface to the inside and water diffusion from the inside to the surface of the fish fillet. Giuffrida et al. (2007) found that the pH values of marinated sea bass, after an initial drastic decrease to under 4.5, fluctuated from 4.4 to 4.9. Gokoglu et al. (2004) also found that the pH value of marinated sardine with 2% acetic acid stored at 4°C fluctuated from 4.01 to 4.56 during 5 months of storage, while the pH value of marinated sardine with 4% acetic acid showed fluctuation from 3.3 on day 60 to 4.18 on day 90. Saltim et al. (2007) reported that the pH of the raw Pacific saury fillets was found 6.32. Brining resulted in a small but significant reduction of the initial pH, while marination with either 2% or 3% acetic acid was resulted in a sharp decrease in the initial pH by about 2 units. This finding is consistent with those reported for anchovies (*Engraulis encrasicholus*) and sardine (*Sardina pilchardus*), in which a sharp decrease in the pH, by about 2-2.5 units, was found after their marination with different concentrations of acetic acid and salt solutions (Sen and Temelli, 2005; Gokoglu et al., 2004).
Acetic acid is generally recognized as safe (GRAS). The application of vinegar as a food preservative is a traditional method of preventing spoilage. Vinegar is an effective acidulant that causes depression of pH below the growth range of many bacteria (Sallam et al., 2007). As soon as the marinating bath comes into contact with the fish, a diffusion of acetic acid and salt takes place into the tissue of the fish flesh until concentration equilibrium is reached (Cabrero et al., 2002). The initial acetic acid content in the brine of 2.5% is reduced to 1.3% when the diffusion process is over, i.e., after 2 or 3 day. With an initial content of 3.4%, a 1.8% acid content in the brine is obtained after same period of time. The final acid content's amount in the marinating bath should be 2.5%, which is an equivalent of 2.3% acid content in fish tissue (Shenderyuk and Bykowski, 1990). Acidity as acetic acid has been determined to investigate the diffusion of acetic acid into the sardine (Sarda pilchardus) tissue. According to acidity results, acetic acid concentration in sardine tissue was prepared with 4% acetic acid increased until 8 h and then remained constant, whereas acetic acid continued to increase up to 16 h in the samples prepared with 2% acetic acid (Gokoglu, 2003). Kilinc and Cakli (2004) claimed that acid content of the fillets of sardine was found 1.09 at the beginning and reached 2.10 after 22 days of storage. Similar results were reported with fish marination in other investigations (Karl et al., 1994; Aksu et al., 1997; Cabrero et al., 2002) showing decreasing pH value and increasing acetic acid concentration of fish fillets in marinades.

Salt preserves fish by dehydrating tissue, increasing waterphase salt and decreasing water activity (Hernández-Herrero et al., 2006). As soon as the marinating bath comes in contact with the fish, a diffusion of acetic acid and salt takes place into the tissue of the fish flesh until concentration equilibrium is reached (Cabrero et al., 2002). The salt present in the marinating bath causes dehydration of the tissue resulting from osmotic process and checks the hydrolysis of proteins caused by enzymes. A higher salt content, therefore, extends the shelf life of marinades. However, if the salt content in the tissue is higher than 4.5%, the product becomes too salty and will not be accepted by consumer. In addition, too high concentration of acid and salt impair the flavor of the marinade (Shenderyuk and Bykowski, 1990). Celik (2004) revealed that salt content in akvades (Tapes decussates) was determined as 2.925% in flesh and 3.023% in brine. Kilinc and Cakli (2004) also reported that NaCl content of the fillets of sardine was found 4.93 at the beginning and 7.12 at the end of the storage of 22 days at 4°C. In traditional brine salting the brine has a specific initial concentration which decreases during the brining process, because of the salt and water exchange between the fish muscle and the surrounding brine (Thorarinssdottir et al., 2004). The concentration of salt in the brine affects the rate of salt diffusion into the muscle and the quantity of water and proteins extracted. The rates of the salt and water diffusion were positively correlated with increasing salt concentration of the brine (Pernomo et al., 1992; Lawrie, 1998). The effect of the salt concentration in the brine has been a matter of controversy, with some indication that higher weight yield and quality may be obtained by using lower salt concentrations than by using a fully saturated brine solution.

CONCLUSIONS

Three different groups of marinating materials were used in this study: scaly fillet, scaleless fillet and skinless fillet. Some important changes have occurred in the first few hours, when the sea bass fillets were taken into pickling solution. These changes were perceptible until the maturation step.

During the storage in pickling solution, these changes showed a balanced and slow increase/decrease.
Maturation times in cold storage 4°C (±1) were; 48th h for scaly sea bass fillets and 30th h for scaleless and skinless fillets.

According to the results, scaly fillets maturated nearly 18 h later than the scaleless and skinless fillets.

In the scaly samples, scales may accumulate on the meat and this may effect the maturation process negatively (instability on the passing process of acetic acid and salt).

Although, the skinless and scaleless samples maturated nearly at the same time, Wastage during the skin removal, outages of time and effort, fillet damages, hygiene requirement and such criterias cause disadvantages for skinless samples.

According to our study results, we advise those people/companies, who will process sea bass marination, that skinless and scaleless samples are more appropriate in terms of maturation. When considering the wastage, effort and quality outages and hygiene, scaleless fillets are more appropriate than skinless fillets for marination process. The results of the study indicate that the kind of fish fillet and brine composition must be taken into account in order to obtain a homogeneous salt and acetic acid content at the end of the marinating process.

REFERENCES


