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Effect of previous chilling storage on quality loss in frozen (–20 °C) sierra (*Scomberomorus sierra*) muscle packed with a low-density polyethylene film containing butylated hydroxytoluene

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Abstract

Rancidity development during frozen storage (–20 °C) of sierra fish (*Scomberomorus sierra*) was studied. Fillets were packed in low-density polyethylene films with and without butylated hydroxytoluene added (BHT-LDPE and LDPE respectively). Fillets stored with no package were used as control. Special attention was given to the effect of previous ice storage (0, 3, 6, 9 and 15 days) on the quality of the frozen fish. Physical (pH and texture) and chemical (peroxide value, PV and thiobarbituric acid index, TBA-i) analyses were carried out. Lipid oxidation increased with ice storage time in fish muscle without film packing, being greater than the film packed muscle (with and without antioxidant). An effect of previous ice storage time was observed on the frozen product (in all treatments). However, fish muscle with film packing containing antioxidant showed less lipid deterioration. Under the conditions applied in this study, the plastic films with antioxidant prevented the lipids oxidation during the cold handling of the sierra muscle.

Keywords: *Scomberomorus sierra*; ice storage; lipid oxidation; antioxidant.

Practical Application: Methods development for quality preservation of fatty fish species during cold storage.

1 Introduction

Commercial value of fish fillets stored at low temperatures may be affected because of the deterioration of its muscle due to lipid oxidation effect, causing both loss in flavor and damage in the product's texture (Pérez-Alonso et al., 2003; Aubourg et al., 2004), mainly in fat species such as sierra (*Scomberomorus sierra*) which contains about 10% lipids (Torres-Arreola et al., 2007), with moderate levels of n-3 fatty acids, namely, eicosapentaenoic acid and docosahexaenoic acid (Murillo et al., 2014). Fatty acids present in this species are highly susceptible to oxidation, this often determines the type of handling, storage, distribution and shelf life of the product (Leland, 1997; Losada et al, 2004; Aubourg et al., 2005; Rodríguez et al., 2007; Chaouqy et al., 2008).

Antioxidants, which prevent the formation of free radicals (hydroperoxides), can be used to delay the deterioration due to lipid oxidation effect (Kim et al., 2006; Sarkardei & Howell et al., 2008; Rostamzad et al., 2010). Another alternative is the use of low temperatures, and the use of oxygen impermeable containers (Rodríguez et al., 2007). Films with added antioxidants have been used in order to prevent the sierra's muscle oxidation during freezing. Torres-Arreola et al. (2007) studied the effect on lipid oxidation of sierra fillets packaging with a film of low density polyethylene containing butylhydroxytoluene, finding a positive effect of the antioxidant material on the quality of the fillets assessed during frozen storage (4 months). However, the fillets were stored at –25 ° C immediately after the capture of the animal, which is not common during the daily handling of the product by fishermen and traders. For this reason, and in order to establish the behavior of the species under a traditional ice handling system. In this study, the effect of using a LDPE film with butylhydroxytoluene during ice handling and subsequent frozen storage (–20 °C) of the sierra (*Scomberomorus sierra*) muscle was established. This contributes to understand the behavior of a tropical species handled at low temperatures and provides information on the relevance of the use of innovative packaging during such handling.

2 Materials and methods

2.1 Antioxidant packaging films

Low density polyethylene added with 40 mg/g of BHT (BHT-LDPE) manufactured by an extrusion process (Torres-Arreola et al., 2007) films were used. Additionally, an LDPE film without BHT was used.

2.2 Fish samples

Sierra fish used in this study were captured with a gill net in the Gulf of California (28,90º N / 108,25º W, 15-18º C) during the autumn season and transported in ice to the Seafood Laboratory at the University of Sonora within 6 h of capture (postrigor state). The fish (200-350 g) were gutted and filleted the same day of catch, and the fillets (120 g) were packed individually in LDPE and BHT-LDPE, the samples were stored on ice for 15 days,

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fillets were kept in direct contact with ice as control. Samples for analytical determinations were taken on days 0, 3, 6, 9, and 15. For determinations of lipid quality parameters, a representative sample was taken after every sampling time during icing storage, which were stored at -20 °C for a period of two months.

2.3 pH

Samples were prepared according to Woyewoda et al. (1986) using a tissue homogenizer M133/1281 (Biospec Products, Bartlesville, OK). pH was monitored using a digital pH-meter (CORNING model 430, New York, USA). Determinations were carried out in triplicate.

2.4 Texture

Portions of 15 fillets from fresh (0-day) and iced fish in contact with BHT-LDPE or LDPE films were subjected to texture analysis and compared to control. The texture was measured by recording the force required to penetrate the material using a Chatillon 2-3b texturometer with a cylindrical plunger of 0.6 cm diameter. Each sample (1 cm × 1 cm × 1 cm) was placed in a position relative to the cylindrical plunger that would result in shearing across the muscle fiber (Dunajski, 1980).

2.5 Peroxide Value (PV)

Lipids were extracted with a water:methanol:chloroform (30:50:100) mixture from a 50 g sample of minced flesh and immediately analyzed. The PV of the lipid extracts were determined according to Woyewoda et al. (1986).

2.6 Thiobarbituric Acid Index (TBA-i)

TBA-i in both, during ice (0, 3, 6, 9 and 15-days) and frozen (2 months) storage was determined using 10 g of fish flesh with colorimetric detection at 538 nm. Standard curve was constructed with 1,1,3,3-tetraethoxypropane (Torres-Arreola et al., 2007). The TBA-i was reported as mg malonaldehyde/kg muscle.

2.7 Statistical analysis

A completely randomized, two-way analysis of variance statistical design was carried out, using the type of film (three levels) and storage time (five levels for ice and frozen storage) as factors. Three fillet from diferent organisms in each storage time were used for PV, TBA-i, and texture (shear force). Data were expresed as mean±SD of three determinations. Tukey´s test was used to determine differences among every storage time. The level of significance was $p < 0.05$. The computer program used for this analysis was JMP 5.00 (Statsoft, Tulsa, OK).

3 Results and discussion

3.1 Quality changes of sierra (Scomberomorus sierra) muscle during its ice storage

pH

pH changes during ice storage of sierra muscle are shown in Figure 1, where after 9 days, the control has a significant increase ($p<0.05$) compared to fresh muscle (day 0), which remains constant after 15 days. Moreover, fillets stored in LDPE and LDPE-BHT showed no such increase throughout the ice storage process ($p\geq0.05$), indicating that the use of packaging delayed changes in sierra muscle pH during ice storage. There are several researches about the increase of pH in fish muscle during ice storage. Erkan & Özden (2008) found that the pH value of whole and gutted sardine (*Sardina pilchardus*) stored 9 days in ice had a significant increase from 6.01 to 6.27. Furthermore, increases in muscle pH indicate the accumulation of different alkaline compounds, which may be derived from microbial action. However, pH value is not an index of microbial growth. Endogenous proteolytic activity may be another factor related with alteration of pH in sea products. Final pH 7 in control samples at 15 days suggests a quality loss of fish muscles, according to several authors who reported that a significant increase in pH indicates a loss in the freshness of fish muscle (Flick et al., 1994; Huss, 1996; Castillo-Yáñez et al, 2007).

Texture

Texture is an important quality factor in sea products, both for those that are consumed raw and those cooked, which depends of species, age and size of animal, fat content and its distribution, quantity and characteristics of their proteins, as well as handling and storage conditions (Haard, 1991; Kagawa et al., 2002).

Figure 2 shows changes in texture of sierra muscle stored on ice. Statistically significant differences ($p<0.05$) among the treatments at 9 days of storage were detected, the control showed the highest loss of firmness, while fillets stored in packaging with antioxidants had more firmness probably due to the effect of antioxidants on lipids present in the muscle, thus delaying possible protein-lipid interactions, as has been documented by Torres-Arreola et al. (2007) that lipid oxidation in fish muscle can cause changes in texture due to the effect of protein-lipid interactions during frozen storage. This protein-lipid interaction effect, together with a modification in the protein-water interactions and endogenous proteolytic activity of the muscle are the main factors that affect the integrity of the muscle fibers.

Several studies have reported a significant decrease in texture of fillets stored on ice, primarily due to the action of calpain and cathepsins (Hultmann & Rustad, 2002). However, such effect cannot be considered under the conditions applied in this research, since the use of LDPE and BHT-LDPE shows no inhibition over these enzymes.

Peroxide Value (PV)

Table 1 shows the values of PV generated by the different treatments after 15 days of storage on ice. It is important to note that after the first 9 days, no values indicating the presence of peroxides in any of the treatments evaluated were detected, this could be attributed first, to an interaction between the peroxide groups and the proteins present in fish muscle since they are highly unstable and easy to react with other compounds (Undeland, 1997), or that formation of free radicals has not begun in the lipids present in sierra muscle after this period of storage. Nevertheless, after 15 days it was possible to detect the presence of peroxides in all three treatments, where the highest values were for the fillets subjected to the control treatment

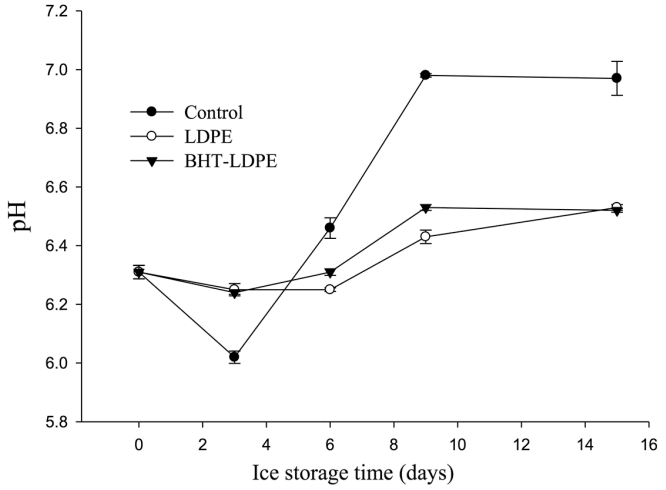

Figure 1. pH values of sierra muscle (*Scomberomorus sierra*) during ice storage. Results represent an average of 3 determinations.

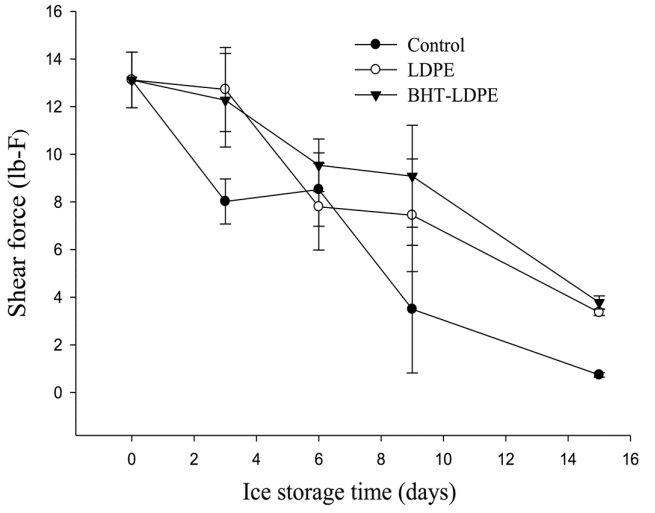

Figure 2. Texture of sierra fish (*Scomberomorus sierra*) fillets during ice storage. Results represent an average of 15 determinations

(p<0.05), while muscle stored in LDPE and BHT-LDPE showed no significant differences among them (p≥0.05). Lipid oxidation often starts in the food surface, between oxygen and substrates, therefore, if the surface of the fish muscle is covered with a barrier, oxidation could then be reduced. However, finding no significant differences between BHT-LDPE and LDPE, suggests that the antioxidant failed to prevent the formation of peroxides in fish muscle after 15 days of storage on ice, then a real effect of packaging with antioxidant over peroxide formation in sierra muscle during this stage of storage cannot be considered. On a research conducted in menhaden oil covered with a film to which Butyl hydroxytoluene (BHT) was incorporated, PV was significantly lower than in the fillets stored directly in contact with air (Huang & Wueng, 1998).

Table 1. Peroxide Value (PV) in sierra fish (*Scomberomorus sierra*) fillets after 15 days of ice storage. Data represents an average of three determinations.

Tratamiento	Peroxide Value (meq active oxygen/kg lipids)
Control	23.17 + 0.24[a]
LDPE	14.20 + 0.83[b]
BHT-LDPE	14.78 + 0.96[b]

Different letters in the same column indicate significant differences (P<0.05) among treatments.

Thiobarbituric Acid Index

Figure 3 shows changes in the TBA-i value (mg of malonaldehyde/kg of muscle) of sierra muscle during ice storage. Statistically significant differences (p<0.05) among treatments were detected during the first 6 days of storage, fillets packed in the control treatment showing a higher value of TBA-i, while the fillets stored in BHT-LDPE showed the lowest values. However, after 9 days, TBA-i value for the control remained without an increase, while the fillets stored in films (with and without antioxidants) showed a significant increase (p<0.05).

Chaouqy et al. (2008) evaluated the effect of refrigerated storage on lipid oxidation in Anchovy (*Engraulis encrasicolus*) muscle, the results showed a significant increase in TBA-i values during the first week of storage, which was maintained for 15 days during which the experiment lasted. In this study, after 15 days of storage, a significant decrease was observed in TBA-i values of the 3 treatments, which agrees with the results reported by Chaouqy et al. (2008), who attributed this behavior to the carbonyl compounds formed high instability and easy reaction with other compounds, such as proteins.

A positive effect of films with antioxidants over sierra muscle oxidation during the first 6 days of storage can be considered; however, from day 9 the effect of such films could not established as they did not show values significantly lower than those presented by the other two treatments.

3.2 Quality changes of lipids in sierra (Scomberomorus sierra) muscle after freezing storage

Peroxide Value (PV)

Significant differences in PV of the three treatments applied during all stages of sampling were found (p<0.05) (Figure 4), where the control showed the highest values compared to the fillets packaged with and without antioxidants (BHT-LDPE and LDPE). For control and LDPE treatments, fillets stored six days in ice prior to freezing were the ones that reached the highest values of IP, while for BHT-LDPE it was shown after 15 days of prior icing, indicating that the BHT incorporated to a LDPE film works by delaying the formation of peroxides. Peroxides are intermediate metabolites during lipid oxidation in foods, so their formation increases up to a maximum value to later start decreasing encouraging the production of aldehydes and ketones as final oxidation products (Badui Dergal, 2006). Therefore, under the conditions used in this study, the use of packaging with antioxidants significantly delayed the formation of peroxides after storage in freezing of the fish fillet, even after having been on ice for prolonged periods.

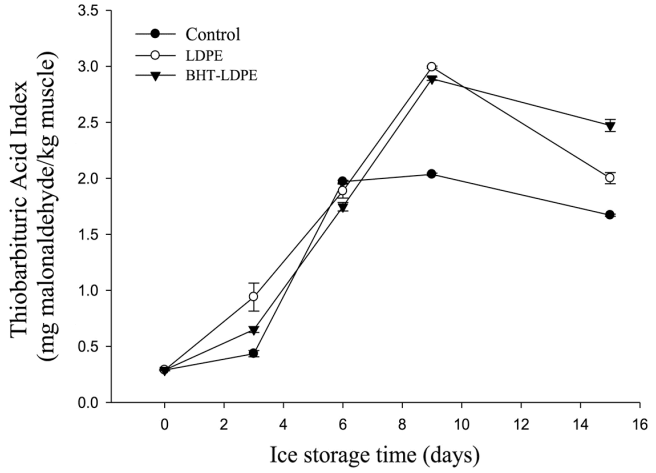

Figure 3. Changes in TBA-i of sierra fish (*Scomberomorus sierra*) fillets during ice sotrage. Results represent an average of 3 determinations.

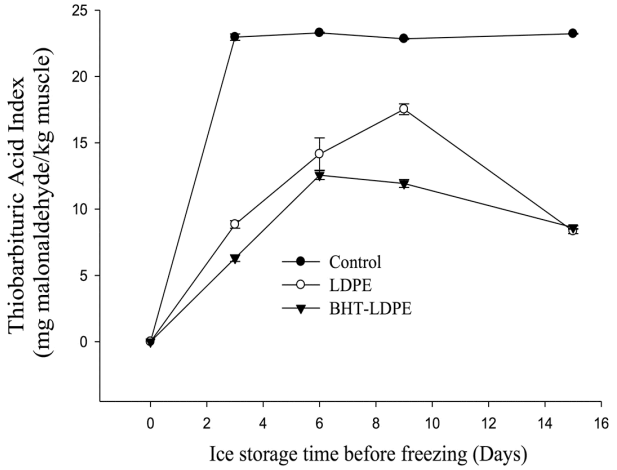

Figure 5. Changes in TBA-i of sierra fish (*Scomberomorus sierra*) fillets after frozen storage. Results represent an average of 3 determinations.

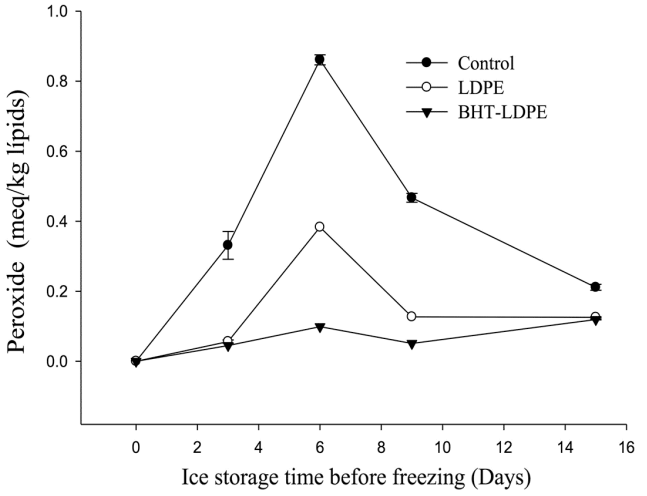

Figure 4. Changes in PV of sierra fish (*Scomberomorus sierra*) fillets after frozen storager. Results represent an average of 3 determinations.

Thiobarbituric Acid Index

From the samples collected on the third day of their handling on ice and subsequent storage in freezing for a period of two months, significant differences were observed ($p<0.05$) in TBA index (mg of malonaldehyde/kg of muscle) among the three treatments applied, being higher in sierra muscle subjected to the control treatment (Figure 5), thus suggesting a marked lipid oxidation in the muscle due to the high interaction with oxygen.

In the fillets stored with BHT-LDPE and LDPE, a maximum value of TBA-i was detected for fillets previously kept 9 days on ice showing later a significant decrease ($p<0.05$). This could indicate, as mentioned above, that carbonyl compounds formed during lipid oxidation in fish muscle are highly unstable and easily react with other compounds (Chaouqy et al., 2008). Torres-Arreola et al. (2007) did not detect the same behavior in sierra muscle stored four months at –25 °C, where the higher TBA-i were reported after 4 months (10 mg malonaldehyde/kg of muscle). However, these authors used fresh muscle as raw material.

Fillets packaged and stored with BHT-LDPE showed TBA-i significantly lower ($p<0.05$) compared with the fillets stored in LDPE, which suggests a significant inhibition of packaging antioxidants on the development of TBA-i in sierra muscle during the development of this study.

4 Conclusions

Both icing and freezing induce changes in the quality of the sierra, especially when the product is handled in direct contact with the ice. A package of low density polyethylene helps keep the muscle more firmly during icing. Moreover, in a period of storage in freezing, after keeping sierra fillets on ice, even for prolonged periods, it delays oxidation of lipids present. However, the addition of butylated hydroxytoluene to the LDPE increases efficiency of the container for softening the sierra (*Scomberomorus sierra*) muscle and delays lipid oxidation and quality loss during ice handling.

References

Aubourg, S. P., RodrÍguez, A., & Gallardo, J. M. (2005). Rancidity development during frozen storage of mackerel (*Scomber scombrus*): effect of catching season and commercial presentation. *European Journal of Lipid Science and Technology*, *107*(5), 316-323. http://dx.doi.org/10.1002/ejlt.200401124.

Aubourg, S. P., Perez-Alonso, F., & Gallardo, J. M. (2004). Studies on rancidity inhibition in frozen horse mackerel (*Trachurus trachurus*) by citric acid and ascorbic acids. *European Journal of Lipid Science and Technology*, *106*(4), 232-240. http://dx.doi.org/10.1002/ejlt.200400937.

Badui Dergal, S. (2006). *Química de los alimentos*. México: Editorial Alhambra Mexicana.

Castillo-Yáñez, F. J., Pacheco-Aguilar, R., Márquez-Ríos, E., Lugo-Sánchez, M. E., & Lozano-Taylor, J. (2007). Freshness loss in sierra fish (*Scomberomorus sierra*) muscle stored in ice as affected by

postcapture handling practices. *Journal of Food Biochemistry*, *31*(1), 56-67. http://dx.doi.org/10.1111/j.1745-4514.2007.00098.x.

Chaouqy, N. E., Gallardo, J. M., El Marrakchi, A., & Aubourg, S. P. (2008). Lipid damage development in anchovy (*Engraulis encrasicholus*) muscle during storage under refrigerated conditions. *Grasas y Aceites*, *59*(4), 309-315.

Dunajski, E. (1980). Texture of fish muscle. *Journal of Texture Studies*, *10*(4), 301-318. http://dx.doi.org/10.1111/j.1745-4603.1980.tb00862.x.

Erkan, N., & Özden, Ö. (2008). Quality assessment of whole and gutted sardines (*Sardina pilchardus*) stored in ice. *International Journal of Food Science & Technology*, *43*(9), 1549-1559. http://dx.doi.org/10.1111/j.1365-2621.2007.01579.x.

Flick, G. J., Lovell, R. T., Enriquez-Ibarra, L. G., & Argañosa, G. C. (1994). Changes in nitrogenous compounds in freshwater crayfish (*Procambarus clarkii*) tail meat stored in ice. *Journal of Muscle Foods*, *5*(2), 105-118. http://dx.doi.org/10.1111/j.1745-4573.1994.tb00524.x.

Haard, N. F. (1991). Biochemical reactions in fish muscle during frozen storage. In Seafood Science and Technology Proceedings of the International Conference Seafood 2000. Malden.

Huang, C.-H., & Weng, Y.-M. (1998). Inhibition of lipid oxidation in fish muscle by antioxidant incorporated polyethylene film. *Journal of Food Processing and Preservation*, *22*(3), 199-209. http://dx.doi.org/10.1111/j.1745-4549.1998.tb00345.x.

Hultmann, L., & Rustad, T. (2002). Textural changes during iced storage of salmon (*Salmo salar*) and cod (*Gadus morhua*). *Journal of Aquatic Food Product Technology*, *11*(3-4), 105-123. http://dx.doi.org/10.1300/J030v11n03_09.

Huss, H. (1996). *Quality and quality changes in fresh fish* (No. 348, pp. 202-219). Rome: FAO Fisheries Technical Paper.

Kagawa, M., Matsumoto, M., Yoneda, C., Mitsuhashi, T., & Hatae, K. (2002). Changes in meat texture of three varieties of squid in the early stage of cold storage. *Fisheries Science*, *68*(4), 783-792. http://dx.doi.org/10.1046/j.1444-2906.2002.00494.x.

Kim, S., Lee, K., Park, J., Lee, H., & Hwang, I. (2006). Effect of natural antioxidants on stored freeze-dried food product formulated using horse mackerel (*Trachurus trachurus*). *Journal of Science and Technology*, *41*(1), 90-95.

Leland, J. (1997). Flavor interactions: the greater whole: the chemistry of flavor interactions. *Food Technology*, *51*(1), 75-80.

Losada, V., Barros-Velázquez, J., Gallardo, J. M., & Aubourg, S. P. (2004). Effect of advanced chilling methods on lipid damage during sardine (*Sardina pilchardus*) storage. *European Journal of Lipid Science and Technology*, *106*(12), 844-850. http://dx.doi.org/10.1002/ejlt.200400991.

Murillo, E., Rao, K. S., & Durant, A. A. (2014). The lipid content and fatty acid composition of four eastern central Pacific native fish species. *Journal of Food Composition and Analysis*, *33*(1), 1-5. http://dx.doi.org/10.1016/j.jfca.2013.08.007.

Pérez-Alonso, F., Arias, C., & Aubourg, S. P. (2003). Lipid deterioration during chilled storage of Atlantic pomfret (*Brama brama*). *European Journal of Lipid Science and Technology*, *105*(11), 661-667. http://dx.doi.org/10.1002/ejlt.200300804.

Rodríguez, A., Losada, V., Larraín, M. A., Quitral, V., Vinagre, J., & Aubourg, S. P. (2007). Development of lipid changes related to quality loss during the frozen storage of farmed coho salmon (*Oncorhynchus kisutch*). *Journal of the American Oil Chemists' Society*, *84*(8), 727-734. http://dx.doi.org/10.1007/s11746-007-1098-5.

Rostamzad, H., Shabanpour, B., Kashaninejad, M., & Shabani, A. (2010). Inhibitory impacts of natural antioxidants (*ascorbic and citric acid*) and vacuum packaging on lipid oxidation in frozen Persian sturgeon fillets. *Iranian Journal of Fisheries Sciences*, *9*(2), 279-292.

Sarkardei, S., & Howell, N. (2008). Effect of natural antioxidants on stored freeze- dried food product formulated using horse mackerel (*triachurus trachurus*). *Journal of Food Science and Technology*, *43*(1), 309-315.

Torres-Arreola, W., Soto-Valdez, H., Peralta, E., Cardenas-López, J. L., & Ezquerra-Brauer, J. M. (2007). Effect of a low-density polyethylene film containing butylated hydroxytoluene on lipid oxidation and protein quality of Sierra fish (*Scomberomorus sierra*) muscle during frozen storage. *Journal of Agricultural and Food Chemistry*, *55*(15), 6140-6146. http://dx.doi.org/10.1021/jf070418h. PMid:17595103

Undeland, I. (1997). Lipid-protein interactions in fish during cold storage. Methods to determine the freshness of fish in research and industry. In Proceedings of the Final Meeting of the Concerted Action "Evaluation of Fish Freshness", AIR3CT94 2283. Nantes, France.

Woyewoda, A. D, Shaw, S. J., Ke, P. J.., & Burns, B. G. (1986). *Recommended laboratory methods for assessment of fish quality* (Canadian Technical Report of Fisheries and Aquatic Sciences, No. 1448, pp. 1-156). Canada: Fisheries and Oceans Canada.