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Research Note

Chemical changes during the chilled storage of Chilean jack mackerel (*Trachurus murphyi*): Effect of a plant-extract icing system

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ABSTRACT

Chilean jack mackerel (*Trachurus murphyi*) is an underutilised medium-fat fish species, captured in large volumes but commercialised in the fish meal and surimi industries. This study provides a first approach including a novel technology for the commercialisation of this fish species as a chilled product for human consumption. Ice prepared from aqueous extracts of oregano (*Origanum vulgare*) and rosemary (*Rosmarinus officinalis*) leaves was applied as chilling system and compared to traditional ice. Chemical changes related to quality criteria were analysed throughout a 23-day chilling period. A marked antioxidant effect ($p < 0.05$) could be detected with fish kept under both plant-extract icing systems, according to peroxide and thiobarbituric acid reactive substance formation; meanwhile, the employment of such icing systems led to lower ($p < 0.05$) scores for pH value and total volatile amine formation. Additionally, the plant extract presence in the chilling medium provided a lower ($p < 0.05$) lipid hydrolysis (free fatty acid formation) development. According to the preservative effect observed for both plant extract systems, further research is envisaged concerning their optimal employment, this including the qualitative and quantitative analysis of active molecules present in the extracts.

1. Introduction

Marine species deteriorate rapidly post mortem due to the effects of a variety of degradation mechanisms. To slow down damage pathways, immediate refrigeration is necessary after the fish capture. Thus, aquatic food products have traditionally been cooled and stored by means of flake ice (Whittle, Hardy, & Hobbs, 1990) or refrigerated seawater (Kraus, 1992). The actual increasing consumer demand for high quality fresh products has led to the development of more advanced technologies. Among them, edible active films (Baker, Baldwin, & Nísperos-Carriedo, 1994), modified-atmosphere packaging (Davies, 1997), slurry ice (Piñeiro, Barros-Velázquez, & Aubourg, 2004) and addition of chemical preservative agents (Hwang & Regenstein, 1995) have been employed successfully.

In cases where the development of lipid damage has been shown to be the limiting factor, attention has been accorded to the employment of extracts obtained from different kinds of plants (Lindberg Madsen, Rud Nielsen, Bertelsen, & Skibsted, 1996; Yanishlieva, Marinová, & Pokorný, 2006). Such extracts have shown a preservative effect that has been explained on the basis of the presence of a wide range of food phytochemicals such as flavonoids, phenolic acids and glycosides. In the case of rosemary (*Rosmarinus officinalis*) plant, the preservative effect has shown to be primarily related to two phenolic diterpenes (carnosic acid and carnosol), followed by other molecules such as rosmanol, epirosmanol, isorosmanol, rosmarinic acid, etc. (Lindberg Madsen, & Bertelsen, 1995; Hopia, Huang, Schwarz, German, & Frankel, 1996). Concerning oregano (*Origanum vulgare*) plant, rosmarinic acid, caffeic acid, carcavrol, thymol, tocopherols, etc. have been shown to be responsible for an antioxidant and antimicrobian effect (Lindberg Madsen, & Bertelsen, 1995; Yanishlieva et al., 2006). Consequently, previous research has accounted for the shelf life extension of refrigerated fish by previous treatment with oregano (Harpaz, Glatman, Drabkin,

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& Gelman, 2003; Giatrakou, Kykkidou, Papavergou, Kontominas, & Savvaidis, 2008) and rosemary (Khalil & Mansour, 1998; Giménez, Roncalés, & Beltrán, 2004; Sarkardei & Howell, 2008) extracts.

Chilean jack mackerel (*Trachurus murphyi*) is an underutilised medium-fat fish species, captured in large capture volumes by countries like Chile, China and Peru (FAO, 2007). Although a great interest has been accorded to its commercialisation (Simpson, Almonacid, & Mitchell, 2004), most efforts have been focused on its employment as a surimi-type product (Ortiz & Aguilera, 2004) and as a fish meal source (Bórquez & González, 1994). Studies on quality changes during processing of this species appear to be scarce, accounting for lipid and protein changes during frozen storage (Dondero, Araya, & Curotto, 1996; Aranda, Mendoza, & Villegas, 2006) and for microbiological activity during storage at room temperature or under refrigeration conditions (Saa, Dondero & Tarky, 1982; Schoebitz, Tamayo, & Davis, 1985).

The present study provides a first approach and includes a novel technology for the commercialisation of Chilean jack mackerel as a chilled product for direct consumption. For it, ice prepared from aqueous extracts of oregano and rosemary leaves was investigated as a chilling system and compared to traditional ice that was employed as control. Chemical changes (lipid damage and volatile amine formation) related to quality criteria were analysed.

2. Materials and methods

2.1. Plant extracts and ice preparation

Three-month-old oregano (*Origanum vulgare*) and rosemary (*Rosmarinus officinalis*) plants were obtained (October, 2006) from the production area of Isla de Maipo (Talagante, Metropolitan Region of Chile) and stored at −80 °C until use.

Before employment, leaves were separated from the plants by hand and air-dried at 25–30 °C for 3 days, the dried sample being chopped into a pot. For each kind of plant, 60 g of ground powder were weighed and placed into a 2-litre Erlenmeyer flask. Then, 1 litre boiling water was added and the mixture stirred during 30 min. After cooling to room temperature (18–20 °C), the mixture was filtered through a Whatman No. 4 filter paper in a Buchner funnel. The extraction of such 60 g sample was repeated two more times (2 × 1 litre) in the same manner, so that finally all filtrates (3 litres) were pooled together, packed in polythene bags and kept frozen (−18 °C) until use.

Concentration of leaf extracts was chosen according to preliminary trials (20–120 g leaves/3 litres) where the resulting fish was visually analysed; thus, a concentration where the best appearance of fish with no presence of odour and colour of the plant extract in fish was chosen. For each kind of plant, the total extraction process and ice preparation was carried out several times in order to prepare enough ice to carry out the experiment. Traditional ice was prepared starting only from water that was packed and kept frozen in the same way as the two other ices. Before addition to individual fishes, the different ices were ground to obtain ice flakes.

2.2. Raw fish, processing and sampling

Fresh Chilean jack mackerel (*Trachurus murphyi*) fish (66 individuals; weight range: 200–230 g) were captured (December, 2006) in the Pacific Ocean near the Valaparaíso (V Región, Chile) coast, transported to the Central Market of Santiago (Chile) and finally carried to the laboratory. Throughout this process (10 h), the fish were maintained in traditional ice. Individual fish gonads were at the $4^{th}/5^{th}$ stage of Maier's scale of gonad maturity.

Upon arrival in our laboratory, three individual fishes were separated and analysed independently ($n = 3$) as starting raw fish (day 0), while the remaining fish were divided into three batches (21 individuals in each batch), placed in boxes and directly surrounded by traditional water ice (WI condition), oregano-extract ice (OI condition) and rosemary-extract ice (RI condition), respectively. In each case, the fish specimens were surrounded by ice at a 1:1 fish-to-ice ratio. All batches were placed in a small (2 m × 2 m, 2.5 m height) refrigerated room (4 °C). Throughout the experiment, individual fish temperature was +0.5 °C in all cases. Boxes employed allowed draining; ice was renewed when required.

Fish samples from the different icing conditions were taken for analysis on days 2, 6, 8, 10, 13, 17 and 23. Three individuals of each batch were analysed independently ($n = 3$) at each sampling point.

2.3. Chemical analyses

The evolution of pH values in Chilean jack mackerel white muscle during the storage time was determined by means of a 6 mm diameter insertion electrode (Crison, Barcelona, Spain).

Total volatile base-nitrogen (TVB-N) contents were measured according to some modifications of the Antonacopoulos (1960) method. Briefly, fish white muscle (10 g) was extracted with 6% perchloric acid and brought up to 50 ml. TVB-N contents were determined, after steam distillation of the acid extracts rendered alkaline to pH 13 with 20% NaOH, by titration of the distillate with 10 mM HCl. The results are expressed as mg TVB-N/100 g muscle.

The lipid fraction was extracted from the fish white muscle by the Bligh and Dyer (1959) method. Quantification results are expressed as g lipid/100 g muscle.

Free fatty acid (FFA) content was determined on the lipid extract by the Lowry and Tinsley (1976) method based on complex formation with cupric acetate–pyridine followed by spectrophotometric (715 nm) assessment. Results are expressed as g FFA/100 g lipids.

The peroxide value (PV) was determined on the lipid extract by means of the ferric thiocyanate method (Chapman & McKay, 1949). The results are expressed as meq active oxygen/kg lipids.

The thiobarbituric acid index (TBA-i) was determined according to Vyncke (1970). This method is based on the reaction between an aq. 5% trichloroacetic extract of the fish white muscle and thiobarbituric acid at high temperature (95–97 °C), the resulting chromophore being measured at 532 nm. Results are expressed as mg malondialdehyde/kg muscle.

2.4. Statistical analysis

Data from the different chemical analyses were subjected to one-way analysis of variance in order to assess differences ($p < 0.05$) among the different icing conditions (Statsoft, 1994). The SPSS 11.5 software for Windows (SPSS Inc., Chicago, IL, USA) was also used to explore the statistical significance of the results obtained, including multivariate contrasts and multiple comparisons by the Scheffé and Tukey tests ($p < 0.05$).

3. Results and discussion

3.1. Assessment of pH value and TVB-N content

The pH values increased with storage period in all treatments ($p < 0.05$) (Fig. 1) due to the action of spoilage bacteria (Whittle et al., 1990). The pH values measured in treatment WI were similar to those previously reported for the same species (Schoebitz et al., 1985) and for related ones (Bennour, El Marrakchi, Bouchriti, Hamama, & El Ouadaa, 1991; Rodríguez, Losada, Aubourg, & Barros-Velázquez, 2005) when kept under similar conditions.

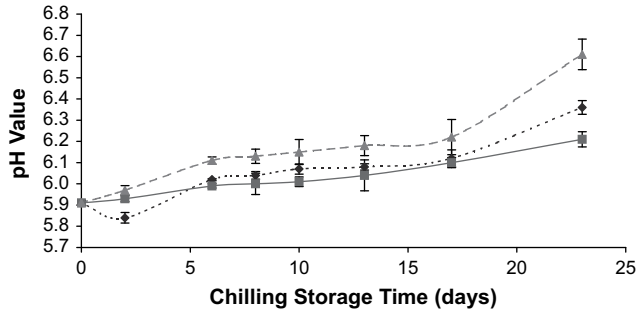

Fig. 1. Evolution of the pH value in Chilean jack mackerel muscle during chilling storage under different icing conditions. Mean values of three ($n = 3$) independent determinations. Standard deviations are indicated by bars. Icing conditions: oregano-extract ice (◆), rosemary-extract ice (■) and traditional water ice (▲).

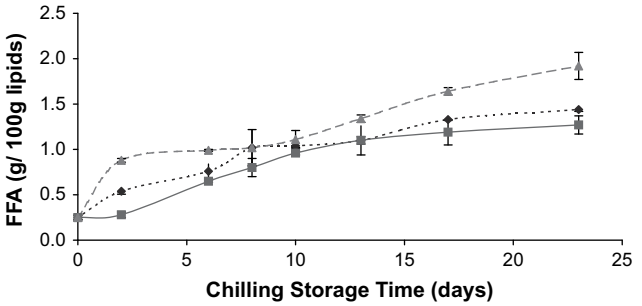

Fig. 3. Free fatty acid (FFA) formation in Chilean jack mackerel muscle during chilling storage under different icing conditions. Mean values of three ($n = 3$) independent determinations. Standard deviations are indicated by bars. Icing conditions: oregano-extract ice (◆), rosemary-extract ice (■) and traditional water ice (▲).

Comparison among icing systems (Fig. 1) showed that fishes kept under traditional conditions developed a higher ($p < 0.05$) pH value than their corresponding individuals kept under ice prepared from vegetable extracts. Some differences could be assessed between individuals kept under both plant-extract icing systems; thus, fish treated under OI condition showed a lower ($p < 0.05$) pH value at day 2, but higher ($p < 0.05$) at day 23 than its counterpart from RI condition, so that a definite difference pattern could not be concluded between both treatments.

An increasing content ($p < 0.05$) on TVB-N could be detected for all kinds of samples with the chilling time (Fig. 2). As for the pH value, this increase can be explained as a result of an increasing microbial activity that could lead to the formation of different kinds of molecules, most of them base-type compounds. Individuals kept under WI condition showed a marked increase after day 13 that can be explained as a result of the end of the lag phase and agrees with previous related research concerning other fish species (Bennour et al., 1991; Aubourg, 2001; Rodríguez et al., 2005). In the present study, all values attained at the end of the experiment are considered below upper limits accepted for human consumption (Oehlenschläger, 1997).

As with the pH evaluation, a higher volatile amine formation ($p < 0.05$) could be observed (Fig. 2) for individuals kept under WI condition, differences being especially marked in the latest stage of the experiment (days 17–23). For TVB-N parameter, no differences ($p > 0.05$) could be outlined between fishes kept under both icing systems including plant extracts. An antimicrobial effect of plant-extract icing systems can be concluded from the analysis of TVB-N values, which confirms previous research where both plant extracts were preliminarily applied to fish food storage (Vareltzis, Koufidis, Gavriilidou, Papavergou & Vasiliadou, 1997; Harpaz et al., 2003; Giatrakou et al., 2008).

3.2. Lipid hydrolysis

Lipid content of the white muscle was included in the 3.5–4.9 g/100 g muscle range and agrees to values expected for a medium-fat fish species. However, values can be considered relatively low and agree with the fact that individuals were captured in the Spring period (Aranda et al., 2006).

A marked increase ($p < 0.05$) in storage time could be observed for FFA content in all kinds of samples (Fig. 3), according to previous research on related fish species (Aubourg, 2001; Losada, Piñeiro, Barros-Velázquez, & Aubourg, 2005). In the present study, lipid hydrolysis development was shown to be higher ($p < 0.05$) in individual fishes kept under WI condition than in their counterparts where a plant-extract icing was employed. This higher hydrolytic activity could be explained on the basis of the marked pH increase (Fig. 1) observed for WI-treated fish, so that an approach towards the optimum activity pH range for lipases (López-Amaya & Marangoni, 2000a) and phospholipases (López-Amaya & Marangoni, 2000b) takes place. Comparison between individuals corresponding to OI and RI conditions led to a lower ($p < 0.05$) lipid hydrolysis development at days 2 and 23 in fish treated under the RI icing system.

During chilling storage, FFA formation has been reported to be produced during a first stage (before the end of the lag phase is attained) as a result of endogenous enzyme (namely, lipases and

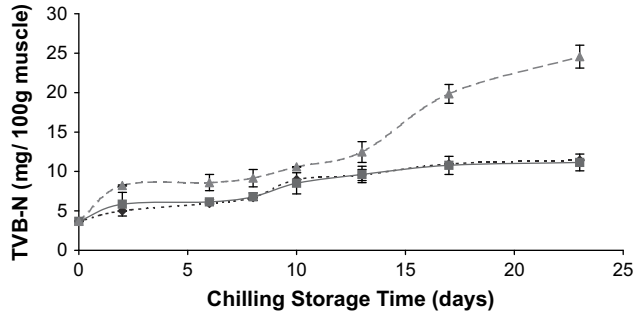

Fig. 2. Total volatile base-nitrogen (TVB-N) content in Chilean jack mackerel muscle during chilling storage under different icing conditions. Mean values of three ($n = 3$) independent determinations. Standard deviations are indicated by bars. Icing conditions: oregano-extract ice (◆), rosemary-extract ice (■) and traditional water ice (▲).

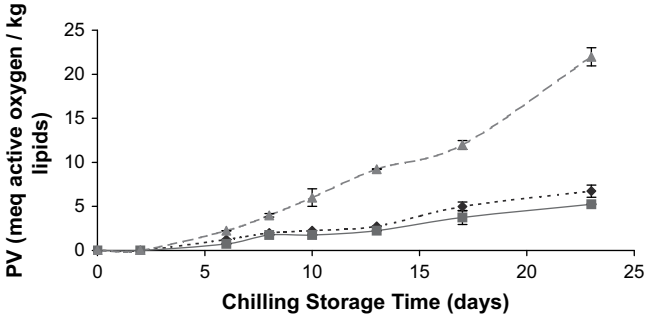

Fig. 4. Evolution of peroxide value (PV) in Chilean jack mackerel muscle during chilling storage under different icing conditions. Mean values of three ($n = 3$) independent determinations. Standard deviations are indicated by bars. Icing conditions: oregano-extract ice (◆), rosemary-extract ice (■) and traditional water ice (▲).

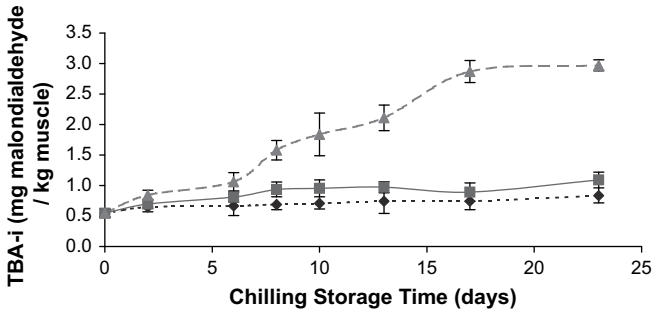

Fig. 5. Evolution of thiobarbituric acid index (TBA-i) in Chilean jack mackerel muscle during chilling storage under different icing conditions. Mean values of three ($n = 3$) independent determinations. Standard deviations are indicated by bars. Icing conditions: oregano-extract ice (◆), rosemary-extract ice (■) and traditional water ice (▲).

phospholipases) activity (Whittle et al., 1990). Later on (after the end of the lag phase), microbial activity should be important, so that FFA formation should mostly be produced as a result of bacterial enzyme activity. According to the present results, a partial inhibitory effect of the plant extract presence on the endogenous enzyme activity is due to occur in the first stage (days 2–6); meanwhile, the antimicrobial effect of the plant extracts would lead in the second stage (days 10–23) to a lower FFA formation in the fish muscle.

3.3. Lipid oxidation

Primary oxidation was measured by means of the PV (Fig. 4). This index exhibited a marked increase in the control samples, in contrast to individual fishes kept under OI and RI conditions. It is concluded that the presence of both extracts in the chilling medium led to a partial inhibition of peroxide formation. However, no significant differences ($p > 0.05$) could be outlined between fish samples corresponding to both plant-extract icing systems.

Secondary lipid oxidation was measured by means of the TBA-i (Fig. 5). A sharp increase after day 6 was observed for control samples, these reaching values above score 2.0 for the 13–23-day period. Individual fishes treated with ice prepared from plant extracts showed a very low thiobarbituric acid reactive substances (TBARS) formation throughout the storage time, which agrees with the low primary oxidation development previously shown (Fig. 4). Comparison between OI and RI conditions showed lower TBARS mean values for fish kept under the OI icing system.

According to PV and TBA-i results, an important antioxidant effect can be attributed to the presence of both plant extracts in the icing system. Such conclusions agree with previous research where both plant extracts were preliminarily applied to a fish food stored under refrigerated (Khalil & Mansour, 1998; Harpaz et al., 2003; Sarkardei & Howell, 2008; Giatrakou et al., 2008) or frozen (Vareltzis et al., 1997; Pérez-Mateos, Lanier, & Boyd, 2006) conditions.

4. Final comments

The present study provides a first approach to the employment of a novel icing system prepared from aqueous extracts of rosemary and oregano. Results obtained show a positive role of active molecules present in such extracts, so that a partial inhibition of chemical changes related to quality loss is obtained.

A large number of reports have shown that active compounds present in plant extracts would depend to a large extent on several factors such as the characteristic distribution during the vegetative cycle, the country in which the plant was grown, the way the plant extract was prepared and the kind of fish material to which it should be applied (Lindberg Madsen & Bertelsen, 1995; Del Baño et al., 2003; Yanishlieva et al., 2006). Meanwhile, previous research has shown that the antioxidant and antimicrobial activity of plant extracts could be dose dependent (Lindberg Madsen & Bertelsen, 1995; Yanishlieva et al., 2006).

Further studies focused on the positive role of the presence of oregano and rosemary extracts during the chilled storage of fish species are envisaged. According to the decisive role of active compound content mentioned above, the next steps would be focused on the qualitative and quantitative analysis of such molecules throughout the chilled storage period; a great effort ought to be addressed towards knowledge of the content range where optimal effects would be obtained.

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