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Effect of Pre-Freezing Iced storage on the Lipid Fractions of *Ariomma indica* during Frozen Storage

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Ariomma indica caught by bottom trawling was frozen onboard after icing for 0, 6 and 12 h. Changes in lipid fractions of the fish during frozen storage at -18°C were monitored up to 315 d. Moisture and total lipid content of fish did not show any change during frozen storage. Phospholipid content decreased by 35% during storage, but no differences were observed between samples stored in ice before freezing. Free fatty acid (FFA) content increased by 124 to 300%, with ice stored samples showing more increase during storage. Hydrolysis of both phospholipid and triglycerides had to occur to account for the observed increase in FFA. Fat oxidation was also more in ice stored samples than in fish frozen immediately after capture. Apparently polyunsaturanted fatty acid content in total fatty acids decreased, while saturated and monounsaturated fatty acids registered an increase, during frozen storage.

Key words : ***Ariomma indica*, lipid changes, frozen storage.**

Ariomma indica (Day), the Indian ariomma is a marine deep water fish of high quality captured by deep sea bottom trawling (Haedrich, 1984). As the exploitation of deep sea resources are increasing, it is essential to know the behaviour of such relatively new resources under various processing conditions. Further, because of the longer duration of deep sea fishing voyages, the catch has to be processed and preserved on board.

Fish lipids and proteins, both undergo deteriorative changes during iced as well as frozen storage. Lipid hydrolysis and oxidation have been observed in various frozen stored fishes (Bligh & Scott, 1966; Nair *et al.*, 1976, 1978; Nair & Gopakumar, 1985; Fazal & Srikar, 1987). *A. indica* being a fatty fish would be particularly vulnerable to such changes. In addition to the hydrolysis and oxidation of lipids, the products of such reactions interfere with the quality. The interaction of the free fatty acids with protein during frozen storage is also well known (Dyer & Freezer, 1959, King *et al.*, 1962).

In this paper we report the changes in the lipid fractions in the muscle of a deep sea fish *A. indica* frozen onboard, after 0, 6 and 12 h of iced storage, during frozen storage up to 315 days.

Materials and Methods

A. indica (10-15 cm) was captured by bottom trawling from the research vessel FORV Sagar Sampada during January 1992 at a depth of 154-158 m off south Karwar coast. After hauling and washing of the catch, one portion was immediately frozen, while the rest were iced in an insulated box with flake ice (1:1). Iced fish were frozen after 6 and 12 h of iced storage. Freezing was done in an onboard blast freezer at -40°C and the frozen fish were packed in 200 gauge polyethylene bags and stored in the freezer hold of the vessel at -20°C. Frozen fish were later transferred and kept at the Institute's frozen storage (-18°C) during storage studies. First sample was drawn after 45d of freezing.

Frozen samples for analysis were kept in sealed polyethylene bags and thawed under running tap water. Moisture in the minced muscle samples was determined by the method of AOAC (1975). For lipid studies, fillets (with skin) were minced and extracted with a chloroform-methanol (2:1) mixture as per Folch *et al.* (1957). Peroxide value (PV) and free fatty acid (FFA) in the extract were determined by AOAC method (1975). Phosphorous in perchloric acid digests of extract was determined by the method of Fiske & Subbarao (1925) and phospholipid (PL) calculated as (Phosphorous x 25) (Shankar & Nair, 1988). Fatty acid methyl esters from the Folch extract were prepared (Metcalfe *et al.*, 1966) and analysed on a Varian gas chromatograph with a 10% Silar 5 CP glass column and flame ionization detector. Operating conditions were: Injector and detector temperatures were 22° and 23°C, respectively. Initial column temperature was 120°C which was increased at the rate of 5° min^{-1} and the final temperature of 200°C was maintained for 60 min. Nitrogen was used as the carrier gas at a flow rate of 40 ml min^{-1}.

Results and Discussion

The frozen samples did not lose excessive moisture during storage as the average moisture content decreased only from 72 to 70.5% even after 300d (Fig. 1). There was also not much difference between the 0, 6 or 12 h iced and frozen samples. The average fat content of the fish was about 9% which did not show any appreciable changes during frozen storage. This is in agreement with previous observations in cod and seer fish (Bligh & Scott, 1966; Fazal & Srikar, 1987).

The average phospholipid (PL) content of the fresh frozen *A. indica* was 430 mg% (Fig. 2) which was about 5% of the

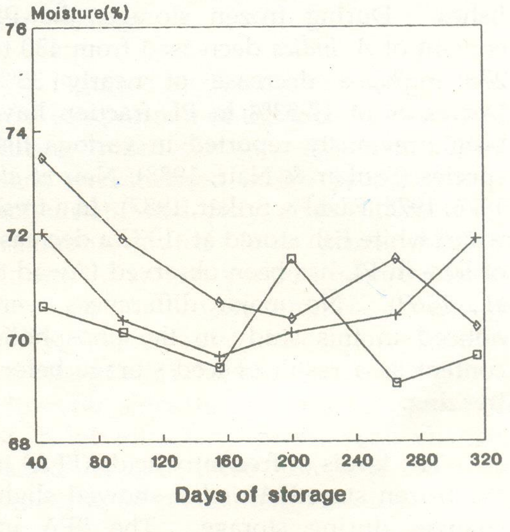

Fig. 1. Changes in the moisture content of *Ariomma indica* stored onboard in ice for 0, 6 and 12h prior to freezing, during frozen storage at -20°C.

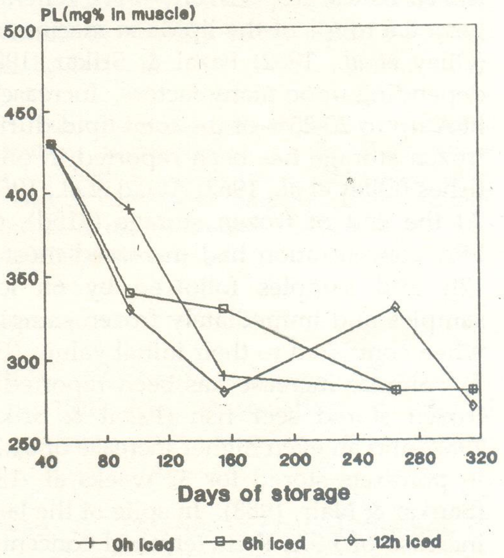

Fig. 2. Changes in phospholipids (PL) of the muscle of *Ariomma indica* stored onboard in ice for 0, 6 and 12h prior to freezing, during frozen storage at -20°C.

total lipids. Phospholipid content in the range of 800-900 mg% has been reported in oil sardine (Nair *et al.*, 1978) and mackerel (Nair *et al.*, 1976), while Olley *et al.*, (1962) found lipid phosphorous in the range of 18.5 to 28 mg% in a number of salt water fishes. During frozen storage, the PL content of *A. indica* decreased from 430 to 270 mg%, a decrease of nearly 35%. Decreases of 17-53% in PL fraction have been previously reported in various fish species (Sankar & Nair, 1988); Nair *et al.*, 1976, 1978; Fazal & Srikar, 1987). In a fresh water white fish stored at -10°C a decrease of 60% in PL has been observed (Awad *et al.*, 1969). No major differences were noticed in this study in the phospholid content as a result of iced storage before freezing.

The levels of free fatty acids (FFA) in the frozen stored *A. indica* showed slight changes during storage. The FFA increased from an initial level of 2.23% of total lipids to 6, 5 and 9% at the end of frozen storage, in 0, 6 and 12 h iced and frozen fishes, respectively. FFA generally form 0.6 to 6% of the lipids in marine fish (Olley *et al.*, 1962; Fazal & Srikar, 1987) depending upon many factors. Increase in FFA up to 20-25% of the total lipid during frozen storage has been reported in other fishes (Olley *et al.*, 1962; Awad *et al.*, 1969). At the end of frozen storage (315d), the FFA concentration had increased most in 12h iced samples followed by 6h iced samples and immediately frozen samples, when compared to their initial values (Fig. 3). Similar increase has been reported in frozen stored seer fish (Fazal & Srikar, 1987) and an even higher increase of 61.7% in pomfrets stored for 32 weeks at -18°C (Sankar & Nair, 1988). In spite of the large increase of FFA, their terminal concentrations did not reflect the influence of pre freezing iced storage, which was discernible only in the quantum of the increase.

The accumulation of FFA in frozen fish muscle is caused by enzymatic hydrolysis of phospholipid and triglycerides

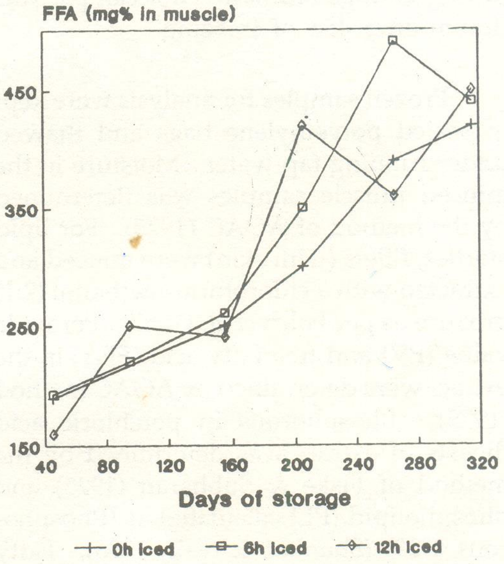

Fig. 3. Changes in free fatty acids (FFA) of the muscle of *Ariomma indica* stored onboard in ice for 0, 6 and 12h prior to freezing, during frozen storage at -20°C.

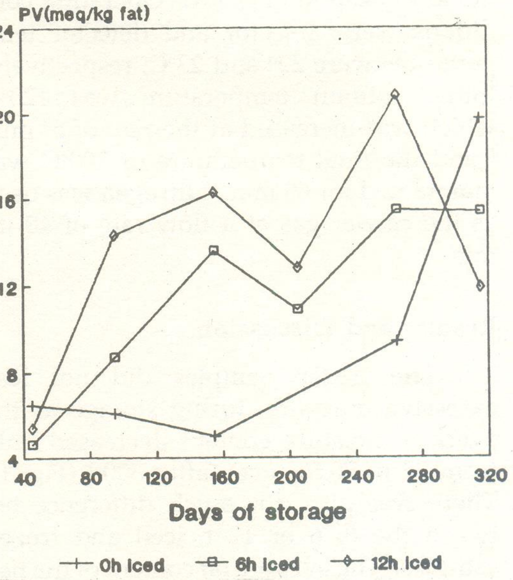

Fig. 4. Changes in peroxide values (PV) of the muscle of *Ariomma indica* stored onboard in ice for 0, 6 and 12h prior to freezing, during frozen storage at -20°C.

(Olley *et al.*, 1962). Since the complete hydrolysis of a mole of PL releases only 31g phosphorous and ca. 600 g of FFA, the maximum amount of FFA that could be released from the decrease seen in the phospholipid fraction was 116 mg%. But the average amount of FFA released during the frozen storage was 230 mg%, which indicates that > 50% of the released FFA was derived from the hydrolysis of triglycerides.

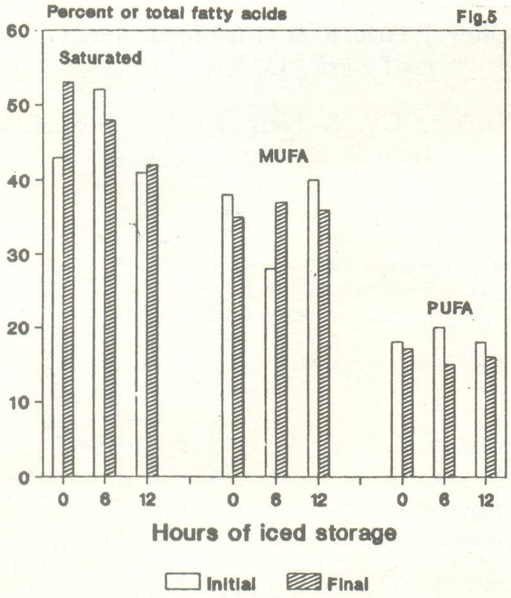

Fig. 5. Changes in saturated, monounsaturated (MUFA) and polyunsaturated (PUFA) fatty acids of the muscle of *Ariomma indica* stored onboard in ice for 0, 6 and 12 h prior to freezing, before and after frozen storage at -20°C for 315 days.

The PV, an index of lipid oxidation increased from 6.5 to 19.8 meq kg^{-1} lipid in fresh frozen fish during storage (Fig. 4). But, in ice stored and frozen samples, the rate of increase in PV especially in earlier stages was faster. The PV declined after 35 weeks in 12h ice stored fish, while it remained at the peak levels in 6h ice stored fish. The decrease in PV after an initial period of increase has been observed earlier (Awad *et al.*, 1969) and is attributed to the breakdown of peroxides formed, to carbonyl compounds. The faster increase in PV of ice stored fish shows that *A. indica* even when iced promptly after catch is subject to faster oxidation during frozen storage when compared to fish frozen immediately.

Figure 5 shows the changes in fatty acid composition of the total lipid fraction during frozen storage. Apparent reductions were noticed in the proportions of polyunsaturated fatty acids (PUFA) and monounsaturated fatty acids (MUFA) during the storage period except in case of 6 h iced and frozen samples. Losses in PUFA fraction have been reported earlier by Nair *et al.* (1978) and Fernandez (1992). However, since the fatty acids are reported as % of total fatty acids, such changes found in the three fractions may be proportional rather than absolute.

Thus, during frozen storage of *A. indica,* the lipids were found to undergo hydrolysis and oxidation. Iced storage of freshly caught *A. indica* prior to freezing resulted in slightly faster lipid oxidation and hydrolysis.

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