Seasonal Variation in the Susceptibility of Pomfret Lipids to Autoxidation

P.G. Viswanathan Nair and T.V. Sankar*

Research Centre of Central Institute of Fisheries Technology, Veraval - 362 265

Seasonal variations in the lipid content of silver pomfret (*Pampus argenteus*) and the extent of peroxide formation of these lipids were studied. Lipid content of small fish (283-400 g) was generally lower than that of big fish (650-813 g) in any season. Maximum lipid content was found during April to June and peroxide formation was maximum during this period. Peroxide formation was more in the lipids of small fish compared to the lipids of large fish. The relationship between peroxide formation and degree of unsaturation was not linear. The level of free fatty acids in the lipids did not affect the rate of formation of peroxides significantly.

Lipid oxidation is one of the major factors contributing to the deterioration of quality in processed and stored marine products. In fatty fishes it is the limiting factor as far as the shelf life of these products are concerned(Castell,1971), The high level of polyunsaturated fatty acids in fish lipids makes them highly susceptible to autoxidation. The process of lipid oxidation in fish muscle is very complex and many factors are involved in determining the course of the reactions. The lipid content of the fish and composition of the lipid are of primary importance in this respect. In many fishes there are variations in lipid content during different periods of the year. Variations in lipid content are associated with variations in composition also (Gopakumar,1974). These changes in the content and composition of lipid in fish muscle during different seasons may influence the susceptibility of these lipids to oxidative changes and consequent development of rancidity.

Silver pomfret (*Pampus argenteus*), which is a very important species commercially, shows seasonal variations in the lipid content (Solanki *et al.*, 1976; Mathew *et al.*, 1977). But no information is available about the seasonal changes in the composition of the lipids or the susceptibility of the lipids of silver pomfret to oxidation during different seasons. This information is of immense use in the processing and storage of this fish. Hence a study on the seasonal variation in the susceptibility of pomfret lipids to oxidation was undertaken.

Materials and Methods

Silver pomfret were collected from landing centres in and around Veraval in very fresh condition. Two grades of fish; namely, small pomfret (283-400 g) and big pomfret (650-813 g) were used in these studies. Immediately after reaching the laboratory the fish were filletted and minced. The mince was mixed thoroughly, packed in polyethylene bags and stored in ice. Samples were drawn at regular intervals and analysed for total lipids (Bligh & Dyer, 1959),iodine value (Wijs) (AOAC, 1975), peroxide value (Wheeler method with modification, Lundberg, 1961) and free fatty acids (AOAC, 1975). The maximum peroxide value of each smaple was determined. The studies were carried out from September 1988 to February 1991.

Results and Discussion

The extent of lipid oxidation in mince is higher than that in whole pomfret because of the favourable conditions for oxidation created during the process of mincing. The

* Present address : Central Institute of Fisheries Technology, Kochi - 682 029

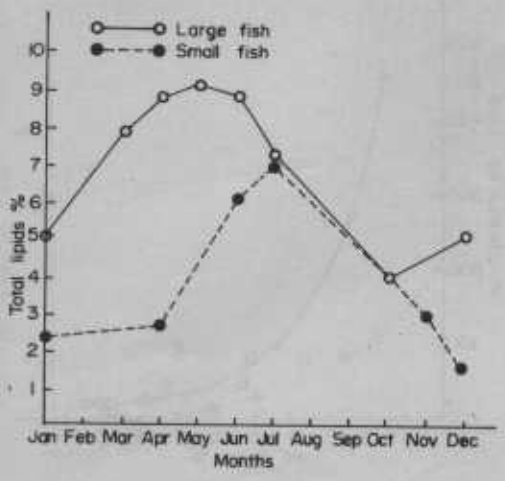

Fig. 1. Changes in lipid contents with season of large and small silver pomfrets

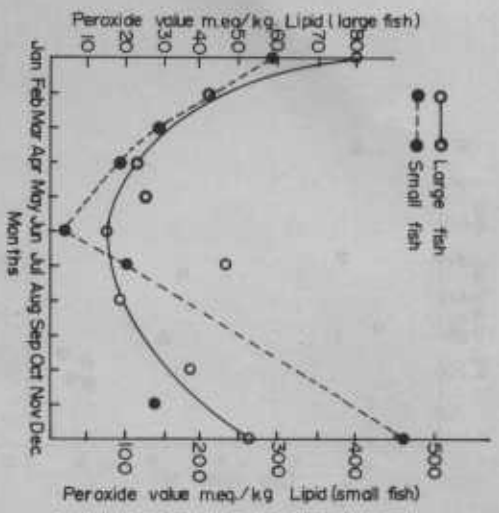

Fig. 2. Changes in maximum peroxide value with season of large and small silver pomfrets

advantage of using mince is the uniformity of the sample.

Fig.1 shows the variations in the lipid contents of small and big silver pomfrets during different seasons. There was a clear seasonal trend in the lipid contents of the big fish. The minimum lipid content was during October to January and the maximum during April to June. The peak spawning period for silver pomfret is from July to September (Personal communication). Maximum lipid level was noticed just prior to this and the decrease in lipid levels coincided with the peak spawning period. The studies of Mathew *et al.* (1977) also indicated that lipid content of muscle was maximum during April and minimum during January-February. In the case of small fish also the trend was similar, but not so well defined (Fig.1). It had maximum lipid content during June-July. There were significant differences between the lipid contents of big and small fish during the period from January to July. In July and October both the fish had comparable lipid contents. The difference in the lipid content had widened by December.

Primary products of lipid oxidation, whether it is autoxidation, photoxidation or enzyme catalysed reaction, are peroxides (Gunstone,1984). The maximum values of peroxides were taken as an indication of the extent of oxidation i.e. as a measure of the susceptibility of the lipids to oxidation. The extent of peroxide formation in big and small fish were significantly different at any given time of the year. The relationship between maximum peroxide value and season (Fig.2) was just the opposite of the relationship between lipid content and season (Fig.1).

The relationship between lipid content and maximum peroxide values was not well defined when big fish alone were considered (Fig.3), but some what clear picture emerged when data for both big and small samples were taken together. Maximum peroxide value decreased sharply as the lipid content increased (Fig.4). The variations were comparatively small when the lipid content was about 8 to 9%. The maximum peroxide value was as high as 460 meg/kg lipid when the lipid content was 1.6% and 16-25 meg/kg lipid when the lipid content was 9% .

Further both the samples analysed in July had similar lipid contents but the

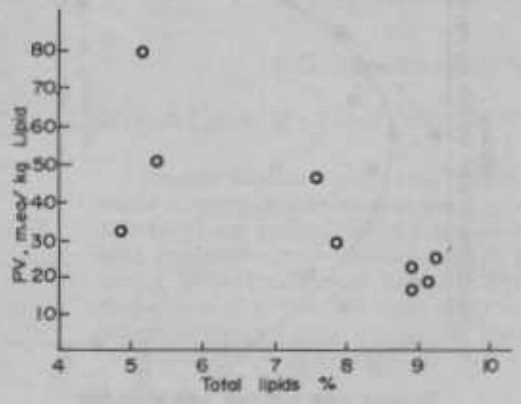

Fig. 3. Changes in maximum peroxide value with changes in lipid content in large silver pomfret

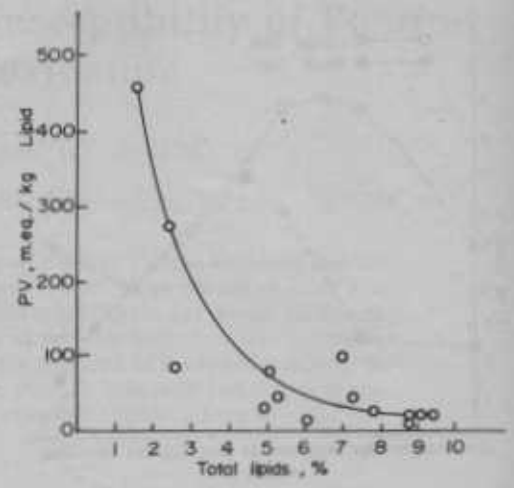

Fig. 4. Relationship between lipid content and peroxide value - composite sample

peroxide values were quite different. The maximum peroxide value for the big fish was 45 meg/kg lipid, while for the small fish it was 102 meg/kg lipid. Thus the lipids of small fish are more prone to oxidation than lipids of big fish, irrespective of the lipid content or season.

The rate at which the lipids are oxidised depends to a very large extent on their degree of unsaturation. The iodine values give a direct measure of the proportion of polyunsaturated fatty acids (Ackman, 1966). The relationship between maximum peroxide values and iodine values are given in Fig.5. Broadly, the peroxide values increase as the iodine values increase. Increase in peroxide value was very sharp when the iodine values were higher than 150. But there were many exceptions. For example for iodine values in the range of 116 to 119, widely varying peroxide values(18 meg/kg lipid to 117 meg/kg lipid) were obtained. Hence the relationship between peroxide formation and degree of unsaturation of the lipids is not a linear one. Many other factors appear to play important roles in influencing the rate of oxidation.

There are different opinions on the effect of lipid hydrolysis and accumulation of free fatty acids in fish tissues on the autoxidation of the lipids. Han & Liston (1988) had hypothesised that peroxidation enhanced phospholipase activity. Castell *et al.* (1966) found that there was a protective effect of free fatty acids against lipid oxidation in a model system of fish muscle homogenate in presence of metal ions. The lower levels of rancidity and higher levels of free fatty acids observed in trout muscle, treated with phospholipase A (Mazeaud & Bilinski, 1976) also support the theory of protective effects of free fatty acids. At the same time Shono & Toyomiza (1973) indicated that formation of free fatty acids accelerated the process of autoxidation. However, in the present study no correlation was observed between the free fatty acid levels and peroxide formation (Fig.6). Castell (1971) had observed that lipid oxidation in lean fish was insignificant in terms of spoilage reactions, but at the same time, if the lipids were extracted from the muscle, they were readily oxidised, developing high TBA values and typical odours of rancid fish oil. This clearly suggests that muscle constituents retard oxidation. According to Castell & Mac Lean (1964) lipids of cod from certain areas were particularly resistant to induced oxidation in June and July and to some extent in August. This was attributed

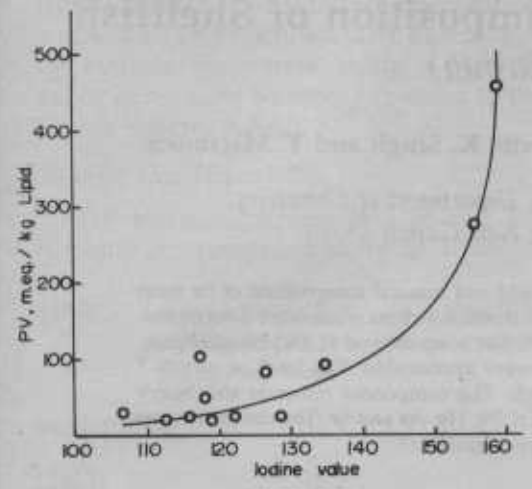

Fig. 5. Relationship between iodine value and maximum peroxide value

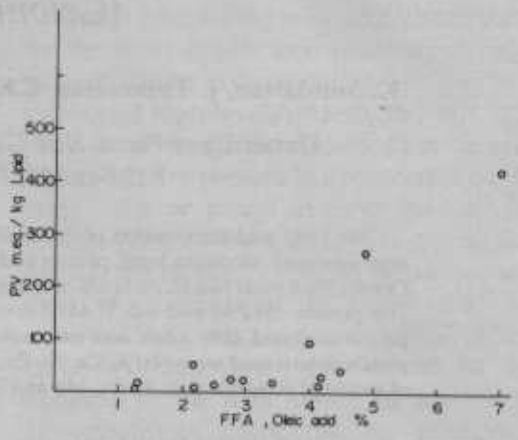

Fig. 6. Relationship between free fatty acids concentration and maximum peroxide value

to the high levels of natural antioxidants present during that period. The potential effects of the changes in the levels of such naturally occurring antioxidants and pro-oxidants in the tissue must also be taken into account while discussing the seasonal variations in the susceptibility of lipids to oxidation.

The results show that development of oxidative rancidity in silver pomfret is maximum during December and January and minimum during June to August. Also, lipids from small silver pomfret develop rancidity more readily when compared with big fish.

The authors are grateful to Shri M.R. Nair, Director Central Institute of Fisheries Technology, Kochi for permission to publish this paper and to Dr.K. Gopakumar and Dr.K. Devadasan, Scientists, CIFT for reviewing the manuscript and giving valuable suggestions. Technical assisfance for the study was given by Shri T. Gangadharan and Shri K.U. Sheikh of this Laboratory.

References

Ackman,R.G. (1966) *J.Am. oil Chem. Soc.* **43**, 385

AOAC (1975) *Official Methods of Analysis* (Horwitz,W, .Ed) 12th Edn., Association of Official Analytical Chemists, Washington

Bligh, E.G. & Dyer, W.J. (1959) *Can.J. Biochem. Physiol.***37**,911

Castell, C.H.(1971) *J. Am. Oil Chem. Soc.* **48**, 645

Castell, C.H. & Maclean, J. (1964) *J.Fish. Res. Bd Can.* **21**, 1361

Castell, C.H., Moore, B.A., Jangaard, P.M. & Neal, W.E. (1966) *J. Fish. Res. Bd Can.* **23**, 1385

Gopakumar, K. (1974) *J.Mar.Biol. Assoc. Ind.* **16**,830

Gunstone, F.D. (1984) *J.Am. Oil Chem. Soc.* **61**,441

Han, J.J. & Liston, J. (1988) *J.Food Sci.* **53**,1917

Lundberg, W.O. (1961) *Autoxidation and Antioxidants* Vol.I,p.36 Inter Science publications, New York

Mathew, P.T., Devadsan, K. & Venkataraman, R. (1977) *Fish.Technol.***14**,66

Mazeaud,F. & Bilinski, E. (1976) *J.Fish. Res. Bd Can.***33**,1297

Shono, T. & Toyomiza, M. (1973) *Bull. Jap Soc. Sci. Fish.***39**,417

Solanki, K.K., Kandoran, M.K. & Venkataraman, R. (1976) *Fish. Technol.* **13**,40