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A Review on Natural Antioxidants in Fish: Stabilizing Effect on Sensitive Nutrients

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Abstract: Antioxidative compounds are found in all fish species to protect their lipids and other compounds that contain double bonds, against damage caused by reactive oxygen species. These compounds belong to various chemical groups and make use of their antioxidative effects via different modes of action. These include amino acids, peptides, ascorbic acid, carotenoids and phenolic compounds such as tocopherols. The occurrence of endogenous antioxidants in fish was reviewed with emphasis on their concentration and antioxidative activity.

Key words: Fish species · Antioxidants · Phenolic compounds · Vitamins

INTRODUCTION

Apart from high amounts of poly unsaturated fatty acids the presence of heme pigments and trace amounts of metallic ions makes the fish, especially dark flesh fatty fish, prone to lipid oxidation [1]. To retard such a quality loss, synthetic antioxidants have been used to decrease lipid oxidation during the processing and storage of fish and fish products [2]. However, the use of synthetic antioxidants has raised questions regarding food safety and toxicity [3,4]. The use of natural antioxidants is emerging as an effective methodology for controlling rancidity and limiting its deleterious consequences. Natural phenolic compounds with antioxidant activity such as rosemary extract, tea catechin, tannins, etc. have been gaining increasing attention due to their safety [5]. Phenolic compounds are bioactive substances widely distributed in plants and are important constituents of the human diet. Plant phenolics comprise a great diversity of compounds, such as flavonoids (anthocyanins,flavonols, flavones, etc.) and several classes of non-flavonoids (phenolic acids, lignins, stilbenes) [6]. In general, phenolic compounds play a role as antioxidants through different mechanisms of action, such as scavenging of free radicals [7], quenching of reactive oxygen species, inhibition of oxidative enzymes [8], chelation of transition metals or through interaction with biomembranes [9]. Therefore, these compounds have been considered as promising candidates as potential protectors against lipid oxidation and biological ageing of tissues. Although the single phenolic compound has been proved as antioxidant, no comparative studies have been conducted among those phenolic compounds, which possess different molecular properties, mode of action, stability etc. Additionally, different phenolic compounds may act as antioxidants at varying degrees in different food systems, depending on the polarity and molecular characteristics. Hydrophilic antioxidants could prevent the oxidation of bulk oil, while its hydrophobic counterpart effectively retards lipid oxidation in oil-in-water emulsion [10]. Fish with its high content of unsaturated fatty acids is highly susceptible towards lipid oxidation [11]. The resulting development of rancidity in fish leads to undesirable changes in flavor, texture, color [12] and nutritional value [13]. In fresh fish the balance between the prooxidative and antioxidative factors which control oxidative reactions is maintained by numerous systems [14]. With processing and prolonged storage time the control of oxidation is lost and the onset of lipid oxidation can no longer be prevented [15]. How long this will take is highly dependent on the type of handling the fish is subjected to and the level of antioxidants present in the fish tissue [16,17].

Fish as Source of Antioxidants: There are several natural compounds that participate in the antioxidative defense mechanism of fish [18,19]. These include enzymes

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(catalase, peroxidase and glutathione and superoxide dismutase), carotenoids, peptides, amino acids and phenolic compounds (tocopherols, ubiquinones). These compounds are found in the cell plasma, mitochondria of cell membranes.

Occurrence of ascorbic acid in fish as antioxidant Fish muscle is generally low in Vitamin C content and the levels may be considered as negligible [20,21]. The ascorbic acid found in white fish muscle averaged 0.33±0.19 mg/100 g with slightly more in oysters and 1.7 mg/100 g in salmon. Sid well and coworkers [22] reported somewhat higher values; 7.1±1.9 in salmon, 1.1±1.1 in trout, 2.6±1.2 in tuna, 1.5±0.6 in shrimp and prawns and 9.0±3.8 mg/100 g in herring. Nettleton and Exler [23] measured ascorbic acid in edible portion of wild and cultivated channel catfish, Coho salmon, rainbow trout, red swamp crayfish and White River crayfish. The vitamin C content of these fish was generally below 1 mg/100 g, except for rainbow trout with 1.8 mg/100 g in wild and 2.9 mg/100 g in cultivated fish and eastern oysters with 3.1 in wild and 3.8 mg/100 g in cultivated oysters. Cultivated fish did not in general contain higher amounts of vitamin C. Nettleton and Exler [23] did also determine the vitamin C content in the relevant fish species after cooking. Vitamin C values for all cooked samples were greater than those in raw samples. The authors proposed that these findings were due to moisture loss during cooking and that vitamin C was well retained after cooking. Other processing of fish like hot smoking has also been found to have little effect on vitamin C in fish. Thus Bhuiyan and coworkers [24] found 4.7 mg/100 g of ascorbic acid in fresh and 4.5 mg/100 g in hot-smoked fillets of Atlantic fall mackerel. Storage time will probably affect the content of vitamin C in fish. Brannan and coworkers [24] measured the effect of frozen storage on the stability of ascorbic acid in fillets and mince of channel catfish (*Ictalurus punctatus*). The initial ascorbic acid concentration in fillets and mince was around 1.47 mg/100 g and decreased by a first order regression equation for both fillets and mince during frozen storage at-6°C. The loss of vitamin C occurred at a faster rate in the mince, especially through the first four months. The ascorbic acid values for the fillets and mince at the end of the storage experiment (6 months) were 1.19 and 0.63 mg/100 g, respectively. Large losses of ascorbic acid in the initial phases of accelerated frozen storage (temperature fluctuations) have also been reported in minced muscle of cultivated channel catfish (*Ictalurus punctatus*) [25-27]. Levels of ascorbic acid in the edible portion of fish and fish products have been reported by Gordon and Martin [28].

Prooxidant Activity of Ascorbic Acid: Although ascorbate is considered to be the terminal small-molecule antioxidant in biological systems, it may act in a prooxidant manner due to its excellent reducing ability [29]. Ascorbate is able to reduce catalytic metals such as Fe3+ and Cu2+ to their more catalytically active valence state Fe2+ and Cu+. In general low concentrations of ascorbate are required for prooxidant conditions, while high concentration is needed for antioxidant conditions. In the presence of ascorbate, catalytic metals will initiate radical chain oxidations, but when ascorbate concentration is high these radical processes will be less significant [30].

Antioxidant activity of amino acids, amines and peptides in fish Amines, peptides and amino acids are known to have significant antioxidant properties. In general, they function as synergists or primary antioxidants. Amino acids, peptides and nucleotides are believed to be important metal chelators present in fish [31]. Most of the amino acids have antioxidant properties depending on the pH of the medium and their concentration. Marcuse [32] found that most amino acids had a significant antioxidative potential even in the absence of primary antioxidants in linoleic acid model system. Amino acids are also known to exert synergistic effect with antioxidants. Various amino acids have been shown to make covalent attachment to Trolox-C, a synthetic derivative of α-tocopherol, to produce Troloxyl-amino acids with higher antioxidant activities than Trolox-C alone [33]. Amino acids are also suggested to have antioxidant properties as reaction products with carbonyls from oxidizing lipids. Various studies have shown results that suggests that reactions between oxidized lipids and amino acids produce many nonenzymic browning reaction compounds, which exert antioxidative properties [34]. The reaction of sugars and carbonyl compounds with amino acids or proteins are known as Maillard reaction or nonenzymatic browning. Their antioxidant properties are attributed to the formation of reductone (enaminone) structures that have both reducing and metal complexing properties [35]. Furthermore the basic amino acids (histidine, lysine and arginine) are known to produce the most effective antioxidant products with sugars [36].

Occurrence of Tocopherols: In marine animals α-tocopherol has been found to be the principal tocopherol [43]. The tocopherol content of foods is influenced by a large numbe of factors e.g. seasonal differences and significant losses may occur during processing and storage of foods [37]. Other factors may also be involved.

Each fish species has characteristic tocopherol levels in its tissue, which, since fish are unable to synthesize the vitamin, are related to diet [38]. The size or the age of the fish may also influence the tocopherol concentration. Thus, López and others [38] found highest values for α-tocopherol in the youngest rainbow trout, but no significant difference was found between sexes in adult samples. Considerable differences in a-tocopherol concentration have been reported between light and dark fish muscle. Ackman and Cormier [39] found α-tocopherol values for the light and dark cod muscle 0.24 and 1.16 mg/100 g, respectively, corresponding to 0.30 and 0.63 mg α-tocopherol/g lipid. Petillo and others [40]. found 4.4 fold difference between the light and dark muscle concentration of tocopherol in mackerel muscle. When expressed per gram of lipid, there was a decrease in differences, where the concentration of α-tocopherol in the light muscle was 0.20 mg/g lipid compared to 0.64 mg/g lipid in the dark muscle. The effect of processing on tocopherol content in fish has been studied. Erickson [41] measured the effect of cooking on minced channel catfish. About 60% of the α-tocopherol remained after 5 minutes of heating at 177°C and over 80% of the α-tocopherol. Other cooking methods like frying in vegetable oil may even increase the tocopherol concentration in fish. Storozhok [42] determined the tocopherol content of peled whitefish (*Coregonus peled*). The α-tocopherol content was 11 mg/100 g tissue in freshly caught fish and 37.1 mg/100 g in whitefish fried in vegetable oil.

Same author reported that the α-tocopherol level was only 4.3 mg/100 g in dry cured whitefish. Lighter processing like freezing also affects the tocopherol content of fish. Syväoja and Salminen [43] measured α-tocopherol in blast-frozen herring fillets. The tocopherol content fell from 420 mg/kg lipid to 270 mg/kg during six months frozen storage, that is over 60% of the α-tocopherol remained. Still, processes like hot-smoking of fall Atlantic mackerel (*Scomber scombrus*) left the vitamin E virtually unchanged [44].

Antioxidant Activity of Tocopherols: Vitamin E is stable to heat and alkali in the absence of oxygen and is unaffected by acids at temperatures up to 100°C. It is, however, slowly oxidized by oxygen to tocopheroxide, tocopherylquinone and tocopheryl hydroquinone as well as to dimmers an trimers [45]. The oxidation rate is greatly enhanced by iron and copper. The esters of vitamin E, e.g. tocopheryl acetate, are stable to oxidation and cannot function as antioxidants. The active hydroxyl group is protected. However, under certain conditions, e.g. acidic aqueous systems (as in the stomach), a slow hydrolysis of the tocopheryl acetate can be observed. The released tocopherol then acts as an antioxidant [46]. Vitamins are organic compounds necessary in the diet for normal fish growth and health. They often are not synthesized by fish and must be supplied in the diet. Vitamins are divided into two groups: water-soluble and fat-soluble [47]. Vitamin E receives the most attention for its importance as an antioxidant [48]. Vitamin E is a fat-soluble vitamin that exists in 8 forms. Each form has its own biological activity, which is the measure of potency or functional use in the body [49]. Alpha-tocopherol (α-tocopherol) is the name of the most active form of vitamin E. It is also a powerful biological antioxidant. Antioxidants, such as vitamin E, act to protect the cells from the effects of free radicals, which are potentially damaging by-products of energy metabolism, or from environmental exposure like radiation. Free radicals may be defined as any molecule that has one or more unpaired electrons. They can damage cells and may contribute to the development of cardiovascular disease, cancer, tissue injury in liver, brain, kidney, lung, nervous system and other organs. The redox cycling of heavy metals, as well as their interaction with organic pollutants is a major contributor to the oxidative stress resulting from aquatic pollution. Small molecule antioxidants such as vitamin E are able to interact with oxidizing radicals directly. Studies are underway to determine whether vitamin E, through its ability to limit production of free radicals, might help prevent or delay the development of the previous diseases (U.S. Department of Agriculture, 2004). Antioxidants from marine sources have attracted the attention of researchers as they are extracted from the by-products of marine processing and don't have side effects. The fishery wastes converted by proteolytic hydrolysis into a more marketable and functional form is called as fish protein hydrolysate. Fish protein hydrolysate have the potential to meet the expanding demand for natural protein sources and it has already been used to enrich food products as a food ingredient and also as a food supplement for human consumption. The peptides present in the fish protein hydrolysate are also found to possess antioxidant properties. The antioxidative activities of *Sphyraena barracuda* (seela) and *Lepturacanthus savala* (ribbon fish) have not been reported yet. Hence the present investigation is aimed to determine the antioxidant capacity and amino acid content of the protein hydrolysates obtained from muscle of these fishes [50].

CONCLUSION

In conclusion, the extracts of fishes species tissues have noticeable antioxidant activities and natural phenolic compounds and vitamins should play important roles in the antioxidative activities. Thus, the fish extract are natural antioxidants that have potentially antioxidative activity.

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