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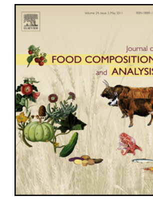

Original Research Article

Determination of urocanic acid, a compound implicated in histamine toxicity, and assessment of biogenic amines relative to urocanic acid content in selected fish and fish products

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ABSTRACT

The contents of *trans*- and *cis*-urocanic acid (*cis*-UCA), NaCl and moisture, and pH of sixty-seven fish and shrimp products, including salted anchovy, different types of salted fish, salted shrimp and shrimp paste collected in Malaysia, were examined. Included in the analysis was determination of the contents of nine biogenic amines. The average levels of *trans*- and *cis*-UCA in salted anchovy, salted fish, salted shrimp and shrimp paste were 9.67 and 7.25, 14.2 and 11.0, 36.6 and 22.5, 6.96 and 18.7 mg/kg, respectively. In general, the average levels of *trans*- and *cis*-UCA were much lower than the histamine levels in fish products. Results showed no strong correlation of pH, salt and moisture contents with *trans*- and *cis*-UCA, nor with histamine. Biogenic amines were also detected in processed fish and shrimp products where the most abundant biogenic amine was putrescine with an average level of 227 mg/kg in shrimp paste. Thus, the high rates of cancers in consumers who consume dried salted fish could be indicative of the synergistic effects of biogenic amines and *cis*-UCA.

1. Introduction

While histamine has been the subject of much research, the role of urocanic acid (UCA) in scombroid fish poisoning (SFP) is largely overlooked. *Cis*-UCA, which is the UV-induced photoisomer of *trans*-UCA, could degranulate mast cells and liberate histamine endogenously. Thus, it has been suggested that UCA and especially *cis*-UCA may play a role in SFP cases when the level of histamine is not adequate for poisoning (Lehane and Olley, 2000; Hungerford, 2010). Furthermore, currently, there is a growing body of evidence that *cis*-UCA, the UV-induced photoisomer of *trans*-UCA, plays a leading role in UV radiation-induced suppression of cell-mediated immunity (Gibbs et al., 2008). It mediates the release of cell-bound (latent) histamine in normal epidermal and dermal mast cells eliciting an immediate-type allergic reaction, and tumour necrosis factor-α (TNF-α), which participates in the development of melanomas and carcinomas in compromised individuals (Ch'ng et al., 2006; Walterscheid et al., 2006; Gibbs et al., 2008; Wasiuk et al., 2010; Harvima and Nilsson, 2011). The combined action of biogenic amines and *cis*-UCA may lead to an increase in the rate of tumour formation, due to the immunosuppressive effect of *cis*-UCA and ability of some biogenic amines such as putrescine and cadaverine to produce carcinogenic nitrosamines. It should also be pointed out that unlike biogenic amines, no detoxification or degradation has been reported for *trans*- and *cis*-UCA during ingestion.

Histamine is produced from histidine *via* a one-step decarboxylation reaction catalysed by histidine decarboxylase, which is found in many species of bacteria (Norval et al., 1989). However, it

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is not the only route through which histidine is metabolised. The other route is its deamination into *trans*-UCA by histidine ammonia lyase (HAL), also known as histidase or histidinase (Lehane and Olley, 2000). Unlike histidine decarboxylase, HAL is found in the muscle and liver of the fish. It has a vast distribution in different species of bacteria as well (Shibatani et al., 1974; Baranowski, 1985). In fact, Baranowski (1985) recommended that UCA should be used as an alternative to histamine as a quality index of fish during storage at low temperature, since UCA has been detected as a predominant metabolite of histidine during incubation of different bacteria at low temperature.

To date there have been only a few reports on the levels of UCA in fish. Mackie and Fernández-Salguéro (1977) detected 52.5 mg/kg total UCA after 18 days incubation of Indian mackerel at 0 °C. Self et al. (2011) also reported 10.25–11.28 mg/kg total UCA in canned and frozen loin of tuna, respectively. In another research, Self and Wu (2013) reported total UCA in different seafood samples, including canned mackerel, frozen raw mackerel, frozen raw mahi mahi fillet, fresh raw sockeye salmon and Thai fish sauce with levels of 30.8, 13.0, 7.0, 0.6 and 25.5 mg/kg, respectively. Because of different properties of *trans*- and *cis*-UCA, determining separate isomers of UCA in fish and fish products is important. Recently, Zare et al. (2013) reported 189.51 and 29.03 mg/kg *trans*- and *cis*-UCA, respectively, after 15 days incubation at 4 °C. However, the levels of *trans*- and *cis*-UCA in many fish and processed fish products are usually not analysed and are, therefore, unknown. Nonetheless, except for a few reports (Zare et al., 2012; Zare et al., 2013), the levels of *trans*- and *cis*-UCA, histamine and other biogenic amines have never been reported together, either in fresh, stored or processed fish and shellfish.

Biogenic amines, which are detected in vast groups of seafood, are considered as antinutritional factors (Bodmer et al., 1999; Önal, 2007). They may cause scombroid fish poisoning (SFP) at high levels and food intolerance in moderate concentrations (Bodmer et al., 1999). Initiation of many pharmacological reactions has also been attributed to biogenic amines (Önal, 2007; Chin-Chen et al., 2013). The role of histamine in SFP is almost certain as high levels of histamine have been detected in many incidences of SFP (Taylor, 1986; Hungerford, 2010; Leuschner et al., 2013). Many researchers believe that ingestion of low levels (8–40 mg) of histamine will not lead to symptoms of poisoning whereas the intake of high levels of histamine by consumption of foods containing 70–1000 mg and 1500–4000 mg of histamine causes moderate and severe poisoning, respectively, in victims (Flick et al., 2001). To control SFP, levels of 50 and 100 mg/kg have been established by the Food and Drug Administration (FDA) of the United State of America and the European Union, respectively, as thresholds of histamine content in fish (EC, 1991; FDA, 2009). The latter has also established 200 mg/kg as the legal limit of histamine in fish products.

Besides histamine, other biogenic amines such as putrescine, cadaverine, tyramine, tryptamine, 2-phenylethylamine, spermine, and spermidine have also been detected in seafood (Al Bulushi et al., 2009; Bakar et al., 2010; Ruiz-Capillas and Jiménez-Colmenero, 2010). Putrescine and cadaverine are usually cited as potentiators of histamine in SFP, while some other biogenic amines such as tyramine and phenylethylamine are important because of their histamine potentiation capacity and toxicity (Halász et al., 1994; Silla Santos, 1996). Cadaverine and putrescine were found to facilitate fish toxicity by increasing the transportation of histamine through the intestine (Flick et al., 2001; Yeh et al., 2006). Nitrosable secondary amines such as putrescine, cadaverine, agmatine, spermine and spermidine are also able to react with nitrite and produce heterocyclic carcinogenic nitrosamines, another important reason to investigate biogenic amines in foods. Salting and smoking can lead to nitrosamine formation in fish while frying and cooking increase the phenomenon (Yeh et al., 2006). Biogenic amine levels in processed fish products are also strongly affected by the quality of raw material along with salt and moisture content, microflora and starter cultures (Silla Santos, 1996; Al Bulushi et al., 2009; Ruiz-Capillas and Jiménez-Colmenero, 2010). Therefore, in general, evaluation of biogenic amines in fish and fish products will help to establish better indices for quality of fish products. Due to the effects of the different biogenic amines, a maximum level of total biogenic amines in fish of 300 mg/kg has been suggested by the European Community (EC, 1991). It has also been suggested by the FDA that information on other biogenic amines is used to evaluate the freshness of fish.

Other than toxicity, the second important reason for biogenic amines determination in fish and fish products is that they have been recommended as a fish quality marker (Ruiz-Capillas and Jiménez-Colmenero, 2010). Research and development, control of the process, raw materials quality control, end product control and fermentation processes monitoring are some applications of the analysis of biogenic amines in fish and fish products (Önal, 2007). Generally, the levels of biogenic amines in very fresh fish are very low while during storage or processing of the fish, they undergo charges in concentration (Ruiz-Capillas and Jiménez-Colmenero, 2010). Increased levels of histamine, putrescine and cadaverine have usually been reported during storage or processing of fish while fluctuation or increase has been reported for spermine and spermidine (Silla Santos, 1996). Base on this, some investigators suggested the quality index and biogenic amines index for evaluation of quality and freshness of fish. However, the accuracy of these indices has not been evaluated (Al Bulushi et al., 2009).

It should also be pointed out that dried salted fish is a big part of the diet in South East Asia, *e.g.* Malaysia, and especially among the Chinese population. Around 4 to 48% of adult southern Chinese population consumes salted fish more than once a week. Furthermore, in some parts of Malaysia such as Selangor, over 90% of Chinese households and 40% of Malay and Indian households consume salted fish regularly. Some people in South East Asia eat salted fish at every meal. Interestingly, exposure to salted fish in some populations commences during and after weaning (IARC Monographs, 2012; Armstrong et al., 1998, 1983).

The relationship between different cancers and consumption of dried salted fish has been discussed by many researchers (Armstrong et al., 1998; Sharif et al., 2008; Al Bulushi et al., 2009). Increasing rates of carcinoma is usually attributed to the presence of biogenic amines and nitrosamines. Thus, the present study was conducted to determine both *trans*- and *cis*-UCA and biogenic amines levels in fish and shrimp products collected from local markets in Malaysia.

2. Materials and methods

2.1. Chemicals

Trans- and *cis*-UCA, tryptamine hydrochloride, 2-phenylethylamine hydrochloride, putrescine dihydrochloride, cadaverine dihydrochloride, spermidine trihydrochloride, spermine tetrahydrochloride, histamine dihydrochloride, tyramine hydrochloride and agmatine sulfate were purchased from Sigma-Aldrich (St. Louis, MO). Octane sulfonic acid, acetonitrile, methanol, ammonium acetate were HPLC grade and obtained from Merck (Darmstadt, Germany). Other chemicals of analytical grade were also obtained from Merck.

2.2. Sample preparation

Sixty seven samples of fish and shrimp products were purchased from local supermarkets and grocery stores in Malaysia between November and December 2012. These samples included