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Effect of using starch on off-odors retention in tuna dark meat

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Abstract: During the process of canned tuna fish, considerable amounts of tuna dark meat are leftover because of its dark color and off-odors as lipid oxidation and fishy odors. The effect of using maltodextrin, corn and rice starch on off-odors retention in tuna dark meat was investigated by total volatile base nitrogen (TVB-N), trimethylamine (TMA), thiobarbituric acid reactive substances (TBARS) and confirmed some oxidized compounds by GC-MS method. 3% of maltodextrin, corn and rice starch solutions were used for washing solutions. A decrease of TVB-N and TMA values in tuna dark meat occurred after washing with those starch solutions. The lowest of TBARS values in tuna dark meat was obtained after washing with maltodextrin solution for 30 min. In addition, volatile compounds peak in term of quality and quantity from the meat washing with maltodextrin solution as 13.06% of peak area was lesser than other treatments particularly control, unwashed sample as 42.71% of peak area. Therefore, maltodextrin solution may have a potential to improve quality of off-odors in tuna dark meat, which could be utilized for further product.

Keywords: Tuna dark meat, maltodextrin, off-odors, retention

Introduction

About 60% of the original weight of fish is wasted. The available protein in fish is discarded or used as animal feedstuff or fertilizer. Generally, fish waste comprises of dark meat, trimmings, including tails, carcasses and skin, which normally are not acceptable in terms of appearance (Simon *et al*., 1981), color and off-odor (Bertoldi *et al*., 2004) as an ingredient in human foods.

The color and odor of tuna meat are very important for acceptability of consumers and the tone color of meat depends on amount of the myoglobin and hemoglobin contents in the muscles (Richards and Hultin, 2002). As well known that the dark muscle contains large amounts of hemeproteins, low molecular weight metal and microbial enzymes (Underland *et al*., 1998) those are causes of fish quality deterioration. Moreover, metmyoglobin and methemoglobin as well as polyunsaturated fatty acid containing in dark meat contribute to lipid oxidation in fish (Chan *et al*., 1997; Lee *et al*., 2003; Sohn *et al.,* 2007). Lipid oxidation is very important problems for fish odor and flavor because the high content of polyunsaturated lipids in meat is directly related to development of rancidity and off-odor (Sohn *et al.,* 2005). As fatty fish products are very susceptible to oxidation and leads to the formation of free radicals and lipid hydroperoxides, primary products of oxidation, which break down to secondary lipid oxidation compounds such as alcohol, aldehydes and ketones (Eymard *et al.,* 2009). The secondary lipid oxidized compounds are normally reported as thiobarbituric acid reactive substances (TBARS) value. This value is not fit for human consumption if it higher than 8 mg/kg oil sample (Huss, 1988).

Total volatile base nitrogen (TVB-N) value is widely used to evaluate the quality of fish and seafood (Li, 2004). This value is a result of endogenous (raw material enzyme) and exogenous (microbial enzyme) enzyme functions. The fish or fish products containing TVB-N more than 30 mg/100 g sample are generally classified as unfit for human food (Özoğul and Özoğul, 2000). However, TVB-N was leached out from the fish by melting ice during storage (Magnússon and Martinsdóttir, 1995).

Interactions between aroma compounds and food involve three mechanisms: the partition of flavor molecules between different phases of the food product, the diffusion of flavor molecules through the food and matrix, and the binding of flavor molecules to food compounds (Taylor, 1998). Starch and starch-based ingredients such as modified starches, maltodextrins and β-cyclodextrins are widely used in the food industry to retain and protect volatile compounds (Boutboul *et al*., 2002). The binding of volatiles to starch has been classified into two types. The first is starch form inclusion complex with volatile molecule then flavor compounds is entrapped in the amylose helix through hydrophobic bonding. The second is interaction of hydrogen bonds from hydroxyl groups of starch and aroma compounds

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(Rutschman and Solms, 1990; Nuessli *et al*., 1997; Boutboul *et al*., 2002).

Starch has ability to form complexes with volatile compounds in particular the linear amylose fraction. The ability to form inclusion complexes with lipids and aroma compounds like alcohols, aldehydes, terpenes, lactones, etc. was reported as a function of amylose chains in starch (Buléon *et al.,* 1998; Heinemann *et al*., 2003; Misharina *et al*., 2003; Jouquand *et al*., 2004). However, retention and release of flavor from native corn starch did not only relate to amylose content but also others such as polarity of compounds and molecular weight of starch used. Moreover, it was found that volatiles were optimum entrapped with maltodextrin when proper molecular weight was applied (Goubet *et al*., 1998). Bangs and Reineccius (1981) reported that the retention of a mixture of 12 aroma compounds depends on the dextrose equivalent (DE) of the maltodextrins as follows: DE 10.0 > DE 15.0 > DE 20.0 > DE 25.0 > DE 36.5.

From the basic knowledge, if some volatile compounds derived from lipid oxidation and protein and/or non-protein nitrogen could be entrapped with food ingredient, then off-odor and off-flavor may reduce after washing. To determine volatile compounds from aqueous sample, solid-phase microextraction (SPME) is famous techniques as its fast, simple, low cost and solvent free properties (Li *et al.*, 2004) as well as could be coupled to gas chromatography-mass spectrometry (GC-MS).

The aim of the present study was to reduce off-odors in tuna dark meat by using various starch type solutions. Furthermore, the abilities of starch to trap the volatile compounds from lipid oxidation were investigated by SPME coupled to GC-MS method.

Materials and Methods

Material and preparation

Skipjack tuna (*Katsuwonus pelamis)* dark meat used in this work was obtained from deskinning and cleaning step during processing of canned tuna (tuna canning factory in Songkhla, Thailand). Then the tuna dark meat samples (flake size 0.5-1.0 cm) were collected and kept frozen at -20°C in closed container and used in the experiment within 12 months.

Starch materials used in this experiment were corn starch, rice starch and maltodextrin. The corn and rice starch were subjected to determine amylose content as method of Juliano (1971). It was found that amylose content in corn and rice starch were 28.44% and 21.14%, respectively while, maltodextrin was declared as containing 9 dextrose equivalents. From preliminary test, TBARS and TVB-N value of sample washed with 3% of maltodextrin for 30 min were lower than unwashed sample. Therefore, each maltodextrin, corn and rice starch solutions were prepared by suspended or dissolved with distilled water to obtain 3% of concentration.

To make the washing process with starch solution, 100 g of tuna dark meat was soaked in 300 ml at 27±2°C of each starch solution and stirred with magnetic stirrer for 10, 20 and 30 min. Then the soaked sample was rinsed with 300 ml of distilled water for 2 times to remove excess starch solution from the meat. The washed samples were brought to determine their pH and off-odor qualities as followed.

pH value

The pH values of the samples were obtained by homogenizing 1 g of sample with 10 ml of distilled water and pH was measured using pH-Meter.

Total volatile base nitrogen (TVB-N) and Trimethylamine (TMA) values

The TVB-N and TMA contents were determined using the Conway microdiffusion assay according to the method of Hasegawa (1987). Sample (2 g) was extracted with 8 ml of 4% trichloroacetic acid (TCA). The mixtures were filtered using Whatman No. 41 then the filtrate was used for analysis. To determine the TMA content, formaldehyde was added to the filtrate to fix dimethylamine (DMA) and ammonia present in the sample. TVB-N and TMA were released after addition of saturated K_2CO_3 and diffused into the boric acid solution. The titrations of solution were performed and the amount of TVB-N or TMA was calculated as mg nitrogen/100 g sample.

Thiobarbituric acid reactive substances (TBARS) value

0.5 g of ground samples was homogenized with 4.0 ml of mixture of 0.037% TBA, 15% trichloroacetic acid and 0.25 N HCl. The mixture was heated in boiling water for 10 min to develop a pink color, then; the sample was cooled down with running tap water and centrifuged at 3,600 rpm for 20 min. The absorbance of supernatant was measured at 532 nm and results were expressed as mg malondialdehyde/ kg sample (Buege and Aust, 1978).

Oxidized compounds

3-g of the washed tuna dark meat was homogenized with a volume of 8 ml saturated NaCl (26% NaCl). The mixture was centrifuged at 3500 rpm for 10 min as method of Iglesias and Medina (2008) to obtain supernatant. Volatile compounds were analyzed by

HS-SPME method, 6 ml of supernatant was heat at 60°C for 10 hr until it reached equilibrium then SPME fiber (50/30 µm Carboxen/polydimethylsiloxane/ divinylbenzene coating) was equipped to absorb the volatiles. The fiber then was immediately desorbed in the gas chromatograph injector at temperature, 270°C, for 15 min and volatile compounds were analyzed with Hewlett-Packard gas-chromatograph model HP 5890, equipped with a Mass Selective Detector 5972 (Atlanta, GA,USA).

Statistical analysis

The data obtained from two batches of materials (three replicates from each batch) and a completely randomized design (CRD) was used. Data were subjected to analysis of variance (ANOVA). Comparison of means was carried out by Duncan's multiple range tests. Significance was declared at $p<0.05$ using the statistical software.

Result and Discussion

Changes in pH

pH of initial tuna dark meat was in the range 5.48 ±0.04 to 5.49±0.08. However, the pH of the tuna dark meat decreased to 4.54±0.06 to 4.89±0.23 after washing with any type of starch solutions (Table 1). A decrease of pH of the washed meat may due to leaching effect as hydrophilic property of volatile base nitrogen as TMA, DMA, ammonia and other amines (Magnússon and Martinsdóttir, 1995).

Table 1. TMA and pH values in tuna dark meat washing with three types of starch solutions

Washing time	TMA (mg/100g of dark meat)	pH
3% maltodextrin solution		
Control (Unwashed sample)	7.23±1.4	5.48±0.08^{a}
10 min	Undetectable	4.78±0.08^{bc}
20 min	Undetectable	4.73±0.10^{c}
30 min	Undetectable	4.89±0.23^{b}
3% Corn starch solution		
Control (Unwashed sample)	6.07±0.81	5.48±0.04^{a}
10 min	Undetectable	4.61±0.11^{b}
20 min	Undetectable	4.63±0.17^{b}
30 min	Undetectable	4.54±0.06^{b}
3% Rice starch solution		
Control (Unwashed sample)	7.47±1.62	5.49±0.08^{a}
10 min	Undetectable	4.78±0.08^{b}
20 min	Undetectable	4.74±0.19^{b}
30 min	Undetectable	4.62±0.15^{c}

$^{a-c}$ Mean within a column within the same condition with different letters are significantly difference ($p<0.05$).

Changes in TVB-N and TMA

The values of total volatile basic nitrogen (TVB-N) in the washed meat were shown in Figure 1. From the result it confirmed that TVB-N values decreased after washing with all starch solutions. The initial TVB-N value could reduce from 26.96 mg nitrogen/100 g of dark meat down to 2.61 mg nitrogen/100 g of dark meat. Based on meat quality judged by TVB-N, it implied that raw material used in this experiment was fair may due to the quality industry plant controlling. However, it was found that type of starch solution had no effect on TVB-N reduction. It implied that volatile base nitrogen compounds could be easily extracted by any starch solutions due to its hydrophilic property then leaching effect occurred. Similar to finding of Magnússon and Martinsdóttir (1995) who mentioned that reduction of TVB-N in iced fish sample caused by melt water.

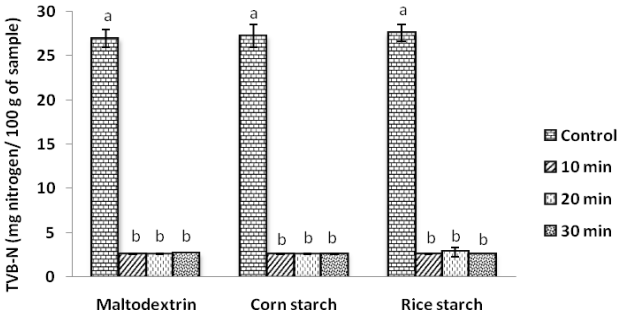

Figure 1. TVB-N value in tuna dark meat washing with three types of starch solutions at 10, 20 and 30 min

Connell (1990) reported that cod containing TMA around 10 to 15 mg nitrogen/100 g of meat is not considered suitable for most uses. It confirmed that initial quality of this present raw material is good for uses. It was also found that washing with any type of used starch could significantly remove TMA from 6.07-7.47 mg/100 g of dark meat to undetectable level as showed in Table1. The most likely explanation was that TMA was washed away with the starch solution in the same manner as described in pH and TVB-N.

Changes in TBARS

Changes in TBARS of tuna dark meat after washing with three types of starch solutions were shown in Figure 2a. The TBARS in control was very high with more than 110 mg/kg sample this may due its nature of dark meat containing high in hemoglobin, myoglobin, and unsaturated lipids as well as heating process. These factors lead to lipid oxidation as addressed by Chan *et al*., 1997; Lee *et al*., 2003 and Sohn *et al.*, 2007. However, the result showed that TBARS values in the tuna dark meat decreased significantly after washing with any starch type solutions at any time compared to unwashed sample.

In addition, decreasing of TBARS values of washed sample with 3% of matodextrin for 30 min was the highest (Figure 2b). Based on washing time,

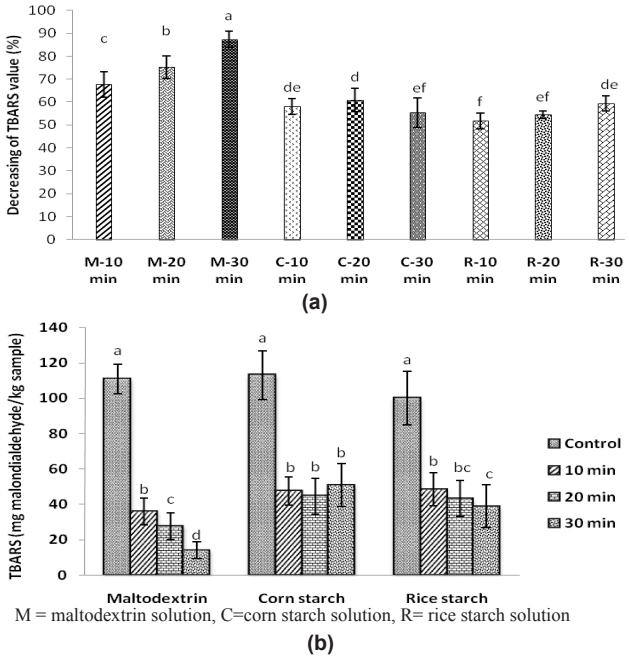

Figure 2. Effect of washing tuna dark meat with three types of starch solutions on TBARS value (a) and % decreasing of TBARS (b)

TBARS decreased as washing time increased only in maltodextrin solutions. It pointed out that contact time was very important for maltodextrin to penetrate and bind with volatile compounds. However, this effect was not show in corn and rice starch solutions.

Arvisenet *et al*. (2002a, b) suggested that the possibility of volatile trapping caused by interaction between volatile compounds and glucose molecule in amylose and/or amylopectin from starch. Moreover, Boutboul *et al*. (2002) mentioned that native starch displayed only minor differences and amylose content did not affect to aroma retention. Missharina *et al*. (2008) reported that a retention of aroma increased as decreased of starch molecular weight. Since maltodextrins are more water soluble when compared with corn and rice starch then it may more increase the retention of volatile (Goubet *et al*., 1998). However, Missharina *et al*. (2004) reported that the retention of volatiles depends on their hydrophobicity. Jouquand *et al.* (2004) reported that hydrophobic molecules such as hexanal, 2-octanone, ethyl butanoate and 2-heptanone would interact with hydrophobic groups in helical cavity of maltodextrin molecule in solution system (Eftink *et al.*, 1989). From the results of TBARS, TVB-N and TMA values, sample treated with maltodextrin solution for 30 min were selected for the determination of oxidized compounds.

Changes in volatile compounds

The oxidized volatile compounds of both unwashed, control, and washed sample were presented in Table 2. Nine compounds as 2-pentenal, 2-hexenal, 2-octenal, (*E,E*)-2,4-decadienal, 2-ethylfuran, 2-(2-propenyl)-furan, 3,5-octadien-2-one, toluene, tetradecanoic acid were not detected in washed sample. Seven compounds as heptanal, 2,4-hexadienal, (*E,E*)-2,4-heptadienal, 2-hendecanone, 2-pentylfuran, 2,6,10,14-tetramethylpentadecane, hexadecanoic acid was reduced by washing with maltodextrin.

Table 2. Volatile compounds, Retention time and Peak area from washed and unwashed sample of tuna dark meat identified by GC-MS

Compounds Name	Unwashed sample (Control)			Washed sample (3% maltodextrin, 30 min)		
	Retention time (s)	Peak area	Peak area (%)	Retention time (s)	Peak area	Peak area (%)
Aldehydes						
2-Pentenal	9.695	1834450	0.405	ND	ND	ND
Heptanal	11.824	17166488	4.340	11.958	47794	1.055
2-Hexenal	13.265	6613337	1.460	ND	ND	ND
2,4-Hexadienal	20.695	4919437	1.086	20.736	3103034	0.734
2-Octenal	21.572	9136009	2.017	ND	ND	ND
(*E,E*)-2,4- Heptadienal	23.847	36276566	8.010	23.878	27404561	6.928
(*E,E*)-2,4- Decadienal	33.177	8802169	1.944	ND	ND	ND
Furans						
2-Ethylfuran	4.352	8404686	1.856	ND	ND	ND
2-Pentylfuran	13.734	18959123	4.793	13.899	6468615	1.428
2-(2-propenyl)-furan	27.761	5726474	1.264	ND	ND	ND
Ketones						
3,5-Octadien-2-one	24.724	19185053	4.236	ND	ND	ND
2-Hendecanone	27.155	6309710	1.393	27.198	5140058	1.299
Aromatic						
Toluene	6.502	16212436	3.580	ND	ND	ND
Noncyclic hydrocarbons						
Dodecamethyl-cyclohexasiloxane	19.954	3763726	0.831	ND	ND	ND
2,6,10,14-Tetramethyl-Pentadecane	29.566	12621350	2.787	29.536	4374263	1.106
Acids						
Tetradecanoic acid	50.846	4856629	1.072	ND	ND	ND
Hexadecanoic acid	52.923	7683331	1.697	52.876	2035332	0.515

ND = not detected

Huss (1995) addressed that lipid oxidation of fish muscle is mostly shorter carbon chain-length such as aldehydes, ketones, small carboxylic acids and alkanes. Aldehydes, the most volatile compounds from lipid oxidation of fish muscle were thought to contribute to the fishy and rancid flavors (Yasuhara and Shibamoto, 1995; Jacobsen *et al*., 2000).

This result confirmed the possibility of interactions between volatile compounds with maltodextrin structure complexes. Jouquand *et al*. (2006) addressed that maltodextrin solutions retain volatile mainly depended on the hydrophobicity of hexanal, (*E*)-2-hexenal and 2-hexanone, short chain fatty acids. Similar to the result of Jouquand *et al.* (2004) who mentioned that maltodextrin solutions with increasing of temperature could increase the retention of volatile compounds such as hexanal, 2-octanone, ethyl butanoate and 2-heptanone due to hydrophobic interaction.

Conclusion

The type of starch solutions did not affect to reduce TVB-N and TMA but a decrease of both values was occurred after washing step. However, TBARS value was the lowest in the tuna dark meat when washing with maltodextrin solution compared with other starch solutions. Oxidized compounds determined by GC-MS confirmed the effectiveness of using maltodextrin as washing solution. Therefore, a low marketable dark meat tuna may be further utilized as human food if washing by suitable starch was applied.

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