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Changes in nutritional composition of skipjack *(Katsuwonus pelamis)* due to frying process

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Abstract

Skipjack is one of Indonesian commodity that can be processed in traditional process (*katsuobushi, dashi,* and smoked fish) and modern process. Frying process is common way to processing skipjack in the local community. Purpose of this research was to determine the changes in skipjack nutritional composition (fatty acids, cholesterol, amino acids, and minerals) due to frying process. The chemical composition of fresh skipjack consisted of 71.76% moisture, 25.29% protein, 0.60% fat, 1.49% ash, and 0.87% carbohydrates, while the fried skipjack's chemical composition consisted of 48.25% moisture, 41.25% protein, 4.80% fat, 4.10% ash, and 1.60% carbohydrate. Fresh skipjack meat contained 30 kinds of fatty acids and 25 kinds of fatty acids after frying process. Cholesterol in skipjack increased due to frying, from 49.12 mg/100 g in fresh, to 173.92 mg/100 g in fried skipjack. Fresh skipjack contained a total of 74.25 g/100 g amino acids, consist of 9 essential amino acids and 6 non-essential amino acids. Mineral content changes namely in potassium, increased from 7966.54 ppm in fresh to 8316.22 ppm in fried skipjack. This research concludes frying process at 180°C for 5 minutes can reduce levels of moisture, protein, EPA, DHA, amino acids, minerals Na, and Zn.

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Introduction

Skipjack *(Katsuwonus pelamis)* is a thriving Indonesian aquatic commodity. Tuna group total production in 2011 was 955.520 tons. Indonesian tuna group export realization in 2011 was 141.774 tons. Generally, fishery exports in 2012 showed an increasing trend, particularly to Japan and the United States (Ministry of Marine Affairs and Fisheries Republic of Indonesia, 2012). In Indonesia, skipjack are generally processed in variety of forms to increase added value such as smoked fish, canned fish, and katsuobushi. Common way to process skipjack is done by frying process. It is a cooking method using cooking oil as heating medium (Muchtadi, 2008). One of frying process ways is deep frying. Deep frying is a frying technique that use cooking oil in large numbers, so that all parts of the food is submerged in hot oil. Deep frying has several advantages, namely short frying time and can fry food (except crust area) below 100°C (Ghidurus *et al.*, 2010).

Frying process can affect the nutritional composition in the food. Tůrkkan *et al.* (2008) stated the frying effect of seabass *(Dicentrarchus labrax)* could reduce 30% eicosapentaenoic acid (EPA) and 28% docosahexaenoic acid (DHA). Domiszewski *et al.* (2011) reported that the frying process at 180°C for 6 minutes on catfish fillets could increase 2.23% to 9.65% fat content. Oluwaniyi and Dosumu (2009) said that amino acid total of Trachurus trachurus decreased 6.21% because of frying process. Utilization of skipjack that many processed in Indonesia unfortunately is not followed by nutrition data information sufficiently. So it is necessary to study the influence of the frying process on the skipjack nutritional content. The purpose of this study was to determine the influence of frying process on the skipack chemical compositions, fatty acids, cholesterol, amino acids, and minerals.

Materials and Methods

Materials and equipments

The main material used was fresh tuna *(K. pelamis)* from PT Graha Insan Sejahtera Muara Baru, North Jakarta captured in June 2013 and palm oil with the brand "Bimoli". The main tools used were gas chromatography (GC) Shimadzu GC 2010 Plus with standard SupelcoTM 37 Component FAME Mix, spectrophotometer UV-200-RS Single Bim, High Performance Liquid Chromatrography (HPLC) Shimadzu RF 20A, and Atomic Absorption

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Spectrophotometer (AAS) Shimadzu AA-7000.

Methods

Stages of the research were morphometric measurement, sample preparation, yield calculation and sensory analysis (Soekarto, 1985), and frying process (modification Domiszewski *et al*., 2011). Testing procedure were proximate analysis (AOAC, 2005), fatty acid analysis (AOAC, 2005), analysis of cholesterol levels used the Liebermann-Buchard Colour Reaction, amino acid analysis (AOAC, 2005), and mineral analysis (AOAC, 1995). Morphometric and yield determination used fresh fish, while the proximate, fatty acids, cholesterol, amino acids, and minerals analysis used fresh and fried fish.

Amino acid analysis

Amino acid analysis performed using HPLC brand Varian 940-LC in four stages, namely the stage of making protein hydrolyzate, drying phase, derivatization phase and injection phase (amino acid analysis). First step were making a protein hydrolyzate by homogenized sample (0.1 g) added with 5 mL 6N HCl were heated (100^0C for 24 hour) and then filtered. Second Phase were drying filtered sample were added 30 mL of mixed solution of methanol, sodium acetate, and trietylamino (2:2:1) then dried until all the solvent evaporates. Third phase were derivatization Derivatization solution of 30 mL were made from a mixture of methanol, picoltiocianat (PITC) and triethylamine (TEA) with ratio (3: 3: 1), then allowed to sit for 20 minutes and then 10 mL of 1 M sodium acetate buffer plus were added. Derivatization process was concluded so that the detector are able to detect substances present in the sample. Final phase were injection into the HPLC of standard solution begins with mixing the stock solution with the standard solution and borate buffer (1: 1). A total of 5 mL of the solution was injected into the HPLC within 30 minutes. The same steps carried out on a sample by mixing the borate buffer with the stock solutions (1: 1). The mixture was injected into the HPLC to detect all the amino acid. Amino acid content in the material is calculated by dividing multiplication of area of the sample, Concentration of standard amino acids (mg / mL), dilution factor and molecular weight of each amino acid by wide and of weight standard sample area and multiplicate them by 100%. HPLC used P1 Cotag column, Motion phase used acetonitrile and phosphate buffers, wavelength were 272 nm, and flow rate were 0.5 mL/ min.

Mineral analysis

Sample undergoes wet ashing process beforehand, 20 g of sample were added 15 mL of 65% HNO_3 and allowed to stand for 60 minutes, then another 10 mL of HNO_3 were added and the solution was heated (80-100^0C) for 6 hours, 2 mL of concentrated H_2SO_4 were added and the solution was heated for 60 minutes, solution were then added $HClO_4$: HNO_3 (2: 1) and heated until it changes color to yellow. Sample solution were then diluted to 100 mL in a flask. A number of standard stock solution of each mineral was diluted using distilled water until the concentration is within the working range of the desired metal, with the addition of 0.05 mL and 5 mL of distilled water. The sample is then cooled and filtered with glass wool and then injected into the AAS.

Standard solution, blank, and sample absorbed into the Atomic Absorption Spectrophotometer (AAS) brand Shimadzu AA-7000. The wavelength used were 422.7 nm for Ca, 766.5 nm for K, 589.0 nm for Na, 324.7 nm for Cu, 248.3 nm for Fe, 213.9 nm for Zn. Making a standard curve made by looking at the relationship between the absorbance standard (dependent variable) and standard ppm (independent variables). Relations between the two variables are described in a form of the linear regression line equation. The equation used to calculate ppm sample by changing the dependent variable with the sample absorbance is detected on the appliance.

Analysis of fatty acids

Analysis of fatty acids carried through the first stage of soxhlet extraction used 20-30 mg of sample in oil form. Second stage were formation of methyl ester (methylation), samples (oil) weighing 20-40 mg were added with 0.5 N NaOH and methanol, heated for 20 minutes in a water bath. 2 mL of 20% BF3 were added after the solution had cooled, and allowed to stand for 20 minutes. 2 mL of saturated NaCl and 1 mL of hexane were added and then homogenously shaken. Hexane layer was transferred by pipette into a tube containing 0.1 g of anhydrous Na_2SO_4, allowed to sit for 15 minutes. The aqueous phase was separated and subsequently injected to GC Hitachi 263-50, with following conditions: Detector: FID, Diethylene Glycol Sukcianat column type, 150°C initial temperature, 180°C final temperature, 5°C/min increased temperature, 200°C Injector temperature, 250°C Detector temperature, 1 kgf/cm^2 Nitrogen flow rate, 0.5 kgf/cm^2 Hydrogen flow rate.

Results and Discussion

Characteristics of skipjack tuna (Katsuwonus pelamis)

Tuna had a fusiform body, the head was very

Table 1. Chemical composition of fresh and fried skipjack

Parameter	Fresh		Fried		Fresh Skipjack*	*Auxis* sp.**
	bb (%)	bk (%)	bb (%)	bk (%)	bb (%)	bb (%)
Moisture	71.76 ±0.42	0.00±0.00	48.25±0.77	0.00±0.00	70.40	73.20
Protein	25.29 ±0.00	89.54±0.00	41.25±0.00	79.71±0.00	21.45	21.80
Fat	0.60±0.00	2.12±0.00	4.80±0.00	9.28±0.00	1.81	1.00
Ash	1.49±0.14	5.28±0.42	4.10±0.13	7.91±0.14	1.27	1.40
Carbohydrate	0.87±0.28	3.07±0.95	1.60±0.64	3.10±1.91	1.81	2.60

*) Matsumoto *et al.* (1984) **) Manzano *et al.* (2007)

thick, and slightly flattened on the side . Tuna had 2 separate dorsal fins. The bodies were not scaly except on the lateral line, there are small dots. Dorsal was dark, but bottom side and belly was silvery with 4-6 pieces of black lines extending on the whole body (Matsumoto *et al.*, 1984). The results of morphometric measurements of skipjack in this study were total length (30.05±1.32 cm), raw length (24.65±1.38 cm), forked length (28.30±1.36 cm), height (7.10±0.46 cm), body width (4.90±0.21 cm) and weight (424.67±8.51 g).

Table 1 showed that the sample were uniform (SD<1.5). The long and high ration was 4:1. This skipjack was small . The sample had a length smaller than the length of the fish first mature gonads. According to Jamal *et al.* (2011), a decent size of skipjack catch is greater than 40 cm. According to Matsumoto *et al.* (1984), skipjack can reach a length about 50-70 cm and a weight about 1500-5000 g. Tanabe *et al.* (2003) stated that skipjack in Pacific Ocean could reach an average length of 35 cm in half a year, 45 cm in 1 year, and 65 cm in 2 years.

According Metusalach (2007) the growth of a biota was influenced by external and internal factors. External factors were habitat, season, water temperature, type of food, and other environmental factors. The internal factors were age, size, gender, eating habits, and other biological factors. Internal factors generally can not be controlled by man while still external factors can be controlled.

The organoleptic value of this sample was 7. The characteristics was little of body mucus, compact texture, clear eyes, and the fresh smell of a specific type. Skipjack meat changed after the frying process. Raw fish meat is white, compact, and fresh smelling like a specific type, while the fried fish meat lightly browned with a more dense texture and delicious smell.

The yield

Skipjack meat yield (58%) was greater than the bone (25%) and offal (17%). This is supported by the characteristics of tuna that has dense and compact meat texture. Meat is part of skipjack's body that is very common utilized. Other skipjack processing are katsuobushi (Mitou *et al.*, 2008) and smoked fish. Utilization of other parts of skipjack namely utilizing fish bone as substitute source to produce gelatin (Astawan *et al.*, 2002), utilizing skipjack waste as animal feed (Leke *et al.*, 2012), and utilizing skipjack bone as fish bone meal (Basmal *et al.*, 2000).

Moisture content

Skipjack moisture content (71.76%) had the same range as the research of Matsumoto *et al.* (1984) that was 70.40% (Table 1). This result had no difference with Auxis moisture content that was 73.2% (Manzano *et al.*, 2000). According to Ayas and Ozugul (2011), moisture content differences may be caused by species, age of biota, differences in environmental conditions, and fresh level of organism. High levels of moisture can cause the fishery products easily damaged if they are not handled well.

Skipjack moisture content decreased 23.50% as a result of the frying process. The decrease in moisture content after frying process was due to the evaporation of the moisture contained in food during the heating process. According to Jacoeb *et al*. (2008), frying process will decrease the amount of moisture in the food. Zahra *et al*. (2013) reported that at higher drying temperatures for long periods, the heat not only is used to vaporize water on the material surface but also evaporates the bound water in the material. The oil will be absorbed into the food during frying process in line with water vaporation from food. Rising oil absorption making the moisture content decreases because the position of the moisture was replaced by oil as the heating medium.

Protein content

The protein content of fresh skipjack was 25.29%. Matsumoto *et al.* (1984) stated that protein content of skipjack was 21.45%. The other species *(Thunnus tonggol)* contained high levels of a protein 21.8% (Manzano *et al.*, 2007). Generally, fish had a high protein content until 20% (Adawyah, 2007).

The protein content of fresh and fried skipjack can be seen on a dry basis, respectively 89.54% and

Table 2. Fatty acid composition in skipjack

Fatty acid	Fresh Skipjack (%w/w)	Fried skipjack (%w/w)	Palm Oil*
Saturated fatty acids			
Caprilic (C8:0)	0.03±0.01	0.04±0.01	0.06
Capric (C10:0)	nd	0.01±0.01	0.01
Lauric (C12:0)	0.04±0.00	0.20±0.00	0.23
Tridecanoic (C13:0)	0.02±0.00	nd	
Myristic (C14:0)	1.74±0.11	0.86±0.03	0.84
Pentadecanoic (C15:0)	0.56±0.04	0.10±0.01	
Palmitic (C16:0)	14.49±0.81	30.46±0.19	36.76
Heptadecanoic (C17:0)	1.00±0.07	0.22±0.01	
Stearic (C18:0)	7.57±0.53	4.03±0.24	
Arachidic (C20:0)	0.41 ±0.03	0.30±0.02	0.16
Heneicosanoic (C21:0)	0.09±0.01	0.08±0.10	
Behenic (C22:0)	0.36±0.03	0.16±0.07	0.06
Lignoceric (C24:0)	0.25±0.02	0.09±0.01	0.07
SAFA Total	26.56	36.55	
Monounsaturated fatty acids			
Myristoleic (C14:1)	0.02±0.00	nd	
Palmitoleic (C16:1)	2.07±0.13	0.36±0.02	
Elaidic (C18:1n9t)	0.09±0.09	0.09±0.01	
Oleic (C18:1n9c)	7.65±0.46	33.45±0.42	49.48
Cis-11-Eicosenoic (C20:1)	0.44±0.03	0.22±0.01	
Erucic (C22:1n9)	0.08±0.01	0.02±0.00	
Nervonic (C24:1)	0.38±0.03	0.08±0.01	
MUFA Total	10.72	34.22	
Polyunsaturated Fatty Acids			
Linolenic (C18:2n6c)	0.97±0.08	8.32±0.42	11.74
Linolelaidic (C18:2n9t)	0.03±0.01	nd	
Linolenic (C18:3n3)	0.28±0.06	0.17±0.01	0.54
γ-Linolenic (C18:3n6)	0.08±0.01	nd	
Cis-11,14-Eicosedienoic (C20:2)	0.18±0.01	0.07±0.01	
Eicosentrienoic (C20:3n3)	0.08±0.01	0.02±0.00	
Cis- 8,11,14- Eicosetrienoic (C20:3n6)	0.09±0.03	nd	
Arachidonic (C20:4n6)	1.31±1.08	0.27±0.01	
EPA (C20:5n3)	3.48±0.16	0.52±0.01	
Cis-13,16-Ducosadienoic(C22:2)	0.03±0.01	nd	
DHA (C22:6n3)	19.27±0.83	3.44±0.12	
PUFA Total	25.85	12.81	
Fatty Acid Total	**63.13±2.47**	**83.58±3.67**	

* Dauqan *et al.* (2011) nt (not detected)

79.71%. There was a decrease of 9.8% protein content. Frying process could carrying protein component of fish meat into the oil being used. Calculation of protein content in this test was describe the total nitrogen in the food material (crude protein), so it was suspected there were the other components of non-protein nitrogen (NPN) counted. Heat caused protein denaturation. Denaturation could be interpreted a change or modification of the secondary structure, tertiary, and quaternary protein molecule without breaking the covalent bonds (Jacoeb *et al.*, 2008). Denaturation changed the physiological protein characteristic, but didn't cause the decrease of total nitrogen in food.

Fat content

Fresh skipjack contained 0.60% fat (wet basis). The results showed that skipjack is classified as low-fat fish that has a fat content <5% (Junianto, 2003). Matsumoto *et al.* (1984) research showed skipjack has 1.81% of fat. Other species within the same family, namely *Auxis* sp. according Manzano *et al*. (2000) also contained a fairly low fat (1%). Fat content on every species would be different. Sample that has lower fat content was caused by sample size that has not entered the age of mature gonads, so that the energy from the fat was used larger for growing than the fish that have entered the age of mature gonads. Heltonika (2009) reported that mature fish has more fat because it requires substantial energy savings form fat to breed.

Fat content of fresh and fried skipjack was 2.12% and 9.28%. Fat content increased 7.16%. Similar result was also shown by Gokoglu *et al.* (2004) that said frying process can raise 9.26% fat levels of rainbow trout *(Oncorhynchus mykiss)*. Fat Increase is the result of palm oil absorption during the frying process. Food will lose water content that contained therein and oil will be absorbed in the food (Zahra *et al*., 2013).

Ash content

The ash content of fresh akipjack in wet basis was (1.49±0.141%). This result was not much different from Matsumoto *et al*. (1984) was 1.27%. Low ash content was also shown in *E. lineatus* was 1.4% (Manzano *et al*., 2000). The ash content of fresh skipjack was (5.275±0.422%) (db) and increased after

Table 3. Amino acids composition in dry basis

Amino Acid	Score (g/100g) Fresh Skipjack	Fried skipjack	Fresh Mackarel **	Yellowfin tuna***
Aspartic acid	7.35±0.11	5.72±0.07	9.84	5.02
Glutamic acid	11.22±0.14	8.48±0.10	15.84	5.25
Serine	2.69±0.04	2.02±0.04	4.24	7.92
Histidine*	6.72±0.12	5.51±0.28	2.72	15.57
Glycine	4.83±0.20	3.00±0.03	4.33	6.74
Threonine*	3.30±0.05	2.69±0.10	4.68	2.83
Arginine	4.85±0.09	3.43±0.08	5.67	6.16
Alanine	5,04±0,09	3.41±0.08	8.49	11.92
Tyrosine*	2.54±0.04	1.99±0.05	-	3.26
Methionine*	2.16±0.04	1.79±0.04	3.65	1.28
Valine*	4.25±0.04	3.43±0.07	8.63	4.54
Phenylalanine*	3.23±0.02	2.50±0.07	-	3.17
Isoleucine*	3.89±0.04	3.07±0.05	4.25	3.21
Leucine*	5.89±0.05	4.54±0.10	7.49	8.04
Lysine*	6.29±0,38	5.13±0.20	7.63	6.13
Total	74.25	56.71	87.46	91.31
essential aa	38.27	30.65	39.05	48.30
non essential aa	35.98	26.06	48.41	43.01

* essential amino acid

** Chalamaiah *et al.* (2012)

*** Buentello *et al.* (2011)

frying (7.913±0.141%) (db). According to Ghidurus *et al.* (2010), the frying process didn't significantly affect the mineral content of food because minerals were relatively resistant to high temperatures and some types of minerals are not soluble in oil but soluble in water. Mineral content in palm oils could also affect the mineral content of fried skipjack. Kok *et al.* (2011) showed that the palm oil containing Fe (5.20 mg/100 g of material), Ca (217±21.2 mg/100 g), and K (693±108 mg/100 g). Frying process can lead the absorption of mineral oil into the food .

Carbohydrate content

Carbohydrates (db) content of fresh and fried skipjack was (3.067±0.953%) and (3.099±1.19%). Fish carbohydrates was a polysaccharide glycogen. Glycogen content of fishery products was approximately 1% for fish (Okuzumi and Fuzii, 2000). Glycogen was found in the sarcoplasmic between myofibrils. Carbohydrate content in fish include (0.05-0.85%) glycogen, 0.038% glucose, and (0.006-0.43%) lactic acid (Adawyah, 2007).

Fatty acid profile

Fresh skipjack contained 30 kinds of fatty acids composed of 12 types of saturated fatty acids (SAFA),7 types of monounsaturated fatty acids (MUFA) and 11 of polyunsaturated fatty acids (PUFA). Result of fatty acid compositions is presented in Table 2. Fatty acids were not detected in meat that were 36.87% of fresh skipjack and 16.42% of fried skipjack. Soxhlet method that used for extraction of fat fatty acids was thought to affect the results obtained. The results of Ozogul *et al.* (2012) said that Soxhlet method is less efficient in extracting fat either polar or non-polar, and less able to prevent loss due to oxidation of PUFAs compared with another (Bligh and Dryer method).

Analysis found that there is trans configuration in a fatty acid compound. According Sartika (2009), the formation of trans fatty acids may be caused by the use of high temperature during the frying process. Suwandi *et al.* (1989) said that the higher temperature will speed up the process of degradation and oxidation of frying oil. Oxidation process at unsaturated fatty acid bonds will cause chain reactions that produces alcohols, aldehydes, hydrocarbons, and trans configurations. According to Salamon *et al.* (2009), fatty acid with cis configuration substantially less stable. So it will be reduced after the heating process.

Frying process 5 minutes at 180^{o}C thought to trigger the formation of trans configuration in the sample. Analysis of fatty acids using Soxhlet method allows the formation of trans fatty acid. Edward *et al.* (2011) said that trans configuration will be more resulting from polyunsaturated fatty acid oxidations. The formation of trans groups will be more harmful to the body because human body has a cis configuration in the unsaturated fatty acid. The composition of the trans is not recognized by the body system, so it will stimulate the expression of several genes in endothelial cells causing endothelial cell damage and atherosclerosis. Change of the unsaturated fatty acids into trans fatty acids can also increase low-density lipoprotein (LDL) and decrease high-density lipoprotein (HDL) which will increase the risk factors

Table 4. Composition of macro and micro mineral in skipjack

Mineral	Total (ppm)			
	Fresh skipjack	Fried skipjack	Fresh skipjack*	Fresh *rainbow trout* **
Macro				
Na	1993.47±268.28	1865.37± 74.33	1373.30	455.00
K	7966.54±834.14	8316.22±141.55	2938.40	3060.00
Ca	506.00± 47.69	843.06± 86.41	359.70	632.00
Micro				
Fe	63.49±14.62	66.03±10.64	32.90	2.10
Zn	24.70± 1.19	20.53± 2.58	17.00	9.68
Cu	-	-	3.90	0.33

* Karunarathna and Attygalle (2009)
** Gokoglu *et al.* (2004)

in atherosclerosis.

Skipjack frying process had n-6/n-3 ratio about 0.11 in fresh condition and 2.07 in after frying. This ratio is in accordance with HMSO recommendation (1994) which stated the maximum n-6/n-3 ratio was 4. Ratio n6/n3 is a index for comparing relative nutritional value of fish oil. Domiszewski *et al.* (2011) reported that if n6/n3 ratio higher than the maximum standard, it will be harmful to health and lead to cardiovascular disease.

Fresh skipjack contained 63.09% fatty acids and fried skipjack contained 82.07%. Fried skipjack fatty acids increased 23.13% in relative terms. These changes were caused by the frying process using cooking oil. Generally, frying process can reduce level of fatty acids. Decreased levels of fatty acid are caused by fat oxidation. Research by Gladyshev *et al.* (2006) about the processing effect on the content of salmon *(Oncorhynchus gorbuscha)* saturated fatty acids mentions that the frying process will produce carbonyl compounds derived from lipid oxidation. Oxidative damage usually occurs in unsaturated fatty acids, but when the oil is heated at ≥100°C, saturated fatty acids also can be oxidized (Jacobson, 1967). Frying process can increase the levels of caprylic, capric, palmitic, oleic, and linoleic acid. Increased levels of palmitate on fried skipjack were caused by cooking oil that has been absorbed into the flesh of the fish during frying process, so the cooking oil fatty acid content was absorbed into the flesh of the fish.

Fresh skipjack contained 3.48% eicosapentaenoic acid (EPA) and 19.27% docosahexaenoic acid (DHA), fried skipjack contained 0.52% EPA and 3.44% DHA. Relative EPA reduction was 85.06% and DHA was 82.15 %. Research by Tůrkkan *et al.* (2008) showed the effect of seabass (Dicentrarchus labrax) frying process can reduce 30% EPA and 28% DHA . According Domiszewski *et al*. (2011), the effect of catfish (*Pangasius* sp.) frying process (6 min 180°C) can reduce both relative EPA and DHA about 71.43% and 72.19%. Different decrease between EPA and DHA caused by sensitive nature of EPA and DHA influenced by 4 factors, namely duration of heating, temperature, composition of fatty acids,

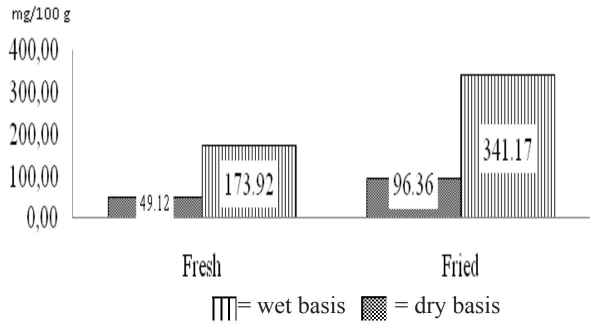

Figure 1. Cholesterol content of fresh and fried skipjack

and position of fatty acid bound in the triglyceride molecule (Ketaren, 1986). Marichamy *et al.* (2009) said that factors such as fat content, processing temperature, fish size and surface contact area can affect the composition of fish fat after cooking process. The longer carbon chain in fatty acids makes up the higher melting point and the lower water solubility of fatty acids (Kusnandar, 2010).

Cholesterol

The average cholesterol was 49.12 mg/100 g for fresh skipjack and 173.92 mg/100 g for fried skipjack (Figure 1). Okuzumi and Fujii (2000) said that skipjack has 0.064% or 64 mg/100 g cholesterol. Cholesterol variation is influenced by several factors such as species, food availability, age, sex, water temperature, geographic location, and season (Sampaio *et al.,* 2006).

Liebermann - Buchard Colour Reaction method is the extraction phase method. This method calculates the levels of cholesterol and other sterols contained in the sample (Kenny, 1952). So that other sterols from cooking oil (palm oil) can be calculated. Palm oil that used contains phytosterol. Phytosterol contains 28-29 atoms alcoholic steroid. Phytosterol and cholesterol have the same structure but phytosterol has an extra methyl or ethyl branches in the chain. The main phytosterols in palm oil are sitosterol 350-410 µg/g oil, campesterol 140-180 µg/g oil, stigmasterol 70-100 µg/g oil, and avenasterol 0-30 µg/g oil (Tabee, 2008).

Amino acids

The composition of skipjack's amino acids in dry basis and comparison with mackerel and tuna could be seen in Table 3. Results of this study indicate that skipjack contained 15 kinds of amino acids consisting of 9 essential amino acids (histidine, threonine, tyrosine, methionine, valine, phenylalanine, i-leucine, leucine , and lysine) and 6 non essential amino acids (aspartic acid, glutamic acid, serine, glycine, arginine, and alanine). Total amino acids in fresh skipjack was 74.25 g/100 g which is the cumulative result of the total essential amino acid was 38.27 g/100 g and non essential amino acid was 35.98 g/100 g.

There were several kinds of essential amino acids were not detected in these tests, tryptophan and cysteine. Hydrolysis process destroyed all the tryptophan and cysteine . Tryptophan can be detected by alkaline hydrolysis (Jacoeb *et al*., 2008). Hydrolysis type in this test was acid hydrolysis. Table 2 showed that the amino acid composition decreased after the frying process. The percentage decrease was 23.62%. These results were supported by Oluwaniyi and Dosumu (2009), showed the total amino acid of Trachurus trachurus decreased 6.21% after frying process. According to Nurhidajah *et al*. (2009), amino acids were reactived by heating. Explained further by Oluwaniyi *et al.* (2010), processed of food contained carbohydrates and protein could cause a Maillard reaction. Maillard reaction was a reaction between the amino group with the aldehyde group of the reducing sugar. It reduced the availability of amino acids. Most of the amino acid content in fried skipjack was reduced and was converted to melanoid pigment in the food.

The highest content of non essential amino acid in the fresh and fried skipjack was glutamic acid with respective values of 11.22±0.14 g/100g and 8.48±0.10 g/100g. The results study of Chalamaiah *et al*. (2012) showed that a high content of glutamic acid was also found in mackerel *(Scomber japonica)* with a value 15.84 g/100 g. According to Oladapa *et al.* (1984), glutamic acid can create the characteristic of aroma and taste of the food. One of the product of skipjack in Japan was katsuobushi, the main ingredient of dashi.

Table 3 showed that the highest content of essential amino acids in skipjack and yellowfin tuna was histidine. Histidine content of the fresh and fried skipjack respectively were 6.72±0.12 g/100 g and 5.51±0.28 g/100 g. This result was lower than histidine content in yellowfin tuna (Buentello *et al*., 2011) was 15.57 g/100 g. The differences of amino acid composition could be caused by fish species, sex, age, environment, food, and fishing season (Nurjanah *et al*., 2005). Histidine can repair the body tissues and produce red blood cells. Histidine also play a role of histamine synthesis (Fitri, 2012).

Limiting amino acid was amino acid that usually lack in foods (Nurhidajah *et al.*, 2009). Limiting amino acid in both of fresh and fried skipjack was methionine, respectively 2.16±0.04 g/100 g and 1.79±0.04 g/100 g. Methionine gave a methyl group for the synthesis of choline and creatinine. Methionine wass also a precursor of cysteine (Harli, 2008). Lack of methionine content in skipjack could be covered by the consumption of other foods that were rich in methionine. Protein quality was determined by the types and proportions of amino acids. High quality protein was the protein that contained all the essential amino acids in a good portion to support the growth (Almatsier, 2006).

Various types of amino acids have a specific function for the body. Tryptophan is the precursor of vitamin niacin and serotonin nerve introduction. Phenylalanine and tyrosine are precursors to form thyroxine and epinephrine hormones. Tyrosine is a materials precursor to form the skin and hair pigment. Arginine and sentrulin involved in the synthesis of urea and liver. Glycine binds toxic materials and turns them into harmless materials (Almatsier, 2006). Leucine helps reduce muscle protein breakdown. Isoleucine supplies energy to muscle and prevent the breakdown of muscle. Isoleucine also plays an important role in the formation of hemoglobin. Cysteine can fight free radicals that cause cell damage. Lysine is important for muscle growth and repair. Lysine and vitamin C play an important role in the formation of collagen (Fitri, 2012).

Mineral

Macro and micro mineral composition of fresh and fried skipjack expressed in dry basis. Macro and micro mineral composition of fresh and fried skipjack and its comparison with the other studies were shown in Table 4. Table 2 showed that skipjack contained macro minerals such as sodium (Na), potassium (K), calcium (Ca), and micro minerals such as zinc (Zn) and iron (Fe). Macro minerals are minerals that needs in the amount of more than 100 mg a day, the micro minerals needed less than 100 mg a day. Frying process caused an increase and a decrease in some minerals . Mineral content of sodium (Na) and zinc (Zn) decreased after the frying process, otherwise the mineral potassium (K), calcium (Ca), and iron (Fe) increased after the frying process. Content of copper (Cu) in this study was not detected. Potassium was highest mineral in this study, 7966.54±834.14 ppm for fresh skipjack and 8316.22±141.55 ppm for fried skipjack. Increased of minerals K, Ca, and Fe could be caused by the absorption of minerals contained in the oil. Palm oin contained 693 ± 108 mg/100 g potassium, 217 ± 21.2 mg/100 g calcium, and 5.20 mg/100 g of iron (Kok *et al*., 2011). Decreased levels of Na caused by the loss of Na with body fluids during the heating process. Sodium is mainly present in the extracellular fluid together with chloride and bicarbonate. The main element is missing when the body fluid lost are sodium (deMan, 1997). Aisyah (2012) added that the loss of sodium during cooking can not be avoided because of sodium can be melted at 97.5^{o}C. Zn levels decreased after processing due to degradation of metallothionine. Zinc is a component of protein that has -SH groups (metallothionine) and act as free radical scavengers (Nurjanah *et al*., 2005). Mineral not affected by chemical and physical treatment during processing (Palupi *et al*., 2007). Minerals are part of the body and plays an important role in the maintenance of body functions, both at the level of cells, tissues, organs, or body functions as a whole .

Comparison of the mineral composition between fresh skipjack in this study, Karunarathna and Atygalle (2009), and fresh rainbow trout (Gokoglu *et al.*, 2004) showed a difference content. Mineral composition of skipjack in this study was higher than both comparator fish. It can be caused by the used of distilled water in this study. Mineral analyzed preferably using deionized water than using distilled water because there is still the possibility of some mineral content in distilled water. Table 2 also showed that the mineral potassium was the highest macro minerals and copper was the lowest micro minerals on the third fish. According to Nurjanah *et al*. (2005), differences in mineral composition can be affected by differences in environmental conditions, species, sex, age, and fishing season.

Conclusion

The frying process in skipjack reduced levels of water, proteins, amino acids, most of the fatty acids such as EPA and DHA, Na, and Zn minerals. The chemical composition of fresh skipjack was 71.76% moisture, 25.29% protein, 0.60% fat, 1.49% ash, and 0.87% carbohydrates, while the chemical composition of fried skipjack was 48.25% moisture, 41.25% protein , 4.80% fat , 4.10% ash , and 1.60% carbohydrate. Fresh skipjack contained 30 kinds of fatty acids (12 SAFA, 7 MUFA , 11 PUFA) and decreased to 25 types of fatty acids (12 SAFA, 6 MUFA, and 7 PUFA) after frying. Cholesterol level of fresh skipjack was 49.12 mg/100 g and increased to after frying became 173.92 mg/100 g. Skipjack contained 9 essential amino acids and 6 nonessential amino acids with a total of 74.25 g/100 g amino acids. The highest mineral content in fresh skipjack was potassium 7966.54 ppm and increased after the frying process became 8316.22 ppm.

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