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Separation and quality of fish oil from precooked and non-precooked tuna heads

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Abstract

Separation of crude oil from precooked and non-precooked skipjack tuna heads by a wet reduction method was carried out. Both heating temperature and time affected the separation and oil quality. Optimum conditions for separation of crude oil involved heating samples at 85°C for 30 min, followed by pressing at 140 tons/m^2 using a hydraulic press. Yields of crude oil prepared from precooked and non-precooked samples were 2.8 and 4.8%, respectively. Crude oil obtained from non-precooked samples showed markedly higher quality than that from precooked samples. Crude oil from precooked samples had a higher peroxide value and much darker colour than that from non-precooked samples. However, crude oil from precooked samples had higher DHA (25.5%) than that from non-precooked samples (18.8%).

1. Introduction

Fish oil has been considered as an available source of long chain polyunsaturated n-3 fatty acids, especially eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA). These fatty acids are recognized to play an essential role in human health and nutrition (Newton, 1996). Consequently, the research with long chain n-3 polyunsaturated fatty acids continues to focus on a myriad of conditions and diseases (Haumann, 1997). Also, increasing research has been conducted on extraction, concentration and stability of fish oil. Fish oil can be produced by several methods, including physical fractionation (Hirata, Saeki, Nonaka, Kawasaki, Ooizumi & Motoe, 1993), low temperature solvent fractionation (Moffat, McGill, Hardy & Anderson, 1993) and supercritical fluid extraction (Dunford, Temelli & LeBlanc, 1997). However, wet reduction, including cooking, pressing and centrifuging to recover the oil from the miscella is the common method used to produce fish oil (Bimbo, 1990; Pigott & Tucker, 1990). Many approaches using an enzymatic method have been carried out to increase the concentration of n-3 fatty acids in fish oil (Moore & McNeill, 1996; Shimada, Marvyama, Sugihara, Moriyama & Tominaga, 1997).

Thailand has become the world's largest exporter of canned tuna and largest importer of fresh and frozen tuna (Crough, 1991). There are 21 tuna-canning factories in the country with a total annual capacity of 647,000 tons (Srikumlaitong, Narkdee, Aiemwat, Arsa, Jenwanichbunjakul & Laichuthia, 1995). During the tuna processing, precooking is a process needed prior to cleaning. Practically, the whole tuna was steamed, followed by deheading (Finch, 1963). Therefore, tuna heads are generated as by-products, which are normally used as animal feeds. So far, pre-cooked tuna heads have been used as a raw material for fish oil production in Thailand.

Deheading of tuna before precooking is an alternative process, which would save energy for precooking and possibly produce higher quality fish oil. However, no information exists about the comparison between the oils produced from non-precooked and precooked tuna head. Therefore, this study aimed to compare the yield as well as the quality of oil from non-precooked and precooked tuna heads.

2. Materials and methods

2.1. Preparation of tuna heads

Non-precooked and precooked skipjack tuna heads were obtained from the tuna processing plant in Hat Yai, Songkhla, Thailand. Skipjack tuna was caught in

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the Indian ocean and shipped to the plant as a frozen whole fish. Precooked samples were previously heated at 100°C for 60 min and cooled down with sprayed water. The samples were kept at −20°C until used.

2.2. Separation of oil from tuna heads

Separation of crude oil was carried out by wet-reduction, according to the method of Bimbo (1990) with a slight modification. The frozen tuna heads were thawed at 4°C overnight. Thawed samples were heated by steam at 75, 85, and 95°C each with heating times of 10, 20 and 30 min, followed by pressing at 140 tons/m^2 using a hydraulic press (Carver model W102, USA). The oil released was recovered by centrifuging the crude oil and water emulsion at 9600×g at 4°C for 20 min (Hitachi, SCR 20B, Japan). Crude oil at the top layer was collected and kept at −20°C until analysed.

2.3. Determination of yield

Yield was expressed as a percentage of oil separated from non-precooked and precooked tuna heads. Yield was calculated as follows:

$$\%\text{Yield} = \frac{\text{wt. of crude oil} \times 100}{\text{wt. of non-precooked or precooked tuna heads}}$$

2.4. Chemical and physical analysis

Chemical compositions and properties, including free fatty acid, peroxide value, unsaponified matter, saponification number and iodine value were determined using the IUPAC (1974) method. Photometric colour index was measured by the AOCS (1986) method.

2.5. Fatty acid analysis

Fatty acid profiles were determined by preparation of methyl esters as described by IUPAC (1974). The fatty acid methyl esters were identified by the gas chromatography (Varian 3400, USA) equipped with flame ionization detector and integrator. A capillary column (30 m×0.25 mm, DB-23, J&W Scientific Co., USA) was used. The temperature for injector and detector were 250 and 300°C, respectively. The fatty acid methyl esters were identified by comparison with standards (Sigma Chemical Co., St. Louis, USA) and were quantified as the area percentage of each fatty acid methyl ester.

2.6. Statistical analysis

The experiment was run in triplicate with a 3×3 factorial in completely randomized design (CRD). The data were subjected to analysis of variance (ANOVA). The differences among the treatments were determined using Duncan's multiple range test (DMRT) (Steel & Torrie, 1980).

3. Results and discussion

3.1. Yield of crude oil from tuna heads

Yields obtained after different treatments are shown in Fig. 1. The highest yield was observed at 85°C ($P < 0.05$). Lower temperatures rendered a lower yield ($P < 0.05$), possibly due to the fact that lipid cells were ruptured to a greater extent with 85°C. Cooking can coagulate the protein of fish, so that liquids and solids can be mechanically separated. Fat cells are also disrupted, releasing oil into the liquid phase (Bimbo, 1990). However, a low yield was found with heating at 95°C. It is postulated that the proteins were denatured and a tightly packed protein structure was generated, leading to the prevention of oil release. Proteins normally undergo irreversible denaturation when heated at 90–100°C for a prolonged period even at neutral pH (Ahren & Klibanov, 1985). A higher yield was generally

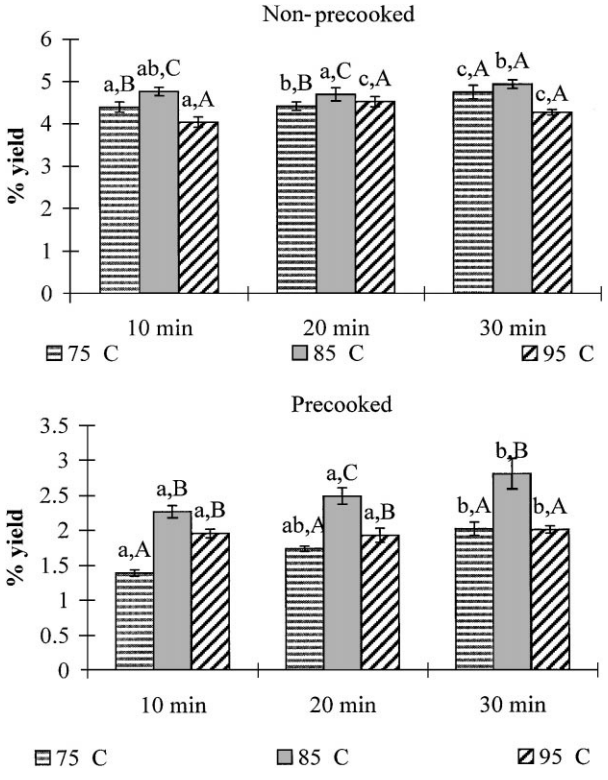

Fig. 1. Yield of oils from non-precooked and precooked tuna heads separated under different conditions. Tuna heads were heated at different temperatures and times, followed by pressing at 140 tons/m^2. Different letters within the same temperature indicate significant differences ($P < 0.05$), and different capital letters within the same separating time indicate significant differences ($P < 0.05$).

observed, when a longer heating time was applied. The optimum conditions for oil separation from both non-precooked and precooked tuna heads were heating the sample at 85°C for 30 min, followed by pressing at 140 ton/m^2 with yields of 4.8 and 2.8%, respectively.

3.2. Free fatty acid (FFA)

FFA content of oils separated under different conditions is presented in Fig. 2. For oils both from non-precooked and precooked samples, a low FFA content was found when heated at 75°C for either 10 or 20 min. However, a high FFA content was obtained when heated at 75°C for 30 min. Generally, oils prepared at higher temperatures had higher FFA. This result indicated that the hydrolysis of ester bonds of triglyceride occurred less at lower temperatures. Oil can undergo hydrolysis in the presence of moisture and heat (Nawar, 1996). Oil prepared from precooked samples heated at 85 or 95°C has a similar FFA content. However, a low FFA content was found in oil prepared from non-precooked samples by heating at 95°C. The loss of volatile FFA probably occurred at very high temperature (95°C), leading to a decreased FFA content. These FFA can be removed during the refining process of oil (Bimbo, 1990).

3.3. Peroxide value (PV)

Oils prepared from precooked samples had extremely high PV (> 200 mg/kg), compared with PVs of about 25 mg/kg in oil from non-precooked samples (Fig. 3). Heat-processing denatures iron-containing proteins, particularly myoglobin, causing release of iron into the catalytic pool (Decker & Welch, 1990). The precipitated iron-containing proteins could associate with lipid membrane and bring iron into closer proximity with the oxidation substrate (Decker & Xu, 1998). Due to the repeated heating of precooked samples, it was feasible that precooked tuna head contained more free iron, resulting in a higher oxidation rate. For oil from precooked samples, PV decreased when samples were heated at either higher temperatures or longer times. This is probably due to the decomposition of hydroperoxides. For non-precooked samples, a low PV was found in oil prepared by heating at 95°C. It was presumed that lipoxygenase in tuna head skin was possibly inactivated completely at high temperature. Lipoxygenase

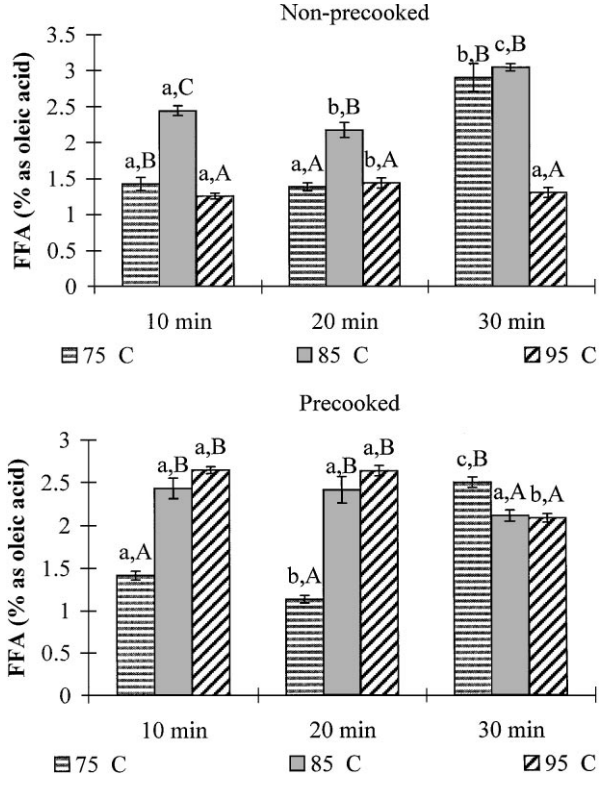

Fig. 2. Free fatty acids of oils from non-precooked and precooked tuna heads separated under different conditions. Tuna heads were heated at different temperatures and times, followed by pressing at 140 tons/m^2. Different letters within the same temperature indicate significant differences ($P < 0.05$), and different capital letters within the same separating time indicate significant differences ($P < 0.05$).

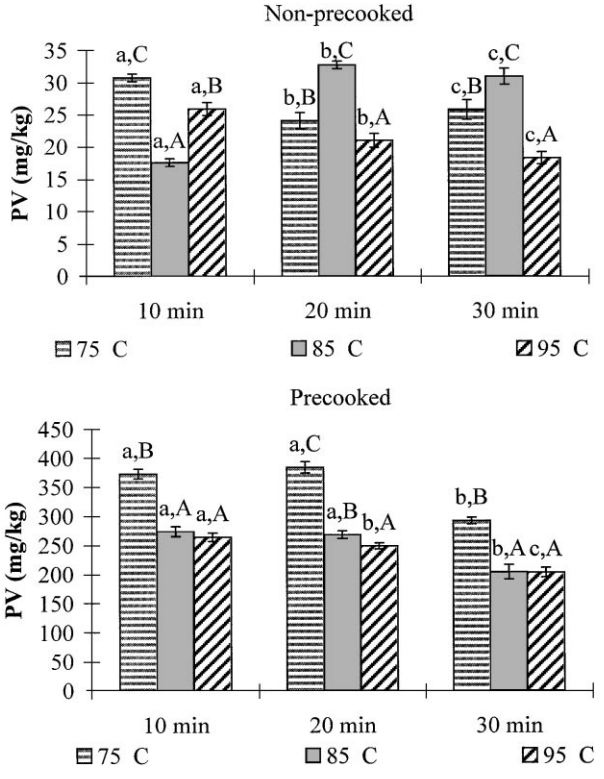

Fig. 3. Peroxide value of oils from non-precooked and precooked tuna heads separated under different conditions. Tuna heads were heated at different temperatures and times, followed by pressing at 140 tons/m^2. Different letters within the same temperature indicate significant differences ($P < 0.05$), and different capital letters within the same separating time indicate significant differences ($P < 0.05$).

in skin could accelerate the lipid deterioration in underlying muscle tissue (German & Kinsella, 1985). Low PV was also possibly due to the decomposition of hydroperoxides. At 85°C, the oil prepared from non-precooked samples had a higher PV as the heating time increased. Oil can undergo oxidation much more as the time increases.

3.4. Iodine value (IV)

For non-precooked samples, oils prepared at lower temperature had higher IV than those prepared at higher temperatures ($P < 0.05$). Double bonds of fatty acid were probably oxidized during heating. No differences were seen in IV in oil from precooked samples prepared with different conditions ($P > 0.05$). IV of non-precooked samples was generally higher than that of oil prepared from precooked samples (Table 1). One of the common trading standards of fish oils is the iodine value (IV). The IV of monoethylenic fatty acid are 90 for 18:1 and 420 for 20: 5 n-3 (Ackman, 1994). It was found that IV of crude oil from tuna heads ranged from 122 to 174. This is due to the fact that crude oil contained a variety of fatty acids.

3.5. Saponification number (SN)

SN of oils prepared from each raw material, non-precooked and precooked samples under different conditions were not different ($P > 0.05$) (data not shown). However, SN of oil from non-precooked samples (159.6–196.9 mg KOH/g) was lower than those of oil from precooked samples (217.3–235.7 mg KOH/g) ($P < 0.05$), indicating that oil from non-precooked samples had higher molecular weight fatty acids than oil from precooked samples (Low & Ng, 1987). From the fatty acid profile, it was found that the both crude oils prepared from precooked and non-precooked tuna heads had similar profiles of fatty acids. Since many oils have similar values, SN is not useful for identification purposes. It is useful for detecting the presence of oil and fats, which contain a high proportion of lower fatty acids (Low & Ng, 1987).

Table 1
Iodine value of crude oils from non-precooked and precooked tuna heads prepared under different conditions

Iodine value (g iodine/100 g)	Heating time (min)	Heating temperature (°C)		
		75	85	95
Non-precooked	10	147a[a]	172a	161a
Precooked		132b	145b	138b
Non-precooked	20	149a	174a	156a
Precooked		146b	123b	145b
Non-precooked	30	160a	173a	147a
Precooked		147b	154b	132b

[a] Means with different letters in each column under the same heating time are significantly different ($P < 0.05$).

3.6. Unsaponified matter (USM)

No differences in USM were observed among the oils prepared under different conditions from both raw materials, precooked and non-precooked samples ($P > 0.05$). However, USM of oil from precooked samples (3.6–4.1%) was much higher than that of oil from non-precooked samples (0.6–1.0%) ($P < 0.05$). It is possible that oil from precooked samples contained non-triglyceride substances, e.g. hydrocarbons, higher alcohols, and sterols, which can be released much more during two steps of heating. Also, degradation products from oxidation reaction probably contributed to the high USM. Bimbo and Crowther (1991) reported that crude oil contains minor amounts of non-triglyceride substances. Some impurities are objectionable because they render the oil dark-coloured, and cause foaming, smoking or precipitation when the oil is further processed.

3.7. Fatty acid profile

Crude oils from both precooked and non-precooked tuna head prepared under optimum conditions (85°C, 30 min) had high amounts of palmitic acid (C16:0), oleic acid (C18:1) and docosahexaenoic acid (C22:6) (> 10%), with myristic acid (C14:0), palmitoleic acid (C16:1), stearic acid (C18:) and behenic acid (C22:0) at more than 5% (Table 2). Among the saturated fatty acids, palmitic acid (C16:0) was a dominant fatty acid. Oleic

Table 2
Fatty acid profiles of oils from non-precooked and precooked tuna heads

Fatty acids (% of total fatty acid)	Non-precooked	Precooked
C6:0	0.0	0.0
C8:0	0.0	0.0
C10:0	0.0	0.0
C12:0	0.1	0.0
C14:0	5.8	5.0
C15:0	1.9	1.7
C16:0	30.3	27.9
C16:1	6.4	5.3
C18:0	7.9	7.5
C18:1	16.5	14.1
C18:2	2.0	1.6
C18:3	0.6	0.6
C18:4	2.0	2.1
C20:0	0.6	0.5
C20:1	2.0	1.8
C20:5	0.1	0.1
C22:0	5.1	6.2
C22:1	0.1	0.1
C22:6	18.8	25.5
C24:0	0.0	0.0

acid (C18:1) was a major monounsaturated fatty acid. The short chain fatty acids were found at very low content. This result was in agreement with Stansby, Schlenk and Gruger (1990) who reported that DHA is often considerably higher in the oils of various species of tuna than in that of most other species. Ando, Ota, Matsuhira and Yazawa (1996) found that tuna orbital oil contained much higher amounts of DHA than EPA. Shimada et al. (1997) reported that tuna oil contained 6.5% EPA and 22.9% DHA. The difference in fatty acid compositions observed in this experiment, comparing them to those reports, was probably due to the differences in raw material and the fish oil process used. Orbital fats of bonito and tuna are excellent sources of 22:6 n-3 (Yazawa, Watanabe, Ichikawa & Kondo, 1991). From this experiment, the eyes in tuna head could be an important source of DHA. However, a very low content of EPA was noted. When the DHA contents in both crude oils from precooked and non-precooked tuna heads were compared, it was found that the former had a slightly higher content of DHA. Double heating possibly resulted in a higher release of phospholipids located in the cell membrane. As a result, unsaponified matter was much higher in the oil from precooked tuna head. Phospholipid has been reported to contain more polyunsaturated fatty acids than triglycerides (Stansby, Schlenk & Gruger 1990). Therefore, the oil from tuna head can be used as a good source of DHA.

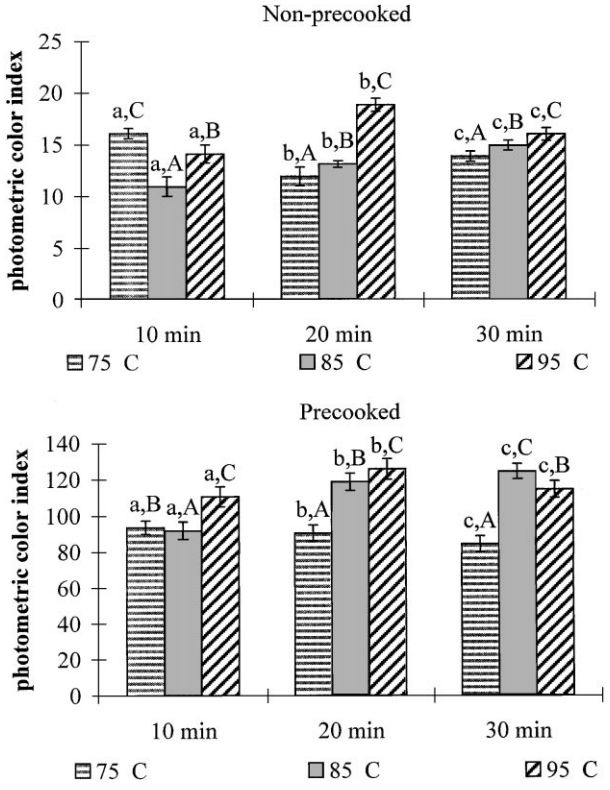

Fig. 4. Photometric colour index of oils from non-precooked and precooked tuna heads separated under different conditions. Tuna heads were heated at different temperatures and times, followed by pressing at 140 tons/m^2. Different letters within the same temperature indicate significant differences ($P < 0.05$), and different capital letters within the same separating time indicate significant differences ($P < 0.05$).

3.8. Colour

Oils from precooked samples had much higher photometric colour indices than oils from non-precooked samples (Fig. 4). During the precooking process, proteins and carbohydrates were decomposed and the degradation products could adulterate the oil, leading to the darker colour (Swern, 1964). The aldehydes in autoxidized fish oil, such as 2-hexenal and acedaldehyde, appear to react by aldol condensation and dehydration to form crotonaldehyde and 2-(1-butenyl)-octa-2,4-dienal, as the main reaction during the early stage of browning (Fujimoto & Kaneda, 1973). Since crude oil from precooked samples had very high PV (Fig. 3), degradation products, e.g. aldehydes, could easily be produced and these undergo browning reaction. As a result, a darker colour was obtained in the oil from precooked samples. Furthermore, the Maillard reaction presumably occurred during precooking, resulting in the brown product formation.

4. Conclusion

Optimum conditions for tuna head oil separation involved heating samples at 85°C for 30 min, followed by pressing at 140 tons/m^2 using a hydraulic press. Oil from non-precooked samples gave a superior yield and quality compared to the oil from precooked samples. Nevertheless, DHA was higher in crude oil from precooked tuna heads.

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