Changes in Quality of Seasoned and Smoked Squid During Processing

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Changes in proximate composition and protein quality were determined to find out appropriate processing conditions of the seasoned and smoked squid(Neon flying squid, Ommastrephes bartrannii). Moisture and crude protein contents were severely reduced (p<0.05), while increasing of fat and ash contents were not apparent. Seasoning and smoking contributed in enhancing TBA value. Trypsin inhibitor(TI) content was not increased severely after those processing steps. TI content checked in the all steps of squid processing was not correlated with the TBA value of squid in the same processing step. An improved digestibility and protein efficiency ratio(PER) were observed in the all products except with steak(mechanically soften product). In vitro enzymatic digestibilities of both raw Neon flying squid meats(mantle and arm) were significantly inferior(p<0.05) to other squid species.

Introduction

Neon flying squid(Ommatrephes bartranii) provide approximately 60% of the total pelagic squid caught in Korea(Kong, 1990), and it is consumed popularly as the seasoned and smoked products. With the decrease in the availability of traditional pelagic squids caught using gillnet fishing, the demand for the effective utilizing appears to be growing. On the other hand, like other fishery products, those squids have been processed only for satisfying consumer's organoleptic appetite by improving its taste with various additives and textural properties without testing the effect of processing conditions on nutritional quality. Due to a growing concern about availability nutritional data of seafoods, it is becoming important to study the beneficial processing conditions that can produce superior products nutritionally rather than satisfying the consumer's organoleptic appetite. Hence, the primary focus of this research was to check the changes of the proximate composition and *in vitro* protein qualities related with trypsin inhibitor(TI) content in the seasoned and smoked squid products through every steps of processing. TBA value was also measured to know the relationship between the peroxides and trypsin inhibitor.

Materials and Methods

1. Sample collection and preparation

Frozen Neon flying squid(Ommatrephes bartranii) was obtained by the courtesy of Suh-Jin Food Co. in Young-Il Korea and its previous history was unavailable. The averages of total length and weight of squid mantle were 42.5 cm and 1,520 gram, respectively. Packaged frozen squids(mantle and tentacles) were thawed in flowing water of 13°C for 3 hours and used them as raw samples. Beka squid (Loligo beka) and Japanese flying squid were purchased from local fish market in the frozen form to compare its protein qualities with Neon flying squid. Skinning was practiced in 55 °C of warm water for 8 minutes with industrial scale (260 kg of thawed mantle in 150 liter of water). The skinned squid was then passed for 5 minutes through continuous conveyor system maintaining the temperature of 95°C and them chilled in water tank of 15°C for 20 minutes. Marinated squid was soaked a mixtured seasoning for 6 hours. The mixtured seasoning contains 15 gram of sucrose, NaCl, monosodium glutamate (MSG) and citrate dissolved in 100 ml of water. Seasoned squid was drained and dried in a hot air blast dryer at 38°C for 6 hours so that its moisture content reached to 55%. Hot-smoking process was employed in preparing the smoked products. The hot air blast dried squid was placed inside the hooded grill having oaktree chips and smoked at 80°C for 50 minutes. After smoking, squid was sterilized using steam heating process (95℃, 30 min.).

2. Chemical analysis

Crude protein($N \times 6.25$) and total lipid content on the edible portions of squid mantle and tentacles were determined by the methods described in AOAC mannual(AOAC, 1984).

Moisture content was determined by drying samples in a vacuum drying oven (15 mmHg) for 8 hours at 100 °C. Samples for ash determination were heated in a muffle furnace at 550°C for 6 hours to constant weight. TBA value was measured by the method of Turner (1954) using 2-thiobarbituric acid reagent. Trypsin inhibitor(TI) content was determined using the procedure of Ryu(1983) which is modified from Rhinehart method (1975). Results of TI are expressed in trypsin inhibitor equivalent, which equals the mg of purified soybean trypsin inhibitor per gram sample. The correlation coefficient between pH and TI content was 0.9935 and the equation for calculation is Y = 4.0307X - 27.63, where Y = purified soybean trypsin inhibitor(mg) and X=pH at 10 minutes incubation.

3. Amino acid analysis

The edible portion of each squid sample was hydrolyzed in 6N HCl under vacuum at $100\,^{\circ}$ C for 25 hours. The hydrolysates were injected into a LKB Autoanalyzer(4150, α -type) for the determination of amion acids. Tryptophan was released using an alkaline hydrolysis by Hugli and Moore method (1972), and sulfur-containing amino acids were quantitatively oxidized using performic acid(Spencer and Wold, 1969).

4. Protein quality

The *in vitro* protein digestibilities of the all samples were measured by the AOAC procedure (1982) using four enzymes including trypsin(Sigma, 14,600 BAEE units/mg solid), α-chymotrypsin(Sigma, 41 units/g solid), peptidase(Sigma, 50 units/g solid) and bacterial protease(Streptomyces griceus, Sigma, 58 units/mg solid). The reference protein used in digestibility assay was ANRC casein. Computed protein efficiency ratio(C-PER), discriminant computed protein efficiency ratio(DC-PER) and predicted digestibility were calculated using the corrected procedure of AOAC(1982). Protein digestibility via a procedure using four enzyme, and amino acid profiles were used in calculation C-PER.

Predicted digestibility and DC-PER were calculated solely from amino acid profiles of sample proteins.

Results and Discussion

1. Proximate composition

The changes of proximate composition of squid products at different stages of processing is shown in Table 1. Mantles and tentacles were sampled and processed separately, and proximate composition of the two kinds of Korean coastal squids, such as Beka squid and Japanese flying squid, were also analyzed to compare the its food quality with Neon flying squid. Moisture contents of both squid samples were not changed until skinning step, and those products contained moisture levels ranging from a low of 78.4% for raw mantle to a high of 82.3% for mantle steak. These values were within the va-

lues reported by Hashimoto et al.(1979), and Suyama and Kobayashi(1980). Boiled products showed a lower moisture content than raw ones by 5%, and there was a significant(p<0.05) reduction(28%) in moisture content of finally smoked squid products. Protein content of squids before boiling stage was about 80% for mantle and 74% for tentacles as moisture free basis. It should be noted that both raw Neon flying squid samples have more protein than those of other coastal squids. Protein levels were lowered by 7% for mantle and 10.4% for tentacles in boiled products because nitrogen compounds were extracted by water. These results were compared well with those reported by Saka-

moto et al.(1979). Crude fat and ash content of raw and processed squids were similar to the results by other researchers(Lee et al. 1974, Suyama and Kobayashi 1980, Jhaveri et al. 1984, Krzynowek et al. 1989). The analysis of the skinned mantle and tentacles showed a decrease in fat and a consequent increase of the ash, as the process of seasoning.

2. Trypsin inhibitor and TBA value

Table 2 shows comparison of TI and TBA value Neon flying squid during processing.

Generally, TI includes typical proteinous inhibitory materials contained in raw sources and indigestible materials induced from the results of intera-

Table 1. Changes in proximate compositions through the commercial seasoned squid processing
% wet basis(% moisture free basis)

Samples	Moisture	Crude protein	Crude fat	Crude ash	
Mantle		(N×6.25)			
Raw	78.4	16.85(78.03)	1.26(5.84)	1.41(6.07)	
Steak	82.3	14.28(80.77)	0.67(3.76)	1.30(7.33)	
Skinned	80.6	15.80(81.28)	0.42(2.17)	1.35(6.97)	
Boiled	75.9	17.15(71.16)	0.48(1.99)	1.39(5.77)	
Seasoned	65.9	20.64(60.49)	0.75(2.21)	3.03(8.91)	
Air blast dried	49.3	31.46(62.00)	1.58(3.11)	3.37(6.64)	
Smoked	48.9	31.08(60.76)	1.12(2.20)	4.09(8.01)	
Rolled	55.2	30.16(67.32)	0.80(1.79)	3.53(7.87)	
Packaged and aged	46.4	31.38(58.59)	2.59(4.83)	4.56(8.52	
Tentacle					
Raw	80.3	12.77(75.11)	0.49(2.25)	1.20(6.07)	
Skinned	80.9	13.83(72.37)	0.50(2.60)	1.12(5.86	
Boiled	75.1	16.11(64.69)	0.65(2.61)	1.84(7.38	
Air blast dried	57.4	20.17(47.38)	1.63(3.82)	2.65(6.23	
Smoked	45.9	23.27(43.02)	1.01(2.29)	3.20(7.26	
Packaged and aged	51.8	22.23(46.11)	1.30(2.70)	3.31(6.87	
Beka squid(<i>Loligo bdka</i>)					
Raw mantle	81.2	13.49(71.76)	1.74(9.23)	1.38(7.35)	
Raw tentacle	81.4	11.07(59.52)	1.37(7.37)	0.91(4.87)	
Japanese flying squid(Todarodes pacificus)					
Raw mantle	80.1	13.41(70.95)	1.30(6.88)	1.46(7.71)	
Raw tentacle	77.6	11.31(50.49)	1.64(7.33)	2.39(10.65)	

ction between protein and other components. When measured by Rhinehart method(1975), about 21 mg/g solid of TI was contained in mantle and 57.5 mg/g solid in tentacles. But those were lost through processing such as boiling or sometimes were increased by the interaction of protein with other components during processing(seasoning and drying). Raw Neon flying squid had more than 2 times of TI, especially 5 times in tentacles comparing with the results of Ryu(1983) using california bay squid as sample. Steak from mantle, which was removing only skin by hands and carving vertical line mechanically in order to soften tissue, has a lower content in TI due to the removal in TI in skin. Boiling contributed in decreasing TI in tentacles but those effect was not revealed in mantle. From the results described above, it could be concluded that TI content during processing was not increased. Unlike the tendency of TI changes, 2 or 3 times more levels of TBA value was checked after seasoning. It could be thought those high levels of TBA

Table 2. Changes in the trypsin inhibitor(TI*) and TBA value during the commercial seasoned squid processing

processing		
Samples	TI (mg/g solid)	TBA (O.D.at 535nm×100)
Mantle		
Raw	21.3	46
Steak	16.0	33
Boiled	16.2	40
Seasoned	22.1	116
Air blast dried	21.8	108
Smoked	19.2	108
Sterilized	19.0	132
Packaged and aged	19.9	109
Tentacle		
Raw	57.5	33
Skinned	51.7	47
Boiled	20.1	45
Seasonned and dried	16.9	1,665
Smoked	20.7	1,697
Packaged and aged	15.9	1,537

^{*} Determined by Rhinehart method(1975)

value is rather the results of interaction between TBA reagents and uncertain materials in the mixtured seasoning than the fat oxidation occurred in processing.

3. Amino acid profiles and in vitro protein quality

The results of amino acid analysis of various smoked squid products are presented in Table 3. Among the essential amino acids, all except lysine (8.47 g/100g protein) showed value within the results reported by Suvama et al. (1980) who analyzed the amino acid content for 4 species of Japanese squid. Tentacles have more total essential amino acids than that in mantles. Proline, histidine, arginine, and alanine were reduced during skinning and boiling, as reported by Suyama and Kobayashi (1980). The in vitro enzymic protein digestibilities and protein efficiency ratios are summarized in Table 4. Protein digestibility of raw mantle and tentacle was 79%, and this was lower by 10% than that of raw coastal squids. However, this species was unsuitable for consuming as raw one. Boiled product showed the greatest value of digestibility (88 %) among all the samples studied, followed by seasoned(87.8%), dried(87.6%) and smoked(87.0 %). These digestibilities were lower than the digestibility of boiled california bay squid(boiled for 1 minute at 95°C), as Ryu(1983). It was noted that digestibility of raw Neon flying squid was improved to considerable level by processing. Though overall protein digestibility of tentacle products was lower than that of mantle, boiled one has a comparable digestibility to mantle product. Predicted digestibility was further calculated based on amino acid profiles and the results did not indicate significant differences among processed samples, so this method is not appropriate to check different digestibility of squid products. The computed protein efficiency ratios(C-PER) fo raw mantle and tentacle were 2.14 and 2.15 for both boiled ones. Processed squid samples showed the value of C-PER around 2.25, without any significant statistical difference between them(p>0.05). Neon flying squid samples were observed to be significantly(p<0.05) inferior to other squids(Lee et al. 1974, Ryu 1983). Discri-

Table 3. Amino acids profiles of the commercial smoked squid product

(g/100g protein)

Amino acids	R	aw	Skir	nned	Во	iled	Air dr	blast ied	Smo	oked		aged aged
acids	M	T	M	T	M	T	M	Т	M	T	M	T
Lys.	8.41	8.81	8.67	8.35	7.66	7.85	8.51	8.21	8.10	8.20	8.03	8.24
His.	2.05	2.08	2.07	2.62	1.99	2.10	2.06	2.34	2.02	1.95	1.98	1.92
NH_3	1.24	1.25	1.25	1.34	1.10	0.91	0.75	1.07	1.30	1.14	1.15	1.16
Arg.	8.37	8.84	8.08	8.52	7.61	7.70	7.96	8.40	7.88	8.61	7.63	7.69
Trp.	1.54	1.40	1.38	1.42	1.31	1.23	1.44	1.36	1.54	1.44	1.38	1.40
Asp.	9.59	8.63	9.64	8.63	8.93	8.72	9.15	10.20	9.44	9.22	10.88	9.89
Thr.	4.54	4.62	4.35	4.62	4.66	4.68	5.10	4.95	4.83	4.81	4.93	4.52
Ser.	4.72	4.90	3.93	4.47	4.08	4.52	4.16	3.95	4.47	4.34	4.91	4.36
Glu.	16.17	17.24	15.37	16.73	14.94	16.11	16.73	17.16	16.81	16.80	16.41	16.63
Pro.	4.37	4.56	4.25	4.10	3.01	3.60	3.61	4.18	4.58	5.30	4.82	4.51
Gly.	4.17	4.74	3.73	4.55	3.87	4.54	4.04	4.40	4.18	4.66	4.20	4.05
Ala.	4.62	4.05	4.51	4.08	4.22	4.03	4.88	4.75	4.71	4.45	4.40	4.63
Cys.	1.20	1.13	1.14	1.11	0.97	1.00	1.31	1.32	1.46	1.38	1.21	1.11
Val.	4.48	4.49	4.00	3.94	5.54	4.58	4.54	3.86	4.32	4.41	4.10	3.66
Met.	2.52	3.31	3.31	3.14	3.11	3.17	3.06	3.38	3.56	3.25	3.57	3.25
Ile.	4.95	4.66	4.87	4.71	5.23	4.55	4.67	4.06	4.69	4.12	4.45	4.95
Leu.	8.20	7.78	8.00	7.88	8.27	7.21	7.61	7.28	7.28	7.06	7.98	7.64
Tyr.	3.46	3.16	3.10	3.21	3.24	3.33	3.27	3.03	3.49	3.25	3.14	3.17
Phe.	4.50	4.53	4.19	4.33	4.87	4.60	4.65	4.97	4.48	4.87	4.07	4.79
Trp.	0.74	0.69	0.70	0.70	0.68	0.72	0.53	0.62	0.53	0.60	0.60	0.72
Total	99.74	99.91	96.54	98.45	96.29	96.15	98.03	99.49	99.67	99.86	99.84	98.29

*M: mantle, T: tentacle

minant computed protein efficiency ratio(DC-PER) of Neon flying squid products approved to inferior to rat-PER of other squids(Lee et al. 1974, Ryu 1983) also, presumably due to lower concentration of proline than that in other seafoods, which plays an important role in calculating C-PER and DC-PER.

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Table 4. Changes in digestibility and PERs during commercial smoked squid processing

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Sample	In vitro digestibility*	Predicted digestibility*	C-PER	DC-PER
Mantle				
Raw	79.14	94.31	2.14	2.11
Steak	80.45	-	-	-
Skinned	84.00	95.54	2.15	2.08
Boiled	88.10	92.98	2.27	2.21
Seasoned	87.80	-	-	-
Air blast dried	87.60	95.44	2.24	2.14
Smoked	87.00	98.31	2.24	2.15
Packaged and aged	86.74	94.82	2.24	2.08
Raw Beka squid	86.96	-	-	-
Raw Japanese flying squid	84.70	-	-	-
Tentacle				
Raw	78.14	96.88	2.14	2.14
Skinned	80.25	96.26	2.15	2.08
Boiled	85.98	97.18	2.24	2.12
Air blast dried	84.85	97.59	2.27	2.08
Smoked	84.12	98.83	2.25	2.13
Packaged and aged	87.75	96.36	2.26	2.07
Raw Beka squid	87.52	·• -	-	-
Raw Japenese flying squid	86.62	-	-	-

^{* %} digestibility

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조미훈연 오징어의 가공중 품질변화

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조미훈연 오징어(Neon flying squid, Ommastrephes bartrannii)의 적절한 가공조건을 찾기 위하여 일반성분변화 및 단백질 품질변화를 측정하였다. 수분, 조단백질함량은 매우 감소하였으나(p < 0.05) 지방, 회분함량은 그다지 증가하지 않았다. 조미, 훈연은 TBA가의 증가를 초래하였다. 여러가지 가공단계들은 TI함량을 크게 증가시키지는 않았다. 오징어 가공전단계를 통해 측정된 TI함량은 같은 가공단계에서의 TBA가와 서로 관련이 없었다. Steak용으로 가공한 것을 제외한 모든 가공품들의 경우, 소화율과 C-PER, DC-PER이 증가하였다. 생시료의 경우, 북태평양산 빨강오징어(몸통, 다리 양쪽 모두)의 효소 소화율은 다른 오징어중에 비해 상당히 낮았다.