魚類脂質脂肪酸組成に関する考察

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Fatty Acid Composition of Lipid from Horse Mackerel Muscle—Discussion of Fatty Acid Composition of Fish Lipid*1

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The fatty acid compositions of whole lipid, neutral lipid (NL), free fatty acid and phospholipid (PL) were determined by GLC on 14 samples of horse mackerel ordinary muscle which contained whole lipid in the range from 1.1 to 11.2%.

Analyses of the fatty acid composition of whole lipid illustrated considerable differences related to variations in lipid content. As for the compositions of NL and PL, they differed but neither showed any obvious change as compared with that of whole lipid except for 18:0 in NL and 16:1 and 20:5 in PL. Consequently, the characteristic fatty acid compositions were recognized in 16:0, 16:1, 18:1 and 22:6 for NL and 16:0, 18:0, 18:1 and 22:6 for PL with species differences.

As a result, the authors postulated that the fatty acid distribution of fish lipid should be discussed not in terms of the fatty acid composition of whole lipid but in terms of the NL and PL fatty acid compositions.

Advances in a method for separating and identifying fatty acid on GLC analysis have contributed to the evaluation of fatty acid compositions of lipids from a variety of marine animals, and classical data from the distillation method have been renewed for the past twenty years. GRUGER *et al.*[1] and UEDA[2] determined the fatty acid compositions of lipids from 17 species and 33 species of fish respectively, and GRUGER[3] reviewed on the fatty acid compositions of lipids from marine animals. They discussed the characteristics of fatty acid distribution with species differences. Such studies, however, are complicated because it has been known that the fatty acid composition of fish lipid is influenced with lipid content, diet, geographical location and season of catch, temperature, maturity, anatomical part etc. Therefore, it is necessary to study the fatty acid composition more extensively.

The present paper is concerned with the fatty acid compositions of whole lipid, neutral lipid (NL) and phospholipid (PL) from horse mackerel muscle having various whole lipid contents.

Materials and Methods

Fish muscle The fresh horse mackerel, *Trachurus japonicus*, was obtained from a market sourse for a period of about one year and a half. The ordinary muscle was

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used unless otherwise indicated. Mackerel scads, *Decapterus muroadi*, was also used for comparison.

Extraction of lipid Prior to the extraction of lipid, the sample of fish muscle was minced in a blender. By use of the procedure of FOLCH *et al.*[4], lipid was extracted with a mixture of chloroform and methanol (2: 1), then washed with 0.2 volume of 0.58% sodium chloride solution, followed by removing water with anhydrous sodium sulfate.

Fractionation of lipid The extracted whole lipid was fractionated into NL, free fatty acid (FFA) and PL by a modified method of MCCARTHY and DUTHIE.[5] In the column chromatography on silicic acid impregnated with potassium hydroxide, the amount of the alkali to be added to 5 g of silicic acid was reduced to 50 mg, one-tenth of the original amount, to prevent from lipid hydrolysis as much as possible during the procedure, and FFA was eluted with 0.2% formic acid in ether.

Determination of fatty acid composition Lipid was subjected to methylation by AOCS method[6] and to programmed GLC analysis with a Shimazu Model GC-4APF under the following conditions. Detector: HFID, Column: 10% DEGS, 3 mm×2 m, Column temperature: 150°–200°C, 4°C/min, Vaporizer temperature: 300°C, N_2 flow rate: 50 m*l*/min.

Fatty acid was identified by using its retention time in constant temperature GLC at 180°C and its equivalent chain length.[7] Fatty acid composition was calculated from peak areas determined by a half-band width method. Dupricate analyses were carried out.

Determination of lipid content Whole lipid content was measured gravimetrically. The contents of NL, FFA and PL were expressed as total fatty acid content (mg/100 g of muscle). For this purpose, the total amount of constituent fatty acids in each lipid was measured in programmed GLC using *n*-octadecane and 16: 0 as an internal standard substance and a standard fatty acid respectively.

Results

The fatty acid compositions of whole lipids in 14 samples of horse mackerel, which contained whole lipids in the range from 1.1 to 11.2%, are listed in Table 1. The main fatty acids were 16: 0, 16: 1, 18: 0, 18: 1, 20: 5 and 22: 6, that was common to all the 14 samples, but their compositional percentages varied widely with the whole lipid content. Usually but not always, increasing whole lipid content tended to increase 16: 1 and 18: 1, on the contrary, decreasing it did to increase 22: 6 and 18: 0. This tendency was remarkable in the sampls of whole lipid content below 4.1%. The connection of fatty acid composition to whole lipid content was observed also in the differences of fatty acid compositions of whole lipids from dorsal and ventral muscle as shown in Table 2.

Table 1. Fatty acid composition of whole lipid from horse mackerel (%)

Fatty acid / Whole lipid cont (%)	14:0	15:0	16:0	16:1	17:0	16:2	18:0	18:1	18:2	18:3	20:1	20:4	22:1	20:5	22:4	22:5 ω6	22:5 ω3	22:6
1.1	1.2	.6	20.3	3.3	1.5	1.4	10.8	12.7	1.4	.7	tr	3.0	tr	6.6	tr	.9	1.9	33.5
1.1	1.5	.5	19.9	3.6	1.4	1.5	9.8	13.1	1.4	1.5	〃	3.5	〃	6.9	〃	tr	2.3	32.3
1.1	2.4	.3	19.8	4.0	1.2	.9	8.1	13.5	1.2	2.7	〃	3.9	3.0	7.8	〃	1.3	2.5	27.0
1.6	2.9	.5	21.0	5.7	1.6	1.2	9.5	19.8	1.0	1.6	〃	2.1	1.4	6.3	〃	tr	1.8	23.4
1.9	2.2	.6	24.7	5.8	1.5	1.3	7.9	15.8	.9	1.2	〃	2.0	tr	7.1	1.1	〃	2.1	24.9
2.6	2.8	.6	23.0	7.1	2.3	1.6	6.1	19.6	2.0	2.4	〃	2.4	1.3	7.4	tr	〃	1.9	18.6
2.7	2.9	.7	24.0	8.1	1.6	1.3	7.7	18.8	1.5	.7	2.3	.8	1.8	6.3	〃	1.8	1.8	17.7
2.9	3.2	.5	24.1	8.5	1.6	1.2	6.4	19.1	1.6	1.8	tr	2.2	tr	7.2	〃	tr	2.1	20.0
3.0	2.6	.4	24.3	8.3	1.1	.8	6.2	19.6	1.5	1.0	2.9	1.1	1.9	6.5	〃	1.3	1.6	18.1
4.1	3.8	.6	21.5	8.1	1.6	1.1	7.7	22.2	1.1	.9	1.6	1.8	1.4	7.4	〃	1.2	2.3	14.9
4.8	4.5	.4	22.7	7.6	1.4	1.1	7.7	22.8	1.3	2.1	.9	3.8	tr	7.2	〃	tr	2.2	13.8
6.2	4.6	.5	21.5	6.9	1.7	1.5	6.4	22.2	2.7	2.8	2.8	1.6	〃	7.4	〃	〃	2.2	14.7
8.2	3.1	.6	28.1	8.0	1.6	.8	6.1	21.3	.9	.5	1.5	1.4	1.0	7.0	〃	1.6	2.0	14.3
11.2	5.0	.6	19.1	9.8	1.5	1.4	7.7	19.5	1.1	3.9	tr	1.3	5.3	8.5	〃	1.1	1.9	12.1
9.3*	3.5	.6	24.5	8.3	1.7	1.6	7.2	24.7	2.0	1.8	.9	1.7	tr	5.7	〃	tr	1.6	13.2

* mackerel scads

Table 2. Difference in fatty acid composition between dorsal and ventral ordinary muscle of horse mackerel (%)

Part of muscle	Fatty acid / Whole lipid cont (%)	14:0	15:0	16:0	16:1	17:0	16:2	18:0	18:1	18:2	18:3	20:1	20:4	22:1	20:5	22:4	22:5 ω6	22:5 ω3	22:6
Dorsal	1.1	1.5	.5	19.9	3.6	1.4	1.5	9.8	13.1	1.4	1.5	tr	3.5	tr	6.9	tr	tr	2.3	32.3
Ventral	1.3	2.5	.5	19.4	4.9	1.4	1.4	10.1	15.2	1.7	1.3	〃	3.2	〃	6.8	〃	〃	2.2	28.5
Dorsal	1.6	2.9	.5	21.0	5.7	1.6	1.2	9.5	19.8	1.0	1.6	〃	2.1	1.4	6.3	〃	〃	1.8	23.4
Ventral	1.9	3.3	.5	21.8	5.9	1.8	1.3	9.4	19.3	1.0	1.6	〃	2.0	1.5	6.6	〃	〃	1.9	22.0
Dorsal	6.2	4.6	.5	21.5	6.9	1.7	1.5	6.4	22.2	2.7	2.8	2.8	1.6	tr	7.4	〃	〃	2.2	14.7
Ventral	10.5	4.7	.8	21.1	7.6	1.4	1.3	5.3	27.5	2.4	2.5	2.4	1.6	〃	6.9	〃	〃	2.1	12.3

For clarifying the cause, whole lipid was fractionated into NL, FFA and PL, and their contents and fatty acid compositions were determined. The contents are shown in Table 3. NL content varied in proportion to whole lipid cotent, while PL content was almost constant without showing any relation to whole lipid content. The fatty acid compositions of NL, FFA and PL are listed in Tables 4, 5 and 6, and the means and the coefficiencies of variation of main fatty acids in whole lipid, NL and PL are shown in Table 7. As for the fatty acid compositions of NL and PL, they were different from each other; the percentages of 16: 1 and 18: 1 were higher in NL, concurrently those of 22: 6 and 18: 0 were higher in PL. Moreover, their main fatty acids maintained relatively low coefficiency of variation in respective lipids except 18: 0 in NL and 16: 1 and 20: 5 in PL regardless of whole lipid content. On the other hand, the main fatty acid distributions in whole lipid varied except 20: 5, and especially 22: 6 and 16: 1 varied considerably as mentioned above. The fatty acid composition of FFA was different from all of them, and the percentages of main fatty acids varied wider than those in NL and PL.

Table 3. Relationship between whole lipid content and contents of neutral lipid, phospholipid and free fatty acid in dorsal ordinary muscle of horse mackerel

Whole lipid (%)	N L*1	P L*1 (mg/100 g of muscle)	FFA*1
1.1	176	388	44
1.3	338	386	50
1.6	525	339	69
1.9	734	332	80
4.1	2417	390	101
4.8	2961	329	42
6.2	3896	337	20
11.2	7810	350	64
9.3*2	6265	356	40

*1 Expressed as total fatty acid content in each lipid.
*2 mackerel scads

In order to summarize the fatty acid compositions of NL and PL in various fish lipids, the main fatty acid distributions in NL and PL from several fish in addition to horse mackerel are shown in Tables 8 and 9 by the present study and the citation of references.[8-13] As a result, the main fatty acid distributions in NL and PL from horse mackerel were resemble to those from mackerel scads, but were different from those from other species.

Discussion

NL in ordinary muscle of horse mackerel is a depot lipid in which the main component is triglyceride,[14] and its content in muscle increased in proportion to whole lipid

Table 4. Fatty acid composition of neutral lipid from horse mackerel (%)

Fatty acid / Whole lipid cont (%)	14:0	15:0	16:0	16:1	17:0	16:2	18:0	18:1	18:2	18:3	20:1	20:4	22:1	20:5	22:4	22:5 ω6	22:5 ω3	22:6
1.1	4.0	.9	21.1	9.0	2.5	3.0	9.0	21.0	2.0	2.0	tr	2.8	tr	6.1	1.2	tr	2.3	12.2
1.3	5.0	.8	21.0	8.3	2.1	1.8	8.6	20.5	2.2	2.7	〃	3.0	〃	6.8	.9	〃	3.7	12.7
1.6	4.4	.8	21.7	8.0	1.6	1.4	8.3	25.5	1.4	2.3	〃	1.3	2.4	6.4	tr	〃	2.1	13.2
1.9	4.5	.7	21.8	8.2	1.7	1.4	8.3	23.5	1.5	2.2	〃	3.6	tr	6.8	〃	〃	2.0	13.7
4.1	4.0	.6	22.3	8.4	1.7	1.2	8.0	22.5	1.1	1.8	〃	3.1	〃	7.5	〃	1.1	2.2	14.5
4.8	4.8	.7	22.5	8.4	2.1	1.4	6.1	23.2	1.6	3.0	1.4	3.8	〃	6.2	〃	1.0	1.8	12.1
6.2	4.8	.9	21.2	8.6	1.7	1.5	6.4	23.0	2.7	2.4	2.7	1.5	〃	7.4	〃	tr	2.1	13.6
11.2	5.8	.4	19.8	10.0	1.3	1.2	7.2	19.9	1.0	3.9	tr	1.1	5.5	8.2	〃	1.1	1.8	11.4
9.3*	3.4	.5	24.2	8.4	1.8	.8	7.4	25.7	2.0	2.2	1.2	1.8	tr	6.0	〃	tr	1.3	13.2

* mackerel scads

Table 5. Fatty acid composition of free fatty acid from horse mackerel (%)

Fatty acid / Whole lipid cont (%)	14:0	15:0	16:0	16:1	17:0	16:2	18:0	18:1	18:2	18:3	20:1	20:4	22:1	20:5	22:4	22:5 ω6	22:5 ω3	22:6
1.1	1.7	.6	21.6	3.6	1.4	.8	11.1	11.4	1.4	.7	tr	2.5	tr	5.5	tr	tr	1.5	35.0
1.3	2.4	.6	21.9	4.4	1.5	1.0	11.3	12.3	1.5	1.0	〃	2.8	〃	6.1	〃	〃	1.5	30.8
1.6	3.7	.6	24.6	6.4	1.2	1.0	12.0	14.9	1.0	1.6	〃	3.4	〃	6.2	〃	〃	1.5	21.9
1.9	3.8	.8	23.6	6.5	1.0	.8	11.3	17.7	1.1	1.0	〃	3.2	〃	6.1	〃	〃	1.5	21.5
4.1	4.0	.8	22.8	6.9	1.5	.8	10.4	18.2	.9	1.6	〃	3.5	〃	6.7	〃	〃	.6	20.2
4.8	2.7	.6	24.5	5.1	1.3	.8	8.8	14.3	1.1	1.0	〃	3.4	〃	7.7	〃	〃	1.6	27.0
6.2	3.5	1.3	27.2	8.0	1.6	1.0	10.8	21.2	3.1	3.3	〃	2.9	〃	6.2	〃	〃	1.1	7.1
11.2	2.3	.6	24.3	7.7	1.4	1.0	9.6	15.0	.9	2.4	〃	1.1	3.9	9.3	〃	〃	1.5	19.0
9.3*	2.8	.8	26.2	5.1	1.2	3.4	10.1	15.7	3.9	2.2	〃	2.6	tr	6.2	〃	〃	.8	17.4

* mackerel scads

Table 6. Fatty acid composition of phospholipid from horse mackerel (%)

Fatty acid / Whole lipid cont (%)	14:0	15:0	16:0	16:1	17:0	16:2	18:0	18:1	18:2	18:3	20:1	20:4	22:1	20:5	22:4	22:5 ω6	22:5 ω3	22:6
1.1	—	—	18.3	1.5	1.3	1.3	11.0	9.3	1.4	.4	tr	3.0	—	6.2	tr	1.3	2.2	41.5
1.3	—	—	18.1	1.4	1.1	1.4	11.1	8.9	1.3	.3	〃	3.2	—	6.3	〃	1.0	1.9	42.6
1.6	—	—	19.5	2.0	1.1	1.4	11.1	9.6	.9	.4	〃	2.8	—	6.5	〃	1.2	2.1	41.2
1.9	—	—	20.2	2.5	1.4	1.2	11.8	9.7	1.0	.8	〃	3.0	—	6.3	〃	1.4	2.1	38.7
4.1	—	—	20.0	2.0	1.3	1.1	11.3	10.4	.9	.6	〃	3.2	—	7.5	〃	tr	2.5	38.8
4.8	—	—	21.3	1.3	.8	.7	11.2	9.1	1.1	.7	〃	2.9	—	8.1	〃	1.2	2.4	38.9
6.2	—	—	18.0	1.8	.9	.9	9.8	10.1	1.7	1.0	〃	3.7	—	9.7	〃	tr	3.1	38.1
11.2	—	—	19.4	2.3	.9	.4	10.3	10.0	.8	1.0	〃	2.7	—	10.1	〃	〃	2.6	38.7
9.3*	—	—	18.1	1.5	1.3	.7	12.4	9.6	1.3	.8	〃	3.4	—	6.7	〃	1.7	1.7	40.6

* mackerel scads

Table 7. Variability of fatty acid distribution in whole lipid, NL and PL from horse mackerel

Fatty acid	Whole lipid			NL			PL		
	$\bar{x}$	σ	$\sigma/\bar{x}\times100$	$\bar{x}$	σ	$\sigma/\bar{x}\times100$	$\bar{x}$	σ	$\sigma/\bar{x}\times100$
16:0	22.4	2.4	11	21.4	.8	3.7	19.4	1.1	5.6
16:1	6.8	1.9	28	8.6	.59	6.9	1.9	.41	22
18:0	7.7	1.4	18	7.7	.99	13	11.0	.58	5.3
18:1	18.6	3.3	18	22.4	1.7	7.7	9.6	.49	5.1
20:5	7.1	.57	8	6.9	.68	9.9	7.6	1.5	19
22:6	20.4	6.6	32	12.9	.95	7.4	39.8	1.6	3.9

$\bar{x}$: Mean. σ: Standard deviation. $\sigma/\bar{x}$: Coefficiency of variation.

Table 8. Fatty acid distribution in NL from various fish

Fish	16:0	16:1	18:1	22:6	
Horse mackerel $\bar{x}$	21.4	8.6	22.4	12.9	
(σ)	(0.8)	(0.6)	(1.7)	(1.0)	
Mackerel scads	24.2	8.4	25.7	13.2	
Cod	15.0	5.0	19.5	9.8	ROUBAL[8]
Sole	16.5	14.4	12.2	7.0	OLLEY & DUNCAN[9]
Halibut	9.6	2.5	12.3	37.6	〃
Dogfish	17.0	4.6	16.1	21.8	〃
Capelin	9.4	16.1	8.3	4.8	ACKMAN *et al.*[10]
Rockfish	16.8	11.7	28.0	20.0	WOOD *et al.*[11]
Coho salmon	10.3	10.7	21.2	10.6	BRADDOCK & DUGAN[12]
Albacore	23.4	3.9	25.8	24.4	SHUSTER *et al.*[13]

Table 9. Fatty acid distribution in PL from various fish

Fish	16:0	18:0	18:1	22:6	
Horse mackerel $\bar{x}$	19.4	11.0	9.6	39.8	
(σ)	(1.1)	(0.6)	(0.5)	(1.6)	
Mackerel scads	18.1	12.4	9.6	40.6	
Cod	20.6	4.2	10.1	35.4	OLLEY & DUNCAN[9]
Sole	20.3	6.1	9.3	21.2	〃
Halibut	18.1	7.2	8.5	42.0	〃
Dogfish	18.6	8.8	10.4	34.4	〃
Capelin	18.3	2.7	11.2	29.3	ACKMAN *et al.*[10]
Rockfish	20.0	5.5	8.9	47.0	WOOD *et al.*[11]
Coho salmon	15.6	4.7	25.3	9.9	BRADDOCK & DUGAN[12]

content. PL is a tissue lipid which largely consists of lecithin and cephalin[14], and its content was almost constant.

In whole lipid from muscle of its content above 4.1%, the total amount of fatty acids in NL was above five times as much as that in PL and FFA, so the fatty acid distribution tended to reflect that of NL. Consequently, the perentages of 16:1 and 18:1 were higher and those of 18:0 and 22:6 were lower than those in whole lipid from muscle of low whole lipid content.

As it has been pointed out that PL contains more polyunsaturated fatty acid than NL when separated from the same sample[9,13,15-17], the percentage of 22: 6 in PL was about three times as much as in NL. Moreover, the percentage of 18: 0 was higher than that in NL. Consequently, in whole lipid from muscle of its content below 4.1%, the percentages of 22: 6 and 18: 0 increased markedly and those of 16: 1 and 18: 1 decreased with the decrease in its content. As for FFA, it showed no significant influence on the fatty acid composition of whole lipid as judged by its low content.

For these reasons, it was concluded that the considerable change in the fatty acid composition of whole lipid is attributed to the differences in NL and PL contents and in their fatty acid compositions.

In the fatty acid compositions of NL and PL, the each of changes in the same lipid was relatively slight regardless of whole lipid content, so the characteristics of fatty acid distribution were recognized in 16: 0, 16: 1, 18: 1 and 22: 6 of NL, and in 16: 0, 18: 0, 18: 1 and 22: 6 of PL with species differences except between horse mackerel and mackerel scads which is its allied species.

As a conclusion, the authors postulated that the fatty acid distribution of fish lipid should be discussed not in terms of the fatty acid composition of whole lipid but in terms of those of NL and PL.

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