JOURNAL OF
AGRICULTURAL AND
FOOD CHEMISTRY

Seasonal Variations of Fatty Acid Compositions in Various Korean Shellfish

JEONGHEE SURH,[†] JONG-SEONG RYU,[§] AND HOONJEONG KWON*,[†]

Department of Food and Nutrition, College of Human Ecology, and School of Earth and
Environmental Sciences (Oceanography), Seoul National University, San 56-1 Shillim-dong,
Kwanak-gu, Seoul 151-742, Korea

Seasonal variations of fatty acids in various Korean shellfish were investigated in relation to the changes in total fatty acids contents, the ratio of polyunsaturated fatty acids to saturated fatty acids (P/S), and that of *n*−3 fatty acids to *n*−6 fatty acids (*n*−3/*n*−6). A distinct seasonal pattern was found in total fatty acids contents with maximal values in early summer and minimal values in late summer. The percentage of monounsaturated fatty acids was lowest in most species throughout the year. In summer months, the proportion of polyunsaturated fatty acids decreased while that of saturated fatty acids increased. The major contributing factor to the seasonal variation of polyunsaturated fatty acids was *n*−3 fatty acids. These results led to the lowest levels of P/S and *n*−3/*n*−6 in summer. Nevertheless, the data suggest that bivalve shellfish would be excellent sources of *n*−3 fatty acids, especially eicosapentaenoic acid and docosahexaenoic acid.

KEYWORDS: Seasonality; fatty acid composition; shellfish; *n*−3 fatty acids/*n*−6 fatty acids (*n*−3/*n*−6); polyunsaturated fatty acids/saturated fatty acids (P/S)

INTRODUCTION

It has been reported that eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) have beneficial effects for the prevention of human coronary heart disease (*1*−*3*). Studies on the lipids of marine organisms have shown that fish and shellfish could be unique sources of *n*−3 polyunsaturated fatty acids (PUFA) such as EPA and DHA (*2*, *4*−*6*). For this reason, it has been suggested that the consumption of seafood would have favorable effects regarding ischemic heart disease and thrombosis (*1*, *2*, *7*, *8*). Because the apparent relationship between the amounts or types of fatty acids consumed and the incidence of ischemic heart disease has been noted, knowledge of the composition of edible fats has been considered to be essential (*1*). Fat content and PUFA composition in seafood are influenced by species (*4*, *9*, *12*, *14*, *15*), season (*4*, *9*−*11*, *13*), availability and composition of food (*4*, *9*), temperature (*4*), geographic regions (*4*), stage of sexual development (*4*), and self-regulation of fatty acid synthesis (*4*). Numerous studies have demonstrated the seasonal variations of the biochemical compositions in bivalves from the viewpoint of marine animal physiology (*11*, *16*−*19*). However, little attention has been paid to the seasonality in the fatty acid compositions of the edible portion of shellfish in terms of the nutritional quality of the seafood.

In the present study, fatty acid contents and compositions in 12 species of shellfish consumed in Korea were investigated in an attempt to assess the seasonal influences on nutritional indices including polyunsaturated fatty acids/saturated fatty acids (P/S) and *n*−3 fatty acids/*n*−6 fatty acids (*n*−3/*n*−6).

MATERIALS AND METHODS

Sample Preparation. The 12 species of shellfish most consumed in Korea were selected for the analysis of fatty acid composition (**Table 1**). Samples were obtained from local markets over several months encompassing four seasons in 1999 and 2000. The samples were live when delivered and were homogenized and then frozen immediately upon arrival. Edible portions of 20−100 shellfish depending on their size were homogenized by a homogenizer (Hanil, Seoul, Korea) at high speed for 1 min without added solvent and stored at −20 °C.

Fatty Acid Analysis. Fatty acids in homogenates were converted to their constituent fatty acid methyl esters (FAME) according to the method of Lepage and Roy (*20*). Two milliliters of methanol/benzene 4:1 (v/v) solution was added to 0.1 g of the homogenate; 100 μg of tridecanoic acid (C13:0) was included in the solution as an internal standard. While stirring, 200 μL of acetyl chloride was slowly added. Glass sample tubes were tightly closed with Teflon-lined caps and subjected to methanolysis at 100 °C for 1 h. Tubes were weighed before and after heating to check leakages of volatile contents. After tubes had been cooled in water, 5 mL of 6% aqueous K_2CO_3 was slowly added to stop the reaction and neutralize the mixture. The reaction mixture was centrifuged, and an aliquot of benzene upper phase was subjected to gas chromatography. All of these reactions were performed in triplicate for each sample.

Analysis of methyl esters was performed by a GC-MSD (Hewlett-Packard; GC-6890, MS-5987, DE) on a fused silica DB-Wax column (60 m length × 0.25 mm i.d.; J&W, Folsom, CA). Carrier gas was helium at a flow rate of 1.0 mL/min and a linear velocity of 26 cm/s. One microliter of the sample was injected with a split ratio of 30:1

---

* Author to whom correspondence should be addressed (telephone 82-2-880-6835; fax 82-2-884-7555; e-mail hjkwon@snu.ac.kr).

[†] Department of Food and Nutrition.

[§] School of Earth and Environmental Sciences (Oceanography).

10.1021/jf026033a CCC: $25.00

Table 1. Types and Spawning Periods of Shellfish Commonly Consumed in Korea

class	order	family	genus species	common name	local name	spawning
Gastropoda	Neogastropoda	Muricidae	*Rapana venosa*	murex shell	pibbulgodoong	May–Aug
Bivalvia	Arcoida	Arcidae	*Scapharca broughtonii*	ark shell	pijogae	July–Oct
			Tegillarca granosa	granulated ark shell	komak	July–Sept
	Mytiloida	Mytilidae	*Mytilus coruscus*	hard-shelled mussel	honghap	March–June
		Pinnidae	*Atrina (Servatrina) pectinata*	pen shell	kijogae	[a]
	Pterioida	Ostreidae	*Crassostrea gigas*	oyster	gool	July–Sept
	Veneroida	Mactridae	*Mactra veneriformis*	surf clam	dongjook	May–Oct
		Tellinidae	*Peronidia venulosa*	pink butterfly shell	bidanjogae	[a]
		Pharellidae	*Sinonovacula constricta*	jack-knife clam	garimatjogae	Aug–Sept
		Veneridae	*Cyclina sinensis*	Venus clam	gamoorak	June–Aug
			Meretrix lusoria	Orient hard clam	baekhap	July–Oct
			Ruditapes philippinarum	little neck clam	bagirak	July–Aug

[a] Information about spawning period was not available.

Table 2. Seasonal Variations of Total Fatty Acids (Grams per 100 g) in Shellfish[a]

species	May	June	July	Aug	Oct	Dec	March	Pr
murex shell	0.67c	2.94ab	1.04c	0.50c	3.80a	1.29c	1.88bc	**
ark shell	0.91b	2.70a	1.47ab	0.97b	1.53ab	2.50a	0.49b	**
granulated ark shell	1.63b	5.41a	2.89ab	[b]	1.29b	3.26ab	2.40b	*
hard-shelled mussel	0.83e	4.77b	6.36a	1.66ed	2.78cd	3.32bc	2.96cd	***
pen shell	1.01abc	1.73abc	2.35a	0.31c	1.65abc	0.59bc	2.01ab	*
oyster	2.27b	6.20a	2.78b	2.21b	4.28ab	4.92ab	5.65a	*
surf clam	0.82bc	2.72a	2.22ab	0.66c	1.44abc	1.69abc	1.27bc	*
pink butterfly shell	1.75b	[b]	3.81a	0.82b	1.60b	[b]	1.05b	**
jack-knife clam	1.17a	2.94a	2.76a	0.67a	3.34a	2.50a	1.91a	
Venus clam	1.32b	4.86a	2.83b	1.67b	2.08b	1.27b	1.35b	*
Orient hard clam	1.12b	2.50ab	6.48a	0.92b	1.31b	0.95b	1.21b	
little neck clam	0.36c	3.61a	2.14ab	0.72bc	1.43bc	1.26bc	1.78bc	**

[a] Total fatty acids were obtained by the summation of the contents of 23 fatty acids (The 23 identified fatty acids were mentioned under Results and Discussion). Values represent means of triplicate. Means with the same letter within rows are not significantly different ($p < 0.05$). *, **, and *** represent significance at 0.05, 0.01, and 0.001, respectively. [b] Samples were not available in local markets.

Table 3. Seasonal Variations of Saturated Fatty Acids (S), Monounsaturated Fatty Acids (M), and Polyunsaturated Fatty Acids (P) in Shellfish[a]

species		May	June	July	Aug	Oct	Dec	Mar	Pr
murex shell	S	44.8d	53.3ab	55.3a	51.3ab	46.3cd	50.0bc	44.4d	***
	M	19.8c	23.1b	25.7a	12.1d	19.8c	11.9d	22.2b	***
	P	35.4ab	23.6c	19.0d	36.6ab	33.9ab	38.1a	33.5b	***
ark shell	S	35.6de	36.4cde	43.1ab	32.1e	39.1bcd	42.0abc	47.5a	**
	M	17.3b	22.6a	16.9b	23.5a	17.2b	16.7b	23.8a	***
	P	47.2a	41.1a	40.0a	44.4a	43.7a	41.3a	28.8b	**
granulated ark shell	S	36.0c	39.0bc	42.9bc	[b]	54.9a	38.8bc	45.6b	**
	M	26.3ab	24.6b	24.3b		25.3ab	19.8c	27.5a	***
	P	37.8a	36.4a	32.8ab		19.8c	41.5a	27.0bc	**
hard-shelled mussel	S	40.5ab	40.5ab	38.1bc	38.6ab	38.9ab	42.0a	34.8c	*
	M	24.8a	20.0cd	20.7c	18.7d	13.8e	18.3d	23.0b	***
	P	34.7c	39.6b	41.2b	42.7b	47.3a	39.7b	42.3b	**
pen shell	S	41.4cd	47.5bc	42.3cd	53.6a	41.9cd	48.5ab	38.7d	***
	M	13.6c	11.4d	17.9a	16.4a	12.0cd	14.2bc	16.0ab	***
	P	45.0ab	41.0ab	39.8ab	30.0c	46.1a	37.4b	45.3a	**
oyster	S	35.2ab	40.2a	38.7ab	38.3ab	39.9a	35.2ab	30.7b	
	M	16.2c	21.0ab	20.8ab	23.1a	20.2ab	16.7c	18.9bc	**
	P	48.7a	37.1b	40.6b	38.6b	40.0b	48.1a	50.4a	***
surf clam	S	40.2ab	41.6ab	43.1ab	45.3a	41.0ab	43.7ab	39.0b	
	M	21.0b	21.0b	21.4b	19.1c	19.9bc	18.8c	25.9a	***
	P	38.7a	37.4a	35.5a	35.7a	39.1a	37.5a	35.1a	
pink butterfly shell	S	35.6d	[b]	40.3c	44.1b	45.5ab	[b]	46.5a	***
	M	25.0a		26.0a	20.6b	15.1c		16.0c	***
	P	39.4a		33.7c	35.3bc	39.4a		37.5ab	**
jack-knife clam	S	35.5b	37.8b	46.0a	50.0a	45.9a	47.4a	37.6b	**
	M	26.0ab	22.9abc	20.5bc	18.6c	27.4a	18.2c	26.1ab	*
	P	38.5a	39.3a	33.4ab	31.4ab	26.7b	34.4ab	36.3a	
Venus clam	S	36.8a	38.5a	37.6a	40.3a	45.1a	41.8a	40.5a	
	M	24.8ab	26.0ab	19.7b	25.9ab	22.6b	19.8b	26.1ab	*
	P	38.3ab	35.5ab	42.7a	33.8b	32.3b	38.5ab	33.3b	
Orient hard clam	S	37.8d	50.6a	43.7bc	44.1bc	47.9ab	46.1b	41.2cd	***
	M	22.6bc	22.8bc	25.6a	15.9d	23.8ab	14.1e	21.6c	***
	P	39.6a	26.7b	30.7b	40.0a	28.3b	39.8a	37.2a	***
little neck clam	S	49.0ab	45.0b	49.6ab	54.5a	53.8a	52.6a	38.3c	***
	M	16.7bc	20.8a	22.0a	16.1bc	19.2ab	14.5c	22.1a	**
	P	34.3ab	34.2ab	28.4b	29.4b	27.1b	33.0ab	39.6a	*

[a] Values are proportions (%) to total fatty acids. Refer to Results and Discussion for the fatty acids within each group. Means with the same letter within rows are not significantly different ($p < 0.05$). *, **, and *** represent significance at 0.05, 0.01, and 0.001, respectively. [b] Samples were not available in local markets.

Table 4. Seasonal Variations of Arachidonic Acid (A), Eicosapentaenoic Acid (E), and Docosahexaenoic Acid (D) in Shellfish[a]

species		May	June	July	Aug	Oct	Dec	Mar	Pr
murex shell	A	8.4bc	8.7bc	8.8bc	9.1b	7.0c	11.6a	7.1c	**
	E	10.7a	7.8c	3.5d	9.3b	8.9bc	9.9ab	9.2b	***
	D	11.9ab	4.6c	2.3c	10.3b	13.7a	11.1ab	12.8ab	***
ark shell	A	2.4c	2.3c	2.7c	1.9d	5.5a	2.5c	4.0b	***
	E	20.5b	21.7b	10.4d	26.1a	10.9d	15.9c	5.9e	***
	D	20.5a	13.5b	22.3a	13.6b	24.9a	20.0a	12.4b	**
granulated ark shell	A	1.2bc	1.7b	3.3a	*b*	1.7b	2.8a	1.0c	***
	E	18.7a	15.9ab	12.2cd		9.4d	19.0a	13.8bc	***
	D	13.8a	15.6a	13.6a		6.3b	15.2a	9.5ab	
hard-shelled mussel	A	2.6c	2.6c	3.8b	4.3a	2.2d	1.5e	1.2e	***
	E	14.4bc	12.5d	13.4cd	14.5bc	14.3bc	17.7a	15.2b	***
	D	14.5c	20.5b	19.6b	21.3b	29.0a	17.9bc	19.9b	***
pen shell	A	1.6d	2.8c	2.3cd	4.2a	3.7ab	3.0bc	2.7c	***
	E	15.9a	12.9b	14.2b	10.4c	10.5c	9.2c	13.2b	***
	D	25.4ab	25.3ab	21.0bc	15.4c	30.4a	25.1ab	24.5ab	*
oyster	A	1.1d	3.1b	2.6bc	2.7b	3.8a	2.2c	1.2d	***
	E	15.3c	11.9d	11.0d	14.7c	16.4c	24.7a	21.4b	***
	D	28.7a	18.7b	22.7ab	17.0b	16.9b	17.8b	22.9ab	*
surf clam	A	1.8c	1.9c	2.6abc	2.3bc	3.1ab	3.4a	2.0c	**
	E	12.8cd	11.1d	11.4d	14.0bc	12.6cd	15.7ab	16.4a	***
	D	20.0a	19.2a	17.4a	16.8a	20.1a	15.6a	9.8b	*
pink butterfly shell	A	1.6c	*b*	1.7c	3.4a	2.9b	*b*	2.0c	***
	E	19.3a		10.7b	9.7b	6.9c		7.7c	***
	D	15.0d		17.2c	18.1c	25.8a		22.7b	***
jack-knife clam	A	1.9cd	1.8d	2.3bc	2.6b	2.2bcd	3.6a	2.1bcd	***
	E	17.3a	12.8b	10.3bcd	7.2cd	11.1bc	6.3d	13.7ab	***
	D	14.4ab	20.1a	14.9ab	15.0ab	10.3b	19.7a	15.8ab	*
Venus clam	A	2.9bc	1.7c	3.7ab	2.0c	3.2bc	4.0ab	5.3a	**
	E	15.8ab	11.2b	11.5b	13.0ab	17.0a	13.1ab	16.9a	
	D	15.6bc	18.1b	23.0a	13.8bc	8.3d	16.7b	11.7cd	***
Orient hard clam	A	2.7cd	3.2c	1.5e	4.8b	3.1c	6.8a	2.4d	***
	E	14.1a	8.6c	9.5bc	9.9bc	8.7c	8.9bc	10.3b	***
	D	20.1ab	9.9d	16.1bc	22.3a	14.0cd	19.8ab	21.4a	***
little neck clam	A	2.2c	2.6bc	2.2c	4.1a	4.8a	3.2b	2.4bc	***
	E	10.1b	9.1bc	9.9b	7.6d	5.0e	7.9cd	13.9a	***
	D	19.0a	18.2a	12.5a	13.3a	15.1a	14.9a	19.0a	

[a] Values are proportions (%) to total fatty acids. Means with the same letter within rows are not significantly different ($p < 0.05$). *, **, and *** represent significance at 0.05, 0.01, and 0.001, respectively. [b] Samples were not available in local markets.

Table 5. Seasonal Variations in the Ratio of Polyunsaturated Fatty Acids to Saturated Fatty Acids (P/S)[a]

species	May	June	July	Aug	Oct	Dec	Mar	Pr
murex shell	0.79a	0.48b	0.34b	0.70a	0.73a	0.79a	0.76a	***
ark shell	1.33ab	1.14abc	0.94c	1.38a	1.10abc	1.02bc	0.61d	**
granulated ark shell	1.05a	0.94a	0.72ab	*b*	0.37c	1.09a	0.59bc	**
hard-shelled mussel	0.84c	0.99bc	1.09ab	1.11ab	1.20a	1.06bc	1.20a	**
pen shell	1.09ab	0.86b	0.96ab	0.56c	1.12ab	0.79bc	1.19a	**
oyster	1.39ab	0.89b	1.17ab	1.00b	0.99b	1.39ab	1.64a	*
surf clam	0.96a	0.89a	0.80a	0.82a	0.94a	0.87a	0.90a	
pink butterfly shell	1.11a	*b*	0.83b	0.81b	0.87b	*b*	0.81b	***
jack-knife clam	1.09a	1.05a	0.75bc	0.64c	0.58c	0.76bc	0.98ab	**
Venus clam	1.05ab	0.93bc	1.15a	0.83bcd	0.72d	0.93bc	0.83cd	**
Orient hard clam	1.05a	0.48c	0.71bc	0.91a	0.59c	0.87ab	0.91a	***
little neck clam	0.70b	0.75b	0.57b	0.54b	0. 53b	0.67b	1.06a	**

[a] Means with the same letter within rows are not significantly different ($p < 0.05$). *, **, and *** represent significance at 0.05, 0.01, and 0.001, respectively. [b] Samples were not available in local markets.

and run in constant flow mode. Chromatographic conditions were as follows: injection port temperature, 250 °C; detector temperature, 250 °C; initial oven temperature, 90 °C for 5 min, rising to 180 °C at 10 °C/min with a hold time of 3 min, to 230 °C at 3 °C/min with a hold time of 3 min, to 245 °C/min at 2 °C/min, and then to 250 °C at 0.7 °C/min with a final hold time of 10 min. Each peak was identified by comparison with the retention times of 35 known standards as well as by their mass fragment patterns. Because saturated fatty acids showed higher GC-MSD response than unsaturated fatty acids, fatty acid concentration was calculated from the standard curves of individual fatty acids. Fatty acids were presented on a monthly basis, and four seasons were defined following the criterion used in a nutrition survey (i.e., spring, March−May; summer, June−August; fall, September−November; winter, December−February).

Statistical Analyses. The fatty acid content and composition are reported as the average of triplicates throughout the paper. Statistical analysis in this study was performed using Duncan's multiple-range test in SAS (*21*).

RESULTS AND DISCUSSION

Fatty acid composition and content were determined over four seasons in 12 species of shellfish common in Korea. **Table 1** lists the shellfish analyzed in this study, categorized according

Table 6. Seasonal Variations in the Proportions of *n*–3 Fatty Acids and *n*–6 Fatty Acids and Their Ratios (R)[a]

species		May	June	July	Aug	Oct	Dec	Mar	Pr
murex shell	*n*–3	23.4a	12.5b	6.1c	22.5a	23.6a	21.9a	22.5a	***
	n–6	12.0bc	11.1c	12.8bc	14.1ab	10.3c	16.2a	11.0c	**
	R	2.0ab	1.1d	0.5e	1.6bc	2.3a	1.4cd	2.1ab	***
ark shell	*n*–3	42.1a	36.2ab	33.1b	40.5ab	36.3ab	36.8ab	19.1c	***
	n–6	5.0c	4.9c	6.9b	4.0c	7.4b	4.5c	9.7a	***
	R	8.4ab	7.5b	4.8c	10.2a	4.9c	8.2ab	2.0d	***
granulated ark shell	*n*–3	34.0a	32.5ab	26.8ab	*b*	16.1c	35.6a	24.0bc	**
	n–6	3.7bc	3.9b	6.0a		3.8bc	5.9a	3.0c	***
	R	9.2a	8.3ab	4.5c		4.3c	6.0bc	8.0ab	**
hard-shelled mussel	*n*–3	30.3c	34.5bc	34.4bc	36.6b	43.7a	36.2b	37.0b	***
	n–6	4.4d	5.1c	6.8a	6.1b	3.7e	3.5e	5.3e	***
	R	6.9c	6.8c	5.1d	6.0c	11.9a	10.4b	7.0c	***
pen shell	*n*–3	42.3a	38.2a	35.5a	25.8b	41.4a	34.4a	38.9a	**
	n–6	2.8c	2.8c	4.3b	4.2b	4.7b	3.0c	6.4a	***
	R	15.3a	13.7a	8.2bc	6.1c	8.9bc	11.3ab	6.0c	***
oyster	*n*–3	45.0a	32.3b	35.9b	34.0b	34.1b	43.4a	46.0a	**
	n–6	3.8c	4.8b	4.7b	4.6b	5.8a	4.7b	4.5bc	**
	R	12.0a	6.8d	7.6cd	7.4cd	5.9d	9.2bc	10.3ab	***
surf clam	*n*–3	33.6a	32.5a	29.2a	31.1a	32.9a	31.3a	27.6a	
	n–6	5.1b	4.9b	6.3ab	4.6b	6.2ab	6.2ab	7.6a	*
	R	6.6a	6.7a	4.6b	6.8a	5.3ab	5.1ab	3.7b	**
pink butterfly shell	*n*–3	35.0a	*b*	28.7c	28.2c	33.2ab	*b*	31.3b	***
	n–6	4.5b		5.0b	7.1a	6.2a		6.2a	***
	R	7.8a		5.8b	4.0c	5.4b		5.1b	***
jack-knife clam	*n*–3	32.6a	34.1a	27.5ab	25.6ab	22.1b	27.6ab	31.0ab	
	n–6	5.9ab	5.2bc	5.9ab	5.8b	4.7c	6.7a	5.4bc	**
	R	5.5ab	6.6a	4.7b	4.4b	4.7b	4.1b	5.8ab	
Venus clam	*n*–3	32.0ab	30.9ab	35.6a	28.5bc	25.8c	31.3ab	29.8bc	*
	n–6	6.3ab	4.6b	7.1ab	5.3b	6.5ab	7.2ab	10.4a	
	R	5.1b	6.7a	5.0b	5.4b	4.0bc	4.4bc	2.9c	**
Orient hard clam	*n*–3	34.5a	18.8e	26.7cd	33.6ab	22.9de	29.0bc	32.2ab	***
	n–6	4.5cd	5.4bc	3.3d	6.3b	5.1bc	7.9a	4.9bc	***
	R	7.6a	3.5d	8.0a	5.4bc	4.5cd	3.7d	6.6ab	***
little neck clam	*n*–3	29.9ab	28.6abc	23.0bcd	21.7cd	20.0d	23.8bcd	33.2a	*
	n–6	4.4e	5.6de	5.4de	7.7b	7.1bc	9.2a	6.3cd	***
	R	6.8a	5.1ab	4.3bc	2.8c	2.8c	2.6c	5.3ab	**

[a] Values of *n*–3 fatty acids and *n*–6 fatty acids are proportions (%) to total fatty acids. R represents ratio of *n*–3 fatty acids to *n*–6 fatty acids. Means with the same letter within rows are not significantly different ($p < 0.05$). *, **, and *** represent significance at 0.05, 0.01, and 0.001, respectively. [b] Samples were not available in local markets.

to the biological classification (*22*, *23*). One species of Gastropoda and 11 species of Bivalvia were included. Twenty-three fatty acids, saturated fatty acids (SFA) C14:0, C15:0, C16:0, C17:0, C18:0, C20:0, C22:0, and C24:0; monounsaturated fatty acids (MUFA) C16:1, C18:1(9), C18:1(13), C20:1, C22:1, and C24:1; $n-3$ PUFA C18:3, C20:3, C20:5, and C22:6; and $n-6$ PUFA C18:2, C18:3, C20:2, C20:3, and C20:4, were detected in the shellfish.

In most species, clear seasonal changes in the contents of total fatty acids were observed, ranging from 0.31 to 6.48 wt % (**Table 2**). Total fatty acids are expected to show slightly lower values than total fat because the latter contains other lipid components besides fatty acids, such as sterols, nonsaponifiable hydrocarbons, and glycerol. However, it is plausible to substitute seasonal changes of lipid with total fatty acids, because fluctuations in total lipid contents are caused predominantly by the variation in triglyceride (*10*). Total fatty acid contents increased to maximum in early summer before spawning and decreased to minimum in late summer after spawning in most shellfishes except murex shell and ark shell (**Tables 1** and **2**). This has been known as a typical pattern described for Bivalvia, because the reproductive activity was shown to dictate the seasonal cycles of energy storage and utilization (*16*, *17*, *19*, *24*). In murex shell and ark shell, the variations were biphasic. The total fatty acids in these two species increased again at the onset of winter and then decreased until spring. It may be explained by the potential of fatty acids as an energy source in some marine bivalves during the winter period of nutritional deficiency (*17*).

Fatty acid compositions are summarized into common fatty acid classes in **Table 3**. The percentage of MUFA was lowest in most species throughout the year. The proportion of PUFAs showed a minimum in summer and early autumn and a maximum in winter or early spring with a gradual change between, whereas SFAs showed the opposite pattern in most species. It has been observed that low environmental temperatures generally increased the degree of unsaturation for the fatty acids in aquatic organisms (*4*, *6*).

The fatty acid spectra in analyzed shellfish were typical of marine animals, with the dominance of palmitic acid (C16:0), EPA (C20:5), and DHA (C22:6). Ackman and Eaton (*25*) pointed out that palmitic acid was a key metabolite in fish. It has been generally accepted that the typical predominance of EPA and DHA is an adaptation to the relatively low temperature of the marine environment, therefore contributing to the maintenance of cell membrane fluidity (*11*, *26*).

The major SFAs were palmitic acid (18.7−34.5%) and stearic acid (4.00−16.7%). Palmitic acid (C16:0) was prominent in all shellfish, contributing to high percentage of SFAs in shellfish (30.7−55.3%). SFAs slightly increased before spawning in most species (**Tables 1** and **3**). Because palmitic acid is not influenced by diet and used as an energy source in shellfish, de novo synthesis of these fatty acids (C16:0 and C18:0) from the period preceding the spawning has been suggested (*18*, *25*). Lipids are the preferable substrates of bivalve mitochondria and oxidized much better than pyruvate or other metabolic intermediates (*18*).

The major MUFAs were oleic acid (18:1,Δ9) (1.43−9.01%) and its positional isomer (18:1,Δ13) (1.94−8.93%). The principal PUFA were EPA (5.0−26.1%) and DHA (6.3−30.4%) in all shellfish except murex shell. Murex shell, the only sample belonging to the Gastropoda class, presented high *n*−6 PUFA (10.3−16.2%), especially arachidonic acid (AA) (7.0−11.6%), and low *n*−3 PUFA (6.1−23.6%) compared to Bivalvia (*n*−6, 2.8−10.4%; *n*−3, 16.1−45.9%). The relative enrichment of the Gastropoda with AA and their impoverishment in DHA have been previously noted (*9*). This discrepancy between two classes may be partially interpreted by the difference of diet. Most bivalve mollusks feed on suspended organic particles, such as planktonic microalgae containing high amounts of EPA and DHA (*4*, *11*, *16*, *27*). On the other hand, murex shell (*Rapana venosa*) is a carnivorous gastropod feeding on bivalves, limpets, and barnacles (*27*). In the present study, the proportion of DHA and EPA in Bivalvia was >20% of total fatty acids throughout the year, whereas that in murex shell varied in large extent with seasons, showing the lowest in July (5.8%; **Table 4**). Pollero et al. (*16*), however, reported that a clear seasonal change of DHA and EPA in some Bivalvia was detected in relation to the type of food and sexual cycle.

Generally, marine fish show higher contents of PUFA due to their diets and, therefore, a high ratio of PUFA to SFA (P/S) (*15*). In contrast, SFA contents were higher (30.7−55.3%), albeit only slightly, than PUFA (19.0−50.4%) in most of the shellfish in this study (**Table 3**), which led to low P/S (0.34−1.39). The opposite tendency of seasonal changes between PUFA and SFA brought about lower P/S in the summer (**Table 5**).

Although it has been believed that the absolute content of PUFA or *n*−3 PUFA influences the prevention of disease, P/S or *n*−3/*n*−6 (ratio of *n*−6 fatty acids to *n*−3 fatty acid) in diet has been emphasized in recent studies (*2*, *4*). Risk factors for certain chronic diseases were observed to be reduced by modulating eicosanoid biosynthesis through the changes in the composition of dietary fatty acids (*2*, *4*, *29*). Piggott and Tucker (*28*) suggested that the *n*−3/*n*−6 ratio was the better index of relative nutritional value from different species. **Table 6** shows that *n*−3/*n*−6 ratios of Bivalvia (2.0−15.4) are much higher than those of Gastropoda (0.5−2.3). *n*−3 fatty acids were the major contributory factor to the seasonal variations of total PUFA, because the proportions of *n*−6 fatty acids were low and relatively unchanged. It was reflected in the seasonal pattern of both *n*−3/*n*−6 and the amount of PUFA (**Table 6**). Beninger and Stephan (*11*) observed the same pattern in adult clams.

Although it is generally recognized that fatty acid compositions in seafood vary with species and seasons, little attention has been paid to the seasonal changes of fatty acid compositions and nutritional values in the edible portion of shellfish in Korea. The present study on Korean shellfish showed the drop of total fatty acid contents in summer and seasonal variations in the proportion of *n*−3 fatty acids. Shellfish provide a significant amount of EPA and DHA to the Korean population, so it is an important component of the diet, providing >10% of the daily protein intake in Korea (*29*). Furthermore, the favorable *n*−3/*n*−6 ratio is expected to enhance the nutritional value of these shellfish.

ABBREVIATIONS USED

PUFA, polyunsaturated fatty acid; MUFA, monounsaturated fatty acid; SFA, saturated fatty acid; P/S, ratio of polyunsaturated fatty acids to saturated fatty acids; *n*−3/*n*−6, ratio of *n*−3 fatty acids to *n*−6 fatty acids; AA, arachidonic acid; EPA, eicosapentaenoic acid; DHA, docosahexaenoic acid.

LITERATURE CITED

(1) Kinsella, J. E. Food component with potential benefits: the *n*−3 polyunsaturated fatty acids of fish oils. *Food Technol.* **1986**, *40* (2), 89−97.

(2) Leaf, A.; Weber, P. C. Cardiovascular effects of n-3 fatty acids. *New Engl. J. Med.* **1988**, *318* (9), 549−557.

(3) Simopoulos, A. P. Summary of NATO advanced research workshop on dietary ω−3 and ω−6 fatty acids: Biological effects and nutritional essentiality. *J. Nutr.* **1989**, *19*, 521−528.

(4) De Moreno, J. E. A.; Moreno, V. J.; Brenner, R. R. Lipid Metabolism of the Yellow Clam, *Mesodesma mactroides*: 1. Composition of the Lipids. *Lipids* **1976**, *11* (4), 334−340.

(5) Ackman, R. G. Concerns for utilization of marine lipids and oils. *Food Technol.* **1988**, 151−155.

(6) Wang, Y. J.; Miller, L. A.; Perren, M.; Addis, P. B. Omega-3 fatty acids in Lake Superior fish. *J. Food Sci.* **1990**, *55* (1), 71−73.

(7) Kinsella, J. E.; Lokesh, B.; Stone, R. A. Dietary *n*−3 polyunsaturated fatty acids and amelioration of cardiovascular disease: possible mechanisms. *Am. J. Clin. Nutr.* **1990**, *52*, 1−28.

(8) Layne, K. S.; Goh, Y. K.; Jumpsen, J. A.; Ryan, E. A.; Chow, P.; Clandinin, M. T. Normal subjects consuming physiological levels of 18:3(*n*−3) and 20:5(*n*−3) from flaxseed or fish oils have characteristic differences in plasma lipid and lipoprotein fatty acid levels. *J. Nutr.* **1996**, *126*, 2130−2140.

(9) Gardner, D.; Riley, J. P. The component fatty acids of the lipids of some species of marine and freshwater molluscs. *J. Mar. Biol. Assoc. U.K.* **1972**, *52*, 827−838.

(10) Clarke, A. Lipid class and fatty acid composition of *Chorismus antarcticus* (Pfeffer) (Crustacea: Decapoda) at South Georgia. *J. Exp. Mar. Biol. Ecol.* **1977**, *28*, 297−314.

(11) Beninger, P. G.; Stehpan, G. Seasonal variations in the fatty acids of the triacylglycerols and phospholipids of two populations of adult clam (*Tapes decussates* L. and *T. philippinarum*) reared in a common habitat. *Comp. Biochem. Physiol.* **1985**, *81B*, 591−601.

(12) Vlieg, P.; Body, D. B. Lipid contents and fatty acid composition of some New Zealand freshwater finfish and marine finfish, shellfish and roes. *N. Z. J. Mar. Freshwater Res.* **1988**, *22*, 151.

(13) Wenne, R.; Polak, L. Lipid composition and storage in the tissues of bivalve, *Macoma balthica*. *Biochem. Syst. Ecol.* **1989**, *17* (7/8), 583−587.

(14) Suriah, A. R.; Teh, S. H.; Osman, H.; Nik-Mat, D. Fatty acid composition of some Malaysian freshwater fish. *Food Chem.* **1995**, *54*, 45−49.

(15) Osman, H.; Suriah, A. R.; Law, E. C. Fatty acid composition and cholesterol content of selected marine fish in Malaysian waters. *Food Chem.* **2001**, *73*, 55−60.

(16) Pollero, R. J.; Ré, M. E.; Brenner, R. R. Seasonal changes of the lipids of the mollusk *Chlamys tehuelcha*. *Comp. Biochem. Physiol.* **1979**, *64A*, 257−263.

(17) Beninger, P. G. Seasonal variations of the major lipid classes in relation to the reproductive activity of two species of clams raised in a common habitat: *Tapes decussates* L. (Jeffreys, 1863) and *T. philippinarum* (Adams & Reeve, 1850). *J. Exp. Mar. Biol. Ecol.* **1984**, *79*, 79−90.

(18) Kluytmans, J. H.; Boot, J. H.; Oudejans, R. C. H. M.; Zandee, D. I. Fatty acid synthesis in relation to gametogenesis in the mussel *Mytilus edulis* L. *Comp. Biochem. Physiol.* **1985**, *81B*, 959−963.

(19) Chu, F. E.; Webb, K. L.; Chen, J. Seasonal changes of lipids and fatty acids in oyster tissues (*Crassostrea virginica*) and estuarine particulate matter. *Comp. Biochem. Physiol.* **1990**, *95A*, 385−391.

(20) Lepage, G.; Roy, C. C. Direct transesterification of all classes of lipids in a one-step reaction. *J. Lipid Res.* **1986**, *27*, 114−120.

(21) SAS Institute Inc. SAS software release 8.1; SAS Institute: Cary, NC, 1999.

(22) The Korean Society of Systematic Zoology. *List of Animals in Korea*; Academybook Publishing: Seoul, Korea, 1997.

(23) Kwon, O. K.; Min, D. K.; Lee, J. R.; Lee, J. S.; Je, J. G. *Korean Mollusks with Color Illustration*; Hangul Publishing: Seoul, Korea, 2001.

(24) Peck, L. S.; Clarke, A.; Holms, L. J. Summer metabolism and seasonal changes in biochemical composition of the Antarctic brachiopod *Liothyrella uva* (Broderip, 1833). *J. Exp. Mar. Biol. Ecol.* **1987**, *114*, 85−97.

(25) Ackman, R. G.; Eaton, C. A. Some commercial Atlantic herring oils: fatty acid composition. *J. Fish. Res. Board Can.* **1966**, *23*, 991.

(26) Farkas, T. Adaptation of fatty acid composition to temperature. A study on planktonic crustaceans. *Comp. Biochem. Physiol.* **1979**, *64B*, 71−76.

(27) Barnes, R. D. *Invertebrate Zoology*; Sanders College Publishing: Fort Worth, TX, 1986; pp 364−379, 407−413.

(28) Piggot, G. M.; Tucker, B. W. *Effects of Technology on Nutrition*; Dekker: New York, 1990.

(29) The Korean Nutrition Society. *Recommended Dietary Allowances for Koreans*, 7th revision; Seoul, Korea, 2000; pp 46−56, 340−380.

Received for review October 14, 2002. Revised manuscript received January 8, 2003. Accepted January 13, 2003. This research was (partly) supported by a grant from the Research Institute of Human Ecology at Seoul National University.

JF026033A