Asian Fisheries Science **13**(2000): 263-270
Asian Fisheries Society, Manila, Philippines

https://doi.org/10.33997/j.afs.2000.13.3.008

Changes in the Volatile Compounds of Yellowtail (*Seriola aureovitata*) During Refrigerated Storage

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Abstract

A variety of significantly odorous compounds of yellowtail (*Seriola aureovitata*) developed during storage at 3ºC for 15 days. Trimethylamine (TMA) and dimethylamine (DMA) were the major volatile basic components. Volatile organic acids which include acetic acid, propionic acid, butyric acid, isobutyric acid and valeric acid were found and their contents increased during six days of storage, but the level of contents didn't reach their odor threshold. Fat oxidation products of carbonyls and alkenals increased greatly during storage. The important compounds were hexanal, hexenal, octanal, octenal, 3,5-octadien-3-one, nonanal, and pent-1-en-3-ol, octen-3-ol. Sulphide compounds were identified after six days of storage.

Introduction

A variety of odoriferous compounds of fresh fish developed during their cold storage. A number of these chemical compounds are used as quality indices of fishery products. Some of these volatile basic nitrogenous compounds resulting from amino acids and trimethylamine oxide have been frequently used (Miller et al. 1972; Toshinaga 1975). Some fishery products produce off-flavors during storage due to the oxidation of highly unsaturated lipids in the muscles and other tissues, which lead to the production of low odor threshold carbonyls and alkenols (Gadbois et al. 1967; Grun et al. 1996; Hsieh et al. 1989; Hughes 1963). Sulphides and precursors which give off odor from spoiled fish have

been dealt with by many researchers (Ronald and Thomson 1964; Ackman and Hingley 1968; Brook et al. 1968; Herbert and Shewan 1975; Herbert and Shewan 1976; Tokunaka 1977). The production of volatile fatty acids correlated with the degradation of fish quality (Miyahara 1961; Kasahara and Nishibori 1975). The odor of deteriorated fish came from different origins and formed different odor patterns. In order to elucidate the quality changes of commercial marine fish yellowtail (*Seriola aureovitata*), volatile compounds of carbonyls and alkanols, organic acids, volatile bases and sulphides were studied.

Materials and Methods

Sample preparation

Live yellowtail weighing about 1.5 kg were caught from the culture station. The fish were packed in ice, transported to the laboratory, excised and separated into white and dark muscles. The muscle samples were stored at 3ºC for 15 days and were analyzed at every three days interval. Each reported value is the mean of three determinations.

Proximate composition of the fish

The contents of moisture, crude protein, and crude fat of samples were determined according to the AOAC method (AOAC 1984).

Lipid extraction and analysis

The total lipids were extracted following the method of Folch using a mixture of solvents $CHCl_3$-CH_3OH. The extracted lipids were esterified following said method (Maeda et al. 1987) while fatty acids were measured by gas-liquid chromatography (HP5890II). The contents of each fatty acid were calculated by normalization.

Volatile basic acid compounds

Five percent TCA extract of muscle tissues were prepared to determine volatile base nitrogen (VBN), trimethylamine (TMA) and dimethylamine (DMA) contents. TMA and DMA were measured simultaneously following the methods of Castell (1973).

Volatile organic acid compounds

Twenty grams of samples were used to extract volatile organic acids by steam distillation and the volatile acids were absorbed with 0.2% NaOH solution. Distilled solution was acidified, organic acid compounds of fish samples were extracted with ethyl ether and concentrated to 1 ml. The contents of acids were determined by gas liquid chromatography using external methods.

Sulphur compounds

Muscle samples were sealed in a 2 ml vial and upper vapor was used to identify volatile sulphur compounds by gas chromatography with FPD Detector.

Carbonyls and alkanols

A dynamic gas purging apparatus was set up for the collection of volatile compounds from fresh fish and spoiled fish samples (Olafsdorttir 1985). Fifty grams of white muscles were homogenized and placed in a bronze cylinder and immersed in a water bath (55ºC). The internal standard tridecane was added and made it to a final concentration of 20 ppb. For the adsorption of volatile compounds, 250 milligrams porous polymer adsorbent (GDX-502) previously treated with polar and nonpolar solvents were packed in the 3 mm steel column. High purity nitrogen was purged through the system at the rate of 300 ml·min for four to five hours, and dried with nitrogen at the rate of 50 ml·min for four to six hours. Volatile compounds were eluted with redistilled ethyl ether from the GDX column and concentrated to 20 microliter for GC and GC-MSD analysis.

Gas chromatography(GC) and mass selective detector (MSD)

The volatile compounds adsorbed by GDX-502 were injected into GC-MSD (HP5890II-HP5971A) with a Carbowax 20 M fused silica capillary column (25 m x 0.3 mm). The column temperature was held at 60ºC for two minutes and then increased at 5 to 190ºC and held for 20 min. Helium was used as carrier gas at a flow rate of 1.5 ml·min. The analysis was performed with the detector in the scan mode, the electron ionization voltage was set at 70 ev and the mass spectrometry interface temperature was set at 280ºC. The identification of volatile compounds based on retention index and the sample spectra matched with those from the GC-MSD Willey library.

Sensory evaluation

A trained panel of nine people evaluated the odor changes of the fish meat during refrigerated storage. Ratings made were as follows: 1-very fresh; 2-fresh; 3-slightly fresh (acceptable); 4-slightly rancid; 5-rancid; and 6-putrid.

Results and Discussion

Proximate composition of muscle sample

Proximate composition of white muscles and dark muscles are shown in table 1. One of the differences between the white and dark muscles was that the fat contents of the dark muscle (19.7%) was much higher than that of the white muscle (3.2%).

Fatty acid composition

The fatty acid composition of the muscle lipids are shown in table 2. The major fatty acids in the muscle lipid of the fish were: C16:0, C18:0, C18:1, C20:5n3, C22:6n3. The most abundant component was C22:6n3 which is higher in the dark muscle than in the white muscle. Highly polyunsaturated fatty acids are the precursors of volatile carbonyls and are easily oxidized.

Volatile basic compounds

The development of TMA in fish muscle stored at 3ºC is shown in table 3. All volatile basic compounds increased during storage. VBN, one of the freshness indices, reached 21.2 mg·100g in the dark muscle at six days of storage. Odor profile of samples indicated that the odor of white muscle was still acceptable after four days of storage and it became slightly rancid after eight days The critical point for white muscles to become unacceptable was the 6th day of storage at 3ºC. The dark muscle had lower VBN value at the initial stage and after six days of storage it developed more volatile basic compounds. TMA and DMA were very little before six days and greatly increased after six days. Since the threshold of TMA is 0.6 mg·kg and DMA is 30 mg·kg, TMA is the most important fishy odor producing component.

Volatile organic acids

Volatile organic acids produced in fish muscle samples during storage at 3ºC are shown in table 4. Acetic acid, propionic acid, butyric acid, isobutyric acid and valeric acid are the major acidic components. Acids composition pattern in spoiled fish varied with different fish species. Volatile acids existed in trace amounts in fresh samples but there is a substantial amount of acetic acid. As the degradation of fish muscles proceeded organic acids resulting from oxidized products of fats and amino acid decomposition increased. Butyric acid and valeric acid played

Table 1. Composition of white and dark muscles of yellowtail (*Seriola aureovitata*) (%).

	Moisture	Crude lipid	Crude protein
White muscle	73.8	3.2	21.9
Dark muscle	67.4	19.7	16.1

Table 2. Fatty acid composition of white and dark muscle lipids of yellowtail (*Seriola aureovitata*) (%).

Fatty acid	White muscle	Dark muscle
C14:0	4.5	3.9
C16:0	19.7	13.4
C16:1	10.0	6.6
C18:0	5.8	6.9
C18:1	17.5	11.4
C18:2n6	1.1	1.3
C18:3n3	1.0	1.1
C20:4n6	1.9	1.6
C20:5n3	5.9	6.7
C22:5n3	3.3	2.2
C22:6n3	15.11	20.9

important roles in the production of spoiled fish odor because of their low thresholds. After six days of storage butyric acid reached 1.1 mg·kg and isobutyric acid amounted to 4.9 mg·kg in the white muscles and both did not reach their thresholds of 3.0 mg·kg and 9.2 mg·kg respectively.

Carbonyls and alkanols compounds

The total ionic chromatograms analyzed by the GC-MSD of fresh white muscles and the muscles stored for 12 days are shown in figures 1 and 2. Volatile compounds identified in the samples are shown in table 5. No volatile carbonyls was detected in the fresh samples and two days of storage samples. After four days of storage, oxidized fish products such as hexanal, heptanal, 2-hexenal, octanal, 3,5-octadien-one were identified. More carbonyls such as 2-oct e- nal, nonanal, 2-undecanone, 4-methyl hexan-2-one were found in the 12 days of storage samples. The odor profile correlated very well with the results of carbonyl compounds and the meat color changed from white to yellow. From the results, hexanal was the most prominent and abundant individual volatile carbonyl component during storage. Hexanal was the oxidized product of n-6 fatty acids (Ajuyah et al. 1993). Ullrich and Grosch (1987) have found that hexenal, octanal, and nonanal existed in “inverted” soy bean oil. More severe fat oxidization of sardine oil

Table 3. Volatile basic compounds of fish meat stored at 3ºC for 15 days (mg·100g).

Storage days		0	3	6	9	12	15
White muscle	VBN	3.5	10.5	21.2	27.5	37.9	71.9
	TMA	0.4	0.8	1.1	13.8	17.4	31.5
	DMA	0.4	0.7	1.0	12.7	13.3	15.4
Dark muscle	VBN	1.2	3.5	15.5	20.2	42.8	88.4
	TMA	0.6	1.3	7.5	13.4	26.7	31.8
	DMA	0.4	1.1	6.8	11.5	13.1	15.6

Table 4. Volatile organic acids of fish muscles during storage at 3ºC (mg·kg).

	Storage days	Acetic acid	Propionic acid	Butyric acid	Isobutyric acid	Valeric acid
White muscle	0	8.8	t	t	t	t
	3	15.7	3.3	.0.8	0.8	0.8
	6	29.8	7.5	0.9	1.6	0.8
	9	32.8	10.6	1.1	4.9	0.9
	12	44.8	12.4	3.1	8.6	3.4
	15	69.6	18.5	3.8	14.0	4.2
	0	t	t	t	t	t
	3	15.0	1.1	1.0	0.4	0.6
Dark muscle	6	36.3	1.1	1.4	0.8	0.8
	9	46.4	3.5	2.1	1.6	1.0
	12	50.2	10.3	2.1	9.8	0.9
	15	65.2	27.3	2.1	46.9	0.9

t means trace amounts.

played an important role in the production of rancid odor (Nakamura 1980). Besides carbonyls, alkanols and alkenols such as pent–1– en–3-ol, octen-3-ol, pentanol, and hexanol were the noticetable compounds in the white muscles after four days of storage. Octen-3-ol has the lowest threshold and gave strong off-odors (Frankel 1991). Pent-1-en-3-ol was the most abundant alkenol in the muscle and an important compound in oxidized sardine oil (Nakamura et al. 1980).

Sulphide compounds

Direct static headspace technique was used to identify volatile sulphide compounds by FPD of GC. It was found that the compounds were produced after six days of storage. Peak areas increased after heavy rancid odor of fish meat developed. Their importance to fish odor have been elucidated by many reporters.

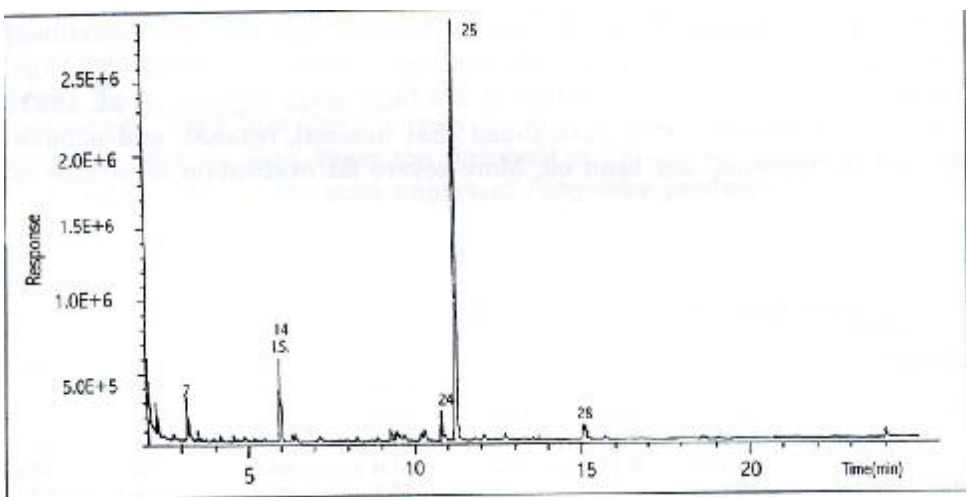

Fig. 1. GC-MSD separation of volatiles from fresh fish after 0 day of storage.

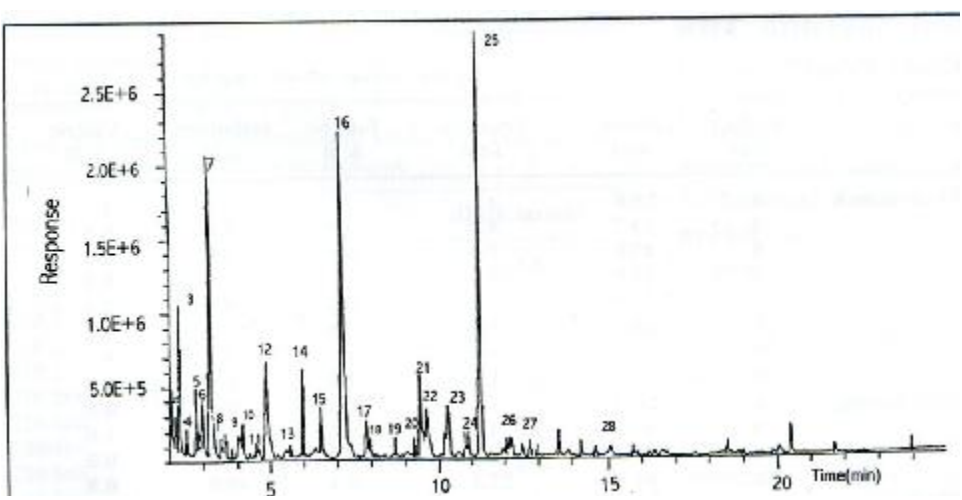

Fig. 2. GC-MSD separation of volatiles from spoiled fish after 12 days of storage.

Table 5. Volatile compounds identified in fresh and spoiled fish.

Peak No	Compounds	Retention weight	Molecular index	Peak area		
				0 day	6 days	9days
1	2,4-pentanedlone	1062	100			L
2	3-methyl butyric acid ethyl ester	1070	130			M
3	hexanal	1087	100		L	L
4	2-methyl-2-propanol	1106	74		S	M
5	ethyl benzene	1108	106			L
6	1,3-dimethyl benzene	1124	106			L
7	1-penten-3-ol	1136	86	S	L	VL
8	pyridine	1156	79			S
9	heptenal	1163	114		S	M
10	2-hexanal	1196	98		M	M
10a	4-heptenal	1198	112		S	
11	4-methyl-2-hexanone	1218	114			S
12	1-pentanol	1235	88		S	L
13	octanal	1268	128		VS	VL
14	tridecane	1285	184	IS	IS	IS
14a	2-penten-1-ol	1306	86		M	
15	6-octen-2-one(Z)	1316	126			L
16	1-hexanol	1341	102		VS	VL
17	2-methyl-4-penten-1-ol	1375	100			M
18	nonanal	1386	142			S
19	2-octenal	1412	126			S
20	Acetic acid	1432	60		S	VS
21	1-octen-3-ol	1435	128		M	L
21a	3-octen-1-ol	1438	128		S	
22	1-heptanol	1439	116			M
23	3,5,5-trimethyl-2-hexene	1462	126		M	M
24	benzaldehyde	1483	106	M	M	M
25	unidentified	1502	118	VL	VL	VL
26	3,5-octadien-2-one	1536	124		S	VS
27	1- Octanol	1540	130			S
28	benzonitrile	1570	103	VS	VS	VS

Peak No. correspond to the peak number in Figure 2. VL, very large; L, large; M, middle; S, small; VS, very small. Peak of 10a,14a,21a were identified after 6 days of storage. IS, internal standard.

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Manuscript received 20 June 1996; Accepted 30 April 1998.