Volatile Components of Boiled and Roasted Short-necked Clam *Tapes philippinarum*

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The volatile components were experimentally produced by heating short-necked clam (*Tapes philippinarum*) with glass beads. Three flavor concentrates, obtained by distillation at three temperature ranges (98–101, 101–115, and 115–160°C), were analyzed by GC-MS. A total of 76 compounds were identified. They included 9 acyclic nitrogen compounds, 9 pyrazines, 6 pyridines, 6 pyrroles, 5 pyrrolidines, 5 acyclic sulfur compounds, and 1-methylpyrrolidine-2,5-dione.

The last concentrate (115–160°C) gave a pleasant roasted odor of short-necked clam was characterized by the following flavor components: 3, 4, 5, 6-tetrahydro-2, 4, 6-trimethyl-2*H*-1, 3, 5-thiadiazine, 5, 6-dihydro-2, 4, 6-trimethyl-4*H*-1, 3, 5-dithiazine, 2-methyl-2-thiazoline, 3-hydroxy-2-methyl-4*H*-pyrone (maltol), and *N,N*-dimethylglycine methyl ester. While the second concentrate (101–115°C) having the boiled odor of the clam contained some pyrazines, some pyridines, and the ester as major flavor components.

Short-necked clam (*Tapes philippinarum*), with a wide range of distribution extending from the Philippine Islands to the Kuril Islands lying in the Sea of Okhotsk,¹⁾ is a delicacy due to its flavor. It also grows on the coasts of Hawaii, California, and Canada, after being introduced from Japan into those regions.¹⁾ It gives an appetizing odor when heated, especially when roasted, although it has merely a weak fishy or marine odor when fresh. However, no literature on capillary gas chromatographic (GC) analysis of heated short-necked clam volatiles is available. Only limited information concerning heated volatiles on short-necked clam and soft-shell clam (*Mya arenaria*) has been published by Nishibori *et al.*,²⁾ Gadbois *et al.*,³⁾ and Mendelsohn and Brooke,⁴⁾ before capillary GC was development. The latter workers have identified more than twenty volatile components from cooked soft-shell clam. Among the components, methylthiomethane was reported to have been the most dominant head gas component and the source of the typical clam odor.⁴⁾ The compound has been recently recognized as a mutually common volatile in bivalves⁵⁾ including short-necked clam and in unicellular algae,^{6,7)} so that there must be the food-chain.⁷⁾ Much information

on volatiles of bivalves has been confined to volatiles arising from raw or during storage.^{3,4,8,9)} Josephson *et al.*¹⁰⁾ have revealed characteristic flavor components of fresh Pacific oyster by using capillary GC. Yasuhara¹¹⁾ has recently reported a comparison of volatiles between fresh and rotten mussel.

This paper reports on the volatile compounds produced by heating short-necked clam. We also describe comparisons among the constitution of volatile components generated in the three temperature ranges of 98–101, 101–115, and 115–160°C.

Materials and Methods

Sample Preparation

Live short-necked clams *Tapes philippinarum*, wrapped with plastic sheets on which a catching place (Tokushima, Japan) was printed, were purchased from a local supermarket in February. Their bodies, along with the juice (426 g), was obtained by hand-shucking from nearly 1 kg of the clams with shells. They were placed into a 2 l round-bottom four-neck flask containing 880 g of dried glass beads (2.3 mm, i. d.). The flask was heated with an electric mantle heater with

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moderate stirring. This glass beads method (tentative name) was previously described with the apparatus and the procedures.^{12,*} The fractions distilled by the three temperature ranges (temperature of the beads) were repeatedly extracted by ether and CH_2Cl_2 until their odors disappeared. The extracts evaporated at reduced pressure till approximately 30, 90, and 300 mg of flavor concentrates remained. They were stored at -20°C and then submitted to GC and GC-MS analyses.

Identification of Compounds

Almost all standard compounds for identification were purchased commercially (Aldrich Chemical Co., Milwaukee; Tokyo Kasei Kogyo, Co., Tokyo; Wako Pure Chemical Co., Tokyo). 3, 4, 5, 6-Tetrahydro-2, 4, 6-trimethyl-2*H*-1, 3, 5-thiadiazine dihydrate (**54**, peak No. in Table 2) and 5, 6-dihydro-2, 4, 6-trimethyl-4*H*-1, 3, 5-dithiazine (**60**, thialdin) were synthesized according to the methods described previously:¹³ **54**, mp. 68.5°C (ref. 69.4°C^{13}), yield 70%; **60**, 46.8°C (ref. 47.3°C^{13}), 95%.

Apparatus for Analysis

The flavor concentrates were analyzed by capillary gas chromatography (GC) on a Hewlett-Packard 5840A chromatograph equipped with a non-polar column; 0.25 mm (i. d.) $\times$ 30 m (0.25 μm film, DB-1 fused silica). The compounds containing sulfur and nitrogen were also recorded on a gas chromatograph; Hitachi 163 equipped with a flame photometric detector (FPD), flame thermionic detector (FTD), together with a flame ionization detector (FID). Volatile components were identified by capillary gas chromatography-mass spectrometry (GC-MS) analysis on a Hitachi M-80A combined with a 0.25 mm (i. d.) $\times$ 50 m capillary column (0.25 μm film,

DB-1 fused silica). Running conditions on these apparatus were the same as described previously.¹² Ionization energy was 20 eV. For each concentrate, 0.6 μl was injected into GC.

Results and Discussion

Alteration of pH during Heating

Table 1 shows thermal effects on distillates generated from the heated short-necked clam-glass beads system; the pH values altered from neutral (pH 6.8) to weakly basic (pH 8.8), and odors of distillates changed from weakly boiled to roasted odors as temperature of the beads elevated.

There is no significant difference in the pH values on the clam juice (pH 6.8–7.0) between the first distillate (pH 6.8) and the second one (pH 7.0). It supports the fact that neither fresh nor boiled short-necked clam contained ammonia as reported by Nishibori *et al.*² As compared with these pH values, the different pH value (pH 8.8) on the last distillate suggests that thermal interactions on short-necked clam principally occurred above 115°C .

On the other hand, as previously reported,* the pH values of distillates obtained from heating dried squid with water (1:1) in the similar manner as the present test, altered from 9.8 (at 101°C) to 8.6 (at 160°C). In the report, we estimated that large generation of ammonia made the distillates basic.

The two initial pH values of the clam juice and the extract of dried squid (pH 6.8, dried squid: water=1:9) were exactly the same before heating, but a large gap in the pH values between their first distillates (pH 6.8 and 9.8) was observed. Therefore, different kinds of volatile constitution must have been formed at higher temperature

Table 1. Alteration of pH and odors of distillates during heating short-necked clam up to 160°C

temperature range	temperature ($^\circ\text{C}$)	time (min)	distillate		odor profile
			(g)	pH	
A	25~98	25			
	98~101	65	224	6.8	weakly boiled odor with unpleasant steam distillation odor
B	101~115	20	80	7.0	boiled odor
C	115~160	15	30	8.8	pleasant roasted odor
total		125	334		

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Fig. 1. Gas chromatogram of the volatile concentrate obtained from heated short-necked clam at the temperature range 98–101°C.

Fig. 2. Gas chromatogram of the volatile concentrate obtained from heated short-necked clam at the temperature range 101–115°C.

Fig. 3. Gas chromatogram of the volatile concentrate obtained from heated short-necked clam at the temperature range 115–160°C.

Table 2. Volatile compounds identified from heated short-necked clam in three temperature ranges 98–101 (A), 101–115 (B), and 115–160 (C) °C

peak No.	compound	KI (DB-1)		GC peak area (%)			MS, KI ref
		unknown	known	A	B	C	
1	ethanal	472	453				
2	diethylether (solvent)						
3	dichloromethane (solvent)						
4	2-butanone	585	560	0.09	0.10	0.05	
5	ethyl acetate	606	595	2.36	0.46	0.07	
6	3-methylbutanal	626	628	0.15	0.10	0.10	
7	2-methylbutanal	637	637	0.11	0.12	0.10	
8	1-methylpyrrolidine	663	665			0.08	
9	3-hydroxy-2-butanone	670	672	0.39	0.11	0.04	
10	2-dimethylaminoethanol	705	708			0.43	
11	pyridine	715	714	1.94	4.81	2.56	
12	methylthiomethane	724	725	0.26	0.50	0.23	
13	pyrrole	727	727			0.39	
14	<i>N,N</i> -dimethylformamide	735	735			0.61	
15	1-ethylpyrrolidine	750	(753)				
						} 0.26	
16	toluene	752	754	1.13	0.15		
17	2-methylpyridine	792	796		0.31	0.29	
18	2-methylpyrazine	796	798	0.08	0.52	0.43	
19	furfural	800	799	0.09	0.07		
20	<i>N,N</i> -dimethylglycine methyl ester	807	810		1.96	1.62	
21	2-methylpyrrole	810	812			0.39	
22	4-hydroxy-4-methyl-2-pentanone	816	815	0.11			
23	1-(methylthio)-1-ethanethiol	820	(822)			0.07	
24	2-furanmethanol	830	830	3.62	5.70		
25	<i>N,N</i> -dimethylacetamide	832	834			1.87	
26	3-methylpyridine	832	834		0.65	1.60	
27	dimethylpyrrole	839				0.12	MS ⁽²⁰⁾
28	2-methyl-2-thiazoline	847	849			0.30	
29	2-oxolanone	857	859	0.27	1.02	0.53	
30	2-acetylfuran	877	880	0.38	1.16	0.35	
31	2,5-dimethylpyrazine	881	883	0.73	1.74	0.45	
32	2-ethylpyrazine	888	887		0.30	0.09	
33	2,3-dimethylpyrazine	892	895	0.48	0.95		
						} 0.35	
34	2,5-dimethylpyrrole	897	902				
35	2,4-dimethylpyridine	906	908			0.18	
36	<i>N,N</i> -dimethylpropionamide*	911	914			0.30	
37	2,3-dimethylpyridine	918	919		0.70	0.11	
38	5-methyl-2-furfural	925	926	0.21	0.61	0.11	
39	benzaldehyde	927	931	0.19	0.17		
40	3-ethylpyridine	929	932		1.76	0.74	
41	methyltrithiomethane	948	949		0.20	0.28	
42	aniline	950	952	0.18	0.15		
43	phenol	958	961	0.13	0.18	0.18	
44	methylethylpyrazine	969			0.35	0.12	MS ⁽²⁰⁾ , KI ⁽²⁷⁾
45	2,3,5-trimethylpyrazine	973	975	1.31	3.24	0.77	
46	unknown (m/e 112, 41, 55, 69, 84)	990		0.42	1.64	0.79	
47	1-methylproline methyl ester	1015	(1017)			0.20	
48	2-acetylpyrrole	1021	1023	0.78	2.41		
49	1-methylpyrrolidine-2,5-dione*	1039	1042		0.60	2.88	
50	unknown (m/e 43, 57, 128, 85, 72)	1041				0.37	

Table 2. Continued

peak No.	compound	KI (DB-1)		GC peak area (%)			MS, KI ref
		unknown	known	A	B	C	
51	2-acetyl-1-methylpyrrole	1046	1045	0.12	0.29		
52	2,5-dimethyl-3-ethylpyrazine	1053	1053	0.68	2.17	0.70	
53	2,6-dimethyl-3-ethylpyrazine	1059	1060	0.89	2.36	0.76	
54	3,4,5,6-tetrahydro-2,4,6-trimethyl-2 <i>H</i> -1,3,5-thiadiazine	1066	1066			0.19	MS ⁽¹²⁾
55	3-hydroxy-2-methyl-4 <i>H</i> -pyrone (maltol)	1076	1079		0.77	1.44	
56	3,5-dimethyl-1,2,4-trithiolane	1107	1109			0.38	
57	1-acetylpyrrolidine	1125	1128			0.37	
58	1,1-bis(methylthio)ethane	1146				0.32	
59	octanoic acid	1155	1158	0.08			
60	5,6-dihydro-2,4,6-trimethyl-4 <i>H</i> -1,3,5-dithiazine	1176	1181			0.77	MS ⁽¹²⁾
61	benzothiazole	1191	1196	0.51	0.55		
62	2-(2-furyl)pyrazine	1226			0.96	0.46	MS ⁽²⁸⁾
63	nonanoic acid	1251	1255	0.32			
64	indole	1260	1264		0.86	0.92	
65	3-(methylethyl)-2,4,5-trithiahexane	1296	(1300)			0.30	
66	decanoic acid	1348	1349	0.36			
67	2- <i>tert</i> -butyl-4-methoxyphenol	1460	1461	0.69			
68	2,6-di- <i>tert</i> -butyl-4-methylphenol	1496	1497	0.32	0.79	1.12	
69	diphenylamine	1590	1596	tr			
70	heptadecane	1701	1700	0.36	0.13		
71	tetradecanoic acid	1750	1758	0.96			
72	hexadecanal	1800	1803	0.89	0.11		
73	proline anhydride	1865	(1870)			0.47	
74	methyl hexadecanoate	1905	1907			0.37	
75	dibutyl phthalate	1922	1922	0.52			
76	hexadecanoic acid	1974	1981	1.74	0.20	0.86	
77	octadecanal	2004		3.54	0.22		
78	methyl octadecanoate	2103	2109			0.11	
79	hexadecanamide	2138	2142		0.27	0.73	
80	<i>N</i> -methylhexadecanamide	2172	(2178)			0.41	

Compounds not fixed with KI (Kovats Indices) are considered to be tentatively identified, solely based on MS (mass spectrum) matching. Compounds with parenthesized KI are identified by comparison with the MS and KI data reported in our previous paper.* Assignment of compound (77) is based on fragment analysis of hexadecanal. Numbers in italics are the molecular weights of the unidentified compounds.

* Asterisked compounds have not been reported previously as volatiles of food.⁽²⁴⁾

ranges between the clam and the dried squid, because ammonia is a well-known natural precursor for heated volatile compounds as well as hydrogen sulfide, methanethiol, and low aliphatic aldehydes.^(14,16) It is very remarkable that both pleasant roasted odors (in Table 1 and in our previous report^(*)) occurred at near pH 9 in nature. The formation of many flavor compounds found from heated food volatiles was reported to have been substantially dependent on pH on the basis of model reactions⁽¹⁸⁻²⁰⁾ (e.g. the thiadiazine having a strong roasted odor has facilely formed under basic conditions from the mixture of ethanal, ammonia, and H₂S⁽¹³⁾).

Characterization of Flavor Concentrates

The three flavor concentrates, having the odors as described in Table 1, were obtained from distillation at the three temperature ranges 98-101 (A), 101-115 (B), and 115-160 (C) °C, and then analyzed by GC-MS. Their GC chromatograms are shown in Fig. 1-3, respectively. The different GC patterns among those Figures show that the volatile constitution became more complicated as temperature rose. They indicate that interactions among low molecular weight compounds arising from heated short-necked clam obviously increased in the flask. The patterns also reflect the difference among the

Table 3. Mass spectral data of volatile compounds found in heated short-necked clam

2-methyl-2-thiazoline (28)	101(M ⁺ , 50), 60(100), 59(43), 55(32), 45(30), 42(28).
<i>N,N</i> -dimethylpropionamide (36)	101(M ⁺ , 58), 72(54), 57(31), 45(73), 44(100), 42(6).
1-methylpyrrolidine-2,5-dione (49)	113(M ⁺ , 60), 85(5), 84(3), 58(12), 57(8), 56(100), 55(6).
1,1-bis(methylthio)ethane (58)	122(M ⁺ , 8), 75(100), 59(18), 47(21), 41(28).
octadecanal (77)	268(M ⁺ , 0), 250(3), 222(6), 182(6), 96(70), 82(100), 68(70), 57(72).

odors.

Table 2 lists 76 identified compounds alongside their corresponding GC peak numbers as in those Figures, accompanying their KI data and GC areas together with MS and KI references. Table 3 compiles MS data of the little known compounds that appear as volatile components of foods.

Methylthiomethane, an easily organoleptical odor associated with marine products, was detected in each distillate and also estimated by the FPD chart. However, its presence based on MS proof was obscure, because of hindrance from covering with peaks of solvents.

The first concentrate possessed 2-furanmethanol (24), octadecanal (77), ethyl acetate (5), and pyridine (11) as major components. Among the identifiable compounds, characteristic impact compounds were lacking in the concentrate. Compounds (1, 4, 6, and 16) have been found from cooked soft-shell clam.^{3,4)}

The second concentrate consisted mainly of the alcohol, the pyridine, some pyrazines (45, 52, and 53), 2-acetylpyrrole (48), *N,N*-dimethylglycine methyl ester (20), and 3-ethylpyridine (40). Compounds (45, 52, and 40) were reported as having the following odors: 45, sweet and caramel²¹⁾; 52, nutty and walnuts²¹⁾; 40, buttery, green, and caramel like odors.²²⁾ The ester, identified as a volatile of roasted dried squid, has an odor of heated dried squid.^{*)} The odor belongs to a fishy odor. 3-Hydroxy-2-methyl-4 *H*-pyrone (55, maltol), well known as giving sweet, caramel, and burnt sugar like odors, occurred in the concentrate. 5-Methyl-2-furfural (38) has sweetish and dusty odors. Consequently, the concentrate was characterized organoleptically by the above dominant but mild-flavor components having sweet, nutty, and other odors, in addition to the ester. The combination of those compounds probably contributes to the boiled odor of short-necked clam.

The last concentrate was composed principally of pyridine (11), 1-methylpyrrolidine-2, 5-dione (49, *N*-methylsuccinimide), *N,N*-dimethylacetamide (25), the ester, 3-methylpyridine (26), and maltol. The pyrrolidine, possessing no odors,

was thought to be formed from an interreaction of succinic acid with methylamine or its analogues, because the large content of the acid in short-necked clam has been determined.²³⁾ The amide has a weak amine like odor. Pyridine (26) was reported to have green, earthy, and hazelnut like odors.²²⁾ However, the concentrate was much characterized by some impact flavor components; the thiadiazine, the dithiazine, and 2-methyl-2-thiazoline (28), together with two considerably large amounts of maltol and the ester.

The thiadiazine has a powerful odor; strong roasted cereal and popcorn like odors which are changeable on pH.¹³⁾ The compound has been quite recently found from dried squid.^{*)} It is considered an important contributor to roasted odors of marine products on the basis of some blending tests. However, it always appeared as a small peak on GC, and its peak on GC was smaller than that on the MS chromatogram. Its small appearance on GC is probably due to its instability upon GC heating along with its high sublimation,¹³⁾ and the gap is most likely caused by the difference between GC and GC-MS thermal systems where GC heating is more strict than GC-MS heating. Whereas, the thiadiazine has two hydrates for its stable form,¹³⁾ such as stable hexahydro-2, 4, 6-trimethyl-1, 3, 5-triazine (acetaldehyde ammonia trimer) has three hydrates. The thiadiazine dihydrate has remained nearly unchanged at -20°C over a few years. However, when put into GC, almost all the hydrate must be changed to the unstable anhydride by GC heating; no anhydrous crystals were obtained even at room temperature.¹³⁾ Its behavior resembles that of the triazine.¹³⁾ Therefore, the genuine thiadiazine in the last concentrate before submission to GC analysis is considered to be much larger than that represented by the GC area in Table 2.

The dithiazine was reported to have a roasted shrimp like odor together with other heated food odors.¹³⁾

Maltol, having a sweet odor as mentioned above, occurred largely in the concentrate. It has been found in many food volatiles from plant origin, with the exception of milk.²⁴⁾ Since short-necked

clam contains glycogen in abundance as a characteristic chemical property of bivalves,²³⁾ the present maltol must have formed through non-enzymatic browning reaction from glycogen or glucose.²⁴⁾

The thiazoline has been recently identified as a volatile component of heated beef, and it was noted to have a meaty odor.²¹⁾ In addition to the odor, it exhibits an irritant roasted odor with fishy and green odors. Also, as having strong odors, indole (64) and some sulfur compounds (23, 56, 58, and 65) can play significant roles in the roasted odor of short-necked clam. The pleasant roasted odor is probably due to these intense flavor components.

Compounds (46 and 50) remained unidentified. Their MS fragmentation patterns respectively resembled those of 2-hydroxy-3-methyl-2-cyclopenten-1-one and 4-hydroxy-2, 5-dimethyl-3 (2 *H*)-furanone, but their KI were inconsistent with authentic ones (KI 1006 and 1031). They seemed to suggest more contributors to sweet and burnt-sugar odors in the concentrate except maltol. 2, 6-Di-*tert*-butyl-4-methylphenol (68, BHT) and 2-*tert*-butyl-4-methoxyphenol (67, BHA) have been frequently detected from volatiles of sea foods wrapped with plastic sheets or packed in such containers (e. g. dried squid and salted cod roe)¹²⁾. The difference in the former GC peak areas depends on its azeotrope.

As described above, higher temperature produced larger amounts of volatiles (in experimental section), more various compounds, and stronger flavor components. Thus, roasting short-necked clam gives more intense, more intricate, more characteristic, and then more favored odors than boiling one.

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