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Volatile Flavor Components in Boiled Snow Crab (*Chionoecetes japonicus*) and Its Concentrated Cooker Effluent

Sung-Hee Choi†, Young-Man Kim and Sook-Kyung Hyun

Department of Food Science and Nutrition, Dong-eui University, Pusan 614-714, Korea

Abstract

The volatile flavor components of snow crabs from the Young-duk coast of Korea and their concentrated cooker effluent were isolated by a modified method from Likens and Nickerson, using a simultaneous distillation and extraction apparatus. The concentrated extract was analyzed and identified by gas chromatography and GC-MS. The flavor profile of boiled crab demonstrated that the favorable flavor characteristic of crab involved a seafood-like note, and that of concentrated cooker effluent demonstrated that the weak boiled crab flavor involved a fishy note. The main flavor components of boiled crab were heterocyclic compounds including alkylpyrazines, thizoles and thiolanes, aliphatic ketones including 2-heptanone and nonanone. On the other hand, the main flavor components of cooker effluent were aldehydes including 3-methylbutanal, alipatic ketones including 2-heptanone and alkanes including 2,6,10,14-tetramethyl-pentadecane. Almost all of heterocyclic compounds, which seem to be important contributors to the flavor of boiled crab, were not identified in concentrated cooker effluent. As a result, there may be a need to add the crab flavor components formed through model experiments of Maillard reactions to the concentrated cooker effluent for human consumption.

Key words: snow crab (*Chionoecetes japonicus*), concentrated cooker effluent (CCE), seafood-like note, heterocyclic compounds

INTRODUCTION

Many cooked crabs are consumed as a popular food throughout the world because of their characteristically favorable odor and taste. The snow crab is processed in some factories located on the eastern coast of Korea. These processed crabs are mainly exported to the United States and Japan (1). Large amounts of cooker effluent (CE) are produced from crab processing. Almost all of this cooker effluent is discarded as processing waste despite its nutritious value and environmental concerns. Cooker effluent produced from processed crab lacks some desirable flavors and forms off-flavors when it is concentrated to about a 1 / 10 ratio by heat. Though most studies on the flavor of boiled crab until now have focused on taste components (2-4), several researchers has been investigating the volatile flavor of some boiled blue crabs (5-7). Cha et al. (8,9) previously reported on volatile flavor components in snow crab cooker effluent. Jaswal (10) reported that amino acid hydrolysates could be produced from crab processing by-product, and Kim et al. (11) also reported the residue after hot water extraction of blue crab was hydrolyzed in order to utilize by-products as seasonings. However, little information has been reported in Korea regarding the comparison of the flavor components of boiled snow crab and its cooker effluent. Our final objective is utilization of concentrated cooker effluent (CCE). This study was carried out in order to compare the flavor quality of boiled snow crab and its CCE to assess the use of cooker effluent for flavor recovery.

MATERIALS AND METHODS

Materials

Fresh snow crabs from Young-duk coast of Korea and its concentrated cooker effluent (CCE) were supplied by Daehosusan Co., Ltd. The concentrated cooker effluent was made by boiling crabs soaked in water, filtering and concentrating the brew to about 1/10 ratio by heat. The materials were stored in a freezer at -30°C until just before use.

Preparation of flavor concentrate

Seven hundred grams of snow crabs plus distilled water [0.7 : 1 (w/v)] and three hundred grams of CCE plus distilled water [0.3 : 1 (w/v)] respectively were extracted for 2 hr with redistilled ether (50 mL) in a SDE (Likens and Nickerson type simultaneous steam distillation and extraction) apparatus as modified by Schultz et al. (12). The extract was dried over anhydrous sodium sulfate and the solvent was removed by the distillation of diethyl ether.

Instrumental methods of flavor concentrates

Gas chromatography (Shimadzu model 17A, Japan) equipped with FID and a HP-5 fused silica capillary column (50 m × 0.32 mm × 0.52 μm film, Hewlett-Packard, USA) was used. The oven temperature was held at 60°C for 5 minutes and

†Corresponding author. E-mail: choish@hyomin.dongeui.ac.kr
Phone: 82-51-890-1590, Fax: 82-51-890-1579

then programmed to 220°C at 2 minutes. Nitrogen was used as a carrier gas and the flow rate was 1.2 mL/min.

GC-MS system consisted of a Hewlett-Packard 6890 GC/ 5973 MS (ionization voltage : 70 eV). The GC conditions were the same as those for the corresponding GC analysis, except that Helium was used as a carrier gas.

RESULTS AND DISCUSSION

The yield of the flavor concentrate in boiled crab was 0.41 mg/100 g based on the raw weight. The yield of the flavor concentrate in concentrated cooker effluent (CCE) was 2.73 mg/100 g. The flavor profile of boiled crab demonstrated that the favorable flavor characteristic of crab involved a seafood-like note, and that of concentrated cooker effluent demonstrated that the weak boiled crab flavor involved a fishy note. The gas chromatograms of the flavor concentrates in boiled snow crab and its CCE are shown in Fig. 1. The identified compounds are summarized in Table 1. Thirty four compounds including 6 aldehydes, 6 alkanes, 4 pyrazines, 4 sulfur-containing compounds, etc., were identified in boiled snow crab. Thirty seven compounds including 15 aldehydes, 3 alkanes, 3 sulfur-containing compounds, etc., were identified in CCE. Many compounds identified in crabs in this study have already been identified in previous papers (5-9). However, many compounds including trans-3,5-dimethyl-1,2,4-trithiolane and cis-3,5-dimethyl-1,2,4,-trithiolane were not identified in previous studies (5-9) about crabs. Many kinds of aldehydes were found in both boiled snow crab and its CCE, while 6 aldehydes were found in boiled snow crab, 15 aldehydes were found in CCE. 2,4-Pentadienal, benzaldehyde, nonanal, tetradecanal were present in both. Though some aldehydes including benzaldehyde may have a desirable effect, almost all of the aldehydes found in CCE may have an unpleasant flavor (5). It seems that large amounts of aldehydes in CCE result in lipid autoxidation during concentration of cooker effluent. Some ketones were found in two samples. Nonanone which has already been detected in the blue crab, was significantly higher in the boiled crab than that in CCE. Alkanes seem to be unimportant contributors to the flavor of foods, and are generally contained in higher amounts in fish. Particularly, 2,6,10,14-tetramethylpentadecane in alkanes was higher in both, which was reported to contribute a green, sweet aroma to crayfish processing waste (13). Kubota (14) reported that this is formed by lipid degradation and may have a desirable effect on fish flavor. Three furans were identified in both samples. Large amounts of 2-ethylfuran were identified only in the boiled snow crab. This compound has been reported to have a sweet note when diluted (7). 2-Pentylfuran known as an off-flavor in fats and oils was identified only in CCE and already reported in crabs (7-9). Four pyrazines were identified in boiled snow crab but these pyrazines were not identified in CCE. Pyrazines were generally associated with desirable nutty (15) and roasted flavors (16,17). Cha et al. (8,9) identified pyrazines in snow crab cooker effluent also. It seems that results differ according to the preparation method of material and experimental conditions. All pyrazines found in boiled snow crab have been previously reported in blue crabs (5). Of five sulfur-containing compounds found in both samples, only trans-3,5-dimethyl-1,2,4-trithiolane and cis-3,5-dimethyl-1,2,4,-trithiolane were identified in boiled snow crab. On the other hand, dimethyltrisulfide was identified only in CCE. Trans and cis type 3,5-dimethyl-1,2,4-trithiolane have not been reported in blue crabs (5,6). Dimethyltrisulfide has been noted as an off-flavor component in the royal red prawn, *hymenopenaeus* sibogae (14). Perhaps dimethyltrisulfide in CCE is formed from degradation of trithiolane during heat concentration of CCE. Trithiolane is formed from the reaction of acetaldehyde with hydrogen sulfide and ammonia (18). It has been found in boiled beef (19) and small shrimps (20,21). 2-Acetylthiazole and benzothiazole previously were reported in crabs (5,8,9). Almost all of heterocyclic compounds such as pyrazines, trithiolane and thiazole were not identified in CCE. These compounds appear to be important contributors to the flavor of boiled snow crab. The odor profile of the boiled crab showed that the favorable characteristic crab odor involved a seafood-like note, and that of the CCE showed that the weak boiled crab odor involved a fishy note. Main odor

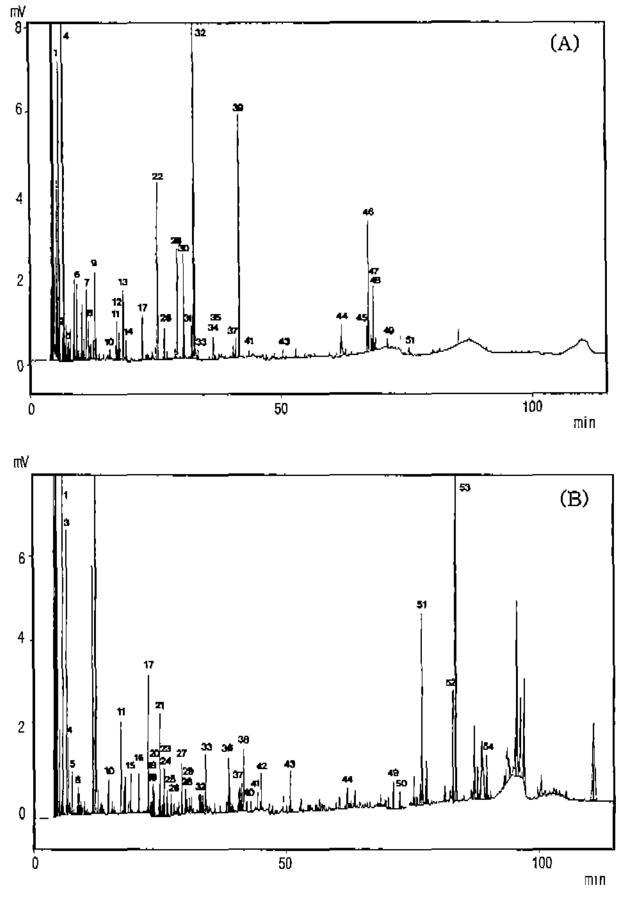

Fig. 1. Gas chromatograms of the volatile flavor concentrates of *Chionoecetes japonicus.* (A) Boiled snow crab. (B) Concentrated cooker effluent.

Table 1. Identified components in the volatile flavor concentrates of *Chionoecetes japonicus*

Peak no.	Compound	Evidence	t_R (min)	Peak area (%)	
				I [1)]	II [2)]
1	ethyl acetate	GC, MS	5.87	2.48	2.58
2	2-methyl-1,3-dioxolane	GC, MS	6.50	0.35	-
3	3-methylbutanal	GC, MS	6.69	-	1.49
4	2-ethylfuran	MS	6.91	5.59	0.44
5	2,4-pentadienal	MS	7.74	0.25	0.30
6	1,1-diethoxyethane	GC, MS	8.90	1.13	0.25
7	hexanal	GC, MS	11.32	1.49	-
8	1,2,3,4-tetrahydroxybutane	MS	11.75	0.70	-
9	2-methylpyrazine	GC, MS	13.04	1.45	-
10	dimethylbenzene	GC, MS	16.03	0.23	0.35
11	2-heptanone	GC, MS	17.48	1.31	1.07
12	cis-4-heptenal	GC, MS	17.81	0.59	-
13	2,5-dimethylpyrazine	GC, MS	18.64	2.74	-
14	2,3-dimethylpyrazine	GC, MS	19.25	0.47	-
15	1-heptanal	GC, MS	19.33	-	0.50
16	methional	MS	20.97	-	0.49
17	benzaldehyde	GC, MS	22.85	1.09	1.76
18	dimethyltrisulfide	MS	23.40	-	0.23
19	1-octen-3-one	MS	23.78	-	0.43
20	2,3-octanedione	MS	23.97	-	0.35
21	2-pentylfuran	MS	25.12	-	1.62
22	trimethylpyrazine	GC, MS	25.56	4.50	-
23	butenylcyclohexene	MS	25.67	-	0.19
24	octanal	GC, MS	25.94	-	0.80
25	trans-2,4-heptadienal	MS	26.59	-	0.35
26	2-acetylthiazole	GC, MS	27.36	0.83	0.27
27	1-methyl-2-nitro-benzene	MS	29.48	-	0.77
28	2,5-diethyltetrahydrofuran	MS	30.20	3.11	0.35
29	2-octenal	MS	30.43	-	0.19
30	phenyloxirane	GC, MS	30.76	3.40	-
31	1-methylethyl formate	MS	32.36	0.78	-
32	2-nonanone	GC, MS	33.12	20.52	0.32
33	nonanal	GC, MS	34.16	0.25	0.97
34	trans-3,5-dimethyl-1,2,4-trithiolane	GC, MS	36.64	1.09	-
35	cis-3,5-dimethyl-1,2,4-trithiolane	GC, MS	37.14	t	-
36	2,3-dihydro-1H-inden-1-one	MS	38.73	-	0.96
37	2-decanone	GC, MS	41.21	0.52	0.53
38	9,12,15-octadecatrienal	MS	41.66	-	0.94
39	11,14,17-trienoic fatty acid methyl ester	MS	41.78	7.65	-
40	1-decanal	GC, MS	42.27	-	0.19
41	benzothiazole	GC, MS	44.37	0.23	0.28
42	cyclohexyl isothiocyanate	MS	44.99	-	0.61
43	4-vinyl-2-methoxyphenol	MS	50.85	0.30	0.65
44	pentadecane	GC, MS	62.02	1.47	0.42
45	1,3,5-undecatriene (isomer)	MS	67.09	0.78	-
46	tetradecatriene-2-one (isomer)	MS	67.41	3.82	-
47	1,3,5-undecatriene (isomer)	MS	67.95	0.49	-
48	tetradecatriene-2-one (isomer)	MS	68.31	1.87	-
49	tetradecanal	GC, MS	71.06	0.28	0.43
50	diphenylamine	GC, MS	72.32	-	0.28
51	2,6,10,14-tetramethyl-pentadecane	GC, MS	76.72	0.27	3.19
52	13-octadecenal or 13-tetradecenal	MS	82.81	-	1.75
53	17-octadecenal	MS	83.43	-	13.02
54	octadecanal	MS	89.48	-	0.87

[1)]Boiled snow crab.
[2)]Concentrated cooker effluent.

components of the boiled crab were heterocyclic compounds including alkylpyrazines, thizoles and thiolanes, aliphatic ketones including 2-heptanone and nonanone, and esters, including ester of unsaturated fatty acid, etc. On the other hand, almost all of the heterocyclic compounds such as alkylpyrazine, thizoles and thiolanes, which seem to be important contributors to the odor of boiled crab, were not identified in CCE. As a result, it is absolutely necessary to add crab flavors formed by model experiments of Maillard reactions in order to utilize CCE for human consumption. The model system of Maillard reaction formed hetrocyclic compounds should be schemed, because those play a large part in the specific crab flavor.

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