



COMPOSITION OF VOLATILE COMPOUNDS FROM VANAME SHRIMP WASTE FLAVOR POWDER BY CONVENTIONAL DRYING METHOD

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Key Words

aroma, flavor powder, shrimp, vaname, volatile component, waste

ABSTRACT

The volatile components impact the commodity's aroma characteristics and its overall acceptance by consumers. The research objective of this study is mainly to identify volatile compounds composition from vaname shrimp waste flavor powder waste which used conventional drying method utilizing Teflon frying pan. This research comprised of several steps, initially volatile flavor compounds was extracted from vaname shrimp waste by boiling process (temperature 65°C, for approximately 90 minutes), followed by drying process by means of Teflon frying pan, extracting samples with the Solid Phase Microextraction (SPME) method (80°C) and finally, identifying the absorbed volatile flavor compounds using Gas Chromatography-Mass Spectrometry (GC/MS) analysis equipment. The resulting data analysis was discussed in a comparative and descriptive manner. The results showed that 147 volatile compounds were detected in vaname shrimp waste with the highest proportion values were pentanal (12%). Most of the components detected came from the aldehyde group, alcohol, hydrocarbons, ketones of organic acids, esters and other compounds.

1. INTRODUCTION

Vaname shrimp (*Litopenaeus vannamei*) is Indonesia's one of the main fishery commodity which is also an export commodity. Based on [1] data, the production volume of vaname shrimp in Indonesia was reaching 411,729 tons a year. This figure certainly has a tendency to increase over the years. The high volume of vaname shrimp production has great potential to be used as raw material in the processing industry which of course later in the process can produce waste. Shrimp processing waste consists of head, skin, tail and legs which constitute 35% - 50% of the initial weight of shrimp [2].

Shrimp waste is sometimes thrown away so that it can cause environmental pollution. Efforts need to be made to prevent pollution, one of which is by utilizing shrimp waste so that it can produce something that can provide added value to fishery product processing businesses. Shrimp waste is utilized by processing it into other valuable products such as chitosan, chitin, enzymes, and pigments [3]. In addition, vaname shrimp waste can also be utilized by extracting useful components such as active flavor compounds [4] and processed as flavor powders.

Flavor is a combination of aroma, taste and other sensations. Flavor can be grouped into two types, namely a volatile flavor component and a non-volatile flavor component. The volatile component is the component that gives the aroma sensation of a product and can only be felt by the sense of smell such as the nose, while the non-volatile component is the component gives the taste sensation of a product and can only be felt by the sense of taste like the tongue. Volatile compounds can derive from products of enzymatic reactions, lipid autoxidation, microbial activity products, and thermal reaction products [5].

Dried form flavor or powdered flavor could originates from a liquid flavor that is absorbed by fillers substance or encapsulated by inert edible polymers such as gum arabic or starch [6]. According to [7], good quality flavor powder has the appearance, color, aroma and taste that consumers like. Drying which is done in making the flavor powder can be done by conventional and non-conventional methods. The conventional or household scale drying process can be practically done using household kitchen utensils such as Teflon frying pan or oven. In addition, the drying process can also be done using a drying equipments such as a spray-dryer, drum-dryer and tray-dryer or what is called non-conventional methods. The conventional method of drying can be easily carried out by the wider community because of its low costs, easily available equipment, but the drawbacks of conventional methods are less optimal drying results and less efficient time [8].

Research on the volatile flavor composition of fishery waste products has been widely conducted abroad. For example, determination of volatile flavor compounds on shrimp heads [9], volatile flavor components in crayfish waste [10], and analysis of volatile flavor compounds in mackerel to assess its quality [11]. Research on the volatile flavor composition of fishery waste products in Indonesia is not readily available. Based on the description above, research on flavor is important to identify volatile flavor compounds in order to determine the aroma characteristics of the product and as basic data for subsequent application studies. The purpose of this study was to identify the composition of volatile flavor compounds in the flavor powder made from vaname shrimp waste with conventional drying methods.

2. MATERIALS AND METHODS

2.1 Samples Preparation

The first stage of this research is taking samples of vanname shrimp from the Karangsong Fish Auction Place, Indramayu in West Java. Fresh vaname shrimp samples as much as 5 kg are stored in a cool box for the transportation process to Fisheries Product Processing Laboratory, Faculty of Fisheries and Marine Sciences, Universitas Padjadjaran. Sample preparation was carried out at that same laboratory, the head and shell of the vaname shrimp are separated from the meat part. Vaname shrimp wastes (head and shell) were then boiled in a boiler pan filled with clean water for 90 minutes at a temperature of 65°C. The boiled water and shrimp waste that had become a broth is then cooled, filtered using a clean filter cloth and packed in an airtight closed glass jar. Filler in the form of 10% maltodextrin (based on the broth volume) was added to the vaname shrimp waste broth gradually and carefully stirred until homogeneous [6].

The sample of liquid broth that has been mixed with maltodextrin was poured thinly until evenly onto the surface of Teflon. After that, heat the thin broth layer over low heat until the broth gradually dries and then transferred it to the container by means of scraping. The time required for the drying stage is approximately 2 minutes. Samples that have dried produce a thin layer of dry flavor which then are crushed using a mortar until it had smooth texture and become fine powder [7]. Samples of the dried powder are wrapped using aluminum foil and cling wrap plastic, labeled and stored in airtight glass jars for analysis. The packaged samples was taken to the Flavour Laboratory, Indonesian Centre for Rice Research, Sukamandi, Subang, West Java for performing analysis of volatile flavor compounds.

2.2 Volatile Compound Analysis

Solid phase microextraction (SPME) is used for extraction by evaporating the volatile compounds contained in the sample. DVB/carboxymethyl/Polydimethylsiloxane fiber is used to absorb volatile flavor compounds in the sample. A total of 6 grams of powder sample was transferred into a specific SPME vial. The extraction temperature of the vaname shrimp powder sample used was 80°C, and it was

carried out in a water bath for 45 minutes. After all of the extraction steps finished the fiber which contained sample's volatile compounds was inserted into the GC/MS sample injector, and then the device was set up according to volatile analysis parameters. The GC column used in this analysis was HP-5MS (325°C: 30 m x 250 μ m x 0.25 μ m) with helium carrier gas. The initial temperature was 45°C (hold for 2 minutes), and then the heat was steadily escalated at a rate of 6°C/min, and the final equipment temperature reaches 250°C (hold for 5 minutes). The total time spent to run this volatile analysis was 36 minutes, and the data obtained is in the form of chromatograms. All procedures were carried out based on the modification from [12] and [13].

2.3 Data Analysis

The mass spectra of the volatile compounds in the flavor powder samples detected by GC / MS were then compared with the mass spectra patterns found in the data center or library of NIST 14 (National Institute of Standards and Technology) stored in a computer device. The component data for these volatile flavor compounds were further analyzed using the Automatic Mass Spectral Deconvolution and Identification System (AMDIS) software [14] to correct the spectral data for compounds that were difficult to read and compared.

3. RESULTS AND DISCUSSION

3.1 Volatile Component

The results of using gas chromatography / mass spectrometry to analyze volatile compounds had successfully identified 147 volatile compounds contained in shrimp waste samples. The results of the analysis of volatile compounds using Gas Chromatography / Mass Spectrometry show that the compounds detected in the sample are compounds from the aldehyde, hydrocarbon, ketone, alcohol, ester, organic acid and other group. The volatile compounds detected are volatile compounds which are generally produced from enzymatic reactions, lipid autoxidation, microbial action, environment and thermal-derived reaction products [5].

The volatile compounds detected from the sample consisted of various groups of compounds. First one, were 14 compounds which classified as aldehyde groups with pentanal (12%) as the type of compound having the largest proportion. The hydrocarbon group was detected as many as 40 compounds with cyclopentane 1,1-diethyl- (1,567%) having the largest proportion. The 15 compounds detected were from the ketone group with ethanone, 1- (2-furanyl) - (3.102%) as the compound having the largest proportion. 20 compounds from the alcohol group were also detected with maltol (2.907%) having the largest proportion. The detected esters consisted of 3 compounds with trifluoroacetic acid and pentadecyl ester (0.210%) as the compounds with the largest proportion. The organic acid group was also detected as many as 3 compounds with nonanoic acid (0.172%) as the compound with the largest proportion. Apart from these groups, compound which categorized in others group were also detected, namely 52 compounds with pyrazine and trimethyl- (4.621%) being the compounds with the highest proportion. The composition of volatile flavor compounds of vaname shrimp waste is presented in Table 1 based on each compound peak area as a semi-quantitative concentration.

Table 1. Volatile compounds detected in vaname shrimp waste flavor powder

Groups	Retention Time	Compounds	Area	Proportion (%)
Aldehydes	1,9367	Butanal, 3-methyl-	191677723	6,40
	2,6562	Pentanal	374285312	12,00
	4,6005	Hexanal	26162547	0,90
	5,2308	Furfural	26582277	1,00
	6,967	Methional	18525745	0,60
	8,4773	Benzaldehyde	29127357	1,00
	11,2897	2-Octenal, (E)-	12357873	0,40
	12,5978	Nonanal	170768881	5,70
	13,686	2-Hexenal, 2-ethyl-	7950906	0,30
	15,5173	Decanal	25930456	0,90
	15,7849	2,4-Nonadienal, (E,E)-	7958599	0,27
	17,0871	2-Decenal, (E)-	8689197	0,29
	21,9568	2,6-Dodecadien-1-al	2435213	0,08
	29,0504	Octanal, 2-(phenylmethylene)-	4886748	0,16
Hydrocarbons	12,253	Cyclopentane, ethyl-	33945386	1,13
	12,4076	1-Octene, 6-methyl-	37701606	1,26
	13,1568	cis-2-Nonene	23080508	0,77
	13,3827	Cyclopropane, 1,1-diethyl-	47041939	1,57
	13,5016	3-Dodecene, (E)-	37861181	1,26
	14,5957	1-Nonene	9883799	0,33

Groups	Retention Time	Compounds	Area	Proportion (%)
	14,7979	Cyclododecane, methyl-	9647546	0,32
	14,9881	Naphthalene	19791872	0,66
	15,2973	Dodecane	22541127	0,75
	15,6898	Undecane, 2,6-dimethyl-	13256546	0,44
	16,3498	Cyclopentane, 1-pentyl-2-propyl-	5393373	0,18
	16,4092	Cyclotridecane	4315531	0,14
	16,9503	2,6-Octadiene-1,8-diol, 2,6-dimethyl-	8746949	0,29
	17,2654	Dodecane, 3-methyl-	4272579	0,14
	17,3308	1-Methyl-2-methylenecyclohexane	2723461	0,09
	18,08	Tridecane	8893128	0,30
	19,4298	Tridecane, 6-methyl-	3342829	0,11
	19,6379	Tridecane, 4-methyl-	6007538	0,20
	20,5179	Cyclotetradecane	3834367	0,13
	20,7201	Tetradecane	12472301	0,42
	21,4098	Caryophyllene	6540389	0,22
	22,2957	Undecane	3430923	0,11
	22,6703	Cyclopropane, nonyl-	25812698	0,86
	23,2233	Pentadecane	5799656	0,19
	23,812	Cyclopentane, 1-pentyl-2-propyl-	4835949	0,16
	24,2044	Hentriacontane	4337638	0,14
	24,7395	Dodecane	5195166	0,17
	26,7076	Hexadecane, 2,6,11,15-tetramethyl-	3822595	0,13
	26,892	Cyclotetradecane	3006749	0,10
	27,5044	1,3-di-iso-propylnaphthalene	5126562	0,17
	27,6114	1,7-di-iso-propylnaphthalene	9090769	0,30
	27,8611	Heptadecane	6577622	0,22
	27,992	Heptadecane, 2,6-dimethyl-	5925425	0,20
	28,2595	Naphthalene, 1,2,3-trimethyl-4-propenyl-, (E)-	5315741	0,18
	28,4855	2,6-Diisopropylnaphthalene	6633778	0,22
	28,5628	1,4-di-iso-propylnaphthalene	3251894	0,11
	28,8244	Octadecane	1624367	0,05
	30,0136	Nonadecane	2931218	0,10
	30,2039	Hexadecane, 2,6,10,14-tetramethyl-	1575193	0,05
	32,0531	Decane	1347939	0,04
Ketones	7,1097	Ethanone, 1-(2-furanyl)-	93117340	3,10
	8,1384	Tropinone	16063486	0,54
	9,0957	2,3-Octanedione	15992416	0,53
	11,6822	Ethanone, 1-(1H-pyrrol-2-yl)-	85379520	2,84
	11,7773	Ethanone, 1-(1-methyl-1H-pyrrol-2-yl)-	36250164	1,21
	15,1487	2-Decanone	9291146	0,31
	16,6173	2,3-Octanedione	7179165	0,24
	17,979	2-Undecanone	5815561	0,19
	19,1027	Pyrethron	2912917	0,10
	19,3703	1-(2-Pyrazinyl)butanone	4563455	0,15
	22,1233	trans-Geranylacetone	17888290	0,60
	22,5454	Cyclohexanone, 2-ethyl-	22,5454	0,00
	22,8487	α -Isomethyl ionone	2533173	0,08

Groups	Retention Time	Compounds	Area	Proportion (%)
	26,4698	Benzophenone	7222999	0,24
	27,7422	1-(4-Benzylphenyl)ethanone	5276595	0,18
Alcohols	5,8432	2-Furanmethanol	74033471	2,47
	6,5389	2-Methylenecyclohexanol	7400161	0,25
	9,0184	1-Octen-3-ol	8088776	0,27
	10,4454	1-Hexanol, 2-ethyl-	66340113	2,21
	12,9427	Maltol	87275502	2,91
	13,7871	(S)-(+)-6-Methyl-1-octanol	19390891	0,65
	14,3935	1-Pentanol, 2,4,4-trimethyl-	7582447	0,25
	14,4708	1-Octanol, 2-butyl-	12455955	0,41
	14,7027	Levomenthol	13110769	0,44
	15,9098	1-Decanol, 2-hexyl-	4108310	0,14
	19,7984	3-Allyl-6-methoxyphenol	16537595	0,55
	20,3514	Phenol, 2,4,6-trimethyl-	3704700	0,12
	21,8795	Cycloheptanol, 2-methylene	1957292	0,07
	23,4433	1-Decanol, 2-hexyl-	1970678	0,07
	23,5325	1-Dodecanol, 2-octyl-	2491803	0,08
	24,026	Acetyleneugenol	8104985	0,27
	24,3411	1-Dodecanol, 2-hexyl-	2300108	0,08
	24,4779	1-Octanol, 2-butyl-	3928501	0,13
	25,7385	1-Decanol, 2-octyl-	4537628	0,15
	26,3092	Epicedrol	2878749	0,10
Esters	17,8006	Trifluoroacetic acid, pentadecyl ester	6307221	0,21
	32,612	Hexadecanoic acid, methyl ester	1416671	0,05
	33,9498	Hexadecanoic acid, ethyl ester	1026875	0,03
Organic Acid	17,6163	Nonanoic acid	5175420	0,17
	24,9179	Nonahexacontanoic acid	3116228	0,10
	28,0693	Nonahexacontanoic acid	2146593	0,07
Others	3,5778	1H-Pyrrole, 2-methyl-	19935379	0,66
	3,8454	Pyrrole	55855874	1,86
	5,0167	Pyrazine, methyl-	39672000	1,32
	7,2881	Pyrazine, 2,3-dimethyl-	135109766	4,50
	8,6973	Dimethyl trisulfide	22389715	0,75
	9,6308	Pyrazine, trimethyl-	138734452	4,62
	9,9043	Pyrrole, 4-ethyl-2-methyl-	17675140	0,59
	10,0411	Pyrazine, 2-ethenyl-6-methyl-	10013644	0,33
	10,1957	Pyrazinamide	20590438	0,69
	10,492	Acetyl pyridine	52566579	1,75
	10,8735	Benzeneacetaldehyde	59548763	1,98
	11,0757	1-Allylazetidine	18217702	0,61
	11,3908	4,5-Dimethyl-2-isobutyloxazole	16266937	0,54
	11,8724	Pyrazine, 2,6-diethyl-	31206090	1,04
	12,041	Pyrazine, 2-ethyl-3,5-dimethyl-	14374950	0,48
	12,1103	2,3-Dimethyl-5-ethylpyrazine	42659891	1,42
	12,8297	1,2,4-Triazolo[4,3-b]pyridazine, 8-methyl-	7497085	0,25
	14,1141	2-Acetyl-3-ethylpyrazine	10635525	0,35
	14,2687	Pyrazine, 3,5-diethyl-2-methyl-	29790446	0,99
	15,0773	Pyrazine, 2,3-dimethyl-5-(1-propenyl)-, (E)-	6258657	0,21

Groups	Retention Time	Compounds	Area	Proportion (%)
	16,0703	Furan, 3-phenyl-	16205834	0,54
	16,2011	4,8-Decadien-3-ol, 5,9-dimethyl-	7832456	0,26
	16,8016	2-Isoamyl-6-methylpyrazine	15104623	0,50
	17,1643	Quinoline, 1,2,3,4-tetrahydro-	8249245	0,27
	17,4081	4-Dimethylaminopyridin-2-amine	9085066	0,30
	17,4616	Benzeneacetaldehyde, α -ethylidene-	12791108	0,43
	18,3357	2-Acetylaniline	16197932	0,54
	18,5795	3-Isoamyl-2,5-dimethylpyrazine	7362606	0,25
	18,9125	2-Oxo-1-methyl-3-isopropylpyrazine	6515353	0,22
	19,1919	2,3-Dimethyl-5-isopentylpyrazine	7966313	0,27
	19,5071	Pyridine, 2-(1-methyl-2-pyrrolidinyl)-	3684435	0,12
	19,953	Disulfide, di-tert-dodecyl	5573295	0,19
	20,1195	Benzimidazole, 2-amino-1-methyl-	11879749	0,40
	20,8509	Bicyclo[3.2.1]oct-3-en-2-one, 4-methyl-	2800989	0,09
	21,7011	3,3'-Bis(1,2,4-oxadiazolyl)-5,5'-diamine	2651479	0,09
	22,932	1,3,5-Triazine-2,4-diamine, 6-phenoxy-	5241172	0,17
	23,3601	Cashmeran	2105798	0,07
	23,6752	Butylated Hydroxytoluene	2549952	0,08
	25,4352	3-Methyl-4-phenyl-1H-pyrrole	4455828	0,15
	25,6136	Diethyl Phthalate	16219106	0,54
	25,2925	Diethyltoluamide	1453199	0,05
	26,5828	3-Hydroxypyridine monoacetate	3107675	0,10
	26,9752	Methyl dihydrojasmonate	3881261	0,13
	27,1655	1,1'-Biphenyl, 2,2',5,5'-tetramethyl-	2583161	0,09
	28,7233	1-Acetyl-4,6,8-trimethylazulene	1803476	0,06
	30,2871	2-Ethylhexyl salicylate	16280731	0,54
	30,5725	Isopropyl myristate	4795169	0,16
	31,292	Galoxolide	5216077	0,17
	31,5358	1-Butyl 2-isobutyl phthalate	2747130	0,09
	33,4087	Butyl 2-ethylhexyl phthalate	1664318	0,06
	27,3914	Phenol, 2,5-di-tert-butyl-	3402484	0,11
	28,6282	Phenol, 4-(1-methyl-1-phenylethyl)-	4892569	0,16

In Table 1 above, there are columns for group, retention time (RT), compound, area, and proportion. Retention time is the time when the compound is detected on GC / MS. Area is a collection of compounds that form peaks as. At these peaks are selected and then adjusted to the NIST library 0.8 so that compounds can be detected as in the table. Pentanal compounds from the aldehyde group were detected to have the highest proportion value compared to other aldehydes compounds, namely 12%. Pentanal is known to have green flavor characteristics [15]. Aldehydes commonly contribute to green-plant scents, paints, metallic, beany, and rancid aromas, and in foods containing lipids [16]. Other compounds detected in the aldehyde group, namely butanal 3-methyl, nonanal, and furfural are all aromatic compounds that contribute to the volatile flavor of the sample.

Ketones sensory characteristics in general are known to have (pleasant) fatty notes [17]. The ethanone 1- (2-furanyl) compound - from the ketone group has the highest proportion value compared to other ketones compounds, namely 3.10% where ethanone 1- (2-furanyl) - is previously known present in cooked apples, morello cherry, grapes, peaches, strawberries, asparagus, baked potatoes, pineapple, bakery products, rice, yogurt and soybeans [18]. In addition to ethanone 1- (2- furanyl) -, there is also ethanone

1-(1H-pyrrol-2-yl) which detected in the sample, where this compound has the second highest proportion value, namely 2.84%. Flavor characteristics of ethanone 1-(1H-pyrrol-2-yl)- contribute to many aromas, one of which is in cereals [19].

The volatile compounds of the hydrocarbon group can be derived from the decarboxylation reaction and the separation of the carbon-carbon chain from fatty acids, a secondary reaction from the thermal oxidation of carotenoids and other unsaturated fats [20]. One of the volatile compounds in the hydrocarbon group that has the highest proportion is cyclopropane 1,1-diethyl- which is 1.57% and the second highest is 1-Octene, 6-methyl- and 3-Dodecene, (E) -, both of which have the highest proportion which is the same, namely 1.26%.

The alcohol group can be formed as a result of the oxidation of fats and fatty acids and the degradation of amino acids during processing [16]. Volatile alcohol compounds are generally a minor contributor to food due to their high threshold unless they are present at high or unsaturated concentrations [5]. The volatile compound in the alcohol group that was detected with the highest proportion was maltol which was 2.91%. Maltol has a fragrant butterscoth caramel aroma and is a natural organic compound that is used as a flavor enhancer [21].

The trifluoroacetic acid compound, pentadecyl ester, is one of the compounds detected and has the highest proportion of the ester group in the sample, namely 0.21%. Esters in general are constituents with high flavor formation properties [22]. The same thing was stated by [12], that esters in general are considered important for food flavor, especially in fruit. Nonanoic acid compounds are compounds with the highest proportion of the organic acid group, namely 0.17%. The nonanoic acid compound is a colorless oily liquid and has an aroma of fatty, coconut, slight odor and rancid [23]. The compound detected in other groups with the largest proportion of vaname shrimp waste was pyrazine trimethyl- with a proportion value of 4.62%. A trimethyl-pyrazine compound commonly found in cereals and cereal products. Trimethyl pyrazine is found in many food ingredients such as asparagus, baked potato, whole wheat bread, Swiss cheese, coffee, black tea, and peanuts, soybeans etc. Trimethyl pyrazine is often used as a flavoring agent and has a roasted nut, baked potato odour [24].

Conclusion

Based on the identification results of the volatile flavor compounds of vaname shrimp waste, it can be concluded that the number of volatile compounds in the vaname shrimp waste sample is 147 compounds. The groups of volatile flavor compounds detected in the sample come from the aldehyde, ketone, alcohol, hydrocarbon, organic acid, ester, and others. The sample has the highest number of compounds in the hydrocarbon group. The compound that has the largest proportion in the vaname shrimp waste sample comes from the aldehyde group, namely pentanal at 12%.

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