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## Research Article

# Determination of Volatile Compounds in Four Commercial Samples of Japanese Green Algae Using Solid Phase Microextraction Gas Chromatography Mass Spectrometry

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Green algae are of great economic importance. Seaweed is consumed fresh or as seasoning in Japan. The commercial value is determined by quality, color, and flavor and is also strongly influenced by the production area. Our research, based on solid phase microextraction gas chromatography mass spectrometry (SPME-GC-MS), has revealed that volatile compounds differ intensely in the four varieties of commercial green algae. Accordingly, 41 major volatile compounds were identified. Heptadecene was the most abundant compound from Okayama (*Ulva prolifera*), Tokushima (*Ulva prolifera*), and Ehime prefecture (*Ulva linza*). Apocarotenoids, such as ionones, and their derivatives were prominent volatiles in algae from Okayama (*Ulva prolifera*) and Tokushima prefecture (*Ulva prolifera*). Volatile, short chained apocarotenoids are among the most potent flavor components and contribute to the flavor of fresh, processed algae, and algae-based products. Benzaldehyde was predominant in seaweed from Shizuoka prefecture (*Monostroma nitidum*). Multivariate statistical analysis (PCA) enabled simple discrimination of the samples based on their volatile profiles. This work shows the potential of SPME-GC-MS coupled with multivariate analysis to discriminate between samples of different geographical and botanical origins and form the basis for development of authentication methods of green algae products, including seasonings.

## 1. Introduction

Seaweeds have been traditionally used as medicines, food, and seasoning [1, 2]. Most seaweeds are of commercial importance in foodstuffs, cosmetics, and dyes. Moreover, they serve as source for biological active compounds. Today 7.5–8 million tons of macroalgae are produced per annum and their estimated value is US\$ 5.5–6 billion [3]. Seaweeds are widely distributed throughout the world and are predominantly consumed in Japan, China, Korea, South Australia, New Zealand, Polynesia, and South America [4].

Certain countries or regions have reputations for producing high-quality green algae, including Aonori (a high quality, merchandised Japanese green seaweed), and are able to demand a significantly higher price for their products. In Japan, high-value production areas include the river Shimanto in Kochi prefecture and river Yoshino in Tokushima prefecture. There is a strong interest in the authenticity of these commercial products and up to now consumers have to rely on package information to provide confirmation that the product is from a high-quality region with a traceability

system, such as the Food Marketing Research and Information Center in Japan [5].

GC-MS techniques coupled with multi-variant analysis are becoming increasingly important tools to monitor the distribution of counterfeit foodstuffs and have been used in authenticating many food products, such as tea, olive oil, honey, cheese, and wine [6–12].

We newly report on nontargeted SPME-GC-MS followed by multi-variant statistical analysis in Japanese green macroalgae. Significant differences in the volatile profiles of green algae from four production areas were detected, implying that markers could potentially be identified using this analytical-statistical approach.

## 2. Experimental

**2.1. Commercial Dried Green Algae Samples.** *Ulva prolifera*, *Ulva linza*, and *Monostroma nitidum*, commercially all sold as “Aonori” (Japanese green algae), were subjected to sensory evaluation and used for solid-phase microextraction (SPME) method development. *Ulva prolifera* (2 samples), *Ulva linza*, and *Monostroma nitidum* were obtained from Okayama, Tokushima, Ehime, and Shizuoka prefecture, respectively. Commercial Japanese green algae were purchased from a wholesale agency in Japan. The samples were placed in air tight plastic bags in the dark at room temperature. Prior to analysis, the samples were ground to a fine powder using liquid nitrogen.

**2.2. Sensory Evaluation.** The sensory tests were carried out by nine untrained panelists consuming regularly green algae. Hedonic sensory attributes evaluated in this study were color, taste, and overall acceptability of four green algae samples. The panelists (6 male, 3 female) were between 26- and 40-year old. A nine point hedonic scale (0–8), anchored by dislike extremely to like extremely for the overall score, light colored to strongly colored for the green color, and weak to intense for the taste, was employed. More precisely, the panelists were asked to evaluate the following aroma attributes animalic, floral, spicy, fatty, green note, marine-like, fresh (waterly), powdery, and leather-like common flavor attributes of green algae. Samples were served in glass beakers and provided randomly to panelists. Sensory evaluation procedures were explained to the panelists prior the tests.

**2.3. Solid Phase Microextraction (SPME).** Polydimethylsiloxane fibers (100  $\mu\text{m}$ ) were mounted in a SPME manual holder (Supelco, Bellefonte, PA, USA). All fibers were conditioned prior to analyses, according to the manufacturer’s recommendations. Various parameters (extraction method, time and temperature) influencing SPME analysis were optimized. For each analysis 10 g of sample was placed in a 40  $\text{cm}^3$  vial, spiked with 1 mg of the internal standard ethyldecanoate, and then sealed with an aluminum crimp cap provided with a needle-pierceable polytetrafluoroethylene/silicone septum. Each sample vial was placed at 50°C for 60 min to equilibrate and then the septum was pierced with the SPME needle. Fibers were exposed to the sample headspace for 60 min.

After the extraction time, fibers were retracted into the needle, transferred immediately to the injection port of a GC, and desorbed at 230°C for 1 min.

**2.4. GC/MS Analysis.** The compounds collected in the headspace above the green algae samples were analyzed by GC connected to a mass spectrometer (MS) (Shimadzu GC-MSQP5000), which was controlled by a Class-5000 workstation. Separation was carried out on a Supelcowax 10 fused silica capillary column 30 m  $\times$  0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness (Supelco, Bellefonte, PA, USA). Injection was in splitless mode for 1 min at 230°C with a specific SPME insert. The GC temperature was raised from 50 to 160°C at 3°C  $\text{min}^{-1}$  and from 160 to 240°C at 10°C  $\text{min}^{-1}$ . The mass spectra were scanned at 70 eV over a mass range from  $m/z$  50 to 280. Nonisothermal linear RI (Kovats type) was calculated after the analysis of a C11–C30 *n*-alkane series (GL Science) under the same conditions. Volatile compounds were tentatively identified by comparing their mass spectra with those of the reference database (NIST Mass Spectral Data 98<sup>l</sup> edition). Compounds were attributed to molecules through their individual mass spectrum, retention indices (RI), and retention time (RT). In addition, pure reference compounds were used to confirm the results. Flavor properties were assigned, based on reported odor descriptions [3, 13, 14].

**2.5. Data Analysis.** The relative peak areas were calculated in relation to the peak area of the internal standard ethyldecanoate. The identified volatile compounds were classified into different groups of molecules, such as alkanes, alkenes, ketones, aldehydes, sulfur compounds, alcohols, and esters. Unidentified compounds were excluded from this analysis. The relative peak areas of the different compounds in each category were calculated as a ratio of the total peak area. Statistical analyses were conducted using XL-STAT, version 2013 (Addinsoft, New York, USA).

## 3. Results and Discussion

The results of the sensory analysis revealed that it was impossible to differentiate between the samples based on the overall score (Figure 1). The same applies also to taste and color (data not shown). Based on the nine aroma attributes (animalic, floral, spicy, fatty, green note, marine-like, fresh (waterly), powdery, and leather-like), it was found that the samples from Okayama, Tokushima, and Ehime prefecture are uniform. However, the sample from Shizuoka prefecture was differently evaluated in respect of its green-note, marine-like, fresh, and powdery aroma (Figure 2).

As a result, it is impossible to distinguish between commercially sold “Aonori” samples based on sensory evaluation. Solely, in taxonomically different samples Okayama, Tokushima, and Ehime (*Ulva* species) versus Shizuoka (*Monostroma* species) somewhat different scores could be obtained.

Volatile compounds are fundamental for algae odor and aroma. Therefore, it is not surprising that volatile compounds in algae have been investigated and reports evaluating volatile

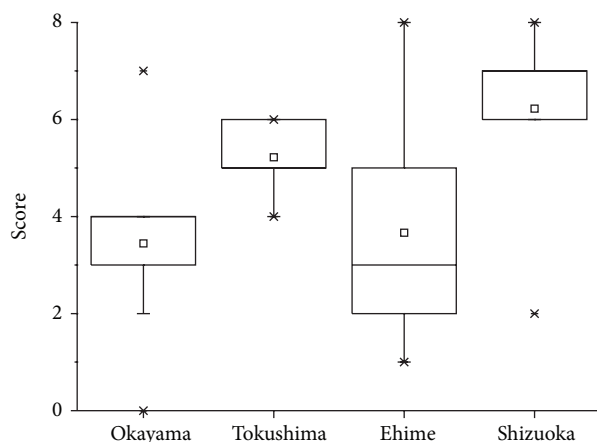


FIGURE 1: Overall scores of the sensory evaluation of green algae samples.

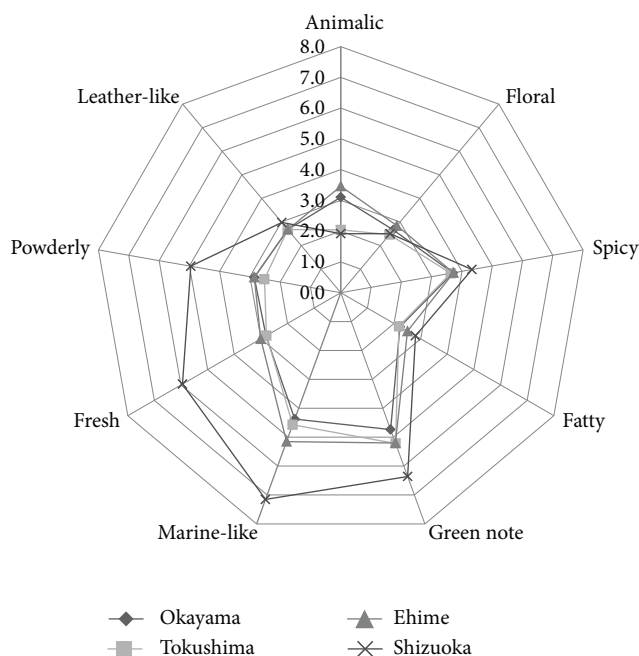


FIGURE 2: Sensory characterisation of green algae samples. The following aroma attributes were determined based on panelist's evaluation: animalic, floral, spicy, fatty, green note, marine-like, fresh (waterly), powdery, and leather-like.

metabolites, for example, in brown and red algae, are available in the current literature [15–18].

GC-MS techniques coupled with multi-variant analysis have been used in authenticating many food products and should be tested in this study for its practicability to distinguish different commercially sold Japanese green algae samples.

Forty-one major volatile compounds, classed as alkanes, alkenes, ketones, aldehydes, sulfur compounds, alcohols, and esters, were identified in the four commercial Japanese green algae (Table 1). These compounds are derived from

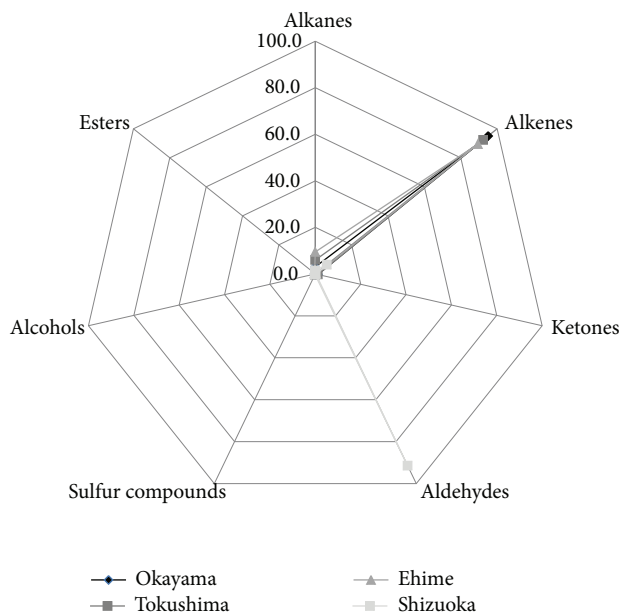


FIGURE 3: Chemical classification of volatile compounds in relative concentrations ( $n = 3$ ) in different commercial green algae samples.

different precursors, including the amino acids, fatty acids, and carotenoids (Table 1).

Hydrocarbons, including alkanes and alkenes (e.g., tetradecene, pentadecane, hexadecane, and octadecene), were abundant in three (Okayama, Tokushima, and Ehime) of the four samples (Figure 3).

The relative concentrations of alkenes vary among the samples from different algae of the order *Ulva*les. Green algae of the *Ulva* species are rich in alkenes: 95% in Okayama, 92.3% in Tokushima, and 89.4% in Ehime prefecture. In contrast, the green algae of the *Monostroma* species from Shizuoka prefecture contain only 6.3% of alkenes. An opposite trend has been found for the relative content of aldehydes. Very low relative contents are present in algae from Okayama (0.2%), Tokushima (0.1%), and Ehime (0.1%) and about 91.5% in algae from Shizuoka prefecture.

Heptadecanes, derived from fatty acids, were identified as major components among all samples. 7-Heptadecane has been reported to be one of the major components in marine green algae (*Ulva pertusa* and *Chara vulgaris*) and is known to be the character impact compound of edible kelp. It also contributes to the off-flavor in water [1, 19]. There is a seasonal variation in the concentration of 7-heptadecene and phytol in marine algae. It was found that 7-heptadecane was usually present in appreciable amounts throughout the year except during summer [20].

Ketones, sulfur compounds, and esters occurred in similar concentration ranges in all of the samples. Principal component analysis was performed to identify key volatiles contributing to the flavor characteristic of the four commercial algae samples. Figure 4 shows the correlation circle of factor 1 against factor 2 and helped us to identify major volatiles contributing to the distinct flavor properties of the commercial samples.

TABLE I: Volatile compounds of different green algae samples presented as relative ratios compared to the internal standard ethyldecanoate.

No.	Volatile compounds	Formula	Class	Origin	Odor description	RI	Relative contents (% averaged GC peak area ratio ( $n = 3$ ))							
							Okayama	STK	Tokushima	STD	Ehime	STD	Shizuoka	STD
1	Dodecane	C <sub>10</sub> H <sub>22</sub>	Alkane		Alkane (B)	1185	ND	ND	ND	ND	ND	1.2	0.0010	
2	Tridecane	C <sub>13</sub> H <sub>28</sub>	Alkane	Fatty acids	Alkane (B)	1297	0.6	0.0003	0.6	0.0008	ND	23.2	0.0298	
3	2,2,6-Trimethylcyclohexanone	C <sub>9</sub> H <sub>16</sub> O	Ketone	Carotenoids	Camphoraceous tobacco notes; thujone-like (A)	1308	0.7	0.0011	0.7	0.0026	ND	ND	ND	
4	Tetradecane	C <sub>14</sub> H <sub>30</sub>	Alkane	Fatty acids	Alkane (B)	1397	3.9	0.0020	11.4	0.0097	7.1	0.0158	0.0065	
5	Tetradecene	C <sub>14</sub> H <sub>28</sub>	Alkene			1444	0.5	0.0013	0.9	0.0005	2.1	0.0025	ND	
6	Pentadecane	C <sub>15</sub> H <sub>32</sub>	Alkene		Alkane (B)	1502	83.6	0.0622	251.1	0.1181	420.5	0.6057	ND	
7	(E,E)-3,5-Octadien-2-one	C <sub>8</sub> H <sub>12</sub> O	Ketone	Fatty acids, carotenoids	Almond (C)	1517	ND	ND	ND	ND	ND	ND	ND	
8	Benzaldehyde	C <sub>7</sub> H <sub>6</sub> O	Aldehyde	Amino acids	Sweet, strong almond (A) almond, burnt sugar (B)	1517	1.7	0.0028	2.3	0.0068	0.9	0.0015	3777.3	7.4504
9	Pentadecene isomer 1	C <sub>15</sub> H <sub>30</sub>	Alkene			1523	2.4	0.0028	3.6	0.0025	4.7	0.0057	11.7	0.0326
10	Pentadecene isomer 2	C <sub>15</sub> H <sub>30</sub>	Alkene			1546	0.7	0.0011	2.3	0.0025	1.0	0.0010	0.5	0.0028
11	Dimethyl sulfoxide	C <sub>2</sub> H <sub>6</sub> OS	Sulfur compound	Amino acids		1557	8.2	0.0457	16.5	0.0944	8.0	0.0500	12.3	0.0221
12	(E,Z)-3,5-Octadien-2-one	C <sub>8</sub> H <sub>12</sub> O	Ketone	Fatty acids, carotenoids	Melon-like (C)	1567	2.7	0.0100	2.1	0.0065	0.6	0.0052	0.3	0.0029
13	Pentadecene isomer 3	C <sub>15</sub> H <sub>30</sub>	Alkene			1576	ND	ND	ND	ND	ND	5.1	0.0085	
14	2,6,6-Trimethyl-2-hydroxycyclohexanone	C <sub>9</sub> H <sub>16</sub> O <sub>2</sub>	Ketone	Carotenoids	Sweet tobacco-like aroma with herbaceous undertones (A)	1594	8.6	0.0237	9.6	0.0223	4.1	0.0053	ND	ND
15	Hexadecane	C <sub>16</sub> H <sub>34</sub>	Alkane		Alkane (B)	1601	4.3	0.0089	5.6	0.0122	7.7	0.0144	28.2	0.0563
16	$\beta$ -Cyclocitral	C <sub>10</sub> H <sub>16</sub> O	Aldehyde	Carotenoids	Fresh (B)	1612	3.5	0.0085	3.5	0.0074	1.4	0.0010	ND	ND
17	Hexadecene isomer 1	C <sub>16</sub> H <sub>32</sub>	Alkene			1619	1.2	0.0010	2.5	0.0027	2.1	0.0025	ND	ND
18	Hexadecene isomer 2	C <sub>16</sub> H <sub>32</sub>	Alkene			1624	0.9	0.0024	1.1	0.0026	2.2	0.0004	ND	ND
19	Safranal	C <sub>10</sub> H <sub>14</sub> O	Aldehyde	Carotenoids		1637	ND	ND	ND	ND	ND	ND	ND	ND
20	Heptadecane	C <sub>17</sub> H <sub>36</sub>	Alkane		Alkane (B)	1707	56.1	0.0610	25.2	0.0936	25.5	0.2227	12.4	0.0993
21	7-Heptadecene	C <sub>17</sub> H <sub>34</sub>	Alkene			1722	2909.7	1.0740	4003.3	3.3306	3954.3	5.5587	155.5	0.3312
22	Heptadecene isomer 1	C <sub>17</sub> H <sub>34</sub>	Alkene			1733	1.8	0.0193	ND	ND	12.0	0.0030	7.0	0.0169
23	Heptadecadiene isomer 1	C <sub>17</sub> H <sub>32</sub>	Alkene			1757	103.4	0.0604	139.2	0.1109	148.7	0.1725	64.3	0.1246
24	Heptadecadiene isomer 2	C <sub>17</sub> H <sub>32</sub>	Alkene			1766	1.0	0.0021	1.2	0.0018	0.5	0.0047	0.7	0.0015
25	Heptadecadiene isomer 3	C <sub>17</sub> H <sub>32</sub>	Alkene			1769	4.3	0.0022	2.2	0.0011	0.8	0.0074	0.7	0.0104
26	Heptadecadiene isomer 4	C <sub>17</sub> H <sub>32</sub>	Alkene			1772	3.8	0.0037	5.3	0.0036	5.9	0.0041	1.1	0.0198
27	Heptadecadiene isomer 5	C <sub>17</sub> H <sub>32</sub>	Alkene			1779	0.8	0.0022	ND	ND	0.3	0.0059	0.5	0.0091
28	Octadecane	C <sub>18</sub> H <sub>38</sub>	Alkane		Alkane (B)	1801	3.0	0.0051	1.6	0.0042	3.2	0.0189	2.1	0.0059
29	Octadecene	C <sub>18</sub> H <sub>36</sub>	Alkene			1817	11.2	0.0072	12.8	0.0059	18.1	0.0085	0.9	0.0081
30	$\alpha$ -Ionone	C <sub>13</sub> H <sub>20</sub> O	Ketone	Carotenoids	Warm, woody, violet-floral (A)	1842	4.6	0.0039	5.6	0.0139	1.8	0.0085	ND	ND

TABLE I: Continued.

No.	Volatile compounds	Formula	Class	Origin	Odor description	RI	Okayama	Relative contents (% averaged GC peak area ratio ( <i>n</i> = 3))	Shizuoka	STD				
								Tokushima	STD	STD				
31	Nonadecane	C <sub>19</sub> H <sub>40</sub>	Alkane		Alkane (B)	1898	2.9	0.0119	1.1	0.0039	2.0	0.0029	0.7	0.0033
32	<i>β</i> -Ionone	C <sub>13</sub> H <sub>20</sub> O	Ketone	Carotenoids	Warm, woody, dry (A)	1927	12.5	0.1087	15.7	0.0144	5.9	0.0040	0.7	0.0031
33	Maltol	C <sub>6</sub> H <sub>6</sub> O <sub>3</sub>	Ketone		Caramel-butterscotch (A)	1960	0.6	0.0082	ND		ND		1.0	0.0059
34	<i>β</i> -Ionone epoxide	C <sub>13</sub> H <sub>20</sub> O <sub>2</sub>	Ketone	Carotenoids	Sweet berry (A)	1980	2.1	0.0181	2.8	0.0025	0.9	0.0006	ND	
35	Methyl tetradecanoate	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	Ester		Faint onion, honey (A), orris (A) (B)	2010	0.9	0.0051	0.0	0.0000	1.3	0.0017	1.7	0.0036
36	Pentadecanal	C <sub>15</sub> H <sub>30</sub> O	Aldehyde		Fresh (B)	2034	1.8	0.0103	3.1	0.0033	1.8	0.0103	ND	
37	6,10,14-Trimethyl-2-pentadecanone	C <sub>18</sub> H <sub>36</sub> O	Ketone	Carotenoids		2139	2.9	0.0168	6.7	0.0174	7.0	0.0160	7.4	0.0427
38	Hexadecanoic acid, methyl ester	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	Ester	Fatty acids		2217	5.2	0.0210	2.2	0.0038	9.0	0.0133	2.2	0.0029
39	Dihydroactinidiolide	C <sub>11</sub> H <sub>16</sub> O <sub>2</sub>	Ketone	Carotenoids	Musky or coumarin-like (A)	2347	3.0	0.0363	8.4	0.0199	4.2	0.0022	0.4	0.0034
40	Methyl linolenate	C <sub>19</sub> H <sub>32</sub> O <sub>2</sub>	Ester	Fatty acids		2566	4.1	0.0390	2.7	0.0063	7.3	0.0268	3.4	0.0057
41	Phytol	C <sub>20</sub> H <sub>40</sub> O	Alcohol	Chlorophyll	Faint floral (A) flower (B)	2580	2.8	0.0191	1.2	0.0050	0.9	0.0023	0.7	0.0071

(A) Food and Agriculture Organization of the united nations (<http://www.fao.org>), (B) Flavornet (<http://www.flavornet.org>), and (C) Hu and Pan, 2000 [14].



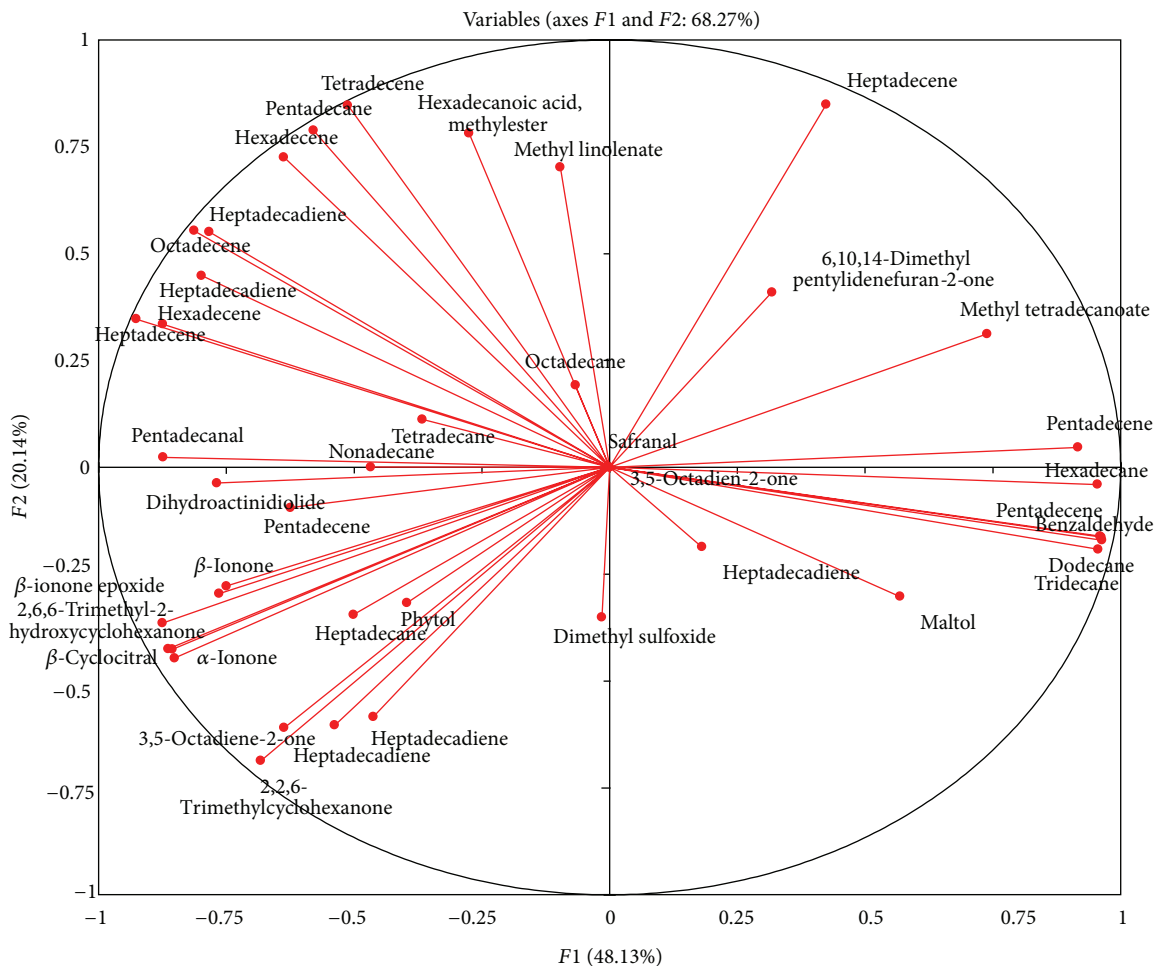


FIGURE 4: Correlation circle of volatile compounds from different green algae samples. The profiling was carried out based on 41 peaks and detected corresponding peak area ratios. Samples were independently analyzed in triplicate. The data was analyzed by PCA using XL-STAT 2013.2.

Our analysis revealed benzaldehyde, an important compound in algae from Shizuoka prefecture, originated from the amino acid biosynthesis pathway. Benzaldehyde contributes to the sweet, almond odor of fruits and flowers and is characterized by low odor thresholds (350–3500 ppb). Benzaldehyde can also be liberated from glycosidically bound precursors in various foods. In addition, it has been reported that concentrations increase during manufacturing processes, for example, production of apple puree or roasting of sesame seeds [21].

Several hydrocarbons such as tridecane, pentadecane, hexadecane, and dodecane were identified as relevant odor compounds in seaweed from Shizuoka prefecture.

It is noticeable that the proportion of volatile apocarotenoids is remarkably high in the investigated algae varieties. The importance of carotenoid-derived flavor compounds in algae has been previously reported. Volatile apocarotenoids, such as the potent flavor compound  $\beta$ -ionone, are produced by a diversity of algae taxa, for example, *Ulothrix fimbriata* and Asakusa Nori (*Porphyra tenera*) [22, 23]. Apart from chemical formation pathways [24], it has been demonstrated that functional carotenoid-cleavage like enzymes

contribute to the formation of volatile apocarotenoids in algae [25].

2,2,6-Trimethylcyclohexanone, (*E*, *Z*)-3,5-octadiene-2-one, 2,6,6-trimethyl-2-hydroxycyclohexanone,  $\alpha$ -ionone,  $\beta$ -ionone, and  $\beta$ -ionone epoxide are abundant in Okayama and Tokushima. Dihydroactinidiolide makes an important contribution to the volatile profile of algae from Tokushima. It is also an important component in green tea, with a sweet peach-like flavor [24]. In addition,  $\beta$ -cyclocitral and phytol are characteristic compounds influencing the flavor of algae from Okayama and Tokushima prefecture: they contribute to fresh and floral odors, respectively [18]. The ketones, such as  $\beta$ -cyclocitral,  $\beta$ -ionone, and  $\beta$ -ionone epoxide and phytol, are generated *via* degradation of carotenoids.  $\alpha$ -Ionone contributes to the violet, wood odor;  $\beta$ -ionone contributes to the violet-like and characteristic seaweed odor;  $\beta$ -ionone epoxide contributes to the sweet berry odor. These are important aroma impact compounds characterized by very low odor thresholds; for example,  $\beta$ -ionone has an odor threshold of 0.007 ppm [26].  $\beta$ -Ionone accounts for 12.5%, 15.7%, 5.9%, and 0.7% of the volatiles in the algae harvested from Okayama, Tokushima, Ehime, and Shizuoka prefecture,

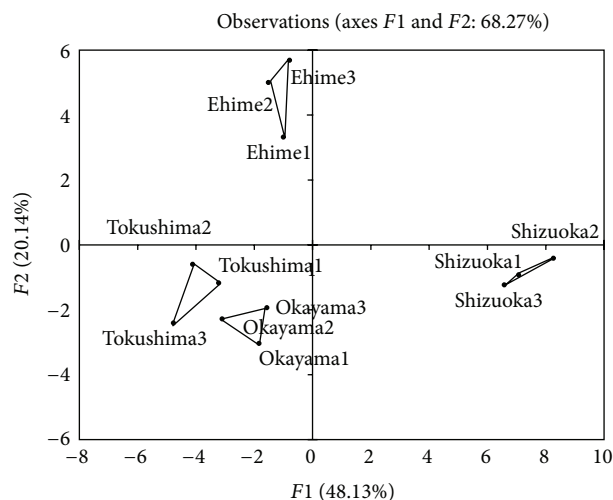


FIGURE 5: Scoring plots of nontargeted profiling of green algae samples of different origin by GC-MS-SPME. The profiling was carried out based on 41 peaks and detected corresponding peak area ratios. Samples were independently analyzed in triplicate. The data were analyzed by PCA using XL-STAT 2013.2.

respectively. Moreover, thermal degradation products of  $\beta$ -carotene, including 2,2,6-trimethylcyclohexanone, benzaldehyde, 2,6,6-trimethyl-2-hydroxycyclohexanone,  $\beta$ -cyclocitral, 5,6-epoxy- $\beta$ -ionone and dihydroactinidiolide, were previously reported [24].

After the removal of undesirable material, green algae are sun dried and packaged. It might be speculated that similar reactions occur during the sun drying processing of green algae and may have a strong impact on the quality of algae products. The occurrence of apocarotenoids is one of the most important indicators of authenticity for *Ulva prolifera*, *Ulva linza*, and *Monostroma nitidum*.

Another class of aroma compounds, the aliphatic acid methyl esters, including hexadecanoic acid, methyl ester, and methyl linolenate, was abundant in algae from Shizuoka prefecture. Methyl linolenate serves as a precursor of (*E*, *Z*)-3,5-octadien-2-one and is one of the most odor-active compounds [27]. It has been found in cod liver oil and *Ulva pertusa* and contributes to the melon-like odor. In this study, (*E*, *Z*)-3,5-octadien-2-one was detected in all samples and was more abundant in *Ulva prolifera*.

To explain the overall characteristics of the four algae samples, further studies are necessary to elucidate the contribution of single components and identify unknown compounds.

Multi-variant analysis of known components was performed on the mass spectral data to explain the overall characteristics of the differences among the samples. PCA was performed using a transformed data set consisting of correlation matrix of 41 variables yielding in 11 eigenvectors. Five factors explained 92.39% of the total variance, indicating that a reduced number of volatile compounds could explain the overall characteristics of the four different samples. Factor 1 explained 48.13% of the total variance and factor 2 explained 20.14% of the total variance. Both factors together

enable discrimination of the four algae samples from different biological and geographical origins (Figure 5). It is interesting that there are fewer differences in the volatile profiles of samples from close geographic origins, such as Tokushima and Okayama, compared with samples which are further away from each other, for example, Tokushima and Ehime. Future studies should be performed with a higher number of replicates and taking into account testing sets.

## 4. Conclusions

The volatile profiles of different commercial Japanese green algae samples, originating from Okayama, Tokushima, Ehime, and Shizuoka, were described for the first time. Multivariate analysis enabled discrimination of the samples, based on their botanical and geographical origin. Hitherto, the authenticity of these commercial products is based on package information and this study could form the analytical basis of authenticity studies of dried green algae samples using the SPME-GC-MS-method, followed by multivariate analysis.

## Conflict of Interests

The authors declare that there is no conflict of interests in the paper.

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