Identification of *Allium* Products Using Flame Photometric Detection Gas Chromatography and Distribution Patterns of Volatile Sulfur Compounds

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An analytical method for the assignment of allium products to the species of *Allium* plants used for their preparation has been developed. It incorporates extraction by a Dean−Stark low-density liquid extractor followed by flame photometric detection gas chromatography and GC/MS. Distribution patterns of volatile sulfur compounds characterizing the origin of the products are evaluated by correlation, cluster analysis, and principal component analysis of the data. Products such as health foods have been identified as allium products by comparison with known *Allium* plants. The results indicate that the computerized GC analysis in this study can be used effectively in the identification of allium products.

Keywords: *Garlic; Allium sativum L. allium products; FPD-GC; volatile sulfur compounds; multivariate data analysis*

INTRODUCTION

Garlic (*Allium sativum* L.) has been historically used as a spice, seasoning, and remedy for common ailments. Medicinal properties of garlic such as antibacterial activity (Johnson and Vaughn, 1969; Al-Delaimy and Ali, 1970), antifungal activity (Yoshida et al., 1987), virucidal activity (Weber et al., 1992), inhibition of platelet aggregation (Gaffen et al., 1984), and reduction of serum cholesterol levels (Lawson, 1993) have been reported. Biologically active sulfur compounds responsible for these properties have been isolated and identified (Cavallito and Bailey, 1944; Ariga et al., 1981; Block and Ahmed, 1984; Block et al., 1986; Lawson et al., 1992). Much attention has been directed to garlic and garlic extracts as potential cardiovascular and anticancer agents (Dausch and Nixon, 1990; Dorant et al., 1993). Garlic products prepared from garlic cloves or extracts have been commercially available as health foods with purported physiological effects to man. However, the quality of these garlic products is of question, and a method has been required for the evaluation and control of the quality of these products.

Characteristic flavor compounds of freshly cut garlic are enzymatically produced from flavor precursors of *S*-alk(en)yl-L-cysteine sulfoxides. Another group of nonvolatile flavor precursors is γ-glutamyl-*S*-alk(en)ylcysteines (Müsch-Eckner et al., 1992). During storage of garlic cloves γ-glutamyl-*S*-alk(en)ylcysteines could be converted to alk(en)ylcysteine sulfoxides (Lancaster and Shaw, 1989; Lawson et al., 1991a). When the garlic tissues are disrupted, alk(en)yl thiosulfinates, the primary flavor compounds of fresh garlic, could be released enzymatically from related alk(en)ylcysteine sulfoxides. Thiosulfinates are thermally unstable and converted to successive compounds of alk(en)yl polysulfides, dithiins, or ajoenes, thus contributing to the flavor of garlic products (Block, 1985, 1992). Plants of the genus *Allium* including garlic, onion, and caucas are sources of various volatile sulfur compounds.

Flavor analysis by using capillary gas chromatography (GC) is an established methodology in food analysis. Pattern recognition techniques such as discriminant analysis, principal component analysis (PCA), and cluster analysis are well-developed multivariate statistical techniques applied to food samples on the basis of GC patterns for quality assurance purposes. Some attempts utilizing pattern recognition analysis for discriminating coffee varieties (Aishima, 1991; Bicchi et al., 1993) and wines (van der Voet and Doornbos, 1984; Rapp and Güntert, 1985; Forina et al., 1986; Etiévant et al., 1989) have been successful.

For the analysis of the alk(en)yl thiosulfinates, HPLC has been suggested as the best method because it is performed at room temperature (Block et al., 1992a; Lawson et al., 1991b). GC was used in this study because of excellent resolution and mass identification capabilities. The GC profile may not always be sufficient to define garlic product quality. When GC is

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insufficient for an unbiased evaluation, a different fraction must be investigated as an alternative to, or combined with, GC. The use of supercritical fluid chromatography−mass spectrometry has been introduced (Calvey et al., 1994; Calvey and Block, 1997).

As a step for developing a simple flavor monitoring system for the identification of allium products, the use of GC patterns with statistical methods was investigated. The methods discussed in this study are correlation, cluster, and PC analysis.

MATERIALS AND METHODS

Materials. Fresh-picked mature garlic (*A. sativum* L.), onion (*A. cepa* L.), rakkyo (*A. chinense* G. Don), and caucas (*A. victorialis* L.) were purchased from local farmers in Aomori, Yamanashi, Fukui, and Kagawa prefectures in Japan. Bulbs were analyzed for garlic, onion, and rakkyo and leaves and stalks for caucas. Garlic and caucas products were purchased from local markets in Japan. A standard of *n*-paraffins (C7−C25) was purchased from Alltech Associates Inc. (Deerfield, IL). Diethyl ether, diallyl disulfide, and dimethyl disulfide were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Filter paper (Whatman phase separator 1 PS) was obtained from Whatman, Ltd. (Maidstone, Kent, England).

Sample Preparation. Samples (1−15 g of chopped *Allium* plants, 0.5−1 g of allium products) were left standing for 30 min with 200 mL of distilled water in a 1 L round-bottom flask. Two drops of silicon, several boiling stones, and 10 mL of diethyl ether as an extracting solvent were added to the flask. The flask was attached to a Dean−Stark (DS) continuous liquid−liquid extraction apparatus (PSJ, 1990; Lau et al., 1995), and the mixture was heated under reflux for 45 min, timed from the start of reflux at the rate of 2 mL/min. After refluxing, the flask was removed and the extracting solvent was passed through a filter paper, diluted to 5 mL with diethyl ether, and dried over anhydrous Na_2SO_4.

GC Analysis. A Shimadzu GC-14A gas chromatograph equipped with a flame photometric detector (FPD) was interfaced with a Shimadzu C-R7A integrator (Shimadzu Co. Ltd., Tokyo, Japan). The fused silica capillary column [SPB-1 sulfur, poly(dimethylpolysiloxane), 30 m × 0.32 mm i.d., D_f 4.0 μm; Supelco Co., Bellefonte, PA] was used to analyze the isolated volatiles. Volatile extracts were injected with a splitless injection and analyzed in duplicate. The operating conditions were as follows: injector temperature, 200 °C; detector temperature, 250 °C; oven temperature, 40 °C (10 min), 2 °C/min, 180 °C, 25 °C/min, 250 °C (5 min); N_2 flow rate, 1 kg/cm^2; linear retention indices were calculated against C7−C25 *n*-paraffins as references (Majlát et al., 1974).

Gas Chromatography/Mass Spectrometry (GC/MS). GC/MS analysis was conducted in a Shimadzu GC-17A gas chromatograph directly coupled to a Shimadzu QP-5000. Mass spectra were obtained by electron ionization (EI), the ion source temperature was 250 °C, and electron energy was 70 eV. The GC column and conditions were the same as described under GC Analysis.

Identification of Volatile Sulfur Compounds. Identification of volatile sulfur compounds in the isolate was mostly based on GC/MS. The structure assignments of sulfur compounds were accomplished by comparing the mass spectra data with those of authentic compounds available from computerized mass spectral databases, Browser-Wiley library, NIST 62 library, or published literature (Kim et al., 1995; Block et al., 1992b; Yu et al., 1989c, 1993, 1994; Yu and Wu, 1989b; Kuo and Ho, 1992a,b; Mazza et al., 1992; Sinha et al., 1992; Kallio and Salorinne, 1990; Vernin et al., 1986; Boelens et al., 1971; Brodnitz et al., 1969).

Pattern Recognition. Twenty-five selected volatile sulfur compounds, which represent dominant polysulfides in the examined *Allium* plants, were classified in 11 groups as shown in Table 1. Peak heights of each volatile of the duplicate GC analyses of each sample were measured, root extracted (as the FPD sulfur response is nonlinear), averaged, and normalized as the ratio to the total peak heights to eliminate effects of absolute amounts of volatiles on pattern recognition. To measure the strength of association of *Allium* plants and their products analyzed, calculation of correlation (Pearson correlation coefficients), cluster analysis (squared Euclidean distances used), and PCA were performed with a commercially available program.

Table 1. Volatile Sulfur Compounds Used for the Identification of *Allium* Products

group	peak[a]	compound	KI[b]	MW
1	4	diallyl sulfide	835	114
	10	diallyl disulfide	1060	146
	22	diallyl trisulfide	1280	178
2	1	allyl methyl sulfide	684	88
	5	allyl methyl disulfide	894	120
	16	allyl methyl trisulfide	1116	152
3	3	allyl propyl sulfide	825	116
4	2	dimethyl disulfide	721	94
	9	dimethyl trisulfide	946	126
	21	dimethyl tetrasulfide	1192	158
5	7	methyl (*Z*)-propenyl disulfide	912	120
	8	methyl (*E*)-propenyl disulfide	919	120
	18	methyl 1-propenyl trisulfide	1144	152
6	6	methyl propyl disulfide	912	122
	17	methyl propyl trisulfide	1132	154
7	11	allyl (*Z*)-propenyl disulfide	1077	146
	12	allyl (*E*)-propenyl disulfide	1081	146
	23	allyl 1-propenyl trisulfide	1306	178
8	13	propyl (*Z*)-propenyl disulfide	1077	148
	15	propyl (*E*)-propenyl disulfide	1098	148
9	14	dipropyl disulfide	1092	150
	24	dipropyl trisulfide	1312	182
10	19	3-vinyl-4*H*-1,2-dithiin	1155	144
	20	2-vinyl-4*H*-1,3-dithiin	1185	144
11	25	3,5-diethyl-1,2,4-trithiolane	1322	180

[a] Peak number refers to Figure 1. [b] Calculated Kováts retention indices.

RESULTS AND DISCUSSION

One of the aims of this study was to develop a method that was quick and easy and provided an objective identification and evaluation of allium products. Therefore, preference was also paid to sample preparation method.

Continuous liquid−liquid extraction in a DS apparatus, low-density liquid extractor, was used for the isolation of volatile sulfur compounds in samples. Extraction with the DS apparatus was rapid, simple, and inexpensive to perform and yielded a sample that was immediately ready for GC analysis. Alk(en)yl thiosulfinates released from *Allium* plants were thermally unstable and transform to polysulfides in the hot refluxing solvent and GC analysis with elevated injector temperatures. Transformation of these compounds was inevitable, and ample decomposition and changes have occurred to the allium samples. However, the composition of such alk(en)yl groups as allyl, methyl, 1-propenyl, and propyl in each plant could not be subject to drastic change and mostly reflects either the original ratio of these groups in the cysteine flavor precursors or thiosulfinates flavorants. The transformation rate of these thiosulfinates to polysulfides in water was found to depend on the conditions of the extraction (Block, 1985; Brodnitz et al., 1971; Yu et al., 1989c). If the volatiles were extracted under identical conditions, the transformation should occur to a similar extent in all of the samples. Therefore, the amount of these polysulfides could be used to represent the original or relative amount of volatile sulfur compounds in *Allium* plants and their products.

The optimum extracting conditions were derived from variation of refluxing solvent, time, and rate using garlic powder sample. The effect of refluxing solvent was compared between diethyl ether and *n*-hexane. Extraction with diethyl ether provided good yields of accumulated major volatiles such as allyl methyl sulfide, diallyl sulfide, allyl methyl disulfide, diallyl disulfide, and allyl methyl trisulfide, whereas extraction with *n*-hexane resulted in poor recoveries, although the amount of diallyl trisulfide exceeded that in *n*-hexane. Reflux times of 15, 30, 45, and 60 min were examined; times <45 min resulted in incomplete extraction, whereas extending the reflux time reduced accumulated major volatiles. Reflux rates of 0.8, 2, and 3 mL/min were considered, and the yields of accumulated major volatiles were maximized at the rate of 2 mL/min.

The pH and thermal effects on the stability and the formation of garlic volatile compounds were reported (Yu et al., 1989a,b; Yu and Wu, 1989a). Formation of 3-vinyl-4*H*-1,2-dithiin and 2-vinyl-4*H*-1,3-dithiin, which were decomposed from allicin, reached their highest levels around pH 5.5. Formation of allyl methyl sulfide, allyl (*Z*)-propenyl disulfide, dimethyl disulfide, methyl (*E*)-propenyl disulfide, allyl methyl trisulfide, and diallyl trisulfide was favored in neutral or weak acidic conditions, whereas formation of diallyl sulfide, allyl methyl disulfide, allyl propyl disulfide, diallyl disulfide, and methyl propyl disulfide was favored around pH 9.0. We selected neutral conditions in this study.

Different types of GC columns were examined for the analysis. Retention times for volatile compounds mostly depended on the polarity of the column used. SPB-1S, a nonpolar column ($D_f = 4.0\ \mu$m) especially developed for sulfur analysis, and HP-1 gave better resolution with good sensitivity.

Differences among *Allium* plants in their volatile sulfur compounds and their compositions have been reported (Bernhard, 1970). Garlic, elephant garlic, wild garlic, and Chinese chive dominantly contained allyl groups. Diallyl disulfide and diallyl trisulfide were the dominant compounds in distilled oil of garlic. On the other hand, 1-propenyl and methyl groups were commonly found in onion, scallion, shallot, leek, and chive (Block et al., 1992b; Sinha et al., 1992; Schreyen et al., 1976; Tokitomo, 1995a,b; Tokitomo and Kobayashi, 1992; Wu et al., 1982; Wu and Wu, 1981). Of the thiosulfinates found in onion, 37−47% contained a 1-propenyl group (Block et al., 1992a). The major volatiles identified in the distilled oils from Welsh onions and scallions were dipropyl disulfide, propyl 1-propenyl disulfide, methyl 1-propenyl trisulfide, and methyl propyl trisulfide (Block et al., 1992a; Kuo and Ho, 1992a,b). The major compounds responsible for the caucas flavor have been reported to be allyl methyl disulfide, diallyl disulfide, dimethyl disulfide, and allyl methyl trisulfide (Nishimura et al., 1971, 1988). Rakkyo, a Japanese name for an *Allium* species similar to scallion or shallot, was reported to contain copious methyl groups (Kameoka et al., 1984). There were marked differences in volatile sulfur compounds among examined *Allium* plants. Dominant compounds of methyl and propyl groups in rakkyo were also observed in our study. On the other hand, the presence of trace quantities of allyl compounds in onion and small quantities of propyl compounds in garlic and in ramp (*Allium tricoccum*; botanically similar to caucas) was found along with major amounts of allyl, methyl, and 1-propenyl groups (Calvey, 1997). Low levels of allyl propyl di- and trisulfides in onion and garlic volatiles were also found (Tokitomo, 1995b; Sinha et al., 1992; Kallio and Salorinne, 1990; Boelens et al., 1971; Kim et al., 1995; Mazza et al., 1992; Yu et al., 1989a). The presence of trace amounts of allyl propyl sulfide, dipropyl trisulfide, and methyl propyl trisulfide in garlic and caucas and of dipropyl disulfide in caucas was found in our study. No trace levels of allyl propyl di- and trisulfide were detected in garlic and onion volatiles. To detect these trace compounds, fairly large amounts of sample might be required. By comparing the patterns of such volatile sulfur compounds as sulfides, we assumed that allium products could be related to the *Allium* plants they were derived from. Typical gas chromatograms of the extracts of allium plants are shown in Figure 1. The identities of the 25 peaks chosen are provided in Table 1, and peak height percent of volatile sulfur compounds in *Allium* plants and their products are shown in Table 2.

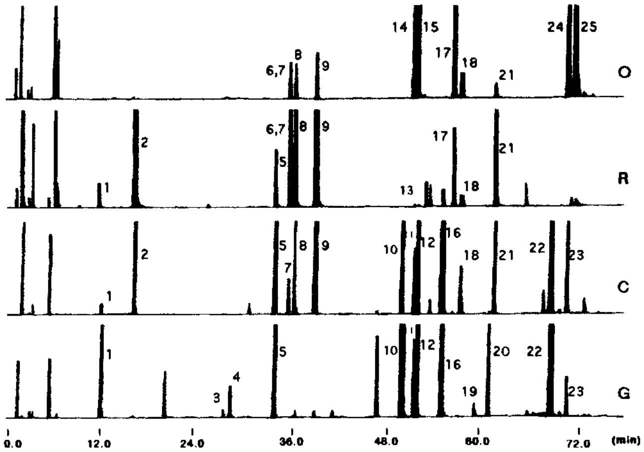

Figure 1. Gas chromatograms of volatile sulfur compounds of *Allium* plants: C, caucas; G, garlic; O, onion; R, rakkyo. Peak numbers refer to Table 1.

The potential success of the pattern recognition program to distinguish allium products on the basis of their volatile sulfur compound distributions was tested by selecting peaks from FPD-GC chromatograms that correspond to only the known sulfur compounds among four *Allium* plants. The algorithms used in this study could not uniquely distinguish *Allium* plants and their products when the nongrouped peaks were used. Bunching peaks that correlate to organic groups enhanced the ability to distinguish the species.

The GC profile similarities were calculated, and a correlation of the data was then produced to examine the relationship between *Allium* plants and their products on the basis of 11 grouped sulfur compounds. A correlation of 0.8−1.0 was considered to be a reasonable indication that the variables are correlated. The correlation coefficients within each plant were highly significant for garlic (0.91−1.00, $n = 10$) and rakkyo (0.91−0.97, $n = 10$), whereas onion and caucas did not show strong correlation and the correlation coefficients were 0.63−0.97 and 0.37−1.00, respectively ($n = 12$). This may be due to growing, storage, and other conditions that might influence the original ratio of alk(en)yl groups in the cysteine flavor precursors. Alk(en)yl polysulfides found in garlic and spice resembled one another, and the correlation coefficients of the alk(en)yl polysufide profiles of the spice for garlic were high (Table 3). High correlation between garlic products and

Table 2. Volatile Sulfur Compounds in *Allium* Plants and Their Products

	peak height (%)												
	caucas[b]	garlic[c]	onion[c]	rakkyo[c]	caucas products[d]			spice[e]			garlic products[f]		
peak[a]	av[g]	av	av	av	min[h]	max[i]	av	min	max	av	min	max	av
1	3.86	4.41	nd[j]	0.32	4.10	22.68	11.88	3.27	10.38	6.33	tr[k]	22.89	3.55
2	7.66	0.71	0.08	19.32	14.86	49.64	33.13	nd	1.51	0.45	nd	14.50	1.12
3	0.21	0.31	0.05	nd	nd			nd	0.42	0.11	nd	1.29	0.05
4	0.21	0.79	nd	nd	tr	3.39	1.73	tr	7.67	3.04	tr	20.35	3.23
5	11.41	8.10	nd	1.61	6.67	23.33	11.81	tr	14.07	5.38	tr	15.00	5.95
6	nd	nd	3.98	7.78	nd			nd			nd		
7	1.63	0.34	–[l]	–[l]	nd	1.59	0.63	nd	0.32	0.06	nd		
8	2.15	0.79	3.82	12.26	nd			nd	1.48	0.61	nd	1.68	0.16
9	12.72	0.91	3.99	34.06	3.54	8.43	6.04	tr	26.99	3.85	nd	11.45	3.10
10	13.03	31.64	nd	0.03	tr	12.13	6.67	tr	35.55	14.86	tr	38.75	16.97
11	2.72	2.67	nd	nd	nd	0.77	0.19	nd	2.72	0.71	nd	1.93	0.37
12	5.75	6.07	nd	0.26	nd	2.78	0.97	nd	4.71	1.18	nd	2.53	0.58
13	nd	nd	0.13	0.55	nd			nd			nd		
14	0.08	nd	25.29	0.74	nd			nd			nd		
15	nd	nd	12.37	1.88	nd			nd			nd		
16	15.14	10.31	nd	1.94	tr	12.11	6.96	7.56	21.22	13.80	tr	34.44	19.31
17	0.40	0.13	11.15	2.95	nd	0.40	0.10	nd	0.80	0.13	nd	0.80	0.08
18	1.10	0.15	5.22	5.76	nd	0.35	0.09	nd	0.57	0.08	nd	0.73	0.03
19	0.22	0.52	nd	0.02	nd			nd	5.70	1.36	nd	0.70	0.05
20	1.39	1.68	nd	nd	nd			nd	17.53	4.69	nd	3.01	0.55
21	1.62	0.01	1.59	8.78	tr	3.20	0.80	nd	1.03	0.14	nd	1.31	0.11
22	11.59	24.45	nd	nd	tr	26.64	7.83	11.71	46.82	30.30	4.91	70.73	35.82
23	2.46	1.58	nd	0.12	tr	4.83	1.32	nd	2.25	0.44	nd	10.72	0.75
24	0.13	0.09	16.26	1.01	nd	1.53	0.44	nd	0.25	0.04	nd		
25	nd	0.04	16.07	0.21	nd			nd			nd		
others	4.53	4.30	tr	0.40	0.95	23.21	9.40	tr	66.46	12.44	tr	48.07	8.03

[a] Peak number refers to Table 1 and Figure 1. [b] $n = 12$. [c] $n = 10$. [d] $n = 4$. [e] $n = 11$. [f] $n = 24$. [g] Average. [h] Minimum. [i] Maximum. [j] Not detectable. [k] Trace. [l] Mixed peak with 6.

Table 3. Summary of Correlated Values Abstracted from the Correlation Matrix for Spice

spice[a]	caucas	garlic	onion	rakkyo
slice A[b]	0.7685	0.9187	−0.4052	−0.1634
slice B[b]	0.8310	0.8700	−0.4810	−0.1378
powder[b]	0.7287	0.9501	−0.3812	−0.1854
minced[b]	0.8147	0.9184	−0.4192	−0.1131
liquid	0.5530	0.9843	−0.3168	−0.1795
extract (liquid)	0.7256	0.9346	−0.3550	−0.1943
grated A[c]	0.6066	0.9829	−0.3713	−0.1849
grated B[c]	0.7397	0.7991	−0.4052	0.3381
grated C[c]	0.5546	0.9820	−0.3069	−0.1866
grated D[c]	0.4618	0.9113	−0.3891	−0.2428
slice C[c]	0.6612	0.9725	−0.3773	−0.1723

[a] Manufactured and distributed in Japan. No lot numbers are given. [b] Dried. [c] Moist.

Table 4. Summary of Correlated Values Abstracted from the Correlation Matrix for Garlic Products

garlic product[a]	caucas	garlic	onion	rakkyo
powder A[b]	0.7865	0.9483	−0.3962	−0.1066
powder B	0.6475	0.9872	−0.3413	−0.1635
powder C	0.7233	0.9697	−0.4071	−0.2317
powder D	0.9458	0.7604	−0.3949	0.2488
tablet A[b]	0.6520	0.9824	−0.3367	−0.1564
tablet B[c]	0.7838	0.9099	−0.3677	−0.1182
tablet C[d]	0.7601	0.9536	−0.3722	−0.0965
tablet D[e]	0.5421	0.9799	−0.3028	−0.1852
tablet E[e]	0.5042	0.9709	−0.2894	−0.1808
tablet F[e]	0.6905	0.9754	−0.3473	−0.1360
tablet G[e]	0.5866	0.9841	−0.3167	−0.1678
tablet H[e]	0.6109	0.9849	−0.3243	−0.1617
tablet I[e]	0.6769	0.9784	−0.3436	−0.1439
tablet J[e]	0.6754	0.9786	−0.3433	−0.1461
tablet K	0.5649	0.9872	−0.3293	−0.1899
tablet L	0.8951	0.8156	−0.3812	0.0650
capsule A[f]	0.7706	0.9659	−0.3978	−0.1268
capsule B[g]	0.6668	0.9877	−0.3652	−0.1643
capsule C[h]	0.6946	0.9740	−0.3634	−0.1272
capsule D[h]	0.7736	0.9391	−0.3815	−0.0989
capsule E[h]	0.7896	0.9250	−0.3838	−0.0954
capsule F[h]	0.5163	0.9775	−0.3068	−0.1817
capsule G[h]	0.5756	0.9888	−0.3260	−0.1879

[a] Manufactured in Japan except capsule C, which was made in the United States. Distributed in Japan. No lot numbers are given. [b] Freeze-dried. [c] Freeze-dried and sugar-coated. [d] Soft tablet. [e] Sugar-coated. [f] Paste contained. [g] Powder contained. [h] Oil contained.

garlic and between caucas products and caucas was also observed (Tables 4 and 5).

To assess the correlation significance of *Allium* plants and their products, cluster analysis was applied in the expectation that allium products and their originating species would form clusters. Different cluster algorithms produced slightly different dendrograms for *Allium* plants and their products used in this study. The groupings were the same using three methods of single, median, and centroid linkage and two methods of complete and average linkage with only the similarity values varying. The dendrogram demonstrated clear separation of garlic and its products and the other three plants. An exception to this was two garlic products that contained reduced amounts of allyl-containing sulfides while showing increased amounts of allyl methyl groups; these were grouped together with caucas. In fact, the products did not have characteristic garlic odor. Soft-drink caucas products fused into the clusters consist of rakkyo, which agreed with the result obtained by correlation. These two products showed the high contents of dimethyl groups with lesser amounts of propenyl groups.

To give an overall picture of the distribution of the volatiles, PCA was performed. The loadings describe how much each variable contributes to the principal component. The loadings for the first three components are summarized in Table 6. The first principal component (PC1) showed a large contribution from groups 8 and 6. The plot of loading 1 against loading 2 accounts

Table 5. Summary of Correlated Values Abstracted from the Correlation Matrix for Caucas Products

caucas product[a]	caucas	garlic	onion	rakkyo
shoyu-zuke[b]	0.9413	0.4170	−0.3393	0.5542
miso-zuke[c]	0.9036	0.8498	−0.4217	0.2957
soft drink A[d]	0.7867	0.0960	−0.2118	0.7640
soft drink B[d]	0.7584	0.0995	−0.2252	0.8318

[a] Manufactured and distributed in Japan. No lot numbers are given. [b] Immersed in soy sauce. [c] Mixed with miso paste. [d] Caucas extract was used.

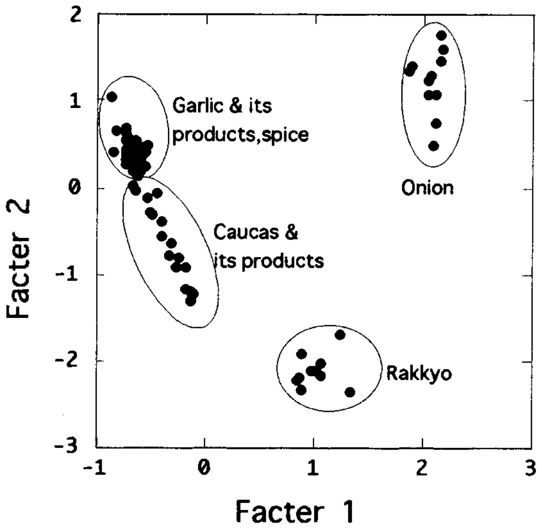

Figure 2. PCA analysis of *Allium* plants and their product volatiles. Factor scores are used for principal components 1 and 2.

Table 6. Loadings of the First Three Principal Components

	principal component		
variable	PC1	PC2	PC3
group 1	−0.813	0.381	−0.182
group 2	−0.845	0.023	−0.094
group 3	−0.203	0.174	0.771
group 4	0.301	−0.911	0.006
group 5	0.772	−0.567	0.221
group 6	0.926	−0.036	0.094
group 7	−0.397	0.018	0.554
group 8	0.901	0.383	0.002
group 9	0.828	0.486	−0.022
group 10	−0.326	0.191	0.316
group 11	0.830	0.486	0.023

for 66.5% of the cumulative variance. Grouping of allium products by origin was displayed graphically on the plane spanned by the first two principal component axes. Garlic, spice, and garlic products are located very close to each other. Caucas and caucas products are also located closely. Onions and rakkyo are clustered separately (Figure 2). PCA shows good separation with regard to different species of *Allium* plants and allowed the unequivocal identification of garlic and caucas products as garlic and caucas origin, respectively.

It is noted, however, that the relative percentage for different alk(en)yl groups could vary with the part of the plant. Also, thiosulfinate or polysulfide variation occurs with the plant variety, developmental stage, and growing and storage conditions (Mazza et al., 1992; Mackenzie and Ferns, 1977). Additional studies regarding the above conditions may be desirable.

In conclusion, an identification method based on FPD-GC analysis of volatile sulfur compound compositions with chemometric evaluation of the data obtained with these methods revealed that it is possible to identify allium products as their originating plants. The use of correlation, cluster, and PC analysis showed a uniform picture and affords a clearer discrimination. Furthermore, a predictive classification model such as *k*th nearest neighbors (KNN) or soft independent modeling of class analogy (SIMCA) may prove useful for prediction of plant sources by analysis of volatile sulfur compounds. It appears that chemometric evaluation of the chromatographic data is a useful method for rapidly obtaining more accurate identification.

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