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Release of volatile compounds from microwave heating of garlic juice with 2,4-decadienals

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Abstract

Garlic (*Allium sativum* L.) juice and 2,4-decadienals were heated in a microwave oven at the full power of 700 W. The volatile compounds of heated samples were isolated using diethyl ether solvent extraction and analysed using gas chromatography and gas chromatography–mass spectrometry. A total of 23 compounds were identified from these samples, among which 14 sulfide compounds, five aldehydes, two alcohols, one acid and one furan were identified. Three tentatively identified compounds, dithio(1-propenyl)propionate, dihydro-2(3*H*)-thiophenthione and *n*-hexanethiol were newly found in deep-fried garlic flavor. During microwave heating, levels of most volatiles decreased as the heating time continued. 2-Pentylfuran, isopropyl alcohol, hexanal and (*E*)-2-octenal were formed from the degradation of 2,4-decadienals. Sulfur dioxide was generated predominantly from the degradation and oxidation of sulfide compounds. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: 2,4-decadienal; Garlic; Microwave heating; Volatile compounds

1. Introduction

Garlic (*Allium sativum* L.) is used widely as a food flavoring and is well known in folk medicine for prevention of stroke, coronary thrombosis, and atherosclerosis (Block, Ahmad, Catalfamo, Jain, & Apitz-Castro, 1986). The most important precursor for the flavor of garlic is allicin (allyl 2-propenethiosulfinate) (Cavallito & Bailey, 1944; Cavallito, Buck, & Suter, 1944; Brodnitz, Pascale, & van Derslice, 1971). Allicin is derived from an odorless thioallyl compound, alliin (*S*-allyl cysteine sulfoxide) by the action of an enzyme alliinase (EC 4.4.1.4). Other precursors such as *S*-methyl cysteine sulfoxide, *S*-(*E*)-1-propenyl cysteine sulfoxide and γ-glutamylalk(en)yl cysteines are also found in intact garlic cloves. When garlic cloves are disrupted, these alk(en)yl cysteine sulfoxides can be converted to related alk(en)yl thiosulfinates by this enzyme (Iberl, Winkler, Muller, & Knobloch, 1990; Block, Ahmad, Catalfamo, Jain, & Apitz-Castro, 1992). However, most of these thiosulfinates are very unstable and can decompose or rearrange to form sulfide compounds, vinyl dithiins, or ajoenes (Block et al., 1986; Lawson, Wood, & Hughes, 1991).

In Chinese-style cooking, stir-frying techniques are commonly used. Before cooking, the wok is preheated with a large flame, and a small amount of oil is then poured in. The oil is spread to coat the surface of the wok, and garlic is then stirred to produce desirable flavor. However, the stir-frying technique might be inapplicable to microwave heating. In addition to the difficulty of cooking with oil, the dielectric constant of cooking oil is too low to penetrate the food during microwave irradiation (Buffler, 1993). Due to the fact that 2,4-decadienal plays an important role in flavor characteristics of deep-fried foods (Ho, Carlin, Huang, Hwang, & Hau, 1987), the direct use of 2,4-decadienal for the substitution of oil might be possible. For the purpose of producing flavors during microwave heating, it is anticipated that the methods for increasing flavors by heating desirable ingredients in a microwave oven will be of great interest. Therefore, the objectives of this study were to investigate the effects of microwave heating on the volatile components of garlic juice with 2,4-decadienals, and to determine the contribution of 2,4-decadienals to fried garlic flavors in order to

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replace the common practices of stir-frying with vegetable oil to produce stir-fried garlic flavors.

2. Materials and methods

2.1. Materials

Garlic cloves were purchased at a local market in Taichung, Taiwan. The mixture of (*E,Z*)- and (*E,E*)-2,4-decadienals (the *E,E*-form > 90%) was obtained from Bedoukian Research Inc., Danbury, CT.

2.2. Sample preparation

Garlic cloves (200 g) were peeled and chopped, and blended with distilled water (600 ml) for 1 min. After the mixture was filtered through filter paper (Whatman no. 4), the filtrate was immediately subjected to the following experimental procedures. Twenty grams of the filtrate, 0.2 ml of 2,4-decadienals (1.4% in methanol), and 0.2 ml of the internal standard (methyl benzyl sulfide, 13 mg in 50 ml methanol/diethyl ether 1:9, v/v) were placed in a 250 ml flask. For simulating the cooking in a microwave oven, a sample was put into a 100 ml flask, and sealed with parafilm, punched with several needle holes and heated in a home-use microwave oven at the full power of 700 W. Immediately after heating for 0, 0.5, 1, 2 and 3 min, each mixture was cooled in an ice-water bath, and stored at 4°C in a refrigerator for further analyses. Three samples from each heating treatment were examined and the experiments were conducted twice.

2.3. Flavor isolation

To each heated sample was added 20 ml of distilled water before solvent extraction. The mixture was then extracted twice with 15 ml of glass-distilled diethyl ether (Merck, Darmstadt, Germany). The combined extracts were dried over anhydrous sodium sulfate and filtered through filter paper (Whatman no. 4). The ether extract was evaporated under the air flow in a hood to a volume of approximately 20 μl, and the concentrate thus obtained was immediately subjected to gas chromatography and gas chromatography–mass spectrometry analyses.

2.4. Capillary gas chromatography (GC)

A DB-Wax column (60 m×0.25 mm i.d., df = 0.25 μm, fused silica WCOT capillary column, J&W Scientific, Folsom, CA) was connected to a flame ionisation detector (FID) in a Hewlett–Packard 5890II gas chromatograph system (Palo Alto, CA). The column temperature was programmed from 40 to 210°C at 3°C min^{-1}. The injector and detector temperatures are both 250°C. Nitrogen carrier gas was used at a velocity of 1.2 ml min^{-1} and controlled by an electron pressure control system in GC. A split ratio of 1:100 was used. Kovats indices were calculated for separate components relative to C_8–C_{25} *n*-alkanes mixture (Alltech Associates, Deerfield, IL) (Schomberg & Dielmann, 1973). Authentic compounds for gas chromatographic analysis were obtained commercially.

2.5. Gas chromatography–mass spectrometry (GC–MS)

The isolated components were analysed by GC–MS using a Hewlett–Packard 5890II gas chromatograph coupled to a Hewlett–Packard 5972A MSD mass spectrometer (Palo Alto, CA). A capillary column (same as that used in the GC analysis) was connected directly into the ion source of a mass spectrometer. The operating conditions were as follows: injector temperature, 250°C; GC–MS interface temperature, 265°C; helium carrier flow rate, 1.0 ml min^{-1}. The oven temperature was held at 40°C for 5 min, programmed to 210°C at 3°C min^{-1}, and then held at 210°C for 30 min. Mass spectra were obtained from electron multiplier voltage and electron ionisation energy at 1294 V and 70 eV, respectively.

2.6. Identification of volatile compounds

Volatile compounds were identified by comparing the mass spectral data with spectra available from the Wiley/NBS mass spectral library (Hewlett–Packard, Palo Alto, CA). Some compounds were further identified using authentic compounds.

3. Results and discussion

The precursor of garlic flavor, allicin, was found to be transformed into 2-vinyl-4*H*-1,3-dithiin and 3-vinyl-4*H*-1,2-dithiin during gas chromatographic analysis (Saito, Horie, Hoshino, Nose, Mochizuki, Nakazawa, & Fujita, 1989). When allicin was dissolved in hexane, diethyl ether or vegetable oils, it was transformed to (*E*)-ajoene, (*Z*)-ajoene, 2-vinyl-4*H*-1,3-dithiin and 3-vinyl-4*H*-1,2-dithiin (Lawson et al., 1991). Therefore, the analysis of allicin might depend on its degraded compounds. Although high performance liquid chromatography (HPLC) has been found to be reliable for the analysis of allicin (Iberl et al., 1990), the separation and identification of some other components present in the garlic extract by HPLC would not be as complete as that in GC. Therefore, this research was carried out using GC and GC–MS analysis.

It has been reported that the components in garlic extracts were unstable at high temperature and, especially at the boiling temperature of water, the major thiosulfinates will be degraded to sulfides (Block et al., 1986; Lawson et al., 1991). Although the simultaneous steam distillation–solvent extraction (SDE) in a modified Likens–Nickerson apparatus is used routinely for the flavor isolation of samples, it is inevitable that the formation of some artifacts during flavor isolation with boiling may occur (Block et al., 1986, 1992). Therefore, solvent extraction was used for flavor isolation of samples in this study.

The identified compounds and their quantitative distribution are listed in Table 1. Totally, 14 sulfide compounds, five aldehydes, two alcohols, one acid and one furan were identified, in which 13 compounds were further confirmed using authentic compounds. As compared to garlic volatile compounds (Brodnitz et al., 1971; Vernin, Heltzger, Fraisse, & Scharff, 1986; Jirovetz, Jager, Koch, & Remberg, 1992; Mazza, Ciaravolo, Chiricosta, & Celli, 1992; Hsu, Jeny, & Chen, 1993; Yu, Wu, & Ho, 1993; Kim, Wu, Kobayashi, & Okumura, 1995), three tentatively identified compounds including dithio(1-propenyl) propionate, dihydro-2(3*H*)-thiophenthione and *n*-hexanethiol were newly found in ether-extracted microwave-heated garlic flavor. As shown in Fig. 1, dithio(1-propenyl)propionate and dihydro-2(3*H*)-thiophenthione were postulated to be derived from the degradation and then cyclisation of 2-vinyl-4*H*-1,3-dithiin, whereas *n*-hexanethiol was from the disintegration of 3-vinyl-4*H*-1,2-dithiin. These three compounds might also have been derived from degradation during sample preparation and separation and/or differences from the solvent extraction.

The carbonyls, including hexanal, nonanal, (*E*)-2-octenal and hexanoic acid, and 2-pentylfuran were apparently derived from the thermal degradation of 2,4-decadienals. These degraded compounds, found at 0 min, originated from the impurity in commercial 2,4-decadienals and/or degradation during sample preparation. It is well known that these carbonyl compounds are related to the lipid degradation of soybean oil and can contribute to the deep-fried flavor (Wu & Chen, 1992). Yu et al. (1993) have also studied the flavor of microwave-heated garlic, but these carbonyl compounds were not found. The discrepancy in the findings reveals that the formation of degraded compounds from fatty acids of soybean oil has not occurred after microwave

Table 1
Volatile compounds released from microwave heating of garlic juice and 2,4-decadienals at various times

Peak no.	Compound	Kovats index (DB-Wax)	Amounts (mg kg^{-1}) at heating time (min)[a]				
			0	0.5	1	2	3
1	Sulfur dioxide	882	507 ± 265.4	814 ± 632.8	1298 ± 595.8	1252 ± 706.5	1246 ± 781.2
2	Allyl mercaptan[b]	895	33.5 ± 5.7	69.7 ± 7.8	66.8 ± 20.4	97.3 ± 40.5	61.8 ± 30.1
3	Isopropyl alcohol	926	3.7 ± 0.5	3.2 ± 1.2	15.1 ± 3.0	13.8 ± 6.4	15.7 ± 3.7
4	Hexanal[b]	1074	2.4 ± 1.6	12.6 ± 8.4	10.0 ± 2.6	11.5 ± 4.0	5.0 ± 1.6
5	Allyl alcohol	1104	15.0 ± 8.6	15.6 ± 10.8	17.6 ± 8.2	11.3 ± 4.5	4.2 ± 2.6
6	Allyl sulfide[b]	1143	3.4 ± 0.5	3.6 ± 0.2	2.4 ± 0.6	1.5 ± 0.4	tr[c]
7	2-Pentylfuran[b]	1243	1.4 ± 0.6	1.4 ± 0.3	1.2 ± 0.4	1.4 ± 0.6	1.2 ± 0.5
8	Methyl allyl disulfide[b]	1271	20.4 ± 4.8	22.1 ± 5.2	19.6 ± 2.5	14.0 ± 6.0	1.4 ± 0.4
9	Unknown	1294	13.8 ± 4.2	11.9 ± 3.2	18.4 ± 4.0	7.6 ± 2.5	tr
10	Dimethyl trisulfide[b]	1368	0.7 ± 0.4	3.8 ± 0.5	2.6 ± 0.8	1.3 ± 0.6	1.3 ± 0.8
11	Nonanal[b]	1376	nd[d]	tr	tr	tr	tr
12	(*E*)-2-Octenal	1429	nd	1.1 ± 0.6	0.4 ± 0.3	0.6 ± 0.2	tr
13	Dithio(1-propenyl)propionate	1451	7.0 ± 0.6	7.7 ± 1.6	7.2 ± 1.6	3.8 ± 0.8	1.3 ± 0.5
14	Diallyl disulfide[b]	1465	48.6 ± 2.5	43.6 ± 10.8	23.2 ± 2.6	17.4 ± 5.1	3.8 ± 2.1
15	Diallyl disulfide	1470	11.3 ± 0.8	10.7 ± 4.6	6.8 ± 2.6	2.1 ± 1.6	0.4 ± 0.3
16	1,2-Dithiacyclopent-3-ene	1510	13.8 ± 1.6	16.3 ± 2.6	18.0 ± 3.6	9.6 ± 1.5	1.6 ± 0.4
17	*n*-Hexanethiol	1578	4.9 ± 1.0	7.2 ± 1.5	6.8 ± 2.6	3.6 ± 0.8	0.4 ± 0.2
18	Methyl benzyl sulfide	1665	is[e]	is	is	is	is
19	Dihydro-2(3*H*)-thiophenthione	1720	22.5 ± 8.9	24.4 ± 10.6	25.5 ± 5.4	11.9 ± 6.0	0.7 ± 0.4
20	3-Vinyl-4*H*-1,2-dithiin[b]	1731	123 ± 40.6	133 ± 42.6	139 ± 10.8	64.7 ± 9.5	3.6 ± 1.2
21	(*E,Z*)-2,4-Decadienal[b]	1739	24.6 ± 4.8	12.7 ± 6.5	2.8 ± 1.8	0.8 ± 0.4	0.4 ± 0.1
22	2-Vinyl-1,3-dithiane	1745	10.6 ± 4.4	7.9 ± 3.6	4.4 ± 1.2	2.3 ± 1.0	tr
23	(*E,E*)-2,4-Decadienal[b]	1788	348 ± 62.9	159 ± 60.3	17.2 ± 5.6	7.9 ± 3.1	9.7 ± 4.2
24	Hexanoic acid[b]	1815	7.4 ± 6.0	2.8 ± 1.0	2.8 ± 1.8	2.0 ± 0.8	0.9 ± 0.5
25	2-Vinyl-4*H*-1,3-dithiin[b]	1824	15.4 ± 5.8	12.8 ± 4.6	15.6 ± 4.6	6.7 ± 4.5	0.5 ± 0.3

[a] Amounts are expressed as mean ± standard deviation.
[b] Mass spectrum and retention index are consistent with those of authentic compounds.
[c] nd: not detected.
[d] tr: less than 0.1 mg kg^{-1}.
[e] is: internal standard.

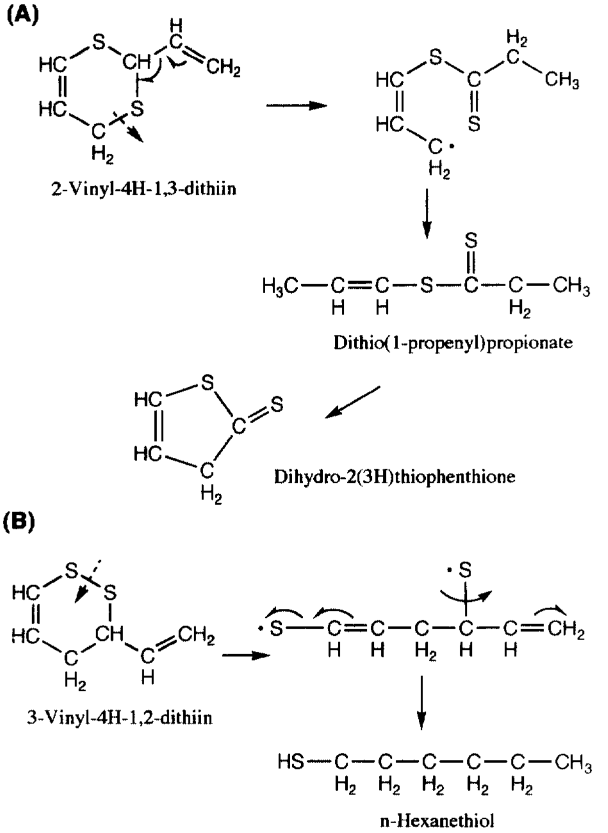

Fig. 1. Postulated degradation of (A) 2-vinyl-4*H*-1,3-dithiin and (B) 3-vinyl-4*H*-1,2-dithiin after microwave heating.

irradiation. Therefore, the deep-fried garlic flavor could not be produced directly from vegetable oils by the microwave heating. Using 2,4-decadienals as the precursor of deep-fried flavor in microwave heating would be one of the most direct methods.

Due to its extremely low odor threshold of 0.07 μg kg^{-1}, 2,4-decadienal is considered as one of the most important flavor characteristics of deep-fried foods (Van Germert & Nettenbrijer, 1977; Ho et al., 1987). 2,4-Decadienals were reported as the primary oxidation products of linoleic acid (Ho, Zhang, Shi, & Tang, 1989) and could thermally degrade to other compounds, such as hexanal, (*E*)-2-octenal, nonanal and 2-pentylfuran via an autoxidation mechanism (Josephson & Lindsay, 1987; Michalski & Hammond, 1972). Hexanal could further oxidise to hexanoic acid (Shahidi, 1994).

Contents of 2,4-decadienals, apparently decreased as the heating time in the microwave oven was prolonged. It was found that some of the degraded compounds from 2,4-decadienals were produced after microwave heating. In fact, some of the degraded carbonyls are thought to be undesirable flavor compounds. 2-Pentylfuran is one of the examples that has been reported as one of the compounds responsible for the reversion flavor of soybean oil (Ho, Smagula, & Chang, 1978). Hexanal, another example, has been proposed as one of the indicators for the development of off-flavor in vegetable oils (Warner, Evans, List, Dupuy, Wadsworth, & Goheen, 1978). However, it must be conceded that the off-flavor from degraded lipids and the deep-fried flavor in fried foods co-existed frequently after heating.

In Table 1, yields of several volatile compounds from microwave-heated samples were apparently different, and most of the compounds were degraded after heating, especially (*E,E*)- and (*E,Z*)-decadienals, vinyldithiins and diallyl disulfide. Sulfide compounds are the major components of garlic flavor. They could be a very important contributor to garlic flavor. Sulfur dioxide was suggested to be formed from the oxidation and degradation of sulfide compounds. The decreased amount of vinyldithiins showed that the amount of allicin was inversely proportional to the heating time in the microwave oven.

In conclusion, this study demonstrated that one of the methods for producing the oily flavor in microwave-heated garlic was the use of 2,4-decadienals as the precursor of the deep-fried flavor. In other words, the microwave heating of garlic with 2,4-decadienals resulted in microwave-fried garlic.

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References

Block, E., Ahmad, S., Catalfamo, J. L., Jain, M. K., & Apitz-Castro, R. (1986). Antithrombotic organosulfur compounds from garlic: structure, mechanistic, and synthetic studies. *Journal of the American Chemical Society, 108*, 7045–7055.

Block, E., Putman, D., & Zhao, S.-H. (1992). *Allium* chemistry: GC-MS analysis of thiosulfinates and related components from onion, leek, scallion, shallot, chive, and Chinese chive. *Journal of Agricultural and Food Chemistry, 40*, 2431–2438.

Brodnitz, M. H., Pascale, J. V., & van Derslice, L. (1971). Flavor components of garlic extract. *Journal of Agricultural and Food Chemistry, 19*, 273–275.

Buffler, C. R. (Ed.) (1993). Dielectric and thermal properties of foods and materials. In *Microwave cooking and processing: engineering fundamentals for the food scientist* (pp. 149–151). New York: van Nostrand Reinhold.

Cavallito, C. J., & Bailey, J. H. (1944). Allicin, the antibacterial principle of *Allium sativum*. I. Isolation, physical properties and antibacterial action. *Journal of the American Chemical Society, 66*, 1950–1951.

Cavallito, C. J., Buck, J. S., & Suter, C. M. (1944). Allicin, the antibacterial principle of *Allium sativum*. II. Determination of the structure. *Journal of the American Chemical Society, 66*, 1952–1954.

Ho, C.-T., Smagula, M. S., & Chang, S. S. (1978). The synthesis of 2-(1-pentenyl)furan and its relationship to the reversion flavor of soybean oil. *Journal of the American Oil Chemists Society, 55*, 233–237.

Ho, C.-T., Carlin, J. T., Huang, T. C., Hwang, L. S., & Hau, L. B. (1987). Flavor development in deep-fat fried foods. In M. Martens, G. A. Dalen, & H. Russwurm, Jr (Eds.), *Flavor science and technology* (pp. 35–42) Chichester, UK: Wiley.

Ho, C.-T., Zhang, Y., Shi, H., & Tang, J. (1989). Flavor chemistry of Chinese foods. *Food Rev. Ins., 5*, 253–287.

Hsu, J. P., Jeng, J. G., & Chen, C. C. (1993). Identification of a novel S-compound from the interaction of garlic and heated edible oil. In P. Schreier & P. Winterhalter (Eds.), *Progress in flavor precursor studies* (pp. 391–394). Carol Stream, IL: Allured Publishing.

Iberl, B., Winkler, G., Muller, B., & Knobloch, K. (1990). Quantitative determination of allicin and alliin from garlic by HPLC. *Planta Med., 56*, 320–326.

Jirovetz, L., Jager, W., Koch, H. P., & Remberg, G. (1992). Investigations of volatile constituents of the essential oil of Egyptian garlic (*Allium sativum* L.) by means of GC-MS and GC-FTIR. *Z. Lebensm. Unters. Forsch., 194*, 363–365.

Josephson, D. B., & Lindsay, R. (1987). Retro-aldol related degradation of 2,4-decadienal in the development of staling flavors in fried foods. *Journal of Food Science, 52*, 1186–1190, 1218.

Kim, S. M., Wu, C. M., Kobayashi, K., & Okumura, J. (1995). Volatile compounds in stir-fried garlic. *Journal of Agriculture and Food Chemistry, 43*, 2951–2955.

Lawson, L. D., Wood, S. G., & Hughes, B. G. (1991). HPLC analysis of allicin and other thiosulfinates in garlic clove homogenates. *Planta Med., 57*, 263–270.

Mazza, G., Ciaravolo, S., Chiricosta, G., & Celli, S. (1992). Volatile flavor components from ripening and mature garlic bulbs. *Flav. Frag. J., 7*, 111–116.

Michalski, S. T., & Hammond, E. G. (1972). Use of labeled compounds to study the mechanism of flavor formation in oxidizing fats. *Journal of the American Oil Chemists Society, 49*, 563–566.

Saito, K., Horie, M., Hoshino, Y., Nose, N., Mochizuki, E., Nakazawa, H., & Fujita, H. (1989). Determination of allicin in garlic and commercial garlic products by gas chromatography with flame photometric detection. *Journal of the Association of Official Analytical Chemists, 72*, 917–920.

Schomberg, G., & Dielmann, G. (1973). Identification by means of retention parameters. *J. Chromatogr. Sci., 11*, 151–159.

Shahidi, F. (1994). Assessment of lipid oxidation and off-flavor development in meat and meat products. In F. Shahidi (Ed.), *Flavor of meat and meat products* (pp. 247–266). London: Chapman & Hall.

Van Germert, L. J., & Nettenbrijer, A. H. (1977). *Compilation of odor threshold values in air and water.* Voorburg, The Netherlands: National Institute for Water Supply.

Vernin, G., Metzger, J., Fraisse, D., & Scharff, C. (1986). GC-MS (EI, PCI, NCI) computer analysis of volatile sulfur compounds in garlic essential oils. Application of the mass fragmentometry SIM technique. *Planta Med., 52*, 96–101.

Warner, K., Evans, C. D., List, G. R., Dupuy, H. P., Wadsworth, J. I., & Goheen, G. E. (1978). Flavor score correlation with pentanal and hexanal contents of vegetable oil. *Journal of the American Oil Chemists Society, 55*, 252–256.

Wu, C. M., & Chen, S. Y. (1992). Volatile compounds in oils after deep frying or stir frying and subsequent storage. *Journal of the American Oil Chemists Society, 69*, 858–865.

Yu, T. H., Wu, C. M., & Ho, C.-T. (1993). Volatile compounds of deep-oil fried, microwave-heated, and oven-baked garlic slices. *Journal of Agricultural and Food Chemistry, 41*, 800–805.