

*Thesis for Degree of Master of Science*

*Comparative Study on the Changes in  
Volatile Flavor Compounds of  
Dried Leeks (*Allium tuberosum* R.) by  $\gamma$ -Irradiation*

*by*

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*Department of Food and Nutrition  
Graduate School of Chosun University*

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in partial fulfillment of the requirement for the degree of  
Master of Science

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## ABSTRACT

### *Comparative Study on the Changes in Volatile Organic Compounds of Dried Leeks (*Allium tuberosum* R.) by $\gamma$ -Irradiation*

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This study was performed to examine the effect of  $\gamma$ -irradiation on the volatile flavor compounds of dried leeks (*Allium tuberosum* R.). Volatile compounds from dried leeks were extracted using simultaneous steam distillation and extraction (SDE) method and analyzed by gas chromatograph/ mass spectrometry (GC/MS). 41 and 42 Compounds were identified in non-irradiated and irradiated at 10 kGy, respectively. These compounds included alcohols, aldehydes, esters, S-containing compounds, N-containing compounds and miscellaneous. The characteristic flavor compounds of irradiated dried leeks were similar to those of non-irradiated samples but the intensities of the peaks were obviously different between them. S-containing compounds were found as dominant compounds in the both of these samples but their amounts were decreased after  $\gamma$ -irradiation in comparison with control. Among S-compounds, dimethyl disulfide, (*Z*)-propenyl methyl disulfide, methyl allyl disulfide, (*E*)-propenyl methyl disulfide, dimethyl trisulfide, 3-ethyl-1,2-dithi-5-ene, (*Z*)-methyl propenyl trisulfide and (*E*)-methyl propenyl trisulfide were dramatically decreased after irradiation. This investigation

indicates that the numbers of volatile compounds in the irradiated dried leeks were increased as compared to non-irradiated sample but the quantities of major volatile compounds were decreased losses by irradiation.

# I

## INTRODUCTION

Plants belonging to genus *Allium* such as garlic, onions, welsh onions, and leeks, have been used as food and medicinal herb in many different cultures of the world since ancient times (1). Taxonomically, the genus *Allium* is included in the family Liliceae and its species grow wild across a wide range of latitudes and altitudes in Europe, Asia, North America and Africa. *Allium* plants are known to accumulate sulfur containing secondary compounds that are derived from cysteine (2). These flavor substances are formed during disruption of plant material by the action of allinase (EC 4.4.1.4) on cysteine derivatives (3).

Leek (*Allium tuberosum* R.), locally called Bu-chu in Korea, is an aromatic herb possesses a characteristic and long-lasting odor resembling the flavor of onion and garlic. This plant is the major ingredient for leek Kim-chi, and has been used for a long time as a folk remedy for the treatment of abdominal pain, diarrhea, hematemesis, snakebite and asthma (4). It is rich in vitamin, fiber, minerals, and sulfur compounds that have antibiotic properties (5). This plant is a source of nitrates as well as sulfur volatiles like thiopropanal S-oxide, thiosulfinates and minor quantities of related compounds (zwiebelanes, capaenes) that contribute to the leeks distinctive flavor (6,7). On the other hand some secondary metabolites are endowed with interesting biological activities. Flavonol glycosides have an antioxdant activity and an

inhibitory activity on human platelet aggregation and atherosclerosis (8). *Allium* plants also possess chitinases with antifungal activity (9,10). These plants also contain high levels of inulin-type fructans with beneficial effects on serum lipids, blood glucose and the human gastro-intestinal tract (11).

Currently, spices are irradiated worldwide on a significant scale. Spices are commercially valued due to their flavor, but there are major problems associated with their storage and export. Heavy microbial contamination, insect infestation, and sprouting can result in quality deteriorations and lower market acceptability (12). Contamination by microorganisms, especially heat-resistant bacteria and molds, has frequently caused serious problems in the food industries. Most spices grown in the tropics under the prevailing production methods contain a large number of microorganisms, capable of causing food spoilage or even diseases in some instances. Until recently, fumigation with ethylene oxide has been used for microbial decontamination of spices in different countries. However, the use of this fumigant has been banned in several regions including the European Union and Japan was phased out by year 2000 in USA because of its toxic residues and occupational health hazards for workers (13). There have been many reports that radiation treatment of spices is a suitable method for inactivation of microorganisms (14,15). Commercial scale use of radiation processing for spices and other food products has been successful in more than 20 countries in recent years (16,17).

The major advantage of food irradiation is that most food can be irradiated successfully in the final stage of packaging. The quality of irradiated food is gradually increased without changing the flavor and other characteristics (18). Extensive research has proven that irradiation is a safe and reliable process,

and it has been approved by the Food and Drug Administration (FDA), the American Medical Association (AMA), and the World Health Organization (WHO) (16). The WHO encourages the use of the irradiation process, which is described as "a technique for preserving and improving the safety of food" (19). The results obtained in the International Project and in national testing programs were repeatedly evaluated by the Joint FAO/IAEA/WHO Expert Committee on the Wholesomeness of Irradiated Food (JECFI). This committee concluded in 1980 that the irradiation of any food commodity up to an overall average dose of 10 kGy presented no toxicological hazard and no special nutritional or microbiological problems (20).  $\gamma$ -Irradiation for microbial decontamination of whole spices and spice powders is legally permitted in some 34 countries world wide and 23 countries are using this technology commercially (21,22).

The complete volatile compound profile for irradiated dried leek has not been clearly described in the literature and it could be an important parameter to evaluate the quality of irradiated samples. Consequently, the objective of this study was to evaluate the profile of volatile compounds in irradiated and non-irradiated dried leeks learn about the effects of  $\gamma$ -irradiation treatment on substances responsible for the characteristic flavor of leek. The present study was therefore, conducted to assess the quality of irradiated spices with respect to their aromatic constituents.

## II

### MATERIALS AND METHODS

#### *A. Materials and analytic apparatus*

##### *1. Plant sample*

Fresh leeks (*Allium tuberosum* R.) were purchased from a local supermarket and freeze drying was performed in the laboratory. Dried leek was irradiated with the dose of 10 kGy at  $12 \pm 1^\circ\text{C}$  using a Co-60  $\gamma$ -irradiator at the Korea Atomic Energy Research Institute. The dose rate was 2.5 kGy/h with a dose rate error of  $\pm 0.02$  kGy. The non-irradiated leek was considered as a control and both samples were stored at  $-18^\circ\text{C}$  until required for the experiments.

##### *2. Reagents*

All the reagents used in the experiments were purchased from Sigma Co. (USA) and Fisher Scientific (USA). The organic solvents used for the extraction and the chromatography were redistilled using a wire spiral packed double distilling apparatus (Normschliff Geratebau, Wertheim, Germany) and Milli-Q water that was generated with a water purification system (Millepore Corporation, Bedford, USA).

### 3. *Analytic apparatus*

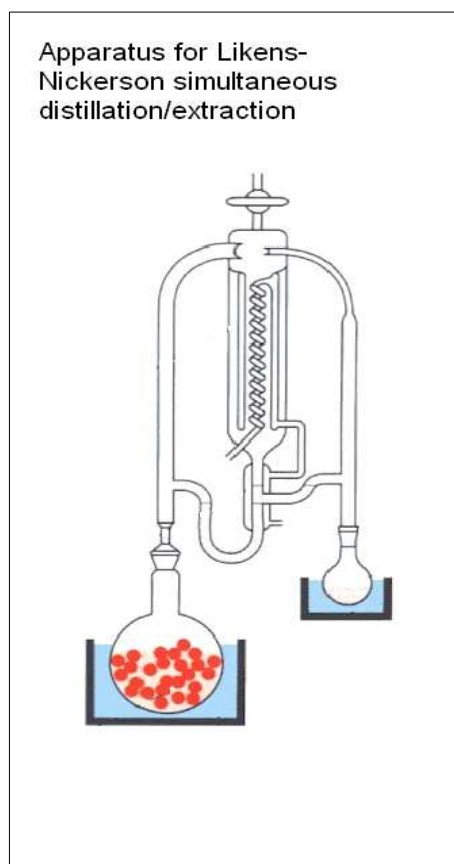
- a. Irradiator : Cobalt-60  $\gamma$ -irradiator  
(at the Korea Atomic Energy Research Institute)
- b. Freeze dryer : Labconco 7754500 (Labconco, Kansas, USA)
- c. Distilling apparatus : Wire spiral packed double distilling apparatus  
(Normschliff Geratebau, Germany)
- d. Blender : Multi mixer (Braun MR 550 CA, Braun, Spain)
- e. pH meter : pH/ION meter (DMS, Korea)
- f. Extraction apparatus (Simultaneous steam distillation and extraction, SDE): Likens & Nickerson type simultaneous steam distillation & extraction apparatus, (Normschliff, Wertheim, Germany)
- g. Concentration column : Vigreux column (250 mL Normschliff, Wertheim, Germany)
- h. Gas chromatograph : Hewlett Packard 5890 II Plus gas chromatograph equipped with FID and HP Chemstation 1050 Data system
- i. Gas chromatography/mass spectrometer : Shimadzu GC/MS QP-5000 equipped with mass spectrum library WILEY 139, NIST 62, NIST 12 (Shimadzu, Japan)
- j. Capillary column : DB-WAX (60 m  $\times$  0.25 mm i.d., 0.25  $\mu$ m film thickness, J&W, USA)

## ***B. Methods***

### ***1. Extraction of volatile flavor compounds***

20 g of samples homogenized in a blender (MR350CA, Braun, Spain) and mixed with 1 L of distilled water. The resultant slurry with maintaining pH 6.5 was used for the quantitative analysis with 1 $\mu$ L of n-butyl benzene added as an internal standard. The volatile compounds were extracted for 2 hr with 200 mL of a redistilled n-pentane/diethyl ether (1:1, v/v) mixture, using a simultaneous steam distillation and extraction (SDE, Likens & Nickerson type) apparatus (23), as modified by Schultz *et al.* (24), under atmospheric pressure (Fig. 1). The extract was dehydrated overnight anhydrous sodium sulfate and concentrated to approximately 1 mL using a Vigreux column. The 1 mL sample was followed by further concentration to final volume 0.2 mL, under the stream of nitrogen. The final sample was then used for the gas chromatograph/mass spectrometry (GC/MS) analysis (Fig. 2).





*Fig. 1. Diagram of simultaneous steam distillation extraction apparatus (SDE) according to Likens-Nickerson.*

## 2. Establishment of retention index

Kovats (25) suggested RI (retention index or Kovats index) as a suitable indication rule for retention indication which was indicated by the same space or compound to retention time for standard alkane.

Retention index as a parameter used for checking a solute from chromatogram by comparing the retention time of both alkane that appeared the above and below of the solute.

$$RI_i = 100 Z + 100 \left\{ \frac{\text{Log } V_{R(i)} - \text{Log } V_{R(Z)}}{\text{Log } V_{R(Z+1)} - \text{Log } V_{R(Z)}} \right\}$$

$RI_i$  : Retention index of compound  $i$

$V_{R(i)}$ ,  $V_{R(Z)}$ ,  $V_{R(Z+1)}$  : Each space revision time of alkane of compound  $I$ , carbon each number  $Z$ ,  $Z+1$

According to definition, retention time of alkane has the value as multiplying carbon number that the compound has to be unrelated with column solid phase, the temperature of separation and requirements of other chromatography. Therefore, n-alkane was indicated as a standard index for  $CH_4$  (RI=100),  $C_2H_6$  (RI=200)  $\cdots$   $C_nH_{2n+2}$  (RI=100n), and even anything in analysis column (26).

For retention index, the dilution mixture of n-alkane; mixture I ( $C_7 \sim C_{17}$ ) and mixture II ( $C_{13} \sim C_{23}$ ), was used as a internal standard.  $1\mu L$  mixture was analyzed to determine the retention time of the internal standard by GC-FID under the condition of Table 1. RI of each peak was established by a basic program that substituted the RT of each peak of n-alkane confirmed at GC chromatogram.

### *3. Analysis and identification of volatile flavor compounds*

#### *a. Analysis of gas chromatograph/mass spectrometer (GC/MS)*

Shimadzu GC/MS QP-5000 (Kyoto, Japan) in the EI (electron impact) mode was used for the quantitative analysis. The ionization voltage and temperature of injector and ion source were 70 eV, 250°C and 230°C respectively. The mass spectrometer scanned from 41 to 350  $m/z$ . A DB-WAX capillary column (60 m  $\times$  0.25 mm i.d., 0.25  $\mu$ m film thickness, J&W, USA) was used for the separation. The oven temperature was programmed as : 40°C (isothermal for 3 min) which was ramped to 150°C at 2°C/min and then to 210°C at 4°C/min. Helium was used as the carrier gas at a flow rate of 1.0 mL/min with an injector volume of 1  $\mu$ L using a 1:20 split ratio (Table 2).

**Table 1. GC conditions for identification of volatile compounds**

---

GC	Hewlett-Packard 5890 series II Plus
Column	DB-Wax(60 m × 0.25 mm I.D., 0.25 μm film thickness, J&W)
Detector	FID
Carrier gas	He(1.0 mL/min)
Make up gas	N <sub>2</sub> (30 mL/min)
Temp. program	40°C(3 min)-2°C/min-150°C-4°C/min-220°C(5 min)
Detector temp.	300°C
Injector temp.	250°C
Injection volume	1 μL

---

**Table 2. GC/MS conditions for identification of volatile flavor compounds from deied leeks**

---

GC/MS	Shimadzu GC/MS QP-5000
Column	DB-Wax(60 m × 0.25 mm I.D., 0.25 μm film thickness, J&W)
Carrier gas	Helium(1.0 mL/min)
Temp. program	40°C(3 min)-2°C/min-150°C-4°C/min-210°C(5 min)
Injector	250°C
Ion source and interface temp.	230°C
Ionization	electron impact ionization(EI)
Ionization voltage	70 eV
Mass range(m/z)	40 ~ 350
Injection volume	1 μL

---

b. Identification and quantitative analysis of volatile compounds

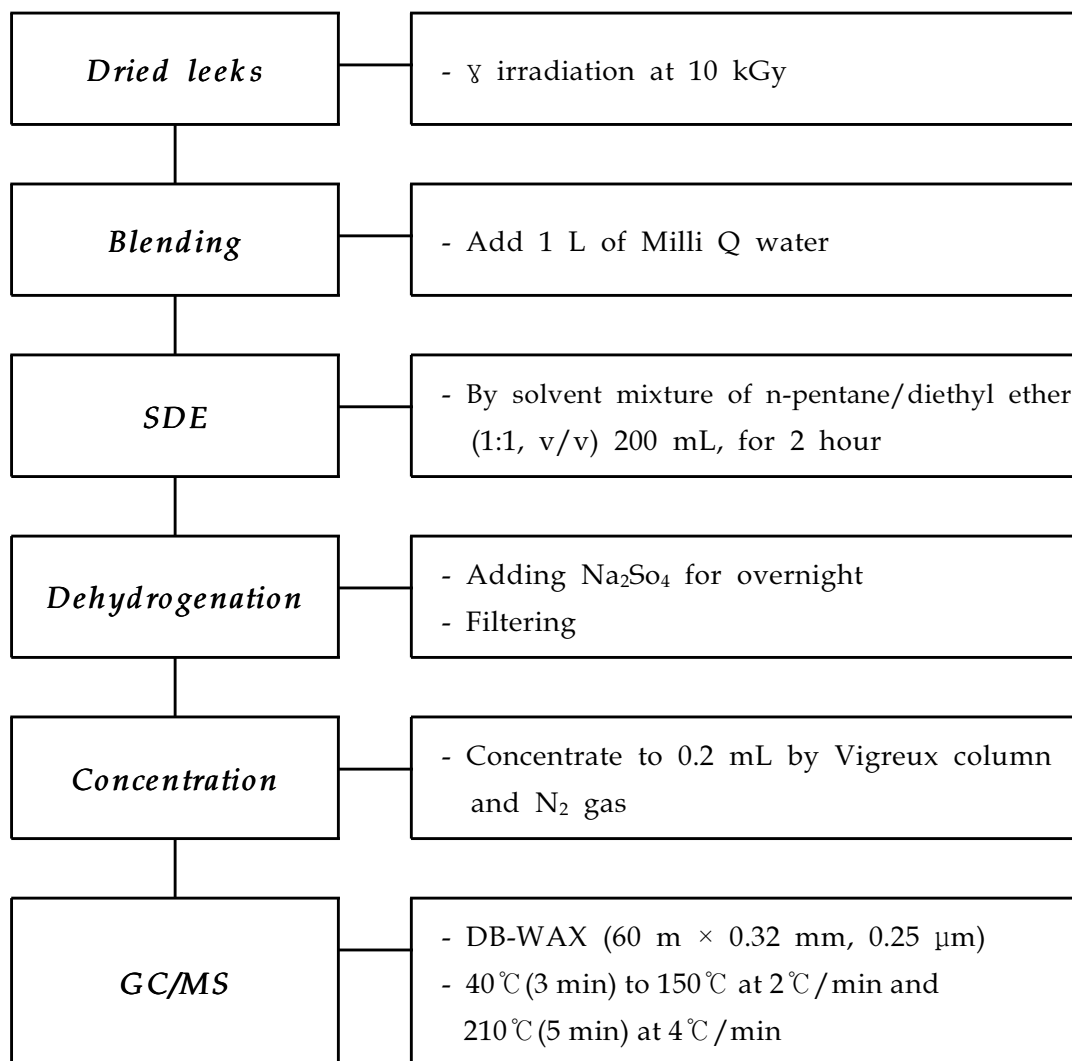
Mass spectra were identified with the aid of our own mass spectral data and those contained within the WILEY 139, NIST 62 and NIST 12 libraries and mass spectral data books (27,28) as well as by the comparison of retention indices to reference data (29,30). The following formula was used for quantitative analysis of volatile compounds.

$$\text{Compounds Content (mg/kg of dried leek)} = \frac{\text{C\%} \times 1000 \text{ g}}{\text{A\%} \times \text{B g}}$$

A% : Peak area% of each sample of internal standard

B% : Amount of sample

C% : Peak area% of each compounds in sample



*Fig. 2. Schematics of an analysis of volatile flavor compounds in non-irradiated and irradiated dried leeks.*

### III

## RESULTS AND DISCUSSION

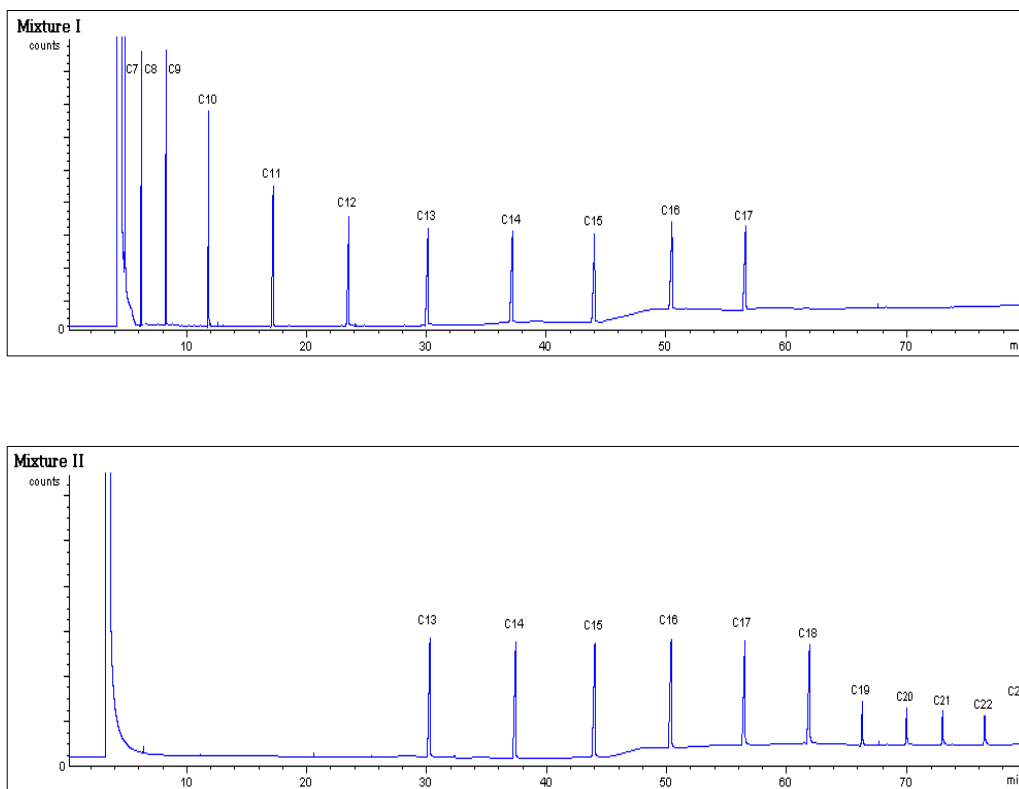
### *A. Analysis of volatile flavor compounds in dried leeks*

#### *1. Retention index of n-alkane*

The standard value of retention index was determined by two different mixture of n-alkane, mixture I (C<sub>7</sub>~C<sub>17</sub>), mixture II (C<sub>13</sub>~ C<sub>23</sub>) considering as an internal standard. 1μL mixture of alkane was analyzed to find out the retention time of internal standard by GC-FID (Fig. 3). RI of each peak was established by a basic program that substituted the RT of each peak of n-alkane confirmed at GC chromatogram (Table 3).

*Table 3. Retention time of n-alkane mixture for gas chromatographic retention index*

Alkanes	Retention time	Alkanes	Retention time	Alkanes	Retention time
C <sub>7:0</sub>	4.957	C <sub>13:0</sub>	30.089	C <sub>19:0</sub>	65.966
C <sub>8:0</sub>	6.119	C <sub>14:0</sub>	36.936	C <sub>20:0</sub>	69.635
C <sub>9:0</sub>	8.289	C <sub>15:0</sub>	43.463	C <sub>21:0</sub>	73.082
C <sub>10:0</sub>	11.598	C <sub>16:0</sub>	49.961	C <sub>22:0</sub>	75.762
C <sub>11:0</sub>	16.858	C <sub>17:0</sub>	56.047	C <sub>23:0</sub>	78.778
C <sub>12:0</sub>	23.25	C <sub>18:0</sub>	61.56		



*Fig. 3. GC chromatograms of n-alkane standard mixture I and II.*



## *2. Extraction of volatile flavor compounds in dried leeks*

Extraction method using SDE apparatus was suggested as an effective method for volatile flavor compounds in foods (23,24).

## *3. Volatile flavor compounds in dried leeks by GC/MS analysis*

Shimadzu GC/MS QP5000 (Kyoto, Japan) in the EI (electron impact) mode was used for the quantitative analysis. The ionization voltage and ion source temperature were 70 eV and 230°C, respectively. The mass spectrometer scanned from 40 to 350 m/z. A DB-WAX capillary column (60 m × 0.25 mm i.d., 0.25 µm film thickness, J&W, USA) was used for the separation. The oven temperature was programmed as : 40°C (isothermal for 3 min) which was ramped to 150°C at 2°C/min, and then to 210°C at 4°C/min. The injector and interface temperatures were 230 °C respectively. Helium was used as the carrier gas at a flow rate of 1.0 mL/min with an injector volume of 1 µL using a 1:20 split ratio.

## ***B. Quantitative analysis of volatile flavor compounds in non-irradiated leeks and dried leeks irradiated at 10 kGy***

### ***1. Volatile flavor compounds in non-irradiated and irradiated dried leeks***

The GC/MS chromatograms are presented in Fig. 3, and the volatile flavor compounds from GC/MS analysis and their relative content are shown in Tables 4-5.

A total of 41 compounds were detected and identified in the control while a 42 compounds were detected in the irradiated samples. In control leeks, the flavor compounds consisted of 7 alcohols, 9 aldehydes, 2 esters, 20 S-containing compounds, 2 N-containing compounds and 1 miscellaneous compound (Table 7).

Qualitative and quantitative analysis of volatile flavor compounds showed that S-containing compounds were characterized as the main volatile flavor compounds in the control. This was in accordance with previous finding that the S-containing compounds are the primary volatile flavor compounds in *Allium* species (33-35). Yu *et al.* (31,32) reported that during the steam distillation of *Allium* species homogenates most of the alk(en)yl-thiosulfinates decomposed to sulfides. The major volatile compounds were monosulfides, disulfides, and trisulfide. The S-containing compounds were found to be the major flavor compounds of fresh leeks, especially dimethyl disulfide, dimethyl trisulfide, (*Z*)-methyl-1-propenyl trisulfide and (*E*)-propenyl methyl disulfide (36). Bernhard (37) and Lopes *et al.* (38) noted that the main components of the essential oil of leek were allyl methyl disulfide, diallyl disulfide and dimethyl disulfide. Our results, which were consistent with previous finding,

are shown in Table 4. The compound dimethyl trisulfide (314.88 mg/kg) was the major compound. The substances (*Z*)-methyl-1-propenyl trisulfide (155.15 mg/kg), dimethyl disulfide (120.33 mg/kg) and (*E*)-propenyl methyl disulfide (103.44 mg/kg) were also detected in large amounts. Methyl allyl disulfide (73.48 mg/kg), 3-ethyl-1,2-dithi-5-ene (49.39 mg/kg) and (*Z*)-propenyl methyl disulfide (38.80 mg/kg) were also the other major compounds (Table 4). Mass spectra with structures of major compounds in dried leeks are presented in Fig. 4.

Composition of volatile compounds from leeks irradiated at 10 kGy were similar to those of non-irradiated leeks, but intensities at peaks were obviously different in irradiated samples. In dried leeks irradiated with 10-kGy doses of radiation, the flavor compounds consisted of 6 alcohols, 9 aldehydes, 2 esters, 21 S-containing compounds, 2 N-containing compounds, and 2 miscellaneous compounds (Table 7). The S-containing compounds featured dimethyl disulfide, (*Z*)-propenyl methyl disulfide, methyl allyl disulfide, (*E*)-propenyl methyl disulfide, dimethyl trisulfide, 3-ethyl-1,2-dithi-5-ene, methyl-(*Z*)-1-propenyl trisulfide and methyl-(*E*)-1-propenyl trisulfide as major components. Among these compounds, dimethyl trisulfide (217.63 mg/kg) was the major compound. Compounds such as dimethyl disulfide (92.67 mg/kg), methyl-(*Z*)-1-propenyl trisulfide (91.62 mg/kg), (*E*)-propenyl methyl disulfide (81.84 mg/kg), methyl allyl disulfide (73.48 m/kg) and (*Z*)-propenyl methyl disulfide (30.06 mg/kg) were also detected in large amounts (Table 5).

According to the results, the S-containing compounds were characteristically detected in both non-irradiated and irradiated samples. Therefore we conclude that S-containing compounds were the dominant group of compounds responsible for the flavor of dried leek.

**Table 4. Volatile flavor compounds identified in non-irradiated dried leek**

<i>Peak no.</i>	<i>RT</i> <sup>1)</sup>	<i>RI</i> <sup>2)</sup>	<i>Compound name</i>	<i>MF</i> <sup>3)</sup>	<i>MW</i> <sup>4)</sup>	<i>mg/kg</i>	<i>Area (%)</i>
1	6.35	813	Ethyl formate	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	74	0.87	0.09
2	6.73	832	2-Propenal	C <sub>3</sub> H <sub>4</sub> O	56	0.05	0.01
3	7.65	874	Ethyl acetate	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88	2.90	0.30
4	9.18	930	Ethanol	C <sub>2</sub> H <sub>6</sub> O	46	2.00	0.20
5	9.78	949	Diallyl methyl sulfide	C <sub>4</sub> H <sub>8</sub> S	88	1.56	0.16
6	10.64	974	Pentanal	C <sub>5</sub> H <sub>10</sub> O	86	0.37	0.04
7	15.21	1073	Dimethyl disulfide	C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>	94	120.33	12.29
8	15.67	1081	Hexanal	C <sub>6</sub> H <sub>12</sub> O	100	0.60	0.06
9	17.56	1113	2-Propenol	C <sub>3</sub> H <sub>6</sub> O	58	1.44	0.15
10	18.95	1137	2-Methyl-4-pentenal	C <sub>6</sub> H <sub>10</sub> O	98	0.32	0.03
11	20.30	1158	2-Methyl-2-pentenal	C <sub>6</sub> H <sub>10</sub> O	98	0.64	0.07
12	22.06	1184	Pyridine	C <sub>5</sub> H <sub>5</sub> N	79	0.90	0.09
13	23.07	1198	Heptanal	C <sub>7</sub> H <sub>14</sub> O	114	0.76	0.08
14	24.23	1216	( <i>E</i> )-2-Hexenal	C <sub>6</sub> H <sub>10</sub> O	98	11.09	1.13
15	25.17	1231	Methyl propyl disulfide	C <sub>4</sub> H <sub>10</sub> S <sub>2</sub>	122	0.99	0.10
16	26.59	1252	2,4-Dimethylthiophene	C <sub>6</sub> H <sub>8</sub> S	112	0.96	0.10
17	26.74	1254	Pentanol	C <sub>5</sub> H <sub>12</sub> O	88	0.21	0.02
18	27.37	1263	( <i>Z</i> )-Propenyl methyl disulfide	C <sub>4</sub> H <sub>8</sub> S <sub>2</sub>	120	38.80	3.96
19	28.57	1280	Methyl allyl disulfide	C <sub>4</sub> H <sub>8</sub> S <sub>2</sub>	120	73.48	7.50
20	29.13	1288	( <i>E</i> )-Propenyl methyl disulfide	C <sub>4</sub> H <sub>8</sub> S <sub>2</sub>	120	103.44	10.56
I.S <sup>5)</sup>	30.77	1311	<b><i>Butyl benzene</i></b>	C <sub>10</sub> H <sub>14</sub>	134	-	-
21	35.51	1381	Dimethyl trisulfide	C <sub>2</sub> H <sub>6</sub> S <sub>3</sub>	126	314.88	32.15
22	35.90	1386	( <i>Z</i> )-3-Hexenol	C <sub>6</sub> H <sub>12</sub> O	100	0.56	0.06
23	36.33	1392	Nonanal	C <sub>9</sub> H <sub>18</sub> O	142	1.07	0.11
24	38.72	1429	( <i>E</i> )-Propenyl propyl disulfide	C <sub>6</sub> H <sub>12</sub> S <sub>2</sub>	148	0.21	0.02

**Table 4. Continued**

<i>Peak no.</i>	<i>RT</i> <sup>1)</sup>	<i>RI</i> <sup>2)</sup>	<i>Compound name</i>	<i>MF</i> <sup>3)</sup>	<i>MW</i> <sup>4)</sup>	<i>mg/kg</i>	<i>Area (%)</i>
25	40.36	1455	Methional	C <sub>4</sub> H <sub>8</sub> OS	104	8.30	0.85
26	40.91	1463	Furfural	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	96	0.44	0.04
27	41.14	1466	3-Ethyl-1,2-dithi-4-ene	C <sub>6</sub> H <sub>10</sub> S <sub>2</sub>	146	15.17	1.55
28	42.15	1481	Diallyl disulfide	C <sub>6</sub> H <sub>10</sub> S <sub>2</sub>	146	17.32	1.77
29	42.57	1487	3-Ethyl-1,2-dithi-5-ene	C <sub>6</sub> H <sub>10</sub> S <sub>2</sub>	146	49.39	5.04
30	42.99	1493	2-Ethyl hexanol	C <sub>8</sub> H <sub>18</sub> O	130	0.41	0.04
31	45.06	1526	N,N-dimethylthioacetamide	C <sub>4</sub> H <sub>9</sub> NS	103	1.14	0.12
32	45.35	1531	Methyl propyl trisulfide	C <sub>4</sub> H <sub>10</sub> S <sub>3</sub>	154	1.06	0.11
33	46.63	1551	Linalool	C <sub>10</sub> H <sub>18</sub> O	154	0.74	0.08
34	49.42	1592	( <i>Z</i> )-Methyl-1-propenyl trisulfide	C <sub>4</sub> H <sub>8</sub> S <sub>3</sub>	152	155.15	15.84
35	49.83	1598	( <i>E</i> )-Methyl-1-propenyl trisulfide	C <sub>4</sub> H <sub>8</sub> S <sub>3</sub>	152	34.07	3.48
36	54.48	1675	S-Methyl methylthiosulphonate	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	126	1.19	0.12
37	54.84	1681	2-Butyl-4-methylthiazole	C <sub>8</sub> H <sub>13</sub> NS	155	0.34	0.03
38	55.35	1689	Cyclohexyl methyl sulfide	C <sub>7</sub> H <sub>14</sub> S	130	3.83	0.39
39	61.08	1792	Diallyl trisulfide	C <sub>6</sub> H <sub>10</sub> S <sub>3</sub>	178	9.62	0.98
40	62.92	1832	Hexanoic acid	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	116	1.18	0.12
41	68.70	1975	1-Phenyl-1-butanol	C <sub>10</sub> H <sub>14</sub> O	150	1.59	0.16
Total						979.37	100.00

R.T.<sup>1)</sup>:Retention time, R.I.<sup>2)</sup>:Retention index, M.F.<sup>3)</sup>:Molecule formula, M.W.<sup>4)</sup>:Molecule weight, I.S.<sup>5)</sup>: Internal standard.

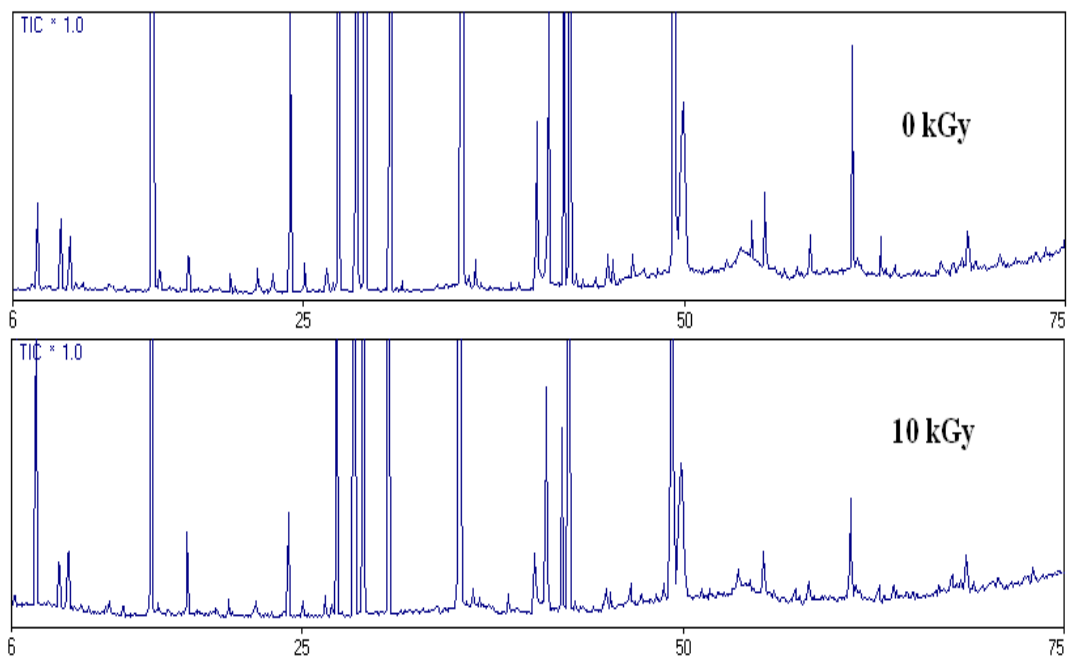
**Table 5. Volatile flavor compounds identified in irradiated dried leek at 10 kGy**

<i>Peak no.</i>	<i>RT</i> <sup>1)</sup>	<i>RI</i> <sup>2)</sup>	<i>Compound name</i>	<i>MF</i> <sup>3)</sup>	<i>MW</i> <sup>4)</sup>	<i>mg/kg</i>	<i>Area (%)</i>
1	6.33	812	Ethyl formate	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	74	3.60	0.53
2	6.70	830	2-Propenal	C <sub>3</sub> H <sub>4</sub> O	56	0.91	0.13
3	7.63	873	Ethyl acetate	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88	7.68	1.12
4	9.16	930	Ethanol	C <sub>2</sub> H <sub>6</sub> O	46	1.34	0.20
5	9.66	946	2-Ethyl furan	C <sub>6</sub> H <sub>8</sub> O	96	0.15	0.02
6	9.76	949	Diallyl methyl sulfide	C <sub>4</sub> H <sub>8</sub> S	88	1.55	0.23
7	12.43	1019	Pentanal	C <sub>5</sub> H <sub>10</sub> O	86	0.10	0.01
8	15.18	1072	Dimethyl disulfide	C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>	94	92.67	13.55
9	15.65	1080	Hexanal	C <sub>6</sub> H <sub>12</sub> O	100	0.40	0.06
10	17.54	1112	2-Propenol	C <sub>3</sub> H <sub>6</sub> O	58	3.08	0.45
11	19.41	1144	Methyl ethyl disulfide	C <sub>3</sub> H <sub>8</sub> S <sub>2</sub>	103	0.09	0.01
12	20.26	1157	2-Methyl-2-pentenal	C <sub>6</sub> H <sub>10</sub> O	98	0.58	0.08
13	22.05	1184	Pyridine	C <sub>5</sub> H <sub>5</sub> N	79	0.72	0.11
14	23.08	1198	Heptanal	C <sub>7</sub> H <sub>14</sub> O	114	0.35	0.05
15	24.19	1215	( <i>E</i> )-2-Hexenal	C <sub>6</sub> H <sub>10</sub> O	98	4.10	0.60
16	25.15	1231	Methyl propyl disulfide	C <sub>4</sub> H <sub>10</sub> S	122	0.75	0.11
17	26.56	1252	2,4-Dimethylthiophene	C <sub>6</sub> H <sub>8</sub> S	112	0.97	0.14
18	26.99	1258	Pentanol	C <sub>5</sub> H <sub>12</sub> O	88	0.48	0.07
19	27.34	1263	( <i>Z</i> )-Propenyl methyl disulfide	C <sub>4</sub> H <sub>8</sub> S <sub>2</sub>	120	30.06	4.40
20	28.52	1279	Methyl allyl disulfide	C <sub>4</sub> H <sub>8</sub> S <sub>2</sub>	120	43.43	6.35
21	29.09	1287	( <i>E</i> )-Propenyl methyl disulfide	C <sub>4</sub> H <sub>8</sub> S <sub>2</sub>	120	81.84	11.97
I.S <sup>5)</sup>	30.74	1311	<b>Butyl benzene</b>	C <sub>10</sub> H <sub>14</sub>	134	-	-
22	35.45	1380	Dimethyl trisulfide	C <sub>2</sub> H <sub>6</sub> S <sub>3</sub>	126	217.63	31.83
23	35.88	1386	( <i>Z</i> )-3-Hexenol	C <sub>6</sub> H <sub>12</sub> O	100	0.65	0.09
24	36.28	1391	Nonanal	C <sub>9</sub> H <sub>18</sub> O	142	0.82	0.12

*Table 5. Continued*

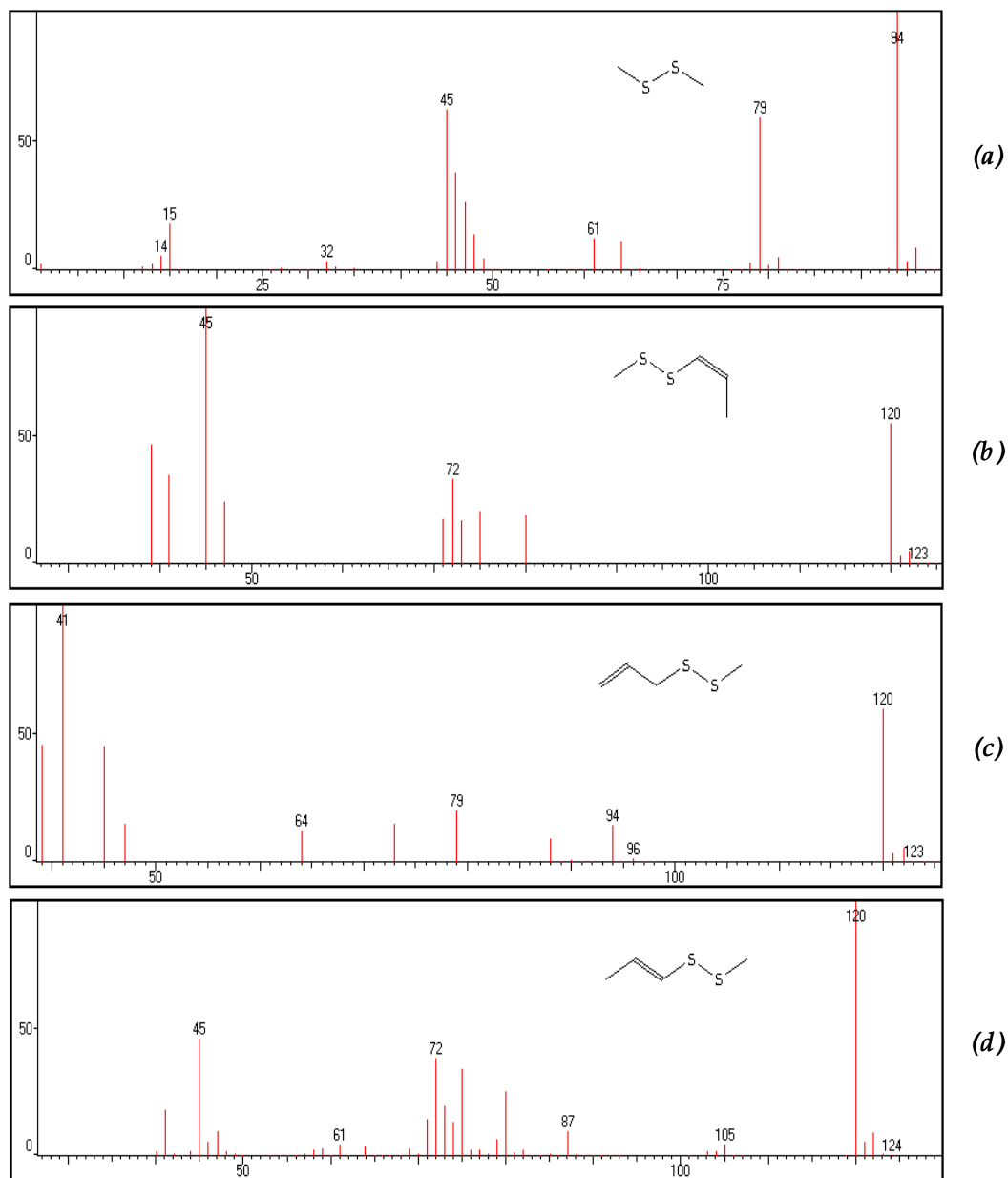
<i>Peak no.</i>	<i>RT<sup>1)</sup></i>	<i>RI<sup>2)</sup></i>	<i>Compound name</i>	<i>MF<sup>3)</sup></i>	<i>MW<sup>4)</sup></i>	<i>mg/kg</i>	<i>Area (%)</i>
25	38.58	1427	( <i>E</i> )-Propenyl propyl disulfide	C <sub>6</sub> H <sub>12</sub> S <sub>2</sub>	148	0.60	0.09
26	40.33	1454	Methional	C <sub>4</sub> H <sub>8</sub> OS	104	3.69	0.54
27	40.89	1463	Furfural	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	96	1.39	0.20
28	41.10	1466	3-Ethyl-1,2-dithi-4-ene	C <sub>6</sub> H <sub>10</sub> S <sub>2</sub>	146	9.52	1.39
29	42.11	1481	Diallyl disulfide	C <sub>6</sub> H <sub>10</sub> S <sub>2</sub>	146	8.85	1.29
30	42.52	1487	3-Ethyl-1,2-dithi-5-ene	C <sub>6</sub> H <sub>10</sub> S <sub>2</sub>	146	32.20	4.71
31	44.84	1523	Benzaldehyde	C <sub>7</sub> H <sub>6</sub> O	106	0.60	0.09
32	45.01	1525	N,N-dimethylacetamide	C <sub>4</sub> H <sub>9</sub> NS	104	1.43	0.21
33	45.33	1530	Methyl propyl trisulfide	C <sub>4</sub> H <sub>10</sub> S <sub>3</sub>	154	1.08	0.16
34	46.62	1550	Linalool	C <sub>10</sub> H <sub>18</sub> O	154	0.87	0.13
35	48.79	1583	Dimethyl sulfoxide	C <sub>2</sub> H <sub>6</sub> OS	78	0.41	0.06
36	49.35	1591	( <i>Z</i> )-Methyl-1-propenyl trisulfide	C <sub>4</sub> H <sub>8</sub> S <sub>3</sub>	152	91.62	13.40
37	49.94	1600	( <i>E</i> )-Methyl-1-propenyl trisulfide	C <sub>4</sub> H <sub>8</sub> S <sub>3</sub>	152	28.04	4.10
38	54.37	1674	S-Methyl methylthiosulphonate	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	126	0.46	0.07
39	55.31	1689	Cyclohexyl methyl sulfide	C <sub>7</sub> H <sub>14</sub> S	130	2.81	0.41
40	61.03	1791	Diallyl trisulfide	C <sub>6</sub> H <sub>10</sub> S <sub>3</sub>	178	4.23	0.62
41	62.89	1831	Hexanoic acid	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	116	1.01	0.15
42	68.67	1974	1-Phenyl-1-butanol	C <sub>10</sub> H <sub>14</sub> O	150	0.93	0.14
<b><i>Total</i></b>						<b>683.69</b>	<b>100.00</b>

R.T.<sup>1)</sup>:Retention time, R.I.<sup>2)</sup>:Retention index, M.F.<sup>3)</sup>:Molecule formula, M.W.<sup>4)</sup>:Molecule weight, I.S.<sup>5)</sup>: Internal standard.



*Fig. 4. GC/MS chromatogram of the volatile flavor compounds in non-irradiated and irradiated dried leek at 10 kGy.*





*Fig. 5. Mass spectra and structures of major S-containing compounds in dried leeks. (a) dimethyl disulfide, (b) (Z)-propenyl methyl disulfide, (c) methyl allyl disulfide, (d) (E)-propenyl methyl disulfide.*

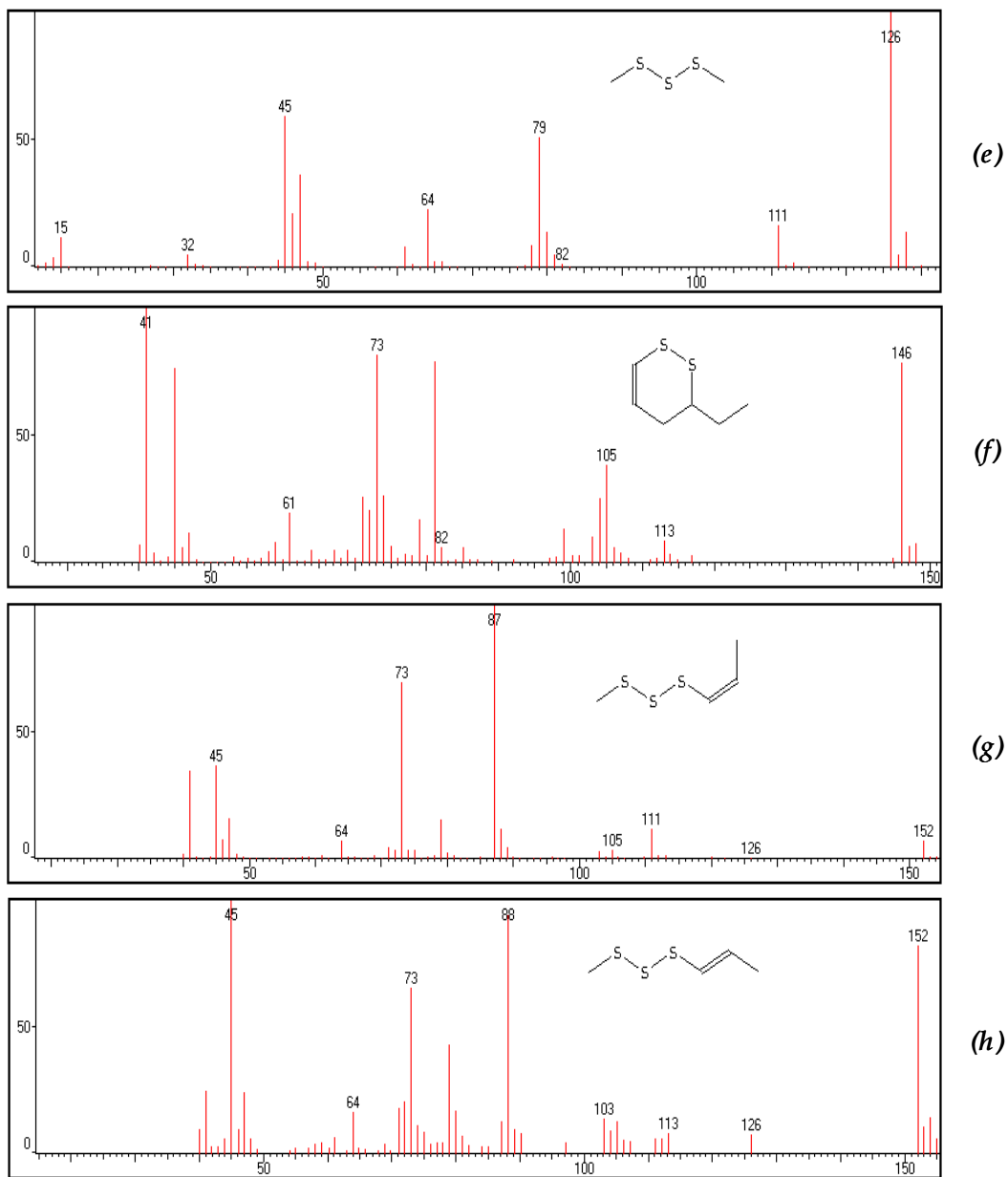


Fig. 5. Continued. (e) dimethyl trisulfide, (f) 3-ethyl-1,2-dithi-5-ene, (g) (Z)-methyl propenyl trisulfide, (h) (E)-methyl propenyl trisulfide.

## ***2. Production of sulfur-containing flavor compounds by alliinase in Allium species***

Since ancient times, garlic (*Allium sativum*), onion (*Allium cepa*), and related species of the leek family (*Alliaceae*) have been used as foods, spices, and herbal remedies in many parts of world. Volatile sulfur-containing compounds are responsible for the characteristic smell and taste of members of the *Alliaceae*. These compounds are alk(en)yl-thiosulfinates formed by the action of allinase (EC 4.4.1.4) on odorless and non-volatile cysteine derived substances *S*-alk(en)yl-L-cysteine sulfoxides. These reactants are released by plant material disruption (Fig. 5) (39-41). Allinase has been preliminary reported to be localized in the bundle sheaths cells of garlic clove (*Allium sativum*) (42) and in foliage leaves of *Allium tuberosum* (43). The reaction of allinase takes place extremely rapidly, as can be observed with the instantaneous appearance of garlic's typical odor when on crush.

*S*-alk(en)yl-L-cysteine sulfoxides are considered to be important in sulfur metabolism, acting as a soluble pool for organic sulfur (44). The general structure of the *S*-alk(en)yl-L-cysteine sulfoxides is shown in Fig. 5. Five *S*-alk(en)yl-L-cysteine sulfoxides differing in R-side group have been described. Four of these have been found in *Allium*. The amounts of the four varieties of R-side group of *S*-alk(en)yl-L-cysteine sulfoxides found in *Allium* sp. plants are presented in Table 6. Intact garlic bulbs contain mostly (+)-*S*-(2-propenyl)-L-cysteine sulfoxide (alliin) with some (+)-*S*-methyl-L-cysteine sulfoxied (methiin). Onions contain (+)-*S*-(1-propenyl)-L-cysteine (isoalliim), while (+)-*S*-propyl-L- cysteine sulfoxide (propiin) the volatile S-containing

compound found in leeks (14,39-41).

The aroma compounds of *Allium* species are pharmacologically active substances that exhibit antibiotic, antioxidant and antitumor activities. They are also involved in inhibition of thrombocyte aggregation lipid-lowering effects. Additionally, epidemiological studies have shown that regular consumption of onion and garlic may prevent stomach cancer (39,45-47). Sulfur-containing substances with one or more allyl residues (e.g., allicin, diallyl sulfide, and diallyl trisulfide) have tumor preventative effects (48,49).

Furthermore, *Allium* oils produced from onion, garlic, or leek by steam distillation are widely used for flavoring food. Breeding experiments involving wild *Allium* species with onions have the potential to increase yields of these volatile sulfur substances.

**Table 6. Kinds of *S-alk(en)yl-L-cysteine sulfoxides* in *Allium***

	<i>Alk(en)yl group</i>	<i>Sources of S-alk(en)yl-L-cysteine sulfoxides</i>
	methyl	garlic, elephant garlic, wild garlic, onion, leek, scallion, shallot, leek
<i>In Allium</i>	propyl	onion, leek, scallion, shallot, chive
	propenyl	garlic, elephant garlic, wild garlic, onion, leek, scallion, shallot, leek, chive
	allyl	garlic, elephant garlic, wild garlic, leek

from Block *et al.* (50).

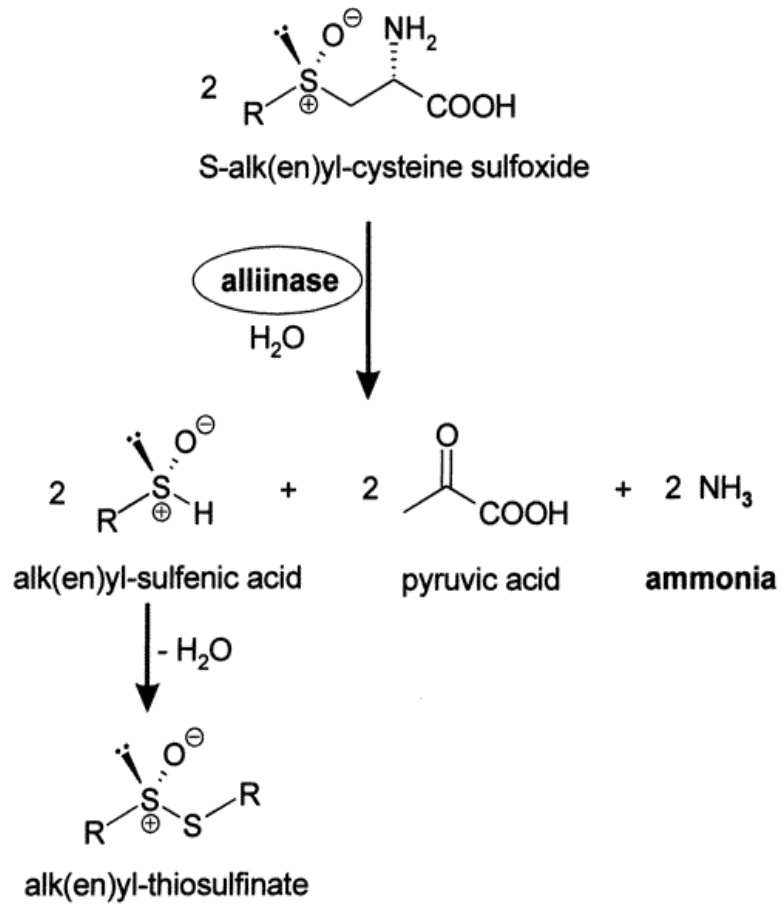


Fig. 6. Enzymatic cleavage of *S*-alk(en)yl-L-cysteine sulfoxides.

### *3. Comparison of the volatile flavor compounds of non-irradiated and irradiated dried leeks*

Table 6 gives the quantitative distribution of the major constituents of the volatile compounds isolated from control and 10 kGy-irradiated dried leek samples. As seen in Fig. 3, GC/MS chromatographic profiles of volatile flavor compounds of control and irradiated samples showed the similarity in their constituents. However, quantitative differences in the volatile flavor compounds between non-irradiated and irradiated sample were observed in the present study. The characteristic volatile flavor compounds of irradiated dried leeks were similar to those of non-irradiated samples but the intensities of the peaks for these substances were obviously different in irradiated samples.

The total volatile flavor compounds in non-irradiated dried leeks were approximately 979.37 mg/kg while samples irradiated at 10 kGy yielded only 683.69 mg/kg. The total amount of volatile flavor compounds was decreased after irradiation. The classifications of volatile flavor compounds by functional groups are shown in Table 7. In non-irradiated dried leeks the relative areas obtained for each functional group of volatile flavor compounds were, in descending order: S-containing compounds (97.00%), aldehydes (1.57%), alcohols (0.71%), esters (0.39%), N-containing compounds (0.21%) and miscellaneous compounds (0.12%). In dried leeks irradiated at 10 kGy the relative areas obtained for each functional group of volatile flavor compounds were as follows: S-containing compounds (95.20%), esters (1.65%), aldehydes (1.34%), alcohols (1.08%), N-containing compounds (0.32%), and miscellaneous substances (0.17%).

After irradiation, a few compounds such as 2-ethyl furan, methyl ethyl disulfide, benzaldehyde and dimethyl sulfoxide appeared. However, concentrations of these compounds were extremely low, which did not change the flavor of dried leeks.

Although significant differences in the levels of individual S-containing compounds were detected between non-irradiated and irradiated samples, the total proportion of these compounds was not dramatically changed by irradiation (from 97.00% to 96.20%). However, the relative percentage of esters was increased almost 4-fold (from 0.39% to 1.34%) after irradiation at 10 kGy. Aldehydes as (*E*)-2-hexenal of exception S-containing compounds were large proportion were markedly decreased after irradiation from 11.09 mg/kg to 4.10 mg/kg. This compound was known as a green note, and polyunsaturated fatty acids of principal ingredients in the cell wall were dissolved lipoxygenase and hydroperoxide lyase, a flavor compound of tea leaves and fruits (51, 52)

Most of the other compounds were also similar major S-containing compounds. The individual constituents of the S-containing compounds constituents between control and irradiated sample. Contents of dimethyl disulfide, (*Z*)-propenyl methyl disulfide, methyl allyl disulfide, (*E*)-propenyl methyl disulfide, dimethyl trisulfide, 3-ethyl-1,2-dithi-5-ene, (*Z*)-methyl propenyl trisulfide and (*E*)-methyl propenyl trisulfide before irradiation were 120.33, 38.80, 73.48, 103.44, 314.88, 49.39, 155.15 and 34.07 mg/kg, respectively. After irradiation at 10 kGy, the amounts of dimethyl disulfide (92.67 mg/kg), (*Z*)-propenyl methyl disulfide (30.06 mg/kg), methyl allyl disulfide (43.43 mg/kg), (*E*)-propenyl methyl disulfide (81.84 mg/kg), dimethyl trisulfide (217.63 mg/kg), 3-ethyl-1,2-dithi-5-ene (32.20 mg/kg), (*Z*)-methyl propenyl trisulfide (91.62 mg/kg) and (*E*)-methyl propenyl trisulfide (28.04 mg/kg) (Fig. 7) were

decreased. Yang *et al.* (53) also reported that the amount of S-containing compounds in dried shiitake mushrooms were decreased during irradiation at doses of 1-2 kGy (54). Similar studies on dry shiitake mushrooms that levels of S-containing compounds in non-irradiated mushrooms were considerably higher than in those irradiated at 1-10 kGy. Gyawali *et al.* (55) reported that, S-containing compounds in dried welsh onions were reduced by irradiation at 10 kGy and 20 kGy. However, dimethyl disulfide and dimethyl trisulfide were increased by irradiation at 10 kGy, which is not in accordance with the present study.

According to the previous studies, levels of volatile compounds were increased by an optimal dose of irradiation but decreased by high doses. Woods *et al.* (56) who reported that when molecules absorb ionizing energy they become reactive and form ions or free radicals that react to form stable radiolysis products. Kim *et al.* (57) reported that volatile compounds of salted and fermented anchovy sauce were increased significantly by irradiation at 5 and 7.5 kGy, but were slightly decreased by high doses of irradiation at 10 kGy. The essential oil of black pepper also showed a few changes due to radiation (58). Wu *et al.* (59) noted that diallyl disulfide was decreased after radiation treatment. Diallyl disulfide contributes most of harsh, pungent, and "garlic-like" flavor of garlic (60,61).

On the contrary, Variyar *et al.* (62) noted that no major qualitative or quantitative change was observed in the essential oils of clove and cardamom irradiated at 10 kGy. Chatterjee *et al.* (63) reported that no detectable difference was observed in the aroma impact compounds of the irradiated turmeric.

In conclusion, the levels of S-containing compounds in dried leeks were considerably lowered when irradiated at a dose of 10 kGy. This investigation



indicates that radiation increased the numbers of different volatile compounds in the dried leeks, but decreased the quantities of major volatile compounds.

*Table 7. Comparison of volatile flavor compounds identified in non-irradiated and irradiated dried onion at 10 kGy*

Peak no.	RT <sup>1)</sup>	RI <sup>2)</sup>	Compound name	MF <sup>3)</sup>	MW <sup>4)</sup>	mg/kg	
						0 kGy	10 kGy
1	6.35	813	Ethyl formate	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	74	0.87	3.60
2	6.73	832	2-Propenal	C <sub>3</sub> H <sub>4</sub> O	56	0.05	0.91
3	7.65	874	Ethyl acetate	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88	2.90	7.68
4	9.18	930	Ethanol	C <sub>2</sub> H <sub>6</sub> O	46	2.00	1.34
5	9.66	946	2-Ethyl furan	C <sub>6</sub> H <sub>8</sub> O	96	-	0.15
6	9.78	949	Diallyl methyl sulfide	C <sub>4</sub> H <sub>8</sub> S	88	1.56	1.55
7	10.64	974	Pentanal	C <sub>5</sub> H <sub>10</sub> O	86	0.37	0.10
8	15.21	1073	Dimethyl disulfide	C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>	94	120.33	92.67
9	15.67	1081	n-Hexanal	C <sub>6</sub> H <sub>12</sub> O	100	0.60	0.40
10	17.56	1113	2-Propenol	C <sub>3</sub> H <sub>6</sub> O	58	1.44	3.08
11	18.95	1137	2-Methyl-4-pentenal	C <sub>6</sub> H <sub>10</sub> O	98	0.32	-
12	19.41	1144	Methyl ethyl disulfide	C <sub>3</sub> H <sub>8</sub> S <sub>2</sub>	103	-	0.09
13	20.30	1158	2-Methyl-2-pentenal	C <sub>6</sub> H <sub>10</sub> O	98	0.64	0.58
14	22.06	1184	Pyridine	C <sub>5</sub> H <sub>5</sub> N	79	0.90	0.72
15	23.07	1198	Heptanal	C <sub>7</sub> H <sub>14</sub> O	114	0.76	0.35
16	24.23	1216	( <i>E</i> )-2-Hexenal	C <sub>6</sub> H <sub>10</sub> O	98	11.09	4.10
17	25.17	1231	Methyl propyl disulfide	C <sub>4</sub> H <sub>10</sub> S <sub>2</sub>	122	0.99	0.75
18	26.59	1252	2,4-Dimethylthiophene	C <sub>6</sub> H <sub>8</sub> S	112	0.96	0.97
19	26.74	1254	n-Pentanol	C <sub>5</sub> H <sub>12</sub> O	88	0.21	0.48
20	27.37	1263	( <i>Z</i> )-Propenylmethyl disulfide	C <sub>4</sub> H <sub>8</sub> S <sub>2</sub>	120	38.80	30.06
21	28.57	1280	Methyl allyl disulfide	C <sub>4</sub> H <sub>8</sub> S <sub>2</sub>	120	73.48	43.43
22	29.13	1288	( <i>E</i> )-Propenylmethyl disulfide	C <sub>4</sub> H <sub>8</sub> S <sub>2</sub>	120	103.44	81.84
I.S <sup>5)</sup>	30.77	1311	<b>Butyl benzene</b>	C <sub>10</sub> H <sub>14</sub>	134	-	-
23	35.51	1381	Dimethyl trisulfide	C <sub>2</sub> H <sub>6</sub> S <sub>3</sub>	126	314.88	217.63
24	35.90	1386	( <i>Z</i> )-3-Hexenol	C <sub>6</sub> H <sub>12</sub> O	100	0.56	0.65

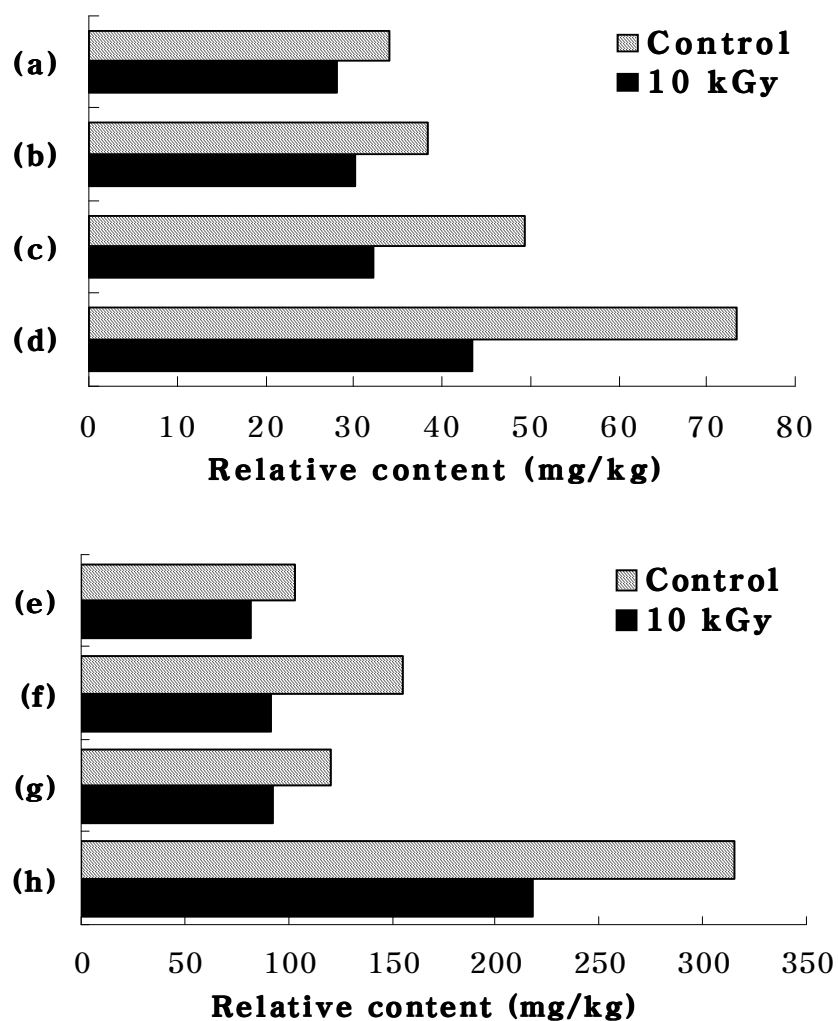
*Table 7. Continued*

Peak no.	RT <sup>1)</sup>	RI <sup>2)</sup>	Compound name	MF <sup>3)</sup>	MW <sup>4)</sup>	mg/kg	
						0 kGy	10 kGy
25	36.33	1392	Nonanal	C <sub>9</sub> H <sub>18</sub> O	142	1.07	0.82
26	38.72	1429	( <i>E</i> )-Propenyl propyl disulfide	C <sub>6</sub> H <sub>12</sub> S <sub>2</sub>	148	0.21	0.60
27	40.36	1455	Methional	C <sub>4</sub> H <sub>8</sub> OS	104	8.30	3.69
28	40.91	1463	Furfural	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	96	0.44	1.39
29	41.14	1466	3-Ethyl-1,2-dithi-4-ene	C <sub>6</sub> H <sub>10</sub> S <sub>2</sub>	146	15.17	9.52
30	42.15	1481	Diallyl disulfide	C <sub>6</sub> H <sub>10</sub> S <sub>2</sub>	146	17.32	8.85
31	42.57	1487	3-Ethyl-1,2-dithi-5-ene	C <sub>6</sub> H <sub>10</sub> S <sub>2</sub>	146	49.39	32.20
32	42.99	1493	2-Ethyl hexanol	C <sub>8</sub> H <sub>18</sub> O	130	0.41	-
33	44.84	1523	Benzaldehyde	C <sub>7</sub> H <sub>6</sub> O	106	-	0.60
34	45.06	1526	N,N-dimethylthioacetamide	C <sub>4</sub> H <sub>9</sub> NS	103	1.14	1.43
35	45.35	1531	Methyl propyl trisulfide	C <sub>4</sub> H <sub>10</sub> S <sub>3</sub>	154	1.06	1.08
36	46.63	1551	Linalool	C <sub>10</sub> H <sub>18</sub> O	154	0.74	0.87
37	48.79	1583	Dimethyl sulfoxide	C <sub>2</sub> H <sub>6</sub> OS	78	-	0.41
38	49.42	1592	( <i>Z</i> )-Methyl propenyl trisulfide	C <sub>4</sub> H <sub>8</sub> S <sub>3</sub>	152	155.15	91.62
39	49.83	1598	( <i>E</i> )-Methyl propenyl trisulfide	C <sub>4</sub> H <sub>8</sub> S <sub>3</sub>	152	34.07	28.04
40	54.48	1675	S-Methyl methylthiosulphonate	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	126	1.19	0.46
41	54.84	1681	2-Butyl-4-methylthiazole	C <sub>8</sub> H <sub>13</sub> NS	155	0.34	-
42	55.35	1689	Cyclohexyl methyl sulfide	C <sub>7</sub> H <sub>14</sub> S	130	3.83	2.81
43	61.08	1792	Diallyl trisulfide	C <sub>6</sub> H <sub>10</sub> S <sub>3</sub>	178	9.62	4.23
44	62.92	1832	Hexanoic acid	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	116	1.18	1.01
45	68.70	1975	1-Phenyl-1-butanol	C <sub>10</sub> H <sub>14</sub> O	150	1.59	0.93
Total						979.37	683.69

R.T.<sup>1)</sup>:Retention time, R.I.<sup>2)</sup>:Retention index, M.F.<sup>3)</sup>:Molecule formula, M.W.<sup>4)</sup>:Molecule weight, I.S.<sup>5)</sup>: Internal standard.

*Table 8. Relative content of functional groups in identified volatile components in non-irradiated and irradiated dried leek at 10 kGy*

<i>Functional group</i>	<i>Relative Peak area (%)</i>			
	<i>0</i>		<i>10</i>	
	<i>Number</i>	<i>Area(%)</i>	<i>Number</i>	<i>Area(%)</i>
Alcohols	7	0.71	6	1.08
Aldehydes	9	1.57	9	1.34
Esters	2	0.39	2	1.65
S-containing compounds	20	97.00	21	95.20
N-containing compounds	2	0.21	2	0.32
Miscellaneous	1	0.12	2	0.17
<i>Total</i>	<i>41</i>	<i>100</i>	<i>43</i>	<i>100</i>



*Fig. 7. Comparison of radiation on major S-containing compounds in dried leek.*

*(a) (E)-methyl propenyl trisulfide, (b) (Z)-propenyl methyl disulfide, (c) 3-ethyl-1,2-dithi-5-ene, (d) methyl allyl disulfide, (e) (E)-propenyl methyl disulfide, (f) (Z)-methyl propenyl trisulfide, (g) Dimethyl disulfide, (h) dimethyl trisulfide.*

## IV

### CONCLUSION

The total content volatile compound dried leeks was decreased after irradiation at 10 kGy in comparison with control. Although significant differences in the contents of S-containing compounds between non-irradiated and irradiated dried leeks were detected, the proportion of these compounds in the total volatile flavor compounds was not dramatically changed after irradiation. S-containing compounds were found as dominant compounds in both samples but their amounts were decreased after  $\gamma$ -irradiation. Among S-compounds, dimethyl disulfide, (*Z*)-propenyl methyl disulfide, methyl allyl disulfide, (*E*)-propenyl methyl disulfide, dimethyl trisulfide, 3-ethyl-1,2-dithi-5-ene, (*Z*)-methyl propenyl trisulfide and (*E*)-methyl propenyl trisulfide were dramatically decreased as by 10 kGy irradiation. An aldehyde compound, (*E*)-2-hexenal, was highly effected to other members of aldehyde and decreased from 11.09 mg/kg to 4.10 mg/kg at 10 kGy, which the same pattern with S-containing compound. The content of the S-containing compounds in dried leeks without irradiation was considerably higher than that of irradiated at 10 kGy. This investigation indicates that the numbers of volatile compounds in the irradiated dried leeks were increased after irradiation. The quantities of the major volatile compounds were decreased by irradiation.

## V

### 요 약

본 연구는 방사선 조사에 의한 건부추의 휘발성 유기성분의 변화를 관찰하기 위하여 수행되었다. 건부추를 10 kGy의 선량으로 조사하고 조사하지 않은 건부추를 control로 하여 SDE방법으로 유기성분을 추출한 후 정유를 GC/MS로 분석하였다. 비조사 시료와 조사시료에서 각각 41종, 42종의 화합물이 분리 동정되었으며, alcohol류, aldehyde류, ester류, 함황화합물, 함질소화합물을 포함하고 있는 것이 확인되었다. 조사된 부추에 함유된 특징적인 휘발성 유기성분은 조사되지 않은 부추에서의 결과와 유사하였으나, 그 농도에 있어서는 눈에 띄는 차이를 보였다. 두 시료 모두에서 함황화합물이 다량 검출되어 주요 화합물임을 알 수 있었으며, 성분들 중에서 다량의 dimethyl trisulfide, (*Z*)-methyl propenyl trisulfide 및 dimethyl disulfide가 함황화합물의 상대적 농도에 크게 기여하는 것으로 확인되었다. 그 외 (*E*)-propenyl methyl disulfide, methyl allyl disulfide, (*Z*)-propenyl methyl disulfide, 3-ethyl-1,2-dithi-5-ene, (*Z*)-methyl propenyl trisulfide와 (*E*)-methyl propenyl trisulfide도 휘발성 유기성분의 조성에 큰 비중을 차지하였다. 이들 주요 함황화합물들은 10 kGy로 조사된 후 그 함량이 크게 감소된 것이 확인 되었으며, 함황화합물을 제외한 화합물중 가장 많은 양을 차지한 (*E*)-2-hexanal 역시 조사 후 그 양이 현저히 감소함을 보였다. 본 연구는 건부추에 대한 방사선 조사가 휘발성 향기성분에 미치는 영향을 확인하기 위해 수행되었으며, 방사선 조사된 후 총 함량 및 주된 화합물인 함황화합물들이 상당량 감소됨을 확인하였다. 본 연구의 결과는 감마선 조사에 의한 건조 향신료의 그 영향을 보여주고 있으며, 현재 활발히 진행되고 있는 감마선 조사식품에 대한 여러 연구들에 대한 기초 자료로 활용될 수 있을 것으로 판단된다.

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