

## Study of Selenium Compound in Favorite Korean Foodstuffs.

by

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### 한국 식품중의 Se 화합물의 함량에 관한 연구

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#### Abstract

Garlic and traditional favorite foodstuffs of plant origin have been analyzed for selenium and sulfur containing amino acid content selenium compound were assayed using a  $^{77m}\text{Se}$  neutron activation analysis, cystine and methionine determination by paper and thin-layer chromatography. The results obtained indicate that the content of selenium and sulfur containing amino acid are highest in garlic. The results also show that the selenium is a more abundant in particular species such as garlics produced in Tan Yang and Wei Sung. The effect of Korean garlic and favorite typically found in the Korean diet has also been studied. Some vegetables known to contain a relatively high level of sulfur and selenium (garlic and onion) do lose significant quantities of selenium as a result of cooking.

#### Introduction

Recent work has shown that the element also have beneficial nutritional effects when present in the diet in trace amount.<sup>(1-4)</sup> The role selenium play a sole of in the biochemistry of higher animal is complex and as yet ill-defined. Increasing evidence that the metabolic role of selenium is for more complex that of a simple periodic relative of sulfur<sup>(5)</sup>. Selenium has been proposed as an essential element in human blood<sup>(6)</sup> and as a placement or adjust to vitamin E.<sup>(7)</sup> Aside from preventing a number of diseases in various animal.<sup>(8)</sup> Garlic, known botanically as *allium* (*sativum*, L.) is used a food, but also as a popular remedy. Its importance had already been recognized, and in ancient Korea. It was regarded as one of the most

treasured foodstuffs and medicinal agent. Until now do detailed studies have been carried out on the constituents of garlic. Recently, Gominato<sup>(9)</sup> have reported the isolation of *allium acoroboprosom* L, from garlic. The inhabitants of ancient Korea attributed a curative action to garlic in numerous disease, such as hemorrhoids, rheumatism, dermatitis, abdominal pain, cough, loss of appetite, and loss of weight.<sup>(10)</sup> Lonicerus<sup>(11)</sup> emphasized the antitoxic properties of garlic, which a having been recognized its value against intestinal worms. That garlic possess an antibacterial action had already been noticed in the early days. Even the enzymes present in garlic<sup>(10)</sup> have been held to exert antibacterial actions. This author<sup>(12)</sup> has also drawn attention to the antibacterial action of allicin against acid-fast bacterial. Most plants obtain their supplies of sulphur

from the sulphate, present in the soil. They transform it into organic compounds which ensures the supply of sulphur-containing amino acid needed by higher animals. It is mentioned that during the chromatographic separation of individual amino a considerable oxidation occurs. (13) Selenium analogues of the common sulphur amino acids are more unstable, consequently separation methods involving the use of mild solvent systems must be employed. (14)

The determinations of were achieved cystine and methionine determination by paper and thin-layer chromatography. (14-15) Gamma spectrometry for determination of radionuclidic purity, of sulfur amino acid was analyzed as described by spackman. (16) In view of the previous report the author (17) has become interested in possible relationships, between selenium content of certain favorite food-stuffs in this country and their acceptance. This study may lead to a better use of garlic. It may also give useful information on the structural features of garlic in selenium content. Selenium, in particular, organic selenium in plants known sometimes as seleniferous vegetation in addition to loss transformation of already known odor us substance such as allyl sulfides namely; allicine. (18-21) Past investigations have shown that normal selenium levels range from 0.005 to 0.5 ppm in animal tissues and from 0.005 to 50 ppm in plants. (22-23) Thus, for effective study on its biological activity and possible food-chain concentrations, analytical procedures must be used which have a sensitivity of less than  $10^{-9}$  gram total selenium and which maintain a higher degree of accuracy. A non-destructive technique where the sample was irradiated and counted directly after an appropriate decay period (24) or the selenium was separated in a radiochemically pure form after irradiation and counted. (25) Relatively few analytical techniques fulfill both criteria of sensitivity and accuracy for the determination of selenium in biological and environmental samples. The literature which deal with the selenium content of human food (26-27) is not much found. Paper attention was called to the fact that cooked or processed foods tended to contain less selenium than raw foods. The propose of the prestant study was to investigate the influence of various cooking and heating treatments on the selenium content of some foodstuffs typically found in the Korean garlic and favorite foodstuffs.

## Experimental method

### 1. Sample

Sample (garlic, onion, welsch, playcodon and water leek) were purchased from local food stores in Seoul. Garlic (*Allium Sativum*) were obtained from Tan Yang and Wei Sung agricultural products. The specimens subjected in the study were collected directly from two cultivated areas with the survey of selenium and sulfur which had been applied to the area of previous time. Precautions in sampling were taken as described previously. (17) The various heating and cooking treatments are described in the tables I. Two series of experiments for onions and garlic were performed during the years 1969~1971.

### 2. Experimental condition

Each sample was transferred to a beaker and dried at 50~70°C in a dry oven. Drying of sample was continued until no further moisture could be driven off at the temperature used. Approximately one gram sample were taken from four different kinds of matrices:

The samples of garlic used in this used were as followings:

- |                     |                                |
|---------------------|--------------------------------|
| Cultivated district | 1. Tan Yang (Korea)            |
|                     | 2. Wei Sung (Korea)            |
| Species             | 1. Brand A (Yok-Chok garlic)   |
|                     | 2. Brand B (Shoen-Chok garlic) |
|                     | 3. Brand C (Chang Son garlic)  |

Table I. Dry Condition

Instruments	Temperature	During
Dry oven	70°C	25 min
Ultra-violet	70°C	3 hr
Beaker	100°C	15 min in water Heating

The selenium content of a particular raw or treated sample were analysed by neutron activation analysis.

(17, 22, 25)

- 1) Reagent : Standard solutions were made by dissolving a weighted quantity of high-purity sodium selenite and elemental selenium in concentrated high-purity nitric acid and diluting to volume with distilled water. The selenium concentration used was 0.50 mg/ml, which was dilute enough to prevent any significant neutron self absorption, the sample and

standard was made comparing the selenium standards with the save sample matrix, contained 1  $\mu\text{g}$  of se/sodium selenite.

- 2) Procedure: For analysis, 0.5 gram sample were encapsulated in cleaned polyethylene vial. Standard solution were encapsulated in the like manner. For rapid operation we used pneumatic rabbit system, and quick-opening rabbit irradiation of short duration, with internal delay between and end of irradiation and the start of the sample. The irradiation were carried out in the pneumatic rabbit system of Triga Mark II reactor at thermal neutron flux of approximately  $3.8 \times 10^{-12}\text{n cm}^{-2}\text{ sec}$  The optimal time was 0.3 min for irradiation. monitors, were not used, as the radical flux variation is less  $\pm 2\%$ . (28)
- 3) Measuring procedure: Time necessary for preparation of vital 0.3 min irradiation is 0.2 min, for handling is 0.2min: for cooling is 0.3 min for life-time measuring is 0.3 min and finally 0.2 min is for spectra subtracion.
- 4) Counting conditions: To eliminate the critical influence of the short half-life each sample was counted using (NaI) detector and 100-channel pulse hight analyzer. The specific activity at the end of the irradiation was compared to the sample for quantitative results.

#### 4. Method of analysis for sulfur amino acid Methionine and cystine

Methionine and cystine were determined as methionine sulfone and cysteic acid, respectively, by the following procedure. (15-16) To approximately 100 mg of sample in a 50 ml coinal flask was added 5 ml of freshly prepared performic acid. (29) After allowing the flasks to set at 0°C for 16 hour, the performic acid was removed by evaporation on a steam bath, for 2 hour. To the day residue was added 5 ml of 20% hydrochloric acid, the suspension was autoclaved at 120°C for 6 hour. (30) The hydrochloric acid was removed by evaporation on a steam bath, the residue dissolved in 5 ml of water, and again reduced to dryness. The latter step was repeated at least once more in order to eliminate completely the hydrochloric acid. The residue was dissolved in 25 ml of pH 2 buffer, filtered, and 0.5 ml of the filtrate was subjected to amino acid analysis as described by Spackman. (16) The hydrochloric acid was removed by repeated concentration in a rotary evaporator and the hydrolysate was finally made up

to a known volume with 10% isopropyl alcohol. Cystine and methionine were determined by the paper chromatography technique. For simple and rapid determination of amino acid, the automatic amino acid analyzer was used.

1) Paper chromatography: It was reported that some sulfur or selenium contained amino acid decompose via oxidation in the process of paper chromatography. (14) However, when  $^{75}\text{Se}$  and  $^{35}\text{S}$ -labelled amino acids were chromatographed on paper with solvent (n-butanol acetic acid water) only slight decomposition observed in present work. A series of experiments were carried out using the following methods: paper chromatography of cystine, methionine (Whatman No. 1) with the solvent system:

(a) n-Butanol-acetic acid-water=60 : 15 : 25 (ascending) volume of 10, 20 and 30  $\mu\text{l}$  of labelled amino acid solutions were pipetted in some cases carrier was also added.

2) Thin-Layer chromatography : Thin-layer chromatography on silica gel plates with the solvent systems:

(a) Ethanol-water=70 : 30

(b) Isopropanol-butanol-water=20 : 60 : 20

(c) n-butanol-acetic acid-water=60 : 20 : 20

Samples from a freshly prepared solution of methionine and cystine were pipetted on thin layer chromatoplate and dried in air for 10 min.

3) Sulfur 35 radioactivity counting: Radioactivity counting for all samples was made with Geiger-Muller counting. The background counts were an average of 20 counts per minute. (c.p.m.) Correction for background counts was made for all data obtained.

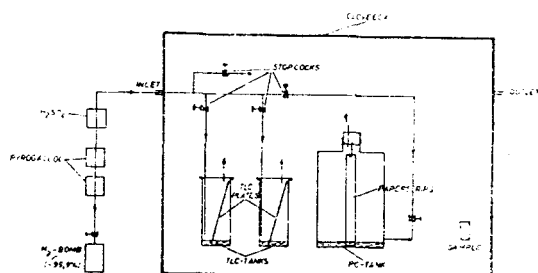


Fig. 1. Working scheme in inert atmosphere.

All operations (pipetting, drying, developing) for

paper and thin-layer chromatography were performed and inert atmosphere of nitrogen.(Fig.1) In parallel, the same samples of L-selenomethionine-<sup>75</sup>Se were handled and developed in air. To prevent any oxidation due to the presence of air, only solvents re-distilled in vacuum and stored. Under nitrogen atmosphere showed that no difference in quality was observed.

### Result

A study on the accuracy of the method was made by analyzing solution of various concentrations of selenium. Radioactivity of selenium standard in some experimental conditions are described in the literature previously reported.<sup>(17)</sup> The results of analysis of selenium in garlic samples are given in Table II. The following table shows the selenium contents in garlic of excellent species grown in the districts of Tan Yang and Wui Sung. The garlic grown in Tan Yang district contains the most amounts of selenium in Korea, showing 0.30  $\mu\text{g}$  more amounts of selenium comparing that in the

Table 2. Comparison of the content of selenium in Korean garlic fresh samples without peel

Sample	Dan-yang products $\mu\text{g se/g}$	wiu-sung products $\mu\text{g Se/g}$	Frenchs garlic(us) $\mu\text{g se/g}$	salt Garlic Fresh(us) $\mu\text{g se/g}$
1.	0.97	0.72		
2.	1.32	0.78		
3.	1.21	0.84		
4.	1.80	0.92		
5.	1.52	0.83		
6.	0.95	0.84		
7.	0.87	0.73		
Average	1.07	0.80	0.02	0.14-0.276

Table 3. Comparison of the content of selenium in Korean garlic species

	Brand A $\mu\text{g Se/g}$	Brand B $\mu\text{g Se/g}$	Brand C $\mu\text{g Se/g}$
1.	0.54	0.51	0.48
2.	0.57	0.53	0.45
3.	0.50	0.48	0.42
4.	0.60	0.46	0.43
5.	0.55	0.50	0.41
Average	0.55	0.49	0.44

garlic grown in Wui Sung district. It seems that the different contents of selenium in garlic is resulted from the difference of soil composition. Further, the difference in selenium contents in garlic between the home produced and the America produced may be resulted from the difference of species, soil composition and the method of cultivation. The interesting observation has been made that the nature and quantity of the components present in garlic vary with the district in which it grows and the character of the soil. It is relationships of the geology and kind of soil formation to the concentration and plant availability of selenium in soils.<sup>(31-42)</sup> There is no doubt that wide variations selenium in plant may be influenced partly by soil composition. Local variation in the selenium content of the diet due to geological factors, especially in light of the recent report of ullrey,<sup>(33)</sup> who found a significant linear correlation between the selenium content of foodstuff and the soil compositions.

The analytical data of selenium contents in garlic of different species but grown in the same area, the author has confirmed that the brand A garlic contains ca. 0.12  $\mu\text{g}$  more selenium than that of brand C garlic. This fact strongly suggests that the contents and the composition of garlic are varied with the species.

The experimental data shows the selenium contents is higher in garlic than other foodstuffs. To verify the relationship between the selenium contents in garlic and the contents of sulfur containing amino acid, some experiment is carried out comparing its contents with other foodstuffs. One variation in the Hoffman<sup>(34)</sup> procedure was necessary when the food sample being assayed contained more than 0.05 se  $\mu\text{g}/\text{gram}$ . Some of the root vegetables contained considerably higher values ranging from 0.015 se  $\mu\text{g}/\text{g}$  for white onion to 0.249 se  $\mu\text{g}/\text{g}$  for garlic. It is interesting that garlic had the highest selenium content of the vegetables assayed. It has been noted that certain selenium compounds have a garlic-like smell.<sup>(34-37)</sup> This could be due to differences in the geographical origin of the samples. Environmental factors, which have been reviewed extensively<sup>(25-26)</sup> may cause the selenium concentrations in foods from different geographical areas to vary widely. The most important factor is the selenium content of the soil. This is due to the volatilization of the selenium during the drying process. Therefore,

both the effects of processing and geographical location much be considered. Thompson<sup>(38)</sup> have shown that 0.04 to 0.10 ppm selenium are needed in the diet to prevent selenium deficiency in chickens depend the vitamin E content of the diet. There is also the possibility that different selenium compounds are present and that more than one type of association, possibly to different proteins, may exist.

Table 4. Selenium contents in some traditional favorite Korean food-stuffs

Sample	$\mu\text{g Se/g.}$
1. Garlic (savitum)	0.582-4.25
2. Onion	0.373-1.25
3. Welsh onion (a stone-leek)	0.301
4. Allium: (monanthum)	0.150
5. Water leek	0.105
6. Ginger. (candied)	0.062
7. Platycodon	0.121
8. Ginseng	0.113

Result are expressed on a dry weight basis<sup>(26)</sup> in order to provide a common among the various treatment. It is considered that the degree of garlic is proportional to the contents of selenium, because garlic contains more selenium than onion. It is further considered that degree of fragrant odor and stimulating power is direct

evidence of selenium contents in species such as garlic, onion, welsch and water leek. The selenium contents in the fresh garlic was found to 0.87 ppm, but ca. 0.45 ppm of selenium was diminished when heated the fresh garlic at 70°C for 20 min. Thereupon, it is believed that the fragrant order of the garlic is proportionally decreased with the decrease of selenium contents. It was also confirmed that the selenium contents was decreased to 1/3~1/2 of the original amounts in cause of heating onion or welsch at 100°C for 15 min. Except the cause of heating in water, the loss of the contents of selenium in the root of chinese ballon flower (platycodon) and the parsley was small comparing these in the others. The present work was undertaken to investigate the composition of garlic. Although, selenium and sulfur amino acid components of garlic was among the constituents, in present work, more emphasis was placed on sulfur-amino acid. The investigation was carried out to determine the cystine and methionine content of garlic and onion. Since data on the amino acid content and biological value are commonly used to assess nutritive quality of the protein foods. From the same table it can be seen that garlic are rich source for the sulfur containing amino acid. It is interesting to note from these finding that there are a loss of selenium counting amino acid in diet.

Table 5. Results from analysis of selenium in favorite foodstuffs

Sample	Garlic	Onion	Welsh	Platycoden	Water Leek
1. Control.(Fresh samples without peel)	0.78	0.45	0.36	0.135	0.123
2. Dry oven 70°C-25 min, dry	0.54	0.26	0.18	0.123	0.098
3. U. V. lamp. 70°C-3hr, dry	0.51	0.20	0.11	0.119	0.073
4. Water 100°C-15min, heating	0.41	0.31	0.09	0.09	0.065

Ewan<sup>(39)</sup> has also reported that corn dried at 93°C lost about 11% of its selenium after 20 min of boiling, garlic lost 35% of its selenium where as onion lost 40% of the selenium originally present. Challenger<sup>(40)</sup> found that asparagized ethanolic of *asparagus tip* yielded dimethyl sulfid after boiling in alkali. The results obtained with boiling, are some what at variance with those of Heinrich<sup>(41)</sup> The two investigators found that 10 to 25% of selenium was lost from various tissue after drying. Selenium is known to occur in different from in various plant depending upon whether the plant is a selenium "accumulor" or a nonaccumula

tor<sup>(42)</sup> Selenium is rather tightly bound in the protein, where as in the onion selenium occur as relatively unstable free selenium compounds that are easily lost upon heating or cooking. This interest was further depend in the light of the fact that, for example, when garlic is treated with heat and moisture, a traditional way of preparation for consumption, it losses its unique taste: It becomes loss hot than the untreated. Since certain foodstuffs commonly consumed as condiment rather than as a more nutrient source it is conceived that lose of unique taste by cooking may be related to volatilization of certain elements. However, from the

view point that allyl sulfides have been employed as toxic substance the author confined the present experiment to that of selenium determination in seleniferous vegetable and its loss upon heat treatment.

**Table 6. Content of cystine and methionine in favorite foodstuffs**

	cystine $\mu\text{g/g}$	methionine $\mu\text{g/g}$
1. Garlic	2.4	2.6
2. Onion	1.8	1.2
3. Welsh onion	1.5	1.2
4. Allium	1.3	1.1
5. Water leek	1.1	0.7
6. Ginger	1.4	0.9
7. Platycodon	1.3	0.8

**Table 8. Analysis result for nutrition value in Garlic and meat**

Foodstuffs species	Calori	Water	Protein	Lipid	Sugar	Ca	Fe	Axerophthol	Thiamine	Riboflavin	Ascorbic acid	Nicin
	Cal	g	g	g	g	mg	mg	IU	mg	mg	mg	mg
Garlic	145	68.4	3.0	9.2	3.2	90	3.0	50	0.33	0.13	20	0.4
Meat	130	72.9	20.9	5.7	5.7	6	1.6	10	0.06	0.08	2	5.0

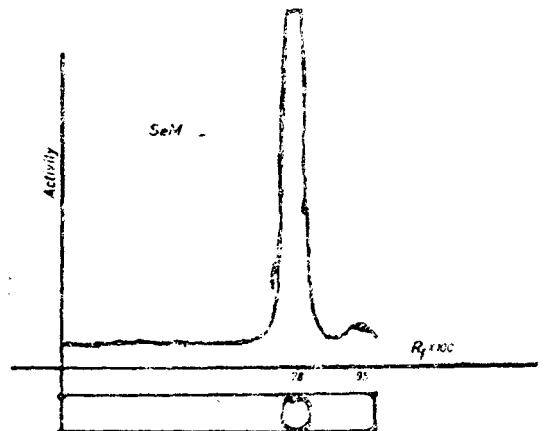
The above tables shows the data obtained for the garlic and most in view of nutrient estimation. It is able to confirm that the garlic contains higher value of nutrient comparing meat showing 2~10 times in contents of lipid, calcium, thiamine, riboflavin and vitamin C. Chromatographic investigation of the acid hydrolysate of garlic indicated the presence of arabinose, xylose, rhamnose, Glucose and galactose or their polymers. Rhamnose formed the major part of the total sugar content. The presence of high amount of rhamnose in the skin of garlic (*Allium cepa*)<sup>(43)</sup> suggests that this sugar may be a characteristic component of allium species. Garlic were also found to contain appreciable amount protein (8.20%). They are thus more promising as a source of proteins than onion which are poor in their content of protein. (0.43%)<sup>(44)</sup>

It may be concluded that the accuracy in the determination of radiochemical purity of methionine and cystine by paper or thin-layer chromatography depends to a great extent on storage and handling in the absence of presence of air because its oxidation leads to the double spotting. This could be interpreted as additional evidence for an anionic combination of selenious radicals to

**Table 7. Content of cystine and methionine in foodstuffs**

	cystine $\mu\text{g/g}$	methionine $\mu\text{g/g}$
1. Rice	0.95	2.1
2. Barley	0.93	1.7
3. Corn	1.82	1.6
4. wheat	4.20	1.4
5. Soybean	0.62	1.2
6. Alfalfa	1.45	0.8
7. Clover	1.65	1.3
8. Potato	0.62	2.3
9. Spinach	1.20	2.1
10. Chlorella	0.90	0.6

the basic ending of other amino-acids. In the chromatography using two solvent(a) and 2(b) Rf, 0.60 and 0.29, was detected respectively. When samples from the same solution were pipetted two days after preparation of the solution and dried for 20 min in air two spots were detected (reaction with ninhydrin) with Rf of 0.6 for solvent 2(b). The second spot with a lower mobility in both cases in due to oxidation products.



**Fig 2. SeM paper chromatogram of L-selenomethionine-<sup>75</sup>Se, first supplier, with carrier(40  $\mu\text{g}$ ), developed in nitrogen atmosphere, solvent 1 (a) redistilled**

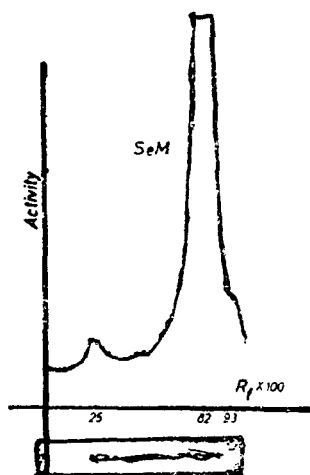


Fig 3. SeM thin-layer chromatogram of L-selenomethionine-<sup>75</sup>Se, first producer, without carrier, developed in nitrogen atmosphere, solvent 2(a). Rf 0.25(6%) and Rf 0.82(92.5%)

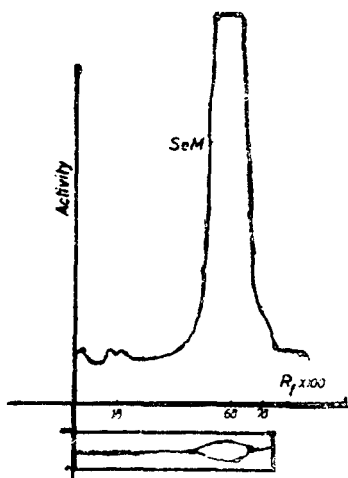


Fig 4. SeM thin-layer chromatogram of L-selenomethionine-<sup>75</sup>Se, first producer, with carrier (15 $\mu$ g), handled and developed in air, solvent 2(a). Rf 0.18(2.5%) and Rf 0.68(96%)

The main types of inorganic and organic sulphur compound have been identified in biological material. Although the function of many of these compounds has yet to be determined, the importance of the sulphur-containing amino acids in biochemical processes is well established. Perhaps a similar difference in the chemical form of selenium exists between vegetable. The procedure is tedious and has exhibited erratic date in replic-

ate analysis of many sample. Increased emphasis on the analysis of trace metal has created the need for more rapid, sensitive and reliable analytic procedures. Trace element in biological materials, may be determined simultaneously.

### Discussion

The importance of selenium in human nutrition is implied from animal studies which show a complex inter-relationship of this mineral with vitamin E. It is also reported that selenium has some behavior of preventing disease caused by the deficient of vitamin E. <sup>(3-4)</sup> Selenium may play an essential role in the synthesis or activation of some the enzymes involved in decarboxylation reaction. <sup>(35-6)</sup> Knowledge and speculation surround biochemistry of selenium. <sup>(45)</sup> Chemically it closely resembles sulfur, is constant contaminant of sulfur compounds and is incorporated into at least six sulfur containing amino acid: cysteine, cystine, methionine, cystathionine, methyl cystine and methyl methionine. <sup>(46)</sup> Together with cystine, methionine and vitamin E selenium compound function in the prevention of certain diseases. <sup>(36-7)</sup> One biological role of selenium appears to be in selenium compound which act as a carrier of vitamin E and effective absorption, protection and transfer of a d- $\alpha$ -tocopherol. <sup>(45)</sup> Studies have also been made of the effect of sulphur compounds on the growth of micro-organisms. <sup>(47)</sup> The amounts required in the diet compared to the requirement for tocopherol are very small. A major function of selenium in animals depend upon the antioxidant activity of some of the selenium compounds. The association of selenium with plant proteins has been thoroughly documented and it is generally believed that the element occurs in the proteins as selenocystine or selenimethionines. <sup>(45)</sup> Some of the metabolic pathways of selenium in plants are shown previously described. <sup>(56)</sup> The clarification of these differences between selenium and sulfur metabolism may provide some interesting tools for biochemical studies of plant genetics <sup>(56)</sup> Hippocrates <sup>(48)</sup> recognized the importance of garlic as a medicinal agent and employed it as a diuretic and emmenagogue and for the treatment of pneumonia and suppuration of wounds. Garlic is still employed today in folk medicine in all parts of the world, both for the prophylaxis and for the cure of a variety of diseases, including acute and chronic infectio

ns gastric and intestinal catarrh, dysentery, typhoid, colera, arteriosclerosis and essential hypertension.

Composition of allin garlic has special fragrant odor and has high nutrient contents but its composition is not precisely. (49) analyzed. It is reported that the garlic contains sulfur containing amino acid and some vaporizable compounds such as allyl sulfide and alicin. The volatile selenium compound in the plants is known to be dimethyl selenide which has a boiling point of 85°C. Important volatile flavor components of onions, garlic have been isolated by methyl disulfide. (51-52) Allin is stable in aqueous solution even at high temperatures. Allin, or S-allyl cysteine sulphoxide, has been isolated from garlic (50) The parent substance of allin is the new, previously unknown amino acid (—)-S-allyl-L-cysteine. Diallyl disulphide occurs in onions and garlic is a breakdown product of the more complex substance alliin. This was thought to be derived from the methyl sulfonium derivative of methionine which occur in cabbage and onion (53) by analogy. We might postulate the formation of the volatile dimethyl selenide from the selenium salt of Se-methyl selenomethionine since this conversion is known to occur in cabbage leaves. (54) The characteristic odor of seleniferous vegetation was probably due to dimethyl selenide. Garlic allicin appears as an intermediate stage in the formation of the more volatile, unpleasant smelling diallyl disulfide in the course of the enzymic cleavage of alliin, a not unpleasant, but typical odor of garlic. The characteristic odor of these plants was due to the release of one or more volatile selenium compounds, although the identity of these compounds has not yet been established. The fragrance of garlic is similar to vaporizable selenium compound. The main cause of its worth as a vigorizing agent for human body is believed to be that it contains some amount of selenium, and there is a direct relationship between the selenium contents and vigorizing action. It is elucidated that there is not any antibiotic action and not any hazardous action on human who intake much amounts of garlic.

Some evidence for selenium antagonist in foodstuffs has been present by Hegue (56) deficiency of this element almost undoubtedly occurs due to a lack of organic sulfur compounds such as cystine and methionine in the diet. The selenium uptake of onions was quite high, and the major portion of the selenium compounds were

water soluble. Beeson (55) has compiled the sources of these plant data and summarized the factors effecting selenium content of plants. When the garlic was heated the characteristic fragrance of the garlic was decreased with selenium contents. Such a phenomenon may be arisen from the volatility of the selenium. Further, the strong volatility of the selenium indicates that the selenium in the garlic is in the form of organo-selenium compounds. It is considered that the garlic plays a role of supplementary supplying of vitamin E and even plays a role of tonic agent to human body. Sulfur-amino acids and some compositions has radiation protective action compared with the other foods. Further, the garlic may play a role of accelerating and aiding the biosynthesis of protein with the unknown trace components in it. Many of the most active forms of selenium (such as sodium selenite) are also the least stable chemically, whereas the relatively inert elemental selenium is essentially without value in alleviating selenium deficiency. Therefore, the total selenium content of foods may not be a valid indicator of their nutritional value. Finally it must be recognized that many selenium compounds are quite volatile and could thus be lost as a result of food cooking processing. The conclusion drawn is that the selenium very probably exists as selenium compounds other than sulphur amino acid. The result in this study indicates that the major sources of selenium in the Korean diet do not lose appreciable amount of selenium in ordinary cooking methods. Some vegetables known to contain relatively high levels of sulfur and selenium (garlic and onion) do lose significant quantities of selenium as a result of cooking.

## 요 약

마늘은 옛부터 정력강장제(精力強壯劑) 및 항균(抗菌) 작용에 효력있는 향신식품으로 구전되어 왔다. 마늘이 정력제의 효력을 나타내는 성분은 미지인바 이를 부분적이라도 밝히고자 하였다.

마늘의 독특한 냄새는 allicin 이의 Se 의 휘발성 냄새에 기인됨을 알았다. Se 는 비타민 E 와 밀접한 관련성이 있으므로 마늘 중에 Se 및 유황 아미노산의 함량을 산지 및 품종별로 분석하였다.

특히 단양, 의성산의 좋은 마늘은 다른 산지의 것보다 Se 의 함량이 훨씬 많았다. 마늘 냄새와 Se 의 함량



은 비례하며 한국산은 외국산보다 Se의 함량이 월등히 많았다. 또 마늘을 요리하는 방법에 따라 Se 손실량이 크게 차이가 있었다.

Se 분석은  $^{75}\text{Se}$ 을 이용한 비파괴 방사화 분석법을 이용하였고 함유량 아미노산은 Label된 Sulfur을 써서 TLC Paper-chromatography로 확인 정량하였다.

### References

- 1) Schwarz, K., and Foltz, C. M. *J. Am. Chem. Soc.*, **79**, 3292 (1957).
- 2) Thompson, J. H. and Scott, M. L. *J. Nutr.*, **100**, 797 (1970).
- 3) Schutte, K. H. *The biology of the trace element: Their role in nutrition.* Crosby Lockwood and Son. Ltd., London (1964).
- 4) Schwarz, K.: *Symposium on nutrition significance of selenium. Fed. Proc.*, **20**, 665 (1961).
- 5) Imbach, A. and Sternberg, J. *Int. J. App. Radiat., and Isotopes*, **18**, 545 (1967),
- 6) Tomilison, R. H. and Dickson, R. C. Proc. 1965 Inter. Conf. modern trend in activation college station. Texas 66, April 19-22 (1965).
- 7) McConnell, K. P. Proc. 1965 Inter. Conf. Modern trend in activation college station. Texas 137: 1, (1961).
- 8) Nesheim, M. C. and Scott, M. L. *Fed. Proc.*, **20**, 674 (1961).
- 9) 小湊 深: 忍辱(大蒜)의 神秘 叢文社(1972).
- 10) Arthus, Stolland and Ewald, Seebeck: *Advance Enzymol*, **11**, 377 (1951).
- 11) Lonicerus.: *Kreuterbuck*, p. 274 (1694).
- 12) Glaser, E. and Drobnil, R. *Arch. expte, pharmkal.*, **193**, 1 (1939).
- 13) Smith, I.: *Chromatographic and electrophoretic techniques* (2nd Ed). Heinemann, London (1960) p. 82.
- 14) Peterson, P. J. and Butler, G. W. *J. Chromatography*, **8**, 70 (1962).
- 15) Jamlian, J. and pellet, P. L.: *J. Sci Fd Agric.*, **19**, 378 (1968).
- 16) Spackman, D.H., Stein, W. H. and Moore, S. *Anal. Chem.*, **30**, 1190 (1958).
- 17) Sea-Yeol Chun.: *Korean J. Food. Sci Technol.*, **4**: 61 (1972).
- 18) Cavillito, J. and Bailey, J. H.: *J. Am. Chem. Soc.*, **67**, 1032 (1945).
- 19) Stoll, A. and Seekbeck, E.: *Helv. Chim. Acta.*, **32**, 197 (1949).
- 20) Stoll, A. and Seebeck, E.: *Experimental*, **3**, 111 (1947).
- 21) Narasimho Rao, P. L. and Verma, S. C. L. *J. Indian Inst. Sci.*, **31**, 315 (1952).
- 22) Allaway, W. H. and Carg, E. E. *Anal. Chem.*, **36**, 1359 (1964).
- 23) Guinn, V. P. L. *Analyse per radioactivation et ses applications aux sciences biologiques D Comar*, D. Presses Universitaires de France, Paris Ed. p. 60.
- 24) Nadkarni, R. A., Ehmann, W.D. and Burdick, D.: *Tobacco Sci.*, **14**, 37 (1970)
- 25) Dams and Hoste, J.: *Anal Chim Acta.*, **41**, 205 (1968).
- 26) Moris, V. C. and Levander, O. A. *J. Nutr.*, **100**, 1383 (1970).
- 27) Lewis, B. G., Hohnson, C. M. and Delwiche, C. C. *J. Agr. Food Chem.*, **14**, 639 (1966).
- 28) Harry L. Rook.: *Anal Chem.*, **44**, 1276 (1972).
- 29) Evans, R. and Bandemer, S. L.: *J. Agr. Food Chem.*, **15**, 439 (1967).
- 30) Schram, E., Moore, S. and Bigwood, E. J.: *Biochem. J.*, **57**, 33 (1954).
- 31) Challenger, F., Lisle, D. B. and Dransfield, B.: *J. Chem Soc P.* 1760(1954)
- 32) 32) underwood, E. J. Trace element in human and animal nutrition 2nd Ed. New York, Academic Press (1962).
- 33) Ullrey, D. E., P. K., Ely, W. T. Grace, A. W. and Miller, E. R. *J. Anim Sci.*, **33**: 240 (1971).
- 34) Hoffman, I. R. J. Westerby and M. Hidioglou.: *J. Ass. Offic Anal Chem.*, **51**, 1039 (1968).
- 35) Rosenfeld, I. and Beath, O. A.: *Selenium-Geobotany, Biochemistry, Toxicity and Nutrition* Academic Press., New York, p. 41-51 (1964).
- 36) Rosenfeld, I. and Beath, O. H.: *Selenium*, New York, Academic Press (1964).
- 37) Hamilton, J. W. and Beath, O. A.: *J. Agr. Food Chem.*, **12**, 371 (1964).
- 38) Thompson, J. N. and M. L. Scott.: *J. Nutr.*, **97**, 335 (1969).
- 39) Ewan, R. C. *J. Anim. Sci.*, **33**, 230 (1970).
- 40) Challenger, F. and Hayward, B. J.: *Biochem.* **58**, iv (1954).

- 41) Heinrich, M., and Kelscy, F. E.: *Fed. Proc.*, **13**, 364 (1954).
- 42) Peterson, D. J. and Butler, G. W.: *Austr. J. Biol. Sci.*, **15**, 126 (1962).
- 43) Lewis, L. A., Quaife, M. L. and Page, I. H.: *Am. J. Physiol.*, **178**, 221 (1954).
- 44) Abdel-Fattah, and A. F. Edress, M.: *J. Sci. Fd Agric.*, **22**, 298 (1971).
- 45) Shrift, A.: *Fed. Proc.*, **20**, 695 (1965).
- 46) H. J. M. Bowen.: *Trace element in biochemistry*, New York, Academic Press (1966).
- 47) Desai, I. D. and Scott M. L.: *Arch. Biochem., Biophys.* **100**, 309 (1965).
- 48) Hipocrates Fuchs *Santl, Werke*.
- 49) Leslie Young and George A. MAW.: *The metabolism of sulfur compound* John Wiely & Son. Inc (1958).
- 50) Hugue, D. E.: *Proc. Cornell Nutr. Conf.*, p. 32 (1958).
- 51) Lewis, B. G., Johnson, C. M. and Delwiche, C. C.: *J. Agr. Food Chem.*, **14**, 638 (1966).
- 52) Muth, O. H., Oldfield, J. E., Weswig, P. H.: *Symposium, Selenium in Biomedicine*, p. 283, AVI Pub. Co. (1967).
- 53) McRorie, R. A., Sutherland, G. L., Lewis, M. S. and Barton, A. D.: *J. Am. Chem. Soc.*, **76** : 115 (1954).
- 54) Lewis, B. G., Johnson, C. M. and Broyer. T.C. *Biochim, Biophys. Acta.*, **237**, 603 (1971).
- 55) Beeson, K. C.: *U. S. Dept. Agr., Hand-book*, 296 (1965).
- 56) Virupaksha, T. K. and Shrift, A.: *Biochim Biophy Acta.*, **107**, 69 (1965).