INFLUENCE OF SOME METALLIC IONS UPON VITAMINS IN FOODS

II. EFFECT OF METALLIC IONS ON THE CONTENT OF VITAMIN C IN RADISH

By

Tae GOTÔ and Masako ARII

Department of Living Science, Faculty of Agriculture, Tohoku University, Sendai, Japan

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The senior author (1) has some time ago reported that a remarkably large quantity of metals is dissolved into cooking water from metallic utensils during cooking. It naturally comes to mind that such dissolved metals might affect vitamins in foods. In the present series of experiments, the effect of such metals on vitamin C in Japanese radish (*Raphanus sativus* L. var. *acanthiformis* Makino) was examined and the results obtained are reported herein.

Experimental

1. Methods

(1) Preparation of the Sample: Ripe Japanese radish root was cut lengthwise into four, one-quarter section was again cut lenghtwise into eight and each cut into triangular shaped slices of 2 mm in thickness. After mixing thoroughly, 10 g of the slices were taken as the sample.

(2) Treatment of the Sample: The fresh samples were treated in three ways: Boiled in water, boiled in water with metallic ions added, and soaked in an aqueous solution containing metallic ions. After these treatments, the amounts of total vitamin C, reducing-type vitamin C, dehydroascorbic acid, and diketoguronic acid were determined, and by comparing such results, effect of metallic ions was observed. Boiling and soaking were carried out in a beaker made of hard glass with 100 cc of distilled water.

As sources of metallic ions, metallic salt solutions such as ammonium ferric sulfate, potassium alum, copper sulfate, zinc chloride, cobalt chloride, and manganese sulfate were used. Concentration of each solution was so adjusted that 1 mg of the metal ion was contained in 100 cc of the solution, which approximates the concentration of metal ions found in cooking water. Both boiling and soaking were carried out during a 5-minute period.

(3) Determination of Vitamin C: Determination of vitamin C followed the method of Roe (2, 3, 4. 5), which uses 2,4-dinitrophenylhydrazine, measuring

the amount of total vitamin C, and the reducing and oxidizing types, and the oxidizing type was determined as dehydroascorbic acid and diketoguronic acid.

Experimental results were submitted to the analysis of variance on E value obtained from Pulfrich's photometer and the values are indicated in the table only in the significant cases.

2. Experimental Results

(1) Content of Vitamin C in Japanese Radish: Samples were obtained from fresh radish immediately after harvesting, and from those stored (buried under soil) for 2, 4, and 5 months. As shown in Table 1, the amount of total vitamin C is the largest in the fresh root, gradually decreasing with passage of time, and the value after five months' storage is about 50 % of the original. The decrease of the reducing type was the most responsible for this decrease and there was observed no definite relationship between the content of the oxidizing type and duration of storage.

Table 1. Vitamin C content in 10 g of Japanese radish

	Total vitamin C (γ)	Reducing type		Oxidizing type		Dehydro-ascorbic acid		Diketoguronic acid		Remarks
		Content (γ)	%	Content (γ)	%	Content (γ)	%	Content (γ)	%	
A	2780±14	2516±30	90.5	263±4	9.5	182±11	6.6	80±10	2.9	Harvest march, analyzed march
B	2334±13	2110±22	90.4	226±8	9.6	71± 7	3.0	155± 4	6.6	Harvest oct. analyzed dec.
C	1441± 8	1262±16	87.6	179±5	12.4	130± 4	9.0	49± 4	3.4	Harvest oct. analyzed next year feb.
D	1844±10	1615±20	87.6	229±7	12.4	98±12	5.3	131± 8	7.1	Harvest oct. analyzed next year feb.
E	1232±10	1010±18	81.9	222±4	18.1	150± 5	12.3	72± 5	5.8	Harvest oct. analyzed nnext year march
F	1505± 7	1172±12	77.9	332±5	22.1	216± 2	14.3	118± 8	7.8	Harvest oct. analyzed next year march

Percentage signifies percentage against total Vitamin C.

Table 2. Effect of cobalt ion on vitamin C content in Japanese radish

V. C	Content in fresh sampl (γ/10 g)	Diff. in content of fresh sample and boiled sample in water (γ/10g)	Diff. in content of fresh sample and boiled sample in water contg. Co(γ/10g)	Diff. in content of sample boiled in water and boied in water contg. Co (γ/10g)	Diff. in content of fresh sample and soaked sample in water contg. Co (γ/10g)
Diketoguronic acid	56± 4	32± 6	28± 6	—	—
Dehydroascorbic acid	130± 4	70± 6	72± 6	—	25± 6
Oxidizing type	179± 5	102± 7	100± 7	—	26± 7
Reducing type	1262±16	713±22	737±22	—	181±22
Total vitamin C	1441± 8	9815±11	836±11	—	208±11

Sample used is sample C in Table 1.
The time for boiling or soaking is 5 min. respectively.

Table 3. Effect of manganese ion on vitamin C content in Japanese radish

V.C	Content in fresh sample (γ/10 g)	Diff. in content of fresh sample and sample boiled in water (γ/10g)	Diff. in content of fresh sample and sample boiled in water contg. Mn (γ/10g)	Diff. in content of boiled in water and sample boiled in water contg. Mn (γ/10g)	Diff. in content of fresh sample and soaked sample in water contg. Mn (γ/10g)
Deketoguronic acid	118± 8	58±12	61±12	—	—
Dehydroascorbic acid	216± 2	133± 2	127± 2	−6±2	13± 2
Oxidizing	332± 5	190± 7	188± 7	—	26± 7
Reducing type	1172±12	767±16	786±16	—	136±16
Total vitamin C	1505± 7	960±10	984±10	—	163±10

Sample used is sample F in Table 1.

The time for boiling or soaking is 5 min. resprectively.

Table 4. Effect of aluminum ion on vitamin C content in Japanese radish

V.C	Content in fresh sample (γ/10 g)	Diff. in content of fresh sample and sample boiled in water (γ/10g)	Diff. in content of fresh sample and sample boiled in water contg. Al (γ/10g)	Diff. in content of boiled in water and sample boiled in water contg. Al (γ/10g)	Diff. in content of fresh sample and soaked sample in water contg. Al (γ/10g)
Diketoguronic acid	80±10	−35±13	—	—	—
Dehydroascorbic acid	182±11	157±15	145±15	—	—
Oxidizing	263± 4	122± 5	122± 5	—	12± 5
Reducing type	2516±30	1517±41	1531±41	—	251±41
Total vitamin C	2780±14	1642±20	1655±20	—	264±20

Sample used is sample A in Table 1.

The time for foiling or soaking is 5 min. respectively.

(2) Effect of Metal Ions on Vitamin C: The metals tested were cobalt, manganese, aluminum, zinc, iron, and copper. In the case of Co, Mn, and Al, as shown in Tables 2 to 4, the amount of total vitamin C, reducing and oxidizing types, all decreased by boiling with water, boiling with water added with metal ion, and soaking in water added with metal ion, as compared to the fresh vegetable. This decrease is assumed to be due to the decomposition and solution of vitamin C in radish. In the case of soaking in water with metal ions added, the total loss of vitamin C and reducing type was only 1/4 to 1/5 of that by boiling.

Since the decrease of vitamin C is approximately the same in boiling with water and with water added with metal ions, the effect of these metallic ions on the loss of vitamin C may be regarded as practically nil.

The oxidizing types, dehydroascorbic acid and diketoguronic acid, was decreased to some extent in boiling but diketoguronic acid did not decrease in the case of soaking in water containing the metal ions.

There seemed to be no mrked effect of Zn and Fe on the loss of vitamin C in all cases. (cf. Tables 5 and 6).

Table 5. Effect of zinc ion on vitamin C content in Japanese radish

V.C.	Content in fresh sample (γ/10g)	Diff. in content of fresh sample and sample boiled in water (γ/10g)	Diff. in content of fresh sample and sample boiled in water contg. Zn (γ/10g)	Diff. in content of boiled in water and sample boiled in water contg. Zn (γ/10g)
Diketoguronic acid	72± 5	44± 7	46± 7	—
Dehydroascorbic acid	150± 5	82± 8	88± 8	—
Oxidizing type	222± 4	126± 5	134± 5	—
Reducing type	1010±18	714±23	703±23	—
Total vitamin C	1232±10	841±14	841±14	—

Sample used is sample E in Table 1.
The time for boiling or soaking is 5 min. respectively.

Table 6. fffect of Ferric ion on vitamin C content in Japanese radish

V.C	Content in fresh Sample (γ/10g)	Diff. in content of fresh sample and sample boiled in water (γ/10g)	Diff. in content of fresh sample and sample boild in water contg. Fe (γ/10g)	Diff. in content of boiled in water and sample boiled in water contg. Fe (γ/10g)	Diff. in content of fresh sample and soaked sample in water contg. Fe (γ/10g)
Diketoguronic acid	155± 4	85±5	72± 5	—	35± 5
Dehydroascorbic acid	71± 7	—	—	—	—
Oxidizing type	226± 8	106±11	94±11	—	—
Reducing type	2110±22	1330±30	1339±30	—	275±30
Total vitamin C	2334±13	1430±18	1430±80	—	293±18

Sample used is sample B in Table 1.
The time for boiling or soaking is 5 min. respectively.

The behavior of Cu ion was somewhat peculiar, as shown in Table 7. The decrease of total and reducing-type vitamin C was clearly greater when boiled in water with metal ion added than by simply boiling in water, indicating the effect of Cu ion.

However, the amount of the oxidizing type increased, though in a small amount. The amount of total and reducing type vitamin C decreased by soaking

the sample in water with the metal ion added but the amount of the oxidizing type increased. Such increase in the amount of the oxidizing type was not observed with any of the other metal ions and indicates the specificity of Cu ion (cf. Table 7).

Table 7. Effect of copper ion on vitamin C content iu Japanese radish

V.C	Content in fresh sample (γ/10 g)	Diff. in content of fresh sample and sample boiled in water (γ/10g)	Diff. in content of fresh sample and sample boiled in water Contg. cu (γ/10g)	Diff. in content of boiled in water (5 min.) and sample boiled in water contg. Cu(γ/10g)	Diff. in content of fresh sample and soaked sample in water contg. Cu (γ/10g)
Diketoguronic acid	131± 8	79±11	36±11	−43±11	—
Dehydroascorbic acid	98±12	49±16	58±16	—	−56±16
Oxidizing type	229±20	128± 9	95± 9	−32± 9	−32± 9
Reducing type	1615±20	973±28	1085±28	112±28	135±28
Total vitamin C	1844±10	1099±14	1176±14	77±14	149±14

Sample used is sample D in Table 1.
The time for boiling or soaking is 5 min. respectively.

(3) Loss of Vitamin C in Japanese Radish by Boiling in water: From the foregoing results, the values of the loss of vitamin C on boiling the sample in water are listed in Table 8. The values are similar in all the sample as to the rate of the loss of total, reducing-type, and oxidizing-type ascorbic acid. Average loss of total vitamin C was 61.4 %, of reducing-type 62.6 %, and of oxidizing type 53.4 %.

The rate of loss of the oxidizing type dehydroascorbic acid and diketoguronic acid was somewhat varied and particularly the amount of diketoguronic acid sometimes increased with boiling.

Table 8. Rate of loss of vitamin C by boiling (5 min.)

Japanese radish \ V.C	Total vitamin C	Reducing type	Oxidizing type	Dehydroascorbic acid	Diketoguronic acid
A	59.1	60.3	46.6	86.3	−43.8
B	61.3	55.6	57.0	28.2	54.8
C	56.3	60.3	55.9	53.9	57.2
D	59.6	70.7	56.7	50.0	60.3
E	68.2	65.5	27.2	54.7	61.1
F	63.8	60.3	46.6	61.6	49.1
Average	61.4	62.6	53.4	—	—

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