

An Investigation of the Precursor of the Naturally Occurring Sulfur Dioxide Detected from Foods Containing Sulfur Compounds

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Summary

Twelve kinds of sulfur compound were examined by use of the bubbling-GC method in order to search the precursor of the naturally occurring sulfur dioxide (SO_2) in foods containing sulfur compounds. SO_2 was found from only 3 kinds of thiosulfinate (synthesized and isolated) by use of pretreatment procedure of standard modified Rankine method. Distillation patterns of SO_2 obtained from thiosulfates on the distillation procedure were similar to those obtained from the foods containing sulfur compounds, however, different from sulfited foods. Relative ratios of SO_2 values obtained from 3 kinds of thiosulfinate by 3 kinds of pretreatment method were similar to those obtained from foods containing sulfur compounds, however, different from sulfited foods.

Thiosulfates, foods containing sulfur compounds and sulfited foods were extracted with chloroform, SO_2 was determined in prepared chloroform extract, water extract and the residue. SO_2 was detected from chloroform extracts prepared from methyl methanethiosulfinate and propyl propanethiosulfinate, and not detected from water extracts. In the case of diallyl thiosulfinate, SO_2 was detected from both of chloroform extract and water extract. SO_2 was not detected from chloroform extracts, and that was detected from water extract and the residue prepared from sulfited foods. SO_2 was detected from all of chloroform extract, water extract and the residue prepared from foods containing sulfur compounds. The detection of SO_2 from the residue prepared from foods containing sulfur compounds is indicated the existence of another precursor of SO_2 except thiosulfates.

The existence of thiosulfates in chloroform extract prepared from foods containing sulfur compounds was confirmed by GC-MS.

From above results, It seemed that thiosulfates are important components as the precursors of SO_2 detected from foods containing sulfur compounds.

Keywords: sulfur dioxide, naturally occurring, food containing sulfur compounds, thiosulfinate, GC-FPD, GC-MS, modified Rankine apparatus

Introduction

Sulfur dioxide (SO_2) and sulfiting agents have been used widely for many kinds of food with the purpose of bleaching, antioxidation, preservation. In Japan, the usage standard has been determined for each food. It is controlled at the residual sulfite quantity. And, the labeling of the use is imposed. Modified Rankine titration method developed by Fujita et al.¹⁾, and modified Rankine colorimetric method developed by Ogawa et al.²⁾, and further improved by Shibata et al.³⁾ were simple, rapid and applicable to many kinds of food. Therefore, they have been adopted as the standard method in Japan⁴⁾.

We developed a improvement colorimetric method (bubbling-colorimetric method)⁵⁾ in order to accurately determine the small amount of sulfite in the food on the basis of modified Rankine colorimetric method²⁾. Furthermore, a gas chromatographic method (bubbling-GC method)⁶⁾ and an ion exchange chromatographic method (bubbling-IC method)⁷⁾ after separation with nitrogen gas bubbling using modified Rankine apparatus were developed in order to more accurately determine the small amount of sulfite in the food.

The 6 kinds of food containing sulfur compounds such as dried garlic powder and dried onion powder were measured by modified Rankine colorimetric method, bubbling-colorimetric method, bubbling-GC method and bubbling-IC method. SO_2 was detected

from these foods by all methods. Values of SO_2 obtained by the modified Rankine colorimetric method were higher than other three methods, and those by the other three methods were good agreement.

In the previous report⁸⁾, we investigated the naturally occurring SO_2 detected from foods containing sulfur compounds by use of the bubbling-GC method. The distillation patterns of SO_2 obtained from the foods containing sulfur compounds were different from those obtained from the sulfited foods. The relative ratios of SO_2 values obtained from the foods containing sulfur compounds by 3 kinds of pretreatment method were greatly different from those obtained from the sulfited foods.

Niegisch et al.⁹⁾ reported that SO_2 exists in the onion flavor components. Brodnitz et al.¹⁰⁾ and Naito et al.¹¹⁾ reported that SO_2 exists in the garlic flavor components. Alkaline hydrolysis of diallyl thiosulfinate yielded SO_2 which was confirmed by titration with permanganate, and precipitation of barium sulfate of oxides after acid distillation using nitrogen gas¹²⁾. However, the precursor of the SO_2 detected from foods containing sulfur compounds by use of modified Rankine colorimetric method, bubbling-colorimetric method, bubbling-GC method and bubbling-IC method was not confirmed.

In this report, we have studied on the precursor of the naturally occurring SO_2 detected from foods containing sulfur compounds. Twelve kinds of sulfur compound were examined by use of the

bubbling-GC method in order to search the precursor. And, behavior of SO₂ generated from sulfur compound by distillation and chloroform extraction was examined. Furthermore, It was confirmed that whether the sulfur compound which generated SO₂ existed in the foods containing sulfur compounds.

Materials and Methods

Samples

Food samples were purchased from supermarkets in Chiba City, Japan.

Reagents

All reagents were analytical or special grade except diallyl disulfide, sodium methyl mercaptan, ethyl methanethiosulfinate, propyl propanethiosulfinate and diallyl thiosulfinate. Dimethyl sulfide, dimethyl disulfide, dimethyl sulfoxide, di-n-propyl sulfide, di-n-propyl disulfide, diallyl sulfide, diallyl disulfide, and 15% sodium methyl mercaptan solution were purchased from Tokyo Chemical Industry Co. Ltd. Allylisothiocyanate was from Wako Pure Chemical Industries Ltd. Methyl methanethiosulfinate, propyl propanethiosulfinate and diallyl thiosulfinate were synthesized according to the method of Matsukawa et al.^{13), 14)}. The reaction solutions were poured into water. Sodium hydrogen carbonate was added to the solutions in order to neutralize acetic acid, and the solutions were extracted by chloroform. Chloroform layers were separated and washed with water. Thiosulfonates were isolated according to the method of Small et al.¹⁵⁾.

- (a) Trapping solution. —Dissolve 10 g triethanolamine in 1 L water.
- (b) Phosphoric acid solution. —25%. Dilute 100 mL of 85% phosphoric acid with water to make 340 mL.
- (c) Phosphoric acid solution. —60%. Dilute 120 mL of 85% phosphoric acid with water to make 170 mL.
- (d) Ferrous sulphate Solution. —Dissolve 2 g ferrous sulphate in 100 mL 0.01N sulfuric acid.
- (e) Alkaline solution. —Dissolve 10 g sodium hydroxide and 25 g potassium sodium tartarate in 800 mL water and add 50 mL ferrous sulphate solution, and dilute to 1 L.
- (f) Sulfite stock standard solution. —100 µg SO₂/mL. Dissolve 162.5 mg sodium hydrogen sulfite in 100 mL of water, then standardised by titration against freshly 0.1 N-iodine to 1000 µg SO₂/mL. Dilute it further with trapping solution to obtain a solution containing 100 µg SO₂/mL.
- (g) Working standard solutions. — Dilute stock solution with trapping solution to appropriate concentrations.

Determination of SO₂ by gas chromatography with frame photometric detection (GC-FPD) or gas chromatography with mass spectrometric detection (GC-MS)

Sample preparation

- (a) Method A⁸⁾—A sample (1-5 g) was subjected to the distillation procedure of the standard modified Rankine method described elsewhere⁴⁾. In brief, 10 mL of trapping solution was placed in the trap. The sample was added 20 mL water and 10 mL 25% phosphoric acid solution, and was distilled for 10 min while nitrogen gas bubbles through at 500 mL/min. After distillation, 5 mL of the trapping solution was measured into a 50 mL Nessler tube. The tube was stoppered tightly, and 1 mL of 60% phosphoric acid solution was injected through the stopper by a syringe. The tube was shaken vigorously for 30 sec, kept for 10 min at room temperature, and the tube was shaken again vigorously for 30 sec. Immediately after, 1 mL of head space gas was withdrawn into a gas tight syringe and injected into GC-FPD or GC-MS.
- (b) Method B⁸⁾—A sample was subjected to the same treatment as the method A except distillation for 80 min.
- (c) Method C⁸⁾—A sample was added 10 mL of alkaline solution, kept at room temperature for 2 hrs under occasional shaking. The sample treated with alkaline solution was added 10 mL water and 10.5 mL 25% phosphoric acid solution, and was subjected to the same treatment (after the distillation operation) as the method A.

GC-FPD conditions

Shimadzu GC-14A system (Shimadzu Corp., Kyoto, Japan). Operating conditions: glass column (3 m × 3 mm id) with APS-1000 (40/60 mesh), column temperature 90°C, injection port temperature 120°C, nitrogen carrier gas 30 mL/min, injection volume 1 mL.

GC-MS conditions

Hitachi RMU-6MG system (Hitachi, Ltd. Tokyo, Japan). Operating conditions: glass column (2 m × 3 mm id) with APS-1000 (40/60 mesh), column temperature 90°C, injection port temperature 120°C, ion source and separator temperature 140°C, helium carrier gas 30 mL/min, injection volume 1 mL.

Preparation of chloroform extract and water extract

Fifty mL water and 50 mL chloroform were added to 20-100 mg each thiosulfonate and shaken for 10 min. The water layer was re-extracted with 50 mL chloroform.

Fifty-90 mL water was added to 10-50 g each food containing sulfur compounds, then the mixture was homogenized for 5 min at 10000 rpm. One hundred fifty mL chloroform was added to the homogenate and shaken for 10 min. The water layer was re-extracted with 150 mL chloroform.

Seventy-five mL water was added to 25 g each sulfited food, then the mixture was homogenized for 5 min at 10000 rpm. One hundred fifty mL chloroform was added to the homogenate and shaken for 10 min. The water layer was re-extracted with 150 mL chloroform. Chloroform layer, water layer and residue prepared in the chloroform extraction procedure described above were

Table 1. Determination of SO₂ in 12 Sulfur Compounds by Method A

Sulfur compound	Amount	
	added (mg)	SO ₂ (μg)
Methyl mercaptan	10	ND
	100	ND
Allylthiocyanate	10	ND
	100	ND
Dimethyl sulfide	10	ND
	100	ND
Di-n-propyl sulfide	10	ND
	100	ND
Diallyl sulfide	10	ND
	100	ND
Dimethyl disulfide	10	ND
	100	ND
Di-n-propyl disulfide	10	ND
	100	ND
Diallyl disulfide	10	ND
	100	ND
Dimethyl sulfoxide	10	ND
	100	ND
Methyl methane thiosulfinate ^a	20	5.20
	100	16.8
Propyl propane thiosulfinate ^a	20	16.0
	100	40.0
Diallyl thiosulfinate ^a	20	54.0
	100	190

ND: not detected (below 0.2 μg)

^a Thiosulfinates were synthesized by the method of Matsukawa et al.^{13), 14)}, and were isolated according to the method of Small et al.¹⁵⁾.

taken out the concentrated extract was used for the determination of SO₂. Certain amount of the water layer and the residue were measured, and used for the determination of SO₂.

Results and Discussion

Search of the sulfur compound with the SO₂-generating property

In order to search the precursor of SO₂ in foods containing sulfur compounds, we determined and identified SO₂ for 12 kinds of sulfur compound by method A using to the distillation procedure of the standard modified Rankine method⁴⁾. Results were shown in Table 1. SO₂ was detected from only 3 kinds of thiosulfinate, i.e., methyl methanethiosulfinate, propyl propanethiosulfinate and diallyl thiosulfinate. Fig. 1 shows distillation patterns of SO₂ obtained from 3 kinds of thiosulfinate on the distillation procedure.

SO₂ was distilled gradually after 10 min for all of 3 kinds of thiosulfinate. Our previous results⁸⁾ were shown in figure 2 and 3. Distillation patterns of SO₂ (Fig. 2) obtained from usual sulfited foods and that (Fig. 3) obtained from foods containing sulfur compounds was different. It is characteristic of the food containing sulfur compounds that SO₂ is distilled gradually after 10 min. Distillation patterns of SO₂ obtained from thiosulfinates were similar to those obtained from the foods containing sulfur compounds.

Table 2 showed amounts of SO₂ obtained from 3 kinds of thiosulfinate by 3 kinds of pretreatment method. SO₂ values obtained by method B were 3.05-12.6 times of those by method A, and those by method C were 0.99-5.20 times of those by method A. It was reported that the difference between relative ratios of SO₂ values obtained from foods containing sulfur compounds and those obtained from sulfited foods by 3 kinds of pretreatment method was greatly in the previous report⁸⁾. On that report, SO₂ values obtained from foods containing sulfur compounds by method B were 2.31-10.5 times of those by method A, and those by method C were 1.23-42.8 times of those by method A. On the other hand, SO₂ values obtained from sulfited foods by method B were 1.03-1.49 times of those by method A, and those by method C were 0.29-1.61 times of those by method A. Three kinds of thiosulfinate showed similar tendency for measured value of SO₂ to foods containing sulfur compounds. It is reported^{10), 12)} that thiosulfinates are contained in food containing sulfur compounds such as garlic. Therefore, it seems to be high possibility that thiosulfinates are the precursor of the SO₂ detected from foods containing sulfur compounds.

Situation on the existence of SO₂ in chloroform extract, water extract and the residue prepared from thiosulfinates, foods containing sulfur compounds and sulfited foods

Table 3 showed amounts of SO₂ obtained from chloroform extract and water extract prepared from 3 kinds of thiosulfinate. SO₂ was detected from chloroform extracts prepared from methyl methanethiosulfinate and propyl propanethiosulfinate, and not detected from water extracts. SO₂ was detected from both of chloroform extract and water extract prepared from diallyl thiosulfinate. This seems to be because the part of diallyl thiosulfinate dissolved in water.

The chloroform extraction procedure was regarded as using for the purification of synthesized thiosulfinates. And, because of free and bound sulfite in sulfited food are water solubility, they would not seem to dissolve in chloroform. It seems to be possible that SO₂ derive from thiosulfinates in food containing sulfur compounds isolate from added sulfite in sulfited food by the chloroform extraction procedure.

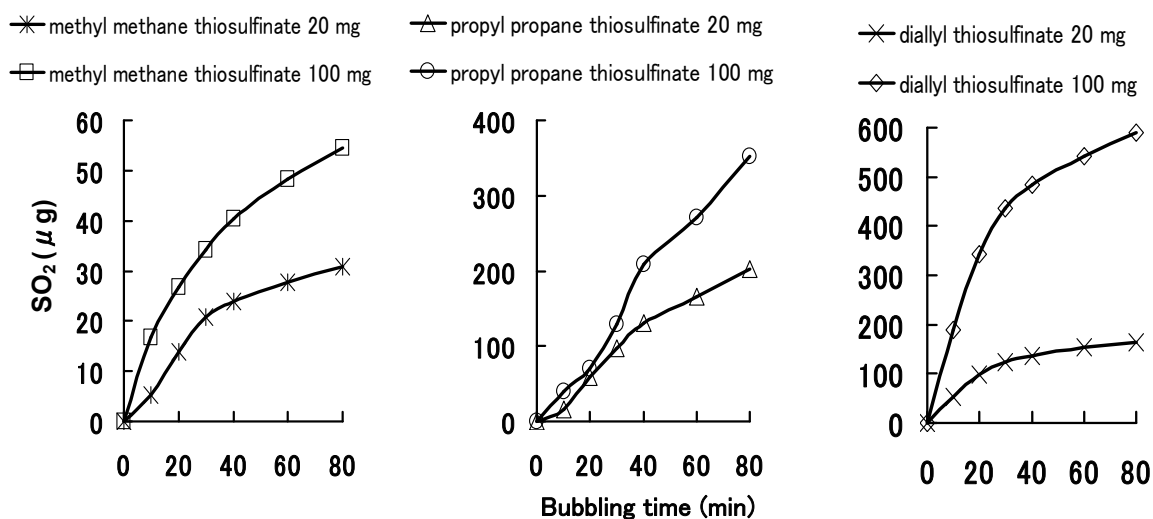


Fig. 1. Distillation patterns of SO₂ in 3 thiosulfates on the distillation procedure

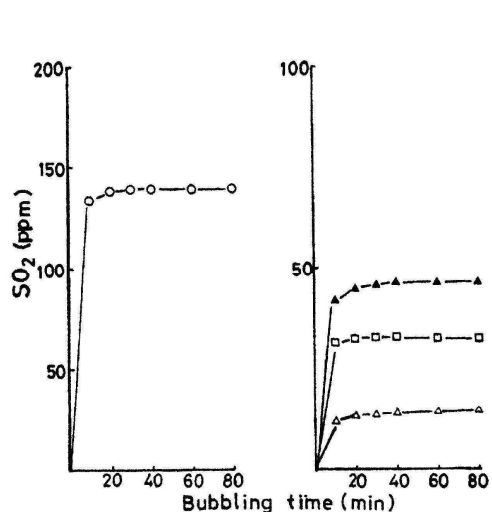


Fig. 2. Distillation patterns of SO₂ in foods treated with sulfur dioxide
○—: white wine; ▲—: frozen peeled shrimps; □—: concentrated orange juice; △—: soy bean paste

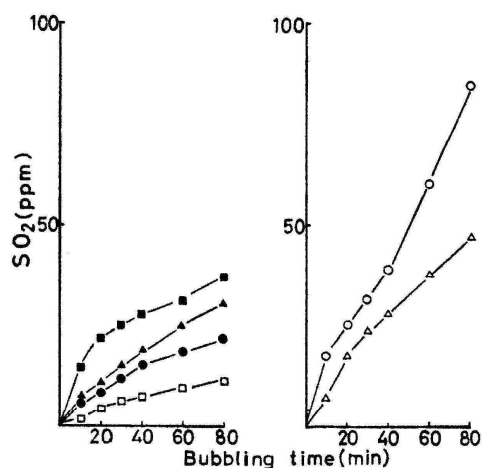


Fig. 3. Distillation patterns of SO₂ in foods containing sulfur compounds
■—: horseradish powder; ○—: garlic powder; ●—: onion powder; △—: dried *Lentinus edodes*; □—: mustard powder; ▲—: shredded and dried Japanese radish roots

Table 2. Determination of SO₂ in 3 Thiosulfates by 3 Methods

Compound	Amount added (mg)	Method A SO ₂ (μg)	Method B SO ₂ (μg)	Ratio (B/A)	Method C SO ₂ (μg)	Ratio (C/A)
Methyl methane thiosulfate ^a	20	5.20	30.8	5.92	6.80	1.31
	100	16.8	54.6	3.25	28.0	1.67
Propyl propane thiosulfate ^a	20	16.0	202	12.6	57.0	3.56
	100	40.0	396	9.90	208	5.20
Diallyl thiosulfate ^a	20	54.0	165	3.05	65.0	1.20
	100	190	589	3.10	188	0.99

^a Thiosulfates: see table 1.

Table 3. Determination of SO₂ in Chloroform Extract and Water Extract Prepared from 3 Thiosulfates

Compound	Amount added (mg)	SO ₂ (μg)			
		Chloroform extract		Water extract	
		Method A	Method C	Method A	Method C
Methyl methane thiosulfinate ^a	20	2.0	4.4	ND	ND
	100	12.0	12.4	ND	ND
Propyl propane thiosulfinate ^a	20	11.0	38.0	ND	ND
	100	0.4	0.8	ND	ND
Diallyl thiosulfinate ^a	20	11.8	16.1	0.75	1.75
	100	31.5	65.5	7.7	9.4

ND: not detected (below 0.3 μg)

^a Thiosulfates: see table 1.**Table 4.** Determination of SO₂ in Chloroform Extract, Water Extract and the Residue Prepared from 5 Sulfited Foods

Sample	SO ₂ (μg/g) ^a					
	Chloroform extract		Water extract		Residue	
	Method A	Method C	Method A	Method C	Method A	Method C
Red wine	ND	ND	108	128	-	-
Sugar beans	ND	ND	44	49	22	22
Dried apricot	ND	ND	280	311	280	344
Soy bean paste	ND	ND	1.7	1.8	1.6	1.8
Frozen peeled shrimp	ND	ND	88	89	86	91

ND: not detected (below 0.02 μg/g for chloroform extract, below 0.04 μg/g for water extract and residue).

^a Sulfur dioxide value was shown at concentration for original sample.**Table 5.** Determination of SO₂ in Chloroform Extract, Water Extract and the Residue Prepared from 6 Foods Containing Sulfur Compounds

Sample	SO ₂ (μg/g) ^a					
	Chloroform extract		Water extract		Residue	
	Method A	Method C	Method A	Method C	Method A	Method C
Dried garlic powder	0.51	0.78	0.88	0.91	0.50	0.50
Dried onion powder	0.07	0.10	0.39	0.49	0.16	0.16
Garlic	1.65	1.92	0.20	0.20	0.45	0.70
Onion	0.14	0.20	Tr	Tr	Tr	Tr
Welsh onion	0.41	0.69	0.16	0.19	Tr	Tr
Chinese chive	0.36	0.59	Tr	Tr	Tr	Tr

ND: not detected (below 0.02 μg/g for chloroform extract, below 0.04 μg/g for water extract and residue).

Tr: trace (0.02~0.04 μg/g for chloroform extract, 0.04~0.08 μg/g for water extract and residue).

^a Sulfur dioxide value: see table 4.

Table 4 showed amounts of SO₂ obtained from chloroform extract, water extract and the residue prepared from 5 kinds of sulfited food. SO₂ was not detected from chloroform extracts, and that was detected from water extract and the residue. In these 5 kinds of unsulfited food, SO₂ was not detected. It was suggested that the precursor of naturally occurring SO₂ did not exist in these 5 foods.

Table 5 showed amounts of SO₂ obtained from chloroform extract, water extract and the residue prepared from 6 kinds of food containing sulfur compounds. SO₂ was detected from all of chloroform extract, water extract and the residue prepared from foods containing sulfur compounds. It was suggested that thiosulfates are precursor of SO₂ detected from chloroform extract

Table 6. Identification of Thiosulfinates and Thiosulfonates in Chloroform Extracts Prepared from 6 Foods Containing Sulfur Compounds by GC-MS

Sample	Methyl methane thiosulfinate	Methyl methane thiosulfonate	Propyl propane thiosulfonate	Diallyl thiosulfinate
Dried garlic powder				○
Dried onion powder	○	○		
Garlic	○			○
Onion	○	○	○	
Welsh onion	○	○		
Chinese chive	○	○		○

Retention time and m/z of each component at the GC-MS (Retention times of methyl methane thiosulfinate and diallyl thiosulfinate were confirmed by the synthesized standard. Retention times of methyl methane thiosulfonate and propyl propane thiosulfonate were confirmed by them which small existed in synthesized standards of methyl methane thiosulfinate and propyl propane thiosulfinate.)

Methyl methane thiosulfinate: retention time 7.5 min m/z 47,64,79,95,110 (library and literature ¹⁹⁾)

Methyl methane thiosulfonate: retention time 10.1 min m/z 47,63,81,111,126 (library and literature ^{17), 20)})

Propyl propane thiosulfonate: retention time 20.9 min m/z 43,76,118,182 (literature ¹⁷⁾)

Diallyl thiosulfinate: retention time 15.1 and 15.8 min m/z 45,71,97,111,144 (literature ¹⁰⁾)

prepared from foods containing sulfur compounds. The detection of SO₂ from the residue prepared from foods containing sulfur compounds would be indicated the existence of another precursor of SO₂. It is known that thiosulfinate is formed from S-alkyl-L-cysteine sulfoxide ^{11), 16)} as sulfur containing amino acid by enzymatic decomposition. S-alkyl-L-cysteine sulfoxide exists in the water extract or the residue, since that is soluble in water. SO₂ might be formed directly from S-alkyl-L-cysteine sulfoxide exists in the water extract or the residue by the distillation procedure.

The confirmation of thiosulfinates in chloroform extract prepared from foods containing sulfur compounds

The existence of thiosulfinates in chloroform extract prepared from foods containing sulfur compounds was confirmed by GC-MS. Table 6 showed that the result of identification of thiosulfinates in chloroform extracts prepared from foods containing sulfur compounds by GC-MS. Methyl methane thiosulfinate was detected from garlic, dried onion powder, onion, welsh onion, chinese chive. Methyl methane thiosulfonate was detected from dried onion powder, onion, welsh onion, chinese chive. Propyl propane thiosulfonate was detected from onion. Diallyl thiosulfinate was detected from dried garlic powder, garlic, chinese chive.

Methyl methane thiosulfinate is very unstable. It is known that stable methyl methane thiosulfonate ¹⁷⁾ is formed by the disproportionation reaction of methyl methane thiosulfinate. Therefore, methyl methane thiosulfonate would be also identified by GC-MS. And, identification of propyl propane thiosulfinate was impossible, since clear peak did not exist at GC-MS. Stable propyl propane thiosulfonate ^{17), 18)} which is the product by the disproportionation reaction of propyl propane thiosulfinate was able to identify by GC-MS. Therefore, propyl propane thiosulfonate

would be identified instead of propyl propane thiosulfinate.

From above results, thiosulfinates as methyl methane thiosulfinate, propyl propane thiosulfinate and diallyl thiosulfinate would exist in 6 kinds of food containing sulfur compounds. It is supposed that these are the precursor of SO₂ detected from chloroform extract.

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含硫黄食品から検出される天然由来の二酸化硫黄の前駆物質について

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要旨

含硫黄食品中の天然由来の二酸化硫黄 (SO₂) の前駆物質を検索する目的で通気-GC 法を用いて 12 種の硫黄化合物を試験した。使用している公定の改良ランキン法の前処理操作で、SO₂ が検出されたのは 3 種のチオスルフィネート (合成、精製したもの) のみであった。チオスルフィネート類から得られた SO₂ の蒸留パターンは含硫黄食品における SO₂ の蒸留パターンと類似していた、しかしながら、亜硫酸塩処理食品の蒸留パターンとは異なっていた。3 種のチオスルフィネート類から 3 種の前処理方法で得られた SO₂ の測定値の相対比は、含硫黄食品から得られた測定値の相対比と類似していた、しかしながら、亜硫酸塩処理食品から得られた測定値の相対比とは違っていた。

チオスルフィネート類、含硫黄食品及び亜硫酸塩処理食品についてクロロホルム抽出を行い、調製したクロロホルム抽出物、水抽出物及び残渣中の SO₂ を定量した。ジメチルチオスルフィネート及びジプロピルチオスルフィネートのクロロホルム抽出物から SO₂ が検出されたが、水抽出物からは SO₂ は検出されなかった。ジアリルチオスルフィネートの場合は、クロロホルム抽出物及び水抽出物の両方から SO₂ が検出された。亜硫酸塩処理食品ではクロロホルム抽出物から SO₂ は検出されなかったが、水抽出物及び残渣からは SO₂ が検出された。含硫黄食品についてはクロロホルム抽出物、水抽出物及び残渣の全てから SO₂ が検出された。含硫黄食品における残渣からの SO₂ の検出は、チオスルフィネート類以外の他の前駆物質の存在を示している。

含硫黄食品から調製したクロロホルム抽出物中のチオスルフィネート類の存在を GC-MS により確認した。

以上の結果から、含硫黄食品から検出された二酸化硫黄の前駆物質としてチオスルフィネート類は重要な成分であると思われた。