Propanethial S-Oxide Content in Scallions (*Allium fistulosum* L. Variety Caespitosum) as a Possible Marker for Freshness during Cold Storage

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Propanethial S-oxide (PSO), known as a precursor of flavor chemicals in *Allium* species, was analyzed in scallions (*Allium fistulosum* L. var. Caespitosum) stored at 0 and 5 °C for 1–5 weeks. The levels of PSO from scallions stored at 5 °C were much higher than those from scallions stored at 0 °C. PSO comprised 80–90% of the total volatiles of all the samples obtained from scallions. The amounts of total volatiles and PSO from scallions stored at 5 °C increased for the first week and then decreased slightly. They gradually increased from the second week to fourth week and then increased dramatically. The amount of PSO from scallions stored at 0 °C increased slightly for the first 4 weeks and then decreased. Over time, the visual changes of scallions stored at 5 °C correlated with the amount of PSO formed. Several sulfur-containing compounds known to be formed from PSO were also identified as main constituents of volatiles from scallions. The formation of PSO during cold storage can be used as a marker for the freshness of scallions.

INTRODUCTION

Respiration is one of the basic processes in the life of fruits and vegetables and is directly related to their maturation. Because chemical reactions of respiration are controlled by temperature, fruits and vegetables should be stored at as low a temperature as possible without damage by freezing to maintain their freshness for extended periods (Salunkhe et al., 1991).

Most *Allium* species are edible and possess characteristic aromas. The composition and formation of volatiles in garlic and onion have been extensively studied (Fenwick and Hanley, 1985; Carson, 1987; Lancaster and Boland, 1990; Block, 1992). It is known that the volatile components of the *Allium* genus are produced by enzymatic splitting of the nonvolatile precursors, S-alk(en)ylcysteine sulfoxides, when the plants are crushed. The alk(en)yl groups are mainly a combination of propyl, 1-propenyl, allyl, and methyl groups, depending on the species. The production of volatile compounds containing a 1-propenyl group was reportedly influenced by storage conditions. For example, the cold storage of garlic increased production of S-(E)-1-propenylcysteine S-oxide, which consequently produced low molecular weight organosulfur compounds (Lawson et al., 1991).

Volatile chemicals of scallions were first studied by Kameoka et al. (1984), who reported sulfides and furanones as the major components in steam-distilled oils from Welsh onions (*A. fistulosum* L. var. Maichuon) and scallions (*A. fistulosum* L. var. Caespitosum). The sulfur-containing volatile compounds, which are possible markers for freshness, constituted 40–48% of the total volatile constituents. Nine different *Allium* species (including scallions) showed that in each case the predominant flavor principles were thiosulfinates and propanethial S-oxide (PSO), with only minimal amounts of polysulfides and other compounds (Block et al., 1992). Recently, Kuo and Ho (1992a) reported 41 novel volatile sulfur-containing compounds in the steam-distilled oils of scallions. Later, the same authors found some thiosulfinates and thiosulfonates, which are heat labile in solvent extracts of scallions (Kuo and Ho, 1992b).

In the present study, the relationship between storage temperature and the content of the major volatile compound (PSO) in scallions was investigated to determine whether or not it could be used as a marker for freshness.

EXPERIMENTAL PROCEDURES

Materials. Scallions (*A. fistulosum* L. var. Caespitosum) were purchased from a local market. Silica gel (60–200 mesh) was obtained from J. T. Baker Inc. (Phillipsburg, NJ). 1-Octanol was purchased from Sigma Chemical Co. (St. Louis, MO). Reclosable polyethylene storage bags ($10^9/_{16}$ in. × 11 in.) were obtained from Payless Drug Stores (Wilsonville, OR).

Cold Storage. Scallions (15–20 g) in storage bags were separately stored in a Precision Model 813 refrigerator (Precision Scientific Inc., Chicago, IL) at 0 or 5 °C for 5 weeks.

Sample Preparations. Every week, scallions (15 g) stored at both temperatures were cut into approximately 1-cm pieces by a scissors and then ground with 5 g of dry ice using a mortar. After the ground samples were spread in a Petri dish in the freezer at −18 °C to evaporate off dry ice, they were stirred with 40 mL of dichloromethane for 30 min in a 200-mL beaker using a magnetic stirrer. The sample mixtures were filtered into a 100-mL flask, and then the filtrates were dried over approximately 2 g of anhydrous sodium sulfate for 12 h. The extracts were passed through a silica gel column (60–200 mesh, 10 cm × 1 cm) to remove chlorophyll and precipitates. All experiments were performed in a cold room (5 °C) up to this point. The samples were then condensed to 0.1 mL in volume under a purified nitrogen stream at room temperature. The concentrated samples were dissolved into 0.5 mL of methanol, and precipitates were filtered off. The volume of each filtrate was adjusted to 0.5 mL with methanol.

1-Octanol (100 μL) solution (40 mg/10 mL of dichloromethane) was added to each sample as a gas chromatographic internal standard immediately before quantitative analysis.

Analysis of Samples. For qualitative analysis of each component, the gas chromatographic Kovats retention index (Kovats, 1965) and the mass spectral fragmentation pattern were compared to those of the authentic compounds. Quantitative analysis of GC components was done by the method described

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Table 1. Main Volatile Compounds Found in Green Onions Stored at 0 and 5 °C over Different Periods

compound	GC/MS scan number	relative GC peak area[a]									
		1st week		2nd week		3rd week		4th week		5th week	
		0 °C	5 °C	0 °C	5 °C	0 °C	5 °C	0 °C	5 °C	0 °C	5 °C
propanethial *S*-oxide	138	43.9	73.8	53.1	64.3	58.6	76.0	80.0	91.2	70.3	123
trans-2-hexenal	287	0.51	1.25	0.48	0.51	0.56	0.59	0.47	0.50	0.40	1.35
dipropyl disulfide	1386	0.87	0.82	1.08	0.77	0.01	0.13	0.61	0.80	1.00	1.03
propyl methanethiosulfonate	1941	0.18	0.16	0.22	0.15	0.17	0.21	0.14	0.13	0.15	0.26
1-propenyl propyl trisulfide	2351	0.12	0.18	0.15	0.14	0.17	0.19	0.16	0.17	0.12	0.32

[a] GC peak area of compound/GC peak area of internal standard (1-octanol).

Table 2. Description of Green Onions at Each Storage Stage

stored at	storage period (weeks)				
	1	2	3	4	5
0 °C	bright green and fresh	slightly light green and fresh	slightly faded by still fresh	slightly yellow and light green	partially yellow and losing freshness
5 °C	slightly yellow	partially yellow	totally yellow with softened texture	dark yellow and shriveled	partially rotted

by Ettre (1967). A Hewlett-Packard (HP) Model 5890 gas chromatograph (GC), equipped with a 60 m × 0.25 mm i.d. DB-5 bonded-phase fused-silica capillary column (J&W Scientific, Folsom, CA), and a flame ionization detector (FID) were used for routine quantitative analysis. The GC peak areas were integrated with an HP 5880A series GC terminal. The injector temperature was 250 °C. The detector temperature was 300 °C. The oven temperature was held at 40 °C for 8 min and then programmed to 180 °C at 2 °C/min. The linear helium carrier gas flow rate was 30 cm/s.

An HP Model 5890 Series II GC interfaced to an HP Model 5971 mass spectrometer was used for MS identification of the GC components. The ionization voltage was 70 eV, and the ion source temperature was 185 °C. The column and oven conditions for GC/MS were as described for the GC/FID analysis.

RESULTS AND DISCUSSION

The main volatile compounds identified in scallions stored at 0 and 5 °C over different periods of time are shown in Table 1. The values are the averages of two replicate experiments. Propanethial *S*-oxide (PSO), *trans*-2-hexenal, dipropyl disulfide, propyl methanethiosulfonate, and 1-propenyl propyl trisulfide were identified as the main components of scallions in the present study. *trans*-2-Hexenal, dipropyl disulfide, and 1-propenyl propyl trisulfide were also previously reported as the main components of scallions (Kuo and Ho, 1992a). PSO comprised 80–90% of the total volatiles of all the samples obtained from scallions in the present study. PSO was not found in the volatiles obtained from scallions by steam distillation (Kuo and Ho, 1992a), but PSO was identified as one of the major constituents of the volatiles recovered from scallions by solvent extraction (Kuo and Ho, 1992b). Also, there are some differences in the composition of volatiles of scallions between the paper by Block et al. (1992) and the results of the present study. This is due to the different conditions used for GC analysis. If elevated temperatures such as 250 °C are used for the GC injector, decomposition of original chemicals occur. In addition, decomposition of flavorants occurs on longer capillary columns such as 60 m (Block et al., 1992; Block, 1993).

Figure 1 shows the relative peak area of total volatiles and PSO in scallion samples at two temperatures over different periods of time. The total amounts of volatiles and PSO in scallions stored at 5 °C were greater than the amounts in scallions stored at 0 °C. The amounts of total volatiles and PSO from scallions stored at 5 °C increased for the first week and then decreased slightly. They gradually increased from the second week to the fourth week and then increased dramatically. The amount of

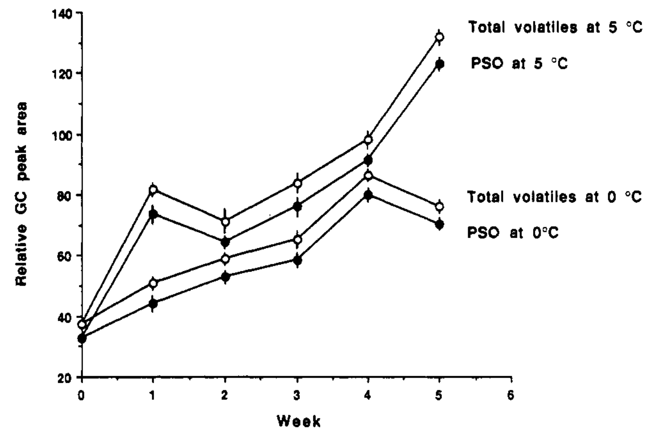

Figure 1. Amounts of total volatiles and PSO formed during cold storage.

PSO from scallions stored at 0 °C increased slightly for the first 4 weeks and then decreased.

In onion, the flavor precursor is *trans*-(+)-*S*-(1-propenyl)-L-cysteine sulfoxide, which is a positional isomer of *alliin*. The enzyme allinase in onion converts it into 1-propenesulfenic acid, which subsequently rearranges to form a lachrymator, PSO (Boelens et al., 1971; Brodnitz and Pascale, 1971). PSO is a precursor of flavor chemicals, such as carbonyl compounds and sulfur-containing compounds, in *Allium* species. In the present study, the chemicals (dipropyl disulfide, propyl methanethiosulfonate, and 1-propenyl propyl trisulfide) hypothesized to be formed from PSO (Boelens et al., 1971) were also found to be the main volatile compounds in scallions (Table 1).

The scallions stored at 0 °C maintained freshness and flavor for 3–4 weeks. On the other hand, the scallions stored at 5 °C maintained freshness for only 1–2 weeks. Neither sample showed freezing or chilling damage. As Table 2 shows, scallions stored at 5 °C underwent appearance changes over time. In particular, scallions stored for 5 weeks at 5 °C were beginning to rot. At the same time, the amount of PSO increased dramatically during 4–5 weeks of storage. Scallions stored at 0 °C maintained freshness for at least 4 weeks, and the amount of PSO formed increased slightly up to 4 weeks of storage. Visible deterioration of scallions stored at cold temperatures correlates with the increase of PSO formed. Consequently, 0 °C is a better storage temperature for scallions than 5 °C. Visual assessment tends to vary among evaluators. Therefore, it is preferable to use chemical or physical methods to evaluate freshness. The linear correlation equations for the PSO formation at 0 and 5 °C over time are $y = 34.88 + 8.32X$ ($r = 0.933$) and $y = 38.35 + 15.17X$ ($r = 0.900$), respectively. The present study suggests that production of PSO is a marker for freshness of scallions.

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