Volatile Compounds Thermally Generated from *S*-Propylcysteine and *S*-Propylcysteine Sulfoxide—Aroma Precursors of *Allium* Vegetables

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Two nonvolatile flavor precursors occurring in *Allium* vegetables, *S*-propyl-L-cysteine and its sulfoxide, were heated in closed model systems at different temperatures (from 80 to 200 °C) in the presence of variable amounts of water (0−98%) for 1−60 min. It seems to be indisputable that thermally generated breakdown products of both *S*-propyl-L-cysteine and particularly *S*-propyl-L-cysteine sulfoxide can significantly participate in the aroma formation of culinary processed *Allium* vegetables. Dipropyl disulfide, dipropyl trisulfide, propylthiol, and dipropyl thiosulfonate were identified as the predominant volatile compounds generated by thermal degradation of *S*-propylcysteine sulfoxide. Dipropyl disulfide and 2-(propylthio)ethylamine were the major breakdown products formed from *S*-propylcysteine. Substantial amounts of various alkyl- and alkylthio-substituted pyridines were also generated from both *S*-propylcysteine and its sulfoxide.

Keywords: *S-Propylcysteine; S-propylcysteine sulfoxide; PCSO; sulfur volatiles; flavor precursor; aroma generation; dipropyl disulfide; pyridines; Allium; onion processing*

INTRODUCTION

S-Alk(en)yl-L-cysteines and their sulfoxides belong to the important secondary plant metabolites occurring in vegetables. *S*-Propylcysteine sulfoxide (PCSO) was first isolated from onion by Virtanen and Matikkala (1959), and their finding was later confirmed by Carson and Wong (1961). Unlike its methyl analogue, which occurs widely in members of many plant families, the distribution of PCSO seems to be restricted only to the genus *Allium* and to the closely related plant *Brodiaea uniflora* Engl. (synonymous with *Ipheion uniflorum* Raf., *Triteleia uniflora*, or *Tristagma uniflora*) (Whitaker, 1976). Its distribution in *Allium* vegetables appears to be quite controversial. It has at times been reported as the major component among all *S*-alkyl-L-cysteine sulfoxides present in onion (Lancaster and Kelly, 1983; Lancaster et al., 1984, 1986; Lancaster and Boland, 1990), whereas others concluded that it occurs only as a minor derivative, if at all (Matikkala and Virtanen, 1967; Yagami et al., 1980; Block et al., 1992a,b; Thomas and Parkin, 1994). On the other hand, PCSO has been considered to be absent in garlic (Ziegler and Sticher, 1989; Lawson et al., 1991). However, recent results of Edwards et al. (1994) and subsequently Calvey et al. (1997) indicated its presence in trace quantities also in garlic.

The typical flavor of *Allium* vegetables is formed by the enzymatic cleavage of *S*-alkyl-L-cysteine sulfoxides when their cellular tissue is disrupted. However, culinary processing such as boiling or frying can cause alliinase inactivation, and thus, a certain amount of the aroma precursors remains unreleased. These can subsequently themselves participate in developing the characteristic flavor of the processed vegetables (Kimura et al., 1990; Yu et al., 1994a−e; Ho et al., 1995; Kubec et al., 1997, 1998; Kubec and Velíšek, 1998). Furthermore, a considerable amount of *S*-propylcysteine and its sulfoxide is bound in γ-glutamyldipeptides (in onion ~0.1% fw) (Whitaker, 1976; Lawson et al., 1991). In that these dipeptides are not cleaved by alliinase, it can be assumed that they also significantly participate in flavor generation of thermally processed vegetables as indicated by the recently published results of both Lawson et al. (1992) and Ueda et al. (1994).

Decomposition of PCSO was first studied by Nishimura et al. (1970, 1971) in connection with flavor deterioration after γ-irradiation of onion. Alanine, cysteic acid, dipropyl disulfide, and dipropyl sulfide were identified as the major degradation products. The effect of onion processing on the PCSO stability was investigated by Freeman and Whenham (1975). They found that the largest losses of PCSO result from hot-air-drying and on a smaller scale from pickling and boiling. However, their study contributed little to our better understanding of volatile formation and nonenzymatic degradation of PCSO.

The effect of water content, time, and temperature of heating on the stability of *S*-propyl-L-cysteine and its sulfoxide is shown in the present study. Arising breakdown products were identified and quantified to understand the formation mechanisms of volatile compounds generated during onion processing.

EXPERIMENTAL PROCEDURES

Synthesis of *S*-Propylcysteine and *S*-Propylcysteine Sulfoxide. *S*-Propylcysteine was synthesized by alkylation of L-cysteine with *n*-propyl bromide according to the procedure of Theodoropoulos (1959). A diastereomeric mixture of (±)-*S*-propyl-L-cysteine sulfoxide was obtained by oxidation of *S*-propylcysteine with hydrogen peroxide. Structures of synthesized amino acids were confirmed by ^{1}H NMR, ^{13}C NMR, and

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10.1021/jf980974z CCC: $18.00
Published on Web 02/20/1999

Table 1. Stability of *S*-Propylcysteine Sulfoxide and Effect of Time, Temperature, and Water Content on Volatile Formation

	time of heating[a]						
	1 min	2 min	4 min	8 min	15 min	30 min	60 min
undecomposed PCSO (%)	99.9	99.2	85.7	34.3	6.6	2.1	1.3
PrCys[b] (mol %)	nd[c]	nd	tr[d]	0.3	0.5	0.9	1.1
total volatiles[e] (mg/g)	0.31	0.98	42.9	228.2	317.6	311.3	299.6
conversion of sulfur[f] (%)	0.07	0.2	11.1	58.5	81.4	80.9	78.7
	temperature of heating[g]						
	80 °C	100 °C	120 °C	140 °C	160 °C	180 °C	200 °C
undecomposed PCSO (%)	89.6	71.3	1.3	0.2	tr	tr	nd
PrCys[b] (mol %)	nd	tr	1.1	0.8	0.3	nd	nd
total volatiles[e] (mg/g)	1.14	58.2	299.6	311.7	317.6	336.7	257.6
conversion of sulfur[f] (%)	0.3	15.1	78.7	75.8	69.4	66.7	50.5

	water content[h]								
	0%	5%	10%	20%	40%	80%	90%	95%	98%
undecomposed PCSO (%)	33.8	18.5	1.3	1.2	1.8	13.5	27.6	41.9	55.3
PrCys[b] (mol %)	nd	0.4	0.8	0.9	1.0	0.7	0.3	tr	tr
total volatiles[e] (mg/g)	3.17	289.9	299.6	284.9	281.5	278.3	211.2	63.5	7.66
conversion of sulfur[f] (%)	0.9	75.4	78.7	75.9	74.9	74.6	56.9	14.8	1.8

[a] At 120 °C and 10% water. [b] Expressed as moles of *S*-propylcysteine (PrCys) formed per mole of PCSO. [c] nd, not detected. [d] tr, traces (<0.1%). [e] Amount of volatiles formed from 1 g of PCSO. [f] Expressed as moles of sulfur bound in volatiles per mole of PCSO. [g] For 60 min and 10% water. [h] At 120 °C for 60 min.

IR spectroscopy. Their purity (>99%) was checked by means of HPLC and TLC.

Synthesis of 2-(Propylthio)acetaldehyde (3-Thiohexanal). Chloroacetaldehyde (10 mL of 45% aqueous solution, 0.068 M, Fluka) was added dropwise to 50 mL of methanolic solution of propyl mercaptane (0.068 M, Fluka) with an intensive external cooling and stirring. After 2 h, the reaction mixture was extracted with 100 mL of diethyl ether, and an ether fraction was dried over sodium sulfate and evaporated in vacuo. Purity of the obtained product was ~90% (according to the GC analysis). Its structure was confirmed by GC/MS (see Table 5).

Synthesis of Dipropyl Thiosulfinate. This compound was synthesized by oxidation of dipropyl disulfide with peracetic acid according to the method of Moore and O'Connor (1966). Its purity (>85%) was checked by means of HPLC.

Thermal Decomposition of Amino Acids. Amino acid (50 mg) was placed in a 5 mL glass tube, water was added, and the tube was sealed. Following equilibration for 24 h, the tube was heated in an oven at temperatures in the range of 80−200 °C, then cooled in the freezer to −18 °C, and crushed under water (total volume of 2.45 mL). The resulting solution was immediately extracted with 5 mL of diethyl ether. The extract obtained was dried using anhydrous sodium sulfate and analyzed by GLC without any further treatment.

Gas Chromatographic Analysis. A Hewlett-Packard 5890 chromatograph equipped with a flame ionization detector and an HP-5 or HP-INNOWax fused silica capillary column (30 m × 0.25 mm i.d.; film thickness of 25 μm; Hewlett-Packard) was used. The operating conditions were as follows: injector temperature, 180 °C; detector temperature, 250 °C; nitrogen carrier gas flow rate, 2 mL/min; temperature program (for HP-5 column), 40 °C (3 min), raised at 4 °C/min to 240 °C (10 min) and (for HP-INNOWax column), 40 °C (3 min), raised at 4 °C/min to 190 °C (10 min); 1 μL of sample was injected, using a split ratio of 1:5. The amount of volatiles was estimated by computing the areas against that of the internal standard [2,6-di-*tert*-butyl-4-hydroxytoluene (BHT)]. The response factors of all compounds to the FID were assumed to be the same.

Gas Chromatography/Mass Spectrometry (GC/MS) Analysis. GC/MS analyses were carried out using a Hewlett-Packard G1800A chromatograph. The operating conditions were the same as described above, with the exception of a helium carrier gas flow rate of 0.6 mL/min. Mass spectra were obtained by EI ionization at 70 eV over the range of 15−300 mass units, with an ion source temperature of 250 °C.

Aroma Extract Dilution Analysis (AEDA). For AEDA experiments the effluent of the HP-5 column was split with a ratio of 1:1 to the FID and the sniffing port (SGE International, Australia) with the addition of humidified air. The analyzed samples were diluted stepwise from 1:2 up to 1:256 with diethyl ether. Odor description and aroma thresholds were evaluated by three trained assessors.

High-Performance Liquid Chromatographic (HPLC) Analysis. Amino acids in the pyrolysates were detected as their *o*-phthaldialdehyde (OPA) derivatives using a slightly modified method of Marks et al. (1992). Three parallel determinations were done.

Thin-Layer Chromatographic (TLC) Analysis. Aqueous extracts of pyrolysates were analyzed on silica gel plates using either *n*-propanol/water (7:3 v/v) or *n*-butanol/acetic acid/water (4:1:1 v/v/v) as mobile phase. Spots of amino acids were visualized by spraying the plates with ninhydrin reagent (0.2% ethanolic solution).

RESULTS AND DISCUSSION

Degradation of *S*-Propyl-L-cysteine Sulfoxide (PCSO). *S*-Propylcysteine sulfoxide seems to be a rather thermolabile amino acid as are most compounds containing a sulfoxide group. As shown in Table 1, the extent of its degradation was strongly dependent not only on temperature and time of heating but also on water content in the reaction system. It decomposed almost completely during 1 h of heating at temperature of 120 °C in the presence of 10−40% of water. It degraded somewhat more slowly when it was heated dry or conversely in more diluted samples. *S*-Propylcysteine, alanine, and pyruvic acid were positively identified among nonvolatile compounds by means of HPLC and TLC. *S*-Propylcysteine could be formed through the reduction of PCSO by dipropyl thiosulfinate, dipropyl sulfides, or propanethiol. Alanine might be generated via amination of pyruvic acid or via a reductive cleavage of sulfoxide group. On the contrary, neither cysteine, cystine, nor any other OPA- or ninhydrin-positive compounds were detected.

Effect of Temperature. A total of 53 compounds generated from *S*-propylcysteine sulfoxide were identi-

Table 2. Volatile Compounds Generated from *S*-Propylcysteine Sulfoxide at Different Temperatures[a]

		Kovats index		mg/g						
no.	compound identified	HP-5	Wax	80 °C	100 °C	120 °C	140 °C	160 °C	180 °C	200 °C
1	propanethiol	<800	<1000		tr[b]	0.32	3.12	27.08	90.55	131.9
2	2-methyl-2-butenal	<800	1095		0.32	0.50				
3	3-methylthiophene	811	1123				0.02	0.30	0.88	0.94
4	2-methylpyridine	816	1219		0.09	0.66	0.88	1.89	2.99	3.07
5	2-methyl-2-pentenal	853	1160		0.30	0.94				
6	3-methylpyridine	864	1292		0.28	0.32	0.38	0.58	0.84	1.35
7	2,4-dimethylthiophene	885	1190				0.20	1.46	3.24	3.32
8	dipropyl sulfide	894	1069		1.35	1.81	1.93	2.07	2.13	1.65
9	2-ethylpyridine	904	1279			0.24	0.35	0.65	0.99	0.98
10	2,5-dimethylpyridine	926	1461		0.56	2.53	2.82	3.34	4.38	3.07
11	2,3(or 2,4)-dimethylpyridine	945	1317		tr	0.38	0.61	1.08	1.50	1.37
12	4,5-dimethylisothiazole	974	1423					0.22	0.64	0.69
13	3,4-dimethylpyridine	999	1352			0.21	0.68	0.71	1.17	1.31
14	ethyl methylthiazole	1002				0.08	0.10	0.25	0.45	0.36
15	ethyl methylpyridine	1007	1383		0.07	0.84	0.92	1.58	2.26	1.59
16	ethyl methylpyridine	1010	1401		0.17	1.64	2.33	4.34	7.02	5.31
17	trimethylpyridine	1024	1463		0.07	1.72	2.13	2.65	3.62	2.51
18	2-(propylthio)ethylamine	1029						tr	tr	0.05
19	ethyl methylpyridine	1037				0.20	0.34	0.38	0.43	0.45
20	2-methyl-5-ethenylpyridine	1040	1509		tr	0.29	0.36	0.47	0.24	0.15
21	ethyl methylpyridine	1102						0.09	0.62	0.76
22	dipropyl disulfide	1109	1374	0.33	6.52	39.95	141.4	186.6	169.7	70.86
23	methyl propylpyridine	1117	1487		0.24	0.62	0.84	1.27	1.92	1.25
24	dimethyl ethylpyridine	1132	1468		tr	0.38	0.53	0.77	0.94	0.71
25	dimethyl ethylpyridine	1132	1510		0.06	0.54	0.74	0.91	1.15	0.81
26	dimethyl ethylpyridine	1144	1545			0.34	0.33	0.36	0.44	0.32
27	trimethylpyridine	1146	1647			0.43	0.62	0.73	0.87	0.67
28	dimethyl ethylpyridine	1149	1551			2.10	2.23	2.41	3.67	2.60
29	unknown1 ($C_6H_{11}NOS$)	1183							tr	tr
30	substituted pyridine ($C_{10}H_{15}N$)	1200					0.22	0.35	0.50	0.37
31	dimethyl ethylpyridine	1220				0.11	0.21	0.25	0.31	0.21
32	substituted pyridine ($C_{10}H_{15}N$)	1223	1595		0.14	0.36	0.45	0.58	0.83	0.65
33	substituted pyridine ($C_{10}H_{15}N$)	1231				0.48	0.55	0.59	0.57	0.42
34	dimethyl propylpyridine	1241	1635			tr	0.78	1.12	1.11	0.85
35	unknown 2 ($C_8H_{18}S_2$)	1268				0.09	0.16	0.47	0.71	0.45
36	dipropyl trisulfide	1328	1662	0.47	39.78	224.2	119.4	47.25	5.77	2.29
37	methyl (propylthio)pyridine	1374			0.34	3.25	3.52	4.18	5.22	3.55
38	dipropyl thiosulfonate	1388	2124	0.34	7.42	8.14	0.09			
39	methyl (propylthio)pyridine	1411	1990			0.17	0.33	0.38	0.53	0.53
40	dimethyl (or ethyl) (propylthio)pyridine	1462	1984		0.08	1.06	1.13	1.27	1.45	0.97
41	ethyl (propylthio)pyridine	1481				0.28	0.44	0.40	0.52	0.36
42	unknown 3	1496				0.09	0.32	0.37	0.42	0.35
43	dimethyl [(propylthio)methyl]pyridine	1501	2076		0.12	1.86	2.06	2.10	2.23	1.58
44	dimethyl (or ethyl) (propylthio)pyridine	1508	2062		tr	0.08	0.37	0.85	0.91	0.49
45	dimethyl (or ethyl) (propylthio)pyridine	1560				0.73	1.17	1.26	1.43	1.02
46	ethyl methyl (propylthio)pyridine	1564					0.09	0.21	0.73	0.46
47	dipropyl tetrasulfide	1569			0.25	0.55	12.71	6.70	1.29	0.62
48	ethyl methyl (propylthio)pyridine	1577			tr	1.12	1.15	1.17	1.38	0.80
49	unknown 4 ($C_8H_{18}S_3$)	1597	2088			tr	1.42	1.95	2.08	0.79
50	unknown 5 (two isomers)	1694					0.56	1.78	2.20	1.52
51	unknown 6	1774					0.36	0.52	2.13	0.41
52	unknown 7	1793					0.39	1.68	1.30	0.39
53	4-methyl-5-ethylthiazole		1492						0.44	0.47

[a] Heated for 1 h in the presence of 10% water. [b] tr, traces (<0.02 mg/g).

fied as summarized in Table 2. Among them were present 23 sulfur-containing volatiles. Of them, dipropyl disulfide (**22**), dipropyl trisulfide (**36**), and at higher temperatures also propanethiol (**1**) were generated as the wholly predominant volatile compounds. With an exception of a temperature of 80 °C, these accounted for >79% of total volatiles. Whereas the content of propanethiol progressively increased with temperature, the formation of dipropyl disulfide and dipropyl trisulfide reached the maximum at 160 and 120 °C, respectively. Their content then greatly decreased, probably due to their breakdown into propanethiol or alternatively due to their incorporation into nonvolatile polymers. A complex mixture of various pyridines (both alkyl- and alkylthio-substituted) was also formed, in particular at higher temperatures. Thirty-two pyridines were identified in the present study. These are considered to be responsible for the pyridine-like odor detected in the model systems. Generally, pyridines possess less pleasant odors than pyrazines and have not received much attention as flavor components. Due to the lack of standard mass spectra, the identification of some of the isomers is considered to be only tentative. On the contrary, none of the pyrazines were detected under any conditions. Anyway, their formation could greatly increase in the presence of other food components, especially sugars. As can be seen in Table 1, into volatiles was incorporated 50.5−78.7% of the starting amount of sulfur bound in PCSO (at temperatures between 120 and 200 °C). The remaining part of sulfur was undoubtedly bound in the typical degradation products of all S-containing amino acids, for example, hydrogen sulfide, sulfur dioxide, and elemental sulfur, as well as in various pigments and other macromolecules.

Table 3. Volatile Compounds Generated from *S*-Propylcysteine Sulfoxide at Different Water Contents[a]

		mg/g								
no.	compound identified	0%	5%	10%	20%	40%	80%	90%	95%	98%
1	propanethiol	tr[b]	0.14	0.32	0.47	0.52	0.25	0.09	tr	tr
2	2-methyl-2-butenal		1.25	0.50	0.07	0.34	1.55	2.07	6.97	0.09
4	2-methylpyridine		1.08	0.66	0.35	0.34	0.22	0.13		
5	2-methyl-2-pentenal		1.78	0.94	0.26	1.50	4.30	3.56	1.50	0.04
6	3-methylpyridine		0.27	0.32	0.14	tr				
8	dipropyl sulfide		2.78	1.81	0.83	0.47	0.34	0.20		
9	2-ethylpyridine		0.32	0.24	0.11	0.08				
10	2,5-dimethylpyridine		3.15	2.53	1.96	1.90	1.19	0.49	0.12	
11	2,3(or 2,4)-dimethylpyridine		0.56	0.38	0.18	0.17	0.16			
13	3,4-dimethylpyridine		0.34	0.21	0.08	0.05				
14	ethyl methylthiazole		0.19	0.08	0.12	0.17	0.09			
15	ethyl methylpyridine		0.90	0.84	0.66	0.58	0.27	0.13		
16	ethyl methylpyridine		2.08	1.64	1.61	1.63	1.53	1.18	0.30	
17	trimethylpyridine		1.72	1.72	1.62	1.59	0.77	0.19		
19	ethyl methylpyridine		0.24	0.20	tr	tr				
20	2-methyl-5-ethenylpyridine			0.29	0.23	0.22	0.16			
22	dipropyl disulfide	1.44	36.50	39.95	41.61	44.41	45.61	29.02	9.47	1.26
23	methyl propylpyridine		0.74	0.62	0.66	0.64	0.57	0.48	0.42	tr
24	dimethyl ethylpyridine		0.31	0.38	0.40	0.45	0.07			
25	dimethyl ethylpyridine		0.46	0.54	0.52	0.60	0.13			
26	dimethyl ethylpyridine		0.34	0.34	0.24	0.14				
27	trimethylpyridine		0.40	0.43	0.38	0.31				
30	substituted pyridine ($C_{10}H_{15}N$)		1.52	2.10	1.74	1.59	1.12	0.73	0.26	
31	dimethyl ethylpyridine		0.08	0.11	0.17	0.20	0.26	0.29		
32	substituted pyridine ($C_{10}H_{15}N$)		0.56	0.36	0.39	0.27				
33	substituted pyridine ($C_{10}H_{15}N$)		0.47	0.48	0.39	0.40	0.38	0.25		
35	unknown 2 ($C_8H_{18}S_2$)		0.11	0.09	0.05					
36	dipropyl trisulfide	1.67	216.8	224.2	214.7	209.7	208.7	163.0	38.98	2.71
37	methyl (propylthio)pyridine	0.03	3.21	3.25	2.60	2.11	1.32	0.85	0.16	
38	dipropyl thiosulfonate		6.51	8.14	7.79	7.88	7.60	7.54	5.96	3.56
39	methyl (propylthio)pyridine		0.23	0.17						
40	dimethyl (or ethyl) (propylthio)pyridine		0.99	1.06	0.75	0.51	0.29	0.18		
41	ethyl (propylthio)pyridine		0.30	0.28	0.18					
42	unknown 3		0.03	0.09	0.05					
43	dimethyl [(propylthio)methyl]pyridine		1.71	1.86	1.48	1.02	0.56	0.29		
44	dimethyl (or ethyl) (propylthio)pyridine		0.05	0.08	0.07	tr				
45	dimethyl (or ethyl) (propylthio)pyridine		0.65	0.73	0.46	0.35				
47	dipropyl tetrasulfide	0.03	0.36	0.55	0.66	0.69	0.78	0.56	0.37	
48	ethyl methyl (propylthio)pyridine		0.83	1.12	0.99	0.71	0.09			

[a] Heated at 120 °C for 1 h. [b] tr, traces (<0.02 mg/g).

Effect of Time of Heating. Naturally, the stability of PCSO decreased with time of heating. On the other hand, the total amount of volatiles initially increased with time, reached the maximum in 15 min, and decreased somewhat with a prolonged time of heating (see Table 1). It can be explained by the formation of various pigments and other macromolecules (in part by self-condensation, in part by reaction with other small molecules, e.g., ammonia, acetaldehyde, and hydrogen sulfide).

Effect of Water Content. As has been already shown in our previous studies (Kubec et al., 1997, 1998; Kubec and Velíšek, 1998), the content of water in the reaction system is one of the crucial parameters, which considerably influences the degradation rate as well as breakdown product structure (Table 3). The formation of volatiles was maximized in the presence of 5−80% of water and decreased greatly at both higher and lower water amounts (see Table 1). In that the fresh onion contains ∼90% of water, it can be expected that the amount of volatiles formed during cooking will be relatively small. In contrast, on frying, baking, or roasting or during a commercial hot-air dehydration, the water content greatly decreases (especially in the outer layers) and the thermal generation of volatiles from PCSO becomes much more significant.

Proposed Volatile Formation Pathways. In general, PCSO decomposes in a similar way to its methyl analogue, *S*-methylcysteine sulfoxide (Kubec et al., 1998). It breaks down into propanesulfenic acid and α-aminoacrylic acid, which can spontaneously hydrolyze to give ammonia and pyruvic acid. The self-condensation of propanesulfenic acid leads to the formation of dipropyl thiosulfinate. It is reasonable to assume its formation, despite its not being detected under any conditions used in our experiments. Thiosulfinates are known to decompose on heating or attempted GC analysis as shown by Block et al. (1992b). They found that decomposition of the thiosulfinates can occur both in the injection port (homogeneously under gas-phase conditions, heterogeneously on heated surfaces) and in the GC column. Mild oven/injector temperature conditions and a short wide-bore column are crucial to minimize their decomposition. Unfortunately, we were not able to analyze dipropyl thiosulfinate using our narrow columns. Total decomposition of the standard sample was observed under any conditions (even when an injection temperature of 120 °C was used). Thus, we could not determine if thiosulfinate decomposed on heating of the sample or during GC analysis. Although dipropyl thiosulfinate was not positively identified, it appeared to be a key breakdown product. It can readily decompose into dipropyl disulfide and dipropyl thiosulfonate, and its self-degradation is probably the most important pathway leading to dipropyl trisulfide formation (Block and O'Connor, 1973; Block and Weidman, 1973). However, the trisulfide

Table 4. Volatile Compounds Generated from *S*-Propylcysteine at Different Temperatures[a]

		Kovats index		mg/g						
no.	compound identified	HP-5	Wax	80 °C	100 °C	120 °C	140 °C	160 °C	180 °C	200 °C
16	ethyl methylpyridine	1010	1401					tr[b]	0.45	0.72
18	2-(propylthio)ethylamine	1029						0.78	8.50	58.25
22	dipropyl disulfide	1109	1374	0.02	0.03	0.05	0.07	0.38	29.56	36.19
23	methyl propylpyridine	1117	1487					tr	1.54	0.87
29	unknown 1 ($C_6H_{11}NOS$)	1183							0.09	3.78
33	substituted pyridine ($C_{10}H_{15}N$)	1231								0.51
36	dipropyl trisulfide	1328	1662	tr	tr	0.03	0.05	0.11	0.13	0.20
37	methyl (propylthio)pyridine	1374							0.23	1.79
38	dipropyl thiosulfonate	1388	2124						0.89	1.61
39	methyl (propylthio)pyridine	1411	1990							0.48
43	dimethyl [(propylthio)methyl]pyridine	1501	2076							0.23
46	ethyl methyl (propylthio)pyridine	1564							0.08	0.76
54	2-(propylthio)acetaldehyde		1688						tr	0.08
	total			0.02	0.03	0.08	0.12	1.27	41.5	105.4
	conversion of sulfur[c] (%)			0.01	0.01	0.02	0.02	0.2	8.5	18.7
	undecomposed PrCys (%)			97.2	89.3	82.9	77.4	71.5	66.6	43.2

[a] Heated for 1 h in the presence of 10% water. [b] tr, traces (<0.02 mg/g). [c] Expressed as moles of sulfur bound in volatiles per mole of PrCys.

Table 5. Mass Spectra of Some Sulfur-Containing Pyridines, Unusual and Unknown Compounds Arising from Thermally Degraded *S*-Propylcysteine and *S*-Propylcysteine Sulfoxide

no.	compound	MS, *m/e* (relative intensity)
18	2-(propylthio)ethylamine	119 (14, M^+), 90 (30), 88 (5), 77 (3), 75 (5), 61 (17), 48 (9), 45 (9), 43 (14), 39 (10), 30 (100)
29	unknown 1 ($C_6H_{11}NOS$)	145 (9, M^+), 128 (44), 113 (34), 99 (6), 95 (5), 86 (60), 74 (53), 70 (34), 54 (10), 45 (15), 43 (38), 41 (32), 39 (13), 30 (100)
35	unknown 2 (see spectra of **42** and **49**)	178 (19, M^+), 138 (3), 103 (100), 93 (3), 87 (2), 61 (54), 59 (12), 43 (26), 41 (19), 27 (12)
37	methyl (propylthio)pyridine	167 (97, M^+), 152 (2), 138 (44), 125 (100), 124 (30), 110 (2), 97 (15), 92 (22), 84 (18), 65 (10), 53 (24), 43 (30), 41 (24), 39 (25)
39	methyl (propylthio)pyridine	167 (91, M^+), 152 (2), 138 (31), 125 (100), 124 (19), 111 (2), 97 (16), 92 (21), 80 (14), 79 (15), 65 (12), 53 (17), 43 (26), 41 (23), 39 (23)
40	dimethyl (or ethyl) (propylthio)pyridine	181 (69, M^+), 180 (31), 166 (2), 152 (12), 139 (22), 138 (100), 124 (9), 111 (8), 106 (7), 94 (7), 77 (9), 67 (4), 51 (5), 43 (12), 41 (16), 39 (13)
41	ethyl (propylthio)pyridine	181 (100, M^+), 152 (29), 139 (90), 140 (50), 124 (7), 111 (9), 106 (18), 97 (24), 94 (11), 77 (17), 53 (33), 43 (12), 39 (16)
42	unknown 3 (M = ?) (see spectra of **35** and **49**)	195 (2), 120 (26), 103 (100), 93 (2), 73 (2), 61 (48), 59 (14), 45 (8), 43 (36), 41 (17), 27 (9)
43	dimethyl [(propylthio)-methyl]pyridine	195 (10, M^+), 181 (4), 167 (0.3), 152 (3), 121 (9), 120 (100), 91 (4), 77 (8), 65 (4), 53 (3), 41 (3)
44	dimethyl (or ethyl) (propylthio)pyridine	181 (100, M^+), 166 (2), 152 (49), 139 (92), 138 (16), 124 (5), 106 (37), 97 (19), 77 (14), 67 (12), 53 (14), 43 (19), 41 (25), 39 (19)
45	ethyl (propylthio)pyridine	181 (76, M^+), 152 (39), 139 (88), 138 (28), 121 (100), 111 (19), 106 (42), 93 (19), 77 (27), 67 (19), 53 (24), 43 (32), 41 (43), 39 (26)
46	ethyl methyl (propylthio)pyridine	195 (100, M^+), 181 (15), 166 (53), 153 (87), 152 (40), 139 (20), 138 (46), 125 (8), 120 (8), 106 (10), 91 (11), 77 (22), 65 (12), 51 (9), 43 (22), 41 (25)
47	dipropyl tetrasulfide	214 (43, M^+), 182 (2), 172 (2), 150 (3), 139 (2), 130 (1.5), 108 (37), 107 (8), 97 (4), 75 (11), 73 (32), 64 (6), 43 (100), 41 (41), 39 (12)
48	ethyl methyl (propylthio)pyridine	195 (83, M^+), 194 (39), 180 (6), 166 (9), 153 (18), 152 (100), 138 (15), 134 (27), 121 (29), 108 (15), 106 (35), 91 (14), 77 (13), 65 (12), 43 (23), 41 (33)
49	unknown 4 ($C_8H_{18}S_3$) (see spectra of **35** and **42**)	210 (1.5, M^+), 181 (1), 167 (1), 103 (100), 93 (4), 89 (3), 73 (6), 61 (72), 43 (50), 41 (24)
50	unknown 5 (two isomers)	229 (4), 215 (13), 186 (1), 172 (2), 154 (2), 140 (4), 128 (3), 114 (6), 102 (100), 89 (7), 87 (8), 69 (14), 61 (18), 60 (94), 56 (16), 43 (21), 41 (26)
51	unknown 6	151 (12), 149 (100), 107 (14), 103 (5), 73 (80), 59 (31), 43 (24), 41 (38)
52	unknown 7	151 (5), 149 (53), 107 (10), 105 (5), 73 (100), 64 (3), 45 (15), 43 (45), 41 (30), 39 (8)
54	2-(propylthio)acetaldehyde	118 (89, M^+), 100 (1), 89 (100), 75 (18), 74 (39), 61 (65), 59 (11), 55 (10), 47 (57), 45 (26), 43 (71), 41 (50), 39 (17)

generation could be more complex, and a certain amount might be formed even via parallel interaction of hydrogen sulfide with propanesulfenic acid and/or dipropyl thiosulfonate. Pyruvic acid can easily decarboxylate to acetaldehyde, by whose aldolization 2-methyl-2-butenal (**2**) is generated. The second aldehyde identified, 2-methyl-2-pentenal (**5**), probably arises through the aldolization of acetaldehyde and propionaldehyde. These carbonyls are proposed to participate significantly in the formation of pyridines found in model systems. Their condensation with ammonia or primary amines (including amino acids) leads to the complex mixture of various alkyl-substituted pyridines (Suyama and Adachi, 1980).

Sensory Properties. Color formation (usually dark brown) during the thermal decomposition of PCSO was very intensive, indicating that besides the formation of volatile compounds some high molecular weight nonvolatile polymers and pigments should also be generated. The overall odor of degraded PCSO samples could be generally described as quite pleasant, resembling boiled onion or leek. Anyway, at higher temperatures burnt and pyridine-like notes prevailed. A sample with 80% water was subjected to AEDA to determine the contribution of the individual components to the overall aroma (Grosch, 1993; Etiévant et al., 1994). Among 26 volatiles identified in the evaluated sample (see Table

3, sixth column), only dipropyl disulfide, dipropyl trisulfide, and dipropyl thiosulfonate were detected by means of an olfactometry detector as important sensory-impact compounds. Dilution factors (FD) of dipropyl disulfide, trisulfide, and thiosulfonate were determined to be 4, 128, and 2, respectively. All of these possess a typical onion-like or leek-like odor. These results are very similar to those obtained in analogous experiments with *S*-methylcysteine sulfoxide (Kubec et al., 1998).

Degradation of *S*-Propyl-L-cysteine (PrCys). *S*-Propyl-L-cysteine appeared to be considerably more stable compared with PCSO. Naturally, its stability decreased with temperature; nevertheless, significant amounts of volatiles were formed as late as at temperatures beyond 180 °C (Table 4). The differences in the stability and yields of volatile compounds between PCSO and PrCys probably result from different degradation pathways of these closely related amino acids. Unlike PCSO, *S*-propylcysteine lacks the extremely thermolabile sulfoxide moiety. Thus, decarboxylation and deamination are the most important mechanisms involved in its thermal breakdown at temperatures <160 °C. 2-(Propylthio)ethylamine (**18**), along with dipropyl disulfide the most abundant volatile, arose as a result of *S*-propylcysteine decarboxylation. This amine could probably serve as a source of propylthio moiety in the formation of propylthio-substituted pyridines (**37**, **39**, **43**, **46**). On the contrary, 2-(propylthio)acetaldehyde (**54**), a product of the Strecker degradation of PrCys, was found only in small amounts. This interesting aldehyde, not previously reported in the literature, possesses a pleasant grassy odor. However, in our hands it appeared to be quite unstable and, on standing by itself for several weeks in the freezer, spontaneously polymerized to form dark brown pigments. Also, its sensory properties became gradually less acceptable and pleasant. With respect to its reactivity, it could be assumed that most of the arising 2-(propylthio)acetaldehyde readily reacted with ammonia and other amino compounds, giving (propylthio)pyridines and various polymers. Beyond a temperature of 160 °C a homolytic cleavage of the labile C−S bond can occur on a large scale, resulting in the formation of propylthio radicals. These subsequently combine giving dipropyl disulfide (**22**), one of the major volatile compound identified. As can be seen in Table 4, into volatiles was incorporated only 8.5 and 18.7% of the starting amount of sulfur bound in PrCys (at temperatures of 180 and 200 °C, respectively). The remaining part of sulfur was probably present in hydrogen sulfide, sulfur dioxide, and various macromolecules. Anyway, no formation of cysteine, cystine, or any other OPA- or ninhydrin-positive compounds was observed under any conditions using HPLC or TLC, respectively.

CONCLUSIONS

On the basis of our results it seems to be evident that the products of nonenzymatic breakdown of *S*-propylcysteine sulfoxide participate in developing the characteristic flavor of processed *Allium* vegetables. On the other hand, the contribution of *S*-propylcysteine is considerably smaller, with respect to its thermal stability and negligible content in vegetables. Amounts of volatiles formed are strongly dependent on temperature and time of heating as well as on water content in the reaction system. The importance of nonenzymatic degradation of these amino acids becomes apparent especially at higher temperatures when water content can decrease, for example, during onion dehydration. The aroma precursors appeared to be rather thermolabile compounds, and thus, the disproportionately high temperatures and long times used during a commercial dehydration process can lead to their great losses and to the deterioration of organoleptic properties. Finally, many factors other than those investigated in the present study are involved in real food systems. We can expect their decomposition to be considerably more complex in the presence of other food components, such as sugars and lipids.

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Received for review September 2, 1998. Accepted December 23, 1998. This work was supported in part by the Research Grant 509/94/0318 from the Grant Agency of the Czech Republic.

JF980974Z