

Supercritical Carbon Dioxide Extraction of Onion Flavors and Their Analysis by Gas Chromatography-Mass Spectrometry

Nirmal K. Sinha,[†] Daniel E. Guyer,^{*†} Douglas A. Gage,[‡] and Carl T. Lira[§]

Departments of Agricultural Engineering, Biochemistry, and Chemical Engineering,
Michigan State University, East Lansing, Michigan 48824

Extraction with supercritical carbon dioxide (SC-CO₂) produced fresh onion-like flavor components from onions. Combined gas chromatography-mass spectrometry analysis of SC-CO₂ onion extract showed the presence of 28 sulfur-containing compounds, including diallyl thiosulfinate (or its isomer, di-1-propenyl thiosulfinate), propyl methanethiosulfonate, dithiin derivatives, diallyl sulfide, diallyl trisulfide, and 6 other tentatively identified compounds. A commercial steam-distilled onion oil analyzed under similar conditions did not contain detectable amounts of the compounds listed above but did have 13 other compounds in common with the SC-CO₂ onion extract. The flavor compounds methyl propyl trisulfide, dipropyl trisulfide, and dipropyl tetrasulfide were detected only in the commercial steam-distilled onion oil and were present in high concentration.

INTRODUCTION

Supercritical carbon dioxide extraction (SC-CO₂), because of its greater solvency, extraction properties at moderate temperatures (25–60 °C), nontoxicity, and minimal reaction with food constituents, can be a viable separation technique in the food industry (Hubert and Vitzthun, 1980; Rizvi et al., 1986). Recent papers suggest its potential in the extraction of lipids and cholesterol from dried eggs (Froning et al., 1990) and in the extraction of annatto pigments (Chao et al., 1991). What distinguishes this process from other separation techniques is the ability to change and "fine tune" its solubilizing power by controlling pressure and temperature. Low operation cost is another attractive feature since the process recycles solvent and can utilize CO₂, a relatively inexpensive material. In this study, SC-CO₂ was used to extract onion flavors. Combined gas chromatography-mass spectrometry (GC-MS) was then employed to identify the individual flavor components in the extract.

The characteristic flavor of onions comes primarily from volatile organic sulfur compounds released enzymatically by the action of alliinase (alliin alkyl-sulfenate-lyase; EC 4.4.1.4) on several nonvolatile, odorless amino acid precursors, namely (+)-*S*-methyl-, (+)-*S*-propyl-, and *trans*-(+)-*S*-1-propenyl-L-cysteine sulfoxides, when the onion bulbs are chopped or crushed (Whitaker, 1976). The primary reaction products of these amino acids are thio-sulfonates, which dissociate to produce various sulfides containing methyl, propyl, and propenyl groups, thiophene derivatives, and other sulfur-containing heterocycles (Carson, 1987). The alkyl thiosulfonates (methyl methane-, propyl methane-, and propyl propanethiosulfonates) have been associated with fresh onion-like flavors, while propyl- and propenyl-containing di- and trisulfides have been associated with cooked onions or steam-distilled onion oils (Boelens et al., 1971).

Onion and onion flavors (onion oil) are important seasonings widely used in food processing. Currently the majority of onion oils used in U.S. food production are

imported. These products, which are usually steam distilled, lack fresh onion flavors, and their quality varies depending on the origin of production and are oftentimes undesirable or inconsistent.

Previous studies (Brodnitz et al., 1969; Boelens et al., 1971; Mazza et al., 1980; Kallio and Salorinne, 1990; Kuo et al., 1990) have reported flavor components of head space, solvent extracts, and distilled onion oils. Block (1985) reviewed the chemistry of garlic and onion. Block et al. (1986) reported synthesis of antithrombotic organosulfur compounds from garlic. The objective of this study was to use a low-temperature extraction process, SC-CO₂, to extract fresh onion flavors. A commercial steam-distilled onion oil was used as a representative sample for simple comparison and differentiation. However, our effort here is not directed toward a comparison of the performance of steam distillation vs SC-CO₂ extraction parameters or a presentation of the optimal SC-CO₂ process parameters for this application but to the presentation of a new flavor and its characteristics obtained by SC-CO₂ extraction.

MATERIALS AND METHODS

Onion Preparation. Michigan-grown onions (*Allium cepa* L.) purchased from a local store were used. The onion bulbs, weighing approximately 200 g, were peeled, cut, and immediately processed with an Acme Juicerator (Model 6001, Acme Juicer Manufacturing Co., Sierra Madre, CA). The onion juice was held at 20–22 °C in a 250-mL glass-stoppered Erlenmeyer flask for 12–15 h before flavor extraction using the SC-CO₂ process. Juice was used in this phase of the project as it allowed for good mixing with the solvent in the extraction vessels and prevented clogging of the capillary restrictor. A sample of steam-distilled commercial onion oil was obtained from a flavoring company and used for simple comparison and differentiation.

SC-CO₂ Equipment and Extraction. Industrial grade CO₂ (AGA gas, 99.5% purity) from a gas cylinder was compressed with a gas booster (Haskel, Inc.) and stored in a 0.5-L reservoir. A pressure regulator positioned between the reservoir and the extraction vessels controlled the extraction pressure. Extraction vessels were fabricated from stainless steel rods which had been bored (16 mm i.d. × 25 mm o.d. × 150 mm length). Three vessels were connected in series to provide a total volume of approximately 100 mL and placed in a temperature-controlled water bath. Each vessel was filled with approximately 20 mL of onion juice prior to pressurization. A 3.2 mm o.d. × 2.70 m length coil of tubing served to preheat the CO₂ before it entered the extraction vessels.

* Author to whom correspondence should be addressed.

[†] Department of Agricultural Engineering.

[‡] Department of Biochemistry.

[§] Department of Chemical Engineering.

Onion flavors were collected in four 25-mL test tubes connected in series. The first collection trap contained a flow restrictor fabricated from 25 μ m i.d. fused silica capillary tubing and was not temperature controlled. The subsequent collection traps were immersed in an ice bath to capture escaping volatiles from the first trap. CO₂ flow was monitored with a flow meter and wet test meter.

The extraction was commenced by slowly raising the pressure in the extraction vessels while the system outlet was closed. After extraction pressure was reached (approximately 10 min), the outlet valve was opened to commence flow. The extraction was performed in duplicate at 35 °C and 204 atm. Flow rate of CO₂ through the extraction vessels and the collection traps was 100–150 STP mL/min. An individual extraction run took approximately 5 h. The operating conditions were selected following a series of trial runs to achieve a measurable recovery of onion flavors for analysis.

Flavor Analysis by GC-MS. Samples from the SC-CO₂ extraction and the commercial onion oil were analyzed in duplicate by GC-MS. The GC-MS system consisted of a Hewlett-Packard HP-5970 mass selective detector connected via a heated interface with a HP-5890 gas chromatograph. A 30-m fused-silica DB-5 column of 0.2 mm i.d. (J&W Scientific, Folsom, CA) was used to separate the flavor components. A 1- μ L methylene chloride solution of SC-CO₂ onion extract or steam-distilled commercial onion oil (ca. 0.1 mg of supercritical onion extract or commercial onion oil was diluted with 100 μ L of methylene chloride) was injected for analysis. The operating conditions were as follows: injector temperature, 280 °C; helium carrier gas flow rate, 1 mL/min; oven temperature, 30–200 °C at 2 °C/min linear. The mass spectra were obtained by electron ionization at 70 eV. Kovat retention indices (I_K) were calculated against the elution of C₇–C₂₆ hydrocarbons coinjected with the samples.

RESULTS AND DISCUSSION

The onion extract produced through the SC-CO₂ process had characteristic fresh onion-like smell in contrast to the rather nonpleasing smell of commercial onion oil. Table I shows the flavor components identified by GC-MS analysis along with their mass spectral data (including the isotope distribution pattern of the molecular ion region) and the relative peak area of the total peak area for all flavor components from both SC-CO₂ onion extract and commercial onion oil samples. The identification of the flavor compounds is based on comparisons of mass spectral data with published works, and in a few cases tentative identifications were made by direct interpretation of the mass spectral data. Where definitive structural characterization could not be made, possible isomeric structures are indicated.

The SC-CO₂ onion extract contained many flavoring compounds which were not detected in the steam-distilled commercial onion oil. Notable among these are diallyl thiosulfinate (allicin) (24) (CH₂=CHCH₂SOSCH₂-CH=CH₂) or its isomer, di-1-propenyl thiosulfinate (CH₃-CH=CHSOSCH=CHCH₃), and propyl methanethiosulfonate (CH₃CH₂CH₂S₂O₂CH₃) (17) (Table I). To our knowledge this is the first time diallyl thiosulfinate has been reported from onions. Bayer et al. (1989) reported five thiosulfates (*trans*-methyl 1-propenylthiosulfinate, *cis*-methyl 1-propenylthiosulfinate, *cis*-propyl 1-propenylthiosulfinate, *trans*-propyl 1-propenylthiosulfinate, dipropyl thiosulfinate) in the chloroform extract of onion juice (*A. cepa* L.), but they did not report diallyl thiosulfinate. The mass spectral data and the isotope peaks in the molecular ion region of compound diallyl thiosulfinate appear to be consistent with the molecular formula of C₆H₁₀OS₂ (Table I). However, in the absence of a synthesized reference compound or supporting NMR or IR spectra, this identification of diallyl thiosulfinate or its isomeric compound is only tentative.

Brodnitz et al. (1971), using IR and NMR analysis, reported diallyl thiosulfinate to be a major constituent of

fresh garlic extracts. These authors indicated that during gas chromatography diallyl thiosulfinate undergoes dehydration, forming two isomeric disulfides: 3-vinyl-1,2-dithi-5-ene and 3-vinyl-1,2-dithi-4-ene. Nishimura et al. (1988) reported 3,4-dihydro-3-vinyl-1,2-dithiin and 2-vinyl-4H-1,3-dithiin in *Allium victorialis* L. These authors also indicated that the decomposition of diallyl thiosulfinate in methanol at room temperature for 7 days produced vinylidithiins (3,4-dihydro-3-vinyl-1,2-dithiin and 2-vinyl-4H-1,3-dithiin), diallyl sulfide, and diallyl trisulfide.

In the head space of crushed onions, Kallio and Salorinne (1990) reported the tentative presence of 3-ethenyl-1,2-dithi-4-ene and 3-ethenyl-1,2-dithi-5-ene. In the present study diallyl thiosulfinate (or its isomer), 3-ethenyl-1,2-dithi-4-ene (20), 3-ethenyl-1,2-dithi-5-ene (15), 3,4-dihydro-3-vinyl-1,2-dithiin (21), and diallyl trisulfide (28) have been found in the SC-CO₂ onion extracts (Table I).

During this study the analysis of SC-CO₂ onion extract was repeated over a period of 3 months to determine if diallyl thiosulfinate (or its isomer) was still present. Diallyl thiosulfinate and dithiin derivatives were still detected after 3 months. However, diallyl trisulfide, which was present in very small quantities (peak area 0.07%) when samples were analyzed within 1 week of extraction (for which the data are reported here), was not detected in the SC-CO₂ onion extract analyzed after being stored for 3 months at 20–22 °C. The presence of diallyl thiosulfinate and also dithiin derivatives in this study suggests that the SC-CO₂ process is able to extract a significant amount of diallyl thiosulfinate. This is perhaps not possible using other methods of extraction, particularly when heat is involved, so that even if a portion of this compound is converted/rearranged to dithiin derivatives during analysis, enough of the compound remains in the SC-CO₂ extracts to be detected.

Thiosulfonates are secondary products arising from thiosulfonates (Abraham et al., 1976). The presence of methyl methanethiosulfonate, propyl methanethiosulfonate, and propyl propanethiosulfonate in dichloromethane extracts of freshly chopped onions has been reported by Boelens et al. (1971). These authors suggest that the absence of these compounds in steam-distilled onion oil is a result of their being soluble in water; thus, they are present in the water layer and do not get transferred to the organic phase during the steam distillation process. In this study only propyl methanethiosulfonate was identified and only in the SC-CO₂ extracts (Table I).

Several other flavor compounds such as dimethyl disulfide (4), 1,3-propanedithiole (6, 7), diallyl sulfide (9), methyl 5-methylfuryl sulfide (23), dibenzothiophene (30), methyl 3,4-dimethyl-2-thienyl disulfide (31), its isomer (33), and an unknown compound (34) containing two sulfur atoms (based on molecular ion isotope distribution) were detected only in the supercritical onion extracts. The identifications of dimethyl disulfide, diallyl sulfide, methyl 5-methylfuryl sulfide, dibenzothiophene, and methyl 3,4-dimethyl-2-thienyl disulfide are based on spectral comparisons with the mass spectral data of Heller and Milne (1978), Wu et al. (1982), Stenhagen et al. (1969), Vernin et al. (1986), Weast and Grasselli (1989), and Kuo et al. (1990), respectively. The identification of 1,3-propanedithiole was based on interpretation of its mass spectral data.

Kuo et al. (1990) reported the presence of methyl 3,4-dimethyl-2-thienyl disulfide [I_K (HP-1), 100% dimethyl polysiloxane column, 1460] in steam-distilled onion oils and suggested thermal reactions were responsible for the formation of these volatile polysulfides. Contrary to their finding, methyl 3,4-dimethyl-2-thienyl disulfide [I_K (DB-

Table I. Flavor Components Analyzed by GC-MS in SC-CO₂ Onion Extracts and in a Commercial Onion Oil

no.	compound	molecular formula and mass (M ⁺)	I _K (DB-5)	mass spectral data ^a	% peak area ^b	
					SC-CO ₂ extract	commercial onion oil
1	1-propanethiol	C ₃ H ₈ S, 76	727	78 (4.4), 77 (4.3), 76 (100), 61 (14.5), 47 (89.5), 46 (25.7), 43 (89.5), 41 (89.7)	0.23	0.56
2	methylthiirane	C ₃ H ₆ S, 74	729	76 (6.0), 75 (4.9), 74 (100), 59 (17.1), 57 (9.6), 47 (17.0), 46 (18.3), 45 (73.4), 41 (90.7)	2.41	1.10
3	methanedithiol ^c	CH ₄ S ₂ , 80	740	82 (8.8), 81 (3.4), 80 (100), 64 (34.4), 47 (19.2), 46 (20.2), 45 (35.0)	2.00	0.85
4	dimethyl disulfide	C ₂ H ₆ S ₂ , 94	770	96 (13.3), 95 (5.8), 94 (100), 79 (58.8), 64 (12.3), 61 (14.7), 48 (10.5), 46 (29.7), 45 (58.1)	0.25	ND ^d
5	methyl ethyl disulfide	C ₃ H ₈ S ₂ , 108	845	110 (7.0), 109 (4.7), 108 (79.6), 79 (13.4), 66 (33.4), 64 (12.7), 47 (13.3), 45 (23.4), 43 (100)	0.70	1.87
6	1,3-propanedithiol ^c	C ₃ H ₆ S ₂ , 106	853	108 (9.4), 107 (4.7), 106 (98.1), 78 (20.8), 66 (12.9), 64 (35.6), 51 (5.9), 47 (18.5), 45 (100), 41 (73.6)	0.43	ND
7	1,3-propanedithiol ^c	C ₃ H ₆ S ₂ , 106	861	108 (9.5), 107 (5.4), 106 (98.9), 78 (20.3), 66 (12.2), 64 (33.4), 51 (5.8), 47 (18.2), 45 (100), 41 (73.2)	0.56	ND
8	3,4-dimethylthiophene	C ₈ H ₈ S, 112	888	114 (3.9), 113 (9.0), 112 (76.3), 111 (100), 97 (51.4), 79 (6.4), 77 (13.7), 69 (9.7), 67 (6.7), 51 (5.0), 45 (26.1)	5.97	0.46
9	diallyl sulfide	C ₆ H ₁₀ S, 114	907	116 (1.7), 115 (2.7), 114 (34.1), 113 (6.3), 101 (4.4), 99 (100), 84 (10.1), 73 (16.2), 72 (2.5), 71 (7.5), 65 (25.9), 60 (12.9), 59 (5.5), 55 (5.9), 45 (22.2), 41 (15.7)	0.44	ND
10	methyl propyl disulfide	C ₄ H ₁₀ S ₂ , 122	913	124 (6.0), 123 (4.1), 122 (68.8), 80 (100), 64 (16.8), 60 (12.0), 47 (15.3), 46 (13.2), 45 (38.0), 43 (46.8), 41 (50.1)	1.07	2.81
11	methyl 1-propenyl disulfide	C ₄ H ₈ S ₂ , 120	922	122 (15.3), 121 (5.5), 120 (89.0), 105 (4.5), 93 (3.0), 89 (22.0), 87 (8.0), 80 (22.6), 75 (40.2), 72 (46.8), 61 (15.4), 49 (10.6), 47 (32.3), 46 (14.3), 45 (100), 41 (58.1)	0.72	1.00
12	dimethyl trisulfide	C ₂ H ₆ S ₃ , 126	950	128 (13.2), 127 (4.5), 126 (100), 111 (17.1), 79 (56.3), 64 (25.3), 61 (7.4), 47 (29.2), 46 (18.3), 45 (53.7)	0.43	2.17
13	dipropyl disulfide	C ₆ H ₁₄ S ₂ , 150	1107	152 (3.0), 151 (2.8), 150 (31.9), 108 (27.7), 75 (4.8), 61 (1.4), 73 (8.0), 66 (10.9), 47 (8.9), 45 (15.6), 43 (100), 41 (42.6)	1.18	22.48
14	1-propenyl propyl disulfide	C ₆ H ₁₂ S ₂ , 148	1116	150 (7.2), 149 (6.6), 148 (80.0), 106 (76.4), 73 (32.8), 72 (29.4), 71 (18.8), 64 (30.9), 61 (16.5), 47 (19.9), 45 (73.6), 43 (60), 41 (100)	0.52	7.24
15	3-ethenyl-1,2-dithi-5-ene	C ₆ H ₁₀ S ₂ , 146	1132	148 (8.4), 147 (3.6), 146 (39.2), 113 (100), 112 (44.6), 111 (68.6), 97 (50.8), 85 (13.1), 79 (31.3), 77 (21.0), 59 (11.8), 45 (43.2), 41 (18.6)	0.70	ND
16	methyl propyl trisulfide	C ₄ H ₁₀ S ₃ , 154	1150	156 (12.8), 155 (6.3), 154 (100), 112 (66.3), 79 (23.6), 64 (28.0), 47 (59.8), 46 (15.3), 45 (37.4), 43 (65.5), 41 (48.7)	ND	14.88
17	propyl methanethio-sulfonate	C ₄ H ₁₀ S ₂ O ₂ , 154	1156	156 (11.7), 155 (6.3), 154 (86.1), 138 (21.7), 112 (58.4), 97 (18.1), 79 (23.3), 73 (21.7), 69 (67.8), 64 (36.9), 47 (58.6), 45 (52.4), 43 (71.4), 41 (100)	0.90	ND
18	methyl 1-propenyl trisulfide ^c	C ₄ H ₈ S ₃ , 152	1160	154 (5.0), 153 (1.9), 152 (31.9), 88 (46.8), 73 (39.7), 64 (14.6), 47 (21.9), 45 (100), 41 (17.4)	ND	1.98
19	methyl 1-propenyl trisulfide ^c	C ₄ H ₈ S ₃ , 152	1170	154 (4.4), 152 (31.8), 111 (23.7), 88 (46.6), 73 (35.3), 64 (16.0), 47 (19.3), 45 (100)	0.82	ND
20	3-ethenyl-1,2-dithi-4-ene	C ₆ H ₁₀ S ₂ , 146	1180	148 (5.6), 147 (3.6), 146 (37.1), 113 (100), 112 (31.9), 111 (45.1), 97 (38.1), 85 (12.6), 79 (32.5), 77 (19.5), 59 (11.2), 45 (37.8), 41 (18.4)	0.76	ND
21	3,4-dihydro-3-vinyl-1,2-dithiin	C ₆ H ₈ S ₂ , 144	1197	146 (9.1), 145 (9.8), 144 (100), 129 (15.9), 111 (85.9), 99 (18.9), 97 (7.7), 85 (11.0), 77 (12.0), 71 (12.3), 69 (16.9), 67 (16.5), 59 (11.0), 45 (33.0), 41 (6.4)	3.94	ND
22	dimethyl tetrasulfide ^c	C ₂ H ₆ S ₄ , 158	1215	(i) 160 (11.6), 159 (3.5), 158 (65.2), 126 (2.7), 111 (10.4), 94 (18.3), 79 (100), 64 (42.1), 61 (9.0), 47 (44.0), 46 (25.8), 45 (67.1)	ND	0.87
			1225	(ii) 162 (7.4), 160 (9.9), 158 (52.5), 113 (92.2), 111 (15.1), 94 (15.8), 87 (33.7), 79 (79.4), 64 (49.3), 61 (4.4), 57 (27.8), 56 (31.8), 55 (26.0), 47 (40.9), 46 (35.0), 45 (100), 43 (85.2), 41 (97.1)	1.13	ND
23	methyl 5-methylfuryl sulfide	C ₆ H ₈ OS, 128	1250	130 (4.8), 129 (8.1), 128 (100), 113 (6.2), 99 (29.8), 85 (68.2), 67 (42.5), 65 (13.4), 59 (16.9), 55 (21.0), 45 (32.6), 43 (13.8), 41 (28.3)	0.54	ND
24	diallyl thiosulfinate ^c	C ₆ H ₁₀ OS ₂ , 162	1324	164 (2.3), 163 (2.1), 162 (22.2), 129 (68.4), 87 (5.7), 99 (3.7), 85 (8.5), 69 (100), 59 (18.4), 45 (37.3)	1.59	ND
25	1-propenyl propyl trisulfide ^c (E/Z)	C ₆ H ₁₂ S ₃ , 180	1345	182 (8.5), 181 (5.7), 180 (60.0), 151 (5.5), 116 (31.1), 115 (36.6), 101 (7.3), 106 (49.5), 87 (12.4), 83 (39.7), 75 (15.7), 74 (79.4), 73 (51.8), 64 (36.1), 59 (25.4), 55 (18.6), 47 (18.1), 45 (77.1), 43 (16.6), 41 (100)	1.36	ND
26	dipropyl trisulfide	C ₆ H ₁₄ S ₃ , 182	1350	184 (7.4), 183 (4.6), 182 (54.1), 150 (1.2), 140 (4.2), 117 (3.2), 98 (12.9), 89 (2.3), 75 (100), 47 (14.0), 45 (15.1), 43 (89.5), 41 (49.6)	ND	23.07
27	1-propenyl propyl trisulfide ^c (E/Z)	C ₆ H ₁₂ S ₃ , 180	1353	182 (6.4), 181 (4.0), 180 (44.4), 138 (1.4), 116 (29.1), 105 (11.2), 87 (2.2), 75 (12.7), 74 (78.6), 73 (100), 59 (8.7), 47 (19.3), 45 (84.6), 43 (60.6), 41 (64.0)	ND	7.11
28	diallyl trisulfide ^c	C ₆ H ₁₀ S ₃ , 178	1373	180 (11.4), 179 (3.8), 178 (41.5), 147 (4.6), 131 (11.7), 114 (49.1), 113 (17.3), 99 (21.7), 79 (11.1), 73 (23.3), 61 (21.4), 47 (17.4), 45 (100), 43 (17.6), 42 (4.0)	0.07	ND
29	dipropyl tetrasulfide ^c	C ₆ H ₁₄ S ₄ , 214	1406	216 (1.8), 215 (1.0), 214 (10.2), 186 (31.4), 158 (21.7), 108 (18.9), 80 (32.0), 79 (55.0), 75 (10.1), 73 (35.5), 64 (35.0), 47 (33.2), 45 (46.8), 43 (100), 41 (53.1)	ND	4.91
30	dibenzothiophene	C ₁₂ H ₈ S, 184	1458	186 (9.2), 185 (11.7), 184 (100), 169 (20.7), 155 (13.2), 151 (34.2), 143 (18.0), 139 (17.0), 125 (19.5), 111 (49.9), 79 (15.3), 85 (20.8), 69 (26.3), 59 (33.6), 45 (71.2), 43 (26.2), 41 (52.0)	0.74	ND
31	methyl 3,4-dimethyl-2-thienyl disulfide	C ₇ H ₁₀ S ₂ , 190	1514	192 (9.7), 191 (7.1), 190 (67.5), 143 (100), 133 (6.1), 111 (18.9), 99 (40.2), 97 (15.1), 69 (18.8), 67 (15.1), 65 (17.9), 59 (15.7), 55 (13.7), 47 (11.7), 45 (54.1), 43 (16.4), 41 (24.4)	0.89	ND
32	dipropyl tetrasulfide ^c	C ₆ H ₁₄ S ₄ , 214	1573	216 (3.6), 215 (2.0), 214 (20.4), 182 (2.6), 150 (4.8), 108 (38.0), 107 (10.0), 75 (13.3), 73 (37.3), 47 (11.0), 45 (16.3), 43 (100), 41 (51.2)	ND	6.55
33	isomer of methyl 3,4-dimethyl-2-thienyl disulfide	C ₇ H ₁₀ S ₂ , 190	1663	192 (0.5), 191 (0.5), 190 (3.3), 159 (0.9), 133 (100), 115 (2.0), 105 (26.2), 91 (2.0), 77 (17.1), 51 (8.1), 43 (1.1)	55.49	ND
34	unknown	C ₁₀ H ₈ S ₂ , ^c 192	1734	194 (0.8), 193 (1.5), 192 (10.3), 161 (1.8), 149 (3.7), 135 (4.0), 108 (68.1), 107 (100), 80 (15.7), 79 (49.3), 78 (13.8), 77 (35.0), 57 (10.1), 51 (8.9), 41 (3.7)	14.17	ND

^a m/z with intensity in parentheses. ^b Average of two analyses. ^c Tentative identification. ^d ND, not detected.

5) 1514] was detected only in the supercritical extract and not in the commercial onion oil.

A number of compounds including 1-propanethiol (1), methylthiirane (2), methanedithiol (3), methyl ethyl disulfide (5), 3,4-dimethylthiophene (8), methyl propyl disulfide (10), methyl 1-propenyl disulfide (11), dipropyl disulfide (13), 1-propenyl propyl disulfide (14), dimethyl trisulfide (12), methyl 1-propenyl trisulfide (18, 19), 1-propenyl propyl trisulfide (25, 27), and dimethyl tetrasulfide (22) were detected both in SC-CO₂ onion extracts and in commercial onion oil (Table I). 1-Propanethiol, methylthiirane, 3,4-dimethylthiophene, methyl propyl disulfide, methyl 1-propenyl disulfide, dipropyl disulfide, 1-propenyl propyl disulfide, dimethyl trisulfide, methyl 1-propenyl trisulfide, and 1-propenyl propyl trisulfide were identified by comparison of the mass spectral data with that of Wu et al. (1982), Weast and Grasselli (1989), Boelens et al. (1971), Brodnitz et al. (1969), and Mazza et al. (1980). The identification of methyl ethyl disulfide and dimethyl tetrasulfide is based on interpretation of their mass spectral data.

The concentration of di- and trisulfides (notably, dipropyl disulfide and 1-propenyl propyl disulfide) was much higher in the commercial onion oil than in the supercritical extracts. Kameoka et al. (1984) also reported very high concentrations of dipropyl disulfide (ca. 28%) and dipropyl trisulfide (ca. 4%) in steam-distilled oil from *Allium fistulosum* L.

The characteristic fresh onion-like flavor present in SC-CO₂ onion extract and not in the steam-distilled commercial onion oil may also be due to the complete absence of methyl propyl trisulfide (16), dipropyl trisulfide (26), and dipropyl tetrasulfide (32) in the former. These compounds were present in a very high concentration in the commercial onion oil only.

CONCLUSION

The above results indicate that a SC-CO₂ extraction process can produce onion extracts with fresh onion-like flavors. Tentatively identified in SC-CO₂ onion extract was diallyl thiosulfinate or its isomer. Propyl methanethiosulfonate, which is associated with fresh flavors, was also detected. Several new components are being reported for the first time in onion from SC-CO₂ extracts, including the two major components tentatively identified as an unidentified isomer of methyl 3,4-dimethyl-2-thienyl disulfide (C₇H₁₀S₃) and another unknown containing two sulfur atoms (C₁₀H₈S₂). The principal components in the steam-distilled commercial sample are 1-propenyl propyl disulfide, dipropyl disulfide, methyl propyl trisulfide, 1-propenyl propyl trisulfide, dipropyl trisulfide, and dipropyl tetrasulfide. Additional studies to confirm the identity of diallyl thiosulfinate, C₇H₁₀S₃, and C₁₀H₈S₂ from extraction with SC-CO₂ are desirable since this is the first time they have been reported as components of onion flavor.

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