# Volatile Constituents of Chinese Chive (*Allium tuberosum* Rottl. ex Sprengel) and Rakkyo (*Allium chinense* G. Don)

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Volatile components were isolated from Chinese chive and rakkyo by simultaneous steam distillation−solvent extraction and analyzed by GC and GC-MS. Sulfur compounds account for 88 and 94% of the total volatiles in the isolated extract of Chinese chive and rakkyo, respectively. In addition to the sulfur compounds commonly reported in the genus *Allium*, 27 novel volatile sulfur-containing components were found in the isolated extracts of both species. Among them were a sulfide, disulfides, trisulfides, and tetrasulfides with ethyl, butyl, and pentyl groups.

**Keywords:** *Volatile; Chinese chive; rakkyo; sulfur compounds*

## INTRODUCTION

The genus *Allium* comprises >600 diferent species found throughout North America, North Africa, Europe, and Asia. Most *Allium* species are edible and possess characteristic aromas (*1*, *2*). Many investigations have been conducted into the nature of the volatile compounds in alliums and their products and the biochemical basis of flavor production, particularly concerning the most common, garlic and onion. It is known that the volatiles are produced by enzymatic splitting of the nonvolatile precursors, *S*-alk(en)yl-L-cysteine 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 (*1*−*4*). Chinese chive (*Allium tuberosum* Rottl. ex Sprengel) and rakkyo (*Allium chinense* G. Don) are cultivated alliums, particularly in Asia. Chinese chive is usually eaten prickled, whereas rakkyo is used as a seasoning. Volatile components of both plants, Chinese chive (*5*−*10*) and rakkyo (*5*, *8*, *11*), have been studied. Most of the volatile constituents were sulfur-containing compounds, although very large differences in chemical composition have been found in these studies.

The present study investigated the volatile constituents of Chinese chive and rakkyo cultivated in Cuba.

## EXPERIMENTAL PROCEDURES

**Materials.** Chinese chives and rakkyos were collected at the experimental field of the Research Institute for Tropical Agriculture, in Havana, in the summer of 1998. Diethyl ether was purchased from Merck (Darmstadt, Germany). It was distilled before use, with a Vigreux fractionation column. A standard of *n*-paraffins ($C_5$−$C_{26}$) was purchased from Alltech Associates, Inc. (Deerfield, IL).

**Sample Preparation.** Leaves (150 g) were cut with scissors into ∼1-cm pieces, blended with 1200 mL of distilled water, and then subjected to a simultaneous steam distillation−solvent extraction with a Likens−Nickerson apparatus (*12*) for 90 min using 25 mL of diethyl ether as extraction solvent. The extracts were dried over anhydrous sodium sulfate, concentrated to near 0.6 mL in a Kuderna-Danish evaporator, and then condensed to 0.1 mL under a purified nitrogen stream at room temperature.

**GC and GC-MS Analyses.** A Pye Unicam 204 gas chromatograph, equipped with a 30 m × 0.32 mm i.d. DB-1 fused silica capillary column (J&W Scientific, Folsom, CA) and a flame ionization detector (FID) were used for qualitative analyses. The injector temperature was 220 °C, and the detector temperature was 250 °C. The oven temperature was held at 60 °C for 4 min and then raised to 250 °C at 4 °C/min. The hydrogen carrier gas flow rate was 0.9 mL/min. Linear retention indices were calculated against those of *n*-paraffins (*13*).

GC-MS analyses were conducted in a JEOL JMS DX 300 system. Mass spectra were obtained at 70 eV, and the ion source temperature was 200 °C. The column and oven conditions for GC-MS were as described for the GC-FID analyses.

## RESULTS AND DISCUSSION

The volatile constituents of Chinese chive and rakkyo were obtained by simultaneous steam distillation−solvent extraction and analyzed by gas chromatography and gas chromatography−mass spectrometry using fused silica capillary columns. The identities of volatile constituents of both plants are listed in Table 1. Identifications was performed by comparing the GC retention indices and mass spectra with either those of authentic compounds or published data (*14*−*17*). When neither an authentic sample nor published information was available, identification was made by interpreting the fragmentation of the mass spectra. Table 2 lists the mass spectral data of some novel compounds identified in the present study.

The volatile compounds found in both *Allium* species may be divided into the following groups: sulfides, disulfides, trisulfides, tetrasulfides, pentasulfides, oxygenated compounds, and terpenes.

Sulfur-containing compounds account for 88 and 94% of the total volatiles of Chinese chive and rakkyo, respectively. Oxygenated compounds make up only 1.5 and 2.3% of the total volatiles in both plants. These include ethyl acetate in Chinese chive and ethyl propi-

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10.1021/jf9907034 CCC: $20.00 
Published on Web 02/13/2001

**Table 1. Volatile Compounds of Chinese Chive and Rakkyo**

| compound | retention index | GC area,[a] % | | ID[b] |
|---|---|---|---|---|
| | | rakkyo | chive | |
| ethyl acetate[e,f] | 601 | 1.5 | –[c] | GC, MS |
| ethyl propionate[e,f] | | – | 1.5 | GC, MS |
| dimethyl disulfide | 731 | 15.0 | 7.3 | GC, MS |
| ethyl *cis*-1-propenyl sulfide[e,f] | 763 | – | 0.5 | MS-I |
| ethyl methyl disulfide[e,f] | 821 | 5.8 | 0.2 | MS |
| diallyl sulfide[e,f] | 850 | tr[d] | – | MS |
| allyl methyl disulfide | 900 | 39.3 | 4.8 | MS |
| methyl propyl disulfide[e] | 914 | 1.3 | 5.5 | GC, MS |
| methyl *cis*-1-propenyl disulfide[e] | 920 | 2.9 | 2.4 | MS |
| dimethyl trisulfide[e] | 949 | 12.6 | 6.0 | GC, MS |
| ethyl propyl disulfide[e,f] | 996 | – | 4.6 | MS-I |
| ethyl *cis*-1-propenyl disulfide[e,f] | 1008 | 1.1 | 3.7 | MS-I |
| ethyl *trans*-1-propenyl disulfide[e,f] | 1012 | 0.6 | – | MS-I |
| butyl methyl disulfide[e,f] | 1016 | – | 0.6 | MS-I |
| limonene[e,f] | 1025 | tr | 1.0 | GC, MS |
| ethyl methyl trisulfide[e,f] | 1030 | 1.1 | 0.2 | MS-I |
| diallyl disulfide[f] | 1056 | t | 0.7 | GC, MS |
| allyl *cis*-1-propenyl disulfide[e,f] | 1067 | 8.6 | 0.6 | MS |
| propyl *cis*-1-propenyl disulfide[e,f] | 1076 | – | 3.2 | MS |
| allyl *trans*-1-propenyl disulfide[e,f] | 1081 | 0.9 | 1.8 | MS |
| dipropyl disulfide | 1094 | – | 5.5 | GC, MS |
| propyl *trans*-1-propenyl disulfide[e,f] | 1099 | – | 3.2 | MS |
| allyl methyl trisulfide | 1112 | 4.5 | 3.4 | MS |
| methyl propyl trisulfide[e] | 1130 | tr | 9.9 | MS |
| methyl *cis*-1-propenyl trisulfide[e,f] | 1139 | 1.3 | 1.2 | MS |
| methyl *trans*-1-propenyl trisulfide[e,f] | 1144 | tr | 1.7 | MS |
| dimethyl tetrasulfide[f] | 1204 | 1.1 | 3.2 | GC, MS |
| butyl methyl trisulfide[e,f] | 1241 | - | 0.3 | GC, MS |
| diallyl trisulfide[f] | 1283 | 0.9 | 0.4 | GC, MS |
| propyl *cis*-1-propenyl trisulfide[e,f] | 1289 | – | 2.8 | MS |
| dipropyl trisulfide[e] | 1313 | – | 6.0 | GC, MS |
| propyl *trans*-1-propenyl trisulfide[e,f] | 1324 | – | 4.9 | MS |
| propyl *cis*-l-propenyl tetrasulfide[e,f] | 1357 | tr | 1.7 | MS |
| methyl pentyl tetrasulfide[e,f] | 1376 | – | 3.7 | MS-I |
| propyl *trans*-propenyl tetrasulfide[e,f] | 1380 | 0.6 | 0.7 | MS |
| dipropyl tetrasulfide[e,f] | 1558 | – | 1.0 | MS |
| allyl propyl tetrasulfide[e,f] | 1567 | – | 1.3 | MS |
| propyl methyl pentasulfide[e,f] | 1614 | – | 0.4 | MS-I |
| 2,3-dihydro-2*n*-octyl-5-methylfuran-3-one[e] | 1626 | – | 0.8 | MS |
| propyl *cis*-l-propenyl pentasulfide[e,f] | 1822 | – | 0.1 | MS-I |

[a] Average of two experiments. [b] GC, MS, and MS-I indicate identification by retention index, mass spectrum comparison, and mass spectrum interpretation, respectively. [c] Not detected. [d] Trace (<0.1%). [e] Not previously identified in Chinese chive. [f] Not previously identified in rakkyo.

**Table 2. Mass Spectra of Some Novel Compounds in Chinese Chive and Rakkyo**

| compound | MW | mass spectral data[a] |
|---|---|---|
| ethyl *cis*-1-propenyl sulfide | 102 | 45 (100), 43 (90), 73 (48), 61 (40), 44 (40), 57 (15), 102 (10), 87 (6) |
| ethyl methyl disulfide | 108 | 63 (100), 78 (73), 45 (65), 43 (60), 47 (50), 61 (38), 73 (15), 94 (15), 108 (12) |
| ethyl propyl dosulfide | 136 | 45 (100), 43 (90), 73 (58), 44 (32), 61 (26), 66 (26), 94 (18), 136 (8) |
| ethyl *cis*-1-propenyl disulfide | 134 | 73 (100), 45 (92), 43 (91), 44 (85), 61 (80), 42 (20), 88 (10), 134 (5) |
| ethyl *trans*-1-propenyl disulfide | 134 | 73 (100), 45 (93), 43 (91), 44 (85), 61 (80), 42 (20), 88 (12), 134 (6) |
| butyl methyl disulfide | 136 | 43 (100), 45 (73), 44 (60), 46 (30), 73 (32), 80 (21), 126 (18), 136 (8) |
| ethyl methyl trisulfide | 140 | 45 (100), 140 (67), 47 (55), 64 (45), 73 (45), 80 (45), 94 (34), 126 (32) |
| butyl methyl trisulfide | 168 | 89 (100), 41 (65), 45 (50), 79 (45), 61 (38), 73 (28), 168 (5) |
| methyl pentyl tetrasulfide | 214 | 43 (100), 185 (58), *41 (55)*, 64 (50), 79 (50), 45 (36), 80 (36), 214 (8) |
| propyl methyl pentasulfide | 218 | 64 (100), 43 (95), 41 (68), 154 (65), 79 (50), 45 (48), 112 (30), 139 (26), 218 (22) |
| propyl *cis*-l-propenyl pentasulfide | 244 | 45 (100), 106 (95), 41 (83), 74 (72), 169 (68), 64 (56), 179 (50) |

[a] *m*/*z* in decreasing values witn intensity in parentheses.

onate and 2,3-dihydro-2*n*-octyl-5-methylfuran-3-one in rakkyo. Neither of the aliphatic esters was not previously reported in these plants. One terpene, limonene, was identified in *Allium* for the first time. The most abundant volatile of Chinese chive extract was allyl methyl disulfide (39.3%), followed by dimethyl disulfide (15%) and dimethyl trisulfide (12.6%). Bernhard (*6*), using GC, has analyzed the composition of many *Allium* species and concluded that the volatile compounds of Chinese chive mainly consisted of allyl methyl disulfide and dimethyl disulfide. Iida et al. (*10*) separated many sulfur compounds from the steam distillate of Chinese chive and identified 29 of them, the most important being dimethyl disulfide (32%), dimethyl trisulfide (16%), allyl methyl trisulfide (10%), and allyl methyl disulfide (8%). These large differences in volatile chemical composition can be explained by the results of MacKenzie and Ferns (*9*), who found a large variation in the volatile compositions in different parts of this plant.

The most abundant volatile of rakkyo extract was methyl propyl trisulfide (9.9%), followed by dimethyl disulfide (7.3%), dimethyl trisulfide (6%), and methyl propyl disulfide (5.5 %). Saghir et al. (*5*) have reported dimethyl disulfide, methyl propyl disulfide, and allyl methyl disulfide as major volatile compounds. In contrast, Freeman and Whenham (*8*) found approximately equal amounts of alkenyl groups in their study, and Kameoka et al. (*11*) found dipropyl disulfide as major volatile compound. The most likely explanation for this discrepancy is that different parts of the plant were analyzed in these studies, although genetic and environmental factors could also contribute to the quantitative variation of volatiles.

Among the 21 and 34 sulfur compounds identified in Chinese chive and rakkyo, respectively, many have not been previously reported in these plants. They include some novel sulfide and polysulfides with ethyl, butyl, and pentyl groups. The presence of these compounds in *Allium* species has been suggested but not confirmed. The *S*-ethyl-, *S*-butyl-, and *S*-pentyl-L-cysteine sulfoxides do not occur naturally. The report of some thioethyl and thiopentyl compounds in *Allium schoenoprasum* (*18*), *Allium fistulosum* (*11*), and *Allium grayi* (*19*) raises the possibility of the occurrence of these *S*-alkyl-L-cysteine sulfoxides.

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Received for review June 28, 1999. Revised manuscript received October 4, 2000. Accepted October 12, 2000.

JF9907034