

Volatile Flavor Compounds Formed in an Interspecific Hybrid between Onion and Garlic

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Volatile flavor compounds formed in an interspecific hybrid between onion (*Allium cepa* L.) and garlic (*Allium sativum* L.) were examined by GC and GC-MS analysis of headspace gas with a purge-and-trap injector. The crushed hybrid bulb formed various flavors including both species-specific and new types. The species-specific flavors were identified as thiopropanal *S*-oxide, which is the major specific flavor and lachrymatory factor in onion, and allyl methyl disulfide and diallyl disulfide, which are major flavors in garlic. The hybrid was thus recognized to be a new plant from the gas chromatographic patterns, which indicated a combination of the species-specific flavors of both parents.

INTRODUCTION

Onion (*Allium cepa* L.) and garlic (*Allium sativum* L.) have been used historically as foods and medicines because of the valuable volatile sulfur compounds they produce. There are species-specific differences in *Allium* with regard to the quantity and quality of their specific flavor precursors, *S*-alk(en)yl-L-cysteine sulfoxides. The non-volatile precursors release volatile sulfur compounds through alliinase activity and chemical degradation, and the compounds have defensive action against animal pests and microorganisms (Block, 1985; Carson, 1987). *S*-1-Propenyl-L-cysteine sulfoxide in onion is the precursor of the major onion flavor and lachrymatory factor, which is irritating and repugnant to certain animals (Block, 1980). Alliin (*S*-allyl-L-cysteine sulfoxide) in garlic is the precursor of allicin, which is the main garlic flavor and also an antibacterial and antifungal factor (Cavallito and Bailey, 1944). No single *Allium* species has yet been found to produce both *S*-1-propenyl-L-cysteine sulfoxide and alliin as major flavor precursors.

In our previous study (Ohsumi et al., 1993), we succeeded in producing an interspecific hybrid between onion and garlic by the nascent embryo rescue technique. The hybridity of the plant was proved by rDNA hybridization, chromosome analysis, and morphological analysis. The hybrid plant produced *S*-1-propenyl-L-cysteine sulfoxide (0.7 mg/g fresh weight), alliin (1.3 mg/g fresh weight), and *S*-methyl-L-cysteine sulfoxide (0.3 mg/g fresh weight) in the bulb. These flavor precursors always occurred in the leaf as well as in the bulb. The sliced hybrid bulb had an odor resembling a mixture of onion and garlic because the level of alliinase activity was similar to that of the parent plants. This paper describes the volatile species-specific flavor compounds formed in the crushed hybrid bulb by headspace vapor analysis using a purge-and-trap injector (Bodings et al., 1985).

EXPERIMENTAL PROCEDURES

Plant Material. Onion (*A. cepa* cv. Sapporoki), garlic (*A. sativum*, Etoh, 1983), and their interspecific hybrid (Ohsumi et al., 1993) were grown in Japan. The bulbs were harvested and

ground completely in liquid nitrogen using a pestle and mortar for suppressing the alliinase activity. The powdered samples were immediately stored in an ultra-low-temperature freezer at -80 °C.

Gas Chromatography. Gas chromatographic analysis was carried out according to the headspace gas method using an automatic purge-and-trap injector system (Chrompack) (Tokitomo and Kobayashi, 1992; Bodings et al., 1985). The gas chromatograph used for headspace gas analysis was a Hitachi G-3000 equipped with a flame ionization detector and a capillary Carbowax column (CP-Wax 52CB 0.25 mm i.d. × 50 m, df = 0.25 μm; Chrompack). The operating conditions were as follows: oven temperature, 40 °C for 10 min, 2 °C/min rise to 100 °C, 5 °C/min rise to 190 °C; carrier gas, helium; flow rate, 1.0 mL/min. GC-MS analysis was conducted using an HP5790 gas chromatograph coupled directly to a JMS-DX300 mass spectrometer and a JMA-DA 5000 mass data system. All conditions for gas chromatography were the same as those for GC analysis, as described above.

Ground plant materials were transferred to a purge-and-trap injector sample flask (15 mL) on dry ice and directly purged in the flask connected with the injector at 30 °C for 20 min: purge gas, helium; flow rate, 10 mL/min. The headspace gas generated from the sample was trapped in the injector at -130 °C. Injection conditions were 200 °C for 5 min. Sample sizes were in the range 1-5 g according to flavor intensity.

RESULTS AND DISCUSSION

The volatile compounds of the interspecific hybrid between onion and garlic were analyzed by GC and GC-MS with a purge-and-trap injector. The gas chromatographic separation is shown in Figure 1. The gas chromatographic profile of the headspace gas from the hybrid was somewhat different from that of onion plus garlic.

The flavors were identified by comparing their GC retention times and mass spectra with the volatile flavor compounds of onion and garlic or with published data (Nishimura et al., 1971; Freeman and Whendam, 1971; Brodnitz et al., 1969). Since the gas chromatographic analysis was done automatically by a purge-and-trap injector, the retention times of the compounds were reproducible. The peak numbers refer to those in Figure 1. The identities of the volatile components of the plants are listed in Table I.

The hybrid produced species-specific flavors as main compounds under the trap condition: thiopropanal *S*-oxide (peak 3), which is the characteristic aroma in onion (Brodnitz and Pascale, 1971), and diallyl disulfide (peak 11) and allyl methyl disulfide (peak 4), which are the characteristic aromas in garlic (Brodnitz et al., 1971). This

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Table I. Identification of Volatile Flavor Components Found in the Hybrid between Onion and Garlic

peak no.	compound	I.D.	MS data
1	dimethyl disulfide	MS, t_R	94 (M^+ , 100), 79 (55), 45 (49), 46 (30), 47 (22), 61 (15), 48 (13), 32 (12)
2	methyl propyl disulfide	MS, t_R	32 (100), 80 (88), 122 (M^+ , 71), 43 (60), 41 (55), 26 (32), 45 (24), 39 (18), 47 (18), 64 (14)
3	thiopropenal S-oxide	MS, t_R	41 (100), 90 (M^+ , 45), 39 (42), 42 (29), 45 (22), 26 (18), 43 (16), 48 (16), 73 (11)
4	allyl methyl disulfide	MS, t_R	41 (100), 120 (M^+ , 52), 39 (27), 45 (21), 73 (9), 64 (6)
5	methyl (<i>E</i>)-1-propenyl disulfide	MS, t_R	120 (M^+ , 100), 45 (75), 32 (63), 72 (52), 41 (42), 75 (36), 39 (30), 73 (28)
6	dipropyl disulfide	MS, t_R	43 (100), 150 (M^+ , 35), 41 (32), 108 (24), 45 (13), 66 (12)
7	(<i>Z</i>)-1-propenyl propyl disulfide	MS, t_R	41 (100), 148 (M^+ , 85), 106 (74), 43 (58), 45 (55), 39 (36), 64 (27), 73 (27), 72 (24), 74 (18), 76 (17)
8	allyl propyl disulfide	MS, t_R	41 (100), 148 (M^+ , 35), 39 (33), 106 (31), 32 (22), 45 (20), 64 (14), 73 (12), 74 (12)
9	(<i>E</i>)-1-propenyl propyl disulfide	MS, t_R	41 (100), 148 (M^+ , 72), 106 (62), 43 (50), 45 (47), 39 (31), 73 (25), 64 (23)
10	allyl (<i>Z</i>)-1-propenyl disulfide	MS, t_R	41 (100), 45 (67), 39 (64), 73 (45), 146 (M^+ , 42), 81 (38), 71 (20), 61 (18), 105 (16)
11	diallyl disulfide	MS, t_R	41 (100), 39 (38), 45 (20), 61 (18), 146 (M^+ , 12), 73 (9), 105 (7), 72 (7)
12	allyl (<i>E</i>)-1-propenyl disulfide	MS, t_R	41 (100), 45 (61), 39 (51), 73 (44), 81 (35), 146 (M^+ , 33), 61 (20), 105 (19), 71 (16)

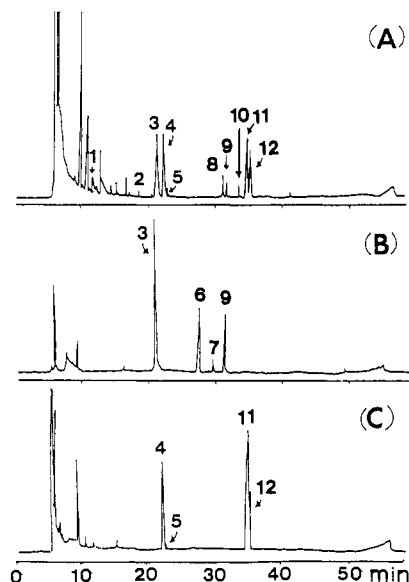


Figure 1. Gas chromatogram of the headspace gas from the interspecific hybrid (A), onion (B), and garlic (C).

suggests that alliinases in the hybrid catalyze the conversion of precursors to flavors in the same manner as the enzymes in the parent plants. Allicin has not been obtained in headspace gas from either the hybrid or garlic because the volatile compound is too unstable to survive gas chromatography. Brodnitz et al. (1971) has shown that allicin tends to decompose to diallyl disulfide and thiosulfonate. Recently, it has been reported that identification of allicin can be made by HPLC analysis (Block et al., 1992a,b; Lawson et al., 1991; Lawson and Hughes, 1992).

The relative amounts of volatile compounds formed in the hybrid were slightly different from those of onion plus garlic under this trap condition. Dipropyl disulfide (peak 6) and 1-propenyl propyl disulfide (two isomers, peaks 7 and 9), which were produced in onion, were little generated from the hybrid. Nevertheless, the level of alliinase activity in the hybrid was similar to that in onion even after freezing (data not shown). This is probably because the kinetic properties of alliinase activity might be changed in the hybrid. Then, the action pattern of the enzyme may be modified by substrates to suppress the production of some of the volatile compounds described above. At least two hybrid volatile compounds containing sulfur were observed as peaks 8 and 10 at relatively high levels (Figure 1). GC and GC-MS data suggested that peak 8 was allyl propyl disulfide. Peak 10 was an isomer of allyl 1-propenyl disulfide, because its mass spectrum was the same as that of peak 12, and these compounds were identified as allyl 1-propenyl disulfide on the basis of their mass spectra. Peak 10 seems to be allyl (*Z*)-1-propenyl disulfide because

the *Z*-form always runs faster than the *E*-form in this Carbowax column.

The quantity and quality of volatile compounds in the hybrid shown in Figure 1 should be due to the occurrence and properties of alliinase as well as the levels of both flavor precursors because the kinetic properties of alliinase differ markedly between onion and garlic, *i.e.*, optimum pH, substrate specificity, and stability (Nock and Mazelis, 1987). Morimitsu et al. (1992) have examined by HPLC the compounds formed on physically mixing onion and garlic. Further studies on the characterization of alliinase activity as well as the levels of flavors formed in hybrid plants are now in progress.

The hybrid has been recognized as a new plant from the gas chromatographic patterns, which combine the species-specific flavors of both parents.

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