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Volatile composition and sensory characteristics of onion powders prepared by convective drying

So Mang Choi [a], Dong-Jin Lee [a], Jong-Yea Kim [b], Seung-Taik Lim [a,*]

[a] Department of Biotechnology, College of Life Sciences and Biotechnology, Korea University, Seoul 136-701, South Korea
[b] Department of Food Science and Biotechnology, Kangwon National University, Chuncheon 200-701, South Korea

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ABSTRACT

Volatile composition and sensory characteristics of onion powders prepared by convective drying at different temperatures (50, 70, and 90 °C) were investigated. Dipropyl disulfide was the major volatile compound in fresh onion (77.70% of total volatile compounds). However it was considerably lost during drying, reaching 6.93–32.25 μg/g solids. Dipropyl disulfide showed a positive correlation with green sensory attribute perceived by descriptive sensory analysis. Thiophenes, which were responsible for caramel and sweet attributes, were produced by drying especially when the drying temperature was high. Aldehydes, another type of volatile compound found in fresh onion, showed a positive correlation with humidity. The aldehyde content in dried onion was the highest at the lowest drying temperature, possibly because the aldehydes were produced by the residual enzymes in fresh onion. Using a low temperature for drying was ideal to retain the aroma of fresh onion.

1. Introduction

Fresh onion (*Allium cepa*) bulbs are susceptible to postharvest pathogens and readily softened because of inherent enzymes, such as polygalacturonase and pectin methylesterase (Coolong, Randle, & Wicker, 2008). Drying fresh onion to powder or chip is one of the most effective processes to extend onion shelf life (Ahvenainen, 1996). According to the Food and Agriculture Organization (FAO, 2015), the global production of dry onion products in 2013 was about 87 million tons, which was approximately 1.5 times greater than the quantity produced in 2003. China is the largest producer of dry onion, contributing 22% of the total global production. Dry onion is widely used as an ingredient in a variety of commercial products, including sauces, snacks, frozen foods and retorted products (Arslan & Özcan, 2010).

In general, volatile compounds contribute to overall sensory characteristics of food products, often determining their acceptability and eating quality (King et al., 2010). Numerous studies have been carried out on the correlation between volatile compounds and sensory attributes of foods, proving the importance of volatile composition for sensory qualities (Johnson, Heymann, & Ebeler, 2015; Álvarez, González-Barreiro, Cancho-Grande, & Simal-Gándara, 2011). For fresh and dry onion products too, various volatile compounds have been identified (Bernhard, 1968; Boelens, De Valois, Wobben, & Van der Gen, 1971; Mondy, Duplat, Christides, Arnault, & Auger, 2002). Among the volatile components in onion, sulfur-containing compounds are known to be major volatiles in fresh onion, which are produced by the action of an inherent enzyme called alliinase. This enzyme catalyzes the hydrolysis of S-alk(en)ly-L-cysteine sulfoxide to produce sulfur-containing volatiles including mono, di and trisulfides (Colina-Coca, González-Peña, Vega, de Ancos, & Sánchez-Moreno, 2013). In addition, various aldehydes have been identified as another type of volatiles in fresh onion. It is widely known that various aldehydes are found in fruits and vegetables as the key aroma components (Gray, Prestage, Linforth, & Taylor, 1999; Noordermeer et al., 2002). Most of the volatile aldehydes consist of six to nine carbons (C6–C9), because the C6–C9 fatty acids are the substrates of the enzymes responsible for the aldehyde formation such as lipoxygenase and hydroperoxide lyase. Some of the volatile aldehydes, however, may induce off-flavor, especially when their residual amounts are too high (Petersen, Poll, & Larsen, 1999).

There have been several studies on the effects of different drying processes using sunlight, convection, vacuum and microwave on the quality of dry onion products (Adam, Mühlbauer, Esper, Wolf, & Spiess, 2000; Arslan & Özcan, 2010). Among the drying methods, convective drying (CD) is the most commonly used to make dry onion products because it is cost-effective and simple to operate. Volatile compounds in fresh onion, however, may be readily lost during convective drying especially when the drying is conducted at high temperature (Bernhard, 1968). However, no

* Corresponding author.
E-mail address: limst@korea.ac.kr (S.-T. Lim).

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study has been reported on changes in volatile compounds and sensory qualities of onion during convective drying.

In the present study, volatile composition and overall sensory quality of dried onion prepared by convective drying at different temperatures were investigated. Also, the correlation between volatile composition and sensory attributes was statistically measured.

2. Materials and methods

2.1. Materials

Fresh onion (*Allium cepa*) was purchased from a local market in Seoul, Korea. The PDMS/DVB-coated solid-phase microextraction (SPME) fiber was supplied by Supelco (Bellefonte, PA). The C7–C40 saturated alkane standard solutions (1000 μg/mL in hexane) and allyl methyl sulfide were purchased from Sigma-Aldrich (St. Louis, MO).

2.2. Convective drying

Onions were cut into slices of approximately 3 mm using a stainless steel knife. One hundred and twenty grams of the onion slices were spread evenly on a stainless steel tray (31 cm × 22 cm × 2 cm), and then dried in a laboratory convective dryer (MOV-112F, Sanyo, Japan) at different temperatures (50, 70, and 90 °C). Drying times of 2.5–48 h were required to reach residual moisture content of 12.46–15.94% (Table 1). The dried onion samples were then ground into powders in a mortar filled with liquid nitrogen. The moisture content of the powders was determined by drying at 105 °C for 20 h. The color of the onion powders was measured by a colorimeter (CR-10; Konica Minolta Sensing Inc., Japan), and the browning index (BI) was calculated using the color values expressed as *L* (whiteness or brightness/darkness), *a* (redness/greenness) and *b* (yellowness/blueness) as described by Maskan (2001) (Table 1):

$$BI = \frac{100(x - 0.31)}{0.17}$$

where

$$x = \frac{a + 1.75L}{5.645L + (a - 3.012b)}$$

2.3. Headspace solid-phase microextraction (HS-SPME)

An HS-SPME analysis of the volatile compounds in fresh onion and dried samples was performed as described in a previous study (Chin et al., 2008) with minor modifications. Five grams of the ground fresh onion or aqueous suspension (10% *w/w* dry solids in distilled water) of dried onion powder were transferred into a 20-mL glass vial. An internal standard solution was prepared by dissolving allyl methyl sulfide in distilled water at a concentration of 1.967 mg/mL (Colina-Coca et al., 2013). An aliquot (20 μL) was subsequently added into the vial. The vial was immediately sealed with a PEFE-silicone septum (Supelco, Bellefonte, PA) and then magnetically stirred at 25 °C for 30 min. A PDMS/DVB-coated (65 μm) SPME fiber which was selected according to a previous study (Zhang, Du, & Li, 2012) was inserted through the septum into the vial to collect the volatile compounds in the headspace of the vial during stirring, which was carried out at 25 °C for 30 min. The fiber was then quickly removed from the vial and inserted into the injector of a gas chromatography for desorption.

Table 1
Moisture content and browning index of onion samples dried under different conditions.

Drying temperature (°C)	Drying time (h)	Moisture content (%)	Browning index
Fresh	0	91.87 ± 0.55	25.76 ± 1.87
50	12	15.94 ± 0.21[a]	30.18 ± 0.98[f]
	24	14.18 ± 0.13[b]	31.20 ± 0.96[f]
	48	12.70 ± 0.11[d]	31.52 ± 0.71[f]
70	4.5	15.85 ± 0.16[a]	37.34 ± 0.79[e]
	6	13.53 ± 0.06[c]	40.71 ± 4.23[de]
	10	12.60 ± 0.14[d]	45.53 ± 1.72[d]
90	2.5	15.86 ± 0.17[a]	52.96 ± 1.70[c]
	2.66	13.49 ± 0.12[c]	58.94 ± 1.01[b]
	3	12.46 ± 0.11[d]	65.54 ± 2.21[a]

Values with different alphabets in the same column are significantly different ($p < 0.05$).

2.4. GC–MS analysis

Identification of volatile compounds was conducted using a gas chromatography (7890A, Agilent Technologies, Santa Clara, CA) coupled to a mass spectrometer (5975C; Agilent Technologies). The volatile compounds isolated by the SPME fiber were separated on a DB-Wax column (30 m length, 0.25 mm ID, 0.25 μm film thickness, J&W Scientific, Agilent). Thermal desorption into the injector was performed by heating at 250 °C for 5 min in splitless mode, using an SPME liner. The GC oven temperature was set at 45 °C for 10 min, increased to 200 °C at a rate of 6 °C /min, and was then maintained at 200 °C for 5 min. Helium was used as a carrier gas with a constant flow rate of 1 mL/min. The mass detector operated in an electron impact (EI) mode at 70 eV. Tentative identifications were based on comparing mass spectra of unknowns with that in the Wiley 07 library with 80% as a minimum matching factor. Identifications of components were confirmed by comparison of their linear retention indices (RI) with those of reference compounds; RI were determined using C7–C40 alkane standards (Van den Dool & Kratz, 1963). Relative concentration of a compound was calculated as follows:

$$Relative\ concentration\left(\frac{\mu g}{g\ dry\ solids}\right) = \frac{peak\ area\ of\ unknown\ compound}{peak\ area\ of\ IS} \times \frac{39.347\mu g\ of\ IS}{amount\ of\ dry\ solids\ (g)}$$

2.5. Sensory analysis

A descriptive sensory analysis (DSA) was carried out to profile the main odor characteristics of onion samples. Fresh onion and dried onion samples prepared at 50 °C for 12 h (CD50_12H), and at 90 °C for 3 h (CD90_3H) were chosen for sensory analysis because the total amount of volatile sulfur and aldehyde compounds in these samples differed significantly. The sensory analysis was performed by 12 panelists (5 male, 7 female, ages 24–30). During training sessions, the panelists smelled fresh and dried onion samples in a blind trial and discussed odor attributes (Coste, Bauzá, Picallo, & Sance, 2010). They determined a final list of 11 descriptive terms by consensus (Table S1). The odor attributes, including pungent, humidity, sulfurous, green, fat, burnt, earthy, cooked vegetables, sweet, onion and caramel attributes as well as general intensity and desirability were evaluated. For a correlation analysis, samples were prepared in the same way as they had been prepared for SPME. The DSA was performed along a scoring line ranging from 0 (none) to 9 (very strong) in triplicate and two samples were present for each analysis.

Table 2
Relative concentrations (μg/g solids) of volatile compounds in onion samples dried under different conditions.

Volatile compounds	CRI[a]	RI[b]	Description of odor[c]	Fresh	CD50			CD70			CD90		
				0	12	24	48	4.5	6	10	2.5	2.66	3
Sulfur compounds													
Dimethyl sulfide	<1000	729[d]	Marine, sulfury[d]	nd	nd	0.20 ± 0.02	0.84 ± 0.04	0.55 ± 0.08	1.67 ± 0.12	3.68 ± 0.60	3.88 ± 0.22	3.07 ± 0.14	3.05 ± 0.19
Dimethyl disulfide	1056	1058[e]	Sulfury, sweaty, onion[l]	2.08 ± 0.10	1.71 ± 0.14	1.59 ± 0.07	1.40 ± 0.24	1.41 ± 0.17	1.66 ± 0.13	2.12 ± 0.25	4.62 ± 0.39	3.72 ± 0.15	6.86 ± 0.20
2,5-Dimethylthiophene	1181	1179[g]	Spring onions, fresh onion[g]	7.98 ± 0.74	10.5 ± 0.76	8.30 ± 0.22	7.25 ± 0.38	4.81 ± 0.33	5.89 ± 0.80	12.0 ± 1.68	24.5 ± 3.33	29.97 ± 3.04	54.2 ± 2.18
Methyl propyl disulfide	1216	1217[g]	Rotten, fried onions, sour cabbage[g]	26.8 ± 5.89	2.20 ± 0.12	3.15 ± 0.22	2.15 ± 0.01	nd	1.12 ± 0.10	2.64 ± 0.35	5.15 ± 1.12	4.74 ± 0.04	8.92 ± 0.34
3,4-Dimethylthiophene	1240	1240[g]	Wood, dry smell, green, book store[g]	244 ± 39.00	74.7 ± 15.0	97.9 ± 9.62	112 ± 12.8	114 ± 11.16	107 ± 4.68	127 ± 16.17	273 ± 4.69	302.53 ± 4.19	400 ± 15.38
trans-Propenyl methyl disulfide	1273	1270[h]		25.4 ± 4.20	21.4 ± 1.48	30.3 ± 2.46	18.0 ± 1.80	3.94 ± 0.04	17.1 ± 1.10	20.2 ± 14.86	142 ± 14.29	139.73 ± 1.60	231 ± 7.64
Dimethyl trisulfide	1361	1356[g]	Solvent, rotten onion, tainted[g]	nd	1.31 ± 0.11	1.92 ± 0.09	0.67 ± 0.02	nd	4.89 ± 0.82	4.32 ± 0.66	45.5 ± 8.40	46.5 ± 1.74	66.7 ± 2.89
Dipropyl disulfide	1363	1365[g]	Strong raw onion, sulfuric, fresh leek[g]	1565.28 ± 166.82	8.98 ± 0.89	6.93 ± 0.89	21.33 ± 2.26	16.71 ± 0.40	11.57 ± 0.80	12.05 ± 2.18	16.08 ± 2.19	21.67 ± 2.12	32.25 ± 2.35
Dipropyl trisulfide	1658	1662[k]	Onion[m]	108.52 ± 1.48	1.41 ± 0.09	0.36 ± 0.02	0.77 ± 0.05	5.69 ± 4.24	0.38 ± 0.07	0.64 ± 0.10	7.48 ± 0.54	7.94 ± 0.31	7.99 ± 5.97
Total of sulfur compounds				1980 ± 132	122 ± 17.8	151 ± 8.74	165 ± 14.49	148 ± 13.91	151 ± 8.43	185 ± 21.81	523 ± 26.0	560 ± 7.23	810 ± 32.7
Aldehydes													
2-Methyl butanal	<1000	907[e]	Nutty, burnt, onion[l]	nd	nd	nd	0.2 ± 0.01	0.11 ± 0.02	0.38 ± 0.01	0.79 ± 0.06	0.70 ± 0.22	0.80 ± 0.05	0.97 ± 0.04
3-Methyl butanal	<1000	911[e]	Chocolate, caramel, green, nutty[l]	nd	nd	nd	0.26 ± 0.03	0.19 ± 0.02	0.59 ± 0.02	1.02 ± 0.10	1.54 ± 0.32	1.75 ± 0.01	1.70 ± 0.06
Hexanal	1067	1068[e]	Green, grass[g]	1.36 ± 0.14	8.09 ± 0.76	9.19 ± 0.88	7.85 ± 0.27	3.89 ± 0.23	4.67 ± 0.25	5.65 ± 0.67	1.98 ± 0.00	1.99 ± 0.13	2.06 ± 0.04
2-Methyl 2-pentenal	1142	1149[f]	Green, grassy, herbal, green cashew[f]	31.7 ± 3.05	144 ± 11.2	72.9 ± 3.60	68.4 ± 4.17	59.6 ± 2.26	33.9 ± 1.63	19.9 ± 1.33	29.5 ± 4.98	28.0 ± 1.04	26.5 ± 2.10
[*E*]-2-Heptenal	1311	1306[g]	Forest, sweat[g]	1.13 ± 0.12	5.59 ± 0.42	5.65 ± 0.32	5.25 ± 0.19	3.83 ± 0.03	3.91 ± 0.12	3.58 ± 2.61	2.90 ± 0.20	2.46 ± 0.41	2.29 ± 0.19
Nonanal	1384	1382[g]	Paint, turpentine[g]	nd	3.20 ± 0.23	13.4 ± 1.70	7.52 ± 0.20	6.83 ± 1.67	9.84 ± 0.78	9.78 ± 12.81	1.80 ± 0.18	1.61 ± 0.05	2.14 ± 0.24
[*E*]-2-Octenal	1416	1412[g]	Soap, old raw leek, compost[g]	nd	2.99 ± 0.18	3.63 ± 0.20	2.6 ± 0.11	2.78 ± 0.12	3.43 ± 0.55	4.47 ± 0.50	4.21 ± 0.67	0.48 ± 0.06	0.69 ± 0.01
Benzaldehyde	1508	1501[i]	Fruity, berry[i]	nd	1.11 ± 0.08	0.74 ± 0.04	0.84 ± 0.05	1.33 ± 0.22	0.72 ± 0.02	0.66 ± 0.16	0.60 ± 0.03	nd	0.84 ± 0.39
Nonenal	1524	1524[j]	Stale, bitter, hay[j]	nd	2.36 ± 0.15	5.40 ± 0.60	3.05 ± 0.19	3.37 ± 0.28	0.39 ± 0.01	2.13 ± 0.21	1.22 ± 0.18	0.91 ± 0.02	1.05 ± 0.03
Total of aldehydes				34.2 ± 3.11	167 ± 12.9	111 ± 5.66	96.0 ± 4.79	82.0 ± 2.14	57.8 ± 2.36	48.0 ± 12.05	44.4 ± 5.09	38.0 ± 1.02	38.2 ± 2.91

nd, not detected.
[a] Calculated retention index (CRI) based on alkanes (C7–C40).
[b] Obtained retention index from literature.
[c] Odor description of volatile compounds in the literature.
[d] Le Guen, Prost, and Demaimay (2000).
[e] Cha, Kim, and Cadwallader (1998).
[f] Garruti, Franco, da Silva, Janzantti, and Alves (2003).
[g] Nielsen et al. (2004).
[h] Yu, Wu, and Liou (1989).
[i] Leão, Sampaio, Pagani, and Da Silva (2014).
[j] Cha and Cadwallader (1998).
[k] Kubec et al. (1998).
[l] Machiels, Istasse, and Van Ruth (2004).
[m] Plagemann, Zelena, Krings, and Berger (2011).

Table 3
Pearson correlation coefficients between volatile compounds and sensory attributes of onion samples dried under different conditions.

	Dimethyl sulfide	2-Methyl butanal	3-Methyl butanal	Dimethyl disulfide	Hexanal	2-Methyl 2-pentenal	2,5-Dimethyl thiophene	Methyl propyl disulfide	3,4-Dimethyl thiophene
Intensity	0.35	0.35	0.35	0.39	−0.41	−0.45	0.33	0.12	0.43
Desirability	0.832**	0.828**	0.833**	0.856**	−0.723*	−0.808**	0.797*	0.24	0.931**
Pungent	−0.932**	−0.937**	−0.937**	−0.918**	0.32	0.43	−0.935**	0.32	−0.725*
Humidity	−0.29	−00.29	−0.29	−0.34	0.925**	0.887**	−0.26	−0.723*	−0.689*
Sulfurous	0.675*	0.702*	0.706*	0.684*	0.08	−0.04	0.709*	−0.53	0.39
Green	−0.958**	−0.960**	−0.959**	−0.941**	0.18	0.31	−0.971**	0.48	−0.673*
Fat	0.968**	0.979**	0.982**	0.970**	−0.35	−0.47	0.972**	−0.31	0.785*
Burnt	0.984**	0.989**	0.989**	0.979**	−0.30	−0.42	0.992**	−0.36	0.767*
Earthy	−0.60	−0.58	−0.58	−0.59	0.761*	0.777*	−0.55	−0.31	−0.727*
Cooked vegetables	0.803**	0.815**	0.816**	0.771*	0.08	−0.04	0.830**	−0.61	0.45
Sweet	0.979**	0.972**	0.971**	0.976**	−0.52	−0.63	0.965**	−0.09	0.901**
Onion	−0.978**	−0.974**	−0.973**	−0.959**	0.32	0.43	−0.976**	0.34	−0.758*
Caramel	0.993**	0.991**	0.991**	0.981**	−0.35	−0.47	0.995**	−0.30	0.802**

	trans propenyl methyl disulfide	[*E*]-2-Heptenal	Dimethyl trisulfide	Dipropyl disulfide	Nonanal	[*E*]-2-Octenal	Benz-aldehyde	Nonenal	Dipropyl trisulfide
Intensity	0.36	−0.37	0.34	0.19	−0.28	−0.40	−0.30	−0.34	0.16
Desirability	0.832**	−0.64	0.819**	−0.04	−0.28	−0.65	−0.22	−0.47	0.00
Pungent	−0.931**	0.17	−0.939**	0.57	−0.28	0.19	−0.34	−0.04	0.53
Humidity	−0.31	0.913**	−0.28	−0.62	0.770*	0.924**	0.63	0.898**	−0.65
Sulfurous	0.687*	0.19	0.707*	−0.675*	0.46	0.16	0.44	0.35	−0.64
Green	−0.955**	0.02	−0.964**	0.678*	−0.42	0.05	−0.48	−0.18	0.65
Fat	0.973**	−0.21	0.978**	−0.53	0.23	−0.23	0.26	0.00	−0.50
Burnt	0.985**	−0.14	0.991**	−0.59	0.30	−0.18	0.37	0.06	−0.55
Earthy	−0.58	0.700*	−0.56	−0.16	0.40	0.692*	0.36	0.59	−0.18
Cooked vegetables	0.798**	0.22	0.822**	−0.835**	0.61	0.21	0.61	0.41	−0.792*
Sweet	0.975**	−0.38	0.970**	−0.37	0.06	−0.41	0.17	−0.19	−0.33
Onion	−0.971**	0.16	−0.975**	0.58	−0.29	0.19	−0.37	−0.04	0.55
Caramel	0.990**	−0.20	0.993**	−0.55	0.26	−0.23	0.35	0.01	−0.51

* Correlations were significant at $p < 0.05$.
** Correlations were significant at $p < 0.01$.

2.6. Statistical analysis

Statistical analysis was performed through one-way analysis of variance (ANOVA) followed by Tukey's test for multiple comparisons using the Statistical Package for the Social Sciences (SPSS 23; IBM Corp., New York, NY). The correlation between volatile compounds and sensory attributes was analyzed by Pearson correlation. Differences were considered to be significant at $p < 0.05$, $p < 0.01$ and $p < 0.001$. Principal component analysis (PCA) was used in the form of multivariate statistics and carried out by Statistica7.0 (Stat Soft Inc., Tulsa, OK). All experiments were performed in triplicate.

3. Results and discussion

3.1. Volatile compounds

Eighteen volatile compounds were identified by satisfying both matching factor (≥80%) and comparison RI. The RI responses of dimethyl sulfide, 2-methylbutanal and 3-methylbutanal were too small to confirm by the analysis used in this study. A list of volatile compounds is provided with their relative concentrations calculated based on internal standards (Table 2). All of the volatile compounds identified were either sulfur compounds or aldehydes. These two chemical groups are found in most *Allium* species, which are reportedly responsible for their characteristic flavors (Nielsen & Poll, 2004). The sulfur compounds accounted for 98.30% of the total volatile compounds in fresh onion, and the aldehydes existed in much smaller quantities (Table 3).

3.1.1. Sulfur compounds

In fresh onion, various flavor precursors exist, such as *S*-methyl cysteine sulfoxide, *trans*-*S*-1-propenyl cysteine sulfoxide, and *S*-propyl cysteine sulfoxide (Jones et al., 2004). Most volatile sulfur compounds are produced from these precursors through the action of alliinase. The sulfur compounds in onion, however, are readily lost during drying (Fig. 1).

All the sulfur compounds identified in this study have the chemical structure of either sulfide or thiophene (Table 2). Among the volatile components, dipropyl disulfide accounted for 77.70% of the total volatile compounds in fresh onion. This sulfur compound, however, was dramatically lost by drying, which was in agreement with previous results reported by Bernhard (1968). It was noteworthy that the amounts of total sulfur compounds in the samples dried at 90 °C were the highest among the dried onion samples (Fig. 1). The amount of sulfur compounds in the onion samples dried at 90 °C continued increasing as drying time increased. Furthermore, some new sulfides, such as dimethyl sulfide and dimethyl trisulfide, which had not been detected in the fresh onion, were found in the dried onion samples (Table 2), especially when the drying temperature was high. The formation of the sulfur compounds might have resulted from the thermal degradation of flavor precursors in fresh onion. It has been reported that *S*-methyl-cysteine might break down into methylsulfenic acid and α-aminoacrylic acid (Ostermayer & Tarbell, 1960). The self-condensation of methylsulfenic acid produces dimethyl thiosulfinate, which can be transformed into dimethyl disulfide and dimethyl thiosulfonate. In addition, the self-degradation of dimethyl thiosulfinate was reported as an important pathway leading to the formation of dimethyl trisulfide (Kubec, Drhová, & Velíšek, 1998). Accordingly, the amounts of dimethyl disulfide and dimethyl trisulfide increased as thermal drying continued to 3 h at 90 °C, reaching 6.86, and 66.74 μg/g solids, respectively, whereas the amount of dimethyl sulfide decreased continually during drying at 90 °C. Therefore, dimethyl sulfide might have transformed to dimethyl disulfide and dimethyl trisulfide through

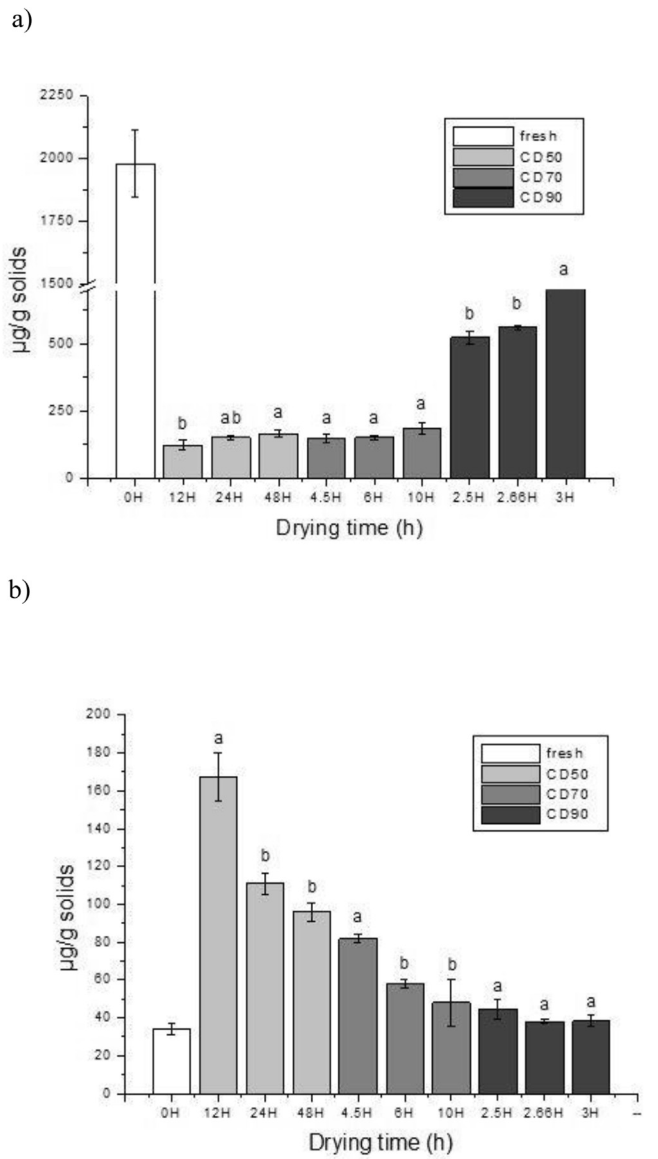

Fig. 1. Total contents of (a) volatile sulfur compounds and (b) volatile aldehydes in onion samples dried at 50 °C (CD50), 70 °C (CD70) and 90 °C (CD90). Values with different letters within the same temperature group are significantly different ($p < 0.05$).

the thermal drying process (Corzo-Martínez, Corzo, & Villamiel, 2007).

Compared to fresh onion, dried onion samples contained substantially smaller amounts of dipropyl disulfide and dipropyl trisulfide, ranging from 6.93 to 32.25, and from 0.36 to 7.99 μg/g solids, respectively. The amounts of these sulfides decreased while drying at 50 °C and 70 °C until the moisture content reached about 14% (24 h at 50 °C, and 6 h at 70 °C), but increased as drying continued to decrease the moisture content (Table 2). The formation of volatile compounds by thermal degradation of the flavor precursor, *S*-propyl cysteine sulfoxide, greatly depended on moisture content (Kubec, Drhová, & Velíšek, 1999).

The amount of thiophenes, such as 2,5-dimethylthiophene and 3,4-dimethylthiophene, increased during thermal drying. Thus, the onion sample dried at 90 °C for 3 h contained the highest amount of thiophenes, accounting for 53.47% of the total volatile compounds (Table 2). Dialkylthiophenes have been reported as thermolysis products derived from di(1-alkenyl) disulfides and alkyl 1-propenyl disulfides (Boelens & Brandsma, 1972). Overall data revealed that the convective drying used for the preparation of dry onion powders induced thermal degradation of flavor precursors in fresh onion. Therefore, it was anticipated that the flavor profile of thermally dried onions would be different from that of fresh onion.

3.1.2. Aldehydes

Aldehydes are another group of major flavor compounds found in onion. There were nine aldehydes identified in fresh and dried onion samples (Table 2). The total aldehyde content appeared to be the highest when onion was dried at 50 °C for 12 h (167 μg/g solids) and the lowest in fresh onion (34.2 μg/g solids) (Fig. 1, Table 2). Hexanal, 2-methyl 2-pentenal and [*E*]-2-heptenal were identified in fresh onion, which accounted for 1.70% of the total volatile compounds. The aldehyde content and composition changed substantially during drying. The aldehyde that was predominant in all fresh and dried onion samples was 2-methyl 2-pentenal, the amount of which ranged from 19.9 to 144 μg/g solids. 2-Methyl 2-pentenal is produced by the sequential transformation from 1-propenylsulfenic acid to thiopropanal-*S*-oxide, which subsequently changes into 2-methyl 2-pentenal (Nielsen, Larsen, & Poll, 2004). The aldehydes newly formed by drying, such as 2-methylbutanal and 3-methylbutanal increased as drying temperature and time increased. As the products of Strecker degradation of isoleucine and leucine, 2-methylbutanal and 3-methylbutanal were produced, respectively (Kraujalytė, Pelvan, & Alasalvar, 2016; Toldrá, Aristoy, & Flores, 2000). Accordingly, it was reported that the residual contents of these two amino acids were found to decrease when onions were dried using hot air (Kang, Kim, & Kim, 2007).

All of the aldehydes identified in this study were C6–C9 aldehydes, which are known to be main contributors to the characteristic aroma of various vegetables (Noordermeer et al., 2002). These aldehydes were derived from fatty acids through the action of residual enzymes such as lipoxygenase and hydroperoxide lyase. The activity of these enzymes could be higher at a drying temperature of 50 °C than that at higher temperatures. It was reported that both enzymes could be inactivated when the temperature was higher than 65 °C (Rodrigo, Jolie, Van Loey, & Hendrickx, 2007).

3.2. Principal component analysis (PCA)

The relationship between volatile compounds and drying conditions was evaluated by PCA, which might be useful in identifying volatile compounds distributed among the samples prepared under different conditions (Álvarez et al., 2011). Fig. 2 shows the biplot of the first two principal components, which explained 80.44% of the variance. The first principal component (PC1) accounted for 52.71% of the variance. It was mainly driven in the positive direction by sulfur compounds and in the negative direction by aldehydes. The samples prepared at 50 and 70 °C (CD50 and CD70) were clustered on the negative axis of PC1, and the amount of the total aldehydes in these samples was higher than that in fresh onion and in the samples dried at 90 °C (CD90) (Fig. 2). In particular, CD50 samples showed high correlations mainly with 2-methyl 2-pentenal and hexanal. On the other hand, CD90 samples were clustered on the positive axis of PC1 and highly associated with 2,5-dimethylthiophene. Not only 2,5-dimethylthiophene but also most sulfur compounds showed high correlations with the CD90 samples. The second principal component (PC2) accounted for 27.73% of the variance. The positive axis of PC2 was highly influenced by methyl propyl disulfide, dipropyl disulfide and dipropyl trisulfide. These three sulfides were the most abundant compounds in fresh onion clustered on the positive axis of PC2. The quantity of these sulfides decreased during the drying process.

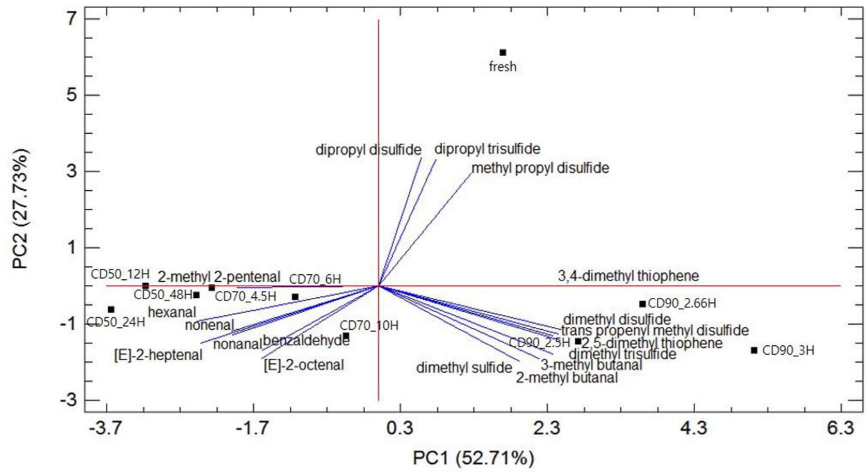

Fig. 2. Principal component analysis (PCA) of 18 volatile compounds and onion samples.

3.3. Sensory evaluation

A descriptive sensory analysis (DSA) was conducted to evaluate the effect of drying conditions on the sensory properties of the onion samples. Fig. 3 shows the DSA profiles of the onion samples. The major flavor characteristics of fresh onion include pungent (5.89), green (4.56) and onion (7.25). The onion sample dried at 50 °C for 12 h (CD50_12H) showed a significant decrease ($p < 0.05$) in green attribute compared to fresh onion but no significant difference in pungent and onion attributes (Table S2). This sample showed the highest humidity attribute ($p < 0.05$), which might be due to the aldehydes existing in the highest quantity in the sample (Petersen et al., 1999). The onion sample dried at the highest temperature (CD90_3H), however, showed a significant decrease in pungent ($p < 0.05$), green ($p < 0.001$) and onion ($p < 0.001$) attributes, compared to fresh onion. It was characterized by significant increases ($p < 0.001$) in fat, burnt, sweet and caramel descriptors. The excessive heat treatment also raised the intensity ($p < 0.05$) of diverse flavor attributes, such as sulfurous, cooked vegetables and desirability. A number of volatile compounds, some of which had not been detected in this study (Table 2), might be produced from the browning reaction induced by drying at high temperature. These compounds were assumed to generate burnt, sweet and caramel attributes which were typical aromas observed in browning products (Lee, Han, & Lim, 2016).

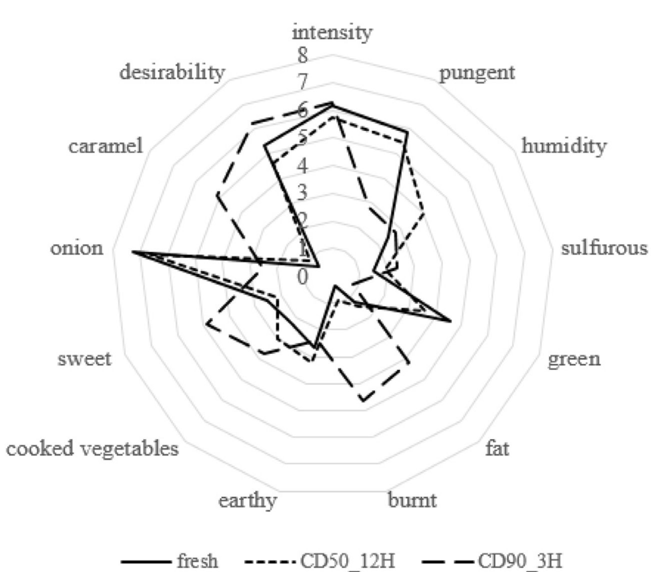

Fig. 3. Descriptive sensory analysis of aroma attributes in onion samples dried under different conditions.

3.4. Correlation between volatile compounds and sensory attributes

Pearson correlation was conducted to determine the relationship between 18 volatile compounds and 13 sensory attributes, including general intensity and desirability. The 2-methyl-2-pentenal and hexanal, which showed close correlations with CD50 samples in PCA, appeared to have a significantly ($p < 0.01$) positive correlation with humidity attribute which was considered to be an off-flavor in onion powder. According to a previous study (Petersen et al., 1999), off-flavor may be generated when the overall quantity of aldehydes is high. The 2,5-dimethylthiophene, which had close correlations with the CD90 samples, has been reported to be responsible for the flavor of spring onion and fresh onion. Compared to a previous study, this compound had high correlations ($p < 0.01$) with caramel, burnt fat, sweet and cooked vegetables flavors. 3,4-Dimethylthiophene, the content of which was the highest in CD90 samples, also had high correlations ($p < 0.01$) with caramel and sweet attributes. In particular, 2-methylbutanal and 3-methylbutanal were the aldehydes which showed correlation with CD90 samples and they have been reported to be responsible for burnt and caramel flavors (Machiels, Istasse, & Van Ruth, 2004). Dipropyl disulfide, which was a predominant volatile compound in fresh onion, was positively related with green attribute ($p < 0.05$). This compound has been reported to be responsible for the flavors of strong raw onion and fresh leek.

As shown in these results, the volatile composition in dry onion samples was much different from that in fresh onion and the volatile composition was not perfectly correlated with the sensory attributes of the onion samples. The volatile compounds exist as mixtures in onion samples, and the sensory attributes from the mixtures are hard to be predicted because these compounds affect each other, often generating unique attributes (Johnson et al., 2015). The relationships between volatile composition and flavor perception of dry onion samples should be further studied for their application in foods.

4. Conclusions

Changes in volatile composition and sensory qualities of onion samples occurred during convective drying. Dipropyl disulfide was found to be the major volatile compound in fresh onion and responsible for green sensory attributes. Various sulfides including dipropyl disulfide appeared to be the predominant odor compounds in fresh onion but dramatically decreased during drying. However, most sulfur compounds increased when onion was dried at relatively high temperature (90 °C in this study), possibly due to thermal degradation. 2,5-Dimethylthiophene, which had close correlations with the onion samples dried at 90 °C, was responsible for caramel, burnt, fat, sweet and cooked vegetable attributes. Aldehydes, such as 2-methyl-2-pentenal and hexanal, were produced from the action of residual enzymes during drying, especially when samples were dried at low temperature (50 °C in this study). These aldehydes were responsible for humidity attribute. The overall sensory quality of dry onion samples appeared not to be generated from the individual volatile compounds, but instead resulted from the complex mixture of these chemicals, which exhibited synergistic and masking effects. Mild drying conditions at relatively low temperature appeared ideal to retain the aroma of fresh onion.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.foodchem.2017.03.129.

References

Adam, E., Mühlbauer, W., Esper, A., Wolf, W., & Spiess, W. (2000). Quality changes of onion (Allium Cepa L.) as affected by the drying process. *Food/Nahrung, 44*(1), 32–37.

Ahvenainen, R. (1996). New approaches in improving the shelf life of minimally processed fruit and vegetables. *Trends in Food Science & Technology, 7*(6), 179–187.

Álvarez, M. G., González-Barreiro, C., Cancho-Grande, B., & Simal-Gándara, J. (2011). Relationships between *Godello* white wine sensory properties and its aromatic fingerprinting obtained by GC–MS. *Food Chemistry, 129*(3), 890–898.

Arslan, D., & Özcan, M. M. (2010). Study the effect of sun, oven and microwave drying on quality of onion slices. *LWT-Food Science and Technology, 43*(7), 1121–1127.

Bernhard, R. A. (1968). Comparative distribution of volatile aliphatic disulfides derived from fresh and dehydrated onions. *Journal of Food Science, 33*(3), 298–304.

Boelens, H., & Brandsma, L. (1972). Formation of dialkylthiophenes by thermolysis of di (1-alkenyl) disulfides and alkyl 1-propenyl disulfides. *Recueil des Travaux Chimiques des Pays-Bas, 91*(2), 141–145.

Boelens, M., De Valois, P. J., Wobben, H. J., & Van der Gen, A. (1971). Volatile flavor compounds from onion. *Journal of Agricultural and Food Chemistry, 19*(5), 984–991.

Cha, Y., & Cadwallader, K. (1998). Aroma-active compounds in skipjack tuna sauce. *Journal of Agricultural and Food Chemistry, 46*(3), 1123–1128.

Cha, Y., Kim, H., & Cadwallader, K. (1998). Aroma-active compounds in kimchi during fermentation. *Journal of Agricultural and Food Chemistry, 46*(5), 1944–1953.

Chin, S. T., Nazimah, S. A. H., Quek, S. Y., Man, Y. B. C., Rahman, R. A., & Hashim, D. M. (2008). Changes of volatiles' attribute in durian pulp during freeze-and spray-drying process. *LWT-Food Science and Technology, 41*(10), 1899–1905.

Colina-Coca, C., González-Peña, D., Vega, E., de Ancos, B., & Sánchez-Moreno, C. (2013). Novel approach for the determination of volatile compounds in processed onion by headspace gas chromatography–mass spectrometry (HS GC–MS). *Talanta, 103*, 137–144.

Coolong, T. W., Randle, W. M., & Wicker, L. (2008). Structural and chemical differences in the cell wall regions in relation to scale firmness of three onion (*Allium cepa* L.) selections at harvest and during storage. *Journal of the Science of Food and Agriculture, 88*(7), 1277–1286.

Corzo-Martínez, M., Corzo, N., & Villamiel, M. (2007). Biological properties of onions and garlic. *Trends in Food Science & Technology, 18*(12), 609–625.

Coste, E., Bauzá, M., Picallo, A., & Sance, M. (2010). Desarrollo preliminar de descriptores para el análisis sensorial de ajos desecados y liofilizados. *Revista de la Facultad de Ciencias Agrarias, 42*(1), 159–168.

Garruti, D. S., Franco, M. R. B., da Silva, M. A. A., Janzantti, N. S., & Alves, G. L. (2003). Evaluation of volatile flavour compounds from cashew apple (*Anacardium occidentale* L) juice by the Osme gas chromatography/olfactometry technique. *Journal of the Science of Food and Agriculture, 83*(14), 1455–1462.

Gray, D. A., Prestage, S., Linforth, R. S., & Taylor, A. J. (1999). Fresh tomato specific fluctuations in the composition of lipoxygenase-generated C6 aldehydes. *Food Chemistry, 64*(2), 149–155.

Johnson, A. J., Heymann, H., & Ebeler, S. E. (2015). Volatile and sensory profiling of cocktail bitters. *Food Chemistry, 179*, 343–354.

Jones, M. G., Hughes, J., Tregova, A., Milne, J., Tomsett, A. B., & Collin, H. A. (2004). Biosynthesis of the flavour precursors of onion and garlic. *Journal of Experimental Botany, 55*(404), 1903–1918.

Kang, N.-S., Kim, J.-H., & Kim, J.-K. (2007). Modification of quality characteristics of onion powder by hot-air, vacuum and freeze drying methods. *Korean Journal of Food Preservation, 14*(1), 61–66.

King, E. S., Kievit, R. L., Curtin, C., Swiegers, J. H., Pretorius, I. S., Bastian, S. E., & Francis, I. L. (2010). The effect of multiple yeasts co-inoculations on Sauvignon Blanc wine aroma composition, sensory properties and consumer preference. *Food Chemistry, 122*(3), 618–626.

Kraujalytė, V., Pelvan, E., & Alasalvar, C. (2016). Volatile compounds and sensory characteristics of various instant teas produced from black tea. *Food Chemistry, 194*, 864–872.

Kubec, R., Drhová, V., & Velíšek, J. (1998). Thermal degradation of S-methylcysteine and its sulfoxide important flavor precursors of Brassica and *Allium* vegetables. *Journal of Agricultural and Food Chemistry, 46*(10), 4334–4340.

Kubec, R., Drhová, V., & Velíšek, J. (1999). Volatile compounds thermally generated from S-propylcysteine and S-propylcysteine sulfoxide aroma precursors of *Allium* vegetables. *Journal of Agricultural and Food Chemistry, 47*(3), 1132–1138.

Le Guen, S., Prost, C., & Demaimay, M. (2000). Critical comparison of three olfactometric methods for the identification of the most potent odorants in cooked mussels (*Mytilus edulis*). *Journal of Agricultural and Food Chemistry, 48*(4), 1307–1314.

Leão, K. M., Sampaio, K. L., Pagani, A. A., & Da Silva, M. A. A. (2014). Odor potency, aroma profile and volatiles composition of cold pressed oil from industrial passion fruit residues. *Industrial Crops and Products, 58*, 280–286.

Lee, D.-J., Han, J.-A., & Lim, S.-T. (2016). Enhancement of antioxidant activity of onion powders by browning during drying process. *Korean Journal of Food Science and Technology, 48*(1), 15–19.

Machiels, D., Istasse, L., & Van Ruth, S. M. (2004). Gas chromatography-olfactometry analysis of beef meat originating from differently fed Belgian Blue, Limousin and Aberdeen Angus bulls. *Food Chemistry, 86*(3), 377–383.

Maskan, M. (2001). Kinetics of colour change of kiwifruits during hot air and microwave drying. *Journal of Food Engineering, 48*(2), 169–175.

Mondy, N., Duplat, D., Christides, J., Arnault, I., & Auger, J. (2002). Aroma analysis of fresh and preserved onions and leek by dual solid-phase microextraction–liquid extraction and gas chromatography–mass spectrometry. *Journal of Chromatography A, 963*(1), 89–93.

Nielsen, G. S., Larsen, L. M., & Poll, L. (2004). Formation of aroma compounds during long-term frozen storage of unblanched leek (*Allium ampeloprasum* Var. *Bulga*) as affected by packaging atmosphere and slice thickness. *Journal of Agricultural and Food Chemistry, 52*(5), 1234–1240.

Nielsen, G. S., & Poll, L. (2004). Determination of odor active aroma compounds in freshly cut leek (*Allium ampeloprasum* var. *Bulga*) and in long-term stored frozen unblanched and blanched leek slices by gas chromatography olfactometry analysis. *Journal of Agricultural and Food Chemistry, 52*(6), 1642–1646.

Noordermeer, M. A., Van der Goot, W., Van Kooij, A. J., Veldsink, J. W., Veldink, G. A., & Vliegenthart, J. F. (2002). Development of a biocatalytic process for the production of C6-aldehydes from vegetable oils by soybean lipoxygenase and recombinant hydroperoxide lyase. *Journal of Agricultural and Food Chemistry, 50*(15), 4270–4274.

Ostermayer, F., & Tarbell, D. S. (1960). Products of acidic hydrolysis of S-methyl-L-cysteine sulfoxide; the isolation of methyl methanethiolsulfonate, and mechanism of the hydrolysis. *Journal of the American Chemical Society, 82*(14), 3752–3755.

Petersen, M. A., Poll, L., & Larsen, L. M. (1999). Identification of compounds contributing to boiled potato off-flavour ('POF'). *LWT-Food Science and Technology, 32*(1), 32–40.

Plagemann, I., Zelena, K., Krings, U., & Berger, R. G. (2011). Volatile flavours in raw egg yolk of hens fed on different diets. *Journal of the Science of Food and Agriculture, 91*(11), 2061–2065.

Rodrigo, D., Jolie, R., Van Loey, A., & Hendrickx, M. (2007). Thermal and high pressure stability of tomato lipoxygenase and hydroperoxide lyase. *Journal of Food Engineering, 79*(2), 423–429.

Toldrá, F., Aristoy, M.-C., & Flores, M. (2000). Contribution of muscle aminopeptidases to flavor development in dry-cured ham. *Food Research International, 33*(3), 181–185.

Van den Dool, H., & Kratz, P. D. (1963). A generalization of the retention index system including linear temperature programmed gas—liquid partition chromatography. *Journal of Chromatography A, 11*, 463–471.

Yu, T. H., Wu, C. M., & Liou, Y. C. (1989). Volatile compounds from garlic. *Journal of Agricultural and Food Chemistry, 37*(3), 725–730.

Zhang, S., Du, Z., & Li, G. (2012). Graphene-supported zinc oxide solid-phase microextraction coating with enhanced selectivity and sensitivity for the determination of sulfur volatiles in *Allium* species. *Journal of Chromatography A, 1260*, 1–8.