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Chemical and sensory profiles of *makgeolli*, Korean commercial rice wine, from descriptive, chemical, and volatile compound analyses

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ABSTRACT

The chemical and sensory profiles of 12 commercial samples of *makgeolli*, a Korean rice wine, were determined using descriptive sensory, chemical, and volatile components analyses. The sample wines were analysed for their titratable acidity, ethanol content, pH, Hunter colour value and total reducing sugars. The chemical compositions of the *makgeolli* samples were found to be significantly different. The volatile compounds were extracted with solid-phase microextraction and analysed by gas chromatography time-of-flight mass spectrometry. In all, 45 major volatile compounds, consisting of 33 esters, 8 alcohols, 1 aldehyde, 1 acid, 1 phenol and 1 terpene, were identified; each *makgeolli* sample included 28–35 volatile compounds. Based on principal component analysis of the sensory data, samples RW1, RW2, RW5, RW8 and RW12 were associated with roasted cereal, mouldy, bubbles, sweet and sour attributes; the other samples were associated with sensory attributes of yellowness, yeast, full body, turbidity, continuation, swallow, alcohol, fruit aroma and whiteness.

1. Introduction

Makgeolli is a traditional Korean rice wine that has been consumed by Koreans for many centuries. The wine is also known by historical names such as *takju*, *dongdongju*, and *nongju*. Traditionally, *makgeolli* is brewed by fermenting *nuruk* (the source of the microorganism) by using yeast in a 2-step process involving saccharification and alcohol fermentation. The raw material rice is prepared by washing and soaking for 1–3 h, followed by steaming and cooling down of the steamed rice to room temperature. After cooling, the rice is thoroughly mixed with *nuruk* and yeast, and water is added for the parallel processes of saccharification and alcohol fermentation. *Nuruk* is a traditional starter culture made from wheat or grits, which allows the growth of various natural types of microorganisms such as fungi, yeast and lactic acid bacteria that saccharify the rice starch during fermentation (Kim et al., 2011). Moreover, several microorganisms from *nuruk* remain alive in the final products after bottling and during distribution. *Makgeolli* is also considered to have health benefits, because it contains various ingredients such as proteins, sugars, vitamins, bioactive compounds and organic acids (Jeong, Nam, Lee, & Lee, 2011; Kim, Kim, Bae, & Ahn, 2010). The wine is characterised by flavours of bitterness, sourness, sweetness, saltiness and *umami* (a savoury taste) (Lee, 1986). Furthermore, *makgeolli* has distinctive characteristics owing to its astringency, pungency, and full body, in addition to its unusual taste that results from the live yeast still present during fermentation and distribution (Lee, Kim, & Lee, 2009).

The addition of various wild-type yeasts and raw materials during fermentation was found to affect the chemical characteristics and volatile compounds profiles in the Korean traditional rice wine *yakju*, which is similar to *makgeolli* (Kim, Kim, Bae, & Ahn, 2010). Among the volatile compounds produced, short- and long-chain esters were affected, depending on the yeast strains present. The types of yeast strains from *nuruk* and the degrees of milling of the rice greatly affected the chemical and volatile compounds of the glutinous rice wines (Kim et al., 2010). An increase in the degree of milling decreases the alcohol, amino acid and organic acid contents, but increases the soluble solids, degree of colour, ultraviolet absorbance and reducing sugar and free sugar contents.

Recently, solid-phase microextraction (SPME), especially headspace (HS)-SPME sampling, has been widely used for the analysis of the volatile compounds in foods and beverages such as fruit juice beverage, vegetable oils, beers, wines and coffees because of its ease of use and sensitivity (Jung & Ebeler, 2003; Song, Gardner, Holland, & Beaudry, 1997). Furthermore, the combination of gas chromatography and time-of-flight mass spectrometry (GC–TOF/MS) can shorten the quantitative and qualitative analyses time, in addition to providing full mass spectra with a mass accuracy above 0.002 Da, even at very low sample concentrations (Song et al., 1997).

The studies on *makgeolli* were weighted towards the enhancement of the fermentation process associated with microorganisms, by varying the addition of raw materials. Sensory evaluations of

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makgeolli were carried out to investigate the changes in flavours that occur as a result of adding new microorganisms that originate from *nuruk* (Yang, Lee, Kim, Seo, & Lee, 2011), different raw materials (Kim et al., 2010), or the developed products (Lee & Lee, 2008). Moreover, few studies have profiled the sensory characteristics of *makgeolli* or examined the relationship between its sensory attributes and flavour characteristics.

Therefore, the objectives of the present study were to quantify the general compositions of several commercial samples of *makgeolli*, identify and quantify the volatile compounds, and compare the volatile components of each sample by carrying out a principal component analysis (PCA). The sensory characteristics of various *makgeolli* samples were also determined to investigate the relationships with their chemical characteristics.

2. Materials and methods

2.1. Materials and chemicals

Twelve *makgeolli* samples, live rice wines, were purchased from different manufacturing companies. The samples that used rice as the primary raw material were not sterilised during processing, and included live microorganisms (e.g. yeast and lactic acid bacteria) in the final products. The 12 *makgeolli* samples included products that had been made by large manufacturers with a large market share, which had won awards at the Korea Liquor Contest, or were locally well-known products. n-Alkane standards (C_8–C_{20} and C_{21}–C_{40}; Fluka, Steinheim, Switzerland) were used to determine the retention index, and 3-octanol (Fluka, GA, USA) was used as an internal standard. Sodium sulphate (Junsei, Tokyo, Japan) and HPLC-grade solvents were used (J.T. Baker, NJ, USA). Other reagents used were purchased from Sigma–Aldrich (MO, USA) and Junsei (Tokyo, Japan).

2.2. Standard chemical analysis and colour measurement

The pH of the *makgeolli* samples was measured with a pH metre (520A; Orion Research Inc., MA, USA). The titratable acidity (lactic acid in grams per litre) was measured by adding 10 g of *makgeolli* sample to 50 mL of deionised water and titrating with 0.1 N sodium hydroxide to an endpoint of pH 8.3 (AOAC, 1990). The total reducing sugars of the samples were measured using the dinitrosalicylic acid method (Miller, 1959), and the OD_{540} value was measured with a UV/Vis spectrophotometer (V-570; JASCO Co., Ltd., Japan). The Hunter colour values *L* (lightness), *a* (redness), and *b* (yellowness) were obtained using a spectrocolorimeter (Ultrascan XE; Hunter Lab, VA, USA). The ethanol concentration in the *makgeolli* samples were analysed using gas chromatography (GC-2010 system; Shimadzu, Kyoto, Japan) with a flame ionisation detector. A BP-20 capillary column (length 30 m × i.d. 0.25 mm × film thickness 0.25 μm; SGE, Ringwood, Australia) was used, with helium as the carrier gas. The injector temperature was 200 °C, with a split ratio of 1:20. The GC oven temperature was first programmed at 45 °C for 5 min and then increased to 200 °C at a rate of 15 °C/min and held at that temperature for 20 min. The column flow rate was 1.10 mL/min, and the sample injection volume was 0.1 μL. All the chemical measurements were repeated 3 times, and the average values are reported.

2.3. Volatile compound analysis

2.3.1. Headspace solid-phase microextraction and gas chromatography mass spectrometry analysis

The *makgeolli* samples were collected 7 days after the production date (bottling; these products are usually consumed within 10 days). Sodium sulphate (5 g) was added to the samples (10 mL) in 20-mL septum-sealed glass vials with screw caps. During sampling, 200 μL of the internal standard 3-octanol (50 ng/mL in distilled water) were added to 10 mL of the sample. The volatile compounds of the samples were extracted and absorbed at 60 °C for 20 min by using SPME fibres (50 μm DVB/CAR/PDMS; Supelco, PA, USA), after shaking the vial at 60 °C for 10 min in an autosampler (Combi PAL G6504-CTC; CTC Analytics, Zwingen, Switzerland). The fibre-absorbed volatiles were then injected into the GC inlet and desorbed for 5 min with the automatic autosampler. A GC (7890A; Agilent Technologies, USA) coupled with a mass spectrometer (TOF-MS, GCT premier; Waters, Manchester, UK) was used, with a DB-Wax column (30 m × 0.32 mm × 0.5 μm; J & W Scientific, CA, USA). The injection port was kept at 220 °C in splitless mode. Helium was used as the carrier gas at a constant flow rate of 2 mL/min. The GC oven temperature was initially maintained at 35 °C for 2 min, raised to 180 °C at 10 °C/min and then to 220 °C at 5 °C/min and finally held at 220 °C for 65 min. The mass detector was operated under electron impact mode (MS-EI) at 70 eV. The ion source temperature was set at 220 °C. The entire analytical procedure was controlled using MassLynx software (Waters, MA, USA), where the spectra were acquired over an *m/z* range of 45–500 a.m.u. and the total ion chromatogram was acquired for peak area integration. For the duration of the GC run, accurate mass measurements were obtained via an external calibration and a single point lock-mass correction at *m/z* 284.9943 for the EI by using 2,4,6-tris(trifluoromethyl)-1,3,5-triazine injected from the outer source as the internal reference. For the exact mass calibration, 9 fragments (obtained in an electron ionisation mode) of this reference compound in centroid mode were used. Once this calibration was made, *m/z* 284.9949 was used as an internal reference mass (lock mass). The exact mass calibration was considered successful if the maximum difference between the measured and theoretical masses was 1.0 mDa. In both cases, 30 final spectra (i.e. 30 points) were used for calculation of the mass resolution and for exact mass calibration during the tuning procedure.

2.3.2. Identification and data processing of volatile compounds

The identification of volatile compounds was achieved by comparing various information, including retention index, NIST library search, spectra and element composition by using the MassLynx 4.0 and ChromaLynx software (Waters Corp.). The volatile compounds were positively identified by comparing their Kovats retention indices (KIs) (Kovats, 1965) with previously reported KIs. The KIs of unknown compounds were determined via sample injection with a homologous series of alkanes (C_6–C_{24}). All MS data, including retention time, *m/z*, and ion intensity, were extracted using the MassLynx 4.0 and ChromaLynx software (Waters Corp.) and assembled into a data matrix. All spectra were aligned and normalised to the total peak intensity. The assignment of volatile compounds contributing to the observed variance was completed through elemental composition analysis by using MassLynx 4.0, with the exact mass (theoretical mass), actual mass (measured mass), mass error (acceptable mass tolerance of the maximum difference between measured and theoretical masses), and i-Fit algorithm (the likelihood that the isotopic pattern of an elemental composition matches a cluster of peaks in the spectrum).

To quantify the volatile compounds, the samples were tested in quadruplicates, and the integrated areas based on the total ion chromatogram were normalised to the areas of the internal standard and averaged. The relative concentrations of volatile compounds in the 12 samples were determined by comparison with the concentration of the internal standard (3-octanol), assuming a response factor of 1. To determine the reproducibility of the quadruplicate injections and identify the peaks that carried across samples, 2-way analysis of variance (ANOVA) (sample, injection)

Table 1
Sensory attributes, definitions and physical standards for *makgeolli*.

Attributes	Code	Written definitions	Standard reference
Appearance			
Whiteness	white	Degree of whiteness	No physical standards
Yellowness	yellow	Degree of yellowness	No physical standards
Turbidity	turbid	Degree of haziness	No physical standards
Bubbles	bubbles	Amount of bubbles in the glass	No physical standards
Aroma			
Alcohol_aroma	alcohol_A	The smell associated with alcohol	25% (w/v) Ethanol
Sour_aroma	sour_A	Sour aroma	0.2 mL Vinegar/100 mL distiled water
Sweet_aroma	sweet_A	The smell associated with grain syrup	15 g Grain syrup/150 mL distiled water
Fruits_aroma	fruit_A	From fruit aroma (e.g. pear)	15 g Crushed pear/100 mL distiled water
Roasted_cereal	cereal_A	From roasted cereal aroma (e.g. roasted barley, similar cereals)	4 g Crushed unpolished rice and barley/20 mL distiled water
Yeast_aroma	yeast_A	From activated yeast aroma	0.1% Yeast in 10% warm sugar solution overnight
Mouldy_aroma	mouldy_A	From mouldy aroma in basement or cellar	10 g *Nuruk*/100 mL warm distiled water
Flavour/taste			
Alcohol	alcohol_T	Fundamental taste of alcohol	25% (w/v) Ethanol
Sweet	sweet_T	Fundamental taste of which sucrose is typical	6% (w/v) Sucrose
Sour	sour_T	Fundamental taste of vinegar	0.25% (w/v) Citric acid
Bitter	bitter_T	Fundamental taste of which caffeine or quinine are typical	0.1% (w/v) Anhydride caffeine
Roasted cereal	cereal_T	From roasted cereal flavour (e.g. roasted barley, similar cereals)	4 g Crushed unpolished rice and barley/20 mL distiled water
Yeast	yeast_T	From activated yeast flavour	0.1% Yeast in 10% warm sugar solution overnight
Mouth feel/aftertaste			
Astringency	astrin	Mouth feel of dryness	0.1% (w/v) Aluminium sulphate
Full body	body	Full-bodied while tasting	No physical standards
Carbonation	carbo	Tingling sensation due to carbon dioxide	No physical standards
Continuation	continue	Feeling of continuing taste	No physical standards
Swallow	swallow	Imitation while swallowing	No physical standards

was performed for each volatile compound peak. All peaks varied significantly across samples, with only 4 varying significantly across replications.

2.4. Descriptive sensory analysis

Sensory evaluation of the 12 *makgeolli* samples was conducted by 10 judges (6 males and 4 females) drawn from Sejong University, Seoul, Korea. Six 1-h training sessions were held for the descriptor development, definitions, and panel training. A total of 22 attributes were generated to characterise the sensory properties of the *makgeolli* samples (Table 1). Standards used to define these aromas and taste descriptors were included during the training and formal sessions. Three samples per session were evaluated, in duplicate, and a total of 8 sessions were conducted. The presentation order of each *makgeolli* sample was randomised for each session. The stimuli were presented in 10-mL aliquots in clear tulip-shaped glasses marked with 3-digit numbers and covered with Petri dishes. The judges scored each attribute on a scale of 0–9, where 9 was the highest intensity and 0 was none. Water was provided to the panellists for rinsing their palate between samples. All evaluations were made in sensory booths at room temperature.

2.5. Statistical analysis

All statistical analyses of the GC and sensory data were performed using SAS ver. 6.12 (SAS Institute, Cary, NC, USA) or XLSTAT ver. 2007.1 (Addinsoft, New York, NY, USA). To evaluate significant differences in the volatile compounds among the 12 *makgeolli*

Table 2
Composition of the 12 *makgeolli* samples.

Sample	Raw materials	Shelf-life[A] (days)	pH	Total acidity (as lactic acid, % v/w)	Reducing sugar (% v/v)	Ethanol (% v/v)	Hunter colour value		
							L	*a*	*b*
RW[B]1	Rice (domestic) 100%, licorice root	30	4.03 ± 0.01^{e}	0.43 ± 0.01^{i}	1.09 ± 0.00^{c}	7.77 ± 1.19^{ef}	17.87 ± 0.20^{f}	3.49 ± 0.04^{bc}	9.29 ± 0.10^{c}
RW2	Rice (domestic organic rice) 100%	20	4.12 ± 0.02^{d}	0.37 ± 0.02^{e}	1.23 ± 0.02^{g}	9.58 ± 3.02^{ab}	15.85 ± 0.19^{g}	3.14 ± 0.12^{d}	$8.74 \pm 0.15d^{e}$
RW3	Rice (imported from USA) 90%, wheat (imported from USA) 10%	15	4.07 ± 0.02^{cd}	0.45 ± 0.01^{d}	1.25 ± 0.05^{b}	12.83 ± 1.33^{ab}	17.32 ± 0.48^{b}	3.48 ± 0.07^{h}	9.61 ± 0.24^{a}
RW4	Rice (domestic) 90%, malto-oligosaccharides 10%	10	3.61 ± 0.01^{c}	0.64 ± 0.01^{a}	1.32 ± 0.03^{e}	8.62 ± 1.00^{ae}	12.47 ± 0.09^{j}	3.52 ± 0.05^{b}	7.66 ± 0.07^{g}
RW5	Rice (domestic) 94%, malt sugar 6%	29	3.86 ± 0.02^{d}	0.38 ± 0.01^{hi}	1.07 ± 0.00^{f}	8.14 ± 0.46^{ef}	19.62 ± 0.31^{d}	2.68 ± 0.23^{e}	9.37 ± 0.17^{c}
RW6	Rice (domestic) 100%	18	3.88 ± 0.02^{e}	0.35 ± 0.01^{fg}	1.05 ± 0.01^{a}	8.39 ± 0.25^{c}	21.98 ± 0.89^{a}	1.31 ± 0.24^{j}	8.67 ± 0.29^{e}
RW7	Rice (domestic) 100%	10	3.74 ± 0.08^{a}	0.67 ± 0.01^{gh}	1.49 ± 0.04^{b}	8.86 ± 0.12^{b}	5.41 ± 0.05^{i}	4.83 ± 0.02^{a}	3.60 ± 0.03^{d}
RW8	Rice (domestic) 80%, wheat (imported) 10%, starch sugars 10%	15	3.84 ± 0.01^{b}	0.46 ± 0.01^{gh}	1.07 ± 0.01^{g}	8.57 ± 0.24^{a}	16.35 ± 0.16^{i}	3.42 ± 0.06^{bc}	9.21 ± 0.10^{f}
RW9	Rice (domestic) 100%	30	4.00 ± 0.01^{c}	0.39 ± 0.03^{f}	1.19 ± 0.01^{b}	7.68 ± 0.43^{d}	16.80 ± 0.18^{c}	5.21 ± 0.06^{g}	10.45 ± 0.10^{b}
RW10	Rice (domestic) 90%, isomalto sugars 10%	10	3.86 ± 0.01^{c}	0.54 ± 0.02^{g}	1.26 ± 0.01^{g}	13.70 ± 0.58^{g}	13.99 ± 0.07^{h}	3.27 ± 0.07^{cd}	8.43 ± 0.06^{f}
RW11	Rice (domestic) 90%, isomalto sugars 10%	10	3.60 ± 0.05^{f}	0.61 ± 0.01^{b}	1.52 ± 0.04^{d}	6.69 ± 0.24^{g}	12.47 ± 0.09^{j}	3.52 ± 0.05^{b}	7.66 ± 0.07^{g}
RW12	Rice (domestic) 100%	20	3.58 ± 0.03^{f}	0.56 ± 0.02^{c}	1.40 ± 0.01^{de}	7.52 ± 0.45^{fg}	18.42 ± 0.25^{e}	1.91 ± 0.02^{f}	9.26 ± 0.10^{c}

All composition data are presented as the mean of triplicates; data with the same letter in a column are not significantly different, with significance set at $p < 0.05$ by Fisher's least-significant difference test.

[A] Shelf-life is the corresponding time in the storage case in a refrigerator (less than 10 °C).

[B] *Makgeolli* samples were named and numbered as RW, of rice wine.

Table 3
Identification of volatile compounds in the *makgeolli* samples by gas chromatography time-of-flight mass spectrometry using solid-phase microextraction fibres (DVB/CAR/PDMS).

No.	Code	Type	KI[a]	Retention time	Identity[b]	Formula[c]	Exact mass[d]	Actual mass[e]	Mass error[f]		i-FIT[g]	MS fragment [EI+]
									mDa	ppm		
1	et1	Ester	510	2.8	Ethyl acetate	$C_4H_8O_2$	88.0518	88.0524	−0.6	−6.8	8.6	70.0, 61.0, 43.0, 88.0
2	al1	Alcohol	678	4.1	Ethanol	C_2H_5O	45.0369	45.0340	2.9	64.4	25.4	45.0, 30.9, 28.9
3	et2	Ester	844	5.8	Isobutyl acetate	$C_6H_{12}O_2$	116.0820	116.0837	−2	−14.6	NC[h]	56.0, 73.0, 43.0
4	et3	Ester	911	6.8	Ethyl butanoate	$C_6H_{12}O_2$	116.0848	116.0837	1.1	9.5	10.1	88.0, 71.0, 91.0
5	al2	Alcohol	938	7.2	1-Propanol	C_3H_8O	60.0583	60.0575	0.8	13.3	9.7	59.0, 42.0
6	al3	Alcohol	1081	9.9	2-Methyl-1-propanol	$C_4H_{10}O$	74.0739	74.0732	0.5	6.8	13.2	74.0, 56.0, 97.1
7	et4	Ester	1092	10.1	3-Methylbut-1-yl ethanoate	$C_7H_{14}O_2$	130.0955	130.0994	−3.9	−30	11.3	70.0, 55.0, 87.0, 43.0
8	al4	Alcohol	1206	13.7	3-Methyl-1-butanol	$C_5H_{12}O$	88.0875	88.0888	−1.3	−14.8	10.7	55.05, 70.0, 41.0
9	et5	Ester	1227	14.2	Ethyl hexanoate	$C_8H_{16}O_2$	144.1165	144.1150	1.5	10.4	10.6	88.0, 99.0, 71.0
10	et6	Ester	1344	17.2	Ethyl heptanoate	$C_9H_{18}O_2$	158.1300	158.1307	−0.7	−4.4	11.9	88.0, 113.0, 101.0, 70.0
11	et7	Ester	1356	17.6	Ethyl-2-hydroxypropanoate	$C_5H_{10}O_3$	118.0668	118.0630	3.8	32.2	10.6	45.0, 75.0, 103.0
12	al5	Alcohol	1389	18.6	3-Ethoxy-1-propanol	$C_5H_{12}O_2$	104.0800	104.0837	−3.7	−35.5	16.6	59.0, 75.0, 86.0, 41.0
13	et8	Ester	1444	20.1	Ethyl octanoate	$C_{10}H_{20}O_2$	172.1465	172.1463	0.2	1.2	11.1	88.0, 101.0, 127.1, 70.0
14	et9	Ester	1452	20.3	2-Methylbutyl caproate	$C_{11}H_{22}O_2$	186.8233	186.1620	−2	−10.7	14.4	99.0, 70.0, 117.0, 43.0
15	ad1	Aldehyde	1527	22.3	Benzaldehyde	C_7H_6O	106.0433	106.0419	1.4	13.2	5.9	106.0, 77.0, 117.0, 145.1
16	et10	Ester	1545	22.7	Ethyl nonanoate	$C_{11}H_{22}O_2$	186.1642	186.1620	2.2	11.8	11.2	88.0, 101.0, 141.1, 73.0
17	al6	Alcohol	1552	22.9	2,4-Butanediol	$C_4H_{10}O_2$	90.0704	90.0681	2.3	25.5	10.6	45.0, 57.0, 75.0, 90.0
18	et11	Ester	1560	23.1	Isobutyl octanoate	$C_{12}H_{24}O_2$	200.1800	200.1776	2.4	12	NC[h]	127.1, 145.1, 57.0
19	et12	Ester	1647	25.2	Ethyl decanoate	$C_{12}H_{24}O_2$	200.1806	200.1776	3	15	13.6	88.0, 101.0, 155.1, 73.0
20	et13	Ester	1666	25.6	Isoamyl octanoate	$C_{13}H_{26}O_2$	214.1942	214.1933	0.9	4.2	11.7	70.0, 127.1, 145.1, 57.0
21	et14	Ester	1674	25.8	Ethyl benzoate	$C_9H_{10}O_2$	150.0673	150.0681	−0.8	−5.3	16.1	105.0, 122.0, 152.1, 51.0
22	et15	Ester	1684	26.1	Diethyl succinate	$C_8H_{14}O_4$	174.0882	174.0892	−0.3	−5.7	7.3	101.0, 129.0, 73.0, 55.0
23	et16	Ester	1696	26.4	Ethyl trans-4-decenoate	$C_{12}H_{22}O_2$	198.1625	198.1620	0.5	2.5	15.0	88.0, 135.1, 55.0, 152.1
24	al7	Alcohol	1726	27.0	3-Methylthiopropanol	$C_4H_{10}OS$	106.0471	106.0452	1.9	17.9	7.4	106.0, 61.0, 73.0, 88.0
25	et17	Ester	1793	28.5	Ethyl phenylacetate	$C_{10}H_{12}O_2$	164.0831	164.0837	−0.6	−3.7	7.0	91.0, 164.0, 65.0
26	et18	Ester	1813	29.0	Ethyl 2-methylbutyrate	$C_7H_{14}O_2$	130.1000	130.0994	0.6	4.6	32.3	87.0, 102.0, 74.0, 60.0
27	et19	Ester	1820	29.2	2-Phenethyl acetate	$C_{10}H_{12}O_2$	164.0827	164.0837	−1	−6.1	8.0	104.0, 91.0, 78.0
28	et20	Ester	1845	29.8	Ethyl dodecanoate	$C_{14}H_{28}O_2$	228.2088	228.2089	−0.1	−0.4	7.8	88.0, 101.0, 157.1, 183.1
29	et21	Ester	1861	30.1	Isopentyl decanoate	$C_{15}H_{30}O_2$	242.2251	242.2246	0.5	2.1	12.5	70.0, 155.1, 173.1, 55.0
30	et22	Ester	1894	31.0	Ethyl 3-methylbutyl succinate	$C_{11}H_{20}O_4$	216.1400	216.1362	3.8	17.6	14.5	101.0, 129.0, 71.0, 55.0
31	al8	Alcohol	1902	31.2	2-Phenylethanol	$C_8H_{10}O$	122.0731	122.0732	−0.1	−0.8	31.2	91.0, 65.0, 122.0
32	et23	Ester	2062	33.9	Ethyl tetradecanoate	$C_{16}H_{32}O_2$	256.2372	256.2402	−3	−11.7	11.6	88.0, 101.0, 157.1, 213.1
33	et24	Ester	2167	35.8	Ethyl pentadecanoate	$C_{17}H_{34}O_2$	270.2533	270.2559	−2.6	−9.6	12.5	88.0, 101.0, 157.1, 70.0
34	et25	Ester	2178	36.0	Hexadec-9-enyl tetradecanoate	$C_{30}H_{58}O_2$	450.4400	450.4437	−3.7	−8.2	NC[h]	88.0, 96.0, 124.1, 83.0.
35	ph1	PHENOL	2207	36.6	4-Ethenyl-2-methoxyphenol	$C_9H_{10}O_2$	150.0689	150.0681	0.8	5.3	11.8	150.0, 135.0, 107.0, 77.0
36	et26	Ester	2227	37.0	10-Methoxy-10-oxo-decanoic acid	$C_{11}H_{20}O_4$	216.1400	216.1362	3.8	17.6	10.9	152.0, 157.1, 111.0, 125.0
37	et27	Ester	2263	37.7	Ethyl hexadecanoate	$C_{18}H_{36}O_2$	284.2745	284.2715	3	10.6	28.1	88.0, 101.0, 73.0, 55.0
38	et28	Ester	2287	38.2	Ethyl (9E)-hexadec-9-enoate	$C_{18}H_{34}O_2$	282.2512	282.2559	−4.7	−16.7	15.8	236.2, 194.2, 69.0, 83.0
39	tp1	Terpene	2303	38.5	1,5,9,9-Tetramethyl-, Z,Z,Z-1,4,8,-cycloundecatriene	$C_{15}H_{24}$	204.1856	204.1878	−2.2	−10.8	11.4	93.0, 121.1, 189.1, 80.0
40	ac1	Acid	2318	38.8	n-Decanoic acid	$C_{10}H_{20}O_2$	172.1473	172.1463	1	5.8	11.4	123.0, 73.0, 104.0, 60.0
41	et29	Ester	2351	39.5	Ethyl heptadecanoate	$C_{19}H_{38}O_2$	298.2873	298.2872	0.1	0.3	15.6	88.0, 101.0, 73.0, 253.2
42	et30	Ester	2431	41.2	Ethyl 15-methylheptadecanoate	$C_{20}H_{40}O_2$	312.3033	312.3028	0.5	1.6	30.9	88.0, 101.0, 157.1, 269.2

(*continued on next page*)

Table 3 (*continued*)

No.	Code	Type	KI[a]	Retention time	Identity[b]	Formula[c]	Exact mass[d]	Actual mass[e]	Mass error[f]		i-FIT[g]	MS fragment [EI+]
									mDa	ppm		
43	et31	Ester	2443	41.5	Ethyl (Z)-octadec-9-enoate	$C_{20}H_{38}O_2$	310.2867	310.2872	−0.5	−1.6	8.4	265.2, 83.0, 97.0, 55.0
44	et32	Ester	2546	43.8	Ethyl-9,12-octadecadienoate	$C_{20}H_{36}O_2$	308.2727	308.2715	3.5	3.9	8.9	67.0, 79.0, 95.0, 109.1
45	et33	Ester	2529	43.4	Ethyl (9Z,12Z,15Z)-9,12,15-octadecatrienoate	$C_{20}H_{34}O_2$	306.2563	306.2559	0.4	1.3	13.5	79.0, 95.0, 67.0, 108.0

[a] KI is the retention index calculated by the Kovats method.
[b,c] The spectra and formula were used in the NIST MS search 2.0 programme, and the volatile compounds were identified by comparing with those in the NIST/EPA/NIH mass spectral database.
[d] Exact mass, the theoretical mass.
[e] Actual mass, the measured mass. The exact mass, mass error and i-FIT of the elemental composition were calculated using the software programme MassLynx 4.0.
[f] Mass error (mDa and ppm), acceptable mass tolerance of the maximum difference between the measured and theoretical masses.
[g] i-FIT, the likelihood that an isotopic pattern of the elemental composition matches a cluster of peaks in the spectrum.
[h] NC, not calculated.

Table 4
Quantitative analysis of volatile compounds in the *makgeolli* samples by gas chromatography time-of-flight mass spectrometry using solid-phase microextraction fibres (DVB/CAR/PDMS).

No.	Identity	Relative area[a] (%)											
		RW1	RW2	RW3	RW4	RW5	RW6	RW7	RW8	RW9	RW10	RW11	RW12
1	Ethyl acetate	0.40	0.25	0.71	0.82	0.25	0.74	3.38	1.72	0.31	1.90	1.93	0.88
2	Ethanol	9.59	9.58	14.39	13.91	9.74	8.27	12.18	7.49	12.41	9.18	21.83	23.31
3	Isobutyl acetate	–	–	–	–	–	0.07	–	–	–	–	–	–
4	Ethyl butanoate	–	–	–	–	–	0.11	–	0.04	–	0.07	–	–
5	1-Propanol	–	–	–	–	–	–	–	–	–	–	0.21	0.14
6	2-Methyl-1-propanol	0.74	0.48	0.36	0.10	–	0.43	–	–	0.21	–	–	–
7	3-Methylbut-1-yl ethanoate	0.57	0.39	0.60	1.01	0.71	2.78	0.12	0.77	0.55	1.42	1.77	0.60
8	3-Methyl-1-butanol	3.78	3.41	4.07	4.23	3.42	5.00	3.17	2.48	4.19	2.97	5.22	4.46
9	Ethyl hexanoate	0.18	0.90	0.55	–	0.52	0.22	0.37	1.15	–	0.92	0.46	0.51
10	Ethyl heptanoate	–	0.06	–	–	0.05	–	–	0.06	–	0.03	0.08	0.07
11	Ethyl-2-hydroxypropanoate	–	–	–	–	–	–	0.40	–	–	–	–	–
12	3-Ethoxy-1-propanol	0.07	–	–	–	–	0.05	–	–	–	0.01	0.11	0.09
13	Ethyl octanoate	0.79	6.68	6.27	5.12	5.38	1.56	5.25	7.26	5.91	4.39	5.37	4.41
14	2-Methylbutyl caproate	0.91	0.09	–	0.11	0.05	–	0.06	0.11	0.05	0.14	0.24	–
15	Benzaldehyde	0.05	0.10	–	0.03	0.08	–	0.01	0.05	0.02	0.02	0.10	0.07
16	Ethyl nonanoate	0.03	0.28	0.16	0.15	0.38	0.12	0.12	0.17	0.09	0.18	0.18	0.23
17	2,4-Butanediol	0.06	0.08	0.31	0.32	–	–	0.32	0.05	0.11	0.10	0.27	0.19
18	Isobutyl octanoate	–	–	–	–	–	–	–	–	–	0.06	–	–
19	Ethyl decanoate	5.76	9.91	8.23	7.93	7.86	3.77	6.85	9.47	9.61	6.82	8.55	6.31
20	Isoamyl octanoate	0.39	0.90	0.70	0.61	0.42	0.14	–	0.68	0.86	0.64	0.66	0.53
21	Ethyl benzoate	–	0.16	0.06	0.11	0.09	0.34	–	–	–	0.13	–	0.15
22	Diethyl succinate	1.42	1.17	6.15	2.86	0.15	0.13	1.66	0.42	6.79	1.93	0.35	0.29
23	Ethyl trans-4-decenoate	0.31	0.17	0.11	–	0.10	0.02	–	0.35	0.10	–	0.59	–
24	3-Methylthiopropanol	0.15	0.05	0.05	0.17	0.05	0.04	0.17	0.09	0.02	0.29	0.25	0.11
25	Ethyl phenylacetate	–	–	0.03	0.15	–	0.02	0.05	0.04	0.03	0.13	–	–
26	Ethyl 2-methylbutyrate	0.49	0.47	0.35	0.73	–	0.14	0.16	0.40	0.15	0.12	0.30	1.07
27	2-Phenethyl acetate	5.87	4.31	4.01	4.25	2.98	7.45	1.13	4.44	4.21	3.65	3.82	3.14
28	Ethyl dodecanoate	4.16	5.18	3.42	3.02	4.17	2.74	2.48	5.54	4.53	6.98	4.42	0.93
29	Isopentyl decanoate	–	–	0.06	0.21	0.14	0.07	–	0.26	0.21	0.04	0.15	0.07
30	Ethyl 3-methylbutyl succinate	–	–	0.42	0.37	–	–	0.03	0.05	0.54	–	–	–
31	2-Phenylethanol	17.19	23.51	22.68	18.69	22.75	21.85	25.70	18.41	24.31	16.75	17.60	25.78
32	Ethyl tetradecanoate	6.31	3.45	2.63	4.11	4.16	2.58	5.77	5.90	1.26	6.46	2.81	1.59
33	Ethyl pentadecanoate	0.14	–	–	–	0.08	–	0.05	0.05	–	0.09	–	–
34	Hexadec-9-enyl tetradecanoate	0.08	0.14	–	–	0.03	–	–	0.04	–	–	–	–
35	4-Ethenyl-2-methoxyphenol	0.69	–	0.27	4.25	0.63	11.54	0.26	4.89	0.14	–	2.84	1.58
36	10-Methoxy-10-oxo-decanoic acid	–	–	–	0.13	0.26	0.01	–	0.04	–	–	0.07	0.20
37	Ethyl hexadecanoate	14.12	10.49	9.61	12.24	9.31	11.82	14.19	10.23	10.62	15.03	9.56	10.37
38	Ethyl(9E)-hexadec-9-enoate	–	0.30	–	0.25	0.73	0.31	0.15	0.28	–	0.33	0.11	0.53
39	1,5,9,9-Tetramethyl-,Z,Z,Z-1,4,8,-cycloundecatriene	–	–	–	–	–	–	0.06	–	–	–	–	–
40	n-Decanoic acid	–	–	–	0.11	–	–	0.08	–	0.13	–	–	–
41	Ethyl heptadecanoate	–	0.23	–	–	0.05	–	–	–	–	0.10	–	–
42	Ethyl 15-methylheptadecanoate	1.77	0.40	0.38	0.70	0.99	0.55	0.41	0.33	0.26	0.57	0.24	0.28
43	Ethyl(Z)-octadec-9-enoate	11.16	8.03	6.49	6.24	11.73	9.00	6.13	8.13	3.70	8.19	4.84	6.10
44	Ethyl-9,12-octadecadienoate	12.49	8.75	6.44	6.87	12.62	8.08	9.06	8.54	8.49	9.92	4.95	5.85
45	Ethyl(9Z,12Z,15Z)-9,12,15-octadecatrienoate	0.27	0.04	–	–	0.11	–	0.12	0.06	0.05	0.15	–	–

-, Not detected.
[a] The relative area % was calculated from the ratio of the peak area of each compound to the total ion chromatogram %.

samples, ANOVA was performed using the general line model procedure. PCA was performed on the mean values of the relative concentrations of the volatile compounds by using a correlation matrix with no rotation. PCA was also applied to clarify the

relationship between the samples and their volatile compounds. The GC data set included 45 identified volatile compounds.

The descriptive data set was initially analysed for significant overall product effects, by employing a 3-way mixed model ANOVA (judges, samples and replications), with all 2-way interactions with judges treated as random. Individual product differences were identified by Fisher's least-significant difference (LSD) test. Correlations between the mean attribute ratings and chemical properties were calculated, and PCA on the mean attribute ratings employing the covariance matrix was conducted.

3. Results and discussion

3.1. General compositions of the 12 commercial makgeolli samples

The general compositions of the 12 *makgeolli* samples are presented in Table 2. The pH values varied from 3.58 to 4.12. Most Korean traditional rice wines such as *takju*, *yakju* and *makgeolli* have an acidic pH of 3.4–4.5 owing to the production of organic acids by the lactic acid bacteria (Jianbo, Kim, Jin, Eom, & Han, 2008).The total acidity of the *makgeolli* samples ranged from 0.37% to 0.67%, which was twice the difference between the lowest value (of sample RW2) and the highest value (of RW7). The total acidity of the *makgeolli* indicated that the overall pH could be changed by the production of various organic acids by the microbes, which is one of the factors related to fermentation properties (Lee, Hwang, Lee, & Son, 2009). Reducing sugars ranged from 1.05% to 1.52%, and were above 1.3% in samples RW4, RW7, RW11 and RW12. The ethanol concentrations of the samples ranged from 6.6% to 8.86%, except for samples RW2, RW3 and RW10, which exhibited an almost 2-fold higher concentration. The ethanol content of Korean *makgeolli* is usually adjusted to 6% through dilution after fermentation and before delivery of the goods. Increases in the ethanol content after delivery are likely caused by continuous fermentation in those products containing live microorganisms such as yeast. The lightness (L) value was in the range of 5.41–21.98. The redness (a-value) of all samples was low (<5.21), whereas the yellowness (b-value) was within a narrow range of 7.99–10.45. Statistical analysis of the general compositions showed that the samples were significantly different in terms of each composition, which implies that no unique trend is present in the many live *makgeolli* varieties produced.

3.2. Compositions of volatile compounds in the 12 commercial makgeolli samples

To compile the aromatic characteristics of the *makgeolli* samples, approximately 70 volatile compounds in the 12 commercial rice wines were extracted with SPME fibre and analysed by GC–TOF/MS. A total of 45 major volatile compounds from the 70 extracted were identified using the MassLynx software; untraceable and/or impurity compounds were excluded. The 45 volatile compounds (Table 3) comprised 33 esters, 8 alcohols, 1 aldehyde, 1 acid, 1 phenol and 1 terpene; each *makgeolli* sample included 28–35 volatile compounds (Table 4).

Based on the quantification of the relative peak areas (Table 4), the esters constituted the largest group of volatile compounds. The most abundant compounds were 2-phenylethanol and ethanol. The predominant volatile compounds, which accounted for 1–10% of the total quantified, included ethyl acetate, ethanol, 3-methyl-1-butanol, ethyl octanoate, ethyl decanoate, diethyl succinate, 2-phenethyl acetate, ethyl dodecanoate, ethyl hexadecanoate, 2-methoxy-4-vinylphenol, ethyl(Z)-octadec-9-enoate, ethyl tetradecanoate and ethyl 9,12-octadecadienoate. Other minor compounds were present at <1.0% each. The compounds ethanol, propan-1-ol, 2-methyl-1-propanol, 2-methylbutan-1-ol, 2-phenylethanol, ethyl acetate, isobutyl acetate, 3-methylbut-1-yl ethanoate, 2-phenethyl acetate, ethyl butanoate, ethyl hexanoate and ethyl octanoate have also been detected in *sake*, a Japanese rice wine (Kiyoshi, 1999). The presence of these compounds in both *makgeolli* and *sake* suggests that they are the major products generated by yeast when using rice as the raw material for wine production. However, unlike *sake*, different final *makgeolli* products have a wide range of flavours due to metabolites produced by the live microorganisms and the addition of ingredients such as medicinal plants or herbs (Lee & Lee, 2008).

Thirty-three esters constituted the largest group among the 45 detected volatile compounds. Among them, 10 esters (ethyl decanoate, ethyl (Z)-octadec-9-enoate, ethyl octanoate, 2-phenethyl acetate, ethyl acetate, 3-methylbut-1-yl ethanoate, ethyl hexadecanoate, ethyl 9,12-octadecadienoate, ethyl dodecanoate and ethyl tetradecanoate) were predominant. Esters are known to be produced by yeasts during fermentation, and they affect the fruity flavours of alcoholic beverages such as wine and beer (Nykänen, 1986). Furthermore, many belong to the apolar ester group, which has fairly low detection odour thresholds, except for ethyl acetate, and contribute fruity and flower notes to the aroma, including ethyl acetate (solvent-like aroma), 3-methylbut-1-yl ethanoate (fruity, banana aroma), ethyl octanoate (pineapple and pear), ethyl hexanoate (apple and violet aromas), ethyl propanoate, ethyl butanoate and 2-phenethyl acetate (flowery, rose and honey aromas) (Lambrechts & Pretorius, 2000). Samples

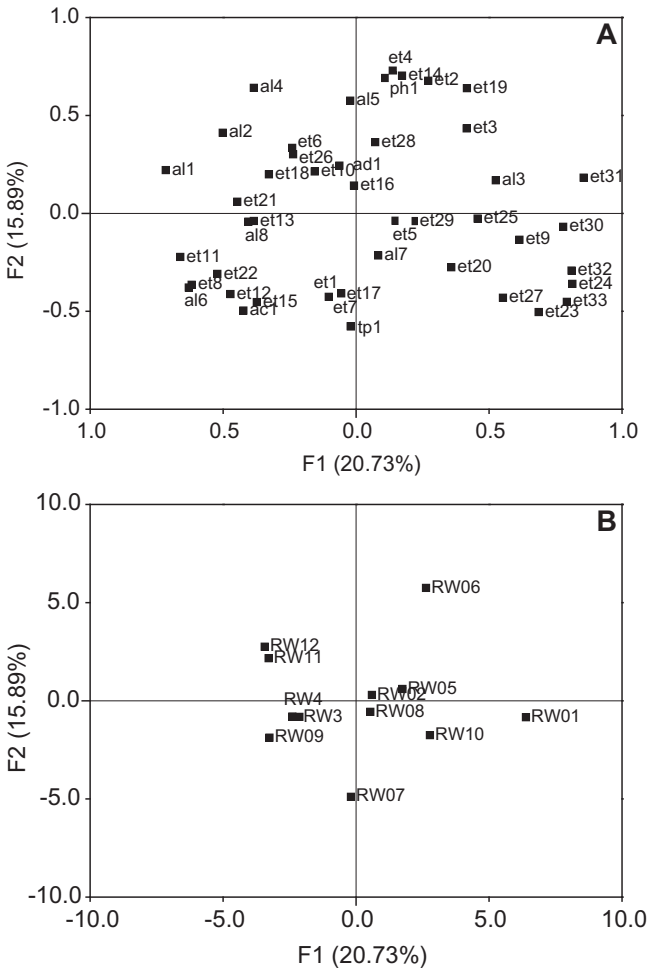

Fig. 1. Principal component analysis loadings for 45 volatile compounds (A) and scores for the 12 *makgeolli* samples (B). The samples and volatile compound codes are defined in Tables 2–4.

RW7 and RW9 were especially enriched with apolar esters. Ethyl octanoate was retained with similar relative peak areas (4.39–7.26%) in most samples, except for RW1 and RW7. Furthermore, most of the *makgeolli* samples contained 2.98–4.44% of 2-phenethyl acetate, which was remarkably high at 7.45% and 5.87% in samples RW7 and RW1, respectively. The levels of ethyl acetate and 3-methylbut-1-yl ethanoate were about 0–3%. Ethyl acetate is distasteful at higher concentrations, which depend on the raw material components and the fermentation conditions produced by microorganisms (Arctander, 1969). Most of the predominant esters in these *makgeolli* samples overlapped with important compounds related to the products of yeast fermentation in previous studies on *yakju*, wine, and beer (Kim et al., 2010; Noble & Ebeler, 2002; Nykänen, 1986).

Among the 7 alcohols, 2-phenylethanol, ethanol and 3-methyl-1-butanol were the dominant compounds, with a combined total of 30.04–53.55% of the relative peak area in the samples. These alcohols have been consistently detected as major components of Korean rice wines by different extraction and analysis methods (Han, Lee, Noh, & Lee, 1997; Kim, Jo, Lee, & Ahn, 2008; Kim et al., 2010). 2-Phenylethanol is included as a natural ingredient in products such as beer, wine, whiskey, olive oil, grapes, green and black teas, apple juice, and coffee because of its rose-like odour. 3-Methyl-1-butanol has an unpleasant, irritating, non-residual and disagreeable odour, which upon dilution becomes agreeably fruity and bitter (Kiyoshi, 1999). Most of the detected alcohols in the 12 *makgeolli* samples were higher alcohols, which are important in wines and distillates, and are divided into 2 categories, aliphatic and aromatic alcohols (Nykänen, 1986). Five higher alcohols detected in the samples were the aliphatic alcohols n-propanol (pungent and harsh aroma), 2-methyl-1-propanol (fuel and spirituous aroma), 2-methylbutan-1-ol and 3-methyl-1-butanol (harsh and nail-polish aroma), and the aromatic alcohol 2-phenylethanol (floral and rose aroma). Small amounts of 3-ethoxy-1-propanol were detected in samples RW1, RW6, RW10, RW11 and RW12.

Among the 12 *makgeolli* samples, RW4, RW7 and RW9 contained trace quantities of only n-decanoic acid. Benzaldehyde, a product of alcoholic fermentation with an odour of bitter almonds (Lambrechts & Pretorius, 2000), was detected in all the *makgeolli* samples, except for RW3 and RW6. Short-chain volatile aldehydes are important to the flavour of a number of foods and beverages, contributing to flavour characteristics ranging from apple-like to citrus-like to nutty, depending on the chemical structure. In particular, 4-ethenyl-2-methoxyphenol was abundant (11.54%) in sample RW6. This volatile compound, produced from free phenolic acids, is detectable in red and white wines and contributes to heavy, phenolic and medicinal odours, giving an undesirable flavour even at low concentrations (Dubois, 1983).

3.3. Comparison of volatile compounds among the makgeolli samples

To determine the overall distribution pattern of the volatile compounds during the separation of the samples, PCA was performed (Fig. 1). PCA is an unsupervised clustering method that does not require any knowledge of the data set, and reduces the dimensionality of multivariate data while preserving most of the variance therein (Noble & Ebeler, 2002). The first and second principal components (PC1 and PC2) accounted for 36.62% of the total variances (20.73% and 15.89%, respectively).

In an examination of the volatile compounds distributions (Fig. 1A and B), sample RW6 on the positive side of a weak PC1 and a strong PC2 was characterised by having higher 4-ethenyl-2-methoxyphenol (clove- and beer-like), 3-methylbut-1-yl ethanoate (fruity), and ethyl benzoate and 2-phenethyl acetate (floral) contents than those in the other samples. 3-Methylbut-1-yl-ethanoate and 2-phenethyl acetate belong to the acetate group. RW6 also included 3-ethoxy-1-propanol, ethyl butanoate, and especially isobutyl acetate, which only rarely existed in the other samples. Thus, sample RW6 was mainly affected by a high number of

Table 5
Sensory attributes intensity ratings for the *makgeolli* samples, as determined by descriptive sensory analysis.

Sensory attributes[A]	Samples[B]											
	RW1	RW2	RW3	RW4	RW5	RW6	RW7	RW8	RW9	RW10	RW11	RW12
Appearance												
Whiteness	4.20^{b}	6.15^{c}	3.80^{b}	$6.55^{c,d}$	6.15^{c}	7.95^{e}	4.45^{b}	3.90^{b}	2.25^{a}	$7.30^{d,e}$	6.80^{cd}	$6.40^{c,d}$
Yellowness	6.40^{f}	$3.75^{b,c}$	6.60^{f}	3.20^{b}	$4.50^{c,d}$	2.05^{a}	5.20^{de}	5.90^{ef}	7.75^{g}	3.35^{b}	3.60^{b}	$3.85^{b,c}$
Turbidity	5.45^{d}	5.65^{d}	5.70^{d}	5.30^{d}	4.05^{b}	2.60^{a}	8.15^{f}	5.60^{d}	6.50^{e}	6.50^{e}	$4.35^{b,c}$	$4.90^{c,d}$
Air bubbles	$6.20^{d,e}$	$5.25^{a,b,c,d}$	$4.65^{a,b,c}$	$4.20^{a,b}$	$6.25^{d,e}$	$4.95^{a,b,c,d}$	$5.85^{c,d,e}$	6.25^{ef}	4.10^{a}	$5.45^{b,c,d,e}$	7.60^{f}	6.65^{ef}
Aroma												
Alcohol_aroma	$3.80^{a,b,c}$	$4.55^{b,c,d}$	$4.45^{a,b,c,d}$	$5.25^{d,e}$	3.35^{a}	$4.70^{b,c,d,e}$	$4.85^{c,d,e}$	$4.25^{a,b,c,d}$	$3.90^{a,b,c}$	5.75^{e}	$3.85^{a,b,c}$	$3.65^{a,b}$
Sour_aroma	$4.00^{a,b,c}$	$4.45^{b,c}$	$4.30^{b,c}$	$4.55^{b,c}$	3.05^{a}	$3.55^{a,b}$	4.95^{c}	$4.50^{b,c}$	$4.25^{b,c}$	$3.60^{a,b}$	$4.35^{b,c}$	$3.80^{a,b,c}$
Sweet_aroma	$3.55^{a,b}$	3.40^{a}	$4.20^{a,b,c}$	$4.60^{b,c}$	$3.60^{a,b}$	5.20^{c}	$3.85^{a,b}$	$3.80^{a,b}$	$4.70^{b,c}$	$4.20^{a,b,c}$	$4.25^{a,b,c}$	$3.70^{a,b}$
Fruits_aroma	$3.45^{a,b}$	3.15^{a}	3.05^{a}	$4.45^{b,c}$	2.95^{a}	5.45^{c}	$3.45^{a,b}$	3.00^{a}	$3.65^{a,b}$	$4.50^{b,c}$	$4.15^{a,b}$	3.20^{a}
Roasted cereal_aroma	$3.15^{a,b,c,d}$	$4.20^{d,e}$	$3.95^{b,c,d,e}$	2.50^{a}	$3.90^{b,c,d,e}$	$3.00^{a,b,c}$	$3.30^{a,b,c,d}$	$3.85^{b,c,d,e}$	4.75^{e}	2.50^{a}	$2.85^{a,b}$	$4.10^{c,d,e}$
Yeast_aroma	$4.45^{b,c}$	$3.80^{a,b,c}$	$4.45^{b,c}$	3.00^{a}	$3.95^{a,b,c}$	2.95^{a}	$4.35^{b,c}$	$4.00^{a,b,c}$	4.70^{c}	$3.35^{a,b}$	$3.50^{a,b,c}$	$4.15^{a,b,c}$
Mouldy_aroma	$3.70^{b,c}$	$2.95^{a,b,c}$	$3.45^{b,c}$	$2.65^{a,b}$	$3.75^{b,c}$	$2.80^{a,b,c}$	$3.25^{b,c}$	$2.95^{a,b,c}$	3.90^{c}	2.05^{a}	$2.75^{a,b,c}$	$3.20^{a,b,c}$
Flavour/taste alcohol	$5.10^{a,b}$	$5.35^{a,b}$	6.60^{c}	$5.30^{a,b}$	$4.45^{a,b}$	$4.65^{a,b}$	4.20^{a}	$4.95^{a,b}$	$4.80^{a,b}$	7.05^{c}	$4.75^{a,b}$	$4.70^{a,b}$
Sweet	3.50^{a}	$5.20^{b,c}$	4.70^{b}	5.40^{bc}	$5.30^{b,c}$	5.90^{c}	3.20^{a}	$5.70^{b,c}$	$5.35^{b,c}$	2.95^{a}	$5.15^{b,c}$	$4.95^{b,c}$
Sour	3.50^{a}	3.70^{a}	$4.30^{a,b,c}$	$5.00^{b,c}$	3.95^{a}	3.50^{a}	7.35^{d}	$4.15^{a,b}$	$4.50^{a,b,c}$	3.80^{a}	$4.20^{a,b,c}$	5.20^{c}
Bitter	$4.15^{b,c}$	2.95^{a}	$4.40^{b,c}$	3.05^{a}	$3.50^{a,b}$	$3.60^{a,b}$	$3.55^{a,b}$	2.80^{a}	$3.55^{a,b}$	5.05^{c}	2.90^{a}	2.75^{a}
Roasted cereal	$4.05^{b,c,d}$	$3.30^{a,b,c}$	$4.10^{c,d}$	$3.55^{b,c}$	$4.00^{b,c,d}$	$3.80^{b,c}$	2.35^{a}	$3.70^{b,c}$	4.90^{d}	$3.15^{a,b,c}$	$3.00^{a,b}$	$3.50^{b,c}$
Yeast	2.40^{a}	$3.55^{b,c,d,e}$	4.50^{e}	$3.20^{a,b,c,d}$	$2.95^{a,b,c}$	$2.50^{a,b}$	$3.80^{c,d,e}$	$3.35^{a,b,c,d}$	$3.90^{c,d,e}$	$4.10^{d,e}$	$2.65^{a,b}$	$3.35^{a,b,c,d}$
Mouth fee/aftertaste												
Astringency	$3.20^{a,b}$	$3.65^{a,b,c}$	$4.45^{c,d}$	$4.05^{b,c}$	$3.55^{a,b,c}$	2.95^{a}	5.15^{d}	$4.05^{b,c}$	5.05^{d}	$4.45^{c,d}$	$3.50^{a,b}$	$3.55^{a,b,c}$
Full body	$4.20^{a,b}$	$4.90^{a,b,c}$	6.30^{d}	$4.85^{a,b,c}$	3.95^{a}	$4.15^{a,b}$	$5.35^{b,c,d}$	$4.55^{a,b,c}$	$5.30^{b,c,d}$	$5.65^{c,d}$	$4.25^{a,b}$	$4.25^{a,b}$
Carbonation	$3.80^{a,b}$	$3.45^{a,b}$	$3.65^{a,b}$	$3.30^{a,b}$	$3.20^{a,b}$	$3.50^{a,b}$	$3.85^{a,b}$	4.10^{b}	$3.95^{a,b}$	$3.25^{a,b}$	$3.15^{a,b}$	2.90^{a}
Continuation	$3.85^{a,b}$	3.55^{a}	5.50^{c}	$4.60^{a,b,c}$	$4.00^{a,b}$	3.70^{a}	$5.05^{b,c}$	$4.10^{a,b}$	$4.45^{a,b,c}$	5.35^{c}	3.50^{a}	$4.05^{a,b}$
Swallow	$4.35^{a,b,c}$	$3.85^{a,b}$	$4.90^{b,c}$	$4.15^{a,b,c}$	$4.00^{a,b,c}$	$4.30^{a,b,c}$	$4.30^{a,b,c}$	$4.15^{a,b,c}$	$4.05^{a,b,c}$	$4.25^{a,b,c}$	3.65^{a}	5.05^{c}

[a–g]Mean values with the same letter in a row are not significantly different, with significance set at $p < 0.05$ by Fisher's least-significant difference test. The intensity of the attributes ranged from 0 to 9 (0, none; 1, very weak; 5, moderate; 9, very strong). The data of sensory evaluation were obtained from a panel of 9 judges, over 2 replications.
[A,B] The sensory attributes and samples are defined in Tables 1 and 2.

members of the phenol and acetate groups. With respect to a negative PC1 and positive PC2, samples RW11 and RW12 were affected predominantly by 3 alcohols (ethanol, 1-propanol and 3-methyl-1-butanol). Sample RW7 on the negative PC1 side was characterised by a sesquiterpene (1,5,9,9-tetramethyl-,Z,Z,Z-1,4,8,-cycloundecatriene) and acetic acid (D-decanoic acid with a rancid and fat odour), which were rarely or not detected in the other samples. On the positive side of PC1 and the negative side of PC2, RW1 and RW10 were separated from the other samples because of their abundant long-chain esters. They were also separated by the presence of 2-methyl-1-propanol (fermented). Many esters were located in the centroid of the plot. They were detected in 2 separate groups of samples, with RW3, RW4 and RW9 on the one side and RW2, RW8 and RW5 on the other side of PC1. In addition, 2-phenylethanol (rose) on the negative side of PC1 was found in small amounts in RW3, RW4 and RW9. Additionally, 3-methylthiopropanol on the positive side of PC1 was a common aspect in samples RW2, RW8 and RW5. Thus, minor esters and 2 alcohols contributed to samples in the central position. Therefore, the characteristics of most of the *makgeolli* samples were determined mainly by the contents and types of esters and alcohols, whereas some samples like RW6 and RW7 were distinguished by their phenols, terpenes and acids.

3.4. Sensory characteristics of makgeolli samples by descriptive sensory analysis

To profile the sensory characteristics of the 12 *makgeolli* samples, the wines were evaluated by descriptive sensory analysis. ANOVA performed on the descriptive data of the 12 rice wines revealed that all attributes, except carbonation, were significantly different across the samples ($p < 0.05$). The mean intensity ratings of the 12 samples and LSDs are presented in Table 5. Sample RW6 exhibited higher levels of the appearance attribute whiteness than did samples RW8, RW3, RW7 and RW9. The aroma in the *makgeolli* samples seemed to have a lower attribute score (<5.0) than did the flavour/taste and mouth feel. Sample RW10 was intense in alcohol_aroma, whereas RW7 exhibited high levels of sour_aroma. The attribute levels of sweet_aroma and fruit_aroma were generally similar among the samples, even though RW6 showed the highest intensity of sweet_aroma, and RW10 especially retained a high intensity of only fruit_aroma. Although the 12 *makgeolli* samples did not use any fruit as a raw material, the esters produced through fermentation may have contributed to the aroma. With regard to roasted cereal_aroma, samples RW2 and RW9 exhibited much higher levels than did RW04, RW10 and RW11. Unpleasant aromas such as yeast_aroma and mouldy_aroma were present at low levels in most of the *makgeolli* samples, with RW9 exhibiting the highest intensity. A comparison of all the flavour/taste attributes revealed alcohol to be at a high level, whereas the other attributes rarely appeared at high levels in the samples. Among the mouth feel attributes, astringency, full body and continuation exhibited similar trends, with samples RW3 and RW7 exhibiting the highest levels.

The principal components of descriptive sensory analysis of the 12 *makgeolli* samples are shown in Fig. 2, and the overall sensory configuration was examined. PC1 and PC2 explained 47% and 21% of the variances across the samples, respectively. There was a contrasting pattern on PC1 between the whiteness and yellowness of appearance, which affected the location between samples RW7 and RW3 on the positive end and RW6 on the negative end, respectively. In addition, the same symmetrical pattern occurred between fruits_aroma and yeast_aroma. In studies on rice wine (Lee & Lee, 2008), attributes such as ripe-fruit, sweet-grain, and fruit taste were found to be in contrast with attributes such as medicinal herb taste and yeast taste, where consumer preference is concerned. Therefore, the whiteness and fruits_aroma attributes in *makgeolli* were expected to be positive factors. In addition, sweet_aroma and sweet_taste on the positive side of PC1 was located on the contrasting side of PC2, which identified the sweet aroma of *makgeolli*. The attributes mouth feel, sour, bitter and alcohol were located on the negative PC1 and positive PC2 sides and were associated with sample RW4. Fermented aroma and flavour/tastes such as yeast, mould, and roasted cereal were associated with the negative sides of PC1 and PC2. Sour, alcohol and roasted cereal were located at similar positions on the plot between the aroma and flavour/taste attributes, and were associated with both of them.

3.5. Correlations between sensory attributes and chemical and volatile compounds

The correlation between the sensory attributes and the chemical characteristics of 7 general compositions and 45 volatile compounds is presented in Table 6. Eleven of 20 sensory attributes were associated with chemical characteristics with a significant correlation coefficient ($p < 0.05$). Relatively higher correlations with sensory attributes were observed for 10 chemical characteristics (correlation coefficient $[r] > 0.7$), including ethyl octanoate, ethyl dodecanoate, ethanol, 2-methyl-1-propanol, 2-phenethyl acetate, b-value, total acidity, ethyl heptanoate, ethyl dodecanoate and ethyl octanoate. The yeast attribute correlated with 3 esters with fruity flavour; namely, ethyl decanoate (grape, oily and wine-like), ethyl octanoate (floral, banana, pear, pineapple

Table 6
Correlation between the sensory attributes and characteristics of volatile compounds and chemical parameters of the *makgeolli* samples.

Sensory attributes[a]	Chemical and volatile components[b] (correlation coefficient[c])
Appearance	
Whiteness	*b*-Value (−0.64)
Yellowness	–
Turbidity	Ethyl caproate (0.59), isoamyl caprylate (0.72), ethyl laurate (0.84)
Bubbles	Isoamyl alcohol (0.58), ethyl heptanoate (−0.60)
Aroma	
Alcohol_aroma	Ethanol (0.76), *b*-value (−0.61), ethyl caprylate (0.68), ethyl caprate (0.58), ethyl palmitate (−0.60)
Sour_aroma	–
Sweet_aroma	Isobutanol (−0.84)
Fruits_aroma	Isobutanol (−0.74), phenethyl acetate (−0.89)
Roasted cereal_aroma	*b*-Value (0.70)
Yeast_aroma	Phenethyl alcohol (−0.63)
Mouldy_aroma	Ethyl butanoate (0.66), benzaldehyde (−0.58)
Flavour/taste	
Alcohol	–
Sweet	–
Sour	Total acidity (0.73), reducing sugar (0.67), isopentyl decanoate (0.66)
Bitter	–
Roasted cereal	pH (−0.59), total acidity (−0.67), ethyl heptanoate (−0.72), benzaldehyde (−0.69)
Yeast	–
Mouth feel/aftertaste	
Astringency	Ethyl caproate (0.62), isoamyl caprylate (0.64), ethyl laurate (0.77)
Full body	Ethyl caproate (0.65), ethyl caprylate (0.65), ethyl caprate (0.63), isoamyl caprylate (0.75), isopentyl decanoate (0.63)
Carbonation	–
Continuation	Ethanol (0.59)
Swallow	–

[a] The sensory attributes are defined in Tables 1 and 4.
[b] Characteristics of chemical parameters and volatile compounds compositions are as in Tables 2 and 5.
[c] The Pearson correlation coefficient showed statistical significance.

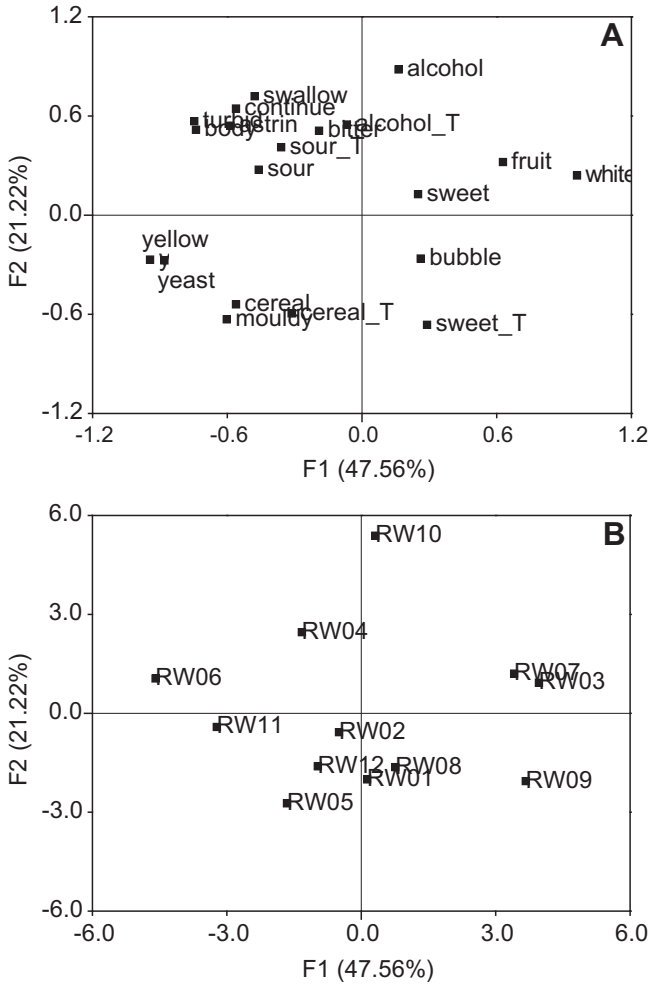

Fig. 2. Principal component analysis loadings for 20 sensory attributes (A) and scores for the 12 *makgeolli* samples (B). The samples and sensory attribute codes are defined in Tables 1 and 5.

and wine-like), and ethyl dodecanoate (fruity and floral). There were reasonable relationships between the sensory and chemical data such as alcohol_aroma and ethanol, sour and total acidity, whiteness and *b*-value, and roasted cereal and benzaldehyde. On the other hand, there were inverse correlations between 2 parameters: sweet_aroma and 2-methyl-1-propanol, and fruits_aroma and 2-methyl-1-propanol and 2-phenethyl acetate. Additionally, the fruit attribute in flavour and taste was negatively associated with ethyl heptanoate (a fruity aroma compound) and benzaldehyde (known for its almond, cherry and sweet aromas). The roasted cereal flavour/taste exhibited an inverse correlation with pH and total acidity. Between the sensory attributes and chemical characteristics, positive and negative scores observed in the aroma attributes were higher than those observed in the other sensory properties, which seemed to be a reasonable and desirable correlation.

4. Conclusions

The differences in chemical characteristics of the general compositions and volatile compounds in 12 commercial *makgeolli* products were investigated. The general compositions of the 12 wine samples were significantly different from one another. The volatile components, extracted with SPME and analysed by GC–TOF/MS, were made up of a total of 45 major volatile compounds, consisting of 33 esters, 8 alcohols, 1 aldehyde, 1 acid, 1 phenol and 1 terpene; each *makgeolli* sample included 28–35 volatile compounds. PCA between the volatile compounds and *makgeolli* samples was characterised depending on the contents of the various esters and alcohols in each *makgeolli*. PCA of the sensory data displayed symmetrical patterns between yellow and yeast on the negative side and white and fruits_aroma on the positive side, properties expected to make an impact upon consumer preference. Between the aroma and flavour/taste attributes, sour, alcohol and roasted cereal were associated with one another. The mouth feel/aftertaste attributes of *makgeolli* were related to sour, bitter and turbidity. Between the sensory attributes and chemical characteristics, the aroma attributes were observed in positively and negatively higher correlations compared with the other sensory properties.

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