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Identification of key volatiles responsible for odour quality differences in popped popcorn of selected hybrids

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Abstract

Volatile compounds from six hot-air-popped popcorn hybrids, being also classified into three types, were evaluated by a gas chromatograph equipped with a mass spectrometer (GC/MS). In addition, 68 panelists determined odour quality differences of the popped kernels by an aroma ranking test. Total number of volatiles detected by GC/MS were 195, of which 51 peaks were positively identified, 92 peaks were tentatively identified, and 52 peaks were unidentified. The relationships between quality/quantity of volatiles and sensory results revealed that 2-acetylpyridine was considered to contribute to the overall popped popcorn aroma quality favorably or not adversely. However, 2,5-dimethylpyrazine, (*E*,*E*)-2,4-decadienal, 2-methylpyrazine, ethylpyrazine, 2-ethyl-5-methylpyrazine and 3-ethyl-2, 5-dimethylpyrazine were found to be important popcorn volatiles, but to contribute negatively to characteristic popped popcorn odour. Numerous other volatiles such as 2-furfurylthiol (2-furanmethanthiol), pyrrole, 3-(methylthio)propanal (methional), 3-furaldehyde, 4-vinyl-2-methoxyphenol (4-vinylguaiacol), 2-pentylfuran, 2-furanmethanol (furfuryl alcohol), hexanal, 1-pentanol, 2-methyl-5-vinylpyrazine, 2-methoxyphenol (guaiacol), 2-acetylpyrrole and others may be responsible in part of typical popcorn aroma characteristics.

Keywords: Popcorn; Aroma; Volatile; Odour; GC/MS

1. Introduction

Buttery, Ling, and Stern (1997) mentioned that a practical method and data to quantitatively analyze aroma components from the large numbers of new popcorn hybrids was needed to produce new hybrids having desirable volatiles in popcorn aroma and flavour. Even though some extensive research had been reported, including that of Buttery group's work on microwave popcorn in 1997, studies on the relationship between sensory results and volatile quality and quantity among several popcorn hybrids have not been reported. Moreover, all studies on determinations of popcorn volatiles, including reports by Walradt, Lindsay, and Libbey (1970), Schieberle (1991, 1995) and Buttery et al. (1997) included either heat treatment during the isolation of volatiles from popped kernels or a relatively lengthy concentration step for solvent volatile mixture.

Therefore, the first objective was to isolate volatiles from 6 hot-air-popped popcorn hybrids by using a simple cold trapping method, which utilized a small amount of solvent and had short concentration periods. Then, the number and amount of volatile compounds in the samples were determined. In addition, key odourants responsible for odour differences in six popped popcorn hybrids were identified from sensory results and volatile aroma composition.

2. Materials and methods

2.1. Materials

Six popcorn hybrids, 25 kg each, in woven laminated polypropylene bags, grown in Colorado or Nebraska and harvested in 1997, were obtained from Rocky Mountain

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Popcorn Company (Fort Collins, CO). The hybrids were BKH, A358W, 019, 1601, 5501 and 353W. The popcorn hybrids were also grouped into three different types based on the colour and shape of popped kernels. Hybrids A358W and 353W were white butterfly type popcorn. BKH and 019 were yellow butterfly, while hybrids 1601 and 5501 were yellow mushroom type popcorn.

2.2. Moisture analysis

The methods for the moisture determination in intact kernels and popped kernels have been reported by Park, Allen, Stermitz, and Maga (2000).

2.3. Moisture adjustment and popping kernels

Similar to the method reported by Maga and Blach (1992), intact kernel moisture content of the hybrids was adjusted to $14 \pm 0.05\%$. Moisture adjustment was done very slowly to minimize physical damage to the kernels. Moisture-adjusted sealed samples were stored at 21 °C. Popcorn was prepared using Presto Hot Air Poppers (National Presto Industries Inc, Eau Claire, WI) from 75 g of intact kernels per popping at 230 °C for 80 s. The poppers were warmed to 230 °C for 30 s before kernels were added.

For sensory evaluation, popcorn was prepared from 600 g of intact kernels per hybrid with three hot air poppers by three operators. The popping of popcorn using the poppers was done in a random order. A total of eight poppings (75 g of intact kernels per popping) were performed with each popper per test day. The popped kernels were held in covered stainless steel containers at 21 °C until mixed and transferred into glass jars for sensory evaluation.

2.4. Volatile determination

Volatile aroma compounds were determined from hot-air-popped kernels, which were prepared from a total of 150 g of moisture adjusted sound intact kernels by two consecutive poppings. Volatile isolation and identification for each hybrid were done twice (two replications). Popped kernels from two batches of popping were blended with a food processor (Cuisinart Co., East Windsor, NJ) for 20 s and placed in a 2000-mL pre-weighed round-bottom flask, and the flask and sample were weighed. Then, 18 ng (0.025 μL) nonane (internal standard) in 5.0 μL pentane was applied to a cotton ball, using a cooled 10-μL micro syringe, and added to the flask. Fresh internal standard solution (3.0 mL) was prepared for each experiment. The cotton ball was prepared from a small piece of Kimwipes and small amount of cotton, by wrapping cotton with the tissue and by tying the Kimwipes' end with cotton thread. The cotton ball was approximately 7 mm in diameter and weighed approximately 70 mg. The cotton ball was cleaned using a Labconco-Goldfish solvent-type extractor (Labconco Co, Kansas City, MO) with 20 mL petroleum ether for 4 h. The solvent was evaporated under a hood at 21 °C and then dried further in an oven at 130 °C for 30 min, desiccated and stored in an air-tight glass jar.

The sample flask was connected to a cold finger condensation trap to isolate volatiles (Fig. 1). The flask was heated from 21 to 100 °C for 5 h. Pure nitrogen was flushed into the flask containing the popcorn sample at a rate of 5.0 mL per min. The volatiles passed through a 250-mm-long Cold Finger condenser (Chemglass, Vineland, NJ) containing 1.0 mL diethyl ether. The condenser was cooled to −73 °C with CO_2 and ethanol in a Dewar flask. The trapping of aroma compounds was continued for 5 h. The holes on the cold finger were sealed tightly with Teflon™ caps after the sample flask was disconnected. The condensation trap was removed, warmed up to 21 °C, and the volatile mixture was washed with previously added 1 mL diethyl ether. The water inside the cold finger was frozen again in a freezer at −23 °C for 30 min. Then, only the volatile/ether mixture was recovered with a 2.0-mL glass syringe and transferred to a 2-mL sample vial. The

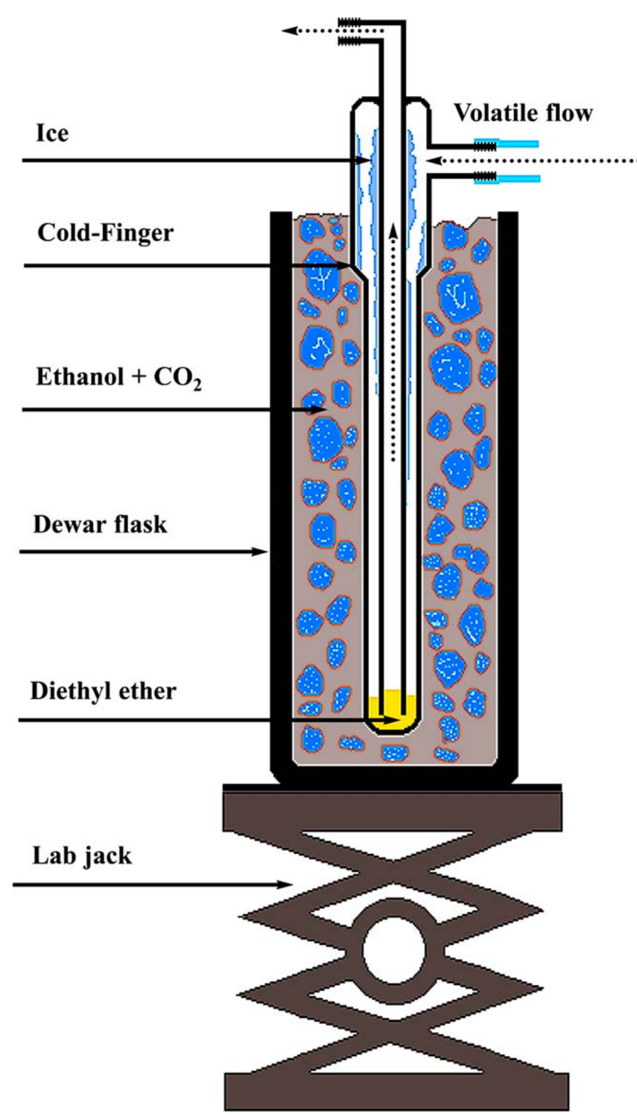

Fig. 1. Cold finger condensation setup.

volatile/ether mixture was placed under a hood and concentrated at 21 °C for 90 min to approximately 200 μL without any heating or air blowing. The modified technique using a cold finger condenser was known to involve minimum heat processing during volatile isolation and concentration, to involve relatively small amounts of solvent to reduce the concentration period, and to eliminate water interference always so common in cold-trapping techniques.

Then, 2 μL of the concentrated sample was injected into a gas chromatograph equipped with a mass spectrometer, using a 10-μL syringe. The volatiles were separated on a 30 m × 0.25 mm (i.d.) DB-1 bonded-phase fused-silica capillary column with a film thickness of 0.25 μm (J&W Scientific, Folsom, CA) in a Hewlett–Packard (HP) 5890A gas chromatograph connected to a HP 5790 mass selective spectrometer (MS). The gas chromatograph was operated with the injection port at 240 °C, the detector at 260 °C and the column heated from 10 to 220 °C at a rate of 4 °C per min; the final temperature was held for 7.5 min. The ionization voltage of the mass detector was 1400 eV. The helium carrier flow rate was 1.4 mL/min. The blank experiments with the internal standard were done as the first experiment and in the middle of the volatile determination to verify efficiency of the glassware cleaning.

Major volatile compounds were positively identified by comparing mass spectra (MS) and literature-reported retention indices (RIs). RIs of the volatiles were measured based on a hydrocarbon standard retention time. Two ASTM hydrocarbon standards (Supelco, Inc, Bellefonte, PA) were mixed and used to determine standard RIs and retention times. The first standard contained propane (C3), butane (C4), pentane (C5), hexane (C6), heptane (C7), *n*-octane (C8) and *n*-nonane (C9). The second standard contained *n*-decane (C10), *n*-undecane (C11), *n*-dodecane (C12), *n*-tridecane (C13), *n*-tetradecane (C14), *n*-pentadecane (C15), *n*-hexadecane (C16), *n*-heptadecane (C17), *n*-octadecane (C18), *n*-eicosane (C20), *n*-tetracosane (C24), *n*-octacosane (C28), *n*-dotriacontane (C32), *n*-hexatriacontane (C36), *n*-tetracontane (C40) and *n*-tetratetracontane (C44). Four replicate runs were done to obtain a polynomial equation for retention times against RIs of the hydrocarbon standards. The polynomial equation was obtained from retention time (*X*-axis) and RI (*Y*-axis) for easy calculation of the RIs for volatile aroma compounds in popped popcorn.

Major volatile peaks were identified positively by comparing mass spectra (MS) and reported RIs, or tentatively identified by mass spectra or RIs. The total quantity and amount of each volatile compound in each sample were determined by the concentration and ion count of the internal standard and ion count of individual compound. The quantity of individual compound and the sum were converted to μg per 1000 g of dry popped popcorn.

The aroma value of selected aroma volatiles was calculated as volatile concentration divided by odour threshold (ppb). The selection of volatiles was done based on the literature reported by Buttery et al. (1997), where special volatiles significantly contributed to popcorn aroma. The aroma volatiles were dimethyltrisulphide, (*E*,*E*)-2,4-decadienal, 3-methylbutanal, 2,5-dimethyl-4-hydroxy-3(2H)-furanone (furaneol), 2-ethyl-3,5-dimethylpyrazine, 2-furfurylthiol (2-furanmethanthiol), propionyl-1-pyrroline, 4-vinyl-2-methoxyphenol (4-vinylguaicol), 1-octene-3-one, 3-(methylthio)propanal (methional), 2-methylbutanal, 2-pentylfuran, hexanal, 2-acetyl-1,4,5,6-tetrahydropyridine, 2-acetyl-3,4,5,6-tetrahydropyridine, 2-methoxyphenol (guiacol), pentanal and 1-methyl-1H-pyrrole-2-carboxaldehyde (*N*-methyl-2-formylpyrrole).

2.5. Sensory evaluation

The subjective aroma characteristics of the popped kernels was evaluated by an aroma ranking test by 68 panelists during the course of 2 days under white fluorescence light in an odour free classroom in the Department of Food Science and Human Nutrition at Colorado State University. Those excluded as panel members were persons with a cold or nasal congestion and who did not like popcorn. The panelists were over 18 years of age and had been recruited by an advertisement on the bulletin board at the Gifford building on campus. Forty-nine females and 19 males (total 68 subjects) completed the aroma ranking test of popped popcorn hybrids. Six other subjects did not finish or did not follow instructions on the score sheet.

Approximately one-half cup of popped kernels was transferred from covered stainless steel holding containers to odour-free glass jars. Glass jars were covered with aluminum (Al) foil to prevent volatile loss and coded on the outside. Within 30 min after popping, each panelist randomly received one sample of each hybrid (6) and a ballet. Panelists were asked to record their gender and age group before the evaluation, and asked to remove the Al foil on top and then to sniff the samples one at a time. After sniffing all samples, panelists were asked to indicate their degree of preference by ranking, best 1 and worst 6.

2.6. Statistical analysis

The effect of hybrids and quantity of individual aroma volatiles and their interactions were evaluated by the *F*-test using SAS/STAT™ (SAS, 1991). Volatile quantity differences among popcorn hybrids were compared by Student Newman Kuels (SNK) multiple comparison methods using SAS (1991) at a significant level of 0.05. Sensory results were evaluated by critical absolute rank sum differences of Friedman rank sums for the analysis of ranked data (Newell & MacFarlane, 1987). The ranking results were converted for the correlation coefficient calculation for easy understanding as following: value used for correlation coefficient = 6 − (mean aroma ranking). The relationships between quantity of selected volatiles and sensory results were evaluated by the Spearman's correlation coefficient test using SAS (1991). Aroma volatiles for determining the relationships were selected based on the *F*-test statistics and aroma value and/or quantity.

3. Results and discussion

Though corn kernels can be quite variable in colour, most popcorn is either yellow or white because the endosperm colour determines the colour of popped flakes (Eldredge & Thomas, 1959). In addition, there are two types of flake, which is used describe the popcorn kernel after it is popped. Popped popcorn which has an irregular, branched or prolonged appearance is called butterfly, which is the most common type. In contrast, popcorn that puffs up into an almost round ball is called mushroom (Eldredge & Thomas, 1959).

Thousands of corn hybrids exist; however, the current study was conducted using six commercially available hybrids, which were systematically selected, and included different types of popcorn available in the market. Among the six hybrids used in the current study, there were two white popcorn hybrids, and four yellow hybrids. Also, two of six hybrids had mushroom type flakes, and four had a butterfly type. Therefore, the current study was designed to involve the major types in US market, but was conducted by using a minimum number of popcorn hybrids. There might be some limitation to apply the results from this research to all popcorn hybrids. However, the study provided valuable information in identifying volatile compounds responsible for aroma differences in different popcorn hybrids and in different popcorn types.

3.1. Volatile compounds

From six hybrids, 195 major peaks (peak area larger than 100,000 ion count) and 11 blank peaks were detected. Among the 195 peaks, 51 peaks were positively identified with RIs and mass spectra, 92 peaks were tentatively identified, and 52 peaks were not identified. A total of 163 peaks (without blank peaks) from hybrid A358W, 171 from hybrid 353W, 169 form hybrid BKH, 159 from hybrid 019, 171 from hybrid 1610 and 187 from hybrid 5501 were detected. The sum total of the volatile concentration in each hybrid was as follows; hybrid A358W: 5.10 mg/kg, hybrid 353W: 5.30 mg/kg, hybrid BKH: 4.63 mg/kg, hybrid 019: 4.88 mg/kg, hybrid 1601: 5.69 mg/kg and hybrid 5501: 7.27 mg/kg. Many more volatile peaks were detected in the current study than in reports by Walradt et al. (1970), Schieberle (1991, 1995) and Buttery et al. (1997).

The concentration of selected volatiles in popped samples is listed in Table 1. The selection was based on the quantity, *F*-test statistics of each volatile concentration and the literature data reported by Buttery et al. (1997), where certain volatiles significantly contributed to popcorn odour. Volatile compounds with a high concentration did not always result in large variation among hybrids; therefore, large amounts of volatiles with no variation were probably responsible for background popped popcorn aroma. Those volatiles included hexanal, 2-furaldehyde, benzaldehyde, *N*-acetyl-4H-pyridine, 2-pentylfuran, 2-methyl-5-vinylpyrazine and 2-acetyl-1,4,5,6-tetrahydropyridine.

In contrast, others such as 2-methylbutanal, 2,5-dimethylpyrazine, 2-ethyl-5-methylpyrazine, 3-ethyl-2,5-dimethylpyrazine, 3-(2-hydroxyphenyl)-(*E*)-2-propenoic acid and 4-vinyl-2-methoxyphenol may be responsible for not only background popped popcorn aroma, but also aroma quality differences among popcorn hybrids. Other numerous volatiles differed in quantity among popped popcorn hybrids, even though low in concentration. However, low in concentration does not always mean minor impact on a food odour because the threshold values of these volatiles are different. Therefore, some of the volatiles may be responsible for the odour quality differences in popped popcorn hybrids to some extent.

The aroma values of 18 selected volatiles of each hybrid are shown in Table 2. Approximately half of the aroma values of the volatile compounds were not significantly different among hybrids. The aroma value of 2-ethyl-3,5-dimethylpyrazine was the highest in hybrid 5501, while it was the lowest in hybrid BKH. That of the 3-(methylthio)propanal was the highest in hybrid 5501 and the lowest in hybrid A358W. The aroma value of 4-vinylguaicol was the highest in hybrid 5501, while it was the lowest in hybrid A358W. Even though our study reported aroma values of selected volatile aroma compounds, the aroma value can be converted to log concentration/threshold values similar to the results reported by Buttery et al. (1997). The mean aroma value of popcorn volatiles over six hybrids was similar to the results reported by Buttery et al. (1997); also, our converted log concentration/threshold values from aroma values of the popcorn volatiles ranged from 2.87 to 0.08, which was similar to values in their report.

3.2. Sensory evaluation

Sensory results showed that numerical ranking for hybrid BKH was significantly lower than those of hybrid A358W, 353W and 1601, but not different from hybrids 5501 and 019 (Table 3). The lower the numerical rank sum reflected the higher the panel preference. Also, the rank sum of hybrid 019 was significantly lower (preferred better) than that of A358W, but did not significantly differ from others. The volatile aroma of hybrid A358W was given the highest numerical ranking (the least preferred) by panelists.

3.3. Relationship between sensory and volatile quantity/quality of popped popcorn

Table 4 shows the correlation between the aroma ranking test and 33 selected volatile concentrations. The selection was done based on concentration variation within hybrids and their concentration. 2-Acetylpyridine was positively

Table 1
Relative concentration of selected[a] aroma volatiles in popped popcorn hybrids

Compounds	Retention index[c]	Volatile aroma concentration (μg/kg)[b]					
		A358W	353W	BKH	019	1601	5501
Aliphatic alcohols							
"1-Pentanol"	671	41.0[d]	42.9[d]	38.8[d]	36.3[d]	43.5[d]	49.6[d]
3-Methyl-2-butanol	674	23.6[de]	23.8[de]	19.0[e]	28.2[de]	24.9[de]	30.5[d]
Aliphatic aldehydes and ketons							
3-Methylbutanal	632	122.1[d]	87.5[d]	83.6[d]	85.9[d]	114.6[d]	89.5[d]
2-Methylbutanal	642	343.4[de]	284.7[e]	239.2[e]	306.0[de]	403.3[d]	253.0[e]
Pentanal	671	38.7[d]	33.8[d]	22.8[d]	47.7[d]	50. 1[d]	30.3[d]
"3-Pentanone"	703	4.1[f]	7.3[e]	tr[g]	3.5[f]	9.8[d]	7.9[de]
Hexanal	778	154.3[d]	139.4[d]	138.1[d]	161.2[d]	182.8[d]	145.0[d]
2-Hexanone	781	27.7[d]	27.4[d]	31.3[d]	30.2[d]	26.3[d]	38.6[d]
4-Heptanone	874	21.9[f]	41.3[e]	28.4[ef]	23.6[f]	33.7[ef]	66.0[d]
1-Octene-3-one	946	17.4[d]	9.0[e]	5.8[e]	tr[f]	tr[f]	18.3[d]
Octanal	983	29.6[d]	38.8[d]	23.5[d]	31.8[d]	26.7[d]	20.0[d]
2,4-Decadienal	1264	11.4[d]	8.6[d]	6.9[d]	9.0[d]	16.3[d]	8.8[d]
(*E*,*E*)-2,4-Decadienal	1285	38.0[e]	42.5[e]	22.3[f]	24.4[f]	53.2[d]	25.5[f]
Nitrogen compounds							
Pyrrole	734	17.3[e]	16.2[e]	17.9[e]	18.9[e]	43.8[d]	24.0[e]
2-Methylpyrazine	795	68.2[d]	61.0[d]	32.3[e]	49.3[de]	48.9[de]	59.2[d]
"2-Ethylpyrrole"	821	22.2[d]	15.2[d]	12.0[d]	10.0[d]	12.6[d]	14.1[d]
"2,4-Dimethylpyrrole"	833	11.2[d]	10.7[d]	5.8[d]	3.9[d]	5.7[d]	11.7[d]
2,5-Dimethylpyrazine	895	144.5[d]	138.8[d]	76.7[f]	81.2[f]	73.4[f]	103.9[e]
2,3-Dimethylpyrazine	895	27.1[d]	22.8[de]	19.6[e]	21.8[e]	16.7[e]	27.9[d]
"Ethylpyrazine"	892	38.9[d]	34.6[de]	20.9[e]	31.0[de]	32.6[de]	38.0[d]
2-Vinylpyrazine	911	3.9[ef]	tr[g]	4.5[e]	2.7[f]	3.1[f]	7.1[d]
1-Methyl-1H-pyrrole-2-carbox-aldehyde (*N*-methyl-2-formylpyrrole)	970	57.4[d]	6.1[f]	57.1[d]	52.7[d]	57.4[d]	25.2[e]
2-Ethyl-6-methylpyrazine	973	28.6[d]	27.8[d]	13.6[e]	23.4[de]	21.5[de]	29.1[d]
2-Ethyl-5-methylpyrazine	976	166.1[d]	147.9[de]	89.9[e]	88.5[e]	101.6[e]	96.0[e]
"*N*-Acetyl-4H-pyridine"	978	89.1[e]	81.2[e]	74.2[e]	71.4[e]	194.6[d]	53.8[e]
2-Methyl-6-vinylpyrazine	980	19.0[e]	13.6[efg]	9.9[fg]	17.4[ef]	6.5[g]	43.6[d]
2-Methyl-5-vinylpyrazine	993	120.9[e]	162.5[e]	92.0[e]	41.7[e]	73.5[e]	350.3[d]
"2-Acetylpyridine"	998	13.9[d]	14.0[d]	25.9[d]	29.3[d]	13.2[d]	23.9[d]
Propionyl-1-pyrroline	1001	29.1[d]	27.9[d]	28.5[d]	26.1[d]	34.6[d]	22.5[d]
2-Acetyl-1,4,5,6-tetrahydropyridine	1016	69.7[d]	27.3[d]	47.0[d]	37.7[d]	31.1[d]	63.5[d]
2-Acetylpyrrole	1031	49.3[d]	43.6[d]	18.9[e]	35.3[d]	39.8[d]	43.1[d]
"3-Ethyl-2,5-dimethylpyrazine"	1053	139.0[d]	127.7[de]	74.7[f]	79.7[f]	85.2[f]	117.2[c]
"2-Ethyl-3,5-dimethylpyrazine"	1057	19.2[ef]	22.7[de]	10.9[g]	18.9[ef]	16.0[f]	25.5[d]
2-Acetyl-6-methylpyrazine	1089	5.2[d]	7.2[d]	4.3[d]	7.7[d]	7.6[d]	tr[e]
"2-Acetyl-3,4,5,6-tetrahydropyridine"	1105	13.4[d]	70.0[d]	14.1[d]	17.4[d]	13.9[d]	30.8[d]
"3,5-Diethyl-2-methylpyrazine"	1130	34.5[d]	35.1[d]	21.0[de]	6.2[e]	30.5[d]	41.6[d]
"1-(2-Furanylmethyl)-1H-pyrrole"	1142	40.9[ef]	35.9[ef]	30.7[ef]	45.8[e]	155.3[d]	26.2[f]
Furans, pyrans, and aromatic compounds							
2-Methylfuran	602	25.5[d]	21.9[d]	19.7[d]	26.0[d]	23.3[d]	30.4[d]
"Ethylfuran"	682	5.9[d]	6.6[d]	4.8[d]	8.5[d]	8.7[d]	10.4[d]
2-Furaldehyde (furfural)	803	378.6[d]	258.5[d]	155.9[d]	343. 1[d]	282.9[d]	289.5[d]
2-Furanmethanol (furfuryl alcohol)	843	64.2[d]	49.6[d]	38.2[d]	82.1[d]	69.0[d]	78.8[d]
"3-Furaldehyde"	846	14.7[de]	12.6[e]	14.5[de]	22. 4[d]	20.6[d]	21.8[d]
1,4-Dimethylbenzene	855	4.5[d]	5.4[d]	5.8[d]	5. 2[d]	7.2[d]	6.1[d]
2-Furfurylthiol (2-furanmethanthiol)	877	tr[e]	4.2[d]	4.6[d]	tr[e]	tr[e]	4.8[d]
Benzaldehyde	927	86.8[d]	78.7[d]	40.9[d]	77.2[d]	88.8[d]	103.4[d]
5-Methyl-2-furancarboxaldehyde (5-methylfurfural)	931	51.1[d]	38.6[d]	25.3[d]	57.7[d]	38.0[d]	49.4[d]
2-Pentylfuran	980	154.1[e]	143.2[e]	165.9[e]	146.8[e]	546.9[d]	196.4[e]
2,5-Dimethyl-4-hydroxy-3(2H)-furanone (furaneol)	1041	16.2[e]	35.0[d]	4.0[f]	14.5[e]	17.7[e]	27.9[d]
2-Methoxyphenol (guaiacol)	1059	12.9[e]	15.8[e]	10.3[e]	tr[f]	8.5[e]	26.6[d]
2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	1113	8.4[e]	3.4[e]	tr[e]	10.7[e]	tr[e]	68.7[d]
5-(Hydroxymethyl)furfural	1159	5.3[d]	4.9[d]	13.9[d]	3.4[d]	tr[d]	7.1[d]
4-Vinyl-2-methoxyphenol (4-vinylguaiacol)	1280	445.3[f]	768.7[d]	625.6[de]	515.0[ef]	468.5[f]	645.7[de]
Vanillin	1350	25.4[e]	21.7[e]	4.7[e]	13.8[e]	27.8[e]	52.5[d]
Acids and lactones							
Heptanoic acid	1065	8.1[e]	9.6[e]	5.6[e]	6.5[e]	4.7[e]	16.2[d]
"3-(2-Hydroxyphenyl)-(*E*)-2 propenoic acid"	1194	121.3[f]	204.7[d]	147.2[e]	76.8[g]	128.1[ef]	145.3[e]

Table 1 (*continued*)

Compounds	Retention index[c]	Volatile aroma concentration (μg/kg)[b]					
		A358W	353W	BKH	019	1601	5501
Others							
"3-Butanethiol"	645	16.2^{e}	15.7^{e}	11.3^{e}	187.3^{d}	19.3^{e}	13.9^{e}
Allyl acetate	669	49.2^{d}	32.6^{d}	37.9^{d}	35.3^{d}	42.4^{d}	43.4^{d}
Diethylsulphide	677	19.8^{e}	20.8^{e}	15.9^{e}	12.3^{e}	15.6^{e}	36.6^{d}
Dimethyldisulphide	714	12.1^{de}	8.3^{e}	8.5^{e}	9.2^{e}	10.6^{e}	16.0^{d}
3-(Methylthio)propanal (methional)	864	9.1^{g}	24.4^{ef}	24.6^{ef}	20.0^{f}	29.0^{e}	46.1^{d}
Dimethyltrisulphide	940	12.3^{d}	7.8^{d}	4. 8^{d}	tr^{e}	10.2^{d}	9.4^{d}
Geranylacetone	1428	tr^{f}	6.2^{ef}	9.8^{e}	5.9^{ef}	11.1^{e}	22.1^{d}

Volatile compounds with quotation mark are tentatively identified.
[tr] Peak area under 100,000 ion count in gas chromatograph.
[a] Volatiles not shown in this table are available in the report by Park (1998).
[b] Average values of two observations.
[c] Determined with hydrocarbon standards on a DB-1 column.
[d–g] Values in the same row with the same letter are not significantly different by Student Newman Kuels test (SNK) at $p \leqslant 0.05$.

Table 2
Aroma values of the selected volatile aroma compounds of popped popcorn hybrids

Compounds	Odour threshold (ppb)	Aroma value (concentration/threshold)[a]					
		A358W	353W	BKH	019	1601	5501
Dimethyltrisulphide	0.01	1233.0^{b}	783.0^{b}	485.0^{b}	0.0^{c}	1021.5^{b}	941.0^{b}
2,5-Dimethyl-4-hydroxy-3(2H)-furanone (furaneol)	0.04	404.0^{c}	874.0^{b}	98.9^{d}	362. 5^{c}	442.4^{c}	697.4^{b}
2-Furfurylthiol (2-furanmethanthiol)	0.006	0.0^{c}	700.8^{b}	763.3^{b}	0.0^{c}	0.0^{c}	793.3^{b}
(*E*,*E*)-2,4-Decadienal	0.07	542.5^{c}	607.0^{c}	319.2^{d}	347.9^{d}	760.4^{b}	364.9^{d}
2-Ethyl-3,5-dimethylpyrazine	0.04	479.0^{cd}	567.2^{bc}	272. 2^{e}	472.0^{cd}	400.4^{d}	637.9^{b}
3-Methylbutanal	0.2	610.7^{b}	437.5^{b}	418.1^{b}	429.5^{b}	573.0^{b}	447.3^{b}
1-Octene-3-one	0.05	347.5^{b}	179.3^{c}	116.8^{c}	0.0^{d}	0.0^{d}	366.3^{b}
Propionyl-1-pyrroline	0.1	290.6^{b}	279.2^{b}	284.8^{b}	260.5^{b}	346.3^{b}	225.4^{b}
4-Vinyl-2-methoxyphenol (4-vinylguaiacol)	3.0	148.4^{d}	256.2^{b}	208.5^{bc}	171.7^{cd}	156.2^{d}	215.2^{bc}
3-(Methylthio)propanal (methional)	0.2	45.4^{e}	121.9^{cd}	123.0^{cd}	100.0^{d}	145.0^{c}	230.6^{b}
2-Methylbutanal	3.0	114.5^{bc}	94.9^{c}	79.7^{c}	102.0^{bc}	134.4^{b}	84.3^{c}
2-Pentylfuran	6.0	25.7^{c}	23.9^{c}	27.6^{c}	24.5^{c}	91.2^{b}	32.7^{c}
Hexanal	4.5	34.3^{b}	31.0^{b}	30.7^{b}	35.8^{b}	40.6^{b}	32.2^{b}
2-Acetyl-1,4,5,6-tetrahydro-pyridine	2.0	34.8^{b}	13.7^{b}	23.5^{b}	18.9^{b}	15.5^{b}	31.7^{b}
2-Acetyl-3,4,5,6-tetrahydro- pyridine	2.0	6.7^{b}	35.0^{b}	7.1^{b}	8.7^{b}	7.0^{b}	15.4^{b}
2-Methoxyphenol (guaiacol)	3.0	4.3^{cd}	5.3^{c}	3.4^{cd}	0.0^{d}	2.8^{cd}	8.9^{b}
Pentanal	12.0	3.2^{b}	2.8^{b}	1.9^{b}	4.0^{b}	4.2^{b}	2.5^{b}
1-Methyl-1H-pyrrole-2-carboxaldehyde (*N*-methyl-2-formylpyrrole)	37.0	1.6^{b}	0.2^{d}	1.5^{b}	1.4^{b}	1.6^{b}	0.7^{c}

[a] Average values of two observations.
[b–e] Values in the same row with the same letter are not significantly different by Student Newman Kuels (SNK) test at $p \leqslant 0.05$.

Table 3
Aroma ranking test results of popped popcorn hybrids

Hybrid	BKH	019	5501	1601	353W	A358W
Rank sum	192^{c}	210^{bc}	221^{abc}	260^{ab}	268^{ab}	277^{a}

[a–c] Values in the same column with the same letter are not significantly different by Friedman rank sum for analysis of ranked data at $p \leqslant 0.05$ (Newell & MacFarlane, 1987).

correlated with panel aroma preference of popped popcorn. However, 3-ethyl-2,5-dimethylpyrazine, 2-ethyl-5-methylpyrazine, ethylpyrazine, 2-methylpyrazine and (*E*,*E*)-2,4-decadienal were very highly negatively correlated with panel aroma ranking. The higher concentration of these volatiles resulted in adverse preference. Moreover, most of the pyrazines gave negative correlations with the sensory results.

Many aroma compounds have been identified in earlier studies. A few compounds have been mentioned as key popcorn aroma volatiles. The volatiles were 2-acetyl-1-pyrroline (2-AP), (*E*,*E*)-2,4-decadienal, 2-furfurylthiol, 4-vinyl-2-methoxyphenol 2,3-dimethyl-6-ethylpyrazine and 2-acetyltetrahydropyridine (Buttery et al., 1997; Schieberle, 1995; Walradt et al., 1970). In addition to these volatiles, Schieberle (1991) reported (*Z*)-2-nonenal, (*E*,*Z*)-2,4-nonadienal, 4,5-epoxy-(*E*)-2-decanal, 2,5-dimethyl-3-ethylpyrazine, 2,3-diethyl-5-methylpyrazine and 2-propionyl-1-pyrroline as being also important volatiles

Table 4
Correlation between selected individual volatile aroma concentration and sensory aroma preference[a] of popped popcorn hybrids

Compounds	Correlation with aroma sensory[b]	p-Value[c]
2-Acetylpyridine	0.77	0.072
2-Furfurylthiol (2-furanmethanthiol)	0.39	0.439
Pyrrole	0.37	0.469
3-(Methylthio)propanal (methional)	0.37	0.469
3-Furaldehyde	0.31	0.544
4-Vinyl-2-methoxyphenol (4-vinylguaiacol)	0.26	0.623
2-Pentylfuran	0.20	0.704
2-Furanmethanol (furfuryl alcohol)	0.09	0.872
4-Heptanone	0.09	0.872
3-(2-Hydroxyphenyl)-(*E*)-2-propenoic acid	0.03	0.957
2-Acetyl-1,4,5,6-tetrahydropyridine	−0.03	0.957
1-Methyl-1H-pyrrole-2-carboxaldehyde (*N*-methyl-2-formylpyrrole)	−0.14	0.784
2-Methyl-6-vinylpyrazine	−0.20	0.704
3-Butanethiol	−0.26	0.623
Hexanal	−0.26	0.623
Diethylsulphide	−0.37	0.469
1-Pentanol	−0.37	0.469
2-Methyl-5-vinylpyrazine	−0.37	0.469
2-Methoxyphenol (guaiacol)	−0.37	0.469
2-Furaldehyde (furfural)	−0.43	0.397
3-Pentanone	−0.49	0.329
Benzaldehyde	−0.49	0.329
2-Ethyl-3,5-dimethylpyrazine	−0.49	0.329
3,5-Diethyl-2-methylpyrazine	−0.54	0.266
2-Methylbutanal	−0.60	0.208
N-Acetyl-4H-pyridine	−0.60	0.208
2,5-Dimethyl-4-hydroxy-3(2H)-furanone (furaneol)	−0.60	0.208
2,5-Dimethylpyrazine	−0.66	0.156
(*E*,*E*)-2,4-Decadienal	−0.77	0.072
2-Methylpyrazine	−0.83	0.042
Ethylpyrazine	−0.83	0.042
2-Ethyl-5-methylpyrazine	−0.94	0.005
3-Ethyl-2,5-dimethylpyrazine	−0.94	0.005

[a] Subjective aroma ranking preference of popped popcorn hybrids, where the values for this computation were calculated as following: value = 6 − (mean ranking of each hybrid).
[b] Correlation was calculated by Spearman's correlation coefficients test.
[c] Calculated under null hypothesis $\rho = 0$ when six observations were used in this computation.

in popped popcorn. Buttery et al. (1997) reported several more volatiles with high log concentration per odour threshold; these were dimethyl trisulphide, 3-methylbutanal, 2-ethyl-3,5-dimethylpyrazine, 1-octen-3-one, 2-methylbutanal, 3-(methylthio)propanal (methional) and hexanal. Most of the volatiles mentioned above were also responsible for the distinct note in the odour profiles of heated cereals such as bread, pastry, cooked rice and corn products (Grosch & Schieberle, 1997). In the current study, however, 2-AP was not identified. Laksanalamai and Ilangantileke (1993) confirmed that 2-AP was a key compound contributing to the popcorn-like aroma in Khao Dawk Mai 105 rice; however, 2-AP was not found in non-aromatic rice and occurred at a low concentration in aged KDMI-105 Thai rice. Moreover, in a recent report by Jezussek, Juliano, and Schieberle (2002), 2-AP was found to be a key odourant in brown rices available in Asia, but not in brown rices available in Europe. On the other hand, 2-amino acetophenone and 4,5-epoxy-(*E*)-dec-2-enal were present and important in brown rices available in two different continents. Therefore, it can be postulated that 2-AP may be a key odourant in some popcorn varieties, but not even present in popped kernels of some varieties.

From the aroma value and correlation results in this study, quantities of most volatiles in popped popcorn were not different from each other. However, some volatiles were considered to contribute to the popcorn odour favorably, and some contributed adversely at high concentration. 2-Acetylpyridine may contribute to the overall popped popcorn aroma quality favorably or not adversely. However, 2,5-dimethylpyrazine, (*E*,*E*)-2,4-decadienal, 2-methylpyrazine, ethylpyrazine, 2-ethyl-5-methylpyrazine and 3-ethyl-2,5-dimethylpyrazine are important popcorn volatiles, but high concentrations may contribute negatively to characteristics popped popcorn odour. Others such as 2-furfurylthiol (2-furanmethanthiol), pyrrole, 3-(methylthio)propanal (methional), 3-furaldehyde, 4-vinyl-2-methoxyphenol (4-vinylguaiacol), 2-pentylfuran, 2-furanmethanol (furfuryl alcohol), hexanal, 1-pentanol, 2-methyl-5-vinylpyrazine, 2-methoxyphenol (guaiacol), and 2-acetylpyrrole may be responsible in part of typical popcorn aroma characteristics. Seitz and Ram (2000) reported that methoxybenzene compounds in grain are associated with off-odour, musty and smoke odours. Grain samples with mostly musty sour and/or smoke odours commonly contained methoxybenzene and 1,2-dimethylmethoxybenzene and/or 2-methoxyphenol (guaiacol) and its 4-ethyl derivative (Seitz & Ram, 2000). In this study, the aroma value of 4-vinylguaiacol was relatively high and gave some variation among popcorn hybrids; however, did not show good relationship with odour preference. Therefore, methoxybenzene compounds in popped popcorn may play a part of typical popcorn odour, but were not responsible for odour quality differences among different popcorn varieties.

4. Other data

Internal standard (18 ng, 0.025 μL nonane) ion count areas in the gas chromatogram of each replicate of six popcorn hybrids ranged from 7243757 to 7761819. The polynomial regression equation for retention time (RT, *X*-axis) of the hydrocarbon standards against retention indices (RI, *Y*-axis) of the hydrocarbon standards was as follows: $RI = 0.000016448RT^5 - 0.002466801RT^4 + 0.142203385RT^3 - 3.677733718RT^2 + 66.129269619RT + 419.\ 497854777$ ($R^2 = 1.000$). All calculated RIs of the hydrocarbon standard by the equation were quite well matched to the known theoretical RIs of the hydrocarbon standards. The retention time and calculated RIs of the hydrocarbon standards by the polynomial equation, and other gas chromatograms of the blank (including solvents and an internal standard), hydrocarbon standards, hybrid A358W, hybrid 353W, hybrid BKH, hybrid 019, hybrid 1601 and hybrid 5501 are available in the report by Park (1998).

5. Conclusions

Only a small number of volatiles were of significance in determining the aroma preference of popped popcorn. The aroma preference differences in popped popcorn hybrids may be subjected to the presence and/or concentration of 2-acetylpyridine, 2,5-dimethylpyrazine, (*E*,*E*)-2,4-decadienal, 2-methylpyrazine, ethylpyrazine, 2-ethyl-5-methylpyrazine and 3-ethyl-2,5-dimethylpyrazine. However, further investigations are needed to confirm the findings.

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