Volatile Flavor Components of Rice Cakes

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Volatiles were obtained from commercially prepared and laboratory-prepared rice cakes using high-flow dynamic headspace isolation with Tenax trapping. Analysis was carried out by capillary GC/MS. More than 60 compounds were identified. Major volatiles included 1-hydroxy-2-propanone, furfuryl alcohol, 2,5-dimethylpyrazine, 2-methylpyrazine, pyrazine, hexanal, furfural, pentanol, 3-hydroxy-2-butanone (acetoin), and ethyl-3,6-dimethylpyrazine. Although not ideally applicable to a dry product, concentration/threshold ratios indicated that the compounds with a high probability of contributing to the aroma and flavor included 3-methylbutanal, dimethyl trisulfide, 2-ethyl-3,5-dimethylpyrazine, 4-vinylguaiacol, hexanal, (*E*,*E*)-2,4-decadienal, 2-methylbutanal, 2-acetyl-1-pyrroline, 1-octen-3-ol, and 1-octen-3-one.

Keywords: *Rice cakes; volatiles; flavor; aroma; identification; concentrations; concentration/threshold ratios*

INTRODUCTION

Rice cakes are a convenient, low-calorie food that are growing in popularity in the United States. The cakes are often prepared from the rice alone and marketed without any additives, but they are also marketed with various flavorings. The present study was undertaken to provide more understanding of the flavor of the basic rice cakes. Various studies have been carried out on the flavor of cooked (mostly boiled) rice, which have been reviewed (Maarse, 1991; Buttery et al., 1988; Maga, 1984), but the process to produce rice cakes uses a short, rapid cooking method in which quite high temperatures are used to puff or pop the rice, which leads to a quite differently flavored product.

MATERIALS AND METHODS

Materials. Rice cakes were purchased from local supermarkets. Two major brands were used, which we will refer to as company A and company B. Both were produced from whole grain brown rice. Rice cakes were also produced in the laboratory in Albany, CA. The process to produce the cakes uses a short (∼10 s) heating process with a relatively high temperature (∼210 °C).

Anhydrous sodium sulfate (>99% pure) was heated at 150 °C for 4 h to remove any possible volatiles and was stored in clean airtight containers. Diethyl ether was freshly distilled, 1−5 ppm of Ethyl Corporation Antioxidant 330 was added, and the distilled ether was stored in the dark. Authentic compounds were obtained from reliable commercial sources or synthesized according to established methods.

Isolation of Volatiles Using Excess Sodium Sulfate. The general method, using sodium sulfate, was described previously (Buttery and Ling, 1998) for other products. With rice cakes, the sample (30 g) was placed in a Pyrex blending jar and blended to a coarse powder. Water (20 mL) was then added and the mixture blended again for 30 s. Anhydrous sodium sulfate (100 g) was next added and the mixture blended. The mixture was then added to a 1 L beaker and as quickly as possible mixed thoroughly with an additional 140 g of sodium sulfate using a glass rod. The resulting mixture was then poured into a Pyrex column 36 mm o.d. × 350 mm long containing a coarse fritted disk at the lower end and ground ball-and-socket joints for connection to a closed loop system. The lower end of the column was connected to a large (∼10 g) Tenax trap, and the column and trap were connected to a precleaned all-Teflon diaphragm pump that recirculated nitrogen around the loop at 3−6 L/min for 3 h (at <25 °C). At the end of the isolation the Tenax trap was removed from the loop and extracted with the freshly distilled ether (∼50 mL). The ether extract was concentrated to ∼50 μL using a warm water bath and a micro-Vigreux distillation column.

Quantitative Analysis. For quantitative studies 2.00 mL of a water solution of internal standards was added to the 20 mL of water used to blend with the powdered rice cakes. The solution of standards consisted of 20.0 μL/L (ppm) each of 2-pentanone, 6-methyl-5-hepten-2-one, and 4-phenyl-2-butanone. Capillary gas chromatography (GC) analysis was carried out with an HP 5890 instrument using flame ionization detection. The fused silica capillary columns used were coated with DB-Wax or DB-1 and were 60 m long × 0.32 mm i.d.

Capillary GC/MS. An HP 5890 GC instrument was used, coupled to an HP 5971 quadrupole mass spectrometer. The capillary columns used were similar to those described above but were 0.25 mm i.d. The injector used a 1/20 split and was at 170 °C. The DB-Wax column was held at 30 °C for the first 4 min after injection and then heated at 2 °C/min to 170 °C and held for a further 60 min. The DB-1 column was held at 30 °C for the first 25 min after injection and then heated at 4 °C/min to 200 °C and held for a further 30 min.

Odor Thresholds. These were values determined in previous studies by some of the authors (Buttery and Ling, 1997).

RESULTS AND DISCUSSION

Isolation Method. The closed-loop high-flow dynamic headspace isolation procedure, using excess anhydrous sodium sulfate, had been previously described by the authors in several publications such as Buttery and Ling (1998) and earlier literature cited therein. This method had been found to give reasonable recoveries of most compounds. As with most dry cereal products, moisture is needed initially to release the volatile compounds. In the mouth, during eating, this comes from saliva. In the current method a small quantity of water was added to the rice cakes. The pH of the rice cakes (on the addition of water) was very close

10.1021/jf990140w
Published on Web 09/04/1999

to neutral (pH 6.9). After this release of volatiles, excess anhydrous sodium sulfate is used to bind the water and so allow reasonable recovery of water soluble compounds.

Identification of Volatiles. Table 1 lists the compounds identified. The mass spectra and GC retention indices were consistent with those of authentic compounds. Also listed in Table 1, for most compounds, are GC retention indices found on the DB-Wax capillary column. The retention times of a few compounds were too long or their peaks were obscured by other peaks on DB-Wax and their GC retention indices on DB-1 are listed. The volatiles identified were in general similar to those found in other cereal products such as popcorn (Waldrat et al., 1970; Schieberle, 1991; Buttery et al., 1997) and tortilla chips (Buttery and Ling, 1998), and major MS ions of these volatiles were listed in the previous publications from our laboratory.

The purpose of this study was aimed mainly at the identification of the volatile compounds, but it also is important to get some idea of the concentration of the identified components. Included in Table 1 are concentrations of compounds determined using three internal standards as described under Materials and Methods. There was some variation with different samples, which is probably related to variations in the raw materials and exact processing conditions. The three internal standards used were chosen to approximate coverage of the volatility range of components. This is most suitable for compounds with volatility and chemical nature similar to those of the standards. However, because such mixtures contain large numbers of compounds with considerable variation in chemical nature, we should probably consider for the general compounds that the data are accurate only within the right order of magnitude. The calculation of these concentrations is based on the assumption of complete quantitative isolation of all components relative to the internal standards. None of the known isolation methods available can do this completely but, in the authors' experience, the high-flow closed-loop sodium sulfate method approaches this ideal for a wide range of volatiles. Recoveries for this method have been described previously by one of the authors (Buttery and Ling, 1998).

The processes involved in producing rice cakes and popcorn have some similarities. Both products are formed using rapid high-temperature heating steps that produce steam at high pressure inside the grain, which causes it to burst (or pop). The main difference is in the type of cereal used, whether corn or rice. The isolation methods used for the analysis of popcorn volatiles were different from the present method used for rice cakes, and this should be kept in mind in direct comparison of the quantitative data. The data obtained indicated that rice cakes generally had lower concentrations of volatiles than found in popcorn. The figures for cracker or popcorn type aroma compounds such as 2-acetyl-1-pyrroline and both isomers of 2-acetyltetrahydropyridine were higher in popcorn than they were in rice cakes. A number of other compounds, not necessarily directly important to flavor, were also indicated as occurring at a higher concentration in popcorn. These included 2,3-butanediol, 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one, γ-butyrolactone, and the sweet aroma compounds Furaneol and maltol.

2-Acetyl-*N*-heterocyclic Compounds. Compounds of this type, which have an acetyl group in close association with a nitrogen generally in a heterocyclic ring, have an odor character frequently referred to as cracker- or popcorn-like. Some mention has been made above of 2-acetyl-1-pyrroline and 2-acetyltetrahydropyridine. The characteristic odor of 2-propionyl-1-pyrroline [first identified in popcorn by Schieberle (1991)] was detected at its expected GC retention time with rice cakes, but we were unable to obtain a mass spectrum of it that was sufficiently above the backround of other interfering components.

2-Acetyl-1-pyrroline had been first found as an important aroma component of aromatic rices (Buttery et al., 1988), and its occurrence in rice cakes was expected. However, the mechanism of its formation at the high-temperature conditions used in producing rice cakes may be different from that involved in boiled rice.

Alkylpyrazines. Alkylpyrazines are common to most food products cooked at temperatures well above 100 °C and were expected in rice cakes. Qualitatively, these were similar to those found in popcorn, but there were some differences quantitatively. The most important to the aroma and flavor appear to be 2-ethyl-3,5-dimethylpyrazine and 2-ethyl-3,6-dimethylpyrazine.

Strecker Degradation and Other Aldehydes. Moderate concentrations of Strecker degradation aldehydes 2- and 3-methylbutanal were found. Phenylacetaldehyde, another commonly occurring Strecker degradation product, was also found in the rice cakes. It is likely that 2-methylpropanal also occurs, but the condition of the isolation method did not allow isolation of such very volatile compounds.

Hexanal is at a moderately high concentration in rice cakes. This is probably related to the fact that rice cakes are made from brown rice and that brown rice and rice bran are relatively susceptible to rancidity due to oxidative lipid breakdown. It is well-known that hexanal is one of the major products formed from lipid autoxidation.

Aliphatic Acids. Low levels of alipihatic acids are common in many foods. Aliphatic acids were also identified in the volatiles of the brown rice used to prepare the rice cakes. They had been also found in popcorn (Buttery et al., 1997). Compared to other products they are relatively weak odorants and are below their water threshold concentration level in rice cakes. The odors of 3-methylbutyric and hexanoic acids were, however, detected using GC sniffing of the volatile isolate.

Probable Contribution to Aroma and Flavor. In studies involving other products, odor threshold determinations in water solution for many components listed in Table 1 had been previously reported by some of us. These include Buttery et al. (1997) and earlier references cited therein. Odor thresholds are listed in Table 2 together with the $\log_{10}$ of the concentration/threshold ratios for rice cakes. As with popcorn, these would be ideally applicable only if we had a highly aqueous food. Like popcorn, rice cakes are quite dry. However, after the rice cakes are chewed in the mouth, an aqueous system is involved in the form of saliva. This aqueous saliva system would necessarily be of the same order of magnitude as the rice cake pieces and would then control the volatility and the relative amounts of components reaching the olfactory senses.

Table 2 shows that a total of 28 compounds occur above their water threshold concentrations in rice cakes.

Table 1. Volatile Compounds Identified and Concentrations Found in Commercial Rice Cakes

compound[a]	KI DB-Wax[c]	concentration in ppb[b] company A	company B
2-methylbutanal	912	350	540
3-methylbutanal	914	440	620
pentanal	974	130	440
2,3-pentanedione	1050	91	250
hexanal	1077	800	960
2-heptanone	1178	15	*d*
heptanal	1180	5	*d*
pyridine	1181	17	20
limonene	1197	34	14
pyrazine	1207	1300	1400
2-pentylfuran	1226	17	16
pentanol	1246	700	720
2-methyl-3-ketotetrahydro-furan	1254	5	15
2-methylpyrazine	1262	1200	2200
2-hydroxy-3-butanone (acetoin)	1278	600	750
octanal	1284	6	7
1-hydroxy-2-propanone	1295	6000	2100
1-octen-3-one	1297	5	4
2,5-dimethylpyrazine	1320	850	1200
2,6-dimethylpyrazine	1326	400	640
2-ethylpyrazine	1331	71	150
2-acetyl-1-pyrroline	1335	10	21
2,3-dimethylpyrazine	1344	90	170
hexanol	1350	70	160
dimethyl trisulfide	1374	3	3
2-ethyl-6-methylpyrazine	1380	78	120
2-ethyl-5-methylpyrazine	1385	80	85
nonanal	1390	9	11
trimethylpyrazine	1404	240	250
(*E*)-2-octenal	1425	27	24
2-vinylpyrazine	1436	20	30
2-ethyl-3,6-dimethylpyrazine	1435	600	280
3-methylthiopropanal (methional)	861 (DB-1)	10	5
1-octen-3-ol	1448	97	79
furfural	1455	700	800
2-ethyl-3,5-dimethylpyrazine	1455	10	3
pyrrole	1507	32	40
benzaldehyde	1516	130	200
propionic acid	1520	61	60
2-acetyl-5-methylpyrazine	1080 (DB-1)	40	*d*
2-acetyl-6-methylpyrazine	1083 (DB-1)	39	*d*
2,3-butanediol	1539	62	38
2-acetyltetrahydropyridine (-1,4,5,6- and -3,4,5,6-)	1585	50	75
5-methylfurfural	1567	40	120
γ-butyrolactone	1623	750	1000
phenylacetaldehyde	1636	88	90
2-acetylthiazole	1641	35	180
furfuryl alcohol	1656	2000	2300
3-methylbutyric acid	1665	80	60
2-methylbutyric acid	1670	10	5
γ-hexalactone	1699	50	170
5-methylfurfuryl alcohol	1720	21	19
pentanoic acid	1730	270	210
(*E*,*E*)-2,4-decadienal	1800	10	*d*
hexanoic acid	1825	280	250
guaiacol (2-methoxyphenol)	1855	200	*d*
γ-octalactone	1916	61	38
maltol	1960	60	29
2-acetylpyrrole	1970	40	42
2-formylpyrrole	2006	65	20
2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (Furaneol)	2030	90	15
4-vinylphenol	1190 (DB-1)	190	*d*
4-vinylguaiacol	2180	550	410
vanillin	1349 (DB-1)	120	*d*
2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one	1115 (DB-1)	110	*d*

[a] Mass spectrum and GC Kovat's retention index found were consistent with those of authentic sample. [b] Parts per billion (10^9) or micrograms of compound per kilogram of rice cake. Data are probably only accurate to the right order of magnitude. [c] Except for those followed by DB-1 where the compounds were only identified on a DB-1 column due to being obscured by other peaks or by being retained too long on DB-Wax. [d] Not measurable due to overlap of other peaks or outside of the range of GC conditions.

Table 2. Odor Thresholds in Water Solution and Log_{10} of Concentration/Threshold Ratios of Components Identified in Commercial Rice Cakes (Company A)[a]

compound	odor threshold ppb[b] (water)	log concentration/ threshold[c]
3-methylbutanal	0.2	3.3
dimethyl trisulfide	0.01	2.5
2-ethyl-3,5-dimethylpyrazine	0.04	2.4
4-vinylguaiacol	3	2.3
hexanal	4.5	2.2
(*E*,*E*)-2,4-decadienal	0.07	2.2
2-methylbutanal	3	2.1
2-acetyl-1-pyrroline	0.1	2.0
1-octen-3-ol	1	2.0
1-octen-3-one	0.05	2.0
2-acetyltetrahydropyridine	1	1.9
phenylacetaldehyde	4	1.9
guaiacol	3	1.8
2-ethyl-3,6-dimethylpyrazine	8.6	1.8
3-methylthiopropanal (methional)	0.2	1.7
4-vinylphenol	10	1.3
trimethylpyrazine	23	1.0
(*E*)-2-octenal	3	0.95
nonanal	1	0.95
octanal	0.7	0.93
γ-octalactone	8	0.88
2,3-pentadione	20	0.65
2-acetylthiazole	10	0.54
2-pentylfuran	6	0.45
vanillin	58	0.30
heptanal	3	0.22
2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (Furaneol)	60	0.18
furfuryl alcohol	1900	0.02
2,5-dimethylpyrazine	1700	0
2-ethyl-5-methylpyrazine	100	−0.09
2,3-dimethylpyrazine	2500	−0.14
2,6-dimethylpyrazine	1500	−0.27
benzaldehyde	350	−0.40
3-methylbutyric acid	250	−0.49
pentanol	4000	−0.76
furfural	3000	−0.77
hexanol	500	−0.85
2-heptanone	140	−0.97
hexanoic acid	3000	−1.0
pentanoic acid	3000	−1.0
5-methylfurfural	500	−1.1
2-hydroxy-3-butanone (acetoin)	8000	−1.1
1-hydroxy-2-propanone	10^5	−1.2
γ-hexalactone	50	−1.5
2-vinylpyrazine	700	−1.5
propionic acid	2000	−1.5
maltol	2500	−1.6
2-methylpyrazine	6×10^4	−1.7
2-acetyl-5-methylpyrazine	3000	−1.9
2-ethylpyrazine	6000	−1.9
pyridine	2000	−2.1
pyrazine	18×10^4	−2.1
2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one	35000	−2.5
2,3-butanediol	$>10^5$	<-3.2
2-acetylpyrrole	17×10^4	−3.6

[a] It should be noted that the concentration/threshold ratios are only ideally applicable to an aqueous food, whereas rice cakes are quite dry. [b] Odor threshold of compounds in water solution in parts of compound per billion (10^9) parts of water or nanoliters per liter. [c] Log_{10} of the ratio of concentration of compound found in the rice cakes/odor threshold concentration of that compound in water.

The compounds 3-methylbutanal, dimethyl trisulfide, 2-ethyl-3,5-dimethylpyrazine, 4-vinylguaiacol, hexanal, (*E*,*E*)-2,4-decadienal, 2-methylbutanal, 2-acetyl-1-pyroline, 1-octen-3-ol, and 1-octen-3-one show the largest log concentration/threshold ratios.

The determination of detection limits of odorants obtained by sniffing the end of the GC column is a powerful tool for pinpointing important aroma compounds and, when quantitatively applied, referred to as the AEDA method (Grosch, 1994). In the present work no quantitative method was used, but odor descriptions were obtained by sniffing the effluent from the GC capillary DB-Wax column using a high dilution factor so that only the most potent odorants could be detected. Recognizable odor descriptions were obtained for and at the retention times of 3-methylbutanal, hexanal, 1-octen-3-one, 2-acetyl-1-pyrroline, dimethyl trisulfide, 2-propionyl-1-pyrroline, 2-ethyl-3,6- and -3,5-dimethylpyrazines, methional, 2-acetyltetrahydropyridine, 3-methylbutyric acid, hexanoic acid, and 4-vinylguaiacol.

Laboratory-Produced Rice Cakes. Volatiles were also studied in rice cakes produced in the laboratory. These cakes differed from the commercial cakes in that besides the brown whole grain rice, a portion (25%) of wheat flour pasta (shaped to resemble rice grains) was also added to the brown rice before the heating (popping) process. The aims behind the addition of the wheat flour pasta included providing other markets for wheat and also as a convenient way to add flavoring compounds or mixtures to the rice cakes. With no added flavor the volatiles isolated from the laboratory-produced rice cakes were found to be similar qualitatively and quantitatively to those found in the commercial rice cakes.

ACKNOWLEDGMENT

We thank Lundberg Family Farms Co., Richvale, CA, for the loan of equipment for the pilot plant preparation of rice cakes.

LITERATURE CITED

Buttery, R. G.; Ling, L. C. Additional studies on flavor components of corn tortilla chips. *J. Agric. Food Chem.* **1998**, *46*, 2764−2769.

Buttery, R. G.; Turnbaugh, J. G.; Ling, L. C. Contribution of volatiles to rice aroma. *J. Agric. Food Chem.* **1988**, *36*, 1006−1009.

Buttery, R. G.; Ling, L. C.; Stern, D. J. Studies on popcorn aroma and flavor volatiles. *J. Agric. Food Chem.* **1997**, *45*, 837−843.

Grosch, W. Determination of potent odourants in foods by aroma extract dilution analysis (AEDA) and calculation of odor activity values (OAVS). *Flavour Fragrance J.* **1994**, *9*, 147−158.

Maarse, H. Rice. In *Volatile Compounds in Foods and Beverages*; Maarse, H., Ed.; Dekker: New York, 1991; pp 79−89.

Maga, J. A. Rice product volatiles, a review. *J. Agric. Food Chem.* **1984**, *32*, 964−970.

Schieberle, P. Primary odorants of popcorn. *J. Agric. Food Chem.* **1991**, *39*, 1141−1144.

Waldradt, J. P.; Lindsay, R. C.; Libbey, L. M. Popcorn flavor: Identification of volatile compounds. *J. Agric. Food Chem.* **1970**, *18*, 926−928.

Received for review February 17, 1999. Revised manuscript received June 14, 1999. Accepted July 6, 1999. We thank Lundberg Family Farms Co., Richvale, CA, for partial support of the work.

JF990140W