

Studies on Popcorn Aroma and Flavor Volatiles

Ron G. Buttery,* Louisa C. Ling, and Don J. Stern

U.S. Department of Agriculture, Agricultural Research Service, Western Regional Research Center,
Albany, California 94710

Capillary GC–MS qualitative studies, with some determination of amounts present, were carried out on flavor and aroma volatiles isolated from microwave oven-produced popcorn. The presence of most previously reported compounds was confirmed, and some additional compounds were identified in popcorn for the first time. These newly identified compounds include dimethyl sulfide, dimethyl di- and trisulfides, 3-methylindole (skatole), α - and β -ionones, 2-methyl-3-hydroxypyran-4-one (maltol), 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one, 5-methyl-4-hydroxy-3(2*H*)-furanone (norfuranol), geranyl acetone, and others. Hydrogen sulfide was found as a major component of the volatiles emitted during popping. Two main methods for isolating the volatiles were used. One involved isolation of the volatiles from the freshly popped dry popcorn including volatiles emitted during popping. The other involved isolating the volatiles from the fresh popcorn blended with water saturated with salt and made moderately basic with sodium carbonate. Odor thresholds in water solution of most compounds found are listed and compared.

Keywords: *Popcorn; volatiles; flavor; identification; concentrations; odor thresholds*

INTRODUCTION

Some of the first gas chromatography–mass spectrometry (GC–MS) studies on popcorn volatiles were carried out by Walradt et al. (1970) who identified 36 volatile components with some certainty and 20 additional components tentatively from microwave oven- and hot oil-produced popcorn. The well-confirmed compounds included the commonly encountered alkylpyrazines such as 2,5-dimethylpyrazine and 2-ethyl-3,6-dimethylpyrazine, furans such as 5-methylfurfural and 2-pentylfuran, alkanals such as hexanal and heptanal, phenols such as 4-vinylguaiaicol and 4-vinylphenol, and pyrroles such as 2-acetylpyrrole and unusual compounds such as *N*-furfurylpyrrole. Probably the most important tentatively identified compounds were 2-acetylpyrazine, which has the most popcorn-like aroma of any of the compounds identified, and 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (Furanol), which has a sweet aroma.

A number of studies of volatiles of popcorn were made in recent years by Schieberle (1990, 1991, 1995) using the method of aroma extract dilution analysis (AEDA) to pinpoint the important primary odorants. In addition to compounds reported by Walradt, Schieberle (1990, 1991) identified 2-acetyl-1-pyrroline, 2-acetyltetrahydropyridine, 2-propionyl-1-pyrroline, 2-furfurylthiol, 4,5-epoxy-(*E*)-2-decenal, (*E*)- β -damascenone, and 1-octen-3-one. Schieberle (1991) showed that 2-acetyl-1-pyrroline, (*E,E*)-2,4-decadienal, 2-furfurylthiol, and 4-vinyl-2-methoxyphenol (4-vinylguaiaicol) contributed the most to the odor (highest flavor dilution (FD) factors) together with 2-acetyltetrahydropyridine and 2-propionyl-1-pyrroline. Some of these compounds had been previously found by Schieberle and Grosch (cf. 1992) in bread volatiles. Using the powerful technique of stable isotope dilution assays, Schieberle (1995) was able to accurately determine the concentrations of 2-acetyl-1-pyrroline, 2-propionyl-1-pyrroline, 2-acetyltetrahydropyridine, 2-acetylpyrazine, and Furanol (Schieberle, 1992) in popcorn.

The current large market in the United States for popcorn produced by home microwave ovens has encouraged further studies on the volatiles responsible for

popcorn aroma and flavor. In evaluating new cultivars a practical method is also needed by the industry to quantitatively analyze the aroma components from the large numbers of such cultivars produced yearly using traditional and modern genetic breeding methods.

MATERIALS AND METHODS

Materials. Corn samples were obtained from commercial production grown in fields in Indiana during the years of 1992 and 1993. Samples were also obtained from local supermarkets. The cultivars chosen were made for the production of popcorn using the microwave method.

Diethyl ether was freshly distilled through a 60 cm Pyrex glass helice column, protected by adding ca. 0.001% Ethyl Corp. antioxidant 330 and stored in the dark. Sodium chloride and sodium carbonate were heated at 150 °C for several hours to remove possible volatiles. All gases were purified by passing through activated charcoal. To remove possible volatiles, high-quality laboratory tissue paper “wipes” were swept with purified air (6 L/min) for 24 h at room temperature.

Isolation of Volatiles Using a “Dry Method”. The corn sample (25 g) was enclosed in a clean 5 L round bottom flask. The neck of the flask (45/50 mm) was covered with an inverted 250 mL beaker. The flask was placed in a large microwave oven and microwaved (800 W) for 2.5 min, whereby most of the corn kernels were “popped”. A suitable Pyrex glass head allowing entry and exit of sweep gas, using clamped ball joints for connections, was then attached to the neck of the flask. A large Tenax trap (ca. 10 g of Tenax) was attached to the head and connected via Teflon tubing through an all Teflon diaphragm pump in a Grob type closed loop system (cf. Grob and Zurcher, 1976) similar to that described previously (Buttery and Ling, 1995). Note that for safety reasons the flask should be placed behind an explosive safety screen because of occasional moderate pressure in the flask. The air of the flask and system was first displaced with nitrogen, through the Tenax trap, before connecting and starting the recycling system. The sweep gas flow through the loop was ca. 3 L/min. In some early studies purified air or nitrogen was used in an open system discarding the gases after they left the Tenax trap. After the 2 h sweeping the volatiles were eluted from the trap with freshly distilled diethyl ether (50–75 mL). The ether was concentrated to ca. 1 mL in a 100 mL pear-shaped flask equipped with a Vigreux column in a warm water bath.

The concentrate was then transferred to a pointed-ended microtest tube and concentrated to ca. 20 μ L using a 50 °C air bath.

Isolation of Volatiles Using a "Wet Method". This was similar to the method described previously by the authors for sweet corn products (Buttery et al., 1994). Corn kernels (25 g) were placed in an inverted Pyrex glass cone (15 cm diameter opening, 15 cm height) supported in a Pyrex dish. The corn kernels were microwaved for 2.5 min at 800 W. The popcorn was then immediately transferred to a Pyrex glass blender containing 150 mL of water. The blender mouth was then covered with aluminum foil and the mixture blended for a few seconds to reduce the volume of the popcorn. Volatile free sodium chloride (54 g) and sodium carbonate (7.5 g) were then added. The blender mouth was again covered with aluminum foil and the mixture blended for 30 s. The mixture was then poured into a clean 1 L flask containing a magnetic stirrer. A suitable Pyrex isolation head was then attached to the flask and the flask headspace swept with a purified stream of air or nitrogen at 3 L/min to a large Tenax trap for 2 h using an open-ended system. The trap was then eluted with diethyl ether and concentrated as for the "dry" method.

A variation of the method for closely neutral conditions (pH 7.4) was also carried out by substituting NaHCO₃ instead of Na₂CO₃.

Capillary GC-MS Analysis. Studies were carried out with both DB-1 and DB-Wax capillary GC columns. The DB-1 column was 60 m long \times 0.25 mm i.d. fused silica, wall coated with bonded methylsilicone DB-1. The injector temperature was 170 °C. The column was held at 30 °C for 25 min and then temperature programmed at 4 °C/min to 200 °C and held at this temperature for a further 20 min. The DB-Wax column was of the same dimensions as the DB-1 column and used the same injector temperature. The column was held at 30 °C for 4 min and then temperature programmed at 2°/min until 170 °C and held at this temperature for another 30 min. The GC instrument was a HP model 5890 which was directly coupled to a HP model 5970 quadrupole mass spectrometer. GC-MS analysis of very volatile compounds was carried out, using a syringe, by drawing 5 mL of vapor through polyethylene film covering the neck of a 5 L flask containing freshly popped corn (25 g) and injecting this directly into the DB-1 capillary GC column.

Quantitative GC Determinations. The GC analysis was carried out using similar GC conditions as described for GC-MS except that the capillary columns were 0.32 mm i.d.

For quantitative determination with the "dry method", a water solution of internal standards (1 mL) supported on two specially precleaned laboratory tissues was added to the flask, after popping, immediately before attaching the isolation head to the neck of the flask. The internal standards used with the dry method were 2-pentanone, 6-methyl-5-hepten-2-one, and 4-phenyl-2-butanone dissolved in water to give 20.0 mg/L of each.

For quantitative determination with the wet method, the internal standards used were 2-pentanone, 3,5-dimethylpyridine, and quinoline each dissolved in water to give 20.0 mg/L of each. The internal standard solution (1 mL) was added to the blender after adding NaCl and Na₂CO₃.

Authentic Compounds. Samples of authentic compounds were obtained from reliable commercial sources or synthesized by well-established methods, e.g., 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one was synthesized from glucose and piperidine as outlined by Kim and Baltes (1996). *N*-Furfuryl-2-formylpyrrole was synthesized by the reaction of *N*-furfurylpyrrole with dimethylformamide and POCl₃. Compounds were purified by preparative GC and verified by spectral (MS or IR) means.

Sensory Studies. Odor thresholds were determined in water following general methods previously described (Guadagni and Buttery, 1978; Buttery and Ling, 1995) using a panel of 18–23 judges. Odor descriptions were obtained from the GC capillary column effluent by turning off the flame (retaining the air flow) and adding a short length of Teflon tubing to the top of the detector (temperature 150 °C) to allow sniffing of the effluent.

RESULTS AND DISCUSSION

Industrial researchers, who had studied popcorn flavor for many years, informed the authors that they felt that the aroma of the volatiles produced during "popping" was important to the public's appreciation of popcorn in addition to those involved in the eating of the popcorn. This led the authors to use both a "dry method" of isolation as well as a "wet method". The "dry method" includes the volatiles produced during popping.

Identification of Volatile Components. Table 1 lists compounds identified with some certainty, having mass spectra and GC retention indices consistent with that of authentic samples. Compounds for which no authentic samples were available, but whose spectral data were consistent with published data (e.g., Shigematsu et al., 1975; Tressl et al., 1982) or MS computer libraries, are listed in quotation marks. Such identification must be considered tentative, although in all cases the spectra matched the published data very well. Figure 1 shows a typical GC analysis of fresh popcorn volatiles isolated using the "dry method".

Concentrations of components found are also listed in Table 1 for both isolation methods. GC quantitative data were obtained from more than 100 different samples of popcorn, and considerable variation was noticed. The figures in Table 1 are means from at least three different samples. Although these quantitative data were measured as carefully as possible, they are only intended to give some idea of the order of magnitude of the concentrations. With the "dry method", as volatiles produced during popping are included, this is more of an apparent concentration than an actual concentration.

Compounds Not Previously Reported. Most of the compounds in Table 1 had been reported previously by Waldradt (1970) or Schieberle (1990, 1991). Compounds not previously reported include dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide, 1-hydroxy-2-propanone, 2,3-butanediol, hexanol, octanol, propanal, 2-heptanone, 3-methylindole (skatole), 5-methyl-4-hydroxy-3(2*H*)-furanone (norfuranol), 2-methyl-3-hydroxypyran-4-one (maltol), 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one (dihydrohydroxymaltol), α -ionone, β -ionone, and geranylacetone. In addition 5-acetyl-2,3-dihydro-1*H*-pyrrolizine and maltoxazine were identified tentatively, their spectra being consistent with published spectra but no authentic samples were available for direct comparison. Some of these compounds had previously been found in other corn products. Both α - and β -ionone had been found at trace levels in corn tortilla-related products by Karahadian and Johnson (1993). This occurrence in tortilla products was later confirmed by us, and in addition we also found the related geranylacetone (Buttery and Ling, 1995). These compounds are usually associated with carotenoids in foods.

5-Methyl-4-hydroxy-3(2*H*)-furanone (norfuranol) is related to 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (Furanol). Furanol had been first reported in popcorn by Waldradt et al. (1970) and later by Schieberle (1991). In the present work other sugar degradation products (maltol and dihydrohydroxymaltol) were also found. The "dry" isolation method facilitated the isolation of these compounds which are very water soluble. Such compounds give extremely low recoveries using other isolation methods which involve aqueous systems, except where direct solvent extraction is used.

Table 1. Compounds Identified in Popcorn^a

compound	Kovats' RT index (DB-1)	concn in popcorn ($\mu\text{g}/\text{kg}$)		compound	Kovats' RT index (DB-1)	concn in popcorn ($\mu\text{g}/\text{kg}$)		
		dry method	wet method			dry method	wet method	
Aliphatic Alcohols								
ethanol	440	60		2,3-butanediol ^b	756	880		
1-hydroxy-2-propanone ^b	620	1800		meso-2,3-butanediol ^b	768	1200		
3-hydroxy-2-butanone ^b	674	140	5800	hexanol	848	12		
pentanol	752	14		octanol	1053	7		
Aliphatic Aldehydes and Ketones								
acetaldehyde	400	4600		2-heptanone	865	17	60	
propanal	480	370		heptanal	876	16		
2-methylpropanal	550	670		1-octen-3-one	953	5		
2,3-butanedione	560	170		nonanal	1082	41		
3-methylbutanal	627	430	1200	(<i>E</i>)-2-nonenal	1133	8		
2-methylbutanal	637	560	2400	decanal	1184	29		
2,3-pentadione	664	200	380	(<i>E,Z</i>)-2,4-decadienal	1240	6		
pentanal	668	36		(<i>E,E</i>)-2,4-decadienal	1287	17		
hexanal	772	140	80					
Nitrogen Compounds								
pyrazine ^b	710	2	2300	2-formylpyrrole ^b	997	41		
pyrrole ^b	725	26	440	"2-propionyl-1-pyrroline" ^b	1000	9	78	
2-methylpyrazine	796	240	3900	2-acetyl-1,4,5,6-tetrahydropyridine	1017	67	250	
2,5-dimethylpyrazine	880	480	2300	2-acetylpyrrole	1024	10		
2,6-dimethylpyrazine	880	71	340	2-ethyl-3,6-dimethylpyrazine	1054	64	240	
2-ethylpyrazine	887	25	480	2-ethyl-3,5-dimethylpyrazine	1054	6	60	
2,3-dimethylpyrazine	890	41	310	"dimethylvinylpyrazine" ^b	1078	5	42	
2-acetyl-1-pyrroline	892	12	55	2-acetyl-3,4,5,6-tetrahydropyridine	1110	350	320	
2-vinylpyrazine	901	20	60	<i>N</i> -furfurylpyrrole	1133	20	250	
<i>N</i> -methyl-2-formylpyrrole	970	40	170	2-acetyl-5-methylpyrazine	1080	4		
2-ethyl-6-methylpyrazine	973	60	130	2-acetyl-6-methylpyrazine	1083	9		
2-ethyl-5-methylpyrazine	975	130	290	3-methylindole (skatole)	1330	2		
2,3,5-trimethylpyrazine	978	210	470	"5-acetyl-2,3-dihydro-1 <i>H</i> -pyrrolizine" ^b	1335	5		
"2-methyl-6-vinylpyrazine" ^c	985	20		<i>N</i> -furfuryl-2-formylpyrrole	1345	15	290	
"2-methyl-5-vinylpyrazine" ^b	992	37	70	"maltoxazine" ^b	1630	17	41	
Furans, Pyrans, and Aromatic Compounds								
furfural	800	610	13000	2,5-dimethyl-4-hydroxy-3(2 <i>H</i>)-furanone	1030	2300		
furfuryl alcohol	827	500	5900	(Furaneol) ^b				
2-acetylfuran	876	16	200	3-hydroxy-2-methylpyran-4-one (maltol) ^b	1070	490		
2-furfurylthiol ^b	880	<5		2-methoxyphenol (guaiacol)	1058	3	2	
benzaldehyde	926	20		2,3-dihydro-3,5-dihydroxy-6-methyl-4 <i>H</i> -pyran-4-one ^b	1115	4000		
5-methylfurfural	927	22	730	5-(hydroxymethyl)furfural ^b	1160	100		
2-pentylfuran	977	17		4-vinylphenol	1190	280	920	
phenylacetaldehyde	1006	97	73	4-vinyl-2-methoxyphenol (4-vinylguaiacol)	1280	500	2800	
5-methyl-4-hydroxy-3(2 <i>H</i>)-furanone (norfuranol) ^b	1020	350		vanillin	1349	3500		
Acids and Lactones								
acetic acid ^b	580	4000		hexanoic acid ^b	975	400		
propionic acid ^b	715	300		heptanoic acid ^b	1064	25		
γ -butyrolactone ^b	854	22000		octanoic acid ^b	1162	19		
pentanoic acid ^b	880	130		nonanoic acid ^b	1260	29		
Others								
dimethyl sulfide	400	70		dimethyl trisulfide	941	3	10	
dimethyl disulfide	722	13	20	α -ionone	1404	2	2	
3-(methylthio)propanal ^b (methional)	861	14	12	geranylacetone	1429	5	5	
				β -ionone	1462	2	2	

^a MS and GLC retention indices are consistent with those of an authentic sample unless indicated. Concentrations of volatiles found in popcorn using the "dry" and "wet" methods of isolation, described in the text. Concentrations are considered of order of magnitude accuracy only. ^b These compounds have very low recovery factors by dynamic headspace sampling and the values are only meant to give an idea of the order of magnitude. ^c Compounds in quotation marks have mass spectra consistent with published spectra but no authentic samples were available for direct comparison. These identifications must be considered tentative.

Sulfur Compounds. Dimethyl sulfide is an important component of sweet corn (cf. Buttery et al., 1994), and it is not surprising to find it in the volatiles formed in the cooking of popcorn. Because of dimethyl sulfide's high volatility, the high temperatures involved, and the open structure of the popcorn, it is probably lost readily from the cooked popcorn. It was only identified in the gases produced during popping and not in the popcorn itself. Traces of dimethyl di- and trisulfide were also detected (GC-MS) using the "wet method" as well as the "dry method" and therefore must occur in the cooked popcorn.

The characteristic odor of hydrogen sulfide was very apparent from the outlet of the Tenax trap using the open-ended "dry method". Its presence was also confirmed from the fact that lead acetate paper rapidly blackened in these exit gases. By passing the exit gases over a 5% solution of lead acetate in water, it was possible to collect the precipitate of lead sulfide and weigh it. This showed that the formation of hydrogen sulfide during the popping was of the order of 17 mg/kg of corn (17 ppm). Hydrogen sulfide is, of course, a potent odorant with a reported threshold < 0.007 mg/m³ in air (Leonardus et al., 1969).

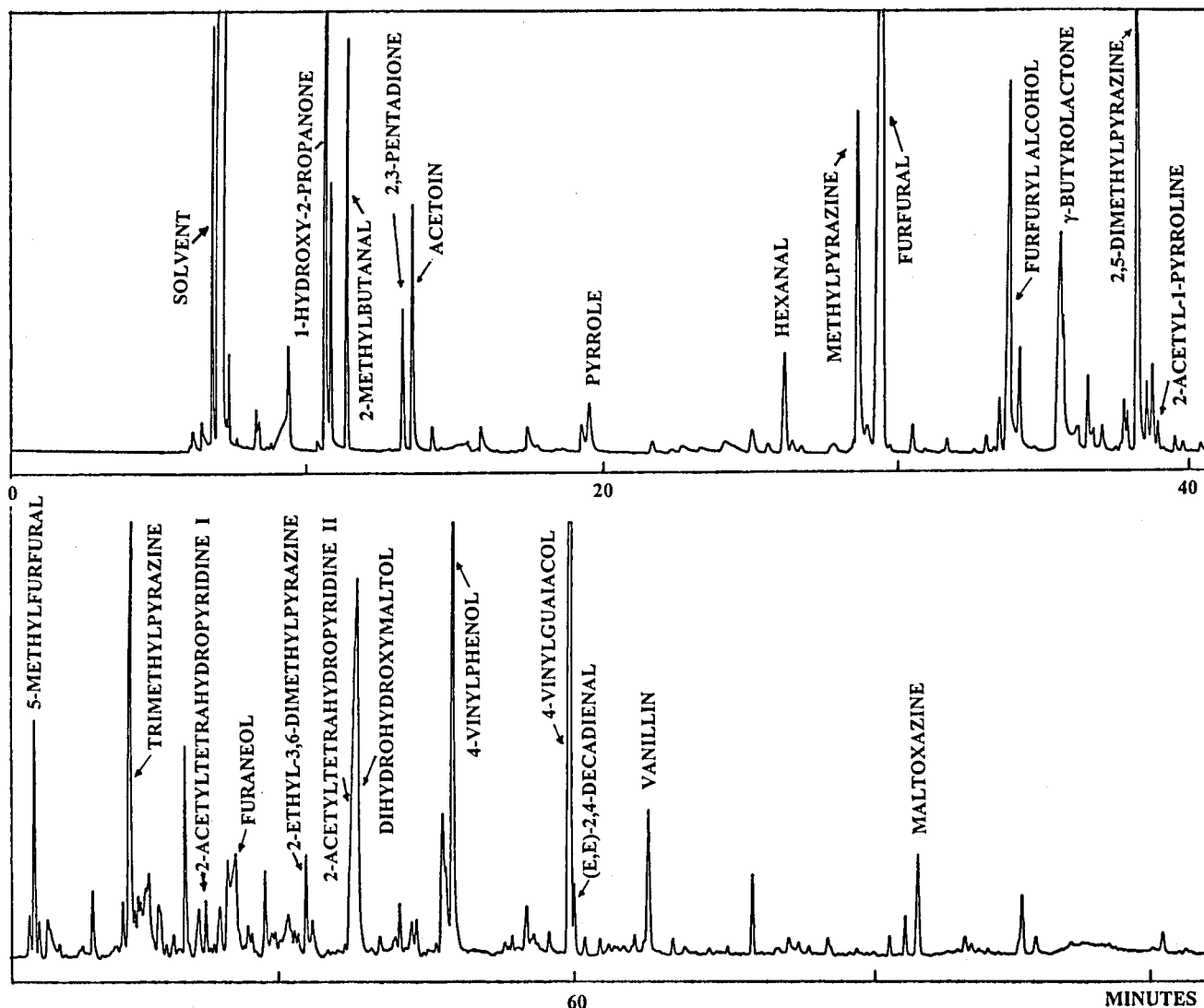


Figure 1. Capillary GC analysis (DB-1) of fresh popcorn volatiles using the "dry method". GC conditions are described in the text.

2-Furfurylthiol had been identified previously in popcorn by Schieberle (1991). We also found mass spectral and GC retention evidence for it. In addition we detected its characteristic odor at the correct retention time when carrying out GLC effluent sniffing. We found it at borderline concentrations for mass spectrometry, and it was only separated sufficiently from other components when using the DB-Wax GC capillary column. Very low recoveries (5–15%) were found for 2-furfurylthiol with isolation using test solutions by the "dry method". The reason for this may be oxidation on the surface of the Tenax during ether extraction or oxidation in the ether extract. Even freshly distilled diethyl ether can contain $\mu\text{g}/\text{kg}$ (ppb) levels of ether peroxide which may be sufficient. The distilled ether contains the BHT type high molecular weight antioxidant Ethyl Corp. antioxidant 330, which may serve to protect most compounds against oxidation, but Hofmann et al. (1996) have shown that antioxidants of the BHT type are not effective in preventing oxidation of thiols.

2-Acetyl Nitrogen Heterocyclic Compounds. Schieberle (1991) has shown that the compounds 2-acetyl-1-pyrroline, 2-propionyl-1-pyrroline, and the two tautomeric forms of the 2-acetyltetrahydropyridines are all important to popcorn aroma. In sensory panel studies some years ago (Buttery et al., 1983), in connection with rice flavor studies, the main odor description used by a

sensory panel evaluating 2-acetyl-1-pyrroline was "popcorn". All four compounds have a very similar odor character, and very likely there is some kind of additive effect of their individual odor contribution. It is quite evident then that these compounds are very important to popcorn aroma. Other related compounds include the considerably weaker odorant 2-acetylpyrazine, which was tentatively identified by Walradt et al. (1970), identified by Schieberle (1991), and not detected by us. We did detect and identify 2-acetyl-5-methylpyrazine and 2-acetyl-6-methylpyrazine which, however, are relatively weak odorants, the 2,5- form having an odor threshold of 3000 nL/L in water solution.

Mass Spectra. The mass spectra of most compounds are well enough known, or the major ions had been listed recently by the authors in studies of other corn products (Buttery et al., 1994; Buttery and Ling, 1995). Major ions for some unusual compounds are listed below (one major ion each 14 mass units with the most intense ions listed first and the molecular ion in *italics*): 5-acetyl-2,3-dihydro-1*H*-pyrrolizine, 134, *149*, 106, 43, 79, 51 (cf. Shigematsu et al., 1975); maltoxazine 150, *179*, 41, 53, 95, 108 (cf. Tressl et al., 1982); 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one, 43, 101, *144*, 55, 72, 115 (cf. Kim and Baltes, 1996); *N*-furfurylpyrrole, 81, *147*, 53, 39, 117, 65; *N*-furfuryl-2-formylpyrrole, 81, *175*, 53, 39, 146, 117.

Isolation Methods. Several isolation methods were tried. A number of preferred factors seemed important in the development of the method. It is important (1) that the method can be carried out in a relatively rapid way in order that it can be used by the popcorn industry as a quality control tool for analyses of large numbers of samples; (2) that the method give a relatively comprehensive analysis, i.e., cover as many as possible volatile aroma compounds in the one process; (3) that the method causes no chemical change to important volatiles.

The commercial "purge and trap" units which use Tenax trapping with thermal desorption meet preferred factor 1 but neither of the others. Such commercial units still use some metal parts such as valves and nickel lines which together with thermal desorption can lead to chemical changes in sensitive compounds such as 2-acetyl-1-pyrroline and 2-acetyltetrahydropyridines which are among the most important volatiles to popcorn aroma. The direct extraction methods described by Schieberle (1991), although meeting the preferred factors 2 and 3 very well, require considerable time to carry out, two main steps being involved: extraction and vacuum transfer.

Two methods were adapted which try to approximate the 1–3 preferred factors, at least enough to be useful. In the first method (called the "dry method") the popcorn (contained in a 5 L flask) was "popped" in a microwave oven and volatiles were isolated using a closed loop Tenax trapping system with nitrogen as the sweep gas. An alternate method used air or nitrogen sweeping the volatiles from the flask through the trap in a continual flow, discarding the effluent gas. This method gave similar results to the closed loop method with no significant observed loss of compounds such as the sensitive 2-acetyl nitrogen heterocyclic compounds when using air. The reason for choosing a 5 L flask, with the dry method, was based on calculations of the volume of steam generated (ca. 4 L) from the moisture (ca. 10%) in 25 g of corn kernels and also the space limitations of a conventional large microwave oven.

With the second method (called the "wet method") the popped corn was blended with water containing added sodium chloride and sodium carbonate. The volatiles were isolated using a sweep gas to transfer them to the Tenax trap in an open-ended system (discarding effluent gas). A similar method had been described previously (Buttery et al., 1994) with studies on sweet corn.

Quantitative Determination. Concentrations of components were determined based on three internal standards which were different for the two methods of isolation. In the case of the dry method the internal standards 2-pentanone, 6-methyl-5-hepten-2-one, and 4-phenyl-2-butanone were used. With the wet method the internal standards were 2-pentanone, 3,5-dimethylpyridine, and quinoline. The standards were chosen based on their stability and recovery under the particular isolation conditions used and also on their retention time positions, i.e., that they did not overlap seriously with important popcorn components.

Recovery factors for components relative to the internal standards were determined using test solutions of the identified components dissolved in water. With the wet method recovery factors for many of the components had been reported previously (Buttery et al., 1994) in studies on sweet corn volatiles. The dry method presented a problem in that the standards could not be added in a homogeneous mixture. Several

methods were tried. A method finally adopted was to add 1 mL of a water solution of the standards to two precleaned laboratory tissue "wipes". The cellulose of the tissue provided a substrate, chemically related to the starch and fiber of the popcorn. The 1 mL of standards was added to the tissue, which was immediately dropped into the flask just before attaching the isolation head. Recovery factors were determined by adding similar tissue "wipes" containing 1 mL of the test solution. Recovery factors found using the dry method included the following: 3-methylbutanal, 58%; 2,3-pentadione, 96%; hexanal, 67%; furfural, 70%; methional, 24%; 2,5-dimethylpyrazine, 90%; 2-acetyl-1-pyrroline, 63%; phenylacetaldehyde, 100%; 2-acetyltetrahydropyridine, 49%; Furaneol, 2.0%; 2-ethyl-3,6-dimethylpyrazine, 90%; 4-vinylguaiacol, 82%; nonanal, 80%; (*E,E*)-2,4-decadienal, 71%; *N*-furfurylpyrrole, 76%; hexanoic acid, 25%; nonanoic acid, 39%. Other factors of related compounds were similar. Although only a 2% recovery factor was found for Furaneol, this was sufficient considering the concentration of Furaneol is much higher than most components. Such recovery factors are, of course, dependent on the particular conditions of each system and operator.

The wet method was chosen to use moderately alkaline conditions (pH 9.8) to facilitate the isolation of the important popcorn aroma, nitrogen heterocyclic compounds such as 2-acetyl-1-pyrroline, 2-propionyl-1-pyrroline, and the two forms of 2-acetyltetrahydropyridine. This method, though, does not fit the preferred factor 2 in that it is not very comprehensive. Furaneol and other sugar degradation products give no detectable recovery. Alkaline conditions also prevent acid recovery and reduce aldehyde recovery. Studies were also carried out at closely neutral conditions (pH 7.4) by substituting NaHCO₃ instead of Na₂CO₃. Qualitatively and quantitatively the analysis at pH 7.4 was very similar to that at the more alkaline conditions.

It can be noticed in Table 1 that the concentrations of many of the polar compounds are many times higher using the wet method. The reason for this may be that the compounds are bound in some way by adsorption in the dry popcorn and are displaced by the addition of water. This property has been observed by authors with other dry foods.

The dry method is the most comprehensive, giving reasonable recoveries of most components. A difficulty with the dry method, however, was that in the analysis of the 2-acetyltetrahydropyridine tautomers, there was more interference (GC peak overlap) from other components. With the wet alkaline method the interfering compounds were not recovered leaving the 2-acetyltetrahydropyridine GC peaks sufficiently separated from other components. Routine analysis in quality control by the industry would most likely be only by GC. The peak shape of 2-acetyltetrahydropyridines on DB-Wax is rather poor, probably because of the tautomerism between the two forms which is influenced by the polar medium of the DB-Wax. The two forms are well resolved on the relatively low polar DB-1. 2-Acetyl-1-pyrroline is found in close GC retention time association with the dimethylpyrazines and ethylpyrazine on both DB-Wax and DB-1 but is better resolved on DB-1.

Sensory Studies. Odor thresholds in water solution, for most compounds, had been determined previously by the authors (cf. Buttery and Ling, 1995) in studies on other products. Others were determined during this study. These are listed in Table 2 together with the log

Table 2. Odor Thresholds of Identified Components in Water Solution and Calculated log Concentration/Threshold Values Based on Concentrations Found Using the "Dry Method"^a

compound ^b	odor threshold (nL/L, ppb) ^c	log conctn/threshold
3-methylbutanal	0.2	3.3
2-furfurylthiol	0.006	<2.9
2-methylpropanal	1	2.8
acetaldehyde	15	2.5
dimethyl trisulfide	0.01	2.5
dimethyl sulfide	0.3	2.4
(<i>E,E</i>)-2,4-decadienal	0.07	2.4
2-acetyltetrahydropyridines	2	2.3
2-methylbutanal	3	2.3
4-vinyl-2-methoxyphenol	3	2.2
2-ethyl-3,5-dimethylpyrazine	0.04	2.2
2-acetyl-1-pyrroline	0.1	2.1
1-octen-3-one	0.05	2.0
2-propionyl-1-pyrroline	0.1 ^d	2.0
2-methoxy-4-formylphenol (vanillin)	58	1.8
3-(methylthio)propanal (methional)	0.2	1.8
2,3-butanedione	3	1.8
β -ionone	0.03	1.8
2,5-dimethyl-4-hydroxy-3(2 <i>H</i>)-furanone	60	1.6
2-ethyl-3,6-dimethylpyrazine	8.6	1.5
hexanal	4.5	1.5
propanal	10	1.5
4-vinylphenol	10	1.4
phenylacetaldehyde	4	1.4
2-ethyl-5-methylpyrazine	100	1.4
2,3-pentadione	20	1.3
3-methylindole (skatole)	0.2	1.0
2,3,5-trimethylpyrazine	23	1.0
heptanal	3	0.7
α -ionone	0.4	0.7
pentanal	12	0.5
2-pentylfuran	6	0.5
furfural	3000	0.2
<i>N</i> -furfuryl-2-formylpyrrole	97	0.2
<i>N</i> -methyl-2-formylpyrrole	37	0.03
2-methoxyphenol	3	0.0
2,5-dimethylpyrazine	1700	-0.5
furfuryl alcohol	1900	-0.6
<i>N</i> -furfurylpyrrole	100	-0.7
2-methyl-3-hydroxypyran-4-one (maltol)	2500	-0.7
2-heptanone	140	-0.9
geranylacetone	60	-1.1
benzaldehyde	350	-1.2
2,6-dimethylpyrazine	1500	-1.3
5-methylfurfural	500	-1.4
2-vinylpyrazine	700	-1.5
hexanol	500	-1.6
2,3-dimethylpyrazine	2500	-1.8
2-ethylpyrazine	4000	-2.2
pentanol	4000	-2.5

^a This comparison would only be strictly valid for an aqueous system. ^b The odor thresholds of many other components, e.g., 2,3-butanediol, γ -butyrolactone, etc., are so high and so weak as odorants that they need not be considered for this comparison. ^c 10^{-9} L/L. ^d Estimate: Schieberle (1991) found 2-propionyl- and 2-acetyl-1-pyrrolines to have essentially the same air threshold.

concentration/threshold values. The authors note than a redetermination of the odor threshold of β -ionone in water gave a figure (0.03 nL/L) somewhat higher than that (0.007 nL/L) obtained in our laboratory more than 25 years previously. The reason for this difference is not known, although ca. 25% of the usual reliable judges seemed anosmic to even quite high levels of β -ionone. The anosmic judges were not taken into account in determining the 0.03 nL/L figure.

GC odor description studies were also carried out by sniffing the capillary GC effluent during the GC separation of the volatile isolate obtained from popcorn. No thorough AEDA method was used (cf. Schieberle, 1991),

but the evaluation was carried out at high dilution where only the most potent odorants could be detected. Recognized odor characters were found for biacetyl, 2- and 3-methylbutanal, 2,3-pentadione, hexanal, methional, 2-furfurylthiol, 2-acetyl-1-pyrroline, dimethyl trisulfide, 1-octen-3-one, 2-propionyl-1-pyrroline, 2-acetyltetrahydropyridine (two tautomer forms), Furanol, 2-ethyl-3,5-dimethylpyrazine, nonanal, 4-vinyl-2-methoxyphenol, 2,4-decadienal, 3-methylindole, and β -ionone at their correct capillary GC retention positions.

Popcorn differs from many foods in that it is a quite dry food. Assuming no added materials, it contains only a very low concentration of water (ca. 2.5%). This would not be expected to be sufficient to lower the vapor pressure of the aroma compounds by aqueous solution effects according to Raoult's law and Henry's law principles. The main effects are probably the adsorption on the predominately starch surfaces, solution effect in the 4–5% lipid present, and possible encapsulation inside. Such threshold data for wet systems as shown in Table 2 are therefore not directly applicable. However, the eating and chewing of popcorn involves saliva, and the concentrations of volatiles in the atmosphere of the mouth, and reaching the olfactory system retronasally, may be determined largely by air–water partitioning. This information (Table 2) then may give us some idea of compounds which are most important to popcorn flavor after the popcorn is chewed.

It can be seen from Table 2 that there are more than 30 compounds which have log concentration/threshold values > 0 which would be above threshold if popcorn was an aqueous system. Popcorn has some similarities to coffee and chocolate in having a large number of potent aroma compounds which must blend to give the integrated aroma and flavor perception. The effect must also be somewhat different depending on whether it is (1) the aroma perceived during popping (where hydrogen sulfide and dimethyl sulfide must also contribute); (2) the aroma of the dry popcorn; (3) the olfactory part of flavor perceived retronasally while eating the popcorn. Relatively water soluble compounds such as Furanol, 2-acetyl-1-pyrroline, and 2-acetyltetrahydropyridines would be expected to be more effective for (1) and (2).

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