Analysis of Headspace Volatiles and Sensory Characteristics of Fresh Corn Tortillas Made from Fresh Masa Dough and Spray-Dried Masa Flour

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Headspace volatiles from nitrogen-purged slurries of commercially prepared fresh tortillas, fresh masa dough, and spray-dried masa flour dough were collected onto Tenax GC. Ether-eluted concentrates were separated by fused silica capillary gas chromatography and identified by mass spectrometry (MS), retention indices (I_E), and odor quality of eluting peaks. Six pyrazines that contribute to the roasted, nutty, and green character of cooked corn products were detected in fresh masa dough, whereas 12 pyrazines were identified in dough made from spray-dried masa flour. 2-Acetyl-1-pyrroline and 2-(methylimino)-3-butanone, which contributed popcorn-like and corn chip-like aromas, respectively, were tentatively identified in spray-dried products. Descriptive sensory analysis of commercially prepared tortillas from fresh masa dough and spray-dried masa flour indicated that tortillas made from spray-dried flours exhibited stronger roasted, cooked corn flavors and aromas.

INTRODUCTION

Fresh corn tortillas have long been a staple food in the diet of Mexican-Americans, and traditionally they have been prepared in the home using fresh-made masa dough. The in-home process involved in the conversion of maize to masa dough typically involves the steeping of maize in the presence of lime (calcium hydroxide) prior to formation of the tortillas (Bressani, 1972). The alkaline process has been shown to increase the availability of niacin (Bressani et al., 1961) as well as calcium (Bedolla and Rooney, 1982; Bressani et al., 1958) while minimizing changes in essential amino acids (Bressani and Scrimshaw, 1958; Ortega et al., 1986) and fatty acids (Bressani et al., 1990) in the final product.

This time-intensive process has been a major part of the in-home duties of Latin American women for many years. Recently, the purchase of fresh tortillas from commercial establishments (tortillerias) by Latin American populations in the United States has increased in popularity (Burum, 1992). This phenomenon, attributed in part to the changing lifestyle of Mexican-Americans, requires an alternative to traditional practices if traditional foods are to be obtained outside the home. To meet the demand, corn product manufacturers have been working to develop commercial ingredients that will allow cost-effective means to increase the production of fresh tortillas while providing products that compare to those made from fresh masa dough in the home.

The processing conditions that are used to convert dried corn into masa dough result in the formation of a distinct corn flavor quality that is sometimes referred to as limed corn flavor. This masa flavor develops from the interactions of corn-contained amino acids, lipids, carbohydrates, and carotenoids when exposed to elevated pHs at moderate temperatures for extended times.

Many studies, of which only a few are cited, have been undertaken to identify the thermally generated aroma and flavor compounds resulting from interactions between amino acids, carbohydrates, and lipids in food systems (Bailey and Einig, 1989; Ho et al., 1989a,b; Huang et al., 1987; Macku and Shibamoto, 1991a,b; Maga, 1982; Mottram and Salter, 1989; Schieberle, 1990; Seifert et al., 1970; Shibamoto, 1989; Shibamoto et al., 1979; Tressel et al., 1989; van den Ouweland et al., 1989; Whitfield, 1992). It has been well established that predictable Maillard browning products can be achieved when precursors, pH, temperature, and time conditions are controlled (Arnoldi et al., 1988; Huang et al., 1987; Koehler and Odell, 1970; Leahy and Reineccius, 1989a,b; Shibamoto and Bernhard, 1976; Wong and Bernhard, 1988). An excellent review that covers the most recent developments in Maillard reaction flavor chemistry has been prepared by Whitfield (1992).

Since the production of spray-dried masa flour requires more extensive heat processing compared to fresh-made masa doughs, it is believed that the flavor characteristics of the end products will be quite different. Therefore, this research was undertaken to assess the chemical and sensory changes that occur in fresh corn tortillas when spray-dried masa flour is used as an ingredient compared to fresh-made masa dough.

MATERIALS AND METHODS

Sample Acquisition. *Freshly Made Corn Tortillas and Spray-Dried Masa Flour.* Spray-dried masa flour and fresh tortillas made from the spray-dried masa flour were commercially prepared using typical processing procedures. Fresh-made tortillas made from masa dough were obtained from a commercial tortilleria in California. Fresh tortillas were packed in blue ice and air shipped to the University of Maryland by overnight carrier. Spray-dried masa flour was also shipped by overnight carrier, but at ambient temperatures in polyethylene bags. The ingredients for all tortillas consisted of lime-processed corn and water only with no preservatives or acids added to any of the tortilla or flour samples evaluated.

Upon arrival, fresh tortillas were held at refrigerated temperatures (4 °C) for up to 24 h until sensory analysis testing was completed. Tortillas that remained after sensory analysis testing were vacuum-packaged (Multivac A300 vacuum packager, Wolfertschwenden, Germany) in oxygen barrier pouches (3.2 oxygen

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transmission; Winpak Vak 3-4, 0.80-mil nylon/2.4-mil EVA copolymer, Holly Sales and Service, Inc., Elkridge, MD) and frozen (-20 °C) until analytical testing was undertaken. The masa flour was stored in its original polyethylene bag at refrigerated temperatures (4 °C) until analyzed.

Preparation of Fresh Masa Dough. Fresh masa dough was prepared in the laboratory at the University of Maryland to simulate traditional masa production procedures (Ortega et al., 1986). Commercial dried white corn was washed, drained, weighed, and placed in a stainless steel sauce pan with an equal amount of water (1:1 w/w) to submerge the kernels. Commercial food grade lime (calcium hydroxide) was added to the mix at an amount equal to 1% of the corn. The corn, water, and lime mixture was heated using a conventional electric stove, and the mixture was stirred semicontinuously while being heated to and held at 88 °C (±5 °C) for 45 min. After holding for 45 min at 88 °C (±5 °C), the mixture was cooled to 60 °C (±5 °C) by adding cold water and lowering the stove temperature. Water-submerged corn kernels were allowed to simmer at 60 °C (±5 °C) for 5–6 h with semicontinuous stirring during the steeping process. After steeping, the corn mixture was drained, washed, and ground in a food processor (Model KFP400, Hobart Corp., KitchenAid Division, Troy, OH) until the masa dough was formed (approximately 5–7 min). The dough was refrigerated (4 °C) in polyethylene bags (420 oxygen transmission; >99.5% polyethylene; Dowbrands, Inc., Indianapolis, IN) if the sample was analyzed within 2 days or was vacuum packaged in the same oxygen barrier pouches as used for the tortillas and frozen (-20 °C) for later use.

Analytical Procedures. *Volatile Headspace Analysis.* (*a*) *Sample Preparation.* Headspace volatiles from samples of fresh tortillas, fresh masa dough, and dough made from spray-dried masa flour were extracted using the Tenax GC trapping method outlined by Olafsdottir et al. (1985) with modifications. A weighed amount of each masa dough made from spray-dried masa flour (1:1 flour:water, 75 ± 1 g), fresh masa dough made from cooked, limed corn (nixtamalized) (75 ± 1 g), or totilla (75 ± 1 g) sample was added to 200 mL of saturated sodium chloride solution and blended for 10 s in a Waring Blendor (Dynamic Corp., New Hartford, CT). Sample slurries were poured into 500-mL round-bottom flasks to which an internal standard (ethyl heptanoate, Aldrich Chemical Co., Milwaukee, WI; 50 μL of an 830 ppm of hexane solution) was added prior to purging. Tenax GC traps were prepared by packing a pasteur pipet with 0.20 ± 0.05 g of adsorbent. After the trap was attached to a glass purge head, the assembly was fitted on top of each flask and headspace volatiles were collected and concentrated by purging agitated samples under a steady stream of nitrogen (240 mL/min) for 3.5 h at room temperature (21 °C). After samples were purged, volatiles were extracted from Tenax GC traps using approximately 0.5 mL of anhydrous diethyl ether (99% +, Aldrich Chemical Co.) and concentrated under a slow stream of nitrogen to 10–15 μL prior to gas chromatographic analysis.

(*b*) *Sample Analysis.* Concentrated ether extracts of headspace volatiles were analyzed using capillary column gas chromatography (GC) for compound quantification, packed column GC for odor assessments of peak areas, and gas chromatography in conjunction with mass spectrometry (GC-MS) for compound identification. Capillary GC separation of volatile compounds was achieved using a gas chromatograph (Hewlett-Packard Model HP 5890A Series II, Avondale, PA) equipped with a Carbowax 20M (30 m × 0.32 mm i.d., 0.25-μm film thickness) fused silica capillary column (Supelco, Inc., Bellefonte, PA) and operated with helium as the carrier gas. A program rate of 50 °C (4-min hold) to 220 °C at 4 °C/min was employed. Chromatographic data were processed with a computing integrator (Hewlett-Packard Model HP 3396A).

Ether extracts were also odor-assessed to identify qualitative characteristics of eluting peaks off a packed column. Odor assessments were achieved using a Varian 3700 gas chromatograph (Varian Associates, Palo Alto, CA) equipped with a variable effluent splitter assembly (SGE, Houston, TX) that was set at 100:1 in favor of the exit port. Packed column separations were carried out with a 3 m × 2 mm i.d. silane-deactivated glass column containing 7% Carbowax 20M on 80–100-mesh Chromosorb AW/DMCS (Alltech Associates, Deerfield, IL) using a temperature program rate of 50 °C (4-min hold) to 220 °C at 4 °C/min.

Mass spectra were obtained using a Finnigan 4500 mass spectrometer fitted with the same Carbowax 20M capillary column and using the same temperature program rate as previously described. Identification of peaks in chromatograms was achieved by matching electron impact (70 ev) mass spectral data to those published in *EPA/NIH Mass Spectral Data Base* (Heller and Milne, 1975, 1980) or those of authentic compounds. Coincidence of retention indices (I_E; Van den Dool and Kratz, 1963) of unknown compounds with authentic compounds and odor quality of peak areas were also employed for compound identification. Standard compounds were obtained from either Aldrich Chemical Co., Pyrazine Specialties, Inc. (Atlanta, GA), or Bedokian Research, Inc. (Danbury, CT) to confirm unknown identities and to establish response factors and recoveries from purged samples.

Response and recovery factors were determined for compounds identified in corn samples when commercial standards were available. Response factors were calculated from peak areas of known weights of each standard compared to that of the internal standard, ethyl heptanoate. Recovery factors were determined by comparing purged quantities of known weights of each standard to the internal standard (ethyl heptanoate) when added to 25 g of wheat flour (Gold Medal, General Mills, St. Paul, MN). Wheat flour was chosen as the carrier to minimize compound interference from corn volatiles while simulating a corn flour matrix. Purging conditions were the same as those employed for the corn samples. Concentrations were calculated from headspace volatiles, and percent recovery was determined after peak areas from a flour-only blank were subtracted. Response factors and percent recoveries were determined on a weight/weight basis.

Proximate Analysis. Fat, moisture, protein, and ash determinations were made on spray-dried masa flour, fresh masa dough, and fresh corn tortillas using AOAC testing procedures (AOAC, 1980).

Taste Panel Procedures. (*a*) *Sample Preparation.* Samples of fresh tortillas were heated on each side for 5–10 on a preheated nonstick griddle (190 ± 10 °C). After heating, tortillas were cut into six pie-shaped wedges. Three wedges were placed in three-digit randomly coded covered glass Petri dishes and placed in a warm oven (110 ± 10 °C) until presentation to the panelists. Samples were held no longer than 10 min in the warm oven.

(*b*) *Taste Panel Protocol.* Thirty-three panelists were recruited from the students, staff, and faculty at the University of Maryland—College Park in the Department of Human Nutrition and Food Systems to participate in the evaluation of corn tortillas. After being familiarized with the product and ballot, panelists were seated in individual booths equipped with standard indoor fluorescent lighting (400 lx). Once seated, panelists were presented with a tray of randomly coded warm tortilla samples, a descriptive flavor analysis ballot consisting of unmarked 7-point linear scales for each attribute (Meilgaard et al., 1987), a glass of water, and unsalted soda crackers. Panelists were asked to evaluate each sample for overall corn odor intensity, fresh corn flavor intensity, toasted corn flavor intensity, sweetness intensity, aftertaste intensity, toughness, and overall preference. Panelists were allowed to choose the order of sampling, which randomized sampling order. Ballots were decoded on a 7-point scale from 1 to 7 (Meilgaard et al., 1987), and data were analyzed using a one-way analysis of variance and least significant differences (LSD) to identify significant differences among samples (Snedecor and Cochran, 1969).

RESULTS AND DISCUSSION

The development of thermally generated volatile compounds in spray-dried masa flours and tortillas results from the interactions of corn-contained amino acids, carbohydrates, lipids, and carotenoids under elevated temperatures and alkaline conditions. Concentrations of headspace volatiles isolated from masa doughs and fresh tortillas using capillary gas chromatographic separations (Figure 1) are listed in Table I. Volatile concentrations

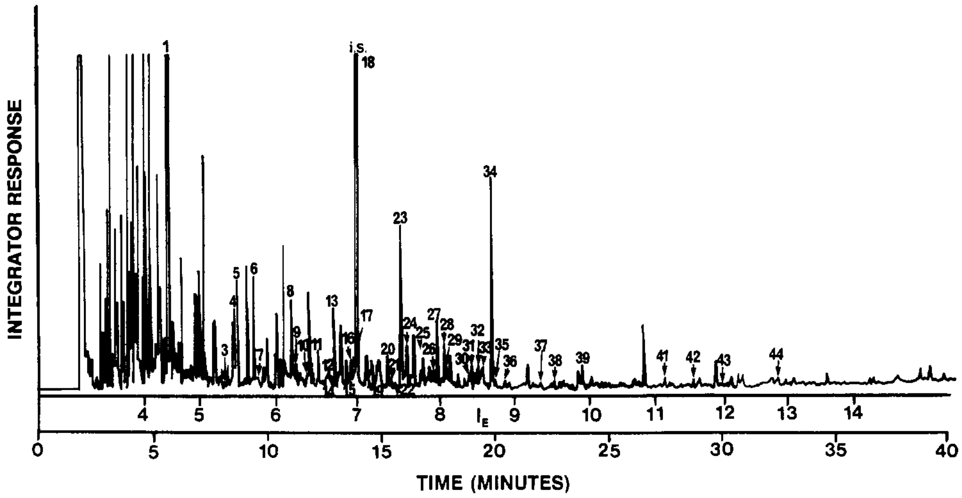

Figure 1. Gas chromatogram of headspace volatiles from masa dough made from spray-dried masa flour separated on a 30 m × 0.32 mm Carbowax 20M fused silica capillary column. The identities of numbered peaks are listed in Table I.

reported in Table I were calculated from wet sample weights; therefore, variations in moisture contents (Table II) may account for some of the small differences observed among samples (Table I).

Many of the volatile compounds isolated from the headspace of masa doughs and fresh tortillas have been previously identified in corn-based (Boyko, 1978; Bruechert et al., 1988; Ho et al., 1989b; Huang et al., 1987) and amine–carbohydrate model systems (Arnoldi et al., 1988; Baltes et al., 1989; Izzo and Ho, 1992; Koehler et al., 1969; Koehler and Odell, 1970; Salter et al., 1988; Tressel et al., 1989; van Praag et al., 1968). Concentrations of protein, carbohydrate, and lipid found in fresh masa dough, spray-dried masa dough, and fresh tortillas provide substantial quantities of the necessary precursors for the formation of volatile flavors and aromas (Table II; Bressani et al., 1990; Ranhotra, 1985; Saldana and Brown, 1984).

Masa-Making Processes That Influence Chemical Reactions. Hydrolysis of the macronutrients present in corn to form free amino acids, monosaccharides, and free fatty acids is aided by the elevated temperatures (60 ± 5 °C), pHs (9–10.5), and moderate steeping times (5–6 h) employed in the masa-making process. Although it has been suggested that washing of steeped masa results in the loss of some suspended and soluble solids (Bressani et al., 1990; Pflugfelder et al., 1988), it is likely that substantial concentrations of amino acids and monosaccharides remain in the masa to provide the necessary precursors to participate in the Maillard browning or Strecker degradation reactions (Hodge, 1953, 1967; Koehler et al., 1969; Koehler and Odell, 1970; Newell et al., 1967; Schonberg and Moubacher, 1952).

In general, moderate temperatures employed in the steeping process (60 ± 5 °C) would not be expected to produce large quantities of reaction flavor compounds (Shibamoto and Bernhard, 1977); however, temperatures greater than 100 °C have been shown to produce substantial concentrations of alkylpyrazines (Koehler and Odell, 1970; Shibamoto and Bernhard, 1976). Although it is not unusual for nonenzymic browning products to develop at low temperatures, the rate of their formation is substantially reduced (Baisier and Labuza, 1992; Leahy and Reineccius, 1989a,b; Rizzi, 1988; Shibamoto and Bernhard, 1976). As noted in Table I, concentrations of all measured volatiles were low in fresh masa dough, with many being absent from the headspace profile. By comparison, concentrations of volatiles in commercially spray-dried products were higher than those found in fresh masa products, which was reflective of the elevated temperatures employed in the various heating processes that are involved in commercial spray-drying.

The final heat treatment in the tortilla-making process occurs after the masa dough is formed into thin shells. Traditional cooking of tortilla shells employs a hot iron plate (200 °C) which is used to cook the tortillas for 2 min on each side (Ortega et al., 1986). In contrast to iron plate cooking where conductive heating predominates, industrially manufactured tortillas are oven-baked in cooking tunnels which utilize convection heating. Therefore, in addition to ingredient variations, differences in cooking techniques may also contribute to variations observed in the flavor and aroma profiles of tortilla samples (Table I).

Formation of Alkylpyrazines. Browning reactions produce many alkylpyrazines and other heterocyclic compounds that exhibit nutty, meaty, toasted, burnt, floral, and planty character notes (Table III; Maga, 1982; Masuda and Mihara, 1988; Mihara et al., 1991). Many of these aromas were observed when GC separations of masa flour and tortilla extracts were odor-assessed (Table I) and were similar to aromas reported for corn germ protein flours (Huang and Zayas, 1991).

Twelve alkylpyrazines were identified in spray-dried masa products; however, coelution, similar mass spectrometry fragment patterns, or overlapping odor characteristics made it difficult to positively identify pyrazines at retention indices of 8.14 and 8.53 (Table I). Many of the pyrazines identified had potent aroma characteristics and could be detected at low concentrations (Table III).

Many studies have shown that a number of amino acids readily react with monosaccharides to form alkylpyrazines (Rizzi, 1972; Shibamoto and Bernard, 1976; 1977; Wong and Bernard, 1988; Leahy and Reineccius, 1989a,b; Whitfield, 1992), and masa flours contain substantial amounts of these amino acid and monosaccharide precursors. Glutamic acid has been reported as the most abundant amino acid in corn protein (18%; Ortega et al., 1986; Sanderson et al., 1978). However, traditional methods of amino acid analysis that employ chemical hydrolysis of peptide bonds readily convert glutamine to glutamic acid, thus resulting in the inability to distinguish between glutamic acid and glutamine content in corn products (Mathews and van Holde, 1990). Although it is unclear as to the percent composition of glutamate and glutamine in corn proteins, either amino acid could participate in browning reactions under elevated temperature and pH conditions.

Table I. Compounds in Masa Doughs and Tortillas Made from Fresh and Spray-Dried Masa Flours

compound	peak no.	CW 20M I_{E}[a]	concn,[c] ppb				ID[b]
			fresh masa dough	tortilla made with fresh masa dough	made with spray-dried masa flour		
					dough	tortilla	
			Pyrazines				
2-methylpyrazine	9	6.20	tr[d]	34	22	183	I_{E}, MS, odor
2,5-dimethylpyrazine	13	6.71	5	8	65	62	I_{E}, MS
2,6-dimethylpyrazine	14	6.76	–[e]	13	8	18	I_{E}, MS
2-ethylpyrazine	15	6.85	tr	2	12	7	I_{E}, MS
2,3-dimethylpyrazine[f]	17	6.98	–	3	11	8	I_{E}, odor
2-ethyl-5-methylpyrazine	20	7.40	–	1	10	7	I_{E}, MS
2-ethyl-6-methylpyrazine	21	7.44	–	–	3	3	I_{E}, MS
2-methoxy-3-isopropylpyrazine[f]	26	7.95	0.6	0.4	3	3	I_{E}, odor
2-ethyl-3,6-dimethylpyrazine	27	8.00	5	1	32	13	I_{E}, MS, odor
2-ethyl-3,5-dimethylpyrazine[g]	29	8.14	–	5	18	53	I_{E}, MS,[h] odor
2-ethenyl-5-methylpyrazine	30	8.39	–	1	6	–	I_{E}, MS
2,3-diethyl-5-methylpyrazine[i]/ 3,5-diethyl-2-methylpyrazine[i]	32	8.53	4	3	7	10	I_{E}, MS, odor
			Lipid Oxidation Compounds				
hexanal	1	4.39	27	54	193	133	I_{E}, MS, odor
2-heptanone	4	5.42	29	3	6	9	I_{E}, MS
heptanal[f]	5	5.45	7	5	14	49	I_{E}, odor
trans-2-hexenal[f]	7	5.74	tr	1	tr	12	I_{E}, odor
3-octanone[j]	8	6.16	1	1	10	10	I_{E}
octanal	11	6.50	2	2	7	16	I_{E}, MS, odor
1-octen-3-one[f]	12	6.62	–	1	3	4	I_{E}, odor
2-nonanone[j]	22	7.50	4	1	1	1	I_{E}
nonanal	23	7.55	4	7	37	19	I_{E}, MS
3-octen-2-one	24	7.64	1	–	8	18	I_{E}, MS
2-octenal	25	7.85	–	2	11	6	I_{E}, MS
1-octen-3-ol[g]	29	8.14	–	tr	tr	tr	I_{E}, MS[h]
trans,trans-2,4-heptadienal	31	8.44	–	–	5	1	I_{E}, MS
decanal	33	8.61	–	5	8	5	I_{E}, MS
trans,cis-3,5-octadien-2-one	35	8.80	1	0.6	2	–	I_{E}, MS
trans-2-nonenal	36	8.89	–	2	3	4	I_{E}, MS
trans,trans-3,5-octadien-2-one	37	9.31	0.7	1	2	1	I_{E}, MS
trans,cis-2,4-decadienal	41	11.11	–	2	3	–	I_{E}, MS
trans,trans-2,4-decadienal	42	11.53	–	–	5	6	I_{E}, MS
ethyl heptanoate, internal standard (i.s.)	18	7.00	i.s.	i.s.	i.s.	i.s.	
			Protein, Carbohydrate, Carotenoid, Lipid Reaction Compounds				
3-methyl-1-butanol	6	5.65	5	8	27	73	I_{E}, MS
2-(methylimino)-3-butanone[k]	19	7.17	2	3	3	7	I_{E}, MS, odor
methional[f]	28	8.08	9	5	23	12	I_{E}, odor
benzaldehyde	34	8.67	2	5	31	13	I_{E}, MS
α-ionone[j]	43	11.94	4	–	–	–	I_{E}
β-ionone	44	12.80	–	35	24	73	I_{E}, MS, odor
			Other Nonenzymic Browning Reaction Compounds				
pyridine[f]	3	5.30	–	3	5	48	I_{E}, odor
2-ethylpyridine[f]	10	6.35	–	–	3	5	I_{E}, odor
2-acetylpyrroline	16	6.91	tr	1	8	10	I_{E}, MS, odor
2-acetylpyridine	38	9.51	–	2	8	–	I_{E}, MS

[a] Retention indices; Van den Dool and Kratz (1963); Carbowax 20M capillary column. [b] I_{E}, retention index; MS, mass spectrometry; odor, odor assessment. [c] Concentrations calculated using % recovery data (Table III). Values reflect the average of at least duplicate runs and are within 20% variation of the mean. [d] Trace amounts detected only by retention indices and odor assessment on a packed column. [e] Not detected analytically. [f] Tentative identification based on retention index and odor assessment. [g] Coelution of compounds prevents separation. [h] MS spectra contained fragment patterns from both 1-octen-3-ol and 2-ethyl-3,5-dimethylpyrazine. [i] Similar retention indices, mass spectra, and odor of 2,3-diethyl-5-methyl- and 3,5-diethyl-2-methylpyrazine made it difficult to determine the identity of the pyrazine at this location. [j] Tentative identification based on retention index of reference standard. [k] Tentative identification by retention index, mass spectrometry, and odor assessment.

In model systems where glutamate and glycine were reacted with glucose for 4 h at 120 °C, 2,5-dimethylpyrazine was preferentially formed over 40 times faster than 2,6-dimethylpyrazine when glutamate was used as the amino acid precursor (Wong and Bernhard, 1988). Concentrations of glutamic acid in corn proteins (18%; Ortega et al., 1986; Sanderson et al., 1978) could account for the presence of 2,5-dimethylpyrazine and 2,6-dimethylpyrazine under masa-making conditions. Results reported in Table I indicate that products undergoing high heat treatment show increased concentrations of 2,5- and 2,6-dimethylpyrazine.

Of the other amino acids present in corn protein, leucine is next in abundance at approximately 12% of the total amino acid profile (Ortega et al., 1986; Sanderson et al., 1978). Its role in alkylpyrazine formation has been demonstrated by Arnoldi et al. (1988), where its reaction with fructose in the presence of cocoa butter and water produced a variety of alkylpyrazines including 2-ethenyl-5-methylpyrazine which was identified in this study (Table I).

An intense earthy potato-like aroma at the retention index of 7.95 in all masa samples suggested the presence of 2-methoxy-3-isopropylpyrazine. Its low threshold concentration (0.002 ppb; Seifert et al., 1970) allowed for its aroma characterization from GC separations of extracts (Table I) even though MS identification was not achievable. Multiple collections and/or use of solvent extractions

Table II. Proximate Analysis and pH Values of Fresh Masa Dough, Fresh Tortillas, Spray-Dried Masa Dough, and Spray-Dried Tortillas

analysis	% composition[a] of fresh masa dough	 tortilla made with fresh masa	 masa dough made with spray-dried masa flour	 tortilla made with spray-dried masa flour
moisture	54.33	49.69	57.81	46.42
protein	4.90	5.70	4.60	5.60
crude lipid	2.30	2.60	2.55	3.00
ash	0.98	0.85	0.84	0.73
carbohydrate by difference	37.49	41.16	34.20	44.25
pH	9.47	6.99	6.89	7.03

[a] Values reflect mean scores of duplicate analysis and vary within ±0.15%.

would be necessary to obtain concentrations high enough for MS identification.

Although 2-methoxy-3-isopropylpyrazine has been associated with volatiles produced in vegetables (Gallois and Grimont, 1985; Seifert et al., 1970), it has not been previously identified in corn-based products. The mechanism responsible for its formation has been recently investigated by Cheng et al. (1991) using cultures of *Pseudomonas perolens* and labeled pyruvate. Enzyme-mediated reactions were shown to be responsible for the conversion of valine, glycine, and methionine to 2-methoxy-3-isopropylpyrazine.

In addition to enzyme-mediated formation, Arnoldi et al. (1988) identified three 2-methoxy-3-alkylpyrazines in model systems containing lysine, cocoa butter, and fructose that appeared to be generated from chemical reactions of precursors under elevated temperatures. Since fructose could be generated in masa products from alkali-catalyzed enolization of glucose to fructose (Speck, 1958), appropriate amino acid/carbohydrate precursors could exist in lime-processed corn products that would allow the formation of this compound. A proposed mechanism responsible for their formation was not discussed; however, these findings suggest that, in addition to enzyme-mediated reactions, chemical reactions involving the interactions of lipid, protein, and carbohydrates could contribute to the formation of 2-methoxy-3-isopropylpyrazine. Further study is necessary to confirm the possibility of chemically forming 2-methoxy-3-isopropylpyrazine under conditions that favor the formation of other browning reaction products.

The presence of methional in masa doughs and tortillas deserves attention at this time because of its aromatic property and flavor-modifying characteristics. It is well established that this Strecker aldehyde (Dunn and Lindsay, 1985; Whitfield, 1992) exhibits a strong boiled potato aroma characteristic when present in concentrations above its threshold (Schieberle, 1991; Schieberle and Grosch, 1989). It was initially believed that the strong potato aroma eluting at the retention index of 8.08 was from the residual potato aroma observed at the retention index of 7.95. However, the two potato aromas exhibited very different potato odor qualities. The compound eluting at the I_E of 7.95 was reminiscent of an earthy-potato aroma which is typical of 2-methoxy-3-isopropylpyrazine whereas the compound eluting at the I_E of 8.08 gave more of a boiled potato aroma that was characteristic of methional (Table III). Because of these odor and retention index differences, the two potato-like compounds were tentatively identified as 2-methoxy-3-isopropylpyrazine and methional.

The concentration of methional in dough made from spray-dried masa flour was above the threshold value reported by Day et al. (1958), and it was generally higher in spray-dried flours and tortillas compared to fresh-made dough products (Table I). Additionally, methional concentrations in tortillas were observed to be lower compared to their corresponding doughs (Table I). Increased concentrations in spray-dried products would be expected because of the higher heat treatment employed. The drop in methional concentration in the finished tortillas compared to the doughs would indicate that the additional heat treatment caused further degradation of the methional to lower molecular weight sulfur compounds or that methional participated in other heat-induced reactions.

From the data presented in Table I, it is observed that concentrations of most alkylpyrazines increased when fresh tortillas were evaluated compared to the fresh masa dough, but only 2-methylpyrazine and 2,6-dimethylpyrazine showed substantial increases after spray-dried flour was made into tortillas.

Increased concentrations of pyrazines in tortilla samples would suggest the development of increased roasted/toasted flavors in the finished product (Tables I and III). When warmed tortillas were evaluated by descriptive flavor analysis, spray-dried masa tortillas were rated higher in toasted corn flavor intensity (mean score of 3.35; Table IV) compared to fresh masa tortillas (mean score of 3.24; Table IV). However, mean scores were not significantly different at the 0.05 level (Table IV). This observation may be explained in part by the presence of higher concentrations of methional, which has been shown to suppress flavor and aroma (Dunn and Lindsay, 1985) and cause undesirable stale flavors when present in concentrations above its threshold (Visser and Lindsay, 1971).

Formation of Compounds Contributing Popcorn and Toasted Corn Chip Flavors. 2-Acetyl-1-pyrroline and 2-(methylimino)-3-butanone are two compounds that have been identified as contributing popcorn-like (Buttery et al., 1983; Buttery and Ling, 1982; Lin et al., 1990; Schieberle, 1991) and corn chip-like (Parliament, 1989) aromas, respectively. Strong popcorn aromas were odor-assessed at the retention index of 6.91 and corn chip-like aromas at an I_E of 7.17. Mass spectral fragment patterns at these retention indices were compared to those previously published for 2-acetyl-1-pyrroline (Lin et al., 1990) and 2-(methylimino)-3-butanone (Parliament, 1989). Ratios of mass fragments were observed to be 43 (100), 41 (54), 69 (40), 55 (36), 111 (18), 58 (17), 38 (14), 68 (10), 83 (10), and 84 (1) for the compound identified as 2-acetyl-1-pyrroline and 56 (100), 43 (72), 42 (49), 55 (46), 41 (44), 69 (23), 57 (12), 85 (8), 54 (3), 40 (3), and 99 (1) for the compound identified as 2-(methylimino)-3-butanone. Since a standard of 2-(methylimino)-3-butanone was unattainable, peak confirmation was considered to be only tentative based on the mass spectral fragment pattern and odor characteristic. Concentrations of 2-(methylimino)-3-butanone were calculated using the response factor and percent recovery determined for 2-acetyl-1-pyrroline because it was observed to be structurally similar to 2-acetyl-1-pyrroline (Parliment, 1989).

Proline is the precursor of 2-acetyl-1-pyrroline (Schieberle, 1989, 1990, 1991). Its Strecker degradation product, 1-pyrroline (Yoshikawa et al., 1965), has been shown to readily react with sugar degradation products to form 2-acetyl-1-pyrroline (Schieberle, 1989, 1990). Since proline is abundant in corn protein (8%; Ortega et al., 1986; Sanderson et al., 1978), it can play a substantial role in the formation of popcorn-like flavors and aromas in masa products.

Table III. Response Factors and Percent Recovery of Compounds in Masa Doughs and Tortillas Made from Fresh Masa Dough and Spray-Dried Masa Flour

compound	response factor[a]	% recovery[b]	threshold,[c] ppm	odor descriptor (flavor/odor)[d]
Pyrazines				
2-methylpyrazine	1.05	12	60 (2)	roasted (4, 11); nutty, green (5); grassy (2)
2,5-dimethylpyrazine	1.09	18	0.8 (3)	grassy, "cornnuts" (2); fine, roasted (4)
2,6-dimethylpyrazine	1.01	14	0.2 (3)	ether-like with corn note (2); roasted, nutty (4)
2-ethylpyrazine	1.04	34	6 (2)	green, roasted (4); buttery, rum (11)
2,3-dimethylpyrazine	1.05	15	2.5 (2)	pleasant, roasted (4); new leather, linseed oil (11)
2-ethyl-5-methylpyrazine	1.03	37		nutty (6)
2-ethyl-6-methylpyrazine	1.04	38	0.1 (3)	nutty (6); grassy (2)
2-methoxy-3-isopropylpyrazine	1.16	104	2×10^{-6} (6)	earthy (1, 5, 10, 12); potato-like (1, 12); nutty (12)
2-ethyl-3,6-dimethylpyrazine	0.81	23	4×10^{-4} (3)	potato-like (9, 10); woody, musty (13); roasted pungent (2)
2-ethyl-3,5-dimethylpyrazine	0.81	16	1×10^{-3} (3)	chocolatey sweet, woody, musty (13)
2-ethenyl-5-methylpyrazine[e]	1.04	38		
2,3-diethyl-5-methylpyrazine	0.97	50		potato-like (9)
3,5-diethyl-2-methylpyrazine[f]	0.97	50		
Lipid Oxidation Compounds				
hexanal	1.09	109	4.5×10^{-3} (1)	green (8)
2-heptanone	0.88	136	3 (1)	blue cheese (13)
heptanal[g]	1.01	61	3×10^{-3} (3)	heavy, planty green (13)
trans-2-hexenal	0.99	100	1.7×10^{-2} (3)	heavy, planty green (13)
3-octanone	0.93	118	5×10^{-2} (5)	earthy, ketonic, mushroom-like (12)
octanal[g]	1.01	61	7×10^{-4} (3)	pungent, slightly fragment (4)
1-octen-3-one[h]	0.87	80	5×10^{-6} (3)	mushroom-like (8)
2-nonanone	0.83	77	7.7 (1)	blue cheese (13)
nonanal	1.01	61	1×10^{-3} (3)	slightly pungent (4)
3-octen-2-one	0.87	80		unripe, green fruit (13)
2-octenal	0.94	48	3×10^{-3} (3)	fatty, nutty (8)
1-octen-3-ol	0.75	58	1×10^{-2} (5)	raw mushrooms (13)
trans,*trans*-2,4-heptadienal	0.95	66		hay-like (13)
decanal	0.91	56	1×10^{-4} (3)	
trans,*cis*-3,5-octadien-2-one[h]	0.87	80		hay-like, oxidized odor (13)
trans-2-nonenal	0.96	41	8×10^{-5} (3)	green, tallowy (8, 9)
trans,*trans*-3,5-octadien-2-one[h]	0.87	80		hay-like, oxidized odor (13)
trans,*cis*-2,4-decadienal	0.96	39		fatty, waxy (9)
trans,*trans*-2,4-decadienal	0.93	22	7×10^{-5} (3)	fatty, waxy (8); fatty, fried fat (9)
Protein, Carbohydrate, Carotenoid, Lipid Reaction Compounds				
3-methyl-1-butanol	1.24	45	4.75 (8)	malty (10)
2-(methylimino)-3-butanone[i]	1.10	57		corn chip-like (7)
methional	1.32	24	1.6×10^{-2} (4)	boiled potato-like (9, 10, 11); cheese cracker-like (14)
benzaldehyde	0.94	81	3×10^{-3} (1)	almond-like (13)
α-ionone	0.83	7		cedar-like, floral (13)
β ionone[j]	0.82	7	7×10^{-6} (3)	cooked carrots, floral (13)
Other Nonenzymic Browning Reaction Compounds				
pyridine	0.92	19	2 (3)	solvent-like (13)
2-ethylpyridine	0.85	50		green, planty (13)
2-acetyl-1-pyrroline	1.10	57	1×10^{-4} (7)	cracker-like (3, 10); roasty (8, 9); popcorn-like (9)
2-acetylpyridine	1.05	14	1.9×10^{-2} (3)	corn chip-like (13)

[a] Response factor calculated in comparison to ethyl heptanoate, the internal standard. [b] Percent recovery obtained by purging known concentrations of standards added to wheat flour compared to ethyl heptanoate, internal standard. [c] Threshold in water; reference indicated in parentheses: 1, Frazzalari (1978); 2, Guadagni et al. (1972); 3, Leffingwell and Leffingwell (1991); 4, threshold in milk, Day et al. (1958); 5, Pyssalo and Suihko (1976); 6, Seifert et al. (1970); 7, Schieberle and Grosch (1989); 8, Sheldon et al. (1971). [d] Descriptive odors of compounds; reference indicated in parentheses: 1, Gallois and Grimont (1985); 2, Boyko (1978); 3, Buttery et al. (1983); 4, Jayalekshmy et al. (1991); 5, Masuda and Mihara (1988); 6, Mihara et al. (1991); 7, Parliment (1989); 8, Schieberle (1989); 9, Schieberle (1991); 10, Schieberle (1990); 11, Schieberle and Grosch (1989); 12, Karahadian et al. (1985); 13, odor of standard as described by the authors; 14, Day et al. (1958). [e] Response factor and % recovery of 2-ethyl-5-methylpyrazine used due to similarity of structure. [f] Response factor and % recovery of 2,3-diethyl-5-methylpyrazine used due to similarity of structure. [g] Response factor and % recovery of nonanal used due to similarity of structure. [h] Response factor and % recovery of 3-octen-2-one used due to similarity of structure. [i] Response factor and % recovery of 2-acetyl-1-pyrroline used due to similarity of structure (Parliment 1989). [j] Percent recovery of α-ionone used because of coelution with peaks in flour-only blank.

Although concentrations of both 2-(methylimino)-3-butanone and 2-acetyl-1-pyrroline were found in highest concentrations in spray-dried masa tortillas, measurable concentrations in other masa products suggest that they may be able to form at lower temperatures if conditions such as elevated pH exist (Table I).

When fresh corn flavor intensities were evaluated by taste panelists, fresh masa tortillas exhibited a fresher corn flavor intensity compared to the spray-dried tortillas (Table IV); however, mean scores were not significantly different at the 0.05 level. When asked to describe the corn flavor of each sample, 45% of the panelists responded that the corn flavor was corn chip-like in the spray-dried sample, whereas only 24% described the fresh tortillas as having a corn chip-like character. Although concentrations of these corn-contributing compounds were slightly higher in spray-dried tortillas (Table IV), it may be possible that their contribution to roasted corn flavor was modified by other compounds in the matrix.

Formation of Lipid Oxidation Products. In addition to browning reaction products, compounds resulting from the oxidation of lipids contribute to the flavors and aromas of food. Typically, lipid oxidation products that are odor/flavor-active are short-chain carbonyl compounds (aldehydes and ketones) and acids (Grosch, 1987; Whitfield, 1992). Many of the degradation compounds formed in

Table IV. Comparative Descriptive Sensory Properties of Corn Tortillas Made from Fresh Masa Dough and Spray-Dried Masa Flour

	sensory attributes (mean scores, n = 33)[a]						
sample description	overall corn odor intensity[b]	fresh corn flavor intensity[b]	toasted corn flavor intensity[b]	sweetness intensity[b]	aftertaste intensity[b]	toughness[c]	overall preference[d]
tortillas made with fresh masa dough	4.33[a]	3.55[a]	3.24[a]	2.93[a]	3.41[a]	3.94[a]	3.79[a]
tortillas made with spray-dried masa flour	3.91[a]	3.28[a]	3.35[a]	2.71[a]	3.76[a]	3.79[a]	3.44[a]
LSD	NS	NS	NS	NS	NS	NS	NS

[a] Mean scores in the same column with the same superscripts are not significantly different ($p < 0.05$). [b] Scale 1 = imperceptible; 7 = very pronounced. [c] Scale: 1 = not tough; 7 = extremely tough. [d] Scale: 1 = dislike extremely; 7 = like extremely.

oxidizing corn products are derived from the oxidation of oleic, linoleic, and small amounts of linolenic acids which are found in corn oils (Snyder et al., 1985) and corn tortillas (Bressani et al., 1990). Consequently, saturated and unsaturated 6-, 8-, 9-, and 10-carbon compounds that would be expected in the volatile headspace profile were observed in this study (Table I). In general, higher concentrations of lipid oxidation products were observed in spray-dried masa products than in products that were made from fresh masa doughs and total volatile concentrations of compounds derived from lipid degradations were lowest in fresh masa doughs (Table I).

It is interesting to note that, in spite of the relatively high concentration of lipids present in masa products (Table II), low concentrations of volatile oxidation compounds were observed in all samples as compared to volatiles produced from oxidizing corn oils (Table I; Snyder et al., 1985). This observation has been made in previous studies where model systems containing lipids, protein, and carbohydrate were allowed to react at elevated temperatures (Ho et al., 1989a,b; Huang et al., 1987; Macku and Shibamoto, 1991a,b).

Various explanations have been proposed to account for this occurrence. α,β-Unsaturated aldehydes produced from lipid oxidations have been shown to undergo retroaldol degradation under elevated temperatures and alkaline conditions (Josephson and Glinka, 1989; Josephson and Lindsay, 1987a,b). Because concentrations of 2,4-decadienal are much lower than would be expected in oxidizing corn oil systems (Snyder et al., 1985), it is possible that the alkaline conditions employed in the masa-making process could encourage the retroaldol degradation of 2,4-decadienal to hexanal and 2-octenal (Josephson and Glinka, 1989; Josephson and Lindsay, 1987a,b). Both 2-octenal and hexanal were produced in masa products, with hexanal showing the highest concentration of all aldehyde oxidation products (Table I). However, hexanal should not be used as the primary indicator of retroaldol reactions because it is also formed from hydroperoxide degradation at the $n - 6$ carbon of linoleic acid.

Bruechert et al. (1988) proposed another explanation for the observed low concentrations of 2,4-decadienal in lipid-containing model systems. They proposed that under elevated temperatures, 2,4-decadienal can undergo cyclization to form benzaldehyde. In this study, benzaldehyde was identified in all samples; however, if substantial concentrations were converted from 2,4-decadienal, one would expect much higher concentrations compared to those observed (Table I).

In addition to retroaldol and cyclization reactions, some of these lipid oxidation products have been shown to react with proteins to form long-chain substituted heterocyclic ring compounds (Bruechert et al., 1988; Chiu et al., 1990; Ho et al., 1989a,b; Huang et al., 1987; Macku and Shibamoto, 1991a,b). It would seem likely that long-chain alkyl-substituted pyrazines would form during spray-drying of masa flours because of the presence of oxidizing lipids (Ho et al., 1989a,b); however, none of these compounds were detected in this study or that of Salter et al. (1988). Studies that successfully isolated and identified these pyrazines employed distillation instead of headspace techniques, which could account for this observation.

Compounds Derived from Carotenoid Oxidations. In addition to unsaturated lipids, other unsaturated compounds such as carotenoids can also undergo oxidation and cleavage to form volatile flavor and aroma compounds. β-Ionone, which exhibits cooked vegetable, floral-like aromas (Table III), results from the oxidation and subsequent cleavage of β-carotene (Ho et al., 1989a; Onyewu et al., 1989). Although many isomers exist, β-ionone is the most predominant isomer produced from β-carotene. Processing conditions as well as exposure to air during storage will result in the formation of this and other ionone compounds. The trends observed for other heat-induced compounds are similar for concentrations of β-ionone in samples of masa flours (Table I). Although concentrations of α-ionone were not measurable in tortillas made with spray-dried flour, a variety of floral and cooked vegetable aromas were observed from odor assessments of sample extracts.

Results from this study have shown that spray-dried masa flour contains higher concentrations of characterizing volatiles as compared to fresh masa dough, which is also generally observed for the fresh tortillas made from these ingredients. Although concentrations of volatiles in masa flours seem to reflect differences in processing parameters, no significant differences were observed in the sensory attributes tested for each tortilla. However, trends were observed in sensory analysis data that indicated tortillas made with spray-dried masa flour had less intense fresh corn aroma and flavor qualities and a more pronounced toasted corn flavor quality. Panelists showed no significant difference in preference for any of the tortilla samples tested (Table IV); however, the small sample size employed in this study can only provide directional information in the evaluation of product preference. More importantly, if producers of fresh tortillas are targeting a specific ethnic population, product preference testing using a large sample size of target consumers needs to be undertaken because even small differences observed in attributes may be perceived as unacceptable to those who are used to the traditional product.

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LITERATURE CITED

AOAC. *Official Methods Analysis*, 13th ed.; Association of Analytical Chemists: Washington, DC, 1980.

Arnoldi, A.; Arnoldi, C.; Baldi, O.; Griffini, A. Flavor components in the Maillard reaction of different amino acids with fructose in cocoa butter-water. Qualitative and quantitative analysis of pyrazines. *J. Agric. Food Chem.* **1988**, *36*, 988–992.

Bailey, M. E.; Einig, R. G. Reaction flavors in meat. In *Thermal Generation of Aromas*; Parliment, T. H., McGorrin, R. J., Ho, C.-T., Eds.; American Chemical Society: Washington, DC, 1989; pp 421–432.

Baisier, W. M.; Labuza, T. P. Maillard browning kinetics in a liquid model system. *J. Agric. Food Chem.* **1992**, *40*, 707–713.

Baltes, W.; Kunert-Kirchhoff, J.; Reese, G. Model reactions on generation of thermal aroma compounds. In *Thermal Generation of Aromas*; Parliment, T. H., McGorrin, R. J., Ho, C.-T., Eds.; American Chemical Society: Washington, DC, 1989; pp 143–155.

Bedolla, S.; Rooney, L. W. Cooking maize for masa production. *Cereal Foods World* **1982**, *27*, 219–221.

Boyko, A. L. Porous polymer trapping for GC/MS analysis of volatile flavor compounds in corn. Ph.D. thesis, Oregon State University, 1978.

Bressani, R. The importance of maize for human nutrition in Latin America and other countries. In *Nutritional Improvement of Maize*; Bressani, R., Braham, J. E., Behar, M., Eds.; INCAP: Guatemala City, Guatemala, 1972; pp 5–29.

Bressani, R.; Scrimshaw, N. S. Lime-heat effects on corn nutrients. Effect of lime treatment on *in vitro* availability of essential amino acids and solubility of protein fractions in corn. *J. Agric. Food Chem.* **1958**, *6*, 774–778.

Bressani, R.; Paz, Y.; Paz, R.; Scrimshaw, N. S. Corn nutrient losses. Chemical changes in corn during preparation of tortillas. *J. Agric. Food Chem.* **1958**, *6*, 770–774.

Bressani, R.; Gomez-Brenes, R.; Scrimshaw, N. S. Effect of processing on distribution and *in vitro* availability of niacin of corn (*Zea mays*). *Food Technol.* **1961**, *15*, 450–454.

Bressani, R.; Benavides, V.; Acevedo, E.; Ortiz, M. A. Changes in selected nutrient contents and in protein quality of common and quality-protein maize during rural tortilla preparation. *Cereal Chem.* **1990**, *67* (6), 515–158.

Bruechert, L. J.; Zhang, Y.; Huang, T. C.; Hartman, T. G.; Rosen, R. T.; Ho, C.-T. Contribution of lipids to volatiles generated in extruded corn-based model systems. *J. Food Sci.* **1988**, *53*, 1444–1447.

Burum, L. Masa central. *Los Angeles Times* **1992**, July 9, H29.

Buttery, R. G.; Ling, L. C. 2-Acetyl-1-pyrroline: an important component of cooked rice. *Chem. Ind.* **1982**, 958–959.

Buttery, R. G.; Ling, L. C.; Juliano, B. O.; Turnbaugh, J. G. Cooked rice aroma and 2-acetyl-1-pyrroline. *J. Agric. Food Chem.* **1983**, *31*, 823–826.

Cheng, T.-B.; Reineccius, G. A.; Bjorklund, J. A.; Leete, E. Biosynthesis of 2-methoxy-3-isopropylpyrazine in *Pseudomonas perolens*. *J. Agric. Food Chem.* **1991**, *39*, 1009–1012.

Chiu, E.-M.; Kuo, M.-C.; Bruechert, L. J.; Ho, C.-T. Substitution of pyrazines by aldehydes in model systems. *J. Agric. Food Chem.* **1990**, *38*, 58–61.

Day, E. A.; Keeney, M.; Stahl, W. H. The role of methional as a flavor compound. *Food Res.* **1958**, *23*, 130–132.

Dunn, H. C.; Lindsay, R. C. Evaluation of the role of microbial Strecker-derived aroma compounds in unclean-type flavors of cheddar cheese. *J. Dairy Sci.* **1985**, *68*, 2859–2874.

Frazzalari, F. A. *Compilations of Odor and Taste Threshold Value Data*; American Society for Testing and Materials: Philadelphia, PA, 1978.

Gallois, A.; Grimont, P. A. D. Pyrazines responsible for potato-like odor produced by some *Serratia* and *Cedecea* strains. *Appl. Environ. Microbiol.* **1985**, *50*, 1048–1053.

Grosch, W. Reaction of hydroperoxides—products of low molecular weight. In *Autoxidation of Unsaturated Lipids*; Chan, H. W. S., Ed.; Academic Press: London, 1987.

Guadagni, D. G.; Buttery, R. G.; Turnbough, T. G. Odour thresholds and similarity ratings of some potato chip components. *J. Sci. Food Agric.* **1972**, *23*, 1435–1444.

Heller, S. R.; Milne, G. W. A. *EPA/NIH mass spectral data base*; U.S. Government Printing Office: Washington, DC, 1975; Vol. 1–4.

Heller, S. R.; Milne, G. W. A. *EPA/NIH mass spectral data base*; U.S. Government Printing Office; Washington, DC, 1980; Suppl. 1.

Ho, C.-T.; Bruechert, L. J.; Zhang, Y.; Chiu, E.-M. Contribution of lipids to the formation of heterocyclic compounds in model systems. In *Thermal Generation of Aromas*; Parliment, T. H., McGorrin, R. J., Ho, C.-T., Eds.; American Chemical Society: Washington, DC, 1989a; pp 105–113.

Ho, C.-T.; Bruechert, L. J.; Kuo, M.-C.; Izzo, M. T. Formation of volatile compounds from extruded corn-based model systems. In *Thermal Generation of Aromas*; Parliment, T. H., McGorrin, R. J., Ho, C.-T., Eds.; American Chemical Society: Washington, DC, 1989b; pp 504–511.

Hodge, J. E. Dehydrated foods, Chemistry of browning reactions in model systems. *J. Agric. Food Chem.* **1953**, *1*, 928–943.

Hodge, J. E. Origin of flavors in foods, nonenzymatic browning reactions. In *Symposium of Foods: The Chemistry and Physiology of Flavors*; Schultz, H. W., Day, E. A., Libbey, L. M., Eds.; AVI Publishing: Westport, CT, 1967; pp 465–491.

Huang, C. J.; Zayas, J. F. Aroma quality of corn germ protein flours determined by sensory and gas chromatographic profiles. *J. Food Qual.* **1991**, *14* (5), 377–390.

Huang, T.-C.; Bruechert, L. J.; Hartman, T. G.; Rosen, R. T.; Ho, C.-T. Effect of lipids and carbohydrates on thermal generation of volatiles from commercial zein. *J. Agric. Food Chem.* **1987**, *35*, 985–990.

Izzo, H. V.; Ho, C.-T. Ammonia affects Maillard chemistry of an extruded autolyzed yeast extract: pyrazine aroma generation and brown color formation. *J. Food Sci.* **1992**, *57* (3), 657–659, 674.

Jayalekshmy, A.; Narayanan, C. S.; Mathew, A. G. Identification of volatile flavor compounds in roasted coconut. *J. Am. Oil Chem. Soc.* **1991**, *68*, 873–880.

Josephson, D. B.; Glinka, J. Formation of influential flavor components through water-mediated retro-aldol conversions of alpha, beta-unsaturated carbonyls. In *Thermal Generation of Aromas*; Parliment, T. H., McGorrin, R. J., Ho, C.-T., Eds.; American Chemical Society: Washington, DC, 1989; pp 242–246.

Josephson, D. B.; Lindsay, R. C. Retro-aldol related degradations of 2,4-decadienal in the development of staling flavors in fried foods. *J. Food Sci.* **1987a**, *52*, 1186–1190, 1218.

Josephson, D. B.; Lindsay, R. C. Retro-aldol related degradations of unsaturated aldehydes: role in the formation of *c*-4-heptenal from *t*-2, *c*-6-nonadienal in fish, oyster, and other flavors. *J. Am. Oil Chem. Soc.* **1987b**, *64*, 132–138.

Karahadian, C.; Josephson, D. B.; Lindsay, R. C. Volatile compounds from *Penicillium sp.* contributing musty-earthy notes to Brie and Camembert cheese flavors. *J. Agric. Food Chem.* **1985**, *33*, 339–343.

Koehler, P. E.; Odell, G. V. Factors affecting the formation of pyrazine compounds in sugar-amine reactions. *J. Agric. Food Chem.* **1970**, *18*, 895–898.

Koehler, P. E.; Mason, M. E.; Newell, J. A. Formation of pyrazine compounds in sugar-amino acid model systems. *J. Agric. Food Chem.* **1969**, *17*, 393–396.

Leahy, M. M.; Reineccius, G. A. Kinetics of formation of alkylpyrazines. Effect of type of amino acid and type of sugar. In *Flavor Chemistry*; Advances in Chemistry Series 388; American Chemical Society: Washington, DC, 1989a; pp 76–91.

Leahy, M. M.; Reineccius, G. A. Kinetics of the formation of alkylpyrazines. Effect of pH and water activity. In *Thermal Generation of Aromas*; Parliment, T. H., McGorrin, R. J., Ho, C.-T., Eds.; American Chemical Society: Washington, DC, 1989b; pp 176–208.

Leffingwell, J. C.; Leffingwell, D. GRAS flavor chemicals-detection thresholds. *Perfum. Flavor* **1991**, *16*, 2–19.

Lin, C. F.; Hsieh, T. C.-Y.; Hoff, B. J. Identification and quantification of the "popcorn"-like aroma in Lousiana aromatic della rice (*Oryza sativa*, L.). *J. Food Sci.* **1990**, *55*, 1466–1467, 1469.

Macku, C.; Shibamoto, T. Headspace volatile compounds formed from heated corn oil and corn oil with glycine. *J. Agric. Food Chem.* **1991a**, *39*, 1265–1269.

Macku, C.; Shibamoto, T. Volatile sulfur-containing compounds generated from the thermal interaction of corn oil and cysteine. *J. Agric. Food Chem.* **1991b**, *39*, 1987–1989.

Maga, J. A. Pyrazines in flavour. In *Food Flavours, Part A. Introduction*; Morton, I. D., Macleod, A. J., Eds.; Elsevier Scientific: Amsterdam, 1982; pp 283–323.

Masuda, H.; Mihara, S. Olfactive properties of alkylpyrazines and 3-substituted 2-alkylpyrazines. *J. Agric. Food Chem.* **1988**, *36*, 584–587.

Mathews, C. K.; van Holde, K. E. *Biochemistry*; Benjamin/Cummings Publishing: Redwood City, CA, 1990; Chapter 5.

Meilgaard, M.; Civille, G. V.; Carr, B. T. *Sensory evaluation techniques*; CRC Press: Boca Raton, FL, 1987; Vol. II.

Mihara, S.; Masuda, H.; Tateba, H.; Tuda, T. Olfactive properties of 3-substituted 5-alkyl-2-methylpyrazines. *J. Agric. Food Chem.* **1991**, *39*, 1262–1264.

Mottram, D. S.; Salter, L. J. Flavor formation in meat-related Maillard systems containing phospholipids. In *Thermal Generation of Aromas*; Parliment, T. H., McGorrin, R. J., Ho, C.-T., Eds.; American Chemical Society: Washington, DC, 1989; pp 442–451.

Newell, J. A.; Mason, M. E.; Matlock, R. S. Precursors of typical and atypical roasted peanut flavor. *J. Agric. Food Chem.* **1967**, *15*, 767–772.

Olafsdottir, G.; Steinke, J. A.; Lindsay, R. C. Quantitative performance of a simple Tenax-GC^R adsorption method for use in the analysis of aroma volatiles. *J. Food Sci.* **1985**, *50*, 1431–1437.

Onyewu, P. N.; Daun, H.; Ho, C.-T. Volatile thermal decomposition products of beta-carotene. In *Thermal Generation of Aromas*; Parliment, T. H., McGorrin, R. J., Ho, C.-T., Eds.; American Chemical Society: Washington, DC, 1989; pp 247–256.

Ortega, E. I.; Villegas, E.; Vasal, S. K. A comparative study of protein changes in normal and quality protein maize during tortilla making. *Cereal Chem.* **1986**, *63*, 446–451.

Parliment, T. H. Characterization of a compound with an intense corn chip/cereal aroma. In *Flavors and Off-Flavors '89*; Charalambous, G., Ed.; Elsevier Science: Amsterdam, 1989; pp 299–304.

Pflugfelder, R. L.; Rooney, L. W.; Waniska, R. D. Dry matter losses in commercial corn masa production. *Cereal Chem.* **1988**, *65*, 127–132.

Pyysalo, H.; Suihko, M. Odor characterization and threshold values of some volatile compounds in fresh mushrooms. *Lebensm. Wiss. Technol.* **1976**, *9*, 371–373.

Ranhotra, G. S. Nutritional profile of corn and flour tortillas. *Cereal Foods World* **1985**, *30*, 703–704.

Rizzi, G. P. A mechanistic study of alkylpyrazine formation in model systems. *J. Agric. Food Chem.* **1972**, *20*, 1081–1085.

Rizzi, G. P. Formation of pyrazines from acyloin precursors under mild conditions. *J. Agric. Food Chem.* **1988**, *36*, 349–352.

Saldana, G.; Brown, H. E. Nutritional composition of corn and flour tortillas. *J. Food Sci.* **1984**, *49*, 1202–1203.

Salter, L. J.; Mottram, D. S.; Whitfield, F. B. Volatile compounds produced in Maillard reactions involving glycine, ribose and phospholipid. *J. Sci. Food Agric.* **1988**, *46*, 227–242.

Sanderson, J.; Wall, J. S.; Donaldson, G. L.; Cavins, J. F. Effect of alkaline processing of corn on its amino acids. *Cereal Chem.* **1978**, *55*, 204–213.

Schieberle, P. Formation of 2-acetylpyrroline and other important flavor compounds in wheat bread crust. In *Thermal Generation of Aromas*; Parliment, T. H., McGorrin, R. J., Ho, C.-T., Eds.; American Chemical Society: Washington, DC, 1989; pp 268–275.

Schieberle, P. Studies on bakers yeast as source of maillard-type bread flavor compounds. In *The Maillard Reaction in Food Processing, Human Nutrition and Physiology*; Finot, P. A., Aeschbacher, H. U., Hurrell, R. F., Liardon, R., Eds.; Birkhauser Verlag: Basel 1990; pp 187–196.

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

Schieberle, P.; Grosch, W. Bread Flavor. In *Thermal Generation of Aromas*; Parliment, T. H., McGorrin, R. J., Ho, C.-T., Eds.; American Chemical Society: Washington, DC, 1989; pp 258–267.

Schonberg, A.; Moubacher, R. The Strecker degradation of alpha-amino acids. *Chem. Rev.* **1952**, *50*, 261–276.

Seifert, R. M.; Buttery, R. G.; Guadagni, D. G.; Black, D. R.; Harris, J. G. Synthesis of some 2-methoxy-3-alkylpyrazines with strong bell pepper-like odors. *J. Agric. Food Chem.* **1970**, *18*, 246–249.

Sheldon, M. R.; Lindsay, R. C.; Libbey, M. L.; Morgan, M. E. Chemical nature of malty flavor and aroma produced by *Streptococcus lactis var. maltigenes*. *Appl. Microbiol.* **1971**, *22* (3), 263–266.

Shibamoto, T. Volatile flavor chemicals formed by the Maillard reaction. In *Thermal Generation of Aromas*; Parliment, T. H., McGorrin, R. J., Ho, C.-T., Eds.; American Chemical Society: Washington, DC, 1989; pp 134–142.

Shibamoto, T.; Bernhard, R. A. Effect of time, temperature, and reactant ratio on pyrazine formation in model systems. *J. Agric. Food Chem.* **1976**, *24*, 847–852.

Shibamoto, T.; Bernard, R. A. Investigation of pyrazine formation pathways in sugar-ammonia model systems. *J. Agric. Food Chem.* **1977**, *25*, 609–614.

Shibamoto, T.; Akiyama, T.; Sakaguchi, M.; Enomoto, Y.; Masuda, H. A study of pyrazine formation. *J. Agric. Food Chem.* **1979**, *27*, 1027–1031.

Snedecor, G. W.; Cochran, W. A. *Statistical methods*; Iowa State University Press: Ames, IA, 1969.

Snyder, J. M.; Frankel, E. N.; Selke, E. Capillary gas chromatographic analyses of headspace volatiles from vegetable oils. *J. Am. Oil Chem. Soc.* **1985**, *62*, 1675–1679.

Speck, J. C. The Lobry de Bruyn-Alberda van Ekenstein transformation. In *Advances in Carbohydrate Chemistry*; Academic Press: New York, 1958; pp 63–103.

Tressel, R.; Helak, B.; Martin, N.; Kersten, E. Formation of amino acid specific Maillard products and their contribution to thermally generated aromas. In *Thermal Generation of Aromas*; Parliment, T. H., McGorrin, R. J., Ho, C.-T., Eds.; American Chemical Society: Washington, DC, 1989; pp 156–171.

Van den Dool, H.; Kratz, P. D. A generalization of the retention index system including linear temperature programmed gas-liquid partition chromatography. *J. Chromatogr.* **1963**, *11*, 463–471.

van den Ouweland, G. A. M.; Demole, E. P.; Enggist, P. Process meat flavor development and the Maillard reaction. In *Thermal Generation of Aromas*; Parliment, T. H., McGorrin, R. J., Ho, C.-T., Eds.; American Chemical Society: Washington, DC, 1989; pp 433–441.

van Praag, M.; Stein, H. S.; Tibbetts, M. S. Steam volatile aroma constituents of roasted cocoa beans. *J. Agric. Food Chem.* **1968**, *16*, 1005–1008.

Visser, M. K.; Lindsay, R. C. Role of methional in the development of off-flavors in beer. *Proc. Am. Soc. Brew. Chem.* **1971**, 230–237.

Whitfield, F. B. Volatiles from the interactions of Maillard reactions and lipids. *Crit. Rev. Food Sci. Nutr.* **1992**, *31* (1/2), 1–58.

Wong, J. M.; Bernhard, R. A. Effect of nitrogen source on pyrazine formation. *J. Agric. Food Chem.* **1988**, *36*, 123–129.

Yoshikawa, K.; Libbey, L. M.; Cobb, W. Y.; Day, E. A. 1-Pyrroline: the odor component of Strecker-degraded proline and ornithine. *J. Food Sci.* **1965**, *30*, 991–994.

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