Aroma Volatiles Generated during Extrusion Cooking of Maize Flour

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Volatile components in maize flour, extruded under different conditions obtained by varying product temperature (120, 150, or 180 °C), moisture level (14, 18, or 22%), and residence time (35 or 60 s), were identified and evaluated by gas chromatography/mass spectrometry (GC/MS) and GC olfactometry (GCO). Eighty compounds were identified in the headspace collections of the extrudates. Increasing the product temperature, reducing the moisture level, or prolonging the residence times generally increased the numbers and quantities of Maillard-derived compounds, such as pyrazines, pyrroles, furans, and sulfur-containing heterocycles. In low-temperature (120 °C) and high-moisture (22%) extrusions, the main volatiles were compounds associated with lipid degradation, with few compounds derived from the Maillard reaction. Increasing the temperature and reducing the moisture level to 18% gave rise to the formation of some pyrazines and thiophenones. A marked increase in quantities of 2-furfural, 2-furanmethanol, and alkylpyrazines occurred in the extrusions at 180 °C and 14% moisture level. Under these conditions, other nitrogen- and sulfur-containing heterocyclic compounds were also generated. GCO assessments identified 2-acetyl-1-pyrroline and 2-acetylthiazole as compounds that contributed to cereal-like odors of the extrudates. Some other sulfur-containing compounds were also believed to be involved in the aroma of extrudates processed at 180 °C and 14% moisture level.

Keywords: *Cereal; maize; extrusion processing; aroma; volatiles; Maillard reaction*

INTRODUCTION

Flavor generation during the extrusion cooking of cereals involves thermally induced reactions, such as the Maillard reaction and degradation of lipids and vitamins. In addition to flavor generation, which forms an important quality aspect of cereals, the extrusion process provides a means of forming, shaping, and texturizing cereal products. In comparison to traditional cereal baking and toasting, extrusion cooking has been regarded as inferior in relation to development of desirable cooked flavor (Maga, 1989). Factors that favor the formation of flavor in extrusion processing are the high temperature, high pressure, and a relatively low moisture level. Compared to traditional cereal baking, water is not lost until the product emerges from the extruder, and this may be less favorable for flavor generation. The short residence time (RT), typically ranging from 5 to 120 s, may also be a factor that limits the flavor forming reactions (Linko and Mercier, 1981). In addition, losses of flavor compounds from the melt leaving the die may contribute to the poor flavor of cereals from the extrusion process (Sadafian and Crouzet, 1987; Nair et al., 1994).

In the analysis of volatile compounds produced in the extrusion of ground and milled malt (Fors and Eriksson,

1986) and potato flakes (Maga and Sizer, 1979), emphasis was given to the effects of temperature, moisture, and time on the yield of pyrazines. This class of compounds was suggested to be important for the toasted and nutty extrudate flavor. Pyrazine formation increased with higher temperature, lower moisture level, and longer RT. More recent investigations reported on other classes of volatile products in extruded cereals, using flours from different grain varieties (Pfannhauser, 1990), maize flour with or without added whey protein (Bailey et al., 1994), taro (Maga and Liu, 1994), and wheat flour (Hwang et al., 1994). These studies focused more on contribution of the cereal feedstock to volatile formation rather than the influence of different process variables to modify flavor generation. The relative contribution of the volatile products in the extrudate flavor was not evaluated in these studies. In extruded oat flour, aroma extract dilution analysis showed that products from lipid degradation, such as 2,4(*E,E*)-decadienal, 2,4(*E,E*)-nonadienal, and (*E*)-4,5-epoxy-2(*E*)-decenal as well as vanillin, which may originate from structural phenols in the flour, were the most important contributors to the fatty, fried, and sweet aroma of the extrudate (Guth and Grosch, 1993).

Recent studies have reported on the effect of different flavor precursors in modifying both aroma and aroma volatiles generated by extrusion cooking. Sensory characterization of the odor properties of wheat flour and starch, enriched with cysteine and pentose or hexose sugars, indicated the important role of the nonstarch fraction of flour on flavor generation in extrusion cooking (Bredie et al., 1997). Other studies reported on

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Table 1. Extrusion Parameters Measured during the Processing of Maize for Aroma Volatile Analyses

sample	temperature attained (°C)				moisture % (w/w)	RT[e] (s)	SME[f] (kJ/kg)	die pressure (MPa)
	stage 1[a]	stage 2[b]	stage 3[c]	product[d]				
120/22/35[g]	125	130	120	125	23.0	35	656	2.16
120/22/60	87	109	115	116	21.7	60	486	2.70
120/18/35	120	130	118	123	18.9	35	678	2.67
120/18/60	73	101	115	118	18.5	60	597	2.98
150/18/35	145	155	147	153	18.4	35	646	1.67
150/18/60	106	150	137	152	18.5	60	472	2.37
180/14/35	170	185	180	182	14.1	35	693	1.70
180/14/60	118	146	172	183	14.1	60	412	2.22

[a] For the screw design giving a residence time (RT) of 35 s, a temperature probe was placed over the partly filled start feed screw in contact with the flour. For the screw design with RT of 60 s, the probe was in good contact with the melt fluid. [b] Probe located in a paddle section. [c] Probe placed over a partly filled screw section in intermittent contact with the melt fluid. [d] Product temperature was measured behind the die channel, in contact with the melt fluid. [e] Different residence times (RT) were achieved by changing the screw configuration; the feed rate was 800 g/min for RT of 35 s and 600 g/min for RT of 60 s; the screw rotation was kept constant at 350 rpm for all the runs. [f] Specific mechanical energy. [g] Target extrusion conditions: temperature expected in product (°C)/moisture level (%)/residence time (s).

qualitative and quantitative changes in the volatile components resulting from the addition of ammonia in the extrusion of autolyzed yeast extract (Izzo and Ho, 1992), proline and ornithine in extrusion of starch (Bredie et al., 1996), and cysteine (Riha et al., 1996) or ammonium bicarbonate and 2-oxopropanal (Izzo et al., 1994) in the extrusion of wheat flour. An investigation of the role of thiamin in flavor generation in extruded cereals has also been reported (Ho et al., 1989). The cereal lipid content has also been shown to influence the generation of volatile compounds. The addition of maize oil in extrusion of model feedstocks with maize flour components showed an increase of secondary oxidation products from lipids and carotenoids, as well as the formation of pyrazines with long alkyl chains (Bruechert et al., 1988). These latter compounds are most likely to be derived from interactions between intermediary products from the Maillard reaction and lipid degradation.

All of these studies have contributed to the identification of the chemical nature of volatile components that are generated in extrusion processing of cereals, and in total >220 compounds have been reported. However, there is insufficient understanding of the mechanisms associated with the flavor formation, the role of these components in the perceived flavor of extruded cereals, and the effect of wetting the cereal matrix on their preferential release.

The extrusion process is characterized by a rapid heating and the formation of a glassy material within a relatively short time after the product leaves the die. The thermal generation of flavor compounds in extruded cereals may therefore be considered as an open-ended series of reactions with the final products immobilized in a glass-like structure. Hence, altering the extrusion process and design variables provides a means of studying the succession of flavor-forming reactions. In an earlier paper, the sensory characterization of aroma in maize and wheat flour extrudates was described (Bredie et al., 1998). The present study aimed to characterize the volatile aroma products in the extrusion cooking of maize flour at different combinations of temperature, moisture, and time to evaluate the different mechanisms associated with their formation.

EXPERIMENTAL PROCEDURES

Extrusion Processing. Maize flour was processed using an APV Baker MPF 50D corotating twin-screw extruder (APV Baker Ltd., Peterborough, U.K.). The maize was a mixture of Dent and Flint varieties and was obtained from Smiths

Flour Mills, Worksop, U.K. The flour was free from any noticeable off-odor prior to extrusion. Analysis of the flour, using standard procedures, showed that it had a particle size of ≈600 μm, a moisture content of 13.5% w/w, and 8.6% protein and 0.8% lipid contents.

Eight extrusion conditions, including four combinations of increasing temperature and decreasing moisture and two levels of RT, were chosen to cover the extreme and intermediate conditions feasible on the APV extruder (Table 1). The independent variables of water and powder feed rate were adjusted by a microcomputer to control the chosen moisture level and overall feed rate. The screw rotation was held at 350 rpm with a variation of <2%. The dependent mass temperature along the screws was adjusted to the chosen profile by heating or cooling of the barrel sections. A measure of the mass temperature in the screw sections along the barrel was obtained from readings of four temperature probes in contact with the fluid mass. Adjustments to this barrel temperature profile were made to provide a constant mass temperature along the screws. Other dependent processing variables, such as torque and die pressure, were kept constant within each run. Motor torque was recorded and expressed as the specific mechanical energy (SME) input. The die pressure was recorded in the die entrance area and provided an approximate estimate of the viscosity of the melt when passed through the die channel.

The screw design, comprising a combination of feed screws and forwarding and reversing paddle elements, has been described elsewhere (Bredie et al., 1998). The standard screw configuration gave a median RT of 35 s at a feed rate of 800 g/min. A longer RT was achieved by modifying the feed and reversing sections, giving a median RT of 60 s at a feed rate of 600 g/min. Twin circular dies with a diameter of 3 mm were used.

Extrudates were cut at a high rate to obtain small pieces. These were collected over a period of 5–10 min, during which time the main extrusion variables showed a coefficient of variation of <3%. The pieces were thoroughly mixed and milled to provide a homogeneous extrudate. The milled samples were packed into plastic polyamide–polyethene laminate bags (Optivac, Vacuum Packaging International, U.K.) and stored at −20 °C until required for analyses.

Volatile Analysis. A sample of each extrudate (10 g) was placed in a 250-mL conical flask fitted with a Drechsel head, and 20 mL of distilled water was added. The mixture was gently shaken until the extrudate powder had absorbed the water. Oxygen-free nitrogen was passed over the sample for 1 h at a rate of 40 mL/min. The volatiles were swept onto a preconditioned glass-lined stainless steel trap, packed with 10 mg of Tenax GC (Unijector system, SGE Ltd., Milton Keynes, U.K.). Throughout the collection, the sample was maintained at 37 °C. The trap was then connected directly to the nitrogen supply for 5 min to remove moisture. One microliter of a 130 mg/L 1,2-dichlorobenzene internal standard in *n*-hexane was then injected onto the trap kept under slight vacuum. Analy-

Flavor Generation in Extruded Maize

J. Agric. Food Chem., Vol. 46, No. 4, 1998 **1481**

ses were performed in duplicate for extrudates from each set of extrusion conditions.

Separation and Identification of Volatiles. A Hewlett-Packard 5980/5988A GC/MS system, equipped with a modified Unijector (SGE Ltd.), connected to a 50 m × 0.32 mm i.d. fused silica capillary column, coated with BPX-5 at 0.5-μm film thickness (SGE Ltd.), was used to analyze the volatiles on the Tenax trap. These were thermally desorbed at 250 °C in the Unijector and cryofocused directly onto the front of the GC column while the oven was held at 0 °C for 5 min. The oven temperature was then raised to 60 °C over 1 min and held for 5 min, before being raised to 250 °C at a rate of 4 °C/min. The helium carrier gas flow was 1.5 mL/min. Mass spectra were recorded in the electron impact mode at an ionization voltage of 70 eV and source temperature of 200 °C. A scan range of m/z 29−400 with a scan time of 0.69 s was employed. The data were controlled and stored by the HP 59970C ChemStation system.

Volatiles were identified by comparison of each mass spectrum with spectra from authentic compounds analyzed in our laboratory or with spectra in reference collections (NIST/EPA/MSDC, 1992; ten Noever de Brauw et al., 1980) or other published spectra. A linear retention index (LRI) was calculated for each compound using the retention times of a homologous series of C_6−C_{22} *n*-alkanes. Wherever possible, mass spectral identifications were confirmed by comparing the LRI with those from authentic compounds run under similar conditions. Where no reference spectra were available, tentative identifications were made by comparison with spectra of related compounds.

GC Olfactometry. After volatile collection and thermal desorption, the volatiles were analyzed on a HP 5890 GC equipped with a humidified odor port (SGE Ltd.). The column effluent (He, 1.6 mL/min) was split at a ratio of 1:1 between the flame ionization detector and the odor port. In the odor port, the GC effluent was enclosed in a stream of humidified air (30 mL/min). The column and oven conditions were similar to those of the GC/MS system.

A trained assessor evaluated the odors from the GC effluent by recording odor descriptions and duration time of the smell. Another assessor was used to verify important odor-active areas in the gas chromatogram. Headspace collections were analyzed in triplicate to distinguish background noise from persistent odors in the GC effluent.

RESULTS AND DISCUSSION

Eight extrudates were produced under different combinations of product temperature, moisture level, and residence time, using maize grits as feedstock material (Table 1). The actual measured extrusion conditions deviated to some extent from the target values. The most noticeable variation between the extrusion runs at different conditions was observed for the SME input. The SME values were higher for the standard screw design, which gave an RT of 35 s, than for the screw giving an RT of 60 s. A lower SME input coincided with a lower temperature in the first three stages of the barrel for the modified screw (Table 1). This screw gave, therefore, a shorter effective heating time at the required temperature than the standard screw. Since temperature is an important parameter in determining the products formed by thermally induced reactions and their rate of formation, a comparison of the effect of RT alone on flavor generation was difficult to make.

Eighty volatile compounds were identified in the maize (Table 2). These included 20 sulfur-containing compounds, 16 pyrazines, 12 aldehydes, 11 pyrroles, 5 alcohols, 5 furans, 4 ketones, 4 hydrocarbons, and 1 pyridine. Some compounds remained unidentified, but these comprised only a small part of the total ion chromatogram. Many of the identified compounds have

been reported previously in extruded cereals. However, the sulfur-containing furans, thiophenones, dithiacycloalkanones, and most pyrroles have not been identified previously in extruded cereals. One compound was tentatively identified for the first time in a food product. The mass spectrum showed three major ions, a molecular ion of 148 with m/z 150 (M + 2) intensity corresponding to two sulfur atoms, and two major fragments at m/z 106 and 78. These two fragment ions appear to have retained two sulfur atoms, which indicated neutral losses of C_3H_6 and C_4H_6O, respectively, from the molecular ion. Other fragments of significance were assigned to S_2^+ (m/z 64), $C_2H_4S^+$ (m/z 60), CH_2S^+ (m/z 46), and $C_2H_2O^+$ (m/z 42). From the spectrum, a structure corresponding to 6-methyl-1,2-dithian-4-one was suggested (Table 2). An alternative structure might be 3,3-dimethyl-1,2-dithiolan-4-one, which has been reported by Tressl and Silwar (1981) and had a similar fragmentation pattern. However, in a meat extract, a compound tentatively identified as 3,3-dimethyl-1,2-dithiolan-4-one was reported to elute earlier on a BP5 column at an LRI of 1199 (Madruga, 1994).

Among the aldehydes, ketones, and alcohols identified in the extrudates, some can be classified as products from Strecker degradation of amino acids (2- and 3-methylbutanal and phenylethanal), some as products from the degradation of phenolic acids associated with hemicelluloses (for example, ferulic acid producing 2-methoxy-4-vinylphenol), and others as products from oxidative or thermal degradation of carotenoids [for example, toluene, 6-methyl-5(*E*)-hepten-2-one, and geranylacetone]. However, the origin of most other aliphatic aldehydes and alcohols, as well as the aliphatic hydrocarbons and 2-pentylfuran, was the oxidative and/or thermal degradation of unsaturated lipids (Grosch, 1982). Lipid autoxidation may occur during storage of extruded cereals, and a direct relationship has been reported between such oxidation and extrusion temperature (Artz and Rao, 1994). In the present work, the extrudates were sealed in bags with low oxygen permeability and stored at −20 °C. This appeared to prevent oxidation during storage, since the quantities of most lipid oxidation products were not appreciably higher in extrudates processed at the higher temperatures and, thus, it may be concluded that the volatiles observed were the products of lipid degradation during extrusion.

The lipid-derived volatile compounds, including 2-pentylfuran, generally increased with the longer RT (Figure 1). However, with conditions of 180 °C and 14% moisture, there was a tendency to produce lower amounts of most of these compounds when the longer RT was employed. The apparent decrease in lipid-derived volatiles may be attributed to an increased formation of Maillard-derived products. Intermediates from the Maillard reaction have been shown to act as free radical scavengers, inhibiting propagation of radical reactions (Lingnert and Eriksson, 1983; Elizalde et al., 1991). The rate of formation of lipid-derived volatiles may therefore decrease when the rate of the Maillard reaction increases in extrusions at higher temperature (≥150 °C) and lower moisture content (≤18%).

The Strecker aldehydes were produced in relatively small amounts in extrudates from the lowest temperature (120 °C) and highest moisture level (22%). The amounts increased with the more severe extrusion conditions, except for the 180 °C/14%/60 s treatment, which showed a decrease (Figure 2). In roasting of

Table 2. Volatile Compounds Identified in the Headspace of Maize Extruded under Different Temperature, Moisture, and Time Combinations

compound	LRI[a]	method of ID[b]	120 °C[d] 22% 35 s	120 °C 22% 60 s	120 °C 18% 35 s	120 °C 18% 60 s	150 °C 18% 35 s	150 °C 18% 60 s	180 °C 14% 35 s	180 °C 14% 60 s
hydrocarbons										
toluene	771	MS+LRI	1	5	6	12	2	8	16	5
octane	800	MS+LRI	2	1	7	11	1	2	12	6
styrene	905	MS+LRI	1	3	4		1	2	12	6
limonene	1040	MS+LRI	4	3	6	7	3		24	17
alcohols										
3-methylbutanol	773	MS[1]	1	1	2					
1-hexanol	873	MS+LRI	1	1	2	5	tr	2	2	
1-octen-3-ol	986	MS+LRI	1	3	6	12	1		13	9
1-nonanol	1169	MS+LRI	1						3	
2-methoxy-4-vinylphenol	1334	MS[3]		2	9	17	3	13	38	48
aldehydes										
3-methylbutanal	661	MS+LRI	3	5	29	18	10	39	130	14
2-methylbutanal	663	MS+LRI		4	4	11	3	21	57	9
pentanal	690	MS+LRI	tr		2					
hexanal	808	MS+LRI	22	62	99	170	24	58	78	9
heptanal	910	MS+LRI	3	8	13	27	4	110	22	6
2(*E*)-heptenal	968	MS+LRI	1	3	8	12	2	3	4	
benzaldehyde	982	MS+LRI	11	20	44	90	10	39	58	59
octanal	1011	MS+LRI	1	3	7	10	2	3		
2-phenylethanal	1064	MS+LRI	tr	4	18	29	10	35	110	43
2(*E*)-octenal	1069	MS+LRI	1	1	5	3		2		
nonanal	1113	MS+LRI	4	10	10	22	5	16	41	37
decanal	1215	MS+LRI	3	5	6	13	4	6	27	
ketones										
2,3-pentanedione	698	MS+LRI		4	6	12	2	6	12	2
2-heptanone	896	MS+LRI	1	4	7	14	3	11	18	5
6-methyl-5(*E*)-hepten-2-one	991	MS+LRI	1	4	5	9	1	8	6	
geranylacetone	1458	MS[1]	1	1	4	5	1	2	5	4
furans										
2-furfural	846	MS+LRI	2	13	24	44	11	41	160	190
2-furanmethanol	868	MS+LRI			2	5	1	9	33	46
2-acetylfuran	923	MS+LRI						4		14
5-methyl-2-furfural	977	MS+LRI					tr	2	21	50
2-pentylfuran	996	MS+LRI	3	8	19	24	5	17	28	6
pyrroles and pyridines										
1-ethyl-1*H*-pyrrole	821	MS[1]							22	7
2-methyl-1*H*-pyrrole	855	MS[1]							7	2
2-acetyl-1-pyrroline	934	LRI+GCO	tr	tr	tr	tr	tr	tr	tr	tr
2-ethyl-4-methyl-1*H*-pyrrole	938	MS[1]							8	10
1-[1(1*H*)-pyrrolyl]-2-propanone	1037	MS[4]							9	9
2-acetylpyridine	1050	MS+LRI		tr	tr			1	tr	6	6
1-ethyl-2-formyl-1*H*-pyrrole	1067	MS[2]						2	22	21
2-formyl-1*H*-pyrrole	1079	MS[1]							3	4
2,3-dihydro-1*H*-indole	1136	MS[1]						2	16	17
1-(2-furanylmethyl)-1*H*-pyrrole	1196	MS+LRI							12	22
2-methyl-1*H*-indole	1423	MS[1]								5
1-(2-furanylmethyl)-2-formyl-1*H*-pyrrole	1443	MS[5]								tr
pyrazines										
pyrazine	739	MS[1]					1	13	7	
methylpyrazine	837	MS+LRI		4	9	19	7	33	240	260
2,5-dimethylpyrazine (or 2,6-)	926	MS+LRI		1	7	26	7	40	260	260
ethylpyrazine	929	MS+LRI					1	5	100	140
2,3-dimethylpyrazine	932	MS+LRI					1	3	34	39
vinylpyrazine	947	MS[1]							15	25
2-ethyl-6-methylpyrazine	1009	MS+LRI					tr	9	56	38
trimethylpyrazine	1014	MS[1]					tr	8	92	69
2-ethyl-5-methylpyrazine	1015	MS[1]						8		22
2-methyl-6-vinylpyrazine	1032	MS[1]							22	35
a methylvinylpyrazine	1038	ms							5	3
(1-propenyl)pyrazine (*E* or *Z*)	1073	MS[1]							2	7
2-ethyl-3,5-dimethylpyrazine	1087	MS+LRI			4	13	3	17	30	17
2,6-diethylpyrazine	1090	MS+LRI							7	8
isopropenylpyrazine	1092	MS[1]						14	15	
3-ethyl-2,5-dimethylpyrazine	1095	MS+LRI							2	2
sulfur-containing compounds										
dimethyl disulfide	753	MS+LRI	1			6				8
dimethyl trisulfide	990	MS[1]	8	6	37	95	11	12	40	130
dimethyl tetrasulfide	1252	MS[1]				5				24
3-methyl-1,2-dithiolan-4-one	1102	MS+LRI					2	4	41	13
1,2-dithian-4-one	1208	MS[6]			2		2	6	27	18

Flavor Generation in Extruded Maize

J. Agric. Food Chem., Vol. 46, No. 4, 1998 **1483**

Table 2. (Continued)

compound	LRI[a]	method of ID[b]	approximate quantity[c] (ng/10 g of extrudate)							
			120 °C[d] 22% 35 s	120 °C 22% 60 s	120 °C 18% 35 s	120 °C 18% 60 s	150 °C 18% 35 s	150 °C 18% 60 s	180 °C 14% 35 s	180 °C 14% 60 s
6-methyl-1,2-dithian-4-one[e] 106, 78 (81), **148** (M[+], 65), 60 (26), 42 (23), 64(18), 41 (16), 59 (12), 84 (11), 39 (10), 45 (10), 46 (10), 115 (10)	1246	ms							10	7
2-[(methyldithio)methyl]furan	1237	MS+LRI							18	29
2-[(methyltrithio)methyl]furan	1490	MS[7]							13	13
2-methyl-3-[(2-furanyl-methyl)dithio]furan	1665	MS+LRI							tr	
bis(2-furanylmethyl) disulfide	1727	MS+LRI							3	5
2,3-dihydro-6-methyl-thieno[2,3c]furan	1215	MS+LRI								18
2-methylthiophene	780	MS[1]							9	
2-vinylthiophene	918	MS[2]							2	1
2-formylthiophene	1024	MS+LRI					1	8	41	49
2-formyl-5-methylthiophene	1109	MS+LRI							9	10
4,5-dihydro-3(2H)-thiophenone	975	MS[1]					tr	2	7	
4,5-dihydro-5-methyl-3(2H)-thiophenone	1006	MS[2]			3	3	1	4	22	18
4-methylthiazole	828	MS+LRI							11	4
2-acetylthiazole	1038	MS+LRI							5	3
2-acetyl-4-methylthiazole	1128	MS[5]							4	8
miscellaneous										
acetic acid	665	MS[1]		3	3	6			3	
1-formyl-5-ethylcyclopentene	1047	MS[8]	1	3	6	9	1	2	2	

[a] Linear retention index on BPX-5 column. [b] MS+LRI, mass spectrum and LRI agree with those of the authentic compound run under similar GC/MS conditions; MS, mass spectrum agrees with literature spectrum, with references indicated by superscript numbers: [1] NIST/EPA/MSDC (1992), [2] ten Noever de Brauw et al. (1980), [3] Ralph and Hatfield (1991), [4] Baltes and Bochman (1987), [5] Stoll et al. (1967), [6] Farmer et al. (1989), [7] Tressl and Silwar (1981), [8] Werkhoff et al. (1993); LRI+GCO, GC peak too small to obtain a mass spectrum, identification based on LRI and odor quality on two columns (BPX5 and BP20) and comparison with authentic compound; ms, interpretation of mass spectrum and comparison with spectra of related compounds. [c] Estimated quantity (ng) in headspace from 10 g of sample, calculated by comparison with 176 ng of 1,2-dichlorobenzene used as internal standard; average values of a duplicate analysis are given, those compounds identified in quantities below 0.5 ng being reported as "tr" (trace). [d] Extrusion conditions, i.e., temperature, moisture, residence time; the screw speed was held constant at 350 rpm. [e] Tentative identification with mass spectrum shown.
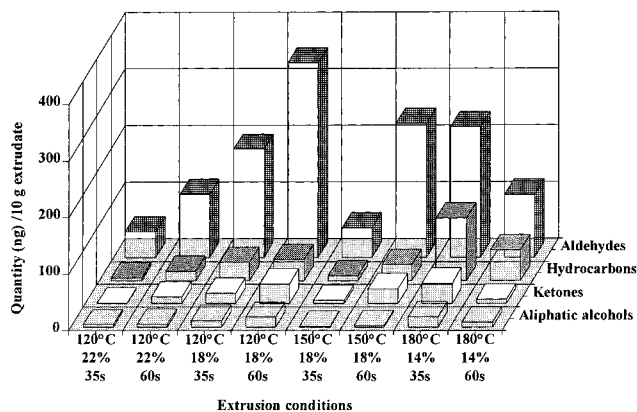

Figure 1. Classes of lipid-derived volatiles formed in extruded maize as affected by extrusion conditions (temperature, moisture, and time).

Figure 2. Formation of Strecker aldehydes in extruded maize as affected by extrusion conditions (temperature, moisture. and time).

malted barley, a decrease in Strecker aldehydes was also observed when the temperature exceeded 150 °C (Beal and Mottram, 1994). The lower level of Strecker aldehydes and lipid-derived aldehydes, in extrudates prepared under the most severe conditions, may indicate that they became involved in further condensation reactions with amines and/or thiols, producing heterocyclic compounds and/or polymeric substances. This has been observed in heated model Maillard systems containing lipids, ribose, and cysteine (Farmer and Mottram, 1992).

Aliphatic sulfur-containing compounds identified in the extrudates were dimethyl di-, tri-, and tetrasulfide, with dimethyl trisulfide present in the highest quanti-
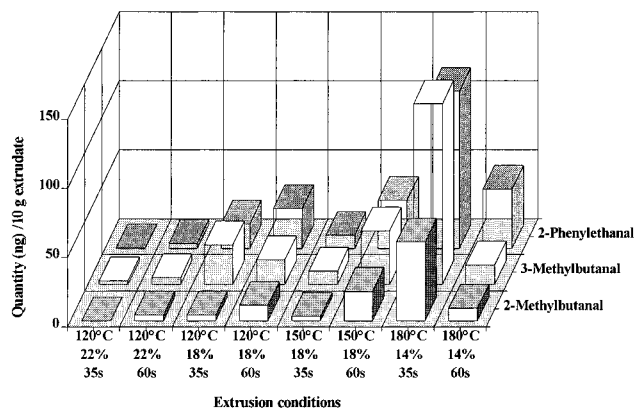
ties. These polysulfides have been reported in trace amounts in extrudates of yeast extract (Izzo and Ho, 1991) and high-gluten wheat flour (Hwang et al., 1994). Possible precursors for these polysulfides are hydrogen sulfide and methanethiol, which may arise from the degradation of sulfur-containing amino acids (cysteine, methionine, S-methylmethionine) (Schutte, 1974).

Fifty heterocyclic compounds were found in the maize extrudates. In contrast to products from lipid degradation, heterocyclic compounds were mostly formed in the extrudates processed at temperatures ≥150 °C and moisture levels ≤18% (Figures 3 and 4). Five furans with sulfur-containing substituents had not been reported previously in extruded cereals. These were
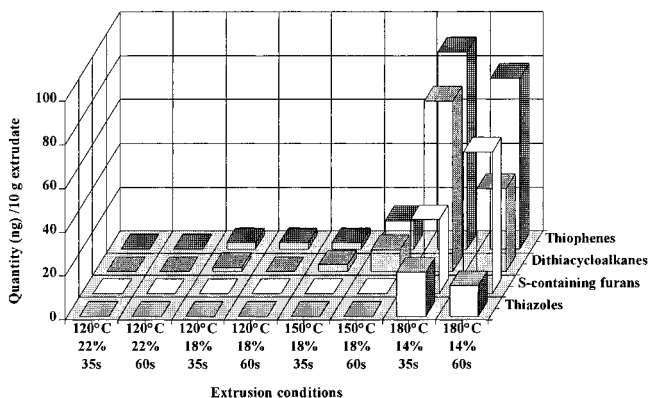
Figure 3. Formation of classes of S-containing heterocyclic compounds in extruded maize as affected by extrusion conditions (temperature, moisture, and time).
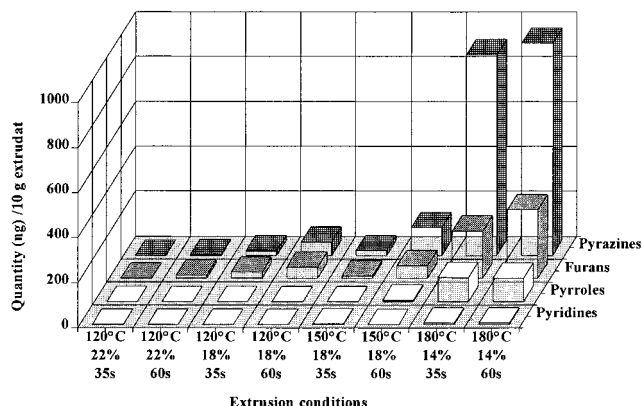

Figure 4. Formation of classes of N- and O-heterocyclic compounds in extruded maize as affected by extrusion conditions (temperature, moisture, and time).

2-[(methyldithio)methyl]furan, 2-[(methyltrithio)methyl]furan, bis(2-furanylmethyl) disulfide, 2-methyl-3-[(2-furanylmethyl)dithio]furan, and 2,3-dihydro-6-methylthieno[2,3-*c*]furan (kahweofuran). They were identified only in the samples extruded at 180 °C and 14% moisture. Their formation coincided with the higher levels of 2-furfural and 2-furanmethanol, which, together with hydrogen sulfide and methanethiol, were their likely precursors. It was noteworthy that most of the sulfur-containing furans had the thio group in the 2-position. The only exception was 2-methyl-3-[(2-furanylmethyl)dithio]furan, which may be formed from the oxidation of 2-methyl-3-furanthiol and 2-furanmethanethiol. Certain roasted and baked cereals, such as popcorn (Schieberle, 1991), roasted sesame seeds (Schieberle, 1993), and bread crust (Baltes and Song, 1994), have been found to contain 2-furanmethanethiol and related sulfides, but 2-methyl-3-furanthiol and related compounds have not been reported. Although 3-thio-substituted furans have been reported in the volatiles of roasted coffee, much higher quantities of the 2-thio-substituted furans were present (Holscher et al., 1990; Tressl and Silwar, 1981). Many 3-thio-substituted furans possess low odor thresholds and characteristic meaty odor notes, while the 2-thio-substituted furans and kahweofuran lack the meaty note and have a more pronounced roasted, sulfur-like character. These observations are in agreement with the toasted, burnt, and puffed-wheat odors found in the sensory profile of these extrudates (Bredie et al., 1998).

Among the thiophenes found in this study, 2-formylthiophene and 2-formyl-5-methylthiophene have also been reported in maize extruded under severe heating (178 °C) and low-moisture (12.5%) conditions (Nair et al., 1994). Addition of cysteine in extrusion cooking of wheat flour (temperature 185 °C, moisture 16%) has been shown to increase the number and amount of several thiophenes (Riha et al., 1996). In the present work, 2-formylthiophene, present in extrudates processed at 150 °C or higher temperatures, was the most abundant thiophene produced. 2-Furfural may have been its precursor via a mechanism involving ring opening and substitution of the oxygen atom with hydrogen sulfide (Shibamoto, 1977). 4,5-Dihydro-3(2*H*)-thiophenone and 4,5-dihydro-5-methyl-3(2*H*)-thiophenone have not previously been described as volatiles in extruded cereals. Unlike the other thiophenes, 4,5-dihydro-5-methyl-3(2*H*)-thiophenone was found in the samples extruded at the lowest temperature of 120 °C with a moisture level of 18%, although the quantity increased under the more severe extrusion conditions. The thiophenones may be derived from the reaction of hydroxyfuranones with hydrogen sulfide or, in the case of 4,5-dihydro-3(2*H*)-thiophenone, from cysteine alone (Shu et al., 1985a). Hydroxyfuranones were not detected in the volatiles from the extrudates, even though they are important Maillard intermediates.

Thiacycloalkanones were also formed under the less severe extrusion conditions and increased in quantity with the higher extrusion temperature and lower moisture level. 1,2-Dithian-4-one and 3-methyl-1,2-dithiolan-4-one have been described earlier among the reaction volatiles in heated model systems containing cysteine and ribose (Farmer et al., 1989). 1,2-Dithiolan-4-one has also been found in the thermal degradation products of cysteine alone (Shu et al., 1985b). The mechanism for the formation of these dithiacycloalkanones may be from the reaction hydroxyfuranones and two molecules of hydrogen sulfide in a reaction similar to the formation of thiophenones (Hartman et al., 1984). This would derive 1,2-dithian-4-one from 4,5-dihydro-3(2*H*)-furanone and 6-methyl-1,2-dithian-4-one from 4,5-dihydro-5-methyl-3(2*H*)-furanone.

Pyrazines were one of the major classes of volatiles identified in the extrudates. Pyrazines have previously received attention in extruded cereals because of their roasted, nutty flavor properties (Maga and Sizer, 1979; Fors and Eriksson, 1986). Nearly 40 different substituted pyrazines have been reported in various extruded cereals, but most of these were identified in model extrusions using an autolyzed yeast extract (Izzo and Ho, 1991, 1992). The pyrazines found in the maize extrudates in this study were common to other extruded cereals and to many heat-processed foods and model systems (Maga, 1992). High temperature, low moistured, and longer RT generally increased the quantities of pyrazines, and the most readily formed were methyl-, 2,5-dimethyl-, and 2-ethyl-3,5-dimethylpyrazine. Formation of other alkylpyrazines required higher extrusion temperatures (≥150 °C) and lower moisture levels (≤18%). Methyl-, 2,5-dimethyl-, and ethylpyrazine were the most abundant pyrazines in the samples extruded at 180 °C and 14% moisture and have also been found in high quantities in extruded green malt (Fors and Eriksson, 1986). Increasing the RT gave higher yields of pyrazines in the extrudates processed at 18% moisture and 120 or 150 °C, but the levels of pyrazines were largely unaffected by varying RT in extrusion at 180 °C and 14% moisture.

Flavor Generation in Extruded Maize

J. Agric. Food Chem., Vol. 46, No. 4, 1998 **1485**

Table 3. Gas Chromatography Olfactometry (GCO) Evaluations of Headspace Concentrates from Selected Maize Extrudates, Showing Compounds That Appear To Elute in the Vicinity of Odor

compound	120 °C 22% 60 s[a]	120 °C 18% 60 s	150 °C 18% 60 s	180 °C 14% 60 s	coinciding odors
3-methylbutanal	−[b]	+[c]	+	+	cheesy, malty
2-methylbutanal	−	+	+	+	cheesy, malty
dimethyl disulfide	−	−	−	+	onion-like, cabbage-like
hexanal	−	+	+	+	grass-like
2,5-dimethylpyrazine	−	+	+	+	grass-like, vegetable-like
2-acetyl-1-pyrroline[d]	+	+	+	+	biscuit-like, popcorn-like
4,5-dihydro-3(2*H*)-thiophenone	−	−	−	+	garlic-like
1-octen-3-ol	+	+	+	+	mushroom-like
dimethyl trisulfide	+	+	+	+	spicy, garlic-like, cabbage-like
trimethylpyrazine	−	−	−	+	sharp, solvent-like
2-ethyl-5-methylpyrazine	−	−	−	+	bread-like, biscuit-like, burnt
2-acetylpyridine	−	−	−	+	biscuit-like, toasted
2-acetylthiazole	+	+	+	+	biscuit-like, toasted, bread-like
2-phenylethanal	+	+	+	+	waxy, caramel-like, sharp
3-methyl-1,2-dithiolan-4-one	+	+	−	+	sharp, burnt, cabbage-like
1-nonanol	+	+	+	+	fatty, damp clothes-like
1,2-dithian-4-one	+	+	−	+	spicy, burnt, yeast extract-like
2-methoxy-4-vinylphenol	−	−	+	+	smoky, burnt

[a] Extrusion conditions (temperature/moisture/residence time). [b] No odor detected or only in one GCO assessment. [c] Odor detected in at least two of the three GCO assessments. [d] Trace of 2-acetyl-1-pyrroline (AP) was responsible for the perceived odor.

Pyrroles and dihydropyrroles were mostly identified in the extrudates processed at 180 °C and 14% moisture, with 1-ethyl-1*H*-pyrrole, 1-ethyl-2-formyl-1*H*-pyrrole, and 1-(2-furanylmethyl)-1*H*-pyrrole found in the highest quantities. Only a few pyrroles have previously been identified in extruded cereals, mainly in maize extruded at high temperature and low moisture (Nair et al., 1994). Recent investigations have shown that moisture affected pyrrole formation in model systems; 1-(2-furanylmethyl)-1*H*-pyrrole and 1-(2-furanylmethyl)-methyl-1*H*-pyrrole were produced in high quantities in dry, heated model systems containing cysteine and ribose, but, in similar systems containing water, these pyrroles were formed in much lower quantities (Mottram and Whitfield, 1995). In other model reactions containing serine and/or threonine without a sugar source, alkylpyrroles were produced in high yields (Baltes and Bochmann, 1987). These authors suggested that alkylpyrroles were formed via a pyrolytic degradation of the amino acids alone, whereas pyrroles containing acyl and furan groups required the presence of a sugar source.

The relative contribution of the different volatile components to the aroma of the extrudates was investigated using GCO on headspace extractions. These showed the number of odor responses to be greater in the extrudates from higher temperatures and lower moisture levels (Table 3). A biscuit-like, popcorn-like odor eluted from the BPX5 column in the LRI range 932−940, but no corresponding GC peak was observed. When the extrudates were analyzed on the more polar BP20 column, the biscuit-like, popcorn-like odor was perceived in the LRI interval of 1356−1360. It was not possible to obtain a mass spectrum, but this trace component was identified as 2-acetyl-1-pyrroline from analysis of an authentic sample that eluted at an LRI of 936 on BPX5 and at an LRI of 1359 on BP20. Although 2,3-dimethylpyrazine had an LRI 932 on the BPX5 column, which was close to where the biscuit-like, popcorn-like odor eluted, this compound was not responsible for the odor, since it gave no odor response on the BP20 column, where it had an LRI of 1379. Biscuit-like, toasted, and bread-like odors were noted for 2-acetylthiazole in all four extrudates analyzed by

GCO. 2-Acetyl-1-pyrroline and 2-acetylthiazole may contribute to the popcorn odor characteristic for the maize extrudate from the 150 °C/18%/60 s treatment (Bredie et al., 1998). Both of these compounds are known to have popcorn-like aromas and have also been associated with the characteristic aroma of baked bread (Grosch and Schieberle, 1991). Few odor responses were found for the pyrazines. Grass-like and vegetable-like odors were noted for 2,5-dimethylpyrazine; a sharp, solvent-like odor was noted for trimethylpyrazine and a biscuit-like, bread-like, burnt odor for 2-ethyl-5-methylpyrazine. The latter two pyrazines gave odor responses only in the 180 °C/14%/60 s sample. These observations suggest that, despite the large numbers of pyrazines generated in the more severely processed extrudates, their contribution to the extrudate aroma appeared to be relatively small.

Some cabbage-like, cooked apple-like, fruity, grass-like, onion-like, stale, and sulfur-like odors were not clearly associated with peaks in the chromatogram as well as caramel-like, biscuit-like, bread-like odors eluting at an LRI interval of 1100−1120. Sulfur-containing compounds, which may be implicated in the perceived aroma of the extrudates, were aliphatic polysulfides, 3-methyl-1,2-dithiolan-4-one, 1,2-dithian-4-one, and 4,5-dihydro-3(2*H*)-thiophenone (Table 3). 2-[(Methyldithio)methyl]furan, which has been described as the "golden brown" aroma compound of white bread (Mulders et al., 1976) and possesses a low flavor threshold of 0.04 μg/L, could not be associated with an odor in GCO analysis of the maize extrudates. This finding agrees with results of other aroma analysis of bread crust (Schieberle and Grosch, 1985, 1987).

In conclusion, the volatile compounds generated under different extrusion conditions indicated that processing at low temperature (120 °C) and high moisture (22%) was associated with products from lipid degradation, the initial stages of the Maillard reaction, and Strecker degradation of amino acids. Increasing the temperature (150 °C) and reducing the moisture level to 18% gave rise to the formation of pyrazines as well as thiophenones, which possibly derived from the reaction of hydroxyfuranones with hydrogen sulfide. Extrusion cooking at 180 °C and 14% moisture level

resulted in a marked increase of 2-furfural and 2-furanmethanol and the formation of related and other N-, NS-, S-, and O-containing heterocycles, resulting from increased Maillard reaction and cysteine degradation. These conditions were also associated with starch and hemicellulose degradation, as evidenced by the increased level of 2-methoxy-4-vinylphenol. Under these conditions, the level of aldehydes tended to decrease, which indicated inhibition of lipid degradation by Maillard reaction products or the participation of aldehydes in further reactions with intermediates of the Maillard reaction. GCO assessments of the extrudates showed that 2-acetyl-1-pyrroline and 2-acetylthiazole contributed to important cereal-like odors.

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J. Agric. Food Chem., Vol. 46, No. 4, 1998 **1487**

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