Effect of pH and Temperature on the Formation of Volatile Compounds in Cysteine/Reducing Sugar/Starch Mixtures during Extrusion Cooking

Jennifer M. Ames,*,† Robin C. E. Guy,‡ and Gary J. Kipping†

School of Food Biosciences, The University of Reading, Whiteknights, Reading RG6 6AP, United Kingdom, and Campden and Chorleywood Food Research Association, Chipping Campden, Gloucestershire GL55 6LD, United Kingdom

Mixtures of cysteine, reducing sugar (xylose or glucose), and starch were extrusion cooked using feed pH values of 5.5, 6.5, and 7.5 and target die temperatures of 120, 150, and 180 °C. Volatile compounds were isolated by headspace trapping onto Tenax and analyzed by gas chromatography–mass spectrometry. Eighty and 38 compounds, respectively, were identified from extrudates prepared using glucose and xylose. Amounts of most compounds increased with temperature and pH. Aliphatic sulfur compounds, thiophenes, pyrazines, and thiazoles were the most abundant chemical classes for the glucose samples, whereas for xylose extrudates highest levels were obtained for non-sulfur-containing furans, thiophenes, sulfur-containing furans, and pyrazines. 2-Furanmethanethiol and 2-methyl-3-furanthiol were present in extrudates prepared using both sugars, but levels were higher in xylose samples. The profiles of reaction products were different from those obtained from aqueous or reduced-moisture systems based on cysteine and either glucose or ribose.

Keywords: *Maillard reaction; extrusion cooking; cysteine; xylose; glucose; pH; temperature; volatiles, 2-furanmethanethiol; 2-methyl-3-furanthiol*

INTRODUCTION

Extrusion cooking is an efficient means of producing a range of cereal foods. Unfortunately, the short cooking times limit flavor formation and, in addition, a proportion of flavor compounds that are formed are volatilized at the die (*1, 2*). Therefore, means of enhancing flavor in extruded products are of great interest, and the application of Maillard reaction chemistry may provide some assistance by providing desirable notes such as "savory", "meaty", and "toasted".

Reactions between ribose or glucose and cysteine under aqueous conditions have been studied extensively over the past 10 years (e.g., refs *3–10*). The effect of pH on volatiles from ribose and cysteine has also been reported (*6*). More recently, the same precursors have been reacted in reduced-moisture or dry systems (*11–15*). In all cases, sulfur compounds were major reaction products, but the relative importance of different chemical classes and of individual compounds varied according to the sugar and to temperature, time, and moisture conditions. This is reflected in the key contributors to flavor in the different systems (*7, 8, 15*).

None of the model systems described above was heated under conditions representative of those encountered during extrusion cooking. Riha et al. (*16*) extruded wheat flour mixed with cysteine and reported sulfur compounds (mainly thiazoles) as the major volatile compounds. Recently, Farouk et al. (*17*) have studied

the effects of different amino acids extruded with wheat flour and glucose on color, odor, and volatile generation. They showed that pyrazine production increased in the presence of all amino acids except cysteine, which enhanced the formation of sulfur compounds. In a sensory study, Bredie et al. (*18*) established that extruding wheat starch or wheat flour with cysteine plus either xylose or glucose results in popcorn, nutty/roasted, puffed wheat, savory, and sulfur-like notes.

The aim of the study reported here was to examine the effects of temperature and extruder feed pH on the profile of volatile compounds produced in cysteine/reducing sugar/starch mixes.

EXPERIMENTAL PROCEDURES

Materials and Reagents. Extruder feeds were prepared from L-cysteine (98%), D-glucose (99%), and D-xylose (99.5%) from Sigma Chemical Co. (Poole, U.K.) and soft wheat starch (Abrastarch) from ABR Foods (Corby, U.K.). The starch had a moisture content of 11.1% (w/w) and a low nitrogen content (<0.15% w/v). Sodium hydroxide was purchased from BDH Chemicals Ltd. (Poole, U.K.).

Preparation of Extrudates. Homogeneous extruder feeds were prepared by premixing cysteine and either xylose or glucose with 1 kg of starch and adding this mixture to the remainder of the starch in a ribbon blender to give a final concentration of 0.044 mol/kg with respect to both the amino acid and sugar. Feeds were cooked in an APV Baker (Peterborough, U.K.) MPF 50D corotating twin-screw extruder to give expanded products. Significant operating conditions were as follows: feed rate, 600 g/min; modal residence time, 35 s; screw speed, 350 rpm; target die temperature, 120, 150, or 180 °C; moisture content, 18%. The pH of the feedstock before extrusion was adjusted to three different levels (7.5, 6.5, and 5.5) by the addition of 34.2, 23.4, and 19.7 g of sodium

* Author whom correspondence should be addressed (telephone +44 118 931 8730; fax +44 118 931 0080; e-mail j.m.ames@afnovell.reading.ac.uk).
† The University of Reading.
‡ Campden and Chorleywood Food Research Association.

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hydroxide per liter of extruder water feed. Full experimental details have been reported previously (*18*, *19*). Immediately following preparation, extrudates were ground to powders and packed into polyamide-polyethylene laminate bags (Optivac, Vacuum Packaging International), hermetically sealed, and stored at −20 °C for no more than two months.

pH Measurements. The pH of the extrudates was based on the AOAC method for flour (*20*). Extrudate (5 g) was mixed with 20 mL of tap water (pH 7.3). After constant stirring for 30 min to give a homogeneous sample, the pH was measured.

Aroma Assessment. Aromas of powdered, dry extrudates (1 g) and moistened extrudates (1 g of extrudate and ∼2.5 mL of distilled water) in brown glass jars were informally assessed by a panel of five assessors who were untrained but who were experienced in flavor research. Assessors were free to choose any term they felt was appropriate to describe each sample.

Isolation of Volatile Compounds. A homogeneous mixture of powdered extrudate (10 g) and distilled water (20 mL) was placed in a 250 mL conical flask fitted with a Drechsel head and a glass-lined stainless steel tube containing 6 mg of Tenax TA (SGE, Milton Keynes, U.K.). Oxygen-free nitrogen (40 mL/min) was passed through the flask and the Tenax tube for 1 h with the flask maintained at 37 °C. The Tenax tube containing the volatile compounds was then connected directly to the nitrogen supply for 5 min, to remove residual water. 1,2-Dichlorobenzene (65 ng in 1 µL of diethyl ether), internal standard, was injected onto the front end of the Tenax tube, under slight vacuum, immediately prior to analysis. Triplicate isolates were prepared for each set of extrusion conditions and blank isolations were also performed using an empty sample flask.

Gas Chromatography—Mass Spectrometry (GC-MS). Analyses were performed using a Hewlett-Packard (Bracknell, U.K.) 5972A mass spectrometer, interfaced with an HP 5890 gas chromatograph, connected to a PC loaded with HP G1034C (version C.01.05) GC-MS workstation software. Tenax tubes, containing the sorbed volatile compounds, were desorbed onto the front end of an ultralow-bleed GC column [50 m long × 0.32 mm i.d., coated with a 0.5 µm film of BPX5 (SGE)] by means of a modified Unijector (SGE). Thermal desorption was carried out at 250 °C for 5 min with the GC column oven held at 0 °C, by means of a subambient accessory, and a helium flow rate of 1.6 mL/min. Following desorption, the column temperature was increased to 60 °C over 1 min, and GC-MS was performed using the following conditions: carrier gas, helium at 1.6 mL/min; temperature program, 60 °C for 5 min, increased to 250 °C at 4 °C/min and held at 250 °C for 10 min; ionization mode, electron impact; electron energy, 70 eV; ion source temperature, 175 °C; ionization current, 50 µA; scan speed, 1.44 scans/s; mass range, 29−300 amu. Compounds were identified by comparing their mass spectra to those held in the mass spectrometer data system library and other libraries (e.g., refs *21* and *22*). Semiquantitative data were obtained from the mass spectral integration report, with reference to the internal standard. Experimental linear retention indices (LRI) were calculated with reference to the retention times of a series of standard alkanes (C_6−C_{22}), run under the same GC−MS conditions, and compared to those of authentic compounds or published in the literature (*23*, *24*). When both the MS and LRI data were consistent with those in the literature or obtained for authentic compounds, identities were considered to be positive. When only MS data were available, identities were considered to be tentative.

RESULTS AND DISCUSSION

The measured variables for all nine sets of extrusion conditions and both sugar−cysteine combinations are shown in Table 1. Specific mechanical energy (SME) values give a measure of the energy to which each product has been subjected. Values generally decreased with temperature for each pH value and decreased with pH for each temperature setting. Product temperature

Table 1. Measured Processing Parameters for Cysteine/Sugar/Starch Extrudates

sugar, target die temp, and pH	extrudate pH	product temp (°C)	die pressure (MPa)	SME (kJ/kg)
glucose				
120 °C, pH 7.5	6.10	120	2.73	673
150 °C, pH 7.5	5.91	148	2.69	603
180 °C, pH 7.5	5.83	182	2.31	534
120 °C, pH 6.5	4.06	125	2.17	700
150 °C, pH 6.5	4.36	154	1.53	479
180 °C, pH 6.5	4.67	194	1.33	415
120 °C, pH 5.5	3.55	117	2.29	578
150 °C, pH 5.5	3.26	146	1.09	425
180 °C, pH 5.5	3.28	173	0.97	371
xylose				
120 °C, pH 7.5	5.60	118	2.87	748
150 °C, pH 7.5	5.50	153	2.05	598
180 °C, pH 7.5	5.40	174	1.24	501
120 °C, pH 6.5	3.98	128	2.20	723
150 °C, pH 6.5	3.96	164	1.28	484
180 °C, pH 6.5	3.90	182	1.20	462
120 °C, pH 5.5	3.10	115	2.30	696
150 °C, pH 5.5	3.09	150	0.50	417
180 °C, pH 5.5	3.13	177	0.54	393

and pH differed from target values and varied between the two sugars. Product temperature ranged from −5 to +14 °C of the target value. The pH of the product always decreased compared to that of the feed; the pH drop was more pronounced at higher temperatures and was usually greater for xylose.

Aroma Assessment. Over 30 different terms were used to describe the aroma of extrudates prepared using each sugar (Tables 2 and 3). Across all of the temperature/pH combinations for both sugars, terms allied to sulfur (e.g., egg, onion, meaty) and cereal-like terms (e.g., puffed wheat, bread, popcorn) were applied. Meaty terms were used more frequently for samples processed at higher temperature or lower pH or prepared using xylose rather than glucose. Samples prepared using glucose were more frequently described as "biscuity" and "nutty". The intensity of the odor increased with pH for samples prepared at the same temperature and using the same sugar. "Burnt", "roast", and "biscuit" terms were used more frequently to describe samples processed at higher temperature, whereas "fruity" descriptors were applied more often to the lower temperature samples. Moistening the extrudates resulted in samples in a state physically similar to that of samples during the isolation of volatile compounds and to food in the mouth. Moistening samples reduced the use of the terms "egg" and "sulfur" and increased the frequency of the terms "onion", "roast", "toast", and "burnt". Bredie et al. (*18*) applied descriptive sensory profiling to two extrudates prepared from wheat starch, cysteine, and either xylose or glucose but processed using a residence time of 45 s (compared to 35 s used here). Their glucose product temperature was 157 °C and its pH was 6.4, whereas their xylose material had a temperature of 154 °C and a pH of 6.1. Significant differences were obtained for the two extrudates for the attributes "wet washing" and "cooked milk", which scored higher for the sample prepared from glucose (*18*).

GC−MS. Eighty compounds belonging to 11 chemical classes and 38 compounds from 9 classes were identified in the glucose and xylose extrudates, respectively (Tables 4 and 5). (No alicyclic compounds or pyridines were identified from the xylose samples.) Three miscellaneous compounds were also identified. The rel-

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Table 2. Descriptors Applied to Cysteine/Glucose/Starch Extrudates

target product temp (°C)	pH 7.5		pH 6.5		pH 5.5	
	dry	wet	dry	wet	dry	wet
120	sulfur, egg, biscuity, perished rubber, cake-like, dough, warm, onion	puffed wheat, onion, cereal, toasted popcorn, sweet, strong, warm, musty, roasted, grilled corn	sulfur, egg, acidic, apples, sweet, burnt	yeasty/fruity, acrid, plasticine/varnish, sweet, strong, meaty, acid, toast, cereal	egg, sulfur, sweet, candy, cheesey	roasted meat, stewed fruit, sweet, plasticine, cheese, savory, acrid, bread, cereal, popcorn
150	sulfur, egg, biscuity, sweet, toast, burnt, bread, puffed wheat, cornflakes, popcorn roasted	puffed wheat, onion, cereal, biscuity, acid, bread, acrid, weak meaty	sulfur, egg, apples	yeast/fruity, acrid, sweet, plasticine/varnish, sulfury, onion, burnt, acid, meaty, rubber, dentist drilling	egg, sulfur, sweet, roasted meat, rotten, savory, mildly acidic, apples, dentist drilling, acrid	roasted meat, stewed fruit, perished rubber, yeast, plasticine, sulfur, mildly burnt
180	sulfur, egg, biscuity, meaty, fruity, puffed wheat, gravy browning, sweet, popcorn	puffed wheat, onion, meaty, old cooking oil, roasted/nutty, acrid, cabbagey, stale, sulfur, garlic, burnt, popcorn, bread, grilled corn	sulfur, egg, garlic, meat-like	yeast/fruity, acrid, sulfur, burnt, cereal, bread, stale, raw onion, roasted/nutty	egg, sulfur, sweet, acidic, apples, dentist drilling, acrid, savory	roasted meat, stewed fruit, cereal, sulfur, wet washing, stale, acidic, popcorn, bread, acrid, dentist drilling, warm, fresh yeast, paint/varnish
common terms	sulfur, egg, biscuity	puffed wheat, onion	sulfur, egg	yeast/fruity, acrid	egg, sulfur, sweet	roasted meat, stewed fruit

Table 3. Descriptors Applied to Cysteine/Xylose/Starch Extrudates

target product temp (°C)	pH 7.5		pH 6.5		pH 5.5	
	dry	wet	dry	wet	dry	wet
120	puffed wheat, cereal, sulfur, egg, rubber, acidic	puffed wheat, cooked meat, slightly acidic, varnish, sweet, cereal, bread, apples	burnt, meaty, acid, sulfur, sweet, egg	puffed wheat, burnt varnish, sharp, sulfur, burnt, corn, bread, roasted	meat, burnt, weak, green apples, wet paint, acidic, roast, sweet, egg	puffed wheat, meat burnt, toast, weak acid, sulfur, old cooking oil, fruity, apples, corn, sweet, putty, roast, acrid
150	puffed wheat, cereal, sulfur, biscuit, burnt, acrid, sharp, onion-like, meaty, sweet	puffed wheat, cooked meat, grilled corn, raw onion, burnt, bread, sharp, roast	burnt, meaty, acid, sulfur, garlic, cereal, acrid, paint	puffed wheat, burnt varnish, sharp, varnish, rubber fruity/ yeasty, roast, bread, sulfur, corn	meat, burnt, weak, sulfur, fatty	puffed wheat, meat, burnt toast, wak, sulfur, roasted, onion, bread
180	puffed wheat, cereal, sulfur, egg, meaty, biscuit, rubber, slightly apples	puffed wheat, cooked meat, sharp, onion, burnt, acrid, stale, acid, metallic	burnt, meaty, acid, toast, acrid, garlic, wet paint, metallic, rubbery, egg	puffed wheat, burnt varnish, sharp, acrid, fruity/yeasty, cereal, onion, toast, stale	meat, burnt, weak, sulfur, biscuit, rubber, onion	puffed wheat, meat, burnt, toast, weak, onion, sharp, rubber
common terms	puffed wheat, cereal, sulfur	puffed wheat, cooked meat	burnt, meaty, acid	puffed wheat, burnt varnish, sharp	meat, burnt, weak	puffed wheat, meat, burnt, toast, weak

ative abundances (RAs) of the classes of compounds at each set of processing conditions are shown in Figures 1−4.

The grand total amount of all compounds was often higher for xylose extrudates, compared to those containing glucose, prepared under the same conditions, especially at 180 °C, and it is well-known that pentoses, such as xylose, participate in the Maillard reaction at a greater rate than hexoses, such as glucose (*25*). In general, amounts of each chemical class increased with temperature, in line with a previous study on extruded maize flour (*19*). For both sugars, grand total yields were highest for the sample prepared at 180 °C and pH 7.5, although some individual compounds did not follow this rule. Total yields were generally lowest for combinations of 120 or 150 °C and pH 5.5 or 6.5.

Excluding miscellaneous compounds, classes that accounted for >20% RA in at least one glucose sample were aliphatic sulfur compounds, thiophenes, and pyrazines, whereas thiazoles were at slightly lower levels (0−14% RA) and sulfur-substituted furans accounted for 4−9% of the total aroma (Figures 1 and 2). For xylose

extrudates, chemical classes (excluding miscellaneous compounds) that accounted for >20% of the RA in at least one sample were non-sulfur-containing furans, thiophenes, and sulfur-containing furans. Pyrazines were in fourth position (1−11% RA) (Figures 3 and 4). Relative amounts of the three most abundant classes (normalized to thiophenes) for the glucose and xylose samples are shown in Figures 5 and 6, respectively. Relative amounts of the three chemical classes varied considerably with processing conditions for both glucose and xylose samples. The data demonstrate the unique effect exerted by each set of processing conditions on the profile of volatile compounds.

Sulfur compounds are always major reaction products of heated cysteine/sugar model systems (*5*). Forty-four of the components reported from the glucose extrudates contained sulfur, and their total amounts ranged from 78 ng/10 g of extrudate (150 °C, pH 6.5) to 1978 ng/10 g of extrudate (180 °C, pH 7.5). The RA of sulfur compounds ranged from 51% (120 °C, pH 7.5) to 72% (120 °C, pH 5.5). In comparison, for xylose, 21 sulfur compounds were identified, and total amounts ranged

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Table 4. Volatile Compounds[a] Identified in the Headspace of Cysteine/Glucose/Starch Extrudates Prepared at Different Temperature and pH Combinations

	LRI		pH 7.5			pH 6.5			pH 5.5		
class and compd	exptl[b]	lit.[c]	180 °C	150 °C	120 °C	180 °C	150 °C	120 °C	180 °C	150 °C	120 °C
carbonyls											
2-butanone	604	604	4	2							
2-methylbutanal	625	652	1	2							
2-pentanone	680	683	15	11	6	4	1	2	7		
pentanal	690	689					1			2	
2,3-pentanedione	709	702	6								
3-hydroxy-2-butanone	720	711		4	4	3					
total carbonyls			26	19	10	7	2	2	7	2	0
aliphatic S compds											
3-mercapto-2-butanone	823	821	438	560	128	46	11	20	90	190	67
3-mercapto-2-pentanone	913	898	39	27	5	5		4			
2-mercapto-3-pentanone	921	904	18	25	6						
bis(1-methyl-2-oxopropyl) disulfide	1478	1476	1	2	2	2					
total aliphatic S compds			496	614	141	53	11	24	90	190	67
alicyclic S compds											
3-methyl-1,2-dithiolan-4-one	1098	1102	39	23	9	21	1	9	15	1	
1,2,4-trithiolane	1157		8	6	3						
3,5-dimethyl-1,2,4-trithiolane	1172		13	3							1
1,3,5-trithiane	1271		4								
3-methyl-1,2,4-trithiane	1287		8	1							
total alicyclic S compds			72	33	12	21	1	9	15	1	1
furans (non-S-containing)											
2-methylfuran	608	606	1								
2,5-dimethylfuran	701	707	2	2			1			2	1
2-ethylfuran	707	705	10	2							
2-vinylfuran	710	720	10	3	1						
2-furfural	838	848				18	5	11	24	8	2
2-furanmethanol	863	867	10	2		3					
2-pentylfuran	990	995	38	68	70	17	8	53	25	34	
total furans (non-S-containing)			71	77	70	39	14	64	49	44	3
pyrroles											
pyrrole	744	748	212	2		7	2	4	34	4	13
1-ethyl-1*H*-pyrrole	818	817	18	13		5		6			
2-methyl-1*H*-pyrrole	850	853	76	136	74	16	4	6			
2-ethyl-1*H*-pyrrole	934	929	8	3	5						
3-ethyl-1*H*-pyrrole	950		5	4							
a trimethylpyrrole	1026		10								
1-(2-furanylmethyl)-1*H*-pyrrole	1195	1196	4	1							
total pyrroles			333	159	79	28	6	16	34	4	13
thiophenes											
thiophene	665	672	72	26	5	21	8	9		2	1
2,3-dihydrothiophene	768		46	8							
2-methylthiophene	771	780	112	56	16	13	4	8	12	6	3
3-methylthiophene	783	784	124								
2-ethylthiophene	872	874	16	10	7	15	3	6	43		
2,5-dimethylthiophene	877	878	20	25	13	13	3	13	10		
2,3-dimethylthiophene	898	896	28	25							
2-vinylthiophene	915		9	4		4		3			
2,4-dimethylthiophene	982		5	3		3					
2(or 3)-thiophenethiol	988		244	196	22	77	25	69	34	5	12
2-thiophenecarboxaldehyde	1001	1000	32	21	5						
2-methyl-3-thiophenethiol	1066		47	48	3	6		6			
2(or 3)-(methylthio)thiophene	1104		15	5	4						
3-acetylthiophene	1107		7	4	4						6
3-methyl-2-thiophenecarboxaldehyde	1109	1119	7	4	3						
2-acetylthiophene	1112	1113	13						2		
5-methyl-2-thiophenecarboxaldehyde	1141	1133	50	14	9	16		12	23	3	
2-pentylthiophene	1165	1165		3	4						
2,3-dihydro-6-methylthieno[2,3*c*]furan	1213		3			10					
thieno[2,3*b*]thiophene	1239		20	4		46					
2-(2-thienyl)furan	1244		3			8			3		
thieno[3,2*b*]thiophene	1282	1248	3								
total thiophenes			876	456	95	232	43	126	133	16	16
S-substituted furans											
2-methyl-3-furanthiol	873	870	31	37	15	7	3	6		6	
2-furanmethanethiol	918	913	106	77	18	18	4	18	32	16	12
total S-substituted furans			137	114	33	25	7	24	32	22	12
pyridines											
pyridine	741	750	7	6	4	1					
2-methylpyridine	824	818	22	16	6	4				12	
total pyridines			29	22	10	5	0	0	0	12	0

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Table 4 (Continued)

class and compd	LRI exptl[b]	LRI lit.[c]	pH 7.5 180 °C	pH 7.5 150 °C	pH 7.5 120 °C	pH 6.5 180 °C	pH 6.5 150 °C	pH 6.5 120 °C	pH 5.5 180 °C	pH 5.5 150 °C	pH 5.5 120 °C
pyrazines											
pyrazine	736	743	82	17	4	5					
methylpyrazine	830	826	274	138	25	18	4	8	12	12	5
ethylpyrazine	923	924	266	140	19	47	2	12	108	32	8
2,3-dimethylpyrazine	931	920	54	25	5						
vinylpyrazine	946	948	31	5							
2-ethyl-5-methylpyrazine	1006	1014	50	14	4	3					
2-ethyl-6-methylpyrazine	1008	1016	54	21		2					
2,6-diethylpyrazine	1089		8								
2,5-diethylpyrazine	1091		4								
2,3-dimethyl-5-ethylpyrazine	1097		16	4							
5-methyl-(5*H*)-6,7-dihydrocyclo-pentapyrazine	1158		12	5	4	4		2			
3,5-diethyl-2-methylpyrazine	1165		4	3						21	
total pyrazines			855	372	61	79	6	22	124	65	13
oxazoles											
4,5-dimethyloxazole	750		154	223	74	26	3	6	23	1	1
trimethyloxazole	852	858	10								
total oxazoles			164	223	74	26	3	6	23	1	1
thiazoles											
thiazole	730	715	82	17	4	5	2	4	5		
2-methylthiazole	815		42	51	15	16	8	18	23		
4-methylthiazole	861		31	16	7	4					
2-methylthiazolidine	893		8	5	4						
2-ethylthiazole	906		14	9	4	4					
4,5-dimethylthiazole	947	943	25	6	5	3	4	24	5	2	
5-ethylthiazole	955	959	31	6	6	8	2	4	6		
trimethylthiazole	1007	1005	27	11							
5-ethyl-2-methylthiazole	1022		84	15	5	15					
2-acetylthiazole	1036	1027	40	9	5	20					
2,5-dimethyl-4-ethylthiazole	1086		13	12	13				7		
total thiazoles			397	157	68	75	16	50	46	2	0
miscellaneous											
hexanenitrile	884	884	17	62	22	9	7	23	4	5	8
limonene	1032	1033	6	11	7	7		6	7		
total miscellaneous			23	73	29	16	7	29	11	5	8
grand total			3479	2319	682	606	116	372	564	364	134

[a] Amounts of compounds are quoted in ng/10 g of extrudate. Figures quoted are the means of triplicate analyses. [b] Calculated linear retention indices for identified compounds. [c] Linear retention indices obtained for authentic compounds analyzed on the same GC column or from the literature (*23*, *24*).

from 52 ng/10 g of extrudate (150 °C, pH 5.5) to 12310 ng/10 g of sample (180 °C, pH 7.5). The RA of sulfur compounds ranged from 5% (180 °C, pH 5.5) to 66% (150 °C, pH 6.5).

3-Mercapto-2-butanone and 3-mercapto-2-pentanone were prominent in extrudates prepared from both sugars, with yields generally increasing with temperature and pH. The related compound 2-mercapto-3-pentanone was also identified in the glucose samples prepared at pH 7.5, together with the oxidation product of 3-mercapto-2-butanone, bis(1-methyl-2-oxopropyl) disulfide, also present at 180 °C and pH 6.5. Aliphatic sulfur compounds were one of the four most abundant classes for glucose (RA = 6.5–52%) (Figure 1) but were never above fourth position for xylose and were not identified under three sets of conditions (RA = 0–7.6%) (Figure 3).

3-Mercapto-2-butanone was first identified from butanedione and hydrogen sulfide by Takken et al. (*26*), and this compound and bis(1-methyl-2-oxopropyl) disulfide are major products of that reaction (*27*). Similarly, 3-mercapto-2-pentanone and 2-mercapto-3-pentanone form from 2,3-pentanedione and hydrogen sulfide (*26*, *27*). All three mercaptoketones identified in the extrudates were also reported as major reaction products in an aqueous cysteine/ribose system (*28*), whereas 3-mercapto-2-butanone accounted for 1.3% of the volatiles in an aqueous pH 6 glucose/cysteine system (*9*). In

contrast to the extrudates, levels of these compounds decrease with increasing pH in aqueous systems (*6*, *29*). They are key odorants in aqueous model systems prepared from both cysteine/ribose (*7*) and cysteine/glucose (*8*). They were not reported in reduced-moisture systems by Mottram and Whitfield (*11*, *12*) or Umano et al. (*13*) and make a lower contribution to the aroma of the reduced-moisture systems of Hofmann and Schieberle (*15*), compared to their aqueous solutions (*7*, *8*). 3-Mercapto-2-butanone and 3-mercapto-2-pentanone possess "sulfury, rotten" and "catty" aromas, respectively (*8*), and possess odor thresholds in air of 0.2–0.8 and 0.05–0.2 ng/L (*7*). These compounds are likely to contribute to the sulfury notes associated with the extrudates (Tables 2 and 3).

Alicyclic sulfur compounds were identified from only glucose samples, and 3-methyl-1,2-dithiolan-4-one was the most prominent representative, being identified under all sets of conditions, except 120 °C and pH 5.5. Amounts of alicyclic sulfur compounds usually increased with temperature and pH but were generally low, compared to most other classes. In contrast, aqueous systems based on cysteine and glucose or ribose produced alicyclic sulfur compounds as major reaction products (e.g., refs *3*–*5*, *9*, *28*), and heating such systems under reduced-moisture conditions resulted in their formation in even higher relative amounts (*11*–*13*). Nevertheless, they were not reported as key odorants

Table 5. Volatile Compounds[a] Identified in the Headspace of Cysteine/Xylose/Starch Extrudates Prepared at Different Temperature and pH Combinations

	LRI		pH 7.5			pH 6.5			pH 5.5		
class and compd	exptl[b]	lit.[c]	180 °C	150 °C	120 °C	180 °C	150 °C	120 °C	180 °C	150 °C	120 °C
carbonyls											
2-pentanone	680	683	98	12	6	40	12	26	11	7	26
2,3-pentanedione	709	702	151	14	10	48		13			26
total carbonyls			249	26	16	88	12	39	11	7	52
aliphatic S compds											
dimethyl disulfide	744	756	13								10
1-pentanethiol	816	822						16			
3-mercapto-2-butanone	823	821	721	43							
3-mercapto-2-pentanone	913	898	736	36	4	106		122			
total aliphatic S compds			1470	79	4	106	0	138	0	0	10
furans (non-S-containing)											
2,5-dimethylfuran	701	707							17		23
2-ethylfuran	707	705	98	7	13	25	28	39	11	6	28
2-furfural	838	848	1670	66	21	1804	93	580	844	76	522
2-pentylfuran	990	995	517	28	116	377	49	438	246	54	305
total furans (non-S-containing)			2285	101	150	2206	170	1057	1118	136	878
pyrroles											
2-methyl-1*H*-pyrrole	850	853	380	26	13						
3-ethyl-1*H*-pyrrole	950		35	2							
total pyrroles			415	28	13	0	0	0	0	0	0
thiophenes											
thiophene	665	672	178	10	4	67	38	19		2	20
2-methylthiophene	771	780	1487	106	62	280	65	264	17		135
3-methylthiophene	783	784	57			768	5			31	
2-ethylthiophene	872	874	32	1		20					
2(or 3)-thiophenethiol	988		103								
4,5-dihydro-2-methyl-3(2*H*)-thiophenone	996	1000		1		71	10	71	53	9	54
2-thiophenecarboxaldehyde	1001	1000				69					
2-methyl-3-thiophenethiol	1066		49	1	2	39		27			45
2-pentylthiophene	1165	1165	143		5	59	8	37	38	10	46
total thiophenes			2049	119	73	1373	126	418	108	52	300
S-substituted furans											
2-methyl-3-furanthiol	873	870	3038	171	44	604		764			400
2-furanmethanethiol	918	913	5346	341	66	1169	124				362
2-methyl-3-[(2-furanylmethyl)thio]furan	1503	1501			5		7	29			21
bis(2-methyl-3-furanyl)disulfide	1541	1547	20				4				
2-methyl-3-[(2-furanylmethyl)dithio]furan	1650	1649			8		7	13			
total S-substituted furans			8404	512	123	1773	142	806	0	0	783
pyrazines											
pyrazine	736	743	86	5	6	26					
methylpyrazine	830	826	872	56	9	135		7			
ethylpyrazine	923	924	708	4	7	80					
2-ethyl-6-methylpyrazine	1008	1016	16	2	2	70	5				
propylpyrazine	1010		316	9	21	66	4	133			
isopropylpyrazine	1060		42		6						
isopropenylpyrazine	1075	1092			9	100	9	50			47
3-ethyl-2,5-dimethylpyrazine	1081	1088	47			57	7	29	23	6	27
total pyrazines			2087	76	60	534	25	219	23	6	74
oxazoles											
4,5-dimethyloxazole	750		664	46	24	176					
thiazoles											
thiazole	730	715	86	5	6	29					
2-methylthiazole	815		195	14	29	135	23	161			82
4-methylthiazole	861		106	7							
total thiazoles			387	26	35	164	23	161	0	0	82
miscellaneous											
hexanal	796	787	1028	90	75	826	49	406	604	74	534
hexanenitrile	884	884	180	12	8	87	10	112	47	15	79
limonene	1032	1033	42	2	14	235	29	246	54	17	256
total miscellaneous			1250	104	97	1148	88	764	705	106	869
grand total			19260	1117	595	7568	586	3602	1965	307	3048

[a] Amounts of compounds are quoted in ng/10 g extrudate. Figures quoted are the means of triplicate analyses. [b] Calculated linear retention indices for identified compounds. [c] Linear retention indices obtained for authentic compounds analyzed on the same GC column or from the literature (*23, 24*).

of cysteine/reducing sugar mixtures heated under either aqueous or reduced-moisture conditions (*7, 8, 15*). The main precursors of alicyclic sulfur compounds are aldehydes and hydrogen sulfide (*30*). The formation of aldehydes via fragmentation of any sugar is favored by neutral/alkaline conditions, thus accounting for in-

creased yields of alicyclic sulfur compounds in the higher pH samples.

Twenty-two thiophenes were identified from glucose extrudates, whereas only nine are reported for xylose products. They made a greater contribution to the total volatiles for glucose samples (RA = 4.4−38.3%) (Figure

Volatiles from Extruded Cysteine/Sugar/Starch

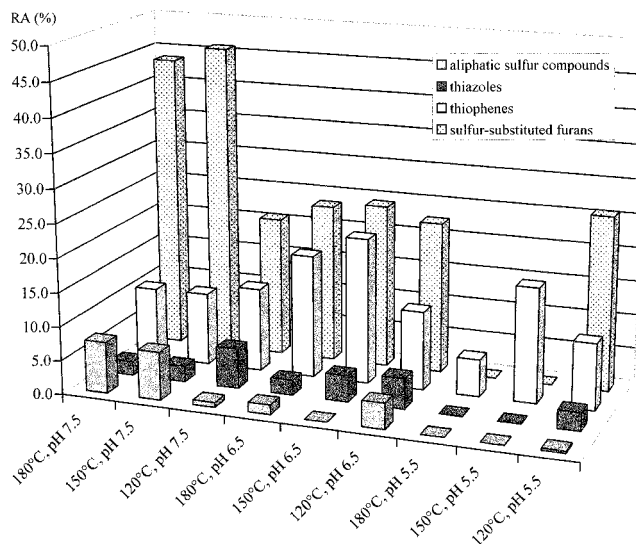*J. Agric. Food Chem.,* Vol. 49, No. 4, 2001 **1891**
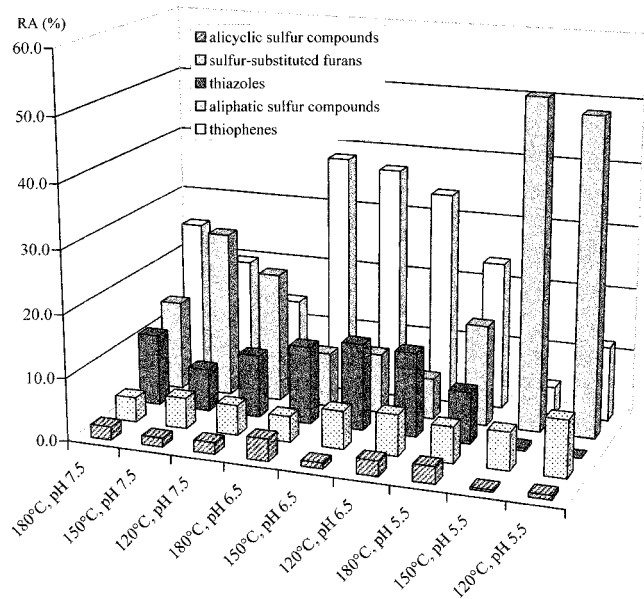
Figure 1. RAs sulfur-containing classes of compounds for cysteine/glucose/starch extrudates.
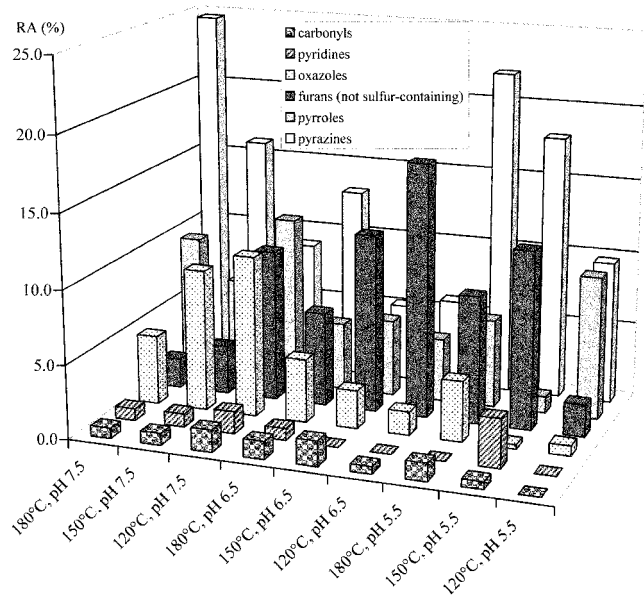
Figure 2. RAs of non-sulfur-containing classes of compounds for cysteine/glucose/starch/extrudates.

Figure 3. RAs of sulfur-containing classes of compounds for cysteine/xylose/starch extrudates.
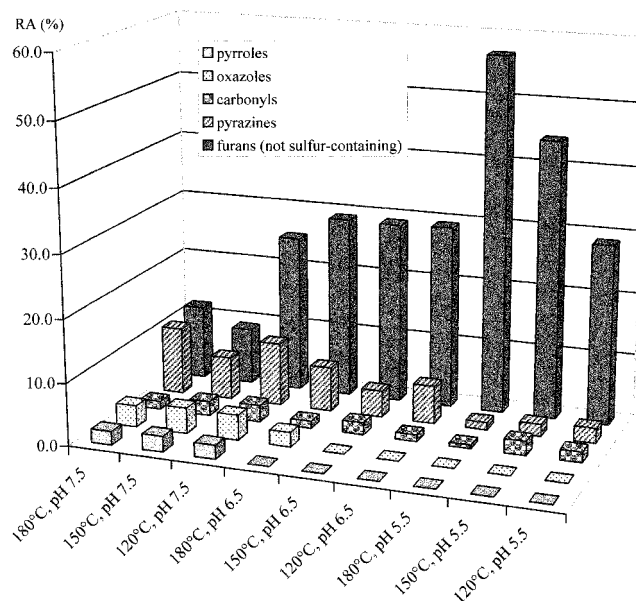
Figure 4. RAs of non-sulfur-containing classes of compounds for cysteine/xylose/starch extrudates.

1) than those prepared from xylose, for which they accounted for 5.5–21.5% of the total amount (Figure 3). Highest relative amounts were obtained under the same conditions (150 or 180 °C and pH 6.5) for both sugars, although absolute amounts were highest at 180 °C and pH 7.5. Thiophenes were a major class of reaction products when cysteine was heated with glucose or ribose under aqueous conditions (e.g., *3–5, 9, 28*), but in reduced-moisture systems they became relatively less important; for example, in aqueous cysteine/glucose systems they had RAs of 41% (*4*) and 17% (*9*), whereas the RA in a dry-heated cysteine/glucose system was 6% (*13*). Thiophenes of particular interest in the present study included the sulfur-substituted compounds and the bicyclic derivatives. 2(or 3)-Thiophenethiol and 2-methyl-3-thiophenethiol were identified in extrudates prepared from both sugars. The latter compound has a meat-like, sulfury odor and a low odor threshold in air of 0.0032–0.0128 ng/L (*7*). It has been identified in

aqueous (*28*) and reduced-moisture (*14*) cysteine/ribose systems. Bicyclic thiophenes were identified only in glucose extrudates. Such compounds have been reported in aqueous cysteine/glucose (*9*), aqueous cysteine/ribose (*3*), and low-moisture cysteine alone and cysteine/ribose (*11*) systems.

Sulfur-substituted furans accounted for up to 45.8% of the compounds identified from xylose extrudates, although they could not be identified in samples extruded at 150 or 180 °C and pH 5.5 (Figure 3). The most abundant representatives were 2-methyl-3-furanthiol (MFT) and 2-furanmethanethiol (FFT), and amounts increased markedly with both temperature and pH. These two compounds were identified at much lower levels in the glucose products. In addition, much lower levels of certain bicyclic compounds are reported under some sets of conditions for xylose.

The observed major differences in yields of FFT and MFT obtained for extrudates prepared using the two sugars are in line with data obtained for both aqueous and low-moisture systems based on cysteine and ribose

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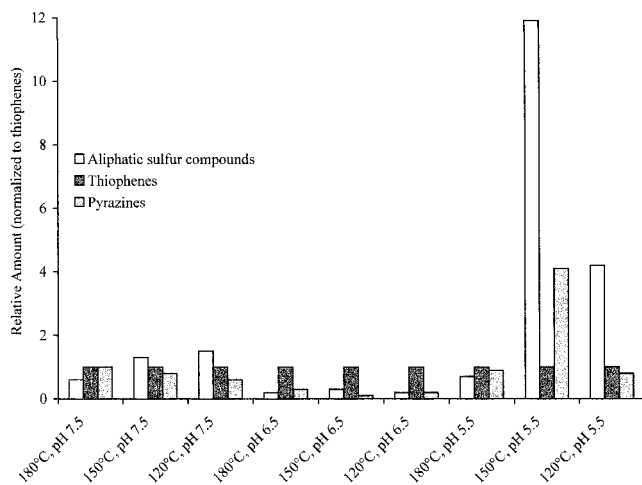
Figure 5. RAs (normalized to thiophenes) of aliphatic sulfur compounds, thiophenes, and pyazines for cysteine/glucose/starch extrudates.
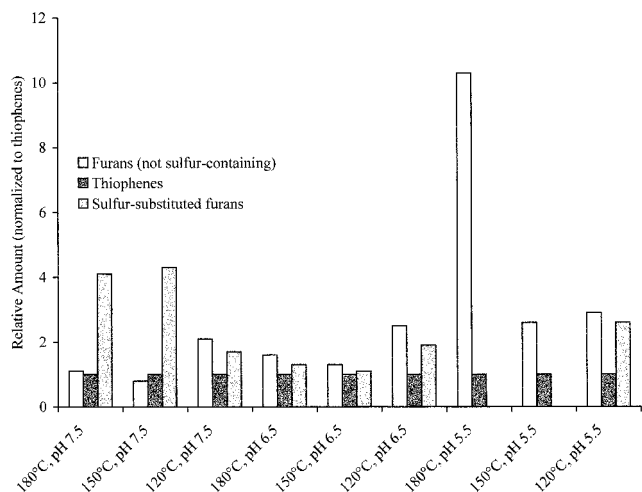
Figure 6. RAs (normalized to thiophenes) of non-sulfur-containing furans, thiophenes, and sulfur-containing furans for cysteine/xylose/starch extrudates.

or glucose (*14*). Moisture has an important effect on the formation of both compounds. Stable-isotope dilution analysis showed that when reduced-moisture pH 5 systems were heated at 180 °C for 6 min, amounts of FFT and MFT from the ribose system increased 8- and 1.3-fold, respectively, compared to aqueous pH 5 systems heated at 145 °C for 20 min. For glucose, the level of FFT halved and the level of MFT more than doubled in the pH 5 reduced-moisture system, compared to the aqueous pH 5 solution (*14*). In other studies, FFT and MFT accounted for 38 and 35%, respectively, of the total volatile compounds when ribose and cysteine were heated at 140 °C for 1 h in phosphate buffer, initial pH 5.7 (*3*), whereas only low levels were recovered in reduced-moisture systems (*11*). In aqueous or dry cysteine/glucose model systems, neither compound was reported (*4, 9, 13, 31*). The different reaction conditions and aroma isolation techniques appear to have dramatic effects on recoveries.

pH has also been reported to affect dramatically yields of FFT and MFT. On heating aqueous systems in the pH range 3−7 at 145 °C for 20 min, levels of both compounds decreased with increasing pH, when ribose was the sugar, but greatest yields for glucose were obtained at pH 5 (*14*). Meynier and Mottram (*6*) also

reported decreased amounts of these compounds with increasing pH over the range 4.5−6.5. The different effect of pH in the glucose systems was shown to be due to different formation mechanisms predominating involving hydroxyacetaldehyde and mercapto-2-propanone (*14*). Tables 4 and 5 show that higher levels of FFT compared to MFT were obtained for all samples, with the exception of the 120 °C, pH 6.5 and 5.5, xylose extrudates. For extrudates prepared from either sugar, levels of FFT were about twice as great as those of MFT. For xylose, this is in closer agreement with the data for a low-moisture pH 5 cysteine/ribose system heated at 180 °C for 6 min, for which levels of FFT were ∼4-fold as great as those of MFT (*14*), than with data for aqueous systems, for which the level of MFT was ∼1.5−3-fold greater than that of FFT. In contrast, the data for the glucose extrudate agree more closely with data for the aqueous model system (∼1.5−2-fold more FFT than MFT) compared to the low-moisture mixture (∼4-fold more MFT than FFT) (*14*). Stable-isotope dilution studies have demonstrated the formation of high levels of FFT from 2-furfural and cysteine (*32*). 2-Furfural, a major pentose degradation product, was recovered in high yields from the xylose extrudates and is likely to be a major precursor of FFT in these samples. The formation of 2-furfural from starch extruded alone (feed pH 5.0) at 150 °C, at a level of ∼2 mg/g of extrudate, has been demonstrated (*33*). Thus, it is also likely to be an important precursor of FFT in the glucose extrudates. This would account for the observed differences between levels of FFT and MFT in the glucose extrudates and in cysteine/glucose systems heated by other means in the absence of starch (*14*) as well as the similar observed FFT/MFT ratios for extrudates prepared from the two sugars (Tables 4 and 5).

FFT is a key contributor to the aroma of aqueous and reduced-moisture ribose/cysteine and glucose/cysteine model systems (*7, 8, 15*), and MFT is also a key aroma compound of an aqueous system prepared from ribose and cysteine. These compounds possess very low odor thresholds in air of 0.0025 ng/L (*7*). FFT possesses an intense roasted and coffee-like odor and contributes to the aroma of commodities such as coffee, popcorn, and roasted sesame seeds (*14*). MFT has a meat-like odor (*7*) and contributes to cooked beef aroma (*34*). Bis(2-methyl-3-furanyl) disulfide, with a meaty aroma, showed a high flavor dilution factor in an aqueous ribose/cysteine model system (*7*). These compounds undoubtedly contribute importantly to the cereal-like and meaty aromas of the extrudates (Tables 2 and 3).

RA values for thiazoles were much higher for glucose samples (up to 13.8%) compared to xylose (up to 5.9%) (Figures 1 and 3). Only three representatives were identified from xylose extrudates, whereas the range was much wider (11 compounds) when glucose was used. Levels of thiazoles generally increased with pH, in line with the literature for aqueous systems (*6, 29*); for example, in a cysteine/ribose system, they were not detected at pH 4.5 but had an RA of 16% at pH 6.5. Thiazoles were identified in much higher relative amounts in reduced-moisture cysteine/sugar model systems (*11−13*), compared to aqueous solutions; for example, they had an RA of 13% in an aqueous pH 7.5 cysteine/glucose system heated at 180 °C for 1 h (*4*), but their RA was 48% for a dry cysteine/glucose system heated at 180 °C for 2 h, largely due to 2-methylthia-zolidine at 38% (*13*). Thiazoles may form from α-dicar-

bonyls, hydrogen sulfide, and ammonia (*26*), and both the Strecker degradation of amino acids and sugar fragmentation lead to these precursors and are favored by elevated pH. However, thiazoles also form on the thermal degradation of cysteine alone (*35*). They are likely to contribute to the terms "puffed wheat", "popcorn", and "cereal" listed in Tables 2 and 3.

Levels of pyrazines increased with temperature and pH, in agreement with the literature (*29, 33*), and their contribution to the total volatiles ranged from 5.2 to 24.6% for glucose extrudates but from only 1.2 to 10.8% for xylose samples (Figures 2 and 4). In contrast, pyrazines accounted for <1% of the volatile products of an aqueous cysteine/ribose system (*3*), and no pyrazines were identified from a pH 6 aqueous glucose/cysteine system heated at 160 °C for 2 h (*9*), although, in a higher pH aqueous system (pH 7.5) of cysteine and glucose heated at 180 °C for 1 h, pyrazines accounted for 12% of the total volatiles (*4*). They were not identified among the key aroma compounds when cysteine was heated with ribose or glucose in aqueous solution (*7, 8*), but their formation was favored in systems of reduced moisture (*15*). When dry or low-moisture systems were heated, 4.7% of the reaction products were pyrazines when the sugar was glucose (*13*) and low levels of pyrazines were identified from ribose/cysteine in the presence of cellulose (*12*). Levels of pyrazines decreased in an extruded cysteine/glucose/wheat flour mixture compared to glucose/wheat flour or wheat flour extruded on its own (*17*). Pyrazines may contribute to the toasted, roasted, nutty, and burnt notes associated particularly with the samples extruded at 180 °C (Tables 2 and 3).

Levels of non-sulfur-containing furans were much higher from samples prepared from xylose, largely due to the increased level of 2-furfural. The yield of this compound was greatest at 180 °C and pH 6.5, and it accounted for 43% of the total volatiles at 180 °C and pH 5.5. It is well established that levels of 2-furfural increase with decreasing pH in aqueous systems (*6, 36*). Also, levels of 2-pentylfuran were often an order of magnitude higher for xylose extrudates, indicating a greater level of oxidation of the low level of lipid in the starch. The identification of 2-pentylthiophene and hexanal, which also form via lipid oxidation, only in xylose samples, supports this.

Relatively low levels of a range of carbonyl compounds were identified, especially from glucose. Some pyrroles and oxazoles were identified, total amounts increasing with temperature and pH. Pyridine and 2-methylpyridine were identified in some glucose samples.

In conclusion, amounts of most compounds generally increased with both temperature and extruder feed pH. Yields of chemical classes were usually higher for extrudates prepared using xylose than those using glucose, under the same processing conditions. Thiophenes and pyrazines were among the most abundant classes of compounds for samples prepared from both sugars. In addition, aliphatic sulfur compounds and thiazoles featured strongly in glucose extrudates, whereas non-sulfur-containing furans and sulfur-containing furans were present at relatively high levels in the xylose products. FFT and MFT were identified in both glucose and xylose samples, levels of FFT being about twice those of MFT for both sugars. 2-Furfural (derived from xylose and/or starch degradation) and cysteine are likely to be its main precursors. The profiles of reaction products were different from those reported in the literature for aqueous or reduced moisture cysteine/sugar systems. Further work is required to understand better the effects of extrusion variables on the course of the Maillard reaction and to be able to apply this knowledge subsequently to the prediction and control of flavor generation in extruded foods.

ABBREVIATIONS USED

FFT, 2-furanmethanethiol; GC-MS, gas chromatography−mass spectrometry; MFT, 2-methyl-3-furanthiol; RA, relative abundance; SME, specific mechanical energy.

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