normal varieties. This could be the reason why sorghum farmers in Ethiopia claim a special sweet flavor for their high-lysine sorghum varieties. This acclaimed taste coupled with the superior protein qualtiy and nutritional value (Ejeta and Axtell, 1987) provide a nutritional basis for the established tradition of consuming the *hl* varieties exclusively at the dough stage in Ethiopia. Further, such combinations of desirable components make the *hl* lines from Ethiopia unique when compared with any of the other known endosperm mutants in corn and sorghum.

Registry No. Starch, 9005-25-8; amylose, 9005-82-7; sucrose, 57-50-1; lysine, 56-87-1.

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Effect of Lipids and Carbohydrates on Thermal Generation of Volatiles from Commercial Zein

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Model systems composed of zein, regular and waxy corn starch, and corn oil were heated in an oven at 120 and 180 °C. The volatile compounds generated were analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). Maillard reaction products and carotenoid decomposition products increased in the presence of corn oil. Two pyrazines identified from the increased number of volatiles generated at the higher temperature were 2-methyl-3(or 6)-pentylpyrazine and 2,5-dimethyl-3-pentylpyrazine. These two pyrazines were characterized as lipid–protein–carbohydrate interaction products.

Thermal interactions between proteins, carbohydrates, and lipids in foods are complicated by extrusion processing. During extrusion, shear force and pressure, as well as temperature, influence the interactions. Protein–carbohydrate interactions during the heat treatment of foods have been given a great deal of attention, and the mechanism proposed by Hodge (1953) for the amino–carbonyl reaction of carbohydrates with proteins has been widely accepted. However, recent discoveries by Hayashi and Namiki (1980, 1981, 1986) indicate that free-radical products form during the early stage of the browning reaction of sugar–amino compounds. Lipids, especially the polyunsaturated lipids, are a well-known source of free radicals. As part of a larger cooperative effort to increase the current understanding of extrusion processing, the effects of corn oil and corn

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Table I. Compositions and Reaction Conditions Used for Model System Study

sample no.	composition: zein, g	regular corn starch, g	waxy corn starch, g	corn oil, g	water, %	temp, °C	reactn time, min
1A	100				30	120	30
1B	100				30	180	30
2A	100	40			30	120	30
2B	100	40			30	180	30
3A	100	40		5	30	120	30
3B	100	40		5	30	180	30
4A	100		40		30	120	30
4B	100		40		30	180	30
5A	100		40	5	30	120	30
5B	100		40	5	30	180	30

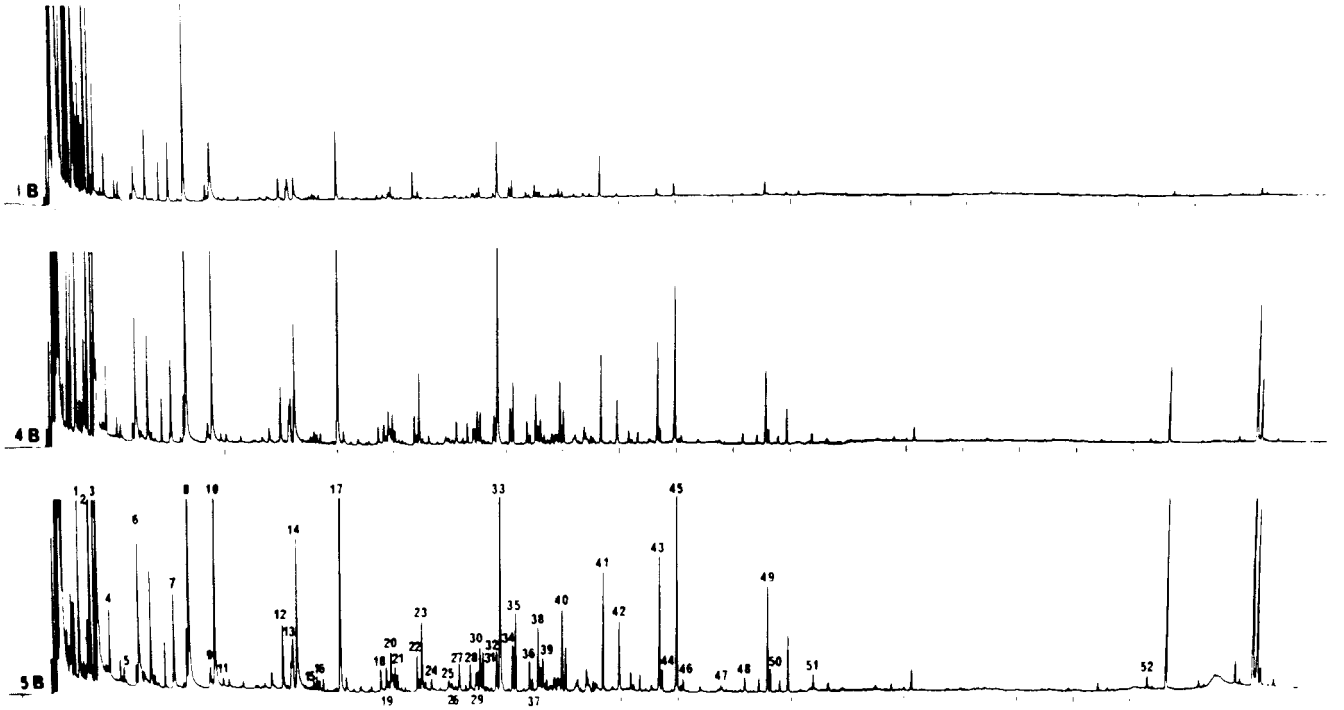

Figure 1. GC profiles of volatile compounds from model systems: (1B) zein; (4B) zein plus waxy corn starch; (5B) zein plus waxy corn starch and corn oil.

carbohydrates on the generation of volatiles from zein were examined over a range of temperatures applicable to the extrusion process.

EXPERIMENTAL SECTION

Materials. Zein was obtained from Sigma Chemical Co. (St. Louis, MO). Corn starch (regular and waxy maize) was obtained from National Starch and Chemical Corporation (Bridgewater, NJ). Regular maize has a relatively high content of amylose, the α-1,4-linked polymer of glucose. Waxy maize has a very high content of amylopectin, a branched polymer constructed of both α-1,4- and α-1,6-linked glucose units. Amioca, used in this study, is reported to be 98% amylopectin. Corn oil was obtained from Corn Products, CPC International (Englewood Cliff, NJ). The major fatty acids in fresh corn oil, as reported by Snyder and co-workers (1985), are linoleic acid (61%), oleic acid (25%), and palmitic acid (11%). Linolenic acid constitutes only 0.9% of the fatty acids.

Sample Preparation. Zein, regular or waxy corn starch, corn oil, and water were mixed in the appropriate ratios according to the following procedure. First the starch and then the corn oil were blended with the zein for uniform distribution. The water was added last with continuous mixing of the dry components. The compositions of the model systems are listed in Table I. Each mixture was kneaded in a Hobart mixer for 10 min and then was wrapped with two layers of aluminum foil and heated in an oven at 120 or 180 °C for 30 min. The doughlike heated product was cut into pieces and ground into powder in a coffee mill with dry ice.

Three additional control systems, 5 g of corn oil and 30 g of water in 100 g of waxy corn starch, 5 g of corn oil and 30 g of water in 100 g of inert diatomaceous earth, and 30 g of water in 100 g of waxy corn starch, were prepared as described for the model systems but were heated only at 180 °C.

Extraction of Volatile Compounds. A 100-g powdered sample was extracted with 500 mL of redistilled ethyl ether twice, and the extract was filtered. The yellow filtrate was steam-distilled on a Nickerson-Likens apparatus (Kontes, Vineland, NJ). The distillate was then dried with anhydrous sodium sulfate and concentrated with a spinning-band still to a final volume of 100 μL.

Gas Chromatographic Analysis. A Varian 3400 gas chromatograph equipped with a flame ionization detector and a nonpolar fused silica capillary column (60 m × 0.25 mm (i.d.); 0.25-μm thickness, SPB-1; Supelco, Inc.) was used to analyze the volatile compounds isolated from the heated model systems. The operation conditions were as follows: injector temperature, 250 °C; detector temperature, 260 °C; helium carrier flow rate, 1 mL/min; split

ratio, 100:1; temperature program, 35 °C for 10 min, 35–235 °C at 2 °C/min, and held at 235 °C for 40 min. Linear retention indices for the volatile compounds were calculated with use of *n*-parrafin (C_6–C_{22}; Alltech Associates) as references (Majlat et al., 1974).

GC/MS Analysis. The concentrated samples were analyzed by GC/MS using a Varian 3400 gas chromatograph coupled to a Finnigan MAT 8230 high-resolution mass spectrometer. The capillary columns were run directly into the source of the mass spectrometer via a heated transfer line. Mass spectra were obtained by electron ionization at 70 eV and a source temperature of 250 °C. The filament emission current was 1 mA, and spectra were recorded on a Finnigan MAT SS 300 data system.

Quantitation of the Volatiles. The peak areas of the GC chromatograms were integrated, and the quantity of each volatile was calculated against 5 μL of a heptadecane internal standard according to

$$\frac{\text{area of sample peak}}{\text{area of IS peak}} = \frac{\mu\text{L of IS} \times d \times p}{\text{g of oil in sample}} = \text{ppm}$$

where IS = internal standard, d = density, and p = purity. The grams of oil in each sample were calculated by adding the amount of bound lipid in the commercial zein to the amount of the added corn oil.

RESULTS AND DISCUSSION

The thermal interactions between corn oil and zein in the presence and absence of corn carbohydrates (regular and waxy starch) were studied by examining the volatile compounds generated. The compositions and reaction conditions of the 10 reaction mixtures studied are listed in Table I. The volatile compounds were isolated with use of a Nickerson-Likens steam distillation–extraction apparatus and analyzed by high-resolution gas chromatography and gas chromatography/mass spectrometry.

The compounds identified in each of the samples, along with their retention indices and mass spectral references, are listed in Table II. The quantitative data of the identified compounds grouped according to their sources of formation are listed in Table III. According to these data, the quantity of volatile compounds generated at 180 °C was greater than that generated at 120 °C for each model system studied. Amylose-containing samples were similar to the corresponding amylopectin samples. Gas chromatograms of the samples, zein, zein plus amylopectin, and zein plus amylopectin and corn oil, reacted at 180 °C are shown in Figure 1 as examples.

From the data in Table III, it is apparent that, in all the samples, the quantity of volatile compounds generated at 180 °C was much higher than that generated at 120 °C.

Straight-chain hydrocarbons, alcohols, aldehydes, ketones, and 2-pentylfuran are common thermal oxidation products of lipids (Frankel, 1985; Nawar, 1985). As shown in Table III, lipid-derived compounds were present in samples with no corn oil added. This indicates that lipids were already present in the commercial zein used. Izzo (1987) reports that commercial zein from Sigma contains 13.8% extractable lipid.

Pentanal, hexanal, heptanal, 2-heptenal, 2-octenal, and 2,4-decadienal were identified in both the corn oil–diatomaceous earth control system and the zein–corn oil model system. The quantities of some of these aldehydes increased noticeably in the zein–corn oil system, but others increased only slightly, and some decreased. It is possible that the aldehydes generated by thermal oxidation of corn lipids will react with primary amino groups in zein, such as those in the amino acid residues arginine and lysine.

Table II. Identification of Volatile Compounds in the Zein–Waxy Corn Starch–Corn Oil Model System

peak[a]	RI[b] (sample)	SPB-1 (std)	interpretation	mass spec ref
1	601	601	3-methylpentane	c
2	630	630	3-methylpentanal	c
3	635		2-methylbutanal	c
4	692	692	pentanal	c
5	700	700	heptane	c
6	721	721	4-methyl-3-hexanol	c
7	763	763	toluene	c
8	784	784	hexanal	c
9	800	800	octane	c
10	807	807	2-methylpyrazine	c
11	814		2,3-dimethyl-2-pentene	c
12	820		1-heptene	c
13	873	873	2-heptanone	c
14	884	884	2,5-dimethylpyrazine	c
15	900	900	nonane	c
16	901	901	2,6-dimethylpyrazine	c
17	915	915	benzaldehyde	c
18	966		6-methyl-5-hepten-2-one	c
19	971	971	2-octanone	c
20	973	973	octanal	c
21	975	975	5-methyl-2-ethylpyrazine	c
22	979	979	2-pentylfuran	c
23	1000	1000	decane	c
24	1003	1003	phenylacetaldehyde	c
25	1014		3-octen-2-one	c
26	1033		C-4 benzene	c
27	1036	1036	1,4-diethylbenzene	c
28	1044	1044	1,2-diethylbenzene	c
29	1056	1056	2,5-dimethyl-3-ethylpyrazine	c
30	1062		C-4 benzene	c
31	1066		C-4 benzene	c
32	1067		3,5-octadien-2-one	c
33	1086	1086	isophorone	c
34	1099	1099	1,2,4,5-tetramethylbenzene	c
35	1102	1102	1,2,3,5-tetramethylbenzene	c
36	1119		2,3-dihydro-5-methylindene	c
37	1122		C-5 benzene	c
38	1129		C-5 benzene	c
39	1134	1134	pentylbenzene	c
40	1156	1156	naphthalene	c
41	1200	1200	dodecane	c
42	1219		2-methyl-3-phenyl-2-propenal	c
43	1267	1267	2,4-decadienal	c
44	1270		2-methyl-3(or 6)-pentylpyrazine	d
45	1291		2,5-dimethyl-3-pentylpyrazine	e
46	1294		8-methyl-1-undecene	c
47	1341		2,7-dimethyl-1-octanol	c
48	1371		3-methyltridecane	c
49	1400	1400	tetradecane	c
50	1401	1402	α-ionone	c
51	1460	1460	β-ionone	c
52	1973	1973	octadecanoic acid	c

[a] Number refers to Figure 1 (sample 3B). [b] Calculated value with *n*-paraffins (C_6–C_{22}) as references. [c] EPA/NIH, 1980. [d] 164 (1), 163 (10), 149 (5), 135 (17), 122 (100), 121 (19), 81 (32), 57 (61). [e] 177 (1), 163 (10), 135 (17), 122 (100), 121 (19), 81 (31), 57 (60).

Schiff base formation between carbonyl functions and primary amino groups is recognized as a key step in the browning reaction of sugars and proteins, and recent reports indicate that similar interactions may occur between lipid-derived aldehydes and amino acid residues (Okitani et al., 1986; Kato et al., 1986).

Several compounds that may originate from carotenoids were detected in samples of the zein model system heated at both 120 and 180 °C. Although the commercial zein used in this study was not analyzed for the presence of carotenoids, identification of these carotenoid decomposition products and the yellow color of the commercial zein support the assumption that carotenoids are present in commercial zein.

The predicted precursors of the volatile carotenoid de-

Table III. Quantitation of Volatile Compounds (at 120 and 180 °C) in the Zein–Waxy Corn Starch–Corn Oil Model System

	quantitation,[a] ppb									
	1		2		3		4		5	
From Lipids										
pentanal	5	44	5	42	10	59	6	39	11	61
heptane	3	13	4	14	5	17	4	12	6	18
hexanal	37	307	41	316	81	698	44	327	86	709
octane	1	19	2	15	5	13	3	8	7	19
2-heptanone	2	19	3	32	6	87	4	34	8	91
nonane	–	3	–	6	–	24	–	12	–	45
2-octanone	–	3	–	5	–	32	–	9	–	34
octanal	3	50	4	43	6	75	6	45	7	80
2-pentylfuran	1	10	2	5	5	39	3	12	6	30
decane	1	22	1	19	4	65	2	11	5	39
3-octan-2-one	–	t[b]	–	2	–	15	–	4	–	15
3,5-octadien-2-one	–	4	–	5	–	44	–	13	–	66
dodecane	4	35	4	35	14	157	5	38	15	130
2,4-decadienal	–	7	–	7	–	85	–	10	–	185
tetradecane	–	11	–	12	–	93	–	38	–	129
octadecanoic acid	–	t	–	t	–	t	–	2	–	17
From Carotenoids										
toluene	2	52	3	68	8	128	5	38	10	115
6-methyl-5-hepten-2-one	1	3	–	6	–	21	–	8	–	26
isophorone	10	60	12	61	22	561	11	228	24	798
α-ionone	–	t	–	t	–	13	–	7	–	28
β-ionone	–	t	–	t	–	9	–	4	–	18
4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butanone	–	t	–	t	–	7	–	3	–	14
From Lipids, Proteins, and Carbohydrates										
2-methyl-3(or 6)-pentylpyrazine	–	t	–	t	–	12	–	7	–	29
2,5-dimethyl-3-pentylpyrazine	–	t	–	t	–	3	–	1	–	6
From Carbohydrates and Proteins										
2-methylpentanal	158	1388	164	1405	159	1497	166	1424	156	1386
2-methylbutanal	42	311	37	325	45	332	41	296	44	356
phenylacetaldehyde	–	t	–	t	–	7	–	t	–	10
2-methylpyrazine	–	14	–	5	–	34	–	19	–	31
2,5-dimethylpyrazine	–	t	6	30	16	217	7	83	18	255
2,6-dimethylpyrazine	–	6	–	8	–	20	–	6	–	17
2-methyl-5-ethylpyrazine	–	t	–	11	–	41	–	15	–	59
2,5-dimethyl-3-ethylpyrazine	–	3	–	2	–	18	–	9	–	31
Miscellaneous										
3-methylpentane	t	111	t	165	32	487	t	176	43	497
2,3-dimethyl-2-pentene	–	t	–	2	–	2	–	4	–	8
4-methyl-3-hexanol	6	26	7	32	17	265	8	35	19	278
benzaldehyde	9	71	11	83	21	421	11	123	20	351
1,4-diethylbenzene	–	1	–	7	–	35	–	13	–	40
1,2-diethylbenzene	–	t	–	t	–	11	–	6	–	12
C-4 benzene (RI 1033)	–	4	–	6	–	20	–	6	–	19
C-4 benzene (RI 1062)	–	5	–	6	–	21	–	7	–	21
C-4 benzene (RI 1067)	–	9	–	11	–	47	–	15	–	47
1,2,3,5-tetramethylbenzene	–	16	–	20	–	87	–	30	–	96
2,3-dihydro-5-methylindene	–	4	–	7	–	28	–	10	–	34
C-5 benzene (RI 1122)	–	t	–	2	–	14	–	4	–	15
C-5 benzene (RI 1129)	–	10	–	14	–	65	–	23	–	76
pentylbenzene	–	5	–	7	–	29	–	8	–	45
naphthalene	–	8	–	13	–	65	–	31	–	105
2-methyl-3-phenylpropenal	–	t	–	t	–	46	–	28	–	103
8-methyl-1-undecene	–	t	–	t	–	8	–	4	–	18
2,7-dimethyl-1-octanol	–	t	–	t	–	9	–	t	–	11
3-methyltridecane	–	t	–	t	–	12	–	4	–	16

[a] Key: 1, zein + water; 2, zein + regular corn starch + water; 3, zein + regular corn starch + corn oil + water; 4, zein + waxy corn starch + water; 5, zein + waxy corn starch + corn oil + water. Quantitative data are average values of two GC determinations. [b] Key: –, not observed; t, trace.

composition products identified in our samples have all been identified in corn grain (Quackenbush et al., 1961) (Table IV). Lutein is reported to be the most abundant carotenoid in corn grain, and isophorone is the most abundant carotenoid decomposition product identified in our model systems. Isophorone may be derived from lutein by the free-radical mechanism proposed in Figure 2. α-Ionone and β-ionone are both well-known oxidation products of α-carotene. β-Ionone can also be derived from β-carotene (Weeks, 1986).

When corn oil was included in the model systems, the quantities of carotenoid decomposition products increased. Corn oil contains small amounts of carotenoids, and the production of carotenoid decomposition products from corn oil would explain the increase of these compounds in model systems containing corn oil. However, thermal oxidation of the corn oil used in this study produced no detectable carotenoid decomposition products. Because free-radical mechanisms have been predicted for carotenoid decomposition, lipid-derived free radicals from corn

Table IV. Predicted Thermal Decomposition Products of Zein Carotenoids

	predicted thermal decomposition product					
caroteinoid	toluene	6-methyl-5-hepten-2-one	isophorone	α-ionone	β-ionone	4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butanone
zeinoxanthin	+					
cryptoxanthin	+			+		
α-carotene	+			+	+	+
lutein	+		+			
zeaxanthin	+					
phytoene	+	+				
phytofluene	+	+				
β-carotene	+			+		+
β-zeacarotene	+	+		+		
ζ-carotene	+	+				

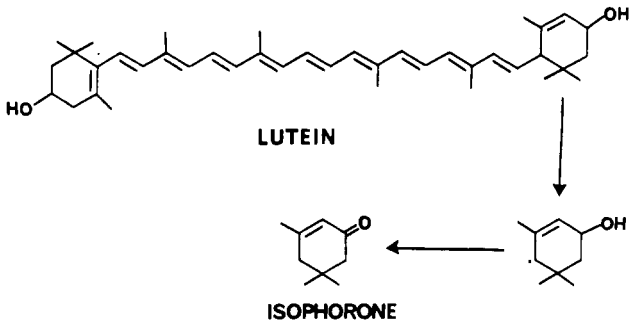

Figure 2. Mechanism for the formation of isophorone.

oil may accelerate carotenoid decomposition in zein.

Two classes of compounds, Strecker aldehydes and alkylpyrazines, were characterized as interaction products between carbohydrates and proteins. Isopentanal, 2-methylbutanal, and phenylacetaldehyde were identified as the Strecker aldehydes of leucine, isoleucine, and phenylalanine. The amounts of Strecker aldehydes identified in the thermally treated zein were not affected by the addition of either corn carbohydrates or corn lipids. These data indicate that Strecker degradation is not affected by the presence of free radicals. They also suggest that commercial zein contains reactive reducing sugars as impurities. It is possible that reducing sugars are present in commercial zein due to incomplete separation of corn starch during processing.

Alkylpyrazines are the most widespread Maillard reaction products found in processed foods. The mechanism for the formation of pyrazines from the thermal interaction of proteins and carbohydrates has been reviewed (Maga, 1982). In the present study, the addition of corn lipids to the zein and carbohydrates favored the formation of alkylpyrazines. No Maillard reaction products were detected in a control system of waxy corn starch and corn oil, so the production of alkylpyrazines from corn oil and carbohydrate is unlikely. However, free-radical products have been reported in the early stage of browning reactions of sugar–amino compound systems (Hayashi and Namiki, 1986). It is possible that the quantities of alkylpyrazines increase in the presence of corn oil due to acceleration of the Maillard reaction by lipid-derived free radicals.

Two alkylpyrazines, 2-methyl-3(or 6)-pentylpyrazine and 2,5-dimethyl-3-pentylpyrazine, tentatively identified by their mass spectra, deserve special attention. These two pyrazines have long-chain (5-carbon) substitution on the pyrazine ring. Only the involvement of lipid or lipid decomposition products in the formation of these compounds could account for the long-chain alkyl substitution. These two pyrazines were accordingly characterized as thermal interaction products of lipids, proteins, and carbohydrates. The mechanism for the formation of 2,5-dimethyl-3-pentylpyrazine was proposed as shown in Figure 3. 3,6-

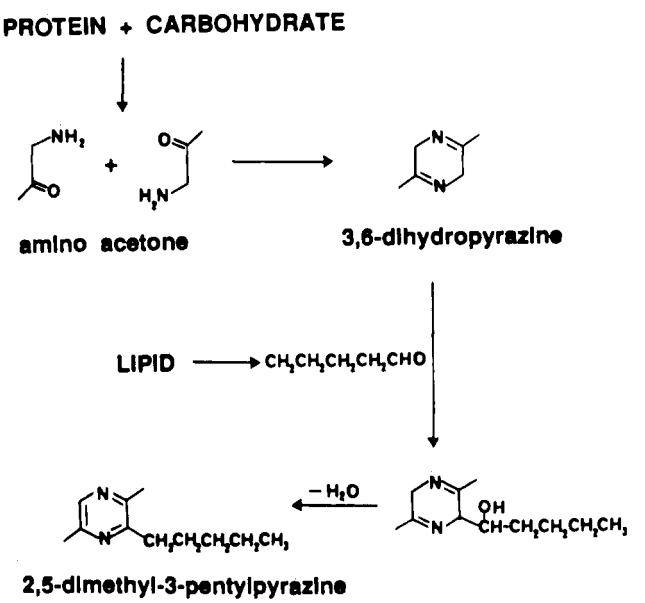

Figure 3. Mechanism for the formation of 2,5-dimethyl-3-pentylpyrazine.

Dihydropyrazine formed by the condensation of amino ketones may react with pentanal, a lipid oxidation product, and result in the formation of 2,5-dimethyl-3-pentylpyrazine. The possible reactivity of 3,6-dihydropyrazine with carbonyl compounds has been discussed by Flament (1981). The involvement of lipid or lipid decomposition products in the formation of heterocyclic compounds has recently been suggested in deep-fat fried foods such as french-fried potatoes (Carlin et al., 1986) and fried chicken (Hwang et al., 1986). The tentatively identified pentylpyrazines have not yet been identified in food systems.

No volatiles of any type were detected in control systems of waxy corn starch alone.

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Isolation of 4-Hydroxy-2-(hydroxymethyl)-5-methyl-3(2*H*)-furanone from Sugar Amino Acid Reaction Mixtures

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From reaction mixtures of glucose with amino acids the compounds extractable by acetonitrile were analyzed. In addition to the well-known 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one (the isomeric **6**), 4-hydroxy-2-(hydroxymethyl)-5-methyl-3(2*H*)-furanone (**5**) was isolated as a further main product for the first time. **5** and **6** react with primary amines (amino acids) forming pyrrolinones of structure **9**, whereas the so-called amino hexose reductones **8** are obtained with secondary amines.

When pentoses are heated with amino acids, proteins, or salts of simple amines in an almost neutral aqueous solution, a comparatively large amount of 4-hydroxy-5-methyl-3(2*H*)-furanone (**1**) is formed (Severin and Seilmeier, 1967). Under suitable conditions, **1** can be obtained in yields of up to 30% (Peer et al., 1968). This compound is also detectable in foodstuff, e.g. beef broth (Tonsbeek et al., 1968). Dihydrofuranone **1** includes a very reactive methylene group and condenses readily with sugar degradation products containing carbonyl functions to colored compounds of general structure **2** (Ledl and Severin, 1978). Thus, substances **2a** and **2b** could be isolated from a mixture of xylose and glycine (Severin and Krönig, 1973). In these compounds the exocyclic methyl group is sufficiently activated in order to react with a second carbonyl component. Thus, the scheme **1** → **2** → **3** generally reflects browning reactions of pentoses under the conditions of the Maillard reaction (Figure 1).

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In a similar way 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (**4**, furaneol) is formed from methyl pentoses (Hodge, 1963). This substance **4** is a very important aroma compound and is available also as a synthetic product (Büchi et al., 1973) (Figure 2).

Because of these results it could be expected that a dihydrofuranone of structure **5** was formed from hexoses. Some years ago already we heated glucose and fructose with amino acids or methylammonium acetate in aqueous solution and analyzed reaction products extractable by ethyl acetate or methylene chloride. The main component we isolated (Severin and Seilmeier, 1968) was not the required compound **5** but an isomeric crystalline substance, which according to Mills et al. (1970) had to be regarded as 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one (**6**). However, substances with structure **5** have been described erroneously in the literature. With a GC–MS system, Tatum et al. (1967) separated and identified volatile products formed during the storage of orange powder. On this occasion, they assigned structure **5** to one of the compounds. But as has been shown by further investigations, this component was again pyranone **6**. Other

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