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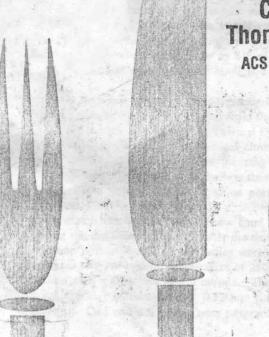
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# in Food Flovors

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was extruded at 185°C, with a 16% moisture feed (w/w), screw speed of 500 rpm, and a mass flow rate of 225 g/min. The other sample was extruded at 160°C, with a 20% moisture feed (w/w), screw speed of 500 rpm, and a mass flow rate of 225 g/min. These extrudates were stored in closed glass jars at 4°C before analysis.

Volatile Isolation from Extrudates. Thirty grams of extrudate were ground in a benchtop grinder (Glen Mills, Maywood, NJ) with dry ice to prevent heat-labile volatiles' destruction. The ground sample (10 g) was packed in the center of a glass tube and the silanized glass wool was placed on the two ends of the tube. One microliter of 1.001 mg/ml deuterated toluene was spiked into the tube as the internal standard. The tube was further sealed in a Scientific Instrument Services, Inc. (SIS) solid sample purge-and-trap apparatus (Ringoes, NJ). Nitrogen was used at a flow rate of 40 mL/min to purge the volatiles into a silanized glass-lined stainless steel desorption tube (4.0 mm i.d. x 10 cm length) from Scientific Instrument Services, Inc. (Ringoes, NJ). It consisted of 3 cm bed volume of Tenax-TA adsorbent and 3 cm bed volume of Carbotrap adsorbent. This volatile isolation was carried out at 80°C for one hour.

Volatile Generation and Isolation from the Heating Process. Two different temperatures (160°C and 180°C) were chosen for the heating process. For each sample, fifty grams of wheat flour, which contained 14% of moisture, were placed in a reaction vessel and heated at a desired temperature for one hour. The heated sample was transferred into a glass tube and the silanized glass wool was placed on the two ends of the tube. One microliter of 1.001 mg/ml deuterated toluene was spiked into the tube as the internal standard. The volatile isolation of the heated samples was carried out by an SIS solid sample purge-and-trap apparatus and the condition was exactly the same as mentioned above.

Volatile Analysis by Gas Chromatography-Mass Spectrometry (GC-MS). The desorption tube which was prepared from the isolation procedure was connected to an SIS model TD-1 Short Path Thermal Desorption unit. This desorption unit was interfaced with a Varian 3400 gas chromatograph coupled with a Finnigan MAT 8320 high-resolution double focusing magnetic sector mass spectrometer (TD-GC-MS). The desorption tube was then injected into the GC and thermally desorbed the volatiles to the injection port of the GC at 220°C for 5 min. However, the temperature of the GC chamber was maintained at -20°C by dry ice to cryofocus the volatiles as a narrow band at the head of the capillary column during the desorption process. After the desorption tube was removed from the injection port of the GC, the volatiles were analyzed by GC-MS. The GC was operated with an injector temperature of 250°C, with a split ratio of 10:1, and a helium carrier flow rate of 1.0 ml/min. The GC column was a nonpolar fused silica capillary column [60 m x 0.32 mm (i.d.), 0.25 µm thickness, DB-1; J&W Scientific Co.] and was temperature programmed from -20°C to 280°C at a rate

of 10°C per minute with a 20 minute hold at the upper limit. Volatiles were semi-quantified via peak area ratio calculation to that of the internal standard, deuterated toluene. Linear retention indices for the volatiles were determined through the use of a C<sub>5</sub>-C<sub>25</sub> n-paraffin standard according to the method of Majlat et al. (11). The mass spectrometer electron ionization was set at 70 eV and the source temperature was 250°C with a filament emission current of 1 mA, scanning masses 35-350, and a 0.8 second interscan time. All mass spectra obtained were identified by utilizing an on-line computer library (NIST).

### Results and Discussion

A total eight-one compounds has identified in Table I. The lipid degradation products identified included aldehydes, ketones, alcohols, hydrocarbons, and 2-pentylfuran. The Strecker aldehydes as well as Maillard reaction-derived heterocyclic compounds such as furans, pyrroles, and pyrazines were also identified. In addition, sulfur-containing compounds such as dimethyl disulfide, thiazoles, and thiophenes were found.

Although the lipid content of wheat flour is low (approximately 2-3% w/w), wheat lipids are rich in linoleic, linolenic, and oleic acids (12). The oxidative products of linoleic acid, which is the most abundant fatty acid in wheat flour (13), included pentanal, hexanal, 2-t-octenal, 4-t-nonenal, 2-t-nonenal, 2,4-nonadienal, 2-t,4-t-decadienal, 1-pentanol, 1-hexanol, and 2-pentylfuran. 2-t,4-t-decadienal, which had a pleasant deep-fat-fried flavor could further convert to a number of components such as 2-octenal, hexanal and acetaldehyde through further oxidation or retro-aldolization reaction (14). Benzaldehyde has also been considered as a thermal degradation product of 2-t,4-t-decadienal and its formation pathway has been suggested by Bruechert et al. (15).

In addition to linoleic acid, oleic acid was also the major fatty acid of the lipids occurring in wheat flour (13). Compounds such as heptanal, nonanal, decanal, and 2-t-decenal were produced from autoxidation of oleic acid. The compounds generated from the autoxidation of linolenic acid included 2-hexenal, 2-t-heptenal, 2-t,4-t-heptadienal, 2-t-penten-1-ol, and 3-t,5-t-octadien-2-one.

The heterocyclics included furans, pyrroles, and pyrazines. These were typical Maillard reaction products. Alkylpyrazines are generally recognized as important contributors to the flavors of all roasted, toasted, or similarly heated foods (16). The most direct route to their formation resulted from the interaction of  $\alpha$ -dicarbonyl compounds with amino acids through the Strecker degradation reaction.

Sulfur-containing compounds were investigated in the present study and were significant contributors to the thermal production of flavors. Those sulfur-containing flavors were generated from the thermal degradation of cysteine and methionine. The formations of dimethyldisulfide, dimethyltrisulfide, and methylpentylsulfide resulted from the interaction of two methylthio radicals, that were produced from methionine degradation, or from the reaction between

Table I. Volatile Aroma Compounds Identified from Extrudates

Compounds		Quantitati	on (ng/g	ng/g of extrudates)		
	$I_k^{\ a}$	E-1 <sup>b</sup>	EA-1b	E-2 <sup>b</sup>	EA-2	
Carbonyls						
butanal	583	_c	4	_	17.59	
pentanal	695	-	214.62	182.50	864.10	
hexanal	807	236.60	778.98	1183.50	830.03	
heptanal	914	56.60	21.50	129.00	200.36	
nonanal	1130	-	34.25	158.40	114.54	
decanal	1238	-	23.56	120.90		
dodecanal	1437	-	27.84	-	24	
3-methylbutanal	662	192.90	122.06	117.50	1.93	
2-methylbutanal	671	123.10	78.03	67.50	7.97	
2-hexenal	790		-	-	59.79	
2-t-heptenal	959		-	-	13.68	
2-t-octenal	1077	-		165.50	24.25	
4-t-nonenal	1122			*	34.08	
2-t-nonenal	1179			72.33	47.45	
2-t-decenal	1320			-	13.87	
2-butyl-2-octenal	1093			-	57.58	
2-t,4-t-heptadienal	1010	121	4.40	-	180.48	
2,4-nonadienal	1275		7.54	-	65.76	
2-t,4-t-decadienal	1350		73.16	74.20	-	
benzaldehyde	970	121.40	75.62	335.10	215.18	
phenylacetaldehyde	1055	61.30	33.65	-	24.25	
4-hydroxy-2-t-octenal	1094		-	1.0	5.73	
2-butanone	598	44.30	-	28.30	-	
2-hexanone	798	34.80	_	-	_	
2-heptanone	904	92.60	28.84	113.80	132.65	
6-undecanone	1333	-	-	-	13.25	
5-methyl-2-isopropyl-						
cyclohexanone	1089		19.21	- *	-	
3-methyl-3-buten-2-one	700	*	26.25	*	23.74	
3-1-octen-2-one	973	-	91.18	-	393.14	
3,4,5-trimethyl-2-cyclo-						
penten-1-one	1066	-	4.	4	24.25	
3-t,5-t-octadien-2-one	1088	-	62.15	126.60	498.59	
2-methyl-5-isopropyl-						
2-cylcohexen-1-one	1276	-	=	35.80		

Table I. continued

Compounds		of extrudate	dates)		
	$I_k^{\ a}$	E-1 <sup>b</sup>	EA-1 <sup>b</sup>	E-2 <sup>b</sup>	EA-2
Carbonyls - continued					
l-hydroxy-2-propanone	717	80.10	12.05		-
3-hydroxy-2-butanone	754		67.73	43.80	
1-hydroxy-2-heptanone	1078		_		314.73
2,3-butanedione	594	55.10	17.94		-
2,3-pentanedione	699	114.60			-
2,3-octanedione	1002	-	-	. 0	33.81
acetic acid	711	178.40	12.05	-	15.67
Alcohols					
l-butanol	689	54.90	200.61	122.70	13.22
l-pentanol	760	-	*	78.30	180.74
l-hexanol	890	86.70	-	390.40	35.85
2-t-penten-1-ol	700			71.10	-
l-octen-3-ol	1004			141.33	126.92
7-octen-4-ol	1024			40.	5.53
3-methyl-1-butanol	788	84.90	23.88	281.30	4.02
4-(1-methylpropyl)-phenol	1353			90.13	
Hydrocarbons					
heptane	723		- 1	60.64	
nonane	936			39.08	35.85
undecane	1147	*		53.74	- X
dodecane	1253		6.63		
tetradecane	1460	-	62.06	156.82	52.03
pentadecane	1569		343.69	261.45	
hexadecane	1673		366.78	133.23	
toluene	778	-	21.50	71.23	
xylene	867	-			17.05
naphthalene	1223		7.54	85.35	34.08
1-methylnaphthalene	1341	-		69.64	
1,8-dimethylnaphthalene	1474	-	28.01	113.65	34.74
trimethylnaphthalene	1599	-		99.77	-

Table I. continued

		Quantitat	ion (ng/g	of extrudate	es)
Compounds	$I_k^{\ a}$	E-1 <sup>b</sup>	EA-1 <sup>b</sup>	E-2 <sup>b</sup>	53.42 165.66 180.48
			_		
Furans					
2-ethylfuran	711	-	~	75.40	53.42
2-acetylfuran	925	-	11.04	~	-
2-furfural	832	-	28.84	243.00	165.66
2-furfuryl alcohol	876	184.50	19.90	*	¥.
2-pentylfuran	1020	¥	64.49	409.50	180.48
Nitrogen-containing compo	ounds				
lH-pyrrole	768	66.00	. H	31.40	*
2-methyl-lH-pyrrole	850	=	-	24.90	~
pyrazine	739	348.80	216.18	35.80	-
methylpyrazine	838	843.50	381.57	**	-
2,5-dimethylpyrazine	931	398.70	430.97	126.60	135.34
2,3-dimethylpyrazine	937	78.00	21.50	-	8
vinylpyrazine	945	70.60	-/		8 .
2-ethyl-5-methylpyrazine	1017	112.30	28.84	31.00	
trimethylpyrazine	1021	-	64.49		-
2-vinyl-5-methylpyrazine	1039	-	16.08	-	_
3-ethyl-2,5-dimethyl-					
pyrazine	1103	-	102.85	56.70	77.36
Sulfur-containing compour	nds				
dimethyldisulfide	749	62.80	2	46.95	17.08
dimethyltrisulfide	987	-	2	51.20	-
thiazole	739	-	2	35.80	_
2-methylthiophene	781	52.30		*	
2-formylthiophene	980	119.10	3.03	-	-
= 10.mj.turopnono	200	112.10	3.03	*	
Total		3954.90	4283.09	6442.84	5397.82

 $<sup>^{8}</sup>I_{k}$  = Calculated retention indices with n-paraffins (C<sub>5</sub>-C<sub>25</sub>) as references;  $^{8}E$ -1 = Extruded at 185°C with a moisture feed of 16% without storage; EA-1 = extruded at 185°C with a moisture feed of 16% after one year storage; E-2 = extruded at 160°C with a moisture feed of 20% without storage; EA-2 = extruded at 160°C with a moisture feed of 20% after one year storage; °Not detected

methylthic radicals and other radicals such as alkyl radicals formed from lipid degradation. Some thiazoles and thiophenes have been reported as volatile compounds derived from the thermal interaction of cysteine and reducing sugars. These thiazoles and thiophenes were involved in the development of "meaty" flavors (17).

The data from Tables I and II shows that the total amounts of volatiles produced from the heating process were 4 to 20 times higher than those from the extrusion process. During the extrusion process, pressure builds up within the extruder barrel as the plasticized material progresses towards the die. As the food exits at the die, steam is flashed off due to the pressure differential between the extrudate and the surrounding environment. Flavors and odors may be lost/removed during expansion at the extruder die (7). Therefore, most of the volatiles were lost at the die. Volatile generation under heating conditions produced a stronger flavor due to less loss. The yield of volatile formation from heating at 180°C was larger than at 160°C. This indicated that temperature enhanced the production of volatile compounds during the heating process.

The volatile compounds were further classified into three different categories that included lipid degradation, Maillard reaction, and others. The relative percentages for these three different types of classifications are shown in Figure 1. Sample E-2, which was extruded at a die temperature of 160°C with a 20% moisture feed, contained about 80% of lipid degradation products, whereas sample E-1, which was extruded at a die temperature of 185°C with a 16% moisture feed, contained larger amounts of Maillard-type of compounds than the lipid degradation products. It has been known that the Maillard reaction has a maximum reaction rate at intermediate moisture levels. It was also reported that the rate of Maillard reactions was enhanced by increasing the extrusion temperature and was offset by increasing the moisture content (18-19). Therefore, it is reasonable that the sample E-1 had dominant Maillard-type flavors addition, the results indicated that the volatile compounds from the Maillard reaction were predominant in both of the heated samples that contained 14% moisture. It also appears that there were more Maillard-type flavors produced when the sample was heated at a higher temperature. The flavor profile of the sample E-1, which was extruded at a higher die temperature, was similar to that of the products formed by the heating process.

Few studies mentioned flavor as a positive attribute of a cooking extruder probably because the volatile compounds are lost as the material exits the extruder at the die. Many extrusion processors have relied on the post-extrusion flavor application or the introduction of thermally resistant flavors prior to the extrusion process (20). Based on the present study, it is suggested that by carefully controlling the extrusion parameters, a desirable flavor profile, which is similar to that of the heating process, could be obtained.

Sample E-1, which contained a large amount of unoxidized fatty acids, was very susceptible to lipid oxidation during the storage process. Therefore, the total yield of the lipid degradation products in sample EA-1, which is sample E-1 stored

Table II. Volatile Aroma Compounds Identified from the Heated Samples

		Quantitatio	n <sup>a</sup>
Compounds	$I_k^{\ b}$	W-160°	W-180°
Carbonyls			
pentanal	695	0.27	0.73
hexanal	807	0.96	1.34
nonanal	1130	0.24	_d
decanal	1238	0.13	-
3-methylbutanal	662	0.37	1.65
2-methylbutanal	671	0.39	2.00
2-methyl-2-t-butenal	737	0.21	*
2-t,4-t-octadienal	893	0.23	0.16
benzaldehyde	970	0.96	4
2-butanone	598	0.92	-
2-hexanone	798	0.17	
2-heptanone	904	0.56	0.69
2-pentadecanone	1701	0.13	-
3-methyl-2-butanone	685	0.11	-
2-methyl-3-pentanone	692	0.14	
2-methyl-5-isopropyl-2-			
cylcohexen-1-one	1276	0.04	-
2-hydroxy-3-pentanone	799	1	0.26
l-(acetyloxy)-2-propanone	850	-	0.18
Alcohols			
I-butanol	689		0.95
I-hexanol	890	0.48	0,93
I-octen-3-ol	1004	0.48	-
3-methyl-1-butanol	788	0.85	0.79
5-methyi-i-butanoi	/00	0.83	0.79
Hydrocarbons			125)
undecane	1147	0.03	-
tetradecane	1460	0.02	-
pentadecane	1569	0.07	-
1-tridecene	1505	0.11	-
naphthalene	1223	0.06	-

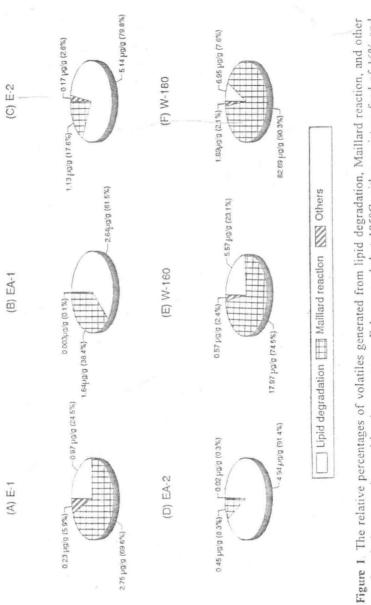
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Table II. Continued

			Quantitatio	n <sup>a</sup>	
Compounds	$I_k^{\ b}$	 V	W-160°	W-180°	
Furans					
2-furfurylalcohol	876		1.64	11.19	
2-pentylfuran	1020			3.08	
2 point, manuar					
Nitrogen-containing compound	ds				
pyrazine	739		0.09	3.91	
methylpyrazine	838		5.38	24.24	
ethylpyrazine	912		4.22		
2,5-dimethylpyrazine	931			21.99	
2,3-dimethylpyrazine	937		0.30		
2-ethyl-5-methylpyrazine	1017		3.07	11.31	
isopropenylpyrazine	1060			0.28	
2-ethyl-3,5-dimethylpyrazine	1075	3:	-	1.26	
3-ethyl-2,5-dimethylpyrazine	1103		0.96	2.78	
3,5-diethyl-2-methylpyrazine	1153		0.16	0.85	
3-isopentyl-2,5-dimethyl-					
pyrazine	1311		0.08		
N.					
Sulfur-containing compounds					
dimethyldisulfide	749		0.21	1.25	
dimethyltrisulfide	987		0.10		
methylpentyldisulfide	1435		0.05		
thiazole	739		0.09		
4-methylthiazole	803		*	0.27	
2-formylthiophene	980		÷	0.37	
2-pentylthiophene	1163		0.08		
Total			24.11	91.53	

 $<sup>^{</sup>a}$ Values in micrograms per gram of wheat flour;  $^{b}I_{k}$  = Calculated retention indices with n-paraffins ( $C_{5}$ - $C_{25}$ ) as references;  $^{c}W$ -160 = Heated at 160°C; W-180 = heated at 180°C;  $^{d}$ Not detected.

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extruded at  $160^{\circ}$ C with a moisture feed of 20% and without storage; EA-2 = extruded at  $160^{\circ}$ C with a moisture feed of 20% and after one year storage; W-160 = heated at  $160^{\circ}$ C; W-180 = heated at  $180^{\circ}$ C. reaction during extrusion and heating processes. E-1 = extruded at 185°C with a moisture feed of 16% and without storage; EA-1 = extruded at 185°C with a moisture feed of 16% and after one year storage; E-2 =

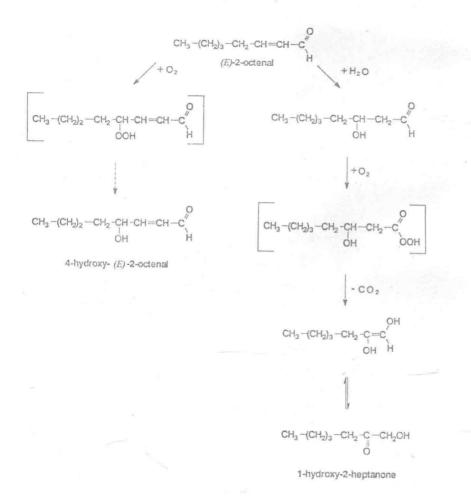


Figure 2. Postulated formation pathways of 4-hydroxy-(E)-2-octenal and 1-hydroxy-2-heptanone from 2-octenal (SOURCE: Adapted from ref. 21. Copyright 1993, American Chemical Society).

for one year, significantly increased (Figure 1). However, the amount of the lipid degradation compounds in sample EA-1 was still lower than that in sample E-2, which was extruded at die temperature of 160°C with a 20% moisture feed. It shows that the rate of lipid degradation was much slower in the storage process than in the extrusion process. Although the total amounts of lipid degradation products did not significantly change between sample E-2 and sample EA-2, which is sample E-2 stored for one year, some of the new lipid degradation products were found in sample EA-2 such as 2-hexenal, 2-t-heptenal, 2-t-decenal, 2-butyl-2octenal, 1-hydroxy-2-heptanone, and 4-hydroxy-2-t-octenal. It implies that the lipid degradation still occurred in sample EA-2; however, it was not shown in the total yield of the lipid degradation products. This was because some lipids gradually degraded to oxidative compounds and some of the oxidative compounds volatilized to air or underwent further reactions. For example, 2-butyl-2-octenal can be formed from the dimerization of hexanals via the aldol addition reaction. These results indicated that the yield of hexanal in sample EA-2 was lower than in sample E-2. In addition, 1-hydroxy-2-heptanone and 4-hydroxy-2-t-octenal identified in sample EA-2 were the degradation products of 2-t-octenal. The formation mechanisms of 1-hydroxy-2-heptanone and 4-hydroxy-2-t-octenal shown in Figure 2 have been proposed by Grein et al. (21). The yields of the Maillardtype flavors decreased in both extrudates during the storage process. Even though the Maillard reaction could occur during storage, its rate was very slow in these studies

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# Chapter 11

# Effect of Packaging on the Lipid Oxidation Storage Stability of Dehydrated Pinto Beans

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This investigation studied the development of lipid oxidation flavors in precooked dehydrated pinto beans stored in different packaging environments. The total lipid content and the fatty acid composition of the beans were determined. The volatile flavor constituents of a commercial product were also characterized. To simulate various packaging environments the precooked, dehydrated beans were stored for up to six months under the following conditions: 1) exposed to air, 2) exposed to air with added butylated hydroxytoluene (BHT), 3) under nitrogen headspace and 4) under nitrogen headspace with added BHT. Throughout the storage stability study, samples were periodically monitored for the presence of hexanal and other oxidative decomposition products. This was accomplished using purge & trap - thermal desorption gas chromatography - mass spectrometry methodology. oxidative stability of the product as influenced by the various storage conditions (in decreasing order of oxidation) was found to be air ≥ air with BHT > nitrogen ≥ nitrogen with BHT.

Pinto beans are a grain legume cultivar of the family Fabaceae, commonly called the pea or bean family, formerly the Leguminocae. Phaseolus vulgaris is the genus and specie. They are a nutritious food source which contains high quality protein, complex carbohydrates, vitamins, minerals, high fiber and a relatively low lipid content that is rich in polyunsaturates. They are the primary ingredient in "refried beans", an ethnic food preparation of Mexican origin that has become increasingly popular in the United States and abroad. Refried beans are typically prepared by soaking pinto beans in water for an extended period (~24 hours) to promote moisture uptake and softening. The soaked beans are then mashed, mixed with additional lipid, salt and/or spices and are cooked by various methods

such as frying or pressure cooking. As a convenience to the consumer, instant refried beans are produced commercially by canning or in a precooked dehydrated form. The dehydrated product is then simply reconstituted with boiling water to produce an instant preparation. The highly polyunsaturated nature of the lipid in the beans limits the oxidative stability of the product, especially after processing. The storage stability and flavor attributes of the precooked dehydrated product are the focus of this investigation.

Numerous studies have been conducted on the chemical composition. processing, cultivation, usage and nutritional aspects of pinto beans. comprehensive review of the early literature has been compiled by Sathe, Deshpande and Saunkhe (1). They report the proximate composition of dry pinto beans as moisture (9%), protein (25%), fat (1.3%), fiber (5%) and carbohydrates (69%). However, it is noted that considerable variation is encountered when analyzing different lots of beans. Presumably, different cultivars and agricultural variation account for these observations. An earlier investigation on the proximate composition of raw dry pinto beans by Meiners et. al. (2) reported moisture content (15%), protein (19%), fat (1.2%), fiber (6%) and ash (4%). The protein quality and anti-nutritional properties of pinto beans were the basis for a study conducted by Hove, King and Hill (3). Based on rat feeding trials they reported a protein efficiency ratio of zero for raw pinto beans. However, after cooking the efficiency ratio increased dramatically indicating that cooked pinto beans offer a source of high quality dietary protein. The poor efficiency observed in the raw beans is attributed to the presence of protease inhibitors and other anti-nutritional factors common to pinto beans and other legume seeds. Although pinto beans offer an excellent source of protein, vitamins, minerals, lipid and carbohydrates consumer acceptability has been limited by its tendency to cause flatulence. This is due to the relatively high content of flatulence-causing sugars such as raffinose and stachyose that are present in the beans. In a study conducted by Borejszo and Khan they reported a reduction in these flatulence-causing sugars following high temperature extrusion of pinto bean high starch fractions (4). Presumably, the high temperature, short time extrusion conditions favored consumption of these sugars via Maillard and/or thermal degradation reactions.

Several early investigations focussed on the lipid composition of pinto beans. Korytnyk and Metzler determined the total lipid content to be 1.85% (5). They reported the fatty acid percentages to be myristic (trace), pentadecanoic (trace), palmitic (32.5), stearic (4.6), oleic (7.2), linoleic (31.2), linolenic (22.0) and behenic (2.5). A study conducted on pinto beans by Takayama, Muneta and Wiese found the total crude lipid and the ratio of triglycerides to phospholipid (6). The crude lipid content of pinto beans obtained from several northeastern U.S. growing areas averaged 3%. The ratio of triglycerides to phospholipid was found to be nearly 1:1. The investigators determined the fatty acid composition on a mole % basis for both forms of conjugated lipid. The triglycerides were found composed of myristic (0.1), palmitic (16.0), stearic (0.5), oleic (8.7), linoleic (26.7) and linolenic (47.9). The fatty acid composition of the phosphatides were palmitic