

# Volatile Components of Roasted Peanuts

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Steam volatile components from roasted Spanish peanuts were fractionated by preparative gas chromatography. Individual fractions were analyzed on a Carbowax 20M 500-ft  $\times$  0.03-in. i.d. open tubular gas chromatographic column coupled to a mass spectrometer. The following compounds are among those reported for the first time from roasted peanuts: seven phenols including 4-vinylphenol and 2-methoxy-4-vinylphenol; propylpyrazine; isopropylpyrazine; tetramethylpyrazine; acetylpyrazine; 2-ethyl-6-acetylpyrazine; vinylpyrazine; 2-methyl-5-vinylpyrazine; 2-methyl-6-vinylpyrazine; 5,6,7,8-tetrahydroquinoxaline; 6,7-dihydro-5H-cyclopentapyrazine; 5-methyl-6,7-dihydro-5H-cy-

clopentapyrazine; 2-methyl-6,7-dihydro-5H-cyclopentapyrazine; 2(or 3),5-dimethyl-6,7-dihydro-5H-cyclopentapyrazine; dipropyl disulfide; 3-methylthiopropionaldehyde; 5-methyl-2-thiophenecarboxaldehyde; tetrahydrothiophen-3-one; 2-methyltetrahydrothiophen-3-one; thiazole; 4-methylthiazole; 4,5-dimethylthiazole; benzothiazole; C<sub>4</sub>, C<sub>5</sub>, and C<sub>8</sub>  $\gamma$ -lactones; pyridine; 2-methylpyridine; 2-pentylpyridine; 2-acetylpyridine; pyrrole; methyl 1-pyrrolyl ketone; 2-methylpyrrole; ethyl 2-pyrrolyl ketone; 1-furfurylpyrrole-2-carboxaldehyde; methyl nicotinate; 27 carbonyls; 16 alcohols; 18 aromatic hydrocarbons; eight esters; and seven terpenes.

Although the flavor of roasted peanuts has wide appeal, it is only recently that progress has been made in the identification of many of the important compounds present in the aroma of roasted peanuts. Mason *et al.* (1966) made the first positive identification in roasted peanuts of alkylpyrazines, followed by identification of the major monocarbonyls (Mason *et al.*, 1967) including acetaldehyde, isobutyraldehyde, benzaldehyde, and phenylacetaldehyde. Johnson and Waller (1970) have reported spectral evidence for 47 new constituents of peanuts, including 23 pyrazines, and Ballschmieter and Dercksen (1970) have reported nine alcohols from roasted peanuts. In this paper we wish to report the identification of additional new components of roasted peanut volatiles and to establish the identity of some of the compounds for which previous structural assignments were tentative or incorrect.

## ISOLATION

Fifty pounds of Spanish peanuts (Starr variety) were roasted to a medium brown and finely ground in a Fitzpatrick mill with five parts by weight of deionized water. The aqueous slurry was distilled at atmospheric pressure in a wiped film evaporator to yield approximately 1 l. of distillate per kilogram of roasted peanuts. After saturating the 22 l. of distillate with sodium chloride (reagent grade) it was continuously extracted for 12 hr in a liquid-liquid extractor with 800 ml of diethyl ether (Matheson Coleman and Bell, ACS Reagent Grade). The ether extract, after drying over sodium sulfate, was initially concentrated in a Kuderna-Danish concentrator (Kontes Glass Co., Vineland, N.J.) to ca. 5 ml and finally to ca. 1 ml using a stream of nitrogen.

## ANALYTICAL METHODS

Preparative glc was carried out on a Tracor MT 220 chromatograph equipped with a Melpar flame photometric detector operated in the dual sulfur-flame mode. A column of medium wall glass tubing 18-ft long  $\times$   $\frac{3}{8}$ -in. o.d. packed with 12% SF 96 + 0.6% Igepal CO-880 on 60-80 mesh AW-DMCS Chromosorb W was used. The column temperature was

programmed from 60° to 190° C at 2° per min with nitrogen carrier gas at a flow rate of 135 ml per min. The column effluent was split approximately 80:1 in favor of the heated collection vent. The injector, splitter, and collector temperatures were 210° C. The total concentrated ether extract was fractionated by repetitive on-column injections of 100- $\mu$ l samples with the gc effluent collected in seventeen 250-mm long  $\times$  3-mm o.d. glass tubes cooled with crushed Dry Ice. The trapped fractions were further resolved using a 500-ft  $\times$  0.03-in. i.d. stainless steel open tubular column coated with Carbowax 20M. The column temperature was programmed from 70° to 190° C at 1° per min with helium carrier gas at a flow rate of 9.7 ml per min, and an injection temperature of 220° C. Peaks corresponding to 4-vinylphenol and 4-vinyl-2-methoxyphenol were trapped from a 12-ft  $\times$   $\frac{1}{8}$ -in. o.d. 10% Carbowax 20M column. Sufficient material was trapped to obtain a very weak ir spectrum of 4-vinyl-2-methoxyphenol, but quite good ir and nmr spectra were obtained for 4-vinylphenol.

Nmr spectra of the samples in deuteriochloroform solution were recorded using a Varian HA-100 spectrometer. Tetramethylsilane was the internal reference compound. Sweep width was 1000-cps with a 50-cps sweep offset.

For gc-ms analysis, a Hewlett-Packard 5750 gas chromatograph was coupled to a Hitachi RMU-6E mass spectrometer. The Carbowax 20M open tubular column was used with the column effluent split so that 5 ml per min was directed through a Watson-Biemann separator (Watson and Biemann, 1965) to the mass spectrometer, while the remainder of the effluent went to the flame ionization detector of the gas chromatograph.

Retention indices ( $I_E$  values) were determined by the method of van den Dool and Kratz (1963) using standards of ethyl esters of *n*-aliphatic acids and programmed temperature glc.  $I_E$  values for the unknown compounds in the gc-ms runs were obtained by interpolation between peaks of unambiguously identified compounds of known  $I_E$  values. For this reason, and because of the influence of other components on retention times, the  $I_E$  values for some of the later eluting peaks could not be determined so precisely as for most of the peaks. The  $I_E$  values obtained on the open tubular column were, in most cases, very close to those obtained on the standard packed columns.

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## METHODS OF SYNTHESIS

4-Vinylphenol and 4-vinyl-2-methoxyphenol were prepared from 4-hydroxycinnamic and 2-methoxy-4-hydroxycinnamic acids, respectively, by injecting an alcoholic solution of the acid into a preparative gas chromatograph. The injection port was maintained at 240° C and the  $\frac{3}{8}$ -in. o.d.  $\times$  10-ft 20% Carbowax 20M column was held at 205° C. The phenolic compound was collected from the exit at greater than 95% purity.

Ethyl- and propylpyrazine were obtained by alkylation of methylpyrazine with iodomethane and iodoethane, respectively, in sodamide/liquid ammonia (Behun and Levine, 1961). Isopropylpyrazine was isolated by preparative gc as a byproduct of the ethylpyrazine synthesis. 2-Ethyl-5-methylpyrazine and 2,5-diethylpyrazine were synthesized similarly from 2,5-dimethylpyrazine (Goldman *et al.*, 1967).

Vinyl- and isopropenylpyrazines were prepared from methyl- and ethylpyrazine, respectively, *via* their Mannich bases (Kamal *et al.*, 1962). The following pyrazines were prepared by the condensation of  $\alpha$ -diketones with  $\alpha$ -diamines followed by oxidation of the dihydropyrazines: 2-ethyl-3-methylpyrazine from 1,2-diaminoethane and pentane-2,3-dione; 2,3,5-trimethylpyrazine from 1,2-diaminopropane and butane-2,3-dione; and 2-ethyl-3,5-dimethylpyrazine and 2-ethyl-3,6-dimethylpyrazine from 1,2-diaminopropane and pentane-2,3-dione.

The methods of synthesis for the alicyclic pyrazines and their occurrence in other food products will be the subject of future publications.

## RESULTS AND DISCUSSION

The compounds identified from all the fractions are listed in Table I. Identification was made by matching the mass spectra of the unknown compounds with reference spectra and verified by comparing the retention index values of the unknown compounds in the gc-ms runs to  $I_E$  values for authentic compounds. Tentative identifications are indicated where the mass spectra were weak, mixed, or reference compounds were not available for comparison. Mass spectral evidence was obtained for several additional pyrazines, but weak spectra or the absence of reference data made structure assignment difficult. Where specific substitution patterns are not indicated for the pyrazines (diethyl methylpyrazine, for example) the assignment could not be made with certainty from available data.

The following alkyl and alkenyl pyrazines have been identified for the first time in the volatiles of roasted peanuts: propyl-, vinyl-, 2-methyl-6-vinyl-, 2-methyl-5-vinyl-, and tetramethylpyrazine. Isopropylpyrazine, in spite of its characteristic mass spectrum, can only be considered to be tentatively identified as it occurs as a small peak on the trailing edge of the large 2,3-dimethyl pyrazine peak and a mixed spectrum was obtained. However, its  $I_E$  value is in excellent agreement with authentic isopropylpyrazine. Isopropenylpyrazine was identified by comparison of  $I_E$  values and mass spectral data (Table I) of the peanut component with synthesized authentic material (Figure 1a shows additional spectral data). The physical data differ significantly from those of the compound for which Johnson and Waller (1970) tentatively assigned the structure isopropenylpyrazine. The correct identity of the latter compound will be discussed below.

Among the pyrazines reported in peanut volatiles for the

first time are the five- and six-membered fused alicyclic pyrazines: 6,7-dihydro-5*H*-cyclopentapyrazine; 2-methyl-6,7-dihydro-5*H*-cyclopentapyrazine; 5-methyl-6,7-dihydro-5*H*-cyclopentapyrazine; 2(or 3),5-dimethyl-6,7-dihydro-5*H*-cyclopentapyrazine; and 5,6,7,8-tetrahydroquinoxaline. In each case the identity of the roasted peanut constituent was confirmed by comparison of mass spectral data and  $I_E$  values with authentic synthesized material. The structures of the synthetic compounds were substantiated by nmr analysis (Figure 1). The mass spectrum, uv, and retention time of 6,7-dihydro-5*H*-cyclopentapyrazine correspond very closely with the component tentatively identified by Johnson and Waller as isopropenylpyrazine (Table II). Similarly, 2-methyl-6,7-dihydro-5*H*-cyclopentapyrazine and the methyl isopropenylpyrazine of Johnson and Waller appear to be the same compound (see Table II for comparison of mass spectra and Figure 1d for uv data). 5-Methyl-6,7-dihydro-5*H*-cyclopentapyrazine corresponds to the compound tentatively identified by the same authors as methyl cyclopentapyrazine (Table II).

5,6,7,8-Tetrahydroquinoxaline is the first saturated six-membered bicyclic pyrazine to be identified from natural sources. Table II shows the mass spectra of the authentic and isolated compounds. Figure 1e shows the nmr spectrum of synthetic 5,6,7,8-tetrahydroquinoxaline.

The presence of several oxygenated pyrazines in the peanut volatiles is also noteworthy. The present report of the methyl and ethyl acetylpyrazines is, to the authors' knowledge, the first report of their natural occurrence. Acetylpyrazine has also been reported as a constituent of sesame oil (Takei *et al.*, 1969).

Seven phenols were found in roasted peanuts, including 4-vinylphenol and 4-vinyl-2-methoxyphenol. The time-averaged nmr spectrum (142 scans) of 4-vinylphenol is shown in Figure 1g. The mass spectrum, shown in Table I, is quite similar to that of 2,3-dihydrobenzofuran (Stoll *et al.*, 1967). However, consideration of the nmr, ir, and retention time clearly indicates that the compound in question is 4-vinylphenol. It is suspected that this may be the compound identified as 2,3-dihydrobenzofuran in deep fat-fried soybeans by Wilkens and Lin (1970).

As illustrated by the preceding discussion, data in addition to mass spectra are highly desirable, if not essential, for positive identification of a compound's natural occurrence. Often, it is extremely difficult to obtain this information due to the small amounts of material which can be isolated. However, the synthesis of the unique compounds postulated from the mass spectral data and subsequent structural verification by appropriate analytical methods allows a direct comparison of mass spectral and retention data of the authentic with the isolated material and, hence, constitutes an important step in the identification process.

## LIKELY PATHWAYS FOR FORMATION OF MORE IMPORTANT FLAVOR COMPOUNDS OF ROASTED PEANUTS

The presence of 4-vinylphenol and 4-vinyl-2-methoxyphenol in peanut volatiles has not been previously reported. Model system studies (Steinke and Paulson, 1964; Fiddler *et al.*, 1967) have demonstrated that 4-vinylphenol and 4-vinyl-2-methoxyphenol can be formed from 4-hydroxycinnamic acid and ferulic acid, respectively. The two phenolic acids have not yet been reported in peanut, but they do occur widely as esters in vascular plants (Neish, 1965) and would

Table I. Compounds Identified from Roasted Peanuts

Pyrazines	First report in roasted peanut	Retention index		Phenols	First report in roasted peanut	Retention index	
		gc-ms	Authentic			gc-ms	Authentic
Pyrazine		5.87	5.87 <sup>b</sup>	<i>o</i> - <i>sec</i> -Butylphenol <sup>a</sup>	X	11.92	
Methylpyrazine		6.42	6.42 <sup>b</sup>	2,6-Di- <i>tert</i> -butyl- <i>p</i> -cresol	X	12.74	12.65
2,5-Dimethylpyrazine		6.86	6.86 <sup>b</sup>	<i>o</i> -Methoxyphenol	X	12.71	13.14 <sup>b</sup>
2,6-Dimethylpyrazine		6.98	6.98 <sup>b</sup>	Phenol	X	13.86	13.46 <sup>b</sup>
Ethylpyrazine		7.06	7.03	<i>p</i> -Ethylphenol	X	15.4	15.05
2,3-Dimethylpyrazine		7.18	7.18	2-Methoxy-4-vinylphenol (4-vinyl-guaiacol)	X	16.4	15.32
Isopropylpyrazine <sup>a</sup>	X	7.32	7.34 <sup>b</sup>	4-Vinylphenol	X	17.5	16.91
2-Ethyl-6-methylpyrazine		7.58	7.53				
2-Ethyl-5-methylpyrazine		7.60	7.62 <sup>b</sup>				
Trimethylpyrazine		7.73	7.73 <sup>b</sup>				
2-Ethyl-3-methylpyrazine		7.73	7.72 <sup>b</sup>				
Methylisopropylpyrazine	X	7.82		<b>Pyridines</b>			
Propylpyrazine	X	7.90	7.85	Pyridine	X	5.55	5.74 <sup>b</sup>
Vinylpyrazine	X	8.06	7.80 <sup>b</sup>	2-Methylpyridine	X	5.85	5.78 <sup>b</sup>
2-Ethyl-3,6-dimethylpyrazine		8.14	8.14 <sup>b</sup>	2-Pentylpyridine	X	9.45	
2-Ethyl-3,5-dimethylpyrazine		8.31	8.27 <sup>b</sup>	Methyl 2-pyridyl ketone	X	9.73	9.65
Methylpropylpyrazine		8.39		Methyl nicotinate	X	11.42	11.51 <sup>b</sup>
Diethylpyrazine <sup>a</sup>	X	8.40					
Tetramethylpyrazine	X	8.43	8.41 <sup>b</sup>	<b>Ketones</b>			
Isopropenylpyrazine	X	8.54	8.56	Acetone	X	1.00	1.00
2-Methyl-6-vinylpyrazine	X	8.58		2-Butanone		2.22	2.22 <sup>b</sup>
2-Methyl-5-vinylpyrazine	X	8.63	8.63 <sup>b</sup>	2,3-Butanedione	X	3.17	3.17 <sup>b</sup>
2,3-Diethyl-5-methylpyrazine		8.65	8.60 <sup>b</sup>	2-Pentanone	X	3.27	3.27
Diethyl methylpyrazine		8.87		4-Methyl-2-pentanone <sup>a</sup>	X	3.61	3.66
Methyl propenylpyrazine <sup>a</sup>	X	9.12		2,3-Pentanedione	X	4.13	4.16 <sup>b</sup>
Diethyl dimethylpyrazine	X	9.19		4-Heptanone <sup>a</sup>	X	4.82	
Acetylpyrazine	X	9.94	9.92 <sup>b</sup>	4-Methyl-3-penten-2-one		4.95	5.02
5-Methyl-6,7-dihydro-5 <i>H</i> -cyclopentapyrazine	X	9.95	9.94 <sup>b</sup>	3-Penten-2-one	X	5.10	5.06 <sup>b</sup>
6,7-Dihydro-5 <i>H</i> -cyclopentapyrazine	X	10.15	10.25 <sup>b</sup>	2-Heptanone	X	5.47	5.49 <sup>b</sup>
2 (or 3),5-Dimethyl-6,7-dihydro-5 <i>H</i> -cyclopentapyrazine	X	10.42	10.39 <sup>b</sup>	Cyclopentanone	X	5.55	5.59
6-Acetyl-2-methylpyrazine <sup>a</sup>	X	10.54		2-Octanone	X	6.55	6.55
5-Acetyl-2-methylpyrazine <sup>a</sup>	X	10.64		Cyclohexanone	X	6.74	6.76
2-Methyl-6,7-dihydro-5 <i>H</i> -cyclopentapyrazine	X	10.75	10.73 <sup>b</sup>	Cyclopentenone	X	7.27	
6-Acetyl-2-ethylpyrazine	X	10.99		2-Undecanone	X	9.67	9.62 <sup>b</sup>
5,6,7,8-Tetrahydroquinoxaline	X	11.12	11.14 <sup>b</sup>	Acetophenone	X	10.17	10.18 <sup>b</sup>
Quinoxaline <sup>a</sup>	X	12.64	12.70 <sup>b</sup>	Ethyl phenyl ketone	X	10.93	10.85
				Benzyl methyl ketone	X	10.97	
				2-Hydroxy-3-methyl-2-cyclopenten-1-one <sup>a</sup>	X		11.71 <sup>b</sup>
<b>Pyrroles</b>				<b>Aldehydes</b>			
1-Methylpyrrole		5.07	5.09 <sup>b</sup>	Acetaldehyde			0.44
Pyrrole	X	8.79	8.73 <sup>b</sup>	Isobutyraldehyde		0.94	1.00 <sup>b</sup>
Methyl 1-pyrrolyl ketone (1-acetylpyrrole)	X	8.76	9.06 <sup>b</sup>	2-Methylbutanal		2.43	2.43 <sup>b</sup>
2-Methylpyrrole	X	9.23		Pentanal	X	3.33	3.33 <sup>b</sup>
Pyrrole-1-carboxaldehyde <sup>a</sup>	X	9.60		Hexanal		4.49	4.49 <sup>b</sup>
1-Ethylpyrrole-2-carboxaldehyde <sup>a</sup>		9.78	9.84 <sup>b</sup>	2-Methyl-2-butenal	X	4.61	4.61
2-Methylpyrrole-1-carboxaldehyde <sup>a</sup>	X	9.84		2-Methyl-2-pentenal	X	5.31	5.34
1-Methylpyrrole-2-carboxaldehyde		9.85	9.86	Heptanal	X	5.51	5.55 <sup>b</sup>
5-Methylpyrrole-2-carboxaldehyde		11.45	11.81	Octanal	X	6.57	6.59
1-Furfurylpyrrole		11.88	11.89 <sup>b</sup>	Nonanal	X	7.64	7.74 <sup>b</sup>
Methyl 2-pyrrolyl ketone (2-acetylpyrrole)		13.26	13.69 <sup>b</sup>	Benzaldehyde		8.97	8.96 <sup>b</sup>
Pyrrole-2-carboxaldehyde		13.69	13.69 <sup>b</sup>	<i>o</i> -Tolualdehyde <sup>a</sup>	X	9.90	10.00
2-Propionylpyrrole	X	13.52	13.66	Phenylacetaldehyde		10.15	10.15 <sup>b</sup>
1-Furfurylpyrrole-2-carboxaldehyde	X	16.1		<i>o</i> -Ethylbenzaldehyde	X	10.25	10.44
				<i>p</i> -Ethylbenzaldehyde	X	10.95	11.00
				<i>trans</i> -2, <i>trans</i> -4-Decadienal		11.67	11.69
				2-Phenyl-2-butenal		12.90	12.90 <sup>b</sup>
				Cinnamaldehyde	X	14.00	14.00 <sup>b</sup>
				5-Methyl-2-phenyl-2-hexenal <sup>a</sup>		13.78	14.19
<b>Thiazoles</b>				<b>Terpenes</b>			
Thiazole	X	6.08	6.07	2(10)-Pinene ( $\beta$ -pinene)	X	4.85	4.85 <sup>b</sup>
4-Methylthiazole	X	6.53	6.55 <sup>b</sup>	4(10)-Thujene (sabinene)	X	4.95	5.00
Benzothiazole	X	12.92	12.91 <sup>b</sup>	Myrcene	X	5.28	5.28 <sup>b</sup>
				<i>p</i> -Mentha-1,8-diene (limonene)	X	5.72	5.75 <sup>b</sup>
<b>Sulfur compounds</b>				1-Isopropyl-4-methylbenzene ( $\gamma$ -terpinene)	X	6.24	6.23
Methyl disulfide		4.49	4.48 <sup>b</sup>	<i>p</i> -Mentha-1,4-diene ( <i>p</i> -cymene)	X	6.45	6.45 <sup>b</sup>
Propyl disulfide	X	7.55	7.55 <sup>b</sup>	4,8-Epoxy- <i>p</i> -menth-2-ene (4-terpineol)	X	9.65	9.65 <sup>b</sup>
3-Methylthiopropionaldehyde	X	8.22	8.14 <sup>b</sup>	<i>p</i> -1-Menthen-8-ol ( $\alpha$ -terpineol)	X	10.65	10.54
2-Methyldihydro-2 <i>H</i> -thiophen-3-one	X	9.05	9.05	<i>p</i> -Mentha-6,8-dien-2-one (carvone) <sup>a</sup>	X	11.04	11.02 <sup>b</sup>
Dihydro-2 <i>H</i> -thiophen-3-one	X	9.31	9.30				
Methyl 2-thienyl ketone (2-acetylthiophene)		11.36	11.37				
5-Methylthiophene-2-carboxaldehyde	X	11.45	11.43 <sup>b</sup>				
Benzyl methyl disulfide <sup>a</sup>	X	13.62	13.60				

Table I. (Continued)

	First report in roasted peanut	Retention index			First report in roasted peanut	Retention index	
		gc-ms	Authentic			gc-ms	Authentic
<b>Furans</b>				<b>Alcohols</b>			
2-Pentylfuran		6.11	5.93	Hexyl alcohol	X	7.15	7.11
2-Furaldehyde		8.31	8.31 <sup>b</sup>	3-Hexen-1-ol	X	7.45	7.35
Furyl methyl ketone		8.71	8.71 <sup>b</sup>	Cyclohexanol	X	7.66	
Furfuryl alcohol, acetate <sup>a</sup>	X	9.05		Heptyl alcohol	X	8.01	8.00
5-Methylfurfural		9.41	9.41 <sup>b</sup>	$\alpha$ -Methylbenzyl alcohol	X	11.61	11.51
Furoic acid, methyl ester	X	9.44	9.42 <sup>b</sup>	Benzyl alcohol	X	12.32	12.32 <sup>b</sup>
Furoic acid, ethyl ester <sup>a</sup>	X	9.61	9.79	Phenethyl alcohol	X	12.55	12.55
Methyl 5-methylfuryl ketone <sup>a</sup>	X	10.04	9.84	<b>Aromatic Hydrocarbons</b>			
Furfuryl alcohol		10.17	10.17 <sup>b</sup>	Benzene	X	2.92	2.42
3-Phenylfuran <sup>a</sup>		11.99		Toluene		4.14	4.14
$\alpha$ -Methylfuranacrolein <sup>a</sup>	X	12.31	11.99 <sup>b</sup>	Ethylbenzene	X	5.00	5.00
<b>Esters</b>				<i>p</i> -Xylene	X	5.10	5.10
Acetic acid, ethyl ester	X	2.00	2.00	<i>m</i> -Xylene	X	5.15	5.17
Butyric acid, ethyl ester	X	4.00	4.00	<i>o</i> -Xylene	X	5.60	5.61
Acetic acid, butyl ester	X	4.30	4.34	Propylbenzene	X	5.86	5.83
Acetic acid, isopentyl ester	X	4.87	4.86	Mesitylene	X	6.25	6.24
Acetic acid, 2-ethoxy ethyl ester	X	6.58		Styrene	X	6.32	6.32 <sup>b</sup>
Acetic acid, phenyl ester	X	9.92		1,2,4-Trimethylbenzene	X	6.59	6.61
Acetic acid, methylphenyl ester	X	11.27	11.23	Butylbenzene	X	6.90	6.91
Propionic acid, phenethyl ester <sup>a</sup>	X	12.40	12.44	Indene	X	8.61	8.61
<b>Lactones</b>				Methyl-2,3-dihydroindene	X	8.76	
4-Hydroxyvaleric acid, $\gamma$ -lactone	X	9.77	9.77 <sup>b</sup>	1,2,3,4-Tetrahydronaphthalene <sup>a</sup>	X	9.05	
4-Hydroxybutyric acid, $\gamma$ -lactone	X	9.96	9.96 <sup>b</sup>	Naphthalene		11.12	11.12 <sup>b</sup>
4-Hydroxyoctanoic acid, $\gamma$ -lactone	X	12.82	12.88	Methylnaphthalene	X	11.99	
<b>Alcohols</b>				Ethyl naphthalene	X	13.08	
Isopropyl alcohol		2.30	2.30 <sup>b</sup>	Dimethylnaphthalene	X	13.22	
Isobutyl alcohol	X	4.35	4.37 <sup>b</sup>	Biphenyl	X	13.46	13.54
2-Pentanol	X	4.35		Dimethylnaphthalene (isomer)	X	13.48	
3-Pentanol <sup>a</sup>	X	4.50	4.51	<b>Miscellaneous</b>			
Butyl alcohol		4.91	4.91	Pentane	X		
1-Penten-3-ol	X	5.07	5.00	Acetaldehyde, dibutyl acetal	X	5.90	5.96
4-Methyl-2-pentanol	X	5.14	5.14	1-Chloro-2-methylbenzene	X	6.87	
2-Methyl-1-butanol	X	5.58	5.54	Hexadecane	X	9.71	9.72
2-Hexanol	X	5.72	5.66	C <sub>17</sub> H <sub>36</sub>	X	10.72	
Pentyl alcohol	X	6.00	6.00	Tolunitrile	X	12.80	
				Benzonitrile	X		9.70
				Tridecane	X		6.74

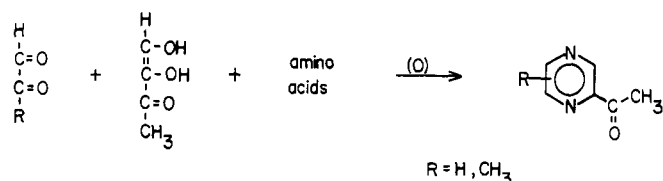
<sup>a</sup> Tentatively identified in roasted peanut. <sup>b</sup> *I*E value obtained on 500-ft  $\times$  0.03-in. i.d. Carbowax 20M capillary. Other authentic *I*E values obtained on packed columns (van den Dool and Kratz, 1963).

be expected to undergo thermal degradation under the conditions of peanut roasting.

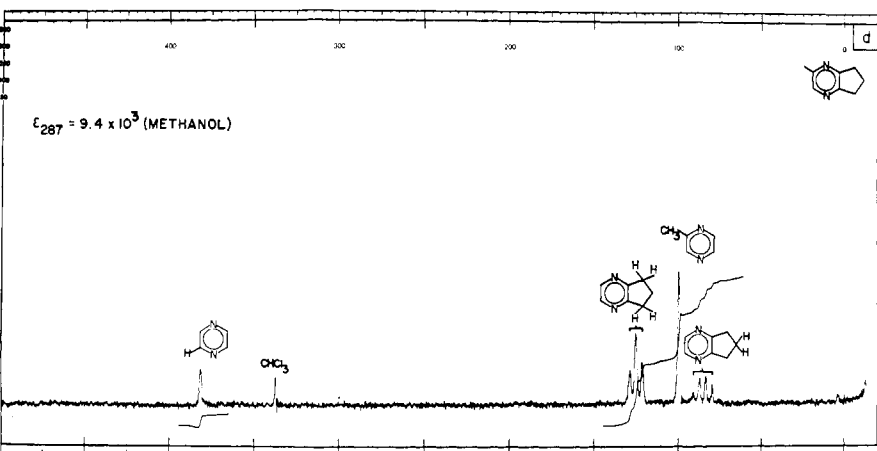
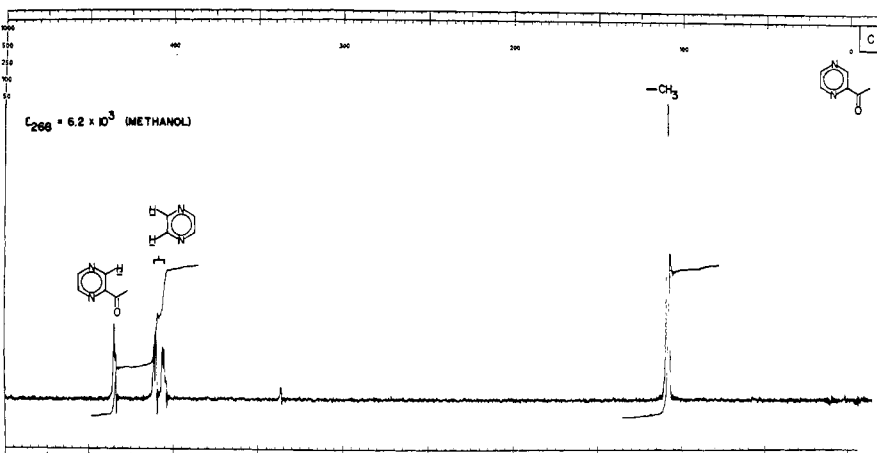
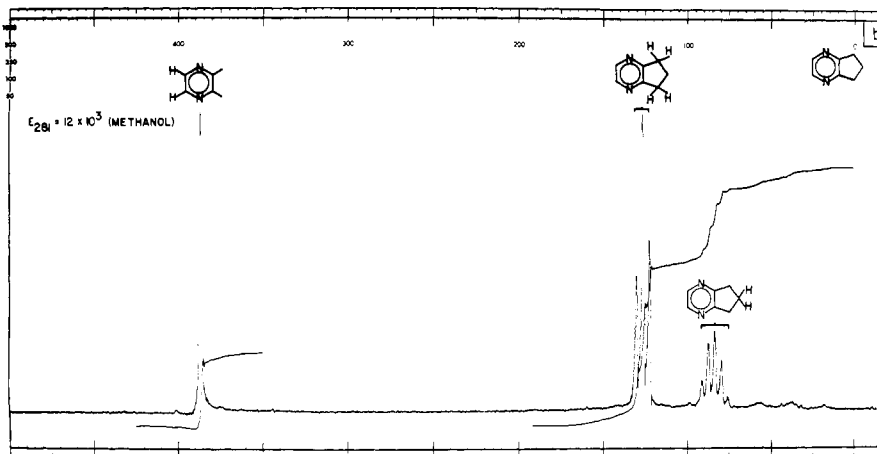
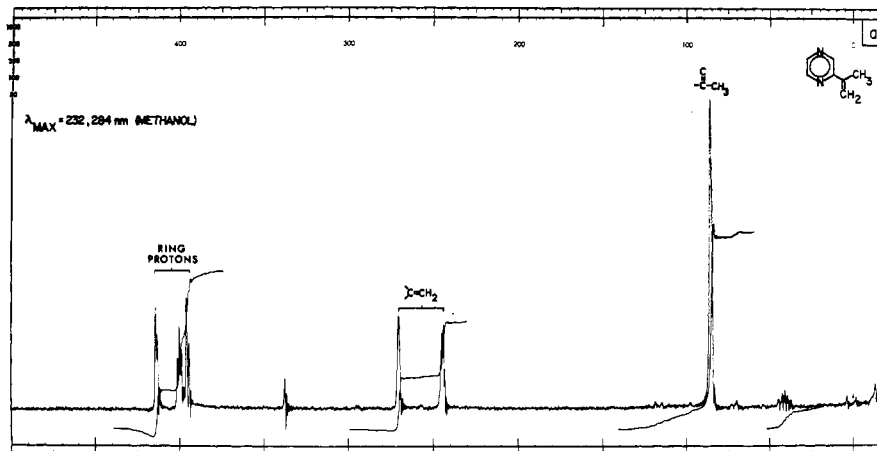
A number of the simple alkylpyrazines have been isolated from several food products which have undergone high temperature processing, notably coffee (Bondarovich *et al.*, 1967; Goldman *et al.*, 1967), cocoa (Marion *et al.*, 1967; Rizzi, 1967; van Praag *et al.*, 1968), popcorn (Walradt *et al.*, 1970), rye crisp bread (von Sydow and Anjou, 1969), and deep fat-fried soybeans (Wilkens and Lin, 1970). As a result of model system studies (Dawes and Edwards, 1966; van Praag *et al.*, 1968; Koehler *et al.*, 1969) possible pathways for the formation of the alkylated pyrazines have been suggested wherein the carbon skeleton of the pyrazine is derived from carbohydrate degradation in the Maillard reaction and the pyrazinic nitrogen originates either directly from amino acids or *via* ammonia. The influence of amino acids on the quantitative distribution of the alkylpyrazines (Koehler *et al.*, 1969) suggests that a mechanism similar to that proposed by Wang *et al.* (1969) is operative for the formation of methyl-substituted pyrazines.

However, with the isolation of pyrazines possessing propyl-, 2,3-diethyl-, 2-methyl-3-isobutyl-, and 2-methyl-3-isoamyl side chains (Bondarovich *et al.*, 1967; Goldman *et al.*, 1967;

Flament *et al.*, 1967), alternative pathways for pyrazine formation must be considered, as it becomes improbable with these complex alkyl groups that the appropriate  $\alpha$ -diketone precursors are formed directly from carbohydrate breakdown. Similarly, the genesis of the alkenyl-substituted pyrazines requires a more complex route, possibly through dehydration of the corresponding hydroxypyrazines (Grimmett, 1965). The formation of acetyl and methyl acetylpyrazines may be explained by the Wang *et al.* (1969) mechanism involving the condensation of *C*-methyl reductone, a browning reaction product (Hodge, 1967), with glyoxal or pyruvaldehyde, respectively, and amino acids.



The pathway(s) by which 6,7-dihydro-5*H*-cyclopentapyrazine and 5,6,7,8-tetrahydroquinoxaline are formed cannot be readily explained on the basis of known precursors. However, the genesis of 5-methyl- and 2(or 3),5-dimethyl-



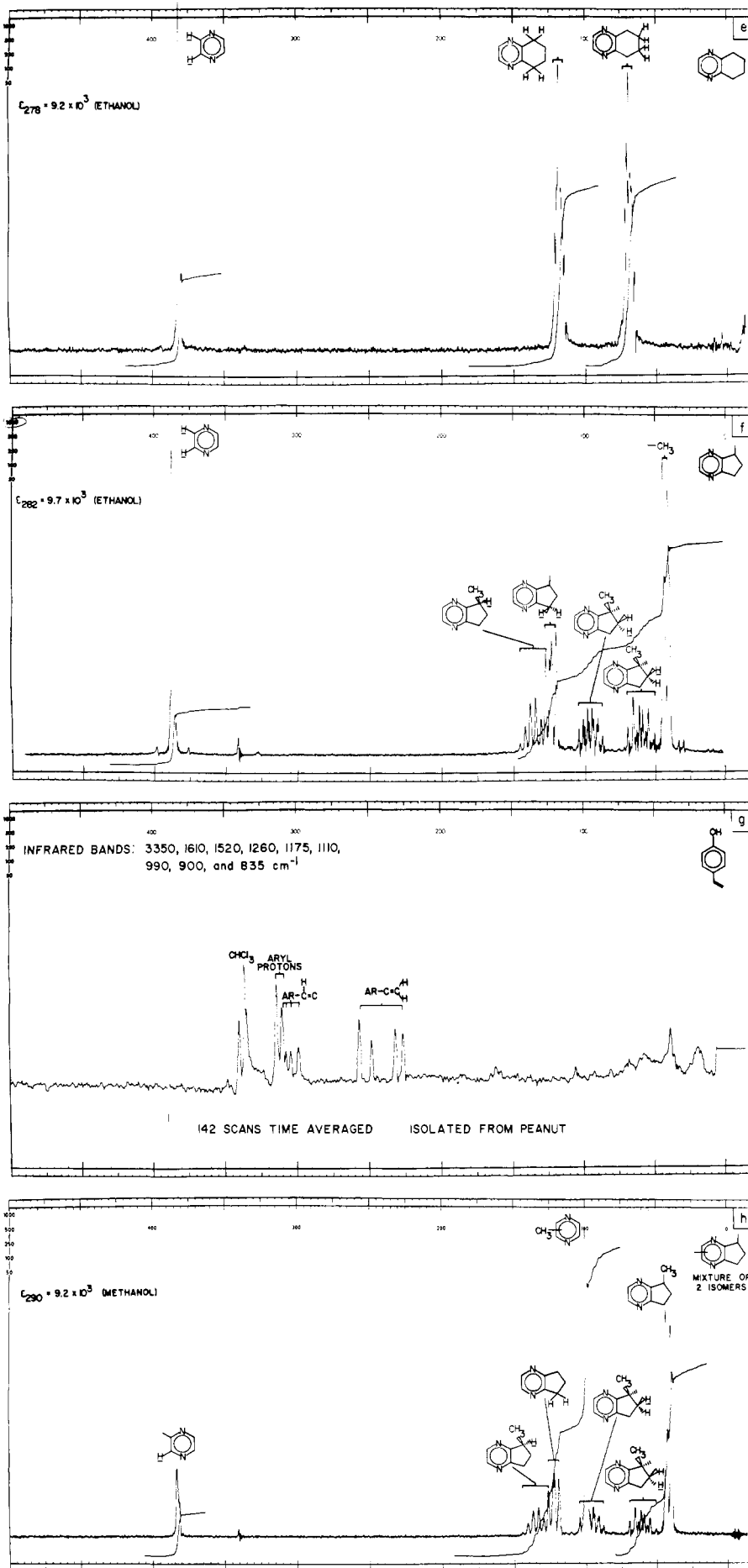


Figure 1. Nmr spectra of synthetic compounds

Table II. Mass Spectra of Compounds Identified in Roasted Peanut

Isopropenylpyrazine, mol wt 120				6,7-Dihydro-5H-cyclopentapyrazine, mol wt 120			
m/e	Relative intensity		m/e	Relative intensity			
	Authentic	Peanut		Authentic	Peanut	Peak T <sup>a</sup>	
39	35	35	39	27	27	8	
41	18	18	41	22	28	7	
52	23	14	65	18	20	10	
67	24	16	66	19	21	13	
94	11	24	93	11	15	9	
119	100	100	119	87	82	84	
120	84	54	120	100	100	100	

Acetylpyrazine, mol wt 122				2-Methyl-6,7-dihydro-5H-cyclopentapyrazine, mol wt 134			
m/e	Relative intensity		m/e	Relative intensity			
	Authentic	Peanut		Authentic	Peanut	Peak W <sup>a</sup>	
43	100	100	39	46	50	22	
52	44	40	40	17	20		
53	34	33	41	15	15		
79	27	30	65	14	17		
80	45	49	66	31	42	29	
122	37	42	107	16	12	15	
			133	69	71	79	
			134	100	100	100	

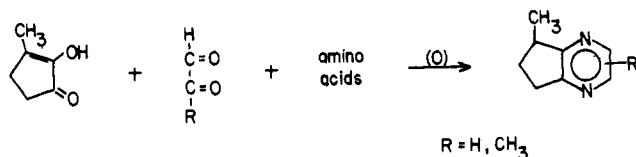
5,6,7,8-Tetrahydroquinoxaline, mol wt 134				5-Methyl-6,7-dihydro-5H-cyclopentapyrazine, mol wt 134			
m/e	Relative intensity		m/e	Relative intensity			
	Authentic	Peanut		Authentic	Peanut	Peak S <sup>a</sup>	
39	37	22	39	21	16	5	
41	28	21	41	12	11	3	
51	25	11	52	16	12	4	
52	42	18	78	12	17	9	
106	33	26	119	100	100	100	
133	56	54	133	25	35	51	
134	100	100	134	48	70	78	

4-Vinylphenol, mol wt 120				2,3-Dihydro-benzofuran <sup>b</sup>			
m/e	Relative intensity		m/e	Relative intensity			
	Authentic	Peanut		Authentic	Peanut	Peak T <sup>a</sup>	
39	19	17	39	26	17		
51	7	12	65	9	5		
63	11	11	79	8	10		
65	14	24	133	100	100		
91	33	60	147	13	22		
119	21	26	148	41	42		
120	100	100					

<sup>a</sup> Johnson and Waller (1970). <sup>b</sup> Stoll *et al.* (1967).

6,7-dihydro-5H-cyclopentapyrazines may be the result of the interaction of glyoxal and pyruvaldehyde, respectively, with amino acids and 2-hydroxy-3-methyl-2-cyclopenten-1-one, a frequently occurring product of carbohydrate degradation.



#### SUMMARY

As a result of this work on the volatiles of roasted peanuts, we have identified 187 compounds; 142 of them, including 17 pyrazines, are reported for the first time. Although many of the identified constituents can be considered to contribute something to peanut flavor, it is not possible on the basis of this study to pinpoint one or more which could be described as definitely peanutlike.

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