roasting. Pertinent to the subject is the work of Reineccius *et al.* (1972) who reported substantially higher concentrations of ketoses in unroasted, fermented Ghana beans compared to the unfermented Sanchez variety.

The percentage compositions of the free sugars fractions of Ghana and Sanchez cocoa beans roasted for varying periods of time at 150°C are recorded in Table V. Ketoses dominated the sugars fraction of Ghana beans and were responsible for most of the total weight of sugars consumed during roasting. This is in contrast to the Sanchez sample in which glucose and fructose were present in comparable amounts after various periods of roasting. Extrapolation of the quantitative data used in Figures 3 and 4 indicated that Ghana beans contained 80% more fructose and sorbose than Sanchez beans, but total sugars was 50% less. Kato *et al.* (1969) reported that the ketoses were about three times more reactive than aldoses in forming volatiles, and Koehler and Odell (1970) obtained a greater yield of pyrazines in heated model systems when fructose was substituted for glucose. The greater reactivity of the ketoses might account for the more rapid and greater generation of pyrazines in fermented Ghana beans.

Hydrolysis of sucrose during roasting was negligible. This indicates that the sucrose concentration in unroasted cocoa beans is not an important variable in the generation of pyrazines during roasting. The rapid and nearly complete hydrolysis of sucrose during the roasting of coffee (Feldman *et al.*, 1969), negligible hydrolysis in roasted peanuts (Newell *et al.*, 1967), and our finding of minor hydrolysis in roasted cocoa is interesting to note.

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Characterization of Some Volatile Constituents of Roasted Pecans

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The volatiles from roasted pecans were separated into carbonyl, basic, acidic, and noncarbonyl oxygenated fractions and qualitatively investigated. Carbonyls were converted to their 2,4-dinitrophenylhydrazones and identified by analysis of the regenerated carbonyls using combined gas chromatography–mass spectrometry, or direct probe mass spectrometry of each crystalline hydrazone isolated by column and thin-layer chromatography. Basic, acidic, and neutral noncarbonyl oxygenated fractions were characterized by gas chromatography and mass spectrometry. Nineteen carbonyls, pyridine, eight pyrazines, seven acids, five alcohols, and one lactone were positively identified by comparison of their mass spectral and gas chromatographic retention data with those of authentic compounds. Pecan oil may be considered as one of the main sources of roasted pecan carbonyls. The possible precursors of the pyrazines are discussed. Compounds believed to contribute to the flavor of roasted pecans are also briefly discussed.

Roasted pecans possess a characteristic pleasant aroma but little is known about the compounds responsible for the aroma. This paper deals with results of a qualitative investigation of volatile compounds from roasted pecans. The origin of the carbonyls and pyrazines identified was also studied in model systems and is discussed.

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EXPERIMENTAL

Materials. Good quality, air-dried, shelled pecans of the Stuart Variety were obtained from the Oklahoma State University Horticulture Department. On identification of components isolated from roasted pecan volatiles, the authentic compounds were obtained from reliable commercial sources or were gifts.

Sample Preparation. About 400 g of raw pecans were dry roasted at 170° C to a deep brown color. The roasted pecan

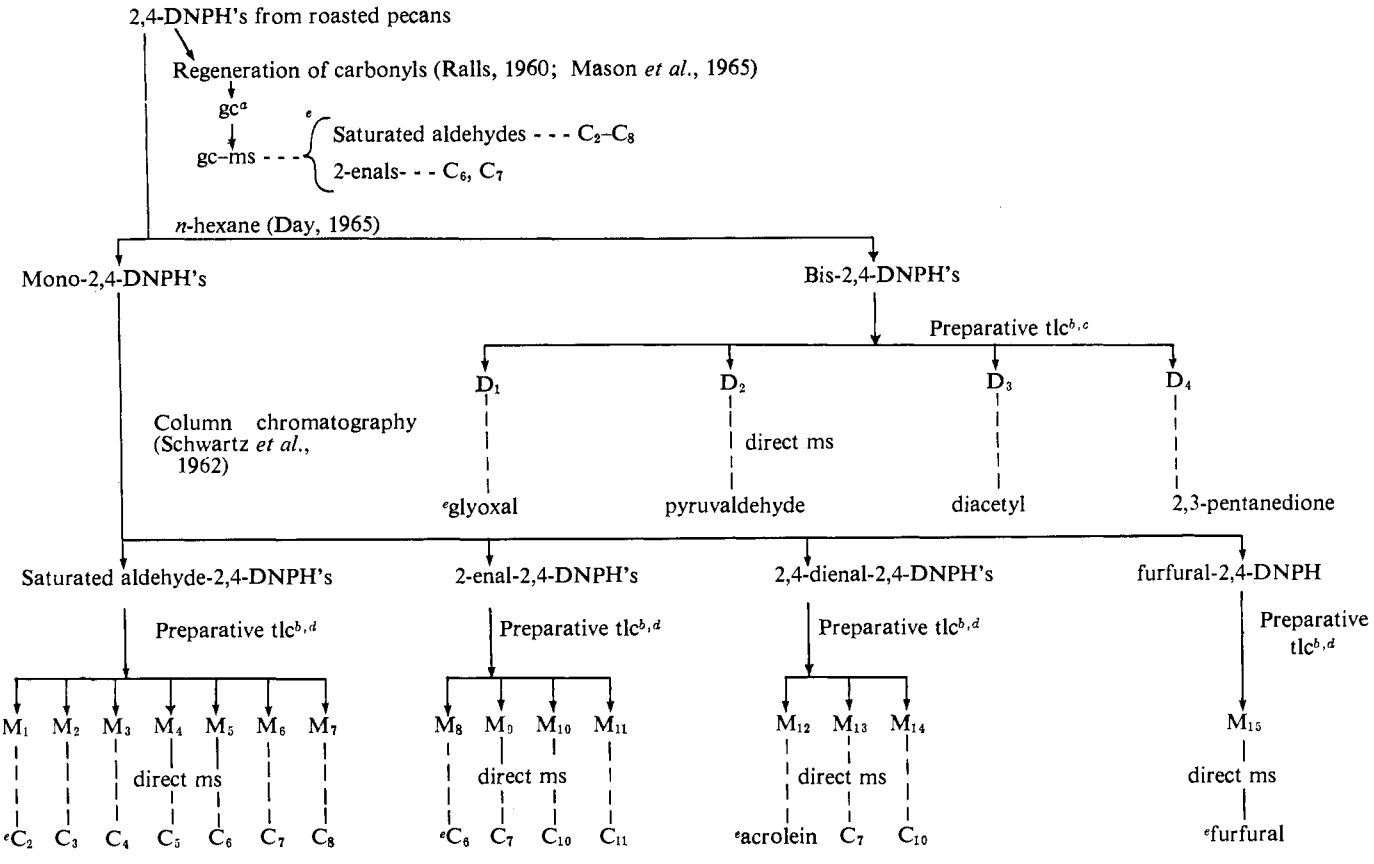

Figure 1. Isolation and identification of 2,4-dinitrophenylhydrazones from volatiles of roasted pecans. (a) Column $I_{(a)}$ was used. (b) 0.25 mm thick silica gel G plates were used. (c) Solvent system, benzene–chloroform, 3:1 (v/v), or benzene–petroleum ether–ethyl acetate, 34:5:1 (Ronkainen, 1967). (d) Solvent system, *n*-hexane–ethyl acetate, 10:1.5 (v/v). (e) Results obtained, *e.g.*, saturated aldehyde C_2 = ethanal, C_3 = propanal, etc.

kernels were ground and subjected to steam distillation at a pressure less than 20 mm in 1.5 l. of distilled water. The distillate was collected in flasks precooled in ice water and Dry Ice–acetone. Sixty grams of NaCl were dissolved in about 800 ml of combined distillate and then extracted three times with 400-ml portions of diethyl ether. The ether extract was concentrated in a rotary evaporator at room temperature. This whole process was replicated several times, and about 250 ml of the ether extract was obtained from a total of about 2 kg of raw pecans. Basic, acidic, and neutral noncarbonyl oxygenated fractions were prepared from the ether extract. The carbonyl fraction was obtained from the steam distillate or directly from the volatiles produced during the roasting of pecans.

Carbonyl Fraction. Another aliquot of raw pecan kernels was roasted under 50–60 ml per min of air flow in an electric roaster [a glass tube of 20 in. × 1 in. i.d. coiled nichrome wire around the tube (Wang *et al.*, 1968)], and the volatiles produced were bubbled directly into a saturated solution of 2,4-dinitrophenylhydrazine in 2 *N* HCl. In a typical preparation, 74 g of raw pecans were roasted and produced about 32 mg of 2,4-dinitrophenylhydrazones (2,4-DNPH's). The hydrazones were also prepared from the above steam distillate. Since the thin-layer chromatograms showed a qualitative similarity between the hydrazone composition obtained from the distillate and those from the volatiles produced during roasting, the hydrazones in the present study were prepared from the volatiles produced during roasting. The procedure of isolation and identification of the hydrazones is shown in Figure 1.

Possible Origin of Carbonyls. About 10 g of pecan oil obtained by extraction of raw pecans with *n*-hexane were heated at 170° C for 3 hr in the electric roaster, and the carbonyls produced were isolated and identified in the same manner as described above. A similar experiment was also conducted with 5 g of pure glycerol.

Basic Fraction. The ether extract (250 ml) from the steam distillate was treated three times each with 50-ml portions of 5% HCl and the resultant aqueous layer was concentrated below 50° C *in vacuo* to near dryness. Ten milliliters of 12 *N* NaOH were added and extracted three times each with 20-ml portions of ether. The combined ether extract was concentrated to about 20 μl and analyzed by glc (Column II, IV; see Gas Chromatography) and gc–ms (Column IV).

Formation of Pyrazines from the Model System of Glycerol–Alanine or Glycine. Glycerol (0.03 mol) was mixed thoroughly with DL-alanine (0.03 mol) and the mixture was heated at 190 ± 5° C for 4 hr in the electric roaster under 50–60 ml per min of air flow. The volatiles produced were collected in two traps cooled with Dry Ice–acetone and then extracted three times each with 30-ml portions of ether. The basic fraction was separated and analyzed by glc (Column II) and gc–ms (Column II) as described above. A similar experiment was also conducted with the glycerol–glycine system.

Acidic Fraction. The ether extract (250 ml, freshly prepared) from the steam distillate was treated three times with 50-ml portions of 5% $NaHCO_3$, and the resultant aqueous layer was concentrated below 50° C *in vacuo* to near dryness. Hydrochloric acid (2 *N*) was added to adjust the pH to 0.5, and the solution was extracted three times with 30-ml por-

Table I. Compounds Identified from Roasted Pecans

Compound	R_f[a] tlc	Retention[b] time, min	ms Identification	Size of[c] peaks
Carbonyls				
Ethanal	1.00	3.2 I_a	+	L
Propanal	1.26	3.9 I_a	+	M
Butanal	1.38	4.9 I_a	+	S
Pentanal	1.48	7.0 I_a	+	L
Hexanal	1.55	10.8 I_a	+	VL
Heptanal	1.61	17.5 I_a	+	M
Octanal	1.67	23.8 I_a	+	M
2-Hexenal	1.57	19.9 I_a	+	S
2-Heptenal	1.64	25.5 I_a	+	M
2-Decenal	1.71		+	
2-Undecenal	1.77		+	
Acrolein	1.42		+	
2,4-Heptadienal	1.69		+	
2,4-Decadienal	1.78		+	
Furfural	1.06		+	
Glyoxal	0.20		+	
Pyruvaldehyde	0.44		+	
Diacetyl	0.61		+	
2,3-Pentanedione	0.75		+	
Basic compounds				
Pyridine		11.5 IV	+	S
2-Methylpyrazine		13.7 IV	+	L
2,5-Dimethylpyrazine		16.6 IV	+	VL
2,6-Dimethylpyrazine		16.8 IV	+	L
2,3-Dimethylpyrazine		17.9 IV	+	S
2-Ethyl-6-methyl-pyrazine		20.1 IV	+	M
2-Ethyl-5-methyl-pyrazine		20.4 IV	+	M
2,3,5-Trimethyl-pyrazine		21.3 IV	+	L
2,5-Dimethyl-3-ethylpyrazine		23.7 IV	+	L
Acids[d]				
Acetic acid		4.9 I_b	+	VL
Propionic acid		6.1 I_b	+	L
Pentanoic acid		10.2 I_b	+	S
4-Methyl-pentanoic acid		11.9 I_b	+	S
Hexanoic acid		13.6 I_b	+	L
Heptanoic acid		17.9 I_b	+	S
Octanoic acid		23.0 I_b	+	S
Alcohols				
Ethanol		6.5 I_b	+	M
1-Pentanol		19.6 I_b	+	L
1-Hexanol		26.0 I_b	+	L
1-Heptanol		32.3 I_b	+	L
1-Octanol		38.8 I_b	+	L
Lactone				
γ-Octalactone		59.9 I_b	+	S

[a] R_f of 2,4-DNPH of carbonyl compound isolated/R_f of 2,4-DNPH of ethanal in benzene–chloroform 3:1, on 0.25-mm thick silica gel G plate. [b] I_a, I_b, and IV refer to retention times on the designated columns and conditions employed. [c] Size of peaks was roughly estimated; S = small; M = medium; L = large; VL = very large. [d] Retention time and peak size data are for methyl ester of the acids.

tions of ether. This ether extract was concentrated to about 5 ml and esterified with diazomethane. The resultant solution was concentrated to about 0.3 ml and submitted to glc (Column $I_{(b)}$, III) and gc–ms analysis (Column $I_{(b)}$).

Neutral Noncarbonyl Oxygenated Fraction. The basic, acidic, and phenolic compounds were removed from the ether extract (250 ml, freshly prepared) of the steam distillate by treatment three times each with 50-ml portions of 5% HCl, 5% $NaHCO_3$, and 5% NaOH. Carbonyls were then removed by treatment with Girard-T reagent (Gaddis, 1961a,b). The hydrocarbon fraction was removed by silicic acid column chromatography (Kirchner and Miller, 1952), and the resultant oxygenated fraction was concentrated to about 50 μl and characterized by glc (Column $I_{(b)}$, III) and gc–ms (Column $I_{(b)}$).

Gas Chromatography. A modified Barber-Colman gas chromatograph (Waller, 1968) Model 8000, with a flame ionization detector was utilized. The four columns were operated under the following conditions.

I. 20-ft × 0.25-in. o.d. coiled glass column packed with 5% Carbowax 20M on 100–120 mesh Gas Chrom Q (w/w). Flow rate 30 ml per min of helium. Temperature held at: (a) 75° C for 12 min then programmed at 5° C per min to 175° C and held at 175° C; (b) 80° C for 7 min then programmed at 2° C per min to 180° C and held at 180° C.

II. 20-ft × 0.25-in. o.d. coiled glass column packed with 10% Carbowax 20M [containing 1% (w/w) KOH additive] on 100–120 mesh Gas Chrom Q (w/w). Flow rate 30 ml per min of helium. Temperature held at 80° C for 7 min then programmed at 2° C per min to 180° C and held at 180° C.

III. 12-ft × 0.25-in. o.d. coiled glass column packed with 10% Triton X305 on 100–120 mesh Gas Chrom Q (w/w). Flow rate 30 ml per min of helium. Temperature held at 60° C for 7 min then programmed at 2° C per min to 200° C and held at 200° C.

IV. 250-ft × 0.01-in. i.d. stainless steel capillary column coated with Carbowax 1540 containing 1% KOH (Cieplinski, 1966). Flow rate 0.8 ml per min of helium. Temperature held at 80° C for 7 min then programmed at 2° C per min to 170° C and held at 170° C.

The injection port and flame ionization detector were held at 220° C and 270° C, respectively, through all operation.

Gas Chromatography–Mass Spectrometry (gc–ms). The columns and the operating conditions employed in gc–ms for analysis of each fraction were as described above. Each column was connected to a prototype of the LKB 9000 gc–ms (Waller, 1968) and operated under the following conditions: ionization voltage, 70 eV; ion source temperature, 250° C; accelerating voltage, 3.5 kV; trap current, 60 μA; electron multiplier voltage, 1.7 to 2.1 kV; separator temperature, 220° C; scan speed, from *m/e* 6 to *m/e* 250 in 5 sec. While the capillary column (Column IV) was in use, additional helium was introduced to the capillary column effluent immediately before the effluent entered the jet separators of the mass spectrometer. This addition of extra carrier gas was necessary for optimum separator efficiency as it requires a column effluent gas flow of 30–40 ml per min.

Direct Probe Mass Spectrometry. Each hydrazone isolated as described above was analyzed by direct probe mass spectrometry. Several micrograms of the sample were gradually heated in the direct probe and the spectra were taken at 120–180° C. The scan speed was from *m/e* 6 to *m/e* 530 in 10 sec and the other conditions were the same as described in gc–ms analysis.

RESULTS AND DISCUSSION

Table I is a summary of the compounds identified and criteria for identity. The identifications were designated positive if mass spectral and retention time data matched authentic compounds analyzed under identical instrument conditions.

Figure 1 is a schematic diagram of procedure and the products obtained in isolation and identification of carbonyls. As shown in Figure 1, the 2,4-DNPH's were investigated by (1) analysis of regenerated carbonyls by gc–ms, or (2) direct

probe mass spectrometry of each crystalline 2,4-DNPH isolated by column and thin-layer chromatography. Method (1) was more simple than method (2) but only the first nine carbonyls listed in Table I (from ethanal to 2-heptenal) were identified by this method. Not only dicarbonyls but also most of the unsaturated aldehydes were not present in the regenerated vapors in sufficient amounts to give glc recorded response or to obtain good mass spectra. Furthermore, some noncarbonyl compounds were found in the regenerated vapors. These could be impurities contained in α-ketoglutaric acid or reagent 2,4-DNPH or could result from the breakdown products produced during the regeneration process. Method (2) utilized column and thin-layer chromatography and was more time consuming; however, all of the carbonyls listed in Table I were identified by this method. There were some advantages of method (2): (a) The molecular ion peak obtained from the direct probe mass spectrometry of 2,4-DNPH itself was much more intense than that from its parent carbonyl (for example, M^+ of 2-heptenal was 6% and M^+ of its 2,4-DNPH was 56% of each base peak, respectively), making it simpler for determination of the empirical formula; (b) Column bleeding, especially at higher temperatures, which may cause confusion in identification, can be prevented; (c) The characteristic colors displayed during chromatography (Schwartz *et al.*, 1962) or after spraying with ethanolic KOH (Neuberg and Strauss, 1945) would give additional information for identification. Furthermore, only a few micrograms of the 2,4-DNPH were adequate to yield a good mass spectrum.

Mass spectral data (above *m/e* 40, intensities in parentheses with base peak taken as 100) of 2,4-DNPH's previously unpublished are listed as follows.

2-Hexenal 2,4-DNPH, M^+ (molecular ion), 278 (77); major ions, 41 (100), 67 (77), 53 (55), 66 (43), 54 (28), 55 (25), 51 (25), 52 (23), 186 (22), 112 (20), 43 (19), 113 (16), 261 (14).

2-Heptenal 2,4-DNPH, M^+, 292 (56); major ions, 235 (100), 41 (61), 67 (42), 231 (41), 216 (41), 53 (31), 55 (25), 275 (22), 189 (22), 95 (19), 63 (19), 170 (17), 81 (14), 80 (14), 78 (14).

2-Decenal 2,4-DNPH, M^+, 334 (35); major ions, 235 (100), 41 (44), 67 (38), 216 (31), 55 (25), 43 (25), 317 (22), 231 (22), 215 (22), 203 (19), 53 (19), 81 (19), 89 (16).

2-Undecenal 2,4-DNPH, M^+, 348 (31); major ions 235 (100), 41 (55), 231 (50), 67 (45), 43 (41), 216 (32), 215 (27), 55 (27), 331 (23), 81 (23), 57 (23), 53 (23), 236 (18), 203 (18), 80 (18), 189 (14), 95 (14), 82 (14), 79 (14).

Acrolein 2,4-DNPH, M^+, 236 (100); major ions, 189 (57), 63 (38), 142 (30), 159 (28), 143 (26), 89 (26), 42 (26), 116 (25), 79 (25), 69 (25), 115 (23), 117 (19), 75 (19), 64 (19), 219 (15).

2,4-Heptadienal 2,4-DNPH, M^+, 290 (30); major ions, 261 (100), 80 (40), 214 (26), 79 (21), 168 (20), 77 (16), 41 (16), 53 (13), 65 (10), 63 (10), 75 (9), 215 (8), 52 (8), 51 (8), 93 (7), 91 (7), 273 (3).

2,4-Decadienal 2,4-DNPH, M^+, 332 (16); major ions, 261 (100), 80 (29), 41 (19), 214 (18), 262 (14), 93 (11), 79 (11), 77 (11), 65 (9), 168 (8), 55 (7), 215 (6), 67 (6), 53 (6), 43 (5), 57 (4), 315 (3).

Glyoxal bis-2,4-DNPH, M^+, 418 (42); major ions, 44 (100), 63 (70), 52 (56), 91 (49), 75 (49), 183 (47), 43 (42), 79 (40), 64 (40), 46 (37), 62 (35), 51 (35), 41 (35), 164 (33), 45 (33), 92 (28), 90 (28), 78 (28), 77 (28), 76 (28), 153 (21), 107 (19), 238 (16).

Pyruvaldehyde bis-2,4-DNPH, M^+, 432 (60); major ions, 43 (100), 63 (72), 250 (70), 75 (56), 183 (53), 77 (53), 51 (42), 79 (40), 78 (40), 52 (40), 249 (37), 91 (35), 76 (35), 64 (35), 90 (33), 62 (30), 153 (23), 44 (23), 50 (19), 415 (14).

Table II. Pyrazine Compounds Formed in the Reaction of Glycerol with Alanine and Glycine

Compound[a]	Glycerol + alanine[b]	Glycerol + glycine[b]
2-Methylpyrazine	M	L
2,5-Dimethylpyrazine (Probably contained 2,6-isomer)	L	VL
2,3-Dimethylpyrazine	VS	S
2-Ethyl-5-methylpyrazine	S	
2,3,5-Trimethylpyrazine	M	VL
2,5-Dimethyl-3-ethylpyrazine	VL	S
Pyrazine with mol wt 136	VS	VS
Second pyrazine with mol wt 136		S
Pyrazine with mol wt 150	VS	VS
Second pyrazine with mol wt 150	VS	VS
Pyrazine with mol wt 164	VS	

[a] Identified by gc–ms (Column II). [b] Size of peaks was roughly estimated: VS = very small; S = small; M = medium; L = large; VL = very large.

Diacetyl bis-2,4-DNPH, M^+, 446 (43), major ions, 43 (100), 44 (57), 42 (47), 264 (35), 75 (35), 41 (33), 77 (31), 63 (29), 78 (27), 55 (25), 91 (24), 51 (24), 263 (20), 429 (17), 233 (16), 183 (16), 181 (14), 90 (14).

2,3-Pentanedione bis-2,4-DNPH, M^+, 460 (24), major ions, 43 (100), 57 (58), 75 (44), 63 (44), 278 (40), 77 (39), 76 (33), 78 (31), 181 (28), 183 (27), 443 (26), 276 (23), 79 (23), 91 (22), 90 (21), 92 (20), 143 (19), 122 (17), 261 (13), 262 (12).

Most of the carbonyls identified were unbranched aliphatic compounds. It is possible that they were the thermal degradation products of triglycerides. Pecans contain about 70% oil; therefore, pecan oil was extracted from raw pecans and heated, and the carbonyls produced were isolated and identified. All carbonyls previously identified in roasted pecans except furfural and 2,3-pentanedione were found. Hence, pecan oil may be considered as one of the main sources of roasted pecan carbonyls. It is known the dicarbonyls are the breakdown products of sugars, but in the present study pyruvaldehyde and glyoxal were identified among the carbonyls produced by heating pecan oil. Endres *et al.* (1962) reported that hydrolysis of the ester linkage between glycerol and the fatty acid occurred during thermal oxidation of the triglycerides. It is possible that the dicarbonyls we identified might be derived from the thermal breakdown of the glycerol portion of triglycerides. Accordingly, pure glycerol was heated, and pyruvaldehyde, glyoxal, formaldehyde, and a small amount of diacetyl were isolated and identified from the volatiles produced.

Most of the compounds identified in the basic fraction were alkylpyrazines (Table I). These pyrazines have been considered to arise from the reaction intermediates of amino acids with sugars (Mason and Johnson, 1966; Newell *et al.*, 1967). The α-dicarbonyls with their related compounds such as glycolaldehyde, 1-hydroxy-2-propanone, 3-hydroxy-2-butanone, which could be the breakdown products from ammonia (amino acid)–sugar reactions, have been postulated to condense with NH_3 to form pyrazines (Praag *et al.*, 1968); or the dicarbonyls might react with amino acids *via* Strecker degradation to form pyrazines (Dawes and Edwards, 1966). In fact, 2,5-dimethylpyrazine was obtained from heating pyruvaldehyde-L-leucine or -L-isoleucine model systems (Wang *et al.*, 1969). Since the dicarbonyls were found in volatiles from heating pecan oil or glycerol in the present study, consequently glycerol was heated with alanine or glycine and the basic compounds formed were analyzed by gc–ms. In each case, as shown in

Table II, pyrazines were obtained. Alanine or glycine, heated alone under the same instrument conditions, did not produce pyrazines. In comparing the pyrazines in Table I and II, the similarity in composition is remarkable. Either triolein or tripalmitin was then mixed with alanine and heated, but contrary to expectation, no pyrazine compounds were detected in this model system. Many peaks were observed in the gas chromatograms of the volatiles produced from heating either triolein or tripalmitin alone, and these thermal breakdown products of triglycerides might interfere with the formation of pyrazines in the triglyceride–amino acid model systems. As well, the amount of α-dicarbonyls formed only from the breakdown of triglycerides (in the absence of sugars) might be insufficient to form pyrazines. However, the formation of pyrazines is still under study and will be the subject of a second paper.

The components listed in Table I were the major compounds produced when pecans were roasted and identified under the conditions described. There are still many compounds, especially those which gave the smaller peaks in the gas chromatograms, which remain unidentified. 2,4-Decadienal has been reported to have a deep-fat-fried aroma (Patton *et al.*, 1959). Furfural, 2,3-pentanedione, pyruvaldehyde, and glyoxal give a slightly burned character to the aroma. Alkylpyrazines probably provide the backbone of "roasted" or "nutty" character of roasted pecans. However, with the removal of the carbonyl and basic compounds, the characteristic aroma of roasted pecans was lost. The odors of most of the acids listed in Table I were unfavorable, but they were also considered to have some influence in the roasted pecan aroma. Alcohols and γ-octalactone were found in the neutral noncarbonyl oxygenated fraction. This fraction gave somewhat coconut-like or floral aroma and the alcohol-like odor could not be perceived. It was evident that alcohols had little effect but γ-octalactone had a significant influence on the aroma of roasted pecans. Although no specific compound has been identified as possessing a characteristic roasted pecan aroma, undoubtedly the compounds identified above are concerned with this aroma.

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