been made to isolate the compound or compounds responsible for this aroma but without success. A special approach will be necessary to fit the high polarity of this compound(s) and its unstable nature.

Importance of the Components to the Aroma of Potato Chips. The authors are in the process of measuring odor thresholds and carrying out qualitative odor studies of the components of potato chips. The results of these studies will be reported when all the information is collected and analyzed. From results obtained so far, it is clear that the aroma of potato chips is a complex mixture. However, the authors believe that some of the more important compounds in the nonbasic fraction include 3-methylmercaptopropanal (methional), 3-methylbutanal, phenylacetaldehyde, and deca-*trans*-2,*trans*-4-dienal.

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Comparison of Carbonyl Compounds in Raw and Roasted Runner Peanuts. I. Major Qualitative and Some Quantitative Differences

David F. Brown,* Vincent J. Senn, James B. Stanley, and Frank G. Dollear

Carbonyl compounds present in oil cold-pressed from raw and roasted peanuts were converted into 2,4-dinitrophenylhydrazones and were identified by comparison of their R_f values, colors, uv, visible, and mass spectra with authentic compounds. Compounds in roasted peanuts included 14 aldehydes, 10 methyl ketones, nine 2-enals, and seven 2,4-dienals. Raw peanuts contained 10 aldehydes, eight methyl ketones, seven 2-enals, and four 2,4-dienals. Hexanal, octanal, nonanal, decanal, and pentanal were the major carbonyl compounds in raw peanuts. Roasted peanuts contained very large concentrations of 2-methylpropanal, 2-methylbutanal, and 3-methylbutanal and large concentrations of 2-heptenal, 2-octenal, 2-nonenal, 2,4-decadienal, hexanal, octanal, and decanal. The average total carbonyl content and the carbonyl content of the dicarbonyl, ketoglyceride, and monocarbonyl fractions in raw peanuts were 62, 30, 24, and 8 μmol per 100 g of oil and in roasted peanuts were 324, 198, 99, and 26 μmol per 100 g of oil, respectively.

The presence of aldehydes and ketones in the aroma and flavor fraction from raw and roasted peanuts has been recognized for several years (Pattee *et al.*, 1965; Young and Holley, 1965; Mason *et al.*, 1967). Significant roles in the overall flavor and aroma of raw and roasted peanuts have been suggested for a few of these carbonyl compounds.

Pattee *et al.* (1965) identified 11 volatile compounds, including nine aldehydes and ketones, in high-temperature-cured, off-flavored peanuts. More recently Pattee *et al.* (1970) related the production of eight compounds, including four carbonyl compounds, to enzyme activities in maturating peanuts, and Pattee *et al.* (1969) strongly implicated hexanal with the characteristic aroma of raw peanuts. Several other saturated aldehydes and 2-nonenal are reported to convey a beany flavor to oxidized milk fat (Kinsella, 1969) and could conceivably impart a beany flavor to raw peanuts too.

The change to a highly desirable roasted peanut flavor that occurs during roasting is ascribed to pyrolytic reactions between amino acids and reducing sugars (Mason *et al.*, 1969) and to the volatile carbonyl compounds (Young and Holley, 1965) and pyrazines (Mason *et al.*, 1966) which are thus produced. More recently Mason *et al.* (1967) positively identified ethanal, 3-methylbutanal, benzaldehyde, and phenylacetaldehyde and tentatively identified four other aldehydes and ketones in condensates from roasted Spanish peanuts. These authors also noted that if the low molecular weight aldehydes were removed from the condensate, the harsh aroma associated with freshly roasted peanuts was no longer present. Ballschmieter and Germishuizen (1968) correlated the production of 2-methylpropanal with the development of roasted peanut flavor but did not find evidence for the presence of

Southern Regional Research Laboratory, Southern Marketing and Nutrition Research Division, Agricultural Research Service, U.S. Department of Agriculture, New Orleans, Louisiana 70179.

phenylacetaldehyde. Johnson (1970) detected the presence of three phenyl alkenals and several carbonyl compounds, which were derivatives of furan, pyrrole, and thiophene, in roasted peanut volatiles.

Even though volatile aldehydes and ketones are known to be major contributors to the flavor and aroma of both raw and roasted peanuts, a detailed comparison of the carbonyl compounds present in the aroma of peanuts before and after roasting has not been reported. Research reported in this paper concerns differences in the total carbonyl content, the carbonyl content of the dicarbonyl, ketoglyceride and monocarbonyl fractions, and the identities of individual carbonyl compounds present in samples of oil expressed from raw and roasted runner peanuts. The term monocarbonyl refers to carbonyl compounds bearing a single carbonyl and no other functional groups.

MATERIALS AND METHODS

Materials and Chemicals. All chemicals and solvents were reagent or spectral grade. Chloroform and hexane were glass distilled. Hexane was rendered carbonyl free (Schwartz and Parks, 1961).

Reference 2,4-dinitrophenylhydrazones (2,4-DNPH's) of commercially available aldehydes and ketones were prepared according to Shriner *et al.* (1956). Several of the 2,4-DNPH's of 2-enals and 2,4-dienals were obtained as gifts.

Analytical grade Celite, Celite 545, Sea Sorb 43, Microcel T-38 and 80–200 mesh adsorption alumina were dried at 150°C, and the alumina was rehydrated with 6% water before use.

Peanuts were 1969 crop, No. 1 grade, Southeastern Early Runners. They were 3-day windrowed, cured artificially at 32°C, and maintained in cold storage at 3°C until utilized.

Preparation of Samples. Peanuts were hand-sorted to remove immature and damaged kernels. Peanuts were roasted at 170°C in a convection oven until judged medium roasted. Testae and embryos were discarded, and the oil in which the carbonyl compounds are dissolved was expressed from the raw or roasted cotyledons at 2,500 lb per in^2 pressure using a laboratory press.

Recovery of Carbonyls as 2,4-DNPH's and Class Separation of Monocarbonyl Derivatives. Carbonyl 2,4-DNPH's were recovered as outlined by Schwartz *et al.* (1963). Carbonyl-free hexane was added to 200 g of peanut oil to give a volume of 1000 ml, and the solution was passed through a column packed with 30 g of Celite impregnated with 2,4-dinitrophenylhydrazine and phosphoric acid. The column was washed with two 100-ml portions of carbonyl-free hexane. The 2,4-DNPH's in the combined eluate were adsorbed on a column packed with 70 g of a 1:1 mixture of Sea Sorb 43 and Celite 545. The monocarbonyl and ketoglyceride fractions were eluted with 300 ml of 25% nitromethane in $CHCl_3$ plus 150 ml of $CHCl_3$, leaving the dicarbonyl fraction on the column. The ketoglyceride fraction was separated from the monocarbonyl fraction on a column of 60 g of alumina using 1:1 benzene–hexane as the eluant.

The 2,4-DNPH's in the monocarbonyl fraction were separated into classes using a modification of the method of Mookherjee and Chang (1963). The initial eluant was chloroform, and 15% methanol in chloroform served as the final eluant.

Separation and Identification of Individual Components Within a Class. The separation of individual methyl ketones, saturated aldehydes, 2-enals, and 2,4-dienals was according to the thin-layer chromatographic procedures described by Schwartz *et al.* (1968). Individual compounds within the classes were identified from uv, visible and mass spectra and by cochromatography and R_f values after tlc on Microcel T-38 impregnated with polyethylene glycol 400 (PEG) plus 1% KOH. The tlc plates (0.375-mm thick) were activated and stored as recommended by Schwartz *et al.* (1968).

Preparative chromatography of 2,4-DNPH's for subsequent uv, visible, and mass spectral examination was carried out on neutral, polyethylene glycol 400 impregnated, Microcel T-38 plates. The tlc plates (0.375-mm thick) were air-dried for 10 min, then heated at 100°C for 5 min and stored over Ascarite. Each band on the developed plate was transferred to a Pasteur disposable pipet which had been plugged with a small plug of glass wool and packed with about 1 g of alumina, and the hydrazones were eluted with benzene (Schwartz and Virtanen, 1968). Absorption maxima were determined in chloroform.

Mass spectra of individual 2,4-DNPH's were obtained on a CEC 21-110 mass spectrometer. The hydrazones were dissolved in methylene chloride and transferred to capillary tubes. After the solvent was evaporated with a stream of nitrogen, the residues were subjected to direct probe analysis. The ionizing voltage was 70 eV, and the filament current was 3.0–3.2 A. The source temperature was increased from 150 to 200°C as the molecular weight of the 2,4-DNPH's increased.

Estimation of Total Carbonyls and Carbonyl Content of Dicarbonyl, Ketoglyceride, and Monocarbonyl Fractions. A modification of the method of Henick *et al.* (1954) was used for estimating carbonyl concentrations. An aliquot of the oil hexane–2,4-DNPH solution or of a hexane solution of the partially purified hydrazones was transferred to a 50-ml volumetric flask. Sufficient hexane was added to bring the sample volume to 10 ml, and 10 ml of ethanolic KOH was added. The reaction mixture was diluted to volume with absolute ethanol and the absorbance was read against a similarly prepared carbonyl-free blank. Instrument parameters and calculations were according to Henick *et al.* (1954).

Estimates of the carbonyl contents of the dicarbonyl fractions were obtained from the difference between the contents measured before and after adsorption on Sea Sorb 43–Celite 545 and subsequent elution from the columns. Estimates of the ketoglyceride concentrations were obtained from the differences between concentrations measured before and after adsorption on alumina and subsequent elution with 1:1 benzene–hexane solvent.

Table I. Estimations of Average Total Carbonyl Content and Carbonyl Contents of the Dicarbonyl, Ketoglyceride, and Monocarbonyl Fractions from Raw and Medium Roasted Runner Peanuts (μmol/100 g of Cold-Pressed Peanut Oil)

Treatment	Replicates	Total carbonyls	Dicarbonyl fraction[a]	Ketoglyceride fraction[b]	Monocarbonyl fraction
Raw	3	62	30	24	8
Medium roasted	3	324	198	99	26

[a] Determined by difference before and after adsorption and subsequent elution of 2,4-DNPH's from Celite 545–Sea Sorb 43 column using 25% nitromethane in chloroform solvent. [b] Determined by difference before and after adsorption and subsequent elution of 2,4-DNPH's from alumina using benzene–hexane solvent.

RESULTS

Carbonyl Contents. The average values of the estimated total carbonyl content and carbonyl contents of the dicarbonyl,

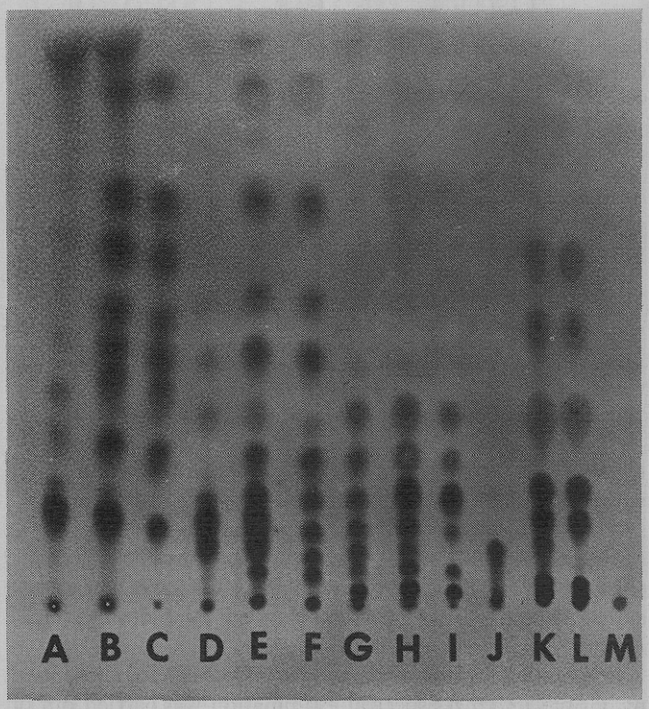

Figure 1. Separation of 2,4-dinitrophenylhydrazones of 2-alkanones, alkanals, 2-alkenals, and 2,4-alkadienals from known mixtures and from medium roasted runner peanuts on Microcel T-38 tlc plates impregnated with polyethylene glycol 400 plus KOH. Compounds chromatographed in the respective lanes are: (A) unknown 2-alkanones; (B) unknown plus authentic 2-alkanones; (C) authentic 2-alkanones [^{C}3,4,5,5(iso),6,7,11]; (D) unknown alkanals; (E) unknown plus authentic alkanals; (F) authentic alkanals [^{C}3,4,5,6,7,9,10,12,16]; (G) unknown 2-alkenals; (H) unknown plus authentic 2-alkenals; (I) authentic 2-alkenals [^{C}4,6,8,9,10,11,14]; (J) unknown 2,4-alkadienals; (K) unknown plus authentic 2,4-alkadienals; (L) authentic 2,4-alkadienals [^{C}5,6,7,11,12,14,16,18]; (M) authentic phenylacetaldehyde

ketoglyceride, and monocarbonyl fractions determined in oil expressed from three raw samples and three medium roasted samples of runner peanuts are recorded in Table I.

Identification of Carbonyl Compounds on KOH Impregnated Microcel T-38 Plates. Figure 1 shows typical separations of unknown and known 2,4-DNPH's of alkanals, 2-alkanones, 2-enals, and 2,4-dienals that can be obtained on Microcel T-38 tlc plates impregnated with KOH plus PEG. The compounds which have been chromatographed in the respective lanes are: (A) unknown 2-alkanones; (B) unknown plus authentic 2-alkanones; (C) authentic 2-alkanones; (D) unknown alkanals; (E) unknown plus authentic alkanals; (F) authentic alkanals; (G) unknown 2-alkenals; (H) unknown plus authentic 2-alkenals; (I) authentic 2-alkenals; (J) unknown 2,4-alkadienals; (K) unknown plus authentic 2,4-alkadienals; (L) authentic 2,4-alkadienals; and (M) authentic phenylacetaldehyde. The 2,4-dinitrophenylhydrazones of methyl ketones were gray, of aldehydes were tan, of 2-enals were pinkish-red, and of 2,4-dienals were rose-red on the basic Microcel T-38 plates, and the colors were of great diagnostic value.

Preparative Separation of Carbonyl Compounds on Neutral, Microcel T-38, TLC Plates. Figure 2 shows a preparative thin-layer chromatographic separation of the 2-enal, 2,4-DNPH's isolated from medium roasted peanuts. The concentration of the 2-enals spotted on this plate represented one-fifth of the fraction isolated from 200 g of cold-pressed peanut oil. The separation of several members of the series of 2-enals from 2-butenal through 2-hexadecenal, which were

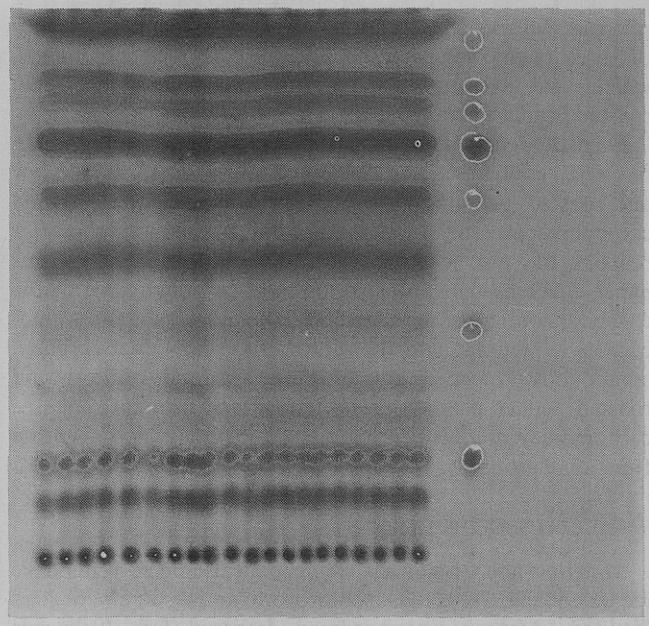

Figure 2. Preparative chromatography of 2,4-dinitrophenylhydrazones of 2-alkenals isolated from medium roasted runner peanuts on Microcel T-38 tlc plate impregnated with polyethylene glycol 400. The loading on the plate represents one fifth of the 2-alkenal class isolated from 200 g of peanuts. The authentic 2-enals chromatographed to the right of the main separation are from top to bottom: ^{C}14,11,10,9,8,6,4

chromatographed in an adjacent lane for reference, is also shown.

Mass Spectrometry. In general the mass spectra obtained from the 2,4-DNPH's eluted from the individual bands on the preparative chromatographic plates were good. Mass spectrograms of a few compounds isolated in very low concentrations could not be interpreted due to the presence of spurious peaks in the spectra. These extraneous peaks are believed to be due to trace impurities, which were present even after rechromatography on alumina.

In addition to the molecular ions, prominent peaks were recorded for the 2,4-DNPH's of higher alkanals at 224 and 206, of 2-alkanones at 238 and 178, for 2-enals at 235, and for 2,4-dienals at 261 mass units. These observations agree with the data reported by Kleipool and Heins (1964) and Badings (1970).

Carbonyl Compounds Identified in Oil Expressed from Raw and Roasted Runner Peanuts. A list of the saturated aldehydes, methyl ketones, 2-enals, and 2,4-dienals which were identified in oil samples expressed from raw and medium roasted runner peanuts is compiled in Table II.

Relative concentrations of the compounds which were isolated from the raw and roasted runner peanuts also are indicated in Table II. A (+) symbol in the column under tlc indicates agreement of the R_f values, results of cochromatography, and of the characteristic colors of known 2,4-DNPH's with those of the carbonyl derivatives isolated from the raw and roasted peanuts. A (+) symbol in the column under ms signifies mass spectral agreement with reference compounds, and a (+) symbol under uv indicates agreement of the absorption maxima with those of known 2,4-DNPH's in chloroform solutions.

The identification of each compound is designated P or T to indicate a "positive" or "tentative" identification. The identifications of several compounds are indicated as "positive," although mass spectra were not obtained for these compounds. The characteristic colors on KOH-impregnated

Table II. Identification of Carbonyl Compounds in Cold-Pressed Oil Samples from Raw and Roasted Runner Peanuts

	Treatment								
	Roasted					Raw			
		Identification method[a]					Identification method[a]		
Compound	Conc[b]	tlc	uv	ms	Remark[c]	Conc[b]	tlc	uv	ms	Remark[c]
Alkanal										
Ethanal	S	+	+	+	P	S	+	+		P
Propanal	S	+	+	+	P	S	+	+		P
Butanal	S	+	+	+	P	S	+	+		P
2-Methylpropanal	VL	+	+	+	P	ND				
Pentanal	M	+	+	+	P	M	+	+	+	P
2-Methylbutanal	VL	+	+	+	P	ND				
3-Methylbutanal	VL	+	+	+	P	ND				
Hexanal	L	+	+	+	P	L	+	+	+	P
Heptanal	S	+	+		P	S	+	+		P
Octanal[d]	L	+	+	+	P	M	+	+		P
Nonanal[d]	L	+	+	+	P	M	+	+		P
Decanal[d]	L	+	+	+	P	M	+	+		P
Undecanal[d]	S	+			T	ND				
Dodecanal[d]	S	+	+		P	S	+	+		T
2-Alkanone										
2-Propanone	VL[e]	+	+	+	P	VL[e]	+	+	+	P
2-Butanone	M	+	+	+	P	S	+	+		P
2-Pentanone[d]	S	+	+	+	P	S	+	+		P
3-Methyl-2-butanone	S	+	+		T	ND				
2-Hexanone[d]	S	+	+		P	S	+	+		P
2-Heptanone[d]	S	+	+	+	P	S	+	+		P
2-Octanone[d]	S	+	+	+	P	S	+	+		P
2-Nonanone[d]	S	+	+	+	P	S	+	+		T
2-Decanone[d]	S	+			T	S	+			T
2-Undecanone[d]	S	+			T	ND				
2-Enals										
Phenyl-2-butenal	S	+	+	+	T	ND				
2-Pentenal[d]	S	+			T	S	+	+		T
2-Hexenal[d]	S	+	+	+	P	S	+	+		P
2-Heptenal[d]	M	+	+	+	P	S	+	+		P
2-Octenal[d]	M	+	+	+	P	S	+	+		P
2-Nonenal[d]	M	+	+		P	S	+	+		P
2-Decenal[d]	M	+	+	+	P	S	+	+		P
2-Undecenal[d]	M	+	+		T	S	+	+		T
2-Dodecenal[d]	S	+			T	ND				
2,4-Dienals										
2,4-Pentadienal[d]	S	+	+		T	ND				
2,4-Hexadienal[d]	S	+	+		T	ND				
2,4-Heptadienal[d]	S	+	+	+	P	S	+	+		P
2,4-Octadienal[d]	S	+	+		T	S	+			T
2,4-Nonadienal[d]	S	+	+	+	P	S	+	+		P
2,4-Decadienal	M	+	+	+	P	S	+	+		P
2,4-Undecadienal[d]	S	+			T	ND				

[a] + = evidence for presence of compound obtained. [b] S = small; M = medium; L = large; VL = very large; ND = not detected. [c] P = positive; T = tentative identification. [d] Not previously reported. [e] Present primarily as an artifact.

tlc plates, absorption maxima, and the results of cochromatography were considered to be strong enough evidence for a definite identification. On the basis of the mass spectra and the aforementioned criteria, 27 monocarbonyl compounds present in roasted and 23 monocarbonyls present in raw runner peanuts were "positively" identified.

The concentrations of some compounds were too low to obtain a mass spectra or to determine the absorption maxima precisely. Therefore, the identifications of 13 aldehydes and ketones from roasted and six monocarbonyls from the raw peanut samples were "tentative."

Table II shows several qualitative and semiquantitative differences between raw and roasted peanuts. Very large concentrations of 2-methylpropanal, 2-methylbutanal, and 3-methylbutanal were present in roasted peanuts, whereas the compounds could not be detected in raw peanuts. Low concentrations of 3-methyl-2-butanone, undecanal, 2-undecanone, 2-dodecenal, 2,4-pentadienal, 2,4-hexadienal, 2,4-undecadienal and the phenyl-2-butenal were detected in roasted peanuts, although these compounds were not detected in nonroasted peanuts. From Table II it also can be seen that the relative concentrations of octanal, nonanal, decanal, 2-butanone, 2-heptenal, 2-octenal, 2-nonenal, 2-decenal, 2-undecenal, and 2,4-decadienal increase during roasting.

DISCUSSION

The total carbonyl content and carbonyl contents listed for the dicarbonyl, ketoglyceride, and monocarbonyl fractions are quantitative estimates. The values include only those carbonyl compounds which are soluble in the hexane–oil effluent after derivatization on the Celite–2,4-dinitrophenylhydrazine reaction columns. The effluent contains the 2,4-DNPH's of the monocarbonyls, semialdehydes, ketoglyc-

erides, and all hexane–oil-soluble dicarbonyl di-2,4-DNPH's, as well as other classes of 2,4-DNPH's which are hexane–oil-soluble (Schwartz *et al.*, 1963). Several low molecular weight dicarbonyl di-2,4-DNPH's, *e.g.*, glyoxal, methyl glyoxal, and diacetyl (Schwartz, 1971), and 2,4-DNPH's of a few other low molecular weight carbonyl compounds, *e.g.*, pyruvic acid, 2-ketoglutaric acid, and benzaldehyde, are virtually insoluble in a 20% solution of peanut oil in hexane and remain on the reaction column.

Total carbonyl contents were determined using aliquots of the hexane–oil eluate from the reaction column, and the values in Table I may be somewhat low, since carbonyls present in the form of glycolytic and Krebs cycle oxoacids and low molecular weight dicarbonyl compounds would not be eluted from the column.

The significance of the quantitative estimates of the carbonyl contents of the dicarbonyl fractions is difficult to assess. The 2,4-DNPH's of oxoacids and all dicarbonyl di-2,4-DNPH's, vicinal and nonvicinal, which are soluble in the oil–hexane effluent from the reaction column are retained on Celite 545–Sea Sorb 43 columns after elution with 25% nitromethane in chloroform (Schwartz *et al.*, 1963). Moreover, saponification of glycerides occurs to some degree on the Celite 545–Sea Sorb 43 columns, and the magnesium salts which are thus formed are also retained on the columns (Schwartz, 1971).

The colors of the di-2,4-DNPH's of α-diketones are violet and of α-ketoaldehydes are blue when adsorbed on Sea Sorb 43–Celite 545, whereas the colors of most of the other classes of 2,4-DNPH's including most oxoacids are either gray, tan, pink, or rose colored (Schwartz *et al.*, 1968). The major portion of the hydrazones which were retained on the Sea Sorb 43–Celite 545 columns were blue or purplish. Therefore, it would appear that the major portion of the fractions was composed of hexane–oil-soluble dicarbonyl compounds and that carbonyl bearing saponification products make up only a small portion of the dicarbonyl fraction. However, the extent to which any nondicarbonyl blue colored 2,4-DNPH derivatives might contribute to the fraction is unknown.

The concentrations of ketoglycerides listed in Table I may be somewhat low (Schwartz, 1971). The most likely cause of low values would be the saponification of glycerides on the Sea Sorb 43–Celite 545 and the retention of the resulting oxoacid derivatives with the dicarbonyl fraction. The extent of this side reaction, however, is not known.

Although the quantitative carbonyl contents of the fraction reported in the present study may not completely account for the carbonyl compounds present in raw and roasted peanuts, there are few data in the literature to which our data may be compared. Young and Holley (1965) analyzed condensed gases from peanut roasters and reported average total carbonyl and dicarbonyl concentrations equivalent to about 1 μmol and 0.5 μmol per 100 g of peanuts in the roaster, but no attempt was made to determine the residual carbonyl content of the peanuts themselves. Recent but unpublished glc results from this laboratory indicate that the concentrations of total volatile carbonyl compounds in oil expressed from raw and roasted runner peanuts are probably 20–30 μmol and 50–60 μmol per 100 g of oil (Dupuy, 1970). In the present study, total carbonyl, dicarbonyl, and ketoglyceride concentrations estimated in oil samples from raw and roasted runner peanuts, respectively, were 62, 30, and 24 μmol and 324, 198, and 99 μmol per 100 g of oil.

The surprisingly large differences between the carbonyl concentrations reported in the three studies are due to the procedures used for isolating the carbonyl compounds and to differences in the volatility of the carbonyl compounds in cold-pressed peanut oil. Young and Holley trapped and estimated the volatile compounds which were driven off during roasting. The values determined by Dupuy are a measure of the concentrations of aldehydes and ketones which can be flash exchanged from peanut oil samples directly into a gas chromatograph. The contributions of ketoglycerides, oxoacids, and the other compounds of low volatility are not measured. In the present study, however, the carbonyl concentrations that were measured included nonvolatile as well as volatile compounds. The high dicarbonyl and ketoglyceride contents indicate that a large proportion of the carbonyl compounds produced during roasting are of low volatility.

As can be seen from Table I the carbonyl contents of all three fractions of carbonyl compounds were dramatically higher in roasted samples. The total carbonyl content increased approximately fivefold, while the carbonyl content of the dicarbonyl, ketoglyceride, and monocarbonyl fractions increased 6.5, four-, and threefold, respectively. The observed increases can be ascribed to the well known acceleration of fat and oil oxidation rates with increased temperature and to a lesser degree to the Maillard reaction (Hodge, 1967) and the Strecker degradation (Mason *et al.*, 1967).

The greater proportional increases in the dicarbonyl fraction and in the ketoglyceride fraction relative to the monocarbonyl fraction during roasting may be the result of the formation and accumulation of nonvolatile dicarbonyls, ketoglycerides, and oxoacids, whereas the monocarbonyl compounds are relatively more volatile and a larger proportion of them tend to be lost during roasting. The much higher values for total and dicarbonyl contents shown in Table I than those reported by Young and Holley (1965) and the approximately 1:1 ratio of dicarbonyl to monocarbonyl compounds trapped by Young and Holley tend to support the suggestion that nonvolatile carbonyls are accumulated in the oil during roasting.

The tlc procedures developed by Schwartz *et al.* (1968) using Microcel T-38 coated plates served admirably for resolving the 2,4-DNPH's isolated from samples of oil pressed from raw and roasted peanuts. Figure 1 shows that Microcel T-38 impregnated with polyethylene glycol 400 plus KOH was an excellent medium for resolving the members of each of the monocarbonyl classes. Good resolution of all the compounds except for the lowest members of the 2,4-dienal class and the C-4, C-5, and C-6 aldehydes, which were grossly overloaded, was observed after a single development with the solvent. The lowest members of the dienal class and the alkanals were resolved satisfactorily through multiple development of the plate.

The presence of other 2-enals, ketones, and aldehydes was shown by spotting increased volumes of the respective fractions. Most of the acetone which was detected was traced to its introduction as an artifact. Traces of acetone were present, since they were detected when freshly prepared samples of the raw and roasted oils were subjected to direct glc examination (Dupuy, 1970).

Resolution of the 2,4-DNPH's was even better on the Microcel T-38 plates impregnated only with polyethylene glycol than on the polyethylene glycol plus KOH impregnated plates. The excellent resolution of the lower member of the 2-alkenal class on the polyethylene glycol 400 impregnated preparative plate, which is seen in Figure 2, prevailed in the other monocarbonyl classes too. Several previously un-

noticed compounds were revealed as a result of the better resolution of the compounds and increased loading possible on the preparative plates. For example, comparison of the bands in Figure 2 with the spots in lane 8 of Figure 1 reveals the presence of four additional compounds in the 2-enal fraction.

Several of the aldehydes and ketones which were isolated from raw and roasted peanuts have been reported previously. The following compounds, which are listed in Table II, have been reported in roasted peanuts: ethanal, 2-methylpropanal, 3-methylbutanal, 2-methylbutanal, pentanal, heptanal, and 3-methyl-2-butanone by Mason *et al.* (1967), propanal and butanal, by Ballschmieter and Germishuizen (1968), hexanal, 2-butanone, and 2-phenyl-2-butenal by Johnson (1970), and 2,4-decadienal by Walradt *et al.* (1970). Several carbonyl derivatives of furan, pyrrole, and thiophene (Johnson, 1970) and phenylacetaldehyde and benzaldehyde (Mason *et al.*, 1967) have been reported to be constituents of peanut volatiles but were not detected in our study. The apparent absence of these compounds is probably a result of the isolation procedure. The 2,4-DNP–hydrazones of aromatic aldehydes and ketones are very difficult to elute from Sea Sorb–Celite columns with chloroform–methanol solutions. That at least traces of phenylacetaldehyde are actually present in the condensed volatiles of roasted runner peanuts was shown gas chromatographically in recent but unpublished work at this laboratory (Senn, 1970).

The occurrence of ethanal, 2-propanone, pentanal, and hexanal in raw peanuts (Pattee *et al.*, 1970) was confirmed. Although methanal, 2-methylpropanal, 3-methylbutanal, 2-methylpentanal, and furfural were detected in high-temperature cured, off-flavor peanuts (Pattee *et al.*, 1965), they were not detected in the raw peanuts used in the present investigation, and methanal, 2-methylpentanal, and furfural were not detected in the roasted peanuts either. Since the presence of 2-methylpropanal, 3-methylbutanal, and furfural are often associated with the Strecker degradation and roasting (Hodge, 1967), nonenzymatic browning reactions similar to those induced by roasting may have occurred during the high temperature (55°C) curing.

The major qualitative differences between roasted and raw runner peanuts are the presence of very large concentrations of 2-methylpropanal, 3-methylbutanal, and 2-methylbutanal in roasted samples, whereas they are absent in nonroasted samples. The three branched chain aldehydes as well as ethanal may be produced by way of the Strecker degradation of the corresponding amino acids, valine, leucine, isoleucine, and alanine, during roasting (Mason *et al.*, 1967).

Other qualitative differences were the presences of low concentrations of 3-methyl-2-butanone, undecanal, 2-undecanone, 2-dodecenal, 2,4-pentadienal, 2,4-hexadienal, and a phenyl-2-butenal in only the roasted nuts. The origin of these compounds is presently unknown. However, undecanal was reported in autoxidized peanut oil by Ellis *et al.* (1961). In addition, 3-methyl-2-butanone (Mason *et al.*, 1967) and 2-phenyl-2-butenal (Johnson, 1970) were reported previously in roasted peanuts. It is noteworthy, however, that van Praag *et al.* (1968) synthesized 2-phenyl-2-butenal as the aldol condensation product of ethanal and phenyl acetaldehyde and that the opposite condensation would give 4-phenyl-2-butenal.

The increases in the concentrations of octanal, nonanal, decanal, 2-butanone, 2-heptenal, 2-octenal, 2-undecenal, and 2,4-decadienal can be attributed to autoxidation of oleic and linoleic acids. All of these compounds except decanal have been identified in roasted peanuts or oxidized peanut oil (Mason *et al.*, 1967; Ellis *et al.*, 1961). Model autoxidation experiments by Ellis and coworkers and Badings (1970) showed that large quantities of octanal and nonanal and smaller quantities of heptanal, decanal, 2-decenal, and 2-undecenal are produced from oleate and large concentrations of hexanal, 2-heptenal, 2-octenal, and 2,4-decadienal, as well as lower concentrations of pentanal, heptanal, octanal, 2-nonenal, and 2,4-nonadienal, are formed by autoxidation of linoleate.

The increase in 2-butanone during roasting may be the result of either decarboxylation of the corresponding β-keto acid or a free radical mechanism (Mookherjee *et al.*, 1965). In the free radical mechanism acyl free radicals, which may be produced readily from propanal, condense with a methyl free radical to yield 2-butanone.

From the standpoint of flavor and aroma, the aldehydes which most probably contribute significantly to the "green or beany" flavor of raw peanuts are hexanal and possibly pentanal, octanal, nonanal, and decanal. The flavors of these compounds are described as beany or green (Kinsella, 1969), and they are in the major components of the monocarbonyl fraction, excluding 2-propanone which is present primarily as an artifact. The flavor thresholds of pentanal, hexanal, octanal, nonanal, and decanal are listed as 0.15, 0.15, 0.46, 0.32, and 1.0 ppm, respectively (Kinsella, 1969), or approximately 0.2, 0.15, 0.4, 0.3, and 0.7 μmol per 100 g of raw peanut oil. Since the average concentration of monocarbonyls detected in the raw oil was 7.8 μmol per 100 g, it seems quite probable that hexanal and quite possible that pentanal, octanal, nonanal, and decanal are major factors in the flavor and aroma of raw runner peanuts.

Several of the alkanals, alkenals, and alkadienals listed in Table II may play significant roles in the flavor and aroma of roasted runner peanuts. Mason *et al.* (1967) suggested that low molecular weight aldehydes are responsible for the harsh aroma associated with freshly roasted peanuts. 2-Methylpropanal, 3-methylbutanal, and 2-methylbutanal are the three compounds which are most likely responsible for this harsh note. They are present in the roasted oil in very large concentrations. They are characterized by harsh or sharp odors, and the flavor threshold values of at least two of them is extremely low. Guadagni *et al.* (1963) gave values of 0.15 ppb for 3-methylbutanal and 0.9 ppb for 2-methylpropanal in water, and Badings (1970) listed 0.030 ppm or 0.05 μmol per 100 g as the flavor threshold of 3-methylbutanal in paraffin oil. By analogy the flavor threshold of 2-methylbutanal is probably in the same range.

Other compounds listed in Table II which may possibly play significant but more subdued roles in the flavor and aroma of roasted runner peanuts are 2-heptenal, 2-octenal, 2-nonenal, and 2,4-decadienal, as well as the five alkanals which were also mentioned in connection with raw peanut flavor. The flavor thresholds of the 2-alkenals and 2,4-decadienal are 0.63, 1.0, 0.1, and 0.28 ppm in paraffin oil (Kinsella, 1969). If the concentrations of the respective compounds exceed these values, the 2-enals and 2,4-decadienal may contribute fatty and deep-fried notes to the overall olfactory sensation of freshly roasted runner peanuts. However, it is unlikely that any of the aldehydes that we have detected are responsible for the "roasted-nutty" flavor of roasted peanuts since the flavors of these compounds are described in quite different terms (Kinsella, 1969; Badings, 1970). The "roasted-nutty" aspect of the flavor is probably due to the presence of one or more other compounds in the volatile,

flavor, and aroma fraction of roasted peanuts or perhaps to the presence of one or more pyrazines as suggested by Mason *et al.* (1966).

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Eating Quality, Sulfhydryl Content, and TBA Values of Turkey Breast Muscle

Jane A. Bowers

Selected flavor and aroma components, juiciness, sulfhydryl groups, and TBA values were determined for freshly cooked and for precooked, frozen, reheated (in gas and in microwave ovens) turkey muscle. In general, freshly cooked muscle had the lowest rancid and stale and highest meaty–brothy flavor and aroma scores; microwave-reheated meat had intermediate scores; and conventionally reheated had the highest rancid and stale and lowest meaty–brothy flavor and aroma scores. Differences in TBA values and sulfhydryl groups were noted between cooked and raw muscle tissue, but not among muscle tissues subjected to the three heating treatments.

Flavor of cooked turkey deteriorates during storage and reheating. Oxidation of muscle lipids has been related to flavor deterioration in cooked meats (Tims and Watts, 1958; Turner *et al.*, 1954) and the thiobarbituric acid (TBA) test has been used to determine extent of oxidation. TBA values increased as off-flavor and odor developed with storage time and storage temperature for precooked meat (Cash and Carlin, 1968; Chang *et al.*, 1961; Keskinel *et al.*, 1964; Jacobson and Koehler, 1970).

Sulfur aroma components have been noted in poultry meat volatiles. An interaction between hydrogen sulfide and carbonyl compounds was suggested by Pippen *et al.* (1965) and may promote off-flavor in reheated meat. Minor *et al.* (1965) suggested that the "meaty" aroma of chicken was due to sulfur compounds. Heating affects protein functional groups of muscle. Hamm and Hofmann (1965) observed a decrease in the number of sulfhydryl groups in beef myofibrils heated to 120°C. They suggested that the decrease was caused by oxidation of the sulfhydryl groups to disulfide groups and to formation of H_2S from myofibrils (which began at about 80°C).

Flavor of microwave-reheated turkey muscle recently has been shown to be more meaty–brothy and less stale than that of conventionally reheated turkey muscle (Cipra *et al.*, 1971); chemical changes that may help explain such a dif-

Department of Foods and Nutrition, Kansas Agricultural Experiment Station, Manhattan, Kansas 66502.