

Comparison of Carbonyl Compounds in Roasted and Nonroasted Spanish and Runner Peanuts

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Carbonyl compounds present in oil cold-pressed from Spanish peanuts were identified as their 2,4-dinitrophenylhydrazones. Forty-one aliphatic monocarbonyl compounds were identified in the roasted and 37 were identified in the raw peanuts. Qualitatively the monocarbonyl compositions of raw and roasted Spanish peanuts were very similar to raw and roasted runner peanuts. Concentrations of 2-methylpropanal, 2-methylbutanal, and 3-methylbutanal in roasted peanuts were very high. Hexanal was the major monocarbonyl

in raw peanuts. The average concentrations of the total carbonyl, dicarbonyl, ketoglyceride, and monocarbonyl fractions in raw Spanish peanuts were 116, 36, 69, and 10 μmol per 100 g of oil and in roasted Spanish were 447, 261, 121, and 65 μmol per 100 g of oil. These values are much higher than in runner peanuts. The increases are attributed primarily to a higher linoleate content and to a lower stability of linoleate toward autoxidation.

Aldehydes and ketones are important constituents in the flavor and aroma fraction of raw as well as of roasted peanuts (Mason *et al.*, 1967; Pattee *et al.*, 1965). The production of several aldehydes and ketones has been related to enzyme activity levels in maturing peanuts (Pattee *et al.*, 1970), and hexanal has been strongly implicated in the characteristic aroma of raw peanuts (Pattee *et al.*, 1969). Brown *et al.* (1971) detected hexanal and octanal in concentrations exceeding their flavor threshold values in raw runner peanuts and suggested that hexanal, octanal, nonanal, and 2-nonenal may contribute significantly to the characteristic "green or beany" flavor of raw peanuts.

Approximately 90 aldehydes and ketones have been identified in the volatile fraction from roasted peanuts (Brown *et al.*, 1971, 1972; Johnson *et al.*, 1971; Mason *et al.*, 1967; Walradt *et al.*, 1971). The list of compounds includes the C₂-C₁₂ alkanals as well as 2-methylpropanal, 2-methylbutanal, 3-methylbutanal, several 2-alkanones, 2-alkenals, and 2,4-alkadienals and numerous carbonyl derivatives of furan, pyrrole, and thiophene. Mason *et al.* (1967) associated the harsh note of freshly roasted Spanish peanuts with low molecular weight aldehydes and ascribed the sweet bouquet of roasted peanuts to the presence of phenylacetaldehyde. The contribution of dicarbonyl compounds *per se* to peanut flavor and aroma is unknown, although they are thought to participate in the formation of the "nutty" and "roasted" flavored pyrazines under roasting conditions (Mason *et al.*, 1969).

A small amount of quantitative data concerning the types of carbonyls and the concentrations of individual carbonyl compounds present in raw and roasted peanuts have been reported. Young and Holley (1965) reported total carbonyl concentrations and dicarbonyl concentrations determined in the roaster condensates from five different varieties of peanuts. More recently Brown *et al.* (1972) determined the total carbonyl content and the monocarbonyl equivalent of the dicarbonyl, ketoglyceride and monocarbonyl fractions isolated in oil expressed from raw and roasted runner peanuts. Concentrations of a few aliphatic monocarbonyl compounds present in oil from raw and roasted runner peanuts also have been reported (Brown *et al.*, 1971).

Research reported in this paper concerns the identities

of individual carbonyl compounds present in samples of oil expressed from raw and roasted Spanish peanuts, as well as the differences in the total carbonyl content and the carbonyl content of the dicarbonyl, ketoglyceride, and monocarbonyl fractions isolated from the oil samples. The qualitative and quantitative compositions of the carbonyl fractions from raw and roasted Spanish peanuts are compared to those previously reported for runner peanuts.

MATERIALS AND METHODS

Materials and Chemicals. All chemicals and solvents were reagent or ultrapure grade. Hexane was rendered carbonyl free (Schwartz and Parks, 1961). Reference 2,4-dinitrophenylhydrazones (2,4-DNPH's) were prepared from commercially available aldehydes and ketones or obtained as gifts. Analytical grade Celite, Celite 545, Sea Sorb 43, Microcel T-38, and adsorption alumina were dried at 150°, and the alumina was rehydrated with 6% water before use.

Peanuts were 1969 crop, No. 1 grade, Dixie Spanish peanuts, grown under similar agronomic conditions at the same location during the same year, as were the Southeastern Early Runner peanuts upon which we previously have reported (Brown *et al.*, 1971). Peanuts were roasted at 170° in a convection oven until judged medium roasted. Testae and embryos were discarded, and the oil was cold-pressed from the raw or roasted cotyledons at 2500 lb per in.² in a Carver laboratory press. Data were obtained for raw and roasted treatments from three independent replicates for both runner and Spanish peanuts. The replicates were processed within a few days of each other.

Isolation and Recovery of Carbonyl Compounds as 2,4-DNPH's. The procedures for derivatizing, isolating, and recovering the carbonyl compounds as their 2,4-DNPH's are reported elsewhere (Brown *et al.*, 1972) and are similar to the procedures developed by Schwartz *et al.* (1963, 1968). Carbonyl compounds present in the oils were converted into their 2,4-DNPH's by passage through a 2,4-dinitrophenylhydrazine reaction column. The 2,4-DNPH's comprising the dicarbonyl fraction were separated from the other 2,4-DNPH's by column chromatography on Celite 545-Sea Sorb 43 columns. The 2,4-DNPH's comprising the ketoglyceride fraction were separated from the 2,4-DNPH's of aliphatic aldehydes and ketones by column chromatography on partially deactivated alumina. The monocarbonyl derivatives were separated into their respective alkanal, 2-alkanone, 2-alkenal, and 2,4-alkadienal classes by rechromatography on Celite 545-Sea Sorb 43 columns. Individual compounds within a class were separated by chromatography on Microcel T-38 thin-layer

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plates impregnated with polyethylene glycol 400 (PEG 400) or PEG 400 plus KOH. For preparative chromatography of 2,4-DNPH's, tlc plates impregnated only with PEG were used: The tlc plates were developed with hexane saturated with PEG 400.

Identification of Individual Carbonyl 2,4-DNPH's. Compounds were identified by comparing their R_f values, characteristic colors on the base-impregnated PEG 400 tlc plates, uv visible absorption maxima, and mass spectra with those of authentic compounds (Brown *et al.*, 1972). The coincident presence of compounds representing another class was detected by a deviation of the absorption maximum from the maximum which is characteristic of the class under investigation. The coincident compounds were identified after rechromatography on a different support (*e.g.*, silica gel, or from the deviations of the absorption maxima themselves) since the absorption maximum of each class differs considerably (Schwartz *et al.*, 1962). Furthermore, if the R_f values were low, then the coincident compound invariably belonged to the class eluting just prior to the class under consideration, and if it had a high R_f value, then it belonged to the class eluting during column chromatography just following the class under consideration.

Quantitation of Total Carbonyls and Carbonyl Content of Dicarboxyl, Ketoglyceride, and Monocarboxyl Fractions. Carbonyl concentrations were estimated using a modification of the method of Henick *et al.* (1954) as previously outlined (Brown *et al.*, 1972). An aliquot of a hexane solution of the partially purified 2,4-DNPH's was transferred to a 50-ml volumetric flask. Sufficient hexane was added to bring the sample volume to 10 ml, and 10 ml of 4% KOH in absolute ethanol was added. The reaction mixture was diluted to volume with absolute ethanol, and the absorbance was read against a similarly prepared carbonyl-free blank.

Estimates of the carbonyl contents of the dicarboxyl 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.

Flavor Threshold Values. Flavor threshold values (ppm) used in this report were determined in paraffin oil by Badings (1970). Threshold values for 2-methylpropanal or 2-methylbutanal were not found in the literature. The values used for 2-methylpropanal and 2-methylbutanal are those of butanal and pentanal, respectively, and are thought to be fair estimates of the threshold values of the branched chain aldehydes (Brown *et al.*, 1971). The flavor threshold as used by Badings is the average minimal concentration of a compound in the solvent, below which aroma and taste are not perceptible to the receptors (Patton and Josephson, 1957).

RESULTS

Carbonyl Contents. The average values of the total carbonyl content and the monocarbonyl equivalents of the dicarboxyl, ketoglyceride, and monocarbonyl fractions determined in oil from three raw and three roasted samples of Spanish peanuts are recorded in Table I. Similar carbonyl determinations obtained for No. 1 grade Southeastern Early Runner peanuts have been reported previously (Brown *et al.*, 1972). The results of these earlier determinations are included in Table I for comparison.

Roasting induced a dramatic increase in the total carbonyl content and in the carbonyl contents of the dicarboxyl, ketoglyceride, and monocarbonyl fractions. Total carbonyl, dicarboxyl, ketoglyceride, and monocarbonyl concentrations in samples of raw Spanish peanuts were,

respectively, 116, 36, 69, and 10 μmol per 100 g of oil and 447, 226, 116, and 65 μmol per 100 g of oil from the roasted nuts. The values determined in runner peanuts were 62, 30, 24, and 8 μmol per 100 g of oil from raw peanuts and 324, 198, 99, and 26 μmol per 100 g of oil from roasted peanuts. In all cases the values for Spanish peanuts were higher than for the runner peanuts. The absolute increases in carbonyl concentrations resulting from roasting were greater for Spanish peanuts than for runners, except for the ketoglyceride fraction.

Monocarboxyl Compounds Identified from Raw and Roasted Spanish Peanuts. A list of the saturated aldehydes, methyl ketones, 2-alkanals, and 2,4-alkadienals which were identified in oil samples expressed from raw and roasted Spanish peanuts is compiled in Table II. Data from our earlier work on runner peanuts (Brown *et al.*, 1972) are also included in Table II for purposes of comparison.

The symbols VL, L, M, S, and ND indicate that the relative concentration of the compound under consideration was very large, large, medium, small, or not detected. 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 tlc plates (Brown *et al.*, 1972), the absorption maxima, and the results of cochromatography were considered to be strong enough evidence for definite identifications. On the basis of these criteria, 28 carbonyl compounds present in roasted and 24 present in raw Spanish peanuts were positively identified.

The concentrations of some compounds were too low to obtain mass spectra or to determine the absorption maxima precisely. Therefore, the identifications of 14 carbonyl compounds in roasted and 13 carbonyl compounds in raw Spanish peanuts were tentative.

It was difficult to separate butanal from 2-methylpropanal and pentanal from 3-methylbutanal by thin-layer chromatography. However, multiple development of the PEG-impregnated Microcel T-38 tlc plates and rechromatography on other adsorbents showed that small quantities of butanal and medium quantities of pentanal were present, along with very large quantities of 2-methylpropanal and 3-methylbutanal in the alkanals from roasted peanuts. On the other hand, mass spectral analysis, multiple development, and rechromatography of the alkanals from raw peanuts revealed the presence of small and medium quantities of butanal and pentanal but no 2-methylpropanal or 3-methylbutanal in the raw peanut samples.

The presence or absence of 2,4-undecadienal in raw and roasted peanuts is uncertain since the compound was recorded in roasted runner and raw Spanish peanuts but not in roasted Spanish and raw runner peanuts. Small concentrations of 2-decanone were detected in runner peanuts in our earlier work, but none was recorded in the present series of experiments with Spanish peanuts. On the other hand, 2-butanal was detected in raw and roasted Spanish peanuts but not in runner peanuts.

Acetone is known to be present in both raw and roasted peanuts (Brown *et al.*, 1972; Walradt *et al.*, 1971). The high concentrations of acetone found in all samples in the present study are considered to be artifacts of the analytical method (Brown *et al.*, 1972; Craske and Edwards, 1971).

As shown in Table II, the major monocarbonyl compound detected in raw Spanish peanuts was hexanal. Octanal, nonanal, and decanal were also detected in relatively large concentrations in the raw peanuts, but concentrations of these three compounds were obviously much lower than that of hexanal. The major saturated aldehydes found in roasted Spanish peanuts were 2-methylpropanal, 3-methylbutanal, 2-methylbutanal, ethanal, propanal,

Table I. Estimations of Average Total Carbonyl Content and Carbonyl Content of the Dicarbonyl, Ketoglyceride, and Monocarbonyl Fractions from Raw and Medium Roasted Spanish Peanuts ($\mu\text{mol}/100\text{ g}$ of Cold-Pressed Peanut Oil)

Determination ^a	Spanish peanuts			Runner peanuts		
	Raw	Roasted	Increase on roasting	Raw	Roasted	Increase on roasting
Total carbonyl	116	447	331	62	324	262
Dicarbonyl fraction ^b	36	226	190	30	198	168
Ketoglyceride fraction ^c	69	116	47	24	99	75
Monocarbonyl fraction	10	65	55	8	26	18

^a Average of three replicates. ^b 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. ^c Determined by difference before and after adsorption and subsequent elution of 2,4-DNPH's from alumina using benzene-hexane solvent.

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

Compound	Treatment ^a					
	Roasted			Raw		
	Spanish ^b	Runner ^{b,c}	Remark ^d	Spanish ^b	Runner ^{b,c}	Remark ^d
Alkanal						
Ethanal	M	S	P ^e	S	S	P
Propanal	M	S	P ^e	S	S	P
Butanal	S	S	P ^e	S	S	P
2-Methylpropanal	VL	VL	P ^e	ND	ND	
Pentanal	M	M	P ^e	M	M	P ^e
3-Methylbutanal	VL	VL	P ^e	ND	ND	
2-Methylbutanal	VL	VL	P ^e	ND	ND	
Hexanal	L	L	P ^e	L	L	P ^e
Heptanal	S	S	P ^e	S	S	P
Octanal	L	L	P ^e	M	M	P
Nonanal	L	L	P ^e	M	M	P
Decanal	L	L	P ^e	M	M	P
Undecanal	S	S	T	S	ND	T
Dodecanal	S	S	P	S	S	T
Tetradecanal	S	ND	T	S	ND	T
2-Alkanone						
Acetone	VL ^f	VL ^f	P ^e	VL ^f	VL ^f	P ^e
2-Butanone	M	M	P ^e	S	S	P
2-Pentanone	S	S	P ^e	S	S	P
3-Methyl-2-butanone	S	S	T	ND	ND	
2-Hexanone	S	S	P	S	S	P
2-Heptanone	M	S	P ^e	S	S	P
2-Octanone	S	S	P ^e	S	S	P
2-Nonanone	S	S	P ^e	S	S	P
2-Decanone	ND	S		ND	S	
2-Undecanone	S	S	T	S	ND	T
2-Alkenal						
2-Butenal	S	ND	T	S	ND	T
2-Phenyl-2-butenal	S	S	T ^e	ND	ND	
2-Pentenal	S	S	T	S	S	T
2-Hexenal	S	S	P ^e	S	S	P
2-Heptenal	M	M	P ^e	S	S	P
2-Octenal	M	M	P ^e	M	S	P
2-Nonenal	L	M	P	S	S	P
2-Decenal	L	M	P ^e	S	S	P
2-Undecenal	L	M	T	S	S	T
2-Dodecenal	M	S	T	S	ND	T
2-Tetradecenal	S	ND	T	S	ND	T
2-Hexadecenal	S	ND	T	S	ND	T
2,4-Alkadienal						
2,4-Pentadienal	S	S	T	ND	ND	
2,4-Hexadienal	S	S	T	S	ND	T
2,4-Heptadienal	S	S	P ^e	S	S	P
2,4-Octadienal	S	S	T	S	S	T
2,4-Nonadienal	M	S	P ^e	S	S	P
2,4-Decadienal	M	M	P ^e	S	S	P
2,4-Undecadienal	ND	S		S	ND	T

^a Average of three replicates. ^b S = small; M = medium; L = large; VL = very large; ND = not detected. ^c From Brown *et al.* (1972). ^d P = positive; T = tentative identification. For both peanut varieties. ^e Mass spectral evidence obtained for presence of compound. ^f Present primarily as an artifact.

hexanal, octanal, nonanal, and decanal. The major unsaturated aldehydes were 2-heptenal, 2-octenal, 2-nonenal, 2-decenal, 2-undecenal, 2-dodecenal, 2,4-nonadienal, and 2,4-decadienal.

Changes in relative concentrations of individual compounds induced in Spanish peanuts during roasting were similar to those induced in runner peanuts during roasting, but concentrations of several of the compounds in raw and roasted Spanish peanuts appeared to be somewhat higher than in the corresponding runner peanut samples. Higher concentrations of hexanal, octanal, nonanal, and decanal were found in raw Spanish than in raw runner peanuts, while higher concentrations of the branched chain aldehydes, as well as ethanal, propanal, octanal, nonanal, decanal, 2-heptanone, 2-heptenal, 2-octenal, 2-nonenal, 2-decenal, 2-undecenal, 2,4-nonadienal, and 2,4-decadienal, were found in roasted Spanish peanuts in comparison to roasted runner peanuts.

DISCUSSION

The major portion of the carbonyl compounds comprising the dicarbonyl fraction is thought to be dicarbonyl di-2,4-DNPH's, although other products are known to be present in this fraction. The ketoglyceride fraction is composed primarily of ketoglycerides plus traces of oxo acids (Brown *et al.*, 1972). The monocarbonyl fraction is composed primarily of aliphatic saturated and unsaturated aldehydes and ketones (Brown *et al.*, 1972; Schwartz *et al.*, 1963). Formation of most of the aliphatic monocarbonyls, ketoglycerides, oxo acids, and many of the dicarbonyls found in raw and roasted peanuts may be attributed to the autoxidation of unsaturated fats (Badings, 1970; Schwartz and Virtanen, 1968; Schwartz *et al.*, 1963).

The higher total carbonyl content and higher carbonyl contents of the dicarbonyl, ketoglyceride, and monocarbonyl fractions and higher concentrations of individual aldehydes in raw Spanish peanuts as compared to raw runner peanuts suggests that autoxidation had progressed to a greater extent in the Spanish peanuts. The two most likely explanations for the apparently higher degree of autoxidation in raw Spanish peanuts as compared to runner peanuts are differences in linoleate content and differences in the length of storage. Oil from Spanish peanuts usually contains a higher concentration of linoleate and is reported to be less stable toward autoxidation than oil from runner peanuts (Fore *et al.*, 1953; Holley and Hammons, 1968), although oil composition and oxidative stability can be modified somewhat through the interaction of environment and planting location (Young, 1970). Secondly, the raw Spanish peanuts were in cold storage approximately 9 months longer than the runner peanuts and were exposed to the potential for autoxidation for a longer period of time.

The possibilities that the apparently higher degree of autoxidation is due to differences in protective factors or differences based on dormancy and nondormancy cannot be ruled out entirely. The tocopherol content of Spanish peanuts is lower than that of runner peanuts (Fore *et al.*, 1953). A lower stability of Spanish peanuts could be the result of a lower tocopherol content. However, Fore *et al.* (1953) noted that the differences in tocopherol content were quite small and concluded that these differences probably were too small to be significant, although differences in possible nontocopherol antioxidants could not be excluded.

Spanish peanuts are nondormant type peanuts, whereas runner peanuts are dormant type peanuts (Holley and Hammons, 1968). Lipoxidase and other enzyme activities in general might be expected to be higher in nondormant peanuts shortly after harvesting and curing. However, differences due to dormancy and nondormancy might be expected to be of little significance in our experiments, since

the curing and postcuring period of 3 months and the period in cold storage of more than a year were probably long enough to allow breaking of dormancy (Harris and Bledsoe, 1951). Furthermore, the much higher carbonyl contents recorded for the Spanish peanuts after roasting tend to indicate that a factor other than dormancy was responsible for the apparently higher rates of autoxidation; *i.e.*, lipid composition or possibly antioxidant content.

The possibilities that the differences in carbonyl contents recorded for raw peanuts are due to differences in climatic conditions, differences in soil conditions, or differences in the locale are minimal. The runner and Spanish peanuts were grown in the same field during the same year, under similar agronomic conditions.

Roasted Spanish peanuts also yielded total carbonyl, dicarbonyl, ketoglyceride, and monocarbonyl values that were much higher than the corresponding values for runner peanuts. Furthermore, Table I indicates that the lipids in Spanish peanuts were less stable toward autoxidation during roasting than the lipids in runner peanuts. The total carbonyl and carbonyl contents of the dicarbonyl and monocarbonyl fractions in Spanish peanuts increased to a greater extent during roasting than did those in runner peanuts. Furthermore, the total monocarbonyls (*i.e.*, ketoglycerides plus monocarbonyls) increased to a greater extent in Spanish peanuts, although ketoglyceride content alone did not. The major factor responsible for the higher carbonyl values in roasted Spanish peanuts and the apparently lower stability of Spanish peanut lipids than runner peanut lipids toward autoxidation during roasting may also be the higher linoleate content of Spanish peanuts and the greater susceptibility of linoleate than oleate or saturated fatty acids toward autoxidation at elevated temperatures (Badings, 1970). The higher monocarbonyl content and higher total carbonyl content of roasted Spanish peanuts than runner peanuts also were due partially to the increased production of branched chain aldehydes in Spanish peanuts during roasting, but the difference is only about 15 μmol per 100 g of oil (Brown, 1971).

Table II shows that the composition of the monocarbonyl fractions isolated from raw runner and raw Spanish peanuts is qualitatively fairly similar. Although nine compounds not detected in raw runner peanuts were detected in raw Spanish peanuts, and one compound detected in raw runner peanuts was not detected in raw Spanish peanuts, the differences occur between compounds which are present at concentrations barely exceeding the limits of detectability. The most likely explanation for the detection of these additional compounds is that the longer period of storage made possible a greater accumulation of trace metabolites and autoxidation products. The higher monocarbonyl content of the raw Spanish peanuts which was noted in Table I is consistent with this hypothesis.

The compositions of the monocarbonyl fractions isolated from medium roasted runner and Spanish peanuts were even more similar to each other than were the fractions from the raw peanuts. Traces of tetradecanal, 2-butenal, 2-tetradecenal, and 2-hexadecenal were found in roasted Spanish but not in roasted runner peanuts, while traces of 2-decanone and 2,4-undecadienal were found in roasted runner peanuts but not in Spanish peanuts. Again the apparent presence of the additional compounds is probably due to the fact that their concentrations were approximately at the limits of detectability.

Model experiments (Badings, 1970; Kinsella, 1969) show that large concentrations of hexanal, 2-heptenal, 2-octenal, and 2,4-decadienal and small concentrations of pentanal, heptanal, octanal, 2-nonenal, and 2,4-nonadienal are formed by autoxidation of linoleate. These compounds, along with ethanal, 2-methylpropanal, 2-

methylbutanal, and 3-methylbutanal, which are the Strecker degradation products of the corresponding amino acids, alanine, valine, isoleucine, and leucine (Mason *et al.*, 1967), were found in medium to very large concentrations in roasted peanuts and in general were found in considerably higher concentrations in roasted Spanish peanuts. It is likely that the higher concentrations of the straight-chained aldehydes are the direct result of higher linoleate content of Spanish peanuts and the higher susceptibility of linoleate to autoxidation noted above. The increased concentrations of the branched chain aldehydes could reflect differences in the protein composition or in the abundance of a particularly labile protein (Mason *et al.*, 1969) or reflect differences in free amino acid concentrations as suggested by Newell *et al.* (1967), but the actual source of the precursor amino acids remains unknown.

One of the objectives of our research has been to relate the flavor of raw and roasted peanuts to the concentrations, flavor threshold values, and reported flavors of individual carbonyl compounds. In our earlier work we found that concentrations of hexanal and octanal in oil expressed from raw runner peanuts exceeded their flavor threshold values of 0.08 and 0.04 ppm, and concluded that hexanal and octanal and possibly nonanal and 2-nonenal contributed to the flavor of raw runner peanuts (Brown *et al.*, 1971). The results of the present investigation tend to indicate that hexanal and octanal and possibly nonanal and 2-nonenal also contribute to the flavor of raw Spanish peanuts, since the concentrations of these compounds in raw Spanish peanuts appear to be as high or higher than in raw runner peanuts.

In oil expressed from roasted runner peanuts, concentrations of 2-methylpropanal, 2-methylbutanal, and 3-methylbutanal exceeded their flavor thresholds by 25-fold or more, and these compounds were implicated in the harsh note of freshly roasted runner peanuts (Brown *et al.*, 1971). Furthermore, the concentrations of hexanal, heptanal, octanal, nonanal, decanal, 2-heptenal, 2-octenal, 2-nonenal, 2-decenal, and 2,4-decadienal in roasted runner peanuts were above their flavor threshold values, and it was concluded that these compounds also might be background notes to the flavor and aroma of roasted runner peanuts. Again the results of the present investigation were similar to those obtained for runner peanuts. Concentrations of the three branched chain aldehydes were obviously even higher than those detected in roasted runner peanuts, and concentrations of hexanal, octanal, nonanal, decanal, 2-heptenal, 2-octenal, 2-nonenal, 2-decenal, and 2,4-decadienal appeared to be at least as high as had previously been found in roasted runner peanuts.

Additive, synergistic, antagonistic, and masking effects are quite common among the various carbonyl compounds (Kinsella, 1969). As a result, some compounds present in raw and roasted peanuts in concentrations above their flavor threshold may not actually contribute to peanut flavor, while other compounds present in concentrations below their flavor thresholds may actually play roles in peanut flavor. We have collected quantitative data on sev-

eral of the major and minor carbonyl compounds found in raw and roasted runner and Spanish peanuts. These data will be presented in a subsequent paper.

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LITERATURE CITED

- Badings, H. T., "Cold-Storage Defects in Butter and Their Relation to the Autoxidation of Unsaturated Fatty Acids," Veenman and Zonen N. V., Netherlands, 1970.
- Brown, D. F., Southern Marketing and Nutrition Research Division, ARS, USDA, New Orleans, La., unpublished data, 1971.
- Brown, D. F., Senn, V. J., Dollear, F. G., Stanley, J. B., *J. Amer. Peanut Res. Educ. Ass.* **3**, 208 (1971).
- Brown, D. F., Senn, V. J., Stanley, J. B., Dollear, F. G., *J. Agr. Food Chem.* **20**, 700 (1972).
- Craske, J. D., Edwards, R. A., *J. Chromatogr.* **57**, 265 (1971).
- Fore, S. P., Morris, N. J., Mack, C. H., Freeman, A. F., Bickford, W. G., *J. Amer. Oil Chem. Soc.* **30**, 298 (1953).
- Harris, H. C., Bledsoe, R. W., in "The Peanut, The Unpredictable Legume," The National Fertilizer Association, Washington, D. C., 1951, pp 89-121.
- Henick, A. S., Benca, M. F., Mitchell, J. H., Jr., *J. Amer. Oil Chem. Soc.* **31**, 88 (1954).
- Holley, K. T., Hammons, R. O., *Ga. Agr. Exp. Sta. Res. Bull.* no. 32 (1968).
- Johnson, B. R., Waller, G. R., Foltz, R. L., *J. Agr. Food Chem.* **19**, 1025 (1971).
- Kinsella, J. E., *Chem. Ind. (London)* **36** (1969).
- Mason, M. E., Johnson, B. R., Hamming, M. C., *J. Agr. Food Chem.* **15**, 66 (1967).
- Mason, M. E., Newell, J. A., Johnson, B. R., Koehler, P. E., Waller, G. R., *J. Agr. Food Chem.* **17**, 728 (1969).
- Newell, J. A., Mason, M. A., Matlock, R. S., *J. Agr. Food Chem.* **15**, 767 (1967).
- Pattee, H. E., Beasley, E. O., Singleton, J. A., *J. Food Sci.* **30**, 388 (1965).
- Pattee, H. E., Singleton, J. A., Cobb, W. Y., *J. Food Sci.* **34**, 625 (1969).
- Pattee, H. E., Singleton, J. A., Johns, E. B., Mullin, B. C., *J. Agr. Food Chem.* **18**, 353 (1970).
- Patton, S., Josephson, D. V., *Food Res.* **22**, 216 (1957).
- Schwartz, D. P., Haller, H. S., Keeney, M., *Anal. Chem.* **35**, 2191 (1963).
- Schwartz, D. P., Johnson, A. R., Parks, O. W., *Microchem. J.* **13**, 37 (1962).
- Schwartz, D. P., Parks, O. W., *Anal. Chem.* **33**, 1396 (1961).
- Schwartz, D. P., Shamey, J., Brewington, D. R., Parks, O. W., *Microchem. J.* **13**, 407 (1968).
- Schwartz, D. P., Virtanen, A. I., *Acta Chem. Scand.* **22**, 1717 (1968).
- Walradt, J. P., Pittet, A. O., Kinlin, T. E., Muralidhara, R., Sanderson, A., *J. Agr. Food Chem.* **19**, 972 (1971).
- Young, C. T., Ph.D. dissertation, Oklahoma State University, Stillwater, Okla., 1970.
- Young, C. T., Holley, K. T., *Ga. Agr. Exp. Sta. Tech. Bull.* no. 41 (1965).

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