Concentrations of Some Aliphatic Aldehydes and Ketones Found in Raw and Roasted Spanish and Runner Peanuts

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ABSTRACT

Carbonyl compounds in oil cold-pressed from raw and roasted peanuts were isolated and quantitated as their 2,4-dinitrophenylhydrazones. Quantitative data were obtained for more than 40 compounds and compared to the flavor threshold values of the compounds in oil. In general, concentrations of aldehydes and ketones in Spanish peanuts were higher than in runner peanuts. Hexanal and octanal and possibly nonanal, 2-octenal and 2-nonenal may contribute to the "green-beany" flavor of raw peanuts. Concentrations of 2-methylpropanal, 2-methylbutanal and 3-methylbutanal vastly exceeded their flavor thresholds and probably contribute significantly to the harsh note of freshly roasted peanuts. Other compounds that could contribute to the flavor and aroma of roasted peanuts are: hexanal, heptanal, octanal, nonanal, dodecanal, 2-heptenal, 2-octenal, 2-nonenal, 2-decenal and 2,4-decadienal.

INTRODUCTION

Flavor is the synchronous sensation of taste and aroma which may be modified to some extent by the simultaneous perception of tactile properties in the mouth (1). Sweet, sour, salty and bitter are the four sensations generally described as taste. Texture, particle size, hardness and solubility contribute to tactile sensation, but the most important factor contributing to flavor is the odor or aroma. Aroma is sensed in the top and back of the nasal passages; in order to possess an odor a substance must be at least partially in the vapor state (1). Characteristic flavors of foods can be attributed for the most part to the volatile compounds that are present, whereas sweetness, sourness, saltiness and bitterness generally contribute to a lesser extent (2).

The chemical composition of the volatile, flavor and aroma, fraction from raw and roasted peanuts has been investigated extensively in the last 10 years (3-7). Several aldehydes, ketones and alcohols as well as ethyl acetate and pentane have been detected in raw peanuts (4,8). The production of several aldehydes and ketones has been related to enzyme activities in maturing peanuts (8), and hexanal, octanal and nonanal have been implicated with the characteristic odor of raw peanuts (4,9).

More than 200 compounds have been identified in the volatiles from roasted peanuts (6,10,11). Mason et al. (5) suggested that the "roasted nutty" note in the aroma of roasted peanuts is imparted by pyrazines. The harsh note of freshly roasted peanuts has been associated with low molecular weight aldehydes (4,12), and the sweet bouquet of roasted peanuts was ascribed to the presence of phenylacetaldehyde (12).

Few quantitative data on the concentrations of individual compounds present in the volatile fraction from raw and roasted peanuts have been published. Pattee et al. (8) measured the areas of gas chromatographic peaks corresponding to individual compounds and compared the recorder responses at various times during the maturation of raw peanuts. The concentrations, flavor threshold values and reported flavors of a few aliphatic monocarbonyl compounds found in raw and roasted runner peanuts have been compared (4), but quantitative data for the majority of the carbonyl compounds found in Spanish as well as runner peanuts have not been reported. The purpose of research reported in this paper was to determine the concentrations of volatile aliphatic aldehydes and ketones present in raw and roasted runner and Spanish peanuts and to attempt to relate the concentrations of these compounds to the flavor of raw and roasted peanuts.

EXPERIMENTAL PROCEDURES

Materials

All chemicals and solvents were reagent or ultrapure grade. Hexane was rendered carbonyl-free (13). 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 C, and the alumina (Fisher Scientific Co.) was rehydrated with 6% water before use (weak alumina).

Peanuts were no. 1 grade, Dixie Spanish and Southeastern Early Runner peanuts, grown under identical agronomic conditions in Tifton, Ga., during 1969. They were 3 day windrowed, cured artificially at 32 C, stored at ambient temperature for ca. 90 days and then maintained in cold storage at 3 C until utilized. Peanuts were roasted at 170 C 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/in.^{2} in a Carver laboratory press.

Isolation of Carbonyl Compounds

The procedures for derivatizing, isolating and recovering the carbonyl compounds as their 2,4-DNPH's are reported elsewhere (11) and are similar to the procedures developed by Schwartz et al. (14,15). The procedures used are outlined in Figure 1. 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 of dicarbonyl compounds, ketoglycerides and other products and the unreactive oils were separated from the 2,4-DNPH's of aliphatic aldehydes and ketones by column chromatography on Celite 545-Sea Sorb 43 and then 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 plates impregnated with polyethylene glycol 400 (PEG 400) or PEG 400 plus KOH. For preparative chromatography of 2,4-DNPH's, thin layer chromatographic (TLC) plates impregnated with only PEG were used.

Identification of Carbonyl Compounds

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 (11). The

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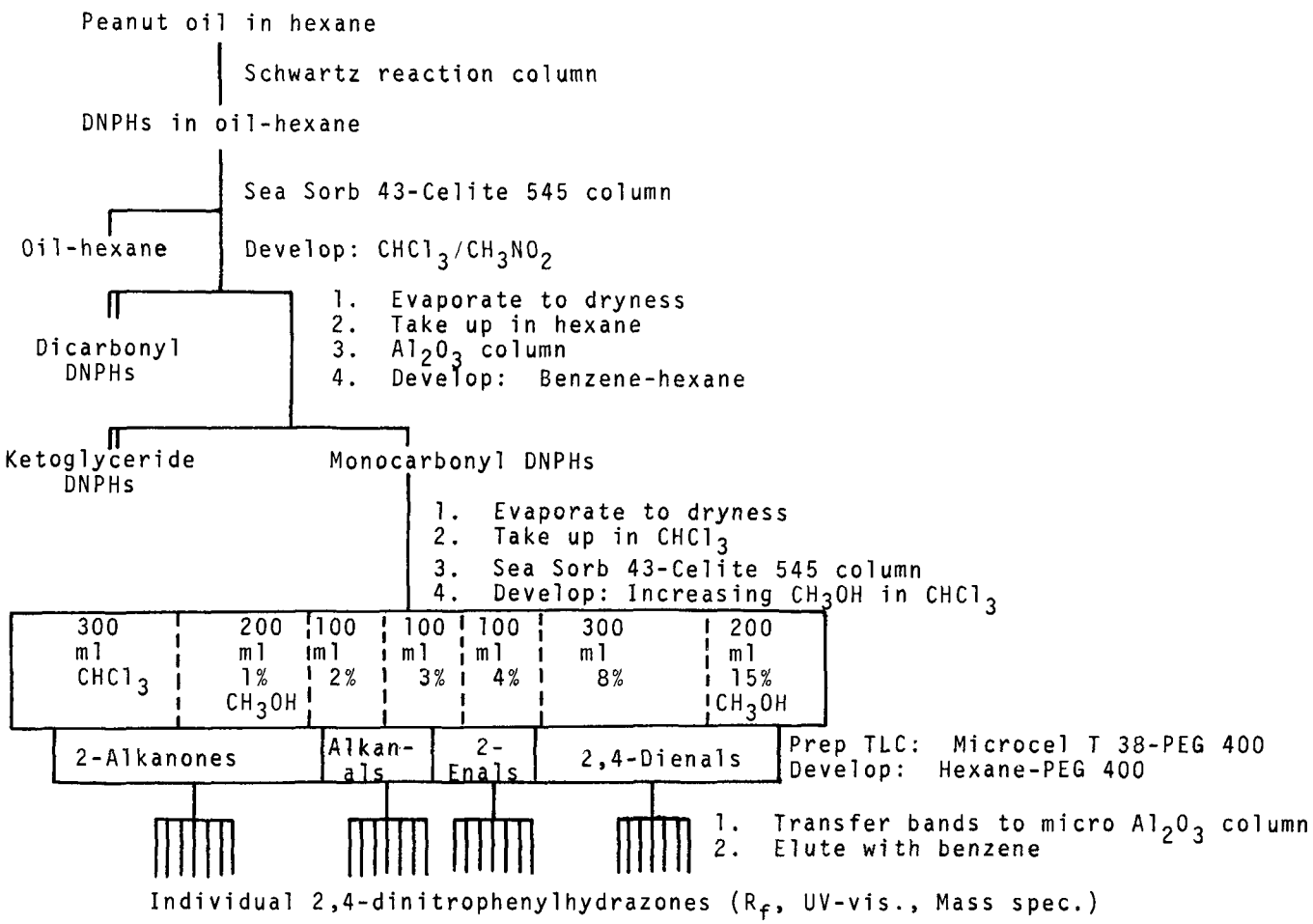

FIG. 1. Schematic diagram for isolation of peanut carbonyls as 2,4-dinitrophenylhydrazones.

coincident presence of compounds representing another class was detected by a deviation of the absorption maximum from the maximum that is characteristic of the class under investigation. The coincident compounds were identified after rechromatography on a different adsorbent, e.g., silica gel, or from the deviations of the absorption maxima themselves, since the absorption maximum of each class differs considerably from those of the other classes (16). Furthermore, if the R_f values were low, the coincident compound belonged invariably to the class eluting just prior to the class under consideration, and if it had a high R_f value, it belonged to the class eluting during column chromatography just following the class under consideration.

Quantitation of Carbonyl Compounds

Quantitative data for individual compounds were obtained after preparative chromatography of an aliquot of each class. Each band was transferred quantitatively to a microcolumn packed with weak alumina, and the 2,4-DNPH's were eluted with benzene. After the solvent was evaporated under a stream of nitrogen on a steam bath, the residue was dissolved in 3 ml chloroform, and the absorbance was measured at its maximum on a spectrophotometer. If two compounds were coincident, the absorbance was apportioned between the two compounds, in proportion to the absorbances of the two compounds after rechromatography and resolution on a different adsorbent, or in proportion to the differences ($m\mu$) between the observed maximum and the maxima of the two individual compounds.

Concentrations were calculated using the molar extinction coefficients listed by Schwartz et al. (16) and are reported as parts per million in the oils. Corrections for losses during TLC and recovery of the 2,4-DNPH's were made by use of correction factors. The correction factors were obtained by dividing the absorbance of each aliquot by the total of the absorbances of all the bands obtained from the class under investigation.

Flavor Thresholds of Carbonyl Compounds

Flavor threshold values (ppm) used in this report were determined in paraffin oil by Badings (17) unless noted otherwise. Threshold values for 2-methylpropanal and 2-methylbutanal are those of butanal and pentanal, respectively, and are thought to be good estimates of the threshold values of the branched chain aldehydes (11). The flavor threshold as used by Badings is the average minimal concentration of a compound in the solvent, below which aroma and taste is not perceptible to 50% of the observers.

RESULTS AND DISCUSSION

Polyethylene glycol 400-impregnated Microcel T-38 thin layer plates were well suited to separating and isolating the derivatives in each of the monocarbonyl classes. Only two pairs of isomers, butanal and 2-methylpropanal, and pentanal and 3-methylbutanal, could not be resolved. Multiple development and rechromatography on other adsorbents demonstrated that the band corresponding to each pair of isomers was comprised almost entirely of the branched chain isomer, but the resolution was not complete enough to permit quantitative determination of each isomer. Therefore butanal and 2-methylpropanal and also 3-methylbutanal and pentanal were determined together, and their concentrations are reported as 2-methylpropanal and 3-methylbutanal.

Concentrations (ppm) of the alkanals, 2-alkanones,

TABLE I

Concentrations of Aldehydes and Ketones Determined in Oil Expressed from Raw and Roasted Spanish and Runner Peanuts (ppm)

Compound	Treatment[a]				Threshold values[c]	Reported flavor[c]
	Spanish peanuts		Runner peanuts			
	Roasted[b]	Raw[b]	Roasted[b]	Raw[b]		
Alkanal						
Ethanal	0.26	0.023	0.01	0.006		
Propanal	0.27	0.010	0.081	0.010	1.6[f]	Sharp, irritating
Butanal	NR	0.021		0.016	0.025	Sharp, irritating
2-Methylpropanal	5.9	ND	1.6	ND	0.025	
Pentanal	NR	0.147		0.038	0.07	Sharp
3-Methylbutanal	3.8	ND	1.8	ND	0.030	Sharp
2-Methylbutanal	5.1	ND	1.7	ND	0.07	
Hexanal	1.1	0.91	1.1	0.34	0.08	Green, beany[d]
Heptanal	0.11	0.045	0.080	0.016	0.055	Oily, putty
Octanal	0.73	0.18	0.41	0.070	0.040	Fatty, beany[d]
Nonanal	1.21	0.38	0.68	0.12	0.20	Tallowy, beany[d]
Decanal	0.59	0.24	0.32	0.10	0.70	Orange peel
Undecanal	0.15	0.024	Trace	Trace	0.09	Citrus
Dodecanal	0.093	0.050	0.068	0.006	0.045	Fatty, citrus
Tetradecanal	0.23	0.095	ND	ND		
2-Alkanone						
Acetone	3.6[e]	3.8[e]	6.2[e]	2.1[e]		
2-Butanone	0.13	0.024	0.11	0.008	79.5[d]	
2-Pentanone	0.055	0.035	0.012	0.002	8.4[d]	
3-Methyl-2-butanone	0.008	ND	0.004	ND		
2-Hexanone	0.089	0.049	0.049	Trace	0.4[d]	
2-Heptanone	0.18	0.062	0.075	Trace	0.7[d]	Blue cheese
2-Octanone	0.088	0.016	0.063	0.014	0.5[d]	
2-Nonanone	0.11	0.037	Trace	0.031	3.5[d]	Blue cheese
2-Decanone	ND	ND	Trace	Trace		
2-Undecanone	0.14	0.069	Trace	ND	15.5[d]	Fruity
2-Alkenal						
2-Butenal	0.007	0.004	ND	ND		
2-Phenyl-2-butenal	0.24	ND	0.25	ND		
2-Pentenal	0.052	0.009	0.045	0.008	1.0	Green, painty
2-Hexenal	0.057	0.034	0.042	0.023	0.6	Green, grassy[d]
2-Heptenal	0.27	0.12	0.23	0.040	0.2	Putty, fatty
2-Octenal	0.37	0.19	0.22	0.039	0.15	Woodbugs, fatty, tallowy[d]
2-Nonenal	0.54	0.090	0.62	0.036	0.04	Tallowy, cucumbers
2-Decenal	0.47	0.13	0.19	0.024	0.15	Tallowy
2-Undecenal	0.43	0.14	0.19	0.022	4.2	Fatty, tallowy
2-Dodecenal	0.22	0.030	0.033	ND	6.3[f]	
2-Tetradecenal	0.061	0.036	ND	ND		
2-Hexadecenal	0.063	0.024	ND	ND		
2,4-Alkadienal						
2,4-Pentadienal	0.001	Trace	0.010	ND		
2,4-Hexadienal	0.003	0.001	0.006	ND	0.04	Fatty, green
2,4-Heptadienal	0.004	0.002	0.014	Trace	0.10	Frying odor
2,4-Octadienal	0.002	0.001	0.002	Trace	0.15[f]	Cardboard
2,4-Nonadienal	0.17	0.07	0.045	0.003	0.46	Fatty, oily
2,4-Decadienal	0.71	0.06	0.31	0.003	0.10	Deep-fried
2,4-Undecadienal	ND	0.002	Trace	ND		Fried, fatty

[a]Average of three replicates.

[b]NR = Not resolved sufficiently for quantitative determination; ND = not detected.

[c]From Badings (17) except as noted.

[d]From Kinsella (19) as determined in milk.

[e]Present primarily as an artifact.

[f]From Meijboom (21).

2-alkenals and 2,4-alkadienals determined in oil from raw and roasted Spanish and runner peanuts are recorded in Table I. In Table I also are listed the flavors attributed to the individual carbonyl compounds and the flavor threshold values reported in the literature. The symbols NR and ND indicate that the compound under consideration was not resolved sufficiently for quantitative determination or was not detected.

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. On the other hand acetone is known to be a constituent of raw and roasted peanuts (10,11), but the high concentrations of acetone found in all of the samples are considered to be artifacts from the derivatization and isolation procedure (11,18).

Table I shows that qualitatively raw Spanish and runner peanuts are quite similar. Although nine additional compounds were detected in raw Spanish peanuts, they were detected in concentrations barely exceeding their limits of detectability. The apparent absence of the compounds in raw runner peanuts is thought to be due to their concentrations being below the limits of detectability rather than to the complete absence of the compounds. This conclusion is supported by the fact that the concentrations of nearly all of the individual carbonyl compounds were higher in Spanish than in runner peanuts.

The qualitative composition of roasted runner peanuts is even more similar to roasted Spanish peanuts. Only four compounds found in roasted Spanish were not found in roasted runner peanuts. Again the apparent absence of the

additional compounds in runner peanuts is thought to be due to the limits of detectability rather than the total absence of the compounds in roasted runner peanuts.

The presence of almost all of the aliphatic monocarbonyl compounds detected in raw and roasted Spanish and runner peanuts can be attributed to the autoxidation of unsaturated fats (11,14,17). The much higher concentrations of several compounds including octanal, 2-heptenal, 2-octenal, 2-decenal, 2,4-nonadienal and 2,4-decadienal in roasted Spanish peanuts than in roasted runners may be explained on the basis of the higher linoleate content of Spanish peanuts and the lower stability of linoleate toward autoxidation.

Acetaldehyde, 2-methylpropanal, 2-methylbutanal and 3-methylbutanal are Strecker degradation products of the corresponding amino acids alanine, valine, isoleucine and leucine (12). The much increased concentrations of these aldehydes detected in roasted Spanish peanuts might reflect differences in the protein composition or in the abundance of a particularly heat labile protein. They may also reflect quantitative differences in the free amino acid compositions of Spanish and runner peanuts. The actual source of the precursor amino acids is 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 the reported flavors of individual carbonyl compounds. However any attempt to correlate flavor with the concentrations of the various aldehydes and ketones detected before and after roasting is difficult. Flavor threshold values are affected by several parameters. The polarity of the dispersing medium affects the apparent flavor thresholds of compounds. Generally the flavor thresholds of carbonyl compounds are lower in polar solvents than in nonpolar solvents (19). Therefore it is important to use flavor threshold values obtained in a solvent similar in character to the food system of interest, when drawing conclusions regarding the potential contribution of a compound to food flavor.

Despite qualitative similarities, the flavors perceived may vary considerably due to differences in relative concentrations of the components. Additive, synergistic, antagonistic and masking effects are quite common among the various carbonyl compounds (19). Furthermore a volatile component may impart a different flavor at high concentration than when it only slightly exceeds its flavor threshold value.

Table I shows that the concentrations of hexanal and octanal determined in oil from raw runner and Spanish peanuts exceed their flavor threshold values. In addition concentrations of nonanal, 2-octenal and 2-nonenal in raw Spanish peanuts exceed their flavor thresholds to a small extent, whereas in raw runners the concentrations of these compounds are slightly below their flavor threshold values.

On the basis of our data the aldehydes that most likely contribute to the "green or beany" flavor of raw peanuts are hexanal, octanal and possibly nonanal, 2-pentenal and 2-nonenal. Badings (17) has described the aroma of hexanal as "green," and hexanal has been implicated previously with raw peanut flavor (9). The flavors of octanal and nonanal and saturated aldehydes in general have been described as beany (19).

The potential contributions of 2-nonenal and 2-octenal to raw peanut flavor are more difficult to assess, since their concentrations were approximately at their threshold values in raw peanuts. The aroma of 2-nonenal has been described as tallowy or cucumber-like (17), while 2-octenal is described as tallowy or fatty (17,19). On the basis of the flavor descriptions and concentrations, it would appear that these two compounds are at most only minor contributors to raw peanut flavor.

The aromas of 2-pentenal and 2-hexenal also have been described as green (17). However the flavor thresholds of these compounds are at least 10-fold greater than the concentrations that were recorded in raw Spanish and runner peanuts. Consequently the possibility that 2-pentenal and 2-hexenal contribute to the flavor of the raw peanuts seems fairly unlikely.

From Table I it can be seen that concentrations of 2-methylpropanal, 2-methylbutanal and 3-methylbutanal exceeded their flavor thresholds by 25-fold or more in roasted runner and 50-fold or more in oil from roasted Spanish peanuts. The concentrations of hexanal, heptanal, octanal, nonanal, dodecanal, 2-heptenal, 2-octenal, 2-nonenal, 2-decenal and 2,4-decadienal exceeded their flavor threshold values by lesser extents. The concentration of undecanal determined in oil from roasted Spanish peanuts was somewhat above its threshold value but was below its threshold value in roasted runner peanuts.

Mason et al. (12) noted that when low molecular weight aldehydes were removed from condensed volatiles of roasted peanuts, the harsh aroma usually associated with freshly roasted peanuts was lost, and thus suggested that aldehydes are responsible for the harsh aroma. The three aldehydes most likely responsible for the harsh note of roasted peanuts are 2-methylpropanal, 2-methylbutanal and 3-methylbutanal. These three compounds are characterized by harsh or sharp aromas, and as noted above their concentrations vastly exceeded the threshold values (see also [20]).

Hexanal, octanal and 2-nonenal were present in roasted peanuts at concentrations of ca. 10-15 times their flavor threshold values, while the concentrations of nonanal and 2,4-decadienal were three to seven times their flavor threshold values. On the basis of the flavor thresholds it seems quite likely that these compounds also could contribute to the flavor and aroma of freshly roasted peanuts. The flavor of 2,4-decadienal is described as deep-fried (17), and this compound probably conveys a deep-fried note in roasted peanuts. However "green beany" and cucumber-like notes are not normally characteristics of roasted peanut flavor. It seems likely that these flavors are completely masked in roasted peanuts or that hexanal, octanal, nonanal and 2-nonenal impart other flavor notes in roasted peanuts. Since 2-nonenal, octanal, nonanal and saturated aldehydes in general also are known to impart tallowy or fatty flavors (17,19), it is quite possible that the compounds contribute fatty and tallowy notes rather than beany, cucumber or green notes in roasted peanuts.

Heptanal, dodecanal, 2-heptenal, 2-octenal and 2-decenal also might be expected to play roles in the flavor of roasted peanuts, since these compounds were detected in concentrations from one to three times their threshold concentrations. The flavors of these compounds are described as fatty, tallowy or oily (17,19), and it seems possible that this group of compounds also might contribute fatty, tallowy and oily notes to the background of roasted peanuts.

Undecanal probably does not contribute significantly to the flavor and aroma of roasted peanuts. The flavor of undecanal is described as citrus-like (17). Since a citrus-like note is not normally a characteristic of roasted peanuts, the flavor of undecanal is either masked or the concentration of undecanal in roasted peanuts is too low to be important. It also seems highly unlikely that any of the aldehydes and ketones that we have detected in peanuts are responsible for the "roasted nutty" flavor of roasted peanuts. This aspect of flavor is probably due to the presence of one or more pyrazines in the volatile flavor and aroma fraction of roasted peanuts (5,7).

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