Correlation of Volatile Components of Peanut Products with Flavor Score I. Shelf Life Studies on Peanut Butter[1]

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ABSTRACT

Samples of three commercial brands of peanut butter stored in the dark at about 25°C were evaluated periodically by direct gas chromatography and by their processors' taste panels. The areas of 9 peaks of each volatiles profile were computed and correlated with flavor scores. The natural logarithm of methylbutanal peak area/hexanal peak area correlated with flavor score of peanut butter in earlier work, correlated well with flavor score for one brand of peanut butter, but other gas chromatographic peak ratios gave better correlations for the two other brands.

Peanut butter, volatiles, direct gas chromatography, flavor.

The flavor of peanut products is a major concern of the peanut industry. Since taste panels are expensive to maintain and often produce highly variable results, an instrumental method is needed to evaluate flavor. Although volatile flavor- and aroma-related components of peanuts have been investigated extensively (1-3, 6-14, 16, 17), the analytical methods used are too slow and complicated for routine use. Fore *et al.* (5) developed a rapid, effective direct gas chromatographic method for obtaining volatiles profiles of peanut butter, and correlated taste panel flavor scores of peanut butter with the natural logarithm of methylbutanal peak area/hexanal peak area determined by direct gas chromatography. A more extensive study, involving samples of three brands of peanut butter, has now been completed, and areas of nine peaks in each volatiles profile have been correlated with taste panel flavor scores, using simple and multiple linear regression analysis.

Materials and Methods

MATERIALS

Peanut butter samples were supplied by three manufacturers. The gas-chromatographic packing, Porapak P, 80-100 mesh, batch 1184, manufactured by Waters Associates, Inc.,[3] Framinghan, Mass., was obtained from TekLab, Inc., Baton Rouge, La. Silicone O-rings, also from TekLab, Inc., were conditioned for 2 hr at 200°C. Sandwich-type silicone septums from Hamilton Co., Reno, Nev., were soaked in chloroform for 15 min. rinsed with chloroform, air-dried, and then conditioned for 2 hr at 200°C. Pyrex brand glass wool, manufactured by Corning Glass Works, Corning, N. Y., was heated at 200°C for about 16 hr to remove volatiles. Liners, 10 x 84 mm, and rods, 4.5 x 65 mm were cut from borosilicate glass tubing and rod, respectively.

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[2]One of the facilities of the Southern Region, Agricultural Research Service, U.S. Department of Agriculture.

[3]Mention of companies or commercial products does not imply recommendation by the U.S. Department of Agriculture over others not mentioned.

GAS CHROMATOGRAPHIC ANALYSIS

A MicroTek 2000 MF gas chromatograph with flame ionization detector, a Westronics LD-11-BD recorder, and an Infotronics CRS 100 integrator were used. A silicone O ring was placed at the base of the inlet and tamped down around the end of the column adapter (see Figure 1). A glass rod was twisted in a freshly opened jar of peanut butter to a depth of about 50 mm until 0.2 g to 0.3 g of peanut butter adhered to it. The rod with the weighed sample was placed immediately in an inlet liner that had been plugged at the bottom with glass wool, and the liner was inserted into the heated inlet of the gas chromatograph. The inlet retainer nut was replaced and tightened against the inlet liner to produce a seal between the lower lip of the liner, the silicone O-ring, and the base of the inlet. When the inlet was closed with the septum and septum nut, the carrier gas was forced to flow upward and then down through the liner, as shown in Figure 1.

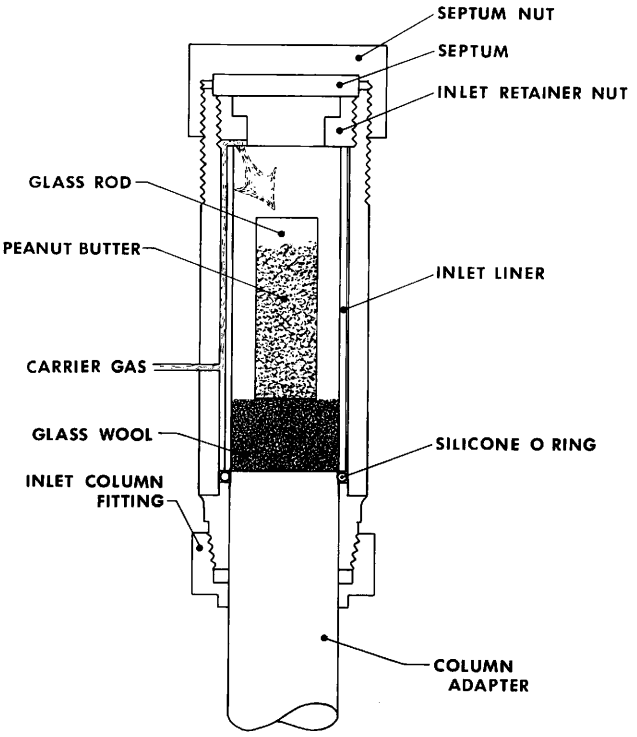

Fig. 1. Cross section of inlet of gas chromatograph with inlet liner containing glass wool and glass rod.

The sweep of the carrier gas and the heat from the inlet promoted rapid and efficient elution of the volatiles, which were swept onto the top portion of the column (maintained at 40°C during an initial hold period of 20 min). The liner containing the spent sample was then removed from the inlet and the volatiles were resolved by programming the temperature of the column oven from 40° to 200°C.

A 2.16 mm ID x 2.29 m stainless steel U-tube packed with Porapak P was used to resolve the volatiles. The Column oven was programmed at 5°C/min for 15 min, 2°C/min for 42.5 min, and then held at 200°c for 30 min. The inlet temperature was set at 120°C and the detector at 300°C. The flow of nitrogen carrier gas was set at 70 ml/min, the hydrogen at 60 ml/min, and the air at 34 liters/hr.

FLAVOR EVALUATION

The taste panels of the processors who supplied the peanut butter made all flavor evaluations. Brands A and

B were scored on a scale of 0 to 10, with 10 the best attainable score, and brand C on a scale of -201 to 192, with 192 the best attainable score.

SHELF LIFE STUDIES

Samples from each of eleven lots of freshly prepared commercial peanut butter from three processors were stored in the dark at approximately 25°C. One sample from each lot was analyzed by direct gas chromatography as soon as it was received from the processor. Peanut butter from other freshly opened jars of each lot was analyzed at intervals of 1 mo or more during the storage period, 12 mo from brands A and B, and 23 mo for brand C. Other jars of the same lots of peanut butter were stored by the processors under similar conditions, and peanut butter from freshly opened jars was flavor scored at similar intervals by the processors' taste panels.

Results and Discussion

The data in Table 1 show that taste panel flavor scores can be represented adequately by linear regressions of flavor score on storage time for all lots of the three brands of peanut butter. However, no relationship existed between initial flavor score and the rate of decrease in flavor score during storage, thus storage time itself is not a useful parameter for estimating flavor score.

Table 1 Linear regression of taste panel flavor scores of peanut butter on days stored.

Brand	Lot	Range of taste panel flavor scores first[1]	last[2]	Correlation[3] coefficient	Standard error	Slope of regression line
A	1	6.6	4.4	-0.86	1.14	-0.015
	2	8.8	6.6	-0.86	0.71	-0.010
	3	8.8	3.2	-0.93	0.70	-0.017
B	1	8.8	4.2	-0.93	0.53	-0.011
	2	8.0	5.0	-0.91	0.62	-0.011
	3	9.2	4.0	-0.89	0.85	-0.013
	4	9.0	2.8	-0.91	0.78	-0.014
	5	9.2	2.6	-0.96	0.51	-0.015
C	1	61	-96	-0.82	32	-0.210
	2	60	7	-0.91	20	-0.086
	3	61	-23	-0.97	7	-0.135

1/ B-2 and -3 were scored 26 days, and all others within 5 days, after production.

2/ Brands A, B, and C were scored for the last time 11, 12, and 21 months after production, respectively.

3/ Correlation for C-1 is significant at 1%. All other correlations are significant at 0.1%.

Changes in volatiles profiles of typical examples of each brand of peanut butter during storage are illustrated in Figure 2. The most striking feature of the profiles is the increase in peaks 2 and 6 during storage. Peak 2 was tentatvely identified as pentane, and 6 as hexanal. Since both pentane and hexanal are produced during autoxidation of linoleates (4, 15), these increases probably denote development of rancidity in the samples. Other changes are less obvious but may also be related to flavor changes. Consequently, the areas of the nine peaks numbered on the chromatograms in Figure 2 were calculatetd for each of the volatiles profiles, and these areas were correlated with estimated flavor scores by both simple and multiple linear regression analysis. Flavor-scoring and gas-chromatographic analysis could not always be done on the same dates, so it was necessary to estimate the flavor score of each jar of peanut butter on the date of gas-chromatographic analysis from the regression line of flavor score on storage time for that lot of peanut butter. Since each of the three brands of peanut butter were flavor-scored by different taste panels, it was necessary to do a separate regression analysis on each brand rather than combine data into a single regression analysis.

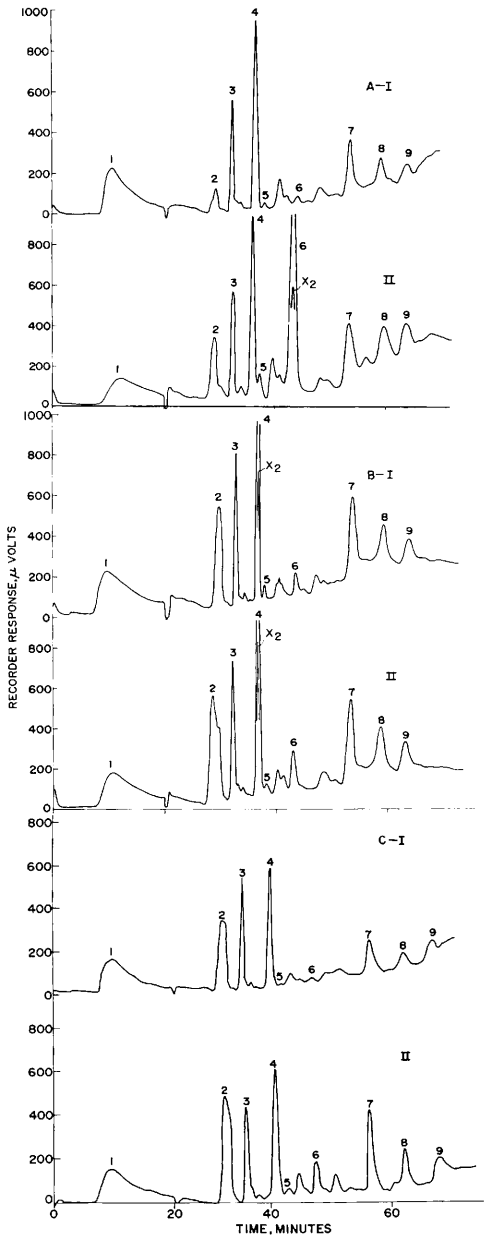

Fig. 2. Gas-chromatographic volatiles profiles: A, two samples of one lot of brand A peanut butter. A—brand A (2 samples from 1 lot)—I, stored 2 wk; II, stored 12 mo. B—brand B (2 samples from 1 lot)—I stored 2 wk; II stored 12 mo. C—brand C (2 samples from 1 lot)—I, stored 3 wk; II, stored 23 mo.
Tentative identification of components: 1 = methanol, acetaldehyde; 2 = pentane (may include some acetone and propanal); 3 = methylpropanal; 4 = methylbutanal; 5 = pentanal; 6 = hexanal; 7 = dimethylpyrazine; 8 = unknown; 9 = phenylacetaldehyde.

The regression analysis data indicated that certain peaks of the volatiles profiles were positively related to flavor quality, and others were negatively related. Peak 3, methylpropanal, was strongly positive for all three brands of peanut butter. The unidentified peak, 8, was strongly positive for brands B and C, but not for A; and peak 4, methylbutanal, was generally positive for brands A and C but negative for B. Peak 6, hexanal, was strongly negative for all brands; peak 2, pentane, and peak 7, dimethyl-pyrazine, were strongly negative for brands B and C, but neutral for A. No conclusions could be drawn regarding the positive or negative bias of the other peaks. The negative bias of the methylbutanal peak for brand B peanut butter and of the dimethylpyrazine peak for brands B and C are unexpected, since both of these compounds develop when peanuts are roasted and pyrazines are credited with the "nutty" flavor of roasted peanuts (8). Possibly compounds that develop as peanut butter deteriorates are being eluted with methylbutanal and dimethylpyrazine.

Table 2 presents correlations found for flavor scores of the three brands of peanut butter with various combinations of areas of the nine peaks numbered on the chromatograms in Figure 2. The natural logarithm of methylbutanal peak area/hexanal peak area, used in earlier work (5), correlates well with estimated flavor score for brand A, but other combinations of components give better correlations for brands B and C. The standard error of regresson 0.87, for correlation of the natural logarithm of methylpropanal peak area/hexanal peak area or methylbutanal peak area/hexanal peak area with estimated flavor score for brand A peanut butter is not statistically different from the standard errors in Table 1 for the regressions of flavor score on days stored used to estimate brand A flavor scores. Likewise, for brand C the standard error of regression values of 22 and 21 for correlation of the natural logartihms of (methylpropanal peak area + area of peak 8)/(pentane peak area + hexanal peak area) and (methylpropoanal peak area + area of peak 8)/(pentane peak area + hexanal peak area + dimethylpyrazine peak area) respectively, with estimated flavor score are not statistically different from the standard errors for the regressions of flavor score on days stored used to estimate brand C flavor scores. Consequently, there is little likelihood that modification of these regression equation models would further reduce the standard error of regression values for these correlations.

Table 2. Linear correlation of natural logarithms of ratios of peak areas of components[1] of volatiles profiles with estimated flavor scores of peanut butter.

Ratios	Brand A		Brand B		Brand C	
	Correlation coefficient[2]	Standard error[3]	Correlation coefficient[2]	Standard error[3]	Correlation coefficient[2]	Standard error[3]
$\frac{4}{6}$	0.89	0.87	0.24	1.34	0.77	30
$\frac{3}{6}$	0.89	0.87	0.29	1.32	0.79	29
$\frac{3}{2}$	0.65	1.43	0.35	1.29	0.83	26
$\frac{3+8}{2+6}$	0.83	1.05	0.37	1.28	0.88	22
$\frac{3+8}{2+6+7}$	0.82	1.08	0.42	1.25	0.89	21
Multiple[4]	0.93	0.68	0.49	1.25	0.94	19

1/ Tentative identification of components: 1 = methanol, acetaldehyde; 2 = pentane (may include some acetone and propanal); 3 = methylpropanal; 4 = methylbutanal; 5 = pentanal; 6 = hexanal; 7 = dimethylpyrazine; 8 = unknown; 9 = phenylacetaldehyde.

2/ For brand B peanut butter, the correlation coefficient of 0.24 is significant at 5% and correlation coefficients of 0.29 and 0.49 are significant at 1%. All other correlation coefficients are significant at 0.1%.

3/ Range of estimated flavor scores: brand A, 9.1 to 2.5 (6.6 units); brand B, 8.7 to 3.3 (5.4 units); and brand C, 59 to -121 (180 units).

4/ Multiple linear regression using all nine peaks.

On the other hand, the standard error of regression 1.25, for the correlation of the natural logarithm of (methylpropanal peak area + area of peak 8) / (pentane peak area + hexanal peak area + dimethylpyrazine peak area) is significantly higher than the standard errors for the regressions of flavor score on days stored used to estimate brand B flavor scores. Probably, there is some unknown factor affecting the brand B flavor scores that has not been measured or considered. Nevertheless, there is a high degree of certainty, 99.9%, that this correlation is real. Correlations resulting from the more complicated linear regression analysis are not appreciably different from the best simple correlations shown in Table 2.

Inspection of the volatiles profiles in Figure 2 and the data in Table 2 suggests that brand A peanut butter differs from B and C in some important respect. Possibly, the lids with rubber gaskets used for brands B and C provided a more effective barrier to air passage than did the waxed-cardboard lined lids used for brand A. When oxygen in the head space of other lots of brands A and B peanut butter was determined with a Beckmann head space sampler and oxygen analyzer, nearly atmospheric quantities of oxygen were found in the head space of all 20 brand A samples and 2 brand B samples, but little or no oxygen was found in the other 18 brand B samples. Volatiles profiles of the two leaking brand B samples were very different from the nonleaking samples but were similar to brand A samples of the same age. Presence or absence of oxygen in the head space may influence the kinds and proportions of voatiles formed during storage.

This study indicates there is a high degree of certainty that a correlation exists between direct gas chromatographic volatiles profiles and flavor scores of peanut butters, but the relationship is very complex. Components giving the best correlations with flavor scores varied from brand to brand, or possibly from taste panel to taste panel, and the correlations for brand B peanut butter were not as good as for brands A and C. Errors may have been introduced from a variety of sources: 1. The peanut butter in different jars of the same lot used for flavor scoring and gas chromatographic analysis may have been different because of slight variations in storage conditions. 2. Air may have leaked into some jars of peanut butter while other jars of the same lot were tightly sealed, causing variations in flavor and volatiles profiles. 3. Inadequate resolution of "positive" and "negative" components of the volatiles profiles could lead to inconsistent results. 4. Results obtained with regression analysis can be no better than the taste panel used to flavor score the samples. 5. Since particular components of the volatiles profiles may be associated with certain flavor notes, any variation in preference or sensitivity for these flavor notes among the three taste panels could affect the correlation of the associated component with flavor score.

Considering the many opportunities for error, the correlations found are surprisingly good. The progress that has been made toward developing an instrumental method for evaluating peanut butter flavor is encouraging, but further work needs to be done under conditions that reduce the opportunities for error.

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