Correlation of Gas Chromatographic Profiles and Organoleptic Scores of Different Fats and Oils after Simulated Deep Fat Frying[1,2]

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ABSTRACT

Five oils and a fat were subjected to simulated deep fat frying using moist cotton balls. The used oils were evaluated by an expert organoleptic panel. Statistically significant differences were found in the odors and flavors of the used oils. Volatile decomposition products of the used oils were quantitatively isolated by high vacuum cryogenic entrainment and then analyzed by gas-liquid chromatography. The volatiles from each used oil yielded a gas chromatogram which was qualitatively and quantitatively different from the others. A statistical analysis was used to correlate the organoleptic scores with the profile gas chromatograms from the used oils. Excellent correlations between gas chromatographic peak areas and organoleptic scores were established. However, limitations in the number of samples tested and limitations in the statistical design do not permit drawing conclusions of cause and effect.

INTRODUCTION

It is of commercial interest to know if there is any real difference in the odor and taste of fried foods caused by the kind of fats and oils used for frying. Chang (1) raised the question in the introduction of a symposium: "What is the effect of different fats and oils upon the organoleptic characteristics of fried foods?" This paper reports a preliminary attempt to answer the question by the use of organoleptic evaluation and instrumentation, as well as their correlation.

The volatile decomposition products produced by fats and oils during deep fat frying have been extensively studied by Chang and his associates. Krishnamurthy et al. (2) developed a method for simulating deep fat frying using moist cotton balls in place of a more chemically complex foodstuff. The method was subsequently used to generate, for study, the volatile decomposition products from deep fat frying oils. The acidic volatiles from corn oil were identified by Kawada et al. (3), and the nonacidic volatiles from corn oil were identified by Krishnamurthy and Chang (4). The acidic volatiles from hydrogenated cottonseed oil were identified by Yasuda et al. (5), and the nonacidic volatiles from hydrogenated cottonseed oil were identified by Reddy et al. (6).

Recently, many attempts have been made to correlate instrumental analysis with organoleptic scores of foods. Powers (7) provided a general description of a computer-assisted method for statistically correlating some chosen measurement of the peaks in profile gas chromatograms of isolated volatiles from foods. Correlation studies of the above type have been conducted for coffee and potato chips (8), cola blends (9), coffee (10), tomato products and peanuts (11), peanuts (12), corn (13), and black currants (14). Dupuy et al. (15) similarly determined edible oil quality by examining the volatiles evolved from a sample heated in a modified gas chromatograph (GC) injector. These investigations met with varying degrees of success in accurately identifying organoleptically differentiated samples by examination of GC data.

A recent publication by Blumenthal and Chang (16) demonstrated a procedure for the preparation of qualitatively and quantitatively reproducible profile gas chromatograms from the isolated volatiles from foods. This method further increased the possibility of correlating instrumental analysis with organoleptic scores.

EXPERIMENTAL PROCEDURES

Oil Samples Used

Corn oil, cottonseed oil, peanut oil, hydrogenated and winterized soybean oil with an iodine value (IV) of 115, hydrogenated and winterized soybean oil IV 89, and hydrogenated soybean shortening IV 70 were obtained from normal plant productions. The samples contained no additives of any kind, and were shipped and stored in 1 qt jars capped off with nitrogen.

These oil samples were kept at room temperature in the dark for 6 weeks from the date of production to allow all samples to have the same period of aging. They were then stored at -20 C until used.

A duplicate sample of cottonseed oil was used throughout the experiment as a control to ensure that all procedures and results were reproducible. Fatty acid composition, free fatty acid level, and IV for each oil were provided by the oil suppliers. Analytical data and organoleptic screening showed the oils were initially of typical good quality, according to common commercial standards.

Simulated Deep Fat Frying

A Sears deep fat fryer (Model 309.6930; 1150 W) with aluminum interior and frying basket was used for the deep fat frying of cotton balls, according to the method of Krishnamurthy et al. (2).

Approximately 2,700 ml of oil were heated to 185 ± 5 C in the deep fat fryer. Ten viscose cotton balls (Johnson and Johnson, New Brunswick, NJ) were strung on an aluminum wire (16 gauge), and each 0.5 g cotton ball was wetted evenly with 1.5 ml of water. The wires were fitted in the bottom of the frying basket so the cotton balls would stay submerged in the oil during the frying process. After frying for 3 min, the cotton balls were drained of oil and discarded. The fryer was left to equilibrate to frying temperature for 15 min. The next set of moist cotton balls was fried, and the entire cycle was repeated for a total of 6 hr. A total of 20 fryings was carried out during this period.

One liter of the used frying oil was placed in a 2 liter

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round bottom flask and stored under nitrogen in a freezer until used for the isolation of volatiles. Another liter of the used frying oil was stored in four 500 ml bottles which were sealed under nitrogen before freezer storage. The latter samples were used for organoleptic evaluation.

Organoleptic Evaluation of the Used Oils

Organoleptic evaluations of the used frying oils were conducted by a panel of 10 trained, experienced members. Preliminary experiments showed clearly that no single score could be used to adequately describe the desirability of either odor or flavor of the deep fat fried oils. For example, a strong odor might be desirable when it was pleasant, or conversely, a strong odor might be undesirable when it was unpleasant. Therefore, two scores were used to describe the odor or flavor: one for its strength and another for its pleasantness.

A hedonic scale of 1 to 9 was used for the scoring of both the strength and pleasantness. For strength, 1 indicates the weakest, 5 the moderate, and 9 the strongest response. For pleasantness, 1 indicates least liked, 5 neutral, and 9 the most liked response.

The used oils with a duplicate of used cottonseed oil were evaluated in two sittings of four samples each. The same used cottonseed oil was put in both sittings as an internal check of panel performance. The four oils served to each panelist at a sitting were randomized.

The oils served in Sitting I were cottonseed oil, peanut oil, cottonseed oil duplicate, and soybean oil IV 70. The oils served in Sitting II were cottonseed oil, soybean oil IV 89, corn oil, and soybean oil IV 115. An incomplete block design was not used for serving samples because this would have required preparation of all oils at each sitting, a requirement which could not be practically implemented.

The panel members were seated in individual booths under yellow light. The samples (5 ml) were served at 60 C in glass creamers. To maintain the temperature during the evaluation period, the creamers were set in holes drilled into heavy aluminum blocks preheated to the desired temperature.

Statistical Analysis of Organoleptic Data

The raw scores were entered into punch cards for computerized statistical analysis. The program used to do the numerous calculations was ANOVAR - Analysis of Variance for Factorial Design, Version of October 14, 1970. The Tukey Test at the 0.05 level was then used to judge the significance of difference among the samples.

The raw scores were then adjusted to compensate for adaptive changes each panelist apparently experienced during the two separate panel sittings. The adjustment for each panelist's scores was based on the response to the used cottonseed oil sample served in both sittings. For example, the scores for used cottonseed oil for panelist #1 was 5.5 and 6.0 in the respective sittings. The mean value of these scores for this panelist was

$$(5.5 + 6.0)/2 = 5.75$$

The scores of this panelist in sitting #1 were then adjusted by 5.75-5.5 or 0.25, and in sitting #2 by 5.75-6.0, or -0.25.

Isolation of Volatile Flavor Compounds from Fresh and Used Oils

The volatiles from the used oils and also from fresh cottonseed oil and fresh soybean oil IV 89, were isolated by subjecting 1 liter of the oil in a 2 liter round bottom flask to 0.05 mm Hg at 90 C for 6 hr. The volatiles were collected in a train of traps cooled with a slurry of solid carbon dioxide in acetone. The volatiles thus collected were washed out with analytical grade ethyl ether, and the solution was concentrated to 3 ml with the use of a 30 plate Oldershaw column.

Gas Chromatography of Volatiles Isolated from Fresh and Used Oils

The volatiles from each sample were gas chromatographed with a Beckman GC-55 instrument which maintained a constant flow rate of carrier gas through the columns regardless of oven temperature. A column effluent splitter was used with 10% of the stream given to the flame ionization detector and 90% to a separately heated sniffer/collection port. The laboratory-prepared column was 1/8 in. x 6 ft stainless steel packed with 5% OV-101 on 80/100 mesh Chromosorb W-HP (DMCS).

The flow rate of helium (99.995% pure) was 33 ml/min through the column and 87 ml/min makeup to the flame ionization detector (FID). The FID was supplied with 250 ml/min of air, and 45 ml/min hydrogen. Signal attenuation was 1 x 16. Temperature settings used were injector 180, lines 240, detector 250, and collector port 180 C. The column oven program was 5 C/min from 50 to 200 C (automatic recycle to lower temperature limit). The recorder was 1 mV/10 in. with a chart speed of ½ in./min. Injection sample size was 3.5 μl.

The gas chromatograms were prepared by the use of the column saturation technique of Blumenthal and Chang (16) in order to obtain qualitatively and quantitatively reproducible profiles.

The profile curves of the volatiles from the used oils were examined to locate coincident peaks (retention volumes) on all the chromatograms. Common peaks were numbered consecutively from 1 to 24 reading from the origins to the ends of the chromatograms. The areas of each of the 24 numbered peaks on each of the seven profile curves were measured with a planimeter. (Some peaks, measuring less than one integration unit in area, were visible but reported as "0".)

Correlation of GC Peak Areas with Organoleptic Evaluation Scores

The area of the 24 peaks common to all the profile curves, and the adjusted organoleptic panel scores were entered on punch cards using a shared coding of sample identity. The program chosen to determine the relationship of peak areas with organoleptic scores was BMD02R-Stepwise Regression-Revised July 17, 1970, from the Health Sciences Computing Facility, UCLA. The stepwise multiple regression analysis program set up a correlation matrix which generated correlation coefficients between each peak area and the average organoleptic scores for the samples in each of the four organoleptic qualities studied.

An equation, $y = a + b_1 X_1 + b_2 X_2$, is established for each organoleptic quality of sample predicting the average organoleptic score, "y." "X_1" is the area of the first peak considered for the sample, and "X_2" is the area of the second peak considered. For evaluation purposes, "a" represents the theoretical (unreal) situation where the values for the first and second peaks are zero; "b_1" is the change associated with a change in organoleptic rating associated with a change of one unit in the first peak area (adjusted for the relationship to the second peak area); "b_2" is the change associated with a change in organoleptic rating associated with a change of one unit in the second peak area (adjusted for the relationship to the first peak area).

RESULTS AND DISCUSSION

Use of Simulated Deep Fat Frying

To fully demonstrate the contribution to the odor and

TABLE I

Relative Ranking of Oils by Adjusted Organoleptic Score

	Strength			Pleasantness	
	Odor	Flavor	Heading, pls	Odor	Flavor
Corn	3.78	4.23	Corn	5.60	5.58
Peanut	3.73	4.63	Cottonseed	5.30	4.96
Cottonseed	5.08	5.03	Peanut	4.45	4.93
Soybean IV[a] 89	5.33	5.08	Soybean IV 89	4.35	4.48
Soybean IV 115	6.53	6.53	Soybean IV 70	3.30	3.03
Soybean IV 70	6.88	7.88	Soybean IV 115	3.00	2.48
Tukey (0.05) q =	2.44	2.40	Tukey (0.05) q =	2.33	2.21

[a]IV = iodine value.

TABLE II

Significant Differences between Oils Deep Fat Fried with Moist Cotton Balls (Tukey 0.05)[a]

Strength of odor	Corn	Peanut	Cottonseed	Soy IV 89	Soy IV 115	Soy IV 70
Strength of flavor	Corn	Peanut	Cottonseed	Soy IV 89	Soy IV 115	Soy IV 70
Pleasantness of odor	Corn	Cottonseed	Peanut	Soy IV 89	Soy IV 70	Soy IV 115
Pleasantness of flavor	Corn	Cottonseed	Peanut	Soy IV 89	Soy IV 70	Soy IV 115

[a]IV = iodine value.

flavor of fried foods by the oil, moist cotton balls were deep fat fried. Such moist cotton balls are similar to inert pieces of potato. However, they do not contribute any odor or flavor to the fried oil. This simulated deep fat frying avoided the use of foods, the odors and flavors of which might be so pronounced as to make the study of the odor and flavor originating from the oil itself most difficult, if not impossible.

This design, of course, assumes that the odor and flavor of the frying oil would contribute to the total odor and flavor of the fried food. It is obvious that if the oil, after being used for frying, has a strong, pleasant odor and flavor, then it would certainly enhance the desirability of the fried foods. On the other hand, if the oil, after being used for frying, develops a strong, unpleasant odor and flavor, it would make the fried food less desirable. While this assumption has no experimental data to support it, it nevertheless appears logical and is therefore used as a preliminary step to approach a complicated problem.

Organoleptic Evaluation of the Used Oils

The average scores of the organoleptic panel of the oils after having been used for simulated deep fat frying are shown in Table I. Differences between panel sittings were leveled by adjusting all raw scores by the difference from the mean of the cottonseed oil used in both sittings as a check.

The adjustment process is similar, both conceptually and practically, to the adjustment process used in incomplete block designs. It is, however, understood that the adjustment process in the incomplete block design would be better due to each treatment appearing in a larger number of blocks without the potential confounding of sittings.

The oils are arranged in increasing order of the strength of either their odor or flavor (with the exception of the odor of peanut oil and corn oil, where the separation between scores was minimal). The oils are also listed in decreasing order of their pleasantness. For example, corn oil has the lowest strength but the highest desirability, both in odor and flavor, while the hydrogenated and winterized soybean oil with an IV of 115 has almost the highest strength but the most undesirable odor and flavor.

Generally, the unhydrogenated oils were ranked higher than the hydrogenated soybean oils. Among the three hydrogenated oils, the one with an IV of 89 ranked the highest. The latter might be due to the fact that its oxidation is stabilized by hydrogenation. At the same time, there was not too much hydrogenation as to yield relatively large amounts of hydrogention flavor (17,18).

Statistical analysis of the differences between the mean organoleptic scores of the six samples was carried out using the Tukey Test at the -.05 level. The single Tukey statistic is presented for simplicity's sake. It is felt that this is reasonable because the sample size used in the calculation is half the true sample size for cottonseed oil, and, as a result, that statistic is conservative.

It should be emphasized that the Tukey Test is a rather conservative statistical procedure which demonstrates only severe differences and ignores subtle ones which might be considered significant by other procedures. With this method, as shown in Table II, any two oils which are not directly connected by a bar are declared significantly different from each other.

For example, in strength of odor, corn oil and peanut oil are significantly different from soybean oil hydrogenated to an IV of 70 and hydrogenated and winterized soybean oil with an IV of 115. For strength of flavor, soybean oil hydrogenated to an IV of 70 is significantly different from all other oils except SBO 115.

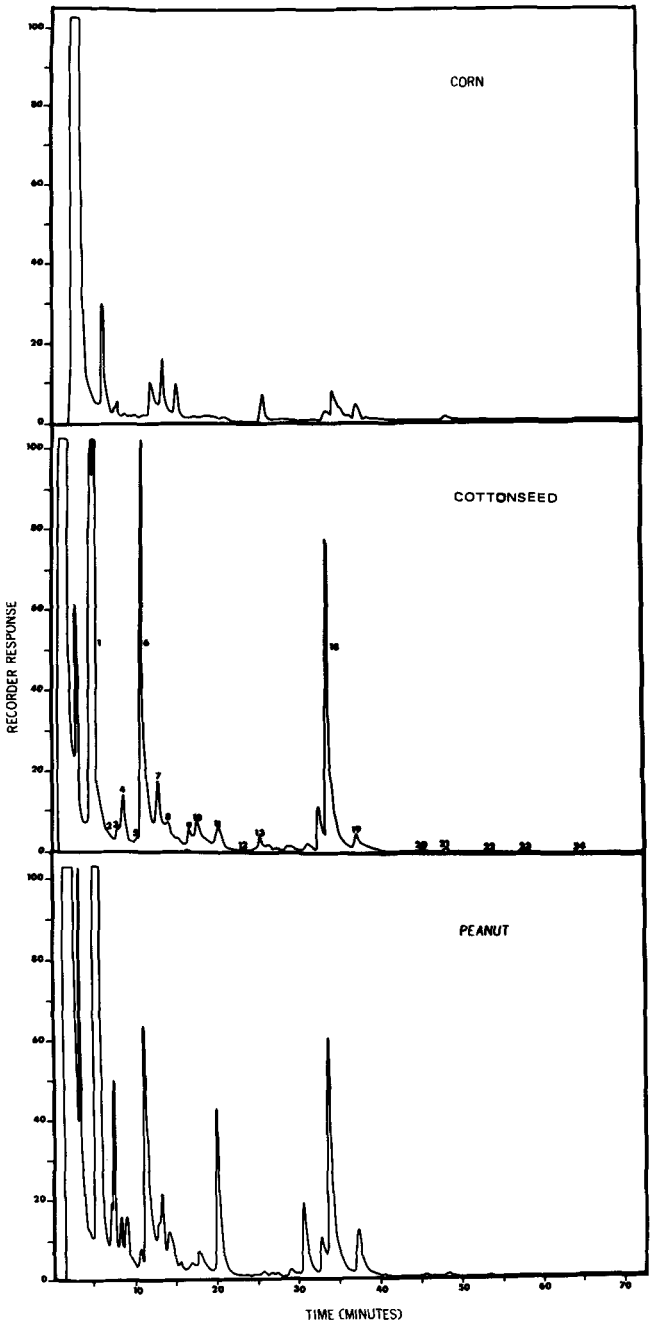

FIG. 1. Gas chromatogram of volatiles isolated from used corn oil (top), used cottonseed oil (center), and used peanut oil (bottom).

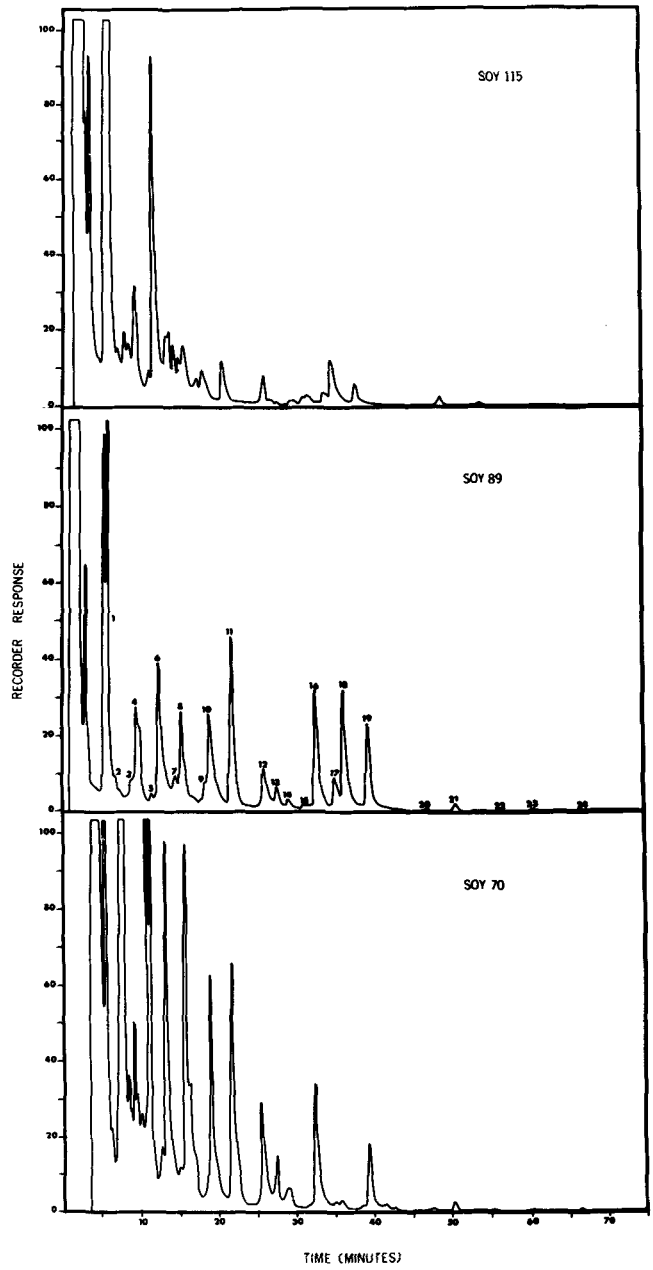

FIG. 2. Gas chromatogram of volatiles isolated from used soybean oil with an iodine value (IV) of 115 (top), IV 89 (center), and IV 70 (bottom).

Gas Chromatography of the Volatiles

By the column saturation technique (16), each of the six oils which have been deep fat fried simulatedly with moist cotton balls yielded a gas chromatogram which was qualitatively and quantitatively different from any other (Fig. 1 and 2). The gas chromatogram could, therefore, be used as the profile of the odor and flavor of the oil.

The profile chromatograms of volatiles from used cottonseed oil and its duplicate were remarkably similar, both qualitatively and quantitatively. This indicated that the procedures used in this investigation were reproducible.

The gas chromatograms of volatiles isolated from fresh cottonseed oil and fresh soybean oil IV 89 showed no peaks under the same conditions as used for the volatiles of used oils. This demonstrated that the peaks adopted for this investigation were those produced during the simulated deep fat frying and were not originally present in the fresh oils.

Correlation of Organoleptic Scores and Gas Chromatograms

An attempt to correlate total GC peak area with the organoleptic scores met with complete failure as expected. By directly sniffing the gas chromatograph's effluent, it was found that some large peaks had little or no odor and that some small peaks had strong, characteristic odors. Furthermore, some peaks had good, desirable odors and some others had objectionable, undesirable odors. Therefore, overall peak area was a composite value, reflecting little of the important organoleptic properties contributed by individual peaks.

Strong correlations between some peak areas (Table III) in the profile curves and the adjusted organoleptic scores were found. Stepwise regression analysis revealed that only two peaks had to be examined in a sample's profile curve in order to closely predict its score for a specific organoleptic

TABLE III

Peak Areas of the Profile Chromatograms Used for Stepwise Regression Analysis[a]

Peak area	Corn oil	Cottonseed oil	Peanut oil	Soy IV 115	Soy IV 89	Soy IV 70
1	22	114	96	153	95	126
2	2	1	19	18	3	32
3	1	1	8	23	7	47
4	1	10	14	34	29	54
5	1	1	5	8	4	19
6	5	65	46	62	29	69
7	8	14	15	17	14	65
8	4	3	14	37	15	23
9	1	2	2	14	10	39
10	2	10	5	10	23	9
11	2	8	21	8	33	45
12	0	0	0	0	12	33
13	3	3	1	5	5	9
14	0	3	1	1	5	10
15	0	2	3	2	3	2
16	0	3	13	6	24	26
17	2	8	11	4	11	3
18	6	53	43	10	20	3
19	3	15	9	3	19	11
20	0	1	0	0	0	1
21	1	1	1	1	2	2
22	0	0	0	0	0	0
23	0	0	0	0	1	0
24	0	0	0	0	0	1

[a]Values of "0" indicate that less than one integral unit was measured by the planimeter even though visually a small peak was indicated on the chromatogram. IV = iodine value.

TABLE IV

Summary of Stepwise Regression Analysis Used to Examine the Relationship between Peak Areas and Organoleptic Scores

	Correlated with peak numbers	R^2 1 Peak	R^2 2 Peaks
Strength of odor	4 and 11	0.7909	0.9158
Pleasantness of odor	8 and 4	0.9172	0.9882
Strength of flavor	3 and 1	0.9303	0.9679
Pleasantness of flavor	8 and 20	0.8778	0.9898

TABLE V

Equations Relating Gas Chromatography Peaks to Organoleptic Panel Scores

Strength of odor:		
$a = 3.92$	$b_4 = 0.092$	$b_{11} = -0.045$
$y = 3.92 + 0.092(x_4) - 0.045(x_{11})$		
Pleasantness of odor:		
$a = 5.71$	$b_4 = -0.021$	$b_8 = -0.055$
$y = 5.71 - 0.021(x_4) - 0.055(x_8)$		
Strength of flavor:		
$a = 3.89$	$b_1 = 0.0073$	$b_3 = 0.064$
$y = 3.89 + 0.0073(x_1) + 0.064(x_3)$		
Pleasantness of flavor:		
$a = 6.04$	$b_8 = -0.096$	$b_{20} = -0.803$
$y = 6.04 - 0.096(x_8) - 0.803(x_{20})$		

quality. The organoleptic qualities, correlated peaks, and the coefficient of determination (R^2) are shown in Table IV.

By placing estimates of the regression parameters, "a," "b_1," and "b_2," into the general formula:

$$y = a + b_1 (x_1) + b_2 (x_2)$$

the equations predicting the values of y from the GC curves alone could be calculated (Table V).

By using such equations, the values for the four organoleptic qualities of the different used oils were calculated (Table VI). These calculated values were all within six-tenths of one unit of the organoleptic scores. It must be mentioned, however, that limitations in the number of samples tested and limitations in the statistical design do not permit drawing conclusions of cause and effect such that the organoleptic properties of an unknown frying oil could be predicted with certainty from a gas chromatogram of the volatile components. Despite the observed good correlation, it is possible that the results could be accounted for by chance, because the number of samples and the number of possible combinations of data do not

TABLE VI

Calculated vs. Observed Organoleptic Scores[a]

	Observed Y	Calculated Y	Obs. - Calc.
Strength of odor:			
CO	3.78	3.92	-0.14
PNO	3.73	4.26	-0.53
CSO	5.08	4.48	+0.60
SBO 89	5.33	5.10	+0.23
SBO 115	6.53	6.69	-0.16
SBO 70	6.88	6.86	-0.02
Pleasantness of odor:			
CO	5.60	5.47	+0.13
CSO	5.30	5.33	-0.03
PNO	4.45	4.64	-0.19
SBO 89	4.35	4.27	+0.08
SBO 70	3.30	3.30	0.00
SBO 115	3.00	2.96	+0.04
Strength of flavor:			
CO	4.23	4.12	+0.11
PNO	4.63	5.10	-0.47
CSO	5.03	4.79	+0.24
SBO 89	5.08	5.03	+0.05
SBO 115	6.53	6.48	+0.05
SBO 70	7.88	7.83	+0.05
Pleasantness of flavor:			
CO	5.58	5.65	-0.07
CSO	4.96	4.95	-0.01
PNO	4.93	4.70	-0.23
SBO 89	4.48	4.60	-0.12
SBO 70	3.03	3.03	0.00
SBO 115	2.48	2.50	-0.02

[a]CO = corn oil, PNO = peanut oil, CSO = cottonseed oil, SBO = soybean oil; numbers following SBO are its iodine value.

eliminate random or chance correlation. Therefore, the observed correlation should be further confirmed with a larger number of samples.

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