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[Received June 19, 1984]

The Estimation of the Composition of Edible Oil Mixtures

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ABSTRACT

The fatty acid, sterol and tocopherol contents of edible oils were used to determine the composition of oil mixtures by means of a weighted least squares estimator with backwards elimination. The model was tested on 93 samples containing known amounts of sunflowerseed oil, groundnut oil, soybean oil, cottonseed oil, maize oil, olive oil and palm oil. Of these samples 75 were binary mixtures, seven were ternary mixtures, one contained seven oils and 10 were pure oils.

Satisfactory results were obtained with 79 of the 93 samples (85%). The differences between the actual and estimated concentrations of the main components were greater than 2.7 times the standard error for six samples; the mean of the absolute differences was 4.7% for all 93 samples. The use of this model is considered superior to the matching of a fatty acid composition, but the model still needs a lot of development.

INTRODUCTION

The identification of edible oils and fats has received a great deal of attention over the years. The Codex Alimentarius Committee on Fats and Oils of the Food and Agriculture Organization/World Health Organization (1) compiled a list of fatty acid ranges for 17 commercial fats and oils to be used for the authentication of these fats and oils. Computer programs (2,3) and a graphic procedure (4) using these values have been put forward for the identification of fats and oils. The ranges contained in this list are, however, so wide that several samples could be classified under more than one type of oil (2). The composition of the unsaponifiable fraction has been included in an effort to overcome the problem of insufficient information from the fatty acids (5-10). In using the results of an analysis for the identification of an oil, the authors considered the concentrations of the compounds in the sample separately or in pairs and a complete picture of the composition of the oil could be formed only subjectively.

Multivariate analysis affords a method of considering the various constituents of the oil simultaneously (11). This has been used *int. al.* to determine the origins of the constituents in blends of peppermint oils (12), the quantitative separation of species in fish mixtures (13) and the determination of the proportion of proteins in a mixture (14). Martens et al. (15) used multiple linear regression and factor analysis to estimate the proportion of three oils in margarine samples. The means from pure samples of coconut oil, soybean oil and hydrogenated marine oil, as well as three factors from the hydrogenated marine oil were used to estimate the composition of four margarine samples fairly accurately.

We approached the problem by analyzing authentic samples of five different oils produced in the Republic of South Africa. The study (16) included sunflowerseed oil (40 samples); soybean oil (40 samples); cottonseed oil (12 samples); groundnut oil (47 samples), and maize oil (45 samples). A limited number of locally produced and imported olive oil samples and imported palm oil samples also were analyzed. The fatty acid composition, sterol content and tocopherol content were determined. Using these results, we evaluated the applicability of a generalized least squares estimator and a weighted least squares estimator with backwards elimination for determining the composition of oil mixtures.

EXPERIMENTAL PROCEDURES

Apparatus and Materials

The gas chromatograph used for the fatty acid analyses was a Varian 3700 with a flame ionization detector and splitter inlet. A glass capillary column (40 m × 0.3 mm internal diameter) coated with XE60 was used isothermally at 220 C with helium as carrier gas at 1.6 ml/min. The split ratio was 1:50.

For sterol analysis, a Carlo Erba Fractovap series 4160 gas chromatograph was used with a splitter inlet and flame ionization detector. A glass capillary column (16 m × 0.3 mm internal diameter) coated with OV17 was used isothermally at 230 C with helium as carrier gas at 2.2 ml/min. The split ratio was 1:20.

The high performance liquid chromatograph consisted of a Varian 5000 pump, Valco inlet valve and a Perkin Elmer 650 fluorescence detector. The slit widths on the detector were both set at 5 nm. Two columns (100 × 2.8 mm), packed with 3 μm Nucleosil 100-3 (Machery-Nagel) were used in series.

Peak areas and retention times for the three chromatographic systems were determined with Hewlett-Packard 3390A reporting integrators. A Hewlett-Packard 9845

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microcomputer with 64K memory was used for data analysis.

Fatty acid standards were obtained from Nu Chek Prep., Inc., Elysian, Minnesota. Stigmasterol and β-sitoserol standards were obtained from Sigma Chemical Company, St. Louis, Missouri.

Methods

The fatty acid composition of the oils was determined by glass capillary gas chromatography. The fatty acid methyl esters were prepared by the method of van Wijngaarden (17), and the individual fatty acids were identified with the aid of standards and the log plot method (18).

The sterols were determined on the unsaponifiable fraction of the oils by glass capillary gas chromatography (16,19).

For the tocopherol determinations the oil was diluted two to five times with n-hexane, filtered through a membrane filter (Millipore HVLP 0.45 μm pore size) and 10 μl was used for liquid chromatography. The method, as previously described (20,21) was modified by using the equipment described in this paper and reducing the flow rate to 1 ml/min to suit the smaller column diameter.

Data Analysis

The linear regression model may be expressed in matrix form as (21):

$$Y = X\beta + \epsilon \qquad [1]$$

Y is a n × 1 vector of observable random variables, that is:

$$Y = \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_i \\ \vdots \\ y_n \end{bmatrix}$$

In our case Y represents the composition of an oil mixture in terms of the fatty acids, sterols and tocopherols present, assuming that n different compounds were determined. X is a n × p matrix containing the known composition of p oils, therefore:

$$X = \begin{bmatrix} x_{11} & x_{12} & \cdots & x_{1j} & \cdots & x_{1p} \\ x_{21} & x_{22} & & & & x_{2p} \\ \vdots & & & & & \vdots \\ x_{il} & & & x_{ij} & & x_{ip} \\ \vdots & & & & & \vdots \\ x_{nl} & \cdots & \cdots & \cdots & \cdots & x_{np} \end{bmatrix}$$

The x_{ij} are known constants, assumed to be measured with negligible error, and represent the expected or mean concentrations of compound i in pure oil No. j.

$$\beta = \begin{bmatrix} \beta_1 \\ \beta_2 \\ \vdots \\ \beta_j \\ \vdots \\ \beta_p \end{bmatrix}$$

The β_j are unknown parameters to be estimated and are the p concentration factors for the p different oils considered to be present in the mixture. In our application of the linear regression model no allowance is made for a constant term. ε is a vector of n unobservable variables, that is:

$$\epsilon = \begin{bmatrix} \epsilon_1 \\ \epsilon_2 \\ \vdots \\ \epsilon_i \\ \vdots \\ \epsilon_n \end{bmatrix}$$

The ϵ_i are the fluctuations or errors in the determination of the y_i. The ϵ_i are assumed to be uncorrelated. By applying the method of least squares (22), the β_j may be estimated from the equation

$$\hat{\beta} = (X'X)^{-1}\, X'Y \qquad [2]$$

The generalized least squares model (22) may be applied when the assumption that the ϵ_i are uncorrelated is not valid. This model assumes the distribution of the ϵ_i to be equal to $\sigma^2 V$ with σ^2 the variance and V a known n × n positive definite matrix. Because of this, there exists a n × n nonsingular matrix K such that $V = KK'$. If we set $Z = K^{-1} Y$, $B = K^{-1} X$ and $\eta = K^{-1} \epsilon$, then we have the model:

$$Z = B\beta + \eta \qquad [3]$$

The least squares estimate of β is:

$$\beta^* = (X'V^{-1}X)^{-1}\ X'\ V^{-1}Y \qquad [4]$$

When applying this model to estimate the composition of oil mixtures, V is taken as the variance-covariance matrix of the mixture. This is unknown and was estimated by a linear combination of the estimated covariances of the compounds for the pure oils expected to be present in the mixture. If σ_{ikj} is the covariance of compound i and compound k in the pure oil j then:

$$\sigma_{ik} = \sum_{j=1}^{p} \quad \beta_j^2 \quad \sigma_{ikj} \qquad [5]$$

where σ_{ik} is the covariance of compounds i and k in the mixture.

Initially all the β_j are set equal to 1/p under the assumption that the p oils are present in equal amounts and the estimated β_j^* subsequently are used in equation 5. A t-test is used to test whether the estimated β_j^* differ significantly from zero.

$$t_j = \frac{\beta_j^*}{SE_j} \text{ with n-p degrees of freedom} \qquad [6]$$

SE_j is the standard error of β_j^* and is determined from:

$$SE_j^2 = \frac{(Y-X\beta^*)'\ V^{-1}\ (Y-X\beta^*)\, a_{jj}}{n-p} \qquad [7]$$

a_{jj} is the element in the j^{th} row and j^{th} column of the matrix $(X'V^{-1}X)^{-1}$. Usually, when applying backwards elimination, the regressor with the smallest value for $|t|$ would be removed from the regression model provided $|t|$ is smaller than a given value t_{min}. In this case, however, a negative β_j^* does not have a physical meaning; therefore, the oil with the smallest value of t is removed first.

From equation 5 a new estimate for σ_{ik} is obtained for p-1 oil standards, and this is used to obtain β^*. The process of elimination and recalculation of the covariances and regression coefficients is repeated until only the regressors with t values larger than t_{min} remain or only a single regressor remains. The normalized concentration (C_j) of each oil j in the mixture may now be calculated from:

$$C_j = \frac{100\,\beta_j^*}{\sum_{j=1}^{v} \beta_j^*} \qquad [8]$$

TABLE I

Composition of Seven Different Types of Plant Oils Analyzed for 38 Compounds

	Sunflowerseed oil SF		Groundnut oil GN		Soybean oil SY		Cottonseed oil C		Maize oil M		Olive oil O		Palm oil P	
	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation
Fatty acid composition (g/100 g fatty acids)														
12:0	.002	.02	.002	.02	.002	.02	.002	.02	.002	.02	.002	.02	.312	.232
14:0	.068	.012	.002	.001	.071	.0169	.834	.237	.037	.0239	.002	.001	1.08	.18
15:0	.002	.0067	.002	.0067	.043	.0067	.03	.0121	.002	.0067	.002	.0067	.002	.0067
16:0	6.05	.353	11.20	.706	9.46	.676	23.02	1.65	12.2	1.02	12.11	1.96	43.7	3.56
16:1	.074	.0135	.011	.0178	.091	.0130	.551	.0377	.145	.0348	.969	.283	.144	.0745
17:0	.055	.0118	.065	.0092	.098	.0075	.086	.0027	.078	.011	.075	.0131	.097	.0056
17:1	.037	.0544	.01	.0166	.052	.0058	.086	.0065	.045	.0059	.127	.0251	.002	.0009
17:2	.002	.0008	.002	.0008	.043	.0084	.052	.0084	.002	.0008	.002	.0009	.002	.0008
a	.002	.004	.002	.004	.002	.004	.268	.041	.002	.004	.002	.004	.002	.004
18:0	5.60	.55	3.65	.77	4.86	.78	2.29	.319	2.33	.396	2.72	.660	4.46	.617
18:1	19.32	2.66	41.1	2.18	21.9	1.89	15.6	1.72	36.9	3.91	71.8	6.16	39.3	2.43
18:2	66.98	2.19	35.5	1.68	52.6	1.71	55.6	1.07	45.9	4.18	10.2	3.26	10.1	1.1
18:3	.078	.023	.0838	.032	7.94	.840	.318	.026	.909	.0964	.745	.194	.195	.131
b	.002	.004	.002	.004	.002	.004	.233	.045	.002	.004	.002	.004	.002	.004
20:0	.36	.03	1.62	.189	.46	.0748	.309	.0438	.565	.0608	.511	.330	.334	.136
20:1	.125	.013	1.07	.25	.188	.025	.051	.0383	.313	.0359	.268	.076	.186	.121
20:2	.002	.0009	.002	.0009	.002	.0009	.002	.0009	.002	.0009	.002	.0009	.002	.0009
22:0	.865	.065	3.32	.354	.497	.08	.169	.0266	.158	.0293	.03	.123	.002	.002
22:1	.002	.005	.123	.048	.002	.005	.002	.005	.002	.005	.002	.005	.002	.005
22:2	.127	.113	.002	.01	.002	.01	.213	.141	.002	.01	.002	.01	.002	.01
c	.002	.009	.002	.009	.002	.009	.002	.009	.002	.009	.473	.091	.002	.009
24:0	.253	.0276	1.38	.267	.156	.0499	.002	.003	.181	.0358	.002	.003	.002	.003
Sterol content (mg/kg oil)														
Cholesterol	0.5	.208	6.23	3.56	.5	.208	.5	.208	.5	.208	.5	.208	.5	.208
Brassicasterol	0.5	.061	0.5	.061	.5	.061	.5	.061	.5	.061	.5	.061	.5	.061
Campesterol	242	36.4	278	91.3	563	105	276	16.4	2655	539	18.8	8.04	88	22.6
Stigmasterol	236	36.3	145	42.5	564	82.9	17.3	4.61	499	123	.5	0.79	42	7.94
β-Sitosterol	1961	242	1145	326	1317	171	3348	190	9187	1579	732	279	252	51.5
Δ^5-Avenasterol	163	61.7	253	69.3	46.1	17.1	85.1	10.1	682	282	77.8	34	.5	34
Δ^7-Stigmastenol	298	84.1	0.5	2.34	92	51	.5	2.34	95.7	40.8	.5	2.34	51	23.4
Δ^7-Avenasterol	99.4	18.2	34.2	12.1	63.2	19.2	17.9	6.53	102	30.8	30	17.7	.5	1.21
24-Methylene-cycloartenol	204	43.7	0.5	2.3	53.0	23.1	0.5	2.31	425	181	580	166	.5	1.15
Tocopherol content (mg/100 g oil)														
α-Tocopherol	56.4	11.6	14.1	3.05	17.9	7.23	40.3	4.85	27.2	11.3	9.0	2.48	9.1	.445
α-Tocotrienol	.013	.012	.007	.0134	.021	.0198	.002	.001	5.37	1.64	.0078	.0134	5.19	1.35
β-Tocopherol	2.45	.375	.396	.107	2.80	1.34	.196	.0705	.214	.335	.16	.076	.153	.073
γ-Tocopherol	.43	.172	13.1	1.95	60.4	6.35	38.3	6.58	56.6	14.6	.471	.283	.84	.632
β-Tocotrienol	.207	.03	.394	.262	.437	.204	.87	.287	1.1	.656	.417	.183	.4	.266
γ-Tocotrienol	.023	.0086	.03	.0517	.078	.0228	.089	.0268	6.17	2.35	.026	.022	13.2	1.92
δ-Tocopherol	.087	.0336	.922	.153	37.1	11.6	.457	.172	2.52	1.16	.043	.01	.002	.01

[a,b] Cyclopropenoic acids.

[c] Unidentified fatty acid eluting between 22:2 and 24:0.

where v is the number of oils remaining in the regression equation.

The weighted least squares model does not take the covariances into account. The matrix V, therefore, is simplified to a diagonal matrix containing only the variances along its diagonal.

The weighted residuals, R, defined as:

$$R = K^{-1} Y - K^{-1} X \beta^{*} \qquad [9]$$

may be plotted against the fitted Y values or compound number (1 to n) as an aid in assessing the goodness of fit of the regression equation.

Computer programs, using extended Basic, were written for the application of these models, and listings may be obtained from the authors on request.

RESULTS AND DISCUSSION

The generalized least squares and weighted least squares models were evaluated by analyzing 30 binary mixtures containing sunflowerseed oil, groundnut oil, soybean oil and cottonseed oil (p = 4 before applying the backwards elimination). The mixtures were analyzed for 36 of the 38 compounds listed in Table I. (The results for 24-methylenecycloartenol and the fatty acid denoted by C were not used). The table also contains the mean values and standard deviations (16) of the compounds in the pure oils. For each compound the same unit of measurement was used for the mixtures and the pure oils. The standard deviations are an indication of both the sampling and analytical error. Some compounds are present in one oil but could not be detected in others and, therefore, are valuable in differentiating between oil types. For computing purposes the value zero could not be assigned where the compounds were absent, because it would implicate division by zero at certain stages in the program. It was, therefore, assumed that in these instances, where a compound could not be detected, the values were distributed normally around a mean equal to half the detection limit. The mean assigned to the missing fatty acids was 0.002%, for the sterols it was 0.5 mg/kg and for the tocopherols 0.002 mg/100g. The corresponding standard deviations were calculated from the range (23), and the covariances were assumed to be zero.

Because of the limited memory capacity of the computer, the program for the generalized least squares model had to be written in such a way that the covariance matrices were re-read from the tape each time they were used in the program. The run time for this program was, therefore, ca. 13 min, while the program for the weighted least squares took only 40 sec for each mixture.

For both models, t_{min} was set at 2 (probability ca. 0.05) and the results obtained with the 30 mixtures are summarized in Table II. The normalized standard error on a percentage base (S.E.) was approximated by:

$$\text{S.E.} = \frac{100\ \text{SE}_j}{\sum_{j=1}^{v} \beta_j^{*}} \qquad [10]$$

The S.E. contained in Table II was calculated for the major component (as estimated by the model) in the mixture.

With the weighted least squares model the differences between the estimated and actual concentrations of the main components in the mixtures were less than 2.7 times the S.E. for the 30 samples. The worst result was obtained for mixture 11 where the program failed to recognize the

TABLE II

The Actual and Estimated Composition of 30 Oil Mixtures Using the Weighted Least Squares and Generalized Least Squares Models and the Standard of Table I

	Actual composition %				Composition from weighted least squares %					Composition from generalized least squares %				
Mixture No.	SF	GN	SY	C	SF	GN	SY	C	S.E. %	SF	GN	SY	C	S.E. %
1	10		90		22		78		7.6			100		3.6
2	25		75		33		67		5.8	19		81		9.3
3	50		50		54		46		5.9	47		53		8.0
4	75		25		76		24		3.3	75		25		3.0
5	90		10		90		10		3.3	90		10		1.7
6	10			90	5			95	3.3				100	1.9
7	25			75	32			68	6.6			15	85	
8	50			50	53			47	5.1	39			61	4.7
9	75			25	72			28	5.1	74			26	3.3
10	90			10	91			9	4.6	92			8	1.4
11	10	90				100			44.7		100			
12	25	75			33	67			6.5	48	52			5.2
13	50	50			54	46			4.1	56	44			2.3
14	75	25			77	23			4.4	81	19			2.4
15	90	10			92	8			3.0	94	6			1.5
16			10	90			10	90	3.2			19	81	3.7
17			25	75			22	78	10.2				100	95
18			50	50			54	46	9.7			55	45	6.6
19			75	25			80	20	11.4			79	21	7.5
20			90	10			96	4	6.0			100		2.0
21		90	10			88	12		28	33	67			
22		75	25			62	38		11.7		55	45		6.7
23		50	50			50	50		8.2		46	54		4.0
24		25	75		18	56	25				26	74		3.9
25		10	90			39	61		16.6		21	79		5.2
26		90		10		75		25	10.4	25	64		11	
27		75		25		68		32	8.1	20	51		29	
28		50		50		45		55	5.2		100			25
29		25		75		28		72	3.4		34		66	7.2
30		10		90		13		87	3.5				100	12.5

SF = Sunflowerseed oil; GN = Groundnut oil; SY = Soybean oil, and C = cottonseed oil.

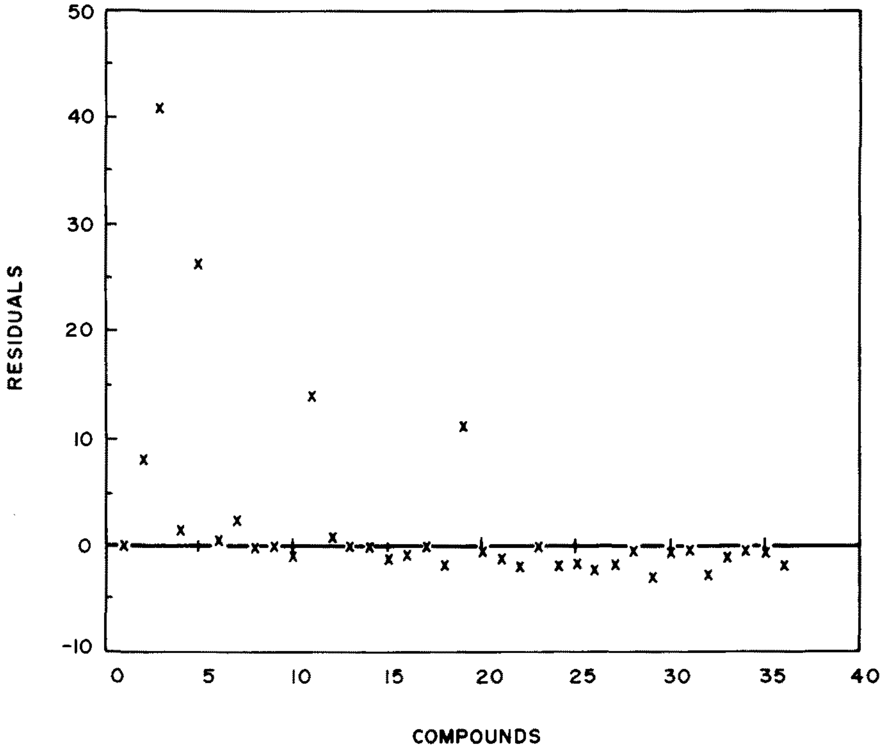

FIG. 1. Graph of the residuals plotted against the compound number for mixture 11. The compounds are plotted in the same order as they appear in Table I (with the exclusion of 24-methylene-cycloartenol and the fatty acid denoted by C).

presence of the sunflowerseed oil and gave a S.E. of 44.7%. With the generalized least squares model the differences between actual and estimated composition were more than 2.7 times the S.E. in six instances; in seven instances the correct components in the mixtures were not indicated. Because of this, all further effort was channeled toward improving the weighted least squares model.

The problems encountered with mixture No. 11 were further investigated by calculating the residuals (equation 9) after changing the values of β^* to 0.1 and 0.9 (the theoretical values for 10% sunflowerseed oil and 90% groundnut oil). The residuals were plotted against the compound number (Fig. 1), and from this it is clear that the residuals of compounds Nos. 2, 3, 5, 11 and 19 are exceptionally high. The actual concentrations of these compounds were 0.034%, 0.031%, 0.101%, 39.3% and 0.01%, respectively. The indications, therefore, are that the program tends to give too much weight to minor compounds.

In order to decrease the importance of compounds which occur at levels close to the detection limit, it was decided to assign larger values to the standard deviations of those compounds which were not detected in the standards. In a trial run we used the smallest standard deviation (for each compound) actually found for any of the seven oils. The standard deviation used for compound 19 in sunflowerseed oil, for instance, was changed from .001 to 0.048. Unfortunately, this change resulted in a greater number of mixtures being identified incorrectly, because too little weight was now given to the minor compounds. As a compromise, one-tenth of the smallest standard deviation was used for further work. Compound 3 presented a special problem in that it was found in sunflowerseed oil in seven out of the 40 samples at levels just above the detection limit. If a standard deviation of 0.0007 (one-tenth of the standard deviation of soybean oil) is used for sunflowerseed oil it would, therefore, give too much weight to this compound by not taking the larger variation into account. To overcome this problem a standard deviation of 0.0067 (equal to that of soybean oil) was used. The optimum values to be assigned to standard deviations of components that are absent in an oil should be determined by an optimization study in the future.

The number of oils used in mixtures was increased from four to seven by adding maize oil, olive oil and palm oil to the other standards ($p = 7$ before applying the backwards elimination). The number of compounds analyzed for also was increased, from 36 to 38. As we had analyzed only a limited number of olive oil and palm oil samples, we estimated the means and standard deviations for these two oils by incorporating results obtained from the literature (8,24,25).

An additional 53 oil mixtures and 10 pure oil samples (derived from various sources) were analyzed. The results were used, together with the 30 original mixtures, to evaluate the weighted least squares model with the extended and revised set of standards (Table I). The value used for t_{min} was increased from 2.0 to 2.7 (corresponding to a probability of ca. 0.01) because it was felt that it was better to err by excluding a minor component of a mixture than by including a component about which there is some doubt. The actual and estimated composition of the 93 samples are given in Table III.

In general, there was good agreement between the estimated and actual composition of the samples, and only 14 presented problems to a greater or lesser degree. The difference between the actual and estimated concentrations of the main components were greater than 2.7 times the S.E. for six samples (Nos. 12, 41, 42, 43, 44, 81) while the mean of the absolute differences was 4.7% for all 93 samples.

Sample 76 is probably the most interesting because it contains equal amounts of the seven different oils. The analytical results of this sample, together with the fatty acid ranges for cottonseed oil(1), are given in Table IV. On the basis of the fatty acids alone it could be concluded that this

TABLE III

The Actual and Estimated Composition of 93 Oil Mixtures using the Weighted Least Squares Model and the Standards of Table I

Mixture No.	Actual composition of mixture %							Estimated composition of mixture by weighted least squares %							
	SF	GN	SY	C	M	O	P	SF	GN	SY	C	M	O	P	S.E. %
1	10		90					0		100					4.7
2	25		75					30		70					6.4
3	50		50					54		46					5.9
4	75		25					78		22					2.9
5	90		10					91		9					3.2
6	10			90				6			94				3.3
7	25			75				30			70				6.4
8	50			50				53			47				4.9
9	75			25				72			28				4.9
10	90			10				91			9				4.1
11	10	90						19	81						6.4
12	25	75						37	63						3.6
13	50	50						55	45						3.6
14	75	25						77	23						3.7
15	90	10						93	7						2.8
16			10	90						10	90				3.2
17			25	75							100				22.6
18			50	50						54	46				9.5
19			75	25						100					10.5
20			90	10						100					5.9
21		90	10						90	10					4.1
22		75	25						79	21					4.5
23		50	50						58	42					4.7
24		25	75						27	73					3.9
25		10	90						6	94					3.7
26		90		10					96		4				4.4
27		75		25					77		23				4.1
28		50		50					49		51				4.1
29		25		75					28		72				3.1
30		10		90					12		88				3.4
31	10				90			14				86			5.9
32	40				60			40				60			3.7
33	90				10			88				12			3.5
34			10		90					7		93			3.1
35			50		50					46		54			3.8
36			90		10					92		8			2.8
37		10			90				5			95			5.2
38		40			60				40			60			5.0
39		90			10				91			9			3.5
40				10	90							100			6.9
41				50	50						36	64			4.8
42				90	10						100				3.4
43					90	10						82	18		2.6
44					60	40						52	48		1.8
45					10	90						7	93		5.1
46					90		10					87		13	3.4
47					50		50					47		53	6.1
48					10		90					18		82	13.4
49	10					90		16					84		17.3
50	40					60		22					78		10.2
51	90					10		91					9		3.3
52			10			90				6			94		6.1
53			50			50				43			57		8.9
54			90			10				87			13		3.3
55		10				90			12				88		4.4
56		40				60			33				67		3.9
57		90				10			87				13		3.3
58				10		90			4		7		89		8.2
59				50		50					39		61		8.2
60				90		10					85		15		2.8
61						90	10					94	6		7.1
62						60	40					71	29		6.8
63						10	90					20	80		10.3
64	10						90	9						91	8.4
65	60						40	55						45	4.0
66	90						10	88						12	5.2
67			10				90			17				83	11.0
68			50				50			44				56	5.9
69			90				10			92				8	5.6
70		10					90		10					90	12.2
71		50					50		50					50	5.1
72		90					10		90					10	4.6
73				10			90							100	38.9
74				60			40				55			45	2.2
75				90			10				100				11.1

TABLE III (continued)

Mixture No.	Actual composition of mixture % SF	GN	SY	C	M	O	P	Estimated composition of mixture by weighted least squares % SF	GN	SY	C	M	O	P	S.E. %
76	14	14	14	14	14	14	14	24	12	14		10	17	22	4.8
77	40		20		40			31		15		54			6.2
78	50	10			40			46	6			48			3.4
79	10	40		50					46		54				4.4
80		40		50	10				48		52				4.4
81	10	20	70						17	83					4.7
82	20	10				70		8	15				77		6.8
83	20		10			70		24		7			69		5.7
84	100							100							3.8
85	100							100							2.9
86					100							100			1.3
87					100							100			1.9
88				100							100				0.8
89		100							100						2.4
90						100							100		3.4
91							100							100	0.7
92			100							100					1.5
93	100							100							10.7

TABLE IV

The Analytical Results for Mixture 76 and the Ranges for Cottonseed Oil

	Mixture 76	Ranges for cottonseed oil[d]
Fatty acid composition (g/100 g fatty acids)		
12:0	.002	0 - 0.1
14:0	.378	0.5 - 2.0
15:0	.002	
16:0	18.8	17 - 29
16:1	.328	0.5 - 1.5
17:0	.083	
17:1	.060	
17:2	.002	
a	.003	
18:0	3.52	1.0 - 4.0
18:1	37.2	13 - 44
18:2	36.5	33 - 58
18:3	1.33	0.1 - 2.1
b	.004	
20:0	.576	0 - 0.5
20:1	.293	0 - 0.5
20:2	.002	
22:0	.618	0 - 0.5
22:1	.002	0 - 0.5
22:2	.002	
c	.004	
24:0	.257	0 - 0.5
Sterol content (mg/kg oil)		
Cholesterol	0.5	< 1
Brassicasterol	0.5	< 1
Campesterol	405	252 - 311
Stigmasterol	170	12 - 29
β-Sitosterol	1817	2903 - 3529
Δ^5-Avenasterol	146	71 - 100
Δ^7-Stigmastenol	38	< 1
Δ^7-Avenasterol	24	6 - 26
24-Methylene-cycloartenol	236	< 1
Tocopherol content (mg/100 g oil)		
α-Tocopherol	23.9	32.7 - 48.4
α-Tocotrienol	.06	< .004
β-Tocopherol	1.2	.11 - .32
γ-Tocopherol	23.8	25.2 - 50
β-Tocotrienol	.37	.5 - 1.26
γ-Tocotrienol	.82	.03 - .13
δ-Tocopherol	5.4	.25 - .89

[a,b] Cyclopropenoic acids.

[c] Unidentified fatty acid eluting between 22:2 and 24:0.

[d] Fatty acid ranges were obtained from reference (1) and sterol and tocopherol ranges obtained from reference (16).

is an authentic sample of cottonseed oil. Only when examining the sterol and tocopherol composition is it clear that this is not the case. The computer succeeded in identifying six of the seven oils but, curiously, failed to indicate the presence of cottonseed oil. We doubt, however, whether manual inspection would have suggested the presence of seven oils.

With three of the ternary mixtures (Nos. 79, 80, 81) the program did not indicate the presence of the minor component (10% of the mixture). The same problem was experienced with three of the binary mixtures (Nos. 1, 20, 42). With mixtures Nos. 17 and 19 a more serious problem was encountered in that the presence of 25% of an extraneous oil could not be detected.

The most serious problem (to our minds) which we met with is the indication of the presence of 4% of groundnut oil (which we did not add) in mixture No. 58. Fortunately, this type of problem did not show up with the 10 samples of pure oils that were included in the study.

In general it can be said that we obtained satisfactory results with 79 of the 93 samples used (85%). If the results of the 14 problematic samples were used in practice, the consequences of the incorrect estimates probably would not be serious except, perhaps, in the case of sample No. 58. We believe that the use of this model is superior to the matching of a fatty acid composition to specified ranges. At the same time, we realize that a considerable amount of effort should still be directed towards the development of an efficient model. Improvements which should be considered, for instance, are constraining the linear regression coefficients so that $\Sigma\beta^*_i = 1$(26), and the use of factor analysis (15). We also should work toward extending the range of the oil standards and improving the reliability of the estimates of the means and standard deviations of these standards.

ACKNOWLEDGMENTS

S.C.C. Smit, A. Fourie and A. Senekal provided assistance, and W.H. van der Walt and Dr. L.M. du Plessis provided advice.

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[Received May 29, 1984]

Factors Affecting Peanut Butter Preference

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ABSTRACT

A sensory evaluation test with 320 subjects provided information pertinent to the preference of peanut butters. Results of paired preference test indicated that more than half the subjects (59%) preferred the "old fashioned" sample; flavor (aroma and taste) would have to be the primary reason since particle size was nearly the same in the prepared test samples. Chi-square tests of independence showed that the preference for the "old fashioned" sample was dependent on age ($P<.05$) and sensory attributes of flavor and textural perception ($P<.05$). Results of the survey showed that 47% of the total responding subjects listed "crunchy" peanut butter as their favorite type. Selection of one's favorite brand of commercial peanut butter was found to be based primarily on its particle size.

INTRODUCTION

Peanut butter is by far the most important product made from peanuts in the United States (1) with the per capita consumption increasing from 1.1 kg in 1950 (2) to 3.8 kg in 1976 (3). Peanut butter, a good protein supplement (25-28% protein), is popular in the U.S. because it has a unique, pleasing and well accepted flavor. It is particularly popular among children.

The product standard of identity requires a minimum of 90% shelled, ground, roasted peanuts, with the remainder consisting of optional ingredients such as salt, sweeteners and emulsifiers (4). "Old fashioned" peanut butters consist solely of ground peanuts, while the "commercial type" peanut butters use salt, sweeteners (such as dextrose and sucrose) and emulsifiers or stabilizers to improve taste and counteract bitterness, as well as to retard oil separation to enhance spreadability. Chemical preservatives, artificial sweeteners and flavors, vitamins, and colorants are not permissible. Peanut butter is classified into three texture types based upon the particle size of the ground peanuts. Smooth peanut butter lacks perceptible peanut particles, while the chunky or crunchy types contain particles greater than 1.59 mm. Medium or creamy peanut butters have intermediate particle size.

Using laboratory profile panel data, Syarief (5) found flavor-by-mouth character notes such as roasted peanut, over-roast, under-roast, sweetness and saltiness were important in sensory perception. Texture notes found significant included adhesiveness, smoothness, perception of particles and initial oiliness.

Although peanut butter is a major item of commerce with more than 97 firms engaged in its production and sale (6), surveys which determined characteristics that affect consumers' product selection and preference have been of a proprietary nature and consequently have not been published. It is apparent that age, sex and race affect the selection and preference for commercial food products (7, 8). Other factors such as rural/urban lifestyles and product formulation also may be important. It is the objective of this study to learn more about these factors with regard to consumers' preference and selection of peanut butters in North Carolina.

MATERIALS AND METHODS

Peanut Butter Preparation

Both "old fashioned" and "commercial" peanut butters were prepared from vacuum packed dry-roasted runner peanuts (Seabrook Blanching Corp.) as outlined by Woodroof (2), who also presented a review on processing parameters and early industrial processes. "Old fashioned" peanut butter was prepared by grinding whole peanut kernels using a fine mill in a Model "B" Olde Tyme peanut butter grinder (East Longmeadow, Massachusetts). The peanut butter corresponded to a medium or creamy texture type in particle size (ca. 1.59 mm) and was presented on the same day to the subjects for evaluation. A "commercial" peanut butter was prepared by grinding whole peanut kernels in a Morehouse Industries 504X stone mill (Fullerton, California). Additives (1% salt, 1.5% dextrose, 1.5% sucrose and 1.5% emulsifier) were added and mixed. The mixture was then reground to the same particle size (ca. 1.59 mm) as the "old fashioned" peanut butter, cooled and de-aerated using a Groen jacketed kettle (Model TDC/2). As with the "old fashioned" peanut butter, the "commercial" product was freshly prepared. Uncoded samples were presented to the subjects for sensory evaluation.

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