Flavor Score Correlation with Pentanal and Hexanal Contents of Vegetable Oil[1]

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ABSTRACT

Samples of commercially processed soybean, cottonseed, and peanut oils were stored under controlled conditions then evaluated for flavor by a 20-member trained, experienced oil panel and for pentanal and hexanal contents by direct gas chromatography. The oils, which contained citric acid and/or antioxidants, were either aged from 0 to 16 days at 60 C or exposed to fluorescent light for 0 to 16 hr. The simple linear regressions of flavor score with the logarithm of pentanal or hexanal content in aged soybean oil gave correlation coefficients of -0.96 and -0.90, respectively; for cottonseed oil, -0.60 and -0.85; and for peanut oil -0.74 and -0.75. Addition of peroxide values to the linear regressions increased the correlation coefficients. Flavor scores of cottonseed and peanut oil can be predicted from pentanal and hexanal contents, but the technique is slightly more reliable for soybean oil based on the treatments used for these oils.

INTRODUCTION

Processed vegetable oils are usually evaluated for the development of off-flavors by trained taste panels, but there is a definite need for objective instrumental methods to measure flavor quality. Much of the research on objective instrumental tests has been focused on gas chromatography (GC) to provide indications of food quality and/or shelf life stability. Methods of headspace and direct analysis by GC both with and without prior enrichment have been developed by Evans et al. (1), Selke et al. (2), Nawar and Fagerson (3), Hoffmann (4), and Dupuy et al. (5-7).

For GC methods to be used, one or more volatile compounds must be selected as indicators to monitor quality and/or stability. The identification of volatile components of a food, the mechanisms for their formation, and/or their characteristic odors and flavors comprise the information needed before GC analysis can be considered reliable and useful for correlation studies. Yasuda et al. (8) have identified 48 volatile components in hydrogenated soybean oil. De Buyn and Schogt (9) reported that in oils, the flavor carriers formed from the odorless and tasteless hydroperoxides are mainly aldehydes. Selke et al. (10) analyzed volatile components from tristearin heated in air and found that the quantities of aldehydes and ketones were present in excess of their taste threshold concentrations. Possible mechanisms for autoxidative rancidity of oils have been proposed by Loury (11). Buttery (12) has studied the formation of carbonyls and hydrocarbons during the autoxidation of potato granules. Smouse and Chang (13) identified 71 volatile flavor compounds in reverted soybean oil. Hoffmann (4) reported that 3-*cis*-hexenal caused the "green bean" flavor in soybean oil. Evans et al. (14) found that the addition of 2-pentyl furan to bland oil produced buttery, rancid, and grassy flavors. Work at this laboratory has shown that hexenal produces grassy flavor responses when added to oil (unpublished data).

Based on the identification of volatiles in food products, researchers are able to choose certain individual or groups of compounds that can be monitored for product quality. Pentane has been chosen by several researchers such as Scholz and Ptak (15), Evans et al. (16), Warner et al. (17), and Fioriti et al. (18) for correlation with flavor scores in vegetable oils. Correlation studies have been reported by Jarvi et al. (19) and Blumenthal et al. (20) using the entire GC profile. Jarvi monitored rancidity of oils while Blumenthal correlated peak area with strength and pleasantness of odors.

Most methods of GC analysis such as solvent extraction and distillation and headspace analysis are time-consuming and complex operations. The direct GC method developed by Dupuy et al. (6) for examining volatiles in oils is a simplified procedure requiring no prior enrichment of the volatiles. The oil is injected directly into the heated inlet of the GC through a liner tube packed with glass wool. Dupuy et al. (7) also found that this technique was sensitive to about 10 parts per billion (ppb) of pentane, pentanal, heptanal, 2-pentyl furan, and nonanal when these were added to good quality oil. This study was undertaken to determine the degree of correlation of flavor scores with volatiles in vegetable oils to learn if flavor characteristics can be reliably assessed by this technique.

Pentanal and hexanal were chosen as the two volatiles which would be monitored in this study because, in regression plots with flavor scores, these two aldehydes produced high correlation coefficients.

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TABLE I

Composition of Oils

Oil[b]	Calculated iodine value	Fatty acid (%) (GC)[a]				
		Pal	St	Ol	Lo	Ln
CSO	114.5	20.6	2.3	17.9	57.2	tr
PO	103.9	13.9	3.5	40.4	36.6	2.2
SBO I	133.4	10.7	3.4	25.2	53.2	7.5
SBO II	132.7	10.4	4.1	25.2	53.1	7.3

[a]GC = gas chromatography; Pal = palmitic; St = stearic; Ol = oleic; Lo = linoleic; Ln = linolenic.

[b]Oil: CSO (cottonseed), PO (peanut), SBO (soybean).

EXPERIMENTAL PROCEDURES

Materials

Evaluations were made on four lots of commercially processed vegetable oil: 2 soybean (SBO); 1 peanut (PO); and 1 cottonseed (CSO). Each lot consisted of one 5-gal can. The fatty acid composition of each oil is shown in Table I. Fatty acid analyses were determined by gas liquid chromatography on a 10% DEGS column (6 ft x 1/4 in.) at 190 C after transesterification with methanol and a sodium methoxide catalyst (21). Both the CSO and PO were purchased as salad oils and redeodorized at the Northern Regional Research Center (NRRC) with addition of citric acid and/or an antioxidant mixture containing BHA, BHT, citric

TABLE II

Soybean Oil I: Effect of Storage on Flavor Scores and Volatiles Content

Additive	Storage days at 60 C	GC integrator counts		Flavor scores
		Pentanal	Hexanal	
None	0	1370	1620	7.9 (0.0)[a]
	2	1440	3680	7.1 (0.3)
	4	3610	5190	6.6 (1.2)
	8	10,290	25,550	5.4 (7.2)
	12	34,160	51,620	3.9 (15.6)
	16	48,210	108,670	3.1 (24.5)
0.01% Citric acid 0.02% TBHQ[b]	0	960	1430	7.5 (0.0)
	2	1070	3950	7.4 (0.2)
	4	11,340	66,460	5.6 (1.1)
	8	10,590	43,880	5.8 (1.8)
	12	15,500	64,560	5.3 (2.4)
	16	11,260	42,190	4.6 (3.0)

[a]Numbers in parentheses are peroxide values at time of tasting.
[b]TBHQ = tertiary butyl hydroquinone.

TABLE III

Correlation Coefficients of Flavor Scores and GC Integrator Counts for Volatiles

Oil	Correlation coefficient	
	Pentanal	Hexanal
Soybean Oil I	-0.99**[a]	-0.99**
SBO I + 0.01% citric acid 0.02% TBHQ	-0.94*[b]	-0.90*
All SBO samples	-0.96*	-0.90*
Cottonseed Oil	-0.71 NS[c]	-0.93 NS
CSO + 0.01% citric acid	-0.49 NS	-0.95*
CSO + 0.076% Tenox 6	-0.75 NS	-0.97*
CSO + 0.01% citric acid 0.076% Tenox 6	-0.36 NS	-0.71 NS
All CSO samples	-0.60*	-0.85**
Peanut Oil	-0.96*	-0.97*
PO + 0.01% citric acid	-0.06 NS	-0.02 NS
PO + 0.076 % Tenox 6	-0.70 NS	-0.89 NS
PO + 0.01% citric acid 0.076% Tenox 6	-0.96*	-0.89 NS
All PO samples	-0.74**	-0.75**

[a]** Statistically significant at the 99% confidence level.
[b]* Statistically significant at the 95% confidence level.
[c]NS, not significant.

acid, and propyl gallate (Tenox 6). The SBO I was purchased as an undeodorized oil and deodorized at NRRC with addition of citric acid and/or tertiary butyl hydroquinone (TBHQ). These oils were steam vacuum deodorized for 3 hr at 210 C in all-glass laboratory equipment. Citric acid and antioxidants were added on the cooling side of deodorization. Oils were blanketed with nitrogen and stored at 0 C until test conditions were begun. The SBO II was purchased as a deodorized salad oil containing citric acid and used without further processing.

Methods

Oils were stored under various controlled conditions prior to flavor and GC evaluations in order to produce different quality oils. Samples were poured from the original containers into 8-oz clear glass bottles (2/3 full). The bottles containing the CSO, PO, and SBO I for the accelerated storage tests were loosely stoppered with cellophane-covered corks and stored in the dark in a forced-draft oven at 60 C for selected time periods as described by Evans et al. (21). For the fluorescent light exposure test, CSO, PO, and SBO II were packaged in 8-oz clear glass bottles with either air or nitrogen in the headspace. The bottles with air in the headspace were loosely stoppered with cellophane-covered corks. Samples containing nitrogen in the headspace were prepared by degassing the oils under vacuum and passing them through three freeze-thaw cycles to ensure complete removal of dissolved ozygen. The headspace was blanketed with nitrogen, and the opening of the bottle was then sealed off with a gas flame. The bottled oil was exposed to fluorescent light for 0 to 16 hr as described by Moser et al. (22). Immediately after storage or light exposure, the oils were evaluated for flavor by the 20-member trained, experienced oil panel using a scale of 10 to 1, with 10 as very good (bland) and 1 as very bad (strong). The evaluation procedures have been previously described by Moser et al. (23). Flavor descriptions were summarized by calculating the flavor intensity values with 1 being weak intensity; 2, moderate; and 3 as strong intensity (24).

Since GC analyses on the oils could not be done immediately after flavor evaluation, a sample from each treatment was packaged in a small glass vial and blanketed with nitrogen. The direct GC procedure developed by Dupuy et al. (7) was used for the rapid elution and resolution of volatiles in the oils. Only pentanal and hexanal contents were used for calculation of correlation coefficients.

Statistical evaluation of the data included simple correlation coefficients which were obtained from linear regression plots of flavor score against the log of integrator counts for the oil components identified by mass spectrometry as pentanal and hexanal (7). Multiple correlation coefficients were also calculated from plots of actual flavor scores against flavor scores predicted by pentanal and hexanal integrator counts (25).

RESULTS AND DISCUSSION

Soybean oil (SBO I) was aged at 0, 8, and 16 days at 60 C. The SBO I with no additives (Table II) was initially scored 7.9 on a scale of 10 to 1, and hexanal and pentanal appeared as relatively small peaks on the chromatogram. As the number of storage days increased, the recorder response increased significantly in the amounts of pentanal and hexanal produced. These data confirm similar results reported by Dupuy et al. (6) using this direct GC method. Correlation coefficients calculated from the flavor scores and pentanal and hexanal contents of SBO I are shown in Table III. The correlation coefficient was -0.99 for each of the two peaks in the SBO I with no additives. When citric acid and TBHQ were added to the oil, peroxide formation was inhibited, the development of aldehydes was altered, and the range of flavor scores was decreased. Correlation coefficients were reduced to -0.96 and -0.90 for pentanal and hexanal. These are significant at the 95% confidence level.

TABLE IV

Cottonseed Oil: Effect of Storage on Flavor Scores and Volatiles Content

Additive	Storage days at 60 C	GC integrator counts		Flavor scores
		Pentanal	Hexanal	
None	0	3360	6650	7.7 (0.5)
	2	3860	32,400	5.5 (1.2)
	4	6040	41,620	5.7 ((4.6)
	8	55,500	329,030	4.7 (8.8)
0.01% Citric acid	0	7080	6610	7.7 (0.7)
	2	8160	24,100	6.2 (1.0)
	4	4690	16,620	6.5 (4.9)
	8	17,900	59,950	5.9 (16.7)
0.076% Tenox 6	0	1200	4480	7.1 (1.0)
	2	4040	6860	6.8 (1.1)
	4	12,080	18,040	6.5 (2.6)
	8	12,000	62,840	5.3 (4.5)
0.01% Citric acid and 0.076% Tenox 6	0	1440	2010	6.7 (1.0)
	2	5450	5910	6.9 (1.5)
	4	4850	16,600	6.0 (2.3)
	8	12,510	28,810	6.3 (4.4)

TABLE V

Peanut Oil: Effect of Storage on Flavor Scores and Volatiles Content

Additive	Storage days at 60 C	GC integrator counts		Flavor scores
		Pentanal	Hexanal	
None	0	720	5560	7.8 (0.1)
	2	9620	26,390	6.3 (4.2)
	4	10,300	42,300	5.4 (9.3)
	8	44,340	201,940	4.8 (9.5)
0.01% Citric acid	0	1130	6930	6.0 (0.3)
	2	2600	13,580	5.8 (0.8)
	4	4350	22,670	5.7 (4.5)
	8	5880	30,840	6.1 (12.9)
0.076% Tenox 6	0	1940	11,850	7.5 (0.0)
	2	2500	17,000	6.6 (0.6)
	4	4770	18,990	6.9 (1.5)
	8	5250	20,650	6.2 (2.8)
0.01% Citric acid and 0.076% Tenox 6	0	1440	8480	7.2 (0.0)
	2	2200	9140	6.8 (1.1)
	4	4870	21,890	5.4 (1.4)
	8	3120	17,760	6.5 (2.7)

TABLE VI

Multiple Correlation Coefficients for Predicting Flavor Scores[a]

	SBO I	CSO	PO
Pentanal and peroxide value (PV)	0.98**	0.77 NS	0.76 NS
Hexanal and peroxide value	0.98**	0.96**	0.77 NS

[a]Model used:

$$\text{Flavor Score} = b_0 + b_1X_1 + b_2PV + b_3X_1^2 + b_4X_1PV + b_5(PV)^2$$

X_1 = log pentanal or log hexanal.

TABLE VII

Correlations within Oil Type Ignoring Additive

	Hexanal	Flavor score	Peroxide value (PV)
Pentanal	0.941**	-0.808**	0.704[a]
Hexanal		-0.837**	0.682**
Flavor Score (FS)			-0.644**

[a]Significant variation between oils in value of r:

SBO I	Pentanal vs. PV	r = -0.96
Cottonseed	Pentanal vs. PV	r = -0.60
Peanut	Pentanal vs. PV	r = -0.74.

It appears that either pentanal or hexanal could be used as indicators of oil quality in SBO, with or without additives.

Correlation coefficients were also calculated for CSO and PO and are presented in Table III. Results of the evaluations of these oils are presented in Tables IV and V. The pentanal content of CSO does not correlate with flavor score. Increases in aldehyde contents were not associated with proportional decreases in flavor scores. Hexanal proved to be a good indicator of quality in CSO containing either citric acid or Tenox 6. Both of the correlation coefficients for these sets of data were significant at the 95% confidence level. The addition of a combination of citric acid and Tenox 6 decreased the amount of hexanal produced and reduced the range of scores for the four samples to 0.9. This resulted in low correlation coefficients which were not statistically significant.

Peanut oil produced the least amount of either pentanal or hexanal in the three oils tested. High correlation coefficients were obtained in PO that had no additives as was the result with SBO I. Peanut oil with citric acid had a low correlation of flavor score against aldehyde content because the range of scores was only 0.4, whereas there was a fivefold increase in amounts of pentanal and hexanal.

The regression lines for the relation between log hexanal (H) contents and log pentanal (P) contents were calculated

TABLE VIII

Correlations between Storage Periods within Additive Group for Ten Oil-Additive Combinations

	Hexanal	Flavor score	Peroxide value (PV)
Pentanal	0.965**	-0.898**	0.886**
Hexanal		-0.936**	0.899**
Flavor Score			-0.883**

by the following equations:

$$\text{SBO } \log H = + 0.01608 + 1.1032 \log P$$
$$\text{CSO } \log H = -0.13058 + 1.1514 \log P$$
$$\text{PO } \log H = + 1.29741 + 0.8319 \log P$$

The regression was linear with no significant curvature. The lines were parallel, but the intercepts varied significantly. The SBO and CSO have hexanal values in a 1:1 ratio with pentanal while the PO shows a 1:10 relationship.

Additional multiple regression correlation coefficients were calculated using peroxide values and either the log of pentanal or hexanal contents so as to predict flavor scores. These data are shown in Table VI. The use of peroxide values reaffirmed the results outlined in Table III. The flavor score can be predicted more precisely for SBO I than for either CSO or PO.

The model equation for predicting flavor score given the log pentanal or hexanal and peroxide value is in Table VI also. The equation can be adapted to other data by calculating constants for b_0 through b_5 and adding observed peroxide values and log pentanal and log hexanal.

Other correlations were calculated, and the results are in Tables VII and VIII. The data in Table VII show significant correlations within oil type, with additives ignored. Pentanal and peroxide values correlated better with SBO I than for PO or CSO. Table VIII shows correlations within each additive type. The data indicate that there were no significant differences between the additives types. The correlation coefficients calculated from hexanal, pentanal, and peroxide value to predict flavor scores are independent of the type of additive used.

Shown in Figure 1 is a plot of actual flavor scores against the flavor scores predicted by pentanal/hexanal multiple regression for PO, CSO, and SBO I. The multiple regression coefficients were all significant at the 99% confidence level. The high correlation coefficient for SBO I indicates that flavor scores can be reliably predicted from the pentanal/hexanal integrator counts. Multiple correlation using pentanal and hexanal together did not significantly improve results over simple regression.

A plot of actual flavor scores against scores predicted by pentanal/hexanal multiple regression for light-exposed SBO II is shown in Figure 2. A highly significant multiple regression correlation coefficient of 0.95 was calculated. Simple correlation coefficients of 0.86 and 0.90 were calculated for pentanal and hexanal, respectively. Samples of light-exposed PO and CSO were also tested, but low correlation coefficients between scores and integrator counts of the two aldehydes were calculated.

Descriptions which the panel members gave for each sample were also analyzed. Flavor descrptions such as grassy, fruity, and light-struck were common to the oils which had the longest periods of fluorescent light exposure. The flavor intensity value (FIV) for grassy increased from 0.2 in fresh SBO II to 1.4 after 8 hr of light exposure for the oil. The sample of PO was least affected by the light exposure. The FIV for grassy was 0.4 in the fresh sample and 0.5 in the one exposed to light for 8 hr.

The direct GC technique developed by Dupuy et al. (6)

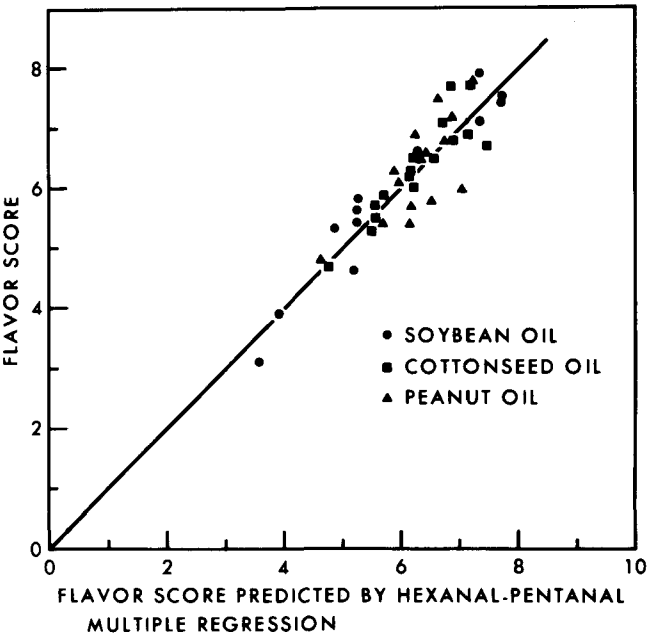

FIG. 1. Correlations of actual and calculated flavor scores for aged vegetable oils.

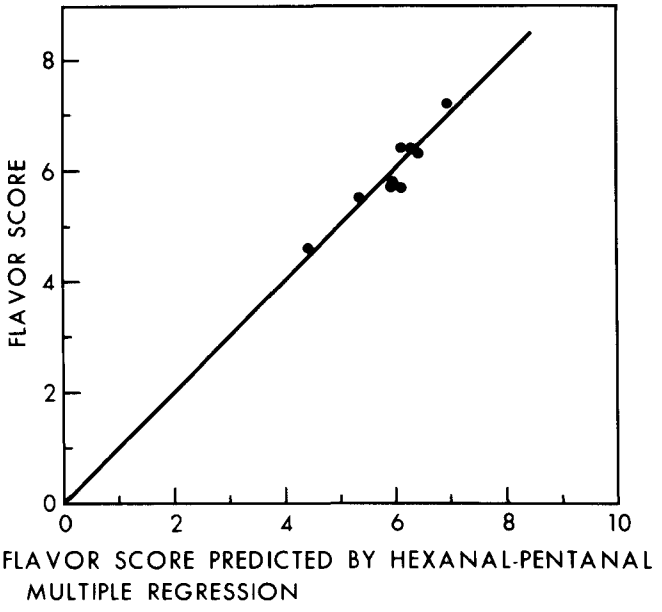

FIG. 2. Correlation of actual and calculated flavor scores for light-exposed SBO II packaged under either air or nitrogen.

for the examination of pentanal and hexanal in oils appears to be a highly reliable method for the objective flavor evaluation of either aged or light-exposed SBO. The method could also provide valuable information on aged PO and CSO by monitoring the hexanal content of the oils.

Further research has recently been conducted by Dupuy et al. (7) and Williams and Wille (26) to measure total volatiles in oils. Dupuy's determinations of correlation coefficients for experimental soybean oil indicate that the total volatiles analysis correlates no better than analyses based on hexanal or pentanal. His correlation coefficients for these two peaks in SBO (7) were much lower (-0.71 and -0.72) than those we are reporting (-0.96 and -0.90). This emphasizes the point that objective-subjective correlations should be established between each taste panel and each instrumental method.

It has been demonstrated that instrumentation can be

effectively utilized in the field of flavor analyses. Much research remains, however, to apply and refine these objective techniques for use with different commodities. Close cooperative efforts between GC analysts and flavor panels should provide the basis for progress in this area.

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