Correlation of the Flavor Scores of Vegetable Oils with Volatile Profile Data[1]

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ABSTRACT AND SUMMARY

One of the most important quality parameters to users of commercial vegetable oils is the flavor. For years, taste panels have been used to rate the overall quality of oils in terms of flavor scores. However, flavor scores are subjective, vary considerably among individuals and laboratories, and are not really diagnostic. The need for more adequate quality evaluation of oils has focused attention on chemical changes and sensitive instrumental methods which can be used to differentiate the stage of freshness or deterioration. Dupuy's direct gas chromatographic method for the examination of the volatile profile of vegetable oils has been applied to 23 fresh soybean oils, and the same 23 oils aged 5 wk in the light at 22 C. High correlation between the volatile profile data and the flavor scores was found. The most significant peaks which were positively correlated with flavor score and those which were negatively correlated were obtained, and a prediction equation of flavor score was calculated from the volatile profile data.

INTRODUCTION

Commercial refiners and users of edible oils are constantly concerned with the quality of the oil that they refine and use in their products. Recently, much effort has been expended trying to define and measure oil quality by physical methods in the domestic and foreign edible oil industry (1-10). Taste assessment is the most common method of grading finished oil quality (11). A panel of experienced tasters rate the flavor of the oil according to an established intensity scale. In industry, flavor ballots with a scoring system from 10-2 or 9-1 are commonly used. Panel members assign numbers as to the intensity of the flavor and, in this manner, an average flavor score (AFS) is obtained. A good oil panel should be able to agree within a standard deviation of ± one flavor unit (12). Off-flavors are often given different descriptive names. Some of the adjectives used to describe the off-flavors and odors are green, grassy, weedy, seedy, fruity, beany, watermelony, nutty, raw, painty, buggy, musty, hydrogenated, metallic, oxidized, light-struck, buttery, rubbery, reverted, fishy, rancid, etc. (13). Agreement between expert panel members as to the type of off-flavor is often poor because this concept of an oil's quality varies both individually and with local food habits.

Sensory methods are well recognized for judging the quality of finished oils. In Figure 1, results from our taste panels are used to illustrate the dramatic drop in the flavor score of commercial soybean oil from 6.5 to 4.0 after 2 wk storage in the light. An example of the limitation of this method, however, is shown by the fact that the taste panels were not able to detect further changes in the oil's flavor even after 12 wk storage in the light. Also, sensory methods do not give information as to the cause of an inferior taste or as to the reason for variation in quality resulting from various refining treatments of different batches of the same raw materials.

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In our search for instrumental methods useful for assessing oil quality deterioration during normal shelf life, we adopted the gas chromatographic (GC) method of Dupuy (15,16). The typical volatile profiles in Figure 2 show that this physical method is a valuable aid in indicating the flavor quality of incoming oils and in following the degradation of vegetable oils upon aging.

An outstanding feature of the direct GC method is the use of Porapak trapping methodology. However, the temperature of 200 C for heat desorption places some limitations on Porapak as a sampling system since bleeding and incomplete desorption of higher molecular weight volatiles can produce artifacts upon analysis (18).

The direct GC method seems to hold promise for: predicting the shelf life of vegetable oils, helping to resolve problems of a customer service nature, and measuring the ability of different processing methods to improve the flavor stability of edible oils.

Methodology

(a) Incoming refined, bleached, and deodorized soybean oil samples were packed in 8 oz flint glass bottles, filled to 1½ in. air headspace, capped with 23 in. lb torque, and labelled. Samples were evaluated by sensory panels to obtain the initial flavor score, and the identical oils were analyzed by oil volatile profile analysis. Identical samples of packaged oils were also stored in the light for 5 wk. These samples were evaluated for flavor and their volatile profiles were analyzed as depicted in Figure 2.

(b) Direct GC analyses of the oil samples were done by the method of Dupuy (15,16). However, the injector port

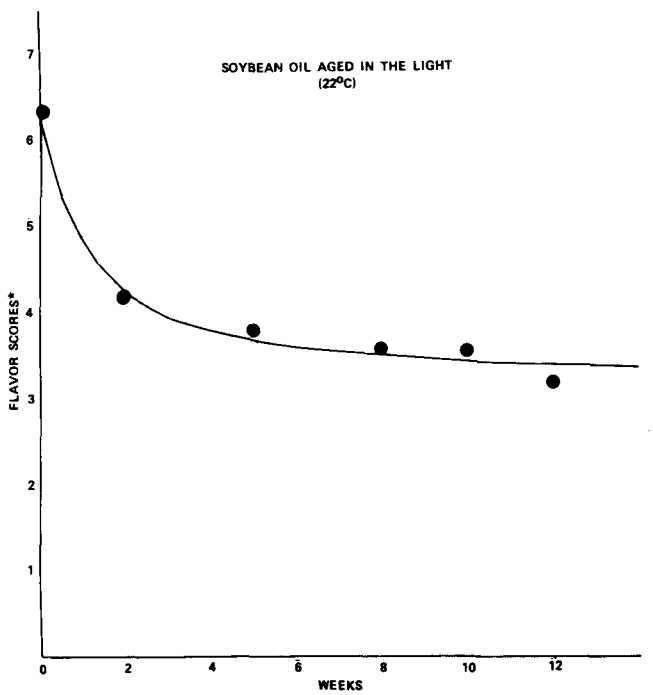

FIG. 1. Change of average flavor scores with storage time. *Each data point represents an average of 15 different taste panels.

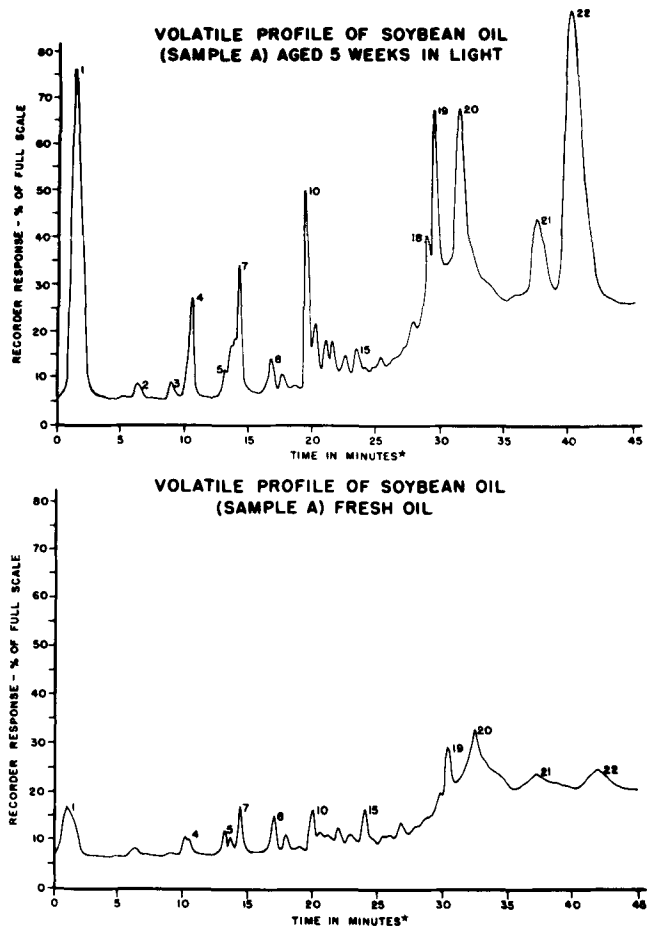

FIG. 2. Typical chromatographs of fresh and aged soybean oil. *Relative retention time based on peak 7.

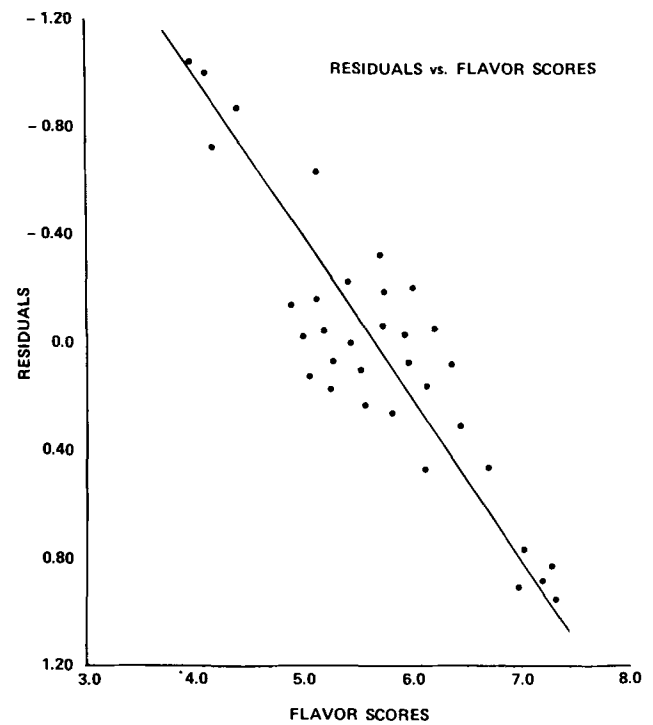

FIG. 3. Magnitude of the errors of computed flavor scores vs. actual flavor scores.

which holds the glass liner was maintained at 170 C throughout the 20 min purge. During this interval, the oil volatiles were swept onto a Porapak P column maintained at room temperature.

(c) The data were analyzed and correlated using the computerized BMDO2R-stepwise multiregression technique.

TABLE I

Summary Table of R^2

Peak Peak number	Multiple R	Multiple R^2	Increase in R^2
X(10)	0.8067	0.6507	0.6507
X(7)	0.8419	0.7087	0.0580
X(19)	0.8681	0.7535	0.0448
X(22)	0.8735	0.7630	0.0095
X(20)	0.8777	0.7704	0.0074

TABLE II

Variable in Correlation Equation

Variable	Coefficient	Standard error	F to remove
(Constant	6.67978)		
X(10)	− .01352	.00509	7.0708
X(7)	− .01872	.00771	5.8898
X(19)	− .01517	.00591	6.5887
X(22)	.00302	.00267	1.2815
X(20)	− .00212	.00135	2.4434

RESULTS AND DISCUSSION

Plot of Residuals

The distribution of the plot of reisduals in Figure 3 indicates that the errors are predictable in the volatile analysis. As we approach oils in the upper or lower range or the borderline area, we make the greatest error. This is to be expected since these types of oils are the hardest to differentiate by the taste panel. Most of the computed flavor scores had an error between ± 0.20 and 0.40.

Correlation Coefficient for Most Significant Peaks

Results obtained in our experiments after statistical analysis using the stepwise multiregression technique are given in Table I and were interpreted as follows:

The correlation coefficient (R) is a measure of the laboratory data and R^2 is the amount of variation in the flavor score measurements that can be explained by fitting the line:

$$Y = C_0 + C_1X_1 + C_2X_2 + C_3X_3 = - C_nX_n$$

where Y = the computed flavor score
C = the coefficient of regression
X = the integration counts of significant peaks in the Volatile Profile.

Correlations of 0.76 to 1.00 are excellent, 0.51 to 0.75 are good, 0.26 to 0.50 are fair, and 0.01 to 0.25 show no correlation (2,19).

In our example, Table I, R is 0.87 and R^2 is 0.77 which shows excellent correlation for raw integrator counts from volatile profile data using the five most significant peaks X(1), X(7), X(19), X(22), and X(20).

Using the nine most significant peaks–X(10), X(7), X(19), X(22), X(20), X(5), X(21), X(4) and X(1)–R^2 is 0.82. This represents an excellent fit; however, the flavor score can be determined within ± one flavor unit using the five most significant peaks. The largest residuals occur as expected at the two extremes. Flavor panel scores cannot easily differentiate among oils with high flavor scores or oils with very low flavor scores.

If the data are fitted by logarithms, the R^2 for the five most significant peaks is not improved.

Dupuy (20) also obtained correlations which could be classified as good using the pentenal, hexenal, 2-5-heptenal, and total volatiles' peaks.

Variables in the Correlation Equation

R and R^2 denote the multiple correlation coefficient and its square. R always increases when an additional peak is added to the regression equation. If, however, the number of samples, N, is small relative to the number of peaks in the equation, p, and apparent improvement in fit of the data to the regression equation, indicated by increasing R, may be spurious. Testing whether R is statistically significantly different from zero will determine if the fit is "real." The value of the standard error of estimate which is a function of $(1-R^2)/(N-p-1)$ may decrease or increase when an additional peak is included in the regression, since, roughly speaking, the increase in R^2 is balanced against the decrease in N-p.

Based on the results in Table II, a prediction equation with five peaks—10, 07, 19, 22, 20—seems the best choice for both GC count and log of GC count. Up to this point, the standard error of estimate is decreasing and R is significantly different from zero at level .01. When a sixth and seventh peak are added, the standard error increases and R becomes not significantly different from zero. The two equations are equally good for predicting taste score (R^2 values of .76 and .77).

The constants obtained from the use of the raw integrator counts to correlate the flavor scores with volatile profiles for all 46 soybean oils (fresh and aged) are given in Table II. Essentially, the constants indicate that the higher molecular weight volatiles reduce the flavor score of the oil. As expected in this study, the "light peak" x (10) (2-*t*-heptenal) is the most important peak and it is negatively correlated with the flavor score. Peaks X(19), X(20), X(21), and X(22) appear to be thermal breakdown products from peak X(10) because oils irradiated with UV light at 0 C will product a larger peak X(10) without peaks X(19), X(20), X(21), and X(22).

The light peak X(10) (2-*t*-heptenal) is produced in oils which are stored in clear glass bottles in the presence of ultraviolet light. Ordinary fluorescent light has enough UV to catalyze production of this peak in oils. Fresh oils usually will show 0.07 ppm of X(10). However, after 5 wk of storage in the light, the light peak X(10) will increase to 5.1 ppm. In the dark, peak X(10) does not increase even after 5 mo storage at 30 C.

We believe that more laboratories should publish their experience with these various gas liquid chromatographic methods so that more exact and reproducible methodology can be developed.

REFERENCES

1. Johanson, G., Chem. & Inds., 902 (1975).
2. Fioriti, J.A., M.J. Kanuk, and R.J. Sims, JAOCS 51:219 (1974).
3. Selke, E., W.K. Rohwedder, and H.J. Dutton, Ibid. 49:636 (1972).
4. Baumann, L.A., D.G. McConnell, H.A. Moser, and C.D. Evans, Ibid. 44:663 (1967).
5. List, G.R., C.D. Evans, W.F. Kwolek, K. Warner, and B.K. Bounty Ibid. 51:17 (1974).
6. Morita, M. and M. Fujimaki, J. Agr. Food Chem. 21:860 (1973).
7. Holm, U., Pre-Manuscript Communications, Presented at S.C.I. and B.F.M.I.R.A. Meeting in Leatherhead, England (1974).
8. Lanser, Alan C., J.O. Ernst, W.F. Kwolek, and H.J. Dutton, Anal. Chem. 45:2344 (1973).
9. Marcuse, R., Rev. Fr. Corps Gras 20:277 (1973).
10. Chang, S.S., Food Technol. 27:27 (1973).
11. Moskowitz, H.R., Lebensm-Wiss U Technol. 8:245 (1975).
12. Moser, H.A., H.J. Dutton, C.D. Evans, and J.C. Cowan, Food Technol. 4:105 (1950).
13. Netherlands Milk and Dairy Journal, Vol. 24 Chapter III, (1970) p. 163.
14. Moskowitz, H.R., Lebensm-Wiss U Technol. 8:249 (1975).
15. Dupuy, H.P., S.P. Fore, and L.A. Goldblatt, JAOCS 48:876 (1971).
16. Dupuy, H.P., S.P. Fore, and L.A. Goldblatt, Ibid. 50:340 (1973).
17. Tassan, C.G., and G.F. Russell, J. Food Sci. 39:64 (1974).
18. Zlatkis, A., A. Lichtenstein, and A. Tishbee, Chromatographia 6:67 (1973).
19. Leporiere, R., Food Prod. Develop. 10:102 (1976).
20. Dupuy, H.P., AOCS Annual Spring Meeting, Paper 98, April, 1976.

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