

✿ Flavor Evaluation of Crude Oil to Predict the Quality of Soybean Oil

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Reliable methods for evaluation of crude oils are needed to assist processing and to improve flavor quality of finished products. The quality of crude oils from soybeans of different sources and treatments was determined by sensory evaluation and by capillary gas chromatographic (GC) analyses of volatiles. Taste panelists were specially trained in using a new technique to evaluate crude oils by dilution and comparison with freshly deodorized oils. The flavor quality of crude oils from untempered soybeans was significantly poorer than that of oils from soybeans steam-tempered at 104 C for four min. Capillary GC analyses of total volatiles and hexanal correlated well with differences in flavor quality and stability. Crude oils extracted from soybeans damaged by storage at 45 C and 13% moisture received decreasing flavor scores with prolonged storage time. Similarly, hexanal and total volatile contents increased with storage times. Commercial crude oils from several geographic locations showed a wide range in flavor scores. However, flavor scores of crude oils showed good agreement with flavor stabilities (decrease in flavor scores after storage at 60 C) of the corresponding oils after refining, bleaching and deodorization. Therefore, the combined use of sensory evaluations and GC-volatile analyses of crude oils can provide convenient, rapid, sensitive and reliable screening methods to assist in improving the quality of finished soybean oils by controlling soybean storage and processing.

The present federal trading specifications for crude soybean oil include such analyses as moisture, volatile matter, free fatty acids, unsaponifiable matter, green color and phosphorus, but do not include flavor standards (1). Under present practice, the flavor quality of soybean oil is generally determined after processing and deodorization (2,3). Analyses of crude and partially processed oils for color, phosphorus and free fatty acids are generally used to monitor processing conditions to meet certain quality standards for finished oils. However, the flavor quality and stability of finished oils is very difficult to predict on the basis of these analytical standards. Improved methods to evaluate crude oils may be more useful to control processing parameters and to predict the flavor stability of finished soybean oils.

Soybean meats are generally conditioned at 65 to 75 C prior to oil extraction to improve the flaking process and to inactivate enzymes. However, these conditions do not completely inactivate enzymes. Steaming or wet heat at temperatures exceeding 82 C are needed to obtain 97% inactivation of lipoxygenase (4). The advantage of heat treatments prior to oil extraction have been well documented (5-8), but this process is reported to lower the extractability of soybeans (5). Previous studies showing the adverse effects of storage and field damage of soybeans on the quality of

the resulting finished oils have been based on chemical and instrumental analyses of the crude oil (9,10), and by flavor evaluation of oil after processing (11).

The decrease in oil flavor stability resulting from damaged soybeans or from the abuse of oils after extraction cannot be completely compensated for by further processing of the oil (12). However, the flavor quality of off-specification oils can be improved by double refining, increased bleaching, higher temperature and longer time of deodorization, and by the use of metal inactivators (13).

How soybeans or crude vegetable oils have been handled or stored prior to receipt at processing plants is generally unknown or often difficult to determine. The effect on oil quality of heating soybeans to inactivate enzymes was evaluated previously by using "sniffing ports" in the empirical Swift stability test to evaluate crude oils (7). Because the relatively high temperature of this stability test (100 C) may cause decomposition and browning of the phosphatides in crude oils, the results may neither reflect flavor quality nor predict flavor stability of the finished processed oils. More reliable evaluations of crude oils would greatly assist processors in improving flavor quality of finished oils.

A method was reported previously to predict flavor stability of different processed vegetable oils by determining induction periods based on the formation of volatile compounds (14). The present study was aimed at developing sensory and volatile gas chromatographic (GC) techniques to evaluate crude oils and to predict the flavor quality of the resulting finished oils. The new methodology was applied to investigate the effects of thermal tempering of soybean meals and of storage damage of whole soybeans, and to evaluate commercial crude oils from different geographic origins, post harvest handling and processing conditions.

EXPERIMENTAL

Materials. Seed grade 1984 Century soybeans were obtained from a local distributor. Crude soybean oils were received from five commercial sources from different U. S. geographic locations. Crude oil samples were stored at 0 C for periods of 1 to 4 weeks before testing.

Storage. After adjusting the moisture contents to 13%, the soybeans were stored in 2.5-kg batches and allowed to generate their own heat endogenously from 35 to 45 C in a forced-draft oven, by the same procedure described previously (10). Samples were withdrawn periodically for analyses and processing.

Processing. Soybeans were first cracked, dehulled and tempered with steam for 4 min at 103 C. Unheated cracked and dehulled soybeans served as control. All samples were flaked and extracted with hexane in a conventional Soxhlet apparatus for 5 hr (15). The oils extracted in the laboratory and commercial crude oils were water-degummed (2% water, 60 C), alkali-refined (10% sodium hydroxide), bleached (1% activated clay)

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and deodorized (3 hr, 210 C) as described previously (16). The oils prepared in the laboratory were treated with 100 ppm citric acid added as a 20% solution in water on the cooling side of deodorization.

Sensory evaluations. Oils were evaluated for flavor at different stages of processing by a taste panel experienced in evaluating finished processed oils. The soy flours were tasted by panelists experienced in evaluating cereal products. Because both commercial and laboratory-prepared crude and partially processed (degummed, refined and bleached) oils had strong hay/grassy flavors, they were diluted in a ratio of 5:95 with good quality freshly deodorized soybean oil containing 100 ppm citric acid. The same lot of refined, bleached and deodorized oil was used for all dilutions. Deodorized oils were evaluated for flavor by procedures described previously (17). The flavor of ground flakes was evaluated as 2% dispersions in carbon-filtered water. A 10-point scale was used to score the samples (10, bland; 1, strong) (18).

Gas chromatographic analyses [GC]. Volatiles were monitored by a direct injection technique (14) with a Perkin-Elmer gas chromatograph (Model 3920, Norwalk, Connecticut) and a Durabond DB-5 fused silica capillary column (30 m × 0.32 mm, film thickness, 1 micron, J & W Scientific, Rancho Cordova, California).

Other analyses. Oils were analyzed at different processing steps for free fatty acids and peroxide values by standard AOCS methods Ca5a-40, Cd8-53 (19). Phosphorus was determined colorimetrically in crude and degummed oils by AOCS method Ca12-55 (19). Anisidine values were also determined in commercial crude oils (11).

RESULTS AND DISCUSSION

Sensory evaluation of crude oils. A method was developed for our oil taste panel to evaluate crude and partially processed oils. The strong flavor of crude oils was diluted by blending 1 to 25% (by volume) crude oil with good quality deodorized soybean oil. Panelists could not detect differences in quality of crude oils at either end of the dilution range tested (Table 1). At the 1% level, the effect of crude oil was not detected and the same score (7.4) was obtained as for the undiluted oil. At the 25% level, the effect of crude oil was too strong, and the flavor score was 3.5. Dilutions at 5 and 10% levels of crude oil were both adequate to detect flavor score differences between oils of varying quality. The 5% dilution level was adopted as an optimum to evaluate crude oils.

For training, panelists were given crude oils of different quality diluted at the 5% level to detect differences in overall flavor intensity and types of flavors. Oils from soybeans that were not thermally tempered were described as predominantly grassy-green and slightly grassy-hay in flavor, whereas oils from heat-tempered soybeans were described as grassy-hay. Crude oils aged at 60 C were used as standards for rancid and painty flavors. Oils from soybeans subjected to different heat treatments were used as standards for "toasted" and "burnt" characteristics. Any samples containing significant amounts of solvent were stripped with a rotating evaporator at 40 to 50 C

TABLE 1

Flavor Evaluation of Two Crude Soybean Oils Diluted with Fresh Refined, Bleached, Deodorized (RBD) Soybean Oil

Samples	Flavor scores/ description	Dilution level (% crude oil by vol)				
		0	1	5	10	25
A	Flavor scores ^a	7.4	7.4	5.5	—	3.5
	Grassy-hay ^b	0.4	0.7	1.6	—	2.2
B	Flavor scores ^a	7.2	—	5.0	4.6	—
	Grassy-hay ^b	0.5	—	2.1	2.0	—

^aBased on a 10-point scoring scale with 10, bland; 1, strong.

^bBased on a 3-point scoring scale with 3, strong; 2, moderate; 1, weak.

under about 1 mm Hg pressure. A well-processed crude oil diluted 95% with good quality deodorized soybean oil was given a score of ca. 6.0. The score decreased as the flavor intensity increased.

Thermal tempering. Soybean meats are generally conditioned by heating to 65-70 C and by adjusting the moisture level to 10.5-11.5% to facilitate flaking (20). Oil quality may be adversely affected by storing the flakes for varying times before extraction (21), or by flaking at relatively high temperatures (6). In this study, soybean meats were tempered at 103 C for four min with steam and the extracted crude oil, defatted flour, partially processed, and deodorized oils were evaluated for flavor quality and compared with the corresponding products from untempered soybeans. The flavor stability of the deodorized oils was also evaluated by aging at 60 C for four days. Flavor scores of crude and partially processed oils, and of the defatted flour from thermally tempered soybeans, were rated significantly higher than the corresponding products from untempered soybeans (Fig. 1). The most marked difference noted was between the flours from thermally tempered and untempered soybeans. Tempering also had a more notable effect on the crude and partially processed oils than on deodorized oils. However, after storage at 60 C the deodorized oil from tempered soybeans was much more stable and gave a significantly higher flavor score than the deodorized oil from untempered soybeans. Crude and partially processed oils from unheated soybeans were described predominantly as grassy-green and grassy-hay. Oils from heat-tempered soybeans lost some of this grassy-hay and all of the grassy-green flavor. Fully processed oils from both tempered and untempered soybeans initially were described as buttery. However, after storage at 60 C for four days, the oil from untempered soybeans had poor flavor and storage stability and was described as rancid.

GC analyses showed good correlation between volatiles and flavor evaluations. Total volatiles decreased significantly in crude and partially processed oils from tempered soybeans when compared to those from untempered soybeans (Fig. 2). Heating soybeans resulted in larger differences in the volatile contents

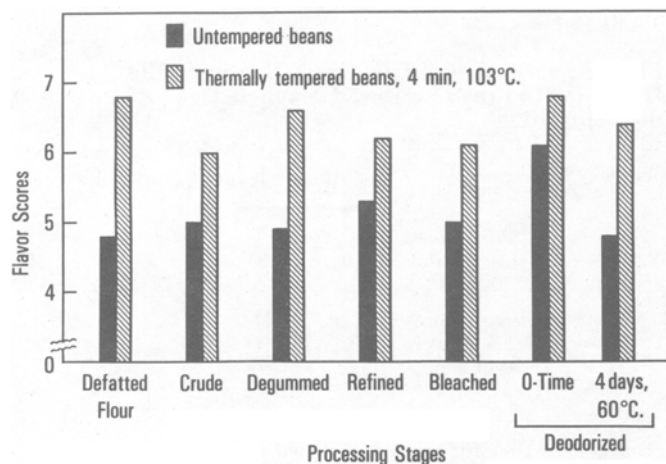


FIG. 1. Mean flavor scores of partially processed and refined, bleached and deodorized (RBD) soybean oils and flour from thermally tempered and untempered soybeans (based on a 10-point scoring scale with 10, bland; 1, strong). Least significant difference (LSD): 0.8.

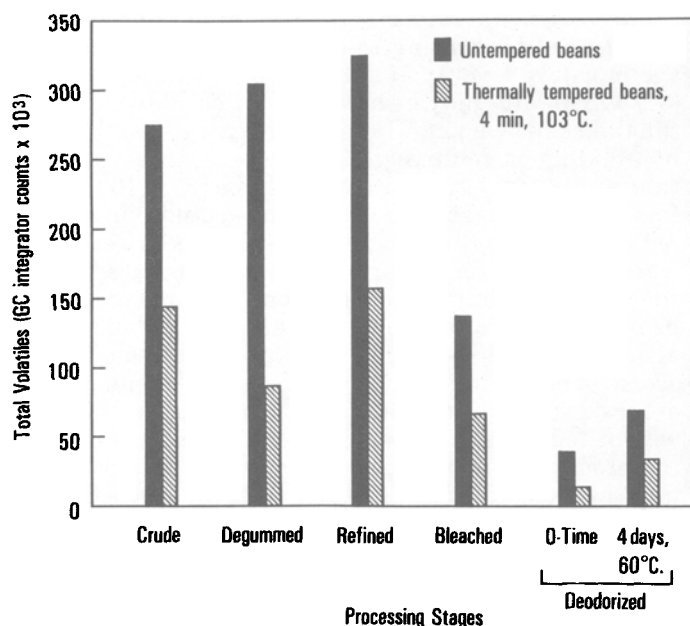


FIG. 2. Capillary gas chromatographic volatiles analyses of partially processed and refined, bleached and deodorized (RBD) soybean oils from thermally tempered and untempered soybeans. LSD = 25×10^3 .

of crude, degummed and refined oils than in the corresponding bleached and deodorized oils. These results confirm previous reports on the beneficial effects of thermal tempering of soybeans on the quality of processed soybean oil (21,6) and demonstrate the usefulness of testing crude oils for flavor to predict the stability of the finished oils.

Soybean storage. Prolonged storage of soybeans under moist conditions is known to decrease the quality of the extracted crude oils and finished processed oils (5,6,8,10). Storage of soybeans at increased moisture levels was shown recently to cause increases in hex-

anal and total volatiles in agreement with increases in free fatty acid and decreases in phosphorus contents (10). For the present work, crude oils were extracted from soybeans stored at 13% moisture for different periods of time. After 80 days of storage, the free fatty acids increased from 0.2 to 1.7% and the phosphorus level decreased from 1,000 to 300 ppm in the oil (Fig. 3). During the same period of storage the flavor quality of the crude oils decreased significantly from an initial score of 6.5 to 4.0 (Fig. 4). The corresponding refined, bleached and deodorized oil showed a similar trend with a decrease in the initial score from 8.0 to 6.5. The storage stability of the deodorized oil was also tested for comparison. After storage at 60 C for four days, the score decreased from 7.0 to 4.6. A highly significant correlation coefficient of 0.95 was calculated between flavor scores of crude oils and the corresponding deodorized oils. Therefore, flavor quality and stability of a finished deodorized oil can be reliably predicted from the flavor scores of the starting crude oil.

Gas chromatographic analyses show a significant increase in total volatiles and hexanal in the crude oils from soybeans stored at 13% moisture (Fig. 5). A correlation coefficient of -0.95 was calculated between flavor scores and total volatile contents of crude oils. These results are in good agreement and confirm our previous analyses based on headspace GC analyses carried out directly on the soybeans and the extracted crude oils (10). Therefore, oxidative deterioration occurring in soybeans by storage under moist conditions can be reliably determined by GC to complement flavor evaluations.

Evaluations of commercial crude oils. The quality of crude oils received in processing plants can vary widely according to the geographic origin of the soybeans, their storage history and other post-harvest handling, the time of the year, and processing conditions prior to and during extraction. A reliable test for flavor quality of crude oils would therefore assist processors in optimizing conditions to prepare stable oils of good quality. A series of 12 commercial crude soybean oils was obtained from October 1985 to March 1986 and stored at 0 C until further processing. The oils varied widely in flavor scores (3.4-5.7), GC volatiles (9.33×10^4 integrator counts), free fatty acids (0.26-1.33%), phosphorus (570-895 ppm) and peroxide values (0-1.9) (Table 2).

Diluted commercial crude oils were described by the taste panel as predominantly grassy-hay when the flavor scores were near 6.0. Increasing intensities of "burnt" descriptions were typically given to the crude oils as their flavor scores decreased. Oils scored below 5.0 were described as having "off" flavors, such as putrid, sulfur, rubbery, musty and metallic. One of the poorest oils, sample L, was described as having the highest intensity of grassy-hay, burnt and "off" flavors including musty, sulfur and tar.

Four of the commercial crude oils ranging widely in flavor scores were selected for further processing to relate the flavor quality of the crude oils with that of the finished deodorized oils. After refining, bleaching and deodorizing, the oils were tested for flavor and oxidative stability by aging at 60 C for eight days.

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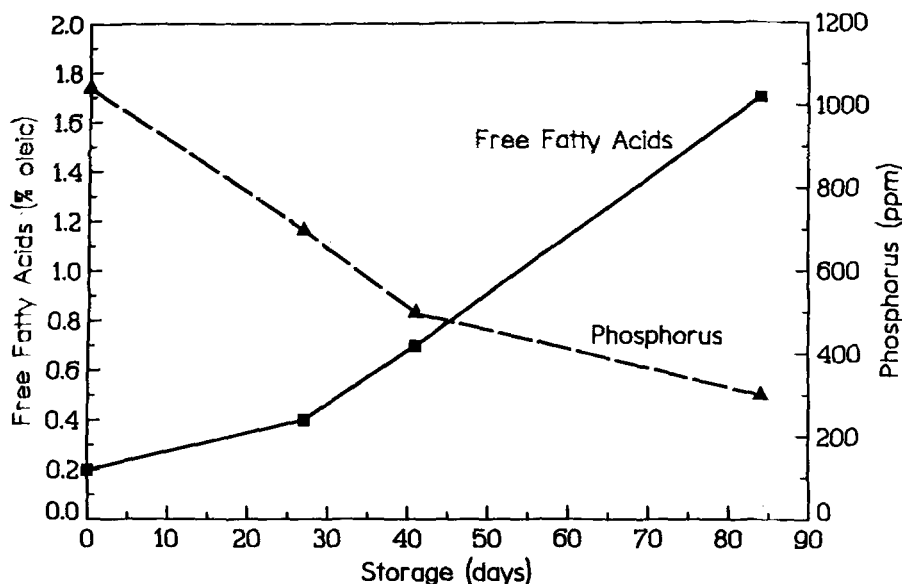


FIG. 3. Effect of storage of soybeans at 13% moisture and 45 C on phosphorus and free fatty acid contents of four crude oils.

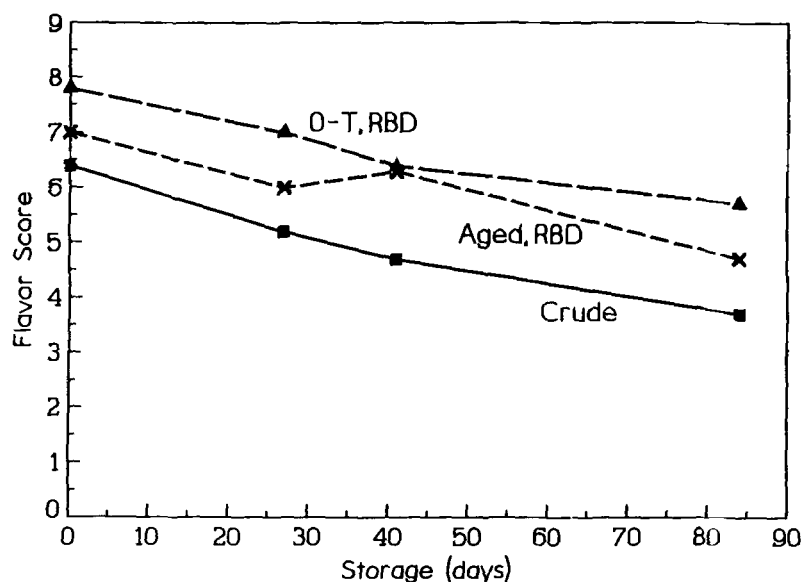


FIG. 4. Effect of storage of soybeans at 13% moisture and 45 C on flavor scores of crude and of refined, bleached and deodorized (RBD) oils at 0-time and after aging at 60 C for four days.

Initial flavor scores of the deodorized oils, ranging from 5.0 to 7.4, showed good correlation ($r = 0.93$) with scores of the corresponding crude oils in three of the four samples (C, D and G, Table 3). After aging at 60 C, the scores of all deodorized oils were in good agreement with the scores of the crude oils ($r = 0.90$). Samples D and G showed the best flavor stability with scores of 5.8 and 6.3 after aging, which corresponded with scores of 5.7 and 5.3 for the crude oils. Samples C and L showed poor flavor stability and quality, with scores of 5.3 and 3.3 after aging and 4.3 and 3.4 for the corresponding crude oils.

GC analyses of deodorized oils showed less increase

in total volatiles due to aging in samples G (70 to 75) and D (80 to 100) than samples C (74 to 100) and L (80 to 160). Free fatty acids, phosphorus analyses and peroxide values of the crude oils did not give any indication of the oxidative or flavor stability of these samples. The respective correlation coefficients were -0.1 , -0.41 and 0.14 between flavor scores of the aged deodorized oils and free fatty acids, phosphorus and peroxide values of the crude oils.

Anisidine values of crude oils also showed a low correlation ($r = 0.18$) with flavor scores of crude oil. However, the anisidine values for unaged deodorized oil had a significant correlation ($r = 0.95$) with flavor

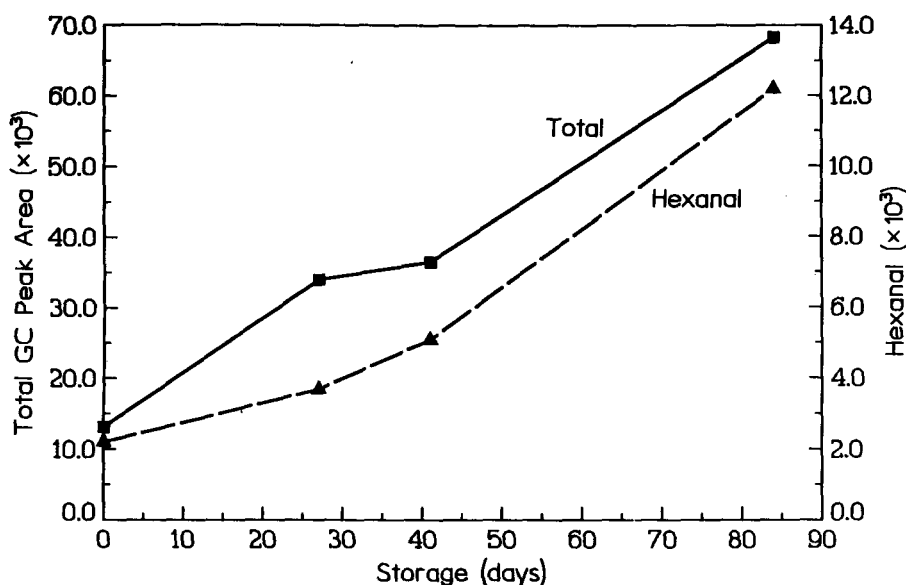


FIG. 5. Effect of storage of soybeans at 13% moisture and 45 C on total volatiles and hexanal in four crude soybean oils.

TABLE 2

Analyses of Commercial Crude Oils

Samples	Flavor scores ^a	GC volatiles pk areas ^b	Free fatty acids, %	Phosphorus (ppm)	Peroxide values (me/kg)
C	4.3	24	1.33	680	1.9
D	5.7	14	0.70	840	1.3
E	5.1	14	0.44	810	0.2
F	5.3	14	0.40	760	1.0
G	5.3	14	0.26	270	0.0
H	4.5	15	0.59	970	0.0
I	5.2	17	0.52	610	0.2
J	4.9	33	0.88	570	1.2
K	3.9	9	0.94	770	0.5
L	3.4	15	0.47	700	0.3
M	3.9	14	0.57	895	0.0
N	3.7	16	0.43	615	0.0

^aCrude oils diluted with 95% fresh refined, bleached, deodorized oil for tasting. Scale: 1-10, 1, strong intensity; 10, bland. Least significant difference: 1.0 ($P < 0.05$).

^bIntegrator counts $\times 10^4$. Peaks eluting after residual solvent.

stability (decrease in flavor scores of deodorized oils from 0 to 8 days of aging). Anisidine values of crude oils had a high correlation coefficient ($r = 0.85$) with total volatiles in the crude oil. The peroxide values and flavor scores of the aged deodorized oils had a high correlation coefficient of -0.93 , but this information was therefore of no value in predicting stability.

The correlation between flavor scores of the aged deodorized oils and the scores of the crude oils was highly significant with a coefficient of 0.93. Also significant was the correlation (-0.87) between total volatiles by GC in deodorized oils after aging and flavor scores of crude oils. Because the commercial oils contained some residual solvents that masked volatile compounds developing during oxidation, such as

2-propenal and pentane, these and other compounds eluting before 2-butenal were not included in the integrations. Therefore, the GC volatile analyses of crude oils given in Table 3 cannot be compared with the total volatile integrator counts for deodorized oils. Oxidative stability, based on the increase in volatiles between fresh and aged deodorized oils, had a good correlation with flavor stability (decrease in scores between fresh and aged oils) for samples L and G but not for samples C and D.

Our flavor evaluations of the quality of crude oils provided the most reliable predictor of future storage stability of deodorized oils. Among the other tests investigated, GC volatile analyses, anisidine and peroxide values were less useful in predicting oxidative dete-

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TABLE 3

Relationship Between Quality Characteristics of Crude and of Refined, Bleached and Deodorized (RBD) Soybean Oils

Samples ^a	Flavor scores ^b	GC volatiles ^c	Anisidine values	Peroxide values (me/kg)
L: Crude	3.4	15	0.4	0.3
RBD: 0 time	7.4	80	92	0.0
8 days ^d	3.3	160	—	15.3
C: Crude	4.3	24	2.1	1.9
RBD: 0 time	5.0	74	10	0.6
8 days ^d	5.3	100	—	6.3
G: Crude	5.3	14	1.1	0.0
RBD: 0 time	7.2	70	3.0	0.0
8 days ^d	6.3	75	—	6.9
D: Crude	5.7	14	1.0	1.3
RBD: 0 time	7.0	80	1.2	0.0
8 days ^d	5.8	100	—	7.0

^aSee Table 2.

^bCrude oils diluted with 95% fresh RBD oil for tasting. RBD oil tasted undiluted. Scale: 1-10, 1, strong intensity; 10, bland.

^cIntegrator counts $\times 10^4$. Peaks eluting after residual solvent for crude oil.

^dAged at 60 C.

rioration than were the flavor evaluations. In this study, free fatty acids and phosphorus determinations had no predictive value. More work is needed with a large number of samples of known histories to gain further insight on how to better predict flavor quality.

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REFERENCES

- Brekke, O.L., in *Handbook of Soy Oil Processing and Utilization*, edited by D.R. Erickson, E.H. Pryde, O.L. Brekke, T.L. Mounts and R.A. Falb, American Soybean Association, St. Louis, MO, and American Oil Chemists' Society, Champaign, IL, 1980, pp. 378-381.
- Mounts, T.L., and K. Warner, *Ibid.*, 1980, pp. 245-266.
- Warner, K., in *Flavor Chemistry of Fats and Oils*, edited by D.B. Min and T.H. Smouse, American Oil Chemists' Society, Champaign, IL, 1985, pp. 207-221.
- Mustakas, G.C., W.J. Albrecht, J.E. McGhee, L.T. Black, G.N. Bookwalter and E.L. Griffin, *J. Am. Oil Chem. Soc.* 46:623 (1969).
- Penk, G., in *Proceedings of the 2nd ASA Symposium on Soybean Processing* (Antwerp, Netherlands), American Soybean Association, St. Louis, MO, 1981, pp. 15-20.
- Kock, M., *J. Am. Oil Chem. Soc.* 60:198 (1983).
- Rice, R.D., L.S. Wei, M.P. Steinberg and A.I. Nelson, *Ibid.* 58:578 (1981).
- Ong, J.T.L., in *Proceedings of the 2nd ASA Symposium on Soybean Processing* (Antwerp, Netherlands), American Soybean Association, St. Louis, MO, 1981, pp. 1-6.
- Robertson, J.A., W.H. Morrison and D. Burdick, *J. Am. Oil Chem. Soc.* 50:443 (1973).
- Frankel, E.N., A.M. Nash and J.M. Snyder, *Ibid.* 63:411 (1986).
- List, G.R., C.D. Evans, W.F. Kwolek, K. Warner, B.K. Boudy and J.C. Cowan, *Ibid.* 51:17 (1974).
- Evans, C.D., E.N. Frankel, P.M. Cooney and H.A. Moser, *Ibid.* 37:452 (1960).
- List, G.R., in *Handbook of Soy Oil Processing and Utilization*, edited by D.R. Erickson, E.H. Pryde, O.L. Brekke, T.L. Mounts and R.A. Falb, American Soybean Association, St. Louis, MO, and American Oil Chemists' Society, Champaign, IL, 1980, pp. 355-376.
- Warner, K., and E.N. Frankel, *J. Am. Oil Chem. Soc.* 62:100 (1985).
- Mounts, T.L., G.R. List and A.J. Heakin, *Ibid.* 56:883 (1979).
- List, G.R., C.D. Evans, K. Warner, R.E. Beal, W.F. Kwolek, L.T. Black and K.J. Moulton, *Ibid.* 54:8 (1977).
- Warner, K., and E.C. Baker, *Ibid.* 61:1861 (1984).
- Warner, K., T.L. Mounts, J.J. Rackis and W. Wolf, *Cer. Chem.* 60:102 (1983).
- Official and Tentative Methods of the American Oil Chemists' Society*, AOCS, Champaign, IL (1981).
- Serrato, A.G., *J. Am. Oil Chem. Soc.* 58:157 (1981).
- Ong, T.L., *Fette, Seifen, Anstrichm.* 82:169 (1980).

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