Electrochemical Hydrogenation of Edible Oils in a Solid Polymer Electrolyte Reactor. Sensory and Compositional Characteristics of Low *Trans* Soybean Oils

K. Warner[a,*], **W.E. Neff**[a], **G.R. List**[a], **and Peter Pintauro**[b]

[a]Food Quality and Safety Research, USDA, ARS, NCAUR, Peoria, Illinois 61604,

and [b]Tulane University, New Orleans, Louisiana

ABSTRACT: Soybean oils were hydrogenated either electrochemically with Pd at 50 or 60°C to iodine values (IV) of 104 and 90 or commercially with Ni to iodine values of 94 and 68. To determine the composition and sensory characteristics, oils were evaluated for triacylglycerol (TAG) structure, stereospecific analysis, fatty acids, solid fat index, and odor attributes in room odor tests. *Trans* fatty acid contents were 17 and 43.5% for the commercially hydrogenated oils and 9.8% for both electrochemically hydrogenated products. Compositional analysis of the oils showed higher levels of stearic and linoleic acids in the electrochemically hydrogenated oils and higher oleic acid levels in the chemically hydrogenated products. TAG analysis confirmed these findings. Monoenes were the predominant species in the commercial oils, whereas dienes and saturates were predominant components of the electrochemically processed samples. Free fatty acid values and peroxide values were low in electrochemically hydrogenated oils, indicating no problems from hydrolysis or oxidation during hydrogenation. The solid fat index profile of a 15:85 blend of electrochemically hydrogenated soybean oil (IV = 90) with a liquid soybean oil was equivalent to that of a commercial stick margarine. In room odor evaluations of oils heated at frying temperature (190°C), chemically hydrogenated soybean oils showed strong intensities of an undesirable characteristic hydrogenation aroma (waxy, sweet, flowery, fruity, and/or crayon-like odors). However, the electrochemically hydrogenated samples showed only weak intensities of this odor, indicating that the hydrogenation aroma/flavor would be much less detectable in foods fried in the electrochemically hydrogenated soybean oils than in chemically hydrogenated soybean oils. Electrochemical hydrogenation produced deodorized oils with lower levels of *trans* fatty acids, compositions suitable for margarines, and lower intensity levels of off-odors, including hydrogenation aroma, when heated to 190°C than did commercially hydrogenated oil.

Paper no. J9563 in *JAOCS 77*, 1113–1117 (October 2000).

KEY WORDS: Fatty acid composition, hydrogenation, margarine, odor, sensory, solid fat index, soybean oil, *trans* fatty acids, triacylglycerol.

Hydrogenation is used by the oil processing industry to change the functional and stability characteristics of liquid oils for applications such as margarines, shortenings, and frying. Conventional chemical hydrogenation not only increases saturated fatty acids and *trans* fatty acids but also contributes distinctive waxy, fruity, and flowery odors and flavors characteristic of hydrogenation (1–4). Health concerns about *trans* fatty acids (5,6) have led to interest in alternatives to hydrogenation such as modified composition oils, interesterification, and blending of saturated and polyunsaturated oils. However, hydrogenation could still be a viable option for food manufacture if *trans* fatty acid levels can be reduced. Alternatives to high *trans*-producing chemical hydrogenation techniques include processes based on supercritical and electrochemical technology (7–9). Pintauro and co-workers (10,11) described a low-temperature electrocatalytic hydrogenation process that produced oils with iodine values (IV) ranging from 100 to 60 and with less than 10% *trans* fatty acids using Pd catalyst and with less than 2% *trans* fatty acids using Pt catalyst. The results of analyses showed satisfactory hydrogenation efficiency, yields and fatty acid profiles indicating potential food use of the hydrogenated oils. To determine the functionality, stability, and odor/flavor of these oils and their suitability in food applications, we examined the compositions of soybean oils that were chemically hydrogenated or electrochemically hydrogenated and their solid fat index profiles. In addition, the odor characteristics of these hydrogenated oils were determined after the oils were heated to frying temperatures.

MATERIALS AND METHODS

Materials. Soybean oils hydrogenated with nickel catalyst to IV of 94 and 68 and refined, unhydrogenated, bleached soybean oil were obtained from a commercial oil processor. Electrochemically hydrogenated oils were prepared in the laboratory from the commercial refined, bleached soybean oil using Pd catalyst at either 50 or 60°C to 104 and 90 IV by procedures described by An *et al.* (10,11) and were then laboratory-deodorized (12).

*To whom correspondence should be addressed at NCAUR, 1815 North University St., Peoria, IL 61604. E-mail: warnerk@mail.usda.ncaur.gov

Chemical/physical analysis. Compositional analyses included fatty acids (13), triacylglycerol (TAG) (14), and regiospecific (15). Fatty acid compositions of the initial oils were determined by capillary gas chromatographic (GC) analysis with a Hewlett-Packard 5890 gas chromatograph (Wilmington, DE) equipped with a SP2330 column (30 m, 0.20 mm i.d., 0.20 micron film thickness; Supelco, Bellefonte, PA). Column temperature was held at 190°C for 5 min and temperature was programmed to 230°C at 20°C/min. Other GC conditions were: injector, 250°C; detector, 260°C. IV was calculated from fatty acid composition. The regiospecific analyses to determine the compositions at carbon 2 were conducted on the TAG using lipolysis, separation by solid-phase extraction, and transmethylation for GC analyses. The compositions of the 1,3-carbons were calculated based on the composition at carbon 2. Details of the procedures have been published by Neff *et al*. (15). The TAG compositions were determined by reversed-phase high-performance liquid chromatography with evaporative light scattering detection and flame-ionization detection. Details of the procedures have been published by Neff and Byrdwell (14). Free fatty acid analysis (FFA), peroxide value (PV), and solid fat index (SFI) were done by AOCS methods (16), Ca 5a-40, Cd 8-53, and Cd 10-57, respectively. Dropping point was measured using a Mettler dropping point cell (17).

Sensory analysis. Room odor analysis at 190°C was conducted using previously published methods (2). The surface-to-volume ratio in the 500-mL glass container simulated deep-fat heating/frying conditions rather than pan frying. Odors generated from the heated oil in the hood were pumped into a $5 \times 8 \times 10$ ft room. Twelve trained analytical sensory panelists experienced in evaluating heated oil odors individually entered each room to evaluate the odors for type and intensity, including overall odor intensity and the intensity of individual odors such as acrid, burnt, doughy, fishy, flowery, fried food, fruity, hydrogenation, waxy, and woody. The scoring scale ranged from 0 = no odor to 10 = strong odor intensity. Sensory data were statistically analyzed by two-way analysis of variance.

RESULTS AND DISCUSSION

Fatty acid composition. The fatty acid compositions for the two commercially hydrogenated oils and the two electrochemically hydrogenated oils and for an unmodified soybean oil are shown in Table 1. The levels of C16:0 for all oils changed only slightly from the unhydrogenated soybean oil; however, levels of C18:0 were higher in the electrochemical samples than in the commercial samples. Monoene levels were higher in the commercial oils, but C18:2 was higher in the electrochemical samples. Linolenic acid was 3.2% in the electrochemical samples but less than 1% in the commercially hydrogenated oils. *Trans* fatty acid contents were 17 and 43.5% for the commercially hydrogenated oils and 9.8% for the electrochemically hydrogenated products. Because the methodology used in this study did not resolve all isomers of C18:2, any isomer containing *trans* was pooled and reported as the total *trans* amount (Table 1). In comparing the fatty acid compositions of the two oils with the most similar IV, commercially hydrogenated soybean oil (NiHSBO-IV 94, where IV 94 = iodine value of 94) and electrochemically hydrogenated soybean oil (PdHSBO-IV 90 where IV 90 = iodine value of 90), the PdHSBO sample had significantly more C18:0, C18:2*c,c* and C18:3. On the other hand, NiHSBO had significantly greater levels of C18:1*t* and C18:1*c*.

TAG composition. The location of fatty acids on the glycerol moiety is an indication of the potential application and oxidative stability of the oil or fat. The TAG fraction of a base stock is responsible for most of a product's physical properties and therefore affects texture and mouthfeel. Table 2 shows the TAG compositions grouped as monoenes, dienes, and trienes (M, D, T) in addition to palmitic and stearic acids

TABLE 1
Fatty Acid Composition, Iodine Values (IV), and Chemical and Physical Analyses of Soybean Oil (SBO), Commercially Hydrogenated Soybean Oils (NiHSBO), and Electrochemically Hydrogenated Soybean Oils (PdHSBO)

Fatty acid/analyses[a]	SBO-IV128	NiHSBO-IV94	NiHSBO-IV68	PdHSBO-IV104	PdHSBO-IV90
C16:0	10.2	10.9	12.1	10.8	11.7
C18:0	4.2	6.4	13.1	12.3	20.6
C18:1*t*	0.1	13.1	42.8	8.2	8.1
C18:1*c*	22.4	40.1	28.9	27.7	23.5
C18:2*c,t/t,c/t,t*	0.2	3.9	0.7	1.6	1.7
C18:2*c,c*	54.8	23.5	2.3	34.8	30.8
C18:3	7.9	0.9	0.2	3.2	3.2
Iodine value	128	94	68	104	90
Dropping point (°C)	—	22.3	41.6	49	56.9
Peroxide value (RB)	—	—	—	0.9	1.0
Peroxide value (RBD)	—	0.1	0.1	0.0	0.2
Free fatty acid (% oleic) (RB)	—	—	—	0.03	0.04
Free fatty acid (% oleic) (RBD)	—	0.01	0.02	0.01	0.02

[a]RB, refined, bleached; RBD, refined, bleached, deodorized; —, not determined.

TABLE 2
Triacylglycerol (TAG) Composition (%) of Hydrogenated Soybean Oils

TAG[a]	NiHSBO-IV94	NiHSBO-IV68	PdHSBO-IV104	PdHSBO-IV90
TDD	0.1	1.8	1.9	2.0
TTM	0.2	0.2	0.8	1.3
DDD	1.1	5.1	9.1	6.1
TDM	1.7	1.7	3.6	3.7
TDP	0.3	0.9	1.4	1.8
DDM	4.7	5.4	11.4	9.6
TMM	5.1	0.5	2.5	0.0
DDP	3.4	4.3	8.8	8.9
TMP	2.2	0.8	1.5	0.0
DMM	12.6	3.2	8.6	6.6
DDS	7.5	2.1	3.6	3.2
DMP	13.2	5.6	9.4	7.9
PDP	1.6	1.7	2.1	2.4
MMM	13.6	12.5	6.2	3.8
DMS	7.0	15.8	5.2	4.7
PMM	9.2	11.7	5.8	5.6
SDP	5.2	3.7	3.4	3.3
PMP	2.9	1.4	1.7	2.7
SMM	3.8	3.3	2.0	2.5
SDS	2.1	9.8	2.2	2.8
SMP	2.2	3.7	2.6	2.4
PPS	0.5	0.8	0.4	1.2
SMS	0.0	1.9	1.9	3.8
PSS	0.0	0.9	1.4	4.8
SSS	0.0	1.1	2.6	9.2

[a]M = 18:1*c* + 18:1*t*; D = 18:2*c,c* + 18:2*t,t*; T = 18.3*c* + 18:3*t*; P = palmitic; S = stearic. For other abbreviatons see Table 1.

(P and S). Patterns in the TAG compositions show that the commercial oil with IV = 68 contained the highest percentage of TAG with monoenes alone or in combination with P or S. Likewise, the commercial oil with IV of 94 had high percentages of monoenes, but they were in combination with the less stable dienes rather than saturated fatty acids. The electrochemical oils had more widespread TAG compositions across all TAG groupings rather than the 4–5 groups found in the commercial oils, indicating less selectivity; however, the monoene-containing TAG in the commercial samples are mixtures of C18:0*c* and C18:0*t*. The electrochemical oil with IV 104 had more monoenes and monoenes in combination with dienes, and the IV = 90 sample had more saturates and saturates with monoenes. TAG compositions can be evaluated for patterns indicative of potential margarine and shortening base stocks with special emphasis on the quantity of

MMM, SMM, PMM, and SDP. The commercial oils had good TAG compositions for base stocks with 31% of the TAG from MMM, SMM, PMM, and SDP for the IV 68 oil and 32% in the other commercial oil whereas the electrochemically hydrogenated oils had 15 and 17% . In comparing the TAG compositions of the two oils with the most similar IV, commercially hydrogenated NiHSBO-IV 94 and electrochemically hydrogenated PdHSBO-IV 90, the PdHSBO sample had significantly more dienes and saturates. The NiHSBO had generally greater amounts of monoenes. The TAG composition also can help predict the relative oxidative stability and frying oil stability. Compositions with no trienes and only one diene would have the greatest oxidative stability (18). Based on this TAG composition, all four of the oils would have good stability in high-stability applications with 99 and 74% of these TAG in the 68 and 94 IV commercial oils, respectively, and 64% and 56% of these TAG in the 90 and 104 IV electrochemical oils respectively.

Regiospecific composition. Compositions at the internal (position 2) and external (positions 1,3) carbons also provide information about suitability as potential base stocks. Natural oils have dienes concentrated at carbon 2 and saturated fatty acids at carbons 1,3 (18). These hydrogenated oils followed the same pattern, with few effects from type of hydrogenation (Tables 3,4). Although unmodified oils have no saturates at the carbon 2 position, base stocks should have saturates at position 2 in order to provide proper functionality (17). Based on these recommendations, the commercial oil with IV of 68 and both electrochemically hydrogenated oils would be appropriate for base stocks.

Chemical/physical analysis. Oxidation and hydrolysis were monitored by PV and FFA as a measure of primary oxidation products and hydrolysis, respectively. Electrochemical hydrogenation exposed oxidatively unstable bleached oil to both water and oxygen, thereby enhancing the potential for both hydrolysis and oxidation. PV for the electrochemically hydrogenated refined, bleached oils were low (0.9–1.0), indicating little oxidation after hydrogenation, and were 0 or 0.2 after deodorization (Table 1). FFA for the electrochemically hydrogenated refined, bleached oils were also low (0.03–0.04), indicating little hydrolysis after hydrogenation. FFA were 0.01–0.02 after deodorization. Both commercially deodorized oils had initial PV of 0.1 and FFA of 0.02. All PV and FFA measurements were low and within standard soy-

TABLE 3
Fatty Acid Composition (%) at TAG Carbon 2 of Hydrogenated SBO[a]

Fatty acid	NiHSBO-IV94	NiHSBO-IV68	PdHSBO-IV104	PdHSBO-IV90
C16:0	0.6	0.1	0.6	1.4
C18:0	3.0	9.7	5.4	3.6
C18:1*t*	16.3	53.6	9.8	7.3
C18:1*c*	42.3	32.2	31.0	28.6
C18:2*t,t/c,t/t,c*	3.8	1.1	2.0	2.5
C18:2*c,c*	32.6	3.1	47.8	51.3
C18:3	1.1	0.0	3.2	4.7

[a]For abbreviations see Tables 1 and 2.

TABLE 4
Fatty Acid Composition (%) at TAG Carbons 1(3) of Hydrogenated SBO[a]

Fatty acid	NiHSBO-IV94	NiHSBO-IV68	PdHSBO-IV104	PdHSBO-IV90
C16:0	16.1	17.8	15.9	16.7
C18:0	8.1	14.6	15.8	28.9
C18:1*t*	11.6	37.0	7.3	8.6
C18:1*c*	39.1	27.0	26.1	20.6
C18:2*t,t/c,t/t,c*	3.9	0.5	1.3	1.3
C18:2*c,c*	18.9	1.9	28.3	20.1
C18:3	0.9	0.2	3.2	2.5

[a]For abbreviations see Tables 1 and 2.

bean oil specifications (19). Readings for the dropping point, a measure of the effect of fatty acid composition on melting point, were significantly higher for the electrochemically hydrogenated products than for the commercial oils. Values of 49 and 56.9°C for the IV 104 and 90 oils, respectively, reflected the effect of low *trans* fatty acid content. Dropping points of 22.3 and 41.6°C were measured for the commercial oils with IV of 94 and 68, respectively. A margarine oil was prepared using 15% of the IV 90 electrochemically hydrogenated oil and 85% liquid soybean oil. The SFI of the blend was compared with that of a liquid margarine. Results (Fig. 1) showed different SFI curves for the two products; however, the SFI for the blend at 33°C was sufficient.

Sensory analyses. Hydrogenation of soybean oil introduces a characteristic aroma and flavor that can be removed by deodorization (1); however, the aroma can be evident when oil is heated at frying temperatures and in fried food es-

pecially in more highly hydrogenated oils (2). This complex aroma/flavor characteristic of hydrogenation, which has been described as waxy, fruity, flowery, and crayon-like (3), can be easily detected in a hydrogenation plant. Hastert (4) stated that although no particular compounds have been identified as definitely responsible for this odor/flavor, isomeric unsaturated acids probably produce the sensory response. Room odor tests not only reflect the odors emanating from a frying operation but also act as an indicator of the potential flavor of the fried food. The odors reported from heated oils in room odor tests have also been detected in flavor analyses of the foods fried in the oils (3). In this study of the room odor of the four hydrogenated oils, both overall odor intensities and hydrogenation odor intensities were significantly higher in the commercial samples than in the electrochemically hydrogenated oils (Fig. 2). The intensities of the hydrogenation odor in the electrochemical samples were at weak levels of 2.0 or less, whereas for the commercial oils the same odor had intensity levels in the moderate range from 4.5 to 5.5. There are many factors that could be responsible for formation of the characteristic hydrogenation odor compounds found in oils hydrogenated under commercial conditions such as high
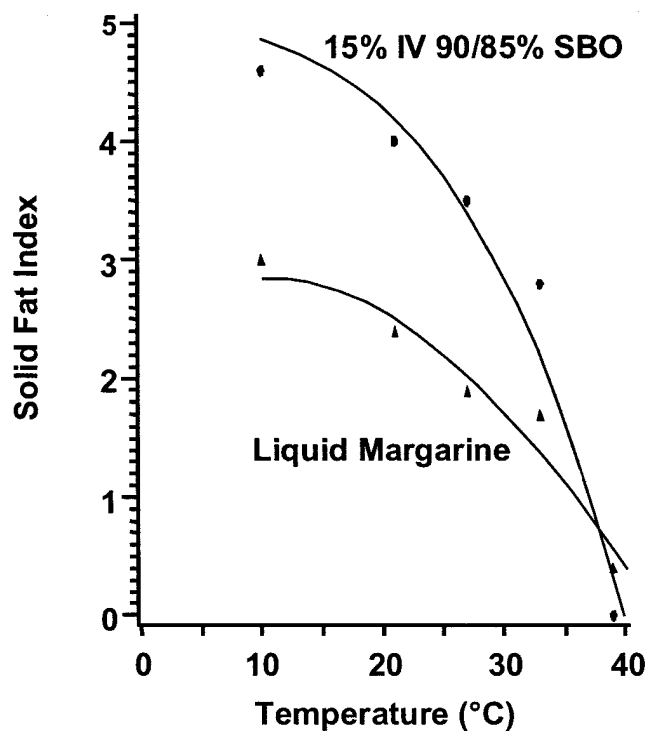

FIG. 1. Solid fat indices of commercial liquid margarine and blend of 15% electrochemically hydrogenated soybean oil (SBO) [iodine value (IV) = 90] with 85% liquid SBO.
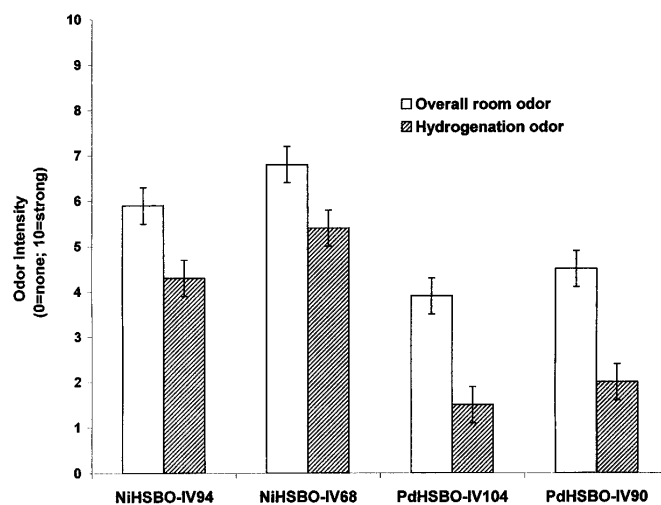

FIG. 2. Overall room odor intensity scores and hydrogenation odor intensity scores of hydrogenated oils. NiHSBO, commercially hydrogenated soybean oil; PdHSBO, electrochemically hydrogenated soybean oil; for other abbreviation see Figure 1. Error bars indicate standard deviations of the means of three replicate samples.

temperature (150–225°C) as well as type of catalyst (such as nickel) (20). Conditions for electrochemical hydrogenation included lower temperatures of 50–60°C as well as Pd or Pt catalysts which might contribute to lower hydrogenation odor intensities.

REFERENCES

1. Brekke, O.L., Deodorization, in *Handbook of Soy Oil Processing and Utilization,* edited by D.R. Erickson, American Soybean Association and American Oil Chemists' Society, St. Louis, 1980, pp. 155–191.
2. Warner, K., T.L. Mounts, and W.F. Kwolek, Effects of Antioxidants, Methyl Silicone and Hydrogenation on Room Odor of Soybean Cooking Oils, *J. Am. Oil Chem. Soc. 62*:1483–1486 (1985).
3. Warner, K., and T.L. Mounts, Frying Stability of Soybean and Canola Oils with Modified Fatty Acid Compositions, *Ibid. 70*:983–988 (1993).
4. Hastert, R.C., Hydrogenation, in *Bailey's Industrial Oil and Fat Products,* 5th edn., edited by Y.H. Hui, John Wiley & Sons, Inc., New York, Vol. 4, 1996, pp. 213–300.
5. Judd, J.T., B.A. Clevidence, R.A. Muesing, J. Wittes, M.E. Sunkin, and J.J. Podczasy, Dietary *trans* Fatty Acids: Effects on Plasma Lipids and Lipoproteins of Healthy Men and Women, *Am. J. Clin. Nutr. 59*:861–868 (1994).
6. Willett, W.C., and A. Ascherio, *Trans* Fatty Acids: Are the Effects Only Marginal? *Am. J. Publ. Health 84*:722–724 (1994).
7. Yusem, G., and P.N. Pintauro, The Electrocatalytic Hydrogenation of Soybean Oil, *J. Am. Oil Chem. Soc. 69*:399–404 (1992).
8. Holliday, R., J. King, J. Snyder, and G.R. List, Selective Hydrogenation of Vegetable Oils Using Mixtures of Supercritical Carbon Dioxide and Hydrogen, American Oil Chemists' Society Annual Meeting and Expo Abstracts, 1998, p. 44.
9. Tacke, T., S. Wieland, and P. Panster, Advanced Lipid Hydrogenation in Supercritical Fluids, *Ibid.,* p. 44.
10. An, W., J.K. Hong, P.N. Pintauro, K. Warner, and W.E. Neff, The Electrochemical Hydrogenation of Edible Oils in a Solid Polymer Electrolyte Reactor: I. Reactor Design and Operation, *J. Am. Oil Chem. Soc. 75*:917–925 (1998).
11. An, W., J.K. Hong, P.N. Pintauro, K. Warner, and W.E. Neff, The Electrochemical Hydrogenation of Edible Oils in a Solid Polymer Electrolyte Reactor: II. Hydrogenation Selectivity Studies, *Ibid. 76*:215–222 (1999).
12. Moulton, K.J., Laboratory Deodorization of Vegetable Oil, *Ibid. 66*:302–308 (1989).
13. Mounts, T.L., K. Warner, and G.R. List, Performance Evaluation of Hexane-Extracted Oils from Genetically Modified Soybeans, *Ibid. 71*:157–161 (1994).
14. Neff, W.E., and W.C. Byrdwell, Soybean Triacylglycerol Analysis by Reversed-Phase High-Performance Liquid Chromatography Coupled with Atmospheric Pressure Chemical Ionization Mass Spectrometry, *Ibid. 72*:1185–1191 (1995).
15. Neff, W.E., M.A.M. Zeitoun, and D. Weisleder, Resolution of Lipolysis Mixtures from Soybean Oil by a Solid Phase Extraction Procedure, *J. Chromatogr. 589*:353–357 (1992).
16. *Official Methods and Recommended Practices of the American Oil Chemists' Society,* 4th edn., edited by D. Firestone, American Oil Chemists' Society, Champaign, 1989.
17. List, G.R., T.L. Mounts, F. Orthoefer, and W.E. Neff, Margarine and Shortening Oils by Interesterification of Liquid and Trisaturated Triglycerides, *J. Am. Oil Chem. Soc. 72*:379–382 (1995).
18. Neff, W.E., T.L. Mounts, and W.M. Rinsch, Oxidative Stability of Purified Canola Oil Triacylglycerols from Genetically Modified Normal, High Stearic and Lauric Acid Canola Varieties as Affected by Triacylglycerol Composition and Structure, *J. Food Sci. Technol. 30*:793–799 (1997).
19. Brekke, O.L., Specifications for Soybean Oil, in *Handbook of Soy Oil Processing and Utilization,* edited by D.R. Erickson, American Soybean Association and American Oil Chemists' Society, St. Louis, 1980, pp. 377–381.
20. Smouse, T.H., Flavor Reversion of Soybean Oil in Flavor Chemistry of Fats and Oils, edited by D. Min and T. Smouse, American Oil Chemists' Society, Champaign, 1985, pp. 85–116.