various tactual factors that may be encountered with other media.

In the initial stages of this study, the vegetable oils were stored in screw-cap vials. The screw caps varied in their ability to maintain a complete seal and as a result, considerable variation was noted in the extent of oxidation from one vial to the next within a sampling period and between periods. Leaky seals might be responsible for the variation. When the oils were dispensed into pyrex vials, the vials degassed at 1 μ Hg and sealed at this pressure, stored samples showed no signs of oxidation over a 16-week period.

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Flavor Evaluation of Natural Soybean Oils of High and Low Linolenate Content

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Abstract

Three varieties of soybeans, Crest, Grant, and Hawkeye, were processed in the laboratory to obtain edible oils containing 10.4, 9.4, and 5.2% linolenate, respectively. Taste panel evaluations were significantly in favor of low-linolenate soybean oils. Both high- and low-linolenate oils gave the typical off-flavors of aged soybean oil. Flavor results indicate that the linolenate content of soybean oil will probably have to be reduced below 5% to achieve a significant quality improvement in commercially processed oils. Soybean oils of excellent quality can be prepared by laboratory processing procedures.

Introduction

THE THEORY THAT LINOLENATE esters are a primary source of off-flavors in soybean oil is widely accepted by the edible oil industry. Elimination of linolenate is a basic and underlying processing trend in the development of improved edible soybean and rapeseed oils in both Europe and America. Reduction in linolenate content of the oil through genetic studies has not been particularly successful for soybeans (16, 18) although it has been accomplished in rapeseed where reductions of over 50% have been reported (3, 14). For soybean oil, practical results on lowering linolenate content have been obtained only by hydrogenation with reduction of total unsaturation. Almost complete removal of linolenate is obtained in shortening products, but in specially prepared liquid cooking and salad oils, 2 to 3% linolenate is retained after partial hydrogenation and winterization (4,11). Processing for removal of linolenate through polymerization, selective extraction, or selective hydrogenation has not been commercially successful.

Comparison of the flavor and oxidative stability of crambe, mustard, rape, and soybean, all linolenate-containing oils, has been reported by Moser et al. (13). Flavor characteristics observed for these four oils agree with the observations of Holm and co-workers (8,9) on the stability of soybean and rapeseed oils. This study was undertaken to determine if oil obtained from beans selected for their linolenic acid content would show a difference in kind or quality of flavor.

Materials and Methods

Three samples of soybeans were furnished by the U.S. Regional Soybean Laboratory at Urbana, Illinois, to members of the Soybean Processors Association, National Soybean Research Council, who were to cooperate in this study. These varieties were identified as Hawkeye, grown near Urbana, Illinois; Crest, near Fosston, Minnesota; and Grant, near Sabin, Minnesota.

The samples of beans, 14 lb each, were cleaned by hand, and weed seeds, dirt balls, and damaged beans removed. The cleaned beans were flaked in pilot-plant milling equipment. Processing consisted of cracking, screening, dehulling by aspiration, heat and moisture conditioning the grits, and flaking. The flakes were immediately placed in a 5-gal Pyrex carboy and extracted with redistilled petroleum ether. The flakes were completely covered with solvent and allowed to soak approximately 2 hr without agitation or stirring at room temperature. The solvent was removed by filtration through several folds of fine-mesh cheesecloth tied over the end of the carboy. Three such extractions were made plus a final washing of the flakes by hand shaking the entire carboy. The miscella was filtered through paper to remove fines and concentrated in rotating evaporators. Final concentration was accomplished by means of evaporation under diminished pressure, obtained from a mechanical vacuum pump while the oil was heated in a water bath. Oil from the Crest variety foamed badly and some was lost in the final stripping.

TABLE I

Processing Data

Variety	Condition	Moisture content, %	Oil yield, %	Oil content,[a] %
Hawkeye	Some bean damage	8.63	21.4	23.3
Crest	Some green, damaged, and broken beans	9.95	18.8	21.1
Grant	Beans rather small; cleanest of 3 lots, but contained some weed seeds	10.15	19.9	20.7

[a] Standard petroleum extraction—AOCS Ac 3-44.

[1] A laboratory of the No. Utiliz. Res. and Dev. Div., ARS, USDA.
[2] A laboratory of the Crops Res. Div., ARS, USDA.

TABLE II

Peroxide Development

Variety	Initial[a]	60C—4 days[a]	AOM (8 hr)
Hawkeye	0.0	1.5	7.5
Crest	0.0	1.4	6.2
Grant	0.0	1.6	15.5
Commercial	0.0	11.1	88.1

[a] Determined at time of tasting.

Refining was done by the cup method in the laboratory by using 7.7% alkali with a 1% excess. The soaps were removed by centrifugation, and the oils were water-washed and separated by centrifugation. Oils were bleached for ½ hr at 97C with 4% bleaching mixture consisting of 15 parts bleaching earth and 1 part carbon. Deodorization was carried out for 3 hr at 210C in a 4-unit, all-glass laboratory deodorizer (15). The three oil samples and a control oil (a commercially refined bleached oil) were deodorized simultaneously, and all were given the same treatment. No metal scavengers or antioxidants were added to the oils.

Flavor evaluation of the oils was made on the freshly deodorized oils and on the same oils after they had been stored in loosely stoppered bottles for 4 days at 60C. The taste panel, composed of 15 members, used a scoring scale of 1 to 10 (10 = best) (12).

Results and Discussion

Selection of seeds and the removal of loose dirt, damaged beans, and weed seeds probably aided in producing an oil of superior stability and quality. Absence of damaged beans undoubtedly reduced the level of various oxidation products, including both volatile and nonvolatile flavors and their precursors. The concentration of dimers and other nonvolatile products resulting from preoxidation has a direct relationship to the quality and stability of refined soybean oil (6). Similar results have been published for rapeseed oil by Holm (9) who used a different method to measure the concentration of preoxidation material in rapeseed oil.

Processing data and yields of crude oil are presented in Table I. Yield of oil was as expected, and it indicated that the laboratory extraction was nearly complete and did not selectively fractionate the oil by removing a more soluble portion.

All laboratory-extracted oils showed exceptionally good oxidative stability when evaluated by chemical tests. Table II shows that peroxides slowly develop when oils are held at 60C or under AOM conditions for 8 hr. When compared to a control soybean oil that was commercially refined and bleached and then laboratory deodorized, the stability of the laboratory-processed oils was excellent and the oil from Hawkeye beans had good flavor stability. Peroxide levels developed in an oil are influenced by a great many factors, and the peroxides may or may not show any relationship to the level of linolenate.

In previous studies, oils with dimer contents of 1% or less were shown to have improved quality and flavor stability. In this study, the low dimer content of the carefully processed oils used imparts good stability to them (Tables II–IV) and confirms results of previous work. Flavor evaluation of the three laboratory samples processed are given in Table IV. Taste tests show that initially the oils are very good and are equal

TABLE III

Oil Characterization

Variety	I.V.	Dimer, %	Polar, %	Linolenate analysis	
				GLC,[a] %	Alkali isomerization,[b] %
Hawkeye	124.0	1.0	0.14	5.2	4.6
Crest	131.0	1.0	0.16	10.4	9.2
Grant	134.0	1.1	0.14	9.4	9.1
Commercial	130.0	1.4	0.17	7.4	....

[a] Average analyses from three cooperators.
[b] Ref. 2.

in quality. Upon aging the oils for 4 days at 60C, the flavor scores for Hawkeye (low in linolenate) are higher in every evaluation made against either Grant or Crest (high in linolenate). On repeated tastings (data not reported), only two tests out of four showed a significant difference at the probability level of 5%. However, one of the nonsignificant tests approached the significant level.

Flavor descriptions show that initially the oils are bland, buttery, and beany. The beany responses are more prominent than usual for freshly deodorized soybean oils. Grassy, rancid, and painty flavors developed in all samples upon aging. Prominent differences in flavor descriptions were not found between the high- and low-linolenate oil.

The quality of oil prepared on a small scale in the laboratory was exceptionally good. Considering all the hand operations and the exposure to air which these manipulations entailed, the results are much better than expected. Refining and bleaching of the processed oils was probably more severe than that used commercially. Two factors, upon which little information is available, are probably responsible for the high quality of the oil. One factor would be that only clean and sound beans were used; the other, that flakes were extracted immediately as they were removed from the flaking rolls. Clean beans plus extraction in glass undoubtedly reduced contamination and trace metal contents of the oils, which would result in improved oil stability. The effect of lipase and lipoxidase activity, as well as other enzymes, on flavor deterioration was not evaluated. Deteriorating effects resulting from enzyme activity would probably be the same if it arose from damaged beans, where a small amount of material can react over a long period of time, or from flaked beans, where a lot of material is exposed to enzyme activity for a relatively short interval. Lipoxidase reportedly is heat sensitive (10). For example, off-flavor of underblanched corn on the cob is attributed to lipoxidase activity (17). Noticeable enzyme inactivation occurs above 20C. Complete inactivation is reported within 4 min at 80C (1). Thus, temperatures attained in tempering and on the flaking rolls (150F) may not be sufficient to cause complete enzyme inactivation.

Oil from old beans is reported to be less stable than oil processed from new beans (5). Evidently these and many other factors contribute to oil quality. Our

TABLE IV

Flavor Evaluation of Oils Processed Experimentally

60C (days)	Hawkeye	Crest	Grant	Commercial[a]	Significance[b]
0	8.4	8.1	7.9	8.3	+
4	6.9	5.9			**
4	6.1		5.8		+
4		5.5	5.8		+
4			5.1	3.2	**
4	5.3			3.4	**

[a] Commercially refined and bleached, laboratory-deodorized.
[b] + None
** Significant at the 1% level.

experience indicates that high-quality soybean oil can be produced only when the many individual factors are controlled, each exhibiting small effects by themselves but in summation having an appreciable effect on quality and stability of the oil.

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Solvent Winterization of Partially Hydrogenated Soybean Oils[1]

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Abstract

Among the important advantages of solvent as compared with conventional winterization of soybean oil are the speed of operation and increased yields up to 25%. Easier and faster filtration results with the solvent system despite the high yields of solids when low iodine value (IV) oils are winterized at low temperatures. Hydrogenated stocks with IV as low as 90 can be winterized easily at temperatures of −16C. The time of winterization can be reduced from several days to a few hours. With all the variations possible in IV, temperature, and solvent selectivity, liquid soybean oil can be produced with specified characteristics and with a minimum linolenate content. Acetone was the best solvent tested for winterization.

Introduction

PARTIALLY HYDROGENATED SOYBEAN oils contain high melting constituents that must be removed to obtain clear, stable salad oils. It has been reported that partially hydrogenated soybean oil can be winterized with considerable success in the same manner as cottonseed oil (6). Some of the problems in the winterization process are low yields of liquid oils, long holding times required for crystallization, and difficulty of filtration. These problems become acute when the fat has been hydrogenated to low levels (IV. 90). Solvents lower the viscosity, and a lower cooling temperature allows formation of hard crystals that are easily filtered and washed. Solvent winterizations have been reported for cottonseed oil (2,4,11) and other edible fatty materials (1,8,15), but for soybean oil most of the fractionations recorded in the literature were done to improve drying oil properties (3,7,9,10,16). The results of extensive solvent winterization of partially hydrogenated soybean oils are reported here.

[1] Presented at AOCS meeting in New Orleans, La., 1964.
[2] A laboratory of the No. Utiliz. Res. and Dev. Div., ARS, USDA.

Materials and Methods

Soybean Oil. Commercially refined and bleached soybean oils (IV. 128) were used in this study.

Catalysts. Two nickel catalysts widely employed by industry for the selective hydrogenation of soybean oil were used. Catalyst A contained 24.4% nickel dispersed in hydrogenated cottonseed oil flakes. Catalyst B contained 65% nickel on kieselguhr.

Hydrogenation. Soybean oil was hydrogenated under selective conditions in a 3-gal stainless-steel convertor at 170C with a hydrogen pressure of 5 lb (6).

Winterization. Conventional and solvent winterization techniques were compared. For the conventional method hydrogenated fats were cooled slowly in Dewar flasks for a minimum of 3 days in a +6C constant temperature room then filtered under vacuum. Solvent winterization was conducted at temperatures ranging from −16C to +6C. The solutions were cooled rapidly and left for a minimum of 3½ hr then filtered under vacuum. The filter cakes were washed with enough solvent at the proper temperature to cover the cakes, and washings were combined with the filtrates. Each winterization fraction was stripped of solvent on rotating vacuum evaporators.

Analysis. Fatty acid content of each fraction was determined as methyl esters by gas-liquid chromatography on a ¼ in. × 3 ft aluminum column containing 25% diethylene glycol succinate on Chromosorb W (17), with a flame ionization detector. Percent isolated *trans* was determined by infrared spectroscopy and calculated as methyl elaidate. The IV of the frac-

TABLE I

Hydrogenated-Winterized Soybean Oil Solvent Concentration

Fractions obtained at 6C	Percent acetone	Yield, %	IV.	Percent *trans*
Hydrogenated SBO	—	—	87.2	31.0
Hydrogenated-winterized SBO				
Liquid	10	60.6	95.6	29.8
Solid	10	39.4	74.8	35.3
Liquid	25	73.4	93.7	29.8
Solid	25	26.6	71.8	34.0
Liquid	80	85.2	93.1	27.2
Solid	80	14.8	56.4	34.7