Flavor and Oxidative Stability of Hydrogenated and Unhydrogenated Soybean Oils: Effects of Antioxidants[1]

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ABSTRACT

Flavor and oxidative stabilities were studied by organoleptic evaluation and chemical analysis of three different samples of soybean oil: unhydrogenated (I); hydrogenated with nickel catalyst (II); and hydrogenated with copper-chromium catalyst (III). Analyses for these oils were:

	I	II	III
Iodine Value	138	109	113
Linolenate, %	8.3	3.3	0.4

Each oil was deodorized with the addition of either citric acid alone or citric acid plus BHA and BHT antioxidants. Addition of antioxidants did not improve the flavor stabilities of the oils in accelerated storage tests but did improve the flavor stabilities of II and III in light exposure tests. All three oils that received the same additive treatment had equivalent flavor stability in both accelerated storage and light exposure tests. However, both hydrogenation and antioxidant treatment improved oxidative stability as measured by the Active Oxygen Method. There was good correlation between flavor score and the logarithm of the peroxide value determined at the time of tasting.

INTRODUCTION

Considerable research at this and other laboratories has provided information concerning the flavor and oxidative stability of soybean oil (1-6). Early reports established the vital role of citric acid as a metal inactivator (1) and the improved storage stability of soybean oils treated with this additive (2). Evans et al. (3) prepared hydrogenated winterized soybean oils of decreasing iodine value (IV) and linolenic acid content, which were deodorized, stabilized with added citric acid, and evaluated organoleptically, using the unhydrogenated oil as a control. They reported that neither the initial flavor nor flavor after 4 days storage at 60 C showed any relationship to either IV or linolenic acid content. Oxidative stability as measured by the active oxygen method varied directly with IV. Cowen et al. (4) reported that the flavor and oxidative stabilities of citrated, copper-reduced oils were inversely related to the linolenic acid content. In comparisons with undydrogenated oils, treatments more severe than 4 days at 60 C were necessary to achieve significant differences in flavor evaluations. Similar results were reported by List et al. (5) when they evaluated oils produced in plant-scale copper hydrogenation runs. Moulton et al. (6) blended laboratory hydrogenated and processed soybean oil and commercially deodorized soybean salad oil to give samples containing increasing amounts of linolenic acid. There was no consistent significant difference between the 0% linolenic acid oil and the 1% and 2% linolenic acid blends. Flavor stability of commercially processed soybean salad oils packaged under air was evaluated during long-term storage at 78 F and 100 F by Evans et al. (7). Partially hydrogenated and antioxidant-treated oil showed little improvement over nonhydrogenated oil at 100 F. At 78 F, improvement was slight and only during the early part of storage.

In studies with tocopherol-free soybean oil (8), antioxidants were shown to be ineffective for improving flavor stability. It is theorized that the high linolenic acid content accounts for the ineffectiveness of antioxidants added to soybean oil. Added antioxidants did improve the flavor and oxidative stability of sunflower oil (9), which has a very low linolenic acid content.

In the present study we have attempted to evaluate the effectiveness of antioxidants in improving the flavor and oxidative stability of soybean oils of decreasing linolenic acid content. At the same time, the flavor and oxidative stability of unhydrogenated and hydrogenated soybean oils were determined and compared.

EXPERIMENTAL PROCEDURES

Materials

To minimize the effects of oil variability, we have used a single lot of refined and bleached soybean (I) oil obtained from Riceland Foods (Stuttgart, AR) for preparation and evaluation of the samples used in this study. Hydrogenations were performed using commercial catalysts: (a) G-15, 25% nickel in tristearin (Girdler Chemical, Inc., Louisville, KY) and (b) Cu-1106P, 39% CuO, 43.5% Cr_2O_3, and 10% BaO (Harshaw Chemical Co., Cleveland, OH). Crystalline butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) antioxidants used to treat the oils were obtained from Eastman Chemical Products, Inc. (Kingsport, TN).

Methods

Two-liter batches of oils were hydrogenated in a 1-gal, 316 stainless-steel vessel, magnetically stirred, and equipped with a gas-dispersing agitator. Nickel-catalyzed reactions were performed at 185 C, 10 psig (H_2), catalyst concentration of 0.1% nickel, by weight; agitation was at 1200 rpm (reaction time: 8.4 min). Copper-catalyzed reactions were performed at 170 C, 30 psig (H_2), catalyst concentration of 0.4% copper, by weight; agitation was 1200 rpm (reaction time: 246 min). Reductions were allowed to proceed so as to produce a partially hydrogenated oil having an IV in the range of 110-115 as estimated by monitoring hydrogen uptake. Four successive hydrogenations were executed with each catalyst. The partially hydrogenated oils from each run were filtered to remove catalysts, bleached with 0.5% activated clay (Super Filtrol), and blended to yield 8 liters each of the nickel-hydrogenated (II) and copper-hydrogenated (III) oils.

Methyl esters were prepared from each of the oils with sodium methoxide catalyst using a modification of the procedure described by Christopherson and Glass (10), in which ethyl ether replaced petroleum ether. Ester compositions were determined from gas chromatography curves obtained with a Varian Aerograph GC instrument equipped with dual 6 ft x 1/8 in. stainless-steel columns packed with 15% EGSS-X on Gas Chrom P 100/120 mesh (Applied Science Laboratories, Inc., State College, PA), and with flame ionization detectors.

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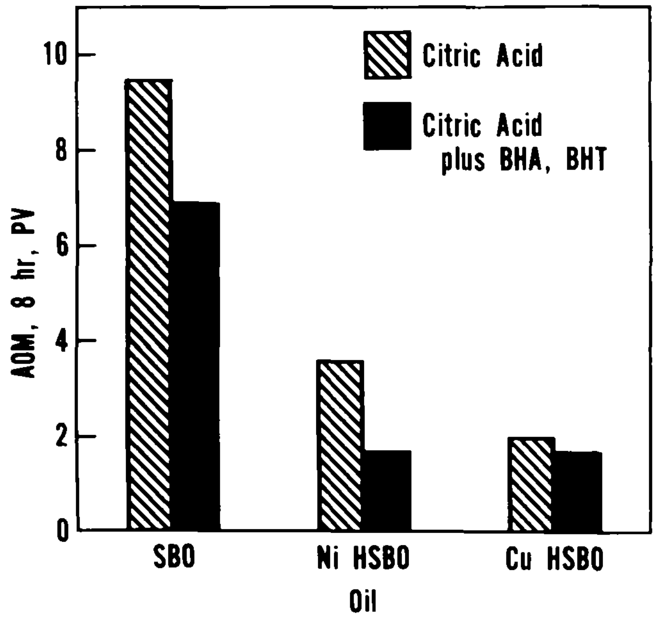


FIG. 1. Modified odor and flavor evaluation system.

The column temperature was 185 C; carrier gas was nitrogen at a flow rate of 20 ml/min. The analog signal from the detector was fed to a Mod-Comp real-time computer programmed to integrate areas under the curves, calculate the composition, and return a formatted report via a laboratory teletype immediately following completion of the chromatogram.

Deodorizations were performed in an all-glass, 4-unit deodorizer, described previously (11). Four 1-liter portions of an oil were deodorized simultaneously at 210 C and 1mm (Hg) for 3 hr, 5% stripping steam. Each portion of oil was treated with citric acid (0.01%), while two of the portions were also treated with the antioxidants BHA (0.01%) and BHT (0.01%). Treatments were made by additions to the oil on the cooling side of deodorization. Citric acid was added as a 20% aqueous solution and the antioxidants as a 10% ethanolic solution. The water and ethanol were removed in the final stages of deodorization during cooling of the oil under vacuum. The two portions subjected to identical additive treatment were blended to yield 2 liters of deodorized oil. Portions of each oil (I, II, and III) were deodorized as described. Repeat deodorizations were performed and blended as necessary to maintain adequate supplies of deodorized oil.

Organoleptic evaluations were conducted by methods described by Moser et al. (12) with a modified score sheet by which the panelist evaluates the oil based on its overall intensity of odor or flavor and provides a description of the odors and flavors perceived, indicating individual intensity values. The score sheet is essentially the same as that illustrated in a previous paper (13). The Odor and Flavor Evaluation System portion of that score sheet has been modified as shown in Figure 1. This modification was designed to yield an evaluation of the oils on the basis of perceived intensity of odor or flavor, rather than on the panelists' subjective conclusion as to whether the oil is good or bad. The goal of the evaluation remains the same, to perceive differences in oils arising from different processing procedures and/or treatments. Sensory evaluation was performed by a 17-member experimental taste panel. Most results were obtained by comparison of two samples, except for some initial evaluations on three freshly deodorized oils. Accelerated storage tests at 60 C and light exposure tests were carried out as described previously (7,14).

Peroxide values were determined at the time of tasting by a modification of the Wheeler method (15). Active oxygen determinations were carried out according to the AOCS official method Cd 12-57 (16).

RESULTS AND DISCUSSION

The fatty acid compositions of the initial oil and the hydrogenated oils, as determined by gas liquid chromatography, are presented in Table I. While both of the hydrogenated oils have IV's in the 109-114 range, the linolenic acid content was 3.3% in II and 0.4% in III. This reflects the greater selectivity of copper catalysis for reduction of linolenic acid (17).

Oxidative stability as measured by the 8-hr AOM peroxide value, was improved by hydrogenation, as would be expected (Fig. 2). Reduction of the linolenic acid content to less than 1.0%, as in III, further enhanced the oxidative stability of the oil. Addition of the antioxidants increased the AOM stability of the oils to some extent.

The results of paired sample evaluations of I and each hydrogenated oil, comparing the oils treated with citric acid only to those treated with citric acid plus the antioxidants, are presented in Table II. All of the deodorized oils had good initial flavor intensity scores. Antioxidants added to I did not enhance the flavor stability as measured after 4- and 8-day accelerated storage tests at 60 C. Although a significant improvement in the flavor stability in II by the addition of antioxidants was indicated after the 4-day accelerated storage test, there was no significant difference between the flavor scores of the oils evaluated after storage for 8 days. Citrated III, with and without added antioxidants, exhibited good flavor stability in accelerated storage tests. Oils evaluated after each storage period showed no significant difference in flavor intensity scores.

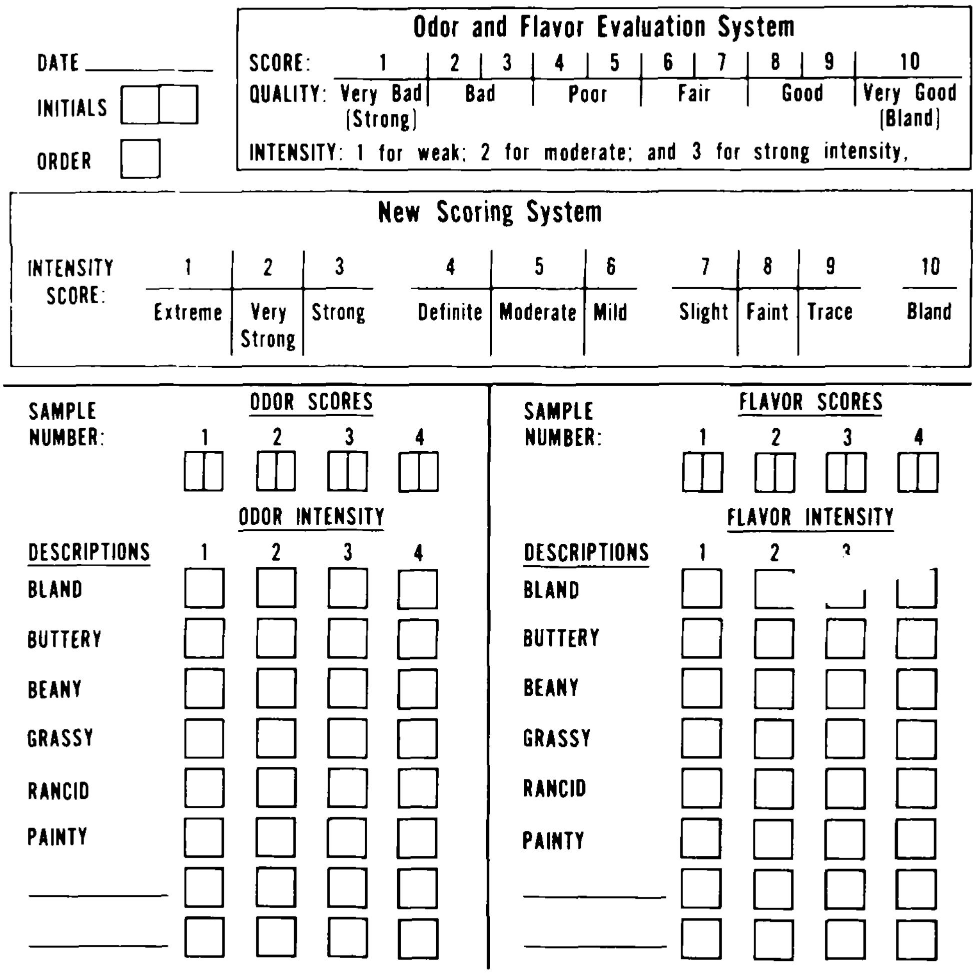
The effect of hydrogenation on flavor stability was evaluated in tests comparing each hydrogenated oil to

TABLE I

Fatty Acid Composition of Soybean Oils (Wt %)

	Unhydrogenated oil (I)	Nickel-reduced oil (II)	Copper chromite-reduced oil (III)
C 16:0	10.2	10.5	10.4
C 18:0	3.4	4.2	3.7
C 18:1	22.3	47.6	41.3
C 18:2	55.5	34.4	44.2
C 18:3	8.6	3.3	0.4
Calc. IV[a]	138	109	113

[a] Iodine value.



DATE ________

INITIALS ☐☐

ORDER ☐

Odor and Flavor Evaluation System

SCORE:	1	2	3	4	5	6	7	8	9	10
QUALITY:	Very Bad (Strong)	Bad		Poor		Fair		Good		Very Good (Bland)

INTENSITY: 1 for weak; 2 for moderate; and 3 for strong intensity.

New Scoring System

INTENSITY SCORE:	1	2	3	4	5	6	7	8	9	10
	Extreme	Very Strong	Strong	Definite	Moderate	Mild	Slight	Faint	Trace	Bland

SAMPLE NUMBER:	ODOR SCORES 1	2	3	4
	☐☐	☐☐	☐☐	☐☐
	ODOR INTENSITY			
DESCRIPTIONS	1	2	3	4
BLAND	☐	☐	☐	☐
BUTTERY	☐	☐	☐	☐
BEANY	☐	☐	☐	☐
GRASSY	☐	☐	☐	☐
RANCID	☐	☐	☐	☐
PAINTY	☐	☐	☐	☐
________	☐	☐	☐	☐
________	☐	☐	☐	☐

SAMPLE NUMBER:	FLAVOR SCORES 1	2	3	4
	☐☐	☐☐	☐☐	☐☐
	FLAVOR INTENSITY			
DESCRIPTIONS	1	2	3	
BLAND	☐	☐	☐	☐
BUTTERY	☐	☐	☐	☐
BEANY	☐	☐	☐	☐
GRASSY	☐	☐	☐	☐
RANCID	☐	☐	☐	☐
PAINTY	☐	☐	☐	☐
________	☐	☐	☐	☐
________	☐	☐	☐	☐

FIG. 2. AOM-oxidative stability of soybean oils.

TABLE II

Effects of Antioxidants

Oil	Citric acid only	Significant	Citric acid plus 0.01% ea. BHA, BHT
	Flavor intensity scores and significance		
		Initial	
I	8.0 (0.1)[a]	+[b]	8.1 (0.4)
II	7.4 (0.4)	+	8.0 (0.5)
III	7.5 (0.0)	+	8.2 (0.0)
		Storage @ 60 C, 4 days	
I	7.2 (1.2)	+	6.7 (1.1)
II	6.2 (0.8)	**[c]	7.6 (0.8)
III	7.1 (1.0)	+	7.5 (1.0)
		Storage @ 60 C, 8 days	
I	5.6 (5.2)	+	5.3 (7.2)
II	6.0 (3.2)	+	6.1 (2.3)
III	6.6 (2.6)	+	5.7 (2.1)

[a] Figures in parentheses are peroxide values determined at the time of tasting.
[b] + Indicates no significance at the 5% level.
[c] ** Denotes significance at the 1% level.

the control SBO and to each other as well. In these tests oils treated with citric acid only were compared to each other, and comparisons were made between those oils which had been treated with citric acid plus antioxidants. Results of these evaluations are presented in Table III. As in previous tests, all of the deodorized oils had good initial flavor scores. There was no significant difference in the flavor scores of any of the oils compared in these paired sample evaluations after 4- and 8-day storage tests.

Limited 4-hr light-exposure tests were conducted, and the results of flavor evaluations of oils subjected to this test are presented in Table IV. The addition of antioxidants did not yield a significant improvement in the flavor scores of I exposed to light. There was a significant improvement, at the 5% level, in the flavor score of II and III by the addition of antioxidants. Comparison between the oils receiving specific additive treatment indicated that there was no significant difference in the flavor stability of the control SBO and hydrogenated

TABLE III

Effect of Hydrogenation

	Flavor intensity scores and significance				
	I		II		III
			Initial		
CA only	7.9 (0.0)[a]	+[b]	7.0 (0.2)	+	7.5 (0.0)
			+		
CA plus BHA, BHT	7.9 (0.0)	+	8.2 (0.1)	+	8.6 (0.0)
			+		
			Storage @ 60 C, 4 days		
CA only	6.4 (1.4)	+	7.0 (1.2)		
	6.8 (0.7)		+		6.8 (1.0)
			6.6 (0.8)	+	7.1 (0.8)
CA plus BHA, BHT	7.0 (1.4)	+	7.3 (1.2)		
	7.2 (0.9)		+		7.2 (0.9)
			6.9 (0.6)	+	6.7 (0.8)
			Storage @ 60 C, 8 days		
CA only	5.1 (10.0)	+	5.7 (6.0)		
	6.2 (10.0)		+		5.7 (4.5)
			5.4 (8.0)	+	5.9 (4.6)
CA plus BHA, BHT	6.1 (6.3)	+	6.2 (2.4)		
	5.3 (6.4)		+		5.5 (3.2)
			6.2 (3.4)	+	7.1 (4.3)

[a] Figures in parentheses are peroxide values at time of tasting.
[b] + Indicates no significance at 5% level.

TABLE IV

Light-Exposure Tests (4 hr)

	Flavor intensity scores and significance Effect of antioxidants		
Oil	CA only	Significance	Ca plus BHA, BHT
I	6.9 (1.2)[a]	+[b]	7.0 (1.6)
II	6.4 (0.9)	*[c]	7.1 (0.9)
III	6.3 (1.1)	*	6.8 (1.2)

[a] Figures in parentheses are peroxide values at time of tasting.
[b] + Indicates no significance at the 5% level.
[c] * Shows significance at the 5% level.

TABLE V

Flavor Intensities of Soybean Oils

		Initial						
			Initial flavor intensity value[b] (FIV)					
Oil	Additive	FIS[a]	Buttery	Beany	Nutty	Grassy	Rancid	Painty
I	Citric acid	7.9	0.6	0.3	0.1	---	---	---
II	Citric acid	7.2	0.6	0.3	---	---	0.1	---
III	Citric acid	7.5	0.7	0.3	0.3	---	---	---
I	Citric acid plus BHA, BHT	8.0	0.6	---	0.4	---	---	---
II	Citric acid plus BHA, BHT	8.1	0.8	0.2	0.1	---	---	---
III	Citric acid plus BHA, BHT	8.4	0.7	---	0.4	---	---	---

[a] Flavor intensity score.

[b] $\text{Flavor intensity value} = \frac{1\ (\text{No. weak}) + 2\ (\text{No. moderate}) + 3\ (\text{No. strong})}{(\text{No. of tasters})}.$

TABLE VI

Flavor Intensities of Soybean Oils

		4 Days storage @ 60 C						
			Flavor intensity value[b] (FIV)					
Oil	Additive	FIS[a]	Buttery	Beany	Nutty	Grassy	Rancid	Painty
I	Citric acid	6.7	0.7	0.3	0.2	0.2	0.4	---
II	Citric acid	7.5	0.8	0.1	---	0.2	0.3	0.1
III	Citric acid	7.0	0.7	0.3	0.3	0.3	0.4	---
I	Citric acid plus BHA, BHT	6.9	0.6	0.4	0.2	0.3	0.3	0.1
II	Citric acid plus BHA, BHT	7.0	0.9	0.1	---	0.1	0.1	---
III	Citric acid plus BHA, BHT	7.2	0.9	0.1	0.1	0.1	0.2	---

[a] Flavor intensity score.

[b] $\text{Flavor intensity value} = \frac{1\ (\text{No. weak}) + 2\ (\text{No. moderate}) + 3\ (\text{No. strong})}{(\text{No. of tasters})}.$

oils after exposure to light.

Based on the concurrent determinations of flavor intensity score and peroxide value as described here, a correlation coefficient of 0.76 was found between the flavor intensity score and the logarithm of the peroxide value. This value compares favorably to the 0.8 correlation coefficient found between the flavor score, as determined using the previous evaluation system, and the logarithm of the peroxide value (1).

A further characterization of the oils is obtained by analyzing the flavor descriptions and flavor intensity values (FIV) (18) which are an integral part of the organoleptic evaluation. The descriptions of FIV's are presented in Tables V-VII for the initial, 4-day and 8-day storage tests. Data in these tables are pooled and averaged values from the multiple tests performed. Buttery was the predominant description given for each of the oils initially, with a few beany and nutty descriptions included. All of these flavors are acceptable and are characteristic of quality soybean oil. After 4 days storage at 60 C (Table VI), the more objectionable flavors, grassy and rancid, were perceived to some extent in all of the oils. After 8 days at 60 C (Table VII), all of the oils showed the effects of this severe storage treatment. Rancid descriptions predominate and painty descriptions which were essentially absent at 0 and 4 days storage, were cited by the panelists.

It appears from the results presented here that while hydrogenation of soybean oil and treatment with antioxidants does improve the AOM oxidative stability of the oil, they do not yield significant improvement of the flavor stability of the oil during storage. Antioxidants increased the flavor stability of hydrogenated oils subjected to light-exposure test conditions.

These findings have great significance for the edible oil industry because they indicate that the added costs inherent in hydrogenation and addition of antioxidants may not be required to ensure the flavor stability of

TABLE VII

Flavor Intensities of Soybean Oils

Oil	Additive	8 Days storage @ 60 C						
		Flavor intensity value[b] (FIV)						
		FIS[a]	Buttery	Beany	Nutty	Grassy	Rancid	Painty
I	Citric acid	5.7	0.5	0.4	---	0.3	0.8	0.5
II	Citric acid	5.9	0.7	0.5	---	0.5	0.7	0.3
III	Citric acid	6.0	0.6	0.4	---	0.4	0.7	0.3
I	Citric acid plus BHA, BHT	5.5	0.4	0.6	0.1	0.4	0.7	0.5
II	Citric acid plus BHA, BHT	6.3	0.8	0.3	---	0.4	0.6	0.1
III	Citric acid plus BHA, BHT	6.4	0.6	0.4	---	0.4	0.6	0.3

[a] Flavor intensity score.

[b] Flavor intensity value = $\frac{1\ (\text{No. weak}) + 2\ (\text{No. moderate}) + 3\ (\text{No. strong})}{(\text{No. of tasters})}$.

soybean oil products for uses other than cooking and frying.

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