

thermally oxidized oil (10,11). Chemical changes of the antioxidants were first indicated by the differential methanol extractabilities of the radioactive material present in the heated oil and in the unheated control. The presence of antioxidant alteration products in the heated oil was subsequently confirmed by the normal-phase HPLC analyses.

Although structures of the alteration products remain unidentified, it appears that the products are less polar than their corresponding parent antioxidants, as indicated by their elution sequence from the silica column. As shown by various model studies (12-14), autoxidation of phenolic compounds or their oxidation by other reagents produced compounds of quinone or epoxide nature. Monte and Maga (15) have demonstrated the formation of BHA dimers in water under stresses of sterilization. Also likely to occur in the frying oil is the radical addition of fatty hydroperoxides to the antioxidants, possibly in a manner similar to the adduct formation between linoleic hydroperoxides and  $\alpha$ -tocopherol (16).

Whatever the nature of the antioxidant alteration products, the real concern is the inevitable human exposure to compounds of undefined toxicity from the use of the additives. As our future goal, we plan to conduct short-term in vitro bioassays of oil fractions that have been enriched with the antioxidant alteration products and, subsequently, to identify and synthesize the ones which

gave positive responses for further toxicological testing in vivo.

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## ✿ Flavor and Oxidative Stability of Hydrogenated and Unhydrogenated Soybean Oil: Effect of Tertiary Butyl Hydroquinone<sup>1</sup>

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#### ABSTRACT

The efficacy of tertiary butyl hydroquinone (TBHQ) treatment for enhancement of the storage stability of soybean oil has been studied by flavor evaluation and chemical analysis. Soybean oils (I) unhydrogenated (IV = 137.7; % linolenate = 8.3), (II) hydrogenated with nickel catalyst (IV = 109.1; % linolenate = 3.3), and (III) hydrogenated with copper-chromium catalyst (IV = 112.8, % linolenate = 0.4) were each deodorized. In the cooling stage of the deodorizer, each oil was treated with citric acid plus TBHQ. These freshly deodorized oils were compared to separate batches of each oil treated with citric acid alone or with citric acid plus butylated hydroxyanisole and butylated hydroxytoluene. An analytical taste panel performed sensory evaluations by a paired sample test using an intensity rating scale system. The oils were also evaluated after being subjected to accelerated storage tests (4 days and 8 days at 60 C) and a fluorescent light exposure test (4 hr, ambient temperature). Peroxide development during storage was beneficially reduced in oils treated with TBHQ. The flavor stability of the three oils was not enhanced by treatment with TBHQ under any test conditions.

#### INTRODUCTION

Monotertiary butyl hydroquinone (TBHQ) was approved as a food grade oil soluble antioxidant in 1972 (1). It has

been reported that treatment of polyunsaturated oils with TBHQ could effect oxidative stabilization to the same extent as could be achieved by partial hydrogenation of the oils (2). Our previous investigation of stored soybean oils (3) showed that treatment with butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) antioxidants did improve the oxidative stability of citrated oils but did not impart improved flavor stability. The flavor and oxidative stability of citrated soybean oils treated with TBHQ now has been evaluated and compared to that of oils treated with citric acid (CA) only and with CA plus BHA/BHT.

#### EXPERIMENTAL PROCEDURES

The oils used in this study were prepared the same as those for our previous study (3), i.e., refined and bleached soybean oil (I), iodine value (IV) = 138, linolenate (Ln) = 8.3%; nickel-catalyzed hydrogenated soybean oil (II), IV = 109, Ln = 3.3%; copper-catalyzed hydrogenated soybean oil (III), IV = 113, Ln = 0.4%. Crystalline BHA, BHT and TBHQ (Eastman Chemical Products Inc., Kingsport, TN) were used for antioxidant treatments. One-liter portions of each oil were deodorized (210 C, 1 mm Hg, 5% sparge steam for 3 hr) (3) and treated with additives on the cooling side of deodorization at about 100 C (3). Additive

<sup>1</sup>Presented at ISF-AOCS Meeting, New York, NY, April 27-May 1, 1980.

**TABLE I**  
**TBHQ Stabilization**

Oil	Flavor intensity scores and significance		
	CA only	Significance	CA + 0.02% TBHQ
	Initial		
I	7.6 (0.0) <sup>a</sup>	+ <sup>b</sup>	7.6 (0.0)
II	7.6 (0.0)	+	7.4 (0.0)
III	8.0 (0.1)	+	7.3 (0.1)
	Storage at 60 C, 4 days		
I	6.8 (1.1)	+	6.7 (0.9)
II	7.0 (0.7)	+	7.3 (0.5)
III	4.7 (0.8)	** <sup>c</sup>	6.5 (0.7)
	Storage at 60°C, 8 days		
I	6.2 (3.3)	+	5.4 (1.3)
II	6.4 (5.0)	+	6.3 (0.4)
III	5.2 (6.7)	+	5.8 (1.2)

<sup>a</sup>Figures in parentheses are peroxide values determined at the time of tasting.

<sup>b</sup>+ Indicates no significance at the 5% level.

<sup>c</sup>\*\*Denotes significance at the 1% level.

**TABLE II**  
**TBHQ Stabilization**

Oil	Flavor intensity scores and significance		
	CA + 0.01 each BHA/BHT	Significance	CA + 0.02% TBHQ
	Initial		
I	7.8 (0.0) <sup>a</sup>	+ <sup>b</sup>	7.7 (0.1)
II	7.6 (0.0)	+	7.7 (0.0)
III	7.7 (0.0)	+	7.5 (0.0)
	Storage at 60 C, 4 days		
I	6.7 (0.9)	+	6.4 (0.8)
II	6.3 (0.5)	+	6.8 (0.5)
III	7.2 (1.3)	** <sup>c</sup>	5.8 (0.5)
	Storage at 60 C, 8 days		
I	5.7 (4.9)	+	5.6 (1.5)
II	7.0 (2.4)	+	6.6 (0.4)
III	6.5 (4.0)	**	5.1 (1.2)

<sup>a</sup>Figures in parentheses are peroxide values determined at the time of tasting.

<sup>b</sup>+ Indicates no significance at the 5% level.

<sup>c</sup>\*\*Denotes significance at the 1% level.

**TABLE III**  
**Effect of Hydrogenation<sup>a</sup>**

Storage at 60 C	Flavor intensity scores and significance		
	I	II	III
Initial	7.8 (0.0) <sup>b</sup> + <sup>c</sup>	7.6 (0.0)	
4 days	7.9 (0.0)	+	8.2 (0.2)
	6.6 (1.2)	+	7.0 (0.5)
8 days	7.4 (1.0)	+	7.8 (0.8)
		7.6 (0.6)	+
	6.4 (1.2)	+	6.3 (1.0)
	5.5 (1.3)	+	5.6 (0.9)
		5.8 (0.9)	+
			5.8 (0.8)

<sup>a</sup>All samples treated with CA + 0.02% TBHQ.

<sup>b</sup>Figure in parentheses are peroxide values determined at the time of tasting.

<sup>c</sup>+ Indicates no significance at the 5% level.

treatments were: 0.01% CA; 0.01% CA plus 0.01% each BHA/BHT; 0.01% CA plus 0.02% TBHQ. CA was added as a 20% aqueous solution, whereas antioxidants BHA, BHT and TBHQ were added as 10% ethanolic solutions. Chemical analyses, storage testing and sensory evaluations were the same as those previously described (3).

**RESULTS AND DISCUSSION**

The results of paired sample evaluations of the oils treated with CA only to those treated with CA plus TBHQ are presented in Table I. There was no significant difference in the flavor intensity scores for oils I and II, either initially or after 4 and 8 days of storage at 60 C. There appears to be some enhancement of flavor stability from treatment of III with TBHQ, since evaluation of the oils subjected to storage for 4 days at 60 C indicated a significant difference. However, no difference was noted when III was evaluated after storage for 8 days.

Flavor stabilization by TBHQ treatment of citrated oils was compared to that achieved by BHA/BHT treatment and the results of the paired sample tests are presented in Table II. The sensory panel noted no significant difference in flavor stability of oils I and II, either initially or after the accelerated storage tests. Treatment with TBHQ appeared to be less effective than BHA/BHT treatment for flavor stability of III, the low linolenate oil.

Results of paired sample evaluations comparing hydrogenated and unhydrogenated oils, all treated with CA plus TBHQ, are presented in Table III. As was observed in our previous study comparing oils treated with CA plus BHA/BHT (3), there was no significant difference in flavor scores in any of the accelerated storage tests.

Results of flavor evaluations of oils after light exposure tests are presented in Table IV. Oils treated with CA plus TBHQ were compared to the same oils treated with CA only or with CA plus BHA/BHT. There was no significant difference in flavor scores in any of the tests. This observation indicated that TBHQ treatment did not enhance the flavor stability during light exposure of the oils studied.

Peroxide development during storage was diminished in the citrated oils treated with TBHQ as compared with that in oils treated with CA only or with BHA/BHT (Tables I and II). These data demonstrate that TBHQ is an effective antioxidant since it retards the formation of peroxides.

As demonstrated here and in our previous study (3), phenolic antioxidants are ineffective in improving flavor stability of soybean oil during storage regardless of the linolenic acid content of the oil. Formation of measurable

**TABLE IV**  
**Light Exposure Tests (4 hr)**

Oil	Flavor intensity scores and significance		
	CA	Significance	CA + 0.02% TBHQ
I	6.8 (0.8) <sup>a</sup>	+ <sup>b</sup>	6.6 (1.2)
II	6.1 (0.8)	+	6.4 (1.1)
III	6.8 (1.0)	+	6.7 (0.7)
	CA + 0.01% each BHA/BHT	Significance	CA + 0.2 TBHQ
I	7.2 (0.9)	+	7.2 (0.8)
II	6.5 (0.9)	+	6.8 (0.7)
III	6.2 (0.9)	+	6.3 (0.6)

<sup>a</sup>Figures in parentheses are peroxide values determined at the time of tasting.

<sup>b</sup>+ Indicates no significance at the 5% level.

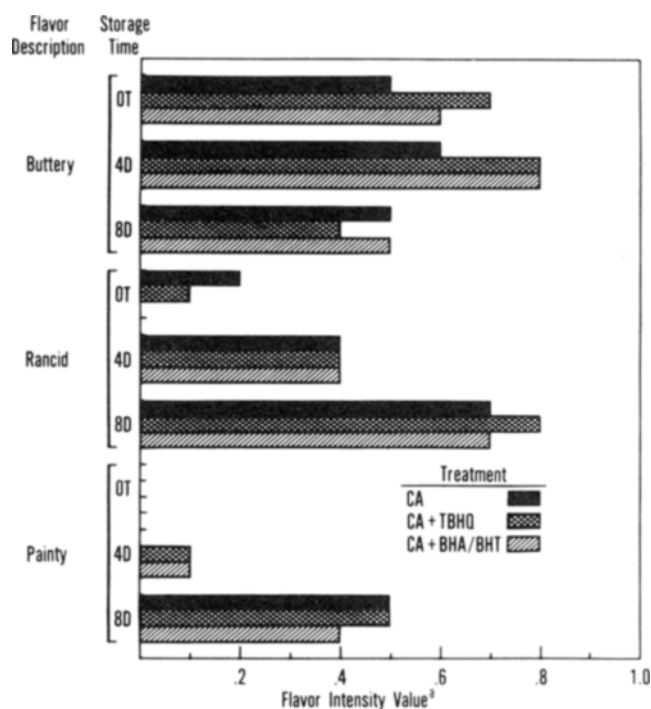


FIG. 1. Flavor deterioration during storage I-SBO. <sup>a</sup>Flavor intensity value (FIV) = 1 (# weak) + 2 (# moderate) + 3 (# strong)/(# tasters).

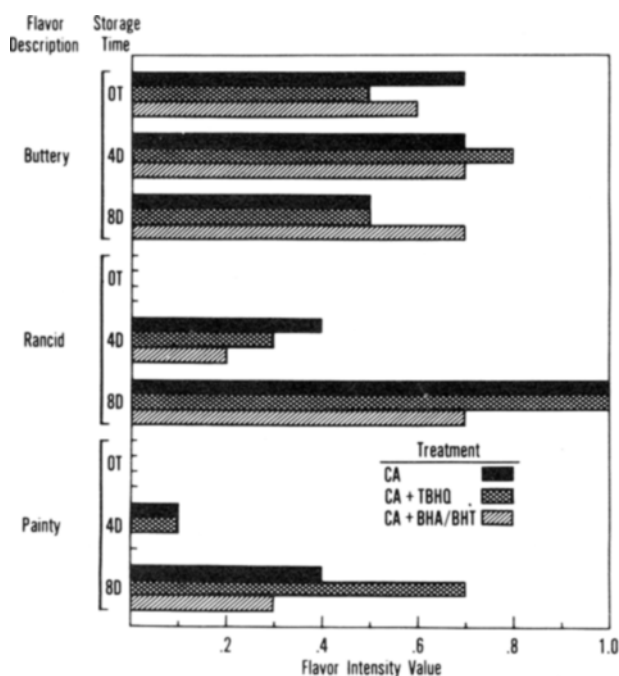


FIG. 2. Flavor deterioration during storage—II-NiHSBO.

peroxides is retarded by antioxidant treatment and this observation would tend to indicate that the flavor deterioration is nonoxidative. However, careful studies with taste panels have established that a very high correlation exists between the flavor score and the logarithm of the peroxide value with samples of similar history (4). Peroxide value, however is not always a measure of flavor quality. Storage, heat and other factors promote decomposition of peroxides. In hydrogenated oils with lowered linolenic acid content, isomeric dienes are formed which may retain a high concentration of terminal pentene radical, thought to

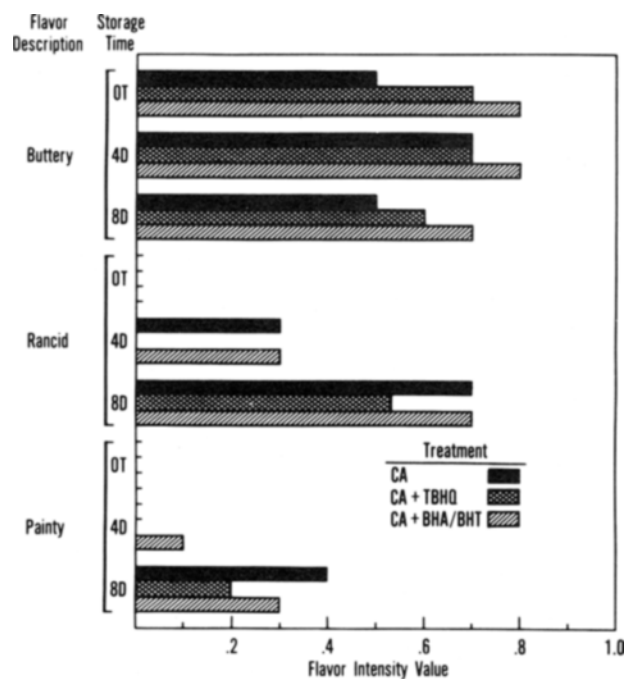


FIG. 3. Flavor deterioration during storage—III-CuHSBO.

be associated with loss of flavor quality. These and other factors of soybean oil flavor deterioration have recently been reviewed by Frankel (5).

Flavor descriptions and flavor intensity values (FIV) were obtained for each oil tested and were indicative of the flavor deterioration that occurs during storage as presented in Figures 1-3. Data plotted in the figures are the pooled and averaged values from the tests performed with each oil, i.e., with CA only and CA + BHA/BIIT treated oils, 2 tests at each storage time period; with CA + TBHQ treated oils, 4 tests. The flavor descriptions presented were the major flavor responses indicated by the panelists and show the progressive deterioration of the oils. Buttery was the predominant flavor description given for all of the oils initially. Rancid and painty descriptions were indicative of flavor deterioration during storage. The pattern of flavor deterioration is generally the same, regardless of additive treatment or content of linolenate in the oil. Rancid descriptions were given to the oils after 4- and 8-day accelerated storage tests. The panelists reported painty flavors only with the oils subjected to the 8-day accelerated storage test which indicated severe flavor deterioration had occurred.

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