Studies on Antioxidant Treatments of Crude Vegetable Oils

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Abstract

Treatments of crude safflowerseed, soybean, sunflowerseed and cottonseed oils with the antioxidant compounds butylated hydroxyanisole (BHA), propyl gallate (PG) and tertiary butylhydroquinone (TBHQ) have been investigated. PG and TBHQ were effective in inhibiting oxidative degradation of the crude oils subjected to long term storage as determined by measurement of peroxide formation in the oils during storage and by determination of AOM and oven (145 F) stabilities of the oils before and after storage. Of particular interest were the oxidative stability characteristics of these oils after they had been stored for relatively long periods in crude form (with and without the antioxidants) and then alkali refined, bleached and deodorized. The data from stability tests on these refined oils indicate that vegetable oils protected with potent antioxidants, such as PG or TBHQ, during storage in the crude form might yield refined, bleached and deodorized oils with somewhat higher initial oxidative stability and with better response to further antioxidant treatment.

Introduction

For over 20 years, synthetic antioxidants, such as butylated hydroxyanisole (BHA) and propyl gallate (PG), have played vital roles in the processing and marketing of vegetable oils for food use. Such antioxidant usage, however, has been primarily in the finished (refined, bleached and deodorized) oils and there has been practically no use of the antioxidants in crude vegetable oils. To some extent, reluctance to use antioxidants in the crude oils likely has stemmed from a general attitude that some oxidative degradation in the crude oil can be tolerated since subsequent refinement, bleaching and deodorization of the oil will remove the oxidation products and provide finished oil of good quality. Furthermore, quantitative removal of antioxidants from the oil during alkali refining, bleaching and deodorization can be demonstrated, hence economic considerations preclude addition of antioxidants to crude oil since they will not carry through into the deodorized product and their value in the crude oil has not been established. Perhaps another important factor discouraging the use of antioxidants in crude vegetable oils has been the lack of antioxidant compounds exhibiting adequate potency in vegetable oils, particularly the more highly unsaturated types such as safflowerseed oil.

A number of published articles have reported on various changes, oxidative and otherwise, occurring in crude vegetable oils during storage and some attempts have been made to relate these changes in crude oils to the quality (oxidative stability, color and other characteristics) of refined oils. Most of these reported studies have been conducted with cottonseed and soybean oils.

It is generally concluded that cottonseed oil cannot be stored satisfactorily in the crude state mainly because of color reversion, an increase in bleach color (1,2). On the other hand, Rao (3) concluded that crude cottonseed oil was very resistant to peroxide buildup when stored in glass and metal containers at 25–30 C. This stability he attributed to the presence of gossypol and certain phosphatides. Harwalker and Saletore (4) observed no noticeable oxidative degradation (peroxide buildup) in crude cottonseed oil under normal storage conditions for 70 days, but they observed a rapid increase in peroxide formation in the resultant refined oil during storage. The color instability of crude cottonseed oil has been related to the oxidation of the complex pigment system and this has been studied in numerous experiments (1,2,4–9). Treatments of crude cottonseed oil with chemical additives to combat color reversion have been investigated (2,10,11), with several chemicals such as para-aminobenzoic acid, sodium bisulfite, sodium sulfanilate and sodium phosphate, having been found somewhat effective. Similar evaluations of the effects of phenolic antioxidants, such as BHA and propyl gallate, on color reversion of cottonseed oil apparently have not been conducted.

With crude soybean oil, oxidation in the oil prior to deodorization has been shown to be detrimental to the flavor and oxidative stability of the finished oil as evidenced by carbonyl buildup (12). In these studies, increase in nonvolatile carbonyl content of the freshly deodorized oil was directly related to the peroxide value of the oil before deodorization. Chang and Kummerow (13,14) have proposed that oxidative polymers injected into soybean oil during processing could serve as precursors of flavor reversion compounds. Baumann et al. (15) demonstrated that crude and refined soybean oils held in drums under conditions simulating field tank storage are not expected to surpass critical levels of peroxide buildup (60 meq/kg) until after 3–4 years of exposure. These data suggest that stored, crude soybean oils with peroxide values under 60 meq/kg could be deodorized to produce salad grade oils with initial flavor quality equal to that of oils processed from stocks having considerably lower peroxide contents.

In the commercial production of safflowerseed oil, the crude oil may often be stored for extended periods before it is refined, bleached and deodorized. Because of relatively low natural antioxidant content and inherent oxidative instability of crude safflowerseed oil, oxidative deterioration may occur quite rapidly in the crude oil during such storage. This paper provides the results of a laboratory program designed primarily to study the effects of several phenolic type antioxidants in retarding oxidation of crude safflowerseed oil and to determine if such antioxidant protection of the crude oil during extended storage might enhance the oxidative stability characteristics of the deodorized oil. [Throughout this paper, the term deodorized oil stands for a finished oil prepared from crude oil by the alkali refinement, bleaching and steam deodorization methods described under Experimental Procedures.]

Since only limited information (3,16) has been developed on similar antioxidant treatments of crude cottonseed and soybean oils, this laboratory program was extended to include these oils. Also, in view of a growing interest in it as a commercial edible vegetable oil and because of the close resemblance of its composition to that of safflowerseed oil, sunflowerseed oil was included in this program.

The antioxidants selected for these studies were BHA and propyl gallate, two commercially available antioxidants commonly used in edible fats and oils, and tertiary butylhydroquinone (TBHQ), a compound which has been shown (17,18) quite effective in polyunsaturated oils but is still not cleared for food use. TBHQ is believed, on the basis of the earlier studies, to be superior in various respects to currently used antioxidants, so it was included in these studies to determine if it might fill the need for a more potent antioxidant to stabilize crude vegetable oils.

Experimental Procedures

Crude safflowerseed (two quantities from separate sources for two series of storage and stability tests), soybean, sunflowerseed and cottonseed oils were obtained from commercial suppliers of these oils. These crude oil samples for the laboratory studies were taken from stocks on hand of the oils intended for commercial usage and, to minimize oxidation prior to their use in the laboratory studies, they were packaged under nitrogen.

The antioxidants evaluated in these studies were butylated hydroxyanisole (BHA) and propyl gallate (PG), which are commercially available for food use, and a refined grade of tertiary butylhydroquinone (TBHQ) which has been evaluated (17,18) extensively in our laboratories as a potential antioxidant for edible fats and oils and is the subject of a petition to the U.S. Food and Drug Administration seeking its clearance for use as a direct food additive under Federal Food Additive Regulations. Where the antioxidants were added to the crude or deodorized oils, as indicated in the tables of data, such applications were carried out by their direct addition to the oils at 70 C with adequate agitation (about 20 min) to insure complete solution of the antioxidants in the oils.

Oxidative stabilities of the crude and deodorized oils were determined by two basic methods, AOM and oven stability tests. The AOM (active oxygen method) stabilities were determined in accordance with the method of Riemenschneider et al. (19) wherein clean, dry air is bubbled through the oil in a special aeration tube held at 210 F. Oxidative degradation of the oil under the AOM conditions is determined by measuring the peroxides in the oil by the iodometric method of Wheeler (20). The AOM stability of the oil was taken as the number of hours until the peroxide content of the oil reached 70 meq/kg oil. The oven stability tests (commonly referred to as Schaal Oven Tests) consisted of holding small samples (approximately 2 oz each) of the oils in capped, glass jars in a convection type, electrically heated oven at 145 F and evaluating the samples periodically for odor degradation attributable to oxidation. The endpoint in the oven stability test was the time in days until a rancid odor was detected in the sample by a majority of the organoleptic panel members.

Alkali refinement of the crude oil consisted of adding cold caustic (16° Baumé + 0.2% excess NaOH) to the oil at 80 F and then holding the mixture at this temperature for 20 min with moderate agitation. The agitation was decreased and the temperature was rapidly raised to 150 F to break the emulsion and to facilitate settling of the soapstock. The soapstock was allowed to settle for 1 hr. The refined oil was separated from the soapstock and washed twice with 10% portions of water.

The refined oil was bleached with a clay-diatomaceous mixture which was added to the oil at 180–200 F with agitation. After an additional 5 min of moderate stirring, a vacuum filtration system was used to separate the bleached oil.

Deodorization of the refined, bleached oil was carried out in a specially devised laboratory apparatus by heating the oil in the presence of steam at 400 F for 3 hr at a pressure of 2–4 mm Hg.

For the long term storage of the crude oils, the oils (about 1500 g for each storage test) were placed in half gallon, clear glass jars with screw caps. The samples were held at the storage temperatures and for the time periods indicated in the experimental data (Fig. 1). The jars were kept tightly closed except when the stored oils were sampled for peroxide determinations which were conducted by the same iodometric procedure as that employed in the AOM tests.

Color evaluations of the deodorized oils were conducted with a Lovibond Tintometer. In the Tintometer, 5.25 in. columns of the oils were matched with standard red and yellow Lovibond colored glasses.

Analyses to confirm the initial antioxidant treatments of the crude oils and to detect carry through of antioxidants into the deodorized oils were carried out by standard colorimetric and polarographic procedures used in our laboratory (21–23).

Results and Discussion

Oxidative Deterioration of Crude Safflowerseed, Soybean, Sunflowerseed and Cottonseed Oils During Storage

As indicated, all three test antioxidants provided, in varying degrees, inhibitory effects (as determined by measurement of peroxide formation) on the oxidation of the four crude oils under the test storage conditions. As was expected on the basis of previous

TABLE I
Stability Studies With Safflowerseed Oil
(Series I)

Antioxidant treatment of crude oil (wt %)	Stability of crude oil			Stability of deodorized oil					
	Unstored		After 2 months' storage	From unstored crude		From 2 months stored crude			
				No antioxidant added to deodorized oil	0.02% TBHQ added to deodorized oil	No antioxidant added to deodorized oil		0.02% TBHQ added to deodorized oil	
	AOM hr	Oven days	AOM hr	AOM hr	AOM hr	AOM hr	Oven days	AOM hr	Oven days
None (control)	4	10	1	8	37	7	7	34	28
0.02 BHA	5	13	2	..	....	8	8	40	30
0.02 PG	9	18	3	..	....	7	7	35	30
0.02 TBHQ	20	31	15	8	37	9	10	36	37

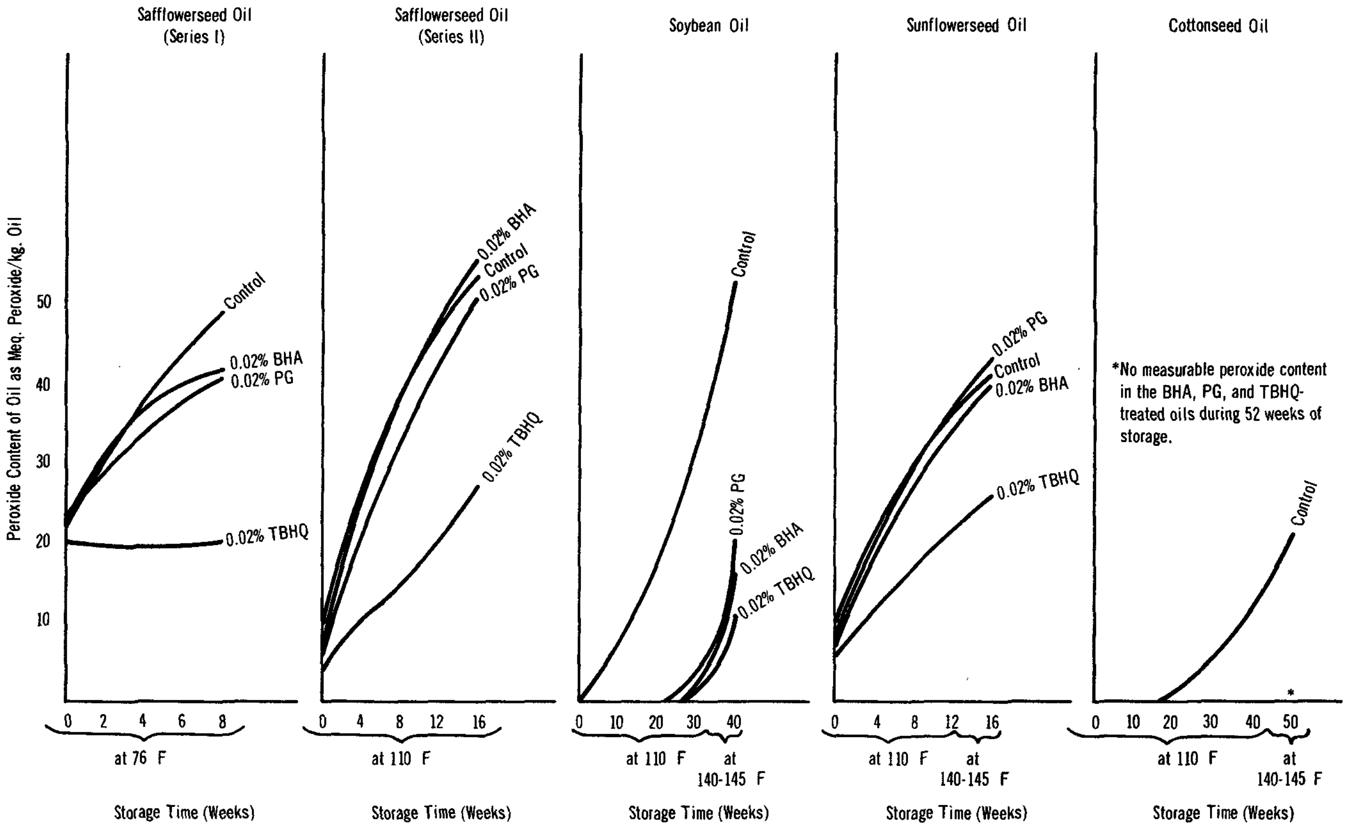

FIG. 1. Peroxide formation in crude vegetable oils during storage.

experience, TBHQ generally provided considerably greater protection to the crude oils than did BHA or PG. In addition to permitting observation of the oxidation tendencies of these crude oils during prolonged storage, an objective of storing the crude oils under the indicated conditions was to create in them (especially in the control samples) an advanced degree of oxidative degradation for purposes of the subsequent stability studies. As shown, the storage tests on each crude oil were terminated when the peroxide content of the control oil had reached 30–50 meq/kg. The storage periods required for the oils to reach this point varied with the different types of crude oil, but it is interesting to note that the order of susceptibility (from least to greatest) of the oils to oxidation was cottonseed, soybean, sunflowerseed and safflowerseed.

Stability Studies with Safflowerseed Oil (Series I)

The oxidative stability of crude safflowerseed oil prior to storage (as measured by AOM and oven storage tests) was greatly enhanced by treatment with TBHQ while PG was considerably less effective and BHA was relatively ineffective. When the crude oil was deodorized immediately, antioxidant treatment of the crude oil appears to have had no noticeable effect on the initial stability of the deodorized oil or its response to further antioxidant treatment. While the stabilities of all the crude oils were greatly reduced at the end of the two-month storage period, the outstanding effect of TBHQ was still evident. Upon deodorization of the crude oils after two months of storage, it appears that the oil produced from the TBHQ-treated crude oil not only had slightly higher initial stability, but also responded somewhat better than the other oils to further treatment with TBHQ. As determined by Lovibond color measurements, there were no differences observed between the colors of the deodorized oils which might be attributable to the presence of antioxidants in the crude oils during storage.

Stability Studies with Safflowerseed Oil (Series II)

Since the safflowerseed oil of Series I had a relatively advanced degree of oxidative degradation (20 meq peroxide/kg oil) as received for the laboratory studies, a second quantity of crude safflowerseed oil was obtained (from a different supplier) for repeat studies to provide data on more typical crude oil. The results from the second series of tests substantiate

TABLE II
Stability Studies With Safflowerseed Oil
(Series II)

Antioxidant treatment of crude oil (wt %)	Stability of crude oil			Stability of deodorized oil from 4 months stored crude			
	Unstored		After 4 months' storage	No antioxidant added to deodorized oil		0.02% TBHQ added to deodorized oil	
	AOM hr	Oven days	AOM hr	AOM hr	Oven days	AOM hr	Oven days
None (control)	8	16	3	7	8	33	31
0.02 BHA	9	17	3	7	9	34	40
0.02 PG	16	19	6	8	13	31	34
0.02 TBHQ	44	52	16	11	16	40	50

TABLE III
Stability Studies With Soybean Oil

Antioxidant treatment of crude oil (wt %)	Stability of crude oil			Stability of deodorized oil from 9 months stored crude		
	Unstored		After 9 months' storage	No antioxidant added to deodorized oil		0.02% TBHQ added to deodorized oil
	AOM hr	Oven days	AOM hr	AOM hr	Oven days	AOM hr
None (control)	45	31	5	12	17	40
0.02 BHA	45	32	14	12	15	42
0.02 PG	53	36	....	14	15	43
0.02 TBHQ	74	57	45	15	18	43

the findings obtained from the first series and show even more clearly an improved stability of deodorized oil resulting from the presence of TBHQ, and to a lesser extent PG, in the crude oil during four months of storage. Also, the deodorized oils having improved initial stability appear to respond somewhat better to further treatment with TBHQ. Lovibond color measurements once again showed that antioxidants in the crude oils had no effect on the color of the deodorized safflowerseed oils.

Stability Studies with Soybean Oil

The crude soybean oil without added antioxidant possessed a high degree of oxidative stability and treatment with a potent antioxidant, such as TBHQ, increased the stability of the crude oil considerably. The high degree of stability of the crude soybean oil agrees with the findings of Baumann et al. (15) who reported on the high degree of stability of crude soybean oil in field tank storage. The presence of TBHQ in the crude oil during the nine months of storage appears to have provided a slight improvement in the stability of the deodorized oil and in the response of the deodorized oil to further antioxidant treatment. There appeared to be no color changes in the deodorized oils attributable to the presence of antioxidants in the crude oil during storage.

Stability Studies with Sunflowerseed Oil

Having a composition much like safflowerseed oil, sunflowerseed oil might be expected to have inherent oxidative stability characteristics and to respond to antioxidant treatment much as safflowerseed oil does. Table IV shows that this was essentially so with the unstored crude oil, the crude oil after four months of storage, and the deodorized oil produced from unstabilized crude oil. However, very unexpected results were obtained with the deodorized oil produced from TBHQ-treated crude sunflowerseed oil after four months of storage. This oil not only had an apparent reduction in stability, as compared with the oils produced from the control and the BHA- and PG-treated crude oils, but its response to further TBHQ treatment was considerably lower than was expected. Also, a notable discoloration was observed in this particular sample of crude oil after four months of storage, and some carry through of this color into the deodorized oil occurred. Further studies should be conducted to determine the relationship between the discoloration and the reduction in stability and to determine if this problem will occur in sunflowerseed oil under more normal storage conditions.

Stability Studies with Cottonseed Oil

Table V indicates TBHQ was quite effective in increasing the oxidative stability of crude cottonseed oil, while BHA exhibited practically no effectiveness and PG was only slightly effective. Substantiating earlier findings by Rao (3) and Harwalker and Saletore (4), the crude cottonseed oil without added antioxidant was found to have good resistance to oxidation during prolonged storage, probably because of its high tocopherol and gossypol content. The apparent increase in stability of the crude oil (with and without antioxidants) during the year's storage cannot be explained on the basis of these studies. The deodorized oils produced from the antioxidant-treated (especially TBHQ-treated) crude oils exhibited slightly increased initial stabilities and the deodorized oil from the TBHQ-treated crude oil seemed to respond slightly better to further treatment with TBHQ.

The color reversion which occurs in crude cottonseed oil during prolonged storage was clearly evident in the deodorized oils obtained in these studies from the stored crude oils. There was no evidence that the presence of phenolic antioxidants in the crude oils had any effect on the color characteristics of the resultant deodorized oils.

In summary, the results of these studies indicate that where there is a need to inhibit oxidation in crude vegetable oils during storage, the adequacy of antioxidants such as BHA and propyl gallate which are currently cleared for use in edible fats and oils may be questionable, but the developmental antioxidant TBHQ appears to be quite effective. These results also provide some evidence that such protection of the crude oils during storage, especially safflowerseed and perhaps soybean and cottonseed to a lesser extent, may provide somewhat improved oxidative stability characteristics in the final deodorized oils. Analyses conducted in conjunction with these stability studies revealed that, with methods

TABLE IV
Stability Studies With Sunflowerseed Oil

Antioxidant treatment of crude oil (wt %)	Stability of crude oil			Stability of deodorized oil from 4 months stored crude			
	Unstored		After 4 months' storage	No antioxidant added to deodorized oil		0.02% TBHQ added to deodorized oil	
	AOM hr	Oven days	AOM hr	AOM hr	Oven days	AOM hr	Oven days
None (control)	8	15	4	8	10	34	44
0.02 BHA	8	21	4	8	11	28	....
0.02 PG	15	19	7	7	11	35	....
0.02 TBHQ	40	54	16	6	11	15	28

TABLE V
Stability Studies With Cottonseed Oil

Antioxidant treatment of crude oil (wt %)	Stability of crude oil			Stability of deodorized oil from 12 months stored crude			
	Unstored		After 12 months' storage	No antioxidant added to deodorized oil		0.02% TBHQ added to deodorized oil	
	AOM hr	Oven days	AOM hr	AOM hr	Oven days	AOM hr	Oven days
None (control)	16	21	19	10	13	32	35
0.02 BHA	16	24	27	12	17	32	41
0.02 PG	20	30	31	11	19	30	36
0.02 TBHQ	34	61	49	14	22	35	45

(21–23) capable of detecting 3–5 ppm TBHQ in vegetable oils such as safflowerseed oil, there was no measurable carry through of the antioxidant from the crude oils into the deodorized oils. Steam distillation techniques (24) have been developed and are in common use for the quantitative removal of phenolic antioxidants from fats and oils for analytical purposes, and in view of this, it is not expected that compounds such as BHA or TBHQ would remain in an oil after deodorization, since deodorization is a steam stripping process which is probably even more efficient than that employed in the analytical procedures. Generally, it seems that the improved stability of the deodorized oils is not due to carry through of trace quantities of the antioxidants which were present in the crude oils.

The results of these studies, being based to a major extent on measurement of peroxides which are recognized as only intermediates in the oxidation of oils, will be somewhat questionable from the standpoint of what they actually mean in terms of the flavor characteristics in deodorized oils produced from antioxidant-treated crude oils. The possible benefits to be derived from having a potent antioxidant such as TBHQ in crude oils during storage should be investigated in greater depth with test methods designed to study flavor qualities (12,25) of the deodorized oils. These additional studies should also include measurement of the end products of oxidation such as the nonvolatile carbonyls in the deodorized oils as determined by the benzidine method proposed by Holm et al. (26) and the dimer content of the crude oils as determined by Baumann et al. (15). The measurement of refractive index has more recently been suggested (27) as a means of gauging the development of oxidative rancidity in fats and oils, and this may be employed as a useful tool in further studies of antioxidants in crude vegetable oils.

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