Conclusions

Some physical and chemical properties of tangerine seed oil were determined. Evidence for the presence of linolenic, linoleic, oleic, palmitic, stearic, arachidic, and an unidentified hydroxy acid was obtained and the percentages of these acids were determined.

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The Flavor Problem of Soybean Oil. V. Some Considerations in the Use of Metal Scavengers in Commercial Operations[1]

H. J. DUTTON, A. W. SCHWAB, HELEN A. MOSER, and J. C. COWAN, Northern Regional Research Laboratory,[2] Peoria, Illinois

CITRIC acid appears to have been used in Denmark as early as 1928 in the refining of soybean oil (1). While its use became widespread in Europe before the second World War, it seems not to have been adopted in this country although numerous studies on its synergistic function with antioxidants have been reported (2).

On receipt of reports by Goss on the water-washing citric acid process used in Germany (3), work was undertaken at the Northern Regional Research Laboratory to evaluate the process. This work, carried out on a laboratory scale, showed that the addition of citric acid to soybean oil did improve its flavor stability (4). Still further studies revealed that certain polyhydric alcohols and certain polybasic acids also increased the oxidative and flavor stability of soybean oil and supported previous suggestions (7, 8) that these compounds might function as metal scavengers by complexing pro-oxidant metals, thus decreasing the rate of oxidation of the oil (9).

After these studies practical considerations in the use of metal scavengers remained to be clarified. These included the concentration of scavenger required, the effect of temperature on the activity of the citric acid, the point during deodorization at which citric acid should be added for best results, the value of the water-washing step, the role of the phosphatides, and the efficacy of metal scavengers in commercial operations. These considerations are the subject of the present communication.

Concentration of Metal Scavenger

To determine the optimal concentration for addition of citric acid and sorbitol to oils, 0.001, 0.01, and 0.1% of each compound as a 20% aqueous solution was flashed into three aliquots of alkali-refined and bleached soybean oil at the beginning of deodorization. These aliquots and a control aliquot were deodorized simultaneously for three hours in the four-sample, glass laboratory deodorizer at 210°C. (10). Oxidative stability was assayed by determining the peroxides of the oil after holding it eight hours under Active Oxygen Method conditions and after holding

it three days at 60°C. The samples held at 60°C. were also evaluated organoleptically according to this Laboratory's procedure (11). Results on citric acid addition are given in Table I. The peroxide data

TABLE I

Effect of the Citric Acid Concentration Upon the Oxidative and Flavor Stability of Soybean Oil

0.1% Citric	0.01% Citric	0.001% Citric	Control	Significant difference[1]
Flavor Score at 0 Time				
8.1 (0.47)[2]	8.5 (0.36)	8.7 (0.39)	8.7 (0.56)	+
After 3 days' storage at 60°C.				
6.9 (1.40) 7.0 (1.30) 6.8 (1.19)	7.1 (1.50)	5.7 (5.23)	4.9 (4.89)	+, *
	7.4 (1.65)	6.2 (5.50)	6.0 (5.66)	*, **
	7.8 (1.56)	5.7 (5.13)	5.8 (5.11)	**, +
Peroxide values (A.O.M. conditions—8 hours)				
6.5	13.1	39.8	56.9	

[1] + No significant difference.
* Significant difference (5% level).
** Highly significant difference (1% level).
[2] Peroxide value at time of organoleptic evaluation.

show that citric acid imparts increasing oxidative stability at concentrations of 0.001, 0.01, and 0.1%. In contrast to the oxidative stability data, flavor stability data indicate that 0.001% affords insufficient protection, but 0.01% is highly effective, and 0.1% appears to hold no advantage over 0.01%.[3] Sorbitol behaves similarly to citric acid as the concentration is varied. Thus the addition of citric acid or sorbitol in concentrations higher than 0.01% does not appear necessary or economically desirable.

Effect of Temperature on the Activity of Citric Acid

Since normal deodorization temperatures are above the decomposition temperature of citric acid, the question is raised thereby whether the application of heat is essential to the activity of citric acid. An answer was sought by the following experiment. To one

[3] In further experiments in which samples were stored at 60°C. and tasted at intervals up to 10 days, no significant difference in flavor scores were found between the 0.1 and 0.01% levels.

sample of deodorized oil, 0.01% of citric acid was added as an aqueous solution. To a second sample was added an equivalent amount of water. The water was then removed by a "room temperature deodorization" at 1 mm. of pressure. Water vapor from the steam generators served to ebullate the mixture. After the water was evaporated, half of each sample was removed from the deodorization flasks and the remaining oil was deodorized for one hour at 210°C. Four samples were thus prepared: 1. A citric acid treated, and 2. control, both with a room temperature deodorization, 3. a citric acid treated, and 4. control sample deodorized at 210°C. From the oxidative and flavor stability data of Table II it is evident that heating is not necessary to activate citric acid.

TABLE II
Effect of Temperature Upon the Activity of Citric Acid [1]

Room temperature		210°C.		Significant difference
Citric acid	Control	Citric acid	Control	
Flavor Score at 0 Time				
8.7 (0.25)	8.8 (0.28)			
		8.2 (0.45)	8.1 (0.42)	‡
After 5 days' storage at 60°C.				
6.9 (1.86)	4.4 (12.16)			**
After 3 days' storage at 60°C.				
		7.1 (1.08)	5.6 (6.09)	*
Peroxide values (A.O.M. conditions—8 hours)				
10.7	38.9	18.1	41.2	

[1] For explanation of symbols, see Table I.

Point of Addition of Citric Acid

Because heat is not required for the activation of citric acid, the question then arose as to the point in deodorization at which the citric acid could be added most advantageously. When glass deodorization apparatus was used, no significant difference was found in the flavor scores of freshly deodorized oils, whether citric acid treated or untreated (e.g., Tables I and II). On the basis of these tests it would be concluded that citric acid affects only stability and not initial quality. However, in commercial plant tests and pilot-plant runs, differences were found in initial flavor scores between "treated" and untreated samples. This is shown, for example, in the zero time data of Tables VI, VII, and VIII. The conditions of commercial deodorizations are undoubtedly more drastic than those in the laboratory, commercial deodorizations being conducted in metal rather than in glass deodorizers with a greater attendant probability of metal contamination. In laboratory deodorizations the temperature of the oil was dropped lower, before breaking the vacuum, than can be practiced commercially. Thus the early addition of metal scavengers holds a distinct advantage in practical operation since the scavenger affords protection throughout the deodorization operation.

Citric acid decomposes at the temperature of deodorization, and it is doubtful if any citric acid exists in the oil after deodorization. The effect of adding further citric acid during the cooling phase of deodorization was therefore investigated. In the data of Table III the stability of a sample of soybean oil treated with 0.01% citric acid before deodorization is compared with the same oil treated both before

TABLE III
Effect of Adding Citric Acid and Iron Before and After Deodorization Upon the Oxidative and Flavor Stability of Soybean Oil [1]

Citric acid before and after deodorization	Citric acid before deodorization, iron after deodorization	Citric acid before, iron after, and citric acid after deodorization	Citric acid before deodorization	Significant difference
Flavor Score at 0 Time				
8.4 (0.70)	4.2 (0.50)	7.8 (0.41)	8.6 (0.67)	
After 5 days' storage at 60°C.				
6.7 (2.04)	3.3 (3.87)	6.2 (1.57)	6.8 (1.71)	**
7.0 (1.59)				+
6.6 (1.64)				+
	3.1 (1.82)	5.7 (3.21)	6.7 (1.54)	**
	3.6 (2.75)	5.9 (1.51)	7.0 (1.45)	*
Peroxide values (A.O.M. conditions—8 hours)				
9.0	208.1	17.8	31.5	

[1] For explanation of symbols, see Table I.

and after deodorization with 0.01% citric acid. An increase in oxidative stability was conferred by the additional citric acid, but no increase in flavor stability was observed.

These samples were stored in glass and free from further metallic contamination. Under practical conditions of packaging and shipping, however, further metal contamination is possible. As shown in Table III, the addition of iron (0.3 p.p.m.) subsequent to deodorization significantly lowered oxidative and flavor stability of oil even though the oil was treated with citric acid at the beginning of deodorization. Further addition of citric acid to this metal-contaminated oil did serve to protect the oil during storage. The implication of these results is that citric acid may be added with advantage during both the heating and the cooling phase of deodorization.

Effect of Phosphatide Addition and of Degumming

Phosphatides have long been recognized as antioxidants (12). It has been suggested that the improved stability afforded by them, in part, is due to the metal scavengering effect of the fat-soluble phosphoric acid (5, 6, 8, 9). To test this hypothesis further, the following experiment was conducted, using acetone precipitated soybean phosphatides: To one aliquot of a refined bleached soybean oil was added 0.02% of phosphatides; to a second, 0.3 p.p.m. of iron as ferric chloride; to a third, 0.3 p.p.m. iron and 0.02% phosphatides. The fourth aliquot served as a control sample. All four samples were then deodor-

TABLE IV
Effect of Phosphatides Upon the Stability of Soybean Oil in the Presence of Added Iron [1]

Phosphatide (0.02%)	Iron (0.3 ppm.)	Phosphatide + Iron	Control	Significant difference
Flavor Score at 0 Time				
8.0 (0.25)	7.1 (0.26)	7.5 (0.24)	8.3 (0.26)	+
After 3 days' storage at 60°C.				
6.5 (1.24)	3.9 (6.78)	5.9 (1.65)	4.9 (6.83)	**
6.8 (1.22)				+
6.5 (1.03)				**
	4.4 (6.32)	6.0 (1.25)	6.4 (7.36)	*
	5.4 (6.73)	6.1 (1.69)	5.7 (6.04)	+
Peroxide values (A.O.M. conditions—8 hours)				
22.3	91.4	37.0	64.4	

[1] For explanation of symbols, see Table I.

ized simultaneously in the four-sample glass deodorizer. Results of this experiment are given in Table IV. The flavor stability of the phosphatide sample was significantly higher than both the control sample and the iron sample. The flavor stability of the phosphatide-iron sample was significantly higher than that of the iron sample and not significantly different from the control sample. Oxidative stability and flavor stability data are thus in agreement in showing that phosphatide addition to the oil during deodorization counteracts the deleterious effect of the added iron.

The concept of lecithin functioning as a fat-soluble metal scavenger is further strengthened by experiments involving the addition of alkyl acid phosphates (butyl, octyl, and lauryl esters). When those compounds were substituted for lecithin in experiments of the type just described, similar results were obtained and the metal scavengering properties of the organic forms of phosphoric acid were apparent.

The concentration of "soybean lecithin" which may be added to soybean oil is of practical interest. Oxidative stability results shown in Table V indicate
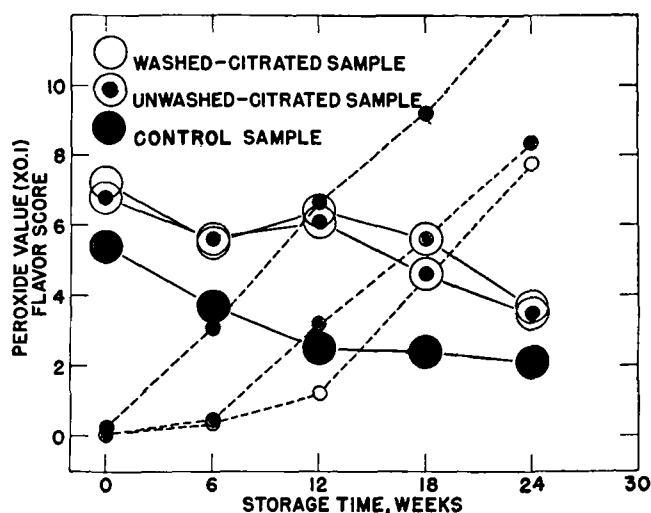

FIG. 1. Changes in flavor scores (solid lines) and peroxide values (broken lines) of commercially produced soybean salad oils stored at room temperature.

TABLE V

Effect of the Phosphatide Concentration Upon the Initial Flavor and Upon the Stability of Soybean Oil [1]

0.05% phosphatide	0.1% phosphatide	0.2% phosphatide	Control	Significant difference
Flavor Score at 0 Time				
8.4 (0.49) 8.3 (0.57) 8.4 (0.46)	7.0 (0.40) 7.7 (0.39) 7.9 (0.49)	7.2 (0.46) 7.0 (0.30) 6.8 (0.00)	8.7 (0.62) 8.3 (0.67) 8.0 (0.50)	+ + + *
After 7 days' storage at 60°C.				
5.6 (8.32)	4.9 (8.87)	4.0 (4.64)	4.1 (28.57)	0.05 * 0.2
Peroxide values (A.O.M. conditions—8 hours)				
7.5	4.2	2.6	65.4	

[1] For explanation of symbols, see Table I.

increasing stability of 0.05, 0.1, and 0.2% levels of addition. In regard to initial flavor the sample containing 0.2% lecithin was graded significantly lower than the control, it being described by terms atypical of soybean oil, such as "melon flavor." While the results after seven days' storage at 60°C. possess less precision than the paired sample tests since they were necessarily tasted four at one time, it appears that lecithin at the 0.2% level introduces extraneous flavors to a significant degree. This sample was again described by atypical flavor terms. On the basis of these tests addition of lecithin at concentrations higher than 0.1% would not be recommended. Since lecithin darkens the oil even at 0.1% this property, rather than its flavor characteristics, may limit its level of addition.

These results largely confirm observations by Eckey and by Bailey and Feuge on the addition of lecithin and phosphoric acid (13, 14). The stabilizing effect of these compounds now appears adequately explained in terms of metal complexing agents.

The present data, showing a beneficial effect of phosphatide addition to the deodorizer, are not in agreement with the opinions of the German processors who attributed reversion to traces of lecithin (3). The German method for combating reversion

called for a thorough degumming prior to refining and bleaching in order to remove the phosphatides and for the addition of citric acid which was thought to "inactivate" the remaining traces of lecithin in the deodorizer. Numerous laboratory experiments involving the exhaustive water-washing of crude soybean oils have been made, but the value of more than one degumming operation has yet to be demonstrated. The ineffectiveness of more than one water-washing operation is apparent also in the results of commercial-scale operations to be described.

Citric Acid Addition in Commercial Operations

The value of citric acid has been demonstrated on a commercial scale in several plants. In the first plant test of the citric acid treatment (Plant A) the value of water-washing was studied also. A quantity of degummed soybean oil was divided into two batches, and one batch was water-washed under conditions similar to the original German process (3). Following alkali refining and bleaching, both the washed and unwashed batches were deodorized with the addition of 0.01% citric acid. To provide a control a portion of the unwashed sample was reserved and subsequently deodorized without the addition of citric acid. The beneficial effect of citric acid upon initial quality is apparent from the data of Table VI;

TABLE VI

Evaluation of Samples From Plant A Using Citric Acid [1]

Washed + citric acid	Unwashed + citric acid	Control	Significant difference
Flavor Score at 0 Time			
7.0 (0.46) 7.3 (0.44)	6.6 (0.96) 7.0 (0.51)	5.3 (0.79) 5.5 (0.86)	+ ** *
After 3 days' storage at 60°C.			
4.5 (21.2) 5.3 (21.7)	4.3 (19.2) 5.3 (16.3)	3.0 (23.0) 2.8 (28.3)	+ ** **
Peroxide values (A.O.M. conditions—8 hours)			
65.8	69.5	213.2	

[1] For explanation of symbols, see Table I.

both the washed citrated and unwashed citrated samples were significantly better than the control at zero time. After storage for three days at 60°C. the citric acid treated sample remained significantly better than the control. After storage at room temperature for 6, 12, 18, and 24 weeks there was no significant difference in flavor scores between the washed citrated sample and the unwashed citrated sample, but there were highly significant differences between the unwashed citrated and control samples and between the washed citrated and control samples (Figure 1).

Since the results of the first commercial trial showed the water-washing step to be of insignificant value, this step was eliminated in the second commercial trial at Plant B. A quantity of refined and bleached soybean oil was divided into two batches. The first batch was deodorized in the usual manner while the second was deodorized in the presence of 0.01% citric acid. As mentioned above, the initial flavor score for the citric acid-treated samples was higher, although not significantly so, than that of the untreated samples (Table VII). After three

TABLE VII
Evaluation of Samples From Plant B Using Citric Acid [1]

Citric acid treated	Control	Significant difference
Flavor Score at 0 Time		
6.5 (0.51)	5.8 (1.00)	+
After 3 days' storage at 60°C.		
5.9 (1.68)	3.6 (8.43)	**
Peroxide values (A.O.M. conditions—8 hours)		
42.4	63.8	

[1] For explanation of symbols, see Table I.

days' storage at 60°C. there was a highly significant difference between the citric acid sample and the untreated sample. Both the oxidative and flavor stability data given in Table VII agree in showing the beneficial effect imparted by citric acid in this commercial operation.

Sorbitol Addition in Commercial Operation

A refined and bleached soybean oil was divided into two batches in the industrial scale trial of sorbitol. The first batch was deodorized in the usual manner while to the other batch 0.01% of sorbitol was added. These samples were then evaluated by the usual organoleptic procedure, and the results are listed in Table VIII. From the data it is concluded

TABLE VIII
Evaluation of Samples From Plant C Using Sorbitol [1]

Sorbitol treated	Control	Significant difference
Flavor Score at 0 Time		
7.3 (0.54)	5.5 (0.50)	*
After 3 days' storage at 60°C.		
6.5 (1.32)	4.8 (6.46)	**
Peroxide values (A.O.M. conditions—8 hours)		
11.7	49.8	

[1] For explanation of symbols, see Table I.

that sorbitol on industrial scale improves the initial quality of the oil as well as protects it from oxidative and flavor deterioration during storage.

Summary
Citric acid and sorbitol were tested on a commercial scale and their use was found to improve the oxidative and flavor stability of soybean oil.

The optimal concentration for the addition of citric acid and sorbitol is of the order of 0.01%, 0.001% being insufficient, and 0.1% giving no significant increase in flavor stability over 0.01%.

Heating is not necessary for the activation of citric acid; however, it is advantageous to add the citric acid at the beginning of the deodorization in commercial operations because of the protection imparted to the oils during deodorization. Since citric acid is destroyed during deodorization, it appears desirable, on the basis of laboratory experiments, to introduce additional citric acid during the cooling phase of deodorization.

Phosphatides added to the deodorizer increase the oxidative and flavor stability of soybean oil and counteract the pro-oxidant effect of added iron. Phosphatides are thus considered to comprise a fat-soluble form of phosphoric acid and to perform the function of a metal scavenger. The value of the second degumming step of the German process is dubious. In neither the laboratory experiments nor in a commercial run were the differences due to this operation found to be significant.

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