TABLE VI

Corrosion Tests in 1 Part Hydrogenated Tallow, 3 Parts 98% Acetic Acid Containing 1% Perchloric Acid at 100°C.

Material	Duration of test (weeks)	Penetration (mm./yr.)
304 S.S.	4	1.2
Carpenter 20	4	0.3
316 S.S.	4	0.1
Haynes 25	10	0.02
Hastelloy C	10	0.001

inactivation until the aqueous acetic acid has been removed in the first part of the distillation. This would raise the triacetin yield by about 1%, w/w on fat charged, due to the molecular weight increase resulting from the re-acetylation.

About 20% of the original unsaturation disappears during the reaction and most of this can be accounted for by the appearance of excess ester value in the products, conversion efficiency of unsaturation to acetoxy being generally around 90%. The high ester value of the earlier distilled fractions shows that the acetoxy acids fail to separate as a clear fraction, and the analyses of the later fractions show that no diacetoglyceride fraction of over 50% concentration was obtained. A redistillation of Fraction IV of Table IV into two equal fractions gave little advance over this figure. While the acetoxy acids do not interfere with the separation of unsubstituted fatty acids from diacetoglycerides, they clearly contaminate both fractions.

Material of Construction

Corrosion tests were carried out at 100°C. using the most severe conditions, i.e., perchloric acid as catalyst, and with daily replacement of the catalyzed reaction mixture. See Table VI.

The first two materials consumed enough catalyst to slow the reaction, and were severely attacked. Type 316 stainless steel did not affect the reaction or show visible pitting, but enough nickel and chromium dissolved to color the test solution at the start. This marginally possible material merits further test with less highly corrosive catalysts. The last two alloys were fully satisfactory. The distillation processes present no novel problem once the catalyst has been inactivated, S.S. 316 being an established satisfactory material.

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Citric Acid: Inactivating Agent for Metals or Acidic Synergist in Edible Fats?[1]

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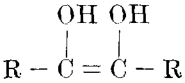
Oxidative stabilities of soybean oil and lard are improved by the addition of either sorbitol or citric acid. Sufficient sorbitol gives enough improvement in stability so that added citric acid gives no increased stability. Unless sorbitol acts as a neutral synergist, forms a powerful acidic synergist in trace amounts or a new antioxidant, the antioxidant activity of citric acid appears to come from its inactivating capacities for metals.

THE MODE OF ACTION that various minor constituents or small amounts of additives have on the oxidative stability of vegetable oils, animal fats, and their derivatives, has been investigated extensively during the past 20 years. These investigations disclose that a series of phenolic derivatives like hydroquinone, catechol, and butylated hydroxyanisole are effective antioxidants for fats (12, 15) and that certain acidic compounds not phenolic in nature, like phosphoric, citric, and carboxymethyl mercaptosuccinic acids, are effective aids to stabilization (2, 8, 12). All the phenolic and related derivatives that are effective antioxidants appear to be enediols



$$R-\overset{OH}{\overset{|}{C}}=\overset{OH}{\overset{|}{C}}-R$$

or vinylogs thereof (12). All acidic compounds that are effective appear to have another property in common, *i.e.*, they are effective inactivating agents of trace metals (2, 3, 5, 15, 18).

Fats are remarkably sensitive to trace amounts of metals, particularly if no natural or added metal-inactivating agent is present. This sensitivity appears to depend in part on the type of unsaturation present in the oil; for example, soybean oil is more sensitive to trace metals than is cottonseed oil (5). Only 0.01 p.p.m. of copper or 0.1 p.p.m. of iron is enough to make an appreciable difference in the rate of autoxidation of soybean oil whereas this amount of added iron may have little effect on cottonseed oil.

Olcott and Mattill (14) found that both a phenolic and an acidic "antioxidant" used together gave unusual stability under certain circumstances. They called this phenomenon a "synergistic effect." At that time Olcott and Mattill were not familiar with the metal-inactivating properties of the acidic compounds because this reaction had not yet been established with certainty. Although Evans (6) suggested that the antioxidant properties of phosphatides in fats and oils were probably based on their metal-inactivating capacities, this inactivation of metals by these acidic compounds was not generally recognized until later. Riemenschneider (15) and Dutton (2) reported data which clearly showed that these acidic compounds could act as metal-inactivating agents.

Lemon (10) examined this problem and concluded that citric acid was both a synergist and a metal inactivator. His conclusion was based primarily on studies with distilled peanut fatty esters. These studies showed that citric acid did improve the stability of the purified (distilled and chromatographed) esters, consequently the acid was considered to be a

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synergist because purified esters were not likely to contain any metallic impurity. Further, when citric acid was added to the purified esters containing added hydroquinone, an additional improvement was made in stability; therefore citric acid was an acidic synergist. If 5 p.p.m. of iron were added to the purified esters, citric acid could be used to control the effect of this addition, *i.e.,* metal inactivation. The difference in stability imparted by citric acid in the presence or absence of added hydroquinone was small. However if a metallic impurity were assumed to be present in the purified peanut esters, citric acid could be acting only as a metal-inactivating agent.

Lips (11), working on the stabilization of linseed shortening, concluded that citric acid exhibited no synergistic or even additive effects with other antioxidants except when used with wheat germ oil and lecithin. Indeed, sometimes citric acid and a second stabilizer, such as tocopherol, gave less protective action than either one alone.

Epstein and others (4) found that sorbitol was effective in delaying but not preventing "reversion" of soybean oil. Sorbitol has been demonstrated to be an effective metal-inactivating agent for iron (2). Consequently the use of sorbitol as a metal-inactivating agent prior to the addition of citric acid might give some interesting data regarding "acid" synergism between phenolic and acidic "antioxidants." Accordingly we investigated the prior additions of sorbitol, followed by the addition of citric acid, on the stability of oils and of oils that contained added metals.

Materials and Methods

Soybean oils used in these evaluations were either undeodorized, commercially refined, and bleached oils or commercially extracted crude oils that were refined and bleached in our pilot plant. Samples of cottonseed salad oil and prime steam lard were commercial samples that had been specially prepared for this investigation. They were processed without the addition of any metal-inactivating agents. In our studies with oils, drum lots are routinely given a clarifying filtration when received and are stored frozen at 0°F. in 5-gal. bottles or other appropriate glass containers. The lard samples were frozen and stored as received.

All deodorizations were carried out in a 4-sample, all-glass unit (17). Liquid oils were deodorized at 210°C. for 3 hrs. under a vacuum of 1 mm. or less. The deodorizaiton of lard and distilled methyl esters was carried out at lower temperatures. At 210°C. one sample of lard gave peculiar results in that both sorbitol and citric acid acted as prooxidants; however this lard behaved more normally when deodorization was performed at 100°C. Sorbitol and α-tocopherol were Eastman white-label, and citric acid was Baker analyzed reagent grade.

In most of the experiments the citric acid or sorbitol was added by increments either during the deodorization or at the end of the deodorization. The addition at the end of deodorization has been referred to as "downgrade addition" since the material is added after the oil has cooled to 70°C. For increment or downgrade addition the deodorizer was cooled and the vacuum broken with nitrogen to afford as much protection as possible to the oil. After increment additions were completed, the system was again evacuated and deodorization continued. Sorbitol and citric acid were added to the oil as 20% aqueous solutions, and tocopherol as a 4% ethyl alcohol solution. Sorbitol was normally added during deodorization, and citric acid was usually added on the downgrade.

TABLE I

Effect of 0.01% Citric Acid on Sorbitol-Treated Soybean Oil

% Added sorbitol	Peroxide values developed under AOM[a] conditions (8 hrs.)				S/C Ratio[c]
	Control	Sorbitol	PF[b]	Citric acid	
......	17			3.2	
0.01	17	4.8	3.5	2.3	2.1
0.05	17	2.2	7.7	2.4	0.9
0.10	17	1.9	8.9	2.4	0.8
1.0	17	1.9	8.9	1.8	1.0
......	38			11	
0.01	38	14	2.7	6.2	2.2
0.05	38	8.6	4.5	6.5	1.3
0.10	38	8.1	4.7	6.5	1.2
......	36			11	
0.01	36	27	1.3	5	5.4
0.05	36	4.6	7.8	2.2	2.1
0.10	36	3.0	12	2.1	1.4
0.01	29	17	1.7		
0.05	29	4.3	6.7		
0.10	29	3.1	9.4		

[a] Active Oxygen Method.

[b] Protective factor $= \frac{\text{Peroxide value of control samples}}{\text{Peroxide value of sorbitol-treated samples.}}$

[c] S/C Ratio $= \frac{\text{Peroxide value of sorbitol-treated samples}}{\text{Peroxide value of citric acid (0.01\%)-treated samples.}}$

The oxidative stabilities were measured by the usual Active Oxygen Method (AOM) (9,16) with titration of the peroxides by the 1-min. Wheeler method (19). Titrations for acid value were made by using the A.O.C.S. Official Method Ca 5a-40—Free Fatty Acid (13); 20-g. samples were used for titration.

Results and Discussion

Soybean Oil. Sorbitol, when used at a 0.01% level during deodorization, improves oxidative stability of soybean oil. Table I shows that the peroxide value developed after 8 hrs. under AOM conditions in sorbitol-treated samples is usually substantially lower than in control samples. In these studies the control sample was treated in a manner similar to the sorbitol sample except for the addition of sorbitol during the deodorization. The protective factor (PF), which is the ratio of the peroxide value of the control to the peroxide value of the sorbitol-treated sample, is usually 2 or greater. These data reconfirm and extend previous observations. Heat was properly used to activate both sorbitol and ctiric acid (1).

The stabilizing effect of sorbitol on soybean oil increases as the amount of sorbitol is increased up to 0.1% or possibly higher. With most samples of soybean oil, 0.1 of sorbitol apparently suffices to give considerable protection. In the first example in Table I no increase in stability was observed when the amount of sorbitol was increased from 0.1 to 1.0%. The optimum level of sorbitol appears to be about 0.1% but may be slightly higher with some samples

TABLE II

Effect of Added Iron and Sorbitol on the Stability of Soybean Oil

Amount of added iron	Amount of added sorbitol	Peroxide values developed under AOM[a] conditions (8 hrs.)	PF[a]
....	0.01	13 (45)[b]	3.5
3 p.p.m.	0.01	88 (230)	2.6
....	0.01	11 (34)	3.1
3 p.p.m.	0.01	19 (63)	3.3
....	0.01	12 (32)	2.7
0.3 p.p.m.	0.01	36 (159)	4.4
....	0.05	9 (37)	4.1
0.3 p.p.m.	0.05	9 (66)	7.3

[a] See Table I for key.

[b] Values in parentheses are peroxide values in the absence of sorbitol.

since extrapolation of data for the lower two samples in the table so indicate.

Table II presents data for samples containing both added iron and sorbitol, and it is evident that sorbitol does counteract the effect of this added metal. Sorbitol is effective at two concentrations of added iron. Apparently, when sufficient sorbitol is used, the same stability can be achieved in the presence or absence of added iron. This result may indicate that sorbitol's only function is that of metal inactivation.

Fig. 1 shows the autoxidation graph that was obtained by plotting peroxide values obtained under AOM conditions against time, for the 0.05% sorbitol and 0.3 p.p.m. iron series of treated soybean oils. Within the limits of these experiments (Tables I, II and Figure 1) the peroxide values at 8 hrs. in the AOM test may be considered an inverse measure of stability. No lines cross on the graph. Admittedly this measure of stabilizing activity is not a precise one, but the calculation of protective factors does give at least a rough method for comparative purposes.

There is no need to demonstrate that citric acid is a metal inactivating agent because ample evidence has already been published (2, 15). However one measure of the synergistic effect of citric acid on soybean oil might be found in the effect of adding citric acid to a sample of oil already treated with sorbitol. The first sample shown in Table I was not improved by the addition of citric acid when the levels of sorbitol used were above 0.05%. The effect of the added citric acid can be readily estimated by either the S/C ratios or the ratios of the peroxide value of the sorbitol samples to peroxide value of the citric acid samples. In these experiments, at levels of 0.05 to 1.0% sorbitol, the ratio dropped to 1 or approached 1. Consequently the added citric acid gave little or no additional stabilizing effect or no synergistic effect. With two of these samples citric acid did show a slight improvement, but as the amount of sorbitol increased from 0.01 to 0.05%, the stabilizing effect of the added citric acid was considerably reduced. A larger amount of sorbitol would most likely give an oil which would not be stabilized further by citric acid. In our opinion these data support the contention that sorbitol at sufficient levels gives as much protection to soybean oil as citric acid.

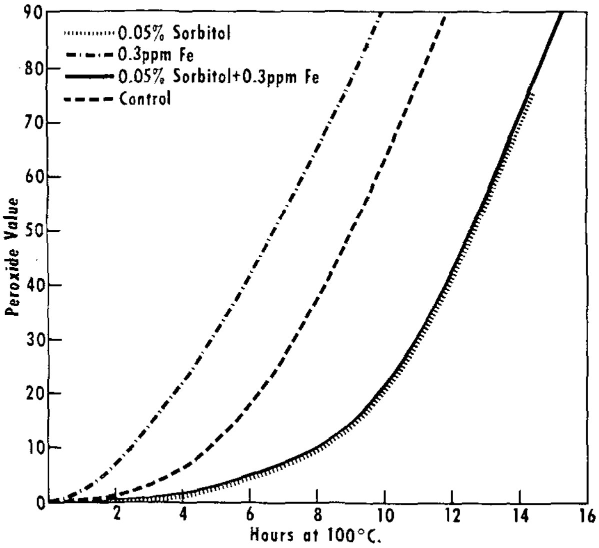

FIG. 1. Effect of 0.05% sorbitol in preventing the oxidation of soybean oil or soybean oil containing 0.3 p.p.m. of added iron under Active Oxygen Method conditions at 100°C.

Fig. 2 presents further evidence that soybean oil is stabilized as much by sorbitol as by citric acid, *i.e.*, both are acting as metal inactivating agents. Here 0.15% sorbitol in a soybean oil sample gave slightly better protection than 0.01% citric acid. Further addition of 0.005% citric acid did not improve the sorbitol sample appreciably.

Other Fats. With different samples of lard we obtained variable results. The effect of increasing the amount of added sorbitol does not appear to be the same as in soybean oil. Results were not always the same with a single lot of lard. Although these variations may be caused by some differences in treatment of the lard samples after adding the sorbitol, in our opinion other factors, such as residual effect of prior autoxidation, amount of metallic impurity, and incomplete destruction of peroxides, may also have an effect. Most lards are not alkali-refined whereas vegetable oils, such as soybean, are usually alkali-refined. It is entirely possible that the differences between the results noted in these samples, and in other experiments with lard, and the results obtained with soybean oil are traceable to the materials which alkali removes. Lard, which is not alkali-refined, may contain materials that adversely affect stabilization with sorbitol. As shown in Table III, it is possible to obtain a considerable degree of stabilization with added sorbitol on some lard samples. However a maximum in the stabilizing effect of either sorbitol or citric acid often occurred when used alone in amounts less than 0.1%. Addition of citric acid to lard samples stabilized with sorbitol often lowered stability. Addition of an antioxidant with either sorbitol or citric acid, or both, improved their effect. More recent work shows that some samples of yellow grease require 0.1 to 0.5% of added metal-inactivating compound (7), *i.e.*, considerable amounts of metallic impurity may be present in some samples.

Autoxidation studies with lard give data which are typical of what would be expected if sorbitol and citric acid were acting only as a metal inactivator. Fig. 3 shows a graph of the peroxide values developed during the autoxidation of lard at 100°C. Sorbitol and sorbitol plus citric acid imparted the same order of stability to the lard because the sample containing the sorbitol plus citric acid was equal to, but no better than the sample containing sorbitol alone. Addition

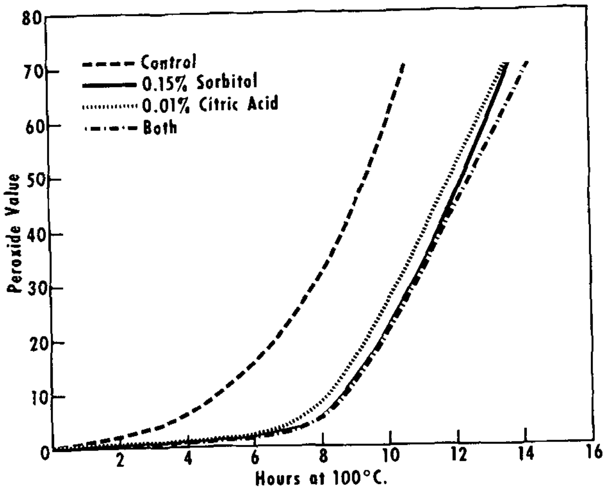

FIG. 2. Stabilizing effect of either 0.15% sorbitol or 0.01% citric acid and the combined effect of 0.15% sorbitol and 0.005% citric acid in soybean oil oxidized at 100°C. under Active Oxygen Method conditions.

TABLE III

Effect of Increasing Amounts of Sorbitol on Stability of Lard

Sample	Peroxide values—AOM[a] conditions (6 hrs.) Levels of sorbitol used				PF[a] (0.05%)
	None	0.01%	0.05%	0.10%	
1	200	210	75	11	18
2	380	120	36	58	10
3	18	9.3	12	16	2
4	100	180	4.9	8.9	20

[a] See Table I for key.

of tocopherol increased the stability considerably, but only a small difference is observed between the tocopherol sample treated with sorbitol plus citric acid and the tocopherol sample treated with sorbitol alone.

It could be argued that sorbitol forms acidic materials when it is added to an oil during deodorization. Samples of methyl esters of cottonseed fatty acids were treated under deodorization conditions with 0.15% sorbitol, 0.1% citric acid, and with both 0.15% sorbitol and 0.005% citric acid added prior to or during deodorization, not on the downgrade. The acid values as compared to the acid value of the sample with no additive did not increase. Indeed it decreased (?) from 1.7 to 1.6 (calculated as oleic acid) for all treated samples. Since both citric acid and sorbitol samples gave slightly reduced acid values, it does not seem likely that an acid synergist is formed from sorbitol. Since sorbitol is comparatively neutral, it cannot act as an acid synergist.

Methyl esters rather than oil were used in these experiments for attempted concentration of any acidic product. Citric acid was normally added on the downgrade, and much of its acidity was retained. For example, in tests with 0.01% of added citric acid, 60 to 85% of the citric acid was retained in the oil as titratable acidity. In experiments with sorbitol and citric acid reported in Table I and Figures 2 and 3, citric acid was retained in the fat to act as a synergist or metal-inactivating agent.

Sorbitol might act in some unknown way to serve as a neutral synergist, form *in situ* an acidic synergist or a new antioxidant. If it does not, the antioxidant properties of citric acid must be attributed to its inactivating capacity for metals. Further work on the effect of sorbitol and its mode of action is beyond the present scope of our investigations.

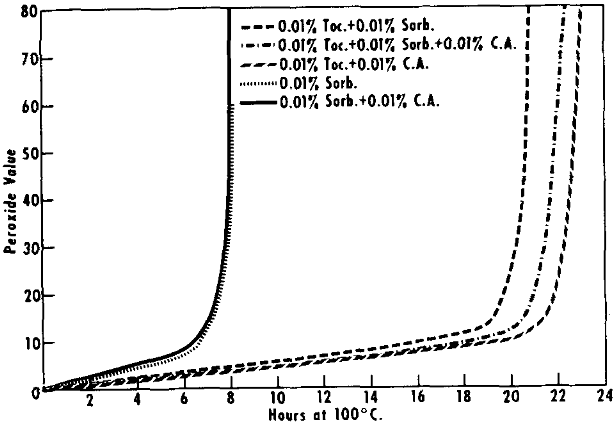

FIG. 3. Stabilizing effect of 0.01% sorbitol (Sorb.) and 0.01% sorbitol plus 0.01% citric acid (C.A.) in lard and in lard containing 0.01% added α-tocopherol (Toc.) oxidized at 100°C. under Active Oxygen Method conditions.

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The Effect of Heat on Pure Triglycerides

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A knowledge of the mechanism of the degradation of triglycerides at temperatures from 190°C. is important in predicting the type of breakdown products likely to be formed in processing oils at elevated temperatures, or in the usage of oils and fats in frying or baking.

The effect of heat on tricaprin and 2-oleo-dipalmitin has been studied both in the absence and in the presence of oxygen. The results show that even a pure fully saturated triglyceride is rendered organoleptically unacceptable, due to breakdown in the temperature range studied, although the mechanism differs according to whether oxygen is present or not. Unsaturated glycerides are more readily degraded, fission at or near the double bonds being superimposed on the processes previously established for saturated triglycerides. Many of the degradation products have been identified.

Degraded triglycerides can be refined to an acceptable standard by conventional means but their keeping times, in the refined state, are considerably less than those of the original pure materials. Hence, it is inferred that precursors of off-flavors persist in the products and survive the refining operations.

EXPERIENCE in handling oils and fats for culinary use has shown that it is difficult to maintain a bland flavor when they are used for long periods. Much is known of the general means by which fatty materials are oxidized or otherwise decomposed in the course of heating during frying or baking conditions, but hitherto such studies have been confined to natural oils and fats, or to blends of such materials. Even if highly sophisticated techniques are used in isolating degradation products to elucidate the mechanism of degradation, such products must be so numerous that interpretation of the mechanism of degradation will be difficult. For this reason, in the present study, use has been made of two pure synthetic triglycerides.