Molecularly Distilled Peanut Oil Antioxidants and Pure Alpha-Tocopherol As Stabilizing Agents for Fats of Poor Keeping Quality[1]

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Evidence that the high stability of hydrogenated vegetable oils is due to the presence of tocopherols or other molecularly distillable antioxidants, and the recent development of successful techniques (4) for conducting molecular distillation on a commercial scale, have directed attention toward the possibility of utilizing distilled vegetable oil concentrates for the fortification of fats of poor stability. The possible use of such concentrates is given significance by the recent discovery (1,3,9) that both pure tocopherols and molecularly distilled vegetable oil antioxidants are most effective at very low concentrations and may in some cases actually serve as pro-oxidants at concentrations above an optimum level.

While peanut oil is not one of the richer sources of tocopherol, it becomes extremely stable upon hydrogenation, and consequently it may be inferred that the mixed antioxidants of peanut oil are relatively potent in fats of a limited degree of unsaturation. It appeared desirable, therefore, to investigate the effectiveness of different concentrations of molecularly distilled peanut oil antioxidants in certain fats of poor keeping quality. For comparison, most of the experiments with the peanut oil antioxidants were paralleled by similar tests with equivalent concentrations of pure alpha-tocopherol.

The fats used in the investigations consisted of a sample of prime steam lard, and hydrogenated samples of two different lots of peanut oil. The hydrogenated peanut oils were inferior in stability to normal peanut oils of equivalent iodine values. One sample with an iodine value of 61.4, for example, had a keeping time at 110° of 11.3 hours, whereas a good peanut oil of this iodine value should keep not less than about 75 hours.

Experimental Details

In preparing the peanut oil antioxidant concentrates, a considerable quantity of refined and bleached peanut oil was first steam deodorized at 210° C. The freshly deodorized oil was then molecularly distilled in an all-glass cyclic still at 210° C. The distillate, consisting of approximately 2.5 percent of the total oil, was then redistilled in successive passes at 90°, 125°, and 140° C.; the fractions distilling at the two latter temperatures were combined. Sterols were then substantially removed from the combined fractions by crystallization from acetone at a low temperature. The final concentrate assayed 11.8 percent tocopherols (calculated as alpha-tocopherol) by the Quackenbush (7) modification of the Furter-Meyer method and 11.75 percent by the Parker-McFarlane (6) modification of the Emmerie-Engel method. The latter modification employs an extraction with sulfuric acid to remove peroxides which interfere with the development of color in the Emmerie-Engle method.

The alpha-tocopherol used was a synthetic product (Merck). Its purity was tested by spectrographic measurements. The extinction coefficient found in ethyl alcohol, $E^{1\%}_{1cm.}$ 292 m(mu) was 71.4 which is in close agreement with the value of 71.0 reported by Robeson (8) for crystalline natural alpha-tocopherol.

The prime steam lard was a sample obtained from one of the larger meat packers; it had an initial peroxide value of 2.5 milli-equivalents per 1,000 gms. of fat. One series of peanut oils (PO-37 of Table 1) was prepared by hydrogenation at 300° F. of a several-months-old lot of refined hydraulic pressed oil from a commercial source. Another sample of peanut oil (PO-41-2 of Table 1) was prepared by the hydrogenation under similar conditions of a lot of peanut oil which had been obtained by solvent extraction in pilot plant equipment. This oil had been in storage in the crude form for several months, during which time its free fatty acid content had increased from 3.3 percent to 5.3 percent. It was refined with caustic soda and bleached prior to hydrogenation. All samples of peanut oil were steam deodorized at 210° C. (410° F.) and had peroxide values of less than 1.

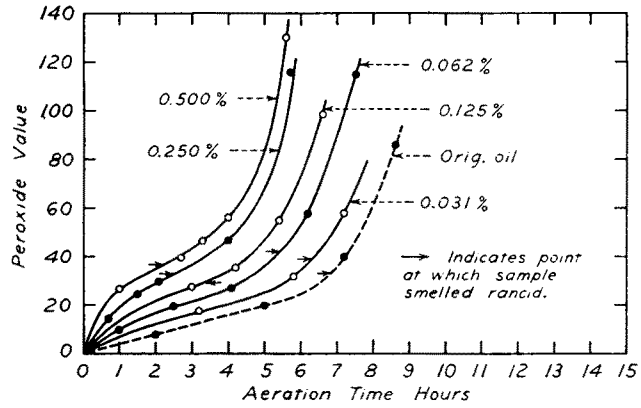

FIG. 1. Stability of hydrogenated peanut oil 37-3 containing different amounts of peanut oil antioxidant concentrate.

Stability tests on the various fat samples were conducted by the Swift or aeration method, using a temperature of 110° C. to accelerate the test, as suggested by Mehlenbacher (5). All peroxide values reported were calculated in terms of milli-equivalents per 1,000 gms. of fat.

Effect of the Antioxidants on Hydrogenated Peanut Oils of Low Stability

Stability data on various hydrogenated peanut oil samples with different percentages of the molecularly distilled peanut oil antioxidants added, are presented in Table 2. In no case did the addition of moderate amounts of antioxidants produce any significant im-

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TABLE 1

Characteristics of Lard and Peanut Oils Used for Tests of Peanut Oil Antioxidants and Alpha-tocopherol.

Fat	Stability, hours*	Tocopherol content, percent**	Iodine value	Thiocyanogen value	Percentage composition of fatty acids		
					Saturated	Oleic	Linoleic
Lard	2.2	nil	69.8	59.1	31.8	55.3	12.9
Peanut oil, PO-37-0	1.5	0.026	93.2	71.7	18.3	55.5	26.2
Above oil hydrog., PO-37-2	2.2	0.029	88.0	70.8	18.9	60.3	20.8
Above oil hydrog., PO-37-3	6.8	0.031	76.7	68.6	20.5	70.0	9.5
Above oil hydrog., PO-37-4	21.2	0.040	65.9	65.0	24.0	75.4	0.6
Above oil hydrog., PO-37-5	56.0	0.053	51.9	51.8	39.0	61.0	0.0
Hydrog. peanut oil PO-41-2	11.3	0.013	61.4	61.8	26.6	73.4	0.0

*-By the aeration method, at 110° C., stability recorded as hours required to develop a rancid odor.
** By the modified Emmerie-Engel method, calculated as alpha-tocopherol.

provement in the stability of the fats, and in most cases there was a progressive decrease in stability with increased concentration of antioxidants. The data for sample PO-37-3, as shown graphically in Figure 1, are typical. Essentially similar results, as indicated in Figure 2 and Table 2, were obtained by the addition of pure alpha-tocopherol to hydrogenated fats. The addition of 0.025 percent commercial soya lecithin to one fat (Figure 3) increased the stability of the fat at all levels of antioxidant concentration, and was equally effective at all levels. In the case of one fat (PO-37-3) similar results were obtained in stability tests conducted at 110° C. and 100° C.

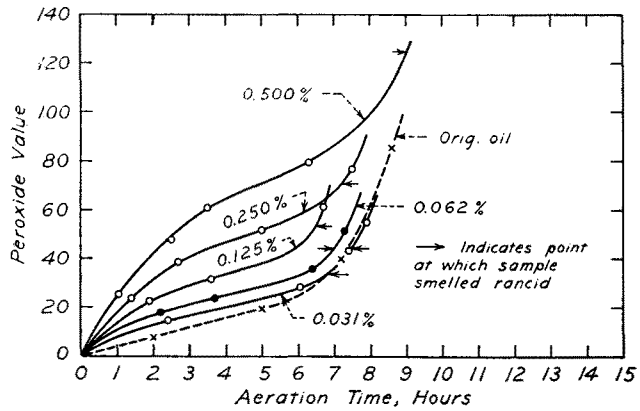

FIG. 2. Stability of hydrogenated peanut oil 37-3 containing different amounts of synthetic alpha-tocopherol.

The results indicate that the relatively poor stability of these particular peanut oils was not due to any deficiency in tocopherols or other distillable antioxidants, but must be attributed to other factors as yet unknown. Thus it would appear that in general neither raw nor hydrogenated peanut oils of poor stability can be improved by increasing their content of distillable antioxidants.

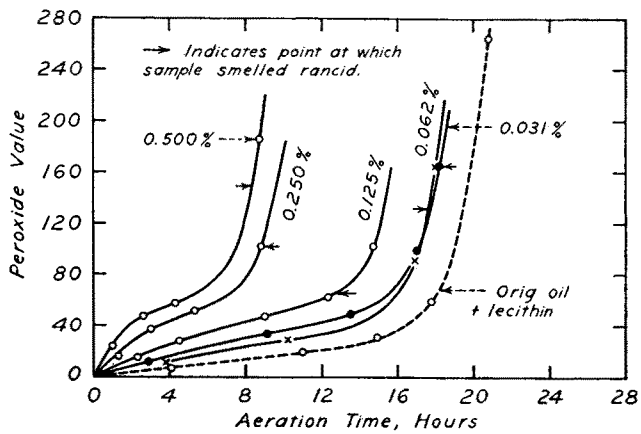

FIG. 3. Stability of hydrogenated peanut oil 37-3 containing 0.025 percent soya lecithin and different amounts of peanut oil antioxidant concentrate.

The behavior of the hydrogenated oils is in marked contrast to that observed previously (1) in the case of molecularly distilled fractions of a hydrogenated peanut oil. These fractions were increasingly stable with the addition of molecularly distilled peanut oil antioxidants up to at least 0.15 percent.

Effects of the Antioxidants on Lard

Stability tests were conducted on the lard alone, and on the lard containing from 0.0019 percent to 1.0 percent of alpha-tocopherol. Results of these tests are shown graphically in Figure 4. This series of tests represents the simplest case of natural antioxidant action, i.e., of a single substance of the tocopherol type in a substrate virtually devoid of antioxidants. The kinetics of the oxidation reaction are therefore of some interest in this case.

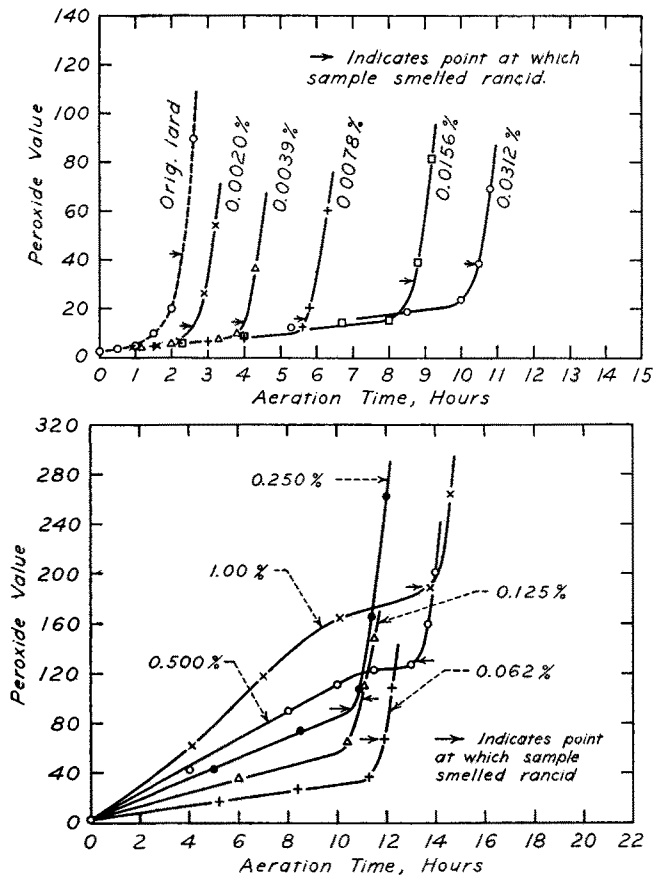

FIG. 4. Stability of prime steam lard containing different percentages of synthetic alpha-tocopherol.

As shown in Figure 4, the stability of the lard was progressively increased by the addition of alpha-toco-

TABLE 2

The Stability of Hydrogenated Peanut Oils With Various Percentages of Molecularly Distilled Peanut Oil Antioxidants and Pure Alpha-tocopherol Added. (Stability expressed in terms of hours' aeration at 110° C. required to produce organoleptic rancidity.)

Test No.	Fat	Antioxidant added	Percent tocopherols added	Stability, hrs.	Peroxide value at which sample became rancid*
A-1	Peanut oil	Peanut oil conc.	0	1.5	22
2	Peanut oil	Peanut oil conc.	.03	1.3	22
3	Peanut oil	Peanut oil conc.	.06	1.2	25
4	Peanut oil	Peanut oil conc.	.12	1.2	33
5	Peanut oil	Peanut oil conc.	.25	1.0	40
6	Peanut oil	Peanut oil conc.	.50	1.2	53
B-1	Hydrog. P. O. 37-2	Peanut oil conc.	0	2.2	25
2	Hydrog. P. O. 37-2	Peanut oil conc.	.03	2.4	28
3	Hydrog. P. O. 37-2	Peanut oil conc.	.06	1.8	28
4	Hydrog. P. O. 37-2	Peanut oil conc.	.12	1.6	36
5	Hydrog. P. O. 37-2	Peanut oil conc.	.25	1.2	41
6	Hydrog. P. O. 37-2	Peanut oil conc.	.50	1.0	42
C-1	Hydrog. P. O. 37-3	Peanut oil conc.	0	6.8	33
2	Hydrog. P. O. 37-3	Peanut oil conc.	.03	6.3	38
3	Hydrog. P. O. 37-3	Peanut oil conc.	.06	5.4	41
4	Hydrog. P. O. 37-3	Peanut oil conc.	.12	3.3	30
5	Hydrog. P. O. 37-3	Peanut oil conc.	.25	2.5	32
6	Hydrog. P. O. 37-3	Peanut oil conc.	.50	2.2	36
D-1	Hydrog. P. O. 37-4	Peanut oil conc.	0	21.2	27
2	Hydrog. P. O. 37-4	Peanut oil conc.	.03	18.7	45
3	Hydrog. P. O. 37-4	Peanut oil conc.	.06	19.0	55
4	Hydrog. P. O. 37-4	Peanut oil conc.	.12	18.8	57
5	Hydrog. P. O. 37-4	Peanut oil conc.	.25	18.0	62
6	Hydrog. P. O. 37-4	Peanut oil conc.	.50	18.0	75
E-1	Hydrog. P. O. 37-5	Peanut oil conc.	0	56	20
2	Hydrog. P. O. 37-5	Peanut oil conc.	.03	52	30
3	Hydrog. P. O. 37-5	Peanut oil conc.	.06	53	31
4	Hydrog. P. O. 37-5	Peanut oil conc.	.12	54	28
5	Hydrog. P. O. 37-5	Peanut oil conc.	.25	69	64
6	Hydrog. P. O. 37-5	Peanut oil conc.	.50	70	75
F-1	Hydrog. P. O. 37-3, with 0.025% lecithin added	Peanut oil conc.	0	17.7	57
2	Hydrog. P. O. 37-3, with 0.025% lecithin added	Peanut oil conc.	.03	17.7	135
3	Hydrog. P. O. 37-3, with 0.025% lecithin added	Peanut oil conc.	.06	18.2	160
4	Hydrog. P. O. 37-3, with 0.025% lecithin added	Peanut oil conc.	.12	12.7	65
5	Hydrog. P. O. 37-3, with 0.025% lecithin added	Peanut oil conc.	.25	8.8	100
6	Hydrog. P. O. 37-3, with 0.025% lecithin added	Peanut oil conc.	.50	8.3	170
G-1**	Hydrog. P. O. 37-3	Peanut oil conc.	0	15.4	40
2**	Hydrog. P. O. 37-3	Peanut oil conc.	.03	15.5	70
3**	Hydrog. P. O. 37-3	Peanut oil conc.	.06	14.2	65
4**	Hydrog. P. O. 37-3	Peanut oil conc.	.12	11.0	50
5**	Hydrog. P. O. 37-3	Peanut oil conc.	.25	7.6	47
H-1	Hydrog. P. O. 37-3	Alpha-tocopherol	0	6.8	33
2	Hydrog. P. O. 37-3	Alpha-tocopherol	.03	7.5	44
3	Hydrog. P. O. 37-3	Alpha-tocopherol	.06	7.0	47
4	Hydrog. P. O. 37-3	Alpha-tocopherol	.12	6.5	53
5	Hydrog. P. O. 37-3	Alpha-tocopherol	.25	7.2	70
6	Hydrog. P. O. 37-3	Alpha-tocopherol	.50	9.2	125
I-1	Hydrog. P. O. 41-2	Peanut oil conc.	0	11.3	20
2	Hydrog. P. O. 41-2	Peanut oil conc.	.03	11.5	29
3	Hydrog. P. O. 41-2	Peanut oil conc.	.06	12.0	43
4	Hydrog. P. O. 41-2	Peanut oil conc.	.12	10.6	43
5	Hydrog. P. O. 41-2	Peanut oil conc.	.25	8.8	38
J-1	Hydrog. P. O. 41-2	Alpha-tocopherol	0	11.3	20
2	Hydrog. P. O. 41-2	Alpha-tocopherol	.03	11.5	31
3	Hydrog. P. O. 41-2	Alpha-tocopherol	.06	11.6	47
4	Hydrog. P. O. 41-2	Alpha-tocopherol	.12	13.3	48
5	Hydrog. P. O. 41-2	Alpha-tocopherol	.25	15.2	51
6	Hydrog. P. O. 41-2	Alpha-tocopherol	.50	18.8	65

* Calculated as milli-equivalents per 1,000 gms. of fat.

** Tests made at 100° C., instead of 110° C.

pherol up to a level of about 0.05 percent. Above this level the further addition of tocopherol had little effect on the stability even up to a concentration as great as 1.0 percent. In the samples containing up to 0.25 percent tocopherol there was a clearly marked induction period during which the peroxide value of the fat increased linearly with aeration time, followed by a period of sharply accelerated peroxide formation, the beginning of which coincided with the incidence of organoleptic rancidity.

In the special case of fats which exhibit a linear increase in peroxide value during the induction period, and which become rancid immediately upon the ending of this period, the stability is a function of two factors. These are the rate of peroxide formation during the induction period and the critical peroxide level corresponding to the end of this period. The stability of the fat is directly proportional to this critical peroxide level, but inversely proportional to the rate of peroxide formation.

The effect of added alpha-tocopherol upon the two factors which thus determine stability is shown graphically in Figure 5. As the concentration of tocopherol is increased, there is a progressive increase in the peroxide value at which the induction period ends. On the other hand, with the same increase in tocopherol concentration, the rate of peroxide formation passes through a minimum at a tocopherol content of about 0.007 percent.

From the standpoint of the stability of the fat, the significant feature of Figure 5 turns upon the relative slopes of the two curves at equivalent tocopherol concentrations. It can be shown mathematically that within any range of tocopherol concentration in

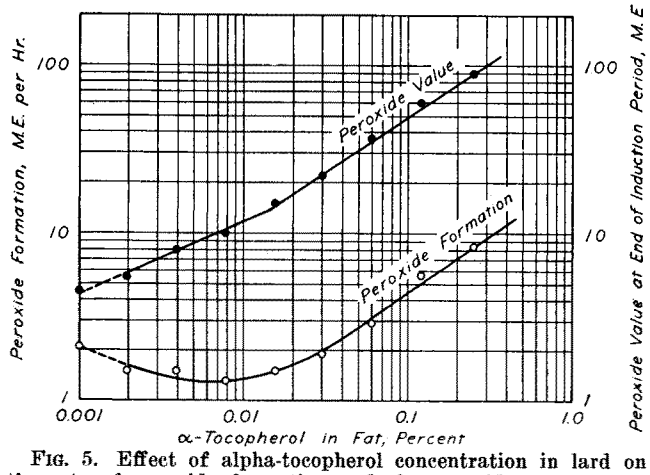

FIG. 5. Effect of alpha-tocopherol concentration in lard on the rate of peroxide formation and the peroxide value corresponding to the end of the induction period.

which the curves are diverging with increasing concentration, the addition of tocopherol increases the stability of the fat. Similarly, if such curves are converging, this is an indication of decreasing stability, and if they are parallel, the stability must be constant within the range of parallelism. In other words, under conditions leading to divergence of the curves, the addition of tocopherol causes the critical peroxide level to rise more rapidly than the rate at which this level is approached, and thus the stability increases. Under conditions corresponding to parallelism of the curves, the addition of tocopherol raises the critical peroxide level at the same rate as it increases the rate of peroxide formation, and thus the stability of the fat remains constant. It will be noted that the curves of Figure 5 diverge up to a tocopherol concentration of about 0.03 percent, after which they are substantially parallel.

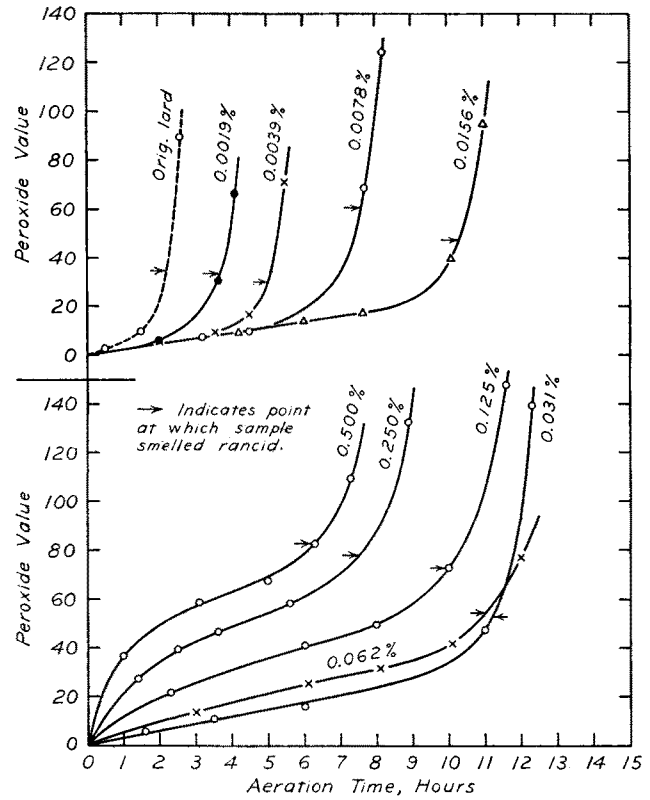

FIG. 6. Stability of prime steam lard containing different amounts of peanut oil antioxidant concentrate.

Results of stability tests on lard with distilled peanut oil antioxidants added are shown in Figure 6. These antioxidants differ from pure alpha-tocopherol in being somewhat more potent at the lower levels of concentration, and in causing a decrease in stability at the higher levels. The relationship between antioxidant concentration and stabiltiy (Figure 7) is very similar to that previously observed (1) in molecularly distilled, antioxidant-free unhydrogenated peanut oil, to which similar antioxidant concentrates were added.

The results shown in Figure 7, indicate that maximum stability in the lard is obtained with a concentration of peanut oil antioxidants corresponding to about 0.04 percent tocopherols, which is close to that occurring naturally in peanut oil. The addition of this optimum amount of antioxidants will increase the stability of the lard 9.1 hours, or from 2.1 to 11.2 hours. However, half this amount of antioxidants, or 0.02 percent tocopherols will be almost as effective, and will increase the stability 8.7 hours. Thus, it may be said that about 96 percent of the maximum antioxygenic effect of the peanut oil antioxidants will be derived from half the optimum addition of these substances. Similarly, about 76 percent of the maximum effect will be obtained from one-fourth the optimum addition, and about 47 percent of the maximum effect will result from one-eighth the optimum addition. Even the addition of as little as 0.0025 percent tocopherols, which is one-sixteenth of the optimum addition, will double the keeping time of the lard, and will confer upon it approximately 37 percent of the maximum stability obtainable. It is evident from extrapolation of the curves of Figure 7 that the original antioxidant content of the lard corresponded to about 0.0006 percent peanut oil tocopherols, or 0.0011 percent alpha-tocopherol. The relationship between stability and tocopherol concentration at the lower concentration levels is similar for peanut oil antioxidants and pure alpha-tocopherol.

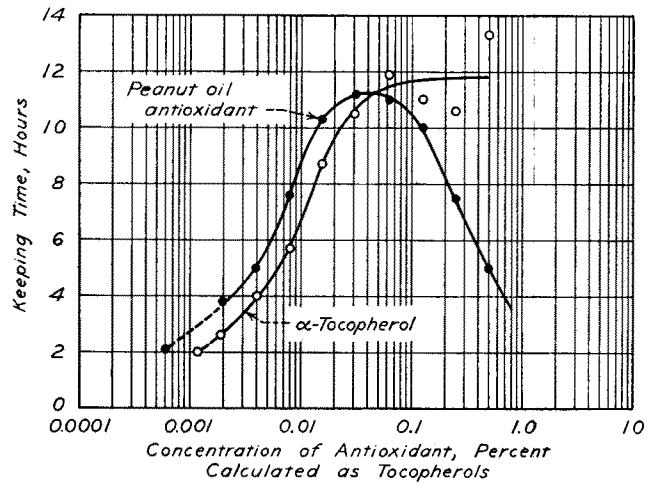

FIG. 7. Effect of peanut oil antioxidant concentrate and pure alpha-tocopherol on the stability of lard.

The addition of 0.02 percent commercial soya lecithin to the lard (Figure 8) had the effect of inhibiting the pro-oxidant effect of high concentrations of the distilled concentrates, and thus produced a series of stability curves somewhat similar to those obtained with pure alpha-tocopherol and lard.

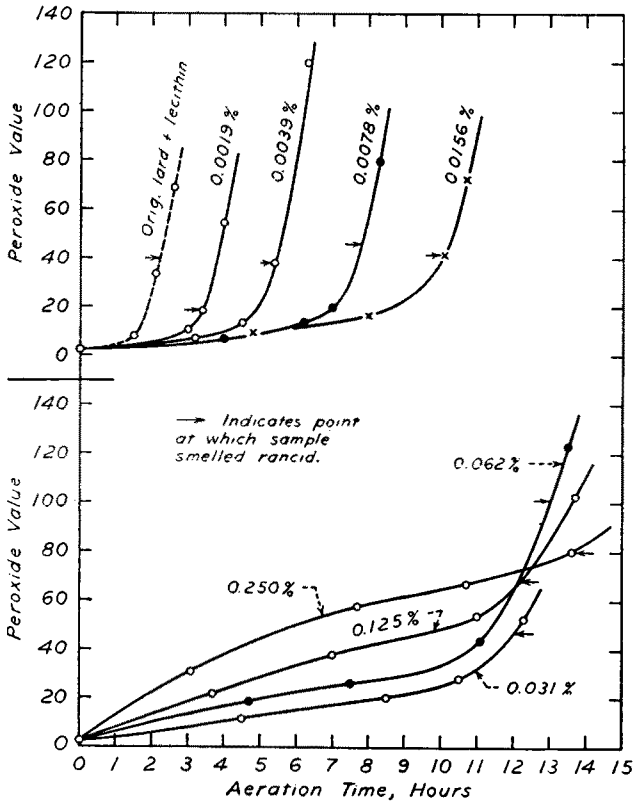

FIG. 8. Stability of prime steam lard containing 0.02 percent soya lecithin and different amounts of peanut oil antioxidant concentrate.

Two experiments were conducted to determine the correspondence between peroxide development and tocopherol disappearance in lard containing high concentrations of tocopherols. In one case, lard containing 0.5 percent alpha-tocopherol was aerated at 110° C., and samples taken periodically were tested for tocopherol content by the modified Emmerie-Engel and Furter-Meyer methods. In the other case, lard containing a corresponding amount of distilled peanut oil antioxidants was similarly treated. Samples of this lard were also tested for their content of chroman-5,6-quinones, by the method used by Golumbic (2,3), in which the step of nitric acid oxidation, as used in the Furter-Meyer assay is omitted. Results of these experiments are shown graphically in Figures 9 and 10.

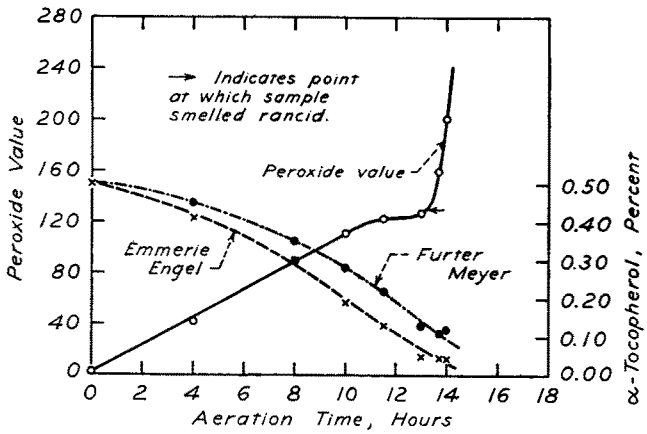

FIG. 9. Assays for tocopherols and related compounds on lard plus alpha-tocopherol during the course of a Swift stability test.

The results are in some respects at variance with the observations of Swift, Rose and Jamieson (9) and of Golumbic (3) relative to the destructive effect of peroxides on tocopherols and the coincidence of complete tocopherol disappearance with the end of the induction period.

If the Emmerie-Engel assay is accepted as the true measure of tocopherols present, there is no evidence that the oxidation of tocopherols is influenced by either the concentration of peroxides in the fat or the rate of peroxide formation. With lard containing peanut oil antioxidants, a plot of aeration time against the logarithm of the tocopherol concentration yields a straight line, indicating that the rate of tocopherol disappearance is simply proportional to its concentration in the fat. The oxidation of alpha-tocopherol in lard follows a somewhat different course, but again the tocopherol does not necessarily oxidize at an appreciably greater rate in the presence of high concentrations of peroxides than in the presence of low concentrations.

It is evident that peroxide formation may become rapid and rancidity may develop in a fat which still contains substantial amounts of tocopherols. In both cases the unoxidized residue of tocopherols remaining in the strongly rancid fat at the end of the induction period was as large as that normally present in fresh peanut oils.

If it is assumed that tocoquinones or other non-reducing substances with the chroman structure are represented by the difference between the Furter-Meyer and Emmerie-Engel assays, it must be concluded that the reaction:

Tocopherols → Non-reducing chromans → Non-chroman substances

follows different courses in the two cases of mixed peanut oil antioxidants and pure alpha-tocopherol.

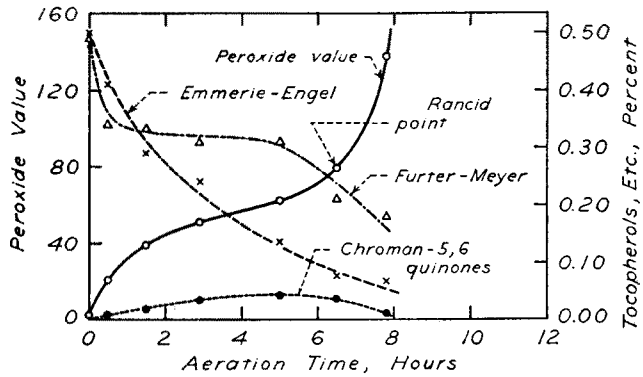

FIG. 10. Assays for tocopherols and related compounds on lard plus peanut oil antioxidants during the course of a Swift stability test.

Altogether, it appears evident that there must be drastic revision of the belief, more or less generally held at present, that the stability of vegetable oils is determined simply by their tocopherol content. The failure of the hydrogenated peanut oil to respond to the addition of antioxidants, the demonstration that a fat can rapidly oxidize and become rancid even while its tocopherol content is relatively high, the various peculiarities of mixed peanut oil antioxidants in comparison with alpha-tocopherol, and the general lack of correlation between stability and tocopherol content, all point very strongly to the existence in these oils of distillable substances capable of inhibit-

ing the action of tocopherols, or otherwise influencing the course of oxidation. These substances may be developed by oxidation, but are not peroxides, since they are stable toward steam deodorization.

Summary

1. Molecularly distilled concentrates of peanut oil antioxidants and pure alpha-tocopherol were tested at 110° C. as agents for the stabilization of lard and abnormal peanut oil products of poor stability.

2. Neither the peanut oil concentrates nor alpha-tocopherol were effective in improving the stability of either raw or hydrogenated peanut oils. In some cases, the addition of these substances materially reduced the stability of the oils. The results indicate that where poor keeping quality is encountered in hydrogenated peanut oils it is not in general due simply to a deficiency in tocopherols or related antioxidants.

3. Both alpha-tocopherol and peanut oil antioxidants were effective stabilizers for lard in concentrations up to approximately 0.06 percent. Above this concentration, the addition of alpha-tocopherol did not materially extend the keeping time of the lard, and the addition of peanut oil antioxidants decreased the keeping time. Essentially similar relationships between antioxidant concentrations and effectiveness were observed at the lower levels of concentration of the two antioxidants.

4. An investigation was made of the kinetics of peroxide formation in lard containing various percentages of alpha-tocopherol. With increasing tocopherol concentration, the peroxide level at which rapid oxidation begins was found to increase constantly, whereas the initial rate of peroxide formation passed through a minimum. This accounts for the antioxidant effect of low concentrations of alpha-tocopherol. At higher tocopherol levels the rate at which the peroxide level rises is balanced by the rate at which peroxide formation is accelerated and there is consequently no stabilizing effect.

5. No correlation was observed between the rate of tocopherol disappearance and either peroxide concentration or rate of peroxide formation in accelerated tests of lard containing 0.5 percent peanut oil tocopherols or 0.5 percent alpha-tocopherol. In these tests there was a considerable residue of unoxidized tocopherols remaining after the fat had become strongly rancid.

6. The experimental results strongly suggest the presence of distillable substances in vegetable oils which are capable of inhibiting the action of tocopherols, or otherwise acting as pro-oxidants. It is possible that such substances are developed by oxidation, but they do not consist of peroxides.

Acknowledgment

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Fatty Acid Esters of Furfuryl Alcohol

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Recently, during some partial saponification experiments using furfuryl alcohol as the solvent, it was observed that the unsaponified oil possessed a much higher iodine number than the original oil. For example, linseed oil of iodine number 170 gave an unsaponified fraction having an iodine number of 214-220 (Rapid Hanus method) (1). Since this high degree of unsaturation could not be due to a selective saponification of saturated glycerides, as evidenced by the iodine number of the saponified material, the formation of furfuryl esters by alcoholysis was suspected. Experiments to confirm this suspicion were initiated in view of the possible enhanced drying properties of such esters, because of their content of conjugated double bonds, known to be especially susceptible to oxidation and polymerization.

A search of the literature revealed that furfuryl palmitate had been used by Japanese workers in some tests described in a journal unavailable to the present authors (2). Other furfuryl esters had been prepared, however; namely the acetate (3), phthalate (4, 5), acetate through valerate (6), furoate (7), p-nitrobenzoate (8) and formate (9). These preparations involved (a) the use of the acid anhydride and mild heat, (b) ester interchange or (c) the use of an acyl halide in pyridine. Direct esterification catalyzed by mineral or strong organic acids must be avoided because of the violent polymerization of furfuryl alcohol in the presence of these acids.

In our first experiment linseed oil was treated with a furfuryl alcoholic solution containing 70% of the amount of potassium hydroxide necessary for complete saponification of the oil. The unsaponified material was extracted with petroleum ether, washed with water to remove furfuryl alcohol, and the petroleum ether removed under reduced pressure. Distillation yielded a product having a saponification equivalent of 358.8 and an iodine number (Rapid Hanus method) of 220.0, compared to the calculated values for linseed furfuryl esters of 358.9 and 219.9, respectively. The method of calculation is described in the experimental section.

In subsequent experiments it was found that much better yields of furfuryl esters could be obtained by

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