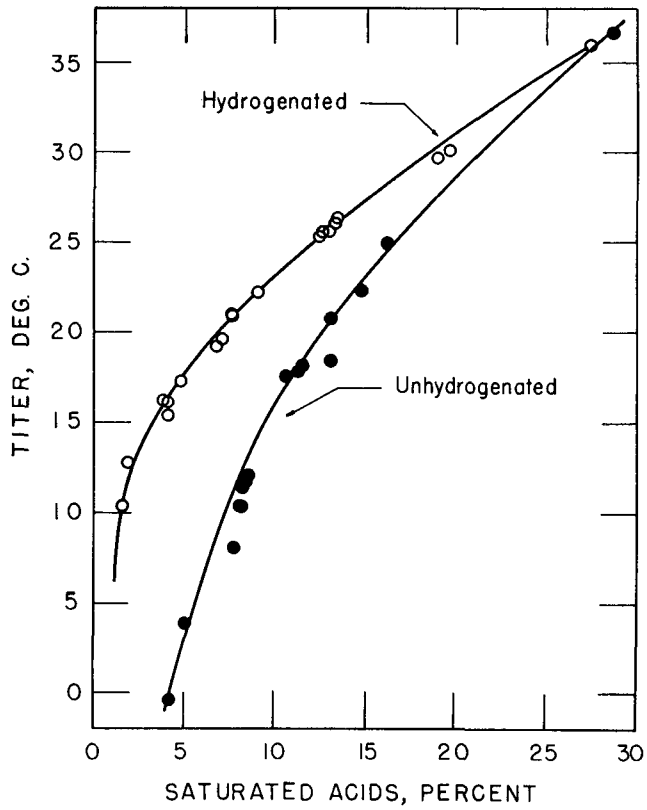

FIG. 5. Relationship between titer and saturated acid content of the liquid acid fractions.

to investigate this feature of the operation. In a single instance, however, involving crystallization of the unhydrogenated acids from Skellysolve B at 15° F., the precipitate from 150 g. of acids was washed on the filter with four successive 300 cc. portions of solvent at 15° F. There were obtained 35.2 g. of washed acids, which had an iodine value of 7.1, and, therefore, consisted of about 95 per cent saturated and 5 per cent unsaturated acids.

Summary

1. An investigation has been made of low-temperature crystallization from organic solvents as a means of effecting practical separations of the solid and liquid acids of unhydrogenated and hydrogenated cottonseed oils.

2. At any fixed temperature the most efficient separations were obtained in the highly polar solvents, acetone and methyl acetate. However, it was possible in any case to make nonpolar petroleum naphtha (Skellysolve B) fully equivalent to the polar solvents simply by conducting the crystallization at a temperature approximately 10° F. lower than that employed with the polar solvents. Ethyl acetate and methyl ethyl ketone were intermediate between petroleum naphtha and acetone or methyl acetate in their effectiveness.

3. By employing a solvent-fatty acid ratio of 4 to 1 by weight and conducting crystallizations at 5° F. or lower from acetone and —5° F. or lower from petroleum naphtha, the liquid fatty acids from unhydrogenated cottonseed oil could be reduced to below —2° C. in titer and to below about 3 per cent in saturated acid content. Under these conditions there was no appreciable crystallization of oleic acid.

4. At a solvent-fatty acid ratio of 6 to 1 and the same temperatures (5° F. for acetone and — 5° F. for petroleum naphtha) equally good separations could be made of the saturated fatty acids present in the mixed acids from hydrogenated cottonseed oil (I.V.=70). Separation of "iso-oleic" acids from the fatty acids of the hydrogenated oil took place over a wide range of temperatures, beginning at 35° F. in acetone and at 25° F. in petroleum naptha, and being incomplete (according to Twitchell analyses of the liquid acids) in either solvent at —15° F. However, the bulk of the higher melting iso-oleic acids was precipitated as the temperature approached —5° F. in acetone and —15° F. in petroleum naphtha.

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Stability Values Obtained by Different Rapid Methods as a Means of Evaluating Antioxidants for Fats and Oils

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THE most widely used rapid methods for determining stability of fats and oils are the active-oxygen (Swift stability test), oxygen-absorption, and oven incubation methods. These methods are also being extensively used to determine the relative effectiveness of antioxidants.

Little is known of the mechanism by which antioxidants inhibit oxidation. It is possible that some antioxidants cause the formation of products different from those normally formed during oxidative rancidification. In this case, use of a pre-established peroxide value or quantity of oxygen absorbed as an end point of the induction period, as commonly employed in rapid tests, might be invalid.

Surprisingly few data have been published that permit a comparison of stability values by different rapid methods for evaluating antioxidants. King, Roschen, and Irwin (1) reported results of a collaborative study in which the stabilities of four lards

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were compared, as determined by the active-oxygen method, an oxygen-absorption procedure, and several incubation tests. Two of these lards contained unspecified antioxidants. The relative order of the samples with regard to stability determined by the various methods was about the same, but the stability values obtained by any one method did not bear a constant relationship to those obtained by any of the other methods. Recently, interest has been stimulated by the finding (2) that certain compounds added to lard may show marked antioxidant activity by the active-oxygen method but pro-oxidant activity by the oxygen-absorption method in which the Barcroft-Warburg apparatus is used and also, that the stability by the latter method agrees more closely with the stability obtained by an "accelerated" storage test.

In an investigation on the improvement of lard, particularly in respect to increasing its resistance to oxidative rancidity by the addition of antioxidants, we have obtained a large number of stability values, which permit a comparison between the active-oxygen and oxygen-absorption methods and oven tests. In some instances, the effects of dry air, dry oxygen, and moist air on the stability values by the active-oxygen method were also investigated.

In general, the protection factors, calculated from stability values obtained by the various methods, show fair agreement. In a few instances, however, the lack of agreement in the protection factors is too great to be attributed to normal errors and may be an indication that certain antioxidants influence the course as well as the rate of oxidation. Little significant difference in stability values was obtained by using dry air instead of moist air in the active-oxygen method.

Experimental

Methods of Determining Stability. Stability values by the active-oxygen method (A.O.M.) were determined by a modified procedure described previously (3). In some experiments dry air or dry oxygen was employed instead of moist air. Dry air was obtained by passing washed air (as obtained in the usual procedure) through two efficient dry-ice traps, a column of Drierite, and finally a column of Dehydrite. Dry oxygen was obtained by subjecting tank oxygen to the same washing and drying treatment. The average moisture content of the moist air and dry air was 19.5 and 0.20 mgs. per liter, respectively. A peroxide value equivalent to 30 milli-equivalents per kilogram of sample was taken as the end point of the induction period. This value has been found to agree more closely with organoleptic tests than the conventional value of 20 milli-equivalents, particularly when antioxidants are used.

Most of the oxygen-absorption measurements were obtained with the Barcroft-Warburg (B-W) apparatus, flasks, technique, and general procedure described by Johnston and Frey (4). In a few instances oxygen-absorption values also were obtained by a macro method (Table 4). For the (B-W) oxygen-absorption measurement, 0.43 g. of fat was placed in the inner cup (2.14 cm. inside diameter) of a special flask (Eck & Krebs Catalogue No. 210) fitted to Warburg manometers containing Brodie solution. Cylinder oxygen was used. The flasks were immersed in a glycerol bath maintained at 100° C. but were not shaken during the period of oxygen absorption. The end point of the induction period was recorded as the time required for absorption of oxygen equivalent to 1 g. per kilogram of sample.

Macro oxygen-absorption measurements were made by a method similar to that described by French, Olcott, and Mattill (5) except that a different type of flask was used and the samples were shaken during the period of oxygen absorption. Jacketed flasks of 250-cc. capacity (Corning Catalogue No. 4510) were used, and heat was supplied by passing steam through the jacket. The flow of steam was controlled to maintain the temperature of the sample at 100°. The end point of the induction was taken as the time required for a 20-g. sample to absorb oxygen equivalent to 1 g. per kilogram.

The oven-stability values were determined by a procedure described in a previous publication (6). A peroxide value equivalent to 30 milli-equivalents per kilogram of sample was considered as the end point of the induction period.

The ratio of the stability of the stabilized sample to that of the control was taken as the protection factor.

With the exception of catechol, nordihydroguaiaretic acid (NDGA), and citric acid, the antioxidants were added directly to the substrate fats, solution being aided in some instances by warming and shaking the mixture *in vacuo*. Catechol, NDGA, and citric acid were added as alcohol solutions. The alcohol was removed by heating the mixture in a deodorizer (7) at 60° under reduced pressure. After the pressure became constant at 1.5 to 2 mm., heating was continued for 10 minutes. An exception to the above was made in the NDGA experiments shown in Table 2, in which a 1.5-percent solution of NDGA in lard was added in amounts required to give the desired concentration of antioxidant. This solution was made by heating the lard containing the NDGA at about 125° C., with stirring, for about 15 minutes.

Results and Discussion

RESULTS of one series of tests, in which stability values were determined only by the active-oxygen and oxygen-absorption methods (B-W), are given in Table 1.

TABLE 1.

Stability Values Obtained by the Active-Oxygen Method (Moist Air) and by the Oxygen Absorption Method (Barcroft-Warburg Apparatus).

Antioxidants added	Stability		Protection factor	
	A.O.M. (moist air) 98.5°	O_2-Abs. (B-W) 100°	A.O.M. (moist air) 98.5°	O_2-Abs. (B-W) 100°
percent	*hours*	*hours*		
Steam-rendered lard-A (control)	6.3	2.8	1	1
+.005 NDGA[1]	27	8.3	4.3	3.0
+.005 NDGA+.005 d-IP[2]	67	26.2	10.6	9.4
+.005 NDGA+.005 citric acid.	53	23.7	8.4	8.5
+.01 lec[3]+.02 d-IP	13	3.8	2.1	1.4
+.01 toc[4]+.01 lec+.02 d-IP	40	14.4	6.3	5.1
Oleo-oil (control)	6	2.7	1	1
+.005 NDGA	43	15.0	7.2	5.6
+.005 NDGA+.005 d-IP	150	37.2	25.0	13.8

[1] Nordihydroguaiaretic acid.
[2] d-Isoascorbyl palmitate.
[3] Commercial soya lecithin.
[4] *a*-Tocopherol.

Results by the two methods, as indicated by the protection factors, are in general agreement. The protection factors obtained by the oxygen-absorption method, however, were lower than those by the active oxygen method; the value for oleo-oil containing both NDGA and d-isoascorbyl palmitate was markedly low.

TABLE 2.

Stability Values Obtained by the Active-Oxygen (Moist Air), Oxygen-Absorption (Barcroft-Warburg Apparatus), and Oven-Incubation Methods on Samples Prepared in Pilot Plant.

Antioxidants added	Stability			Protection factors		
	A.O.M. (moist air) 98.5°	O_2-Abs. (B-W) 100°	Oven test 63°	A.O.M. (moist air) 98.5°	O_2-Abs. (B-W) 100°	Oven test 63°
percent	*hours*	*hours*	*days*			
Steam-rendered lard-B (control)	0.4	0.2	0.3	1	1	1
+10.0 hyd. soy oil[1]	5	2.5	3.1	12.5	12.5	10.3
+10.0 hyd. soy oil +.01 lec[2]+.01 d-lP[3]	29	13.5	18	73	68	60
+.01 toc[4]+.01 lec +.01 d-lP	25	12.2	15	63	61	50
+.005 NDGA[5]	2	1.4	1.6	5.0	7.0	5.3
+.005 NDGA +.005 citric acid	36	17.2	30	90	86	100
+.005 NDGA +.005 d-lP	44	16.1	42	110	81	140
+.005 NDGA +.01 lec	12.5	6.7	10	31	34	33
+.01 NDGA	7.5	5.0	6.6	19	25	22
Drip-rendered lard (control)	4.5	1.3	.....	1	1	.....
+.01 NDGA	65	21	.....	14.4	16.1	.....

[1] Soy oil hydrogenated to an iodine number of 60.0 was added, and the mixture was deodorized.
[2] Commercial soya lecithin.
[3] d-Isoascorbyl palmitate.
[4] A mixture of tocopherols was added as a concentrate (34% in vegetable oil).
[5] Nordihydroguaiaretic acid.

The reason for such a large discrepancy in this instance has not been determined.

The samples for the series of experiments summarized in Table 2 were prepared in pilot-plant equipment. Unavoidable difficulties and delays during the preparation of the series related to control lard-B resulted in products of unusually low stability. Nevertheless, the results were considered of sufficient interest to be presented as a contrast to those obtained on samples prepared from controls of higher stability. Stability values determined by an oven test (6) are given in Table 2 in addition to those by the active-oxygen and oxygen-absorption methods.

The differences in the protection factors reported in Table 2 might reasonably be expected since an error of even 0.1 unit in a control having such low stability obviously would produce enormous differences in the protection factors. For that reason, no particular significance can be attached to them other than that they give a rough indication of agreement between the methods. Comparison of the protection factors of the stabilized samples from a control having low stability with those from controls of greater stability (Tables 1, 2, and 3) shows clearly the fallacy of indiscriminate use of these factors as a means of comparing antioxidants. Comparisons of the effectiveness of antioxidants by means of protection factors may be valid only if the same substrate is used. Synergism was much more pronounced with lard of low stability (Table 2) than in the series in Table 3 with lard of good stability.

The stability values in Table 3 were determined by the active-oxygen and oxygen-absorption (B-W) methods; dry air as well as moist air was employed in the active-oxygen method. The stabilized samples were prepared in the laboratory from lard of good stability. The protection factors show fair agreement in most cases. In a few instances, however, the differences are significant and are not attributed to lack of reproducibility of the stability values. The variation in reproducibility of each method was about 5%. The preparations containing benzylhydroquinone gave significantly lower protection factors by the oxygen-absorption method; those containing catechol gave significantly higher factors. The differences between the stability values or protection factors obtained by the active-oxygen method using moist air as compared with those obtained when dry air was used may be of little significance from a practical viewpoint.

The order of increasing effectiveness of the tocopherols [2] as antioxidants was α, β, γ, although the relative differences between them was much less than that reported by Olcott and Emerson (8), who found that at 75° the β and γ were about 2 and 3 times, respectively, as effective as α.

The samples represented in Table 4, with the exception of those containing NDGA, were prepared in pilot-plant equipment. As in the preceding tables, the protection factors indicate a general but not close agreement between the various methods. In

[2] Contributed by Merck & Co., Inc.

TABLE 3.

Stability Values and Protection Factors of Stabilized Lard Obtained by the Active-Oxygen Method With Moist and With Dry Air and by the Oxygen-Absorption Method (Barcroft-Warburg Apparatus).

Antioxidants added	Stability			Protection factors		
	A.O.M.		O_2-Abs. (B-W) 100°	A.O.M.		O_2-Abs. (B-W) 100°
	(moist air) 98.5°	(dry air) 98.5°		(moist air) 98.5°	(dry air) 98.5°	
percent	*hours*	*hours*	*hours*			
Steam-rendered lard-C (control)	7	6	3.0	1	1	1
+.01 α-tocopherol	20	19	8.6	2.9	3.2	2.9
+.01 β-tocopherol	24	21	11.0	3.4	3.5	3.7
+.01 γ-tocopherol	28	30	14.5	4.0	5.0	4.8
+ 6.4[1] refined corn oil	20	20	12.3	2.9	3.3	4.1
+.01 α-tocopherol +.01 citric acid	21	21	11.0	3.0	3.5	3.7
+.005 benzylhydroquinone	43	44	11.0	6.1	7.3	3.7
+.005 benzylhydroquinone +.01 citric acid	50	50	14.1	7.1	8.3	4.7
+.005 propyl gallate	40	42	20.1	5.7	7.0	6.7
+.005 propyl gallate +.01 citric acid	50	50	24.8	7.1	8.3	8.3
+.005 NDGA[2]	58	50	26.9	8.3	8.3	9.0
+.005 NDGA +.01 citric acid	67	62	32.8	9.6	10.3	10.9
+.01 catechol	44	43	28.9	6.3	7.2	9.6
+.01 catechol +.01 citric acid	48	48	43.2	6.9	8.0	14.4

[1] Equivalent to .01% tocopherol.
[2] Nordihydroguaiaretic acid.

TABLE 4.

Stability Values and Protection Factors of Stabilized Lard Obtained by Various Rapid Stability Tests.

Antioxidants added	Stability						Protection factors					
	A.O.M.			O_2-Abs. (macro) 100°	O_2-Abs. (B-W) 100°	Oven test 63°	A.O.M.			O_2-Abs. (macro) 100°	O_2-Abs. (B-W) 100°	Oven test 63°
	(moist air) 98.5°	(dry air) 98.5°	(dry O_2) 98.5°				(moist air) 98.5°	(dry air) 98.5°	(dry O_2) 98.5°			
percent	*hours*	*hours*	*hours*	*hours*	*hours*	*days*						
Steam-rendered lard-D (control).	2	1.8	1.5	1	1.2	1.5	1	1	1	1	1	1
+.01 toc[1]+.04 lec[2]+.04 d-IP[3]..	30	24	15	15	14	16	15	13	10	15	12	11
+.02 NDGA[4].....	37	33	34	22	....	49	19	18	23	22	....	33
Steam-rendered lard-E[5](control).	5.5	5.5	4	3.3	2.8	4	1	1	1	1	1	1
+.01 toc +.04 lec +.04 d-IP[6]..	68	53	23	23	19	33	12	10	6	7	7	8
+.01 toc +.04 lec +.04 d-IP[7]..	84	66	30	29	28	44	15	12	8	9	10	11
+.02 NDGA.....	64	57	45	41	....	51	12	10	11	12	....	13

[1] A mixture of tocopherols was added as a concentrate (34% in vegetable oil).
[2] Commercial soya lecithin.
[3] d-Isoascorbyl palmitate.
[4] Nordihydroguaiaretic acid.
[5] The same lard as (D) except that about 12% of hardened lard had been added and then deodorized.
[6] After the addition of tocopherol, the lard was deodorized; then lecithin and d-isoascorbyl palmitate were added.
[7] The tocopherol, lecithin, and d-isoascorbyl palmitate were added after the lard was deodorized.

this series of tests (Table 4), the use of dry air in the active-oxygen method gave lower stability values than did the use of moist air. Differences due to dry air were most significant for preparations containing tocopherol, lecithin, and d-isoascorbyl palmitate. When dry oxygen was employed, the stability values were somewhat comparable with those obtained by the oxygen-absorption methods. In this series, owing to the relatively low stability of the control, protection factors by the different methods are exaggerated and may be subject to greater error.

Summary

A COMPARISON was made of stability values and protection factors as determined by three widely used rapid methods—the active-oxygen, oxygen-absorption, and the oven-test methods. In most instances there was fair agreement between the results by the active-oxygen and oxygen-absorption methods, as indicated by protection factors. In general, use of dry air instead of moist air in the active-oxygen method resulted in little significant difference in the stability values although in some preparations, differences were found that may be significant. Use of dry oxygen in the active-oxygen method gave results comparable with those obtained by the oxygen-absorption method. In experiments in which an oven test was also used, the protection factors in most cases were in general agreement with those obtained by the other two methods.

The synergistic antioxidant effect of acidic compounds with phenolic antioxidants was most pronounced when lard of low stability was used. Likewise, the protection factors were disproportionately greater when antioxidants were added to lard of low stability than when added to lard of good stability. The results indicate that comparison of antioxidants by means of protection factors is valid only when the same substrate is used. Protection factors so obtained help to evaluate the order of effectiveness of various antioxidants but do not yield a strict quantitative comparison of the protective power of the antioxidants when applied to other substrates.

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Allylic Esters of Polymeric Fat Acids

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THE CHEMISTRY of the acids obtained by polymerization of the polyunsaturated fat acid components of vegetable and cereal oils of the northern region has been studied extensively at this laboratory. Since organic compounds containing the allyl grouping have been widely investigated as sources of industrially useful polymers, it was of interest to study allylic esters of these polymeric fat acids.

This paper reports the preparation and polymerization of the allyl, β-methallyl, and β-chlorallyl esters of polymeric soybean fat acids and of purified dilinoleic acid which is the principal constituent of these acids. Bradley and Johnston (1, 2) and Cowan (7) have described the preparation, properties, and composition of polymeric fat acids; and Bradley and Johnston (2) and Cowan and Wheeler (6) have reported the isolation of dilinoleic acid and its physical and chemical properties.

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Materials

Polymeric fat acids prepared from soybean oil were obtained from the Procter and Gamble Company. The acids had the following constants: acid value, 191; iodine value [3 min. Wijs (10, 11)], 76.5; saponification number (2 hours), 193; n_D^{30} 1.4871.