deodorizer distillates from edible oil processing plants. Various deodorizers give different quantities of tocopherol in the distillates. In one controlled experiment on a mixture of refined and hydrogenated soybean and cottonseed oils, a 5% loss of tocopherols was observed. We, therefore, estimate that the loss during commercial deodorization is only a few per cent.

Summary. A method for the analysis of the total tocopherols in soybean oil has been presented, and judged by distillation and other procedures is estimated to be accurate to within 10%. A discussion is made of the tocopherol losses in various steps of soybean oil refining.

REFERENCES

1. Baxter, J. G. Biological Symposia XII, (1947).
2. Baxter, J. G., and Stern, M. H. Analytical Chemistry. In press.
3. Dam, H., *et al.* Kgl. Danske Videnscab Selskab. Biol. Med. *16*, 7 (1941).
4. Evelyn. J. Biol. Chem. *115*, 63-75 (1936).
5. Hickman, K. C. D. Ind. Eng. Chem., Anal. Ed. *14*, 253 (1942).
6. Kaunitz, H., and Beaver, J. J. J. Biol. Chem. *156*, 653-51 (1944).
6a. Olcott, H. S. J. Biol. Chem. *105*, lxv (1934).
7. Parker, W. E., and McFarlane, W. D. Can. J. Res., Sect. B, *18*, 405 (1940).
8. Quaife, M. L., and Biehler, R. J. Biol. Chem. *159*, 3 (1945).
9. Quaife, M. L., and Harris, P. L. Ind. Eng. Chem., Anal. Ed., *18*, 707 (1946).
10. Rawlings, H. W. Oil & Soap *21*, 257 (1944).
11. Stern, M. H., Robeson, C. D., Weisler, L., and Baxter, J. G. J. Am. Chem. Soc. *69*, 869 (1947).
12. Weisler, L., Robeson, C. D., and Baxter, J. G. Analytical Chemistry. In press.

Delta-Tocopherol as an Antioxidant in Lard[1,2]

JANICE GRIEWAHN and B. F. DAUBERT

THE antioxidative properties of α-, β-, and γ-tocopherols, isolated and named by Evans and co-workers (1), have been known for some time, having first been demonstrated by Olcott and Emerson (2) in 1937 and later verified by Hove and Hove (3). γ-Tocopherol was shown to be a more effective antioxidant in lard than β-tocopherol, which in turn was more effective than α-tocopherol. "The tocopherols function most effectively at lower levels of concentration and with decreasing efficiency at higher levels," as indicated by Swift, Rose, and Jamieson (4), and also by Golumbic (5). Stern, Robeson, Weisler, and Baxter (6) recently announced the isolation and properties of another tocopherol, which they named δ-tocopherol. They demonstrated that this newly-isolated tocopherol is more effective as an antioxidant for vitamin A acetate at 39° and 55°, and for β-carotene at 39°, in olive oil, than α-, β-, or γ-tocopherol. The purpose of this paper is to compare the relative antioxygenic effects of the four tocopherols in concentrations of 0.02 and 0.1% using lard as a substrate.

Experimental[3]

Oxidation was accelerated by means of a modified Swift Stability Test (7, 8). Compressed air, washed with a solution of potassium dichromate, was dried through a system of concentrated sulfuric acid, sodium hydroxide pellets, and anhydrous calcium chloride. Molten lard with added tocopherol was poured into a three-necked flask and maintained at 100°C. by means of a thermoregulated oil bath. The air was bubbled through the lard at a rate such that the lard was saturated with air. Samples were removed by means of a pipette at intervals in accordance with the rate of oxidation. Peroxides were determined by a modified Wheeler method (9).

[1] The subject matter of this paper has been undertaken in cooperation with the Committee on Food Research of the Quartermaster Food & Container Institute for the Armed Forces. The opinions or conclusions contained in this report are those of the authors. They are not to be construed as necessarily reflecting the views or indorsement of the War Department.

[2] Contribution No. 653 from the Department of Chemistry, University of Pittsburgh.

[3] The δ-tocopherol was supplied through the courtesy of James G. Baxter of Distillation Products, Inc., Rochester, N. Y.

Results and Discussion

The tocopherol effects, at 0.02% concentration, on the oxidation of lard at 100°C. by the modified Swift Stability Test are shown in Fig. 1. The endpoint of

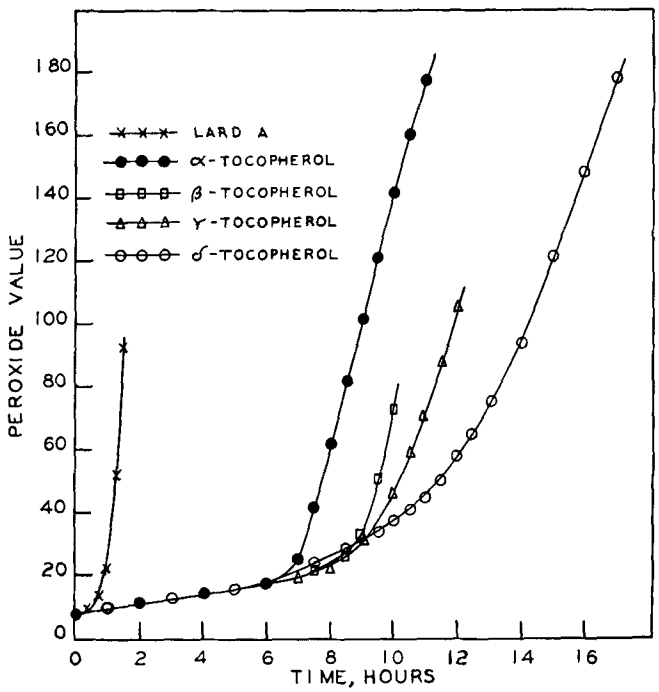

FIG. 1. The tocopherol effect on the oxidation of lard at 100°C. at a concentration of 0.02% in lard.

the induction period was chosen arbitrarily as a peroxide value equivalent to 40 milliequivalents per kilogram of sample. This value is somewhat higher than the value of 30 milliequivalents used by Riemenschneider, *et al.* (10). The induction periods in hours, therefore, for the tocopherols were approximately as follows: α-tocopherol, 7.5; β-tocopherol, 9; γ-tocopherol, 9.5; and δ-tocopherol, 11. The ratios of the relative activities of α-, β-, γ- and δ-tocopherols as

antioxidants for lard are 1:1.2:1.3:1.5, respectively. The order of increasing effectiveness of α-, β-, and γ-tocopherols as antioxidants are in general agreement with that reported by Riemenschneider, *et al.*, for 0.01% concentration except that the difference between β- and γ- is much smaller at the 0.02% concentration.

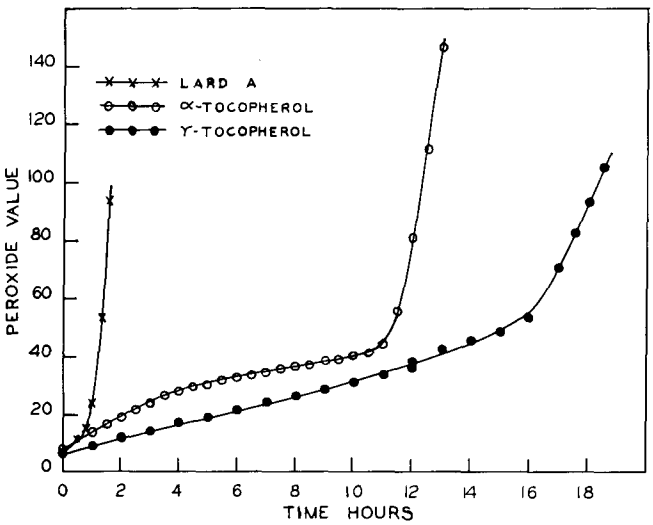

FIG. 2. The tocopherol effect on the oxidation of lard at 100°C. at a concentration of 0.1% in lard.

The comparison of the antioxidative properties of the tocopherols at a concentration of 0.1% was also made, as shown in Fig. 2 and 3. Two different lard specimens were used for these determinations: Lard A, with an induction period of one hour, was used for the 0.02% (Fig. 1) and 0.1% (Fig. 2) concentrations. Lard B, with an induction period of 10 hours, was the substrate used for the determinations at 0.1% as shown in Fig. 3. The induction periods were approximately as follows: Lard A (Fig. 2), α-tocopherol, 11 hours; γ-tocopherol, 13 hours; Lard B (Fig. 3), α-tocopherol, 17 hours; β-tocopherol, 22 hours; γ-tocopherol, 35 hours; and δ-tocopherol, 42 hours. The ratios of the relative activities of α-, β-, γ-, and δ-tocopherols at 0.1% concentration are 1:1.3:2:2.5, respectively.

According to Fig. 2, an increase from 0.02% to 0.1% tocopherol increased the lengths of the induction periods. The rate of peroxide formation, however, became more rapid at the beginnings of the induction periods with an increase in tocopherol content, in agreement with the observations of Swift, Rose, and Jamieson (4) on methyl esters of cottonseed oil. Swift, *et al.*, have attempted to explain this phenomenon. Since antioxidants function to relieve fatty acid peroxides of excess energy and thereby prevent peroxide accumulation rather than to remove the

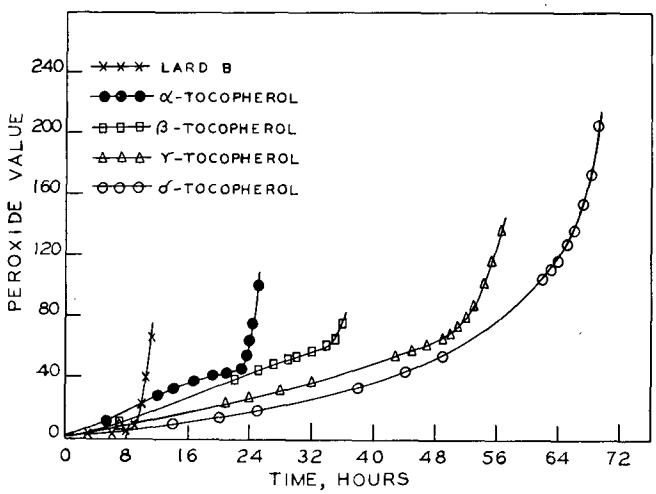

FIG. 3. The tocopherol effect on the oxidation of lard at 100°C. at a concentration of 0.1% tocopherol in lard.

peroxides when added to oxidizing fats, they suggested the existence of two kinds of peroxides. As they point out, and as is shown in Fig. 1 and 2, "the rate of peroxide accumulation, as well as the stability of the samples, was observed to increase upon the addition of successively higher amounts of tocopherol. Since the tocopherol was presumably oxidized in reaction with the least stable peroxides, it appears that those peroxides which accumulated were of the more stable type."

A comparison of the four tocopherols at a concentration of 0.1% in lard as plotted in Fig. 3 shows that δ-tocopherol is also the most effective antioxidant under these conditions.

Summary

Comparison of the antioxidative properties of α-, β-, γ-, and δ-tocopherols at concentrations of 0.02% and 0.1% tocopherol in lard have been made by means of a modified Swift Stability Test at 100°C. In order of increasing antioxidative effectiveness, the tocopherols are: α, β, γ, and δ.

REFERENCES

1. Evans, H. M., *et al.*, J. Biol. Chem., *113*, 319 (1936); Science, *83*, 421 (1936).

2. Olcott, H. S., and Emerson, O. H., J. Am. Chem. Soc., *59*, 1008 (1937).

3. Hove, E. L., and Hove, Z., J. Biol. Chem. *156*, 623 (1944).

4. Swift, C. E., Rose, W. G., and Jamieson, G. S., Oil and Soap, *19*, 176 (1942).

5. Golumbic, C., Oil and Soap, *20*, 105 (1943).

6. Stern, M. H., Robeson, C. D., Weisler, L., and Baxter, J. G., J. Am. Chem. Soc., *69*, 869 (1947).

7. King, A. E., Roschen, H. L., and Irwin, W. H., Oil and Soap, 10, 105 (1933).

8. Mehlenbacher, V. C., Oil and Soap, *19*, 137 (1942).

9. Wheeler, D. H., Oil and Soap, *9*, 89 (1932).

10. Riemenschneider, R. W., Luddy, F. E., Herb, S. F., and Turer, J., Oil and Soap, *22*, 174 (1945).