Tocopherols as Carry-Through Antioxidants

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THE ANTIOXIDANT ACTIVITY OF TOCOPHEROLS has long been recognized. The activity of the various tocopherols has been compared and found to vary inversely with the order of their biological vitamin E activity. Olcott and Emerson (7) with animal fats, and Hove and Hove (3) with carotene and ethyl oleate showed that gamma was more effective than beta, which in turn was more effective than alpha tocopherol. Stern *et al.* (9) used vitamin A and beta carotene, and Griewahn and Daubert (2) used lard to show that delta tocopherol is a more effective antioxidant than the other tocopherols.

It is generally accepted that the tocopherols are primarily responsible for the stabilities of the vegetable oils. Quaife (8) demonstrated the presence of various tocopherols in some of the vegetable oils, and Lange (5) listed the tocopherol content of a great number of food products including fats and oils. Little mention has been made of the carry-through activity of the tocopherols. McGuine *et al.* (6) found that hydrogenated lard was stabilized by adding tocopherols and that some carry-through stability was imparted to crackers made with lard or oleo oil containing 0.03% of a 30% tocopherol concentrate.

This report is concerned with the carry-through activity and antioxidant activity of tocopherols in comparison with and in combination with other antioxidants in lard.

Experimental Methods. Stability of treated fats was determined by the Active Oxygen Method (4). Carry-through activity was evaluated from the keeping time of crackers, pastry, and potato chips prepared with the stabilized lards and incubated at 63°C. in loosely capped, 4-oz. glass jars. Rancidity was assessed by organoleptic means. Crackers and pastry were prepared from standardized test formulas. Potato chips were prepared by frying five 100-g. lots in 1,500 g. of fat and discarding the first three lots. The last two lots of potato chips were combined for keeping time tests.

Results and Discussion of Carry-through of Tocopherols. Tocopherols can be obtained in purified form, but the most readily available are in a vegetable oil concentrate. Concentrates produced from soybean oil have approximately 30% tocopherols, which are mostly gamma tocopherol.

Tocopherols from such a concentrate were used to stabilize lard for AOM and carry-through tests in comparison with BHA and BHT, which are known to have carry-through activity. The concentrate was used in one test to provide 0.005% and in a second test to provide 0.01% tocopherol in lard. BHA and BHT were each used at 0.01% in both tests. The results of these tests are shown in Table I. Tocopherols were slightly less effective in providing AOM stability than BHA or BHT, and tocopherols proved to have carry-through activity in each test. The use of 0.01% tocopherol did not provide an appreciably better AOM stability or carry-through effect than the use of 0.005%. The carry-through activity of tocopherols was much less than that provided by BHA or BHT.

The use of purified α- and γ-tocopherols was studied

TABLE I

Carry-through Activity of Tocopherols Compared with BHA and BHT

Antioxidant		AOM Stability (hrs.)	Oven Stability at 63°C. (hrs.)		
			Crackers	Pastry	Potato Chips
Control lard No. 1		10	117	123	44
BHA	0.01%	34½	995	1194	576
BHT	0.01%	36	885	722	278
Tocopherols [a]	0.005%	28½	305	271	230
Control lard No. 2		8¾	111	170	42
BHA	0.01%	30¾	830	1067	583
BHT	0.01%	33½	816	812	359
Tocopherols	0.01%	29	233	295	228

[a] Supplied by a concentrate containing 30% tocopherols, mostly gamma.

to compare their relative carry-through activity with one another and BHA. The data in Table II reveal that α-tocopherol has very little carry-through effect but that γ-tocopherol has a marked effect. The carry-through effect of γ-tocopherol in the one lard tested was not equivalent to that provided by BHA. It followed the pattern shown by the AOM stability

TABLE II

Carry-through Activity of Alpha- and Gamma-Tocopherols Compared with BHA

Antioxidant		AOM Stability (hrs.)	Oven Stability at 63°C. (hrs.)		
			Crackers	Pastry	Potato Chips
Control lard		13	271	239	66
BHA	0.01%	50½	820	1056	521
d, α-Tocopherol	0.01%	34	393	230	125
d, γ-Tocopherol	0.01%	44	510	483	285

of the treated lard in that BHA provided the greatest stability, followed in turn by γ-tocopherol and α-tocopherol.

Interesting results were obtained when combinations of BHA and tocopherols were used in lard. BHA was used at a constant level of 0.01% and a tocopherol concentrate at levels to provide 0.01, 0.05, and 0.1% tocopherols in the lard. Results are shown in Tables III and IV.

It was shown by Swift *et al.* (10) and by Golumbic (1) that an optimum quantity of γ-tocopherols exists for stabilization of fats. A quantity in excess of this amount will provide lesser stability through an apparent pro-oxidant effect.

TABLE III

Carry-through Activity of BHA-Tocopherol Combinations

Antioxidant		AOM Stability (hrs.)	Oven Stability at 63°C. (hrs.)		
			Crackers	Pastry	Potato Chips
Control lard		5	273	197	48
Tocopherol [a]	0.01%	26	992	547	489
Tocopherol	0.05%	29	1603	1128	1253
Tocopherol	0.10%	25	1915	1488	1507
BHA	0.01%	31	1329	849	408
Tocopherol BHA	0.01% 0.01%	28	1469	1267	1109
Tocopherol BHA	0.05% 0.01%	24	1762	1536	1493
Tocopherol BHA	0.1 % 0.01%	21	1867	1734	1593

[a] Supplied by a concentrate containing 30% tocopherols, mostly gamma.

TABLE IV
Carry-through Activity of BHA-Tocopherol Combinations

Antioxidant		AOM Stability (hrs.)	Oven Stability at 63°C. (hrs.)		
			Crackers	Pastry	Potato Chips
Control lard		7	163	307	67
Tocopherol [a]	0.01%	29	288	518	566
Tocopherol	0.05%	27	984	1339	2045
Tocopherol	0.10%	23	1497	1747	2496
BHA	0.01%	31	1044	1805	1133
Tocopherol BHA	0.01% 0.01%	33½	798	2006	1709
Tocopherol BHA	0.05% 0.01%	27	1257	2370	2473
Tocopherol BHA	0.10% 0.01%	24	1680	2342	2781

[a] Supplied by a concentrate containing 30% tocopherols, mostly gamma.

The maximum AOM stability was provided by 0.01% tocopherols in one lard and by 0.05% in the other lard. Increasing the concentration of tocopherols then provided less stability in conformance with the observations of other workers, as noted above. The maximum stability provided by the combination with BHA resulted from use of 0.01% tocopherols, and when increased levels of tocopherols were used, a decreased stability resulted. The presence of BHA did not prevent the pro-oxidant effect of the higher levels of tocopherols. There was no positive synergistic activity between antioxidants in either lard.

The carry-through tests revealed a different situation. The higher levels of tocopherols provided increased oven stability in all test foods. The higher levels of tocopherols in combination with BHA provided a further increase in oven stability. The combinations with BHA provided greater stability than the corresponding level of tocopherol used alone. Generally the combination of 0.01% tocopherols with 0.01% BHA provided better carry-through stability than BHA used alone at 0.01%. It was observed in lards and foods made with lard containing 0.05% and 0.1% tocopherols that a pronounced off-flavor, described as fishy, was developed.

The reasons for the increased carry-through activity with higher levels of tocopherols are not clearly apparent. Perhaps the heat treatment involved in cooking may destroy or modify tocopherols to a level where they do not exert the pro-oxidant effect. There is also the possibility that the function of the tocopherols is altered in the complex system of a food so that the effect is reversed.

These studies indicate that tocopherols are indeed carry-through antioxidants. It is implied that improved stability of foods made with fats containing tocopherols can be accomplished by the use of BHA although the AOM stability of the fat may not be improved significantly.

Studies designed to test the effectiveness of tocopherols with other antioxidants revealed a negative synergistic effect with all tested except BHT. The antioxidant effect with BHT seemed to be merely additive. The antioxidants showing a negative synergism under conditions of the AOM test with the tocopherol concentrate in lard were BHA, nordihydroguariaretic acid, diphenyl-p-phenylenediamine, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, and p-hydroxydiphenylamine.

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Summary

1. Tocopherols have been found to be carry-through antioxidants in lard.
2. Gamma tocopherol, which is a better antioxidant than alpha tocopherol, is also a better carry-through antioxidant.
3. Higher levels of tocopherol provide increased carry-through stability although the AOM stability of lard is decreased.
4. Combinations of BHA with tocopherol in lard provide increased carry-through stability but do not increase the AOM stability.

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New Integrated Refining Process for Edible Oils[1]

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SINCE JANUARY, 1950, at least 30 papers have been presented before this Society or in the Journal of the American Oil Chemists' Society dealing with the problems and virtues of recovering oil from vegetable and animal source material by means of solvents. This attests to the considerable interest shown by the industry in this type of oil recovery. For a number of years the research facilities of Ranchers Cotton Oil have concentrated on solving some of the problems associated with this type of operation.

One of the major problems encountered in a solvent type of operation is buyer resistance to dusty solvent meal. The desirable economic factor of an additional 20 to 50 lbs. of oil per ton of vegetable source material processed is in part offset by a meal that is difficult to sell in competition with Expeller or hydraulic pressed meal which contains 2% to 4% more oil.

We have successfully resolved the dusty meal prob-

[1] Presented before the Spring Meeting of the American Oil Chemists' Society in Houston, Tex., April 22–25, 1956.