Antioxidant Properties of the Fatty Alcohol Esters of Gallic Acid

STEWARD G. MORRIS, LILLIAN A. KRAEKEL,[1] DOROTHY HAMMER, J. S. MYERS, and R. W. RIEMENSCHNEIDER

Eastern Regional Research Laboratory[2]
Philadelphia 18, Pennsylvania

PREVENTION of rancidity in fats and oils has received considerable attention during the last 15 to 20 years. Recently several reviews on the subject of antioxidants have been published (1,2,3,4). In general it is agreed that the polyphenolic compounds which have hydroxyl groups in ortho or para relation to each other are most effective. Powerful antioxidants of this type are nordihydroguaiaretic acid (NDGA) (5) and gallic acid.

One disadvantage of these antioxidants is their low solubility in fats and oils. This lack of solubility gives rise to technical difficulties in the process of incorporating the antioxidants into the fat.

The effect of fat solubility and the lipophilic character of an antioxidant on its carry-over into baked goods has been recognized for some time, but no systematic study has been reported. The fat solubility of a phenolic type of compound may be increased by introducing an alkyl group into the nucleus. A convenient method of improving the fat solubility of the hydroxybenzoic acids, for example, gallic acid, is esterification with fatty alcohols. A United States patent was issued to Sabalitschka and Böhm (6) in 1941 on the use of methyl, ethyl, propyl, and butyl gallates as antioxidants for fats and oils. These gallates have been classified among the best antioxidants. Furthermore, gallic acid and its esters in the small amounts required for use as fat antioxidants are generally considered non-toxic. Lea (1) pointed out that gallic acid is widely distributed as a constituent of the tannins present in many vegetable foods, particularly in tea. In recent pharmacological tests with mice (3) ethyl gallate was fed or injected in quantities greatly exceeding anything which would be taken in food stabilized with this substance. There were no apparent ill effects.

[1] Present address: Rohm and Haas, Philadelphia, Pa.

[2] One of the Laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

In studying the effect of fat solubility on the carry-over into baked goods, it was considered desirable to use antioxidants of greater solubility than that of the lower gallates. For this purpose, therefore, the higher gallates—octyl, dodecyl, tetradecyl, hexadecyl, and octadecyl were prepared (7). These higher esters were readily soluble in fats and oils. The present paper is a continuation of this work and is a report on the evaluation of the antioxidant properties of these compounds.

Experimental

The lard used was a good-quality, steam-rendered lard consisting of 25% killing fats and 75% cutting fats. The hydrogenated vegetable shortening was a commercial grade purchased in the local retail market. The cottonseed oil was alkali refined and bleached.

Stability Tests: The modification of the active oxygen method (A.O.M.) previously described (8) was employed for evaluating the antioxidants in the fat substrates. The gallic acid and NDGA were incorporated by means of alcoholic solutions, and the solvent was removed as described in a previous paper (9).

Baking Tests: The effectiveness of the antioxidants in bakery goods was determined by piecrust tests. The recipe for the piecrust consisted of 100 g. pastry flour, 44 g. lard, 2.5 g. salt, and 33 cc. water. The pastry was mixed in a mechanical mixer and then rolled to one-eighth-inch thickness with a motor-driven sheeter. The dough was cut into round wafers one inch in diameter and baked on a sheet of aluminum at 200°C. for 17 minutes. The thermostatically controlled oven was of the reel type with four shelves which rotated vertically, so that the wafers were evenly exposed to the heat. In comparative baking tests, it is extremely important that the various batches of bakery products be browned to the same degree. The greater the degree of browning of a piecrust, the more rapidly rancidity will develop.

TABLE I.

Evaluation of Antioxidants at Different Concentrations.

Substrate	Anti-oxidant	Stability by the Active Oxygen Method					
		NDGA	Gallic Acid	Gallic Acid Esters			
				Propyl	Octyl	Dodecyl	Octadecyl
	%	*hours*	*hours*	*hours*	*hours*	*hours*	*hours*
Lard[1]	0.05	73	141	114	110	113	104
Lard	0.02	85	103	91	80	70	68
Lard	0.01	85	66	70	60	45	44
Lard	0.005	55	38	50	43	33	31
Lard	0.10	62	....	....	....	....	....
Lard	0.083[4]	....	....	....	106	....	....
Lard	0.10[4]	....	....	....	....	101	....
Lard	0.20	....	....	....	....	97	....
Lard	0.124[4]	....	....	....	....	....	108
HVO[2]	0.05	199	....	294	....	229	....
HVO	0.01	112	....	138	....	113	....
CSO[3]	0.01	8	13	10	11	10	9

[1] Lard-control, 7 hours.
[2] Hydrogenated vegetable oil—control 78 hours.
[3] Cottonseed oil—control 8 hours.
[4] Concentration of the gallate is equal to the molecular equivalent of 0.05% gallic acid.

The wafers were placed in 6-oz. wide-mouth bottles, covered with small watch glasses, and stored at 38° C. and at 63° C. Rancidity was determined organoleptically.

Results and Discussion

The stability values on lard in Table I show a somewhat higher protective action for gallic acid than for its esters. The difference, however, is not so great as might be expected since the functional portion (gallic acid radical) of octadecyl gallate, for example, is only about 40% of its molecular weight. Thus, when gallic acid and the esters were added in equal molecular concentrations (gallic acid equal to 0.005% concentration, Table II) the esters gave greater protection than gallic acid. On the other hand, gallic acid at the high concentration of 0.05% gave somewhat higher protective action than did the esters in molecular equivalent amounts, Table I. This concentration, however, is above the optimum level for the esters. The differences between the individual esters may not be significant. None of the antioxidants gave much protection for cottonseed oil, whereas they markedly enhanced the stability of hydrogenated vegetable oil.

TABLE II.

Stability Values for Lard Containing 0.005% NDGA, 0.005% Gallic Acid, and Esters of Gallic Acid in Corresponding Molecular Equivalent Amounts.

Antioxidant	A.O.M. Stability
	hours
NDGA	43
Gallic acid	33
Propyl gallate	44
Hexyl gallate	55
Octyl gallate	52
Dodecyl gallate	42
Tetradecyl gallate	45
Hexadecyl gallate	54
Octadecyl gallate	55
None	8

The usual synergistic effects of certain acidic compounds were also noted. As shown by the stability values in Table III, isoascorbyl palmitate (6-palmityl-d-isoascorbic acid) was the most effective. In general, the synergists were more effective when used with NDGA than with the gallates.

The results of baking tests in which piecrust wafers were stored at two temperatures are shown in Table IV. The effectiveness or carry-over of the antioxidant properties of the higher gallate esters in piecrust was much superior to that of propyl gallate or gallic acid. This was true at both storage temperatures but was shown more strikingly in the tests at 63°C. When the antioxidants were added in 0.05% concentrations, rancidity developed in 1 and 3 days, respectively, in wafers containing gallic acid and propyl gallate, while 8, 9, and 10 days, respectively, were required for rancidity to develop in the wafers containing octyl, dodecyl, and octadecyl gallates.

TABLE III.

Evaluation of the Synergistic Effect of Phosphoric Acid, Isoascorbyl[1] Palmitate, and Citric Acid on Antioxidants in Lard.

Antioxidant	A.O.M. Stability			
	Without Synergist	With 0.01% H_3PO_4	With 0.02% Isoascorbyl[1] Palmitate	With 0.02% Citric Acid
	hours	*hours*	*hours*	*hours*
0.02% NDGA	79	105	147	109
0.02% Gallic Acid	93	....	133	....
0.02% Propyl Gallate	93	89	119	82
0.02% Octyl Gallate	71	....	103	....
0.02% Dodecyl Gallate	58	71	94	75
0.02% Hexadecyl Gallate	63	71	89	61
None	5.5	....	....	....

[1]6-palmityl-d-isoascorbic acid.

Most antioxidants in oils have an optimum concentration, above which there is no appreciable increase in the protective value as measured by the active oxygen method. In Table I there was no increase in protective value when the concentration of the antioxidant was raised above 0.05%. In baking tests, however, the optimum concentration of antioxidants was considerably higher. In Tables IV and V, the results of baking tests indicate that the dodecyl and octadecyl gallates are much more effective at 0.1% concentrations than they are at 0.05%.

TABLE V.

Days Required for Development of Rancidity in Piecrust Wafers Made With Lard Containing 0.05% Gallic Acid and the Esters of Gallic Acid in Corresponding Molecular Equivalent Amounts.

Antioxidant	Days Required for Development of Rancidity	
	At 38°C.	At 63°C.
0.05% Gallic Acid	26	1
0.1% Dodecyl Gallate	>185	53
.124% Octadecyl Gallate	>185	79
0.1% NDGA	48	5
Control	18	2

In a few preliminary tests on baked crackers, the degree of carryover of the gallates was considerably less than that reported for piecrust wafers.

The substantially better carry-over of the antioxidant action of the higher gallates than that of gallic acid or propyl gallate suggests that fat solubility of the antioxidant is an important factor. More work with different series of compounds, however, is required before any general conclusions can be drawn.

Summary and Conclusions

The antioxidant properties of octyl, dodecyl, tetradecyl, hexadecyl, and octadecyl gallates in lard substrate were determined by the active oxygen method. The order of their effectiveness was about the same as that of the more active antioxidants, nordihy-

TABLE IV.

Days Required for Development of Rancidity in Piecrust Wafers Made With Lard Containing Different Amounts of Antioxidants.

Temperature of Storage	Antioxidant	Days Required for Development of Rancidity					
		NDGA	Gallic Acid	Gallic Acid Esters			
				Propyl	Octyl	Dodecyl	Octadecyl
	%						
38°C.	0.05	49	26	35	60	46	60
Control, 18 days	0.02	27	26	35	46	60	42
63°C.	0.05	6	1	3	8	9	10
Control, 2 days	0.02	2	1	2	5	6	4

droguariaretic acid and gallic acid, that have been reported. The carry-over of the antioxidant properties into baked goods was determined by storage tests on piecrust at 38° and 63°C. The results show that the higher gallates have good protective action in baked piecrust and are much superior to gallic acid and propyl gallate.

These higher esters of gallic acid are readily soluble in fats. This factor is of great importance in commercial stabilization of fats.

REFERENCES

1. Lea, C. H., J. Soc. Chem. Ind. *63*, 107 (1944).
2. Bergel, F., Chem. and Ind. *1944*, 127.
3. Hilditch, T. P., Chem. and Ind. *1944*, 67.
4. Mattill, H. A., Oil and Soap *22*, 1 (1945).
5. Lundberg, W. O., Halverson, H. O., and Burr, G. O., Oil and Soap *21*, 33 (1944).
6. Sabalitschka and Böhm, U. S. Pat. 2,255,191 (1941).
7. Morris, S. G., and Riemenschneider, R. W., J. Am. Chem. Soc. *68*, 500 (1946).
8. Riemenschneider, R. W., Turer, J., and Speck, R. M., Oil and Soap *20*, 169 (1943).
9. Riemenschneider, R. W., Luddy, F. E., Herb, S. F., and Turer, J., Oil and Soap *22*, 174 (1945).

Effect of Drying and Storing Tung Seeds On Quality of the Oil and Milling Characteristics of the Seeds*

RAIFORD L. HOLMES and FRANK C. PACK
Bureau of Agricultural and Industrial Chemistry
Agricultural Research Administration, U. S. Department of Agriculture
Bogalusa, Louisiana

and

S. G. GILBERT
Bureau of Plant Industry, Soils, and Agricultural Engineering
Agricultural Research Administration, U. S. Department of Agriculture
Gainesville, Florida

ONE of the major problems with which the tung oil industry is confronted is that of drying tung fruits or seeds sufficiently to be milled or stored. As production is increased this problem becomes even more important. The tung fruits contain 60% to 70% moisture when they fall from the trees, and they cannot be stored in bins in layers more than about a foot in depth until they have dried to 15% to 20% moisture, nor can the oil be pressed efficiently from tung seeds until the seeds have dried to about 9% moisture. Drying to even 20% moisture requires several weeks in the orchard. Without the use of driers it is not possible to start the milling operations until about two months after the fruits have matured. Also, in some years rainfall is so heavy that it is almost impossible to dry the fruits sufficiently in the orchard to store or to mill them.

Since there is a considerable investment in the processing plant, it is desirable to run the mill as long each season as feasible, and in many seasons the mills have operated into June. The fruits need to be off the ground by the first of April at the latest so that field operations can begin, and some form of storage would be necessary to accomplish this and enable the mills to operate as late as June. These facts point out the need of being able to dry and store tung fruits or seeds.

Obviously, it would be desirable to remove the hulls before drying or storage because of the smaller amount of heat required for the drying and the smaller storage capacity required for the hulled fruits. Even if there should be a market for the dried hulls it probably would not be feasible to dry the whole fruits before hulling because of the loss of kernel fragments in hulling fruits that are too dry.

In practice, most of the hulling has been done in the tung mills by disc hullers, and this type of huller in addition to removing all of the hulls ordinarily removes about half of the shells and breaks some of the kernels, the amount of breakage varying with conditions of the fruits and setting of the discs. A huller has been developed by the Agricultural Engineering Division of the Bureau of Plant Industry, Soils and Agricultural Engineering which breaks a low percentage of shells (5). This huller can be built small enough to be used as a portable huller or as large as it needs to be. The storage experiments reported in this paper were carried out on seeds that had been hulled in one of these portable hullers, on the assumption that if hulled seeds are to be stored such storage would be limited to seeds with the least possible proportion of broken shells.

Drying and storage are so intimately connected that it is almost impossible to study the latter without considering the former. Also, drying and storage conditions may have considerable effect on the behavior of the seeds in the screw press. For these reasons experiments were designed in which seeds were dried under controlled conditions, stored for different periods, and then processed in a commercial screw press, thus permitting studies on all of these phases with the same material.

In general, it is well known that in handling other oil seeds such as cottonseed there is a certain moisture content above which development of acidity takes place rather rapidly at ordinary temperatures. The upper limit of moisture content for safe storage of these seeds is about 13% (3). These same principles would presumably apply to tung seeds. It is thought

*Agricultural Chemical Research Division Contribution No. 180. Presented at annual meeting of the American Tung Oil Association, Pensacola, Florida, April 26-27, 1946.