The Antioxidant Properties of Gallic Acid and Allied Compounds

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On the basis of the ability to stabilize animal or vegetable fats against autoxidative rancidity, Olcott and Mattill (1) made a tentative classification of three groups of antioxidants. One of these, the inhibitols, (1,2) delayed the autoxidation of animal but not of vegetable fats. The reverse was true of certain acid inhibitors; such acids as citric, tartaric and phosphoric had little or no stabilizing effect on animal fats but were very good antioxidants for certain vegetable fats. In general these acid-type inhibitors displayed a reinforcing or "synergistic" activity with inhibitols when both were added to animal fats, purified fat acids and other unsaturated substrates; that is, when both types of stabilizers were used together, the resulting induction period was much longer than the sum of the induction periods when they were used separately. Indeed, the protection afforded vegetable fats by the acid-type stabilizers alone constitutes a demonstration of this synergism, in that these fats already contain inhibitols. With the exception of pyruvic acid the organic acid inhibitors were di- or tri-carboxylic acids, and were primarily alike only in the possession of ionizable hydrogen atoms. Their synergistic capacity was shown to be contingent upon the presence of free carboxyl groups; that of pyruvic acid was ascribed to the accessory activating effect of its carbonyl group. It is doubtful however that synergism can be explained merely on the basis of varying acid strength because there is no correlation between the ionization constants of the acid inhibitors and their relative synergistic efficiency.

In a third group were certain phenolic compounds which protected both animal and vegetable fats; examples are such natural products as catechol, pyrogallol and gallic acid. This preliminary classification of inhibitors was made solely for the purposes of orientation and no claims were made for completeness; there may be other kinds of fat antioxidants (3) for which a place must be found in a more comprehensive classification.

In order to explore the limitations and usefulness of this classification, the antioxygenic properties of gallic acid were studied in some detail. It was of particular interest to determine whether this compound which is both phenol and acid would also exhibit dual antioxygenic properties. Experimentally, this was found to be the case. The acid is not only a powerful antioxidant for lard and vegetable oils but also shows a marked synergistic action with inhibitols in animal fat substrates and in vegetable fats as well, when further amounts of inhibitols are added to them in the form of concentrates (Table I).

Inasmuch as benzoic acid is not an acid-type inhibitor, it is apparent that the phenolic groups as well as the carboxyl group of gallic acid are involved in its synergistic activity. When both groups are bound, as in ethyl triacetyl gallate, all synergistic activity is lost (Table II). This derivative, as well as all others in which the pyrogallol portion of the molecule is no longer free, possess no antioxygenic activity. This is not necessarily true of the synergistic activity; thus, trimethoxy gallic acid is ineffective as a synergist whereas triacetyl gallic acid can still enhance the antioxygenic effect of inhibitols (Table II) even though it is no longer effective as an antioxidant. Evidently, in the former compound, some essential but as yet unknown property of the carboxyl group has been nullified but remains unaffected in the acetyl derivative. When the pyrogallol portion of gallic acid is uncombined, the free carboxyl group is no longer indispensible for the appearance of synergistic activity. Thus, ethyl gallate although somewhat less effective than gallic acid as an antioxidant, has synergistic properties similar to those of the parent compound.

TABLE I

The Antioxygenic Action of Gallic Acid

Test Fat	Induction Period—Hours [1] With Inhibitor	Induction Period—Hours [1] Control
Lard + 0.01% gallic acid	22½	17
	21	15
Lard + 0.06% gallic acid	213	12
	43½	17
Lard + 0.04% inhibitol concentrate (C-3-1)[2]	30	15
Lard + 0.01% gallic acid + 0.04% C-3-1	> 90	17
	>192	15
Crude ethyl esters of cotton seed oil [3]		
+ 0.01% gallic acid	83½	12
+ 0.10% C-3-1	3	12
+ 0.01% gallic acid + 0.10% C-3-1	>312	12
	Induction Period—Days [4]	
Hydrogenated cottonseed oil	32, 40	
+ 0.001% gallic acid	30, 39	
+ 0.02% C-3-1	39, 41	
+ 0.001% gallic acid + 0.02% C-3-1	>50	

[1] By the method of oxygen absorption, at 75°.
[2] An inhibitol concentrate prepared from cottonseed oil, as described previously (1).
[3] Prepared as previously described (1).
[4] By the oven test at 63°.

In view of the ability of ethyl gallate to act as an acid-type inhibitor, it was of interest to determine if pyrogallol also had this property. It does act in this fashion (Table II) in addition to being one of the most powerful of phenolic inhibitors.

The other isomeric trihydric phenols, hydroxyhydroquinone and phloroglucinol, also shared this dual nature in their antioxygenic properties (Table II). Phloroglucinol is exceptional in that it is rather of the acid type and is more effective on vegetable than on animal fat substrates. This behavior is doubtless related to its well-known keto-enol isomerism. Acetylacetone, an open chain compound which is structurally related to phloroglucinol and shows the same keto-enol tautomerism, was also effective on the vegetable fat substrate (antioxygenic index = 4).

It is apparent that classification of inhibitors solely on response of fat substrates to their action leads to considerable complication and gives no clear insight into the mechanism of synergistic action. In their study of the synergistic action of tocopherol and ascorbic acid, Golumbic and Mattill (4) showed that the oxidation of the phenolic inhibitor was retarded at the expense of the other. For such a coupled reaction to occur a difference in oxidation potential between the two inhibitors is necessary. Such differences also exist between the synergists reported here. Thus the oxidation potentials of gallic acid and of the trihydric phenols (5) are appreciably higher than the apparent oxidation potential of α-tocopherol (6). The possibility of a rational classification of fat inhibitors based on their oxidation potentials is being investigated. The role of inorganic acid inhibitors, e.g. phosphoric acid, in such an arrangement will be discussed in a subsequent report.

TABLE II

The Antioxygenic Action of Gallic Acid and Related Compounds

Compound	(Phenolic) Antioxygenic Index (Lard)[1]	(Acid) Antioxygenic Index (Crude C.S.O.[2] Esters)	Synergism with Inhibitol [3] (Lard)	Synergism with Inhibitol [4] (Crude C.S.O. Esters)
Gallic acid	18 [5]	7-10	+	+
Ethyl gallate	4	6	+	+
Triacetyl gallic acid	1	3	+	+
Ethyl triacetyl gallate	1	1	—	—
Trimethoxy gallic acid	1	1		—
Pyrogallol	>60 [6]	32		+
Hydroxy hydroquinone	>60 [6]	18		+
Phloroglucinol	2	16	+	+

[1] This is the ratio of the induction period (in hours) of the protected fat to the induction period of the substrate fat alone. Unless otherwise indicated the concentration of the inhibitor was 0.02% of the fat.

[2] The concentrations of gallic acid, ethyl gallate and pyrogallol were 0.01%, of the others 0.02%, in cottonseed oil esters.

[3] The inhibitol concentrations ranged from 0.04% to 0.10%.

[4] The inhibitol concentration was 0.10%.

[5] The concentration of gallic acid was 0.06%.

[6] These indices were previously published and are included here for comparison.

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Summary

The differences between animal fats and common vegetable oils as regards their protection by antioxidants are briefly reviewed; in general, the former can be stabilized by di- and poly-phenolic inhibitors and by inhibitols, the latter by acid-type inhibitors such as tartaric, phosphoric and other acids; these acids reinforce the action of the inhibitols which occur naturally in vegetable oils or which may be added to animal fats.

A study has been made of the antioxygenic action of the polyphenols on both kinds of fats. The trihydric phenols, gallic acid and ethyl gallate are effective stabilizers in animal and vegetable fats and enhance the antioxygenic activity of inhibitols; they thus demonstrate the properties of both phenolic and acid inhibitors.

The possible mechanism of this synergistic action is briefly discussed.

REFERENCES

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Report of the Uniform Methods and Planning Committee—1941-1942

Owing to conditions at the present time only very few of the committees reported their work. This is easily understood because all of us have been particularly burdened with various things required of us in our own organization. In the report which follows we will only cover the committees that have submitted reports.

Oil Characteristics Committee:

During the past few years there has been considerable discussion as to the advisability of adopting so-called standards for oils and fats by the American Oil Chemists' Society. Owing to the expression of opinions of various members of the Society when the report was read the Uniform Methods and Planning Committee recommend that the Governing Committee be requested to pass on the policy of adopting standards for oils and fats. Until the Board has voted their approval further consideration of the report will be withheld.

Color Committee:

The Color Committee reported progress and also suggested that it be continued for another year and that they study the Spencer Colorimeter during that time. The Uniform Methods and Planning Committee have approved this recommendation.

Cellulose Yield Committee:

This committee made the following recommendations:

"1. That the Cellulose Yield procedure be adopted as an official method to be known as 'The American Oil Chemists' Society Cellulose Yield Method.'

"2. That check samples be sent out several times during the next year."

The Uniform Methods and Planning Committee have approved the above recommendations.

Soap in Refined Oil Committee:

This Committee has been doing some work on a method during the past year, but feel that the results obtained to-date are not definite enough to make any recommendations as to the adoption of a method. The Uniform Methods and Planning Committee approve their report and recommend that the committee be continued for another year.