of sodium chloride containing small percentages of glycerol.

Procedure

Weigh approximately 50 grams ± 0.10 gram of the sample and transfer to a 500 ml. volumetric flask. Partially fill the flask with water and shake until the sample is completely dissolved. Dilute the solution to a volume of 500 ml. by the further addition of water. Allow the solution to stand until any insoluble dirt that is present has settled out.

Pipette a 50 ml. aliquot of the clear solution into a 500 ml. tall type beaker and evaporate on the steam bath to a pasty consistency. This operation usually requires about two hours.

Slowly add 30 mls. of concentrated sulfuric acid to the sample, and allow to stand on the steam bath for about one hour after the frothing has completely subsided. The frothing usually ceases in about ten minutes. This operation should be carried out under a hood with a strong draft.

Remove the sample from the steam bath, cool, and proceed to oxidize, or, if more convenient, allow to stand overnight at room temperature before oxidizing. Proceed to oxidize by the method of the American Oil Chemists' Society (1) for the determination of glycerol in soap bearing in mind that the sample already contains sufficient sulfuric acid for the oxidation.

TABLE III

Bichromate Oxidation of Recovered Salt Before and After Decomposition With Concentrated Sulfuric Acid

Sample	Oxidation of salt as received	Oxidation of salt after decomposition with H_2SO_4	Difference
	Pct. oxidizable as glycerol	*Pct. oxidizable as glycerol*	*Pct. oxidizable as glycerol*
A	0.74	0.47	—0.27
A	0.77	0.45	—0.32
B	0.68	0.41	—0.27
B	0.69	0.40	—0.29
C	1.20	0.81	—0.39
C	1.21	0.80	—0.41

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(1) Official and Tentative Methods of The American Oil Chemists' Society, p. D-5 (1941).

The Antioxygenic Action of Phosphoric Acid in Association With Tocopherols and Hydroquinones*

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The capacity of tocopherols to act as inhibitors of fat autoxidation is greatly enhanced by small amounts of certain acids, both organic and inorganic, which have little or no stabilizing properties in themselves (1, 2, 3, 4).

A kinetic study has been made of the tocopherol-phosphoric acid-lard esters system. The data of Table I show that phosphoric acid retards the oxidation of α-tocopherol and thereby increases the antioxygenic activity of the phenolic constituent. Phosphoric acid likewise augments the stabilizing capacity of hydroquinones.

TABLE I

The Oxidation of α-Tocopherol in the Ethyl Esters of Lard in the Presence and in the Absence of Phosphoric Acid

Time in hours	Amount of Tocopherol in 1 gram Ester	
	(no H_3PO_4) γ	(0.10% H_3PO_4) γ
0	1000	1000
5	66	660
10	trace	
20	0	376
66		trace
68		0
Induction period hours	11	68

A clue to the mechanism of action of phosphoric acid is provided by the observations recorded in Table II. α-Tocoquinone and phosphoric acid, both ineffective by themselves, nevertheless powerfully stabilized the fat substrate when they were used together. This unexpected stability could only mean a regeneration of some tocopherol because tocohydroquinone like its corresponding quinone is ineffective as an inhibitor (5). The presence of tocopherol in the stabilized substrate was confirmed by biological assay. After exposure to oxygen at 75° for at least a day, the stabilized substrate was fed to three vitamin E-deficient female rats in amounts sufficient to provide each animal with at least 4 mgs. of tocopherol; all three animals had litters. The amount of α-tocopherol formed was determined by photometric analysis according to the Emmerie-Engel method (6) (Table III). Evidently the fat itself serves as a reducing agent for the

TABLE II

Antioxygenic Action of Mixtures of Quinones With Phosphoric Acid

Substrate	% Inhibitor Added	Antioxygenic Index [a] at 75°
Ethyl esters of Lard fatty acids	0.20 Phosphoric Acid	1
	0.10 α-Tocoquinone	1
	0.10 α-Tocoquinone + 0.20 Phosphoric Acid	>82[b]
	0.02 Benzoquinone	4
	0.02 Benzoquinone + 0.20 Phosphoric Acid	>110[b]

[a] Ratio of induction period of stabilized ester to that of control.
[b] When discontinued, these samples were still fresh.

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tocoquinone, and the phosphoric acid catalyzes its cyclization to tocopherol. In alcoholic solution phosphoric acid also cyclizes tocoquinone provided a reducing agent is present. Such cyclization occurs in the presence of other mineral acids (7).

TABLE III

Reduction of α-Tocoquinone in the Presence of Phosphoric Acid at 75°[a] Substrate: Ethyl Esters of Lard Fatty Acids

Time hrs.	0	26	78	167
α-Tocopherol formed[b], %	0.0	0.04	0.04	0.07

[a] The initial concentration of α-tocoquinone was 0.20%; that of phosphoric acid was 0.40%.

[b] Biological assays and stability tests indicated that no substantial amounts of α-tocohydroquinone were present.

Evidence that the autoxidation of a fat may proceed in part through a dehydrogenation mechanism has been presented by Deatherage and Mattill (8) and hydrogen has been identified among the products arising from the autoxidation of fats (9, 10).

In the case of benzoquinone, some reduction to hydroquinone was detected even in the absence of phosphoric acid. The amount thus formed, determined quantitatively by the ferric chloride-dipyridyl reagent of Emmerie and Engel (6), was small (Table IV),

TABLE IV

Reduction of *p*-Quinone in the Absence[a] and Presence[b] of Phosphoric Acid at 60° Substrate: Lard

Time, in days	0	7	14	28	42
Hydroquinone formed[a], %	0	0.001	0.001	0.001	0.001
Hydroquinone formed[b], %	0	0.006	0.008	0.008	0.014

The initial concentration of quinone was 0.02%, and of phosphoric acid, when present, 0.10%.

but was nevertheless sufficient to account for the antioxygenic activity of the quinone. The inhibition of oxidation by certain other *p*-quinones (11) may be explained on the same basis.

When phosphoric acid was used in conjunction with benzoquinone, the amount of hydroquinone formed was several times greater than that produced in the absence of the acid. The observed powerful synergistic action of this combination (Table II) is thus not surprising. Possibly the phosphoric acid influences the hydrogen ion concentration of the fat substrate even at the low concentrations of acid employed. Nothing is known regarding the acidity of phosphoric acid in fat media but Hall and Conant (12) have demonstrated that in other non-aqueous solvents, mineral acids produce acidities ("super acid solutions") far in excess of their hydrogen ion activities in water systems.

Our results suggest that the addition of a quinone or a hydroquinone to an autoxidizing fat leads to the formation of a hydroquinone ⇄ quinone equilibrium which is shifted to the left by phosphoric acid. The tocoquinones constitute a special case of this relationship because here reversal of the reaction involves cyclization in addition to reduction.

The action of phosphoric acid is to be distinguished from that of acids such as ascorbic and tartaric, since the latter do not function synergistically with tocoquinone (3), apparently because they cannot cyclize tocohydroquinone to tocopherol.

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Summary

Phosphoric acid greatly augments the antioxygenic activity of hydroquinones and tocopherols and their corresponding quinones in autoxidizing fats. In such media, *p*-quinones are partly reduced to hydroquinones. Phosphoric acid promotes this reaction and thus enhances, in a synergistic manner, the antioxygenic activity of both quinones and hydroquinones. With tocoquinones, cyclization as well as reduction occurs, and tocopherol is thereby regenerated.

The results suggest that a hydroquinone ⇄ quinone system is set up upon the addition of either the oxidant or the reductant to an autoxidizing fat, and that the resulting equilibrium is shifted in favor of the reductant by phosphoric acid.

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The Processing of Tung Fruit for Oil*

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The personnel of the U. S. Tung Oil Laboratory at Gainesville, Florida, have been considering for some time the possibility and advisability of hulling the tung fruit on the farm. The hull, which constitutes about 50% of the tung fruit, has no value for oil production. The oil comes only from the kernel, but a part of the shell is mixed with the ground kernels to prepare the meal from which tung oil is pressed at the mill.

Hulling the fruit on the farm would not only decrease by 50 per cent the weight of material hauled to the mill, but would leave the hulls on the farm where they could be used as a mulch. The hulls could also be used for their fertilizer value since they contain about 0.70 per cent nitrogen, 0.20 per cent phosphoric acid, and 3.1 per cent potash.

Because of the wide variation in size, and in the hardness of air-dried tung fruit, it has been impossible to remove the hulls with the present type of huller without damaging a considerable proportion of the seeds and kernels. It was believed, from experience with other oil-bearing seeds, that unless the damaged or abraded kernels are pressed almost immediately there would be a marked rise in the free-fatty acid content of the expressed oil, as well as a marked

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