Preservation of Lipids With Malic Acid

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Abstract

This paper deals with an evaluation of malic acid in a number of different lipids of animal and vegetable origin under comparable conditions. An Active Oxygen Method was used, with citric acid as the standard of comparison. In most cases, the performance of the acids was determined in the presence and absence of added iron salts and antioxidants butylated hydroxyanisole and butylated hydroxytoluene. Mathematical evaluation of the data shows malic acid to be at least as effective as citric acid in most cases. In very few instances, a reversal of performance was observed depending on experimental conditions used. In a few experiments, malic acid was also tested against phosphoric acid and found to be equal to or better than the latter. Phosphoric acid caused darkening of the oils at the test temperature used.

Introduction

The retarding effect of malic acid on oxidative deterioration of lipids is well known both in non-food uses (1–6) and in the stabilization of edible oils and fats (7–13). The published literature, however, gives a somewhat inconsistent picture of the performance of this acid. For example, Dutton et al. (9), in a study of soybean oil by the active oxygen method (97.8 C) found citric acid to be markedly more effective than malic acid in preventing peroxide buildup. On the other hand Olcott and Mattill (8), in an investigation of hydrogenated cottonseed oil by the oxygen absorption method (75 C), found these two acids to be nearly equally effective. More recent data published by Japanese workers (12) on the protective effect of malic acid on olive oil containing added copper oleate, at 50 C, show malic acid to be as good as or better than citric acid.

Citric acid is widely used by the lipid industry as an antioxidant synergist and trace metal deactivator. Hence, a comparison with this acid provides a convenient measure of the value of a substance as a lipid preserver. Based on the above-cited tests, the relative performance of malic acid ranges from fair to excellent. The inconsistent results in the literature may be due to the use of slightly different experimental conditions. To provide a clear comparison of malic acid and citric acid, it was deemed of interest to study their relative performance under strictly comparable test conditions; a few tests against phosphoric acid are also included for comparison. Such experiments, on a number of different lipids, are the subject of this paper.

TABLE I
Lipids Used and Their Characteristics

Lipids	Initial peroxide value, meq/kg oil	AOM value, hr[a]	Metal content, ppm[b]		
			Fe	Cu	Ni
Soybean oil	11	5.5	0.2	0.03	....
Hydrogenated soybean oil	0	63	0.5	0.05	0.9
Cottonseed oil	42	3.1	0.8	0.03	....
Prime steam lard	0	3.4	0.2	0.03	....
Top white tallow	4	2.4	1.2	0.04	....
Fancy bleachable tallow	0	2.2	1.2	0.05	....
Yellow grease	0	5.3	5.2	0.08	....

[a] Time required for sample to attain an AOM peroxide value of 100 mek/kg of oil.
[b] By atomic absorption spectrophotometry.

Experimental Procedure

Materials

Table I shows the lipids used in this study and some of their characteristics. These materials were obtained from commercial sources and contained no added antioxidants or metal deactivators. In some cases, they were carefully processed in the laboratory to ensure freedom from these additives.

Anhydrous citric acid (Chas. Pfizer & Co.) and Pomalus food grade malic acid (Allied Chemical Corp.) were used in all tests. Butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) were food grade materials supplied by UOP Chemical Division and Eastman Chemical Products, Inc., respectively. Phosphoric acid (85–87%) and ferric chloride were reagent grade materials supplied by Baker & Adamson. Ferrous distearate was supplied by Witco Chemical Co.

Method

Oxidative stability of the lipids was determined at 99–100 C by the Active Oxygen Method (AOM) (14) with iodometric titration of the peroxides (14,15). A value of 100 meq of peroxide per kilogram of lipid was taken as the rancidity point in all cases. Time corresponding to this value was determined graphically, from peroxide value-aeration time plots. The apparatus used was built essentially as described in Reference 14 except that additional ballast volume was included in the air distribution system between flowmeters and aeration tubes to smooth the motion of the flow-indicating ball. A constant temperature silicone bath was used. Most experiments were run in duplicate; however, only the average result is tabulated. The additives were incorporated into the oils at room temperature either as solids or in the form of aqueous solutions. In experiments involving the higher levels of acid addition, the solubility limits of the acids may have been exceeded initially; however, as aeration at the test temperature proceeded, nearly total solubilization usually occurred.

Precision and Significance

The coefficient of variation (standard deviation expressed as a per cent of the AOM value) was determined from the data tabulated below and from data obtained in preliminary experiments not reported here. The value found for this coefficient is 6%. The coefficient of variation given in AOCS Tentative Method Cd 12–57, which is very similar to the method used by us, is 13.4%. The latter value refers to interlaboratory precision most likely based on round-robin tests. The better precision of our data is undoubtedly due to the fact that all tests were performed by the same personnel; it reflects the precision of the method and excludes between-laboratory variance.

For purposes of interpreting the tabulated data presented here which show AOM values in hours, not in percentages, the repeatability value can be used. In our case, this value is 17% (38% for the AOCS method). This means that two measurements differing by 17% are different at the 5% significance level ($\alpha = 0.05$).

Dutton et al. (9) report statistical information on the precision of their AOM data in somewhat ambiguous terms ("The standard deviations of means for these control samples . . . are approximately ±15%") making an accurate comparison with our findings difficult. However, from all indications, our measure of variation reflects greater precision than that reported by these workers.

Analysis of the results for significance is based on a statistical t-test (16).

Results and Discussion

Performance of Malic Acid

Experimental results are summarized in Table II. Examination of these results from the standpoint of the relative performance of malic acid shows the following.

Soybean Oil (Tests 1–5). In the presence of added iron, malic acid was more effective than citric acid; in the absence of added iron, neither acid was effective.

Hydrogenated Soybean Oil (Tests 6–20). With increasing acid concentration, in the absence of other additives, malic acid showed greater effectiveness than citric acid (Expt. 7,8,10–13). In all other experiments, the two acids performed equally well. Malic acid also compared well against phosphoric acid. However, at the end of aeration, the samples containing phosphoric acid were markedly darker than those containing malic or citric acid which were very light in color.

Cottonseed Oil (Tests 21–25). The two acids showed equal effectiveness in all tests.

Prime Steam Lard (Tests 26–36). In the absence of additives, malic acid was more effective than either citric or phosphoric acid. In all other experiments,

TABLE II

Effect of Malic vs. Citric Acid on Oxidative Stability of Some Lipids

Oil	Test No.	Additives, ppm							AOM value hr	Statistical significance of difference
		Malic acid	Citric acid	Phosphoric acid	Iron (III) as		BHA	BHT		
					Chloride	Stearate				
Soybean	1	......	......	......	....	....	......	......	5.5	
	2	100	......	......	....	....	100	......	6.0	NS[a]
	3	......	100	......	....	....	100	......	5.9	
	4	100	......	......	5	....	100	......	4.4	$\alpha^{b} < 0.001$
	5	......	100	......	5	....	100	......	2.2	
Hydrogenated soybean	6	......	......	......	....	....	......	......	63	....
	7	100	......	......	....	....	......	......	87	NS
	8	......	100	......	....	....	......	......	88	
	9	......	......	100	....	....	......	......	86	
	10	250	......	......	....	....	......	......	101	NS
	11	......	250	......	....	....	......	......	85	
	12	500	......	......	....	....	......	......	105	$\alpha = 0.05$
	13	......	500	......	....	....	......	......	82	
	14	......	......	......	....	....	100	100	86	
	15	100	......	......	....	....	100	100	96	NS
	16	......	100	......	....	....	100	100	96	
	17	......	......	100	....	....	100	100	102	
	18	......	......	......	0.3	....	......	......	21	
	19	100	......	......	0.3	....	250	250	93	NS
	20	......	100	......	0.3	....	250	250	94	
Cottonseed	21	......	......	......	....	....	......	......	3.1	
	22	100	......	......	....	....	100	......	3.1	NS
	23	......	100	......	....	....	100	......	3.0	
	24	100	......	......	....	5	100	......	2.2	NS
	25	......	100	......	....	5	100	......	2.0	
Prime steam lard	26	......	......	......	....	....	......	......	3.4	
	27	100	......	......	....	....	......	......	5.5	$\alpha = 0.001$
	28	......	100	......	....	....	......	......	3.5	
	29	......	......	100	....	....	......	......	3.3	
	30	......	......	......	....	....	100	100	56	
	31	100	......	......	....	....	100	100	77	NS
	32	......	100	......	....	....	100	100	71	
	33	......	......	100	....	....	100	100	72	
	34	......	......	......	0.3	....	250	250	31	
	35	100	......	......	0.3	....	250	250	65	NS
	36	......	100	......	0.3	....	250	250	62	
Top white tallow	37	......	......	......	....	....	......	......	2.4	
	38	100	......	......	5	....	......	......	6.0	NS
	39	......	100	......	5	....	......	......	6.0	
	40	500	......	......	5	....	100	......	108	NS
	41	......	500	......	5	....	100	......	105	
	42	500	......	......	....	5	100	......	109	NS
	43	......	500	......	....	5	100	......	104	
Fancy bleachable tallow	44	......	......	......	....	....	......	......	2.2	
	45	100	......	......	....	....	......	......	3.5	NS
	46	......	100	......	....	....	......	......	4.0	
	47	300	......	......	....	....	50[c]	......	18	$\alpha < 0.001$
	48	......	300	......	....	....	50[c]	......	8.3	
	49	100	......	......	....	....	100[c]	......	17	$\alpha < 0.001$
	50	......	100	......	....	....	100[c]	......	28	
	51	500	......	......	....	....	100[c]	......	52	$\alpha = 0.02$
	52	......	500	......	....	....	100[c]	......	37	
	53	500	......	......	5	....	100[c]	......	25	$\alpha = 0.005$
	54	......	500	......	5	....	100[c]	......	37	
Yellow grease	55	......	.....	......	....	....	......	......	5.3	
	56	100	......	......	....	....	......	......	51	$\alpha = 0.01$
	57	......	100	......	....	....	......	......	72	
	58	500	......	......	....	....	......	......	211	NS
	59	......	500	......	....	....	......	......	212	
	60	100	......	......	....	....	100	......	172	$\alpha = 0.01$
	61	......	100	......	....	....	100	......	116	
	62	500	......	......	....	....	100	......	236	NS
	63	......	500	......	....	....	100	......	244	

[a] NS = not significant.

[b] Probability that two numbers are different when they are not (type-1 error). In this paper, significant differences are indicated by $\alpha \leq 0.05$.

[c] In propylene glycol solution.

the acids showed equal effectiveness. The effect on color of the aerated samples was the same as for hydrogenated soybean oil; phosphoric acid gave darker oils than did malic or citric acid, which showed practically no effect on color.

Top White Tallow (Tests 37–43). The two acids showed equal effectiveness in all tests.

Fancy Bleachable Tallow (Tests 44–54). The two acids showed equal effectiveness in the absence of other additives (Tests 45,46). At the lower level of BHA, malic acid was more effective than citric acid (Tests 47, 48); at the higher level of BHA (Tests 49–54), relative performance of the two acids varied.

Yellow Grease (Tests 55–63). At the higher level of acid (500 ppm), malic acid and citric acid showed equal effectiveness regardless of the presence of BHA (Tests 58,59;62,63). At the low level of acid (100 ppm), malic acid was more effective in the presence of BHA, whereas citric acid showed greater effectiveness in the absence of BHA.

The above results show that, in the vegetable oils, lard and top white tallow, malic acid was equal to or slightly better than citric acid; in fancy bleachable tallow and yellow grease, the relative performance of the two acids varied, with malic acid being more effective in some cases and citric acid in others.

The greater effectiveness of malic acid observed in many of the above tests may be due to the lower molecular weight of this acid (134 vs. 192 for citric acid). This hypothesis is based on the assumption of a 1:1 molecular metal-acid chelate. For comparable chelate stability, the lower molecular weight acid would then be expected to have greater metal binding efficiency.

The overall conclusion based on these laboratory tests is that malic acid is potentially a very valuable lipid stabilizer. Since commercial processing conditions vary markedly with respect to temperature, lipid history, trace metal contamination, etc., and since the two acids have different physical and chemical properties, their relative performance under practical conditions may differ from that observed in the laboratory. For example, the lower melting point of malic acid (129 C vs. 153 C for citric acid) may prove beneficial in promoting dispersion and rate of solution of the acid in hot oil. The performance of malic acid at oil processing temperatures should, to a degree, depend also on the effectiveness of its thermal degradation products which at this time is not well known. Evaluations of malic acid on a commercial scale should resolve some of these uncertainties.

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