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Control of Lipid Oxidation in Cooked Meats by Combinations of Antioxidants and Chelators

F. Shahidi, L. J. Rubin

Department of Chemical Engineering and Applied Chemistry,
University of Toronto, Toronto, Ontario, Canada M5S 1A4

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D. F. Wood

Food Research Centre, Agriculture Canada, Ottawa, Ontario, Canada K1A 0C6

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ABSTRACT

The degree of oxidation in cooked meats treated with phosphates or polyphosphates and sodium ascorbate (SA) or one of its related compounds was determined using the 2-thiobarbituric acid (TBA) test. Combinations of ascorbates with a polyphosphate effectively retarded lipid oxidation in cooked pork during a 5-week storage period at refrigerator temperature. Addition of a phenolic antioxidant—butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG), tert*-butylhydroquinone (TBHQ) or trihydroxybutyrophenone (THBP)—to the above mixtures did not affect the TBA numbers substantially ($\leq 0{\cdot}1$ TBA unit). Ethylenediaminetetraacetic acid disodium salt (Na_2EDTA) with sodium ascorbate, with or without a phenolic antioxidant, was effective in protecting cooked pork from oxidation (TBA numbers of ≤ 1). Commercial antioxidant systems, Tenox A and Tenox II, were also effective in retarding meat rancidity, but Ronoxan A and Ronoxan D20 were only slightly effective.*

INTRODUCTION

Oxidative deterioration represents a major problem in the production of many lipid-containing foods. Oxidation of unsaturated lipids (Younathan & Watts, 1960) not only gives rise to unacceptable odours and flavours but

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can also decrease the nutritional quality as the meat lipids oxidize and react with other meat constituents such as proteins, carbohydrates and vitamins (Labuza, 1971). In addition, oxidation adversely affects the safety of foods through the formation of the carcinogenic initiator and mutagen, malonaldehyde, which is a breakdown product of peroxidized poly-unsaturated fatty acids (Shamberger *et al.*, 1974, 1977). Thus, whereas cooked uncured meat develops a stale flavour, known as warmed-over flavour, within a day or two during refrigerated storage, this does not happen with cured meat. Sodium nitrite, which is used for curing, is an excellent antioxidant in meat systems, but has been shown to produce carcinogenic *N*-nitrosamines in some cured meat products (Sen *et al.*, 1973). Therefore, there is an interest in eliminating its use in the curing process entirely (Shahidi *et al.*, 1984).

To reproduce the antioxidant effect of nitrite, we have examined a number of antioxidants (Shahidi *et al.*, 1986*a*) and chelators (Shahidi *et al.*, 1986*b*). Among the antioxidants used BHA and TBHQ were the most effective, even at 30 ppm, for retarding fat oxidation during 35 days of refrigerated storage as measured by the 2-thiobarbituric acid (TBA) test. Among the food-grade chelators, ethylenediaminetetraacetic acid (EDTA) and sodium pyro- and tripolyphosphates (SPP and STPP, respectively) were effective (Shahidi *et al.*, 1986*b*).

This paper reports on the synergistic effect of phosphates and polyphosphates with sodium ascorbate. The effect of adding antioxidants to mixtures of Na_2EDTA or STPP with sodium ascorbate was also tested. In addition, common commercial antioxidant systems, namely Ronoxan A and D20 and Tenox A and II, were examined.

MATERIALS AND METHODS

All chemicals used were reagent or food-grade and were used without any further purification. Ascorbyl acetal (Bharucha *et al.*, 1980) was obtained from Canada Packers Research Centre, Toronto. Ronoxan A (25% ascorbyl palmitate, 5% DL-α-tocopherol, 0·8% citric acid, 1% mono- and diglycerides and dextrose) and Ronoxan D20 (4·8% ascorbyl palmitate, 1·6% DL-α-tocopherol, 0·8% citric acid, mono- and diglycerides and dextrose) were obtained from Hoffmann-La Roche and Co., Toronto. Tenox A and II, also referred to as Dadex A (40% BHA and 8% citric acid in propylene glycol) and Dadex II (20% BHA, 6% PG and 4% citric acid in propylene glycol) were obtained from Daminco Inc., Mississauga, Ontario. The levels of addition for antioxidants and chelators are given in the individual tables.

Fresh pork loin was deboned and trimmed to remove most of the surface fat. It was then ground twice using an Oster meat grinder, model 990-68. Additives were added directly to the meat followed by the addition of 20% by weight of distilled water. The mixture was then thoroughly mixed and cooked in a thermostatted water bath at 80°C for *ca.* 40 min to reach an internal temperature of 75 ± 1°C and then cooled to room temperature. Each meat system was well mixed and stored in a plastic bag at 4°C until use. The amount of oxidation in the meat samples was determined after cooking (day 1) and after 7, 14, 21, 28 and 35 days of storage at 4°C by the TBA test of Tarladgis *et al.* (1960) as modified by Shahidi *et al.* (1986*a*).

RESULTS AND DISCUSSION

The TBA numbers for meats treated with different additives, individually or in combination, are given in Tables 1 to 3. The results are averages of three determinations.

The TBA values for phosphates and polyphosphates (Table 1) follow a similar trend to that reported previously (Shahidi *et al.*, 1986*b*). Only the polyphosphates, particularly sodium tripolyphosphate (STPP) and sodium

TABLE 1
Effect of Combinations of Phosphates and Polyphosphates with Ascorbates on the TBA Values of Cooked Pork during Storage at 4°C[a]

Experiment number	*Additive system*	*Storage time (days)*					
		1	*7*	*14*	*21*	*28*	*35*
1	No additive	3·17	6·63	8·55	10·0	10·62	13·05
2	Sodium ascorbate (550 ppm)	1·35	4·23	7·38	6·82	7·10	7·80
3	Monosodium phosphate (3000 ppm)	4·68	9·44	10·53	11·06	12·32	13·40
4	(2) + (3)	1·26	8·14	7·42	5·70	5·82	6·49
5	Disodium phosphate (3000 ppm)	4·96	9·18	10·42	11·25	11·15	11·81
6	(2) + (5)	1·08	5·65	2·85	3·20	3·81	4·25
7	Sodium hexametaphosphate (3000 ppm)	1·20	3·08	3·83	4·46	6·62	7·71
8	(2) + (7)	0·14	0·14	0·26	0·25	0·25	0·29
9	Sodium pyrophosphate (3000 ppm)	0·34	0·42	0·52	0·61	0·86	1·66
10	(2) + (9)	0·19	0·21	0·24	0·23	0·25	0·23
11	Sodium tripolyphosphate (3000 ppm)	0·22	0·36	0·97	1·13	1·21	1·86
12	(2) + (11)	0·17	0·16	0·20	0·31	0·44	0·27
13	(11) + Ascorbyl palmitate (1000 ppm)	0·18	0·16	0·15	0·20	0·16	0·18
14	(11) + Ascorbyl acetal (1000 ppm)	0·10	0·20	0·20	0·20	0·18	0·19
15	(2) + Sodium nitrite (150 ppm)	0·32	0·48	0·50	0·49	0·58	0·53
16	(12) + Sodium nitrite (150 ppm)	0·20	0·31	0·29	0·35	0·34	0·35

[a] The cooked meats contained 70·97 ± 0·18% water and 9·55 ± 0·11% fat.

TABLE 2

Effect of Combinations of Antioxidants with Sodium Ascorbate and Sodium Tripolyphosphate or Ethylenediaminetetraacetic Acid on the TBA Values of Cooked Pork during Storage at 4°C[a]

Experiment number	*Additive system*	*Storage time (days)*					
		1	*7*	*14*	*21*	*28*	*35*
1	No additive	3·17	6·63	8·55	10·0	10·62	13·05
2	Sodium tripolyphosphate (3000 ppm)	0·22	0·36	0·97	1·13	1·21	1·86
3	(2) + Sodium ascorbate (550 ppm)	0·17	0·16	0·20	0·31	0·44	0·27
4	(3) + BHA (30 ppm)	0·16	0·14	0·20	0·20	0·19	0·20
5	(3) + BHT (30 ppm)	0·17	0·16	0·18	0·20	0·17	0·20
6	(3) + PG (30 ppm)	0·16	0·16	0·19	0·19	0·16	0·18
7	(3) + TBHQ (30 ppm)	0·19	0·16	0·20	0·18	0·19	0·18
8	(3) + THBP (30 ppm)	0·17	0·14	0·16	0·20	0·16	0·20
9	Na_2EDTA (500 ppm)	0·18	0·17	0·25	0·25	0·25	0·29
10	(9) + Sodium ascorbate (550 ppm)	0·19	0·21	0·24	0·23	0·25	0·23
11	(10) BHA (30 ppm)	0·19	0·21	0·24	0·23	0·25	0·23
12	(10) + BHT (30 ppm)	0·20	0·18	0·22	0·24	0·24	0·23
13	(10) + PG (30 ppm)	0·20	0·20	0·24	0·24	0·20	0·23
14	(10) + TBHQ (30 ppm)	0·21	0·18	0·22	0·22	0·21	0·22
15	(10) + THBP (30 ppm)	0·20	0·20	0·24	0·23	0·22	0·21

[a] The cooked meats contained 70·97 ± 0·18% water and 9·55 ± 0·11% fat.

pyrophosphate (SPP), show the ability to lower the TBA numbers substantially (Table 1, experiments 9 and 11). Protection of cooked meats by polyphosphates has been related to their ability to sequester metal ions, particularly those of iron (Tims & Watts, 1958). Addition of sodium ascorbate (SA) to mono- or disodium phosphate caused a decrease in the TBA numbers (Table 1, experiments 4 and 6). However, this decrease was not enough to give the necessary protection (i.e. a TBA number of less than one, Tarladgis *et al.*, 1960) to the cooked meat. The antioxidant ability of sodium ascorbate at levels ≥100 ppm has already been reported (Sato & Hegarty, 1971; Shahidi *et al.*, 1986*b*). For polyphosphates, however, a strong synergism with SA was observed. This synergism was particularly noticeable for sodium hexametaphosphate (SHMP) (Table 1, experiment 8). A possible explanation for this synergistic effect was offered by Schubert & Derr (1978). They found that mixed-chelating systems such as ethylenediaminetetraacetic acid–salicylic acid and diethylenetriamine–pentaacetic acid–salicylic acid showed a very powerful chelating effect, very much greater than that by the individual components. The TBA numbers decreased even further when ascorbyl acetal (AA) or ascorbyl palmitate (AP) were used in place of SA, perhaps due to their greater fat solubility (Table 1, experiments 13 and 14). The TBA numbers for meats

TABLE 3
Effect of α-Tocopherol and Commercial Antioxidant Systems on the TBA Values of Cooked Pork during Storage at 4°C[a]

Experiment number	*Additive system*	*Storage time (days)*					
		1	*7*	*14*	*21*	*28*	*35*
1	No additive	3·84	7·91	8·63	11·21	10·62	13·59
2	DL-α-tocopherol[b] (200 ppm)	1·95	7·52	6·37	6·77	7·21	8·36
3	(2) + Ascorbyl palmitate (1000 ppm)	0·30	0·86	1·17	1·10	1·30	1·22
4	Ronoxan A (1000 ppm)	0·48	2·74	3·54	3·48	3·49	3·84
5	Ronoxan D20 (5000 ppm)	0·62	3·38	3·91	4·35	4·48	4·56
6	Tenox A (200 ppm)	0·09	0·11	0·13	0·13	0·15	0·17
7	Tenox II (200 ppm)	0·09	0·12	0·13	0·13	0·10	0·15

[a] The cooked meats contained 71·80 ± 0·20% water and 10·12 ± 0·15% fat.
[b] Shahidi *et al.* (1986a).

treated with mixtures of polyphosphates and SA, AP or AA were generally lower than those for nitrite-cured meats (Table 1), indicating effective inhibition of fat oxidation by these systems in cooked pork.

Addition of phenolic antioxidants to meats along with STPP and SA or Na_2EDTA and SA was studied, and the results are given in Table 2. The protection of meat against oxidation by Na_2EDTA was excellent (Table 2, experiment 9; Shahidi *et al.*, 1986*b*), and this was equivalent to some of our best systems (for example, experiments 8, 10 and 12 in Table 1). The TBA numbers for these systems were only slightly lowered by the addition of a phenolic antioxidant. However, in preliminary organoleptic tests, untrained panelists showed a preference for meats cooked with SA, STPP and TBHQ or BHA as compared with the samples which did not contain the phenolic antioxidants. The panelists did not detect any difference between the pork treated with the nitrite-free systems and the nitrite-cured pork (Yun *et al.*, 1987). Therefore, the phenolic antioxidants may play a role in enhancing the flavour, but this was not reflected in the TBA numbers.

Table 3 summarizes the TBA numbers of meats treated with α-tocopherol and commercial antioxidant systems. The activity of α-tocopherol alone was minimal. Much better results were obtained in the presence of ascorbyl palmitate. Ronoxan A and D20 had a modest activity. However, in all cases the reduction in TBA numbers was not sufficient to give an organoleptically acceptable product (i.e. TBA number of ≤ 1). Ronoxan A is a brown paste containing a mixture of antioxidants and is used for stabilizing vegetable oils and animals fats, as well as fat-containing foods. At the highest level of use (i.e. 1000 ppm) suggested by the manufacturer, it provides 250 ppm of ascorbyl palmitate, which is not sufficient to give the necessary protection to meat. Ronoxan D20 is a

product specially developed for the meat industry. This antioxidant mixture may be effective for short-term protection of meat products. Antioxidant systems containing phenolic antioxidants such as Tenox A (40% BHA and 8% citric acid in propylene glycol) or Tenox II (20% BHA, 6% PG and 4% citric acid in propylene glycol) were sufficiently effective in protecting cooked pork from oxidation (Table 3). Moerck & Ball (1973) reported that Tenox II was effective in preventing lipid oxidation in mechanically deboned chicken and Dawson *et al.* (1978) showed that Tenox A and Tenox II were equally effective in preventing oxidation in mechanically deboned turkey. Thus, Tenox A provides 80 ppm of BHA, which should be enough to give low TBA values; similarly, Tenox II provides 40 ppm of BHA.

In conclusion, combination of sodium ascorbate (550 ppm) with sodium tripolyphosphate, sodium hexametaphosphate or sodium pyrophosphate (3000 ppm), with or without a phenolic antioxidant (30 ppm), effectively protects cooked meat from oxidation. Sodium tripolyphosphate in combination with the fat-soluble ascorbic acid derivatives, ascorbyl palmitate and ascorbyl acetal, were perhaps even more effective. These mixtures are at least as effective as sodium nitrite (150 ppm) in the presence of sodium ascorbate (550 ppm). Addition of sodium nitrite to meat containing SA and STPP did not have any further effect in the control of lipid oxidation. Ethylenediaminetetraacetic acid disodium salt (Na_2EDTA) with sodium ascorbate, with or without a phenolic antioxidant, protected cooked pork from oxidation and the TBA numbers after 5 weeks of storage at 4°C were $\leq 0{\cdot}29$. α-Tocopherol or its commercial blends were unable to control oxidation in cooked pork effectively. Tenox A and Tenox II were highly effective in the prevention of oxidation in cooked-meat samples.

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