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CONTROL OF LIPID OXIDATION IN COOKED MEATS

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INTRODUCTION

The curing of meat is an ancient art which originiated in salting, one of the first methods used for preserving meat. Current meat-curing practice involves the addition of nitrite, at times nitrate, and salt; sugars, ascorbates, polyphosphates, and spices may also be added. Sodium nitrite and salt are the most important ingredients of the curing mixture. Nitrite has the ability to impart colour, flavour, antimicrobial activity, and antioxidant properties to the meat, (MacDougal et al, 1975; Hadden et al, 1975; Hauschild et al., 1982) the latter being responsible for the elimination of the warmed-over flavour (Igene and Pearson, 1979). The use of nitrite is certainly not without its problems. Although nitrite is not particularly dangerous per se, it does under certain conditions, such as the high temperature reached in frying bacon, brings about the formation of nitrosamines in cured-meat products (Sen et al., 1973). Some of these compounds, such as N-nitrosopyrrolidine and N-nitrosodimethylamine, formed by the reaction of nitrite with amines, are known to be carcinogens. As a result of concern over health hazards associated with nitrite, efforts are being made to reduce its level of addition, or eliminate it entirely (Shahidi et al., 1984).

Since no single compound is expected to impart all of the key functions of nitrite, we have been involved in the preparation of a multicomponent curing system. To achieve this, we have now synthesized the cooked cured-meat pigment, dinitrosyl ferrohemochrome (DNFH), in good yield and in pure form from beef red blood cells (Shahidi et al., 1985). To achieve oxidative stabi[illegible], the curing mixture must also include an antioxidant and/or a sequestrant, individually or in c[illegible]ation. An antimicrobial agent, such as potassium sorbate, may also be added to ensure micr[illegible]ological stability, especially against the outgrowth of Clostridium botulinum spores, thus preventing toxin formation.

Lipid oxidation is due to the reactivity of unsaturated fatty acid moieties towards oxygen, and this is of critical importance for polyunsaturated fatty acids with three or more double bonds, which in meats are associated with the phospholipids (Allen and Foegeding, 1981).

In this paper we report on the use of a number of common antioxidants and/or chelators, individually or in combination, with or without an antimicrobial agent, and DNFH, to impart oxidative stability to cooked meats, as measured by the TBA test.

MATERIALS AND METHODS

The meat, 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 addition of 20% (w:w, based on the weight of the meat) of distilled water. The mixture was then thoroughly mixed.

The blended meat samples were cooked in a thermostated bath for a period of ca. 40 min to reach an internal temperature of 75±1°C, while stirring frequently with a glass rod. After cooling to room temperature, the cooked-meat samples were homogenized in a Waring blender and stored in plastic bags at 4°C.

The oxidative state of the meat samples after cooking was evaluated on day 1, and after 7, 14, 21, 28 and 35 days by a modified version of the 2-thiobarbituric acid (TBA) test of Tarladgis et al. (1960).

In all cases 10 g of sample was weighed on a weighing paper and transferred into a 500 mL round-bottom flask containing 97.5 mL distilled water, 2.5 mL of 4N HCl, a few drops of Dow antifoam A, and several glass beads. The mixture was then distilled. In all cases 50 mL distillate was collected over a period of ca. 20 min.

In a vial containing 5 mL of the distillate, 5 mL of a 0.02 M aqueous solution of 2-thiobarbituric acid was added. A blank containing 5 mL of distilled water and 5 mL of the TBA solution was used. The vials were then cooled to room temperature, and the absorbance of the resultant pink-coloured chromogen was measured at 532 nm (maximum) using a Beckman DU-7 spectrophotometer.

A solution of 1,1,3,3-tetramethoxypropane (TMP) was used as a standard to obtain the conversion factor for absorbance values to TBA numbers.

RESULTS AND DISCUSSION

To convert the absorbance to TBA numbers, defined as mg of malonaldehyde equivalent per kg of the mixture, a value of 8.1 was obtained using the TMP standard solutions. This compares well with the value of 7.8 reported by Tarladgis et al. (1960).

The TBA numbers for the meat samples, untreated or treated, are reported in the tables: antioxidants (Table 1), chelators (Table 2), and the usual pickle ingredients and DNFH (Table 3). The results for combination of antioxidants, chelators, and ascorbates, with or without the cooked cured-meat pigment (DNFH), and possibly also an antimicrobial agent, are given in Table 4.

Among the antioxidants used, the following were found to be the most effective at both 200 and 30 ppm addition levels - butylated hydroxyanisole (BHA), t-butylhydroquinone (TBHQ) and trihydroxybutyrophenone (THBP). Propyl gallate (PG) was also highly effective (TBA number < 1) at an addition level of 200 ppm (Table 1).

The chelators which proved effective were ethylenediaminetetracetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and to a lesser extent the polyphosphates (Table 2). The polyphosphates used were sodium tripolyphosphate (STPP), sodium pyrophosphate (SPP), and sodium hexametaphosphate (SHMP).

The pickle ingredients, sodium nitrite and ascorbates, especially ascorbyl acetal (Bharucha et al., 1980) and ascorbyl palmitate, showed pronounced antioxidant effects, while salt showed almost no effect (Table 3). Sucrose and the antimicrobial agents had little influence on the TBA numbers. The cooked cured-meat pigment (DNFH), showed a weak antioxidant effect. As expected, sodium nitrite at 150 ppm showed strong antioxidant properties.

Combinations of antioxidants, chelators, and ascrobates were found (Table 4) which were as effective as sodium nitrite in preventing lipid oxidation. These combinations consist of polyphosphates, or EDTA and DTPA, and soium ascorbate or one of its related compounds, with or without BHA or TBHQ. The strong synergism between the polyphosphates and sodium ascorbate is to be particularly noted. When combined with the cooked cured-meat pigment in comminuted pork, a product was obtained which had the characteristic colour and showed the same resistance to lipid oxidation as nitrite-cured meat. Preliminary organoleptic evaluation showed that meat "cured" by some of our better systems was similar in flavour to nitrite-cured meat. An antimicrobial agent, such as potassium sorbate, sodium hypophosphite or monoethyl fumarate, was also added to some of the mixtures to ensure the microbiological stability of the systems.

A "meat-curing" system has thus been developed which simulates the multiple functions of nitrite reasonably well. The cured-meat pigment is preformed from a readily available raw material. Oxidative stability is achieved by several combinations of chelators and antioxidants which, at the same time, preserves the cured-meat flavour. The system is completed by the addition of an approved antimicrobial agent. Further research on the antimicrobial activity of some of the more promising systems, with and without antimicrobial agents, is in progress.

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REFERENCES

Allen, C.F. and Foegeding, E.A. 1981. Food Technol. 35:253.
Bharucha, K.R., Cross, C.K. and Rubin, L.J. 1980. J. Agric. Food Chem. 28:1274.
Hadden, J.P., Ockerman, H.W., Cahill, V.R., Parrett, N.A. and Borton, R.J. 1975. J. Food Sci. 40:626.
Hauschild, A.H.W., Hilscheimer, R. Jarvis, C. and Raymond, D.P. 1982. J. Food Protec. 45:500.
Igene, J.O. and Pearson, A.M. 1979. J. Food Sci. 44:1285.
MacDougal, D.B., Mottram, D.S. and Rhodes, D.N. 1975. J. Sci. Food Agric. 26:1743.
Roffo, A.H. 1939. Presna. Med. Argent. 26:619.
Sen, N.P., Miles, W.F., Donaldson, B., Panalaks, T. and Iyenger, J.R. 1973. Nature 245(5420):104.
Shahidi, F., Rubin, L.J., Diosady, L.L., Chew, V. and Wood, D.F. 1984. Can. Inst. Food Sci. Technol. J. 17:33.
Shahidi, F., Rubin, L.J., Diosady, L.L. and Wood, D.F. 1985. J. Food Sci. 50:272.
Tarladgis, B.G., Watts, B.M. and Younathan, M.T. 1960. J. Am. Oil Chem. Soc. 37:44.

Table 1. Effect of Some Common Antioxidants on the TBA Numbers.[a]

No.	Meat System	Days of storage at 4°C					
		1	7	14	21	28	35
1	no additive	4.39	11.49	11.0	13.28	13.26	15.46
2	dl-α-tocopherol (200 ppm)	1.95	7.52	6.37	6.77	7.21	8.36
3	BHA (200 ppm)	0.23	0.50	0.53	0.48	—	0.47
4	BHA (30 ppm)	0.25	0.43	0.50	0.46	0.59	0.44
5	BHT (200 ppm)	1.33	1.92	2.33	1.99	2.04	1.89
6	BHT (30 ppm)	2.31	4.41	4.17	4.30	4.13	4.31
7	PG (200 ppm)	0.19	0.27	0.30	0.30	0.27	0.38
8	PG (30 ppm)	1.07	2.66	2.79	2.68	2.66	3.03
9	TBHQ (200 ppm)	0.39	0.44	0.38	0.40	0.45	0.45
10	TBHQ (30 ppm)	0.32	0.58	0.30	0.38	0.40	0.35
11	THBP (200 ppm)	0.39	0.43	0.30	0.40	0.43	0.45
12	THBP (30 ppm)	0.63	2.12	1.23	1.73	1.62	1.77

[a] The meats contained 70.1 ± 0.2% water and 10.7 ± 0.2% fat.

Table 2. Effect of Sequestrants on the TBA Numbers[a]

No.	Meat System	Days of Storage at 4°C					
		1	7	14	21	28	35
1	no additive	4.95	8.96	10.50	11.67	12.12	13.73
2	citric acid (500 ppm)	2.74	8.08	8.77	10.01	10.79	12.62
3	monoglyceride citrate (500 ppm)	5.40	8.57	8.23	9.92	9.39	9.16
4	Na_2EDTA (500 ppm)	0.31	0.64	0.71	0.86	0.90	0.96
5	DTPA (500 ppm)	0.29	0.38	0.33	0.34	0.33	0.36
6	monosodium phosphate (3000 ppm)	5.60	10.56	10.53	10.06	10.66	11.01
7	disodium phosphate (3000 ppm)	4.56	9.19	9.58	9.89	10.49	9.20
8	SHMP (3000 ppm)	1.41	3.46	4.70	6.00	7.88	8.78
9	STPP (3000 ppm)	0.31	0.58	0.90	1.05	1.39	2.07
10	SPP (3000 ppm)	0.35	0.32	0.39	0.48	0.69	1.13

[a]The meats contained 72.4 ± 0.2% water and 10.5 ± 0.2% fat.

Table 3. Effect of Pickle Ingredients on the TBA Numbers[a]

No.	Meat System	Days of Storage at 4°C					
		1	7	14	21	28	35
1	no additive	4.39	11.41	11.00	13.28	13.76	15.46
2	salt (2%)	7.04	11.36	11.06	12.40	14.60	15.75
3	sucrose (1.5%)	5.61	10.36	11.05		12.83	—
4	sodium ascorbate (550 ppm)	1.98	5.73	7.32	7.40	7.82	8.23
5	ascorbic acid (500 ppm)	1.63	5.45	5.39	5.81	7.01	—
6	erythorbic acid (500 ppm)	1.53	5.89	5.67	5.65	7.80	—
7	ascorbyl acetal (1000 ppm)	0.47	0.90	0.68	0.55	0.63	1.27
8	ascorbyl palmitate (1000 ppm)	0.34	0.85	0.48	0.63	0.72	1.06
9	sodium nitrite (25 ppm)	1.10	2.90	2.82	3.38	4.62	6.79
10	sodium nitrite (50 ppm)	0.82	2.63	2.60	3.10	3.86	3.90
11	sodium nitrite (150 ppm)	0.50	0.55	0.58	0.58	0.60	0.63
12	DNFH (12 ppm)	0.39	8.10	7.32	9.64	9.08	9.89
13	DNFH (24 ppm)	0.09	4.98	4.26	5.70	5.06	7.14
14	sodium hypophosphite	5.54	9.54	9.92	11.47	12.43	12.08
15	potassium sorbate	7.21	9.79	10.61	9.04	9.49	10.07
16	monoethyl fumarate	4.02	8.10	8.18	8.41	9.73	10.16

[a]The meats contained 70.1 ± 0.2% water and 10.7 ± 0.2% fat.

Table 4. Effect of Alternative Curing Mixtures on the TBA Numbers[a]

No.	Meat System	Days of Storage at 4°C					
		1	7	14	21	28	35
1	no additive	4.95	8.96	10.50	11.67	12.12	13.73
2	salt (2%) + sugar (1.5%) + sodium ascorbate (550 ppm)	1.35	7.74	8.46	9.64	—	15.93
3	(2)+STPP (3000 ppm)	0.58	0.53	0.51	0.66	0.86	1.32
4	(2)+DNFH (12 ppm)	0.59	6.81	8.66	—	—	—
5	(3)+DNFH (12 ppm)	0.24	0.35	0.34	0.37	0.37	0.45
6	(5)+sodium hypophosphite (3000 ppm)	0.27	0.34	0.36	0.33	—	0.30
7	(5)+potassium sorbate (2600 ppm)	0.64	0.53	0.74	0.46	—	0.47
8	(5), but with SHMP (3000 ppm)	0.38	0.27	0.33	0.49	0.35	0.31
9	(5), but with SPP (3000 ppm)	0.33	0.30	0.29	0.35	0.29	0.30
10	(5), but with Na_2EDTA (500 ppm)	0.40	0.76	0.36	0.78	0.57	—
11	(5), but with DTPA (500 ppm)	0.51	0.31	—	0.53	0.43	—
12	(5)+BHA (30 ppm)	0.28	0.27	0.24	0.27	0.38	0.28
13	(5)+TBHQ (30 ppm)	0.22	0.20	0.20	0.22	0.21	0.21

[a] The meats contained 69.9 ± 0.1% water and 10.6 ± 0.1% fat.