EFFECT OF ANTIOXIDANTS AND FUNGISTATIC AGENTS ON RANCIDITY IN DRIED SPLIT-SALTED BISUGO (*Nemipterus taeniopterus* Cuvier and Valencienes)

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ABSTRACT

The effects of antioxidants butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and propyl gallate (PG) and fungistatic agents potassium sorbate, sodium propionate and sodium benzoate on the stability of dried bisugo against oxidative rancidity were evaluated using sensory and chemical analyses as indices. Each of the antioxidants and fungistatic agents was applied at a level of 0.1% in saturated brine. Sensory evaluation indicated that the antioxidants exerted potent antioxidative effect while the fungistats showed accelerating effects on the development of oxidative rancidity of the dried samples. Chemical analyses, TBA (thiobarbituric acid) and peroxide tests supported and confirmed the results indicated by the sensory data. The 7 treatments could be arranged, in the order of decreasing antioxidative effect as: BHA > PG > BHT > control > sodium benzoate > potassium sorbate > sodium propionate.

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KEY WORDS: Bisugo. *Nemipterus taeniopterus.* Antioxidant. Fungistat. Rancidity.

INTRODUCTION

Drying is a common method of fish processing in the Philippines. At present, one of the problems in processing is the development of rancidity, attributed chiefly to the atmospheric oxidation of the fish oils. The highly unsaturated nature of the fatty acids of fish oils makes them very susceptible to rancidification through the formation and decomposition of peroxides and hydroperoxides, the products of which are mainly responsible for the undesirable odors and flavors formed (Sacharow and Griffin, 1970; Pyke, 1964). The development of rancidity in food lowers the palatability and impairs the nutritive value by reducing the content of various fat-soluble vitamins and essential fatty acids (Aurand and Woods, 1973; Lea, 1939).

Rancidity tests have been developed to establish sensitive control of the stability of fats in food. The more common are the peroxide and thiobarbituric acid tests. Although rancidity can be detected by organoleptic tests, determination of the degree of rancidity can be difficult since rancidity does not develop uniformly in fish. Chemical tests, when combined with organoleptic assessment of rancidity, are of great assistance where the purpose of the investigation is to trace the course of the chemical deterioration for the storage test.

This study presents the relative potencies of commonly used antioxidants and fungistatic agents against oxidative rancidity during storage using chemical and sensory evaluations as indices.

MATERIALS AND METHODS

Fresh bisugo fish samples measuring about 12 to 15 cm long and weighing about 50 to 60 g were split, eviscerated and washed thoroughly in clean water. These were randomly divided equally into 7 lots (Table 1).

Each of the antioxidants and fungistatic agents was applied at a concentration of 0.1% in saturated brine. Fish samples were allowed to remain in the treated brine for 1 hr at room temperature after which they were rinsed lightly and sun-dried until a moisture range of 30-35% was attained in the flesh (Uyenco et al., 1970). After drying, the samples were placed in medium-sized bamboo baskets, stored at room temperature and were evaluated weekly for rancidity. Rancidity development on the different treatments was monitored through chemical analyses (thiobarbituric acid and peroxide determinations) and organoleptic evaluation by a panel of 15 trained tasters. TBA (thiobarbituric acid) values, expressed as mg malonaldehyde per

Table 1. The different treatments with their corresponding fungistatic agent/antioxidant used.

Treatment	Chemical	Action
1	None (Control)	—
2	Potassium Sorbate	Fungistatic
3	Sodium Propionate	Fungistatic
4	Sodium Benzoate	Fungistatic
5	Butylated Hydroxyanisole	Antioxidant
6	Butylated Hydroxytoluene	Antioxidant
7	Propyl Gallate	Antioxidant

kg sample, were determined using the direct TCA (trichloroacetic acid) extraction method (Vyncke, 1970). Peroxide values, milliequivalents of peroxide per 1000 g sample were analyzed using the method described by Pearson (1973). Three hundred g of sample from each treatment were fried at 180-200°C for 2 min each time using fresh cooking oil. Samples were then presented to the panel for evaluation of intensity of rancid odor and flavor.

RESULTS AND DISCUSSION

TBA and Peroxide Tests.

Changes in TBA and peroxide values of the antioxidant- and fungistat-treated dried bisugo with storage time are shown in Figs. 1 and 2. Statistical analyses strongly indicated significant differences among treatment means (Table 2). The group of fungistats composed of potassium sorbate, sodium propionate and sodium benzoate exhibited higher rates of increase in TBA and peroxide values with respect to time compared with the control group, which means that these had accelerating or pro-oxidative effects on the fat of fish (Table 3). On the other hand, the antioxidant group composed of

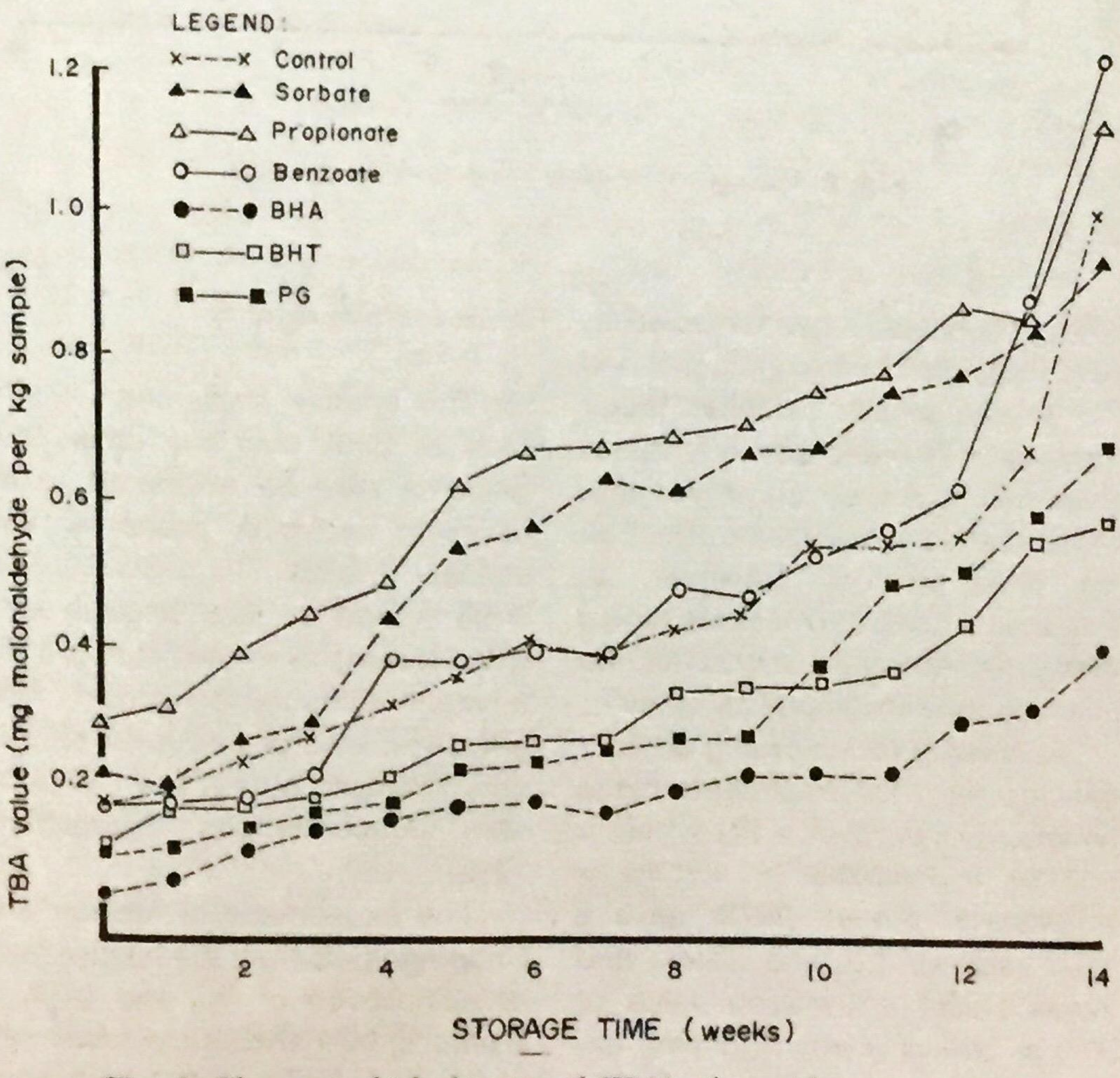

Fig. 1. Changes in thiobarbituric acid (TBA) values with storage time.

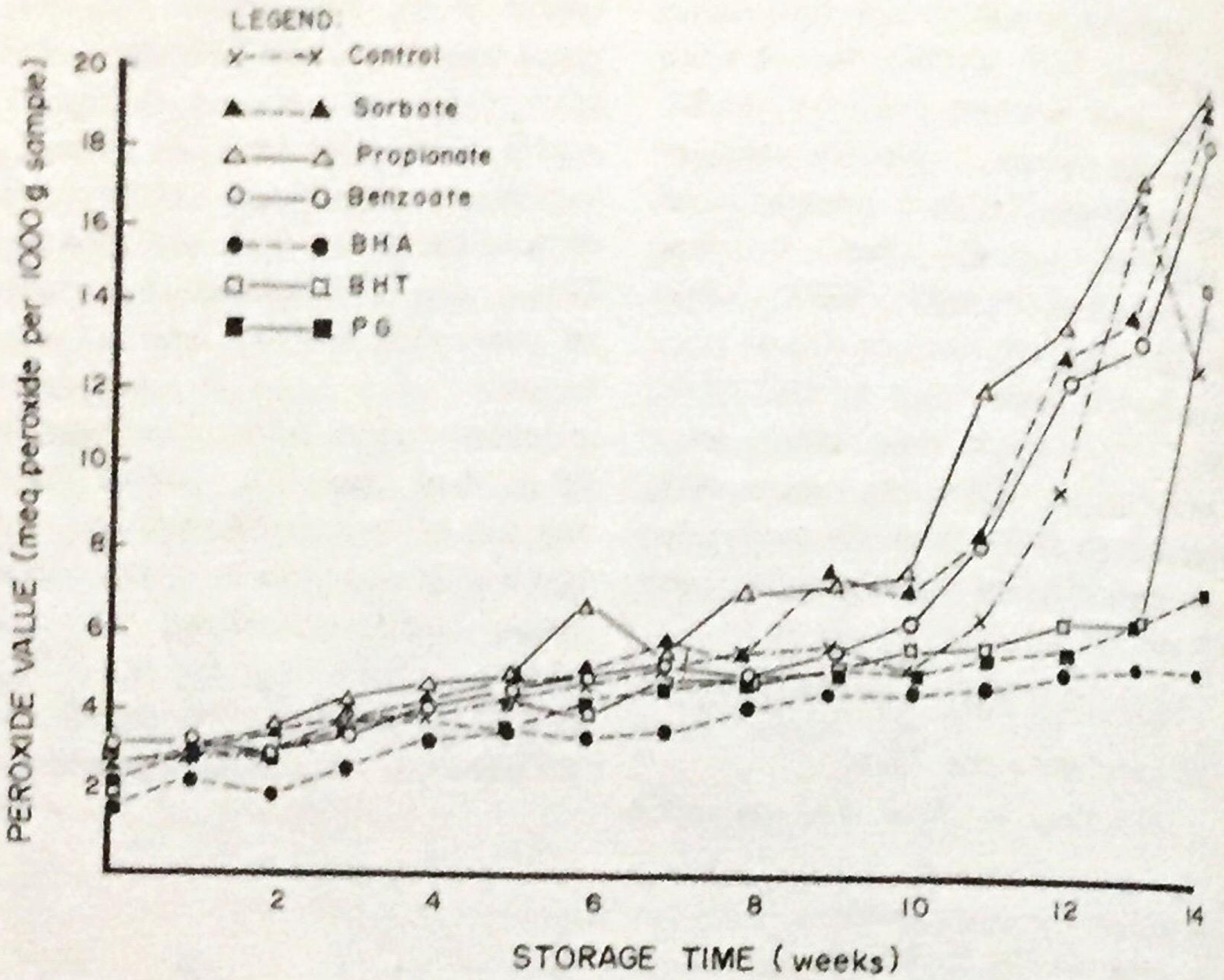

Fig. 2. Changes in peroxide values with storage time.

BHA (butylated hydroxyanisole), BHT (butylated hydroxytoluene) and PG (propyl gallate) exhibited lesser increase in TBA and peroxide values than the control, which proved that these exerted antioxygenic effect on the dried product. However, all treatments tended to become rancid with time and varied only in the rate in which they developed rancidity.

According to increasing antioxidative effect, the treatments could be arranged as: BHA > PG > BHT > control > benzoate > sorbate > propionate. Sweet (1973) gave a TBA value of 1.0, and Chang and Watts (1950) a peroxide value of 20.0 as critical points signifying onset of rancidity.

Antioxidative Agents.

The relative superiority in efficacy of BHA over the other antioxidants may be attributed to its excellent carryover properties and stability to heat. The destruction of BHA is slow so that enough antioxidant remains in the fat to protect it for some time. Although BHT may also show reliable carryover properties, it is less potent than BHA at low concentrations (Borgstrom, 1968).

The experiment of Mahon and Chapman (1953) on the relative rates of destruction of PG and BHA in oxidizing lard showed a faster rate of disappearance of PG with time.

Table 2. Mean values[1] for chemical and sensory analyses of dried bisugo during 14 weeks of storage at room temperature.

TREATMENT	CHEMICAL		SENSORY	
	TBA Value[2]	Peroxide Value[3]	Rancid Odor*	Rancid Flavor*
Control	0.43d	6.07cd	1.86cd	1.86cd
Sorbate	0.56b	7.21ab	2.10b	2.34b
Propionate	0.64a	8.10a	2.73a	3.06a
Benzoate	0.48c	6.76cb	1.96bc	1.96c
BHA	0.19f	3.85f	1.48e	1.45f
BHT	0.31e	5.19ed	1.89cd	1.63e
PG	0.31e	4.63ef	1.77d	1.73de

[1] Each value presented is the average of weekly means. Means in the same column having a common letter are not significantly different at 5% level, DMRT.

[2] mg of malonaldehyde per kg sample

[3] meq of peroxide per 1000 g sample

* 1 - absent; 2 - threshold; 3 - slightly rancid; 4 - rancid; 5 - rancid, strong but still acceptable; 6 - rancid, objectionable

The rate of destruction of PG was approximately constant with respect to time while that of BHA occurred in 2 stages: an initial slow loss which was partially attributed to evaporation of BHA from the surface of the lard, followed by a period of rapid decrease which was initiated coincidentally with the disappearance of PG. The gallates are not carry-through antioxidants and their power to stabilize fatty foods is low (Chipault, 1962). Incidentally, temperature during sun drying (60-65°C) was enough to initiate destruction of the antioxidants, especially the non-carrythrough.

Fungistatic Agents.

The pro-oxidative effect of the fungistats may be explained by the following contributing factors: First, they lack that ability to inhibit the chain of reactions that involves the oxidation of fat. In other words they do not have that "chain breaking" (breaking of free radical reaction chains) propensity possessed by the antioxidants. Second, metals and their salts generally increase the rate of oxidative deterioration of food lipids (Lea, 1939; Castell et al., 1965). It should be noted that the fungistats were incorporated into the fish in the form of potassium and sodium salts. Third, salt (NaCl) has been shown to have an accelerating effect on rancidity of herring (Banks, 1937) and cod muscles (Castell et al., 1965). This study revealed that the fungistat-treated samples had relatively higher salt content compared to those of the antioxidant-treated and control groups.

Sensory Evaluation.

Tables 2 and 4 show the effect of various treatments on the rancid odor and flavor of dried bisugo as evaluated by panelists. The trend of overall average scores of undesirable rancid odor and flavor at different periods was in general agreement with chemical changes measured by TBA and peroxide values. Both rancid odor and flavor scores increased with time of storage concurrent with increase in TBA and peroxide values. The order of efficacy of the treatments using sensory data was the same with that obtained using chemical measurements indicating the reliability of the sensory evaluation.

Regression analysis and equations showed increasing linear trend in flavor/odor scores with time (Table 5). From this linear trend, the number of weeks required for the various treatments to become rancid (sensory score of 4) was predicted as presented in Table 6.

Table 3. Changes in TBA and peroxide values in antioxidant/fungistat-treated dried bisugo during 14 weeks of storage at room temperature.

TREATMENT	TBA VALUE[1]			PEROXIDE VALUE[2]		
	Initial	After 14 weeks	Rate of Increase[3]	Initial	After 14 weeks	Rate of Increase[4]
Control	0.179	1.04	0.032	2.590	12.75	0.416
Sorbate	0.211	0.952	0.053	2.860	19.75	0.685
Propionate	0.296	1.120	0.047	3.035	19.91	0.804
Benzoate	0.157	1.229	0.039	2.935	18.52	0.609
BHA	0.049	0.392	0.025	1.740	5.41	0.255
BHT	0.120	0.579	0.023	1.990	15.05	0.296
PG	0.104	0.691	0.031	2.100	7.8	0.279

[1] mg malonaldehyde per kg sample

[2] meq of peroxide per 1000 g sample

[3] mg malonaldehyde per kg sample per week

[4] meq of peroxide per 1000 g sample per week

Table 4. Sensory evaluation of the changes in rancid odor and flavor of antioxidant/fungistat-treated dried bisugo during 12 weeks of storage at room temperature.

TREATMENT	RANCID ODOR[1]			RANCID FLAVOR[1]		
	Initial rancidity	After 12 weeks	Rate of increase[2]	Initial rancidity	After 12 weeks	Rate of increase[2]
Control	1.50	3.08	0.138	1.25	2.79	0.142
Sorbate	1.58	3.25	0.174	1.33	3.75	0.248
Propionate	1.33	4.42	0.306	1.42	5.16	0.389
Benzoate	1.25	3.16	0.152	1.16	2.83	0.126
BHA	1.00	2.08	0.095	1.00	2.16	0.105
BHT	1.16	3.00	0.194	1.08	2.75	0.147
PG	1.08	2.75	0.146	1.16	2.58	0.139

[1] 1 - absent; 2 - threshold; 3 - slightly rancid; 4 - rancid; 5 - rancid, strong but still acceptable; 6 - rancid, objectionable

[2] amount of increase in rancid odor/flavor score per week

Table 5. Estimated linear relationships between rancid odor/flavor and time for the various treatments.

TREATMENT	Regression Equation	Correlation Coefficient (r)
	Odor	
Control	$Y^1 = 0.960 + 0.126X^2$	0.89
Sorbate	$Y = 0.973 + 0.174X$	0.94
Propionate	$Y = 0.745 + 0.306X$	0.96
Benzoate	$Y = 0.972 + 0.152X$	0.92
BHA	$Y = 0.859 + 0.095X$	0.93
BHT	$Y = 0.636 + 0.194X$	0.93
PG	$Y = 0.822 + 0.146X$	0.97
	Flavor	
Control	$Y = 0.938 + 0.142X$	0.95
Sorbate	$Y = 0.726 + 0.248X$	0.98
Propionate	$Y = 0.534 + 0.0389X$	0.97
Benzoate	$Y = 1.136 + 0.126X$	0.85
BHA	$Y = 0.771 + 0.104X$	0.95
BHT	$Y = 0.679 + 0.146X$	0.95
PG	$Y = 0.822 + 0.139X$	0.96

[1] rancid odor/flavor score

[2] time (in weeks)

Table 6. Predicted time for rancidity development in antioxidant/fungistat-treated dried bisugo during storage at room temperature.

Treatment	Odor		Flavor	
	Weeks	Months	Weeks	Months
Control	22	5.50	22	5.50
Sorbate	18	4.50	13	3.25
Propionate	11	2.75	9	2.25
Benzoate	20	5.00	23	5.75
BHA	33	8.00	31	7.75
BHT	17	4.25	23	5.75
PG	22	5.50	23	5.75

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