

EFFECT OF BUTYLATED HYDROXY TOLUENE AND POTASSIUM SORBATE ON DEVELOPMENT OF RANCIDITY IN SMOKED MULLET

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ABSTRACT

Mullet fillets were smoked and divided into groups according to the type of brine solution used: (1) 10-percent brine, (2) 0.1-percent butylated hydroxy toluene in 10-percent brine, (3) 1.0-percent potassium sorbate in 10-percent brine, and (4) 0.1-percent butylated hydroxy toluene and 1.0-percent potassium sorbate in 10-percent brine. The fillets were stored at 37° F. and were analyzed for the development of rancidity at intervals of 2 weeks.

Butylated hydroxy toluene gave the longest protection against rancidity. Potassium sorbate, however, protected the fillets against rancidity throughout the marketable life of the smoked product.

INTRODUCTION

Preservation of fishery products by smoking is a method that has long been in use, but in these days of modern refrigeration, smoke preservation is being used less extensively. More consumers, however, are becoming aware of the delicious taste of smoked fish. Many species of fish and shellfish are smoked and distributed today, but because of the short shelf life of these products, distribution is often restricted to those areas near the source of the material. The major problem--that of short shelf life--is due to two causes: (1) the rapidity with which this type of product develops surface molds and (2) the rapidity with which it develops rancid flavors.

To solve the first difficulty, that of mold development, researchers have tried various mold inhibitors. The use of potassium and sodium sorbate in extending the shelf life of smoked fish has been investigated by Geminder (1959). The use of potassium sorbate on smoked mullet fillets has been further investigated, at this laboratory, by Waters (1960). In both studies, it was found that potassium sorbate was effective in preventing mold deterioration of smoked fishery products.

The next problem was that of rancidity. The constituents of smoke have been shown to have an antioxidant effect on fatty fish fillets (Erdman, Watts, and Ellias, 1954). Rancid flavors become evident in smoked mullet in a short time, however, effectively keeping the shelf life of this product short. The retardation of the development of rancidity in fresh frozen mullet has been studied in detail by Saenz and Dubrow (1959), who found that the shelf life of frozen vacuum-packed mullet fillets could be extended 4 to 5 months through proper application of antioxidant.



Fig. 1 - Chemist analyzing smoked mullet fillets for rancidity by the thiobarbituric acid method.

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To determine further the effects on rancidity development of the antioxidant and antimycotic and a combination of both as used in previous experiments concerned with mold spoilage (Waters 1960), techniques found in the literature were applied to smoked mullet. This report will describe the effects of butylated hydroxy toluene, potassium sorbate, and a combination of both on rancidity in smoked mullet fillets.

EXPERIMENTAL PROCEDURE

A large lot of mullet (Mugil cephalus) was obtained from a local seafood concern. These mullet had been caught in Breton Sound, Miss., iced, and processed within 24 hours.

PROCESSING METHODS: The mullet were scaled and eviscerated. They were then randomly divided into four groups according to the type of brine to be employed. The brines used were as follows:

- (1) Control--10-percent brine.
- (2) Butylated hydroxy toluene--0.1-percent butylated hydroxy toluene in 10-percent brine.
- (3) Potassium sorbate--1.0-percent potassium sorbate in 10-percent brine.
- (4) Butylated hydroxy toluene and potassium sorbate--0.1-percent butylated hydroxy toluene and 1.0-percent potassium sorbate in 10-percent brine.

The effective concentration of butylated hydroxy toluene and potassium sorbate had been previously determined by Waters (1960). The fillets were allowed to remain in the brine for 30 minutes at room temperature (75° F.). They were then removed from the solution and drained. Six fish from each group were removed and dried in an oven as a negative control for use in determining the amount of added TBA color development, if any, contributed by substances in the brining process. The remainder of the fish were smoked according to the procedure developed in this laboratory and previously recorded by Waters (1960). After being smoked, the fish were vacuum-packed in "cryovac" bags and stored at 37° F. The following day, six fish from each group were removed from the 37° F. room and analyzed as positive controls to determine TBA color development contributed by substances in the smoking process. Samples of six fillets of each group were removed at intervals of 2 weeks for analysis.

CHEMICAL METHODS: A butterfly fillet of mullet was ground three times in a General food grinder and a 1-gram sample was removed and analyzed for rancidity according to the thiobarbituric acid method (Yu and Sinnhuber 1957; Sinnhuber and Yu 1958). The amount of aldehyde produced during the rancidification of oils, as measured by the formation of a red color through the reaction of malonaldehyde with thiobarbituric acid, has been used as a measure of rancidity by these authors. $E_{1\%}^{1\text{cm}}$ at 535 m μ . was measured in a Bausch and Lomb "Spectronic 20" colorimeter. The factor for conversion of absorbancy to rancidity value (TBA value) was determined for this colorimeter with 1,1,3,3-tetraethoxypropane standard solution. A factor of 57 was found; in other words, an absorbance of 1.0 indicated 57 milligrams of aldehyde per 1.000 gram sample.

Each individual sample was analyzed for moisture and oil. Moisture was determined according to the method of the Association of Official Agricultural Chemists (1955) for fishery products, with the exception that Ottawa sand was used instead of asbestos. The AOAC (1955) acid hydrolysis method of oil analysis was employed.

ORGANOLEPTIC TESTS: Limited organoleptic tests were also used to indicate progress towards rancidity. The following classifications were employed: good--prime quality; fair--smoky flavor still discernible; rancid--rancid-oil flavor definitely noticeable. Fillets that were rated good or fair did not have a discernible rancid flavor, and these classifications merely serve to indicate progressive loss of smoky flavor. Fillets that were rated rancid ranged from those fillets with a barely discernible rancid flavor to those with a distinct rancid flavor.

from 1.5 percent to 15.0 percent and averaged 6.4 percent. The TBA values were not corrected to the average oil content.

Thiobarbituric acid is known to form the characteristic red pigment with a number of oxidation products of unsaturated fatty acids (Tarladgis, Watts, and Younathan 1960) and aldehydes from other sources, as well as a characteristic yellow pigment with certain other aldehydes (Patton 1960). Since the smoke deposit on the surface of fish fillets is known to contain a variety of aldehydes (Shewan 1949), it was necessary to ascertain the amount of TBA color that could be attributed to the smoke constituents. For the same reason, fillets that had not been smoked but had been brined were analyzed to determine the effect of the brining solutions on the development of the TBA color. The fillets that were not smoked comprised the negative control and those that were smoked comprised the positive control.

The group of fish comprising the negative control had been treated identically with the smoked fish up to the point where the fish were dried during the smoking process. The negative control group was dried in a laboratory oven for a length of time and at a temperature similar to that used in smoking the fish fillets. The average TBA value of the fish brined in 10-percent salt solution was 0.6; in 0.1 percent butylated hydroxy toluene, 1.5; in 1.0-percent potassium sorbate, 0.7; and in the combination of 1.0-percent butylated hydroxy toluene and 1-percent potassium sorbate, 0.9.

The positive control consisted of six fish from each group, which were analyzed the day immediately following smoking. The average TBA values of the six fish from each group were as follows: control, 2.9; 0.1-percent butylated hydroxy toluene, 2.9; 1.0-percent potassium sorbate, 4.3; and 0.1-percent butylated hydroxy toluene and 1.0-percent potassium sorbate, 3.6. It thus is apparent that when the negative control of each group is subtracted from the positive control of the same group, a certain amount of apparent TBA value is due to substances deposited during the smoking process. The error of the mean of the four groups at the critical 6-week interval ranged from 0.4 (0.1-percent butylated hydroxy toluene) to 1.6 (control) and averaged 0.9. The average TBA value found to be due to the smoking process was 2.5, and since this value exceeded the average error of the mean, it was subtracted from all succeeding TBA values. In addition, the apparent TBA value due to the brining process found in each negative control group was subtracted from subsequent TBA values. The TBA values reported in table 1, therefore, can be considered for the purpose of this paper to be due to an increase in rancidity alone.

In the correlation of the organoleptic scores with the TBA values found, it becomes apparent that the fillets with a TBA value less than 7.8 could be considered as not rancid, and the fillets with TBA value greater than 7.8 could be considered rancid (95-percent confidence level). Fillets with a TBA value of less than 5.0 could be considered good (95-percent confidence level). Those with TBA values ranging from 5.0 to 7.8 could be classified as fair. For the purposes of this experiment, then, fillets with a TBA value ranging from 0.0 to 5.0 were considered good, those ranging from 5.0 to 7.8 were considered fair, and those with values 7.8 and above were considered rancid. The organoleptic tests correlated to a high degree (99-percent confidence level) with the TBA values, indicating that the TBA test for rancidity is reliable in the case of smoked mullet fillets.

After 2 weeks' storage of the smoked fillets, the average TBA value (4.5) of the six fillets in the control group showed them as being in the good class. Within 4 weeks, the average TBA value (7.3) showed these fillets to be fair, whereas after 6 weeks, the fillets had become rancid (8.8).

In the group of fillets brined with the addition of 0.1-percent butylated hydroxy toluene, it was found after 2 weeks of storage that the average TBA value of the fillets was well within the good class (1.6). After storage for 4 weeks, the average TBA value (3.9) showed that the fillets had remained in the good class, and after storage for 6 weeks, the average TBA value (5.3) showed that they had passed into the fair class. The average TBA values showed these fillets as remaining in the upper range of the good class throughout the remainder of the experiment.

In the case of the fillets brined in 1.0-percent potassium sorbate, the average TBA value (2.5) after 2 weeks of storage showed the fillets to be in the good class; after 4 weeks of stor-

age, the average TBA value (3.8) showed the fillets to remain in the good class; and after 6 weeks' storage, the average TBA value (4.8) showed the fillets remaining in the upper range of the good class. Within 8 weeks the average TBA value (8.6) showed the fillets as having passed into the rancid class.

After 2 weeks' storage of the fillets brined in 0.1-percent butylated hydroxy toluene and 1.0-percent potassium sorbate, the average TBA value (2.0) showed the fillets as being in the good class; after 4 weeks' storage, the average TBA value (4.3) showed that the fillets had remained in the good class; and, after 6 weeks' storage, the average TBA value (4.1) showed that the fillets had still remained in the good class. Within 8 weeks, the average TBA value (8.8) showed that the fillets had passed into the rancid class.

DISCUSSION

A rather marked disappearance of the smoky flavor was noticed by the taste panel after approximately 6 weeks' storage. This disappearance of smoky flavor, due to the slow volatilization or degradation of the smoke flavor components, has been recognized by the commercial industry. The time limit for protection against the development of rancidity has been suggested to be approximately 6 weeks. It can be noted from figure 2 that at approximately 6 weeks, the average TBA value had progressed from the upper range of the good class to the fair group. The treated groups followed a different pattern from that of the nontreated group through approximately the first 6 weeks of storage. From the 6th to the 8th week, the rate of rancidification of the fillets treated with 1.0-percent potassium sorbate and with the combination 0.1-percent butylated hydroxy toluene and 1.0-percent potassium sorbate approached that of the control group, whereas the development of rancidity in the 0.1-percent butylated hydroxy toluene group was retarded.

From a marketing standpoint, 6 weeks appears to be the limit of the shelf life of smoked mullet fillets. The limiting factor here is not the development of mold or rancidity, but the loss of smoky flavor. There is a significant difference between the means of the TBA values of the treated groups and the mean of the control group until the 6th week of storage. No significant difference is noted between the means of the TBA values of the three treated groups, but at the 6th week there is no significant difference between the means of all four groups. It thus seems that in the use of potassium sorbate to retard the development of mold, an additional benefit is secured in sufficiently lengthening the induction period before the development of rancidity to permit the storage of the fillets for the desired market life of 6 weeks.

Although the marketable life of the mullet fillets had been determined as 6 weeks, the experiment was carried on for a period of 6 additional weeks to study the effects of the butylated hydroxy toluene, potassium sorbate, and the combination of both on the development of rancidity. It became apparent that butylated hydroxy toluene was the most effective antioxidant, since the rancidity, as indicated by the average TBA values, increased slowly, leveled, and remained the same. From the 6th to the 10th week, the group treated with 1.0-percent potassium sor-

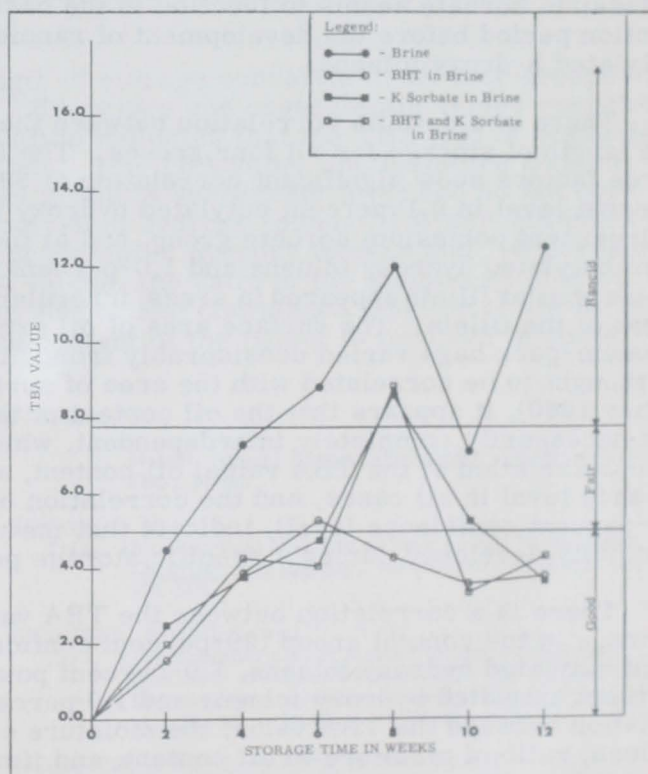


Fig. 2 - Change in TBA values with storage time. The relative position of the average TBA values within the organoleptic classes is shown for the four groups--(1) control, 10-percent brine, (2) 0.1-percent butylated hydroxy toluene in 10-percent brine, (3) 1.0-percent potassium sorbate in 10-percent brine, and (4) 0.1-percent butylated hydroxy toluene and 1.0-percent potassium sorbate in 10-percent brine.

bate and the group treated with 0.1-percent butylated hydroxy toluene and 1.0-percent potassium sorbate exhibited the same pattern of increase and decrease of TBA value as did the control samples. From the 10th to the 12th week, the average TBA value of the control sample increased, whereas the average TBA values of the treated groups decreased or remained the same. These trends could perhaps be due to the production of a compound capable of producing a color with thiobarbituric acid and its subsequent destruction during the rancidification process. The next step in the degradation process could then be seen as being the formation in the control group of another such compound, which is absent from the other groups.

There is little evidence in the literature to suggest that potassium sorbate had previously been considered as being an antioxidant or as having antioxidant properties. It has been suggested that the mechanism of the antimycotic action of potassium sorbate is due to the fact that once deposited on the meat of the fish, it hydrolyzes into sorbic acid. Sorbic acid is an unsaturated fatty acid similar to those formed in the enzymatic dehydrogenation reaction necessary to sustain mold growth, and when present in excess it tends to inhibit this reaction and consequently the growth of the mold (Pfizer 1955). It is possible that (1) by preventing the dehydrogenation of fatty acids in the mullet oil, it prevents the formation of free radicals necessary to the development of rancidity or (2) because of its fatty acid structure, it preferentially selects the available oxygen. The latter course seems the more likely, since the potassium sorbate seems to function in the case of smoked mullet merely to lengthen the induction period before the development of rancidity but is not as effective in this regard as is butylated hydroxy toluene.

There is a definite correlation between the TBA value, the oil content of the fillets, and the length of storage for all four groups. The F values obtained in the correlation of these three factors show significant correlation at 99-percent level in the control group, at the 99-percent level in 0.1-percent butylated hydroxy toluene group, at the 95-percent level in the 1.0-percent potassium sorbate group, and at the 99-percent level in the combination 0.1-percent butylated hydroxy toluene and 1.0-percent potassium sorbate group. The deposits of oil in the mullet fillets appeared in areas, irregular in size and shape, between the skin and the meat of the fillets. The surface area of oil exposed to the limited supply of oxygen in the vacuum-pack bags varied considerably from fillet to fillet. Since the rate of oxidation of oil is thought to be correlated with the area of surface exposed to the air (Polmater, Yu, Sinnhuber 1960), it appears that the oil content of the fillet and the development of rancidity are not necessarily completely interdependent, which would account for the variation in F values. The correlation of the TBA value, oil content, and length of storage above the 95-percent confidence level in all cases, and the correlation of the TBA value and organoleptic tests (at the 99-percent confidence level), indicate that the value of the TBA is dependent on the degree of rancidity developed during a specific storage period.

There is a correlation between the TBA values, the moisture content, and the length of storage in the control group (99-percent confidence level). The groups treated with 0.1-percent butylated hydroxy toluene, 1.0-percent potassium sorbate, and the combination of 0.1-percent butylated hydroxy toluene and 1.0-percent potassium sorbate show no significant correlation between the TBA value, the moisture content, and the length of storage. The TBA values, ratio of moisture to oil content, and time of storage, however, correlate at the 99-percent confidence level for the control group and the 0.1-percent butylated hydroxy toluene group, at the 97-percent confidence level for the 1.0 percent potassium sorbate group and, at the 90-percent confidence level, for the combination 0.1-percent butylated hydroxy toluene and 1.0-percent potassium sorbate group. The increase in correlation that was found by the use of the ratio of moisture to oil content rather than the moisture content alone seems to suggest that there is a relationship between the oil and moisture contents of the fillets and the development of rancidity as evidenced by the TBA value.

SUMMARY

Mullet fillets were smoked and divided into groups according to the following four types of brine solution used:

(1) 10-percent brine solution.

(2) 0.1-percent butylated hydroxy toluene in 10-percent brine solution.

(3) 1.0-percent potassium sorbate in 10-percent brine solution.

(4) 0.1-percent butylated hydroxy toluene plus 1.0 percent potassium sorbate in 10-percent brine solution.

The fillets were then stored at 37° F. for 12 weeks, with samples being analyzed for the development of rancidity by the thiobarbituric acid method at intervals of 2 weeks.

Organoleptic tests indicated that smoky flavor gradually disappeared and that after a period of 6 weeks the fillets were considered not suitable for marketing for this reason. For 6 weeks, the butylated hydroxy toluene, potassium sorbate, and combination of both prevented the development of discernible rancidity. After 6 weeks, potassium sorbate and the combination of potassium sorbate and butylated hydroxy toluene allowed an increase in the rate of the development of rancidity, whereas the butylated hydroxy toluene did not. Apparently, it is possible to utilize potassium sorbate both as an antimycotic and as an agent to lengthen the induction period preceding the development of a noticeable rancidity during the marketable life of the smoked mullet fillets.

The TBA value, the oil content, and the length of storage correlate in all four groups at or above the 95-percent confidence level. The TBA values and organoleptic values correlate at the 99-percent confidence level. This correlation indicates that the TBA test is adequate for prediction of rancidity in smoked mullet fillets. The TBA value, the moisture content, and the length of storage correlate in the control group at 99-percent level and do not correlate for the groups treated with 0.1-percent butylated hydroxy toluene, 1.0-percent potassium sorbate, and the combination of 0.1-percent butylated hydroxy toluene and 1.0-percent potassium sorbate. On the other hand, the TBA values, the ratio of the moisture to the oil content, and the time of storage correlate at the 90-percent confidence level or above for all groups. This finding indicates that the moisture content of the fillets is involved in some manner in the development of rancidity.

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