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The Antioxidant Behavior of the Isomers of Butylated Hydroxyanisole[1,2]

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BUTYLATED hydroxyanisole (BHA) has been shown to have very desirable properties as an antioxidant for animal fats and for foods made with these fats (1, 2, 4, 5, 6, 7, 9). It provides long shelf-life for crackers, pastry, and potato chips and, in combination with propyl gallate and citric acid, imparts stability to good lards comparable to that of the best hydrogenated vegetable oils.

The commercially prepared BHA is primarily composed of the two isomers of BHA. These are 3-tertbutyl-4-hydroxyanisole and 2-tertbutyl-4-hydroxyanisole which will be referred to hereafter as the 3-isomer and the 2-isomer, respectively. Since the 3-isomer belongs to the class of "partially hindered phenols" whereas the 2-isomer is an unhindered phenol, the question naturally arises as to whether there is a difference in their effectiveness as an antioxidant. Rosenwald and Chenicek (8) reported that the 3-isomer is 3 to 5 times as effective as the 2-isomer when tested by the Active Oxygen Method (AOM) in one sample of lard. They noted that the 3-isomer was approximately 2.5 times as effective as the 2-isomer in delaying rancidity in crackers made with a single lard.

We compared the effect of the two isomers on the AOM stability in 11 different lards and the effect on carry-through stability with crackers, pastry, and potato chips on four different lards. The maximum increase found in AOM stability with the 3-isomer was 1.64, and the average increase 1.5 times that obtained with the 2-isomer. In carry-through stability the 3-isomer was only slightly more effective than the 2-isomer.

AOM Studies of Antioxidant Effectiveness

For this study highly purified samples of the two isomers were obtained (Table I). The isomers were tested separately and in specially prepared mixtures to provide known weight ratios of each isomer in each mixture. The mixtures of the isomers were prepared to provide 75/25, 50/50, and 25/75 per cent ratios. Due to the fact that antioxidant effectiveness will vary with the initial stability of a lard, the isomers and mixtures of isomers of BHA were tested at 0.01% in 11 different lards. The effectiveness of commercial BHA was determined at the same time in the same lards. The tests made were AOM stability of the lard and Schaal oven stability of crackers, pastry, and potato chips, which were prepared to illustrate the carry-through activity of the antioxidants.

TABLE I

Composition of Isomers and Mixtures of Isomers of BHA[a]

	Per Cent by Weight	
	3-isomer	2-isomer
3-isomer BHA, m.p. 60-61.2°C.	99.5	0.5
2-isomer BHA, m.p. 50-51.5°C.	1.0	99.0
75% 3-isomer BHA 25% 2-isomer BHA	72.1	27.8
50% 3-isomer BHA 50% 2-isomer BHA	50.7	49.3
25% 3-isomer BHA 75% 2-isomer BHA	22.4	77.6

[a] Infrared analyses furnished by the Tennessee Eastman Company.

The AOM stabilities imparted to lards obtained from four packinghouses widely distributed in the Middle West are shown as lards 1 to 4 in Table II. In all cases the 3-isomer is the most effective antioxidant, and the 2-isomer is the least effective. The mixtures of isomers fall between the pure isomers and are respectively more effective as an antioxidant as the amount of the 3-isomer is increased in the mixture. The commercial BHA tested was equal to or superior in effectiveness to the mixture containing 50% of each isomer when tested in each of the lards. These lards are those which were used for the culinary studies to be discussed later. The AOM stability values for the mixed isomers in six different lards and for the pure isomers in the same lards and in one different lard are shown as lards 5 to 11 in Table II. The same pattern of effectiveness was found as for the four lards used in the culinary tests.

The term inhibitor ratio (I.R.) has been used (8) to describe the effectiveness of an antioxidant referred to another antioxidant chosen as a standard. The I.R. may be defined: $IR = \frac{S_x - S_c}{S_s - S_c}$ where S_c refers to the AOM stability of the control lard, S_s to the stability of the lard treated with the "standard" antioxidant, and S_x the stability of the lard when treated with the antioxidant being compared with the "standard." Since the 3-isomer has been referred to as a "standard" (8), it will be used as a standard for purposes of this discussion. The IR for the 3-isomer will, of course, be 1.00 while all antioxidants that are less effective will have an IR less than 1.00. The IR for the 2-isomer of BHA is variable with the lard used as would be expected. The average IR for the 2-isomer in the first four lards is 0.65, which means that the

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TABLE II
AOM Stability of Lards Treated with the Isomers of BHA

Antioxidant[a]	AOM Stabilities of Various Lards										
	1	2	3	4	5	6	7	8	9	10	11
	hrs.	*hrs.*	*hrs.*	*hrs.*	*hrs.*	*hrs.*	*hrs.*	*hrs.*	*hrs.*	*hrs.*	*hrs.*
Control (no antioxidant)	9.5	12	7.5	0.8	2	4	6	8	10.8	10.8	8
3-Isomer BHA	33.5	43.5	30.3	18	20	23	29	30	34	40	36.5
2-Isomer BHA	26	33	21.5	11.5	14	17	22	22	27	30	26.5
75% 3-Isomer BHA 25% 2-Isomer BHA	32	42.3	29	16.5	19	24	28	28	33	38.5	
50% 3-Isomer BHA 50% 2-Isomer BHA	30.5	39.8	27	15	17	24	26	26	32	37.5	
25% 3-Isomer BHA 75% 2-Isomer BHA	29	37.5	25.3	13.5	16	21	24	24	31	35.5	
Commercial BHA	30.5	40	28	15.3	16.5	21.5	25.5	24.5	32.5	36	

[a] Total antioxidant in each lard—0.01%.

3-isomer is approximately 1.5 times as effective on the average as the 2-isomer. In the other seven lards it is 0.68, which makes the 3-isomer 1.47 times as effective as the 2-isomer. The IR for the mixtures fall intermediate to those for the purified isomers, with the IR being greater with the greater quantity of the 3-isomer in each mixture.

The average increase in IR from that for the 2-isomer to that for the mixture containing 75% 2-isomer and 25% 3-isomer is 0.13 while the average increase from the IR for the mixture containing 25% 2-isomer and 75% 3-isomer to that for the 3-isomer alone is only 0.05. This difference in increased IR values indicates that any mixture of the isomers is better than the 2-isomer used alone, and it also indicates that use of the pure 3-isomer has little advantage over mixtures of the isomers. Golumbic (3) has indicated that a mutual synergistic effect may be obtained when two phenolic antioxidants with differing oxidation-reduction potentials are used in a fat system subjected to oxidation. The oxidation-reduction potentials of the isomers of BHA, while not known, would undoubtedly be different. It may be that a mutual synergism between these isomers in a mixture may account for the greater IR increase between the 2-isomer and the mixture containing it in 75% concentration than is found between the mixture containing 75% of the 3-isomer and the 3-isomer alone.

The amount of synergism afforded by each mixture of isomers may be calculated if one assumes that the effect of varying the concentration of each isomer will have essentially a proportional effect on the stability imparted by that isomer whether used alone or in a mixture of the isomers. For example, the 50/50 mixture of isomers in lard 2 may be calculated to impart a stability of 21.75 hours due to the 3-isomer, and a stability of 16.5 hours due to the 2-isomer. The sum of these is 38.25 hours, whereas the measured stability was 39.75 hours. The difference of 1.5 hours may then be due to synergism between the two antioxidants. Although the synergism measured in each instance is small, it follows the same pattern in each lard by increasing as the amount of the 3-isomer is decreased in the mixture.

The IR for the commercial BHA averaged 0.89 for the first four lards, which means that the 3-isomer is only about 1.1 times as effective by the AOM as the commercial BHA.

The 3-isomer is demonstrated to be more effective as an antioxidant than the 2-isomer when tested by the AOM. When mixtures of isomers are tested, an effect which may be due to a mutual synergism reduces the advantage the 3-isomer would be expected to have over a given mixture and increases the advantage a given mixture would be expected to have over the 2-isomer.

Culinary Carry-Through Studies

The lards used in the AOM studies were prepared in sufficient quantities for making crackers, pastry, and potato chips to evaluate the carry-through effectiveness of the isomers and the prepared mixtures. The pastry was a standard formula, and the crackers were prepared according to the method outlined by the Technical Institute of the Independent Biscuit Manufacturers Company Inc., Chicago, Ill. The potato chips were prepared by frying five 100-gm. lots in 1,300 gm. of fat at 375°F. The chips from the fourth and fifth fryings were combined and used for evaluation purposes. This evaluation does not give data which will assess the effectiveness in commercial frying operation but serves to compare the relative effectiveness of the antioxidants to prevent rancidity in potato chips. All carry-through evaluations were performed by organoleptic testing for rancidity on the products stored in small loosely capped screw-top jars at 145°F.

TABLE III
Carry-Through Effectiveness in Lard of the Isomers and Mixtures of Isomers of BHA

Antioxidant[b]	Schaal Oven Stability —145°F.		
	Crackers[a]	Pastry[a]	Potato Chips[a]
	hrs.	*hrs.*	*hrs.*
Control Lard	161	135	98
3-isomer BHA	777	1166	1003
75% 3-isomer BHA 25% 2-isomer BHA	707	1157	924
50% 2-isomer BHA 50% 3-isomer BHA	670	1101	778
25% 3-isomer BHA 75% 2-isomer BHA	697	1115	755
2-isomer BHA	633	1107	759
Commercial BHA	743	1071	795

[a] Average values from 4 lards.
[b] Total antioxidant concentration in each test—0.01%.

The results of the carry-through studies in the first four lards are shown in Table III. Values shown are the average values from the four lards. Note that in all cases the average stability imparted by the 3-isomer is greater than that imparted by the 2-isomer or any of the mixtures of isomers. The difference in stability from the greatest to the least value in pastry has no significance. In crackers the difference is such as to have only slight significance, and only in potato chips is there any really significant increase in stability due to use of the pure 3-isomer of BHA. Even in potato chips the stability imparted by the pure 3-isomer is not significantly greater than that imparted by the mixture containing 75% 3-isomer and 25% 2-isomer. Use of commercial BHA in the same lards shows that it compares favorably with the better values obtained with the pure isomers and mixtures of isomers.

Comparison of the Commercial BHA Products

The commercially available BHAs have been compared in a number of different lards. The comparisons have been made between the antioxidants alone, in combination with citric acid, and in combination both with citric acid and propyl gallate. The average AOM stabilities obtained in a number of different lards are shown in Table IV. Note that they are essentially equivalent. This holds true both when the antioxidants are tested alone in the lard or in synergistic combination with propyl gallate and citric acid. A statistical analysis of the data shows odds of 1.2 to 1 in favor of BHA 2 when the antioxidants were used alone. Odds of 1.15 to 1 in favor of BHA 1 when citric acid was used with the BHA, and odds of 2.7 to 1 in favor of BHA 2 were found when the combination mixture included propyl gallate and citric acid. Since the odds would have to be 19 to 1 to be significant, it is obvious that no advantage accrues to either commercial preparation due to a difference in composition.

TABLE IV

Comparison of Commercial BHA Preparations

Antioxidant	Avg. AOM Stabilities[a]	Carry-Through Effectiveness—Schaal Oven (145°F.)[b]	
		Crackers	Pastry
	hrs.	*hrs.*	*hrs.*
Control (no antioxidant)	4.6(9)	143	20
0.01% BHA No. 1	20.4(7)	556	278
0.01% BHA No. 2	20.6(7)	475	257
0.01% BHA No. 1 0.002% Citric Acid	26.4(4)	452	291
0.01% BHA No. 2 0.002% Citric Acid	26.25(4)	386	266
0.01% BHA No. 1 0.002% Citric Acid 0.003% Propyl Gallate	57.8(7)		
0.01% BHA No. 2 0.002% Citric Acid 0.003% Propyl Gallate	59.0(7)		

[a] Number in ( ) indicates number of lards.
[b] Avg. values obtained in two la ds.

Carry-through studies were conducted in two lards to compare the commercial BHAs. Crackers and pastry were prepared and tested as outlined above. While the results illustrated in Table IV are somewhat more variable than those from the AOM studies, no advantage can be claimed for either commercial BHA in the carry-through studies.

From AOM studies of the stabilities of lards treated with the pure isomers of BHA, with the mixtures of isomers of BHA, and with the commercially available preparations of BHA, it is apparent that the 3-isomer is somewhat more effective than the 2-isomer, but when the two isomers are used in admixture, the advantage is reduced so that no significant advantage can be ascribed to the 3-isomer over mixtures containing at least 50% of this isomer.

In the culinary studies of carry-through the difference is even less clear-cut, and the 3-isomer can be said to have little advantage over the 2-isomer or any of the mixtures of the isomers.

Summary

1. The antioxidant effectiveness of the purified isomers of BHA and prepared mixtures of these isomers was studied in 11 lards.

2. The 3-isomer is more effective in providing AOM stability than the 2-isomer, and the mixtures of isomers fall between the purified isomers in antioxidant effectiveness. The mixtures of isomers are more effective as the amount of the 3-isomer is increased in the mixture. The commercial BHA is equivalent or superior to the mixture containing 50% of each isomer. A mutual synergistic effect between the isomers may account for the fact that mixtures of the isomers are more effective than would be expected from the effectiveness of the purified isomers when used alone.

3. When four lards were treated with the isomers and mixtures of isomers of BHA and used for the preparation of crackers, pastry, and potato chips, carry-through was demonstrated in all cases. The 3-isomer is generally most effective and the 2-isomer is the least effective in antioxidant carry-through. Little significant advantage lies with the 3-isomer over the 2-isomer and the mixtures of isomers in antioxidant carry-through. The commercial BHA compared favorably with the isomers and mixtures of isomers in antioxidant carry-through tests.

4. The commercially prepared BHAs were compared in a number of different lards. No significant advantage could be ascribed to one over the other although the composition in terms of relative proportions of the isomers of BHA may be somewhat different.

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REFERENCES

1. Cecil, S. R., and Woodruff, J. G., Food Ind., *23* (2), 81-84, 223-224 (1951).
2. Dugan, L. R. Jr., Kraybill, H. R., Ireland, Louise, and Vibrans, F. C., Food Technol., *4*, 457-60 (1950).
3. Golumbic, Calvin, Oil and Soap, 23, 184-186 (1946).
4. Kraybill, H. R., Beadle, B. W., Vibrans, F. C., Swartz, VeNona, Wilder, O. H. M., and Rezabek, Helen, American Meat Institute Foundation Bull. 2 (1948).
5. Kraybill, H. R., Dugan, L. R., Beadle, B. W., Vibrans, F. C., Swartz, VeNona, and Rezabeck, Helen, J. Am. Oil Chem. Soc., *26*, 449-453 (1949).
6. Kraybill, H. R., Dugan, L. R., Vibrans, F. C., Swartz, VeNona, and Bondi, Vera, American Meat Institute Foundation Bull. 4 (1949).
7. Magoffin, J. E., and Bentz, R. W., J. Am. Oil Chem. Soc., *26*, 687-690 (1949).
8. Rosenwald, R. H., and Chenicek, J. A., J. Am. Oil Chem. Soc., *28*, 185-188 (1951).
9. Van Allsberg, E. J., Biscuit and Cracker Baker, *39*, 28, 41 (1950).

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