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Comparative Antioxidant Potency of 2,4,5-Trihydroxyphenones

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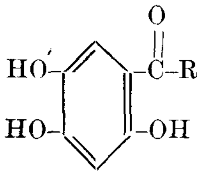
THIS REPORT is concerned with the results of testing 2,4,5-trihydroxyphenones as antioxidants for fats, paraffin wax, and mineral oil. The use of antioxidants for stabilizing various organic materials has grown fairly rapidly the last few years. More and more specific applications are being discovered as more antioxidant compositions are produced in the laboratory and become available for testing. Included in the current applications are cracked gasolines, leaded aviation gasoline, turbine oil, jet fuel, certain vitamins (such as carotene), rubber, paraffin wax, polymeric materials (such as polyethylene), and fats and oils. The increasing use of fats in cattle and poultry feeds will undoubtedly point out the need for antioxidants in these materials.

Antioxidants in edible fats serve two purposes: a) they prolong storage life by preventing rancidity development and b) they increase shelf life of foods cooked with or containing the stabilized fat. At present there are several compounds which are approved by the Food and Drug Administration for use in foods. These compounds are butylated hydroxyanisole (BHA), propyl gallate (PG), citric acid (CA), butylated hydroxytoluene (BHT), nordihydroguaiaretic acid (NDGA), guaiac acid, tocopherols, lecithin, phosphoric acid, 3,3′-thiodipropionic acid, dilauryl and distearyl esters of 3,3′-thiodipropionic acid, and ascorbic acid.

It might be expected that antioxidants for edible fats should also be antioxidants for non-edible fats. This is indeed true, but in many cases the non-edible varieties are more difficult to stabilize.

A series of compounds was tested as antioxidants for several different media by means of the Swift Active Oxygen Method (AOM). These compounds are represented by the formula



in which R is hydrogen, alkyl, cycloalkyl, aralkyl, or aryl. These compounds, in most AOM tests, are highly potent antioxidants. They are outstandingly good in lard, paraffin wax, and mineral oil and have some degree of potency in the various oils tested.

Discussion

Table I presents some AOM data for lard stabilized with the 2,4,5-trihydroxyphenones and also shows corresponding data for BHA, BHT, and PG. The data show that 2,4,5-trihydroxyphenones have very high potencies in lard and that the potency decreases with increasing molecular weight. This is shown graphically in Figure 1, in which AOM values are plotted against the number of carbon atoms in the R group. It is noted that the two compounds with branched R groups do not fall on the same line as that for the compounds with straight-chain R groups.

In Figure 2 AOM values for lard are plotted against antioxidant concentration. This plot shows that the AOM values for the 2,4,5-trihydroxyphenones are more nearly proportional to concentration than is the case with BHA, BHT, or PG.

In Table II AOM stability data for some of the 2,4,5-trihydroxyphenones in certain edible oils are given. In all cases the AOM life was increased. In peanut oil the effectiveness was most pronounced; the increase approached four-fold in this particular sample. In cottonseed oil the life increase was nearer

TABLE I

Results of Tests with Lard

Antioxidant		Stability, Hrs. (20 meq. peroxide)		
Compound	Concn., % by wt.	Sample A	Sample B	Sample C
None	......	13	13	12
BHA	0.02	31	35	31
PG	0.02	89	127	92
BHT	0.02	44	54	47
R Group of Phenone				
Hydrogen	0.01	96	......	......
	0.02	193	......	......
Methyl	0.01	128	......	......
	0.02	205	......	......
Propyl	0.005	67	......	......
	0.010	122	......	......
	0.020	163	......	......
Isopropyl	0.02	167	......	......
Propenyl	0.01	......	72	......
Amyl	0.02	......	......	106
3-Amyl	0.02	......	......	75
Heptyl	0.005	......	71	......
	0.010	......	88	......
	0.020	160	168	......
3-Heptyl	0.02	......	......	69
Nonyl	0.02	......	......	106
Undecyl	0.02	......	......	106
Heptadecyl	0.01	......	74	......
Benzyl	0.02	......	......	120
Cyclohexyl	0.02	......	......	87
Phenyl	0.01	100	......	......
	0.02	172	......	......
2-Furyl	0.005	64	......	......
	0.010	84	......	......
	0.020	127	......	......

two-fold. The lack of sufficient data on corn oil prohibits the drawing of any conclusions.

Some AOM data for paraffin wax and mineral oil are presented in Table III. It should be noted that data are shown for both 100°C. and 150°C. The higher temperature is more convenient in that the time required for the test is much shorter. The 2,4,5-trihydroxyphenones that were tested appeared to be quite effective in preventing peroxide formation under the test conditions.

In Table IV AOM data for two of the 2,4,5-trihydroxyphenones in castor, palm, sperm, and sesame oils are given. The two phenones were fairly effective in all of these oils and increased AOM life considerably. None of the antioxidants shown were very potent in palm or sperm oils.

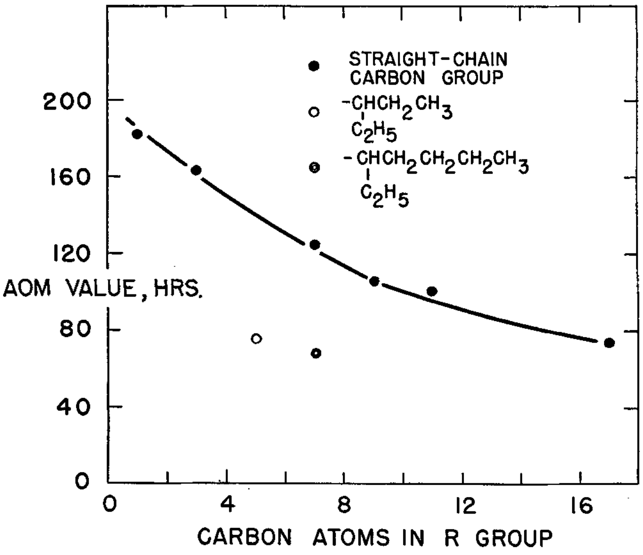


FIG. 1. Effect of R group on AOM keeping quality of lard stabilized with 2,4,5-trihydroxyphenones.

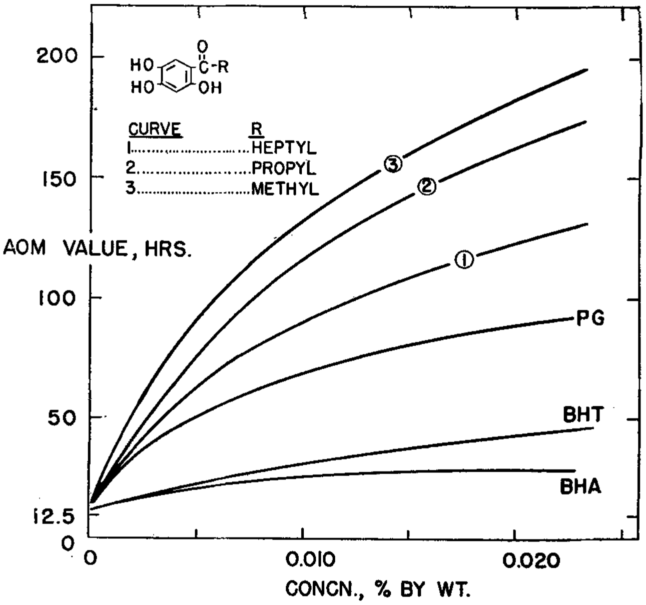


FIG. 2. Effect of antioxidant concentration on AOM keeping quality of lard.

AOM data for tallows and greases stabilized with various antioxidants are shown in Table V. All of the compounds were effective in tallows, but none were outstandingly good in greases except when used with citric acid. By using citric acid as a

TABLE II

Results of Tests with Cottonseed, Peanut, and Corn Oils

Antioxidant[a]	Stability, Hrs. (70 meq. peroxide)			
	Cottonseed		Peanut	Corn
	Sample A	Sample B		
None	11	11	12	6
BHA	11	11	12	6
PG	27	53	48	11
BHT	11	11	25	11
R Group of Phenone				
Hydrogen	30	....	47	11
Methyl	28	....	48	15
Propyl	23	....	62	....
Isopropyl	....	23	55	....
Propenyl	....	18	....	....
Heptyl	....	20	52	....
Heptadecyl	....	17	45	....
Phenyl	41	....	52	....

[a] Concn. = 0.02% by wt.

TABLE III

Results of Tests with Mineral Oil and Paraffin Wax at 100°C. and 150°C.

Antioxidant		Stability, Hrs. (50 meq. peroxide)			
		Paraffin wax[a]			Mineral oil[b] 150°C.
Compound	Concn., % by wt.	Sample A	Sample B		
		150°C.	100°C.	150°C.	
None	......	1.7	54	1	0.5
BHA	0.02	18	....	....	....
PG	0.01	....	670	17	17
BHT	0.01	....	135	5	6
R Group of Phenone					
Methyl	0.01	29	475	15	17
Propyl	0.01	62	>1,000	29	21
Heptyl	0.01	....	....	26	20
Isopropyl	0.01	....	....	21	....
Nonyl	0.01	....	....	21	....
Undecyl	0.01	....	....	23	....
Phenyl	0.01	....	....	25	....

[a] Aristowax, amp. 130/134.

[b] Primol D, flash point 433°F.(223°C.).

TABLE IV

Results of Tests with Castor, Palm, Sperm, and Sesame Oils

Antioxidant[a]	Stability, Hrs. (70 meq. peroxide)			
	Castor	Palm	Sperm	Sesame
None	91	3.0	1.0	4.5
PG	210	3.5	1.0	16.0
BHT	97	4.0	2.0	5.5
BHA	95	4.0	3.5	4.5
R Group of Phenone				
Methyl	139	4.5	3.0	25.0
Propyl	117	4.0	2.5	12.5

[a] Concn. = 0.02% by wt.

TABLE V

Results of Tests with Tallows and Greases

Antioxidant	Stability, Hrs. (20 meq. peroxide)						
	Tallows			Greases			
				Choice white		Yellow	
	Fancy	Choice	Prime	A[a]	B[b]	A[a]	B[b]
None	28	10	23	0.5	1.0	2.0	30.0
BHA	170	>260	83	0.5	46.0	5.0	74.0
PG	89	>260	35	0.5	63.0	3.5	57.0
BHT	95	197	43	0.5	14.0	3.0	32.0
R Group of Phenone							
Methyl	100	>260	31	0.5	10.0	5.5	60.0
Propyl	96	>260	40	0.5	5.0	6.0	71.0

[a] 0.01%antioxidant.
[b] 0.01% antioxidant plus 0.05% citric acid.

metal scavenger, or synergist, the greases were stabilized satisfactorily.

Conclusions

On the basis of AOM tests run to date it appears that 2,4,5-trihydroxyphenones are quite potent antioxidants for many applications. Some of the lower members of the series, such as 2,4,5-trihydroxybutyrophenone, are outstandingly effective in lard, paraffin wax, mineral oil, and peanut oil. In other media, such as cottonseed oil, corn oil, castor oil, sesame oil, and tallows, they are less effective but still fairly active. In greases, palm oil, and sperm oil, they are only moderately effective. Over-all the 2,4,5-trihydroxyphenones compare quite favorably with current commercial products. It would appear that as more testing is done, more applications for these compounds may be found.

Subacute toxicity studies made with 2,4,5-trihydroxyacetophenone and 2,4,5-trihydroxybutyrophenone indicate that they are of a low order of toxicity. Long-term feeding tests on rats and dogs are underway with the butyrophenone, and after four months there are no apparent ill effects.

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Present Status of the Filtration-Extraction Process for Cottonseed[1]

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DEVELOPMENT of the various phases of the filtration-extraction process for cottonseed has been reported in previous papers (1, 2, 3, 4). Since the publication of these papers many important improvements or "process refinements" have been made, and some of these have been applied commercially in the first large-scale plant which was installed in Mississippi. Many of these improvements have been developed on a cooperative basis with the Mississippi Cottonseed Products Company [3] and the Lukenweld Division of Lukens Steel Company.[3]

Improvements or changes in the processing procedures and operating features, which depict the present status of the development of the process for cottonseed, involve the following phases of the process: conditioning of the meats or flakes prior to cooking; extraction temperature; effect of screw conveying both flakes and cooked meats; effect of an open-weave type filter medium; effect of recycling the initial concentrated miscella filtrate; effect of reforming cooked material; effect of cake thickness; and product quality. The following brief discussion of the filtration-extraction process is required better to understand the application of the process refinements.

Essential steps of the process are shown in Figure 1. Prepared cottonseed flakes are cooked in conventional four-to-six-high stack cookers, using lower temperatures and shorter cooking time than normally used for hydraulic cooking. Moisture content of the material is maintained throughout the cooking period at levels higher than for hydraulic cooking. The cooked material is "crisped" by evaporative cooling and by reducing the size of any large agglomerates formed during the cooking operation. The conditioned material is mixed with one of the miscella filtrates to form a slurry which is held for 25 to 40 min. The slurry is filtered, and the resulting cake countercurrently washed three times on a horizontal rotary vacuum filter. Total time on the filter is only 2 to 4 min. The solvent damp extracted meal (marc) is discharged to a conventional desolventizer for meal and solvent recovery. The concentrated miscella is pumped to the oil recovery system for separation of oil and solvent.

Conditioning of Meats or Flakes. Cottonseed used in the earlier pilot-plant runs had a normal average moisture content of 9 to 11%. The moisture of the resulting flakes was increased to the required 16 to 22% in the first or second ring of the cooker. In some of the recent runs the use of cottonseed having a moisture content of 6 to 8% showed the preferability of altering the method of adding the water. The drier meats from this seed tended to produce more fines when flaked to 0.008 to 0.010 in.; and the resulting flakes required the addition of more water to at-

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[1] Presented at the 45th annual meeting of the American Oil Chemists' Society, San Antonio, Tex., April 11-14, 1954.

[2] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

[3] The Agricultural Research Service has memorandum of understanding with this Company.