Components	Composition % (theoretical)	Types of organic compounds found	Percentage found
Coconut fatty acid isopropanol amide	0.8	Fatty acid alkylol amide	0.5
Na-palmitate	1.5	Fatty acid soap	1.5 (average number of C atoms per molecule 16.5)
Alkyl benzene sulphonate	1.9 (mol. wt.=342)	Alkyl benzene sulphonate	2.2 average mol. wt. 352
"TEEPOL" (sec. alkyl sulphates)	3.9	sec. alkyl sulphates	3.9
Builders: soda ash, Na-CMC, sodium pyrophosphate and sodium sulphate	4.9	....	....
Water	87.9	....	87 (determined according to Dean and Stark ASTM D 95-46)

termines not only the different types (alkyl sulphates, alkylaryl sulphonates, polyethene condensation products) but also the degree of branching of the alkyl sulphate, the chain length of non-ionics based on polyethene oxide and, for the anion-active compounds, the cation present. In addition, this method can be used for quantitative analyses.

Recently Sadtler (13) has also suggested analyzing synthetic detergents by means of infrared absorption.

Both Delsemme's and Sadtler's method may be valuable to those who have an apparatus for infrared spectrography. An advantage of these methods is that the spectra can be filed so that new products can immediately be compared with previous ones.

Acknowledgment

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Summary

An identification scheme for surface-active agents is given which enables these agents or their mixtures to be detected in commercial products. Use is made of the acid resistance of the various types, which make it possible to separate the different compounds step by step from the mixture.

An important feature of the method is that it can be used also for quantitative analyses by weighing the extraction residues obtained and determining their physical and chemical constants.

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Bisphenol Derivatives as Antioxidants for Carotene

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PHENOLIC antioxidants have been shown to possess marked ability to prolong the induction period of autoxidizing paraffin wax (4) and, under certain conditions, to protect carotene similarly (1). The success achieved in these tests with several compounds related to the bisphenols prompted a more extensive investigation of these materials and related compounds as antioxidants for carotene during storage. As far as possible, the compounds tested were chosen to permit observation of change in activity with systematic change in structure. The present report deals with the results of these stability tests.

Experimental

Stability of Oil Solution. The effectiveness of the antioxidants for the protection of carotene in oil solution was first determined. The substrate used for testing the antioxidants was a solution of purified crystalline carotene in a highly refined mineral oil.

The details of the stability test for carotene in oil solution have been published previously (6). It consists of a determination of the time required for breakdown of 20% of the carotene in the oil solution stored as a thin layer at 75°C. under specified conditions. As in previous work (1), the antioxidants were incorporated on an equivalent molecular basis rather than on a weight basis in order to facilitate the comparative evaluation of the antioxidants in the oil solution.

Stability in Alfalfa Meal. To test the effect of the antioxidants on the stability of carotene in alfalfa meal, a rapid, simple method of incorporating the antioxidant was employed. This involved spraying a Cellosolve (ethylene glycol monoethyl ether) solution of the antioxidant on a 200-g. sample of meal while it was tumbled at 12 r.p.m. in a rotary mixer. Samples were then stored for 2 weeks at 65°C. Results so obtained were comparable to about eight months' storage at 25°C. Details of this technique have been described fully in an earlier report (5).

Results

Bisphenol Derivatives in Mineral Oil Solution. Since all of the experiments reported here followed the same pattern, the quantitative data can be concisely reported in one table. Column 3 of Table 1 shows the comparative stabilizing effect of the various compounds tested for carotene in mineral oil solution. The Stability Value$_{20}$ of the control (*i.e.*, the time in hours for 20% loss of carotene in the absence of added antioxidants) was 2 hours.

Certain of the bisphenols were very effective antioxidants for carotene in oil solution, others were less effective, and some were completely ineffective. In attempting to correlate structure with antioxidant activity, a number of general observations may be made. It is immediately evident that the methylene group of the methylene bisphenols is of great importance. Effective antioxidants were obtained when the methylene bridge was either *ortho* or *para* to the hydroxyl groups on the rings; the most effective antioxidants were ortho-linked compounds. Whenever both hydrogens of methylene were substituted in the 2,2′-methylenebisphenols, there was a great loss of activity (compounds 3, 4, 42) although comparable substitution in the 4,4′-methylenebisphenols did not cause loss of activity (compounds 15 and 19).

Phenyl substitution of one of the hydrogens on the methylene group of a 2,2′-methylenebisphenol to form the triphenyl derivative (compound 14) decreased the antioxidant activity to one-third that of the parent compound. Replacement of only one of the hydrogens of the methylene group with a low molecular weight alkyl group such as ethyl, propyl, or isopropyl produced little influence on the antioxidant effectiveness of the parent compound (compounds 30, 31, 32, 33).

The addition of alkyl groups to the ring markedly influenced the efficiency of the compound as an antioxidant. Usually, the addition of a second alkyl group to the ring increased the antioxidant activity of the compound (compounds 21 and 39). The nature of the alkyl groups on the ring also had an important bearing on the effectiveness of the compound. Thus the 2,2′-methylenebisphenols which contained two methyl groups in the 4 and 6 positions on the ring were more effective than the corresponding compounds, which contained two-*t*-butyl groups in these positions (compounds 24 and 39). Furthermore the relative positions of the alkyl groups on the ring were very important. Thus 2,2′-methylenebis(6-*t*-butyl-4-methylphenol) was three times as effective as 2,2′-methylenebis(4-*t*-butyl-6-methylphenol). Addition of a third alkyl group to the ring of a dialkyl substituted bisphenol occasionally destroyed most of the antioxidant effectiveness of the compound (compounds 9 and 24).

In passing from the two-ring to the related three-ring compound, in some cases no increase and, in others, only a moderate increase in antioxidant efficiency was obtained (compounds 41, 42 and 21, 27). This does not agree with the observations of Morawetz (4), who found a great increase in antioxidant efficiency in passing from the two-ring to the related three-ring compound.

Previous work on the efficiency of antioxidants for stabilizing paraffin wax had indicated that halogens in the para position caused a substantial improvement in the antioxidant efficiency of the compound (4). This was not borne out in the present work with carotene, wherein it was found that substitution of chlorine in the ring destroyed almost all of the antioxidant effectiveness of the compound (compound 7).

A sulfur link between two phenolic nuclei contributed to antioxidant efficiency to approximately the same extent as did the methylene group (compounds 13, 21 and 38, 42). The disulfide group was much less effective whereas the sulfoxide link completely inactivated the phenol (compounds 5, 11, 38).

Bisphenol Derivatives for Carotene in Alfalfa Meal. Column 4 of Table 1 shows the comparative stabilizing effect of the various compounds tested for carotene in alfalfa meal. The compound, 2,2′-methylenebis(6-*t*-butyl-4-methylphenol), which was one of the most effective antioxidants for carotene in mineral oil solution was also the most active for carotene in alfalfa meal. Several related compounds, in which one of the hydrogens on the methylene groups was replaced with an alkyl group, were also quite effective (compounds 26 and 28). However the related 3-ring compound, 2,6-bis(3′-*t*-butyl-2′-hydroxy-5′-methylbenzyl)-4-methylphenol, was relatively less effective in alfalfa meal than it was in mineral oil solution. Furthermore a number of other compounds which were effective antioxidants for carotene in mineral oil solution had little or no activity for carotene in alfalfa meal (compounds 25, 29, 31, 32, 33, 35, 39). At least two antioxidants for carotene in mineral oil were pro-oxidants in alfalfa meal (compounds 9 and 17).

Discussion

In general, the results of this investigation have confirmed and extended the earlier observations that certain bisphenols were effective antioxidants for hydrocarbon systems. However it appears to be difficult to predict at this time whether an antioxidant will afford the same order of magnitude of protection in different media. Thus, although certain bisphenol derivatives were effective for stabilizing carotene in mineral oil solution as well as in alfalfa meal, others were much less effective in the meal than in the oil solution. This is in accordance with previous work from this laboratory which showed that certain derivatives of pyrogallol possessed marked activity for carotene in mineral oil but not in alfalfa meal (2).

There exists no easily apparent explanation for the diversity of results in the two systems. The solubility of an antioxidant in the media in which its activity is being observed is an important factor. Thus, in a heterogeneous mixture such as alfalfa meal, the antioxidant must be soluble in that phase which it is designed to protect, a fact which may account for the decreased activity of certain of the bisphenol derivatives toward carotene in alfalfa meal. Furthermore a complex media such as alfalfa meal contains a number of substances which are subject to autoxidation either selectively or concurrently, and the individual stability of each of these components is affected markedly by the presence of the others.

It has been shown that alfalfa meal is rich in naturally occurring antioxidants (3) so that the possibility of synergistic action of the added antioxidants with those naturally present must be taken into account. It has even been demonstrated in this study that under different conditions an antioxidant may not only lose all activity but may even appear to act as a pro-oxidant. It should therefore be emphasized that generalizations which may be made regarding nuclear substitution of bisphenols and their stabilizing effect apply only under the conditions studied. That

TABLE I

Efficiency of Antioxidants for Stabilizing Carotene in Mineral Oil Solution at 75°C. and in Alfalfa Meal at 65°C.

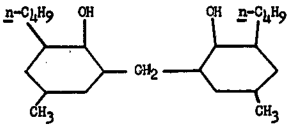
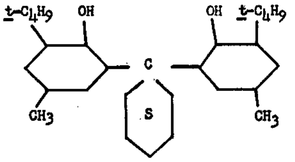
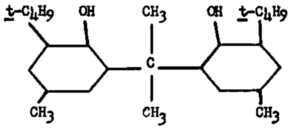
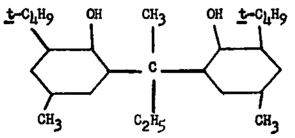
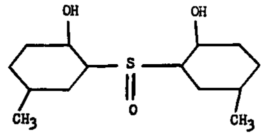
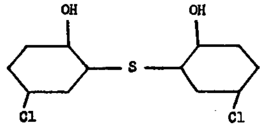
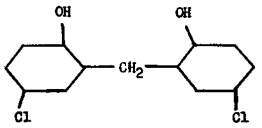
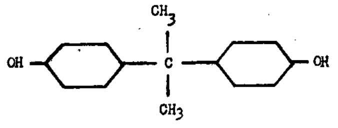
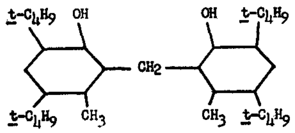
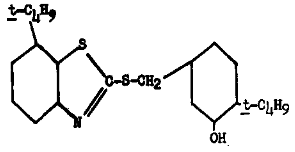
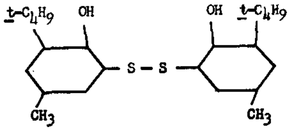
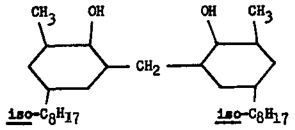
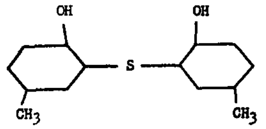
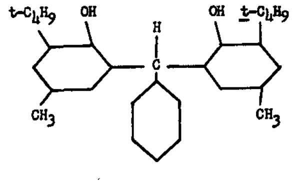
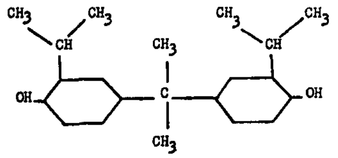
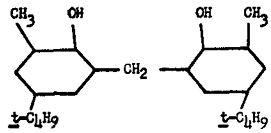
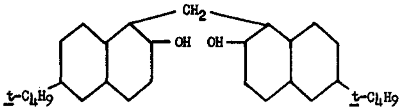
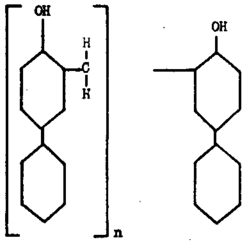
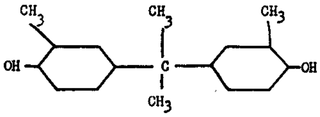
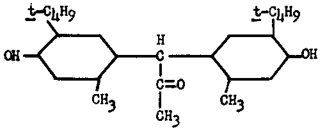
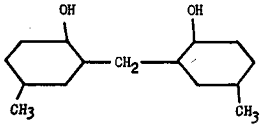
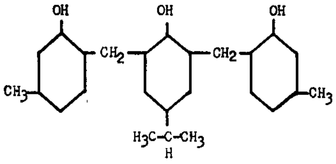
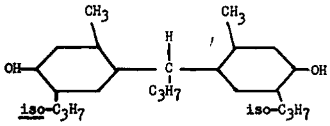
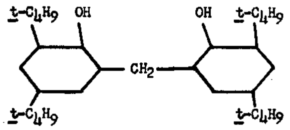
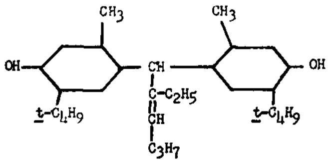
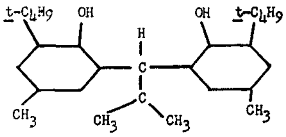
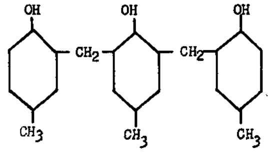
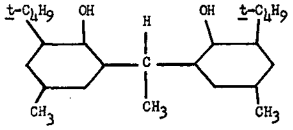
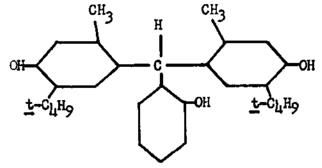
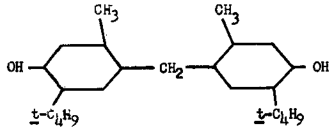
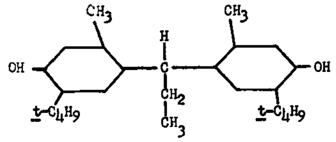
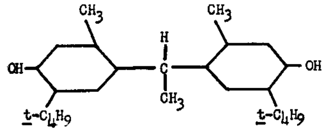
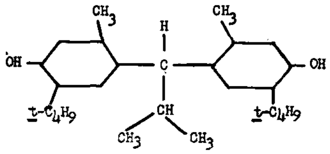
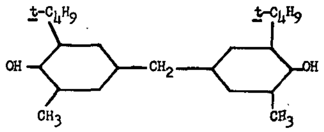
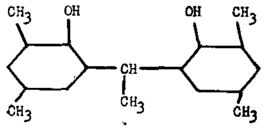
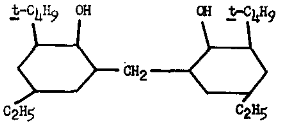
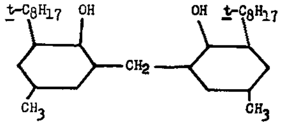
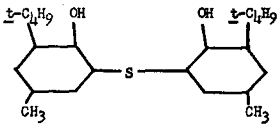
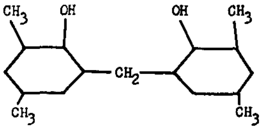
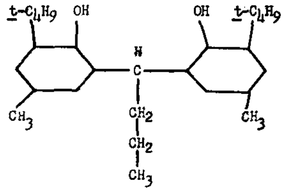
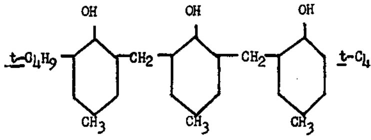
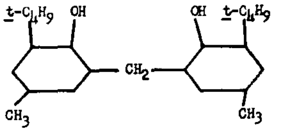
Compound Number	Structural Formula and Name	Effect on Carotene Stability	
		Oil[a]	Alfalfa Meal[b]
		Hours	*% Retained*
	Control	2	21
1	 2,2'-Methylenebis(6-*n*-butyl-4-methylphenol)	2	23
2	 2,2'-Cyclohexylidene-bis(6-*t*-butyl-4-methylphenol)	2	25
3	 2,2'-Isopropyl-idenebis(6-*t*-butyl-4-methylphenol)	2	25
4	 2,2'*sec.*-Butylidene-bis(6-*t*-butyl-4-methylphenol)	2	27
5	 2,2'-Dihydroxy-5,5'-dimethyldiphenyl-sulfone	2	23
6	 2,2'-Dihydroxy-5,5'-dichlorodiphenyl sulfide	3	24
7	 2,2'-Methylenebis (4-chlorophenol)	5	25
8	 4,4'-Isopropylidene diphenol	5	23
9	 2,2'-Methylenebis(4,6-di-*t*-butyl-3-methylphenol)	13	16
10	 7-*t*-Butyl-2-(4'-*t*-butyl-3'-hydroxybenzylmercapto) benzothiazole	16	28
11	 3,3'-Di-*t*-butyl-2,2'-dihydroxy-5,5'-dimethyl-phenyl disulfide	28	17
12	 2,2'-Methylenebis(4-*iso*-octyl-6-methylphenol)	47	25
13	 2,2'-Dihydroxy-5,5'-dimethyl-phenyl sulfide	48	24
14	 2,2'-Benzylidenebis (6-*t*-butyl-4-methylphenol)	52	26
15	 4,4'-Isopropylidenebis (2-*iso*propylphenol)	52	23
16	 2,2'-Methylenebis(4-t-butyl-6-methylphenol)	55	23

TABLE I (Continued)

Compound Number	Structural Formula and Name	Effect on Carotene Stability	
		Oil[a]	Alfalfa Meal[b]
		Hours	*% Retained*
17	 1,1'-Methylenebis(6-t-butyl-2-naphthol)	66	28
18	 Formaldehyde condensation product	66	24
19	 4,4'-Isopropylidenebis (2,2'-methylphenol)	68	23
20	 1,1-Bis(5-t-butyl-4-hydroxy-o-tolyl)-2-propanone	72	25
21	 2,2'-Methylenebis(4-methyl-phenol)	78	26
22	 2,6-Bis-(4'-methyl-2'-hydroxybenzyl)-4-t-butylphenol	34	26
23	 4,4'-Butylidenebis(3-methyl-6-t-butylphenol)	85	23
24	 2,2'-Methylenebis(4,6-di-t-butylphenol)	85	22
25	 4,4'-(2-ethyl-2-hexene-1-ylidene)bis (6-t-butyl-3-methylphenol)	100	23
26	 2,2'-Isobutylidenebis(6-t-butyl-4-methylphenol)	105	36
27	 2,6-Bis(5'-methyl-2'-hydroxy-benzyl)-4-methylphenol	105	26
28	 2,2'-Ethylidenebis(6-t-butyl-4-methylphenol)	115	35
29	 4,4'-o-Hydroxybenzylidene-bis(6-t-butyl-3-methylphenol)	115	23
30	 4,4'-Methylenebis(6-t-butyl-3-methylphenol)	120	29
31	 4,4'-Propylidenebis(6-t-butyl-3-methylphenol)	120	24
32	 4,4'-Ethylidenebis(6-t-butyl-3-methylphenol)	125	24

(TABLE I (Concluded)

Compound Number	Structural Formula and Name	Effect on Carotene Stability	
		Oil[a]	Alfalfa Meal[b]
		Hours	*% Retained*
33	 4,4'-Isobutylidenebis(6-t-butyl-3-methylphenol)	125	23
34	 4,4'-Methylenebis(6-t-butyl-2-methylphenol)	130	27
35	 2,2'-Ethylidenebis (4,6-dimethylphenol)	135	23
36	 2,2'-Methylenebis(6-t-butyl-4-ethylphenol)	140	32
37	 2,2'-Methylenebis (4-methyl-6-t-octylphenol)	140	32
38	 3,3'-Di-t-butyl-2,2'-dihydroxy-5,5'-dimethyl-phenyl sulfide	145	28
39	 2,2'-Methylenebis (4,6-dimethylphenol)	150	24
40	 2,2'-n-Butylidenebis(6-t-butyl-4-methylphenol)	150	31
41	 2,6-Bis(3'-t-butyl-2'-hydroxy-5'-methylbenzyl)-4-methylphenol	155	28
42	 2,2'-Methylenebis (6-t-butyl-4-methylphenol)	155	38

[a] Time in hours for 20% loss of carotene at 75°C.

[b] Percentage of initial carotene retained after two weeks' storage at 65° C.

the generalizations do not always hold is shown in this study as well as in comparison with other work. They may or may not apply to other systems.

Summary

Relative values for the carotene-stabilizing effects in mineral oil solutions of a number of bisphenol derivatives were determined. Certain relationships between molecular structure and antioxidant activity were observed. Alkyl substitutions in the reactive *ortho* and *para* positions were shown to improve the stabilizing efficiency of the compounds studied. High activities were obtained with bisphenols linked by methylene or sulfur. Several of the most effective antioxidants were found to be also effective for stabilizing carotene in alfalfa meal.

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