Acknowledgment

The authors wish to thank William U. Pokela, former chemical engineering senior, for his help in obtaining some of the data on rapeseed, sunflower, and tung oils reported in this paper.

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[Received September 25, 1956]

Antioxidant Activity of Phenols as Related to Effects of Substituent Groups[1]

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IN A RECENT COMPARISON of alkyl phenols as antioxidants for lard (1) it was observed that compounds having alkyl groups in the 2 position invariably showed some activity and that compounds with alkyl groups in both the 2 and 6 positions showed substantially higher activity. Similar observations were made with gasoline (2) and lubricating oils (3) as substrates. Since the alkyl groups provide some steric hindrance in the region of the phenolic group, the term "hindered phenols" has sometimes been applied to such compounds. However the thought that antioxidant activity is not attributable solely to a steric effect was suggested by the observation (1) that the comparatively large nitro-, bromo-, or iodo-groups imparted no such antioxidant activity to the phenol molecule.

The purpose of the present work was to learn more about the nature of substituents which can impart antioxidant activity to phenols, especially substituents in the 2 and 6 positions.

Experimental

Materials and Procedure. Few of the desired substituted phenols were available from commercial sources, and it was necessary therefore to synthesize most of them. The compounds, some of their properties, and their sources are indicated below. Melting points are not corrected.

2,6-di-*tert*-butyl-4-methylphenol, m.p. 69.5°C. (The Dow Chemical Company and Koppers Company Inc.). Recrystallized three times from aqueous ethanol.

2,6-di-bromo-4-methylphenol, m.p. 47–48°C. Prepared as reported by Ruderman (4).

2,6-di-iodo-4-methylphenol, m.p. 60.5°C. Iodination performed as reported by Datta and Prosad (5).

2,6-di-nitro-4-methylphenol, m.p. 78.5°C. Synthesized in manner of Monti and Cianetti (6).

2,6-di-benzoyl-4-methylphenol, m.p. 163–164°C. Procedures of Newman and Pinkus used in the synthesis (7, 8, 9).

2,6-di-methoxymethyl-4-methylphenol, b.p. 124°C., 1–2 mm. Hg. This phenol was prepared by acetolysis of 2,6-di-acetoxymethyl-4-methylphenylacetate as reported by Barthel (10). The 2,6-di-acetoxymethyl-4-methylphenylacetate (b.p. 180–187°C. approx. 1 mm. Hg.) was prepared from 2,6-di-(di-methylaminomethyl)-4-methylphenol as Bruson *et al.* (11) prepared 2,4,6-tri-acetoxymethylphenylacetate from 2,4,6-tri-(dimethylaminomethyl)phenol.

2,6-di-hydroxymethyl-4-methylphenol, m.p. 129°C. The synthesis was performed as reported by Granger (12).

2,6-di(dimethylaminomethyl)-4-methylphenol, b.p. 132–135°C., approx. 1 mm. Hg. Synthesized in the manner reported by Bruson and MacMullen for synthesis of 2,4,6-tri-(dimethylaminomethyl)phenol (11). The compound 4-methylphenol was used as starting material instead of phenol. Auwers (13) has shown that formaldehyde adds to the 2,6 positions of 4-methylphenol and that this reaction is involved in the synthesis.

2,6-di-methoxyphenol, m.p. 54.5–55.5°C. (Eastman Organic Chemicals).

2,6-di-methoxy-4-propylphenol. Synthesized as reported by Hunter and Hibbert (14), who used the procedure of Hurd and Fowler (15). Because of low yield the compound was purified by molecular distillation. A light yellow oil was obtained.

2,6-di-methoxy-4-propionylphenol, m.p. 106.5–108°C. Prepared as reported by Hunter and co-workers (16) in the manner of Coulthard *et al.* (17).

2,6-di-*tert*-butyl-4-methylphenylbenzoate, m.p. 168–169°C. Synthesized in the manner of Stillson *et al.* (18).

2,6-di-methoxyphenylpropionate, b.p. 127–133°C., approx. 1 mm. Hg. Esterification was performed as reported by Hunter *et al.* (16), who used the procedure developed by Miller and co-workers (19).

3,5,3′,5′-tetra-*tert*-butylstilbene-4,4′-quinone, m.p. 308°C. Synthesized in manner of Cook *et al.* (20).

1,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethane, m.p. 169°C. Prepared by reduction of preceding quinone in the manner of Yoke and co-workers (21). Purified by passing heptane solution through activated clay[3] and then crystallizing from aqueous acetone.

The substrate used was a bleached, deodorized, and dried lard which had very little, if any, antioxygenic material present. The method for its preparation and the method for testing antioxidant effectiveness have been reported previously along with an explanation of the term *catechol index* used to express relative effectiveness (4). All of the compounds were tested at a concentration of one micromole per gram of lard except Compound XIV, which was tested at 0.5 micromole per gram of lard. All of the compounds were either recrystallized or distilled until a constant antioxidant activity was obtained.

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Antioxidant Activity in Relation to Size of Ortho-Substituents. Among the known alkyl phenols 2,6-di-*tert*-butyl-4-methylphenol is the most active antioxidant for lard. However 2,4,6-tri-methylphenol is approximately half as active (1). To compare the effects of other sizeable non-alkyl groups in the 2 and 6 positions of 4-methylphenol, four other derivatives were prepared, each with 2,6 substituents of sufficient size to exert some steric hindrance on the reactivity of the phenolic group (Compounds II to V, Table I).

TABLE I

Comparative Antioxidant Activity of Compounds Added to Lard

Compound	Activity[a] (Catechol Units)	Standard Error[b]
I. 2,6-di-*tert*-butyl-4-methylphenol	2.35	0.09
II. 2,6-di-bromo-4-methylphenol	0.00	
III. 2,6-di-iodo-4-methylphenol	0.00	
IV. 2,6-di-nitro-4-methylphenol	0.00	
V. 2,6-di-benzoyl-4-methylphenol	0.00	
VI. 2,6-di-methoxymethyl-4-methylphenol	0.31	0.04
VII. 2,6-di-hydroxymethyl-4-methylphenol	0.34	0.01
VIII. 2,6-di-(dimethylaminomethyl)-4-methylphenol	0.12	0.03
IX. 2,6-di-methoxyphenol	0.53	0.01
X. 2,6-di-methoxy-4-propylphenol	0.70	0.02
XI. 2,6-di-methoxy-4-propionylphenol	0.33	0.03
XII. 2,6-di-*tert*-butyl-4-methylphenylbenzoate	0.00	
XIII. 2,6-di-methoxyphenylpropionate	0.00	
XIV. 1,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl) ethane	1.11	0.01
XV. 3,5,3',5'-tetra-*tert*-butylstilbene-4,4'-quinone	0.00	

[a] Active compounds tested five times; inactive three times.
[b] Standard error expressed in catechol units.

Radii reported (22) for these groups (in Angstroms) are $-CH_3$, 1.73; –I, 2.20; –Br, 2.11; $-NO_2$, 1.92. The results of antioxidant tests showed decisively that the halogen, nitro, and benzoyl, groups in the *ortho* position were incapable of imparting antioxidant activity to the phenolic group. The 4-methyl substituent did not exert sufficient influence to distinguish these compounds from their corresponding trinitro or tri-halogen derivatives (1). It was evident that other factors, besides simple steric hindrance, must be considered in attempting to understand the antioxidant activity of alkyl phenols, and attention was turned to electrostatic behavior of the different groups.

Electron-Attracting vs. Electron-Repelling Effects of Substituents. Arresting of the chain reaction in the autoxidation of a fat is presumed to require easy donation of a free hydrogen by the interposing antioxidant (23). However phenols tend toward hydrogen ionization, and this tendency is increased by electron-attracting substituents (K_a, phenol $= 1 \times 10^{-1}$; K_a, tri-nitrophenol $= 4.2 \times 10^{-1}$ (24). On the other hand, the tendency of a phenol to ionize is diminished by an *ortho*-methyl substituent [K_a 2,4-dinitrophenol $= 1 \times 10^{-4}$ (25); K_a, 2,4-dinitro-6-methylphenol $= 4.5 \times 10^{-5}$ (26)]. A similar influence is also shown by other alkyl groups. Coggeshall and Glessner (27) have reported that 2,6-di-*tertiary*-butyl-4-methylphenol does not ionize completely in 5-M sodium hydroxide solution.

It was of interest therefore to compare the antioxidant effectiveness of phenols which have electron-repelling substituents other than alkyls in the 2 and 6 positions. For this purpose di-methoxymethyl, di-hydroxymethyl, and di-(dimethylaminomethyl) derivatives were prepared (Compounds VI, VII, VIII, Table I). All showed activity as antioxidants; however none was so active as the corresponding 2,6-dimethyl compound (1). Evidently antioxidant activity is not proportional to the electron-repelling force of the 2,6 substituents.

Activity was shown also by 2,6-di-methoxyphenol (Compound IX) but the potency was about one-fifth that of the desmethyl analog, pyrogallol (28). A similar relationship had been noted previously with these compounds in mineral oil by Bickoff *et al.* (30). Ability of pyrogallol to form an *ortho*-quinone complicates any interpretation of this difference in terms of electron repulsion. However it was observed that pyrogallol was three times as active as the dihydroxy benzene, catechol (28); perhaps this reflects the presence of another strong electron-repelling *ortho* group (hydroxy) in the pyrogallol molecule. Activity of the di-methoxy compound was enhanced by introduction of a propyl group in the 4-position but was reduced by nearly half when a 4-propionyl group was present (Compounds X, XI, Table 1). Since propyl gallate is about half as active as pyrogallol (28), it is suggested that electron-attracting carbonyl groups in the 4-position may detract from activity of 2,6 substituted phenolic antioxidants. Wasson and Smith (3) found that the most effective tri-alkylphenols contained *normal* alkyl substituents in the 4-position.

Importance of the Free Phenolic Group. It has been known for some time that di-or polyphenolic antioxidants lose their activity when derivatized (29, 30). However the *ortho*-substituted phenols constitute a specialized group of antioxidants in that the substituents impart activity to an otherwise inactive nucleus. Cook (31) has called attention to a reactivity of the 4-alkyl substituent in *ortho*-di-*tert*-butylphenols, which is evidenced in their ease of dimerization, and has commented that the apparent easy formation of substituted benzyl radicals for 2,6-di-*tert*-butyl-4-methylphenol introduces the possibility of chain reaction stoppage by the hydrogen so released. A question may then be raised as to whether in this type of compound a free phenolic group is essential for antioxidant activity; to answer this question benzoyl and propionyl esters (Compounds XII and XIII) of two of the active compounds were prepared. Neither ester showed any activity in lard. It appears likely therefore that the hydrogen atom involved in chain-stoppage is furnished by the phenolic group from mono- as well as polyphenolic antioxidants. In a recent article Cook has concluded that the first step in the antioxidant action of monophenolic antioxidants may be the removal of a hydrogen from the phenolic hydroxyl (20).

Cook (31) has reported that when 2,6-di-*tertiary*-butyl-4-methylphenol is heated in petroleum oil, a dimer is formed, and this oxidizes further to the corresponding stilbene-quinone (Compounds XIV and XV, Table I). He has offered this sequence as evidence of a proposed mechanism of antioxidant participation in arresting the chain reaction in autoxidation. It was of interest therefore to observe changes which might occur when the alkyl phenol was heated in lard in the presence of air. The procedure used was as follows: six 10-g. samples of bleached, deodorized, and dried lard were weighed into 100-ml. beakers. To one of the beakers were added 5 ml. of purified ethanol (distilled over KOH), containing 0.05 g. of 2,6-di-*tert*-butyl-4-methylphenol; to another, 5 ml. of ethanol containing 0.5 g. of the phenol; to a third, 5 ml. of ethanol containing 2.0 g. of the phenol; and to two of the remaining beakers

5 ml. of the ethanol alone. To the final beaker 5 ml. of ethanol containing 1.0 g. of the phenol were added, and then 3 g. of copper pellets. The ethanol was then removed from all six samples on a steam bath, and the samples were placed in an air oven at 100° ± 1.5°C. for six weeks. All developed a reddish color during this period. After six weeks' time 5 g. of each of the samples were dissolved in 25 ml. of commercial heptane, which had been purified by distillation over KOH after percolation through silica gel. To one of the two samples consisting of lard alone were added 2.5×10^{-3} g. of the stilbene quinone (Compound XV) in heptane, and then all of the samples were diluted to 100 ml. with heptane. Spectral absorption was recorded from 410 to 470 millimicrons with matched 1-cm. Pyrex cells in a Beckman Model DU spectrophotometer.

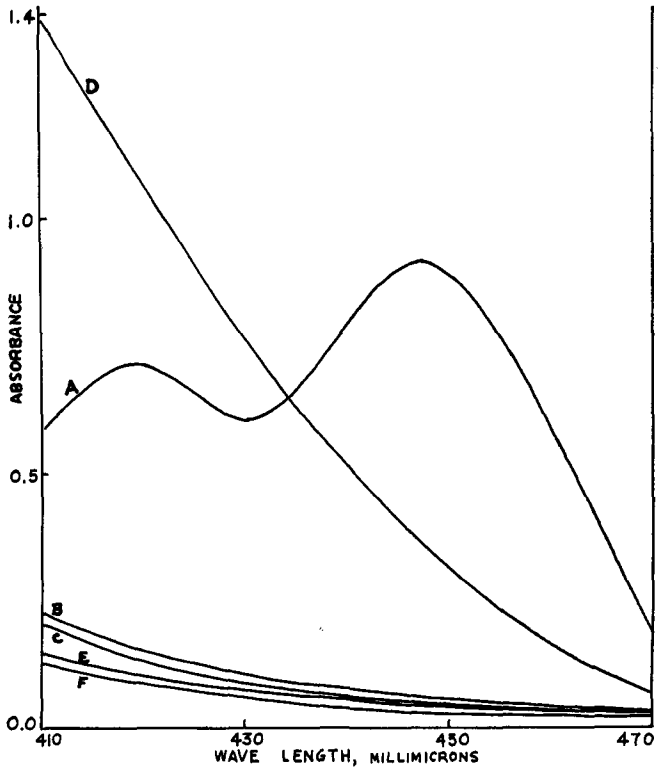

FIG. 1. Spectral absorption of lard solutions.
A. Autoxidized lard (six weeks at 100°C.) plus 0.025%, 3,5,3′,5′-tetra-*tert*-butylstilbene-4,4′-quinone.
B. Autoxidized lard (six weeks at 100°C.).
C. Lard plus 0.5% 2,6-di-*tert*-butyl-4-methylphenol after mixture had oxidized for six weeks at 100°C.
D. Lard plus 1% 2,6-di-*tert*-butyl-4-methylphenol after autoxidation with copper (six weeks at 100°C.).
E. Lard plus 5% 2,6-di-*tert*-butyl-4-methylphenol after autoxidation without copper (six weeks at 100°C.).
F. Lard plus 20% 2,6-di-*tert*-butyl-4-methylphenol after autoxidation without copper (six weeks at 100°C.).

Curves A and B in Figure 1 showed that compound XV, when added to oxidized lard, exhibited characteristic absorption maxima in the region of 410 to 470 millimicrons while oxidized lard alone exhibited almost complete transmission through this region. This property was used to determine whether compound XV was produced in oxidized lard when compound I had been added prior to the oxidation. Curves C, E, and F proved that, regardless of the concentration of compound I originally present in lard, there was no measurable amount of compound XV present at the end of a six-week oxidation period. Curve D showed that the concurrent presence of a metallic catalyst did not result in the appearance of compound XV even though there was an indication that a high degree of oxidation of the lard had occurred. To ascertain whether the stilbene quinone might be present in the early stages of oxidation, three 25-g. samples of lard were weighed into three 50-ml. beakers and treated as follows: to No. 1 were added five ml. of ethanol containing 0.25 g. of 2,6-di-*tert*-butyl-4-methylphenol; to No. 2, five ml. of ethanol containing 0.25 g. of the stilbene quinone; and to No. 3, five ml. of the ethanol as a control. After removal of the ethanol on a steam bath the samples were placed in an oven at 100°C. Beginning on the second day 0.03- to 0.10-g. portions of each sample were removed periodically and diluted to 25 ml. with purified heptane. The absorbance of each was determined. No absorption attributable to quinone was observed in the portions from beaker No. 1 even during the early stages of oxidation; the added quinone in beaker No. 2 fell off quite rapidly and in two weeks had disappeared. Therefore it is evident that the reactions of compound XIV in lard are different from those in mineral oil; apparently in lard the compound is oxidized beyond the quinone stage.

Summary

Antioxidant activity in lard was exhibited by all phenols which had electron-repelling groups in the 2 and 6 positions. No activity was shown by those which had electron-attracting groups in these positions.

The mechanism of antioxidant action of alkyl phenols in lard does not appear to differ from that of di- or polyphenols. A free phenolic group was shown to be essential, and spectral absorption studies after autoxidation did not reveal any evidence for a dimer of the alkyl phenol. The dimer, stilbene quinone, reported isolated from oxidized petroleum oil, disappeared quite rapidly when added to oxidizing lard.

Acknowledgment

The authors wish to express their appreciation to Swift and Company, Chicago, Ill., for a grant in support of this work and for their generous supplies of bleached, deodorized lard. Liberal amounts of some of the phenols used in this study were also kindly furnished by the Dow Chemical Company and by Koppers Company Inc.

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[Received November 13, 1956]

Chemical Changes Which Take Place in an Edible Oil During Thermal Oxidation[1,2]

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PREVIOUS STUDIES on the nature of the chemical changes which take place in fats and oils and fatty acid esters during oxidation have usually been carried out at temperatures ranging from 0 to 100°C. (2, 5, 11). At these temperatures it has been shown that the peroxide value increased rapidly and large amounts of carbonyl compounds were formed. Polymeric material was produced, possibly through carbon to oxygen linkages (2).

Studies at higher temperatures (250°–300°C.) have generally been carried out in inert atmospheres and have shown that molecular weight and viscosity increase, resulting partially from the formation of polymers through the Diels-Alder type of condensations (3, 10, 13). Cyclic monomers were also believed to be produced under these conditions (12).

To date the combined effects of oxidation and thermal treatment have not been studied extensively. Although changes in acid value and iodine value have been reported, the effect of specific conditions, *e.g.*, temperature, aeration, and the length of the heating period on the nature of these changes has not been studied. The present study was designed to provide information on the effect of thermal treatment at a temperature of 200°C. when aeration and the time of thermal treatment were varied.

Methods

The thermal oxidation (aeration) was carried out in a five-liter, stainless steel beaker. The apparatus was similar to that used in our previous studies (5). The sample of oil was heated to 200°C., and the aeration was begun when the oil had reached the desired temperature.

The saponification, free fatty acid, and Wijs iodine values were determined by official methods (9). The peroxide determination was made according to the modification of Wheeler (14), and the mixed fatty composition was determined by the spectrophotometric method of Brice *et al.* (1). Carbonyl values were obtained by using a modification of the procedure suggested by Lappin and Clark (7). The solvent used was a 1:1 mixture of carbonyl-free methanol and ethanol, and decyl aldehyde was used as standard. The carbonyl value was expressed as milliequivalents per kilo of oil.

A standard set of conditions was selected for the initial experiment. Further experiments were then carried out, using variations in the time, temperature, and amount of aeration from these following four standard conditions: a) sample weight, 1,500 g. of commercially refined corn oil; b) temperature, 200° C. ± 10°; c) time of treatment, 24 hrs.; and d) rate of aeration, 150 ml. of air per kilo of oil per minute.

Results

The iodine value of corn oil decreased at a relatively constant rate during the first 10 to 12 hours of treatment under the standardized conditions (Figure 1). As the iodine value decreased, a corresponding decrease was observed in the amount of nonconjugated dienoic acids present. A marked increase in the percentage of conjugated diene in the oil indicated that at least part of the dienoic acid was conjugated before further reactions took place. A careful comparison of the decreases in iodine value and linoleic acid content indicated that the linoleic acid decreased more rapidly than the total unsaturation. The percentage of monounsaturated fatty acids in the corn oil increased from 26.1% in the fresh corn oil to 39.9% in oil which had been heated for 24 hrs. This suggested that only one of the double bonds of linoleic was attacked or utilized during the initial period.

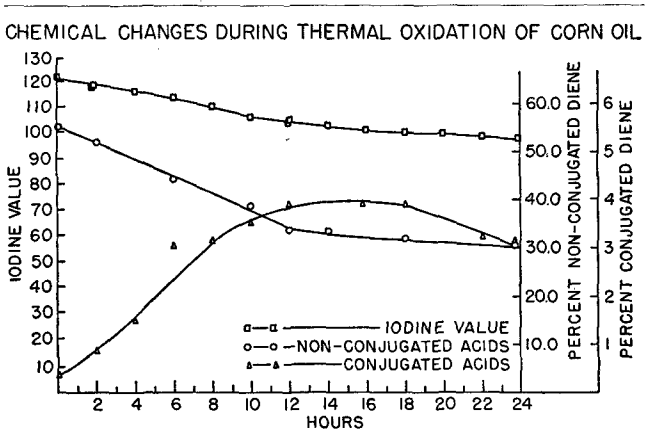

FIG. 1. Chemical changes during thermal oxidation of corn oil.

The total oxygen content of the oil increased during the first 10 to 12 hrs. and then began to decrease

[1] This study was supported in part by funds from the American Dairy Association and Armour and Company.
[2] Presented at fall meeting, American Oil Chemists' Society, Sept. 24–26, 1956, Chicago, Ill.