237°C., $[\alpha]_D = -9.5°$ (2% soln. in 95% EtOH). This quantity of tetrahydroresin acids represents 5% of the total acid content of disproportionated rosin.

Peak 3, p.e.v. = 650. Fractions 56–80 were combined. The acid was recovered by precipitation of the cyclohexylamine salt from the isooctane solution. The salt was converted to the free acid in ether solution with dilute HCl. After evaporation of the ether the acid crystallized upon wetting with ethanol. The dehydroabietic acid obtained had a m.p. = 170–172°C., $[\alpha]_D = +61.7°$ (2% soln. in 95% EtOH), and showed maximum characteristic ultraviolet absorption at 276 mμ, $a = 2.37$ and 268 mμ, $a = 2.15$.

Peak 4; p.e.v. = 1040. The acids in this peak were not isolated since they represented only 2% of the acidic portion of the disproportionated product. The position of the peak effluent volume indicates that they are more polar than the characterized resin acids.

Detection of Diene-Resin Acids in Disproportionated Rosin. This chromatographic method is satisfactory for the detection of as little as 1% of the diene-resin acids in a completely disproportionated product since the peak effluent volumes of these acids range from 290 to 510 (Figure 1, curve 1). It is of interest to note that on disproportionation with 5% palladium on carbon catalyst all of the diene unsaturated acids in the rosin were converted to their di-, tetra, and dehydro derivatives. This includes the pimaric as well as the abietic-type acids.

Chromatographic Investigation of Commercially Disproportionated Rosins. The chromatographic curves of three samples of commercially disproportionated rosin are shown in Figure 2. The variations in the extent of disproportionation is apparent from examination of these chromatograms. No attempt was made to isolate the various components of these samples. The degree of separation obtained shows that the method is applicable to all of the products examined and that the percentage of dehydroabietic acid in the acidic portion of the rosin can be determined. On that basis Table I shows the percentages of the various acids or groups of acids divided into three categories: a) acids eluted prior to dehydroabietic acid, b) dehydroabietic acid, c) acids eluted after dehydroabietic acid.

TABLE I

Distribution of Acids in Commercially Disproportionated Rosins

Sample	Acids eluted prior to dehydroabietic acid	Dehydroabietic acid	Acids eluted after dehydroabietic acid
1	26	51	23
2	30	59	11
3	40	58	0

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The Antioxidant Properties of Some 6-Hydroxychromans And 5-Hydroxycoumarans

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H. S. OLCOTT AND O. H. EMERSON (1) related the antioxigenic properties of the unsaponifiable matter of wheat germ oil to its tocopherol content. They noted the great difference in the antioxidant power of β and α tocopherols which differ chemically only by the reversal of the methyl group and the unsubstituted position on both sides of the phenolic hydroxyl. C. Golumbic (2) investigated the relation between antioxidant activity and constitution in the case of hydroquinone and 6-hydroxychroman, the basic ring system common to all tocopherols. He compared the effect that C-methylation of the aromatic ring had on the antioxidant properties of hydroquinone and 6-hydroxychroman in lard. He concluded that methylation is detrimental, especially in the case of hydroquinone, which becomes practically inactive in lard. The 6-hydroxychroman still retains some activity even when completely methylated in the aromatic ring. In 1943 R. H. Rosenwald and J. A. Chenicek (3) showed that the introduction of a tert-butyl group ortho to the free hydroxyl into the monomethyl ether of hydroquinone greatly increased the inhibitor activity over that of the parent compound. The introduction of two tert-butyl groups in the 2 and 5 positions does not improve the low inhibitor potency of methoxyphenol. The 6-hydroxychroman may be considered structurally related to a monoalkylated alkoxyphenol, in which the introduction of a tert-butyl group should depress the inhibitor activity. Therefore the effect of the introduction of a tert-butyl group into a 6-hydroxychroman could not be predicted and could only be determined empirically. The 5-hydroxycoumaran was investigated also because of its close chemical relation.

The chromans and coumarans selected were the 2,2-dimethyl-6-hydroxychroman and the 2,2-dimethyl-5-hydroxycoumaran. The two compounds were prepared as suggested by C. D. Hurd and W. A. Hoff-

man (4), who showed that this 6-hydroxychroman can easily be prepared free of the isomeric coumaran and the 2,2-dimethyl-5-hydroxycoumaran equally free of the isomeric chroman. Both compounds were readily alkylated in 85% H_3PO_4 at 70–80° with tert-butyl alcohol, yielding 6-tert-butyl-2,2-dimethyl-5-hydroxycoumaran and 7-tert-butyl-2,2-dimethyl-6-hydroxychroman (5).

The stability times in a lard having an induction period of 5 hrs. were determined according to the modified Active Oxygen Method of R. W. Riemenschneider, J. Juros, and R. M. Speck (6). Results in Table I show that the 2,2-dimethyl-5-hydroxycoumarans differ from the corresponding 2,2-dimethyl-6-hydroxychromans in the following respects: they are more effective; they reach their maximum efficiency at lower concentrations; and they respond more to synergists.

TABLE I

Effectiveness of 5-Hydroxycoumarans and 6-Hydroxychromans in Lard

Uninhibited Lard = 5 hrs. Stability Time

Antioxidant, Wt. %	A.O.M. Time, hrs.		
	0.005%	0.01%	0.02%
2,2-dimethyl-6-hydroxychroman	16	22	26
2,2-dimethyl-7-tert-butyl-6-hydroxychroman	19	26	33
2,2-dimethyl-7-tert-butyl-6-hydroxychroman + 0.0001% 85% Phosphoric acid	23	26	31
2,2-dimethyl-7-tert-butyl-6-hydroxychroman + 0.001% Citric acid	21	26	32
2,2-dimethyl-5-hydroxycoumaran	26	26	26
2,2-dimethyl-6-tert-butyl-5-hydroxycoumaran	47	49	41
2,2-dimethyl-6-tert-butyl-5-hydroxycoumaran + 0.0001% 85% Phosphoric acid	52	54	41
2,2-dimethyl-6-tert-butyl-5-hydroxycoumaran + 0.001% Citric acid	53	60	47

In both classes of compounds the introduction of a tert-butyl group ortho to the phenolic hydroxyl increases the potency. This effect is not very strong with the 6-hydroxychroman while it practically doubles the activity of the 5-hydroxycoumaran on a weight basis. The effect is even greater, if calculated on a molar basis, because the introduction of the tert-butyl group decreases the molar concentration of the phenolic hydroxyl in the 2,2-dimethyl-5-hydroxycoumaran by 25%.

Table II shows the effects the different chromans and coumarans have on the induction period of a thermally cracked gasoline. This induction period was determined according to U.O.P. Method H-6-40 (7). The differences in the alkylated 5-hydroxycoumaran and the 6-hydroxychroman in this gasoline are not as marked as in lard. Both are effective inhibitors at concentrations of 0.006% and over while they do not perform quite as well at lower concentrations. Washing of the gasoline with a methanolic potassium hydroxide prior to inhibition did not yield any clear-cut results. The purpose of this procedure is to remove any naturally occurring phenols.

The 5-hydroxycoumaran is a better inhibitor than the 6-hydroxychroman, both in lard and gasoline. When tertiary butylated, its activity is approximately doubled both in lard and gasoline at low concentrations, at higher concentrations less. The behavior of the 6-hydroxychromans is quite different. In lard, alkylation does not add much potency. As a matter of fact, the inhibitor potency of both chromans is only fair but, in gasoline, alkylation triples the effectiveness of the 6-hydroxychroman at the low concentration. Table II shows that 2,2-dimethyl chroman lengthens the induction period by 60 min. and the 2,2-dimethyl-7-tert-butyl-6-hydroxychroman by 175 min., a three-fold increase. However the absolute activity of the tert-butylated 6-hydroxychroman is not better than that of the corresponding coumaran.

One can explain why the 7-tert-butyl-6-hydroxychroman and the 6-tert-butyl-5-hydroxycoumaran are better inhibitors than the 2,5-di-tert-butyl-4-methoxyphenol, since the latter is a relatively poor inhibitor (11), but it is not possible to explain in the present state of knowledge why the 5-hydroxycoumarans are better inhibitors than the 6-hydroxychromans in lard but are substantially the same in gasoline.

THE MAIN ACTION all inhibitors have in common is the transfer of a hydrogen atom from the inhibitor to a chain-propagating free radical like the alkyl peroxy free radical: ROH + ROO° ⟶ RO° + ROOH; where ROH = Inhibitor (8). This is chain termination. The first task of an antioxidant is to supply this hydrogen atom, but not every compound which is able to do so is a good antioxidant. Many phenols can supply hydrogen atoms but are not good antioxidants. The crucial characteristics and properties of a good antioxidant rest with the activity of the remaining free radical or semiquinone. If the remaining semiquinone shows sufficiently high reactivity, it could become a chain starter for autoxidation by removing a hydrogen atom from a molecule of the substrate. This would therefore nullify its first chain-stopping action when a hydrogen atom was transferred to peroxy-free radical, or, in other words, it would act as a chain-transfer agent.

The necessary decrease of the reactivity of the semiquinone is supplied by the resonance energy, which is really a negative energy factor. Its presence connotes a lower energy content, thereby creating greater stability. It is not surprising that most commercial inhibitors operating at ambient temperatures consist of aromatic systems carrying hydroxyl and/or

TABLE II

Effectiveness of 5-Hydroxycoumarans and 6-Hydroxychromans in Cracked Gasoline

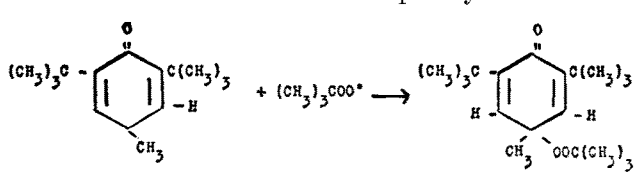
Antioxidant, Wt. %	Induction Periods in Minutes at 100 lbs. O_2 and 210°F. in a Pennsylvania Thermally Cracked Gasoline of 100 min. Induction Period					
	0.003%		0.006%		0.01%	
	Treated[a]	Not treated	Treated	Not treated	Treated	Not treated
2,2-dimethhyl-6-hydroxychroman	160	160	230	225	275	285
2,2-dimethyl-7-tert-butyl-6-hydroxychroman	275	275	380	410	570	510
2,2-dimethyl-5-hydroxycoumaran	190	210	290	290	355	390
2,2-dimethyl-6-tert-butyl-5-hydroxycoumaran	290	285	440	385	535	495

[a] The treatment consisted of washing the gasoline three times with 10 vol. % of a solution containing 50% methanol, 25% H_2O, 25% KOH. The induction period values are the averages of four determinations.

amino groups. Aromatics can supply greater amounts of resonance energy than any other conjugated system. The first free radical found was the triphenyl methyl radical stabilized by the resonance energy of three phenyl groups. The resonance energy of this system has been calculated by L. Pauling and G. W. Wheland (9).

The stability of the triphenyl methyl radical rests on the number of phenyl groups which deactivate the methyl radical by their resonance energy. Many of the effective phenolic antioxidants carry an alkoxy group in the para position to the free phenolic group like methoxy in butylated hydroxyanisole and the heterocyclic part of the coumarans and chromans. These groups have an electron releasing effect on the benzene system, a +M effect, according to C. K. Ingold (10), and thereby decrease the electron deficiency on the site of the odd electron. In addition, the resonance from the 4-site structures of the odd electron diminishes the reactivity of the semiquinone even more. Another corollary of resonance is the shortening of bonds; anything which tends to counteract this will diminish the resonance energy. That is why planarity of the molecule enhances the resonance energy and anything that will strain the bonds of groups attached to the aromatic ring will decrease the resonance energy.

Although 2-tert-butyl-5-methyl-4-methoxyphenol is not as effective as 2-tert-butyl-4-methoxyphenol (BHA), it is nevertheless much better than 2,5-di-tert-butyl-4-methoxyphenol (11). The 5-tert-butyl group acts sterically on the 4-methoxy group, forcing it out of the plane of the aromatic ring, setting up a strain, and diminishing the resonance energy thereby. The effect of the 5-methyl group is much smaller, therefore the inhibitor potency of BHA is much less disturbed. The reactivity of the semiquinone is decreased further by adding a tert-butyl group ortho to the phenolic oxygen carrying the odd electron. Steric hindrance thus created prohibits the approach of any save the smallest atoms, like the hydrogen atom. If the last-mentioned contingency occurs, the inhibitor is reconstituted and could act again. As to the further actions of the semiquinone, T. W. Campbell and G. M. Coppinger (12) have shown for the 2,6-di-tert-butyl-p-cresol that its mesomeric cyclohexadienone free radical can combine with a peroxy free radical:



It is not known whether the semiquinones formed from BHA and the hydroxy-tert-butyl chromans and coumarans will react in the above indicated manner with high reactive radicals and thereby stop another chain reaction. R. H. Rosenwald and J. A. Chenicek (11) suggest dimerization in the ortho position for BHA. As to the fate of the chromans and coumarans, C. Golumbic (13) recognized tocoquinones as the immediate oxidation products of tocopherols in fats. Orthoquinones, namely the chroman-5,6-quinones, were also found but only in autoxidized vegetable fat, never in animal fat.

In view of these experiments in which the oxidation of the antioxidant proceeds by different pathways, even in so closely related substrates as animal and vegetable fats, it is too early to correlate the results C. E. Boozer and G. S. Hammond (14) obtained concerning the fate of the inhibitor when working in simplified systems.

Summary

The inhibitor activity of some 6-hydroxychromans and 5-hydroxycoumarans in gasoline and lard was investigated. The coumarans are the more effective in both substrates. Introduction of a tertiary butyl group ortho to the hydroxyl group increases the activity of 2,2-dimethyl-5-hydroxycoumaran in both substrates, but the activity of the 2,2-dimethyl-6-hydroxychromans is increased only in gasoline.

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Improved Method for Determining Gossypol in Crude Cottonseed Oils

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THE USE OF newer cottonseed processing methods has resulted in the commercial production of crude oils in which the gossypol content can vary from as little as 0.1 to as much as 0.7% (5, 11). With increased use of these methods more consideration may be given to the amount of gossypol in crude oils, particularly since evidence has been presented (2, 5, 11, 12) to indicate that this pigment and its derivatives are primarily responsible for increases in refined and bleached oil color resulting from the storage of some crude oils at elevated temperatures.

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