

TABLE IX
 Reflectance and Color Changes in Clear and Pigmented Films as Determined by the Color Difference Meter

Polymer	Pigmentation	Unexposed			Covered 14 Days ^a			Exposed to UV ^b 14 Days		
		Rd	a	b	Rd	a	b	Rd	a	b
		Re ^c	Red	Yellow	Ref	Red	Yellow	Ref	Red	Yellow
DCP(3)CL(1).....	Clear	50	6	36	55	2	33	65	-2	25
	Pigmented	70	0.5	19	71	-1	17	79	-3	8
CP(1.4)CS(1).....	Clear	15	22	28	20	20	17	60	0	33
	Pigmented	40	7	22	45	6	20	70	0	15
CP(1.5)CL(1).....	Clear	19	21	30	25	17	30	60	1	31
	Pigmented	43	7	22	45	6	20	70	0	14

^a This section of the panel covered with aluminum foil during the exposure to UV.

^b General Electric type S-1 sun lamp was placed 12 in from panel surface. Panels were placed on a rotating table and a fresh lamp was used after every 72 hr of operation.

^c Ref = Reflectance.

known to be compatible with vinyl ethers. Blends were made at ratios of 1:9 and 9:1 by volume. A number of these blends resulted in clear, haze-free solutions. However, hydrogenated rosin was the only resin to produce clear, wrinkle- and tack-free films. This lack of compatibility is somewhat surprising. The compatibility with recently prepared styrenated vinyl ether polymers varies but is improved, and appears to be associated with composition of the vinyl ether polymer, as well as with the extent of styrenation. Research is now being conducted on the styrenation reaction and on properties of the polymers from it (7,11).

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Methods for the Determination of Cyclopropenoid Fatty Acids. I. Aqueous Hydrochloric Acid Method¹

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Abstract

An analytical method is described for the estimation of long-chain cyclopropenoid fatty acid derivatives. It is based upon the quantitative addition of a molecule of hydrogen chloride at the cyclopropene ring when the sample is shaken with concentrated hydrochloric acid. The cyclopropenoid content can be calculated, as sterculeic acid, from the increase in chlorine content. Epoxy compounds and hydroperoxides interfere and must be removed by one of the accepted pretreatment methods.

Introduction

THIS IS ONE of a series of reports resulting from a search for improved methods for the quantitative determination of long-chain cyclopropenoid fatty acids. These acids, which respond to the Halphen test,



contain the group $\text{—C}=\text{C—}$ near the middle of the

carbon chain. In sterculeic acid, a 19-carbon acid which is the major fatty acid constituent of *Sterculia foetida* seed oil, this group is in the 9-10 position. The cyclopropenoid acid which is present as a minor constituent in cottonseed oil fatty acids has been reported to be predominantly malvalic acid, the corresponding 18-carbon acid with the cyclopropene group in the 8-9 position (1,2,3).

A number of methods of analysis have been suggested. Deutschman and Klaus (4), and Shenstone and Vickery (3), used modifications of the Halphen color test. Gas chromatographic analysis was applied by Miwa et al. (5) to the methyl esters, and by Smith, Wilson, and coworkers (6,7) to the methyl esters after dihydrogenation of the cyclopropene ring.

Another method, developed by Smith, Wilson, et al. (6,7,8), involves titration with a standard solution of hydrogen bromide in glacial acetic acid (Durbetaki reagent) after first destroying the epoxy acids by lithium aluminum hydride reduction or cold acetolysis. The number of moles of hydrogen bromide added equals the number of moles of cyclopropenoid moiety present. The titration is time-consuming and unsatis-

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factory because of the extreme slowness of the reaction involved and the difficult end point. A modification of this hydrogen bromide titration method, to be described in a separate publication (9), overcomes these difficulties by titrating epoxy acids, if present, below room temperature, and the cyclopropenoid derivatives at an elevated temperature.

Kühn and Bengen reported (10) in 1906 that cottonseed oil no longer gives the Halphen test after treatment with aqueous hydrochloric acid (sp gr 1.18–1.19). This was confirmed for cottonseed oil and also for *Sterculia foetida* seed oil. It was also found that the infrared absorption bands at 5.35 and 9.91 μ , associated with the cyclopropene group in *Sterculia foetida* oil, disappeared as a result of the treatment. Results of experiments on *Sterculia foetida* oil alone, and in admixture with corn oil, showed that the increase in chlorine and bromine contents resulting from the hydrochloric acid treatment and the hydrobromic acid titration, respectively, were stoichiometrically equal and directly proportional to the concentration of the *Sterculia foetida* oil in the mixture. Thus, the number of moles of cyclopropene moiety present in the sample can be calculated from the number of equivalents of hydrogen chloride taken up.

The experimental data reported below show that this method of analysis is applicable to cyclopropenoid materials which are substantially free from epoxy compounds. Should epoxy or other interfering substances reacting with hydrohalogens be present, they can be eliminated by one of the accepted pretreatments developed in connection with the hydrogen bromide titration method (6,7,8).

Experimental

Sterculia foetida oil was particularly suitable for use in these experiments because it contains no appreciable quantity of epoxy compounds (7,8). The dehulled seeds were extracted with several portions of low-boiling petroleum ether in a Waring Blendor at room temperature. The combined extracts were filtered and freed from solvent under reduced pressure on a rotary evaporator without heating above 60°C. The oil was immediately sealed in evacuated tubes and stored in the refrigerator until used. The corn oil was a commercial salad oil.

Procedure. The oil sample was intimately mixed with an equal volume of concentrated aqueous HCl (sp gr 1.18–1.19) by shaking for 1 hr under a nitrogen blanket on a mechanical shaker and extracted with hexane. The hexane extract was washed with water until free from mineral acid, dried over anhydrous sodium sulfate, and freed from solvent under reduced pressure. Chlorine analyses were made in duplicate on 20–30 mg samples by the method of Cheng (11). The cyclopropenoid acid content was calculated as sterculic acid from the corrected chlorine content.

$$\% \text{ Sterculic acid} = \frac{294.47x}{35.47(100-1.028x)}$$

where x = % chlorine (corrected).

Results and Discussion

Table I gives the results obtained on two series of corn oil-*Sterculia foetida* oil mixtures prepared from *Sterculia foetida* oils extracted from two different batches of seeds. These mixtures represent a range of sterculic acid concentrations from 2.25–45.79%.

TABLE I
Analyses of Corn Oil-*Sterculia foetida* Oil Mixtures

% <i>S. foetida</i> oil	% Chlorine	% Cyclopropenoid acid ^a		Deviation from theory
		Observed ^b	Theory ^c	
0.00	0.15	0.00	0.00
10.02	0.69	4.69	4.59	+0.10
20.03	1.10	8.15	9.17	-1.02
40.02	2.26	18.28	18.32	-0.04
60.01	3.24	27.10	27.48	-0.38
79.97	4.19	35.79	36.61	-0.82
100.00	5.26	45.79	45.79
Second series ^d				
4.83	0.37	1.88	2.25	-0.37
9.44	0.61	3.92	4.40	-0.48
17.09	1.09	8.04	7.97	+0.07
49.98	2.80	23.10	23.31	-0.21
49.98	2.85	23.54	23.31	+0.23
50.00	2.85	23.54	23.32	+0.22
66.52	3.73	31.51	31.02	+0.49
				Av. 0.37

^a Calculated as sterculic acid.

^b Corrected for the corn oil contribution and for the chlorine content of the untreated *Sterculia foetida* oil.

^c Calculated from the observed value for the 100% sample in the first series and that for the 49.98% compositions in the second series.

^d Using *Sterculia foetida* oil from another batch of seed.

The percentage of cyclopropenoid acids (as sterculic) in each of the mixtures (column 3) was calculated from the average of duplicate chlorine analyses (column 2). Correction was applied for the original chlorine content of the *Sterculia foetida* oil, 0.04%, and for the fact that blank determinations on the corn oil showed a final chlorine content of 0.15%.

The theoretical sterculic acid values in column 4 were calculated from the weight percentages of *Sterculia foetida* oil in the mixtures (column 1) and the observed sterculic acid concentration for the 100% *Sterculia foetida* oil in the first series and for the 49.98% mixture in the second series.

The average deviation of the observed from the theoretical values (column 5) is 0.37% sterculic acid. The average of the deviations from the mean of the duplicate chlorine analyses was about 0.025%, corresponding to 0.21% sterculic acid. Thus, a higher precision should be attainable by the hydrochloric acid method if a more precise method or larger samples were used for chlorine analysis.

The mechanism of the hydrohalogenation reactions involved can be deduced from iodine values and infrared absorption spectra (12). The hydrochloric acid treatment of the sterculic acid moiety results in the appearance of a strong absorption band at 11.05 μ . This has been used as the basis of another method for estimating cyclopropenoid acids which will be described in a separate report.

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