TABLE III

Stabilization of DOP Plasticized Vinyl Resin by Mixtures of Ba-Cd Soaps at a 1% Level

Ba-Cd Soaps	UV Light Stability Hours to color change[a] in Atlas Weather-Ometer			Heat Stability Hours to color change[a] in 160C oven		
Ratio	Wool wax	Lauric	Stearic	Wool wax	Lauric	Stearic
1/0	96	72	96	2	2	2
10/1	120	120	96	2	2	2
7/1	120	120	144	2	1½	1½
3/1	120	144	120	2	1½	1½
1/1	72	96	96	2	2	2
1/3	120	120	96	2	1½	1½
1/5	72	96	96	2	2	2
0/1	120	96	96	2	1½	1½

[a] Time reported is for first appearance of a color change.

Table III. Also reported in Table III are comparison tests with similar ratios of barium and cadmium soaps of lauric and stearic acids.

From the data given in Table III one can conclude that the mixed barium-cadmium soaps of lauric acid and those of the wool wax acids are effective as stabilizers in ratios from 3/1 to 10/1 (Ba/Cd). These mixtures are superior to the individual soaps in both heat and light stabilizing effectiveness. Synergism is demonstrated by two facts: discoloration of the film during heat aging is gradual compared to the abrupt change observed with cadmium soap stabilized films, and films stabilized with mixed soaps showed increased light stability compared to those stabilized with barium soaps.

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Sterculic Derivatives and Pink Egg Formation[1,2]

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Abstract

Sterculyl alcohol has been methylated and reduced to form the methoxyl and hydrocarbon derivatives. These two derivatives, sterculyl alcohol and the polymers of sterculic acid and methyl sterculate were fed to laying hens. The sterculic derivatives caused pink egg formation but the polymers did not.

THE FEEDING of malvalic and sterculic acids to hens has been reported to cause pink discoloration in cold stored eggs (1,2). These acids give a positive Halphen test (3,4), which has been postulated to be specific for the cyclopropene ring (5). However, the property of derivatives of these fatty acids, such as the hydrocarbon or the alcohol, to produce these effects has not been reported.

Sterculic acid is sensitive to heat, forming a polymer the structure of which has been established (6). The loss of the characteristic infrared bands at 5.38 μ and 9.92 μ indicates that the cyclopropene ring is gone. Further evidence for this destruction is a negative Halphen test. The glyceride or methyl ester of the acid is considerably more stable to heat than the acid.

Nunn, in isolating sterculic acid (7), noted that the cyclopropene ring is resistant to lithium aluminum hydride reduction (LAH) by the method of Nystrum (8). This resistance was also observed by Smith (9) when LAH was used to differentiate cyclopropene fatty acids from oxirane oxygen-containing fatty acids. The cyclopropene ring has also been reported to be stable during saponification of Sterculia foetida oil at room temperature with 10% alcoholic KOH (1).

Very few methylation and reduction studies on fatty alcohols to form methyl ethers and hydrocarbons have been reported. Sekera and Marvel (10) reported preparation of saturated fatty acid tosylates in very good yields. Strating (11) prepared hexadecane from LAH reduction of cetyl tosylate in 98% yield. Although methoxy derivatives of hydroxy fatty

acids and dimethoxy derivatives of fatty aldehydes have been reported in the literature, 1-methoxy-9-octadecene and similar compounds have not been hitherto reported. Studies of the methylation of sterculyl alcohol and oleyl alcohol with methyl iodide and silver oxide in dimethyl formamide revealed the presence of numerous side products. Methylation with methyl sulfate in tetrahydrofuran produced a methylated product in nearly quantitative yields.

The work reported in this paper shows that the hydrocarbon, ether, and alcohol of sterculic acid produce pink discoloration in eggs and give positive Halphen reactions.

Methods

Oil was extracted at room temperature from 2 kg of ground Sterculia foetida seeds[3] with Skellysolve F (3 x 3 1). The extracts were dried over anhydrous Na_2SO_4 and the solvent removed by distillation at room temperature under reduced pressure. The yield was 568 g of a golden yellow oil.

Transesterification. Transesterification of 200 g of Sterculia foetida oil was carried out at room temperature. The oil was added to 1 l of dry methanol containing 1% sodium methoxide. The heterogeneous solution was stirred rapidly for 45 min at which time the solution had turned homogeneous and a dark orange in color. The mixture was transferred to a separatory funnel and 500 ml diethyl ether was added followed by 250 ml of ice water. The aqueous layer was extracted with Skellysolve B (3 x 300 ml). The extracts were combined and washed with water (3 x 300 ml), 10% sodium carbonate (2 x 300 ml), 5% sodium bicarbonate (2 x 300 ml), and water (2 x 200 ml) to pH 7–8. The ether solution was dried over anhydrous sodium sulfate and the solvent removed on a rotovac. The yield was 186.5 g of methyl esters.

Fractionation. The methyl esters (125 g) were added to urea-saturated boiling methanol (125 g urea in 365 ml dry methanol). After 3 hr of occasional shaking the adducts were filtered and washed with 100 ml of urea-saturated methanol. Filtrate and washings were combined. A second urea adduct on the combined filtrate and washings removed essen-

[3] Seeds procured through the courtesy of F. R. Amos, Director of Forestry, Manila, Philippines.

tially all the saturated esters. The second filtrate was extracted with Skellysolve F with the aid of 200 ml of ice water. The Skellysolve solution was washed free of methanol with water (3 x 200 ml), dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure. The yield was 36.6 g of methyl sterculate. The methyl sterculate was crystallized from a 10% solution of methanol at −35C. The crystals obtained at this temperature were pure methyl sterculate as determined by gas-liquid chromatography (GLC), $n_D^{20} = 1.4571$. Distillation of 750 mg of the ester under reduced pressure (bp 123C/.035 mm) revealed no appreciable polymerization or decomposition. Quantitative infrared spectral analysis on the crystallized and on the distilled ester were identical (bands at 5.38, 8.27, 8.55, 9.11, 9.92 μ). The yield of crystallized methyl sterculate was 20.8 g.

Sterculic acid was prepared from 1 g of the methyl sterculate by conventional saponification at room temperature, $n_D^{20} = 1.4656$ [lit. (12), $n_D^{25} = 1.4650$] I.R. bands at 5.38, 8.61, 9.15, 9.92 μ.

Sterculyl Alcohol. Sterculyl alcohol was prepared according to Nunn, $n_D^{20} = 1.4647$ [lit. (7), $n_D^{30} = 1.4617$]. The yield was 8.5 g (93.5%) from 10 g of methyl sterculate. I.R. analysis showed bands at 2.80, 5.38, 8.52, and 9.92μ.

Methyl Sterculyl Ether [1-octyl, 2-(1-methoxy)-octyl, cyclopropene]. Sterculyl alcohol (5 g) in 60 ml of freshly distilled tetrahydrofuran and 4.0 g of powdered NaOH were combined and the heterogeneous mixture stirred rapidly for 10 min. Four ml of methyl sulfate were added. After 30 min of rapid stirring a gentle exothermic reaction was noted. The mixture was stirred 16 hr and then diluted with 70 ml of ice water and extracted with 40 ml of Skellysolve F. The Skellysolve solution was washed with water (3 x 70 ml) until neutral to pH paper, dried, and solvent removed on a rotovac at room temperature. The yield was 4.9 g (93.3%). Distillation of 0.5 g of the product under reduced pressure revealed no appreciable decomposition and identical I.R. spectra for the distilled and undistilled preparation, bp 116C/0.35 mm, $n_D^{20} = 1.4567$, I.R. bands at 5.38, 8.98, 9.92 μ.

Sterculene (1,2-dioctylcyclopropene). One g of sterculyl alcohol was dissolved in 20 ml of freshly opened pyridine in a 125-ml Erlenmeyer flask containing a magnetic stirrer. The solution was placed in an ice bath and 1.1 g of p-toluenesulfonyl chloride added over a period of 10 min. The reaction mixture was stirred at ice bath temperature for 4 hr. A precipitate of pyridine hydrochloride was noted after 1 hr. The mixture was transferred to a separatory funnel with 15 ml. of Skellysolve F and 20 ml of water. The aqueous-pyridine layer was extracted with 30 ml. of Skellysolve F. The combined extract was washed 3 times with water to a pH of 7–8. The solution was dried and solvent removed on a rotovac at room temperature. The yield was 1.43 g (92.5%) of a yellow oil.

The oil (1.2 g) was dissolved in 20 ml of anhydrous ether. This solution was added dropwise to 0.3 g of LAH in a 200 ml three-neck reaction flask fitted with stirrer, funnel, and condenser over a 30 min period. After 1 hr the excess LAH was decomposed by addition of ethyl acetate followed by ice water. Thirty ml of Skellysolve F was added and the mixture shaken and filtered through fine grain filter paper into a separatory funnel. The Skellysolve layer was washed with water (3 x 30 ml), dried over anhydrous Na_2SO_4 and solvent removed on a rotovac at

room temperature. The yield was 0.69 g (94.6%). Upon distillation no appreciable decomposition was noted, bp 102C/.040 mm, $n_D^{20} = 1.4541$, I.R. 5.38, 9.92 μ. The I.R. spectra of the distilled hydrocarbon lacked the weak band at 2.8 μ (free hydroxyl group) found in the I.R. spectra of the undistilled hydrocarbon. The elimination of this band is good evidence that distillation removed any unreacted sterculyl alcohol.

Methyl Oleyl Ether (1-methoxy, 9-octadecene). Commercial grade oleic acid, containing approximately 80% oleate as determined by chromatography (GLC), was reduced to oleyl alcohol and subsequently methylated in the manner described previously for methyl sterculate.

Sterculic Acid and Methyl Sterculate Polymers. The method followed was essentially that of Rinehart (6). The *Sterculia foetida* acids were prepared from *Sterculia foetida* methyl esters by cold saponification with 10% KOH in ethanol. Fifteen g of *Sterculia foetida* fatty acid was heated for 26 hr at 150C. The polymer was removed from the oil bath and allowed to cool to approximately 60C. The polymer was washed free of any monomers by rinsing with warm methanol (3 x 50 ml), and the methanol decanted. The polymer was taken up in ethyl ether and dried over Na_2SO_4. The *Sterculia foetida* methyl ester polymer was prepared in a similar manner. The solvent-free polymers gave negative Halphen tests.

Analysis. The purities of the methyl sterculate, sterculyl alcohol, and sterculyl alcohol derivatives preparations assayed at 98% or better by GLC (Aerograph No. A-100-C, 5 ft. diethylene glycol succinate column, 200C, 30 psi). Halphen tests were run on the derivatives by the method of Deutschman and Klaus (4). For I.R. analysis concentrations of 6% sample in CCl_4 were run on a Perkin-Elmer Model 137 Infracord.

Feeding Experiments. Three feeding experiments containing 4 lots of 5 laying White Leghorn hens were conducted. The hens were individually caged in order to identify the eggs, fed a practical laying ration and given water, *ad libitum*. The various sterculic derivatives were administered orally by capsule once daily for 15 days. The eggs were collected daily after the 5th day of supplemental diet for 15 consecutive days. They were stored at 2C for periods of 1 to 3 mo.

The capsules were prepared to contain an amount of cyclopropene equivalent to 25 mg of *Sterculia foetida* oil. In 10 of 12 trials the derivatives were diluted to 125 mg with corn oil per capsule. The capsules were stored at 7C until administered. The supplemental diets are given in Table I.

The eggs were examined for pink discoloration and pH change after 1 mo storage. The degree of discoloration was rated visually on a 5-point scale as used by Kemmerer *et al.* (17). The pH of the whites and the yolks were determined with a Beckman pH meter.

Results and Discussion

The stability of the cyclopropene ring toward neutral or alkaline reagents is illustrated in the analysis of the preparations presented in this paper. In all the steps of the preparations the most gentle treatment possible was carried out on the cyclopropene ring compounds. No attempt was made to determine the limits of these treatments. It may be noted that preparation of methyl sterculate by transesterification as described in this paper eliminates the use of heating sterculic acid with HCl or esterification with

Expt. no.	Lot no.	Composition of capsule	Egg (16) discoloration	pH	
				White	Yolk
1	1	125 mg corn oil	0	9.05	6.20
	2	100 mg corn oil 25 mg oleyl ether	0	9.05	6.20
	3	100 mg corn oil 25 mg *Sterculia foetida* oil	5	8.70	8.25
	4	108 mg corn oil 17 mg "sterculyl ether"	5	8.75	8.25
2	5	125 mg corn oil	0	9.05	6.15
	6	75 mg corn oil 50 mg sterculia acid polymer	0	9.00	6.20
	7	75 mg corn oil 50 mg sterculyl ester polymer	0	9.05	6.00
	8	100 mg corn oil 25 mg *Sterculia foetida* esters	5	8.45	8.00
3	9	125 mg corn oil	0	9.10	6.35
	10	17 mg sterculyl alcohol	4	8.70	7.60
	11	18 mg "sterculene"	5	8.60	7.90
	12	100 mg corn oil 25 mg *Sterculia foetida* esters	5	8.60	8.15

diazomethane. Both of the latter methods give some destruction of the cyclopropene ring.

The authenticity of these preparations is clearly shown by examining the infrared spectrophotometric data and comparing with reported standard bands (13,14,15). The large band at 9.92 μ and the weak band at 5.38 μ attributed to the cyclopropene ring, are found in all six sterculyl derivatives and all are of the same magnitude. No decrease in intensity was noted in the 9.92 μ band when the ester, ether, and hydrocarbon were distilled.

In addition to the bands given under the various preparations, bands at 3.47, 3.56, 6.85, and 7.30 μ were found for all five compounds. These bands have been characterized as due to C-H stretching, C-H bending, and symmetrical deformation vibrations of the CH₃ group, which are characteristic of long chain aliphatic material.

The doublet at 7.79, 7.83 μ found in the acid spectrum is due to C-O vibration. When the acid is esterified with a methyl group this doublet is changed into a triplet with bands at 8.07, 8.40, and 8.55 μ. Two bands are characteristic of fatty alcohols, these being 9.38 μ due to the bending motion of the OH group and the 2.8 μ band indicating a normal "free" alcoholic O-H vibration. It was noted that these

bands are absent for the methylated alcohol and for "Sterculene." A band at 8.98 μ in the methoxy spectrum indicates a CH_2-O-CH_3 bonding system. The hydrocarbon spectrum is free of any acid, ester, alcohol or ether bands.

Halphen tests run on these derivatives did not produce deviations from the normal behavior of the Halphen reagents on cyclopropene ring containing oils. This indicates that the color of the Halphen test is not affected by the carboxyl group of the fatty acids.

In the biological experiments performed with laying hens *Sterculia foetida* oil, sterculyl ether, *Sterculia foetida* esters, and sterculene all produced pink discoloration in the eggs in about the same degree (Table I). Also the pH changes in the yolks were in the same direction. These facts combined with the absence of pink discoloration of eggs from hens fed sterculic acid polymer and methyl sterculic polymer indicate that the cyclopropene ring but not the COOH group is necessary for discoloration.

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The Determination of Mutton Tallow in Mutton/Beef Tallow Mixtures

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A method is proposed for the determination of the mutton tallow content of mixed beef and mutton tallow samples. The calculation is based on the determination of conjugated diene, *trans* acids, and mono *cis* unsaturated acids in the sample. The analytical findings are employed in a single equation which is weighted to minimize uncertainty due to natural variation. The method is largely independent of the degree of "seeding" of the tallow prior to sampling and is accurate to approximately ± 14%. This accuracy is considered reasonable in view of the natural variations of the two fats and their close analytical similarity.

TALLOW in its various grades and qualities is a raw material of considerable importance to Australian industry, comprising as it does by far the greatest proportion of indigenously produced fats and oils. In the edible fat industry its significance is enhanced on the one hand by cost considerations and on the other by certain legislature requirements.

Under these circumstances, factors affecting quality of crude edible tallows and of products made therefrom have received much attention. In the case of certain grades of "mixed" tallows the problem