

Hydrogenation of Cyclopropenoid Fatty Acids Occurring in Cottonseed Oil

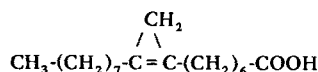
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ABSTRACT

The hydrogenation of cyclopropenoid acids and their relative reactivities during hydrogenation as compared to linoleic and oleic acids were examined. Pure methyl sterculate and purified *Sterculia foetida* oil and its methyl esters, which have a cyclopropene content more than 60 times that of cottonseed oil, were used for the hydrogenation experiments. Nickel, palladium and platinum catalysts were used. The effect of temperature and type of catalyst were demonstrated in a series of hydrogenation experiments of safflower and *S. foetida* oil mixtures, and methyl oleate and methyl dihydrosterculate mixtures. Partial hydrogenation of methyl sterculate formed as many as twenty compounds in addition to the cyclopropenoid derivatives. Most of these compounds were monounsaturated. The cyclopropene group hydrogenated very readily compared to the 9,12-diene system in linoleate. The cyclopropane group obtained by hydrogenating the cyclopropenoid acids group was quite resistant to further attack by hydrogen and nickel catalyst had little effect. With palladium catalyst, a temperature of 180 C was necessary for the reaction to go to completion. Platinum in acetic acid was a good system for hydrogenolysis of the cyclopropane group at 80 C.

INTRODUCTION

The presence of malvalic acid in the triglycerides of cottonseed oil was established by Shenstone and Vickery (1), who subsequently found sterculic acid also was present but in smaller proportion (2). Malvalic acid differs from sterculic



acid in having one less methylene group between the cyclopropene and carboxyl groups. Analyses made in our laboratory indicate that oils from domestic cottonseed usually contain less than 1% cyclopropenoids, calculated as malvalic acid (3).

Malvalic and sterculic acids occur in other seed oils of the order Malvales. The seed oil of *Sterculia foetida* is particularly rich in these cyclopropenoid acids, containing about 60%. However, the only commercially important oil other than cottonseed oil from plants of the order Malvales is kapok seed oil which apparently contains about 20% cyclopropenes (4).

Lowenstein (5) and Moore (6) showed that limited hydrogenation rendered cottonseed oil Halphen negative (AOCS Method Cb 1-25). It was also demonstrated that under certain conditions a light hydrogenation which reduced the iodine value of cottonseed oil by only 1.7 units gave a Halphen-negative, virtually cyclopropene-free oil (7). A continuous hydrogenation process has been devised which will hydrogenate the cyclopropenes of cottonseed oil to a Halphen-negative level in a time as short as 2 min (8).

Nunn, in proving the structure of sterculic acid, subjected it to a stepwise hydrogenation (9). The first step yielded dihydrosterculic acid, a cyclopropanoid acid, and the second step yielded a mixture of *n*-nonadecanoic acid and two methyloctadecanoic acids. Apparently, the possi-

bility that other compounds could be formed during the hydrogenation of sterculic acid has never been raised. Yet, it is known that the hydrogenation of cyclopropane on nickel catalysts is a complicated reaction which yields methane, ethane, and propane (10,11). The objective of the present investigation was to examine in a more critical manner the hydrogenation of esters of malvalic and sterculic acids and their relative reactivities to linoleic and oleic acids. To simplify the experimental work, *S. foetida* oil and methyl esters derived from it were employed rather than cottonseed oil and its derivatives.

EXPERIMENTAL

Materials

S. foetida oils were obtained from two lots of seed. Each lot was dehulled separately and the crushed kernels were extracted with hexane at room temperature. The oils, which were recovered from the hexane at about the boiling point of the latter, were alkali-refined, bleached with neutral activated clay, diluted with petroleum ether and passed through alumina (1 part oil : 4 parts alumina). Ca. 0.02% butylated hydroxyanisole was always added to each oil after the petroleum ether was removed. The oil used in practically all of the experimental work contained, according to a titration with hydrogen bromide, 62.4% cyclopropenoid acids, calculated as tristerculin. The ratio of sterculic acid to malvalic acid was calculated on the basis of cyclopropene content and gas liquid chromatographic (GLC) data to be 16.9:1. The content of linoleoyl groups, calculated as trilinolein, was 6.83%. The second oil (used in only two hydrogenations, as indicated in the text), contained 58.1% cyclopropenoid acids calculated as tristerculin.

The safflower oil was a commercially refined, bleached, and deodorized product which was further purified by passage through alumina (1:4). The purified oil contained linoleoyl groups equivalent to 75.8% trilinolein.

Pure methyl sterculate was prepared from the *S. foetida* oil containing 62.4% cyclopropenoid acids. A sodium methoxide catalyzed methanolysis was conducted at room temperature and the methyl esters were subjected to a series of urea clathrations and fractional crystallizations from methanol. Shortly before use, each sample or portion of sterculate was dissolved in petroleum ether and the solution was passed through an alumina column (1 part sterculate : 4 parts alumina). The petroleum ether was removed under vacuum by stripping at a low temperature with purified nitrogen. The final methyl sterculate was 100% pure based on analyses by GLC and thin layer chromatography (TLC), titration with hydrogen bromide, reaction with methyl mercaptan, analysis by nuclear magnetic resonance (NMR), and behavior on hydrogenation.

The methyl esters of palmitic, oleic, linoleic, and dihydrosterculic acids were all analyzed by GLC and TLC and found to have a purity of 98-100%.

Hydrogenation Apparatus and Procedures

Two hydrogenators were employed. The larger of the two,

^aRetired.

TABLE I

Operational and Analytical Data on the Hydrogenation of *Sterculia foetida* Oil/Safflower Oil Mixtures^a

Run no.	<i>S. foetida</i> to safflower oil, wt ratio	Catalyst type and conc.	Temp, C	Time, min	Reduction in HIV ^b	Composition, wt % ^c		
						Cyclopropenes	Cyclopropanes	Linoleins
1	1:1	0.1% Ni	130	23	22.8	7.0	8.2	33.4
2	1:1	0.1% Ni	150	28	23.0	11.1	4.5	32.1
3	1:1	0.1% Ni	180	21	23.3	4.4	5.0	32.0
4	1:1	0.1% Pt	150	24	24.0	18.5	2.2	24.9
5	1:1	0.1% Pd	150	13	24.1	9.9	5.3	26.5
6	1:0	0.5% Ni	80-120	d	60.7	0.0	51.6	0.0
1:1 Mixture before hydrogenation						31.2	0.0	41.0

^aBatches of 25 g each, except run no. 6, which was 15 g.^bHIV means hydrogen iodine value.^cCyclopropenes, cyclopropanes, and linoleates calculated as tristerculin, tridihydrosterculin, and trilinolein, respectively.^dHydrogenated until uptake of hydrogen virtually stopped.

which was essentially the apparatus described previously (10), except that a constant-temperature oil bath was substituted for the electric heating mantle, consisted of a glass vessel 28 mm in diameter and 200 mm long to which was charged 25 g of the material to be hydrogenated. Hydrogen at atmospheric pressure was circulated continuously by an external pump and the uptake of hydrogen was measured with the aid of a gas-holder. The temperatures of the oil bath and charge were measured with thermocouples and were maintained within a degree or two of those desired.

The second hydrogenation apparatus was an all-glass unit (11) originally designed for analytical hydrogenations of 1 or 2 g of material. The hydrogenations were conducted at atmospheric pressure in small round bottom flasks or test tubes fitted with standard taper glass joints. Agitation was provided by Teflon-coated, magnetic stirring bars. Hydrogen uptake was measured with a gas burette graduated in 0.1 mL. The temperature was controlled with an oil bath. Three different catalysts were used in the hydrogenations. The nickel catalyst was a commercial product (G-70, Chemical Products Division, Chemetron Corp., Louisville, KY) of the supported type. Its nominal composition was 25% nickel, 1% zirconium, 14% Kieselguhr, and 60% fat. The fat was removed before the catalyst was used. The palladium catalyst consisted of 10% palladium on carbon (Engelhard, Newark, NJ). The platinum catalyst was platinum dioxide (Fisher Scientific Co., Fair Lawn, NJ).

Hydrogenation to convert methyl sterculate to methyl dihydrosterculate was carried out in heptane (1g/100 mL) at ambient temperature in the presence of 1.25% zirconium promoted nickel catalyst. The catalyst was first activated by hydrogenation at 150 C in methyl laurate. The laurate was removed by washing with heptane, care being taken that the catalyst never approached dryness. The heptane and the catalyst were mixed first under hydrogen, pure methyl sterculate was then added. Hydrogenation was continued until hydrogen uptake virtually stopped.

Hydrogenations of the methyl dihydrosterculate-methyl oleate mixtures were all carried out in solvents. The solvents used at lower temperatures were heptane and acetic acid. Acetic acid could not be used with the nickel catalyst since the nickel reacted with acetic acid, releasing hydrogen and forming nickel acetate (as indicated by the green color of the solution and increased pressure inside the hydrogenation vessel). The solvents chosen for the higher temperatures (150-180 C) were decane and methyl laurate.

Methods of Analysis

Cyclopropene contents were determined by a titration with

hydrogen bromide (12) when interfering substances were absent. Otherwise, analyses were made with the infrared (IR) spectrophotometer and cyclopropene contents calculated from the absorption band at 9.9 μm . Whenever methyl esters were analyzed in the spectrometer, an equal molar concentration of methyl oleate was used in the reference cell to cancel the absorption of the -OCH₃ group.

Cyclopropane contents usually were calculated from the 9.8 μm absorption band in the IR spectra of samples which did not contain cyclopropenes or in which the cyclopropenes had been destroyed by treatment with methanolic silver nitrate (13). As an alternative, the methyl esters of the cyclopropane and other fatty acids were fractionated on a silver nitrate-silicic acid column (see below) and the saturated fraction containing the cyclopropanes was analyzed by GLC.

Linoleoyl groups were determined by AOCS Method Cd 7-58 (14). Extensive experiments were conducted to establish that this method gave correct results in the presence of cyclopropenes and their hydrogenation products.

Partially hydrogenated methyl sterculate and partially hydrogenated methyl dihydrosterculate-methyl oleate mixtures were fractionated on a silver nitrate-silicic acid column by a slight modification of the De Vries method (15). A column 1 in. in diameter was packed with a mixture of 150 g silver nitrate-silicic acid and 75 g diatomaceous earth (Hyflo Super-Cel, Johns-Manville, New York, NY). A sample of 0.2 g was put on the column and eluted successively with 300-mL portions of 10%, 15%, and 20% benzene in petroleum ether, 200 mL of 30% benzene in petroleum ether, 100 mL benzene, and 100 mL diethyl ether. The eluant was collected in 20 mL fractions. After evaporation of the solvent at 60 C under a stream of nitrogen, the test tubes were brought to constant weight. The weight of methyl esters was plotted against the test tube number. Nine peaks were obtained. Each peak was analyzed by GLC, hydrogenation to completion, ozonolysis, and by IR spectroscopy. Ozonolysis was conducted at 0 C in the presence of methanol and the ozonides were treated with hydrogen peroxide in the presence of formic acid (16). The resulting monobasic and dibasic acid-containing mixture was treated with methanol-boron trifluoride to form methyl esters.

Content of dimers and polymers in the hydrogenation products was determined by TLC on silicic acid plates. The developing solvent for methyl esters was 8% diethyl ether in petroleum ether and for triglycerides, 15% diethyl ether in petroleum ether.

GLC analyses were conducted with a 15 ft, 1/8 in.

TABLE II

Relative Reactivities of Linoleoyl to Cyclopropene Acid Groups in the Hydrogenation of *Sterculia foetida* and Safflower Oils

Catalyst	Temp, C	Reactivity, cyclopropene to linoleoyl groups
0.1% Ni	130	7.4:1
0.1% Ni	150	4.2:1
0.1% Ni	180	7.9:1
0.1% Pt	150	1.0:1
0.1% Pd	150	2.6:1

diameter diethylene glycol succinate column in a Barber-Coleman Model 20 instrument, equipped with a tritium detector. The sampler temperature was maintained at 250 C, the detector at 195 C, the column at 140-187 C, depending on the resolution desired.

RESULTS AND DISCUSSION

Reactions in the Absence of Hydrogen

The behavior of the cyclopropene groups during hydrogenation is complicated by side reactions induced by heat and by the catalysts in the absence of hydrogen. Heating pure methyl sterulate at 150 C under nitrogen for 90 min caused about 12% of the sterulate to polymerize. Adding 0.2% nickel in catalyst form and heating under otherwise identical conditions caused 19% to polymerize, while heating with 0.2% platinum in catalyst form caused 22% to polymerize. Analysis of these products by GLC revealed that the unpolymerized portion apparently was unchanged methyl sterulate. During the hydrogenation of methyl sterulate these polymerization reactions occurred at a lower

rate. Thus, the hydrogenation of methyl sterulate at 150 C with 0.2% nickel produced a total content of polymers of only 6 to 8%.

The changes in composition resulting from polymerization induced by heat and by nickel and platinum in catalyst form were a minor factor in most of the hydrogenations conducted with the 1:1 mixtures of *S. foetida* and safflower oils. Heating such mixtures either alone or in the presence of 0.1% nickel or palladium for 30 min at 150 C lowered the cyclopropene content only 1-2 units from its original value of 31.2%, calculated as tristerculin.

Results obtained with palladium catalyst differed greatly from those of nickel and platinum. Heating methyl sterulate under nitrogen at 150 C with 0.5% palladium in the form of a 10% palladium-on-carbon catalyst destroyed practically all of the sterulate in 30 min; and when the reaction was stopped after 90 min, no trace of sterulate remained. Analysis by TLC indicated the presence of no more than 50% methyl esters of unchanged molecular weight, mostly conjugated dienes. An investigation of the reaction between cyclopropenes and palladium catalyst has been described previously (17).

The rate of cyclopropene destruction by palladium catalysts under a nitrogen atmosphere was found to be lower for a freshly activated, hydrogen-containing catalyst than for a catalyst entirely free of hydrogen. As will be shown later, during hydrogenation the types of reaction discussed here are markedly retarded. With a low concentration of catalyst and a high rate of hydrogen dispersion, these reactions can be retarded even further.

Relative Reactivities of Cyclopropene and Linoleoyl Groups

The relative reactivities of the cyclopropene and linoleoyl acid groups during hydrogenation were calculated from

TABLE III
Derivatives of Methyl Sterulate Formed on Hydrogenation^a

Structure	Amount, %	ECL	ECL after complete hydrogenation
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}=\text{CH}- \end{array}$	29.9	18.60	18.35
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}=\text{CH}-\text{CH}- \end{array}$	22.9	19.00	18.35
$\begin{array}{c} \text{CH}_2 \\ / \quad \backslash \\ -\text{C} \quad \text{C}- \\ \backslash \quad / \\ \text{H} \quad \text{H} \end{array}$	17.9	19.30	85% 18.35 and 15% 19.00
-CH=CH-CH ₂ -	8.0	19.35	19.00
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}-\text{CH}_2- \end{array}$	7.1	18.35	18.35
$\begin{array}{c} \text{CH}_2 \\ \\ -\text{C}-\text{CH}_2- \end{array}$	5.0	19.15	18.35
-CH ₂ -CH ₂ -CH ₂ -	4.6	19.00	19.00
Chain cleavage products	1.5	ca. 10.0	
Unidentified	3.1	18.10-18.20	

^aAdded 1.04 mole hydrogen per mole of methyl sterulate. Conditions, 0.1% Ni catalyst, 150 C, atmospheric pressure.

TABLE IV

Ozonolysis Products of Unsaturated Derivatives of Methyl Sterculate After Hydrogenation

Unsaturated derivatives	Ozonolysis products	
	Monofunctional	Difunctional
1. a $\begin{array}{c} \text{CH}_3 \\ \\ \text{-HC=C-} \end{array}$	C ₉ monoester 31%	C ₁₀ ketoester 31%
b $\begin{array}{c} \text{CH}_3 \\ \\ \text{-C=CH-} \end{array}$	C ₁₀ ketone 16%	C ₉ diester 16%
2. $\begin{array}{c} \text{H} \quad \text{CH}_3 \\ \diagdown \quad \\ \text{-C=C-CH-} \\ \\ \text{H} \end{array}$	C ₇ monoester 27%	Branched C ₁₁ diester 27%
$\begin{array}{c} \text{CH}_3 \quad \text{H} \\ \quad \\ \text{-C-C=C-} \\ \\ \text{H} \end{array}$	Branched C ₁₁ monoester 21%	C ₇ diester 21%
3. $\begin{array}{c} \text{CH}_2 \\ \\ \text{-C-CH}_2\text{-} \end{array}$	C ₁₈ ketoester 90%	
4. $\text{-CH=CH-CH}_2\text{-}$	monoesters C ₆ -2%, C ₇ -4%, C ₈ -9%, C ₉ -20%, C ₁₀ -9%, C ₁₁ -5% diesters C ₈ -5%, C ₉ -9%, C ₁₀ -20%, C ₁₁ -9%, C ₁₂ -4%, C ₁₃ -2%	

data obtained in the hydrogenation of the 1:1 mixtures of *S. foetida* and safflower oils (Table I). In calculating the relative rates, the concept of affinity constants proposed by Bailey and Fisher (18) were employed. That is, the decrease in concentration of each type of fatty acid group for a given extent of hydrogenation was used to calculate a reactivity constant using the equation for a first-order reaction, i.e., extent of reaction was substituted for time. The ratio of the constants for the cyclopropene and linoleoyl groups then gives the relative rates of the two. For this analysis, the first-order equations are valid regardless of whether the reactions proceed in true first order fashion. They become invalid only if the relative reaction rates change. As is evident from Table I, the reactivities were calculated from a limited drop in hydrogen iodine value and little change in relative reaction rates would be expected. The reactivities are recorded in Table II.

Judging from the relative reactivities with Ni catalyst at 130 C and 150 C, the degree of preferential hydrogenation of the cyclopropene groups over the linoleoyl groups decreases as the temperature increases. This effect agrees with data obtained in an experiment in which a solution of methyl sterculate and methyl linoleate in hexane was hydrogenated with the nickel catalyst at 85 C. The sterculate hydrogenated completely while very little of the linoleate hydrogenated. The apparent high relative reactivity at 180 C is complicated by thermal polymerization.

In a previously reported investigation (8), it was found that cottonseed oil (0.4% cyclopropenes, calculated as malvalic acid) could be rendered Halphen negative (less than 0.01% cyclopropenes) by hydrogenating to an iodine value drop of 2 units when the reaction was conducted at 120 C and atmospheric pressure and with 0.1% nickel. Calculating the relative reactivities from these data gives a ratio of approximately 99:1 for the cyclopropene groups to the linoleoyl groups.

The relative reactivities of the cyclopropenes obtained with the nickel catalyst at 180 C and 150 C (Table II) does not mean that the relative rate of actual hydrogenation

increased as the temperature increased. Calculations using data from run 3 (Table I) reveal that the total decrease in cyclopropenes and linoleins is greater than can be accomplished by a decrease of 23.3 in hydrogen iodine value. Therefore, the relative reactivity of 7.9 at 180 C is influenced to a significant degree by the thermal degradation of the cyclopropene acid groups.

By analogous reasoning, it can be shown that the relative reactivity of the cyclopropenes in the presence of palladium catalyst at 150 C is actually the sum of the reactivities, actual hydrogenation and degradation of the cyclopropenes by the palladium. The palladium catalyst is as unselective as the platinum catalyst in preferentially hydrogenating cyclopropene groups over linoleoyl groups.

Structure of Derivatives of Methyl Sterculate Formed on Hydrogenation

The structures of the derivatives formed by adding one mole of hydrogen to one mole of methyl sterculate are shown in Table III. The position of double bonds was determined by ozonolysis. Further hydrogenation identified products as branched chain or straight chain derivatives. IR spectroscopy and NMR confirmed a higher number of methyl groups in methyl substituted hydrogenated derivatives. (See Table IV). IR data also indicated that all carbon-carbon double bonds formed had hydrogen in the *trans* position, and it was established from GLC data (by comparison with known standards) that all the cyclopropane groups formed had hydrogens in the *cis* position.

Relative Reactivities of Cyclopropane Acid and Oleoyl Groups

The dihydrosterculate obtained by hydrogenation of sterculate was quite resistant to further hydrogenation. The relative reactivities of the cyclopropane and oleoyl groups were calculated from data obtained in the hydrogenation of the 1:1 mixtures of methyl dihydrosterculate and methyl oleate (Table V).

TABLE V

Operational and Analytical Data on the Hydrogenation of Methyl Dihydrosterculate and Methyl Oleate Mixtures

Run no.	Methyl dihydrosterculate to oleate wt ratio	Solvent	Catalyst type and conc.	Temp (C)	Time (min)	Reduction in HIV	Cyclopropanes	Composition, wt %			
								Saturated C-19 branched chain	Saturated C-19 straight chain	Methyl oleate	
1	1:1	Decane	0.1% Ni	150	60	33.13	50	0	0	11.3	38.7
2	1:1	Decane	0.1% Pd	150	30	31.23	47.9	1.9	0.2	15.4	34.6
3	1:1	Decane	0.1% Pt	150	30	18.80	47.2	1.5	0.3	29.6	20.4
4	1:0	Acetic acid	0.1% Pt	80	180 ^a	83.5	0	84.8	15.2		
5	1:0	Methyl laurate	0.1% Pd	150-180	180 ^a	84.2	0	85.2	14.8		

^aHydrogenated until uptake of hydrogen virtually stopped.

Relative reactivities were calculated the same way as for Table II for 0.1% nickel, palladium, and platinum catalysts and values of 38.7:0, 16.5:1, and 11.3:1, respectively, were obtained.

To hydrogenate the dihydrosterculate further, the cyclopropane ring has to be opened. The data in Table V indicate that nickel catalyst in decane will not cleave the cyclopropane ring even at 150 C. Platinum and palladium, however, will do so even though the cyclopropane group hydrogenation is slow in comparison to the oleoyl groups. Platinum in acetic acid hydrogenated dihydrosterculate to completion at 80 C. With nickel, as previously mentioned, acetic acid could not be used as solvent because of its reactivity. Platinum, as well as palladium, preferentially cleaved the cyclopropane ring to produce a branched chain compound (Table V).

In addition, all the ring-opening reactions are exothermic and great care must be taken to keep the temperature from rising once the reactions start.

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