Reaction of Cyclopropene Esters With Hydrogenation Catalysts[1]

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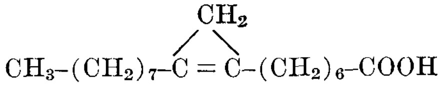
Abstract

Methyl esters of sterculic and malvalic acids were heated under nitrogen in the presence of various hydrogenation catalysts, and the effect on the cyclopropene moiety was established. Similar tests were conducted with cottonseed oil, which contains glycerides of sterculic and malvalic acids. Palladium catalysts, and some palladium compounds which were tested, readily gave cyclopropene-free products, while nickel and platinum catalysts did not. Palladium catalysts freshly activated with hydrogen were not as active as those freed of adsorbed hydrogen. The catalysts could be reused. Heating cottonseed oil (0.73% cyclopropenes, calculated as trimalvalin) with 0.02% palladium, as a 10% palladium-on-carbon catalyst, gave a cyclopropene-free oil after 2 hr at 150 C. The treated oil was unaltered in appearance, and the non-cyclopropene components were unaffected. Heating methyl sterculate with palladium catalyst produced a mixture of unsaturated condensation products and a number of unsaturated monoesters of practically unchanged molecular weight. The palladium treatment was shown to cleave the cyclopropene ring and produce methyl and methylene substituted fatty acid groups.

Introduction

Cottonseed oil contains the cyclopropene acids, malvalic and sterculic, at a level which usually ranges from 0.5% to 1.0%. The ratio of malvalic acid



$$CH_3\text{-}(CH_2)_7\text{-}\overset{CH_2}{C = C}\text{-}(CH_2)_6\text{-}COOH \qquad [I]$$

to sterculic its C_{19} homolog, is about 6:1. Because both acids are physiologically active, their presence in cottonseed oil has been of considerable interest even though the amounts present are quite small.

As might be expected, the cyclopropene moiety is chemically quite reactive. It polymerizes, reacts with organic and inorganic acids, and hydrogenates readily (1–5).

The possibility that hydrogenation catalysts in the absence of hydrogen might alter the cyclopropene moiety of these fatty acids or their esters apparently has never been investigated. Indeed, the possibility seems rather remote on the basis of previous reports concerning the behavior of cyclopropene acid groups on hydrogenation. In our own laboratory we succeeded in hydrogenating methyl sterculate almost quantitatively into the corresponding cyclopropane, methyl dihydrosterculate. Nevertheless, these previous experiments did not prove that the cyclopropene acid groups could not be destroyed by hydrogenation catalysts.

In preliminary tests with a number of hydrogenation catalysts the discovery was made that some catalysts could be made to destroy the cyclopropene moiety. The experiments were extended with the thought that treating cottonseed oil with such catalysts might be a suitable technique for producing a cyclopropene-free oil. Also, some effort was devoted to determining the structure of the compounds formed on destroying the cyclopropene moiety by interaction with an effective catalyst.

Comparison of Catalysts

To establish the relative cyclopropene destroying activity of the catalysts ordinarily available in the laboratory for the hydrogenation of double bonds, a series of tests was made with a commercially refined and bleached cottonseed oil containing 0.73% cyclopropenes, calculated as trimalvalin. The oil and the selected catalyst were mixed in the reaction vessel, and the catalyst was kept in suspension by bubbling dry nitrogen through the mixture. All air was excluded. The reaction vessel with the suspension of catalyst in oil was immersed for 2 hr in an oil bath at 150 C. At the end of the heating period the mixture was cooled, and the catalyst was removed by filtration. The treated oil was then subjected to the Halphen test (AOCS Method Cb 1–25), which gives a red color or positive reaction when cyclopropenes are present at a level above about 0.01%. The intensity of the red color developed ranges from orange (just barely positive) through pink, to dark red. The responses of some of the treated oils to the Halphen test are recorded in Table I.

The 10% palladium-on-carbon catalyst represented in the Table was a hydrogenation catalyst purchased from a laboratory supply house. Tests also were con-

TABLE I

Response of Cottonseed Oil to Halphen Test After Heating With Various Catalysts or Additives[a]

Catalyst or additive	Concentration,[b] wt. %	Response to Halphen test[c]
None (control)	—	+++
10% Palladium on carbon	0.01	+(?)
10% Palladium on carbon	0.02	—
10% Palladium on silica	0.03	—
Palladium black	0.10	+
$PdCl_2$	0.10	—
$Pd(NO_3)_2$	0.10	—
Nickel catalyst No. 1	0.20	+++
Nickel catalyst No. 2	0.10	+++
Nickel formate	0.10	+++
$NiO + Ni(OH)_2$ on silica (unreduced hydrogenation catalyst)	0.10	+++
PtO_2 catalyst	0.10	++
Reduced PtO_2 catalyst	0.10	+++
Activated carbon, alkaline	0.10	+++
Activated carbon, acidic	0.10	+++
Al_2O_3 (adsorbent grade)	0.30	++

[a] Each sample heated under nitrogen at 150 C for 2 hr.

[b] Calculated on weight of metal in metal-containing catalysts or compounds and on actual weight of metal-free additives.

[c] Response: —, Negative (less than 0.01% cyclopropenes); +, positive; ++, strongly positive; and +++, very strongly positive.

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TABLE II

Effect of Palladium Concentration and Temperature on the Destruction of the Cyclopropenes of Cottonseed Oil[a]

Palladium,[b] %	Halphen test after heating[c]		
	100 C	150 C	200 C
0.2	+(?)	–	–
0.1	+	–	–
0.05	++	–	–
0.02	+++	–	–
0.01	+++	+(?)	+(?)
0.005	+++	+	+

[a] Heated for 90 min under nitrogen.

[b] Amount of metal in form of 10% palladium on carbon.

[c] Halphen test response: –, Negative; +(?), questionably positive; +, positive; ++, strongly positive; +++, very strongly positive.

TABLE III

Equivalent Chain Lengths and Percentages of Mono- and Diesters Derived From the Unpolymerized Portion of Methyl Sterculate Heated with Palladium-on-Carbon Catalyst

ECL[a]	Monoesters, wt. %	Diesters, wt. %
6.0	1.4	6.5
7.0	......	2.0
7.4–7.6	9.4	20.0
8.0	44.7	19.0
9.0	30.5	34.9
9.4	11.1	14.5
10.0	2.8	3.0
10.4	0.8	......

[a] ECLs for the mono- and diesters are based on the ECLs of standard mono- and diesters, respectively, on a diethylene glycol succinate column.

ducted with other palladium-on-carbon catalysts with results similar to those shown. The palladium-on-silica catalyst was prepared in the laboratory. The two nickel catalysts were commercial products of the supported type prepared specifically for the hydrogenation of fats and oils. The PtO_2 was of the type used in the laboratory hydrogenation of double bonds.

The palladium-on-carbon catalyst used at a level of 0.01% palladium gave an oil with a questionable or just barely positive Halphen test. The palladium black and the palladium salts were tested only at the one level shown. Obviously, palladium and its compounds were unique among the catalysts and compounds tested. It should be noted that three pluses in the Table means that the treated oils contained large proportions of cyclopropenes as measured by the Halphen test but that these proportions were not necessarily equal.

The palladium catalysts employed generally were completely free of adsorbed hydrogen. One of the very active palladium-on-carbon catalysts had been stored in dry form in our laboratory for over 20 years and during this time had been opened repeatedly, which either desorbed or oxidized the hydrogen. The freshly prepared palladium-on-carbon catalysts did not contain sufficient hydrogen to destroy 1% of the cyclopropenes which were destroyed (6). The $PdCl_2$ and $Pd(NO_3)_2$ of course contained no hydrogen.

Besides not being necessary, the presence of hydrogen on the palladium catalysts was actually undesirable. Catalysts freshly treated by heating them in the presence of gaseous hydrogen were less efficient in destroying cyclopropenes than were the untreated catalysts. The 10% palladium-on-silica catalyst destroyed cyclopropenes more effectively on being dried and exposed to air than did the same catalyst on being protected from air by being directly immersed in cottonseed oil.

The palladium catalysts could be reused for the destruction of cyclopropenes. However, as might be expected, some catalyst poisoning occurred, as indicated by reduced activity of the catalyst. Regeneration could be effected to some extent by washing the spent catalyst with a 0.1 N salution of sodium hydroxide in 95% ethanol.

Noncyclopropene Components

Olefin-palladium chloride complexes, as well as other palladium complexes have recently been found by others to be efficient catalysts for the low-temperature, liquid-phase isomerization of olefins such as 4-methylpentene-1 and 1-pentene (7,8). The reaction reportedly is specific for isomerization of double bonds and does not rearrange the carbon structure. This suggested the possibility that palladium catalysts employed under conditions which destroyed the cyclopropenes of cottonseed oil might also produce changes in the double bond structure of other unsaturated fatty acid groups.

Infrared spectrophotometric analyses and gas liquid chromatographic analyses were made of treated cottonseed oils and methyl esters derived from these oils. Also, methyl esters of linseed oil fatty acids and tung oil fatty acids were prepared, treated with palladium catalysts, and examined. No evidence of isomerization of oleic, linoleic, linolenic or eleostearic acid groups was found.

Reaction Rates

To obtain information on the reaction rate of the cyclopropenes a series of tests was conducted with purified methyl esters of *Sterculia foetida* oil fatty acids. These methyl esters, which contained 58.4% cyclopropenes, calculated as methyl sterculate, were mixed with 0.5% palladium in the form of palladium-on-carbon catalyst and portions of the suspension were heated under nitrogen for varying periods of time at 150 C. The treated samples were analyzed for cyclopropene content by infrared spectrophotometry. The following results were obtained: 0 min, 0% cyclopropenes destroyed, 20 min, 62%; 40 min, 97%; and 90 min, 100%.

After 90 min all traces of cyclopropene had disappeared and even the Halphen test was negative.

A commercial nickel catalyst tested under similar conditions destroyed only 10% to 15% of the cyclopropenes, which was about the same percentage destroyed by heat alone.

To establish the effect of temperature on the ability of the palladium-on-carbon catalyst to destroy the cyclopropenes of cottonseed oil, samples of the oil were heated with different amounts of catalysts and at different temperatures (Table II).

As is evident from the first column of the Table, destruction of the cyclopropene moiety proceeded quite slowly at 100 C. A level of 0.2% palladium yielded an oil still containing a trace of cyclopropenes. At 150 C the reaction proceeded at about the maximum rate, and no significant increase in rate occurred on raising the temperature to 200 C.

Tests similar to those represented in Table II were conducted at 150 C using 0.01% palladium and varying the time. After 1 hr the Halphen test gave a light red color, after 2 hr the color was a faint pink, and after 3 hr it was difficult to determine whether the test was positive or negative.

Properties of Reaction Products

Outwardly, the properties of cottonseed oil did not change on being rendered Halphen negative by treatment with palladium catalysts. It still retained its characteristic color and bland flavor. There was no

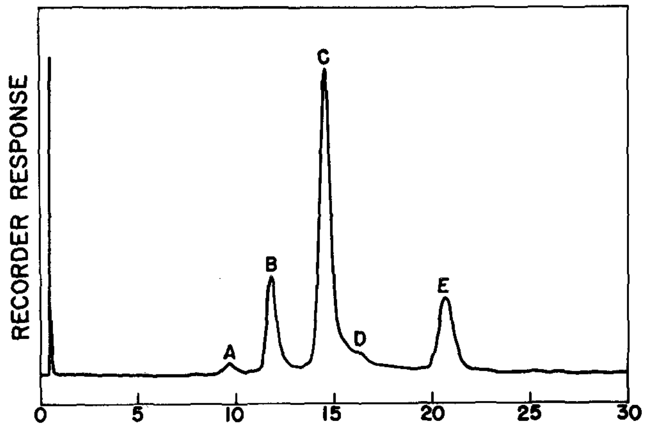

FIG. 1. Gas liquid chromatogram (diethylene glycol succinate column) *of unpolymerized reaction product obtained on heating* a dilute solution of methyl sterculate in the presence of palladium. The weight percentages and equivalent chain lengths (ECLs) of the fractions were, respectively, as follows: A, 1.9, 18.7; B, 15.8, 19.4; C, 58.0, 20.15; D, 4.8, 20.2; and E, 18.9, 21.15.

detectable change in viscosity. Infrared spectra of the oil before and after treatment were identical with the exception that sometimes a barely detectable band appeared at 10.3 μ after treatment. This band indicates the presence of a small proportion of *trans* bonds. Because the original concentration of cyclopropenes in the cottonseed oil was only 0.73% much change in the overall composition of the oil after treatment would not be expected.

Pure methyl sterculate heated with 0.5% palladium (as 10% palladium on carbon) at 150 C for 2 hr to destroy the cyclopropene groups was more appropriate for establishing the nature of the reaction products. The average molecular weight of the treated methyl sterculate, determined osmometrically, was 540, compared to 308.5 for the untreated methyl sterculate. Thin layer chromatographic (TLC) analyses on silicic acid plates indicated a content of about 50% polymers, which had R_f values much smaller than those of the unpolymerized esters.

The high content of polymer was a function of the concentration of methyl sterculate and its reaction products. When a 5% solution of methyl sterculate in decane was treated, rather than the solvent free methyl sterculate, the content of polymer was only about 25%. This polymer was readily separated from the other reaction products by passing the solution through a short silicic acid column. Gas liquid chromatographic (GLC) analyses before and after fractionation revealed no change in the unpolymerized fraction.

Composition of Unpolymerized Portion of Reaction Product

GLC analysis of the unpolymerized portion of the reaction product obtained on treating with palladium catalyst the 5% solution of methyl sterculate in decane revealed that at least five compounds of about the same molecular weight as methyl sterculate were formed (Fig. 1). In addition to the five compounds shown in Figure 1, about 0.4% of compounds having an equivalent chain length (ECL) of C_9 were formed.

When the fraction of the reaction product represented in Figure 1 was dissolved in decane and hydrogenated in an analytical hydrogenator (9) with the aid of a palladium-on-carbon catalyst, and the resulting product was analyzed by GLC on a diethylene glycol succinate column, a single, symmetrical peak containing over 98% of the total area under the chromatogram and having an ECL of 18.45 was obtained. This is exactly the ECL of the methyl esters of methyl substituted stearic acids. Further proof of such identity was found by chromatography on silicic acid-silver nitrate plates and infrared and ultraviolet spectroscopy in reference to known mixtures containing methyl substituted stearate.

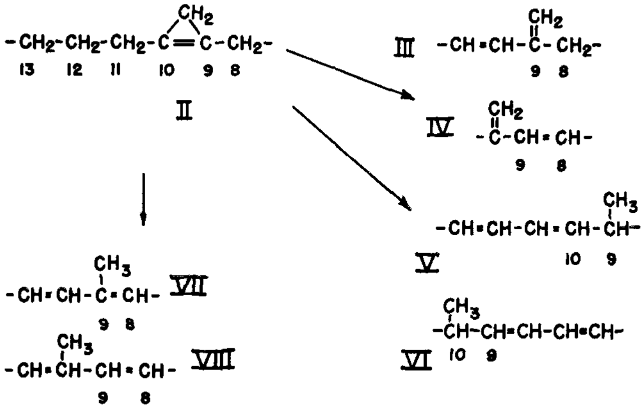

FIG. 2. Major structures formed on heating methyl sterculate with palladium catalyst under nitrogen at 150 C.

An analytical hydrogenation (9) of a portion of the unpolymerized fraction of the reaction product indicated the presence of two double bonds per ester group.

These findings indicate that the catalytic cleavage of the cyclopropene ring produces methyl or methylene substituted fatty acid groups or both which may undergo further polymerization reactions.

Infrared and ultraviolet spectra of the unpolymerized reaction product resulting from treating with palladium the 5% solution of methyl sterculate in decane were obtained. Ultraviolet spectra revealed a very strong absorption band at 232 mμ, indicating a very large proportion of compounds containing conjugated dienes. No conjugated trienes were found. Infrared spectra had a strong absorption band at 10.37 μ, indicating a large proportion of *trans* bonds. These spectra also had absorption peaks at 11.33 and 11.20 μ, indicating the presence of two types of methylene substituted fatty acid groups. Gellerman and Schlenk (10) obtained similar infrared absorption bands with products resulting from the silicon dioxide catalyzed pyrolysis of methyl sterculate. The major structures represented in Figure 2 are identical with those which have been reported to be obtained by heating cyclopropenes in the presence of alumina and silicon dioxide (10,11).

Another unpolymerized portion of the reaction product was ozonized in methanol, the ozonides were oxidized with hydrogen peroxide and formic acid, and then they were treated with boron trifluoride to obtain a mixture of methyl esters of mono- and dibasic acids (Table III).

In other research on the cyclopropene acids it was established that the substitution of a methyl group for a hydrogen atom in a saturated hydrocarbon chain increased the ECL on a diethylene glycol succinate column by 0.4. Thus, an ECL of 9.4 for a methyl ester would indicate a methyl substituted pelargonic acid group.

A portion of the reaction product obtained by treating with palladium the 5% solution of methyl sterculate in decane was further analyzed by passing it through a silicic acid-silver nitrate column, which removed the approximately 25% of polymer and effected some fractionation of the unpolymerized methyl esters. The various unpolymerized fractions and combinations of these fractions were analyzed before and after ozonolysis and before and after hydrogenation. Infrared and ultraviolet spectrochromatograms were obtained. GLC and TLC analyses were made and compared with known compounds. Also, TLC analyses on alumina and infrared analyses were made with fractions treated with mercuric acetate in methanol containing a small proportion of acetic acid (12,13). The methylene-substituted esters apparently reacted more readily with the mercuric acetate than did the other unsaturated esters, and marked differences in TLC patterns were obtained.

It was concluded that the main unpolymerized compounds obtained on treating methyl sterculate with palladium (Fig. 1, Fraction C) were methylene-substituted, conjugated octadecenoates. Some other fractions were rich in methyl substituted, conjugated octadecadienoates. The main structures resulting from the cleavage of the cyclopropene ring are believed to be those shown in Figure 2.

Structures III and IV in Figure 2, which were believed to have produced Peak C of Figure 1 amounted to over 50% of the unpolymerized reaction product. There is evidence that the compounds responsible for Peak C contained a *trans* double bond in the chain and that Peak D represented the *cis* isomers of structures III and IV. Structures VII and VIII are believed to be represented by B, while structures V and VI are represented by E. Small proportions of structures other than those shown undoubtedly were produced. However, little cleavage of the hydrocarbon chain occurred.

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