

Acetoxylation of Methyl Oleate with a Resin Catalyst¹

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Abstract

The reaction of methyl oleate with acetic acid in the presence of a reticulated cation exchange resin produces methyl acetoxyesterate. Saponification of this compound and subsequent acidification yields hydroxystearic acid. Time, temperature, acetic acid:ester ratio, and resin:ester ratio were examined for their effect on yield of methyl acetoxyesterate. A yield of approximately 45% of theory was reached under the best conditions. The cation exchange resin promoted ester interchange with the formation of oleic acid, acetoxyesteric acid, and methyl acetate. An estolide polymer was formed, probably by ester interchange between acetoxyated methyl oleate and oleic acid. Acetoxy esters were separated from unreacted methyl oleate and ester polymers by fractional distillation. Molecular weight and GLC data substantiate the product structure. Several other short-chain carboxylic acids were reacted with methyl oleate but gave lower yields of acyloxyated product than acetic acid.

Introduction

SYNTHESIS OF HYDROXY and dihydroxy fatty acids from oleic acid has been accomplished through several mechanisms. Deatherage and Mattill (1) synthesized dihydroxystearic acid through autoxidation of oleic acid to form an epoxy group across the double bond. After the ring was opened by reaction with a carboxylic acid, the resulting ester could be saponified to the dihydroxy acid. Knight and his associates (3) showed that 9,10-dihydroxy acids could be prepared from oxidized oleic acid which contained hydroperoxides. Wallace and co-workers (12) used polystyrene sulfonic acid ion exchange resins with hydrogen peroxide and acetic acid to obtain 9,10-dihydroxystearic acid directly. Roe and co-workers (8) prepared mono-hydroxystearic acid in good yields by sulfonation and hydrolysis. Fore and Bickford (2) synthesized an equimolar mixture of methyl 9- and 10-mono-hydroxystearic acid through the hydrogenation of methyl oleate. Several workers have shown that an unsaturated fatty acid could be formoxylated or acetoxyated by one of two means: a) addition of formic or acetic acid to the double bond in the presence of a strong acid catalyst (4,7), or b) reaction of hydrogen peroxide with formic or acetic acids to form the peracid intermediate which reacts directly with the double bond (10,11).

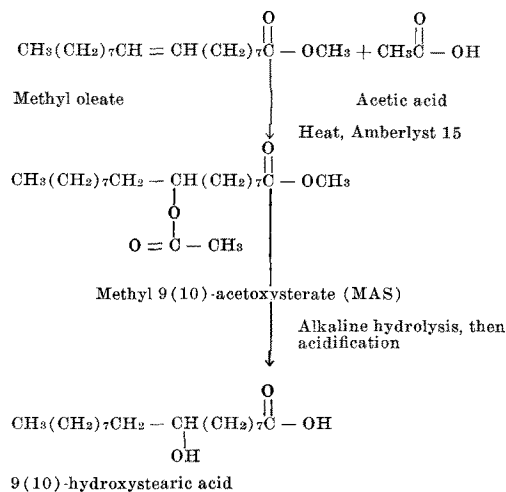
This paper describes a simplified method for the acyloxylation of methyl oleate and conversion of the product to the monohydroxy acid. Acetoxyated stearic esters may be efficient low-temperature plasticizers for poly(vinylchloride) (5).

Our preparation is similar to the acetoxylation procedures carried out above (4,7,10,11) except that the hydrogen peroxide or strong acid catalyst was replaced with Amberlyst 15 cation exchange resin (6,9,14).

Amberlyst 15 is a bead form, strongly acidic resin

that functions well in nonaqueous media and that possesses a so-called macroreticulated structure and therefore has a high degree of true porosity. The resin has excellent resistance to various types of attrition in spite of its high porosity and will withstand prolonged exposure to temperatures of 150°C. It may be easily recovered after the reaction, washed with methanol, dried, and reused with essentially no loss in activity, provided it is not poisoned by organic peroxides or heavy metal inorganic salts (9).

The reaction of methyl oleate with acetic acid in the presence of a reticulated cation exchange resin yields methyl 9(10)-acetoxyesterate (MAS) as shown in the following equation:



The relative amounts of the 9- and 10-isomers were not determined but, by analogy to other similar methods of preparation, approximately equimolar amounts should be expected to be formed.

The reaction was conducted under controlled conditions for varying periods of time to yield acetoxy esters and fatty acids, unreacted esters, and acids and polymeric material. The acetoxyated product and unreacted materials were separated from the polymer by distillation. The fatty acids were formed by inter-esterification between fatty acid methyl esters and acetic acid, catalyzed by the resin. MAS was converted to monohydroxystearic acid by alkaline hydrolysis and acidification.

Experimental

MAS was prepared as follows: The reaction was carried out in a 2-liter, 3-necked, round-bottom flask equipped with a heating mantle, water condenser, thermometer and a Teflon stirring blade driven by a variable-speed motor. The stirrer shaft was fitted with a ground-glass seal to prevent evaporation of the boiling acid. Fifty grams of dry resin, then 100 g of commercial methyl oleate were added to the flask. Methyl oleate content, determined by gas-liquid chromatography (GLC), was 73%. A molar ratio of 50:1 glacial acetic acid to methyl oleate was added to the flask, and the stirrer speed was adjusted so that the resin was kept suspended in the acetic acid-methyl oleate solution. The mixture was refluxed for 8 hr, after which it was allowed to cool and the resin to

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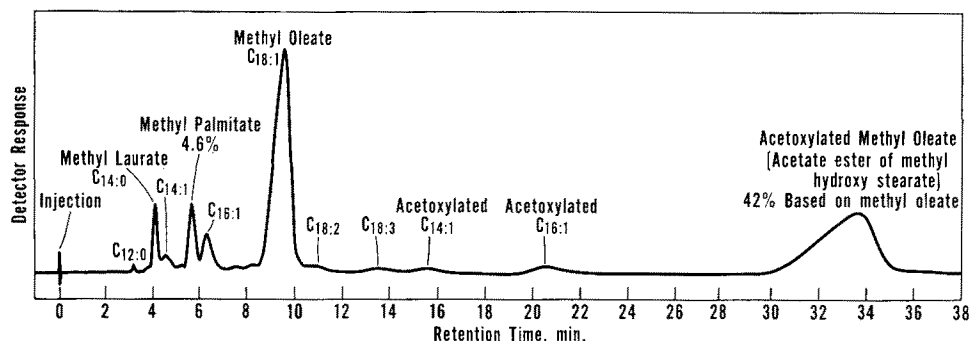


FIG. 1. Gas-liquid chromatogram of a sample of commercial methyl oleate after reaction with acetic acid in the presence of reticulated resin.

settle. The liquid was decanted into a 2-liter separatory funnel with 800 ml of water. Contents of the separatory funnel were thoroughly mixed, and the product layer was allowed to separate. After two more water washings the oil layer was dried with anhydrous sodium sulfate and filtered under vacuum. Although the final product was clear, its color was darker than the original methyl oleate.

The product was esterified by using methanol, dimethoxypropane, and 1% sulfuric acid to convert any fatty acids to esters, then analyzed by GLC (Fig. 1) on a 9-ft \times $\frac{1}{4}$ in. stainless-steel column packed with 20% diethylene glycol succinate on 80/100 mesh Gas-Chrom P. The oven temperature was 225C with an injection temperature of 300C and a detector temperature of 320C. The sensing device was a thermal conductivity detector. A flow rate of 75 cc/min was used for the carrier gas, helium.

In addition to quantitation of the peaks shown on the chromatogram, the amount of polymeric material retained on the column was calculated. The original methyl oleate contained 4.6% methyl palmitate, which was used as an internal standard. Nonvolatile material was calculated according to the following equation: $X = 100 [(C/P) - A]/(C/P)$ where

C = area count of methyl palmitate in the sample chromatogram

P = fraction of methyl palmitate in the original methyl oleate

C/P = total area count which should be present in the sample chromatogram if no polymeric material were retained on the column

A = actual area count present in the sample chromatogram

X = percentage of nonvolatile material

The esterified reaction product was separated into three portions by fractional distillation through a Vigreux column. The low-boiling fraction contained nearly all the unreacted material. The second fraction, which was collected over a boiling range of 158–178C at 13 μ pressure, was 97% pure MAS. The undistilled fraction was the nonvolatile polymeric material. Crystallization of the second fraction from acetone yielded pure MAS.

Results and Discussion

Ester Identification

The acetoxyated ester was identified by subjecting it to alkaline saponification, followed by acidification. Infrared analysis showed a strong OH absorption at 3300 cm^{-1} . The hydroxystearic acid was esterified by using an acid catalyst, methanol and dimethoxypropane and was then chromatographed. The reac-

tion product had a retention time 1.47 times that of the MAS but identical with that of methyl 9(10)-monohydroxystearate. The hydroxy ester and a standard sample of methyl 9(10)-monohydroxystearate were acetylated with acetic anhydride at room temperature by the method of West et al. (13). The two acetylated esters each yielded peaks with the same retention time as the original MAS.

The molecular weight of the acetoxyated ester was 350, as determined by vapor pressure osmometry (theory 356.5). A saponification equivalent run on the purified ester yielded a value of 180.2, almost exactly half of the molecular weight (theory 178.2).

Conditions for Maximum Yield

The effect on yield of varying acid:ester ratio, resin:ester ratio, and reaction temperature was studied. The effect of changing the acid:ester ratio (Fig. 2) was examined by reacting 100 g of methyl oleate and 25 g of dry resin with 10:1, 25:1 and 50:1 molar ratios of glacial acetic acid to methyl oleate. The reaction temperature was the boiling point of glacial acetic acid (118C), and reaction times were 2, 4, 8, 16 and 32 hr. A yield of 42% MAS was obtained after 32 hr with an acid:ester ratio of 50:1 while only 33% MAS was obtained with an acid:ester ratio of 10:1. The reaction rate curves were similar at all acid:ester ratios.

The effect of varying the resin:ester ratio (Fig. 3) was determined by reacting 965 cc of glacial acetic acid with 100 g of methyl oleate (50:1 molar ratio) with 1:1, 1:2 and 1:4 weight ratios of dry resin to methyl oleate. The reaction was carried out at 118C for 2, 4, 8, 16 and 32 hr. The higher the ratio of resin

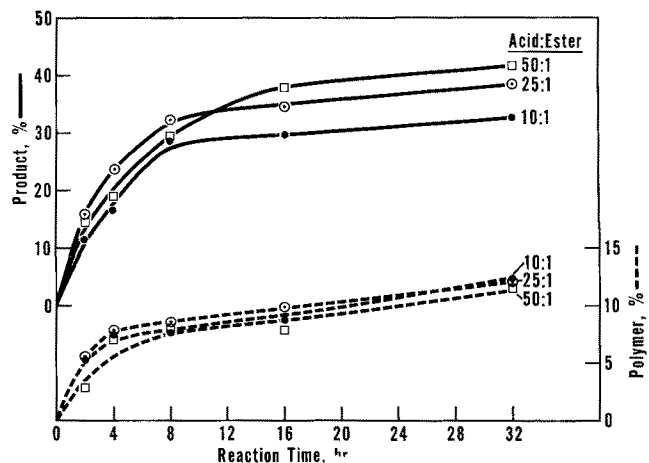


FIG. 2. Effect of reaction time and acid:ester ratio on yields of acetoxyated product and polymeric material.

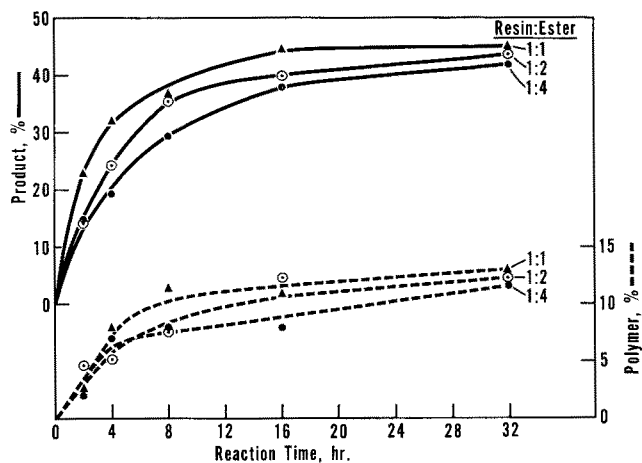


FIG. 3. Effect of reaction time and resin:ester ratio on yields of acetoxyated product and polymeric material.

to ester, the faster the reaction proceeded. However, after a 32-hr reaction period, the yields of MAS were similar regardless of the resin:ester ratios.

The effect of reaction temperature (Fig. 4) was examined by reacting 100 g of methyl oleate, 965 cc of glacial acetic acid, and 25 g of dry resin at 100, 118, and 140°C (2 atmospheres pressure) until the reaction neared completion. As expected, the lower temperatures gave much slower reaction. Our studies indicate that to produce maximum yield of MAS (45%) in a minimum time (8 hr), without using a pressure vessel, the methyl oleate should be reacted with a high ratio of acid:ester (50:1) and a high ratio of resin:ester (1:1) at the boiling point of acetic acid (118.6°C).

The formation of fatty acids by ester interchange has been found to occur during the reaction. A direct correlation was found between the quantities of fatty acids produced and the amounts of acid and resin used and the reaction time and temperature.

The reaction also produces 10–15% polymer (Fig. 2–4), and only slight correlation is observed between

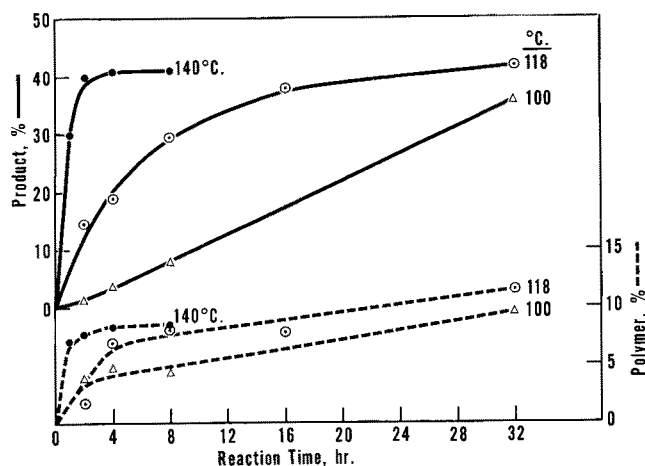


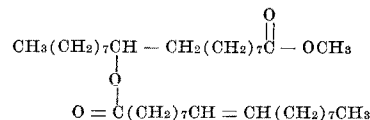
FIG. 4. Effect of reaction time and temperature on yields of acetoxyated product and polymeric material.

the amounts of acid and resin in the reaction and the amount of polymer formed.

Acyloxylation with Other Acids

Several carboxylic acids other than acetic acid were tried; however yields were lower. The resin did not catalyze the reaction between formic acid and the methyl oleate. Monochloroacetic acid produced either a compound of low volatility which would not elute from the chromatograph or extensive polymer formation. Propionic and butyric acids reacted similarly to acetic acid to form their respective acyloxyated products but, as would be expected, their yields were lower. When octane was added to the acetoxylation reaction as a diluent, final yields were the same, but a longer reaction time was required.

The nonvolatile polymer fraction probably contained some dimer believed to be an estolide.



This estolide is formed from the interchange reaction of acetoxyated methyl oleate with oleic acid, as evidenced by the hydroxystearic acid and oleic acid obtained from saponification of the polymer. A small amount of methyl linoleate present in commercial methyl oleate may have reacted with the acetic acid at both double bonds to yield methyl diacetoxyate but, if formed, this was not eluted from the GLC column.

This acetoxylation reaction has also been applied to the methyl esters of soybean oil. In addition to MAS, the soybean methyl esters yielded a monoacetoxyated octadecenoate and a monoacetoxyated octadecadienoate. The identity of these compounds was established by acetoxyating pure methyl octadecadienoate and methyl octadecatrienoate and comparing them by GLC with the soybean product. On hydrogenation of the mixture, the unsaturated products were converted to MAS and gave a single peak by GLC. The products derived from the acetoxylation of soybean methyl esters were not completely characterized.

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