A Convenient Preparation of 10-Hydroxydecanoic Acid

ABSTRACT

The alkaline cleavage of ricinoleates may be carried out in ethanol at temperatures of 190-200 C using two to three equivalents of NaOH to give yields up to 69% of pure 10-hydroxydecanoic acid. This method avoids the use of large excesses of alkali as well as the use of high boiling alcohols as reaction media.

Formation of 10-hydroxydecanoic acid by causic fusion of ricinoleates suffers from a number of preparative disadvantages. Alkaline fusion at temperatures lower than those used for production of sebacic acid, i.e., 180-200 C, gives a low yield of hydroxy acid (1). Base treatment in the presence of a high boiling alcohol such as 2-octanol gives much better results, presumably because of the reducing capability of the added alcohol (2,3). However the large excess of this material must be removed during workup. Additionally the amount of NaOH used (up to 8.5:1 over ricinoleate) presents considerable neutralization problem. The method described here eliminates both of these objections and provides a convenient laboratory procedure for preparation of 10-hydroxydecanoic acid. The easily removable solvent, ethanol, is used as reaction medium and reducing agent, and a much lower base ratio is employed.

In this investigation a 300 ml stainless steel autoclave equipped with glass insert was routinely used as a suitable reaction vessel. Some etching of the glass occurred during each run, but the liner remained usable after 10 runs. An ordinary laboratory oven was used to heat the container, and no agitation was found to be necessary.

In a typical experiment we placed 46.8 g (150 mmoles) of methyl ricinoleate and a solution of 12.0 g (300 mmoles) of NaOH in 100 ml of 95% ethanol. The autoclave was placed in an oven at 190-200 C for 16-18 hr and then cooled to room temperature, vented to remove a certain amount of ethylene (identified by its mass spectrum) produced during heating and opened. After dissolving the semisolid contents in about 500 ml of water, the resulting solution was extracted with three 200 ml portions of ether to remove neutral material. This step may be omitted if it is not desired to retain the 2-octanol formed as coproduct. The aqueous phase was then acidified with 30 ml of concentrated hydrochloric acid, and the liberated acids extracted with two 200 ml portions of ether. After drying over magnesium sulfate and evaporation under reduced pressure to give about 35 g of solid, the crude acids were then dissolved in 100 ml of warm ethyl acetate and 100 ml of heptane was added. After standing overnight at 0 C the mixture deposited 20.2 g of crystals, mp 71.5-74.5 C which on recrystallization from benzene, 140 ml, yielded 19.4 g (104 mmoles, 69%) of 10-hydroxydecanoic acid, mp 73-75 C (lit. 75-76 C [4]).

The above conditions are optimal when methyl ricinoleate is utilized, but the cleavage will proceed at lower temperatures. At 160 C about 41% yield of product was obtained after approximately the same reaction time. Prolonged heating at 190-200 C did not give a higher yield, nor did higher temperatures appear to be beneficial. Neither did it appear necessary to use a base ratio higher than 2:1. The conditions described may be applied to ricinoleic acid; however, the amount of water present in the medium appears to be critical, and 100% ethanol must be used in this case to obtain maximum yields. Sodium ricinoleate may be cleaved in 95% ethanol using one equivalent of added hydroxide. Castor oil may also be used, but best results are obtained with three equivalents of sodium hydroxide for each equivalent of ester in the glyceride, and absolute ethanol is necessary for best results. In none of the examples mentioned does sebacic acid appear as contaminant in the final product.

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The mass spectrum of ethylene was obtained by W.F. Haddon of this laboratory.

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High Resolution NMR for Purity Determination of Cyclopropenoid Concentrates

ABSTRACT

High resolution nuclear magnetic resonance is proposed as a method for assaying the cyclopropenoid concentration of methyl sterculate and methyl malvalate concentrates. Spectra obtained on a 220 MHz instrument are analyzed and compared with that obtained on a 60 MHz instrument. Calculation of cyclopropene concentration based on methoxy protons and cyclopropene protons is discussed.

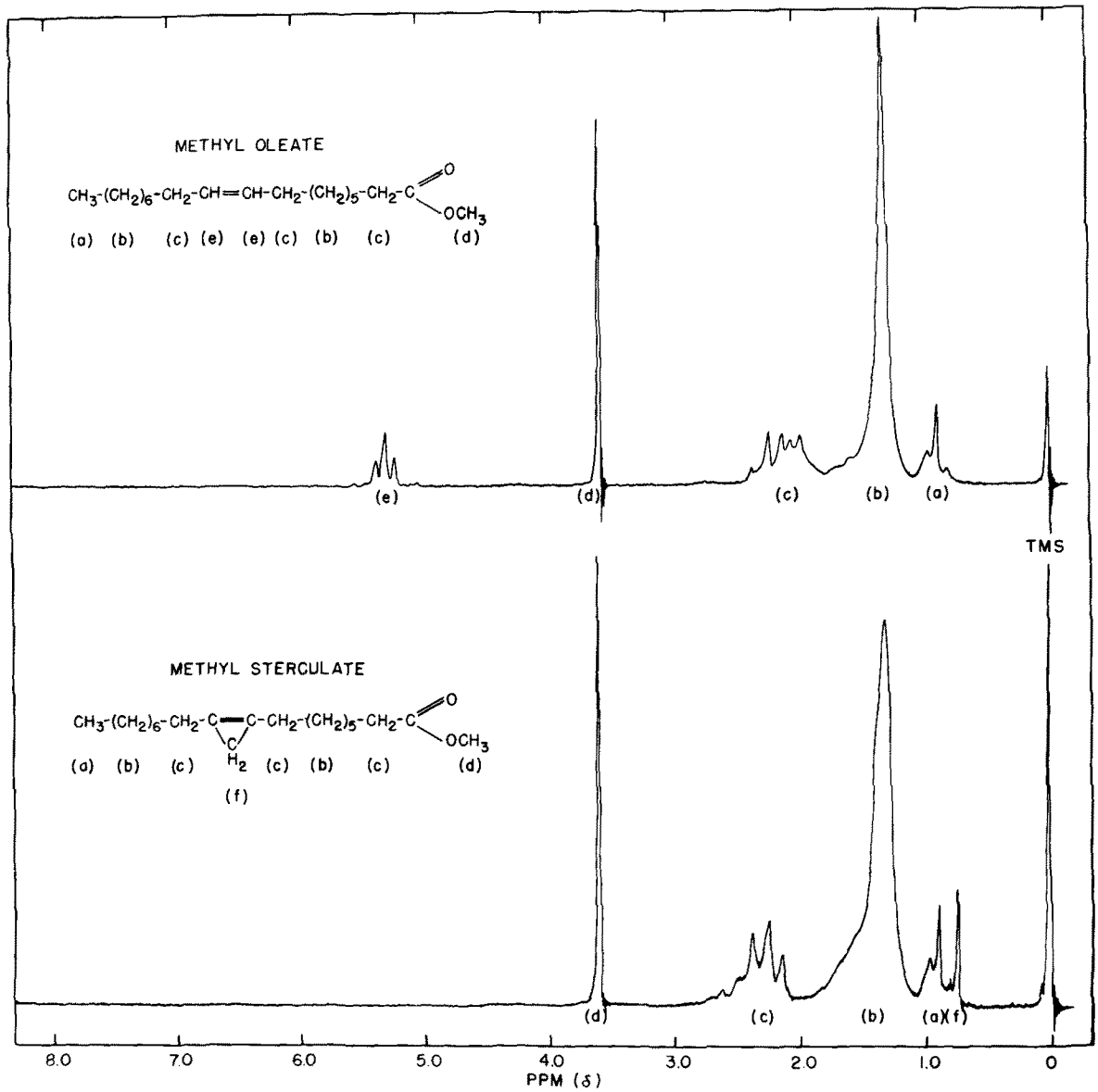

FIG. 1. 60 MHz spectra of methyl oleate and methyl sterculate.

Numerous methods have been proposed for the analysis of the cyclopropenoid fatty acid esters—methyl sterculate and methyl malvalate. The HBr and modified HBr titration procedures (1-3) rely on a stoichiometric reaction between HBr and the cyclopropene ring. The modified Halphen test methods, which involve a complicated color reaction (4,5), are based in turn on an HBr standard. Each of the procedures is reported to give good results for specific applications (6), but none is specific for either ester alone without prior knowledge of its identity. Gas liquid chromatographic procedures have been developed but appear to lack reliability. Elaborate techniques have been proposed for structure identification but are poorly applicable to purity analyses. In the present report high resolution nuclear magnetic resonance (NMR) at 220 MHz is proposed as a method of establishing the purity of methyl sterculate and methyl malvalate concentrates.

Methyl oleate is one of the major impurities found in cyclopropenoid concentrates. Ordinary high resolution NMR (60 MHz) gives spectra (Fig. 1) in which the olefinic methine protons are easily identified at 5.5 ppm down field from tetramethylsilane (TMS), and the quantity present can be estimated by a proton count. On the other hand the cyclopropene methylene protons, although readily identified at 0.73 ppm, are not sufficiently resolved from the chain methylene protons at 1.3 ppm to allow an accurate proton count to be made. Spectra obtained on a 220 MHz instrument exhibit much better resolution and provide significantly more information. Illustrated in Figure 2 are spectra for methyl sterculate obtained on 60 and 220 MHz instruments. Whereas the protons *beta* to the cyclopropenoid and carbonyl groups and those adjacent to the other methylene protons have nearly the same chemical shifts and are only partially resolved in the 60 MHz spectrum, they are seen as two distinct signals at 1.3 ppm and 1.5 ppm, shifted to the terminal methyl, 0.87 ppm, and the cyclopropenoid, 0.73 ppm, protons in the 220 MHz spectrum.

It is interesting to note that those protons *alpha* to the carbonyl and *alpha* to the cyclopropenoid group are seen as two partially resolved triplets at ca. 2.4 ppm. With the improved resolution and in the absence of signals indicative of impurities, the cyclopropenoid composition can be calculated based on a proton count with the total protons being indicative of the carbon chain length. The ratio of methoxy to cyclopropene or cyclopropene plus terminal methyl protons would be precisely 3:2 or 3:5, respectively, and the ratio of methylene to methoxy protons would be 28:3 or 26:3 for either pure methyl sterculate or pure methyl malvalate. Pure methyl sterculate analyzed by this

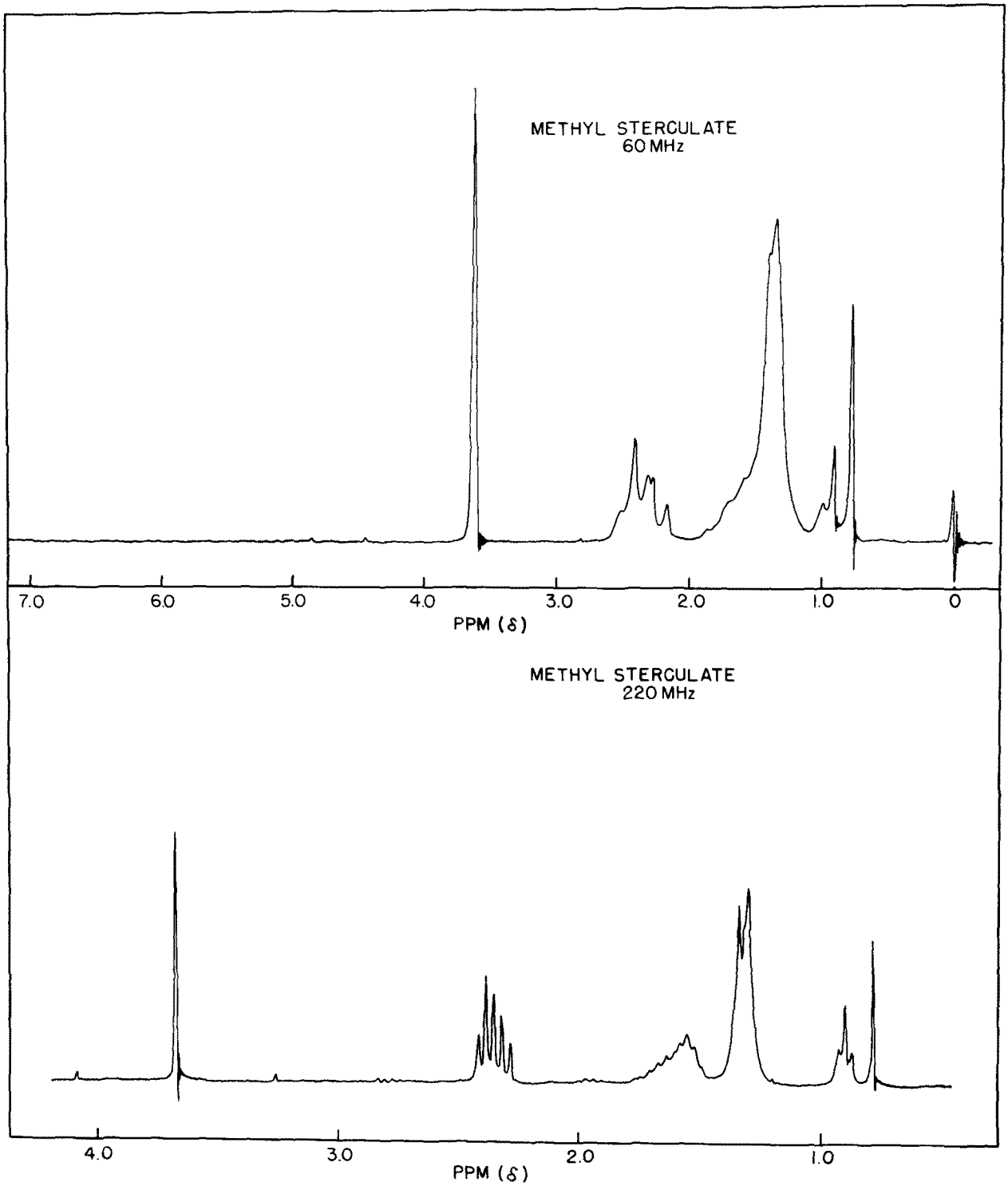

FIG. 2. 60 and 220 MHz spectra of methyl sterculate.

procedure was indicated to be greater than 98% pure as compared to 100% by the HBr titration method. The procedure, which cannot claim high precision because of the inherent instrumental error in integrating the area under the curve, is suggested as a rapid, nondestructive method for assaying the purity of methyl sterculate and methyl malvalate concentrates.

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