

HYDROLYSIS AND HYDROXYLATION OF CASTOR OIL TO TRIHYDROXY HEPTADECANOIC ACID

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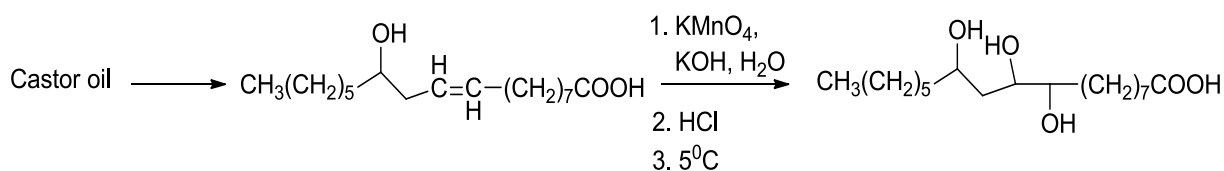
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ABSTRACT

Castor oil was hydrolysed with potassium hydroxide. The ricinoleic acid released was hydroxylated without first isolating the free acid to obtain trihydroxy heptadecanoic acid in good yield. The product obtained was confirmed with the aid of FTIR spectroscopy.



Key words: Hydrolysis, hydroxylation, castor oil, trihydroxy heptadecanoic acid

INTRODUCTION

Castor oil is the natural source of ricinoleic acid. Ricinoleic acid is about 80% of castor oil. Ricinoleic acid is hydrolysed to trihydroxy heptadecanoic acid using potassium permanganate in alkaline condition. The same alkaline conditions required for the hydrolysis of castor oil to yield ricinoleic acid. It was previously reported (Hill and Mc Ewan, 1933) that ricinoleic acid polymerizes if allowed to stand and hence causes a decrease in yield upon hydroxylation. We decided to carry out the hydrolysis and hydroxylation reactions simultaneously without first isolating the ricinoleic acid. This will be a very useful industrial process in production of polyhydroxy fatty acids (Polyols) or polyurethanes as it eliminates several unnecessary steps.

MATERIALS AND METHODS

Experimental

5.0g of castor oil was added to a solution of 4.5g (0.080mol) of KOH in 50mL of 95% ethanol. The mixture was placed in a 250mL flask equipped with a reflux condenser and refluxed for 1hr. The solution was allowed to cool to room temperature and then it was poured into 800mL of ice water and 200g of crushed ice. With the mixture maintained at 5°C, a solution of 4.0g (0.0253mol) of potassium permanganate in 80mL of water was added as rapidly as possible while stirring vigorously. After five minutes, the mixture was decolorized with KHSO₃. 80mL of 1 molar Hydrochloric acid solution was added and the mixture cooled in ice-water for a further 1 hr. The precipitate was filtered and dried at room temperature in a vacuum desiccator to give 3.58g (72 %) of trihydroxy heptadecanoic acid, m.p. 141-

143⁰C. FTIR (cm⁻¹, nujol mull): 1744(C=O), 2855(CH₃), 2982 (CH₂), 3300-3600 broad (-OH, -COH).

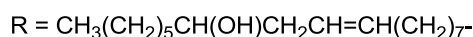
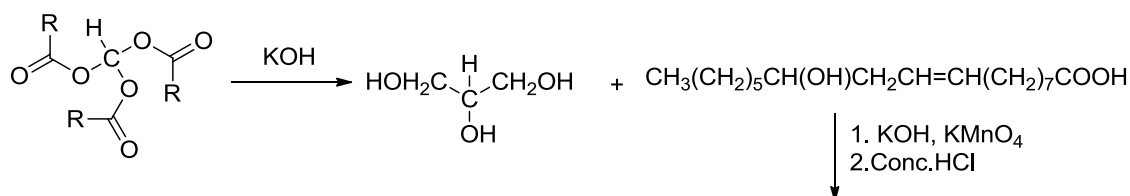
RESULTS

3.58g (72 %) of trihydroxy heptadecanoic acid was obtained with the melting point between 141 and 143⁰C. FTIR (cm⁻¹, nujol mull): 1744(C=O), 2855(CH₃), 2982 (CH₂), 3300-3600 broad (-OH, -COH).

DISCUSSION

A quantitative yield of over 70% indicates that this procedure is appropriate if the objective is the preparation of the trihydroxy derivative of ricinoleic acid. The by-products: glycerol and saturated fatty acids remained in the aqueous solution or remain as oily liquid while the product was isolated as solid precipitate.

When the FTIR spectra of raw castor oil is compared to that of the product, the band

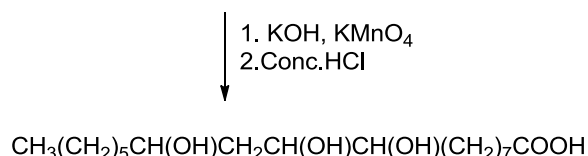


due **CH=CH**hydrogen atoms at 3008 cm⁻¹ are not found.

The alternative procedures for oxidation of fatty acid double bonds – epoxidation and catalytic ring opening or epoxidation and ring opening prior to hydrolysis (Chen *et al*, 2015, Dahlke *et al*, 1995) is not suitable for simultaneous hydrolysis and hydroxylation.

Another advantage of this procedure is that if ricinoleic acid is isolated and allowed to stand, polymerization occurs. Hill and McEwan (1933) reported that the polymerized acid gives very poor yields in the oxidation by nitric acid.

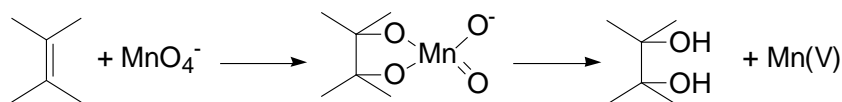
A relatively high concentration of the alkali is required for the hydrolysis of the triglyceride, neutralization of the OH group already present in the fatty acid moiety as well as the incipient carboxylic acid of the ricinoleic acid.



The permanganate oxidation of the double bond to obtain the trihydroxy acid also requires an alkaline medium.

According to Wiberg and Saegerbarth (1957), Wagner, Boeseken and Criegee, were the earliest workers on the permanganate oxidation of olefins to diols.

They proposed that a *cis* diol is formed through an intermediate cyclic ester in alkaline conditions i.e. Lapworth and Motram conditions: 1.45 KMnO₄: 1.00 olefin bond (Wiberg and Saegerbarth, 1957). This mechanism has been accepted and is the basis of most permanganate oxidation of double bonds today.



It is generally known that the oxidation of olefins in the presence of permanganate results in either a diol or a cleavage of the double bond depending on the reaction temperature. Oxidation at near zero temperature results in the formation of the dihydroxy product while oxidation at elevated temperatures result in the cleavage of the olefins into corresponding aldehydes or ketones. The decolourization of the permanganate in the mixture can also be achieved with NaHSO_3

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