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SYNTHESIS AND CHARACTERIZATION OF ESTER FROM DIHYDROXYSTEARIC ACID

The esterification of dihydroxystearic acid as a source of hydroxy fatty acid and monohydric fatty alcohols (C8-C18) was successfully carried out. The reaction was done at 180°C in the absence of catalyst and the yield of the ester obtained was 80%-96%. The products were analysed by infrared spectroscopy, and some of their physical properties determined.

Keywords: Esterification, dihydroxystearic acid, fatty alcohol.

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INTRODUCTION

Hydroxy fatty acids and their derivatives are used in cosmetics, lubricants, paints, coating, and food industries. They are useful intermediates in the synthesis of fine chemicals and pharmaceuticals (Ghosh and Bhattacharyya, 1992; Weber *et al.*, 1995).

Hydroxy fatty acids occur in appreciable proportions in the seed oils of some higher plants. For example, castor oil contains ricinoleic acid, which incorporates a hydroxyl group at C12. Hydrogenation of ricinoleic acid gives 12-hydroxystearic acid. Hydroxy stearate is usually known in the form of wax esters, where its major application is in the manufacture of multipurpose grease. High-pressure lithium-based greases derived from hydrogenated castor oil are used as a gelling agent for performance improvement. Such greases have higher drop points, more resistant to water and gives better lubricity, which are important for automotive and military uses (Naughton, 1974).

Wax esters can be produced by hydrogenating castor oil fatty acid esters, or by reacting a, fatty acid and an alcohol directly at a higher temperature, in the presence of catalyst. In the present study, ester from dihydroxystearic acid was synthesized. The effect of alcohol chain lengths on the esterification reaction, and some physical properties of the ester were studied.

MATERIALS AND METHODS

Materials

Dihydroxystearic acid was prepared in the laboratory. Fatty alcohols, such as octanol, dodecanol and octadecanol were purchased from Sigma Chemicals, whereas decanol, tetradecanol and hexadecanol from Merck. All the other reagents were of analytical grade and used as received.

Esterification Process

The esterification was carried out in a three-necked round bottom flask equipped with a magnetic stirrer, a thermometer, an inert gas inlet tube and a condenser. Fatty alcohol was placed in a reaction flask and heated until melted. Dihydroxystearic acid was heated separately and then added to the reaction flask. The reaction mixture was heated to the desired temperature. An oil bath was used to maintain a constant temperature. The reaction mixture was stirred continuously under dry nitrogen atmosphere, for a predetermined reaction period.

Several sets of experiments were carried out under different conditions to standardize the process variables. The percentage esterification was calculated by the following equation.

$$\% \text{ Esterification} = [(B-A) \times 100]/B$$

Where

A = free fatty acid remaining in the sample

B = free fatty acid in the unreacted sample

Analytical Methods

The products obtained were tested for different physical properties. The acid value was determined using AOCS Official Method Te 1a-64 and iodine value using AOCS Official Method Tg 1-64. Determination of the slip melting point and the saponification values were carried out using PORIM's Test Methodp3.1 andp4.2 (1995).

RESULTS AND DISCUSSION

To prove that esterification had occurred, infrared (IR) spectra of the starting materials and final products were compared (Figure *1*). In the IR spectra of the product, an OH absorption band at 3340-3302 cm^{-1}, indicating that the hydroxyl group of the parent acid was retained and unaffected by the reaction. The absorption band at 1709 cm^{-1} assigned to C=O stretching in the IR spectrum of the starting material, has shifted slightly to 1736 cm^{-1} after esteritication, which suggested the fact that the reaction has already taken place. Other absorption peaks were quite similar, indicating that the overall structure of dihydroxystearic acid was retained during the reaction.

Several sets of experiments with different variables were carried out to optimize the esterification (Figures 2 to *5*). The maximum yield was obtained from the reaction carried out at 180°C with the mole ratio of 1:2 (dihydroxystearic acid to alcohol). The suitable reaction time was found to be 420 min. It was also indicated by ***Figures*** 4 and 5 that by varying the ratios of the reactants, the initial rate of the esterification process was also affected. However, the rates of the reaction for the fatty alcohols despite their chain lengths were quite similar.

The physical properties of the crude esters are presented in ***Table*** I. The slip melting points gradually increased by 4°C-6°C, possibly due to the presence of the additional $-CH_2-CH_2-$ group in the product obtained from various fatty alcohols with various chain lengths from C8-C18 carbon. The saponification value decreased with increasing chain length of the alcohol part of the ester. The iodine value showed an inverse relationship with increasing molecular weight. This was in agreement with the results reported by Ghosh and Bhattacharyya (1992).

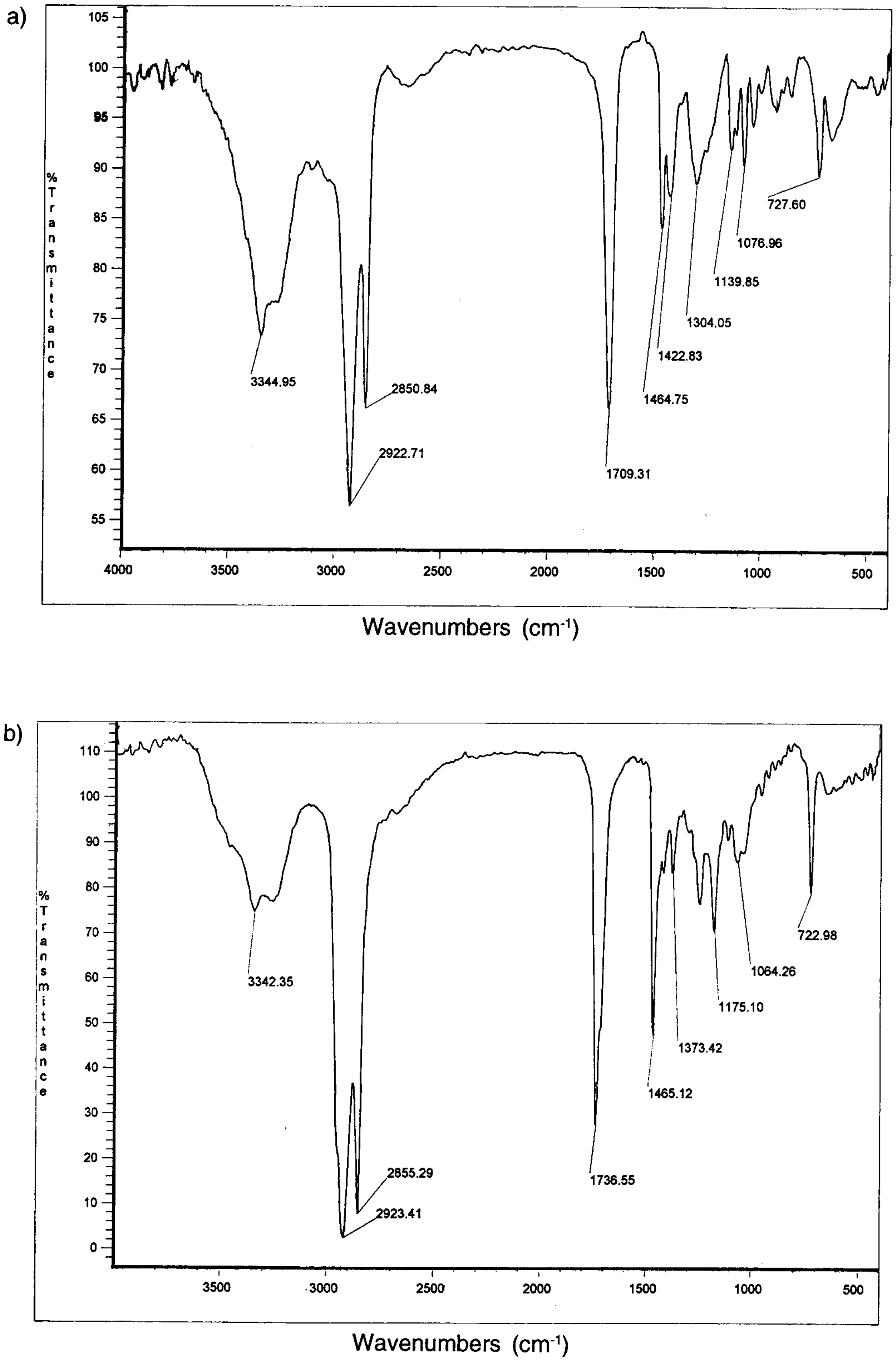

Figure 1. Infrared spectrum of (a) dihydroxystearic acid and (b) product obtained.

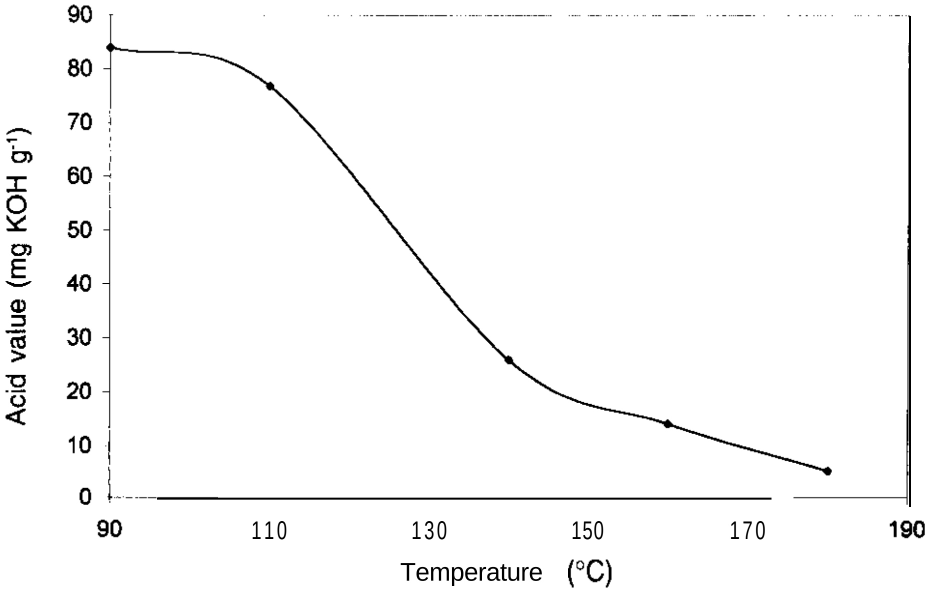

Figure 2. Effect of temperature on acid value.

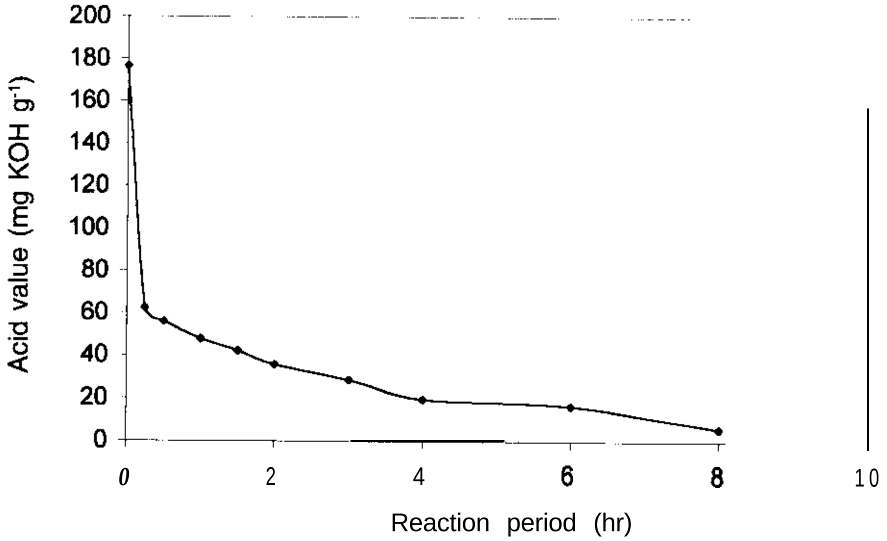

Figure 3. Effect of reaction time on acid value.

Based on the above results, we have successfully shown that the dihydroxystearic acid can be esterified with long chain fatty alcohol quite easily without affecting the parent hydroxyl group. The direct esterification route is also found to be economically viable.

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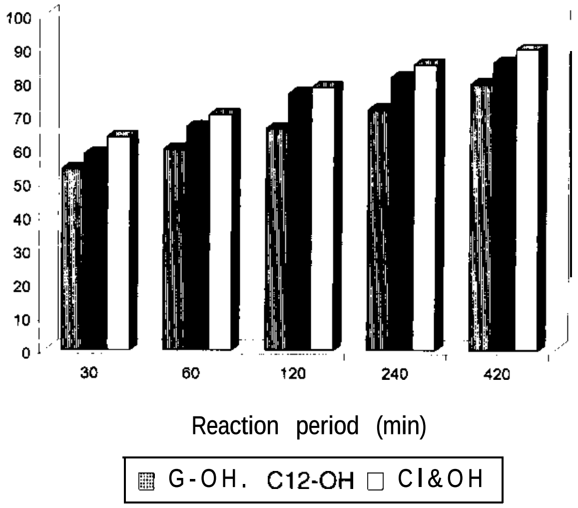

Figure 4. Percentage esterification ofdihydroxystearic acid with different fatty alcohols as a function oftime (1:1 mole ratio of acid and alcohol).

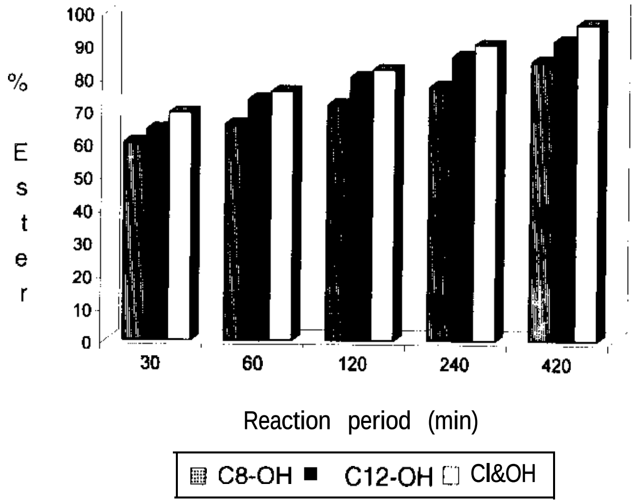

Figure 5. Percentage esterification ofdihydroxystearic acid with different fatty alcohols as a function oftime (1:2 mole ratio of acid and alcohol).

TABLE 1. PHYSICAL PROPERTIES OF DIHYDROXYSTEARIC ACID ESTERS

Characteristics	**Dihydroxystearic acid ester**					
	C8	**C10**	**C12**	**C14**	**C16**	**C18**
Slip point (°C)	35.1	**40.8**	**44.3**	**48.6**	**53.0**	**57.8**
Iodine value	15.8	**13.3**	**11.9**	**11.0**	**10.9**	**10.2**
Sap. value	183.0	178.0	166.0	149.0	142.0	131.0

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