

DESCRIPTION

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TITLE

Preparation of dihydroxy compound from unsaturated raw materials.

TECHNICAL FIELD

The present invention relates to a process for the preparation of dihydroxy compound using palm fatty acid or unsaturated hydrocarbon as the starting materials.

BACKGROUND ART

Hydroxy fatty acids have great interest to the industry because of their different behavior compared with ordinary fatty acids. Hydroxy fatty acids and their derivatives have many applications, *e.g.*, as additives in lubricants, in cosmetics, and surfactants. Their uses as a corrosion inhibitor in lubricants (German Patent DE 3203491 A1) and as auxiliaries for the textile industry (German Patent DE 3638918 A1) have been investigated. Currently, the main source of hydroxy acids supplied by nature is castor oil. Ricinoleic acid (12-hydroxy-9-octadecenoic acid) is present in castor oil at ca. 90%.

Because castor oil is not available in Malaysia, other means to produce the compound need to be studied. Preparation of hydroxy fatty acids by functionalization of the alkyl chain of unsaturated fatty acids derived from common triglycerides (fats and oils) offer an alternative. Oleic acid (9-octadecenoic acid) is an important raw material for preparing this type of compound. It can be obtained by splitting oils/fats containing the acid, for example, tallow (50% oleic acid), tall oil (45% oleic acid) and palm oil (40% oleic acid).

A number of di- or poly-hydroxy fatty acid compounds have been synthesized from mono or polyunsaturated fatty acids using oxidants/catalysts such as selenium oxide/*tert*-butyl hydroperoxide, hydrogen peroxide/tungstic acid, ruthenium tetroxide and osmium tetroxide. The oxidants convert unsaturated fatty acid to an epoxide or

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epoxides and this (these) is (are) then hydrolyzed to the di- or poly-hydroxy compounds. The epoxide ring can be catalytically-opened by adding acetic (US patent 2,443,280) or formic acid (US patent 4,101,589 & European patent EP 0025944031), which led to saponification of the esters to results in the desired vicinal diols. The hydroxylation of monounsaturated fatty acid by oxidant such as osmium tetroxide is a well-known reaction. However, this system suffer from several disadvantages including overoxidation of the diol to cleavage products, the tedious removal of reduced oxidants and the chemical used is expensive and toxic.

A US patent, application No. 4,851,593 reported that dihydroxy and polyhydroxy fatty acid compounds can be obtained from polymerized fatty acids by a liquid phase reaction at a temperature at about 260 °C (500 °F) to about 343 °C (650 °F), pressure up to about 1000 psi in the presences of a catalytic amount of hydrogenation catalyst.

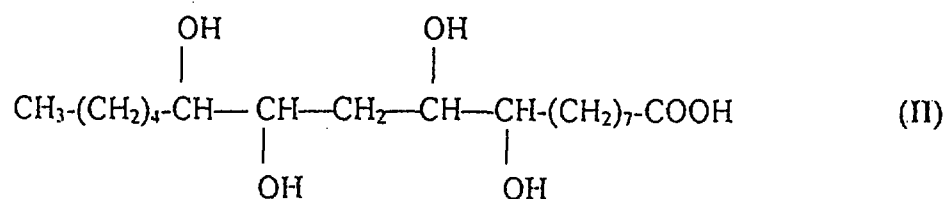
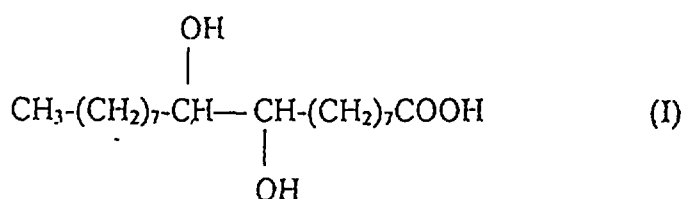
The oxidation of the alkali metal salts of oleic and undecylenic acid with ruthenium and osmium tetroxide is also reported by other researchers. With osmium tetroxide, hydroxylation of the double bond of potassium olcate gives a yield of *erythro*-9,10-dihydroxy stearic acid. The osmium tetroxide oxidation of sodium undecylenate results in the formation of 10,11-dihydroxy undecanoic acid and the cleavage product sebacic acid in varying yields.

Hydrocarbon lacking a full complements of hydrogen atoms, and thus characterized by one or more double or triple bonds between carbon atoms. Hydrocarbons having only one double bond between adjacent carbon atoms in the molecule are called olefin. Unsaturated hydrocarbons readily attract additional hydrogen, oxygen, or other atoms, and are therefore highly reactive. Linear alpha olefins are highly versatile chemical intermediates and base fluids for a number of applications-from detergents and cleaning products to oil field drilling mud. As co-monomers in the production of polyethylene, alpha olefins also offer clarity and flexibility to plastic products. The low potential for environmental impact enhances the appeal of linear alpha olefins.

SUMMARY OF THE INVENTION

I) Unsaturated Fatty Acids to Dihydroxy Fatty Acids (DHFA)

An object of the present invention is to provide a dihydroxy fatty acids (DHFA) based on palm based oleic acid and a cheaper process for preparing the compound. The compound can be converted to surfactants, emulsifiers and lubricants and also useful in the formation of urethanes. According to the fatty acids compositions of the oleic acid used, therefore the product of the invention is not only 9,10-dihydroxy stearic acid (9,10-dihydroxyoctadecanoic acid) but also 9,10,12,13-tetrahydroxy stearic acid (9,10,12,13-tetrahydroxyoctadecanoic acid) or other side products and are represented by the formula (I) and (II)



Due to the development of oleochemical industry in Malaysia, palm based unsaturated fatty acids (especially oleic acid) is easily available and provides an easy source of raw materials for this invention. However, this invention is applicable to oleic acids derived from other types of oils/fats.

Palm based oleic acids or oleic acids derived from other oils/fats are seldom pure. Besides oleic acid (C 18:1), they also contain saturated fatty acids of various chain lengths (C8, C10, C12, C14, C16, C18 and C20), unsaturated fatty acids especially linoleic (C18:2) and linolenic acids (C18:3) and they are in various percentages. The fatty acids compositions (FAC) of an oleic acid sample can be determined by Gas Chromatography [AOCS Method] while the degree of unsaturation present can be measured using Iodine Value (IV) [AOCS Method]. Other chemical characteristics used to identify oleic acid are Saponification Value [AOCS Method] and Acid Value [AOCS Method].

Below are the chemical characteristics of palm based oleic acid produced in Malaysia.

Table 1: Characteristic of Palm Based Oleic Acid Produced in Malaysia

PARAMETERS	RANGE
FATTY ACIDS COMPOSITION	
C 8:0	0.1-0.8
C10:0	Trc-1.2
C12:0	0.9-2.4
C14:0	0.3-1.5
C16:0	3.1-5.5
C16:1	0.1-0.3
C18:0	1.2-7.6
C18:1	71.4-78.0
C18:2	11.8-17.3
C18:3	Trc-0.6
C20:0	0.1-0.5
Others	To 100
IODINE VALUE ($g\ I_2/100g$)	87-95
ACID VALUE ($mg\ KOH/g$)	180-204
SAPONIFICATION VALUE ($mg\ KOH/g$)	182-203

Hydroxylation of unsaturated palm fatty acids with peroxyacetic acid was chosen in this invention. The use of peroxyacetic acid as an oxidant has an advantage because the chemicals are inexpensive compared to other oxidants/catalysts and the oxidation process can be carried out under mild and controlled conditions therefore, reducing the possibility of overoxidation. In contrast to the previous inventions, the epoxide ring is

catalytically opened by hydrolyzing the epoxidized compound in acid solutions of very low concentrations (0.1%).

II) Unsaturated Hydrocarbons to Diols

An object of the present invention is to provide a dihydroxy compound (diol) which is useful as starting material for other downstream products, mainly esters. Alpha olefin was used as starting material in this invention. Diols can be obtained from alpha olefin via epoxidation of the olefin with peroxyacetic acid, followed by hydrolysis of the epoxide to corresponding diol. Alpha olefin is cheap product that is also used in the personal care industry in the form of the sulphonated products.

DETAILED DESCRIPTION OF THE INVENTION

The present invention involves a two-step process. The first step is the preparation of peroxyacetic acid by reacting glacial acetic acid with hydrogen peroxide (30% to 50%) in the presence of a catalyst. A ratio of 2.06:1 glacial acetic acid to hydrogen peroxide in the presence of 1% to 2% catalyst gave the highest peroxyacetic acid content. Once the formation of peroxyacetic acid is completed, the catalyst is neutralized with sodium acetate and the actual weight of peroxyacetic acid available in the mixture is determined.

In the second step of this inventive process, the peroxyacetic acid prepared in step (I) is reacted to the oleic acid. Based on the percentage of the peroxyacetic acid obtained and iodine value of oleic acid used, the required amount of oleic acid to react with the available peroxyacetic acid is calculated. Generally, the reaction is carried out within a temperature range of 60°C to about 95°C but most preferably in the range of 75°C - 80°C. The mole ratio of peroxyacetic acid to oleic acid is in the range of 0.5:1.0 to about 1.5:1.0, preferably from 0.75:1.0 to about 1.0:1.0. When the addition of peroxyacetic acid is completed, the reaction mixture is allowed to stir, typically for about 0.5 to 3 hours, most preferably from 1.5 to 2 hours.

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EXAMPLE 1

Preparation of Peroxyacetic Acid

Glacial acetic acid (968.8 g) and 18.8 g sulfuric acid were mixed in a passivated apparatus, heated and maintained at 40°C. 889.6 g of hydrogen peroxide was then added at a rate of 50-60 g per minute with continuous stirring. During the addition the temperature would increase. It is necessary to regulate the temperature increased and it should be maintained at 60-65°C. When the addition was completed, the mixture was allowed to stir for an additional 4 hours after which a maximum percentage of peroxyacetic acid would be obtained. The catalyst was then neutralized with 26.8 g sodium acetate.

Preparation of Dihydroxy Fatty Acid

Based on the percentage of the peroxyacetic acid obtained, iodine value of oleic acid used, and the mole ratio of peroxyacetic acid to oleic acid is 1.0:1.0, the required amount of oleic acid to react with the available peroxyacetic acid is calculated (Appendix 1).

Oleic acid (1280.5 g) was placed in a round bottom flask, equipped with a mechanical stirrer. Peroxyacetic acid was then added dropwise to oleic acid with continuous stirring. When the addition of peroxyacetic acid was completed, the mixture was stirred for 2 hours and the temperature maintained at 75°-80°C. The reaction mixture was separated from unreacted peroxyacetic acid and poured into an excess of water and heated under reflux for 1 hour. The product was then washed several times with distilled water and dried over anhydrous sodium sulphate.

The product obtained has a hydroxyl value of about 220.3; an acid value of about 167.5; a saponification value of about 208.0. The yield is about 85% of the acid feed.

FTIR: 3336 cm^{-1} -3242 cm^{-1} , 1237 cm^{-1} , 1140 cm^{-1}

$^1\text{H-NMR}$ (90 MHz, CD_3OD): δ 4.85(OH), 3.37(-CH-O-), 2.28(CH_2 at C2), 1.60-1.29(CH_2) and 0.90(CH_3).

EXAMPLE 2

Example 1 was repeated. After complete addition of peroxyacetic acid the reaction mixture was maintained at 88°-93°C for 2 hours. The product has a hydroxyl value of about 130.5, an acid value of about 166.9, a saponification value of about 239.8. The yield is about 50%.

EXAMPLE 3

Example 1 was repeated. The mole ratio of peroxyacetic acid to oleic acid was 1.5:1.0. After the addition of peroxyacetic acid was completed, the reaction mixture was allowed to stir for 2 hours at 75°-80°C. The product has a hydroxyl value about 118.4, an acid value of about 166.9, a saponification value of about 222.5. The yield is about 44%.

EXAMPLE 4

Example 1 was repeated. Alpha olefin was used as starting material instead of oleic acid. Alpha olefin was melted. Peroxyacetic acid was then added dropwise to alpha olefin with continuous stirring. When the addition of peroxyacetic acid was completed, the mixture was stirred for 2 hours and the temperature maintained at 80-90°C. The reaction mixture was separated from unreacted peroxyacetic acid and poured into an excess of acid solution and heated under reflux for 1h. The product was then washed several times with water and dried in a dessicator.

The product obtained has a hydroxyl value of about 145-148, melting point 79-80°C. The yield is about 70-80% based on iodine value.

FTIR: 3449 cm^{-1} , 1061 cm^{-1} , 723 cm^{-1}

$^1\text{H-NMR}$ (60 MHz, CDCl_3): δ 3.56 (-CH-O-), 1.26 (CH_2) and 0.88 (CH_3)

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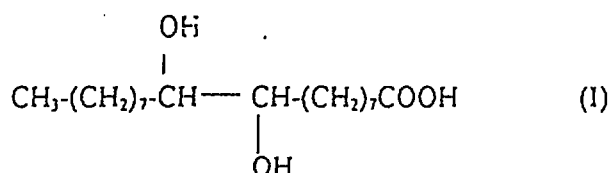


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CLAIMS:

1. A process for producing Dihydroxy fatty acid from oleic acid, said process comprising the steps of
 - (i) reacting glacial acetic acid with hydrogen peroxide in the presence of a catalyst;
 - (ii) reacting the thus formed product of step (i) with oleic acid.
2. A process as in claim 1 wherein the composition of hydrogen peroxide is 30% to 50% w/w.
3. A process as in claim 1 wherein the temperature range for the reaction is 60°C to 95°C.
4. A process as in claim 1 wherein the mole ratio of product formed in step (i) to oleic acid is in the range of 0.5:1.0 to 1.5:1.0
5. A process as in claim 1 wherein the oleic acid is derived from palm oil
6. A 9,10-dihydroxystearic acid represented by the formula (I)



as produced according to the process of Claims 1 - 5.

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APPENDIX I

Calculation on the amount of oleic acid to be used

In the previous example:

Percentage of peroxyacetic acid	= 19.45
IV of oleic acid	= 94.34
m.w. of oleic acid	= 282.47
amount of peroxyacetic acid	= $\frac{(968.8 + 889.6) * 19.45}{100}$
	= 361.46 g

Moles of peroxyacetic acid	= $361.46 / 76 = 4.76$ moles
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The mole of unsaturation in 1 g of oleic acid	= $\frac{(94.34)(282.47)}{(100)(253.8)}$
	= 1.050 moles

Assuming that:

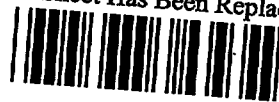
One mole of unsaturation will react with one mole of peroxyacetic acid.

Therefore, the weight of oleic acid containing 4.76 moles of unsaturation is

	= $\frac{(4.76)(282.47)}{1.050}$
	= 1280.5 g



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