

A Process For Producing Estolide Compounds

Field of The Invention

- 5 The present invention relates to a process for producing estolide compounds and products manufactured therefrom.

Background of The Invention

- 10 An estolide is a unique oligomeric fatty acid that contains secondary ester linkages on the alkyl backbone of the molecule. These linkages are more resistant to hydrolysis than those of triglycerides. This estolide may be used in lubricants, cosmetics and coating. As a lipophilic surfactants, derivatives from estolides are known.
- 15 US Patent No. 2, 785 978 discloses surface active compounds prepared by esterification between polycondensed hydroxycarboxylic acid having at least 8 carbon atoms and polycondensed polyhydric alcohols having at least 3 carbons atoms. Another US Patent No. 3, 429, 820 discloses power steering process and lubricating compositions containing estolides of 12-hydroxystearic acid having a neutralization
- 20 number of not more than 30.

Estolide has been found in nature and has been synthesized in the laboratory. Typically, it can be prepared by homopolymerization of castor oil fatty acid (Modak *et al.*, JAOCS 42: 428 (1965)) or 12-hydroxystearic acid (Raynor *et al.*, J. Chromatogr. 505:179 (1990)) under thermal or acid-catalyzed conditions. Erhan *et al.* (JAOCS, 70: 461 (1993)), reported the production of estolides from unsaturated fatty acid using a high temperature and pressure condensation over clay catalyst. Yamaguchi *et al.*, (Japanese patent 213, 387 (1990)) described a process for enzymatic production of estolides from hydroxy fatty acids present in castor oil using



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lipase. However, there is no disclosure on the production of estolide from dihydroxystearic acid.

Summary of The Invention

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It is therefore an object of the present invention ~~is~~ to provide a process for producing estolide from fatty acid preferably dihydroxystearic acid (DHSA).

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It is a further object of the present invention to provide a process for producing estolide by condensation of DHSA or mixtures of DHSA and ~~ordinary~~ non-hydroxy_fatty acids.

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Another object of the present invention is to produce estolide having utility as thickening agent, emulsifier, and additive in cutting fluid as well as starting material for producing surfactant.

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The process for producing estolide compounds according to the present invention ~~comprising condensing of DHSA or mixtures of DHSA and ordinary non-hydroxy fatty acid. The condensation reaction may be performed at a temperature from 120°C to 200°C for a period between about 2 to 10 hours depending upon the degree of~~ condensation desired. comprises condensing a dihydroxystearic acid or mixtures of a dihydroxystearic acid and a non-hydroxy fatty acid in the presence or absence of a catalyst under an inert gas at a temperature range of 120°C to 170°C for 2 to 10 hours.

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In the preferred embodiment of the present invention, the dihydroxystearic acid is 9,10-dihydroxystearic acid obtainable bleed from vegetable oil preferably palm oil. More preferably, the dihydroxystearic acid is prepared according to Singapore patent 86353.

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A catalyst may be added to the reaction mixture. The suitable catalyst including ~~sulfuric acid,~~ p-toluene sulfonic acid, perchloric acid as well as hydrochloric acid.

A composition comprising estolide obtainable according to the process of the present invention may be produced.

- 5 The estolide having lower acid value of about 30 to 40 mgKOHg⁻¹ are suitable for use as an emulsifier in cosmetic formulation.

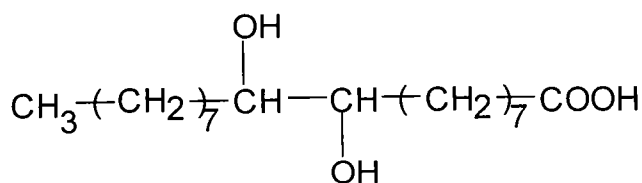
The estolide having acid value above 45mgKOHg⁻¹ and not more than 75 mgKOHg⁻¹ are suitable for use in shampoo formulation.

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Detailed Description of The Preferred Embodiment

- The present invention relates to a process for producing estolide or polyestolide from fatty acid by condensation. Preferably, the fatty acid is dihydroxystearic acid, more preferably palm-based dihydroxystearic acid (DHSA). In the preferred embodiment of the present invention, DHSA was prepared according to Singapore patent 86353. In another embodiment of the present invention the DHSA may be derived from any other oleic acid. The DHSA used in the present invention is preferably 9,10-dihydroxystearic acid, which is represented by Formula 1.

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Formula 1

- 25 The fatty acid compositions (FAC) of DHSA and product obtained can be determined by gas chromatography. Other chemical characteristics used to identify DHSA and the products are acid value (AOCS Method), hydroxyl value (AOCS Method) and saponification value (AOCS Method). Below are the characteristics of palm-based DHSA used in this invention. However, it may be varied depending on the sources of

oleic acid used for the production of DHSA. The process is applicable to crude and purified DHSA.

Table 1a: Characteristic of Purified Palm-Based DHSA

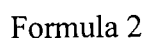
Parameter	
Hydroxyl Value, mgKOH/g	309.3
Acid Value, mgKOH/g	180.3
Iodine Value, $\text{gI}_2/100\text{g}$	1.1
Saponification Value, mgKOH/g	178.5
Melting Point, $^{\circ}\text{C}$	90.6
Fatty acid composition, % C16:0	2.8
C18:0	1.8
C18:2OH	93.2
Unknown	2.2

Table 1 b: Characteristic of Crude Palm-Based DHSA

Parameter	
Hydroxyl Value, mgKOH/g	196.0
Acid Value, mgKOH/g	179.3
Iodine Value, $\text{gI}_2/100\text{g}$	10.2
Saponification Value, mgKOH/g	178.0
Melting Point, $^{\circ}\text{C}$	61.9
Fatty acid composition, % C18:2OH	67.2
C12-C18	14.2
Unknown	18.6

The estolide of this invention is obtained by intermolecular esterification reaction between hydroxyl group and carboxyl group present in DHSA. As the condensation reaction proceeds, the molecular weight of the product increases, and the property changes from solid to paste and then to wax. The upper limit of n value in the formula 2 is not restricted, but it is less than 10. If the reaction is carried out at longer time or under more severer conditions, the n value can be higher than 10. The reaction product is an estolide containing hydroxyl group in a molecule. The reaction

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Example 1

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Reaction Time, h	Acid Value, mgKOH/g		Estolide Number (EN)	
	Crude DHSA	Purified DHSA	Crude DHSA	Purified DHSA
0	182.8	176.3	-	-
2	106.1	87.2	0.66	1.00
3	104.4	70.7	0.69	1.50
4	87.1	55.9	1.03	2.16
6	67.3	35.8	1.63	3.95
8	63.3	23.7	1.70	6.47

The formation of estolides compound was confirmed by NMR spectroscopy. The proton NMR spectra show some key features of a typical estolide. The ester methine (-CH-O(C=O)-) signal at 4.86-4.83 ppm is indicative of an estolide linkage. Another distinctive feature is the α -methylene proton shift ($\text{CH}_2(\text{C}=\text{O})\text{-O-CH-}$), (2.25 ppm) adjacent to the ester and the α -methylene proton shift ($\text{-CH}_2(\text{C}=\text{O})\text{-OH}$), (2.32 ppm) adjacent to the acid. The carbon NMR spectrum contains the expected estolide signals. There are two different carbonyl signals present at 179.2 ppm (acid) and 173.7 ppm (ester).

Example 2

Example 1 was repeated. Instead of variable reaction time, the reactions were carried out at different temperature for about 6h.

Reaction Temperature, °C	Acid Value, mgKOH/g
120	151.04
140	121.99
160	71.66
180	29.05

Example 3

The same procedure was followed as in Example 1, except that 0.3% of five different acids were used as catalyst. The reaction mixture was carried out at 150°C for 4h.

	Catalyst	Acid Value, mgKOH/g
5	H ₂ SO ₄	122.45
	H ₃ PO ₄	138.39
	HClO ₄	135.47
	HCl	136.57
	p-TSA	136.74

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Example 4

Use of DHSA-estolide as a thickening agent

			Viscosity / cP			
			Dimer	Trimer	Tetramer	Hexamer
15	Castor oil	549.0	577.8	579.9	583.4	591.6
	POME	5.35	7.75	7.87	7.98	8.34
	IPM	1.27	2.49	4.39	4.45	4.61

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Example 5

Use of DHSA-estolide as an additive in water-based cutting fluid composition

	Sampel	Rust inhibitor + test duration		Surface tension, mN/m
		24h	72h	
25	DHSA	9	6	36.50
	DIMER	10	8	34.11
	TRIMER	10	8	34.87
30	TETRAMER	10	6	32.96
	HEX AMER	8	6	30.81

Aqueous solutions of adduct (1g), triethanolamine (2g) and water (97g) were used as the test solution.

Example 6

Use of DHSA-estolide as an emulsifier in W/O emulsion system

Emulsion test of the samples synthesized were carried out as follows. 70parts of castor oil and 10 parts of samples were placed in a beaker. Under enough agitation, 20 parts of distilled water was added. The mixture was mixed for additional 5 minutes.

After this time, the mixture was poured into a test tube. Emulsion was observed after 24hours, 1 week and 2 week storage.

Estimation of emulsion 100 x emulsion layer / total layer			
SAMPLE	24hr	7 days	14 days
DIMER	100%	100%	50%
TRIMER	100%	100%	50%
TETRAMER	100%	100%	100%
HEXAMER	100%	100%	100%

Example 7

Use of DHSA-estolide as a compound in shampoo formulation

Ingredients	% by weight
Deionised water	To 100
Sodium laureth sulfate	8.0
Cocamidedopropyl betaine	2.0
Cocamide DEA	5.0
PEG-7 glyceryl cocoate	1.0
EDTA	0.05

	Sodium lactate	2.0
	DHSA-estolide	2.0
	Perfume	0.1
	Preservative	0.1
5	Citric acid / NaOH	To pH 5.5

The shampoo thus obtained fully functioned as a shampoo.

10 It is to be understood that the present invention may be embodied in other specific forms and is not limited to the sole embodiment described above. However modification and equivalents of the disclosed concepts such as those which readily occur to one skilled in the art are intended to be included within the scope of the claims which are appended thereto.

Claims

1. ~~A process for producing estolide compounds comprising condensing of dihydroxystearic acid or mixtures of dihydroxystearic acid and ordinary non-hydroxy fatty acid under conditions effective to provide estolide compounds with a pre-~~
5 ~~determined acid value as desired.~~

2. ~~The process according to Claim 1, wherein said dihydroxystearic acid is 9,10-~~
10 ~~dihydroxystearic acid.~~

3. ~~The process according to Claim 1, wherein said conditions are performed at a temperature in the range of about 120°C to 200°C for a period in the range of about 2 to 10 hours depending upon the degree of condensation desired.~~

15 4. ~~The process according to Claim 1, wherein said process further comprises adding a catalyst into the reaction mixture.~~

5. ~~The process according to Claim 3, wherein said catalyst is any one of or combination of sulfuric acid, p-toluene sulfonic acid, perchloric acid and hydrochloric acid.~~
20 ~~acid.~~

6. ~~The process according to Claim 1, wherein said process further comprises passing an inert gas through the reaction mixture while heating is continued.~~

25 7. ~~A composition comprising estolide compounds obtainable from any one of the preceding Claims.~~

8. ~~A cosmetic formulation comprising estolide compounds obtainable from any one of the preceding Claims as emulsifier.~~
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~~9. The cosmetic formulation according to Claim 8, wherein said estolide compounds having acid value in the range of about 30 to 40 mgKOHg⁻¹.~~

~~10. A shampoo formulation comprising estolide compounds obtainable from any one of the preceding Claims.~~

~~11. The shampoo formulation according to Claim 9, wherein said estolide compounds having acid value in the range of about 45 to 75 mgKOHg⁻¹.~~

~~12. A thickening agent comprising estolide compounds obtainable from any one of the preceding Claims.~~

1. A process for producing estolide compounds comprising condensing a dihydroxystearic acid or mixtures of a dihydroxystearic acid and a non-hydroxy fatty acid in the presence or absence of a catalyst under an inert gas at a temperature range of 120°C to 170°C.

2. A process according to claim 1, wherein the dihydroxystearic acid is 9,10-dihydroxystearic acid.

3. A process according to claims 1 or 2, wherein the catalyst is p-toluene sulfonic acid, perchloric acid, hydrochloric acid or a combination of any two and more thereof.

4. A process according to claims 1 to 3, wherein the estolide compounds produced is a polymer with dihydroxystearic acid and/or non-hydroxy fatty acid molecules not more than 12.

5. A cosmetic formulation comprising estolide compounds obtained by condensing a dihydroxystearic acid or mixtures of a dihydroxystearic acid and

a non-hydroxy fatty acid in the presence or absence of a catalyst under an inert gas at a temperature range of 120°C to 170°C, wherein the estolide compounds having an acid value in the range of 30mgKOHg⁻¹ to 40mgKOHg⁻¹.

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6. A shampoo formulation comprising estolide compounds obtained by condensing a dihydroxystearic acid or mixtures of a dihydroxystearic acid and a non-hydroxy fatty acid in the presence or absence of a catalyst under an inert gas at a temperature range of 120°C to 170°C, wherein the estolide compounds having an acid value in the range of 45mgKOHg⁻¹ to 75mgKOHg⁻¹.

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