

CHARACTERIZATION OF ESTOLIDES FROM DIHYDROXYSTEARIC ACID

ROILA AWANG*; AMINAH NOR AZIZAN**; SALMIAH AHMAD* and WAN MD ZIN WAN YUNUS**

ABSTRACT

Dihydroxystearic acid estolides (DHSA-estolides) were produced by intermolecular esterification between the hydroxyl group and carboxyl group in dihydroxystearic acid (DHSA). The products obtained were characterized by Fourier transform infrared (FTIR), proton and carbon nuclear magnetic resonance spectroscopy (¹H-NMR, ¹³C-NMR). The appearance of two ester peaks at 1734 cm⁻¹ and 1740 cm⁻¹ wavenumber revealed the formation of DHSA-estolides. The ester methine signal at 4.84 ppm was an indication of an estolide linkage in the ¹H-NMR spectrum while the ¹³C-NMR showed two carbonyl signals at 178.78 ppm for acid and 172.08 ppm for estolide. Titration of carboxylic acid with a standardized base was used to determine the average molecular weights of the estolides as well as their estolide numbers (EN).

Keywords: condensation reaction, dihydroxystearic acid, estolides, estolide number, polyestolides.

Date received: 23 September 2006; **Sent for revision:** 30 October 2006; **Received in final form:** 15 January 2007; **Accepted:** 12 March 2007.

INTRODUCTION

An estolide is a unique oligomeric fatty acid that contains secondary ester linkages on the alkyl backbone of the molecule (Isbell *et al.*, 1994; Isbell and Kleiman, 1994; Cermak and Isbell, 2001). These linkages are more resistant to hydrolysis than those of triglycerides. The estolides made from ricinoleic acid have been used as a viscosity controller for chocolate and emulsifier in margarine (Yoshida *et al.*, 1997). Estolides were reported to improve intra-fibre moisture retention and thereby impart protection from thermal damage, restore elasticity and reduce friction on the cuticle surface to prevent mechanical damage in hair care products (www.fancorp.com). Estolides from 12-hydroxystearic acid were found to increase lubricity as well as water retention in cosmetics (Higaki, 1981).

Estolides occur naturally but have also been synthesized. Typically, they are prepared by

homopolymerizing of castor oil fatty acid or 12-hydroxystearic acid under thermal or acid-catalyzed conditions (Modak and Kane, 1965). Erhan and Isbell (1997), reported the production of estolides from unsaturated fatty acids using a high temperature and pressure condensation over clay catalyst. However, there is no report on the production of estolide from dihydroxystearic acid (DHSA). In this study, we performed a series of experiments to explore estolide formation for DHSA-estolides.

MATERIALS AND METHODS

Materials

DHSA was prepared in the laboratory via epoxidation and hydrolysis of oleic acid (Awang *et al.*, 1998). Sodium hydroxide, sodium sulphate, potassium hydroxide, potassium iodide and sodium thiosulphate were purchased from MERCK (Darmstadt, Germany) and used without further purification. All other reagents were of analytical grade and used as received.

Condensation Reaction

DHSA-estolides were prepared according to Malaysian patent application PI20050185 (Awang *et al.*, 2005). DHSA was placed in a three-neck round bottom flask equipped with a magnetic stirrer,

* Malaysian Palm Oil Board,
P. O. Box 10620,
50720 Kuala Lumpur,
Malaysia.
E-mail: roila@mpob.gov.my

** Department of Chemistry,
Faculty of Science,
Universiti Putra Malaysia,
43400 UPM Serdang,
Selangor, Malaysia.

thermometer, nitrogen gas inlet and condenser. The reaction mixture was stirred continuously under dry nitrogen atmosphere for a pre-determined reaction period at 180°C.

Analysis of the Product

All the analyses were performed in duplicate according to the standard methods (AOCS official methods): acid value, Te 1a-64 (89); saponification value, TI 1a-64(93); hydroxyl value (OHV), Cd I3-60 (89) and iodine value Cd Id-92 (92) (11). Fourier transform infrared (FTIR) was recorded on a Nicolet Magna-IR550 (Nicolet, Madison, WI). The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on a Varian Unity Inova (Palo Alto, USA, 500 MHz) spectrometer in deuterated chloroform with tetramethylsilane (TMS) as internal standard.

RESULTS AND DISCUSSION

FTIR Characterization of Estolides

The condensation of DHSA was expected to produce saturated estolides as shown in *Figure 1*. To prove that condensation had occurred, FTIR spectra

of DHSA and reaction products were compared. The FTIR spectrum of DHSA shows a C=O stretching band at 1703 cm^{-1} wavenumber, while the transmittance peak at 3305 cm^{-1} wavenumber indicates the presence of a hydroxyl group in the DHSA structure (spectrum not shown). The FTIR spectra of the reaction product obtained from the condensation of DHSA at different reaction times are shown in *Figure 2*. The decrease in carboxylic acid transmittance peak at 1703 cm^{-1} indicated that the acid had converted to DHSA-estolides as the reaction proceeded. Only one carbonyl (C=O) ester transmittance peak was observed for the DHSA-estolides obtained after 2 hr reaction time. For the DHSA-estolides obtained from the reaction after 4 hr and above two ester transmittance peaks were observed (*Figure 3*), where ester with more electronegative which is C=O group bonded to the acid backbone appeared at 1734 cm^{-1} (E1) wavenumber, while ester with less electronegative, which is C=O group bonded to the ester backbone appeared at 1740 cm^{-1} (E2). This observation suggests that DHSA-estolides with more than one ester linkage formed after 2 hr reaction time. The presence of CH_2 bending at 720 cm^{-1} wavenumber indicates long-chain compound.

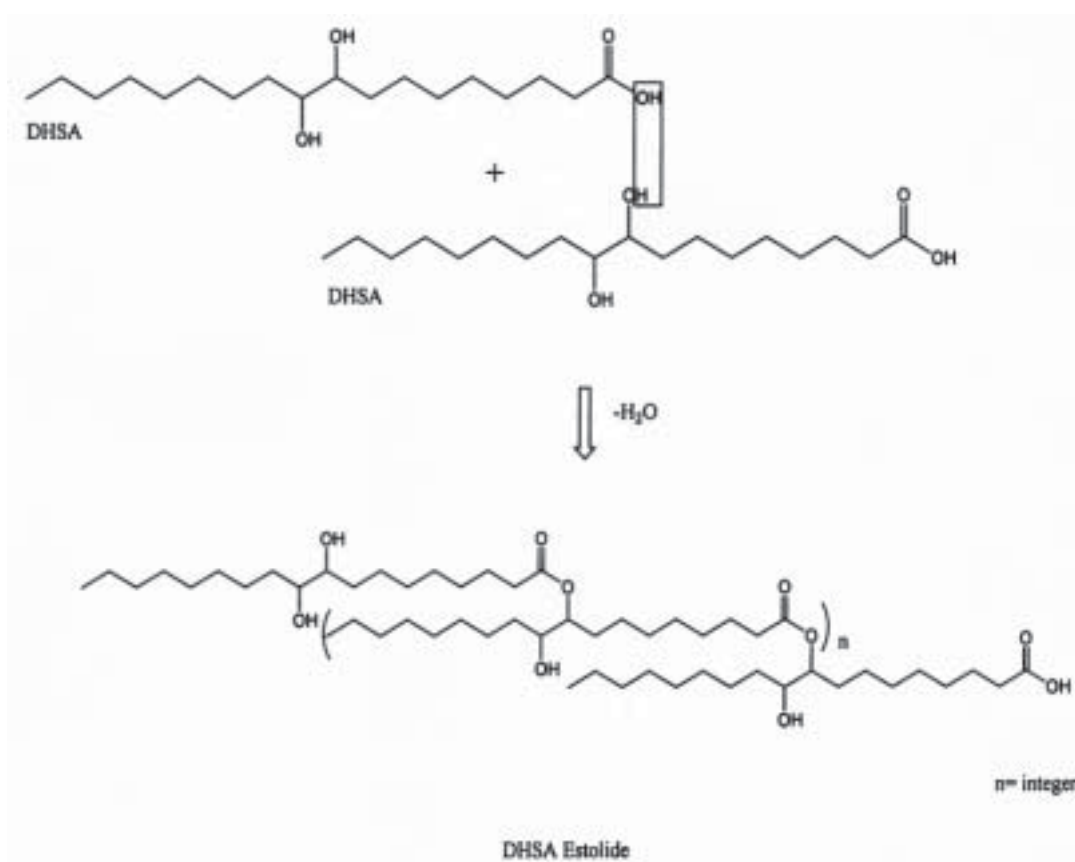


Figure 1. The condensation of DHSA.

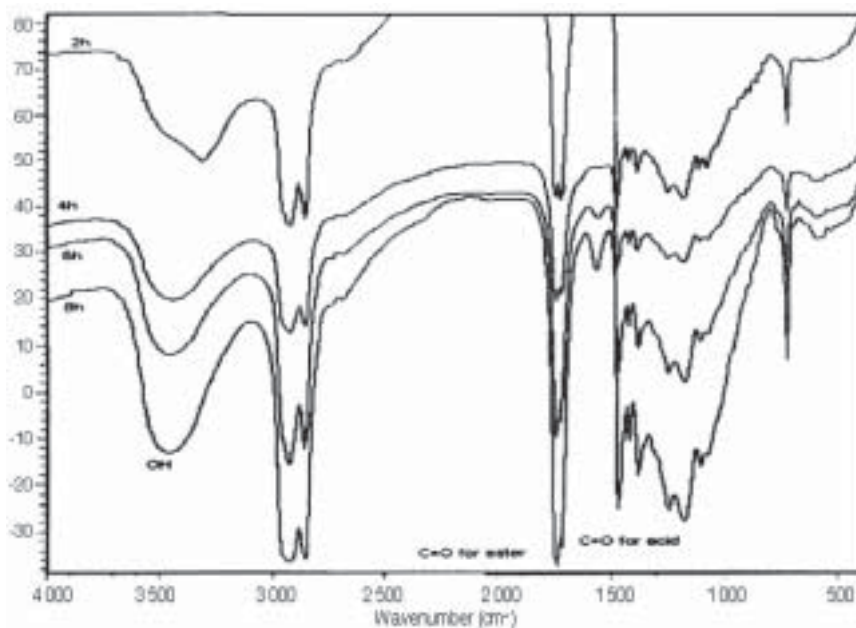


Figure 2. Overlay FTIR spectra of dihydroxystearic acid estolides (DHSA-estolides) obtained from various reaction times.

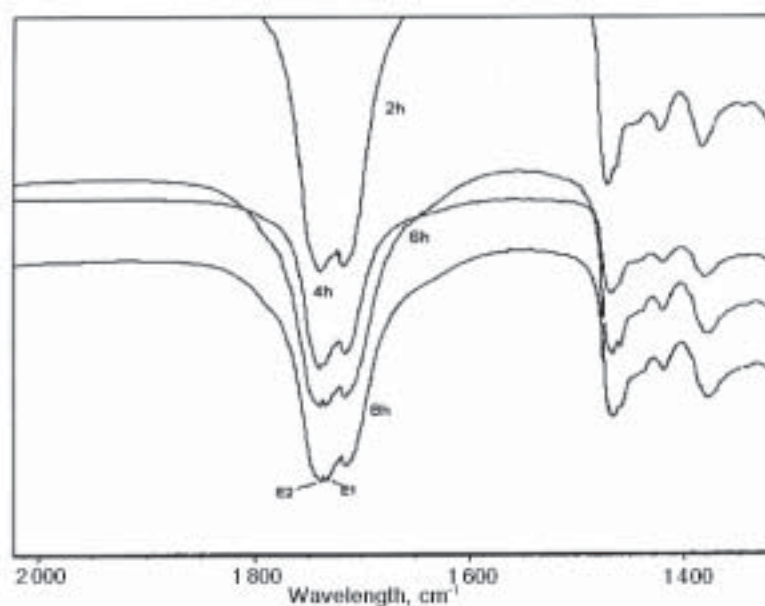


Figure 3. Enlarged FTIR spectra of dihydroxystearic acid estolides (DHSA-estolides) obtained from various reaction times (1600 cm^{-1} -1800 cm^{-1}).

NMR Characterization of DHSA-Estolides

The ^1H -NMR spectrum for the DHSA-estolides in Figure 4 shows some of the key features for a typical estolide. The ester methine signal (H_m) at 4.84 ppm is indicative of an estolide linkage. Another distinctive feature is the α -methylene proton shift at 2.36 ppm adjacent to the acid, and the α -methylene proton shift at 2.30 ppm adjacent to the ester. Although Isbell and Kleiman (1994) reported that the ratio of α -ester/ α -acid can be used as a means to determine the EN for oleic-estolides, the method cannot be applied for this compound since the NMR

is far more complex than those for the traditional oleic-estolides. The proton attached to CH-OH, which has the chemical shift range at 3.20-3.80 ppm for DHSA, is now shifted downfield to 4.00-5.20 ppm because of the formation of ester linkages. The ^{13}C -NMR spectrum contains the expected estolide signals (Figure 5). There are two different carbonyl signals at 178.78 ppm (acid) and 172.08 ppm (estolide ester). The other distinctive signal was methine carbon at 72.84 ppm, which is common to esters. Carbon bonded to -OH was still observed at 74.70 ppm.

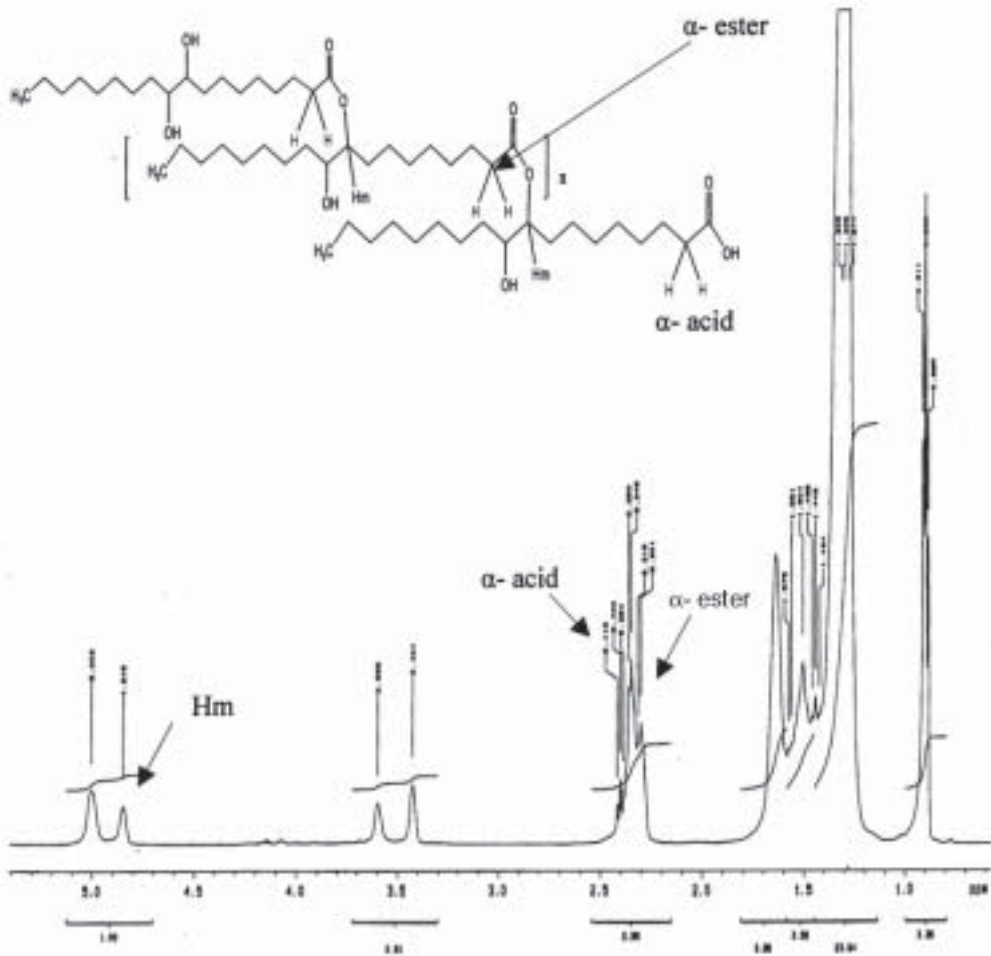


Figure 4. Typical ¹H-NMR spectrum of dihydroxystearic acid estolides (DHSA-estolide).

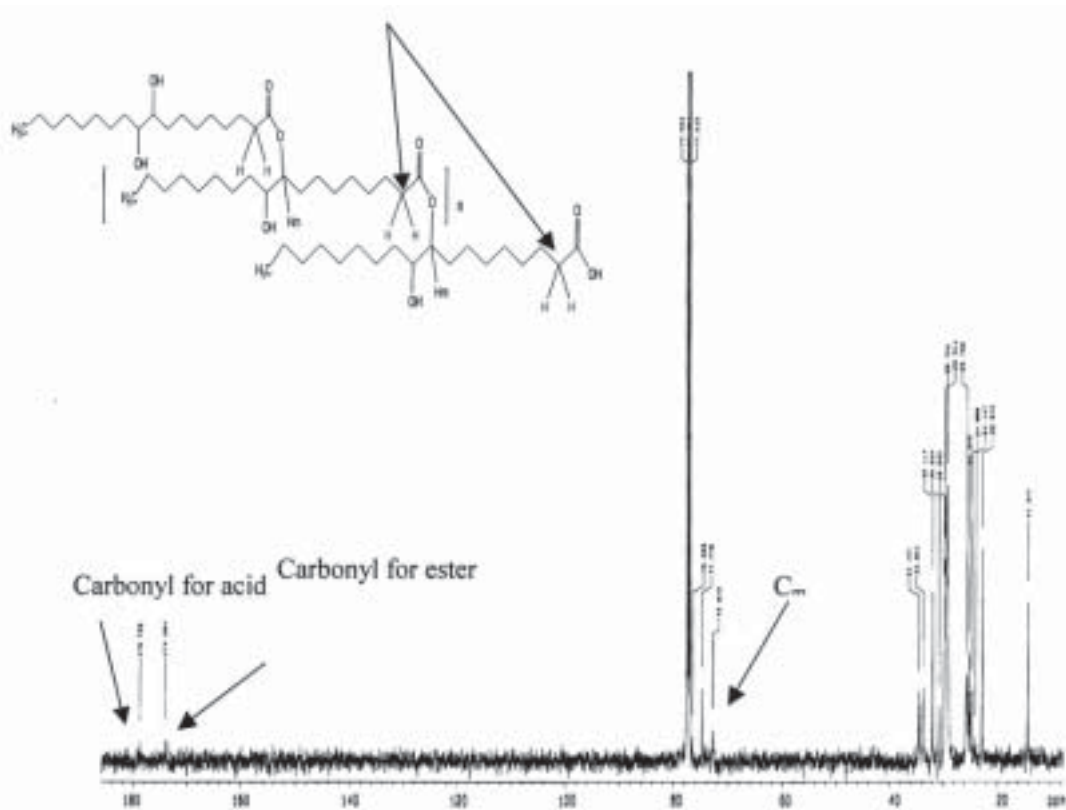


Figure 5. Typical ¹³C-NMR spectrum of dihydroxystearic acid estolides (DHSA-estolide).

Chemical Analysis and Estolide Number Determination

The acid value (AV), saponification value, OHV and iodine value (IV) of the DHSA-estolides obtained from various reaction times are shown in *Table 1*. Both the acid value and hydroxyl value decreased as the reaction time increased. This may be due to the increasing molecular weight of the product. The saponification value did not show any trend. Although the DHSA-estolides produced were expected to be saturated compounds, the IV of the product increased with the reaction time, possibly due to dehydration of the hydroxyl group of DHSA into diene compounds. It has been reported that dehydration of 9,10-DHSA at high temperature followed by distillation, gave a distillate which was primarily a mixture of diene compounds and their esters (Modak and Kane, 1965). However, the FTIR spectrum of DHSA-estolide did not show any unsaturation peak at 1600-1660 cm⁻¹ wavenumber nor at 3000 cm⁻¹. The ¹H-NMR and ¹³C-NMR also did not show any peak for double bond carbon at 100-150 ppm and 6.0-6.5 ppm. Therefore, we conclude that IV obtained was due to replacement of the hydroxyl groups in the DHSA-estolide structure by iodine.

Acid Value as a Means to Determine EN

Isbell and Kleiman (1994) reported a good correlation between the AV technique and HPLC and GC methods for determining the extent of polyestolide formation. In this study, AV was determined according to the AOCS method. Titration not only provided the acid number but also yielded the neutralization equivalent (NE)-(Equation 1), which is the average molecular weight of the DHSA-estolides mixture. The estolide number was then calculated using Equation 2.

$$\text{Neutralization equivalent, NE} = (1000 \times 56.1) / \text{acid value} \quad (1)$$

$$\text{Estolide number, EN} = (\text{NE} - 316.47) / 316.47 \quad (2)$$

The NE and EN of the DHSA-estolides from various reaction times are summarized in *Table 2*. The average molecular weights of the DHSA-estolides obtained from the various reaction times were also calculated based on other end-group analyses. As shown in *Table 3* the molecular weights calculated based on the AV and saponification value showed good correlation with the theoretical molecular weight. The average molecular weights calculated based on OHV were slightly higher. This difference cannot be explained at the moment.

TABLE 1. CHEMICAL PROPERTIES OF DIHYDROXYSTEARIC ACID (DHSA)-ESTOLIDES OBTAINED FROM VARIOUS REACTION TIMES

| Sample | Reaction time (hr) | Chemical property | | | |
|----------|--------------------|--------------------------------------|--------------------------------------|-------------------------------|--|
| | | Acid value (mg KOH g ⁻¹) | Sap. value (mg KOH g ⁻¹) | OHV (mg KOH g ⁻¹) | Iodine value (g I ₂ 100 g ⁻¹) |
| DHSA | 0 | 176.28 | 172.08 | 260.05 | 3.74 |
| DHSA-E2h | 2 | 92.62 | 209.71 | 174.57 | 7.41 |
| DHSA-E4h | 4 | 67.91 | 211.54 | 168.72 | 7.62 |
| DHSA-E6h | 6 | 41.70 | 210.99 | 155.32 | 7.73 |
| DHSA-E8h | 8 | 29.42 | 201.02 | 115.42 | 9.29 |

Note: OHV – hydroxyl value.

TABLE 2. NEUTRALIZATION EQUIVALENT AND ESTOLIDE NUMBER OF DIHYDROXYSTEARIC ACID (DHSA)-ESTOLIDE OBTAINED FROM VARIOUS REACTION TIMES

| DHSA-estolide | Acid value (mg KOH g ⁻¹) | Neutralization equivalent (NE) | Estolide number (EN) | Description |
|---------------|--------------------------------------|--------------------------------|----------------------|---------------|
| DHSA-E2h | 92.62 | 605.80 | 0.91 | Monoestolide |
| DHSA-E4h | 67.91 | 826.24 | 1.61 | Diestolide |
| DHSA-E6h | 41.70 | 1 345.56 | 3.25 | Triestolide |
| DHSA-E8h | 29.42 | 1 907.20 | 5.03 | Pentaestolide |

TABLE 3. AVERAGE MOLECULAR WEIGHTS OF DIHYDROXYSTEARIC ACID (DHSA)-ESTOLIDE BASED ON END-GROUP ANALYSIS *vs.* THEORETICAL MOLECULAR WEIGHTS

| Sample | Molecular weight calculated based on end-group analysis | | | Theoretical molecular weight |
|---------------|---|------------|----------|------------------------------|
| | Acid value | Sap. value | OHV | |
| DHSA | 318.30 | 326.06 | 431.53 | 316.00 |
| Monoestolide | 605.80 | 535.12 | 964.25 | 614.00 |
| Diestolide | 756.91 | 795.74 | 1 445.00 | 912.00 |
| Triestolide | 1 345.56 | 1 345.74 | 1 944.55 | 1 216.00 |
| Pentaestolide | 1 907.20 | 1 674.75 | ND | 1 809.00 |

Note: OHV – hydroxyl value.

CONCLUSION

DHSA-estolides were successfully prepared by intermolecular esterification between the hydroxyl and carboxyl groups in DHSA. As the reaction proceeded, the molecular weight of the product increased and its state changed from solid to paste and then to wax. The estolides obtained may find uses in cosmetics and personal care products as well as in the food industry.

ACKNOWLEDGEMENT

The authors thank the Director-General of MPOB for permission to publish this paper.

REFERENCES

- AWANG, R; AHMAD, S and KANG, Y B (1998). Preparation of dihydroxy fatty acid from oleic acid. Malaysian patent application PI9804456.
- AWANG, R; AHMAD, S; NOR AZIZAN, A and WAN YUNUS, W M Z (2005). A process for producing estolides. Malaysian patent application PI20050185.
- AOCS (1995). *Official Methods and Recommended Practices of the American Oil Chemists' Society*. 4th Edn. AOCS Press, Champaign.
- CERMAK, S C and ISBELL, T A (2001). Biodegradable oleic estolide ester having saturated fatty acid end group useful as lubricant base stock. US patent 6316649.
- ERHAN, S M and ISBELL, T A (1997). Estolide production with modified clay catalysts and process conditions. *J. Amer. Oil Chem. Soc.*, 74: 249-254.
- HIGAKI, Y (1981). Oligoesterification products and cosmetics containing the same. Japanese patent JP 56-108739.
- ISBELL, T A; KLEIMAN, R and PLATTNER, B A (1994). Acid-catalyzed of oleic acid into estolide and polyestolide. *J. Amer. Oil Chem. Soc.*, 71: 169-174.
- ISBELL, T A and KLEIMAN, R (1994). Characterization of estolides produced from the acid-catalyzed of oleic acid. *J. Amer. Oil Chem. Soc.*, 71: 379-383.
- MODAK, S N and KANE, J G (1965). Studies in estolides. I. Kinetics of estolide formation and decomposition. *J. Amer. Oil Chem. Soc.*, 42: 428.
- YOSHIDA, Y; KAWASE, M; YAMAGUCHI, C and YAMANE, T (1997). Enzymatic synthesis of estolides by a bioreactor. *J. Amer. Oil Chem. Soc.*, 74: 261-267.
- www.fancorp.co/specs/specmeadowestolide-htm. Accessed on 25 June 2005.