The Malaysian Journal of ANALYTICAL SCIENCES ISSN 1394-2506

SYNTHESIS OF ESTOLIDE 2-ETHYLHEXYL ESTER FROM *RICINUS COMMUNIS*

(Sintesis Estolida 2-Etilheksil Ester dari *Ricinus Communis*)

Nazrizawati Ahmad Tajuddin[1,2]*, Nor Habibah Rosli[1], Jumat Salimon[2], Mohd Firdaus Mohd Yusoff [2], Noraishah Abdullah[2]

[1]*Department of Chemistry, International Education College, UiTM Section 17, 40200 Shah Alam, Selangor, Malaysia*
[2]*Oleochemistry Programme, School of Chemical Science and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia,43000 Bangi, Selangor, Malaysia*

**Corresponding author: nazriza@salam.uitm.edu.my*

Abstract

Estolide 2-ethylhexyl ester synthesized through condensation reaction between ricinoleic acid from castor oil (*Ricinus communis*) and lauric acid, and then capped with 2-ethylhexyl alcohol. The reaction was continuously conducted under vacuum for 24 hours. Product of 2-ethylhexyl ester was characterized by using Fourier Transform Infrared (FTIR) to determine functional group and Nuclear Magnetic Resonans (NMR) for structure's determination. The presence of ester group at 1738.23 cm^{-1} wavenumber indicates that the formation of estolide ester has occurred. The vibration peak of C-O at 1174.60 cm^{-1} and 1117.10 cm^{-1} support the formation of ester. The presence of CH_2 bending indicated the long-chain compound. The ester methine signal at 3.8669 ppm indicated the estolide linkage in the ^{1}H-NMR spectrum while the ^{13}C-NMR showed two carbonyl signals at 173.41 ppm for acid and 173.56 ppm for ester.

Keywords: Castor oil, ricinoleic acid, estolide ester, biodegradable, biolubricant study

Abstrak

Estolida 2-etilheksil ester disintesis melalui tindakbalas kondensasi antara asid risinoleik dari minyak jarak (*Ricinus communis*) dan asid laurik yang kemudiannya ditutup dengan 2-etilheksil alkohol. Tindakbalas ini dijalankan secara berterusan selama 24jam. Hasilan 2-etilheksil alkohol ester dikenalpasti dengan menggunakan Fourier Transform Infrared (FTIR) untuk pengecaman kumpulan berfungsi dan Magnetic Resonan Nuclear (NMR) digunakan untuk menentukan struktur estolida yang terhasil. Getaran C-O pada puncak 1174.60 cm^{-1} dan1117.10 cm^{-1} mengesahkan kehadiran ester di dalam sebation yang terbentuk. Kehadiran CH_2 bengkokan menunjukkan kehadiran kompaun berantai panjang. Signal ester methane yang hadir pada 3.8669 ppm dalam ^{1}H-NMR spectrum dan signal karbonil pada 173.56 ppm dalam ^{13}C-NMR mengesahkan kompaun terhasil adalah ester.

Kata kunci: Minyak jarak, asid risinoleik, estolida ester, biodegradasi, kajian biolubrikan

Introduction

The depletion of the world's crude oil reserve, increasing crude oil prices, and issues related to conservation have brought about renewed interest in the use of bio-based materials. Emphasis on the development of renewable, biodegradable, and environmentally friendly industrial fluids, such as lubricants, has resulted in the widespread use of natural oils and fats for non-edible purposes. The desire to replace petroleum-based material with environmental friendly and sustainable alternatives has stimulated the development of vegetables oil-based materials as biolubricants [1] such as castor oil.

Castor bean oil contains ricinoleic acid, a hydroxy monounsaturated fatty acid as main constituent of its fatty acid profile [2]. Ricinoleic acid, a monounsaturated, 18-carbon fatty acid, is unusual in that it has a hydroxyl functional

group on the 12th carbon. This functional group causes ricinoleic acid and castor oil to be unusually polar, and also allows chemical derivatization that is not practical with most other seed oils. It is the hydroxyl group which makes castor oil and ricinoleic acid valuable as chemical feedstocks. Estolide have been shown to have certain physical characteristics that could eliminate common problems associated with vegetable oils as functional fluids [3].

Ref [4] reported that vegetable oil-based lubricants and derivatives have excellent lubricity and biodegradability properties for which they are being more closely examined as a base stock for lubricants and functional fluids. However, vegetable oil as functional fluids has two major problems; low resistance to thermal oxidative stability [5] and poor low temperature properties [6]. The properties still can be improved but only at the sacrifice of biodegradability, toxicity and cost.

An estolide is a unique oligomeric fatty acid that contains secondary ester linkage on the alkyl backbone of the molecule [7,8,9]. These linkages are more resistance to hydrolysis than those of triglycerides. Estolides are formed when the carboxylic acid functionality of one fatty acid links to the site of unsaturation of another fatty acid to form oligomeric ester [10]. Typically, estolides were synthesized by homo-polymerization fatty acid from vegetable oil acidic conditions.

Estolide from oleic and saturated fatty acids and their 2-ethylhexyl ester have excellent low temperature properties when synthesized at 45°C. These estolide esters were more suitable as a base stock for biodegradable lubricants and functional fluids than commercial materials [11] So far, there is no reference on ricinoleic acid from castor oil being synthesize with 2-ethylhexyl alcohol have been reported. In this paper we synthesized estolide 2-ethylhexyl ester from ricinus communis and being capped by 2-ethylhexyl alcohol for biolubricant purposes where perchloric acid has been used as catalyst.

Materials and Methods

Materials

Samples (castor bean) were collected from four different areas; Meru-Kapar (Klang); Salak Tinggi(KL); Sungai Chua (Kajang) and Plant House (UKM, Bangi). 2-ethylhexyl alcohol, lauric acid and percholoric acid were purchased from Sigma-Aldrich, USA. Hexane (for extraction) and potassium hydroxide were obtained from SYSTERM.

Extraction of Castor Oil

The samples went under pretreatment of drying (80^{o}C, 8 hours) and grinding before being extracted using Soxhlet Extractor apparatus. Castor oil was extracted according to Soxhlet method and hexane being used as solvent. Extraction was carried out for 6-12 hours at 65°C in order to assure the oil was fully extracted. The collected oil was separated by using rotavapor.

Hydrolysis of Castor Oil

Hydrolysis was performed to produce fatty acid of ricinoleic acid. 25 g of castor oil was added with 65 ml ethanol, 5.71g KOH and 11 ml distilled water. The mixture were reflux for 1 hour with maintain temperature 50°C. Then 50 ml distilled water was added and quenched with 100 ml hexane (2x). Soap matter was acidized to pH 1 by using 25 ml HCl 6N. The product was quenched again with 50 ml hexane. Sodium sulphate was added and the process proceeded with rotavapor. Isolation been done by adding 40 ml ethanol and 60 ml distilled water. The mixture was quenched with 40 ml hexane. The final product was added with sodium sulphate and rotavap.

Synthesis of Estolide Ester

Synthesis of estolide 2-ethylhexyl ester were conducted based on Ref [10] with modification by using ricinoleic acid as first fatty acid reacted with lauric acid and capped with 2-ethylhexyl alcohol. Ricinoleic acid (50 g, 177 mmol) and saturated fatty acid, lauric (17.75g, 88.5 mmol) were combined together and heated to 60 ^{o}C under vacuum. Once the desired temperature was reached, 11.5 ml perchloric acid was added and stirred for 24 hours. All the reactions were conducted in a three-neck round flask, connected to a recirculating vacuum in a fume hood. After 24 hours, 2-ethylhexyl alcohol (33.75 ml, 228.8 mmol, 29.8 g) was added to the vessel, vacuum was restored and the

mixture was stirred for 2 additional hours. The complete reaction was quenched by 25 g KOH in 90% ethanol/water (10 ml) solution.

The reactor was disconnected from the circulating bath and the solution was allowed to cool for 30 minutes. The organic layer was dried over sodium sulphate and filtered. The material was distilled at 105^{o}C to remove any excess alcohol and water contents.

Analysis and Characterization

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy analysis was carried out to determine the functional group presence in estolide ester based on the spectrum peaks. In this analysis, Perkin Elmer GX FTIR Spectrophotometer was used to get the information of all functional groups in each sample. Samples which were in liquid form were sandwiches between two sodium chloride (NaCl) plates while samples in solid form were diluted before being placed between two potassium bromide (KBr) plates.

The functional group to be monitored for is ester carbonyl (1735 cm^{-1}), hydroxyl –OH (2900-3300 cm^{-1}), sp^3 stretching carbon (2800-3000cm^{-1}), long chain (720cm^{-1}) and other functional groups which may appear as a characteristic of the product. Spectrums for all raw materials (ricinoleic acid and 2-ethylhexyl alcohol) were compared to product's to observe the differences between each spectrum.

Nuclear Magnetic Resonance (NMR)

NMR spectroscopy been used to detect ^{1}H proton and carbon ^{13}C in the estolide structure. Samples were eluted in chloroform and injected in Delta NMR ECP 400 (1D complex) using probe proton/carbon (400 MHz ^{1}H/100.61 MHz ^{13}C).

Results and Discussion

Synthesis of Estolide Ester

Generally, formation of estolide ester is influences by two major factors; acid catalyst and the reaction temperature used. Perchloric acid was added in this reaction act as catalyst. Perchloric acid provide significantly faster rate (5-8 times) of estolide formation compare to sulphuric acid and produce more yield of estolide [7]. Addition of sulphuric acid to unsaturated fatty acid will produce sulfated oils. The sulfated oil is stable at low temperature (≤20°C) in the presence of acid, but at elevated temperature (50°C), the sulphate esters quickly decompose, estolides and lactones are observed.

Estolide esters formation also influences by the temperature. At room temperature (27°C), the rate of reaction catalyzed by perchloric acid becomes slow. However, at higher temperature, the formation become too fast due to the rate is accelerated even though the concentration of perchloric acid is reduced and the side reactions begin to predominate, chiefly the formation of lactones [7]. Hence, an optimum temperature, 60°C has been applied in this study. Synthesis was carried out within 24 hours in order to assure all the reactions are complete.

Figure 1 shows C7 on ricinoleic acid tend to interact with OH group from lauric acid to form ester and also for capping the chain. Carbonyl group tends to form bonding with OH because carbonyl group are easier to disconnect compared to double bond, which is more stable. By capping the fatty ester, the compounds no longer had the opportunity to undergo either intra- or intermolecular hydrogen bond interaction [11]. Yield produced is about 82.25%.

FTIR Characterization of Estolides

Synthesis of estolide 2-ethylhexyl ester was expected to produce unsaturated estolides as shown in Figure 1. To prove that condensation had occurred, FTIR spectra of estolide 2-ethylhexyl ester and reaction product were compared. The FTIR spectrum shows a strong stretching band at 1738.23 cm^{-1}. This peak indicates the presence of ester group in the estolide as ester shows a strong peak at range 1750-1735 cm^{-1} [12]. This assumption was supported by the presence of two C-O streching bonds.

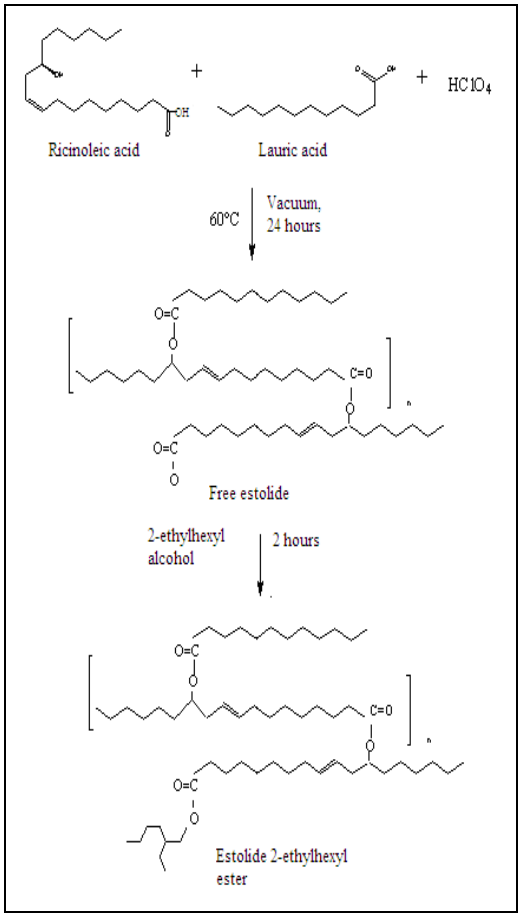

Figure 1. Reaction of estolide 2-ethylhexyl ester

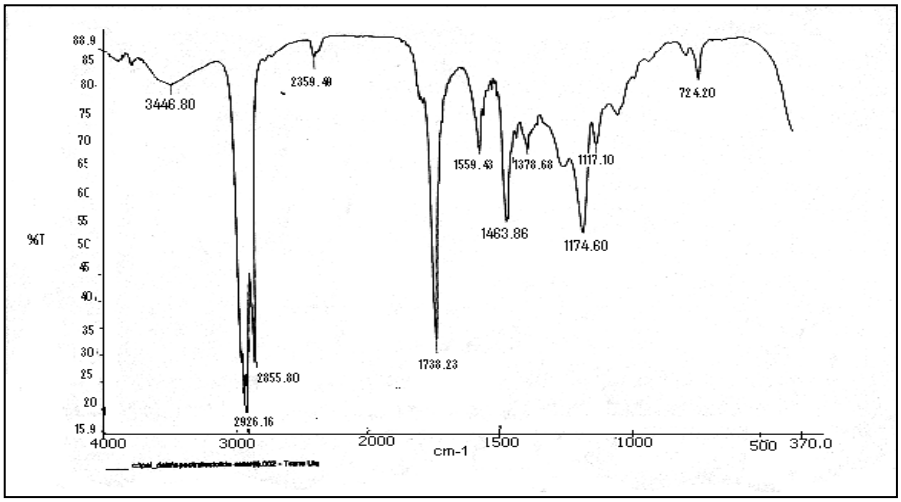

Figure 2. Estolide 2- ethylhexyl ester

At 1174.60 cm^{-1} wavenumber which is more electronegative as the C-O group bonded to the acid backbone while ester with is less electronegative, which is C-O ester bonded to the ester backbone appeared at 1117.10 cm^{-1}.

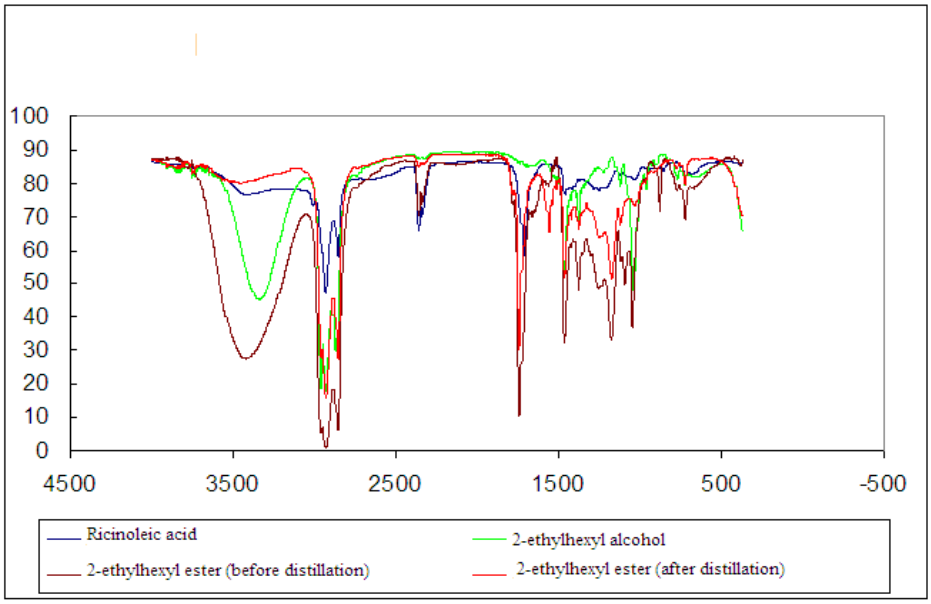

Figure 3. Differentiate spectrum in formation of estolide ester before and after distillation

NMR Characterization of estolide 2-ethylhexyl ester

The 1H-NMR spectrum for estolide 2-ethylhexyl ester shows in Figure 4 contains the expected estolide signals. The ester methine signal (Hm) at 2.157 ppm indicates the estolide linkage. Another distinctive feature is the α-methelyne proton shift at 4.5438 ppm adjacent to the acid and the α- methelyne proton shift at 3.8669 ppm adjacent to the ester (Table 1).

Table 1. Data elucidation of NMR ^{1}H spectrum

Node	Shift (ppm)	Group
CH_3	0.7712	Methyl
CH_2	1.1641	Methylene ($CDCl_3$ peak)
	1.4929	Methylene
	4.5438	Methylene (α- acid)
CH	2.1570	Methine (ester linkage)
	3.8669	Methine (α-ester)

Although the ratio of α- ester/ α- acid can be used as a means to determine the estolide number (EN), the method cannot be applied for this compound since the NMR is more complex [8]. The ^{13}C NMR spectrum for estolide 2-ethylhexyl ester shows in Figure 5 contains some of the key features for a typical estolide and all the shift data are listed in Table 2. There are two carbonyl signals at 173.4091 ppm (acid) and 173.5697 ppm (ester). Methine carbons were appeared at 76.9122-77.5545 ppm which is common to estolides. Estolide ester is supposed to have ethylene peak at 130.6 ppm in the spectrum due to double bond from ricinoleic acid. However, spectrum of estolide 2-ethylhexyl ester shows inverse result where there is no ethylene peak or very small signal observed [10] expected cause by the impurity of ricinoleic acid**.**

Table 2 Data elucidation of NMR ^{13}C spectrum

Node	Shift (ppm)	Group
CH_3	10.8630-13.9675	Methyl
CH_2	22.9137-30.43	Methylene
	64.7010-66.3602	Methylene
CH	38.7722	Methine
	76.9122-77.5545	Methine ($CDCl_3$ peak)
C-O	173.4091	Carbonyl (acid)
	173.5697	Carbonyl (ester)

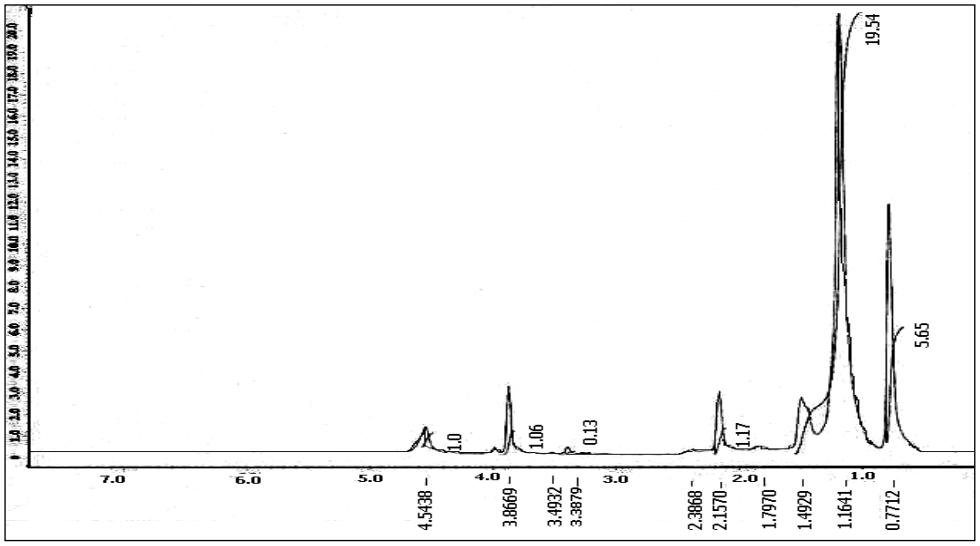

Figure 4. Spectrum of NMR ^{1}H estolide 2-ethylhexyl ester.

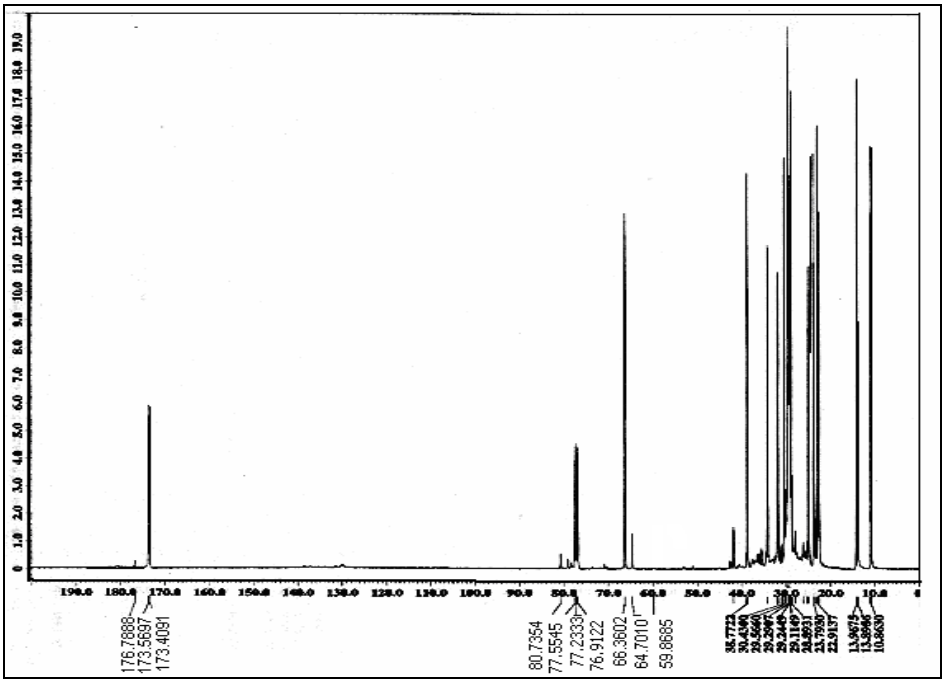

Figure 5. Spectrum of NMR ^{13}C estolide 2-ethylhexyl ester.

Conclusion

Estolide 2-ethylhexyl ester was successfully synthesized between ricinoleic acid from castor oil and lauric acid with addition of 2-ethylhexyl alcohol where perchloric acid acted as catalyst. Data elucidation from FTIR and NMR described the characteristic of the product. The result shows significant value with the estimation and matched with the molecular structure, hence possibly been use as biolubricant material.

Acknowledgement

Thanks to Universiti Kebangsaan Malaysia for research funding, OUP-BTT-28/2007 and supporting staff of Science and Technology Faculty for expert technical assistance. And thank you to International Education College, UiTM Section 17 for Accommodation & Travelling sponsored.

References

1. Lin, J.T. & Chen, G.Q. 2010. Acylglycerols Containing Trihydroxy Fatty Acids in Castor Oil and the Regiospecific Quantification of Triacylglycerols. *Journal of the American Oil Chemists' Society*. 87:1371-1379
2. Jumat, S., Neeranjini, N., Nadia, S. & Bashar, M.A. 2011. Synthesis and Physical Properties of Estolide Ester Using Saturated Fatty Acid and Ricinoleic Acid. *Journal of Automated Methods and Management in Chemistry*.2011: 1-4
3. Cermak, S.C. & Isbell, T.A. 2002. Physical prop of saturated estolides and their 2-ethylhexyl ester. *Industrial Crops Products*. 16: 119-127.
4. Zaher, F.A. & Nomany, H.M. 1988. Vegetable oils and lubricants. *Grases Aceities (Seville).* 39: 235-238
5. Becker, R. & Knorr, A. 1996. An evaluation of antioxidants for vegetable oil at elevated temperatures. *Lubri. Sci.* 8: 95-117.
6. Asadauskas, S. & Erthan, S.Z. 1999. Depression of pour points of vegetable oils by blending with diluents used for biodegradable lubricants. *J.Am.Oil Chem.Soc.* 76: 313-316.
7. Isbell, T.A., Kleiman, R. & Plattner, B.A. 1994. Acid.Catalyzed Condensation of Oleic Acid into Estolides and Polyestolides. *J.Am.Oil Chem.Soc*: 71.

8. Isbell, T.A. & Kleiman, R. 1994. Characterization of Estolides Produced from the Acid-Catalyzed Condensation of Oleic Acid. *New Crops Research.* 71:379-383.
9. Cermak, S.C. & Isbell, T.A. 2001. Synthesis of estolides from oleic and saturated fatty acids. *J.Am.Oil.Chem.Soc.* 78: 557-565.
10. Cermak, S.C. & Isbell, T.A. 2003. Synthesis physical properties of estolide-based functional fluids. *Industrial Crops Products.* 18:183-196.
11. Cermak, S.C., Brandon, K.B. & Isbell, T.A. 2006. Synthesis and physical properties of estolides from lesquerella and castor fatty acid esters. *Industrial Crops Products*.23:54-64.
12. Pavia, D.L., Lampman, G.M. & Kriz, G.S. 2001. Introduction to spectroscopy, 3rd ed. America:Thomson Learning.