

Lewis Acidic Ionic Liquids As New Addition Catalyst For Oleic Acid To Monoestolide Synthesis

Nadia Farhana Adnan¹, Nor Asikin Mohamad Nordin², Noraini Hamzah^{1,3},
Mohd Ambar Yarmo¹

¹ School of Chemical Science and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia , 43600 Bangi, Selangor Darul Ehsan, Malaysia.

² Department of Science, UTM SPACE, Universiti Teknologi Malaysia International Campus Jalan Semarak, 54100 Kuala Lumpur, Malaysia.

³School of Chemical Sciences and Environmental, Faculty of Applied Sciences, University of Technology MARA, 40450 Shah Alam, Selangor Darul Ehsan, Malaysia.

Abstract

Estolide compound has a large potential in many industrial applications such as biodegradable lubricants and in cosmetic formulation. In this study, monoestolide can be prepared by addition reaction of oleic acid under vacuum-reflux and solvent free condition for 10 hours at 85 °C in the presence of solid zinc chloride anhydrous (ZnCl₂), choline chloride (ChCl) and ionic liquids (IL) ChCl-ZnCl₂, ChCl-FeCl₃, ChCl-SnCl₂, ChCl-CuCl₂ as homogenous acid catalysts. These reactions were compared with common homogenous catalyst namely sulfuric acid (H₂SO₄). The FTIR analysis show that addition reaction using the above catalysts showed the presence of three new peaks at 1732 cm⁻¹ for C=O ester, 967.0 cm⁻¹ for trans-CH=CH and 1176 cm⁻¹ for C-O-C which confirmed the existence of monoestolide. The LC-MS results showed peak for the present of new monoestolides at retention time (tR) 12.3 min corresponding to *m/z* 563.48. Among the IL, ChCl-ZnCl₂ surprisingly exhibited higher activity which is 98 % acid oleic conversion and 80 % selective for the synthesis of monoestolides. As a result, this IL gave two potential functions as a solvent as well as a green catalyst for monoestolide synthesis from oleic acid.

1 INTRODUCTION

Vegetable oils and their derivatives is good alternative as a substitution for petroleum as environmental friendly lubricant but it had some limitation such as poor thermal oxidative stability [1,2,3] and poor low temperature properties [4]. Estolides were developing to overcome all the limitation of vegetable oils such as dramatic improvement in oxidative stability and excellent low temperature properties over vegetable oils [5,6]. Estolides are class of ester based on vegetable oils form from one fatty acid react on unsaturated of another fatty acid to form an ester linkage [1].

Estolides were found in nature or be synthesized in laboratory shown promise as cosmetics, coating and biodegradable lubricants [5]. A monoestolide is formed when carboxylic acid from some fatty acid is linked to the unsaturated carbon of some other fatty acid through the ester bond. Polyestolides formed when three, four or more fatty acids are added up onto the estolides unit as shown in Fig 1. The number of oligomerizations that takes place is expressed as the estolides number (EN), which is defined as the average number of fatty acid molecules added to the parent fatty acid [7].

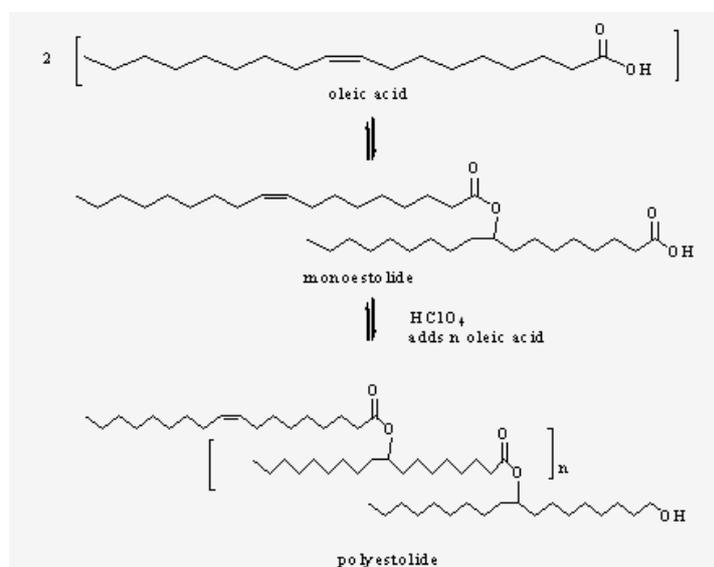


Figure 1 : Monoestolide and polyestolides structures [8].

Existence technology of estolides process required 'non-green' acidic catalyst such as H₂SO₄ and HClO₄ are well known in the literature [2,4,5,6]. These

mineral acids provide high yields of estolides after isolation by Kogelrohr distillation which is H_2SO_4 gave 60% while gave HClO_4 75%. These catalysts undergo many problem for example production process required high cost stainless steel equipment which can enhance operational cost. Furthermore, in every production expensive separation and purification also were needed due to the usage of highly corrosive acidic homogeneous catalyst [9]. To overcome these disadvantages effort has been made to the development IL catalyst system.

The replacement of the acidic homogeneous catalyst with IL have many attractive features such as environmental friendly and permit a continuous operation in very economical way. IL was known as a molten salt at room temperature. The term of IL is used for the salt which is melting point lower than $100\text{ }^\circ\text{C}$ [10]. IL is emerging as a green reaction media which is as catalyst and solvent at the same time. In this paper, we report the synthesis of monoestolides using four types of Lewis acidic IL as a catalyst, namely ChCl-ZnCl_2 , ChCl-FeCl_3 , ChCl-SnCl_2 and ChCl-CuCl_2 . Oleic acid is a desirable reactant in this reaction because it is readily available from agriculture source and inexpensive.

2 EXPERIMENTAL

Materials

Oleic acid (90 %w/w) and choline chloride (ChCl) were purchased from Sigma-Aldrich. Sulfuric acid (98 %w/w), Urea and iron chloride were purchase from System. Zinc chloride was purchase from Merck. All the materials were used without any further purification.

Preparation of Catalyst

Choline chloride salt (20 mmol) were mixed with chloride salt (zinc chloride or iron chloride)(80 mmol) in a 1:4 molar ratio and heated at $150\text{ }^\circ\text{C}$ in air with stirring until clear colourless liquid solution obtain [15].

Method

The acid oleic addition reaction perform by acid catalyzed with some modification describe by previous studies[6]. These reactions was carried out under low vacuum-reflux and solvent free condition complete with two-necked round bottom flask equipped with a magnetic stirrer, thermometer and fitted with a Dean Stark adapter and a condenser for reflux. This reaction were carried out at $85 \pm 1.0\text{ }^\circ\text{C}$ using IL, ZnCl_2 , ChCl and $65\text{ }^\circ\text{C}$ H_2SO_4 as a catalyst for 10 hours. IL catalyst was used at molar ratio 1:1 to the reactant. ZnCl_2 , ChCl and H_2SO_4 were used as comparison. The product from IL

catalyst was purified using urea to remove catalyst and impurities. Organic solvent in the sample were remove by rotary evaporator.

Product characterization

All liquid products were concentrated in a rotary evaporator. The product then analysed by Fourier transform infrared (FTIR) spectrometry to determined the changes to functional groups. The FTIR instrument used was a Perkin Elmer Model GX 1605. Sodium chloride cell (NaCl) is used as a medium for the liquid sample to identify the reaction. HPLC analyses were performed on a Waters 2795 separation module fitted with an auto injector (20- μ L injection loop), couple to a Varian 385-LC evaporative light scattering detector. Reverse-phase column chromatographic analyses were carried out on a C-18 column supplied by Phenomenex Jupiter from USA. The column was eluted by flow rate of 0.2 mL/ min (0 to 30 min, 80% acetonitrile: 20% acetone). The ELSD drift tube was set at 55 °C with nebulizer gas set 20 psi (138 kpa) and N₂ flow rate of 2.0 mL per minutes. LC-ESI-MS analyses were performed on Bruker MicrotofQ Daltonics mass spectrometer and linked to Ultimate 3000 Dionex LC.

3 RESULT AND DISCUSSIONS

The acid catalyzed with IL process was expected to convert the oleic acids to estolides under vacuum (2mBar) at 85°C and all other reaction parameter were held constant. As a control reaction, a reaction of oleic acid was performed without the present of a catalyst. The estolides obtained was a light and golden yellow. Next, the product undergoes urea purification to remove excess IL. In this process ionic liquid were removed when it form eutectic solvent after ChCl was mixed with urea[11]. Then, the final product underwent HPLC to calculate the conversion and selectivity. Their catalytic performances for formation of estolides were presented in Table 1. The results obtained were then compared to common acid catalyst reported in the literature for homogenous H₂SO₄. Among the IL catalyst screened the IL ChCl-ZnCl₂ (Sample 2) showed good catalytic activity to estolides synthesis. When using IL ChCl-FeCl₃ (Sample 3), IL ChCl-SnCl₂ (Sample 4) and IL ChCl-CuCl₂ (Sample 5), the results determined by HPLC indicate that there are no chemical reaction take place. This may be due to feeble acidity of this catalyst and the amount use in the reaction not suitable to obtain good yield of estolides product. The Lewis acidity of metal chloride IL will increase in order CuCl₂<FeCl₃<ZnCl₂<AlCl₃ [12]. This result obtained might be due to the differences properties of Lewis acid present in the catalyst. The catalytic activity of the IL observed in Table 1 was consistent with the Lewis

acidity order. Evidently, stronger Lewis acidity of the catalyst is advantageous for the activation of estolides production. Therefore, the catalytic performance of IL depends on the cation character. As compare with simple salt ZnCl_2 (Sample 7) with ChCl-ZnCl_2 (Sample 2) shows that IL displayed higher activity.

Table 1 : Catalytic performance of ionic liquid for the estolides synthesis.

Sample	Catalyst	T(°C)	t (h)	Conversion (%)	Selectivity (%)
1	H_2SO_4	65	10	99	63
2	ChCl-ZnCl_2	80	10	98	80
3	ChCl-FeCl_3	80	10	0	0
4	ChCl-SnCl_2	80	10	0	0
5	ChCl-CuCl_2	80	10	0	0
6	ChCl	80	10	19	43
7	ZnCl_2	80	10	46	66

Remark: Molar ratio of $\text{ChCl/MCl}_x=1:3$

The emergence of infrared absorptions for the ester function of estolides was monitored by FTIR spectrometry. Table 2 shows the data obtain from FTIR analyses of the reaction of oleic acid (oa), with or without a catalyst. The FTIR spectrum recorded from control reaction ao without catalyst, ChCl-FeCl_3 , ChCl-SnCl_2 , ChCl-CuCl_2 showed peaks at 1713.6 cm^{-1} for C=O of carboxylate group, 2926.1 cm^{-1} for C-H groups and 723.8 cm^{-1} for the cis CH=CH bond. In contrast, the IR spectrum recorded from the reaction oa catalyzed by homogenous sulfuric acid and ChCl-ZnCl_2 shows three new infrared absorption at 1732.8 cm^{-1} for the ester carbonyl group, 967.0 cm^{-1} for the -CH=CH- trans bond and 1176.2 cm^{-1} for the group C-O-C [1]. All the formation of the estolide had been monitored in this way by the formation these three new peaks [1,13,14]. A comparison of FTIR spectra from the reaction of oa without catalyst and using all ionic liquid discuss above shown in Fig.2. When using ChCl-ZnCl_2 , the FTIR spectrum show a peak for the C=O of ester estolide similar to C=O bond observed from homogenous H_2SO_4 as a catalyst. Our observation suggest that reaction using IL as a catalyst required slightly higher temperature compare to H_2SO_4 to complete the chemical reaction [15].

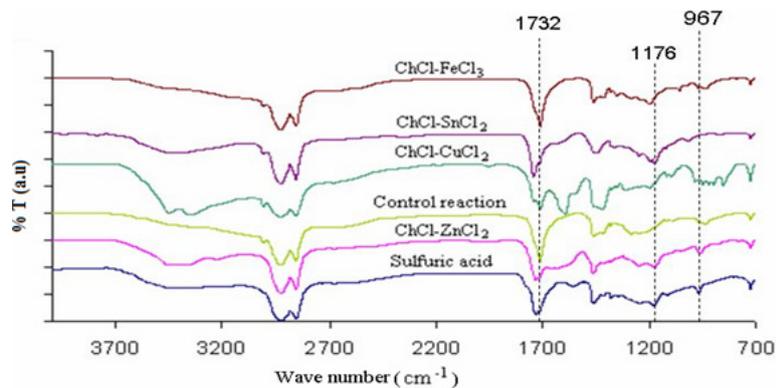


Figure 2 : FTIR spectra recorded from condensation reaction using different catalyst in same reaction condition.

Table 2 : FTIR data from samples of reaction and control (without catalyst)

Entry	IR bands (cm ⁻¹)	Functional moiety	Illumination
1, 2, 3, 4, 5	2929 and 2855	C-H	Alkane, medium (stretch, sharp/intense peak)
1, 2	1732	C=O	Carbonyl of ester group (sharp/intense peak)
1, 2, 3, 4, 5	1713	C=O	carbonyl of acid group (sharp/intense peak)
1, 2	1176	C-O-C	Anti-symmetric C-O-C strach (sharp/intense peak)
1, 2, 3	967	CH=CH, trans	=C-H, out of plane bending (sharp/intense peak)
1, 2, 3, 4, 5	723	CH=CH, cis	=C-H, out of plane bending (sharp/intense peak)

Remark: Entry 1: control reaction (H₂SO₄)

LC-ESI-MS show that typical ion chromatogram (TIC) of oa and the product using ChCl-ZnCl₂ (Sample 2) as a catalyst was taken under negative-ion mode are presented in Fig. 3. The LC peaks detected peak 3-5 in Fig. 3A from the control reaction. It consist of linoliec acid (LA), oleic acid (OA) and stearic acid (SA), respectively. The mass spectrum corresponding to peak 3 at tR 5.5 indicated to LA at *m/z* 279.25. Peak 4 at tR 6.4 min produced major peaks at *m/z* 281.20 for OA. Peak 5 indicated SA at tR 8.20 and 283.20 *m/z*. LC-

MS analysis of sample 2 produced seven chromatographic peaks which design as peak 1, 2, 3, 4, 5, 6 and 7 (Fig. 3B). The chromatographic peaks 3, 4 and 5 represent the same compounds as chromatographic peaks 3, 4 and 5 of control reaction. Thus, peak 3, 4 and 5 were identified as OA and SA, respectively. Peak number 6 at tR 12.3 min was identified as monoestolides from oleic-oleic estolides and it give major spectral at m/z 563.50.

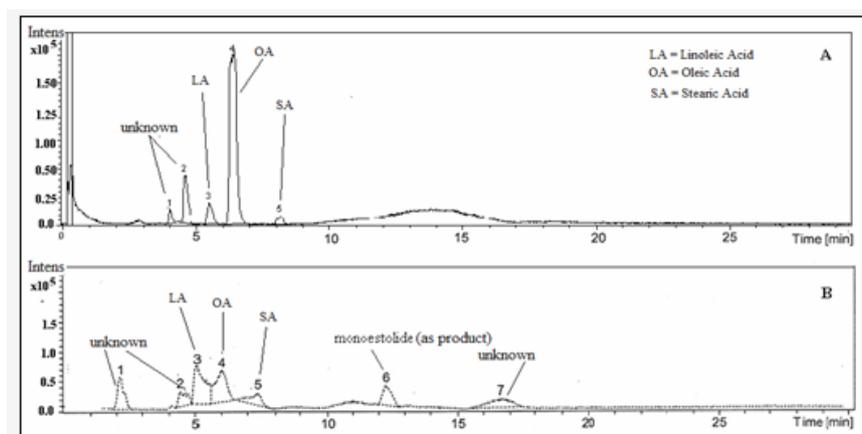


Figure 3 : Negative ion LC-ESI-MS chromatogram recorded from control reaction (without catalyst) (A) and entry 2 which is using ChCl-ZnCl_2 (B)

4 CONCLUSION

This study showed monoestolide was successfully synthesis using IL ChCl-ZnCl_2 as a catalyst and this catalyst system exhibit better catalytic performance than H_2SO_4 catalyst. IL ChCl-ZnCl_2 catalyst gave 98% conversion of OA and 80% selectivity to monoestolide. The present of peak 1732cm^{-1} from FTIR spectrum shows the ester linkage are produced and LC-MS identified monoestolide with major spectral m/z 563. The result obtained suggest the reaction 10 hours, temperature $85\text{ }^\circ\text{C}$, 1:1 molar ratio IL ChCl-ZnCl_2 : ao was sufficient to estolide synthesis. Therefore, IL ChCl-ZnCl_2 is a new catalyst that can be used to estolides synthesis using oleic acid and also provided an environmental friendly approaches.

ACKNOWLEDGMENT

The authors would like to thank UKM for UKM-ST-07-FRGS0002-2008 and UKM-GUP-NBT-08-27/113 research grant. We also would like to thank research staffs and friends.

REFERENCES

- [1] S.C Cermak and T.A Isbell, J. (2001). "Synthesis of Estolides from Oleic and Saturated Fatty Acids" in American Oil Chemist Society Vol. 78. pp. 557-565
- [2] Becker, R., Knorr, A. (1996). "An evaluation of antioxidants for vegetable oils at elevated temperatures" in Lubricant Science, Vol. 8. pp. 95-117
- [3] Cermak S.C & Isbell, T.A. (2003). "Improved Oxidative Stability of Estolides Esters" in Industrial Crops and Products Vol. 18. pp. 223-230.
- [4] Erhan, S.M., & Asadauskas, S. (2000). "Lubricant base stock from vegetable oils" Industrial Crops and Products Vol. 11. pp. 277-282.
- [5] Isbell, T.A. & Kleiman, R. (1994). "Characterization of estolides produced from acid catalyzed condensation of oleic acid" in Ibid Vol. 71. pp. 379-383.
- [6] Cermak, S.C, Skender, A.L., Deppe, A.B. & Isbell, T.A. (2007). "Synthesis and physical properties of tallow-oleic estolide 2-ethylhexyl esters" in Journal American Chemical Society Vol. 84. pp. 449-456.
- [7] Erhan, S.M., Kleiman, R. & Isbell, T.A. (1993). "Estolides from meadowfoam oil fatty acids and other monounsaturated fatty acids" in Journal American Chemical Society Vol. 70. pp. 461-465.
- [8] Cermak, S.C. & Isbell, T.A. (2001). "Synthesis of Estolides from Oleic and Saturated Fatty Acids" in Journal American Oil Chemist Society (2004) Vol. 78. pp. 557-565.
- [9] H. Wang, B. Lu, X. Wang, J. Zhang & Q. Chai, (2009) "Highly Selective Synthesis of Dimethyl Carbonate from Urea and Methanol Catalyzed by Ionic Liquids" in Fuel Processing Technology Vol. 90. pp. 1198-1201.
- [10] Welton, T. (1999). "Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis" in Chem. Rev. Vol. 99. pp. 2071 – 2083.

- [11] Abbott, A.P., Capper, G., Davies, D. L., Rasheed, R. K., & Tambyrajah, V. (2003). "Novel solvent properties of choline chloride/urea mixtures" in *Chemical Communications* pp. 70-71
- [12] Yang Y. L., Y. Kou,. (2004). "Determination of the Lewis acidity of ionic liquids by means of an IR spectroscopic probe" in *Chem. Commun* pp. 226-227.
- [13] Isbell. T. A., Lowery, B.A., DeKeyser, S,S., Winchell, M.L. & Cermak, S.C. (2006). "Physical Properties of Triglyceride Estolides from Lesquerella and Castor Oils" in *Industrial Crops adds products* Vol. 23. pp. 256-263.
- [14] Erhan, S.M. & Kleiman, R. (1997). "Biodegradation of estolides from Monosaturated Fatty Acid" in *Journal of American Oil Society* Vol.74. No. 5 pp. 671-674.
- [15] Sunitha, S., Kanjilal, S., Reddy, P.S., & Prasad, R.B.N. (2007). "Liquid – liquid Biphasic Synthesis of Long Chain Wax Esters Using the Lewis Acidic Ionic Liquid Choline Chloride.2ZnCl₂" in *Tetrahedron Letters* Vol. 48. pp. 6962 – 6965.