ZULFAQAR International Journal of
Defence Science, Engineering & Technology

Journal homepage: www.zulfaqar.upnm.edu.my

Synthesis of Epoxidized Fatty Hydrazides from Palm Olein: A Preliminary Study

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ARTICLE INFO

Article history:
Received
22-12-2018
Received in revised
25-12-2018
Accepted
25-12-2018
Available online
31-12-2018

Keywords:
epoxidized palm olein,
epoxidized fatty
hydrazides,
n-hexane

e-ISSN:
Type: Article

ABSTRACT

Epoxidized fatty hydrazides (EFHs) which have amine, amide and epoxide functional groups in their molecules are a versatile starting material for synthesizing of many industrially important compounds. In this report we describe the results of our preliminary study of synthesizing these compounds using a chemical reaction of epoxidized palm olein (EPO) and hydrazine monohydrate. The products were characterized by using Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) technique and CHN elemental analyser. The optimum reaction conditions for the hydrazide preparation were investigated by studying effect of each important reaction parameters on the product yields. The study shows that the optimum conditions to produce EFHs were using EPO to hydrazine monohydrate (mol ratio of 1 to 12), n-hexane as the solvent and at the temperature of 69°C.

Introduction

Fatty hydrazides, as multifunctional group compounds with general chemical structure (R-C=O-NH-NH_2) are versatile starting materials for many industrially important organic chemicals. The products include ionic surfactants [1], corrosions inhibitors [2], polyurethane based appliances [3], thermoplastics [4] and resins [5]. In addition, hydrazide derivatives have also good prospect to be used as antimicrobial [6, 7], anticancer [8, 9] and anti-tuberculosis [10] agents.

To date, there are varieties of methods that have been developed to produce hydrazides. The most widely used method is refluxing corresponding esters or amides with hydrazine monohydrate [11]. In addition, fatty hydrazides can be also prepared from vegetable oils such as palm oil [12-14], non-traditional oil such as neem, rice bran and karanja oils [15] and soybean oil [16].

Although epoxidized fatty hydrazides has been synthesised from epoxidized soy oil (ESO) more than half decade ago [17] followed by synthesis of epoxidized fatty hydrazides from palm oil by enzymatic method [18]. The literature search apparently indicates that, there are lacks of studies done on synthesis of fatty hydrazides from epoxidized palm olein without using enzyme as a catalyst. This report describes the results of our preliminary study on synthesis of epoxidized fatty hydrazides directly from epoxidized palm olein without the use of enzyme as a catalyst for the reaction.

Materials and Methods

i. Materials

EPO was a gift from Advance Oleochemical Technology Division (AOTD) of Malaysian Palm Oil Board. Hydrazine monohydrate of reagent grade (64-65%) and phosphorus pentoxide were supplied by Sigma Aldrich (St. Louis Missouri, USA) and used as received. n-hexane was purchased from Fisher Scientific (New Hampshire, USA). Ethanol, cyclohexane, n-heptane and chloroform were obtained from Merck Company (New Jersey, USA). All other solvents are of analytical grade.

ii. Experimental set up and procedure

EPO (1 mmol) and chosen amounts hydrazine monohydrate and n-hexane were mixed in a 100 ml conical flask. The mixture was then stirred at 150 rpm for 12 hours at 69˚C. Immediately after the reaction period was over, the white paste formed was transferred into a bigger conical flask, mixed with 10 ml ethanol, heated at 60-70˚C for almost 15 minutes and left at room temperature (28˚C) to obtain a precipitation. The solid was then isolated using a Whatman 4B filter paper in a Buchner funnel under a reduced pressure and dried in a reduced pressure desiccator in the presence of phosphorus pentoxide. This method was a modified procedure which was described in earlier publications [14, 19].

iii. Characterization

FTIR spectra in the range of 4000-300 cm^{-1} were obtained using a Spectrum BX Fourier Transform Infrared (FT-IR) spectrometer (Perkin Elmer, Waltham, Massachusetts, United States). ^{1}H NMR spectra of deuterated chloroform sample solutions were recorded using a Bruker 600 MHz NMR Spectrophotometer. Nitrogen content in the EFH was analysed by using a LECO Elemental Analyzer 932.

Result and Discussion

i. Effect of molar ratio of epoxidized palm olein to hydrazine monohydrate

The highest yield of EFHs was obtained when the mol ratio of hydrazine monohydrate to EPO was 12.0: 1.0 (Fig.1). Decrease of the yield as molar ratio is increased is probably due to the inhibitory effect of the excess of hydrazine monohydrate that reacts with the fatty acid chain [14].

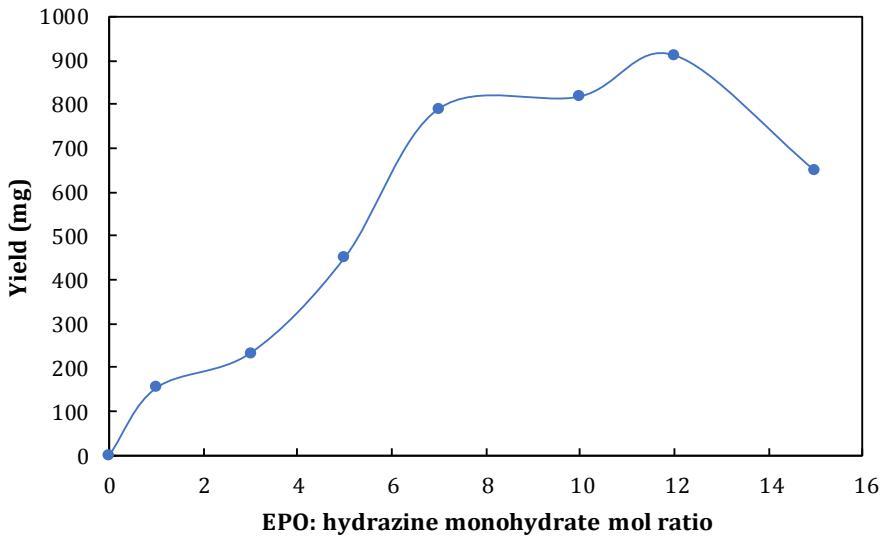

Fig.1: Effect EPO hydrazine monohydrate mol ratio on the product yield (Reaction conditions: solvent = 8 ml of n-hexane, temperature = 69 ˚C, time = 12 hours)

ii. Effect of solvent volume

Solvent plays important role in this synthesis reaction as vary the amount of the solvent affects the efficiency of the conversion [20] . Fig.2 shows that the yield is slightly increases as the volume of hexane is increased until the optimum yield is reached. The solvent volume of 8.0 ml gives the highest yield of fatty hydrazides. Similar trend was observed by other researchers [14]. The decrease of the yield may be due to the reduction the reactant molecule collisions as their concentrations are reduced.

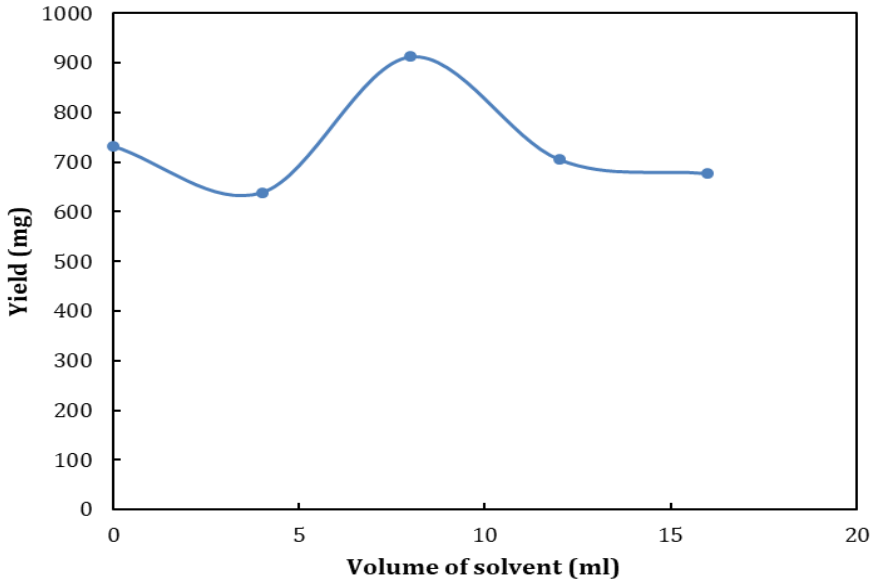

Fig. 2: Effect amount of solvent on the yield of fatty hydrazide production (Reaction conditions: EPO hydrazine monohydrate mol ratio = 12 mmol, solvent = n-hexane and temperature = 69 ˚C)

iii. Effect type of solvent

Changing of organic solvent offers possibility of the yield improvement as its affect the solubility of substrate and products [19]. In this part of the study, effect of various solvents on the yield was investigated. Four solvents of different polarity, i.e. chloroform (log P = 2.0), cyclohexane (log P = 3.2), n-hexane (log p = 3.5) and n-heptane (log P = 4.0) were tested and the results were shown in Fig.3. This study indicates that n-hexane is the most effective solvents for EFH production while chloroform gives lowest yield of the products.

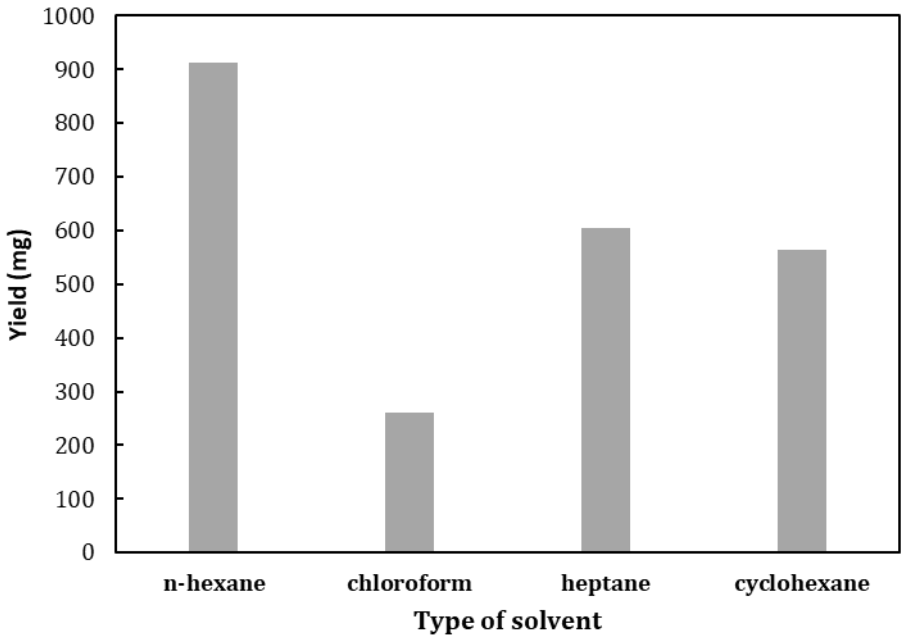

Fig. 3: Effect of various solvents on hydrazinolysis of EPO (Reaction conditions: EPO hydrazine monohydrate mol ratio = 12, solvent volume = 8 ml, reaction period = 12 hours and temperature = 69°C)

iv. FTIR spectra

FTIR spectra of EPO and EFHs are shown in Fig.4. EPO spectrum shows the characteristics absorption bands at 2920.61 cm $^{-1}$ and 2854.07 cm^{-1} corresponding to C-H stretching of long alkyl chain. Absorption band appears at 1739.30 cm^{-1} is due to C=O stretching. Then, absorption peak at 839.24 cm^{-1} corresponds to C-O-C stretching of oxirane vibration which belongs to epoxide group present in the EPO structure. This observation is almost same as observed in previous work [21]. FTIR spectrum for the product shows the characteristics absorption band of hydrazides. The peaks at 3314.15cm $^{-1}$ and 3197.20 cm^{-1} correspond to N-H group stretching for primary amine. Then, the absorption band at 1626.84 cm^{-1} is due to amide carbonyl stretching. Another important band is 1532.76 cm^{-1} which is due to N-H bending of primary amine. The absorption band at 845.05 cm^{-1} is for C-O-C stretching from oxirane vibration of the EFH. These results show that the epoxide functional groups are present in the products, in addition to N-H groups which are produced from hydrazine monohydrate treatment of the EPO.

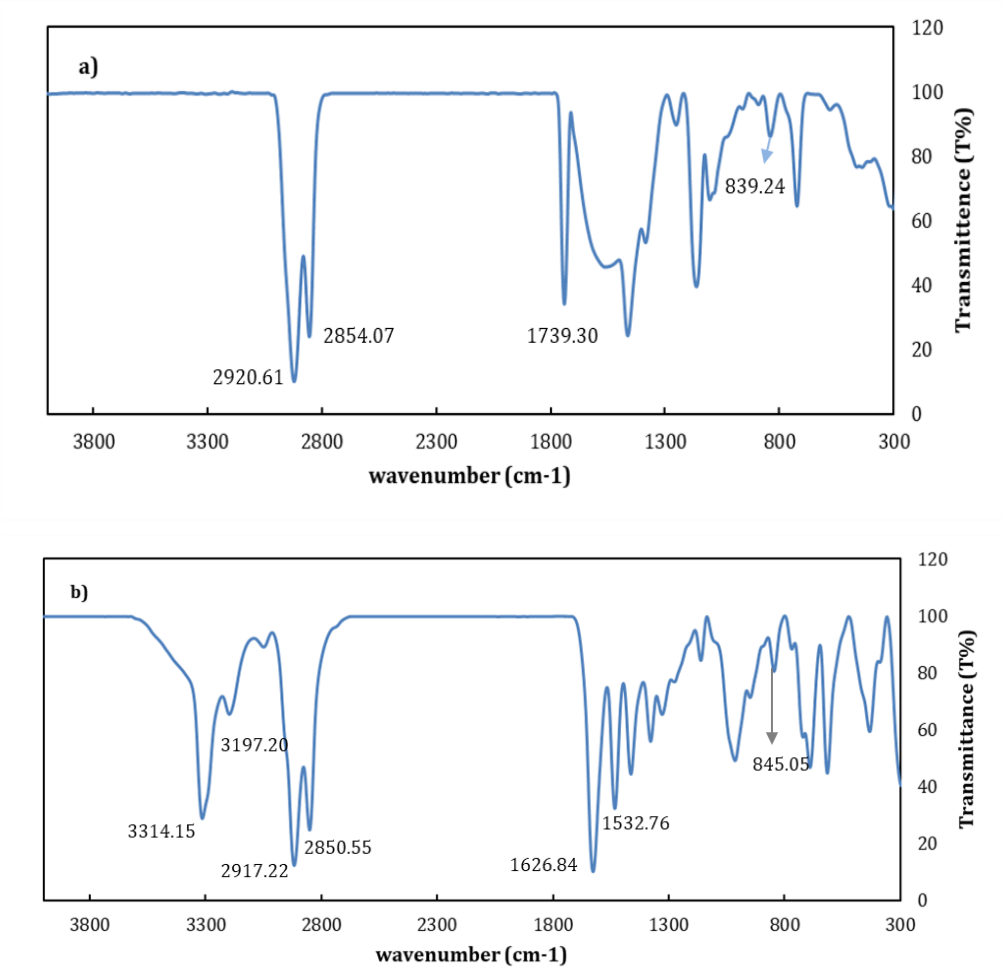

Fig. 4: FTIR spectra of a) epoxidized palm olein (EPO) and b) epoxidized fatty hydrazide (EFHs)

v.^{1}H-NMR analysis of epoxidized fatty hydrazides

The structure of EFH was investigated by using NMR spectrometry. The EFH powder sample was dissolved in deuterated chloroform ($CDCl_3$- d_6). Fig.5 shows the proton NMR spectra of EFH, in which, the $CDCl_3$-d_6 signal appears at (δ) 7.27 ppm [22, 23]. The peak at (δ) 0.88 ppm belongs to terminal methyl proton $-CH_3$ (Ha). The peak at (δ) 1.39 ppm is due to the protons of $-CH_2CH_2CH_3$ (Hb) in the methylene groups which adjacent to the methyl group, whereas the strongest peaks at (δ) 1.24 ppm is due to the methylene protons in the chains of fatty acid $-CH_2CH_2CH_2$- (Hc). Other important peaks in the spectra is at the range of (δ) 2.86 – 2.90 ppm which is attributed to the methane of epoxy ring proton (Hd), while peak at the region of (δ) 1.45-1.48 ppm could be due to the methylene group of alpha position of the epoxy group (epoxy-CH_2-CH_2-) (He). The protons of the peak at (δ) 1.63-1.64 ppm which is labelled as (Hf) belongs to the (epoxy-CH_2-epoxy) [24]. Furthermore, the peak at (δ) 3.76 ppm is due to proton at NH_2 of the nitrogen at R-C=ONHNH_2 which is labelled as (Hi). The peak at 7.09 ppm (Hh) in the range of 5.00 – 9.00 ppm [23] is attributed to the N-H of the amide group.

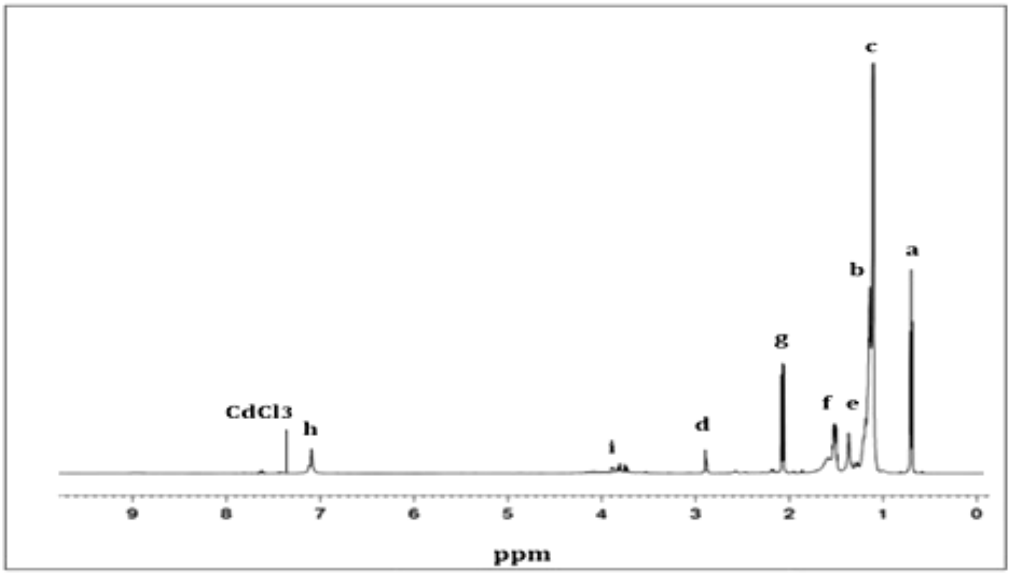

Fig.5: ^{1}H NMR Spectrum of epoxidized fatty hydrazides

vi. Elemental analyser

The nitrogen content of the EFHs was analysed using the elemental analyser. The presence of 10.3% of nitrogen in the EFHs indicates that hydrazinolysis of EPO by hydrazine monohydrate was successfully carried out.

Conclusion

This preliminary study shows that, EFHs which consists of amine, amide and epoxide functional groups in its molecule has been successfully synthesized via reaction of EPO with hydrazine monohydrate. The study also suggests that, the optimum conditions for preparing the EFH is using EPO hydrazine monohydrate mole ratio of 12 with reaction period of 12 hours at 69^0 C and n-hexane as a solvent. The characterization of EFH using FTIR and NMR techniques and CHN analysis verify that the important functional groups are present in the product

Acknowledgment

The authors would like to thank the Ministry of Higher Education Malaysia for funding this study through the Fundamental Research Grant Scheme (FRGS/2/2014/SG05/UPNM/01/1) and to AOTD of Malaysian Palm Oil Board for providing the EPO.

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