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Chemical synthesis and characterization of N-hydroxy-N-methyl fattyamide from palm oil

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ABSTRACT

In this study, N-hydroxy-N-methyl fattyamide (HMFA) has been synthesized by refluxing of palm oil and N, methyl hydroxylamine. The products were characterized using the complex formation test of hydroxamic acid group with copper(Π), various technique methods including nuclear magnetic resonance (^{1}H NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy and elemental analysis. Parameters that may affect the conversion of palm oil to HMFA including the effect of reaction time, effect of organic solvent and effect of, M, methyl hydroxylamine /oil molar ratio were also investigated in this study. Results of characterization indicate that HMFA was successfully produced from palm oil. The conversion percentage of palm oil into N-hydroxy-N-methyl Fattyamide was around 79. Results also showed that hexane is the best organic solvent to produce the HMFA. The optimum reaction time to achieve the maximum conversion percentage of the palm oil into HMFA was found to be 16 hours, and the optimum molar ration of M, methyl hydroxylamine/oil was found to be 6.5:1.0.

Key words: N-hydroxy-N-methyl Fattyamide, N,methyl hydroxylamine, palm oil, reflux.

INTRODUCTION

Hydroxamic acid and its derivatives have attracted much attention due to their biological activities as antibiotics, antifungal agents, food additives and chelators[1,2]. In addition, they are of considerable interest as efficient surfactants in the detergent industry[3]. Their complexes with various metal ions were used as organic reagents for extraction and separation of metal ions from aqueous solution in analytical application[4].

The hydroxamic acids were synthesized by reaction of an alkyl or aryl ester with hydroxylamine in the presence of alkali using adopting Blatt's procedure[5]. Many studies were carried out to synthesize of hydroxamic acids from acids or esters with hydroxylamine[6-8]. Alkanohydroxamic acids (N-acyl hydroxylamines) were synthesized using *Rhizomucor miehei* lipase catalyzed hydroxylaminolysis of fatty acids and soybean methyl ester[9]. Fatty hydroxamic acids from palm oil products were also synthesized using immobilized lipase as the catalyst[10]. The synthesis of erucamide by ammonolysis of erucic acid was investigated. The optimum conditions for the synthesis of erucamide were determined. 4.0: 1.0 molar ratio of urea to erucic acid and 190 C temperature[11]. Al-Mulla *et. al.,* (2009) reported that N,N'-carbonyl difatty amides were synthesized from palm oil using sodium ethoxide as catalyst. Ethyl fatty esters and glycerol were produced as by-products. Palm oil was converted to 79% N,N'-carbonyl difatty amides after 8 hours and molr ratio of urea to palm oil was 6.2: 1.0[12].

In this study, N-hydroxy-N-methyl Fattyamide was synthesized by refluxing method from palm oil and N,methyl hydroxylamine. Palm oil is a mixture of triacylglycerides, just like any ordinary fat, which are esters of glycerol with different saturated and unsaturated fatty acids. Malaysia is currently the world's largest producer and exporter of palm oil and it is the major source of vegetable oil for industrial application[13].

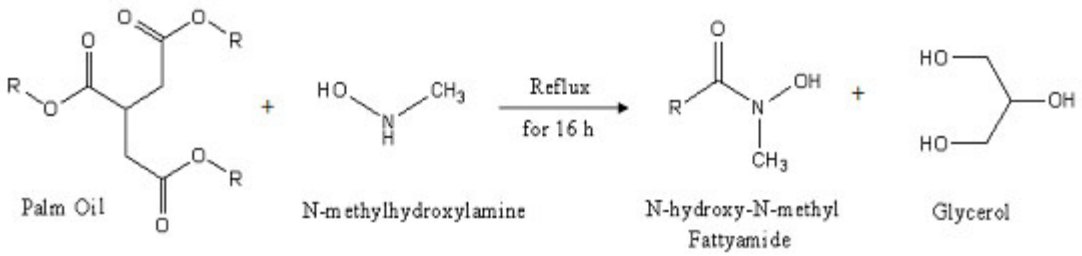
MATERIAL AND METHODS

Materials

The N,methyl hydroxylamine was purchased by local supplied from Fluka, Switzerland. Palm oil was obtained from Ngo Chew Hong oils and fats (M) Sdn.Bhd. Malaysia. Hexane, cyclohexane, chloroform and n-butane were supplied by T. J. Baker, USA.

Synthesis of HMFA

Palm oil was dissolved in hexane with N,methyl hydroxyl amine by refluxing at the boiling point of hexane for 16 hrs using a thermostated round bottom flask equipped with water-cooled condenser and mechanical stirrer .After the reaction had finished (product changed the colour to green with copper(Π) due to its ability to form complex),the product was dissolved in hot hexane and separated from bottom layer by separating funnel. The hexane phase was cooled in an ice bath for 4h to obtain HMFA filtered and then washed by hexane for three times and dried in a vacuum desiccators over phosphorous pentoxide. Scheme 1 shows the equation of reaction. The above procedure was carried out using various solvents including cyclohexane, chloroform, n-butane as well as hexane.



R= C_{12}: 0, C_{14}: 0, C_{16} : 0, C_{18} :0, C_{18} : 1, C_{18} : 2, C_{18} : 3, C_{20} : 0

Scheme 1: The reaction equation of N-hydroxy-N-methyl Fattyamide from palm oil

Qualitative analysis of amide group on HMFA was carried out by observing the coloured complex formed after methanolic solution of the HMFA reacted with copper(Π) in the dilute hydrochloric acid solution. The amount of the hydroxamic acid group was estimated based on nitrogen content of the dry HMFA determined by elemental analyzer model 932 (LECO, USA). The presence of amide in HMFA was also determined by FTIR spectra, The measure range of FTIR spectra was 4000- 280 cm^{-1} in a Parkin-Elmer 1650 infrared Fourier transform spectrometer, using the KBr pellet technique (about 1 mg of sample and 300 mg of KBr were used in the preparation of the pellets). The mixture was then pressed under 8 tons load for 1 min to produce the disc.

^{1}H Nuclear Magnetic Resonance (NMR) spectra were recorded using NMR spectrophotometer (Joel Ltd., Tokyo, Japan).

RESULTS AND DISCUSSION

Measurement of conversion

The conversion of palm oil into N-hydroxy-N-methyl Fattyamide was carried out by using the optimum reaction conditions as presented in Table 1. The conversion percentage of the product was calculated via the following equation (equation 1).

$$\text{Conversion (\%)} = \frac{\text{mmol of PRODUCT}}{\text{mmol of fatty acid in PALM OIL}} \times 100$$

Depending on nitrogen content of dry N-hydroxy-N-methyl Fattyamide analyzed by the elemental analysis; the amount of mmol product was determined. The amount of mmol fatty acid in the palm oil was calculated from mmol of potassium hydroxide required to saponify 1g of palm oil[14].
Characterization of HMFA

Complex formation

The colour of complexes of HMFA with copper(II) is green, Haron *et al.* (1994) reported that the same colour was observed after reaction between these metals with fatty amides[15].

Fourier Transform Infrared (FTIR) spectroscopy

Results of FTIR spectra of palm oil and HMFA are graphically depicted in Fig. 1. FTIR spectrum conducted on palm oil reveals peaks at wavenumber of 2857 cm^{-1} and 2925 cm^{-1} which correspond to C-H stretching of alkyl chain. The peak at 1745 cm^{-1} corresponds to C=O stretching and at 1459 cm^{-1} corresponds to C-H aliphatic bending, respectively. The peak observed in FTIR spectrum of HMFA was at wavenumber of 3420 cm^{-1} which corresponds to O-H stretching. Absorption bands at 1650 cm^{-1} which correspond to C=O of amide group and at 1041 cm^{-1} which corresponds to C-N stretch indicating that fatty amide was formed[13].

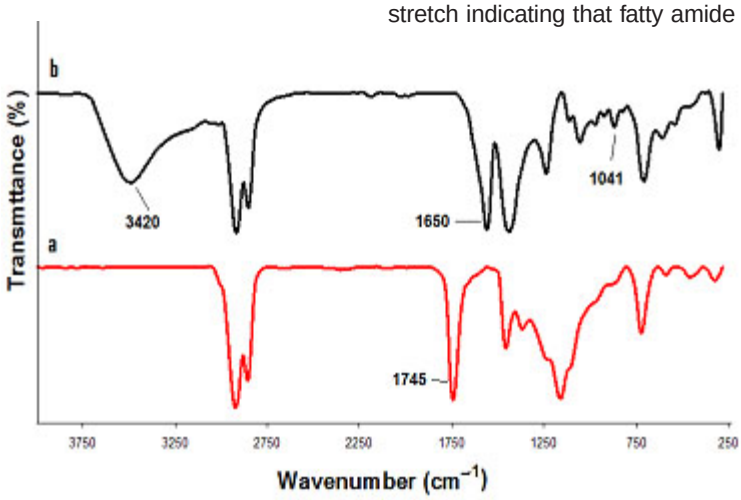


Fig. 1: FTIR spectrum conducted on (a) Palm oil and (b) HMFA

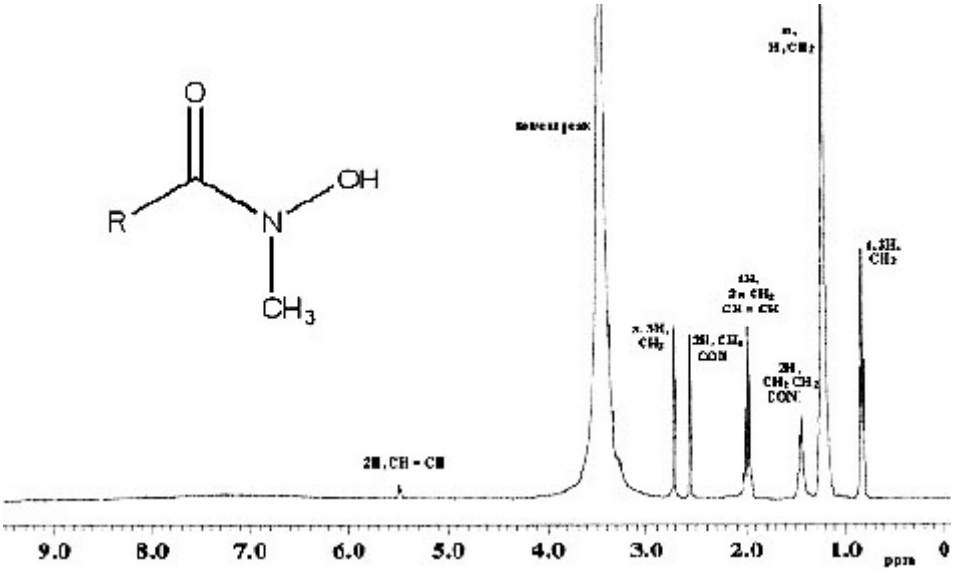


Fig. 2: ^{1}H NMR Spectra of HMFA

^{1}H NMR Spectra of N,hydroxy-N,methyl Fattyamide

(400MHz) ($CDCL_3$): δ 0.88 (t, J = 8.5 Hz, 6H, 2 x CH_3), 1.29 (m, H, CH_2), 1.94 (2H, CH_2 CH_2 C=O N), 2.02 (H, OH), 2.18 (2H, CH_2 CH = CH), 2.58 (t, J = 10.4 Hz, 2H, 2 x CH_2 CO N), 2.72 (s, 3H, CH_3), 5.49 (2H, CH = CH).

Elemental Analysis

Results of the elemental analysis conducted on HMFA reveals the presence of nitrogen atoms in the product. The nitrogen content of N-hydroxy-N-methyl Fattyamide was found to be 5.01%.

Table 1:Optimum reaction conditions of conversion Palm Oil into N-hydroxy-N-methyl Fattyamide

Parameter	Condition
Solvent	Hexane
Reaction time	16 h
Temperature	69 °C
Ratio N-hydroxy-N-methyl Fattyamide (mmol): Palm oil (mmol)	6.5: 1.0

CONCLUSIONS

This paper describes the synthesis and characterization of N-hydroxy-N-methyl Fattyamide from palm oil with N,methyl hydroxylamine using refluxing method.

Based on test results, the following conclusions can be drawn:

- FTIR spectrum, ^{1}H NMR and elemental analysis tests conducted on HMFA reveal that HMFA were successfully produced from palm oil
- The optimum reaction time for all palm oil was found to be 16 hrs.
- The conversion percentage of palm oil to HMFA was found to be substantially affected by the organic solvent used in the production process. Hexane solvent results in the highest conversion percentage of palm oil to HMFA.
- A molar ratio of 6.5: 1.0 (N,methyl hydroxyl amine to oil) results in the maximum conversion percentage of palm oil to HMFA.

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