Derivatization of Fatty Acid with 2,4 dibromoacetophenom by BF3 (Boron Triflouride).

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International Journal of Sciences: Basic and Applied Research (IJSBAR)

ISSN 2307-4531
(Print & Online)

http://gssrr.org/index.php?journal=JournalOfBasicAndApplied

Derivatization of Fatty Acid with 2.4 Dibromoacetophenone by BF_3 (Boron Triflouride) Catalyst

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Abstract

The research of derivatization process of fatty acid using 2.4 dibromoacetophenone with BF_3 catalyst has been done. Derivatization process aims to improve the detection of UV detector on HPLC instrument, because the fatty acid can only absorb the UV light at small wavelength. Results show that the fatty acid derivatization process using 2.4 dibromoacetophenone with BF_3 catalyst can't make to phenacyl oleic but methyl oleic form. Product derivatization with BF_3 catalyst with methanol or n-hexane as solvent get the same product that is methyl oleic. This phenomenon, because BF_3 catalyst in methanol. The conclusion of this research is BF_3 catalyst can't be used in the derivatization process for fatty acid with 2.4 dibromoacetophenone.

Keywords: Fatty Acids; Derivatization Process; BF3 catalyst.

1. Introduction

The derivatization process of fatty acids with 2.4 dibromoacetophenone done to make the absorption of fatty acid to higher wavelength. The derivatization process will change the bathochromic shift process (red shift). The derivatization process to improve the specificity and sensitivity analysis.

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Reference [1] reported that the derivatization of fatty acids can be used to separate from the disturbance peak between the products and reagents /solvents. Development of derivatization process of fatty acid to change the chromophore group can be performed with 2.4 dibromoacetofe and triethylamine [2]. The research on derivatization of fatty acids can also be used reagent 2,4-dinitrophenylhydrazine (2,4-DNPH) with a base catalyst [3]. While [4] also did a short chain fatty acid derivatization with 2,4-dibromoacetophenone (DBAP) and triethylamine (TEA). Other research from [5] have also been done derivatization of fatty acids with penderivat 2-(2-naphthoxy) ethyl 2-(piperidino) ethanesulfonate (NOEPES) with 18-crown-6 in toluene (20 mM) and potassium carbonate. The derivatization process of fatty acids can be done with 2-(11H-benzo[a]carbazol-11-yl)-ethyl-4-methylbenzenesulphonate (BCETS) and K_2CO_3 with solvent acetonitril [6]. The derivatization process that can be applied in the analysis by HPLC with different types of detectors such as ultraviolet (UV), fluorescence and mass spectrometry (MS) [7].

This literature shows a lot of derivatization process carried out in an alkaline catalyst. This process can do the derivatisation process used an acid catalyst. This is usually done in the esterification or transesterification process of fatty acids. Some studies esterification and transesterification of fatty acids can be carried out with the catalyst NaOH [8], K_2CO_3 [9], KOH [10], H_2SO_4 [11, 12], BF_3 [13, 14] and several catalysts such as hydrotalcite [15].

This study determine the derivatization process of fatty acids with 2.4 dibromoacetophenone using BF_3 catalysts. The derivatisation process of fatty acid carried out in acid catalyst. The catalyst use in this process is BF_3. It's as acid catalyst and usually used in the process of derivatisation especially esterification fatty acid process. This study focused to use BF_3 catalyst in the fatty acid derivatisation process. It's seeing the BF_3 ability as an acid catalyst in this derivatization process.

2. Material and Method

Materials: Oleic acid (Fluka) , 2.4 Dibromoacetophenone (Merck), BF_3 20 % in methanol (Merck), saturated NaCl , distilled water, n -Hexane (Merck) and methanol (Merck).

Derivatization of Fatty Acid using 2.4 Dibromoacetophenone

The optimization of derivatization process of fatty acids with 2.4 Dibromoacetophenone done by weighing 25 mg of oleic standard dissolved in 10 ml of n-hexane and put in a 25 ml flask was added n-hexane to mark boundaries. Taken 3 ml solution, then added 100 ul BF_3 in methanol and added 500 uL of 2.4 Dibromoacetophenone, Then vortex until a homogeneous solution for 4 minutes. After that followed by heating for 40 minutes at a temperature of ± 80 °C. After the process of heating the solution was added with 1.5 ml saturated NaCl, and centrifuged for 10 minutes. Separated a n-hexane layer, then read on GC-MS (Shimadzu 2010) and Uv-vis spectrophotometry (Shimadzu 1700) . The same process is done using solvent is methanol.

3. Result and Discussion

The derivatization process of fatty acid derivatization process with 2.4 dibromoacetophenone will form a new

compound. This has a chromophore groups to be responsible for UV absorption. The derivatization results shown are expected to shift the wavelengths of UV absorption to be higher wavelengths (Figure 1).

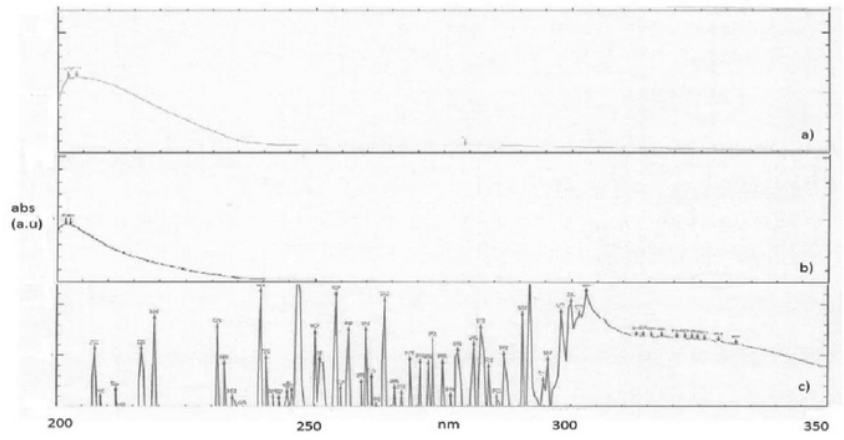

Figure 1: The maximum wavelength ; a) Triglycerides (205 nm), b) Free Fatty Acid (202 nm), c) Derivatization of Fatty Acid with 2.4 dibromoacetophenone using BF_3Catalyst (305 nm) .

Figure 1. Shows about change the wavelength triglycerides and fatty acids. The difference wavelength between triglyceride at 205 nm and free fatty acids of about 202 nm. the derivatization process change the wavelength to 316 nm. This indicates a bathochromic shift after derivatization process. Therefore, it is necessary to identify the results of derivatization using GC-MS (Figure 2).

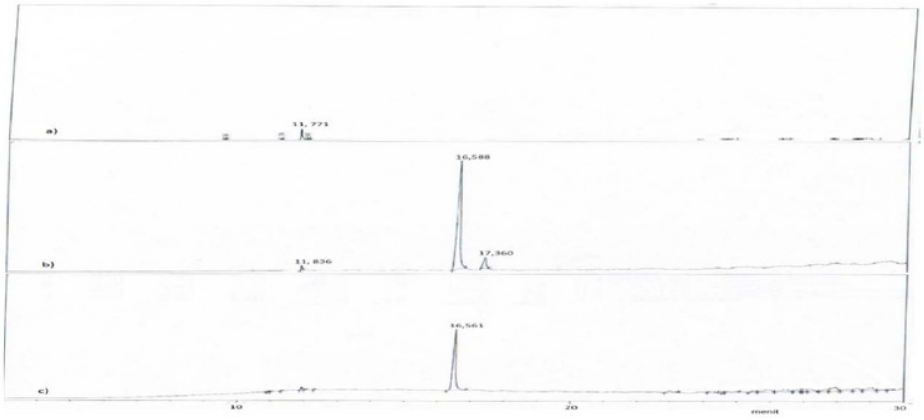

Figure 2: Result of GC-MS chromatograms of Standard Fatty Acids in Derivatisation Process with methanol as Solvent ; a) chromatogram with 2.4 Dibromoacetophenone, b) Derivatization of Oleic Acid with 2.4 Dibromoacetophenone and c) Derivatization of Oleic Acid with 2,4 Dibromoacetophenone (GC-MS conditions; oven temperature: 0^0C-50^0C (Hold 5 minutes), 50^0C-200^0C (Hold 1 minute, the increasing temperature rate of 20^0C), 200^0C - 250^0C (Hold 1 minute, the increasing temperature rate of 3^0C)

Figure 2 shows two chromatogram for oleic form that are oleic methyl ester and oleic acid are appear at the retension time 16.588 minutes and 17.485 minutes. The presence of oleic acid after derivatization process shows the derivatization conditions are not perfect or their reaction decomposition from oleic methyl ester. The results show that derivatization process of oleic acid with 2.4 dibromoacetophenone does not occur. The derivatization process of oleic acid with 2.4 dibromoacetophenone produce oleic methyl esters form. The oleic methyl ester with BF_3 catalyst in the methyl trans 9-octadecanoic form based on the MS (Figure 3).

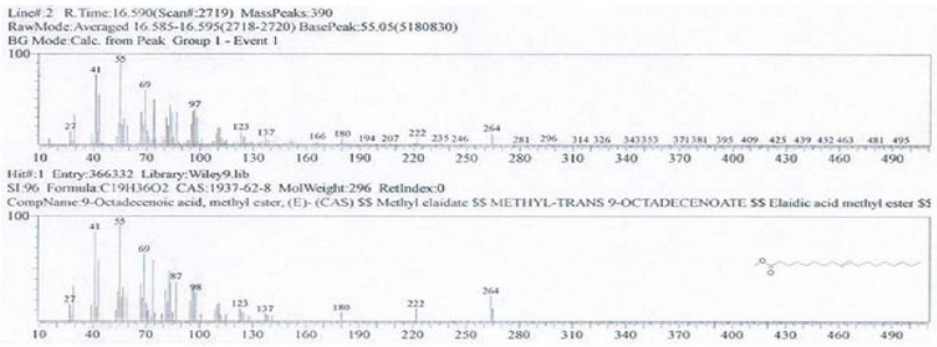

Figure 3: Results of oleic methyl esters fragmentation by GC - MS appearing at a retention time of 16.590 minutes

The result of MS Fragmentation show that the compound has a molecular weight 264 g/mol. Its typical from the oleic methyl ester. Results by wiley 9 has a similarity of 96% indicates a oleic compound in the trans structure (figure 3). Other than that appear peak from 2.4 dibromoacetophenone at a retention time 11.835 minutes . These results have of MS similarity 92% (Figure 4)

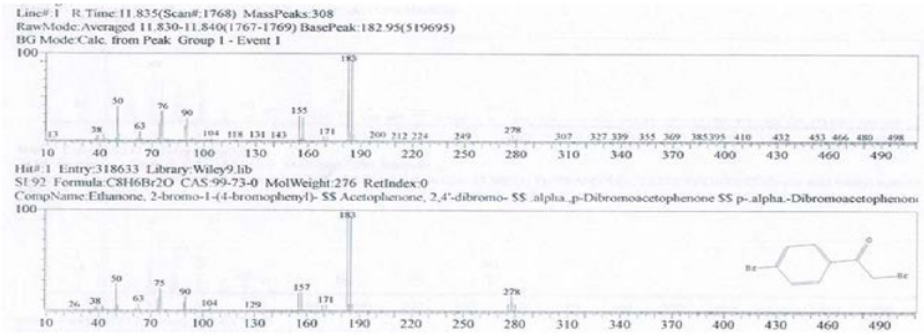

Figure 4: Results of fragmentation 2.4 dibromoacetophenone by GC - MS appears at a retention time of 11.835 minutes

The result of GC-MS identification showed that the bathochromic shift in the maximum wavelength is not from the derivatisation process between oleic acid with 2.4 dibromoacetophenone. This results showed the reaction between oleic acid and methanol to produce a oleic methyl esters form. This wavelength shift from the

compound of 2.4 dibromoacetophenone. This is evidenced because presence of 2.4 dibromoacetophenone peak at a retention time 11.835 minutes. Derivatization process mechanism is illustrated as Figure 5.

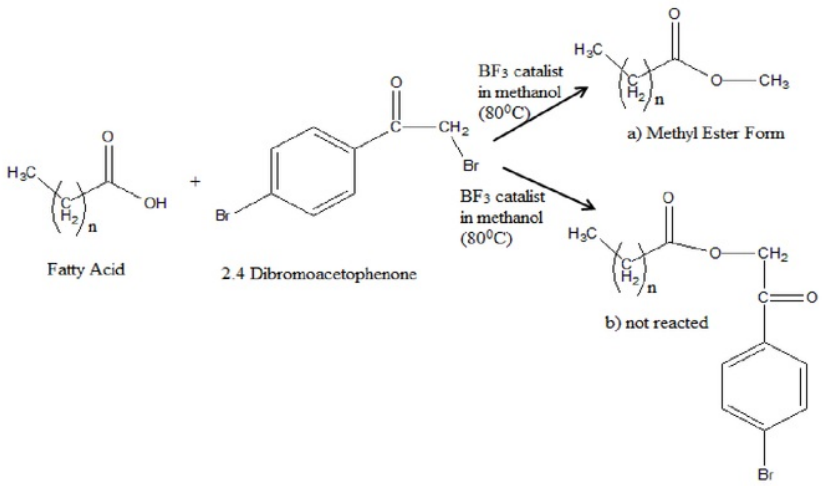

Figure 5: The Derivatization Process of Fatty Acids with 2.4 dibromoacetophenone with BF_3 Catalyst in Methanol; a) Methyl Ester Form (Result of Derivatization Process), b) 2.4 dibromoacetophenone Ester Form (not Reacted)

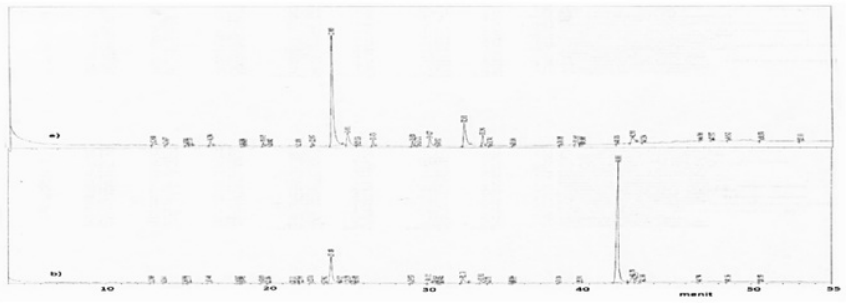

Figure 6: The GC-MS Chromatograms of Fatty Acids Standard in Derivatisation Process using 2.4 Dibromoacetophenone with n hexane solvent ; a) Chromatogram Penderivat 2.4 Dibromoacetophenone, b) Derivatization of Oleic Acid with 2.4 Dibromoacetophenone (GC-MS conditions; oven temperature : 0^0C - 50^0C (hold 5 minutes) , 50^0C - 260^0C (hold 8 minutes, the increasing the temperature rate of 5^0C)

The result of oleic methyl ester formation in n hexane solvent in the FAME form (Figure 6). The results shown that derivatization process of oleic acid with 2.4 dibromoacetophenone in the n-hexane solvent indicates an oleic methyl ester appears at a retention time 41.800 minutes (Figure 6). The compound 2.4 Dibromoacetophenone after derivatization process is appears at a retention time of 23.985 minutes and 32.161 minutes. This problem is

common with use methanol as a solvent. Therefore, the use of BF_3 catalyst in the process of derivatization of oleic fatty acids with 2.4 dibromoacetophenone produce the methyl ester form. This phenomenon is possible because the BF_3 catalyst methanol solvent, so the fatty acid will react with the methanol to oleic methyl esters form.

4. Conclusion

The derivatization product with BF_3 catalyst and using solvent like methanol or n hexane can produce the same product. The derivatization product as methyl ester form. This problems because BF_3 in methanol solvent. Therefore, application of BF_3 catalyst will produce methyl ester form. This result shown that BF_3 catalyst can't be used in the derivatisation process with 2.4 dibromoacetophenone

Acknowledgements

We would like to acknowledge and thanks for Grants Higher Education 2015 on fundamentals Scheme given in the Research of optimization methods in the halal products analysis.

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