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**Research Article**

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# Synthesis of Alkyl Esters from Vegetable Oils Catalyzed by Lemon Juice as Natural Catalyst and Ethanol as Reagent

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## ABSTRACT

*This study was to develop green methodology to convert vegetable oils into ethyl esters of fatty acids using lemon juice (pH=2.8) as a natural catalyst and ethanol as reagent. It is a first application of lemon juice to synthesize ethyl esters from fatty acids of vegetable oils. We used the sulfuric acid as a control to compare the catalytic activity of lemon juice to that of sulfuric acid.*

**Keywords**: Waste cooking oil; Sunflower oil; Lemon juice; Fatty acid esters

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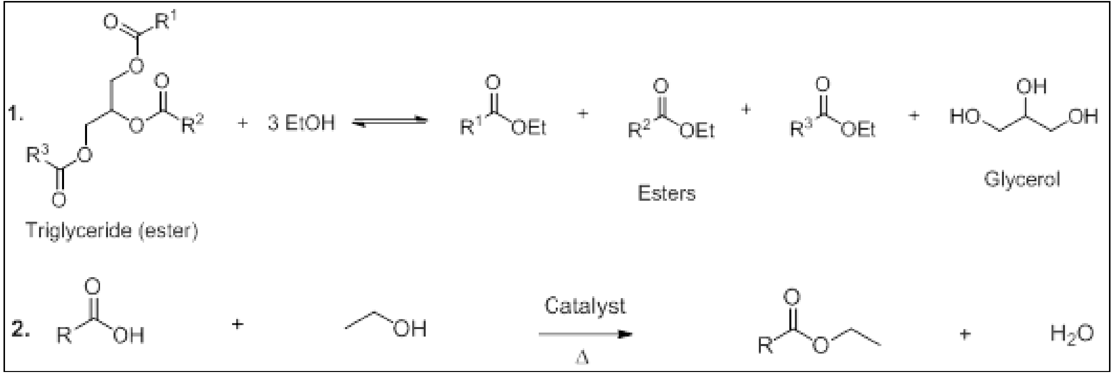
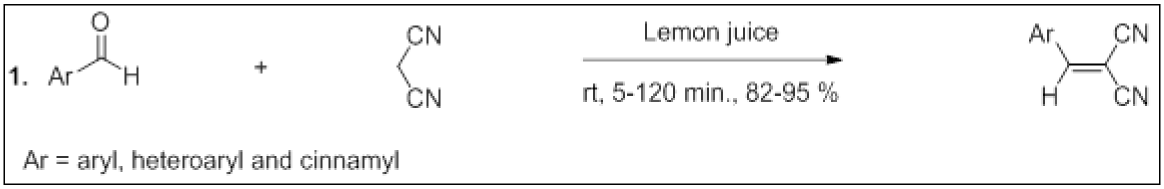
## INTRODUCTION

Vegetable oils are triglycerides or esters of fatty acids and glycerol containing long hydrocarbon chains (R) insoluble in water (Scheme 1, reaction 1). Indeed, a comparative study showed no significant difference, from a structural and spectroscopically point of view, can be observed between waste cooking oil and refined vegetable oils. However, the results indicated that only the degree of saturation, monounsaturated fatty acids, viscosity and acidity index of used cooking oils were considerably higher compared to those of refined vegetable oils [1]. Thus, these two types of oils consist essentially of triglycerides of fatty acids, which may be converted to alkyl fatty acid esters. In terms of organic synthesis, trans-esterification (Scheme 1, reaction 1) and esterification (Scheme 1, reaction 2) are adequate methods to generate alkyl esters from vegetable oils [2-7].

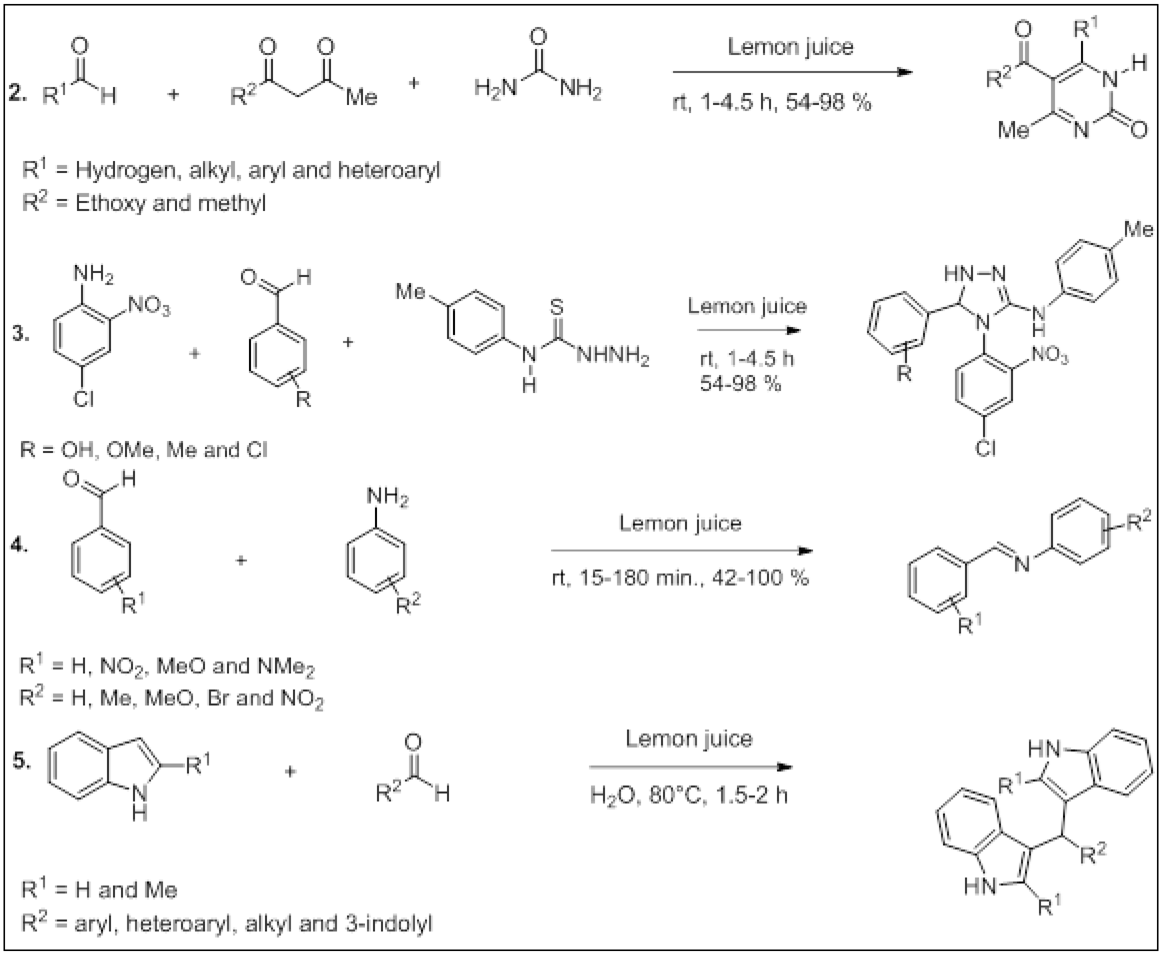


**Scheme 1 : Trans-esterification and esterification to generate alkyl esters from vegetable oils**

Due to its acid behavior, lemon juice is a potential catalyst. It has already been used as a natural catalyst in the Knoevenagel condensation (Scheme 2, reaction 1), in the synthesis of dihydropyrimidinones (Scheme 2, reaction 2), in the synthesis of triazoles derivatives (Scheme 2, reaction 3), in the synthesis of Schiff bases (Scheme 2, reaction 4) as well in the coupling of aldehydes and indoles to generate bis-, tris-, and tetra-indoles (Scheme 2, reaction 5) [8-11].



**Scheme 2a: Synthesis of dihydropyrimidinones**



**Scheme 2b: Synthesis of Schiff bases**

However, lemon juice has not yet been used as natural catalyst in the chemical modification of vegetable oils. In this fashion, this study shows, for the first time, the catalytic potential of lemon juice in the chemical modification of fatty acids to the corresponding esters. Let us recall here that one of the major challenges for Chemists, is to find and develop simple chemical processes, and less hazardous by identifying environmentally benign reaction conditions [8-11]. In this perspective, the main objective of this study was to develop a green methodology to convert vegetable oils into corresponding ethylated esters, by exploiting catalytic properties of lemon juice and using ethanol as an appropriate reagent. Lemon is rich in citric acid, calcium, phosphorus, potassium and vitamins E, K, B and C. Phenol compounds have also been identified in the lemon juice [12]. This diversity of chemical constituents makes lemon, a highly sought fruit, for its therapeutic properties, antiseptic and antioxidant.

## EXPERIMENTAL PROCEDURES

### Processing oils

The work began with the collection of vegetable oils and required reagents. The vegetable oils were, initially, hydrolyzed. At the end of this operation, the resulting fatty acids were then esterified in the presence of catalysts such as, sulfuric acid and lemon juice. The corresponding ethylated esters have been purified by silica gel column chromatography and analyzed by $^1$H NMR and Infrared spectroscopy. In this experiment, it was used the waste cooking oil and the refined sunflower oil as starting materials. In fact, before converting waste vegetable oil into ethyl esters, it was necessary to remove the impurities it contains. The oil was allowed to stand for 48 hours at room temperature to settle the solid particles of food. The supernatant was collected by decanting. This fraction was subjected to vacuum filtration to remove residual impurities and placed in an oven at 110°C overnight to remove any trace of water. On the other hand, refined sunflower oil was used without any particular treatment.

### Quantitative analysis of waste cooking oil and refined sunflower oil

The amount of free fatty acids in oils was determined by dissolving 2 g of oil in 10 mL of ethanol and 3 to 5 drops of phenolphthalein were added as an indicator. The solution was stirred to obtain a homogeneous mixture and a solution of NaOH was added drop wise until color change. The tap of the burette was closed when the coloration persisted for at least ten seconds.

### Obtaining fatty acids

50 ml of oil (waste cooking oil or refined sunflower oil) were taken using a test tube and introduced into an Erlenmeyer. 50 mL of 8 N NaOH solution and 100 mL of ethanol were added. The reaction mixture was kept at reflux under magnetic stirring for about 45 minutes. The solution was cooled to room temperature and then a saturated NaCl solution was added. The solution containing the precipitate was filtered and the solid obtained was dried in open air. The solid obtained is a sodium salt or soap. Thereafter, the soap was dissolved in an aqueous solution containing sulfuric acid. The mixture was heated at 55°C and maintained under stirring until complete dissolution of the solid salt. The mixture was then transferred to a separatory funnel to separate the two phases. The organic phase was concentrated under vacuum (rotary evaporator) to afford 83.21 g of waste oil (91.48%) and 86.99 g of refined sunflower oil (95.28%). The fatty acids were used, without purification, to synthesize the corresponding esters.

### Synthesis of fatty acid esters

10 g of fatty acids were introduced into an Erlenmeyer and ethanol was added and the catalyst. The solution was stirred until complete homogenization. The reaction mixture was heated to 80°C and kept under stirring for one hour. After that, the solution was cooled and then transferred to a separatory funnel to separate the organic phase containing crude ethylated esters. The corresponding ethyl esters have been purified by silica gel column chromatography, using petroleum ether and ethyl acetate in a ratio of 95: 5 as eluent, to yield 7.21 g (71.27%) in the presence of sulfuric acid and 2.94 g (29%) in the presence of lemon juice when refined sunflower oil fatty acids were used as starting materials (Scheme 3). In the same perspective, 6.61 g (66%) were obtained when sulfuric acid was used as a catalyst and waste cooking oil fatty acids as starting materials. When waste cooking oil fatty acids were mixed with ethanol, in the presence of lemon juice, a light transformation was observed because the thin layer chromatography showed a single spot of the reaction with an $R_f$ (0.15) compared with the $R_f$ (0.11) of the starting material. All he compounds were characterized by IR and $^1$H NMR.

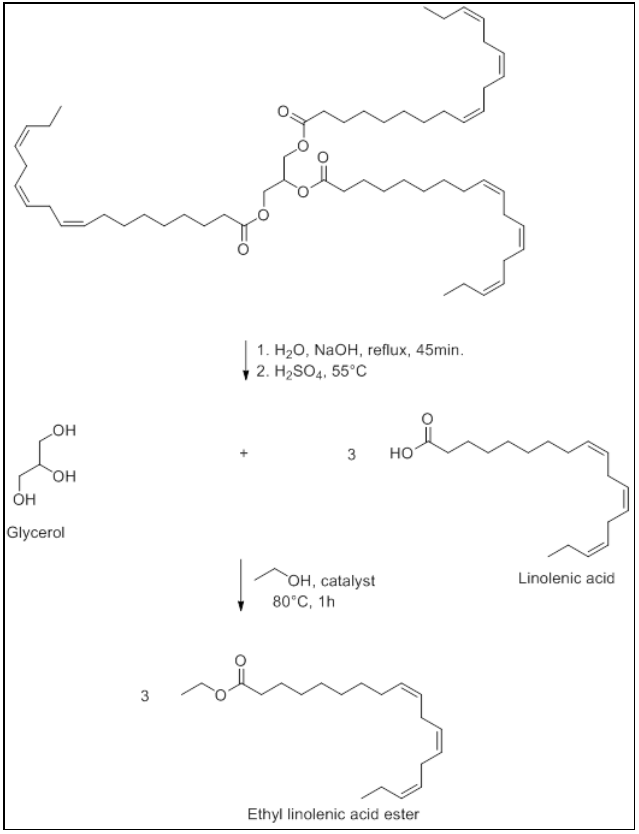
### Spectral data for ethyl esters of waste cooking oil fatty acids obtained in the presence of sulfuric acid

$^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.23-1.30 (3H, m, $CH_3$-$CH_2$-O-CO-R), 4.09-4.14 (2H, q, $CH_3$-$CH_2$-O-CO-R), 2.30-2.35 (2H, m, $CH_3$-$CH_2$-O-CO-$CH_2$-R), 1.55-1.64 (2H, m, $CH_3$-$CH_2$-O-CO-$CH_2$-$CH_2$-R), 1.23-1.30 (8H, m, $CH_3$-$CH_2$-O-CO-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-R), 1.98-2.05 (4H, m, R-$CH_2$-CH=CH-$CH_2$-CH=CH-$CH_2$-CH=CH-$CH_2$-$CH_3$), 2.26-2.35 (2H, m, $CH_3$-$CH_2$-O-CO-$CH_2$-R), 2.77-2.78 (4H, m, R-CH=CH-$CH_2$-CH=CH-$CH_2$-CH=CH-R), 5.31-5.38 (6H, R-HC=CH-$CH_2$-CH=CH-$CH_2$-CH=CH-$CH_2$-$CH_3$), 0.93-0.98 (3H,m, R-CH=CH-$CH_2$-$CH_3$). IR (film): 2924, 2854, 1736, 1466, 1373, 1180, 1034, 725 $cm^{-1}$.

**Spectral data for ethyl esters of refined sunflower oil fatty acids obtained in the presence of lemon juice**
$^1$H NMR (400 MHz, $CDCl_3$): δ = 1.21-1.39 (3H, m, $CH_3-CH_2-O-CO-R$), 4.09-4.15 (2H, q, $CH_3-CH_2-O-CO-R$), 2.22-2.37 (2H, m, $CH_3-CH_2-O-CO-CH_2-R$), 1.52-1.64 (2H, m, $CH_3-CH_2-O-CO-CH_2-CH_2-R$), 1.21-1.39 (8H, m, $CH_3-CH_2-O-CO-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-R$), 2.00-2.07 (4H, m, $R-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH_3$), 2.22-2.37 (2H, m, $CH_3-CH_2-O-CO-CH_2-R$), 2.75-2.78 (4H, m, $R-CH=CH-CH_2-CH=CH-CH_2-CH=CH-R$), 5.31-5.38 (6H, $R-HC=CH-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH_3$), 0.93-0.98 (3H, m, $R-CH=CH-CH_2-CH_3$). IR (film): 2924, 2854, 1736, 1458, 1373, 1242, 1180, 1095, 1034, 725 cm$^{-1}$.

## RESULTS AND DISCUSSION

As a part of our ongoing research in natural products, we report herein our results in the synthesis of fatty acid esters catalyzed by sulfuric acid and by lemon juice in the presence of ethanol as reagent. The slight transformation could be explained by residual traces of NaOH which have probably neutralized the lemon juice acidic behavior. Nevertheless, lemon juice was effective in the esterification process of fatty acids of refined sunflower oil (Scheme 3). We also analyzed the pure ethyl esters by $^1$H NMR and Infrared spectroscopy. We noticed that the $^1$H NMR and Infrared (IR) spectra of ethyl esters obtained by lemon juice are identical with those of the ethyl esters obtained by sulfuric acid (Scheme 3). It is important to note that, we used the sulfuric acid as a control to compare the catalytic activity of lemon juice to that of sulfuric acid. It is also important to mention that fatty acid ethyl esters present hydrogen chemical shifts well established in the educative literature [13].



**Scheme 3: Esterification process of fatty acids of refined sunflower oil**

In fact, the methyl hydrogen atoms attached to methylene, which is, attached to the oxygen of the ester group and hydrogen atoms belonging to methylene attached to the oxygen of the ester group are visible on the $^1$H NMR spectra. The hydrogen atoms attached to three alkenes groups are also visible on the $^1$H NMR spectra, including hydrogen atoms of the other methylene groups, and the hydrogen atoms of the methyl group attached to the end of the carbon chain. Comparing with the educative literature, $^1$H NMR data indicate that the ethyl linolenic acid esters were synthesized, in the presence of sulfuric acid and lemon juice (Scheme 3). In the same perspective, the ethyl linolenic acid esters are also confirmed by the IR spectra. IR spectra show an intense band characteristic of the ester group at 1736 $cm^{-1}$ and two bands resulting from the symmetric and asymmetric stretch C-H methylene groups of the hydrocarbon chain at respectively 2924 $cm^{-1}$ and 2854 $cm^{-1}$. The band at 725 $cm^{-1}$ results from the rotation plane C-H methylene group, the bands 1458 and 1373 $cm^{-1}$ respectively refer to symmetrical and asymmetrical deformations of the C-H bonds of methyl groups and finally some of the bands between 1242 $cm^{-1}$ and 1034 $cm^{-1}$ correspond to the C-O stretching vibration. The lack of broadband characteristic of the OH group between 3300 and 2500 $cm^{-1}$ and the presence of the characteristic band of the ester group at 1736 $cm^{-1}$ show that ethylated esters were synthesized. The amount of free fatty acids in oils was determined by the method reported by Ding's research group [14]. In fact, the quantitative analysis showed that the waste cooking oil contains large amounts of free fatty acids (2.23 mg of NaOH/g waste cooking oil), while refined sunflower oil contains a small amount (1.12 mg of NaOH/g refined sunflower oil). This could be explained by the formation of free fatty acids that occur when frying foods.

## CONCLUSION

Lemon juice acidic behavior and sulfuric acid allowed us to complete the conversion of vegetable oils in corresponding fatty acid ethyl esters. Indeed, according to the results of this experiment, lemon juice and sulfuric acid have proven to be potential catalysts in such conversion. Given the interest in this study, the further research should focus on using other natural organic products as potential catalysts in various organic reactions.

## ACKNOWLEDGEMENT

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**Conflict of interest**

We declare that we do not have conflict of interest regarding the publication of this paper.

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