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## Oleochemicals from Water Melon (*Citrullus lanatus*) Seed Oils

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**Abstract** The use of watermelon seed oil as feedstock for oleochemicals was studied. Oil was extracted from the seeds which was homopolymerized using  $\text{HClO}_4$  as catalyst. The homopolymer was used to prepare a variety of oleochemicals namely amine, amide, epoxide and copolymerized Phenol-*Citrullus-lanatus* polymer (CPCLP). Iodine value was determined for the oil, homopolymer (CLH) and the CPCLP as a measure of unsaturation. Viscometry studies were carried out to determine the molecular weights of products. FTIR and proton NMR were used to determine the structure of the oleochemicals.  $^{13}\text{C}$  NMR was used to further characterize the CPCLP.

The percentage oil yield is 56.86%. The iodine values were respectively 196.13g/100g, 127.96g/100g and 123.3g/100g for *Citrullus-lanatus* oil (CLO), homopolymer (CLH) and CPCLP. The molecular weights ( $\times 10^7$ ) of the oleochemicals were 510.8g/mol, 536.8g/mol, 543.8g/mol, 410.3g/mol, 566.8g/mol, and 759.0g/mol respectively for CLO, *Citrullus-lanatus* amide (CLAmide), *Citrullus-lanatus* amine (CLAmine), CLH, Epoxidized *Citrullus-lanatus* polymer (ECLP) and CPCLP. FTIR spectra showed absorptions at (1720-1740)  $\text{cm}^{-1}$  of carbonyl group. The major peaks found in the proton NMR spectrum are vinyl protons (C=C-H) at (4.5-5.5) ppm,  $\alpha$ -carbonyl protons and allylic protons at (2-3 and 1.8) ppm. CLAmine shows N-H peaks at 4.444 ppm and 4.490 ppm while CLAmide showed the CONHR peak at 5.775 ppm and 5.621 ppm respectively. CPCLP showed aromatic protons between 6.6ppm and 7.1ppm. The  $^{13}\text{C}$  NMR also confirm CPCLP structure.

The results showed that watermelon oil can be used to prepare useful oleochemicals that are of great importance to the economy with little or no environmental impairment.

**Keyword:** Oleochemical, Watermelon, Green chemistry, Feedstock, Environment

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### Introduction

Petroleum based chemicals have extensively been used by man to produce several important materials that are useful for man such as plastics, industrial chemicals, additives, polymers, heavy chemicals and all other petroleum based products [1]. These products have generated environmental pollution beyond man's control over the years. Majority of the products from unsaturated hydrocarbons and haloalkanes are non- biodegradable *i.e.* Lindane (*gamma*-hexachlorocyclohexane), plastic bottles and DDT (Dichlorodiphenyltrichloroethane), they therefore pose threat to the unborn generation as they gradually destroy our world [2-3]. Some of them have strong bond energies that are not easily broken-down hence can contribute to the depletion of ozone layer, blue baby syndrome, death, extinction of aquatic species and reduction of quality nutrients in the soil for plant growth which affect the food chain and later results into famine [4].

Infertility and reduction to life expectancy are other problems that are associated with the continuous use of petroleum chemicals. The best resolution to this so far has been to convert the poisonous gases coming from these petroleum products ( $\text{CO}$ , hydrocarbons, nitrogenous compounds,  $\text{H}_2\text{S}$ ) into more benign state and the use of



catalytic converters (CO<sub>2</sub> and N<sub>2</sub>) [5-6]. The existence of excess CO<sub>2</sub> had led to an increase in temperature of polar regions which leads into flooding and extinction of some small aquatic species that cannot survive the effect of the heat [7]. All these factors result from imbalance in energy which is based on the first law of thermodynamics brought about by the dependence of man on petroleum based resources [4].

The concept of green chemistry serves as alternative source to these myriads of problems. Green chemistry offers the privilege of producing chemicals from natural materials such as carbohydrates, vegetable oils, animal fats, plants and lignin [7-8]. These chemicals have similar applications to those of petroleum products and pose less harm than them. The major reason for this is that they are biodegradable due to the presence of carbonyl group in their structure which are not found in the chain of hydrocarbons used in petrochemicals. Chemicals that are derived from vegetable oils are called oleochemicals. Several products and chemicals from these natural materials have been reported in literature [9-11]. Linoleum was obtained from linseed oil, several polymer additives such as stabilizers, plasticizers and lubricants were obtained from soybean oil, stearic acid and rapeseed oil respectively [12]. Building blocks for polymers have also been obtained from vegetable oils such as polyamides, polyesters, polyols, polyurethanes and alkyd resins from tall oil, soybean oil, castor oil, sunflower oil and linseed oil [13-15].

Many surfactants have also been reported from carbohydrates and vegetable oils mixture at various proportions. These include anionic surfactants, cocomonoglyceride sulfate and the nonionic sugar surfactant alkyl polyglycoside [12,16]. These products are used especially as mild surfactants in cosmetic formulations and polymer applications. Those rich in unsaturated fatty acids are used as plastic additives or components for composites or polymers like polyamides and polyurethanes [17]. The basic way in which surfactants act is determined by their structure. With their hydrophilic head and hydrophobic tail, surfactant molecules interpose themselves between water and water-insoluble substances [12]. By far the most important field of surfactant application is the washing and cleansing sector as well as textile treatment and cosmetics; these use more than 50% of the total amount. Other uses are in the food sector, in crop protection, in mining, and in the production of paints, dyes, and paper [18]. The hydrophobic (or lipophilic) hydrocarbon chain is formed by a fatty alcohol (dodecanol/tetradecanol) obtained from palm kernel oil or coconut oil [9]. The hydrophilic part of the molecule is based on glucose (dextrose) obtained from starch [19]. The development of surfactants based on carbohydrates and oils is the result of a product concept that is based on the exclusive use of renewable resources [20]. Vegetable oils have shown to also be a profitable raw material [12]. They are completely biodegradable, both aerobically and anaerobically.

Watermelon seed (*Citrullus lanatus*) oil contains high amounts of unsaturated fatty acids with linoleic and oleic acid as the major acids [21]. It also shows a good quality yield of oil, with some literatures reporting 50% [22]. The seed samples are not useful and are hardly consumed hence they are majorly discarded after the consumption of the flesh [23]. Several oils from vegetables have been reported for various polymeric materials and its building blocks, however, highly reduced number of literatures or non-are available on the potential oleochemicals from watermelon seed oil, water melon as raw materials for producing green monomers, precursors, polymers and grafted copolymers. This research therefore attempts to bridge this gap and tries to bring this oil into focus such as been observed with soybean oils, Linseed oil, rape seed oil and Jathropha curcas oil with the sole aim of adding one important seed oil as additional feedstock to the oleochemical industries.

## Experimental

### Materials

The chemicals used include N-Hexane, Phenol, Perchloric acid (HClO<sub>4</sub>), Calcium chloride, Phosphoric acid triethanolamine and hydroquinone (All chemicals were from Sigma Aldrich, Germany). The reactor used was locally fabricated.

### Methods

#### Samples treatment and Oil extraction

The fruits of *citrullus-lanatus-sinensis* were cut with a knife, squeezed and the seeds were separated from the juice. They were washed with tap water and dried at 110°C for 1hour in an electric air draughtoven. These seeds were deshelled to obtain the seeds, they were blended using an industrial blender. Oil was extracted from the blended



seeds at 60 °C for 6 hours with n-Hexane and a sohxlet extractor. A yellow oil was obtained. It was placed in an air tight glass bottle and stored in a refrigerator. The percentage oil yield was calculated using the relationship.

$$\text{Percentage oil yield} = \frac{A - B \times 100}{W}$$

Where: A = weight of flask + oil, B = weight of flask only and W = weight of sample

#### Determination of Physiochemical parameters

The iodine, free fatty acid, saponification and peroxide values were determined according to AOAC, 1984 [24]. The phenolic content was also determined.

#### Iodine value

This was carried out for crude oil sample, homopolymer, and CPCLP according to AOAC, 1984. A blank test, omitting the sample was simultaneously made. The iodine value was calculated using the formula:

$$\text{Iodine value} = \frac{(x - y) \times 1.269}{W}$$

where x = ml of thiosulphate solution required by the blank, y = ml of thiosulphate solution required in the test. w = weight of sample. The factor 1.269 is for an accurate 0.1N solution of sodium thiosulphate [27].

#### Total Phenolic Content

The content of total phenolic compounds in the oil sample was determined by the Folin Ciocalteu method (SINGLETON; ROSSI, 1965). One ml of the oil was pipetted into a test tube and then 3 ml of methanol was added. The test tube was vortexed and then centrifuged at 3.000 rpm for 10 minutes, and the supernatant was collected. This procedure was repeated two more times. An aliquot (0.1 ml) of methanolic extract was placed in a volumetric flask (10 ml) and the Folin-Ciocalteu reagent (0.5 ml) was added. After 3 minutes, saturated sodium carbonate (1.5 ml) was added. The flask was filled with water up to 10 ml. After 2 hours of reaction at ambient temperature, absorbance at 765nm against a reagent blank was measured using a Visible spectrophotometer (Shimadzu, Kyoto, Japan). Calibration was performed using gallic acid (Sigma-Aldrich, St Louis, EUA), and a calibration curve was obtained in the range of 0 to 500 mg. L<sup>-1</sup>. Based on the measured absorbance, the concentration of phenolics was read (mg/ml) from the calibration line; then the content of phenolic in extracts was expressed in terms of gallic acid equivalent (mg of GA/g of extract).

#### Homopolymerization of water melon (*Citrullus lanatus*) seed oil (CLH)

The oil sample was homopolymerized before further polymerization process using a modified method by Petrov, 2010. One litre reactor was charged with 400g of crude oil sample and 1% of pure perchloric acid (HClO<sub>4</sub>) was added as catalyst. The oil/catalyst mixture was stirred at room temperature for 30 minutes under protective atmosphere of nitrogen. During this interval of time, the color of the reaction mass changed from the initial yellow color to dark brown, The *Citrullus-lanatus* sample turned darker. This observation may be due to the formation of cationic active centers-conjugated allyl cations. The temperature was then increased to 90°C and was maintained between 88-92°C for 6 hours. In the first 3-4 hours, the viscosity of the reaction mass increased slowly, however, it increases rapidly from the 4th hour to 5th hour. After 6 hours, the reaction was stopped and the homopolymerized oil containing the super acid catalyst was purified. The purification consists of the removal of catalyst and of some volatile compounds by treating the product with 3% (w% against the oil) of powdered calcium hydroxide for 5 hours at room temperature. The dark brown color of polymerized oil changed to yellow gradually after prolonged contact with solid Ca(OH)<sub>2</sub>. The color change is probably explained by the decomposition of cationic active centers because of the neutralization of the super acid catalyst. The oil obtained was light yellow, the volatile compounds were eliminated in a rotary evaporator. The product was analyzed using FTIR, proton NMR and Viscometry techniques. The iodine value of the homopolymer was determined. The product obtained was named *Citrullus-lanatus* homopolymer (CLH).



### Copolymerization of phenol and *Citrullus-Lanatus* homopolymer (CPCLP)

300g of homopolymerized sample were mixed with 100g of molten phenol under inert atmosphere at 50–60°C. The catalyst (HClO<sub>4</sub>) was added to the reaction mixture (1 % of the mixture) and the reaction was maintained for 4–6 h at 90°C under nitrogen. The reaction mass became red–brown and after 20–40 minutes a notable increase in the viscosity was observed. The final product was between a red brown to brown viscous liquid. The unreacted phenol was removed by distillation. Calcium hydroxides were added to ensure that the catalysts were recovered. The iodine value of the product obtained was determined. The product obtained were analyzed using Viscometry, FTIR, <sup>1</sup>NMR, and <sup>13</sup>C NMR. The product obtained was named Copolymerized Phenol-*Citrullus lanatus* polymer. (CPCLP)

### *Citrullus Lanatus* amide (CLAmide)

An Amide was prepared from the sample using the modified Schmid method. One litre three necked batched reactor was charged with 200g of the homopolymer. 50ml of distilled water was added and was heated for 1 hour at 50°C. 50ml of acetone was added and the temperature was left to stabilize. This was allowed for another 1 hour. 2g of finely crushed sodium hydroxide pellets were added and the reaction was refluxed for 30 minutes. 30ml of ammonium chloride was introduced thrice at 25 minutes' intervals. The reaction continued for 2 hours and was stopped. The product was cooled for 1 hour before filtering and the highly viscous product (filtrate) obtained was kept in a closed container for analysis and application. Characterization of the product was done using Viscometry, FTIR and proton NMR.

### *Citrullus lanatus* amine (CLamine)

An amine was prepared from water melon seed oil using a modified method based on the one described by Woodwork, 2012. Triethanolamine (100ml) and 200g of homopolymer were mixed and homogenized for 20 minutes in a one litre three necked batch reactor at room temperature. They were then heated with sodium methoxide (5% of the mixture) under nitrogen atmosphere for 6 hours at 90 °C. Reaction was cooled down to room temperature and the product obtained was dissolved in propanone and washed with 15% KCl (aq) which was filtered and dried over sodium sulphate for 24 hours. The viscous product obtained was not purified further and was analyzed using proton NMR. FTIR and Viscometry.

### Epoxidation of *Citrullus Lanatus* oil (ECLP)

200g of *Citrullus-lanatus* homopolymer and 100g of peracetic acid were stirred for 30 minutes at room temperature. They were charged into 1 litre three necked batch reactor at room temperature and 1% of 1M HCl was added to the mixture as catalyst. The total mixture was stirred again for 10 minutes at room temperature. The reaction was allowed to continue for 5 hours after which it was stopped. Calcium hydroxide was added to the product obtained to neutralize the catalyst. The product was cooled for 2 hours. It was filtered and the remaining volatile compound present in the viscous filtrate was removed using a rotary evaporator. The product obtained was characterized using Viscometry, FTIR and proton NMR. The product was named epoxidized *citrullus-lanatus* polymer (ECLP).

### Molecular weight determination of the *citrullus-lanatus* oil and the oleochemical

This was determined using Oswald viscometer. Various very low concentrations of the polymers were prepared in toluene. The flow-time of the toluene and the polymer solutions were measured. From the concentration and time of flow, the inherent and reduced viscosity were calculated using the following equations

$$\text{Inherent Viscosity} = \frac{\ln \eta_r}{C}$$

$$\text{Reduced Viscosity} = \frac{\eta_{sp}}{C}$$

Where  $\eta_{sp}$  = specific viscosity, C = Concentration (g/ml) and  $\ln \eta_r$  = Inherent Viscosity.

A graph was drawn by plotting reduced viscosity against concentration and inherent viscosity against concentration. Intrinsic viscosity was obtained by extrapolating the graph to zero concentration. From the values of intrinsic



viscosity, the viscosity average molecular weight of each polymer was obtained using Mark-Houwink-Sakurada equation [25].

$$[\eta] = KM^a$$

Where  $\eta$  = intrinsic viscosity, K and a are constants depending on the polymer solvent ratio, M = Molecular weight.

### FTIR Analysis

The oil sample and oleochemicals were qualitatively characterized by the FT-IR technique. These were obtained on a Perkin Elmer Fourier transform infrared spectrometer. The spectra were recorded between 4000-350 $\text{cm}^{-1}$  using KBr disc.

### Proton and carbon 13 NMR Analysis of Citrullus- lanatus oil and the oleochemicals

The oil sample and their corresponding monomers and copolymers were quantitatively characterized by proton NMR technique and  $^{13}\text{C}$  NMR technique. These were obtained on a Bruker av400 MHz NMR.

## Results and Discussion

### Viscometry analysis

The molecular weights of *Citrullus-lanatus* oil (CLO), homopolymerized *citrullus -lanatus* polymer (CLH), Copolymerized Phenol-*Citrullus-lanatus* polymer (CPCLP), Epoxidized *citrullus-lanatus* polymer, *Citrullus-Lanatus* amide (CLAmide) and *Citrullus-lanatus* Amine (CLAmine) were obtain using Viscometry method. The molecular weights are shown in Table 1. The high molecular weight of the homopolymer is an evidence that homopolymerization of the crude oil (CLO) had taken place. CLamine and CLAmide showed lower molecular weights than the homopolymer because they are purely oleochemicals and not polymer products. The copolymerized product (CPCLP) showed a great increase in mass to confirm that copolymerization had occurred between the homopolymer backbone and the phenolic group. The FTIR and proton NMR result also complement the Viscometry result.

**Table 1:** Molecular weight of crude oil and its oleochemicals

Sample	Molecular weight ( x 10 <sup>7</sup> gmol)
<i>Citrullus-Lanatus</i> oil (CLO)	510.0
<i>Citrullus-Lanatus</i> homopolymer (CLH)	538.0
<i>Citrullus-Lanatus</i> Amide (CLAmide)	536.2
<i>Citrullus-Lanatus</i> Amine (CLAmine)	545.0
Epoxidized <i>Citrullus-Lanatus</i> Polymer (ECLP)	566.0
Copolymerized Phenol- <i>Citrullus Lanatus</i> Polymer (CPCLP)	756.0

### Physiochemical Parameters

The iodine value, peroxide value, saponification value, free fatty acids and the phenolic contents were determined for the oil samples. The results obtained are shown in Table 2.

The percentage oil yield for the sample was 56.86%. This is close to the value reported by Baboli and Kordi, 2010. The oil yield is very large and of good commercial quantity for any interested organization as a starting raw material for the oleochemical industries. The iodine value of the oil sample was 196.13g/100g. the homopolymerized product has an iodine value of 127.96g/100g and the Copolymerized Phenol *Citrullus -lanatus*polymer has an iodine value of 122.3g/100g. Iodine value measures the degree of unsaturation in a fat or vegetable oil. It determines the stability of oils to oxidation and allows the overall unsaturation of the fat to be determined qualitatively [26]. These values are indicators that the oil is rich in unsaturation. It was reported from literature that the seed oil is rich in oleic and linoleic acid, the high iodine value complements this result (Table 2). The homopolymer showed a decrease in unsaturation. Introducing phenol to the homopolymers chain showed a further decrease in unsaturation of the copolymer product obtained. These observations are evidences that polymerization has actually occurred around the vinyl centres in the vegetable oil moiety. The result of the iodine value shows that watermelon seed oil and its derivatives (Table 2) has the potential to replace petroleum based unsaturated hydrocarbons in producing polymeric materials such as plastics, tyres, rubber, adhesives, resins, insulators, conjugated materials and drug carrying



polymers since they all involve polymerization processes. It does this with the advantage of been biodegradable and green.

Peroxide value (PV) is used as a measure of the extent to which rancidity reactions have occurred to oils during storage, it could be used as an indication of the quality and stability of fats and oils [27]. Values below 10meq/kg indicates no rancidity while values around 30 and 40 meq/kg show that the oil is rancid [16]. The results showed that the peroxide value is 1.51 meq/kg. This showed that the sample is not rancid. Saponification value (SV) is an index of average molecular mass of fatty acid in an oil sample. The lower value of saponification suggests that the mean molecular weight of fatty ester is lower or that the number of ester bonds is less. The saponification value of the water melon oil sample is 189.67mgKOH/g, the value agrees with those found in literatures for oils [28-30]. The high value shows a higher ester bond and tendency to have a high molecular weight (Table 1). Due to this high value, the oils have potentials for use in industrial processes.

The acid value measures the presence of corrosive free fatty acids and oxidation products. This is important because the lower the free fatty acid the better the quality of the oil. The acid value for the oil is 7.26%. It is an indication of the presence of unsaturated fatty acid chains which substantiate the ability of the oils to undergo polymerization. It also complements the iodine value. The phenolic content shows the amount of phenol present in the oil samples. These values are close to those reported for the same seed oil by Zahra and Baboli, 2010 (Table 2). The phenolic content in the samples is 2.7g/kg. All these properties show that the sample is a viable industrial raw material. The homopolymerized and grafted product from the sample are other potential starting materials in the oleochemical and material processing industries (Table 3).

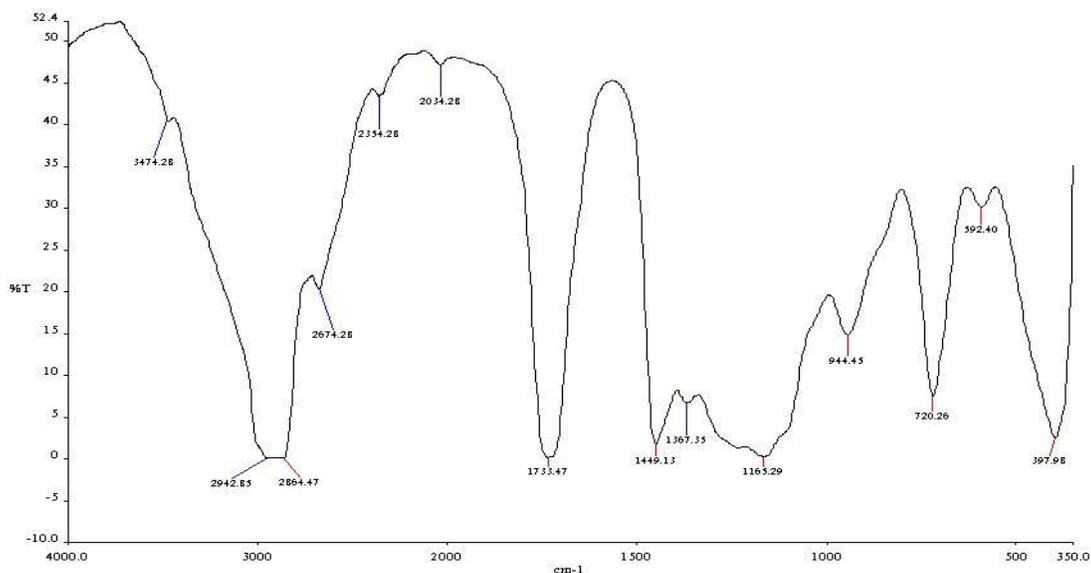
**Table 2:** Physicochemical properties of watermelon seed oil

Physicochemical Parameters	Values	Zahra and Baboli,2010
Iodine value	196.13g/100g	156 g/100 g
Peroxide value	1.51meq/kg	2.4 meq/kg
Saponification value	189.67mgKOH/g	200 mg KOH/g
Acid value	7.26%	3.24%
Phenolic content	2744.16mg/kg	

**Table 3:** Comparison of iodine values of oil and the modified samples

Samples	Iodine value(g/100g)
Watermelon oil	196.13
Homopolymerized polymer	127.96
CPCLP	122.30

#### FTIR results of *Citrullus Lanatus* oil and its oleochemical



**Figure 1:** FTIR spectrum of *Citrullus Lanatus* oil (CLO)



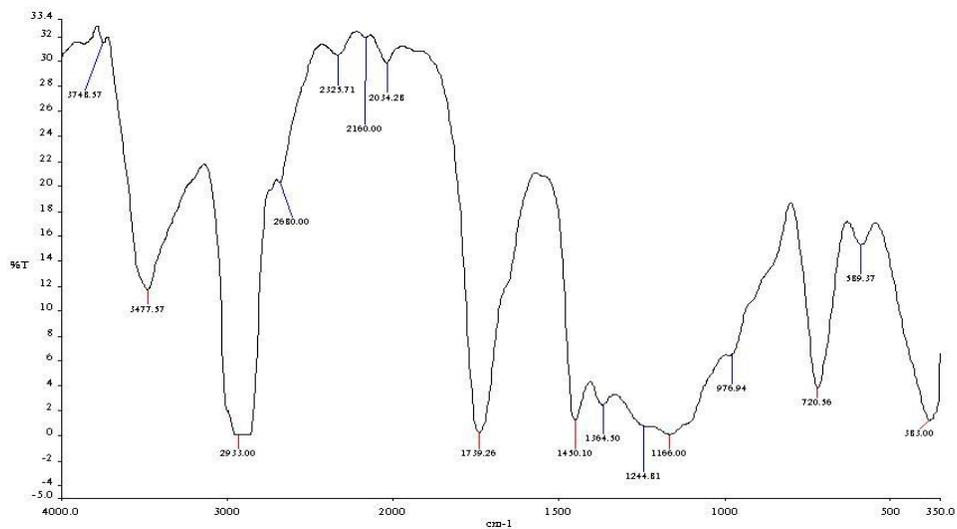


Figure 2: FTIR spectrum of *Citrullus lanatus* homopolymer (CLH)

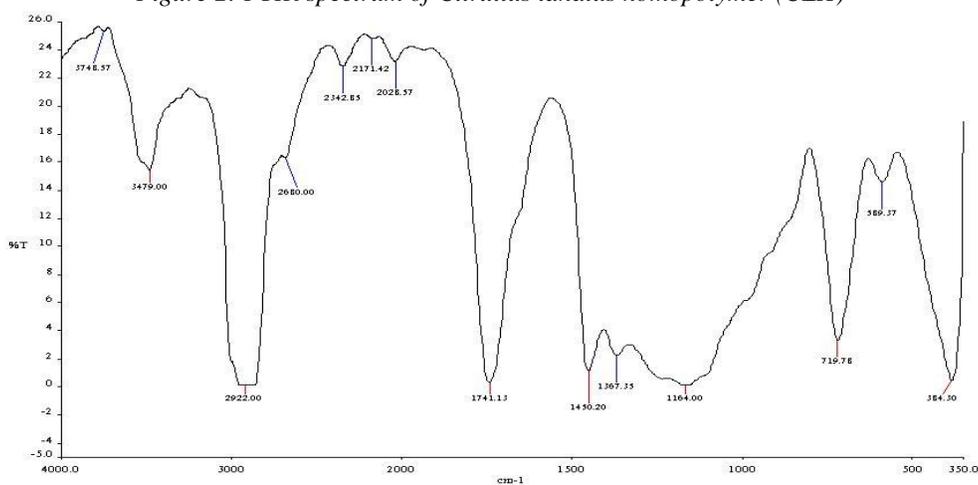


Figure 3: Epoxidized *Citrullus lanatus* oil (ECLP)

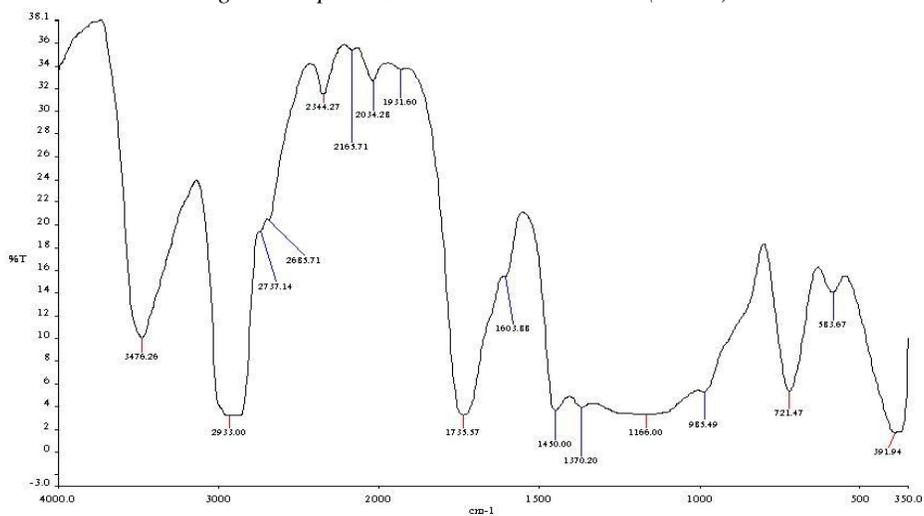


Figure 4: FTIR spectrum of Copolymerized Phenol-*Citrullus lanatus* polymer (CPCLP)



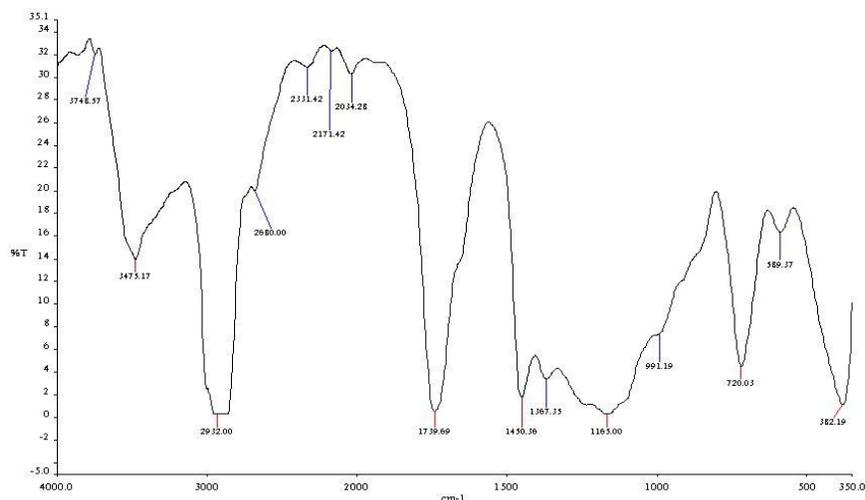


Figure 5: FTIR spectrum of *Citrullus lanatus* Amide (CLAmide)

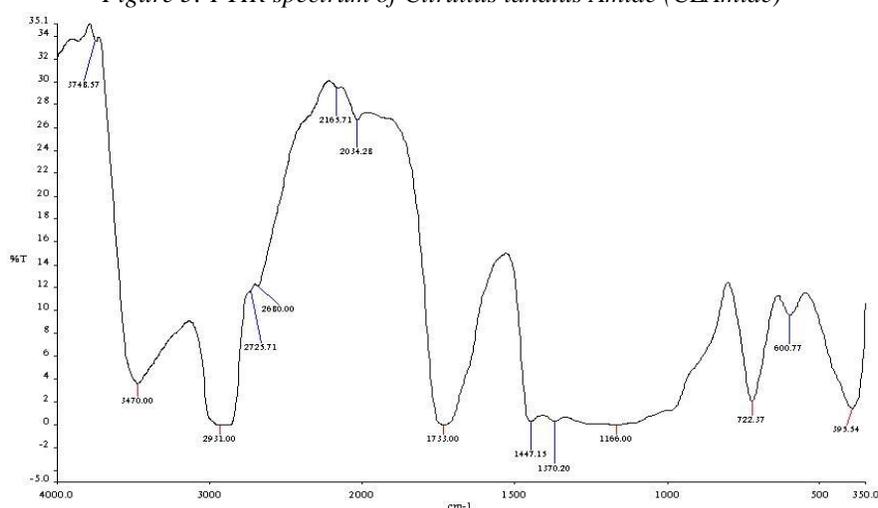


Figure 6: FTIR spectrum *Citrullus lanatus* amine (CLAmine)

### FTIR Analysis

Figure 1 is the spectrum of *citrullus-lanatus* oil (CLO), the spectrum showed strong C=O stretch of ketone at  $1740\text{ cm}^{-1}$ . This is also common to all the spectra. C=C and C-H bends of aromatics at  $1450.06\text{ cm}^{-1}$  and  $1364.50\text{ cm}^{-1}$ . These peaks show that the oil contains an unsaturated ketone group. The peaks at  $965.54\text{ cm}^{-1}$ ,  $917\text{ cm}^{-1}$  and  $718\text{ cm}^{-1}$  showed the traces of phenyl group. This indicates the presence of phenolic content in the sample. The spectrum complements the physiochemical parameters, mostly the iodine value and phenolic content for the oil. These functional groups present in the crude oil as an unsaturated fatty ester which when hydrolyzed, transesterified and modified makes the oil a potential important feedstock for industrial chemicals such as lubricant and organic solvent. They can also serve as green feedstock for producing other useful products like nylon, plastics and similar useful biodegradable products in polymerization processes. The results are in tune with Sanchez reports for oils in 2014 [31].

Figure 2 is the spectrum of *Citrullus-lanatus* homopolymer (CLH). The prominent peak found in the FTIR of the homopolymers is  $1740.20\text{ cm}^{-1}$  due to strong C=O stretch of an ester. The peak is close to the wave number obtained for the crude oil sample (Table 4). The peaks at  $1450\text{ cm}^{-1}$ ,  $1367.14\text{ cm}^{-1}$  and  $1236.26\text{ cm}^{-1}$  are evidences that the homolymer is unsaturated. The peaks are due to C=C bending and C-H bending of phenolic. The peak at  $1236.26\text{ cm}^{-1}$  was not found in the original sample (Table 3). The peak results from Ar-O bond. It also establishes the presence of phenolic group in the structure as found in CLO (Figure 1). The peak serves as good evidence for the homopolymerization reaction. The peaks at  $1164.80\text{ cm}^{-1}$  results from C-O stretch. The peaks at  $982.64\text{ cm}^{-1}$ ,  $914.25$



$\text{cm}^{-1}$  and  $719.70 \text{ cm}^{-1}$  were due to phenolic groups. The results showed that homopolymerizing vegetable oils can bring about an increase in its concise functionality. The result obtained is in tune with Ionescu and Petrovic report for the homopolymerization of soyabean oil in 2007.

Figure 3 is the FTIR spectrum of epoxidized *Citrullus- lanatus* polymer. The peak at  $1741.13 \text{ cm}^{-1}$  is due to C=O stretch. C=C and C-H bending of aromatics occurred at  $1447.55 \text{ cm}^{-1}$  and  $1370.20 \text{ cm}^{-1}$ . C-O stretch was found at  $1166.00 \text{ cm}^{-1}$  and C-H stretch occur at  $2931.00 \text{ cm}^{-1}$  (Table 4). The peak at  $722.37 \text{ cm}^{-1}$  is due to phenolic group. These peaks confirm the presence of phenolics. Similar result was reported for the physiochemical property (Table 2). The presence of a new peak at  $3479 \text{ cm}^{-1}$  was attributed to the ether group ROR stretching, indicating that the epoxy group might be opened. The result is in tune with what Saremi *et al.*, 2012 reported for epoxides [32].

Copolymerizing Phenol and the homopolymer of *Citrullus-lanatus* oil was carried out to improve the functionality of the vegetable oils. Figure 4 is the FTIR spectrum of CPCLP. The spectrum (Figure 4) shows the presence of C=O stretch peak at  $1735.57 \text{ cm}^{-1}$ , C=C and C-H bends at  $1450.00 \text{ cm}^{-1}$  and  $1370 \text{ cm}^{-1}$ . These peaks are confirming the presence of aromatic structure. The peak at  $1603.88 \text{ cm}^{-1}$  however confirms the copolymerization. The C-O peak occurring between  $1000-1300 \text{ cm}^{-1}$  was almost no longer present in the spectrum above which implies that it is the point where polymerization had taken place. The absence of any peak around  $1200 \text{ cm}^{-1}$  confirms this. The peaks at  $985.49 \text{ cm}^{-1}$  and  $721.47 \text{ cm}^{-1}$  confirms the presence of phenolic group in the structure. The peak at  $3476 \text{ cm}^{-1}$  shows the presence of O-H stretch of phenol (Table 4). The peaks at  $2165.71 \text{ cm}^{-1}$ ,  $2034.28 \text{ cm}^{-1}$  are due to unsaturation. The high number of peaks in the aromatic region serve as evidence for cloud of pi electrons surrounding the aromatic moiety. This is strong evidence of increase in the functionality of the new product.

Figure 5 is the FTIR spectrum for *Citrullus lanatus* amide (CLAmide). The Fatty amide structure show a carbonyl group at  $1739.69 \text{ cm}^{-1}$ , C-H stretch at  $2932.00 \text{ cm}^{-1}$ , N-H which is a singlet (meaning that the compound is a substituted amide) at  $3475.17 \text{ cm}^{-1}$ , C=C and C-H bending at  $1450.36 \text{ cm}^{-1}$  and  $1367.35 \text{ cm}^{-1}$ , C-N stretch at  $1165.00 \text{ cm}^{-1}$ . All these confirms that the compound is a secondary amide (Table 4). Phenolic group were found at  $720.03 \text{ cm}^{-1}$  and  $991.19 \text{ cm}^{-1}$ . The absorption at  $2171.42 \text{ cm}^{-1}$  is due to jugation of alkene. The product will play a very important role as either a lubricant or an inhibitor due to the lone pairs present in the nitrogen atom and the pi bonds associated with the unsaturated group.

Figure 6 is the FTIR spectrum of the amine obtained from the *Citrullus lanatus* homopolymer (CLamine). It shows the presence of C=O at  $1733.00 \text{ cm}^{-1}$ , N-H group at  $3470.00 \text{ cm}^{-1}$ , C-H stretch at  $2931.00 \text{ cm}^{-1}$ , Peaks at  $1447.15 \text{ cm}^{-1}$  and  $1370.20 \text{ cm}^{-1}$  confirms C=C and C-H bending of aromatics (Table 4). C-N bond was confirmed by the peak at  $1166.00 \text{ cm}^{-1}$ . The phenolic group was confirmed by the  $722.37 \text{ cm}^{-1}$  absorption. All these functional groups with the support of the proton NMR spectrum confirmed the oleochemical an amine.

**Table 4:** Comparison of FTIR values in watermelon crude oil and its Oleochemicals

Functional groups and properties	CLO (cm <sup>-1</sup> )	CLH (cm <sup>-1</sup> )	ECLP (cm <sup>-1</sup> )	CLA (cm <sup>-1</sup> )	CLa (cm <sup>-1</sup> )	CPCLP (cm <sup>-1</sup> )
C=O, Strong	1740.91	1740.20	1741.13	1739.69	1733.00	1735.57
C=C, bending	1450.06	1450.25	1450.20	1450.36	1447.15	1450.00
C-H, bending	1364.50	1367.34	1367.35	1367.35	1367.35	1370.20
C-O, stretch	1164.25	1164.80	1164.00	1165.00	1166.00	1166.00
C-H, stretch	2927.00	2931.73	2922.00	2932.00	2931.00	2933.00
Ar-O	965.54,917.09, 718.67	982.64, 914.24 719.70	719.78	991.19, 720.03	722.37	985.49, 721.47
C=C, alkene						1603.88
N-H, bending				3475.17	3470.00	
O-H Stretch			3479.00			

**CLO** = *Citrullus lanatus* oil.

**CLH** = *Citrullus lanatus* homopolymers

**ECLP** = Epoxidized *Citrullus lanatus* polymer

**CLAmide** = *Citrullus lanatus* amide

**CLAmine** = *Citrullus lanatus* amine

**CPCLP** = Copolymerized Phenol- *Citrullus lanatus* polymer



**<sup>1</sup>NMR results of *Citrullus lanatus* oil and its Oleochemicals**

The proton NMR analysis was carried out using Agilent - 400 MHz, temperature of 31°C and CDCl<sub>3</sub> as solvent.

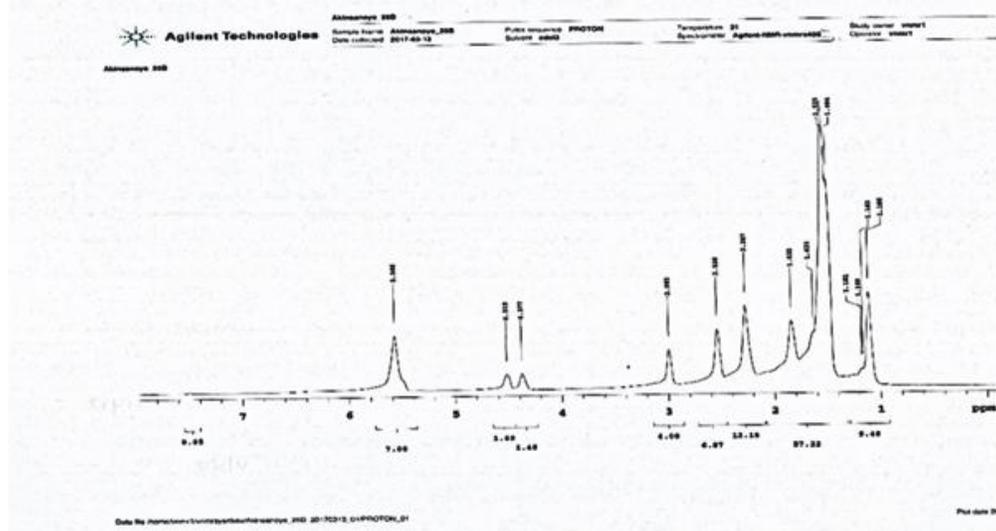


Figure 7: <sup>1</sup>NMR spectrum of *Citrullus lanatus* oil (CLO)

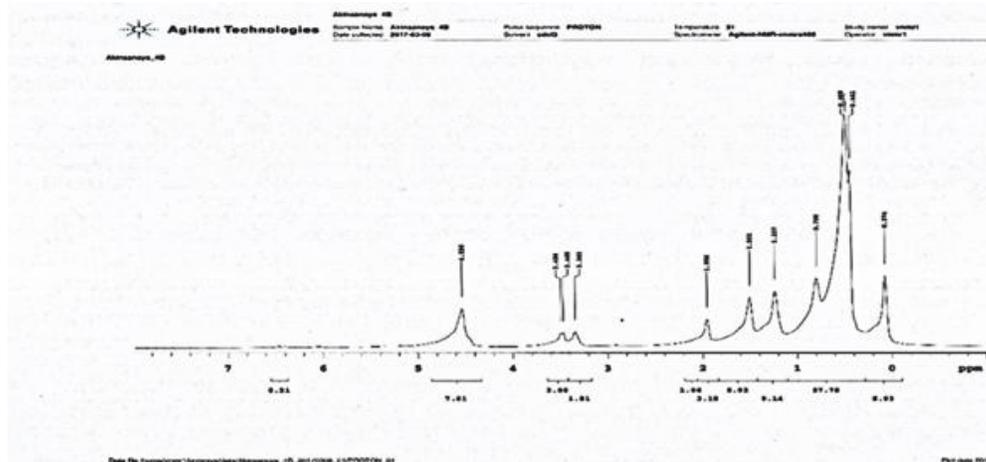


Figure 8: <sup>1</sup>NMR spectrum of *Citrullus lanatus* Homopolymer (CLH)

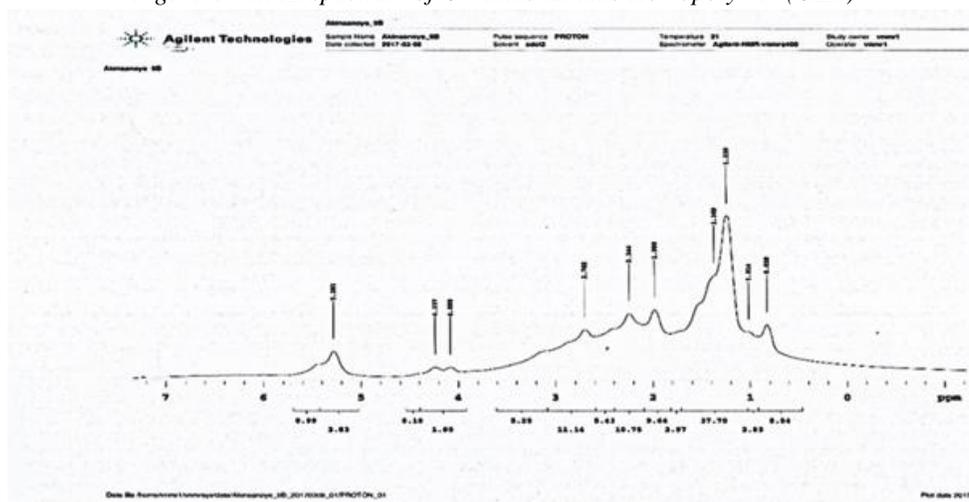


Figure 9: <sup>1</sup>NMR spectrum of Epoxidized *Citrullus lanatus* polymer (ECLP)



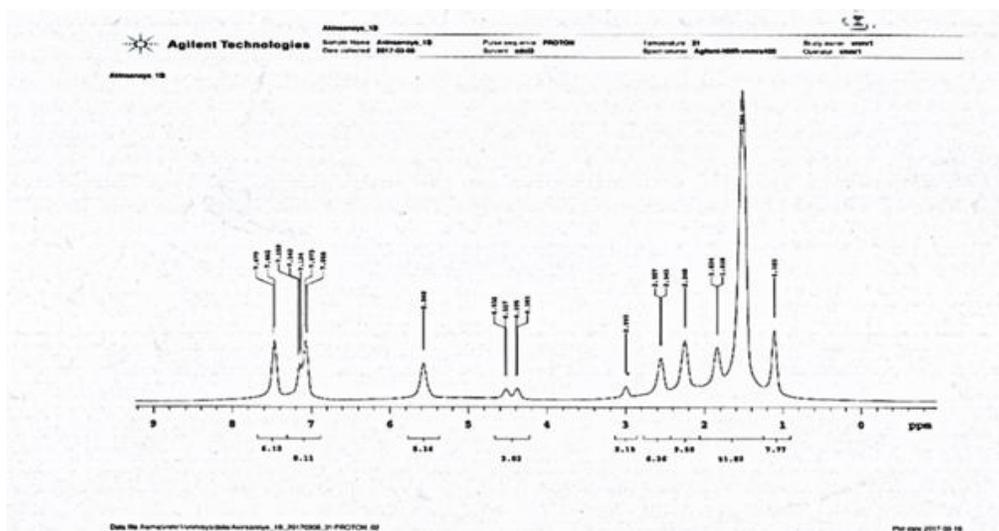


Figure 10: <sup>1</sup>H NMR spectrum of Copolymerized Phenol- Citrullus lanatus polymer (CPCLP)

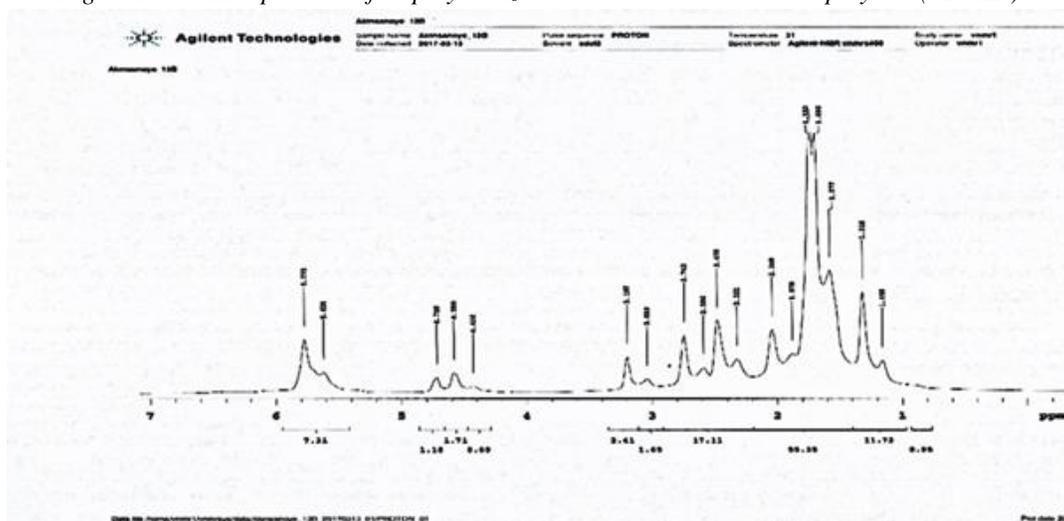


Figure 11: <sup>1</sup>H NMR spectrum of Citrullus lanatus Amide (CLAmide)

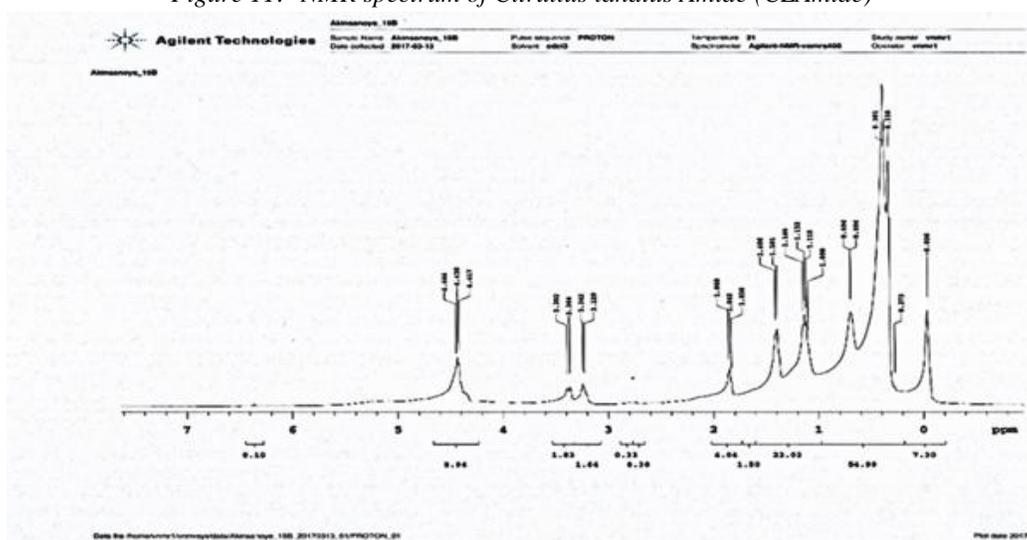
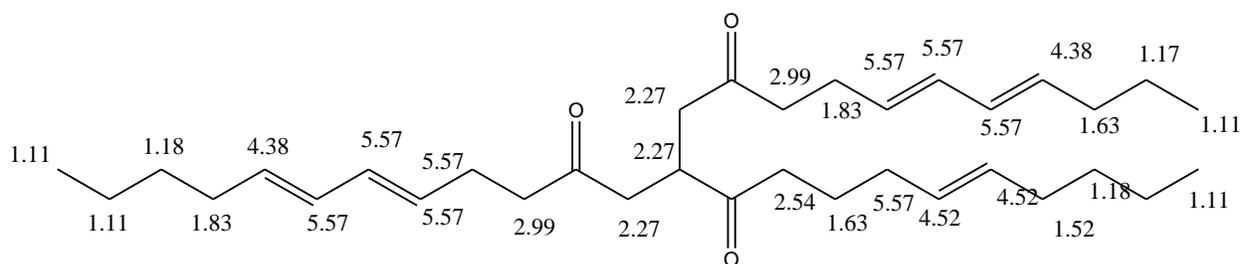


Figure 12: <sup>1</sup>H NMR spectrum of Citrullus lanatus Amine

### Discussion of NMR results

Figure 7 shows the proton NMR spectrum of *Citrullus lanatus* oil. The spectrum shows a small absorption in the aromatic region (0.005%). This confirms the presence of phenolic group in the structure of the oil in trace amount. It complements the physicochemical properties result for phenolic content (Table 1). There is a doublet occurring at 4.377 ppm and 4.519 ppm due to vinylic protons (H-C=C-H). This shows that the sample is rich in oleic acid. The peak at 5.57 ppm corresponds to vinylic conjugated proton. This implies that the sample is rich in conjugated alkene (possible presence of linoleic acid in the chain structure of the sample). The peaks at 2.993 ppm, 2.538 ppm and 2.267 ppm are  $\alpha$ -carbonyl protons (O=C-CH<sub>2</sub>). The result complements the FTIR values (Table 4 and Figure 1) and iodine values (Table 1) in establishing that watermelon seed oil is rich in unsaturation. Peaks at 1.833 ppm and 1.631 ppm are allylic protons (C=C-CH<sub>2</sub>). This confirms that the oil is rich in linoleic acid as suggested in literatures for the seed sample [33-34]. The presence of oleic acid and linoleic acid in the crude oil sample makes it a potential important feedstock for the oleochemical industries. The peaks at 1.523 ppm and 1.484 ppm are due to 3° aliphatic protons. Peaks at 1.181 ppm, 1.169 ppm, 1.163 ppm and 1.106 ppm are secondary and primary aliphatic protons respectively. The proposed structure based on the NMR spectrum, FTIR and Viscometry is as shown in Figure 13 with <sup>1</sup>NMR labels.



(4E,6E,17E,19E)-12-((E)-dec-5-enoyl)tetracos-4,6,17,19-tetraene-10,14-dione

Chemical Formula: C<sub>34</sub>H<sub>54</sub>O<sub>3</sub>

Exact Mass: 510.41g

Molecular Weight: 510.79g/mol

Figure 13: Proposed structure and name for *Citrullus lanatus* oil

### <sup>1</sup>NMR analysis of the spectrums of *Citrullus lanatus* oil homopolymer (CLH)

The <sup>1</sup>NMR spectrum of the homopolymers shows vinyl proton at 4.535 ppm, this is like the peak found in the crude sample (Figure 7). It also shows the presence of phenolics in a very small amount. These are similar to the result of the physicochemical parameters and the FTIR reported for the sample. The doublet found at 3.494 ppm and 3.464 ppm results from the proton of fatty esters (RCOO-CH). This similarly account for the peak at 3.345 ppm (Figure 8). These peaks suggest that the homopolymers possess the C-O stretch. The observation is similar to the Baeyer-Villiger oxidation of ketones or lactones to fatty esters using peroxyacids [35-36]. The peak at 1.956 ppm results from protons close to the carbonyl group (HCC=O) while the peak at 1.501 ppm confirm the presence e of allylic proton (C=C-CH<sub>2</sub>). The peaks at 0.798 ppm, 0.488 ppm, 0.441 ppm (doublets) and 0.074 ppm are all aliphatic protons. The spectra are like the crude oil sample and shows decrease in unsaturation with concise functionalities. The increase in the number of methyl protons shows that additional polymerization had occurred in the molecule with the catalyst or water moiety supplying the additional protons in the reaction. It corroborates the accuracy of the result obtained for the iodine value as well (Table 2). The proposed structure for the homopolymers based on the Proton NMR spectra, Viscometry and FTIR are shown in Figure 14.



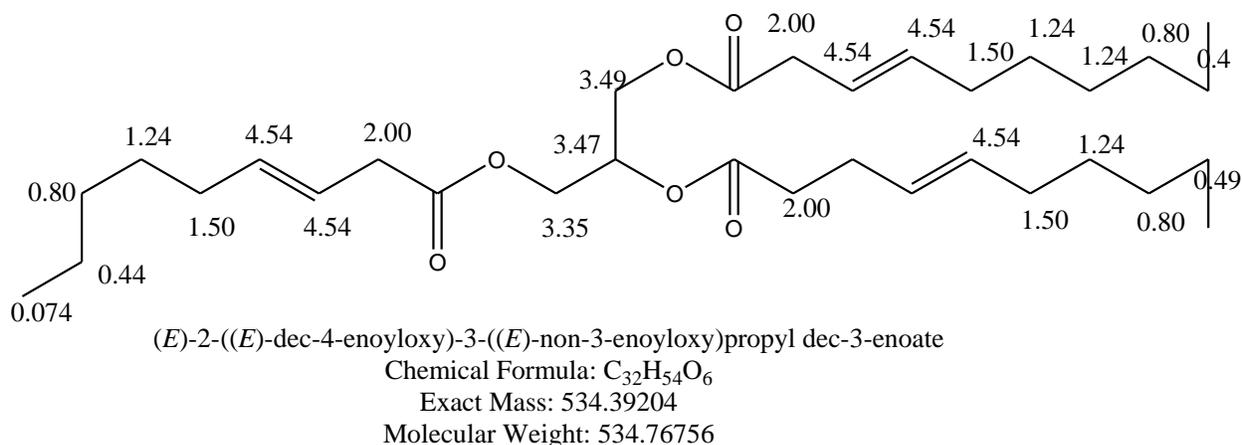


Figure 14: Suggested structure and name for *Citrullus lanatus* homopolymer

#### Proton NMR of epoxidized *Citrullus lanatus* polymer (ECLP)

From the spectrum of epoxidized *citrullus-lanatus* polymer (ECLP), the peaks at 2.703 ppm and 2.244 ppm (Figure 9) are evidences of ketone types of proton, this is complemented with the fact that there is no C-O stretch in the spectrum, this is like the peak found in the seed oil sample (Figure 7). Peaks at 5.281 ppm shows the existence of vinyl proton meaning that there is a level of unsaturation in the ring structure. The peak at 1.980 ppm occur due to the presence of allylic protons. The peaks at 4.237 ppm and 4.080 ppm are evidences for the epoxidation process since the peaks occur due to R-O-R bond [37]. The suggested structure for epoxidized *Citrullus Lanatus* oil is presented in Figure 15.

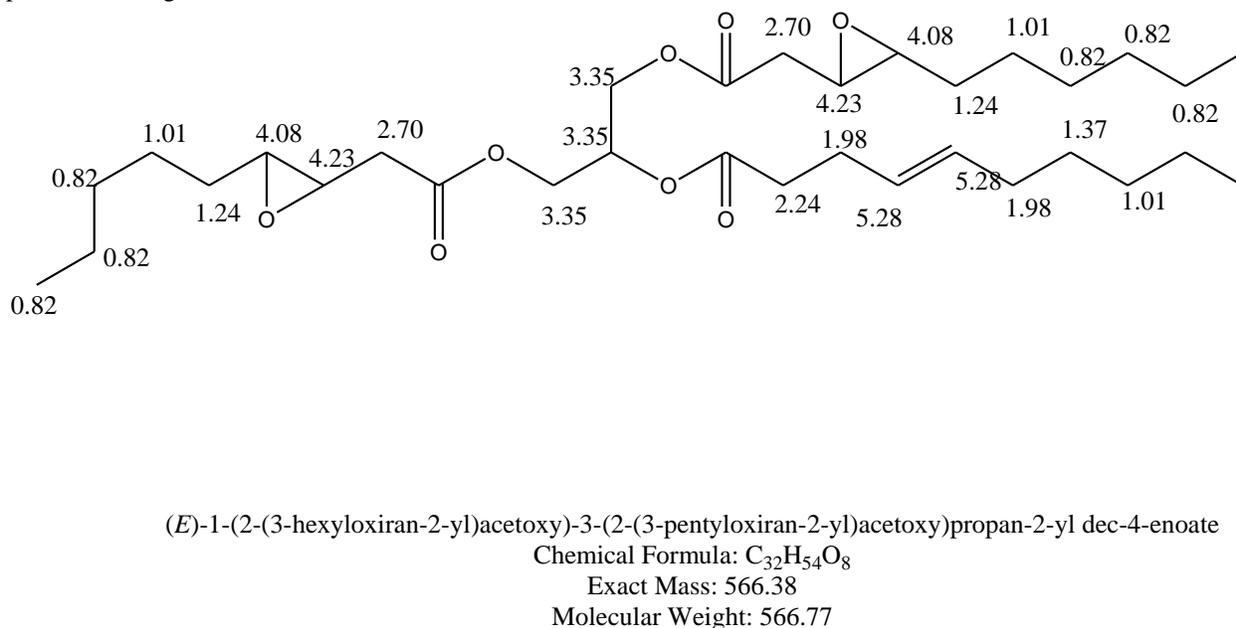


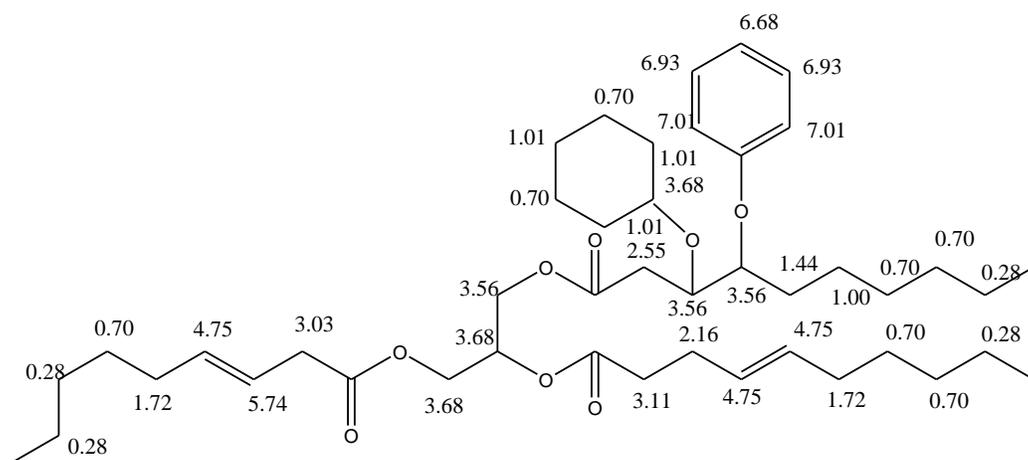
Figure 15: Suggested structure and name for epoxidized *Citrullus lanatus* polymer

#### Proton NMR spectrum of Copolymerized Phenol-*Citrullus lanatus* polymer (CPCLP)

The spectrum of copolymerized Phenol-*Citrullus lanatus* polymer is presented in Figure 10. Absorptions at 7.102 ppm, 6.934 ppm and 6.675 ppm are due to aromatic protons. This peaks account for 0.13% which is around 4 % increment from the 0.005 % present in the original sample. This is an evidence for the copolymerization reaction. This is because there was no major absorption in this region from the crude oil sample and the homopolymer. The presence of cyclohexanol ring in the structure of the new polymer is evidence that one of the phenolic structures that



attack the vinyl group in the fatty ester moiety has been hydrogenated completely (Figure 16). Introduction of phenol into the vegetable oil structure increases functionality of the new product. The cloud of pi electrons present in the phenolic group will improve the functionality of the vegetable oil backbone. This is evidence that a new reactive feedstock has been produced. The peak at 4.746 ppm shows the presence of vinyl protons. The peak at 5.044 ppm confirms the presence of OH group attached to phenol. Peaks at 3.680 ppm, 3.556 ppm, 3.030 ppm are the protons close to C-O bond present in the fatty ester moiety. Peaks at 2.548 ppm, 2.468 ppm and 2.159 ppm occur due to  $\alpha$ -carbonyl protons. The peak at 1.716 ppm is due to allylic protons ( $\text{CH}_3\text{-CH}=\text{CH}_2$ ). The peaks occurring at 1.440 ppm, 1.009 ppm, 0.701 ppm, 0.283 ppm and 0.607 ppm are all aliphatic protons. The grafting of Phenol to the vegetable oil homopolymer showed a great increase in molar mass and molecular weight which is also evidence that polymerization had occurred (Table 3). The product obtained is biodegradable and meet the norm required for green chemicals. It is less harmful than phenol since a very small amount of phenol was used for copolymerization. The product can be a useful precursor to the preparation of plastics and tyres in the oleochemical industries with little or no environmental impairment [38].



(*E*)-1-((3,4-dimethoxydecanoyl)oxy)-3-((*E*)-non-3-enoyloxy)propan-2-yl dec-4-enoate compound with benzene and cyclohexane (1:1:1)  
 Chemical Formula:  $\text{C}_{46}\text{H}_{78}\text{O}_8$   
 Exact Mass: 758.56967  
 Molecular Weight: 759.10672

Figure 16: Proposed structure for Copolymerized Phenol- *Citrullus lanatus* polymer based on proton NMR

#### Proton NMR analysis of *Citrullus lanatus* amide (CLAmide)

The absorption at 5.775 ppm and 5.621 ppm results from the presence of free substituted amide group ( $\text{O}=\text{C}-\text{NHR}$ ). The small peak at 7.500 ppm must have occurred due to hydrogen bonded amide group (Figure 11). The trend of the result is similar to the physiochemical parameters result (Table 1) and the FTIR result (Figure 6). The C-O peak found in the homopolymer is no longer found in this present product, this shows that the C-O bond must have given way to form the C-N bond found in this present structure (Figure 17). Hence the polymerization must have occurred at the carbonyl section of the homopolymer used in preparing the amide. Similar reactions have been reported for preparing amides from esters [39].

Peaks at 4.718 ppm, 4.580 ppm and 4.426 ppm results from vinyl protons ( $\text{H}-\text{C}=\text{C}=\text{H}$ ). These protons are evidence for the formation of an unsaturated amide. Peaks at 3.197 ppm, 3.039 ppm, 2.742 ppm, 2.748 ppm, 2.321 ppm and 2.040 ppm confirm the presence of  $\alpha$ -carbonyl protons. Peaks at 1.878 ppm, 1.732 ppm, 1.690 ppm, 1.557 ppm are due to allylic protons (55.35%) substantiating that oleic acid present in the fatty ester structure were also present in the amide formed. Peaks at 1.312 ppm and 1.158 ppm confirms the presence of methylene protons in the structure. The peak at 0.99 ppm is a methyl proton. Based on the  $^1\text{NMR}$  and FTIR values the amide can be classified as N-substituted amide which is a secondary amide. It can be a very good organic solvent, good lubricant or inhibition



material due to the presence of lone pairs on the nitrogen atoms. The structure was deduced using the spectrum obtained from the  $^1\text{NMR}$ , FTIR and Viscometry. Labels were based on the proton NMR values.

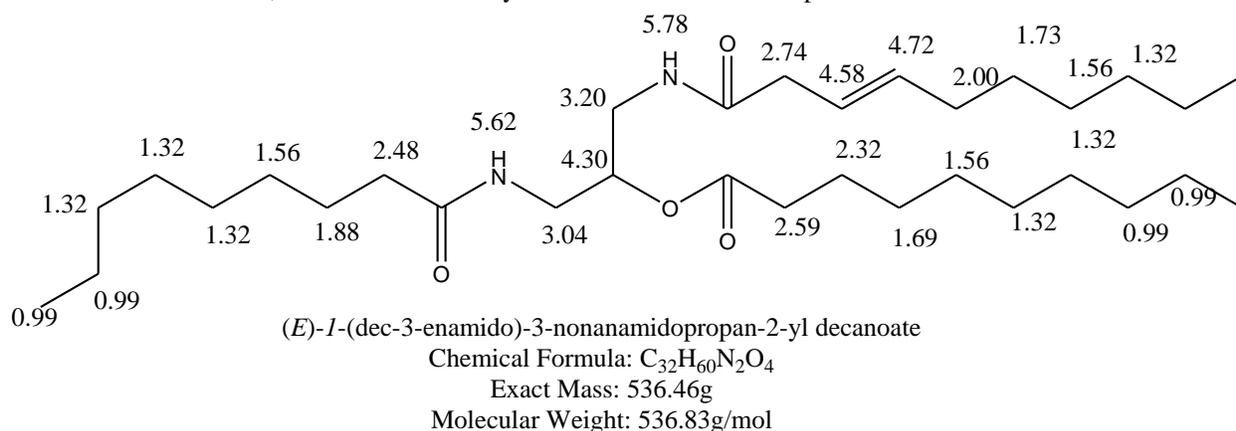


Figure 17: Shows the suggested structure and name for the amide product

#### Proton NMR analysis of *Citrullus lanatus* amine (CLamine)

The peaks at 4.444 ppm and 4.430 ppm and 4.417 ppm relatively confirm the  $\text{O}=\text{C}-\text{O}-\text{NH}_2$  group proving that the compound is an amine (Figure 12). The peaks at 3.392 ppm, 3.364 ppm, 3.342 ppm and 3.242 ppm confirms  $\text{H}_2\text{-C}-\text{O}-\text{C}=\text{O}$  group. These peaks show that the vinyl group is present in the crude sample has been hydrogenated during polymerization. This is also confirmed by the FTIR. The Viscometry also show a high molecular weight for this sample (Table 3) to suggest that hydrogenation had taken place in the conjugated sites to give a saturated aliphatic amine [39]. Peaks at 1.406 ppm, 1.391 ppm, 1.146 ppm, 1.132 ppm, 1.115 ppm, 1.098 ppm, 0.694 ppm, 0.96 ppm, 0.381 ppm, 0.330 ppm, 0.273 ppm, 0.036 ppm are all aliphatic protons resulting from hydrogenation of the unsaturated areas on the fatty acid moiety. The structure was suggested based on the proton NMR, FTIR and Viscometry result and is displayed in Figure 18.

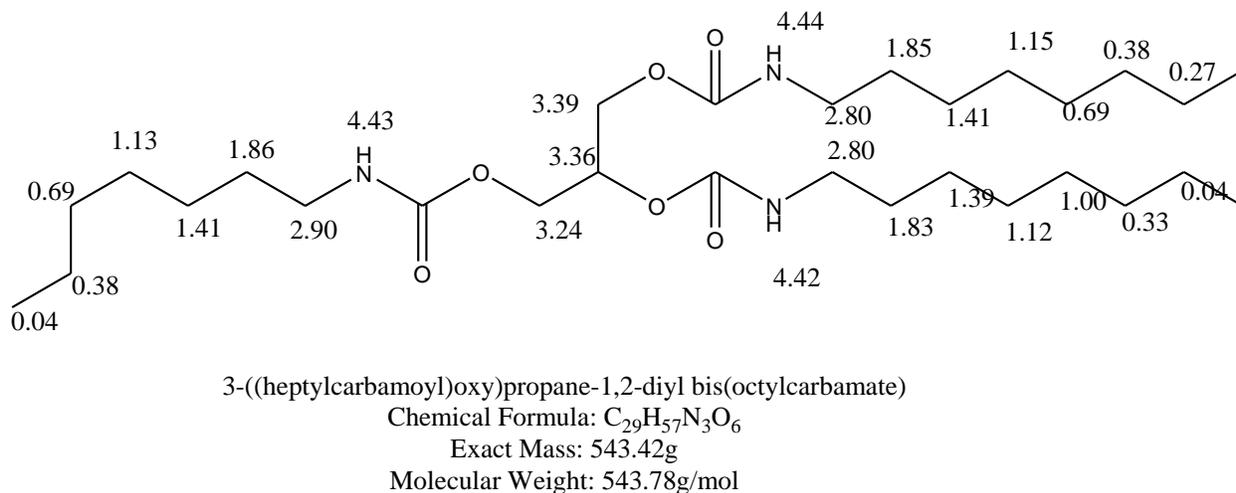


Figure 18: Proposed structure and name of the *Citrullus-lanatus* amine (CLamine)

#### $^{13}\text{C}$ NMR analysis of copolymerized phenol/*Citrullus Lanatus* polymer

The  $^{13}\text{C}$  NMR analysis was carried out using Agilent -400 MHz, temperature of 31 °C and  $\text{CDCl}_3$  as solvent. This was used to further characterize the product obtained from copolymerizing Phenol and *Citrullus lanatus* homopolymer.



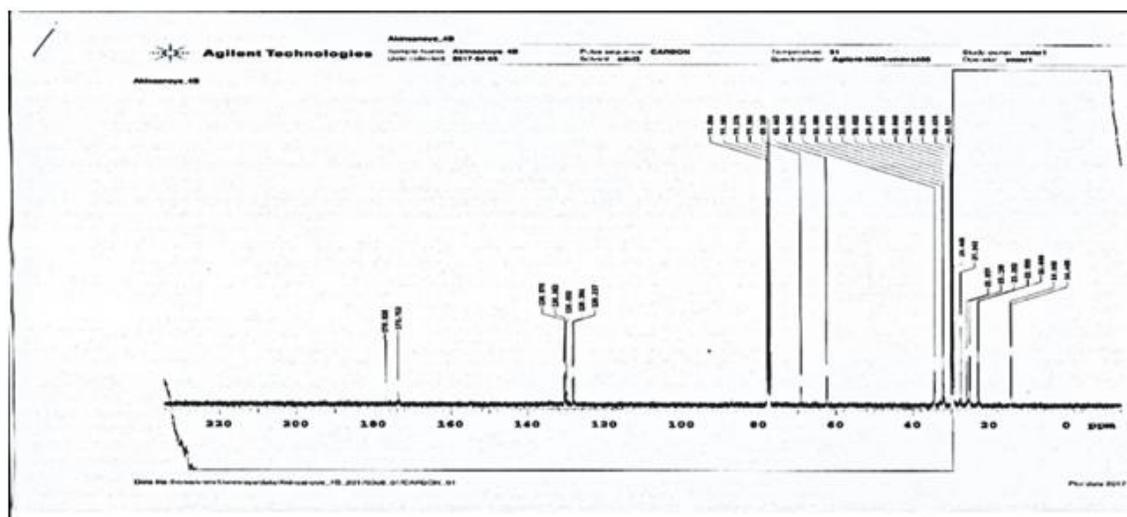
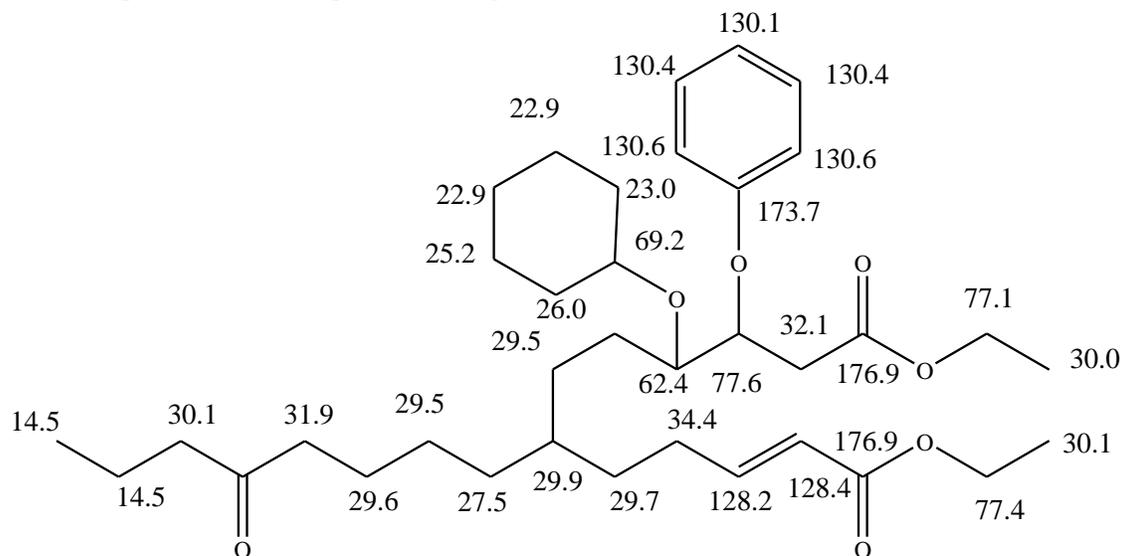


Figure 19:  $^{13}\text{C}$  NMR for copolymerized phenol *Citrullus lanatus* polymer (CPCLP)

The peak at 176.920 ppm is due to the presence of carbonyl group of esters present in the sample. Peaks at 173.712, 130.575 ppm, 130.363 ppm, 130.052 ppm are aromatic carbon atoms. Peaks at 128.343 ppm, 128.217 ppm occur due to the presence of vinyl carbons. Peaks at 77.694 ppm, 77.580 ppm, 77.325 ppm, 77.064 ppm, 69.169 ppm and 63.443 ppm occur due to the presence of C-O stretch in the ester and phenolic group. The peaks at 34.3600 ppm, 29.726 ppm, 29.696 ppm, 30.022 ppm, 29.468 ppm are aliphatic carbon atoms resulting from the hydrogenation of the unsaturated points in the fatty ester moiety and the hydrogenation of one of the phenolic group. Resonance peaks occurring at 27.542 ppm, 22.886 ppm, 14.506 ppm and 14.460 ppm are from saturated carbon atoms present in the ring structure. The result agrees with the Viscometry, proton NMR and FTIR results. The proposed structure based on carbon 13 and product obtained is presented in Figure 20.



(*E*)-diethyl 9-(cyclohexyloxy)-10-methoxy-6-(5-oxooctyl)dodec-2-enedioate compound with benzene (1:1)

Chemical Formula:  $\text{C}_{37}\text{H}_{60}\text{O}_7$

Exact Mass: 616.43390

Molecular Weight: 616.86810

Figure 20: Proposed structure for Copolymerized phenol *Citrullus lanatus* polymer based on  $^{13}\text{C}$  NMR



## Conclusion

Fatty esters are gaining increasing importance as biodegradable replacement for mineral oils. In some application areas such as chain saw oil, gear box, hydraulic oils, and lubricants for crude oil production, the oleochemical products are established. However, certain specific sources of fatty esters are yet to be exploited for this similar purpose. This research therefore probes into one of the less utilized source of fatty esters in watermelon. The oil from the seeds shows a high-quality yield, poses important functional groups for modification and as a result was used to prepare a variety of oleochemicals which showed quality materials in comparison to the regularly used oils feed stocks for oleochemicals after characterization. The homopolymers obtained showed sharp vinyl protons for continuous polymerization reaction, the amides obtained are good lubricants for gearbox, hydraulics, chainsaw oil, demulsifiers in oil production and good inhibitors because of the lone pairs on the *nitrogen* atom present in the structure and the carbonyl group present in the structure. The copolymerized Phenol –*Citrullus lanatus* oils can be used as lubricant, it can also serve as intermediate chemicals for tyres, plastic, resins and synthetic nylon production. This implies that watermelon based oleochemicals can reduce dependence on seeds that are edible as feedstock, create job opportunities, produce environmental friendly chemicals in line with the green chemistry policy and environmental sustenance and inline with other green feedstock will sufficiently and efficiently replace mineral oil based chemicals.

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