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A Novel Cardanol-Based Monoglyceride Using Cashew Nut Shell Liquid

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Abstract: Phenol is a widely used non-renewable petrochemical resource in many organic syntheses, hence sourcing phenolic derivatives from renewable resources is an important concern. In this study, a novel monoglyceride (MG) was synthesized utilizing "cardanol" as a starting material, which is an eco-friendly and natural phenolic derivative. Cardanol was obtained by the decarboxylation of anacardic acid present in raw cashew nut shell liquid (CNSL). It was then reacted with maleic anhydride (MA) to synthesize a novel mono-phenyl maleate (MPM) derivative with a purity of 65.5%. This product was subjected to a direct esterification with glycerol to obtain the novel MG. Based on the periodic oxidation method, the percentage composition of the monoglyceride was obtained to be 70.1%. It showed high thermal stability up to 250 °C. This MG being a thermally stable di-functional compound makes it a potential novel monomer that can be used to synthesize novel alkyd resins with enhanced properties in the future.

Keywords**:** monoglyceride, cashew nut shell liquid, cardanol, thermal stability

1. Introduction

Petroleum is a non-renewable resource that serves as a primary source of basic organic compounds.[1] With rapid consumption of non-renewable resources, there is a growing emphasis on renewable alternatives, like cardanol present in cashew nut shell liquid (CNSL). Cardanol, an economical and eco-friendly phenolic derivative, shows promise in various applications, including surface coatings, paintings, and varnishes.[2]

The cashew tree (*Anacardium occidentale* L.) believed to have first originated in Brazil,[3] is an evergreen tropical tree with a commercially significant nut. Despite the Cashew nutshell being considered an agro waste,[4] the liquid within the honeycomb shell structure has drawn significant attention due to essential chemical compounds present,[5] including anacardic acid, cardanol, cardol, and methyl cardol.[6] Extraction methods, influenced by the temperature[7] and the geographical distribution[8] affect the percentage composition of these components. Common extraction methods such as (1) solvent, (2) thermal, and (3) mechanical extractions result in different compositions. Low temperatures extractions (below 100 °C) yield higher anacardic acid levels (60-65%), while high temperatures lead to elevate cardanol levels (60-65%)[9] due to the decarboxylation of anacardic acid in CNSL into cardanol.[10,11]

Raw CNSL with a high anacardic acid percentage is acidic and corrosive.[10] The applications of raw CNSL are

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limited due to its instability at elevated temperatures. Raw CNSL is subjected to thermal treatments for converting the anacardic acid into cardanol to produce technical CNSL (t-CNSL). The optimal temperature for this reaction was reported to be 140 °C[10] in which the decarboxylation reaction is predominant in contrast higher temperatures result in thermal polymerizations.[10] Cardanol, the major component in t-CNSL serves as a crucial green starting material in organic syntheses offering versatility for various transformations through hydrogenation, halogenation, epoxidation, and cross-linking owing to the functionality of its hydrocarbon chain and the aromatic ring.[5]

This study focused on utilizing cardanol in a two-step synthesis to synthesize a novel monoglyceride. Synthesis of mono phenyl maleate (MPM) derivative by reacting cardanol with maleic anhydride (MA) was the first step. MPMs, known as aromatic esters have diverse applications in the food, pharmaceutical, and cosmetic industries.[12]

The structure of a cardanol-based MPM resembles a long-chain fatty acid having unsaturation. The second step of this synthesis is similar to the reaction between fatty acid and glycerol to synthesis monoglyceride (MG).[13] The novel MG of this synthesis can serve as a monomer in alkyd resin synthesis via polyesterification with suitable acid anhydrides such as phthalic anhydride (PA) or maleic anhydride (MA). The primary goal objective of this study was to synthesize a novel cardanol-based MG from CNSL offering a potential novel monomer with advanced properties and contributing to the field of green chemistry.

2. Materials and methodology

2.1 *Extraction of cashew nut shell liquid*

Soxhlet extraction method was employed to extract raw CNSL. Initially, 300.00 mL of Acetone was filled into the round bottom flask of the soxhlet apparatus. Subsequently, 50.00 g of clean cashew nut shells were charged into the thimble of the extractor. The extraction was conducted at 60 °C in runs of two hours. The excess acetone was removed via rotary evaporation to obtain raw CNSL.[14]

2.2 *Characterization of cashew nut shell liquid*

A Thin layer chromatography (TLC) analysis was performed using a solvent mixture of chloroform, hexane, and ethanol in the ratio of 25:25:2 as the mobile phase solvent system.[15] Additionally Fourier-Transform Infrared (FTIR) spectrum was obtained to characterize the liquid.

2.3 *Decarboxylation of cashew nut shell liquid*

Extracted CNSL was decarboxylated at 140 °C, in an open beaker placed in an oil bath using the magnetic stirrer for two hours, until the effervescence ceased.[16] The acid value was monitored until it reached a constant minimum.

2.4 *Isolation of cardanol*

Decarboxylated CNSL (10.00 g) was dissolved in 32.00 mL of methanol along with a 20.00 mL solution of 25% ammonium hydroxide and stirred for 15 minutes. The resulting solution was then extracted using *n*-hexane (4 × 20.00 mL). The organic layers were combined and washed successively with 10.00 mL of 5% HCl and 10.00 mL of distilled water. Subsequently, 1 g of Activated charcoal was added to the organic layer stirred for 15 minutes and filtered through celite. The filtrate was then dried over anhydrous sodium sulphate and subjected to rotary evaporation to remove hexane.[9]

2.5 *Characterization of raw CNSL, decarboxylated CNSL and cardanol*

Raw and decarboxylated CNSL were characterized for their viscosity, specific gravity, and acid value. Additionally, FT-IR spectroscopy was performed using the ATR mode in the range of 600 $\mathrm{cm^{-1}}$ to 4,000 $\mathrm{cm^{-1}}$ to compare raw and decarboxylated CNSL. GC-MS spectrum of cardanol was obtained by dissolving 1 mg of the sample in 10.00 mL of dichloromethane. 1 µL of the solution was injected into the Agilent GC 7890A/MS 5975C (GC-MS system) equipped with HP-5MS UI capillary column (30 m × 0.250 mm, 0.25 μm film thickness). Helium was used as the carrier gas at a flow rate of 0.5 mL/min. The temperature program involved an increment from 50 to 250 °C at 10 °C/min and maintained at 250 °C for 30 minutes.[16]

2.6 *Synthesis of MPM derivative of cardanol*

Since the direct esterification of phenolic compounds is impossible, the synthesis was conducted in two steps. The first step involved synthesizing the potassium phenolate of cardanol followed by the reaction with MA in the second step.

A volume of 25.00 mL of distilled water was used to dissolve 40 mmol of potassium hydroxide, which was then mixed with 40 mmol of cardanol in a beaker. The resulting mixture was agitated until it formed a viscous paste which underwent vacuum evaporation to remove water.[12]

Subsequently, 40 mmol of MA was dissolved in 25.00 mL of 95% v/v ethanol. The dried potassium phenolate derivative of cardanol was transferred into a clean three-neck round bottom flask along with the ethanolic MA solution. This mixture was refluxed for three hours at 78 °C. At the end of the reaction, the mixture was acid-washed using an acidic solution prepared by adding 2.50 mL of concentrated HCl to 25.00 mL of water. The reaction product was extracted using three portions of 15 mL of chloroform, followed by evaporation to isolate the product.[12]

2.7 *Synthesis of the novel monoglyceride*

A quantity of 40 mmol of MPM and 40 mmol of glycerol were transferred into a clean three-neck round bottom flask along with 250.00 mL of toluene as the solvent. The reaction was carried out at 110 °C for three hours. The product was freed from glycerol by washing with a brine solution.[17]

2.8 *Characterization of the novel monoglyceride*

The novel MG was characterized using FTIR performed in the range of 600 cm^{-1} to 4,000 cm^{-1} using ATR mode. The thermal stability of the novel MG was determined using Thermogravimetric analysis (TGA) with a scanning rate of 10/min from 27 to 400. Additionally, the differential thermal analysis (DTA) curve was plotted using TGA data. The percentage of α-MG was determined using the Per-iodic oxidation method.[17]

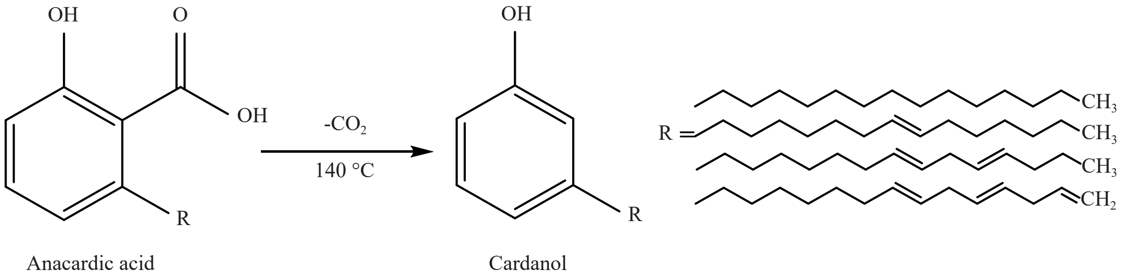

Figure 1. Decarboxylation pathway of anacardic acid into cardanol

3. Results and discussion

3.1 *Extraction and characterization of raw CNSL*

Raw CNSL was a brownish viscous liquid with an acid value of 117 mg KOH/g. Its viscosity was obtained as 198 cP and the specific gravity was 0.997 at 30 °C. The percentage yield of extraction was 18%. Four components were determined with the R_f values of 0.22, 0.49, 0.71, and 0.81 for anacardic acid, cardol, methyl cardol, and cardanol respectively aligning closely with literature reported 0.22 for Anacardic acid, 0.49 for cardol, and 0.82 for cardanol.[15]

The decarboxylation of CNSL resulted in a 12.1% weight loss and a decrease in viscosity. The decarboxylated CNSL resulted in a reddish-brown appearance and reduced turbidity. By the end of 160 minutes, the acid value decreased from 117 mg KOH/g to a minimum constant of 9 mg KOH/g. The extent of reaction was calculated as 92.3%. The decarboxylation pathway of anacardic acid into cardanol is given in Figure 1.

In the FT-IR spectrum, the peak corresponds to the -C=O stretch is characteristic, of the raw CNSL since the carboxylic group is absent in the decarboxylated CNSL. This peak appeared at 1,643 cm^{-1} in raw CNSL and is tallied with the literature reported values[18] is clearly absent in the decarboxylated CNSL indicating the completion of the decarboxylation reaction. Further, the sharpening of the broad peak at 3,384 cm^{-1} corresponding to the phenolic O-H stretching in decarboxylated CNSL in contrast to decarboxylated CNSL indicates the decarboxylation.[18]

3.2 *Characterization of cardanol*

The average yield of extraction of cardanol from the decarboxylated CNSL was obtained as 82.37%. The presence of cardanol was confirmed by the GCMS analysis. Accordingly, cardanol was obtained with a retention time of 24.7 minutes. The mass spectrum of cardanol is depicted in Figure 2.

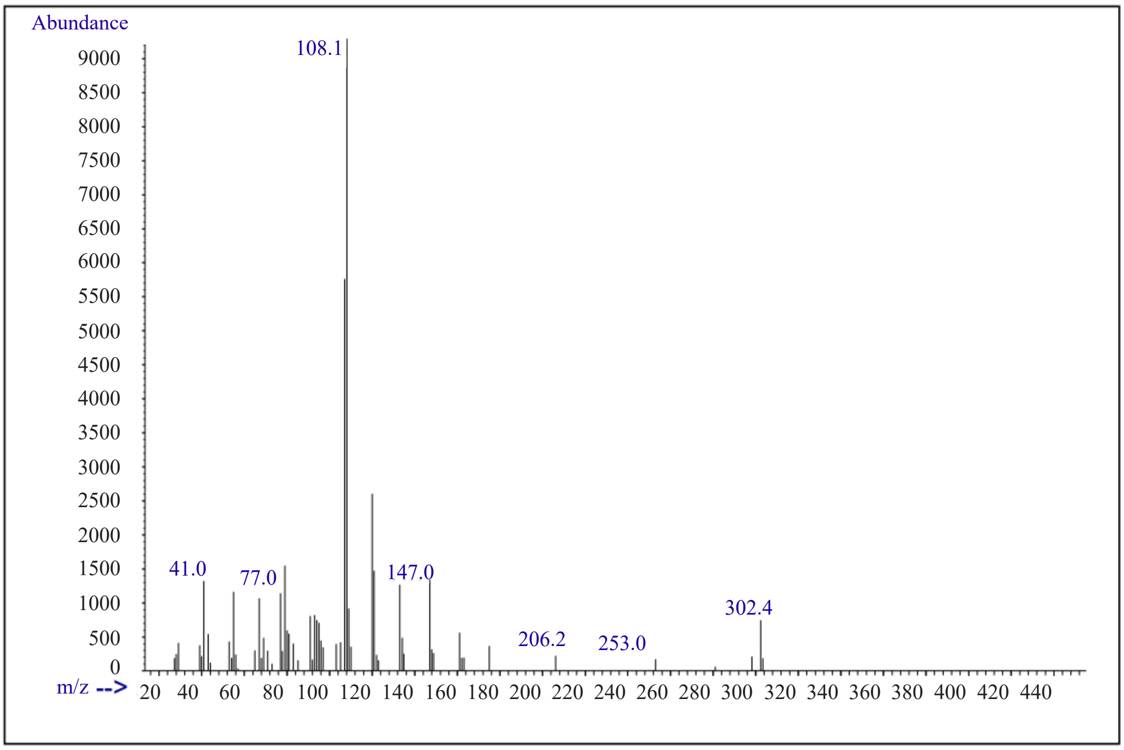

Figure 2. Mass spectrum of cardanol

The mass spectrum of cardanol aligns with the published data.[19] The molar mass of monoene cardanol is 302.4 g mol^{-1}. The peak m/z at 302 can be assigned to the molecular ion of cardanol which is clear evidence for the presence of cardanol. Additionally, the appearance of a peak m/z at 108.1 indicates the characteristic alkyl benzene fragments, derived through the β cleavage of the aliphatic chain of the cardanol structure. This rearrangement is known as Mclaferrtry rearrangement and is attributed to the presence of a long aliphatic chain attached to a benzyl ring.[16]

3.3 *Characterization of cardanol based mono phenyl maleate*

The percentage yield of the potassium phenolate derivative of cardanol was 90.38%. The theoretical acid value for a 100% pure MPM derived from cardanol is 140.1 mg KOH/g, corresponding to 0.2496 mol/g of acidic substance. The experimentally obtained acid value was 91.9 mg KOH/g, indicating 0.1638 mol/g of acidic substance. This disparity suggests the presence of non-acidic substances in the product mixture. Consequently, the purity of MPM was determined as 65.5%.

The characteristic peak of the FT-IR spectrum used to confirm the formation of MPM is at 1,263 cm^{-1} corresponding to the sp^2 C-O stretching of the ester linkage. The literature reported value for this peak is 1,258 cm^{-1}.[18] Other important peaks can be assigned at 3,370 cm^{-1}, 1,718 cm^{-1}, and 1,454 cm^{-1} corresponding to the hydroxyl stretching, carbonyl stretching and the C-H bending of methylene in aliphatic chains respectively in accordance with the literature reported values at 3,305-3,363 cm^{-1}, 1,682 cm^{-1} and 1,450 cm^{-1} respectively.[18] The proposed synthetic pathway for the formation of MPM is given in Figure 3.

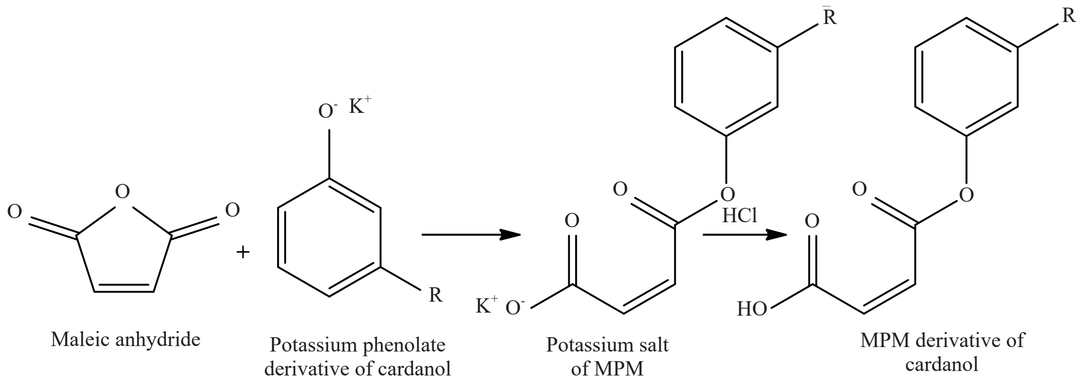

Figure 3. Synthetic pathway for the formation of novel MPM

3.4 *Characterization of the novel monoglyceride*

According to the periodic oxidation method, the percentage of alpha MG in the product mixture was determined to be 70.1%, thereby confirming the formation of the product.[17] However, impurities deriving from the previous stages as well as the products from side reactions could contribute to the decrease in yield to 70%. The proposed reaction pathway of this synthesis is given in Figure 4 as follows.

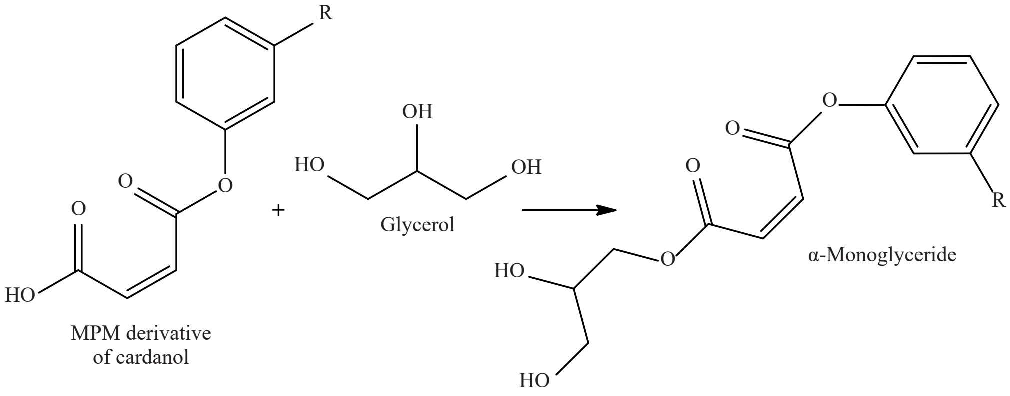

Figure 4. Synthetic pathway for the formation of novel monoglyceride

The formation of the novel MG is further supported by FT-IR data as well. A broad absorption band at 3,412 cm^{-1} is assigned to the OH stretching. The sharpening of this peak is an indication of the presence of MG, which is a characteristic peak for MG. Also, the intensification of the adsorption band at 2,925 cm^{-1} and 2,847 cm^{-1} can be assigned to the asymmetric and symmetric C-H stretching respectively in the glycerol moiety and long aliphatic chain of the cardanol moiety. The intense peak at 1,710 cm^{-1} is assigned for the carbonyl group and 1,260 cm^{-1} peak can be assigned for the ester linkage, C-O-C stretching mode.[18] The sharpening of this peak indicates the formation of new ester bonds in the MG synthesis.

The thermal stability of this structure was determined using TGA and the spectrum is given in Figure 5.

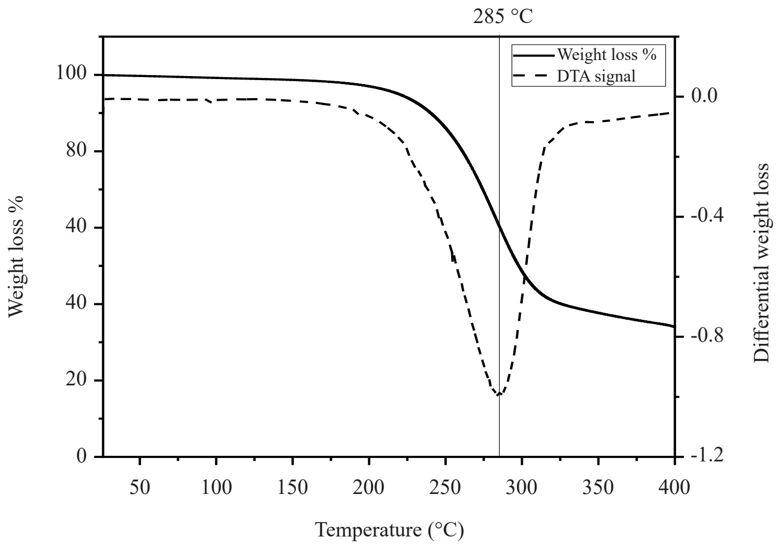

Figure 5. The TGA and DTA spectrum of the novel MG

This novel MG exhibits stability up to approximately 250 °C without undergoing any thermal decomposition. However, the decomposition is prominent at 284 °C. The decomposition can be attributed to the breakdown of unsaturated aliphatic side chains presented in the cardanol structure.[20] High thermal stability is an essential property for this compound to serve as a potential monomer.

4. Conclusion

Raw CNSL was extracted with a yield of 18% and four major components; anacardic acid, cardol, methyl cardol, and cardanol were identified. The initial properties were an acid value; 117 mg KOH/g, viscosity; 198 cP, and specific gravity; 0.997. Decarboxylation of Anacardic acid into Cardanol was indicated by the decrease in acid value from 117 mg KOH/g to 9 mg KOH/g, with a weight loss of 12.1%. Cardanol was isolated from decarboxylated CNSL with a yield of 82.37%. Cardanol was reacted with MA to synthesize a novel MPM derivative, with a purity of 65.5%. A novel MG was synthesized by the reaction of the MPM derivative of cardanol with glycerol and the yield was 70.1%. TGA studies showed its thermal stability up to about 250. This di-functional and thermally stable novel MG derived from cardanol and glycerol offers potential as a polyesterfication monomer and contributes greatly to green chemistry.

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Conflict of interest

No potential conflict of interest.

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