

## Article

# Isolation of Cardanol Fractions from Cashew Nutshell Liquid (CNSL): A Sustainable Approach

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**Abstract:** Exploring sustainable approaches to replace petroleum-based chemicals is an ongoing challenge in reducing the carbon footprint. Due to the complexity and percentage variation in nature-generated molecules, which further varies based on geographical origin and the purification protocol adopted, a better isolation strategy for individual components is required. Agrowaste from the cashew industry generates phenolic lipid (cardanol)-rich cashew nutshell liquid (CNSL) and has recently shown extensive commercial utility. Cardanol naturally exists as a mixture of three structurally different components with C<sub>15</sub>-alkylene chains: monoene, diene, and triene. The separation of these three fractions has been a bottleneck and is crucial for certain structural designs and reproducibility. Herein, we describe the gram-scale purification of cardanol into each component using flash column chromatography within the sustainability framework. The solvent used for elution is recovered and reused after each stage (up to 82%), making it a cost-effective and sustainable purification strategy. This simple purification technique replaces the alternative high-temperature vacuum distillation, which requires substantial energy consumption and poses vacuum fluctuation and maintenance challenges. Three components (monoene 42%, diene 22%, and triene 36%) were isolated with good purity and were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR, GC-MS, HPLC, and FTIR spectroscopy. The present work demonstrates that greener and simpler strategies pave the way for the isolation of constituents from nature-sourced biochemicals and unleash the potential of CNSL-derived fractions for high-end applications.

**Keywords:** cardanol; chromatography; solvent recovery; purification; sustainable process; separation; flash chromatography; NMR of cardanol; cardanol monoene; cardanol diene; cardanol triene; epoxidation of cardanol triene



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## 1. Introduction

Society is challenged to meet the escalating global demand for chemicals while transitioning from petroleum-based products to more sustainable alternatives [1]. Waste generated by agro-based industries and the abundance of biosynthons in plant sources offer two natural alternatives that have the potential to substitute products derived from current fossil feedstocks in various applications. The utility of such resources has appeared as an advancement in material science as these bio-based resources act as feedstock and simultaneously enriches new structural design of materials with unique set of properties [2,3]. In this context, the substantial growth of the polymer industry over the years has led to excessive consumption and over-dependence on non-renewable petroleum-sourced raw materials. Alternatively, several polymers have been developed using renewable sources like plant oils, starch, cellulose, chitosan, and isosorbide [4]. Among phenols, bisphenol-A (BPA) is a major constituent for designing several polymers such as epoxy, phenol–formaldehyde, polycarbonate, polyether ketones, polyesters, etc. However, BPA has been identified as an endocrine disruptor, affecting biological functions associated with the reproductive,

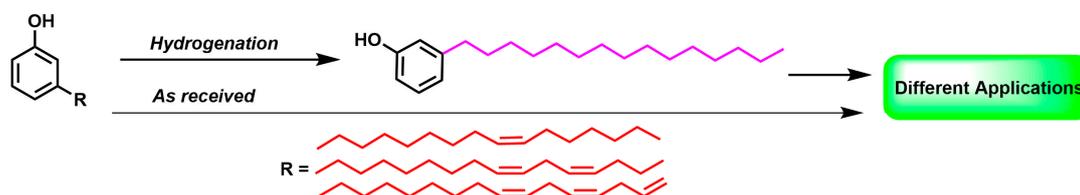
immune, and neuroendocrine systems. Additionally, it can induce multiorgan toxicity by entering the receptor pathways, leading to either disruption or alteration in pathways, inhibiting enzymes, the modulation of immune and inflammatory responses, and even affecting genotoxic and epigenetic mechanisms. Furthermore, exposure to BPA has illicit health effects [5,6], impacting reproductive, growth, metabolism, immunity, respiratory, liver, and kidney functions, along with signs of carcinogenesis. Even biomagnification of BPA, once entered into the food chain, is potentially lethal. Due to the rising environmental concerns, the EFSA (European Food Safety Authority) and other governmental regulators have set strict limits on BPA-based plastics, especially those in food contact [7]. To alleviate this, developing and exploring other safe phenolic alternatives to synthesize BPA-free plastics is in a continuous surge. The synthesis of bisphenol analogues via altering the synthetic design of the isopropylidene linker between the two hydroxyphenyl functionalities using petroleum-based feedstocks has shown itself to be a promising approach [8]. Alternatively, several naturally occurring phenols hold potential [9]. Interestingly, other inherent additional functionalities provide excellent opportunities for structural engineering at a molecular level, possessing similar or advanced functional properties to form BPA-mimic polymers [10].

Phenolic resins constitute one of the oldest thermosets with the highest tonnage consumption for industrial applications [11]. Thus, plant phenolics represent important and time-honored raw materials for innumerable industrial products, including thermoset [12] and thermoplastic [13] polymers [14,15]. Furthermore, the inherent presence of various functionalities is one of the vivid features as it enables various structural modifications to design and stimulate diversity in bio-based precursors for polymers [16–18] and nanoparticles/nanofibers [19,20]. The simplest method of extracting these phenolics is via a direct isolation route, either from natural sources or by transforming waste from agro-based industries [21].

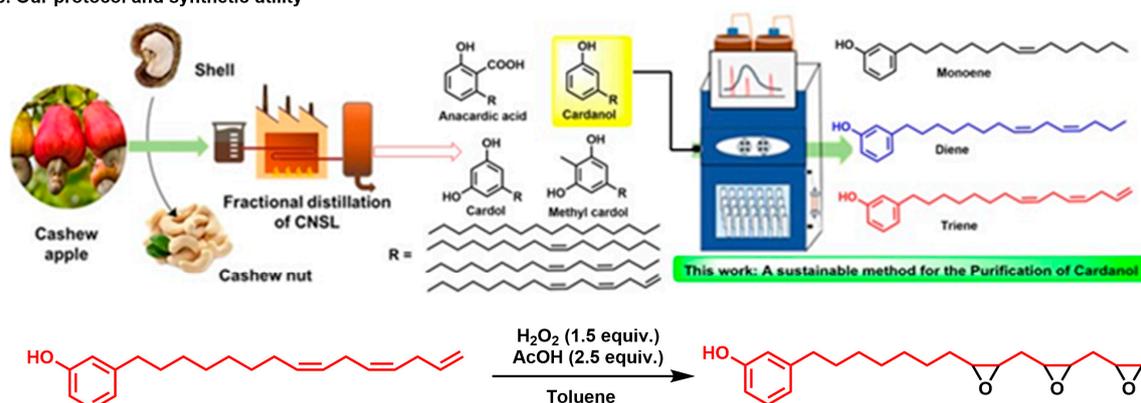
Among naturally occurring phenols, cardanol is a plant phenolic lipid extracted from the spongy mesocarp of cashew nutshells obtained from cashew trees, *Anacardium occidentale*, largely grown in coastal regions of India, Vietnam, Indonesia, Brazil, and Mozambique. Cashew nutshell liquid (CNSL), a reddish-brown viscous liquid (~25–30 wt.%), is derived from the most diffused roasted mechanical processes of cashew shells and is generally discarded as a pollutant from the cashew agro-industry [22]. Cardanol-based polymer offers specific properties, such as strong corrosion, heat and chemical resistance, and good adhesion properties, enabling their usage in many applications such as paints [23,24], surfactants [25], coatings [26–28], bio-plasticizers [29], larvicidal [30], antibacterials [31,32], adhesives [33–35], flame retardants [36,37], self-healing [38,39] cathode [40], and photovoltaic [41] materials, etc., for naval constructions, industrial machinery, and automotive components. Interestingly, even food, drug, and beverage industries also extensively use CNSL due to its antioxidant properties [42,43] and possible flavoring and mineral oil additive. Low viscosity further enables its use as a reactive diluent [44,45]. Natural CNSL is a complex mixture of phenolic compounds, and depending on the source, it mainly consists of anacardic acid (70%), cardanol (5%), and cardol (18%), and each type has varying degrees of unsaturation at the meta-substituted C<sub>15</sub>-long aliphatic side chain (Figure 1). Till date, extraction, and isolation of CNSL are given major importance, rather than separating it into individual cardanol components. Conventional approaches for CNSL extraction include the hot oil pyrolysis process, solvent extraction, mechanical extraction, vacuum distillation, and supercritical carbon dioxide extraction [46,47]. CNSL is commercially available in natural and technical grades. Natural grade (cold-processed CNSL) contains anacardic acid [48] and cardol as the major components. In the case of the hot oil method, roasting the shell at high temperatures mediates the flow of CNSL, and decarboxylation of anacardic acid occurs, leading to enrichment in cardanol content. In contrast, the technical grade (hot-processed CNSL) consists of cardanol and cardol in major quantities and a minor fraction of 2-methylcardol. Heat-extracted cardanol is further processed via distillation at a

reduced pressure, resulting in a distilled technical-grade CNSL with a composition of 78% cardanol, 8% cardol, and 2% polymeric material [49].

a. Earlier strategies



b. Our protocol and synthetic utility



**Figure 1.** Previous strategies for the utilization of CNSL vs. our protocol for the separation process adopted to isolate monoene, diene, and triene from cashew nutshell and its synthetic utility.

Tyman et al. [50] used a laborious solvent (carbon tetrachloride and petroleum ether) extraction method yielding CNSL ~15–30% in a maximum duration of 14 days. The use of organic solvents for CNSL extraction is suitable for small-scale analysis but appears challenging for large-scale purification, making the process non-green due to unsafe and high-cost solvents. CNSL enrichment with cardanol is also achieved via the decarboxylation of anacardic acid in toluene using a Dean–Stark apparatus [51]. On refluxing the decarboxylated CNSL in a methanol–formaldehyde–diethylenetriamine solution, cardanol is obtained in a 50% yield. Among greener approaches, the extraction of CNSL using supercritical carbon dioxide ( $\text{Sc-CO}_2$ ) yielded cardanol at ~85% yield, a significantly higher yield than the conventional techniques mentioned earlier. However, maintaining a high and constant pressure of 300 bar at 60 °C is crucial for achieving this level of enrichment.

As well as being a versatile and inexpensive phenolic compound, the existence of three reactive sites—phenolic–OH, an aromatic ring, and an alkenyl chain (benzylic– $\text{CH}_2$ , allylic– $\text{CH}_2$ , and  $\text{C}=\text{C}$  bond)—provide scope for further structural modifications and polymerization mechanisms. However, CNSL is a complex mixture and structurally consists of phenolic compounds with meta-substituted  $\text{C}_{15}$ –long alkylene chains. The existence of double and triple bonds in an R-chain meta to the phenol group is unique and challenging to synthesize otherwise; however, nature accomplishes this adeptly. The aliphatic side chain varies from saturated (3-*n*-pentadecylphenol, 20–30%) to monoene (3-(pentadeca-8-enyl)phenol, 70–80%), diene (3-(pentadeca-8,11-dienyl)phenol, 5%), and triene (3-(pentadeca-8,11,14-trienyl)phenol, <5%) [52]. The degree of unsaturation in the alkylene chain varies from saturated to monoene, diene, and triene, each differing by two proton mass units. In general, one of the major bottlenecks is the purification of CNSL into individual constituents. Therefore, various synthetic and material utilities or applications [53] of this phenolic waste involve its usage either as saturated cardanol (with reduced alkylene chain) or unpurified CNSL (Figure 1a) [13,54,55]. Using CNSL (as received) affects the reproducibility of data, as the weight ratio of each component

varies depending on the geographical origin of the cashew tree. Alternatively, purifying cardanol into its constituents is a challenging problem, which is worth exploration for advancing its utility. CNSL has a boiling point of  $\sim 360$  °C (at 7600 mm of Hg) and  $\sim 225$  °C (10 mm of Hg). Vacuum distillation seems a promising alternative purification process, but a very high and similar boiling points of the components make the separation strategy very challenging. Also, this process relies on substantial energy consumption and often faces challenges due to vacuum fluctuation and maintenance. Synthetically, the unsaturated alkylene chain components (monoene, diene, and triene) in CNSL can be converted into a single product, 3-pentadecylphenol/hydrogenated cardanol (alkyl side chain), via a hydrogenation reaction. However, the former process demands an unsafe hydrogenation process using costly catalysts, rendering the whole process uneconomical. Additionally, hydrogenation leads to the loss of the characteristic unsaturation degree, which is otherwise difficult to achieve synthetically, thus eliminating any opportunity for further modification (epoxidation, hydroxylation, halogenation, etc.).

Nevertheless, the challenge lies in increasing the CNSL content and its effective separation [56]. Importantly, purifying cardanol based on unsaturation content becomes crucial to unlocking new chemistry with this remarkable natural molecule [57,58]. Therefore, there is a need to develop a purification method that could be sustainable and practical. Here, we have established a gram-scale simple purification technique for purifying CNSL into cardanol monoene, diene, and triene fractions using flash column chromatography, following a sustainable, less-energy-intensive (low-boiling solvent) purification strategy. The solvent used for elution is recovered and reused (including the column) after each stage, achieving up to 82% recovery, which makes it cost-effective compared to the alternative of high-temperature vacuum distillation. From CNSL, three components (monoene 42%, diene 22%, and triene 36%) were isolated with good purity and fully characterized via  $^1\text{H}$  and  $^{13}\text{C}$  NMR, GC-MS, HPLC, and FTIR spectroscopy. The present work demonstrates that simpler strategies pave the way to isolate constituents from nature-sourced biochemicals and unleash the potential of CNSL-derived fractions for high-end applications.

## 2. Materials and Methods

### 2.1. Materials

Cardanol (technical grade) was received as a gift from Satya Cashew Chemicals Pvt. Ltd., Chennai, India, acetonitrile (HPLC grade) from Sigma Aldrich (St. Louis, MO, USA), acetic acid from Qualigens, and chloroform-d ( $\text{CDCl}_3$ ) from Eurisotop. All chemicals were used as received. Merck thin-layer chromatography (TLC) plates silica gel 60 F254 coated on aluminium plates was used.

### 2.2. Characterization

The purification of monoene, diene, and triene cardanol was carried out on a Grace Reveleris<sup>®</sup> X2 Flash chromatography (W. R. Grace & Co., Columbia, MD, USA) companion touchscreen consisting of an evaporative light scattering detector (ELSD) and UV detector equipped with C18 column (4 g, 40  $\mu\text{m}$ , Grace Reveleris<sup>®</sup>, W. R. Grace & Co., Columbia, MD, USA). The peaks were detected via UV absorption in wavelengths 220, 254, and 280 nm with a diode array detector. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet iS20 spectrometer (Thermo Scientific<sup>™</sup>, Waltham, MA, USA) equipped with an interferometer with a KBr/Ge-coated beam splitter, dynamic alignment, a thermoelectrically cooled deuterated triglycine sulfate (DTGS) detector, and an attenuated total reflectance diamond (iD5-ATR) accessory. Spectra were recorded in the range of  $4000\text{--}400$   $\text{cm}^{-1}$  with a resolution of  $16$   $\text{cm}^{-1}$ , and 64 scans were co-added to each spectrum.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 400 MHz (nuclear magnetic resonance) NMR spectrometer in deuterated chloroform, and spectra were calibrated to the signals of residual proton in the NMR solvent or tetramethylsilane as an internal reference. Spectra were processed in MestRenova 8.1 software (Mestrelab Research SL; Santiago de Compostela, Spain). HPLC analysis was performed on an Agilent 1260 Infinity LC system (Agilent Technologies, Inc.,

Santa Clara, CA, USA) and carried out at room temperature on a column of GRACE Alltima C18 (150 mm × 4.6 mm, 5 μm, W. R. Grace & Co., Columbia, MD, USA). Detection was performed at the wavelength of 280 nm.

### 2.3. Purification of Crude CNSL via Flash Column Chromatography

Flash column chromatography separated monoene, diene, and triene cardanol from crude CNSL. Typically, a 2.0 g sample was injected into the C18 Reveleris column (12 g, stationary phase, W. R. Grace & Co., Columbia, MD, USA), and eluent, elution time, and flow rate were varied. The eluted peaks were detected via UV absorption at wavelengths 220, 254, and 280 nm.

#### 2.3.1. Method 1

The mobile phase was a mixture of MeCN–MeOH (70:30) for 155 min at a flow rate of 35 mL/min. The major fractions were collected, dried over sodium sulfate, and concentrated over a rotary evaporator.

#### 2.3.2. Method 2

The mobile phase was a mixture of MeCN–H<sub>2</sub>O–AcOH (80:20:1) for 72 min at a 50 mL/min flow rate. Pure fractions were collected and evaporated over a rotary evaporator to recover acetonitrile, and the residue was washed with water until the pH was neutral (checked with pH paper). The isolated fractions were separately dried over sodium sulfate and concentrated on a rotary evaporator. The purity of the components was confirmed using HPLC, and structural characterization was conducted using NMR, FTIR, and mass spectrometry.

### 2.4. Characterization Details of the Purified CNSL Fractions

#### 2.4.1. Monoene Cardanol

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ = 7.14 (dd, *J* = 6.0 Hz, 1H), 6.76 (d, *J* = 6.0 Hz, 1H), 6.67–6.54 (m, 2H), 5.40–5.33 (m, 2H), 2.56 (t, *J* = 6.0 Hz, 2H), 2.05–2.01 (m, 4H), 1.63–1.57 (m, 2H), 1.31–1.28 (m, 17H), 0.91–0.88 (m, 3H). <sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>) δ = 155.6, 145.1, 130.1, 130.0, 129.5, 121.1, 115.5, 112.6, 31.9, 31.4, 29.9, 29.5, 29.4, 29.1, 27.4, 27.3, 14.2.

#### 2.4.2. Diene Cardanol

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.15 (dd, *J* = 6.0 Hz, 1H), 6.77 (d, *J* = 6.0 Hz, 1H), 6.69–6.67 (m, 2H), 5.40–5.39 (m, 4H), 2.82 (m, 2H), 2.57–2.54 (m, 2H), 2.08–2.07 (m, 4H), 1.60–1.59 (m, 2H), 1.45–1.35 (m, 10H), 0.98–0.91 (m, 3H). <sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>) δ = 156.0, 145.3, 130.6, 130.4, 129.8, 129.0, 128.4, 121.3, 115.8, 113.0, 31.7, 30.1, 30.0, 29.7, 27.7, 26.1, 23.2, 14.2.

#### 2.4.3. Triene Cardanol

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.15 (dd, *J* = 6.0 Hz, 1H), 6.74 (d, *J* = 6.0 Hz, 1H), 6.66–6.64 (m, 2H), 5.86–5.78 (m, 1H), 5.43–5.38 (m, 4H), 5.07–4.98 (m, 2H), 2.84–2.77 (m, 3H), 2.56–2.53 (m, 2H), 2.18 (m, 1H), 2.05–2.02 (m, 2H), 1.67 (m, 1H), 1.60–1.57 (m, 2H), 1.35–1.28 (m, 7H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 155.8, 145.3, 137.3, 129.8, 128.0, 127.3, 121.4, 115.8, 115.2, 113.0, 36.3, 32.0, 31.7, 30.1, 29.8, 29.7, 27.7, 26.0, 21.5, 14.5.

## 3. Results

### 3.1. Purification Strategy

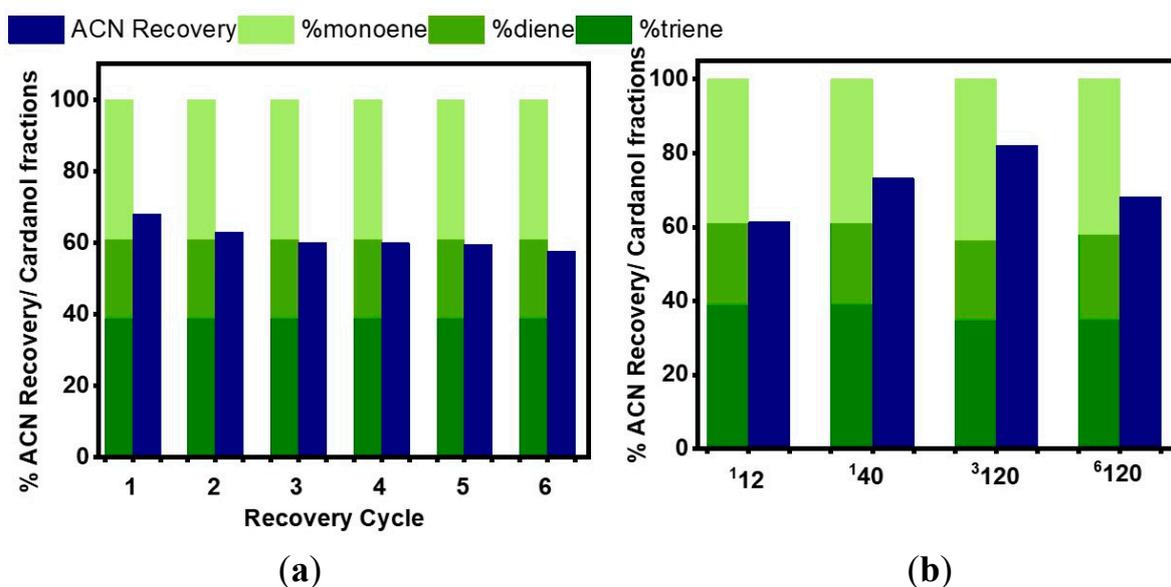
As a preliminary study, we separated the crude mixture of CNSL over the TLC using 20% ethyl acetate in hexane and showed three major spots identified by iodine stains with *R<sub>f</sub>* values as 0.85, 0.6, and 0.35, as depicted in Figure S1 (Supplementary Materials).

Furthermore, mono, di, and triene derivatives of cardanol were purified from crude through column chromatography at milligram scales (200 mg) using hexane and 2–5% and 10% EtOAc in hexane as eluent. Notably, these fractions were evaporated under reduced

pressure followed by a high vacuum and analyzed via various spectroscopy techniques. Understanding the gravity column chromatography was laborious and time-consuming, thus limiting the industrial utility. Therefore, flash column chromatography was attempted using the same eluent further to validate the purification technique at the gram scale. Unfortunately, no pure fraction was obtained. Therefore, we further optimized the eluent system for the flash column chromatography and found that MeCN–MeOH (70:30) as a mobile phase (Method 1, Figure S2) was able to separate the mixture with a flow rate of 30 mL/min for 152 min for 2 g crude. To reduce the elution time, a run at a fast flow rate of 50 mL/min under the optimized condition was performed. However, collected fractions revealed impure compounds. In continuation to our efforts towards the solvent optimization, we found the solvent system acetonitrile–water–acetic acid (80:20:1) as a mobile phase (Method 2, Figure S3) at a flow rate of 50 mL/min, which reduced the time from 152 min to 72 min (Method 1 vs. Method 2). Thus, Method 2 is relatively practical and time efficient. According to the flow rate (50 mL/min) vs. run time (72 min.), a 3.6 L mobile phase purified 2 g crude.

### 3.2. Acetonitrile Recovery

To make the process more sustainable, cost-effective, and practical, recovery of acetonitrile and the effect of crude CNSL loading on variable-size column cartridges is also important. The sample analysis is denoted as  $^Y_X$  where 'X' is the weight of cartridge (in g) and 'Y' is the amount of crude CNSL (in g). For example, if 3 g of cardanol is loaded on a 120 g cartridge then it is denoted as  $^3_{120}$ . In analogy with flash chromatography results (2 g of crude on 12 g cartridge i.e.,  $^2_{12}$ ), the acetonitrile recovery/cycle was ~68%, and it was marginally affected in consecutive cycles (Figure 2a) up to the sixth cycle. Furthermore, the eluate revealed pure fractions of cardanol as monoene (39%), diene (22%), and triene (39%) in each cycle, confirming the robustness of the process. To study the effect of loading on the cartridge, weight of cartridge changed from 12 to 120 g, and amount of cardanol varied from 1 to 6 g. With the decrease in loading of cardanol from 2g to 1 g on 12 g cartridge (i.e., from  $^2_{12}$  to  $^1_{12}$ ) (Figure 2b), neither effect on average solvent recovery nor percentage elution were observed.



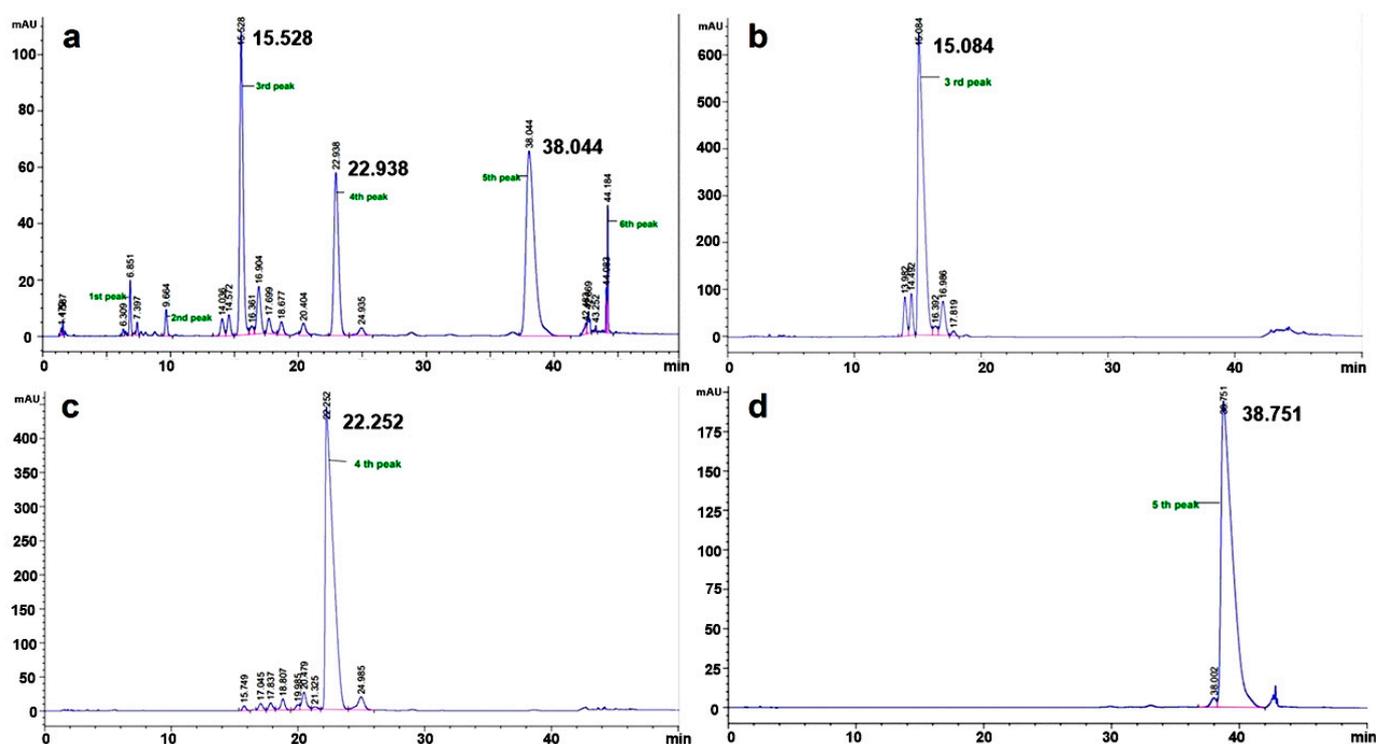
**Figure 2.** (a) Acetonitrile recovery after consecutive six cycles using the same cartridge (cardanol loading of 2 g on 12 g cartridge,  $^2_{12}$ ). (b) Effect of cartridge size with/without variation in CNSL loading in the recovery of acetonitrile.

Expectedly, an increase in the cartridge to 40 g, as in <sup>1</sup>40, delivered the 73% recovery of acetonitrile with the same ratio of mono, di, and triene. Meanwhile, in the case of <sup>3</sup>120, a superior recovery of acetonitrile (82%) with 43% monoene, 22% diene, and 35% triene is observed. In the next attempt, a two-fold increase in cardanol content, i.e., <sup>6</sup>120, led to a 68% acetonitrile recovery with 42% monoene, 22% diene, and 36% triene. These results suggested that the ratio of crude cardanol to cartridge size as 1:4 ensures optimal performance and could be scalable. Finally, different techniques, such as HPLC, IR, NMR, and GC-MS, characterized the collected fractions.

### 3.3. Characterization of Cardanol Fractions

#### 3.3.1. HPLC Analyses

The purity of eluted cardanol monoene, diene, and triene was determined via HPLC using stationary phase as Grace Alltima C-18 column, 150 × 4.6 mm, and mobile phase MeCN—H<sub>2</sub>O—AcOH (80:20:1 *v/v*) at a wavelength of 280 nm and flow rate of 1.5 mL/min for 40 min. A 30 μL sample (monoene, diene, and triene cardanol) was injected separately before recording the HPLC of crude CNSL. Figure 3 shows the HPLC trace of the samples. As received, CNSL revealed several peaks, with major peaks at 15.53, 22.94, and 38.04 min. Interestingly, significant peaks at elution time (purity%) due to triene, diene, and monoene were observed at 15.08 min (82%), 22.25 min (92%), and 38.75 min (99%), respectively.



**Figure 3.** HPLC analysis of (a) crude, (b) triene, (c) diene, (d) monoene.

#### 3.3.2. FTIR Analyses

To further confirm the *cis*/*trans* double bond in alkyl side chains, FTIR of cardanol was recorded (Figure 4). Each fraction showed the characteristic phenolic O–H stretch (3348 cm<sup>-1</sup>), C–H stretching vibration of the unsaturated hydrocarbon and aromatic (3012 cm<sup>-1</sup>), C–H asymmetric and symmetric stretching vibrations of saturated methylene in the side chain (2926, 2852 cm<sup>-1</sup>), and stretching bands for C=C *cis*-alkene (1587 cm<sup>-1</sup>), C–H bending alkane (1453 cm<sup>-1</sup>), and the C–H(C=C)<sub>*cis*</sub> out of plane deformation (693 cm<sup>-1</sup>). Expectedly, only triene showed a terminal vinyl group observed in triene (910 cm<sup>-1</sup>).

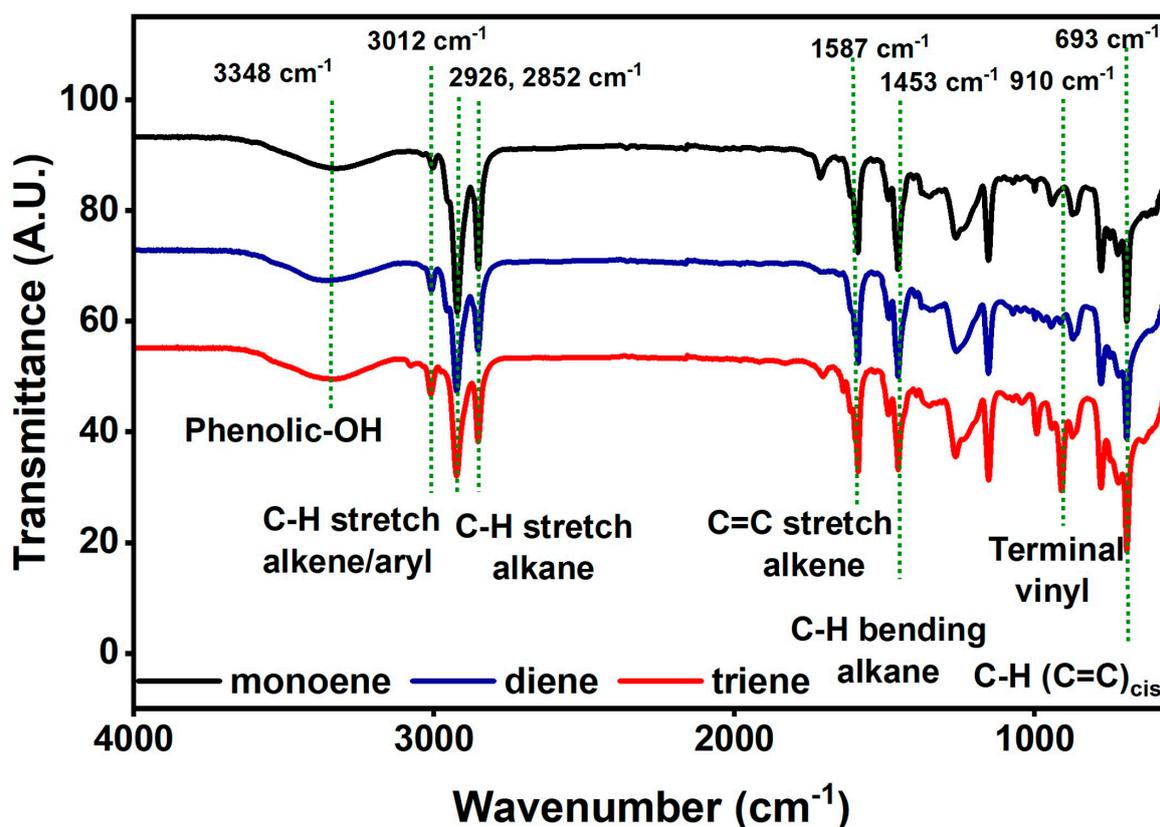


Figure 4. Stacked FTIR spectra of monoene, diene, and triene cardanol.

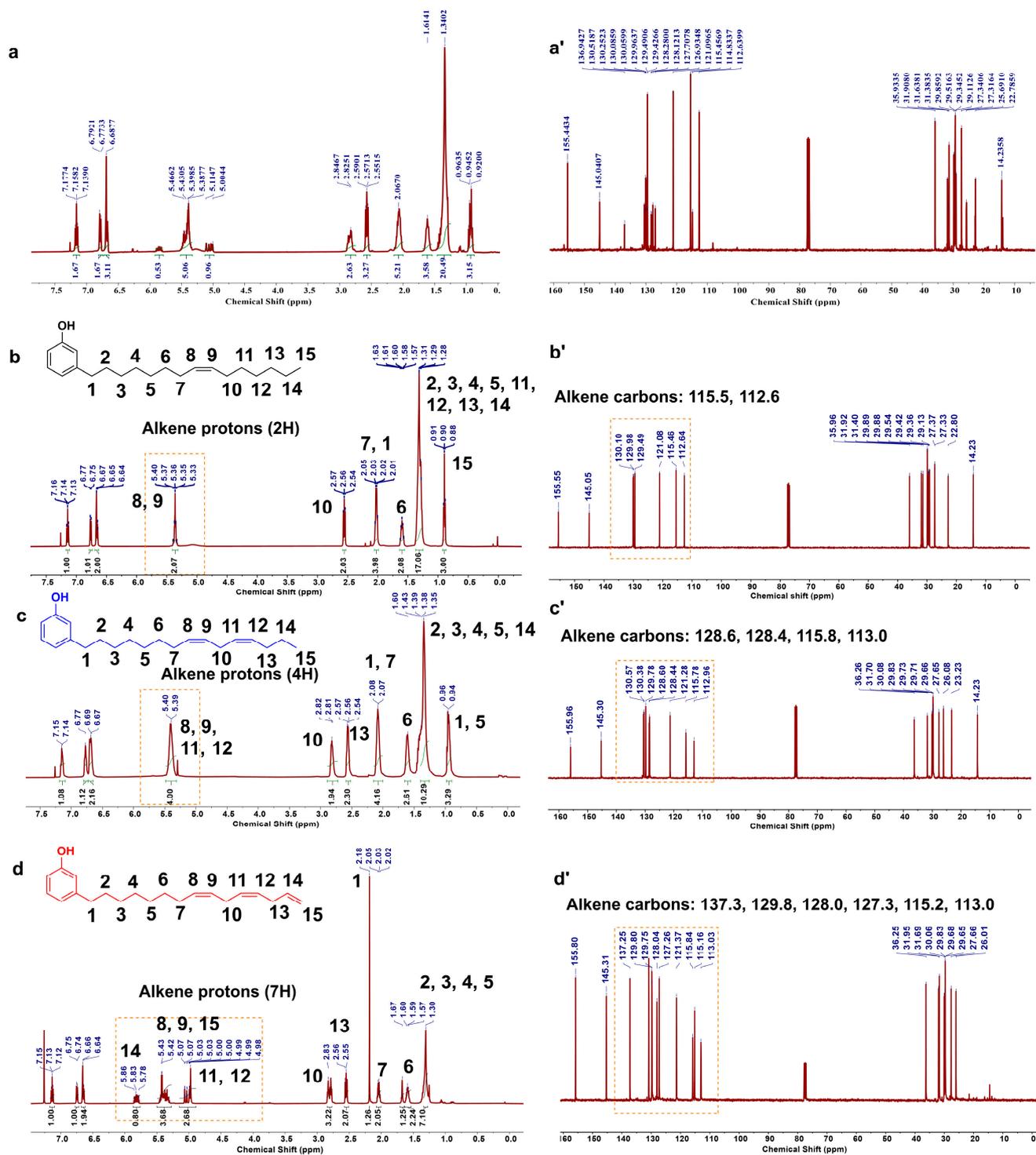
### 3.3.3. NMR Analyses

Figure 5 shows the  $^1\text{H}$  and  $^{13}\text{C}$  NMRs of crude CNSL, monoene, diene, and triene cardanol. Crude CNSL showed several signals with significant overlaps, especially  $\delta = 6.0\text{--}4.0$  ppm (137.0–112.6 ppm), due to olefinic protons accounting for the complexity of the composition. The isolated fractions allowed for the complete assignment of protons, including olefinic protons and carbons. In the case of monoene, diene, and triene, the characteristic olefinic signals at  $\delta = 5.4\text{--}5.3$ ,  $5.40\text{--}5.38$ , and  $5.9\text{--}4.9$ , respectively, are clearly observed. In  $^{13}\text{C}$  NMR, the C-OH was observed at  $\sim 155$  ppm. Respective olefinic carbons in monoene (115.5 and 112.6 ppm), diene (128.6, 128.4, 115.8, and 113.0 ppm), and triene (137.3, 129.8, 1128.0, 127.3, 115.2, and 113.0 ppm) are observed. Additionally, the signal at 14.2 ppm due to the methyl group ( $-\text{CH}_3$ ) is absent in triene, confirming the presence of the ( $-\text{CH}=\text{CH}_2$ ) terminal vinyl group, corroborating the FTIR results.

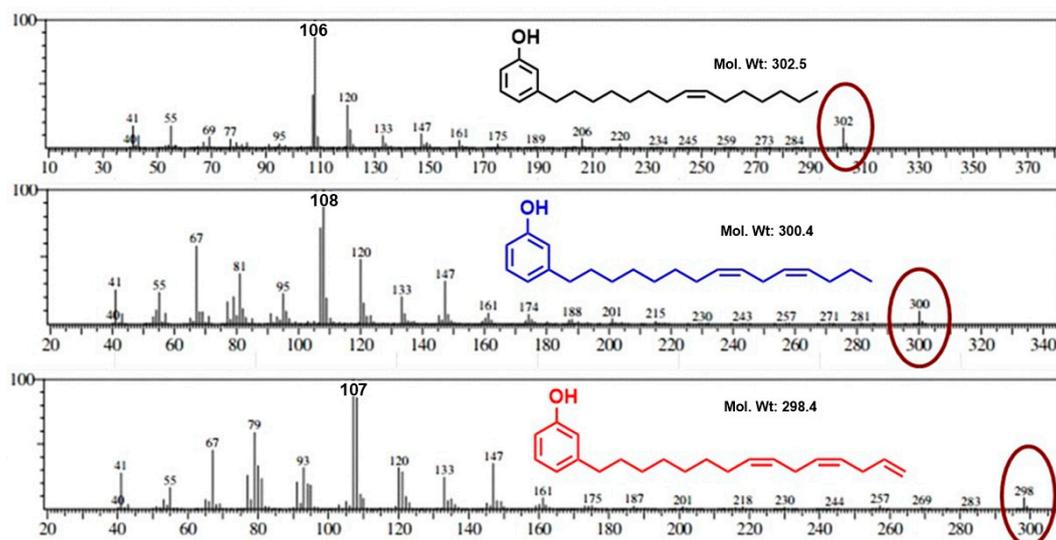
### 3.3.4. GC-MS Analyses

GC-MS spectra are shown in Figure 6. Molecular ion fragments at  $m/z = 302$ ,  $300$ , and  $298$  due to monoene, diene, and triene cardanol, respectively, are observed. The difference of two units in each component confirms the variation in the number of double bonds in each side chain.

The synthetic utility of purified cardanol triene was demonstrated following the reported epoxidation method (see supporting information).  $^1\text{H}$  NMR of the epoxide product obtained from purified cardanol triene vs. as-received from CNSL [59] clearly shows the benefit of the presented strategy. In the near future, our group will undertake structural modifications of isolated cardanol fractions.



**Figure 5.** <sup>1</sup>H and <sup>13</sup>C NMRs of crude (a,a'), monoene (b,b'), diene (c,c'), and triene (d,d') cardanol. Recorded in CDCl<sub>3</sub> ( $\delta = 7.25$  ppm for <sup>1</sup>H NMR and 77.5 ppm for <sup>13</sup>C NMR). Monoene, diene and triene of cardanol were distinguished by the characteristic signals of alkenes which are presented in the yellow box.



**Figure 6.** GC–MS plots of cardanol monoene, diene, and triene. Red circles represent the desired molecular weight for individual fractions of cardanol confirming the purity of sample.

#### 4. Conclusions

A highly practical and sustainable method for purifying crude CNSL through flash column chromatography into its constituent monoene, diene, and triene fractions with a good mass balance is demonstrated. The recovery of acetonitrile (b.p. 80 °C) in the developed method requires only 45 °C under very mild reduced pressure (unlike that required for vacuum distillation of oil, 225 °C, at 10 mm of Hg), representing a substantial sustainable approach in the current work. The process achieved a maximum 82% recovery of acetonitrile, and the reusability of the solvent (including column) in subsequent purifications illustrates the environmentally friendly nature of the process. The purified fractions (monoene, diene, and triene) showed high purity in HPLC, and their structures were characterized via NMR, GC-MS, and IR techniques, based on the structural differences observed in these fractions. Furthermore, the synthetic utility of the triene fraction is explored through an epoxidation strategy. This suggests its potential future utility in contributing to new materials and prospects in materials science.

**Supplementary Materials:** The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/suschem5020006/s1>, Figure S1: TLC image. crude CNSL, 1 stands for triene, 2 for diene, and 3 for monoene; Figure S2: Method 1 used for flash column chromatography purification of crude CNSL; Figure S3: Method 2 used for flash column chromatography purification of crude CNSL; Figure S4: <sup>1</sup>H NMR of crude cardanol tri-epoxide.

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