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Studies on effect of various solvents on extraction of cashew nut shell liquid (CNSL) and isolation of major phenolic constituents from extracted CNSL

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ABSTRACT

Cashew nut shell liquid (CNSL) and its derivatives are widely used in polymer-based industries, synthesis of chemicals and intermediates including bactericides, insecticides and surface active agents. Commercially available CNSL mainly contains phenolic constituents such as anacardic acid, cardanol and cardol. Cardanol contains polymerizable side chain and phenolic group. Cardanol and its various derivatives have found numerous industrial applications. In the present study, extraction of CNSL from cashew nut shell was performed using soxhlet extraction method in presence of various polar and non polar solvents. Among all the solvents acetone gives maximum amount of CNSL. From the extracted CNSL, anacardic acid was selectively isolated and acid free CNSL was treated with liquor ammonia to separate the cardanol and cardol in stepwise manner. They were all characterized using quantitative analysis by HPLC. Technical CNSL provided higher content of cardanol compared to natural CNSL.

Keywords: Cashew nut shell, Soxhlet extraction, Anacardic acid, Cardanol, Cardol.

INTRODUCTION

The cashew tree is evergreen. The Cashew nut has a shell of about 1/8 inch thickness, with a soft honeycomb structure inside, containing a dark brown viscous liquid. It is called cashew nut shell liquid (CNSL), which is pericarp fluid of the cashew nut. [1] CNSL is extraction from cashew nut shell (CNS) by using of different methods. The heating process (roasting) can be achieved by open recipients or drums. [2] The cashews can also be heated by CNSL in a process denominated as thermo – mechanic (hot oil process). [3] In the cold, the CNSL can be obtained by extrusion, in solvents or by pressing. The cashew's liquid obtained by the cold is denominated as natural

CNSL and when extracted in hot is denominated technical CNSL. CNSL was extracted from cashew nut shell (CNS) by using soxhlet extraction equipment. Polar and non-polar solvents were used in extraction of CNSL from the CNS and comparison was made between them. [4] Solvent-extracted CNSL contains anacardic acid (60–65%), cardol (15–20%), cardanol (10%) and traces of methyl cardol. Technical CNSL is obtained by roasting shells and contains mainly cardanol (60–65%), cardol (15–20%), polymeric material (10%), and traces of methyl cardol. [5] In view of its biological and industrial applications it was considered necessary to develop a simple and efficient method for the isolation of all the major phenolic constituents of CNSL. Because of the thermo ability of the carboxylic group of anacardic acid (tendency to get converted to cardanol), CNSL constituents cannot be separated by fractional distillation. [6] In previous reported methods to isolation of anacardic acid from CNSL the purity of the product was not supported by using modern chromatographic or spectral data and not suitable for large scale isolation and not much attention was given for the isolation of cardol and cardanol. [7-8-9]

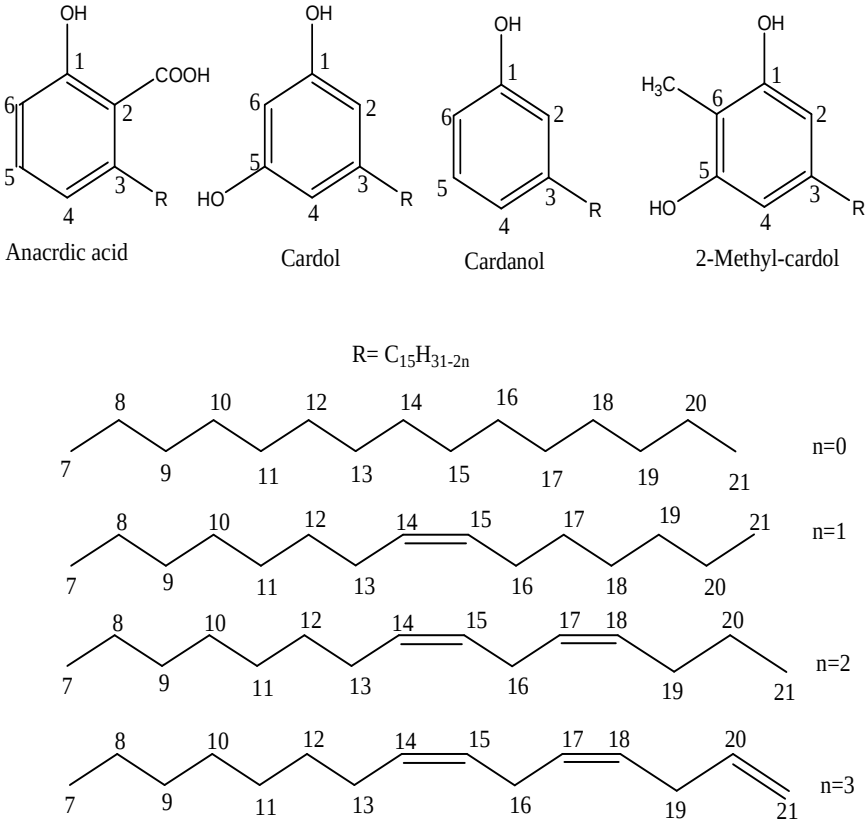


Figure 1. Structure of main components of CNSL [5]

We report a novel method for isolation of anacardic acid from CNSL to obtain a stable salt with calcium and separation of cardanol and cardol. They were all characterized using quantitative analysis by HPLC and comparison with standard samples. [10] CNSL and its derivatives have been reported to be useful in innumerable applications in polymer-based industries like friction linings, paints, primers, and varnishes, [11] laminating resins, and rubber compounding resins, surfactants, epoxy resins, wood preservatives and polyurethane-based polymers. [5] Cardanol is a phenolic compound with a C_{15} aliphatic chain in the meta position, obtained from cashew nut

shell liquid, that find many applications in the form of phenol formaldehyde resins in vanishes, paints, and brakes linings. Derivatives of cardanol find applications in form of dye stuffs, plasticizers, and ion-exchange resin. Chlorinated products of cardanol were found to have pesticidal action. Sulfonated derivatives of cardanol, tetra hydro cardanol, and their phenolic ethers are used as surface-active agents. [12]

MATERIALS AND METHODS

Cashew nut shell was obtained from Gujarat Cashew industrial (Kutch). The soxhlet apparatus was used for the extraction of CNSL from CNS. This experiment can be set up required of round bottom flask, bubble type condenser, heating mantle, and simple distillation unit for solvents recovery from CNSL. Mixture of solvents and water recovery using of dean-stark assembly. All polar and non-polar solvents were obtained from Merck (India), and Thin layer chromatography was performed on absence of acid coated with silica gel GF254, using of hexane and ethyl acetate, as the solvents system and spots were visualized under UV radiation. All the components characterized using quantitative analysis by HPLC in COE (vapi,India).

Extraction from cashew nut shell liquid

The extraction of CNSL from CNS by using soxhlet extractor and used as polar and non-polar solvents. Five hundred milliliters (500 ml) of solvents was charged into the round bottom flask of soxhlet apparatus. 50 g of crushed cashew nut shell was charged in to the thimble and fitted into the soxhlet extractor. The solvent in the set-up was heated to its boiling point and the vapour produced was subsequently condensed by water flowing in and out of the extraction set-up. This process of heating and cooling continued until a sufficient quantity of CNSL was obtained. At the end of the extraction, the thimble was removed while the remaining solvent in the extractor was recharged into the round bottom flask for a repeat of the process. Finally, the set-up was then re-assembled and simple distillation unit using of solvent recovery from the oil.

Figure 2. Soxhlet extraction

Isolation of anacardic acid from CNSL

Extracted CNSL (50 g) was dissolved in acetone (300 ml), and calcium hydroxide (30 g) was added in portions under stirring. After completed the calcium hydroxide, the temperature of the reaction mixture was raised to 50^{o}C and stirring was continued for 3.5 h and cheak the TLC for

the absence of anacardic acid. After completion of the reaction, the precipitated calcium anacardate was filtered and washed with acetone (160 ml), and dried at 2 h. The filtrate was preserved for subsequent isolation of cardol and cardanol. Calcium anacardate (50 g) treated with distilled water (200 ml) and 11M HCL (40 ml) was added and constant stirred for ½ h. The resultant solution was extracted with petroleum ether (2 x 150 ml). The combined organic layer was washed with distilled water (2 x 100 ml), dried over anhydrous sodium sulfate, and to get 26 g anacardic acid obtained.

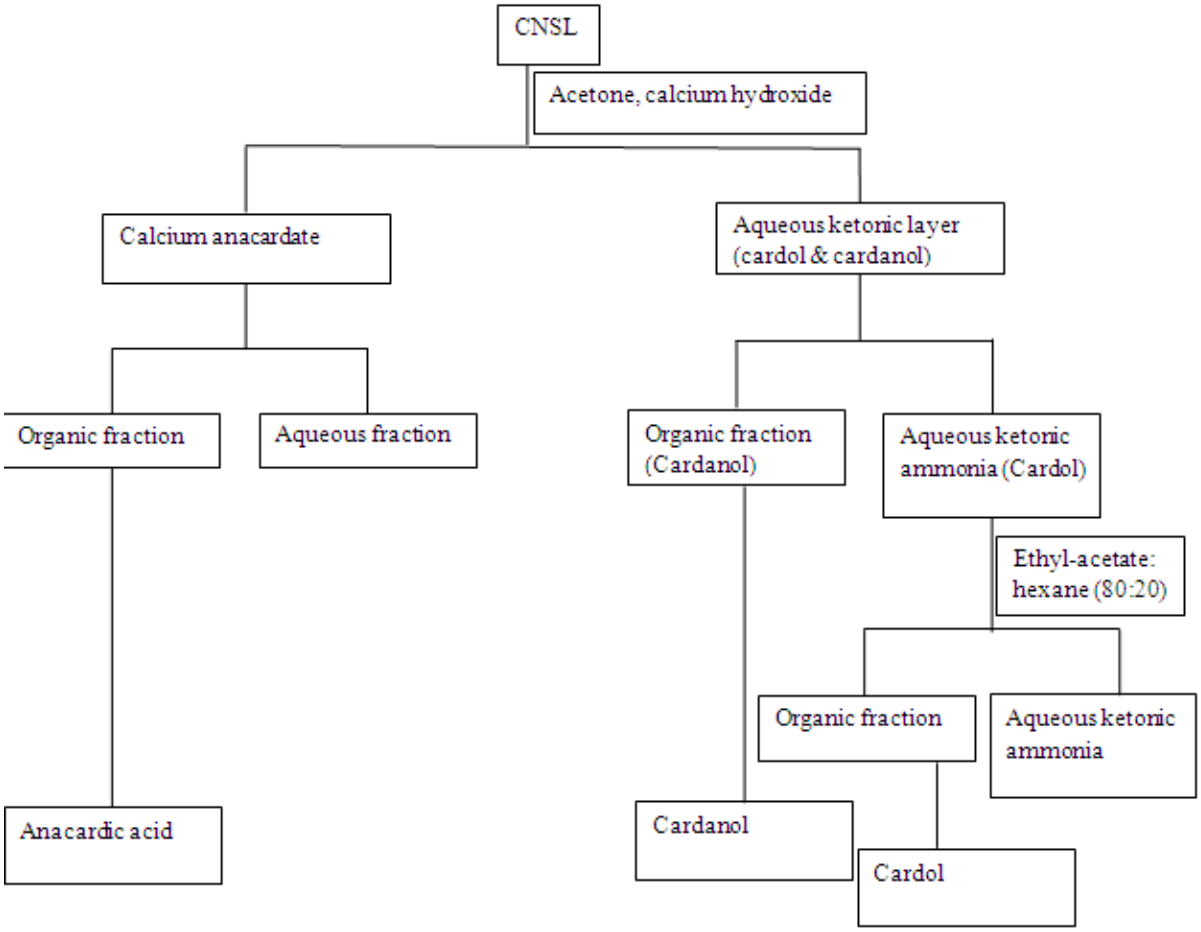


Figure 3. Flow chart for separation of anacardic acid, Cardanol and Cardol from the CNSL

Separation of Cardol and Cardanol

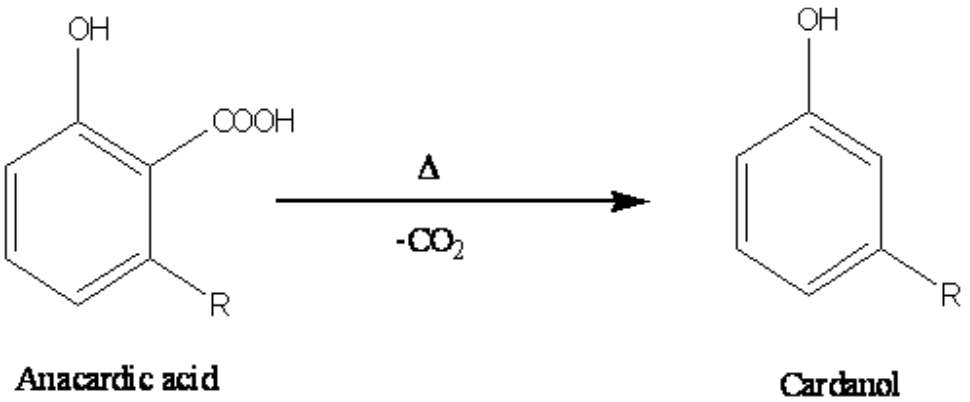
The ketonic solution obtained after filtration of the Calcium anacardate. Liquor ammonia (80 ml) was added and stirred for 15 min. This solution was extracted with hexane/ethyl acetate (98:2) (3 x 100 ml). The combined organic layer was washed with NaOH solution (2.5%, 200 ml) followed by 5% HCl solution (100 ml) and distilled water (100 ml). The organic layer was dried over anhydrous sodium sulfate and concentrated to get pure cardanol (7 g). Aqueous ammonia solution was extracted with ethyl acetate/ hexane (80:20) (100 ml). The organic layer was washed with 5% HCl (50 ml) followed by distilled water (50 ml), dried over anhydrous sodium

sulfate, and concentrated to yield pure cardol (14 g). The identity of cardanol and cardol was confirmed by HPLC and comparison with standard samples. [13]

Decarboxylation of CNSL

The extracted CNSL (100 g) was mixed with toluene (150 ml) in a round bottom flask and refluxed for 3 h by using dean-stark apparatus and check the TLC for the absence of anacardic acid. Then the decarboxylated CNSL (50 g) and 200 ml methanol were placed in a 500 ml round bottom flask. Then 20 ml of 40% formaldehyde solution and 3.0 ml diethylenetriamine were added in this solution. This mixture was heated until boiling under reflux for 2 h. After the solution was allowed to reach room temperature, a phase separation occurred, showing a slightly reddish upper solution, and a dark brown solidified lower phase. The upper phase was subsequently decanted, and treated with distilled water (40 ml) followed by petroleum ether. The petroleum ether layer was evaporated to dryness, yielding a reddish residue of cardanol (26 g). [14-15]

Figure 4. Structure of anacardic acid to conversion to cardanol



RESULTS AND DISCUSSION

Physiochemical parameters of compounds are presented in Table 1. All compounds were colored. They were soluble in polar and non-polar solvents but acid compound soluble in water.

Physico-chemical characteristic of cashew nut shell liquid and yield of extraction product (CNSL)

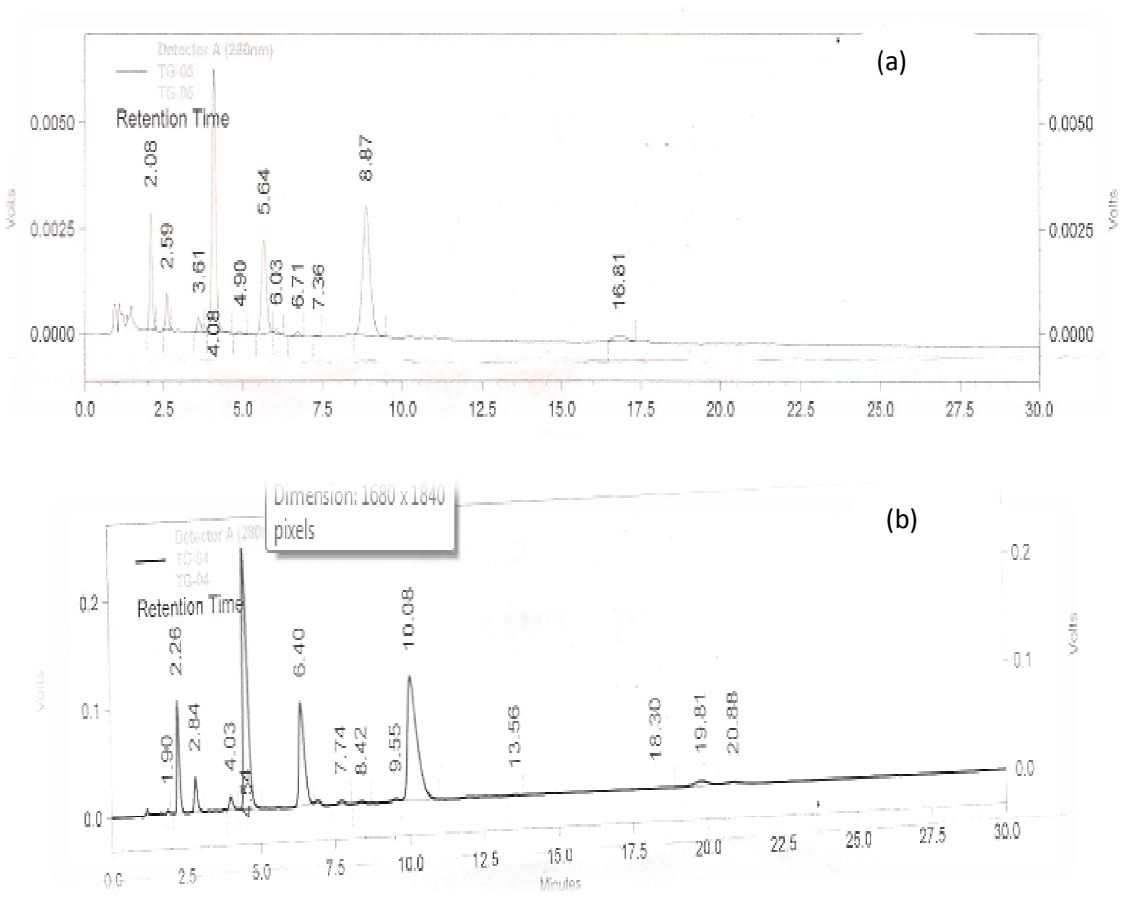
The different types of polar and non- polar solvents were used in solvent extraction method to extracted CNSL from CNS. The comparative studies were carried out on the properties of CNSL obtained using the different solvents mentioned above. By comparing all the above determined properties of CNSL using different solvents, ketonic solvent was more efficiency than other solvents. The results of determining the characteristic properties of the CNSL are given in Table 1. Table 1 gives the pH result (4.9) of the CNSL and is indicted the presence of anacardic acid. From the available information in the literature, the specific gravity of CNSL is 1.07 g/cm^3, [16] whereas the specific gravity of the present work is 0.91 g/cm^3. The slight variation in the specific gravity may be attributed to the extraction technique cum operating conditions employed during the experiment. By using of methanol, solvent extraction of CNSL from CNS, the yield of product was low, so, not measurements of physical parameter.

Table 1. Physico-chemicals Characteristic of CNSL extracted at 100-110°C and 1 atm Pressure

Parameters	S-CNSL	CNSL extracted 80-100°C from CNS from Solvents			
		Acetone	Hexane	Toluene	Methanol
pH	4.9	4.6	5.5	4.6	5.0
Viscosity (poise)	58.9	47	46.4	46	-----
Specific gravity (g/cm3)	0.98	0.9155	0.9118	0.9145	-----
Refractive index	1.48	1.4645	1.4625	1.4620	-----
Quantity (gm)	------	16.54	15.26	11.60	2.49
Color	Dark Brown				
	Theoretical yield in CNSL (g)	**Experimental yield in CNSL (g)**		**% Yield of each components**	
Anacardic acid	32.5	26		80	
Cardanol	8	7		71	
Cardol	16	14		87.5	
Decarboxylated Cardanol	32.5	19		59.46	

High-performance Liquid Chromatography (HPLC)

High-performance liquid chromatography analysis was done on a modular HPLC instrument comprising two 510 reciprocating pumps, a 481 variable-wavelength detector, and a Rheodyne injector, all from Waters Corporation (Milford, MA). A Supelcosil LC-18 (150 mm x 4.6 mm i.d., 5 µm particle size) column was used, and the mobile phase was acetonitrile/water/ac etic acid (80:20:1) at 1.80 mL/min; absorbance was monitored at 280 nm. Each analysis was carried out by dissolving 25 mg of sample in 5 ml of acetonitrile, passing that through a C18 Sep- Pak cartridge (Waters Associates, Milford, MA), and injecting a 20-µL sample. [15]



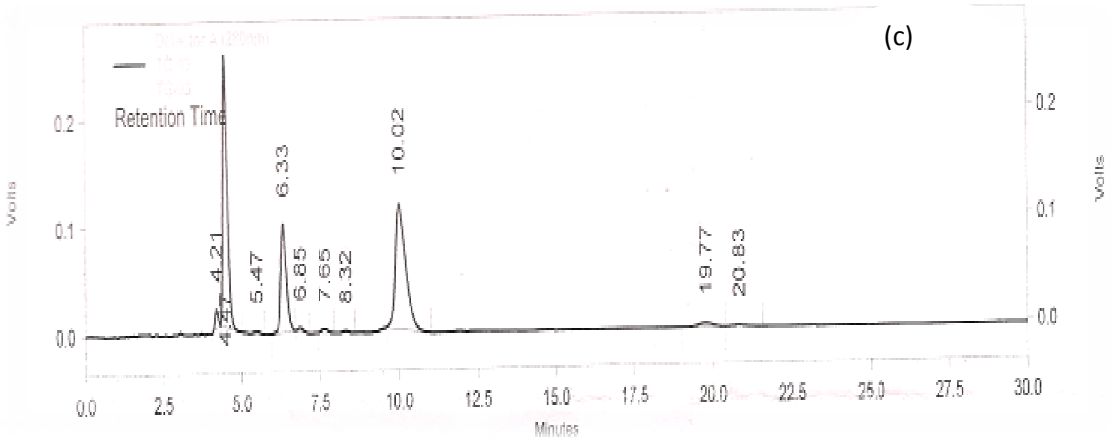


Figure 5. HPLC profiles of (a) Anacardic acid (b) Conventional cardanol (c) De- carboxylated cardanol, using Supelcosil, LC-18 and acetonitrile/water/acetic acid (80:20:1) as mobile phase at 280 nm.

Purity of all compounds was confirmed by HPLC. Isolated compounds were confirmed by compared with reported HPLC.[15] The results reported above are averages of four experiments performed at 100 g, 200 g, 500 g, and 1 kg scale. The yield and purity are consistent in all batches. The procedure described above and summarized in is superior to existing methods, as it accounts for the complete isolation of the major phenolic constituents in quantitative yield.

In the initial step, which anacardic acid was precipitated from CNSL as calcium anacardate. It was also observed that during precipitation of the calcium anacardate, excess if calcium hydroxide had to be added in order to get the product as a free flowing power. The optimum reaction temperature for the salt formation of calcium anacardate was found to be 50^{o}C. At this temperature the salt formation was completed in 3 h. and recovery of anacardic acid from CNSL was good (60-65%).

The mother liquor obtained after the filtration of calcium anacardate contained primarily the other two major phenolic constituents cardol and cardanol of CNSL. It was stirred with liquor ammonia and then extracted with a mixture of hexane/ethyl acetate (98:2). Cardol remained in the ammonical solution while the cardanol was extracted into the organic layer. Subsequently, extraction of the ammonical solution with a mixture of ethyl acetate/hexane (80:20) yielded cardol in high purity. Use of the hexanes-ethyl acetate mixture instead of ethyl acetate gave proper partitioning of aqueous and organic layers. Purity of all compounds was confirmed by HPLC.

Yield of Cardanol was increase by using decarboxylated of CNSL at above 100^{o}C for 3 h refluxed by using dean-stark assembly. The decarboxylated product cardanol was characterized by analysis of HPLC. This decarboxylated product in added of formaldehyde solution and diethylenetriamine used as a catalyst was mixed in methanol. After 30 min phase separation occur, the upper phase treated with water followed by extraction petroleum ether, then purify cardanol 70% yield obtained.

CONCLUSION

The extraction of CNSL obtained from CNS by using soxhlet apparatus. Different types of polar and non-polar solvents were used in the extraction of CNSL from CNS. The comparison of % yield obtained after extraction using different solvents was carried out. Among all of the solvents, acetone gives maximum amount of CNSL. Higher % yield of anacardic acid obtained from Isolation method and higher % yield of cardanol obtained from decarboxylated method. Extracted, isolated and decarboxylated cardanol can be use as one of the cost effective and renewable raw material for polyurethane synthesis.

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