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Process for Isolation of Cardanol from Technical Cashew (*Anacardium occidentale* L.) Nut Shell Liquid

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Commercially available technical cashew (*Anacardium occidentale* L.) nut shell liquid (CNSL) contains mainly cardanol (decarboxylated anacardic acid) and cardol. Cardanol, the monophenolic component of technical CNSL, is widely used as a synthon for the preparation of a number of polymers and agricultural products. This paper describes the separation of cardanol from toxic cardol. Technical CNSL was dissolved in a mixture of methanol and ammonium hydroxide (8:5) and extracted with hexane to obtain cardanol. The resultant methanolic ammonia layer was extracted with a mixture of ethyl acetate and hexane to yield cardol. This is the first industrially feasible process based on solvent extractions for the isolation of cardanol from technical CNSL.

KEYWORDS: Anacardic acid; cardol; cardanol; cashew nut shell liquid; *Anacardium occidentale* L.

INTRODUCTION

Cashew (*Anacardium occidentale* L.) nut shell liquid (CNSL) is a unique natural source for unsaturated long-chain phenols (*1*). Obtained as a byproduct of the cashew industry, this renewable material has wide applications in the form of brake linings, surface coatings, paints, and varnishes. The main applications of CNSL are in the polymer industry (*2*). Compared with conventional phenolic resins, CNSL polymer has improved flexibility (due to the internal plasticization effect of the long chain) and thus betters processability. The side chain imparts a hydrophobic nature to the polymer, making it water repellant and resistant to weathering (*3*). The low "fade" characterization on friction, a significant property of CNSL polymer, makes it an essential additive for most of organic brake-lining formulations (*4*). CNSL-based resins possess outstanding resistance to the softening action of mineral oils and high resistance to acids and alkalis (*5*). CNSL polymers also have useful characteristics such as heat and electrical resistance, antimicrobial properties, and termite and insect resistance (*6*).

On the basis of the mode of extraction from cashew nut shell, CNSL is classified into two types, solvent-extracted CNSL and technical CNSL. A typical solvent-extracted CNSL contains anacardic acid (60−65%) (**Figure 1**, **1**−**4**), cardol (15−20%) (**Figure 1**, **5**−**8**), cardanol (10%) (**Figure 1**, **9**−**12**), and traces of methylcardol. Technical CNSL is obtained by roasting shells and contains mainly cardanol (60−65%), cardol (15−20%), polymeric material (10%), and traces of methylcardol. Among the CNSL constituents, anacardic acid possesses antimicrobial, antiacne, and many other medicinal properties (*7*, *8*). Cardol, the dihydric component, accounts for CNSL's vesicant activity and toxicity (*9*). With its polymerizable side chain and phenolic group, cardanol has been widely studied for its polymeric properties (in the form of phenol−formaldehyde resins). Simple derivatives of cardanol were reported to possess industrially important properties. Chlorinated products of cardanol were found to have pesticidal action. Sulfonated derivatives of cardanol, tetrahydrocardanol, and their phenolic ethers are used as surface-active agents (SAA). Derivatives of cardanol find applications in the form of dyestuffs, plasticizers, and ion-exchange resin (*6*).

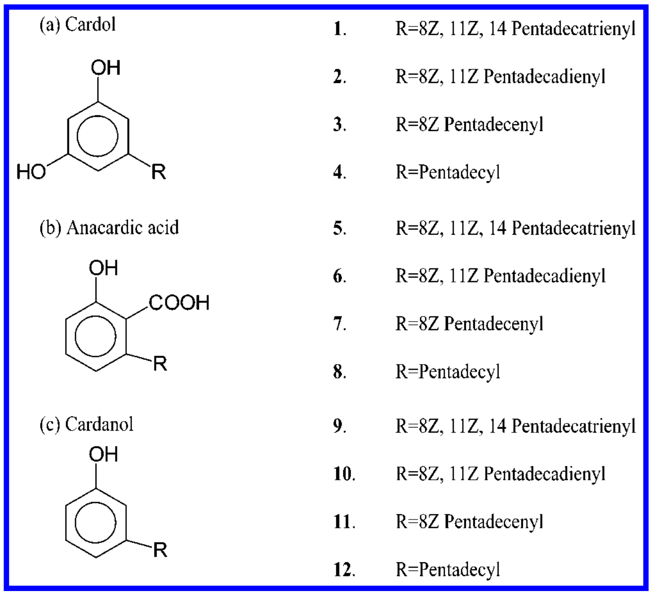

Figure 1. Structures of CNSL constituents.

Among the innumerable potential uses of CNSL, only a few have become commercially successful. CNSL could effectively

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compete with any phenol-based polymer and even other types of polymers. It has a major drawback in that it is a mixture of monomers; to achieve a high molecular weight polymer, purity of the monomer is of great significance. The polymerization products of CNSL are generally dark brown in color, and therefore the application of CNSL in the surface-coating industry has been limited. The dark color formed during the polymerization of CNSL was attributed to the dihydric component, cardol. It was also observed that the presence of cardol and methylcardol results in cross-linked polymers, affecting the uniformity of polymer. In view of the industrial applications of cardanol, there is a need for the development of an efficient, industrially feasible process to separate it from cardol.

Various methods of purifying technical CNSL are known. Pure cardanol, free from cardol, has been obtained by column chromatography, but this method is expensive, time-consuming, and not commercially viable. Tyman et al. (*10*) reported an efficient method to reduce the dihydric component in technical CNSL, based on formation of an amine−cardol adduct (amine should have basicity above that of diethylamine and should be nonvolatile) and distillation of cardanol under high vacuum. Although this method is efficient, it has a few drawbacks: (1) distilled cardanol contains ∼6% of cardol as an impurity; (2) the selection of base becomes difficult and expensive due to basicity and volatility restrictions (as mentioned above); (3) high-vacuum distillation could lead to amine contamination in cardanol. Recently we reported a method (*11*) for the separation of cardol and cardanol by solvent extraction. Although this is the most efficient method reported to date, it is applicable only for solvent-extracted CNSL and not for technical CNSL. As a part of our ongoing project, a novel method for the isolation of cardanol from technical CNSL has been developed.

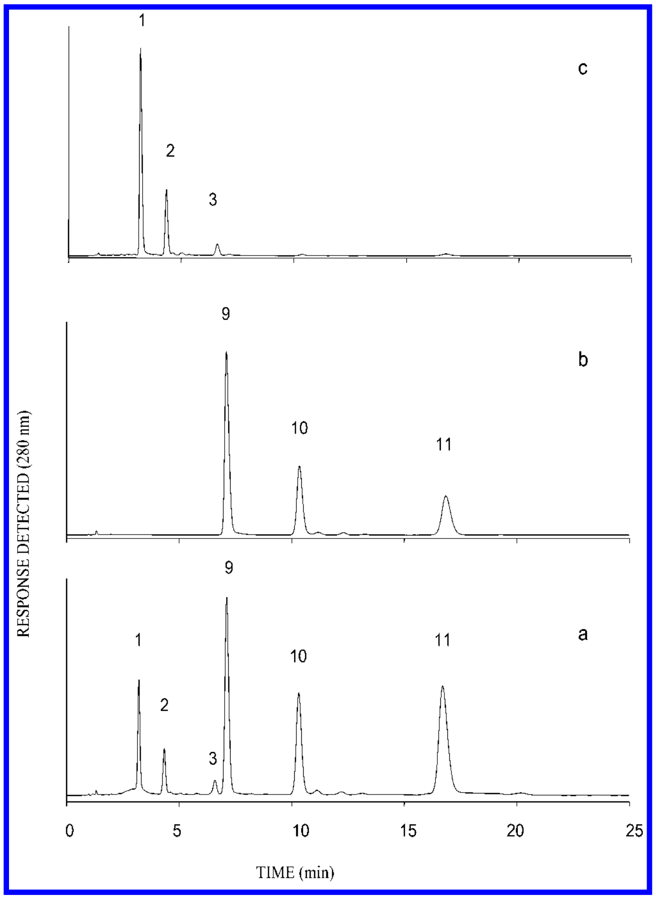

Figure 2. (a) Technical CNSL; (b) cardanol isolated from technical CNSL; (c) cardol isolated from technical CNSL.

MATERIALS AND METHODS

Technical CNSL. Technical CNSL was obtained from the cashew nut processor, Mangalore. It contained 22% cardol and 67% cardanol as quantitated by HPLC.

Chemicals and Solvents. All organic solvents, chemicals, and TLC plates (silica gel GF254) were obtained from Merck.

NMR. NMR (^{1}H and ^{13}C) spectra were taken on a Bruker DPX200 (40 MHz for ^{13}C and 200 MHz for ^{1}H) and FT-NMR spectra in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. In the case of ^{1}H NMR typically 500 scans were accumulated. All signals were referred to TMS to within ±0.01 ppm. Typically 1000−2000 scans were accumulated for the proton noise decoupled ^{13}C NMR spectrum. All of the signals were referenced to TMS to within ±0.1 ppm.

GC-MS. GC-MS analysis was carried out using a Hewlett-Packard GC 5890 and a Hewlett-Packard 5970 mass selective detector, on an HP-1 ultra-2 column. Sample (1 mg) was dissolved in 10 mL of dichloromethane, and 1 μL of this solution was injected into the GC-MS. The temperature was programmed from 50 to 250 °C at 10 °C/min and maintained at 250 °C for 30 min.

HPLC. HPLC analysis was done on a modular HPLC instrument comprising two 510 reciprocating pumps, a 481 variable-wavelength detector, and a Rheodyne injector (20 μL loop), all from Waters Corp. A Supelcosil LC-18 (4 mm × 150 mm) column was used. The mobile phase was acetonitrile/water/acetic acid (80:20:1) at a flow rate of 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 and filtering through a C_{18} Sep-Pak cartridge (Water Associates, Milford, MA).

Separation of Cardanol from Cardol. Technical CNSL (100 g) was dissolved in methanol (320 mL), and ammonium hydroxide (25%, 200 mL) was added and stirred for 15 min. This solution was then extracted with hexane (4 × 200 mL). The organic layer was washed with 5% HCl (100 mL) followed by distilled water (100 mL). Activated charcoal (10 g) was added to the organic layer, stirred for 10 min, and filtered through Celite (15 g). The filtrate was dried over anhydrous sodium sulfate and concentrated to get pure cardanol (65 g). The methanolic ammonia solution was extracted with ethyl acetate/hexane (4:1) (2 × 200 mL). The resulting organic layer was washed with 5% HCl (100 mL) followed by distilled water (100 mL), dried over anhydrous sodium sulfate, and concentrated to yield pure cardol (20 g). The purity of cardanol and cardol was confirmed by HPLC (**Figure 2**) and comparison with standard samples as previously described (*12*).

Hydrogenation of Cardanol. Cardanol (30 g) was dissolved in methanol (120 mL). Five percent Pd/C (palladium adsorbed on carbon) (0.75 g) was added slowly, and this solution was transferred to a 250 mL hydrogenation flask. Hydrogenation was carried out with 2.5 kg/cm^2 pressure for 2 h, and the solution was filtered through a Celite bed to obtain catalyst-free solution. This was evaporated under vacuum to get crude saturated cardanol, which was recrystallized from petroleum ether (40−60 °C). The resulting solid was found to have a melting point of 52−53 °C (lit. mp 51−52 °C; *13*).

RESULTS AND DISCUSSION

This process is an extension of the work reported for solvent-extracted CNSL by our group (*11*). In this method, technical CNSL was dissolved in a mixture of methanol and ammonium hydroxide. It was observed that the ratio of methanol and ammonium hydroxide was crucial. A series of experiments were done with different ratios of methanol and ammonium hydroxide, and the optimum was found to be 8:5. In the case of our earlier reported method (*11*) for solvent-extracted CNSL, the methanol and ammonium hydroxide ratio was 4:5. This solution was extracted with hexane to obtain cardanol in the pure form. In the case of solvent-extracted CNSL (*11*), ethyl acetate (2−5%) in hexane was essential to isolate pure cardanol. This is due to the presence of a higher percentage of cardol than

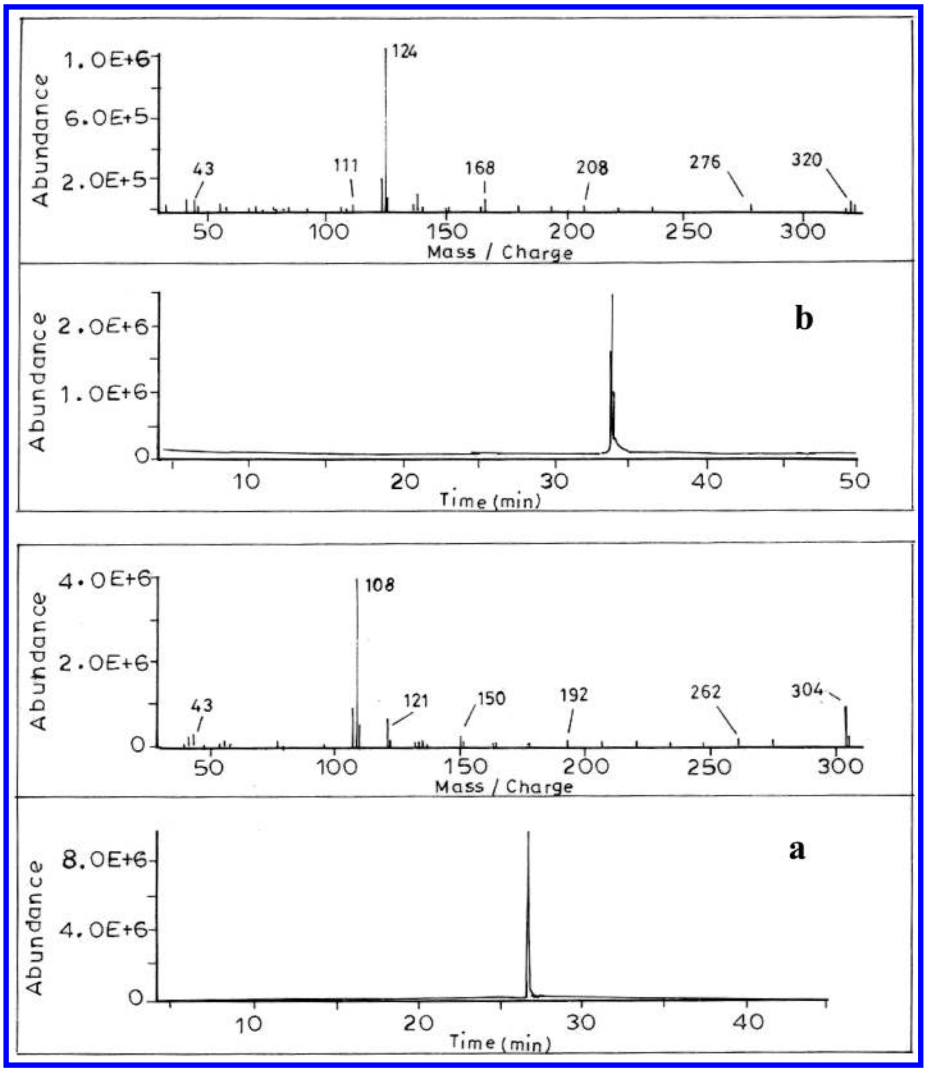

Figure 3. GC-MS profile of (a) saturated cardanol and (b) saturated cardol.

cardanol. Because of this, traces of cardol impurity present in the hexane layer were removed by treatment with 2.5% NaOH. In the case of technical CNSL, due to the presence of a higher percentage of cardanol than cardol, extraction with hexane is sufficient to obtain cardanol (**Figure 2b**). The cardanol obtained by this process requires a charcoal treatment to remove the colored impurity. Subsequently, the methanolic ammonia layer was extracted with a mixture of ethyl acetate and hexane (8:2) to obtain cardol (**Figure 2c**). Here, the role of hexane is to give an efficient separation of the methanolic ammonia layer and organic layer. For industrial convenience, the percentage of hexane could be increased for better visualization of the separation between layers. Upon concentration of the organic layer, cardol was obtained, and its purity and identity were confirmed by HPLC. For further confirmation, cardanol was hydrogenated and an NMR spectrum was obtained that was consistent with reported NMR results (*14*). GC-MS analysis of saturated cardol and cardanol also confirmed the purity (**Figure 3**). The results reported above are an average of four experiments performed at 100 g, 200 g, 500 g, and 1 kg scales. The yield and purity are consistent in all experiments (see **Table 1**).

Hence we report an efficient method for the separation of mono- and diphenolic components from technical CNSL. We feel this industrially feasible process widens the scope for the study of cardanol-based polymers as a substitute for phenol−formaldehyde resins. This paper also aids studies directed toward the development of cardanol as an alternate fuel additive for petroleum products, due to its rich carbon content.

Table 1. Results of Separation of Cardol and Cardanol from Technical CNSL at Different Batch Scales

sample	CNSL (g)	cardanol (g)	cardol (g)	% recovery (cardanol + cardol)	% efficiency
1	100	65	20	85	95.5
2	200	126	40	83	93.3
3	500	320	105	85	95.5
4	1000	640	196	83.6	94

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