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Synthesis of Cardanol-Based Acetaldehyde Novolac Resin from Cashew Nut Shell Liquid (CNSL)

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Abstract

Polymers are currently in the limelight. Phenolic resin is one of the polymer products obtained from the polymerization process, either from natural or synthetic sources. One of the natural compounds that can be applied to polymers is cardanol. This study aimed to synthesize cardanol-based acetaldehyde novolac resin from Cashew Nut Shell Liquid (CNSL). Isolation of cardanol from CNSL was done by liquid-liquid extraction method with acetone and purified by gravity column chromatography in a mixture of n-hexane and ethyl acetate in a ratio of 9:1. HPLC analysis showed that cardanol compounds had aliphatic chains with different levels of saturation and the yield was 18.48%. The cardanol-acetaldehyde novolac resin was synthesized through a condensation polymerization reaction with a cardanol-acetaldehyde mole ratio (1:0.5), using HCl as a catalyst. FTIR and ^{1}H-NMR analysis were employed to identify the novolac resin structure. The product was a brownish-orange solid with a yield of 12.80 mg (40%) and followed *ortho-ortho* substitution. Cardanol is one of the natural phenol sources that might be utilized to manufacture novolac resins.

1. Introduction

Cardanol is a promising natural resource since it is obtained from a by-product of the cashew nut industry known as cashew nut shell liquid (CNSL). Utilization of CNSL as a source of cardanol is secure and more environmentally friendly [1]. This compound can be employed as a source of natural phenol in manufacturing phenol-formaldehyde resins because it contains a C15 unsaturated hydrocarbon chain with one to three meta-position double bonds in the phenol group [2, 3]. Cardanol has a series of unsaturated hydroxy groups, aromatic rings, and hydrophobic alkyl groups, which make it a potential renewable polymer material [4]. Cardanol has been extensively researched as a modifier for phenolic resins due to its simple polymerization and structural similarity to phenol. Cardanol can react with formaldehyde under various conditions to produce resole or novolac resins, depending on the catalyst used [5]. Cardanol structure is shown in Figure 1.

The production of novolac resin is done with a certain mole ratio using an acid catalyst such as adipic acid, oxalic acid, succinic acid, sulfuric acid, hydrochloric acid, or tricarboxylic acid, for instance, citric acid [6, 7]. Tiwari *et al.* [8] have synthesized novolac resin by reacting cardanol and formaldehyde with a mole ratio of 1:0.8 using citric acid as a catalyst. Sangeetha [6] synthesized novolac resin using cardanol-formaldehyde (1:0.9) with a malonic acid catalyst.

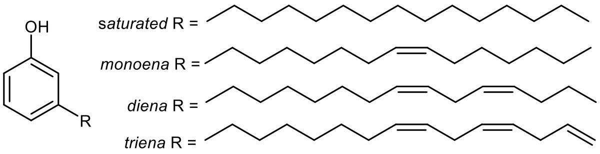

Figure 1. The chemical structure of cardanol [9]

Most novolac resins are derived from cardanol and formaldehyde, although the acquired products are unsatisfactory. Synthesis of novolac resin using cardanol-formaldehyde still has some drawbacks, such as weak chemical stability, low flexibility, and poor adhesion; therefore, novolac resin must be modified to improve its chemical stability, flexibility, and adhesion [10, 11]. A modification was developed by reacting cardanol and acetaldehyde to obtain a novolac resin with improved characteristics. Acetaldehyde is abundant and has lower toxicity than formaldehyde [12, 13]. In addition, the literature related to the study of cardanol-acetaldehyde resins has not been widely reported.

2. Methodology

2.1. Materials and instruments

Materials. Technical CNSL (Cashew Nut Shell Liquid) (PT. Guna Mete Mojosongo), acetaldehyde (40%, Merck), calcium hydroxide ($Ca(OH)_2$) (Merck), ammonia solution (Merck), sodium hydroxide (NaOH) (2,5 %, Merck), hydrochloric acid (HCl) (5%, Merck), anhydrous Na_2SO_4 (Merck), methanol (analytical grade, Merck), technical acetone, technical ethyl acetate, technical n-hexane, distilled water, filter paper, aluminum plate coated with silica gel 60 PF254 0.25 mm, cerium(IV) sulfate tetrahydrate (Merck), and silica gel 60 (0.063-0.200 mm) (Merck).

Tools. Analytical balance (Ohaus), hot plate (Thermolyne type 1000 Stirrer plate), Fourier Transform InfraRed (FTIR) (Shimadzu IR Prestige-21), Nuclear Magnetic Resonance (NMR) (Agilent) recorded in $CDCl_3$ operating at 500 MHz and High-Performance Liquid Chromatography (HPLC) Alliance e2695 UV detector. CNSL and isolates were identified using HPLC with a reversed-phase column (7 µm, 150 mm) at about 25 minutes with an eluent flow rate of 1.8 mL/minute with a UV detector. The eluent used was acetonitrile: water: acetic acid (80:19:1), according to research belonging to Phani Kumar *et al.* [14] and Gandhi *et al.* [15].

2.2. Experiments

2.2.1. Isolation cardanol from CNSL

The cardanol isolation procedure was based on the study of Gandhi *et al.* [15] with slight modifications. CNSL (10 g) was dissolved in 60 mL acetone, followed by adding 6 g $Ca(OH)_2$, and then stirred using a magnetic stirrer. After mixing the solution with $Ca(OH)_2$, the reaction temperature was raised to 50℃ for 3.5 hours. The mixture was then filtered to obtain a filtrate containing cardanol and calcium anacardate as a precipitate.

The filtrate was added with 16 mL of ammonia solution and stirred with a magnetic stirrer for 15 minutes. The mixture was then extracted with n-hexane: ethyl acetate (98:2) and repeated twice. The organic layer was then washed with 40 mL of 2.5% NaOH solution, followed by 20 mL of 5% HCl solution and 20 mL of distilled water. The organic layer on top was added anhydrous Na_2SO_4 and concentrated to obtain isolate [15]. The extracted isolates were analyzed by TLC employing an n-hexane: ethyl acetate (9:1) eluent. Based on the TLC profile, the isolate was then purified using gravity column chromatography with 60 silica gel as the stationary phase (0.063-0.200 mm) and 2×100 mL of n-hexane: ethyl acetate (9:1) as eluent. Column chromatography results were grouped based on the TLC profile. The purity of the isolated cardanol compounds was known from TLC analysis using three different types of eluents: n-hexane: ethyl acetate (9:1), n-hexane: chloroform (1:1), and n- hexane: chloroform: ethyl acetate (7:3:1). Cardanol compounds were then further analyzed using FTIR and HPLC.

2.2.2. Synthesis of cardanol-acetaldehyde resin

The cardanol-acetaldehyde resin was prepared with the mole ratio of cardanol: acetaldehyde (1:0.5). The hydrochloric acid catalyst (5%) (1% by weight of cardanol) was dissolved in 5 mL methanol. Half of the solution was added to acetaldehyde and half to cardanol. Cardanol and catalyst solution were mixed in a three-neck flask and stirred using a magnetic stirrer. The flask was heated in an oil bath equipped with a Leibig thermometer and condenser. The system was heated to 65℃ then acetaldehyde solution (0.5 mol) and catalyst were gradually added. The system temperature was raised to 140℃, and the reaction lasted 6 hours [7].

Purification of the synthesized resin was performed using the column chromatography method using silica gel 60 (0.063-0.200 mm) eluted with a mixture of eluent n-hexane: chloroform (18:1) [16]. The fractions obtained were analyzed using TLC with the mobile phase of n- hexane: chloroform (18:1) and viewed with a UV lamp at λ 254 nm and then sprayed with $Ce(SO_2)_2$ staining reagent. The purified compounds were then analyzed using an FTIR and ^{1}H-NMR spectrophotometer.

3. Results and Discussion

3.1. Cardanol isolation

Cashew Nut Shell Liquid (CNSL) contains the main compounds: cardanol, cardol, anacardic acid, and 2- methylcardol. Cardanol is the primary compound of CNSL. Cardanol was successfully isolated from CNSL using the extraction method and purified by column chromatography method. The fraction from column chromatography was tested using TLC to determine its profile. The TLC profile is shown in Figure 3.

Figure 3 reveals that the TLC profile for fractions 2 to 8 shows a single spot. In addition, a purity test was conducted using three different eluent systems to determine if the spot was a pure isolate. These results demonstrate that the isolated chemical is pure cardanol with 18.48% of yields (Figure 4).

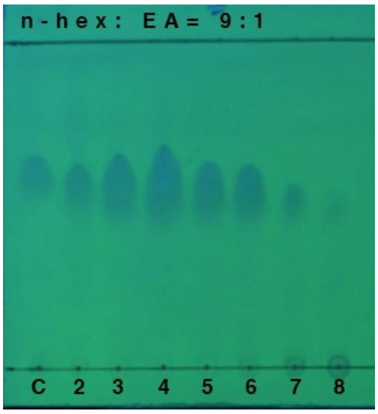

Figure 3. TLC profile of column chromatography results with n-hexane eluent: ethyl acetate (9:1)

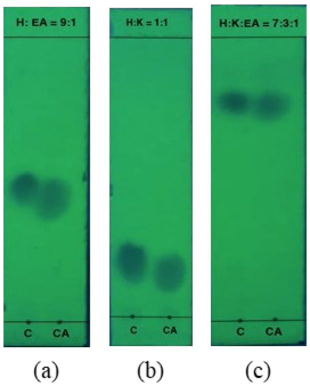

Figure 4. TLC profile of cardanol (a) n-hexane: ethyl acetate (9:1), (b) n-hexane: chloroform (1:1), and (c) n- hexane: chloroform: ethyl acetate (7:3:1)

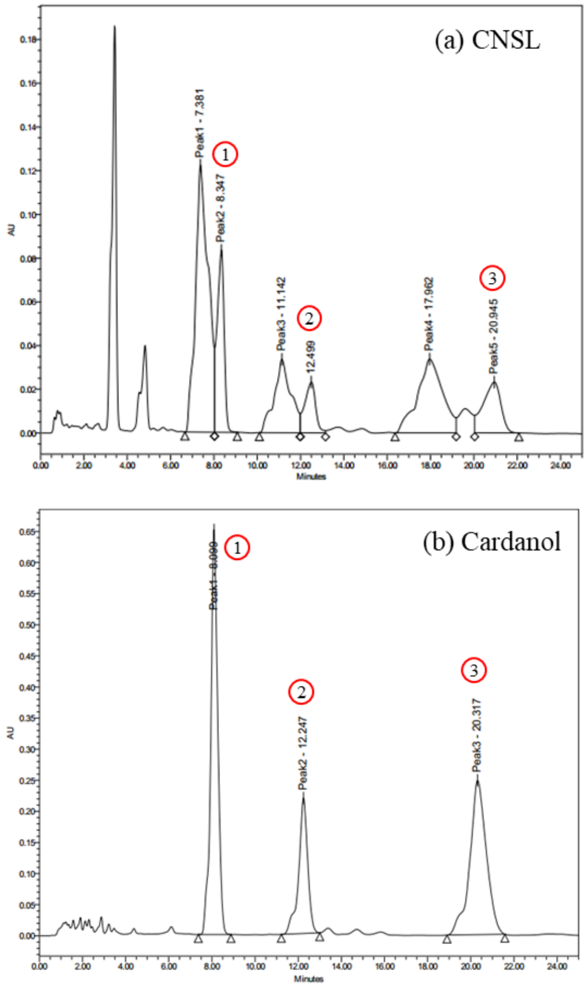

Figure 5. Chromatogram profiles of (a) CNSL and (b) Cardanol

Isolated cardanol and CNSL were identified using HPLC and FTIR. There are numerous peaks on the chromatogram of the CNSL, indicating that it still includes various components. According to the HPLC analysis results (Figure 5), cardanol has three chromatogram peaks with different retention times, showing that cardanol has different degrees of saturation in the aliphatic chain. The peak chromatogram 1 showed a retention time of 8.009 minutes (42.76%), while the peaks of chromatograms 2 and 3 had a retention time of 12.247 minutes (18.59%) and 20.317 minutes (38.65%), respectively. This is reinforced by research conducted by Phani Kumar *et al.* [14], which showed chromatogram peaks 1, 2, and 3 each cardanol with side chains of 8,11,14-pentadecatrienyl (triene), 8,11-pentadecadienyl (diene), 8-pentadecyl (monoene). The structure of these aliphatic chains can be seen in Figure 1.

Spectroscopic identification using FTIR at the absorption range of 250–4000 cm⁻¹ of CNSL and cardanol is shown in Figure 6. Similar wavenumbers may be seen in the FTIR spectra of CNSL and cardanol, except for the absence of the C=O group in cardanol at 1670–1640 cm⁻¹. The C=O group originates from anacardic acid, a carboxylic acid [17]. The absence of the carbonyl group suggests that cardanol was successfully isolated from CNSL. The absorption peaks of the hydroxyl groups (-OH) in CNSL and cardanol appear at 3172 cm⁻¹ and 3327 cm⁻¹, respectively. According to FTIR spectrum analysis, it can be seen that the OH group of cardanol has a sharper absorption band than CNSL. The OH group in CNSL is derived from carboxylic acid groups (anacardic acids) and phenolic compounds (cardanol, cardol, and methyl cardol). The influence of the OH group from anacardic acid causes the absorption band to broaden.

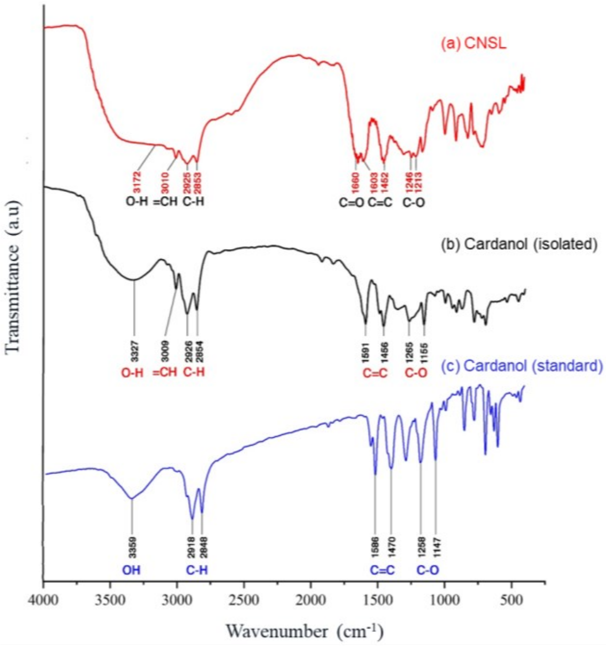

Figure 6. FTIR spectra (a) CNSL, (b) Cardanol isolated, and (c) Cardanol standard

The peaks of aromatic =CH and aliphatic C-H of CNSL are detected at 3010 cm⁻¹ and 2925-2853 cm⁻¹, while of cardanol at 3009 cm⁻¹ and 2976-2854 cm⁻¹. The C=C bond is found in the aromatic ring and side chain of cardanol, making the absorption appear strong. The absorption peak at 1591 cm⁻¹ corresponds to the C=C bond in the aromatic ring, whereas the peak at 1456 cm⁻¹ indicates the C=C bond present in the side chain [12]. Meanwhile, the C=C group is seen in CNSL at 1603-1452 cm⁻¹. The appearance of peaks at 1213-1246 cm⁻¹ in CNSL and 1265-1155 cm⁻¹ in cardanol indicates the emergence of the C-O group from phenolic. Isolated and regular cardanol have wavenumbers that are not significantly different.

3.2. Cardanol-acetaldehyde novolac resin synthesis

The novolac resin was synthesized from cardanol and acetaldehyde compounds under an acidic environment using an HCl catalyst. The product obtained was a brown viscous liquid. The product was purified by column chromatography and analyzed by TLC, as shown in Figure 7. The TLC profile shows that a pure compound was obtained from novolac resin, a brownish-orange solid with 12.80 mg of yields (40%).

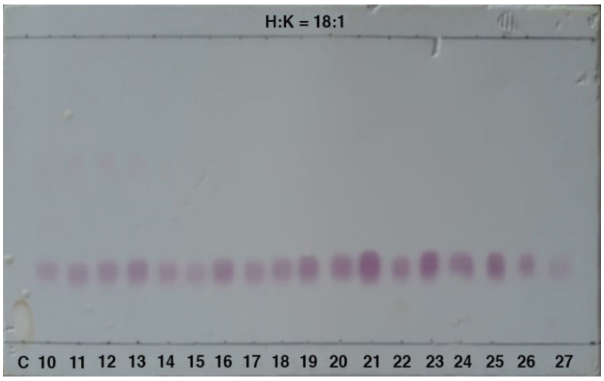

Figure 7. TLC profile of novolac resin as a result of column chromatography with n-hexane: chloroform (18:1) eluent

This resin is formed by a condensation polymerization reaction in which cardanol possesses reaction sites on aromatic rings and side chains with varying saturation levels, allowing it to be polymerized in several ways [17]. The polymerization reaction can be seen in Figure 8.

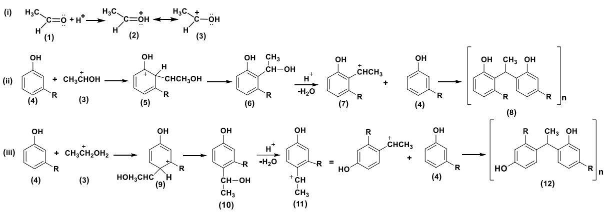

Figure 8. The reaction for the formation of cardanol-acetaldehyde resin substitution (ii) *ortho* and (iii) *para* [18]

The reaction between cardanol and acetaldehyde in the presence of an acid catalyst was performed through a stepwise polymerization reaction. In the first step (i), acetaldehyde (1) undergoes protonation under acidic conditions to form hydroxyethylene carbonium ion (3). This ion acts as a hydroxy alkylating agent and reacts with cardanol (4) via electrophilic aromatic substitution. Nucleophilic attack on electrophilic may occur from the *ortho* (ii) or *para* (iii) position because cardanol can experience resonance [19]. The formation of the reaction can be characterized by the formation of alkyl (ethylene) bridges and the release of simple molecules [20]. The ethylene bridge (C_2H_4) connects the aromatic nuclei in the *ortho-ortho* (8) and or *ortho-para* (12) positions by releasing water molecules (H_2O). This reaction was repeated until a polymer chain was formed.

3.3. FTIR identification of cardanol-acetaldehyde novolac resin

The FTIR spectra of cardanol-acetaldehyde novolac resin are shown in Figure 9. The substitution occurs at the *ortho* position at the 720 cm^{-1}, which forms an ethylene bridge and is confirmed by the presence of a CH_3 group at the 1370 cm^{-1} region. In addition, the aliphatic chain does not react with acetaldehyde. This is also evidenced by the appearance of peaks at 2925-2853 cm^{-1}, which correspond to C-H str absorption, and C=C absorption shown at a frequency of 1642-1502 cm^{-1}. The absorption band demonstrates the presence of the C-O group at 1132-1093 cm^{-1}. The absorption at 991 cm^{-1} indicates that substitution in the benzene core occurred. The FTIR analysis of the novolac resin also reveals an absorption at 720 cm^{-1}, which corresponds to a benzene core substitution at the *ortho* position. *Ortho* substitution in the benzene nucleus is also present at 720 cm^{-1}. The presence of a peak at a frequency of 3441 cm^{-1} is caused by hydroxy groups [6].

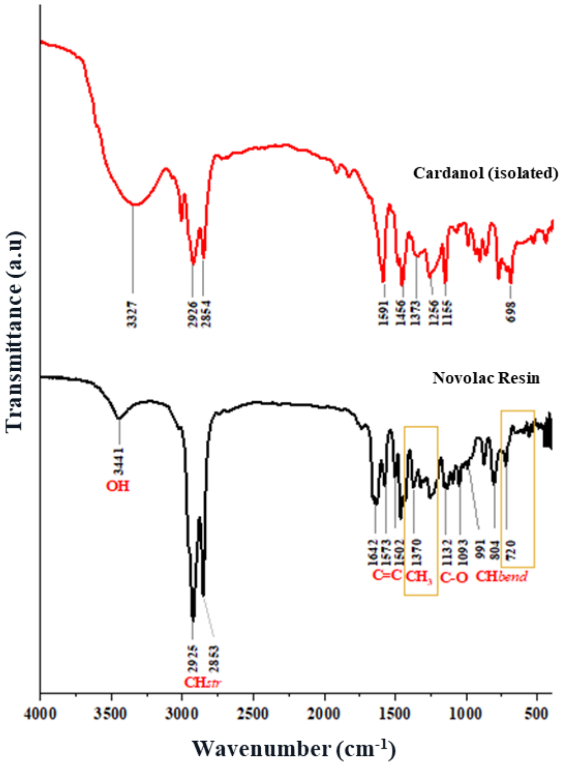

Figure 9. FTIR spectra of (a) Cardanol and (b) Novolac resin

3.4. Identification of ¹H-NMR novolac cardanol-acetaldehyde resin

Spectral data from ¹H-NMR analysis (500 MHz, $CDCl_3$) were identified to determine the proton signals in cardanol compounds and cardanol-acetaldehyde resins. Figure 10 discloses the comparative ¹H-NMR spectra of cardanol and novolac resin. The ¹H-NMR spectra of cardanol can be seen in Figure 10a, indicating the presence of an aromatic proton signal substituted with δH 7.15 ppm (1H, *t*, *J*= 7.7 Hz, H-5), 6.78 ppm (1H, *d*, *J*= 7.5 Hz, H-4), and 6.67 ppm (2H, *m*, H-2, and H-6). The proton signal of the phenolic hydroxy group is present at δH 5.11 ppm (*s*, OH). The meta-substituted aliphatic chain is shown at δH 2.57 (2H, *m*), 1.60 ppm (2H, *dd*, *J*= 14.6; 7.1

Hz), 1.31 ppm (24H, *m*), and 0.91 ppm (3H, *t*, *J*= 6.9 Hz). The ^{1}H-NMR spectroscopy data from the present study were in line with cardanol data from the literature (Table 2).

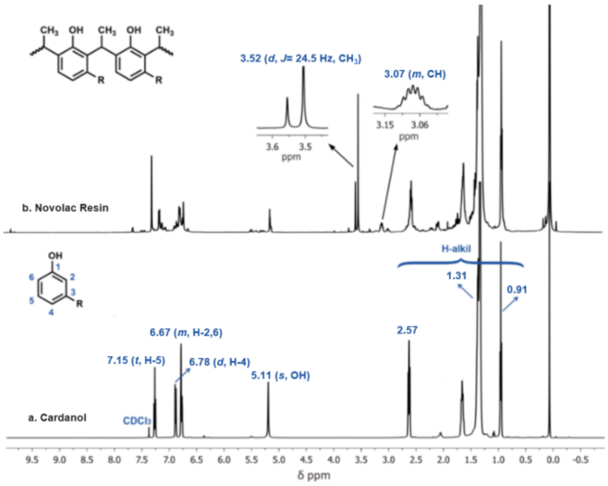

Figure 10. ^{1}H-NMR spectra of (a) Cardanol and (b) Novolac Resin

The results of the proton analysis of cardanol-acetaldehyde resin are shown in Figure 10(b). According to the synthesized resin spectra, a new chemical shift appeared at δH 3.07 ppm (1H, *m*), indicating the presence of methine protons (CH), and at δH 3.52 ppm (3H, *d*, *J* = 24, 5Hz) the methylene protons (CH_3) were detected. The tendency of methine and methylene protons to undergo deshielding is influenced by the presence of the highly electronegativity OH group. This shift indicates the presence of ethylene (C_2H_4) bridges connecting the aromatic nuclei at *ortho-ortho* positions, which is supported by the high J value of the coupling on the methylene proton (24.5 Hz).

The reaction for forming cardanol-acetaldehyde resin based on the identification results using FTIR and ^{1}H-NMR data analysis follows the substitution reaction (ii), which is *ortho-ortho* products. The *ortho-ortho* bridge product of ethylene is between the OH groups (compound 8), while the *ortho-para* product of the ethylene bridge is between the R group and the OH group (compound 12). The formation of these *ortho-ortho* products is preferable to *ortho-para* products, which can be due to the steric hindrance factor of the R group on cardanol which is a long-chain group.

Table 2. Comparison of cardanol ^{1}H-NMR data with literature

No. C	δ_H (multiplicity, J in Hz) ppm	
	Cardanol	Cardanol*
2	6.67 (*m*)	6.72 (*m*)
4	6.78 (*d*, *J* = 7.5 Hz)	6.83 (*m*)
5	7.15 (*t*, *J* = 7.7 Hz)	7.21 (*m*)
OH	5.11 (*s*)	5.78 (*s*)

Cardanol: measured in CDCl3 500 MHz; Cardanol*: measured in CDCl3 400 MHz [21]

4. Conclusion

Cardanol can be isolated from CNSL by liquid-liquid extraction and purified using gravity column chromatography and obtained a yield of 18.48%. The novolac resin can be synthesized from cardanol-acetaldehyde via a condensation polymerization reaction at *ortho-ortho* positions, producing a brownish-orange solid with 12.80 mg of yields (40%).

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References

[1] Yiping Shi, Paul C. J. Kamer, David J. Cole-Hamilton, Synthesis of pharmaceutical drugs from cardanol derived from cashew nut shell liquid, *Green Chemistry*, 21, 5, (2019), 1043-1053 https://doi.org/10.1039/C8GC03823F

[2] Faleh Setia Budi, Luqman Buchori, Optimasi Proses Polimerisasi CNSL dengan Formaldehid untuk Aplikasi Coating Furniture, *Jurnal Ilmu Lingkungan*, 11, 1, (2013), 10-15 https://doi.org/10.14710/jil.11.1.10-15

[3] Denial Mahata, Ahindra Nag, Santi M. Mandal, Golok B. Nando, Antibacterial coating on in-line suction respiratory catheter to inhibit the bacterial biofilm formation using renewable cardanyl methacrylate copolymer, *Journal of Biomaterials Science, Polymer edition*, 28, 4, (2017), 365-379 https://doi.org/10.1080/09205063.2016.1277623

[4] Ayman M. Atta, Hamad A. Al-Hodan, Reda S. Abdel Hameed, Abdelrahman O. Ezzat, Preparation of green cardanol-based epoxy and hardener as primer coatings for petroleum and gas steel in marine environment, *Progress in Organic Coatings*, 111, (2017), 283-293 https://doi.org/10.1016/j.porgcoat.2017.06.002

[5] Dinesh Balgude, Anagha S. Sabnis, CNSL: an environment friendly alternative for the modern coating industry, *Journal of Coatings Technology and Research*, 11, 2, (2014), 169-183 https://doi.org/10.1007/s11998-013-9521-3

[6] N. J. Sangeetha, Synthesis and characterization of cardanol-formaldehyde resins, *Journal of Chemistry and Chemical Sciences*, 8, 3, (2018), 625-629

[7] Nilesh L. Jadhav, Sai Krishna C. Sastry, Dipak V. Pinjari, Energy efficient room temperature synthesis of cardanol-based novolac resin using acoustic cavitation, *Ultrasonics Sonochemistry*, 42, (2018), 532-540 https://doi.org/10.1016/j.ultsonch.2017.12.001

[8] Dileep Tiwari, Archana Devi, Ramesh Chandra, Synthesis of cardanol based phenolic resin with aid of microwaves, *International Journal of Drug Development & Research*, 3, 2, (2011), 171-175

[9] Tatiana Loureiro, Rocio Macarena Moyano Dip, Elizabete Lucas, Luciana Spinelli, Cardanol polymerization under acid conditions by addition and condensation reactions, *Journal of Polymers and The Environment*, 26, 2, (2018), 555-566 https://doi.org/10.1007/s10924-017-0969-6

[10] S. G. Andrews, V. Rama, C. V. Mythili, Synthesis and characterization of polymer resins from renewable resource, *International Journal of Plastics Technology*, 21, 2, (2017), 427-443 https://doi.org/10.1007/s12588-017-9195-2

[11] Sayekti Wahyuningsih, Ari H. Ramelan, Surya D. Marliyana, Putri Rahmawati, Development of Cardanol-Based Phenolic Resin as Natural Adhesive for Uniting Fossil (Metacarpal Bone of Bovidae Family) Fragments *Proceedings of 175th The IIER International Conference*, Bangkok, Thailand, 2018

[12] Indah Purnamasari, Hary Sulistyo, Kinetika Reaksi Polimerisasi Urea-Asetaldehid dalam Proses Enkapsulasi Urea, *Jurnal Rekayasa Proses*, 6, 2, (2012), 37-42

[13] Imre Kovács, Arnold Péter Farkas, Ádám Szitás, Zoltán Kónya, János Kiss, Adsorption, polymerization and decomposition of acetaldehyde on clean and carbon-covered Rh (111) surfaces, *Surface Science*, 664, (2017), 129-136 https://doi.org/10.1016/j.susc.2017.05.016

[14] P. Phani Kumar, R. Paramashivappa, P. J. Vithayathil, P. V. Subba Rao, A. Srinivasa Rao, Process for isolation of cardanol from technical cashew (*Anacardium occidentale* L.) nut shell liquid, *Journal of Agricultural and Food chemistry*, 50, 16, (2002), 4705-4708 https://doi.org/10.1021/jf020224w

[15] Tejas Gandhi, Mayank Patel, Bharat Kumar Dholakiya, Studies on effect of various solvents on extraction of cashew nut shell liquid (CNSL) and isolation of major phenolic constituents from extracted CNSL, *Journal of Natural Product and Plant Resources*, 2, 1, (2012), 135-142

[16] F. F. M. da Silva, A. K. de Medeiros Costa, P. T. Barbosa, J. C. de Paiva Mota, T. L. G. de Lemos, Extraction, Isolation and Chemical Modification of the Anacardic Acids from the Peel of the Cashew Nuts (*Anacardium occidentale* L.) and Biological Assay, *Current Research in Bioorganic & Organic Chemistry*, 2018, 02, (2018), 1-9 https://doi.org/10.29011/2639-4685.100010

[17] Francisco Cardona, Thiru Aravinthan, Jessica Fedrigo, Clarisse Moscou, Synthesis of phenolic bio-resins for advanced composites in civil engineering structures, *Proceedings of the Southern Region Engineering Conference (SREC 2010)*, Australia, 2010

[18] M. Natarajan, S. C. Murugavel, Synthesis, spectral and thermal degradation kinetics of novolac resins derived from cardanol, *High Performance Polymers*, 25, 6, (2013), 685-696 https://doi.org/10.1177/0954008313482955

[19] Ranjana Yadav, Poonam Awasthi, Deepak Srivastava, Studies on synthesis of modified epoxidized novolac resin from renewable resource material for application in surface coating, *Journal of Applied Polymer Science*, 114, 3, (2009), 1471-1484 https://doi.org/10.1002/app.30581

[20] Yongsheng Zhang, Production and applications of formaldehyde-free phenolic resins using 5-hydroxymethylfurfural derived from glucose in-situ, Chemical and Biochemical Engineering, The University of Western Ontario, 2014

[21] Mitsuhiro Shibata, Yusuke Itakura, Hironori Watanabe, Bio-based thermosetting resins composed of cardanol novolac and bismaleimide, *Polymer Journal*, 45, 7, (2013), 758-765 https://doi.org/10.1038/pj.2012.195