Synthesis and Characterisation of Cardanol Acetate and Cardanol Ether as Reactive Diluents for Alkyd Coatings

Njuku, F.W*. Muturi, P. M Thiong'o, G. T
Department Chemistry, Jomo Kenyatta University of Agriculture and Technology
P.O. Box 62,000-00200, Nairobi, Kenya
*Corresponding author E-mail: njukufrancis@ymail.com

Abstract
Alkyd resins are viscous, tacky materials that are difficult to handle. Most often, these handling problems are overcome by dissolving the resins in organic solvents, which evaporate into the atmosphere as volatile organic compound (VOC), giving rise to regulations. A reactive diluent is a compound that acts as a solvent in the liquid paint, lowering the viscosity, and chemically reacts into the final film during the curing process to give a more environmentally friendly coating and the amount of traditional solvent can be decreased. Cashew nut shell liquid (CNSL) is not currently utilized in Kenya and the objective of this work was to develop reactive diluents from chemically modified CNSL products and evaluate their compatibility with alkyd coatings. A standard reactive diluent should have low viscosity, increase drying time of less than 50 %, and be nontoxic. Cardanol was isolated using methanol and ammonia solution as the solvents in a ratio of 8:5 respectively. The percentage yield of cardanol obtained was 63.94 %. The yield of cardanol acetate obtained was 58.94 %. The cardanol acetate was also characterized by FT-IR and it showed the presence of the C=O stretch functional group characteristic of the ester and the absence of the OH group that was present in cardanol. The cardanol acetate synthesised showed a low viscosity (45 Cps) and a reduced drying time of about 25–35% compared to conventionally prepared formulations.

Keywords: Cashew nut shell liquid, Cardanol, Reactive diluent, Cardanol acetate.

1.0 INTRODUCTION

Since the implementation of the clean air act 1990, Alkyd resin and coating producers have been under increasing pressure to reduce the hazardous air pollutants and volatile organic compounds content of their products. New nationals and regional rules such as Ozone Transport Commission, state Architectural and Industrial Maintenance (AIM) rules will soon mandate that certain categories of alkyd coatings contain as little as 50 grams of VOCs per liter of paint (Daniel *et al.*, 2004). Cashew nut shell liquid (CNSL) is a viscous liquid found in the honeycomb structure of the cashew nuts shell having a bitter taste and it is dark brown in color. It is essentially a mixture of 4 phenolic compounds namely anacardic acid, cardanol, cardol and 2-methyl cardol (Francisco *et al.*, 2006). Natural CNSL contains about 90% by weight anacardic acid, a derivative of O-carboxyphenol that readily decarboxylates on heating and converts to cardanol. The remaining 10% of CNSL consists of cardol, a resorcinol that is mainly responsible for the vesicative activity of the CNSL (Cornelius, 1966).

2.0 MATERIALS AND METHODS

2.1 *Chemicals and Solvents.*

All organic solvents and chemicals were obtained from Kobian Chemicals and were purified before using them. Other equipments used in analyses were a pH meter, a viscometer (Brookfield), a pycnometer, Gas Chromatography-Mass Spectrum (GC-MS), and Fourier Transformed Infrared Spectroscopy (FTIR).

2.2 *Separation of Cardanol from Cardol.*

Decarboxylated CNSL (10 g) was dissolved in methanol (32 mL), and ammonium hydroxide (25%, 20 mL) was added and stirred for 15 min. This solution was then extracted with hexane (4 × 20 mL). The organic layer was washed with 5% HCl (10 mL) followed by distilled water (10 mL). Activated charcoal (10 g) was added to the organic layer, stirred for 10 min, and filtered through filter papers. The filtrate was dried over anhydrous sodium sulfate and concentrated to get pure cardanol (Kumar *et al.,* 2002).

2.3 *GC-MS.*

GC-MS analysis was carried out using a Finnigan GC 8000 series and interfaced with a voyager EI-mass selective detector, on a RTX-5MS 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 (Kumar *et al.,* 2002).

2.4 *Synthesis of cardanol acetate*

Cardanol (31.6 g), acetic anhydride (15.8 g), concentrated sulphuric acid (0.4 g) and acetonitrile (10 ml) mixed together. The reaction mixture was refluxed at 80 °C in an oil bath for 4.5 hrs. After completion of the reaction, the mixture was filtered off. The product was extracted with ethyl acetate and washed with water and finally dried over anhydrous sodium sulphate to obtain pure product (Saeid and Somayeh, 2010).

2.5 *Synthesis of cardanol ether*

Cardanol (23.5 g), methyl iodide (30.3 g), anhydrous potassium carbonates (34.6 g) and 100 ml of acetone were mixed together. The mixture was rufluxed in a hot plate for 8 hours. After completion of the reaction, the mixture was poured into 500 ml of water in a beaker. The organic layer was separated and extracted with (3 × 20 ml) diethyl ether. The combined organic layer and diethyl ether extract was washed with 2 M sodium hydroxide solution and dried over anhydrous sodium sulphate. The diethyl ether was removed in a rotor vapor under reduced pressure to obtain pure product (Brian, 1989).

RESULTS

TABLE 1: RESULTS OF CHARACTERISTICS OF CARDANOL ACETATE AND CARDANOL ETHER

Parameter	**Cardanol acetate**	**Cardanol ether**
Specific gravity @25 °C, g/cm^3	0.96	0.93
Viscosity @ 40 °C,cps	42.06	36.10
Iodine value, g/100 g	232.4	232.6
Moisture content	Negligible	Negligible
pH @25 °C	6.23	7.01

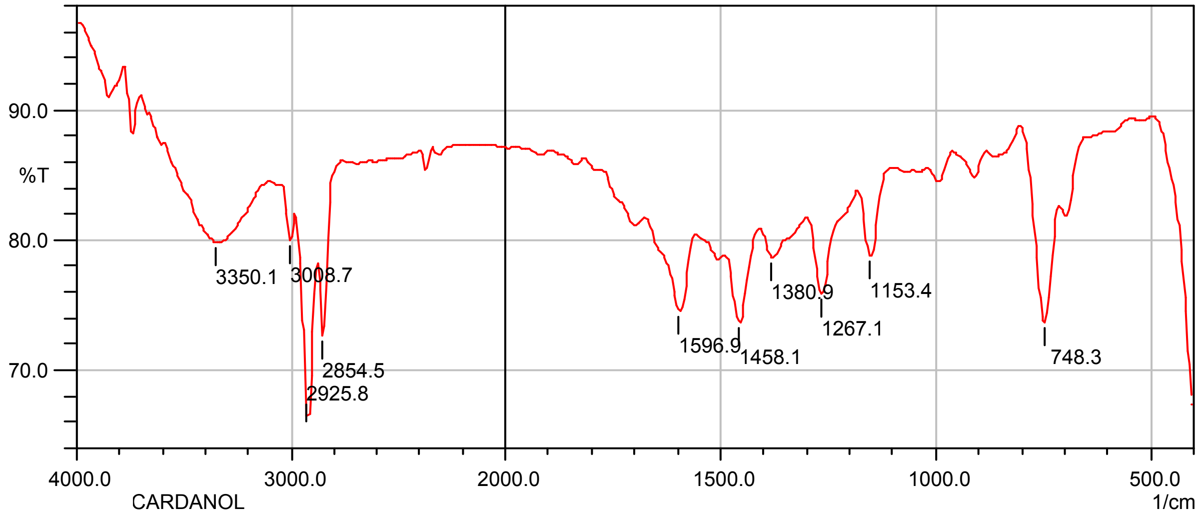


FIGURE 1: FTIR SPECTRUM OF CARDANOL

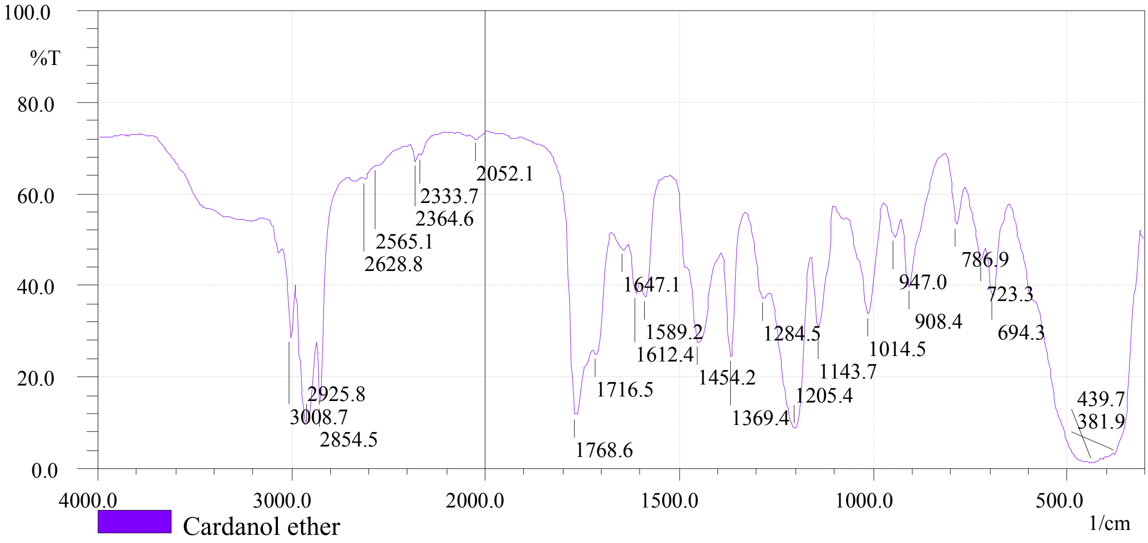


FIGURE 2: FTIR SPECTRUM OF CARDANOL ETHER

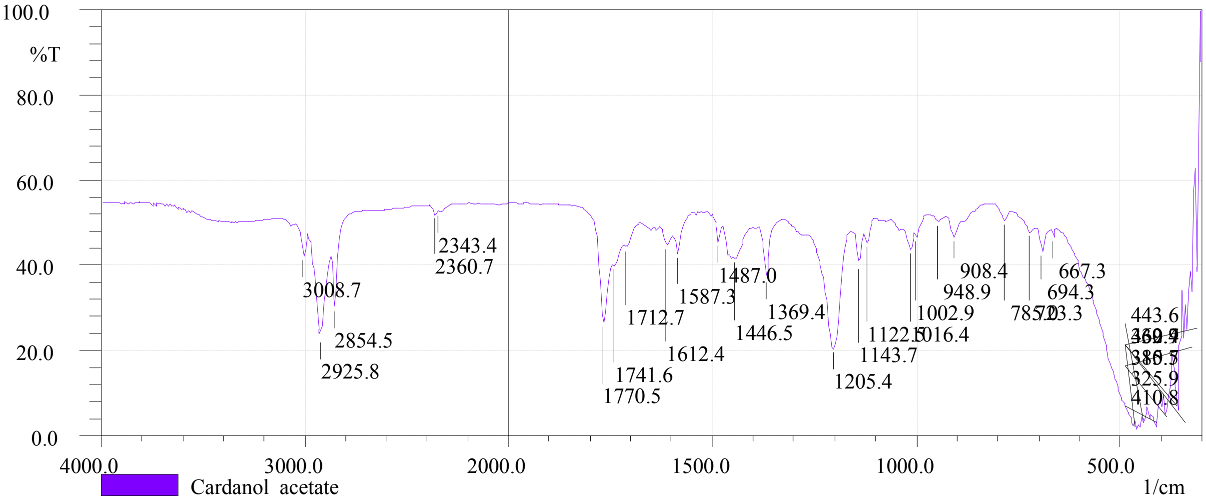


FIGURE 3: FTIR SPECTRUM OF CARDANOL ACETATE

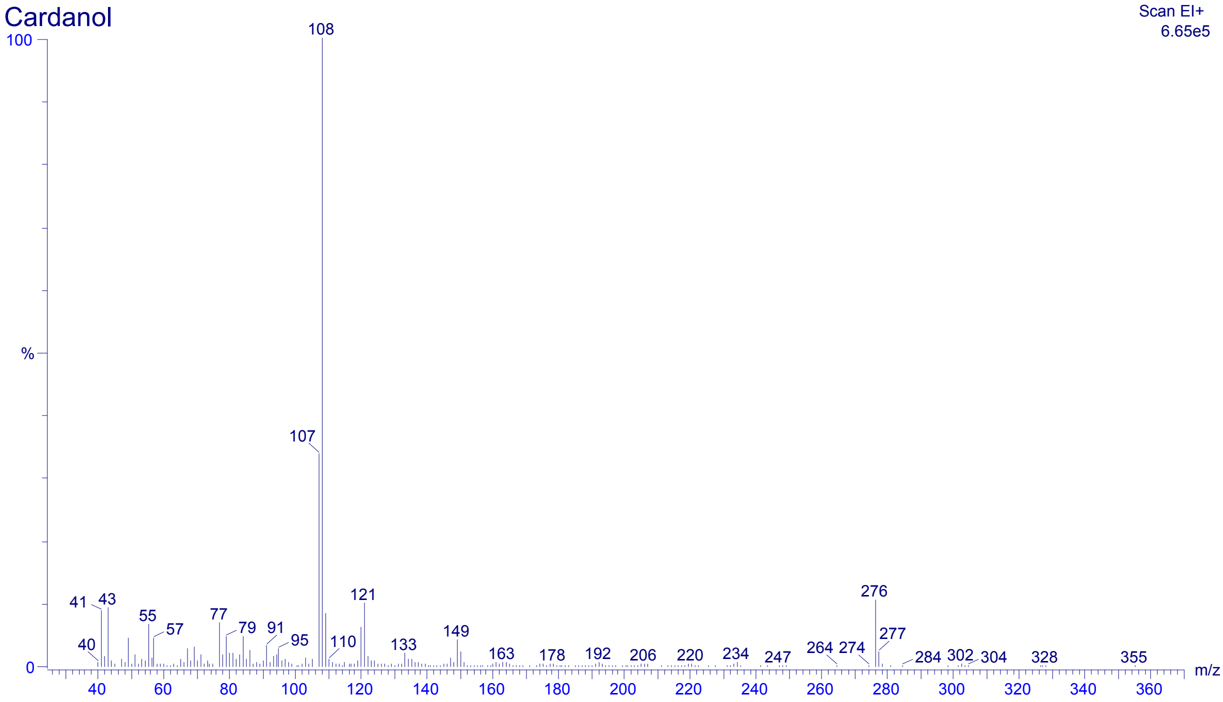


FIGURE 4: GC MS PROFILE OF CARDANOL

CARDANOL ACETATE

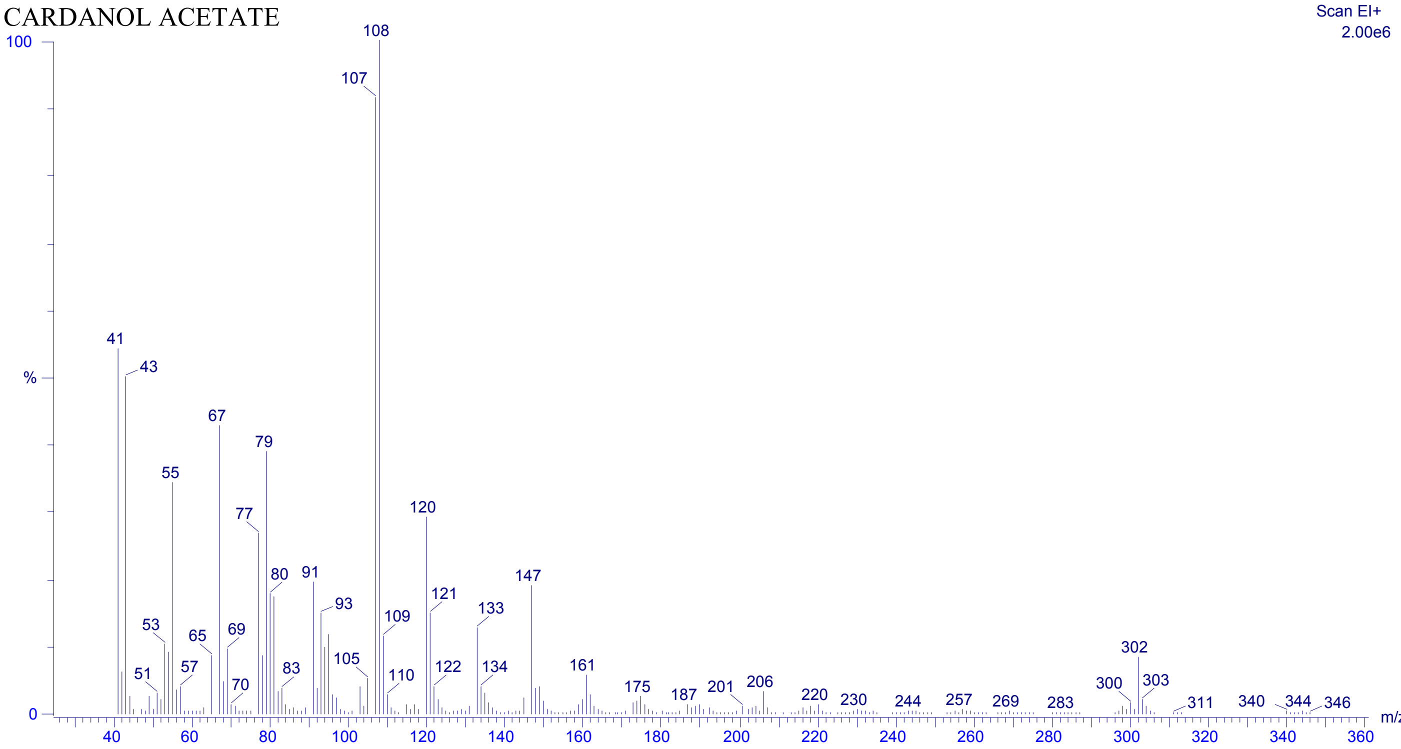


FIGURE 5: GC MS PROFILE OF CARDANOL ACETATE

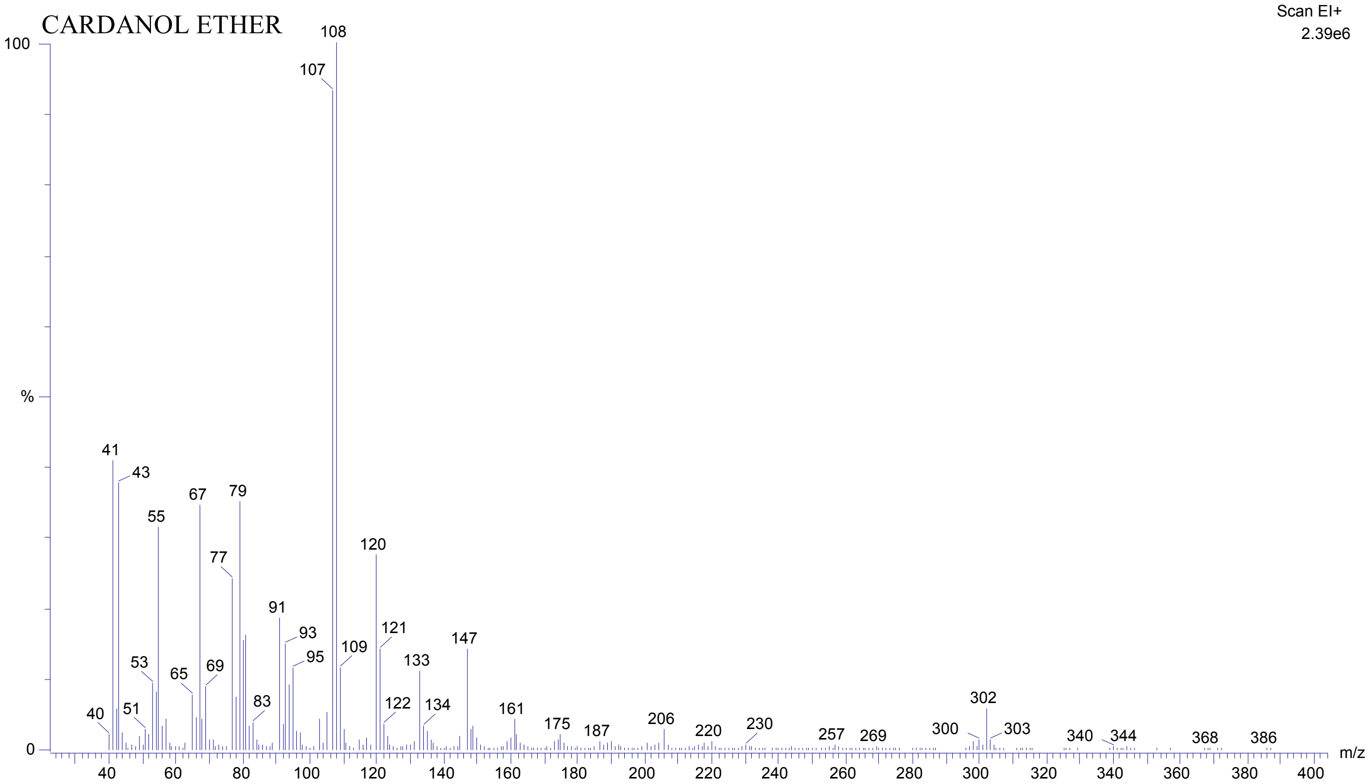


FIGURE 6: GC MS PROFILE FOR CARDANOL ETHER

DISCUSSION

Characteristics of Cardanol Acetate and Cardanol Ether

There is A Significance Difference in the Viscosity Values of Cardanol Acetate and Cardanol Ether (Table 1). Cardanol Ether Has A Low Viscosity than Cardanol Acetate Because of the Architecture of the Molecule, The Substituents in The Phenyl Core Orient Themselves in Such A Way that the Molecules Do not Interact as They Flow Down the Capillary Tube. There is Reduced Shear Rate and as A Result the Shear Strain Increases and the Molecule Flows Easily as Compared to Cardanol Acetate. in Cardanol Acetate, There is Molecular Interaction Which Results into the Entanglement of the Long Aliphatic Chain and the Viscosity is Reduced. There is no Significance Difference in the Iodine Values of Cardanol Ether and Cardanol Acetate as Shown in Table 1. This Shows that Methylation and Acetylation of Cardanol with Methyl Iodide and Acetic Anhydride Respectively Does not Affect the Unsaturation of the Side Chain. There is a Significance Difference in the Density Values of Cardanol Ether and Cardanol Acetate (Table 1); This is Because Acetylation Increases the Molecular Weight of the Phenyl Backbone. There is no Significance Difference in the Moisture Content of Cardanol Ether and Cardanol Acetate as Shown In Table 1.

Identification Using the FTIR for cardanol

The peak of absorption that appeared at frequency of 3350.1 cm $^{-1}$ indicated the presence of OH group of phenolic compounds (Figure 1). The peaks that appeared at frequency of 3008.7 cm^{-1} indicated the presence of C-H branch chains of the aromatic compounds (Figure 1). The peak that appeared at frequency 2925.8 cm-^{1} indicated the presence of methylene C-H symmetrical stretch of the long aliphatic chain (Figure 1). The Spectra that appeared at 1265.2 cm^{-1} area indicated C-O groups of the phenolic compounds (Figure 1). The absorption peak that appeared in the 1596.9 cm^{-1} frequency indicated C=C bonds of the long aliphatic chain, while the peak that appeared in the 1458.1 cm^{-1} frequency indicated the C=C stretch of the aromatic chains.

Identification Using the FTIR for cardanol acetate

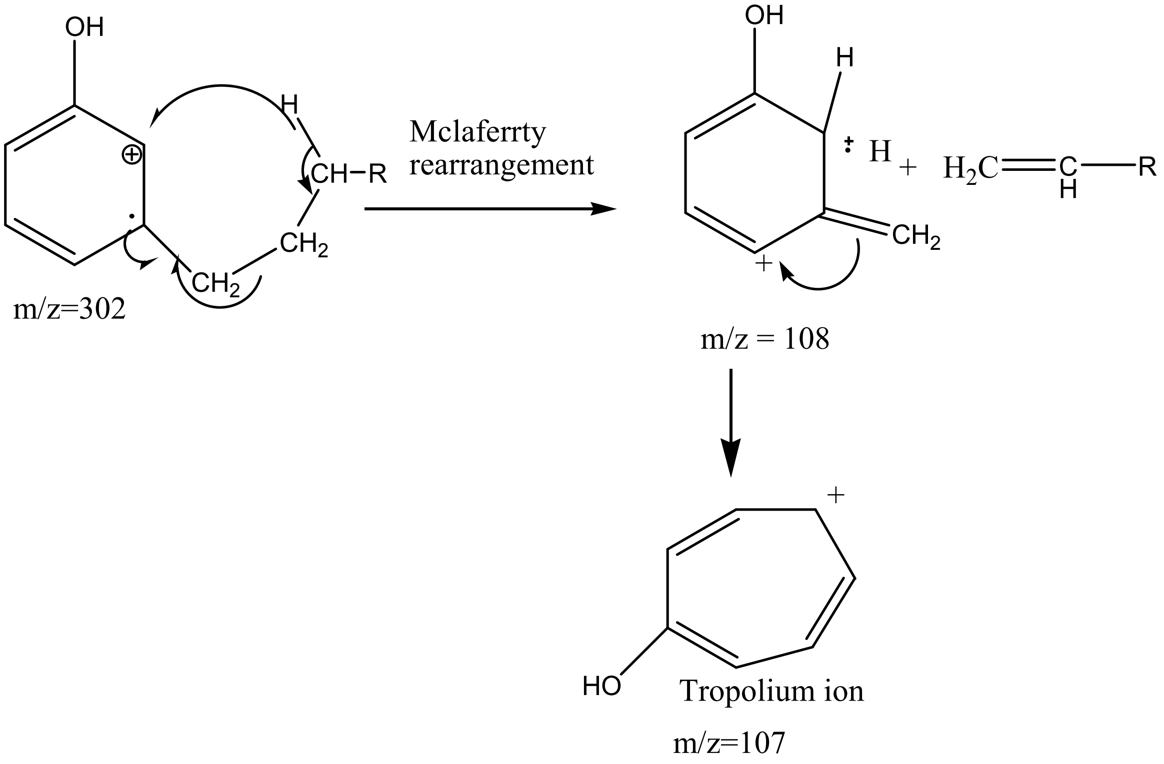
The peak of absorption that appeared at frequency of 3008.7 cm^{-1} indicated the presence of C-H branch chains of the aromatic compounds (Figure 3). The peak that appeared at frequency 2925.8 cm-^{1} indicated the presence of methylene C-H symmetrical stretch of the long aliphatic chain (Figure 3). The peak that appeared at frequency 1770.5 cm-^{1} indicated the presence of C=O stretch for an ester (Figure 3). The Spectra that appeared at 1205.4 cm^{-1} area indicated C-O symmetrical stretch characteristic of an ester (Figure 3). The absorption peak that appeared in the 1587.3 cm^{-1} frequency indicated C=C bonds of the long aliphatic chain, while the peak that appeared in the 1446.1 cm^{-1} frequency indicated the C=C stretch of the aromatic chains.

Identification Using the FTIR for cardanol ether

The peak of absorption that appeared at frequency of 3008.7 cm^{-1} indicated the presence of C-H branch chains of the aromatic compounds (Figure 2). The peak that appeared at frequency 2925.8 cm-^{1} indicated the presence of methylene C-H symmetrical stretch of the long aliphatic chain (Figure 2). The Spectra that appeared at 1205.4 cm^{-1} area indicated C-O symmetrical stretch characteristic of an ester (Figure 2). The absorption peak that appeared in the 1587.3 cm^{-1} frequency indicated C=C bonds of the long aliphatic chain, while the peak that appeared in the 1446.1 cm^{-1} frequency indicated the C=C stretch of the aromatic chains

Interpretation of GC MS profile for cardanol

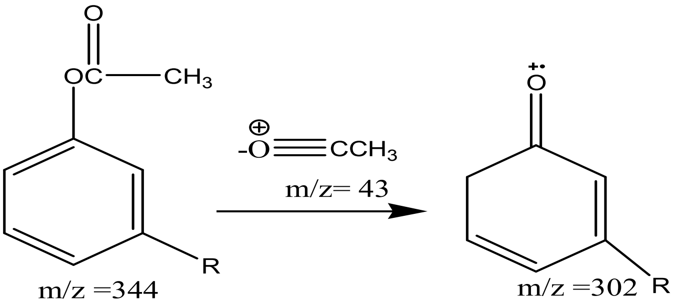
The base peak at m/z = 108 of the spectra can be rationalized in accordance with the main characteristic of alkyl benzene as derived from the molecular ions and is attributed through the β cleavage of the aliphatic chain as shown in figure 3. There is the Mclaffetry rearrangement due to the long aliphatic chain attached to the benzyl ring. The Peak at m/z = 302 and 304 correspond to the molecular weights of the two fractions of cardanol. Scheme 1 below shows the fragmentation.



Scheme 1: Fragmentation of cardanol acetate

Interpretation of GC MS profile for cardanol acetate

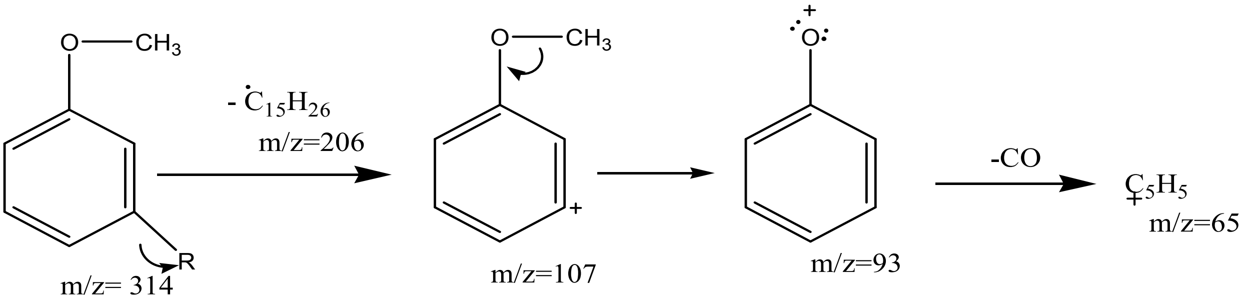
The base peak at m/z = 108 of spectra can be rationalized in accordance with the main characteristic of alkyl benzene as derived from the molecular ions and is attributed through the β cleavage of the aliphatic chain as shown in figure 3 above. The peak at m/z = 302 is attributed due to the cleavage of $\underset{+}{C}OCH_3$ m/z= 43 group from molecular ion as shown in scheme 3. The Peak at m/z = 340, 344 and 346 correspond to the molecular ions of the three fractions of cardanol acetate. Scheme 2 shows the fragmentation pattern.



Scheme 2: Fragmentation of cardanol acetate

Interpretation of GC MS spectra for cardanol ether

The main fragmentation ions of cardanol ether are those at *m/z* 108 due to McLafferty rearrangement and m/z 107 due to formation of tropolium ions. Scheme 3 below shows how the fragmentation occurs.



Scheme 3: Fragmentation of cardanol acetate

CONCLUSION

The characteristics of cardanol ether differed from those of cardanol acetate by a small amount. Cardanol ether had a low viscosity and a low specific gravity as compared to cardanol acetate.

ACKNOWLEDGMENTS

The authors wish to thank Research, production and extension for financial support of this work and Mr. Tom Oddo of college of health sciences for their technical assistance in the study.

Reference

Alp, H. A., Kevin, D., Rhonda, R., Crystal, S., James, W. R. and Sarah, E. M. (2011). Synthesis and evaluation of tetra (2, 7-octadienyl) titanate as a reactive diluent for air-drying alkyd paints. *Journal of coatings technology and Research*, 8 (1): pp 45–52.

Brian, S. F., Antony, J. H., Peter, W. G .S. and Austin, R. T. (1989). Vogels text book of practical organic chemistry, 5th ed, pp 986. John wiley and sons, New york

Akinhanmi, T. F., Atasie, V. N. and Akintokun, P. O. (2008). Chemical composition and physicochemical properties of cashew nut oil and cashew nut shell liquid. *Journal of Agriculture and food chemistry,* 2 (1): pp 1-10.

Atul, M., Sudhir, J and Powar, A. G. (2011). Cashew nut processing: Sources of environmental pollution and standards. *Indian Journal*, 1: pp 05-11.

Bambang, Susilo. (2000). Roasting experiment of cashew nut in traditional industry. *Journal of Agricultural and Technology,* 1: pp 64-69.

Barrett, K. E. J. and Lambourne, R. (1966). Air-drying alkyd paints. The effect of incorporation of non-volatile monomers on film properties. *Journal of the Oil and Colour Chemists Association,* 49(6): pp 443-63.

Bruson, H.A. (1947). *U.S. Patent 2,414,089.*

Cornelius, J. A. (1966). Cashew nut shell liquid and related materials. *Tropical science*, 8: pp 79-84.

Daniel, B. P and Scott, E. S. (2004). High-Solids Alkyd Resins with Improved Properties Based on Styrene Allyl Alcohol Resinous polyols. *Journal of Coatings technology*, 1: pp 40-47.

De Lima, S. G., Feitosa, C. M., Cito, A. M. G. L., Neto, M. J. M., Lopes, J. A. D., Leite, A. S., Brito, M. C., Dantas, S. M. M. and Melo Cavalcante, A. A. C. (2008). Effects of immature cashew nut shell liquid (*Anacardium occidentale*) against oxidative damage in *Saccharomyces cerevisiae* and inhibition of acetylcholinesterase activity. *Journal of Genetics and Molecular Research,* 7 (3): pp 806-818.

Dieter, S and Werner, F. (1998). Paints, Coatings and Solvents. Book, 2ed, pp 41-50, New York: Wiley-Vs.

Food and Agriculture Organization (FAO) (2008). Global production of cashew nut. A technical report to Food and Agriculture Organisation of the United Nation Production database, http://apps.fao.org/ page/collections.

Francisco, H. A. R., Judith P. A. F., Nagila, M. P. S. R., Francisco C. F. de Franca., Jose O. B. C. (2006). Antioxidant activity of cashew nut shell liquid (CNSL) derivatives on the thermal oxidation of synthetic *cis*-1, 4-polyisoprene. *Journal of Brazilian Chemical Society*, 17: pp 1.

Hatsuo, I and Tarek, A. (2011). Handbook of Benzoxazine Resins: Study of a cardanol-Based Benzoxazine as Reactive Diluent and Toughening Agent of Conventional Benzoxazines. pp 365, Elsevier B.V.

Hochberg, S. (1965). The chemistry of the vinyl cyclic acetals and their air-drying reactions. *Journal of the Oil and Colour Chemists Association*, 48: pp 1043-1064.

James, J. L. (2003).Coating materials for electronic applications: *Polymer processes, reliability, testing*.2ed: pp 71-73.Voges publication/William Andrew (USA).

Johansson, K and Johansson, M. (2006). Progress in organic coatings: *A model study on fatty acid methyl esters as reactive diluents in thermally cured coil coating systems*. 55: pp 382-387.

Knop, A. and Scheib, W. (1979). Chemistry and Applications of Phenolic Resin-Polymer Properties and Applications; 2ed, Springer Verlag: Berlin, Germany.

Khumar. P. P., Paramashivappa, P. J., Vithayatil, P. V. S. R, and Rao, A. S. (2002). Process for isolation of cardanol from technical cashew (*Anacardium occidentale*) nut shell liquid. *Journal of Agriculture and Food Chemistry*, 50: pp 4705-4708.

Larson, D. B. and Emmons, W. D. (1983). Chemistry of high-solids alkyd/reactive diluent coatings. *Journal of Coatings Technology*, 55(702): pp 49-56.

Mahanwar, P. A. and Kale, D. D. (1996).Effect of cashew nut shell liquid (CNSL) on properties of phenolic resins. *Journal of Applied Polymer Sciences*, 61: pp 2107-2111.

Marcionilia, F. P., Denis, D. L., Leonardo R. M., Adilson B., Sandra, T. S., Leticia, V. C. L. (2009). Ecotoxicological analysis of cashew nut industry effluents, specifically two of its major phenolic components, cardol and cardanol. *Pan-American Journal of Aquatic Sciences*, 4(3): pp 363-368.

Maria Lucilia dos Santos and Gouvan C. de Magalhaes. (1999). Utilization of Cashew Nut Shell Liquid from *anacardium occidentale* as starting Material for organic synthesis: A novel route to Lasiodiplodin from Cardols. *Journal of Brazilian Chemical Society,* 10(1): pp 13-20.

Menon, A. R. R.; Pillai, C. K. S. and Mathew, A. G. (1985). Cashew nut shell liquid-its polymeric and other industrial products. *Journal of Science in Industrial research*, 44: pp 324-338. 2381-2383.

Muizebelt, W. J., Hubert, J. C., Nielen, M. W. F., Klaasen, R. P., Zabel, K. H. (2000). Crosslink mechanisms of high-solids alkyd resins in the presence of reactive diluents. *Progress in Organic Coatings*, 40(1-4): pp 121-130.

Muturi, P., and Arunga, O. R. (1988). Cashew nut shell liquid: a review of production and research in Kenya. *Tropical Science,* 28*:* pp 201 - 218.

Muturi, P. (1984a). Coatings formulation from cashew nut shell liquid and their characteristics. *Kenya journal of Science and Technology*, 5 *(1 and 2)*: pp 53-61.

Ranjana, Y. and Deepak, S. (2008). Studies of cardanol based epoxidized novalac resin and its blends. *Indian journal of Chemistry and Chemical technology*, 2: pp 173-184.

Risfaheria, T. T. I., Nur, M. A and Illah, S. (2009). Isolation of Cardanol from Cashew Nut Shell Liquid using the vacuum distillation method. *Indonesian journal of Agriculture,* 2(1): pp 11-20.

Saeid, F and Somayeh, P. (2010). Decatungstodivanadogermanic heteropoly acid (H6GeW10V2O40.22H2O): A novel, green and reusable catalyst for efficient acetylation of alcohols and phenols under solvent-free conditions. *European Journal of Chemistry*, 1 (4): pp 335-340.

Satoru, E. (1978). Study of reactive diluent for air-dried alkyd paints. *Journal of Applied Polymer Science,* 22(1): pp 253-65.

Tyman, J.H.P. (1973). Long chain phenols.Part III. Identification of the components of a novel phenolic fraction in *Anacardium occidentale* (cashew nut shell liquid) and synthesis of the saturated member. *Journal of chemical Society of Perkins Transport*. 1: pp 1639-1647.

Ursula, B., Werner, B., Ralf, H., Willi, F and Jurgen, O. M. (2009). Esters of calendula oil and tung oil as reactive diluents for alkyd resins, *European journal of lipid Science and technology*, 112: pp 103-109.

Wicks, Z. W., Jones, F. N. and Pappa, P. S. (1992).Organic Coatings: Science and Technology. 2ed. New York: Wiley-Interscience.

Zabel, K.H., Klaasen, R.P., Muizebelt, W.J., Gracey, B.P.,Hallet C., Brooks, C.P. (1999). Design and incorporation of reactive diluents for air drying high solid alkyd paints. *Progress in organic coatings*, 35(1-4): pp 255-264, Eiseviers equiol.

Zeno, W. W., Frank, N. J. and Peter, S. P. (2007). Science and technology. Organic coatings 3rd ed, pp 313, John Wiley and sons.