EVALUATION OF CASHEW NUT SHELL LIQUID (CNSL) BASED PRODUCTS AS REACTIVE DILUENTS FOR ALKYD COATINGS

F.W. Njuku, P. M. Muturi and G. T.Thiong'o
Department Chemistry, Jomo Kenyatta University of Agriculture and Technology, Nairobi, Kenya
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.

Key words: 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 purified before uses. 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 sulphate and concentrated to get pure cardanol (Kuma*r 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 refluxed 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).

2.6 Formulation of Alkyd with Reactive Diluent

The alkyd resin was diluted with the two reactive diluent at weight percentages of 5%, 10%, 15% 20%, and 25%. Metal driers were added at levels of 1% and 0.6% for lead naphthenate and cobalt octoatet respectively (Table 1). In addition, white spirit was incorporated at weight percentages of 45%, 40%, 35%, 30% and 25%.

Table 1: Composition of clear alkyd coating formulations based on long oil alkyd resin (70% wt solids)

Alkyd resin (70 % wt solid)	White spirit (g)	Lead Naphthenate (32%)	Cobalt octoatate (10%)	Reactive diluent (g)
100 g pure resin	45	1 % (3.13 g)	0.6 % (6 g)	5
100 g pure resin	40	1 % (3.13 g)	0.6 % (6 g)	10
100 g pure resin	35	1 % (3.13 g)	0.6 % (6 g)	15
100 g pure resin	30	1 % (3.13 g)	0.6 % (6 g)	20
100 g pure resin	25	1 % (3.13 g)	0.6 % (6 g)	25

2.0 Results and Discussion

2.1 Characteristics of Raw CNSL, Decarboxylated CNSL and Cardanol

There is a significant difference in the density values of raw CNSL, decarboxylated CNSL and cardanol (Table 2). Raw CNSL has a high relative density because it has anarcadic acid as the major fraction. There is intermolecular attraction between the electronegative oxygen atom and the partially positive hydrogen atom of the phenol core, and as a result the molecules are closely packed together. A large mass occupies the same volume of the density bottle and hence a high relative density. The decrease in specific gravity in decarboxylated CNSL is due to the release of CO_2 gas from anacardic acid to form cardanol after decarboxylation, which has a smaller specific gravity than raw CNSL. The molecules are not closely packed together as there are no strong dipole-dipole attractions.

There is no significant difference in the iodine values of raw CNSL, decarboxylated CNSL and cardanol as shown in Table 2. This is because iodine value is a measure of the amount of unsaturation in given oil and the unsaturation in raw CNSL, decarboxylated CNSL and cardanol is equal. The high iodine values of more than 140 in the fractions show that they are drying oils. There is a significance difference in the viscosity values of raw CNSL, decarboxylated CNSL and cardanol (Table 2). Raw CNSL has anarcardic acid as the major fraction with the –COOH group in the ortho position of the phenol core and therefore there is strong dipole–dipole attraction between the partially positive charged hydrogen atom and the strong electronegative oxygen atom. There is the effect of intramolecular hydrogen bonding which results in the molecule being entangled together as it flows down the capillary tube as a result the shear rate increases and thus a high viscosity in CNSL as compared to decarboxylated CNSL and cardanol. There is a significance difference in the acid values of raw CNSL, decarboxylated CNSL and cardanol. Acid value is a measure of free acids in a given oil, this shows that there is a lot of free acids in raw CNSL. Decarboxylated CNSL and cardanol have low acid value. There is significant difference in the pH value of raw CNSL, decarboxylated CNSL and cardanol as shown in table 2. The Raw CNSL used is highly acidic with a pH of 3.07 as compared to decarboxylated CNSL pH 6.02 and cardanol pH 6.16 indicating that the carboxylic acid content in the liquid is very high. Decarboxylated CNSL and Cardanol are less acidic because heating CNSL decomposed the anacardic acid into cardanol and the carboxylic acid group was lost as a gas. There is significant difference in the moisture content of raw CNSL, decarboxylated CNSL and cardanol as shown in Table 2. This is because during processing, cashew nut shells are soaked in water so that the kernel can be removed and this increases the moisture content. There is negligible moisture content in decarboxylated CNSL because during decarboxylation at 140 oC water is lost.

Table 2: Results of characteristics of raw CNSL, decarboxylated CNSL and cardanol

Parameter	Raw CNSL	Decarboxylated CNSL	Cardanol
Specific gravity @ 25 ^{o}C, g/ cm^3	0.99	0.96	0.95
Viscosity @ 40 ^{o}C, Cps	52.36	46.56	45.31
Acid value, g/100 g KOH	12.64	1.73	1.18
Iodine value, g/100 g	231.5	231.2	232.0
pH @ 25 ^{o}C	3.07	6.02	6.16
Moisture content (%)	0.55	Negligible	Negligible

2.2   Characteristics of Cardanol Acetate and Cardanol Ether

There is a significance difference in the viscosity values of cardanol acetate and cardanol ether (Table 3). 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 3. 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

3); 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 3.

Table 3: Results of characteristics of cardanol acetate and cardanol ether

Parameter	Cardanol acetate	Cardanol ether
Specific gravity @25 ºC, g/cm³	0.96	0.93
Viscosity @ 40 ºC,cps	42.06	36.10
Iodine value, g/100 g	232.4	232.6
Moisture content	Negligible	Negligible
pH @25 ºC	6.23	7.01

2.3 Identification Using the FTIR for Decarboxylated CNSL

The peak of absorption that appeared at frequency of 3352.1 cm-1 indicated the presence of OH group of phenolic compound (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.
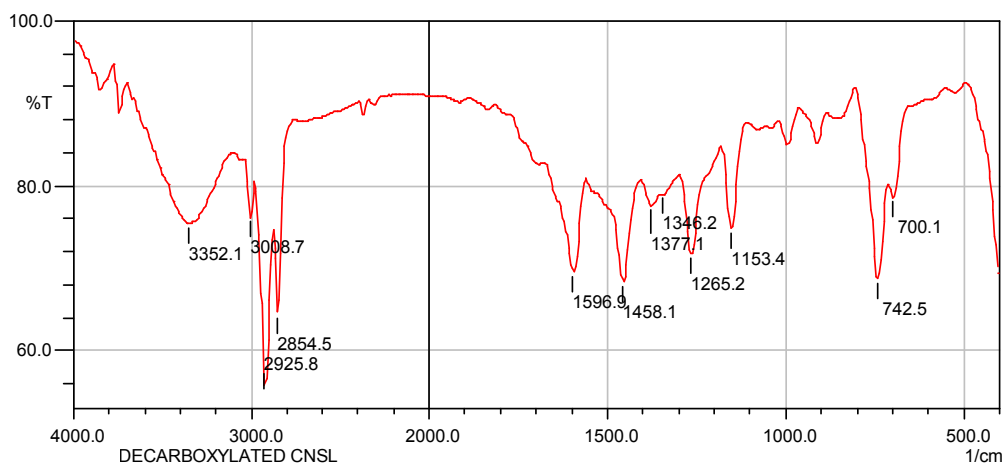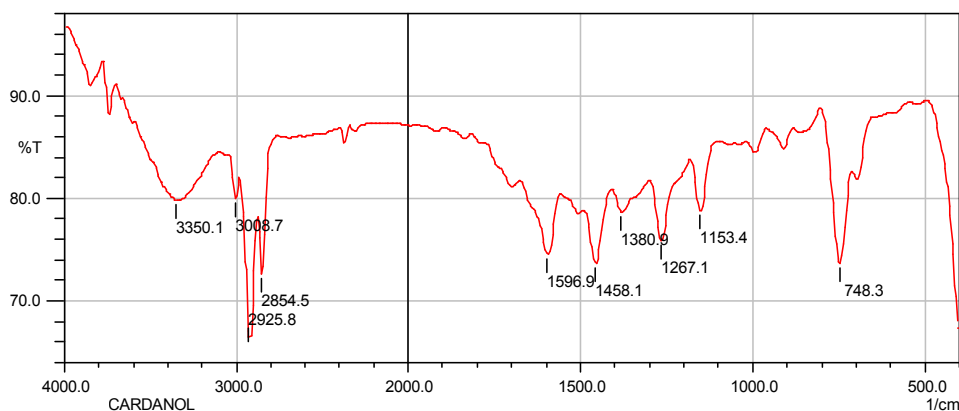

Figure 1: FTIR spectrum of decarboxylated CNSL

2.4 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 2). The peaks 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 1265.2 cm^{-1} area indicated C-O groups of the phenolic compounds (Figure 2). 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.
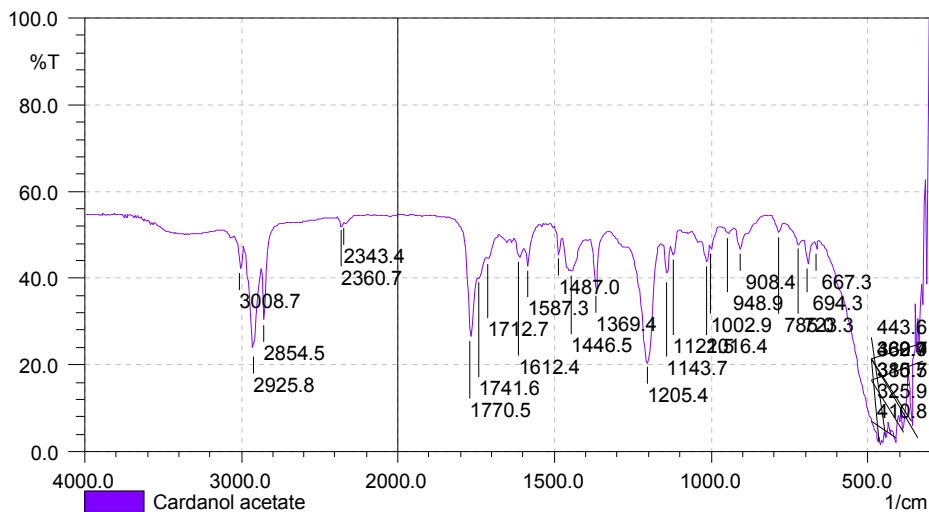
Figure 2: FTIR spectrum of cardanol

2.5   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 2). The peak that appeared at frequency 1770.5 cm^{-1} indicated the presence of C=O stretch for an ester (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.
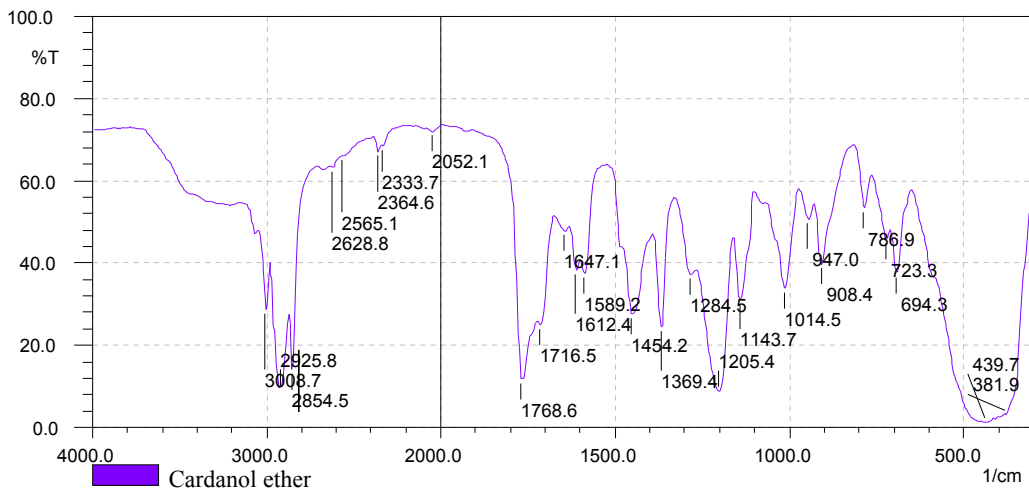

Figure 3: FTIR spectrum of cardanol acetate

2.6   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 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 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.

Figure 4: FTIR spectrum of cardanol

2.7 Interpretation of GC MS Spectra for CNSL

A phenolic compound consisting of an aliphatic chain will experience fragmentation in the β position of the alkyl chain to form tropolium ions which are more stable. This position will give a base of m/e =108 as shown in Figure 6 and scheme 1. The peaks at m/z 300,302 and 304 correspond the molecular ion of 3(-8Z,11Z pentadecadienyl) - phenol, 3(-8Z-pentadecenyl)- phenol, 3(-pentadecyl) phenol respectively and are as a result of fragmentation of the COOH group of anarcardic acid to form cardanol since the identification was done at a high temperature of 100 – 250°C.
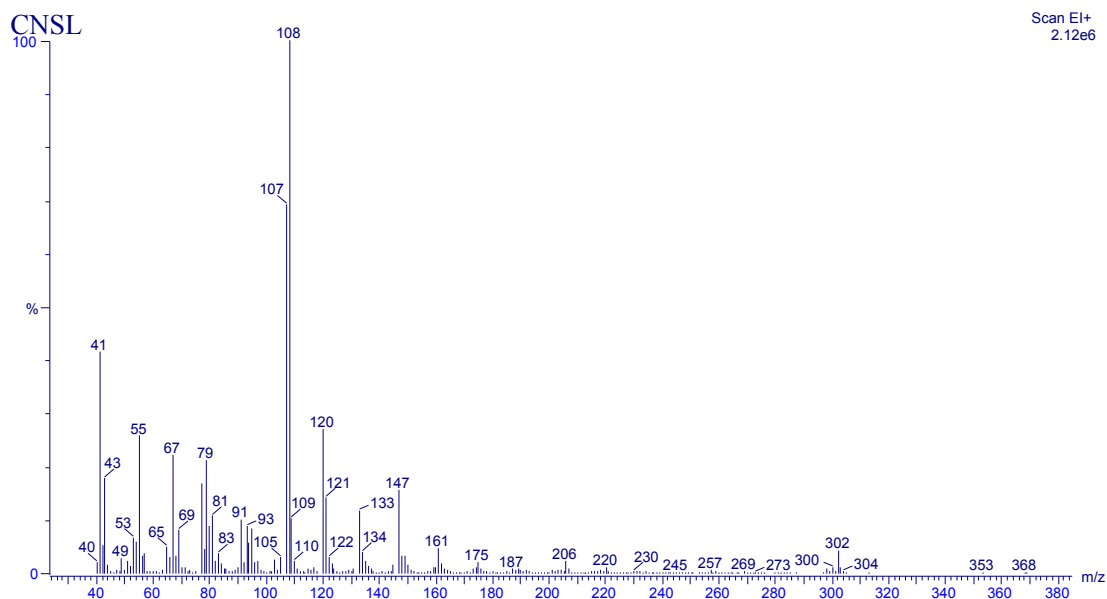
Figure 5: GC MS profile of CNSL
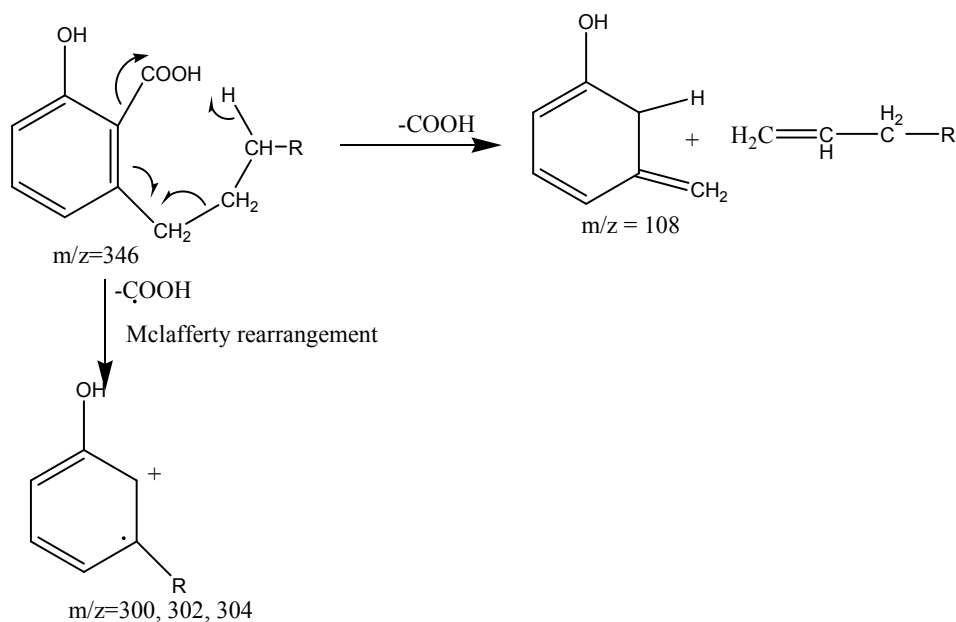
Scheme 1: Fragmentation of anarcardic acid
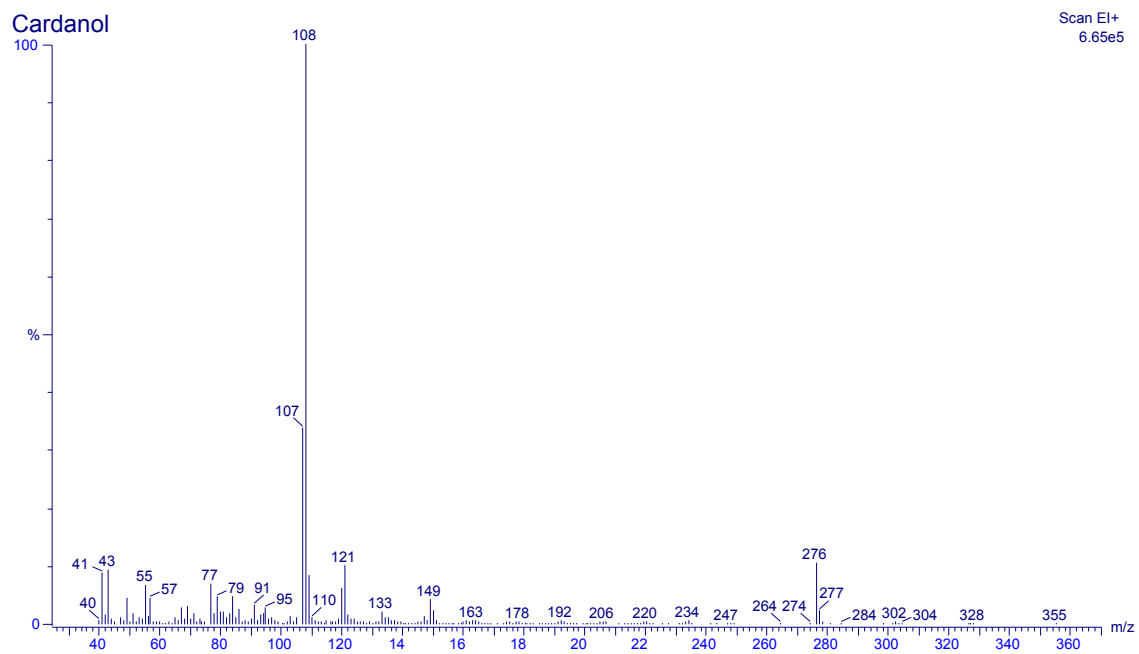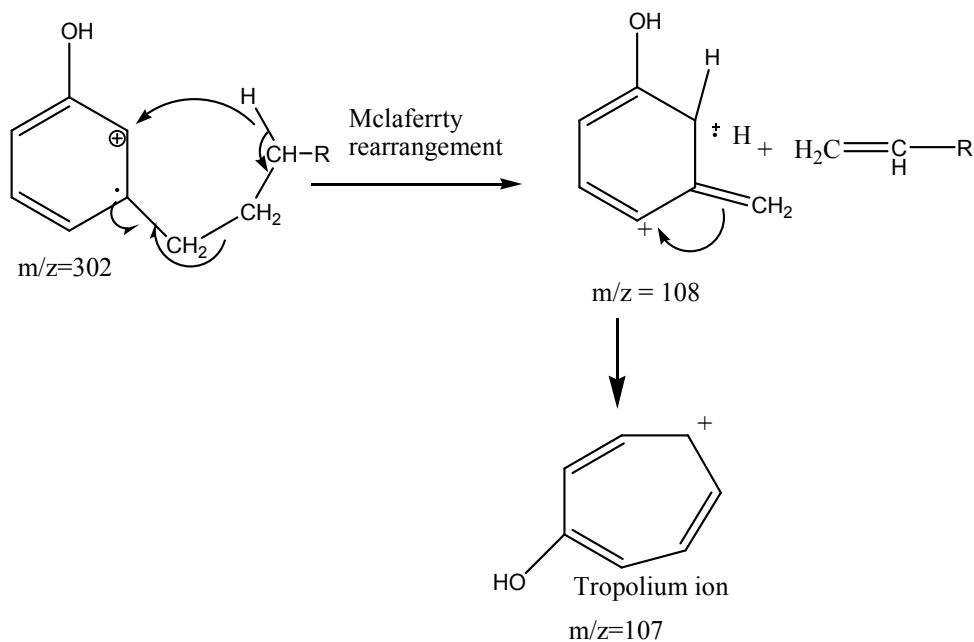
2.8 Interpretation of gc ms Spectra for Cardanol

Figure 6: GC MS spectra 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 7. 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 2: Fragmentation of cardanol

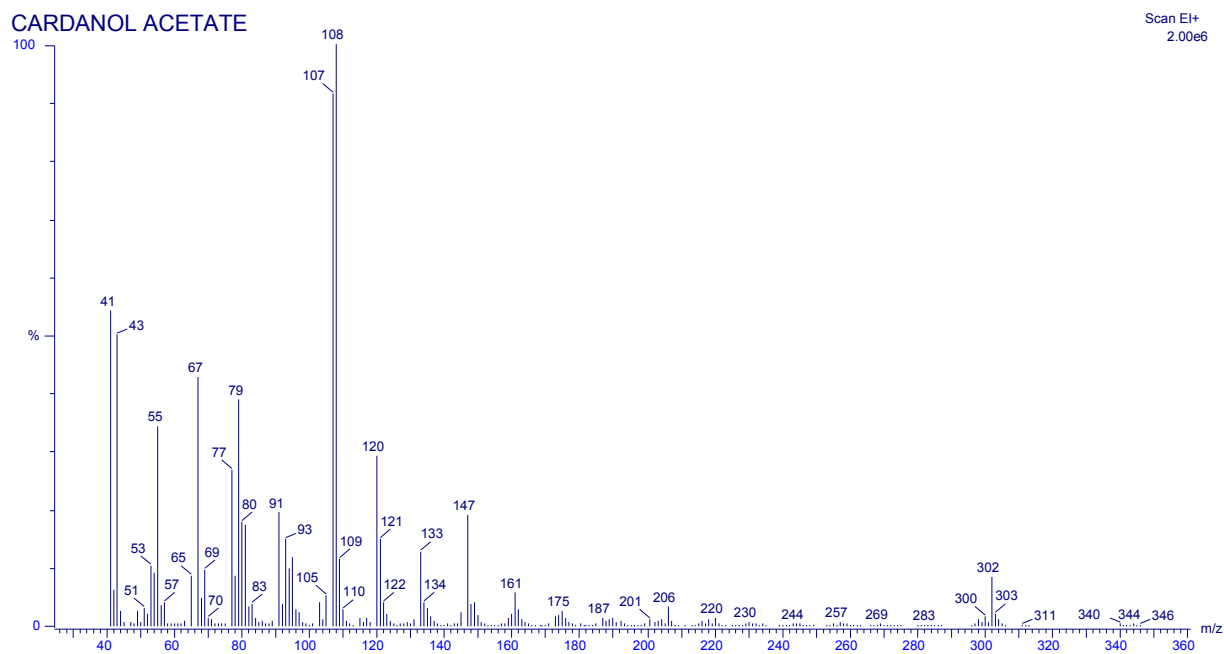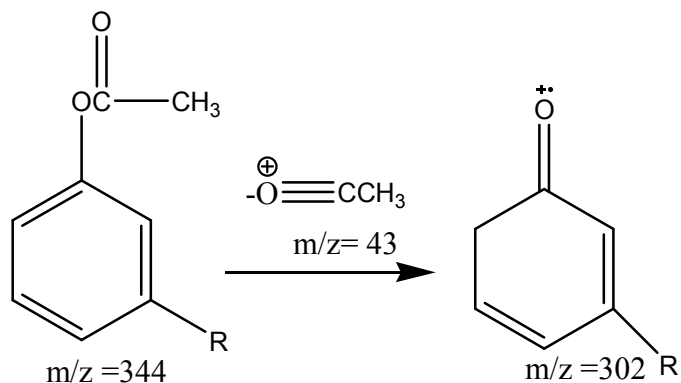## 2.9 Interpretation of gc ms Spectra for Cardanol Acetate

Figure 7: 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 $\overset{+}{C}OCH_3$ 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 3: Fragmentation of cardanol acetate

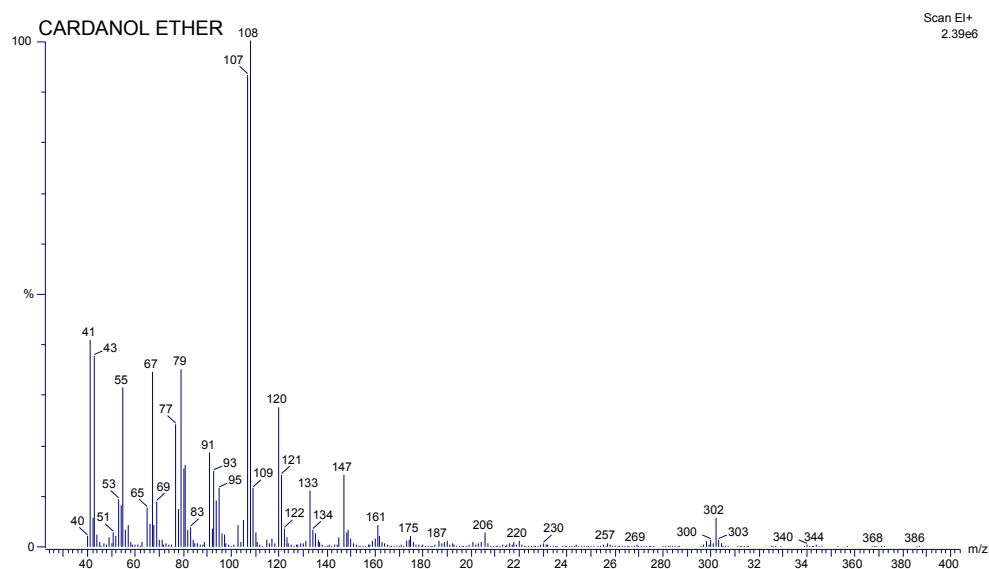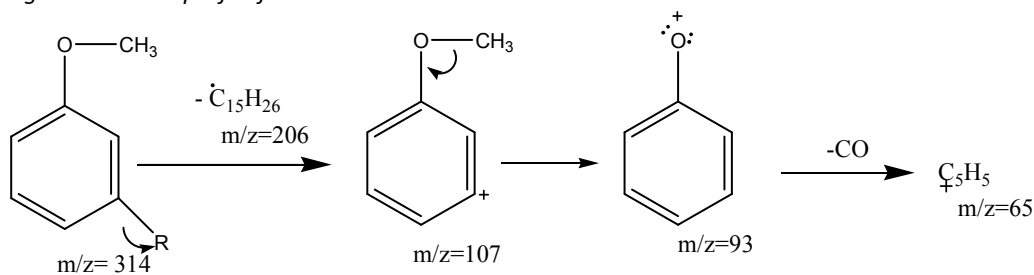## 2.10 Interpretation of gc ms Spectra for Cardanol Ether

Figure 1: GC MS profile for cardanol acetate

Scheme 4: Fragmentation of cardanol acetate

180

3.0   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.

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