

## Synthesis of Semiochemicals and Related Fine Chemicals from Cashew Nut Shell Liquid

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### Abstract

This paper reports on syntheses of 3-hydroxybenzaldehyde (**1**) and tetradecanal (**2**) from the same renewable starting material (cashew nut shell liquid or CNSL), thus demonstrating the potential of the agro-waste cashew nut shells (CNS) as a source of valuable fine and industrial chemicals. The strategy employed in accomplishing the synthesis started with extraction of CNSL followed by isolation of anacardic acid (**4**) and decarboxylation to give cardanol (**5**). Compound **5** was hydrogenated followed by protection of phenolic group to give 3-pentadecylphenyl acetate (**7**). Benzylic oxidation of compound **7** followed by reduction and dehydration resulted into formation of 3-(pentadec-1-en-1-yl)phenol (**9**). Ozonolysis of compound **9** furnished tetradecanal (**2**) and 3-hydroxybenzaldehyde (**1**). Since the transformation of compound **1** to *m*-propylphenol (**3**) has been reported in literature, the synthesis of compound **1** from anacardic acid constitutes a formal synthesis of **3**.

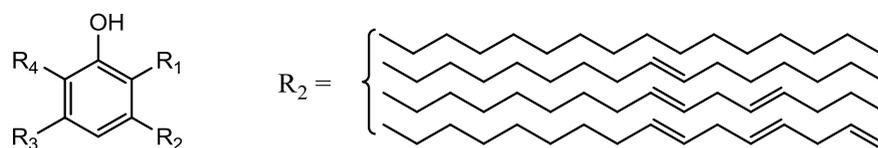
**Keywords:** semiochemicals isocardanol, 3-hydroxybenzaldehyde, *m*-propylphenol, tetradecanal

### Introduction

Beginning from the 1970s, semiochemicals have emerged as prominent alternatives or complements of synthetic pesticides in the battle against numerous pests. Since then, many semiochemicals from different organisms have been identified, synthesized, field-tested and applied in Integrated Pest Management (IPM) programmes. These compounds are very useful due to the fact that most of them are environmentally friendly, harmless to human

health compared to insecticides, volatile, highly specific, effective in small quantities and biodegradable (Heuskin et al. 2011). The simple phenolic compound *m*-propylphenol (**3**) is a component of a kairomone which has been shown to exhibit pheromonal, allomonal and kairomonal properties in different insects.

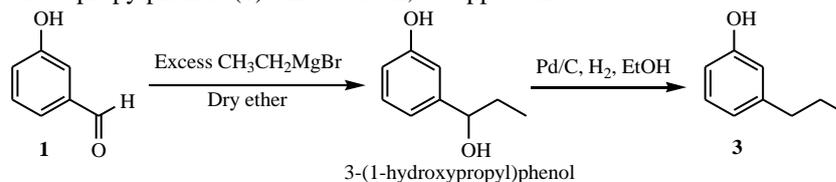
This paper reports on the successful synthesis of 3-hydroxybenzaldehyde (**1**) starting from anacardic acid which is a component of CNSL (Figure 1).



R<sub>1</sub> = CO<sub>2</sub>H, R<sub>3</sub> = R<sub>4</sub> = H: Anacardic acids; R<sub>1</sub> = R<sub>3</sub> = R<sub>4</sub> = H: Cardanols;  
R<sub>1</sub> = R<sub>4</sub> = H, R<sub>3</sub> = OH: Cardols; R<sub>1</sub> = H, R<sub>3</sub> = OH, R<sub>4</sub> = CH<sub>3</sub>: Methyl cardols

**Figure 1:** The sixteen components of cashew nut shell liquid.

Since the synthesis of *m*-propylphenol from compound **1** had been accomplished by Ujváry and Mikite (2003) [Scheme 1], this work, which has employed simple bench top chemistry methods, constitutes a formal synthesis of *m*-propylphenol (**3**). In addition,



**Scheme 1:** Synthesis of 3-propylphenol (**3**) from **1** (Ujváry and Mikite 2003).

Cashew Nut Shells (CNS), an agro-waste of cashew industry, was the source of Cashew Nut Shell Liquid (CNSL) used as starting material for the syntheses of compounds **1** and **2** being reported in this paper. Solvent extraction method was adopted to obtain the cashew nut shell liquid (Gandhi et al. 2012). Isolation of anacardic acid was achieved by precipitating it as calcium anacardate salt by reacting with  $\text{Ca}(\text{OH})_2$ . Treatment of the calcium anacardate cake with HCl followed by workup of the mixture gave the free acid as oil.

## Materials and Methods

### Material, reagents, instruments and general procedures

The cashew nut shells (from *Anacardium occidentale*) left after removal of cashew kernels were collected as industrial waste from Southern Jumbo Cashew Nuts Ltd in Dar es Salaam in October 2013. All chemicals and reagents used were purchased from Sigma Aldrich, South Africa. All glassware apparatus were cleaned and oven dried before use. All organic extracts obtained from aqueous workup of the reaction mixture were dried over anhydrous  $\text{MgSO}_4$ . For product purification column chromatography techniques were employed, whereby 755500 silica gel MFC (about 0.125 to 0.250 mm and 60 to 120 mesh) were used as stationary phases. Reactions' progresses were monitored by Thin Layer Chromatography (TLC) using MERCK 20 cm

the strategy leads to the synthesis of another important semiochemical, the  $\text{C}_{14}$  aldehyde, tetradecanal (**2**). Previously the synthesis of compound **3** from CNSL was reported by Mmongoyo et al. (2012) employing a different approach.

x 20 cm silica gel 60 F<sub>254</sub> plates coated on plastic plates and observed under UV light of 120 volts, 60 Hz and 0.70 Amps. Alpha ATR FT-IR Spectrometer Bruker Optic GmbH 2011 was used for IR data collection. <sup>1</sup>H-NMR spectra were recorded in deuterated chloroform ( $\text{CDCl}_3$ ) at 300/600 MHz on a Bruker A.G. spectrometer with Tetramethylsilane (TMS) as the internal standard and desktop 60 MHz NMReady. Throughout the synthesis, distilled water from Still Aquatron /A4000/ was used. The process of separating the solvent from the products was achieved by rotary evaporator (BUCHI RotarVapor R-205, vacuum controller V-800 Heating bath B-490 and vacuum aspirator B-169).

### Isolation of anacardic acid (**4**)

Cashew nut shells (2500 g) were soaked in 5000 mL of 99% ethanol for three days, decanted to yield 4000 g of the extract and solvent. The extract was concentrated to give 700 g (28%) of CNSL. The extracted CNSL (50 g) was dissolved in 300 mL of 5% aqueous methanol followed by addition of 5 g of calcium hydroxide over 15 minutes while stirring. The temperature of the reaction mixture was raised and maintained at 50 °C for 3 hours. The precipitates formed were filtered, washed through with 50 mL methanol and dried in an oven for 2 hours to give about 34 g of calcium anacardate. Anacardic acid was obtained from the calcium salt by adopting the

method used by Paramashivappa et al. (2001): Calcium anacardate precipitates obtained were suspended in 250 mL of 6 M HCl and stirred for 1 hour. The solution obtained was extracted with 75 mL x 3 ethyl acetate and the combined organic layer was washed with distilled water (50 mL x 3), dried over anhydrous magnesium sulphate and filtered. The organic layer obtained was concentrated under reduced pressure to give anacardic acid (**4**) (30 g, 97.17% yield) as viscous brown oil. FT-IR: (film): 3231-2550  $\text{cm}^{-1}$ , 3007.65  $\text{cm}^{-1}$ , 2923.19  $\text{cm}^{-1}$ , 2852.96  $\text{cm}^{-1}$ , 1643.96  $\text{cm}^{-1}$ , 1606.83  $\text{cm}^{-1}$ , 1576.58  $\text{cm}^{-1}$ , 1446.36  $\text{cm}^{-1}$ .

#### Synthesis of cardanol (**5**)

Thermo-labile anacardic acid (**4**) obtained was converted to key intermediate cardanol (**5**) which has structural resemblance with the target semiochemicals. Decarboxylation was achieved by heating 25 g of compound (**4**) at 200 °C for 2 hours. The whole process was performed in a sand bath under solvent free condition (Njuku et al. 2014). Cardanol (20 g, 91.65%) was obtained as amber coloured oil. FT-IR (film): 3426.27  $\text{cm}^{-1}$ , 3007.88  $\text{cm}^{-1}$ , 2923.13  $\text{cm}^{-1}$ , 2852.92  $\text{cm}^{-1}$ , 1712.19  $\text{cm}^{-1}$ , 1663.80  $\text{cm}^{-1}$ , 1607.26  $\text{cm}^{-1}$ , 1588.57  $\text{cm}^{-1}$ , 1452.79  $\text{cm}^{-1}$ .

#### Synthesis of 3-pentadecylphenol (**6**)

Cardanol (**5**), obtained above was the natural mixture whose  $\text{C}_{15}$  side chain consists of saturated, monoene, diene and triene components. The mixture (20 g) was dissolved in methanol followed by addition of Pd/C catalyst. Hydrogen gas was then bubbled into this solution for two hours. The product obtained was filtered in a vacuum pump to afford 18 g (90%) of 3-pentadecylphenol (Somboonthanakij et al. 2007). FTIR (film): 3396.20  $\text{cm}^{-1}$ , 2922.09  $\text{cm}^{-1}$ , 2852.25  $\text{cm}^{-1}$ , 1672.13  $\text{cm}^{-1}$ , 1608.98  $\text{cm}^{-1}$ , 1588.10  $\text{cm}^{-1}$ , 1453.64  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 0.92 (t,  $J$  = 8, 3H), 1.34 (m, 20 H), 1.70 (m, 2H), 2.03 (m, 4H), 2.59 (t,  $J$  = 7.0, 2H), 4.75

(s, 1H), 5.40 (d, 1H), 6.67 (s, 1H), 6.80 (d,  $J$  = 7.5, 1H), 7.18 (t,  $J$  = 7.5, 1H).

#### Synthesis of 3-pentadecylphenyl acetate (**7**)

At room temperature, 1.824 g (6 mmol) of saturated cardanol (**6**) was mixed with acetic anhydride (0.21 g, 30 mmol) and stirred for 24 hours while monitoring the reaction progress by TLC. The reaction mixture was diluted with 10% aqueous sodium hydrogen carbonate and the organic phase was extracted with dichloromethane (3 x 50 mL) and dried over  $\text{MgSO}_4$ . The product obtained was recrystallized from a mixture of hexane and ethyl acetate to give pure compound **7** (1.5 g, 72.25% yield) as described by Heravi et al. (2007). FTIR (film): 2957.32  $\text{cm}^{-1}$ , 2914.16  $\text{cm}^{-1}$ , 2848.72  $\text{cm}^{-1}$ , 1756.02  $\text{cm}^{-1}$ , 1738.02  $\text{cm}^{-1}$ , 1611.62  $\text{cm}^{-1}$ , 1587.41  $\text{cm}^{-1}$ , 1486.95  $\text{cm}^{-1}$ , 1470.96  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 0.87 (t,  $J$  = 7.8, 3H), 1.31 (m, 24H), 1.59 (m, 2H), 2.28 (s, 3H), 2.59 (t,  $J$  = 7.1, 2H), 6.89 (d,  $J$  = 7.5, 1H), 7.04 (d,  $J$  = 7.5, 1H), 7.26 (m, 2H).

#### Synthesis of 3-pentadecanoylphenyl acetate (**8**)

Using pestle and mortar, 3.0 g of potassium permanganate was ground to fine powder and mixed with 0.4 g of 'active' manganese dioxide. 30 mL of methylene chloride was added to the mixture followed by addition of pentadecylphenyl acetate (1.386 g, 4 mmol) and stirred. At the fourth hour, 3 drops of sulfuric acid were added followed by another 3 drops at the eighth hour. The reaction mixture was stirred continuously at room temperature for 48 hours. After completion of the reaction, 15 mL of methylene chloride were added to the reaction mixture followed by filtration. The residues were washed with additional methylene chloride (2 x 10 mL) and the combined organic solution obtained was dried with anhydrous magnesium sulfate and concentrated in rotary evaporator to give 1.08 g (75% yield) of 3-pentadecanoylphenyl acetate. FTIR (film): 2922.15  $\text{cm}^{-1}$ , 2852.50  $\text{cm}^{-1}$ ,

1767.52  $\text{cm}^{-1}$ , 1738.69  $\text{cm}^{-1}$ , 1711.57  $\text{cm}^{-1}$ , 1610.77  $\text{cm}^{-1}$ , 1587.39  $\text{cm}^{-1}$ , 1456.07  $\text{cm}^{-1}$ , 1446.59  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 0.88 (t,  $J$  = 7.0, 3H), 1.26 (m, 22H), 1.72 (m, 2H), 2.32 (s, 3H), 2.93 (t,  $J$  = 7.1, 2H), 7.30 (d,  $J$  = 7.4, 1H), 7.46 (t,  $J$  = 7.5, 1H), 7.84 (s, 1H), 7.87 (d,  $J$  = 7.4 1H).

#### Synthesis of 3-(pentadec-1-en-1-yl)phenol (9)

Compound **8** was reduced and dehydrated to give compound **9** by adopting the procedure of Zeynizadeh and Behyar (2005). Compound **8** (0.722 g, 2 mmol) was placed in a round bottomed flask and mixed with wet  $\text{SiO}_2$  (0.26 g, 30% w/w) followed by three drops of dilute sulphuric acid and stirred for 5 minutes. To the mixture was added fine powder of  $\text{NaBH}_4$  (0.152 g, 4 mmol) while stirring in an oil bath at 80 °C for further 20 min. The progress of the reaction was monitored by TLC. At the end of reaction the mixture was cooled and washed with dichloromethane (3 x 6 mL) and dried over anhydrous  $\text{MgSO}_4$ . The resulting crude product was purified in a short column over silica gel (hexane/ethyl acetate, 5:1) to give 0.36 g, (59.1% over four steps) of compound **9** from calcium anacardate. FTIR (film): 3345.68  $\text{cm}^{-1}$ , 2916.12  $\text{cm}^{-1}$ , 2849.24  $\text{cm}^{-1}$ , 1589.74  $\text{cm}^{-1}$  and 1457.46  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 0.89 (t,  $J$  = 7.0, 3H), 1.31 (m, 20H), 1.45 (m, 2H), 2.17 (m, 2H), 2.31 (s, 1H), 6.21 (m, 1H), 6.33 (d,  $J$  = 15.0, 1H), 6.73 (d,  $J$  = 7.5, 1H), 6.75 (d,  $J$  = 7.4, 1H), 6.89 (m, 1H), 7.27 (s, 1H).

#### Synthesis of 3-hydroxybenzaldehyde (1) and Tetradecanal (2)

Ozonolysis was carried out by adopting the method of Schiaffo and Dussault (2008). The substrate **9** (0.30 g, 0.99 mmol) was introduced in a round bottomed flask containing 6.62 mL of 95:5 acetone/water (v/v), followed by addition of Sudan III indicator. The solution was cooled in an ice bath to 0 °C and a stream of  $\text{O}_3/\text{O}_2$  (approximately 0.5 mmol/min  $\text{O}_3$ ) was bubbled into the reaction solution for 2 hours. The crude solution obtained was worked up by diluting with 25 mL of water and the resulting solution was extracted with  $\text{CH}_2\text{Cl}_2$  (2 x 25 mL). The product was separated and purified via flash chromatography with ether/hexane to give 3-hydroxybenzaldehyde. 0.06 g (49.50%) and tetradecanal 0.16 g (75.99%) FT-IR (film): of 3-hydroxybenzaldehyde and tetradecanal are: 3374.34  $\text{cm}^{-1}$ , 2953.01  $\text{cm}^{-1}$ , 2917.47  $\text{cm}^{-1}$ , 2849.68  $\text{cm}^{-1}$ , 1706.21  $\text{cm}^{-1}$ , 1607.61  $\text{cm}^{-1}$  and 2992.26  $\text{cm}^{-1}$ , 2951.44  $\text{cm}^{-1}$ , 1725.50  $\text{cm}^{-1}$ , 1447.37  $\text{cm}^{-1}$  and 1435.09  $\text{cm}^{-1}$ , respectively.

$^1\text{H}$  NMR (60 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 3.32 (s, 1H), 7.14-7.42 (m, 4H), 10.02 (s, 1H) for 3-hydroxybenzaldehyde and:  $\delta_{\text{H}}$  = 0.88 (t,  $J$  = 8.0, 3H), 1.26-2.42 (m, 24H) and 9.77 (1H) for tetradecanal. GC-MS Spectral technique analysis for compound **1** showed single strong peak at retention time 15.505 min and base peak 122.10 as shown in Figures 2(a) and 2(b) while compound **2** showed single strong peak at retention time 20.08 min and base peak 57.05 as indicated in the Figures 3(a) and 3(b).

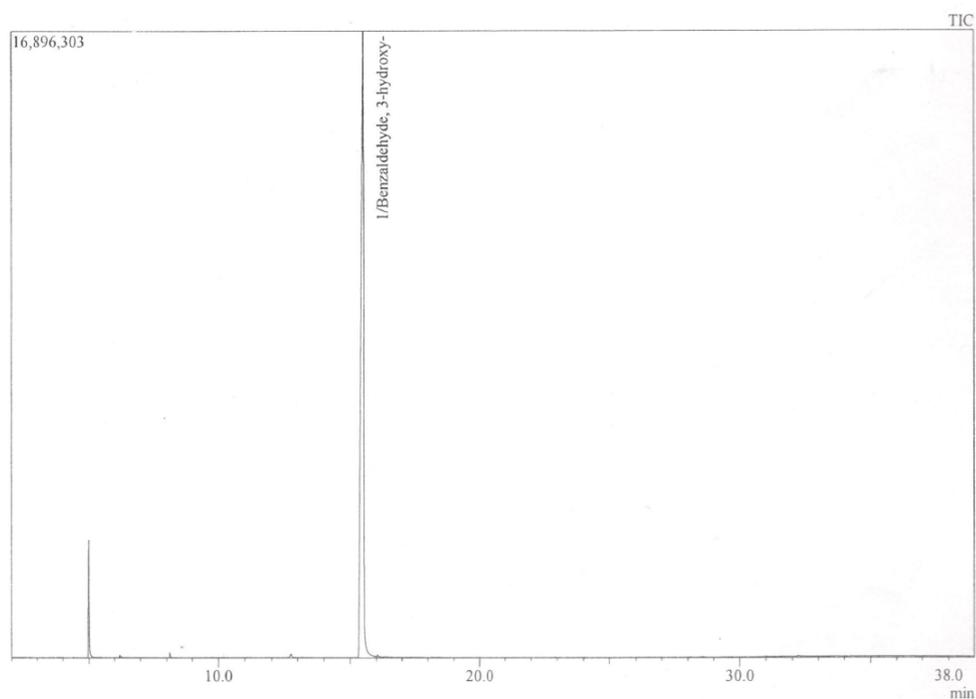


Figure 2(a): GC chromatogram for compound 1.

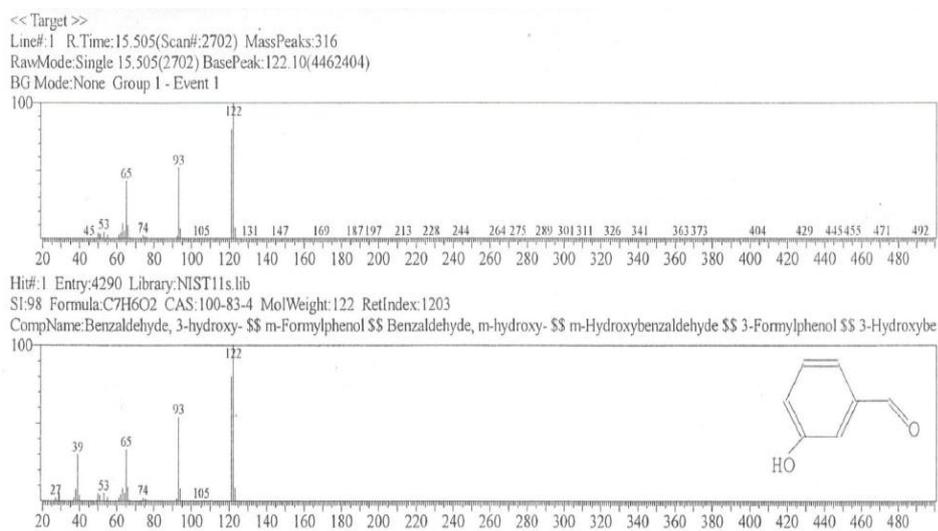


Figure 2(b): MS spectrum for compound 1.

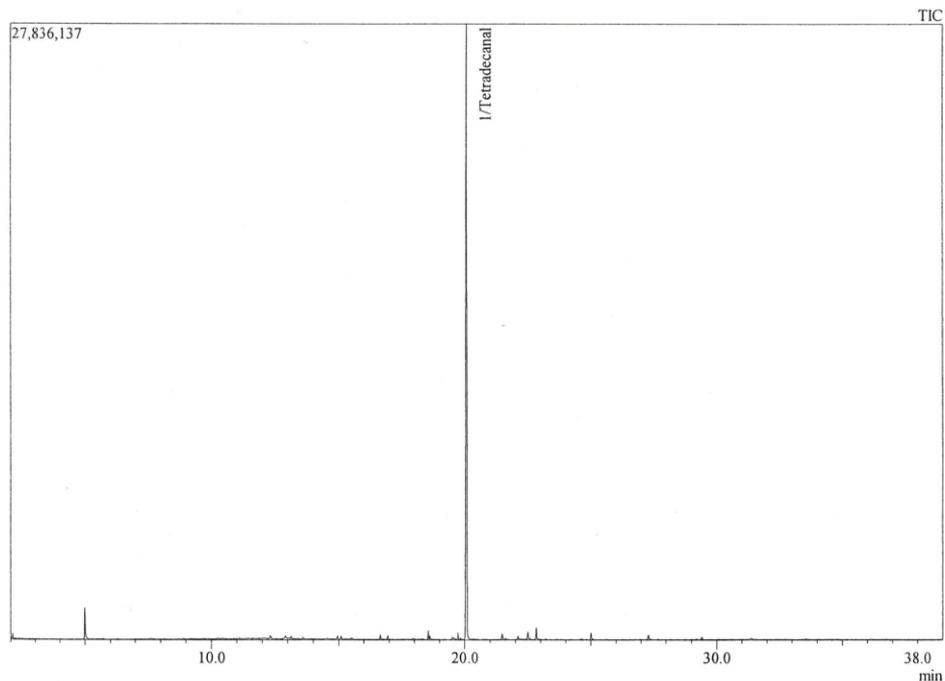
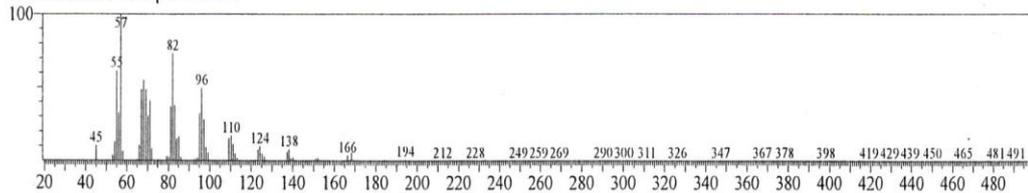


Figure 3(a): GC chromatogram for compound 2.

<< Target >>

Line#: 1 R. Time: 20.080(Scan#: 3617) MassPeaks: 333  
RawMode: Single 20.080(3617) BasePeak: 57.05(3061726)  
BG Mode: None Group 1 - Event 1



Hit#: 1 Entry: 19156 Library: NIST11s.lib  
SI: 97 Formula: C14H28O CAS: 124-25-4 MolWeight: 212 RetIndex: 1601  
CompName: Tetradecanal \$\$ Myristaldehyde \$\$ Myristylaldehyde \$\$ Tetradecylaldehyde \$\$ n-Tetradecanal \$\$ Aldehyde C-14 \$\$ Aldehyde C-14, myristic S

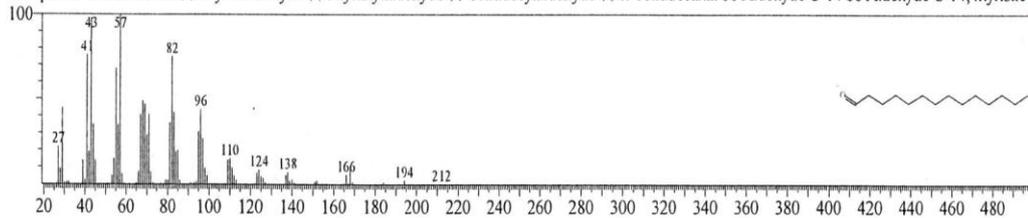


Figure 3(b): MS spectrum for compound 2.

## Results and Discussion

### Synthesis of 3-(pentadec-1-en-1-yl)phenol (9) from CNSL

The infra-red broad absorption band at 3231-2550  $\text{cm}^{-1}$  (*s*) indicated the presence of O-H stretch for a carboxylic acid group. A sharp absorption band at 3007.65  $\text{cm}^{-1}$  was due to a C-H stretch of  $\text{sp}^2$  hybridized carbon, whereas absorption bands at 2923.19  $\text{cm}^{-1}$  (*s*) and 2852.96  $\text{cm}^{-1}$  (*s*) are attributed to a C-H stretch of  $\text{sp}^3$  hybridized carbon. Furthermore, the band at 1643.96  $\text{cm}^{-1}$  (*m*) corresponded to a C=C stretch of alkenes and the band at 1606.83  $\text{cm}^{-1}$  (*m*) is for the C=C stretch of aromatic ring.

Decarboxylation of compound **4** converted it to cardanol (**5**) [Scheme 2]. This process removed the carboxyl functional group as carbon dioxide in form of effervescences. The fact that decarboxylation had occurred was deduced from the FT-IR spectrum of the product which showed disappearance of the broad strong band at 3231.49 to 2550.43  $\text{cm}^{-1}$  as the key absorption peak for carboxylic acid. The strong absorption band at 3426.27  $\text{cm}^{-1}$  is due to phenolic O-H stretch where as the band at 3007.88  $\text{cm}^{-1}$  (*s*) is due to C-H stretch of  $\text{sp}^2$  hybridized carbon indicating presence of unsaturation in  $\text{C}_{15}$  side chain and the band at 1607.26  $\text{cm}^{-1}$  (*m*) indicated C=C stretch of aromatic moiety. The FT-IR spectral data as whole confirmed the formation of cardanol (**5**).

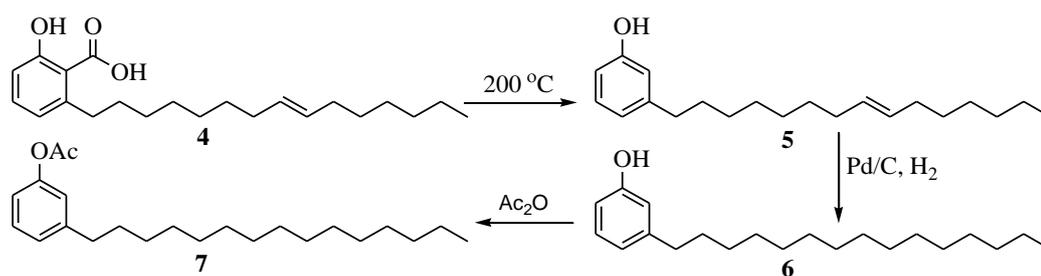
The cardanol obtained following decarboxylation was bubbled with hydrogen gas in the presence of Pd/C catalyst to saturate the  $\text{C}_{15}$  side chain. The product formed was characterized by IR spectroscopy, which indicated disappearance of a C-H absorption band for hydrogen of  $\text{sp}^2$  hybridized carbon at 3007.88  $\text{cm}^{-1}$  and retention of strong broad band for O-H stretch at 3396.20  $\text{cm}^{-1}$  (*s*), 2922.19  $\text{cm}^{-1}$  and 2852.25  $\text{cm}^{-1}$  for C-H stretch for hydrogens on  $\text{sp}^3$  hybridized carbons. Also the band at 1606.83  $\text{cm}^{-1}$  (*m*) for the aromatic C=C stretch was retained in the hydrogenated product. The hydroxyl group in 3-pentadecylphenol (**6**) obtained was protected so

as to prevent its involvement in subsequent reactions. The protection was effected through acetylation using acetic anhydride to obtain 3-pentadecylphenyl acetate (**7**). The FT-IR spectrum for compound **7** showed absorption band at 1756.02  $\text{cm}^{-1}$  due to ester carbonyl C=O stretch. The C-O stretch appeared at 1203.79  $\text{cm}^{-1}$  and 1141.54  $\text{cm}^{-1}$  and the disappearance of absorption band at 3396.20  $\text{cm}^{-1}$  indicated full protection of the hydroxyl group following acetylation. The C-H stretch of the hydrogen on  $\text{sp}^3$  hybridized carbon was observed at 2914.16  $\text{cm}^{-1}$ , while the C=C stretch due to the aromatic ring appeared at 1587.41  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum for compound **7** [see Scheme 3 for carbon atom numbering] exhibited a singlet signal for the  $\text{CH}_3$  protons of the acetate group at  $\delta_{\text{H}}$  2.28 ppm (H-1) and a triplet signal at  $\delta_{\text{H}}$  0.877 (H-23) for three protons located at the terminal  $\text{CH}_3$  of pentadecyl side chain, two multiplet at  $\delta_{\text{H}}$  1.31 ppm and 1.59 ppm were observed for methylene protons H-11 to H-22 and H-10, respectively. The signal for benzylic protons appeared as triplet at  $\delta_{\text{H}}$  2.59 ppm (H-9) while aromatic protons appeared as doublets at  $\delta_{\text{H}}$  6.89 ppm (H-6) and  $\delta_{\text{H}}$  7.04 ppm (H-8) and multiplet at  $\delta_{\text{H}}$  7.26 ppm for both (H-7 & 4).

The oxidation at benzylic carbon under solvent-free condition in which 3-pentadecylphenyl acetate (**7**) was oxidized with  $\text{KMnO}_4$  supported on active manganese dioxide in methylene chloride catalyzed with few drops of sulfuric acid gave the reasonable yield. The FT-IR spectrum for compound **8** showed long and sharp absorption peak at 1711.57  $\text{cm}^{-1}$  indicating C=O stretch of carbonyl functional group formed following oxidation. Absorption peaks at 1767.52  $\text{cm}^{-1}$  and 1738.69  $\text{cm}^{-1}$  showed the persistence of the acetate group during the oxidation. The absorption bands at 2922.15  $\text{cm}^{-1}$  and 2852.50  $\text{cm}^{-1}$  indicated C-H stretch in the side chain alkyl group, while the existence of the benzene ring was identified by the peak at 1587.39  $\text{cm}^{-1}$ . The  $^1\text{H}$ -NMR spectrum for compound **8** showed a signal for the three  $\text{CH}_3$  protons of

the acetyl group as a singlet at  $\delta_H$  2.32 ppm (H-1, See **Scheme 3** for carbon atom numbering). The protons for the terminal  $CH_3$  group (H-23) appeared as a triplet at  $\delta_H$  0.88 ppm. The methylene ( $CH_2$ ) groups' signal appeared at  $\delta_H$  1.26 ppm as a multiplet. The two protons

adjacent to the newly formed keto functional group (H-10) appeared as a triplet at  $\delta_H$  2.93 ppm. Aromatic protons appeared as follows: a singlet at  $\delta_H$  7.84 ppm (H-4), doublets at  $\delta_H$  7.87 and 7.30 ppm (H-6 & 8) and a triplet at  $\delta_H$  7.46 ppm (H-7).



**Scheme 2:** Synthesis of 3-pentadecylphenyl acetate (7).

Reduction of compound **8** using the relatively mild reducing agent  $NaBH_4$  with inexpensive and readily available wet  $SiO_2$  under solvent-free condition (Shaabani et al. 2004) resulted into formation of compound **9**, which was the key intermediate toward the targeted semiochemicals **1** and **2**. The successfully reduced keto group of compound **8** gave an alcohol which was dehydrated with dilute sulfuric acid *in situ* to form 3-(pentadec-1-en-1-yl)phenol (**9**). The purification of the product was done through flash column chromatography on silica gel. The IR spectrum of product **9** showed the disappearance of the band at  $1711.57\text{ cm}^{-1}$ , indicating that the keto  $C=O$  group had been reduced. Formation of a new band at  $3345.68\text{ cm}^{-1}$  and disappearance of absorption bands at  $1767.52\text{ cm}^{-1}$  and  $1738.69\text{ cm}^{-1}$  is an indication of reformation of O-H function group initially protected as the acetate group in compound **8**. The  $^1H$  NMR spectrum of compound **9** (See **Scheme 3** for carbon atom numbering) showed signals for the aromatic protons at  $\delta_H$  6.73 and 6.75 ppm as doublets having a single proton each (H-4 and H-6). The other aromatic proton signals appeared at  $\delta_H$  6.89 ppm (H-5) and 7.27 ppm (H-2) as a multiplet and a singlet, respectively. A doublet signal at  $\delta_H$  6.33 ppm (H-7) was assigned to the benzylic proton. The proton of

the hydroxyl group (H-1) appeared as a singlet at  $\delta_H$  2.31 ppm, whereas the methylene ( $CH_2$ ) groups' protons appeared as multiplet at  $\delta_H$  1.31 ppm. The terminal methyl group protons (H-21) of the pentadecenyl side chain were observed as triplet of three protons at  $\delta_H$  0.89 ppm.

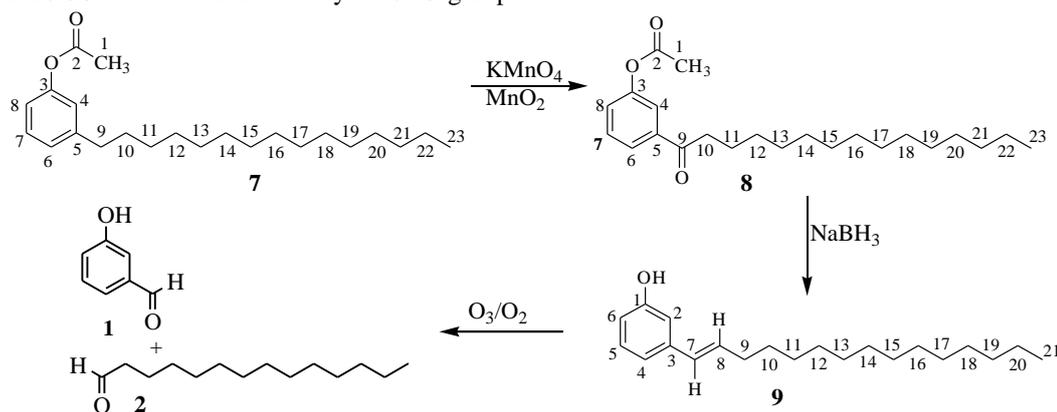
#### Synthesis of 3-hydroxybenzaldehyde (**1**) and tetradecanal (**2**)

The major targets for this study were 3-hydroxybenzaldehyde (**1**) and tetradecanal (**2**). A successful preparation of aldehyde **1** would constitute a formal synthesis of *m*-propylphenol (**3**). On the other hand, tetradecanal (**2**) is a semiochemical in its own right. Thus, ozonolysis of compound **9** using acetone as solvent formed compounds **1** and **2** (**Scheme 3**). Acetone was the preferred solvent because it is ozone stable at low temperature. The structural elucidations of compounds **1** and **2** were carried out by employing different spectroscopic techniques. The FT-IR spectrum of 3-hydroxybenzaldehyde (**1**) showed newly formed aldehyde ( $-CHO$ ) functional group due to presence of an absorption band at  $1706.21\text{ cm}^{-1}$ . The absorption band at  $3374.34\text{ cm}^{-1}$  was due to OH vibration and the absorption band at  $1607.61\text{ cm}^{-1}$  was assigned to  $C=C$  stretching vibration in the aromatic ring.  $^1H$  NMR

spectral data also gave evidence to formation of compound **1**. The spectrum exhibited three proton signals. A signal at  $\delta_{\text{H}}$  3.32 ppm appeared as singlet (1 H) due to proton of the hydroxyl group. It was observed that the aromatic ring displayed multiplet proton signal (4 H) appearing between  $\delta_{\text{H}}$  7.17 and 7.42 ppm. A signal at  $\delta_{\text{H}}$  10.02 ppm appeared as singlet (1 H) and was assigned for the proton of the aldehyde group. GC-MS spectra of compound **1** exhibited strong peak at retention time of 15.505 min and base peak at  $m/z$  122.10, with the assistance of NIST library software of the technique the compound's molecular formula and weight were found to be  $\text{C}_7\text{H}_6\text{O}_2$  and 122, respectively.

The second product from the ozonolysis reaction exhibited an IR absorption band at  $1725.50\text{ cm}^{-1}$  due to the aldehydic  $\text{C}=\text{O}$  group.

The absence of absorption band around  $1600\text{ cm}^{-1}$  indicated absence of benzene ring and, thus pointing to the  $\text{C}_{14}$  aldehyde **2**. Likewise, the  $^1\text{H}$  NMR spectrum displayed a triplet at  $\delta_{\text{H}}$  0.88 ppm (3 H) due to the terminal methyl proton. A multiplet at  $\delta_{\text{H}}$  1.26-2.42 ppm (24 H) was assigned for methylene protons and the singlet at  $\delta_{\text{H}}$  9.77 ppm (1 H) was assigned for the proton of the aldehyde group. These spectral data provided evidence for compound **2** as the second product of the ozonolysis reaction. GC-MS spectra of compound **2** showed strong peak at retention time of 20.080 min and base peak at  $m/z$  57.05, with the aid of the NIST library software of the technique the compound molecular formula identified was found to be  $\text{C}_{14}\text{H}_{28}\text{O}$  and the molecular weight was 212.



**Scheme 3:** Synthesis of 3-hydroxybenzaldehyde (**1**), tetradecanal (**2**) and carbon atom numbering.

### Conclusion

The paper has reported on the syntheses of expensive semiochemicals 3-hydroxybenzaldehyde (**1**) and tetradecanal (**2**) from anacardic acid while maximizing atom economy. The successful synthesis of these important agro-chemicals has demonstrated once again the potential of CNS/CNSL as industrial raw materials. The key feature of the synthesis involved the simultaneous reduction-dehydration of benzylic ketone to alkene in one step.

### Declaration of Competing or Conflict of Interest

The authors declare that there is no competing or conflict of interest.

### References

- Gandhi T, Patel M and Dholakiya BK 2012 Studies on effect of various solvents on extraction of cashew nut shell liquid (CNSL) and isolation of major phenolic constituents from extracted CNSL. *J. Nat. Prod. Plant Resour.* 2: 135-142.

- Heravi MM, Behbahani FK and Bamoharram FF 2007 Acetylation of alcohols, phenols and salicylic acid by heteropoly acid in acetic anhydride: A green and eco-friendly protocol for synthesis of acetic salicylic acid (aspirin). *Arkivoc* xvi: 123-131.
- Heuskin S, Verheggen FJ, Haubruge E, Wathelet JP and Lognay G 2011 The use of semiochemical slow-release devices in integrated pest management strategies. *J. Biotechnol. Agron. Soc. Environ.* 15: 459-470.
- Mmongoyo JA, Mgani QA, Mdachi SJM, Pogorzelec PJ and Cole-Hamilton DJ 2012 Synthesis of kairomone and other chemicals from cardanol, a renewable resource. *Eur. J. Lipid Sci. Technol.* 114: 1183-1192.
- Njuku FW, Mwangi PM and Thiong'o GT 2014 Evaluation of cardanol acetate a reactive diluent for alkyd coatings. *Int. J. Adv. Res.* 2: 928-941.
- Paramashivappa R, Kumar PP, Vithayathil PJ and Rao SA 2001 Novel method for isolation of major phenolic constituents from cashew (*Anacardium occidentale* L.) nut shell liquid. *J. Agric. Food Chem.* 49: 2548-2551.
- Schiaffo CE and Dussault PH 2008 Ozonolysis in solvent/water mixtures: direct conversion of alkenes to aldehydes and ketones. *J. Org. Chem.* 73: 4688-4690.
- Shaabani A, Mirzaei P and Lee DG 2004 The beneficial effect of manganese dioxide on the oxidation of organic compounds by potassium permanganate. *Catal. Lett.* 97: 119-123.
- Somboonthanakij S, Mekasuwandumrong, Panpranot J, Nimmanwudtipong T, Strobel R, Pratsinis SE, Prasertdam P 2007 Characteristics and catalytic properties of Pd/SiO<sub>2</sub> synthesized by one-step flame spray pyrolysis in liquid-phase hydrogenation of 1-heptyne. *Catal. Lett.* 119: 346-352.
- Ujváry I and Mikite G 2003 A practical synthesis of 3-*n*-propylphenol, a component of tsetse fly attractant blends, *Org. Process. Res. Dev.* 7: 585-587.
- Zeynizadeh B and Behyar T 2005 Fast and efficient method for reduction of carbonyl compounds with NaBH<sub>4</sub>/wet SiO<sub>2</sub> under solvent free condition. *J. Braz. Chem. Soc.* 16: 1200-1209.