

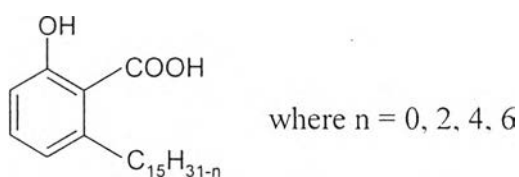


## CHAPTER IV

### RESULTS AND DISCUSSION

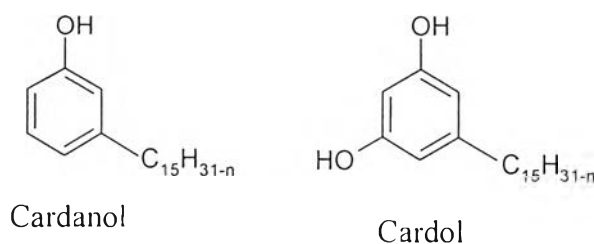
#### 4.1 The CNSL and decarboxylated CNSL

Cashew nut shell liquid (CNSL) was obtained from the hexane extracts of spongy layers of cashew nut shells (*Anacardium occidentale*). It was a dark brown viscous liquid, insoluble in water, freely soluble in organic solvents, alcohol, and petroleum ether. Its major component was anacardic acid, whose structure is shown below.



The infrared spectrum of CNSL (Fig. 4-1) showed absorption peaks at  $3300\text{-}2500\text{ cm}^{-1}$  (OH-stretching of carboxylic acid),  $3016\text{ cm}^{-1}$  and  $2929\text{ cm}^{-1}$  ( $=\text{C-H}$  stretching of aromatic),  $2852\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1649\text{ cm}^{-1}$  (C=O stretching of carboxylic acid),  $1608\text{ cm}^{-1}$  and  $1454\text{ cm}^{-1}$  (C=C ring stretching of aromatic), and  $1311\text{ cm}^{-1}$  and  $1250\text{ cm}^{-1}$  (C-O stretching). Moreover, the  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ ) of CNSL showed prominently a signal of the C=O group of a carboxylic acid at  $\delta_{\text{C}} 176.0\text{ ppm}$  (Fig. 4-2).

CNSL was decarboxylated by heating at 110 °C for 3 hrs to yield decarboxylated CNSL, which was a dark brown viscous liquid, freely soluble in organic solvents, and alcohol. TLC on silica gel (25% ethyl acetate in hexane) revealed two major products (intense UV absorption) with the  $R_f$  value of 0.52 and 0.64; these two products were probably cardanol and cardol, whose structures are depicted below.



where  $n = 0, 2, 4, 6$

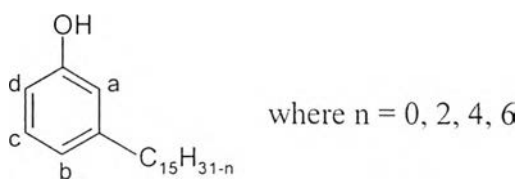
The infrared spectrum of decarboxylated CNSL (Fig. 4-3) showed absorption peaks at  $3354\text{ cm}^{-1}$  (O-H stretching of phenol),  $3011\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2929\text{ cm}^{-1}$  and  $2852\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1603\text{ cm}^{-1}$  and  $1465\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1352\text{ cm}^{-1}$  (O-H bending of phenol), and  $1265\text{ cm}^{-1}$  (C-O stretching of phenol). No C=O absorption at  $1630\text{-}1700\text{ cm}^{-1}$  (C=O stretching of carboxylic acid) was observed. The  $^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ ) of decarboxylated CNSL did not show the C=O signal of the carboxylic acid (Fig. 4-4).

Both  $^{13}\text{C}$ -NMR data and infrared spectral data of decarboxylated CNSL conclusively confirmed that anacardic acid was completely decarboxylated to cardanol.

## 4.2 Cardanol

The decarboxylated CNSL was partially purified by reacting dihydric phenol (e.g. cardol and 2-methylcardol) with formaldehyde and diethylenetriamine to give high molecular weight products while leaving cardanol unreacted. As a result, cardanol was removed from the reaction after working up. TLC analysis revealed that this residue contained mainly cardanol, with a small amount of cardol and unidentified polar compounds.

Partially purified cardanol was obtained as light brown and less viscous liquid. The structure of cardanol is shown below.



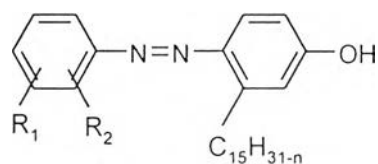
The infrared spectrum of partially purified cardanol (Fig 4-5) showed absorption peaks at  $3354\text{ cm}^{-1}$  (O-H stretching of phenol),  $3010\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2921\text{ cm}^{-1}$  and  $2859\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1598\text{ cm}^{-1}$  and  $1457\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1369\text{ cm}^{-1}$  (O-H bending of phenol), and  $1264\text{ cm}^{-1}$  (C-O stretching of phenol).

The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol (Fig. 4-6) showed signals at the positions a, b, c, and d at  $\delta_H$  6.70 (*br s*), 6.80 (*d*, 7.5 Hz), 7.10 (*t*, 7.6 Hz), and 6.60 (*br s*), respectively. In addition, the spectrum also demonstrated the signal of methylene protons adjacent to the aromatic at  $\delta_H$  2.80.

The  $^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ ) of partially purified cardanol (Fig. 4-7) revealed the presence of an oxycarbon in the aromatic ring at  $\delta_c$  155.4, methylene and methyl groups at  $\delta_c$  14.1-35.8, and double bonds in the aromatic ring and side chain at  $\delta_c$  112.5-136.8.

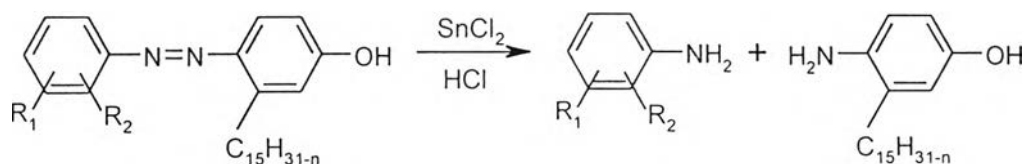
### 4.3 Synthetic marker dyes

Marker dyes were prepared from the coupling reaction between diazotized aniline derivatives and 3-alkylphenoxide ions, which were derived from cardanol in an alkali solution. General chemical structures of marker dyes in this research are shown below.



Where  $n = 0, 2, 4, 6$ ;  $R_1$  and  $R_2$  are each nitro, chloro groups and etc.,

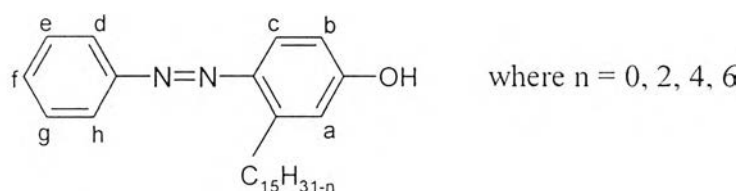
The presence of azo group ( $\text{N}=\text{N}$ ) was confirmed by reducing the marker dye with stannous chloride in an acid solution, yielding aniline derivatives and amino-cardanol; this reaction was easily observed, because the yellow reaction mixture changed to colorless.



where  $n = 0, 2, 4, 6$

### 4.3.1 Cardanol-phenyl azo

Cardanol-phenyl azo was prepared by reacting aniline diazonium salt with 3-alkylphenoxide ions, to yield a yellowish-brown azo dye. The structure of cardanol-phenyl azo is:



The infrared spectrum of cardanol-phenyl azo (Fig. 4-8) showed absorption peaks at  $3354\text{ cm}^{-1}$  (O-H stretching of phenol),  $3010\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2926\text{ cm}^{-1}$  and  $2859\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1603\text{ cm}^{-1}$  and  $1462\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1364\text{ cm}^{-1}$  (O-H bending of phenol), and  $1244\text{ cm}^{-1}$  (C-O stretching of phenol).

The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-phenyl azo (Fig. 4-9) revealed the presence of a benzene ring in the marker dye at  $\delta_H$  7.90 (2H, *d*, 7.5 Hz, positions d and h), 7.50 (2H, *t*, 7.8 Hz, positions e and g), and 7.45 (*t*, 7.0 Hz, position f). This spectrum also demonstrated the existence of a coupled cardanol in the marker dye, whose  $\delta_H$  at the positions a, b, and c were at 6.80 (*br s*), 6.75 (*dd*, 1.6 and 8.7 Hz), and 7.70 (*d*, 8.7 Hz), respectively. In addition, the  $\delta_H$  of the methylene adjacent to the aromatic of a coupled cardanol was shifted downfield from 2.80 (in unreacted cardanol) to 3.15 (in the marker dye product); this downfield shift may be due to the presence of azo substituted cardanol. As seen on the  $^1\text{H-NMR}$  spectrum of cardanol-phenyl azo, a quantitative amount of

unreacted cardanol (indication by the size of the protons of unreacted cardanol at  $\delta_H$  2.80) was observed. The assignments are concluded in Table 4-1.

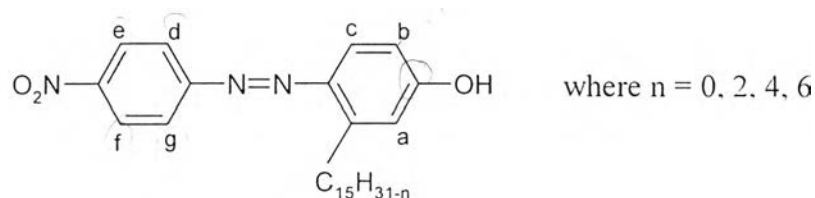
Table 4-1: The  $^1\text{H-NMR}$  spectral data of cardanol-phenyl azo.

| Position | $\delta_H$ , multiplicity, $J$ (Hz) |
|----------|-------------------------------------|
| a        | 6.80, <i>br s</i>                   |
| b        | 6.75, <i>dd</i> , 1.6 and 8.7       |
| c        | 7.70, <i>d</i> , 8.7                |
| d        | 7.90, <i>d</i> , 7.5                |
| e        | 7.50, <i>t</i> , 7.8                |
| f        | 7.45, <i>t</i> , 7.0                |
| g        | 7.50, <i>t</i> , 7.8                |
| h        | 7.90, <i>d</i> , 7.5                |

The  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-phenyl azo (Fig. 4-10) revealed the presence of oxycarbon in an aromatic ring (C-OH) at  $\delta_C$  158.4, methylene and methyl groups at  $\delta_C$  14.1-35.8, and double bonds in an aromatic ring and side chain at  $\delta_C$  112.5-136.8.

### 4.3.2 Cardanol-*p*-nitrophenyl azo

Cardanol-*p*-nitrophenyl azo was prepared by the reaction of *p*-nitroaniline diazonium salt and 3-alkylphenoxide ions, to yield a reddish-brown azo dye. The structure of cardanol-*p*-nitrophenyl azo is:



The infrared spectrum of cardanol-*p*-nitrophenyl azo (Fig. 4-11) showed absorption peaks at  $3380\text{ cm}^{-1}$  (O-H stretching of phenol),  $3013\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2922\text{ cm}^{-1}$  and  $2855\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1606\text{ cm}^{-1}$  and  $1467\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1529\text{ cm}^{-1}$  (N=O asymmetric stretching of the  $\text{NO}_2$  group),  $1348\text{ cm}^{-1}$  (N=O symmetric stretching of the  $\text{NO}_2$  group),  $1244\text{ cm}^{-1}$  (C-O stretching of phenol), and  $866\text{ cm}^{-1}$  (C-N stretching vibration of C-N bond).

The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-*p*-nitrophenyl azo (Fig. 4-12) showed the presence of a *para*-substituted azo benzene ring at  $\delta_H$  8.37 (2H, *d*, 8.7 Hz, positions e and f), and 7.95 (2H, *d*, 8.9 Hz, positions d and g). The  $^1\text{H-NMR}$  spectrum of cardanol-*p*-nitrophenyl azo also demonstrated the existence of a coupled cardanol in the marker dye, whose  $\delta_H$  at the positions a, b, and c were at 6.80 (*d*, 2.2 Hz), 6.75 (*br d*, 8.6 Hz), and 7.70 (*d*, 8.8 Hz). In addition, the  $\delta_H$  of the methylene adjacent to the aromatic of a coupled cardanol was shifted downfield from 2.80 (in unreacted cardanol) to 3.15 (in the marker dye product);

this downfield shift may be due to the presence of azo substituted cardanol. The  $^1\text{H-NMR}$  spectrum of cardanol-*p*-nitrophenyl azo also implied that there was a quantitative amount of unreacted cardanol in the reaction mixture, as suggested by the size of unreacted cardanol at  $\delta_{\text{H}}$  2.80. The assignments are concluded in Table 4-2.

Table 4-2: The  $^1\text{H-NMR}$  spectral data of cardanol-*p*-nitrophenyl azo.

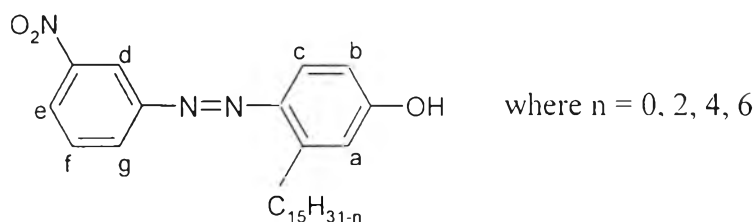
| Position | $\delta_{\text{H}}$ , multiplicity, $J$ (Hz) |
|----------|--|
| a        | 6.80, <i>d</i> , 2.2                         |
| b        | 6.75, <i>br d</i> , 8.6                      |
| c        | 7.70, <i>d</i> , 8.8                         |
| d        | 7.95, <i>d</i> , 8.9                         |
| e        | 8.37, <i>d</i> , 8.7                         |
| f        | 8.37, <i>d</i> , 8.7                         |
| g        | 7.95, <i>d</i> , 8.9                         |

The  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-*p*-nitrophenyl azo (Fig. 4-13) showed prominently at  $\delta_{\text{C}}$  120.9 and 124.7, attributable to carbon positions d and g, and e and f, respectively. The  $^{13}\text{C-NMR}$  spectrum of this marker dye also revealed the presence of oxycarbon in an aromatic ring (C-OH) at  $\delta_{\text{C}}$  156.3, methylene and methyl groups at  $\delta_{\text{C}}$  14.1-35.8, and double bonds in an aromatic ring and side chain at  $\delta_{\text{C}}$  112.5-136.8.



### 4.3.3 Cardanol-*m*-nitrophenyl azo

Cardanol-*m*-nitrophenyl azo was prepared by the reaction of *m*-nitroaniline diazonium salt and 3-alkylphenoxide ions, to yield a yellowish-brown azo dye. The structure of cardanol-*m*-nitrophenyl azo is:



The infrared spectrum of cardanol-*m*-nitrophenyl azo (Fig. 4-14) showed absorption peaks at  $3370\text{ cm}^{-1}$  (O-H stretching of phenol),  $3009\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2927\text{ cm}^{-1}$  and  $2855\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1601\text{ cm}^{-1}$  and  $1472\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1539\text{ cm}^{-1}$  (N=O asymmetric stretching of the  $\text{NO}_2$  group),  $1353\text{ cm}^{-1}$  (N=O symmetric stretching of the  $\text{NO}_2$  group),  $1249\text{ cm}^{-1}$  (C-O stretching of phenol), and  $876\text{ cm}^{-1}$  (C-N stretching vibration of C-N bond).

The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-*m*-nitrophenyl azo (Fig. 4-15) showed the characteristic of a *meta*-substituted azo benzene ring of the dye product at  $\delta_{\text{H}}$  8.70 (*s*, position d), 8.30 (*dd*, 2.2 and 8.0 Hz, position e), 7.60 (*t*, 8.0 Hz, position f), and 8.20 (*d*, 8.0 Hz, position g). The  $^1\text{H-NMR}$  spectrum of cardanol-*m*-nitrophenyl azo also demonstrated the existence of a coupled cardanol in the marker dye, showing a typical set of protons at the positions a, b, and c at  $\delta_{\text{H}}$  6.8 (*d*, 2.5 Hz), 6.75 (*dd*, 2.3 and 8.6 Hz), and 7.75 (*d*, 8.7 Hz), respectively. Moreover, the downfield shift of the methylene next to the aromatic of a coupled

cardanol was observed; this downfield shift may be due to the presence of azo substituted cardanol. The  $^1\text{H-NMR}$  spectrum of cardanol-*m*-nitrophenyl azo also revealed a quantitative amount of unreacted cardanol left in the reaction mixture. The assignments are concluded in Table 4-3.

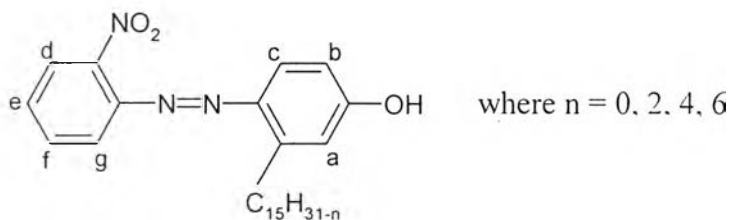
Table 4-3: The  $^1\text{H-NMR}$  spectral data of cardanol-*m*-nitrophenyl azo.

| Position | $\delta_H$ , multiplicity, $J$ (Hz) |
|----------|-------------------------------------|
| a        | 6.80, <i>d</i> , 2.5                |
| b        | 6.75, <i>dd</i> , 2.3 and 8.6       |
| c        | 7.75, <i>d</i> , 8.7                |
| d        | 6.75, <i>s</i>                      |
| e        | 8.30, <i>dd</i> , 2.2 and 8.0       |
| f        | 7.60, <i>t</i> , 8.0                |
| g        | 8.20, <i>d</i> , 8.0                |

The  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-*m*-nitrophenyl azo (Fig. 4-16) revealed the presence of an oxycarbon in an aromatic ring (C-OH) at  $\delta_C$  159.6, methylene and methyl groups at  $\delta_C$  13.8-35.8, and double bonds in an aromatic ring and side chain at  $\delta_C$  112.5-136.8. The  $^{13}\text{C-NMR}$  spectrum of cardanol-*m*-nitrophenyl azo also showed  $\delta_C$  147.2 and 148.9 (attributable to nitro group, C- $\text{NO}_2$ ), and  $\delta_C$  153.5 and 155.4 (of an azo substituted benzene).

#### 4.3.4 Cardanol-*o*-nitrophenyl azo

Cardanol-*o*-nitrophenyl azo was prepared by the reaction of *o*-nitroaniline diazonium salt and 3-alkylphenoxide ions, to yield a reddish-brown azo dye. The structure of cardanol-*o*-nitrophenyl azo is:



The infrared spectrum of cardanol-*o*-nitrophenyl azo (Fig. 4-17) showed absorption peaks at  $3329\text{ cm}^{-1}$  (O-H stretching of phenol),  $3004\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2926\text{ cm}^{-1}$  and  $2853\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1603\text{ cm}^{-1}$  and  $1488\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1535\text{ cm}^{-1}$  (N=O asymmetric stretching of the  $\text{NO}_2$  group),  $1363\text{ cm}^{-1}$  (N=O symmetric stretching of the  $\text{NO}_2$  group),  $1233\text{ cm}^{-1}$  (C-O stretching of phenol), and  $876\text{ cm}^{-1}$  (C-N stretching vibration of C-N bond).

The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-*o*-nitrophenyl azo (Fig. 4-18) revealed the presence of an *ortho*-substituted azo benzene ring at  $\delta_H$  7.80 (*d*, 8.1 Hz, position d), 7.65 (*br s*, positions e and g), and 7.50 (*m*, position f). The  $^1\text{H-NMR}$  spectrum of cardanol-*o*-nitrophenyl azo also demonstrated the existence of a coupled cardanol in the marker dye, whose  $\delta_H$  at the positions a, b, and c were at 6.80 (*br s*), 6.70 (*br d*, 7.6 Hz), and 7.70 (*d*, 7.4 Hz), respectively. In addition, the  $\delta_H$  of the methylene adjacent to the aromatic of a coupled cardanol was shifted downfield from 2.80 (in unreacted cardanol) to 3.15 (in the marker dye product);

this downfield shift may be due to the presence of azo substituted cardanol. The  $^1\text{H-NMR}$  spectrum of cardanol-*o*-nitrophenyl azo indicated that there was a quantitative amount of unreacted cardanol left in the reaction mixture. The assignments are concluded in Table.4-4.

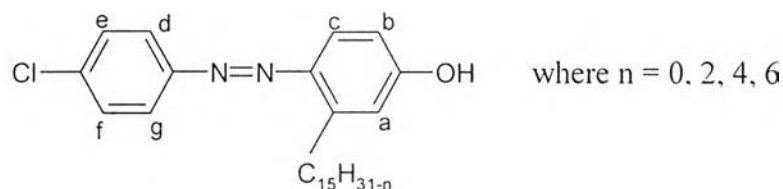
Table 4-4: The  $^1\text{H-NMR}$  spectral data of cardanol-*o*-nitrophenyl azo.

| Position | $\delta_H$ , multiplicity, $J$ (Hz) |
|----------|-------------------------------------|
| a        | 6.80, <i>br s</i>                   |
| b        | 6.70, <i>br d</i> , 7.6             |
| c        | 7.70, <i>d</i> , 7.4                |
| d        | 7.80, <i>d</i> , 8.1                |
| e        | 7.65, <i>br s</i>                   |
| f        | 7.50, <i>m</i>                      |
| g        | 7.65, <i>br s</i>                   |

The  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-*o*-nitrophenyl azo (Fig. 4-19) revealed the presence of oxycarbon in an aromatic ring (C-OH) at  $\delta_C$  155.5, methylene and methyl groups at  $\delta_C$  14.1-35.8, and double bonds in an aromatic ring and side chain at  $\delta_C$  112.5-132.7.

### 4.3.5 Cardanol-*p*-chlorophenyl azo

Cardanol-*p*-chlorophenyl azo was prepared by the reaction of *p*-chloroaniline diazonium salt and 3-alkylphenoxide ions, to yield a yellowish-brown azo dye. The structure of cardanol-*p*-chlorophenyl azo is:



The infrared spectrum of cardanol-*p*-chlorophenyl azo (Fig 4-20) showed absorption peaks at  $3360\text{ cm}^{-1}$  (O-H stretching of phenol),  $3009\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2922\text{ cm}^{-1}$  and  $2860\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1591\text{ cm}^{-1}$  and  $1461\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1363\text{ cm}^{-1}$  (O-H bending of phenol),  $1244\text{ cm}^{-1}$  (C-O stretching of phenol), and  $1098\text{ cm}^{-1}$  (C-Cl stretching vibration of C-Cl bond).

The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-*p*-chlorophenyl azo (Fig. 4-21) showed the presence of a *para*-substituted azo benzene ring at  $\delta_H$  7.85 (2H, *d*, 8.6 Hz, positions e and f), and 7.50 (2H, *d*, 8.6 Hz, positions d and g). This spectrum also indicated the characteristic of a coupled cardanol in the marker dye, whose  $\delta_H$  at the positions a, b, and c were at 6.80 (*d*, 2.4 Hz), 6.75 (*br d*, 8.8 Hz), and 7.70 (*d*, 8.7 Hz), respectively. Furthermore, the  $\delta_H$  of the methylene adjacent to the aromatic of a coupled cardanol was shifted downfield from 2.80 (in unreacted cardanol) to 3.15 (in the marker dye product), conclusively confirmed the presence of the marker dye product in the reaction mixture. The  $^1\text{H-NMR}$

spectrum of cardanol-*p*-chlorophenyl azo revealed a quantitative amount of unreacted cardanol in the reaction mixture. The assignments are concluded in Table 4-5.

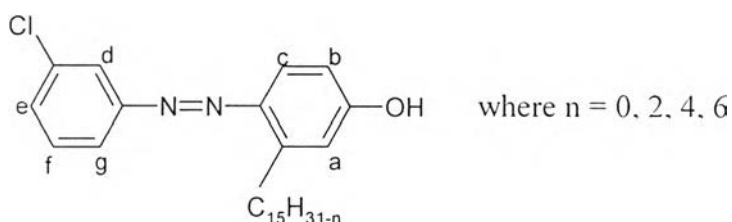
Table 4-5: The  $^1\text{H}$ -NMR spectral data of cardanol-*p*-chlorophenyl azo.

| Position | $\delta_H$ , multiplicity, $J$ (Hz) |
|----------|-------------------------------------|
| a        | 6.80, <i>d</i> , 2.4                |
| b        | 6.75, <i>br d</i> , 8.8             |
| c        | 7.70, <i>d</i> , 8.7                |
| d        | 7.50, <i>d</i> , 8.6                |
| e        | 7.85, <i>d</i> , 8.6                |
| f        | 7.85, <i>d</i> , 8.6                |
| g        | 7.50, <i>d</i> , 8.6                |

The  $^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ ) of cardanol-*p*-chlorophenyl azo (Fig. 4-22) indicated the presence of oxycarbon in an aromatic ring (C-OH) at  $\delta_C$  155.4, methylene and methyl groups at  $\delta_C$  14.1-35.8, and double bonds in an aromatic ring and side chain at  $\delta_C$  112.5-136.8.

### 4.3.6 Cardanol-*m*-chlorophenyl azo

Cardanol-*m*-chlorophenyl azo was prepared by the reaction of *m*-chloroaniline diazonium salt and 3-alkylphenoxide ions, to yield a yellowish-brown azo dye. The structure of cardanol-*m*-chloroaniline azo dye is:



The infrared spectrum of cardanol-*m*-chlorophenyl azo (Fig. 4-23) showed absorption peaks at  $3350\text{ cm}^{-1}$  (O-H stretching of phenol),  $3009\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2922\text{ cm}^{-1}$  and  $2865\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1601\text{ cm}^{-1}$  and  $1467\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1363\text{ cm}^{-1}$  (O-H bending of phenol),  $1250\text{ cm}^{-1}$  (C-O stretching of phenol), and  $1089\text{ cm}^{-1}$  (C-Cl stretching vibration of C-Cl bond).

The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-*m*-chlorophenyl azo (Fig. 4-24) showed the presence of a *meta*-substituted azo benzene ring at  $\delta_H$  7.85 (*s*, position d), 7.80 (*br d*, 7.4 Hz, position e), 7.42 (*t*, 8.2 Hz, position f), and 7.45 (*d*, 7.8 Hz, position g). This spectrum also demonstrated the existence of a coupled cardanol in the marker dye, whose  $\delta_H$  at the positions a, b, and c were at 6.80 (*d*, 2.3 Hz), 6.75 (*dd*, 2.3 and 8.8 Hz), and 7.70 (*d*, 8.7 Hz), respectively. In addition, the  $\delta_H$  of the methylene adjacent to the aromatic of a coupled cardanol was shifted downfield from 2.80 (in unreacted cardanol) to 3.15 (in the marker dye product); this readily confirmed the existence of the marker dye product in the

reaction mixture. The  $^1\text{H-NMR}$  spectrum of cardanol-*m*-chlorophenyl azo revealed a quantitative amount of unreacted cardanol in the reaction mixture. The assignments are concluded in Table 4-6.

Table 4-6: The  $^1\text{H-NMR}$  spectral data of cardanol-*m*-chlorophenyl azo.

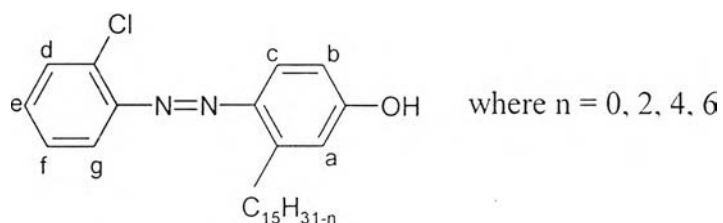
| Position | $\delta_H$ , multiplicity, $J$ (Hz) |
|----------|-------------------------------------|
| a        | 6.80, <i>d</i> , 2.3                |
| b        | 6.75, <i>dd</i> , 2.3 and 8.8       |
| c        | 7.70, <i>d</i> , 8.7                |
| d        | 7.85, <i>s</i>                      |
| e        | 7.80, <i>br d</i> , 7.4             |
| f        | 7.42, <i>t</i> , 8.2                |
| g        | 7.45, <i>d</i> , 7.8                |

The  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-*m*-chlorophenyl azo (Fig. 4-25) revealed the presence of oxycarbon in an aromatic ring (C-OH) at  $\delta_C$  155.8, methylene and methyl groups at  $\delta_C$  14.1-35.8, and double bonds in an aromatic ring and side chain at  $\delta_C$  112.5-136.8.



### 4.3.7 Cardanol-*o*-chlorophenyl azo

Cardanol-*o*-chlorophenyl azo was prepared by the reaction of *o*-chloroaniline diazonium salt and 3-alkylphenoxide ions, to yield a yellowish-brown azo dye. The structure of cardanol-*o*-chlorophenyl azo is:



The infrared spectrum of cardanol-*o*-chlorophenyl azo (Fig. 4-26) showed absorption peaks at  $3355\text{ cm}^{-1}$  (O-H stretching of phenol),  $3009\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2922\text{ cm}^{-1}$  and  $2860\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1601\text{ cm}^{-1}$  and  $1472\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1373\text{ cm}^{-1}$  (O-H bending of phenol),  $1239\text{ cm}^{-1}$  (C-O stretching of phenol), and  $1070\text{ cm}^{-1}$  (C-Cl stretching vibration of C-Cl bond).

The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-*o*-chlorophenyl azo (Fig. 4-27) indicated the presence of an *ortho*-substituted azo benzene ring at  $\delta_H$  7.55 (*d*, 9.2 Hz, position d), 7.35 (*m*, positions e and f), and 7.65 (*d*, 9.6 Hz, position g). This spectrum also demonstrated the existence of a coupled cardanol in the marker dye, whose  $\delta_H$  at the positions a, b, and c were at 6.80 (*d*, 2.2 Hz), 6.75 (*dd*, 2.3 and 8.6 Hz), and 7.80 (*d*, 8.8 Hz), respectively. In addition, the downfield shift of the methylene next to the aromatic of a coupled cardanol was observed; this downfield shift may be due to the presence of azo substituted cardanol. The  $^1\text{H-NMR}$  spectrum of cardanol-*o*-chlorophenyl azo revealed a quantitative amount

of unreacted cardanol left in the reaction mixture. The assignments are summarized in Table 4-7.

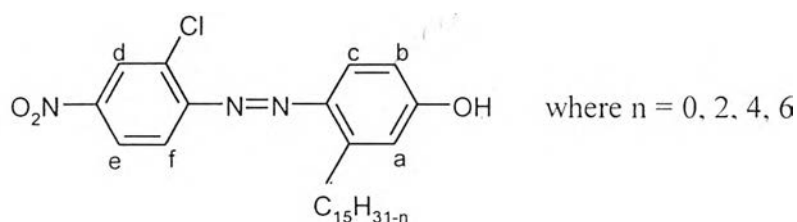
Table 4-7: The  $^1\text{H}$ -NMR spectral data of cardanol-*o*-chlorophenyl azo.

| Position | $\delta_H$ , multiplicity, $J$ (Hz) |
|----------|-------------------------------------|
| a        | 6.80, <i>d</i> , 2.2                |
| b        | 6.75, <i>dd</i> , 2.3 and 8.6       |
| c        | 7.80, <i>d</i> , 8.8                |
| d        | 7.55, <i>d</i> , 9.2                |
| e        | 7.35, <i>m</i>                      |
| f        | 7.35, <i>m</i>                      |
| g        | 7.65, <i>d</i> , 9.6                |

The  $^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ ) of cardanol-*o*-chlorophenyl azo (Fig. 4-28) indicated the presence of oxycarbon in an aromatic ring (C-OH) at  $\delta_C$  155.4, methylene and methyl groups at  $\delta_C$  14.1-35.8, and double bonds in an aromatic ring and side chain at  $\delta_C$  112.5-130.7.

### 4.3.8 Cardanol-2-chloro-4-nitrophenyl azo

Cardanol-2-chloro-4-nitrophenyl azo was prepared by the reaction of 2-chloro-4-nitroaniline diazonium salt and 3-alkylphenoxide ions, to yield a reddish-brown azo dye. The structure of cardanol-2-chloro-4-nitrophenyl azo is:



The infrared spectrum of cardanol-2-chloro-4-nitrophenyl azo (Fig. 4-29) showed absorption peaks at  $3370\text{ cm}^{-1}$  (O-H stretching of phenol),  $3009\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2923\text{ cm}^{-1}$  and  $2855\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1597\text{ cm}^{-1}$  and  $1457\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1524\text{ cm}^{-1}$  (N=O asymmetric stretching of the  $\text{NO}_2$  group),  $1348\text{ cm}^{-1}$  (N=O symmetric stretching of the  $\text{NO}_2$  group),  $1239\text{ cm}^{-1}$  (C-O stretching of phenol),  $1055\text{ cm}^{-1}$  (C-Cl stretching vibration of C-Cl bond), and  $896\text{ cm}^{-1}$  (C-N stretching vibration of C-N bond).

The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-2-chloro-4-nitrophenyl azo (Fig. 4-30) indicated that there was a marker dye product, with a quantitative yield, formed in the reaction mixture (as suggested by the methylene signal resonanced at  $\delta_H$  3.15). The  $^1\text{H-NMR}$  spectrum of this marker dye showed the typical pattern of a coupled cardanol, and protons at the positions a, b, and c resonanced at  $\delta_H$  6.80 (*br s*), 6.75 (*br d*, 7.6 Hz), and 7.82 (*d*, 8.8 Hz), respectively. Protons at the positions d, e, and f were assigned at  $\delta_H$  8.45 (*d*, 2.3

Hz), 8.20 (*dd*, 2.3 and 8.7 Hz), and 7.70 (*d*, 8.8 Hz), respectively. The assignments are concluded in Table 4-8.

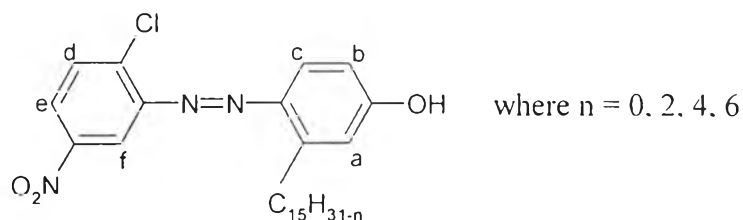
Table 4-8: The  $^1\text{H-NMR}$  spectral data of cardanol-2-chloro-4-nitrophenyl azo.

| Position | $\delta_{\text{H}}$ , multiplicity, $J$ in (Hz) |
|----------|---|
| a        | 6.80, <i>br s</i>                               |
| b        | 6.75, <i>br d</i> , 7.6                         |
| c        | 7.82, <i>d</i> , 8.8                            |
| d        | 8.45, <i>d</i> , 2.3                            |
| e        | 8.20, <i>dd</i> , 2.3 and 8.7                   |
| f        | 7.70, <i>d</i> , 8.8                            |

The  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-2-chloro-4-nitrophenyl azo (Fig. 4-31) revealed the presence of oxycarbon in an aromatic ring (C-OH) at  $\delta_{\text{C}}$  152.7, methylene and methyl groups at  $\delta_{\text{C}}$  14.1-35.8, and double bonds in an aromatic ring and side chain at  $\delta_{\text{C}}$  112.4-130.2.

### 4.3.9 Cardanol-2-chloro-5-nitrophenyl azo

Cardanol-2-chloro-5-nitrophenyl azo was prepared by the reaction of 2-chloro-5-nitroaniline diazonium salt and 3-alkylphenoxide ions, to yield a yellowish-brown azo dye. The structure of cardanol-2-chloro-5-nitrophenyl azo is:



The infrared spectrum of cardanol-2-chloro-5-nitrophenyl azo (Fig. 4-32) revealed absorption peaks at  $3360\text{ cm}^{-1}$  (O-H stretching of phenol),  $3004\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2928\text{ cm}^{-1}$  and  $2855\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1601\text{ cm}^{-1}$  and  $1457\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1534\text{ cm}^{-1}$  (N=O asymmetric stretching of the  $\text{NO}_2$  group),  $1348\text{ cm}^{-1}$  (N=O symmetric stretching of the  $\text{NO}_2$  group),  $1248\text{ cm}^{-1}$  (C-O stretching of phenol),  $1061\text{ cm}^{-1}$  (C-Cl stretching vibration of C-Cl bond), and  $885\text{ cm}^{-1}$  (C-N stretching vibration of C-N bond).

As seen on the  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-2-chloro-5-nitrophenyl azo (Fig. 4-33), protons a, b, c, d, e, and f were assigned at  $\delta_{\text{H}}$  6.80 (*d*, 2.3 Hz), 6.75 (*br d*, 7.4 Hz), 7.82 (*d*, 8.9 Hz), 7.70 (*d*, 9.1 Hz), 8.20 (*dd*, 1.9 and 8.6 Hz), and 8.50 (*d*, 3.0 Hz), respectively. Methylene protons adjacent to a coupled cardanol resonanced at  $\delta_{\text{H}}$  3.15, indicating the marker dye product formed in the reaction mixture. The assignments are concluded in Table 4-9.

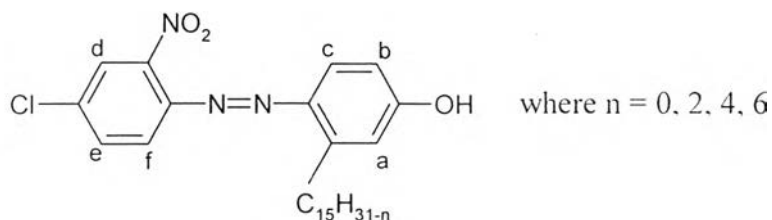
Table 4-9: The  $^1\text{H}$ -NMR spectral data of cardanol-2-chloro-5-nitrophenyl azo.

| Position | $\delta_H$ , multiplicity, $J$ (Hz) |
|----------|-------------------------------------|
| a        | 6.80, <i>d</i> , 2.3                |
| b        | 6.75, <i>br d</i> , 7.4             |
| c        | 7.82, <i>d</i> , 8.9                |
| d        | 7.70, <i>d</i> , 9.1                |
| e        | 8.20, <i>dd</i> , 1.9 and 8.6       |
| f        | 8.50, <i>d</i> , 3.0                |

The  $^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ ) of cardanol-2-chloro-5-nitrophenyl azo (Fig. 4-34) revealed the presence of oxycarbon in an aromatic ring (C-OH) at  $\delta_C$  155.4, methylene and methyl groups at  $\delta_C$  14.1-35.8, and double bonds in an aromatic ring and side chain at  $\delta_C$  112.5-131.3.

#### 4.3.10 Cardanol-4-chloro-2-nitrophenyl azo

Cardanol-4-chloro-2-nitrophenyl azo was prepared by the reaction of 4-chloro-2-nitroaniline diazonium salt and 3-alkylphenoxide ions, to yield a reddish-brown azo dye. The structure of cardanol-4-chloro-2-nitrophenyl azo is:



The infrared spectrum of cardanol-4-chloro-2-nitrophenyl azo (Fig. 4-35) revealed absorption peaks at  $3345\text{ cm}^{-1}$  (O-H stretching of phenol),  $3013\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2928\text{ cm}^{-1}$  and  $2860\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1597\text{ cm}^{-1}$  and  $1462\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1534\text{ cm}^{-1}$  (N=O asymmetric stretching of the  $\text{NO}_2$  group),  $1353\text{ cm}^{-1}$  (N=O symmetric stretching of the  $\text{NO}_2$  group),  $1243\text{ cm}^{-1}$  (C-O stretching of phenol),  $1107\text{ cm}^{-1}$  (C-Cl stretching vibration of C-Cl bond), and  $890\text{ cm}^{-1}$  (C-N stretching vibration of C-N bond).

As seen on the  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-4-chloro-2-nitrophenyl azo (Fig. 4-36), protons a, b, c, d, e, and f were assigned at  $\delta_H$  6.80 (*d*, 2.4 Hz), 6.75 (*dd*, 2.2 and 8.8 Hz), 7.65 (*d*, 9.9 Hz), 7.80 (*br s*), 7.60 (*dd*, 1.5 and 8.2 Hz), and 7.70 (*d*, 9.2 Hz), respectively. Methylene protons adjacent to a coupled cardanol resonanced at  $\delta_H$  3.15, indicating the marker dye product formed in the reaction mixture. The assignments are concluded in Table 4-10.

Table 4-10: The  $^1\text{H}$ -NMR spectral data of cardanol-4-chloro-2-nitrophenyl azo.

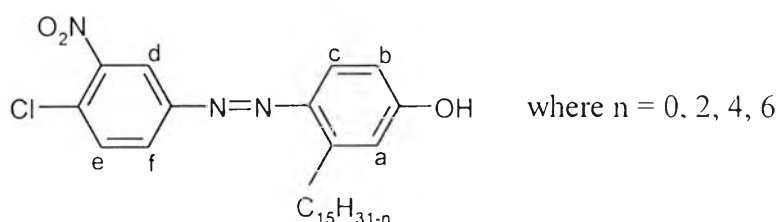
| Position | $\delta_H$ , multiplicity, $J$ (Hz) |
|----------|-------------------------------------|
| a        | 6.80, <i>d</i> , 2.4                |
| b        | 6.75, <i>dd</i> , 2.2 and 8.8       |
| c        | 7.65, <i>d</i> , 9.9                |
| d        | 7.80, <i>br s</i>                   |
| e        | 7.60, <i>dd</i> , 1.5 and 8.2       |
| f        | 7.70, <i>d</i> , 9.2                |

The  $^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ ) of cardanol-4-chloro-2-nitrophenyl azo (Fig. 4-37) revealed the presence of oxycarbon in an aromatic ring (C-OH) at  $\delta_C$  155.5, methylene and methyl groups at  $\delta_C$  14.1-35.8, and double bonds in an aromatic ring and side chain at  $\delta_C$  112.5-132.8.



### 4.3.11 Cardanol-4-chloro-3-nitrophenyl azo

Cardanol-4-chloro-3-nitrophenyl azo was prepared by the reaction of 4-chloro-3-nitroaniline diazonium salt and 3-alkylphenoxide ions, to yield a yellowish-brown azo dye. The structure of cardanol-4-chloro-3-nitrophenyl azo is:



The infrared spectrum of cardanol-4-chloro-3-nitrophenyl azo (Fig. 4-38) revealed absorption peaks at  $3345\text{ cm}^{-1}$  (O-H stretching of phenol),  $3009\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2928\text{ cm}^{-1}$  and  $2855\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1597\text{ cm}^{-1}$  and  $1462\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1540\text{ cm}^{-1}$  (N=O asymmetric stretching of the  $\text{NO}_2$  group),  $1363\text{ cm}^{-1}$  (N=O symmetric stretching of the  $\text{NO}_2$  group),  $1254\text{ cm}^{-1}$  (C-O stretching of phenol),  $1050\text{ cm}^{-1}$  (C-Cl stretching vibration of C-Cl bond), and  $871\text{ cm}^{-1}$  (C-N stretching vibration of C-N bond).

As seen on the  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-4-chloro-3-nitrophenyl azo (Fig. 4-39), protons a, b, c, d, e, and f were assigned at  $\delta_H$  6.80 (*br s*), 6.75 (*br d*, 7.6 Hz), 7.75 (*d*, 8.8 Hz), 8.35 (*d*, 1.8 Hz), 7.70 (*d*, 8.5 Hz), and 8.00 (*dd*, 2.2 and 8.3 Hz), respectively. Methylene protons adjacent to a coupled cardanol resonanced at  $\delta_H$  3.15, indicating the marker dye product formed in the reaction mixture. The assignments are concluded in Table 4-11.

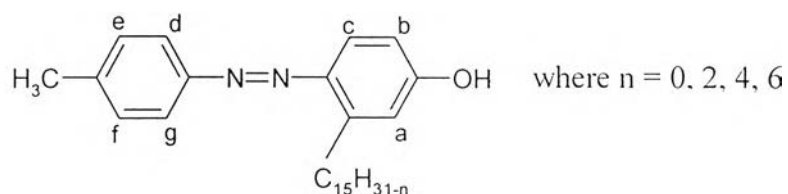
Table 4-11: The  $^1\text{H-NMR}$  spectral data of cardanol-4-chloro-3-nitrophenyl azo.

| Position | $\delta_H$ , multiplicity, $J$ (Hz) |
|----------|-------------------------------------|
| a        | 6.80, <i>br s</i>                   |
| b        | 6.75, <i>br d</i> , 7.6             |
| c        | 7.75, <i>d</i> , 8.8                |
| d        | 8.35, <i>d</i> , 1.8                |
| e        | 7.70, <i>d</i> , 8.5                |
| f        | 8.00, <i>dd</i> , 2.2 and 8.3       |

The  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-4-chloro-3-nitrophenyl azo (Fig. 4-40) revealed the presence of oxycarbon in an aromatic ring (C-OH) at  $\delta_C$  155.3, methylene and methyl groups at  $\delta_C$  14.1-35.8, and double bonds in an aromatic ring and side chain at  $\delta_C$  112.5-132.8.

### 4.3.12 Cardanol-*p*-methylphenyl azo

Cardanol-*p*-methylphenyl azo was prepared by the reaction of *p*-toluidine diazonium salt and 3-alkylphenoxide ions, to yield a yellowish-brown azo dye. The structure of cardanol-*p*-methylphenyl azo is:



The infrared spectrum of cardanol-*p*-methylphenyl azo (Fig. 4-41) revealed absorption peaks at  $3350\text{ cm}^{-1}$  (O-H stretching of phenol),  $3009\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2923\text{ cm}^{-1}$  and  $2860\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1591\text{ cm}^{-1}$  and  $1457\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1363\text{ cm}^{-1}$  (O-H bending of phenol), and  $1255\text{ cm}^{-1}$  (C-O stretching of phenol).

The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-*p*-methylphenyl azo (Fig. 4-42) showed the presence of a *para*-substituted azo benzene ring at  $\delta_H$  7.32 (2H, *d*, 8.1 Hz, positions d and g), and 7.80 (2H, *d*, 8.2 Hz, positions e and f). This spectrum also demonstrated the existence of a coupled cardanol in the marker dye, whose  $\delta_H$  at the positions a, b, and c were at 6.80 (*d*, 2.6 Hz), 6.75 (*br d*, 7.6 Hz), and 7.70 (*d*, 8.7 Hz). The methyl moiety on the aromatic ring resonated characteristically at  $\delta_H$  2.75. In addition, the downfield shift of the methylene next to the aromatic of a coupled cardanol was observed; this downfield shift may be due to the presence of azo substituted cardanol. As seen on the  $^1\text{H-NMR}$  spectrum of cardanol-*p*-methylphenyl azo, the quantitative

amount of unreacted cardanol was observed. The assignments are concluded in Table 4-12.

Table 4-12: The  $^1\text{H}$ -NMR spectral data of cardanol-*p*-methylphenyl azo.

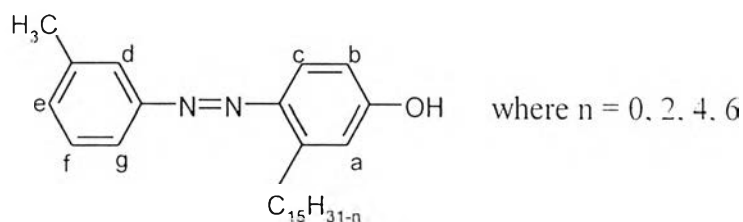
| Position | $\delta_H$ , multiplicity, $J$ (Hz) |
|----------|-------------------------------------|
| a        | 6.80, <i>d</i> , 2.6                |
| b        | 6.75, <i>br d</i> , 7.6             |
| c        | 7.70, <i>d</i> , 8.7                |
| d        | 7.32, <i>d</i> , 8.1                |
| e        | 7.80, <i>d</i> , 8.2                |
| f        | 7.80, <i>d</i> , 8.2                |
| g        | 7.32, <i>d</i> , 8.1                |

The  $^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ ) of cardanol-*p*-methylphenyl azo (Fig. 4-43) revealed the presence of oxycarbon in an aromatic ring (C-OH) at  $\delta_C$  155.3, methylene and methyl groups at  $\delta_C$  14.1-35.8, and double bonds in an aromatic ring and side chain at  $\delta_C$  112.5-132.8.



### 4.3.13 Cardanol-*m*-methylphenyl azo

Cardanol-*m*-methylphenyl azo was prepared by the reaction of *m*-toluidine diazonium salt and 3-alkylphenoxide ions. to yield a yellowish-brown azo dye. The structure of cardanol-*m*-methylphenyl azo is:



The infrared spectrum of cardanol-*m*-methylphenyl azo (Fig. 4-44) revealed absorption peaks at  $3355\text{ cm}^{-1}$  (O-H stretching of phenol),  $3007\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2930\text{ cm}^{-1}$  and  $2858\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1609\text{ cm}^{-1}$  and  $1470\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1370\text{ cm}^{-1}$  (O-H bending of phenol), and  $1255\text{ cm}^{-1}$  (C-O stretching of phenol).

The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-*m*-methylphenyl azo (Fig. 4-45) showed the positions of protons d, e, f, g, and h at  $\delta_H$  7.75 (*br s*), 7.72 (*br s*), 7.40 (*t*, 8.2 Hz), and 6.75 (*d*, 7.7 Hz), respectively. This spectrum also demonstrated the existence of a coupled cardanol in the marker dye, whose  $\delta_H$  at the positions a, b, and c were at 6.80 (*br s*), 6.75 (*br d*, 7.7 Hz), and 7.70 (*d*, 8.8 Hz). The methyl moiety on the aromatic ring resonated characteristically at  $\delta_H$  2.50. In addition, the downfield shift of the methylene next to the aromatic of a coupled cardanol was observed; this downfield shift may be due to the presence of azo substituted cardanol. As seen on the  $^1\text{H-NMR}$  spectrum of cardanol-*m*-

methylphenyl azo, the quantitative amount of unreacted cardanol was observed.

The assignments are concluded in Table 4-13.

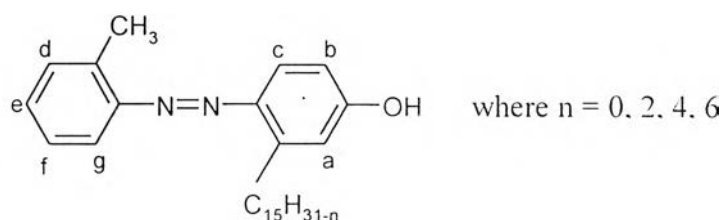
Table 4-13: The  $^1\text{H}$ -NMR spectral data of cardanol-*m*-methylphenyl azo.

| Position | $\delta_H$ , multiplicity, $J$ (Hz) |
|----------|-------------------------------------|
| a        | 6.80, <i>br s</i>                   |
| b        | 6.75, <i>br d</i> , 7.7             |
| c        | 7.70, <i>d</i> , 8:8                |
| d        | 7.75, <i>br s</i>                   |
| e        | 7.72, <i>br s</i>                   |
| f        | 7.40, <i>t</i> , 8.2                |
| g        | 6.75, <i>d</i> , 7.7                |

The  $^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ ) of cardanol-*m*-methylphenyl azo (Fig. 4-46) revealed the presence of oxycarbon in an aromatic ring (C-OH) at  $\delta_C$  155.3, methylene and methyl groups at  $\delta_C$  14.1-35.8, and double bonds in an aromatic ring and side chain at  $\delta_C$  112.5-132.8.

#### 4.3.14 Cardanol-*o*-methylphenyl azo

Cardanol-*o*-methylphenyl azo was prepared by the reaction of *o*-toluidine diazonium salt and 3-alkylphenoxide ions, to yield a yellowish-brown azo dye. The structure of cardanol-*o*-methylphenyl azo is:



The infrared spectrum of cardanol-*o*-methylphenyl azo (Fig. 4-47) revealed absorption peaks at  $3355\text{ cm}^{-1}$  (O-H stretching of phenol),  $3007\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2930\text{ cm}^{-1}$  and  $2858\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1598\text{ cm}^{-1}$  and  $1470\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1365\text{ cm}^{-1}$  (O-H bending of phenol), and  $1250\text{ cm}^{-1}$  (C-O stretching of phenol).

The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-*o*-methylphenyl azo (Fig. 4-48) showed the positions of protons d, e, f, g, and h at  $\delta_{\text{H}}$  7.65 (*d*, 7.7 Hz), 7.35 (*br s*), 7.30 (*m*), and 7.35 (*br s*), respectively. This spectrum also demonstrated the existence of a coupled cardanol in the marker dye, whose  $\delta_{\text{H}}$  at the positions a, b, and c were at 6.80 (*br s*), 6.75 (*br d*, 7.6 Hz), and 7.70 (*d*, 8.8 Hz). The methyl moiety on the aromatic ring resonated characteristically at  $\delta_{\text{H}}$  2.75. In addition, the downfield shift of the methylene next to the aromatic of a coupled cardanol was observed; this downfield shift may be due to the presence of azo substituted cardanol. As seen on the  $^1\text{H-NMR}$  spectrum of cardanol-*o*-

methylphenyl azo, the quantitative amount of unreacted cardanol was observed.

The assignments are concluded in Table 4-14.

Table 4-14: The  $^1\text{H}$ -NMR spectral data of cardanol-*o*-methylphenyl azo.

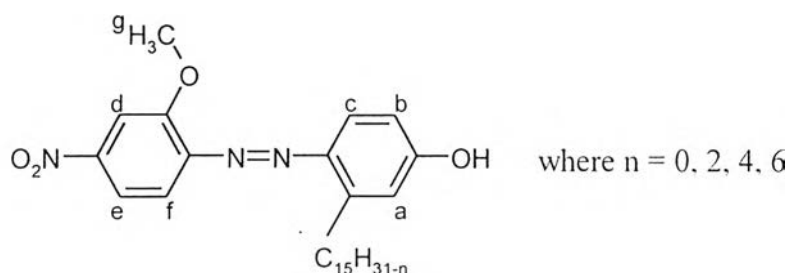
| Position | $\delta_H$ , multiplicity, $J$ (Hz) |
|----------|-------------------------------------|
| a        | 6.80, <i>br s</i>                   |
| b        | 6.75, <i>br d</i> , 7.6             |
| c        | 7.70, <i>d</i> , 8.8                |
| d        | 7.65, <i>d</i> , 7.7                |
| e        | 7.35, <i>br s</i>                   |
| f        | 7.30, <i>m</i>                      |
| g        | 7.35, <i>br s</i>                   |

The  $^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ ) of cardanol-*o*-methylphenyl azo (Fig. 4-49) showed the presence of oxycarbon in an aromatic ring (C-OH) at  $\delta_C$  155.3, methylene and methyl groups at  $\delta_C$  14.1-35.8, and double bonds in an aromatic ring and side chain at  $\delta_C$  112.5-132.8.



#### 4.3.15 Cardanol-2-methoxy-4-nitrophenyl azo

Cardanol-2-methoxy-4-nitrophenyl azo was prepared by the reaction of 2-methoxy-4-nitroaniline diazonium salt and 3-alkylphenoxide ions, to yield a reddish-brown azo dye. The structure of cardanol-2-methoxy-4-nitrophenyl azo is:



The infrared spectrum of cardanol-2-methoxy-4-nitrophenyl azo (Fig. 4-50) showed absorption peaks at  $3365\text{ cm}^{-1}$  (O-H stretching of phenol),  $3012\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2930\text{ cm}^{-1}$  and  $2853\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1603\text{ cm}^{-1}$  and  $1460\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1531\text{ cm}^{-1}$  (N=O asymmetric stretching of the  $\text{NO}_2$  group),  $1347\text{ cm}^{-1}$  (N=O symmetric stretching of the  $\text{NO}_2$  group),  $1255\text{ cm}^{-1}$  (C-O stretching of phenol), and  $881\text{ cm}^{-1}$  (C-N stretching vibration of C-N bond).

The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-2-methoxy-4-nitrophenyl azo (Fig. 4-51) indicated that there was a marker dye product, with a quantitative yield, formed in the reaction mixture (as suggested by the methylene signal resonanced at  $\delta_H$  3.15). The  $^1\text{H-NMR}$  spectrum of this marker dye showed the typical pattern of a coupled cardanol, and protons at the positions a, b, and c resonanced at  $\delta_H$  6.80 (*br s*), 6.75 (*br d*, 7.6 Hz), and 7.72 (*d*, 8.8 Hz),

respectively. Protons at the positions d, e, and f were assigned at  $\delta_H$  7.95 (*br s*), 7.92 (*br s*), and 7.65 (*d*, 8.7 Hz), respectively. The methoxy methyl protons (position g) resonanced characteristically at  $\delta_H$  4.10. The assignments are concluded in Table 4-15.

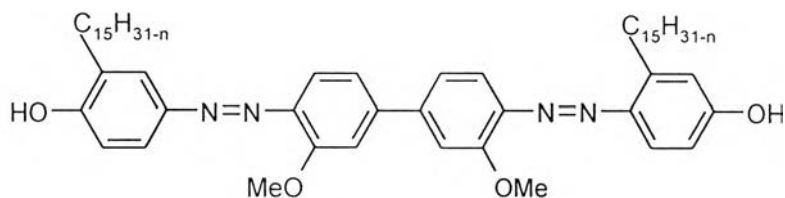
Table 4-15: The  $^1\text{H-NMR}$  spectral data of cardanol-2-methoxy-4-nitrophenyl azo.

| Position | $\delta_H$ , multiplicity, $J$ (Hz) |
|----------|-------------------------------------|
| a        | 6.80, <i>br s</i>                   |
| b        | 6.75, <i>br d</i> , 7.6             |
| c        | 7.72, <i>d</i> , 8.8                |
| d        | 7.95, <i>br s</i>                   |
| e        | 7.92, <i>br s</i>                   |
| f        | 7.65, <i>d</i> , 8.7                |
| g        | 4.10, <i>s</i>                      |

The  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-2-methoxy-4-nitrophenyl azo (Fig. 4-52) revealed the presence of oxycarbon in an aromatic ring (C-OH) at  $\delta_C$  155.5, methylene and methyl groups at  $\delta_C$  14.1-35.8, and double bonds in an aromatic ring and side chain at  $\delta_C$  112.5-130.4. The  $^{13}\text{C-NMR}$  spectrum of cardanol-2-methoxy-4-nitrophenyl azo also showed  $\delta_C$  56.7 (attributable to methoxy group, C-OCH<sub>3</sub>).

#### 4.3.16 Cardanol-Fast Blue B azo

Cardanol-Fast Blue B azo was prepared by the reaction of Fast Blue B diazonium salt and 3-alkylphenoxide ions, to yield a reddish-brown azo dye. The structure of cardanol-Fast Blue B azo is:



where  $n = 0, 2, 4, 6$

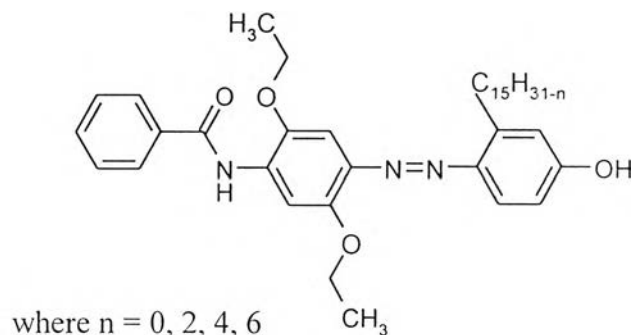
The infrared spectrum of cardanol-Fast Blue B azo (Fig. 4-53) showed absorption peaks at  $3360\text{ cm}^{-1}$  (O-H stretching of phenol),  $3012\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2925\text{ cm}^{-1}$  and  $2858\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1598\text{ cm}^{-1}$  and  $1465\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1370\text{ cm}^{-1}$  (O-H bending of phenol), and  $1255\text{ cm}^{-1}$  (C-O stretching of phenol).

The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-Fast Blue B azo (Fig. 4-54) indicated that there was a marker dye product, with a quantitative yield, formed in the reaction mixture (as suggested by the methylene signal resonanced at  $\delta_H$  3.15). The  $^1\text{H-NMR}$  spectrum of this marker dye also showed the methoxy methyl protons at  $\delta_H$  4.15. However, the  $^1\text{H-NMR}$  spectrum of this marker dye is too complex, since there are many aromatic protons in the molecule, therefore, the aromatic protons of this marker dye could not be conclusively assigned.

#### 4.3.17 Cardanol-Fast Blue BB azo

Cardanol-Fast Blue BB azo was prepared by the reaction of Fast Blue BB diazonium salt and 3-alkylphenoxide ions, to yield a yellowish-brown azo dye.

The structure of cardanol-Fast Blue BB azo is:

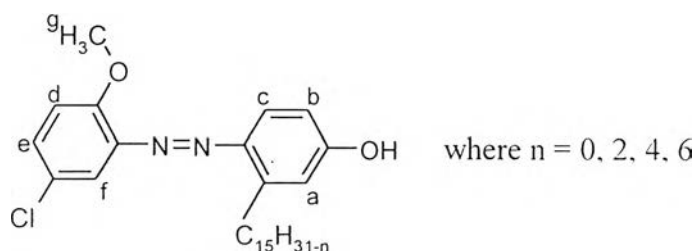


The infrared spectrum of cardanol-Fast Blue BB azo (Fig. 4-55) showed absorption peaks at  $3370\text{ cm}^{-1}$  (O-H stretching of phenol),  $3007\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2925\text{ cm}^{-1}$  and  $2858\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1598\text{ cm}^{-1}$  and  $1460\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1360\text{ cm}^{-1}$  (O-H bending of phenol), and  $1265\text{ cm}^{-1}$  (C-O stretching of phenol).

The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-Fast Blue B azo (Fig. 4-56) suggested that poor yield of this marker dye was obtained from the reaction mixture. The oxymethylene of the ethylene group resonanced characteristically at  $\delta_H$  4.35 and 4.20, as seen on the  $^1\text{H-NMR}$  spectrum. However, the  $^1\text{H-NMR}$  spectrum of this marker dye is too complex, since there are many aromatic protons in the molecule, therefore, the aromatic protons of this marker dye could not be conclusively assigned.

#### 4.3.18 Cardanol-Fast Red RC azo

Cardanol-Fast Red RC azo was prepared by the reaction of Fast Red RC diazonium salt and 3-alkylphenoxide ions, to yield a reddish-brown azo dye. The structure of cardanol-Fast Red RC azo is:



The infrared spectrum of cardanol-Fast Red RC azo (Fig. 4-57) revealed absorption peaks at  $3365\text{ cm}^{-1}$  (O-H stretching of phenol),  $3011\text{ cm}^{-1}$  (=C-H stretching of aromatic),  $2925\text{ cm}^{-1}$  and  $2853\text{ cm}^{-1}$  (C-H stretching of aliphatic),  $1598\text{ cm}^{-1}$  and  $1460\text{ cm}^{-1}$  (C=C ring stretching of aromatic),  $1365\text{ cm}^{-1}$  (O-H bending of phenol),  $1276\text{ cm}^{-1}$  (C-O stretching of phenol), and  $1168\text{ cm}^{-1}$  (C-Cl stretching vibration of C-Cl bond).

The  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ ) of cardanol-Fast Red RC azo (Fig. 4-58) indicated that there was a marker dye product, with a quantitative yield, formed in the reaction mixture (as suggested by the methylene signal resonanced at  $\delta_H$  3.15). The  $^1\text{H-NMR}$  spectrum of this marker dye showed the typical pattern of a coupled cardanol, and protons at the positions a, b, and c resonanced at  $\delta_H$  6.80 (*br s*), 6.75 (*br d*, 7.6 Hz), and 7.68 (*d*, 8.2 Hz), respectively. Protons at the positions d, e, and f were assigned at  $\delta_H$  7.18 (*d*, 8.9 Hz), 7.40 (*br d*, 8.6 Hz), and 7.62 (*d*, 2.5 Hz), respectively. The methoxy methyl protons of this marker dye (position g)

resonanced characteristically at  $\delta_H$  4.10 (*s*). The assignments are concluded in Table 4-8.

Table 4-16: The  $^1\text{H}$ -NMR spectral data of cardanol-Fast Red RC azo.

| Position | $\delta_H$ , multiplicity, <i>J</i> (Hz) |
|----------|--|
| a        | 6.80, <i>br s</i>                        |
| b        | 6.75, <i>br d</i> , 7.6                  |
| c        | 7.68, <i>d</i> , 8.2                     |
| d        | 7.18, <i>d</i> , 8.9                     |
| e        | 7.40, <i>br d</i> , 8.6                  |
| f        | 7.62, <i>d</i> , 2.5                     |
| g        | 4.10, <i>s</i>                           |

The  $^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ ) of cardanol-Fast Red RC azo (Fig. 4-59) revealed the presence of oxycarbon in an aromatic ring (C-OH) at  $\delta_C$  155.4, methylene and methyl groups at  $\delta_C$  14.1-35.8, and double bonds in an aromatic ring and side chain at  $\delta_C$  112.5-131.3. The  $^{13}\text{C}$ -NMR spectrum of cardanol-Fast Red RC azo also showed  $\delta_C$  56.6 (attributable to methoxy group, C-OCH<sub>3</sub>).

#### **4.4 Suitable extraction system for the detection of marker dyes in fuel oils**

Gasoline containing 2 ppm of cardanol-2-chloro-4-nitrophenyl azo was used for the determination of suitable extraction system. The appropriate extraction system was chosen from the basis of the color developed in the extracted phase, the intensity and stability of the developed color, and the ability to separate from an oil phase.

The extraction systems in this research were divided into 3 major systems on the basis of the type of bases used, which were potassium hydroxide, ethylenediamine, and diethylenetriamine. After the dyed gasoline was extracted individually with each bases, the UV/VIS absorption at the maximum wavelength were measured and summarized in Table 4-17.

Table 4-17: The absorbance of the developed color with various base-types, when extracted cardanol-2-chloro-4-nitrophenyl azo (2 ppm) in gasoline.

| Extraction systems   | $\lambda_{\max}$<br>(nm) | Absorbance | Visual<br>color | Ability to<br>separate |
|--|--------------------------|------------|-----------------|------------------------|
| <b>System A:</b>   |                          |            |                 |                        |
| A1. 1% potassium hydroxide in 1:1 ethylene glycol and methanol | 528.5                    | 0.3989     | Purple          | Easy                   |
| A2. 2% potassium hydroxide in 1:1 ethylene glycol and methanol | 528.2                    | 0.3897     | Purple          | Easy                   |
| A3. 3% potassium hydroxide in 1:1 ethylene glycol and methanol | 527.7                    | 0.3969     | Purple          | Easy                   |
| A4. 4% potassium hydroxide in 1:1 ethylene glycol and methanol | 528.0                    | 0.3838     | Purple          | Easy                   |
| A5. 5% potassium hydroxide in 1:1 ethylene glycol and methanol | 528.9                    | 0.3656     | Purple          | Easy                   |
| <b>System B:</b>   |                          |            |                 |                        |
| B1. 10% ethylenediamine in 1:1 ethylene glycol and methanol    | 540.5                    | 0.3480     | Purple          | Easy                   |
| B2. 20% ethylenediamine in 1:1 ethylene glycol and methanol    | 547.3                    | 0.4070     | Purple          | Easy                   |
| B3. 30% ethylenediamine in 1:1 ethylene glycol and methanol    | 554.8                    | 0.4262     | Violet          | Easy                   |



Table 4-17 (cont.): The absorbance of the developed color with various base-types, when extracted cardanol-2-chloro-4-nitrophenyl azo (2 ppm) in gasoline.

| Extraction systems   | $\lambda_{\max}$<br>(nm) | Absorbance | Visual color  | Ability to separate |
|--|--------------------------|------------|---------------|---------------------|
| <b>System B (cont.):</b>                                       |                          |            |               |                     |
| B4. 40% ethylenediamine in 1:1 ethylene glycol and methanol    | 562.1                    | 0.4642     | Violet        | Easy                |
| B5. 50% ethylenediamine in 1:1 ethylene glycol and methanol    | 568.4                    | 0.4731     | Bluish-violet | Easy                |
| <b>System C:</b>   |                          |            |               |                     |
| B1. 10% diethylenetriamine in 1:1 ethylene glycol and methanol | 538.9                    | 0.3378     | Purple        | Easy                |
| B2. 20% diethylenetriamine in 1:1 ethylene glycol and methanol | 547.0                    | 0.4044     | Purple        | Easy                |
| B3. 30% diethylenetriamine in 1:1 ethylene glycol and methanol | 554.0                    | 0.4098     | Violet        | Easy                |
| B4. 40% diethylenetriamine in 1:1 ethylene glycol and methanol | 561.1                    | 0.4352     | Violet        | Easy                |
| B5. 50% diethylenetriamine in 1:1 ethylene glycol and methanol | 568.6                    | 0.4586     | Bluish-violet | Easy                |

From Table 4-17, it was shown that extraction systems A-C were very easy to separate from an oil phase, these results may be due to ethylene glycol, which itself could be acted as phase separation enhancer [2].

The extraction system A, employing a strong alkali (potassium hydroxide) to react with the marker dyes, developed unstable colors that resulted in the errors during the quantitative determination of the marker dyes. This system was therefore not suitable for the extraction of marker dyes, although its cost was the lowest when comparing with the extraction systems B and C.

The extraction systems B and C were weak alkali solutions of ethylenediamine, and diethylenetriamine, respectively. Both systems gave clearly defined and deep colors with high absorbance at the maximum wavelength of the developed colors in an extracted phase. However, when comparing the costs of ethylenediamine and diethylenetriamine, the cost of ethylenediamine was lower than that of diethylenetriamine. Thus, the extraction system B was the most suitable system for the extraction of marker dyes from fuel oils.

Regarding to the percentages of base used in extraction system B and the maximum wavelength obtained, it was found that when the percentage of base was increased, the maximum wavelength of the developed color would shift to the longer wavelength, this effect is called "Bathochromic shift" or "Red shift". This bathochromic shift presumably resulted from a reduction in the energy level of the excited state accompanying dipole-dipole interaction, and hydrogen bonding between ethylenediamine and marker dyes. It was shown that the extraction system B5 (50% ethylenediamine) gave the highest absorbance at the maximum

wavelength (Table 4-17). The extraction system B5 was therefore chosen as the most appropriate extraction system for the marker dyes in this research.

The synthetic marker dyes (each with 5 ppm) were dyed in gasoline and diesel fuel, they were subsequently extracted with 50% ethylenediamine in a solution of 1:1 ethylene glycol and methanol. The UV/VIS absorbance at their maximum wavelengths and visual colors were observed as shown in Table 4-18.

Table 4-18: The UV/VIS absorbance at their maximum wavelengths and visual colors in the extracted phase of marker dyes (each with 5 ppm).

| Marker dye                              | Gasoline              |                  | Diesel fuel           |                  |
|---|-----------------------|------------------|-----------------------|------------------|
|   | $\lambda_{\max}$ (nm) | Visual color     | $\lambda_{\max}$ (nm) | Visual color     |
| 1. cardanol-phenyl azo                  | 418.1                 | Yellow           | 424.0                 | Yellow           |
| 2. cardanol- <i>p</i> -nitrophenyl azo  | 537.5                 | Purple           | 538.2                 | Purple           |
| 3. cardanol- <i>m</i> -nitrophenyl azo  | 470.3                 | Yellowish-orange | 471.2                 | Yellowish-orange |
| 4. cardanol- <i>o</i> -nitrophenyl azo  | 479.1                 | Orange           | 483.0                 | Orange           |
| 5. cardanol- <i>p</i> -chlorophenyl azo | 418.3                 | Yellow           | 454.0                 | Yellow           |
| 6. cardanol- <i>m</i> -chlorophenyl azo | 432.4                 | Yellow           | 450.4                 | Yellow           |
| 7. cardanol- <i>o</i> -chlorophenyl azo | 434.2                 | Yellow           | 462.5                 | Yellow           |
| 8. cardanol-2-chloro-4-nitrophenyl azo  | 567.7                 | Bluish-violet    | 569.8                 | Bluish-violet    |
| 9. cardanol-2-chloro-5-nitrophenyl azo  | 490.2                 | Orange           | 495.6                 | Orange           |

Table 4-18 (cont.): The UV/VIS absorbance at their maximum wavelengths and visual colors in the extracted phase of marker dyes (each with 5 ppm).

| Marker dye                               | Gasoline              |                | Diesel fuel           |                |
|--|-----------------------|----------------|-----------------------|----------------|
|  | $\lambda_{\max}$ (nm) | Visual color   | $\lambda_{\max}$ (nm) | Visual color   |
| 10. cardanol-4-chloro-2-nitrophenyl azo  | 495.2                 | Reddish-orange | 500.6                 | Reddish-orange |
| 11. cardanol-4-chloro-3-nitrophenyl azo  | 480.9                 | Orange         | 495.3                 | Orange         |
| 12. cardanol- <i>p</i> -methylphenyl azo | 407.3                 | Yellow         | 420.7                 | Yellow         |
| 13. cardanol- <i>m</i> -methylphenyl azo | 407.8                 | Yellow         | 420.9                 | Yellow         |
| 14. cardanol- <i>o</i> -methylphenyl azo | 407.4                 | Yellow         | 421.3                 | Yellow         |
| 15. cardanol-2-methoxy-4-nitrophenyl azo | 546.3                 | Purple         | 550.8                 | Purple         |
| 16. cardanol-Fast Blue B azo             | 507.0                 | Reddish-orange | 510.5                 | Reddish-orange |
| 17. cardanol-Fast Blue BB azo            | 478.3                 | Orange         | 480.6                 | Orange         |
| 18. cardanol-Fast Red RC azo             | 436.6                 | Yellow         | 450                   | Yellow         |

Visual colors in an extracted phase when extracted the dyed fuel oils in this research were compared with those in the master thesis of Thowongs, K. [3], and Silapakampeerapab, S. [4] as shown in Table 4-19.

Table 4-19: The visual colors in extracted phase of marker dyes in this research comparing with marker dyes obtained from the master thesis of Thowongs, K., and Silapakampeerapab, S.

| Aniline                    | Color in extracted phase |                |                  |
|----------------------------|--------------------------|----------------|------------------|
|                            | Marker dye A*            | Marker dye B** | This research    |
| 1. <i>p</i> -nitroaniline  | -                        | Red            | Purple           |
| 2. <i>m</i> -nitroaniline  | -                        | Yellow         | Yellowish-orange |
| 3. <i>o</i> -nitroaniline  | -                        | Orange-yellow  | Orange           |
| 4. <i>p</i> -chloroaniline | Yellow                   | -              | Yellow           |
| 5. <i>m</i> -chloroaniline | Yellow                   | -              | Yellow           |
| 6. <i>o</i> -chloroaniline | Yellow                   | -              | Yellow           |

\* Marker dyes in master thesis of Thowongs, K. [3]

Extraction solution was 10% potassium hydroxide in methanol

\*\* Marker dyes in master thesis of Silapakampeerapab, S. [4]

Extraction solution was 2% potassium hydroxide in ethylene glycol

In chloroaniline series, the colors in the extracted phase of marker dyes set A, and marker dyes in this research were yellow. Therefore, it could be concluded that the use of 10% potassium hydroxide in methanol, and 50% ethylenediamine in

a solution of 1:1 ethylene glycol and methanol for the extraction of marker dyes in chloroaniline series from the dyed fuel oils were not significantly different.

On the other hand, when extracted the marker dyes in nitroaniline series, the colors in extracted phase of marker dyes in this research were clearer and deeper than the ones obtained from the extraction of marker dyes set B. Therefore, it could be concluded that 50% ethylenediamine in a solution of 1:1 ethylene glycol and methanol was more appropriate for the extraction of marker dyes in nitroaniline series from the dyed fuel oils than 2% potassium hydroxide in ethylene glycol.

These marker dyes could be detected in the dyed fuel oils by extraction into 50% ethylenediamine in a solution of 1:1 ethylene glycol and methanol. The detection of marker dyes (each with 5 ppm) in fuel oils are shown below.

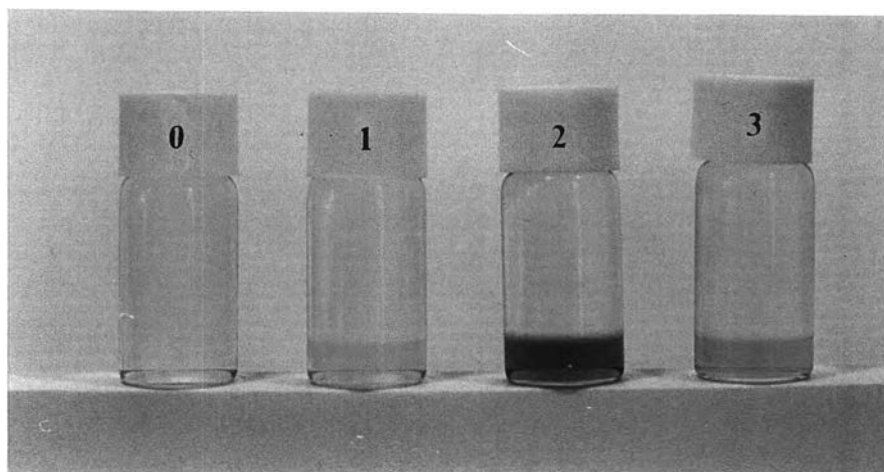


Fig. 4-60: The detection of cardanol-phenyl azo (1), cardanol-*p*-nitrophenyl azo (2), and cardanol-*m*-nitrophenyl azo (3) in gasoline comparing with undyed gasoline (0).

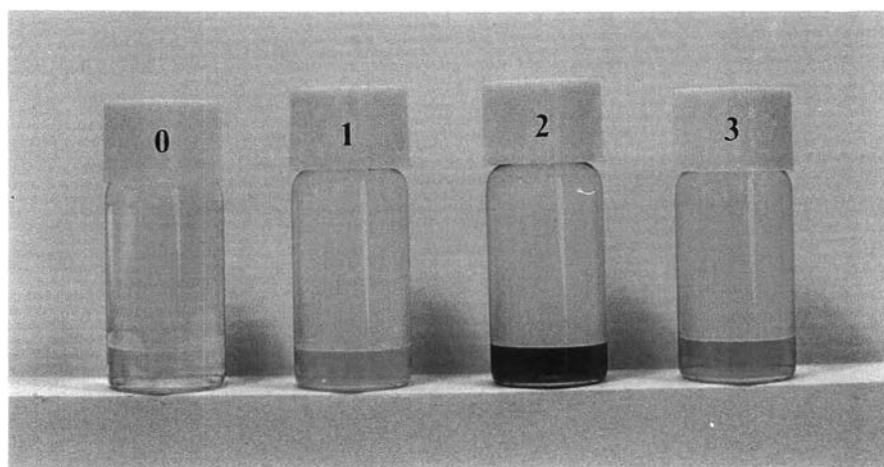


Fig. 4-61: The detection of cardanol-phenyl azo (1), cardanol-*p*-nitrophenyl azo (2), and cardanol-*m*-nitrophenyl azo (3) in diesel fuel comparing with undyed diesel fuel (0).



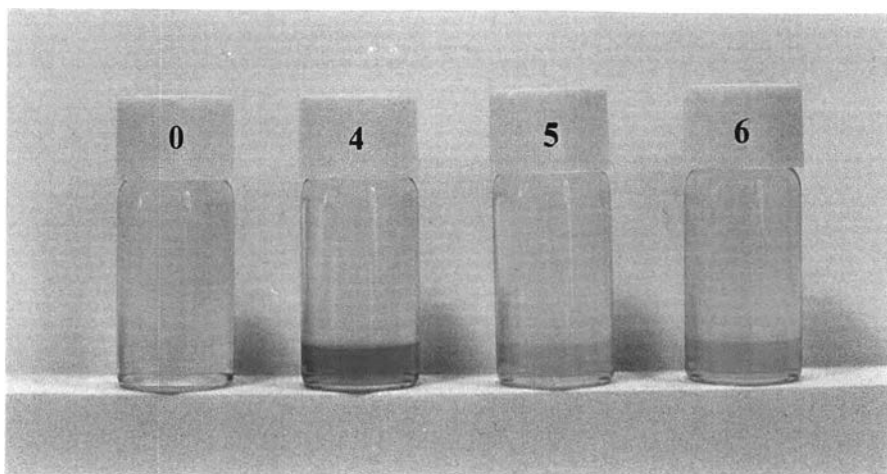


Fig. 4-62: The detection of cardanol-*o*-nitrophenyl azo (4), cardanol-*p*-chlorophenyl (5), and cardanol-*m*-chlorophenyl azo (6) in gasoline comparing with undyed gasoline (0).

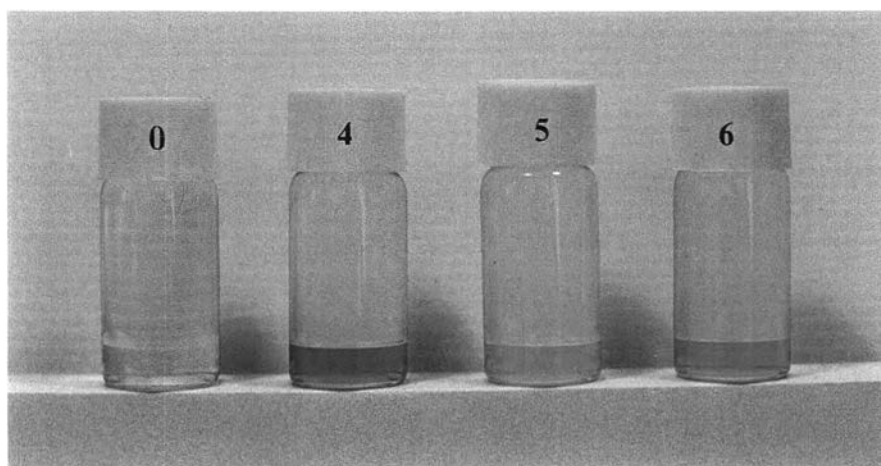


Fig. 4-63: The detection of cardanol-*o*-nitrophenyl azo (4), cardanol-*p*-chlorophenyl (5), and cardanol-*m*-chlorophenyl azo (6) in diesel fuel comparing with undyed diesel fuel (0).

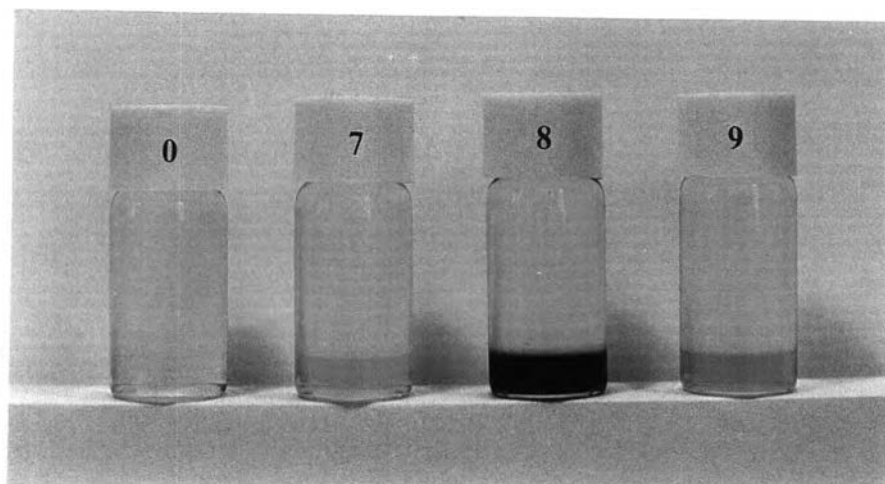


Fig. 4-64: The detection of cardanol-*o*-chlorophenyl azo (7), cardanol-2-chloro-4-nitrophenyl azo (8), and cardanol-2-chloro-5-nitrophenyl azo (9) in gasoline comparing with undyed gasoline (0).

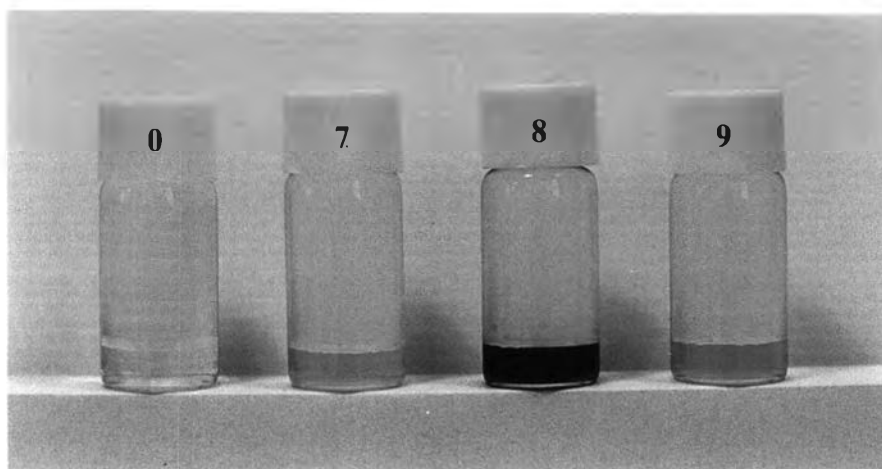


Fig. 4-65: The detection of cardanol-*o*-chlorophenyl azo (7), cardanol-2-chloro-4-nitrophenyl azo (8), and cardanol-2-chloro-5-nitrophenyl azo (9) in diesel fuel comparing with undyed diesel fuel (0).

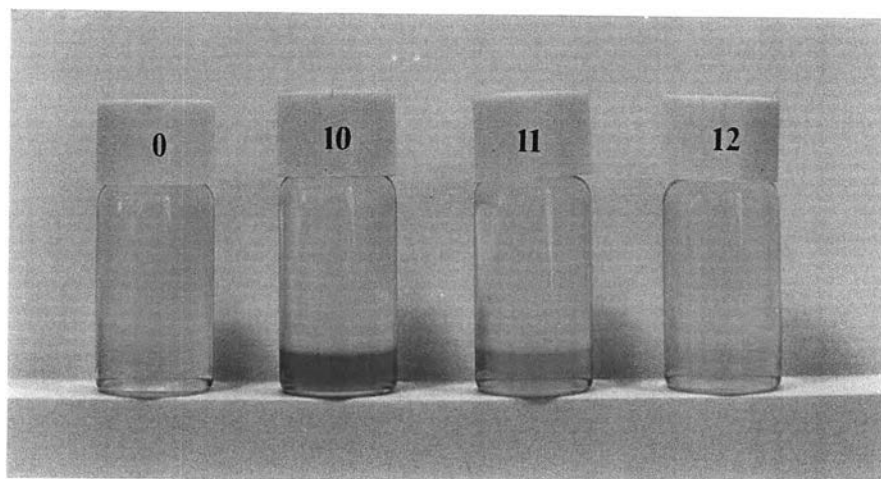


Fig. 4-66: The detection of cardanol-4-chloro-2-nitrophenyl azo (10), cardanol-4-chloro-3-nitrophenyl azo (11), and cardanol-*p*-methylphenyl azo (12) in gasoline comparing with undyed gasoline (0).

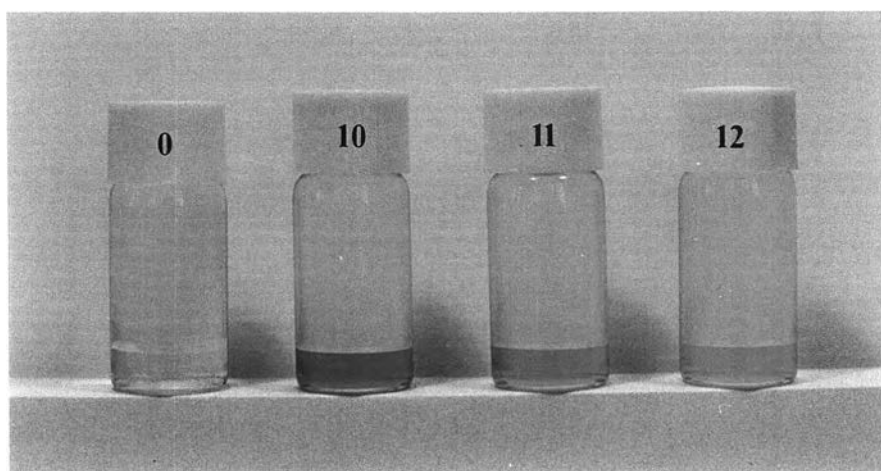


Fig. 4-67: The detection of cardanol-4-chloro-2-nitrophenyl azo (10), cardanol-4-chloro-3-nitrophenyl azo (11), and cardanol-*p*-methylphenyl azo (12) in diesel fuel comparing with undyed diesel fuel (0).

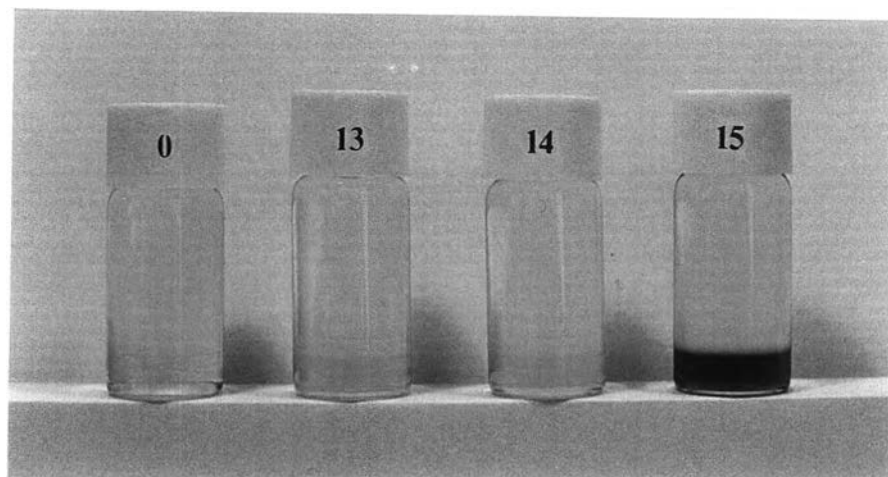


Fig. 4-68: The detection of cardanol-*m*-methylphenyl azo (13), cardanol-*o*-methylphenyl azo (14), and cardanol-2-methoxy-4-nitrophenyl azo (15) in gasoline comparing with undyed gasoline (0).

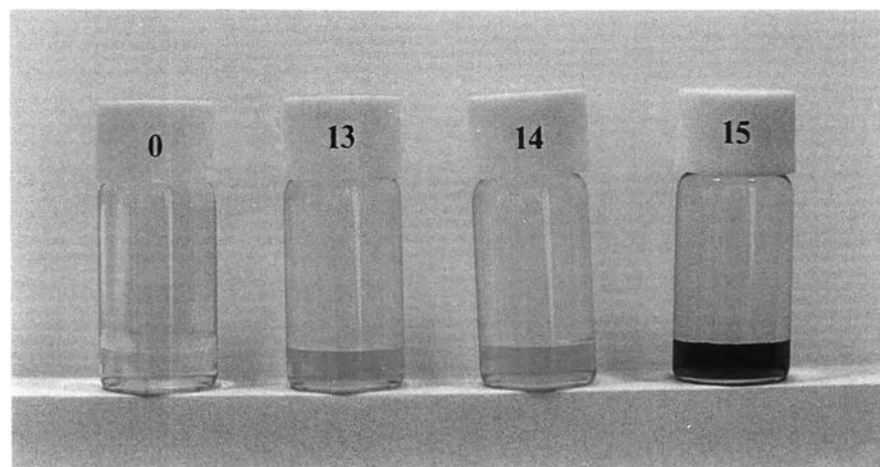


Fig. 4-69: The detection of cardanol-*m*-methylphenyl azo (13), cardanol-*o*-methylphenyl azo (14), and cardanol-2-methoxy-4-nitrophenyl azo (15) in diesel fuel comparing with undyed diesel fuel (0).

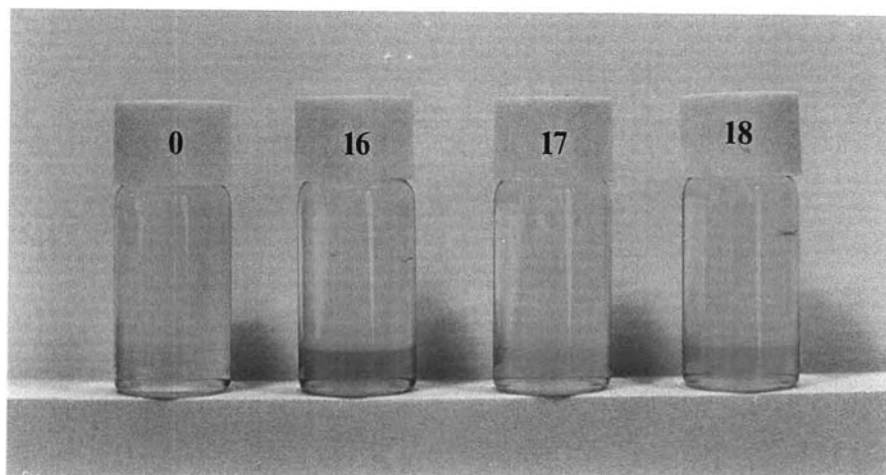


Fig. 4-70: The detection of cardanol-Fast Blue B azo (16), cardanol-Fast Blue BB azo (17), and cardanol-Fast Red RC azo (18) in gasoline comparing with undyed gasoline (0).

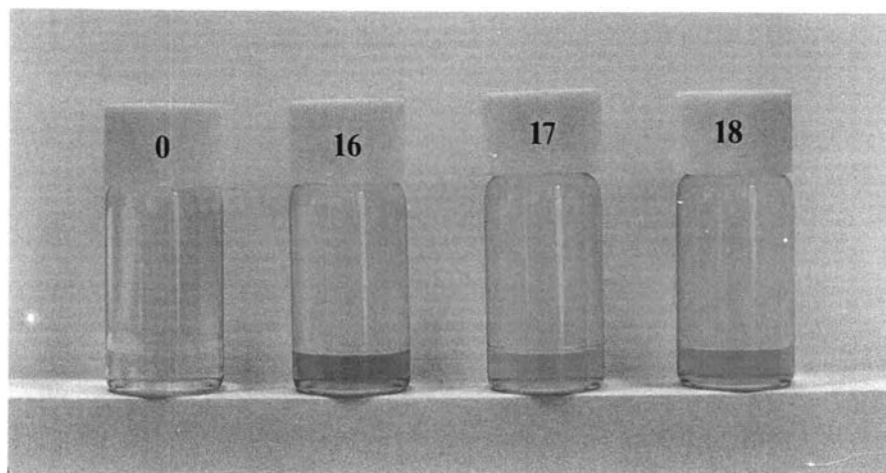
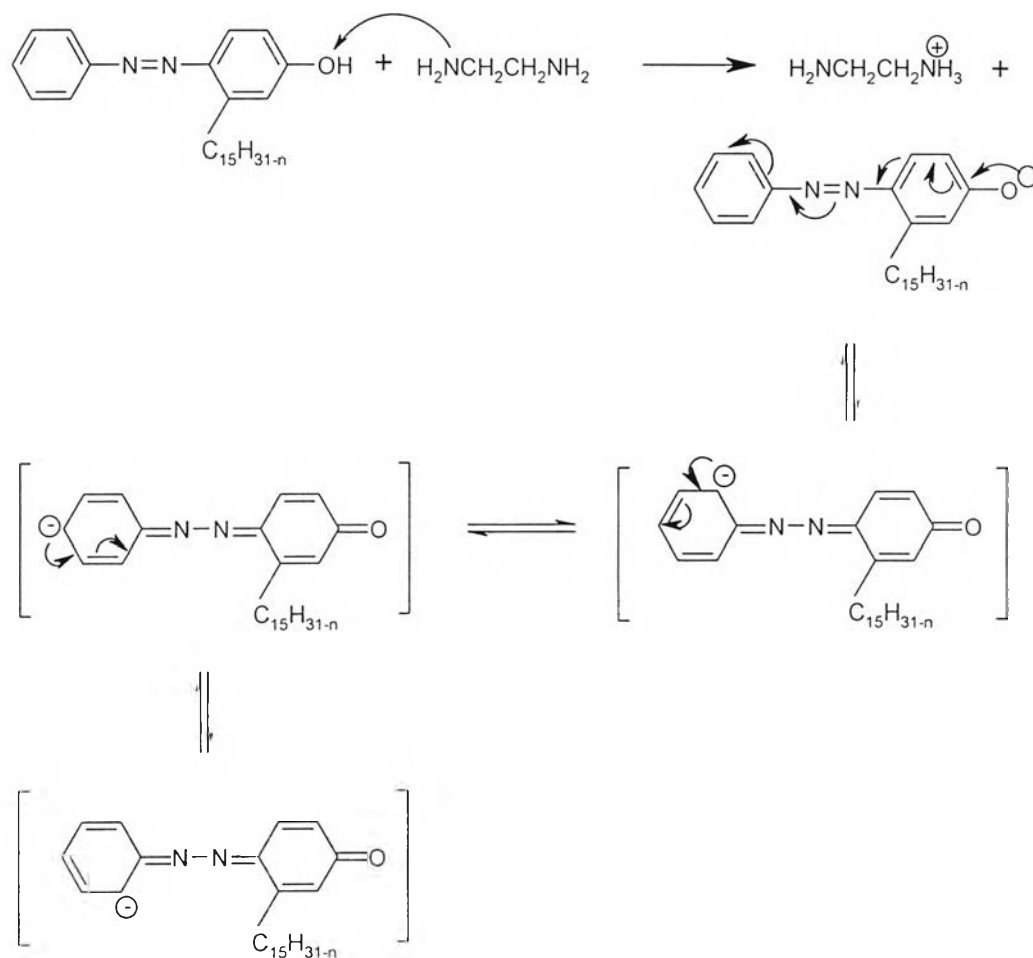


Fig. 4-71: The detection of cardanol-Fast Blue B azo (16), cardanol-Fast Blue BB azo (17), and cardanol-Fast Red RC azo (18) in diesel fuel comparing with undyed diesel fuel (0).

The colors of the marker dyes were visible by complexation reaction of ethylenediamine and marker dyes. These reactions resulted in the oil-soluble marker dyes being rendered soluble in an aqueous medium, thus extractable into an aqueous phase. The complexation mechanism is schemed below.



From this mechanism, it is shown that the negative charge would appear in the *para* and *ortho*-position to the azo group. If the *para* or *ortho*-position to the azo group is occupied by an electron-withdrawing group, such as nitro group, the structure is stabilized by an inductive effect. Moreover, if the substituent at the *para* or *ortho*-position to the azo group is the nitro group, the structure is stabilized

not only by the inductive effect but also the resonance effect, because nitro group could distribute the negative charge through its structure.

From Table 4-18, the color in the extracted phase of cardanol-*p*-nitrophenyl azo was purple, while the color in the extracted phase of cardanol-*o*-nitrophenyl azo was orange. Both ionized structures were stabilized by the inductive, and the resonance effects, but the differences in colors supported that the substitutions of the electron-withdrawing group at the *ortho*-position were less effective than the substitutions of the electron-withdrawing groups at the *para*-position to the amino moiety.

#### **4.5 Effects of marker dye on the physical properties of dyed fuel oils**

Physical properties of dyed fuel oils were determined and compared with the undyed fuel oils. The marker dyes suitable for the fuel oils are the marker dyes that do not give any effects on the physical properties of the dyed fuel oils.

##### **4.5.1 Effects of marker dye on the physical properties of dyed gasoline**

Gasoline containing 2 ppm of cardanol-2-chloro-4-nitrophenyl azo was employed for testing physical properties, using the ASTM methods. The physical properties of dyed and undyed gasoline were compared. The results are listed in Table 4-20.

Table 4-20: The effects of marker dye on the physical properties of dyed and undyed gasoline.

| Test items   | ASTM   | Limit   | Result |        |
|--|--------|---------|--------|--------|
|  |        |         | Dyed   | Undyed |
| API gravity @ 60 °F                                | D 1298 | Report  | 56.0   | 58.2   |
| Specific gravity @ 60 / 60 °F                      | D 1298 | Report  | 0.7547 | 0.7459 |
| Octane number                                      |        |         |        |        |
| - Research method (RON)                            | D 2699 | 95      | 96.6   | 95.2   |
| Reid vapor pressure @ 37.8 °C ,kPa                 |        |         |        |        |
| - Oxygenated blends                                | D 5191 | 62 max  | 56.0   | 59.7   |
| Copper strip corrosion, Number<br>(3 hrs, @ 50 °C) | D 130  | No. 1   | No. 1  | No. 1  |
| Distillation: (Correct. temp.)                     | D 86   |         |        |        |
| IBP, °C  |        | Report  | 36.5   | 37.2   |
| 10 %vol. evaporated, °C                            |        | 70 max  | 54.1   | 52.2   |
| 50 %vol. evaporated, °C                            |        | 70 –110 | 87.6   | 80.4   |
| 90 %vol. evaporated, °C                            |        | 170 max | 153.7  | 149.5  |
| End point, °C                                      |        | 200 max | 191.9  | 187.6  |
| Recovery, %vol.                                    |        | Report  | 97.8   | 97.3   |
| Residue, %vol.                                     |        | 2.0 max | 1.0    | 1.0    |
| Color  | D 1500 | 2.0 max | < 0.5  | < 0.5  |
|  | Visual | -       | Yellow | Yellow |
| Total acid number, mg KOH/ g                       | D 974  | -       | 0.008  | 0.004  |



The physical properties of dyed gasoline were not significantly different from those of undyed gasoline (Table 4-20). Both dyed and undyed gasoline gave similar specific gravity, distillation properties, and color. The Research Octane Number (RON) of dyed gasoline was slightly greater than undyed gasoline; this effect may be due to the contamination of toluene from the marker dye stock solution. However, toluene contamination did not show significant effect on physical properties of the gasoline. From these reasons, this marker dye was applicable as the marker in gasoline.

#### **4.5.2 Effects of marker dye on the physical properties of dyed diesel fuel**

Diesel fuel containing 2 ppm of cardanol-2-chloro-4-nitrophenyl azo was used for testing physical properties, using the ASTM methods. The physical properties of the dyed and undyed fuel oils were compared. The results are shown in Table 4-21.

Table 4-21: The effects of marker dye on the physical properties of dyed and undyed diesel fuel.

| Test items   | ASTM   | Limit     | Result |        |
|--|--------|-----------|--------|--------|
|  |        |           | Dyed   | Undyed |
| API gravity @ 60 °F                                | D 1298 | Report    | 38.8   | 38.9   |
| Specific gravity @ 15.6 / 15.6 °C                  | D 1298 | Report    | 0.8309 | 0.8304 |
| Calculated cetane index                            | D 976  | 47 min    | 55.7   | 55.5   |
| Kinematic viscosity @ 40 °C, cSt                   | D 445  | 1.8 - 4.1 | 3.1    | 3.1    |
| Pour point, °C                                     | D 97   | 10        | -2.0   | -2.0   |
| Sulfur content, %wt                                | D 4294 | 0.05      | 0.03   | 0.03   |
| Copper strip corrosion, Number<br>(3 hrs, @ 50 °C) | D 130  | No. 1     | No. 1  | No. 1  |
| Flash Point (P.M), °C                              | D 93   | 52        | 62     | 61     |
| Distillation: (Correct. Temp.)                     | D 86   |           |        |        |
| IBP, °C  |        | Report    | 173.7  | 171.6  |
| 10 % rec., °C                                      |        | Report    | 213.4  | 210.5  |
| 50 % rec., °C                                      |        | Report    | 276.8  | 275.4  |
| 90 % rec., °C                                      |        | 357 max   | 354.0  | 352.1  |
| Color  | D 1500 | 2.0 max   | < 0.5  | < 0.5  |
|  | Visual | -         | Yellow | Yellow |
| Total acid number, mg KOH/ g                       | D 974  |           | 0.007  | 0.004  |

The physical properties of dyed diesel fuel were not significantly different from those of the undyed diesel fuel (Table 4-21). Both dyed and undyed diesel fuels provided similar specific gravity, calculated cetane index, pour point, flash point, distillation properties, and colors. Since the marker dye did not have effects on the physical properties of diesel fuel, it is therefore possible to use this marker dye as the marker in diesel fuel.

#### **4.6 Quantitative determination of marker dyes in dyed fuel oils**

The standard calibration curve of each marker dyes in gasoline and diesel fuel was prepared by adding each marker dyes into fuel oils at different concentrations. This dyed fuel oils was then extracted with 50% ethylenediamine in a solution of 1:1 ethylene glycol and methanol, and the standard calibration curve was a plot between absorbance and the concentration of the marker dye in fuel oil.

The standard calibration equations of marker dyes in gasoline and diesel fuel are listed in Table 4-22, while the standard calibration curves of marker dyes are shown in the Appendix section.

Table 4-22: The calibration equations for the quantitative determinations of marker dyes in gasoline and diesel fuel.

| Marker dye                              | Standard calibration equation  |  |
|---|--|--|
|   | Gasoline   | Diesel fuel  |
| 1. cardanol-phenyl azo                  | $Y = 2.862000 \text{ e-}03 + 9.888300 \text{ e-}02 * x$<br>$(\lambda_{\text{max}} = 418.1, r = 0.999915)$  | $Y = 1.394000 \text{ e-}03 + 1.193835 \text{ e-}01 * x$<br>$(\lambda_{\text{max}} = 424.0, r = 0.999921)$  |
| 2. cardanol- <i>p</i> -nitrophenyl azo  | $Y = -5.200000 \text{ e-}05 + 1.794930 \text{ e-}01 * x$<br>$(\lambda_{\text{max}} = 537.5, r = 0.999968)$ | $Y = 3.320000 \text{ e-}03 + 1.867790 \text{ e-}01 * x$<br>$(\lambda_{\text{max}} = 539.0, r = 0.999930)$  |
| 3. cardanol- <i>m</i> -nitrophenyl azo  | $Y = 4.200000 \text{ e-}03 + 1.760640 \text{ e-}01 * x$<br>$(\lambda_{\text{max}} = 470.3, r = 0.999901)$  | $Y = -2.890000 \text{ e-}03 + 1.827310 \text{ e-}01 * x$<br>$(\lambda_{\text{max}} = 471.2, r = 0.999859)$ |
| 4. cardanol- <i>o</i> -nitrophenyl azo  | $Y = -9.720000 \text{ e-}04 + 1.550150 \text{ e-}01 * x$<br>$(\lambda_{\text{max}} = 479.1, r = 0.999936)$ | $Y = -6.280000 \text{ e-}03 + 1.579850 \text{ e-}01 * x$<br>$(\lambda_{\text{max}} = 424.0, r = 0.999868)$ |
| 5. cardanol- <i>p</i> -chlorophenyl azo | $Y = 3.316000 \text{ e-}03 + 5.782900 \text{ e-}02 * x$<br>$(\lambda_{\text{max}} = 418.3, r = 0.999891)$  | $Y = 8.458000 \text{ e-}03 + 1.287205 \text{ e-}01 * x$<br>$(\lambda_{\text{max}} = 454.0, r = 0.999827)$  |

Table 4-22 (cont.): The calibration equations for the quantitative determinations of marker dyes in gasoline and diesel fuel.

| Marker dye                              | Standard calibration equation  |  |
|---|--|--|
|   | Gasoline   | Diesel fuel  |
| 6. cardanol-2-chloro-4-nitrophenyl azo  | $Y = -3.116000 \text{ e-}03 + 2.389930 \text{ e-}01 * x$<br>$(\lambda_{\text{max}} = 567.7, r = 0.999917)$ | $Y = -6.436000 \text{ e-}03 + 1.629490 \text{ e-}01 * x$<br>$(\lambda_{\text{max}} = 569.8, r = 0.999800)$ |
| 7. cardanol- <i>p</i> -methylphenyl azo | $Y = 1.146216 \text{ e-}03 + 3.380318 \text{ e-}02 * x$<br>$(\lambda_{\text{max}} = 407.3, r = 0.999891)$  | $Y = -4.181622 \text{ e-}03 + 8.677993 \text{ e-}02 * x$<br>$(\lambda_{\text{max}} = 420.7, r = 0.999843)$ |
| 8. cardanol-2-methoxy-4-nitrophenyl azo | $Y = 4.974000 \text{ e-}03 + 1.064645 \text{ e-}01 * x$<br>$(\lambda_{\text{max}} = 546.3, r = 0.999914)$  | $Y = 1.814000 \text{ e-}03 + 1.077675 \text{ e-}01 * x$<br>$(\lambda_{\text{max}} = 550.8, r = 0.999970)$  |
| 9. cardanol-Fast Blue B azo             | $Y = 8.475472 \text{ e-}04 + 3.210590 \text{ e-}02 * x$<br>$(\lambda_{\text{max}} = 507.0, r = 0.999964)$  | $Y = 1.351321 \text{ e-}03 + 3.487759 \text{ e-}02 * x$<br>$(\lambda_{\text{max}} = 510.5, r = 0.999953)$  |

From Table 4-22, it was concluded that marker dyes in this research gave the precisely quantitative determinations since their correlation coefficients ( $r$ ) in the standard equations were closed to 1. Therefore, the marker dyes in this research could be used as markers in gasoline and diesel fuel with precisely quantitative determinations.

#### 4.7 Stability of marker dyes in dyed fuel oils

Stability of marker dyes in fuel oils was studied by monitoring the quantities of marker dyes in fuel oils for 3 months, using the UV/VIS spectroscopic technique. The marker dyes, cardanol-*p*-nitrophenyl azo (2 ppm), cardanol-2-chloro-4-nitrophenyl azo (2 ppm), and cardanol-2-methoxy-4-nitrophenyl azo (5 ppm) in gasoline and diesel fuel were used for this study. The results of the stability of marker dyes in fuel oils are in Tables 4-23 to 4-25.

Table 4-23: The stability of cardanol-*p*-nitrophenyl azo (2 ppm) in gasoline and diesel fuel in the period of 3 months.

| Month | Concentrations in gasoline |      |      | Concentrations in diesel fuel |      |      |
|-------|----------------------------|------|------|-------------------------------|------|------|
|       | 1                          | 2    | Ave  | 1                             | 2    | Ave  |
| 1     | 1.99                       | 2.03 | 2.01 | 2.10                          | 2.18 | 2.14 |
| 2     | 2.05                       | 2.00 | 2.03 | 2.12                          | 2.20 | 2.16 |
| 3     | 2.04                       | 2.01 | 2.03 | 2.11                          | 2.16 | 2.14 |

Table 4-24: The stability of cardanol-2-chloro-4-nitrophenyl azo (2 ppm) in gasoline and diesel fuel in the period of 3 months.

| Month | Concentrations in gasoline |      |      | Concentrations in diesel fuel |      |      |
|-------|----------------------------|------|------|-------------------------------|------|------|
|       | 1                          | 2    | Ave  | 1                             | 2    | Ave  |
| 1     | 2.02                       | 2.04 | 2.03 | 2.05                          | 2.00 | 2.03 |
| 2     | 2.05                       | 2.09 | 2.07 | 2.08                          | 2.05 | 2.07 |
| 3     | 2.05                       | 2.08 | 2.07 | 2.07                          | 2.11 | 2.09 |

Table 4-25: The stability of cardanol-2-methoxy-4-nitrophenyl azo (5 ppm) in gasoline and diesel fuel in the period of 3 months.

| Month | Concentrations in gasoline |      |      | Concentrations in diesel fuel |      |      |
|-------|----------------------------|------|------|-------------------------------|------|------|
|       | 1                          | 2    | Ave  | 1                             | 2    | Ave  |
| 1     | 4.99                       | 5.02 | 5.01 | 5.02                          | 5.05 | 5.04 |
| 2     | 5.01                       | 5.03 | 5.02 | 5.10                          | 5.07 | 5.09 |
| 3     | 5.00                       | 5.05 | 5.03 | 5.10                          | 5.14 | 5.12 |

From Tables 4-23 to 4-25, the concentrations of marker dyes in fuel oils were slightly different from the original concentrations, so it is concluded that these marker dyes are stable, at least 3 months in fuel oils. Generally, each batch of fuel oils is consumed within 3 months, after release to the market. It is concluded that these marker dyes could be applied as markers in commercial fuel oils.