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Phytochemical studies of *Prunus domestica Linn* shoots extract and its corrosion inhibition potential

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Abstract
This project aims to study the phytochemical constituents of *Prunus domestica* shoots extract by GC-MS & FTIR techniques and to investigate its corrosion inhibition potential by Tafel techniques. Ethanolic extract of *P. domestica* was fractionated using an n-hexane solvent, which was further resolved via column chromatography using different solvents (non-polar to the polar solvent). Three major subfractions were obtained from the n-hexane fraction; subjected to further analysis. These subfractions mainly constituted esters, alkanes, and alcohols and exhibited corrosion inhibition potential of up to 95.78%. It was established that *P. domestica Linn* shoot extract has good potential to serve as a green corrosion inhibitor.
Keywords: Prunus domestica, extract, inhibition potential, corrosion

1. INTRODUCTION

The breakdown of metals and alloys due to chemical or electrochemical contact with the environment is known as corrosion. Wet and dry corrosion are two categories used to categorize corrosion reactions based on the characteristics of the corrosive environments. Corrosion can be classified into general corrosion, pitting, crevice corrosion, intergranular corrosion, environmental degradation, delamination, galvanic corrosion, and erosion-corrosion based on the metal damage caused [1]. Coatings, alloying, cathodic, and anode protection are all techniques for preventing corrosion in metals. Lasers have been employed for this recently. It is thought that metal surface treatment enhances the qualities of metal, such as its hardness, corrosion resistance, and roughness [2]. Nitrogen, sulfur, and oxygen-containing organic compounds had high inhibitory efficacy. However, many artificial inhibitors have hazardous effects on the environment and living things. Therefore, it is important to highlight low-cost, readily available, biodegradable, and environmentally acceptable corrosion inhibitors with high inhibitory efficiency [3]. There is currently a great need for corrosion inhibitors that are both effective and environmentally safe for the acidizing process. 15% hydrochloric acid (HCl) is used during acidization, which corrodes N80 steel [4]. Mild steel is frequently used in industry, due to its appealing mechanical features and inexpensive price. However, it degrades when exposed to corrosive environments [5]. The green corrosion inhibitors derived from plant extract are the most extensively studied since they are affordable, renewable, biodegradable, and, most importantly, safe for the environment and people. Plant extracts are effective at inhibiting corrosion, with an inhibition efficacy of above 80%. The highly concentrated active components known as phytochemicals account for this great efficiency [6]. The word phytochemical is used to a wide range of biologically active substances found in plants such as steroids, alkaloids, flavonoids and terpenoids [7]. The characteristics of the active phytochemicals and various pharmaceutical properties already documented are highlighted in the literature. Four Chinese plums have been used to separate the main phytochemicals, including polyphenols, flavonoids, and anthocyanins. Varying edaphic environments may cause the same variety to have different antioxidant capabilities [8]. Seasonal fruit *P. domestica* L. contains a variety of bioactive phytonutrients, including vitamins, flavonoids, phenolics, antioxidants, tannins, and anthocyanins. The use of an edible coating, controlled and modified atmospheric pressure, high-pressure thermal processing, ozone pretreatment, irradiation, and novel methods for creating extracts from plum flesh, peel, and seeds are just a few of the cutting-edge plum-processing technologies [9]. Many problems have arisen by using polyaniline as a coating material without using an environmentally favorable method. Here, cost-effective emulsion polymerization is used to create green Prunus domestica gum grafted polyaniline (PDG-g-PANI) composite, which is intended to be used as an effective anticorrosion material for mild steel (MS) and stainless steel (SS) in corrosive environments [10]. Pino & Quijano [11] identified the volatile compounds in *P.domestica* and analyzed them via headspace-solid phase microextraction and Simultaneous Distillation-Extraction. These techniques were combined with GC-FID and GC-MS techniques. Through this analysis, they have identified 148 compounds, out of which 23 are terpenoids, 58 are esters, 11 alcohols, 9 are alkanes, 14 aldehydes, 3 phenols, 10 ketones, 7 acids, 4 lactones including 9 structures of different compounds having different functional groups. Treutter et al., [12] studied the flavonoid and phenylpropanoid content of fruit skin of 28 plum varieties. The 49 phenolic contents were extracted from the fruit skin of *P. domestica.* for quantitative analysis, these contents are evaluated via an HPLC-DAD-based metabolomic study. The high content of peonidin and cyanidin glycosides of anthocyanins was found, while the principal flavanol was rutin. The main hydroxycinnamic acids found were n-chlorogenic acid and neochlorogenic acid. Khallouki and coworkers [13] have done

the phytochemical screening of flesh and peels of *P. domestica* fruit and found linoleic acid and oleic acid were the major constituents of oil from the fruit. The peels consist of rutin and 3,4-dihydroxybenzoic acid, while the flesh of the fruit comprises echinoids. The pits of the fruit consist of different phenolic compounds amygdalin, dihydro-coniferyl aldehyde, vanillin glucoside , vanillin, and guajacyl-glycerin-coniferyl aldehyde isomers. Navarro et al., [14] studied the flesh and skin phenolic content of *P. domestica Linn* shoot extract via High-Resolution Mass Spectrometry coupled with Ultra Performance Liquid Chromatography (UPLC-DAD-ESI-MS). A total of 52 compounds were identified, including 15 flavonoids (naringenin, kaempferol, quercetin derivatives), two isoprenoid glycosides derivatives of vomifoliol, nine phenolic acids (hydroxycinnamic acid, caffeoylquinic, and protocatechuic derivatives), five hydroxy chalcones (3-hydroxyphloretin derivatives and phloretin derivatives) and 21 proanthocyanidins. High phenolic content was measured for *P. domestica* fruit skin (0.3mg gallic acid equivalents/g extract). 5.19 µg/mL was the antioxidant potential by the DPPH method with IC50. Organic inhibitors typically have heteroatoms. Oxygen, sulphur, and nitrogen-containing organic compounds have been studied to reduce steel corrosion. Most organic inhibitors adsorb on metal surfaces by pushing away water molecules and generating a barrier. Because inhibitor molecules have p- and nonbonded (lone pair) electrons, electrons can easily travel from the inhibitor to the metal. Transferring electrons from the inhibitor to the metal surface creates a coordinated covalent connection. The donor atom's electron density and polarizability affect chemisorption bond strength. Substituting a ring H with -NH2, -NO2, -CHO, or -COOH improves inhibition. [15].

Given all the factors discussed above, it can be reasonably concluded that many flavanols, phenols, esters, and alkanes are reported from *P. domestica* flesh, and the skin of the fruit and natural products could be effectively used since they are readily available and relatively cheaper. Therefore the aim of this project is to study the phytochemical constituents of *Prunus domestica Linn* shoot in n-hexane solvent using advanced technologies and their application as a corrosion inhibiter potential for the safety of metals from corrosion through green technology as future innovative technology.

2. EXPERIMENTATION

2.1. Plant material collection and preparation

The shoots of *P. domestica Linn* (5 Kg) were collected from various regions of KPK, Pakistan, .and transported to Lab where they dried in the shade, sliced, and ground. Then, at room temperature, the plant material was soaked in 80% aqueous ethanol for 15 days. The ethanolic extract was evaporated to obtain a thick dark paste of liquid. This ethanolic extract was extracted using n-hexane solvent.

2.2. Extraction using n-hexane

The extraction was performed by using an n-hexane solvent. A total of three extractions were done with this solvent. The ethanol bark extract formed the lower layer, and the n-hexane extract formed the upper layer, as the n-hexane was less dense than the ethanol bark extract. The n-hexane was collected from a separatory funnel into separate collecting tubes. The extracts were diluted, so they were concentrated using a rotary evaporator.

2.3. Separation

This experiment used silica gel column chromatography as a separation technique. It has a stationary phase and a mobile phase. The stationary phase in this experiment was silica, and the mobile phase was n-hexane solvent. The column was a burette, and its preparation required two steps that were column packing and column loading.

For packing the column, a cotton plug was soaked in 2 ml of n-hexane solvent and loaded into the column. After that, 10 ml of n-hexane was added to the column. The silica was activated by placing it in the oven at 65-70 °C for 30 minutes. About 40 g of silica was dissolved in 100 ml of n-hexane solvent, forming a slurry, and loaded into the column. The different solvent was collected in a conical flask from the bottom of the column. For loading the column, about 3 g of activated silica was mixed with the concentrated n-hexane solvent extract. It was stirred with a spatula and evaporated at room temperature until a homogenous powdered form was obtained. Then this powder was loaded into the column. An opaque silica solution and the respective solvent were then topped onto the sample in the column. Also, while loading, the column was tapped from time to time to ensure there was no bubble forming in the silica slurry.

The column was run using three solvent systems that were 300mL n-hexane, 300mL n-hexane + chloroform (1:1), and 300ml chloroform. As silica is polar and n-hexane is non-polar, the separation was done within 3 hours, which was the fastest compared to other solvents used in column chromatography in this experiment. The samples from each solvent system were collected separately and were concentrated using a rotary evaporator. These fractions were analyzed by GC-MS techniques and resulted in the identification of 10 compounds.

2.4. GC-MS analysis

Helium was used as the carrier gas for the GC-MS analyses, and a mass spectrometer served as the detector. The column's initial temperature was set to 80°C and held there for one minute. In two minutes, the temperature increased to 160 degrees Celsius. After reaching 260°C, the temperature was maintained there for 12 minutes. The injector temperature and detector

temperature were set to 300°C during this conditioning.

2.5. FTIR analysis

FTIR analysis was used to investigate the phytochemical components of the *Prunus domestica* Linn shoots extract. A sample that will be examined is exposed to infrared rays. Bonds begin to vibrate as a result of radiation absorption, and they do so at various characteristic frequencies. The functional groups that are present in the molecule can be identified using this feature. Data on infrared absorbance were gathered over the wave number range of 4000 cm^{-1} to 400 cm^{-1} and were expressed in cm^{-1}.

3. RESULTS AND DISCUSSION

These n-hexane extracts were characterized using GC-MS and FTIR techniques and its application was identified by corrosion inhibition assay.

3.1. GC-MS Analysis of the extract

The GC-MS results were identified using the turbo mass software and reported in Table (1). The results were matched with The National Institute of Standards and Technology (NIST) library, and the compounds with the highest similarity were identified (Table 1). For the *P. domestica* hexane extract (PD-H-H), the compound L- isoleucine ethyl ester was identified at the peak 7.479, 1,2,3,4-hexadecane tetrol was identified at the peak 5.279, pyridazine-3-phenyl-5-nitro was identified at the peak 8.945, and Cyclo decylamine was identified at the peak 17.233. For the sample *P. domestica* hexane extract and chloroform solvent (1:1) (PD-H-H+C), 4-cyanobenzoic acid decyl ester was identified at the peak of 19.484, 3,5-dibutyl hexahydrol-H-pyrolozine was identified at the peak of 16.628, and 1,12-dodecanediol identified at the peak 12.176. For the sample *P. domestica* hexane extract in chloroform solvent (PD-H-C), 4-cyanobenzoic acid heptyl ester was identified at the peak of 19.484, hexadecane dinitrile was identified at the peak of 10.045, and N-heptadecanol-1 was identified at the peak of 18.279.

Table 1. Prunus domestica hexane extract in different combination of solvents

Sample Name	Compounds Identified
PD-H-H	L- isoleucine ethyl ester
	1,2,3,4-hexadecane tetrol
	pyridazine-3-phenyl-5-nitro
	cyclodecyl amine
PD-H-H+C	4-cyanobenzoic acid, decyl ester
	3,5-dibutyl hexahydrol-H-pyrolozine
	1,12-dodecanediol
PD-H-C	4-cyanobenzoic acid, heptyl ester
	hexadecane dinitrile
	N-heptadecanol-1

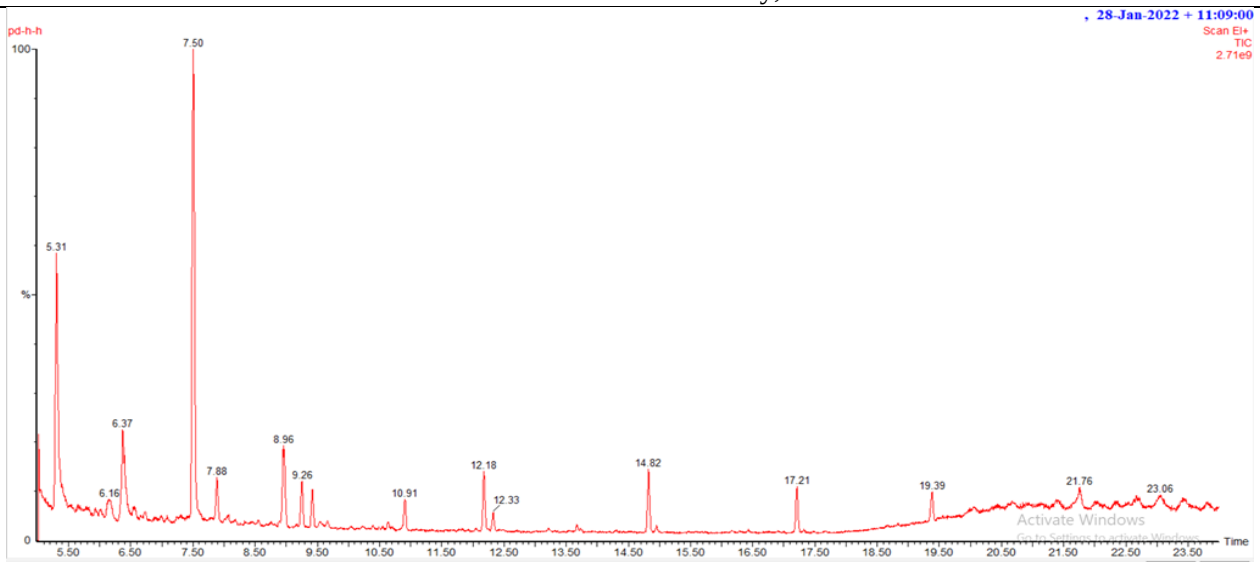

Figure 1 GC-MS of Prunus domestica hexane extract in hexane solvent (PD-H-H)

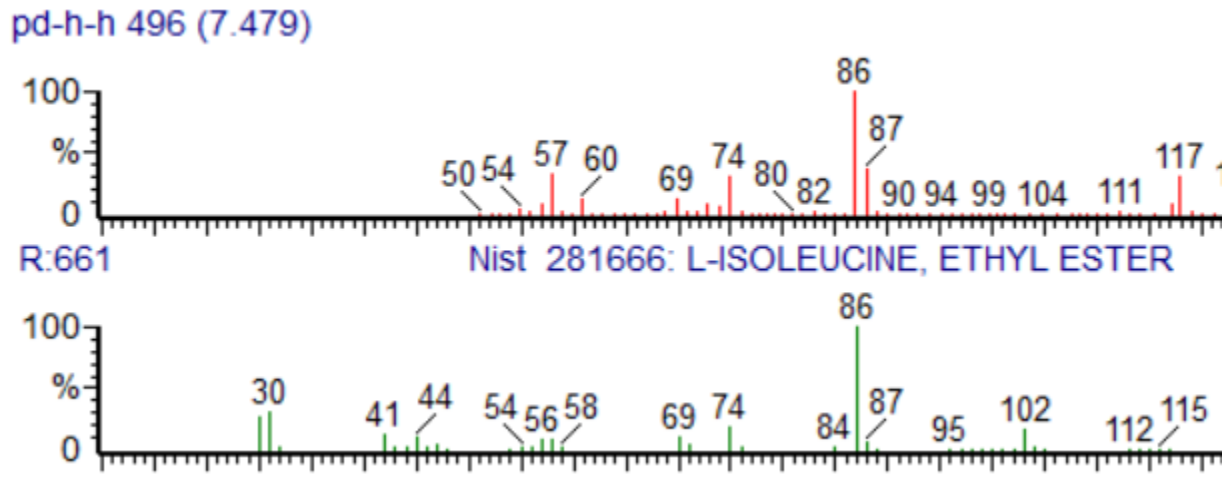

Figure 2 Mass spectrum of L- isoleucine ethyl ester in PD-H-H

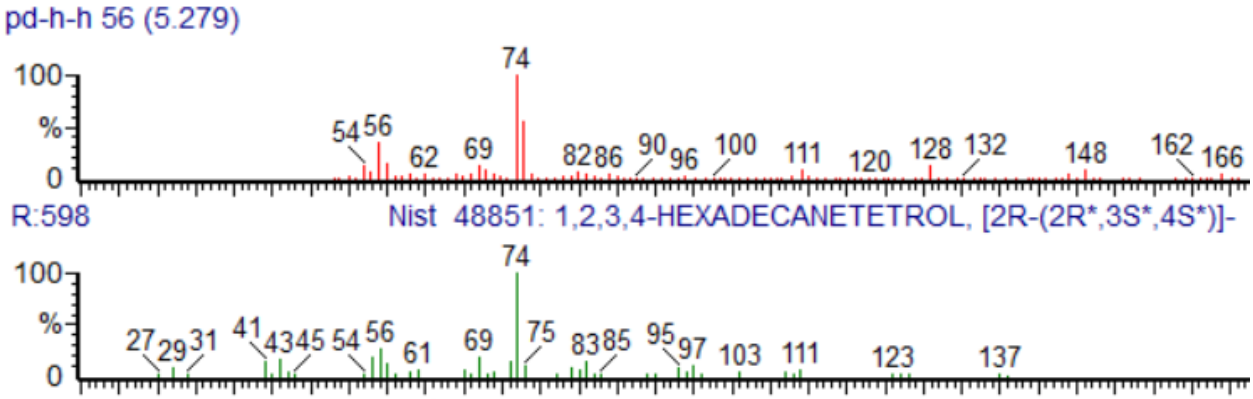

Figure 3 Mass spectrum of 1,2,3,4-hexadecane tetrol in PD-H-H

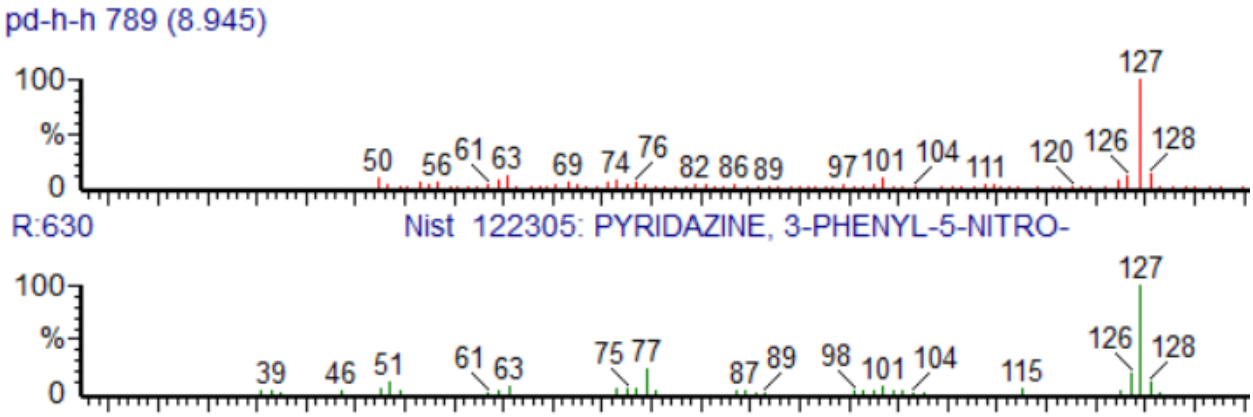

Figure 4 Mass spectrum of pyridazine-3-phenyl-5-nitro in PD-H-H

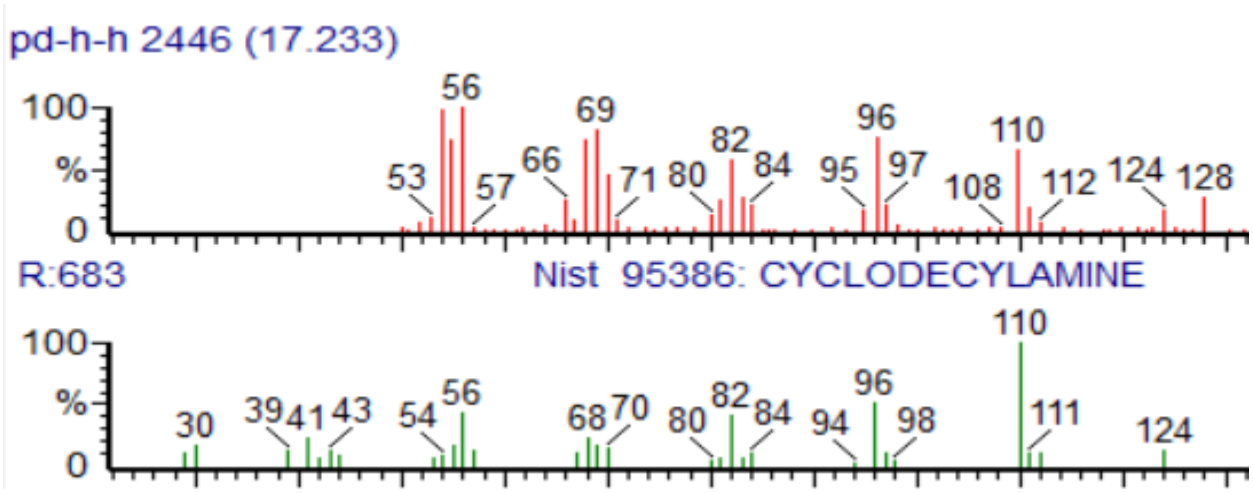

Figure 5 Mass spectrum of cyclodecyl amine in PD-H-H

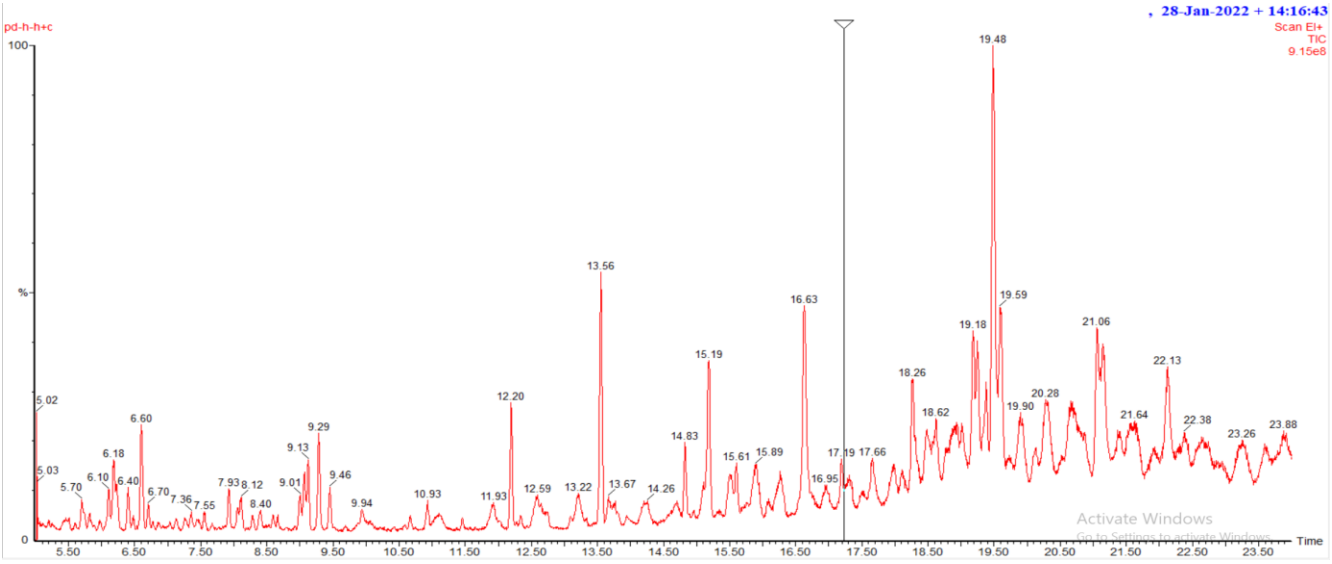

Figure 6 GC-MS of Prunus somestica hexane extract in hexane and chloroform solvent(1:1) (PD-H-H+C)

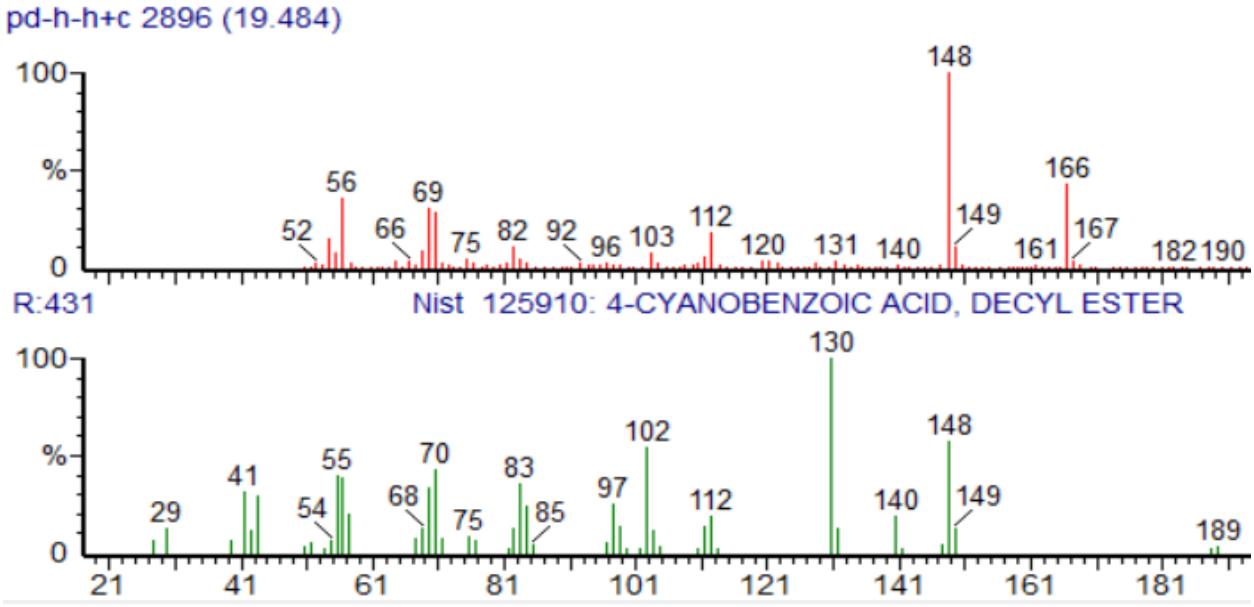

Figure 7 Mass spectrum of 4-cyanobenzoic acid, decyl ester in PD-H-H+C

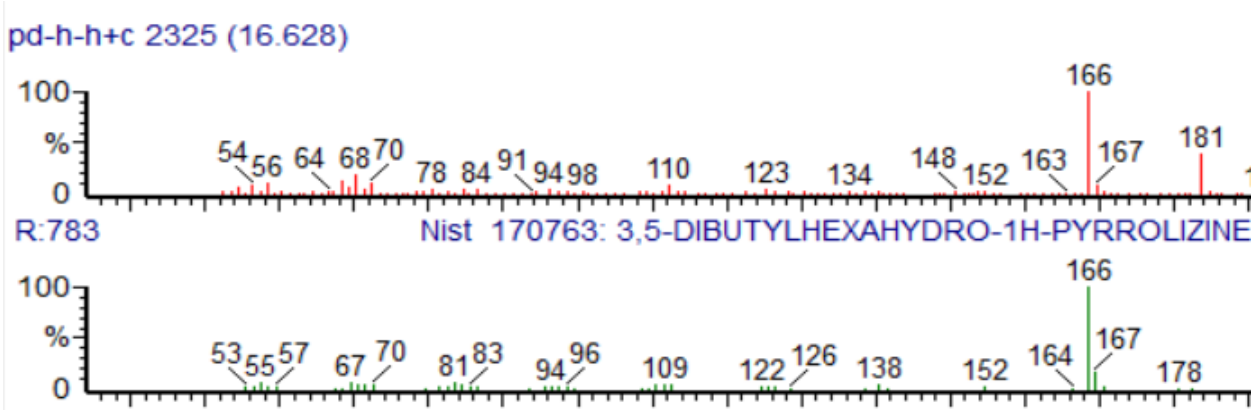

Figure 8 Mass spectrum of 3,5-dibutyl hexahydrol-H-pyrolozine in PD-H-H+C

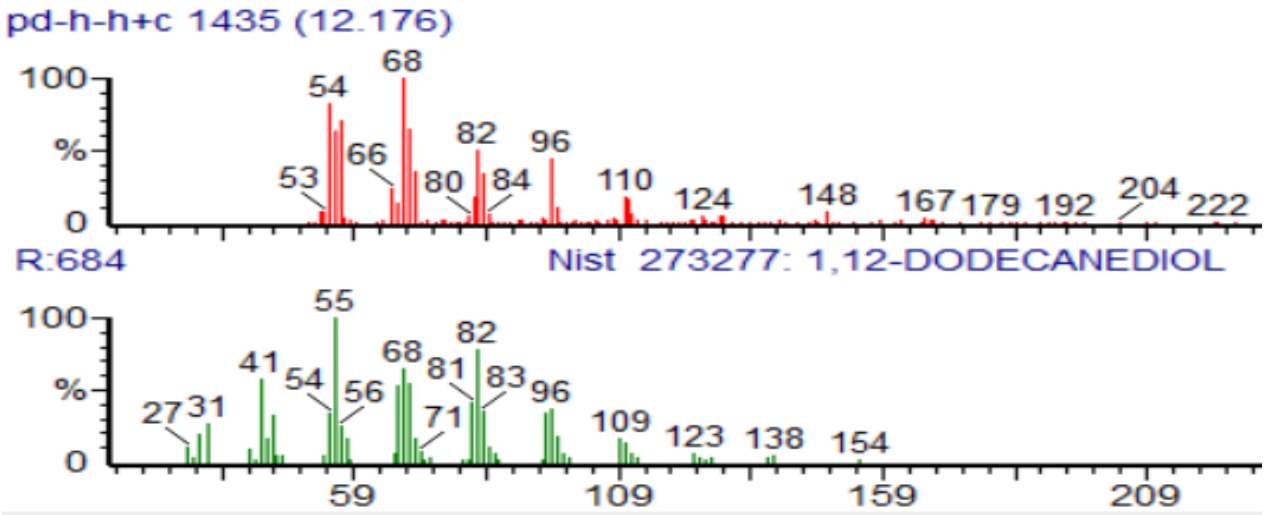

Figure 9 Mass spectrum of 1,12-dodecanediol in PD-H-H+C

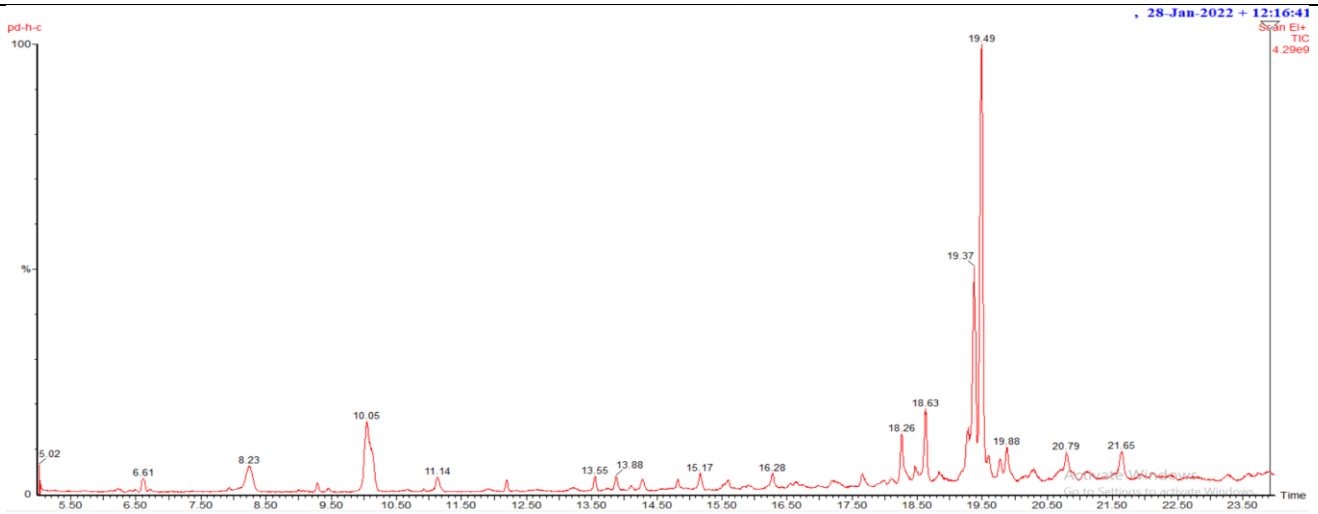

Figure 10 GC-MS of Prunus domestica hexane extract in chloroform solvent (PD-H-C)

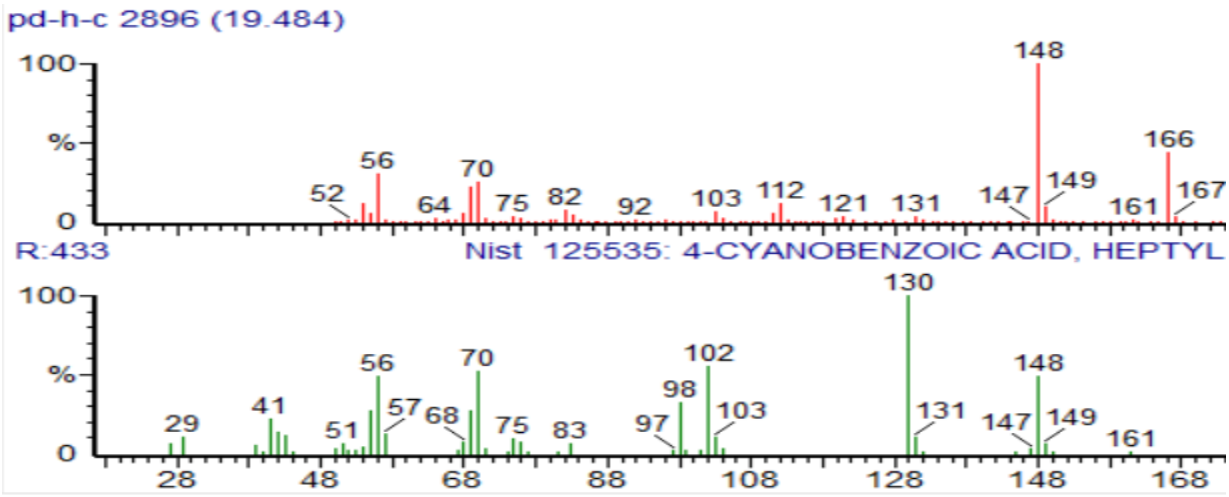

Figure 11 Mass spectrum of 4-cyanobenzoic acid, heptyl ester in PD-H-C

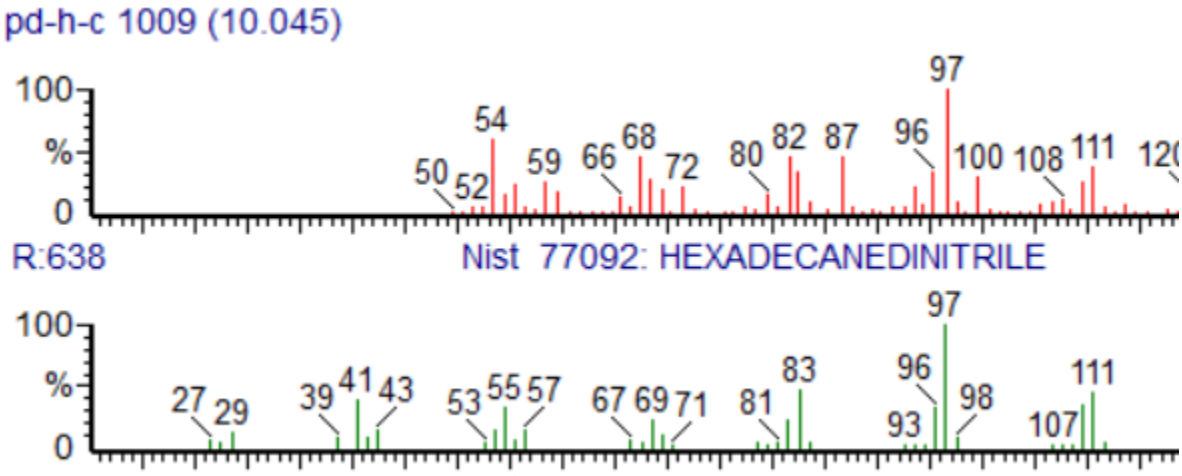

Figure 12 Mass spetcrum of hexadecane dinitrile in PD-H-C

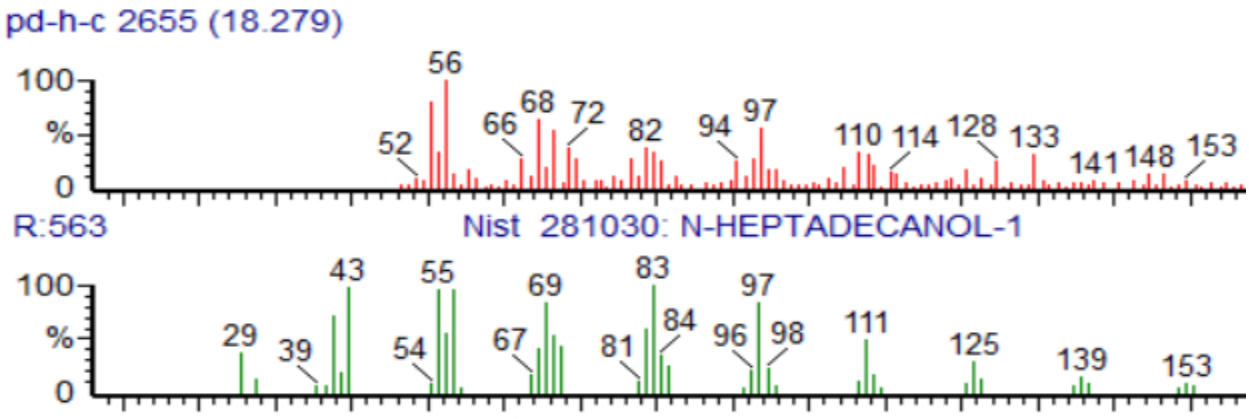

Figure 13 Mass spectrum of N-heptadecanol-1 in PD-H-C

3.2. FTIR analysis

3.2. FTIR of *Prunus domestica* hexane extract in hexane solvent (PD-H-H):

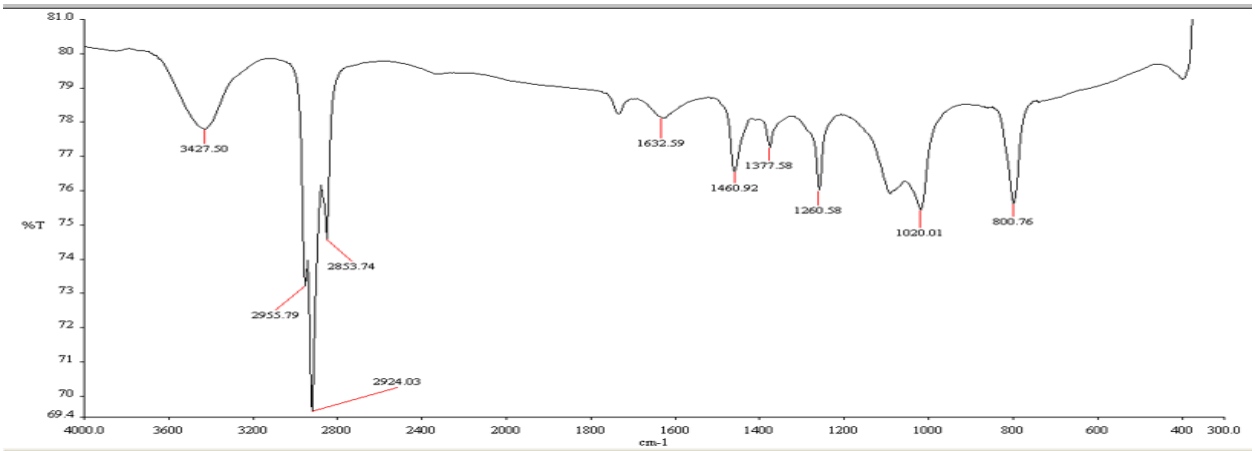

Figure 14 FTIR of PD-H-H

The FTIR spectrum from *figure 14* gave a very strong absorption band at 3400cm-1 due to O-H stretch in 1,2,3,4-hexadecane tetrol. The bands in the range of 2955-2924 are due to sp3 C-H stretch in our sample. The strong bands between 1020-1100 cm^{-1} are due to C-O stretch in L- isoleucine ethyl ester.

3.3. FTIR of *Prunus domestica* hexane extract in hexane and chloroform solvent (1:1) (PD-H-H+C)

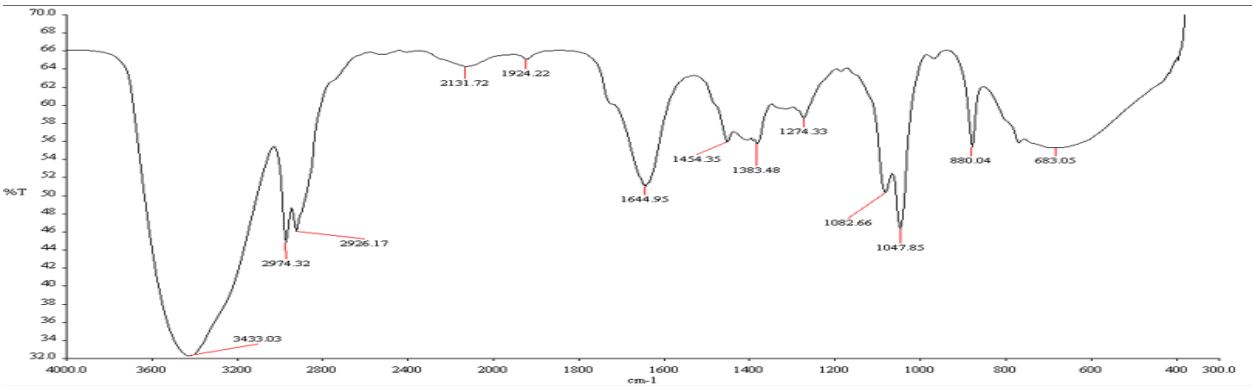

Figure 15 FTIR of PD-H-H+C

The FTIR spectrum from *figure 15* the strong band at 3433 cm^{-1} is due to the O-H stretch in 4-cyanobenzoic acid. Conjugation with the benzene ring reduces the C=O stretch from 1700 to 1645 cm^{-1}. The bands at 1082-1048cm^{-1} appear due to the C-O stretch in our sample.

3.3. FTIR of *Prunus domestica* hexane extract in chloroform solvent (PD-H-C)

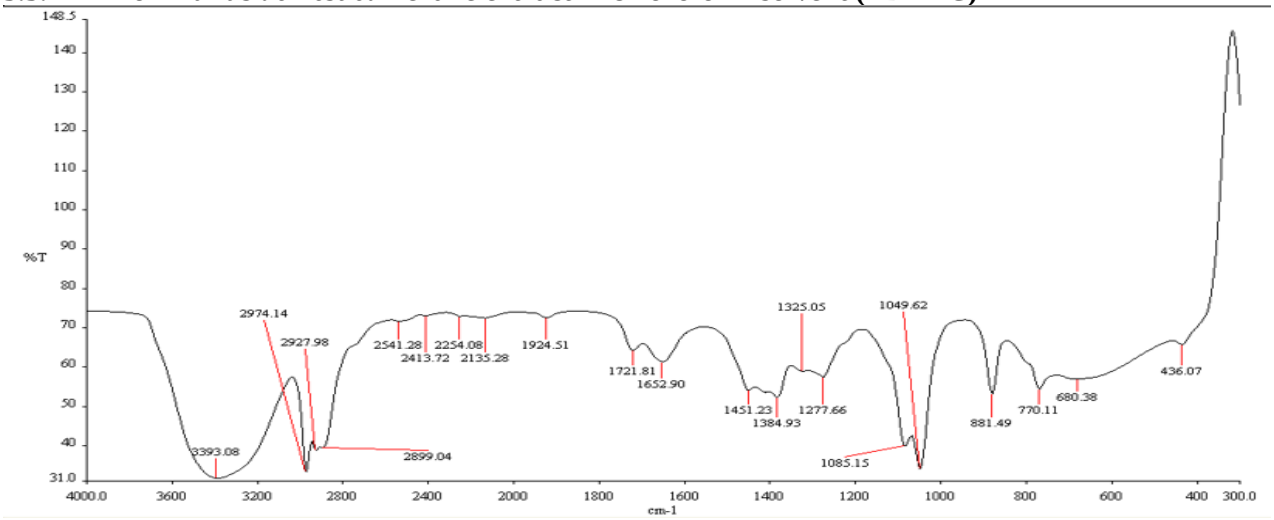

Figure 16 FTIR of PD-H-C

The FTIR spectrum from *figure 16* shows the broad band at around 3393cm^{-1} is due to the hydrogen-bonded O-H stretch in the sample, while bands at around 2900cm^{-1} are due to sp3 C-H stretch. The strong absorption bands around 1050-1085cm^{-1} are due to the C-O stretch in 4-cyanobenzoicacid heptyl ester.

3.3. Corrosion inhibition assay

A corrosion inhibition assay was established to determine whether the samples obtained via column chromatography possessed corrosion inhibition capability. On mild steel, the corrosion inhibition potential was evaluated using a potentiometer. In the corrosion cell, prepared electrodes were used as the working electrode, platinum wire as the counter electrode, and saturated calomel as the reference electrode. The electrolyte was made with 9.5 ml of 3.5% NaCl and 0.5 ml of the suitable sample extract. This 10 ml solution's anticorrosion capabilities were evaluated. These were subjected to potentiodynamic polarization scanning using Gamry Reference 3000 equipment. To plot Tafel curves, potentiodynamic graphs were obtained at a scan rate of 0.5 mV/sec. These curves relating electrochemical corrosion potential (E) and current were plotted (I). This procedure was performed for each sample. Before combining the material with the NaCl solution, a test utilizing only the NaCl solution was conducted. The corrosion current density (I_{corr}) from the potentiodynamic graphs obtained with a NaCl solution and 0.5 ml of samples was compared with the I_{corr} value of the blank, and the corrosion inhibition efficiency (%) of the samples was then determined using the formula.

$$\eta\% = \frac{I_o - I}{I_o} \times 100$$

here I_o is the corrosion current density in the absence of extract/fraction, i.e., without the blank and I is the corrosion current density in the presence of extract/fraction with the NaCl solution. (I_{corr})

3.3.1 Corrosion Current Density of Blank

The value of I_{corr} of the blank was obtained, labeled as Io to avoid confusion, and then compared with the I_{corr} values of the sample extracts to measure the η%. Io value for the blank was 45.40 µA obtained from Table 2 I_{corr} of the blank.

Table 2 Icorr of blank

Parameter	Value
Beta A	1.202 V/decade
Beta C	1.925 V/decade
I_{corr}	45.40 µA
E_{corr}	-498.0 mV
Corrosion Rate	41.51 mpy
Chi Squared	109.3e^{-3}
Data File	SS-2cm-200s.DTA

3.3.2 Corrosion Inhibition Efficiency of n-Hexane Column Extracts

The corrosion inhibition efficiency of the extracts from the n-hexane column was calculated for each extract obtained from the three solvent systems.

The first extract was from the 300 ml n-hexane solvent of the n-hexane column. The I_{corr} obtained for this sample extract was 22.50 μA from Table 3 I_{corr} of extract from n-hexane . The corrosion inhibition efficiency (η%) was calculated to be 50.89% as the value of I_o was 45.40 μA, and I_{corr} was 22.54 μA.

Table 3 Icorr of extract from n-hexane *solvent*

Parameter	Value
Beta A	252.9e^{-3} V/decade
Beta C	202.9e^{-3} V/decade
I_{corr}	22.50 μA
E_{corr}	-982.0 mV
Corrosion Rate	20.77 mpy
Chi Squared	7.107
Data File	PD-H-H.DTA

The second extract was from the 300 ml n-hexane + chloroform solvent, which was in 1:1 concentration, of the n-hexane column. The I_{corr} obtained for this sample extract was 2.42 μA from Table 4 I_{corr} of extract of hexane and chloroform solvent. The corrosion inhibition efficiency (η%) was calculated to be 94.67% as the value of I_o was 45.40 μA and I_{corr} was 2.42 μA.

Table 4 I_{corr} of extract of hexane and chloroform solvent

Parameter	Value
Beta A	129.7e^{-3} V/decade
Beta C	124.8e^{-3} V/decade
I_{corr}	2.420 μA
E_{corr}	-941.0 mV
Corrosion Rate	2.242 mpy
Chi Squared	12.14
Data File	PD-H-H+C.DTA

The third extract was from the 300ml chloroform solvent of the n-hexane column. The I_{corr} obtained for this sample extract was 2.00 μA from Table 5 I_{corr} of extract from chloroform solvent. The corrosion inhibition efficiency (η%) was calculated to be 95.41% as the value of I_o was 45.40 μA and I_{corr} was 2.00 μA.

Table 5 I_{corr} of extract from chloroform solvent

Parameter	Value
Beta A	78.20e^{-3} V/decade
Beta C	214.8e^{-3} V/decade
I_{corr}	2.000 μA
E_{corr}	-679.0 mV
Corrosion Rate	1.849 mpy
Chi Squared	18.41
Data File	PD-H-C.DTA

4. APPLICATION

In the previous studies, the phytochemical constituents of *P. domestica* seeds, skin and flesh of the fruit were discussed [9] and have shown corrosion inhibition potential above 80% [6]. In this project, the phytochemical constituents of *P. doemstica* shoot extract were studied, and identified the corrosion inhibition potential of the shoots extract. The compounds identified through GC-MS analysis are alkanes, esters, and alcohols. The corrosion inhibition potential of these compounds was identified on mild steel and showed corrosion inhibition potential of 50.89%, 94.67%, and 95.41%, respectively. The outcome of this project would have a significant impact on the steel industry as these extracts have anticorrosion properties, which could enhance the durability of metals and extend its efficiency. This method is environmentally friendly and is in accordance with sustainable development goals (SDGs). The extracts of *P. domestica* L. might be a potent source of bioactive green corrosion inhibitors.

5. CONCLUSION

It was concluded that fractions from the shoots of *P. domestica Linn* offer substantial corrosion protection validated by a corrosion inhibition assay and the formula for the % efficiency of each fraction. The hexane extract exhibited the highest anticorrosion activity (95.41%) when the chloroform solvent system was utilized. Therefore, it is reasonable to assume that the shoot extract of *P. domestica Linn* can be employed as an effective green corrosion inhibitor.

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