



INVESTIGATION ON CHEMICAL CONSTITUENTS IN DAMMAR RESIN EXTRACT FROM STINGLESS BEE HIVE AND ITS POTENTIAL AS CORROSION INHIBITOR

(Penyiasatan Konstituen Kimia dalam Ekstrak Resin Dammar daripada Sarang Lebah Tanpa Sengat dan Potensinya Sebagai Perencat Kakisan)

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Abstract

This study aimed to determine the major compounds present in local dammar resin and its potential as an anticorrosive property. Dammar resin from a stingless bee hive was subjected to solvent extraction using an aqueous system; 70:30 v/v of ethanol: water. The yield of extraction was characterized through Fourier transform infrared (FTIR) and gas chromatography-mass spectrometry (GC-MS). A linear polarization resistance (LPR), potentiodynamic polarization, and weight loss test were performed to evaluate the corrosion rate of steel. The result shows that longipinane (18%) was the major compound present in the extract, followed by ursolic aldehyde (14%), 1H-cycloprop[e]azulene (6.85%), 3,4-dichlorophenyl thiocyanate (6%), azulene, 1,2,3,3a,4,5,6,7-octahydro-1,4-dimethyl-7-(1-methylethenyl) (4.48%), and 2,4-heptadienal (4%). The existence of aromatic structure, phenyl group, C=C, and C=O provides an active site for adsorption on the metal surface to inhibit steel corrosion. LPR and weight loss test revealed the lowest corrosion rate at the 600 ppm dammar extract and recorded about 60% and 74% inhibition efficiency respectively. Tafel analysis showed a decrease in current density from 5.8×10^{-3} to 8.0×10^{-4} after 600 ppm dammar extract was employed in the corrosive medium of 3% NaCl, eventually, giving an inhibition efficiency at 86.2%. This research signifies that the local dammar resin of stingless bee hives has great potential as a corrosion inhibitor.

Keywords: dammar resin, gas chromatography-mass spectroscopy, corrosion rate, corrosion inhibition, Tafel

Abstrak

Kajian ini bertujuan untuk menentukan sebatian utama yang terdapat dalam resin dammar tempatan dan mengenalpasti potensi sifat antikarat. Dammar daripada sarang lebah tanpa sengat telah melalui pengekstrakan pelarut menggunakan sistem akueus; 70:30 v/v etanol: air. Hasil pengekstrakan telah dicirikan melalui inframerah transfromasi Fourier (FTIR) dan kromatografi gas-

spektrometri jisim (GC-MS). Rintangan polarisasi linear (LPR), pengutuban potensiodinamik dan ujian kehilangan berat telah dilakukan untuk menilai kadar kakisan keluli. Keputusan menunjukkan bahawa longipinan (18%) merupakan sebatian utama dalam ekstrak, diikuti oleh aldehid ursolik (14%), 1H-cycloprop[e]azulene (6.85%), 3,4-diklorofenil tiosianat (6%), azulena, 1,2,3,3a,4,5,6,7-oktahidro-1,4-dimetil-7-(1-metiletanal) (4.48%) dan 2,4-heptadienal (4%). Kewujudan struktur aromatik, kumpulan fenil, C=C dan C=O menyediakan tapak aktif untuk penjerapan pada permukaan logam bagi menghalang kakisan keluli. Keputusan LPR dan ujian kehilangan berat menunjukkan kadar kakisan terendah pada ekstrak dammar 600 ppm, dan masing-masing merekodkan kira-kira 60% dan 74% kecekapan perencatan. Analisis Tafel menunjukkan penurunan ketumpatan arus dari 5.8×10^{-3} kepada 8.0×10^{-4} selepas ekstrak dammar 600 ppm digunakan dalam medium 3% NaCl, akhirnya memberikan kecekapan perencatan 86.2%. Penyelidikan ini menunjukkan resin dammar sarang lebah tanpa sengat yang diperoleh dari sumber tempatan berpotensi besar sebagai perencat kakisan logam.

Kata kunci: dammar, kromatografi gas-spektrometri jisim, kadar kakisan, perencatan kakisan, Tafel

Introduction

The strategies in managing the degradation of metal and its structure must always synchronize with the aspect of cost, energy, time, nature of the environment, and materials. Failure in handling the strategies can cause severe damage and losses, especially on a metal structure with complex designs as well as hidden structures that are hard to inspect routinely. An effort in using good substances or chemicals in controlling the corrosion attack such as corrosion inhibitors is the most practical in such conditions. The organic inhibitors adsorb on the metal surface, form a thin protective film, and give protection from the corrosive environment. Since the principle of corrosion inhibitors is to alter the corrosiveness of the environment, the technology in exploiting natural sources and organic chemicals is encouraged as well in coatings. Attempts have been made on using metals and plant-based extracts as corrosion inhibitors such as carbon, carbon black, graphene, graphite, silver, glycosides, alkaloids, amino acids, flavonoids, and many more [1-3].

However, another less researched potential source is the organic chemical originating from natural sources such as dammar resinous or propolis from beehives. This native chemical is one of the potential materials to be introduced in corrosion control strategies. It offers abundance, availability, and renewable as compared to other metallic inhibitors. Dammar resinous or propolis is a resinous substance formed by honeybees from buds, leaves, and exudates of trees and plants mixed with pollen, wax, and enzymes secreted from the bees [4, 5]. The resinous substance is generally composed of approximately 50% resin (polyphenolic fraction), 30% wax, 10% essential oils, 5% pollen, and 5% various

organic and inorganic compounds. Chemicals compounds (such as flavonoid and polyphenol) in dammar and propolis or beehive extract were found to have an antioxidant property that reflects the role for inhibits an oxidation process. The use of the dammar resinous or propolis extract from bee hives as corrosion inhibitors has developed interest among researchers. Rizvi et al. reported the ethanolic extract of propolis at 250 ppm was able to inhibit steel corrosion at 70% efficiency with comprehensive adsorption [6]. While Gapsari et al. stated that 2000 ppm bee wax propolis extract was feasible to inhibit the stainless steel corrosion in sulfuric acid with up to 97% efficiency with the formation of the complex and protective film [7]. The inhibition was reported due to physisorption and temperature-dependent. The efficiency of propolis also has been discussed by Fouda et al. who explained the inhibitive action based on the adsorption of the stable complex at the carbon steel surface [8, 9].

Apart from steel, other metals also have been treated by dammar resin/bee nest/wax base [7]. A study by Hachelef et al. revealed that the efficiency of propolis extract as a corrosion inhibitor for copper alloy in NaCl gives the maximum value of the inhibitory (73.28%) at an optimum concentration of 1.25 g/L of propolis extract [8]. Varvara et al. investigated the ability of propolis against the corrosion of bronze and found that 100 ppm propolis gives up to 98% with 12h exposure to weak acid of sodium sulphate and sodium bicarbonate [9]. The inhibitory effect was reported due to the adsorption of flavonoids and phenolic compounds on the bronze surface. The anticorrosive behaviour of propolis in combating aluminium corrosion was studied by Islami et al. and it was found that the high concentration of

propolis extract may cause agglomeration thus decreasing the efficiency [10].

However, not much literature on the chemical constituents of propolis from stingless bee hives has reported the inhibition properties [4, 11]. The composition of raw propolis depends on the geographical location, nature of plants, and bee species. A study by a group of Malaysian researchers has found that the local propolis extract is composed of volatile and non-volatile compounds [12]. While Leonhardt et al. revealed the propolis from the stingless bees in Borneo comprise terpenes, alkanes, and alkenes [13]. A constituent of triterpenes and flavonoids from stingless bee hives originated from Northeast Brazil also has been explored by Freitas et al. through chemical isolation and characterization [14]. In another study, Kartal et al. reported that flavonoids, aromatic acids, diterpenic acids, and phenolic compounds were the major components accountable for the biological activities of propolis samples [15]. Since the geographical was a strong factor in the variation of bee hive constituents, hence, each of the bee hive extracts may compose of a unique constituent locally.

The extraction methods play crucial roles in determining the obtained green inhibitor's functional compounds. It includes soaking, heating reflux, enzymatic hydrolysis, Soxhlet extraction, and ultrasonic extraction methods [16]. However, in this research, the usage of the aqueous extraction technique is preferred as compared to the organic extracts as it gives polar phytochemicals that

offer strong bonding with the metallic surface than the non-polar in the latter technique [2]. The preferred aqueous method using ethanol is cost-saving and commonly known as a green extractant in providing high yield efficiency [17].

Therefore, the study of potential chemical constituents extracted from local bee hives was embarked as a corrosion inhibitor focusing on properties of the main constituent present in the extract of a stingless bee hive that may contribute to the potency of anticorrosive properties against steel. This work begins with the extraction, characterization, and identification of bee hives constituents through chemical analysis, followed by a corrosion inhibitors test.

Materials and Methods

Extraction of dammar resin

Dammar resin from a stingless bee hive (Figure 1a) or locally known as *damar kelulut* was collected from a local bee farm in Merbok, Kedah, Northern Peninsular Malaysia. The dried dammar resin was crushed into a fine powder and subjected to solvent extraction in 70:30 v/v of ethanol: water. The solvent mixture was heated below 60 °C, stirred for 24 hours, filtered, and kept at 4 °C for 3 days before removing the ethanol using a rotary evaporator. The light brown solution obtained was dried using a freeze-dryer to remove water and moisture and kept in a closed container before characterization. Light brown powders of dammar resin extracts were obtained (Figure 1b). The powder was used to form an inhibitors solution (Figure 1c).

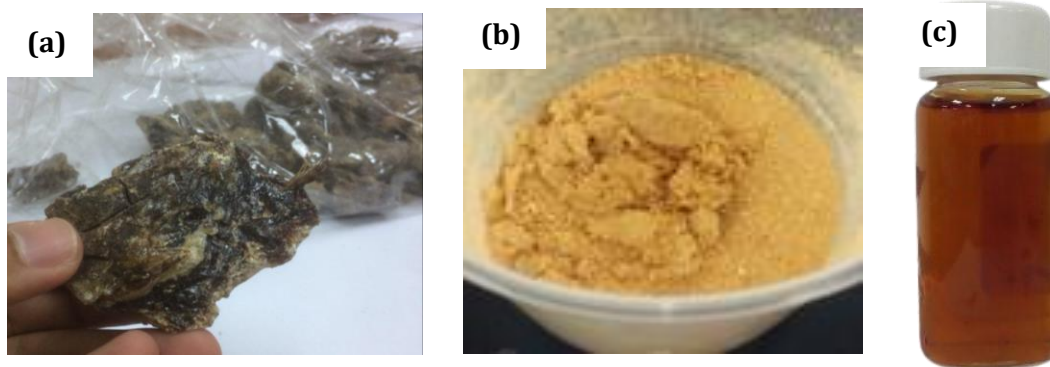


Figure 1: (a) Dammar resin; (b) Dammar resin powder after the extraction; (c) Dammar resin extract in ethanol/water system 70:30)

Characterization of dammar resin

Characterization of dammar resin extract was performed via Fourier transmission infrared (FTIR) and gas chromatography-mass spectrometry (GC-MS). FTIR analysis was carried out on a powder of dammar resin (before and after extraction) to identify the functional group present. The chromatograph and mass spectrometer calibration was performed using GC-MS Agilent 7890A gas chromatograph with a triple-axis detector. The chromatographic column used was SGE BPX-5 (30 m x 0.32mm i.d x 0.25 μ m film thickness) with 5% phenyl polyphenylene-siloxane at a temperature from 50 °C for 2 min, then 20 °C min⁻¹ to 280 °C for 10 min, and finally 20 °C min⁻¹ to 320 °C for 50 min.

Preparation of metal sample and corrosion inhibitor solution from dammar resin extract

A carbon steel S50C with a dimension of 1 cm x 1 cm x 0.6 cm was embedded in an epoxy resin with an exposed area of 1 cm². The specimen was polished by using different sizes of emery paper grades (from 400 to 1200), washed thoroughly with distilled water, and rinsed with ethanol [18, 19]. A solution of 3 wt.% NaCl was prepared in the 1 L flask and was used as a corrosive medium in a glass cell corrosion test. The carbon dioxide gas was purged for 1 hour to provide the glass cell containing 3 wt.% NaCl with saturated gases.

Electrochemical test

Linear polarization resistance (LPR) measurement was performed via ACM Instrument Gill 12 Weld Tester for

data acquisition. A typical three-electrode glass cell was used consisting of a saturated calomel electrode AgCl (SCE) as a reference electrode and graphite as the counter electrode. The experiment was carried out at a constant temperature (within $\pm 1^\circ$ C). The potentiodynamic polarization test was performed for 24 hours. The measurement of LPR was recorded at a constant sweep rate of 0.167 mVs⁻¹ and the scanning range was from -250 to +250 mV with respect to the open circuit potential (OCP). Inhibition efficiencies percentage (%IE) were determined from the corrosion current densities, I_{corr} calculated by the Tafel extrapolation method. The persistence test was carried out by immersing the metal sample in dammar extract for 1 hour to form a film. The metal samples were then dried before being exposed to a corrosive medium. The introduction of an inhibitor in 3 wt.% NaCl was carried out after a 2-hour measurement for stabilization of open circuit potential (OCP). The concentration of dammar extract as an inhibitor for this test was selected from the maximum inhibition efficiency achieved by the weight loss and LPR analysis.

Weight loss test

The weight loss test (immersion test) was carried out in a 1 L glass cell beaker containing 3 wt.% NaCl with different concentrations of dammar extract (200-1000 ppm). The immersion test was performed for 24 hours and the weight before and after immersion was recorded. The corrosion rate, CR was calculated using Eq. (1);

$$CR \text{ (mm/y)} = \frac{W}{(D \times A \times T)} \times K \quad (1)$$

Where, W = weight loss in grams, K = constant (87600), D = metal density in g/cm³, A = area of the specimen (cm²), and T = time (hour).

The inhibition efficiency was quantified using Eq. (2);

$$IE\% = \frac{CR_0 - CR_i}{CR_0} \times 100 \quad (2)$$

Where, CR₀ = Corrosion rate of the uninhibited system, and CR_i = Corrosion rate of the inhibited system.

Results and Discussion

Characterization of functional group in dammar extract via FTIR

Figure 2 illustrates the combination of the FTIR spectrum for dammar resin powder before extraction, after extraction and dammar extract in an aqueous solution of 70% ethanol; designated as (a), (b) and (c) respectively. The peak assignment for each spectrum was shown in Table 1.

In Figures 2 (a) and 2 (b), the spectrum shows an absorption around 3400 cm^{-1} assigned to the OH broadened band of either hydrogen bonded or hydroxyl group in the phenolic and aliphatic compounds. The absorption peaks at 2929 and 2943 cm^{-1} were due to the C-H stretch band of a methyl group. The peaks at 2868 and 2869 cm^{-1} were assigned as alkyl units of CH for a sample before extraction and ethanoic content for a sample after extraction correspondingly. The intense peak around 1693 and 1694 cm^{-1} were assigned as carboxylic acid groups (C=O). While the vibration around 1513 , 1515 , 1456 , and 1453 cm^{-1} shows the presence of aromatic groups, C=C [7, 9]. Several peaks

around 1380 , 1313 , 1273 , 1109 , 1087 , and 1046 cm^{-1} for both samples exhibit the C-O stretching band of the carbonyl group and C-OH bending band. Meanwhile, a peak around 887 and 826 cm^{-1} was attributed to primary and secondary alcohol for a sample after extraction [6]. The existence of C=O, C=C, and OH in the dammar extract might contribute to the anticorrosive properties as the common criteria for a corrosion inhibitor is to have oxygen, functional groups, and aromatic rings for the best site of interaction [20, 21].

Spectra in Figure 2 (c) represent the FTIR result for dammar extract in aqueous 70% ethanol. The broad peak was observed at 3358 cm^{-1} corresponding to the OH group. Meanwhile, a peak around 2976 and 2893 cm^{-1} was assigned as ethanoic content for an extract in an aqueous solution. A peak at 1648 cm^{-1} was attributed to the C=C of the alkene and aromatic group. Several bands at 1453 , 1382 , 1086 , and 1045 cm^{-1} were considered alcoholic functional groups of the C-O bond. Meanwhile, a band of 879 and 672 cm^{-1} is also related to the primary and secondary alcohol.

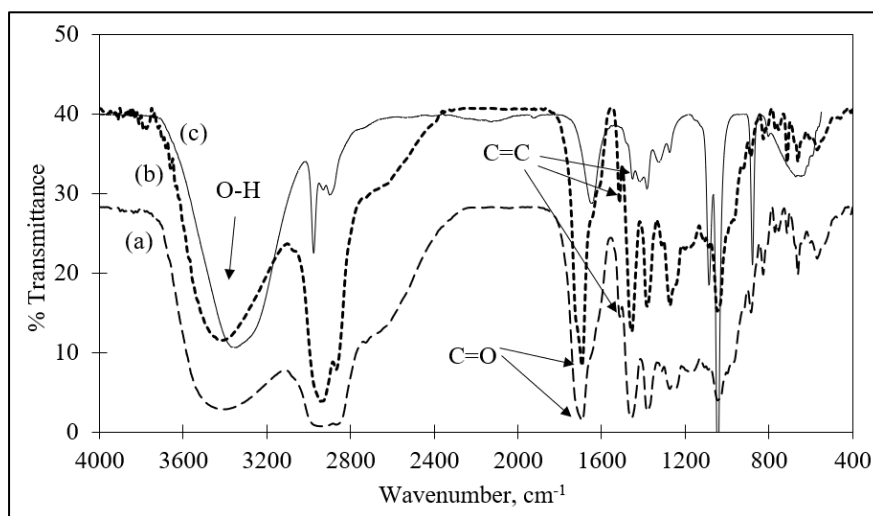


Figure 2. A powder of dammar resin (a) before extraction; (b) after the extraction; and (c) dammar extract in an aqueous solution of 70% ethanol

Table 1. Peak assignment of the FTIR spectrum for 3 samples, dammar resin powder before extraction, dammar extract powder after extraction and dammar extract in aqueous

Detected Wavenumber			Signal Peak Assignment
(a) Dammar Resin Powder Before Extraction	(b) Dammar Extract Powder After Extraction	(c) Dammar Extract in Aqueous	
3402	3411	3358	OH group
2929	2943	-	C-H stretch
2868	-	-	Alkyl CH
-	2869	2976, 2893	ethanoic content
1693	1694		carboxylic acid groups (C=O)
1513	1515, 1456	1648, 1453	C=C of alkene and aromatic group
1380, 1314, 1243, 1243, 1109, 1046	1380, 1273, 1109, 1047	-	alcoholic functional groups of C-O bond
		1382, 1086, 1045	C-O stretching band of carbonyl group and C-OH bending band
827, 753, 662, 570	887, 826	879, 672	primary and secondary alcohol

Identification of chemical constituents in dammar extract via GC-MS

A total of 46 constituents were finally identified via GC-MS analysis of dammar resin extract in 70% ethanol within 62.4 minutes as depicted in Table 2. The first compound, 1,3,6-Heptatriene, 2,5,6-trimethyl was

detected around RT=19.5 min with an amount of 0.35%. The highest amount 18.42% was detected at RT=56.8 assigned as longipinane. The less volatile in this extract was methyl 3 beta-hydroxyolean-18-en-28-oate since it was the last compound detected, with 3.33% amount.

Table 2. Chemical constituent of dammar extract in dammar resin (70:30 of ethanol:water) identified via GC-MS

Peak Number	RT	Compound Detected	Total Amount (%)
1	19.457	1,3,6-Heptatriene, 2,5,6-trimethyl	0.35
2	20.635	Copaene	1.40
3	20.85	(-)-.beta.-Bourbonene	0.62
4	20.992	Cyclohexane, 1-ethenyl-1-methyl-2, 4-bis(1-methylethenyl)-	1.39
5	21.459	1H-Cycloprop[e]azulene, 1a,2,3,4,4a,5,6,7b-octahydro-1,1,4,7-tetramethyl	6.85
6	21.62	1H-Cyclopropa[a]naphthalene, 1a,2,3,3a,4,5,6,7b-octahydro-1,1,3a,7-tetramethyl	0.80
7	21.782	Caryophyllene	3.61
8	22.037	4H-1-Benzopyran-4-one, 2-amino	0.55
9	22.385	2,4-Heptadienal	4.02
10	22.693	Humulene	1.07
11	22.803	(1R,9R,E)-4,11,11-Trimethyl-8-methylenebicyclo[7.2.0]undec-4-ene	0.78

12	23.164	.gamma.-Muurolene	0.58
13	23.334	Germacrene D	0.81
14	23.442	1-Isopropyl-4,7-dimethyl-1,2,3,4,5,6-hexahydronaphthalene	0.80
15	23.575	(3R,6R)-3-Hydroperoxy-3-methyl-6-(prop-1-en-2-yl)cyclohex-1-ene	1.39
16	23.689	(1S,2E,6E,10R)-3,7,11,11-Tetramethylbicyclo[8.1.0]undeca-2,6-diene	1.25
17	23.989	1,8-Nonadiene, 2,7-dimethyl-5-(1-methylethenyl)-	0.22
18	24.228	Naphthalene, 1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-,	1.00
19	25.494	Azulene, 1,2,3,3a,4,5,6,7-octahydro-1,4-dimethyl-7-(1-methylethenyl)	4.48
20	25.674	(3aS,4R,7R)-1,4,9,9-Tetramethyl-5,6,7,8-tetrahydro-4H-3a,7-methanoazulene	3.09
21	25.782	Caryophyllene oxide	1.13
22	25.89	2-Methyl-3-(3-methyl-but-2-enyl)-2	0.40
23	26.095	1,4-Methanocycloocta[d]pyridazine,1,4,4a,5,6,9,10,10a-octahydro-11,11-dimethyl	0.63
24	26.429	Cyclohexene, 4-(1,5-dimethyl-1,4-hexadienyl)-1-methyl-	0.60
25	26.741	Humulane-1,6-dien-3-ol	1.77
26	26.972	Methyl 10,12-pentacosadiynoate	0.46
27	27.164	(-)-Neoclovene-(I), dihydro	1.10
28	27.478	.alpha.-Cadinol 85709 000481-34-5 5	0.48
29	27.558	1R,4S,7S,11R-2,2,4,8-Tetramethyltricyclo[5.3.1.0(4,11)]undec-8-ene	0.39
30	29.9	Bicyclo[6.1.0]nonane, 9-bromo-9-methyl	0.17
31	31.269	2-Cyclohexen-1-one, 4-ethyl-4-meth	0.42
32	53.286	Ethyl 3-[2,2-bis(ethoxycarbonyl)ethyl]-5-methoxy-1H-pyrrolo[2,3]pyridine-2-carboxylate	0.55
33	53.521	Propanedioic acid, (triphenyl)phosp	0.42
34	53.673	N-(2-Chloro-1-ethoxyethyl)-N'-cyano -N',N'',N'''-tetramethyl-1,3,5-triazine-2,4,6-triamine	0.49
35	54.034	2-Isopropenyl-4a,8-dimethyl-1,2,3,4,4a,5,6,7-octahydronaphthalene	0.76
36	55.739	1H-Isoindole-1,3(2H)-dione, 5,5'-oxybis[2-phenyl-	1.45
37	56.004	3-Hydroxy-4-phenyl-5-isopropyl-1,2,4-triazole	1.64
38	56.113	Cyclohexa-2,5-diene-1,4-dione, 2-methyl-5-(4-morpholinyl)-	0.68
39	56.54	Pimelic acid, 2-(2-methoxyethyl)hexyl pentyl ester	2.95
40	56.754	Longipinane	18.42
41	57.05	3-Bromo-4-methoxyphenol	2.14
42	57.482	Ursolic aldehyde TMS ether	14.13
43	57.762	9H-Fluorene-4-carboxylic acid, 9-oxo-, phenethylamide	0.62
44	58.07	3,4-Dichlorophenyl thiocyanate	6.17
45	59.319	Skatole	0.64
46	62.419	Methyl 3. beta.-hydroxyolean-18-en-28-oate	3.33

Chemical structure of major identified compounds in dammar resin extract

Figure 3 shows the chemical compounds found in dammar extract deduced from GC-MS. Out of 46 constituents in dammar extract, about 6 main compounds were identified in the range of 4 to 18%. Longipinane (18%) was the most abundant compound

present followed by ursolic aldehyde (14%), 1H-cycloprop[e]azulene (6.85%), 3,4-dichlorophenyl thiocyanate (6%), azulene, 1,2,3,3a,4,5,6,7-octahydro-1,4-dimethyl-7-(1-methylethenyl) (4.48%) and 2,4-heptadienal (4%). Most of the components present in dammar extract are classified as terpenoids.

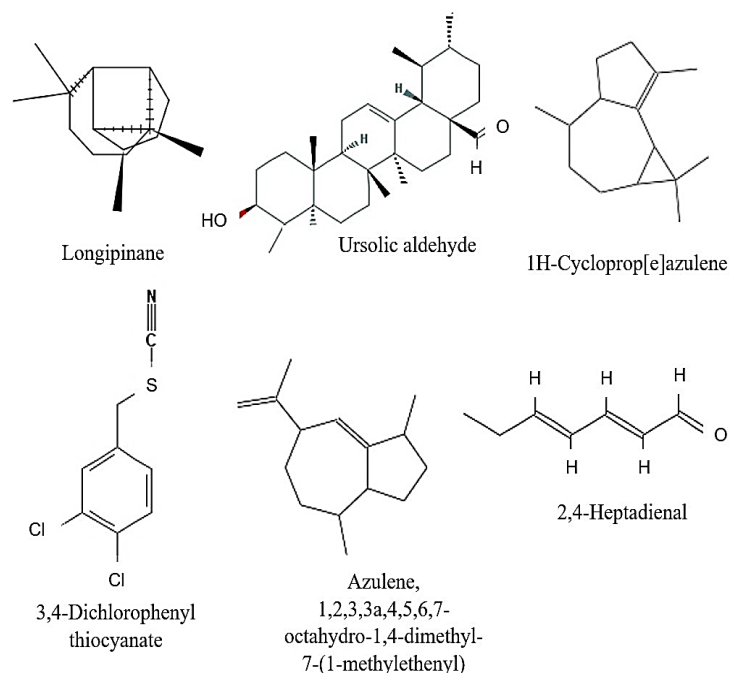


Figure 3. A main chemical compound present in dammar extract as deduced from GC-MS

Molecular structure criteria for corrosion inhibition

Table 3 summarized the main compound contains in propolis obtained from different regions. The listed propolis types have been extracted and analyzed for corrosion studies. The main compound was reported to have an anti-corrosive property.

Most of the chemical compounds in extracted dammar or propolis were built with an aromatic structure, for example, quercetin, cinnamic, and caffeic acid. Aromatic structure with delocalized electrons and functional groups provides an optimum site for interaction with metal. It is found that organic compounds containing aromatic rings and polar substituents are served as the most effective corrosion inhibitors. This agrees with studies that report each extract consists of complex phytochemicals (polar

functional groups and multiple bonds) providing electron-rich sites and aiding in the adsorption of phytochemicals on a metal substrate [2, 23].

Aliphatic groups also may contribute to the interaction since their structure may occupy the limited adsorption site to retard the corrosion process. However, corrosion inhibition affected by the structure of inhibitors depends on its orientation, size, and the distribution of the electrons cloud. In agreement with a study by Varvara et al., besides aromatic structure, the presence of oxygen atoms in functional groups and various phenolic compounds are also factors for the corrosion inhibition of bronze corrosion in sodium solution [24].

Besides, the existence of methyl, CH_3 in almost all structures identified in both extracts plays an important

role in inhibition as methyl also provides a significant reaction site. The presence of particular repeating units (such as methyl and phenyl groups) of the parent chain

and other substituent groups may improve the bonding strength of the group on the metal [21].

Table 3. List of main compounds in propolis discovered from different types and regions

Propolis Type	Extraction Method	Analysis	Main Compound	Ref
Bee wax propolis	Liquid-liquid extraction	FTIR and HPLC	Quercetin (2-(3,4-dihydroxyphenyl)-3,5,7- trihydroxy-4H-chromen-4-one)	[7, 9]
Propolis sample collected from Henan province (China)	Solvent extraction using ethanol	FTIR and HPLC	Pinos-trobin, trans-cinnamic acid, galangin and pinocembrin	[6]
Ethanolic extract of propolis was provided by the Duzce University Beekeeping Research, Development and Application Centre, Yigilca, Turkey	Solvent extraction using 96% ethanol	FTIR and HPLC	3,4-dimethoxycinnamic acid, pinobanksin, caffeic acid, apigenin, isorhamnetin, curcumin, naringin, myristic acid and luteolin	
Collected from Daqahlia province (delta Nile) of Egypt	Water extraction	Not included	Pinocembrin, caffeic acid, phenyl ester, quercetin and galangi	[5, 22]
Croatian propolis	Commercial alcoholic extract of propolis	Not included	Luteolin, 7-O- prenylpinocembrin, Cearoin, Linalool, P- methoxycinnamic acid, 3-prenyl-4- hydroxy-suberosin cinnamic acid, 3- prenylresveratro, l 6-methoxydiphyllin and Prenylated coumarin	
Propolis collected from the region of Bordj El Menaïel in Algeria	Ethylene glycol (30%) / water (70%)	FTIR	Not included	[8]

Linear polarization resistance (LPR)

Table 4 shows the resistance polarization value, R_p obtained from the LPR measurement. The R_p value for the blank solution without inhibitors (0 ppm) shows the lowest value with only 1225 Ohm.cm². Meanwhile, the highest values of R_p with 2971 Ohm.cm² are shown by the inhibitor's concentration at 600 ppm. It can be seen that the R_p value was increased as the concentration inhibitors increased from 200 to 600 ppm. However, the value then declined when the addition of inhibitors concentration was increased up to 800 and 1000 ppm.

The lowest value of R_p demonstrates small resistance to corrosion since no dammar extract was applied in the

systems. Thus, the corrosion of steel might increase with a decrease in resistance. The greater value of R_p shown at 600 ppm was assigned that the dammar extract was capable to provide resistance to corrosion. This attributes to good inhibition which resists the chloride attack against the steel surface. The decrease in R_p values as the concentration of extract increased was due to the overdosage of inhibitor molecules that may promote the complexation. This phenomenon affects the formation of a protective film to resist corrosive ions due to repulsive interactions, thus weakening the adsorption for inhibition [25].

Table 4. Resistance polarization (R_p) value of steel corrosion by dammar extract at different concentrations

Concentration Inhibitor (ppm)	R_p (Ohm.cm ²)
0	1225
200	1413
400	2750
600	2971
800	1469
1000	1397

Corrosion rate measurement

Figure 4 shows the corrosion rate measurement employed through the weight loss method and LPR technique. The high values of corrosion rate were shown in all measured concentrations via the LPR technique compared to the weight loss method. The highest value of corrosion rate was shown by the steel sample without corrosion inhibitors (0 ppm) for both the weight loss method (0.19 mm/yr) and LPR (0.25 mm/yr). The addition of 200 to 600 ppm dammar extract reduced the corrosion rate concentration and gradually increased as the inhibitors were increased. The lowest corrosion rate was achieved via weight loss methods at 0.05 mm/yr for 600 ppm. Above the 600 ppm dammar resin, the increase in inhibitor concentration has increased the corrosion rate values up to 0.22 mm/yr. The corrosion rate values for both measurement methods showed a similar trend.

In this result, the low concentration of dammar extract provides low corrosion protection as inhibitors were unable to prevent the corrosive ion, (eg: Cl^-). Consequently, the corrosion rate was increased due to insufficient dammar extract to interact on the surface for better corrosion inhibition. Meanwhile, the overdosage of dammar extract contributes to the excess of inhibitor molecules in the solution. Eventually, various ions in the solution create the Van der Waals effect where the mutual repulsion or attraction force is triggered among the inhibitors molecules and ions in the metal/solution interface [25]. Therefore, the high corrosion rate at high inhibitor concentration is also due to the complexity of dammar extracts composition causing the desorption process [26].

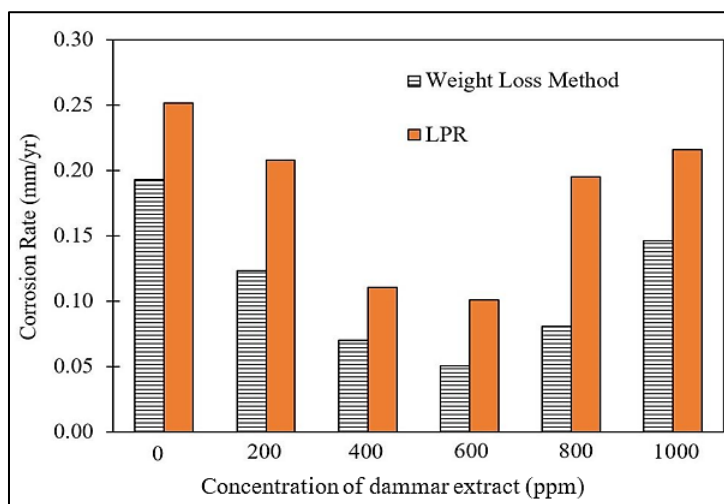


Figure 4. Corrosion rate of steel measured via LPR and weight loss method

Table 5 shows the inhibition efficiency value of steel corrosion calculated from corrosion rate values obtained via LPR and weight loss analysis in different concentrations of inhibitor. Generally, the addition of

corrosion inhibitors shows enhanced corrosion inhibition. However, our results showed the inhibition efficiency was dependent on the concentration of the inhibitor.

Table 5. Inhibition efficiency of steel corrosion by dammar extract at a different concentration calculated from corrosion rate values obtained via LPR and weight loss analysis

Concentration (ppm)	Inhibition Efficiency (IE%)	
	LPR Analysis	Weight Loss Analysis
0 ppm	0	0
200 ppm	17	36
400 ppm	56	64
600 ppm	60	74
800 ppm	22	58
1000 ppm	14	24

From the tabulated data, it can be seen that the inhibition efficiency increased up to 60% and 74% as 600 ppm dammar resin was used in LPR and weight loss methods correspondingly. While the use of 1000 ppm dammar resin exhibits the lowest efficiency. The values decreased as the concentration become increased to 1000 ppm. The highest efficiency was achieved at the concentration of 600 ppm of dammar resin. The maximum efficiency was shown by the 600 ppm dammar resin for both methods. It is believed that the inhibitor molecules affect the reactions and adsorbed on the mild steel plate by blocking the active sites situated on the metal surface hence inhibiting the corrosion reaction. The compounds establish a barrier associated with mass charge transfer. The hindrance against the transport of corrosive ions into the solution was contributed by the adsorption of phenolic compounds via an aromatic ring, as well as the heteroatoms of nitrogen and oxygen upon the steel plate [1].

This situation also explained the phenomenon of limiting or critical concentration and the solubility effect [27-29]. At the concentration of 600 ppm, the dammar resin molecules have covered an optimum surface coverage and inhibit the corrosion at high efficiency. As

more inhibitors are added into the corrosive medium, there is a limited site for adsorption. It is observed that before and after the 600 ppm, the inhibition efficiency in both LPR and weight loss method was lesser than 60% and 74% respectively. The low efficiency shown by the highest concentration (1000 ppm) was due to the desorption process. This indicates the presence of improper surface protection on the metal substrate. The weak interaction among the inhibitor molecules and metal surfaces generated from dipole-dipole interactions has declined the adsorption capability [25]. Therefore, the adsorption and inhibition were controlled by the major structure of the chemical components in the inhibitors [27, 30] such as alkyl chain length in the inhibitor, presence of heteroatoms and heterocycles in the molecule, existence of electron donating/withdrawing functionalities, and size of rings in the inhibitors molecules as can be further investigated in Figure 3.

Figure 5 shows the Tafel plots obtained from the electrochemical measurement of steel exposed to 3% NaCl solution. The presence of 600 ppm dammar extract in 3% NaCl was measured and the electrochemical parameter was summarized in Table 6.

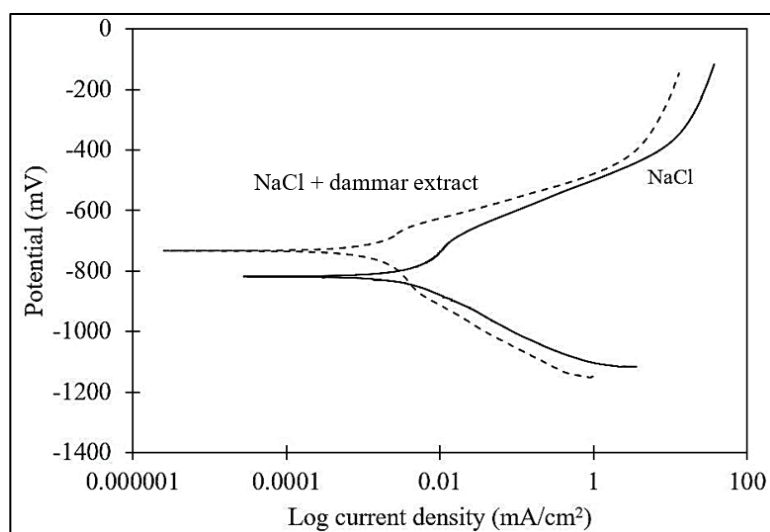


Figure 5. Potentiodynamic polarization curve of steel in NaCl and the absence and presence of 600 ppm dammar extract

Table 6. Tafel parameter obtained from potentiodynamic polarization test

Inhibitor System	Corrosion Potential, E_{corr} (mv)	Current Density, I_{corr} (mA/cm ²)	Inhibition Efficiency (IE%)
NaCl	-818	5.8×10^{-3}	0
NaCl + dammar extract	-725	8.0×10^{-4}	86.2

The presence of dammar extract inhibitors in 3% NaCl has shifted the E_{corr} value to a more positive potential. This signified the dammar extract inhibitors act as an anodic inhibitors type by decreasing the steel dissolution. Simultaneously, the value of current density, I_{corr} was reduced from 5.8×10^{-3} to 8×10^{-4} mA/cm² assigned the flow of electrons is hindered by the mass of dammar extract molecules. The changes of both E_{corr} and I_{corr} values attribute the corrosion inhibition due to the adsorption of dammar extract on the steel surface. The dammar extract molecules have hindered the corrosive ions from NaCl from further attacking the steel.

Conclusion

The overall findings from this study can be concluded as follows: The chemical constituents of dammar extract have been determined and the six major compounds were found; longipinane (18%), ursolic aldehyde (14%), 1H-cycloprop[e]azulene (6.85%), 3,4-dichlorophenyl thiocyanate (6%), azulene, 1,2,3,3a,4,5,6,7-octahydr o-1,4-dimethyl-7-(1-methylethenyl) (4.48%) and 2,4-

heptadienal (4%). The existence of various functional groups such as C=C, C=O, C-OH, CH₃, phenyl group, and aromatic structure contributed to the good anticorrosive properties of the local *kelulut* dammar extract towards steel corrosion. The best concentration of dammar extract was 600 ppm with 86.2% inhibition efficiency may exhibit a practical, efficient, and excellent potential for alternative green corrosion inhibitors. Below 600 ppm, the adsorption of inhibitor on the metal surface happened at an intermediate level of inhibition. Whilst, more crowding inhibitor molecules at the metal/solution interface do not improve the corrosion inhibition. The inhibition efficiency of the dammar extract obtained from LPR and weight loss measurements were in good agreement.

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