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Modified Glucomannan Derivative with p-Aminobenzoic Acid as Mild Steel Corrosion Inhibitor

**Hapin Afriyani[a]*, Ilim[a], Devi Nur Anisa[a], Dian Septiani Pratama[a],
Qori Hikmah Faranida[a,b], Rekia Enrik[a]**

Abstract. Indonesia's tropical climate, influenced by high temperatures and humidity, accelerates corrosion processes, especially in industrial and marine environments. Numerous studies have explored natural materials as corrosion inhibitors; however, most organic inhibitors suffer from poor thermal stability due to degradation of their chemical structures. This study aims to develop a heat-resistant and eco-friendly corrosion inhibitor using modified glucomannan from Amorphophallus onch (porang flour). The modification included using periodate oxidation to create an intermediate compound (GA-1), and then reacting it with para-aminobenzoic acid (pABA) to form a yellow-colored product. The synthesized compound was evaluated for its corrosion inhibition activity on mild steel in artificial seawater using various immersion times. At a concentration of 0.5 mg/L, the inhibitor exhibited an efficiency of 93.74% after 12 hours, decreasing slightly to 92.06% after 24 hours and 89.65% after 36 hours. The way it works is thought to be by the compound sticking to the steel surface, creating a protective layer that prevents harmful ions from interacting with the metal and slows down both the rusting of the metal and the reactions involving oxygen. These results indicate that the glucomannan–pABA derivative is a potentially effective eco-friendly corrosion inhibitor that can be used in tropical areas where corrosion is a problem.

Keywords : glucomannan, p-aminobenzoic acid, corrosion inhibitor, mild steel.

[a]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, University Of Lampung, Bandar Lampung, 35145, Indonesia*
[b]*PT Nusa Veritas Inspektama, Kebon Jeruk, West Jakarta, 11620*
Correspondence and requests for materials should be addressed to Hapin Afriyani
(email: hapin.afriyani@fmipa.unila.ac.id)

Introduction

The extensive use of mild steel in manufacturing industries, particularly in developing countries, stems from its advantageous mechanical characteristics, including high ductility, excellent thermal conductivity, cost-effectiveness, and ease of fabrication. With a carbon content ranging between 0.022% and 0.3%, mild steel is widely applied in structural and engineering components. However, its primary drawback lies in its susceptibility to corrosion, which can significantly shorten equipment lifespan and cause issues such as product contamination, unplanned shutdowns, and financial losses [1] [2].

Several corrosion control techniques have been developed, including external coatings, cathodic protection, and the use of corrosion-resistant alloys. Yet, for internal corrosion, especially in pipelines and enclosed systems, the use of corrosion inhibitors remains the most practical and cost-effective solution. Recently, attention has shifted toward natural-based corrosion inhibitors due to their biodegradability, low toxicity, and eco-friendly nature. Natural extracts such as pineapple peel [3], banana peel [4], Dayak onion leaf [5], and mangosteen peel [6] have shown promising results. Despite their advantages, many organic inhibitors suffer from poor thermal stability, which limits their industrial applicability under harsh conditions.

To overcome these limitations, chemical modification of natural polymers has emerged as an effective strategy. Glucomannan, a polysaccharide derived from Amorphophallus onchophyllus (porang tuber), offers enormous potential due to its film-forming ability, biocompatibility, and biodegradability [7], [8]. Functionalizing glucomannan can enhance its affinity for metal surfaces and improve its performance as a corrosion inhibitor.

Previous studies have shown that glucomannan changed with nitrogen-rich compounds such as dopamine, thiazole, and Schiff bases can be very good at stopping corrosion, achieving effectiveness rates of up to 98.8% when conditions are just right. This study proposes a new type of glucomannan by incorporating para-aminobenzoic acid (pABA) into its structure using Schiff base formation. pABA is a thermally stable, bifunctional aromatic compound possessing both amino ($-NH_2$) and carboxyl (–COOH) groups. The $-NH_2$ group helps form imine (C=N) bonds with dialdehyde groups added to glucomannan using periodate oxidation, and the aromatic ring structure allows it to attach to metal surfaces by interacting with their electrons.

Although p-aminobenzoic acid (pABA) has been extensively researched in medicine and plastics, its use for improving natural polymers to prevent rust has not been studied much. In this study, glucomannan is changed chemically by adding pABA, creating a structure that has two useful functions and a better ability to stick to mild steel surfaces. This design is expected to enhance heat resistance and how well it sticks to surfaces, making it a promising option for a sustainable and effective rust blocker in harsh conditions.

Experimental

Porang flour was obtained locally and used as the source of glucomannan. Other chemicals used were ammonium chloride (NH_4Cl), 96% ethanol, 1% acetic acid, sodium periodate ($NaIO_4$), para-aminobenzoic acid (pABA), benzoyl peroxide (BPO), 1,4-dioxane, and deionized water, all of which were of high quality for testing. Mild steel specimens were cut into 2 × 1 cm pieces, polished with silicon carbide (SiC) sandpaper (grit 100–800), rinsed with distilled water and ethanol, and dried at room temperature. Standard laboratory equipment included glassware, a magnetic stirrer, an oven, a centrifuge, an analytical balance, and an IR spectrophotometer.

Extraction of Glucomannan. Glucomannan was isolated by dissolving 4 g of porang flour in 50 mL of 0.1% NH_4Cl and 100 mL of warm water (75 ° C). The mixture was stirred for 30 minutes and centrifuged at 2000 rpm for 30 minutes. The filtrate was combined with 150 mL of 96% ethanol to precipitate glucomannan, which was filtered under vacuum and oven-dried at 60°C for 24 hours. The obtained glucomannan was characterized using infrared spectroscopy to confirm functional groups.

Synthesis of Modified Glucomannan. Fifty milligrams of glucomannan was oxidized by adding 5 g of $NaIO_4$ in 100 mL of deionized water and heating at 60°C for 24 hours. After the reaction, methanol was added to separate the intermediate compound (GA-1), which was then filtered and cleaned with a mixture of cyclohexane and ethyl acetate.

Subsequently, 20 mg of GA-1 was dissolved in 100 mL of absolute ethanol, and 100 mg of pABA and 0.08 g of BPO were gradually added. The mixture was refluxed at 80°C for 12 hours. The product was filtered and then cleaned up using column chromatography with silica gel and a mixture of cyclohexane and ethyl acetate in a 3:1 ratio. The final product was characterized by IR spectroscopy.

Corrosion Inhibition Assessment (Weight Loss Method). Weight loss measurements were performed to evaluate corrosion inhibition. Mild steel samples were weighed until they had the same weight and then placed in CO_2 -saturated artificial seawater with inhibitor levels of 0, 0.1, 0.2, 0.3, 0.4, and 0.5 mM for 24 and 36 hours. After immersion, the samples were washed, dried, and reweighed. The corrosion rate (CR) was calculated using Equation 1.

$$CR\ (mpy) = \frac{W\ x\ K}{DAT} \qquad (1)$$

where W is the mass loss (g), K is a constant (3.45×10^6), D is the density of the metal (g/cm^3), A is the surface area (cm^2), and T is the exposure time (hours).

The efficiency of inhibition (E) was evaluated by Equation 2.

$$E\ (\%) = \frac{X_a - X_b}{X_a}\ x\ 100\% \qquad (2)$$

In this equation, X_a represents the corrosion rate without the inhibitor, while X_b denotes the corrosion rate with the inhibitor [3].

Result and Discussion

Isolation of Glucomannan. The isolation of glucomannan from porang flour was carried out by dissolving 80 g of flour in 0.1% ammonium chloride solution and 2 l of warm distilled water. The extraction process was accelerated by adding water at 75°C, followed by homogenization and centrifugation at 2000 rpm. The supernatant containing glucomannan and amylose was separated from the insoluble amylopectin residue. Glucomannan was then precipitated using 96% ethanol as a precipitating agent to reduce the polarity of the solution.

The isolated glucomannan precipitate was dried in an oven at 50°C for 48 hours until a dry sample was obtained. The dried glucomannan appeared as thin, rigid, and brittle sheets. Weighing the dried sample yielded 10.6809 grams of glucomannan, indicating an isolation yield of 13.35%. The milling process significantly influences the isolated glucomannan content. Porang tubers that undergo repeated heating and washing before milling typically produce flour with relatively lower glucomannan content but have the advantage of reduced oxalate levels. The isolation process was then repeated to obtain sufficient material for the synthesis of glucomannan-derived compounds.

The glucomannan taken from porang flour was analyzed with an IR spectrophotometer to find out how it absorbs different wavelengths, as shown in Figure 1.

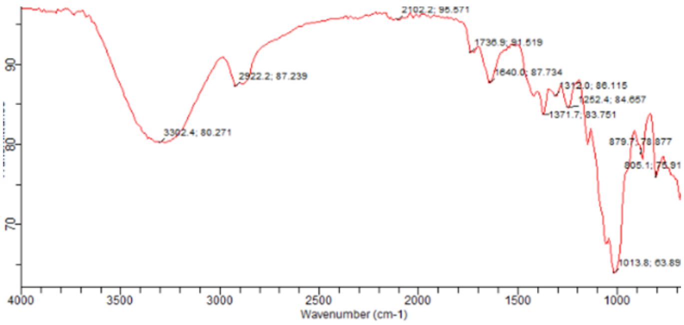


Figure 1. IR spectrum of isolated glucomannan

Based on the spectrum in Figure 1, the isolated compound is confirmed to be glucomannan, characterized by the following peaks: a broad absorption at 3400–3200 cm^{-1} indicates the presence of O–H groups, while peaks at 2920–2900 cm^{-1} and 1410–1390 cm^{-1} correspond to C–H stretching in aliphatic chains. A peak at 1650–1640 cm^{-1} indicates C=O stretching. Wu et al. reported that glucomannan spectra are dominated by O–H and water vibrational bands [10]. The CH_2 group vibration at 2922 cm^{-1} aligns with [11]. The C–O–C functional group appears at 1021 cm^{-1}, similar to Iftari et al. [12], who observed it at 1019–1016 cm^{-1}. Peaks at 805 cm^{-1} and 872 cm^{-1} indicate glycosidic bonds of mannose and glucose in β-pyranose form.

Syntesis of GA-1 Compound. The first step in the synthesis of glucomannan derivatives involved the preparation of the intermediate compound GA-1. A total of 50 mg of isolated glucomannan was dissolved in 100 mL of deionized water, and 5 g of sodium periodate ($NaIO_4$) was gradually added into a 250 mL round-bottom flask. The reaction mixture was heated in an oil bath at 60°C for 24 hours.

The periodate oxidation cleaved the C–C bonds between adjacent hydroxyl groups in the glucomannan polymer, resulting in the formation of

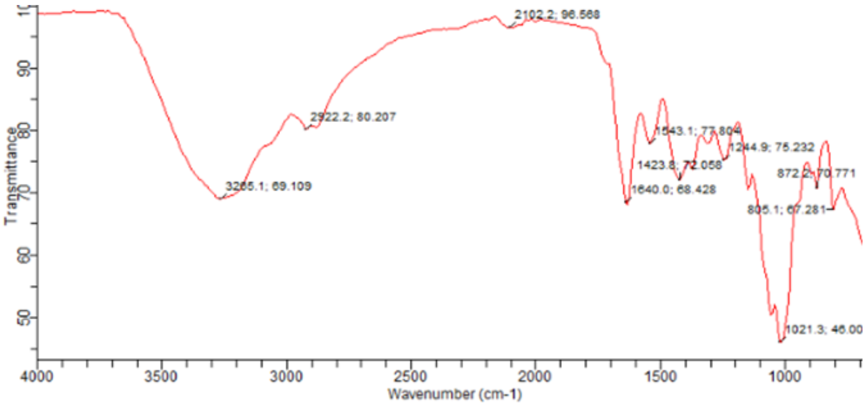


Figure 2. IR spectrum of GA-1

aldehyde groups. Upon addition of methanol, sharp white crystals were formed. These crystals were cleaned with a mix of cyclohexane and ethyl acetate (3:1 v/v) to get rid of any leftover impurities and chemicals, resulting in a cleaner GA-1 compound. The solvent mixture successfully got rid of nonpolar impurities, while the polar GA-1 compound stayed the same.

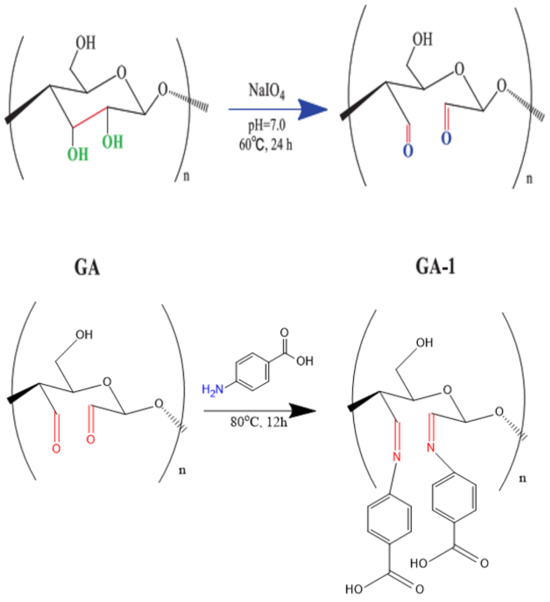
Theoretical analysis suggests that when $NaIO_4$ oxidizes the C2 and C3 positions of the pyranose ring in glucomannan, it causes the ring to open and creates dialdehyde structures [10].

This structural change provides reactive sites for further derivatization. The GA-1 intermediate was analyzed with infrared (IR) spectroscopy to check for new functional groups, as shown in Figure 2.

The IR spectrum of GA-1 (Figure X) shows a clear peak between 1720 and 1740 cm^{-1}, which means that carbonyl (C=O) groups are present due to periodate oxidation. A broad band at 3200–3600 cm^{-1} corresponds to hydroxyl groups or residual moisture. Peaks at 2720–2920 cm^{-1} represent C–H stretching from aldehyde groups, confirming successful functionalization. The band between 1000 and 1150 cm^{-1} shows the stretching of C–O–C bonds from the glycosidic connections in the glucomannan structure.

Synthesis of Glucomannan Derivative Compound. The second step in making glucomannan derivatives involved mixing 20 mg of GA-1 with 100 mg of p-aminobenzoic acid in 100 mL of dry ethanol. Benzoyl peroxide (BPO, 0.08 g) was added as a radical initiator. The reaction was carried out under reflux at 80°C for 12 h. After completion, the product was filtered and purified using column chromatography with silica gel and cyclohexane/ethyl acetate (3:1) eluent.

The product, a yellowish liquid, was characterized by IR spectroscopy. The presence of C=N stretching (~1650 cm^{-1}) confirmed the formation of imine. Additional peaks at ~1500 cm^{-1} (aromatic ring) and 3000–3300 cm^{-1} (–OH group) indicated the structural features of the derivative. The decrease in the intensity of the aldehyde peak (C=O) confirmed the success of the condensation. The aromatic imine bond in the glucomannan framework is expected to improve the stability of the compound and its potential corrosion inhibition properties. Figure 3. generally depicts the reaction that takes place.



Corrosion Inhibition Activity. The synthesized final compound was evaluated for corrosion inhibition in artificial seawater. Pre-cleaned mild steel samples were weighed to a steady weight and placed in CO_2-saturated artificial seawater with different amounts of the inhibitor (0; 0.1; 0.2; 0.3;

0.4; 0.5 mM) for 24 and 36 hours. After immersion, samples were rinsed with distilled water and ethanol, dried at 25°C, and reweighed to assess weight loss. The testing procedure is illustrated in Figure 4.

Steel plates (2×1×0.1 cm) were used. In the gravimetric method, the entire surface was immersed, whereas in the potentiostatic method, only half of the plate was submerged. The exposed surface area was calculated accordingly.

The gravimetric method, which measures weight [13], was used to find out how fast mild steel corrodes and how effective the inhibitors are by looking at the weight loss. Table 1 summarizes the results of weight loss, corrosion rate, and inhibition efficiency. Based on the data in Table 1. the relationship between inhibitor concentration and inhibition efficiency is illustrated in Figure 5.

The results showed a consistent increase in inhibition efficiency with higher inhibitor concentrations. At 0.1 mg/L, inhibition was low and decreased slightly over time (17.57% at 12 h to 13.91% at 36 h), indicating limited stability of the protective layer. At 0.3 mg/L, the efficiency peaked at 69.70% after

Figure 4. Testing activity of anticorrosion

Table 1. Corrosion test result data

Inhibitor Concentration (mg/L)	W_0 (g)	Wt (g)	ΔW	Volume (cm^3)	Density (g/cm^3)	Cr (mpy)	% Protection
12 hours							
0	4.5709	4.5674	0.0035	0.480	9.514	8.058646	**0.00%**
0.1	4.9528	4.9500	0.0028	0.548	9.044	6.643130	**17.57%**
0.2	4.6409	4.6389	0.0020	0.554	8.378	5.209973	**35.35%**
03	4.9408	4.9392	0.0016	0.563	8.778	3.978115	**50.64%**
0.4	5.2879	5.2873	0.0006	0.620	8.535	1.451798	**81.98%**
0.5	5.1780	5.1778	0.0002	0.596	8.686	0.504832	**93.74%**
24 hours							
0	4.4409	4.4371	0.0038	0.501	8.861	9.392054	**0.00%**
0.1	4.5674	4.5642	0.0032	0.520	8.788	8.006938	**14.75%**
0.2	4.3985	4.3961	0.0024	0.487	9.025	5.977154	**36.36%**
0.3	4.4309	4.4297	0.0012	0.469	9.440	2.845735	**69.70%**
0.4	4.6409	4.6401	0.0008	0.554	8.378	2.048901	**78.18%**
0.5	4.9408	4.9405	0.0003	0.563	8.778	0.745897	**92.06%**
36 hours							
0	4.0950	4.0918	0,0032	0,555	7.377	9.274768	**0.00%**
0.1	5.2879	5.2846	0,0033	0,620	8.535	7.98489	**13.91%**
0.2	5.1780	5.1762	0,0018	0,596	8.686	4.543486	**51.01%**
0.3	4.5550	4.5539	0,0011	0,556	8.199	2.961894	**68.07%**
0.4	4.9761	4.9752	0,0009	0,519	9.591	2.063745	**77.75%**
0.5	5.3291	5.3287	0,0004	0,614	8.681	0.959664	**89.65%**

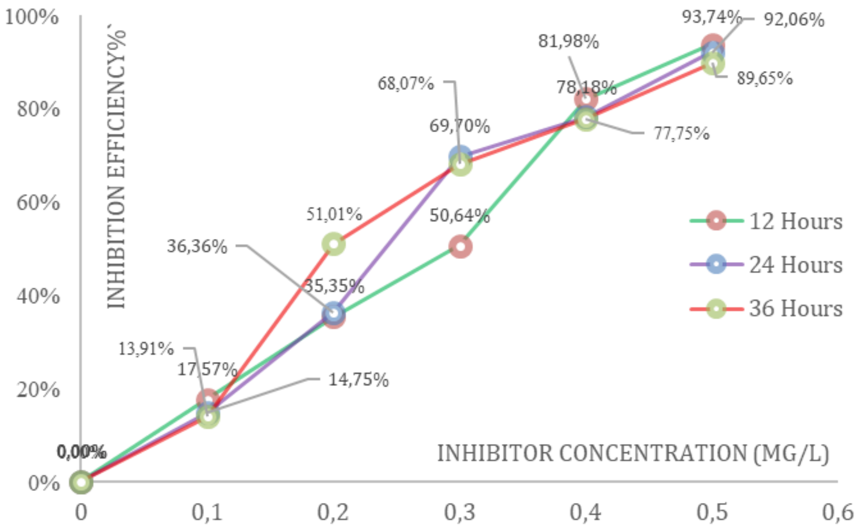


Figure 5. Testing activity of anticorrosion

24 hours and remained relatively stable. At the highest concentration (0.5 mg/L), the efficiency exceeded 90% at all time points, with only a slight decrease observed, indicating excellent and long-lasting corrosion protection. These data confirm that higher inhibitor concentrations result in more effective and stable inhibition over a long period.

Corrosion is an electrochemical process involving the dissolution of the anode metal and the acceptance of electrons by the cathode, which is often accelerated by the presence of aggressive ions such as Cl^-, F^-, or SO_4^{2-} [14]. Inhibitors are compounds that reduce the rate of corrosion by adsorbing to the metal surface and forming a protective layer that inhibits the redox reaction.

The final synthesized compounds likely function through an adsorption mechanism. Functional groups such as –OH, $–NH_2$, and –COOH interact with the steel surface, forming a passive barrier that prevents chloride and oxygen from accessing the metal [15]. Increased surface coverage by the inhibitor correlates with higher inhibition efficiency. In this study, inhibition was more effective at higher inhibitor concentrations but decreased during longer immersion times, indicating weak physisorption interactions such as Van der Waals forces. This resulted in gradual desorption and loss of protection in a saturated environment.

Conclusion

Glucomannan was successfully isolated from porang flour with a yield of 13.35% and characterized using IR spectroscopy, which confirmed the presence of O–H, C–H, C=O, and C–O–C functional groups. The compound was subsequently oxidized using $NaIO_4$ to produce an intermediate compound, GA-1, containing aldehyde groups. This intermediate was further reacted with p-aminobenzoic acid to form a glucomannan derivative featuring an imine bond. Corrosion inhibition tests on mild steel in CO_2-saturated artificial seawater demonstrated that the synthesized compound effectively inhibited corrosion, particularly at a concentration of 0.5 mg/L, which achieved an inhibition efficiency exceeding 90%. The inhibition mechanism involves the adsorption of active functional groups onto the metal surface, forming a protective layer. However, a slight decrease in efficiency was observed over time due to the physical nature of the adsorption interaction. Overall, the glucomannan derivative exhibits promising potential as an effective and environmentally friendly natural corrosion inhibitor.

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Author Contributions

H.A. and Q.H.F. carried out the isolation, synthesis, and characterization of the glucomannan derivative. I. and R.E. performed tests for corrosion inhibition activity. D.N.A. and D.S.P. designed the research framework and interpreted the data. All authors contributed to data analysis and manuscript preparation and approved the final version of the article.

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