EVALUATION OF TANNIN FROM *RHIZOPHORA APICULATA* AS RUST CONVERTER

by

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Thesis submitted in fulfillment of the requirements
for the degree of
Master of Science

March 2005

DECLARATION

Saya mengisytiharkan bahawa kandungan yang dibentangkan di dalam tesis ini adalah hasil kerja saya sendiri dan telah dijalankan di Universiti Sains Malaysia. Tesis ini juga tidak pernah diserahkan untuk ijazah yang lain sebelum ini.

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ACKNOWLEDGEMENTS

I would like to take this opportunity to acknowledge many individuals who have helped me throughout my research. First and foremost, I would like to express my gratitude to my supervisor, Assoc. Prof. Dr. Mohd. Jain. Noordin Mohd. Kassim for his superb guidance, advice, inspiration, support and help.

My thanks also go to Pn. Afidah Abdul Rahim, for her generous advice and assistance in some of my experimental. I would like to acknowledge the technical staff of the School of Chemical Science, in particular Mr. Ali for his help throughout my work in laboratory, Mr. Sobri for his guidance in HPLC analysis and Mr. Aw Yeong for his assistance in FTIR study.

My gratitude also goes to all of my friends and colleagues for their help and encouragement. And last but not least, my sincere appreciation to my family back in Indonesia for giving me this chance to complete postgraduate study and for their encouragement and support.

Henny Sumilo Santoso

March 2005

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ABSTRAK

Tujuan utama daripada kajian ini adalah memformulasikan penukar karat berasaskan tanin dan mengkaji keberkesanannya sebagai penukar karat. Tanin yang digunakan dalam kajian ini diekstrak daripada kulit kayu bakau (*Rhizophora apiculata*) yang merupakan bahan buangan dalam industri arang kayu. Pengekstrakan daripada kulit kayu bakau dengan 70 % akueus aseton meghasilkan 23.6 % tanin campuran, yang mengandungi 12.3 % tanin terhidrolisis dan 8.7 % tanin terkondensasi. Beberapa pengujian dilakukan untuk mengkaji tanin, seperti ujian Prussian blue untuk penentuan fenol total, ujian vanillin dilakukan untuk menganggarkan tanin terkondensasi, ujian Stiasny untuk menganggarkan peratus flavanoid yang bertindak balas dengan formaldehid. Pengenalpastian monomer yang terkandung dalam tanin terkondensasi dilakukan dengan HPLC. Rawatan serbuk karat dengan pelbagai peratusan larutan tanin menghasilkan penukaran hasil karat besi kepada ferik tanat atau hasil fasa besi lainnya. Dalam formulasi penukar karat satu pek berasaskan tanin, kajian FTIR menunjukkan bahawa campuran asid fosforik dan tanin lebih efektif daripada tanin atau asid fosforik sahaja dalam menukarkan karat. Penukar karat yang mengandungi 9 % tanin menunjukkan keupayaan untuk menukar hasil karat besi sepenuhnya. Formula penukar karat berasaskan resin polivinil-butiral (PVBR) yang mengandungi gabungan tanin dan zink fosfat dengan nisbah 1 : 1 mempunyai potensi yang besar sebagai penukar karat. Penukar karat yang hanya mengandungi tanin atau zink fosfat sahaja tidak menunjukkan keberkesanannya sebagai penukar karat.

ABSTRACT

The main objective of this research is to formulate rust converter formulations based on tannin and to evaluate their rust conversion performance. The tannins that were used in this study were extracted from mangrove (*Rhizophora apiculata*) barks which are the waste product from charcoal industry. The extraction of mangrove bark with 70 % aqueous acetone produced 23.6 % mixed tannin, which contained 12.3 % hydrolysable tannin and 8.7 % condensed tannin. The quantifications of tannin have been carried out by several assays, such as Prussian blue assay for total phenolic determination, vanillin assay to estimate condensed tannin, Stiasny test to provide the estimation of the total flavanoid that react with formaldehyde. The identification of the tannin monomer of condensed tannin was carried out by reverse phase HPLC. Treatment of rust powder with various percentage of tannin solution resulted in the transformation of iron rust products into ferric tannate or other iron phase products. In single pack rust converter formulations based on tannin, the FTIR study showed that a mixture of phosphoric acid and tannin is more effective than the tannin or phosphoric acid alone in converting or transforming the iron rust products. Rust converter which contained 9 % of tannin had been showed to be able to convert completely all the iron rust products. Rust converter based on a polyvinyl-butyral resin (PVBR) containing tannin in combination with zinc phosphate in the ratio of 1 : 1 had great potential as rust converter. Using tannin or zinc phosphate alone was not effective as rust converter.

1.0 INTRODUCTION

1.1 Corrosion

Corrosion may be defined as the destruction or deterioration of metal or metal alloy by chemical or electrochemical reactions with its environment [1]. The serious consequences of the corrosion process have become a problem of world wide significance. In addition to our everyday encounters with form of degradation, corrosion causes plant shutdown, waste of valuable resources, loss or contamination of products, reduction in efficiency, costly maintenance, and expensive overdesign. It can also jeopardize safety and inhibit technology progress. It is estimated that roughly 3% of the annual production of steel is lost by corrosion [2] and approximately 5% of an industrial nation's income is spent on corrosion preventions and maintenance or replacement of products lost or contaminated as a result of corrosion reactions [3].

The corrosion characteristics are influenced by many variables including relative humidity, pollutant, temperature, sulfur dioxide content, hydrogen sulfide content, chloride content, amount of rainfall, dew formation, dust and even the position of the exposed metal. Geographic location also plays an important part. All types of corrosion may take place depending on the specific contaminants present and the material of construction [4].

1.1.1 Corrosion of Iron

Iron corrodes in reaction with the environment because of the thermodynamically unstable condition of iron after it has been extracted from its ores. Corrosion is essentially the conversion of iron into a hydrated form of iron oxide, i.e. rust. The driving force of the reaction is the tendency of iron to combine with oxygen [2]. Iron rusts owing to the presence of anodic and cathodic sites on its surface. During corrosion, more than one oxidation and one reduction reaction may occur.

In the anodic zone, the iron ionizes:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad \text{...} \quad (1.1)$$

In the presence of water and oxygen, hydroxyl ions are produced in the cathodic zone:

$$H_2O + {}^1/_2O_2 + 2e^- \rightarrow 2OH^- \quad \text{...} \quad (1.2)$$

If no other oxidation or reduction reaction occurs, the total electrochemical reaction is just the sum of reaction (1.1) and (1.2) to form ferrous hydroxide:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad \text{...} \quad (1.3)$$

In the presence of atmospheric oxygen, the $Fe(OH)_2$ is rapidly oxidized to reddish brown color rust which is generally written as FeO.OH or hydrated iron (III) oxide ($Fe_2O_3.H_2O$):

$$4Fe(OH)_2 + O_2 \rightarrow 4\gamma\text{-}FeO.OH + 2H_2O \quad \text{..............................} \quad (1.4)$$

Lepidocrocite (γ-FeO.OH) can be transformed into the more stable goethite (α-FeO.OH) or, in deficiency of oxygen, reduced to magnetite (Fe_3O_4).

$$Fe(OH)_2 + 2\gamma\text{-}FeO.OH \rightarrow Fe_3O_4 + 2H_2O \quad \text{..............................} \quad (1.5)$$

Later, the magnetite produced is re-oxidized in air by oxygen in the presence of water to regenerate γ-FeOOH:

$$Fe_3O_4 + {}^1/_4O_2 + {}^3/_2\,H_2O \rightarrow 3\ \gamma\text{-}FeOOH \quad \text{..............................} \quad (1.6)$$

From the reactions above, it serves to illustrate that the electrochemical nature of rusting and the essential parts played by moisture and oxygen [2]. However, in the presence of electrolyte such as sodium chloride, the reactions are modified, ferrous chloride is formed at the anode and sodium hydroxide is formed at the cathode [2]. These two compounds are very soluble and not easily oxidized, so that they diffuse away from the sites of formation and react at a distance from the metal surface to form ferrous hydroxide, or a basic salt, which then combines with oxygen to form rust with the regeneration of sodium chloride:

$$FeCl_2 + 2NaOH \rightarrow Fe(OH)_2 + 2NaCl \quad \text{..............................} \quad (1.7)$$

$$4Fe(OH)_2 + O_2 \rightarrow 4FeOOH + 2H_2O \quad \text{..............................} \quad (1.8)$$

Goethite (γ-FeOOH), lepidocrocite (γ-FeO.OH) and magnetite (Fe_3O_4) are the main constituents of atmospheric corrosion of steel. The proportions of each depend on pH, temperature, the atmosphere in which the rust forms and the presence or absence of atmospheric pollutants [5]. Akaganeite (β-FeOOH) is often observed as a corrosion product of iron in chloride-containing environments, such as marine atmospheres [6].

1.1.2 Corrosion Protection

While corrosion will always remain as a threat, there are many ways that can be deployed to protect a structural metal against the environment corrosion severity. Basically, there are five essential ways of corrosion control; they are based on the application of good design practice, a sensitive approach to materials selection, the use of inhibitors, the application of protective coating and finally using anodic or cathodic protection [7]. Most of the structural steels are protected from corrosion by surface coating, principally by painting schemes. Paint coating will provide long-term protection only if applied to well prepared substrate. Thus, proper surface preparation is the key to obtain maximum protection performance by a surface coating.

The main function of a protective coating is to isolate structural metal from environmental corrosives. A coating must provide to a substrate a continuous barrier, any imperfection can become a focal point for degradation and corrosion of the substrate. A paint system often comprising at least three coats of paints viz. a primer, an undercoat and a topcoat. The primer is a universal component of all anticorrosive coatings and is considered to be one of the most important elements of a protective system. A good primer generally provides the ability to retard the spread of corrosion and adhere well to the base metal. Generally, the primer consists of anticorrosive pigment such as lead and chromates or sacrificially metallic pigment which is more base than the metallic structure being protected [5,8].

The major problem in preparing a steel surface to be painted is the removal of all mill scale, rust and associated contaminants from the substrate [9]. It is either technically impossible or economically undesirable to achieve surface preparation to bright steel finish [10]. The excessive cost and inconvenience associated with the mechanical methods such as hand tool, power tool, and sandblasting cleaning have incited efforts to develop alternative surface preparation methods, which can be applied to marginally prepared surfaces. The efforts have centered on rust conversion coating or so-called rust converter that either impregnate rust, convert rust to inactivate soluble salt, or convert iron oxides to other products [10].

1.2 Rust Converter

Rust converters are water-based coatings that are applied to corroded surfaces to convert rust into a water-insoluble, coherent and protective layer over which further paint coatings or topcoat may be applied, which provide protection against corrosion

[11]. The rust converter convert corrosion products of iron into iron compounds that are more stable and corrosion resistant than oxides and oxyhydroxides of iron, therefore do not further react with corrosive agents and impede steel corrosion. If rust is stabilized so that it can no longer redox between Fe(II) and Fe(III) states, the cathodic cycle in the atmospheric corrosion process will cease and corrosion should be prevented [12]. These rust converter formulations could be applied on partially rusted substrate, reducing the effort and cost needed for cleaning the surface by sandblasting or other methods.

The results on protection efficiency of rust converters are controversial due to several factors include finding the appropriate components and their optimal concentrations, the proper time of reaction of the converters with the rust and the application method. The type and concentration of alcohol used as solvent is another important factor. However, the nature of the rust layer (e.g. thickness and composition) and its time of formation at the corroded steel surface are other factors influencing the converter protection efficiency. Younger rust reacts better with the converters than the rust with considerable time of formation, because of its high reactivity [11,13].

The vast majority of commercial rust converters incorporate some type of polyhydroxylated or tannin-like compound as the pigments [9]. In relation to the composition, it is well known that the most common prime candidates to be used in rust converters are based on tannin and phosphoric acids and their derivatives. The dramatic transformation of rusty steel to the typical blue-black coating, which occurs after the application of the product, has been attributed to the complexation of the polyphenolic moiety of the tannin resin to the iron oxide and hydroxides in rust. The blue-black coating that is formed is known as ferric tannate complex. This complex formation can be used to disturb the kinetic of reactions involved in corrosion.

1.3 Tannin

The term "tannins" have a long and well-established usage in the scientific literature which relate specifically to the application of certain plant extracts [14]. They are very complex group of secondary metabolism of plants [15]. Tannins are the most widespread polyphenols in plants after lignin [16]. They are found in approximately 80% of woody, 15% of herbaceous dicotyledonous species and in nearly every species of higher plants, both gymnosperms and angiosperms, and can occur at high levels in some forages, animal feeds and human foods of plant origin, leaves, fruits and galls [17,18]. They are absent or only found in small quantities in lower plants (algae, mosses, lichens, fungi, ferns) and comparatively rare in monocotyledons [19]. In a few families, many species contain tannin in large quantities, e.g. Rhizophoraceae and Combretaceae [19].

Tannins are water-soluble phenolic compounds with molecular weight approximately between 500 and 3000 Daltons [20]. However, this definition does not include all tannins, since, more recently, molecules with molar mass up to 20000 Daltons have been isolated, and that should also be classified as tannins on the basis of their molecular structures [21]. Besides giving the usual phenolic reaction, tannins contain sufficient phenolic hydroxyl groups that permit them to have special properties such as capable of forming stable cross-linking and/or precipitating proteins, collagens, alkaloids, gelatins and minerals (Figure 1.1) [22,23].

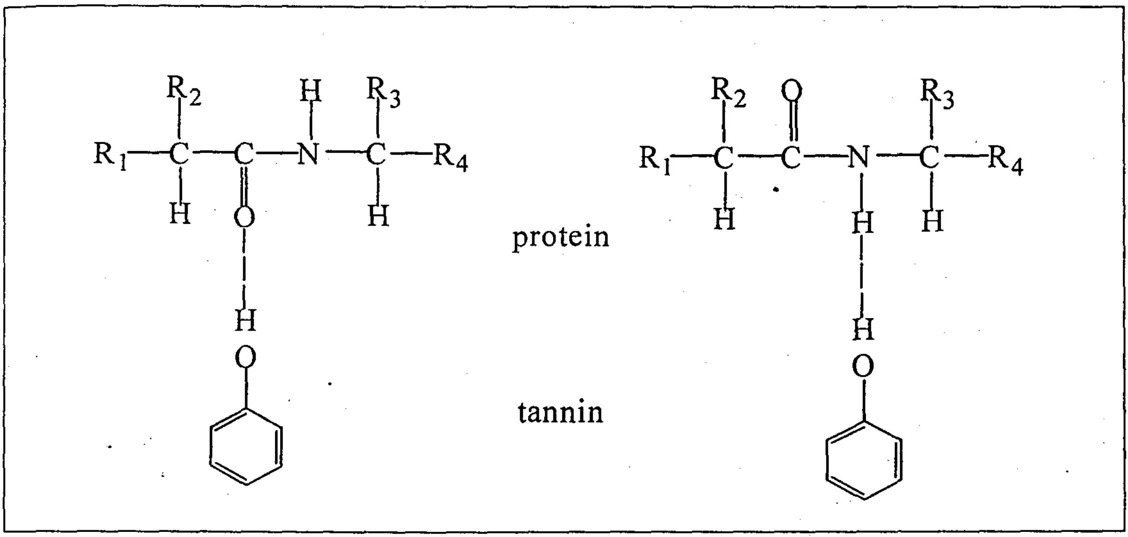


Figure 1.1: Reaction of tannin with protein [24].

Chemically the extracts of tannins fall into two main categories, on the basis of their structural types and their reactivity toward hydrolytic agents, particularly acids; which are largely unrelated apart from the fact that both contain polyhydric phenols within their structures. They are classified as hydrolysable tannins and condensed tannins [25,26]. The latter present complex structures such as dimmers, trimes, oligomers and polymerics [20]. Condensed tannins are widely distributed in higher plants, whereas hydrolysable tannins are of limited distributed in nature [23].

1.3.1 Hydrolysable tannin

Hydrolysable tannins, being polyester, are readily hydrolyzed by acids, alkalis or enzymes into sugars or related polyhydric alcohols and phenol-carboxylic acids [27]. Hydrolysable tannins are further subdivided on the basis of the phenol-carboxylic acids yielded on hydrolysis. The two major groups of hydrolysable tannins are gallotannins, which are derived from gallic acid and ellagitannins, which are derived from hexahydroxydiphenic acid. The structural variation amongst these compounds is caused by oxidative coupling of neighboring gallic acid units or by oxidation of aromatic rings [28].

1.3.1.1 Gallotannin

The gallotannins are the simplest hydrolysable tannins [18]. Gallotannins consist of a central polyol (generally glucose) as a central core, which is surrounded by several gallic acid units (3,4,5-trihydroxyl benzoic acid). The prototypical gallotannin is pentagalloyl glucose, which is the central point for many complex tannin structures [22]. The best-known and the most widely used hydrolysable tannins are tannic acid, which is a gallotannin that has five identical gallic acid units which involve aliphatic hydroxyl groups of the core sugar (Figure 1.2) [27]. Gallic acid may be further esterified or oxidatively cross linked to yield more complex hydrolysable tannins. Further gallic acid units can be attached through a *meta-* or *para-* despide bond (Figure 1.3) [18].

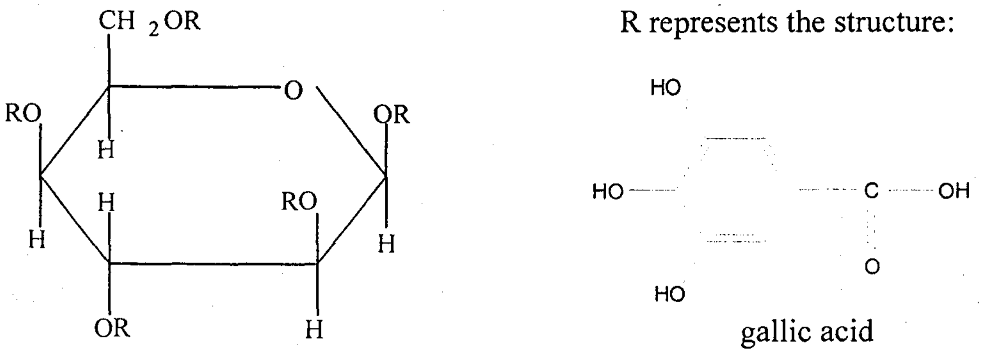


Figure 1.2: The structure of tannic acid, the best-known hydrolysable tannin [26].

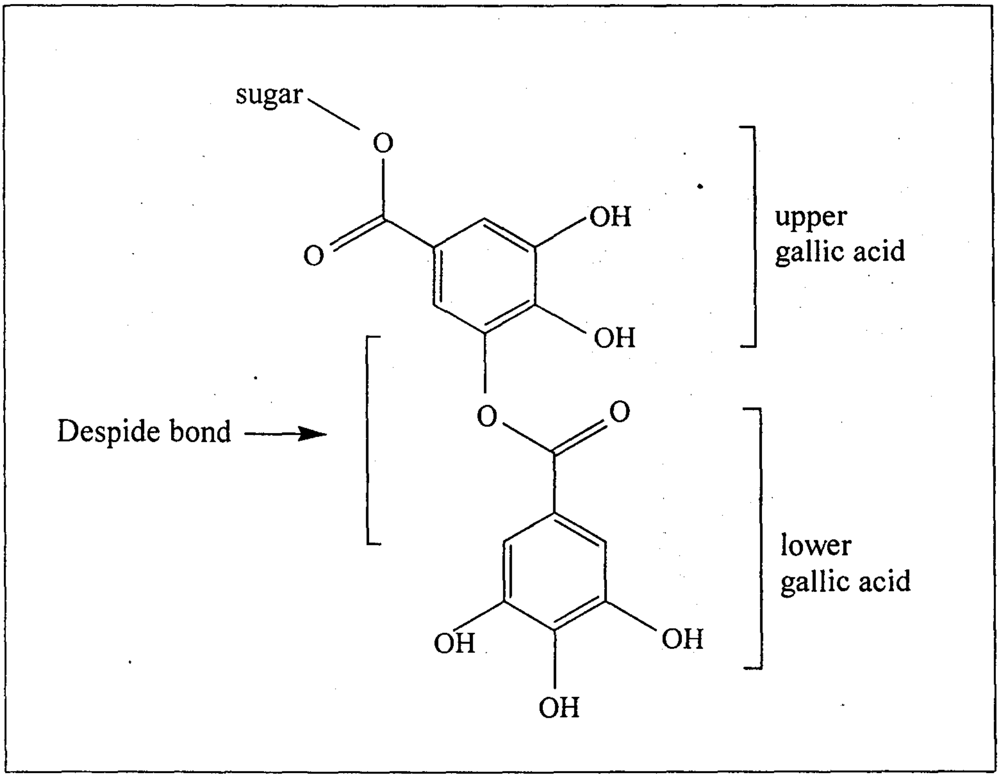
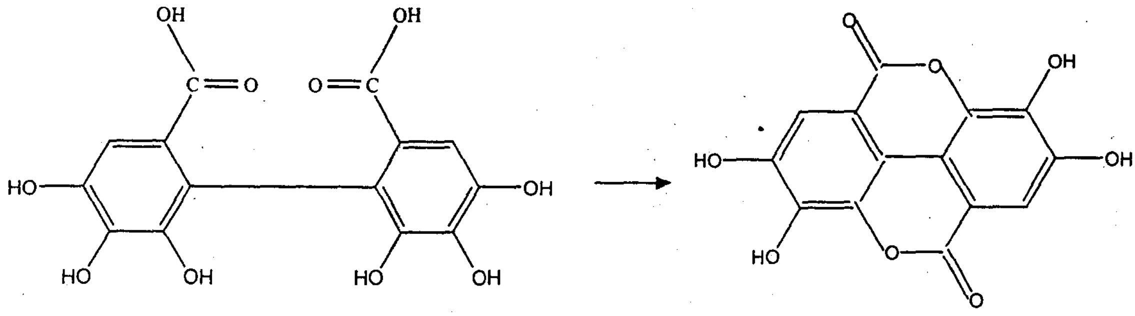


Figure 1.3: Example of despide bond which is formed between the phenolic group of the upper and the acid group of the lower gallic acid units [18].

1.3.1.2 Ellagitannin

In contrast to the rather limited occurrence of gallotannins, ellagitannins are widely distributed and have been found to occur in many plant families and have a strong tendency to combine to higher aggregates [29]. Ellagitannins are derived biosynthetically from pentagalloyl glucose (gallotannin) by oxidative reactions between at least two gallic acid units [20]. The simplest ellagitannins are esters of hexahydroxydiphenic acid. Hexahydroxydiphenic acid spontaneously lactonizes to ellagic acid in aqueous solution (Figure 1.4).



hexahydroxydiphenic acid ellagic acid

Figure 1.4: The structure of the simplest ellagitannin, hexahydroxydiphenic acid and its stable dilactone, ellagic acid [25].

1.3.2 Condensed Tannin

Condensed tannins are high-molecular-weight polymers [27]. Condensed tannins, or commonly referred to as proanthocyanidins [23], are flavanoid polymers, with carbon-carbon bonds joining the individual flavanoids monomers [30]. Condensed tannins are not polyester, therefore are not hydrolyzed by acids, they contain only small amount of carbohydrate and polymerize under the action of acids [30].

The polyflavanoid of condensed tannin consist essentially 2-50 monoflavanoid units linked as a straight chain or with branching [31]. The monoflavanoid is a diverse group of metabolites based on the heterocyclic ring system (C-ring, containing one oxygen atom) derived from two benzene rings, which are phenylalanine (B-ring) and polyketide biosynthesis (A-ring) (Figure 1.5) [32,33]. The basic structures of condensed tannins can be represented by the anthocyanidin, flavanone, flavone and flavonol (Figure 1.6) [22]. The monoflavanoid units of condensed tannin are bound together to form a polymeric chain (Figure 1.7) through the C4-C6 inter-flavanoid bonds or if a hydroxyl group is present on the C5 position, the crosslinking occurs at the carbon atoms in the 4 and 8 positions; other hydroxylation pattern occur, but there are much less common [34,35].

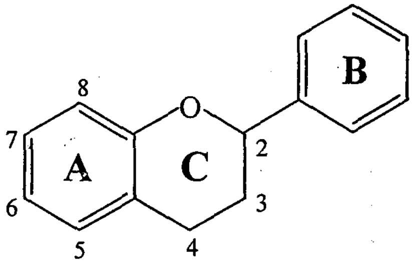
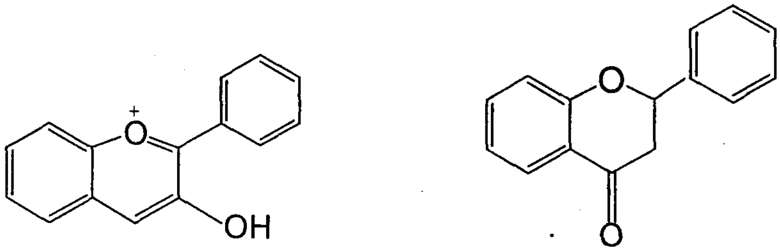
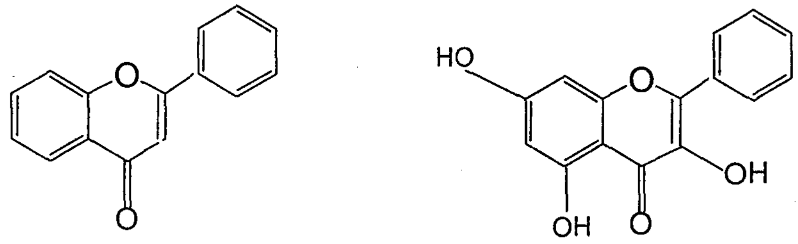


Figure 1.5: The heterocyclic ring system of condensed tannin [33,36].



anthocyanidin
(a)

flavanone
(b)



flavone
(c)

flavonol
(d)

Figure 1.6: The structures of (a) anthocyanidin, (b) flavanone, (c) flavone and (d) flavonol [37].

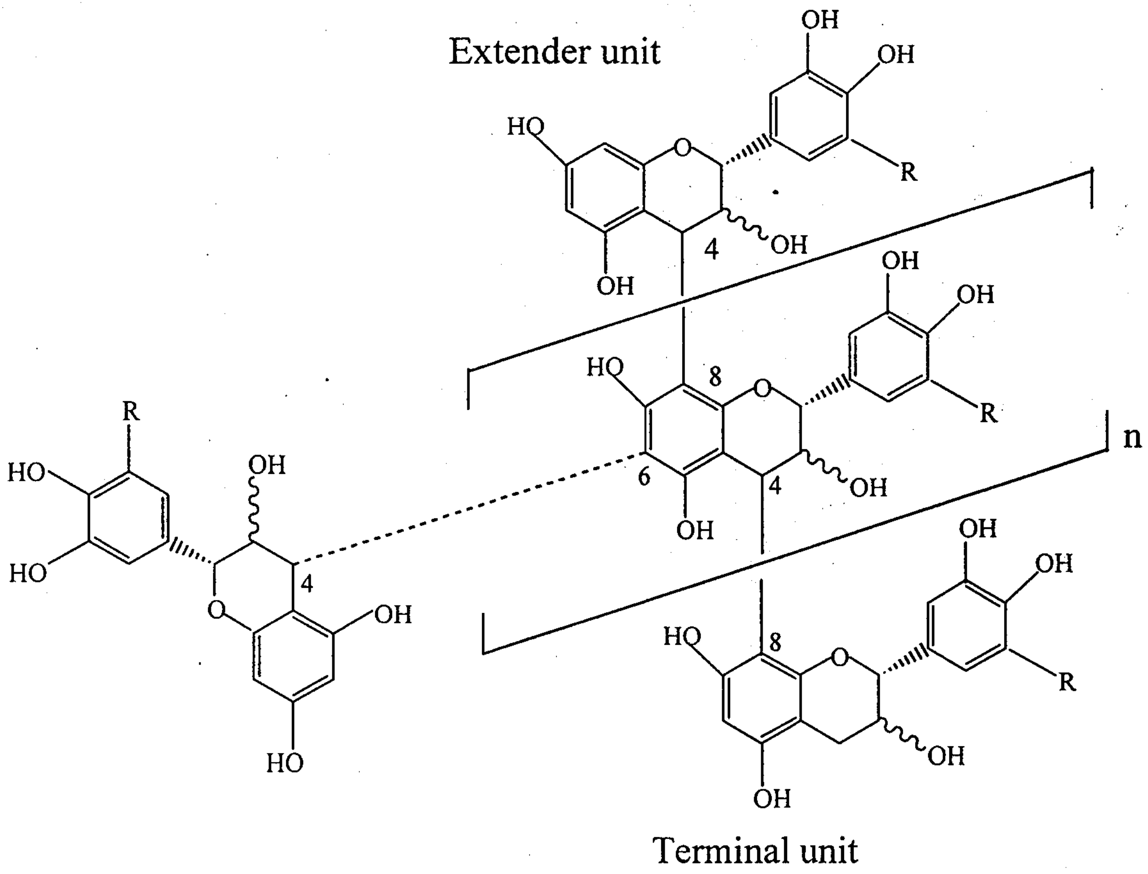
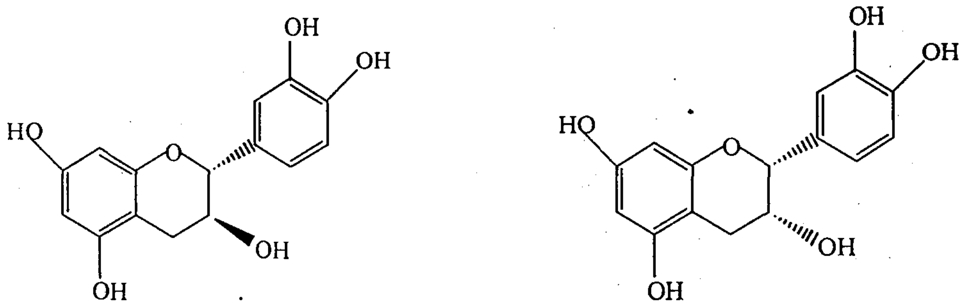


Figure 1.7: Model structure for a condensed tannin. The 4→6 linkage (dotted line) is an alternative interflavan bond. The terminal unit is at the bottom of such a multi-unit structure [34].

1.3.2.1 Flavan-3-ol

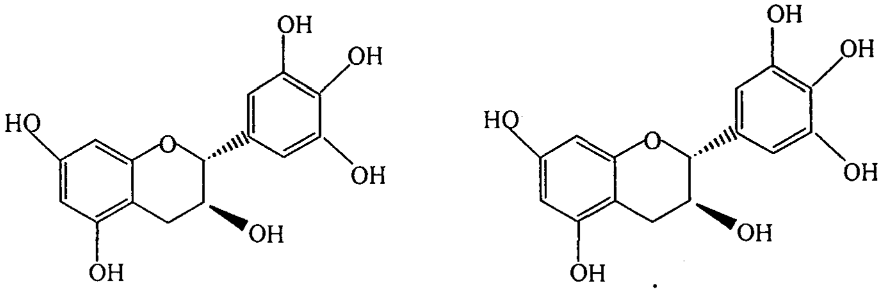
The chemistry of flavan-3-ol is intimately linked to progress in the understanding of the oligomeric proanthocyanidin [33]. Common classes of proanthocyanidin are the procyanidin which consist of chains of the flavan-3-ol(+)-catechin and (-)-epicatechin (Figure 1.8). The catechin and epicatechin monomer has asymmetric centers at position 2 and 3 in ring C [38]. The stereochemistry of (+)-gallocatechin and (-)-epigallocatechin were subsequently related to that of catechin (Figure 1.9) [34]. Flavan-3-ols have two hydroxyl groups on the A-ring and two (catechin and epicatechin) or three (gallocatechin or epigallocatechin) hydroxyl groups on the B-ring.



catechin

epicatechin

Figure 1.8: The structures of flavan-3-ol(+)-catechin and (-)-epicatechin [39].



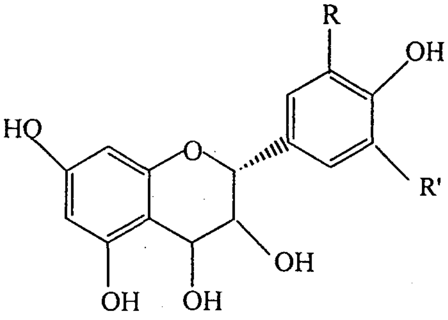
gallocatechin

epigallocatechin

Figure 1.9: The structures of (+)-gallocatechin and (-)-epigallocatechin [40].

1.3.2.2 Flavan-3,4-diol

Other important units involved in proanthocyanidin structure are the flavan-3,4-diols (Figure 1.10) or leucoanthocyanidins (Figure 1.11). Leucoanthocyanidins are monomeric flavanoids which yield cyanidin and delphinidin by cleavage of a C-O bond upon heating with mineral acid [33].

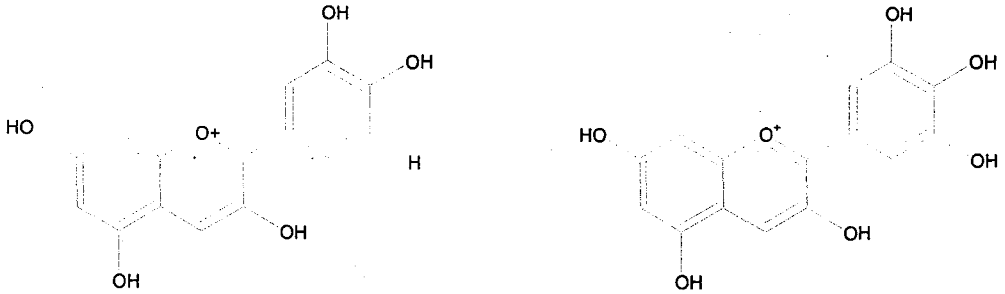


R = H, R' = OH, leucocyanidin

R = R' = H, leucopelargonidin

R = R' = OH, leucodelphinidin

Figure 1.10: The structure of flavan-3,4-diol [22,33].



cyanidin

delphinidin

Figure 1.11: The structures of cyanidin and delphinidin that are yielded from flavan-3,4-diol [37].

1.3.2.3 Flavan-4-ol

The flavan-4-ols (Figure 1.12) are also leucoanthocyanidins, but they are unique in their lability. They may be chemically, and presumably also biosynthetically, derived by a single reduction step from a flavanone. They yield anthocyanidins upon treatment with alcoholic acid at room temperature [33].

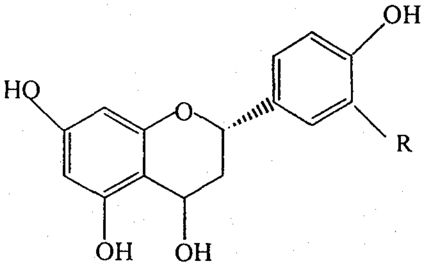


Figure 1.12: The structure of flavan-4-ol [33].

1.3.3 Complex Tannin

Recent accumulated data of tannin structural studies have shown that they may be classified into three major groups based mainly on the structural features rather than on chemical properties [28]. The term "complex tannin" appears to be established as a descriptor for the class of polyphenols that contain both hydrolysable and condensed tannin [33]. They are often difficult to recognize in their sometimes highly modified structures.

From their structural features, they are further divided into three groups. The most commonly occurring is flavano-ellagitannin, in which a flavan-3-ol (catechin, epicatechin or gallocatechin), representing a constituent unit of the condensed tannins, is connected to the glucose portion of the ellagitannin, which representing hydrolysable tannin, through a carbon-carbon linkage [33]. The second is procyanidino-ellagitannin that contains both proanthocyanidins and ellagitannins, and the third is the flavono-ellagitannin in which a flavonoid glucoside is linked to an ellagitannin moiety through a carbon-carbon bond [28].

Originally tannins were used by humankind over several thousand years for tanning leather, as an ingredient in the synthesis of wood adhesives and in several industrial applications, such as in the production of paint, paper, glue, ink, cosmetic and in food industry as natural colorant and preservative [41]. Interest is now based on the use of tannin as anti-corrosive pigment in rust converter for the protection of steel structures as an alternative to toxic anti-corrosive inhibitor such as lead or chromate [42]. Tannins are polyphenols of vegetal origin, therefore they are environmentally safe and are obtained from renewable sources [43]. The proximity of hydroxyl groups on the aromatic rings makes them able to form chelate with iron ions.

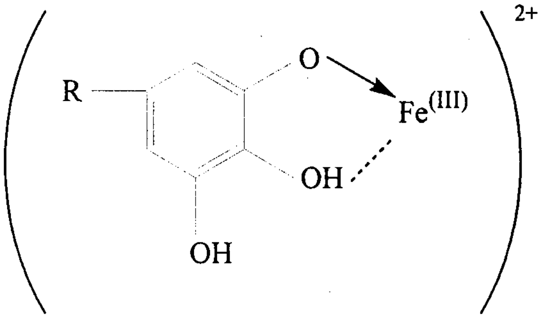
1.4 Reaction of Tannin with Iron

Tannin and phosphoric acid and their derivatives are the most common prime candidates to be used in rust converter [11]. Tannin and phosphoric acid treatments are useful on rusted steel where it is impossible or undesirable to remove all rust. They will delay the onset of rusting and thereby retard the breakdown of subsequent paint films [44].

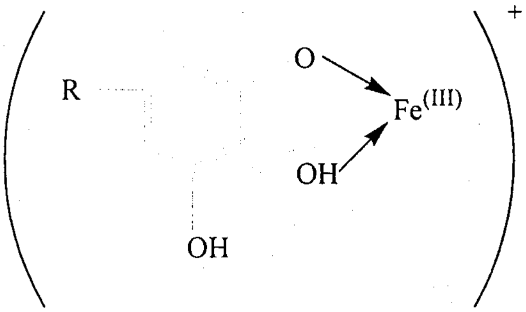
The polyphenolic groups of the tannins confer them the ability to form complexes (chelates) with iron and other metallic cations. This complex formation can be used to disturb the kinetic of reactions involved in corrosion [12,42]. The mechanism of the reaction of tannin with rust is characterized by three general steps: (1) absorption of tannin to the rusty surface, (2) complexation of ferric ions or complexation of surface iron hydroxides/oxides followed by dissolution, and (3) partial or complete readsorption of the iron-tannate complexes to the substrate [9].

Tannin reacts with iron or rusty steel to form an intense blue-black ferric tannate complex, which is the basis of the corrosion protective coating [10]. The ferric tannates are highly insoluble and act as electric insulators between cathodic and anodic sites on the metal surfaces [12,43].Tannins with low molecular weights have lower reactivity with iron and lower capacity to absorb oxygen [8]. As tannin molecules are generally polymeric in nature with flavanoid structure, each molecule could react with a number of ferric ions to form a network structure [44]. Seavell [45] described that the reaction with ferric ions involve the C3 and C4 adjacent hydroxyl groups of tannin, this reaction is common to all flavanoid units. Reaction between ion Fe^{3+}(aq) and the phenolic hydroxyl groups gives an insoluble bis-chelate (Figure 1.13). With chelation giving oxonium ions, reaction is formed under conditions which reduce acidity. The tris-chelate is not likely to form, except under alkaline conditions [45].

It might be expected that the Fe^{3+} would complex as the follow structure:



However, despite the high pKa value for the hydroxyl group at the C4 position of the singly ionized anion, the greater stability of the doubly ionized chelate leads to the formation of the ortho-diphenol complex:



The bis-chelate that is formed between Fe^{3+}(aq) and tannin:

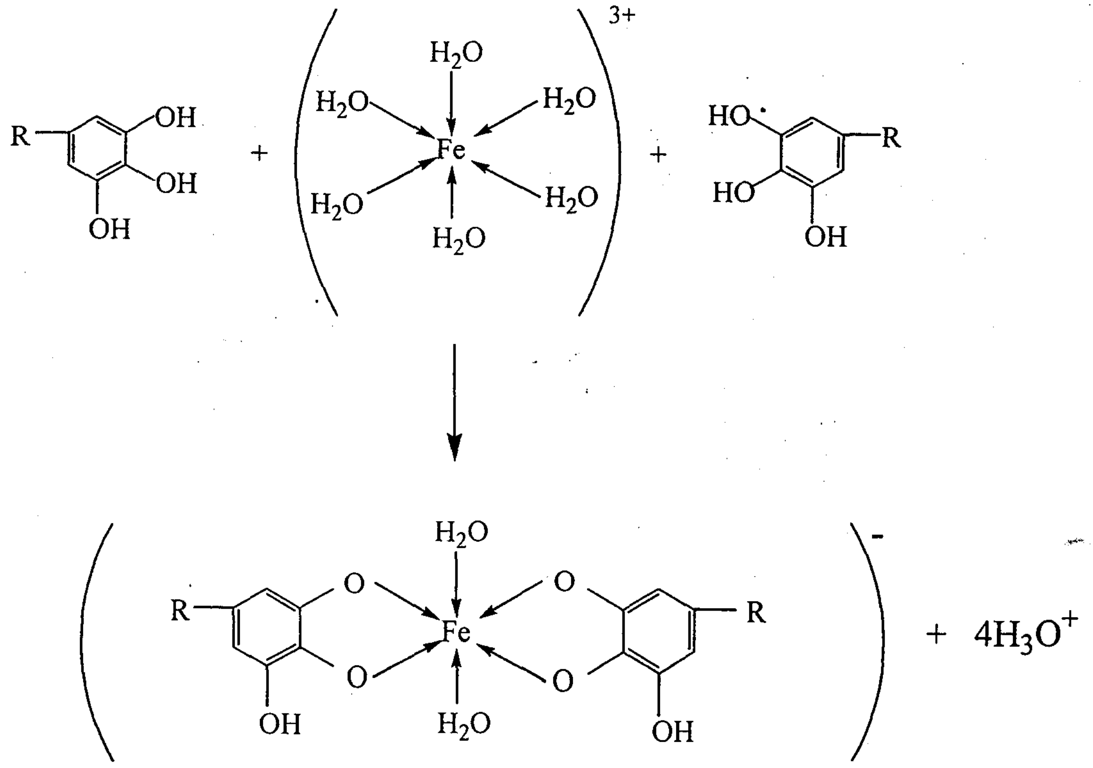


Figure 1.13: Ferric tannate chelate where R represents the rest of the tannin molecule [45,46].

The tannin chelates with Fe^{3+}(aq) but not with Fe^{2+}(aq). Although Fe^{2+}(aq) ions do not chelate with phenolic hydroxy groups, they are readily oxidized to Fe^{3+}(aq), especially if the reaction is carried out under conditions when there is ready access of air to supply oxygen for the oxidation [45]:

$$4Fe^{2+} + 2H_2O + O_2 \rightarrow 4Fe^{3+} + 4OH^- \quad \text{...} \quad (1.9)$$

Work done by Seavell [12] showed that the tannin functions by reacting with the Fe^{3+}(aq) ion and not by direct reaction with either iron or rust. The reactions of tannin and Fe^{3+}(aq) ion were proposed as follows [8]:

$Fe + 3H^+ + {}^3/_4O_2 \rightarrow Fe^{3+} + {}^3/_2H_2O$ .... (1.10)

$Fe + 2H^+ + {}^1/_2O_2 \rightarrow Fe^{2+} + H_2O$ .... (1.11)

$Fe^{2+} + {}^1/_4O_2 + H^+ \rightarrow Fe^{3+} + {}^1/_2H_2O$ .... (1.12)

$Tannin\text{-}OH + Fe^{3+} \rightarrow (Tannin\text{-}O\text{-} Fe^{3+})^{2+} + H^+$ .... (1.13)

$Tannin\text{-}2OH + Fe^{3+} \rightarrow (Tannin\text{-}2O\text{-} Fe^{3+})^{+} + 2H^+$ .... (1.14)

$Tannin\text{-}2OH + (Tannin\text{-}2O\text{-} Fe^{3+})^{+} \rightarrow (Tannin\text{-}4O\text{-} Fe^{3+})^{-} + 2H^+$ .... (1.15)

If the steel presented oxides in its surface (i.e., lepidocrocite, FeOOH and/or magnetite, Fe_3O_4), the tannin primer reacted with ferrous or ferric ions, according to the following reactions:

$FeOOH + 3H^+ \rightarrow Fe^{3+} + 2H_2O$ .... (1.16)

$Fe_3O_4 + 8H^+ \rightarrow 2Fe^{3+} + Fe^{2+} + 4H_2O$ .... (1.17)

$Fe^{2+} + {}^1/_4O_2 + H^+ \rightarrow Fe^{3+} + {}^1/_2H_2O$ .... (1.18)

Ferric ions formed in Reactions (1.16) and (1.17), in turn, reacted with tannin according to Reactions (1.13) and (1.14), generating iron tannates that contain corrosion inhibitor characteristics. A study done by Deslauriers [9] showed that the performances of rust converter depend more on the barrier properties of the entire paint system and the amount of the rust present on the surface than on its ability to form ferric tannate chelates.

1.5 Reaction of Phosphoric Acid with Iron

Phosphoric acid alone is not recommended as rust converter because of their reputation of poor performance [47]. However, the addition of phosphoric acid to a tannin solution produced a coating which showed better corrosion resistance than that formed by either of the individual constituents alone [43]. Nigam *et al.* [48] concluded that the rust conversion performance using phosphoric acid solution depends strongly on the concentration of the acid and the condition of the surface. It is only above 8 M concentrations that ferric phosphate is formed. Below this concentration level, the transformation is dependant on the initial corroding medium [43].

In formulation containing phosphoric acid alone, it was found to migrate and react with the surface of the steel. This resulted in the formation of metal phosphates such as $Fe(H_2PO_4)_2$, $FeHPO_4$, $Fe_3(PO_4)_2$, $FePO_4$, etc. These compounds are thought to passivate the substrate and provide the proper functionalities for the condensation reactions with binder [43]. When reacts with metallic iron and magnetite, concentrated phosphoric acid form a mixture of $FePO_4.4H_2O$ and $Fe_3(PO_4)_2.8H_2O$, whereas with oxyhydroxides like goethite and lepidocrocite, it forms acid ferric phosphate $Fe_3(PO_4)_2.5H_2O$ that exhibits a relatively high stability [49]. A test carried out by Nasrazadani [50] concluded that the reaction of phosphoric acid is fastest with lepidocrocite, a little slower with magnetite, and slowest with goethite.

Phosphoric acid solution with low concentration reacts with iron corrosion product to form iron phosphate precipitation, which act as corrosion protection, according to Reactions (1.18) and (1.19) [47]. However, according to Gust [51], if phosphoric acid with medium and high concentration were applied, the iron seems to be unable to allow the iron phosphate precipitation.

$$6H_3PO_4 + 3Fe \rightarrow 3Fe(H_2PO_4)_2 + 3H_2 \quad \text{..........................} (1.18)$$

$$3Fe(H_2PO_4)_2 \rightarrow Fe_3(PO_4)_2\downarrow + 4\,H_3PO_4 \quad \text{..........................} (1.19)$$

Tannin, as well as phosphoric acid, reacts with phase components of rust, converting them into ferric tannates and ferric phosphates, respectively. While agent containing both tannin and phosphoric acid, they convert the phase components into mixtures of original compounds, which are ferric tannates and ferric phosphates [51].

1.6 Objective

It is well known that tannin and phosphoric acid are the most prime candidates to be used in rust converter due to their ability to convert corrosion products of iron into more stable and corrosion resistant iron compounds. Therefore, the objectives of this study are:

1. To extract and quantify tannin from mangrove (*Rhizophora apiculata*) bark with different types of solvent.
2. To evaluate the chemical and physical properties of the tannins that are extracted by means of infrared spectroscopy (FTIR), UV-VIS and several tannin assays such as Prussian blue assay, vanillin assay and Stiasny test.
3. To identify the tannin components (monomer) by means of reverse phase HPLC.
4. To optimize the condition of the reaction between Fe(III) ion with tannin and phosphoric acid using infrared spectroscopy.
5. To formulate and evaluate the rust converter formulations based on *Rhizophora apiculata* tannins by salt spray test (ASTM B 117).

2.0 MATERIALS AND METHODS

The mangrove barks (*Rhizophora apiculata*) were collected from charcoal industry at Larut Matang, Perak, Malaysia. The barks were dried under the sun until constant weight and then were ground into powder form with the mesh size of 150 µm. The ground barks were kept in closed container at room temperature for subsequently extraction. All the chemicals and solvents used in this study were AR grade and been used without further purification.

2.1 Tannin Extraction

A 150.0 g of ground *Rhizophora apiculata* bark was wrapped with cotton cloth and immersed in 600 mL of 70 % aqueous acetone for 24 hours with occasionally stirred at ambient temperature. The immersion was repeated with new solvent for three times. Acetone extracts were reduced to the aqueous phase by rotary evaporation under reduced pressure and the resulting aqueous solution was freeze-dried to obtain raw tannin powder.

The raw tannin (1.5 g) that was obtained by extraction of 70 % acetone was redissolved in 150 mL water and extracted with 50 mL of n-hexane using separating funnel to remove lipid. The residue was then extracted with 50 mL ethyl acetate to remove the non-tannin containing extract include low molecular weight tannin. Traces of ethyl acetate were removed from the ethyl-acetate soluble fraction (upper phase) by rotary evaporation to obtain low molecular weight tannin. The ethyl acetate was also removed from the remaining aqueous fraction (lower phase) to obtain mixed tannin (mixture of hydrolysable and condensed tannin).

Mixed tannin (1 g) was diluted in 100 mL of 50 % aqueous methanol and applied to a 2.5 cm x 20 cm Sephadex LH-20 column. The column was first eluted with 50 % aqueous methanol until the eluate was clear to recover hydrolysable tannin and condensed tannin was eluted from the column with 50 % aqueous acetone. The type of tannin that was fully applied in the whole experimental was mixed tannin, unless stated in the experimental.

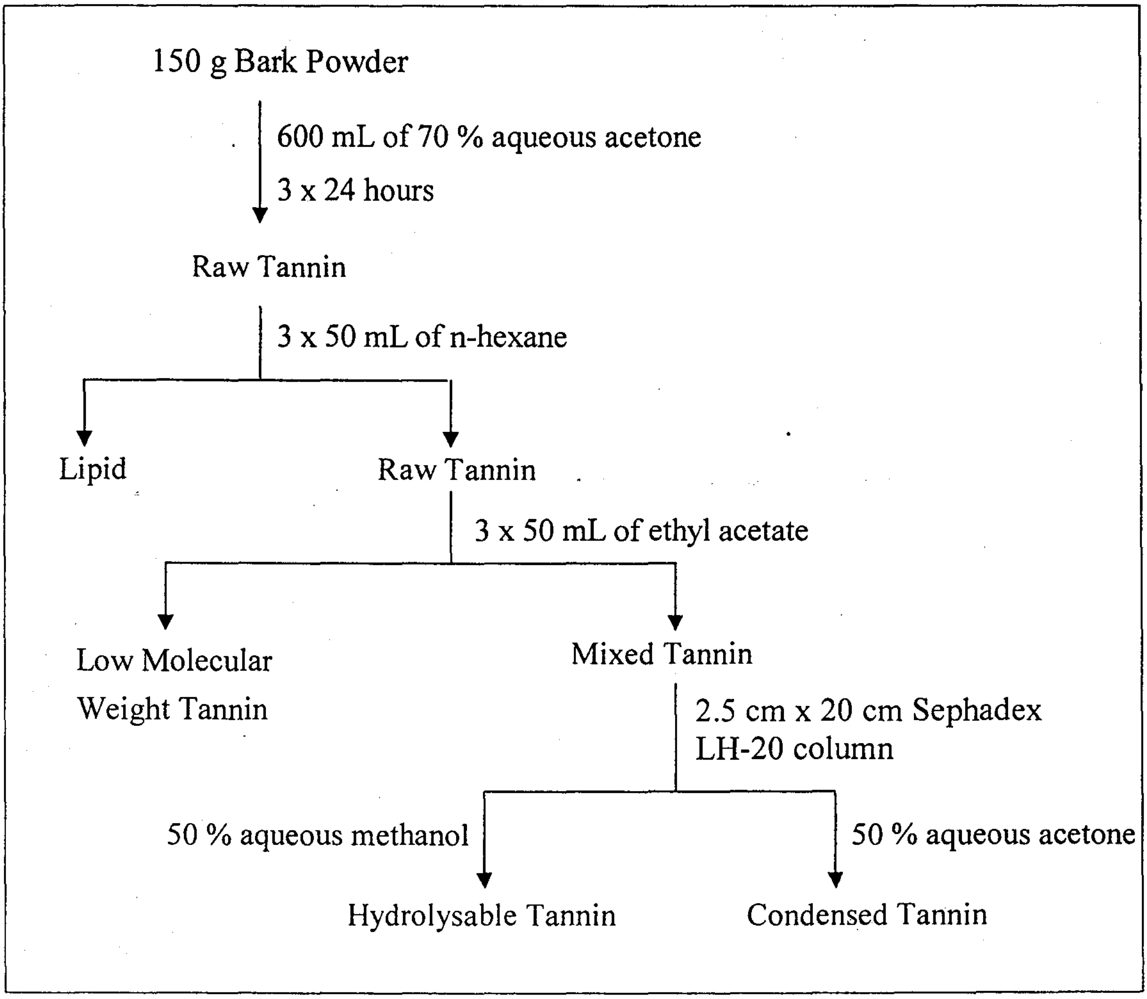


Figure 2.1: Procedure in tannin extraction from *Rhizophora apiculata* bark.

2.2 Assays for The Quantification of Tannin

2.2.1 Prussian Blue Assay for Total Phenols [52]

Gallic acid was obtained from Sigma-Aldrich and was used without further purification. All other reagents were of analytical grade.

2.2.1.1 Preparation of Reagents

(1) 0.10 M $FeNH_4(SO_4)_2$ in 0.10 M HCl

Concentrated HCl was diluted to 0.10 M by bringing 8.3 mL of the concentrated acid to 1 L with distilled water. A 48.2 g of dodecahydrate salt ($FeNH_4(SO_4)_2.12H_2O$) was dissolved in 1 L of 0.10 M HCl to obtain a pale yellow solution of $FeNH_4(SO_4)_2$.

(2) 0.008 M $K_3Fe(CN)_6$

A yellow solution of 0.008 M $K_3Fe(CN)_6$ was prepared by dissolving 2.63 g potassium ferricyanide in 1 L distilled water.

2.2.1.2 Assay Procedure

Tannin sample (0.01 g) was dissolved in 10 mL methanol. A 0.10 mL of the sample was dispensed into a 125 mL Erlenmeyer flask, followed by adding 50.0 mL distilled water. Three millimeters of 0.10 M $FeNH_4(SO_4)_2$ was added and swirled. Exactly 20 minutes after the addition of 0.10 M $FeNH_4(SO_4)_2$, three millimeters of 0.008 M $K_3Fe(CN)_6$ was added and swirled. Absorbance at 720 nm was read 20 minutes after the addition of 0.008 M $K_3Fe(CN)_6$. Solvent-only blank was prepared in the same manner. The absorbance of the blank was subtracted from the absorbance obtained for each sample. All determinations were done in duplicate. The absorbance was read with U 2000, Hitachi, Japan UV-Vis spectrophotometer.