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Computational and FTIR-spectroscopic study on the reactivity of some polyphenolic compounds with HCHO

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ABSTRACT

A semi-empirical computational approach was used to study the reaction of some polyphenolic compounds with formaldehyde in an aqueous alkaline system. Mulliken charges were calculated for the reactive sites on the aromatic rings of the polyphenolic compounds to predict their reaction pathways with formaldehyde. Semi-empirical calculations at RHF/PM3 model were performed on a series of polyphenolic compounds with different chain lengths using HyperChem and GAMESS softwares. The results were compared with the experimental Fourier Transform Infra Red (FT-IR) data. The results indicate that the initial gallic acid formaldehyde resin forms predominantly via CH₂OCH₂ links. It was found that C3-C6 link is formed between the B-ring of the two flavanoid units and the link formed is a CH₂OCH₂ type link. Based on analysis study the negative charges at reactive sites C3' and C6' of catecholic B-ring complexed with Zn²⁺ ions have increased, affinity of the reactive sites towards formaldehyde. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Computer modeling;
Configuration;
Cross linking;
Geometry optimization;
Semi-empirical calculations;
Adsorption.

INTRODUCTION

Tannins are complex phenolic molecules of high molecular weights, ranging from 500 to 20,000. They can be divided into two major groups: (a) condensed tannins (proanthocyanidins) and (b) hydrolysable tannins (polyesters based on gallic and/or ellagic acid and their derivatives). Generally, tannins are soluble in water, with exception of some very high molecular weight compounds^[1]. Gallic acid (Figure 1) has been suggested as a precursor of hydrolysable tannins^[2].

Gallic acid consists of an aromatic ring bearing a carboxyl group (position 1) and three adjacent hydroxyl

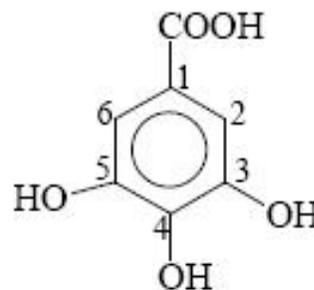


Figure 1 : Structure of gallic acid

groups (positions 3, 4, and 5), leaving two free sites on the ring. Reactivity considerations show that the hydroxyl groups in 3 and 5 activate the free positions, while the remaining groups deactivate them^[3].

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On the other hand, the condensed type of tannin contains a polymeric structure containing 4-8 flavanoid units (Figure 2). They are natural compounds with the structure based on flavan-3-ol units. Previous studies have stated that the A-rings of the tannin serve as very reactive nucleophiles and B-rings provide antioxidant properties and excellent sites for complexation with metals and biopolymers due to the presence of ortho-hydroxyl groups^[4,5].

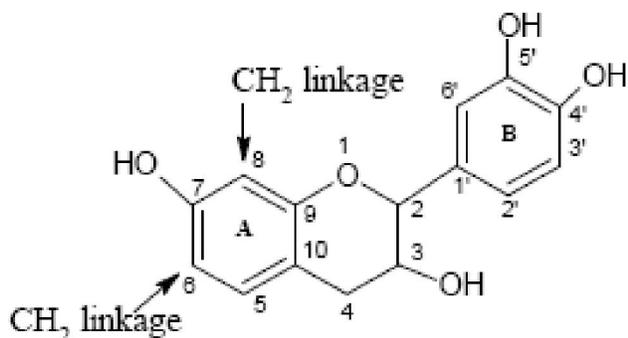


Figure 2 : Structure of flavanoid unit of pine type tannin

Tannins of plant origins have been extensively studied as potential replacements for phenol in the manufacture of formaldehyde based resins. However, some of the studies conducted have revealed that the tannin-formaldehyde molecule formed does not form into a large molecular structure as one would expect. The replacement of phenol with a complex molecule like a tannin molecule makes the understanding of the mechanism of the reaction difficult addressing the problems of the above nature difficult. In addition, this makes the control of the polymerization reaction difficult and thereby the control of the properties of the end products manufactured^[6-9].

According to^[3,10] there are two possible condensation reaction paths for the reaction of gallic acid and formaldehyde, leading to the formation of a methylene bridge (Figure 3). The first step of two mechanisms, methylation, is an electrophilic aromatic substitution reaction [Figure 3(a)]. The second step is a condensation reaction. The two mechanisms involve reaction of a hydroxymethyl group either with a proton of the aromatic ring (ortho position) releasing a water molecule [Figure 3(b)], or with another hydroxymethyl group releasing a water molecule [Figure 3(c)] and a formaldehyde molecule, subsequently [Figure 3(d)]. In both cases, a methylene bridge is created. Thus, the formal-

dehyde reaction at the ortho position of a sufficiently large number of galloylated rings of gallic acid, would initiate the formation of a three dimensional cross-linked structure depending on reaction conditions. Similarly, formaldehyde molecules react with condensed tannins to produce polymers through methylene linkages at reactive positions on the flavanoid molecules, mainly via the A-rings^[6,7].

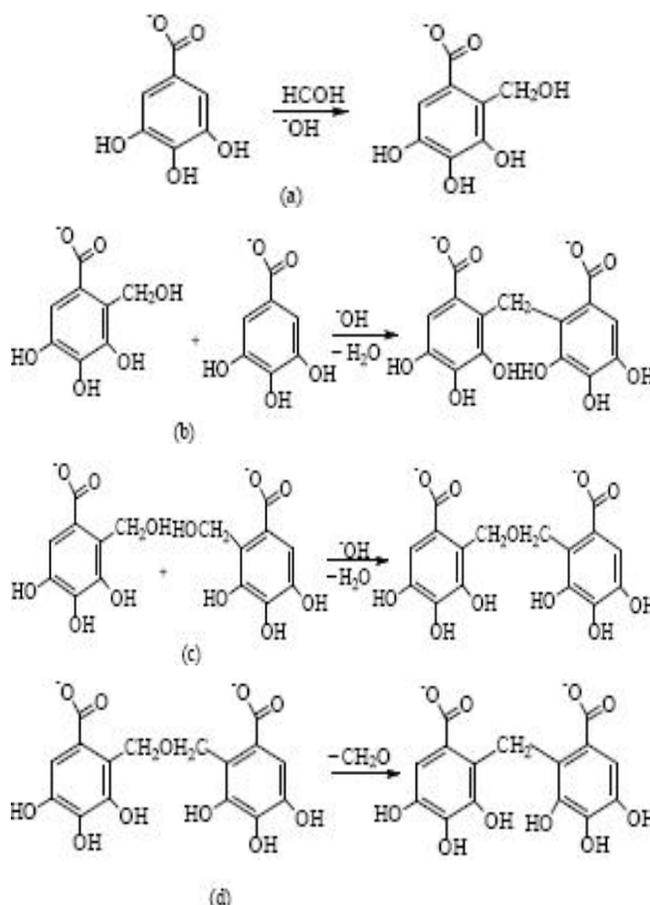


Figure 3 : Reaction of galloyl group with formaldehyde. (a) Methylation reaction of galloyl unit; (b–d) condensation reaction path of galloyl unit in gallic acid³

Pizzi and coworkers^[8,9] have reported that while catecholic or pyrogalloic B-rings of the flavanoid unit do not react with formaldehyde at pH lower than 10, the addition of bivalent metallic ions such as Zinc ions to the reaction mixture induced the B-rings to react with formaldehyde at lower pHs, the optimum being in the pH 4.5–5.5 range.

In order to utilize tannin based resins effectively in various applications and to develop new resins, it is important to understand the reactions of tannin molecules with formaldehyde. However, to date, most of

the studies on polyphenolic resins have concentrated mainly on kinetic studies^[1-3,10,11]. These studies involved not only the calculation of reaction rates but also complex and cumbersome processes for isolation and identification of the reaction products. However, computational chemistry approaches have introduced novel techniques, which allow analysis of reaction mechanisms and prediction of the reactivity of reactants. Therefore, computational chemistry could be used to predict the reactivity of tannin molecules with formaldehyde and thereby to provide new insight into the reaction mechanisms. Such information may be useful in developing strategies to formulate polyphenolic resins for applications such as adhesives and ion-exchange resins. This insight would also serve to decrease the time needed to optimize properties of new resins, experimentally^[11-15].

The main objective of this study is to investigate some important aspects of the reaction mechanisms of hydrolysable and condensed tannins with formaldehyde using the semi-empirical computational approach. While the gallic acid (Ga) was used to represent hydrolysable tannin, pine type tannin (Pt) molecule was chosen to represent condensed tannins. The possible reaction sites of catecholic B-rings of the pine type tannin for the reaction with formaldehyde were investigated. Further, the influence of incorporation of bivalent cations to pine type tannin on the reactivity of catecholic B-rings of the tannin molecule was also studied using the computational approach. The experimental FT-IR spectroscopic evidences were used to confirm results obtained from the theoretical computational approach.

EXPERIMENTAL

Preparation of gallic acid formaldehyde resin

A 25 g sample of gallic acid dissolved in 50 mL of distilled water was heated in a 500 mL three-necked boiling flask to 60 °C. A 40 mL volume of formalin solution (38 % w/w) was added to the reaction mixture. The pH of the mixture was adjusted to 10 using NaOH solution (33 % w/v). The reactants mixture was reacted at 60 °C for an hour. Thereafter, the reaction mixture was cooled and freeze-dried. A sample (15 mL) was removed from the reaction mixture and was freeze-dried in order to be used for the FT-IR analysis. The resin prepared was cured in an air-circulating oven at

100 °C for an hour to obtain the completely cross linked resin and FT-IR spectrum of the resin was recorded.

Preparation of tannin formaldehyde resin

A sample of pine type tannin powder (12.50 g) was dissolved in 50 mL of distilled water. Methanol (10 mL) and 1.0 g of pumice stone were added to the tannin solution. The pH of the mixture was kept at 10 using a solution of NaOH (33 % w/v). To this mixture, a 65 mL volume of formaldehyde solutions (38 % w/w) was added drop-wise while maintaining the temperature at 40 °C. The temperature of the mixture was increased to 80 °C. The mixture was kept at 80 °C for an hour. Then, the mixture was neutralized using a solution of dilute HCl (0.01 mol/dm³). The resultant mass was cooled and allowed to harden. The lump of material obtained was mechanically broken into pieces. The resin particles obtained were thoroughly washed with distilled water to remove unreacted substances and cured in an oven at 100 °C to impart further cross linking for an hour. Finally, the resin was stored for FT-IR analysis.

Preparation of metal adsorbed resin

A mixture of 10 g of pine type tannin, 25 mL of formaldehyde solution (38 % w/w) and 25 mL of Zinc acetate solution (0.01 mol/dm³) were mixed in a reagent bottle. The pH value of the reaction mixture was adjusted to 4.7 using a solution of dilute HCl (0.01 mol/dm³). The mixture was then immersed in a boiling water bath while gently stirring with a glass rod until gelation occurred. The product obtained was cooled and allowed to harden. Finally, FT-IR spectrum was recorded.

FT-IR Spectroscopy

FT-IR spectra of the resins prepared were recorded using a FT-IR instrument (Thermo Nicolet, USA). Potassium bromide disks were prepared mixing 1 mg of dried and ground samples of resins with 200 mg of KBr (spectrometry grade) at 10,000 kg cm⁻² pressure. The spectra were recorded by carrying out 100 scans at 4 cm⁻¹ resolution.

COMPUTATIONAL CALCULATION

Two series of polymer structures were constructed

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to depict the structures of polymers formed by gallic acid and formaldehyde using the software HyperChem version 6^[16]. First, a polymer chain linked with a CH_2 link through C2 and C6 positions of two adjacent gallic acid molecules was constructed as shown in Figure 4. Then, the chain length of the resulting polymer was increased one by one to incorporate up to eight gallic acid molecules linking them through C2 and C6 positions of two adjacent gallic acid molecules. Secondly, another series of structures were constructed replacing the CH_2 link with a CH_2OCH_2 link between C2 and C6 positions of two adjacent gallic acid molecules (Figure 5).

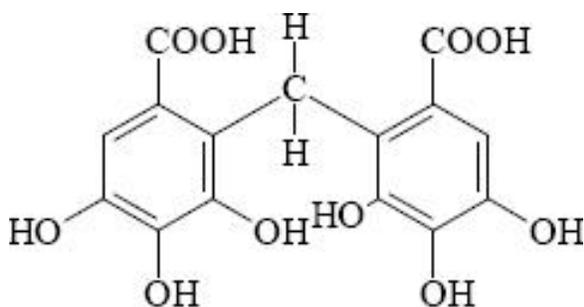


Figure 4 : Gallic acid formaldehyde molecule with single CH_2 link

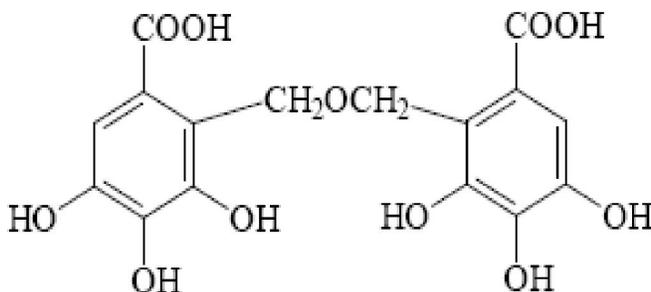


Figure 5 : Gallic acid formaldehyde molecule with single CH_2OCH_2 link

In the case of tannin, a polymer chain linked with a CH_2OCH_2 link in Head to Tail configuration through C6' and C3' positions of B-rings of two adjacent flavanoid units was constructed using the software HyperChem version 6 (Figure 6)^[16]. Then, the chain length of the resulting polymer was increased one by one to incorporate up to five tannin units linking them through C6' and C3' of B-rings of two adjacent flavanoid units. Similarly, a structure where a Zinc ion complexed with two hydroxyl groups attached to the B-ring of the flavanoid unit of pine type tannin was drawn to study the reactivity of tannin molecule influenced by bivalent cations towards formaldehyde (Figure 7).

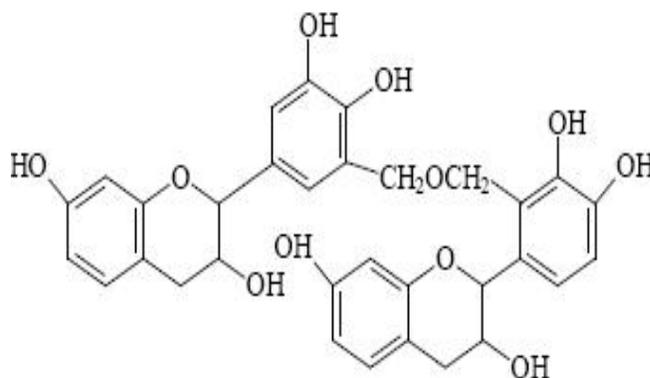


Figure 6 : Tannin formaldehyde molecule with single CH_2OCH_2 link

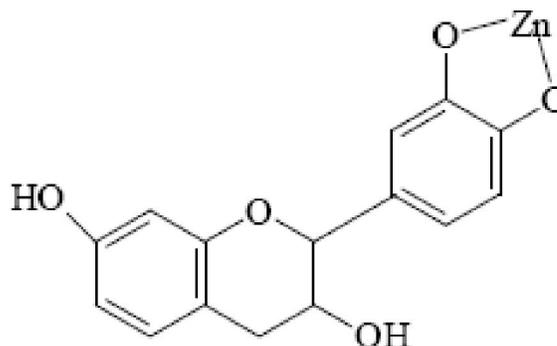


Figure 7 : A Zinc ion complexed with a flavanoid unit

Semi-empirical optimization was performed on two series of structures using version 6 of HyperChem software. The conjugate gradient method was used in the semi-empirical optimization. The optimization calculation was performed with a Root-Mean-Square (RMS) gradient of 0.1 kcal/ (\AA mol). The full geometry optimizations were carried out by minimization of the molecular energies.

The optimized structures with C1 symmetry obtained from HyperChem were used as the starting structures for calculations at the Restricted Hartree Fock/Parameterized Model number 3 (RHF/PM3) level of theory using GAMESS software^[17]. The data files that contain PM3 basis set and Huckel electronic states obtained were used to calculate Mulliken charges in atomic unit (au) using GAMESS software.

Calculations of the Mulliken charges at reactive carbon centers of catecholic B-rings of the pine type tannin in the tail of the phenolic compounds were carried out for the reaction of pine type tannin molecules with formaldehyde. Similarly, Mulliken charges were calculated for two gallic acid based series. In addition, the Mulliken charges for reactive sites of flavanoid mol-

ecule which has a catecholic B-ring complexed with a Zinc ion were calculated.

RESULTS AND DISCUSSION

Initial semi-empirical calculation conducted on the gallic acid at RHF/PM3 level of the theory provided the Mulliken charges for each atomic nucleus. The Mulliken charges obtained for carbon atoms attached to the aromatic ring of the gallic acid molecule are given in the TABLE 1. According to the results, the highest (-0.1130) and the second highest negative charges (-0.1019) are located at C2 and C6 positions of aromatic ring of gallic acid, respectively. Hence, the reaction of gallic acid with formaldehyde occurs via C2 and C6 positions.

TABLE 1 : Mulliken charges distribution obtained by PM3 method in gallic acid

Atom	Mulliken charges (au)
C1	-0.0736
C2	-0.1019
C3	0.0262
C4	-0.0560
C5	0.0900
C6	-0.1130

The Mulliken charges obtained from the semi-empirical RHF/PM3 calculation at the reactive carbon center of the tail of gallic acid formaldehyde molecules linked with CH_2OCH_2 and CH_2 linkages plotted against the number of cross links are depicted in the Figure 8. The Mulliken charges of the reactive center of CH_2OCH_2 linked molecules are much more negative compared to charges of those linked with CH_2 . Further, it can be observed that a steady increase of charges with the increase of the number of CH_2 -linkages. Further, the curve that depict Mulliken charges of the reactive center of CH_2OCH_2 linked molecules goes through a maximum between two to three CH_2 cross links. This could be due to the fact that the approaching formaldehyde molecule faces highest steric hindrance in this range. Although, one could also observe very little increase in Mulliken charges for polymer containing CH_2OCH_2 cross links in this range, before decreasing to very low values towards the end, the values recorded are very low compared to those of CH_2 cross links.

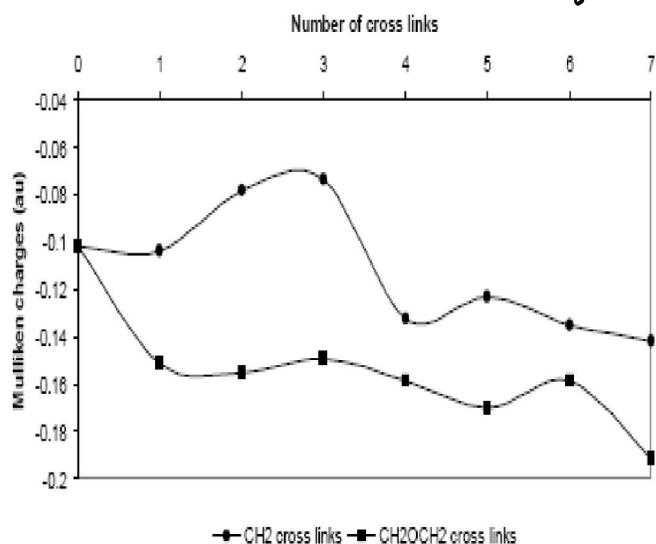


Figure 8 : Variation of Mulliken charges of the reactive carbon at the tail of the gallic acid molecules linked with CH_2 and CH_2OCH_2 in the gallic acid formaldehyde polymer

Hence, the formation of CH_2OCH_2 linkages favors to the formation of CH_2 linkages in the reaction of gallic acid with formaldehyde. This indicates that the cross linking reaction initially proceeds through CH_2OCH_2 linkage to form the gallic acid formaldehyde resin. Further, the presence of peak around $1200\text{-}1210\text{ cm}^{-1}$ that can be attributed to C-O stretching of CH_2OCH_2 group^[18] in the FT-IR spectrum of gallic acid formaldehyde resin produced initially, which disappeared completely in the spectrum obtained after curing at 100°C , confirms the formation of CH_2OCH_2 links at low tem-

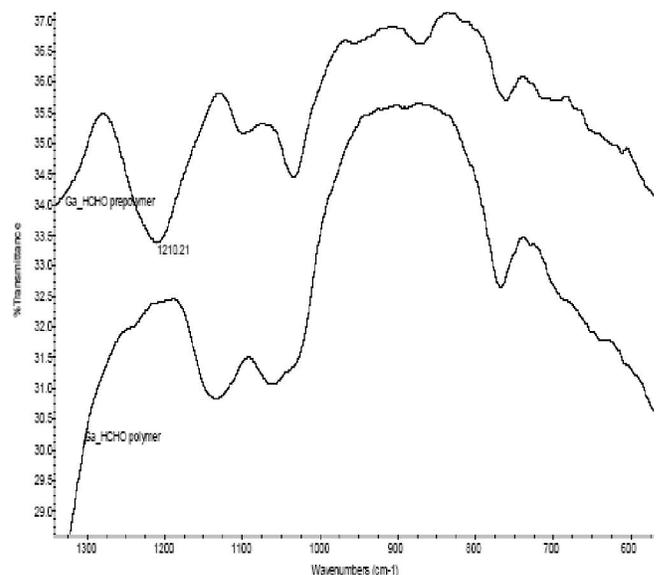


Figure 9 : FT-IR spectra of gallic acid polymer before curing (Ga_HCHO_prepolymer) and gallic acid polymer after curing at 100°C (Ga_HCHO polymer)

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peratures (Figure 9). These evidence support the second mechanism out of two mechanisms proposed by^{13, 10]} for the formation of gallic acid formaldehyde resin.

The FT-IR spectra obtained for the pine type tannin and the tannin formaldehyde resin produced are depicted in the Figure 10. The characteristic peak present in the range of 1085-1150 cm^{-1} which can be attributed to CH_2OCH_2 links could be seen in the spectrum of the tannin formaldehyde resin. This confirms the formation of CH_2OCH_2 links to join two pine type tannin molecules, initially. Hence, it is reasonable to assume that the tannin formaldehyde reaction occurs via the formation of CH_2OCH_2 links as in the case of gallic acid formaldehyde resin, initially (i.e. in the pre-polymer).

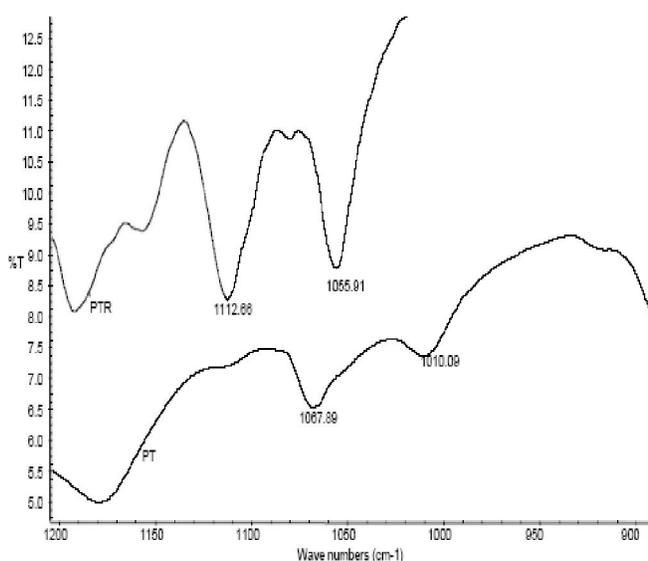


Figure 10 : FT-IR spectra of pine type tannin (PT) and pine type tannin formaldehyde resin (PTR)

TABLE 2 : Calculated Mulliken charges at RHF/PM3 level for the pine type tannin formaldehyde molecules with varying number of CH_2OCH_2 cross links

Number of CH_2OCH_2 cross links	Charges at each reactive center/au		
	C2'	C3'	C6'
0 (monomer)	-0.0752	-0.1559	-0.0926
1	-0.0964	-0.1934	-
2	-0.0977	-0.1983	-
3	-0.0987	-0.1801	-
4	-0.1014	-0.1465	-

Hence, the semi-empirical calculations were performed on the structures drawn to delineate the polymer that contains tannin type molecules joined by CH_2OCH_2 links. The results of the semi-empirical cal-

culations carried out at RHF/PM3 level on the flavanoid unit of pine type tannin compounds are given in the TABLE 2.

According to the charges given in the TABLE 2, initially, large negative charges are located at the C6' (-0.0926), C2' (-0.0752), and C3' (-0.1559) positions of aromatic ring of the pine type tannin (Figure 2). Consequently, one could expect that the positively charged carbon of formaldehyde may react at these three sites. However, the site C2' is more sterically hindered than sites C6' and C3' for formaldehyde molecule due to the heterocyclic group and the OH groups attached to heterocyclic ring. This is reflected by the relatively less negative charge at C2'. Hence, the formaldehyde molecule could react with the B-ring of the pine type tannin compound only at C6' and C3'. Having a CH_2OCH_2 link between C6' and C3' of two tannin molecules, in the molecules with more than one CH_2OCH_2 link, only sites which will be free to react with a formaldehyde molecule are C2' and C3'. Hence, charges were calculated for C2' and C3' (see TABLE 2). It can be observed that C3' remains as the favorable site throughout the reaction compared to C2'. This shows that the formation of tannin-formaldehyde-tannin linkage occurs between C6' and C3' active centers of the B-ring of the pine type tannin molecule.

As the final part of this study, the effect of incorporation of Zn^{2+} ions to tannin molecule was studied using the semi-empirical method. The Zn^{2+} ion was used as a model compound as many other metal ions have been reported to act as accelerators for the reaction of phenolic compounds with formaldehyde^[19]. It was assumed that Zn^{2+} ion makes a coordination complex via two hydroxyl groups attached to the B-ring of the pine type tannin. As in the case of earlier calculation, Mulliken charges were calculated at C6', C2' and C3' positions of the pine type tannin molecule.

The results obtained from the semi-empirical study given in the TABLE 3 show that the calculated atomic

TABLE 3 : Distribution of charges in a pine type flavanoid unit with Zn^{2+} ion as a ligand

Reactive center	Mulliken charges (au)
C2'	0.0789
C3'	-0.1627
C6'	-0.1508

charges at reactive sites of aromatic B-ring coordinated with Zn^{2+} ions have changed. While the negativity of the charge at C2' has decreased from -0.0752 to 0.0789, negativity of charges at C3' and C6' have increased to -0.1627 and -0.1508, respectively. Hence, reactive sites C3' and C6' have become more favorable sites for the reaction with formaldehyde molecule. Many heavy metal catalysts are known to depend on the ability of the metal ion to exist in more than one oxidation state. In such cases the metal may act as an electron carrier and may act catalytically in a manner which is fundamentally different from the catalytic activity of hydrogen ions. The action of the Zn^{2+} ion as an electron carrier might have increased the negativity of sites C3' and C6' of the tannin molecule^[19].

The peak that represents methylol group (C-O) at the region of 1150–1012 cm^{-1} in the spectrum of pine type tannin formaldehyde resin (PTR) found to be broadened by the adsorption of Zn^{2+} ion to the resin (Figure 11)^[18].

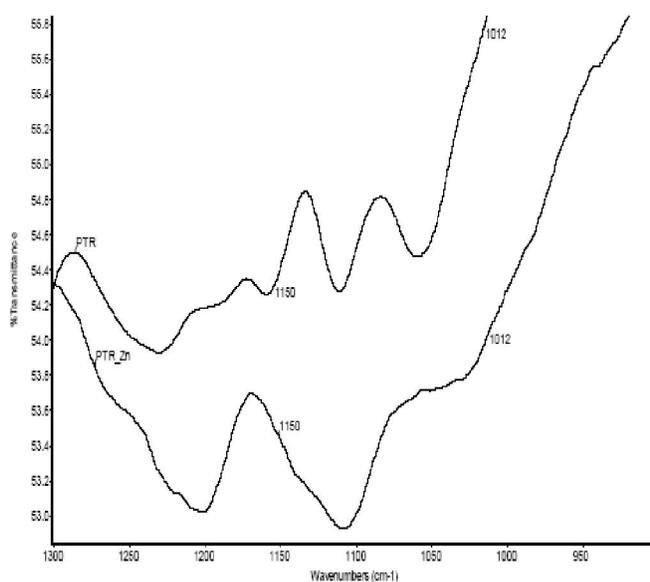


Figure 11 : FT-IR spectra of pine type tannin formaldehyde resin (PTR) and Zinc adsorbed pine type tannin formaldehyde resin (PTR_Zn)

These changes support findings of the semi-empirical calculation, which indicate the increase of charges at reactive centers (see TABLE 3) where the formation of methylol groups would occur. These findings confirm that the increase of activity of active sites of B-ring of the flavanoid unit in the reaction with formaldehyde when induced by bivalent metal ions^[20, 21].

CONCLUSIONS

The semi-empirical calculation and FT-IR results show that the formation of gallic formaldehyde polymer proceeds through CH_2OCH_2 linkages at low temperatures. Further, it was found that the C3-C6 link is formed between the B-ring of the two flavanoid units and the link formed is a CH_2OCH_2 type link. The negative charges at reactive sites C3' and C6' of catecholic B-ring complexed with Zn^{2+} ions have increased, showing an increased affinity of the reactive sites towards formaldehyde type molecules. The results of this study indicate that semi-empirical calculations can be used to explain the reaction mechanism between the polyphenolic compounds and formaldehyde.

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