forming linear chains (xxviii).
With the 8- and 6-positions providing the nucleophilic function in the phloroglucinolic and resorcinolic flavonoids respectively, self-condensation continues as the 4-carbonium ion electrophile is generated from the flavan-3,4-diols. This mechanism results in oligomeric units with greater than 10 linked flavonoids resulting in high molecular weight tannins. Wattle tannins have a number average mass of 1250 compared with 1784 for quebracho and in the case of pine a number average mass of 4300 has been established.[5]

1.4 The Reactivity of Macromolecular Tannins

In addition to the reactions expected of flavan-3-ol units, condensed tannins exhibit unique reactions due to their macromolecular structure. These reactions affect their industrial application in adhesives.

1.4.1 Positional Selectivity of Electrophilic Substituents on Flavonoids

Selective bromination was used to examine the relative accessibility and reactivity of the flavonoid units.
(+)-Tetra-o-methyl catechin (xxiv), representing a phloroglucinol-type flavonoid, was reacted with pyridine hydrobromide perbromide[10]. Bromination occurred preferentially at the 8-position and only commenced at the 6-position once the former was filled. The B-ring was found to be very unreactive, although in the presence of excess brominating agent a low degree of substitution was noted at the 6' position[11]. Thus for phloroglucinol based tannins the positions of

reactivity are 8>6>>6'.
Using(-)-tri-o-methylfustin as a model for resorcinol, the substitution sequence for the A-ring was found to be 6>8>>6' (xxv).
The preferential 8- and 6-substitution in phloroglucinol- and resorcinol-type flavonoids, respectively, appears to be related to the greater accessibility of these positions in each instance.

1.4.2 A- and B-Ring Reactions with Aldehydes

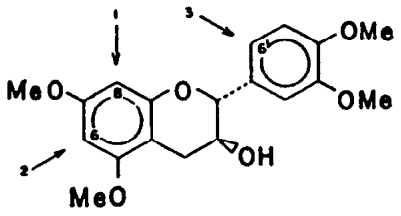
Being phenolic in nature, tannins are able to undergo the same well-known base- or acid-catalysed reactions of phenols with formaldehyde. The nucleophilic centres on the A-rings of the flavonoid units tend to be more reactive than those on the B-rings, since in addition to the hydroxyl substituent activation of the ring, the A-ring has localised effects causing further activation.

Formaldehyde reacts with tannins producing polymerisation through methylene linkages to reactive positions of the flavonoid units, mainly on the A-ring (tannin-CH_2-tannin). In condensed tannins, the A-rings of the oligomeric flavonoid units retain only one reactive nucleophilic centre with the remaining active centres being involved in interflavonoid bond formation. The B-rings only participate in the reaction with formaldehyde at high pH values where the reactivity of the A-rings toward formaldehyde is so high that any tannin-formaldehyde adhesives prepared have unacceptably short pot-lives. Thus, only the A-rings are used to cross-link the network.[5]

Owing to their great size and bulky shape, tannin molecules become immobile at low levels of condensation with formaldehyde. This ensures that the available reactive sites become too far apart for further methylene bridge formation, resulting in incomplete polymerisation which in turn leads to weakness and brittleness, characteristic of many tannin-formaldehyde adhesives.
To solve this problem, bridging agents with longer molecules, such as phenolic and aminoplastic resins, have been used to bridge the distances too large for methylene bridges.

Regarding pH dependence of the tannin-formaldehyde reaction, it is generally accepted that the reaction rate of pine tannins with formaldehyde is at its minimum in the pH range 3.3 to 3.9, compared with 4.0 to 4.5 for wattle tannins. The variation is due to the variation in the structures of the two types of tannin (figure 1.1).

Formaldehyde is generally the aldehyde used in the preparation, setting and curing of tannin adhesives, despite the problem of incomplete cross-linking. The formaldehyde is normally added to the tannin extract solution at the desired pH, both as liquid formalin solution and in its polymeric form of paraformaldehyde. The latter is capable of fairly rapid depolymerisation in the aqueous conditions normally employed in adhesive preparation.



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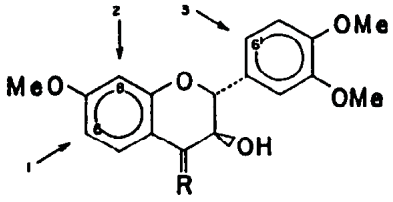

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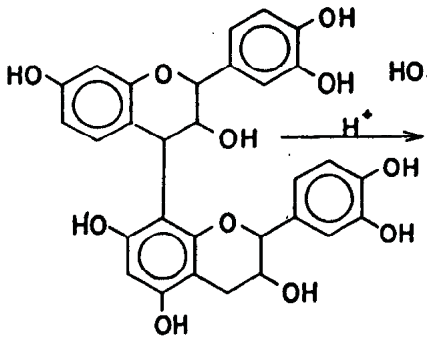

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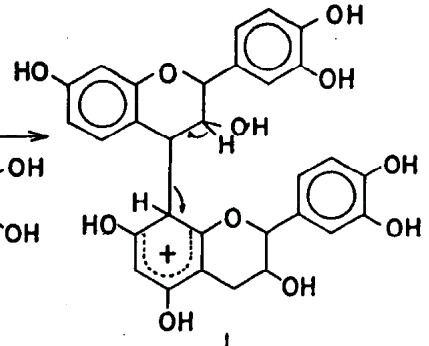
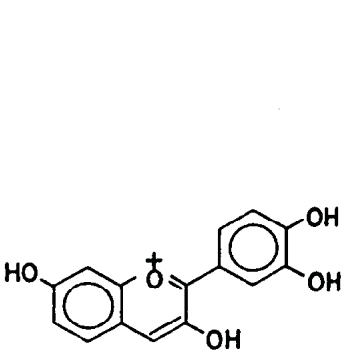
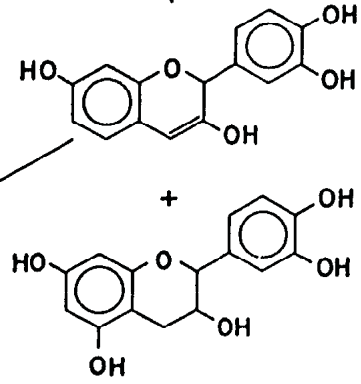
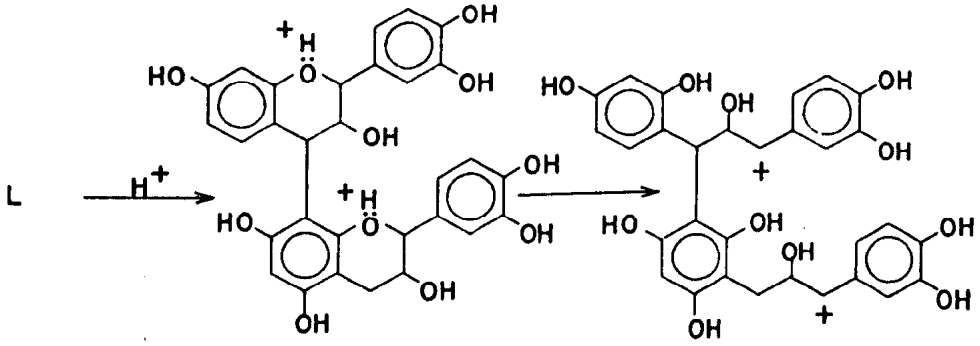






(+) - Catechin



Substitution on poliflavonoids (tannins)

Phlobaphenes

1.4.3 Hydrolysis and Autocondensation

Tannins are subjected to two competing reactions when heated in the presence of strong, mineral acids. Degradation occurs in the one where fission of the interflavonoid bond leads to anthocyanidin and catechin formation.[8] (cf figure 1.2). Whilst this reaction should cause a decrease in the overall molecular weight, it has been noted that a secondary reaction occurs where the anthocyanidins formed can condense forming angular triflavonoids and higher oligomers.[12] These can precipitate as the condensation increases, forming a red insoluble mass of higher than expected molecular weight.[13]
The second reaction is condensative, occurring as a result of hydrolysis of the heterocyclic rings.
The resultant p-hydroxybenzylcarbonium ions condense randomly with the nucleophilic centres on other tannin units forming high molecular weight, insoluble "phlobaphenes" or "tanner's reds" (cf figure 1.2).[14]

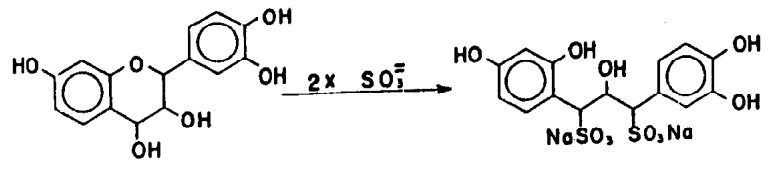
Some phlobaphenes are formed naturally and are complex mixtures of high molecular weight condensed tannins which have, in some instances, been found associated with carbohydrates and which contain higher proportions of methoxyl groups.[15]
There is speculation as to the differences between the phlobaphenes formed naturally, which could include extraneous matter and which are therefore variable, and those formed by acid treatment.[15]

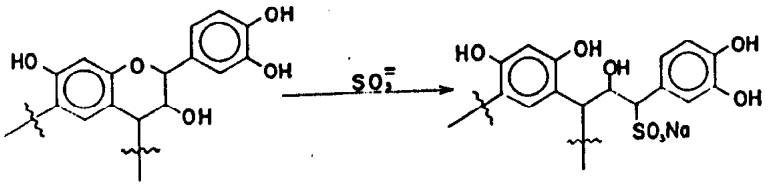
Under alcoholic conditions (80 - 100% ethanol) hydrolysis and anthocyanidin formation predominate.

Conversely, under aqueous conditions, the phlobaphene formation reaction is preferred.[8]
In strongly alkaline conditions, partial autocondensation takes place. Practically, this has been observed by the considerable viscosity increases at high pHs.[8]

1.4.4 Sulphitation

One of the oldest and most useful reactions in flavonoid chemistry is the sulphitation of tannins. Sulphitation affects both the physical and chemical properties of the tannins and is as such, very useful in the preparation of tannin based adhesives.[8]
Sulphitation generally causes an increased solubility of the tannin extract and serves to decrease the viscosity of the resultant solution.[14]
The mechanism whereby this is achieved is thought to be due to at least one of two effects.
One possible mechanism is a ring opening of the heterocyclic ring at position 2. The resultant molecule would contain sulphonic acid functionalities which enhance the hydrophilicity of the molecules.[8]





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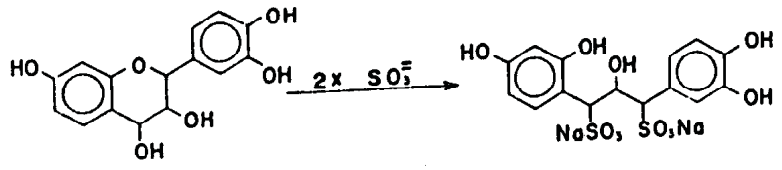

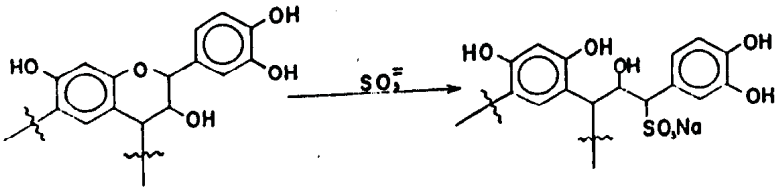

A second mechanism is the cleavage of the interflavonoid linkage forming procyanidin-4-sulphonates.[16]

The former mechanism explains the increased solubility by the elimination of the heterocyclic, hydrophobic ether group and the introduction of the hydrophilic sulphonic and hydroxyl groups. A corresponding decrease in the rigidity and steric hindrance of the tannin molecule and a decrease in the intermolecular hydrogen bonding obtained by opening the ring can explain the decreased viscosity.[5]
The latter mechanism explains the increased solubility by the presence of the sulphonic groups which improve the hydrophilicity of the molecule. The decrease in the molecular weight due to interflavonoid bond cleavage explains the decrease in viscosity.[16]

The advantages of sulphitation in adhesive applications are the improved concentration of tannin phenolics, due to the enhanced solubility and decreased viscosity, and the higher moisture retention by the tannin resins at the glueline.[18] In addition, sulphited tannins are more reactive to formaldehyde, due to the enhancement of their nucleophilicity by the opening of the ring, and they are more readily available for the reaction with formaldehyde because of the increased mobility of the tannin molecule as a whole.[5] These factors improve the cross-linking of the resin and thus improve its strength.
Disadvantages are, however, also present. Sulphonate groups enhance the sensitivity of the resin to moisture which can cause deterioration of the resin if

cross-linking is inadequate or if exposure to the moisture is excessive and no fortifier is present.[18]

1.5 Tannin Adhesives

The purity of vegetable tannin extracts varies considerably. Pine bark yields an extract containing only 50 to 60% active phenolic ingredients compared with 70 to 80% for commercial wattle extracts.[17]
The nontannin fraction consists mainly of sugars and high molecular weight hydrocolloid gums which cannot participate in resin formation with formaldehyde. They do, however, affect the quality of the resin. Sugars have been found to reduce the strength and water resistance of the resin in proportion to the amount present (figure 1.3). The hydrocolloid gums have a more marked effect on the original strength and water resistance of the resin (figure 1.4). The effect on the tannin based adhesive will then be such that unfortified pine tannin/formaldehyde adhesives will effect only 50 to 60% of the performance of synthetic adhesives while unfortified wattle adhesives will achieve 70 to 80%.[5]
The demands on the glueline in many glued wood products are so high that the use of unmodified tannin adhesives are unsuitable. Two possibilities exist:

refining the extracts
fortification of the extracts

Refining the extracts has been unsuccessful for two main reasons. The intimate association between the various constituents of the extract makes industrial fractionation difficult to execute and this in turn

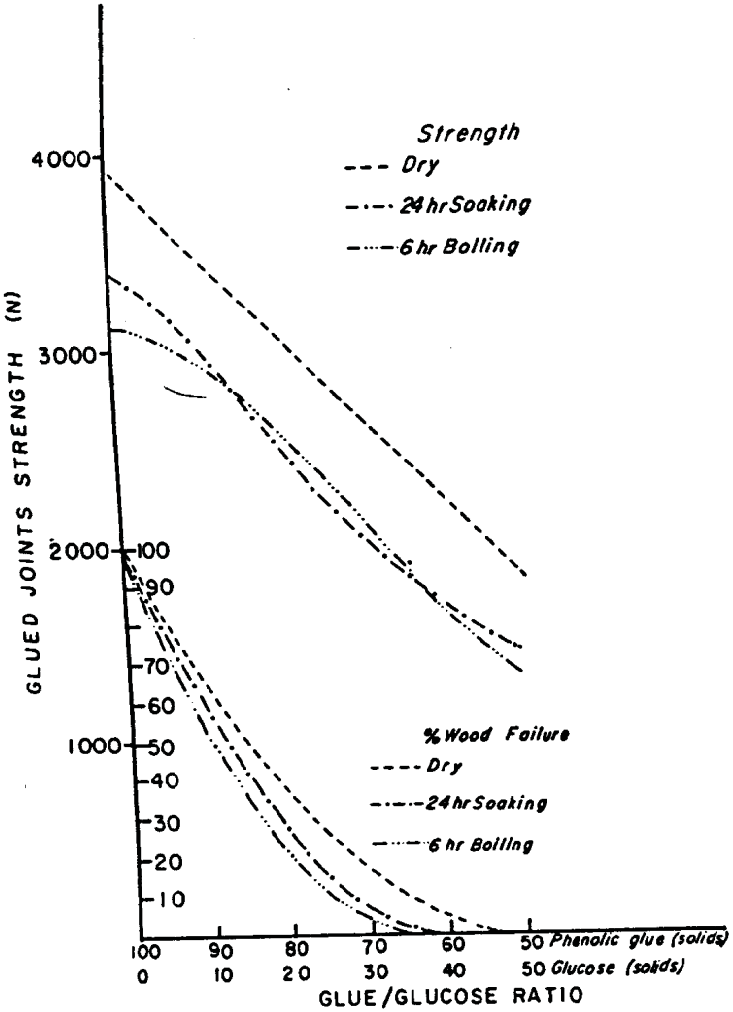

Fig. 1.3 Influence of glucose on glued-joint quality. [From A. Pizzi, *J. Macromol. Sci., Rev. Macromol. Chem.* C 2(18):247–315 (1980).]

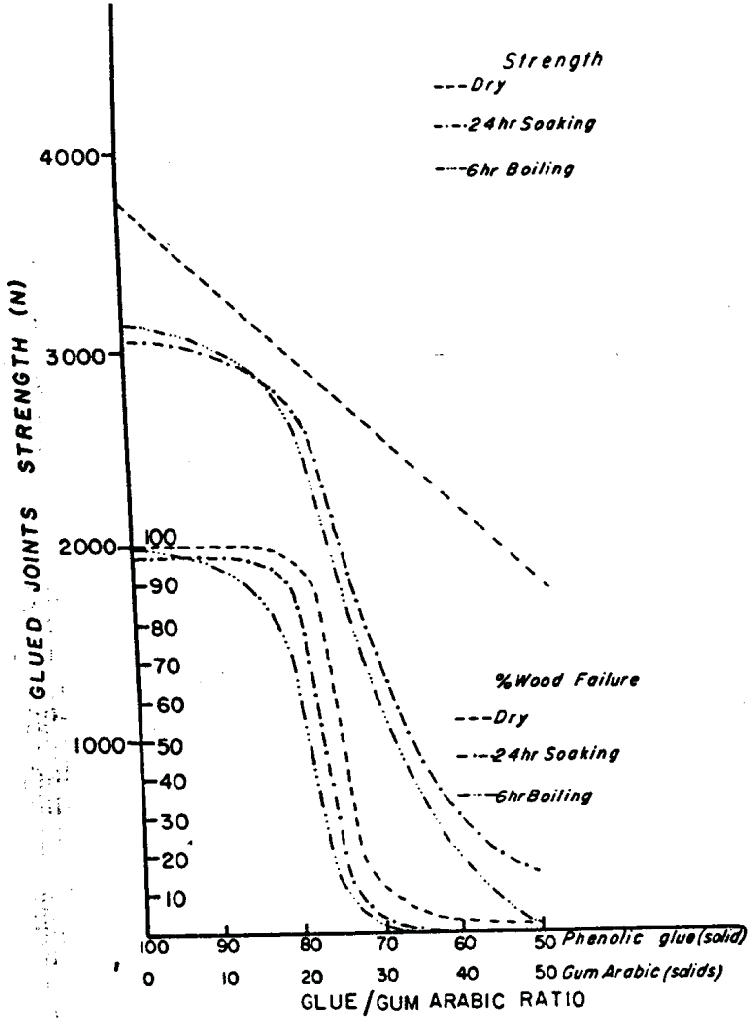

Fig. 1.4 Influence of gum arabic on glued-joint quality. [From A. Pizzi, *J. Macromol. Sci., Rev. Macromol. Chem.* C 2(18):247–315 (1980).]

makes the process economically nonviable[5].
The most practical approach to reducing the effects of the impurities is by fortifying the resin. Fortification generally consists of copolymerising the tannin with phenolic or aminoplastic resins.[19] This process can be effected during the manufacture of the adhesive, during the glue-mix assembly or during adhesive use.
The most successful wattle tannin based adhesives contain sufficient synthetic resins to reduce the nontannin fraction to below 20%.
The fortification of pine tannin adhesives has another advantage in that it not only reduces the effect of the nontannins but it also provides the tannins with longer and more mobile cross-linking agents.[5]
Synthetic resins used in fortification include phenol/formaldehyde and urea/formaldehyde resoles and phenol/formaldehyde/resorcinol terminated resins.[5]

Since tannin molecules are very large, the rate of molecular size increase in relation to the rate of linkage is high, causing tannin based adhesives to have fairly short pot-lives. Phloroglucinolic (pine) tannins have both a higher average molecular weight and higher reactivity than resorcinolic (wattle) tannins. This can be demonstrated by their relative gel times at their pH of minimum reactivity : 960 seconds for wattle extract and 65 seconds for pine extract (figure 1.1).
Since reducing the molecular size is not easily achieved, the pot-life can be increased by lowering the initial viscosity by dilution, retarding the reaction. This can be achieved by:

1) Addition of alcohols to the glue-mix to form hemiacetals with the formaldehyde, retarding the tannin-formaldehyde reaction and lengthening the pot-life.
2) Adjusting the pH of the adhesive.
3) Addition of additives other than alcohols to retard the tannin-formaldehyde reaction such as sodium sulphite which reacts with the tannin decreasing the viscosity (see 1.4.4) as well as with the formaldehyde.

The viscosity of the tannin solutions is strongly dependent on the concentration and increases rapidly above a concentration of 50%. Thus, tannin extracts are more viscous at the concentrations normally required in adhesives.

1.6 Comparison of Pine and Wattle Tannins

Although the distribution of conifers is greater than that of acacia mearnsii (mimosa wattle), the commercialisation of tannin extraction from conifers is not wide-spread due to several difficulties. In contrast, wood adhesives based on mimosa tannins have been commercial for many years in South Africa, Zimbabwe and Australia[5].

The reasons for the lack of commercialisation of pine tannins are many.
During the extraction of pine tannins from the bark, a low extraction yield is obtained. At parity of tannin content in the extract, the percentage of extract obtainable from pine bark, under industrial conditions,

is 15% (on dry bark mass)[20] compared with a value greater than 30% for mimosa extract. Higher extraction yields have been obtained in laboratory extractions but these have also extracted higher proportions of other polymeric components such as carbohydrates, decreasing the percentage tannin in the extract itself. The low yield of tannin extracted industrially, requires that more bark be extracted for the desired quantity of tannin, resulting in increased production costs and decreasing the viability of the process.

A second difficulty experienced, is the formation of high molecular weight insoluble phlobaphene precipitates, or tanners' reds. These are formed during the extraction of the tannins from the bark via an autocondensation process. The precipitation of a proportion of the extract results in a further decrease in the available tannin and introduces another cost-increasing factor, since the phlobaphenes must be disposed of.[20]

Extracted pine tannins have a higher viscosity than the equivalent mimosa extracts, a result of the higher average molecular weight of the pine tannins compared with wattle tannins. This results in difficulties in obtaining solutions of the desired concentration, since a requirement for acceptable results in several adhesives' applications is for solutions of low viscosity and high resin content.[5]

The reactivity of pine tannins toward formaldehyde is considerably greater than that experienced by mimosa or quebracho tannins. The increased reactivity is attributable to the more reactive phloroglucinolic A-ring in the structural monomer of the pine tannin. The high reactivity towards formaldehyde, is

problematic with respect to the pot-life and curing time of any pine tannin based resin.

Whilst these disadvantages enhance the usefulness and acceptability of wattle adhesives, the latter have a major disadvantage in their limited distribution worldwide. This prevents their being commercially produced in many countries and reduces their viability. Since conifers are easily grown in almost any climate, the potential for their commercial production for use in adhesives and other phenolic-type compounds is very great, if the problems highlighted above can be overcome.

The potential advantages for the use of pine tannins in wood adhesives has resulted in a numerous studies and research into their use in as wood adhesives.[21] However, a lack of adequate adhesive formulations has yet to be surmounted.

From this, it can be clearly seen that if the extraction yield of pine tannins from the bark could be increased, without using expensive and hazardous reagents, the potential profit obtainable industrially would be great. In particular, it would increase the viability of commercialisation of the extraction of pine tannins for use in wood adhesive and other resin formulations.
In addition, if the formation of phlobaphenes during the extraction could be eliminated or, at least minimised, this too would increase the viability and profitability of the extraction process.

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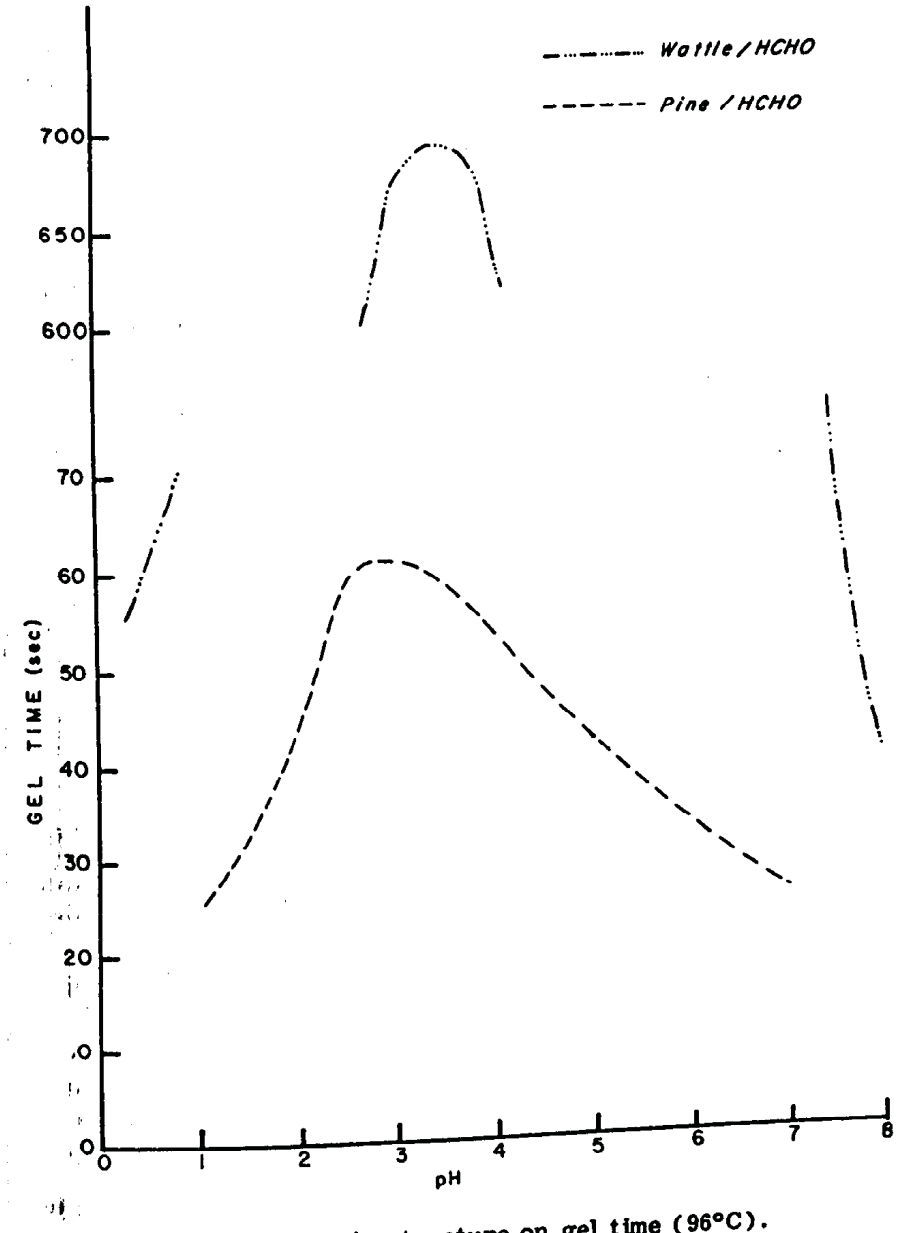
If a reduction in phlobaphenes could not be achieved, a method for their solubilisation would prevent them being a wasted product, but would, in turn, result in their providing an economical contribution.
Finally, research into successful formulations for the use of pine tannins in wood adhesives would result in possible profitable commercialisation of pine tannins and their use in wood adhesive formulations.



Effect of tannin structure on gel time (96°C).

CHAPTER 2 DISCUSSION - PART

INCREASING THE TANNIN EXTRACTION YIELD

A major limitation in the usage of pine tannins is the relatively low extraction yield obtained during the extraction process. In industry, an average yield of 15% pine tannin by mass of pine bark is obtained[20]. This can be compared with approximately 30-33% wattle tannin obtained during the extraction of the wattle bark[22]. There is evidence[23] which suggests that a large proportion of the pine tannins remain in the bark, even after extraction. This so, since when extracted with an organic solvent, such as ethanol, the extraction process has been shown to effectively extract much higher quantities of pine tannin.[7] Since pine tannin phlobaphenes dissolve in ethanol, the indication is that during the heated aqueous extraction of the bark, phlobaphenes form within the bark and are not extracted.

In addition, air oxidation of the tannins during growth of the tree and after the bark has been stripped from the trunk, occurs. Both of these phenomena allow polymerisation of the pine tannins to occur, resulting in linear growth of the molecules, an

increased degree of polymerisation and the formation of higher molecular weight fractions within the bark. Thus to increase the extraction yield, two methods of approach can be used:

i) linear auto-polymerisation of the pine tannin during extraction could be minimised
ii) a solvent could be sought to extract all of the oxidised and cross-linked products.

The use of solvents other than water on an industrial scale can be problematic especially in the areas of pollution, recycling and cost. For these reasons, the second approach in increasing the extraction yield was not investigated.

2.1 Model Compound Studies

Model compounds were used, primarily, to establish whether a decrease in the polymerisation of the tannin molecules could be effected. Early studies[24] indicated that catechin was able to self-condense forming a polymer. Since catechin resembles the monomeric unit of pine tannins, an investigation into the self-condensation of catechin could be used to model that of the tannins. Catechin has also been observed to form condensation products with phloroglucinol[25,26]. Since the catechin could react with the phloroglucinol, it was believed that any self-condensation would decrease in proportion with the reaction with the phloroglucinol. Once this had been established, other inhibitors to the self-condensation process were sought, which could be tested on the pine tannins themselves, to effectively

decrease the self-condensation of the tannin molecules, thereby increasing the yield.

2.1.1 Catechin Self-Condensation

Catechin, in the presence of dilute acid, was seen to react with itself, at 25°C according to thin-layer chromatography (tlc) (cf 5.3.2, 5.3.1)
The presence of two spots after developing the plate (table 2.1.1) indicated a reaction had occurred. Since the catechin had an Rf of 0.91, the self condensation product could be identified at Rf 0.56.
The reaction was followed over time (table 2.1.1) and the formation of this product was found to occur almost instantly.
The effect of temperature variation on the self-condensation of catechin was also examined. Increasing the temperature from 25°C to 35°C and 70°C respectively (cf 5.3.2), appeared to have no marked effect on the condensation products, with the condensation again being rapid. (Table 2.1.2).
The isolation of the condensation product proved difficult since both the pure catechin and the self-condensation product extracted into ethyl-acetate. However, the catechin appeared to extract first into the ethyl-acetate, leaving the condensation product in the aqueous fraction. During these extractions, tlc was used to ensure an effective separation had been achieved.
After extraction of the catechin, evaporation of the aqueous layer demonstrated that only approximately 1% by mass of the catechin had self-condensed. However, while the aqueous layer, which according to tlc had

had all of the catechin extracted, was allowed to stand before evaporation, catechin was again noted using tlc. This seemed to indicate the presence of an equilibrium process in the formation of the self-condensation product and resulted in difficulties in obtaining pure condensation product for analysis being encountered.

2.1.2 The Effect of Phloroglucinol and m-Phenylenediamine on the Catechin Self-Condensation

Phloroglucinol and m-phenylenediamine were separately added to dilute acid solutions, containing dissolved catechin (cf 5.3.3 and 5.3.4 respectively) and the effects of these additives on the catechin self-condensation were noted. On analysis of the respective tlc plates, various products could be located. The catechin and phloroglucinol or m-phenylenediamine and the catechin self-condensation product were fairly easily identified (cf 5.3.1) and in all instances at least one product could be identified which could be attributed to a mixed condensation product.

a) Temperature effects

As the temperature was increased from 25°C to 35°C and 70°C, variations in the product distribution and the number of products was noted.

i) Phloroglucinol

In the case of phloroglucinol, (cf 5.3.3, table 2.1.3), as the temperature increased, so the

number of reaction products observed increased. From the tlc analyses, the catechin self-condensation product, present in the solution at 25°C, decreased until it disappeared at the higher temperatures as the phloroglucinol condensed with the catechin. Possible structures for this reaction were advanced by Mayer, et al[35] (figure 2.1)

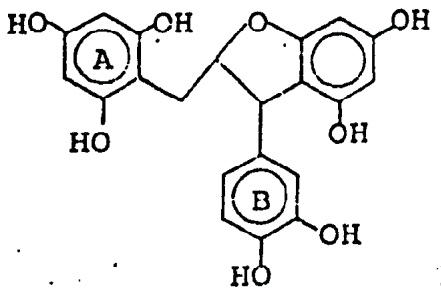


Figure 2.1

ii) m-Phenylenediamine

A similar effect was noted when m-phenylenediamine was added to the catechin solution. (cf 5.3.4, table 2.1.4).
Here, however, the tlc was further complicated by the presence of impurities in the m-phenylenediamine. At 25°C, a possible condensation product from the catechin reacting with the m-phenylenediamine was noted in addition to the catechin self-condensation product (table 2.1.4). As the temperature was increased so the catechin self-condensation product seemed to decrease (by about 50% on spot size). As the self-condensed product's spot disappeared, a new spot at a different Rf

value (table 2.1.4) appeared and was attributed to a second type of catechin-m-phenylenediamine reaction product. This product may have been due to the reaction between two different m-phenylenediamine molecules with the catechin or due to a different product configuration to that giving rise to the first spot. (figure 2.2)

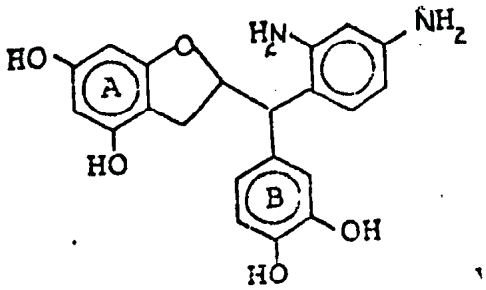


Figure 2.2

Thus, It appeared that an increase in temperature and the presence of phloroglucinol or m-phenylenediamine decreased the catechin self-condensation in dilute acid solution.

b) Concentration effects

Having established that phloroglucinol and m-phenylenediamine were effective in decreasing the catechin self-condensation, when present in equimolar quantities, the effects of increasing the catechin concentration with respect to these inhibitors were examined. This so, in order to establish whether the self-condensation could be inhibited when lower quantities of the inhibiting molecules were present, since equimolar quantities of a self-condensation inhibitor would not be

viable industrially.

i) Phloroglucinol

In the presence of phloroglucinol, the catechin concentration was doubled. (cf 5.3.3, table 2.1.5) At 25°C, only the catechin self-condensation product was noted in addition to the two pure compounds (table 2.1.5). At 35°C, the catechin self-condensation product was no longer evident, whilst the same reaction product between the catechin and the phloroglucinol, as observed in the equimolar investigations, was noted (table 3.1.5, 3.1.3). At 70°C, a new product appeared which could possibly have been due to a reaction between two catechin molecules and one phloroglucinol molecule.

i.e. 2 catechin + phloroglucinol =
catechin-phloroglucinol-catechin

The formation of this particular product was postulated since twice as much catechin was present in the reaction as the phloroglucinol.

ii) m-Phenylenediamine

Despite the higher concentration of the catechin, the catechin self-condensation product was only observed in the 25°C reaction. (cf 5.3.4, table 2.1.6) In the reactions at 35°C and 70°C a complete absence of the self-condensation product was observed (table 2.1.6). In addition, a second reaction product between the catechin and the m-phenylenediamine was noted at the higher temperature. If the reaction between the catechin and the m-phenylenediamine in the

equimolar reaction had resulted in a complex formation (figure 2.2), it seemed possible that the second reaction product would contain twice as much catechin as m-phenylenediamine, owing to the solution stoichiometry. Thus a postulated form of the reaction is as follows:

2 catechin + m-phenylenediamine =
catechin-mphenylenediamine-catechin

2.1.3 The Effect of Urea and Ammonia on the Catechin Self-Condensation

Having established that the self-condensation of catechin was partially minimised in the presence of both phloroglucinol and m-phenylenediamine, cheaper yet effective alternatives were sought. Two relatively inexpensive chemicals, industrially, urea and ammonia were selected. Urea contained a highly reactive carbocationic centre, representative of the reactive centres of the phloroglucinol and the more reactive m-phenylenediamine. The reactive centre of the ammonia was an amine group. This was chosen in order to establish whether a small, reactive and labile molecule would be effective in blocking the catechin self-condensation sites, despite the lack of a carbocationic site. The same reaction conditions as examined using phloroglucinol and m-phenylenediamine, were used with urea and ammonia, to facilitate comparison.

a) Urea reactions (cf 5.3.5)
The presence of the urea caused a decrease in the catechin condensation product as expected. (Table 2.1.7)

i) Temperature effects

In the stoichiometrically equivalent reaction, the urea was unable to totally inhibit the self-condensation reaction at ambient temperature. This was noted when the self-condensation product was observed on the tlc plates (table 2.1.7). However, at elevated temperatures ($70^{o}C$), the presence of a new reaction product was noted, in addition to small amounts of the self-condensation product. Thus, it appeared that a decrease in the self-condensation of catechin in the presence of urea, was more effective at an elevated temperature.

ii) Concentration effects

At high concentrations of catechin (2:1 ratio of catechin to urea), the presence of two reaction products at high temperature was noted (table 2.1.7). One of these products was identical, both to that obtained at ambient temperature and to the reaction product obtained in the stoichiometrically equivalent solution (Rf 0.40-0.44). This product was possibly due to a 1:1 combination of the urea with catechin. The variation in the Rf values was possibly due to the presence of varying molecular weight oligomers. Since the reaction stoichiometry was 2:1 catechin to urea, it seemed possible that the second high temperature product depicted the reaction stoichiometry in its formation (Rf 0.64). Thus, a possible reaction scheme could be:

2 catechin + urea =

catechin-urea + catechin-urea-catechin

When the urea was present in higher concentrations than the catechin, (2:1 ratio of urea to catechin), two reaction products were again noted (table 2.1.7). The first was similar to that obtained at the other concentrations, thought to be a 1;1 urea-catechin reaction product. The second product, at a lower Rf value than the high temperature product, was thought not to have been due to the reaction between one catechin and two urea molecules. It was considered more possible that the spot may have been due to the observation of a higher or lower molecular weight oligomer of the 1:1 reaction product, especially as the Rf values were relatively close together (0.37, 0.44).

b) Ammonia reactions

On addition of the concentrated liquid ammonia to the catechin solution (cf 5.3.6), it was noted that the time for the reaction of the ammonia with the catechin appeared to take much longer than those discussed previously. In general, the reactions between catechin and phloroglucinol, m-phenylenediamine or urea were almost instantaneous whilst those with ammonia were slower at ambient temperature. (Table 2.1.8)

i) Temperature effects

The ammonia appeared to be less effective in reducing the catechin self-condensation at

ambient temperature than at 70°C (table 2.1.8). However, it also appeared that the higher temperature inhibited the rate of the reaction slightly. At 25°C, whilst the catechin self-condensation product was always present, after 30 minutes, a different product appeared. This spot was very small and did not reappear until 24 hours had passed. In contrast, at the higher temperature, it took longer (60 minutes) before a reaction product was observed, but this remained present and was present at almost double the concentration compared with the lower temperature.

ii) Concentration effects

On doubling the catechin concentration with respect to the ammonia, it was noted that ammonia-catechin reaction products appeared after only fifteen minutes at the higher temperature (70°C). In addition, very little self-condensation product was observed (table 2.1.8). At ambient temperature, the presence of a reaction product was erratic and appeared in conjunction with the self-condensation product.

The presence of two different Rf values for the reaction product (Rf 0.40, 0.50) could be explained by the presence of different molecular weight oligomers reacting with the ammonia. A less likely explanation was that the ammonia had become the centre of a branched molecule, due to the presence of more than one removable proton at its reactive centre.

When the ratio of the ammonia to the catechin

was increased to 2:1, no second reaction product was noted. This indicated either a lack of different catechin oligomers, or more likely, that the separation of the components of the system was incomplete.

iii) pH effects

In the reactions between catechin and urea, m-phenylenediamine or phloroglucinol, the pH of the solution remained that of the dilute hydrochloric acid. However, the addition of the ammonia caused a change in the pH.

When the ratios of the catechin and ammonia were 1:1 and 2:1, the solution pH was 2.85. This would explain the decrease in the speed of the reaction since the catalyst concentration for the activation of the catechin had been decreased. The formation of the self-condensation product would still be possible however. When the ammonia concentration was doubled with respect to the catechin concentration, the pH measured 9.27 and two observations were made.

The first was the almost complete lack of the self-condensation product at both ambient and elevated temperatures, due to the lack of proton catalyst. This indicated that, on increasing the pH, the catalyst had effectively been removed from the system and effective elimination of the self-condensation product was observed. The second was the lack of any condensates different from those formed in the stoichiometrically equivalent reaction, probably a 1;1 ammonia:catechin product.

2.1.4 Conclusions from the Model Compound Studies

From the model compound studies, it was observed that self-condensation of catechin could be decreased by adding an inhibitor. The function of the inhibitor, such as phloroglucinol or m-phenylenediamine, was to react with the catechin, effectively blocking the site through which self-condensation occurred. On increasing the temperature in the catechin self-condensations, a higher degree of self-condensation was observed. For the blocking agent to be effective, it too would have to block more effectively at the higher temperatures. In general, this effect was observed. From the temperature studies, it was generally noted that an increased temperature did result in increased efficiency in the prevention of self-condensation, with less self-condensation product being observed at these temperatures. This observation was also made when the urea and ammonia were tested as blocking agents.

The local variation in the Rf values obtained for all of the reactions could possibly be attributed to slight variations in the separating solvent, each time it was prepared. Another explanation could be that catechin self-condensation occurred to a small degree, eg a dimer formed, and this was blocked from further condensation by reaction with phloroglucinol or m-phenylenediamine. This would have resulted in a different Rf value being obtained.

From the studies, it appeared that the most effective reagent in preventing self-condensation was the ammonia when it was present in the highest concentration. Its effectiveness was probably due to

its pH effects rather than entirely to its blocking abilities (cf 2.1.3 b iii). However, variations in pH, whilst not obviously important in the model compound studies, could prove problematic when encountered by tannin solutions. This so, since the pH affects the tannin structure which in turn could affect the industrial viability and usefulness of the extract. However, when the pH increase effected by the ammonia was small, the ammonia was also successful in decreasing the catechin self-condensation. For this reason, the ammonia was considered as a potential blocking agent for testing with the tannins, on condition that the pH change was not too marked.
Urea also proved to be a potential tannin self-condensation blocking agent, since in the reactions with catechin it had been as successful as phloroglucinol in decreasing the self-condensation observed.
Although phloroglucinol and m-phenylenediamine had both proved effective in decreasing the self-condensation, with m-phenylenediamine being more efficient, their high cost prevented them from being seriously considered on an industrial scale.

2.2 Effect of Urea and Ammonia on Phlobaphene Precipitation from Pine Tannin Solutions

The results obtained in the model compound study were extended to pine tannins themselves. Prior to confirming the results in an extraction of the pine bark, phlobaphenes were precipitated from pinus radiata tannin solutions in the presence of urea or ammonia, using hydrochloric acid or sodium sulphite.