INDUSTRIAL POLYMERS

BASED ON

PINE TANNIN PHLOBAPHENES

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ABSTRACT

This dissertation centres on improving the extraction yield of pine tannin obtained from the bark of pinus radiata D.Don - Chile and the solubilisation of pine tannin phlobaphenes and their application in adhesive formulations.

Initial studies with catechin as a model compound for tannins indicated that phloroglucinol, m-phenylenediamine, ammonia and urea were successful in decreasing the self-condensation of catechin. These results were successfully extended to the extraction of pine tannins from bark both on laboratory and industrial scale. Economic considerations and health hazards resulted in the final choice of urea to be used in the extraction of pine tannins. Adhesive formulations were prepared, examining the effects of urea on the performance of the tannin extracts.

Phlobaphenes were precipitated from aqueous solution using acid. These phlobaphenes were successfully redissolved to a 40% solids concentration, using sodium sulphite, ethanol and water. Once redissolved, the phlobaphenes were successfully employed in both thermosetting and fast-setting honeymoon adhesive formulations, which were tested in particle boards and fingerjoints respectively.

DECLARATION

I declare that this dissertation is my own work and that any technical and industrial assistance has been acknowledged.

It is being submitted for the degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted for any degree or examination in this or any other University.

Vanessa Jenifer Sealy-Fisher

Tuesday, 8th day of January, 1991.

ACKNOWLEDGEMENTS

Numerous people have offered assistance and advice during the course of my studies - to all of these I extend my sincere and grateful thanks.
In particular, I wish to thank the following:

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  for being an exciting supervisor who always found time to share his great adhesives knowledge. His tremendous support and advice and the stimulating discussions we had, in addition to his limitless patience especially during the preparation of this dissertation, definitely do not go unappreciated!
- **Senor Ernst von Leyser of DITECO, Ltda**
  who supplied all the natural and sulphited tannin extracts used in the research, who welcomed me in Chile and who graciously placed DITECO factory at my disposal for industrial trials.
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  for supplying the South African pinus radiata bark
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  and all others in and about lab 122
  for the fun and laughter, the encouragement to keep going and for being great friends - despite the chocolate-coloured sticky tannins I prepared!

Finally, last but by no means least

- to my husband, **Peter**
  for his constant love, support and encouragment and for faithfully keeping me going through the last few years of studying - I couldn't have coped without him.

to the only God
our Saviour
be glory, majesty, power and authority,
through Jesus Christ our Lord,
before all ages, now and forevermore!
Amen.

ERRATA AND ADDENDA

Table 2.2.3 3.0 ml HCl yields 70% precipitate

Page 28 line 7 being encountered. The isolation of catechin from the condensation products may, however, have been more successful if a non-polar solvent such as ethyl ether had been employed in the separation.

Page 29 line 8 advanced by Mayer, et al[25] (figure 2.1).

Page 41 line 13 There were no exceptions, since the calculation error in table 2.2.3 has been rectified. Thus the trend of increasing acidity resulting in increased precipitation of phlobaphenes was observed throughout. This corresponded to the increased presence of acid catalyst in the tannin solution.

Page 49 line 31 extracts. However, some of the reagents used in the laboratory extraction of the tannins (such as phloroglucinol) appeared to have caused interference in the absorption of the radiation by the tannins. This probably affected the estimation of the tannin concentration in those solutions, from the calibration curve in figure 2.3.2.

Page 69 line 33 decrease in adhesive strength. In addition, the very low Stiasny numbers may have been attributable to an unusually high carbohydrate content in the samples. However, since the concentration of carbohydrates was not established, this could not be confirmed.

Page 142 line 4 solubility of the former. The relative intensities of the bands assigned to the S=O groups (lower in the phlobaphenes than in the tannins) and ether bonds (higher in the phlobaphenes than in the tannins) could also suggest that the precipitate obtained after extraction was due to a low degree of sulphitation in the tannins.

Page 147 line 11 supplied as 32% (mass/volume) by Unilab, SAARChem.

Page 183 reference 7 J. Baeza, J. Freer, N. Rojas, N. Duran: Bol. Soc. Chil. Quim. 31, (1986), 115-121

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INTRODUCTION

Adhesives based on tannin extracts from acacia mearnsi (black wattle) have been successfully applied in the timber industry for over twenty years. However, due to the limited distribution of the wattle, the commercial use of these adhesives has been limited to a few countries in the southern hemisphere.

Tannin based adhesives appear to be an ideal replacement for the traditional phenolic resins which, with the oil crises, are becoming more expensive and less available. Since the distribution of the wattle is limited, another rich source of tannin is required.

Conifers contain large quantities of phloroglucinolic flavonoids, or tannin, easily accessible in their bark and needles. In addition, the distribution of conifers is worldwide where they grow with varying degrees of success. They constitute a potentially enormous, renewable industrial resource of renewable phenolic material.
However, the use of coniferous tannins to replace or supplement traditional synthetic phenolics has proved problematic. These problems include the relatively low extraction yield compared with the relatively high tannin concentration within the bark. Water-insoluble phlobaphenes or tanner's reds precipitate during the extraction and the resultant soluble tannins are highly reactive with formaldehyde and other components of the adhesive resulting in difficulties in preparing wood adhesives meeting the required standards.
This research was aimed at solving some of these problems.

CHAPTER 1 LITERATURE SURVEY

1.1 Background

After the second world war, large petrochemical industries built for wartime fuel production turned their attention to preparing inexpensive, synthetic, petrochemical-based products, including phenol and resorscinol.[1] Many of these products were included in the manufacture of adhesives of good strength, durability and low cost.

Phenol and to a lesser extent, resorscinol were combined with formaldehyde to produce highly cross linked, strong adhesives suitable for use in a variety of interior and exterior applications. The first applications were in resinous form as bakelite. However, the adaptability of the resins to be used as wood adhesives was soon established. Phenol-formaldehyde resins were successfully employed in exterior applications where the advantage of their water resistance resulted in them being the preferred choice as wood adhesives for exterior use.

However, the energy crisis in 1973 brought a rapid end to the easy availability and low cost affordability of these oil-derived raw materials.

When production of these adhesives was limited, alternative, energy-saving methods were sought to alleviate the shortage of adhesives and the future was seen to be progressively based on a renewable resource.

Investigations conducted immediately after the war had led to the discovery that on mixing tannins, used during the leather tanning process, with formaldehyde, adhesives could be prepared.[2] To demonstrate this, pinus radiata, Douglas Fir and Western Hemlock bark extracts were used in experiments aimed at preparing wood adhesives in the late 1950's.[3]
The use of tannins in adhesives was originally suggested when it was established that the bark of woody trees contained a fairly high concentration of phenolic- and polyphenolic-type compounds which could replace synthetic phenol used in adhesives.[4].
Further research into the usefulness of tannin based adhesives was conducted in early 1970's in an attempt to release the wood-based industries from the apparent stranglehold of oil-based adhesives.

Prior to the investigations into the use of tannins as a source of polyphenolics for adhesives, research had been conducted to investigate the use of the bark and wood of different tree species.
This resulted in the realisation that although tannins were present in most dicotyledenous plants of the vegetable kingdom, very few had sufficient water soluble tannins present in the bark for successful commercial extraction and subsequent exploitation.[4]

1.2 Tannins

"Tannins" were originally defined as those astringent vegetable substances which had the property of tanning leather. This loose definition incorporated two important classes of naturally occurring phenolic-based compounds - namely: hydrolysable tannins and condensed tannins.

1.2.1 Hydrolysable Tannins

Hydrolysable tannins are mixtures of simple phenols, such as pyrogallol and egallic acid, with oligomers of gallic acid derivatives as esters of simple sugars, such as glucose.[2] They obtained their name from the ease of their hydrolysis to gallic acid and its dimer egallic acid, in the presence of specific enzymes or dilute hydrochloric acid (cf figures i, ii, iii, iv, page 4).[3] Hydrolysable tannins occur naturally in such species as:

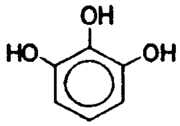
myrobolans (Terminalia and Phyllantus species)

dividivi (Caesalpina coraria)

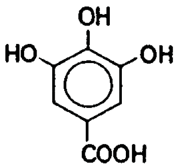
and in trees of the chestnut species.[5]

These tannins have not been isolated in conifers.[2]

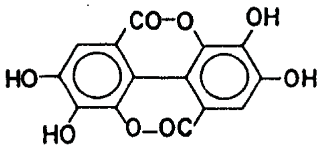
Hydrolysable tannins have been successfully employed in the production of phenol-formaldehyde resins where they can be used to partially substitute the phenol. This can be achieved since they are analogous to simple phenols in their low reactivity with formaldehyde.
They are of little economic importance owing to their limited availability, low worldwide production, high cost, lack of macromolecular structure and low nucleophilicity.[5]



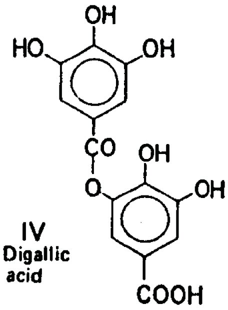
I
Pyrogallol



II
Gallic acid

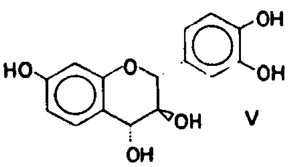


III
Ellagic acid

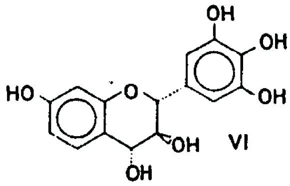


IV
m - Digallic acid

A. Flavan-3,4-diols

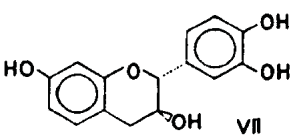


V
(+) - leucofisetinidin

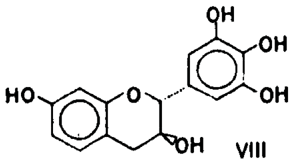


VI
(+) - leucorobinetidin

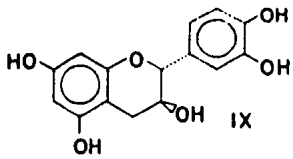
B. Flavan-3-ols



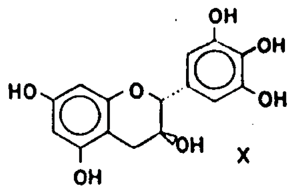
VII
(−) - fisentinidol



VIII
(−) - robinetinidol

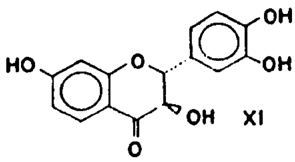


IX
(+) - catechin

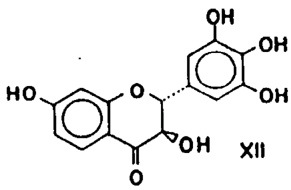


X
(+) - gallocatechin

C. Dihydroflavonols

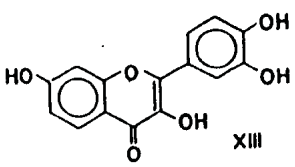


XI
(+) - fustin

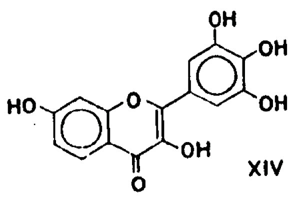


XII
(+) - dihydrorobinetin

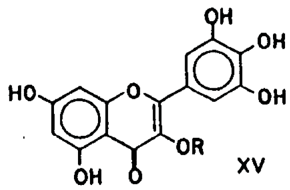
D. Flavonols



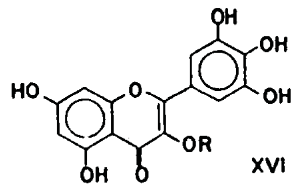
XIII
fisetin



XIV
robinetin

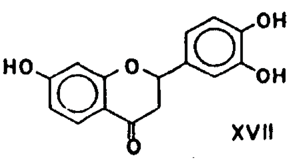


XV
quercetrin (R = rhamnose)



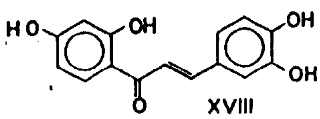
XVI
myricitrin (R = rhamnose)

E. Flavanones

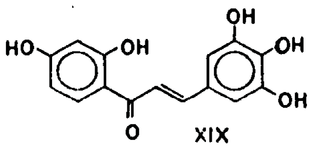


XVII
(±) - butin

F. Chalcones



XVIII
butein



XIX
robtein

1.2.2 Condensed Tannins

Condensed tannins and their precursors are one of the most abundant classes of natural phenolic compounds and are found extensively throughout the plant kingdom. Although their functions and uses have not as yet been fully elucidated, they are thought to be involved in several defence mechanisms, protecting the plant from both pathogens and herbivores and in some cases increasing the plants' drought resistance.[6]

Condensed tannins constitute approximately 90% of the worldwide production of tannins, materials which are very interesting for the potential production of adhesives and resins.[5] Commercially, these are currently extracted from *Acacia* (wattle) bark and *Schinopsis* (quebracho) wood, predominantly in the southern hemisphere.[5] The lack of commercial production of condensed tannins in the northern hemisphere is probably attributed to the limited distribution of the wattle and quebracho species in addition to the extraction problems experienced with the tannin rich conifer species. Despite the problems experienced in the extraction of condensed tannins from these trees, the extraction of condensed tannins from the bark of various *pinus* species was recently commercialised in Chile.[7]

1.3 The Chemistry of Condensed Tannins

Condensed tannins, consist of flavonoid units which have undergone varying degrees of ionic-based self-condensation. Naturally, these polyflavonoid structures are often found in association with their immediate precursors, including flavan-3-ols, flavan-3,4-diols and other flavonoid analogues (cf figures v-xix, page 4).[8] Extracts containing condensed tannins and their precursors are also associated with simple carbohydrates and glucuronates whose presence is sufficient to affect the viscosity and sometimes, other physical properties.[8]

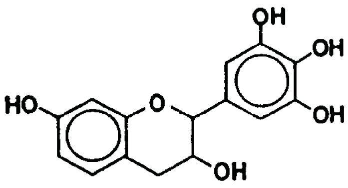
Condensed tannins or proanthocyanidins are classified according to the combinations of resorcinol and phloroglucinol (A-rings) with catechol, phenol and pyrogallol (B-rings). Two major classes are generally defined:

i) Those containing predominantly resorcinol-type A-rings - confined to tropical and sub-tropical hardwoods (including wattle) and until recently the only ones of economic importance. (cf 1.3.1)

ii) Those containing predominantly phloroglucinol-type A-rings - very common in monocotyledonous and dicotyledonous plants (including conifers) which recently became economically important. (cf 1.3.1)

1.3.1 Monoflavonoids

Monoflavonoids are classified as 'phenolic nontannins' and owing to their relative simplicity, are the most widely studied group in the tannin extracts. They include flavan-3-ols (catechins), flavan-3,4-diols (leucoanthocyanidins), dihydroflavonoids (flavonols), flavanones, chalcones and coumaran-3-ones (cf figures v-xix, page 4).[5]



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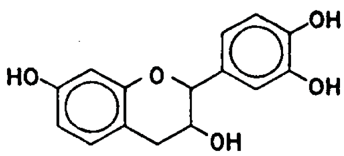
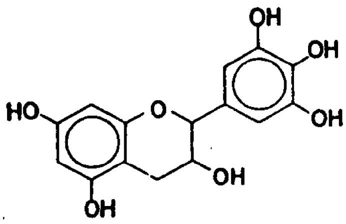


XXI



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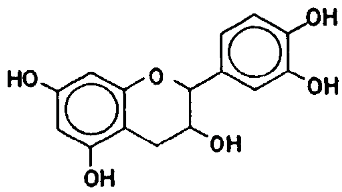

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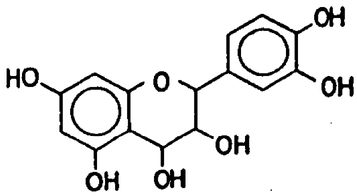

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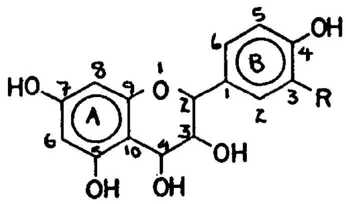
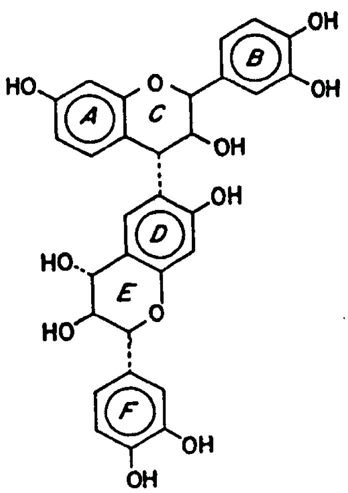


XXV



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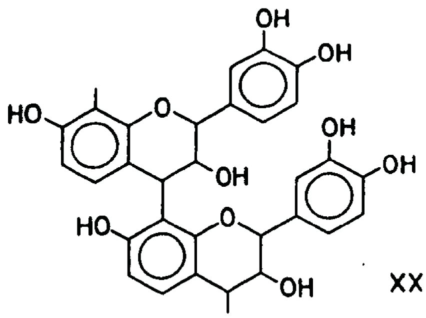
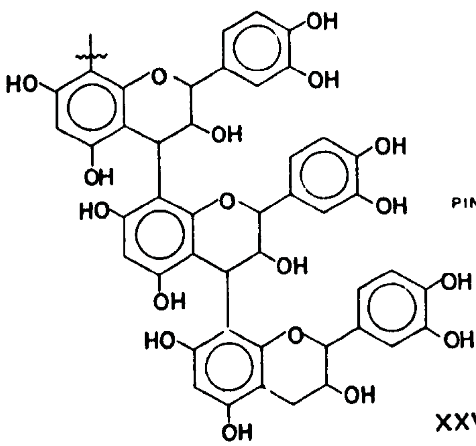


XXVII



PINE TANNIN

XXVIII

Condensed tannins appear to be formed by flavan-3,4-diols and some flavan-3-ols whilst the remaining structures do not appear to be involved in tannin formation.
In black wattle bark extract the main polyphenolic patterns are represented by flavonoid analogues on resorcinolic A-rings. Approximately 70% of the extract consists of resorcinol A- and pyrogallol B-rings (xx) and 25% is represented by the resorcinol A- and catechol B-rings (xxi). Small amounts of phloroglucinol A-pyrogallol B (xxii) and phloroglucinol A-catechol B (xxiii) are also present.
In contrast, however, pine tannins have completely different patterns and relationships. In general, most coniferous species (including pinus radiata, taeda, sylvestris, patula and pinaster) present only two main patterns. The more important pattern is based on phloroglucinol A- and catechol B-rings (xxiii). Also known as procyanidins, these phloroglucinol-catechol condensed tannins have been established to be the most widely spread condensed tannins in the plant kingdom. A lesser evident pattern is based on phloroglucinol A- and phenol B-rings (xxiv). The complete lack of resorcinol A-rings has important consequences in the use of these tannins in adhesives.

1.3.2 Biflavonoids

Flavan-3-ols and flavan-3,4-diols participate in tannin formation via an autocondensation process which relies on the nucleophilicity of the A-ring and available reactive positions. Since the other flavonoids are all substituted at position 4 on the heterocyclic ring, the nucleophilic character of the A-rings is reduced and inhibition of autocondensation occurs.

In the flavan-3,4-diols and flavan-3-ols the meta-substitution of hydroxyl groups and the heterocyclic oxygen cause strong nucleophilic centres in the C6- and C8- positions on the A-rings. In addition, charge delocalisation stabilises the benzylcarbonium ion formed at the C4-position of the heterocyclic ring (xxv). Together, these enhance the possibility of autocondensation based on an ionic mechanism.[8]
Since there are two positions for attack on the A-ring, namely the 6- and 8-positions, two types of biflavonoid are expected. Both products, 4->6 (xxvi) and 4->8 (xxvii), have been isolated although the 4->8 product does predominate under ideal conditions. In phloroglucinol derived condensed tannins, or procyanidins, 4->8 interflavonoid linkages are more common and are found in an approximate ratio of 3:1 (4->8 : 4->6), in comparison with the predominance of the 4->6 linkage in wattle extracts.

1.3.3 Oligomeric Flavonoids

Some oligomeric flavonoid structures have been elucidated and found, in general, to be an extension of the low molecular weight flavonoid structures. Thus the 4->6 and 4->8 linking patterns have been found to continue in the higher oligomers.[9]
In pine extracts, as all the flavonoids are phloroglucinolic in nature, the condensation pattern is accepted to be via 4->8 interflavonoid linkages only,