A ^{13}C NMR Study of Polyflavonoid Tannin Adhesive Intermediates. I. Noncolloidal Performance Determining Rearrangements

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SYNOPSIS

Chemical and heat treatments introduce noticeable modifications on the structure of four different polyflavonoid tannin extracts during their modification for use as tannin-formaldehyde polycondensates. Such modifications are performance determining and account for the profound differences in behaviour of the four tannin extracts when used as tannin-formaldehyde adhesives. Such modifications are directly followed by ^{13}C NMR on the tannin extracts. Although some of the modifications observed by ^{13}C NMR appear to correlate well with previous findings by model compounds studies, others could only be observed by ^{13}C NMR of the modified tannin extracts themselves. Structural rearrangements to phlobatannins, depolymerization, recyclation, rearrangement of the type of interflavonoid monomer links, and autocondensation have been followed by ^{13}C NMR and found to occur to different extents in the four tannins accounting for many of their differences in adhesive performance and characteristics. A novel reaction of autocondensation was observed for pecan nut pith tannins, which is different in applied characteristics from other polyflavonoid tannin adhesives. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Thermosetting polyflavonoid tannin-formaldehyde resins non-"fortified" by the addition of any other synthetic resin have performed well in industrial applications as phenolic exterior adhesives for wood particle board for the last 20 years.[1] It is well known that most nonmodified tannin extracts do not usually perform adequately as tannin-formaldehyde adhesives due to several shortcomings such as high viscosity, lower cross-linking density, and so forth.[1]

Industrial polyflavonoid tannin extracts are mostly composed of phenolic polyflavonoids, in particular flavan-3-ols, and of smaller fractions of polysaccharides as well as simple sugars.[1] The reaction of the formaldehyde with the extract occurs at reactive sites on the phenolic polyflavonoid tannins; polysaccharides and simple sugars also create conditions that influence the reactions and performance

of the extract-formaldehyde adhesive. The most diffuse and used industrial tannin-formaldehyde formulation used for particle board is based on a mimosa extract modified by a series of precise acid and base treatments well before its reaction with formaldehyde.[2] The chemical modification of the tannin extract is done at 80–90°C by the addition of minor amounts of an anhydride (acetic or maleic anhydride) followed by the addition of minor amounts of phenylacetate and by the subsequent addition and digestion of sodium hydroxide for a well-defined period of time.[1,2] That such a simple treatment and procedure is capable of transforming a tannin extract into a high performance adhesive indicates that, although the amount of chemicals used are really minor, they are likely to induce major modifications in the tannin structure, or in the interaction between the different components of the extract, or influence markedly the physicochemical characteristics of the extract. The ^{13}C NMR study presented is aimed at indicating on the tannin extracts themselves, not only on models, which are the main modifications and reactions contributing to the perfor-

mance of the tannin-formaldehyde resin, in regard to both the structure of the polyflavonoid tannin itself and particularly the physicochemical influence of the polysaccharide components. The study is extended to four types of commercial tannin extracts, namely black wattle or mimosa (*Acacia mearnsii* formerly *mollissima, de Wildt*) bark extract, quebracho variety chaqueno (*Schinopsis balansae*) wood extract, pine (*Pinus radiata*) bark extract, and pecan (*Carya illinoensis*) nut pith extract. All tannins in these extracts present the characteristic flavonoid repeating units
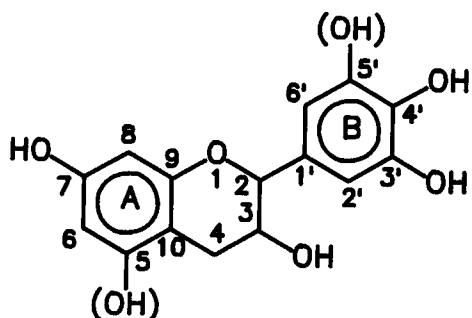
linked to each other, 4–6 or 4–8.[1]

The combination of reactions leading to the different behaviour of these tannin extracts as polycondensate wood adhesives for particle board will be detailed and correlated with performance, at first with model compound systems and then with the tannin extract themselves. In this first article the structural characteristic variation induced by the treatment detailed above of the four polyflavonoid tannin extracts, independent from the colloidal state of the extract, observable by ^{13}C NMR, will be discussed as well as to what extent they are likely to be responsible for adhesive performance.

This article is also aimed at determining if modifications of tannins forecast through applied and fundamental adhesives work and model compounds work, (i) do or do not occur on the concentrated solution of the tannin itself and (ii) such modifications can be followed on the tannin itself by simple ^{13}C NMR techniques. The extent to which such modifications are likely to influence tannin adhesives performance is also addressed.

EXPERIMENTAL

^{13}C NMR

Solutions of ^{13}C NMR spectra were obtained on a Bruker AC200 FT-NMR spectrometer at a fre-

quency of 50.3 MHz and with the sample spectra at 25 Hz. Chemical shifts were calculated relative to $(CH_3)_3Si(CH_2)_3SO_3Na$ for NMR control. $(CH_3)_3Si(CH_2)_3SO_3Na$ was dissolved in D_2O, run separately, and the shifts for the four signals were set. All the spectra were run overnight. Acquisition time was of 1.08 s and number of transients approximately 10000. All spectra were run with identical relaxation delay of 5 s and were accurate to 1 ppm. The spectra were run with nOe enhancement, spectral width was 15000 Hz, digital resolution 0.925 Hz/point with exponential multiplication. The WALTZ decoupling programme was used. Typical spin-lattice relaxation times were not measured but standard values shown in the literature were used.[3] The ^{13}C NMR band intensities reported in the tables are integrated intensities. The samples were prepared by diluting 40% mass/mass aqueous solutions of tannin extracts before and after treatment with D_2O in 1 : 4 mass proportion, except for monomeric catechin alone for which deuterated methanol was used as the solvent. Distortionless enhancement by polarization transfer (DEPT) ^{13}C NMR spectra were also obtained to add confirmatory evidence of correct assignment for CH—, —CH_2—, —CH_3, and quaternary carbon shifts. The ^{13}C NMR band intensities were reported to a 100% band intensity for the C3′,C4′ 145–146 ppm band, for parity of comparison for the untreated tannin extracts. The chemically treated tannin extracts were reported to the same intensity of the C1′ band at 131 ppm, also for parity of comparison with the untreated samples. Results are shown in Table I for the tannin extracts and on Table II for model compounds. The 60–90 ppm region relating to signals from the hydrocolloid gums present in the extracts was not reported in the tables because this region has already been examined in depth.[4]

Chemical/Heat Treatment

The chemical/heat treatment was used on the following solutions:

1. 50% mimosa tannin extract in water;
2. 45% natural quebracho tannin extract in water;
3. 45% natural pine tannin extract in water;
4. 45% pecan nut tannin extract in water.

The above were treated on tannin extract solids with 3.5% by mass of acetic anhydride at 80°C, under mechanical stirring for 45 min, followed by 5.5% by mass NaOH solids (as a 30% water solution) at 90°C

Table I ^{13}C NMR Relative Band Intensities of Untreated and Chemically/Heat Treated Polyflavonoid Tannin Extracts

Group	C=O	C5,C7	C9	C3′,C4′	C1′	C6′	C5,C2′	C4–C8 Link	C10	C6	C8	C4	Catechinic Acid	—CH₃
Band (ppm)	181–182	156–157	155	145–146	131	120–121	115–117	110	101	96–98	95–96	27–28	31–32	24–25
Mimosa	—	53	30	100	44	25	26	51	19	21	31	21	—	—
Quebracho	—	63	33	100	66	56	99	40, 52	25	20	20	32	—	—
Pine	—	71	71	100	49	39	76	60	37	47	23		—	—
Pecan nut	—	66	70	100	62	30	33	66	42	40	29	37	79	—
Treated														
Mimosa	21	43	34, 28	74	44	27	34	45	18	19	18	22	—	38
Quebracho	35	51, 46	40	76	66	51	78	35, 41	27	25	27	27	—	55
Pine	61	44	44	51	49	37	58	34	26	35	24		—	147
Pecan nut	130	39	39	65	62	37	45	56	43	45	34	38	59	210

Table II ^{13}C NMR Relative Band Intensities of Treated and Untreated Catechin Monomer Model Compound

Group	C=O	Ester	C5,C7	C9	C3,C4′	C1′	C6′	C5,C2′	C4–C8 Link	C10	C6	C8	C2	C3	Catechinic Acid	C4	CH₃
Band (ppm)	184	159–160	156–158	150–155	146–147	137	132–133	117–118	110–111	101–103	97	95–96	83	68–69	31	27	25
Catechin monomer	—	—	97, 100	—	72, 76	—	73	98, 96	—	68	88	97	92	93	31	27	25
Catechin monomer + acetic anhydride	448	—	100, 54	22	72, 91	—	79	79, 68	29	68	44	51	60	64	51	80	1350
Catechin monomer + gum arabic + acetic anhydride	356	72	100, 81	39	69, 98, 79	29	33, 57	72, 48	20	20	34	43	53	49	45	31	1070

under mechanical stirring for a period of 3 h, then cooled rapidly to ambient temperature and the pH adjusted to 7.0 for all four cases before ^{13}C NMR analysis was carried out. Catechin monomer (A.R. grade) was treated only with acetic anhydride at 80°C for 1 h in the following two cases:

1. 25% catechin monomer alkaline water solution + 3.5% acetic anhydride, by mass, on catechin solids;
2. 25% catechin monomer and 15% gum arabic alkaline water solution + 3.5% by mass acetic anhydride on catechin solids.

Gel Times and Viscosity

The gel-times with formaldehyde of the eight treated and untreated tannin extract solutions were determined at pH 5.6, 94°C using the following method. Gelation is defined by the point at which the tannin extract solution ceases to be a viscous liquid and becomes an elastic, rubbery solid. The end point of this determination is very sharp and reproducible for tannin-formaldehyde reactions. Tannin extract solution, 10 g was weighed in a test tube and to it were added 0.3 g 96% paraformaldehyde fine powder. A wire spring was placed in the test tube and the extract solution and paraformaldehyde gently mixed for a few seconds at ambient temperature. The test tube was then placed in a boiling water bath (94°C), the wire spring manually moved rapidly by upward/downward hand movements, and the time taken to gel measured by stopwatch. The test was done in duplicate. This test is a FESYP standard method[5] and is used extensively in Europe for wood adhesives. The gel time measurement was used to relate to the reactivity of the phenolic material, in this case the tannin extracts. Shorter gel times indicated more reactive phenolic materials. The results obtained are shown in Table III.

Viscosities of the treated and untreated tannin solutions were measured at 20°C using a Haake Hoeppler type viscometer. The results obtained are shown in Table III.

DISCUSSION

The relative intensities of the ^{13}C NMR bands of the adhesive intermediates derived from chemically treated tannin extracts indicate that a variety of modifications were induced by the hot chemical treatment used (Table I). The correct assignment of the ^{13}C NMR spectra was originally deduced from the work of other authors[6] and then refined according to data reported in a preceding article.[7] The first ^{13}C NMR bands of interest are those characteristic of the free C6 and free C8 sites and C4–C8 interflavonoid linkage at 96–98, 95–96, and 110 ppm, respectively. These are indicative and important diagnostic bands as the free C6 and C8 are mostly the sites through which subsequent reaction with formaldehyde and cross-linking occur in the adhesive. Comparing the relative intensities of these bands among the different treated tannins and with the untreated tannins, mimosa tannin extract shows little variation of the free C6 band and a clear decrease of the free C8 band, indicating that some autocondensation occurs in C4–C8, although not too extensively. This is due to its mainly profisetinidin/prorobinetinidin (resorcinol A-rings) nature. It is supported by a decrease of the 110-ppm band, thus very low or no amounts of C4–C8 cleavage that is only due to the small but significant proportion of phloroglucinol type units present in this tannin.[8,9] Instead in pine tannin autocondensation is more evident, particularly treatment-induced autocondensation at C6: the free C6 relative band intensity decreases noticeably with the free C8 band remaining unaltered, or increasing slightly. This implies

Table III Comparative Viscosities and Gel Times of Four Tannins Before and After Chemical/Heat Treatment

	Viscosity[a] (Centipoises)		Gel Time (sec)[b]	
	Before Treatment	After Treatment	Before Treatment	After Treatment
Mimosa 50% extract solution	1480	550	210	180
Quebracho 40% extract solution	1250	300	495	447
Pine 40% extract solution	630	450	77	70
Pecan nut 40% extract solution	2700	5700	42	42

[a] At 20°C.
[b] At pH = 5.6.

that although very noticeable tannin cleavage at the C4–C8 interflavonoid link must have occurred, in the subsequent autocondensation the flavonoid units affected by such cleavage appear to have recombined randomly both C4–C8 and C4–C6 (Fig. 1). Equally this effect could infer a rotation/recyclation rearrangement via 5-OH (Fig. 1).

This is known to occur in model compound reactions of fisetinidin/catechin dimers.[10] It is however less likely or less abundant in pine tannin, as interflavonoid cleavage is more favoured in this type of tannin. As pine tannin is mainly a procyanidin/ prodelphinidin type[6,11] (phloroglucinol A-ring type) and thus the repeating units are mostly C4–C8 linked, it means that cleavage of C4–C8 links and partial recombination of the units by C4–C6 links should cause a noticeable decrease in relative intensity of the 110 ppm C4–C8 band: this was indeed the case (Table I). Thus, after treatment, pine tannin appeared to show clear autocondensation and has shown some C4–C6 recombination. Equally, the lack of increase in free C8 sites appeared to indicate that the chemical/heat treatment has caused further autocondensation, and not only recombination, leading to an increased degree of polymerization of the tannin mostly through additional C4–C6 links (in this type of tannin the free C6 being the most available site for further autocondensation).[1]

In the case of quebracho tannin the free C6, C8 bands increased indicating that some interflavonoid link cleavage has occurred, although less extensively than in pine tannin, with such cleavage occurring in similar proportion at C6 and C8. The 110 ppm (C4–C8) clear decrease in relative intensity showed not only that C4–C8 interflavonoid links involving catechin-type units have been cleaved, but confirms that the procyanidin polymers proportion, or catechinic units proportion, is noticeably greater in quebracho tannins than in mimosa.[8] Of note was that autocondensation by recombination does not appear to have occurred, due to the predominance in this tannin of the profisetinidin/prorobinetidin fraction, in which interflavonoid link cleavage is known to be difficult.[12] Thus, in quebracho tannin the chemical treatment has a definite effect in decreasing the degree of polymerization of the tannin, contrary to the other three tannins; this is also noticeable in the greater decrease in viscosity caused by the chemical treatment (Table III).

Pecan nut tannin, the other procyanidin/prodelphinidin type of tannin, shows some similar and some very different responses than pine tannin. Thus, the free C6 relative band intensity increased indicating the presence of C4–C6 linkages, an un-

thought of finding, as well as the lack of C4–C6 recombination. Free C8 increased indicating much clearer cleavage of the predominant C4–C8 linking pattern than in pine: this appears to be confirmed by the marked decrease in relative intensity of the 110 ppm C4–C8 band. All this again indicated a more noticeable proportion of C4–C6 interflavonoid linkages in this natural tannin than in pine. The response of this tannin to treatment is very different from the other three tannins, a fact observable from the viscosity after treatment (Table III) and by its characteristic applied behaviour already reported.[13]

The C4–C6 interflavonoid link band at 122.7 ppm also appeared to confirm the above. Such a band increased after chemical treatment for all four tannins. This indicated that in all four tannins C4–C6 autocondensation and/or recyclation induced by the chemical or heat treatment occurred and was quite noticeable. It also indicated that artificially induced autocondensation favours further C4–C6 links formation, whatever the main linking pattern (C4–C8 or C4–C6) present in the natural tannin before treatment. This band often, but not always, overlaps the C6' band, but its contribution to it is always quite small.

It is interesting to compare what was observed in the actual tannin extracts with that observed with model compounds, namely catechin and catechin plus gum arabic. In unreacted catechin monomer the intensities of both the free C6 and free C8 bands are very high, but the C4–C8 interflavonoid link band at 110 ppm does not appear.[7] This is consistent with catechin being a monomer. In catechin and catechin plus gum arabic, chemically treated with anhydride, a very marked decrease of the free C6 and C8 bands, and the definite appearance of the C4–C8 interflavonoid band, were noticeable. The chemical and heat treatment of catechin appeared then to have caused autocondensation in which C6 and C8 were involved to a similar extent: heat-induced autocondensation of catechin is well known.[14] However, in the case of the mixture of catechin and gum arabic, the decrease of free C6 and C8 sites was more marked, indicating possibly more autocondensation, and the increase in C4–C8 was less marked than in pure catechin, indicating the reverse. These contradictory indications are of interest as they infer for the first time that other reactions are also likely to occur when the system is in a colloidal state. This will be expanded in the next article.

The next band of interest in Table I was the C9 band at approximately 155 ppm. The intensity of this band should decrease after chemical treatment because of heterocycle opening by cleavage of the

a) Mimosa   (a) small amount of autocondensation at C8

(b) little or no change of interflavonoid link

(c) phlobatannin rearrangement (acid and alkaline induced) main reaction
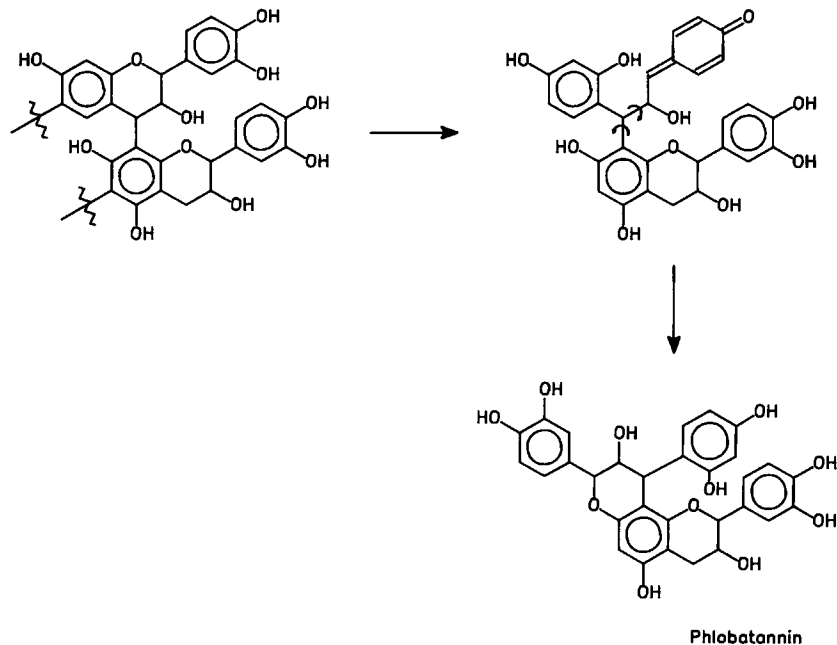
Phlobatannin

(b)Quebracho   (a) extensive interflavonoid clevage

(b) depolymerization by C4—C8 clevage at phloroglucinol units

(c) closure of heterocycles by phlobatannin rearrangement
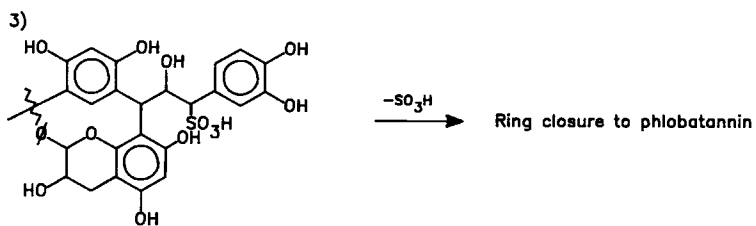
1)

decrease in DP
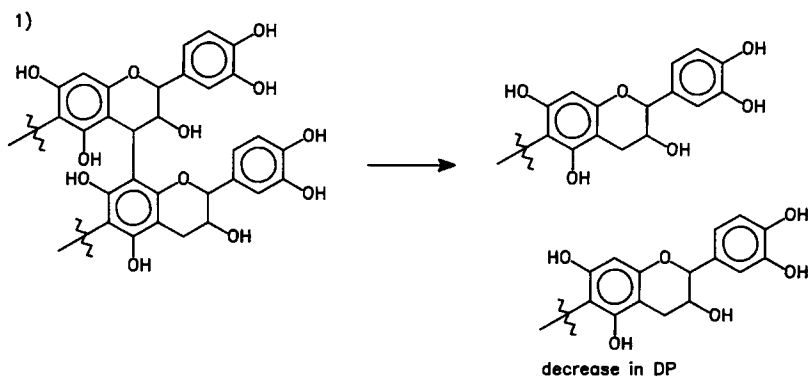
2) As main reaction in mimosa

3)

−SO₃H

Ring closure to phlobatannin

Figure 1 Schematic of the main reactions occurring in polymer modification by chemical/ heat treatment of mimosa and quebracho tannin to be used for polycondensate adhesives.

bond O1–C2. The relative intensities of this band indicate that the chemical treatment did not affect the number of close heterocycle rings in mimosa tannin. This is patently absurd as it is now well-known that heterocycle cleavage is facile in mimosa[12,15] (contrary to interflavonoid link cleavage which is difficult). This is then an indication that the heterocycle rings, after opening, reform most likely via the now proven phlobatannin rearrangement[15] (Fig. 2) and/or through recyclation. Quebracho tannin instead showed a certain amount of closure of heterocycles: in this natural tannin, due to the use of sulphite or metabisulphite for its extraction, a certain proportion of open heterocycles in which the reactive C2 was blocked from further condensation from a sulphonic acid group was present. Elimination of some sulphonic group from C2 due to heat and chemical treatment will lead to a C2 site reactive enough to form a new heterocycle via the same phlobatannin rearrangement and/or recylation of mimosa. Equally, some heterocycle opening will occur during chemical treatment just as for mimosa. As such phlobatannin rearrangement is particularly noticeable when a resorcinolic and a phloroglucinolic unit are linked, the higher proportion of phloroglucinol A-rings in quebracho will effectively lead to an increase in the closures of heterocycle rings by formation of phlobatannins. Pine and pecan nut tannins instead appeared to behave very differently. The main effect was one of heterocycle opening, as shown by the marked decrease in intensity of the C9 band. Here, however, due to the great predominance of greatly reactive phloroglucinol A-rings, condensation of the reactive C2 with the phloroglucinol A-ring of a flavonoid unit in another chain is likely to be very much favoured. This was the case at least for pecan nut tannin, and the overall effect is predominantly one of autocondensation through C2–C8 and/or C2–C6 interflavonoid linkages superimposed to that possibly involving the C4 sites. The phlobatannin rearrangement did not appear to occur. Although interflavonoid cleavage was the favourite reaction in predominantly procyanidin tannins,[12] heterocycle opening also occurred, particularly considering that proportions of profisetinidins were also present. The higher the amount of profisetinidins the higher the amount of heterocycle opening, the higher the C2–C8 and C2–C6 autocondensation. The above infers that in predominantly procyanidin tannins the higher the proportion of units with a resorcinol A-ring, the higher will be the autocondensation of the tannin, and the more noticeable the increase in viscosity after the chemical and heat treatment. This was borne out by the increase in viscosity of pecan nut tannin after chemical treatment being much greater than for pine tannin (Table III). It also explains the already reported viscosity instability of pecan nut tannin adhesives[13] and the reasons why systems used to stabilise it by blocking the reactive C2 or C4 position are so effective.[13,16] The behaviour of the model compounds (Table II) also appeared to confirm this: both catechin and catechin gum arabic showed clearly extensive heterocycle opening, as in pine and pecan nut tannins. Again, as before with C4–C8/C4–C6 autocondensation, the catechin/gum arabic mixture showed after chemical/ heat treatment less heterocycle opening than pure catechin. This was the second indication of a difference, this time in extent, of a reaction occurring when the flavonoids are in a colloidal solution. It implies for instance that less heterocycle opening occurred because less acid from the anhydride is available to cause heterocycle cleavage. This also will be expanded in the next article.

The behaviour of the intensity of the ^{13}C band of the free C4 site (not involved in an interflavonoid link), although this band is not very sensitive, also confirmed many of the arguments exposed. In mimosa the chemical/heat treatment caused no noticeable change in the relative intensity of the free C4 signal, as expected. In quebracho there was a clear small decrease in band intensity again confirming that this tannin undergoes depolymerization to some limited extent during the chemical treatment. In pecan nut tannin, where the very noticeable increase in viscosity[13] and other factors,[13] clearly indicate tannin autocondensation, the intensity of this band did not change; this appears to confirm again that the predominant and very marked autocondensation caused by the chemical treatment in pecan nut appears to be C2–C8/C2–C6 and not C4–C8/C4–C6. In pine tannin the free C4 band was not very noticeable both before and after the chemical/heat treatment indicating a very condensed tannin. Although variation was small it appeared to indicate a similar behaviour as pecan nut tannin but to a much smaller extent.

The ^{13}C NMR study thus clarified for the first time several interesting aspects of the effect of the chemical heat treatment in tannins. In mimosa tannin a very moderate chemical treatment as the one used does not introduce the phlobatannin reaction to an excessive extent, an unthought of finding. Such a reaction in theory introduces a more reactive resorcinol ring in a configuration of higher mobility. In reality higher mobility can only be achieved in the upper and possibly lower flavonoid units of the
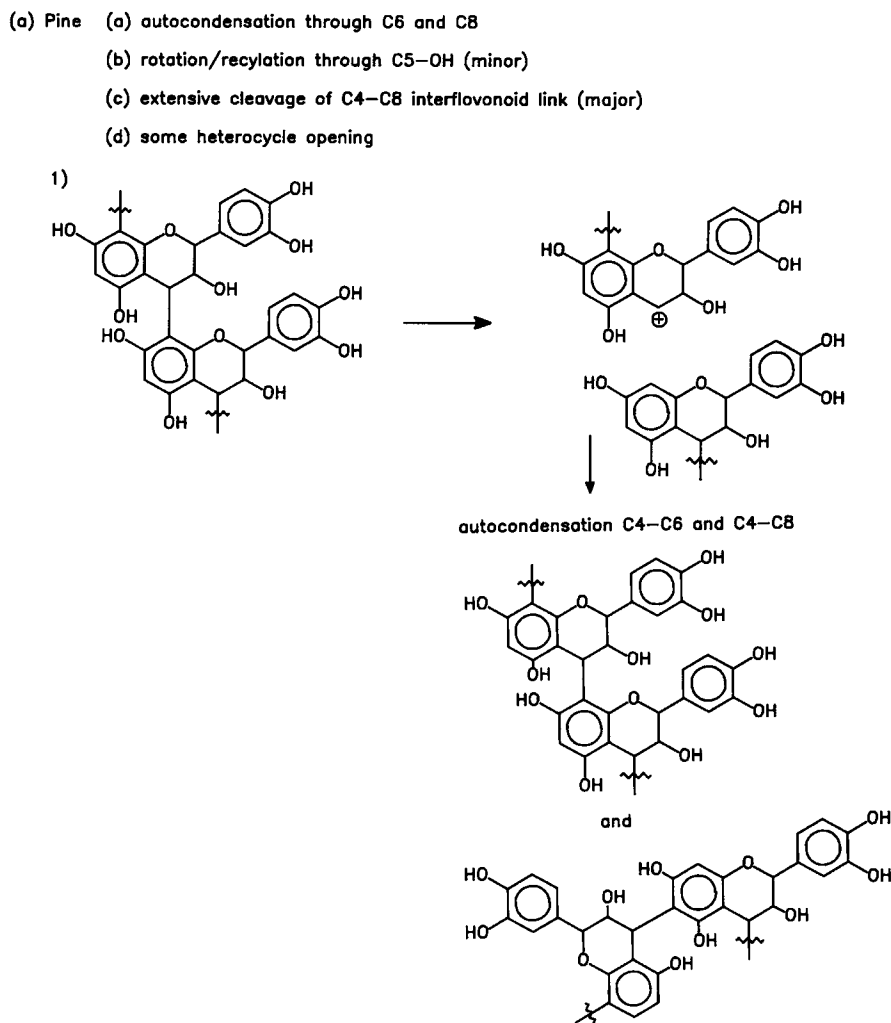
(a) Pine   (a) autocondensation through C6 and C8

(b) rotation/recylation through C5—OH (minor)

(c) extensive cleavage of C4—C8 interflovonoid link (major)

(d) some heterocycle opening

1)

autocondensation C4—C6 and C4—C8

and

Figure 2   Schematic of the main reactions occurring in polymer modification by chemical/ heat treatment of pine and pecan nut tannin to be used for polycondensate adhesives.

polymer. The limited amount of more reactive resorcinol rings will lead to faster reactions with formaldehyde, but not to an extreme extent, as confirmed by moderately faster gel times (Table III). Possibly a somewhat higher density of cross-linking due to the resorcinol-type A ring being in a configuration more accessible to formaldehyde attack could also be achieved in the case of upper and lower terminal flavonoid units in the polymer. Phlobatannin rearrangements that instead occurred in nonterminal flavonoid units, although still contributing to higher reactivity toward formaldehyde, present resorcinol rings whose mobility is still severely hindered (Fig. 1). Their contribution to cross-linking density is then likely to be no different than that of units in untreated tannins. In both cases the number of potential cross-link sites did not change. The

properties improvement was then mostly based on increased rate of reactivity with formaldehyde and its limited extent only partially accounts for the improvement of the properties of the tannin extract as an adhesive: other factors, discussed in the next article, have at least comparable importance on the adhesive performance of the two less reactive tannins, mimosa and quebracho. An excessive chemical treatment, by unduly increasing the amount of, or time of treatment with, sodium hydroxide has been observed experimentally[1,17] to introduce some disadvantages to the adhesive. This is because the greater proportion of phlobatannin rearrangements induced does not correspond to any further increase in cross-linking but only some further small increase in reactivity. Concurrent noticeable increases in viscosity[1,13,17] due to this rearrangement and auto-
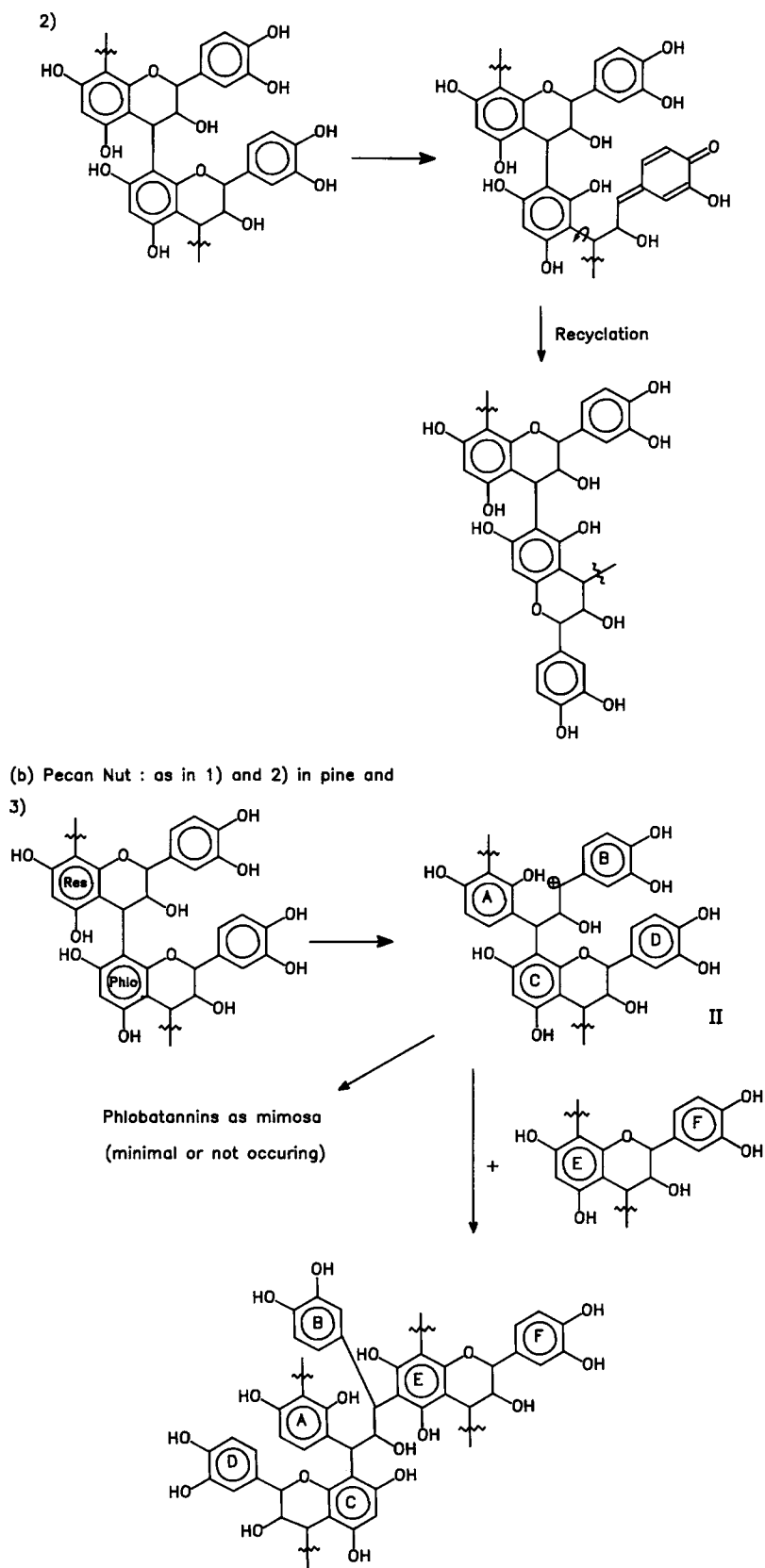
2)

Recyclation

(b) Pecan Nut : as in 1) and 2) in pine and

3)

Phlobatannins as mimosa

(minimal or not occuring)

II

+

Figure 2   (*Continued from the previous page*)

● sites highly reactive with formaldehyde· Number remains the same throughout sequential
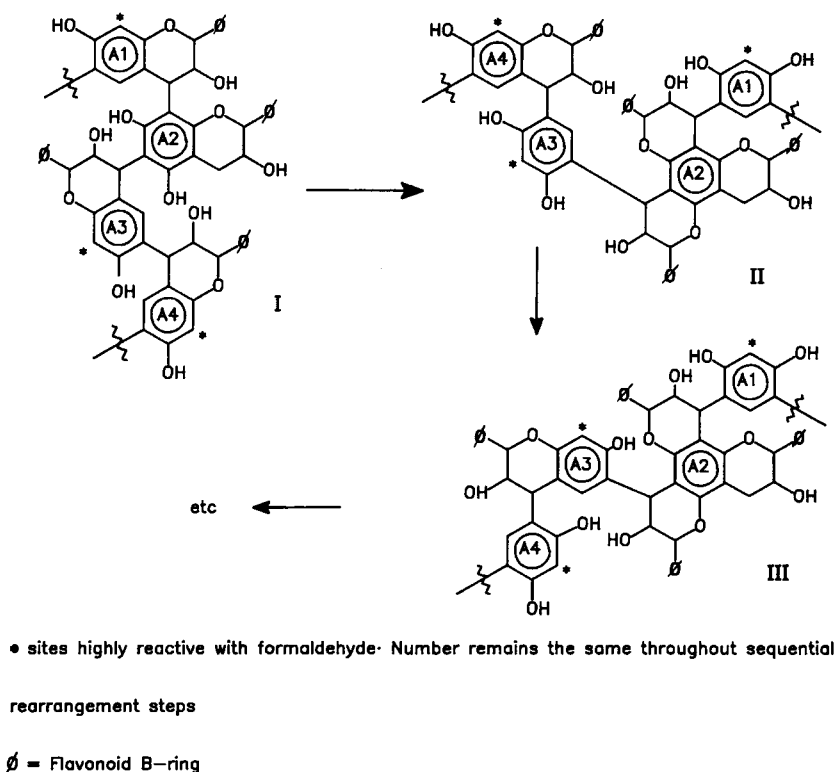
rearrangement steps

∅ = Flavonoid B—ring

Figure 3 Schematic illustration of the limit of improvement caused by phlobatannin rearrangement in tannins to be used for polycondensation adhesives.

condensation also occurred. The further and greater disadvantage of a more marked chemical treatment is that multiple phlobatannin reactions will lead to less resorcinol rings in the more reactive configuration, further, only those of the lower and upper flavonoid units in the polymer, as illustrated in Figure 3. This situation does not appear to be too damaging in tannins of lower average degree of polymerization (DP_n) such as mimosa (average 4–5 condensed units) for which the treatment was originally conceived.[2,18,19] It appears however to be a contributory cause to the less marked effect, or lack of it, noticed in higher molecular mass tannins such as pine and pecan nut. In the higher molecular mass quebracho tannin, the clear depolymerization noted by ^{13}C NMR contributed to a decrease in the DP_n, enough to render the treatment still effective.

CONCLUSIONS

In conclusion the main structural modifications that appeared to affect the performance of the modified tannin extracts for adhesives during their reaction with formaldehyde are summarised in Figures 1 and

3. Some of these modifications were forecast by model compounds work, or deduced or inferred by applied adhesive work already reported, but never checked on concentrated solutions of the tannins as used in adhesives. Their relative importance for different tannins in regard to adhesive applications has not been examined previously. Model compounds findings have also not been related to the extent to which some of these modifications might or might not occur in the tannin itself, and to the relative importance, or lack of it, to the final performance of the tannin as an adhesive. The importance, or for some tannins mostly the lack of it, of some reactions previously believed to be performance determining was then for the first time put into its correct perspective directly on the tannin itself and for different tannins. In mimosa, the phlobatannin reaction introduced a more reactive resorcinol ring in a configuration of higher mobility. This led to faster reactions, as observed by faster gel times (Table III), and only in some cases possibly a somewhat higher density of cross-linking due to the resorcinol ring being in a configuration of higher mobility. Quebracho behaved very similarly to mimosa, with possibly a more extensive proportion of phlobatannin
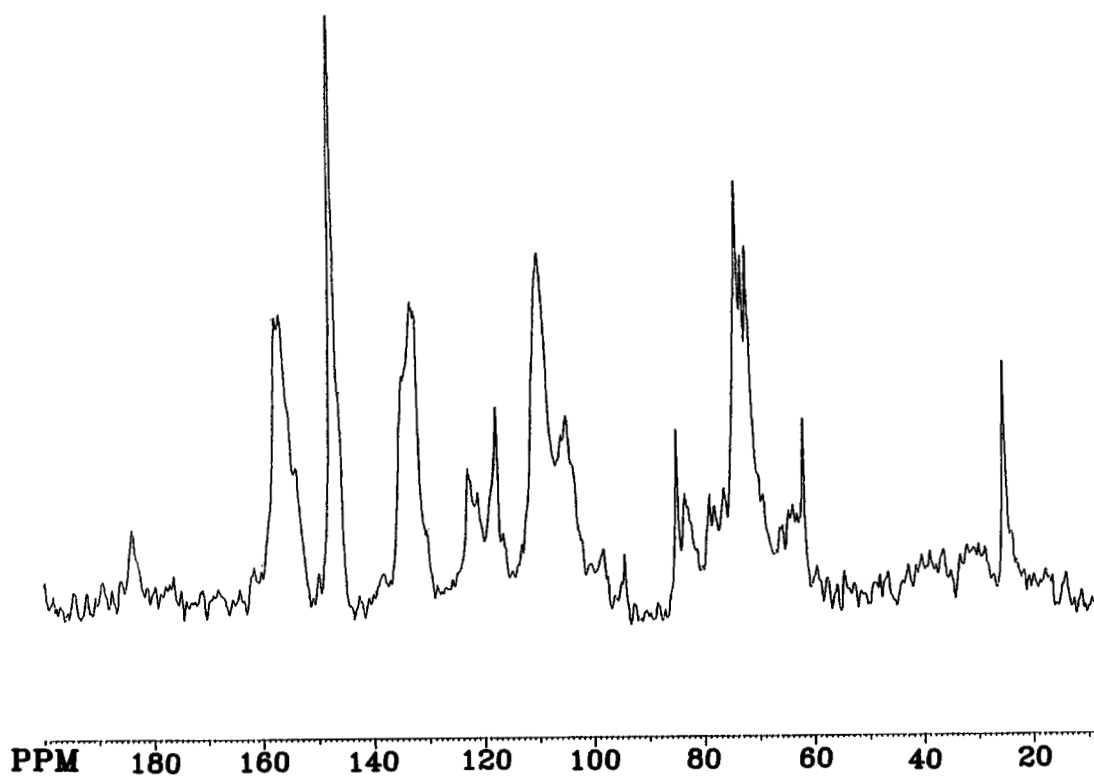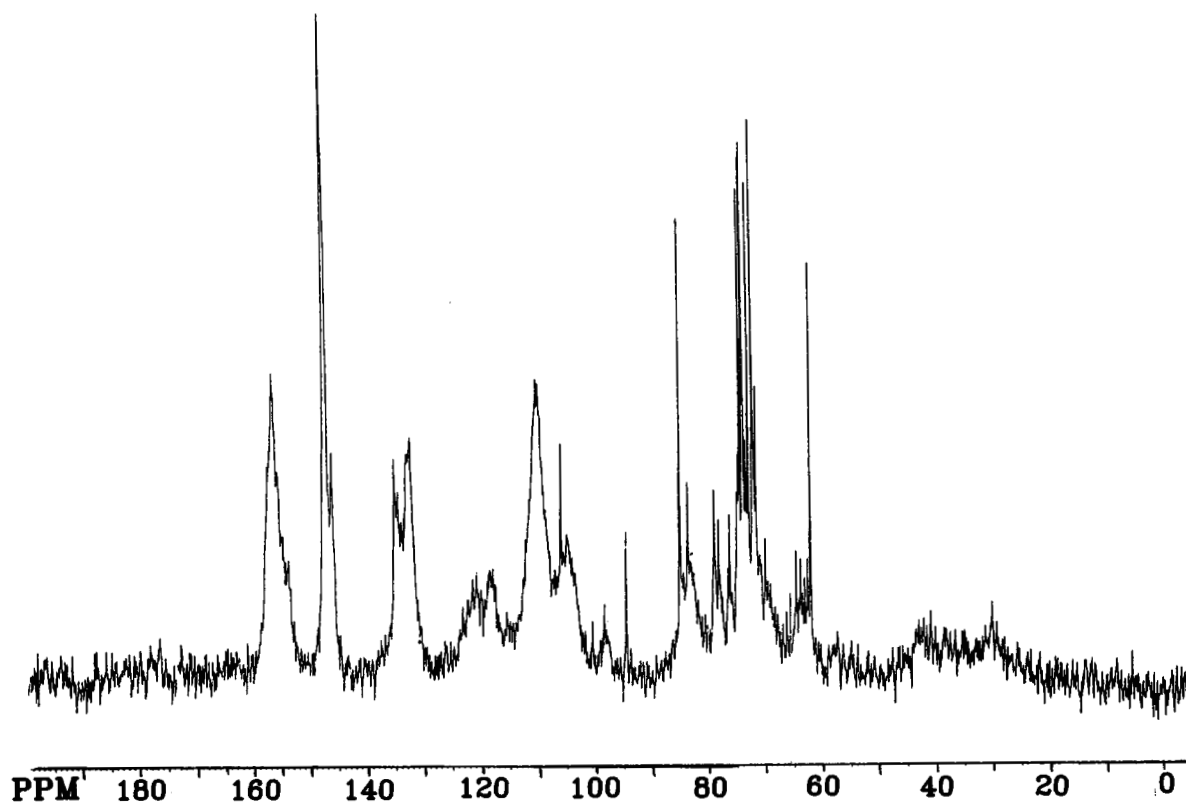
Figure 4 ^{13}C NMR of mimosa tannin extract (a) before and (b) after chemical/heat modification.
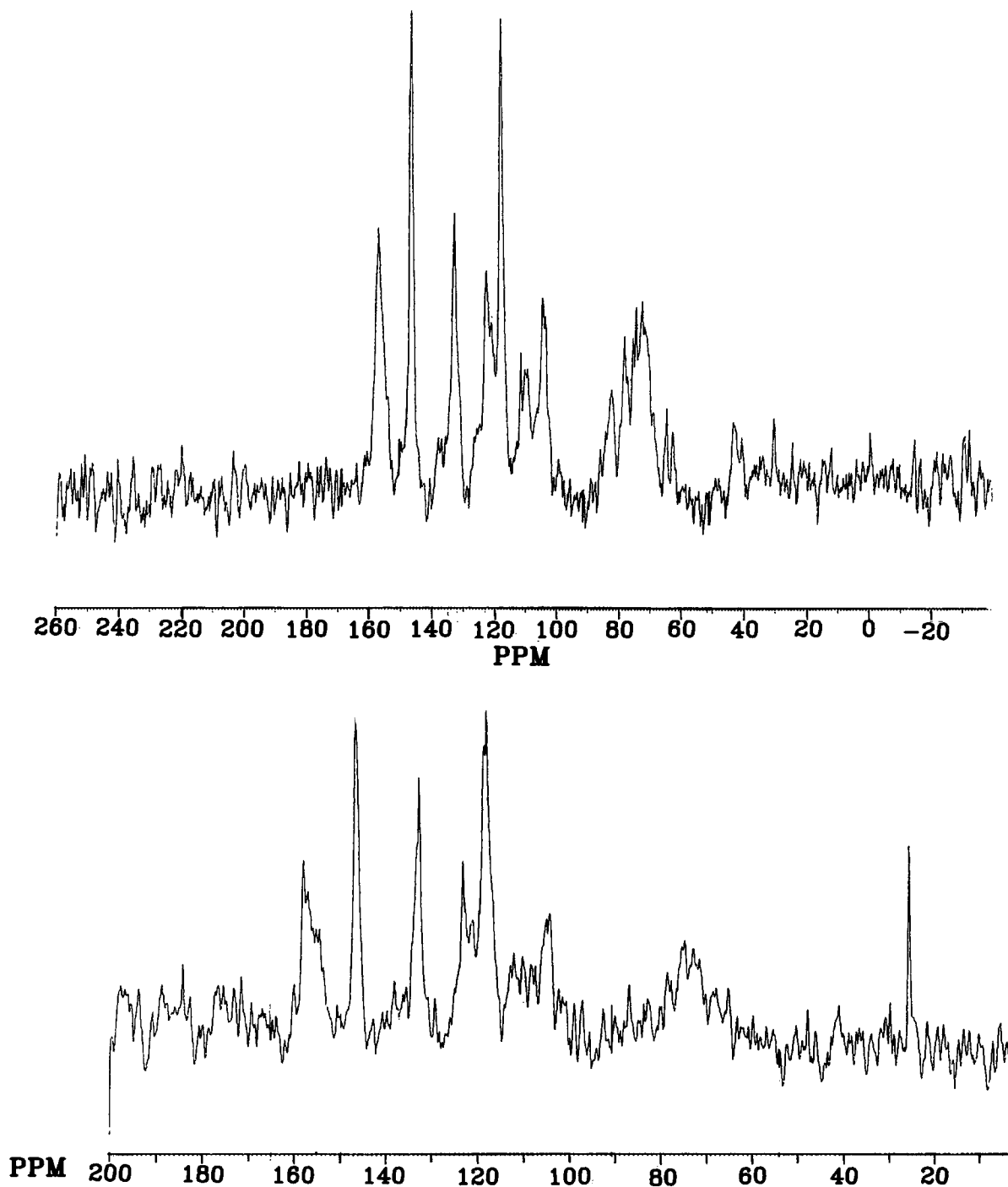
Figure 5   ^{13}C NMR of quebracho tannin extract (a) before and (b) after chemical/heat modification.

rearrangement, but also with some decrease of degree of polymerization. The sum of the two effects gave an overall effect similar, but slower than that for mimosa (Table III) as regards reactivity, indicating quebracho depolymerization to be possibly more extensive than the phlobatannin rearrangement, a fact also indicated by the more noticeable decrease in viscosity.

The two more reactive tannins, pine and pecan nut, their already much higher reactivity being due
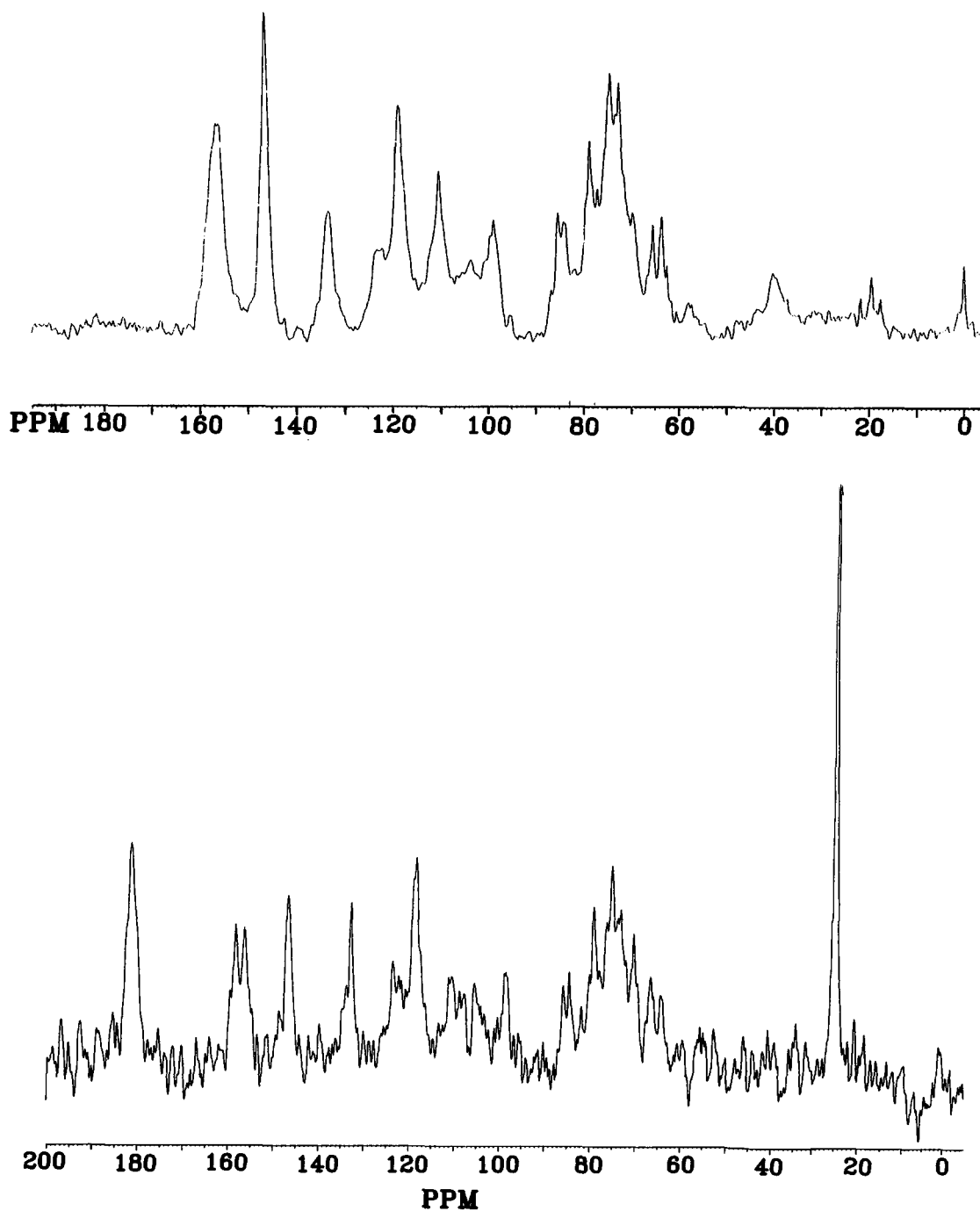
Figure 6 ^{13}C NMR of pine tannin extract (a) before and (b) after chemical/heat modification.

to the predominant amount of phloroglucinol A-ring in their constituent units, presented very different behaviour. In the case of pine the chemical treatments did not really improve the situation in regard to reactivity or degree of cross-linking: the improvements noted were due to reactions in that col-

loidal state that will be discussed in the following article. In pecan nut tannin the chemical treatments detailed were instead positively deleterious. The predominant autocondensation No. 3 in Figure 2 for pecan nut tannin, which has not been reported before but originally inferred from applied findings,
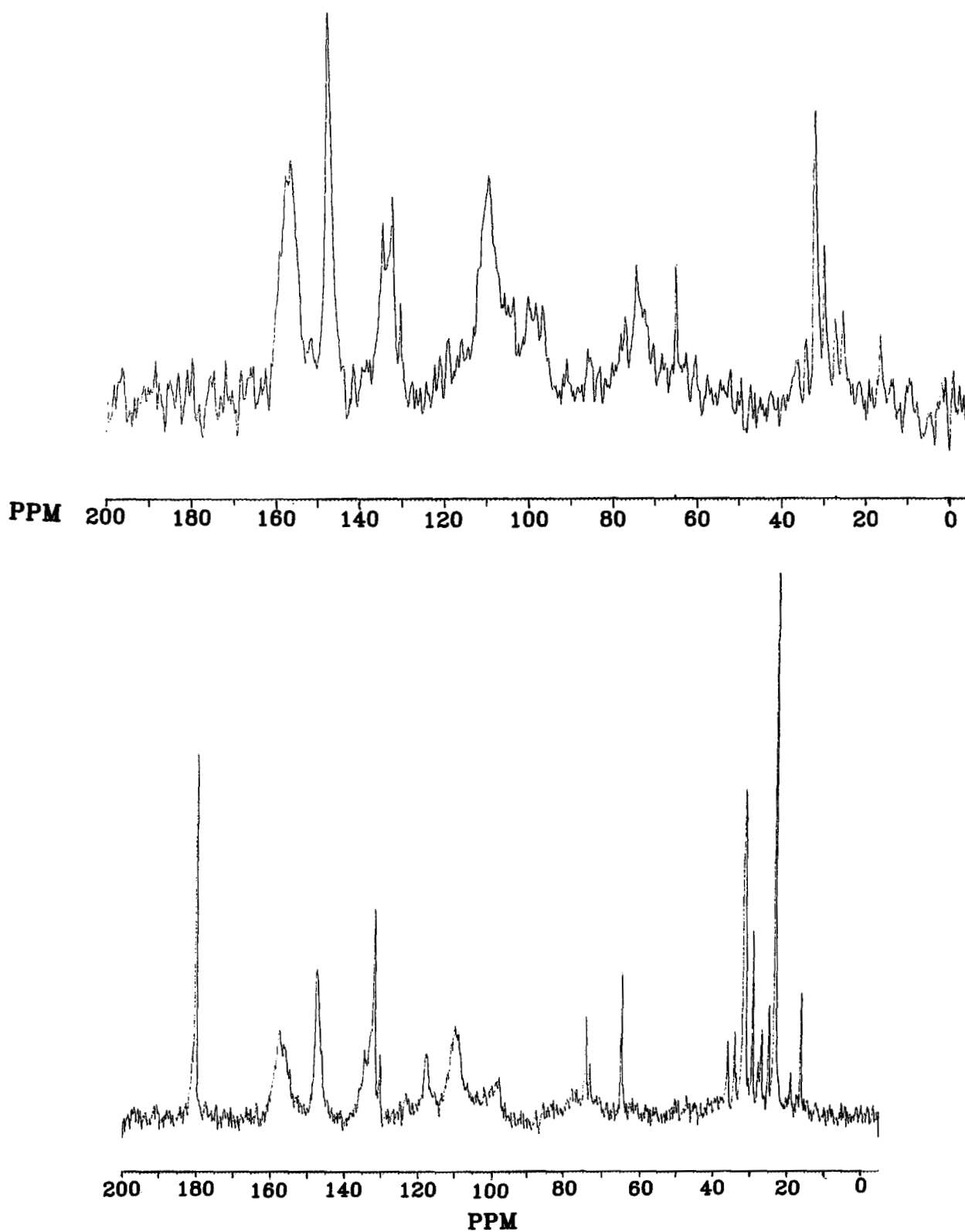
PPM 200   180   160   140   120   100   80   60   40   20   0

200   180   160   140   120   100   80   60   40   20   0

PPM

Figure 7 ^{13}C NMR of pecan nut tannin extract (a) before, (b) after chemical/heat modification, and (c) after chemical/heat modification when tannin extract is stabilized by the addition of 7% urea.
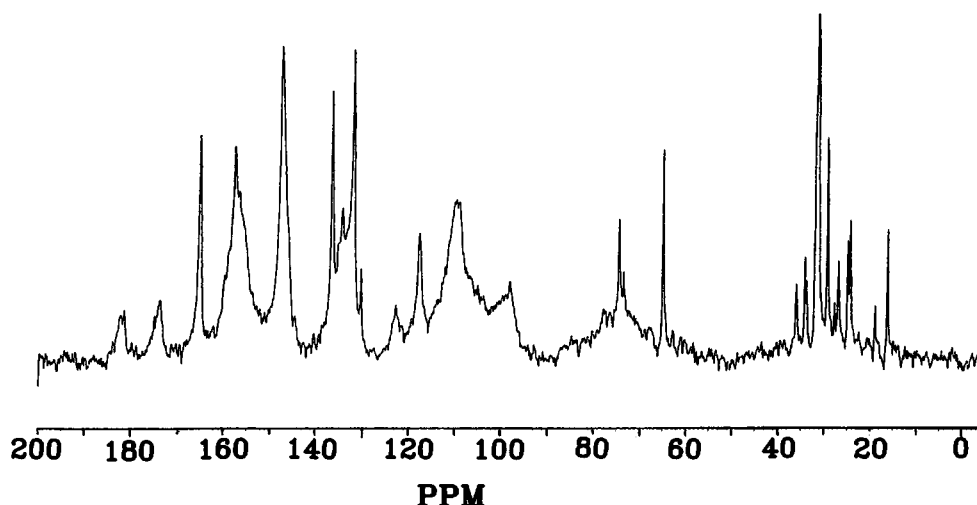
Figure 7 (*Continued from the previous page*)

led to an unchecked increase in viscosity that renders the tannin unusable for adhesives if chemically and heat treated. The same autocondensation occurring during hot bonding, while the tannin-formaldehyde reaction is also occurring, also helped this

tannin to outperform, as an adhesive, all the other tannins in their modified and unmodified forms.[13] It is easy to understand how a simple treatment with urea as already reported,[13,16] at ambient or higher temperature was able to check the increase in viscosity to a considerable extent.
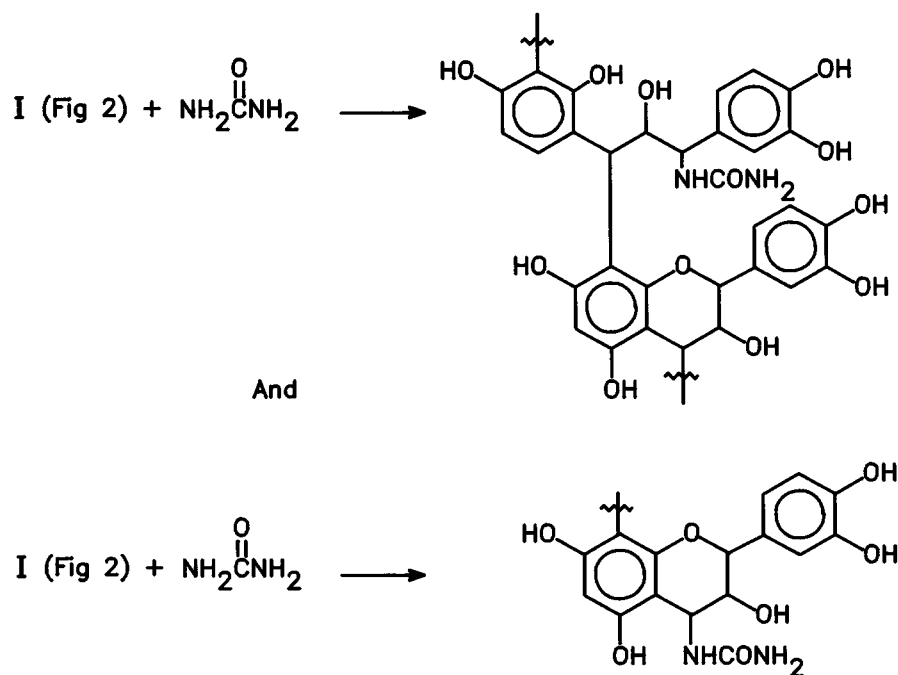
The second of these reactions was observed occurring by the noticeable decrease of the ^{13}C NMR C4 band intensity once small amounts of urea were added to the tannin before chemical and heat treatment. From the ^{13}C NMR spectra, there were several clear indications that both the mechanisms above

occur in pecan nut tannin pretreated with 5–7% urea. The C2, two bands at 74.2–74.6 ppm and 73.5, indicating two different C2 states (one of phloroglucinol and the other resorcinol units), varied considerably. On chemical and heat treatment the 73.5

ppm band decreased markedly. On addition of urea followed by chemical and heat treatment the 74.2–74.6 ppm band also decreased indicating that the second mechanism shown in the reaction scheme above occurred. That the first mechanism occurred as well is shown by an intense sharp band beside the C1′ one at 136.5 ppm (the C1′ is at 132.1 ppm) indicating a different state of the C1′ due to an amide group linked to C2 in an open heterocycle unit.

From the mechanisms at play observed by ^{13}C NMR, pine, mimosa, and quebracho could probably be modified to a certain extent to upgrade their performance to the level of pecan nut tannin. To this effect the addition of some pine tannin or gambier tannin both catechinic to mimosa or quebracho,

most likely could upgrade their performance by the same mechanism observed in pecan nut tannin alone. It will work best in upgrading pine tannin performance as an adhesive by the addition of small amounts of mimosa or quebracho extracts to again induce pecan nut like autocondensation on tannin-formaldehyde adhesive curing.

It is interesting to note than in the ^{13}C NMR spectra of pecan nut tannin extract pretreated with urea and then chemically and heat treated, there were indications of an interesting side reaction. The carbonyl signal of urea appears at 165 ppm[20–22] and although the intensity of the $C = O$ band of acetic acid was lower than usual, a third carbonyl band at 173.7 ppm clearly appeared. This was due to the reaction
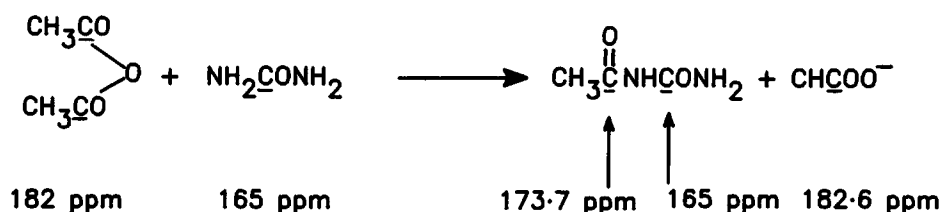
Such a reaction also subtracted anhydride from both a-set attack,[23,24] which was of no interest anyhow in this tannin, as well as contributing to a decrease in heterocycle cleavage and thus in autocondensation in pecan nut tannins.

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