NOTES

^{13}C-NMR of Zn^{2+} Acetate-Induced Autocondensation of Polyflavonoid Tannins for Phenolic Polycondensates

INTRODUCTION

The autocondensation of polyflavonoid tannins induced by weak Lewis acids has recently been described.[1-3] It opens up the possibility of new applications of polymeric tannins as adhesives and resins.[1-5] Small amounts of weak Lewis acids such as silica, silicic acid, boric acid, and aluminum trichloride induce rapid autocondensation of concentrated tannin solutions to hardened resins.[1,3-5] The mechanism of autocondensation was found to be based on Lewis acid acceptance of electrons from the ether oxygen of the flavonoid unit pyran ring with concurrent and consequent facilitation of base-induced heterocycle opening. Ionic and, in particular, radical mechanisms were shown to be present and to be superimposed or not under well-defined reaction conditions.[1-6] The reactive site formed (C2) was shown to condense with the A-ring of another flavonoid unit in another polymer chain[1,5] without intramolecular rearrangements to catechinic acid or phlobatannins occurring.[1,3-5] This leads to crosslinking and networking of the material to a hardened state.[1,2,4] The presence of this mechanism was also shown to reverse the relative ease of cleavage between interflavonoid bond and heterocycle opening in procyanidin tannins.

Zinc (2+) acetate also appears to cause a similar type of autocondensation, but this is much slower, occurs mostly at higher curing temperatures, and not at ambient temperatures as for the other materials already examined,[1] and leads to a much softer gel. This indicates that differences in the mechanism between zinc acetate and the materials reported previously might exist. This article was aimed at examining such differences.

EXPERIMENTAL

Gel Times

The gel times with SiO$_2$ and with (CH$_3$COO)$_2$Zn2H$_2$O were done on a 40% water solution of commercial pecan (*Carya illinoensis*) nut pith tannin extract over the range of pHs shown in Table I. Gelation is defined by the point at which the tannin extract–water solution ceases to be a viscous liquid and becomes an elastic rubbery solid. The end point of this determination is sharp. Ten grams of 40% tannin extract–water solution adjusted with 30% NaOH to the pHs indicated in the table is placed in a test tube and to it are added solid fine powder SiO$_2$ or a 40% zinc acetate–water solution. The percentages added were of 6% SiO$_2$ and of 6% and 23% zinc acetate on tannin extract solids. A wire spring is placed in the test tube and the extract solution gently mixed for a few seconds at ambient temperature. The test tube is then placed in a boiling water bath (100°C), the wire spring is normally moved rapidly by upward/downward hand movements, and the time taken to gel is measured by a stopwatch. The test is done in duplicate. This is a FESYP standard test method and is used extensively in Europe for wood adhesives.* The gel time measurement is used to relate to the reactivity of the resin, in this case, the tannin extract. Shorter gel times indicate more reactive materials. The results obtained are shown in Table I.

^{13}C-NMR

The zinc acetate gelled samples of pecan nut tannin extract were used. Contrary to the SiO$_2$ cases,[1] CP-MAS ^{13}C-NMR could not be carried out due to the softer nature of the gel due still to the presence of considerable amounts of water and portions of ungelled material in the specimens. One-pulse ^{13}C-NMR spectra were obtained in a Bruker MSL 300 FT-NMR spectrometer, at a frequency of 74.47 MHz. Chemical shifts were calculated relative to TMS for NMR control. The spectra were run with suppression of spinning side bands and at a spinning speed of 4500 Hz. Spectral width was 20,000 Hz. Relaxation delay was 5 s. Typical spin lattice relaxation times for the types of compounds analyzed were taken from the literature.[7-9]

DISCUSSION

Pecan nut pith tannin extract is composed of a 1 : 5 molar proportion of procyanidins : prodelphinidins when

* FESYP, European Federation of Particleboard Manufacturers.

Table I Comparison of Gel Times in Function of pH of Pecan Nut Tannin Extract with 6% SiO₂ and 6% Zinc Acetate

| | Hardener | |
pH	SiO₂ (s)	Zinc Acetate (s)
8.00	80	Does not gel
9.00	56	Does not gel
9.50	50	1980
10.00	48	1865

acetone–water extracts are examined[10–12] and of 1 : 2 in the case of the thiolitic cleavage products.[10–12] Such results were obtained after considerable manipulation and are affected both by the type of extraction used, which leaves behind some of the material which is normally extracted by an industrial sodium sulfite/carbonate water extraction, and by the chromatographic separation which also leaves behind a noticeable fraction of the material. The molar ratio of procyanidins : prodelphinidins from industrial extracts showed, instead, a value of 1 : 4.[13] All these results clearly indicate that a considerable proportion of procyanidins are present in pecan nut pith tannin extract even if this tannin is predominantly of a prodelphinidin nature. The gel time of pecan nut tannin extract using 4% zinc acetate is, however, much slower and starts at much higher pHs than what was obtained with 4% SiO₂ (Table I). The gel obtained is also softer.

The ^{13}C-NMR spectra of pecan nut tannin extract without and at two levels of addition of zinc acetate indicate well-defined reaction trends (Figs. 1–3). Pyran ring opening and subsequent autocondensation are indicated by a decreased intensity of the C2 band at 83 ppm with an increasing amount of zinc acetate used (Figs. 1–3). This is confirmed by the decrease and, finally, the disappearance of one of the peaks (135 ppm) of the doublet signal of the C1' (at 131 and 135 ppm), transforming this signal into a single band (131 ppm). The C1' band decreasing in intensity is the one belonging to the prodelphinidins[13] and, thus, to flavonoid units presenting a pyrogallol B-ring. This indicates that prodelphinidins in the tannin open and autocondense with the A-rings of other flavonoid units. The C1' band at 131 ppm belonging to procyanidins remains, instead, unaltered, indicating that, contrary to the SiO₂ case,[1,13] the pyran ring of procyanidins appears to be unaffected by zinc acetate.
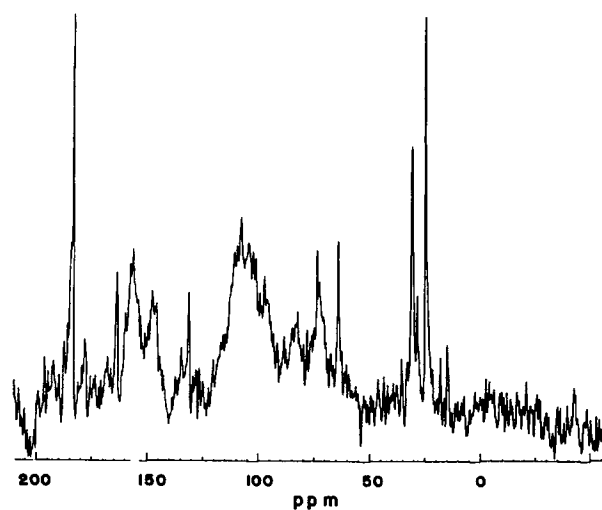
C2 — C6/C2 — C8 autocondensation of prodelphinidins is also evident by the increase in intensity of the 105 ppm band,[13–15] the increase being very evident even at low percentages (6%) of zinc acetate. Some C4 — C8 cleavage and depolymerization might also occur as shown by the slight decrease of the 110 ppm band characteristic of the C4 — C8 interflavonoid bond accompanied by the slight increase of the free C6/C8 band at 97–98 ppm. The latter, however, is not proportional to the amount of zinc acetate used: Passing from 0 to 6% zinc acetate, the increase can be observed, but passing from 6 to 23%, the intensity of this band appears to remain unaltered. The slight depolymerization is most likely due to interflavonoid bond cleavage in procyanidins, confirming that procyanidins are unaffected by zinc acetate, and a first indication that interflavonoid bond and heterocycle cleavages' relative ease of reaction is not inverted by zinc acetate, contrary to what was shown to occur with SiO₂.[1,5,6] The decrease in intensity of the free C4 band at 31–32 ppm with increasing zinc acetate, particularly at the 23% level, indicates also that some later C4 — C8 autocondensation does occur, as expected.[14,15]

Of interest are also other trends observable from the ^{13}C-NMR spectra. Treatment with zinc acetate decreases considerably the C3'/C4' at 145–148 ppm signals of the aromatic C — OH of the flavonoids B-rings. It is well known that Zn²⁺ and other metal ions form ortho-
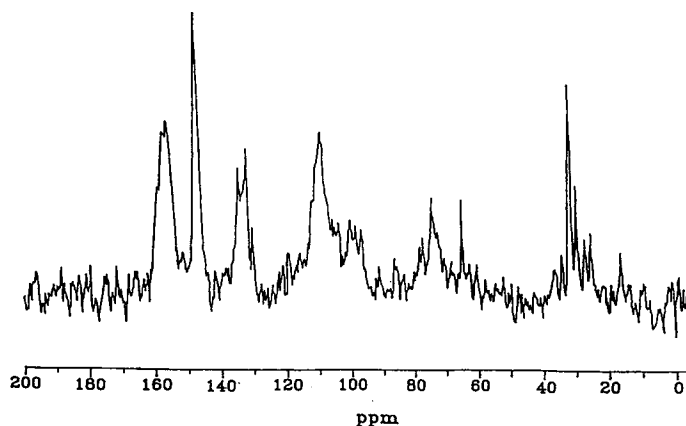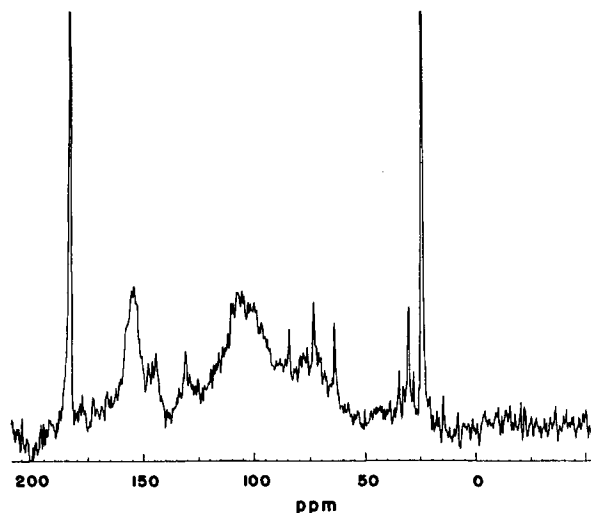

Figure 1 ^{13}C-NMR of pecan nut tannin extract.

diphenol complexes with flavonoids.[16] This is of importance, as the second step of the autocondensation needs a "pegging" action of the opened flavonoid structure to address the subsequent reaction toward condensation with another chain[1,2,5] rather than internal rearrangement to catechinic acid. In the case of Zn^{2+}, the formation of such complexes would supply, in a different manner from SiO_2, such a "pegging" effect. The A-rings C5, C7 signal at 155–157 ppm also slightly decreases but to a considerably lesser extent than does the C3'/C4' band. Apart from the action of Zn^{2+}, an acetylation of some phenolic —OH's within the mycelles formed in water by the colloidal tannins[17] may also be occurring.[17,18] The evidence suggests that, possibly, both zinc complexation and some acetylation might take place. That some acetylation in the mycellar phase also occurs is suggested by the decrease in intensity of the C3 band at 62–63 ppm, The alcoholic —OH at C3 possibly also presenting some acetylation.

The mechanism which then emerges in the case of the zinc acetate-induced autocondensation of tannins is that prodelphinidin heterocyclic rings open while the procyanidin ones do not. Zn^{2+} then appears to be capable of causing prodelphinidin pyran ring opening, pegging the open unit possibly by a B-ring *ortho*-diphenol complexation, but its effect is too weak to affect the procyanidins. This indicates that autocondensation will only occur at higher pH's than for SiO_2 and that it will be much slower as well as leading to softer gels, which indeed is the case. As a consequence, zinc acetate does not appear to produce an effect strong enough to invert the relative ease of interflavonoid bond cleavage and pyran ring opening in procyanidins, which, instead, SiO_2 has been shown to be capable of.[1,5] Thus, in the presence of zinc acetate, autocondensation will occur of prodelphinidins to prodelphinidins and prodelphinidins

Figure 3 ^{13}C-NMR of pecan nut tannin extract 40% water solution hardened at 100°C with 23% zinc acetate.

to procyanidins, but never or rarely of procyanidins to procyanidins.

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Figure 2 ^{13}C-NMR of pecan nut tannin extract 40% water solution hardened at 100°C with 6% zinc acetate.

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