NOTES

Induced Accelerated Autocondensation of Polyflavonoid Tannins for Phenolic Polycondensates. III. CP-MAS ^{13}C-NMR of Different Tannins and Models

The autocondensation of polyflavonoid tannins induced by weak Lewis acids has recently been described.[1] It opens the possibility of new applications of polymeric tannins as adhesives.[2,3] Foremost could be the use of tannins as wood adhesives without the use of any aldehyde hardener, leading to environmentally friendly, zero-aldehyde-emission natural binders.

Traces of 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] 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. The reactive site so formed (C2) is blocked, by the charge of the Lewis acid counterion, from undergoing the intramolecular bonds rotations associated with the catechinic acid[4] and phlobatannin rearrangements observed on monomeric model compounds.[1] These then do not occur, or occur to a much reduced extent on the polymeric natural tannin.[1] The effect hence addresses the subsequent condensation of the reactive site formed, away from internal rearrangements but toward condensation with a flavonoid unit in another polymer chain.[1,3] This leads to crosslinking and networking of the material to a hardened state.[1,3] The presence of this mechanism was also shown to reverse the relative ease of cleavage between interflavonoid bond and heterocycle opening in procyanidin tannins.[1]

An important aspect remains to be investigated: the extent and type of reactions occurring when using different tannins in relation to what is observed for monomeric flavonoid model compounds.

EXPERIMENTAL

^{13}C-NMR

Solid-state (CP-MAS) ^{13}C-NMR spectra of gelled concentrated water solutions of (+)-catechin at pH 12 with 4% silica and of pine tannin extract and pecan nut tannin extract also gelled at pH 12 with 3% silica were obtained on a Bruker AC200 FT-NMR spectrometer, at a frequency of 50.3 MHz with the sample at 40 Hz. Tannin extracts dried from concentrated (40%) solutions in water at pH 12 and at the natural pH of the tannin (pecan natural pH = 5.1) were also examined.

Chemical shifts were calculated relative to $(CH_3)_3$ $Si(CH_2)_3SO_3Na$ for NMR control in D_2O.

All the spectra were run overnight. Aquisition time was of 0.094 s and number of transients was 20,000. All spectra were run with relaxation delay of 5 s and were accurate to 1 ppm. The spectra were run with nuclear Overhauser effect (nOe) enhancement, and spectral width was of 22,000 Hz. Typical spin lattice relaxation times were as used for the same materials as reported.[1]

DISCUSSION

The ^{13}C-NMR spectra of (+)-catechin monomer, pine tannin (procyanidins) bark extract, and pecan nut tannin (prodelphinidins) pith extract, with and without the addition of silica, show well-defined trends and some clear differences. (+)-Catechin monomer diluted water solutions reacted with 4% silica at pH 12 and at ambient temperature form a definite soft gel after about 4 weeks, a result that is not obtained when silica is absent. The ^{13}C-NMR spectrum of the gelled material Figure 1(a) shows clear indications of catechinic acid rearrangement[4] with the quinoid and enolic bands characteristic of catechinic acid at 207, 188, and 173 ppm being evident.[4,5] This is confirmed by the much lower intensity of the band at 100–103 ppm characteristic of the flavonoid C10, indicating transformation of the aromatic nature of the flavonoid A-ring to the triazone ring of catechinic acid,[4] and the decrease and disappearance of the C5, C7 band at 150–154 ppm. Superimposed but both quite strong are the bands of the interflavonoid bonds at 110 ppm and at 105–106 ppm, indicating not only C4-C8/C4-C6 autocondensation but also C2-C8/C2-C6 autocondensation. It is remarkable that C4-C8/C4-C6 autocondensation appears to occur to a greater extent in the catechin–silica system, while by heat autocondensation of catechin alone, at the same pH, in absence of silica, the C2-C6/C2-C8 type of autoconden-
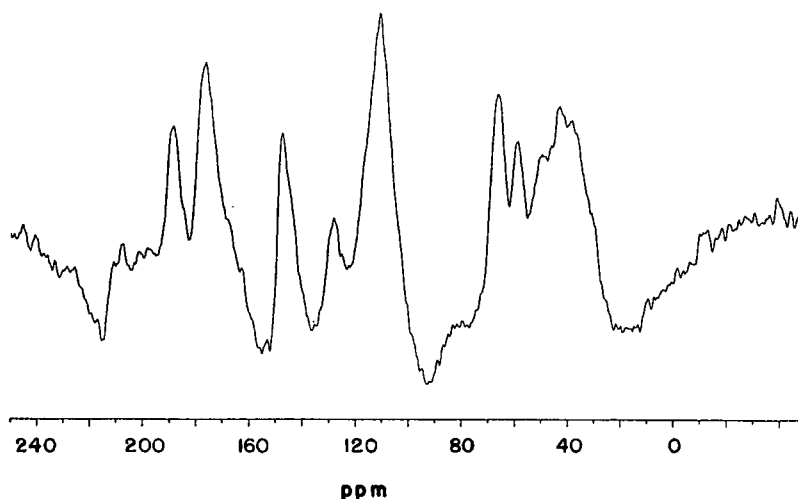
Figure 1   CP-MAS NMR spectrum of concentrated (+)-catechin water solution gelled over a period of one month at pH 12 by addition of 4% silica.

sation is the favorite one (Fig. 1). A new methylene band, very noticeable at 59 ppm, also appears, also related to the catechinic acid rearrangement.

The situation appears to be very different with the two natural, polymeric tannins. In the case of procyanidin tannin (pine) hardened with 3% silica at pH 10 [Fig. 2(a)]
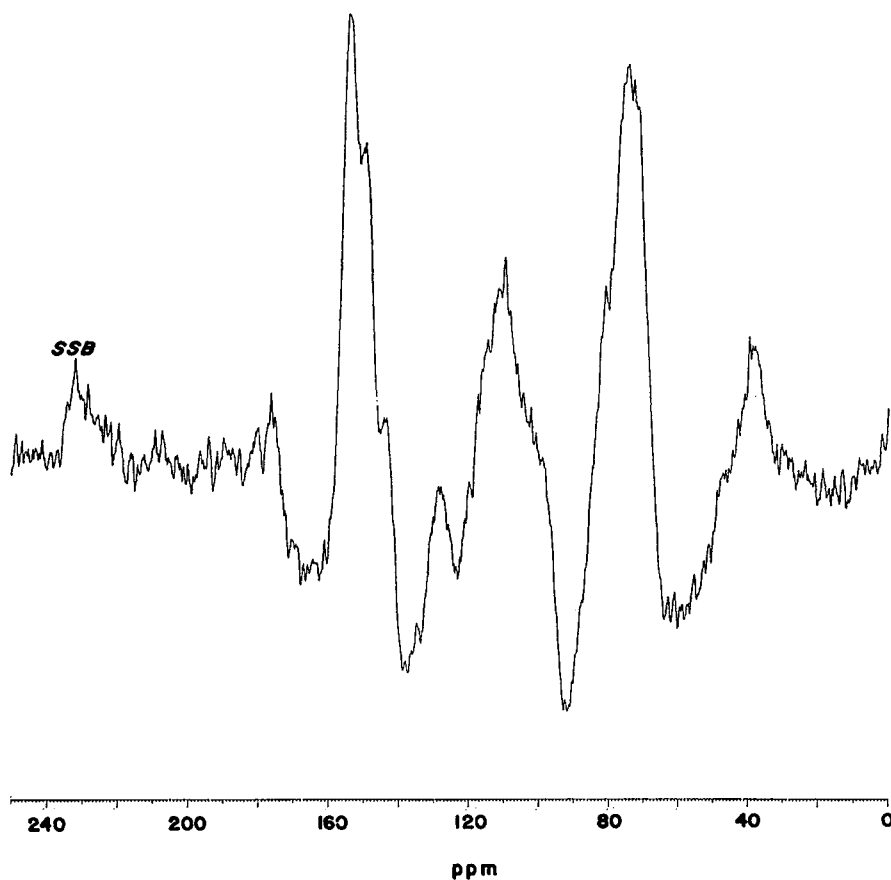

Figure 2a   CP-MAS NMR spectrum of pine tannin extract concentrated (40%) water solution at pH 12, by the addition of 3% silica over a period of 10 min at pH 12. (SSB = spinning side band)
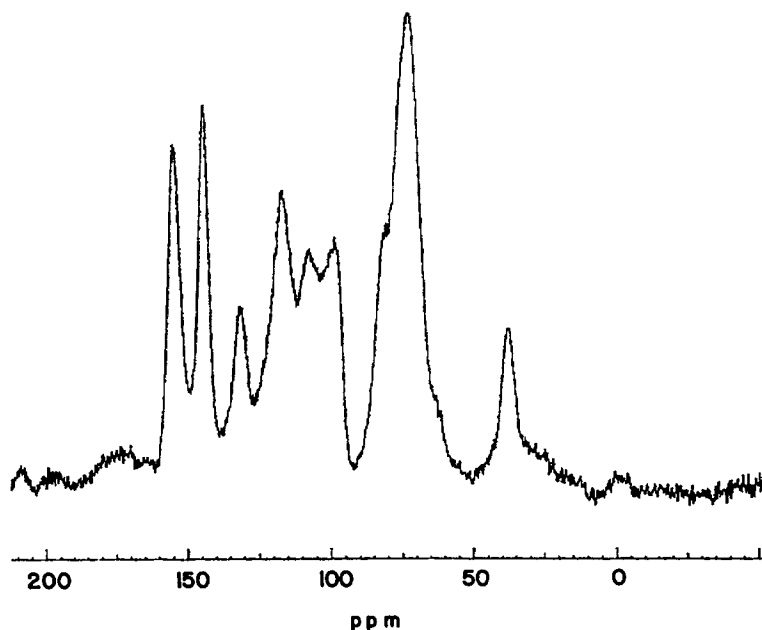
Figure 2b   CP-MAS NMR spectrum of pine tannin extract concentrated water solution obtained dried by vacuum evaporation of water.

very small amounts of quinonoid structures (232 and 176 ppm) appears to be present, the 232-ppm band definitely not belonging to catechinic acid. The small band at 176 ppm belonging to a small proportion of the enolic form of the flavonoid B-ring quinone in which some configurations are "frozen," as already found for prodelphinidin tannins (pecan).[1] The intensity of the 176-ppm band is orders of magnitude lower than in silica-hardened prodelphinidins, this being a major difference between procyanidin and predominantly prodelphinidins tannins. It appears that the prodelphinidins pyrogallol B-ring is able to stabilize better the open heterocycle form, hence the appearance of more marked 176-ppm band. Thus, in both tannins,

the catechinic acid rearrangement does not appear to occur when silica is present. This is confirmed by the very well developed C5,C7 band at 154 ppm in pine tannin indicating that the transformation of C5 and C7 to nonaromatic quinoid structures[4] does not occur. Of equal interest is that the catechinic acid rearrangement also does not occur, or occurs to a minimal extent, at pH 12, also in the absence of silica [Figs. 2(b), 3(b)], even when the tannin is examined in its solid hardened state, as already observed for tannins in solution.[1-3] The considerable increase of the 105-106 ppm band characteristic of C2-C6/C2-C8 auto-condensation in pine [compare Figs. 2(a) and 2(b)] to fill the gap between the 110 ppm (C4-C8/C4-C6) and 100 ppm
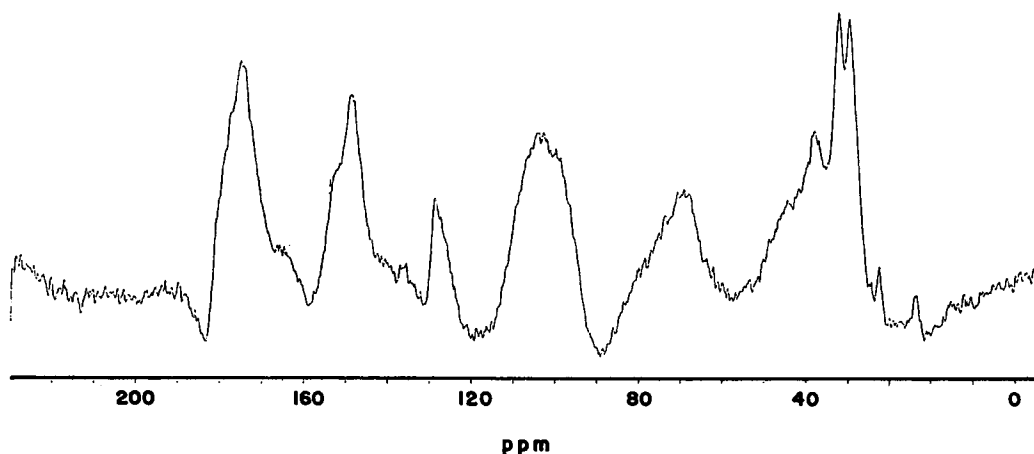

Figure 3a   CP-MAS NMR spectrum of pecan nut tannin extract concentrated water solution (40%) at pH 12, by the addition of 3% silica over a period of 10 min.
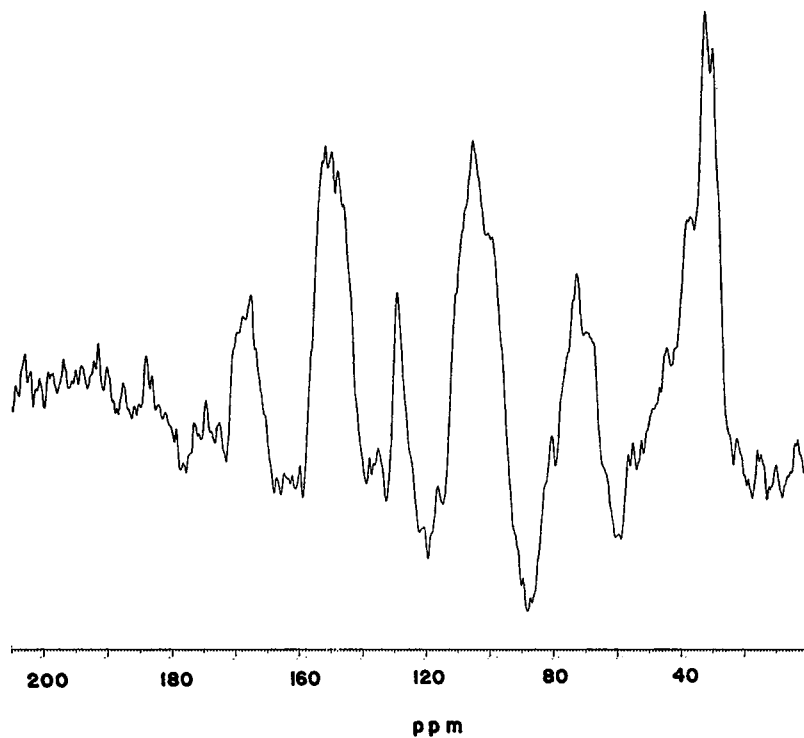
Figure 3b   CP-MAS NMR spectrum of pecan nut tannin extract concentrated water solution at pH 12, dried by vacuum evaporation of water.
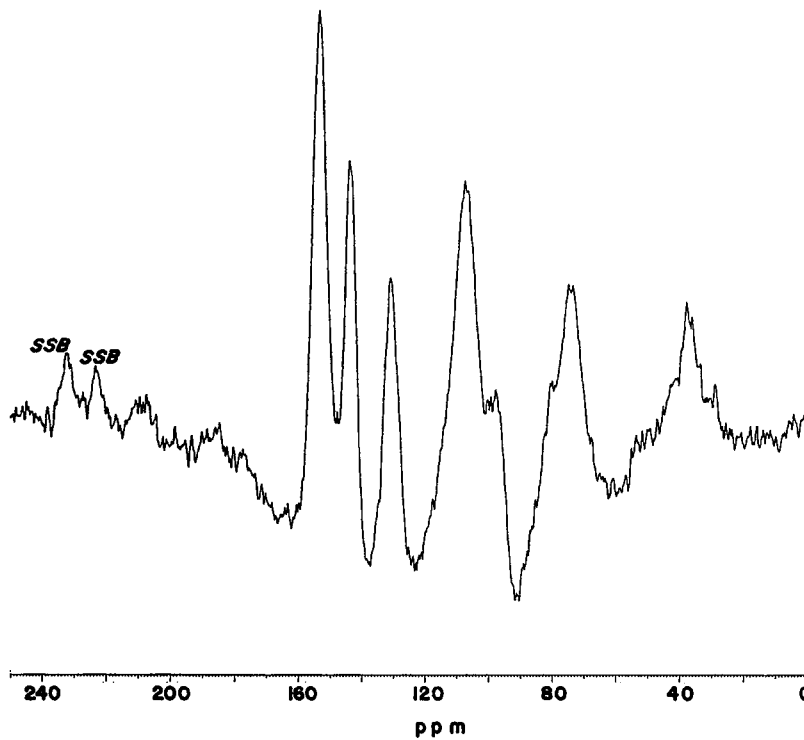

Figure 3c   CP-MAS NMR spectrum of dry pecan nut tannin extract at its natural pH (5.1). (SSB = spinning side bands).

(C10) bands indicates clearly that C2-C6/C2-C8 autocondensation has occurred and is quite extensive; furthermore, neither further C4-C8/C4-C6 interflavonoid bond formation by autocondensation nor interflavonoid cleavage has occurred.

Thus, in the case of silica-hardened procyanidins the shift to heterocycle opening rather than interflavonoid bond cleavage is confirmed on the hardened material: this indicates a major shift in the relative importance of the two reactions.

In the case of silica-hardened pecan nut tannin, as already observed,[1] the intense band at 176 ppm is assigned to enolic forms of B-rings quinoid structures obtained by base opening of the heterocycle pyran ring; some of these remain frozen in such a conformation due to the stabilizing effect of the pyrogallol, rather than catechol, B-ring in prodelphinidins. Notable is the appearance of these forms, and of the 176-ppm band, already at pH 12 without any silica, and their greater intensity when silica is present [compare Figs. 3(a), 3(b), 3(c)]. This indicates that in pecan nut tannin in which rapid autocondensation is well-known to occur[5,6] even without silica (but not to gelation) part of the 176-ppm band is due to the ease of heterocycle opening of prodelphinidins[1-3,5,6] and part is due to the "pegging" effect of the $-Si(OH)_4^-$ counterion already reported.[1,3]

In conclusion, it is then apparent that both of the two different types of tannin behave very differently to what can be observed with model compounds. Catechin monomer, procyanidin and prodelphinidin tannins clearly all gel in the presence of dissolved silica and other weak Lewis acids due to intermolecular C2-C6/C2-C8 autocondensation. The similarity of behavior, however, ends there: in the case of the model compound because intermolecular crosslinking competes with the catechinic acid rearrangement,[4] the latter rearrangement being equally or even more marked than autocondensation. In the case of the natural polymeric tannins instead, the catechinic acid intramolecular rearrangement is completely absent when dissolved silica is present leading to the predominance of intermolecular autocondensation and crosslinking. This contributes to explaining why both tannins gel in a matter of minutes at ambient temperature, while under the same conditions catechin monomer gels in about one month.

This illustrates that there appears to be little correspondence between monomeric model compounds reactions and reactions of the polymeric natural tannins. Some definite differences in behavior between the two types of tannins also occur, but these are small, mainly centering on the inversion of the relative ease of cleavage of the interflavonoid bond in relation to heterocycle opening in procyanidin tannins.

References

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