

Induced Accelerated Autocondensation of Polyflavonoid Tannins for Phenolic Polycondensates. I. ^{13}C -NMR, ^{29}Si -NMR, X-Ray, and Polarimetry Studies and Mechanism

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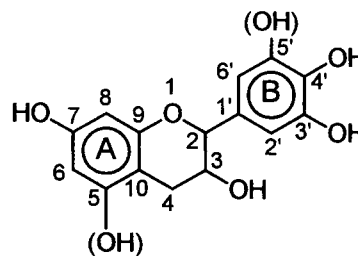
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SYNOPSIS

Polyflavonoid tannins have been found to autocondense and harden when in presence of small amounts of SiO_2 at high pH. Small amounts of boric acid and AlCl_3 were found to have the same effect. The mechanism of tannin autocondensation to hardening was found to depend on the Lewis acid behaviour of the additives used. Such mechanism involves Lewis acid acceptance of electrons from the ether oxygen of the flavonoid unit pyran ring with subsequent facilitation of base-induced heterocycle opening. The reactive C2 site created by heterocycle opening proceeds to autocondense with the reactive A-ring of a flavonoid unit on another chain denying to the flavonoid the possibility of intramolecular rearrangements to catechinic acid and phlobatannin which occur in model compounds. Si has been shown to pass through a coordination state of 5, by CP-MAS ^{29}Si -NMR. The portion of Si, which has not been able to complete the reaction due to premature hardening, remains attached to the flavonoids, in this coordination state, in the hardened network. The Si portion, which has completed the reaction and caused the hardening, reverts instead to SiO_2 and is detached from the flavonoid. The SiO_2 , H_3BO_3 , and AlCl_3 mechanism shows that their presence also reverses the relative facility of cleavage between interflavonoid bond and heterocycle opening in mainly procyanidin and profisetinidin tannins. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Thermosetting polyflavonoid tannin-formaldehyde resins have performed well in industrial applications as phenolic exterior adhesives for wood for the last 20 years.^{1,2} Industrial polyflavonoid tannin extracts are mostly composed of flavan-3-ols repeating units, and smaller fractions of polysaccharides and simple sugars.¹ Polyflavonoids in such tannin extracts present phloroglucinol or resorcinol A-rings and catechol or pyrogallol B-rings.



Scheme 1

The repeating units are linked to each other C4-C6 or C4-C8, the former predominating in tannins mostly composed of fisetinidin (resorcinol A-ring; catechol B-ring) and robinetinidin (resorcinol A-ring; pyrogallol B-ring) repeating units. The C4-C8 interflavonoid linkage instead predominates in tan-

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Table I Gel Times in Seconds as a Function of pH of Commercial Polyflavonoid Tannin Extracts By Autocondensation Induced By 3% SiO₂ (Mass/Mass Tannin Extract)

pH	Natural		Natural		Natural		Semi-sulphited		Semi-sulphited		PF	PRF
	Pecan	Mimosa	Pine	Quebracho	Pine	Quebracho	Pine	Quebracho				
Powder SiO ₂ (94°)												
-0.37	—	823	—	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel
0.40	225	Does not gel	—	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel
1.0	540	Does not gel	—	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel
4.22	—	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel
7.69	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel
8.00	85	230	119	752	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel
9.00	60	104	85	—	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel
9.50	—	—	—	110	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel
10.00	52	87	60	98	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel
11.00	43	73	42	73	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel
12.00	35	63	30	—	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel
Dissolved SiO ₂ (25°C)												
12.00	Instantaneous	Instantaneous	Instantaneous	Instantaneous	Instantaneous	Instantaneous	Instantaneous	Does not gel	Does not gel	Does not gel	Does not gel	Does not gel

nins composed of catechin (phloroglucinol A-ring; catechol B-ring) and gallic acid (phloroglucinol A-ring; pyrogallol B-ring) repeating units. When the polymeric tannins are composed of fisetinidin/robinetinidin units the polymers are respectively called profisetinidin/prorobinetinidin; when they are composed of catechin/gallic acid the polymers are called procyanidin/prodelphinidin, respectively.³ The free C6 and/or C8 sites on the A-ring are sites reactive with formaldehyde, due to their strong nucleophilicity, to form adhesives under the usual conditions in which these materials are used.

While the reactions of these natural polymeric materials with formaldehyde to give polycondensates have been used extensively, autocondensation reactions characteristic of these materials have never been used to prepare adhesive polycondensates in absence of aldehydes. Tannins autocondensations are known, but as they have been studied only on monomeric model compounds, their effect on polymeric systems has neither been studied nor even considered for resin preparation and hardening. Recently, a predominantly prodelphinidin tannin, pecan nut pith tannin extract (*Carya illinoensis*) has been found to undergo fairly rapid autocondensation reactions,⁴ although not to such an extent as to lead to cross-linked, hardened resins. This autocondensation reaction is based on the opening, under alkaline or acid conditions, of the O1-C2 bond of the gallic acid repeating unit and subsequent autocondensation between the carbocation at C2 of the open unit with the free C6 or C8 sites on a gallic acid unit of another polymer chain.

Although this reaction leads to noticeable increases in viscosity^{4,5} of concentrated (40%) tannin solutions, gelling does not occur. The work presented in this article was prompted by the chance finding that concentrated water solutions of pecan nut tannin extract gelled and hardened in a very short time by addition of small, even trace, amounts of silica, even at ambient temperature.

This article is then aimed at studying the reaction of autocondensation on the polymeric tannin itself, at accelerating it to lead to gelation and hardening of the material without the need for aldehyde-induced cross-linking, and in expanding this concept to other polyflavonoid tannins: In this regard the findings obtained on pecan nut (*Carya illinoensis*) pith tannin extract were also tested on pine (*Pinus radiata*) bark extract (a predominantly procyanidin tannin), black wattle or mimosa (*Acacia mearnsii* formerly *mollissima*, de Wildt) bark extract (a predominantly prorobinetinidin extract) and quebracho (*Schinopsis balansae*) wood extract (a predominantly

Table II Gel Times in Seconds As a Function of % SiO₂ (Mass/Mass Tannin Extract) of Pecan Nut Pith and Mimosa Bark Tannin Extract at Two Comparable pHs

Silica (%)	Mimosa pH 8.29 (seconds)	Mimosa pH 10.60 (seconds)	Pecan pH 8.30 (seconds)	Pecan pH 10.60 (seconds)
1	Does not gel ^a	Does not gel ^a	210	135
2	516	197	92	59
3	241	91	77	50
4	189	71	72	47
6	141	55	65	42

^a = No gel after 3600 s.

profisetinidin extract).⁶ All are commercially produced and used for adhesives.

EXPERIMENTAL

Gel Times

The gel times with SiO₂, boric acid and AlCl₃ of the four extracts in 40% water solutions were determined over the range of pHs shown in Tables I, II, and III, at 34°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 in the cases tried. 10 g of 40% tannin extract water solution adjusted with 30% NaOH to the pHs indicated in the tables is placed in a test tube and to it is added solid finely powdered

SiO₂ smoke (Aerosyl), or a 40% water solution of boric acid or AlCl₃. The percentage by mass of the autocondensation accelerating compound added was always 3% on the mass of solid tannin extract. Solutions of tannin extracts at high pH (pH 12) to which SiO₂ predissolved in 30% NaOH is added gelled and hardened within seconds at ambient temperature: on these latter ones (Table I) gel time determinations could not be carried out. 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 (94°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 method and is used extensively in Europe for wood adhesives.⁷ The gel time measurement is used to relate to the reactivity of the resin, in this case the

Table III Gel Times By Autocondensation of Polyflavonoid Pecan Nut Tannin Extract Induced at Different pHs By Different Lewis Acids

pH	pKa = 10	pKa = 9.22	pKa = 8.6	Strong acid
	SiO ₂ (s)	Boric Acid (s)	AlCl ₃ (s)	Phosphoric and Polyphosphoric Acid (s)
4.49	Does not gel	5400	—	Does not gel
4.65	Does not gel	2040	—	Does not gel
4.96	Does not gel	1800	—	Does not gel
5.50	Does not gel	1140	—	Does not gel
6.00	Does not gel	280	—	Does not gel
6.53	Does not gel	102	—	Does not gel
7.18	Does not gel	83	—	Does not gel
7.88	112	(270) ^a	—	Does not gel
8.66	60	(360) ^a	—	Does not gel
9.55	49	(360) ^a	780	Does not gel
12.00	35	—	—	Does not gel

^a Rapid agglutination at ambient temperature causing apparent lengthening of gel time.

Table IV ¹³C NMR Relative Bond Intensities of Catechin Model Compounds With and Without SiO₂

ppm	Group	Cat. acid keto		C=O	176-180	169	162	Quinone acid and enol B-ring		C5, C7	C9	C3', C4'	C1'	C6'	C5', C2'	C4-C8/ C2-C8		C10	Free		C4	
		C=O	C=O					C6	C8							C2	C3		Cat. acid			
212		192	183	176-180	169	162	156-158	150-159	146-147	131	128	120	116-118	110-111	106	101-103	97	95-96	83	68-69	31	27-29
	Catechin monomer, unreacted	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Catechin, + 10% SiO ₂	—	—	—	—	—	127; 132	—	95; 100	96	—	127	126	—	—	89	115	128	121	122	—	105
27	25°C, pH 12.5	47	33	28	60	36	56	45	100	44	60	55	97; 62	67	42	44	33	38	51	38	43	
	Catechin alone	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	93°C, pH 12.5, 4 hours	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
34	BLANK	53	—	40	47	100	—	27	27	—	52	56	60	24	54	40	32	36	53	34	54	
	Catechin + 10% SiO ₂	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
91	93°C, pH 12.5, 4 hours	126	44	48	44	91	39	37	100; 55	56	71	66	69	85	46	38	38	39	133	48	48	35

tannin extract. Shorter gel times indicate more reactive materials.

¹³C-NMR

Solutions ¹³C-NMR and solid state (CP-MAS) ¹³C-NMR spectra were obtained on a Bruker AC200 FT-NMR spectrometer, at a frequency of 50.3 MHz with the sample spectra at 35 Hz for liquid and 40 Hz for solid spectra. Chemical shifts were calculated relative to (CH₃)₃ Si(CH₂)₃ SO₃ Na for NMR control in D₂O. All the spectra were run overnight. Acquisition time was 1.08 seconds for liquid and 0.094 seconds for solids with the respective number of transients of 10,000 and 20,000. All spectra were run with relaxation delay of 5 seconds and were accurate to 1 ppm. The spectra were run with nOe enhancement, spectral width was 15,000 Hz (liquid) and 22,000 Hz (solids), digital resolution was 0.825 (liquids) and 1,327 (solid). Typical spin-lattice relaxation times were not measured but standard values shown in the literature were used.⁷ The ¹³C NMR bond intensities reported in the tables are integrated intensities. The liquid samples were prepared by diluting 40% mass/mass aqueous solutions of tannin extracts with D₂O in 1 : 4 mass proportion. In Tables IV and V the ¹³C NMR bond intensities were reported to a 100% bond intensity for the C3', C4' bond for parity of comparison between the different cases. Results are shown in Tables IV and V and Figures 1 a, b, c, and 2 a, b.

²⁹Si-NMR

The solid-state ²⁹Si-NMR spectra was obtained on a Bruker AH300 FT-NMR spectrometer and a DAB probe, at a frequency of 59.63 MHz, MAS ω_r 3,000 Hz, relaxation delay of 10 seconds and 22,700 transients. ²⁹Si chemical shifts were calculated relative to (CH₃)₃ Si(CH₂)₂ COONa for NMR control equal to 0. The spectrum obtained is shown in Figure 3a. The liquid ²⁹Si-NMR spectra of catechol, pyrogallol and (+)-catechin flavonoid monomer + 4% SiO₂ were obtained on a Bruker AC 200 FT-NMR spectrometer.

Crystallography

A 4% SiO₂ hardened tannin resin was analyzed by x-ray diffraction. SiO₂ fine powder and a mixture of 4% SiO₂ powder mechanically mixed with spray-dried tannin powder were also analyzed by the same technique. The x-ray diffraction patterns of the

samples were recorded on a Philips powder diffractometer. Cu radiation ($2\theta^\circ = 1.5405 \text{ \AA}$) was used with a nickel filter. The powdered samples were placed on the aluminium sample holder of the camera. The traces were recorded with a detection speed of $2^\circ/\text{minute}$. The traces obtained and the reflections relative intensities and angles are shown in Figure 4 and Table VI.

Potentiometry

Potentiometry of water solutions 0.05 M pyrogallol and of 0.05 M pyrogallol + 0.05 M SiO_2 , titrated with 0.5 M KOH on a Metrohm at a consistent 22°C . The results are shown in Figure 5.

Tannin Extracts

The tannin extracts used were commercially produced ones and were obtained from the following sources: Pecan nut pith tannin extract from Bakelite AG, Duisburg, Germany and Advanced Resins Systems, Memphis, USA. Pine tannin bark extract from Diteco Ltda, Concepcion, Chile. Mimosa tannin bark extract from Bisonboard South Africa (Pty) Ltd, Boksburg, South Africa. Quebracho tannin wood extract from Indunor, Silva-Ledoga, Buenos Aires, Argentina.

DISCUSSION

The trends in gel times at 94°C and ambient (Table I) show that gelation and hardening of 40% water solutions of pecan and tannin extract occur readily on addition of small amounts of SiO_2 dissolved in sodium hydroxide. From just these data (Tables I and II) it is not possible to deduce if tannin cross-linking occurs because dissolved silica acts as a hardener, or because it acts as some sort of catalyst for tannin autocondensation. The percentage of silica used does influence the rate of gelation but over a few percentages not to a great extent, possibly inferring that a catalytic effect is involved (Table II). Nondissolved SiO_2 clearly does not present the same behavior, and the tannin does not harden: the rate of gelation varies according to the pH used (Tables I and II), this depending somewhat from the solubility or lack of it, of SiO_2 at different pHs.

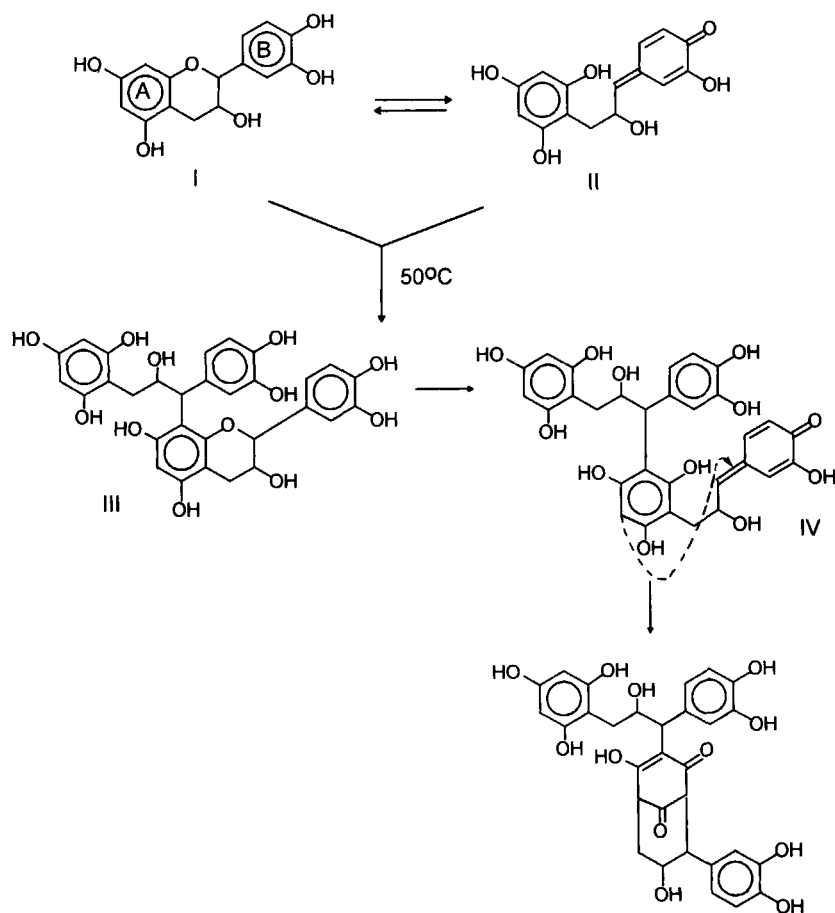
^{13}C -NMR spectra of the autocondensation of the model compound monomeric catechin in presence or absence of 10–20% dissolved SiO_2 give some additional insight (Fig. 1a–c, Table III). Monomeric

Table V ^{13}C NMR Relative Bond Intensities (ppm) of Commercial Polyflavonoid Pecan Nut Tannin Extract With and Without SiO_2

Group	Catec. acid		ArC=O	C5, C7 (C9)	C9	C3', C4'	C1'	C4-C6/		C2-C8	C6	C8	cat. acid	C4
	C=O 2/3	C=O 196						link	link					
Pecan tannin extract natural pH = 5.6	—	—	—	66; 70	—	100	62	66	41	40	29	—	—	37
Pecan tannin extract pH = 12.0	37	42	49	60	—	100	60	77	55	37	32	51	—	39
Pecan tannin extract + 3% SiO_2 , pH = 12.0	—	—	112	—	75	100	64	79	86	25	25	—	—	40

catechin when in solution in alkaline environment autocondenses readily to give the well known catechinic acid rearrangement.⁸ In this rearrangement

the two ketones carbonyls and the enolic carbon signals of the nonatrione ring formed appear at 203, 186, and 173 ppm, respectively.⁸



Scheme 2

In all the spectra of the catechin model autocondensation these three bonds are all present indicating that extensive catechinic acid rearrangement has occurred. However, there are also clear differences between the spectra of catechin autocondensation in the presence or absence of dissolved SiO_2 (Table III). First, in all cases the C2-C8 signal of the interflavonoid bond at 105–106 ppm appears clearly. Second, in the SiO_2 /catechin cases the C4-C8 interflavonoid bond at 109–111 ppm also appear clearly while it does not when SiO_2 is absent. Third, when SiO_2 is present, under the identical conditions of pH, temperature and reaction time, autocondensation appears to be much more extensive (compare 25°C SiO_2 with 4 h 93°C no SiO_2 , Table II). The indications are then that (i) catechin has autocondensed more rapidly (not more extensively) when

dissolved SiO_2 is present and that (ii) the autocondensation has occurred mainly by hererocycle opening and formation of C2-C8 interflavonoid linkages, but also (iii) some lesser C4-C8 and C4-C6 autocondensation, an unexpected finding, has occurred. The presence of C4-C8 linkages might be explained by mechanisms already detected involving heterocycle opening at C4,⁹ but it is more likely by attack of the benzylic C4 on the C8 site of another monomer; the free C4 signals at 31 ppm decreasing, as would be expected in both of the above two cases. The promotion by SiO_2 of the C4-C8/C4-C6 linkage is minimal and must involve a SiO_2 -promoted mechanism. In all the model compounds spectra however, a broad band at 176–178 ppm also appears. This can be assigned to a para alkyl quinone structure of aromatic character, according to Pretsch et

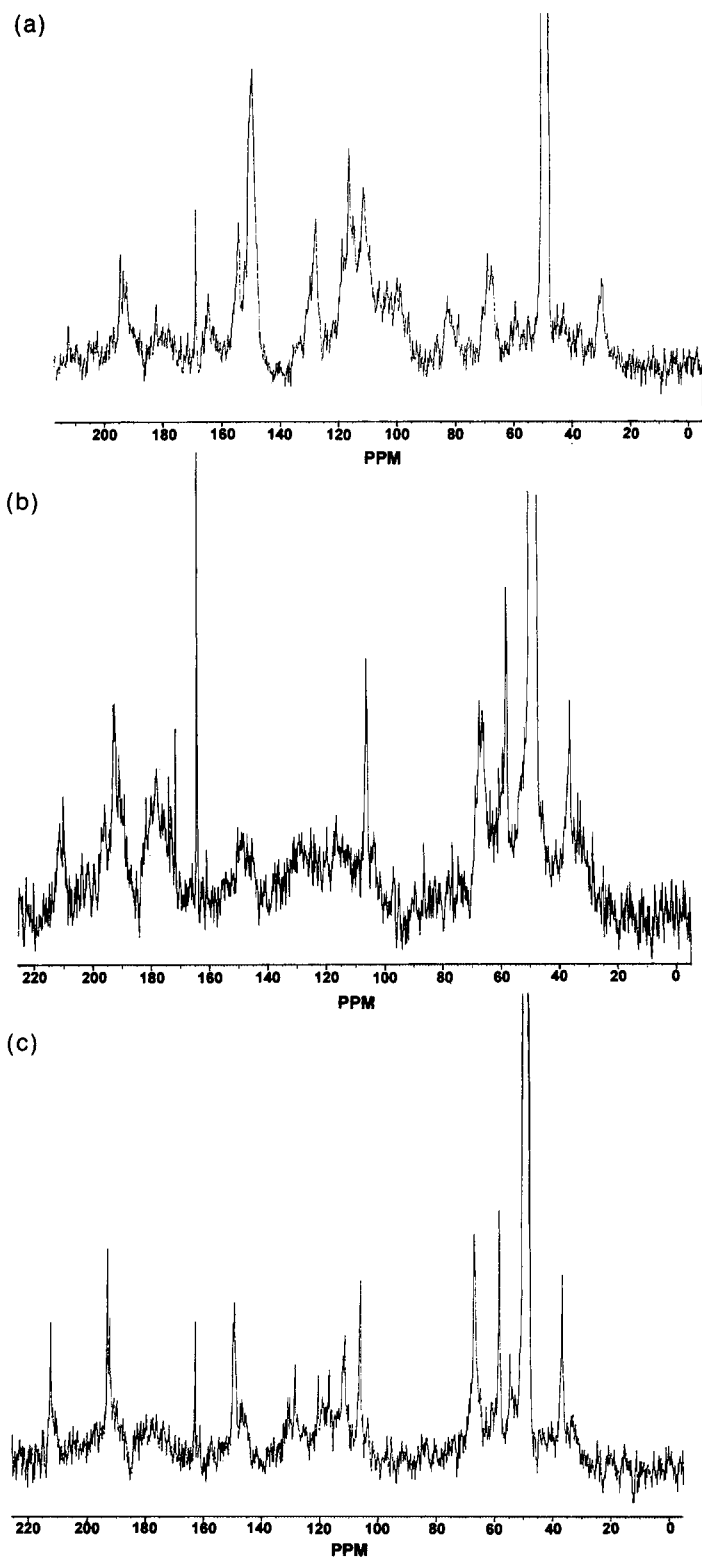


Figure 1 ^{13}C -NMR of catechin model reacted (a) for 30 min with 10% by mass SiO_2 at ambient temperature 25°C , pH 12.5, (b) by itself for 4 h at 93°C , pH 12.5, and (c) with 10% mass of SiO_2 , for 4 h at 93°C , pH 12.5.

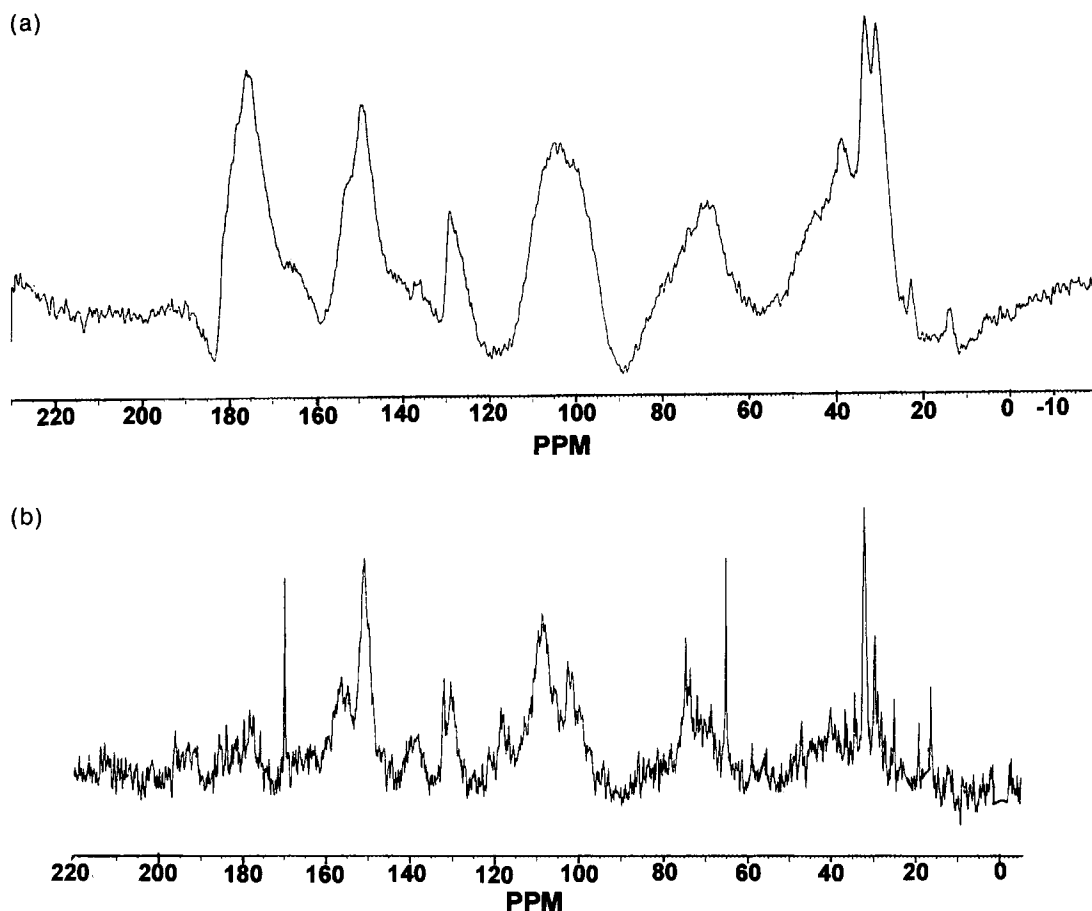


Figure 2 (a) ^{13}C -NMR (CP-MAS) of pecan nut tannin extract hardened with 4% SiO_2 , at pH 12; (b) ^{13}C -NMR of concentrated pecan nut tannin extract without any SiO_2 , at pH 12.

al.¹⁰ This would have a shift of $180.4 - 2.8 = 177.6$ ppm, which considering the precision of ± 1 ppm of the spectra fits well with the observed 176–178 ppm. This band is then the carbonyl signal of the aromatic alkyl quinone from the B-ring in structures II and IV, or of an alkyl quinone formed on the A-ring.

The solid-state ^{13}C -NMR spectrum obtained from pecan nut tannin extract hardened with 4% SiO_2 at pH 12, using a cross-polarization (CP) pulse sequence to improve signal to noise ratio and magic angle spinning (MAS) to improve line width, gives some indication of what has occurred (Fig. 2a, 2b; Table V). Comparing unreacted with SiO_2 -reacted tannin two main differences are evident from the ^{13}C -NMR spectra: firstly, the C2-C8 band at 105–106 ppm characteristic⁵ of C2-C8 autocondensation induced by heterocycle opening has noticeably and considerably increased in intensity. The C4-C8 band at 109–111 ppm is still present but has increased to a much lesser extent. Furthermore a very noticeable,

intense new band at 176 ppm has appeared (the alkyl quinone structure of the B-ring as in the model compounds). What is most noticeable is the absence of the two carbonyl and the enolic bands at 203, 186, and 173 ppm: hence, no catechinic acid rearrangement occurs nor C4-C8 interflavonoid bond cleavage. These are important differences between what is observed with monomeric model compounds and what instead is observed on the natural polymer. Extensive heterocycle opening then definitely occurs in the natural tannin polymer, much more extensively than when dissolved SiO_2 is absent. This is supported by the small increase of the C5, C7, and C9 band at 150–155 ppm due to C9 increase by heterocycle opening, the C1' band at 125–131 ppm remaining unaltered, the C4-C6/C4-C8 band at 103–111 ppm increasing somewhat and particularly the C2-C6/C2-C8 band at 105–106 ppm increasing considerably indicating mainly C2-C6 (and some C2-C8) autocondensation, but also some C4-C6/C4-C8

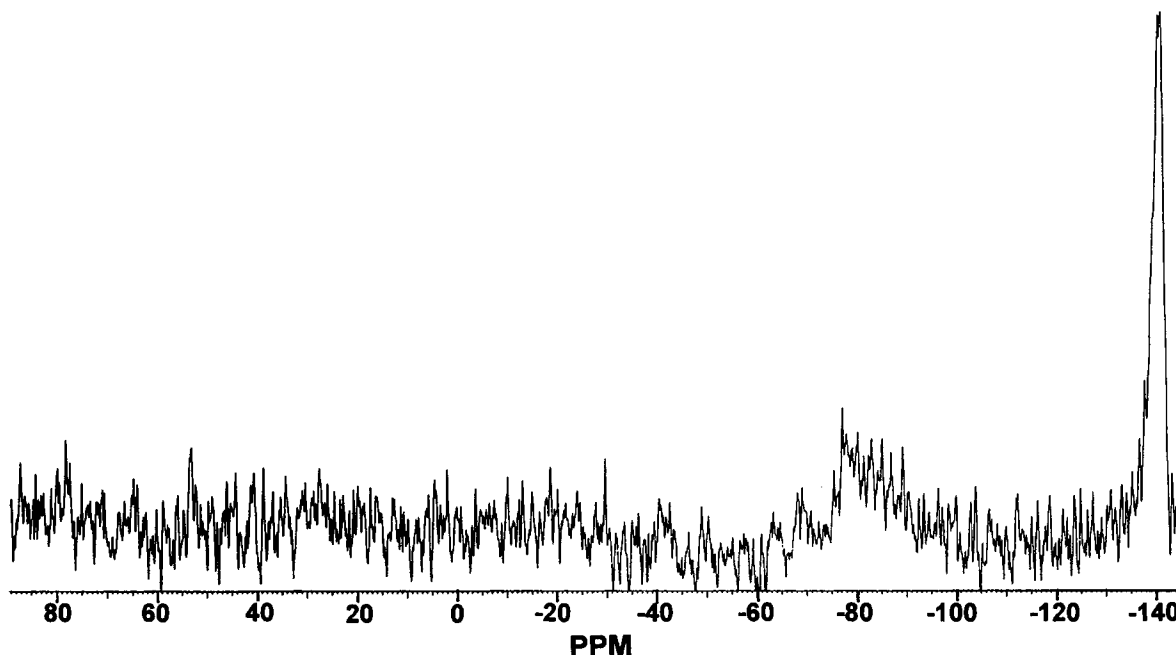


Figure 3a ^{29}Si -NMR (CP-MAS) of pecan nut tannin extract hardened with 4% SiO_2 , at pH 12.

further autocondensation. The free C6 band at 96–98 ppm decreases markedly confirming that C2–C6 is the predominant mode of autocondensation, while the free C8 band at 95–96 ppm also decreases, but to a lesser extent, indicating that, possibly C2–C8

bands are also formed to a smaller extent (involving the upper terminal units of the chain which have free, reactive, C8 sites). The C4 band at 27–31 ppm remains mostly the same indicating that under the conditions used the new mechanism of heterocycle

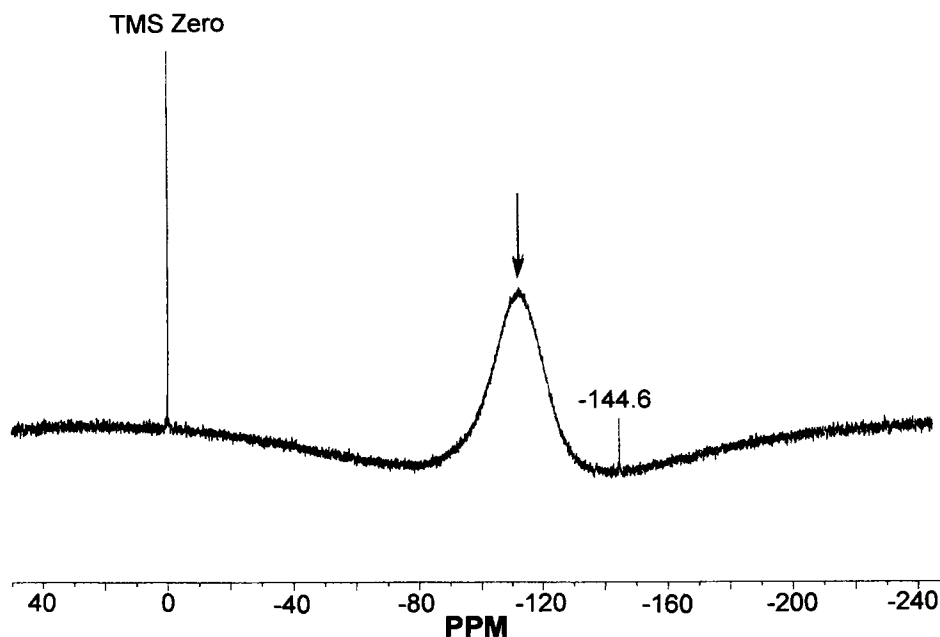
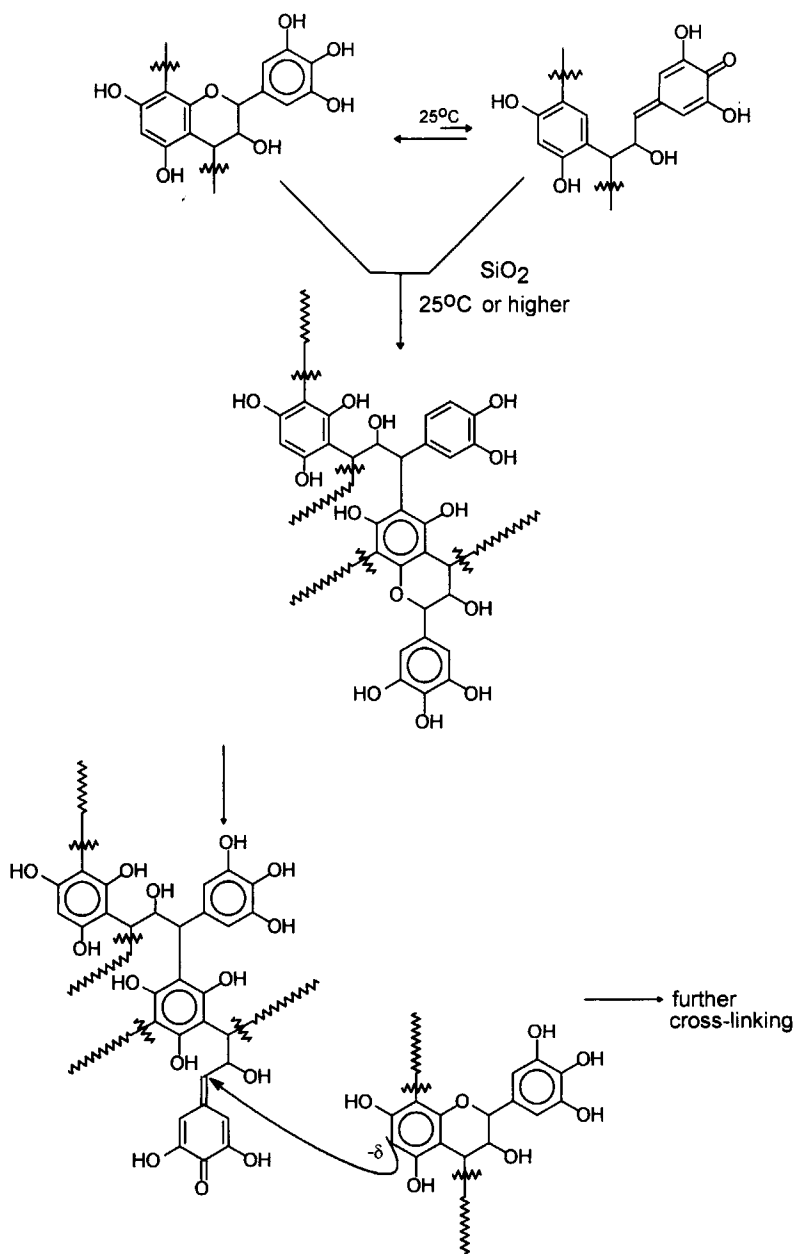


Figure 3b ^{29}Si -NMR of catechol plus 4% SiO_2 at pH 12.

opening at C4⁹ does not occur to any great extent in concentrated solutions of the natural polymer under the conditions used. Thus, considering that the catechinic acid rearrangement involves as a first step C2-C8 autocondensation this (mostly C2-C6) is shown to occur also in the natural polymer. In the model compounds the second reaction step to a nonatrione ring does however ensue only because rotation around the C4-C10 and C4-C3 bonds necessary for the rearrangement to occur is, in practice, unhindered in the lower terminal unit of the dimer

obtained. This is not the case for the natural polymer in which a repeating unit is part of a long chain and is thus severely hindered by a number of other repeating units preceding and following it along the same chain. Equally, the acceleration by SiO₂ of heterocycle opening decreases interflavonoid cleavage of the terminal units which are those causing catechinic acid rearrangement (Fig. 2b). Such severe hindrance ensures that the reactive C2 rather reacts with the free C6 or C8 sites of a flavonoid unit in another chain, leading to cross-linking. Thus, the proposed reaction is as follows:



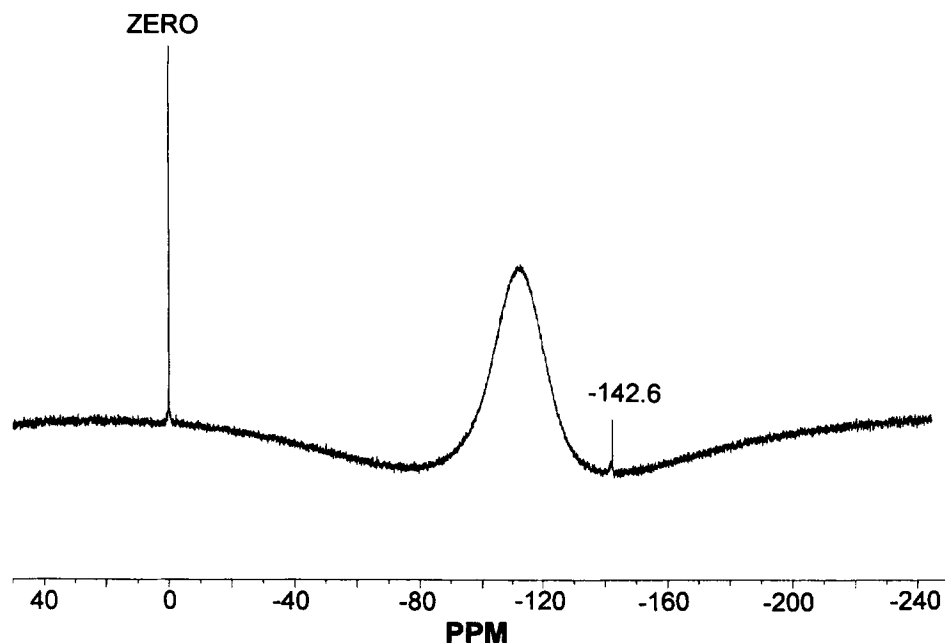
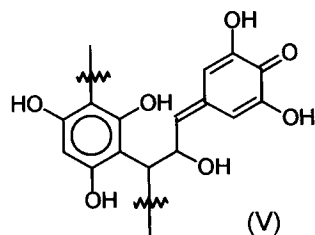


Figure 3c ^{29}Si -NMR of pyrogallol plus 4% SiO_2 at pH 12.

Because of the length of the polymers and their high functionality, many of the heterocycles which open later, when the process of gelation is already well underway, are likely not to be able to participate in cross-linking. Many such groups will then remain "frozen," in the already solid tridimensional network, in the B-ring quinone configuration (V):



Scheme 3

These are the source of the strong ^{13}C -NMR band at 176 ppm observed in the CP-MAS spectrum. This band spans from 160 to 182 ppm indicating that this is not the enolic form of the conjugated diketone observed in the catechinic acid rearrangement of the models, especially because the two other keto bands characteristic of catechinic acid⁸ are not present (Fig. 2a and b). This also implies that, under the conditions used for these polycondensations in concentrated solutions of natural tannin polymers the mimosa tannin favored alkaline-induced phlobatannin rearrangement can occur, but not to any great

extent, for the identical reasons which prevent the catechinic acid rearrangement in pecan tannin. If the phlobatannin rearrangement occurred and went to the same conclusion obtained for model compounds work on dimers, mimosa tannin could not autocondense rapidly in presence of dissolved SiO_2 : another example of the different routes rearrangements take when studied with diluted model compounds rather than concentrated solutions of the natural polymer. A second generalization which is found wanting by the results outlined is that the favorite cleavage of procyanidin/prodelphinidin polymers is at the C4-C8 interflavonoid links rather than at the heterocycle. This is now found to be correct for predominantly procyanidin tannins (pine) but it is definitely incorrect for predominantly prodelphinidin ones (pecan). Equally, that the favorite cleavage of profisetinidin/prorobinetinidin tannins is at the heterocycle, is an incorrect generalization: it is correct for predominantly prorobinetinidin tannins (mimosa), but it is not for predominantly profisetinidin ones (quebracho) where C4-C6 and C4-C8 cleavage is instead favored. In the case of quebracho this should lead to extensive depolymerization on alkaline heat treatment, as confirmed already by ^{13}C -NMR on the natural polymer.^{5,6} It also leads, in the same study,⁶ to the incorrect conclusion of pecan being a mixed resorcinol/phloroglucinol A-ring type of tannin, due to the facile ring opening generalization;¹¹ while it is

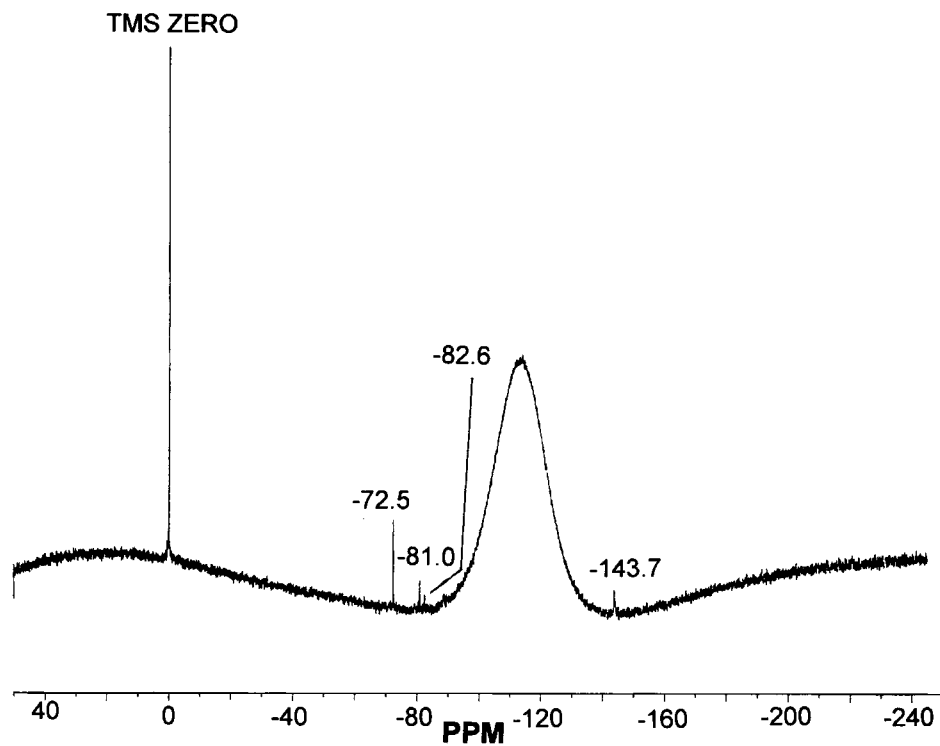


Figure 3d ^{29}Si -NMR of (+)-catechin (flavonoid monomer) plus 4% SiO_2 at pH 12.

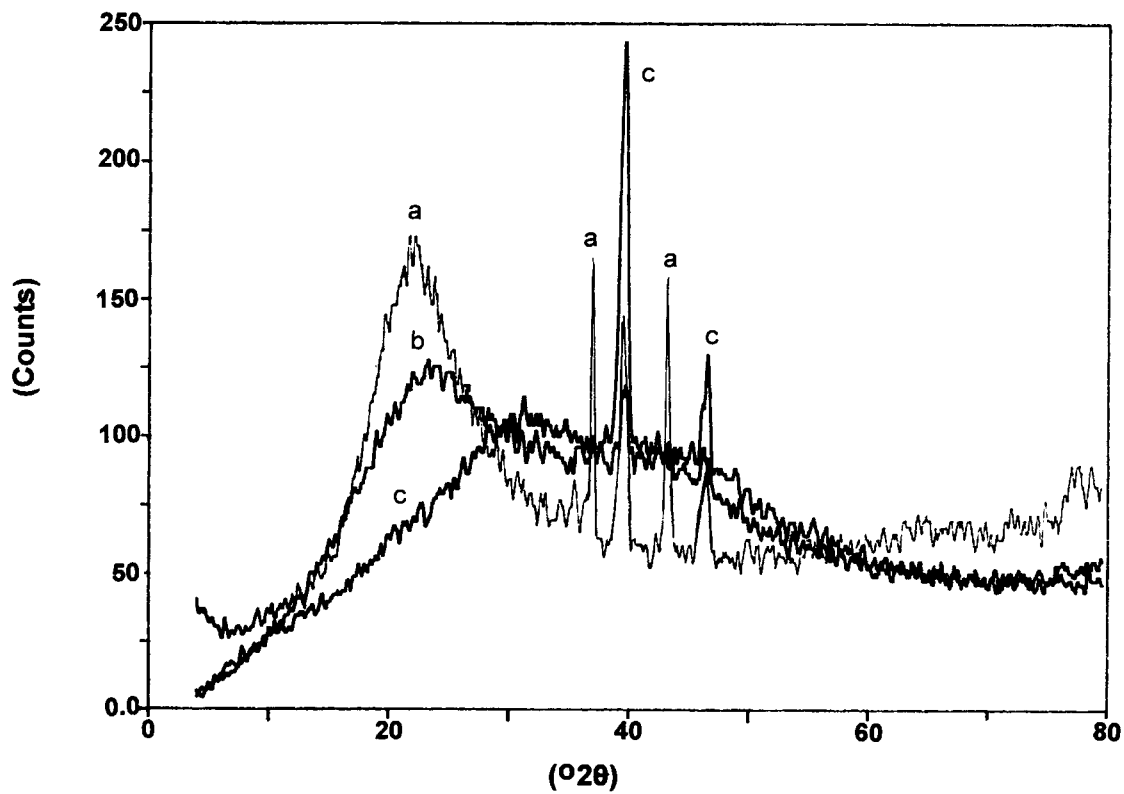


Figure 4 X-ray diffraction traces of (a) SiO_2 powder, (b) mechanical mixture of unreacted powder pecan tannin extract and 4% powder SiO_2 , and (c) 4% SiO_2 hardened pecan nut tannin extract.

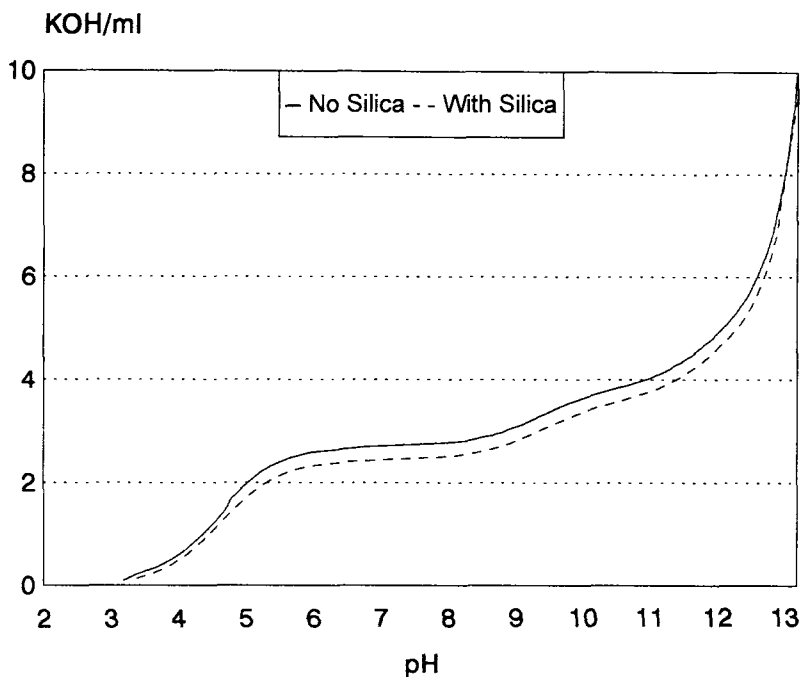


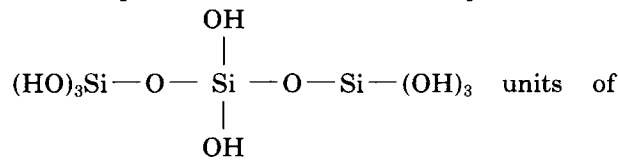
Figure 5 Potentiometric curves of KOH vs pH of (a) pyrogallol alone and (b) pyrogallol + 25% dissolved SiO_2 .

not a mixed tannin but predominantly a prodelphinidin one, the facile ring opening being due to the pyrogallol B-ring predominant in the units.

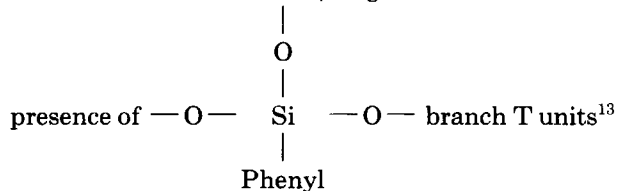
Why does SiO_2 dissolved in sodium hydroxide, or diluted sodium silicate, catalyse the autocondensation of the tannin? The ^{29}Si -NMR (CP-MAS) spectrum (Fig. 3a) of the pecan tannin/ SiO_2 hardened material and the ^{29}Si -NMR liquid spectra of SiO_2 of catechol, SiO_2 /pyrogallol and SiO_2 /(+)-catechin supply some indications (Figs. 3b, 3c, 3d). About one third of the silicon (Fig. 3a) is present in a series of peaks from -77 to -90 ppm while two thirds of the silicon is present as a compound of shift -140 ppm in the solid-state tannin-silicon spectrum. As low a shift as -140 ppm cannot be reached by any siloxanes (down to -110 ppm minimum)¹² or even by compounds in which Si is indirectly linked to C or to Si.¹³ It implies a coordination number of the Si higher than 4¹² for at least some of the Si atoms, by themselves or in a polysiloxane chain. Higher coordination number Si compounds have high shielding, hence the shift to values of -130 to -180 ppm for such compounds. Compounds of higher coordination number form with ease in the case of Si: for instance SiF_5^- and SiF_6^{2-} ions form readily from SiF_4 because silicon can accept more electrons in its valence shell on the third orbital and even when the octet in the 3s and 3p orbitals is complete.¹³ In this

reaction it behaves as a Lewis acid. The ^{29}Si NMR shift at -140 ppm implies a Si of coordination 5, linked at some site on the flavonoid unit. This gives a lead on what the acceleration mechanism is likely to be. First, it indicates that the formation of *ortho*-diphenol complexes by $\text{Si}(\text{OH})_4$ on the B-ring is not contributing to the mechanism because these are not detected in the ^{29}Si -NMR CP-MAS, second, because those complexes are likely to be very weak^{14,15} and, third, because silicic acid *ortho*-diphenol complexes are not likely to be present with silicon in coordination number higher than 4. To this effect potentiometric titrations of pyrogallol with or without dissolved SiO_2 present (Fig. 5) over the pH range 3–13 clearly indicate that dissolved SiO_2 does not form *ortho*-diphenol complexes; the two curves follow exactly the same trend (Fig. 5). That this is the case can be seen from the ^{29}Si NMR spectra of 4% SiO_2 with the model compounds catechol, pyrogallol and (+)-catechin. In these, at whatever pH, > 99% of the silica is present in $\text{Si}(\text{OH})_4$ only, with much less than 1% in the -140 ppm range (Fig. 3b–d). The approximately one third of Si at -77 to -90 ppm in the ^{29}Si -NMR (CP-MAS) (Fig. 3a) appears to be due to $-\text{O}-\text{Si}-(\text{OH})_3$ polysiloxane. ^{29}Si -NMR (CP-MAS) (-77 ppm to -82 ppm) (Fig. 3a) appears due to $-\text{O}-\text{Si}-(\text{OH})_3$ polysiloxane terminal M units¹³ and chain D units¹³ of configura-

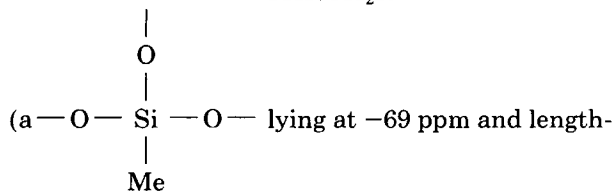
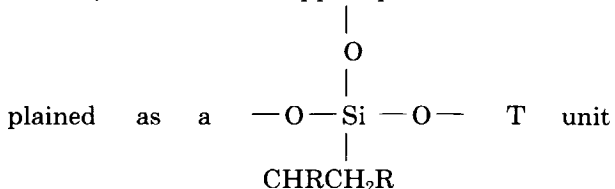
tion —O— Si —O—. The relative abundance of the peaks indicate thus the presence of



units of number average degree of polymerization of approximately 3. The —77 peaks itself which although small is the most evident, might also indicate the



in which a phenyl group is directly attached to the silicon. That a small amount of direct bonding Si-C occurs in such system can be noticed from the SiO₂/(+)-catechin model ²⁹Si NMR liquid spectrum (Fig. 3d): while the small peaks at —82.6 and —81.0 are clearly due to polysiloxanes —O—Si—(OH)₃ terminal M units,¹² the absence of —85—–90 ppm indicating that there are dimers,¹² the —72.5 ppm peak can be ex-



ening of the alkyl chain adding —3 ppm to the shift¹²). The only alkyl chain present in the flavonoid monomer (+)-catechin is the one of the heterocyclic pyran ring, an indication that (1) the small amount of Si linkage to carbon might not be specific (to an alkyl chain in the model, possibly to a phenyl ring in the tannin) or that (2) in the case of the flavonoid monomer model an initial attack of Si to the C2, and opening of the pyran ring, is actually detectable. Equally, the well-documented¹⁶ reaction of phenolic resins hydroxyls with siloxanes to form Si—O—Ar bonds is not involved, or is not the determining reaction by itself because such a mechanism alone did

not lead to gelation of PF resins (Table I) and thus would not account by itself for the gelation of the tannin.

It is of interest (Table III) what other materials do give gelling of the tannins, and which others do not. The finding is that it is not the polymeric nature of the acid determining gelling (Table III), but that the weaker the acid the faster is the gelling. The common thread in Table III is that all the materials which do gel the tannin behave as Lewis acids. Boric acid ionizes in an unusual way in water: instead of donating one of its H⁺ to water, it removes an OH[–] from a water molecule, leaving an H⁺ which combines with water to form H₃O⁺.¹³ Thus, B(OH)₃ also behaves in water as a Lewis acid, the Boron atom having a vacant 2p orbital which can accept an electron pair from H₂O or from other lone pair-carrying groups.¹³ AlCl₃ also is well known to behave in this manner as a Lewis acid.¹⁴

Mono and dimeric model compounds studies of procyanidins (pine) and profisetinidins (quebracho) tannins have indicated that alkali interflavonoid bond cleavage precedes the opening of the pyran ring.¹⁷ It is known now that in predominantly prodelphinidin (pecan) and prorobinetinidin (mimosa) tannins the opening of the pyran heterocycle precedes instead the interflavonoid bond cleavage (if interflavonoid cleavage occurs extensively at all):⁶ this is due to the greater susceptibility to cleavage of the O1-C2 bond induced by the base deprotonation of the C4' hydroxyl¹⁸ as a consequence of the stronger nucleophilicity of the pyrogallol B-ring. Thus, in procyanidin and profisetinidin tannins, when catalysts such as SiO₂ are not present, the reaction in alkali will take a course already reported¹⁹ which does not lead to autocondensation nor to an increase in molecular mass. Prodelphinidin and prorobinetinidin tannin solutions however, without SiO₂ do not gel by themselves but rather, due to the limited number of units undergoing pyran ring opening and autocondensation in absence of a catalyst, should present a noticeable increase in viscosity just on standing at ambient temperature, or being heated, at high pH: this increase in viscosity has been observed and reported.^{4,6,20} This indicates that, in predominantly prodelphinidin (pecan) and prorobinetinidin (mimosa) tannins, gelling is induced by the acceleration or greater extent of pyran ring openings induced by the dissolved SiO₂: the reaction is then highly specific to cleavage of the pyran ring. In predominantly procyanidin (pine) and profisetinidin (quebracho) tannins, the specificity of the acceleration by dissolved SiO₂ for pyran ring cleavage ensures that interflavonoid cleavage does not

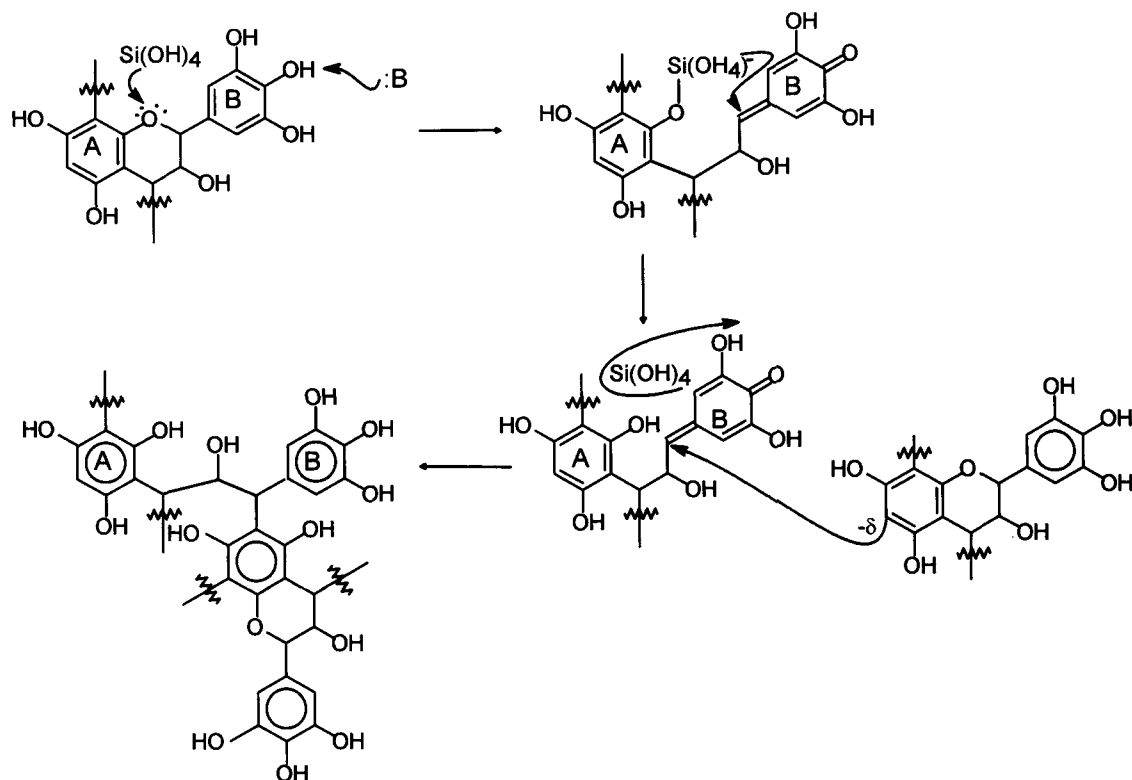
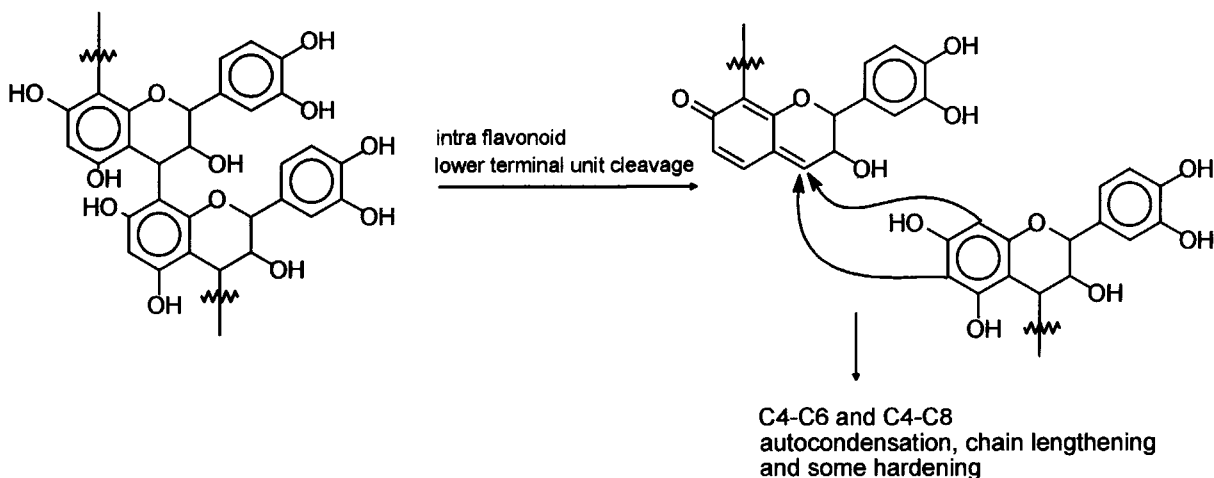


Figure 6 Proposed autocondensation mechanism of SiO_2 and Lewis acids-induced autocondensation and hardening of polyflavonoid tannins.

remain the favored reaction. If acceleration of pyran ring opening is very marked, then interflavonoid bond cleavage will not occur anymore, or to a much reduced extent: the behavior of these two tannins will now be identical to what is observed for pecan and mimosa, as indeed is the case (Table I). A mechanism can then be proposed (Fig. 6). It is interesting to note that the mechanism proposed in Figure 6 would also be consistent with the more recent concept of a one-electron (radical) mechanism being involved in pyran ring cleavage.²¹

The ^{13}C -NMR CP-MAS of the SiO_2 autocondensed pecan tannin does clearly indicate that no catechinic acid rearrangement has occurred by the absence of its characteristic bands at 213, 186, and 173 ppm. The monomeric and dimeric model compounds ^{13}C -NMRs instead show extensive catechinic acid rearrangement. This has some importance, because in the mechanism proposed in Figure 6, after the initial attack of the $\text{Si}(\text{OH})_4$ to cleave the pyran ring the negative $-\text{OSi}(\text{OH})_4^-$ group could itself block the C2 site, ensuring that no catechinic acid or phlobatannin intramolecular rearrangement takes place. This further blockage to intramolecular rotation at the interflavonoid C4-C8 and of the C3-C4 bonds might or most likely might not occur. If

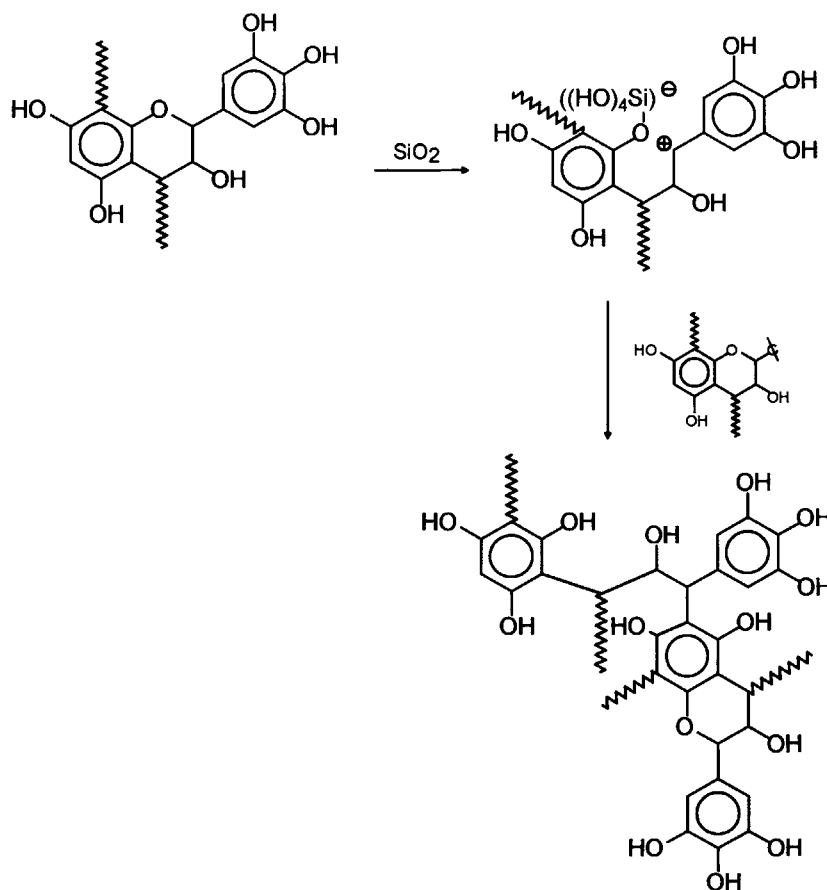
it does occur it further ensures that attack at C2 comes only from an A-ring of a flavonoid unit on another chain. In reality, catechinic acid rearrangement signals are absent in their ^{13}C -NMR when any of the four tannins is heat treated at a mild pH 8, 90°C for 3 hours^{12,21} in absence of SiO_2 . This indicates that in concentrated solutions the steric hindrance exercised by the long chain segments preceding and following the opened flavonoid unit already severely limits bond rotations and intramolecular rearrangements in concentrated natural tannin polymer solutions unless more drastic conditions are used. The above does not explain the lack of such rearrangement in the terminal units of the chain at the very drastic pH of 12: again all the ^{13}C -NMR evidence⁶ on concentrated solutions of the four natural tannins indicates that both in presence or absence of SiO_2 such rearrangements still do not appear to occur at pHs of up to 8. In procyanidin (pine), in absence of SiO_2 , cleavage of the C4-C8 interflavonoid linkage holding the lower terminal unit will create the residual chain fragment to which the departed terminal unit belonged. This has been reported to form an A-ring quinone¹⁹ which is then likely to autocondense with another chain without any rearrangement.



Scheme 4

The latter explaining perhaps the slight increase in C4-C8 linkages observed in the ^{13}C -NMR spectra. It is interesting to note that even the monomeric, departed lower terminal unit does not appear to form any catecholic acid derivative, again by the absence of its characteristic ketoenolic signals in ^{13}C -NMRs

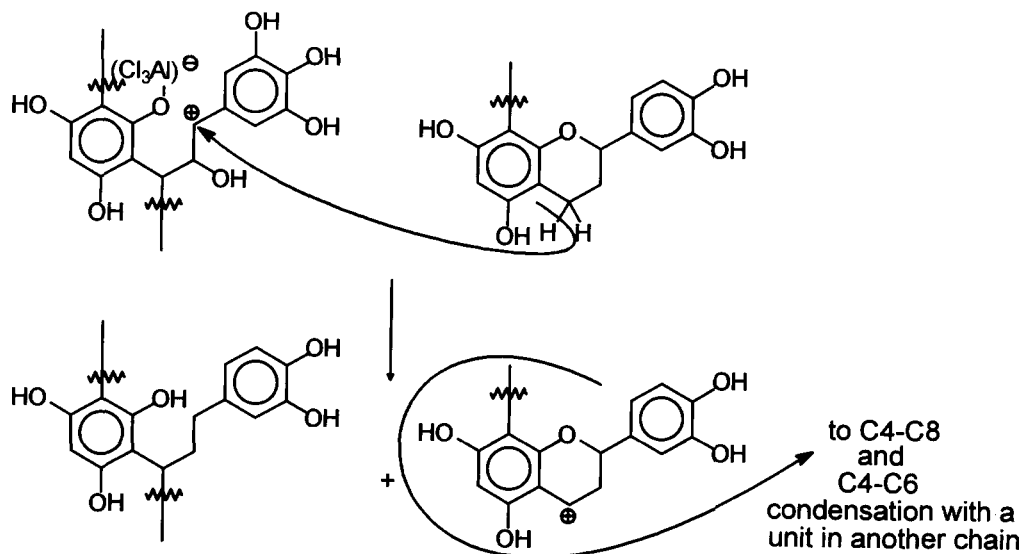
of concentrated natural tannin polymer solutions. The reaction can also be better explained by a carbocation mechanism, this because it occurs also at neutral and mildly acid pHs, indicating that base-induced deprotonation of phenolic-OHs contributes only to facilitate the reaction at high pHs, but is not the determining cause of it.



Scheme 5

A carbocation mechanism would also explain the higher than expected increase in C4-C8/C4-C6 interflavonoid linkages. It is well known that in chain

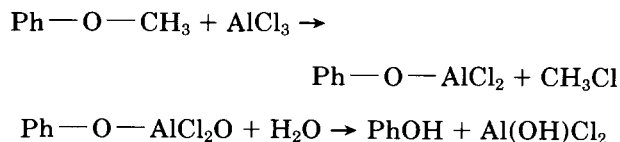
transfer in cationic polymerization an hydride ion can often be extracted by the carbocation from the α -carbon to a double bond or aromatic ring of another molecule.^{22,23} Thus,



Scheme 6

indicating that it is the additional contribution from the flavonoid chains lower terminal units which is likely to lead to the appearance and increase in the intensity of the C4-C2/C4-C6 ¹³C-NMR band. It also indicates that the counterion $-\text{OSi}(\text{OH})_4^-$ charge contributes to peg the unit on the carbocation formed at C2 avoiding bond rotation and eliminating catechinic acid rearrangements.

In the case of one of the catalysts used, AlCl_3 , reactions of cleavage of aromatic ethers with formation of phenols, according to



have already been reported a long time ago²⁴⁻²⁷ although the mechanism reported²⁴⁻²⁷ might well not be as shown above.

Some qualitative confirmatory evidence of Si being in a coordination number higher than four is also obtained by powder x-ray diffraction traces of solid SiO_2 , of unreacted powder mixtures of pecan tannin extract and SiO_2 (4% by mass) and of the reacted pecan tannin/ SiO_2 (4% by mass) solid network (Table VI; Fig. 4). The diffraction trace of SiO_2 alone shows a considerable amount of amorphous material present (Fig. 4, broad peak at $2\theta^\circ$ max = 21) and four clear intense reflection peaks at $2\theta^\circ = 36.9$;

39.5; 43.3 and 46.6. The unreacted mixture of powder pecan tannin with 4% by mass of powder SiO_2 shows that the same reflection peaks are present but at very low intensity as would be expected at such low levels of SiO_2 . The reacted pecan nut tannin + 4% SiO_2 network instead shows that amorphous silica is no longer present, a small amount of amorphous material of tannin origin being visible at $2\theta^\circ = 31$, but most interestingly it shows that only two crystalline reflection peaks remain: the $2\theta^\circ = 46.6$ and the $2\theta^\circ = 39.7$. The latter is particularly noticeable by presenting a considerable increase in intensity, disproportionate to the small percentage of SiO_2 added (Table VII; Fig. 4) indicating that rather than the peaks disappearing a shift has taken place, thus the increase in intensity of one peak. The fact that the peaks for both silica and silica/tannin are at the same reflection suggests that the silica in both samples is in the same orientation, the change being brought about by a small change in the orientation of the silica. Such shift could be brought about by (i) new covalent bonds between silica and tannin and (ii) secondary forces interactions between silica and tannin. It is probable that the presence of the tannin decreases the silica crystallinity in one dimension without affecting or increasing the crystallinity in another. From this it appears then that SiO_2 has maintained some orientations of its original crystalline state but that the original SiO_2 network has been considerably distorted. This confirms the

Table VI X-Ray Diffraction Traces Results of SiO₂ Alone and of Pecan Nut Tannin Extract Treated With 4% SiO₂ (Mass/Mass of Tannin Extract)

Angle [2θ°]	d-Value [Å]	Peak Width [2θ°]	Peak Intensity [counts]	Relative Intensity [%]	Significance
SiO₂ Alone					
35.575	2.5277	0.400	7	8.4	0.80
36.940	2.4374	0.080	86	100.0	1.03
39.535	2.2776	0.560	40	45.9	4.42
43.285	2.0886	0.240	43	56.7	3.89
46.605	1.9472	0.400	12	13.4	1.01
77.200	1.2377	0.360	3	3.7	0.94
Pecan Tannin/4% SiO₂ Coreacted					
39.730	2.2725	0.240	146	100.0	2.41
46.585	1.9528	0.320	35	23.8	1.32
56.550	1.6301	0.480	6	4.3	1.00

²⁹Si-NMR result indicating the change of coordination number of Si, and the introduction of another atom in the Si(O_{1/2})₄ network. The distance between reflection planes corresponding to 2θ° = 39.7 is 2.27 Å (Table V) indicating that the reflection planes involved are those, respectively, passing through the

Si
 \
Si, the O and the Si of a O linkage. If the tannin
 /
 Si

polymers are attached to the Si(O_{1/2})₄ network to form planes around the silicon, because in the new structure formed the distance between the reflection planes is indirectly linked to the structure of Si(O_{1/2})₄, while the network would be severely distorted, some of the original reflections would remain and increase noticeably in intensity, as observed. This confirms that a good part of Si(O_{1/2})₄ is linked to the tannin, as found by ²⁹Si NMR. The low amount of tannin in the amorphous state (solid tannins are completely amorphous) also infers that a noticeable amount of the tannin is involved in the new crystalline, or paracrystalline, structure. While one cannot be sure from the traces presented which tannin site Si is linked to, some deductions can also be made. If an Si—C bond had been formed, a different 2θ°, intense, peak would have appeared while the 2θ° = 39.7 would not increase in intensity. While a 2θ° = 56.6 peak appears, this is very small (Table VI; Fig. 4) inferring that the fifth coordinated atom is an oxygen from the tannin, in line with the ²⁹Si NMR result.

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