

Comparative Kinetics of the Induced Radical Autocondensation of Polyflavonoid Tannins. III. Micellar Reactions vs. Cellulose Surface Catalysis

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SYNOPSIS

Cellulose surface catalysis of the induced autocondensation of tannins has been found to occur also for the radical mechanism of the reaction. Equally effective in accelerating pyran ring opening of polyflavonoids by radical mechanisms appears to be the presence of any substance leading to micellar structures in the tannin solution. Thus, soaps and synthetic and natural polymeric colloids have been found to accelerate the reaction. The micellar effect is distinct and different from the surface catalysis of the process induced by cellulose. Amorphous and crystalline cellulose appear to differ somewhat as regards the extent of catalytic activation. As for ionic mechanisms, also for catalyzed radical mechanisms, procyanidins invert their favorite reaction of cleavage of the interflavonoid bond to favor, instead, pyran ring opening. This inversion of the favorite reaction is induced both by the presence of cellulose and by the level of the micellar state of the reaction. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Recently, the radical mechanism of the reaction of autocondensation to hardened resins of polyflavonoid tannins induced by weak Lewis acids, in particular, silica and silicic acid, has been described.¹⁻⁴ Both ionic and radical mechanisms have been found to exist for this reaction for all polyflavonoid tannins.^{1,5-7} The relative balance of their contribution to hardening of the two types of mechanism differs according to the type of tannin used—hence, with the difference in structure of the tannin repeating unit,^{1,5,7} with the degree of polymerization of the tannin,⁷ and with the level of the colloidal state of the tannin solution.^{2,5-7,8-11} Autocondensation of tannins by cellulose surface-induced catalysis has also been identified in the context of ionic mechanisms.^{2,4} What has not been checked is (i) if cellulose is also capable of inducing radical-based autocondensation mechanisms in tannin and (ii) if the cel-

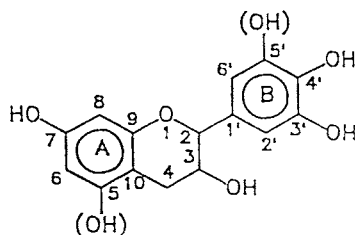
lulose-induced catalysis and the colloidal/micellar acceleration of the reaction are due to two distinct effects or are two different expressions of the same effect. The answer to these questions are of importance in the preparation of formaldehyde-free tannin-based wood adhesives¹² and other applications such as faster wine aging and consequent taste improvement by flavonoid tannin silica, weak Lewis acids, and wood-induced accelerated autocondensation (it is well known that the pleasant taste developing during wine aging is, among others, due to the increase in degree of polymerization of flavonoid tannins induced by absorption and desorption of the wine on the oak of the barrel^{13,14}), cement superplasticizers, and others for which the tannin autocondensation system is starting to be considered.^{2,12-16}

Polyflavonoid tannins in industrial tannin extracts are composed mainly of flavan-3-ols repeating units. Four types of repeating units can exist and predominate in these tannins,^{17,18} namely:

5 = 5' = H = Profisetinidins
5 = 5' = OH = Prodelphinidins
5 = OH, 5' = H, Procyanidins

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5 = H, 5' = OH, Prorobinetinidins



Polymers of structure (I) are called prodelphinidins; of structure (II), procyanidins; of structure (III), prorobinetinidins; and of structure (IV), profisetinidins.^{17,19} Such differences in structure, although they might appear minor, impart, instead, rather marked and well-defined characteristics to different tannins.

This last article of this series was then aimed at ascertaining (i) if radical mechanisms of tannin autocondensation induced by a lignocellulosic substrate are of importance and at quantifying their importance for different tannins, and (ii) what the distinction is between the polymeric carbohydrate surface accelerating effect and the micellar/colloidal acceleration effect of the reaction.

EXPERIMENTAL

Tannin Types

Five types of commercial polyflavonoid tannin extracts were used. These were the following:

- Natural quebracho (*Schinopsis balansae*, variety chaqueno) wood tannin extract
- Pecan (*Carya illinoensis*) nut pith tannin extract
- Pine (*Pinus radiata*) bark tannin extract
- Mimosa (*Acacia mearnsii*, formerly *mollissima*, de Wildt) bark tannin extract
- Carbohydrate-free quebracho wood tannin extract.

Tannin extract water solutions of 20% concentration were prepared by dissolving spray-dried powders of the different types of tannin extracts in water and adjusting the pH to 12 with a 30% sodium hydroxide solution. The additives used were analytical-grade amorphous cellulose powder (20% on tannin extract solids), 1 and 5% on tannin extract solids of a surfactant (Rhom & Haas Triton-X100), 10% on tannin extract solids of four different types of poly(ethylene

glycol) (PEG 300, PEG 2000, PEG 8000, PEG 10000), 50% on tannin extract solids of cotton wool cellulose fiber (>90% crystallinity), and 10% gum arabic.

Electron Spin Resonance (ESR) Spectra

ESR spectra of the tannin solutions with and without the different additives listed above were recorded at 298 K on a Bruker ER 200 D spectrometer (X-band) equipped with a TE₁₀₂ sample cavity. Fine structures of the phenoxide anion radicals were studied in the range 3465–3495 Gauss with a field modulation intensity of 0.8 and scan times of 500 s. The tannin phenoxide signals were observed at 3482.4 Gauss and all had $g = 2.003$. Spectra were centered on the signal of DPPH as the standard²⁰ at 3843 Gauss. Decay of the radical concentration and the variation in intensity of the peaks of the fine structure of the phenoxide signal as a function of time were followed by scanning the material after base or both additive and then base addition at 5 min intervals for a period of 1 h or more. The first-order kinetic equations of the second step of the reaction, namely, the radical decay reaction, were expressed as signal intensity units (r) as a function of time. Pecan tannin responded to a kinetic equation of a more complex kind⁷ also in the presence of additives, and what was found for this tannin appeared to be the case for all other tannins with the proviso that for pecan tannin the composite nature of the curve could be clearly followed. Pine could not be exactly modeled by a simple first-order exponential kinetic law, although good information on its behavior could be derived by a first-order kinetic law. Maximum intensities reported are the experimental values, while half-reaction times are derived from the kinetic laws fitted. The radical decay reactions reported were obtained by dividing the rate of the same reaction expressed in signal intensity units per s⁻¹ by the maximum intensity of the signal; their unit is then (s⁻¹).

DISCUSSION

To distinguish between the existence or not of a radical mechanism when the tannin is on the surface of cellulose and rather a micellar/colloidal accelerating effect and, equally, to determine which of the two effects predominate, electron spin resonance (ESR) spectra were done in the presence of amorphous cellulose powder and of cotton wool fibers (>90% crystallinity) in the presence of different

amounts of a soap and in the presence of a noncarbohydrate colloid [poly(ethylene glycol) [PEG] of different grades]. The four most common commercial tannins were used, namely, pecan nut tannin (mainly a prodelphinidin¹⁷⁻¹⁹) extract, pine bark tannin (a procyanidin^{17,18}) extract, mimosa bark tannin (a prorobinetinidin/proflsetinidin with the former predominating^{17,19,21,22}) extract, and quebracho wood tannin (also a prorobinetinidin/proflsetinidin but with the latter predominating¹⁷).

In Table I, the results for pecan tannin alone, in the presence of 1 and 5% of a soap, and in the presence of amorphous cellulose powder are reported. In all cases, phenoxide radical anion signals representing the characteristic structure of flavonoids⁵ are present. Addition of 1% soap does not appear to change either the radical signal intensity (related

to the first step of the reaction: radical formation⁷) or the radical rate of decay (related to the second step of the reaction⁷). However, addition of 5% soap markedly increases the intensity of the signal—hence, increases markedly the radical concentration (by almost three times), as well as accelerating considerably the rate of radical decay, both expressed as a half-reaction time or as a rate in seconds¹ (Table I), i.e., at 1%, the soap concentration is under the critical micellar concentration, and, hence, micelles do not form, while at 5% soap concentration, micelles have definitely formed. Thus, both steps of the radical reaction, within the micelles, are considerably faster.²³

A marked increase in signal intensity as well as in the rate of radical decay is noticeable for the case of pecan tannin in the presence of suspended amor-

Table I Kinetic Law, Half-time of Reaction, Radical Decay Rate, and Initial Maximum Peak Intensities of Induced Radical Reactions of Pecan Nut Tannin Extract Alone, with Soap Added, and on Amorphous Cellulose

Peak (Gauss)	Kinetic Law	Intensity (10 ⁵)	Half-reaction Time (s)	Rate (s ⁻¹)
Pecan only				
3480.3	$162.6439[e^{-0.0037t} - e^{-0.2848t}] + 210.1181e^{-0.4276t}$	209	7086	0.0035
3481.3	$102.6986[e^{-0.0053t} - e^{-0.8308t}] + 203.8904e^{-0.6418t}$	208	389	0.0038
3483.9	$178.2659[e^{-0.0046t} - e^{-0.8305t}] + 258.2672e^{-0.7858t}$	262	4205	0.0036
3485.1	$238.7545[e^{-0.0041t} - e^{-0.1716t}] + 367.7329e^{-0.3973t}$	377	289	0.0048
Average		264	2992	0.0039
Pecan + 1% soap				
3480.4	$130.7921[e^{-0.0015t} - e^{-0.4134t}] + 207.5003e^{-0.5219t}$	208	9261	0.0044
3481.5	$97.4513[e^{-0.0070t} - e^{-1.5720t}] + 197.1730e^{-0.9931t}$	202	241	0.0027
3484.1	$147.8579[e^{-0.0056t} - e^{-1.5720t}] + 238.1182e^{-1.1156t}$	242	2320	0.0024
3485.1	$174.4457[e^{-0.0016t} - e^{-0.3325t}] + 362.1124e^{-0.5162t}$	363	199	0.0060
Average		254	3007	0.0039
Pecan + 5% soap				
3480.3	$287.4650[e^{-0.0058t} - e^{-0.1481t}] + 588.1996e^{-0.6642t}$	596	79	0.0097
3481.3	$164.4449[e^{-0.0068t} - e^{-0.3777t}] + 670.8624e^{-0.8555t}$	678	60	0.0127
3483.9	$277.1040[e^{-0.0056t} - e^{-0.2302t}] + 584.9707e^{-0.6451t}$	593	95	0.0090
3485.1	$386.8655[e^{-0.0052t} - e^{-0.1463t}] + 1018.2406e^{-0.7413t}$	1030	60	0.0115
Average		724	75	0.0107
Pecan + amorphous cellulose				
3480.8	$162.2305[e^{-0.0055t} - e^{-0.2645t}] + 649.4558e^{-0.8427t}$	652	58	0.0129
3481.8	$104.0390[e^{-0.0072t} - e^{-1.7856t}] + 839.4527e^{-1.1313t}$	851	48	0.0151
3484.6	$175.7920[e^{-0.0069t} - e^{-1.7318t}] + 674.5719e^{-1.1855t}$	681	64	0.0122
3485.6	$206.8614[e^{-0.0046t} - e^{-0.2479t}] + 1234.8424e^{-0.8251t}$	1241	56	0.0130
Average		856	57	0.0134

Table II Half-times of Reaction, Initial Maximum Peak Intensities, and Radical Decay Rates Responding to a First-order Kinetic Law for Pine Tannin Extract Alone and on Amorphous Cellulose

Peak (Gauss)	Intensity (10^5)	Half-reaction Time (s)	Rate (s^{-1})	Intensity Ratio
<u>Pine only</u>				
3479.7	490	341	0.0047	
3480.9	476	202	0.0058	
3481.9	391	133	0.0059	
3482.4	345	160	0.0057	
3483.4	445	615	0.0026	
3484.6	500	842	0.0032	
Average	441	382	0.0047	
<u>Pine + amorphous cellulose</u>				
3479.6	944	124	0.0074	1.93
3480.8	923	92	0.0079	1.94
3481.7	836	101	0.0079	2.14
3482.3	602	108	0.0079	1.74
3483.2	780	215	0.0063	1.75
3484.4	883	179	0.0067	1.77
Average	828	137	0.0074	1.88

phous cellulose powder. Cellulose powder suspended in a water solution of the tannin does not contribute at all to the level of the colloidal state of the system. It is then evident that the radical mechanism of the reaction is induced not only by weak Lewis acids,¹ but also (i) by a surface catalysis effect by cellulose and (ii) is favored by the micellar state of the solution. Exactly the same behavior on amorphous cellulose is noticeable for pine tannin (Table II), a procyanidin. Thus, at least the very similar prodelpinidins and procyanidins present the same type of cellulose surface catalysis and the same intramolecular reaction effects appear to occur, with the effects appearing to be slightly more marked for prodelpinidins (compare signal intensities, and radical decay rates and half-reaction times, with and without cellulose in Tables I and II).

In the case of pine tannin, it is not possible to model to a reasonable level of exactness its radical decay kinetic law, because while the curve of decrease of signal intensity as a function of time forms "bulges," an occurrence often found also for all the other tannins,⁷ these form so early and so rapidly (compare Figs. 1 and 2) that it is difficult to do anything else other than modeling such a curve as a simple exponential. It is for this reason that a ki-

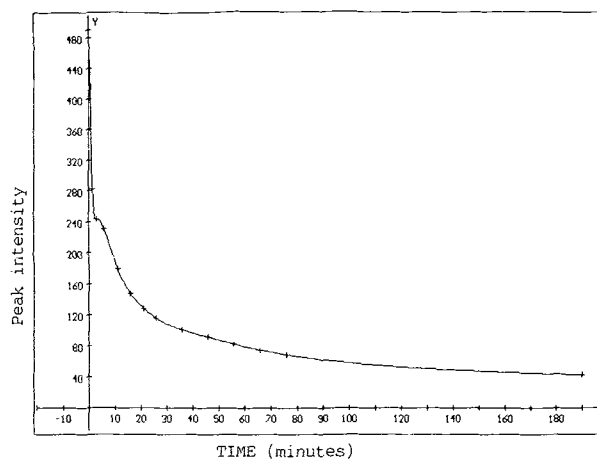


Figure 1 Graphic representation of the variation in intensity of pine tannin alone (peak at 3479.7 Gauss) as a function of time. Note early-on "bulge," the influence of which is not negligible on the fitting of a simple first-order kinetic law.

netic expression for pine is not given in Table II, where the half-reaction times, etc., are derived from a simple exponential regression.

In the case of procyanidins, the signal intensity surge and the more rapid radical decay rate in the presence of cellulose again confirm that the pyran ring opening reaction is being favored over the interflavonoid bond cleavage. This is then valid not only for ionic mechanisms, but also for radical mechanisms even when the reaction is catalyzed by a cellulose substrate, confirming more applied results already reported.^{2,12}

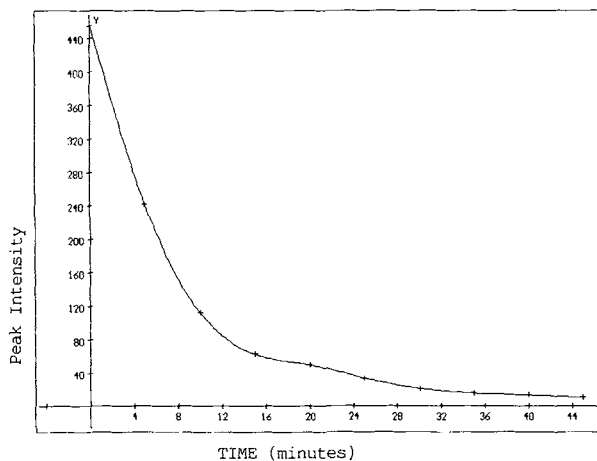


Figure 2 Graphic representation of the variation in intensity of quebracho tannin + silica (peak at 3477.9 Gauss) as a function of time. Note the late "bulge," the influence of which is negligible on the fitting of a simple first-order kinetic law.

The situation is rather different for prorobinetinidin/profisetinidin tannins. For predominantly prorobinetinidin tannins, such as mimosa tannin^{21,22} (Table III), the presence or not of amorphous cellulose in suspension does not appear to change the course of the reaction: Signal intensities and radical concentration remain almost the same, while for radical decay, the half-time of reaction does not change, while the actual radical decay rate becomes faster. At least for mimosa tannin if any surface catalysis by amorphous cellulose occurs through a radical mechanism, then (i) it does not apply to the first step of the reaction, as shown before,⁷ and (ii) it might only apply to the second step of the reaction, or (iii) the predominant mechanism which has already been shown to exist² is an ionic one, at least under the well-defined sets of conditions used.

The effects observed are again different for the other prorobinetinidin/profisetinidin tannin (but in which profisetinidins greatly predominate¹⁷), namely, quebracho tannin, and more in line with

what was already observed for both prodelpinidins and procyanidins. In Table IV, the results obtained in the presence of 10% PEG of different average molecular mass indicate that at least for the radical mechanism, (i) first, the presence of an added colloid unrelated to polymeric carbohydrates both increases the rate of the first reaction step as indicated by the higher signal intensities for all the PEG types (Table IV), and (ii) the intensity of the micellar effect increases with increasing average molecular mass of the synthetic polymeric colloid. More in detail, while a clear improvement is noticed by adding any type of PEG, little difference is noticeable between the effect of PEG 300 and PEG 2000. Very marked improvements are instead noticeable with both the PEGs 8000 and 10000. The rate of radical decay, hence, the second reaction step, is, instead, affected very little, and for this reaction step, some very small differences commence to be noticed, only starting with PEG 8000. In the case of the micelles formed in the 5% soap for a quebracho extract from which

Table III Kinetic Law, Initial Maximum Peak Intensities, Half-times of Reaction, and Radical Decay Rates for Mimosa Tannin Extract Alone and on Amorphous Cellulose

Peak (Gauss)	Kinetic Law	Intensity (10 ⁵)	Half-reaction Time (s)	Rate (s ⁻¹)
<u>Mimosa only</u>				
3477.6	$r = 7059.4491e^{-0.4200t}$	6856	99	0.0047
3478.3	$r = 9145.4573e^{-0.3499t}$	8267	119	0.0043
3479.3	$r = 4672.0804e^{-0.4155t}$	4577	100	0.0043
3480.3	$r = 6402.6318e^{-0.4215t}$	6291	99	0.0043
3481.2	$r = 9911.9506e^{-0.3841t}$	9407	108	0.0042
3482.2	$r = 4204.0585e^{-0.3286t}$	3703	127	0.0062
3482.9	$r = 8926.0383e^{-0.3566t}$	8443	117	0.0038
3483.8	$r = 6600.2790e^{-0.4038t}$	6495	103	0.0042
3485.7	$r = 7418.1233e^{-0.4145t}$	7272	100	0.0042
3486.5	$r = 7434.7977e^{-0.4254t}$	7236	98	0.0045
Average		6854	107	0.0044
<u>Mimosa + amorphous cellulose</u>				
3477.5	$r = 6271.8603e^{-0.4183t}$	6138	99	0.0072
3478.3	$r = 8141.7422e^{-0.3943t}$	7842	106	0.0068
3479.3	$r = 4208.5114e^{-0.3998t}$	4069	104	0.0068
3480.3	$r = 6162.8621e^{-0.4142t}$	6048	100	0.0070
3481.1	$r = 10334.9796e^{-0.3935t}$	10,012	106	0.0068
3482.2	$r = 5388.0147e^{-0.3105t}$	4647	134	0.0060
3482.8	$r = 9392.6062e^{-0.3682t}$	9180	113	0.0063
3483.8	$r = 6336.5091e^{-0.3892t}$	6256	107	0.0065
3485.6	$r = 6843.9279e^{-0.4035t}$	6740	103	0.0068
3486.4	$r = 6597.5256e^{-0.4247t}$	6510	98	0.0072
Average		6744	107	0.0067

Table IV Kinetic Law, Initial Maximum Peak Intensities, Half-times of Reaction, and Radical Decay Rates for Quebracho Tannin Extract in Presence of PEG of Increasing Molecular Mass and of Carbohydrate-free Quebracho Tannin in Presence of a Soap

Peak (Gauss)	Kinetic Law	Intensity (10^5)	Half-reaction Time (s)	Rate (s^{-1})
Quebracho + PEG 300				
3480.3	$r = 71.7568e^{-0.1986t}$	128	209	0.0019
3481.3	$r = 68.7292e^{-0.2177t}$	139	191	0.0018
3482.8	$r = 120.1711e^{-0.1475t}$	215	282	0.0014
Average		161	227	0.0017
Quebracho + PEG 2000				
3480.3	$r = 97.0514e^{-0.1268t}$	145	328	0.0022
3481.2	$r = 106.5912e^{-0.0946t}$	134	440	0.0013
3482.8	$r = 103.0845e^{-0.1606t}$	186	259	0.0015
Average		155	342	0.0017
Quebracho + PEG 8000				
3480.6	$r = 262.5718e^{-0.1368t}$	306	304	0.0020
3481.6	$r = 360.4231e^{-0.1269t}$	390	328	0.0020
3483.1	$r = 439.5648e^{-0.1245t}$	500	334	0.0018
Average		399	322	0.0019
Quebracho + PEG 10000				
3480.2	$r = 493.3816e^{-0.1431t}$	532	291	0.0022
3481.3	$r = 691.7302e^{-0.1294t}$	700	321	0.0021
3482.8	$r = 744.5231e^{-0.1284t}$	806	324	0.0020
Average		679	312	0.0021

all the colloidal components from the polymeric carbohydrates have been removed (Table IV), the same micellar acceleration effect occurs, with the signal intensities being greater with the soap present and the rate of radical decay remaining almost invariable (although variation of the half-time of reaction occurs). The effect appears to be less intense than in the case of the micellar state being achieved by addition of a colloid (PEG).

Thus, the radical mechanism for prodelpinidins and procyanidins appear to be much more sensitive to micellar-based acceleration, both reaction steps being affected, than for prorobinetinidins/profisetinidins where for profisetinidins the first step of the reaction might be affected while the second is not, while for prorobinetinidins, the whole reaction does not appear to be affected much.

For quebracho tannin, the same behavior is observed for amorphous cellulose-induced catalysis of the radical mechanism (Table V). Thus, signal in-

tensity and radical concentration markedly increase for the first reaction step when carried out in the presence of amorphous cellulose suspended in the tannin solution. The radical decay rate instead, as for the soap case, appears to remain unaffected. The suggestion, already advanced,⁷ that radical mechanisms are of importance for the first step of the autocondensation reaction while ionic mechanisms might be of greater importance for the second reaction step,⁷ the condensation step proper, then appears to gain some additional confirmation from this behavior.

As regards tannin behavior on cellulose substrates of different structure (amorphous and > 90% crystalline^{24,25}), some differences in behavior appear to exist, but these might well be due to diffusion problems in the case of the cotton cellulose fibers (Table V), and, thus, a definite conclusion on this point cannot really be reached with the data available, contrary to what already was concluded in the

Table IV (Continued)

Peak (Gauss)	Kinetic Law	Intensity (10 ⁵)	Half-reaction Time (s)	Rate (s ⁻¹)
Carbohydrate-free quebracho only				
3479.0	$r = 86.2049e^{-0.0839t}$	97	496	0.0012
3479.7	$r = 53.5013e^{-0.0382t}$	61	1089	0.0006
3481.2	$r = 79.0252e^{-0.0726t}$	85	573	0.0011
3482.0	$r = 42.8921e^{-0.0334t}$	45	1245	0.0005
3483.5	$r = 32.7756e^{-0.0285t}$	49	1459	0.0003
3484.2	$r = 80.4662e^{-0.0517t}$	97	804	0.0007
3485.1	$r = 126.7039e^{-0.0753t}$	143	552	0.0011
Average		82	888	0.0008
Carbohydrate-free quebracho + 5% soap				
3479.1	$r = 139.6252e^{-0.0420t}$	138	990	0.0007
3479.8	$r = 88.4847e^{-0.0373t}$	91	1115	0.0006
3481.3	$r = 73.0154e^{-0.0358t}$	59	1162	0.0007
3482.1	$r = 47.6990e^{-0.0278t}$	50	1496	0.0004
3483.6	$r = 43.7429e^{-0.0299t}$	77	1390	0.0003
3484.3	$r = 106.5219e^{-0.0382t}$	126	1089	0.0005
3485.2	$r = 178.7929e^{-0.0445t}$	192	935	0.0007
Average		105	1168	0.0006

case of ionic mechanisms.² What is clearly noticeable, however, is the interesting behavior of both the tannin solution once separated from the cellulose fibers and of the cotton cellulose fibers still impregnated with the tannin solution. For the tannin solution, once the fibers are separated from it, the radical concentration is still high and the radical concentration decays as a function of time as in the other cases. The cellulose fiber might then have only functioned as the trigger for the first step of the reaction to occur (Table VI).

ESR spectra of the cotton cellulose fiber impregnated with the tannin solution, of the cellulose fiber separated and mechanically squeezed of the tannin solution (but still with some tannin solution on it), of the cotton fiber partially dried on filter paper and then even dried on a vacuum filter show some interesting results, too (Table VI). The signal of cellulose fibers just impregnated with the solution has an intensity comparable to that of the solution just separated from contact with some fibers. More interesting, however, is the fact that if a good part of the tannin solution is mechanically squeezed out of the cellulose fiber; hence, in the case that is in great excess in relation to the tannin solution, the cellulose surface catalysis effect is so strong that the ESR signal intensity, hence, the average radical concentration, continues to increase with time even 76 min

after contact between the two materials (Table VI). In this case, it can then be assumed that there is effectively a greater area of contact between the fiber and a very high proportion of the tannin solution and, thus, just about the whole solution, even tannin structures which might normally have greater difficulties in undergoing radical cleavage, undergoes direct contact catalysis by the fiber surface. While the total average continues to increase, there are peaks which then precipitously start to decrease (peaks at 3476.9, 3478.4, 3479.2, 3480.7, 3481.4, 3484.0, and 3484.7), while others continue to increase (peaks at 3480.0, 3482.4, 3483.2, 3486.4).

It also explains the sometime appearance of "bulges" in the radical decay curves previously reported,⁷ these being due to the tannin structures which are slower in giving radical cleavage undergoing the first step of the reaction at the same time the more reactive structures are already undergoing the second step of the reaction. This has been shown clearly and has been quantified in the kinetic equations for pecan nut tannin⁷ (Table I) for some of the ESR peaks for which the process is clearly visible. For pecan tannin, at least the contribution of the two effects, with or without cellulose, has been quantified. All the other tannins often present a similar behavior (see Fig. 2, for quebracho tannin), but due to the position of the "bulges" on the curve,

Table V Kinetic Law, Initial Maximum Peak Intensities, Half-times of Reaction, and Radical Decay Rates of Quebracho Tannin Extract Alone, on Amorphous Cellulose, and on Mainly Crystalline Cotton Cellulose Fibers (the Latter After the Cellulose Fibers were Subtracted from the System)

Peak (Gauss)	Kinetic Law	Intensity (10 ⁶)	Half-reaction Time (s)	Rate (s ⁻¹)	Intensity Ratio
Quebracho only					
3479.6	$r = 98.3680e^{-0.1168t}$	116	356	0.0017	—
3479.0	$r = 75.1567e^{-0.1223t}$	80	340	0.0019	—
3480.7	$r = 110.8841e^{-0.1287t}$	135	323	0.0018	—
3482.9	$r = 126.4532e^{-0.1361t}$	153	306	0.0019	—
Average		121	331	0.0018	—
Quebracho + amorphous cellulose					
3479.0	$r = 512.6993e^{-0.1113t}$	529	374	0.0018	—
3480.0	$r = 664.5836e^{-0.1081t}$	676	385	0.0018	8.49
3481.5	$r = 695.1106e^{-0.1031t}$	704	403	0.0017	5.23
3484.2	$r = 239.3794e^{-0.1081t}$	264	385	0.0016	1.73
Average		543	386	0.0017	5.15
Quebracho + cotton cellulose fibers					
3479.0	$r = 388.2251e^{-0.1299t}$	416	320	0.0020	—
3480.0	$r = 537.6898e^{-0.1221t}$	557	341	0.0020	6.99
3481.5	$r = 617.4467e^{-0.1140t}$	670	365	0.0018	4.98
3484.2	$r = 145.5302e^{-0.1316t}$	191	316	0.0017	1.25
Average		458	335	0.0019	4.41

the effects cannot be clearly quantified. It is interesting to note that the peaks which continue to increase are mainly (but not only) the flavonoid B-ring peaks, confirming that it is the initial very fast surge of A-ring radicals and the consequent shifting to the right of the A \rightleftharpoons B ring radical equilibrium which is the likely cause of this effect. That it is this

equilibrium which is the one causing such an effect can be deduced by the S-shape curve of some peaks' radical surge and decay as a function of time (i.e., the peaks at 3482.4 and 3484.0 Gauss, clearly both B-ring radical peaks; 3484.0 is the more interesting one, as it first decreases [Table VI] from 838 to 820 units and then the equilibrium takes over and the

Table VI Different Initial Peak Intensities and Their Variation as a Function of Time of Different Proportions of Quebracho Tannin Extract Solution on Mainly Crystalline Cotton Cellulose Fibers

Time (min)	Peak Intensity										
	3474.6	3476.3	3477.1	3477.6	3478.6	3479.1	3480.2	3481.0	3481.8	3482.8	3484
Cotton cellulose fiber impregnated of natural quebracho solution											
0.0	221	229	488	613	1037	672	740	370	318	205	231
Cotton cellulose fiber after quebracho solution excess has been squeezed out											
41.0	379	461	760	707	475	120	558	839	816	570	478
46.0	373	520	827	940	693	—	680	820	944	662	516
51.0	385	576	896	1124	920	—	940	1228	1009	706	544
76	343	—	—	1378	—	—	1304	1368	—	—	499

Table VII Peak Intensities for the Radical Reaction of Carbohydrate-free Quebracho Tannin in the Presence of Different Types of Additives

Time (min)	Peak Intensity							Average
	3479.0	3479.7	3481.2	3482.0	3483.5	3484.2	3485.1	
<u>Carbohydrate-free quebracho only</u>								
0.0	97	61	85	45	49	97	143	82
15.0	46	46	46	41	57	79	83	
<u>Carbohydrate-free quebracho + silica</u>								
0.0	78	53	69	38	40	80	114	67
15.0	37	36	29	24	36	51	55	
<u>Carbohydrate-free quebracho + gum arabic</u>								
0.0	113	75	59	44	70	113	169	92
15.0	120	88	73	50	49	112	167	
<u>Carbohydrate-free quebracho + 5% soap</u>								
0.0	139	94	82	44	57	124	192	105
15.0	93	78	60	44	43	95	126	

peak intensity then starts to increase). The only peak where it is possible to calculate very approximately the combined law of the radical surge as a function of time and of the equilibrium is the A-ring radical signal at 3480.0 Gauss where the increase in radical concentration between 41 and 76 min follows a logarithmic law of the type signal intensity = 1010.207 ln time (s) - 7090.66 (coefficient of correlation $r = .953$).

With the same carbohydrate-free quebracho tannin used before,⁷ thus of low or no colloidal level,⁷ the results in Table VII confirm again what was deduced for the first step of the reaction. Thus, addition of silica gives a less intense signal, again confirming that the induced catalysis is dependent on the micellar state of the solution, while it is also faster once a micelle-forming compound, namely, a colloid such as gum arabic in one case or soap in another case (Table VII) is present even in the absence of silica.

In conclusion, radical mechanisms for monomeric flavonoids which have already been described for monomeric model compounds²⁶⁻²⁸ have now been shown not only to exist for polymeric flavonoid tannins, and not only for base-induced pyran ring opening, but also for cellulose and micellar-induced reactions. This infers that it is also the conditions under which the tannin finds itself which greatly influences the outcome, the route, the facility, and

the rate of the reaction, the results found indicating that previous studies on just noncolloidal isolated and diluted solutions of monomeric model compounds alone could not hope to describe what really occurs with colloidal solutions of commercial polymeric tannin extracts under their real conditions of application (on wood).

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