Antioxidant Characteristics of Hydrolysable and Polyflavonoid Tannins: An ESR Kinetics Study

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ABSTRACT: As part of an investigation of the role of tannin as antioxidants, the radical formation and radical decay reactions of some polyflavonoid and hydrolysable tannins has been followed by electron spin resonance (ESR) techniques. Comparative kinetics were determined for both light-induced radicals and by radical transfer from a less stable chemical species for the tannin alone and when the tannin is in a methanol solution. The five parameters which appear to have a bearing on the very complex pattern of the rates of tannin radical formation and radical decay were found to be (1) the extent of the colloidal state of the tannin in solution, (2) the stereochemical structure at the interflavonoid units linkage, (3) the ease of heterocyclic pyran ring opening, (4) the relative numbers of A- and B-rings hydroxy groups, and (5) solvation effects when the tannin is in solution. It is the combination of these five factors that appears to determine the behavior as an antioxidant of a particular tannin under a set of application conditions. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 475–482, 1997

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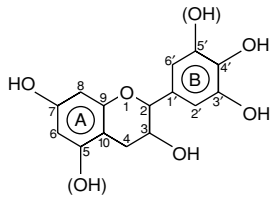
INTRODUCTION

The capability of phenols to produce rather stable phenoxyl radicals, capable by their presence of retarding or even inhibiting the progress of radical addition polymerization, is well known.[1,2] Recently, in the ambit of research on the improvement of the antioxidant capabilities of surface finishes for wood protection, natural phenolic and polyphenolic materials, such as hydrolysable and polyflavonoid tannins and their model compounds, have been shown by the use of stopped-flow techniques to be capable of similar, but rather more intense effects.[3] However, both a simpler to handle and more rapid technique to measure tannins antioxidant capabilities, as well as a screening of the antioxidant capabilities of a variety of different hydrolysable and polyflavonoid tannins, is needed.

Polyflavonoid tannins are mainly flavan-3-ols polymeric materials of natural origin[4] which are soluble in water. They contain an elevated number of phenolic hydroxyls and their characteristic structure lends itself to the stabilisation of radicals not only by mechanisms characteristic of all phenols but also by the existance of side reactions, such as heterocycle pyran ring opening and others. The structures of their monomer units are as follows



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The polyflavonoid tannins in industrial tannin extracts are composed mainly of flavan-3-ols and present four main types of repeating units. Thus, prodelphinidins have structure composed of a phloroglucinol A-ring and a pyrogallol B-ring; procyanidins present phloroglucinol A-ring and catechol B-ring structures; prorobinetinidins present resorcinol A-ring and pyrogallol B-ring; and profisetinidins present resorcinol A-ring and catechol B-ring.[5]

Also recently, electron spin resonance (ESR) has been used with good results to study the reactions of radical formation and decay induced by bases and weak Lewis acids in polyflavonoid tannins[6–8] and their model compounds.[6–11] It is for this reason that ESR was then tested as an alternative, simpler technique for the determination of the antioxidant properties of tannins.

This paper's aim is to study how (1) the structure of different tannins influences the rate of radical transfer from DPPH to a tannin and the subsequent rate of radical decay of the phenoxyl radical formed and (2) the effect of the presence or absence of solvent and of the type of solvent; but it is mainly aimed at (3) studying the rate of increase in phenoxyl radical concentration by light irradiation in different tannins and the subsequent radical decay rate once the inducing light is removed.

EXPERIMENTAL

The tannins used were commercial mimosa (*Acacia mearnsii* formerly *mollissima,* de Wildt) bark tannin extract, commercial quebracho (*Schinopsis balansae,* variety chaqueno) wood tannin extract, commercial pecan (*Carya illinoensis*) nut pith tannin extract, commercial gambier (*Uncaria gambir*) shoots tannin extract, commercial pine (*Pinus radiata*) bark tannin extract (all these being polyflavonoid tannins), and commercial oak (*Quercus spp.*) tannin extract, an hydrolysable tannin. Also, the tannin extract of chestnut (*Castanea sativa*) wood, an hydrolysable tannin, was tested but far too variable results were obtained, and, thus, the results for this tannin could not be reported.

The stable 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical at 0.1% concentration in methanol was used as the radical species from which transfer of the radical to the tannin was carried out. Other solvents were tried but ultimately rejected: toluene because DPPH was insoluble in it; acetone, as this solvent gave ESR spectra that were of too low intensity to allow any measure; and dioxane solutions gave measurable spectra, but the solvent appeared clearly to interfere with both radical formation and radical decay. The few cases in dioxane solution that were measurable are also reported in the tables. The ESR spectra were carried out on a Bruker ER 200 D spectrometer (X-band) equipped with TE_{102} sample cavity, with sample ultraviolet-visible irradiation capability by Xenon vapor lamp with a delivery light flux of 10 mW/cm^2 at 355 nm. The instrument setting was as follows: field set = 3483 gauss; scan range = 40 gauss; gain = 50,000; modulation = 2 Gpp; scan time = 180 s. The starting time of all spectra was always at 210 s. The variation of all the phenoxyl radicals peak was followed. All had g = 2.003. Spectra were centered on the signal of the DPPH as standard and decay of the radical concentration; hence, of the ESR signals, intensity as a function of time was followed for 280 min. First-order kinetics were fitted to the results to be able to compare all the different results.

For the light-induced radical experiments on solid tannins, after an initial measurement without any light to obtain the base spectrum of each tannin, the light was switched on. After stabilization of the signal intensity, which occurred in 60 min in cases in which vacuum was not used and in 120 min in cases in which the experiment was done under vacuum, the light was switched off, and the radical decay reaction followed as function of time. The types of curves obtained are shown in Figures 1 and 2. All the experiments were carried out both in quartz and in glass sample-holders, the field set being of 3406 for the quartz and of 3398 for the glass sample holder. ESR equipment parameters maintained constant were scan range = 40 gauss, scan time = 120 s, modulation = 2 Gpp., and gain = 5000.

The results obtained are shown in Tables I, II, and III.

DISCUSSION

One of the more necessary steps to take at the start of such a type of study is to define what is intended for antioxidant capabilities of a tannin. In relation to light-induced degradation of a wood surface, to measure the antioxidant capabilities of any surface finish could be defined as the measurement of two different parameters. These are as follows.

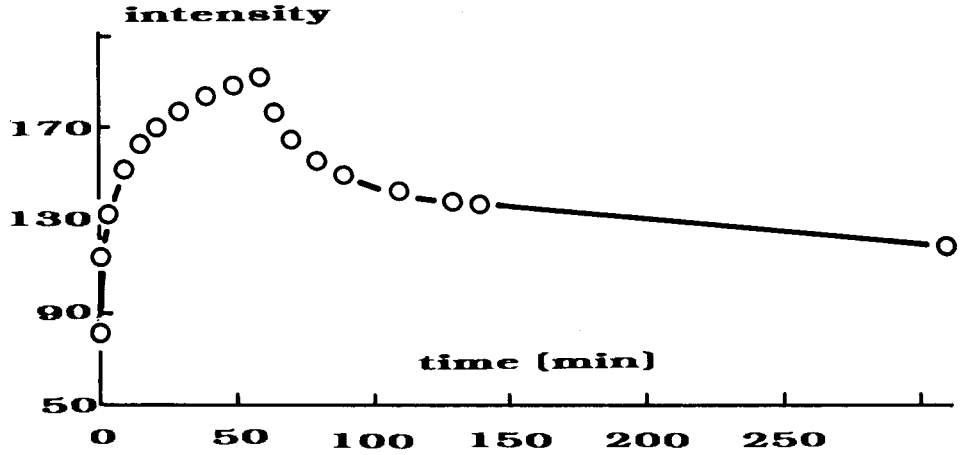

Figure 1 Intensity increase and decrease of the average of the two opposite symmetrical peaks representing the ESR signal during UV irradiation experiments of Quebracho flavonoid tannin extract powder without vacuum, in air, and in a quartz sample holder. The initial part of the curve up to the maximum of intensity describes the increase in radical concentration as a function of time during irradiation, while the decreasing intensity section describes the radical decay reaction from the moment the UV lamp has been switched off.

1. The rate at which the tannin is able to form a radical, which is determined either by the rate of radical transfer from a preexisting radical species to the tannin to form a more stable phenoxyl radical or by the rate of radical formation on light irradiation of the tannin.
2. The rate of radical decay of tannin phenoxyl radicals formed. The first parameter defines the ease and readiness of the tannin in subtracting a radical from, for instance, the substrate; the easier and the more rapid this transfer is, the greater the antioxidant capabilities of the tannin. The second pa-

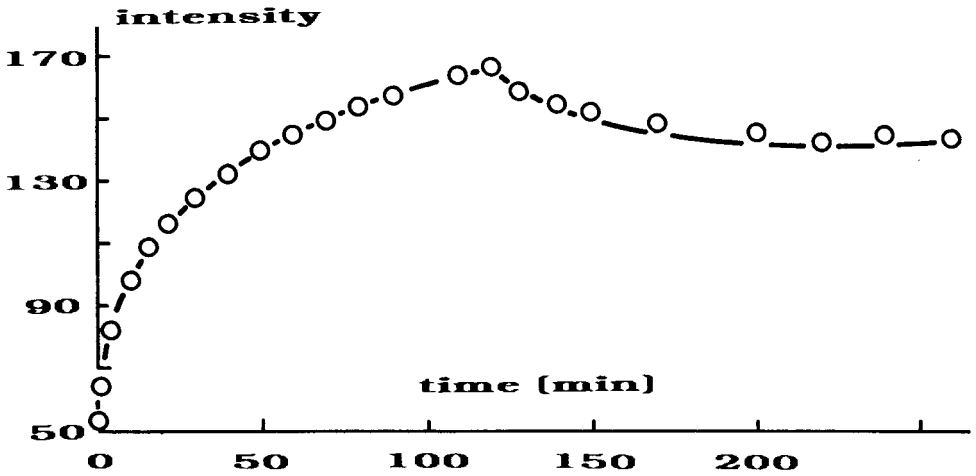

Figure 2 Intensity increase and decrease of the average of the two symmetrical, opposite peaks representing the ESR signal during UV irradiation experiments of Mimosa flavonoid tannin extract powder under vacuum and in a glass sample holder. The initial part of the curve up to the maximum of intensity describes the increase in radical concentration as a function of time during irradiation, while the decreasing intensity section describes the radical decay reaction from the moment the UV lamp has been switched off.

Table I Radical Formation (=First Reaction Step) Kinetics According to a First-order Kinetic Law Derived from Electron Spin Resonance Experiments

Tannin	Vacuum Conditions	Cell Material	Parameters			
			a	k (s^{-1})	r	$t_{1/2}$ (s)
Mimosa	without	quartz	1.4974	1.549×10^{-4}	0.809	4474
	vacuum	glass	1.5069	1.510×10^{-4}	0.786	4604
Mimosa	with	quartz	1.7192	1.120×10^{-4}	0.838	6187
	vacuum	glass	1.6806	1.148×10^{-4}	0.839	6038
Quebracho	without	quartz	1.5546	1.513×10^{-4}	0.784	4580
	vacuum	glass	1.6545	1.605×10^{-4}	0.770	4316
Quebracho	with	quartz	1.4770	0.580×10^{-4}	0.832	11939
	vacuum	glass	1.8611	0.744×10^{-4}	0.806	9319
Pecan	without	quartz	1.1835	0.442×10^{-4}	0.668	15671
	vacuum	glass	1.2018	0.463×10^{-4}	0.672	14968
Pecan	with	quartz	1.6345	0.652×10^{-4}	0.827	10634
	vacuum	glass	1.6595	0.558×10^{-4}	0.823	12424
Oak	without	quartz	1.1748	0.610×10^{-4}	0.792	11360
	vacuum	glass	1.2057	0.581×10^{-4}	0.742	11927
Oak	with	quartz	1.1050	0.383×10^{-4}	0.898	18079
	vacuum	glass	1.2253	0.496×10^{-4}	0.902	13962

rameter defines how stable is the tannin phenoxyl radical. Here two interpretations are possible: in general, the more stable the radicals, hence, the slower is the rate of radical decay, the more marked is the inhibition of radical degradation of the substrate and, hence, the better the antioxidant properties of the tannin are.

Table II Radical Decay (=Second Reaction Step) Kinetics According to a First-order Kinetic Law Derived from Electron Spin Resonance Experiments

Tannin	Vacuum Conditions	Cell Material	Parameters			
			a'	k' (s^{-1})	r	$t_{1/2}$ (s)
Mimosa	without	quartz	0.909	0.874×10^{-4}	0.92	7931
	vacuum	glass	0.928	0.639×10^{-4}	0.90	10839
Mimosa	with	quartz	0.927	0.227×10^{-4}	0.89	30586
	vacuum	glass	0.951	0.148×10^{-4}	0.87	46896
Quebracho	without	quartz	0.901	0.559×10^{-4}	0.91	11571
	vacuum	glass	0.846	0.379×10^{-4}	0.81	18294
Quebracho	with	quartz	0.950	0.024×10^{-4}	0.92	289665
	vacuum	glass	0.920	0.028×10^{-4}	0.92	249264
Pecan	without	quartz	0.886	0.163×10^{-4}	0.71	42402
	vacuum	glass	0.886	0.076×10^{-4}	0.61	91184
Pecan	with	quartz	0.951	0.147×10^{-4}	0.86	47185
	vacuum	glass	0.936	0.020×10^{-4}	0.75	344069
Oak	without	quartz	0.931	0.102×10^{-4}	0.74	68177
	vacuum	glass	0.934	0.197×10^{-4}	0.71	35012
Oak	with	quartz	0.987	0.043×10^{-4}	0.80	160107
	vacuum	glass	0.997	0.055×10^{-4}	0.93	127249

Table III Radical Formation Reaction, Maximum Intensity (10^{-5}), and Starting Intensity (10^{-5}) in Intensity Units of ESR Signal and of Relative Radical Concentration

Tannin	Vacuum Conditions	Cell Material	Peak Intensity (Relative Radical Concentration) Maximum (at 60 min)	Starting (at 0 min)	Difference (Units %)	
Mimosa	without	quartz	95	41	54	132
	vacuum	glass	67	29	38	131
Mimosa	with	quartz	179	65	114	177
	vacuum	glass	145	53	92	174
Quebracho	without	quartz	191	80	111	139
	vacuum	glass	164	63	101	160
Quebracho	with	quartz	450	230	220	96
	vacuum	glass	311	115	196	170
Pecan	without	quartz	182	137	45	33
	vacuum	glass	147	109	38	35
Pecan	with	quartz	471	207	264	128
	vacuum	glass	343	153	190	124
Oak	without	quartz	222	160	62	39
	vacuum	glass	182	128	54	42
Oak	with	quartz	651	511	140	27
	vacuum	glass	349	229	120	52

3. In the case of tannin radicals, however, considerably more reactive than the substrate, hence, where radical termination reactions between two tannin radicals are favorite, the rate of radical decay is faster. Hence, the faster the quenching between themselves of the tannin radicals formed, the better are the antioxidant properties of the tannin. Cases (1) and (2) define two different effects. While case (1) has general applicability in all cases, case (2) might assume disproportionate importance in the case of experiments, like those reported here, in which the substrate is not present. This discussion is then limited at evaluating the importance of the radical decay reaction only from the point of view of case (2): the slower the radical decay rate, the greater the antioxidant power of the tannin. An example of the type of cumulative curve obtained is shown in Figures 1 and 2.

The increase in intensity of the ESR signal, which corresponds to the reaction of radical formation due to the irradiation of the three flavonoid and one hydrolysable tannins examined, can be modelled by a first-order kinetic law of the type $I/I_o = ae^{kt}$ (Table I). Comparison of the rate constants or of the semitransformation times $t_{1/2}$ allows a few deductions as follows.

1. In absence of vacuum, thus, in presence of singlet oxygen, mimosa and quebracho tannins present the faster radical formation reaction, while pecan and oak tannins are somewhat slower.
2. In vacuum, thus in absence of singlet oxygen, mimosa tannin shows the more rapid rate of formation, followed by quebracho and pecan tannins, which are almost comparable, finally followed by oak tannin, which is the slowest of them all.
3. With a few exceptions, the results in quartz and glass cells are comparable.

For a wood surface finish application, in air, the above results (Table I) indicate that mimosa and quebracho should present the best antioxidant characteristics with the results of mimosa under vacuum indicating a greater consistency, while pecan and oak tannin appears to have poorer antioxidant characteristics.

Equally, the decrease in intensity as a function of time of the ESR signal after stopping the irradiation of the specimen, hence, the radical decay reaction itself, correctly described by first-order

kinetics of the form $I/I_0 = a'e^{-k't}$ and shown in Table II, indicate the following.

1. In general, without vacuum, oak and pecan maintain the radical for much longer than quebracho and even longer than mimosa tannin.
2. In general, with vacuum, quebracho presents the slowest radical decay reaction, followed by oak, then pecan, and lastly by mimosa tannin.
3. Differences in the behavior between quartz and glass cells are noticeable. With vacuum, for instance, pecan in a glass cell appears to have the slowest radical decay rate, an unexpected occurrence considering all the other results.

Thus, in radical formation, the order of faster to slower rate remains the same with just differences in relative rates determined by the conditions used (vacuum or not, quartz or glass), and is

$$\text{mimosa} = \text{quebracho} \gg \text{pecan} \geqq \text{oak}$$

In the radical decay reaction, instead, the slower to faster rate changes quite considerably according to the conditions, particularly, but not only, according to the presence or absence of vacuum. Thus, without vacuum and the air singlet oxygen present, the rate of radical decay is

$$\text{mimosa} > \text{quebracho} \gg \text{pecan} = \text{oak}\ (>\text{faster than})$$

while under vacuum

$$\text{mimosa} > \text{pecan} \geqq \text{oak} \gg \text{quebracho}$$

In air, then, the balance of the two reactions indicate that the differences between the various tannins should not be major. As, however, radicals have to form before they can decay, the rapidity of radical assumption or formation is the most likely important factor; thus, mimosa and quebracho should be considerably better as antioxidants than the other two tannins. If it is considered that quebracho is as rapid as mimosa to form radicals but that its radicals definitely present a slower radical decay rate, the first conclusion which could be drawn is that quebracho appears to have a slightly better overall antioxidant behavior than mimosa but that such a difference is not likely to be very marked. All three flavonoid tannins appear to have considerably better behavior as antioxidants than the hydrolysable tannin.

The general behavior of tannins described above can also be seen, however, from a point of view of relative intensity of the ESR signals, thus, total radicals formed, rather than just from a purely kinetic rate point of view. Table III puts in perspective the relative quantities of radicals formed, directly related to the surge in intensity during a fixed period of time of 60 min (which, in all the cases without vacuum, corresponds to the peak of maximum radical concentration obtained at which the inducing light was switched off). From Table III, it is easy to see that differences in ESR intensity units, hence, in radical concentration, is much higher for quebracho (Table III) than for all the other three tannins, with the exception of pecan tannin in the vacuum/quartz case. The results for the other tannins are comparable to each other, presenting only minor differences. Expressing the same results (Table III) in percentages show mimosa to give comparable results to those of quebracho; this gives a false idea of the situation because it is the difference in units, which is directly related to the increase in radical concentration on the tannin; thus, the percentage should not be considered. The percentages are shown in Table III to warn about this error in interpretation. These results confirm again that quebracho has the best antioxidant characteristics but also show that there is not much difference between the other tannins.

In the cases with vacuum in which the role of the singlet oxygen is minimized (radical formation in flavonoids is generally considerably easier in presence rather than absence of air, hence, of singlet oxygen, as shown by both more rapid radical formation and decay without rather than with vacuum in Tables I, II, and III); thus, the real dependence of radical formation from just the characteristic structure of the tannin can be deduced. Here, the difference in units follows the order

$$\text{pecan} \geqq \text{quebracho} \gg \text{oak} > \text{mimosa}$$

It is interesting to relate such a scale to the structural and chemical characteristics of the three flavonoid tannins in question. Formation of radicals on the flavonoid B-rings generally leads to heterocycle ring opening, and pyran ring opening is most favorite in prodelphinidins (pecan)

because of their pyrogallol B-ring/phloroglucinol A-ring structure, which ensures better stabilization by delocalization of the radical on a greater number of possible sites. For this reason, mimosa (a 70% prorobinetinidin) should then be better than quebracho (mainly a profistinidin), which is not the case. There must then be at least another major structural reaction influencing the above scale. The other frequent bond cleavage reaction characteristic of flavonoid polymers is the cleavage of the interflavonoid linkage. Radical formation is also likely to be stabilized through this reaction. Interflavonoid bond cleavage is relatively easy in pecan and quebracho tannins and notoriously difficult in mimosa tannin.[12,13] It appears that it is the ease of this reaction superimposed onto the ease of pyran ring opening that is likely to lead to the scale shown above.

ease of pyran ring opening =

pecan = mimosa > quebracho

+

ease of interflavonoid bond cleavage =

pecan = quebracho ⩾ mimosa

This appears to indicate that, in general, the higher the number of —OHs on the flavonoid B-rings, and particularly, the higher the number of —OHs on the flavonoids A-rings, the greater the antioxidant behavior of the flavonoid tannin appears to be, although this characteristic is again overcome by the ease of interflavonoid bond cleavage. The fact that interflavonoid bond cleavage appears to be strongly related to antioxidant behavior under vacuum might not mean that this reaction determines radical formation or stability. It might only mean that the stereochemistry of tannins which present easier bond cleavage is such, for instance, that the structure is more open and that radical formation and uptake are facilitated.

The structural parameters that influence the antioxidant properties of the tannins change of importance in the presence of air, hence, in the presence of singlet oxygen. The total scale is mimosa = quebracho ⩾ pecan ≧ oak. Here, it appears that there is a clear inverse relationship between the number of A-rings, —OHs, and of ease of interflavonoid bond cleavage with the rates of radical formation and decay; namely, in the presence of air, the greater the number of A-rings —OHs and the easier the interflavonoid links cleavage, the lesser is the antioxidant activity of the tannin. Thus, the parameters of importance are the same in the presence or absence of air, but the effect is exactly opposite in the two cases. This indicates that another tannin property might also have a bearing on the antioxidant capability of the tannin, namely, its colloidal state. Flavonoid tannins present decreasing colloidal state according to the scale mimosa = quebracho > pecan.[14] In the presence of singlet oxygen, the effect of migration of such a radical species within the colloidal micelles will afford much more rapid radical formation or uptake by the tannin, and thus, improve its radical uptake characteristics (and, at the same time, possibly also accelerate radical decay within the micelles). This is indeed the case from the results in Tables I and II. If the singlet oxygen is not present, hence, in absence of air, the effect of the colloidal state is nonexistent for the radical formation reaction and radical formation is much slower. The effect might have very little bearing on the radical decay reaction, although with the data available, it is impossible to say.

In conclusion, the four parameters the combination of which appears to have a bearing on the antioxidant capabilities of a tannin are (1) the extent of its colloidal state, (2) the ease of interflavonoid bond cleavage (or, better, its stereochemical structure), (3) the ease of pyran ring opening, and (4) the relative numbers of A- and B-rings —OH groups. It is the combination of these four factors that will determine the behavior as an antioxidant of a particular tannin under each set of particular application conditions. With the data presently available, it is impossible to quantify the relative extent of the four effects as a function of application conditions.

The experiments of radical transfer from DPPH to a tannin in solution also gave some interesting results. Three solvents were tried. Tetrahydrofurane was discarded because it did not dissolve the tannins. Dioxane dissolved the tannin but presented problems of radical transfer between DPPH and tannin. Some of the few reliable results in dioxane are reported in Table IV. Solutions of tannin and DPPH in methanol instead gave reliable results; these are also shown in Table IV. These show that as regards the radical decay reaction mimosa is slower, thus, has better antioxidant power than quebracho. This result closely matches and supports what already obtained by radical transfer in solvent with the stopped-flow apparatus experiments.[3] This result supports

Table IV First-order Kinetics of Radical Decay Reaction After Radical Transfer to Tannin from DPPH in Methanol[a]

	Radical Decay Reaction					
Tannin	a'	k' (s^{-1})	r	$t_{1/2}$ (s^{-1})	Max Peak Intensity ($\times 10^5$)	Radical Formation
Quebracho	1.092	8.3×10^{-5}	0.978	8349	38	15 int. units in 1200 s
Mimosa	0.972	1.7×10^{-5}	0.952	40765	5	too fast to measure
Pecan	0.932	5.5×10^{-5}	0.988	12600	19	too fast to measure
Pine	0.977	1.03×10^{-5}	0.848	67282	55	44 int. units in 1200 s
Gambier	0.999	0.14×10^{-5}	0.945	498561	117	105 int. units/13000 s
Oak	0.934	1.96×10^{-5}	0.708	35357	21	too fast to measure

[a] In dioxane, only two radical decay rates could be reliably measured: Quebracho ($a' = 0.900$; $k' = 4.24 \times 10^{-5}$ s^{-1}; $r = 0.960$) and Gambier ($a' = 1.053$; $k' = 6.7 \times 10^{-5}$ s^{-1}; $r = 0.953$).

again the use of ESR techniques for this type of determination. Regarding the other tannins, the increasing order of the rate of the radical decay reaction (thus passing from the slowest to the fastest radical decay rate) (Table IV) is as follows:

$$\text{gambier} < \text{pine} \leqq \text{mimosa} \leqq \text{oak} < \text{pecan} < \text{quebracho}$$

which presents quite a different order from the experiments done without solvent and simply by light irradiation. The order of quebracho, pecan, and oak in the above scale reproduces what was obtained without vacuum in the experiments without solvent, except for the relative position of mimosa tannin in the scale, which is now completely different. It is clear then that solvation parameters also appear to play an important role under certain conditions. This goes to show the complexity of the interrelation of parameters in tannins radical reactions. Regarding the radical formation reaction, the results obtained can be calculated only in a very few cases, the reaction in the other cases being either too fast or too unreliable (Table IV).

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