

Comparative Kinetics of Induced Radical Autocondensation of Polyflavonoid Tannins. I. Modified and Nonmodified Tannins

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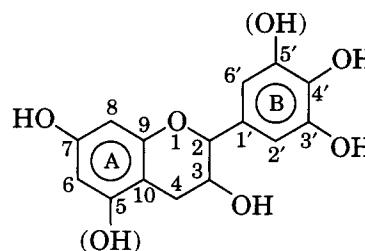
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SYNOPSIS

Comparative kinetics of the radical autocondensation induced by SiO₂ of a polyflavonoid tannin, namely quebracho tannin a mostly profisetinidin/prorobinetinidin tannin, in its natural extract state, sulfited, carbohydrate free, and in its adhesive intermediate form were carried out by electron spin resonance (ESR). The results obtained not only confirmed the existence of strong radical mechanisms of tannin autocondensation in the presence of dissolved SiO₂, but also pointed out new effects of interest in such a reaction. The SiO₂ induced autocondensation proceeds at a faster rate, and radical surge and concentration decay appear to be more marked and more rapid the more colloidal the tannin solution is. This appears to indicate that a colloid-induced intramolecular radical mechanism of the reaction is at work. As a consequence the intensity and rate of the radicals surge and decay decreases passing from more colloidal to less colloidal tannin solutions. Thus, the decay rate decreases passing from natural tannin to adhesive intermediate, to carbohydrate-free tannin, to almost disappear for sulfited tannin. The colloidal state of the solution appears to depend mostly, but not only, on the presence of the polymeric carbohydrates in the extract. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Thermosetting polyflavonoid tannin-formaldehyde resins have performed well in industrial applications as phenolic wood adhesives for more than 20 years.¹ Industrial polyflavonoid tannin extracts are mostly composed of flavan-3-ols repeating units, and smaller fractions of polysaccharides and simple sugars.¹ Recently, the autocondensation to hardened resins, without the use of any aldehydes, of polyflavonoid tannins induced by weak Lewis acids, in particular silica and silicic acid, were described.^{2,3} The mechanism of autocondensation was found to be based on the Lewis acid acceptance of electrons from the ether oxygen of the flavonoid unit heterocyclic ring, with consequent easing of the base-induced heterocycle opening at the O1—C2 bond.^{2-c}



The subsequent autocondensation of the reactive site formed (C2) with the A ring of the flavonoid unit in another polymer chain leads to resin hardening. Both ionic and in particular radical mechanisms have been found to exist for this series of reactions for all polyflavonoid-type tannins.⁴ The relative balance in the contribution to hardening of the two types of mechanism differs according to the type of tannin used with differences in the structure of the tannin repeating unit and polymer.⁴ The differences in the kinetics of the reaction as a function of the structure of the tannin can be investigated

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according to two different approaches: by tannin treatment to induce known modifications to its structure, composition, and characteristics, and by comparison of natural tannins of different types and from different sources, but of well-known differences in structure.

In this article the first approach is taken, with investigation of the reaction kinetics of the radical reaction for a natural tannin (Quebracho tannin extract, from *Schinopsis balansae* variety chaqueno, from Argentina, and mainly a prorobinetinidin tannin⁵) and three of its industrially used modifications, namely sulfited tannin extract, organic solvent-treated extract to yield a carbohydrate-free tannin² (W. McKillip, Pers. commun.), and a tannin extract modified to yield a tannin adhesive intermediate.⁶⁻⁸

EXPERIMENTAL

Tannin Types

Four types of commercial tannin extracts were used. All were based on quebracho (*Schinopsis balansae*, variety chaqueno) wood tannin extract. The four extracts were as follows:

1. natural quebracho tannin extract, prepared by countercurrent extraction with 2% sodium sulfite in hot water;
2. sulfited quebracho tannin extract, derived from the natural tannin extract by sulfitation with 10% sodium sulfite to increase solubility in hot water;
3. solvent extracted, carbohydrate-free quebracho tannin extract, derived from the natural tannin extract by extraction with ether/ethyl acetate to eliminate the carbohydrate fraction of the extract; and
4. tannin adhesive intermediate, derived from natural quebracho tannin extract treated in concentrated solution at 90°C with 3% maleic anhydride and 4–5% sodium hydroxide according to procedures already reported.⁶⁻⁸

All four products were commercial products obtained from Indunor, Argentina.

Tannin Extracts Solutions

Tannin extracts water solutions of 30% concentration were prepared by dissolving spray-dried powders of the four types of quebracho tannin extracts described and adjusted to a pH of 12 with 30%

sodium hydroxide solution. Solutions of (+)-catechin monomer at the same pH were used as a control.⁴

Electron Spin Resonance (ESR) Spectra and Kinetics

ESR spectra of the above solutions with and without 10% fine SiO₂ powder (aerosyl) were done. ESR spectra were recorded at 298 K on a Bruker ER 200 D spectrometer (X-band) equipped with a TE₁₀₂ sample cavity. Fine structure of the phenoxide radicals were studied in the range 3465–3495 Gauss with field modulation intensity of 0.8 and scan times of 500 s. The spectra in air, due to the requirement of the presence of singlet oxygen for the radical mechanism of pyran ring opening of flavonoids to occur,⁹ are the ones reported. The tannin phenoxide signal was observed at 3482.4 Gauss and all had $g = 2.003$. Spectra were centered on the signal of DPPH as standard¹⁰ at 3843 Gauss. Decay of the radical concentration, and of 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 silica addition at 5-min intervals for a period of 1 h. The results obtained are shown in Table I and Figures 1–4.

RESULTS AND DISCUSSION

The results of the comparative kinetics of radical concentration decay for the four types of tannin extracts (natural, sulfited, carbohydrate-free, and adhesive intermediate) are shown in Table I, and show several features of interest. It was already shown that dissolving SiO₂ in an alkaline tannin extract solution leads to an immediate surge in radicals, or better in anion-radicals concentration in the solution.⁴ This can again be seen by comparing the relative intensities at time 0 of the ESR peaks of tannins with 10% SiO₂ (on tannin extract solids) with the same tannins without SiO₂ the former being considerably more intense than the latter. This appears to be valid for all four types of tannin (Table I). From the fine structure of the phenoxide radical signal, it is again confirmed that the balance of the relative intensities between the A-ring and B-ring radicals of the polyflavonoids is severely altered by the addition of SiO₂⁴: the former is generally more intense than the latter when SiO₂ is present (with the exception of the natural quebracho tannin extract, Figs. 2, 3). In this respect it is interesting to note that the greater intensities of A-ring phenoxide

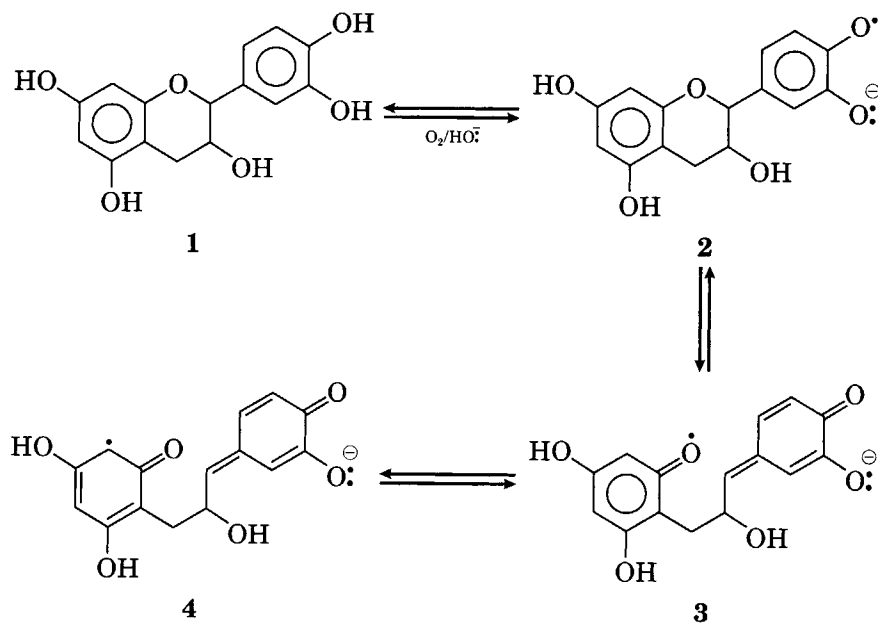
Table I Rate of Decay of Peaks of Fine Structure of ESR Phenoxide Signal

Alkali Alone (pH 12)					Alkali (pH 12) + 10% SiO ₂				
Peak (Gauss)	Ring	Kinetic Law	Reaction Half-Time (s)	Peak Intensity at $t = 0$ ($\times 10^{-5}$)	Peak (Gauss)	Kinetic Law	Reaction Half-Time (s)	Peak Intensity at $t = 0$ ($\times 10^6$)	Ratio
Natural									
3476.9	A	$r = 98.3680$ $e^{-0.1168t}$	356	115.92	3476.0	$r = 233.3830$ $e^{-0.1366t}$	304	240.48	2.07
—	A	—	—	—	3477.9	$r = 441.1190$ $e^{-0.1392t}$	299	454.68	—
—	B	—	—	—	3478.9	$r = 502.0077$ $e^{-0.1354t}$	307	523.36	—
3479.95	B	$r = 75.1567$ $e^{-0.1223t}$	340	66.97	3479.34	$r = 376.2258$ $e^{-0.1566t}$	266	380.09	5.65
3480.70	B	$r = 110.8841$ $e^{-0.1287t}$	323	134.52	3480.38	$r = 531.9474$ $e^{-0.1279t}$	325	576.28	4.28
3482.06	A	—	—	143.70	3482.20	—	—	330.89	2.30
3482.86	A	$r = 126.4532$ $e^{-0.1361t}$	305	153.02	3483.04	$r = 310.8174$ $e^{-0.1082t}$	384	347.24	2.27
Adhesive intermediate									
3475.0	A	$r = 11.7988$ $e^{-0.0819t}$	508	16.67	3475.0	$r = 268.3209$ $e^{-0.0994t}$	418	276.34	16.5
3476.7	A	—	—	—	—	—	—	—	—
3477.5	A	$r = 29.9595$ $e^{-0.1138t}$	365	33.17	3477.5	$r = 68.1916$ $e^{-0.0806t}$	516	61.42	1.85
3479.8	B	—	—	10.0	—	—	—	—	—
3480.6	B	—	—	—	—	—	—	—	—
3481.9	B	$r = 40.3733$ $e^{-0.0576t}$	722	63.22	3480.58	$r = 34.7620$ $e^{-0.0684t}$	608	61.18	0.97
3484.4	A	—	—	26.74	3481.99	$r = 216.0935$ $e^{-0.0922t}$	419	263.34	9.85
3485.1	A	$r = 24.0722$ $e^{-0.0671t}$	620	27.37	3482.80	$r = 312.1792$ $e^{-0.1028t}$	405	354.54	12.95
Carbohydrate free									
3476.0	A	—	—	108.40	3476.0	$r = 190.3690$ $e^{-0.0300t}$	1386	225.63	2.08
3476.7	A	—	—	76.67	—	—	—	131.62	1.71
3478.2	B	—	—	56.5	—	—	—	35.60	0.63
3479.2	B	—	—	77.66	3479.3	—	—	142.31	1.83
3479.9	B	—	—	132.38	3480.0	—	—	146.21	1.10
3481.3	A	—	—	129.62	3481.2	$r = 208.8325$ $e^{-0.0289t}$	1439	258.30	1.99
3482.1	A	—	—	159.18	3482.2	$r = 287.8222$ $e^{-0.0263t}$	1581	333.32	2.09
Sulfited									
3476.0	A	—	—	—	—	—	—	—	—
3476.7	A	—	—	9.5	3476.7	—	—	39.0	4.11
3477.6	A	—	—	11.82	3477.6	—	—	48.0	4.06
3478.3	B	—	—	10.0	3478.3	—	—	27.0	2.70
3479.5	B	—	—	—	—	—	—	—	—
3481.7	A	—	—	27.94	3481.4	—	—	90.46	3.24
3482.9	A	—	—	—	—	—	—	—	—

Reaction time = 3 min for the four types of quebracho tannin, with and without addition of silica.

radicals concentration on addition of SiO_2 appears to occur in the natural tannin followed by the adhesive intermediate, then by the carbohydrate-free tannin extract, and last by the sulfited tannin. Another feature of interest is the radical decay half-time of reaction indicating that radical decay becomes slightly slower passing from natural tannin

extract to adhesive intermediate but is then considerably slower passing to the carbohydrate-free tannin (Table I). Thus for an average half-time of 314 s for natural tannin extract, the radical concentration decay half-time is 473 s for the tannin adhesive intermediate and 1469 s for the carbohydrate-free tannin (Table I).



All the above indicates that several factors appear to be at play. First of all, the extensive opening of the heterocycle in sulfited tannin, and extensive or complete degradation of the polymeric hydrocolloid gums also caused by the reaction with sulfite,¹ indicate that not many radicals can be formed, particularly for the first of the reasons listed: the disappearance of the great majority of closed heterocycles as a consequence of the reaction of sulfitation and the introduction of a sulfonic acid group at the potentially reactive C2 site of the flavonoid subtract the main form of radical stabilization from the system. The results for sulfited tannin appear to confirm this (Table I).

In the other three types of tannins the factors at play appear to be the same: the availability and proportion of closed heterocycle rings of the flavonoid still susceptible to opening and the presence of the colloidal state of the tannin extract solution, which is mostly dependent on the presence of the hydrocolloid gums (polymeric carbohydrates)⁸ but also on the presence of tannins of high molecular weight. These two factors combine to give different

results in the three types of tannin. In natural tannin the high proportion of available closed heterocycles leads to a marked surge in radical concentration once SiO_2 is added, but not to a greater proportion of A-ring radicals over B-ring radicals. The colloidal state of the solution⁸ also ensures that radical decay is the most rapid, and indicates that radical formation and decay was induced by silica addition. Hence, heterocycle opening and subsequent autocondensation is a function of the colloidal micelles present in the solution. This type of effect has already been noticed for similar reactions involving synthetic phenolic resins in a colloidal solution.¹¹ Heterocycle ring opening, radical formation, and radical decay caused by the subsequent reaction of autocondensation then occurs within the colloidal micelles mainly induced by the presence of polymeric carbohydrates, and are therefore quite rapid. It is not possible at this stage to say if the first steps of the reaction, namely the base attack on the hydroxyl groups of the B ring and the SiO_2 attack on the ether oxygen of the pyran ring, occur outside or inside the micelles.

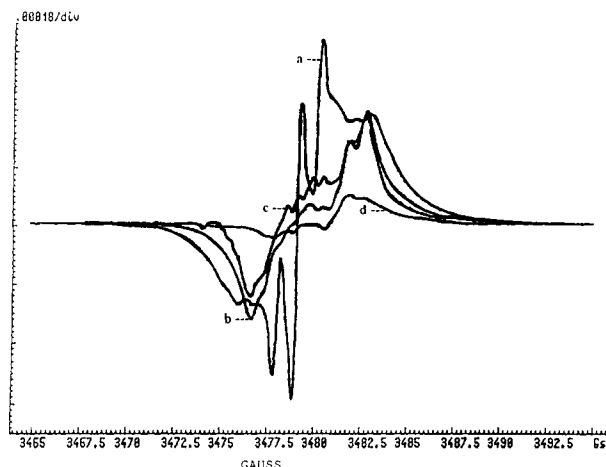


Figure 1 Comparative fine structure of phenoxide radical signal in ESR spectra at time = 3 min (after SiO_2 addition), at pH 12, 20°C of (a) natural quebracho tannin extract + 10% SiO_2 , (b) quebracho tannin adhesive intermediate + SiO_2 , (c) carbohydrate-free quebracho tannin + SiO_2 , and (d) sulfited (>10%) quebracho tannin extract + SiO_2 .

Once the tannin extract is treated to give the tannin adhesive intermediate, the chemical and heat treatment it underwent caused several changes in both the structure and colloidal state of the tannin solution. The treatment considerably decreased but did not eliminate the colloidal nature of the solution^{7,8,12} due to a certain extent of acid and alkaline hydrolysis of the hydrocolloid gums.¹ As a consequence, the number of micelles is likely to be

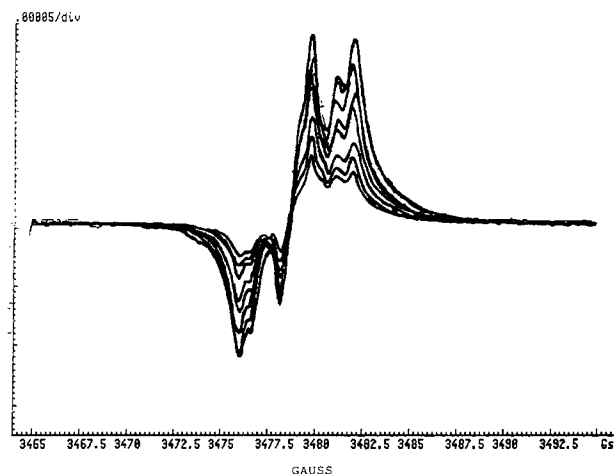


Figure 2 Variation of the fine structure of the ESR phenoxide radical signal as a function of time (more intense signal time = 3 min, lowest intensity signal time = 45 min), at 20°C and pH 12 of carbohydrate-free quebracho tannin alone (ordinate scale = 5×10^{-5} divisions).

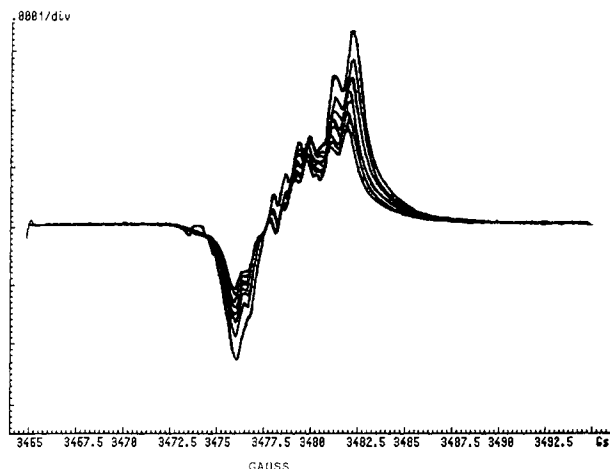


Figure 3 Variation of the fine structure of the ESR phenoxide radical signal as a function of time (most intense signal time = 3 min, lowest intensity signal time = 45 min), at 20°C , pH 12, of carbohydrate-free quebracho tannin + 10% SiO_2 (ordinate scale = 1×10^{-4} divisions).

lower, translating in both a lower initial radical concentration and in a slower rate of radical decay. There is then a lower number of rapidly reacting intramicellar radicals and a greater relative proportion of slower reacting radicals outside the micelles in the solution. This can be seen by the much lower radical concentration in the case in which SiO_2 was not added. Addition of SiO_2 also activates the radical mechanism within the micelles (the solution is still colloidal^{8,11}), but this time both the peak intensity (=radical concentration) is lower and radical decay

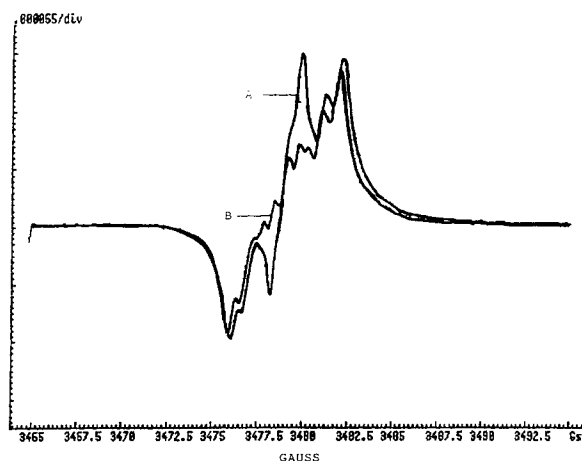


Figure 4 Variation of the fine structure of the ESR phenoxide radical signal at pH 12, 20°C , of (a) carbohydrate-free quebracho tannin alone and (b) carbohydrate-free quebracho tannin + 20% gum arabic, at time $t = 10$ min (ordinate scale = 5.5×10^{-5} divisions).

is slower, as a good part of the reaction does not proceed within micelles.

In the case of the carbohydrate-free tannin solutions, the effects already noticed with the adhesive intermediate are brought one step further. In this material some colloidal state can exclusively be maintained by the fraction of tannins of higher molecular mass. It is interesting to note that the average radical concentration without SiO_2 is higher than in the case of the adhesive intermediate. This is an indication that the treatment to form the adhesive intermediate induces rather noticeable depolymerization of quebracho tannin in particular, a peculiarity of this tannin observed by ^{13}C -NMR and already reported.^{5,7} In the carbohydrate-free tannin the carbohydrate-generated micelles do not exist, but the number of high molecular weight tannin-generated ones is higher than in the preceding case. As a consequence of this, alkali alone will give a higher radical concentration than in the adhesive intermediate case. The alkali + SiO_2 case will again give a surge in radicals concentration, but this will instead be of a similar intensity to the adhesive intermediate case. The rate of radical decay is much slower than in the previous two cases (Table I), indicating that the polymeric carbohydrates are the ones that induce the greater proportion of the colloidal state in tannin solutions. It is also interesting to note that the introduction of 20% polymeric carbohydrates (gum arabic was used) again shows a very marked variation of the fine structure of the spectra, with the signal for the flavonoid B ring almost disappearing, and the A-ring signals dominating again without the addition of any silica. This is an indication that it is the colloidal state of the solutions that favor the radical reaction, whatever its initiator. It is then this colloidal state that allows the dominance of A-rings over B-rings radicals. This implies that, at least under the conditions used, the radical component of the mechanism is of considerable importance.

The last case, sulfited quebracho tannin extract, marks the near total destruction of the colloidal state of the solution. Extensive sulfite treatment, which is used commercially to both markedly decrease tannin solution viscosity and improve water solubility, causes nearly the total destruction of the colloidal state of the tannin solution. The polymeric carbohydrates are extensively degraded to simple sugars; the tannins are almost completely in solution for extensive opening of the pyran heterocycle and the blocking by insertion of sulfonic acid groups of the C2 reactive site as well as the solubilizing effect of the $-\text{SO}_3\text{H}$ group introduced.¹ Some decrease

in the average degree of polymerization of the tannin as a consequence of this treatment¹⁰ also contributes to the loss of colloidal state of the solution. It is interesting to note that once the colloidal nature of the tannin extract solution disappeared, the effect of the addition of silica was considerably less intense (Table I). This could well be due to the nonavailability of suitable heterocycles to open, but also to the silica initiation reaction mainly occurring within micelles.

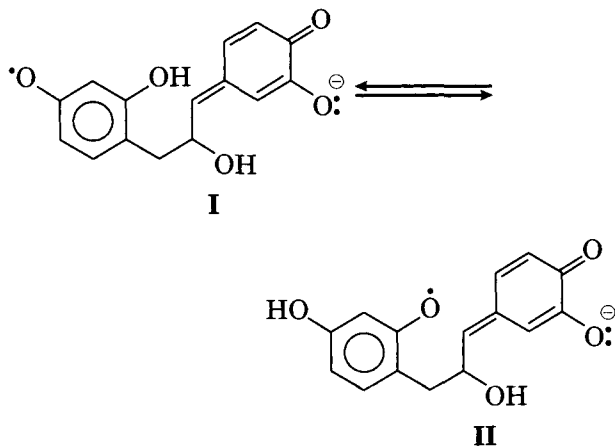
The above also relates well with past experiences with model compounds (catechin monomer⁴). The silica induced autocondensation of catechin monomer does occur, but at a much slower rate than with polymeric tannins; but it is greatly accelerated by the addition of gum arabic, imparting colloidal characteristics to its solution.^{4,7,11}

It is also interesting to note that the results are consistent with the catalytic acceleration of autocondensation that polymeric carbohydrates not in colloidal form can induce in both tannin and other resin polycondensations.¹¹ In this regard natural tannins containing the greater amount of polymeric carbohydrates appear to react faster than, for instance, the tannin adhesive intermediate in which polymeric carbohydrates still exist (but in which they present a lower degree of polymerization), and react much faster than the carbohydrate-free extract, as would be expected.¹¹ This aspect is also of some interest because it means that not only heterogeneous catalysis,^{11,12} but also homogeneous catalysis induced by polymeric carbohydrates on both tannin autocondensation and on other types of polycondensations might not be limited only to ionic reactions,^{7,10-12} but could also extend to radical reactions.

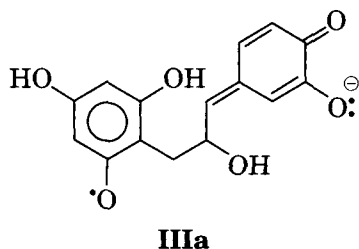
As regards the rate equations given in Table I for the different radical decay processes, the exponentials presented represent the values of $1/k$, where k is the apparent rate constant for the different radical decay reactions. The apparent kinetic law followed in all the cases is of the first order (Table I).

It is also interesting to consider if peaks in the ESR spectrum correspond to well-defined anion radicals in the equilibrium of the different, possible flavonoid radicals. It was already determined which peaks in the fine structure of the phenoxide signal belong to the flavonoid B-ring radicals and which belong to the A-ring radicals.⁴ All the anion radicals present only phenoxide radical signals, and thus no other radical types appear to exist; this allows the exclusion of the existence of anion radicals of type 4, confirming previous results.⁴ The flavonoid B rings present two signals often combined into one

single more intense signal (Table I, Figs. 1–4). The two more noticeable signals correspond to the two resonance anion radicals in which radical and anion charge, respectively, invert on the two vicinal phenolic *ortho*-hydroxy groups. A small third peak sometimes appears due to the small proportion of B rings presenting a third *ortho*-hydroxy group.^{5,13} More interesting, however, are the signals belonging to the A rings. In purely profisetinidin/prorobinetinidin tannins only two signals should be noticeable, the ones due to the following structures:



As quebracho tannin contains up to 20% catechin type units,¹³ then a third, possibly more feasible signal should be present, from the structure:



The three signals then correspond to the two main signals coming from structures I and II and to the three more feasible signals coming from structures of type Ia, IIa, and IIIa. In the four cases inves-

tigated, two and sometimes three peaks are observed in the A ring region of the signal (Fig. 1). However, only two of these peaks are always very intense. Thus, these are the ones corresponding to the structures directly obtained by silica attack, structures I and Ia, or conversely they correspond to anion radicals I and II given the considerably higher amount of profisetinidin/prorobinetinidin structures in the tannin used. The limited data available at present do not allow more precise deductions at this stage.

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